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The evaluation of the chromaticity of a series of fluorescent Lewis adducts with highly luminescent dithienophospholes enables the unequivocal determination of the strength of Lewis acids. Our method provides a simple, robust, and efficient avenue to discern an exhaustive list of species from across the period table.

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Fluorescent Lewis Adducts: A Refined Guide for Lewis Acidity

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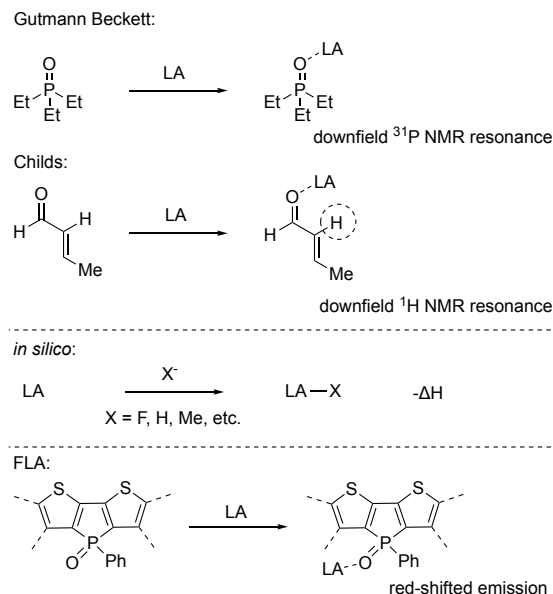
Abstract

Experimentally determining the strength of a Lewis acid is a highly desirable and important task that has implications across the chemical sciences. However, unlike the pK_a scale for Brønsted acids, there is no established universal scale for Lewis acids. Recently, we developed a unifying fluorescence-based method to evaluate the Lewis acidity of a small series of Lewis acids across the main-group and d-block with great precision. In the present report, we provide our refined approach toward these Fluorescent Lewis Adducts (FLAs) that alleviates the uncertainties that we identified with our original method. Moreover, we expand the scope of the FLA method in a true universal sense, by systematically investigating the strength of over 50 Lewis acids. Notably, a number of the investigated Lewis acids have never been experimentally measured before. Our refined guide clearly shows that the FLA method is robust, accurate, simple, and extremely sensitive to small structural or electronic perturbations, without the need for complex NMR experiments, equilibrium studies, or *in silico* analyses.

Introduction

One hundred years after initially defined as an electron-pair acceptor,^[1] Lewis acids remain of significant importance in the chemical sciences. However, unlike their Brønsted acid counterparts, no universal scale for Lewis acid strength exists to date. This is in part due to the simple definition of a Lewis acid. While defined as an electron pair acceptor, Lewis acidity can be derived from scenarios that involve empty p- or d-orbitals, although this concept has begun to change with the discovery of potent Lewis acids with energetically accessible σ^* -orbitals.^[2-4]

From a practical standpoint, Lewis acids have been pivotal to a range of research fields. The recent renaissance in main group chemistry has established their increasing utility as reagents,^[5] catalysts,^[6] functional materials, and sensors.^[7] Recent successes in metal-free catalysis, have shown that main group Lewis acids are useful alternatives to transition metal catalysts. Representative examples in this context include the hydro-silylation and hydrogenation of unsaturated substrates,^[8] as well as the direct C–H borylation of aromatic molecules.^[9] As new Lewis acids, derived from p-block elements, transition metals, or more exotic scaffolds are being realized, it is critical to evaluate their Lewis acidity, as it has direct implications on their functionality and applicability.



Scheme 1. Established methods for Lewis acid (LA) strength determination.

Currently, the predominant method for measuring Lewis acidity is the Gutmann-Beckett method (GB; Scheme 1),^{[10],[11]} which uses Et₃PO as a probe; the Lewis acid strength is evaluated via ³¹P NMR spectroscopy. Another common NMR-spectroscopic method is the Childs method that uses crotonaldehyde as a probe via ¹H NMR analysis.^[12] Moreover, *in silico* methods, such as fluoride-ion affinity (FIA) have become popular due to their relative ease of use,^[13] but recently, hydride- and methyl-ion affinities have also been explored as complementary scales.^[14] However, these experimental and computational methods each suffer from individual drawbacks, and they all

utilize only a single Lewis basic probe to measure Lewis acid strength. Since Lewis adducts are in equilibrium with the free acid and base, the measurement against one probe can skew the results by biasing against external factors, such as sterics, temperature, or their hard-/soft-ness (i.e., HSAB theory). Furthermore, while generally adopted by the community, these methods have given inconsistent results throughout the literature.^[15]

Upon adduct formation, the emission of the dithienophosphole oxide probe undergoes a bathochromic shift. By evaluating the chromaticity of the resulting FLAs, we discovered a strong correlation between Lewis acidity and their respective commission internationale de l'éclairage (CIE) coordinates. In our initial report, we analyzed 15 Lewis acids, whose strength was quantified by arbitrary Lewis acid units (LAU).^[16] Using this approach, we were able to accurately compare classical main-group, cationic, and transition-metal-based Lewis acids on the same scale for the first time. Notwithstanding, our method ultimately revealed a few uncertainties, specifically around three points: i) the use of only three Lewis bases led to larger than desirable error margins; ii) the small window of defined LAU values for the measured Lewis acids made it difficult to assess differences between species of similar strength; and iii) some of the FLAs with strong Lewis acids were found to emit into the near-IR region, which is outside the defined chromaticity space.

Building on our initial proof-of-concept study, we now expand the scope of our method as we push towards developing a more refined, universal scale for Lewis acidity. Herein, we report the improvement of our methodology to confront the issues above, and significantly expand the scope of the investigated Lewis acids.

Results and Discussion

As indicated above, the chromaticity/CIE coordinates of the FLAs are the cornerstone for our method. Chromaticity is determined directly from the emission spectrum of a given compound. The universal CIE space is defined within the visible spectrum between 380 nm and 780 nm, or in other words, the colors that the human eye can see. Each color is defined by the unitless variables x , y , and z that describe a specific color as a function of hue, saturation, and intensity (Figure 1).

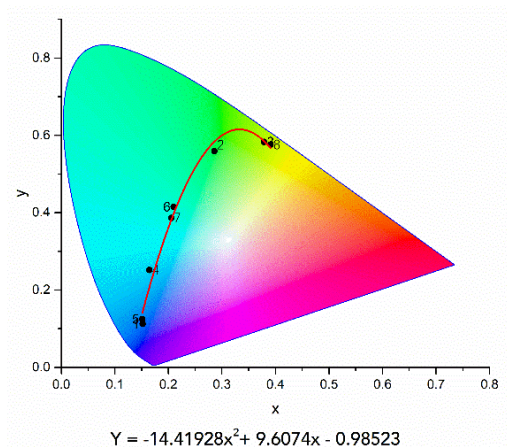


Figure 1. CIE diagram overlaid with the parabolic fit for the eight dithienophosphole probes.

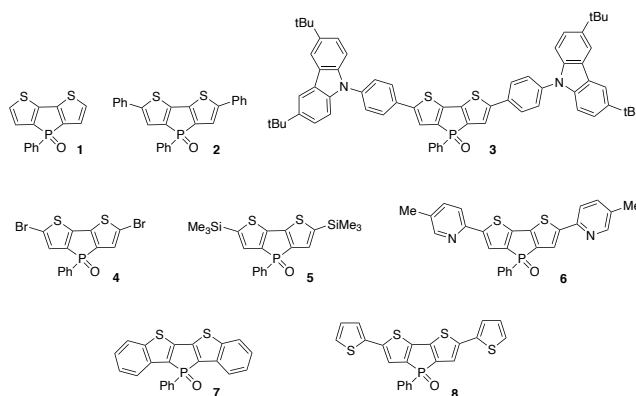


Figure 2. Dithienophosphole probes used in this work.

In our original report, Lewis acid strength was based on the three FLA chromaticity coordinates formed with probes **1**, **2**, and **3** (Figure 2). We found that both, free probes as well as their FLAs could be expressed as two intersecting parabolic functions. The x-coordinate of the intercept then allowed us to accurately extrapolate the relative Lewis acidities in LAUs (*vide infra*).

Since three points are mathematically the minimum necessary to define a parabola, experimental error could unfortunately not be discussed. We resolved this issue by acquiring the chromaticities of the FLAs with additional probes. To improve the fit of the free-probe parabola and to minimize the potential uncertainties as much as possible, we included additional probes in the original report (**1-6**; Figure 2) and two more probes as part of this study. To this end we used the benzo-fused

dithienophosphole oxide species (**7**) with a blue/green emission at $\lambda_{\text{max}}(\text{em}) = 483 \text{ nm}$.^[17] To maximize the use of the color space, we also included the thienyl-extended dithienophosphole oxide **8** with similar photophysical properties to that of **3** ($\lambda_{\text{max}}(\text{em}) = 545 \text{ nm}$).^[18] To our satisfaction, the new probes **7** and **8** fit well onto the parabolic function containing the free dithienophosphole oxide probes **1-6** from our original work, forming a representative parabolic trend in the CIE space (Figure 1).

With new probes in hand, we found that adding more data points to a parabolic fit gave diminishing improvement to the R^2 value and similarly a minimal change in standard deviation. The calculated fits generally have R^2 values of 0.98 with several producing near perfect fits (Supporting Information). This demonstrates another strength of this method; it produces highly self-consistent results. The results obtained across three, four, or five probes suggests that any combination of three could practically be used to determine the Lewis acid strength with satisfactory accuracy. However, the use of one or two additional probes affords the most accurate results and allows to easily check that the data is self-consistent. In the case when only three probes are used, emissions that span the chromaticity space (e.g., **1**, **2**, **3** or **1**, **7**, **8**) are preferred over those of similar chromaticity (e.g., **1**, **4**, **5** or **4**, **6**, **7**).

In our original study, we also found that some FLAs with strong Lewis acids had emission spectra extending beyond 780 nm into the near-IR spectral region (Supporting Information). When converted into CIE space, we were concerned that this would underestimate the strength of strong Lewis acids, as the chromaticity is based on the integral of the emission spectrum. However, using different sets of probes that did not generate FLAs with emission into the near-IR region revealed that this is not a major source of error for strong Lewis acids, as is evident in the LAUs determined by the refined method herein (*vide infra*; Supporting Information).

The second perceived shortcoming of our initial study was the fact that the LAU values obtained by extrapolation of the CIE x-coordinate only provided a very narrow window between 0.54 and 0.77 LAUs.^[16] This was sufficient to distinguish between the 15 previously tested Lewis acids, but this resolution is insufficient when expanding the Lewis acid scope, as several LAUs were separated by only a fraction of a decimal. We hypothesized this being the result of only utilizing

the x-coordinates of the CIE diagram. Chromaticity defines color in a two-coordinate space; our initial method only utilized the x-coordinate of the intercept (Figure 3a), corresponding to an ideal FLA,^[16] leaving half of the available data out of the equation. In order to address this issue, we decided to refine the data of our intercepts by incorporating the y-coordinate as well. By using both the x and y coordinates that define the color at the intersection point, we expect to be able to more precisely define Lewis acid strength.

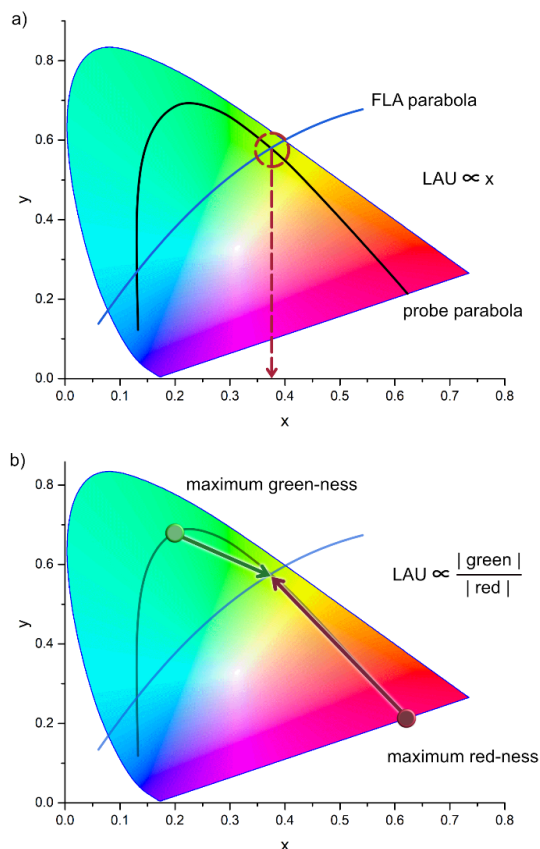


Figure 3. FLA method a) original (LAU range: 0.5 – 1.0); b) refined (LAU range: 0 – >50).

As established earlier, an increasing x-coordinate of the intercept can be correlated with Lewis acid strength.^[16] Upon closer inspection of the original data, we also recognized that the y-coordinate decreases concurrently. We decided that a vector-based approach would be most appropriate to exploit the full information a CIE diagram provides. To be able to mathematically utilize both coordinates, the ratio of two vectors with defined magnitudes is needed.^[19] The most suitable origins for these vectors are at fixed points within the CIE space, at the apex and the root of the dithienophosphole oxide probe parabola, corresponding to the theoretically weakest (green)

and strongest (red) possible Lewis acids, respectively (Figure 3b). One vector is generated from the apex of the parabola, to the intersection point with the FLA parabola, representing the "greenness" of the ideal FLA that is used to derive the Lewis acid strength. The second vector is defined from the point where the probe parabola intersects with the edge of the chromaticity space (maximum x), which represents the "red-ness" of the ideal FLA. The ratio of the magnitude of the two vectors is then used to define the Lewis acid strength. Note that now as x increases, the Lewis acid strength increases, while an increase in y correlates with a decreasing Lewis acid strength. This two-dimensional approach consequently widens the measurable LAU range from 0 to theoretically infinity and should allow for a large number of Lewis acids to accurately be measured. In line with our initial iteration of the FLA method, the refined analysis still only requires determining the intersection point of the dithienophosphole oxide probe chromaticity curve, and the FLA chromaticity curve. Given the x and y coordinates, Equation 1 can be used to calculate the new LAU values (for details, see Supporting Info).

$$Strength = \frac{\sqrt{(x-0.333)^2 + (y-0.615)^2}}{\sqrt{(x-0.511)^2 + (y-0.164)^2}} * 100 \quad (1)$$

With these improvements in hand, we sought to establish the robustness and sensitivity of our method by considerably expanding the scope of Lewis acids measured. To this end, we incorporate a wide variety of Lewis acids, ranging from classical main group species, to metal salts, to charged and hypervalent Lewis acids. Notably, the strength of a considerable number of the Lewis acids tested had not been investigated before, for various reasons (e.g., stability, reactivity, etc.).

Neutral Borane Derivatives

Boranes are among the most popular Lewis acids by being easily synthetically accessible and highly tunable through their substituents. However, measurements and scaling of Lewis acid strength for numerous derivatives is inconsistent.^[20] To alleviate this issue, several *in silico* approaches have been developed that analyze different variables, but their results were also found to differ considerably.^[21] B(C₆F₅)₃ has become a staple in Lewis acid catalysis as it is capable of performing a variety of selective reactions.^[22] However, other arylboranes of varying electron deficiency can also facilitate certain reactivity; even weak Lewis acids such as triphenylborane have been utilized in catalysis.^[23] It is evident that due to their high popularity, an accurate ordering

of the boranes by Lewis acid strength is needed. As such, we investigated a wide range of fluorinated arylboranes with different aromatic substitution patterns (Figure 4).^{[24],[26]}

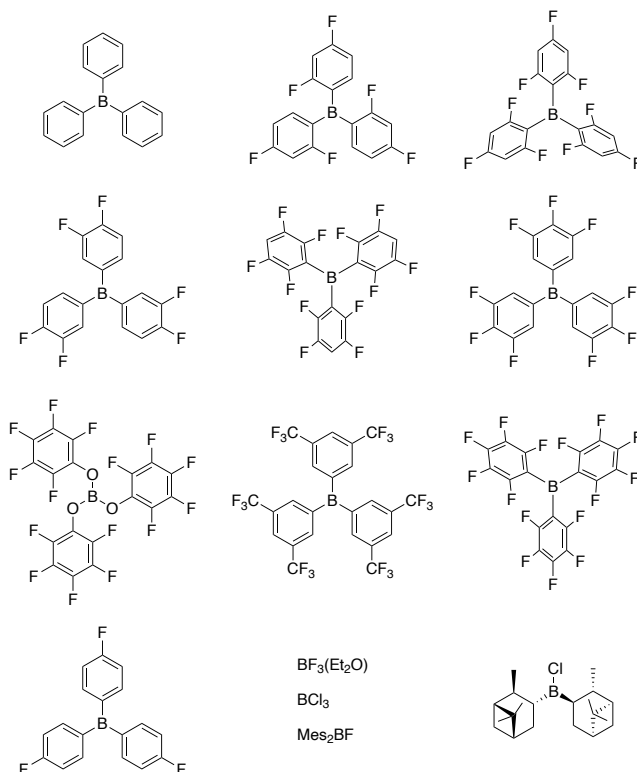


Figure 4. Borane derivatives investigated.

The observed trend in Lewis acidity with the FLA method correlates with what is generally found in the literature, but more importantly, our method provides clarity for a number of disputed results. For instance, the FLA method indicates that $\text{B}(\text{C}_6\text{F}_5)_3$ is a stronger Lewis acid than $\text{B}(3,5\text{-(CF}_3)_2\text{C}_6\text{H}_3)_3$ (Figure 5). This has been subject to debate in the literature and Blagg and Wildgoose explored this issue extensively with a number of different methods, including examining the reduction potential, Gutmann-Beckett, and other NMR spectroscopic techniques.^[27] The reduction potentials suggest that $\text{B}(\text{C}_6\text{F}_5)_3$ is a stronger Lewis acid, whereas the GB method implies the opposite. We have shown in our original study^[16] that the FLA probes are less sterically encumbered than Et_3PO and therefore can better interact with bulky Lewis acids. Our method strongly corroborates the fact that $\text{B}(\text{C}_6\text{F}_5)_3$ is the strongest Lewis acid in the series. Excitingly, this result may even support unexpected discrepancies in reactivity. A recent example by Gagné shows distinct differences in chemoselectivity when applying $\text{B}(\text{C}_6\text{F}_5)_3$ or $\text{B}(3,5\text{-(CF}_3)_2\text{C}_6\text{H}_3)_3$ as a

Lewis acid catalyst for the reduction of natural products and sugars.^{[28],[29]} Additionally, $\text{B}(\text{OC}_6\text{F}_5)_3$, which differs by only ether linkages from $\text{B}(\text{C}_6\text{F}_5)_3$, was found to be a weaker Lewis acid on our scale (Figure 5). This can be attributed to lone pair donation from the oxygen atoms to the empty p-orbital on boron. The reported strength of this Lewis acid in the literature is also contradictory, as the GB method suggests that $\text{B}(\text{OC}_6\text{F}_5)_3$ is a stronger Lewis acid, while the Childs method implies the opposite.^{[20],[30],[31]} The FLA method clearly supports that $\text{B}(\text{OC}_6\text{F}_5)_3$ is the weaker Lewis acid as anticipated from the adjacent donor atoms. The remaining boranes follow the expected Lewis acidity trend, based on the number and positioning of the fluorine substituents, providing strong evidence for the robustness and sensitivity of the FLA method. Interestingly, the distinct differences between $\text{H}_2\text{B}(\text{C}_6\text{F}_5)$ and Piers' borane $\text{HB}(\text{C}_6\text{F}_5)_2$ on the one side, and $\text{B}(\text{C}_6\text{F}_5)_3$ on the other side, provide a strong testament to the commonly observed dimeric nature of hydridoboranes (Figure 5).^{[32],[33]}

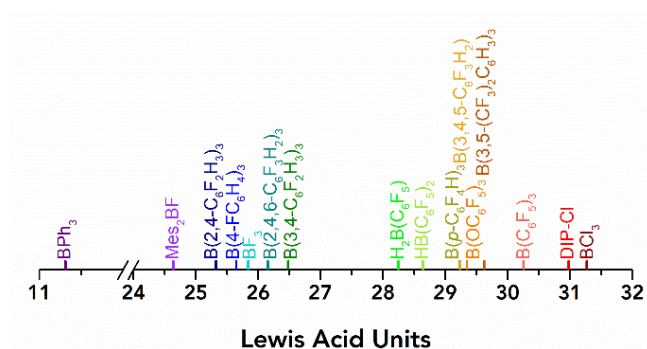


Figure 5. LAUs of neutral boranes derivatives.

Our refined method confirmed that BPh_3 is still the weakest Lewis acid ($\text{LAU} = 11.31$). This was followed by a significant increase in strength ranging from $\text{B}(2,4\text{-C}_6\text{F}_2\text{H}_3)_3$ (24.64), $\text{B}(2,4,6\text{-C}_6\text{F}_3\text{H}_2)_3$ (25.84), $\text{B}(3,4\text{-C}_6\text{F}_2\text{H}_3)_3$ (26.41), $\text{H}_2\text{B}(\text{C}_6\text{F}_5)$ (28.25), $\text{HB}(\text{C}_6\text{F}_5)_2$ (28.64), $\text{B}(p\text{-C}_6\text{F}_4\text{H})_3$ (29.23), $\text{B}(3,4,5\text{-C}_6\text{F}_3\text{H}_2)_3$ (29.24), $\text{B}(\text{OC}_6\text{F}_5)_3$ (29.35), $\text{B}(3,5\text{-(CF}_3)_2\text{C}_6\text{H}_3)_3$ (29.63), to $\text{B}(\text{C}_6\text{F}_5)_3$ (30.25). Interestingly, we could not confidently assign a LAU value to $\text{B}(4\text{-FC}_6\text{H}_4)_3$ (25.32*) because it was evident in the chromaticity measurements that additional emissive species were present in solution (Supporting Information).^[34]

In our initial publication, we also reported the measurement of boron trihalides $\text{BF}_3 \cdot \text{OEt}_2$ and BCl_3 . The revised method provides a similarly accurate measurement of the two, with LAUs of 25.72 and 31.27, respectively. We further explored how steric hinderance would impact haloboranes by

testing Mes_2BF and (–)-B-chlorodiisopinocampheylborane (DIP-Cl). The only electron withdrawing substituent on these boranes is the singular halogen atom. Their LAUs were determined to be 22.74 and 30.98, respectively. This nicely compares to the LAU for the other haloboranes, $\text{BF}_3\cdot\text{OEt}_2$ and BCl_3 . In both cases, the Lewis acidity of the fluoroboranes is reduced due to the electron donation from the F-lone pairs.

Heavier Group 13 Lewis Acids

Generally, Lewis acidity decreases down a group in the periodic table. However, the trend is also strongly dependent on the substituents surrounding the Lewis acidic center. To verify the trend with a given group, we first investigated the heavy analogues of $\text{B}(\text{C}_6\text{F}_5)_3$: $\text{Al}(\text{C}_6\text{F}_5)_3$, $\text{Ga}(\text{C}_6\text{F}_5)_3$, and $\text{In}(\text{C}_6\text{F}_5)_3$.^{[35],[36]} These Lewis acids are intriguing as their reactivity is drastically different – particularly $\text{Al}(\text{C}_6\text{F}_5)_3$ is known to be a highly reactive species.^[37] Nevertheless, the FLA method provided LAUs of 28.82, 25.65 and 22.74 for the Al, Ga, and In species, respectively. These values make all of these Lewis acids weaker than $\text{B}(\text{C}_6\text{F}_5)_3$, which agrees with the periodic trends, but conflicts with some observed experimental evidence that $\text{Al}(\text{C}_6\text{F}_5)_3$ is more reactive than $\text{B}(\text{C}_6\text{F}_5)_3$.^[38] A possible explanation for this observation could be the unique ability of $\text{Al}(\text{C}_6\text{F}_5)_3$ to form stable adducts with even very weak donor molecules,^[39] which supports the sensitivity of our method.

Subsequently, we analyzed several heavier main-group congeners with halide and triflate substituents and found that the FLA method again provides reliable results. The results were as follows: AlOTf_3 (30.31), GaCl_3 (29.39), AlCl_3 (28.89), GaOTf_3 (27.85), Ga_2Cl_4 (27.77), AlBr_3 (27.28), InBr_3 (27.07), InOTf_3 (26.99), and $\text{Ga}(\text{NO}_3)_3$ (17.65) (Figure 6). While the determined trend does not clearly distinguish between the substituents around the center atom, it nevertheless confirms the decreasing Lewis acidity down the group. Interestingly, our method was able to probe Ga_2Cl_4 , which has been shown to catalyze C-H type activations.^[40] This species can be represented as either the divalent Ga_2Cl_4 or as the mix-valent ionic $[\text{Ga}][\text{GaCl}_4]$ and exhibits a lower LAU than that of GaCl_3 (Figure 6). Since the obtained LAU value is close to that of GaOTf_3 , it is prudent to assume that the ionic form is more likely to exist in toluene solution.

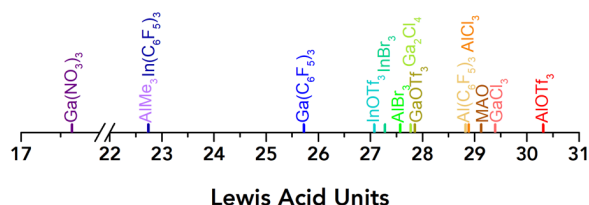


Figure 6. LAUs of heavier group 13 species.

With our FLA method successfully matching the expected trends for a large group of Lewis acids so far, we then sought to push the boundaries further. We previously reported the Lewis acidity of AlMe₃ (LAU = 22.73) and thought it would be a highly valuable endeavor to provide some insight into the Lewis acidity of methylaluminoxane (MAO). MAO is a key co-catalyst for organometallic olefin polymerization, but the structure still remains a “black box” to date.^[41] The chloride ion binding energy has previously been calculated showing that MAO will more strongly bind chloride than AlMe₃.^[42] This could indirectly be related to Lewis acidity, but no further experimental approaches have been made to measure the Lewis acidity of MAO. Using our FLA approach, we were able to successfully determine the Lewis acidity of MAO, again showing the robustness of this method. MAO has a LAU of 29.13, thus making it a stronger Lewis acid than AlMe₃ (Figure 6) and putting it on-par with the commonly used borane co-catalysts for olefin polymerization.

Cationic Lewis Acids

Cationic Lewis acids are generally much stronger than their neutral counterparts. Consequently, experimentally assessing Lewis acidity (other than via *in silico* methods) has been met with major challenges so far. To better understand the impact of a charge on Lewis acidity, we investigated the borinium cation [Mes₂B]⁺ (used as [Mes₂B][B(C₆F₅)₄]).^{[43],[44]} This stable species has been shown to possess exceptional Lewis acidity, providing unprecedented reactivity with CO₂ and H₂. Due to its high reactivity, the Lewis acidity of this species could not be established to date. However, we were able to clearly determine a LAU of 31.59 with our FLA method, stronger than all neutral boranes tested. This number is in line with the thermodynamic stability provided by the sterically bulky mesityl substituents. With this success, we expanded our studies to other mono- and dicationic Lewis acids. For this study, we focused mainly on exploring highly Lewis-acidic group 13, 14, and 15 species (Figure 7). It should be noted that the group-15 Lewis acidity is

derived from σ^* orbitals that is distinct from the group 13 and 14 Lewis acids with empty p orbitals. Given these fundamental differences, we sought to explore, if the FLA method could be applied to these systems as well.

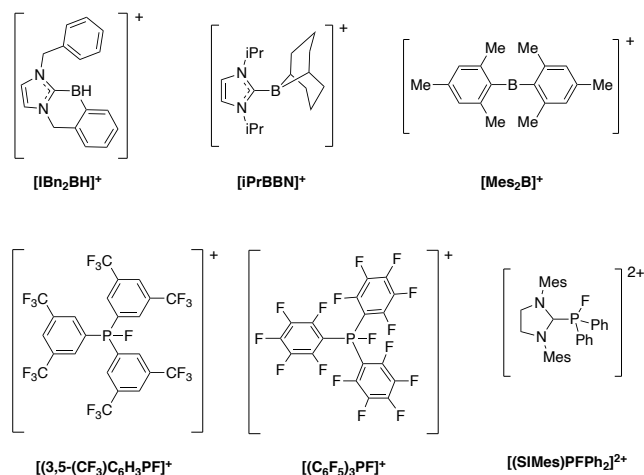


Figure 7. Cationic Lewis acids investigated.

In addition to $[\text{Mes}_2\text{B}][\text{B}(\text{C}_6\text{F}_5)_4]$, we explored two previously reported N-heterocyclic carbene stabilized borenium cations, $[\text{IBn}_2\text{BH}]^+$ (IBn = 1,3-dibenzylimidazol-2-ylidene) and $[(\text{iPr}_2)(\text{BC}_8\text{H}_{14})][\text{B}(\text{C}_6\text{F}_5)_4]$ ($[\text{iPrBBN}]^+$) (Chart 3).^{[45],[46]} We were able to determine that their Lewis acidities increase in the order: $[\text{Mes}_2\text{B}]^+ < [\text{IBn}_2\text{BH}]^+ < [\text{iPrBBN}]^+$ with LAUs of 31.59, 32.97, and 34.54 respectively (Figure 8). Of the borenium cations, only $[\text{iPrBBN}]^+$ has previously been measured. Ingleson and co-workers explored the hydride ion affinity of a series of borenium cations at the M06-2X/6-311G(d,p) level of theory and noted that this Lewis acid has a higher hydride affinity than $\text{B}(\text{C}_6\text{F}_5)_3$.^[47] If this is to be taken as a measure of Lewis acidity, then our FLA method supports this result. Even though $[\text{Mes}_2\text{B}]^+$ has been reported to have the most unique reactivity, it is in fact, the weakest of the three boron-based cations according to the FLA method. This may be due to the significant steric protection provided by the mesityl substituents.

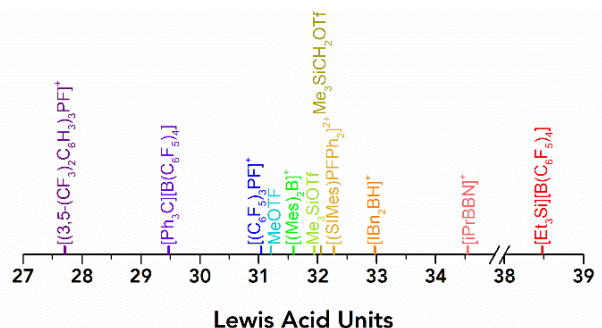


Figure 8. LAUs of cationic Lewis acids.

We also revisited several cationic group 14 Lewis acids, which were covered in our original study. $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$, Me_3SiOTf , and $[\text{Et}_3\text{Si}][\text{B}(\text{C}_6\text{F}_5)_4]$ all remain in the same relative order with the revised method, with LAUs of 29.47, 31.94, and 38.48, respectively. As an expansion, we then explored the Lewis acidity of other pseudo-carbocations such as MeOTf and $\text{Me}_3\text{SiCH}_2\text{OTf}$. While these species are predominantly known as alkylating reagents, they could in theory still provide an estimate for the Lewis acidity of the “free” CH_3^+ and $\text{Me}_3\text{SiCH}_2^+$ cations. Interestingly, the FLA method was able to handle these reagents and LAUs of 31.20 and 32.01 were determined, respectively (Figure 8). These numbers provide an interesting baseline as Lewis acids that generate higher LAUs would in theory be a stronger than simple methyl cations in solution.

For group 15 Lewis acids, we focused our attention on electrophilic phosphoniums cations (EPCs).^[2] Due to the nature of these Lewis acids, determining the Lewis acidity experimentally has proven difficult to date. We began with $[(\text{C}_6\text{F}_5)_3\text{PF}][\text{B}(\text{C}_6\text{F}_5)_4]$ and found a Lewis acidity of 31.04 LAU. This agrees well with the experimental data obtained so far, as it has been reported to be a stronger Lewis acid than $\text{B}(\text{C}_6\text{F}_5)_3$ but weaker than $[\text{Et}_3\text{Si}][\text{B}(\text{C}_6\text{F}_5)_4]$. Encouragingly, we were also able to apply our method to EPCs, whose Lewis acidity could not be determined directly before. The Lewis acid $[(3,5\text{-(CF}_3)_2\text{C}_6\text{H}_3\text{PF}][\text{B}(\text{C}_6\text{F}_5)_4]$ was indirectly found to be a weaker Lewis acid than $[(\text{C}_6\text{F}_5)_3\text{PF}][\text{B}(\text{C}_6\text{F}_5)_4]$, but unfortunately this Lewis acid reacts with Et_3PO .^[48] Gratifyingly, this Lewis acid is compatible with our FLA method – again highlighting the exceptional robustness of our method. It was found to have a Lewis acidity of 27.57 LAU, indicating it is indeed a weaker Lewis acid than $[(\text{C}_6\text{F}_5)_3\text{PF}][\text{B}(\text{C}_6\text{F}_5)_4]$. Finally, with the group 15 EPCs, we also have the ability to test dicationic Lewis acids. Through a series of competition experiments the dicationic Lewis acid $[(\text{SIMes})\text{PFPh}_2][\text{B}(\text{C}_6\text{F}_5)_4]_2$ ($\text{SIMes} = 1,3\text{-dimesitylimidazolidin-2-ylidene}$) was reported to be one of the strongest EPC Lewis acids.^[49] Direct measurement was previously not possible due to decomposition. Once again, the FLA method proved robust enough to measure the Lewis acidity of this highly reactive species, resulting in a LAU of 32.13, making it the strongest EPC to date, supporting the literature data (Figure 8).

Donor-Acceptor, Metal, and Cationic Group 16 Lewis Acids

Lastly, we investigated the ability of the FLA method to establish the Lewis acidity of donor-acceptor Lewis acids, metals, and cationic Group 16 systems (Figure 9). Donor-acceptor Lewis

acids are defined as having one or more adjacent substituents with a lone-pair that can partially quench the Lewis acidity. To evaluate the gradual reduction of Lewis acidity from neighboring donor atoms, we have tested Ph_2NBMe_2 and Ph_2PBMe_2 . These species are expected to be very weak Lewis acids and periodic trends predict a stronger orbital overlap in the B-N species. This is clearly reflected by the measured Lewis acidity with LAUs of 13.86 and 14.10 for the nitrogen and phosphorus species, respectively. The difference in Lewis acidity is marginal, yet measurable. Increasing the Lewis acidity of the boron center is possible through the introduction of pentafluorophenyl substituents leading to a LAU of 15.17 for $\text{Ph}_2\text{NB}(\text{C}_6\text{F}_5)_2$. The influence of the donor nitrogen atom can clearly be visualized by comparing the Lewis acidity to that of Piers' borane $\text{HB}(\text{C}_6\text{F}_5)_2$ (LAU = 28.64), confirming a considerable N-B double bond character in $\text{Ph}_2\text{NB}(\text{C}_6\text{F}_5)_2$.

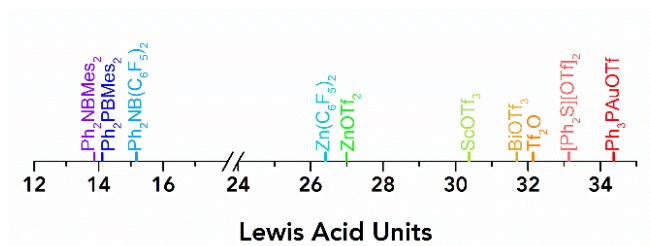


Figure 9. LAUs of donor-acceptor, metal, and cationic group 16 Lewis acids.

With this study, we did not want to neglect group 16, as some cationic chalcogens exhibit Lewis-acidic behavior as well, but they are not abundant in the literature.^[50] One sulfur(IV) dicationic species in particular, which can be prepared *in situ* from Ph_2SO and Tf_2O , has been found to mediate the arylation of carbonyls.^[51] *In situ* generation of the sulfuranylenium (IV) Lewis acid, $[\text{Ph}_2\text{S}][\text{OTf}]_2$ results in an LAU = 32.05. As a control, we also tested Tf_2O to compare any differences, although it is technically not a Lewis acid. As expected, we found that Tf_2O (LAU = 32.05) is slightly weaker than $[\text{Ph}_2\text{S}][\text{OTf}]_2$ (LAU = 33.12). It should be noted that we cannot discern whether the sulfuranylenium(IV) is of the form $[\text{Ph}_2\text{S}][\text{OTf}]_2$ or $[\text{Ph}_2\text{SOTf}][\text{OTf}]$, but it is irrelevant in so far that the relative Lewis acidity in solution is measured. Qualitatively, it is one of the stronger Lewis acids in our collection, and its acidity is in line with the other tested cationic species.

Though we have primarily focused on main-group Lewis acids so far, transition metals are intrinsically Lewis acidic, but their reactivity is more complex given the complications of different

redox states and accessible d-orbitals. Notwithstanding, transition metals have an established reactivity. They enable many catalytic transformations and so their Lewis acidity based on our method serves as a good comparison. We therefore selected a representative mix of transition metals with either filled (Zn, Au) or empty (Sc) d-shell configurations, as well as a catalytically active main group metal.

Zinc species such as $\text{Zn}(\text{C}_6\text{F}_5)_2$ (LAU = 26.16) and $\text{Zn}(\text{OTf})_2$ (LAU = 26.48) show considerable Lewis acidity, but interestingly the organozinc species is slightly less Lewis acidic than the more ionic compound. Based on earlier observations, a C_6F_5 motif induces high Lewis acidity and would de-shield the Zn center more than other electron-withdrawing groups. This is an ideal contrast between inductive effects and a formal charge, as $\text{Zn}(\text{OTf})_2$ is likely accessible as a Lewis acid in the form $[\text{Zn}(\text{OTf})]^+$. On the other hand, $\text{Sc}(\text{OTf})_3$ (LAU = 30.37), being a d^0 complex, is evidently much stronger than $\text{Zn}(\text{OTf})_2$, due to the filled d-shell in the latter (Figure 9).

Finally, bismuth-catalyzed transformations have been gaining recent attention.^[52] While technically a pnictogen, Bi nevertheless exhibits a very strong metallic character, which justifies its inclusion in this section. Recently, $\text{Bi}(\text{OTf})_3$ has found application as a water-compatible Lewis acid catalyst^[53] and our FLA method supports its highly Lewis acidic character with a measured LAU of 31.69. Cationic gold(I) species are also garnering increased attention in a catalysis context. These have found vast application in organic synthesis, particularly in the activation of alkyne substrates.^[54] This activation motif requires a very strong Lewis acidic metal center and we representatively investigated the complex Ph_3PAuOTf as a model compound as part of this study. To our satisfaction, we were able to determine that this is indeed a very strong Lewis acid with a LAU of 34.37 (Figure 9). As a control to ensure that we are measuring the Lewis acidity of the cationic Au complex, we also examined the Lewis acidity of Ph_3PAuCl with the FLA method, but this species was too weak to be detected (Supporting Info).

Conclusion

In conclusion, we have provided a considerable improvement for the measurement of Lewis acidity. Our previously introduced method that leverages the red shift of Fluorescent Lewis Adducts (FLAs), provided a strong foundation toward a unified Lewis acidity scale, but also

revealed some areas for improvement, which are addressed in this article. By taking a vector-based approach that incorporates both the x and y coordinates of the CIE diagram, we were able to get more accurate measurements and concurrently better resolution for Lewis acidic species of similar strength. In order to validate the strength and robustness of our refined method, we were able to evaluate an exhaustive list of representative Lewis acids (Figure 10). Species investigated include neutral and charged main group species, transition metals, as well as unique hypervalent compounds, whose Lewis acidity is based on anti-bonding orbitals. Notably, several of the evaluated species could not be measured experimentally before, due to their high reactivity. The most notable species include MAO, $[\text{Mes}_2\text{B}]^+$, as well as fluorophosphonium cations and dications. From this extended study, it is clear that our method is very powerful, as being able to unify very different types of Lewis acids – in terms of chemical composition and reactivity – which had not been possible with any of the established methodologies. We are currently further expanding the scope of the FLA method by expanding it to other Lewis acids that have shown high practical value for chemical syntheses. We are also looking at other important features that impact Lewis acidity, such as solvent polarity, as our studies so far have exclusively focused on toluene solutions. These studies will be reported in due course.

Experimental

The synthesis of the dithienophosphole oxide probes has previously been reported (see Supporting Info for references). All previously known Lewis acids tested were either purchased from Sigma-Aldrich or prepared via literature procedures (see references throughout the manuscript); $(\text{C}_6\text{F}_5)_2\text{BNPh}_2$ is a new compound and full details can be found in the Supporting Information.

All samples for optical spectroscopy measurements were prepared in an inert-atmosphere glovebox under $\text{N}_{2(g)}$. A 0.025 mM stock solution of each probe was prepared by serial dilution in toluene. Lewis acids in stock solutions, such as BF_3OEt_2 and BCl_3 , were applied to the probe solution using Schlenk techniques, followed by cuvette sample preparation in the glovebox. All other Lewis acids were prepared to final concentrations of either 0.125 mM or 0.25 mM in toluene. For FLAs that required a large excess of Lewis acid to reach full saturation, their emission spectra were used to establish the number of equivalents required (see SI). Lewis acids of low solubility were added directly to the probe solutions in excess, then sonicated to form the FLAs. Following formation of the FLA, cuvettes were capped with a Teflon seal inside the glovebox and wrapped

with parafilm. Optical spectroscopy measurements were performed immediately upon the removal of cuvettes from the glovebox.

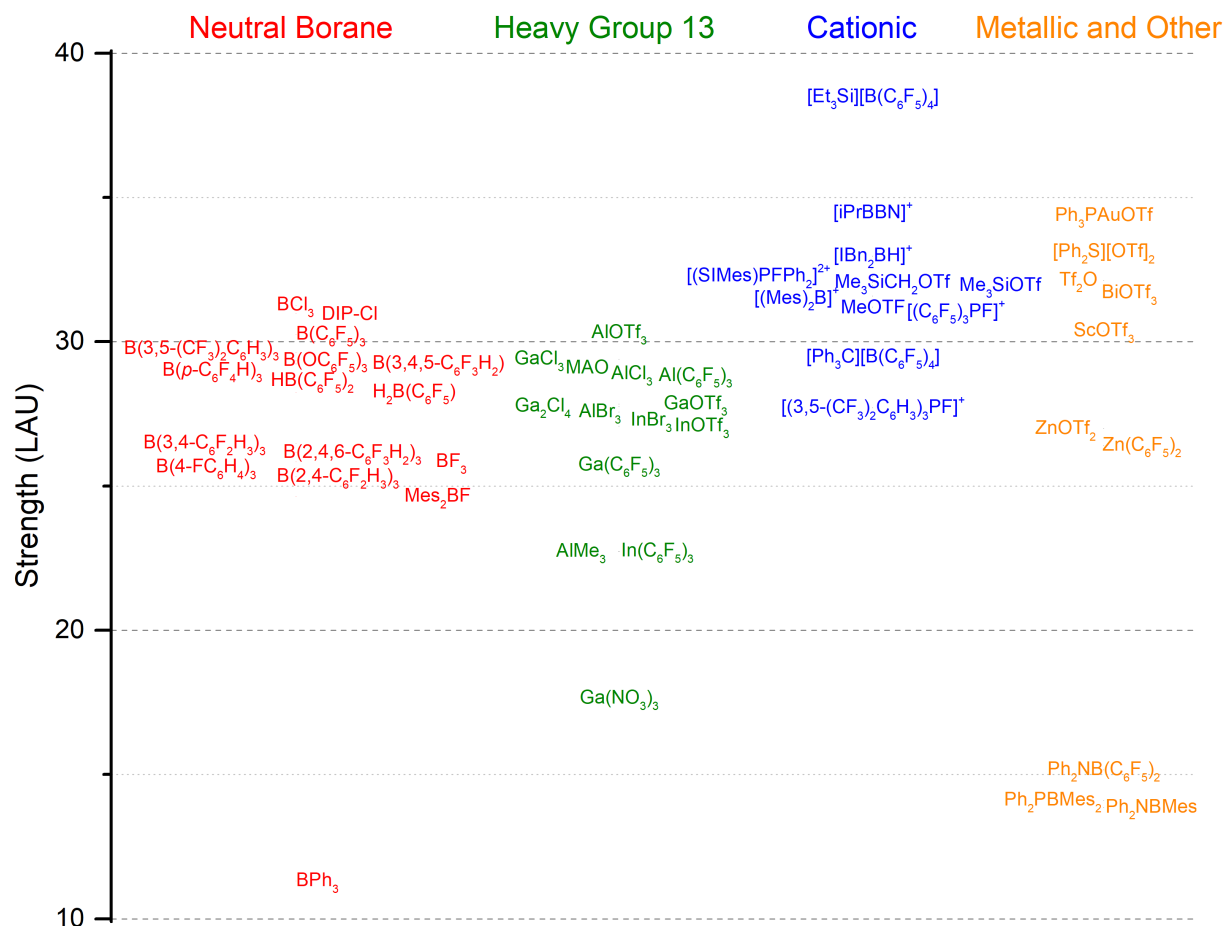


Figure 10. LAU values of all Lewis acids measured relative to one another.

Acknowledgements

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References

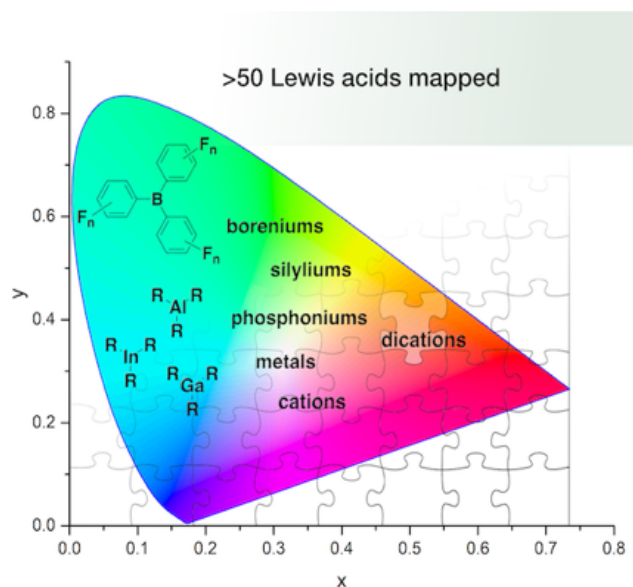
- [1] G. N. Lewis, *J. Am. Chem. Soc.* **1916**, *38*, 762–785.
- [2] C. B. Caputo, L. J. Hounjet, R. Dobrovetsky, D. W. Stephan, *Science* **2013**, *341*, 1374–1377.

- [3] B. Pan, F. P. Gabbaï, *J. Am. Chem. Soc.* **2014**, *136*, 9564–9567.
- [4] T. W. Hudnall, Y.-M. Kim, M. W. P. Bebbington, D. Bourissou, F. P. Gabbaï, *J. Am. Chem. Soc.* **2008**, *130*, 10890–10891.
- [5] H. Yamamoto, *Lewis Acids in Organic Synthesis*. Wiley-VCH, **2008**.
- [6] D. W. Stephan, *Science* **2016**, *354*, aaf7229.
- [7] *Main Group Strategies towards Functional Hybrid Materials* (Eds.: T. Baumgartner, F. Jäkle), Wiley, **2017**.
- [8] M. Oestreich, J. Hermeke, J. Mohr, *Chem. Soc. Rev.* **2015**, *44*, 2202–2220.
- [9] M. A. Légaré, M. A. Courtemanche, É. Rochette, F. G. Fontaine, *Science* **2015**, *349*, 513–516.
- [10] U. Mayer, V. Gutmann, W. Gerger, *Monatshefte Chem.* **1975**, *106*, 1235–1257.
- [11] M. A. Beckett, G. C. Strickland, J. R. Holland, K. S. Varma, *Polymer* **1996**, *37*, 4629–4631.
- [12] R. F. Childs, D. L. Mulholland, A. Nixon, *Can. J. Chem.* **1982**, *60*, 801–808.
- [13] K. O. Christe, D. A. Dixon, D. McLemore, W. W. Wilson, J. A. Sheehy, J. A. Boatz, *J. Fluor. Chem.* **2000**, *101*, 151–153.
- [14] H. Böhrer, N. Trapp, D. Himmel, M. Schleep, I. Krossing, *Dalton Trans.* **2015**, *44*, 7489–7499.
- [15] L. Greb, *Chem. Eur. J.* **2018**, *24*, 17881–17896.
- [16] J. R. Gaffen, J. N. Bentley, L. C. Torres, C. Chu, T. Baumgartner, C. B. Caputo, *Chem* **2019**, *5*, 1567–1583.
- [17] Y. Dienes, M. Eggenstein, T. Kárpáti, T. C. Sutherland, L. Nyulászi, T. Baumgartner, *Chem. Eur. J.* **2008**, *14*, 9878–9889.
- [18] Y. Dienes, S. Durben, T. Kárpáti, T. Neumann, U. Englert, L. Nyulászi, T. Baumgartner, *Chem. Eur. J.* **2007**, *13*, 7487–7500.
- [19] J. Stewart, *Single Variable Calculus: Early Transcendentals* (Eighth Edition). Boston, MA, USA: Cengage Learning, **2016**
- [21] I. B. Sivaev, V. I. Bregadze, *Coord. Chem. Rev.* **2014**, *270–271*, 75–88.
- [21] B. L. Durfey, T. M. Gilbert, *Inorg. Chem* **2011**, *50*, 7871–7879.
- [22] J. R. Lawson, R. L. Melen, *Inorg. Chem.* **2017**, *56*, 8627–8643.
- [23] D. Mukherjee, D. F. Sauer, A. Zanardi, J. Okuda, *Chem. Eur. J.* **2016**, *22*, 7730–7733.

- [24] J. R. Lawson, L. C. Wilkins, R. L. Melen, *Chem. Eur. J.* **2017**, *23*, 10997–11000.
- [25] Q. Yin, Y. Soltani, R. L. Melen, M. Oestreich, *Organometallics* **2017**, *36*, 2381–2384.
- [26] J. A. Nicasio, S. Steinberg, B. Inés, M. Alcarazo, *Chem. Eur. J.* **2013**, *19*, 11016–11020.
- [27] R. J. Blagg, T. R. Simmons, G. R. Hatton, J. M. Courtney, E. L. Bennett, E. J. Lawrence, G. G. Wildgoose, *Dalton Trans.* **2016**, *45*, 6032–6043.
- [28] Y. Seo, J. M. Lowe, M. R. Gagné, *ACS Catal.* **2019**, *9*, 6648–6652.
- [29] T. A. Bender, P. R. Payne, M. R. Gagné, *Nature Chem.* **2018**, *10*, 85–90.
- [30] G. J. P. Britovsek, J. Ugoletti, A. J. P. White, *Organometallics* **2005**, *24*, 1685–1691.
- [31] R. C. Neu, E. Y. Ouyang, S. J. Geier, X. Zhao, A. Ramos, D. W. Stephan, *Dalton Trans.* **2010**, *39*, 4285–4294.
- [32] G. Ménard, D. W. Stephan, *Dalton Trans.* **2013**, *42*, 5447–5453.
- [33] W. E. Piers, T. Chivers, *Chem. Soc. Rev.* **1997**, *26*, 345–354.
- [34] We confirmed that at high concentrations required to reach saturation with a weak Lewis acid, B(4-FC₆H₄)₃ aggregates and starts to emit white light (Supporting Info).
- [35] Y. Ning,; E. Y.-X. Chen, *Macromolecules* **2006**, *39*, 7204–7215.
- [36] M. Xu, J. Possart, A. E. Waked, J. Roy, W. Uhl, D. W. Stephan, *Phil. Trans. R. Soc. A* **375**: 20170014.
- [37] J. Chen, E. Y.-X. Chen, *Angew. Chem.* **2015**, *127*, 6946–6950; *Angew. Chem. Int. Ed.* **2015**, *54*, 6842–6846.
- [38] A. Y. Timoshkin, G. Frenking, *Organometallics* **2008**, *27*, 371–380.
- [39] J. Chen, E. Y.-X. Chen, *Dalton Trans.* **2016**, *45*, 6105–6110.
- [40] Z. Li, G. Thiery, M. R. Lichtenthaler, R. Guillot, I. Krossing, V. Gandon, C. Bour, *Adv. Synth. Catal.* **2018**, *360*, 544–549.
- [41] E. Y.-X. Chen, T. J. Marks, *Chem. Rev.* **2000**, *100*, 1391–1434.
- [42] T. Yamasaki, *Catal. Today* **1995**, *23*, 425–429.
- [43] K. L. Bamford, Z.-W. Qu, D. W. Stephan, *J. Am. Chem. Soc.* **2019**, *141*, 6180–6184.
- [44] Y. Shoji, N. Tanaka, K. Mikami, M. Uchiyama, T. Fulushima, *Nature Chem.* **2014**, *6*, 498–503.
- [45] J. M. Farrell, D. W. Stephan, *Angew. Chem.* **2015**, *127*, 5303–5306; *Angew. Chem. Int. Ed.* **2015**, *54*, 5214–5217.
- [46] J. M. Farrell, J. A. Hatnean, D. W. Stephan, *J. Am. Chem. Soc.* **2012**, *134*, 15728–15731.

- [47] E. R. Clark, A. Del Grosso, M. J. Ingleson, *Chem. Eur. J.* **2013**, *19*, 2462–2466.
- [48] J. H. W. LaFortune, K. M. Szkop, F. E. Farinha, T. C. Johnstone, S. Postle, D. W. Stephan, *Dalton Trans.* **2018**, *46*, 11411–11419.
- [49] M. H. Holthausen, M. Mehta, D. W. Stephan, *Angew. Chem.* **2014**, *126*, 6656–6659; *Angew. Chem. Int. Ed.* **2014**, *53*, 6538–6541.
- [50] F. A. Tsao, A. E. Waked, L. Cao, J. Hofmann, L. Liu, S. Grimme, D. W. Stephan, *Chem. Commun.* **2016**, *52*, 12418–12421.
- [51] X. Huang, M. Patil, C. Farè, W. Thiel, N. Maulide, *J. Am. Chem. Soc.* **2013**, *135*, 7312–7323.
- [52] T. Ollevier, *Org. Biomol. Chem.* **2013**, *11*, 2740–2755.
- [53] S. Kobayashi, C. Ogawa, *Chem. Eur. J.* **2006**, *12*, 5954–5960.
- [54] D. Pflästerer, A. S. K. Hashmi, *Chem. Soc. Rev.* **2016**, *45*, 1331–1367.

TOC Figure



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Fluorescent Lewis Adducts: A Refined Guide for Lewis Acidity

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1. General Considerations, Materials, and Instrumentation

All manipulations were performed using an MBraun LABstar Glove Box Workstation under N₂ atmosphere or by employing Schlenk techniques. All glassware was oven-dried at 110 °C before being transferred into the glove box. Solvents were prepared from an MBraun MB-SPS 800 solvent drying system under N₂ atmosphere. Compounds **1–8** were synthesized according to literature procedures.^{S1,S2,S3,S4} Chloroform-d and benzene-d₆ were transferred to Strauss flasks and dried over activated molecular sieves, then degassed using freeze-pump-thaw techniques, followed by immediate transfer to the glovebox. Experiments monitored by NMR spectroscopy were conducted in NMR tubes (8" x 5 mm) sealed with standard plastic caps and wrapped with Parafilm. ¹H, ¹¹B, ¹³C{¹H}, and ¹⁹F{¹H}, and ³¹P{¹H} NMR spectra were acquired at 25 °C on either a Bruker 700 MHz Spectrometer, Bruker DRX 600 MHz Spectrometer, Bruker ARX 400 MHz Spectrometer, or Bruker ARX 300 MHz Spectrometer. Chemical shifts are reported relative to SiMe₄ and referenced to the residual solvent signal (¹H, ¹³C{¹H}) to CDCl₃ (δ 7.26, 77.16 ppm). ¹¹B and ¹⁹F{¹H} NMR spectra were referenced relative to 15% BF₃•Et₂O. ³¹P{¹H} NMR spectra were referenced relative to H₃PO₄. NMR spectra were analyzed using either TopSpin 4.0.1 or MestReNova 6.0.2-5475 software. Chemical shifts are reported in ppm and coupling constants as scalar values in Hz. The conventional abbreviations were used as follows: s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublets), m (multiplet), br (broad). Absorption measurements were recorded with a Cary 5000 UV-Vis-NIR Spectrophotometer from Agilent Technologies. Recordings were obtained at 25 °C and taken with the instrument operating in single beam mode and referenced to toluene. Emission and excitation measurements were recorded with an Edinburgh Instruments FS5 fluorescence spectrometer. Emission spectra were excited at their respective absorption maxima. All absorption and fluorescence experiments were conducted in quartz cuvettes (1 cm x 1 cm) equipped with a Teflon seal.

2. FLA Method 101 (From acid to LAU) – A step-by-step guide.

Begin by generating a solution of the Lewis acid and one of the eight dithienophosphole oxide probes in toluene. Ensure to afford complete mixing. For a single measurement, the sample only needs to be of typical concentration for photophysical measurements (~1e-5 M). The Lewis acid, however, must be added in sufficient amount to saturate the Lewis base so that the only fluorescent species in solution is the FLA. Be aware that, while strong Lewis acids typically require near 1:1 stoichiometry with the probe, weak Lewis acids may require up to several thousand equivalents to generate a saturated solution. Saturation concentrations can be determined precisely as described in our original manuscript on this method⁴ but are typically not necessary. The absorbance spectrum must then be measured for the FLA solution. This will provide both the excitation wavelength and may indicate if an additional species may be present in solution, which may invalidate the measurement. The emission spectrum can then be

^{S1} *Angew. Chem. Int. Ed.* **2004**, *45*, 6197-6201.

^{S2} *Chem. Eur. J.* **2005**, *11*, 4687-4699.

^{S3} *Chem. Eur. J.* **2007**, *13*, 7487-7500.

^{S4} *Chem* **2019**, *5*, 1567-1583.

measured, from which the chromaticity is derived. An excitation spectrum may be collected to assess if any additional emissive species are present which may invalidate the measurement. Repeat the process with the same Lewis acid, but replace the dithienophosphole oxide probe with one of the other seven. At least three separate measurements must be taken with three distinct probes, however, more may be used to ensure internally consistent data. Record the chromaticity values as the x and y coordinates generated for the 1931 CIE space and use a graphing or analysis software, such as OriginLab's Origin or Microsoft Excel, to generate a polynomial fit of second order (parabola) to the data. Using the parameters of the fit equation that was generated, find the intersection between this curve and the parabolic fit of the dithienophosphole oxide probes, Equation S1 below. This can be performed by setting the two equations equal, and either solving the quadratic equation for the zeros of the resultant equation, or by using an equation solving software such as Wolfram Mathematica or WolframAlpha online. The solution generates two intercepts, from which the right-most (larger) will be used for the remaining calculations. This is the x-coordinate of the intersection between the two trends, the y coordinate can be calculated by solving either the dithienophosphole oxide fit function, or the FLA fit function at this x value (they should be identical). The x and y coordinates are the chromaticity value of the adduct between the Lewis acid being measured and a "theoretical dithienophosphole oxide" of a specific strength so that the adduct saturated the base in a 1:1 ratio. Use the Equation S2, below, with the x and y coordinates obtained to generate the Lewis acid strength in LAUs.

$$y = -14.41928x^2 + 9.6074x - 0.98523 \quad \text{Eq. S1}$$

$$\text{Strength} = \frac{\sqrt{(x-0.33314)^2 + (y-0.61495)^2}}{\sqrt{(x-0.511)^2 + (y-0.16409)^2}} * 100 \quad \text{Eq. S2}$$

3. Chromaticity Data and LAUs

Table S1 Chromaticity data of all Lewis acids tested. Strength is reported in Lewis acid units; x and y corresponds to the chromaticity x-coordinate and y-coordinate respectively at the FLA fit/probe fit intercept; green vector is the magnitude of the vector from intersection to the weakest FLA measurable; red vector is the magnitude of the vector from the intersection to the strongest FLA measurable.

Lewis Acid	Strength	x	y	Green Vector	Red Vector
BPh ₃	11.31	0.37634	0.5882	0.05088	0.44986
Ph ₂ NBMes ₂	13.86	0.38274	0.57963	0.06097	0.43978
Ph ₂ PBMes ₂	14.10	0.3833	0.57883	0.06189	0.43885
Ph ₂ NB(C ₆ F ₅) ₂	15.17	0.38569	0.57528	0.06593	0.43475
Ga(NO ₃) ₃	17.65	0.39085	0.56708	0.07507	0.42543
Al(Me) ₃	22.73	0.39988	0.55088	0.09261	0.40736
In(C ₆ F ₅) ₃	22.74	0.39989	0.55085	0.09264	0.40733
Mes ₂ BF	22.74	0.39989	0.55085	0.09264	0.40733
B(2,4-C ₆ H ₂ H ₃) ₃	24.64	0.40283	0.54507	0.09879	0.40096
B(4-C ₆ FH ₄) ₃	25.32	0.40385	0.54301	0.10097	0.39871
Ga(C ₆ F ₅) ₃	25.65	0.40432	0.54204	0.102	0.39765
BF ₃ ·Et ₂ O	25.72	0.40443	0.54182	0.10223	0.39741
B(2,4,6-C ₆ F ₃ H ₂) ₃	25.84	0.4046	0.54148	0.10259	0.39703
Zn(C ₆ F ₅) ₂	26.16	0.40505	0.54054	0.10358	0.39601
B(3,4-C ₆ F ₂ H ₃) ₃	26.41	0.40541	0.53979	0.10437	0.39519
ZnOTf ₃	26.48	0.40551	0.53958	0.10459	0.39496
InOTf ₃	26.99	0.40622	0.5381	0.10615	0.39335
InBr ₃	27.07	0.40634	0.53784	0.10642	0.39306
AlBr ₃	27.28	0.40662	0.53724	0.10705	0.39241
[(3,5-(CF ₃) ₂ C ₆ H ₃ PF)][B(C ₆ F ₅) ₄]	27.57	0.40702	0.53639	0.10794	0.39149
Ga ₂ Cl ₄	27.77	0.40729	0.53582	0.10855	0.39086
GaOTf ₃	27.85	0.4074	0.53559	0.10879	0.39061
H ₂ B(C ₆ F ₅)	28.25	0.40793	0.53445	0.10998	0.38937
HB(C ₆ F ₅) ₂	28.64	0.40845	0.53332	0.11117	0.38814
Al(C ₆ F ₅) ₃	28.82	0.40869	0.5328	0.11172	0.38757
AlCl ₃	28.89	0.40877	0.53262	0.1119	0.38738
MAO	29.13	0.40908	0.53194	0.11261	0.38664
B(<i>p</i> -C ₆ F ₄ H) ₃	29.23	0.40922	0.53165	0.11292	0.38632
B(3,4,5-C ₆ F ₃ H ₂) ₃	29.24	0.40923	0.53162	0.11295	0.38629
B(OC ₆ F ₅) ₃	29.35	0.40937	0.5313	0.11328	0.38595
GaCl ₃	29.39	0.40943	0.53118	0.11341	0.38582
[Ph ₃ C][B(C ₆ F ₅) ₄]	29.47	0.40952	0.53097	0.11362	0.3856
B(3,5-(CF ₃) ₂ C ₆ H ₃) ₃	29.63	0.40973	0.53052	0.11409	0.38511
B(C ₆ F ₅) ₃	30.25	0.41052	0.52877	0.11593	0.3832
AlOTf ₃	30.31	0.4106	0.5286	0.1161	0.38302
ScOTf ₃	30.37	0.41067	0.52843	0.11628	0.38284
(-)-B-chlorodiisopinocampheylborane	30.98	0.41142	0.52675	0.11803	0.38102
[(C ₆ F ₅) ₃ PF][B(C ₆ F ₅) ₄]	31.04	0.41149	0.52659	0.1182	0.38085

MeOTf	31.20	0.4117	0.52612	0.11868	0.38035
BCl ₃	31.27	0.41177	0.52594	0.11887	0.38015
[Mes ₂ B][B(C ₆ F ₅) ₄]	31.59	0.41216	0.52508	0.11978	0.37921
BiOTf ₃	31.69	0.41229	0.52478	0.12008	0.3789
[Me ₃ Si][OTf]	31.94	0.41258	0.52411	0.12078	0.37817
Me ₃ SiCH ₂ OTf	32.01	0.41266	0.52392	0.12098	0.37796
Tf ₂ O	32.05	0.41272	0.5238	0.12111	0.37784
[(SiMes)PFPh ₂][B(C ₆ F ₅) ₄]	32.13	0.41281	0.52358	0.12133	0.3776
IBn ₂ BH	32.97	0.41379	0.52132	0.12368	0.37516
[Ph ₂ S][OTf] ₂	33.12	0.41397	0.5209	0.12412	0.37471
PPh ₃ AuOTf	34.37	0.41538	0.51759	0.12755	0.37115
[(<i>i</i> Pr ₂)(BC ₈ H ₁₄)] [B(C ₆ F ₅) ₄]	34.54	0.41557	0.51712	0.12804	0.37065
[Et ₃ Si][B(C ₆ F ₅) ₄]	38.48	0.41971	0.50703	0.13846	0.35984

Table S2 Fit data of the parabolic functions generated where *a*, *b*, and *c* are the parameters of the parabolic fit ax^2+bx+c and R^2 is the root mean squared error of the fit function.

Lewis Acid	Strength	a	b	c	R ²
None	--	-14.41928	9.6074	-0.98523	0.984
BPh ₃	11.31	-11.84876	8.35913	-0.87952	0.998
Ph ₂ NBMes ₂	13.86	-10.52488	7.49106	-0.74218	0.924
Ph ₂ PBMes ₂	14.10	-12.36018	8.50915	-0.86679	1
Ph ₂ NB(C ₆ F ₅) ₂	15.17	-9.66448	7.35887	-0.82531	0.980
Ga(NO ₃) ₃	17.65	-7.18431	5.55326	-0.50591	1
Al(CH ₃) ₃	22.73	-4.95917	3.94981	-0.23558	1
In(C ₆ F ₅) ₃	22.74	-4.97452	3.96589	-0.23958	0.994
Mes ₂ BF	24.64	-4.76967	3.84351	-0.22923	0.997
B(2,4-C ₆ H ₂ H ₃) ₃	25.32	-4.33093	3.48901	-0.15967	0.994
B(4-C ₆ FH ₄) ₃	25.65	-4.53161	3.94483	-0.31213	0.997
Ga(C ₆ F ₅) ₃	25.72	-4.00857	3.24184	-0.11362	0.986
BF ₃ ·Et ₂ O	25.84	-4.36572	3.51542	-0.16619	0.998
B(2,4,6-C ₆ F ₃ H ₂) ₃	26.16	-4.01908	3.23405	-0.11002	0.991
Zn(C ₆ F ₅) ₂	26.41	-4.3631	3.58884	0.04649	0.995
B(3,4-C ₆ F ₂ H ₃) ₃	26.48	-4.00656	3.20468	-0.10112	0.990
ZnOTf ₃	26.99	-6.02409	4.96031	-0.48281	0.994
InOTf ₃	27.07	-4.13955	3.34113	-0.1363	0.997
InBr ₃	27.28	-3.91884	3.15079	-0.09599	0.981
AlBr ₃	27.57	-3.60988	2.86506	-0.03171	0.989
[(3,5-(CF ₃) ₂ C ₆ H ₃ PF)][B(C ₆ F ₅) ₄]	27.71	-1.86997	1.1851	0.3635	1
Ga ₂ Cl ₄	27.77	-3.6992	2.97442	-0.0199	0.988
GaOTf ₃	27.85	-4.11296	3.33473	-0.14033	0.994
H ₂ B(C ₆ F ₅)	28.25	-3.38934	2.70644	-0.00558	0.983
HB(C ₆ F ₅) ₂	28.64	-3.41092	2.72424	-0.01035	0.987
Al(C ₆ F ₅) ₃	28.82	-3.30385	2.65081	0.00127	0.986
AlCl ₃	28.89	-3.45971	2.77372	-0.0231	0.989
MAO	29.13	-3.62185	2.94486	-0.06664	0.985
B(<i>p</i> -C ₆ F ₄ H) ₃	29.23	-3.19367	2.52158	0.06369	0.988

B(3,4,5-C ₆ F ₃ H ₂) ₃	29.24	-3.43674	2.7394	-0.01388	0.977
B(OC ₆ F ₅) ₃	29.35	-3.91189	3.15698	-0.1055	0.983
GaCl ₃	29.39	-3.50377	2.81283	-0.03313	0.997
[Ph ₃ C][B(C ₆ F ₅) ₄]	29.47	-1.81185	1.14904	0.36428	0.997
B(3,5-(CF ₃) ₂ C ₆ H ₃) ₃	29.63	-3.14101	2.5007	0.03322	0.983
B(C ₆ F ₅) ₃	30.25	-2.92587	2.29836	0.07833	0.990
AlOTf ₃	30.31	-4.02818	3.31378	-0.15292	1
ScOTf ₃	30.37	-3.64527	2.97419	-0.07821	0.999
(-)-B-chlorodiisopinocampheylborane	30.98	-3.84172	3.10749	-0.10146	0.984
[(C ₆ F ₅) ₃ PF][B(C ₆ F ₅) ₄]	31.04	-1.92862	1.29272	0.32121	0.999
MeOTf	31.20	-2.97888	2.34242	0.06666	0.990
BCl ₃	31.27	-2.84	2.19778	0.1025	0.984
[Mes ₂ B][B(C ₆ F ₅) ₄]	31.59	-2.89022	2.27119	0.07996	0.993
BiOTf ₃	31.69	-3.05634	2.41371	0.04916	0.989
[Me ₃ Si][OTf]	31.94	-3.15361	2.50105	0.02904	0.994
Me ₃ SiCH ₂ OTf	32.05	-3.01768	2.38683	0.05273	0.993
Tf ₂ O	32.13	-3.20391	2.56855	0.00924	0.994
[(SiMes)PFPh ₂][B(C ₆ F ₅) ₄]	32.27	-2.41722	1.79047	0.19604	1
Bn ₂ IBH	32.97	-2.82547	2.19157	0.09825	1
[Ph ₂ S][OTf] ₂	33.12	-2.81368	2.19331	0.09512	0.998
PPh ₃ AuOTf	34.37	-3.03104	2.42355	0.03387	.997
[(IIPr ₂)(BC ₈ H ₁₄)] [B(C ₆ F ₅) ₄]	34.54	-3.40971	2.85151	-0.07903	0.992
[Et ₃ Si][B(C ₆ F ₅) ₄]	38.48	-2.956	2.43905	0.00406	1
PPh ₃ AuCl	--	-14.63509	9.80413	-1.03634	0.997

4. Limitations and Error Analysis

Chromaticity values across repeated experiments exhibited variance no higher than 1e-4. The sum of the RMS error of the typical fit function was on the scale of 1e-5 to 1e-4. The theoretical error of the parabola fit function, typically the result of utilizing a limited range of values to generate the fit function, ranged between 1% and 7% error. Data that poorly spans the parabola results in higher theoretical error, however this has no correlation between theoretical error and Lewis acid strength. Taking this into account, we proposed that Lewis acids with strength values within 0.25 LAU of one another are of equivalent effective strength in toluene, and strictly as a Lewis acid, may be interchangeable. This value was generated by removing the chromaticity data from one of the probes used in the fit function of a specific Lewis acid and determining the variance upon recalculating the strength of the Lewis acid using the reduced data set. The average variance was compared between samples to determine the 0.25 value above. An example of this process is shown below for both B(C₆F₅)₃ (average error 0.754 LAU) and the trityl cation (average error 0.198 LAU). In general, the average variance upon removing a single probe was approximately ± 0.5 LAU. The removal of some specific probes, however, lead to a substantial increase in error. This is typically due to the theoretical error afforded to a reduced data set. For example, probe **1** can be removed or replaced when the FLA with probe **4** was measured as both probes are strong bases that emit in the blue region, however, if no blue probe is used, the theoretical error increases drastically due to the poorly defined parabola. Similarly probes **3** and **8** can be exchanged as well as **2** and **7**. Note in the example below that the complete removal of a blue-region probe from the data for B(C₆F₅)₃ significantly increases the error,

and the resultant strength value is similarly decreased. However, the removal of a blue region probe from the data for the trityl cation results in a less substantial increase in error and the corresponding strength value is less impacted. As the removal of an individual probe impacts each Lewis acid fit function differently, the average variance was used. Note that $B(C_6F_5)_3$ exhibits an average error higher than 0.25 LAU. As an extreme example of the statement above, when probes **2** and **7** are removed, the resulting data set can be defined by a nearly linear fit. This affords a minimal fit error, but a significant error in the Lewis acid strength. Incorporating these data into the average error results in a skewed average error.

Table S3 Calculation of error in Lewis acid strength measurement upon removing individual probes when determining the strength of trityl cation and $B(C_6F_5)_3$.

Lewis acid	Removed Probe	Fit Error	Strength	Strength Error
$B(C_6F_5)_3$	None	1%	30.25	--
$B(C_6F_5)_3$	1	19%	15.67	48%
$B(C_6F_5)_3$	2	1%	27.80	8.1%
$B(C_6F_5)_3$	3	9%	30.09	0.5%
$B(C_6F_5)_3$	7	1%	35.99	19%
$B(C_6F_5)_3$	8	9%	30.07	0.5%
$[Ph_3C][B(C_6F_5)_4]$	None	3%	29.47	--
$[Ph_3C][B(C_6F_5)_4]$	2	15%	29.44	0.1%
$[Ph_3C][B(C_6F_5)_4]$	3	32%	30.73	4.3%
$[Ph_3C][B(C_6F_5)_4]$	7	7%	28.15	4.5%
$[Ph_3C][B(C_6F_5)_4]$	8	9%	30.31	2.9%

As an example of the relevance of this error analysis, a note regarding $ScOTf_3$ and $ZnOTf_2$. These two transition metal species were the only Lewis acids that underwent significant change to their relative strength when utilizing this new method in comparison to our original method. In brief, due to the poor solubility of the zinc species in toluene a peak corresponding to the scattering of the onset light could be detected. This scattering peak was particularly apparent when using probe **1**. This off-set the chromaticity toward blue and resulted in a weaker strength value. By utilizing additional probes, with which the scattering peak could be virtually eliminated without impacting the emission spectra, an appropriate strength value could be measured. The scandium species is an example of the difference between theoretical and experimental error. The FLA of $ScOTf_3$ and probes **1**, **2**, and **3** were used to fit the original parabola, however, as three points define a parabola no experimental error could be determined. The incorporation of an additional probe demonstrated that the FLA of $ScOTf_3$ and probe **3** fell off of the parabolic trend with the measured chromaticity shifted toward the free probe. This is typically an indication of a sub-saturated solution. By incorporating additional data points, a fit could be formed and the experimental error inherent in the original data could be discussed as the RMS error of the fit. Upon removal of the chromaticity data for the FLA with probe **3**, the strength value remains consistent with the newly reported value.

While this method has shown to be robust and able to easily measure the Lewis acidity of Lewis acids that are too reactive or troublesome for alternative methods, it is not without limitations. Phosphonium Lewis acids with a P-O-R moiety, such as $[(C_6F_5)_3P(OC_6F_5)]^+$, show signs of reactivity with several of the dithienophosphole oxide probes. Phosphonium cation Lewis acids lacking a P-O-R moiety, such as $[(3,5-(CH_3)_2C_6H_3)_3PF]^+$, do not exhibit this reactivity and can be measured appropriately as discussed.

5. Synthesis

Ph₂NB(C₆F₅)₂: Sodium hydride (51.9 mg, 2.16 mmol) was added to diphenylamine (182.9 mg, 1.08 mmol) in THF (10 mL) and stirred until the evolution of gas stopped. The solvent was removed *in vacuo* and the residue was suspended in dichloromethane (10 mL), followed by the dropwise addition of (C₆F₅)₂BCl (411.2 mg, 1.08 mmol); the reaction mixture was stirred for 12 h. The mixture was then filtered, concentrated, and then triturated with pentanes. The resulting precipitate was vacuum filtered to afford the product as a beige powder.

Yield 0.51 g (91%). C₂₄H₁₀BF₁₀N (513.08 g/mol): calcd %. C 56.18; H 1.96; N 2.73%; found C 56.24, H 2.66, N 3.08%.

¹H NMR (400 MHz, Benzene-*d*₆) δ: 6.96 (d, *J* = 5.4 Hz, 2H), 6.80 (t, 1H), 6.78 – 6.71 (m, 2H). ¹¹B NMR (128 MHz, Benzene-*d*₆) δ: 37.12. ¹³C NMR (101 MHz, Benzene-*d*₆) δ: 146.94, 146.08 (d, *J* = 251.8 Hz), 142.26 (d, *J* = 254.9 Hz), 137.55 (d, *J* = 251.5 Hz), 129.32, 127.42, 126.71. ¹⁹F NMR (377 MHz, Benzene-*d*₆) δ: -132.36 (dd, *J* = 9.4, 23.3 Hz), -151.24 (t, *J* = 20.5 Hz), -161.45(m).

6. Photophysical Data

6.1. Emission Spectra

6.1.1. $\text{Al}(\text{C}_6\text{F}_5)_3$

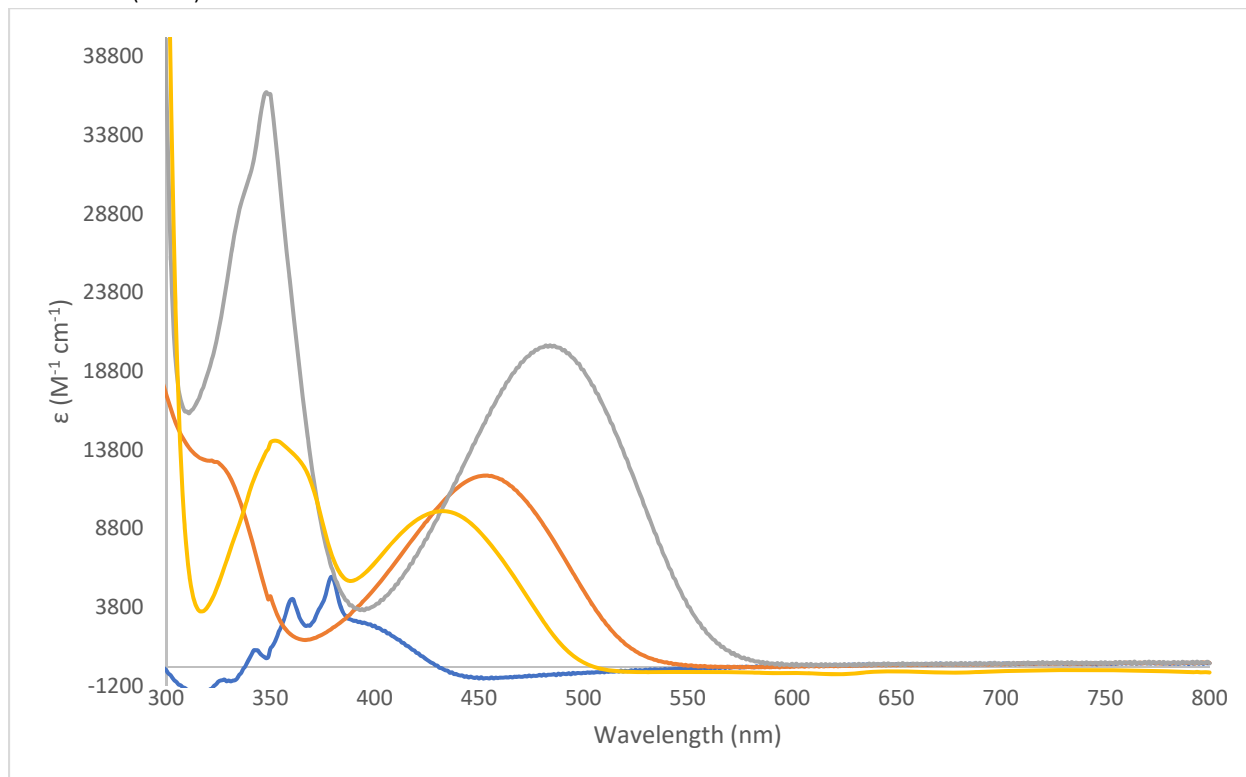


Figure S1 Stacked UV-Vis absorption spectra of **1** (blue, 5 eq), **2** (orange, 5 eq), **3** (grey, 5 eq), and **7** (yellow, 1000 eq) with $\text{Al}(\text{C}_6\text{F}_5)_3$; 12.5 μM samples.

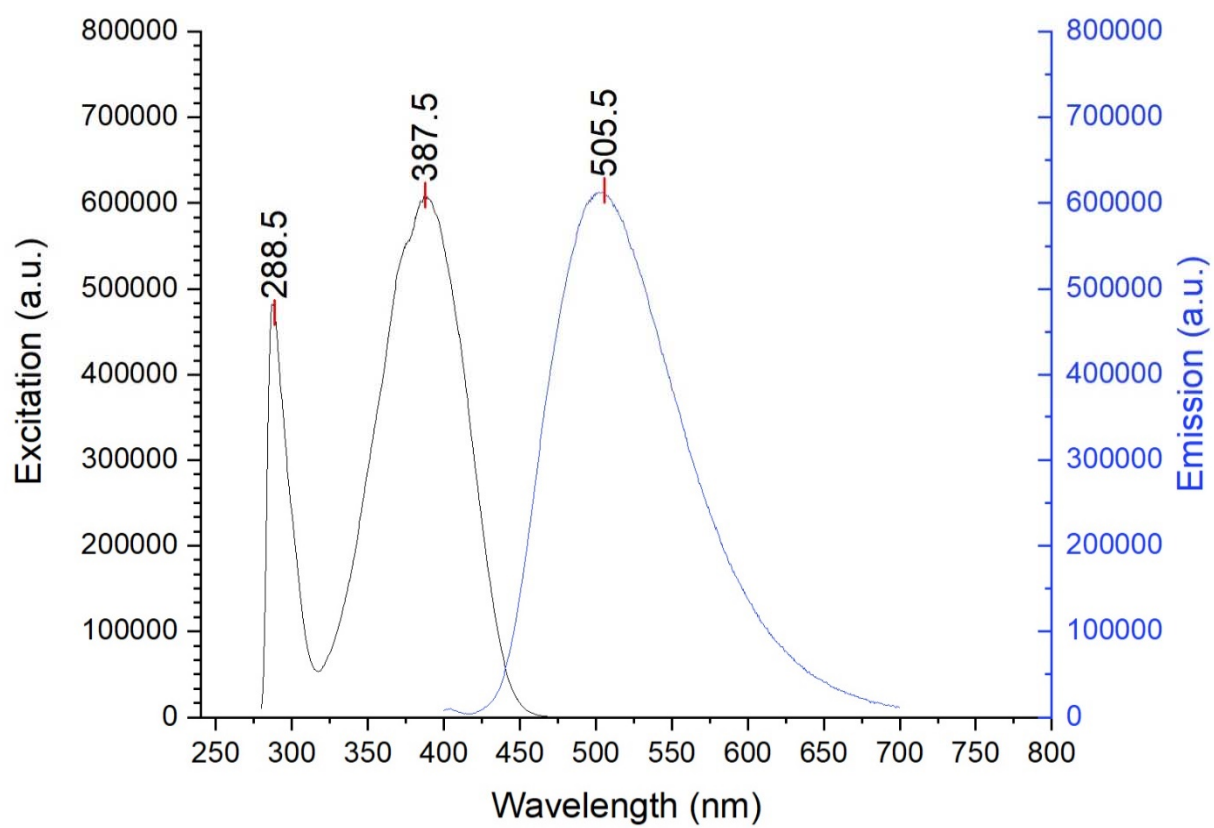


Figure S2 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.2 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.2 nm) spectra of compound 1 and $\text{Al}(\text{C}_6\text{F}_5)_3$; 12.5 μM sample.

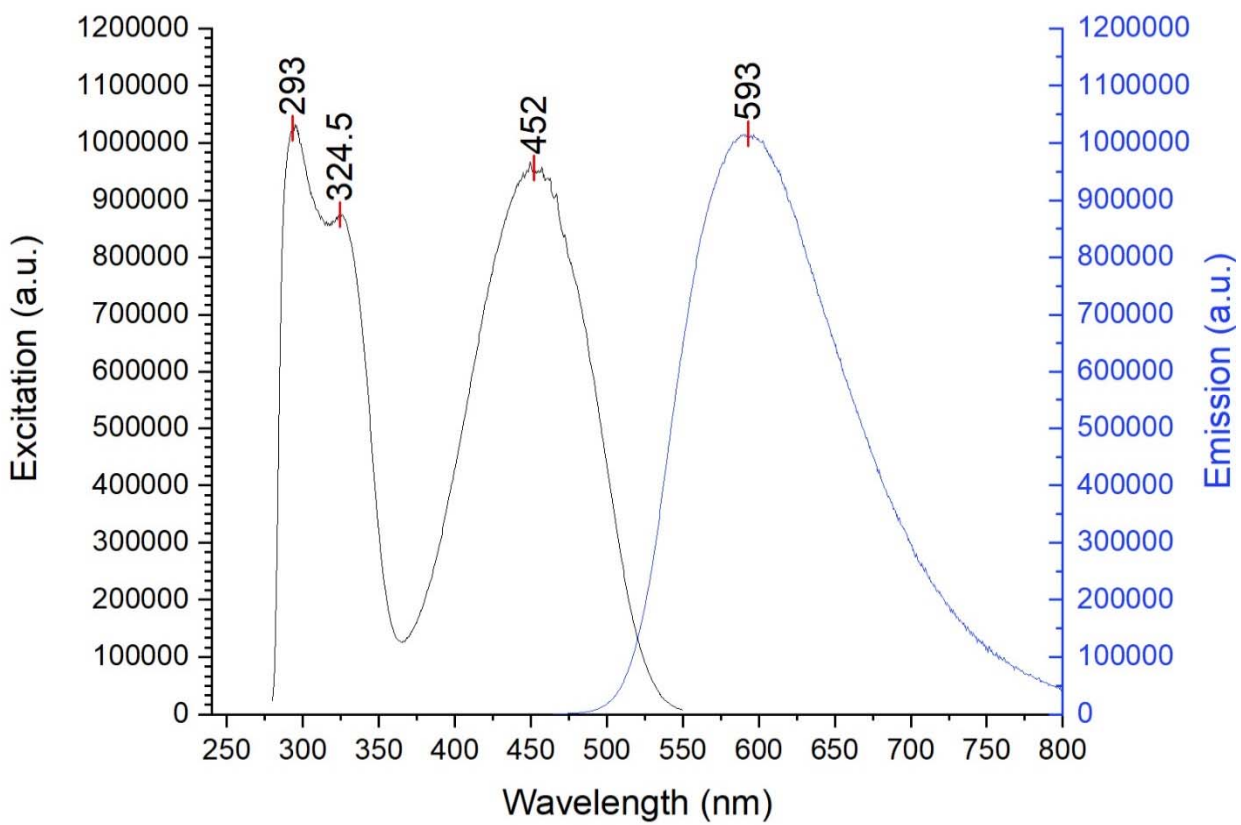


Figure S3 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.2 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.2 nm) spectra of compound **2** and $\text{Al}(\text{C}_6\text{F}_5)_3$; 12.5 μM sample.

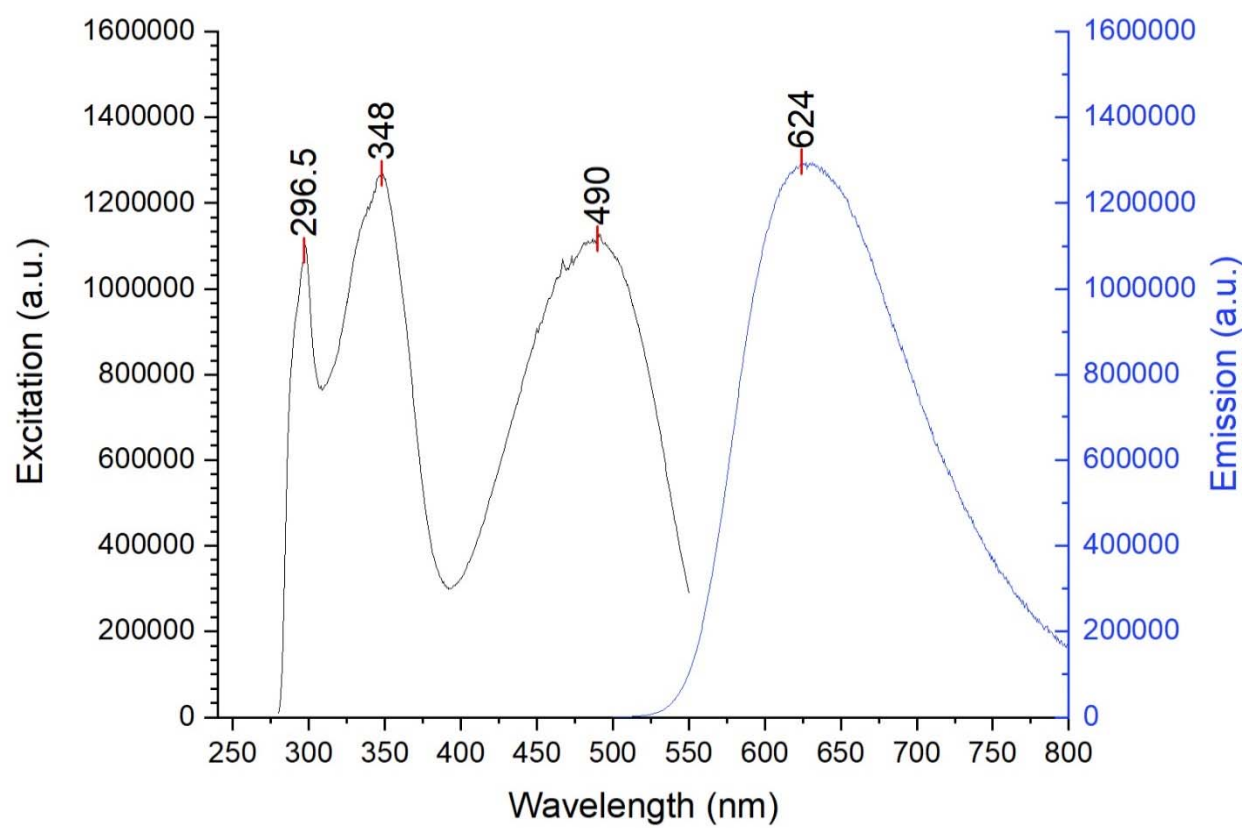


Figure S4 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.2 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.2 nm) spectra of compound **3** and $\text{Al}(\text{C}_6\text{F}_5)_3$; 12.5 μM sample.

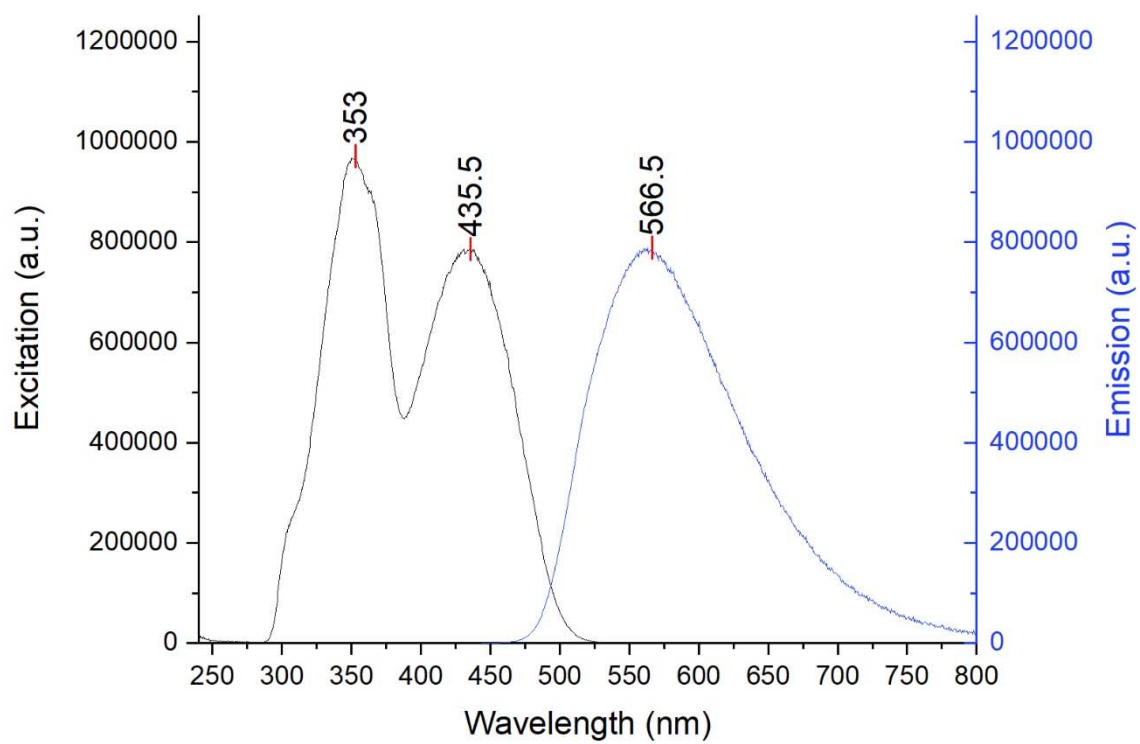


Figure S5 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.2 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.2 nm) spectra of compound **7** and $\text{Al}(\text{C}_6\text{F}_5)_3$; 12.5 μM sample.

6.1.2. AlCl_3

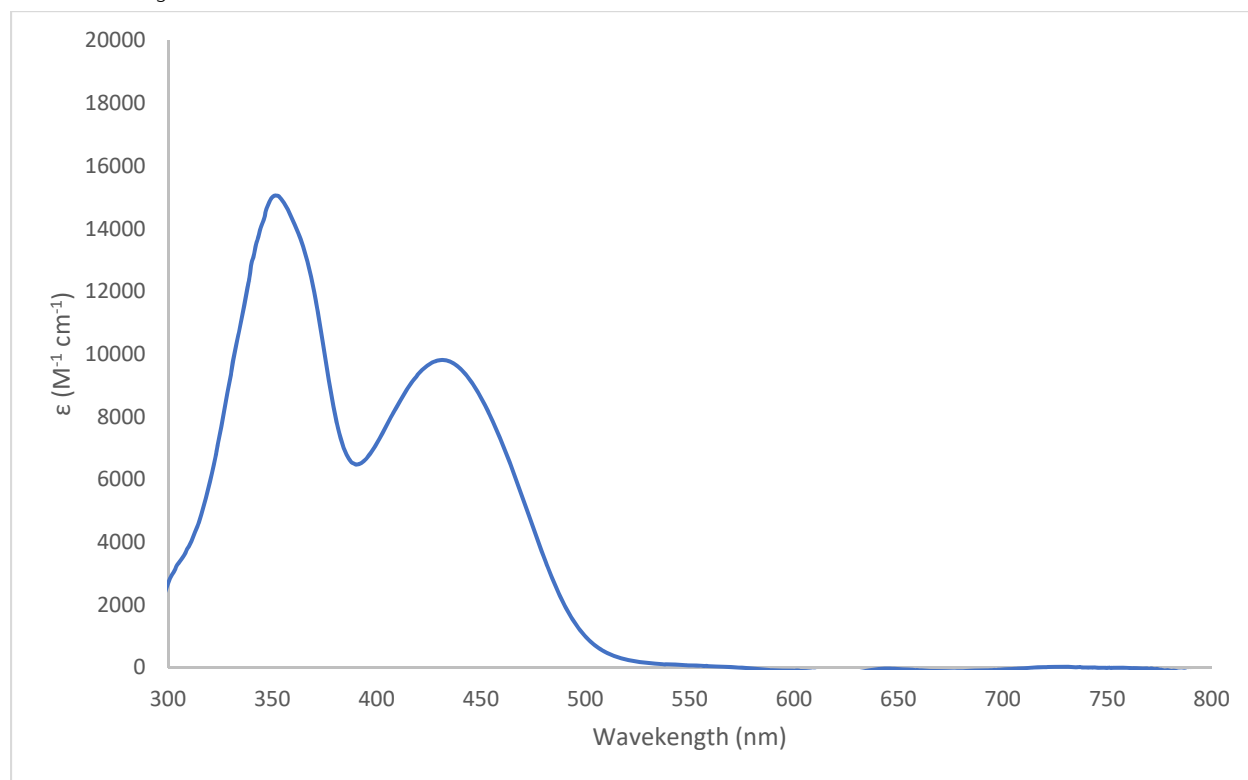


Figure S6 Stacked UV-Vis absorption spectra of **7** (blue) with AlCl_3 (100 eq.); 12.5 μM samples.

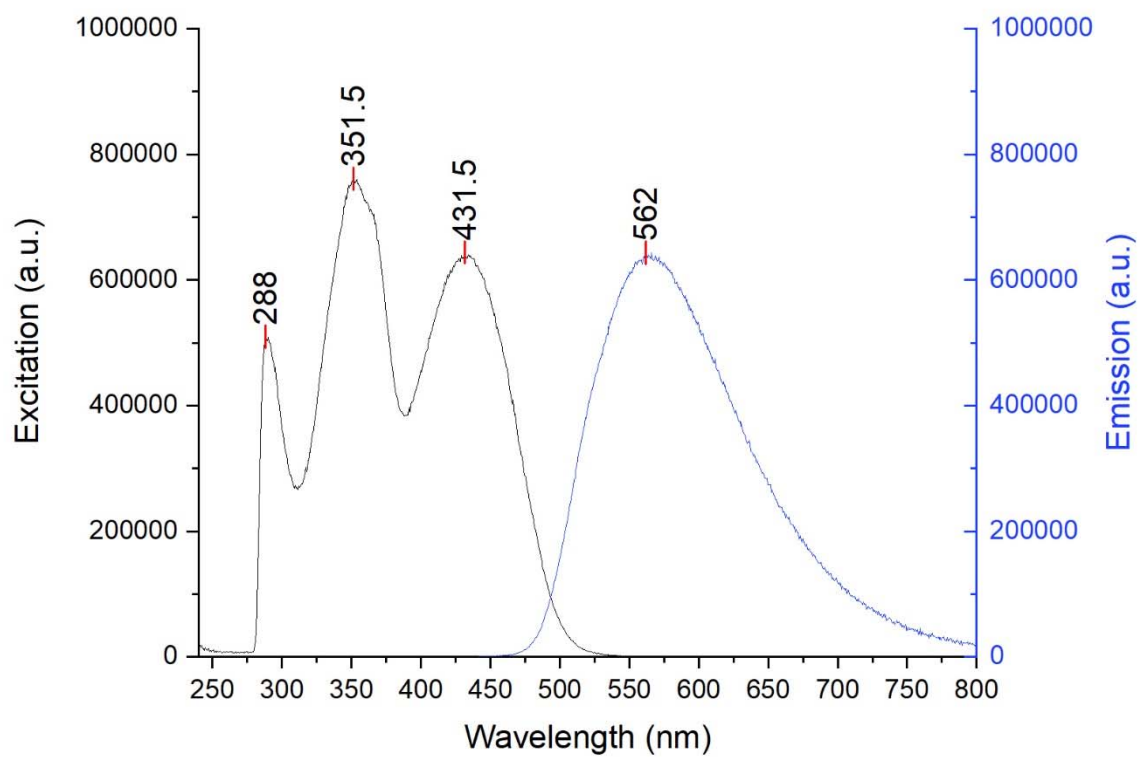


Figure S7 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.2 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.2 nm) spectra of compound **7** and AlCl_3 ; 12.5 μM sample.

6.1.3. AlBr_3

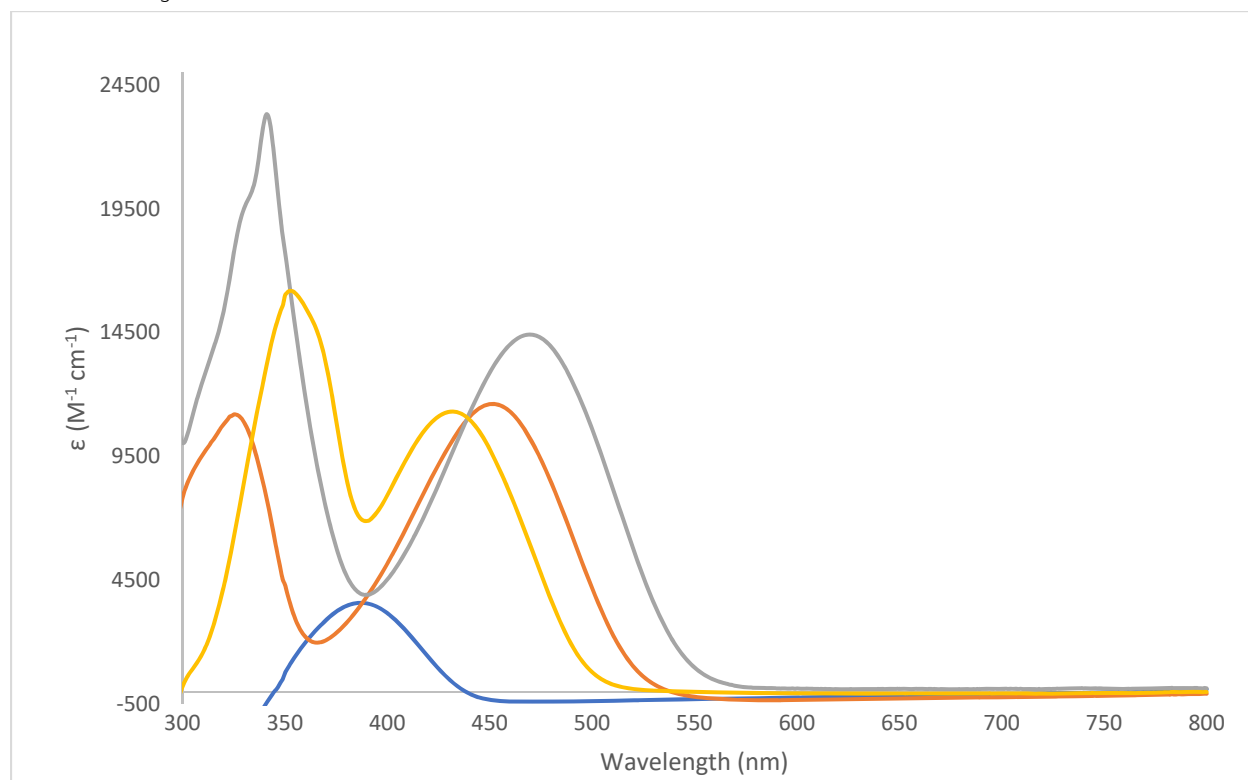


Figure S8 Stacked UV-Vis absorption spectra of **1** (blue), **2** (orange), **3** (grey), and **7** (yellow) with AlBr_3 (3 eq.); $12.5 \mu\text{M}$ samples.

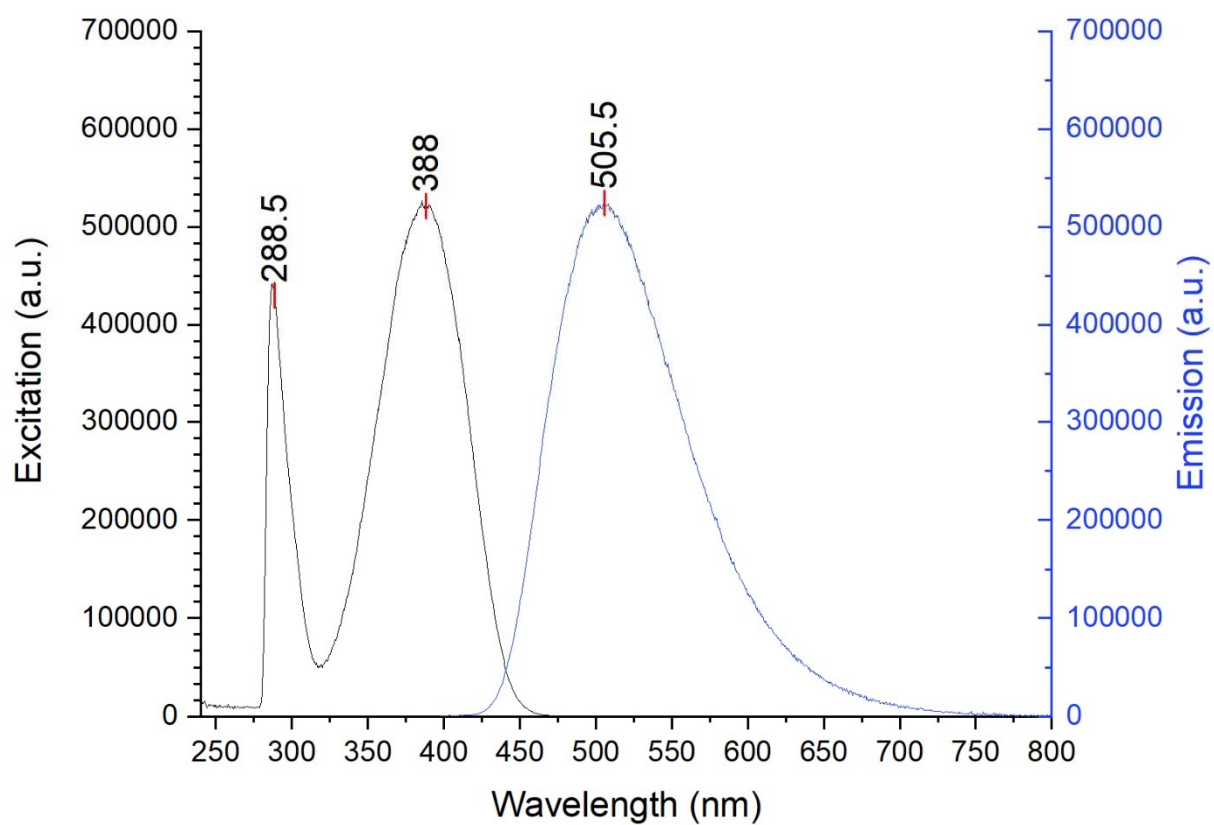


Figure S9 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.2 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.2 nm) spectra of compound **1** and **AlBr₃**; 12.5 μ M sample.

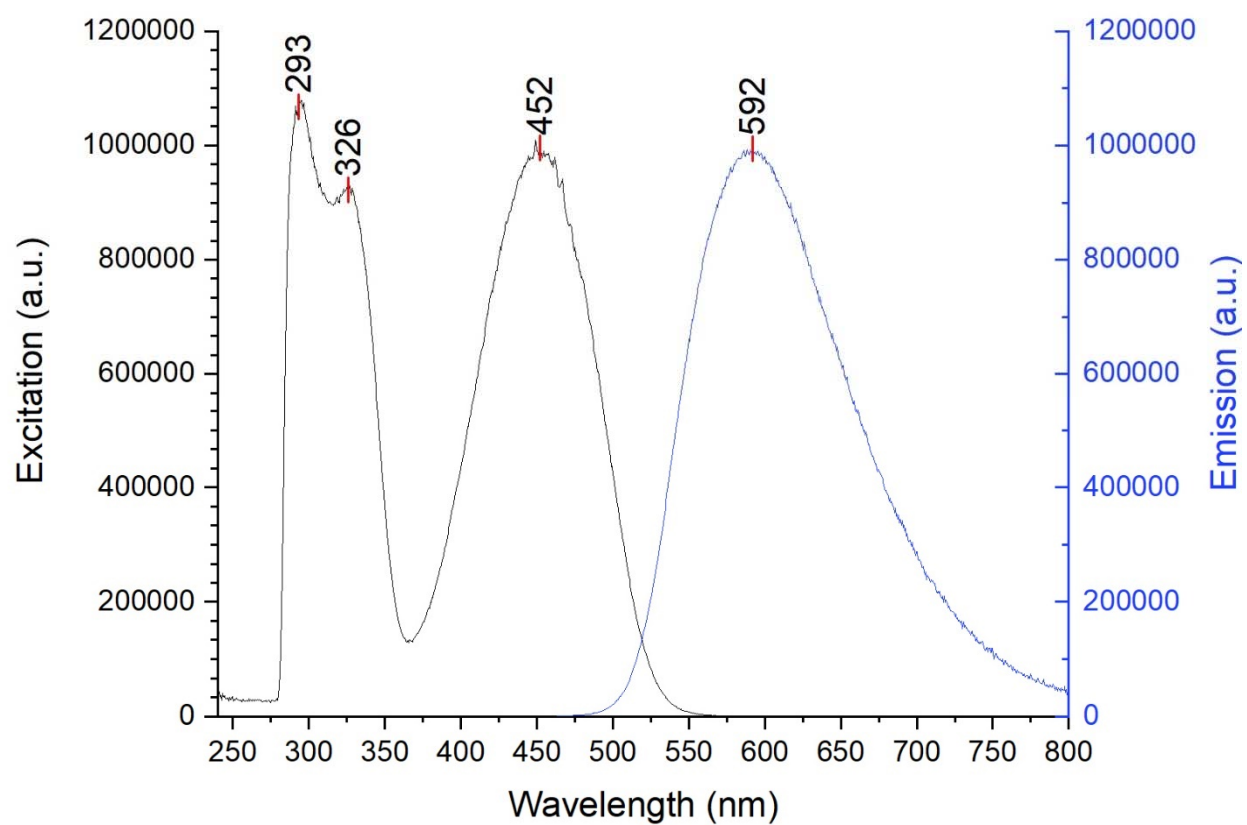


Figure S10 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.2 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.2 nm) spectra of compound **2** and AlBr_3 ; 12.5 μM sample.

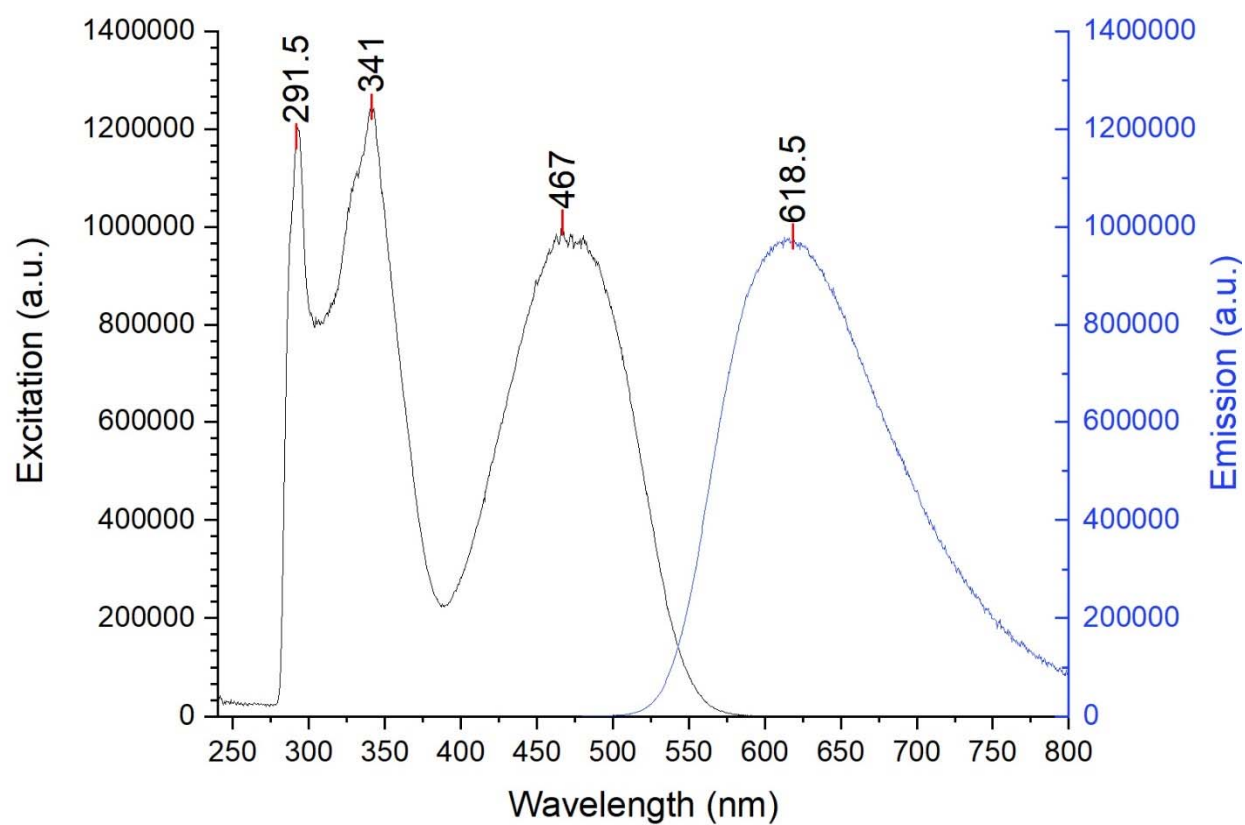


Figure S11 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.2 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.2 nm) spectra of compound **3** and AlBr_3 ; 12.5 μM sample.

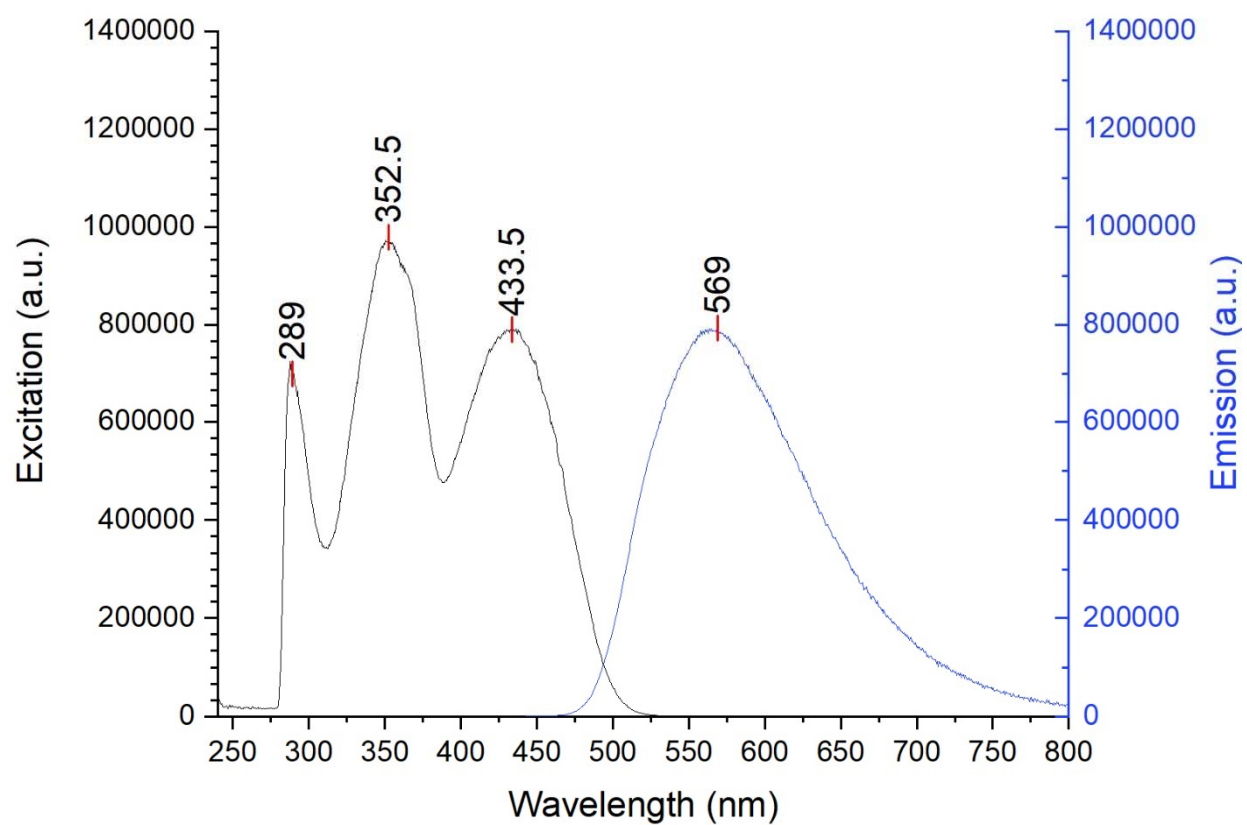


Figure S12 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.2 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.2 nm) spectra of compound **7** and AlBr_3 ; 12.5 μM sample.

6.1.4. AlMe_3

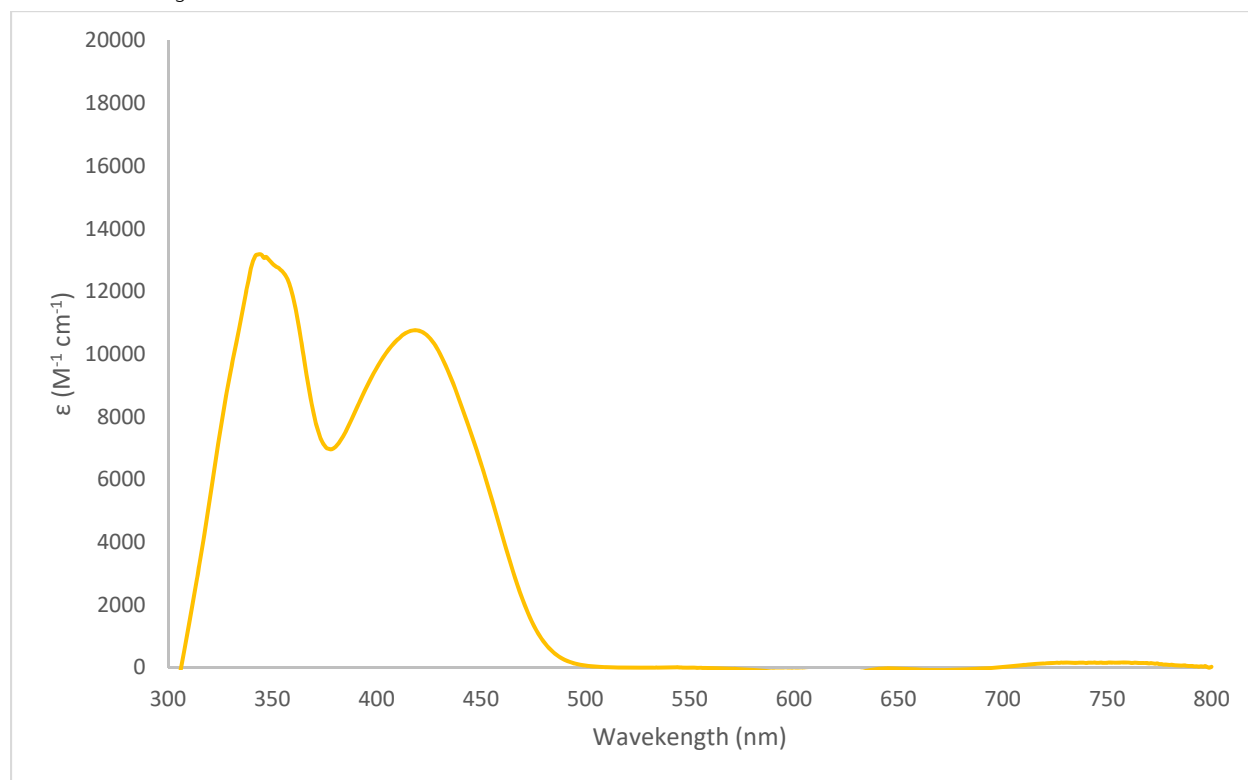


Figure S13 Stacked UV-Vis absorption spectra of **7** (yellow) with AlMe_3 (10 eq.); 12.5 μM samples.

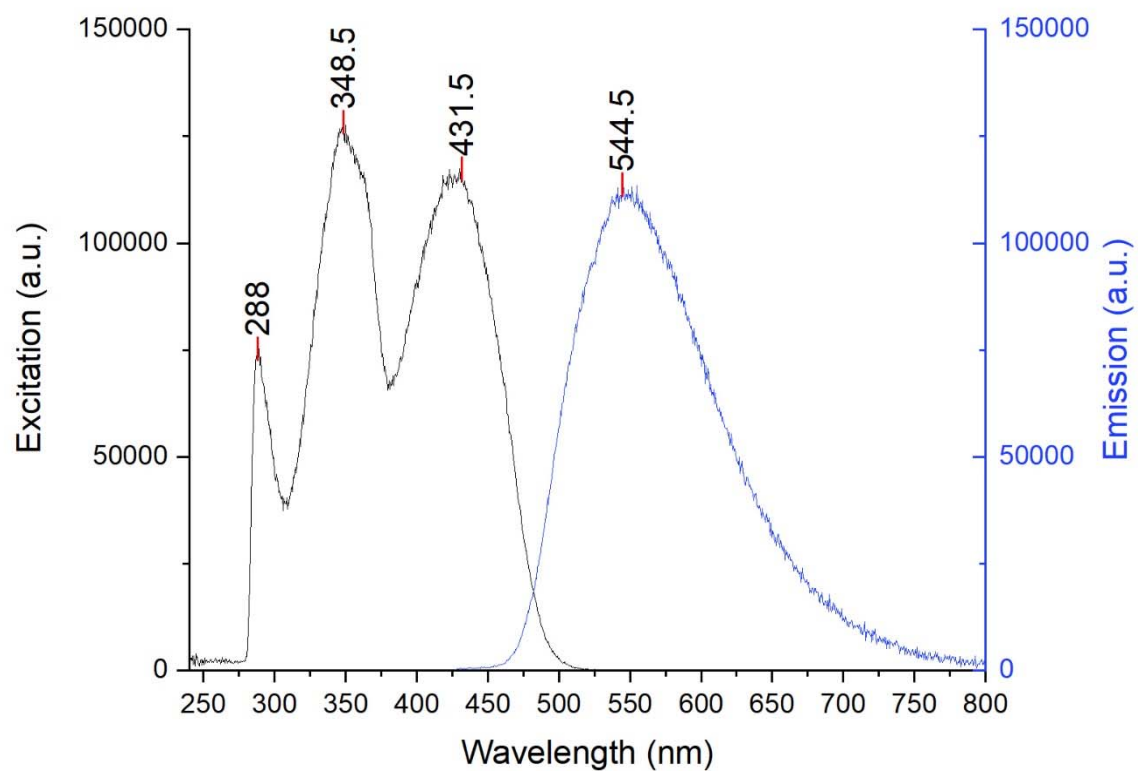


Figure S14 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.2 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.2 nm) spectra of compound **7** and AlMe_3 ; 12.5 μM sample.

6.1.5. $\text{Al}(\text{OTf})_3$

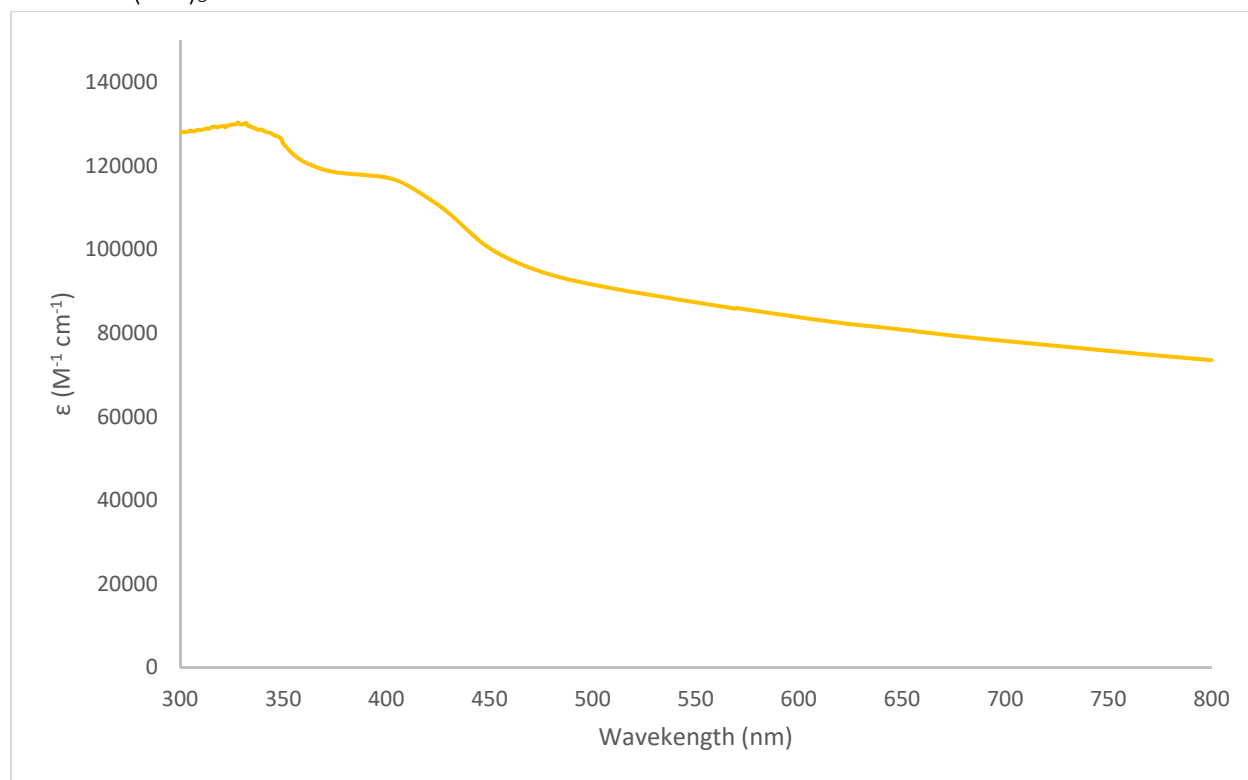


Figure S15 UV-Vis absorption spectrum of **7** (yellow) with $\text{Al}(\text{OTf})_3$ (1000 eq.); 12.5 μM samples.

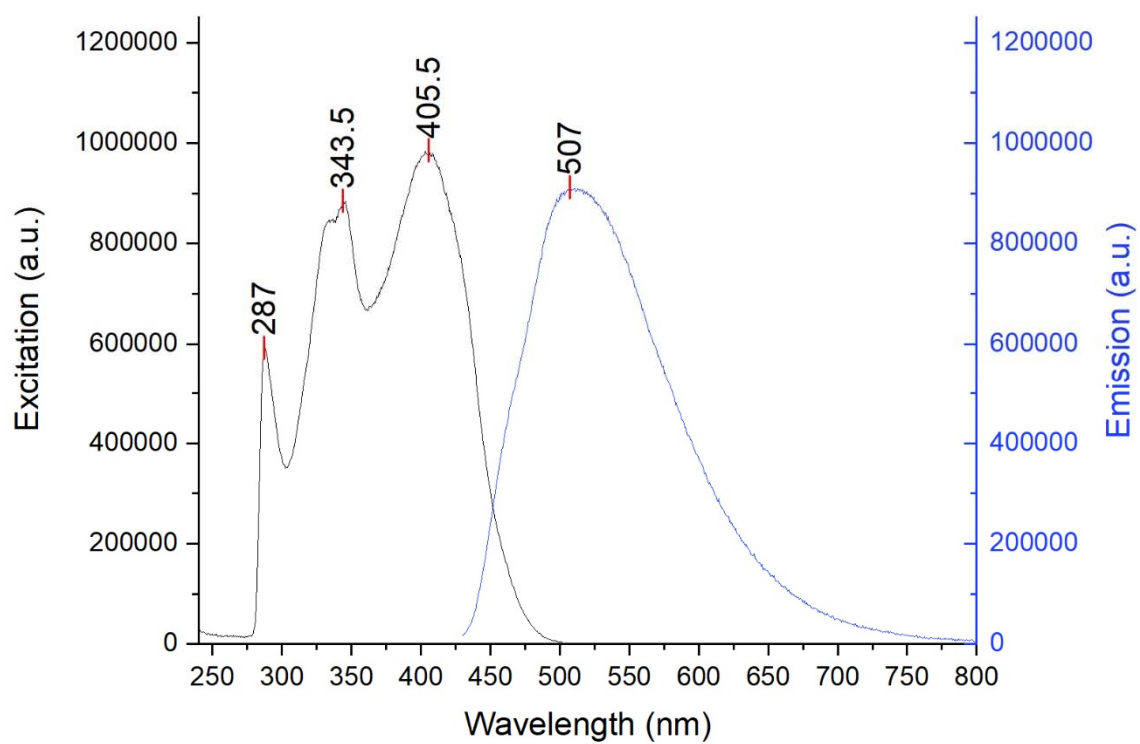


Figure S16 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.2 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.2 nm) spectra of compound **7** and $\text{Al}(\text{OTf})_3$; 12.5 μM sample.

6.1.6. BCl_3

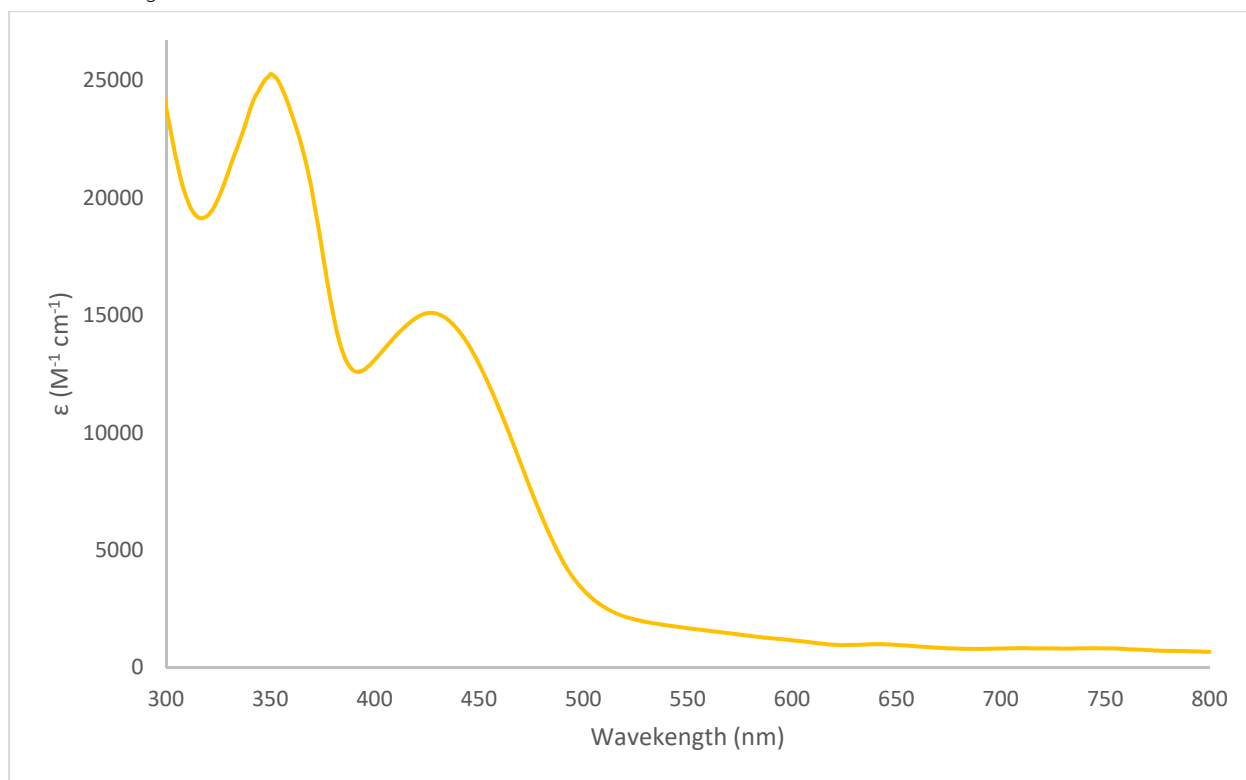


Figure S17 UV-Vis absorption spectrum of **7** (yellow) with BCl_3 (excess); 12.5 μM samples.

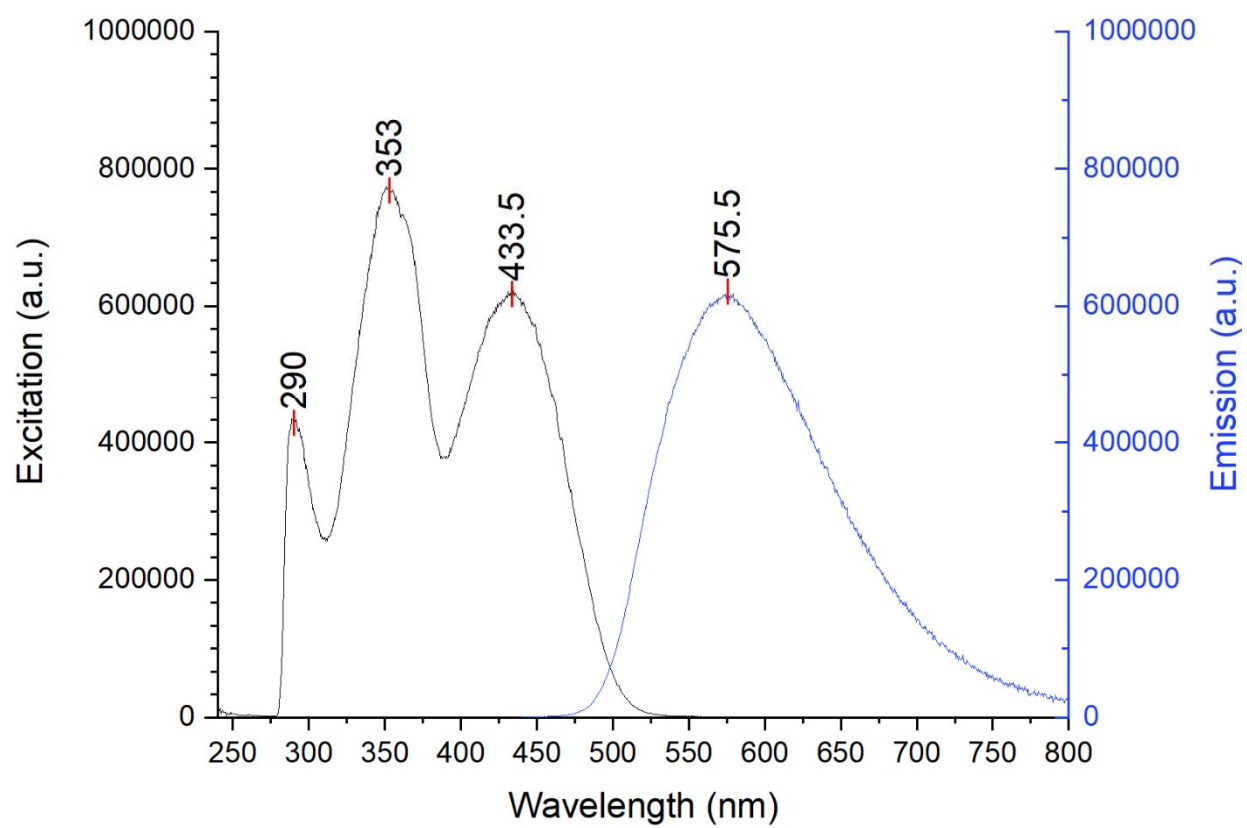


Figure S18 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.2 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.2 nm) spectra of compound **7** and BCl_3 ; 12.5 μM sample.

6.1.7. BF_3OEt_2

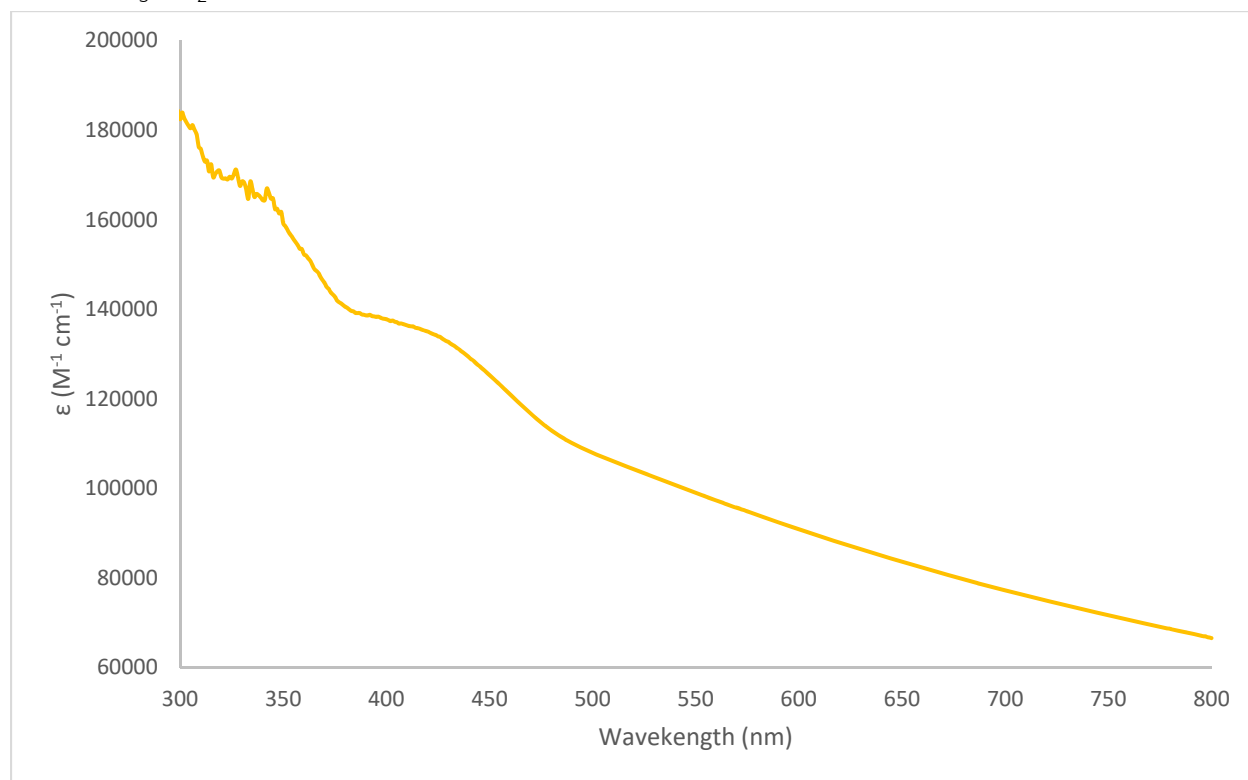


Figure S19 UV-Vis absorption spectrum of **7** (yellow) with BF_3OEt_2 (excess); 12.5 μM samples.

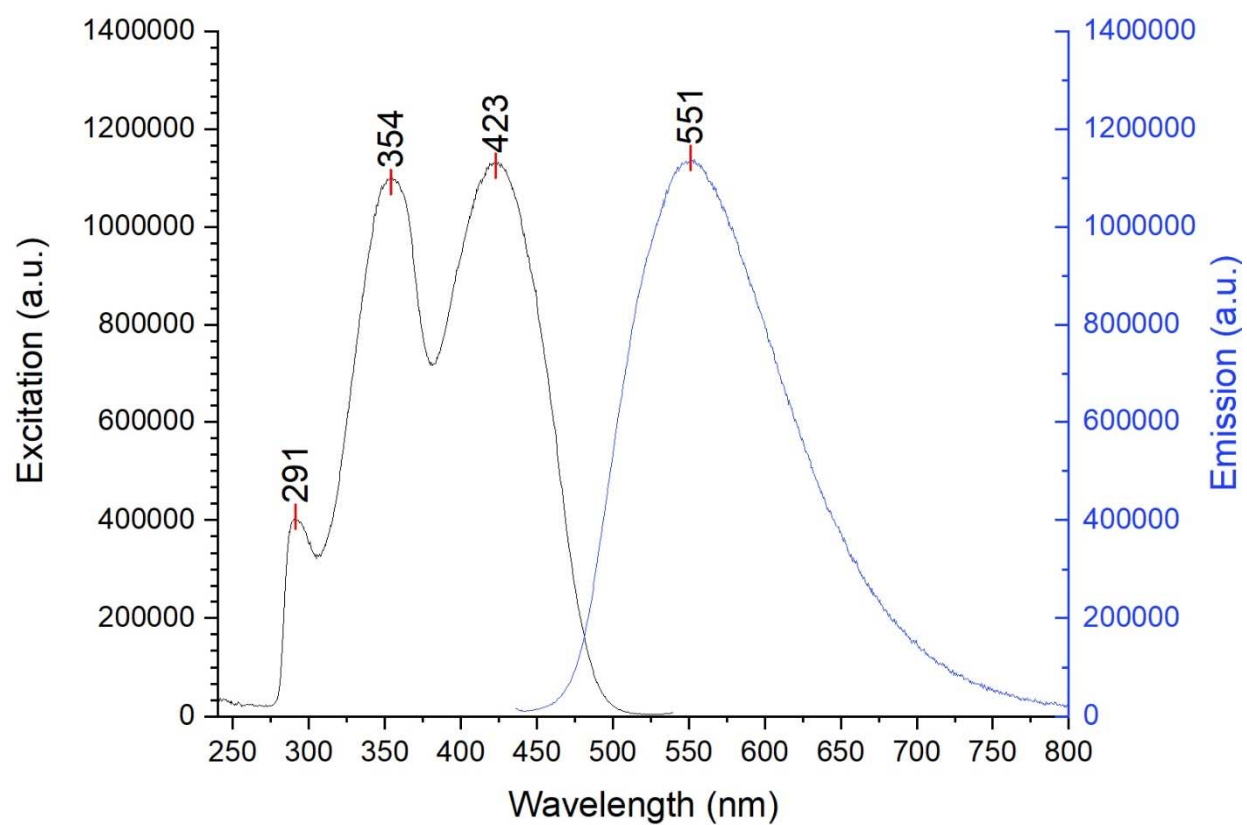


Figure S20 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.2 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.2 nm) spectra of compound **7** and BF_3OEt_2 ; 12.5 μM sample.

6.1.8. Mes₂BF

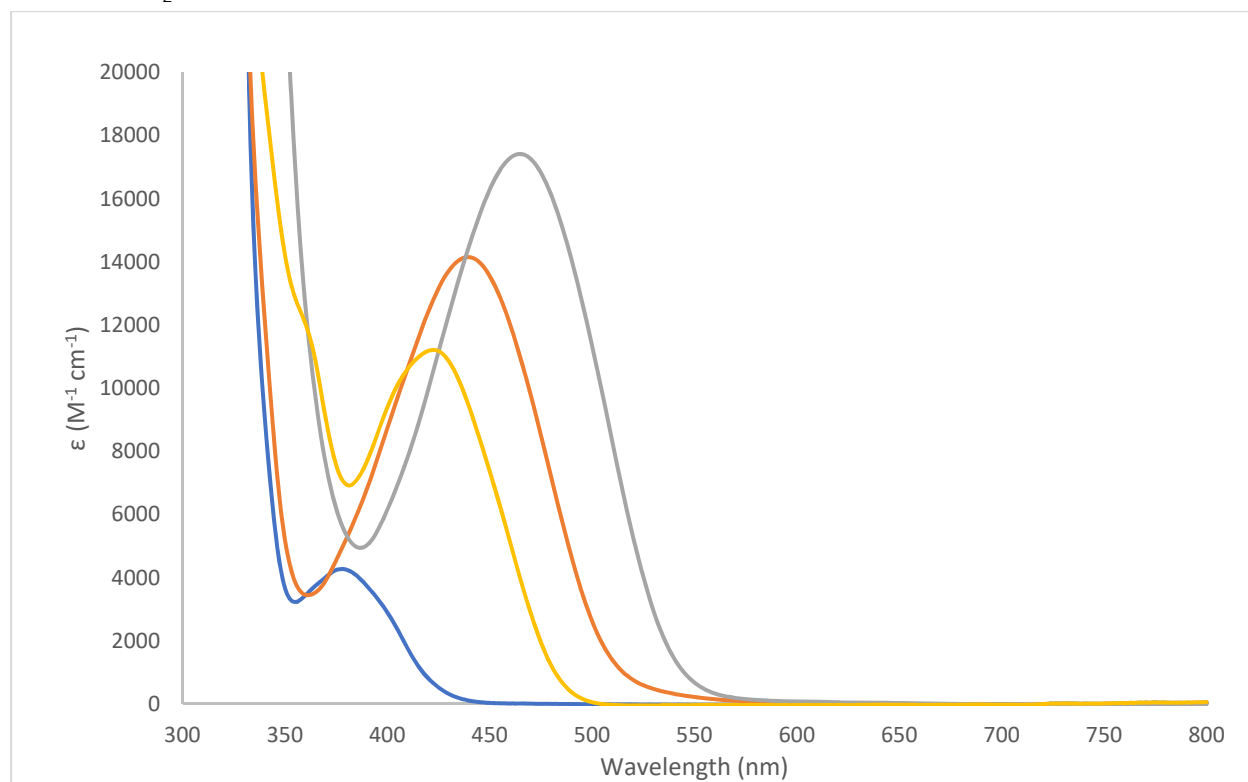


Figure S21 Stacked UV-Vis absorption spectra of **1** (blue), **2** (orange), **3** (grey), and **7** (yellow) with **Mes₂BF** (excess); 12.5 μ M samples.

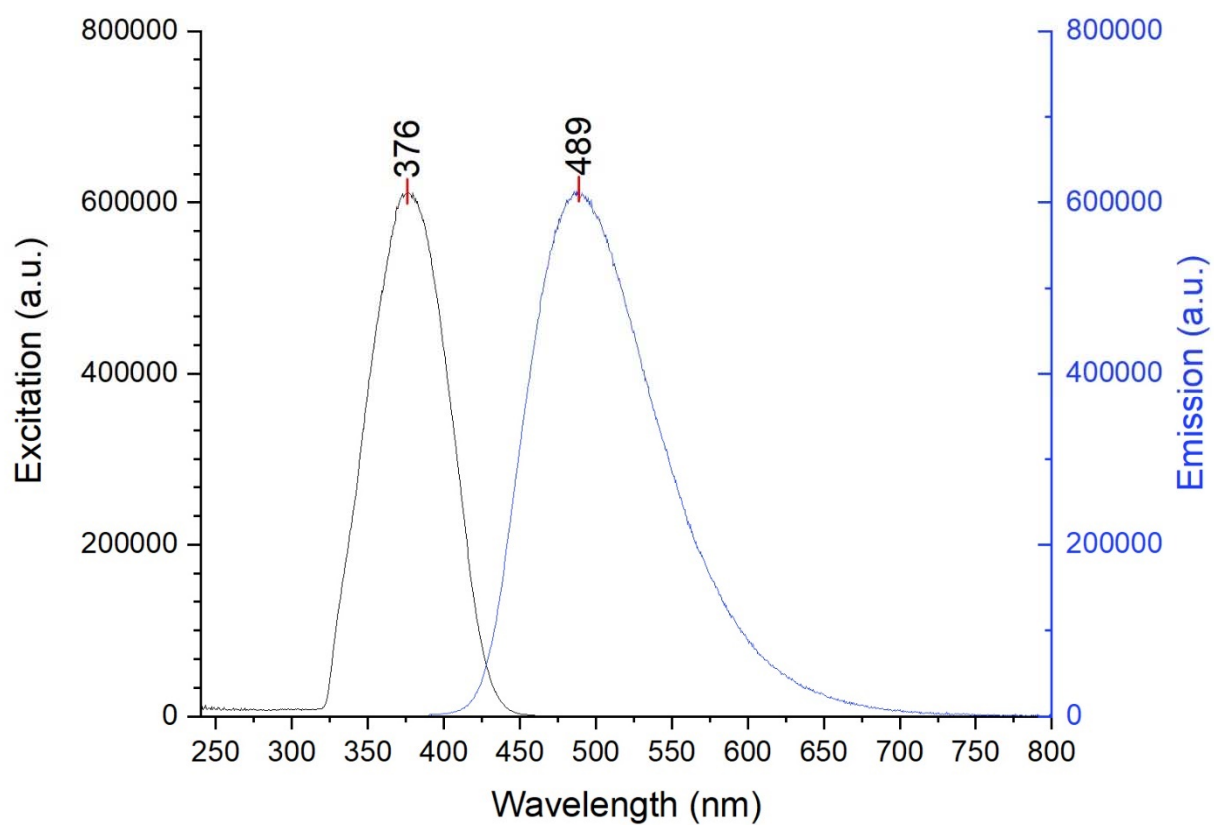


Figure S22 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.2 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.2 nm) spectra of compound **1** and Mes₂BF; 12.5 μ M sample.

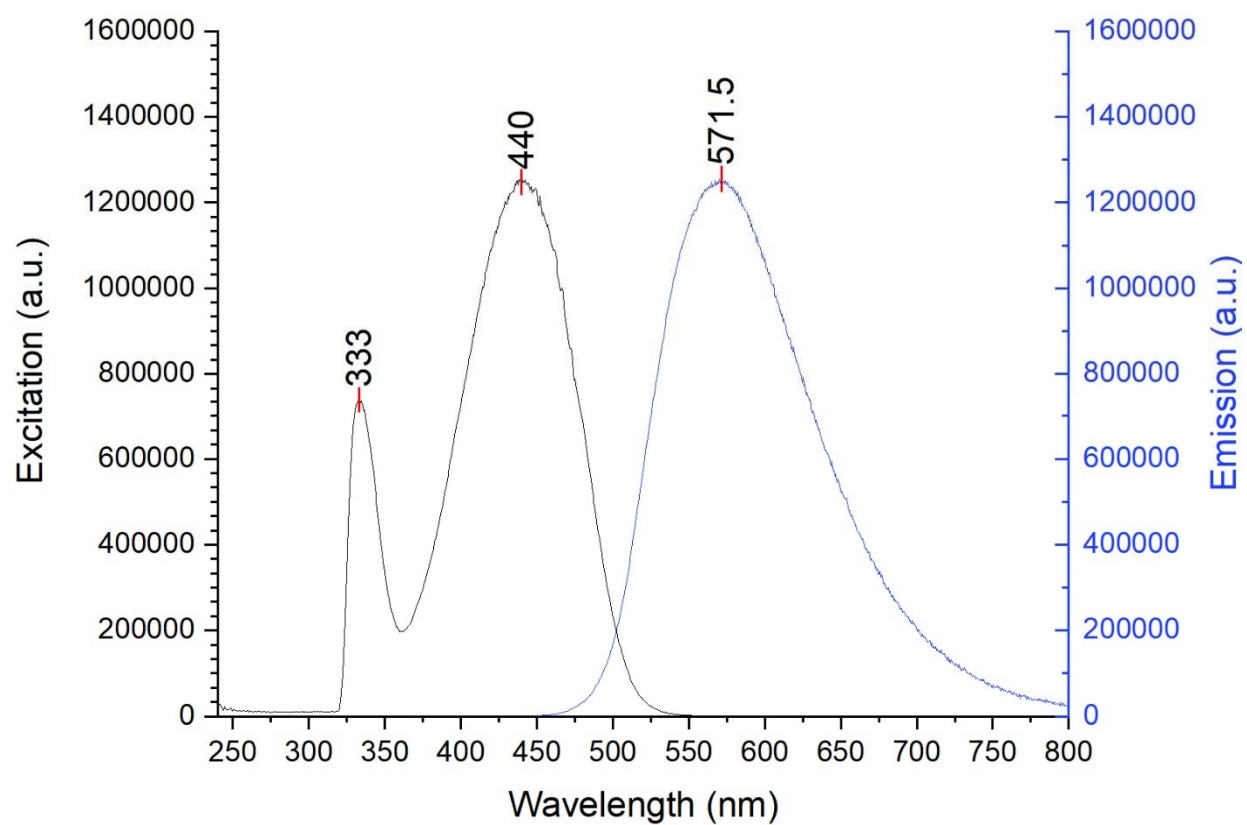


Figure S23 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.2 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.2 nm) spectra of compound **2** and **Mes₂BF**; 12.5 μ M sample.

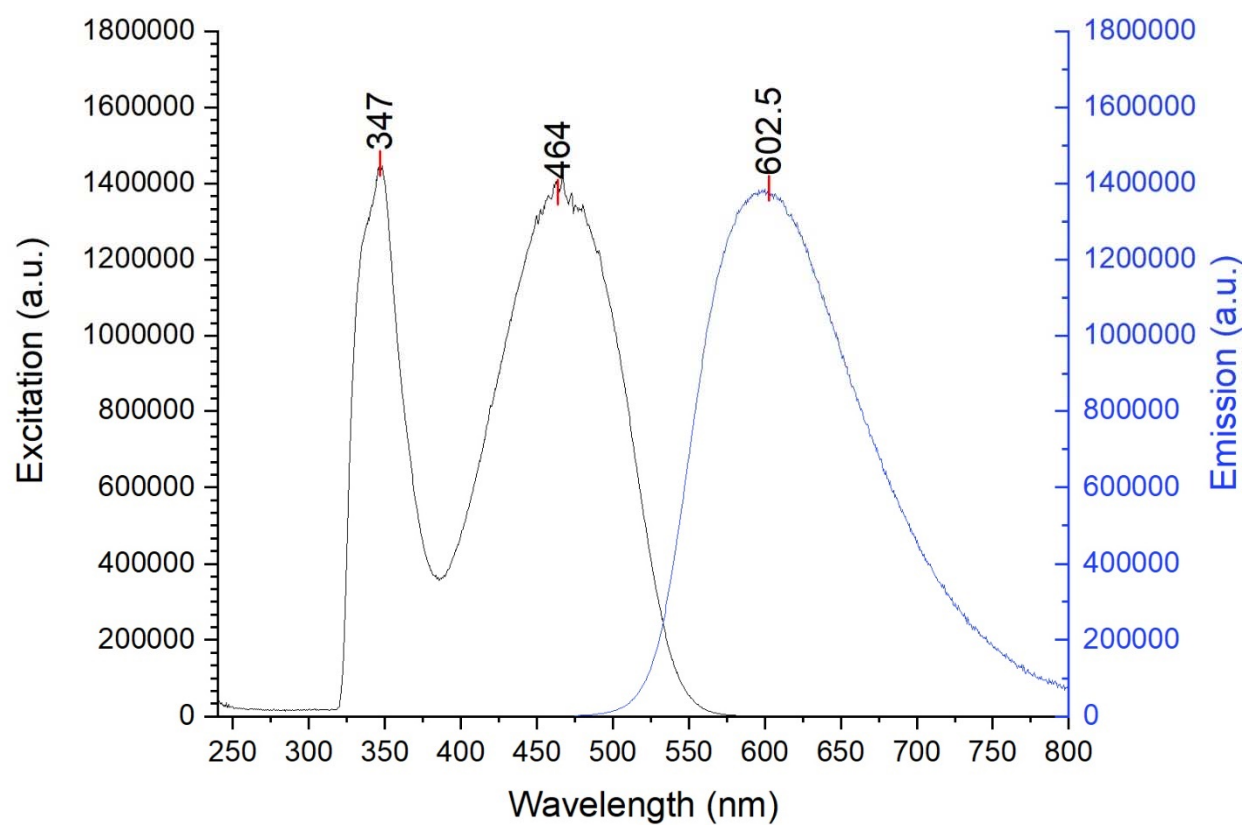


Figure S24 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.2 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.2 nm) spectra of compound **3** and **Mes₂BF**; 12.5 μ M sample.

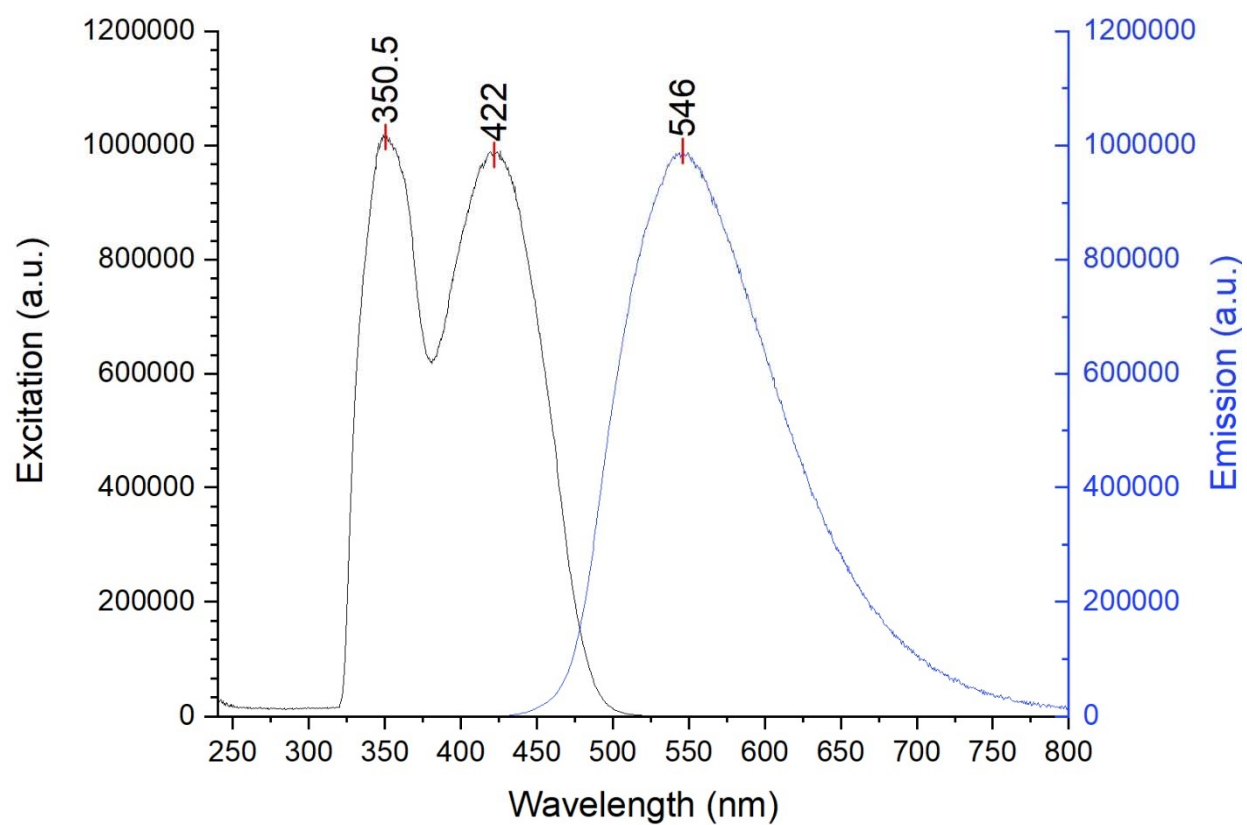


Figure S25 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.2 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.2 nm) spectra of compound **7** and **Mes₂BF**; 12.5 μ M sample.

6.1.9. $B(4-F-C_6H_4)_3$

*UV-Vis absorption spectroscopy was not feasible due to the necessary amount of Lewis acid required to prepare the FLA samples.

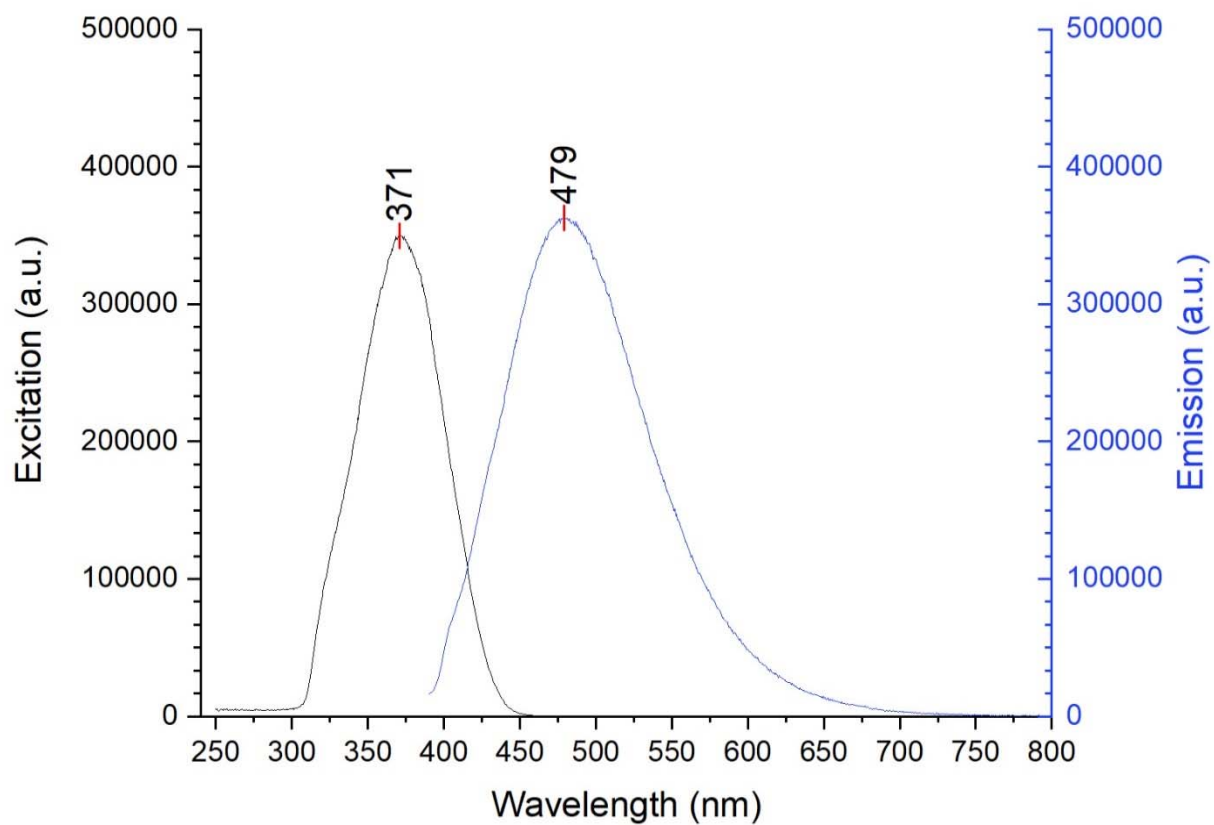


Figure S26 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) spectra of compound **1** and $B(4-F-C_6H_4)_3$ (>1000 eq.); 12.5 μ M sample.

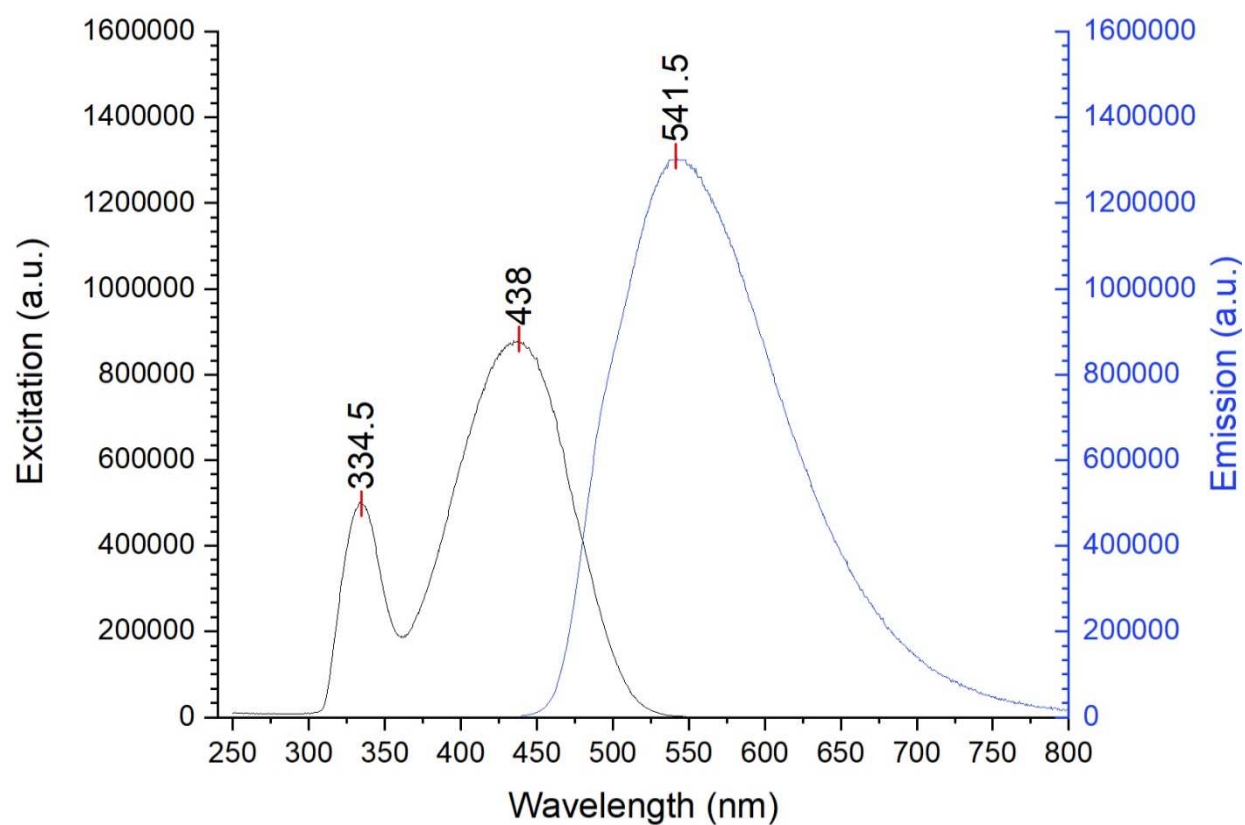


Figure S27 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) spectra of compound **2** and **B(4-F-C₆H₄)₃** (>1000 eq.); 12.5 μ M sample.

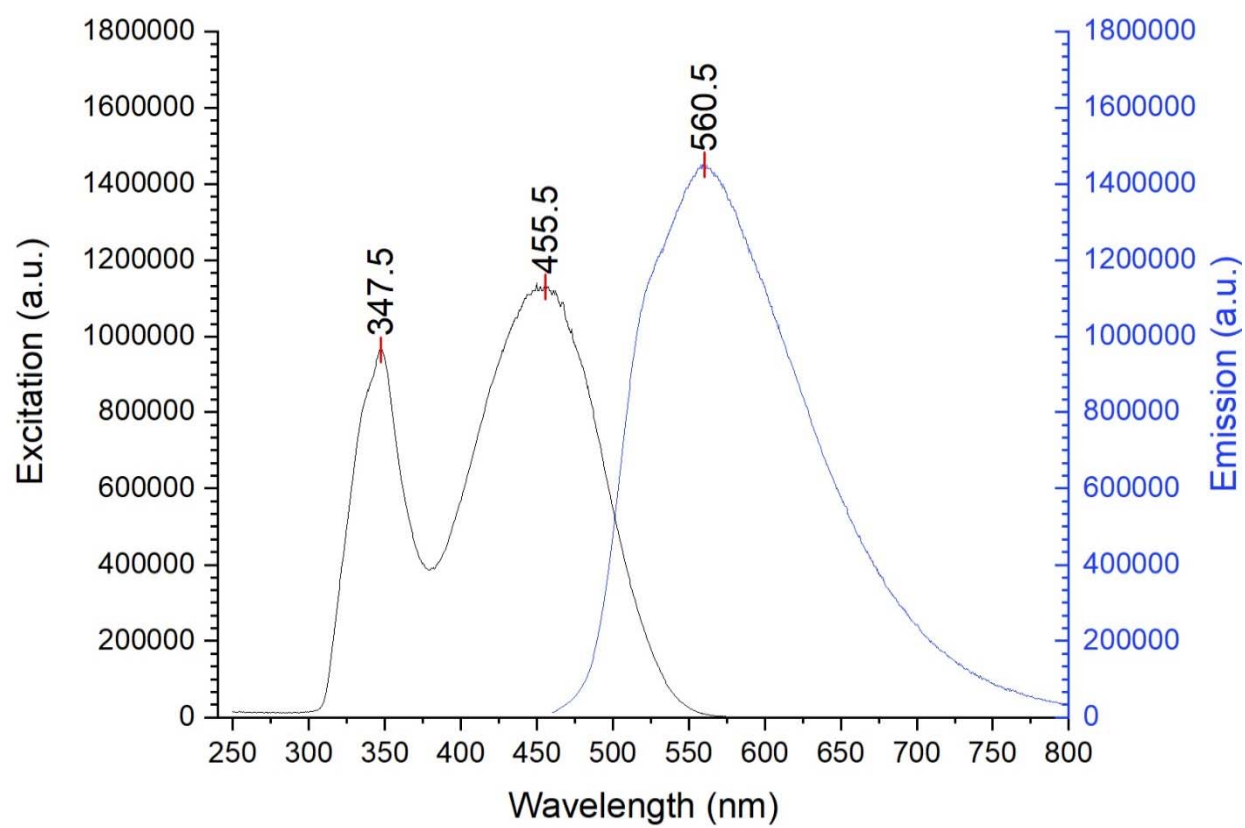


Figure S28 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) spectra of compound **3** and **B(4-F-C₆H₄)₃** (>1000 eq.); 12.5 μ M sample.

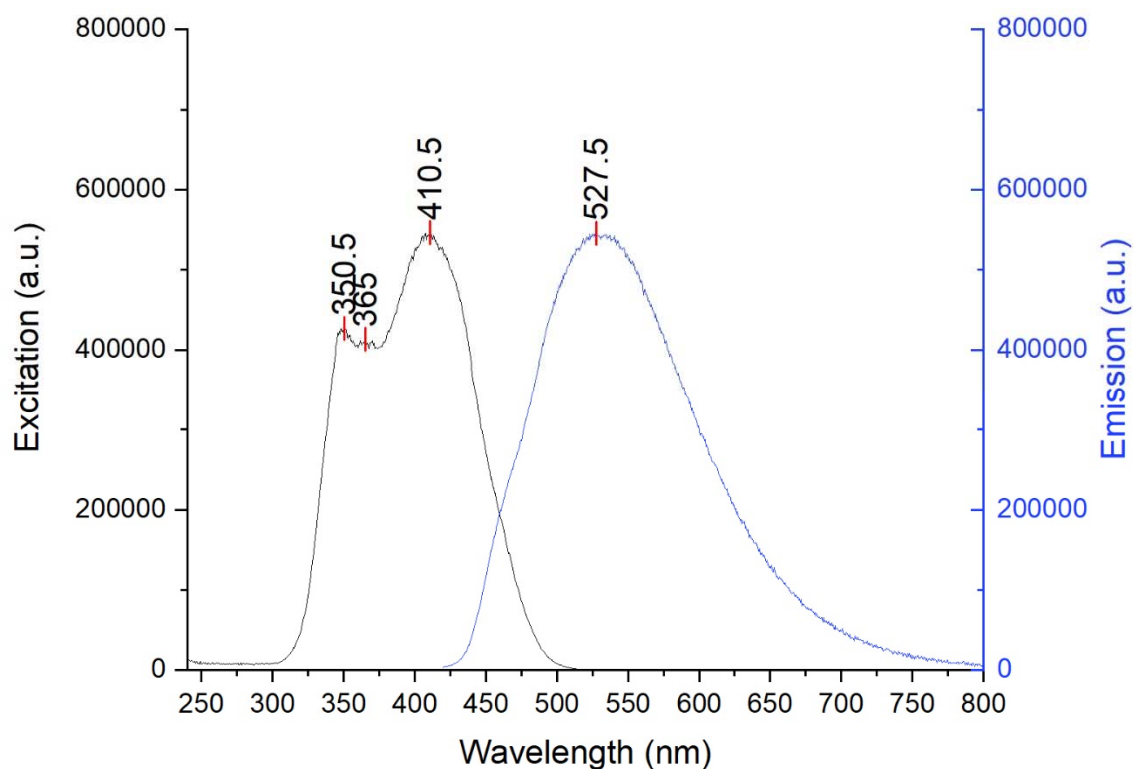


Figure S29 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) spectra of compound **7** and $B(4-F-C_6H_4)_3$ (>1000 eq.); 12.5 μM sample.

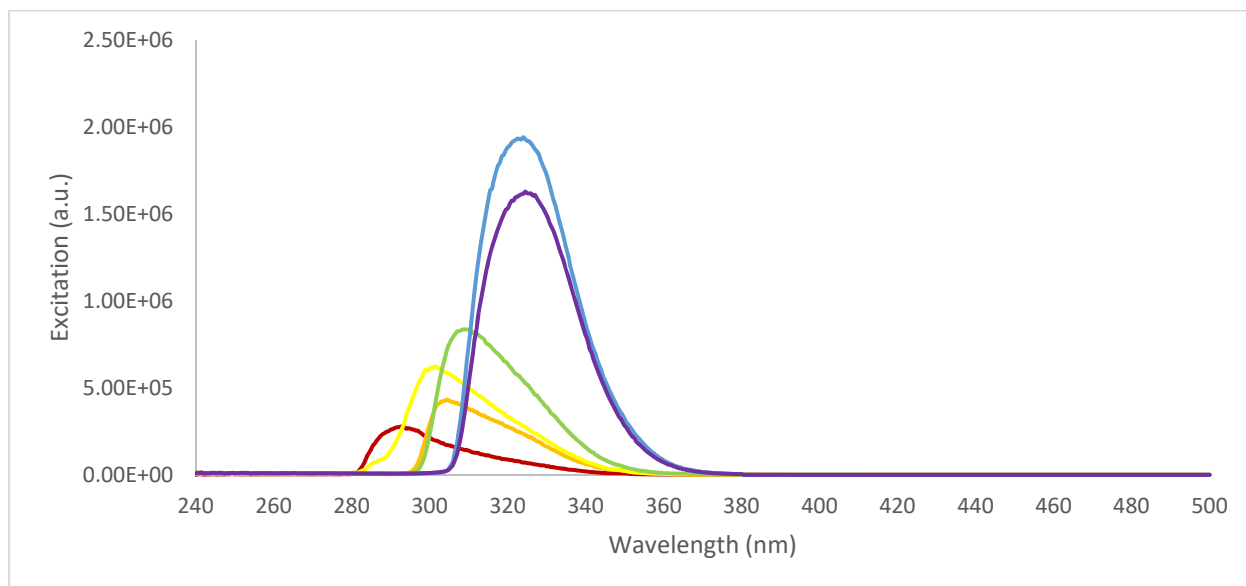


Figure S30 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) spectra of $B(4-F-C_6H_4)_3$ at 0.3125 mM (red), 0.6250 mM (orange), 1.25 mM (yellow), 2.5 mM (green), 5.0 mM (blue), 10.0 mM (purple).

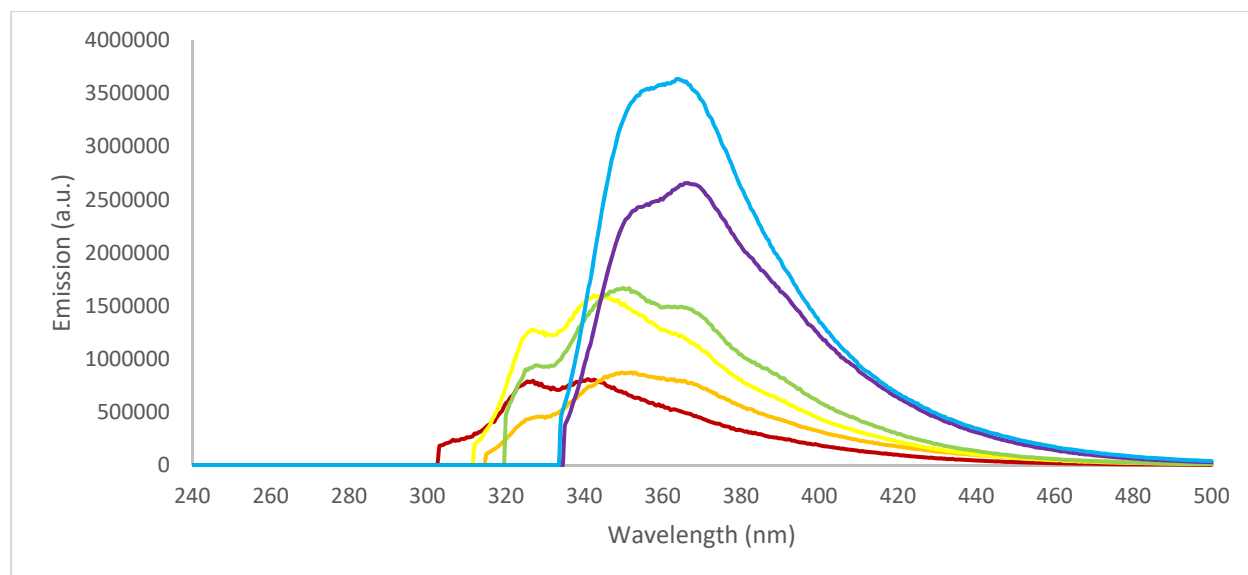


Figure S31 Stacked emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) spectra of $B(4-F-C_6H_4)_3$ at 0.3125mM (red), 0.6250mM (orange), 1.25mM (yellow), 2.5 mM (green), 5.0 mM (blue), 10.0 mM (purple).

6.1.10. $B(2,4-F_2-C_6H_3)_3$

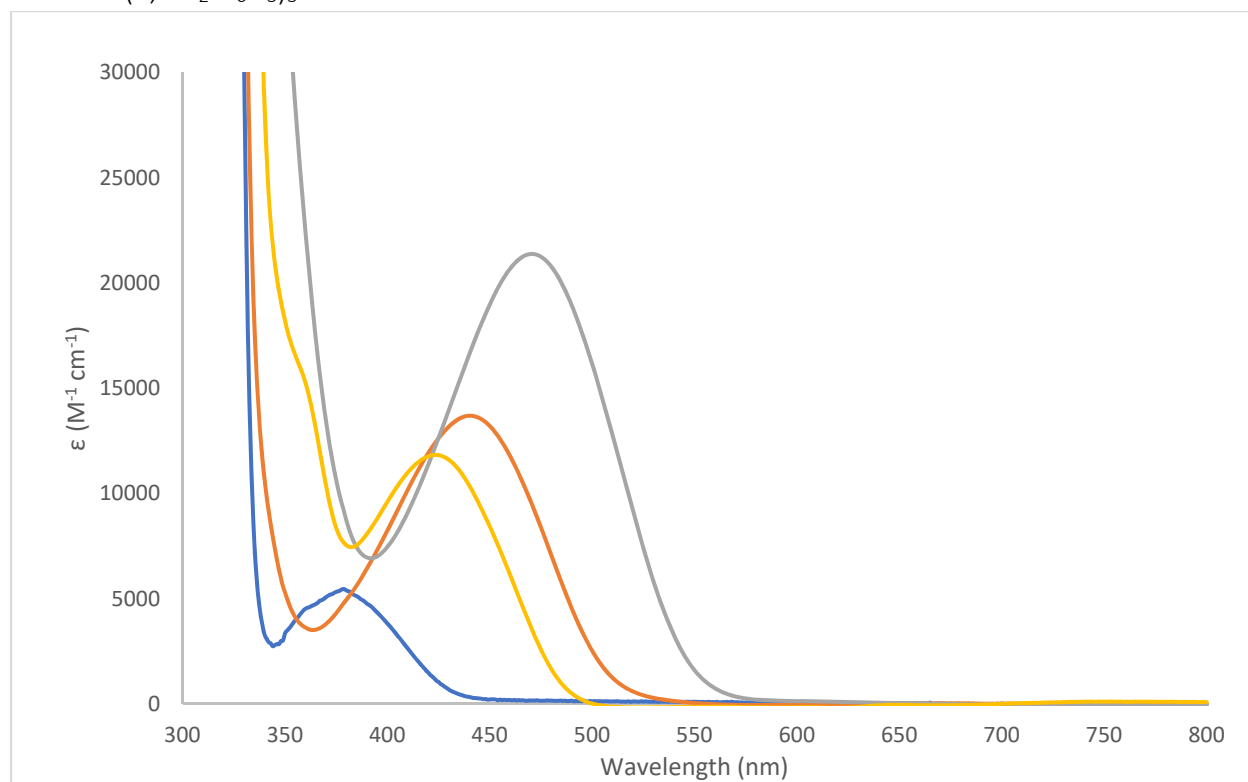


Figure S32 Stacked UV-Vis absorption spectra of **1** (blue), **2** (orange), **3** (grey), and **7** (yellow) with $B(2,4-F_2-C_6H_3)_3$ (1000 eq.); 12.5 μM samples.

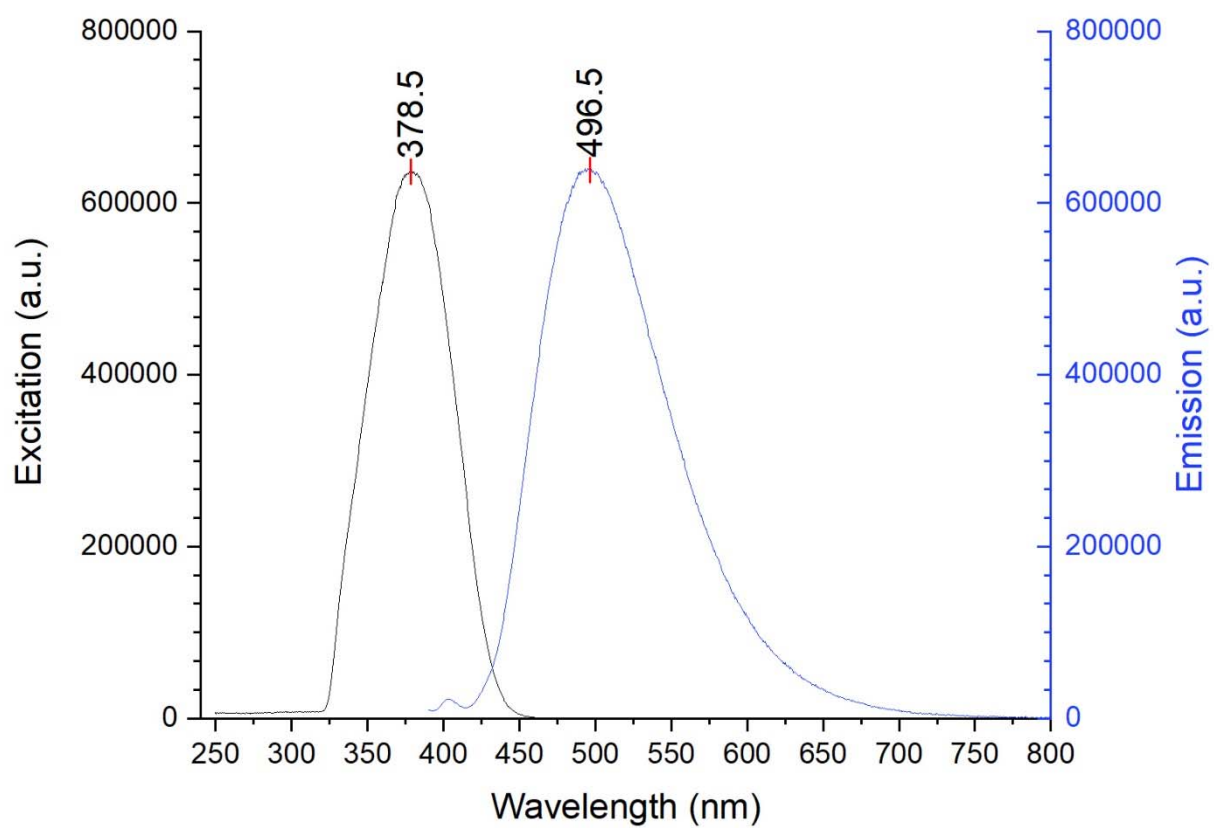


Figure S33 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.2 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.2 nm) spectra of compound **1** and **B(2,4-F₂-C₆H₃)₃**; 12.5 μ M sample.

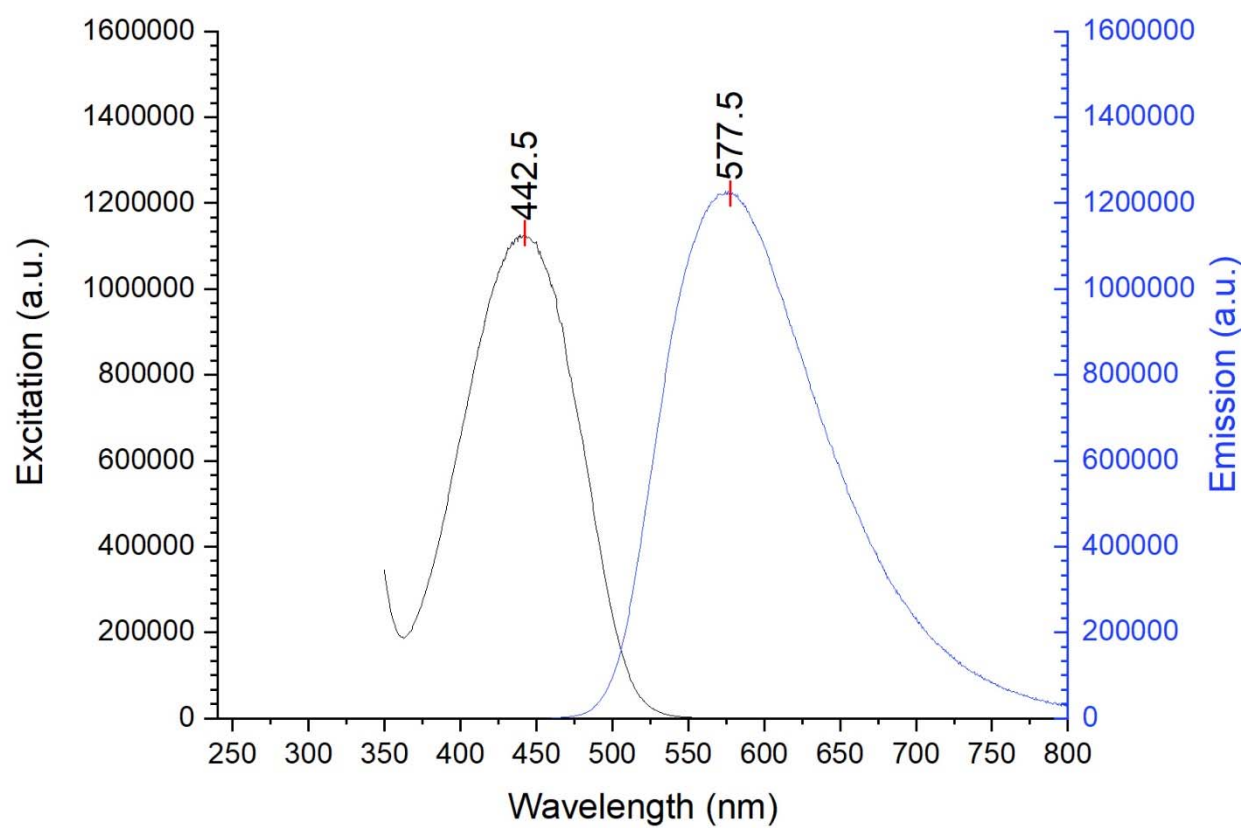


Figure S34 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.2 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.2 nm) spectra of compound **2** and **B(2,4-F₂-C₆H₃)₃**; 12.5 μ M sample.

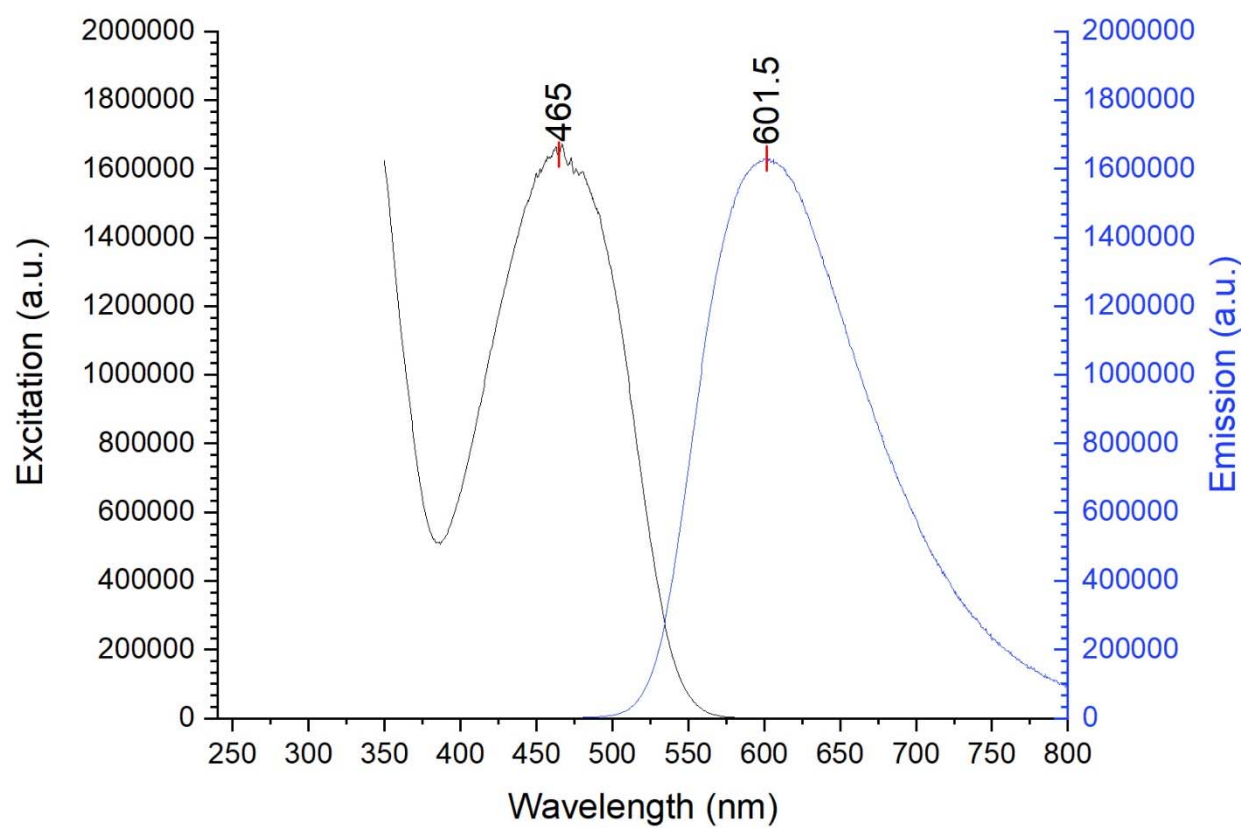


Figure S35 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.2 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.2 nm) spectra of compound **3** and $B(2,4-F_2-C_6H_3)_3$; 12.5 μ M sample.

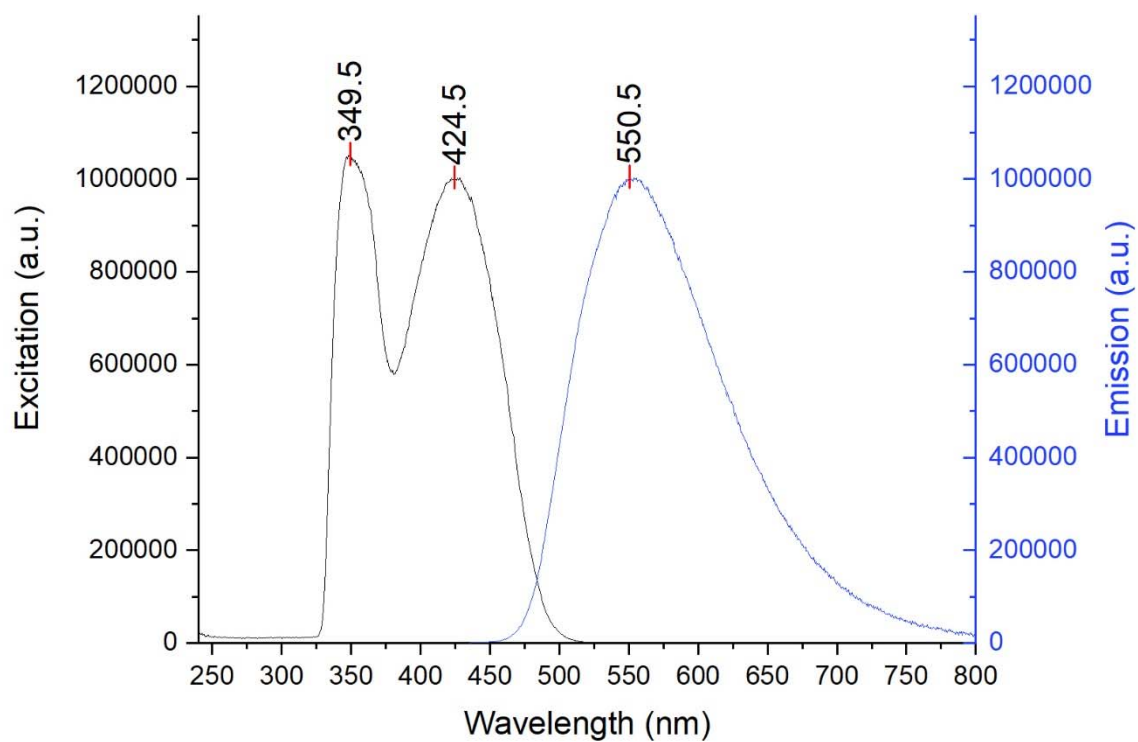


Figure S36 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.2 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.2 nm) spectra of compound **7** and **B(2,4-F₂-C₆H₃)₃**; 12.5 μ M sample.

6.1.11. $B(3,4-F_2-C_6H_3)_3$

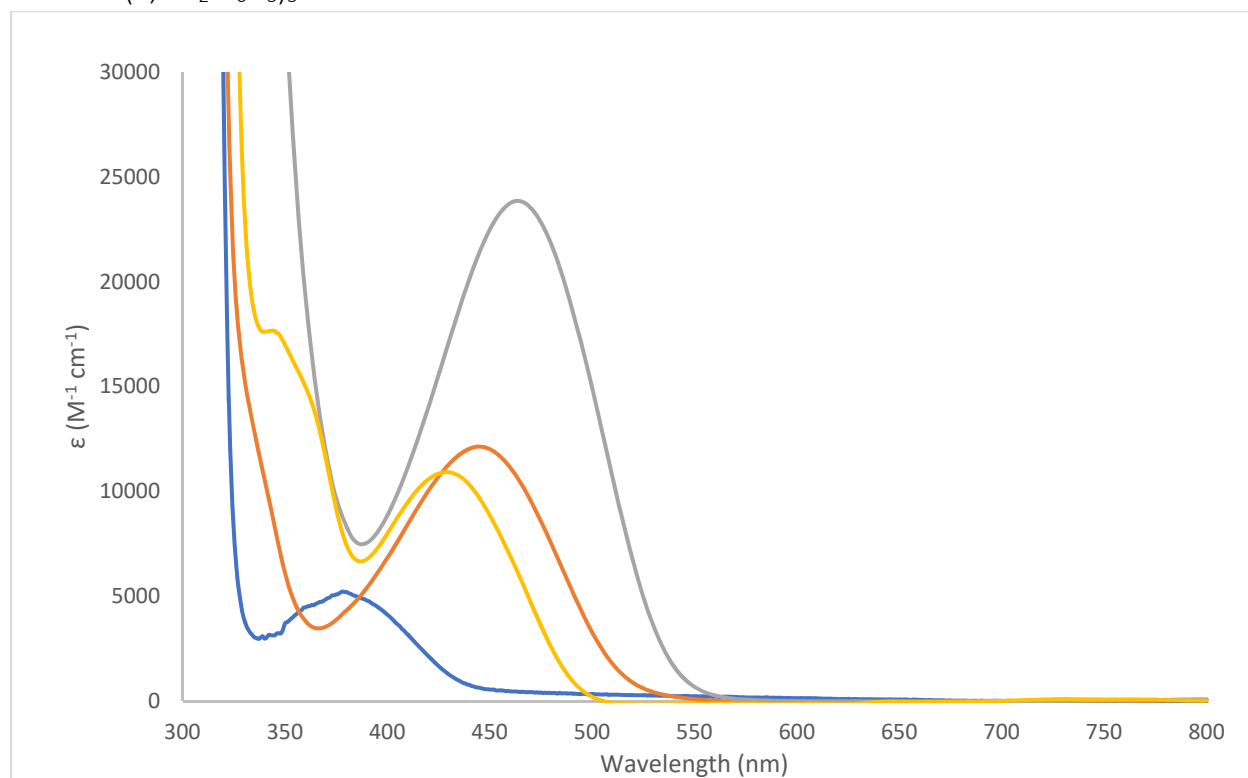


Figure S37 Stacked UV-Vis absorption spectra of **1** (blue), **2** (orange), **3** (grey), and **7** (yellow) with $B(3,4-F_2-C_6H_3)_3$ (1000 eq.); 12.5 μM samples.

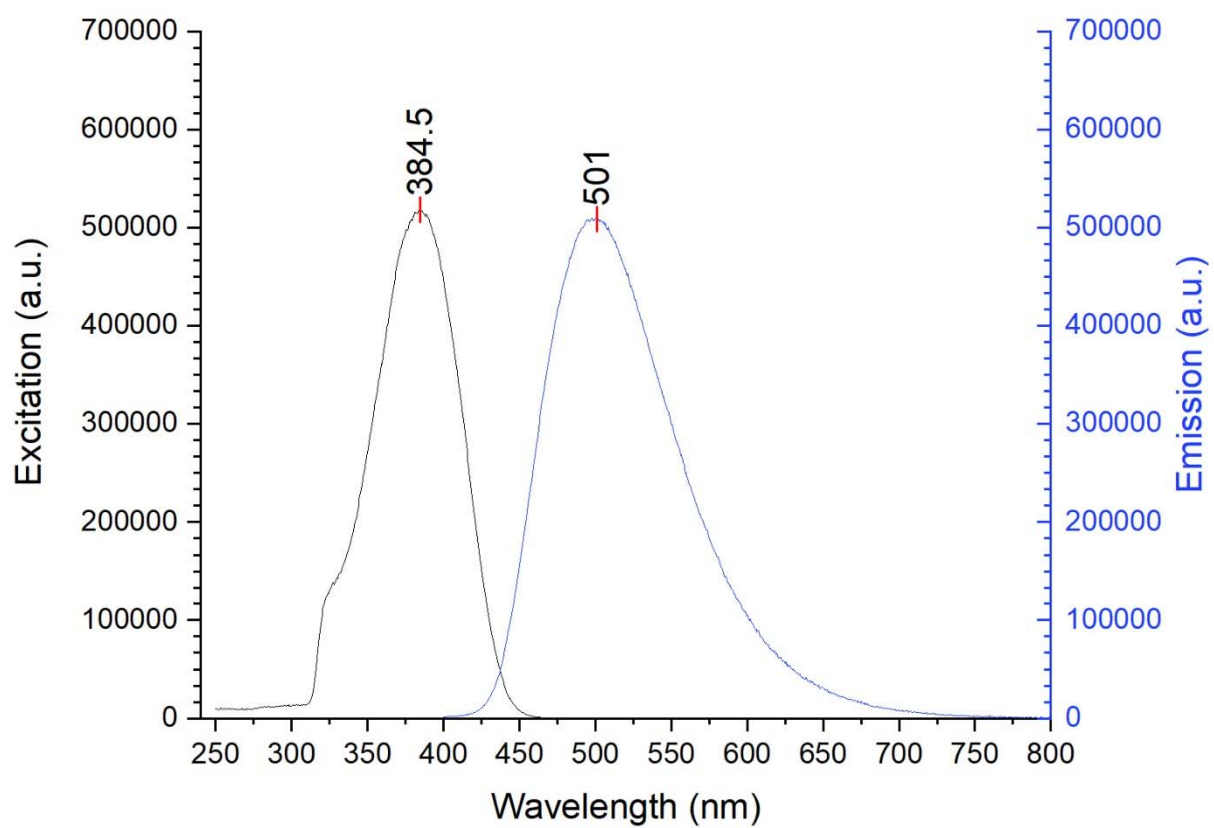


Figure S38 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.2 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.2 nm) spectra of compound **1** and **B(3,4-F₂-C₆H₃)₃**; 12.5 μ M sample.

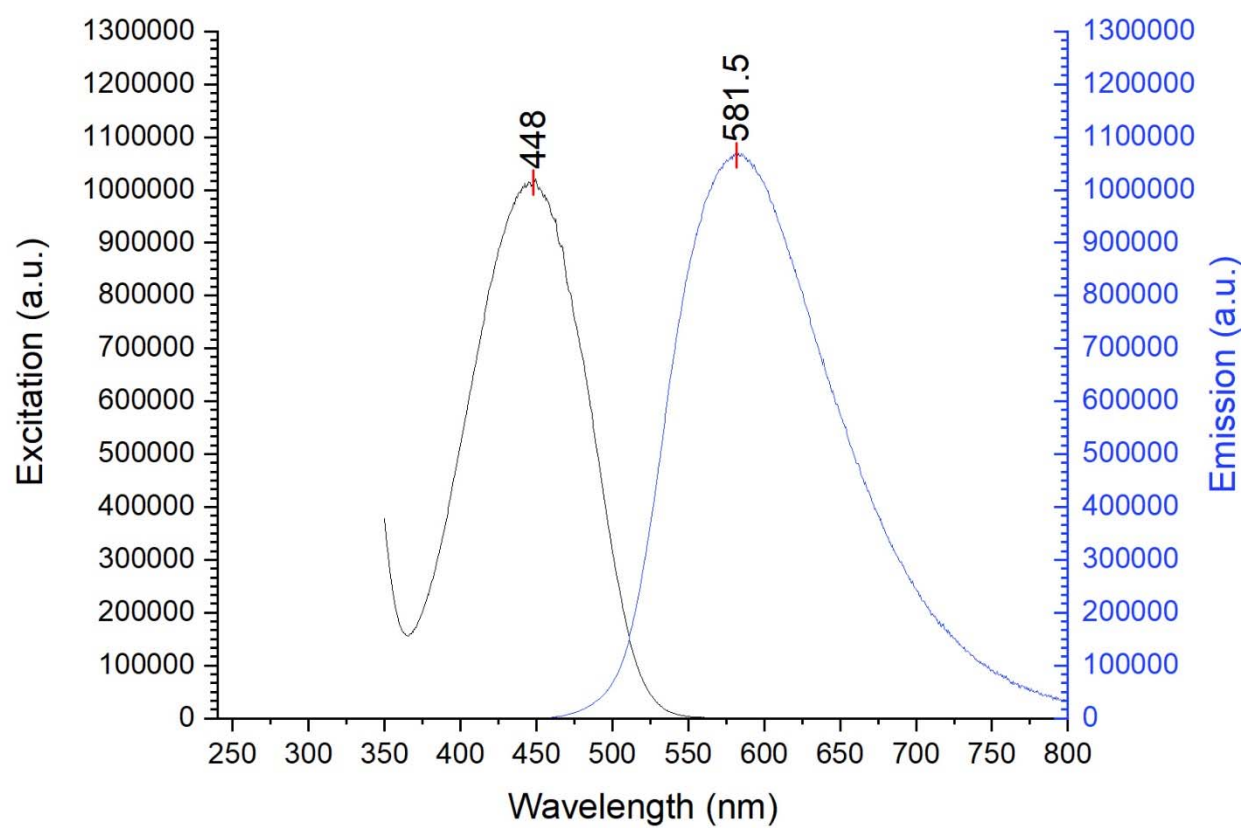


Figure S39 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.2 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.2 nm) spectra of compound **2** and **B(3,4-F₂-C₆H₃)₃**; 12.5 μ M sample.

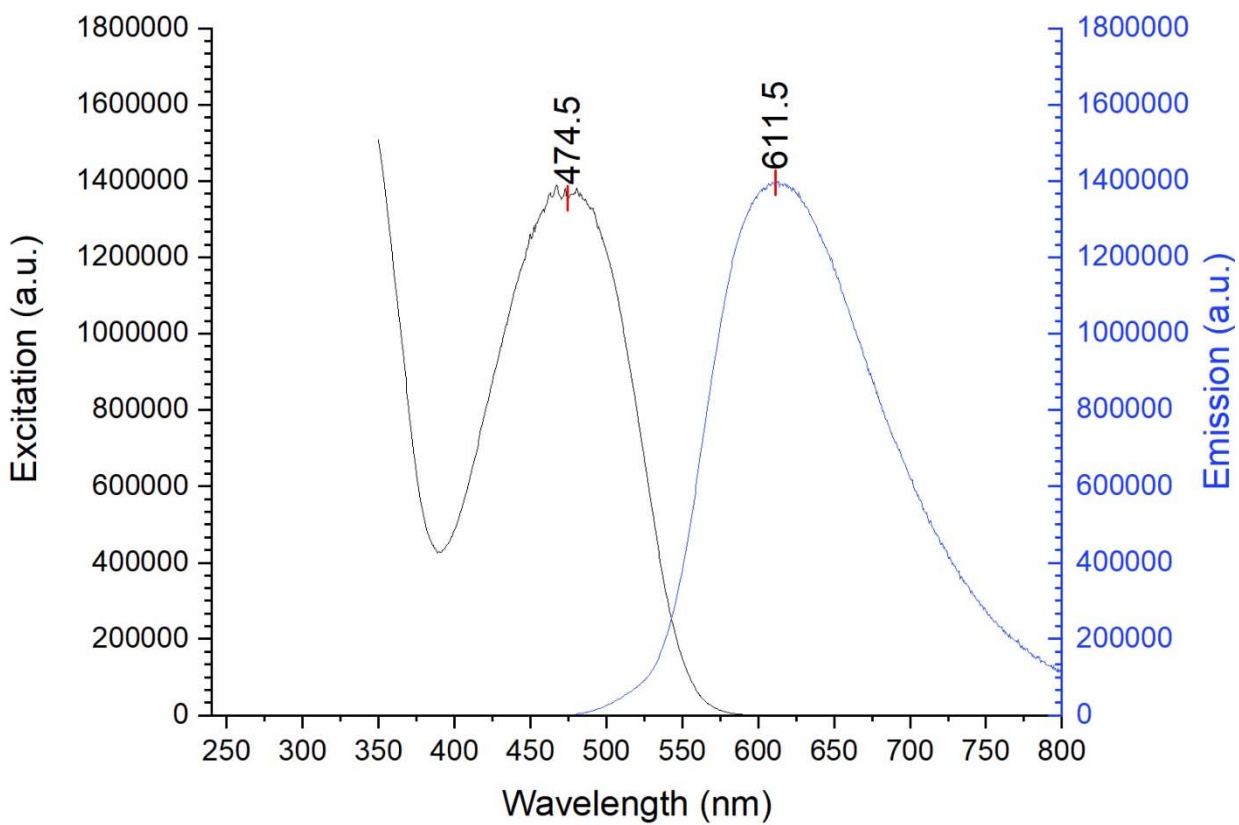


Figure S40 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.2 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.2 nm) spectra of compound **3** and **B(3,4-F₂-C₆H₃)₃**; 12.5 μ M sample.

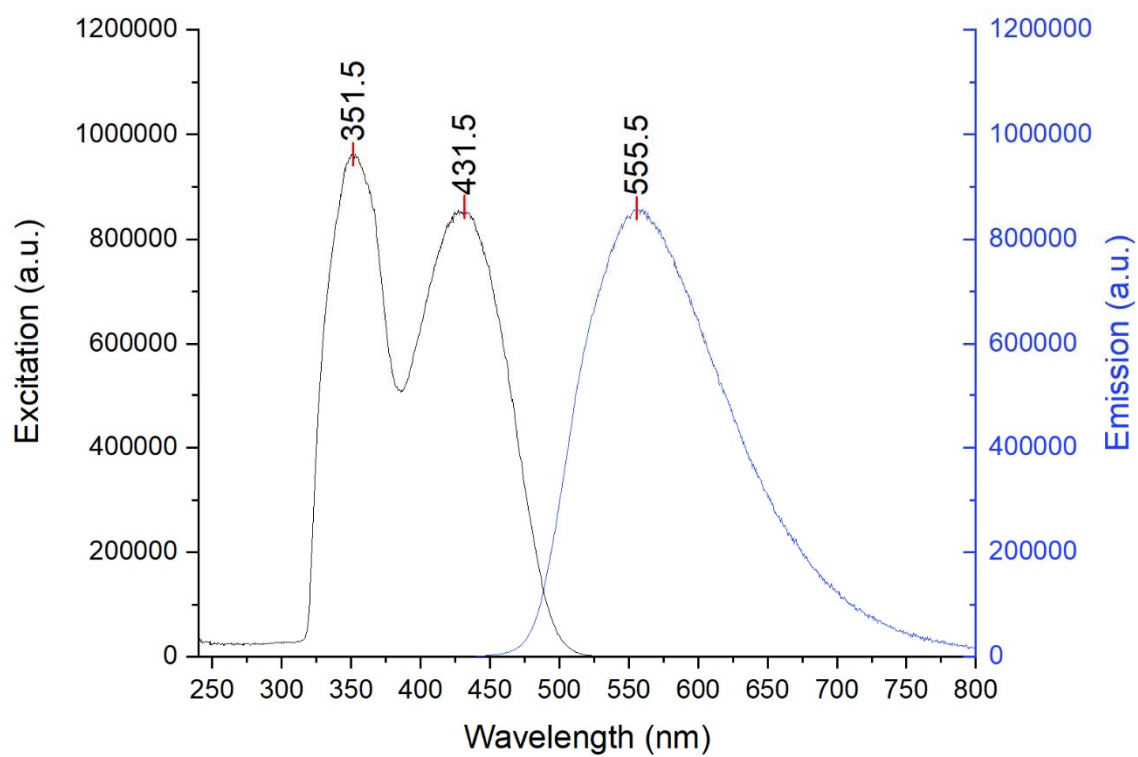


Figure S41 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.2 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.2 nm) spectra of compound **7** and **B(3,4-F₂-C₆H₃)₃**; 12.5 μ M sample.

6.1.12. $B(2,4,6-F_3-C_6H_2)_3$

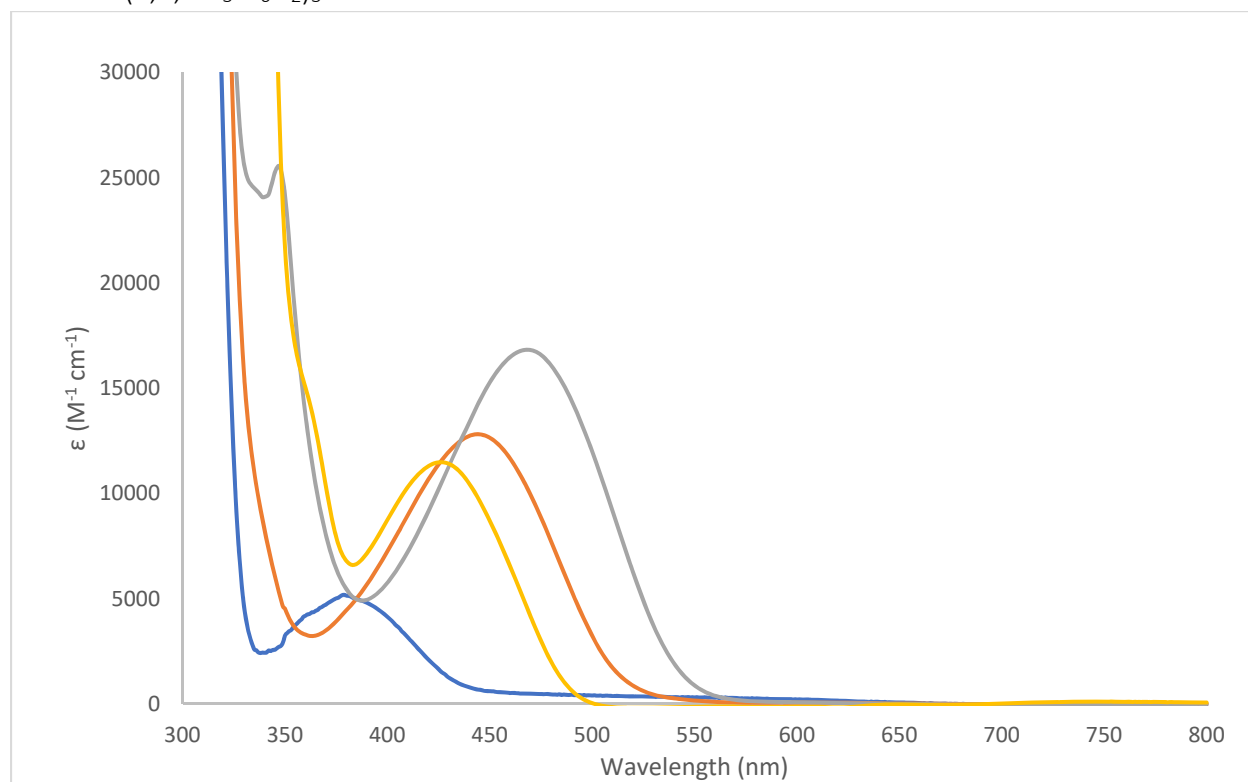


Figure S42 Stacked UV-Vis absorption spectra of **1** (blue), **2** (orange), **3** (grey), and **7** (yellow) with $B(2,4,6-F_3-C_6H_2)_3$ (1000 eq.); 12.5 μM samples.

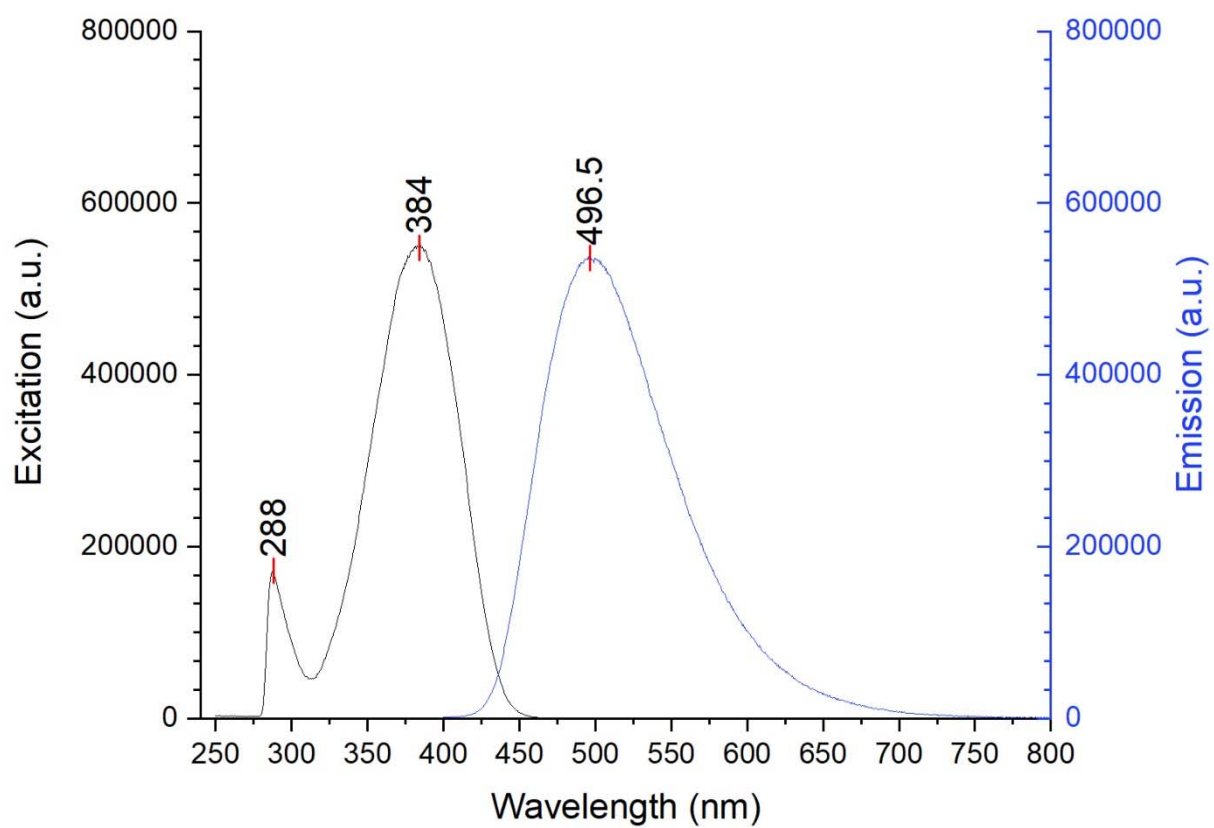


Figure S43 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.2 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.2 nm) spectra of compound **1** and **B(2,4,6-F₃-C₆H₂)₃**; 12.5 μ M sample.

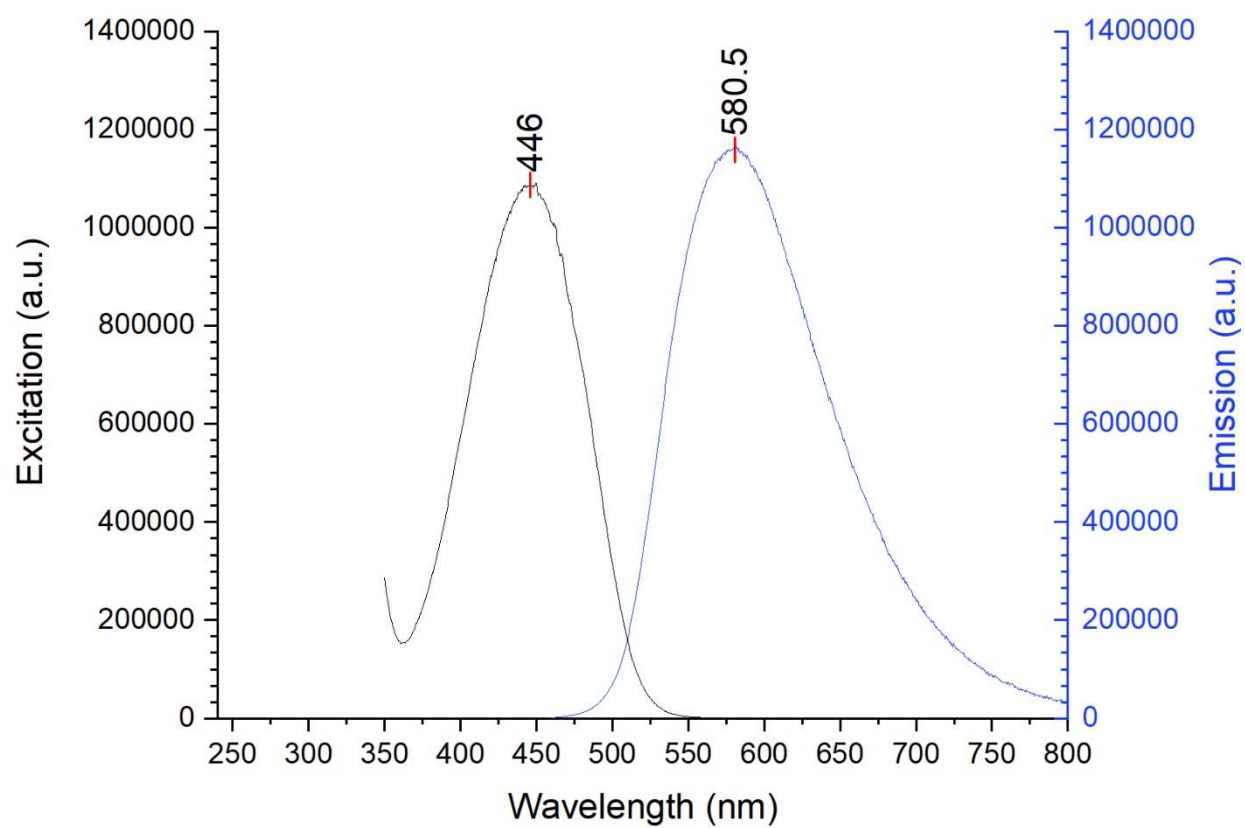


Figure S44 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.2 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.2 nm) spectra of compound **2** and **B(2,4,6-F₃-C₆H₂)₃**; 12.5 μ M sample.

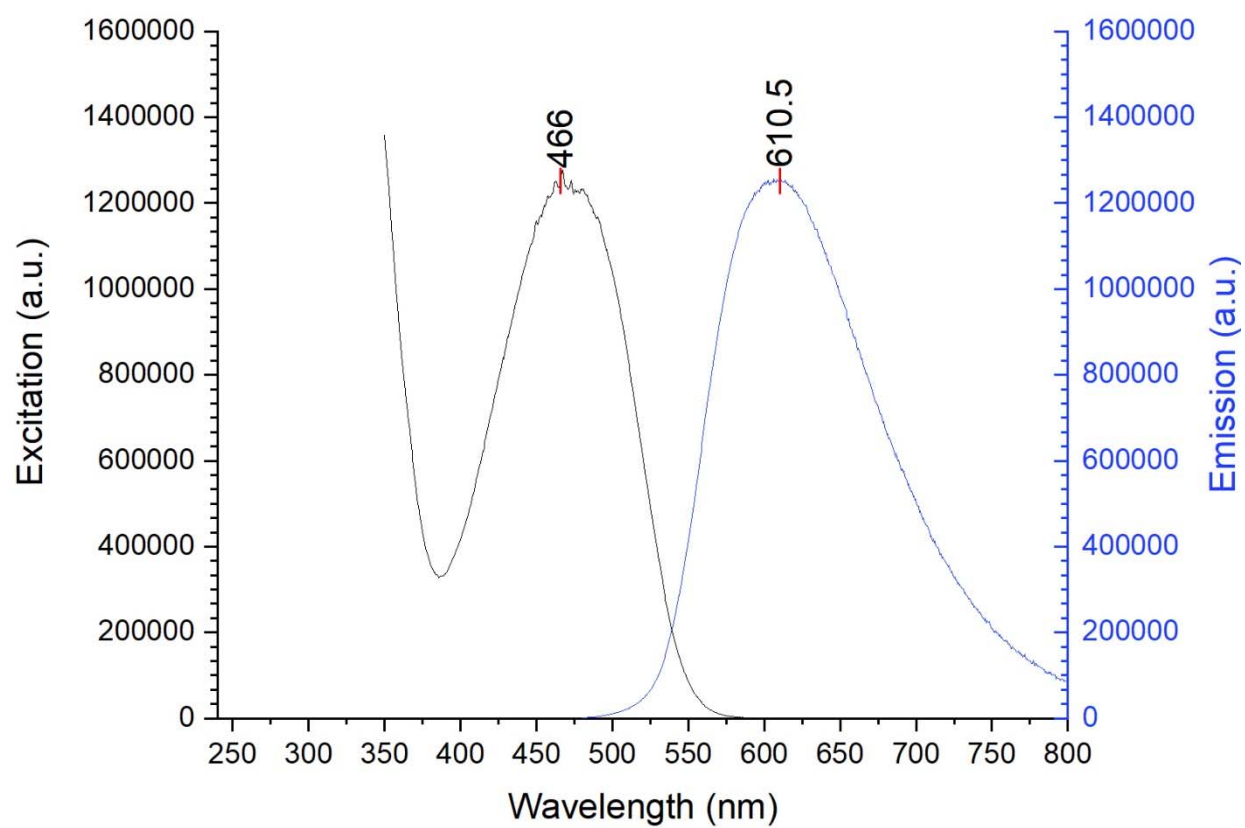


Figure S45 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.2 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.2 nm) spectra of compound **3** and **B(2,4,6-F₃-C₆H₂)₃**; 12.5 μ M sample.

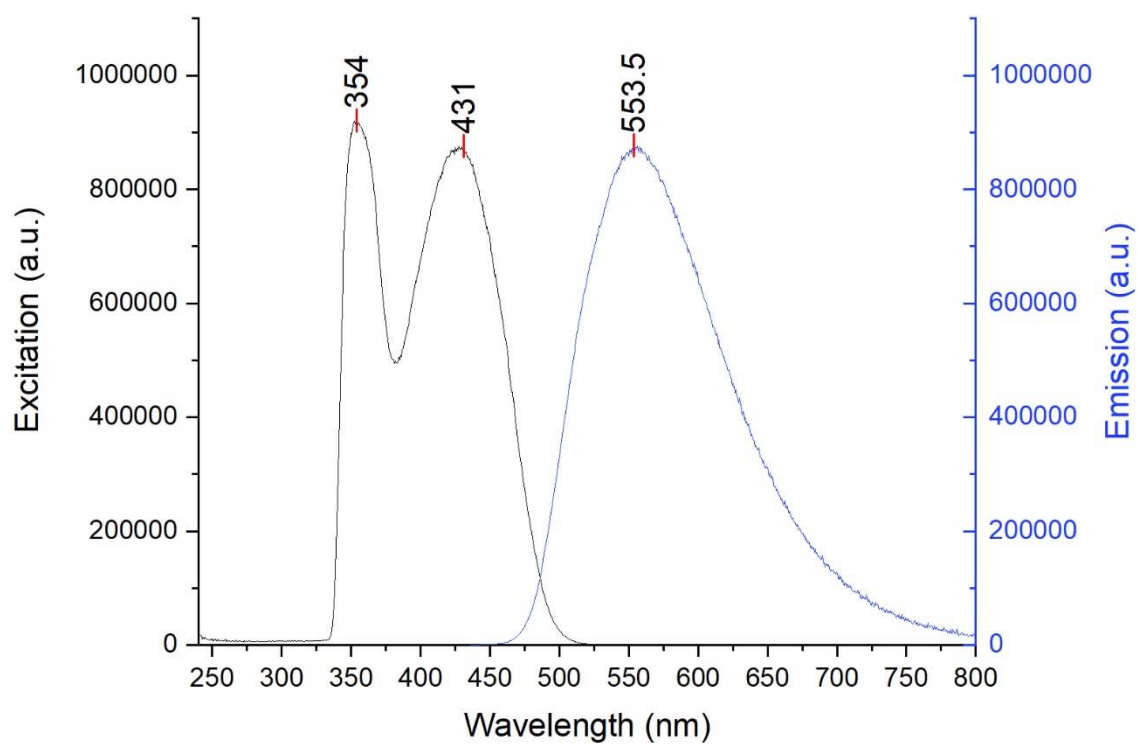


Figure S46 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.2 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.2 nm) spectra of compound **7** and **B(2,4,6-F₃-C₆H₂)₃**; 12.5 μM sample.

6.1.13. $B(3,4,5-F_3-C_6H_2)_3$

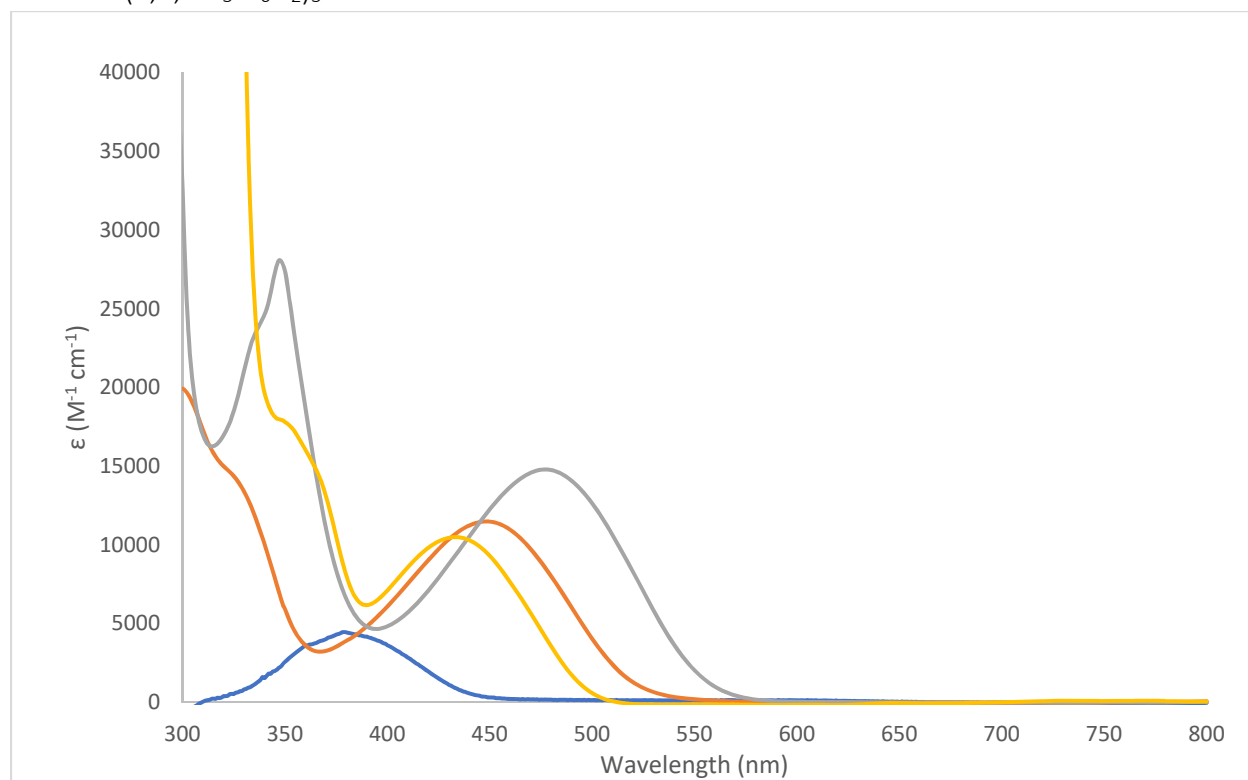


Figure S47 Stacked UV-Vis absorption spectra of **1** (blue), **2** (orange), **3** (grey), and **7** (yellow) with $B(3,4,5-F_3-C_6H_2)_3$ (1000 eq.); 12.5 μM samples.

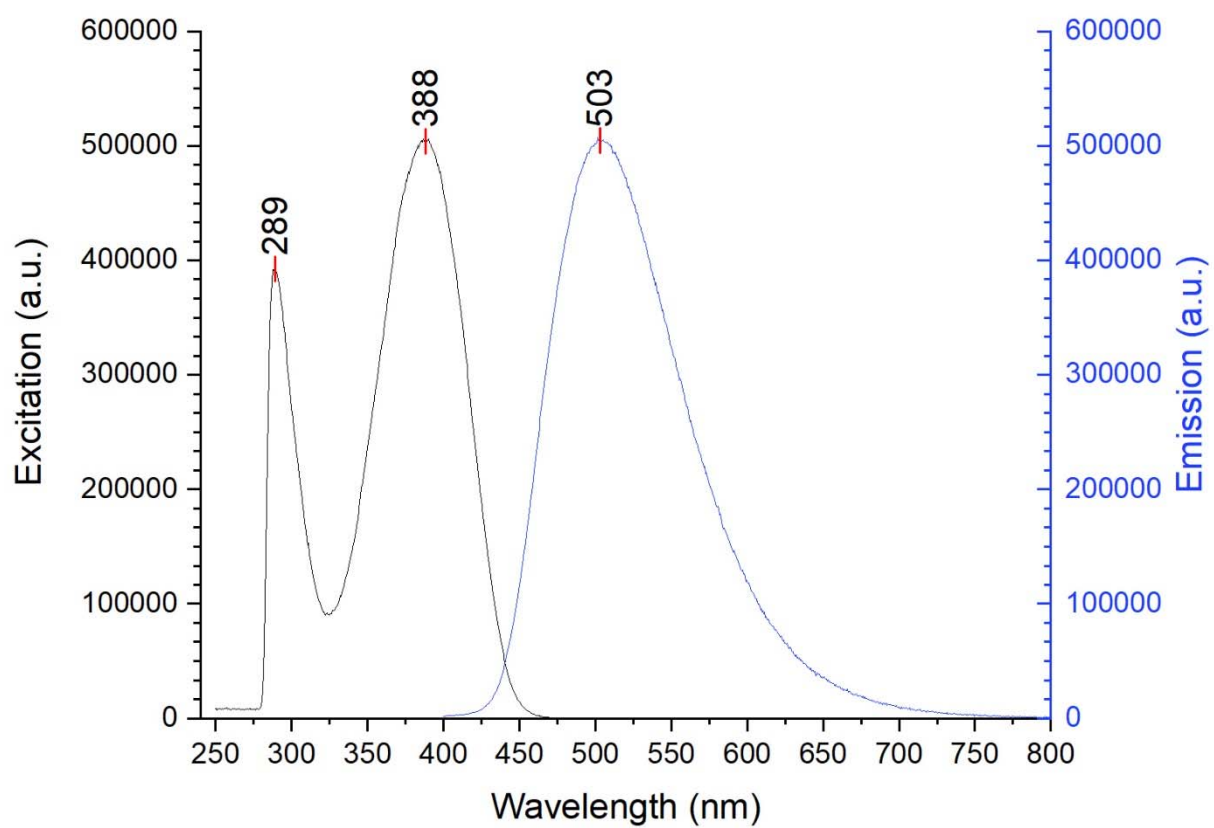


Figure S48 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.2 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.2 nm) spectra of compound **1** and **B(3,4,5-F₃-C₆H₂)₃**; 12.5 μ M sample.

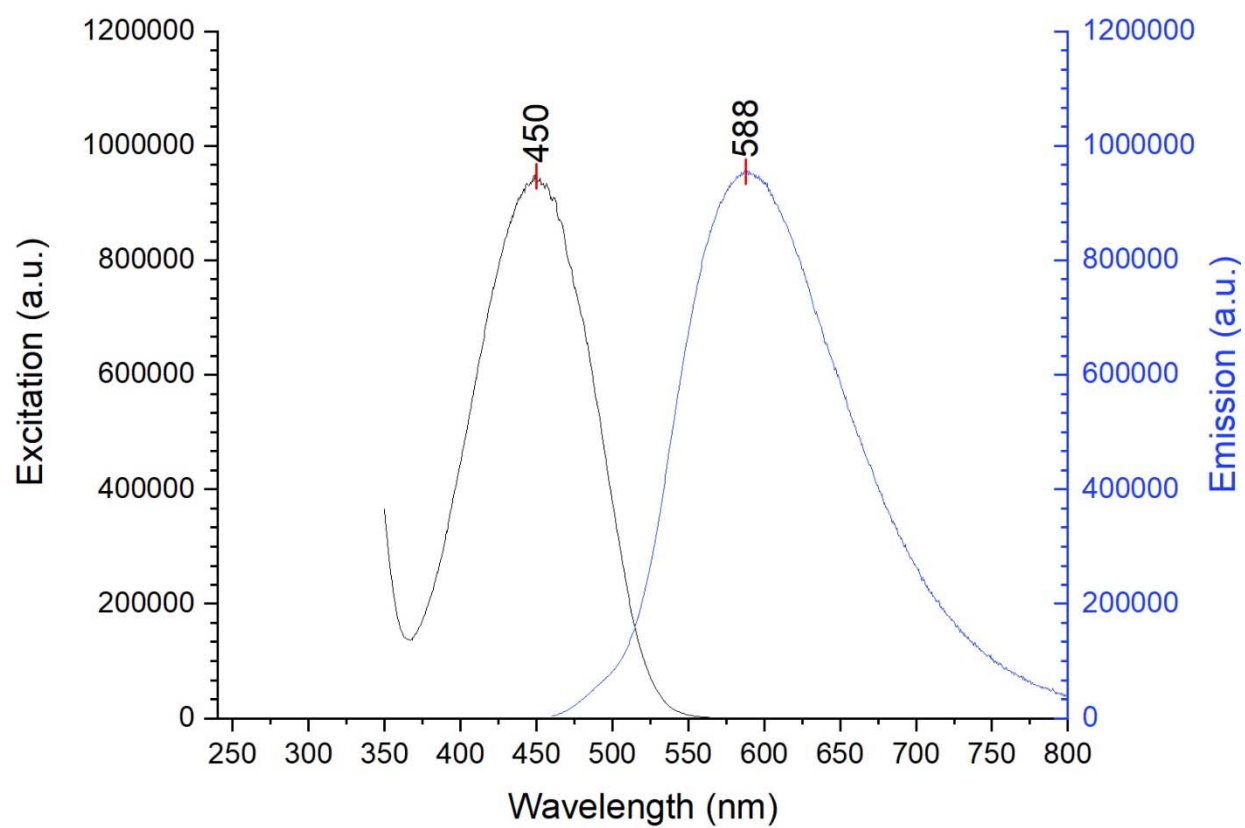


Figure S49 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.2 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.2 nm) spectra of compound **2** and **B(2,4,6-F₃-C₆H₂)₃**; 12.5 μ M sample.

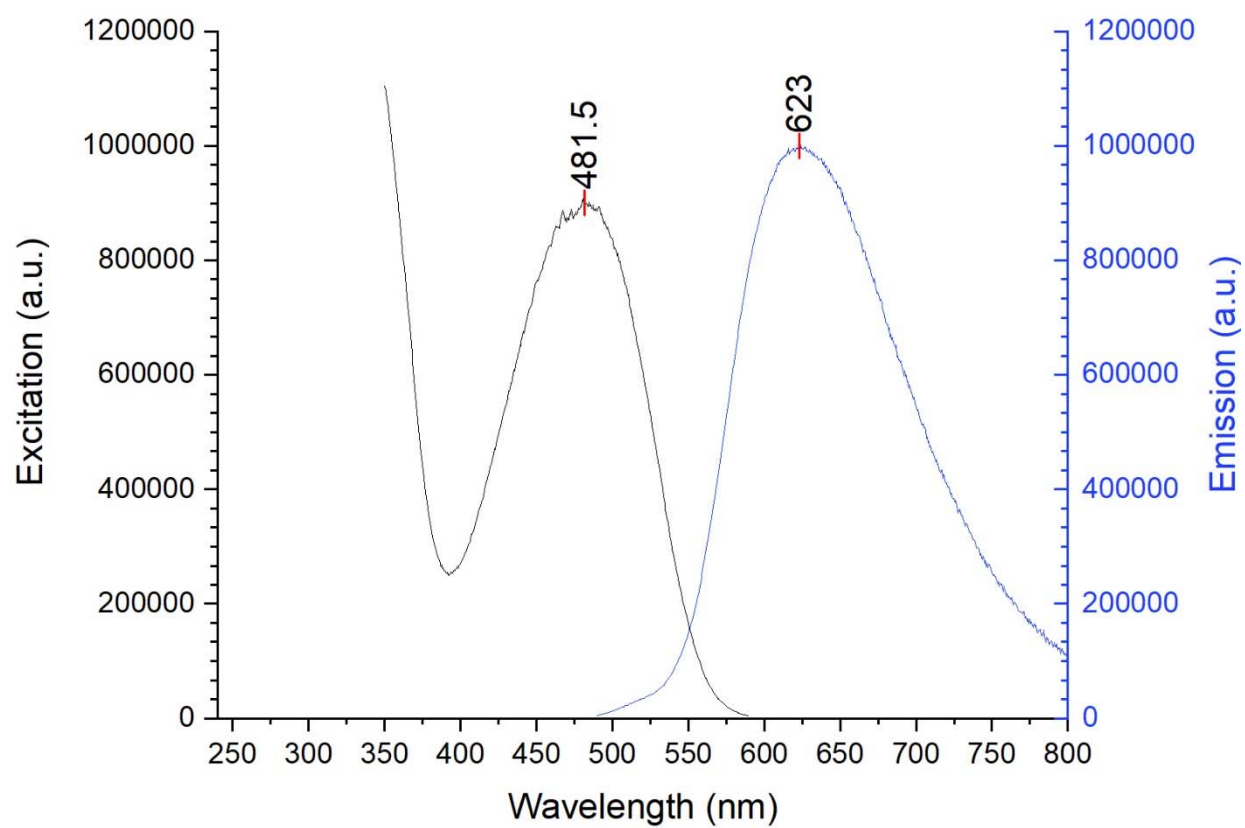


Figure S50 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.2 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.2 nm) spectra of compound **3** and **B(2,4,6-F₃-C₆H₂)₃**; 12.5 μ M sample.

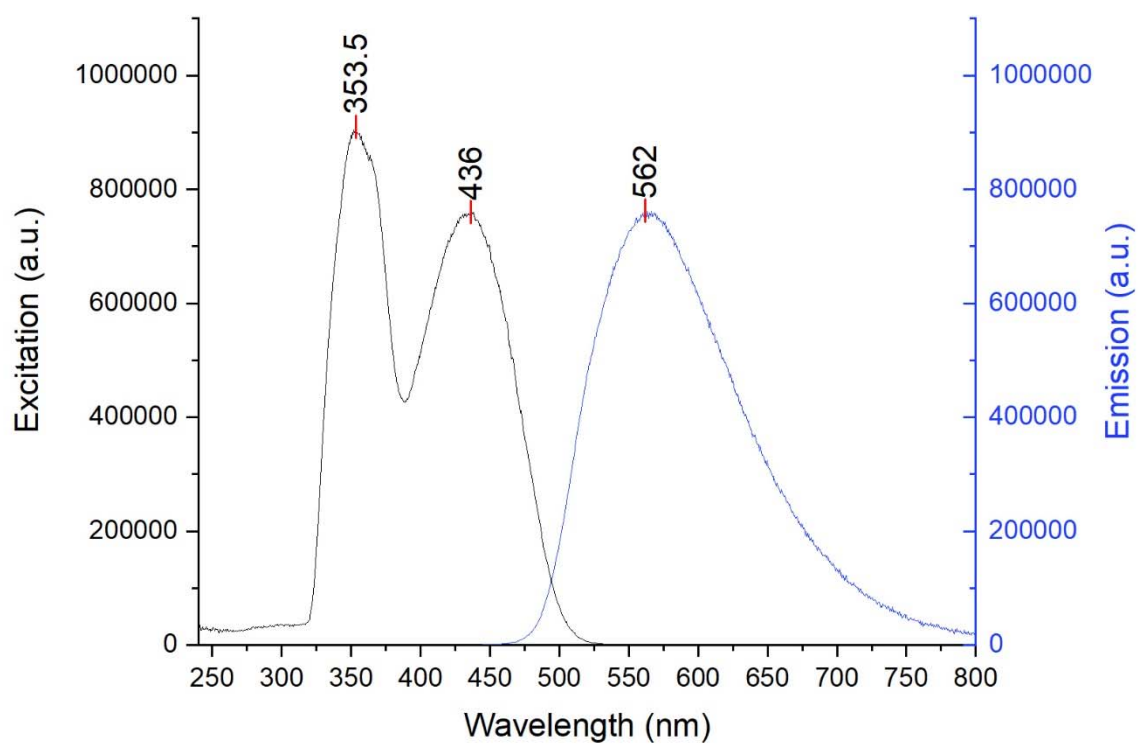


Figure S51 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.2 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.2 nm) spectra of compound **7** and **B(2,4,6-F₃-C₆H₂)₃**; 12.5 μM sample.

6.1.14. $(\text{Ph}_2\text{N})_2\text{B}(\text{C}_6\text{F}_5)$

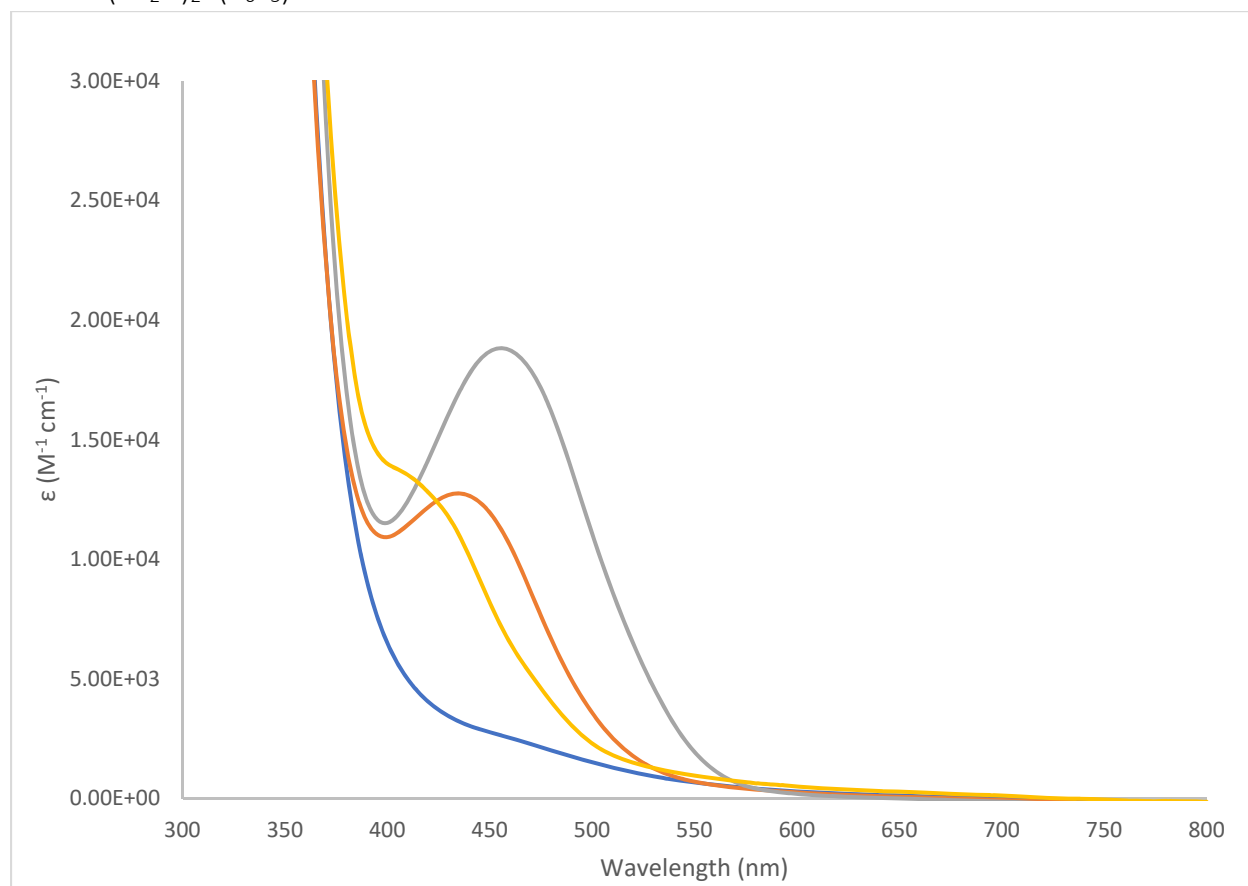


Figure S52 Stacked UV-Vis absorption spectra of **1** (blue), **2** (orange), **3** (grey), and **7** (yellow) with $(\text{Ph}_2\text{N})_2\text{B}(\text{C}_6\text{F}_5)$ (100 eq.); 12.5 μM samples.

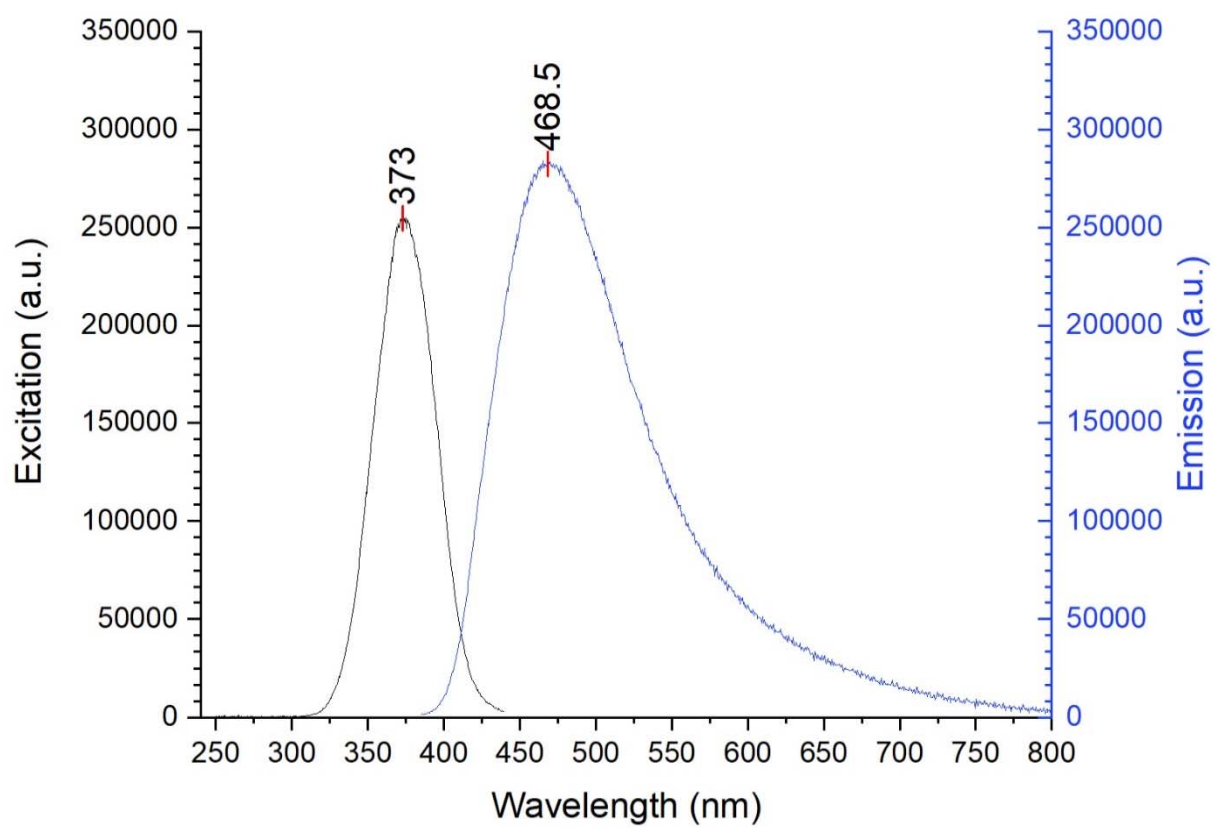


Figure S53 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.2 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.2 nm) spectra of compound **1** and $(\text{Ph}_2\text{N})_2\text{B}(\text{C}_6\text{F}_5)$; $12.5\ \mu\text{M}$ sample.

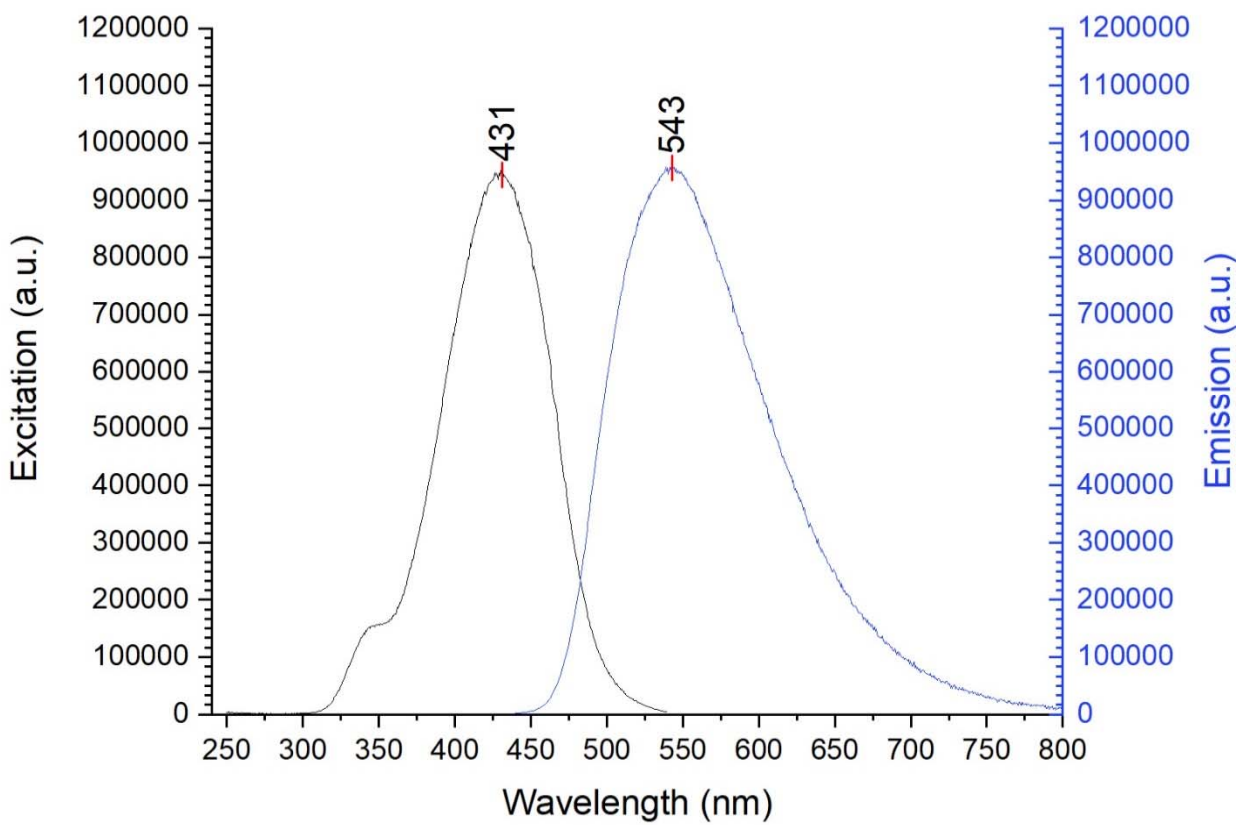


Figure S54 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.2 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.2 nm) spectra of compound **2** and (Ph₂N)₂B(C₆F₅)₃; 12.5 μM sample.

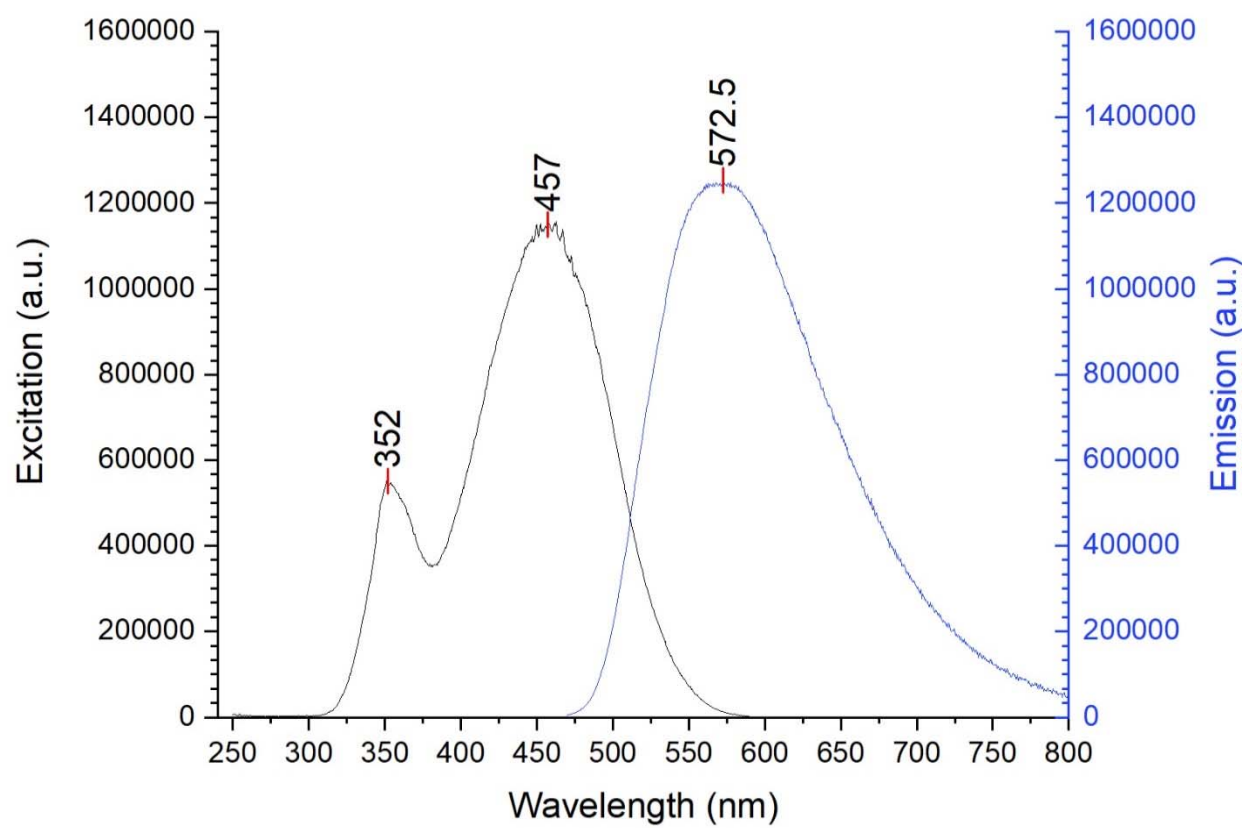


Figure S55 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.2 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.2 nm) spectra of compound **3** and $(\text{Ph}_2\text{N})_2\text{B}(\text{C}_6\text{F}_5)$; $12.5\ \mu\text{M}$ sample.

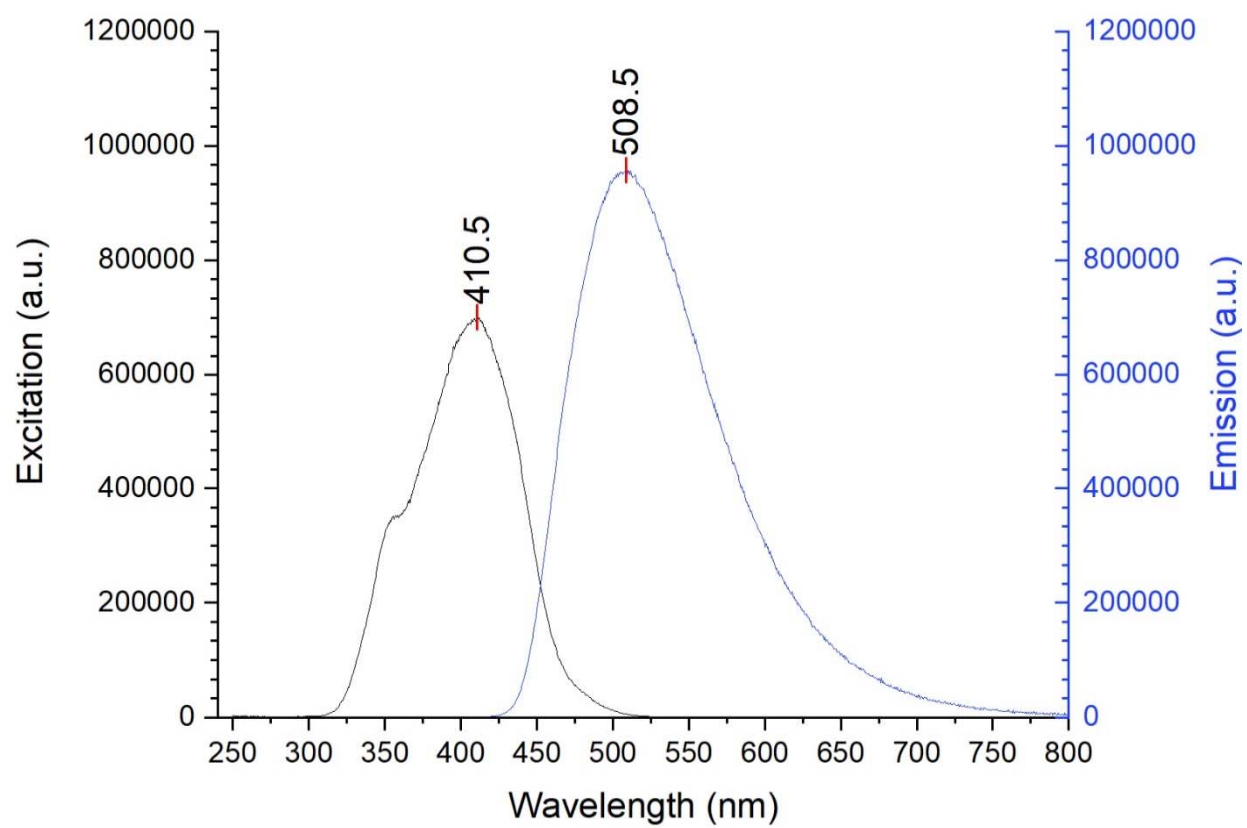


Figure S56 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.2 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.2 nm) spectra of compound **7** and $(\text{Ph}_2\text{N})_2\text{B}(\text{C}_6\text{F}_5)_3$; 12.5 μM sample.

6.1.15. $B(OC_6F_5)_3$

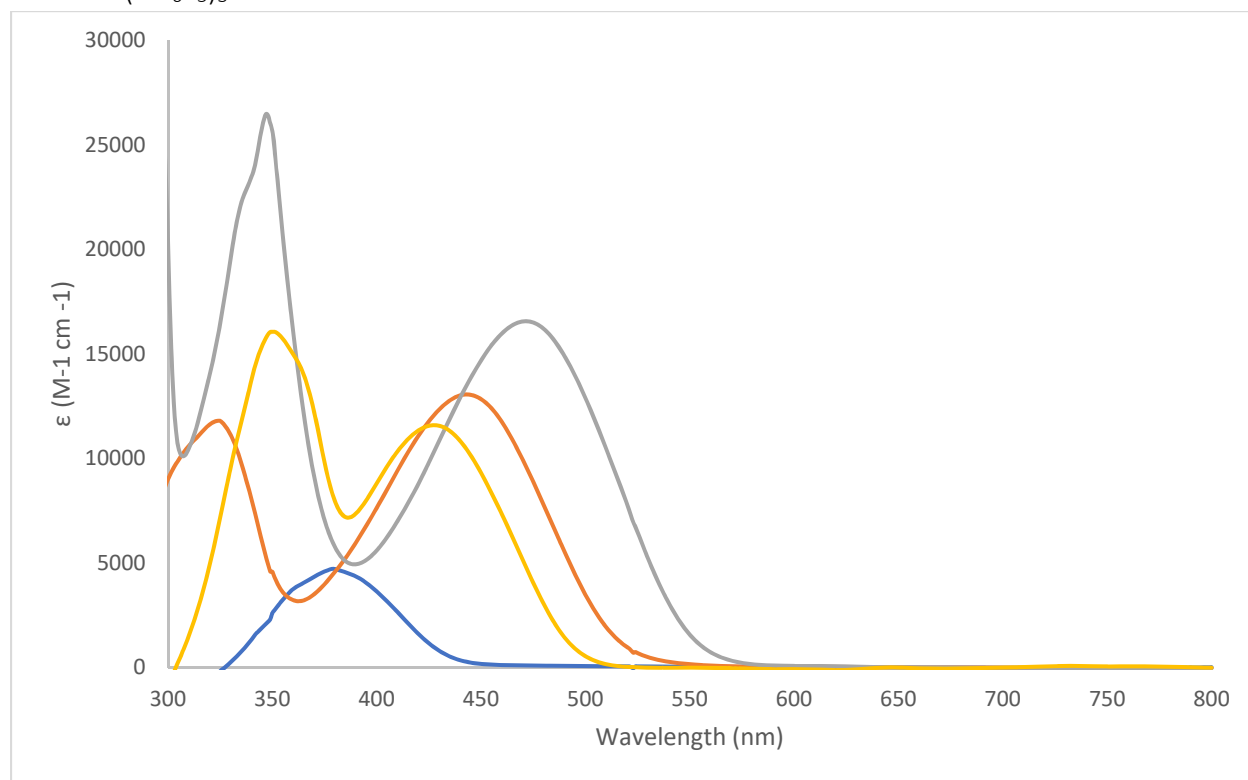


Figure S57 Stacked UV-Vis absorption spectra of **1** (blue), **2** (orange), **3** (grey), and **7** (yellow) with $B(OC_6F_5)_3$ (1000 eq.); 12.5 μM samples.

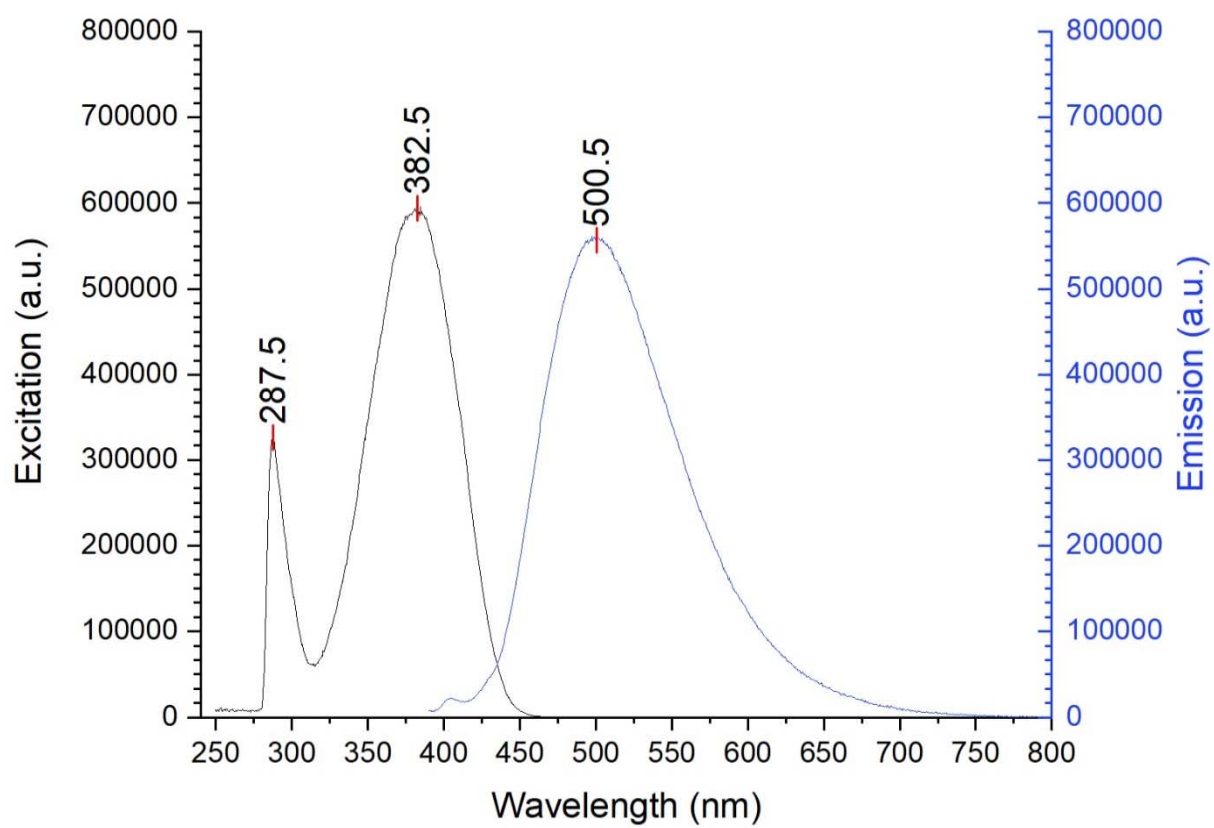


Figure S58 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.2 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.2 nm) spectra of compound **1** and **B(OC₆F₅)₃**; 12.5 μ M sample.

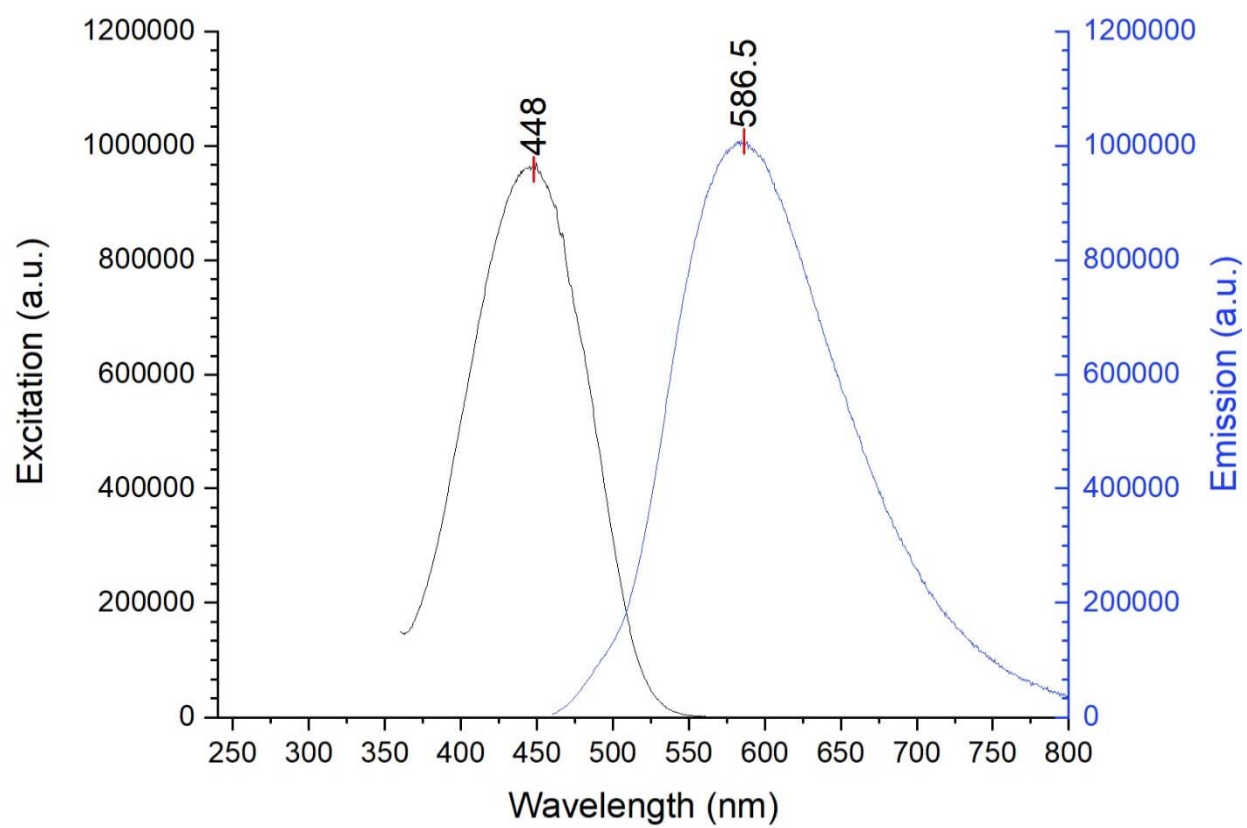


Figure S59 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.2 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.2 nm) spectra of compound **2** and **B(OC₆F₅)₃**; 12.5 μ M sample.

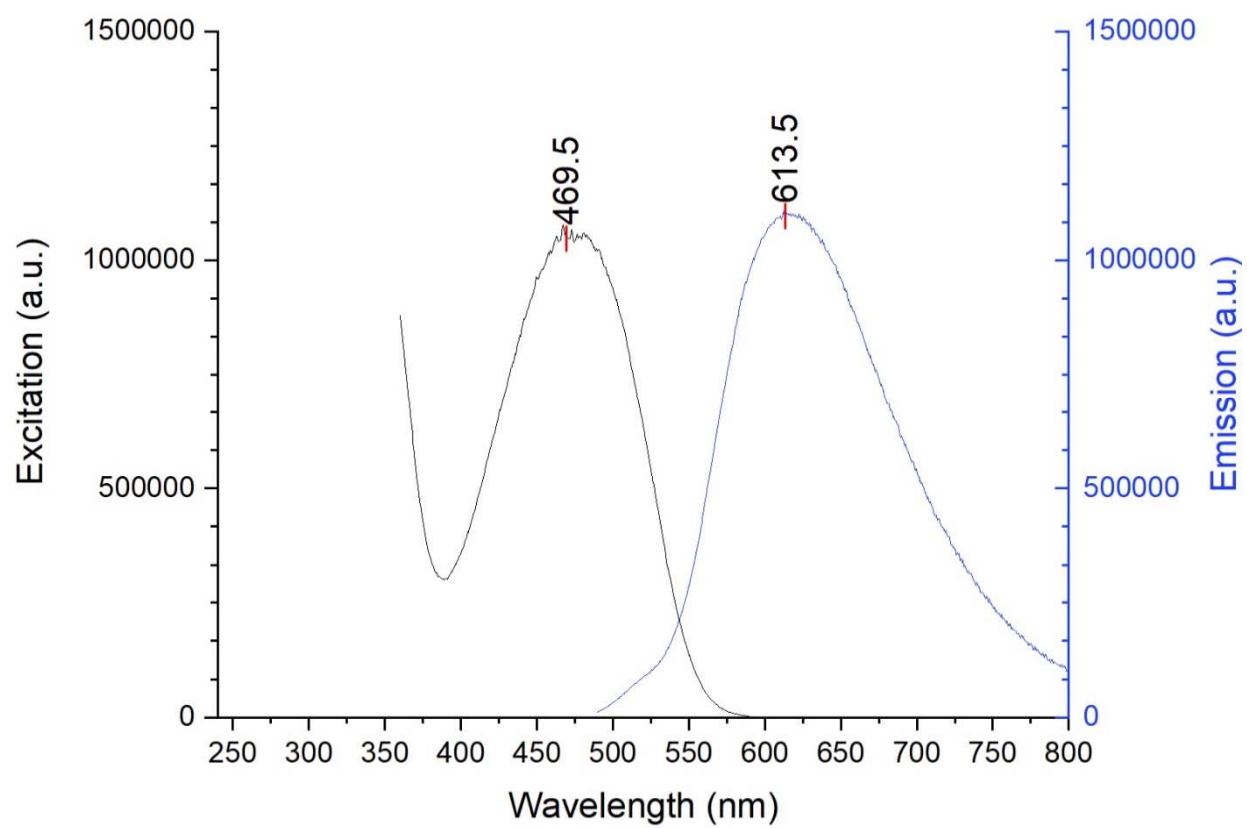


Figure S60 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.2 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.2 nm) spectra of compound **3** and $B(OC_6F_5)_3$; 12.5 μM sample.

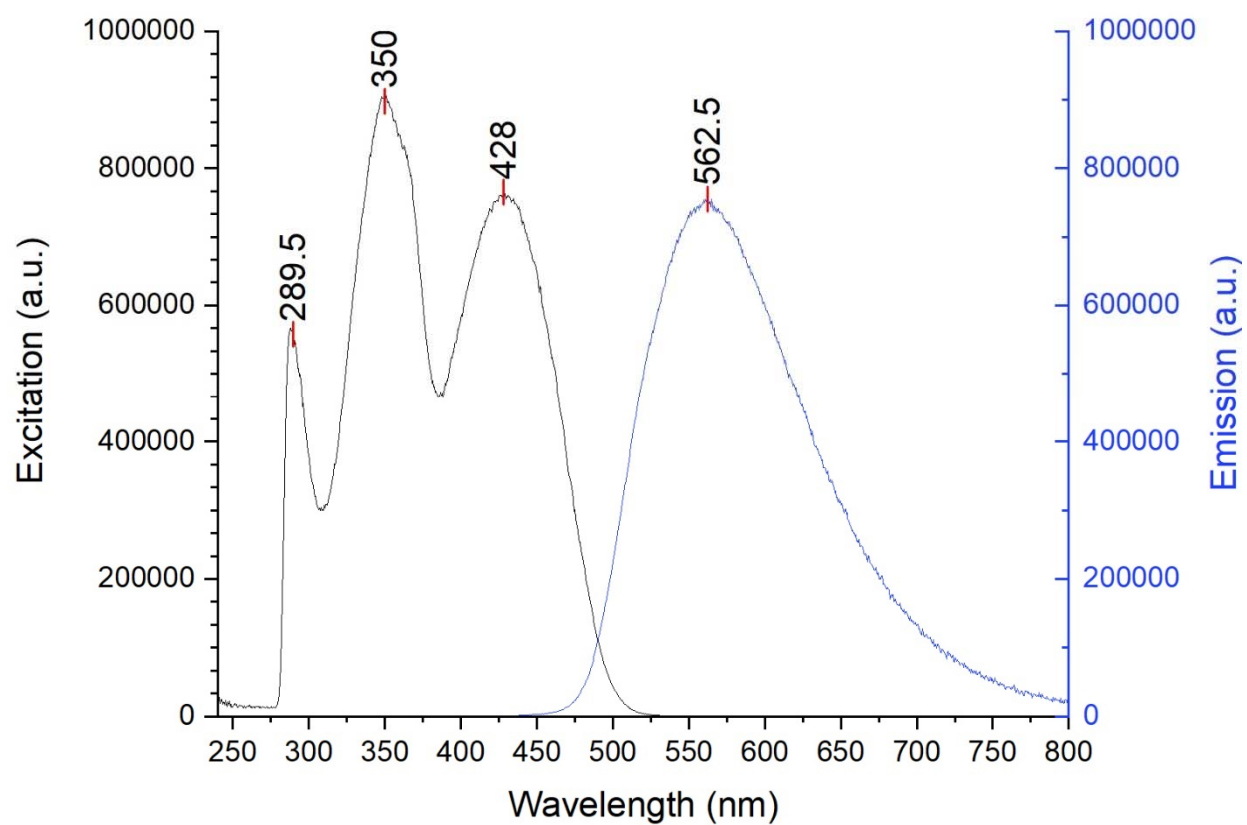


Figure S61 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.2 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.2 nm) spectra of compound **7** and **B(OC₆F₅)₃**; 12.5 μ M sample.

6.1.16. Bi(OTf)₃

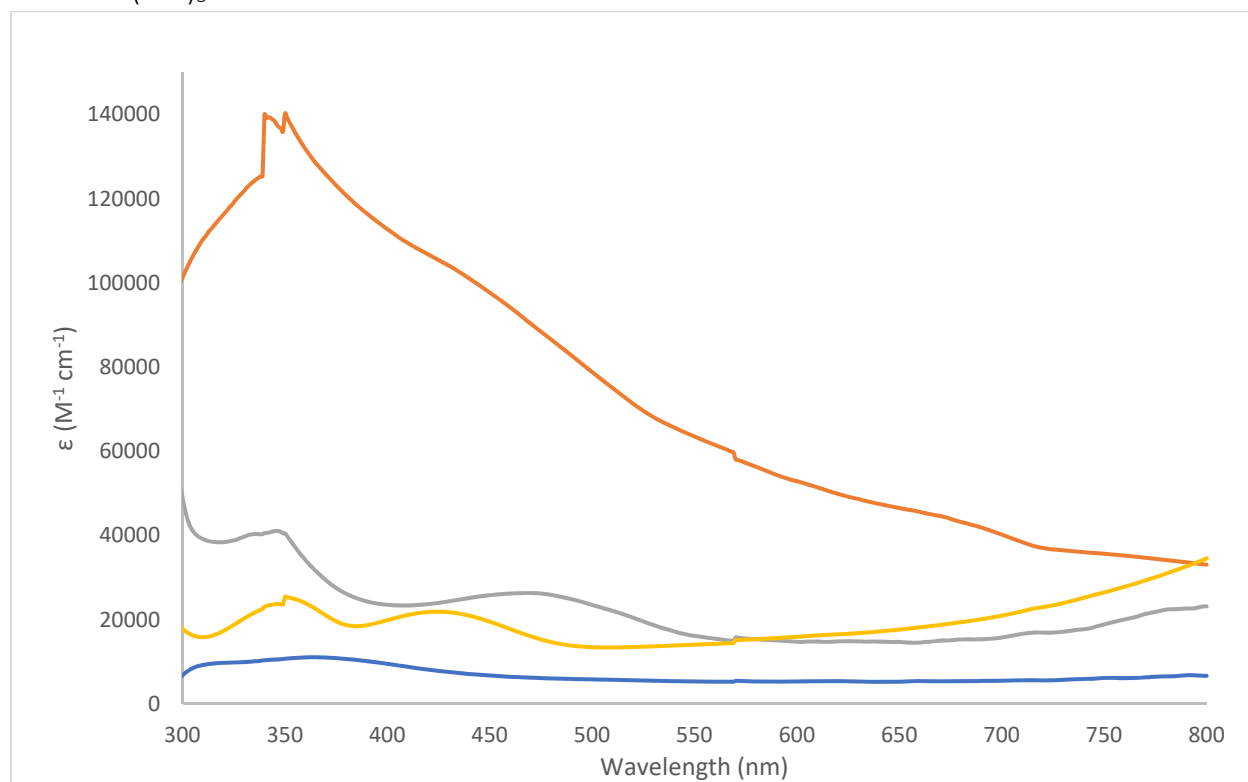


Figure S62 Stacked UV-Vis absorption spectra of **1** (blue), **2** (orange), **3** (grey), and **7** (yellow) with Bi(OTf)₃ (excess); 12.5 μ M samples.

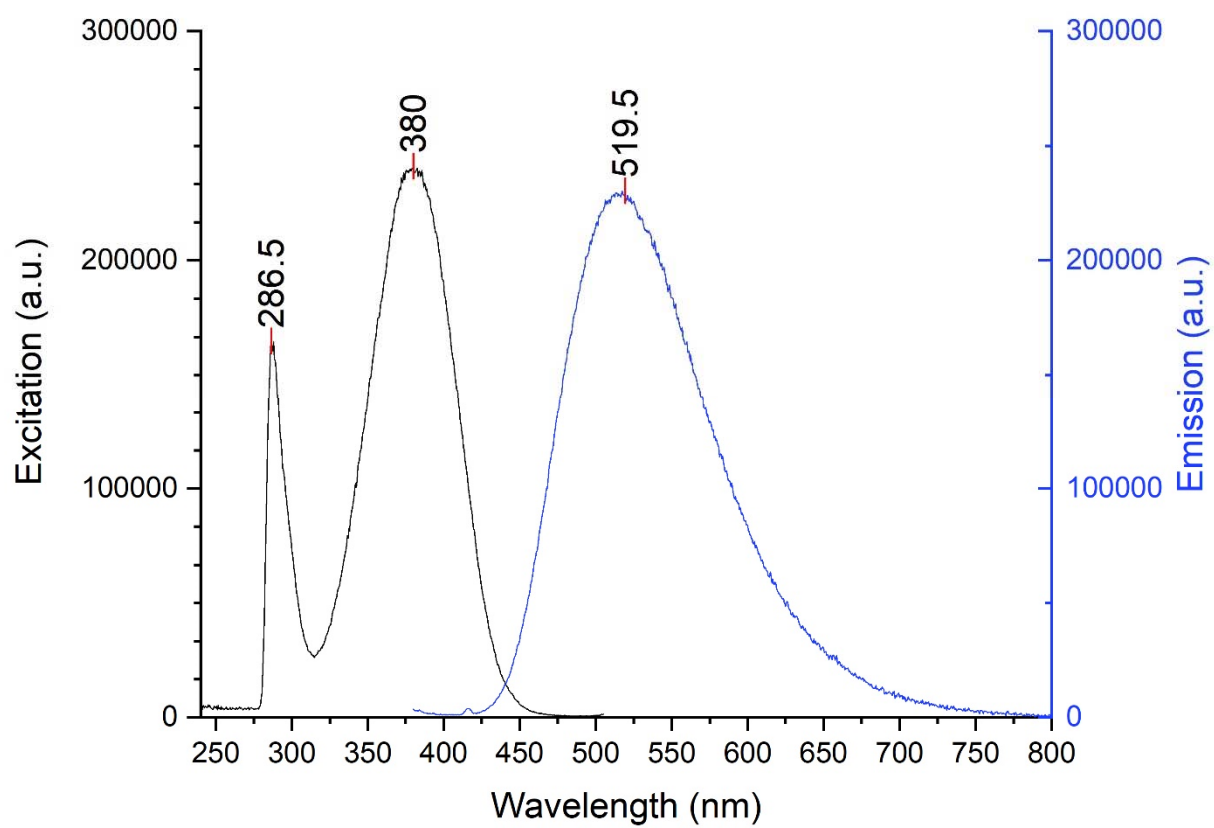


Figure S63 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.2 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.2 nm) spectra of compound **1** and **Bi(OTf)₃**; 12.5 μ M sample.

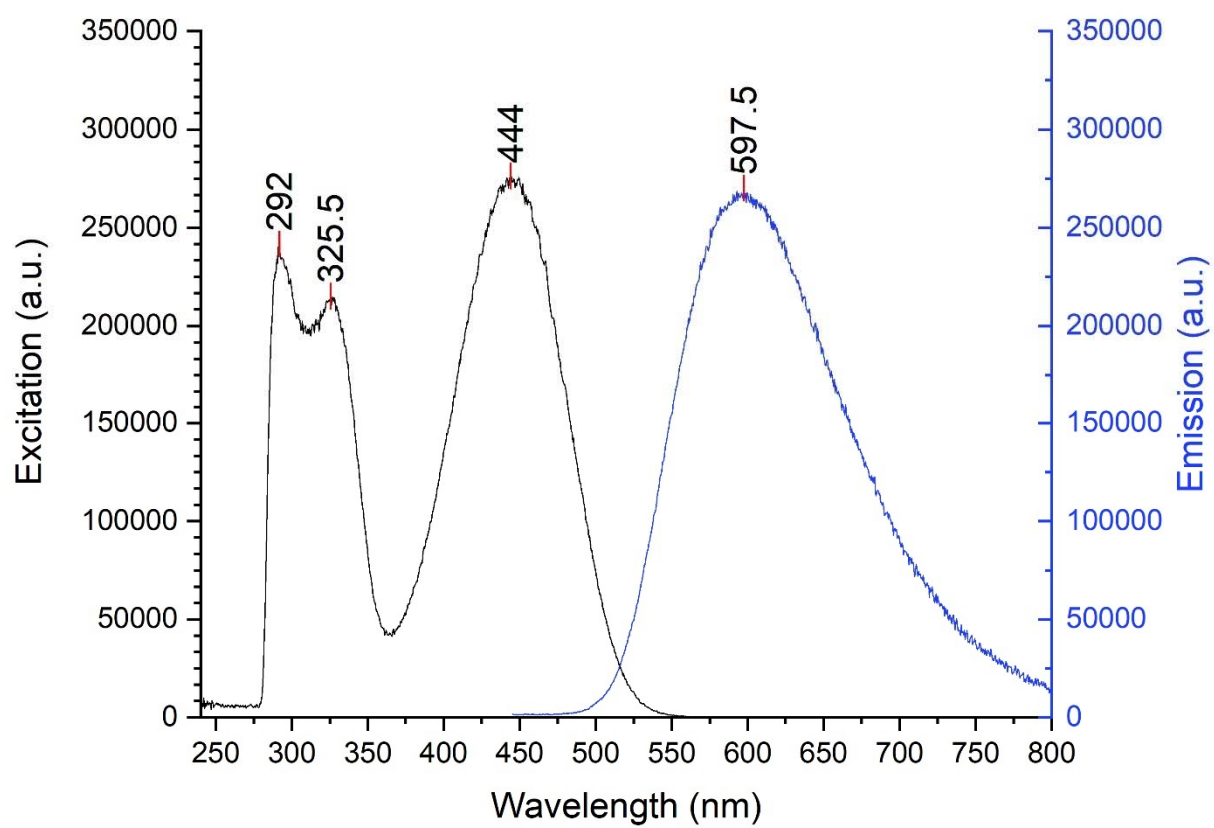


Figure S64 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.2 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.2 nm) spectra of compound **2** and $\text{Bi}(\text{OTf})_3$; 12.5 μM sample.

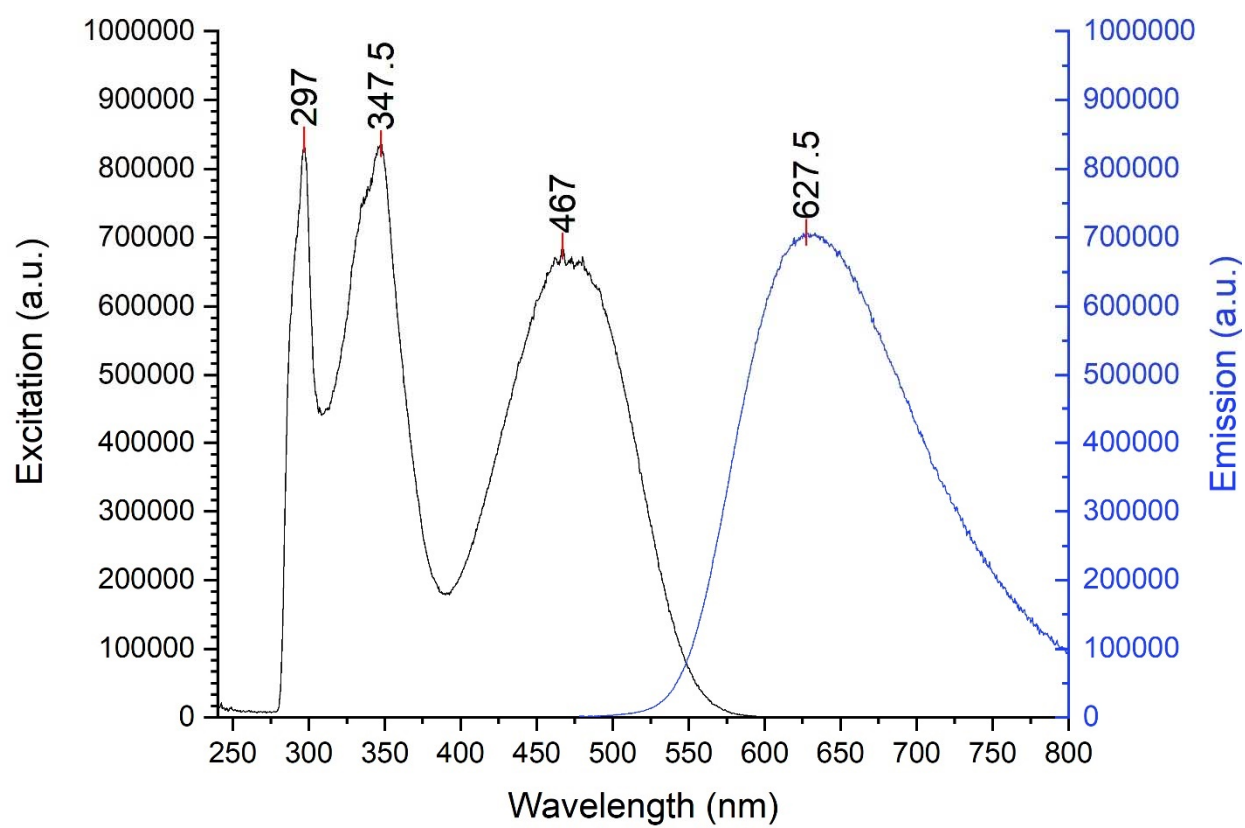


Figure S65 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.2 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.2 nm) spectra of compound **3** and $\text{Bi}(\text{OTf})_3$; 12.5 μM sample.

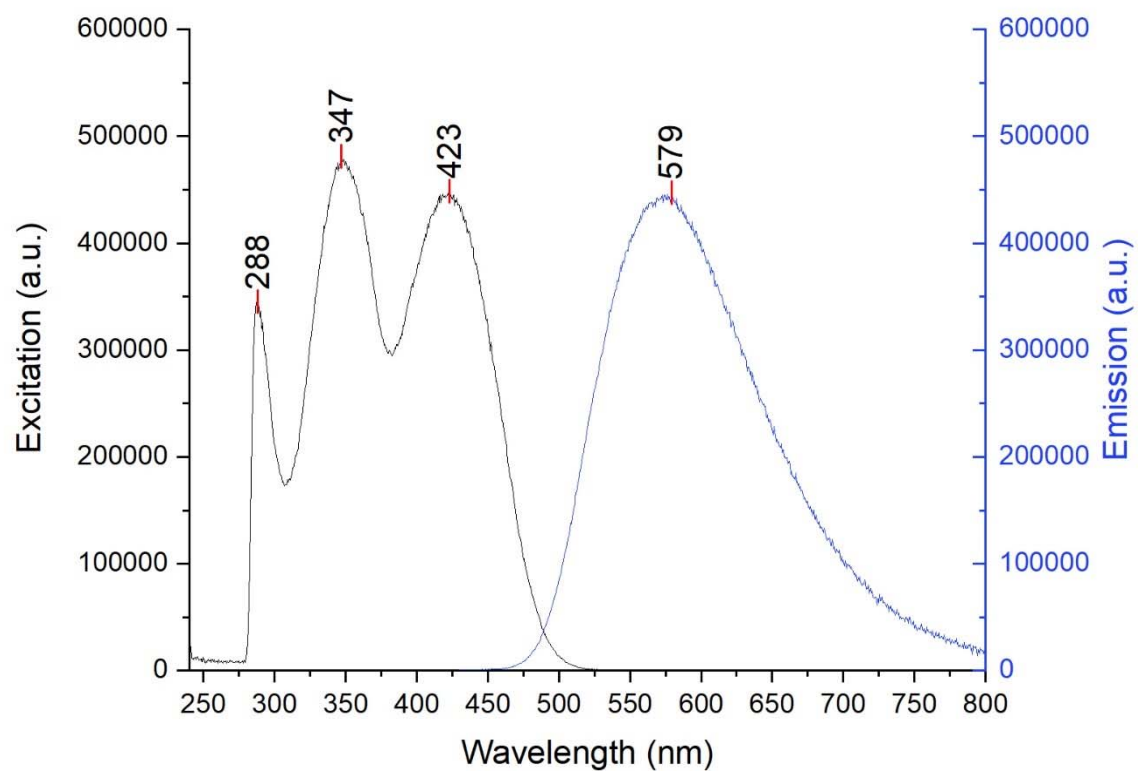


Figure S66 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) spectra of compound **7** and $\text{Bi}(\text{OTf})_3$; 12.5 μM sample.

6.1.17. [Mes₂B][B(C₆F₅)₄]

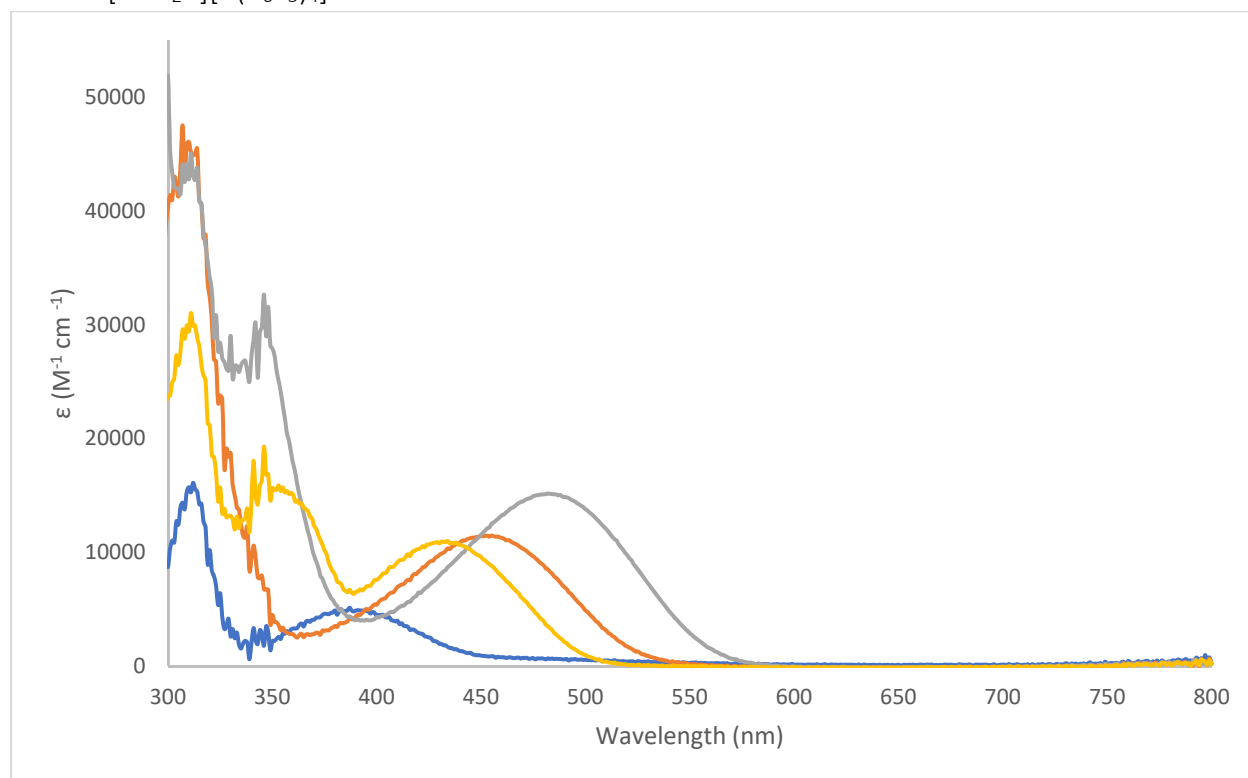


Figure S67 Stacked UV-Vis absorption spectra of **1** (blue), **2** (orange), **3** (grey), and **7** (yellow) with [Mes₂B][B(C₆F₅)₄] (2 eq.); 12.5 μ M samples.

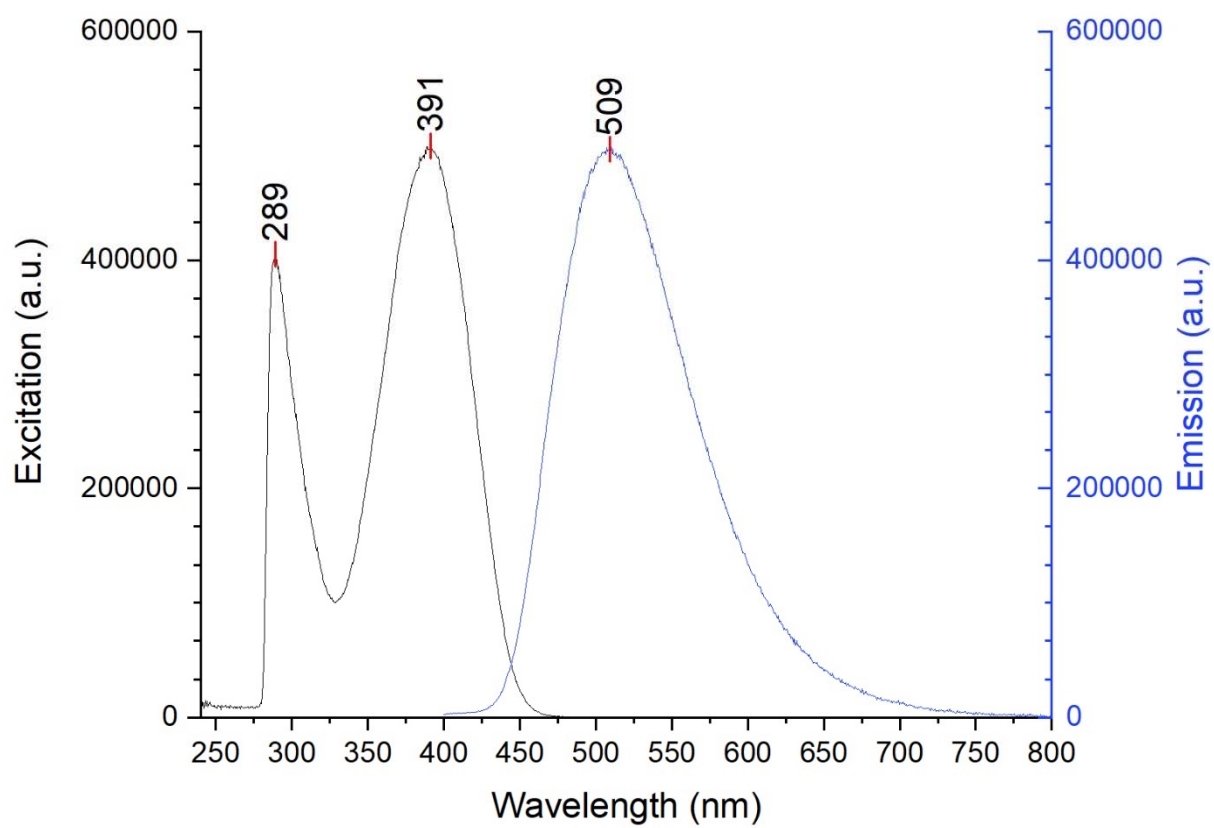


Figure S68 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) spectra of compound **1** and **[Mes₂B][B(C₆F₅)₄]**; 12.5 μM sample.

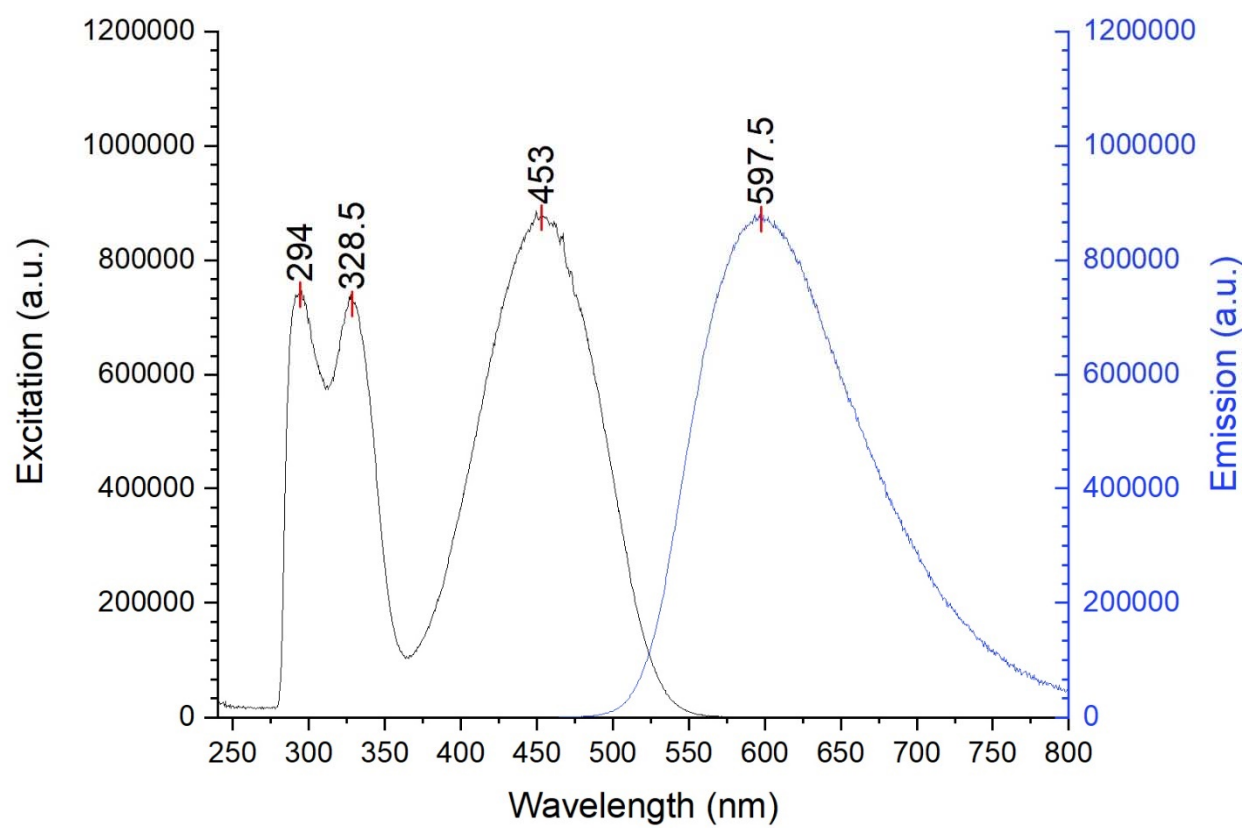


Figure S69 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) spectra of compound **2** and $[\text{Mes}_2\text{B}][\text{B}(\text{C}_6\text{F}_5)_4]$; 12.5 μM sample.

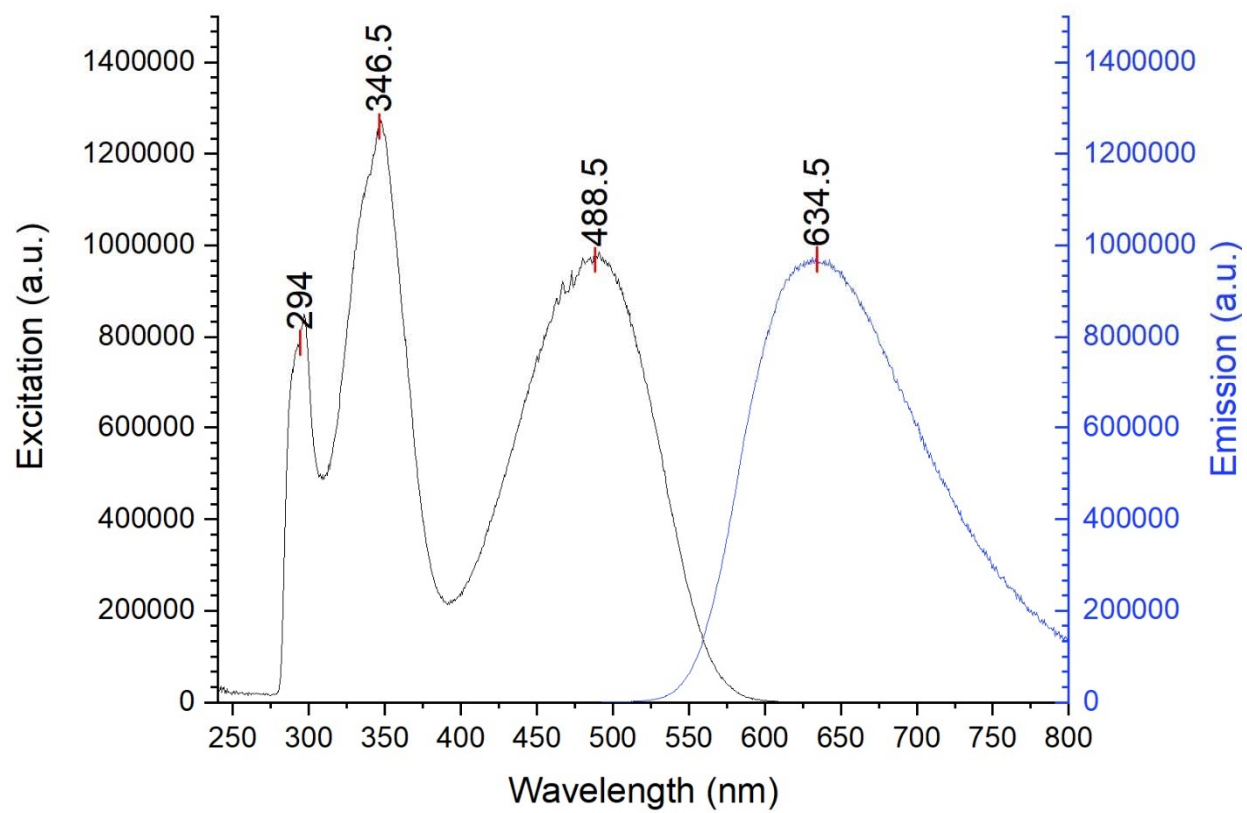


Figure S70 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) spectra of compound **3** and $[\text{Mes}_2\text{B}][\text{B}(\text{C}_6\text{F}_5)_4]$; 12.5 μM sample.

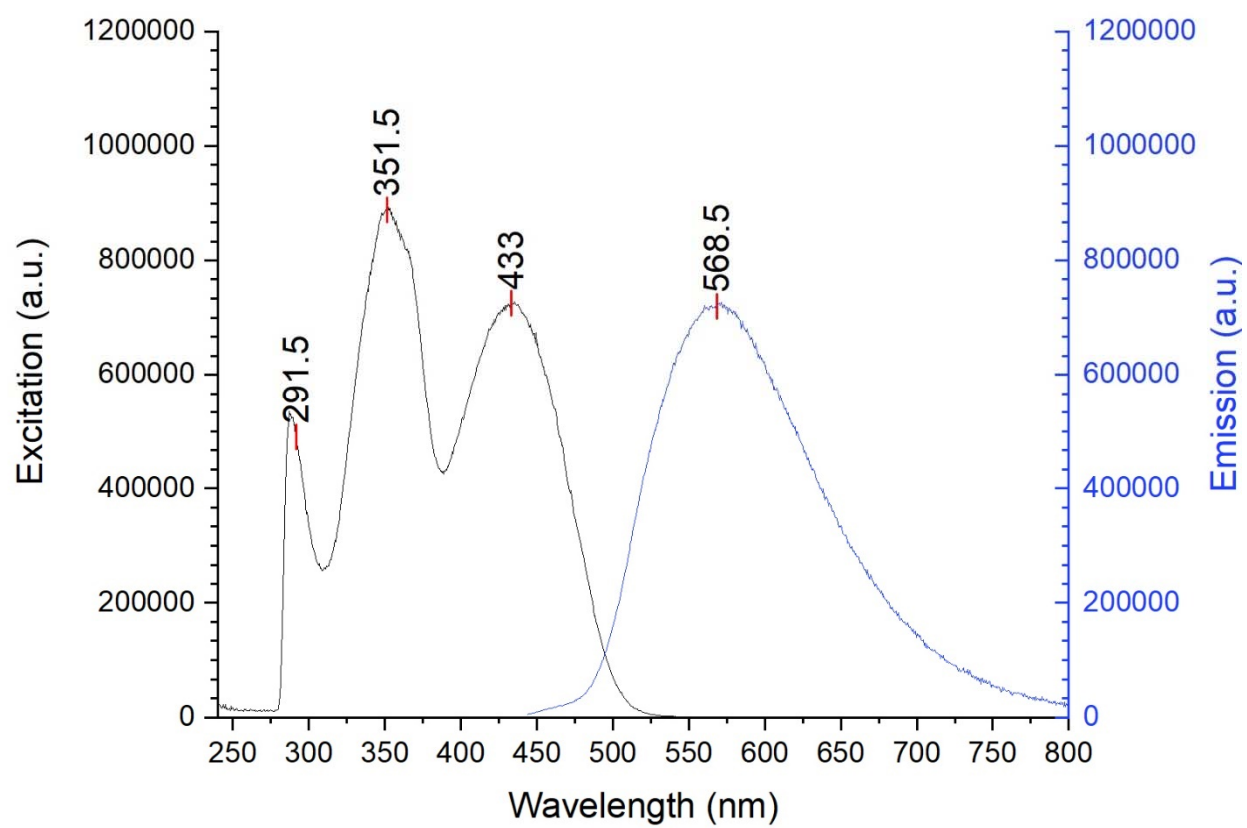


Figure S71 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) spectra of compound **7** and $[\text{Mes}_2\text{B}][\text{B}(\text{C}_6\text{F}_5)_4]$; 12.5 μM sample.

6.1.18. $B(C_6F_5)_3$

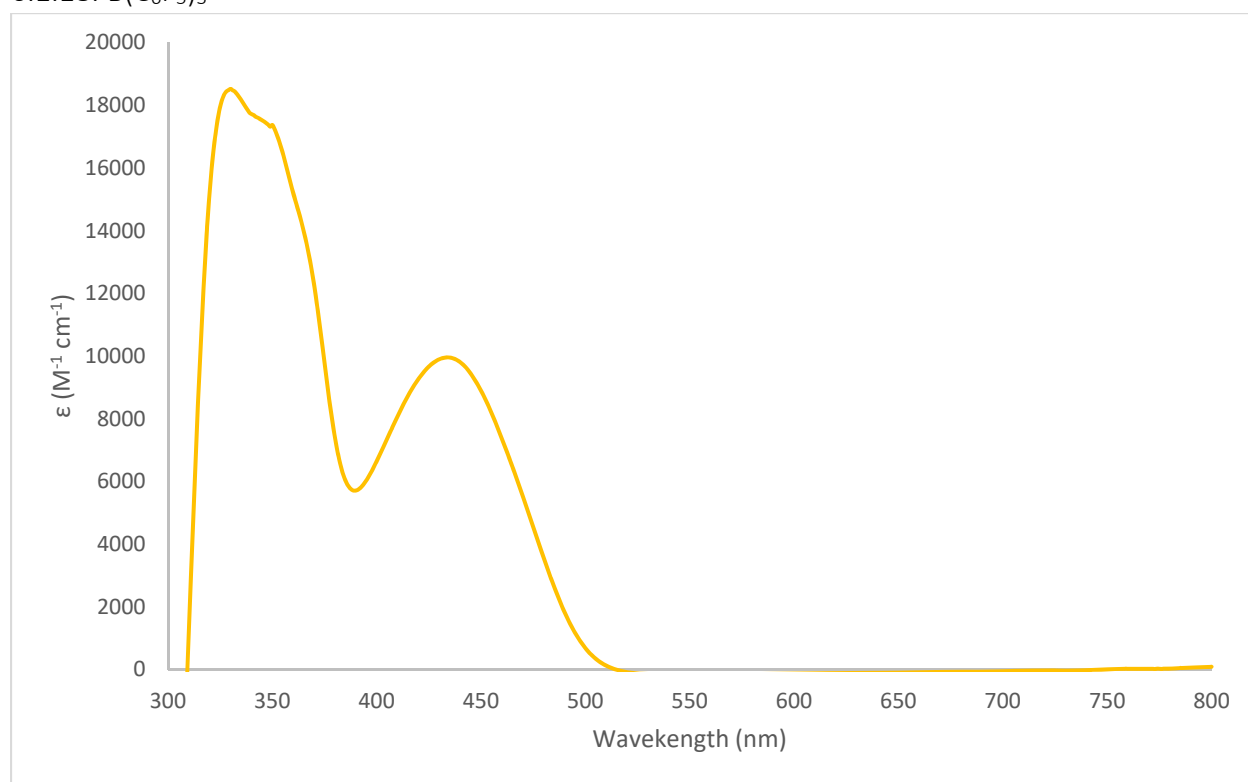


Figure S72 Stacked UV-Vis absorption spectra of **7** (yellow) with $B(C_6F_5)_3$ (5 eq.); 12.5 μM samples.

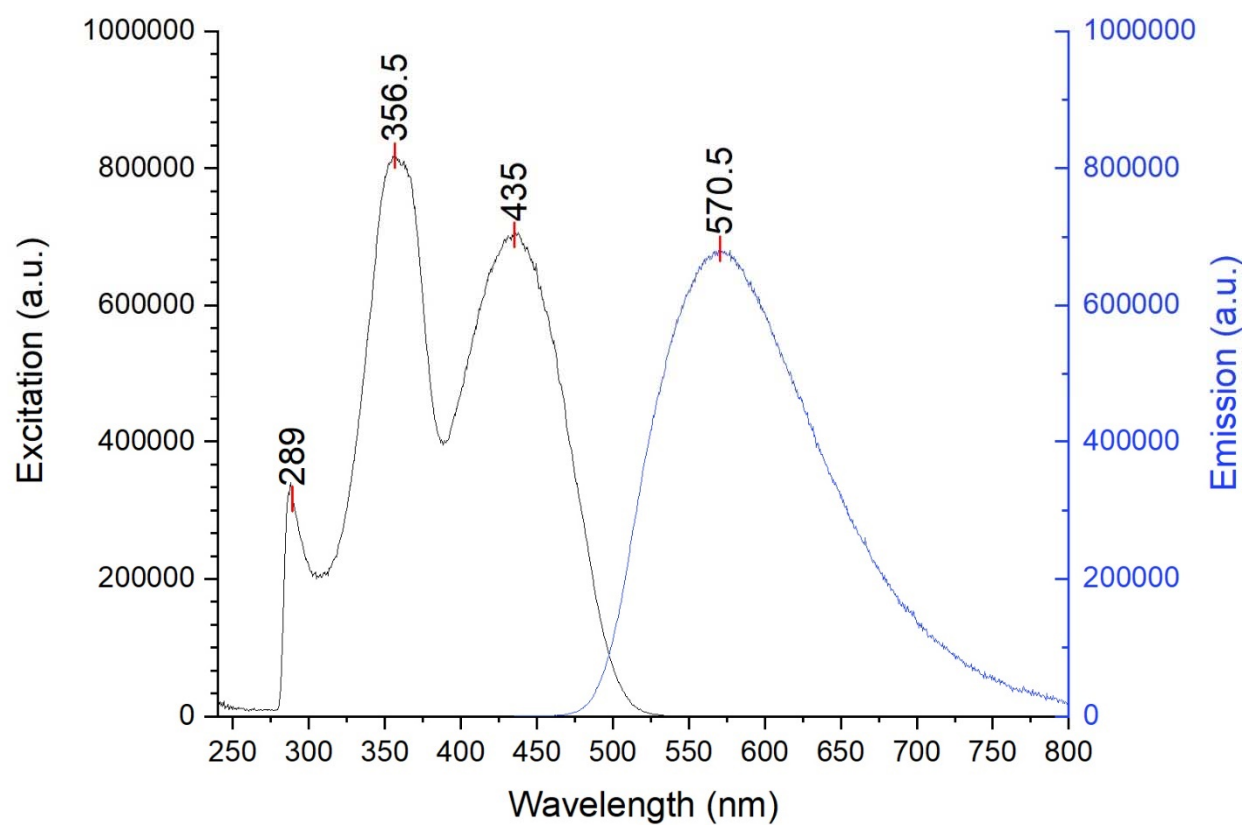


Figure S73 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.2 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.2 nm) spectra of compound **7** and **B(C₆F₅)₃**; 12.5 μ M sample.

6.1.19. $B(m\text{-XyF}_6)_3$

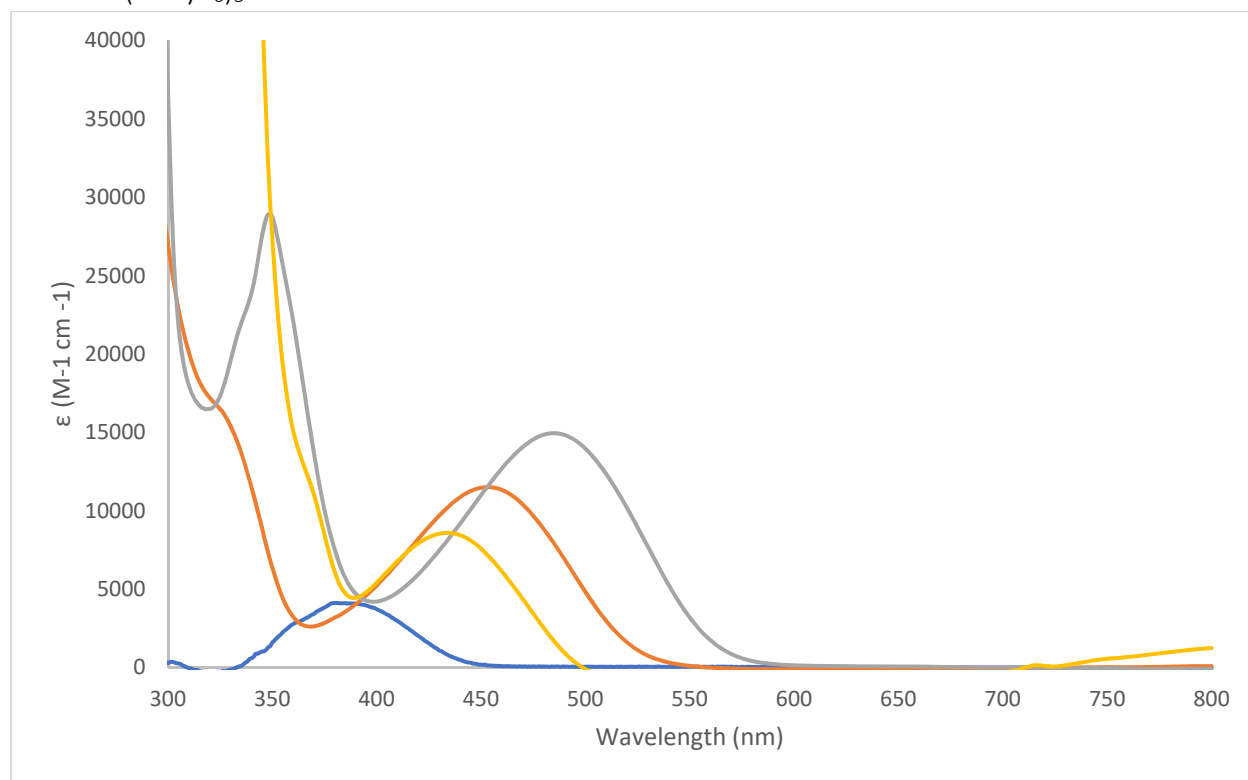


Figure S74 Stacked UV-Vis absorption spectra of **1** (blue, 5 eq), **2** (orange, 5 eq), **3** (grey, 5 eq), and **7** (yellow, 1000 eq) with $B(m\text{-XyF}_6)_3$; 12.5 μM samples.

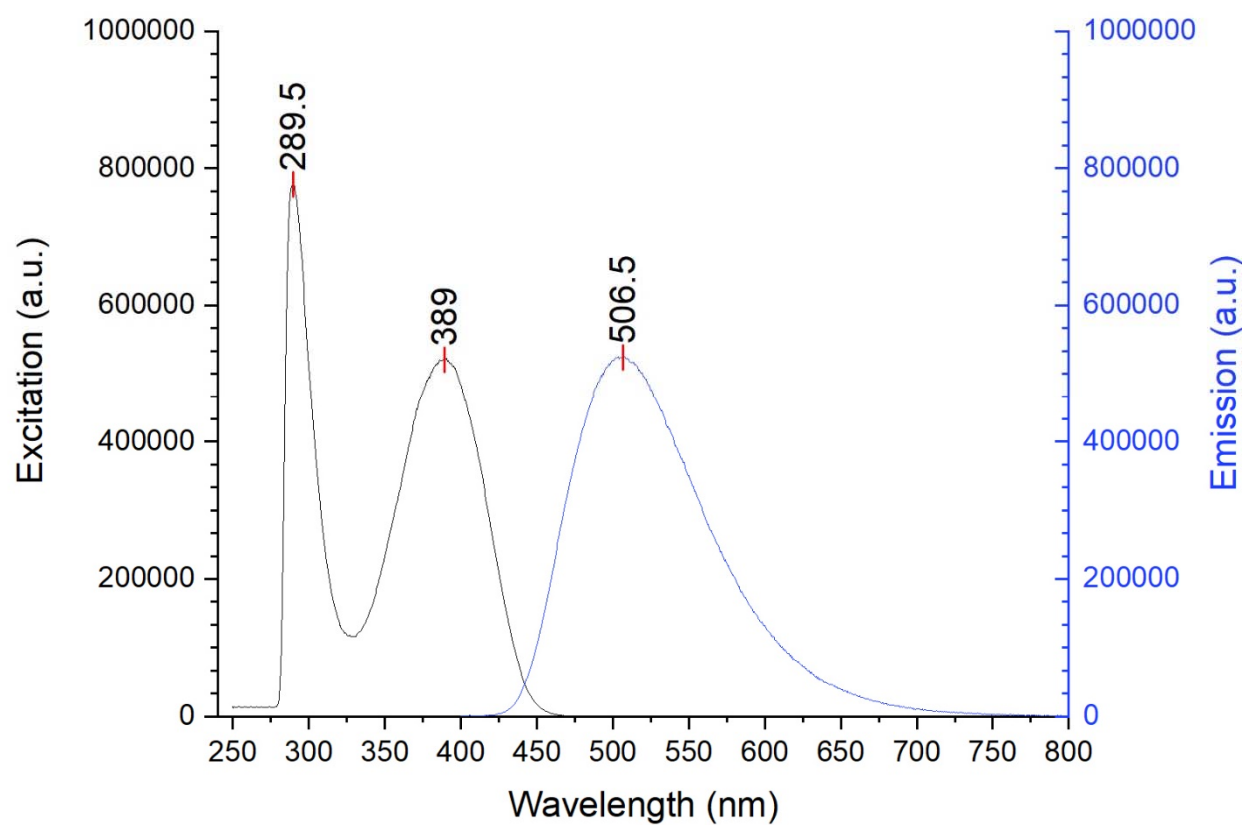


Figure S75 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.2 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.2 nm) spectra of compound **1** and **B(m-XyF₆)₃**; 12.5 μ M sample.

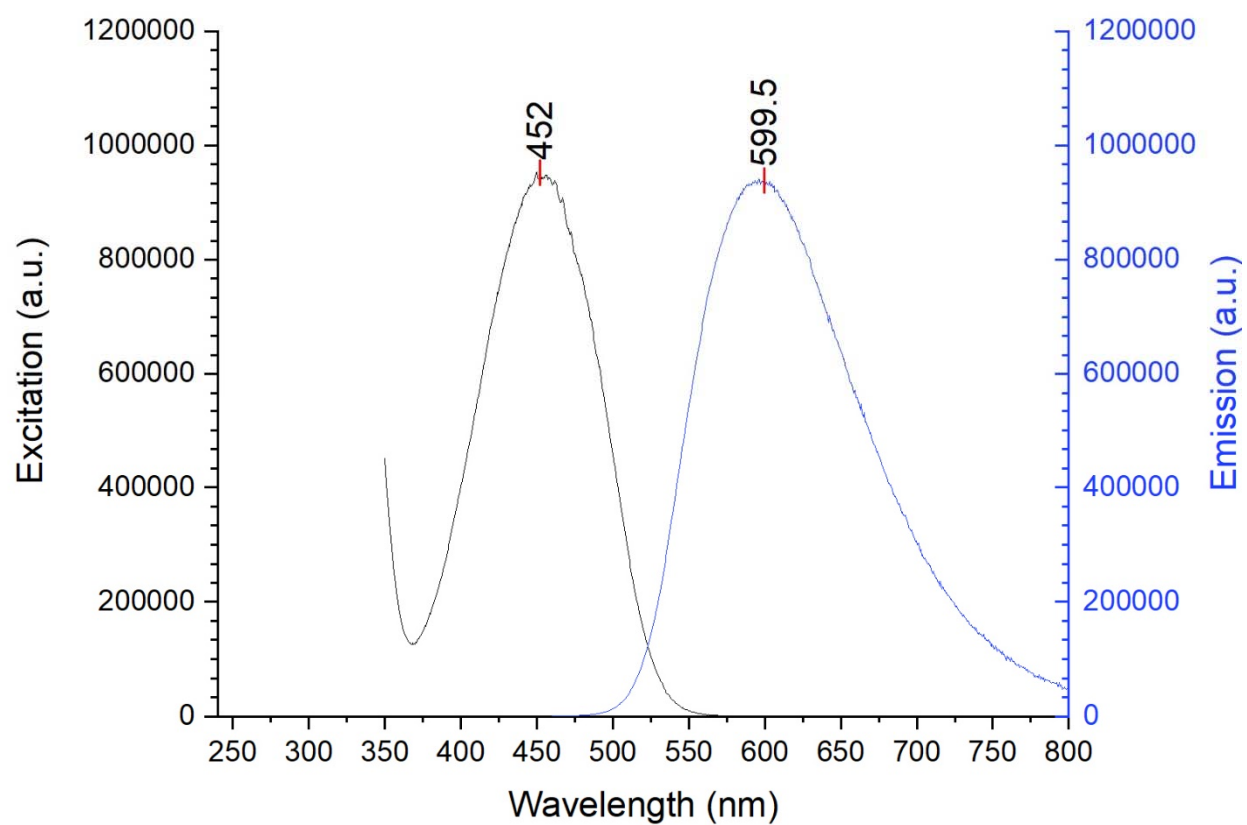


Figure S76 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.2 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.2 nm) spectra of compound **2** and **B(m-XyF₆)₃**; 12.5 μ M sample.

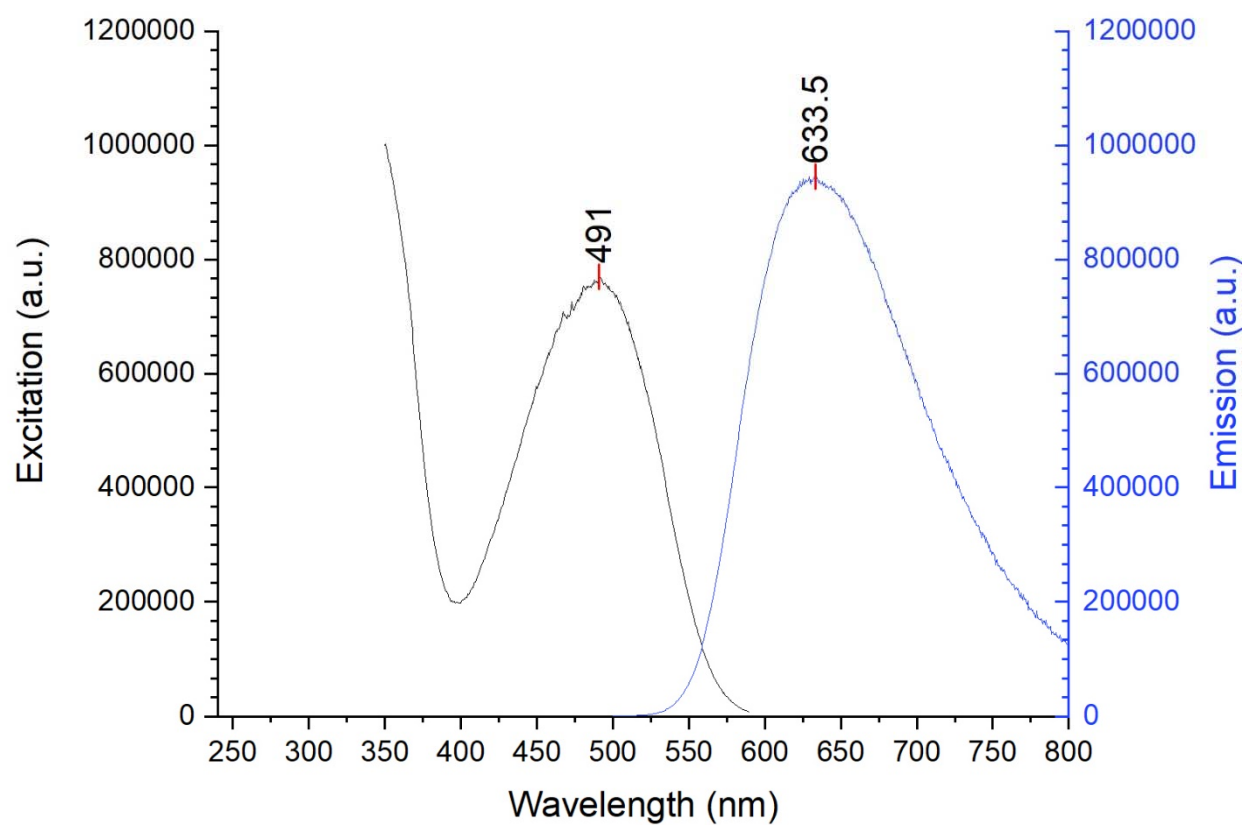


Figure S77 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.2 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.2 nm) spectra of compound **3** and **B(m-XyF₆)₃**; 12.5 μ M sample.

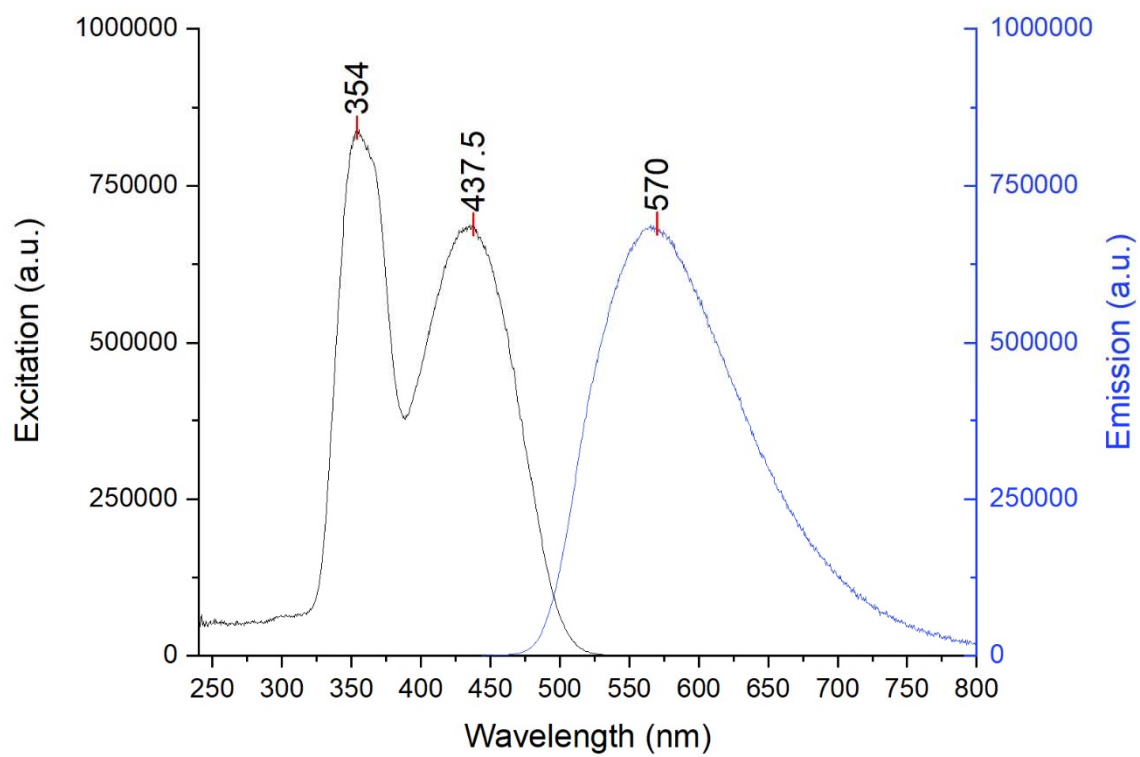


Figure S78 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.2 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.2 nm) spectra of compound **7** and **B(m-XyF₆)₃**; 12.5 μ M sample.

6.1.20. $[\text{Bn}_2\text{IBH}][\text{B}(\text{C}_6\text{F}_5)_4]$

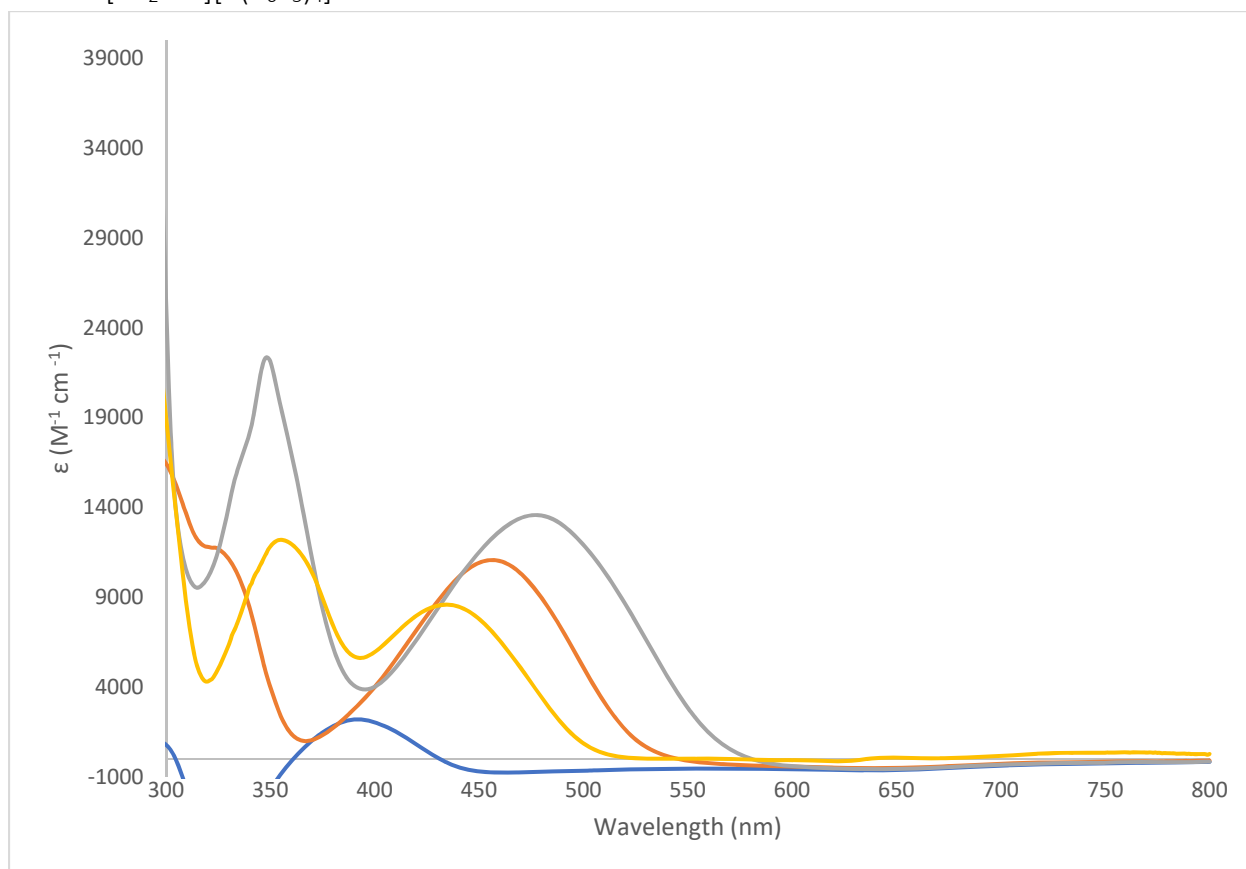


Figure S79 Stacked UV-Vis absorption spectra of **1** (blue, 5 eq), **2** (orange, 5 eq), **3** (grey, 5 eq), and **7** (yellow, 10 eq) with $[\text{Bn}_2\text{IBH}][\text{B}(\text{C}_6\text{F}_5)_4]$; 12.5 μM samples.

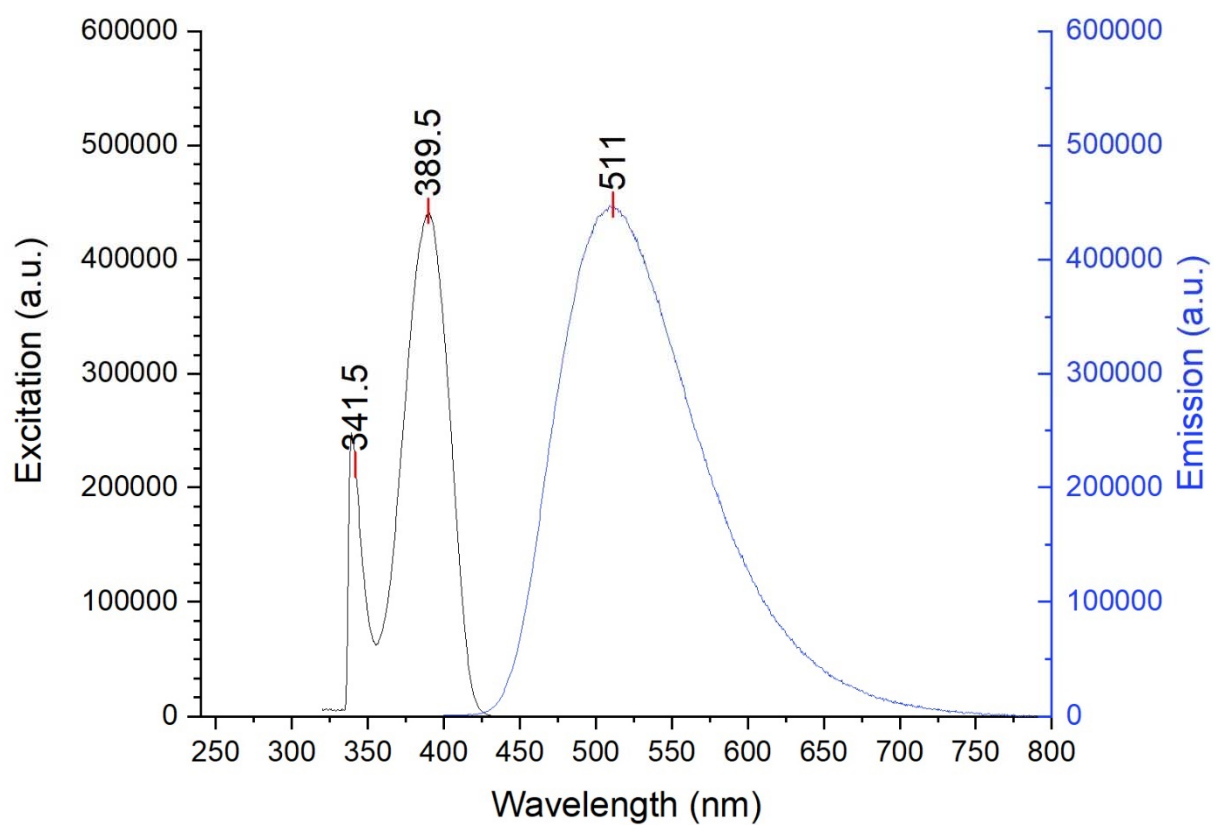


Figure S80 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) spectra of compound **1** and [Bn₂IBH][B(C₆F₅)₄]; 12.5 μ M sample.

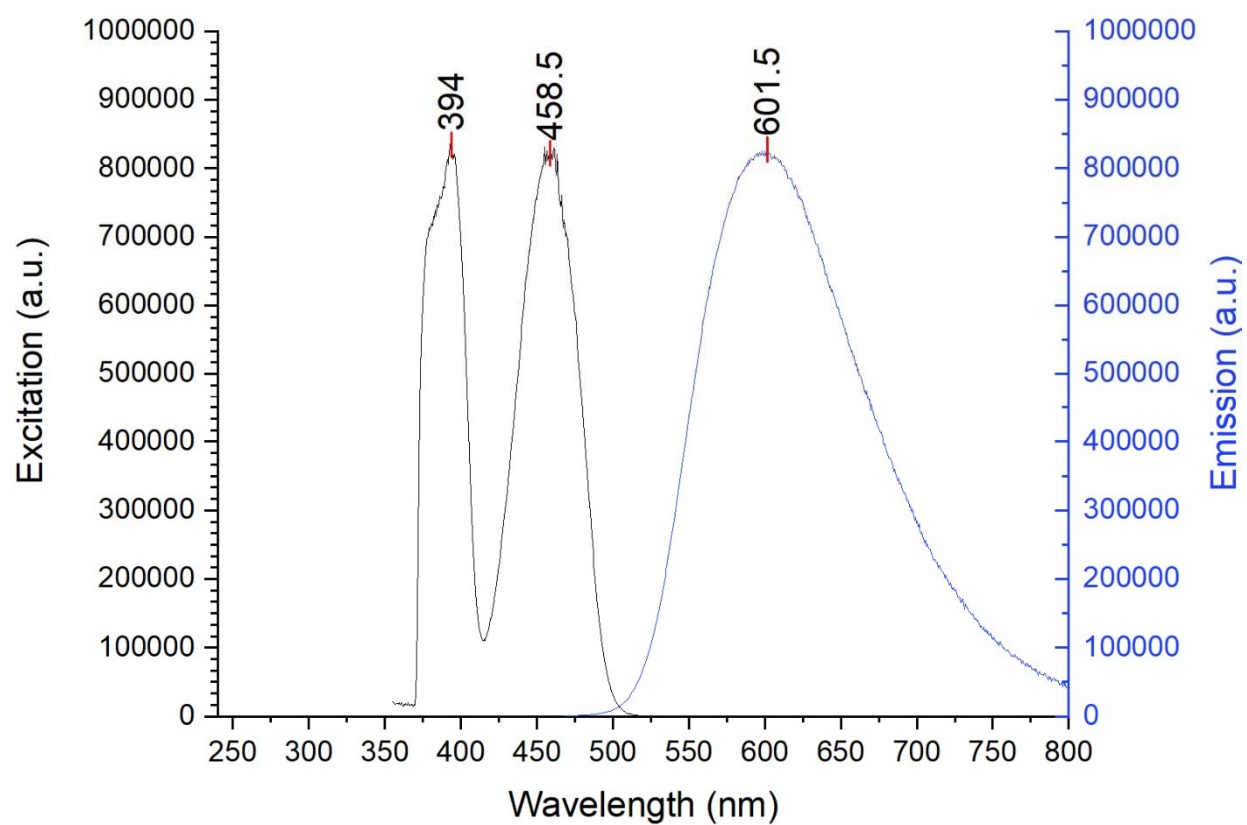


Figure S81 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) spectra of compound **2** and [Bn₂IBH][B(C₆F₅)₄]; 12.5 μM sample.

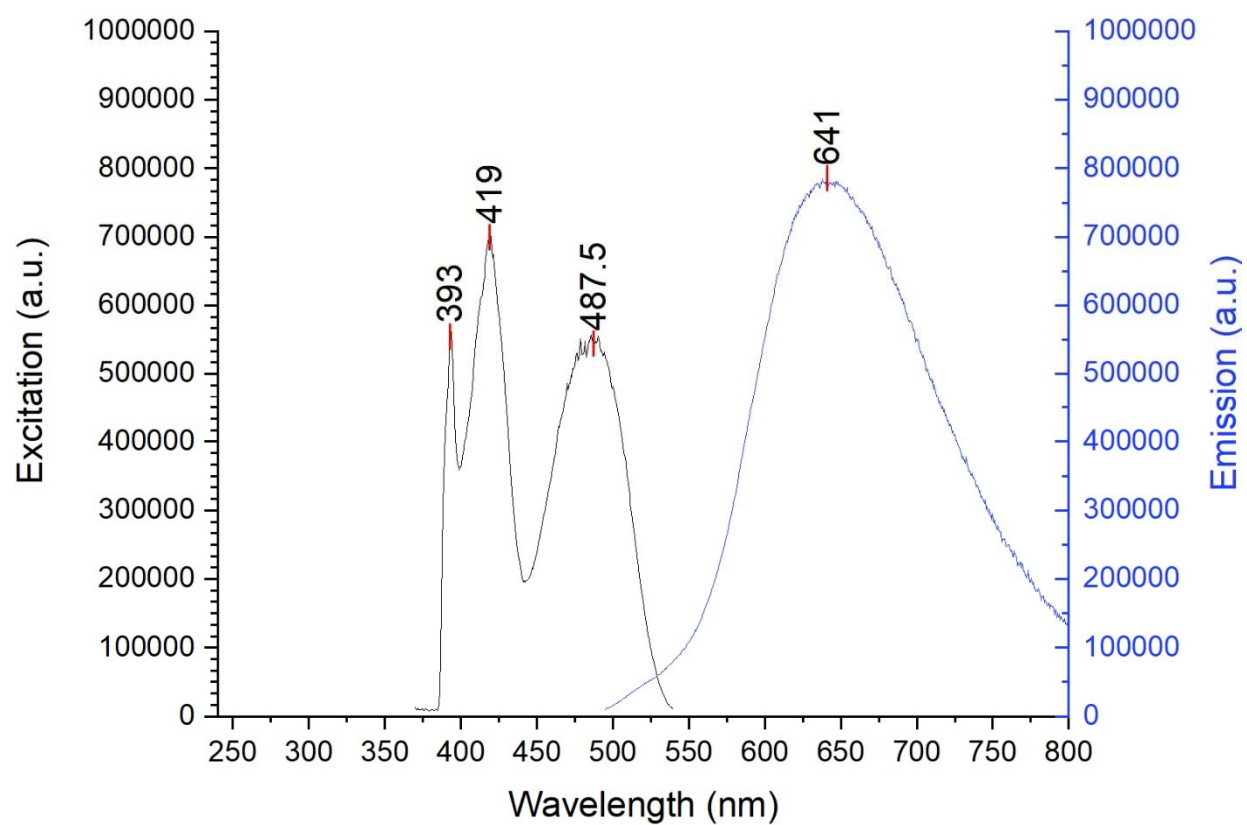


Figure S82 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) spectra of compound **3** and $[Bn_2IBH][B(C_6F_5)_4]$; 12.5 μ M sample.

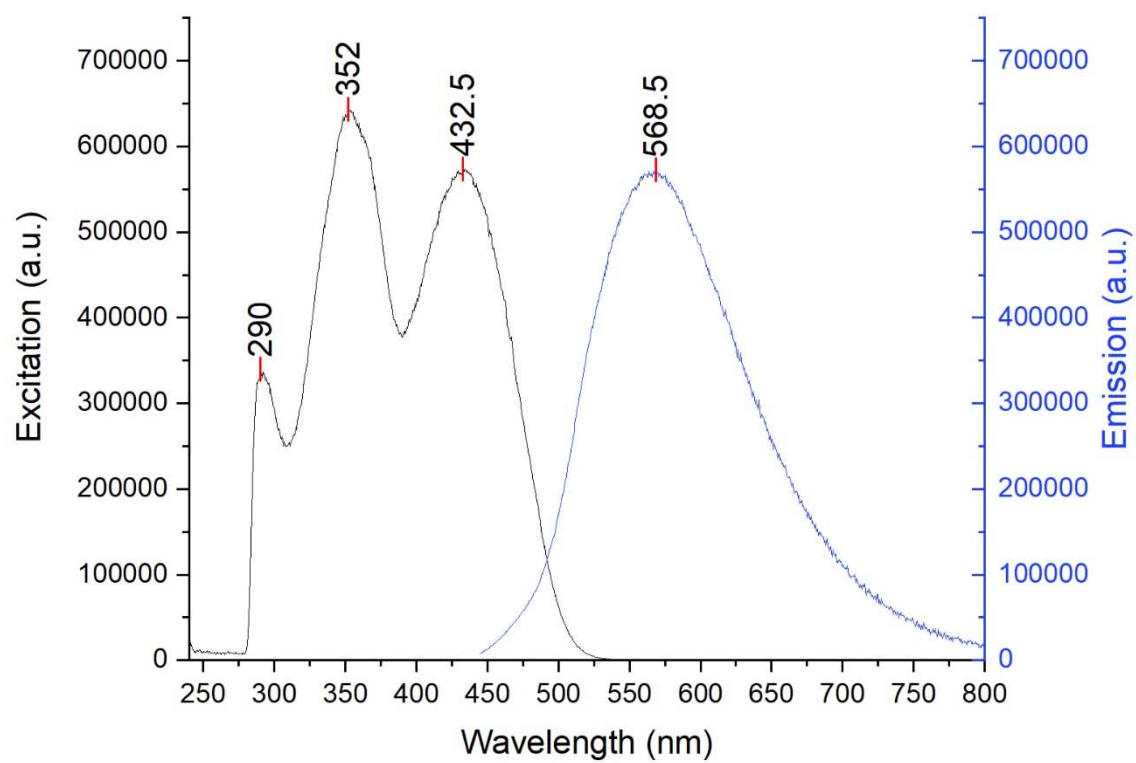


Figure S83 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) spectra of compound **7** and $[\text{Bn}_2\text{IBH}][\text{B}(\text{C}_6\text{F}_5)_4]$; 12.5 μM sample.

6.1.21. $B(Ph)_3$

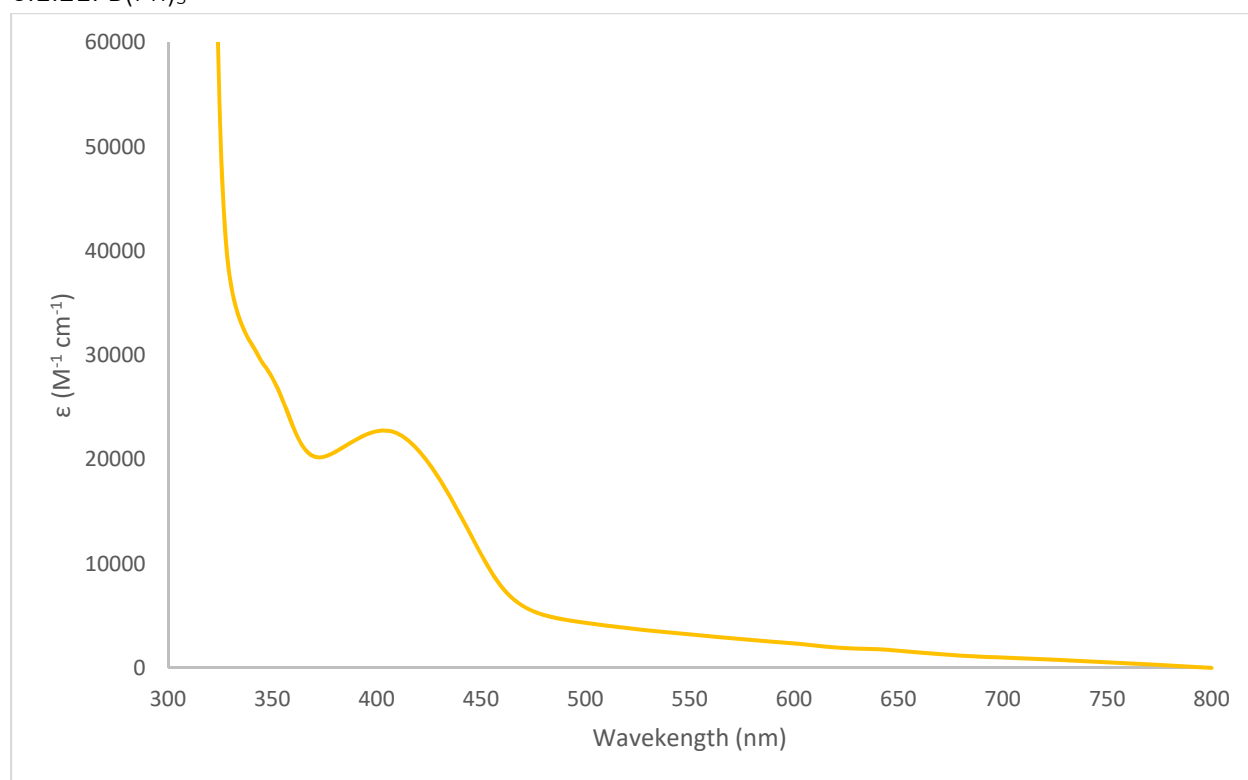


Figure S84 Stacked UV-Vis absorption spectra of **7** (yellow) with $B(Ph)_3$ (excess); 12.5 μM samples.

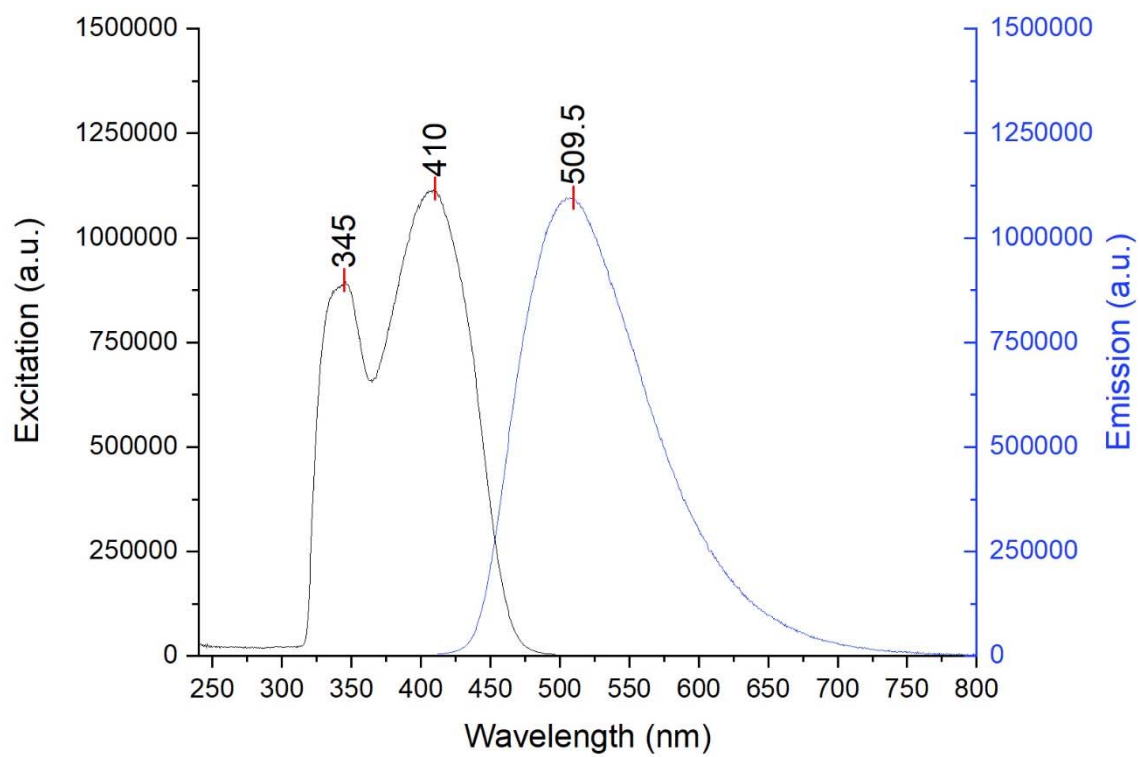


Figure S85 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) spectra of compound **7** and **B(Ph)₃**; 12.5 μ M sample.

6.1.22. $B(p\text{-HC}_6\text{F}_4)_3$

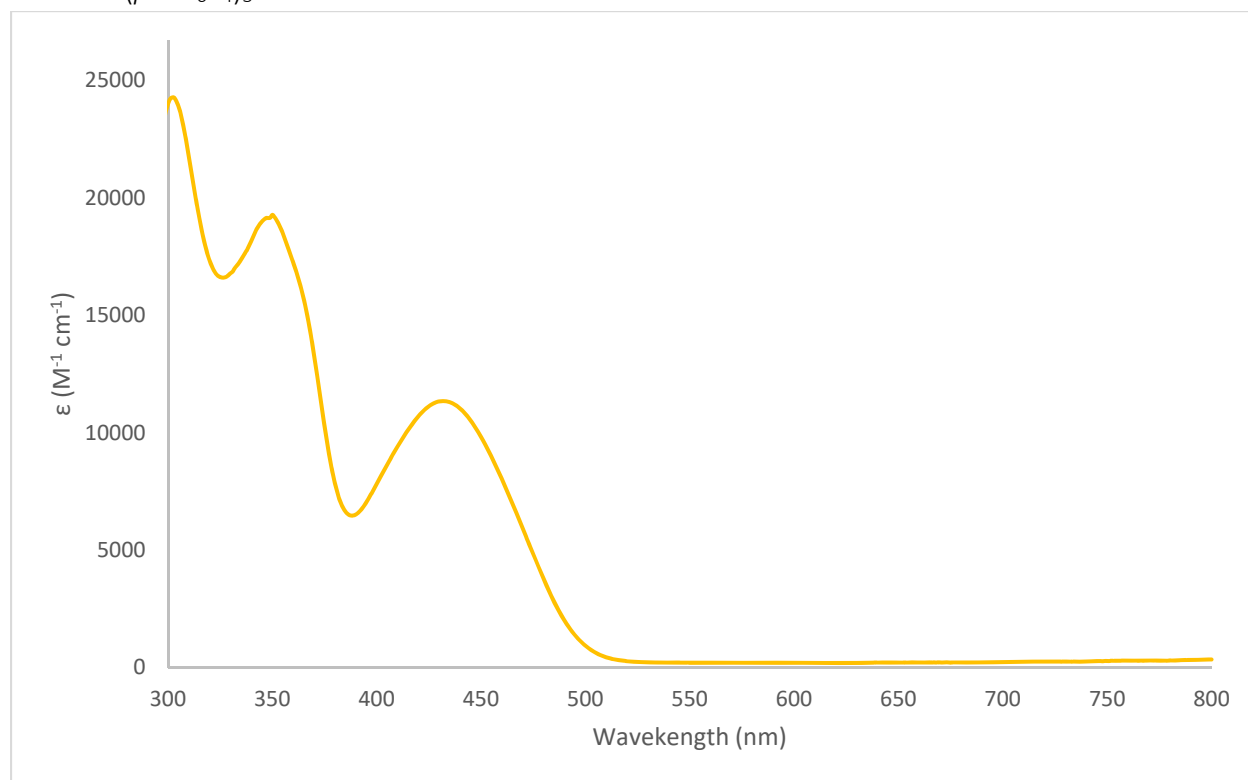


Figure S86 Stacked UV-Vis absorption spectra of **7** (yellow) with $B(p\text{-HC}_6\text{F}_4)_3$ (5 eq.); 12.5 μM samples.

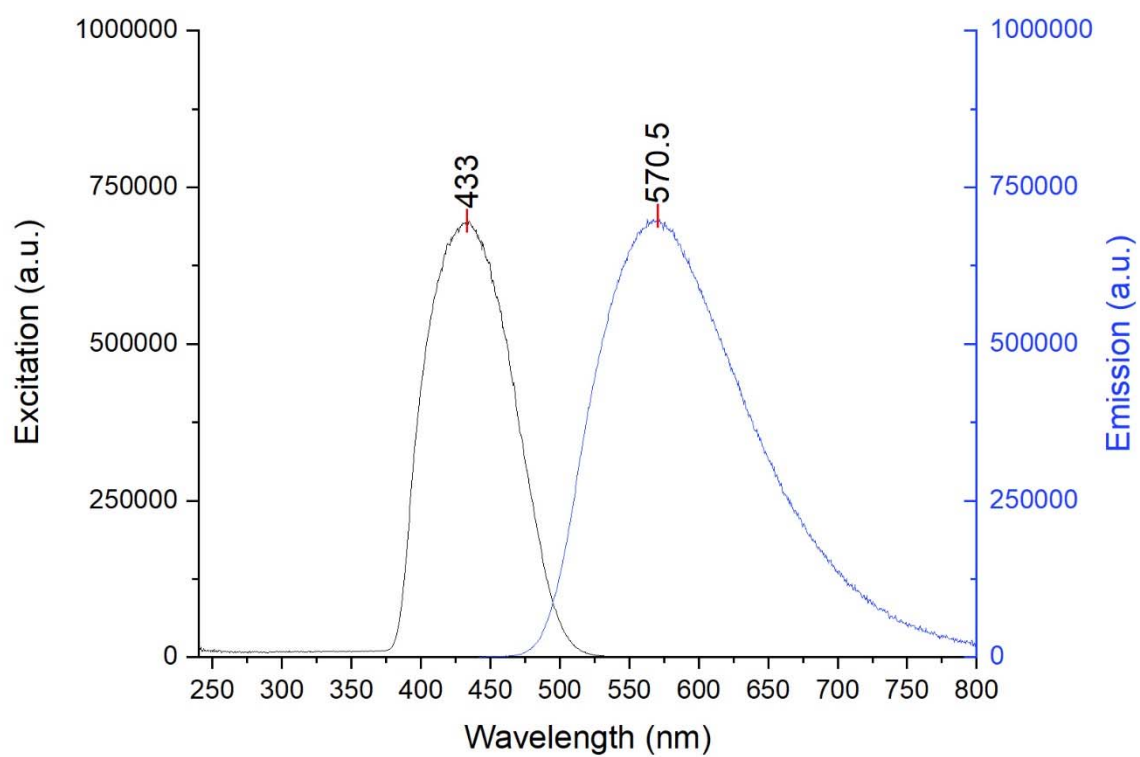


Figure S87 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) spectra of compound **7** and **B(p-HCF₄)₃**; 12.5 μ M sample.

6.1.23. (–)-B-chlorodiisopinocampheylborane (DIP-Cl)

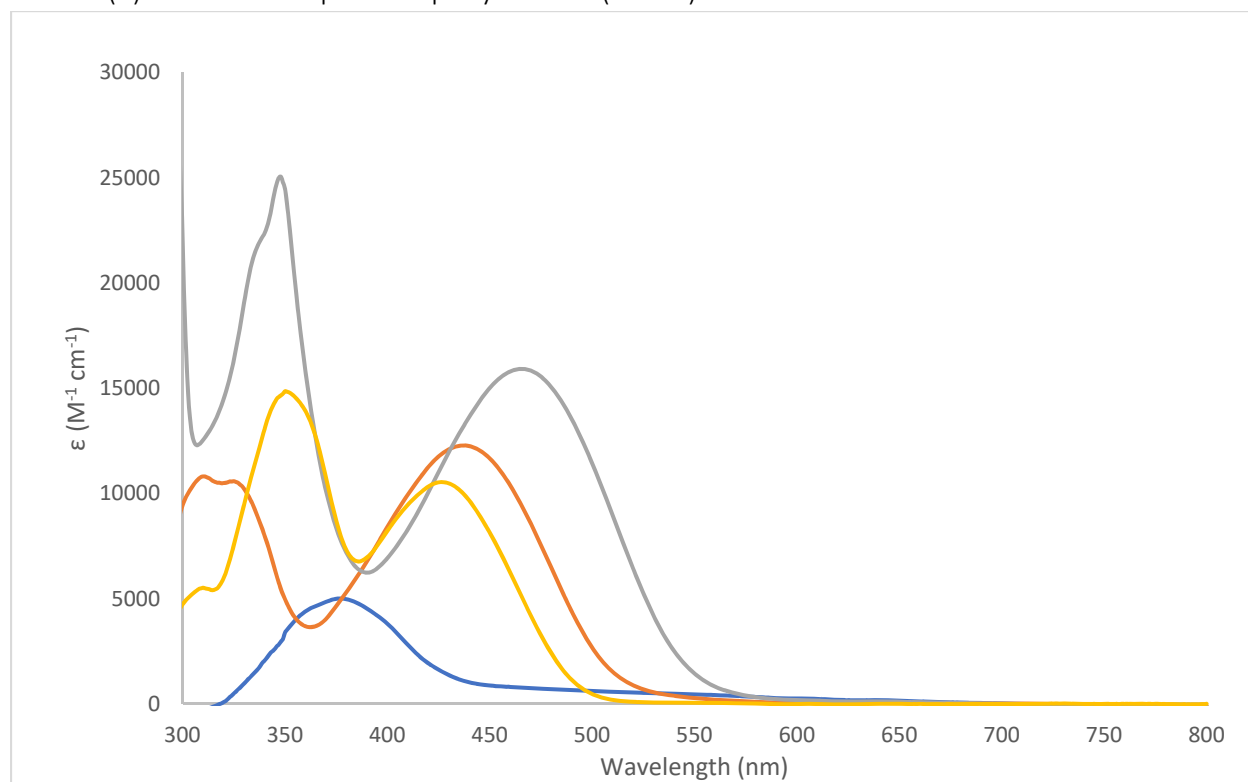


Figure S88 Stacked UV-Vis absorption spectra of **1** (blue), **2** (orange), **3** (grey), and **7** (yellow) with **DIP-Cl** (excess); 12.5 μM samples.

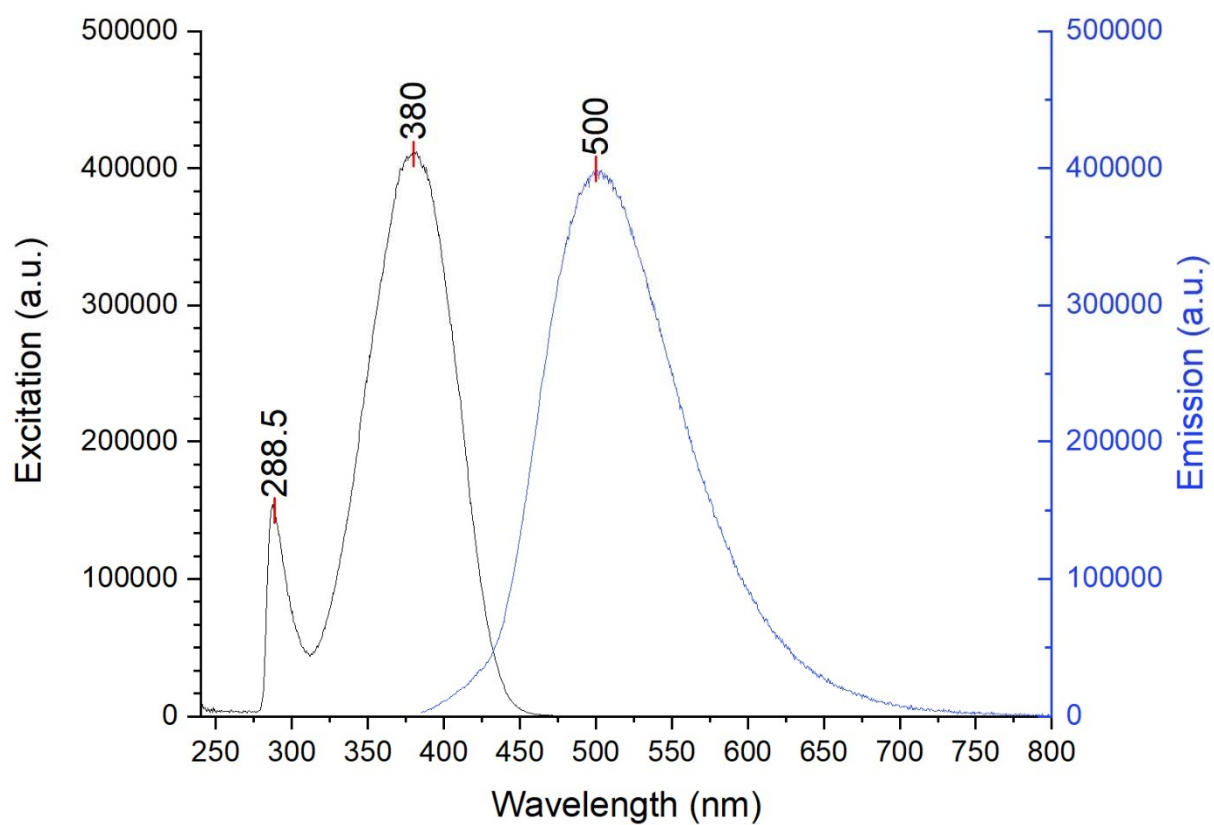


Figure S89 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) spectra of compound **1** and **DIP-Cl**; 12.5 μ M sample.

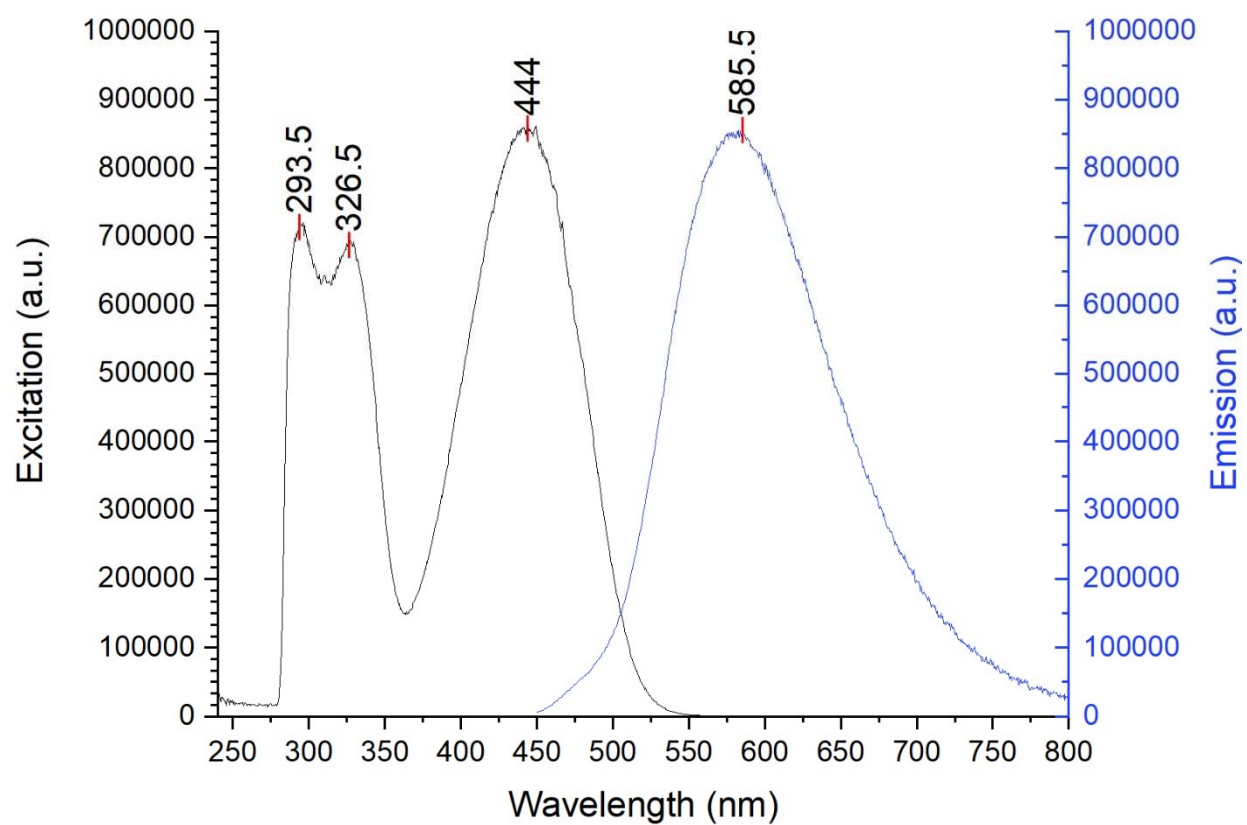


Figure S90 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) spectra of compound **2** and **DIP-Cl**; 12.5 μ M sample.

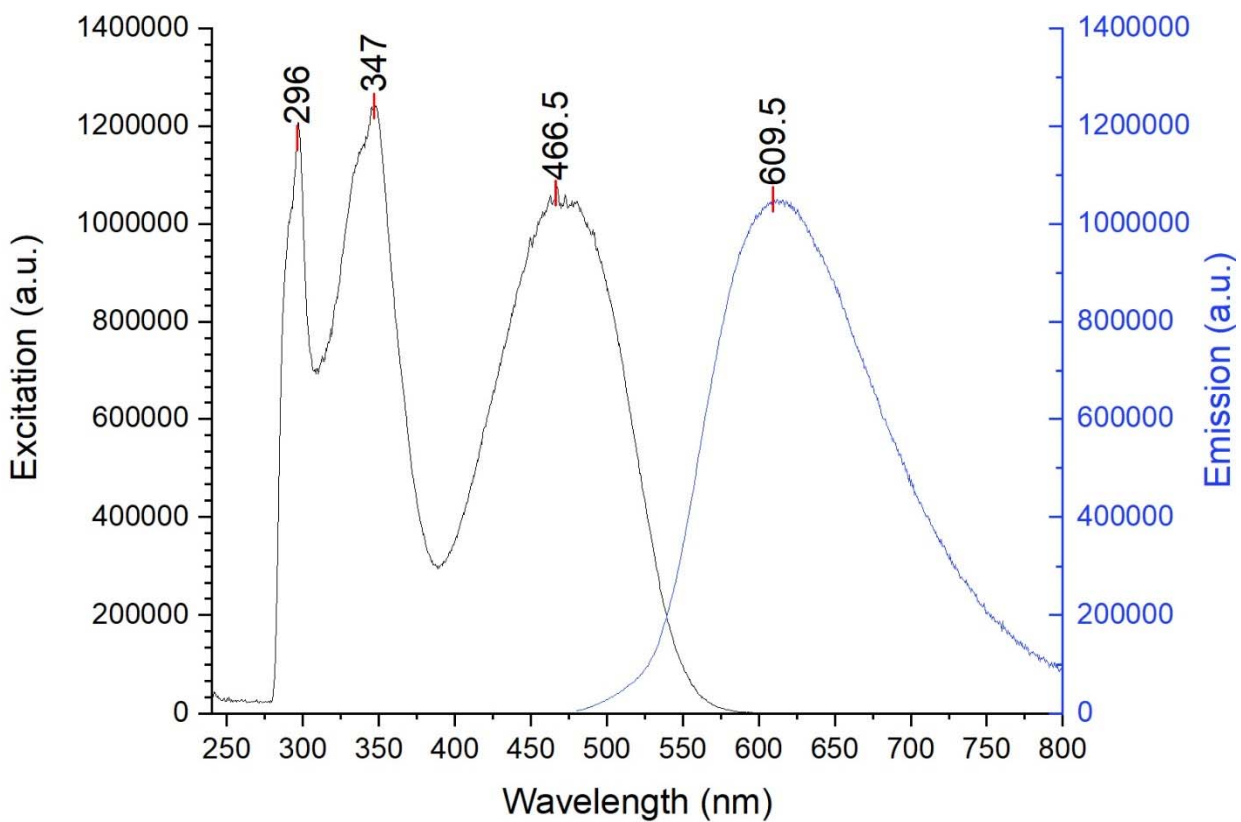


Figure S91 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) spectra of compound **3** and **DIP-Cl**; 12.5 μM sample.

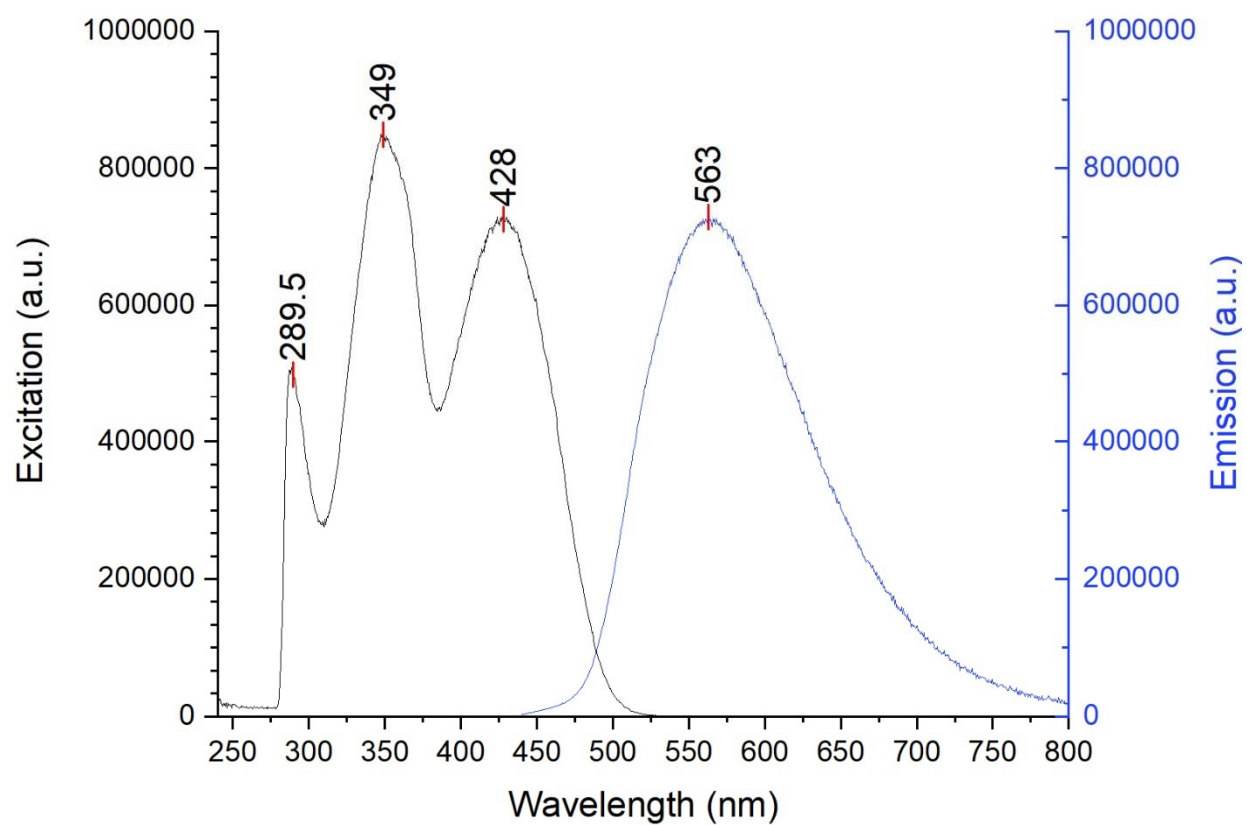


Figure S92 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) spectra of compound **7** and **DIP-Cl**; 12.5 μ M sample.

6.1.24. $[(C_6F_5)_3PO(C_6F_5)][B(C_6F_5)_4]$

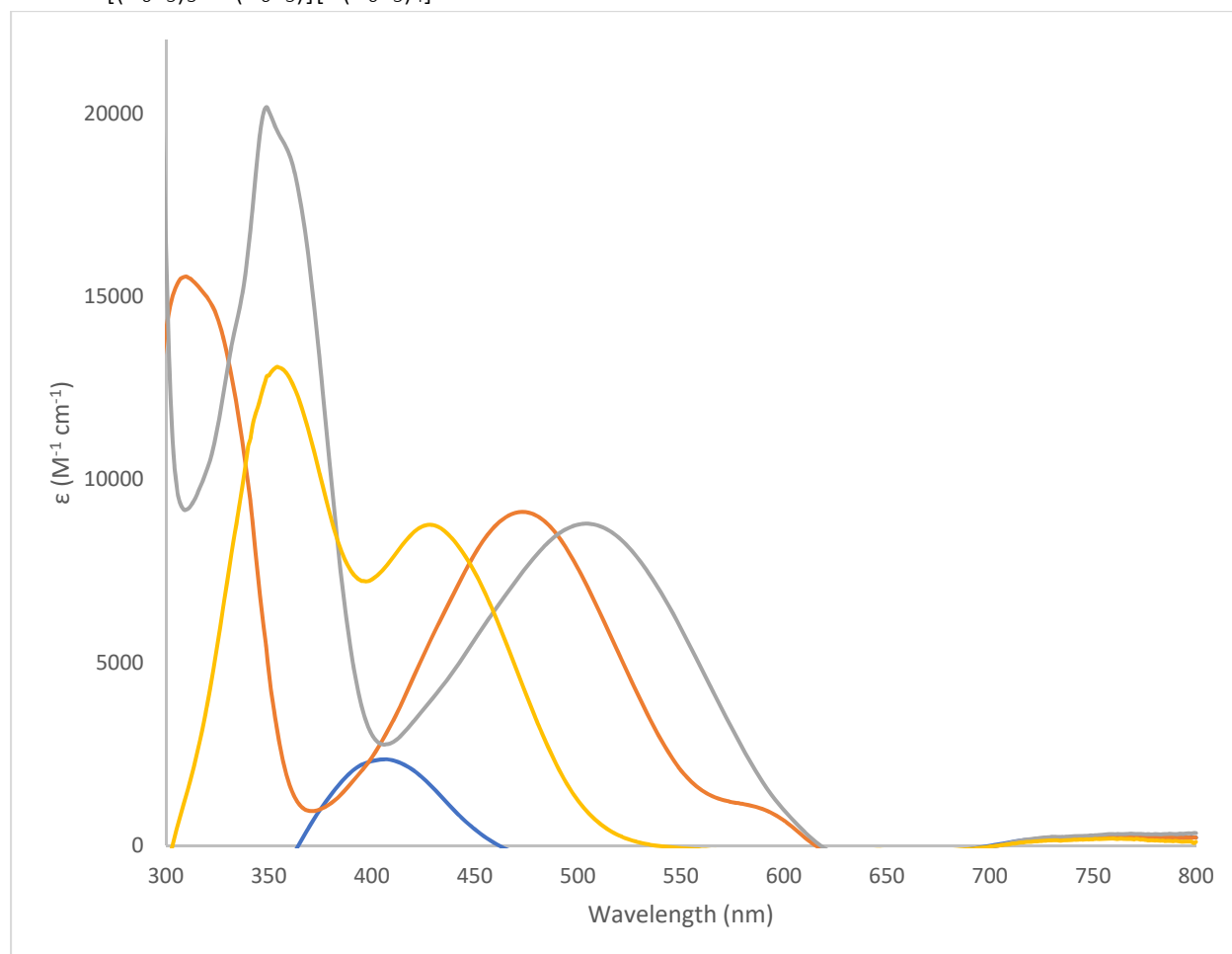


Figure S93 Stacked UV-Vis absorption spectra of **1** (blue, 5 eq), **2** (orange, 5 eq), **3** (grey, 5 eq), and **7** (yellow, 10 eq) with $[(C_6F_5)_3PO(C_6F_5)][B(C_6F_5)_4]$; 12.5 μM samples.

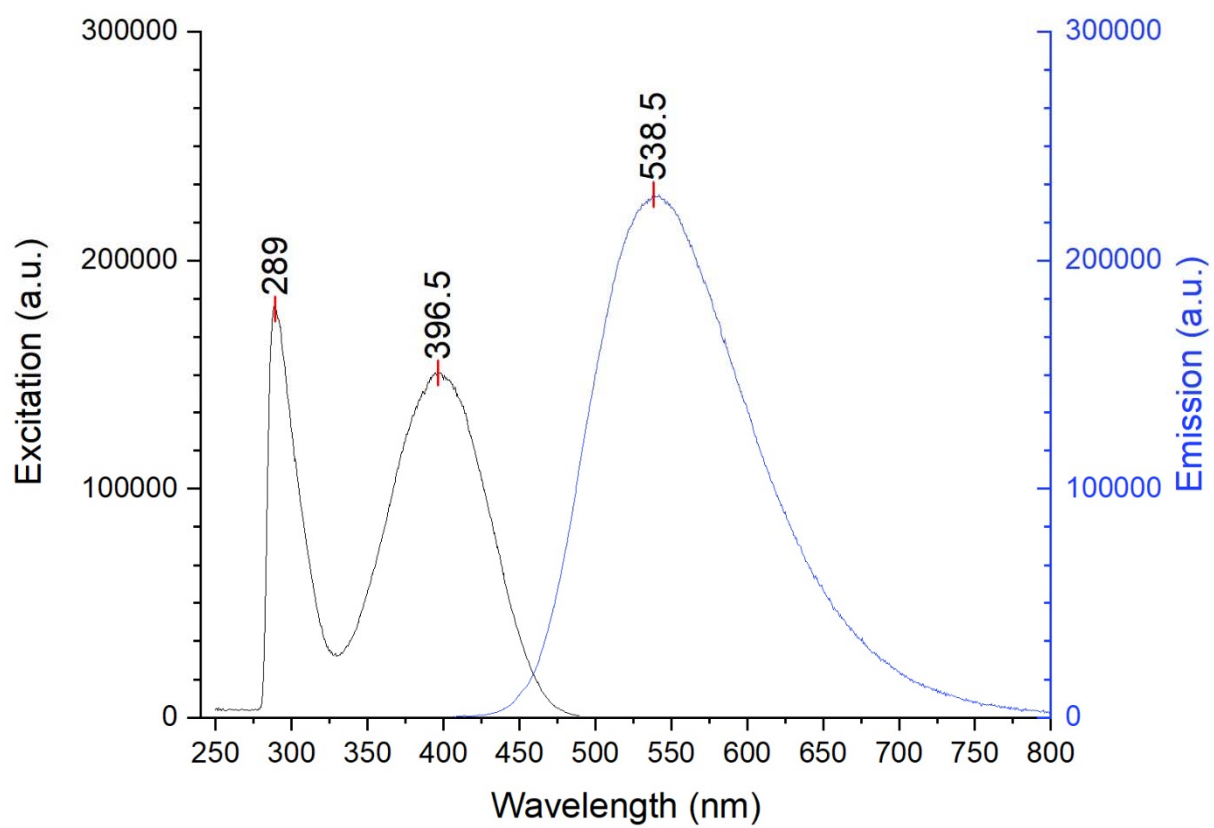


Figure S94 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) spectra of compound **1** and $[(C_6F_5)_3PO(C_6F_5)] [B(C_6F_5)_4]$; 12.5 μ M sample.

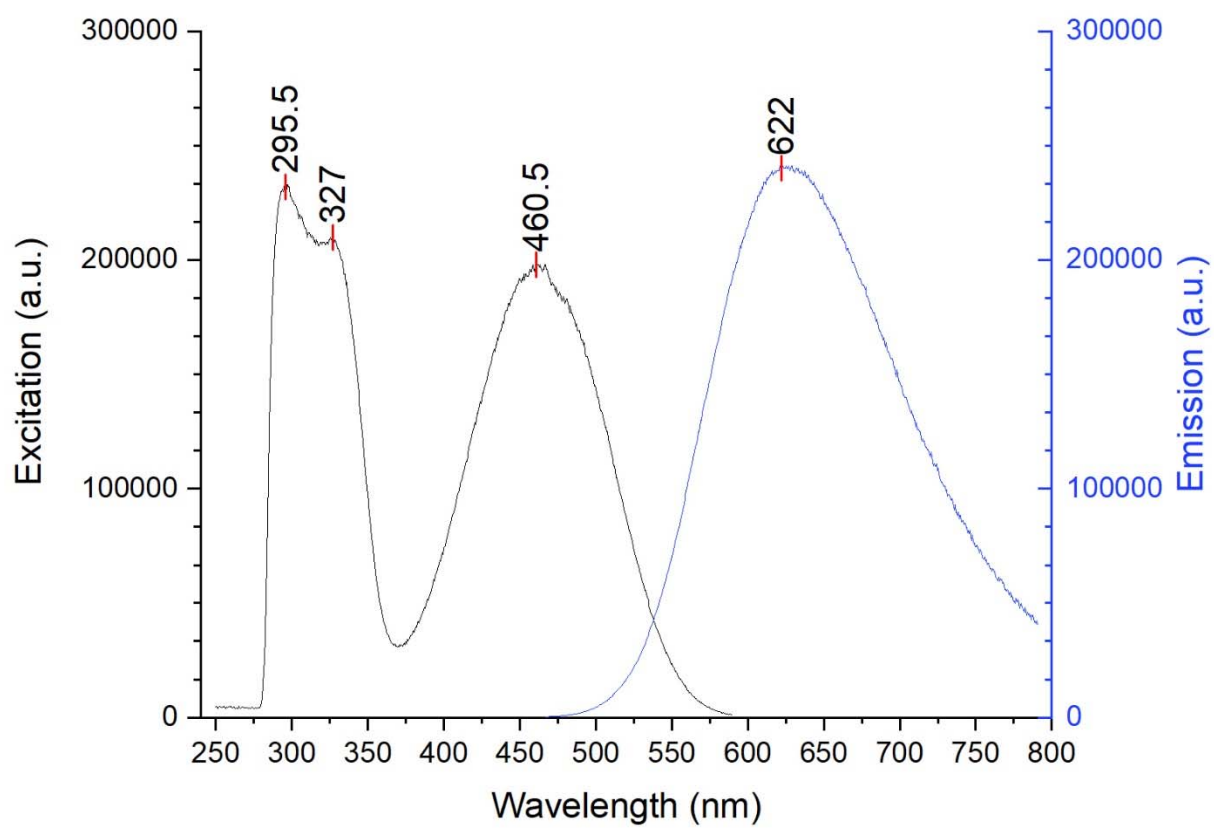


Figure S95 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) spectra of compound **2** and $[(C_6F_5)_3PO(C_6F_5)][B(C_6F_5)_4]$; 12.5 μ M sample.

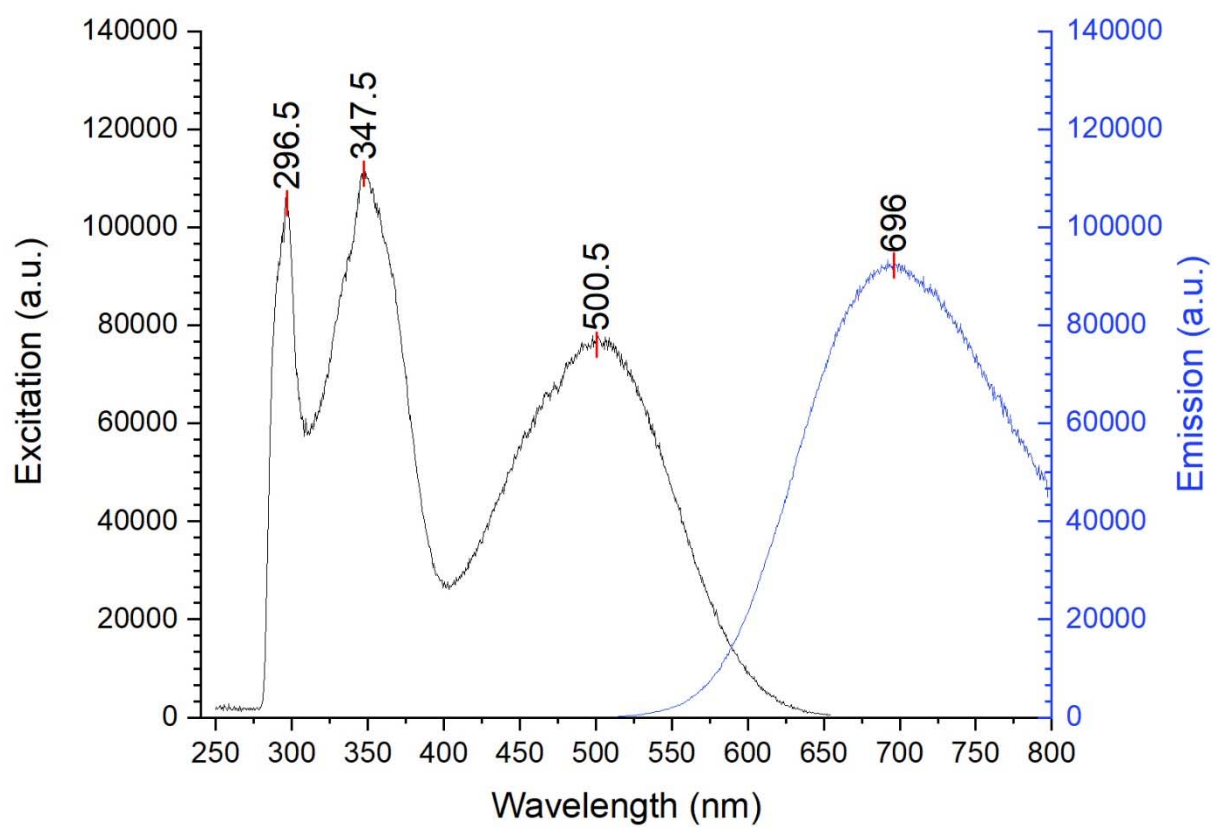


Figure S96 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) spectra of compound **3** and $[(C_6F_5)_3PO(C_6F_5)][B(C_6F_5)_4]$; 12.5 μ M sample.

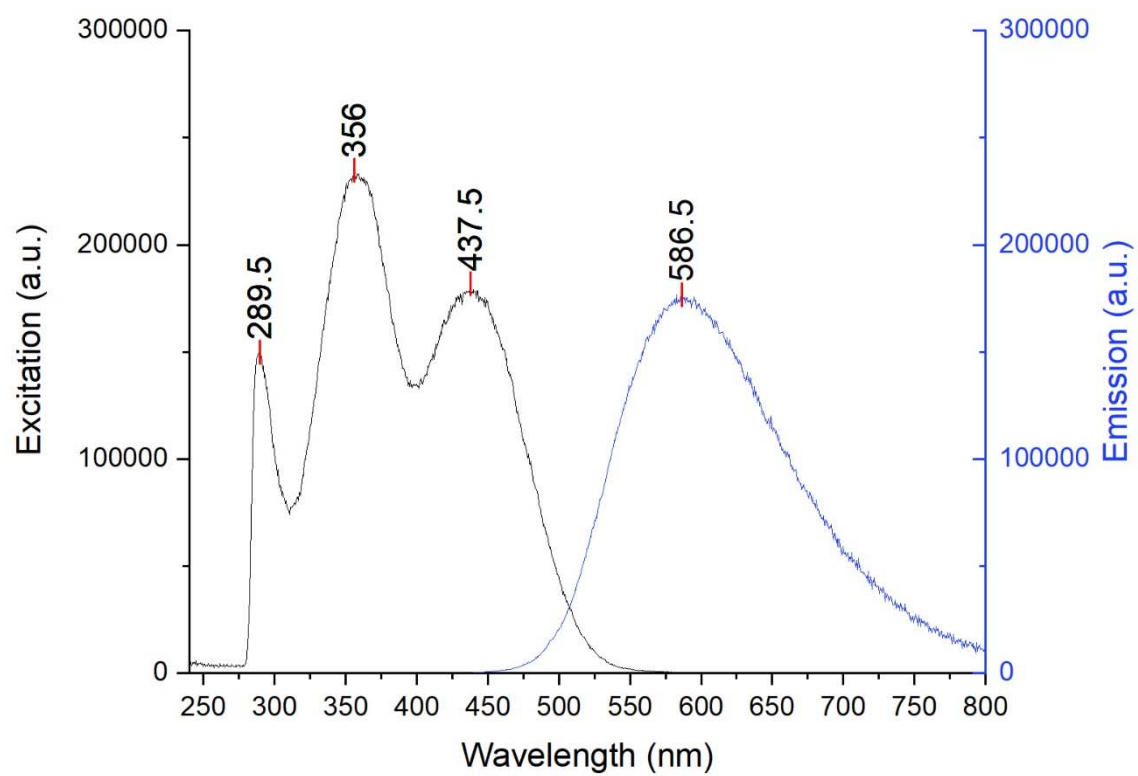


Figure S97 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) spectra of compound **7** and $[(\text{C}_6\text{F}_5)_3\text{PO}(\text{C}_6\text{F}_5)][\text{B}(\text{C}_6\text{F}_5)_4]$; 12.5 μM sample.

6.1.25. $[\text{Et}_3\text{Si}][\text{B}(\text{C}_6\text{F}_5)_4]$

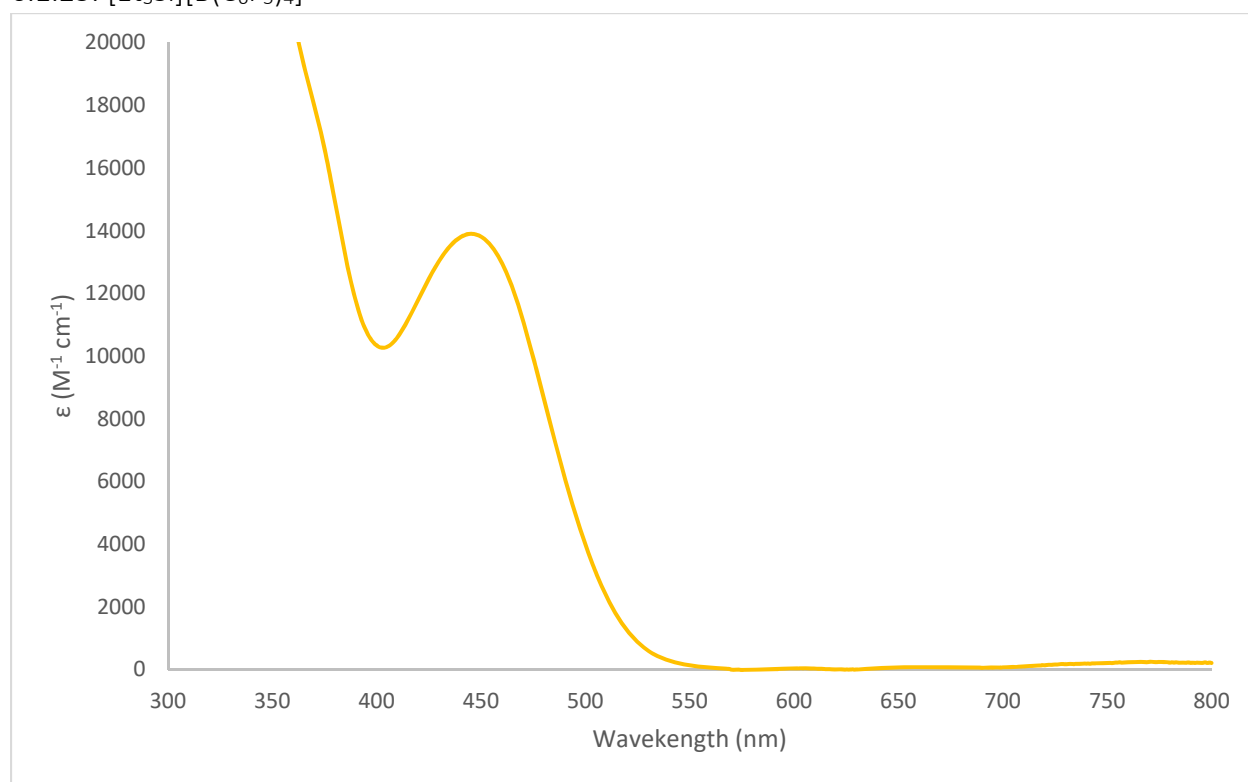


Figure S98 Stacked UV-Vis absorption spectra of **7** (yellow) with $[\text{Et}_3\text{Si}][\text{B}(\text{C}_6\text{F}_5)_4]$ (10 eq.); 12.5 μM samples.

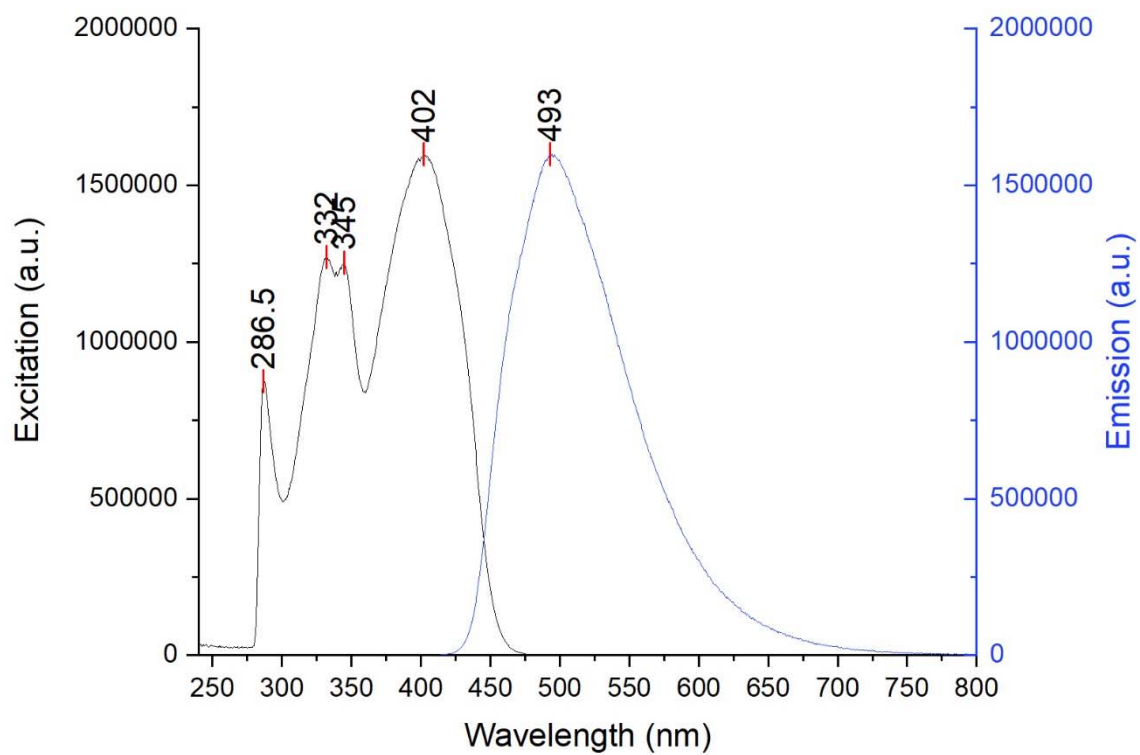


Figure S99 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) spectra of compound **7** and $[\text{Et}_3\text{Si}][\text{B}(\text{C}_6\text{F}_5)_4]$; $12.5\ \mu\text{M}$ sample.

6.1.26. $[(C_6F_5)_3PF][B(C_6F_5)_4]$

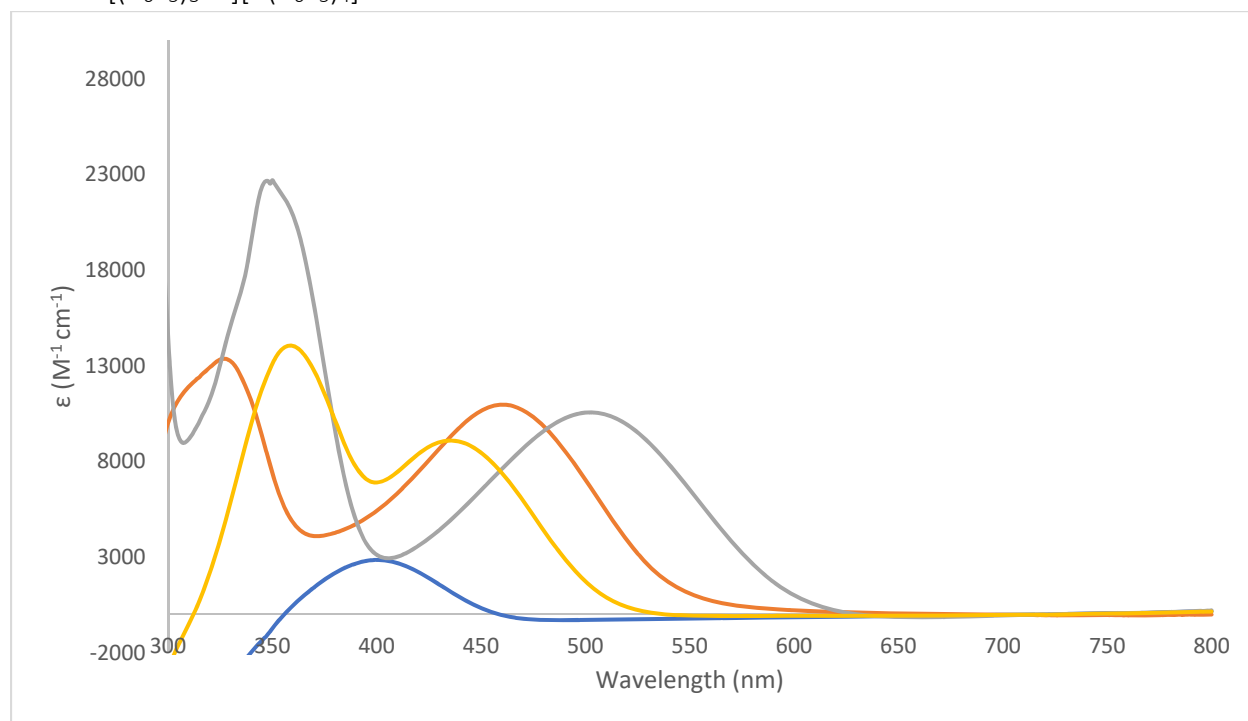


Figure S100 Stacked UV-Vis absorption spectra of **1** (blue), **2** (orange), **3** (grey), and **7** (yellow) with $[(C_6F_5)_3PF][B(C_6F_5)_4]$ (5 eq.); 12.5 μM samples.

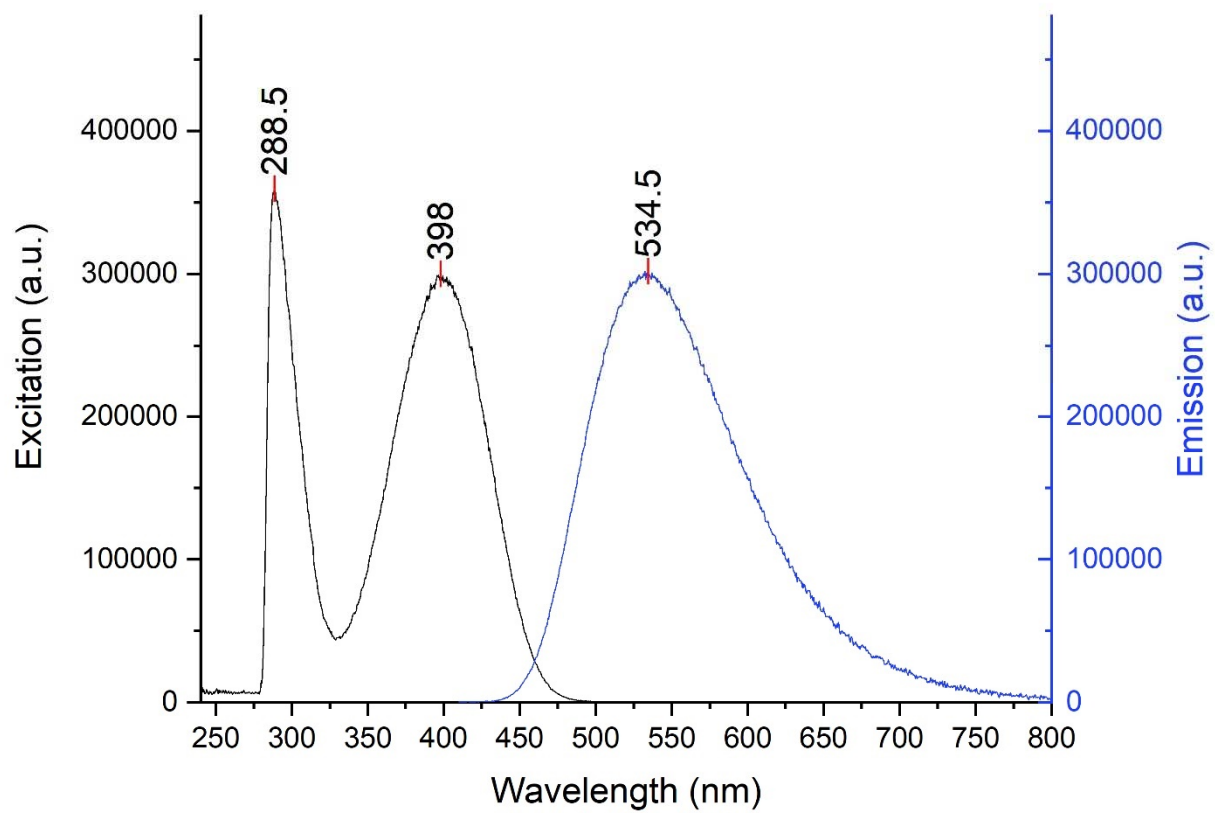


Figure S101 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) spectra of compound **1** and $[(\text{C}_6\text{F}_5)_3\text{PF}][\text{B}(\text{C}_6\text{F}_5)_4]$; 12.5 μM sample.

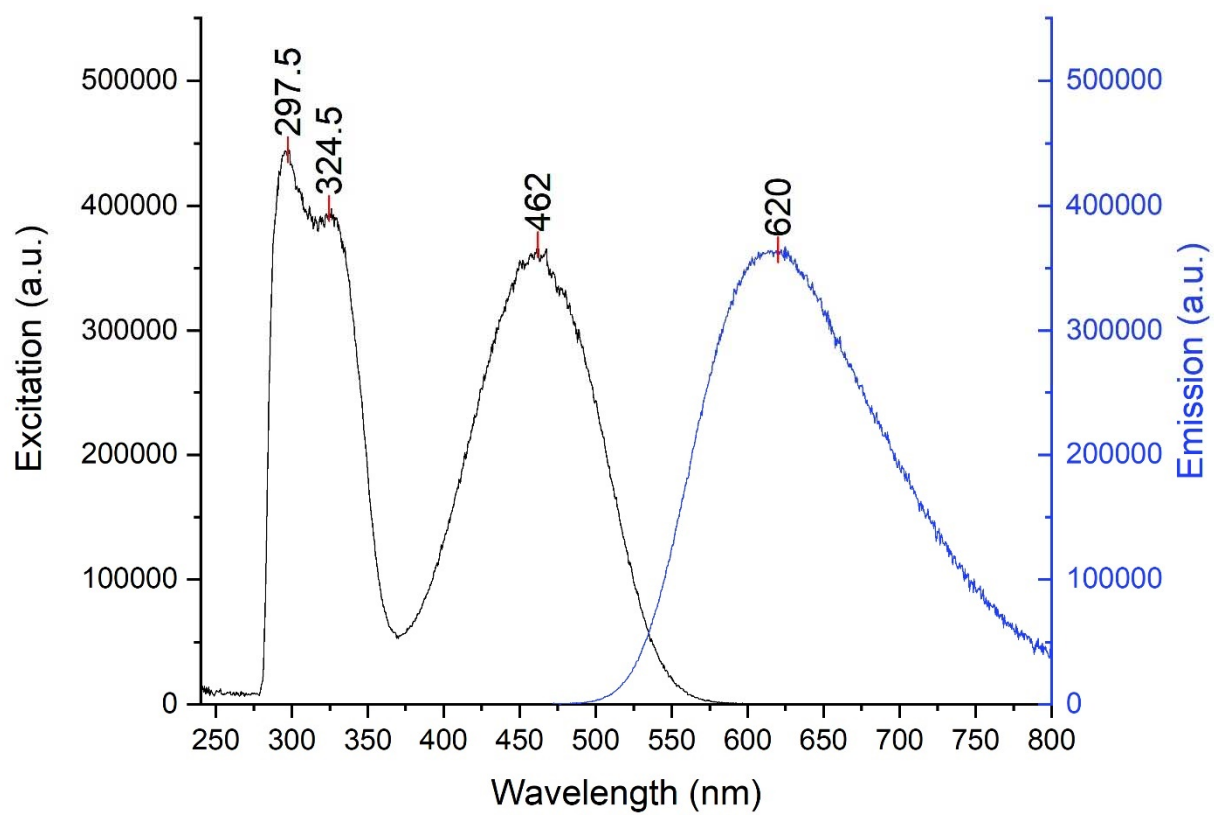


Figure S102 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) spectra of compound **2** and $[(\text{C}_6\text{F}_5)_3\text{PF}][\text{B}(\text{C}_6\text{F}_5)_4]$; 12.5 μM sample.

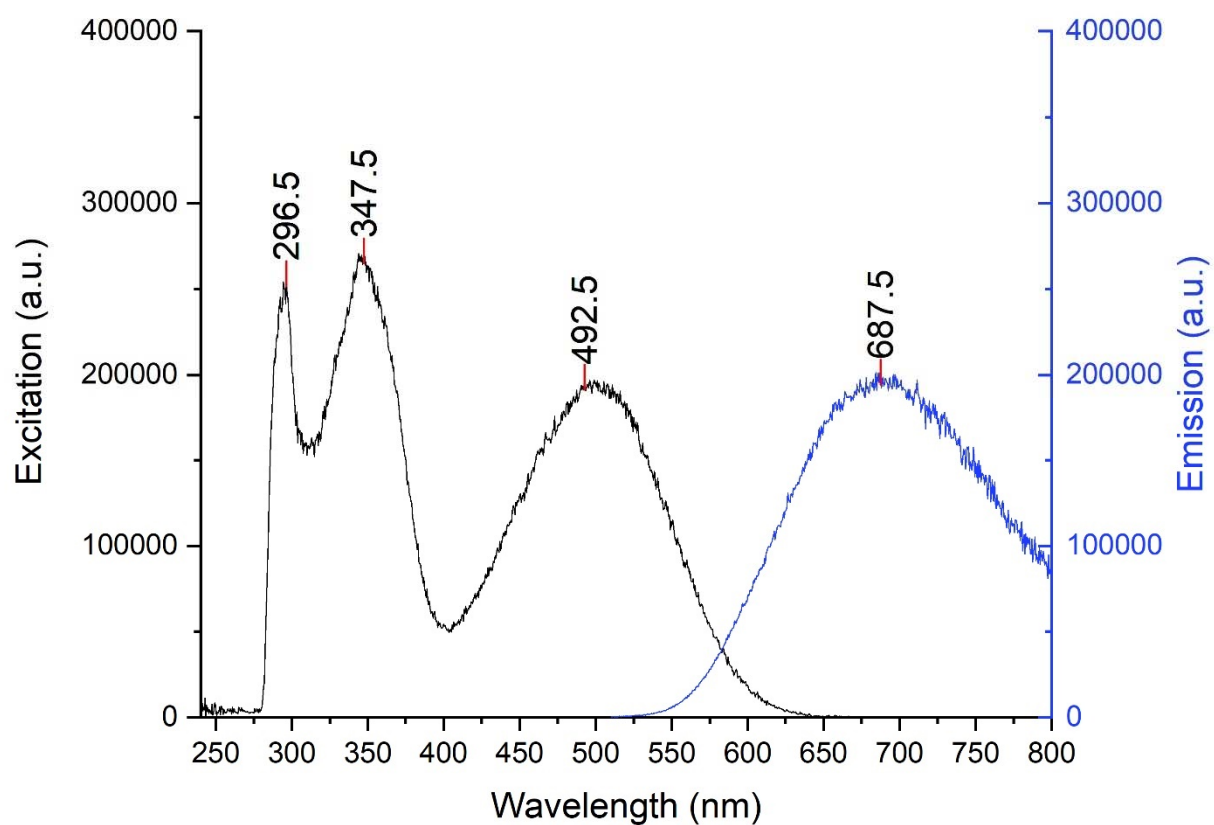


Figure S103 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) spectra of compound **3** and $[(C_6F_5)_3PF][B(C_6F_5)_4]$; 12.5 μ M sample.

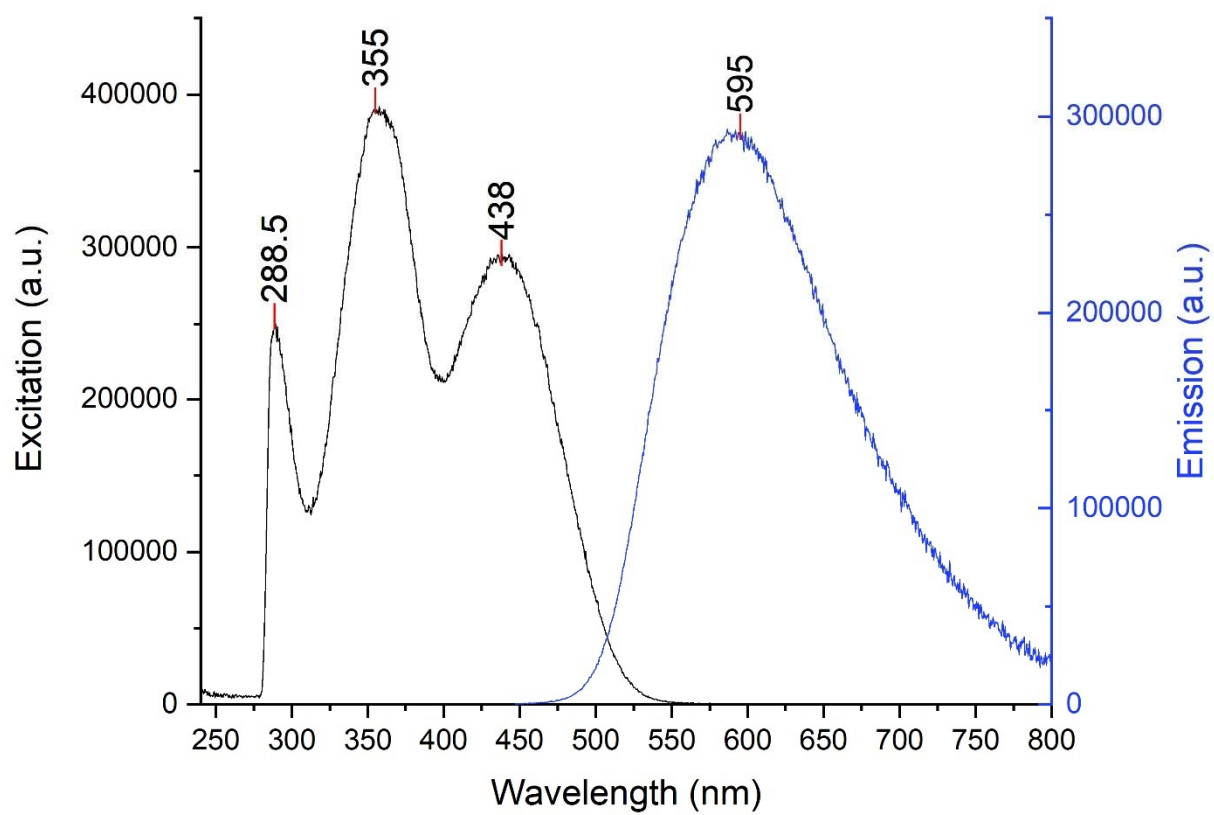


Figure S104 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) spectra of compound **7** and $[(C_6F_5)_3PF][B(C_6F_5)_4]$; 12.5 μM sample.

6.1.27. Ga₂Cl₄

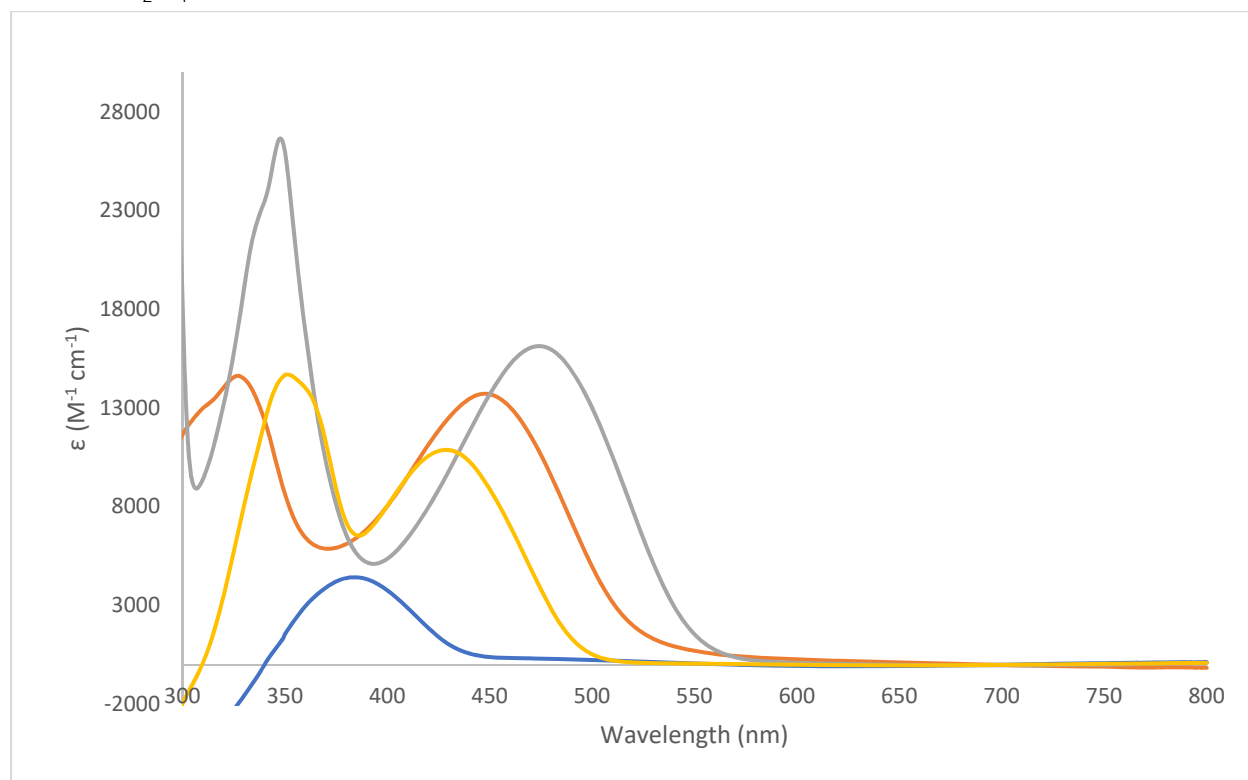


Figure S105 Stacked UV-Vis absorption spectra of **1** (blue), **2** (orange), **3** (grey), and **7** (yellow) with Ga₂Cl₄ (excess); 12.5 μ M samples.

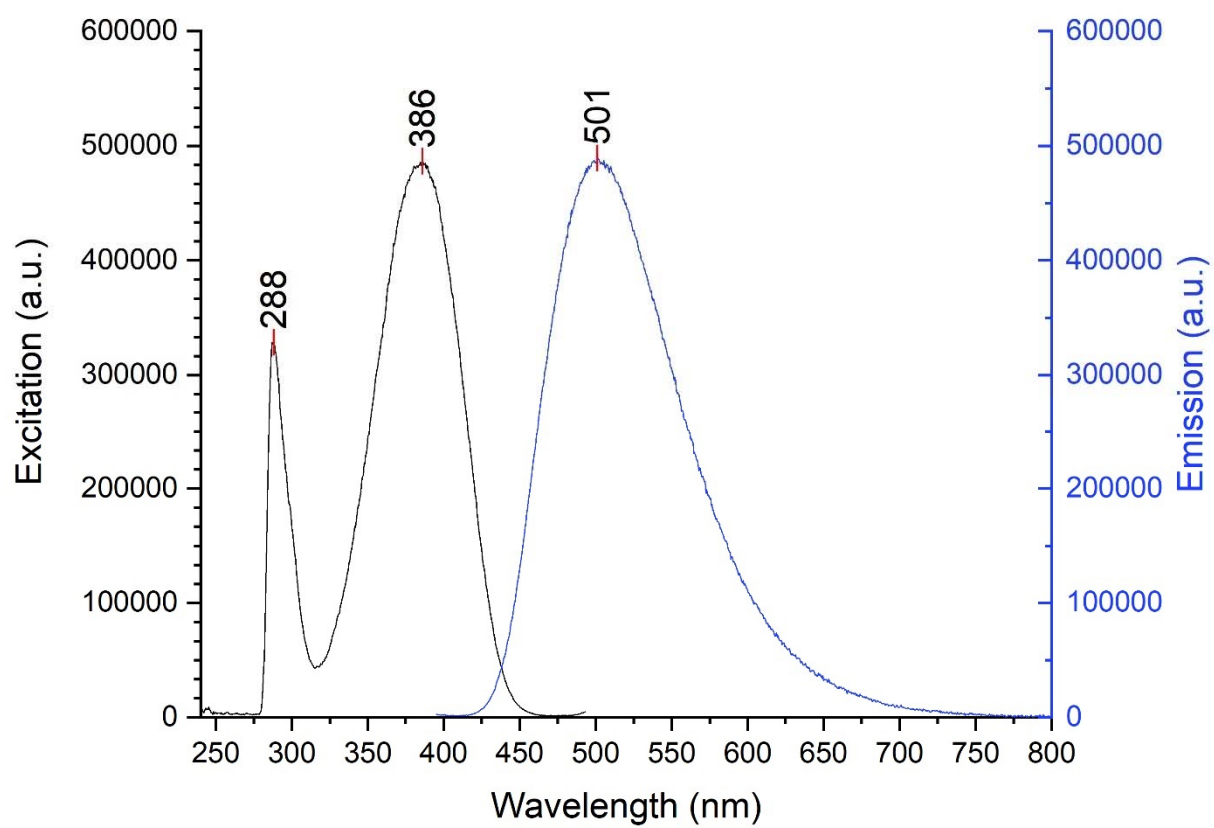


Figure S106 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) spectra of compound **1** and Ga₂Cl₄; 12.5 μM sample.

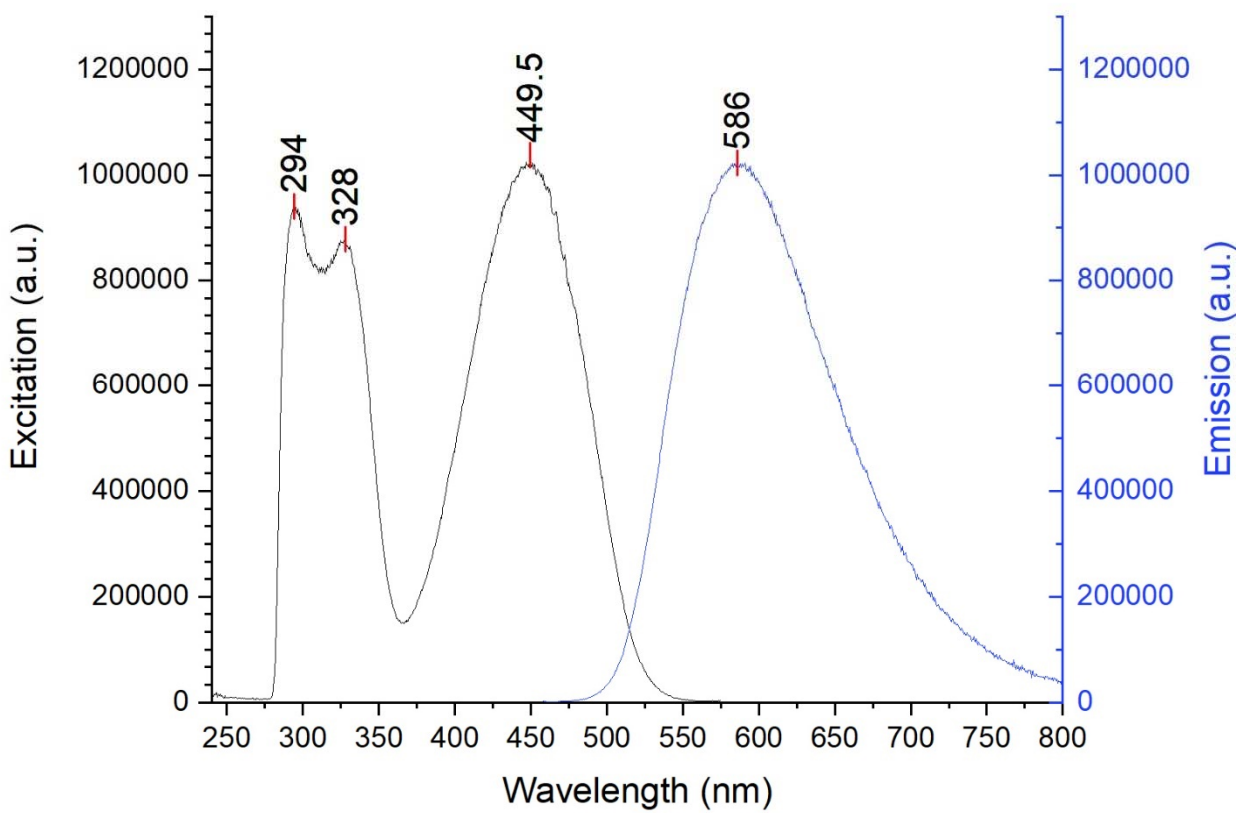


Figure S107 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) spectra of compound **2** and Ga_2Cl_4 ; 12.5 μM sample.

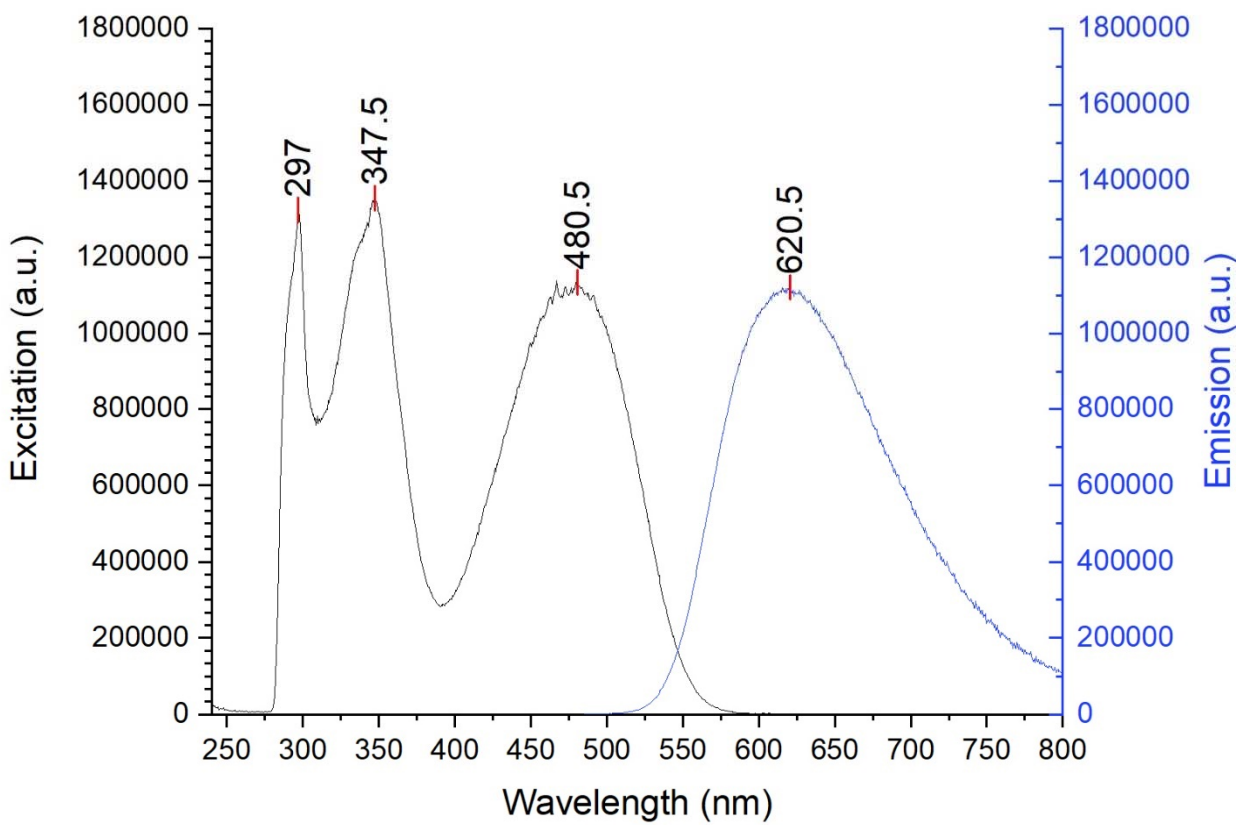


Figure S108 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) spectra of compound **3** and Ga_2Cl_4 ; 12.5 μM sample.

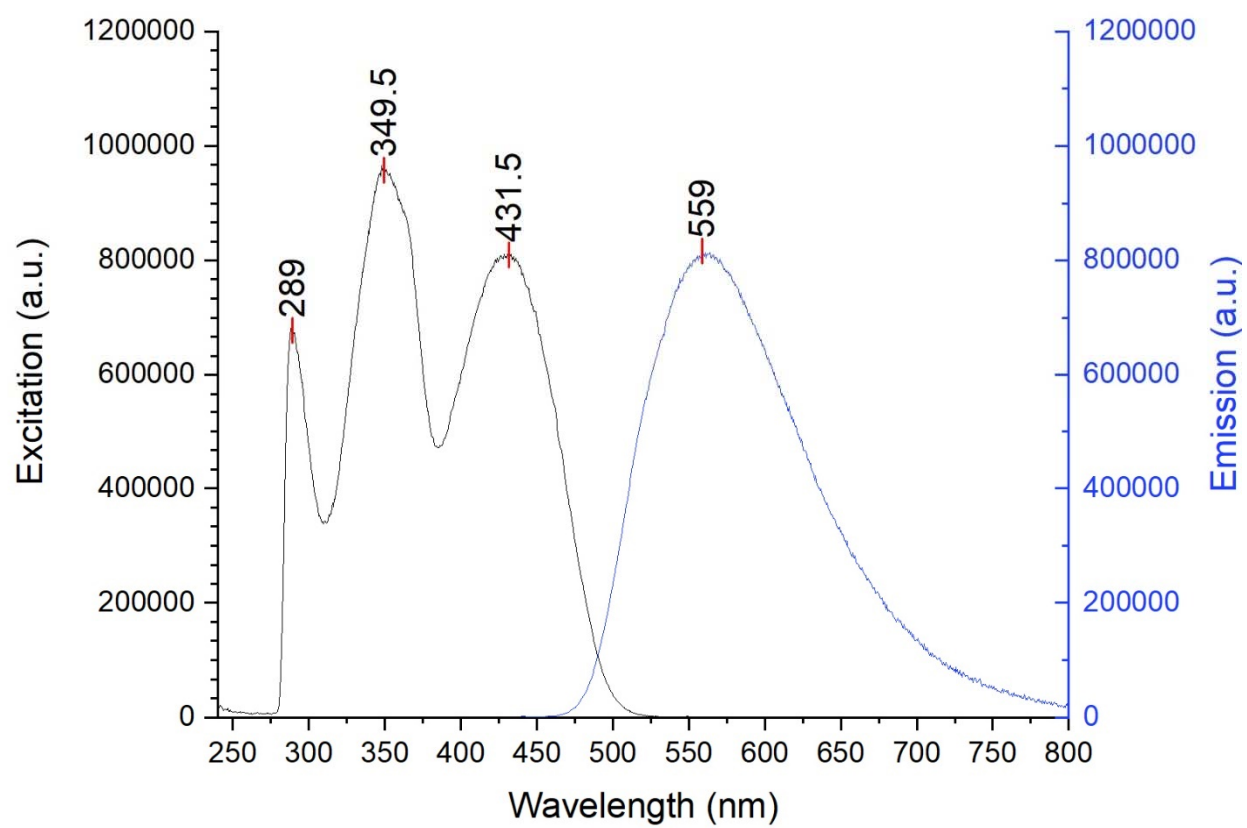


Figure S109 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) spectra of compound **7** and Ga_2Cl_4 ; 12.5 μM sample.

6.1.28. $\text{Ga}(\text{C}_6\text{F}_5)_3$

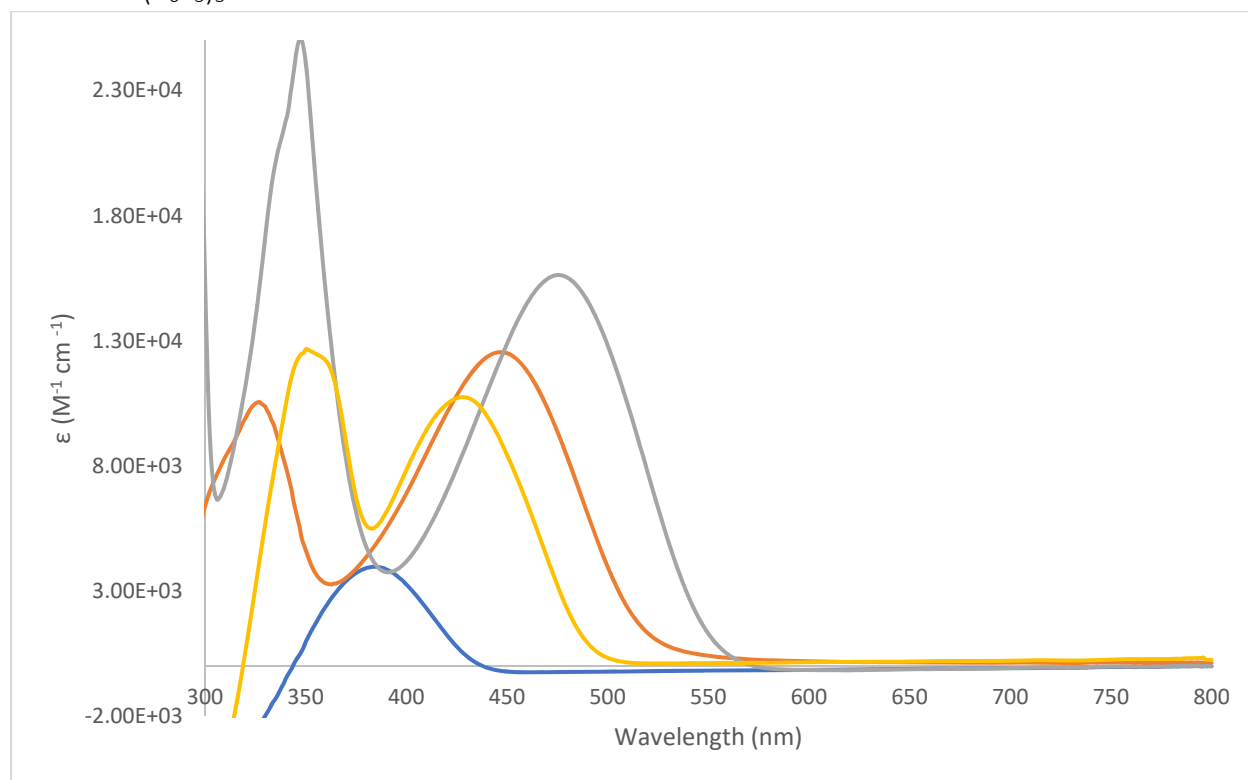


Figure S110 Stacked UV-Vis absorption spectra of **1** (blue), **2** (orange), **3** (grey), and **7** (yellow) with $\text{Ga}(\text{C}_6\text{F}_5)_3$ (5 eq.); 12.5 μM samples.

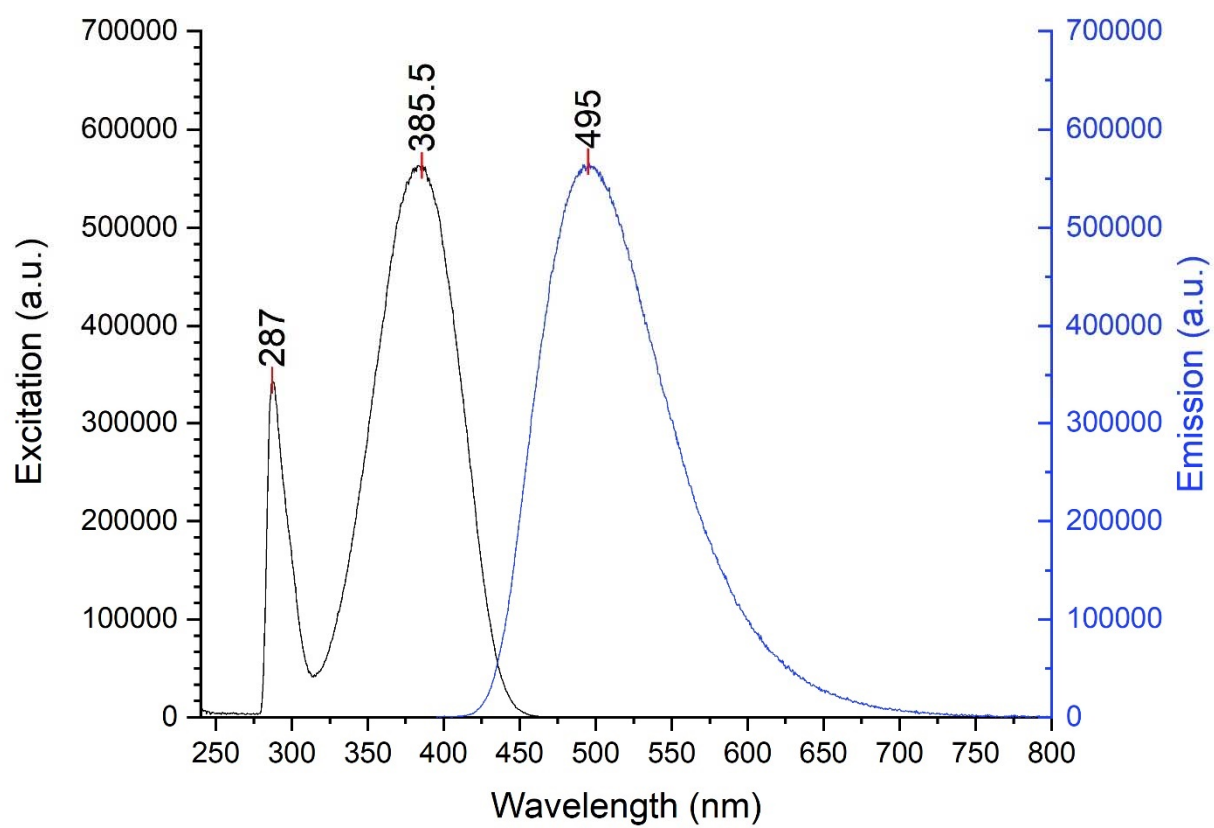


Figure S111 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) spectra of compound **1** and **Ga(C₆F₅)₃**; 12.5 μ M sample.

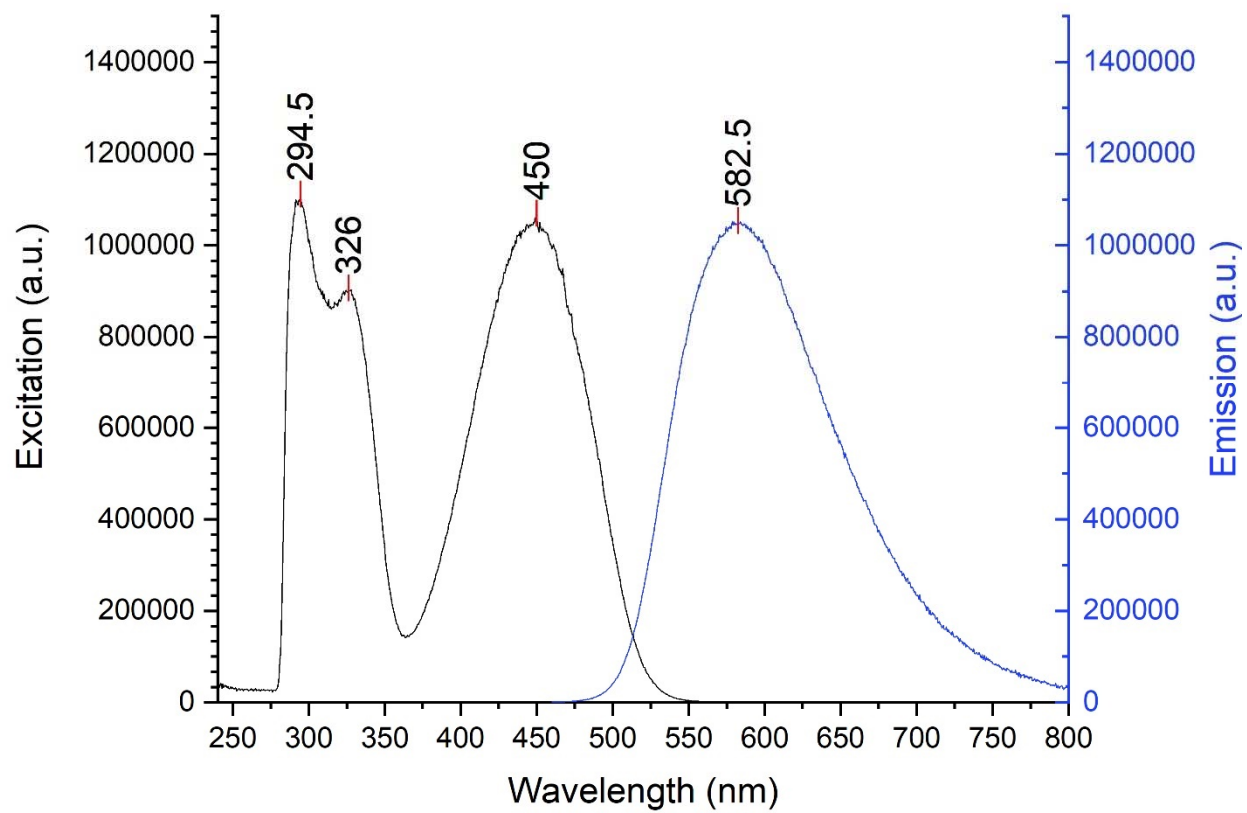


Figure S112 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) spectra of compound **2** and $\text{Ga}(\text{C}_6\text{F}_5)_3$; 12.5 μM sample.

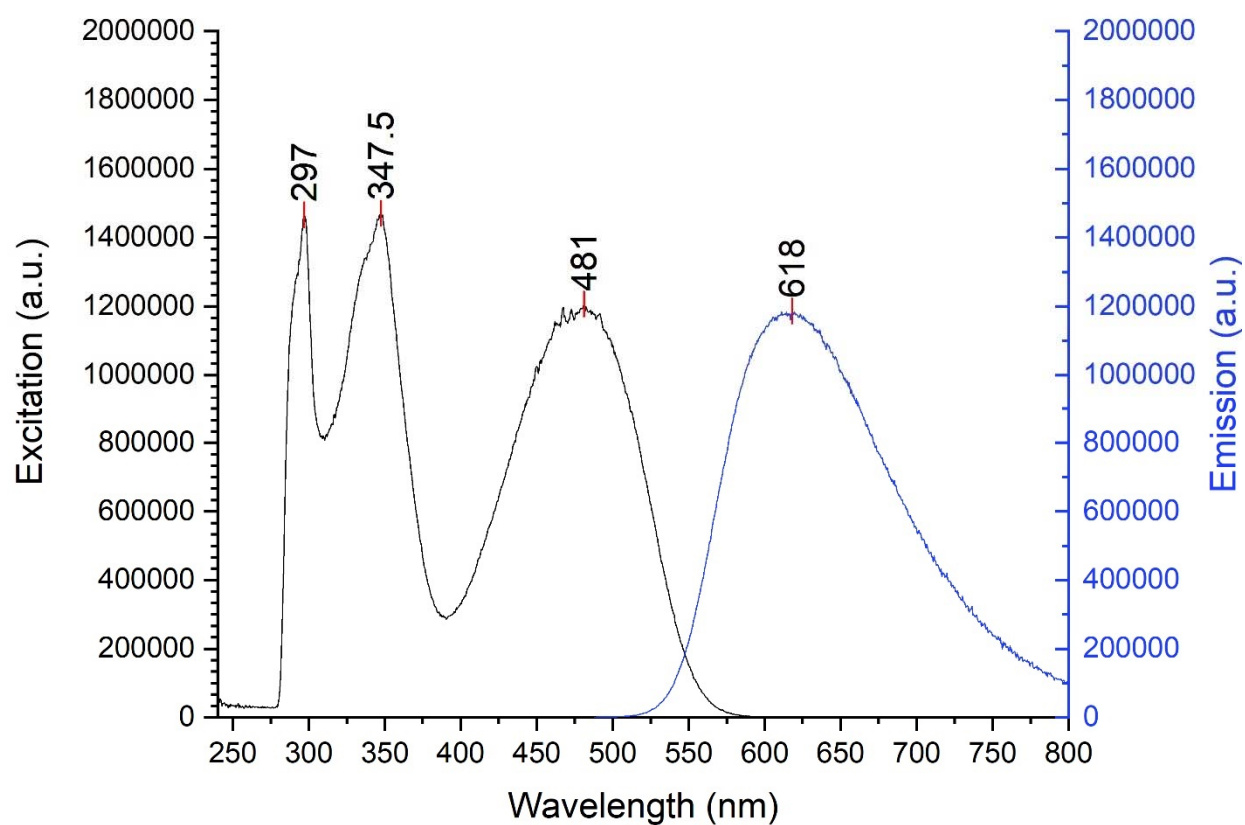


Figure S113 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) spectra of compound **3** and $\text{Ga}(\text{C}_6\text{F}_5)_3$; 12.5 μM sample.

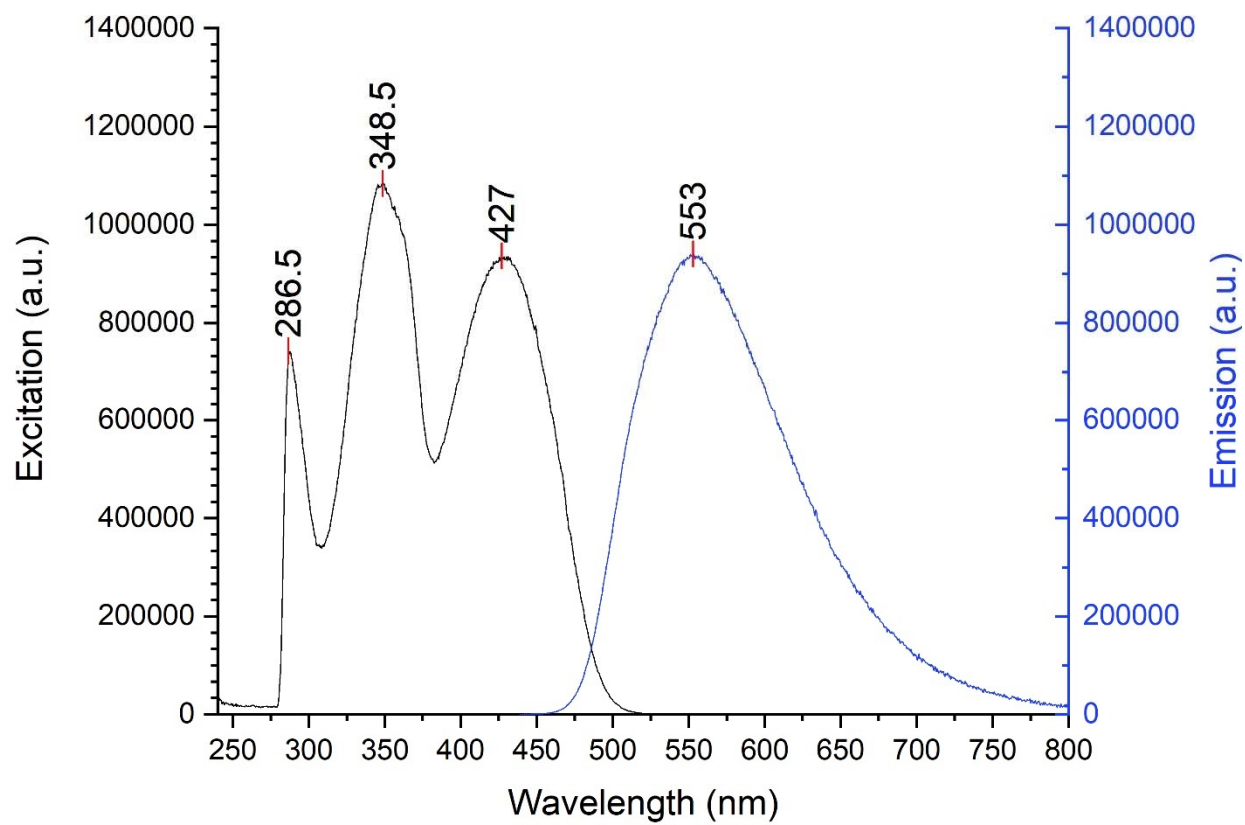


Figure S114 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) spectra of compound **7** and $\text{Ga}(\text{C}_6\text{F}_5)_3$; 12.5 μM sample.

6.1.29. GaCl₃

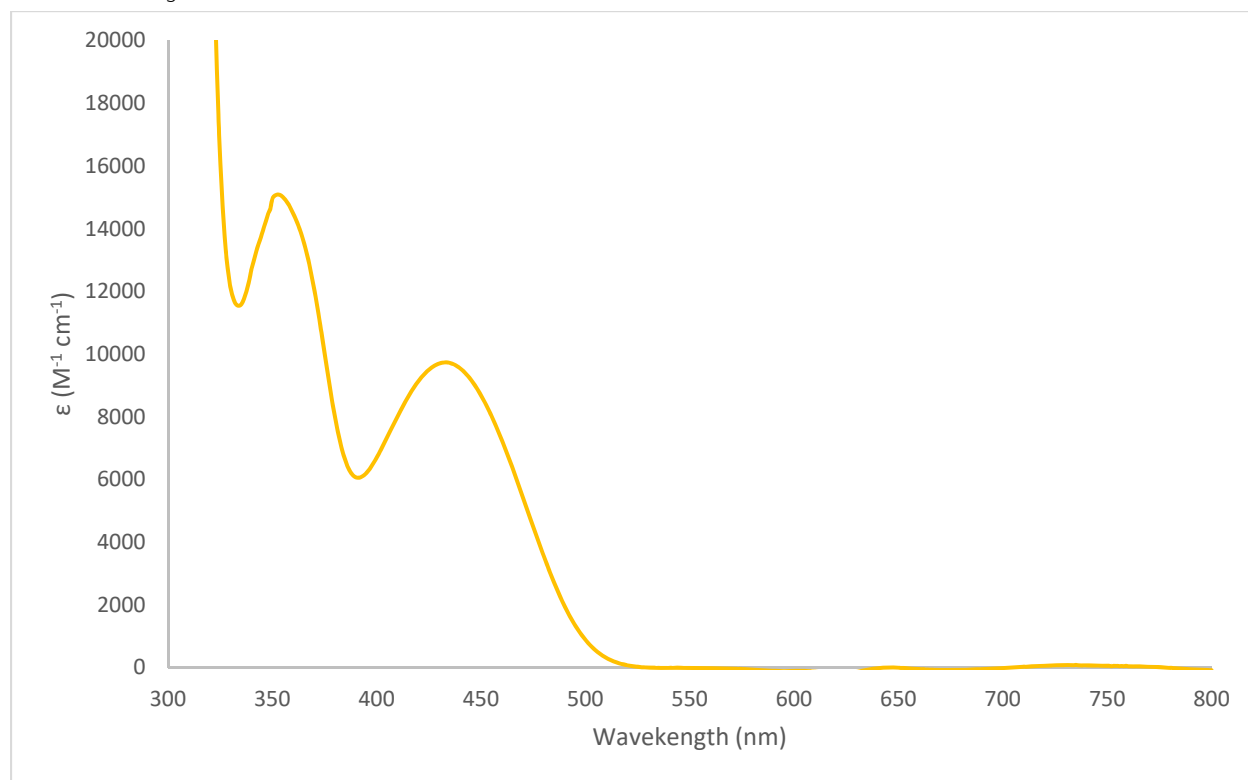


Figure S115 Stacked UV-Vis absorption spectra of **7** (yellow) with **GaCl₃** (1000 eq.); 12.5 μM samples.

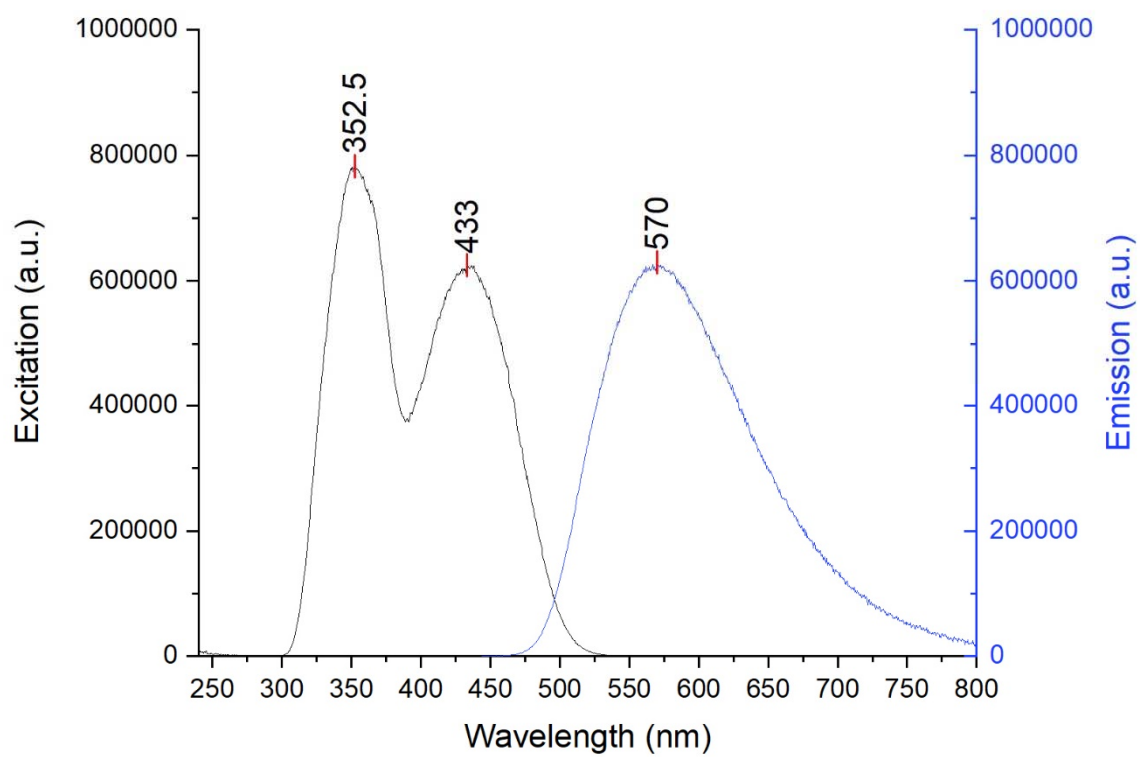


Figure S116 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) spectra of compound **7** and GaCl_3 ; 12.5 μM sample.

6.1.30. $\text{Ga}(\text{NO}_3)_3$

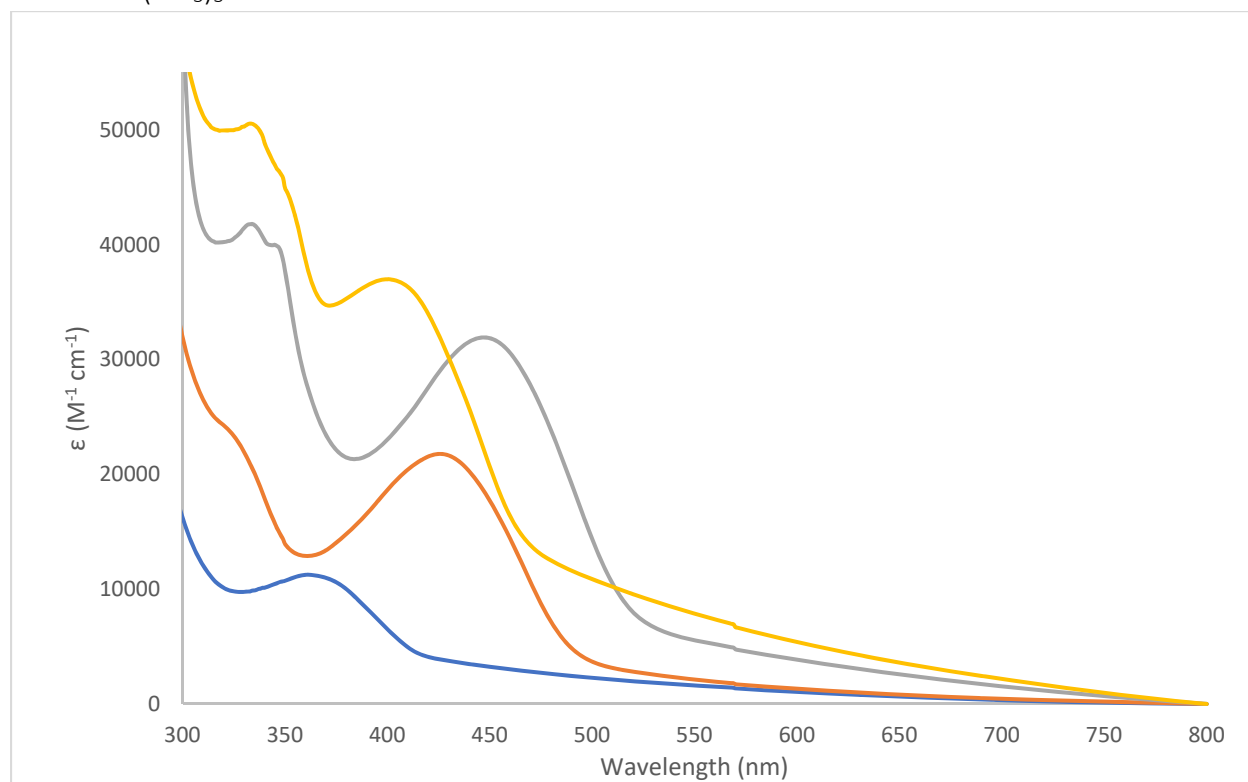


Figure S117 Stacked UV-Vis absorption spectra of **1** (blue), **2** (orange), **3** (grey), and **7** (yellow) with $\text{Ga}(\text{NO}_3)_3$ (excess); $12.5 \mu\text{M}$ samples.

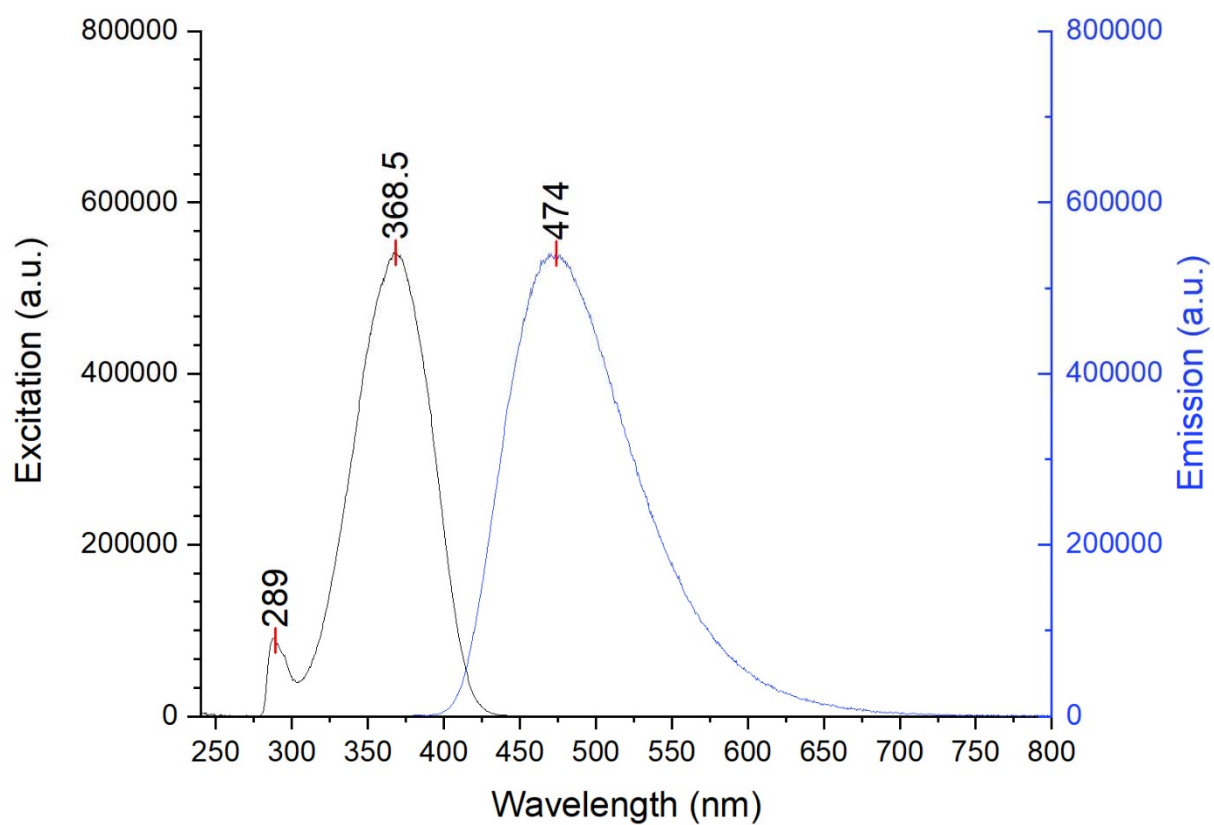


Figure S118 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) spectra of compound 1 and $\text{Ga}(\text{NO}_3)_3$; 12.5 μM sample.

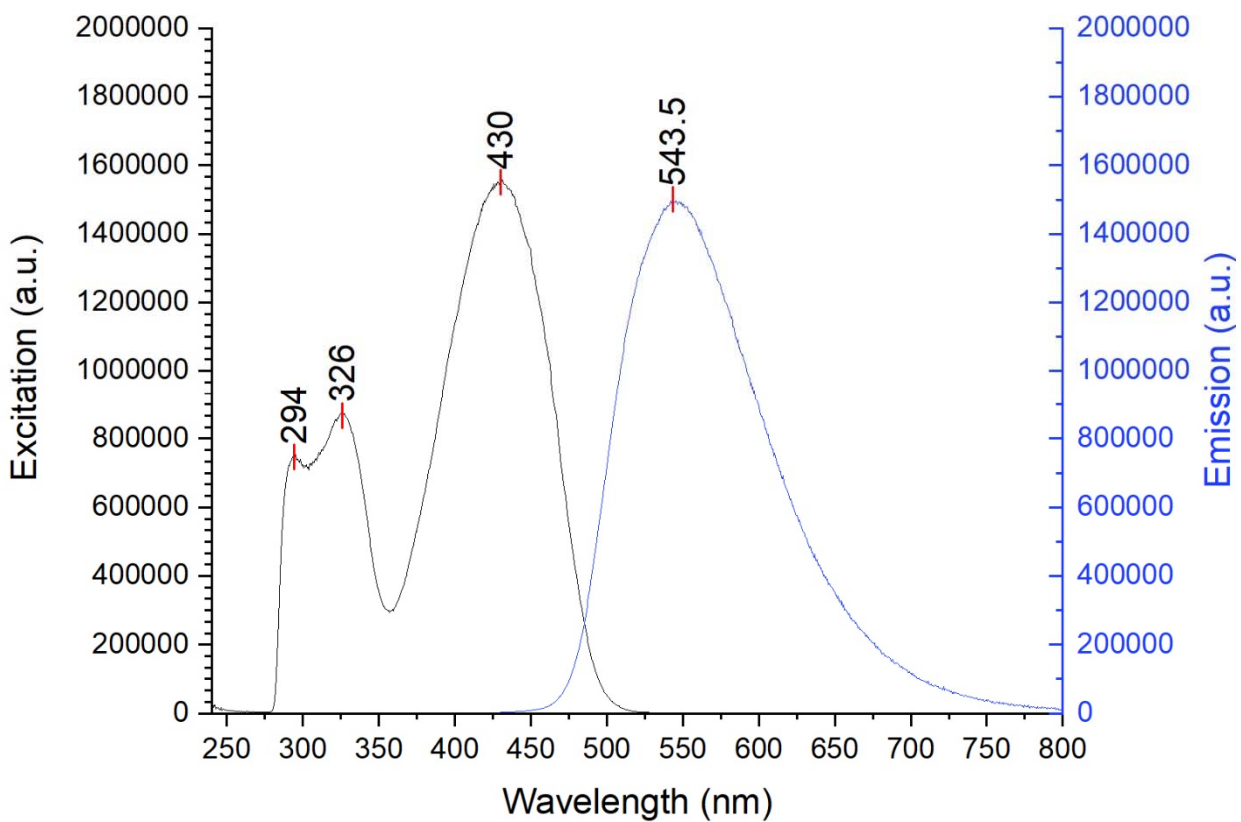


Figure S119 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) spectra of compound **2** and $\text{Ga}(\text{NO}_3)_3$; 12.5 μM sample.

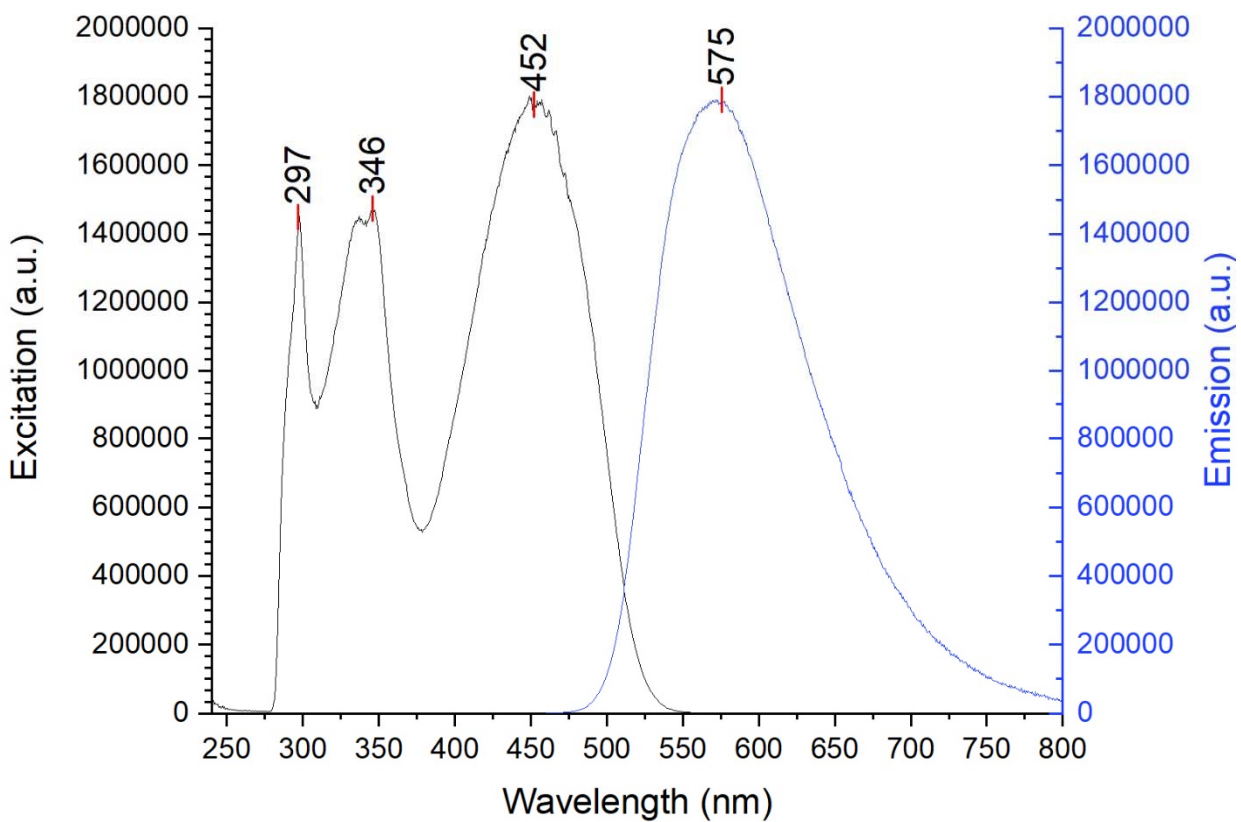


Figure S120 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) spectra of compound **3** and $\text{Ga}(\text{NO}_3)_3$; 12.5 μM sample.

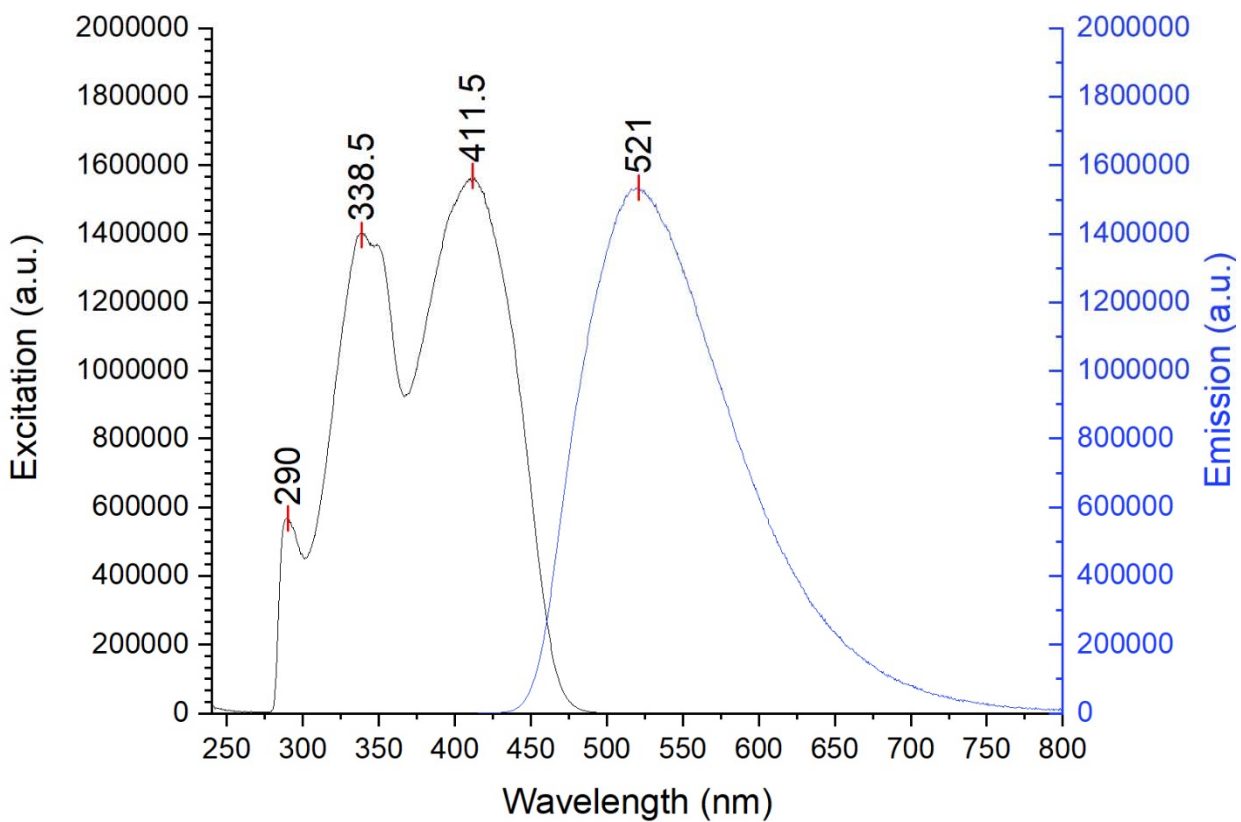


Figure S121 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) spectra of compound **7** and $\text{Ga}(\text{NO}_3)_3$; 12.5 μM sample.

6.1.31. Ga(OTf)₃

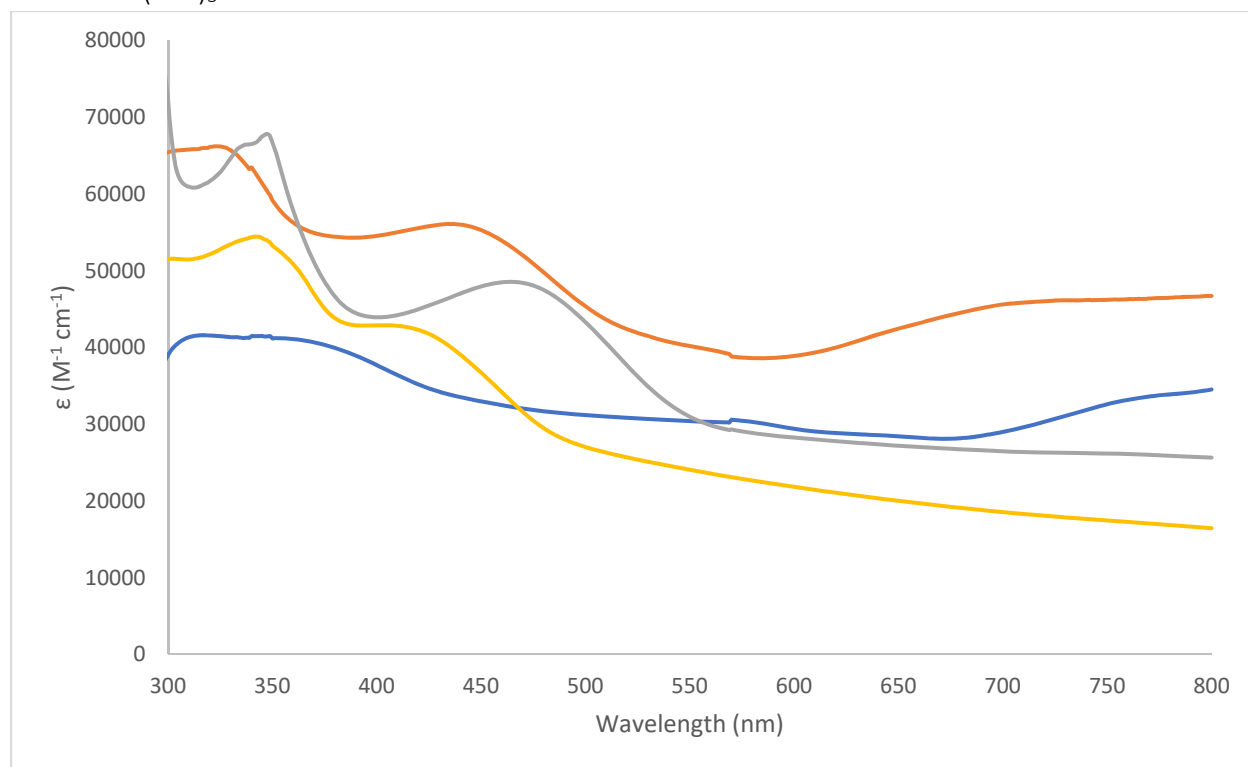


Figure S122 Stacked UV-Vis absorption spectra of **1** (blue), **2** (orange), **3** (grey), and **7** (yellow) with Ga(OTf)₃ (1000 eq.); 12.5 μM samples.

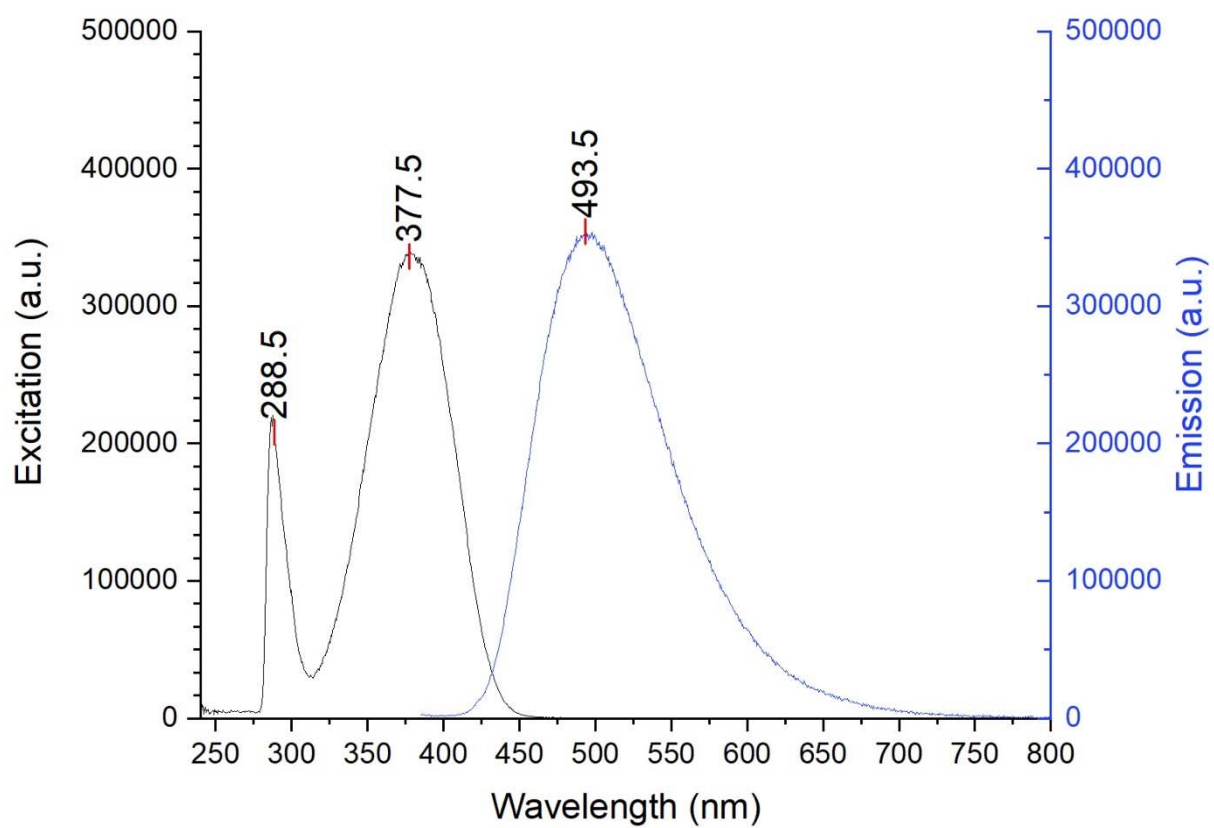


Figure S123 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) spectra of compound **1** and **Ga(OTf)₃**; 12.5 μ M sample.

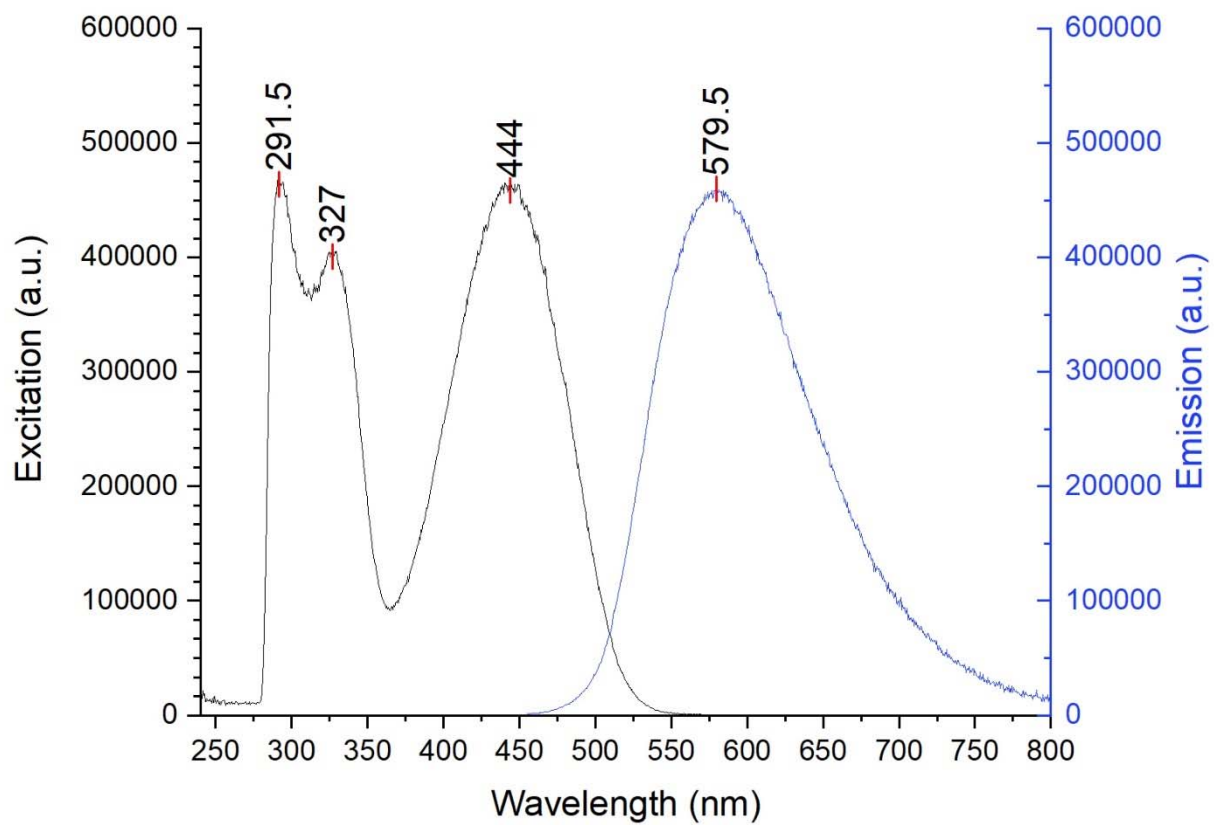


Figure S124 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) spectra of compound **2** and **Ga(OTf)₃**; 12.5 μ M sample.

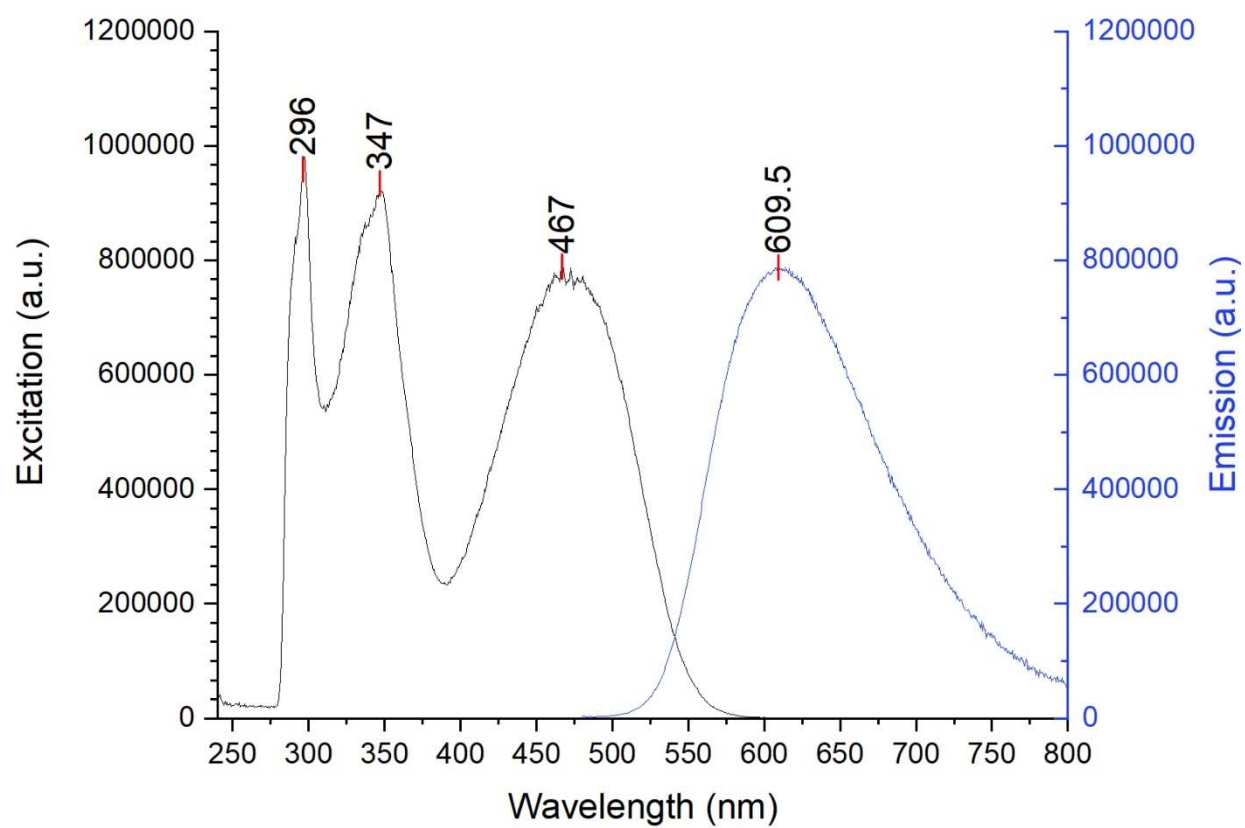


Figure S125 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) spectra of compound **3** and **Ga(OTf)₃**; 12.5 μ M sample.

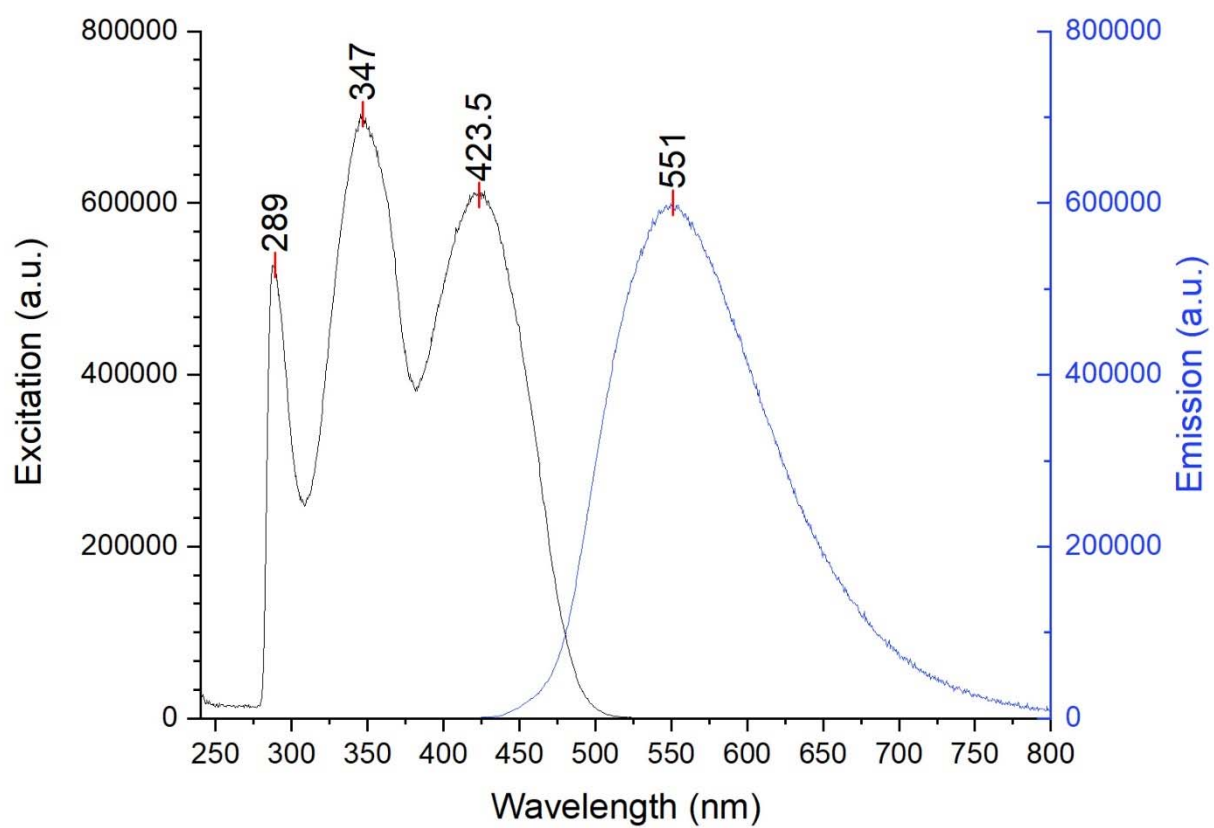


Figure S126 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) spectra of compound **7** and $\text{Ga}(\text{OTf})_3$; 12.5 μM sample.

6.1.32. $\text{H}_2\text{B}(\text{C}_6\text{F}_5)$

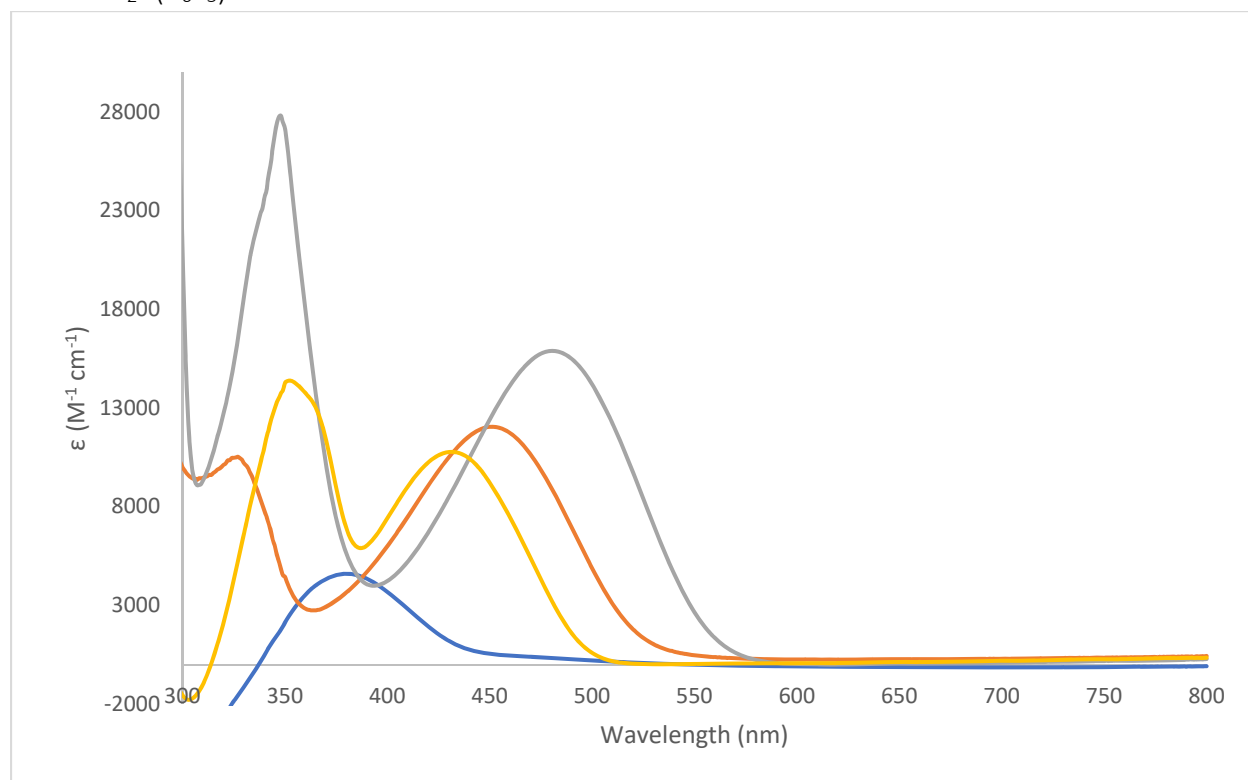


Figure S127 Stacked UV-Vis absorption spectra of **1** (blue), **2** (orange), **3** (grey), and **7** (yellow) with $\text{H}_2\text{B}(\text{C}_6\text{F}_5)$ (500 eq.); 12.5 μM samples.

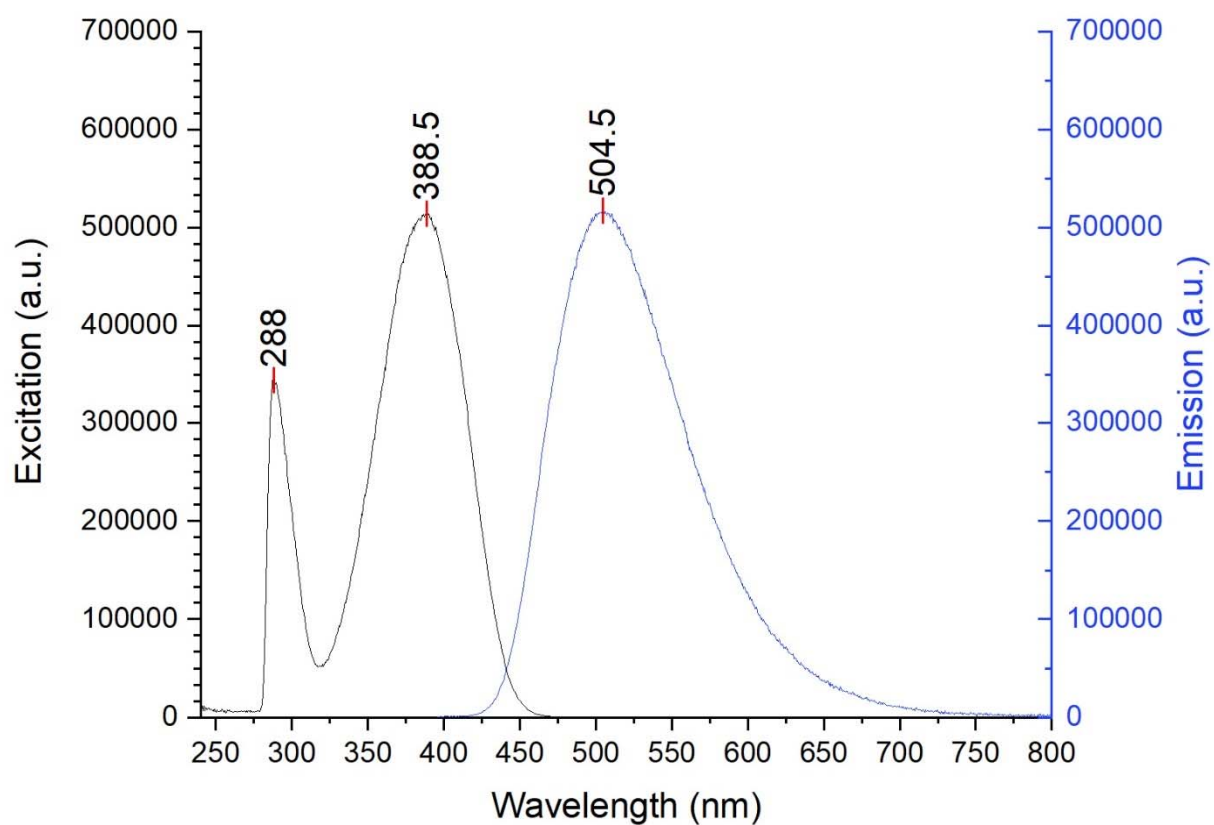


Figure S128 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) spectra of compound **1** and **H₂B(C₆F₅)**; 12.5 μM sample.

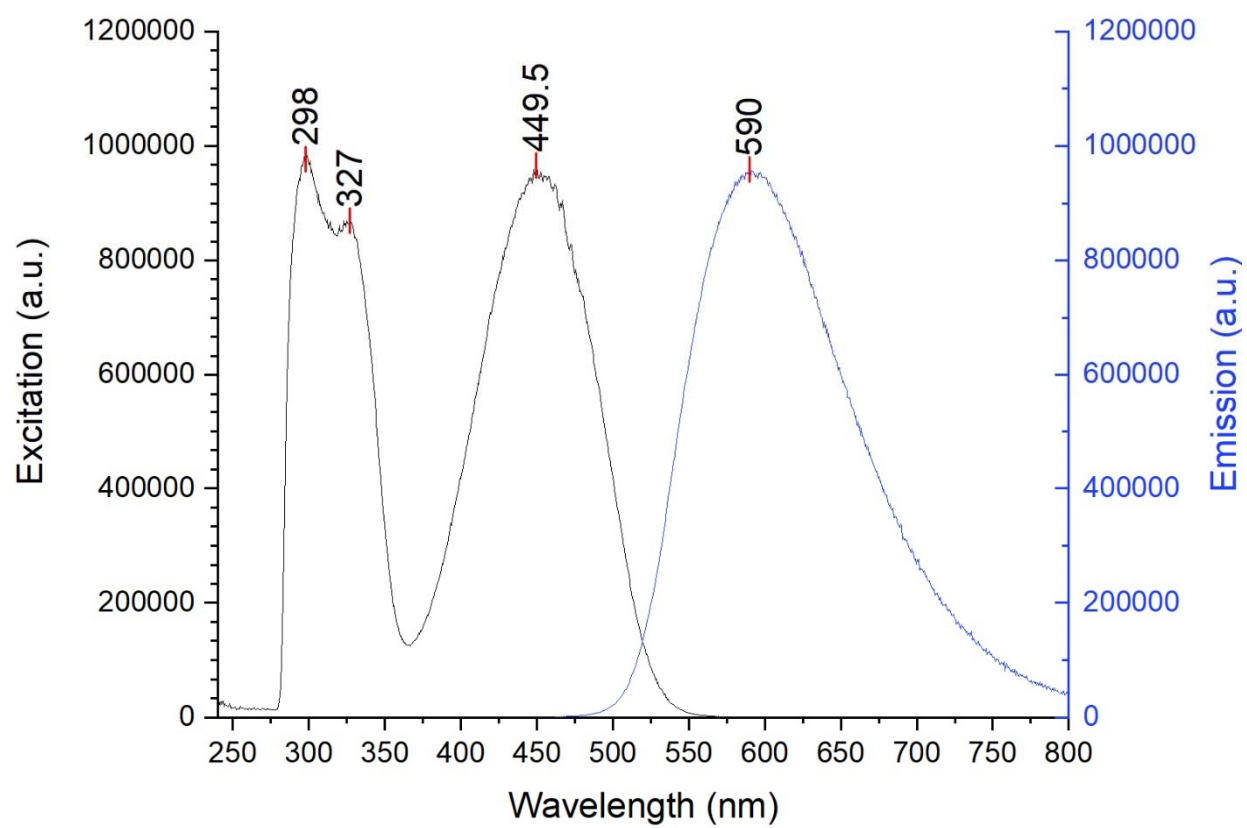


Figure S129 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) spectra of compound **2** and $\text{H}_2\text{B}(\text{C}_6\text{F}_5)_3$; 12.5 μM sample.

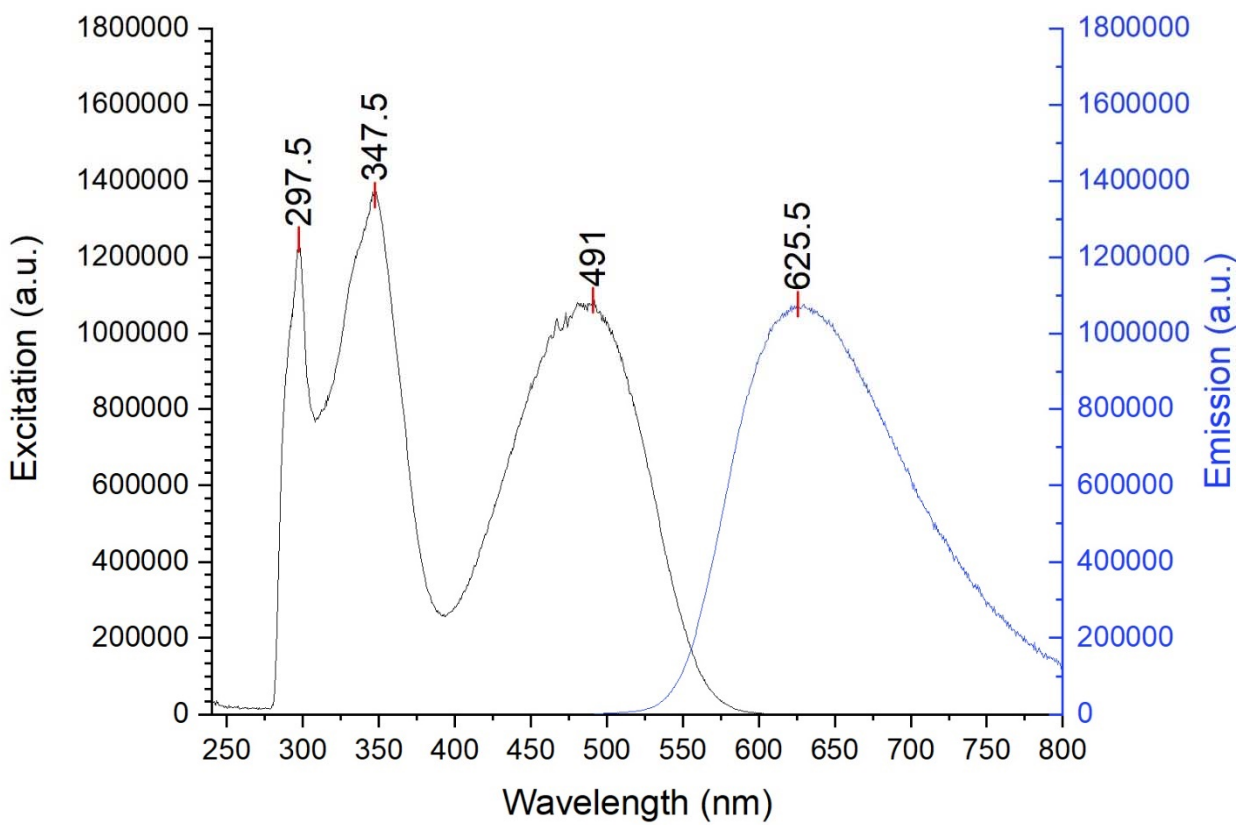


Figure S130 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) spectra of compound **3** and $\text{H}_2\text{B}(\text{C}_6\text{F}_5)$; $12.5\ \mu\text{M}$ sample.

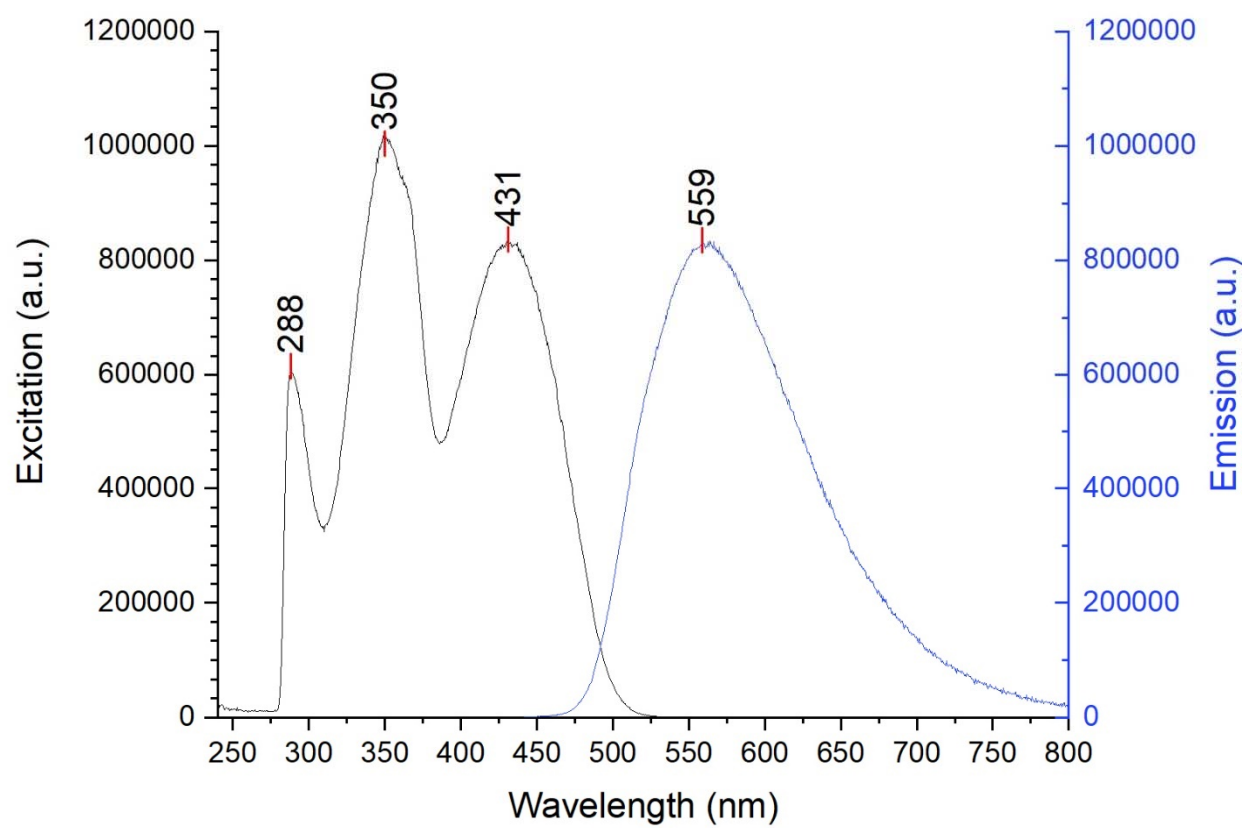


Figure S131 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) spectra of compound **7** and $\text{H}_2\text{B}(\text{C}_6\text{F}_5)$; $12.5\ \mu\text{M}$ sample.

6.1.33. $\text{HB}(\text{C}_6\text{F}_5)_2$

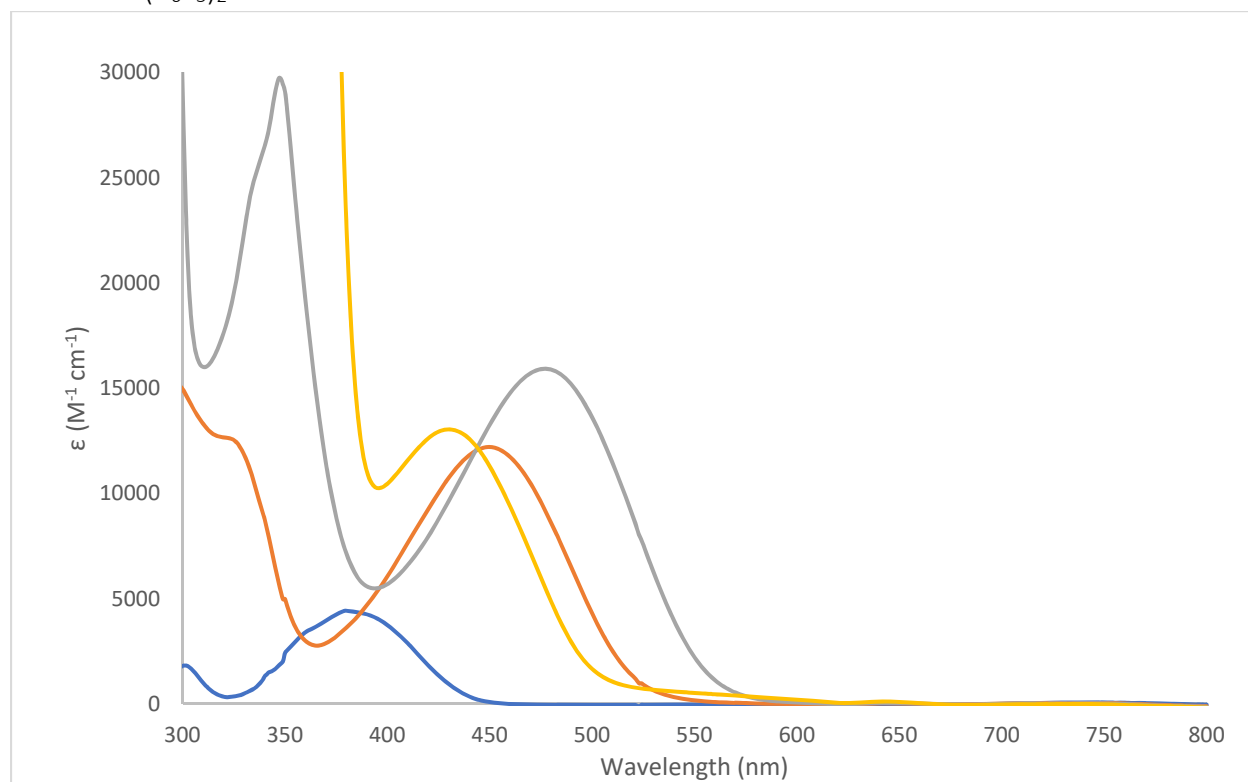


Figure S132 Stacked UV-Vis absorption spectra of **1** (blue), **2** (orange), **3** (grey), and **7** (yellow) with $\text{HB}(\text{C}_6\text{F}_5)_2$ (1000 eq.); 12.5 μM samples.

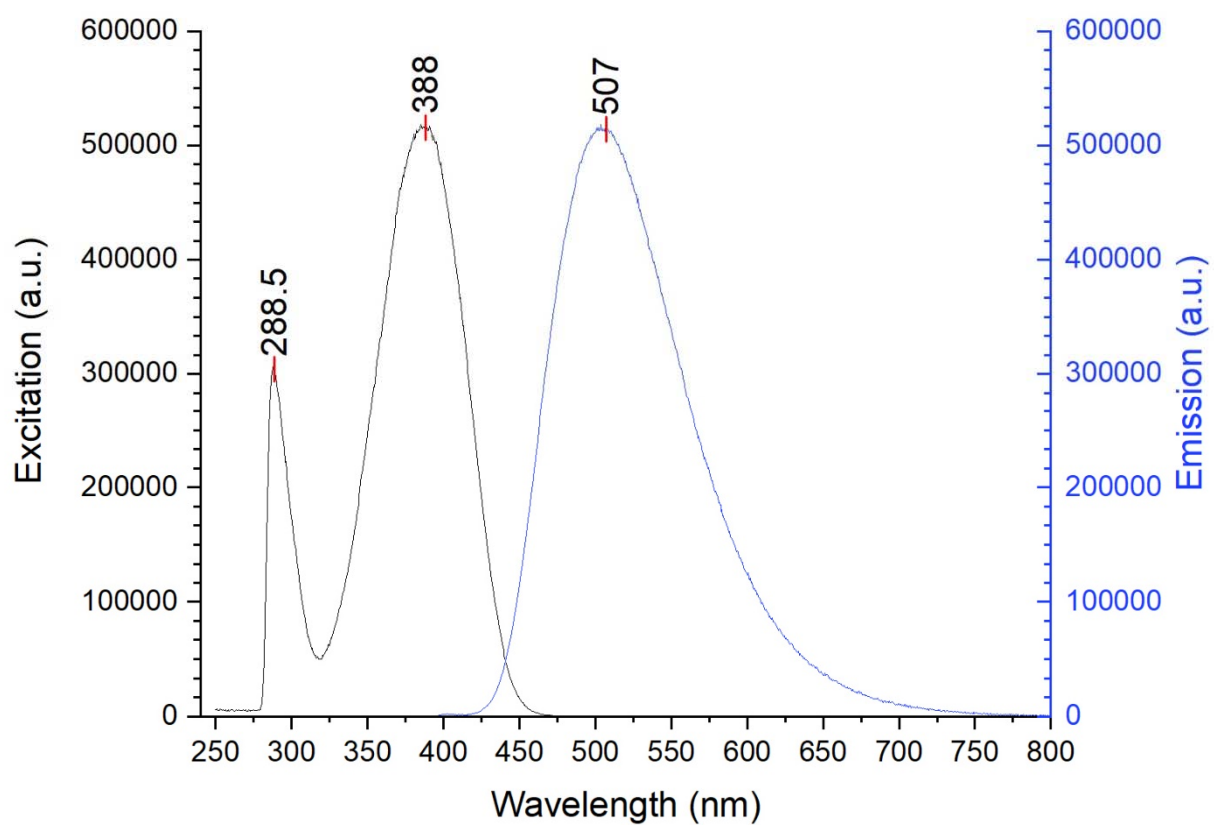


Figure S133 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) spectra of compound **1** and **HB(C₆F₅)₂**; 12.5 μ M sample.

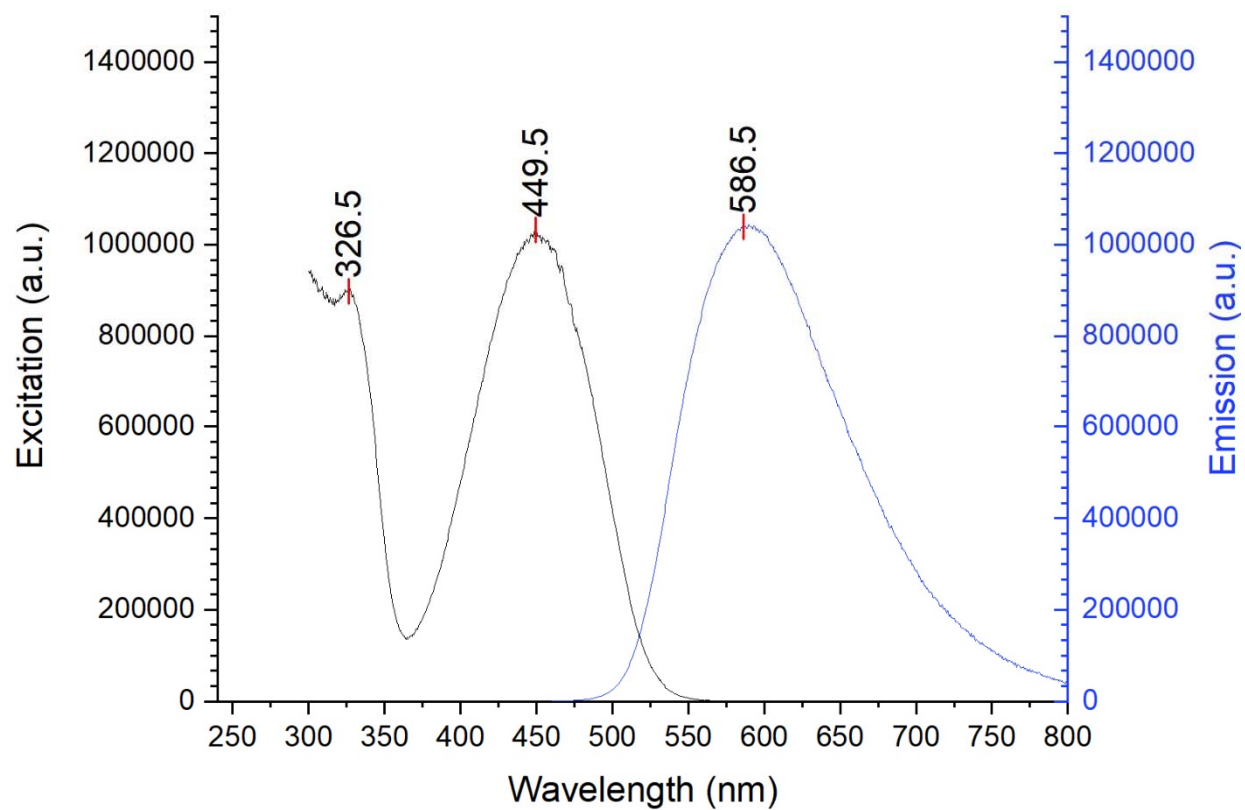


Figure S134 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) spectra of compound **2** and $\text{HB}(\text{C}_6\text{F}_5)_2$; 12.5 μM sample.

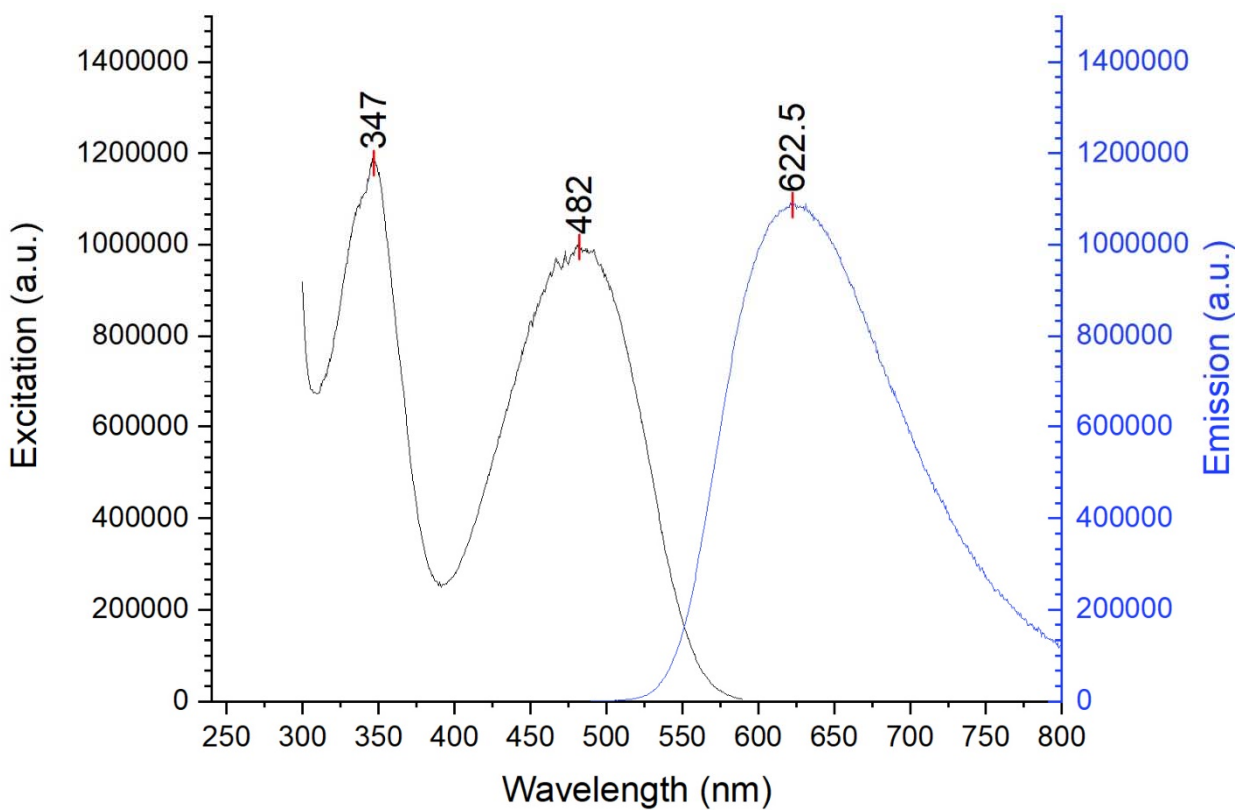


Figure S135 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) spectra of compound **3** and $\text{HB}(\text{C}_6\text{F}_5)_2$; 12.5 μM sample.

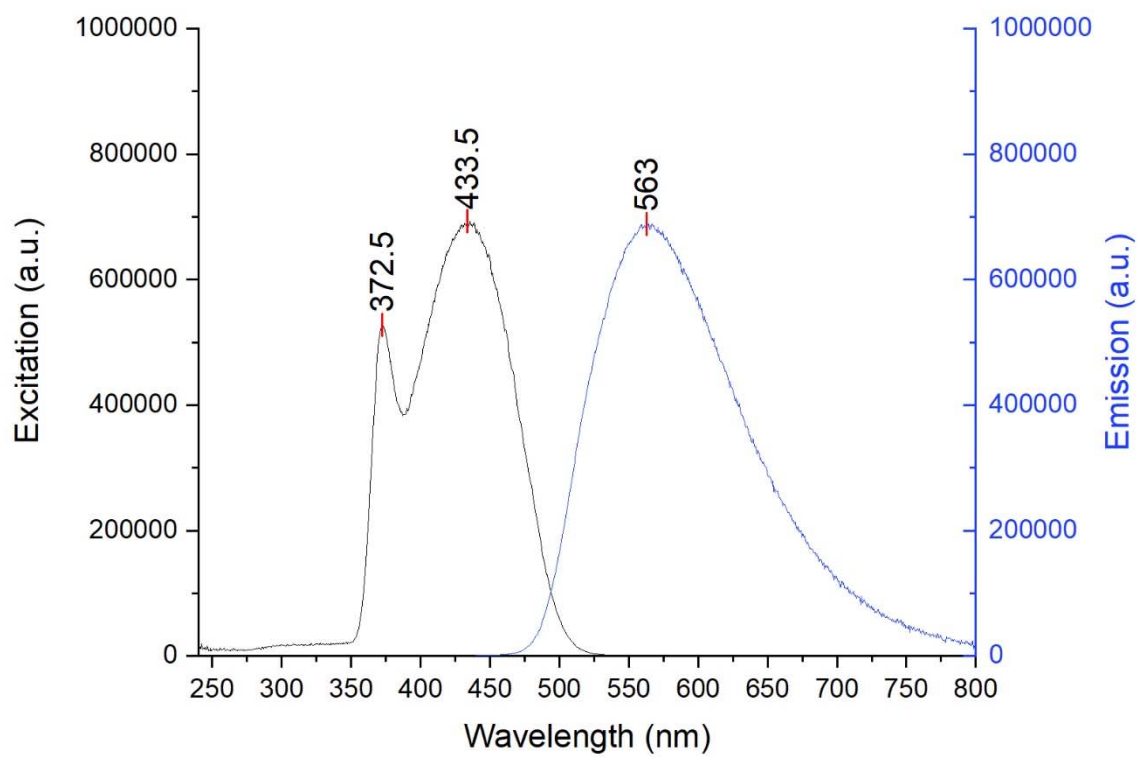


Figure S136 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) spectra of compound **7** and $\text{HB}(\text{C}_6\text{F}_5)_2$; 12.5 μM sample.

6.1.34. InBr_3

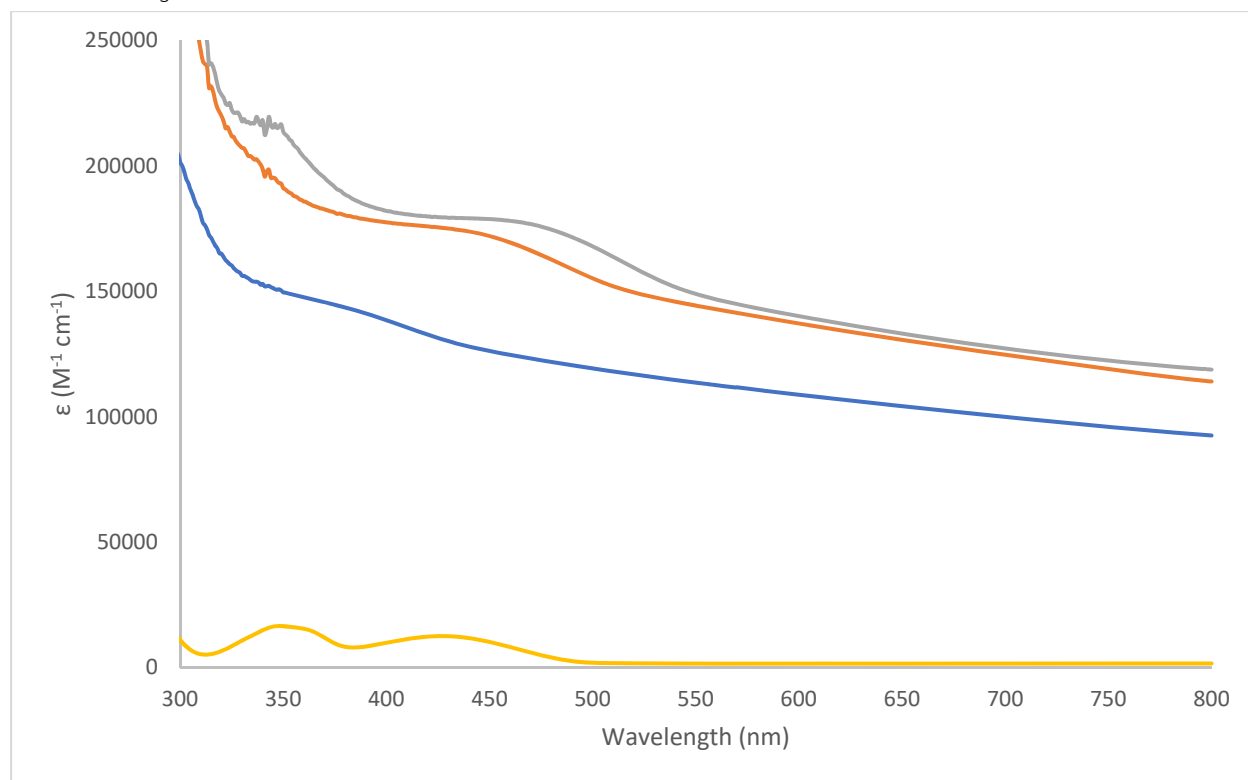


Figure S137 Stacked UV-Vis absorption spectra of **1** (blue), **2** (orange), **3** (grey), and **7** (yellow) with InBr_3 (1000 eq.); 12.5 μM samples.

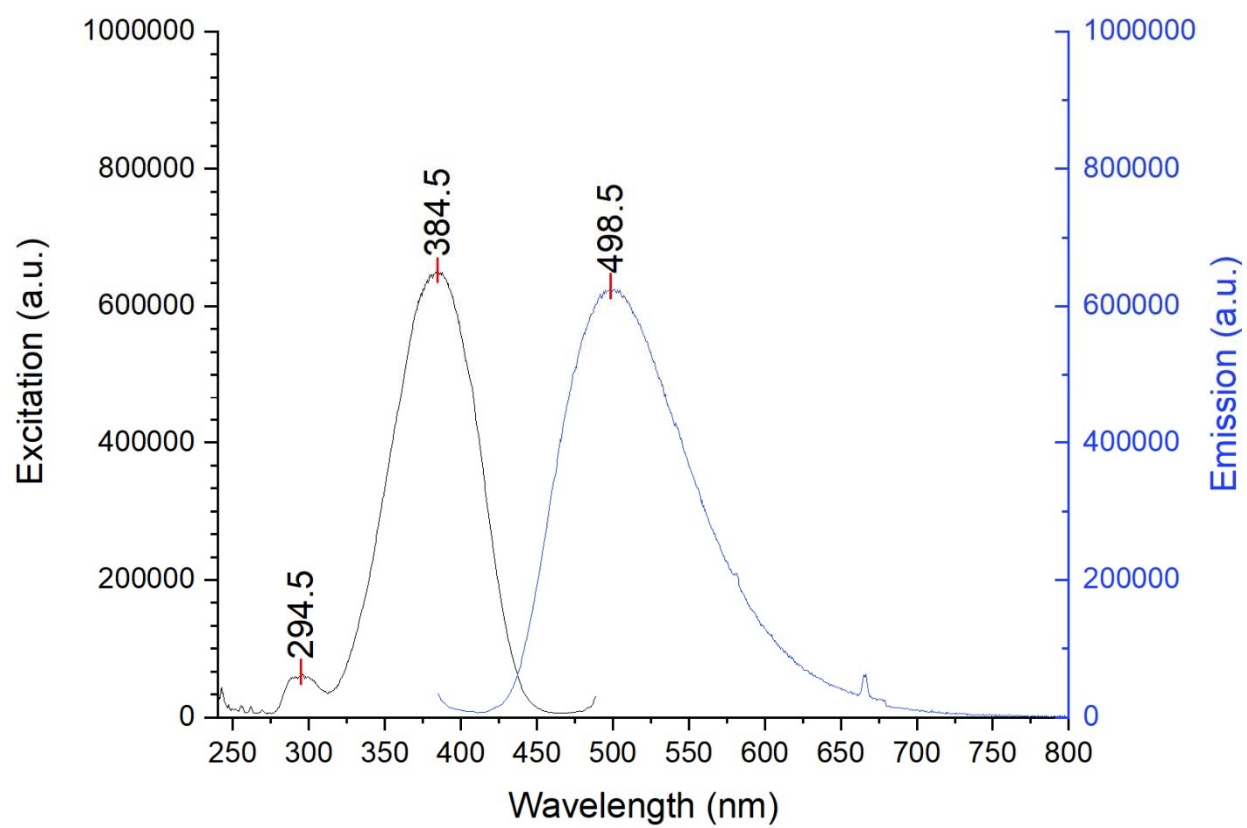


Figure S138 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) spectra of compound **1** and InBr_3 ; 12.5 μM sample.

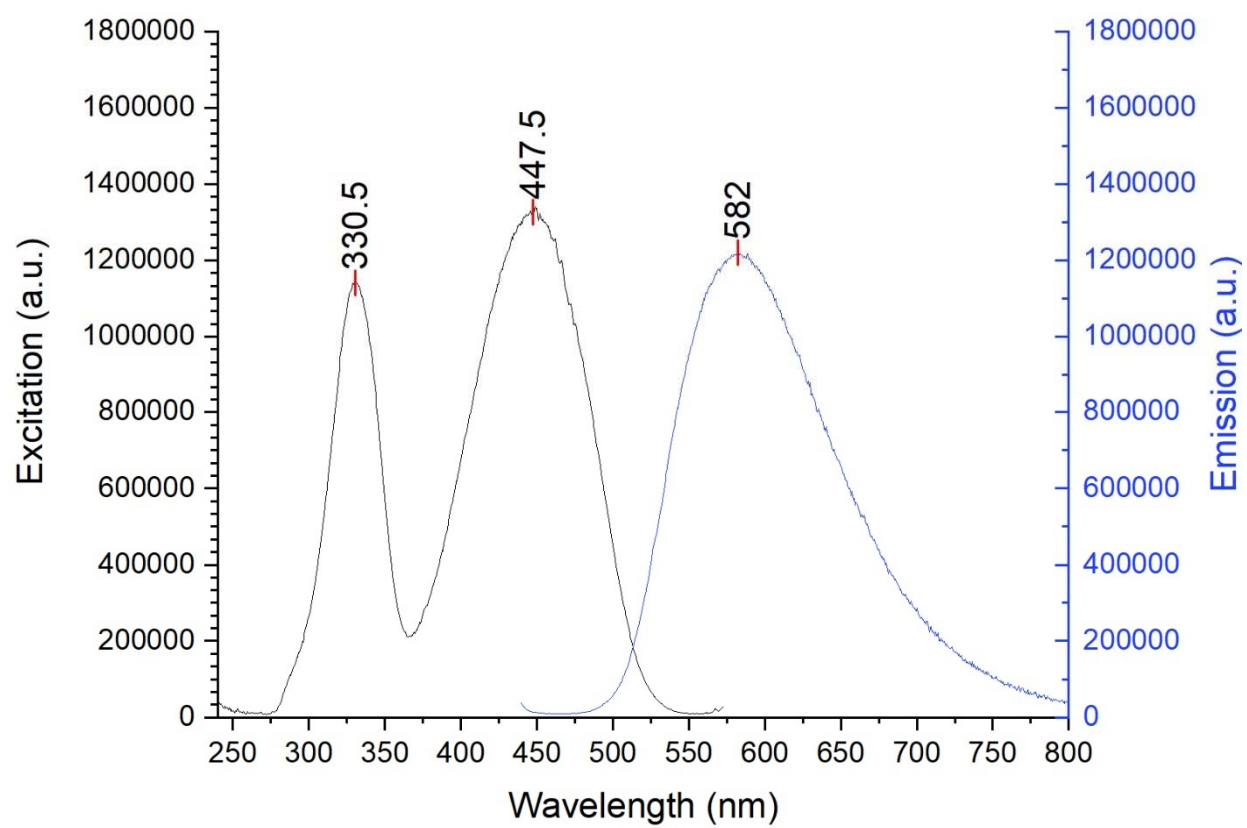


Figure S139 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) spectra of compound **2** and InBr_3 ; 12.5 μM sample.

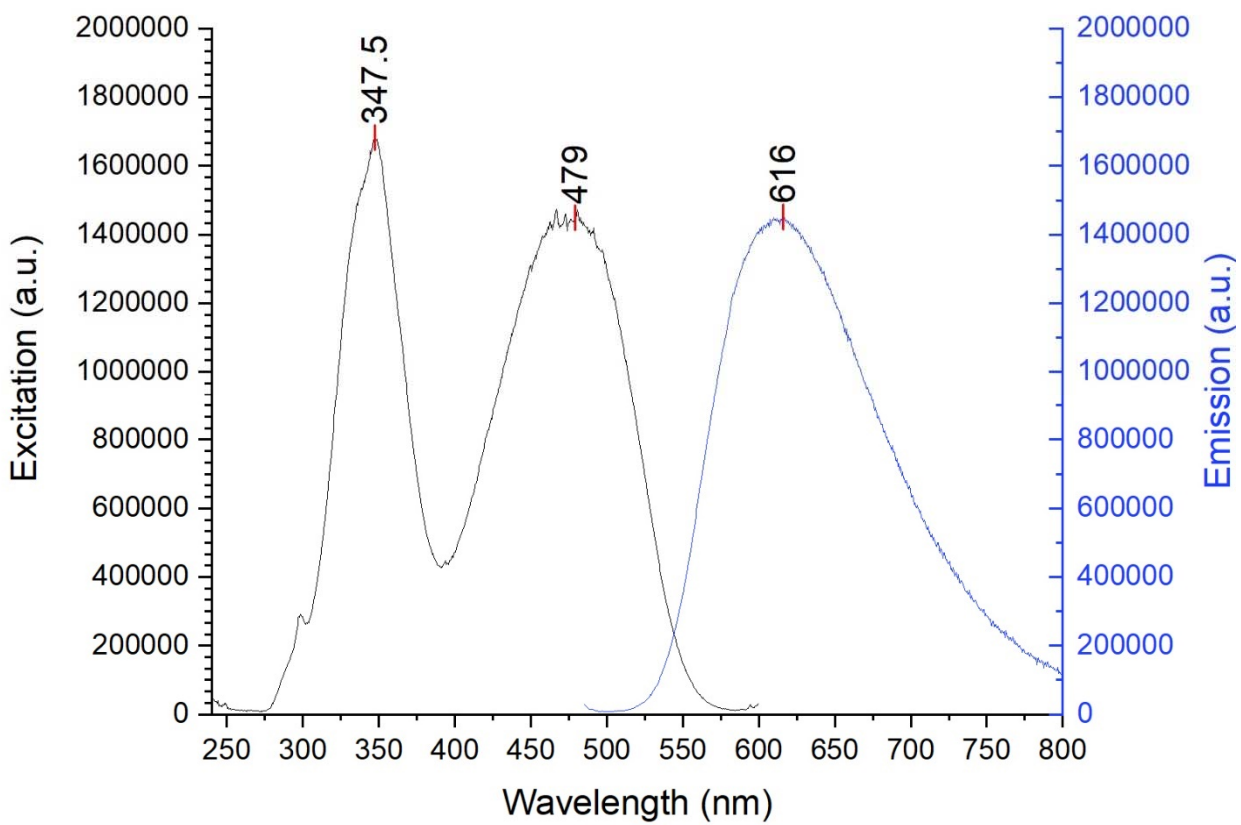


Figure S140 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) spectra of compound **3** and InBr_3 ; 12.5 μM sample.

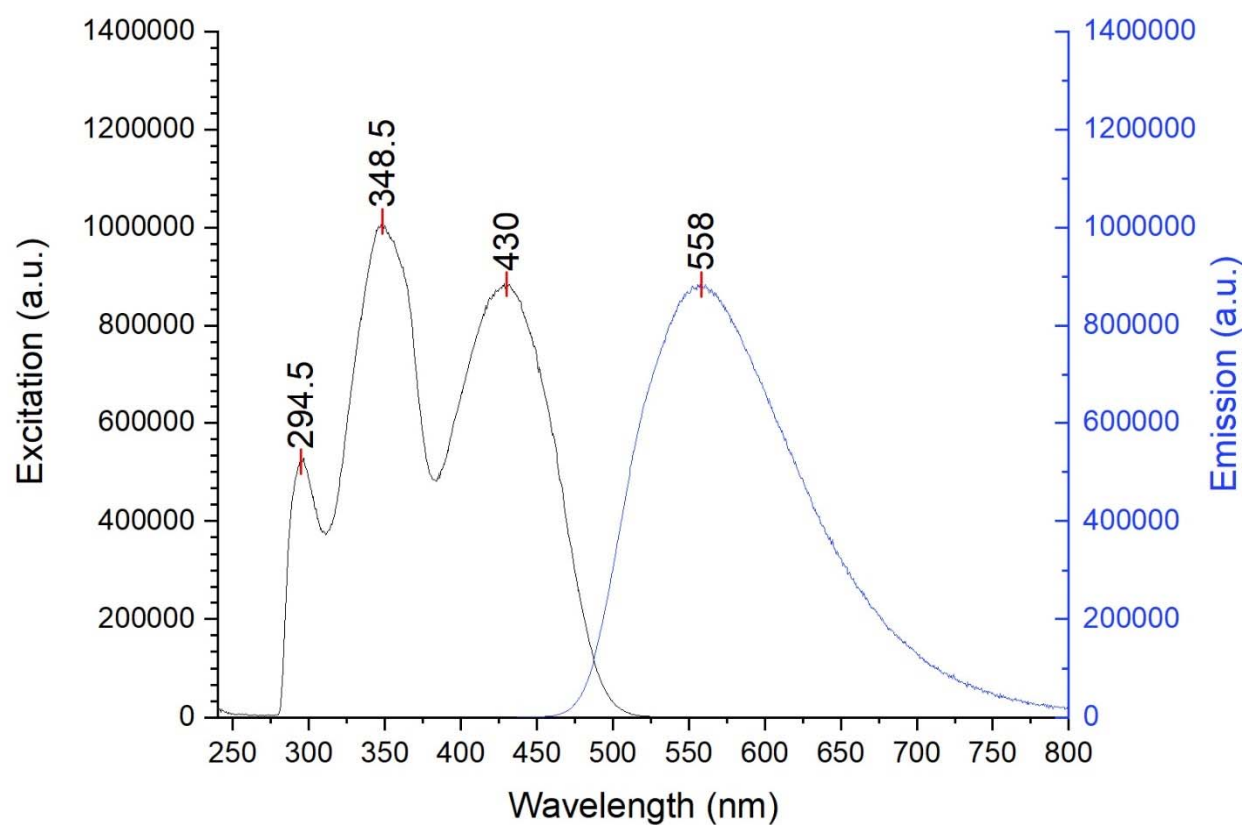


Figure S141 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) spectra of compound **7** and InBr_3 ; 12.5 μM sample.

6.1.35. $\text{In}(\text{C}_6\text{F}_5)_3$

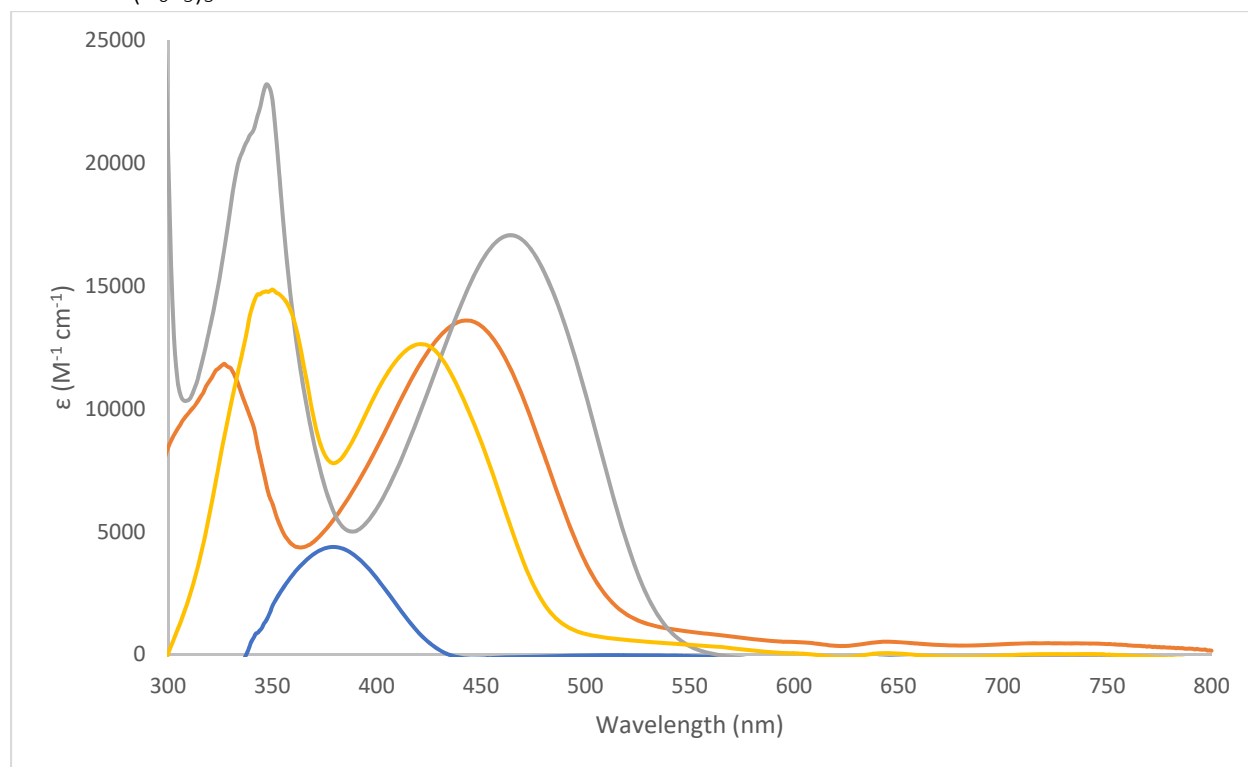


Figure S142 Stacked UV-Vis absorption spectra of **1** (blue), **2** (orange), **3** (grey), and **7** (yellow) with $\text{In}(\text{C}_6\text{F}_5)_3$ (10 eq.); 12.5 μM samples.

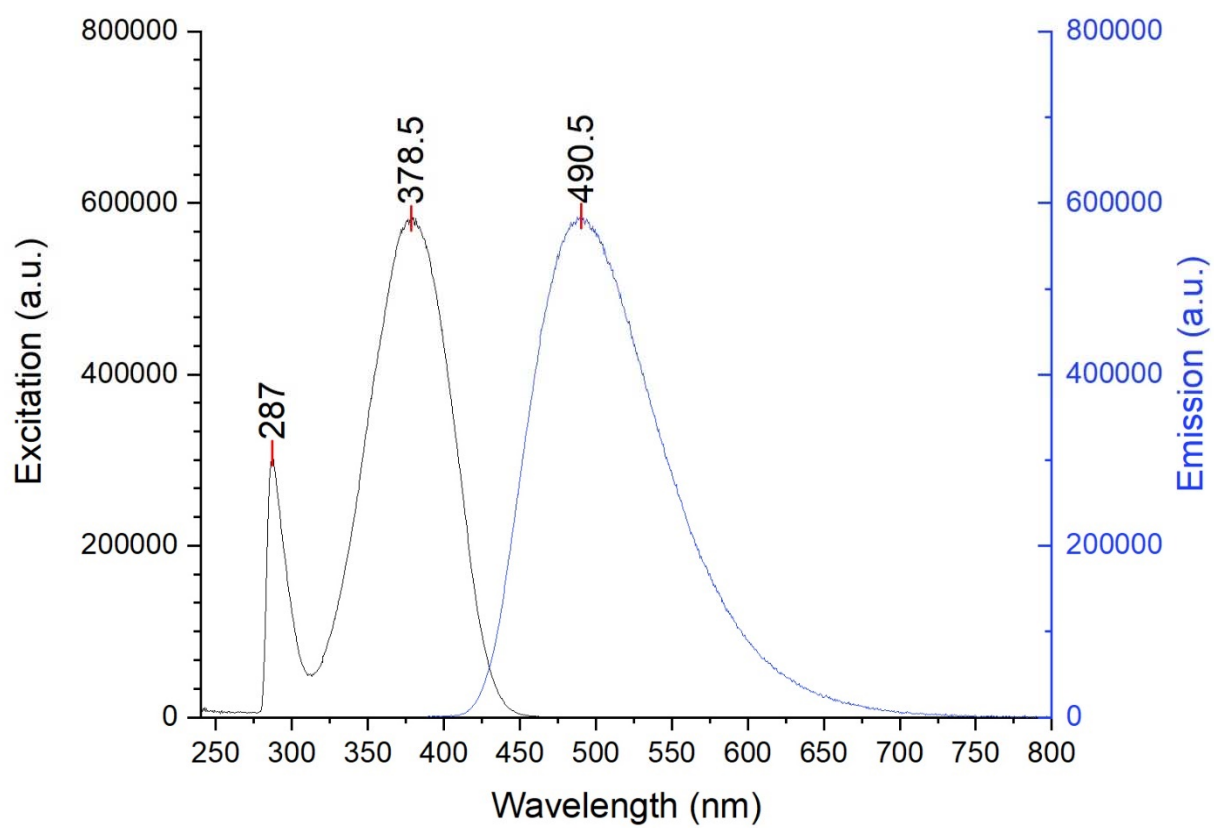


Figure S143 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) spectra of compound **1** and $\text{In}(\text{C}_6\text{F}_5)_3$; 12.5 μM sample.

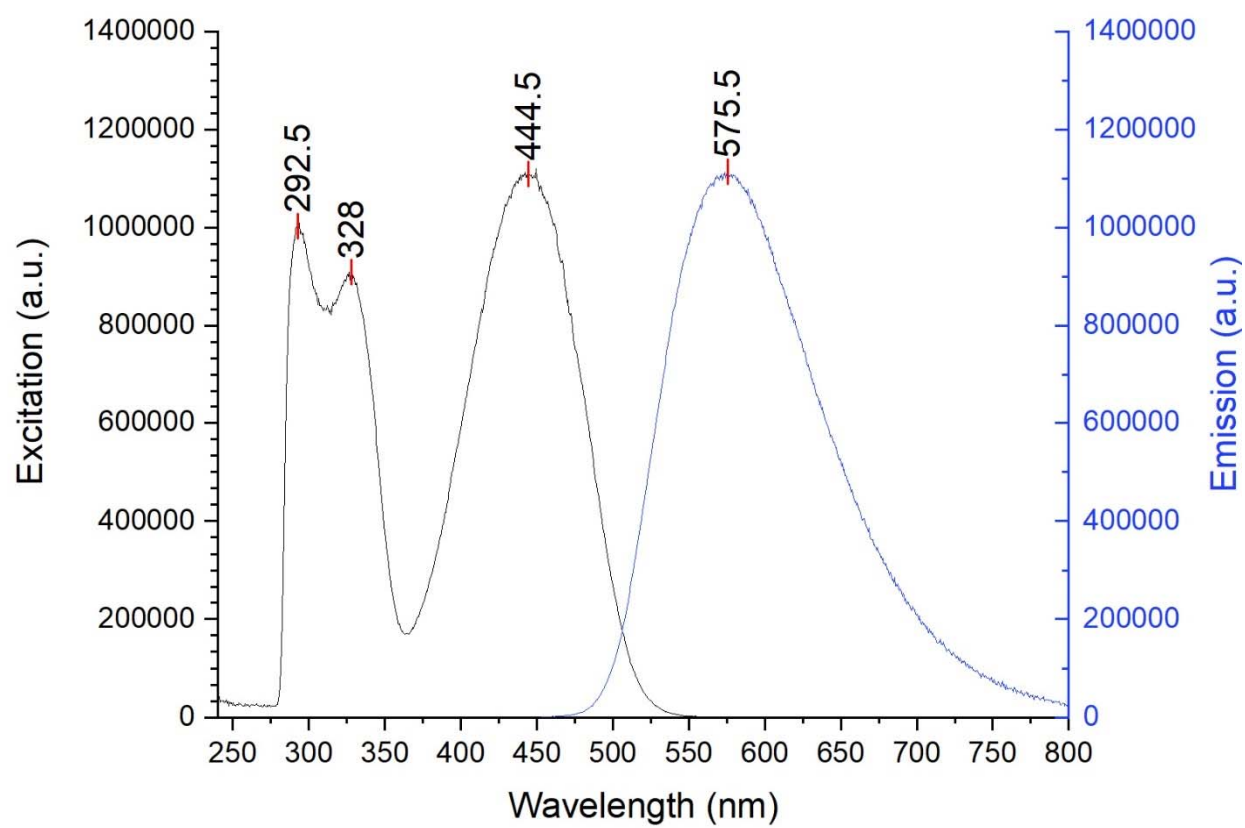


Figure S144 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) spectra of compound **2** and $\text{In}(\text{C}_6\text{F}_5)_3$; 12.5 μM sample.

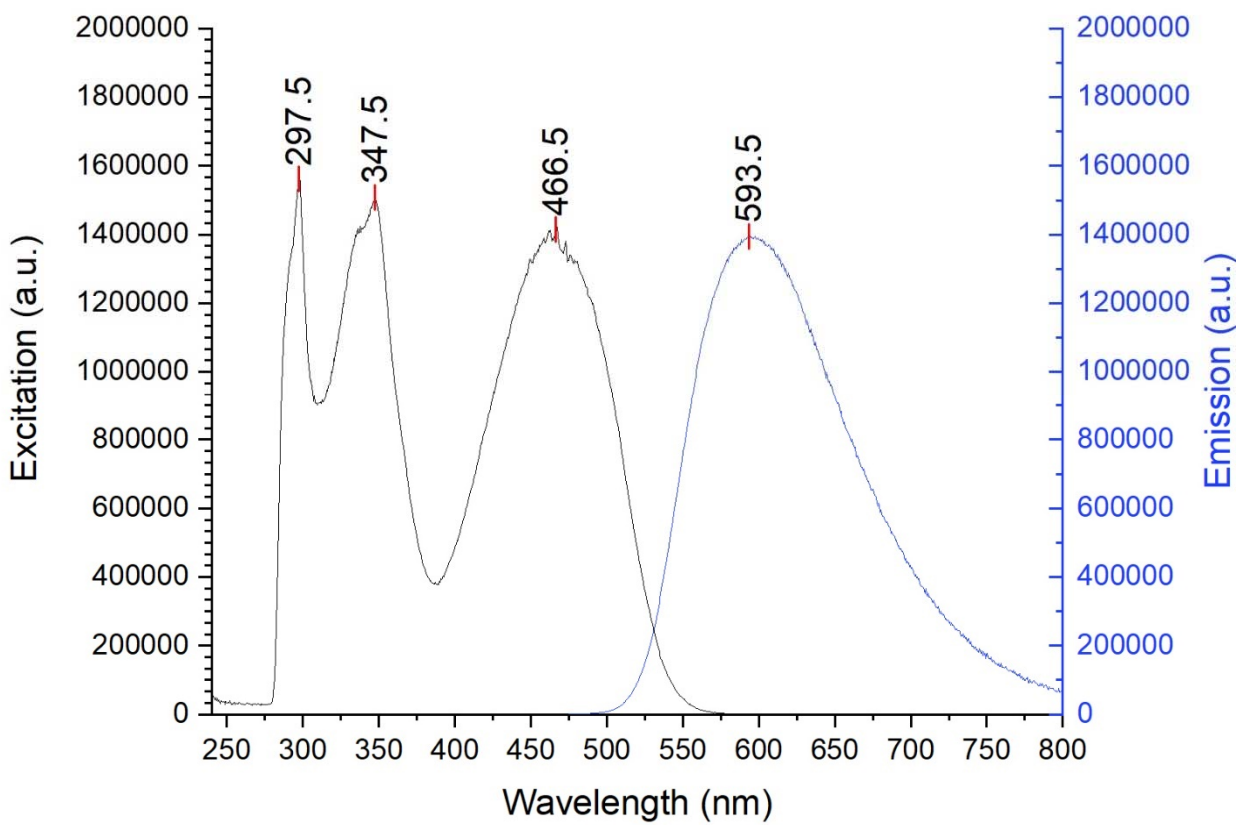


Figure S145 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) spectra of compound **3** and $\text{In}(\text{C}_6\text{F}_5)_3$; 12.5 μM sample.

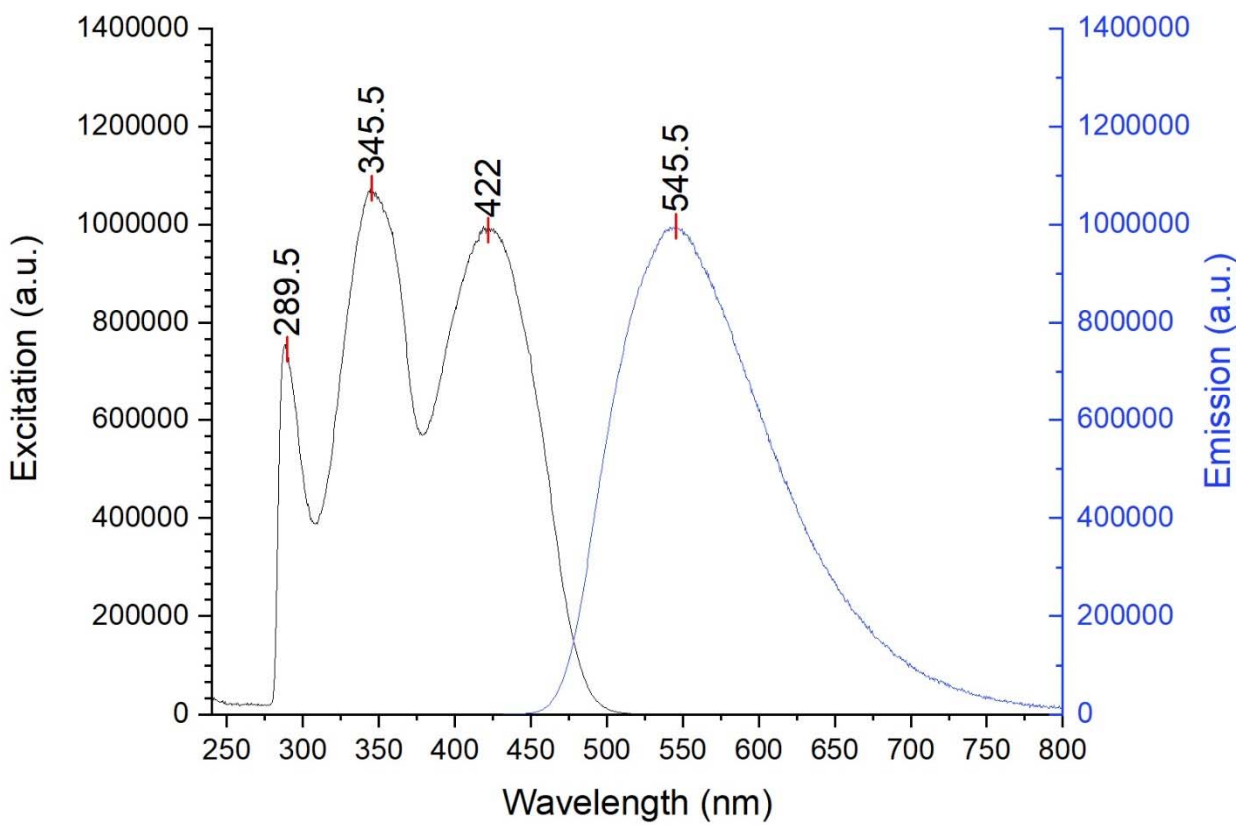


Figure S146 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) spectra of compound **7** and $\text{In}(\text{C}_6\text{F}_5)_3$; 12.5 μM sample.

6.1.36. $\text{In}(\text{OTf})_3$

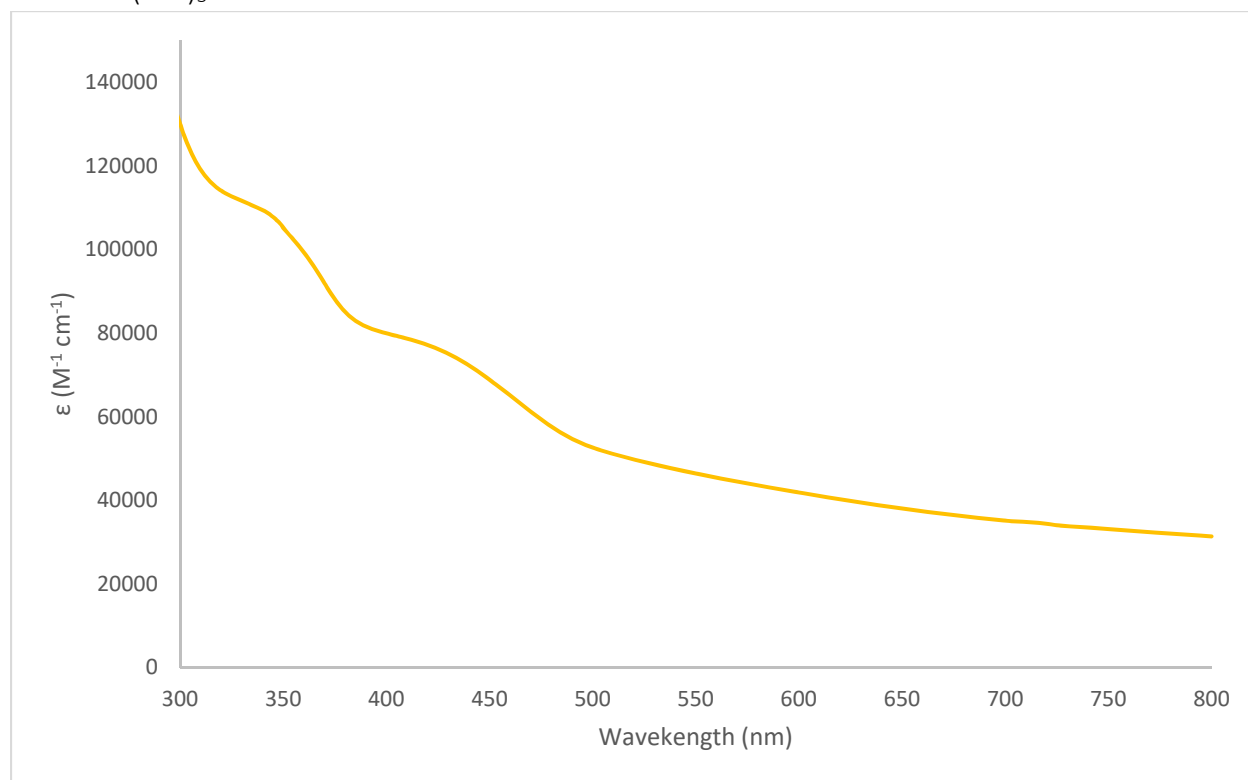


Figure S147 Stacked UV-Vis absorption spectra of **7** (yellow) with $\text{In}(\text{OTf})_3$ (excess); 12.5 μM samples.

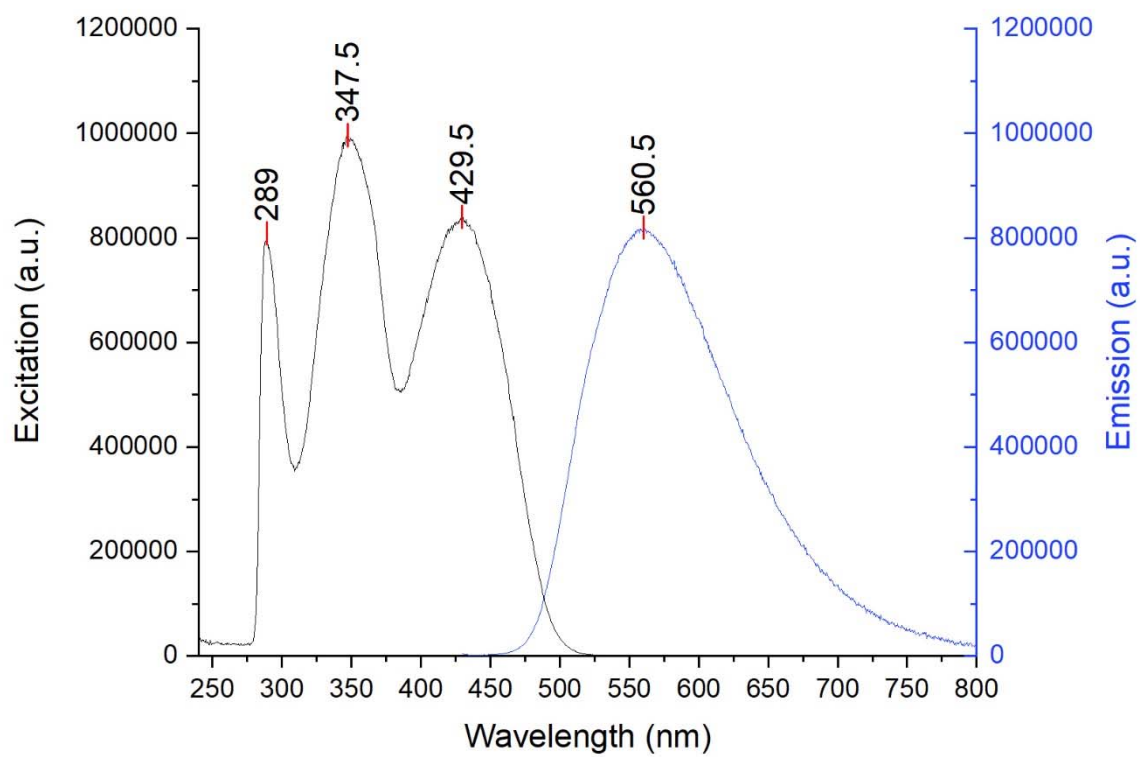


Figure S148 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) spectra of compound **7** and $\text{In}(\text{OTf})_3$; 12.5 μM sample.

6.1.37. $[\text{iPrIBBN}][\text{B}(\text{C}_6\text{F}_5)_4]$

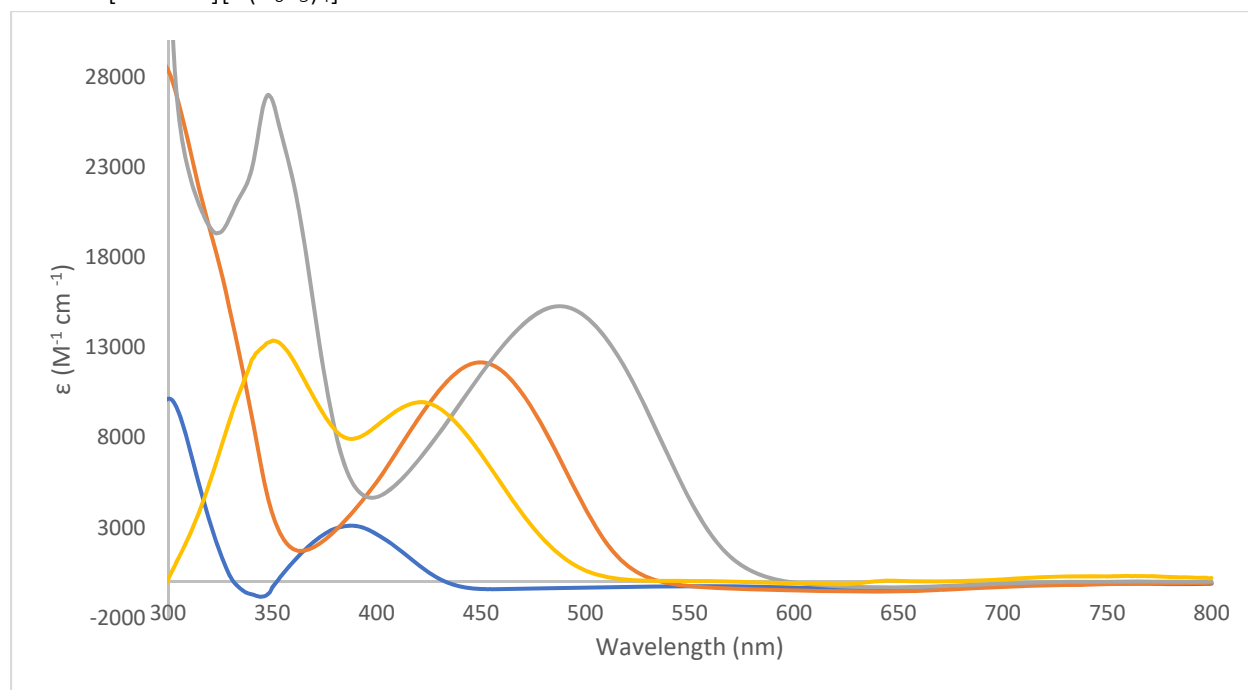


Figure S149 Stacked UV-Vis absorption spectra of **1** (blue, 5 eq), **2** (orange, 5 eq), **3** (grey, 5 eq), and **7** (yellow, 10 eq) with $[\text{iPrIBBN}][\text{B}(\text{C}_6\text{F}_5)_4]$; 12.5 μM samples.

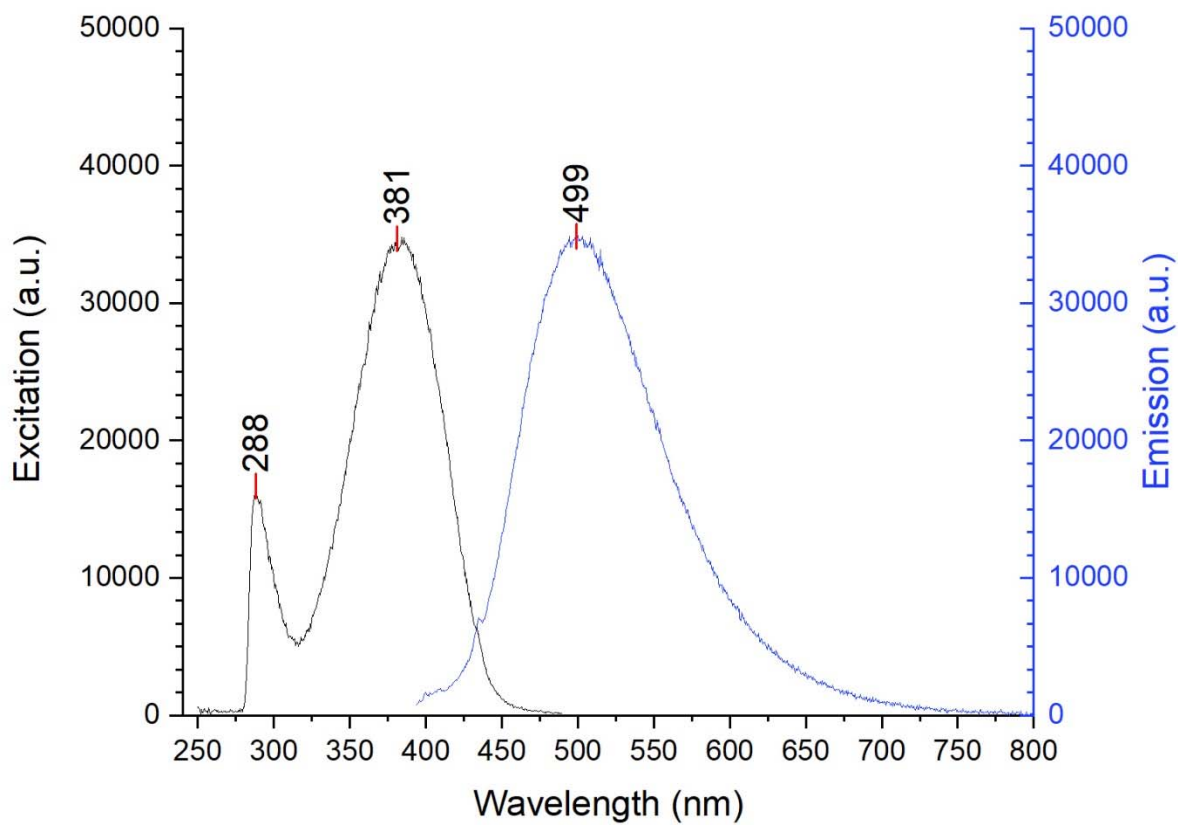


Figure S150 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) spectra of compound **1** and [iPrIBBN][B(C₆F₅)₄]; 12.5 μM sample.

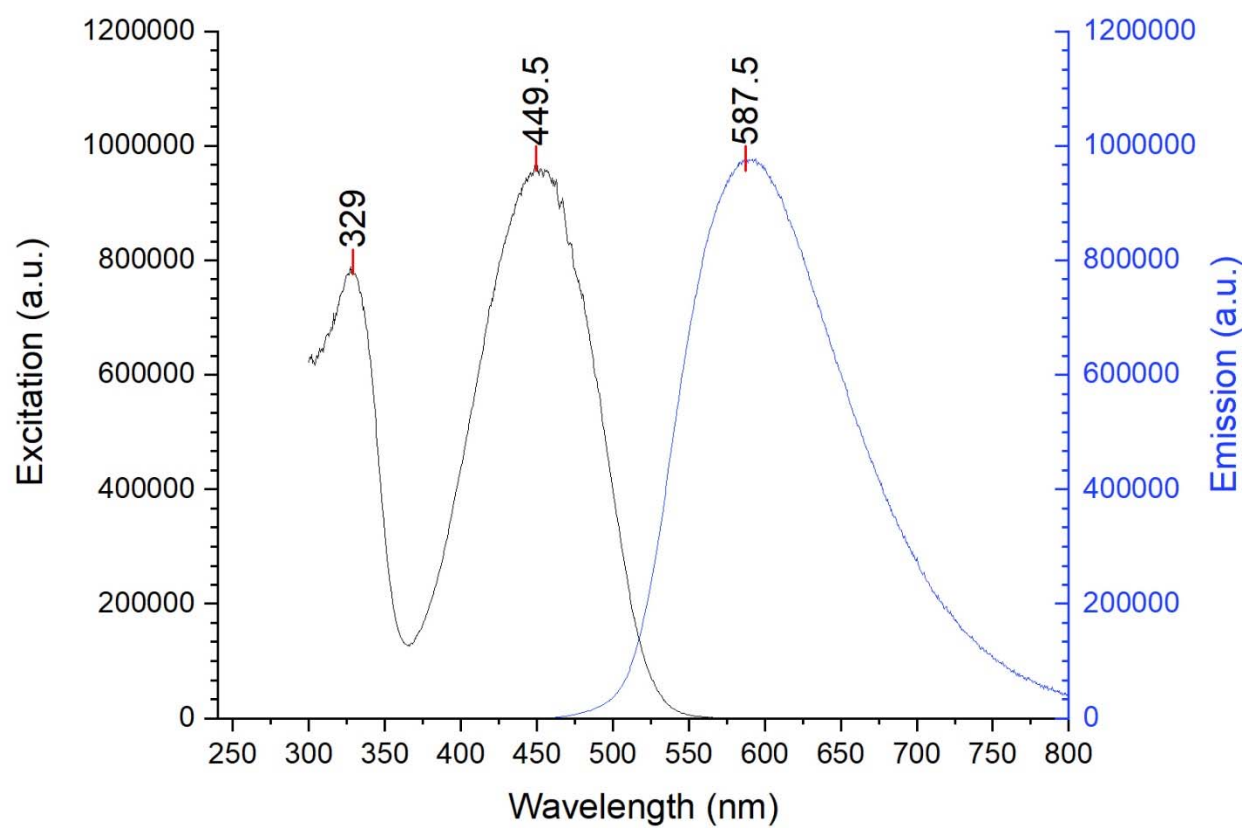


Figure S151 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) spectra of compound **2** and [iPrIBBN][B(C₆F₅)₄]; 12.5 μ M sample.

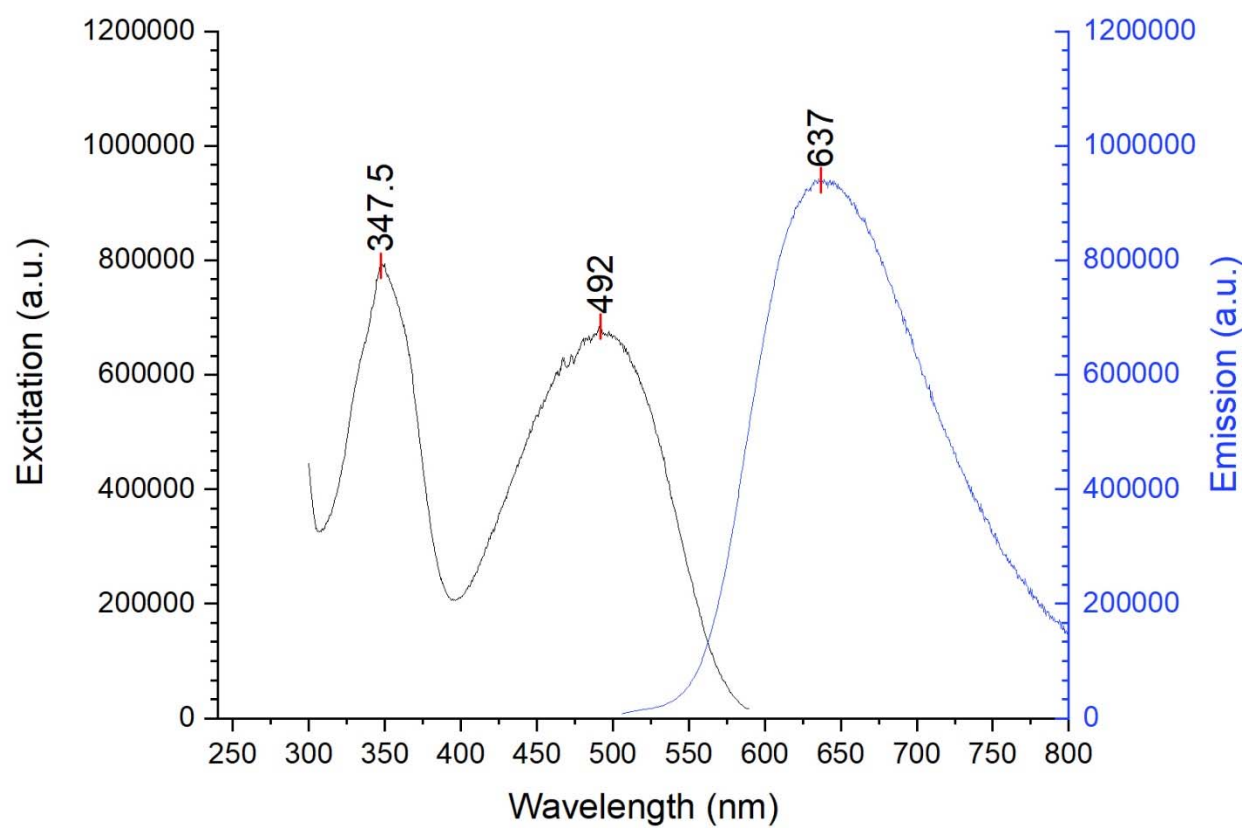


Figure S152 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) spectra of compound **3** and $[iPrIBBN][B(C_6F_5)_4]$; 12.5 μM sample.

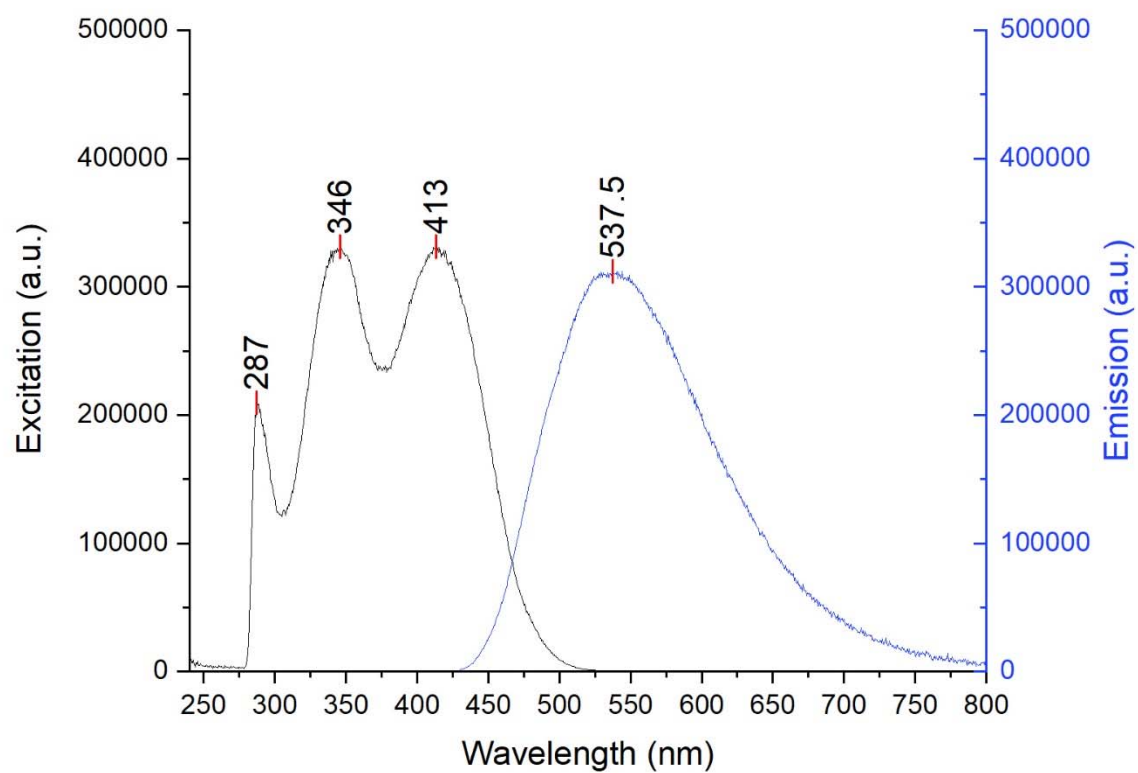


Figure S153 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) spectra of compound **7** and $[iPrIBBN][B(C_6F_5)_4]$; 12.5 μM sample.

6.1.38. $[(\text{SIMes})\text{PFPh}_2][\text{B}(\text{C}_6\text{F}_5)_4]_2$

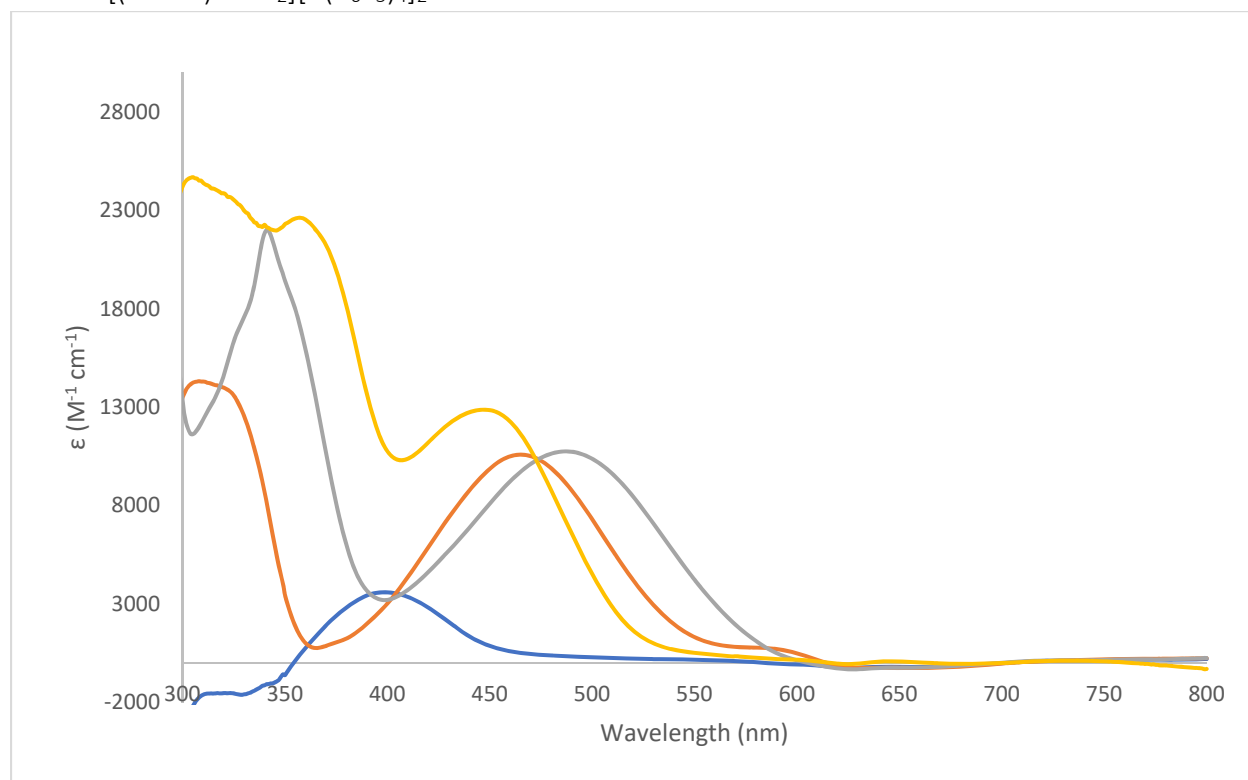


Figure S154 Stacked UV-Vis absorption spectra of **1** (blue, 5 eq), **2** (orange, 5 eq), **3** (grey, 5 eq), and **7** (yellow, 10 eq) with $[(\text{SIMes})\text{PFPh}_2][\text{B}(\text{C}_6\text{F}_5)_4]_2$; 12.5 μM samples.

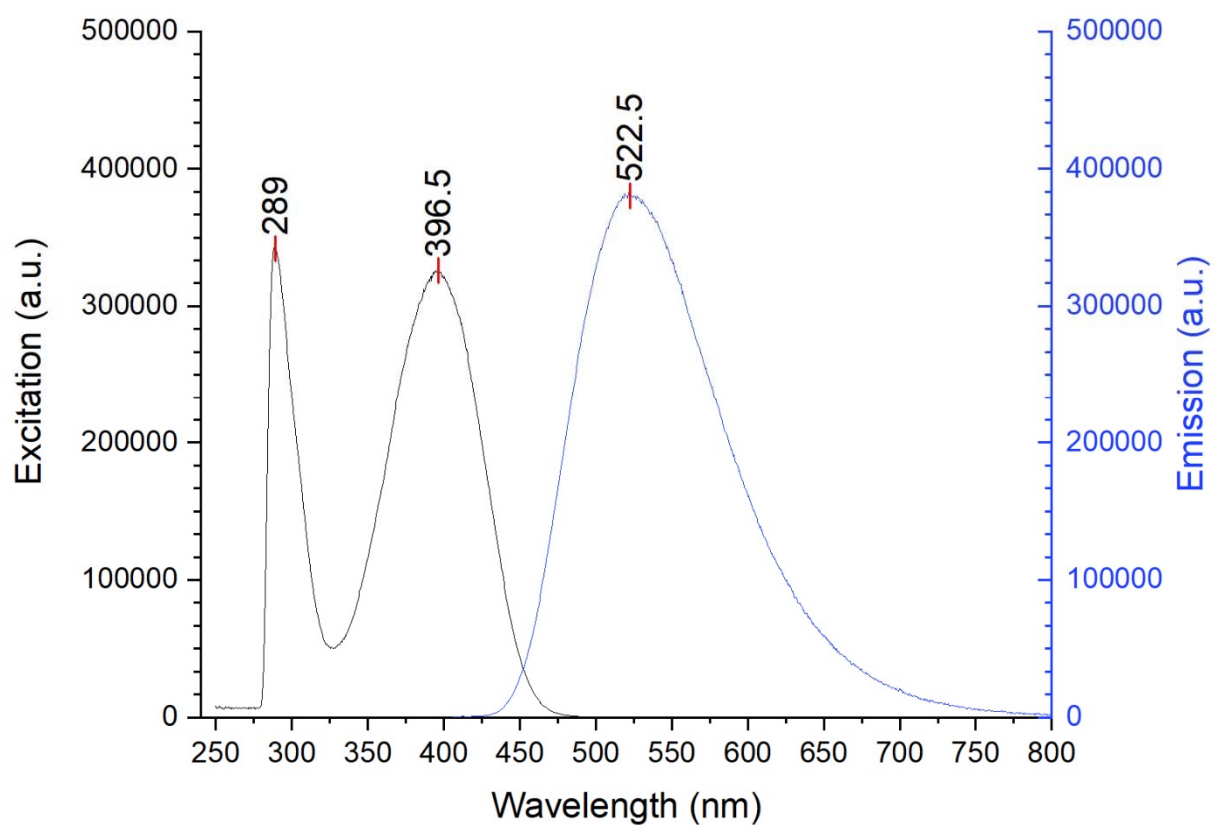


Figure S155 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) spectra of compound **1** and $[(\text{SIMes})\text{PPh}_2][\text{B}(\text{C}_6\text{F}_5)_4]_2$; 12.5 μM sample.

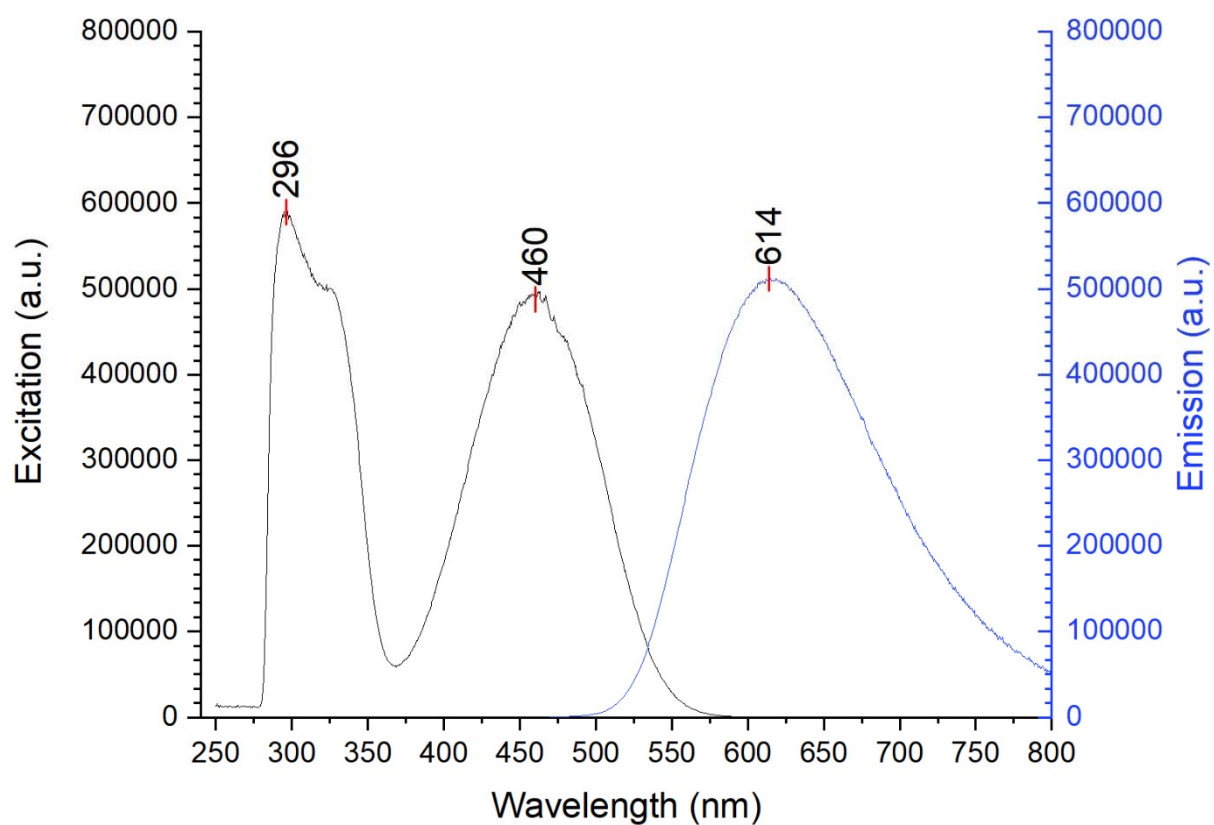


Figure S156 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) spectra of compound **2** and $[(\text{SIMes})\text{PFPh}_2][\text{B}(\text{C}_6\text{F}_5)_4]_2$; 12.5 μM sample.

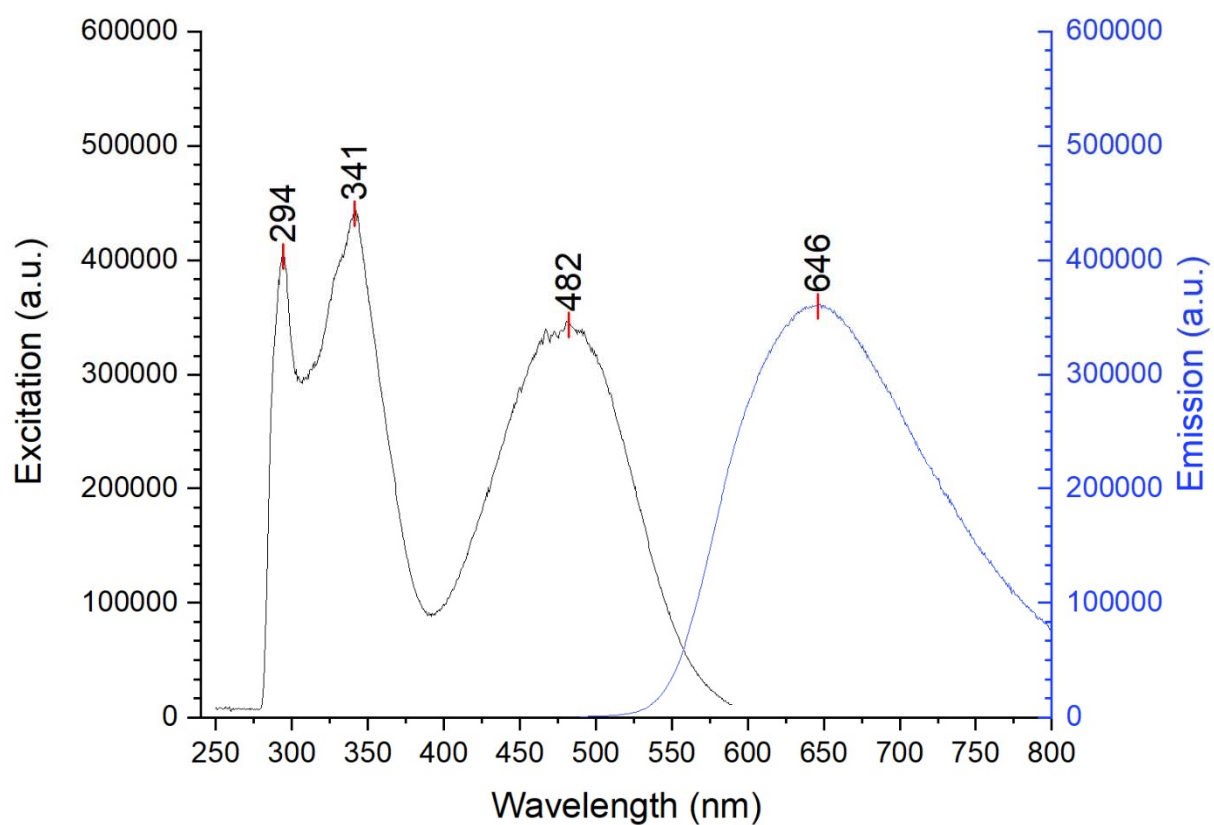


Figure S157 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) spectra of compound **3** and $[(\text{SIMes})\text{PFPh}_2][\text{B}(\text{C}_6\text{F}_5)_4]_2$; 12.5 μM sample.

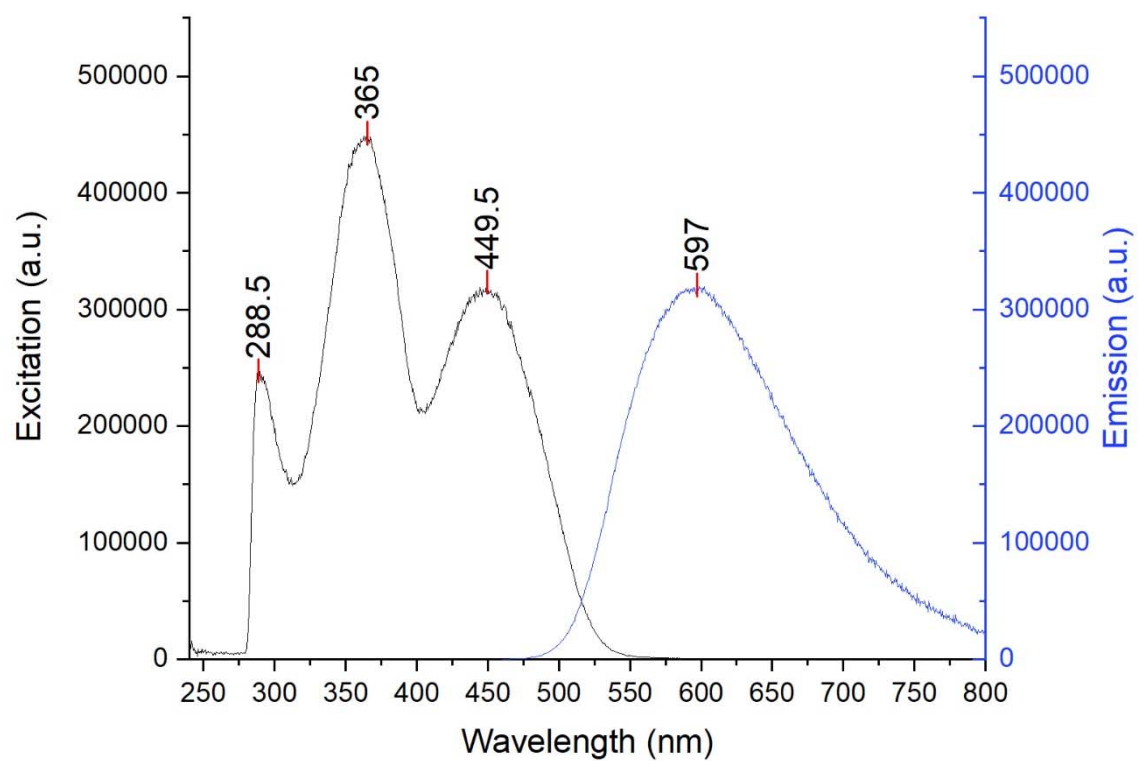


Figure S158 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) spectra of compound **7** and $[(\text{SIMes})\text{PFPh}_2][\text{B}(\text{C}_6\text{F}_5)_4]_2$; 12.5 μM sample.

6.1.39. MeOTf

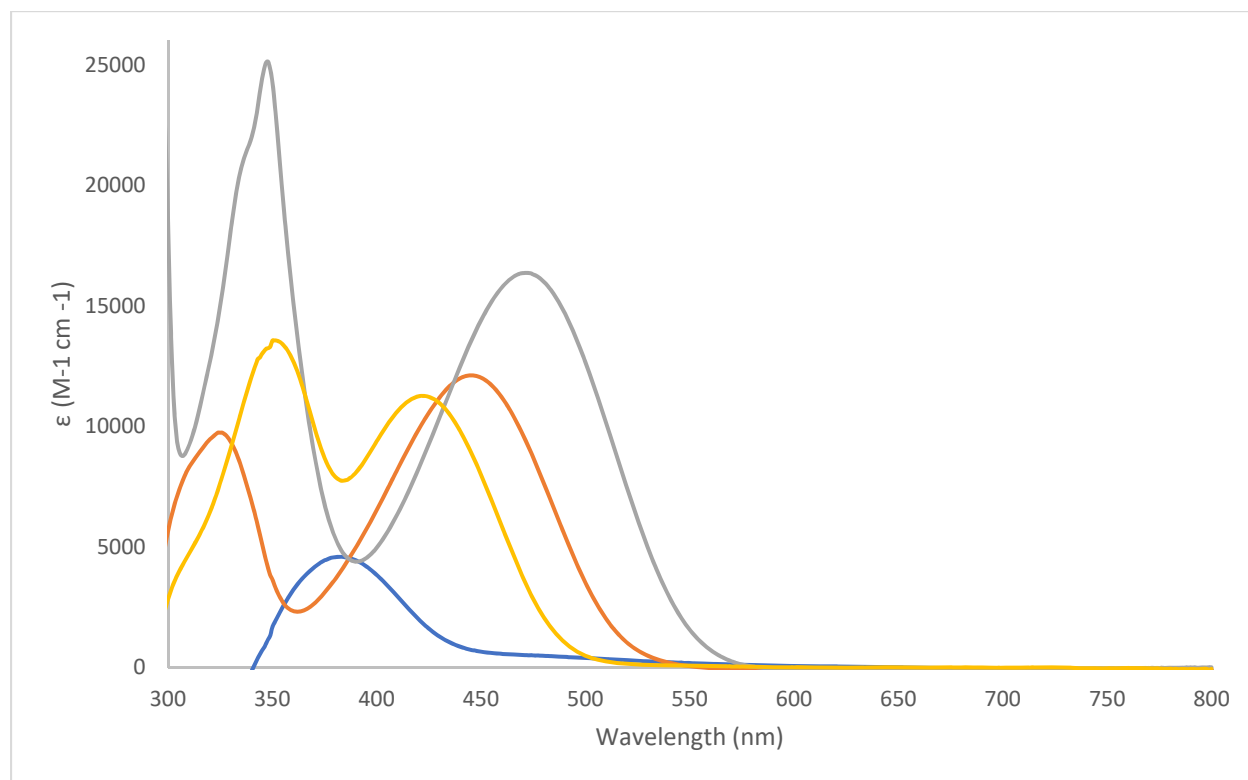


Figure S159 Stacked UV-Vis absorption spectra of **1** (blue), **2** (orange), **3** (grey), and **7** (yellow) with **MeOTf** (excess); 12.5 μM samples.

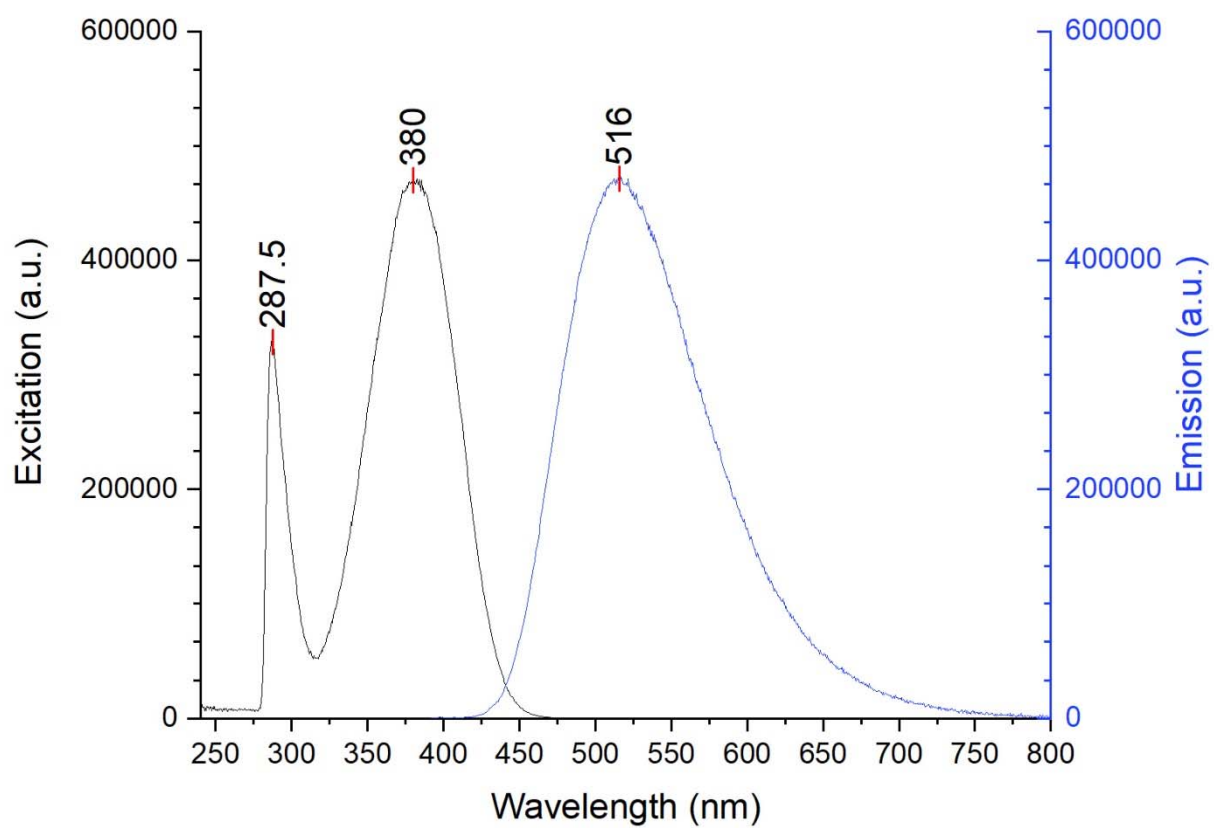


Figure S160 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) spectra of compound **1** and **MeOTf**; 12.5 μ M sample.

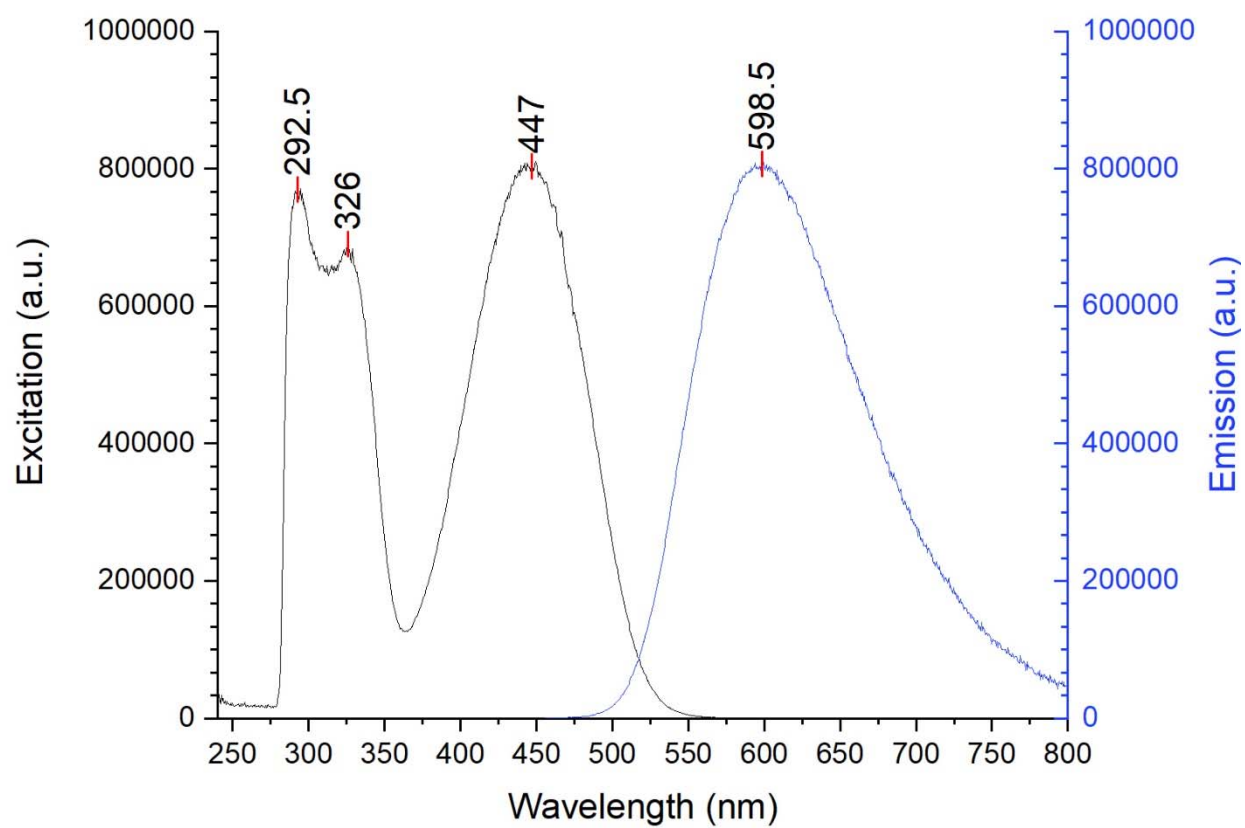


Figure S161 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) spectra of compound **2** and **MeOTf**; 12.5 μ M sample.

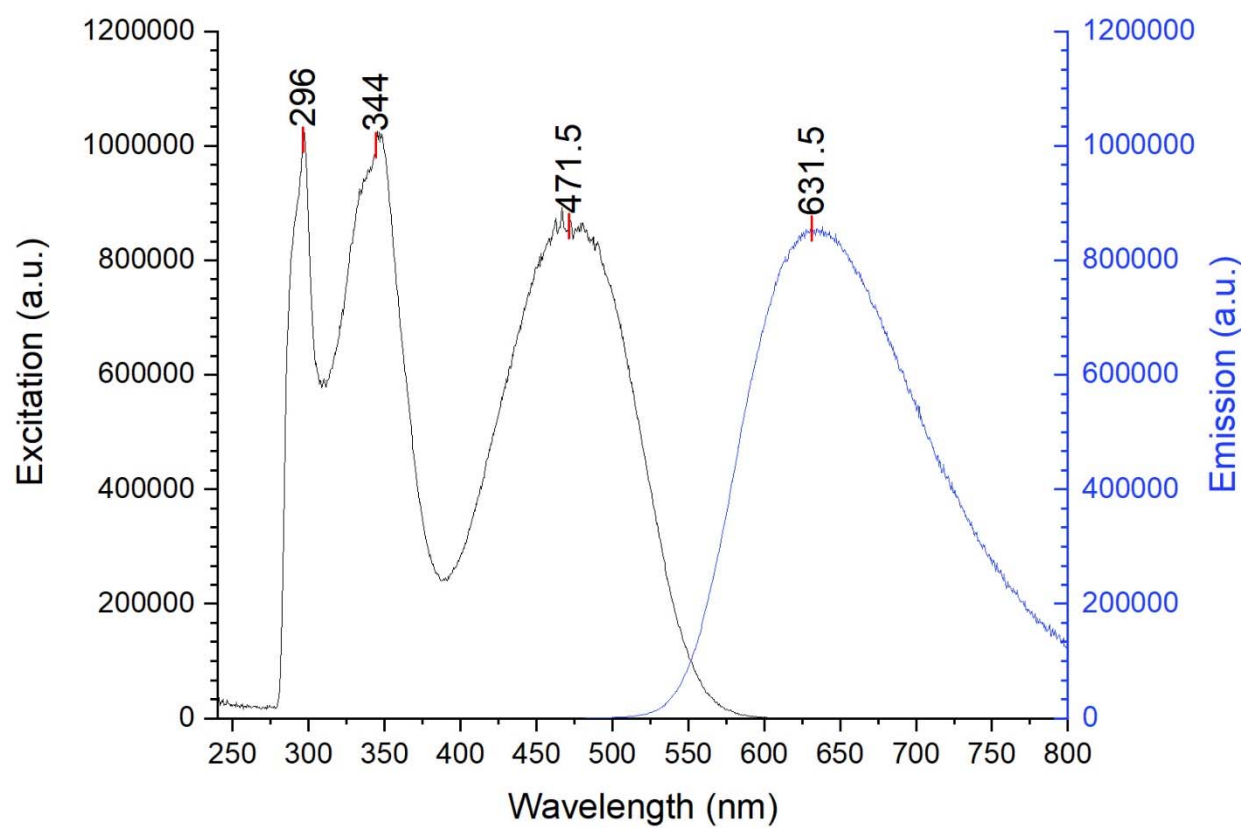


Figure S162 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) spectra of compound **3** and **MeOTf**; 12.5 μM sample.

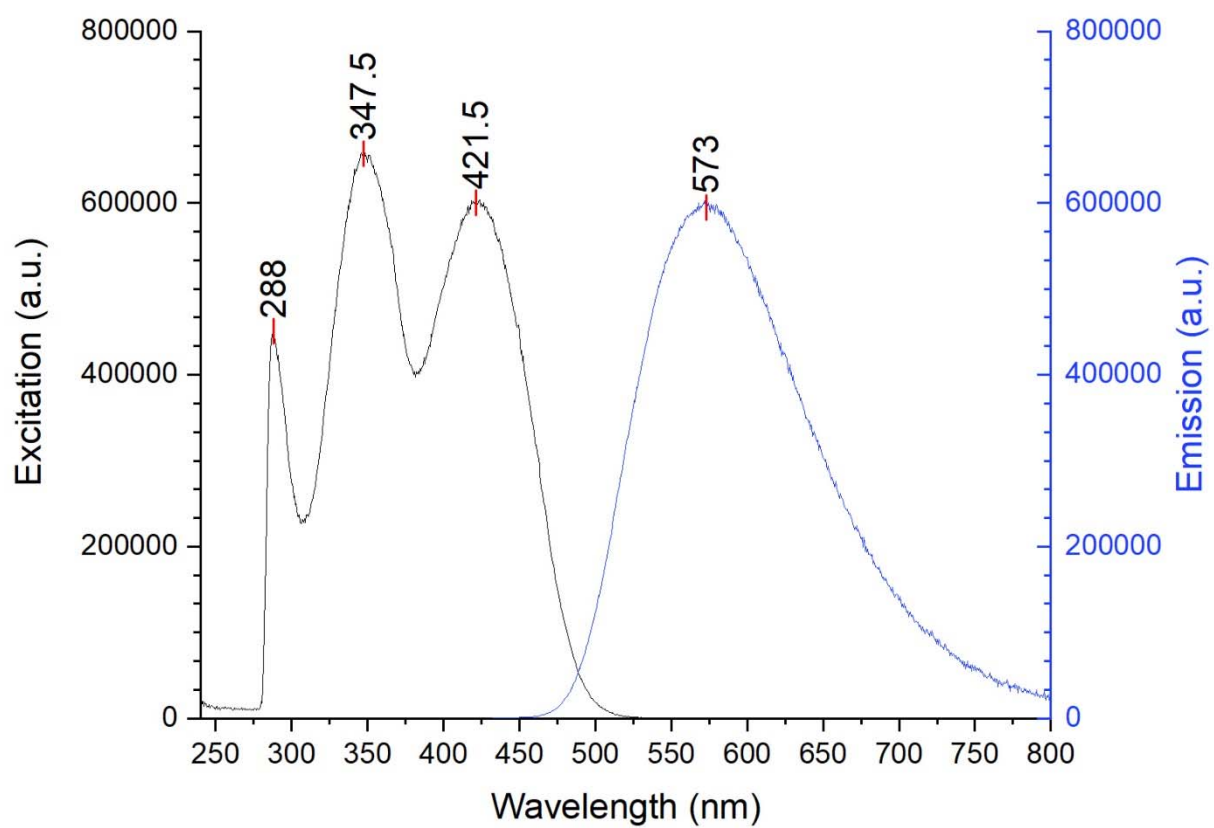


Figure S163 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) spectra of compound **7** and **MeOTf**; 12.5 μ M sample.

6.1.40. Methylaluminoxane (MAO)

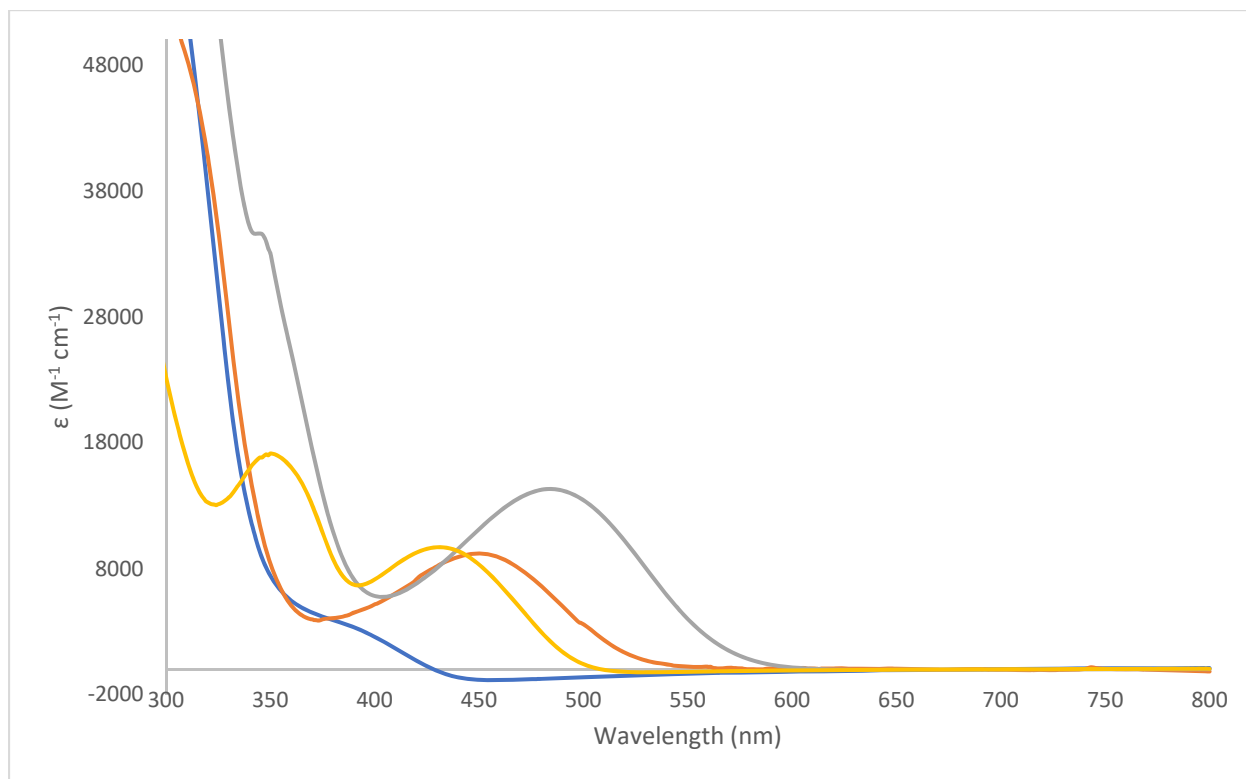


Figure S164 Stacked UV-Vis absorption spectra of **1** (blue), **2** (orange), **3** (grey), and **7** (yellow) with **MMAO** (excess); 12.5 μM samples.

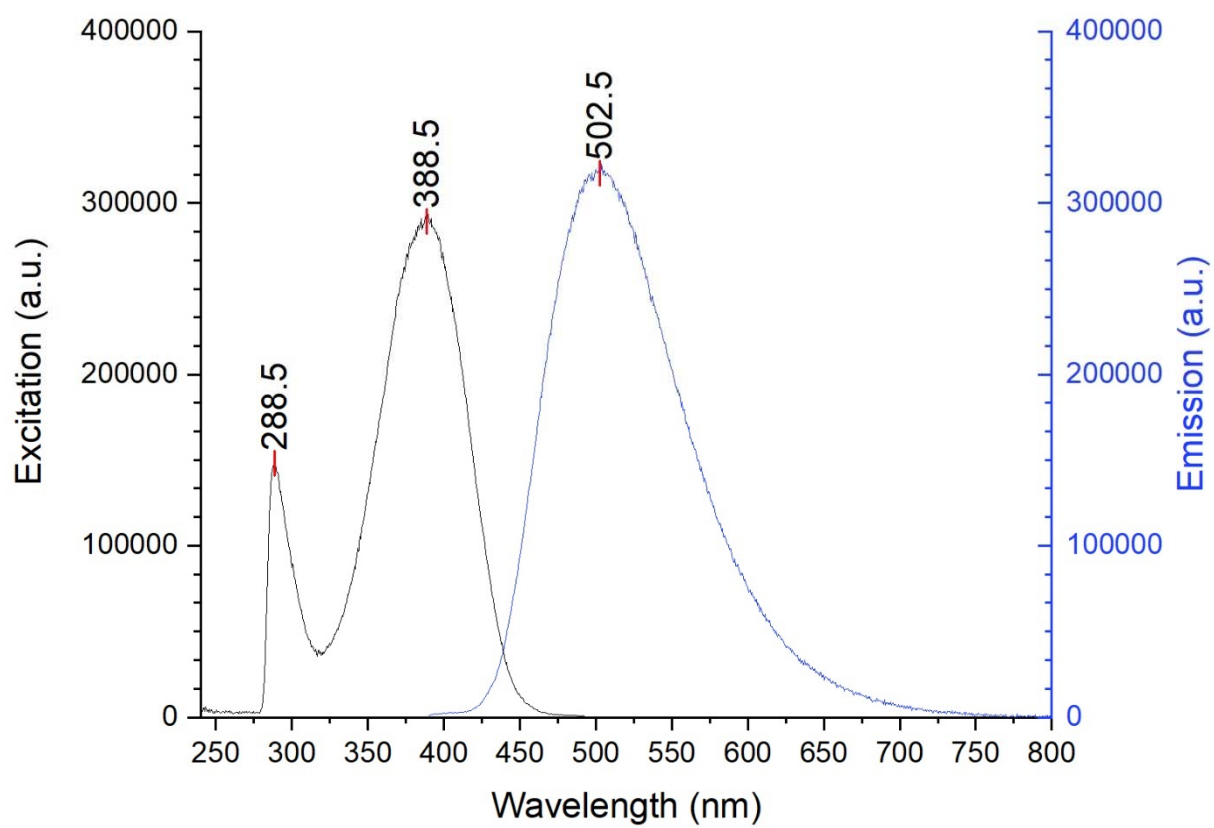


Figure S165 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) spectra of compound **1** and **MMAO**; 12.5 μ M sample.

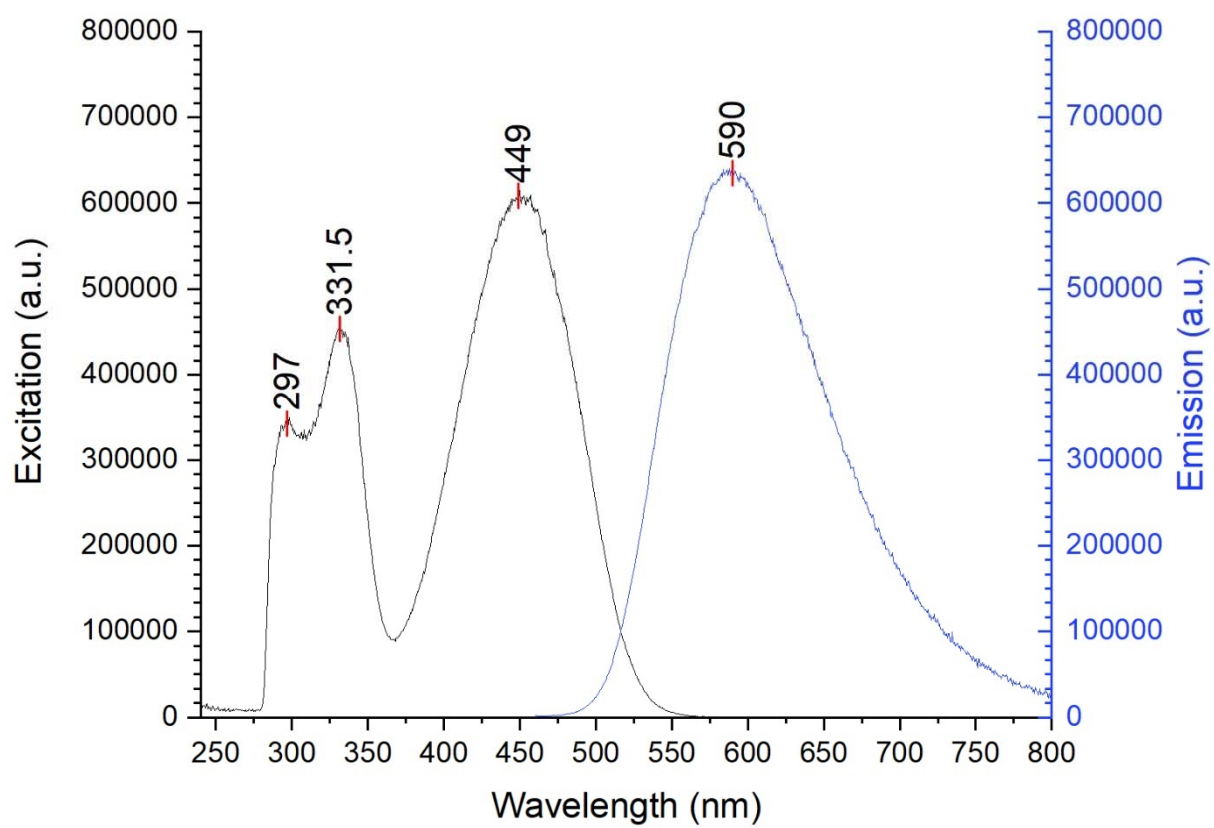


Figure S166 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) spectra of compound **2** and **MMAO**; 12.5 μ M sample.

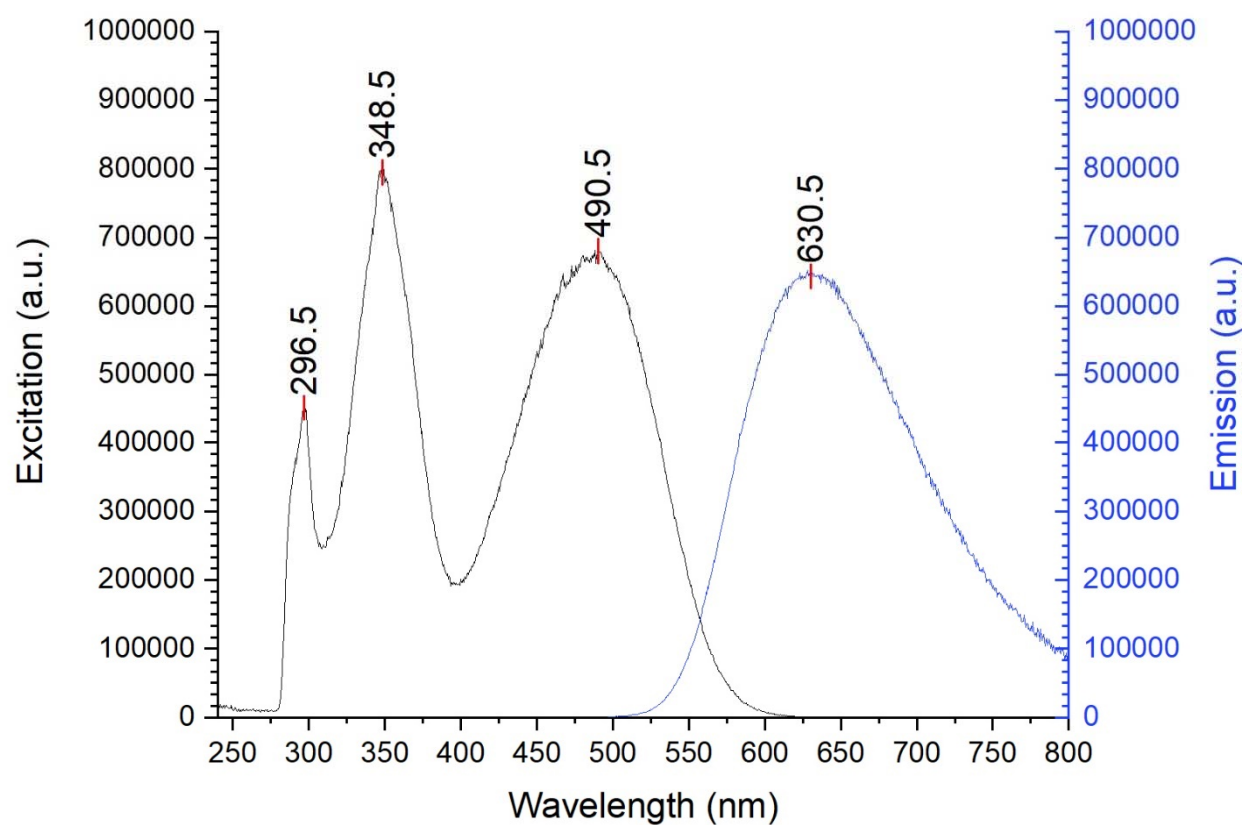


Figure S167 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) spectra of compound **3** and **MMAO**; 12.5 μ M sample.

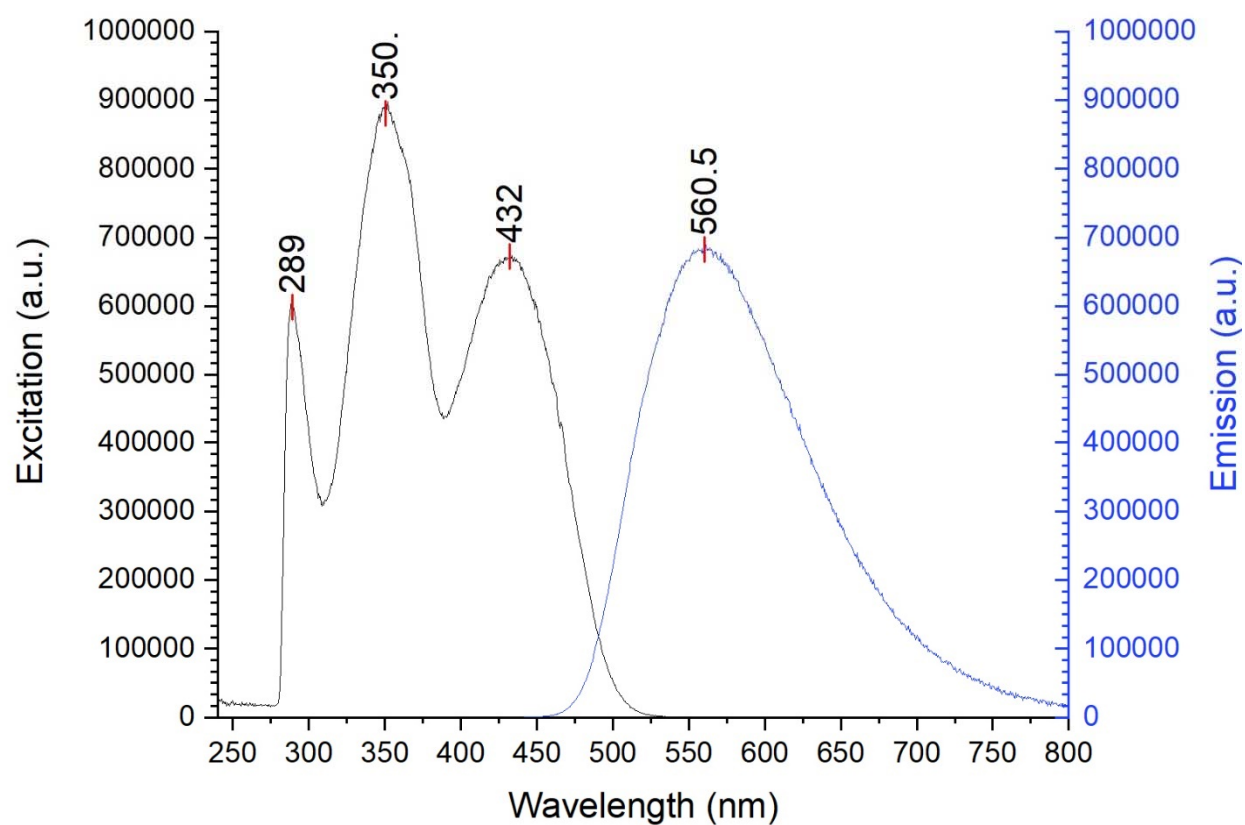


Figure S168 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) spectra of compound **7** and **MMAO**; 12.5 μ M sample.

6.1.41. $[(m\text{-XyF}_6)_3\text{PF}][\text{B}(\text{C}_6\text{F}_5)_4]$

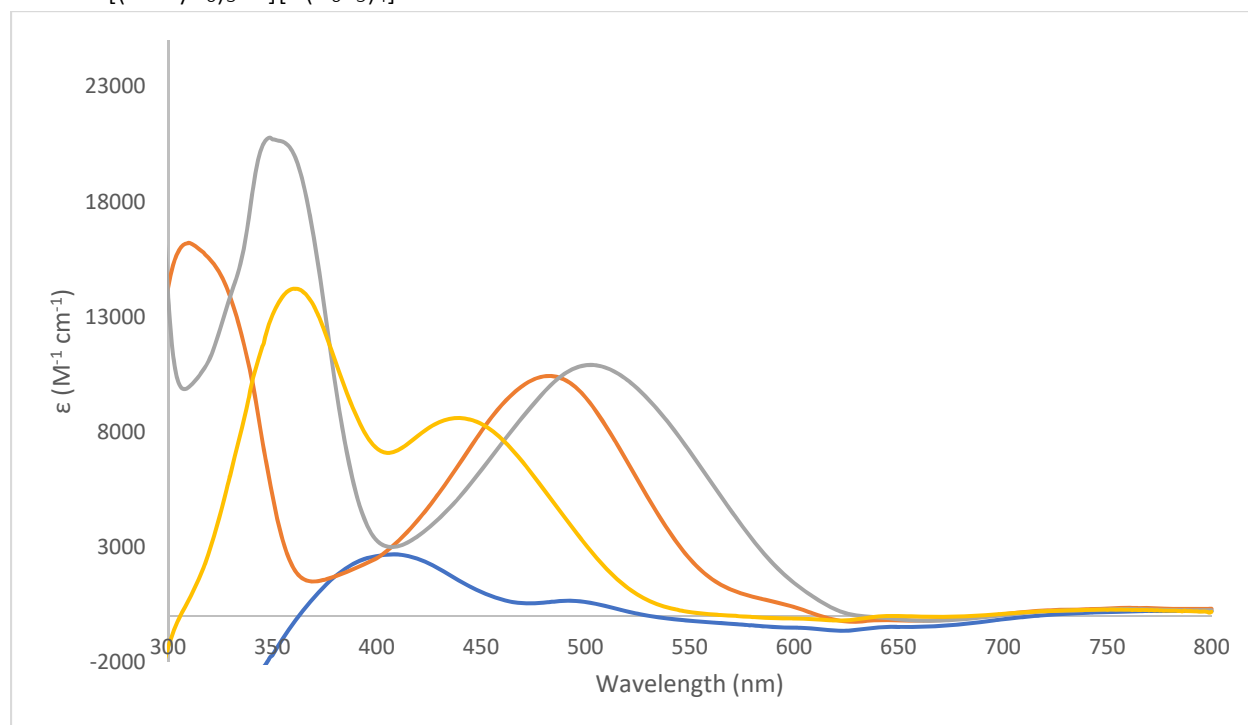


Figure S169 Stacked UV-Vis absorption spectra of **1** (blue, 5 eq), **2** (orange, 5 eq), **3** (grey, 5 eq), and **7** (yellow, 10 eq) with $[(m\text{-XyF}_6)_3\text{PF}][\text{B}(\text{C}_6\text{F}_5)_4]$; 12.5 μM samples.

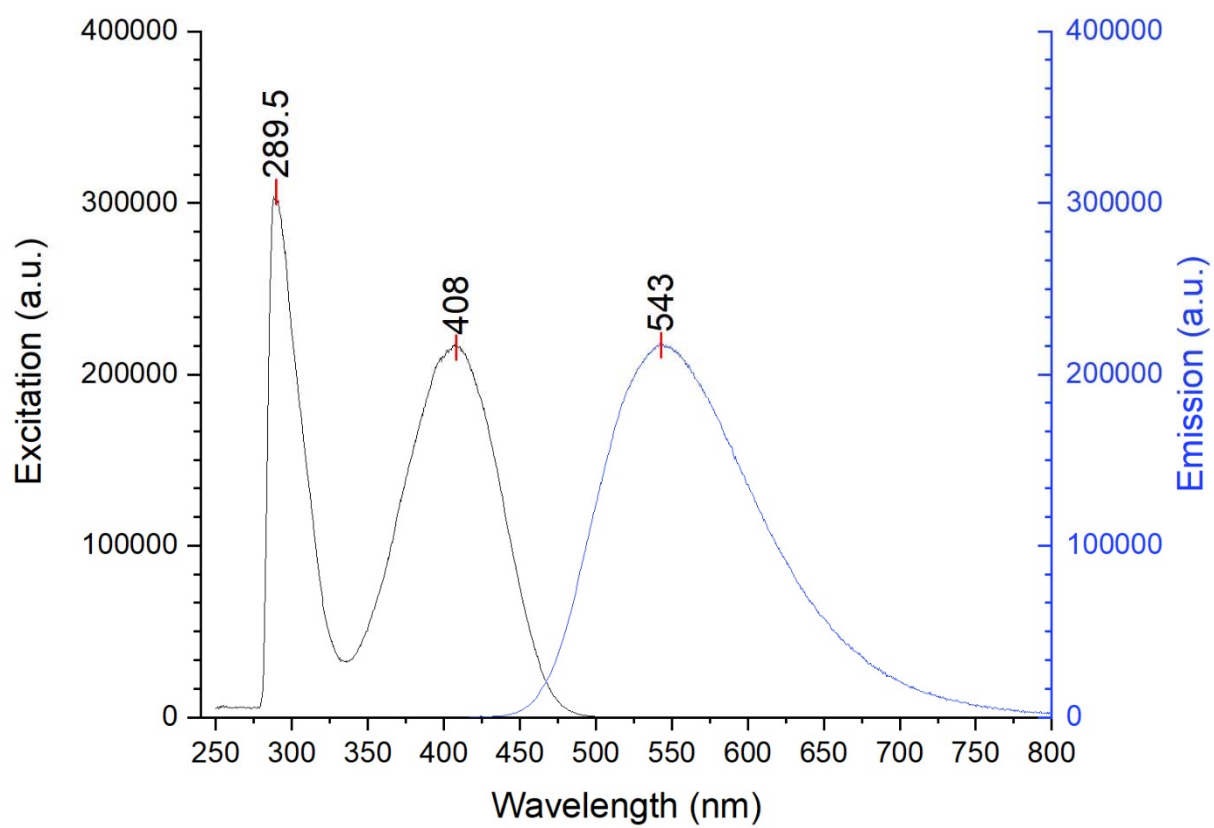


Figure S170 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) spectra of compound **1** and $[(m\text{-XyF}_6)_3\text{PF}][\text{B}(\text{C}_6\text{F}_5)_4]$; 12.5 μM sample.

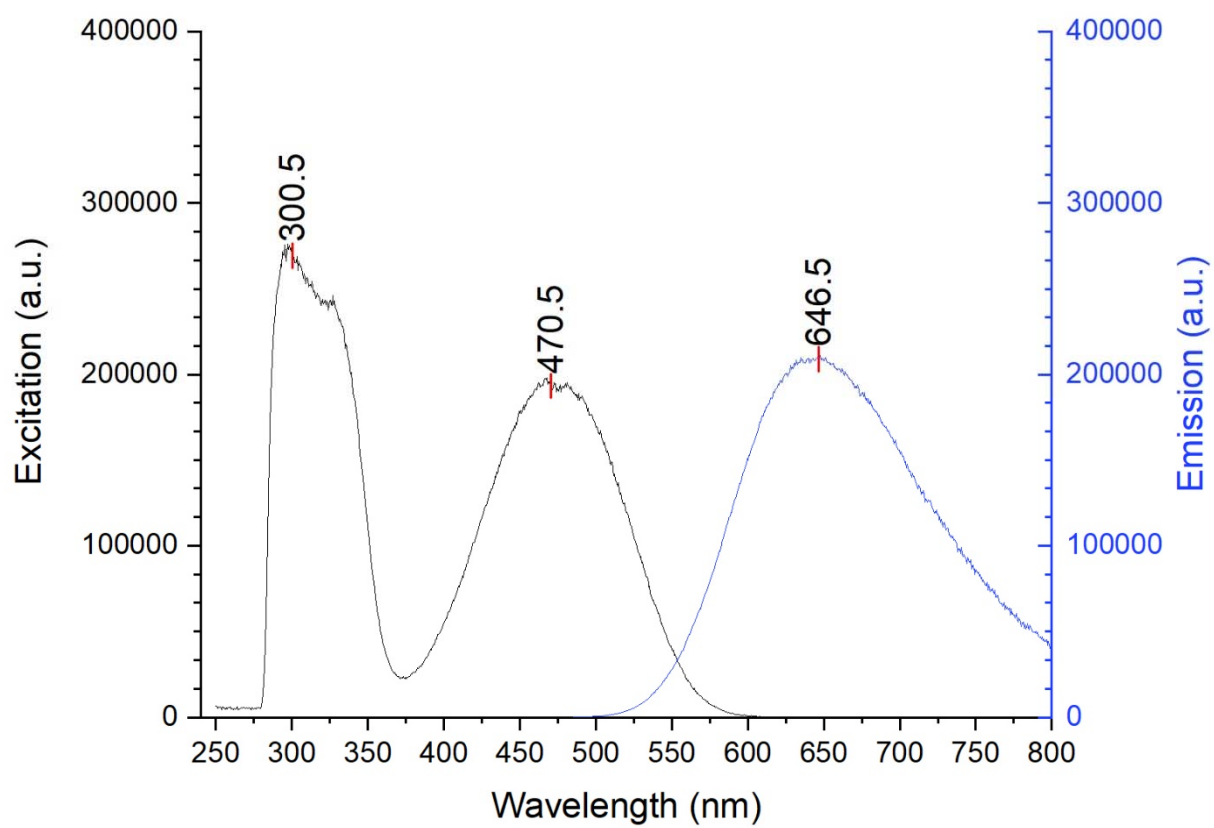


Figure S171 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) spectra of compound **2** and $[(m\text{-XyF}_6)_3\text{PF}][\text{B}(\text{C}_6\text{F}_5)_4]$; 12.5 μM sample.

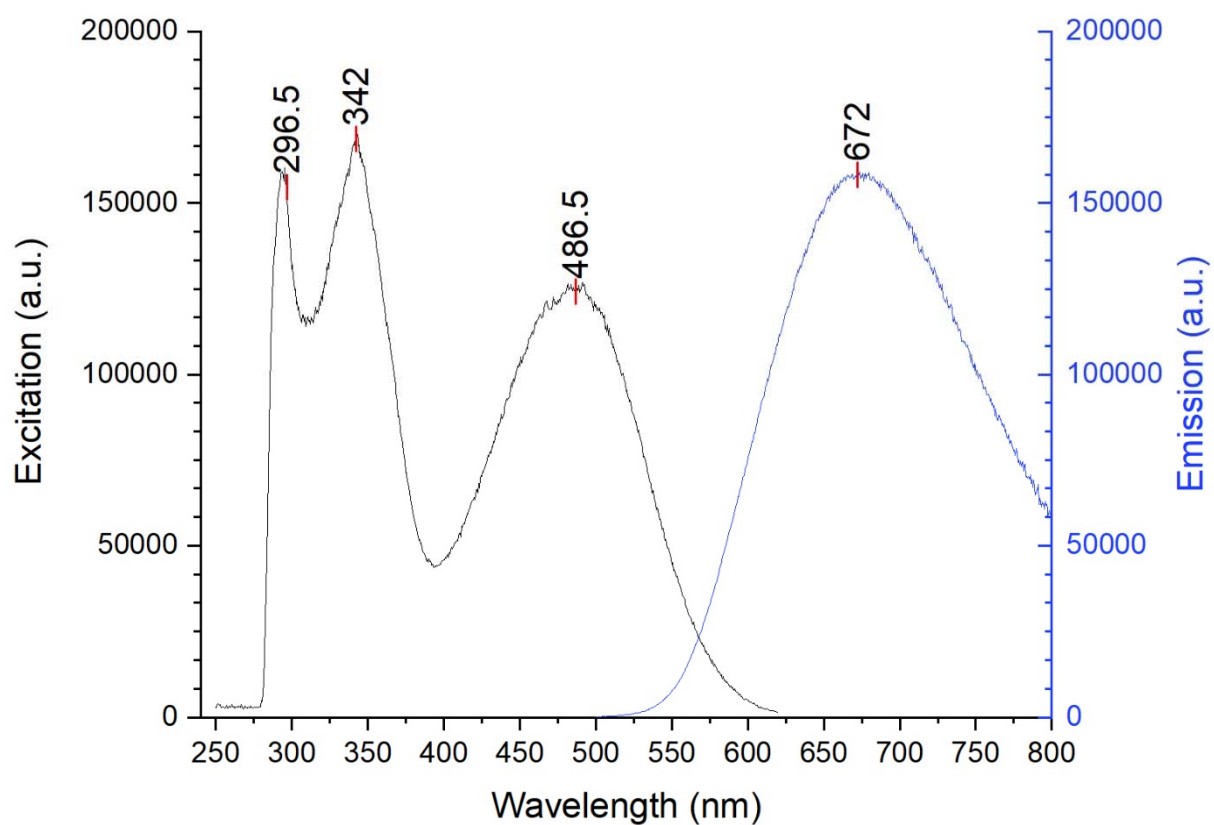


Figure S172 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) spectra of compound **3** and $[(m\text{-XyF}_6)_3\text{PF}][\text{B}(\text{C}_6\text{F}_5)_4]$; 12.5 μM sample.

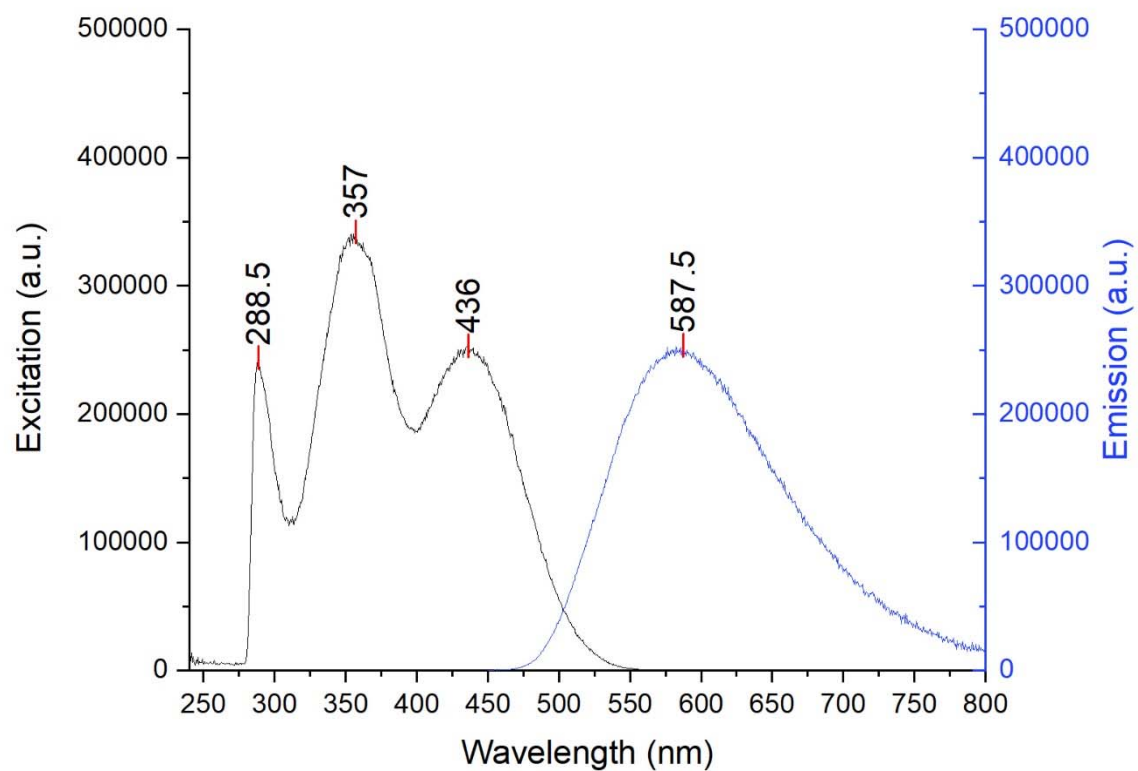


Figure S173 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) spectra of compound **7** and $[(m\text{-XyF}_6)_3\text{PF}][\text{B}(\text{C}_6\text{F}_5)_4]$; 12.5 μM sample.

6.1.42. Ph₂NBMes₂

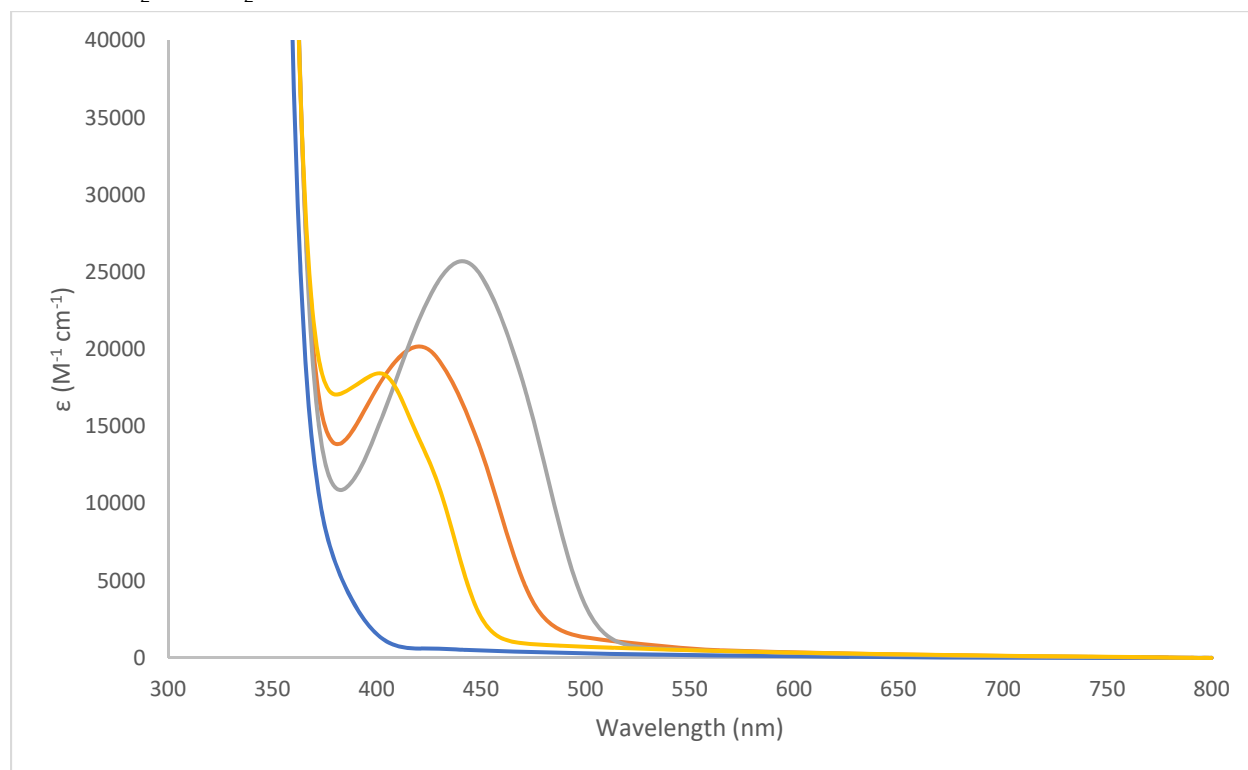


Figure S174 Stacked UV-Vis absorption spectra of **1** (blue), **2** (orange), **3** (grey), and **7** (yellow) with Ph₂NBMes₂ (excess); 12.5 μ M samples.

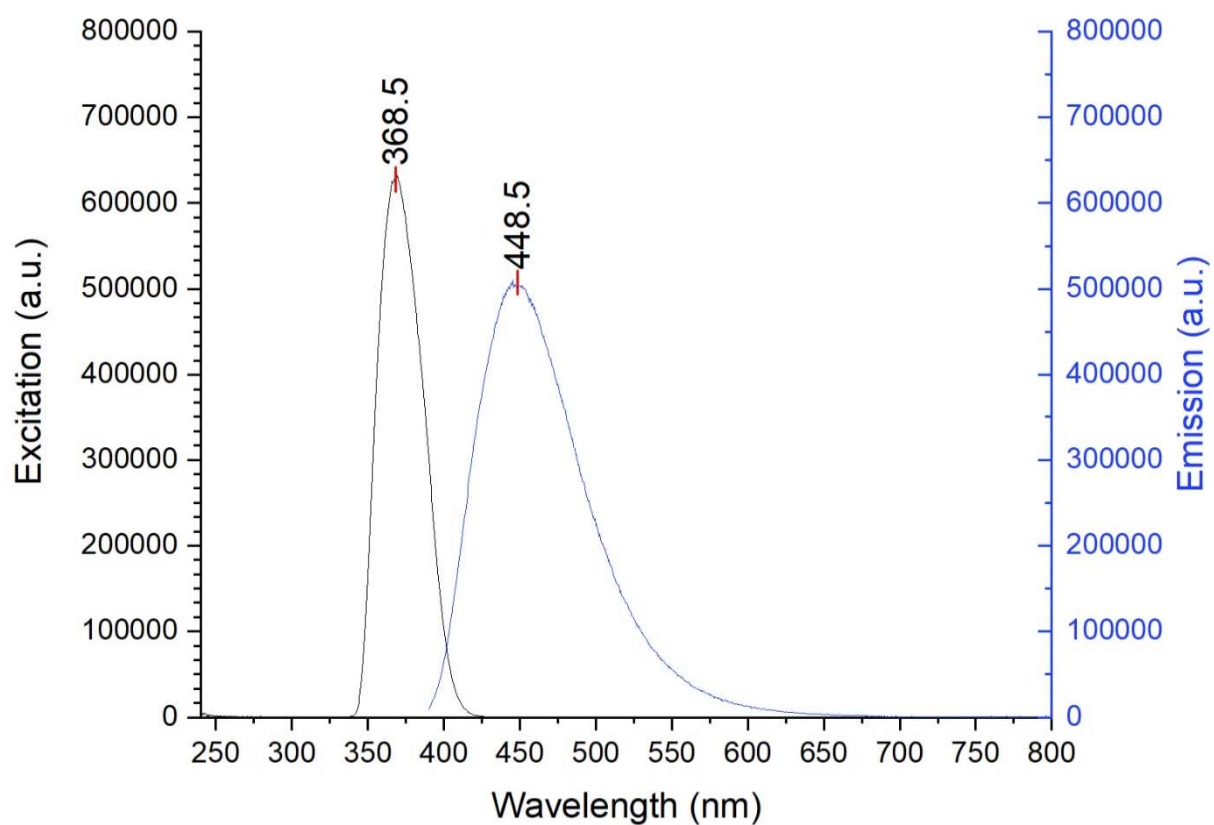


Figure S175 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) spectra of compound **1** and **Ph₂NBMes₂**; 12.5 μ M sample.

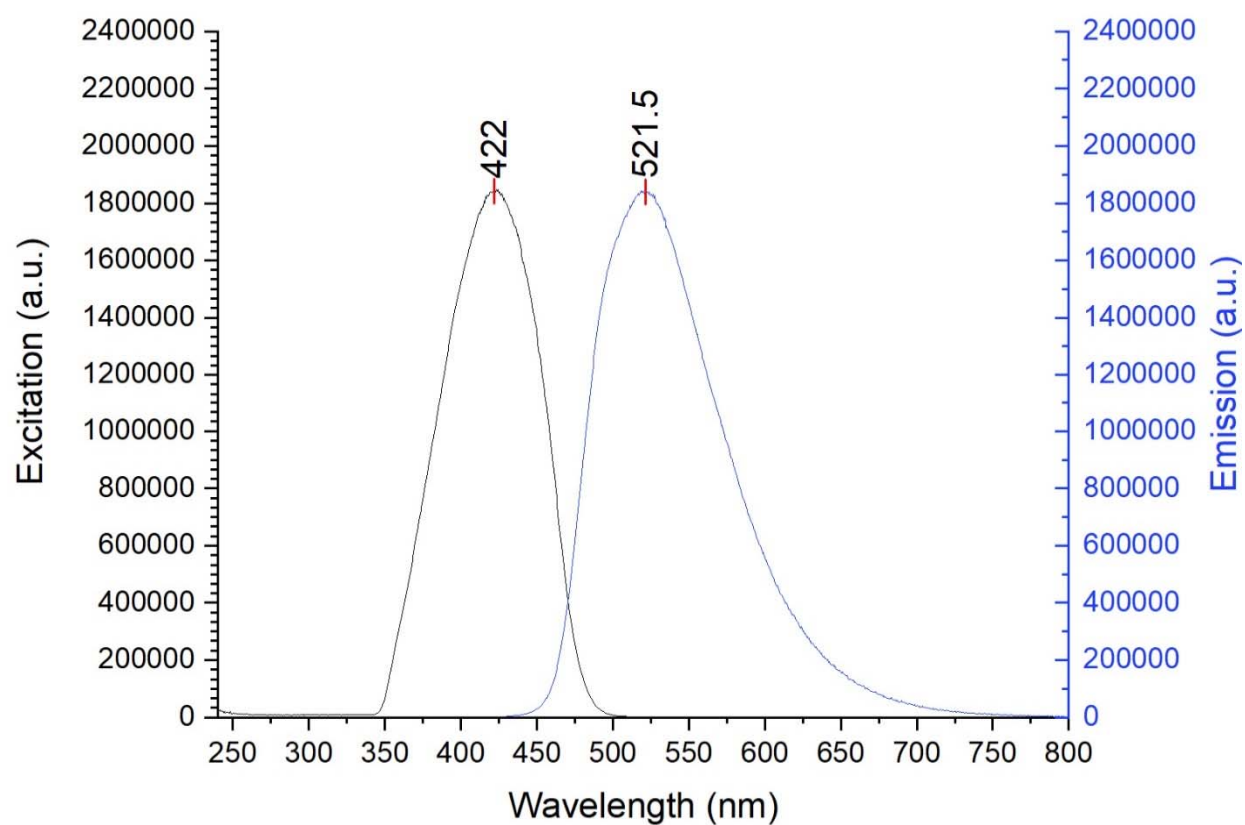


Figure S176 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) spectra of compound **2** and Ph₂NBMes₂; 12.5 μ M sample.

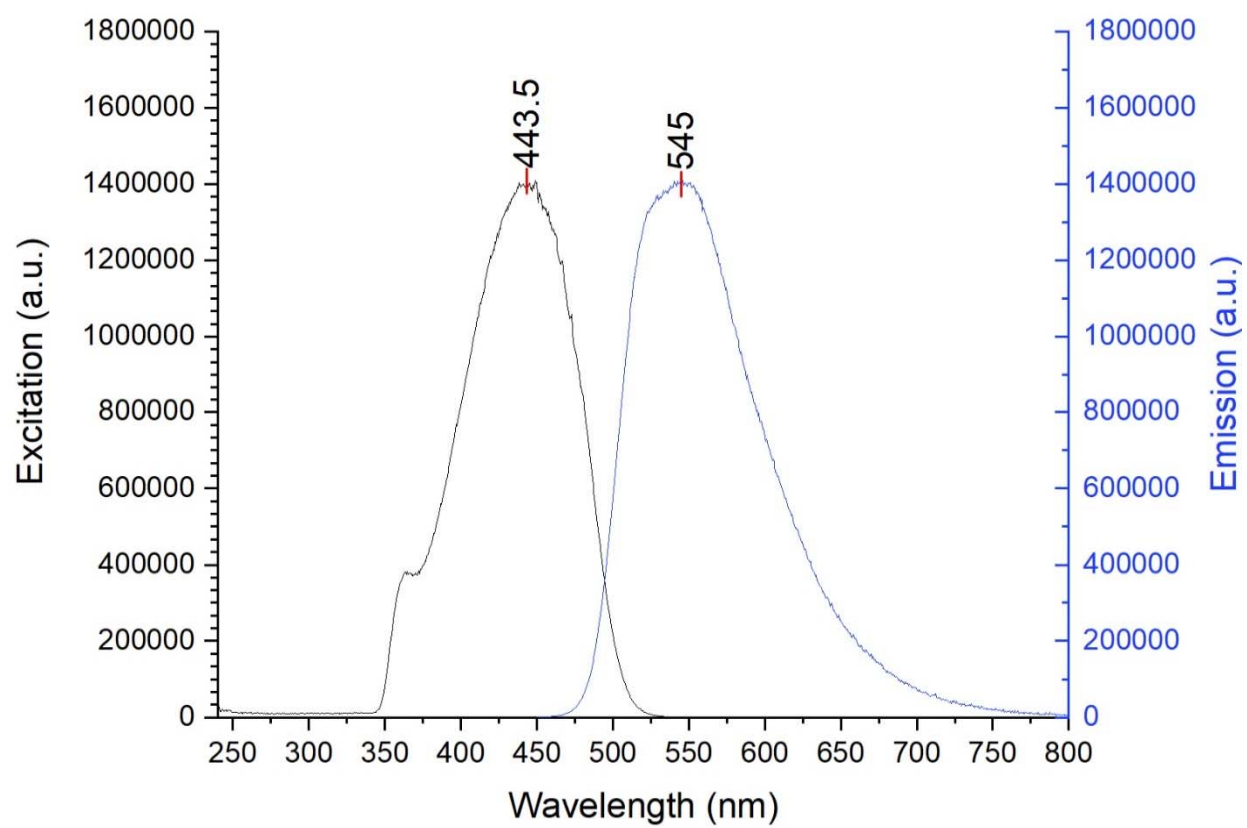


Figure S177 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) spectra of compound **3** and **Ph₂NBMes₂**; 12.5 μ M sample.

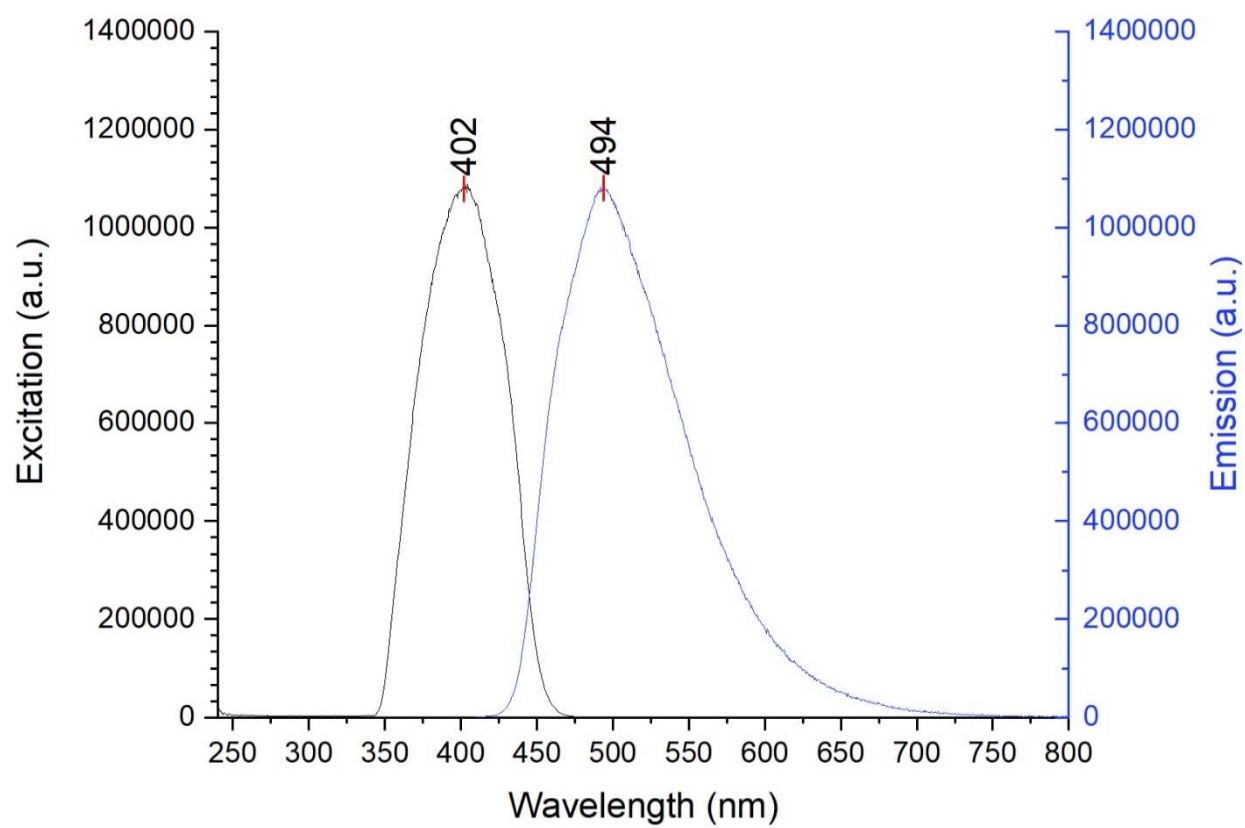


Figure S178 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) spectra of compound **7** and **Ph₂NBMes₂**; 12.5 μ M sample.

6.1.43. Ph₂PBMes₂

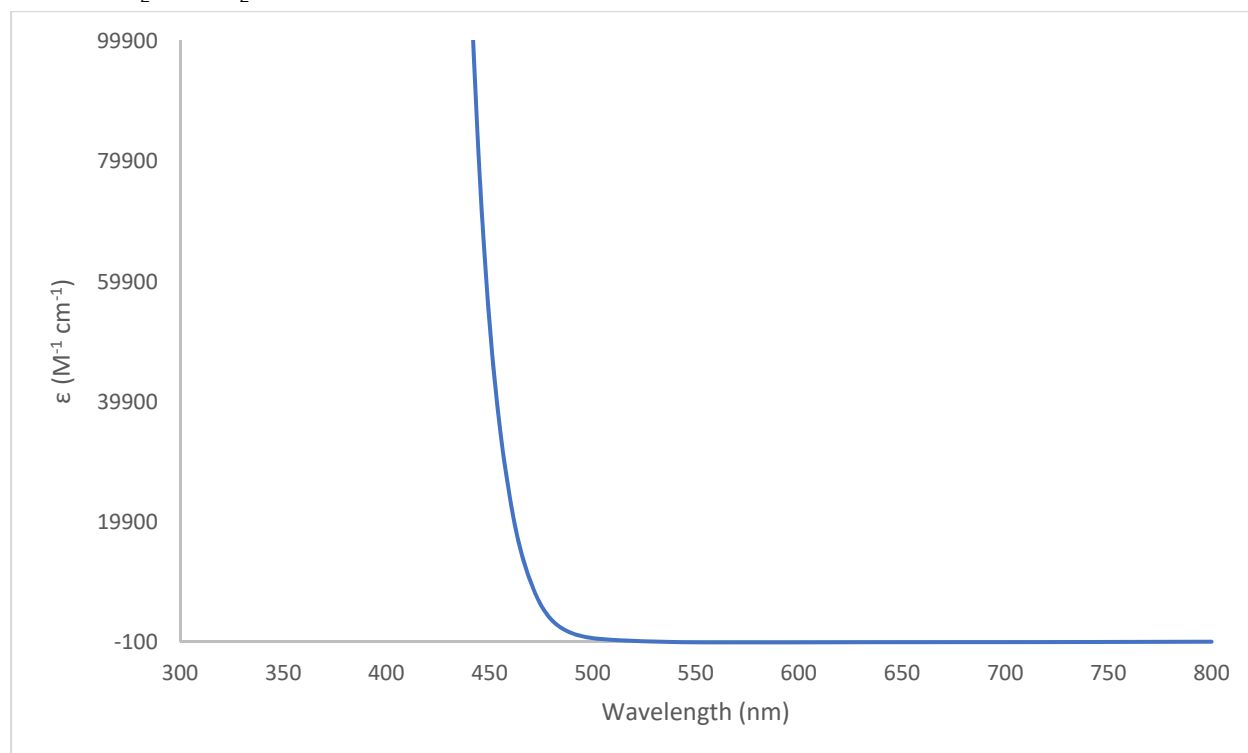


Figure S179 Stacked UV-Vis absorption spectrum of **1** (blue) with **Ph₂PBMes₂** (excess); 12.5 μ M samples. Adduct absorption with additional probes could not be measured due to the high concentrations colored Lewis acid, thus not yielding acceptable UV-Vis absorption spectra.

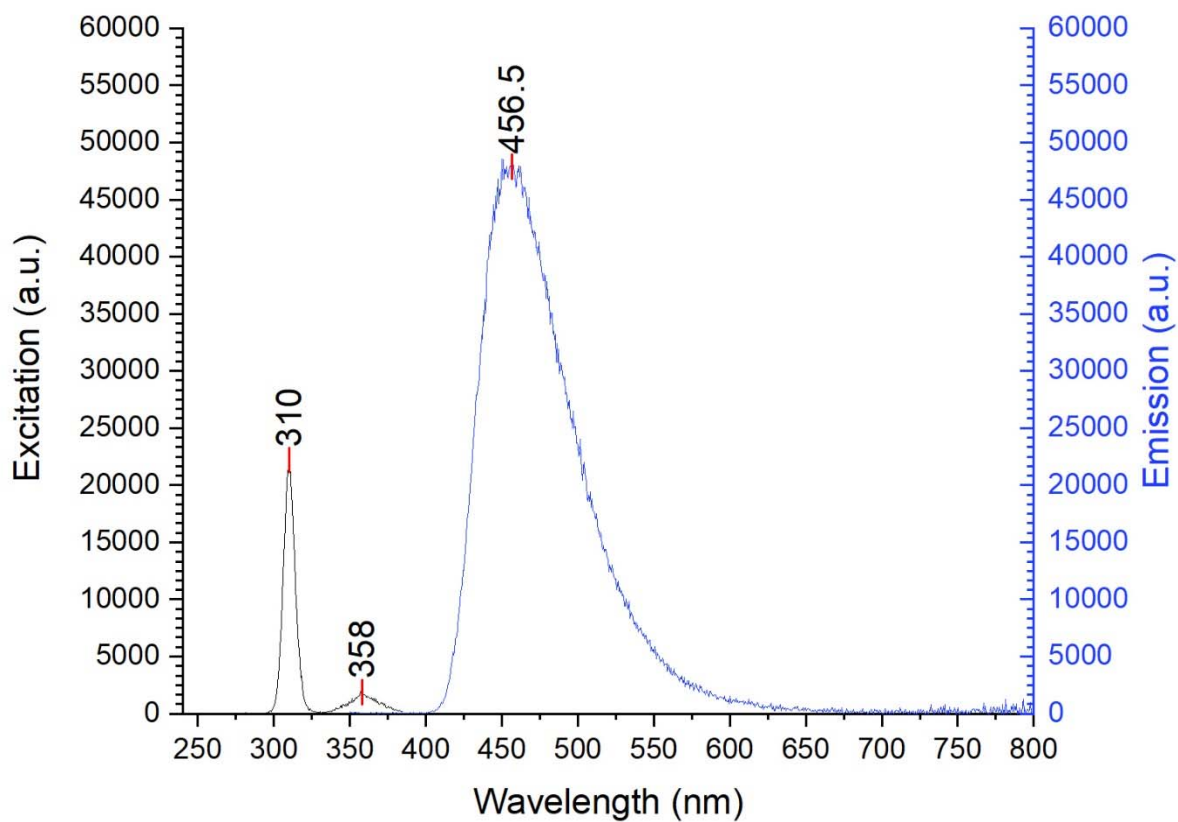


Figure S180 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) spectra of compound **1** and **Ph₂PBMes₂**; 12.5 μ M sample.

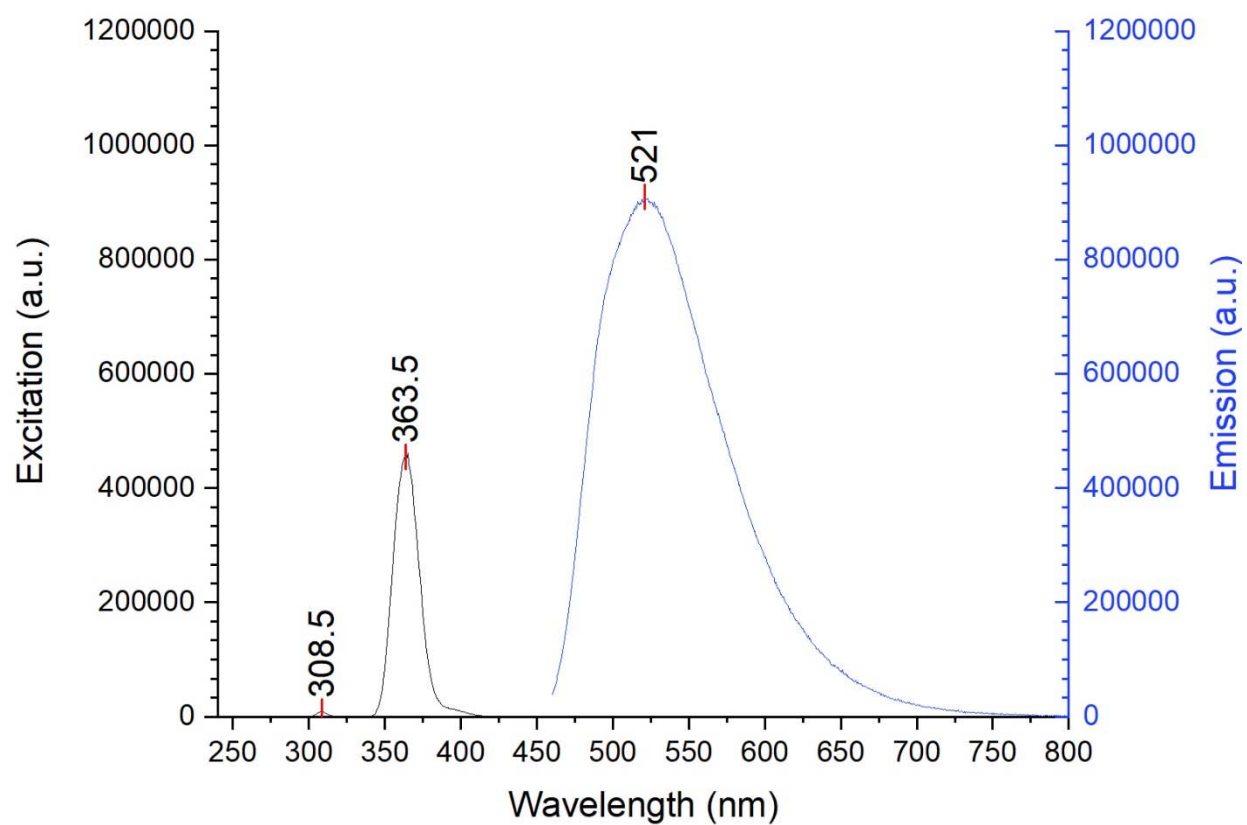


Figure S181 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) spectra of compound **2** and **Ph₂PBMe₂**; 12.5 μ M sample.

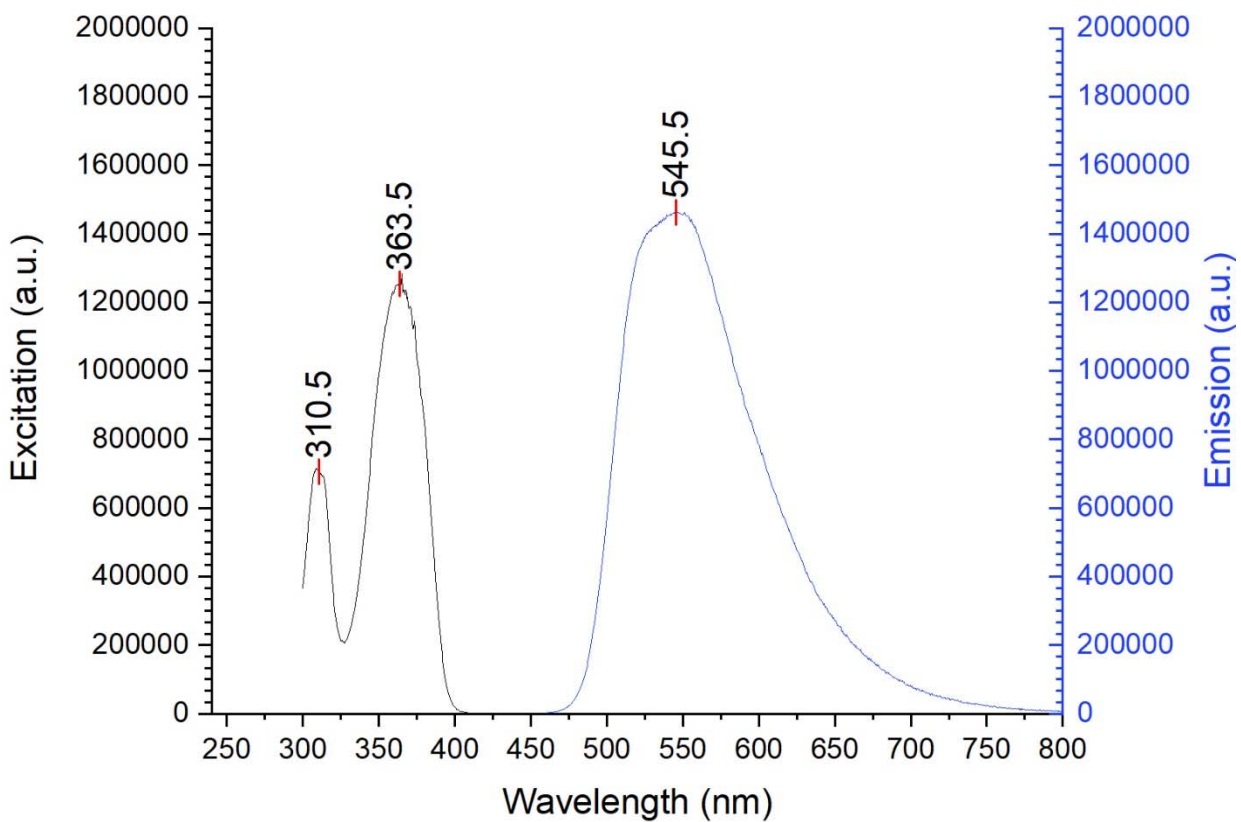


Figure S182 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) spectra of compound **3** and **Ph₂PBMe₂**; 12.5 μ M sample.

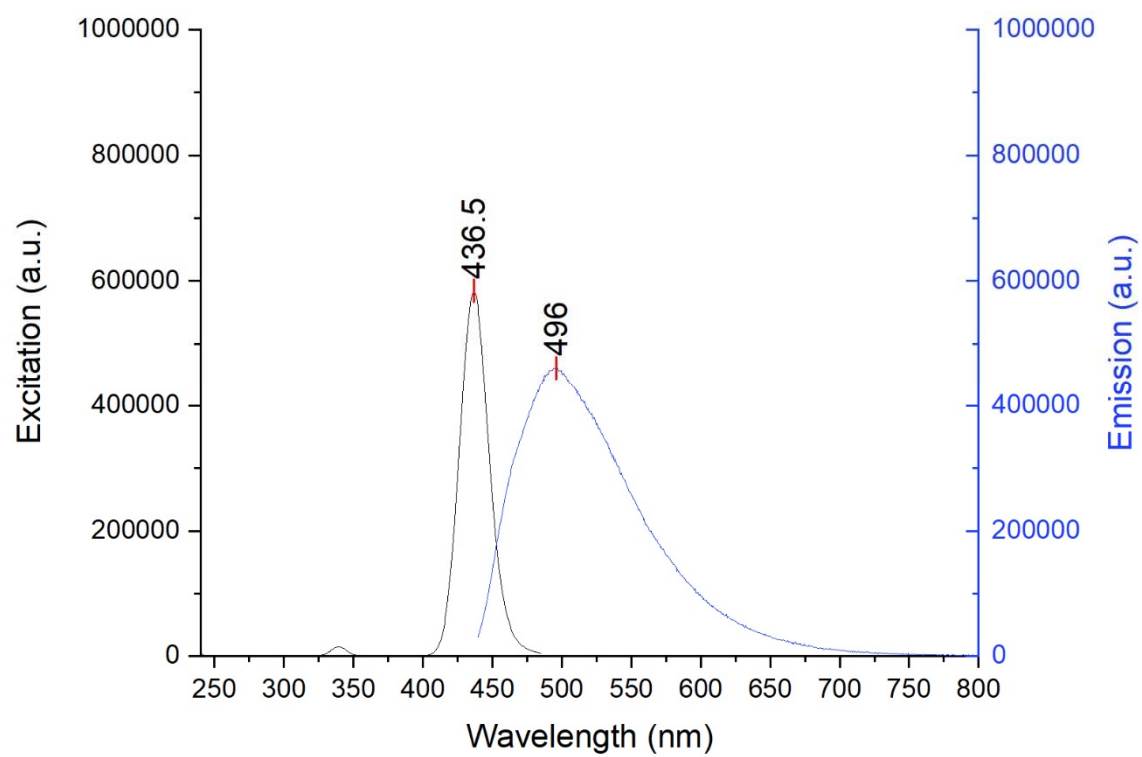


Figure S183 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) spectra of compound **7** and Ph_2PBMe_2 ; 12.5 μM sample.

6.1.44. $[\text{Ph}_2\text{S}][\text{OTf}]_2$

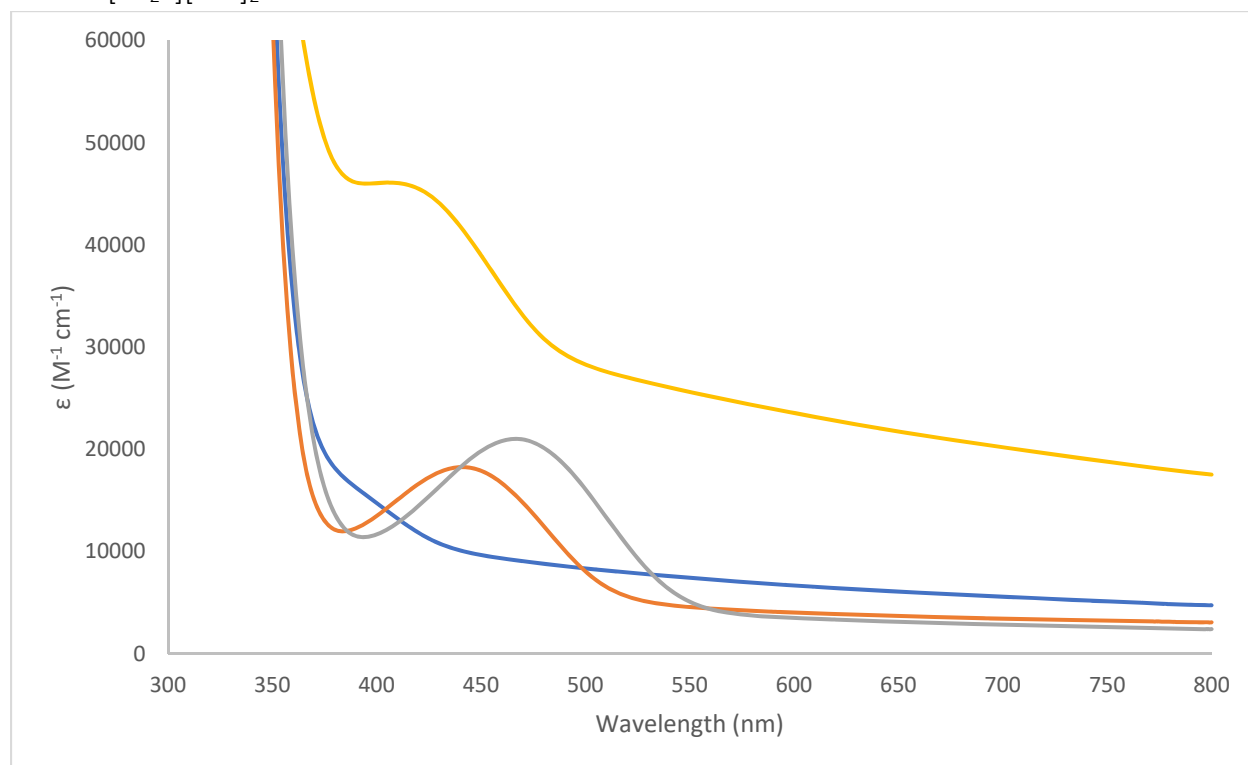


Figure S184 Stacked UV-Vis absorption spectra of **1** (blue), **2** (orange), **3** (grey), and **7** (yellow) with $[\text{Ph}_2\text{S}][\text{OTf}]_2$ (excess); 12.5 μM samples.

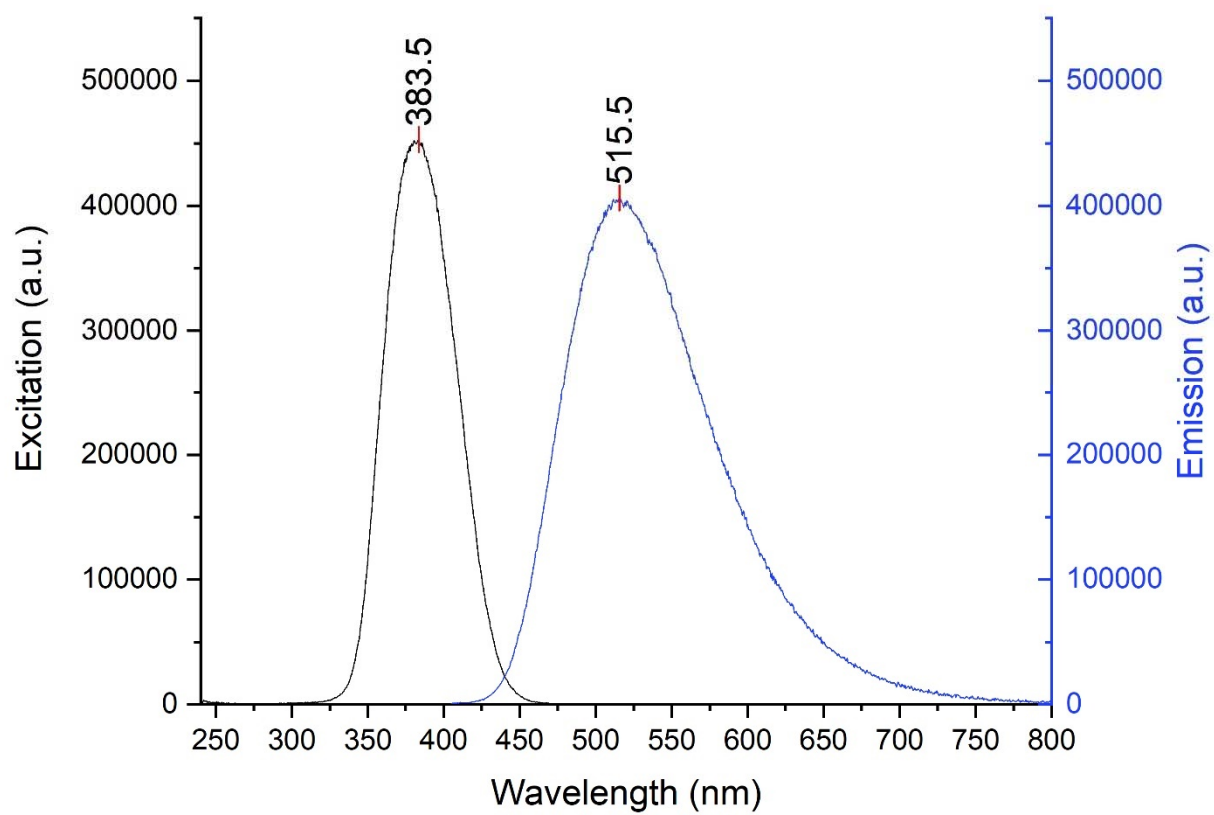


Figure S185 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) spectra of compound **1** and [Ph₂S][OTf]₂; 12.5 μM sample.

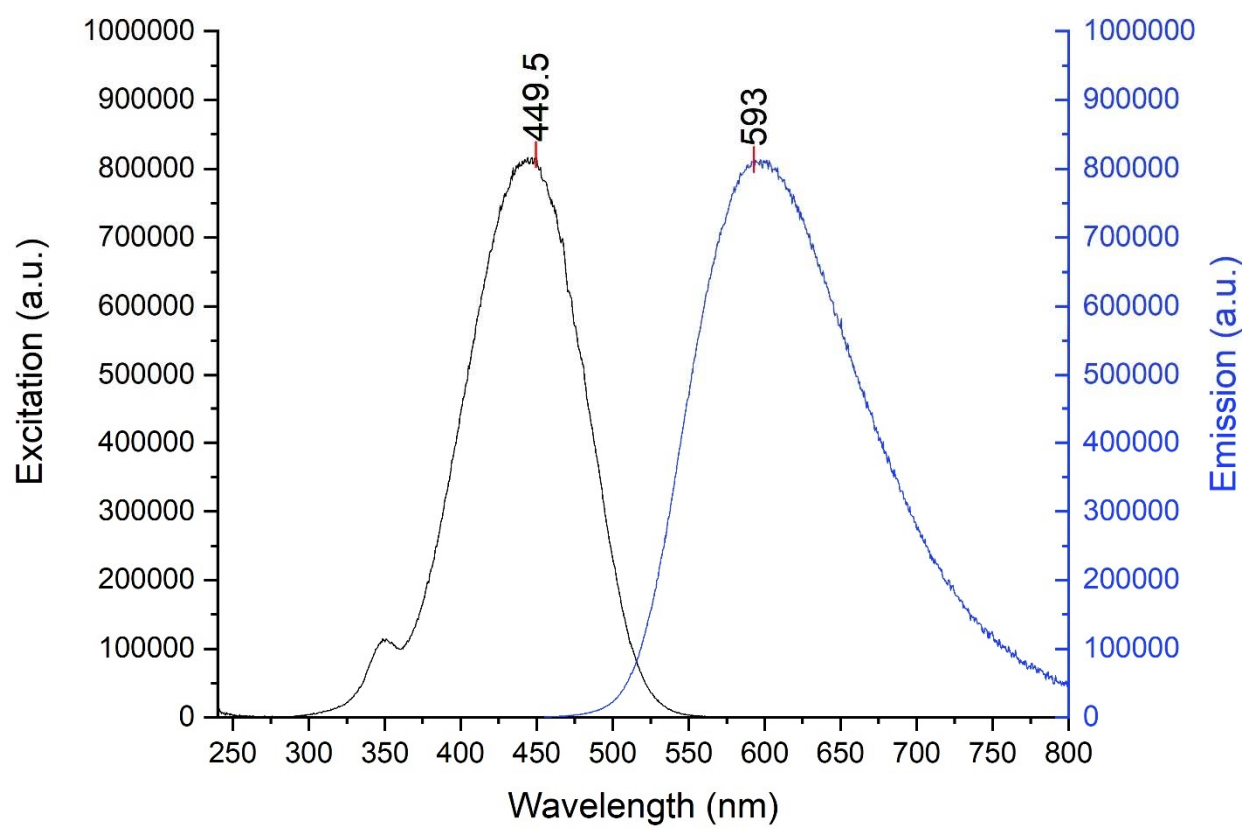


Figure S186 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) spectra of compound **2** and $[\text{Ph}_2\text{S}][\text{OTf}]_2$; 12.5 μM sample.

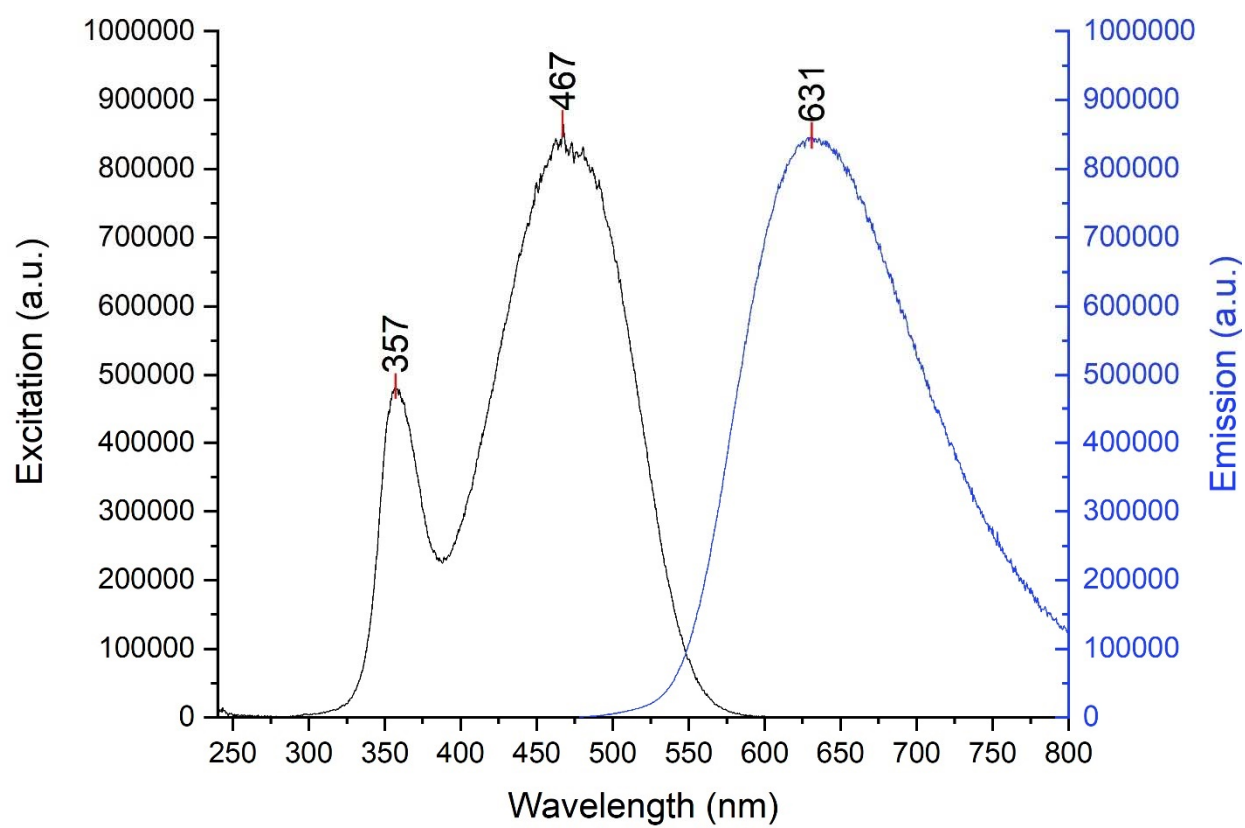


Figure S187 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) spectra of compound **3** and $[\text{Ph}_2\text{S}][\text{OTf}]_2$; 12.5 μM sample.

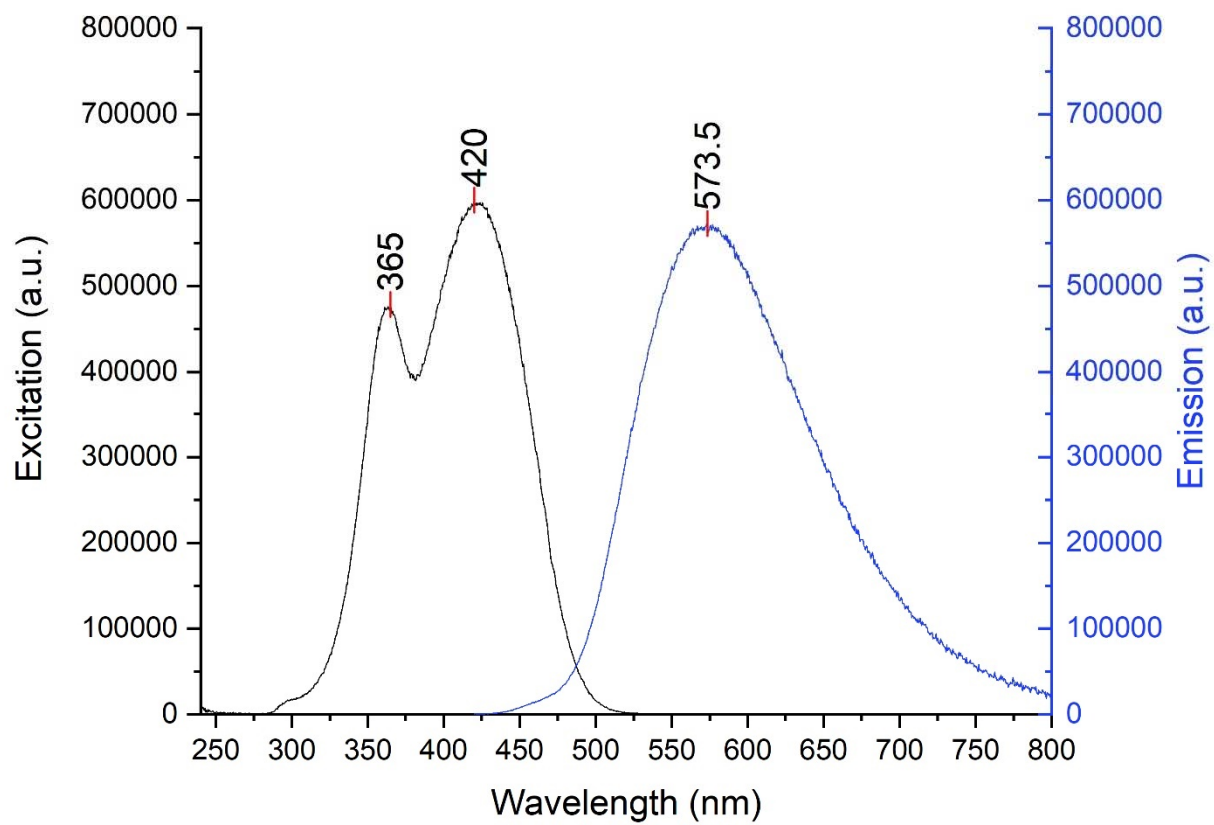


Figure S188 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) spectra of compound **7** and $[\text{Ph}_2\text{S}][\text{OTf}]_2$; 12.5 μM sample.

6.1.45. $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$

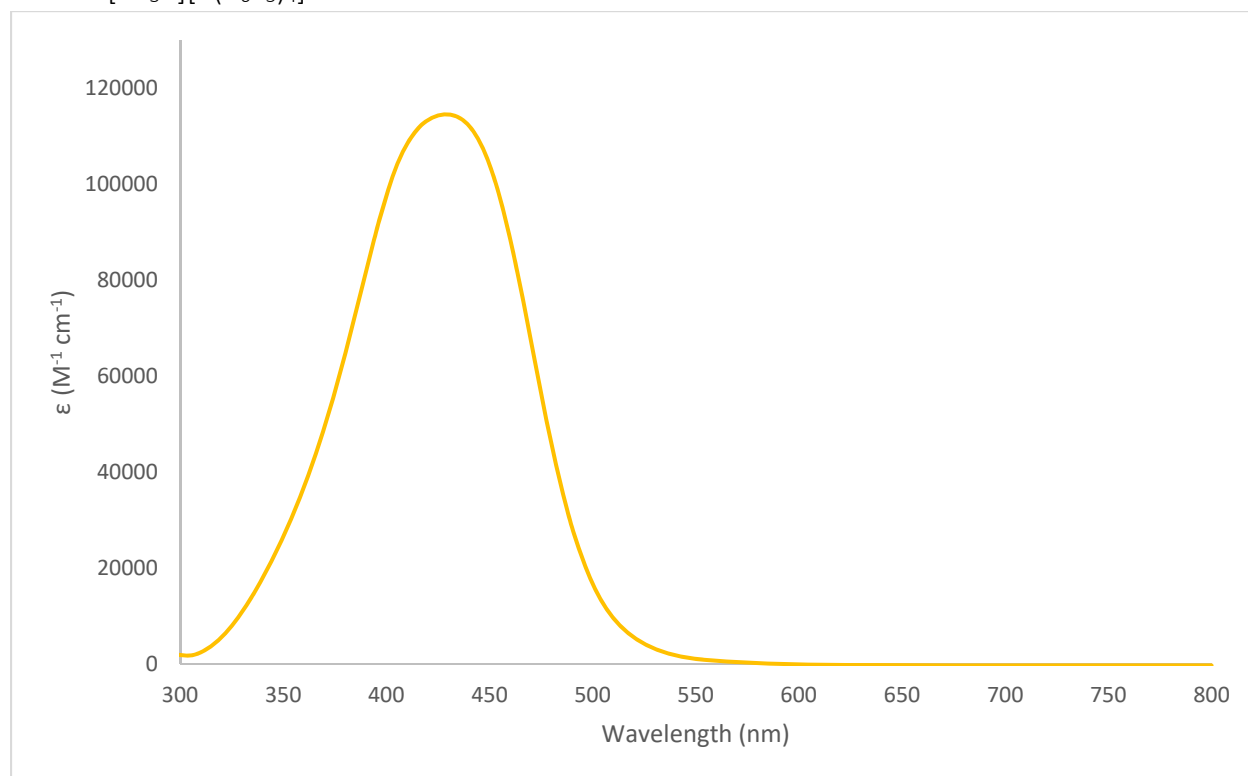


Figure S189 Stacked UV-Vis absorption spectra of **7** (yellow) with $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ (5 eq.); 12.5 μM samples.

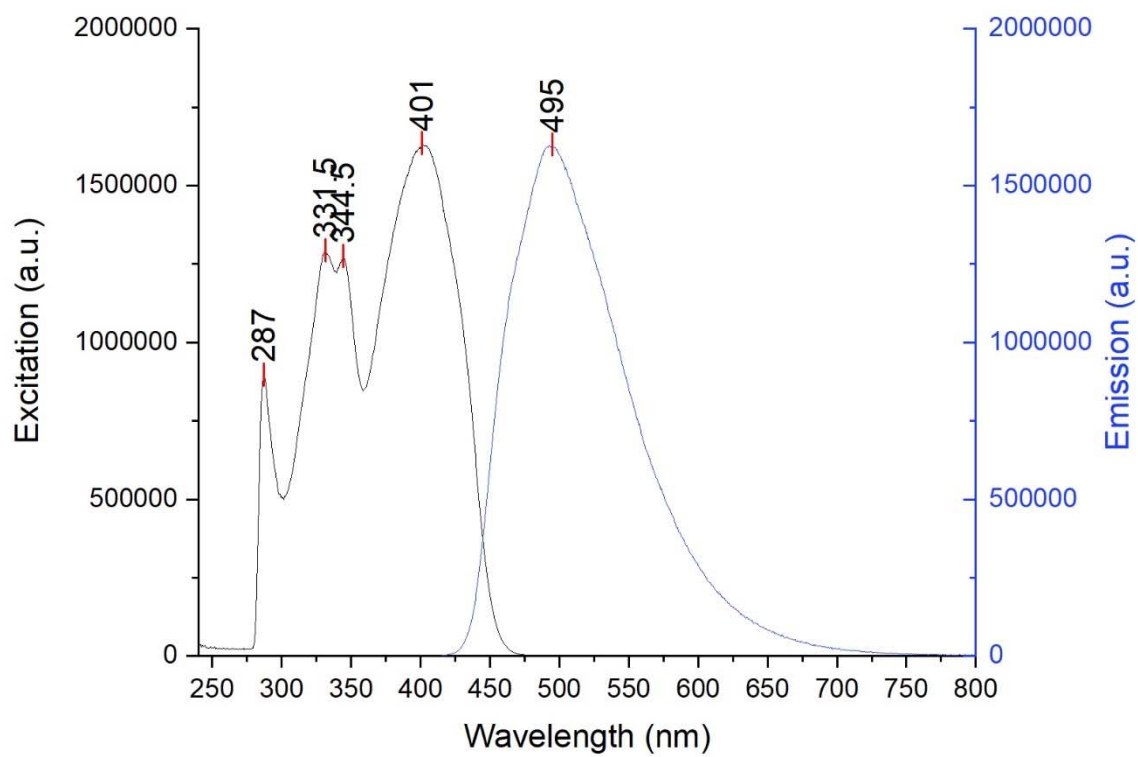


Figure S190 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) spectra of compound **7** and $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$; $12.5\ \mu\text{M}$ sample.

6.1.46. $[\text{Ph}_3\text{PAuCl}]$

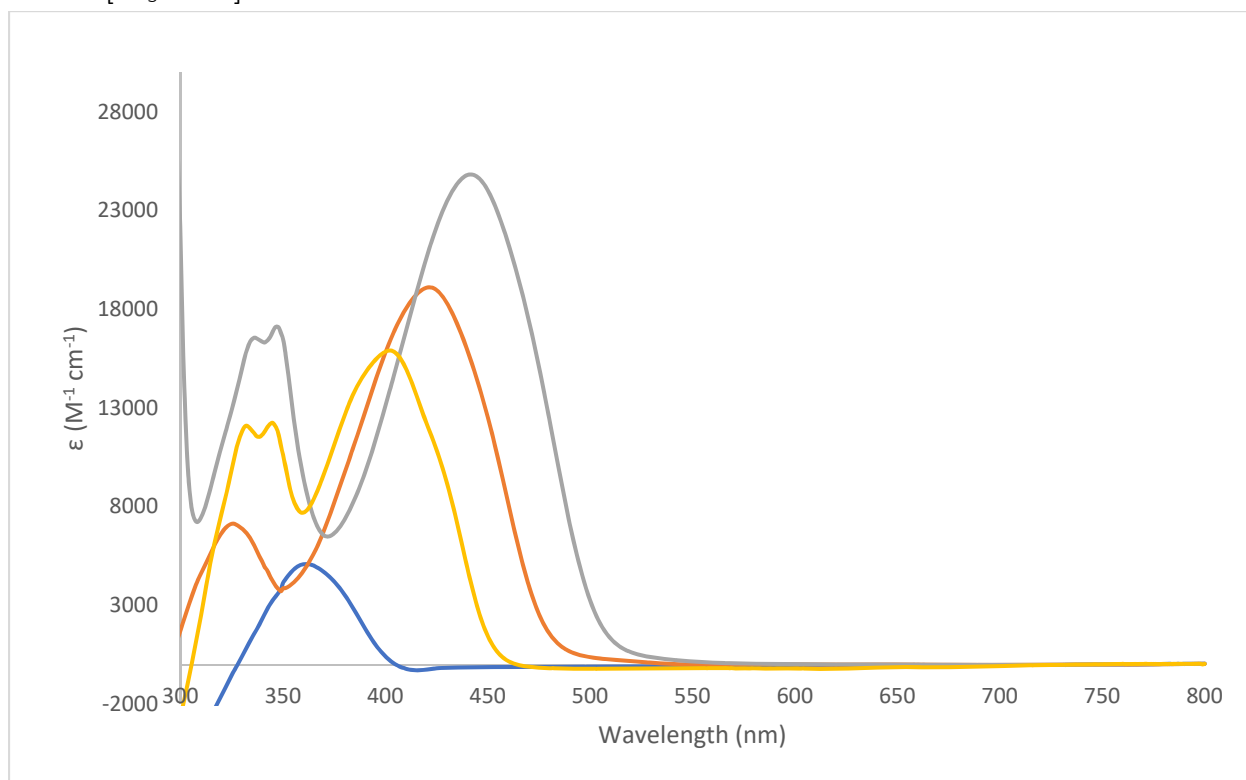


Figure S191 Stacked UV-Vis absorption spectra of **1** (blue), **2** (orange), **3** (grey), and **7** (yellow) with $[\text{Ph}_3\text{PAuCl}]$ (500 eq.); 12.5 μM samples.

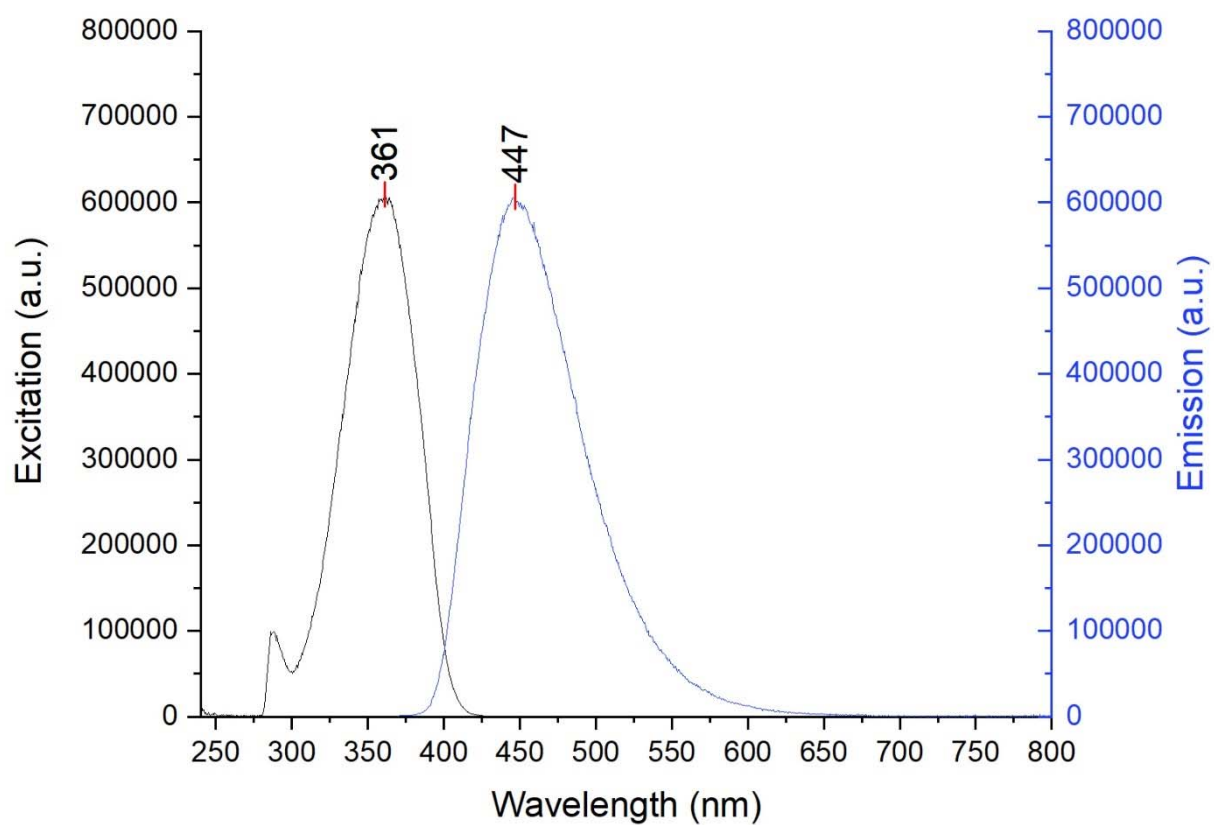


Figure S192 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) spectra of compound **1** and [Ph₃PAuCl]; 12.5 μM sample.

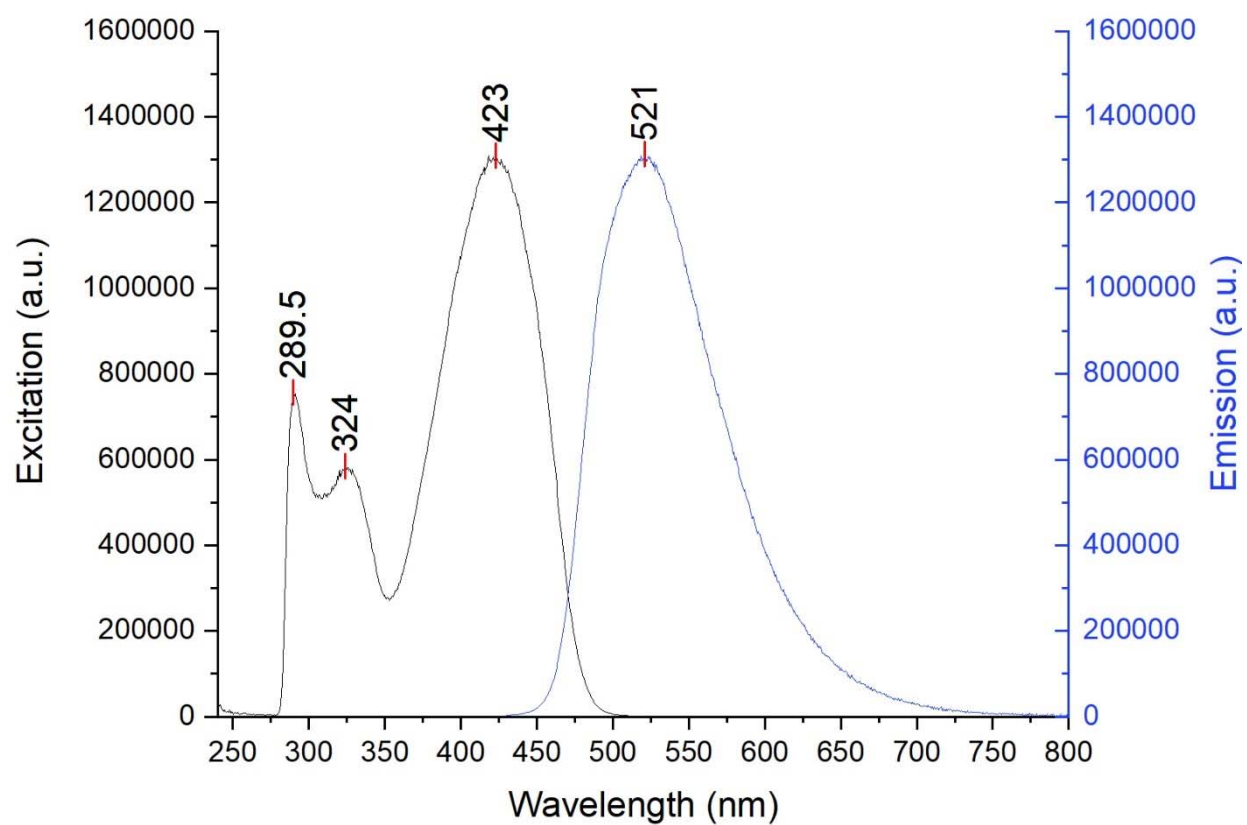


Figure S193 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) spectra of compound **2** and [Ph₃PAuCl]; 12.5 μM sample.

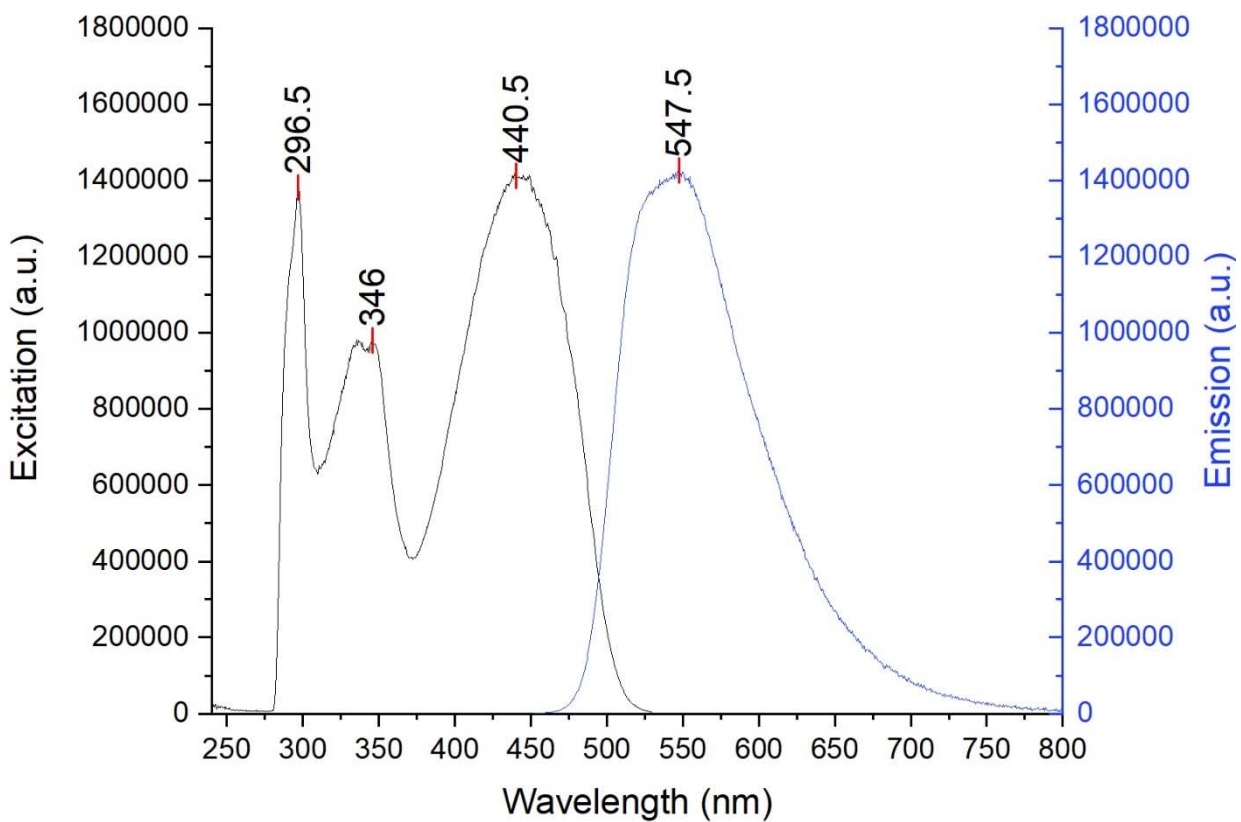


Figure S194 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) spectra of compound **3** and $[\text{Ph}_3\text{PAuCl}]$; 12.5 μM sample.

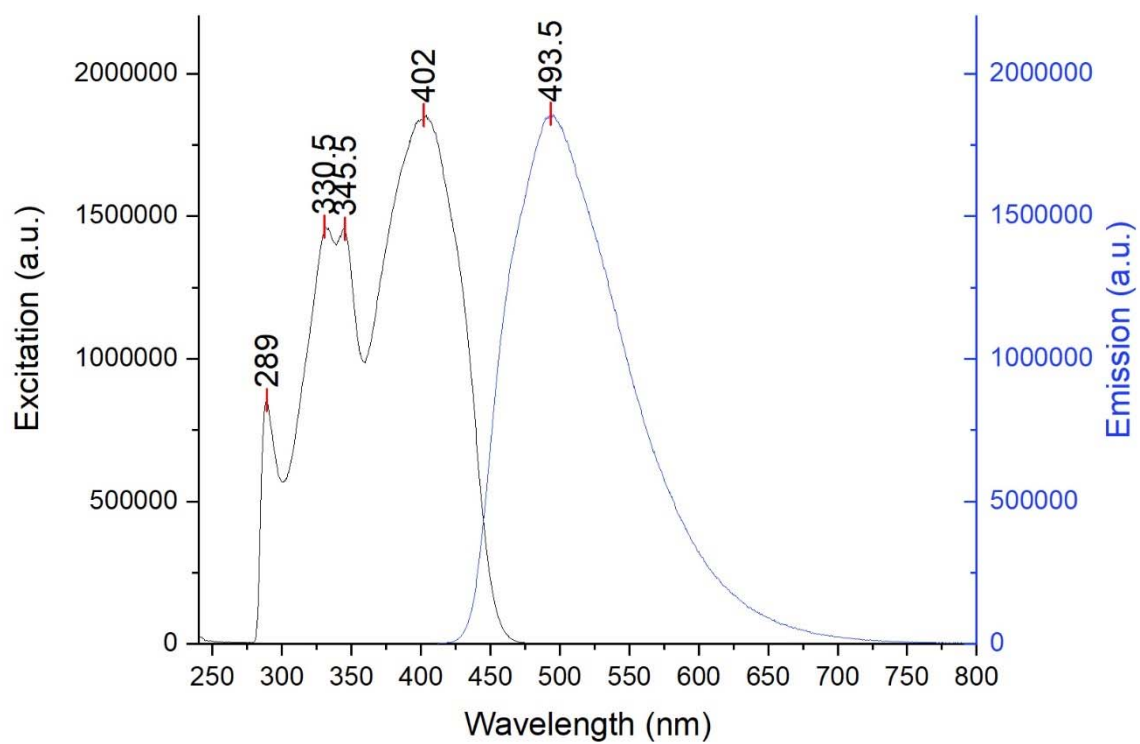


Figure S195 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) spectra of compound **7** and $[\text{Ph}_3\text{PAuCl}]$; 12.5 μM sample.

6.1.47. $[\text{Ph}_3\text{PAuOTf}]$

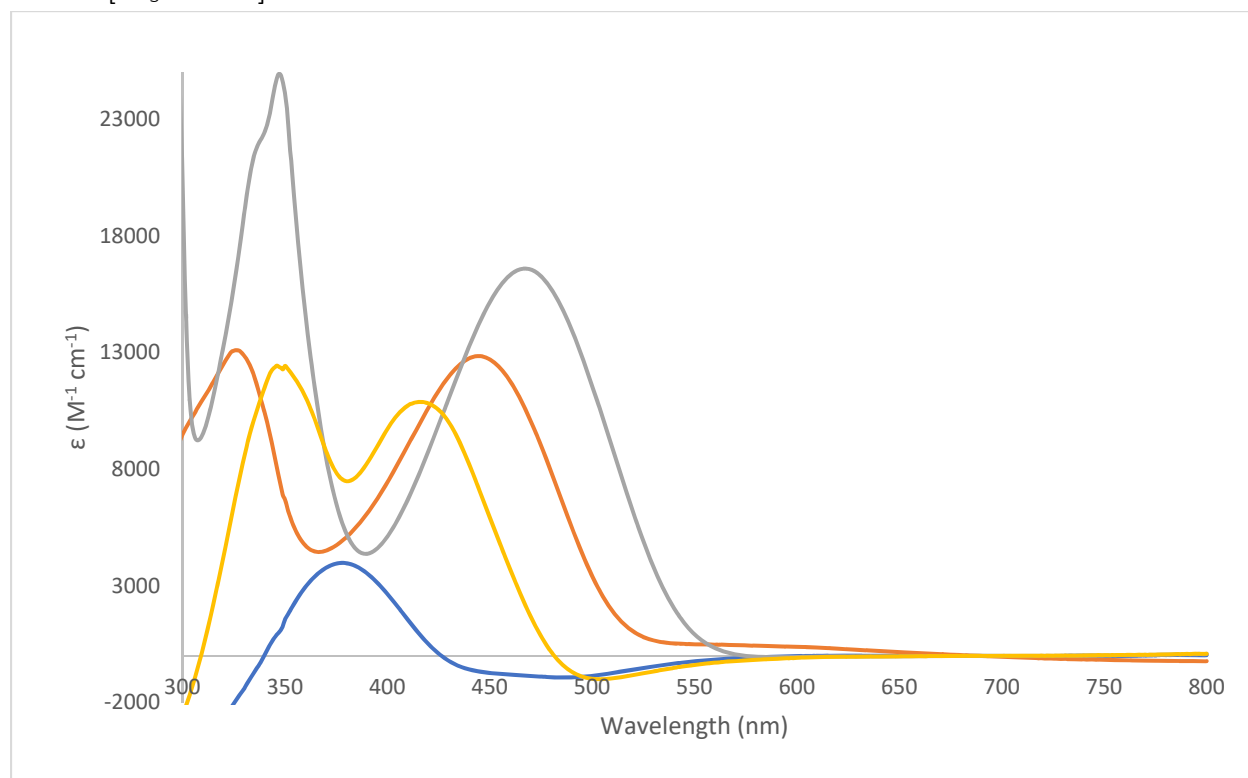


Figure S196 Stacked UV-Vis absorption spectra of **1** (blue), **2** (orange), **3** (grey), and **7** (yellow) with $[\text{Ph}_3\text{PAuOTf}]$ (excess); 12.5 μM samples.

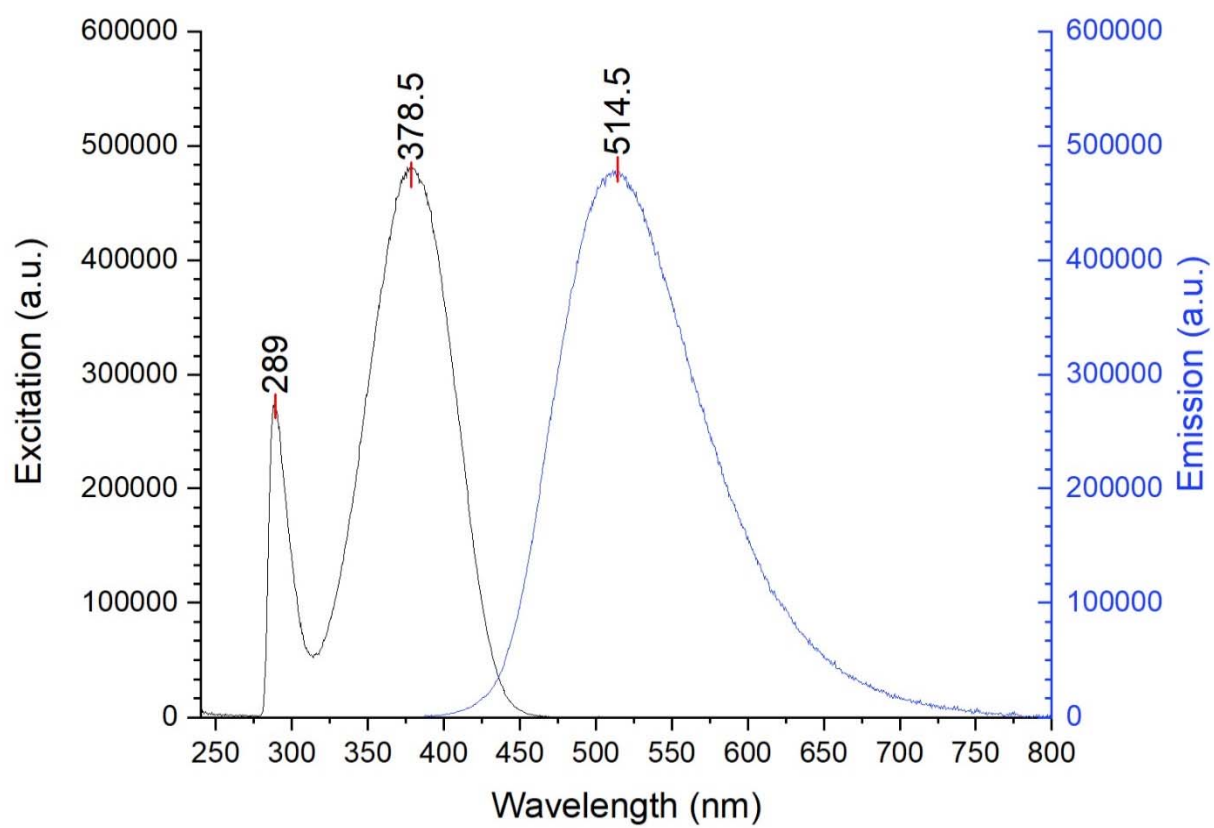


Figure S197 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) spectra of compound **1** and **[Ph₃PAuOTf]**; 12.5 μM sample.

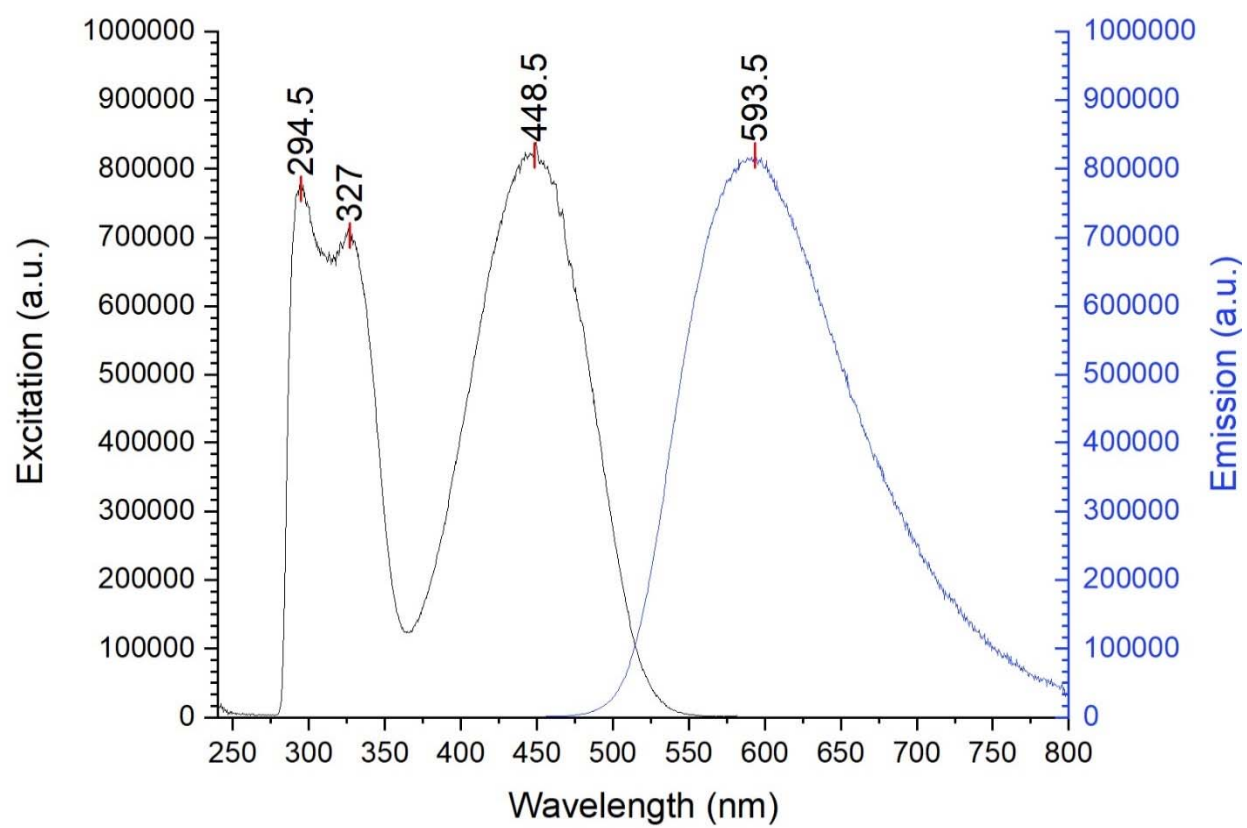


Figure S198 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) spectra of compound **2** and $[\text{Ph}_3\text{PAuOTf}]$; 12.5 μM sample.

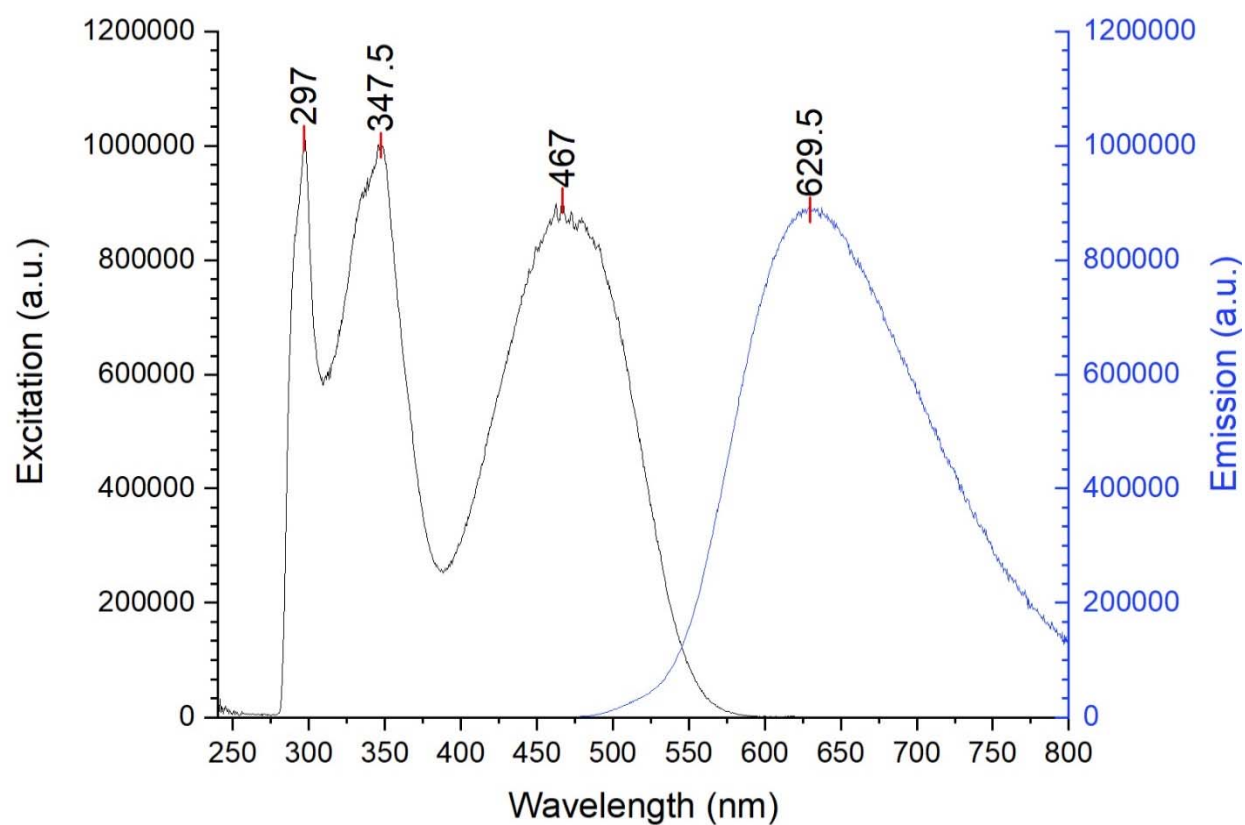


Figure S199 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) spectra of compound **3** and $[\text{Ph}_3\text{PAuOTf}]$; 12.5 μM sample.

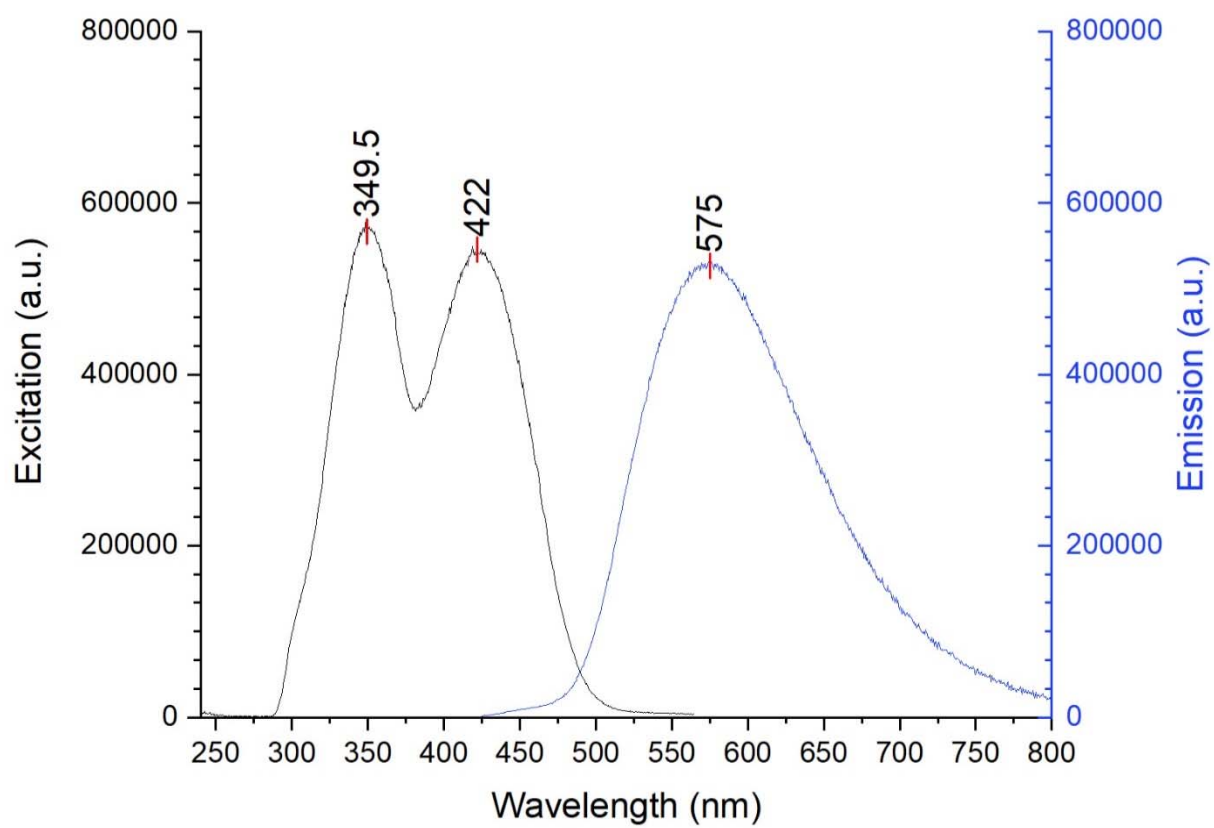


Figure S200 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) spectra of compound **7** and $[\text{Ph}_3\text{PAuOTf}]$; 12.5 μM sample.

6.1.48. $\text{Sc}(\text{OTf})_3$

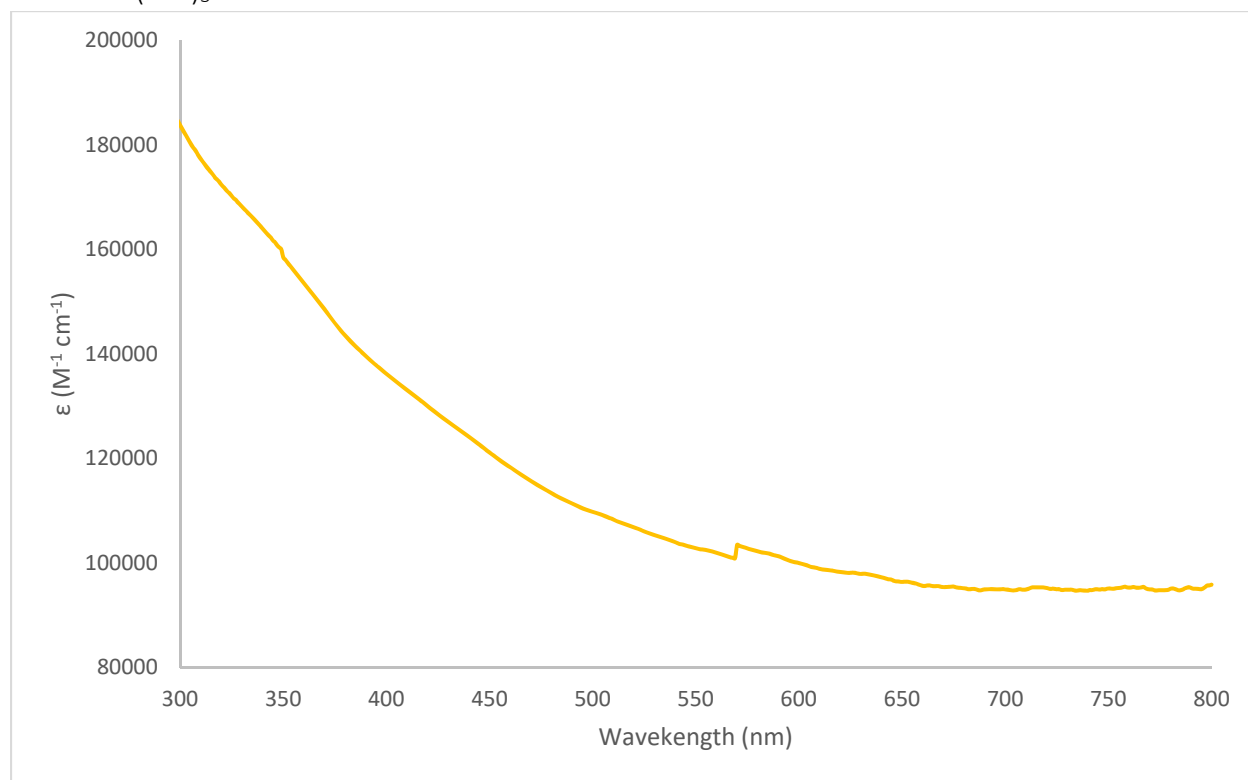


Figure S201 Stacked UV-Vis absorption spectra of **7** (blue) with $\text{Sc}(\text{OTf})_3$ (excess); 12.5 μM samples.

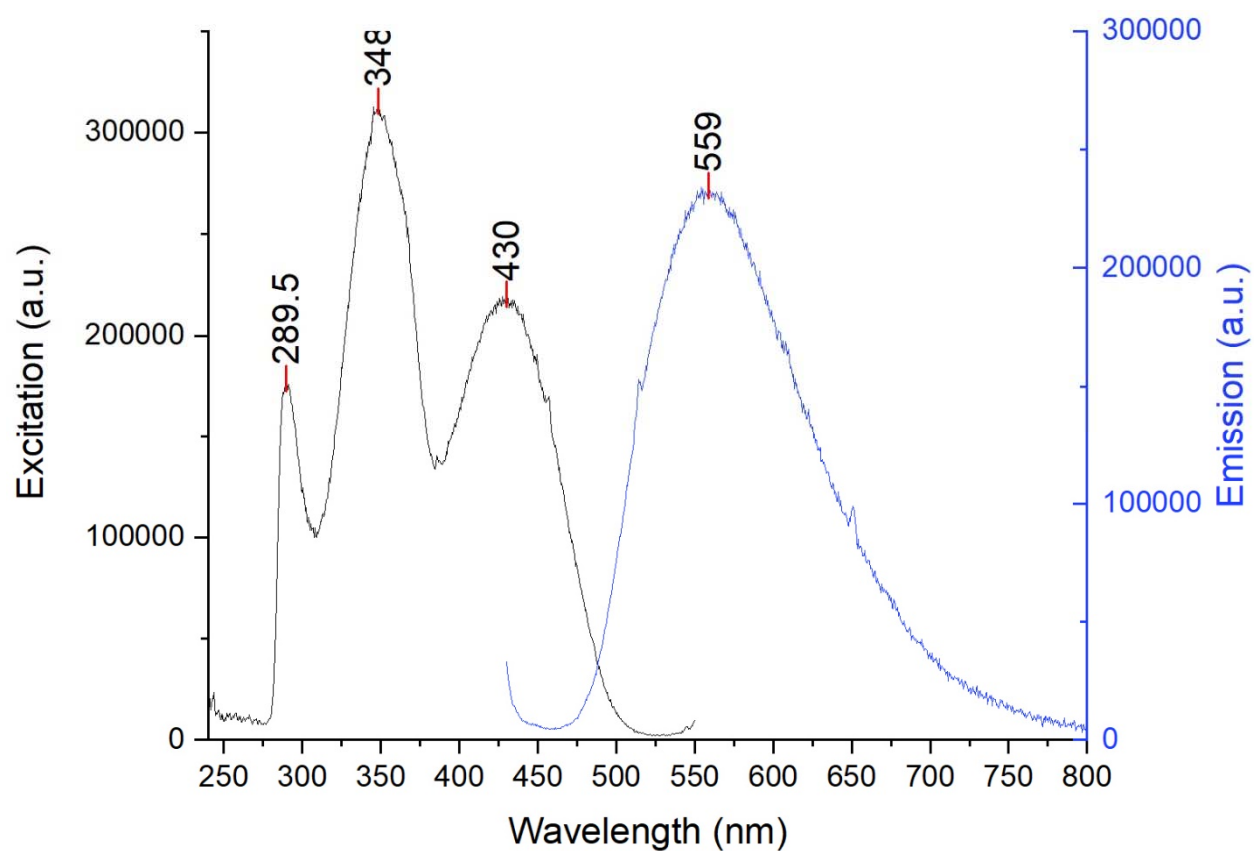


Figure S202 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) spectra of compound **7** and $\text{Sc}(\text{OTf})_3$; 12.5 μM sample.

6.1.49. Tf₂O

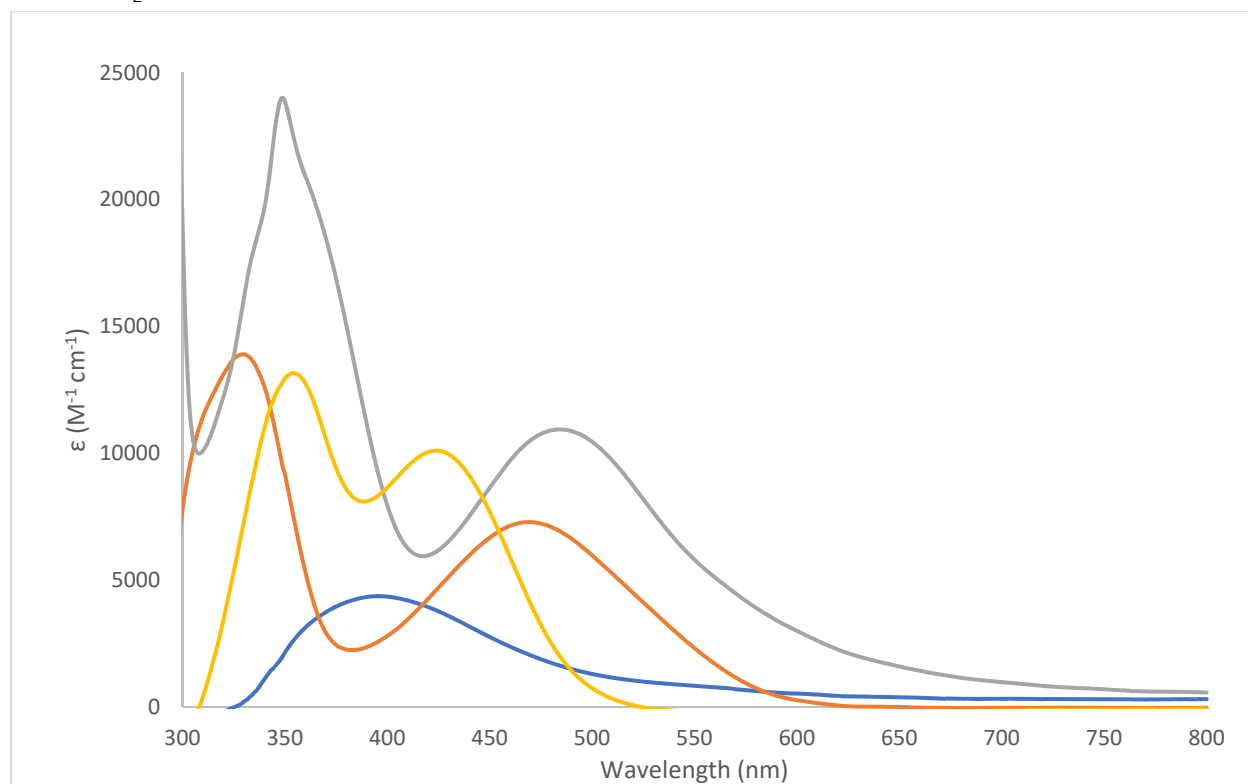


Figure S203 Stacked UV-Vis absorption spectra of **1** (blue), **2** (orange), **3** (grey), and **7** (yellow) with Tf₂O (excess); 12.5 μ M samples.

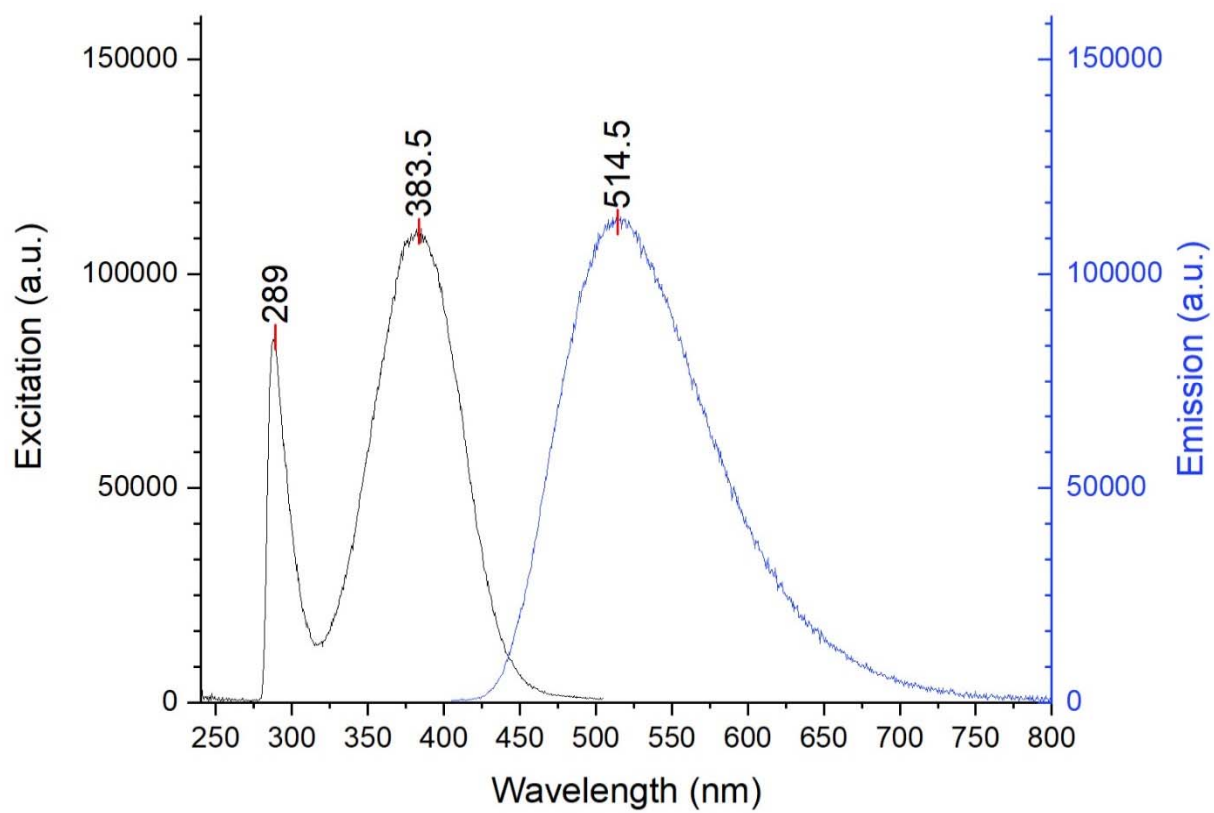


Figure S204 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) spectra of compound **1** and **Tf₂O**; 12.5 μ M sample.

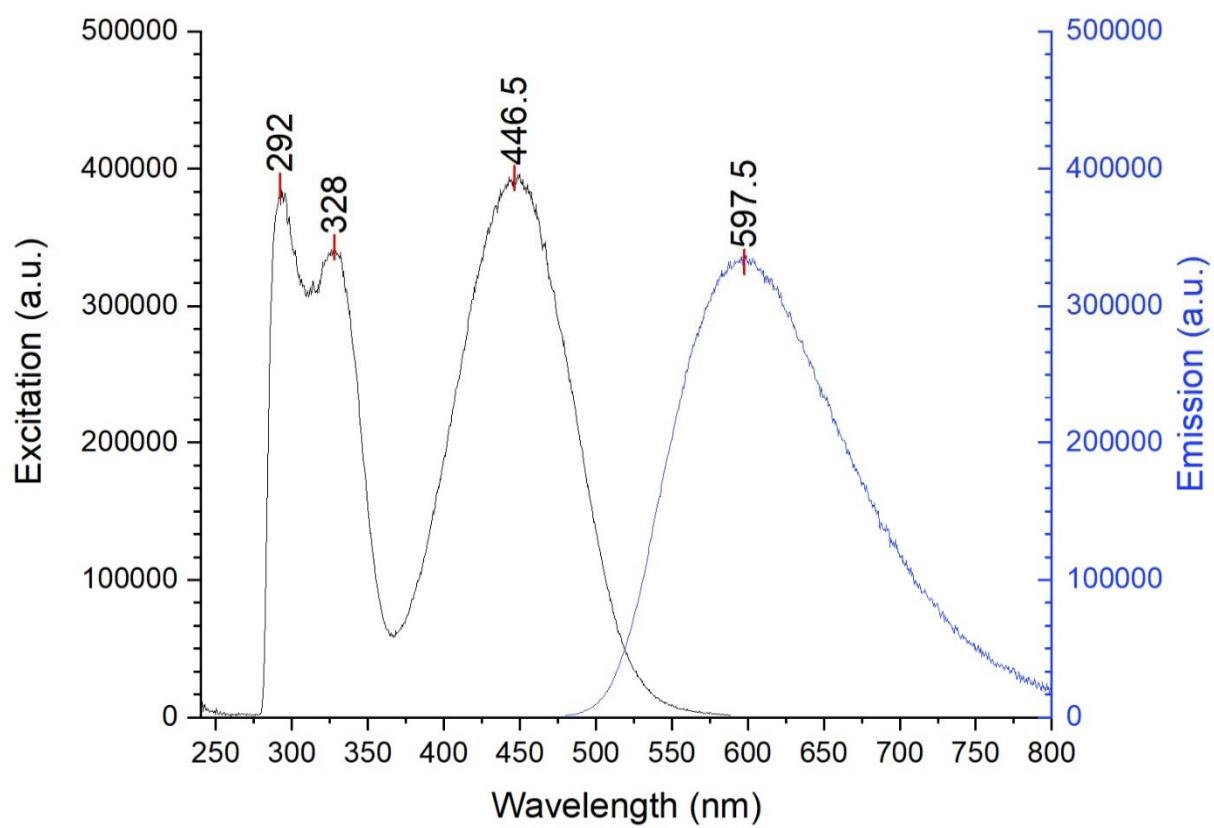


Figure S205 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) spectra of compound **2** and Tf_2O ; 12.5 μM sample.

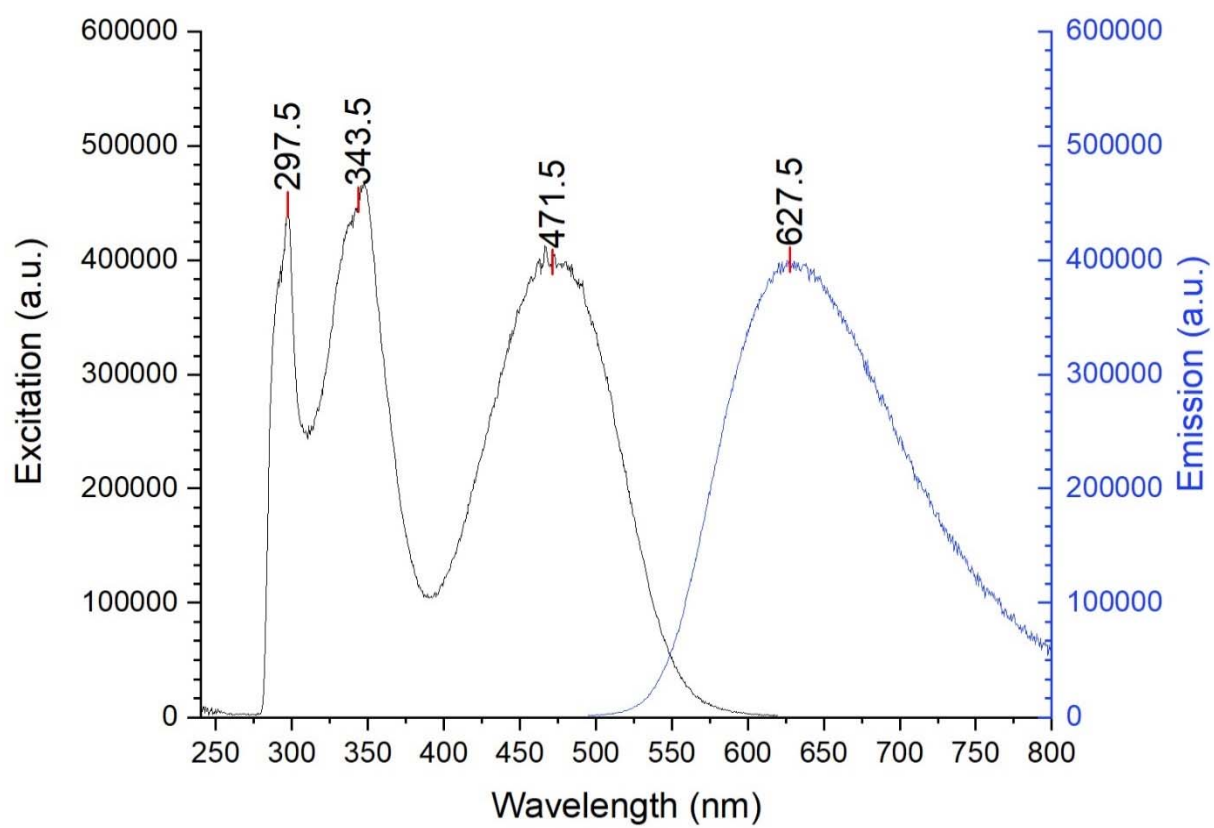


Figure S206 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) spectra of compound **3** and Tf_2O ; 12.5 μM sample.

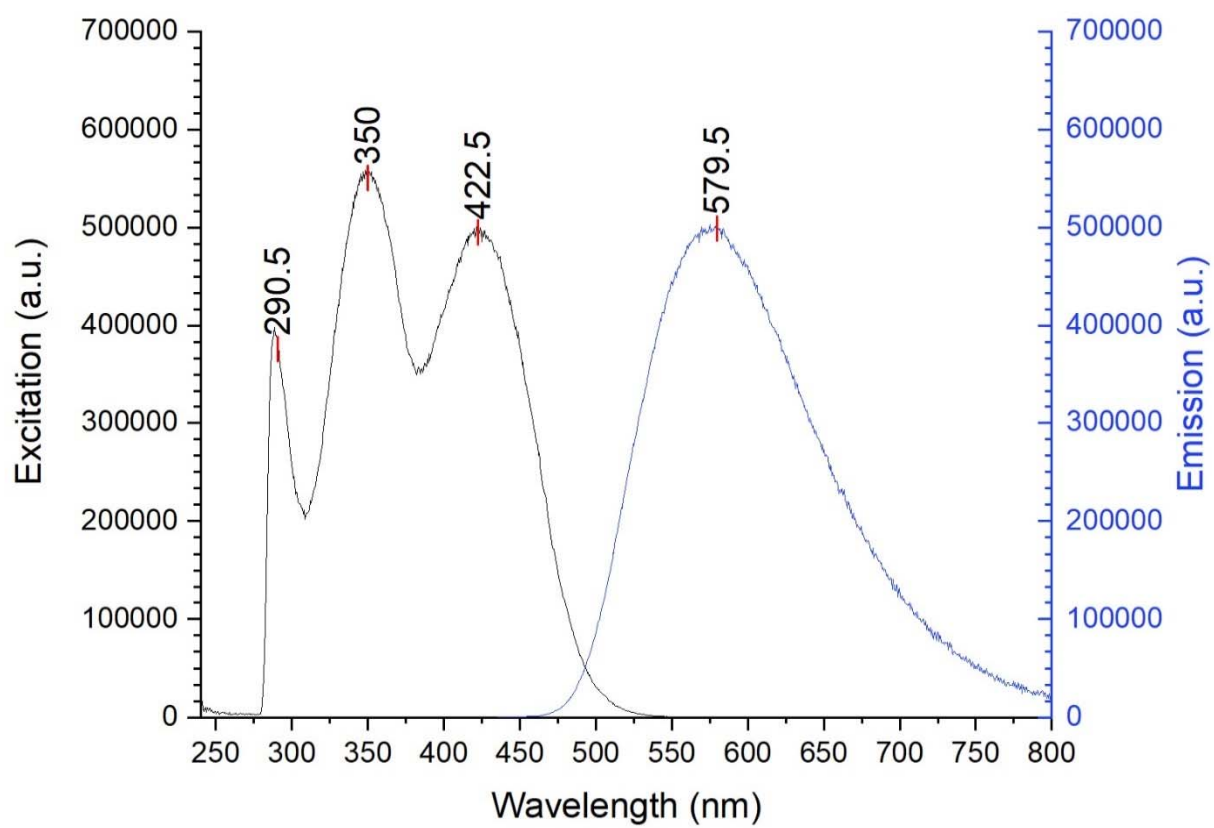


Figure S207 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) spectra of compound **7** and Tf_2O ; 12.5 μM sample.

6.1.50. [Me₃SiCH₂OTf]

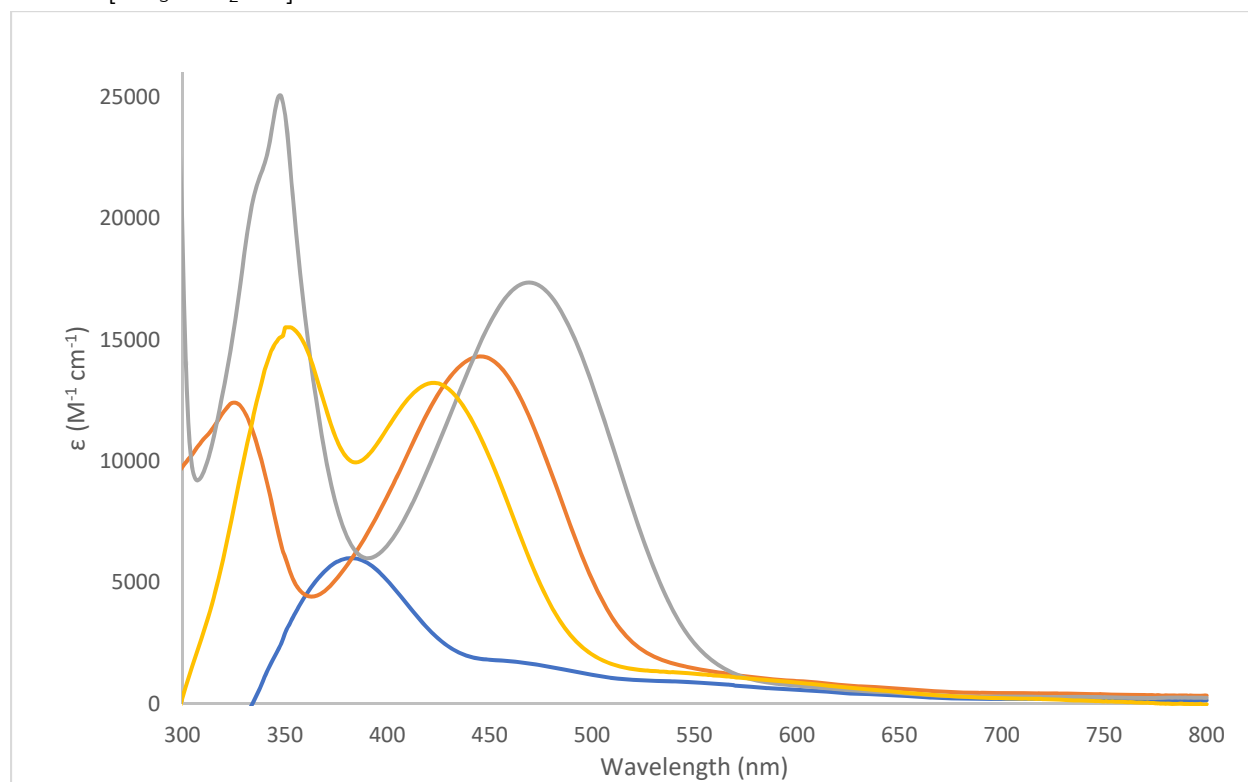


Figure S208 Stacked UV-Vis absorption spectra of **1** (blue), **2** (orange), **3** (grey), and **7** (yellow) with [Me₃SiCH₂OTf] (excess); 12.5 μ M samples.

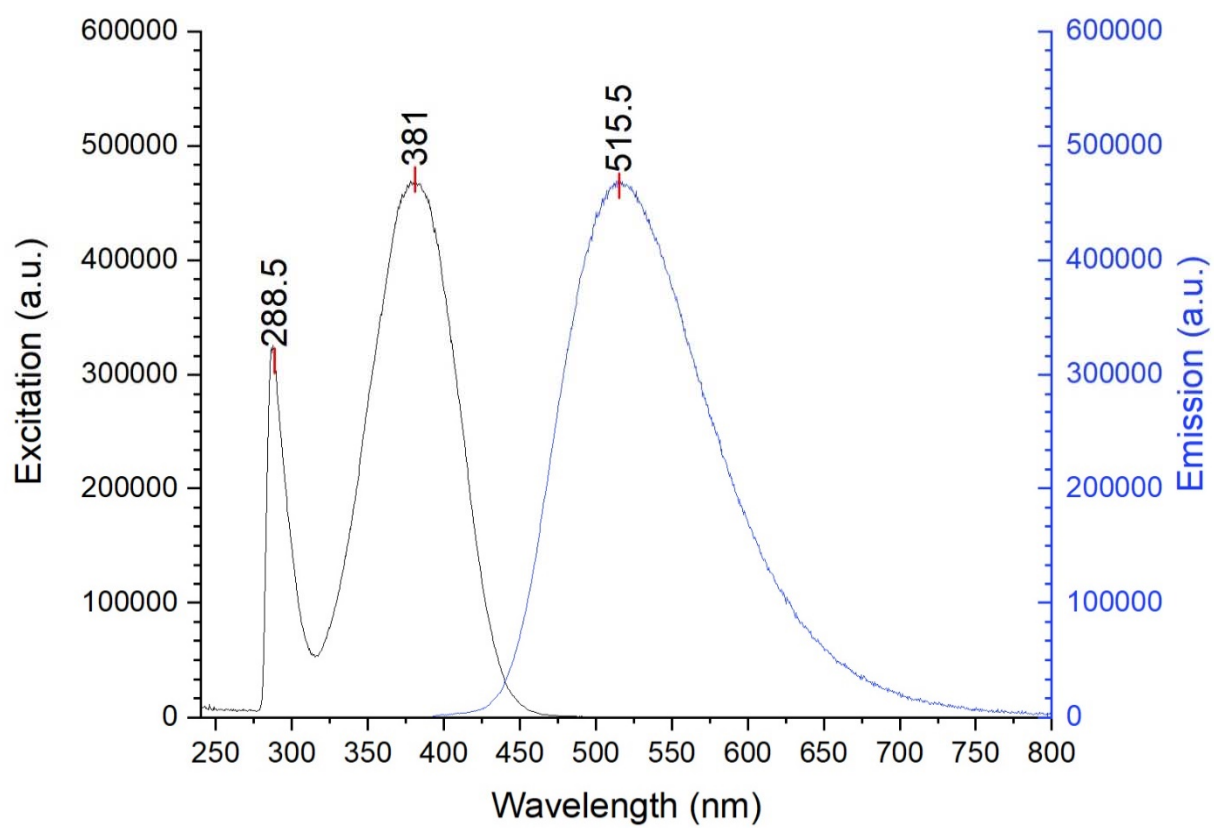


Figure S209 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) spectra of compound **1** and **[Me₃SiCH₂OTf]**; 12.5 μM sample.

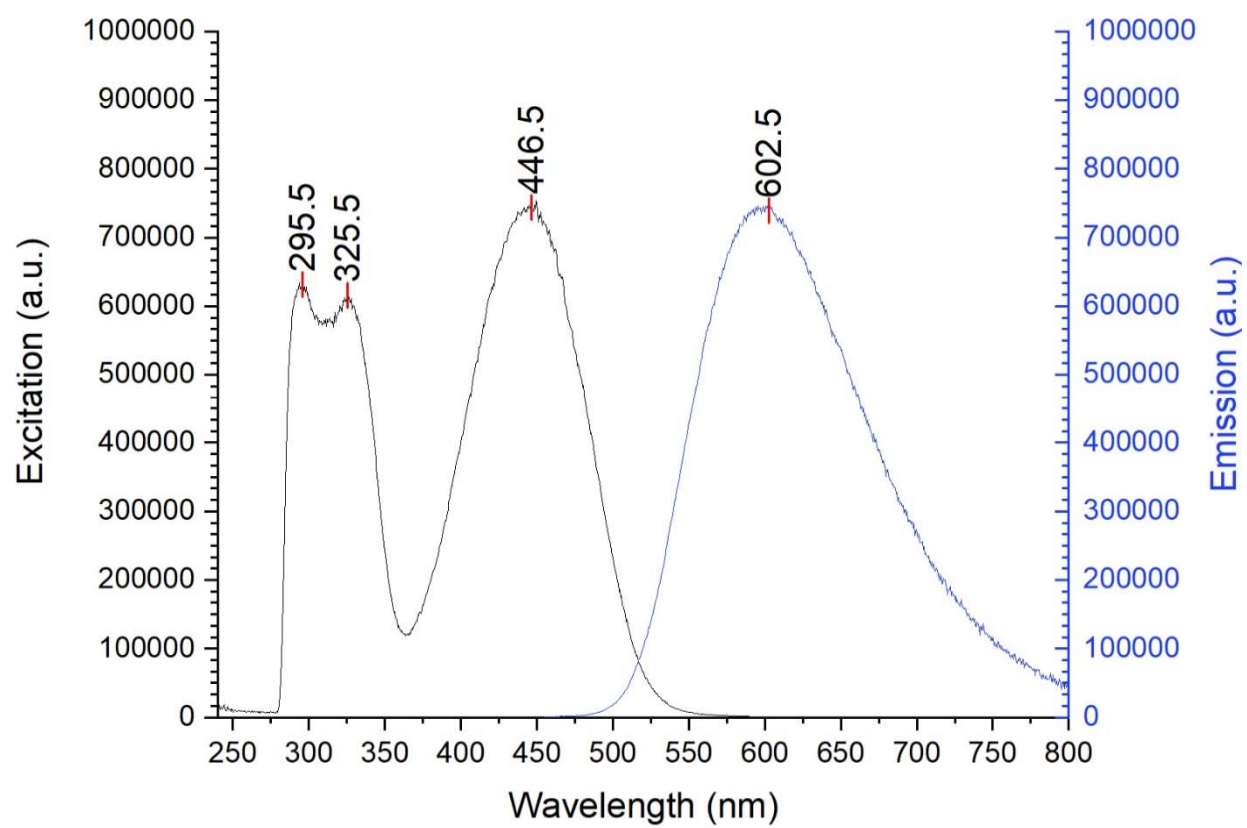


Figure S210 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) spectra of compound **2** and $[\text{Me}_3\text{SiCH}_2\text{OTf}]$; 12.5 μM sample.

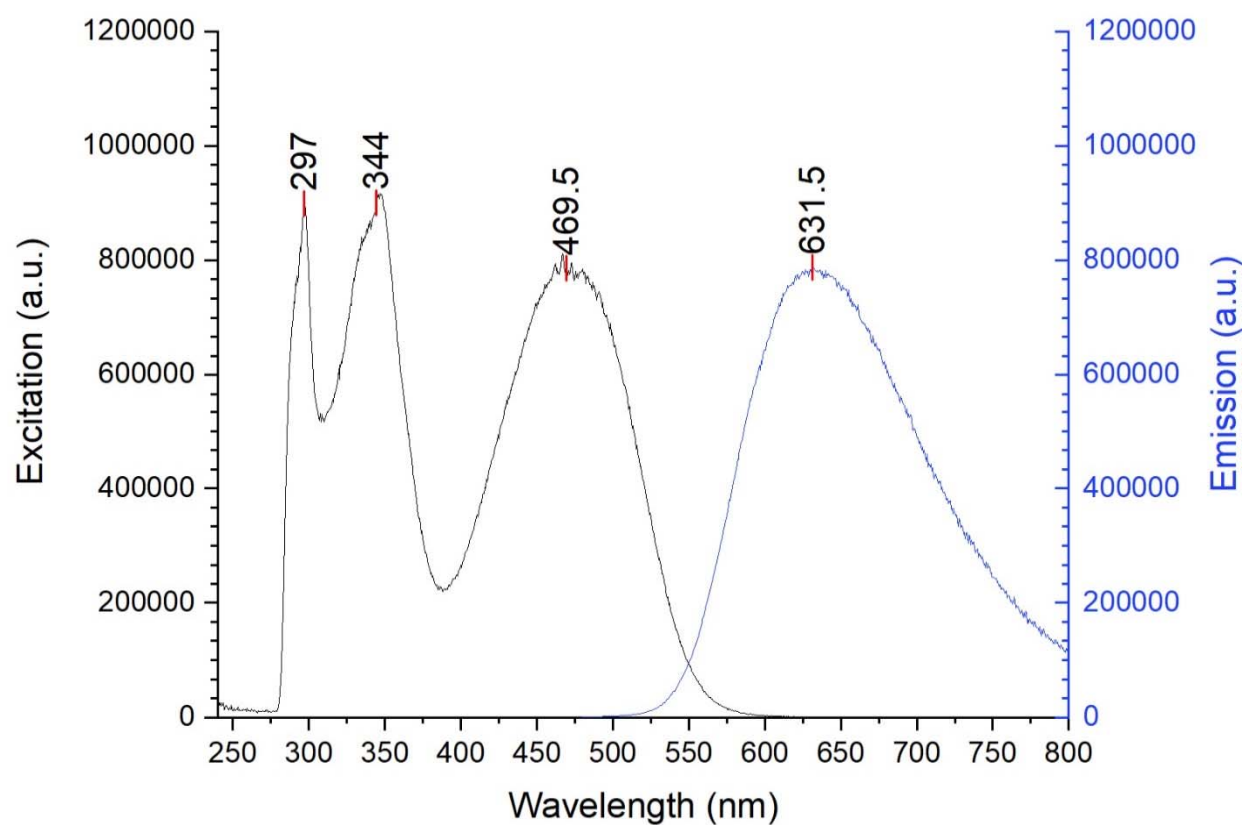


Figure S211 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) spectra of compound **3** and **[Me₃SiCH₂OTf]**; 12.5 μM sample.

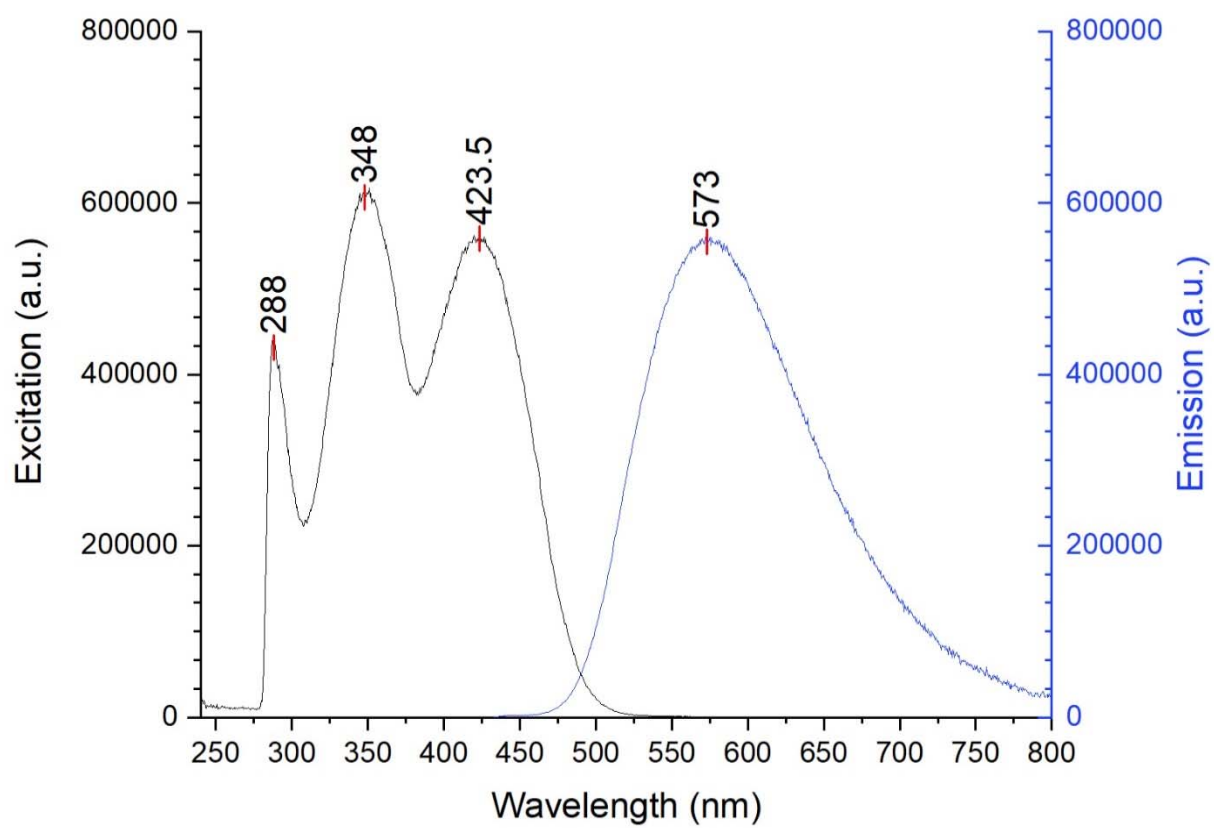


Figure S212 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) spectra of compound **7** and **[Me₃SiCH₂OTf]**; 12.5 μ M sample.

6.1.51. [Me₃SiOTf]

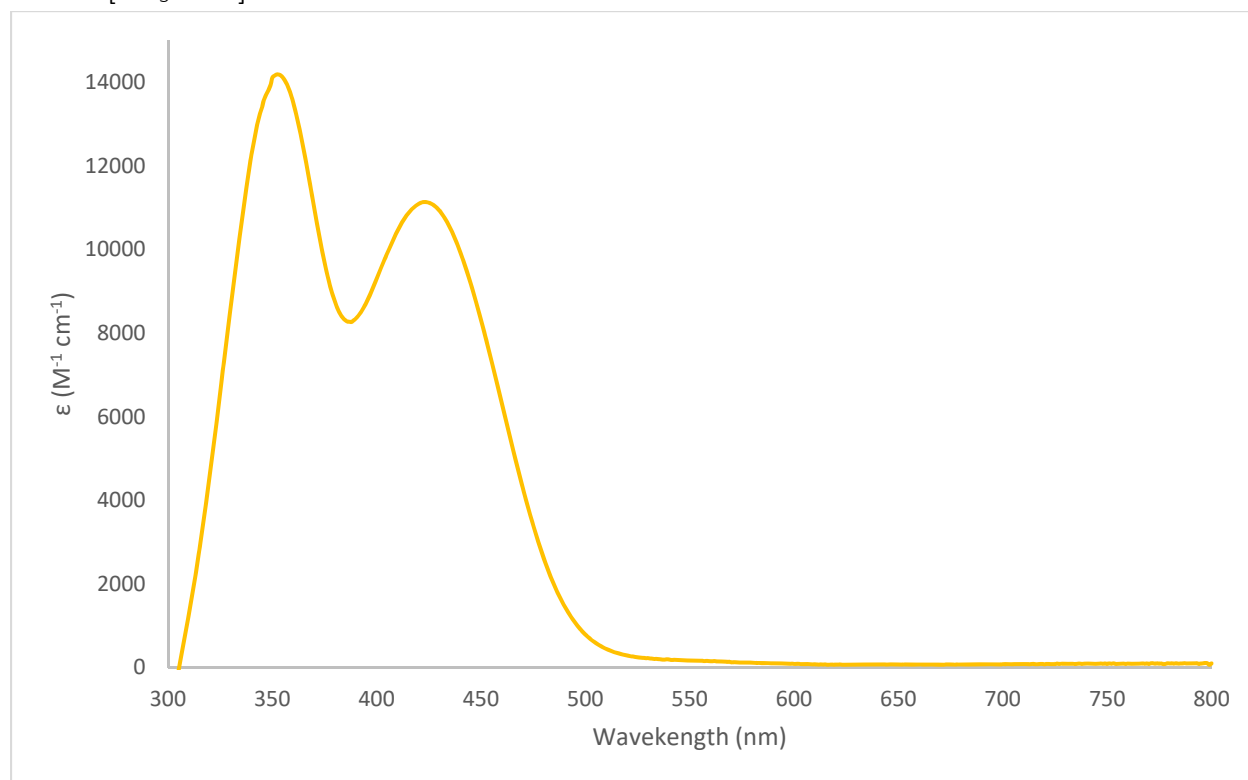


Figure S213 Stacked UV-Vis absorption spectra of **7** (blue) with [Me₃SiOTf] (excess); 12.5 μM samples.

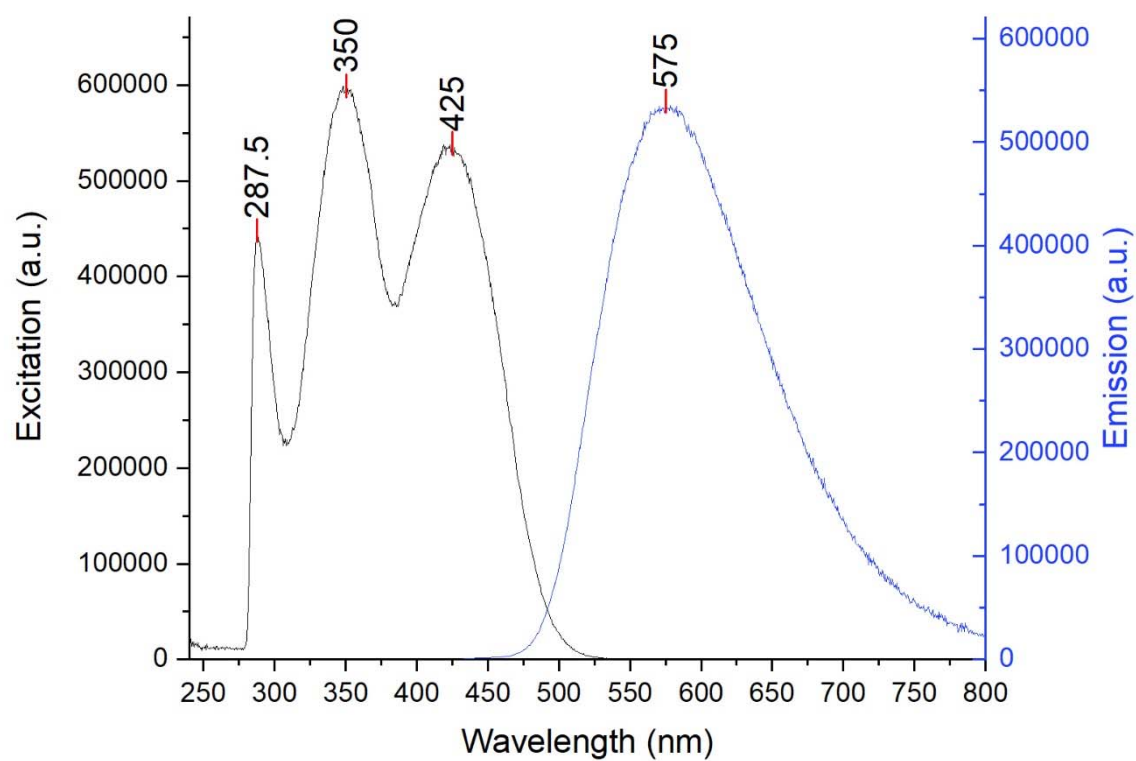


Figure S214 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) spectra of compound **7** and $[\text{Me}_3\text{SiOTf}]$; 12.5 μM sample.

6.1.52. $\text{Zn}(\text{C}_6\text{F}_5)_2$

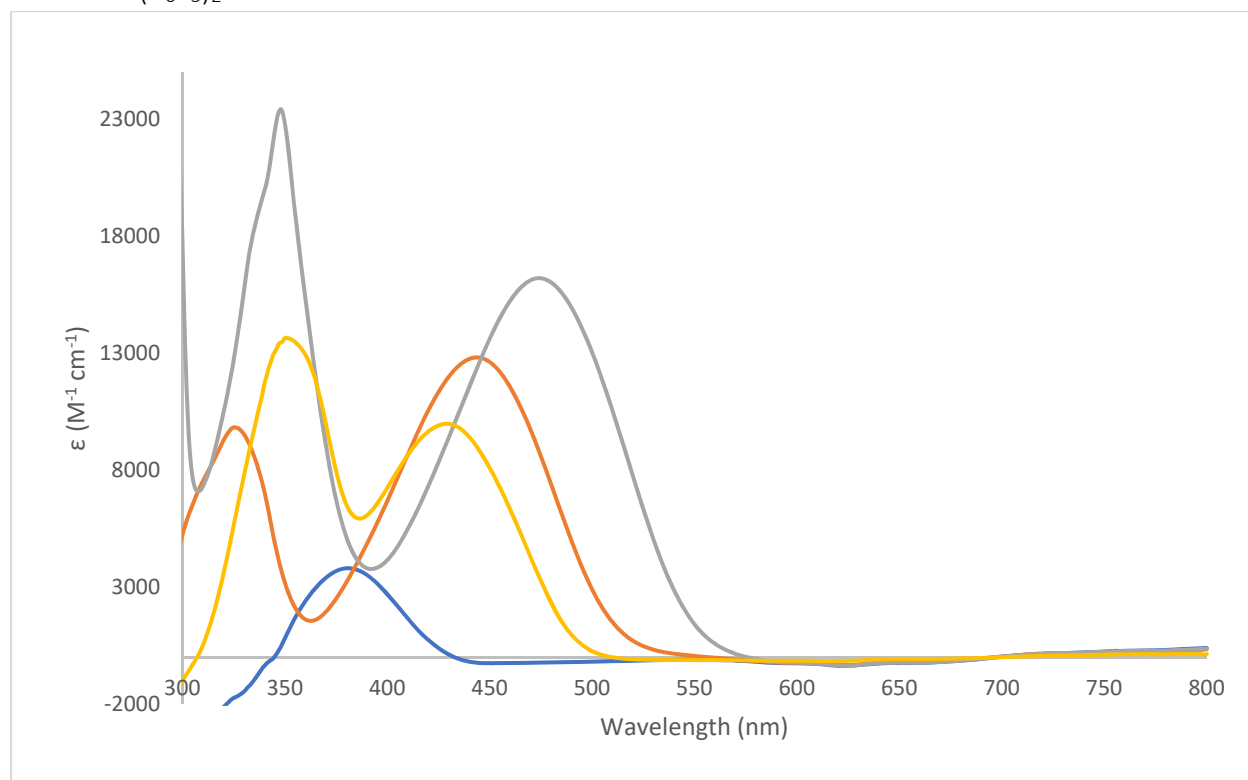


Figure S215 Stacked UV-Vis absorption spectra of **1** (blue), **2** (orange), **3** (grey), and **7** (yellow) with $\text{Zn}(\text{C}_6\text{F}_5)_2$ (1000 eq.); 12.5 μM samples.

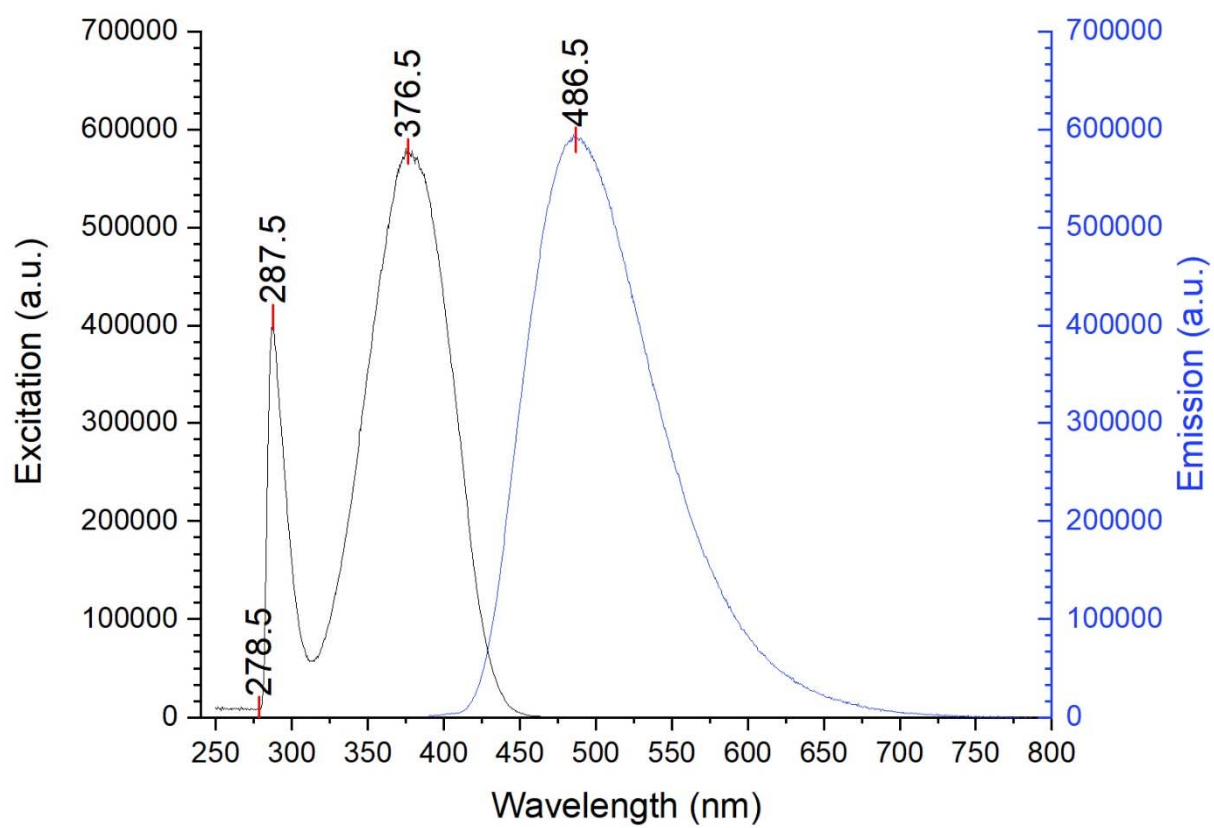


Figure S216 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) spectra of compound **1** and $\text{Zn}(\text{C}_6\text{F}_5)_2$; 12.5 μM sample.

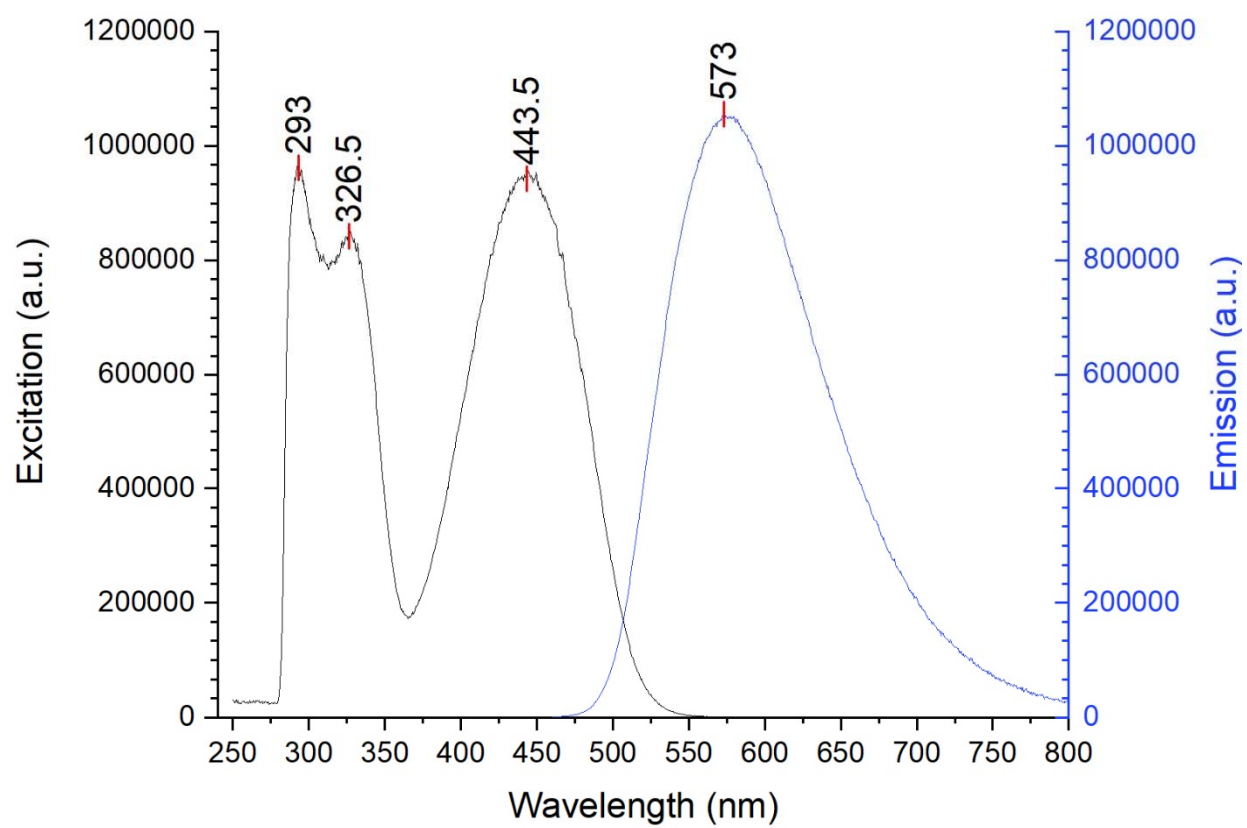


Figure S217 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) spectra of compound **2** and $\text{Zn}(\text{C}_6\text{F}_5)_2$; 12.5 μM sample.

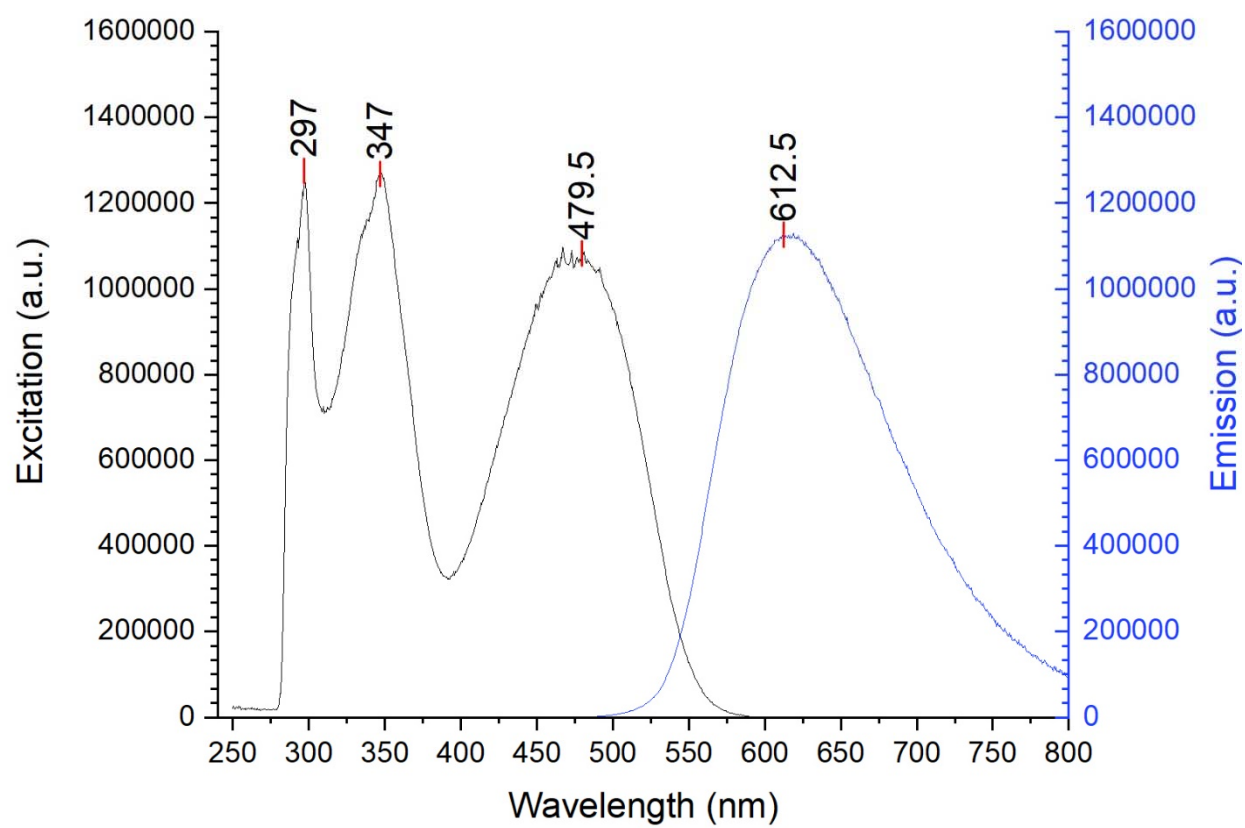


Figure S218 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) spectra of compound **3** and $\text{Zn}(\text{C}_6\text{F}_5)_2$; 12.5 μM sample.

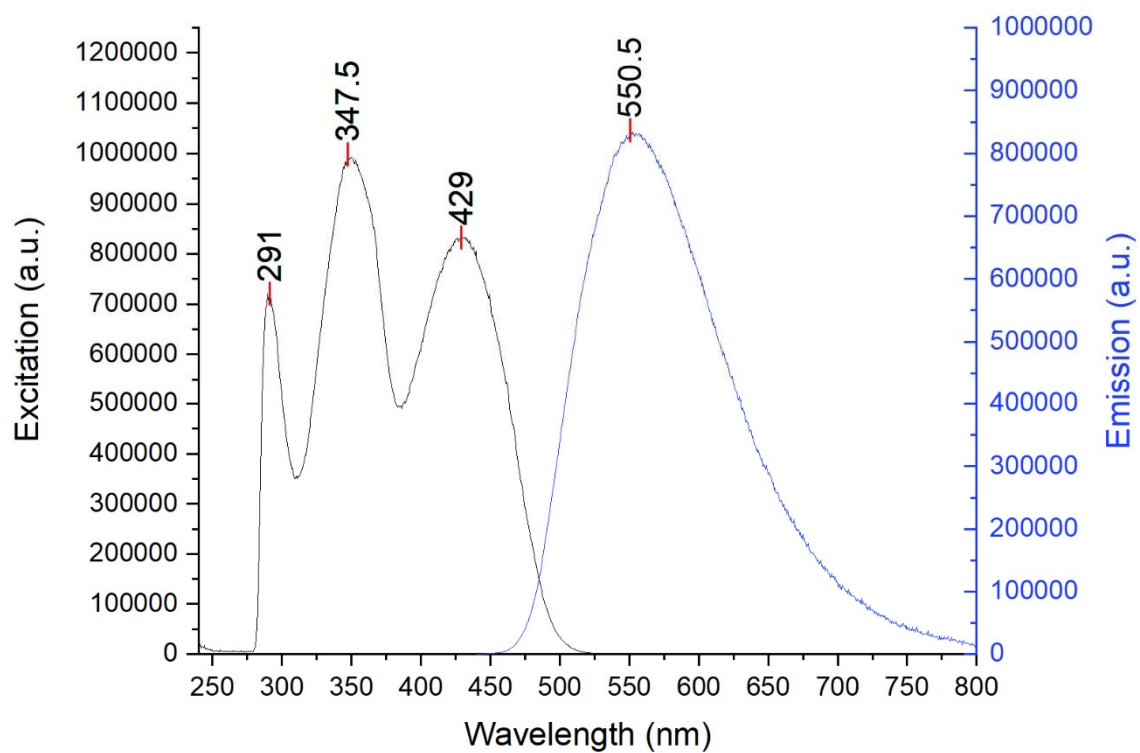


Figure S219 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) spectra of compound **7** and $\text{Zn}(\text{C}_6\text{F}_5)_2$; 12.5 μM sample.

6.1.53. $\text{Zn}(\text{OTf})_2$

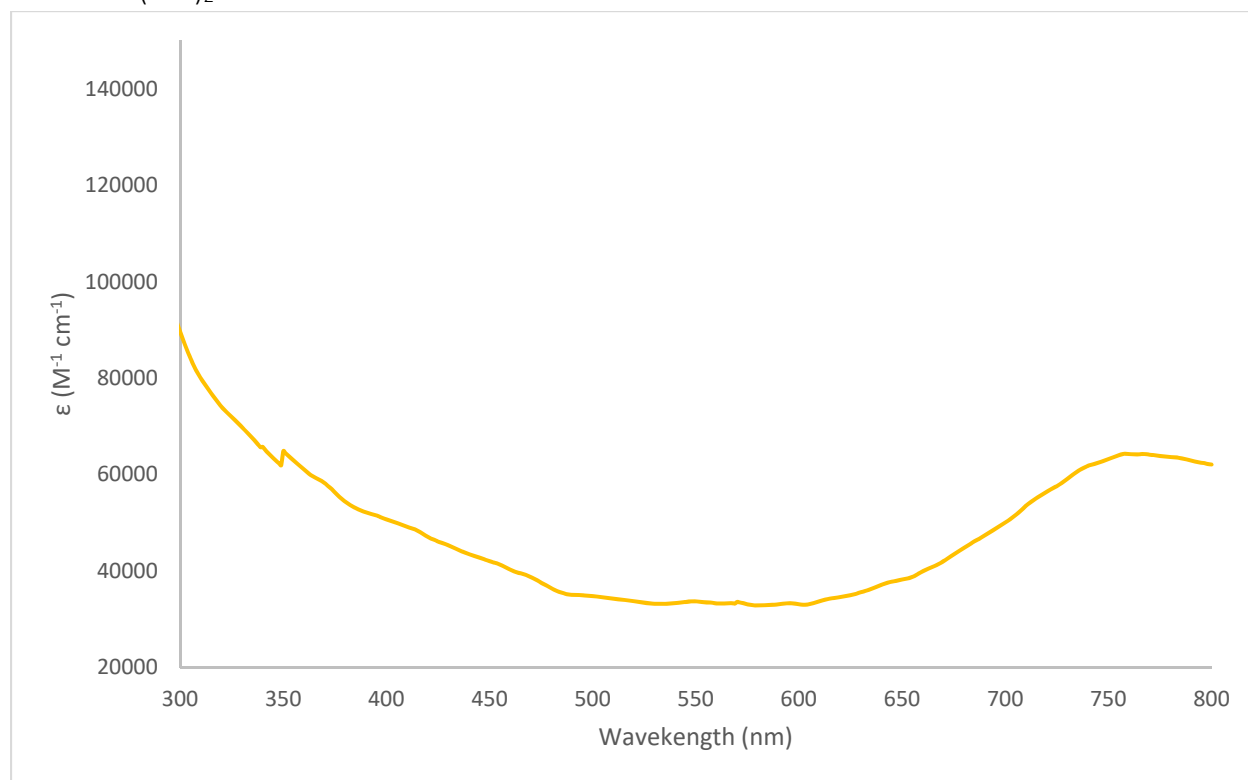


Figure S220 Stacked UV-Vis absorption spectra of **7** (blue) with $\text{Zn}(\text{OTf})_2$ (excess); 12.5 μM samples.

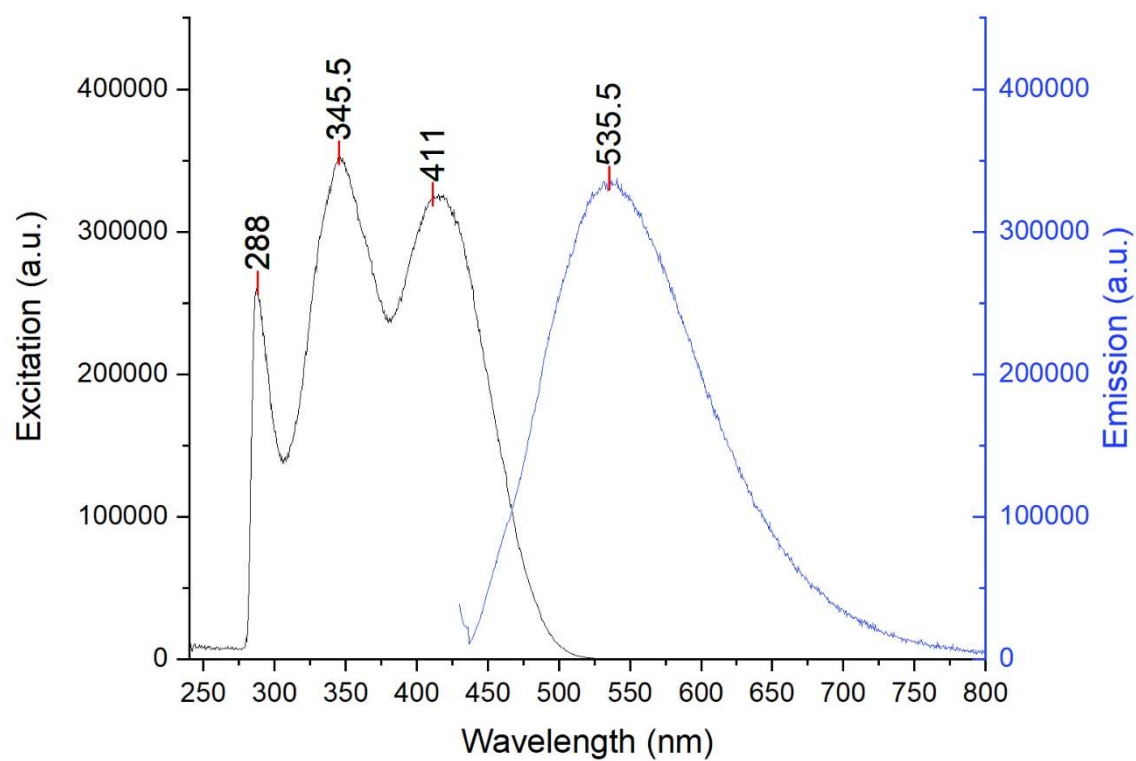


Figure S221 Stacked excitation (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) and emission (step: 0.5 nm/s, dwell time: 0.125 s, slit width: 1.0 nm) spectra of compound **7** and $\text{Zn}(\text{OTf})_2$; 12.5 μM sample.

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>50 Lewis acids mapped

