Electronic Supporting Information

Multifunctional Self-Assembled Macrocycles with Enhanced Emission and Reversible Photochromic Behaviour

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1. Synthesis and characterization of the compounds:

Scheme S1: Synthetic routes for the preparation of the AIE active acceptor.

Scheme S2: Synthetic routes for the preparation of the aldehyde donor.
Scheme S3: Synthetic routes for the preparation of the photochromic donor.

1.1 Materials and Methods:

General chemicals and the solvents were purchased from commercially available suppliers and were used without further purification. Precursor compounds 1, a, 10, 13 and acceptor a1 were synthesized according to the reported literature procedures. The IR spectra were recorded in a BRUKER ALPHA FT-IR Spectrometer. The NMR spectra of the newly prepared materials were recorded on a BRUKER 400 MHz spectrometer. The chemical shifts (δ) in the 1H NMR spectra were reported in ppm relative to the tetramethylsilane, which was used as an internal standard (δ = 0.00 ppm) or the resonance of the proton resulting from partial deuteration of the NMR solvents: CDCl3 (δ = 7.26 ppm) and D6-DMSO (δ = 2.50 ppm). 13C NMR spectra were recorded using the same instrument at 100 MHz and all the chemical shifts (δ) were reported in ppm relative to external CDCl3 and DMSO-d6 at 77.8-77.2 ppm and 40.5 ppm, respectively. The 31P NMR spectra were recorded at 120 MHz and the chemical shifts (δ) are reported in ppm relative to external 83% H3PO4 at 0.0 ppm. Electrospray ionization mass spectra were recorded using Agilent 6538 Ultra-High Definition (UHD) Accurate Mass Q-TOF spectrometer along with the use of standard spectroscopic grade solvents. Electronic absorption spectra and emission spectra were recorded on a LAMBDA 750 UV/Vis spectrophotometer and HORIBA JOBIN YVON made Fluoromax-4 spectrometer. Time-resolved fluorescence measurements were carried out on a Fluorolog instrument using 325 nm and 350 nm nano-LED source. Dynamic light scattering (DLS) experiments were performed on the Zeta-seizer instrument ZEN3600 (Malvern, UK) with a 173° back scattering angle and He-Ne laser (λ=633 nm). The DCM/hexane mixtures with various water fractions were prepared by slowly adding ultra-pure hexane into the DCM...
solution of samples. The SEM image was obtained using Zeiss Ultra-55 SEM instrument with the sample coated on a carbon tape. TEM analysis was performed on a JEOL 2100F instrument. The photochromic experiments were performed in a custom-made wood box decorated with 8 alternatively positioned 254 and 365 nm UV light source which were fitted vertically and was centred around the position of the cuvette. The absolute fluorescence quantum yields of the solid samples were measured by Quanta-ϕ Horiba Instrument coupled with Fluorolog spectrophotometer.

1.2 Synthesis

Synthesis of 2:
A 100 mL Schlenk flask was charged with diiodotriphenylamine aldehyde (3.4 g, 6.58 mmol), dibenzethene phosphate (2.00 g, 6.58 mmol) and freshly distilled THF (70 mL) was added. Then the mixture was cooled to 0º C and KOtBu (2.2 g, 19.74 mmol) was added. Slowly the temperature was raised to r.t and the crude was stirred for 24 h. After completion of the reaction, the solvent was evaporated and water was added. The medium was neutralized with dilute hydrochloric acid. Then the crude was extracted in CHCl3 and purified by column chromatography using silica gel (60-120 mesh) with EtOAc/Hex (5%) as eluent to afford 2 as yellow solid (55%). 

1H NMR (CDCl3, 400 MHz): δ = 7.50 (d, 4H), 7.35 (m, 3H), 7.31 (m, 5H), 7.24 (m, 2H), 6.90 (d, 3H), 6.80 ppm (d, 6H). 

13C NMR (100 MHz, CDCl3): δ = 147.2, 145.6, 143.7, 142.1, 140.9, 138.7, 133.1, 131.1, 130.1, 129.3, 128.7, 127.8, 126.5, 123.8, 86.6 ppm.

Synthesis of 3:
An oven-dried 100 mL two-neck round-bottom flask was charged with 2 (1.00 g, 1.48 mmol), CuI (0.02 g, 0.5 mol %), triphenylphosphine (0.04 g, 10 mol %) and [Pd(PPh3)2Cl2] (0.03 g, 3 mol %). Freshly distilled triethylamine (50 mL) was added to the mixture, which was heated at 50º C for 15 min. Trimethylsilylacetylene (0.65 ml, 4.44 mmol) was added to the hot solution and the mixture was heated at reflux for 2 days. After completion of the reaction (as monitored by TLC), the solvent was removed and the compound was purified by column chromatography on silica gel (60-120 mesh) with EA/Hex (10%) as eluent to afford 3 as a yellow product (95 %). 

1H NMR (CDCl3, 400 MHz): δ = 7.35 (m, 3H), 7.30 (m, 3H), 7.24 (m, 2H), 6.90 (m, 5H), 6.80 (m, 2H), 0.24 ppm (s, 18 H). 

13C NMR (100 MHz, CDCl3): δ = 147.5, 145.5, 143.8, 142.1, 140.9, 133.5, 131.0, 130.6, 128.7, 127.8, 124.4, 123.9, 117.7, 105.5, 94.1 ppm.

Synthesis of 4:
A mixture of compound 3 (0.90 g, 1.46 mmol) and K2CO3 (0.61 g, 4.38 mmol) was dissolved in a mixture of CH2Cl2 and MeOH (30:15) and stirred for 48 h. The solvent was removed under reduced pressure and the crude product was purified by column chromatography with EA/Hex (10%) as the eluent to give 4 as a yellow solid (90 %). 

1H NMR (CDCl3, 400 MHz): δ = 7.34 (m, 12H), 7.23 (m, 2H), 6.96 (d, 4H), 6.91 (m, 3H), 6.83 (d, 2H) 3.04 ppm (s, 2H). 

13C NMR (100 MHz, CDCl3): δ =147.7, 145.4, 143.7, 142.3, 140.9, 133.6, 131.1, 130.6, 129.2, 128.7, 127.8, 124.6, 123.9, 116.6, 84.0 ppm.
Synthesis of 5:
Compound 4 (0.30 g, 0.64 mmol), trans-[Pt(PEt$_3$)$_2$I$_2$] (1.31 g, 1.91 mmol) and CuI (0.02 g, 10 mol %) were added to a freshly distilled mixture of toluene (30 mL) and diethylamine (15 mL) in a Schlenk flask. The flask was degassed under vacuum and refilled with nitrogen three times. The reaction mixture was stirred for 48 h at room temperature. The solvent was removed under vacuum and the crude product was purified by column chromatography with CH$_2$Cl$_2$/hexane (6:4) as the eluent to afford 5 as a light yellow solid (72 %).

$^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ = 7.37 (m, 3H), 7.33 (m, 4H), 7.24 (m, 2H), 7.12 (d, 4H), 6.90 (m, 5H), 6.86 (m, 2H), 6.84 (d, 2H), 2.21 (m, 24H), 1.16 ppm (m, 36H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 146.5, 145.0, 143.9, 141.2, 141.1, 131.9, 130.7, 129.2, 128.6, 128.0, 127.7, 124.7, 123.6, 122.8, 100.2, 89.1, 17.1, 8.8 ppm.

$^{31}$P NMR (120 MHz, CDCl$_3$): $\delta$ = 8.56 ppm.

Synthesis of a2:
Compound 5 (0.05 g, 0.03 mmol) was dissolved in freshly distilled CH$_2$Cl$_2$ (5 mL) in a 20 mL drum vial. When the solution was treated with AgNO$_3$ (0.01 g, 0.07 mmol), a yellow precipitate started to form. The mixture was covered with aluminium foil and stirred in the dark at room temperature for 24 h. The mixture was filtered through Celite by using glass fibre. Diethyl ether was added to induce the formation of an off-white precipitate, which was dried to afford the final product a2 (60 %).

$^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ = 7.36 (m, 3H), 7.32 (m, 4H), 7.29 (m, 3H), 7.04 (m, 4H), 6.89 (m, 5H), 6.85 (m, 2H), 6.78 (m, 2H) 1.94 (m, 24H), 1.20 ppm (m, 36H);

$^{31}$P NMR (120 MHz, CDCl$_3$): $\delta$ = 20.06 ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 146.3, 145.3, 143.9, 141.2, 141.1, 132.2, 131.8, 130.7, 130.6, 129.2, 128.6, 127.9, 127.7, 124.5, 122.9, 103.4, 14.8, 8.2; HRMS (ESI): C$_{60}$H$_{83}$N$_3$O$_6$P$_4$Pt$_2$, [M - 2NO$_3$]$^{2+}$ = 665.7334 (calcd), found: 665.7496 (30%).

Synthesis of 6:
A clean and dry 100 mL two-neck round-bottom flask was charged with 1 (3.00 g, 5.71 mmol), CuI (0.054 g, 5 mol %), triphenylphosphine (0.300 g, 20 mol %) and [Pd(PPh$_3$)$_2$Cl$_2$] (0.120 g, 3 mol %). Freshly distilled triethylamine (60 mL) was added to the mixture, which was heated at 50$^\circ$C for 15 min. Trimethylsilylacetylene (3.0 mL, 17.12 mmol) was added to the hot solution drop wise under high nitrogen flow and the mixture was refluxed for 24 h. After completion of the reaction (as monitored by TLC), the solvent was removed, and the compound was purified by column chromatography on silica gel (60:120) with EA/Hex (5%) as eluent to afford 6 as a yellow product (95 %).

$^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ = 9.84 (s, 1H), 7.11 9d, 2H), 7.40 (d, 4H), 7.07 (d, 2H), 7.03 (d, 2H), 0.24 (s, 18H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 191.2, 152.7, 146.3, 134.1, 131.6, 131.0, 125.6, 122.1, 119.9, 104.9, 94.9, 0.74.

Synthesis of 7:
A mixture of compound 6 (4.00 g, 8.58 mmol) and K$_2$CO$_3$ (3.00 g, 21.47 mmol) was dissolved in a mixture of CH$_2$Cl$_2$ and MeOH (30:15) and stirred for 24 h. The solvent was removed under reduced pressure and water was added. Then it was neutralized with dilute HCl (6N). The crude was extracted in dichloromethane to afford brown sticky product 7 (90
%) and was used without further purification. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ = 9.86 (s, 1H), 7.75 (d, 2H), 7.45 (d, 4H), 7.14 (d, 2H), 7.10 (d, 4H), 3.12 (s, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 190.9, 152.5, 146.7, 134.0, 131.8, 131.1, 125.6, 122.1, 118.7, 83.5.

Synthesis of d1:

A dry two-neck 100 mL round-bottom flask was charged with 7 (1.30 g, 4.04 mmol), 4-bromopyridine (3.14 g, 16.18 mmol), CuI (0.038 g, 5 mol %), and triphenylphosphine (0.211 g, 20 mol %). Freshly distilled triethylamine (40 mL) was added to the mixture, which was heated at 50°C for 15 min. [Pd(PPh$_3$)$_2$Cl$_2$] (0.113 g, 3 mol %) was added to the hot solution and the mixture was refluxed for 24 h. Upon completion of the reaction (as monitored by TLC), the solvent was removed, and the compound was purified by column chromatography with neutral alumina as static phase and THF/Hexane mixture (10%) as eluent. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ = 9.89 (s, 1H), 8.60 (d, 4H), 7.77 (d, 2H), 7.51 (d, 4H), 7.37 (d, 4H), 7.14 (m, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 191.0, 152.4, 151.1, 150.4, 147.1, 133.9, 132.6, 132.5, 132.4, 131.8, 131.5, 129.0, 128.9, 127.7, 126.0, 125.6, 122.7, 118.6, 94.0, 87.4; HRMS (ESI): C$_{33}$H$_{21}$N$_3$O, [M+H]$^+$ = 476.1700 (calcd) found: 476.1761 (100%).

Synthesis of 9:

An oven-dried 100 mL two-neck round-bottom flask was charged with 8 (1.00 g, 2.82 mmol), CuI (0.026 g, 5 mol %), triphenylphosphine (0.072 g, 10 mol %) and [Pd(PPh$_3$)$_2$Cl$_2$] (0.06 g, 3 mol %). Freshly distilled triethylamine (60 mL) was added to the mixture, which was heated at 50°C for 15 min. Trimethylsilylacetylene (0.8 mL, 4.22 mmol) was added to the hot solution drop wise under high nitrogen flow and the mixture was refluxed for 24 h. After completion of the reaction (as monitored by TLC), the solvent was removed, and the solid was purified by column chromatography on silica gel (60:120) with EA/Hex (5%) as eluent. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ = 7.39 (s, 1H), 7.30 (m, 8H), 7.28 (m, 2H), 7.22 (m, 1H), 7.13 (m, 1H), 6.92 (m, 1H), 6.86 (d, 1H), 6.68 (d, 1H), 6.58 (d, 1H), 5.76 (d, 1H), 2.77 (s, 3H), 1.13 (s, 3H), 1.22 (s, 3H), 0.30 (s, 9 H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 155.33, 148.53, 137.07, 134.09, 131.00, 129.20, 128.11, 121.97, 120.62, 119.73, 119.22, 115.61, 115.07, 107.32, 105.57, 105.18, 92.70, 52.30, 29.33, 26.35, 20.54, 0.55 ppm.

Synthesis of 10:

A mixture of compound 9 (0.70 g, 1.87 mmol) and KOH (0.21 g, 3.74 mmol) was dissolved in a mixture of CH$_2$Cl$_2$ and MeOH (30:15) and stirred for 24 h. The solvent was removed under reduced pressure and water was added. Then it was neutralized with dilute HCl (6 N). This was extracted in dichloromethane to afford brown sticky product 10 (90 %) which was used without further purification. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ = 7.50 (m, 1H), 7.28 (m, 1H), 7.22 (m, 1H), 7.12 (d, 1H), 6.88 (d, 1H), 6.68 (d, 1H), 6.58 (d, 1H), 5.76 (d, 1H), 3.02 (s, 1H), 2.77 (s, 3H), 1.33 (m, 3H), 1.29 (m, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$=155.4, 148.5, 137.0, 134.2, 131.0, 129.2, 128.1, 122.0, 120.7, 119.8, 115.7, 114.0, 107.3, 105.2, 84.0, 76.0, 52.3, 29.3, 26.3, 20.5. ppm.
Synthesis of 12:

In a two-neck 250 mL round-bottom flask, dipyridylamine (1.22 g, 7.13 mmol), 1,4-diiodobenzene (7 g, 21.40 mmol), CuSO\(_4\) (0.56 g, 3.56 mmol) and K\(_2\)CO\(_3\) (3.98 g, 25.53 mmol) were taken together and degassed. Then 100 mL diphenylether was added to the mixture under N\(_2\) atmosphere. The mixture was stirred at 50°C for 30 minutes followed by addition of 18-Crown-6 (0.02g, 0.07 mmol). The crude was then stirred at 170°C for 4 days. After completion of the reaction, the solvent was removed under reduced pressure. The crude product was purified by column chromatography using neutral alumina as the stationary phase and THF/CHCl\(_3\) (1:1) as eluent to afford white solid (75%). \(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta = 8.40\) (d, 4H), 7.70 (d, 2H), 6.91 (m, 6H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 152.3, 151.4, 144.3, 139.8, 129.6, 117.0, 91.7, 71.1\).

Synthesis of d2:

An oven-dried 100 mL two-neck round-bottom flask was charged with 12 (0.25 g, 0.67 mmol), spiropyranalkyne (10) (0.3g, 1mmol), CuI (0.01 g, 5 mol %), and triphenylphosphine (0.02 g, 10 mol %). Freshly distilled triethylamine (40 mL) was added to the mixture, which was heated at 50°C for 15 min. [Pd(PPh\(_3\))\(_2\)Cl\(_2\)] (0.03 g, 3 mol %) was added to the hot solution and the mixture was heated at reflux for 24 h. After completion of the reaction (as monitored by TLC), the solvent was removed, and the compound was purified by preparative TLC with MeOH/EA (10%) as eluent. \(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta = 8.44\) (d, 4H), 7.52 (d, 2H), 7.25 (m, 2H), 7.20 (d, 1H), 7.13 (m, 2H), 7.08 (d, 1H), 6.97 (d, 4H), 6.86 (m, 2H), 6.69 (d, 1H), 6.54 (d, 1H), 5.73 (d, 1H), 2.73 (s, 3H), 1.30 (s, 3H), 1.17 (s, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 155.4, 152.5, 151.4, 148.5, 143.9, 137.0, 133.7, 129.5, 127.5, 122.6, 121.9, 120.8, 119.7, 119.4, 117.2, 115.8, 114.7, 107.3, 105.3, 91.1, 87.3, 52.4, 29.4, 26.3, 20.5 ppm. HRMS (ESI): C\(_{37}\)H\(_{30}\)N\(_4\)O, [M+H]\(^+\) = 547.2497 (calcd) found: 547.1571 (100%).

Synthesis of M1:

Acceptor a1 (12.8 mg, 0.01 mmol) was treated with newly synthesized aldehyde functionalized donor d1 (4.8 mg, 0.01 mmol) in (1:1) molar ratio in dry DCM (5 mL). The reaction mixture was heated to reflux, and the reaction was continued for 24 h. Upon completion of the reaction, the solvent was removed under reduced pressure and the crude was washed with cold ether several times to afford the desired final product (M1) (isolated yield: 82 %). \(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta = 9.84\) (s, 3H), 8.57 (m, 12H), 7.85 (m, 6H), 7.67 (s, 9H), 7.53 (m, 12H), 7.44 (m, 15H), 7.39 (m, 21H), 7.17 (m, 12H), 7.07 (m, 12H), 6.62 (s, 3H), 1.80 (m, 72H), 1.16 ppm (m, 108H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 191.75, 152.58, 149.32, 148.29, 148.11, 147.50, 147.11, 146.50, 135.69, 134.25, 134.19, 133.90, 133.82, 132.86, 132.16, 131.86, 129.68, 129.59, 126.27, 125.91, 125.65, 125.43, 125.16, 125.07, 124.77, 124.30, 123.82, 123.60, 123.47, 123.08, 94.49, 87.01, 85.90, 49.23, 49.02, 48.81, 48.59, 48.38, 48.17, 47.95, 29.89, 14.55, 7.79. \(^{31}\)P\(^{\text{[1H]}\}) NMR (120 MHz, 295K, CDCl\(_3\)): \(\delta = 15.92\) ppm (195Pt satellites, \(J_{\text{Pt-P}} = 2887.6\) Hz). ESI-MS (m/z) = 990.3368 [M-5NO\(_3\)]\(^{5+}\), 814.7788 [M-6NO\(_3\)]\(^{6+}\). IR = 2966 (m), 2213 (m), 2122 (m), 1688 (m), 1584 (s), 1498 (s), 1318 (s), 1275 (s), 1166 (m), 1034 (s), 827 (s), 732 (s).
Synthesis of M2:

An equimolar mixture of acceptor $a_1$ (12.8 mg, 0.01 mmol) and newly prepared photochromic donor $d_2$ (5.46 mg, 0.01 mmol) was dissolved in dry DCM (5 mL) and stirred for 15 min. The reaction mixture was heated to reflux for another 24 h. The solvent was removed under vacuum and the afforded solid was subjected to solvent wash with ample amount of cold diethyl ether. Finally, the residual solid was dried to afford the desired final product M2 (Isolated yield: 75 %).

$^1$H NMR (CDCl$_3$, 400 MHz): $\delta = 8.34$ (d, 12H), 7.66 (d, 12H), 7.47 (m, 15H), 7.28 (m, 9H), 7.23 (m, 21H), 7.10 (m, 12H), 6.95 (m, 6H), 6.70 (d, 3H), 6.54 (d, 3H), 5.74 (d, 3H), 2.74 (s, 9H), 1.84 (m, 72H), 1.13 (s, 9H) 1.18 ppm (m, 117H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 152.96, 152.86, 148.51, 147.60, 146.25, 137.02, 134.66, 133.80, 132.28, 130.63, 129.78, 129.40, 129.28, 128.12, 124.99, 124.01, 123.73, 121.97, 120.77, 120.02, 119.76, 119.44, 115.83, 114.53, 107.33, 105.35, 87.12, 52.36, 29.35, 26.34, 20.54, 14.74, 8.43. $^{31}$P{$^1$H} NMR (120 MHz, 295K, CDCl$_3$): $\delta = 16.16$ ppm. ($^{195}$Pt satellites, $J_{P-P} = 2892$ Hz); ESI-MS (m/z) = 1306.5741 [M-4NO$_3$]$^4^+$, 1032.7936 [M-5NO$_3$]$^5^+$, 850.3211 [M-6NO$_3$]$^6^+$. IR = 3440 (w), 2966 (w), 2122 (m), 1592 (s), 1490 (s), 1336 (s), 1030 (m), 826 (m), 735 (s).

Synthesis of M3:

Freshly prepared AIE-active acceptor $a_2$ (14.6 mg, 0.01 mmol) was treated with the photochromic donor $d_2$ (5.46 mg, 0.01 mmol) in dry DCM (5 mL) and the mixture was refluxed for 24 h. The solvent was removed and the obtained solid was washed with cold diethyl ether several times to afford the desired final product M3 (Isolated yield: 76 %).

$^1$H NMR (CDCl$_3$, 400 MHz): $\delta = 8.61$ (m, 12H), 7.67 (d, 6H), 7.47 (m, 12H), 7.29 (m, 24H), 7.26 (m, 15H), 7.07 (m, 18H), 6.97-6.85 (m, 36H), 6.70 (m, 3H), 6.54 (d, 3H), 5.74 (d, 3H), 2.73(s, 9H), 1.83 (m, 72H), 1.30 (s, 9H), 1.18 ppm (m, 117H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 155.51, 152.87, 141.14, 137.04, 134.70, 133.80, 132.27, 132.15, 130.81, 130.67, 129.24, 128.65, 128.12, 127.76, 124.49, 121.97, 120.79, 119.99, 119.76, 119.46, 115.84, 107.33, 105.35, 92.29, 87.23, 52.36, 29.35, 26.33, 20.54, 14.75, 8.42. $^{31}$P{$^1$H} NMR (120 MHz, 295K, CDCl$_3$): $\delta = 16.26$ ppm, ($^{195}$Pt satellites, $J_{P-P} = 2852$ Hz). ESI-MS (m/z) = 1440.0334 [M-4NO$_3$]$^4^+$, 1139.6400 [M-5NO$_3$]$^5^+$, 939.3665 [M-6NO$_3$]$^6^+$. IR = 3440 (w), 2966 (w), 2122 (m), 1592 (s), 1490 (s), 1336 (s), 1030 (m), 826 (m), 735 (s).

Synthesis of Nanoaggregates:

Initially, stock solutions ($10^{-3}$ M) of M1, M2 and M3 were prepared using spectroscopy grade DCM. The required amounts of the aliquots from the stock solutions were transferred to 4 mL glass vials. After addition of the appropriate amount of DCM for dilution, spectroscopy grade hexane was added to the solutions under vigorous stirring to afford ($10^{-5}$ M) solutions with varying hexane-DCM ratios (10%-90%). The photophysical studies were carried out immediately.
DLS Analysis:
For DLS analysis, 2 mL solutions of the samples with varying hexane fractions in DCM were placed in a quartz cuvette with all transparent sides. The samples were passed through a 1-micron filter paper to remove inconsistent bigger particles formed due to rapid agglomeration. The cuvette was placed into the instrument sample chamber during the data collection and each data was recorded at least 10 times to obtain a consistent value.

SEM Analysis:
For SEM analysis, 1cm² sized carbon tapes were first fitted on a steel-based sample holder. Using a micropipette, 10μL solution of different samples were drop cast on the carbon tapes and was dried subsequently under vacuum for at least 6 hr. The as-dried samples were kept in dark prior to data collection to avoid any deformities caused by light sensitivity.

TEM Analysis:
For TEM analysis solutions with different hexane fraction in DCM (80% and 90%) were selected to examine the effect of hexane fraction on particle size formation. Each sample (10μL) was drop cast on Cu grid and was dried under vacuum for at least 6 h before data collection. Due to light sensitivity, all the samples were kept under dark before data collection.

Fluorescence Quantum Yield Measurement:
For fluorescence quantum yield measurement, quinine sulphate was chosen as reference. The quantum yields were measured using the following equation

$$\phi_c = \left(\frac{\phi_r \{(1 - 10^{-A_c}) \times N_c^2 \times D_c\}}{(1 - 10^{-A_r}) \times N_r^2 \times D_r}\right)$$

Where $\phi_m$ and $\phi_r$ is the radiative quantum yields of the compounds and reference respectively; $A_c$ is the absorbance of the compound and $A_r$ is the absorbance of the reference; $D_c$ is the area of emission of the compound and $D_r$ is the area of emission of the reference, $N_c$ and $N_r$ are the refractive indices of the compound and reference solutions, respectively. For solid-state quantum yield measurement, a Quanta-ϕ instrument coupled with Fluorolog spectrophotometer was used and barium sulphate was used as filler substrate.

Solvent Dependent Fluorescence:
For solvent dependent fluorescence, stock solutions of the macrocycles were made in DCM (10⁻³ M) and from the stock solution 20 μL was transferred into a quartz cuvette and was diluted with the corresponding solvent under study.

Optimisation Methods:
All the theoretical calculations were performed using Gaussian 09 package.¹ The M1, M2 and M3 were optimized using PM6 semi-empirical method. In all other calculations, the hybrid B3LYP functional has been used. The 6-31G basis set was used for all calculations. But for Pt centre the basis set was changed to LANL2DZ.² No symmetry constraints were used during the optimization procedure.
For theoretical calculation the model was chosen in such a way that it incorporates the basic building unit common to all the macrocycles. Hence the ligand was coordinated to a platinum(II) centre which was also coordinated to two PEt₃ groups and was terminated with acetylene moiety.

**Photochromic Experiments:**
For the photochromic experiments, all the samples were prepared using spectroscopy grade DMSO as the solvent and the concentration was maintained at 10⁻⁵ M. During experiments, the samples (2 mL) were placed in an all transparent quartz cuvette and the cuvette was positioned into the sample chamber of the custom-made box decorated with 8 UV light source. The samples were irradiated for 2 min for photo-conversion and subsequently were wrapped with aluminium foil before photophysical experiments. It was found that if kept unprotected, the sample returns to its original form just under 1 min exposure of the normal tube light fitted in the laboratory. For photochromism reversibility experiment, the sample was repeatedly exposed to the UV chamber and normal light source and their absorption spectra were measured each time to verify the interconversion. For acid-base experiment, dilute nitric acid was chosen as the sample already contains nitrate counter ions and dilute triethylamine solution was used as the base. Addition of an equivalent amount of acid arrests the ring-opened form by protonation and the addition of base again deprotonates the ring to facilitate faster cyclisation.

1.3 Self-assembly of M1:

**Scheme S4:** Synthetic scheme for M1

![Scheme S4](image-url)
Figure S1: $^1$H NMR spectrum of M1 (CDCl$_3$, 298 K).

Figure S2: $^{31}$P NMR spectrum of M1 (CDCl$_3$, 298 K).
Figure S3: $^{13}$C NMR spectrum of M1 (CDCl$_3$, 298 K).

Figure S4: 2D-DOSY spectrum of M1 (CDCl$_3$ at 298 K),
According to Stokes-Einstein equation: $D = \frac{(K_b T)}{6\pi \eta r}$, where $K_b$ is Boltzmann’s constant, $T$ is temperature, $\eta$ is viscosity index of the solvent and $r$ is the hydrodynamic radius of the M1, the estimated diameter of the molecule was found to be 6.34 nm which is comparable with the calculated value from optimised.

**Figure S5**: $^1$H-$^1$H COSY spectrum of M1 (CDCl$_3$ at 298 K). The rectangular position shows the interaction between neighbouring protons.
Figure S6: $^1$H NMR spectrum of the acceptor $a_1$ (a), $M_1$ (b) and donor $d_1$ (c) respectively and the upfield and downfield shift of the building blocks.

Figure S7: $^{31}$P NMR spectra of the acceptor $a_1$ (a) and $M_1$ (b) respectively.
Figure S8: Total Electrospay ionization Mass Spectrum of M1, ([M1 - 6NO$_3$]$^{6+}$ = 814.7879, [M1 - 5NO$_3$]$^{5+}$ = 990.137) and isotopic distribution pattern of 5+ charge (inset), experimental (red) and simulated (green).
Figure S9: IR spectra of M1 with precursor acceptor and donor.

1.4 Self-assembly of M2:

Scheme S5: Synthetic scheme of M2
Figure S10: $^1$H NMR spectrum of M2 (CDCl$_3$, 298 K).

Figure S11: $^{31}$P NMR spectrum of M2 (CDCl$_3$, 298 K).
Figure S12: $^{13}$C NMR spectrum of M2 (CDCl$_3$, 298 K).

Figure S13: 2D-DOSY spectrum of M2 (CDCl$_3$ at 298 K). The estimated diameter of the molecule was found to be 7.7 nm which is comparable with the calculated value from optimized structure.
Figure S14: $^1$H-$^1$H COSY spectrum of M2 (CDCl$_3$ at 298 K). The rectangular position shows the interaction between neighbouring protons.
Figure S15: $^1$H NMR spectrum of the acceptor, macrocycle and donor a1 (a), M2 (b) and d2 (c), respectively.

Figure S16: $^{31}$P NMR spectrum of the acceptor a1 (a) and M2 (b).
Figure S17: Total Electrospray ionization Mass Spectrum of M2, ([M2 - 6NO₃]⁶⁺ = 850.3211, [M2 - 5NO₃]⁵⁺ = 1032.7936, [M2 - 4NO₃]⁴⁺ = 1306.4751) and isotopic distribution pattern of 5+ charge (inset), experimental (red) and simulated (green).

Figure S18: Electrospray ionization Mass Spectrum of M2 with 4+ charge, simulated (a) and experimental (b) and 6+ charge experimental (d) and theoretical (c).
Figure S19: IR spectra of M2 with precursor acceptor and donor.

1.5 Synthesis of M3:

Scheme S6: Synthetic scheme of M3
Figure S20: $^1$H NMR spectrum of M3 (CDCl$_3$, 298 K).

Figure S21: $^{31}$P NMR spectrum of M3 (CDCl$_3$, 298 K).
Figure S22: $^{13}$C NMR spectrum of M3 (CDCl$_3$, 298 K).
Figure S23: 2D-DOSY spectrum of M3 (CDCl₃ at 298 K). According to Stokes Einstein equation the estimated diameter of the molecule was found to be 5.6 nm which is comparable with the calculated value from optimized structure.
Figure S24: $^1$H-$^1$H COSY spectrum of M3 (CDCl$_3$ at 298 K). The rectangular position shows the interaction between neighbouring protons.
Figure S25: Total Electrospray ionization Mass Spectrum of M3, \([\text{M3} - 6\text{NO}_3]^{6+} = 939.3655, [\text{M3} - 5\text{NO}_3]^{5+} = 1139.6419, [\text{M3} - 4\text{NO}_3]^{4+} = 1440.0334\) and isotopic distribution pattern of 6+ charge (inset), experimental (red) and simulated (green).

Figure S26: IR spectra of M3 with precursor acceptor and donor.
2. Normalized absorption and emission spectra of the macrocycles and building blocks in DCM:

**Table 1.** Absorption and Emission Maxima of the Building Blocks, Macrocycles, and their Corresponding Quantum Yields and Lifetime.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Absorption Maxima (nm)</th>
<th>Emission Maxima (nm)</th>
<th>Quantum Yield</th>
<th>Lifetime (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a2</td>
<td>370</td>
<td>510</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>a1</td>
<td>357</td>
<td>470</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>d1</td>
<td>374</td>
<td>495</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>d2</td>
<td>326</td>
<td>380</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>M1</td>
<td>372</td>
<td>500</td>
<td>67</td>
<td>3.21</td>
</tr>
<tr>
<td>M2</td>
<td>331</td>
<td>475</td>
<td>9.8</td>
<td></td>
</tr>
<tr>
<td>M3</td>
<td>335</td>
<td>515</td>
<td>13</td>
<td>3.24</td>
</tr>
</tbody>
</table>

**Figure S27:** Normalized absorbance and emission spectra of acceptor a2 in DCM.
Figure S28: Normalized absorbance and emission spectra of donor d2 in DCM.

Figure S29: Normalized absorbance and emission spectra of M2 in DCM.
Figure S30: Normalized absorbance and emission spectra of M3 in DCM.

3. Absorption and emission spectra of the macrocycles and building blocks in different solvents:

Figure S31: Normalized absorption spectra of donor d1 in different solvents.
Figure S32: Normalized absorption spectra of M2 in different solvents.

Figure S33: Normalized absorption spectra of M3 in different solvents.
Figure S34: Fluorescence spectra of donor d1 in different solvents, $\lambda_{\text{max}} = 370$ nm.

Figure S35: Solvent dependent fluorescence of donor d1 under UV light (365 nm).
Figure S36: Fluorescence spectra of M2 in different solvents, $\lambda_{\text{max}} = 330$ nm.

Figure S37: Solvent dependent fluorescence of M2 in under 365 nm UV light.
**Figure S38:** Fluorescence spectra of M3 in different solvents, $\lambda_{\text{max}} = 330$ nm.

**Figure S39:** Solvent dependent fluorescence of M3 under 365 nm UV light.
4. Absorption and emission spectra of the compounds in different fraction of Hexane-DCM mixture:

**Figure S40:** Absorption spectra of acceptor a2 in different solvent fraction of hexane in DCM.

**Figure S41:** Absorption spectra of donor d1 in different solvent fraction of hexane in DCM.
**Figure S42:** Absorption spectra of M1 in different solvent fraction of hexane in DCM.

**Figure S43:** Absorption spectra of M2 in different solvent fraction of hexane in DCM.
**Figure S44:** Emission spectra of acceptor a2 in different solvents fraction of hexane in DCM, $\lambda_{\text{max}} = 330$ nm

**Figure S45:** Images of the acceptor a2 in different solvents fraction of hexane in DCM when irradiated with 365 nm light inside the UV chamber.
Figure S46: Emission spectra of donor d1 in different solvent fraction of hexane in DCM, $\lambda_{\text{max}} = 370$ nm.

Figure S47: Colours of donor d1 in different solvent fraction of hexane in DCM under 365 nm UV light.
Figure S48: Emission spectra of M1 in different solvents fraction of hexane in DCM, $\lambda_{\text{max}} = 370$ nm.

Figure S49: Colours of M1 in different solvents fraction of hexane in DCM under 365 nm UV light.
Figure S50: Emission spectra of M2 in different solvents fraction of hexane in DCM, $\lambda_{\text{max}} = 330$ nm.

Figure S51: Visual colours of M2 in different solvents fraction of hexane in DCM under 365 nm UV light.
5. NMR of the intermediate and acceptor and donor compounds:

**Figure S52:** $^1$H NMR spectrum of compound 2 (CDCl$_3$, 298 K).

**Figure S53:** $^{13}$C NMR spectrum of compound 2 (CDCl$_3$, 298 K).
Figure S54: $^1$H NMR spectrum of compound 3 (CDCl$_3$, 298 K).

Figure S55: $^{13}$C NMR spectrum of compound 3 (CDCl$_3$, 298 K).
Figure S56: $^1$H NMR spectrum of compound 4 (CDCl$_3$, 298 K).

Figure S57: $^{13}$C NMR spectrum of compound 4 (CDCl$_3$, 298 K).
Figure S58: $^1$H NMR spectrum of compound 5 (CDCl$_3$, 298 K).

Figure S59: $^{31}$P NMR spectrum of compound 5 (CDCl$_3$, 298 K).
Figure S60: $^{13}$C NMR spectrum of compound 5 (CDCl$_3$, 298 K).

Figure S61: $^1$H NMR spectrum of compound a2 (CDCl$_3$, 298 K).
Figure S62: $^{31}$P NMR spectrum of compound a2 (CDCl$_3$, 298 K).

Figure S63: $^{13}$C NMR spectrum of compound a2 (CDCl$_3$, 298 K).
Figure S64: $^1$H NMR spectrum of compound 6 (CDCl$_3$, 298 K).

Figure S65: $^{13}$C NMR spectrum of compound 6 (CDCl$_3$, 298 K).
Figure S66: $^1$H NMR spectrum of compound 7 (CDCl$_3$, 298 K).

Figure S67: $^{13}$C NMR spectrum of compound 7 (CDCl$_3$, 298 K).
Figure S68: $^1$H NMR spectrum of compound d1 (CDCl$_3$, 298 K).

Figure S69: $^{13}$C NMR spectrum of compound d1 (CDCl$_3$, 298 K).
Figure S70: $^1$H NMR spectrum of compound 9 (CDCl$_3$, 298 K).

Figure S71: $^{13}$C NMR spectrum of compound 9 (CDCl$_3$, 298 K).
Figure S72: $^1$H NMR spectrum of compound 10 (CDCl$_3$, 298 K).

Figure S73: $^{13}$C NMR spectrum of compound 10 (CDCl$_3$, 298 K).
Figure S74: $^1$H NMR spectrum of compound 12 (CDCl$_3$, 298 K).

Figure S75: $^{13}$C NMR spectrum of compound 12 (CDCl$_3$, 298 K).
Figure S76: $^1$H NMR spectrum of compound d2 (CDCl$_3$, 298 K).

Figure S77: $^{13}$C NMR spectrum of compound d2 (CDCl$_3$, 298 K).
6. Mass spectra of the acceptor and donor compounds:

Figure S78: Mass spectrum of compound a2. Inset: experimental (red) and theoretical (green) isotopic distributions of 2+ charge.
Figure S79: Mass spectrum of compound d1.

Figure S80: Mass spectrum of compound d2.
7. Dynamic light scattering data of compounds M3 in DCM/hexane mixture:

Figure S81: Particle size distribution of M3 with 80% hexane in DCM.
8. Scanning Electron Microscopy images of compounds M1 and M3 in DCM/hexane mixture with varying solvent fraction:

Figure S82: SEM images of the M1 with various hexane/DCM fractions. 80% (a) and 90% (b).

Figure S83: SEM images of the M3 with various hexane/DCM fractions 80% (a) and 90% (b).
9. Transmission Electron Microscopy images of compounds M1 and M2 in DCM/hexane mixture with varying solvent fraction:

**Figure S84**: TEM images of the M1 with various hexane/DCM fractions. 80% (a) and 90% (b)

**Figure S85**: TEM images of the M2 with various hexane/DCM fractions. 80% (a) and 90% (b)
10. Photochromic behavior of donor d2 and M2:

**Figure S86:** Photochromic behaviour of the building block d2 after exposure to 365 nm UV irradiation for 2 minutes followed by visible light exposure of 2 min.

**Figure S87:** Photochromic behaviour of M2 after exposure to 365 nm UV irradiation for 2 minutes followed by visible light exposure of 2 min.
**Figure S88.** Energy minimized geometry of the free ligand and metal coordinated model. Color codes: Carbon (grey), Nitrogen (blue), Phosphorus (pink), Platinum (orange).

**Figure S89:** Acidochromic behaviour of M2 after exposure to 365 nm UV irradiation for 2 minutes followed by addition of acid, UV exposure, and neutralization with base followed by visible light exposure of 2 min.
**Figure S90:** Reversible photochromic behaviour of M2 after exposure to 365 nm UV irradiation for 2 minutes followed by visible light exposure of 2 min.

**Figure S91.** Stacked $^{31}$P NMR spectra of M2: initial (a), 1st cycle (b), 2nd cycle (c), 3rd cycle (d) in CDCl$_3$ with 100 µL MeOD.
Figure S92: Image of the hexagonal UV chamber (a) outside and (b) inside, decorated with 12 UV lamps of (254 and 365 nm).

References:
