A “Simple” Donor-Acceptor AIEgen with Multi-Stimuli Responsive Behavior

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Abstract: At present, there is still an urgent demand for novel smart materials that can achieve a diverse range of practical applications in synthetic material area. Herein, we developed a simple but versatile aggregation-induced emission luminogen (1) with a donor-acceptor structure and pronounced intramolecular charge transfer property. Compound 1 showed a remarkable color change in sensitive response to polarity change making it to serve as a promising imaging probe for detecting environmental polarity in cells and selective visualization of lipid droplets in live tissues. Additionally, this compound exhibited a wide range of thermoresponsive behavior with ratiometric luminescence change and noticeable fluorescence color switching. It also can respond to anisotropic shearing force and isotropic hydrostatic pressure with prominent but contrast luminescence conversion due to the distinct disturbance of the weak intermolecular interactions and charge transfer processes. Meanwhile, compound 1 was sensitive to external electric stimulus and displayed reversibly three-color switched electrochromism and on-to-off electroluminochromism. Such property allowed the fabrication of high-performance non-doped OLED with a high external quantum efficiency of 5.22%. The present results may offer an important guideline for multifunctional molecular design and provide an important step forward to expand the real-life applications of AIE-active smart materials.

1. Introduction

In this amazing and beautiful world, living systems, plants or animals, show various adaptive behaviors and a wide variety of intriguing ways to response to stimulus of their surrounding environment.[1-3] Today, scientists and engineers are bewitched by these distinctive and glamorous stimuli-responsive behaviors because investigation of these behaviors may bestow new inspirations for developing diverse bio-inspired and smart materials for real-world applications.[4] One common principle learned from these natural creatures is that their unique and complex physiological functions are derived from their selective integration capability of each particular function related to different kinds of specialized cells.[4a] And this principle has been efficiently utilized for fabrication of various novel materials by researchers through assembling different structural components with special function into composite systems at the molecular level to achieve multi-functional materials.[5]

So far, there is still an urgent demand for novel smart materials that are able to support more efficient technologies and to achieve a diverse range of practical applications in synthetic material area.[6-9] By utilizing the integration strategy, synthetic scientists have
developed a wide variety of new smart systems that are able to response to multiple environmental stimuli. For instance, Thayumanavan et al. reported a novel triple stimuli sensitive block copolymer assembly with responses to changes in temperature, pH and redox potential by incorporating an acid-sensitive THP-protected HEMA and a temperature-sensitive PNIPAM with a redox sensitive disulfide linker. Weder’s group reported the first supramolecular polymer materials with thermomechanical characteristics of a supramolecular polymer glass by combining mechanoresponsive luminescent compounds with the concept of supramolecular polymerization. Wang and co-workers prepared triple stimulus sensitive supramolecular hydrogel that responded to changes in temperature, light and reduction through the combination of cyclodextrin-based host–guest complexes, poly(N-isopropylacrylamide) chains, azobenzene groups and disulfide bonds. Accordingly, these multiple responsive systems are generally constructed by the integration of multiple components with specific responsive ability. Thus precise control of each unit and even intricate and time-consuming organic synthesis are required.

Owing to the vacant p-orbital on the central boron atom, triarylborons (TAB) serve as excellent electron acceptors. When associating with amine-based electron donors, the incorporated donor-acceptor (D-A) small-molecule systems show unprecedented photophysical and photochemical properties resulting from the eminent and unique intramolecular charge transfer (ICT), and relevant extensive applications in optical storage and memory, optoelectronic and display devices, chemical sensors, security inks and papers, etc. have been developed. Indeed, many pioneering and elegant TAB-amine systems with intriguing stimuli-responsive properties have been developed by researchers through rational design. While a majority of them displayed only one specific responsive function, little effort had been placed to explore their versatility and capacity in multifarious applications. In this respect, it would be desirable and amazing if we could integrate these individual responsive properties into a single small-molecule system without involving tedious synthetic tasks. More importantly, developing simple and versatile small molecule materials with various kinds of environmental responses would solve the limitations of smart materials in practical applications and further expand their application scope.

Herein, we report a simple but versatile TAB-containing molecule with D-A structure, aggregation-induced emission (AIE) and pronounced ICT effect (Figure 1A). This luminogen is sensitive to multiple stimuli, including solvent polarity, temperature, mechanical shearing force, hydrostatic pressure and electric field. Each of them could been specifically visualized by the prominent photoluminescence (PL) color change. To the best of our
knowledge, the realization of such multifunctional properties, including solvatochromic PL and further environmental polarity detection in cells, thermo-chromic PL, mechano-chromic PL, electrochromism and electroluminochromism as well as electroluminescence, in a single small molecule have not been reported to date. Another unique aspect of the present system is that each responsive behavior has their own specialties and we will elaborate their stories in the forthcoming contents.

Figure 1. (A) The molecular structure of compound 1. (B) PL spectra of 1 (1.0 × 10⁻⁵ M) in DMF/water mixtures with different water fraction (f_w). λ_ex = 390 nm. (C) Plot of relative PL intensity (α_AIE) at 500 nm versus f_w of the DMF/water mixtures of 1, where α_AIE = I/I₀ and I₀ = emission intensity in pure DMF solution. Inset: photos of DMF solution and DMF/water mixture (f_w = 90%) of 1 taken under 365 nm UV light.

2. Results and Discussions

2.1. AIE, Solvatochromic Photoluminescence and Biological Application

The target compound 1 was facilely prepared in a high yield of 79% through a simple one-step reaction along the synthetic route as presented in Scheme S1 in the Supporting Information. The product was well characterized by NMR and high-resolution mass spectroscopy with satisfactory results. Detailed information were provided in the Supporting Information (Figures S1-S3). The structure of 1 was further confirmed by single crystal X-ray diffraction (details see below) and the associated data was summarized in Table S1.
As anticipated, compound 1 featuring propeller shape exhibited typical AIE property (Figure 1).[21] When the sample of 1 was dissolved in pure DMF solvent at low concentration, the solution was completely non-emissive. However, with the addition of water, its emission boosted with a dramatic ~27000-fold enhancement when the water fraction reached 40%, while the luminescence intensity remained almost unchanged with the further increase of water fractions. As demonstrated in our previous work,[20a,22] the single crystal structure of 1 bears a very twisted molecular conformation with the corresponding torsion angles of 31.23 ($\theta_1$), 39.34 ($\theta_2$), 39.32 ($\theta_3$), 57.85 ($\theta_4$), and 47.72 ($\theta_5$), respectively, as shown in Figure S4 (Supporting Information). Accordingly, the rotations of multiple flexible aryl rotors are greatly restricted in different aggregate states as verified by the viscosity test (Figure S5), which blocks the radiationless consumption of the excitation energy and facilitates the radiative decay channel, and thus compound 1 molecule becomes highly emissive. We also measured the THF-water mixture system and found it exhibited aggregation-induced PL change (Figure S6) due to the coexistence and competition of AIE and the twisted intramolecular charge transfer (TICT) process.[15]

**Figure 2.** (A) PL spectra of compound 1 measured in different solvents. (B) Linear correlation of the orientation polarization ($\Delta f$) of solvent with Stokes shift ($\nu_a - \nu_f$) for 1 ($R^2 = 0.991$). Inset: CIE chromaticity diagram showing the temperature dependence of the (x, y) color coordinates of 1. Concentration: $1.0 \times 10^{-5}$ M; $\lambda_{ex} = 390$ nm. Abbreviation: TEA = triethylamine, IPE = isopropyl ether, DEE = diethyl ether, EA = ethyl acetate, THF = tetrahydrofuran, DCM = dichloromethane, DMF = $N,N'$-dimethylformamide, ACN = acetonitrile.

As literatures well documented,[15,23] a large molecular dipole of D-A structures is considered to reveal intriguing photoluminescence behavior depending on the solvent polarity due to the conversion between less polarized locally excited (LE) state and polarized TICT
state. As expected, compound 1 demonstrated a strong solvatochromic effect (Figure 2). When the solvent polarity was increased gradually from low-polarity hexane to high-polarity acetonitrile, the emission of its solution exhibited a dramatic bathochromic shift and the intensity gradually weakened due to the susceptibility of the TICT state to various nonradiative quenching processes (details see Table S2 in the Supporting Information). Meanwhile, its solution colors changed from bright blue in nonpolar hexane over green, yellow and orange in lower polar solvents (such as ether, ethyl acetate, THF and DCM) and then to dark red in high polar solvents (acetone, DMF and acetonitrile), thus covering the whole visible region as shown in the CIE diagram obtained from the PL spectra (Figure 2B), and allowing even a visual estimate of the solvent polarity. In sharp contrast, its absorption spectra displayed no obvious change as the solvent polarity increased (Figure S7). Quantitatively, the relationship between the Stokes shift ($\nu_a - \nu_f$) of the luminogen and solvent parameters, or the orientation polarizability $f(\varepsilon, n)$ can be described by the Lippert–Mataga equation:

$$\hbar c (\nu_a - \nu_f) = \hbar c (\nu_a^0 - \nu_f^0) + \frac{2(\mu_e - \mu_g)}{a^3} f(\varepsilon, n)$$

Where $\hbar$ is Plank’s constant, $c$ is the velocity of light, $f$ is the orientational polarizability of the solvent, $\nu_a^0 - \nu_f^0$ corresponds to the Stokes shifts when $f$ is zero, $\mu_e$ is the excited-state dipole moment, $\mu_g$ is the ground-state dipole moment, $a$ is the solvent Onsager cavity radius, and $\varepsilon$ and $n$ are the solvent dielectric and the solvent refractive index, respectively (Table S2, Supporting Information). As shown in Figure 2B, the experimental data of 1 obeys a good linear relationship expected by Lippert–Mataga equation in the whole range of solvent polarity, further confirming its typical TICT character. Additionally, obvious charge separation in its natural transition orbitals (NTO) of the first singlet excited state also verified the large molecular dipole of compound 1 further reflecting its ICT character (Figure S8). The aforesaid solvatochromic PL behavior is essentially a visualization for marked solvent polarity changes which takes place on a molecular-microscopic level.

Herein, it is noteworthy to mention that polarity is an utmost important parameter in chemistry, nanotechnology, and even life science. In biological systems, especially at the cellular level, polarity determines the interaction activity of large numbers of proteins and enzymes or reflects the permeability of membrane compartments. Furthermore, abnormal changes in polarity are closely linked with disorders and diseases (e.g., diabetes, liver cirrhosis). However, the environmental polarity change in biological systems is relatively subtle, thus it is very difficult to realize its measurement in a straightforward manner, let
alone its macroscopic visualization. Therefore, our present system, featuring remarkable polarity dependence and obvious fluorescence change, is expected to provide a valuable tool for the detection of biological environmental polarity change.

**Figure 3.** (A, B) Two-photon microscopic images of MCF-7 cells treated without (A) or with (B) oleic acid (OA) and then stained with compound 1 for 5 h. (C) Reconstructed 3D two-photon microscopic images of the excised mesenteric adipose tissues of nude mouse stained with compound 1 for 30 min. Two-photon excitation wavelength: 780 nm. The two-photon fluorescence emitted from 1 were captured through two filters: 420-460 nm (blue, A1-C1) and 495-540 nm (green, A2-C2). A3-C3: merged images of blue and green channels (bright field). Scale bar: 20 μm.

To demonstrate the practical application of 1 as a fluorescent bioimaging probe for the environmental polarity in biological systems, two-photon fluorescence imaging in live cells was performed by using a two-photon microscope (Olympus FV1200MPE) and MCF-7 cells as model (Figure 3). Prior to live cell imaging, the cytotoxicity of 1 was assessed by the standard MTT assay and the results indicate that 1 exhibits no cytotoxicity towards MCF-7
cells (Figure S9). After incubation with MCF-7 cells for 1 h, weak green fluorescence detected in the range of 495-540 nm of 1 was observed from the cells (Figure S10A), and the signal was greatly intensified by extending the incubation time to 5 h (Figure 3A). Further co-staining experiment with commercial Lysotracker Red indicated that 1 was mainly localized in lysosome (Figure S11A). Given that lipid droplets (LDs) are extremely hydrophobic and their polarity is lower than other intracellular regions,[1] we anticipated that hydrophobic 1 should be more inclined to target LDs and the detected fluorescence should be blue-shifted and the corresponding intensity should be much stronger than in the lysosome. To verify our presumption, MCF-7 cells were treated with oleinic acid (OA) to induce the formation of LDs intracellularly. As expected, in addition to the original green fluorescence signal, newly appeared and strong blue fluorescence signal in the range of 420-460 nm was detected in the OA-treated MCF-7 cells. More importantly, the blue signal was relatively dominant and the resulting merged images were blue emissive as clearly shown in Figure 3B and Figure S10B. As shown in Figure S12, a much better colocalization of 1 with BODIPY, a commercial lipid droplet dye, was observed, further verifying that probe 1 was dramatically enriched in the hydrophobic lipid droplets and thus signals their much lower polarity. Therefore, the above noticeable difference in the fluorescence signals observed before and after OA treatment explicitly demonstrates that the drastic color change of 1 realized a discrimination of the cellular environmental polarity. It is noteworthy to mention that the above study also indicates that probe 1 is highly suitable for direct and selective lipid droplet visualization in biological systems. Furthermore, given that two-photon fluorescence microscopy in tissue imaging exhibits remarkable advantages over traditional fluorescence techniques such as deep penetration, high 3D resolution, and in situ visualization with simple operation.[2] We further applied compound 1 for two-photon microscopic images of the excised mesenteric adipose tissues of nude mouse (Figure 3C and Figure S13). As shown in Figure 3C, the reconstructed 3D two-photon microscopic images of the ex vivo tissues displayed similar noticeable and dominant blue fluorescence signal to that observed in MCF-7 cells, indicative of the excellent lipid droplets imaging property of probe 1 in tissues.

2.2. Thermochromic Photoluminescence

In general, the luminescence of organic compounds in solution state is quenched with the increase of temperature. And most of the TICT systems also have the same quenching problem at high temperature.[16] However, it is intriguing that our present system can achieve a continuously enhanced emission by increasing temperature. From another perspective, this temperature effect is also a powerful evidence to reinforce that the TICT process is really
involved. Typically, in THF solvent with a moderate polarity, two discernible bands centered at 556 and 596 nm, respectively, could be observed. As demonstrated in Figure 4, increasing the temperature from 29 °C to 47 °C led to a change of their relative intensities. Additionally, there is an excellent linearity between their intensity ratio ($\lambda_{556}/\lambda_{596}$) and the temperature in the range from 29 °C to 47 °C, including a vital physiological temperature range, suggesting that the present ratiometric system may be useful for the quantitative determination of temperature. More interestingly, a noticeable luminescence color transition from dark orange to bright yellow was accompanied with the above temperature elevation process. Therefore, our system could realize a visual and ratiometric temperature detection.

It has been recognized that solvent polarity is heavily temperature-dependent. In weak polar toluene, similar intensity-intensified and blue-shifted tendency could be observed with the increase of temperature, while these variations were comparatively more conspicuous and were accompanied by striking color changes in relatively higher polarized solvents, i.e. dichloroethane and o-dichlorobenzene, as shown in Figure S14.

**Figure 4.** (A) Temperature-dependent fluorescence spectra of 1 in THF solution ($1 \times 10^{-5}$ M; $\lambda_{\text{ex}} = 390$ nm). (B) Plot of the corresponding intensity ratio ($\lambda_{556}/\lambda_{596}$) with temperature ($R^2 = 0.988$).

In another aspect, thermochromic solutions of compound 1 also allow a simple quantitative determination of the temperature dependence, thus possessing great potential to be used as luminescent thermometer. In order to test its response range and facilitate its application, we have selected tetraethylene glycol dimethyl ether (TRIEDM) with a very high boiling point of 275 °C and ideal stability as the solvent. As shown in Figure 5, its emission band gradually blue shifted and the corresponding intensity was continuously enhanced with the increase of temperature. What is exciting that its luminescence color also exhibited obvious conversion from orange to bright yellow-green. Due to the limitations of the
temperature control device, we only detected up to 175 °C, but it is reasonable to predict that the above change tendency would be continuous if temperature condition permits and its solution colors probably cover the whole visible region as shown in the CIE diagram in Figure 5C. Moreover, there is also a good linear relationship between the intensity ratio \( \frac{\lambda_{535}}{\lambda_{600}} \) and the temperature in a wide range of 25 to 175 °C. It should be mentioned that the above temperature-dependent emission evolution and color conversion are completely reversible. Such intriguing properties inspired us to fabricate a simple liquid thermometer by utilizing the above TRIEDM solution system. As illustrated in Figure 5D, when we heated the above solution from the top and synchronously cooled it from the bottom, apparent color changed pattern, corresponding to specific temperature gradient, could be directly observed with our naked eyes. This is only a very simple trial but it is reasonable to anticipate that the above color switching should be much more prominent if higher temperature can be achieved. In light of the above excellent properties, our system should be a promising candidate for high performance thermometers with a wide detection range and high upper limit.

**Figure 5.** (A) Temperature-dependent fluorescence spectra and (B) plot of the corresponding intensity ratio \( \frac{\lambda_{535}}{\lambda_{600}} \) of 1 in tetraethylene glycol dimethyl ether with temperature \((1 \times 10^{-5} \text{ M}, \lambda_{\text{ex}} = 390 \text{ nm}, R^2 = 0.993)\). (C) CIE chromaticity diagram showing the temperature
dependence of the \((x, y)\) color coordinates of \(1\). (D) The gradient fluorescence of \(1\) solution in a quartz tube.

We were then interested in unveiling the underlying mechanism of the above polarity-dependent and thermochromic PL behaviors, which was envisaged to provide an initial guideline for the design of new polarity and temperature responsive materials. Taking all the experimental data together, we proposed that raising temperature will lead to the increase of solvent hydrophobicity, thus benefiting the planar geometry and resulting in intensified emission intensities and blue-shifted luminescence.\(^{[15g,28]}\) As the literature documented,\(^{[15g]}\) we also measured the mixed system composed by polar THF and nonpolar hexane to verify our presumption above (Figure S15). As expected, the results demonstrated that the emission was gradually enhanced and blue shifted with the increase of solvent hydrophobicity brought from the increase of hexane fraction. Given that temperature switching is considered to induce dynamic changes in molecular conformations. We then devoted to obtain persuasive evidence from the theoretical calculations. Considering there are multiple flexible aryl rotors of our present system, we performed plenty of attempts on various conformations of the excited state \(S_1\). Ultimately, we found that the central plane formed by atoms C16, N2 and C25 is the pivot to determine the flexible conformation, and is also the critical position linking the charge separated donor and acceptor units. Upon excitation to \(S_1\), the molecule rotates around the N2–C25 bond, and the associated C16–N2–C25–C30 dihedral angle varies from \(\sim 30^\circ\) to \(\sim 90^\circ\), thus possessing a more twisted conformation as demonstrated in Figure 6A. Combined with the most populated transitions of molecular orbitals, the twisting degree of molecular conformations could be well elucidated by the variation of central dihedral angle C16–N2–C25–C30. In order to clarify its influence on the photoluminescence, we calculated the PL spectra of eight different conformations by scanning different twisting angles of C16–N2–C25–C30 (computational details see the Supporting Information). As shown in Figure 6B, a gradual red shift and attenuation of photoluminescence could be observed with the dihedral angle varying from 0° to 90°. These results reveal that more planar conformation should greatly facilitate the fluorescence emission. We also calculated the potential energies of these eight conformations in the excited states. The potential energy of the planar conformation with 0° is about 14 kcal/mol higher than that of the twisted conformation with 90° (Figure 6), thereby further indicating much higher stability of the latter. The theoretical calculations together with the evidences from the polarity-dependent and thermochromic studies reinforced our previous envision that both the polarity and the temperature strongly influenced the dynamic equilibrium between the planar and the twisted conformations, and
lower polarity and higher temperature are suggested to facilitate the stability of planar geometry, further resulting in blue-shifted and enhanced photoluminescence.

**Figure 6.** (A) Molecular structures of the ground state and the excited state of I based on TDDFT calculations at B3LYP/6-31G(d) level. (B) Simulated fluorescence spectra and (C) calculated potential energies of different conformations in the excited state of I.

### 2.3. Mechanochromic Photoluminescence

Excitingly, this compound is also very sensitive to the external shear force stimulus and exhibits attractive tribochromic PL behavior (Figure 7). We found that the solid showed red-shifted and remarkably enhanced emission when the powder was ground under shearing force. Upon grinding, its emission color changed from blue to yellow-green with the maximal fluorescent peak shifted from 480 nm to 509 nm, and the corresponding quantum yield also dramatically increased up to 86% from the original 52% (Figure 7A and 7C). It’s also appealing that the color transition after grinding could be directly observed with naked eyes in daylight (Figure S16). When the ground powder was exposed to dichloromethane (DCM) vapor, the original blue state could be restored completely as the PL spectra verified, indicative of a reversible tribo-responsive process. Given its excellent triochromic PL behavior, we further explored the practical application in rewritable paper. By immersing the filter paper into the DCM solution of I and then drying by blower, we prepared a blue emissive rewritable paper, on which we can write any legible and yellow-green letters such as...
“AIE” with a sharp rod. When exposing the filter paper in DCM atmosphere for a few minutes, the written letters can be easily erased. And the above writing-erasing process could be repeated many times. Accordingly, this compound could potentially be applicable for security inks and papers.[29]

Figure 7. (A) PL spectra of 1 before grinding, after grinding, and after treatment with dichloromethane vapor. $\lambda_{ex} = 390$ nm. (B) photographs taken under irradiation with 365 nm UV light. (C) Writing and erasing of letters “AIE” on the filter paper using 1 taken under UV light. (D) Photos of 1 powder taken under different pressure. (E) Fluorescent spectra of 1 powder during compression and (F) decompression via DAC (diamond anvil cell). Excitation wavelength was 365 nm.
To get more insight into the tribochromic PL mechanism, powder X-ray diffraction (pXRD) measurement was performed on 1 sample in different states. As demonstrated in Figure S17, the pristine state of 1 exhibits sharp and intense diffraction peaks, suggesting a well-defined crystalline state; while relatively weak reflections could be observed after grinding, indicative of significant destruction of crystalline state by mechanical forces. In this state, the amorphous species should be predominantly produced. Upon fuming in the DCM atmosphere, the original sharp signals could be restored, which reveals the recovery of the crystalline state. Therefore, the observed tribochromic PL behavior of 1 is explicitly involved in a reversible morphological transformation between the blue crystalline state and the amorphous yellow-green state.\textsuperscript{[30]}

Given that this compound can respond to anisotropic shearing force, we also explored its responsive behavior to isotropic hydrostatic pressure. As shown in Figure 7D, compound 1 suffered remarkable and continuous color variation over three stages from blue to yellow and then to orange with the \textit{in situ} pressure increasing. Concomitantly, the fluorescence spectra exhibited a gradual red shift from 481 nm to 588 nm (Figure 7E), but its intensity decreased continuously, which is noticeably different from that of its ground state. However, once the pressure was released, it gradually reverted back to the initial state (Figure 7F and Figure S18). To probe the structural change during the above piezochromic PL process, \textit{in situ} high-pressure Raman experiment was performed on this compound\textsuperscript{[31]} As demonstrated in Figure S19, all the Raman peaks displayed blue-shift with elevated external pressure, which is presumably attributed to the simultaneously shortened bond lengths and decreased intermolecular distances.

Combined with the DFT calculation results (Table S3), the peaks at 709, 723, and 740 cm\textsuperscript{-1} are attributed to the C–H bond off-plane wagging vibrations, and their respective intensities gradually decreased with the increase of pressure; while the peaks ascribed to breathing vibrations of benzene ring at 997 cm\textsuperscript{-1} (P1, P2 and P4) and 1002 cm\textsuperscript{-1} (P3 and P5) gradually blue shifted and fused into one single peak with the increase of high pressure. Accordingly, it’s reasonable to think that the intermolecular interactions would be enhanced under increasing hydrostatic pressure and this isotropic force mainly influences the intermolecular interactions, where all the molecules are squeezed into a quite compact condition during the compression process.\textsuperscript{[29b,32]} Once the pressure was released, it can return to the initial state.
The above observations raise a question: why the mechanical grinding and hydrostatic pressure triggered distinct luminescence alterations? The analysis of crystal structure was expected to provide some clues to address this issue. As shown in Figure 8A, multiple weak intermolecular C–H···π interactions (distances ranging from 3.06 to 3.43 Å) between the adjacent molecules could be observed, which play a vital role in fixing the orientation of the diamine donor and the triarylboron acceptor. Additionally, we also noted that the intermolecular amine donor and the boron acceptor units get very close to each other (Figure 8B), which is enough to cause intermolecular charge transfer processes. In the molecular packing, the molecules form ordered but very loose arrangements (Figure S20). Accordingly, regarding the mechanism of tribochromic PL behavior, we presume that these weak intermolecular interactions and the intermolecular charge transfer processes should be perturbed by the anisotropic stimulus of mechanical grinding, which is also accompanied by the intramolecular conformational planarization, and both factors synergistically result in a red-shifted and remarkably enhanced emission (Figure 8C). While the situation is presumably
different for the piezochromic PL process. The isotropic high pressure is strong enough to squeeze the adjacent molecules close enough that inevitably generates intermolecular π–π interactions and can facilitate intermolecular charge transfer processes, thus jointly leading to the red-shifted and annihilated emission (Figure 8C).[33] The above analyses further imply the significant role of molecular packing in controlling the solid-state luminescence.

2.4. Electrochromic and electroluminescent properties

The electrochemical behavior of compound 1 was investigated by cyclic voltammetry and square-wave voltammetry in deaerated CH₂Cl₂ containing 10⁻¹ mol/L n-Bu₄NPF₆ as the supporting electrolyte (Figure S21). Compound 1 exhibited two well-defined reversible oxidation peaks at 0.81 and 1.10 V (vs. Ag/Ag⁺), respectively, and one quasi-reversible reduction peak at -2.00 V (vs. Ag/Ag⁺). The oxidation peaks are ascribed to stepwise oxidation of the diamine donors and the reduction process is attributed to reduction of the diarylboron acceptor.[34] In addition, the HOMO and LUMO energy levels of compound 1 were determined to be -5.18 and -2.34 eV, respectively, and the HOMO-LUMO band gap was 2.84 eV (Table S4).

![Figure 9](image)

**Figure 9.** (A and B) Electrochromism and (C) electroluminochromism of 1 in THF/0.1 M n-Bu₄NPF₆ at 298 K. Inset: Photos of 1 at different oxidation states taken under (A and B) day light and (C) 365 nm UV light.
Interestingly, compound 1 can also respond to the external electric stimulus and exhibited remarkable change in its electronic spectra in the near-infrared (NIR) region and different colors associated with its different oxidation states during the *in situ* spectroelectrochemical measurements (Figure 9). As demonstrated in Figure 9A and 9B, the completely reversible conversion among three different colors could be readily achieved by modulating the redox potentials of compound 1, *i.e.* light yellow, vivid green, and dark green, corresponding to neutral, monocationic, and dicationic states, respectively, which could be directly observed with naked eyes. Therefore, the above distinct properties of 1 indicate that this compound has great potential to be used as an electroswitchable electrochromic material. Regarding its emission spectra, it can also realize a transformation from turn-on state to turn-off state upon slow oxidation to the mono-cationic state with its orange luminescence gradually weakened (Figure 9C), also pointing to its potential application in information recording and storage devices.

**Figure 10.** (A) EQE versus brightness curve (inset: EL spectrum at 10 mA cm$^{-2}$), (B) Current density–voltage–luminance plot. (C) Voltage-dependent EL spectra and (D) CE and PE versus brightness curve of a EL device with a configuration of ITO/HATCN (5 nm)/TAPC (25 nm)/Emitter (35 nm)/TmPyPB (55 nm)/LiF (1 nm)/Al.
Table 1. EL performance of OLED.

<table>
<thead>
<tr>
<th>Emitter</th>
<th>( \lambda_{EL} ) (nm)(^a)</th>
<th>( V_{on} ) (V)(^b)</th>
<th>( L ) (cd/m(^2))(^\text{a})</th>
<th>( \eta_c ) (cd/A)(^\text{a})</th>
<th>( \eta_p ) (lm/W)(^\text{a})</th>
<th>EQE (%)(^\text{a})</th>
<th>CIE (x, y)(^c)</th>
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<td>1</td>
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<td>4.1</td>
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<td>16.23</td>
<td>11.69</td>
<td>5.22</td>
<td>(0.289, 0.551)</td>
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\(^a\) The luminescence (\( L \)), current efficiency (\( \eta_c \)), power efficiency (\( \eta_p \)), and external quantum efficiency (\( \eta_{ext} \)) are the maximum values of the device.  
\(^b\) \( V_{on} \) is the turn-on voltage at 1 cd/m\(^2\).  
\(^c\) CIE coordinates at 10 mA/cm\(^2\).

In light of its excellent luminescent behavior of 1 at solid state, we were accordingly encouraged to evaluate its potential application as solid-state emitter. Thermogravimetric analysis (TGA) was also performed to analyze the thermal properties of 1 under nitrogen atmosphere, as shown in Figure S22 and Table S4. The pertinent data indicated that compound 1 exhibits desirable thermal stability with a decomposition temperature up to 376 \(^\circ\)C, thus demonstrating that this compound is stable enough for thermal evaporation. We tentatively prepared its film by vacuum evaporation. As shown in Figure S23, its film exhibited a very bright yellow-green fluorescence (\( \tau = 6.9 \) ns) with a maximal peak at 501 nm and a very high quantum yield of 84\%, thus indicating a very similar status to its ground amorphous state we discussed above. Accordingly, we further fabricated non-doped OLED with the device configuration of indium tin oxide ITO/HATCN (5 nm)/TAPC (25 nm)/1 (35 nm)/TmPyPB (55 nm)/LiF (1 nm)/Al (120 nm), where HATCN (dipyrazino[2,3-f:2’,3’-h]quinoxaline-2,3,6,7,10,11-hexacar-bonitrile) and LiF serve as the hole- and electro-injection layer, respectively; TAPC (di-(4-(N,N-ditolyl-amino)-phenyl)cyclohexan) and TmPyPB(1,3,5-ti(m-pyridin-3-ylphenyl)benzene) serve as the hole- and electron-transporting layer, respectively; and ITO (indium tin oxide) and Al are used as the anode and electrode, respectively. The schematic energy level diagrams of the devices, EQE (external quantum efficiency) versus luminance curves, the electroluminescence (EL) spectra, the current density–voltage–luminance (J–V–L) characteristics, voltage-dependent EL spectra, the current efficiency and power versus luminance curves of the non-doped OLEDs are presented in Figure 10. The key device performances are summarized in Table 1. The EL spectra of compound 1 is close to that of the nondoped PL spectrum (vacuum-deposited) and very stable at various driving voltages, indicating that the emissive excitons were well confined in the emitting layer. The EL shows a bright green emission peak of 516 nm and CIE coordinate of (0.289, 0.551). The maximum luminance (\( L_{max} \)), current efficiency (\( \eta_c \)), power efficiency (\( \eta_p \)), and EQE values are as high as 4622 cd m\(^{-2}\), 16.23 cd A\(^{-1}\), 11.69 lm W\(^{-1}\), and 5.22 \%, respectively. Impressively, the EQE value (5.22\%) is practically reaching the theoretical limit.
value of traditional organic emitters, which makes compound 1 a promising candidate for OLED application.

3. Conclusion

In this work, we designed and synthesized a twisted AIE-active small molecule containing TAB and amine units, which showed response to multiple external stimuli including solvent polarity, temperature, mechanical shearing force, hydrostatic pressure and electric field. As a typical D-A molecule, remarkable solvent-dependent behavior accompanied by obvious PL change from blue to red was observed by gradual increasing the solvent polarity. Accordingly, it can be utilized as a useful imaging probe for the environmental polarity in cells and allows selective visualization of lipid droplets in live tissues. Additionally, the ICT also endowed it with unique thermochromatic property. It exhibited ratiometric luminescence signal changes and noticeable fluorescence color switchings with the change of temperature. Additionally, a wide detection range of temperature and a high upper limit were facilely realized. Another equally fascinating behavior was that it could respond to anisotropic shearing force and isotropic high pressure with remarkable but contrast luminescence conversion from uniform blue to highly-enhanced yellow-green and greatly-weakened red, respectively. XRD results demonstrated that the tribochromic PL involved a reversible morphological transformation between the crystalline state and the amorphous state. Crystal structure analysis combined with \textit{in situ} Raman spectra further indicated that the emission enhancement induced by grinding was attributed to the perturbation of weak intermolecular interactions and charge transfer processes and conformational planarization, while intermolecular $\pi-\pi$ interactions and intermolecular charge transfer processes jointly led to the emission annihilation under high pressure. Meanwhile, this compound was sensitive to external electric displaying threecolor switched electrochromism and on-to-off electroluminochromism. And it could serve as an emitter for fabrication of a non-doped OLED device with a high EQE value of 5.22%. Therefore, the present system featuring multi-stimuli responsive properties is potential for multifarious real-life applications, including probing the environmental polarity in biological systems and selective visualization of lipid droplets in live tissues, wide-range liquid thermometer, security inks and papers, electroswitchable electrochromic and electroluminochromic material for information recording, storage device and OLED. The results presented here are anticipated to provide an efficient guideline for the design of multifunctional materials.

4. Additional information
Materials, instrumentation, and detailed experimental procedures can be found in the Supporting Information. Additional data are available from the corresponding author upon reasonable request.

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