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Electronic Supplementary Information for

Synergistic Combination of ACQ and AIE Moieties to Enhance the Emission of Hexagonal Metallacycles

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1. Materials and methods

All reagents were commercially available and used as supplied without further purification. Deuterated solvents were purchased from Cambridge Isotope Laboratory (Andover, MA). Compounds **3**[S1] was prepared according to the literature procedures. NMR spectra were recorded on a Varian Unity 300 MHz spectrometer. ^{1}H and ^{13}C NMR chemical shifts are reported relative to residual solvent signals, and $^{31}P\{^1H\}$ NMR chemical shifts are referenced to an external unlocked sample of 85% H_3PO_4 (δ 0.0). The solutions of metallacycles in dichloromethane were used for ESI-TOF-MS analysis. Mass spectra were recorded on a Micromass Quattro II triple-quadrupole mass spectrometer using electrospray ionization with a MassLynx operating system. The UV-vis experiments were conducted on a Hitachi U-4100 absorption spectrophotometer.

The fluorescent experiments were conducted on a Hitachi F-3000 fluorescence spectrophotometer. Solid-state quantum yields were measured using a Horiba FMax-4 instrument equipped with a Quanta-Phi integrating light sphere. The quantum yields were measured on solid samples obtained via precipitation and solvent removal. The solids were placed between two quartz discs and excited at 360 nm.

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

2. ^{1}H NMR and ^{31}P{^{1}H} NMR spectra of TPE-based di-Pt(II) acceptor ***3***

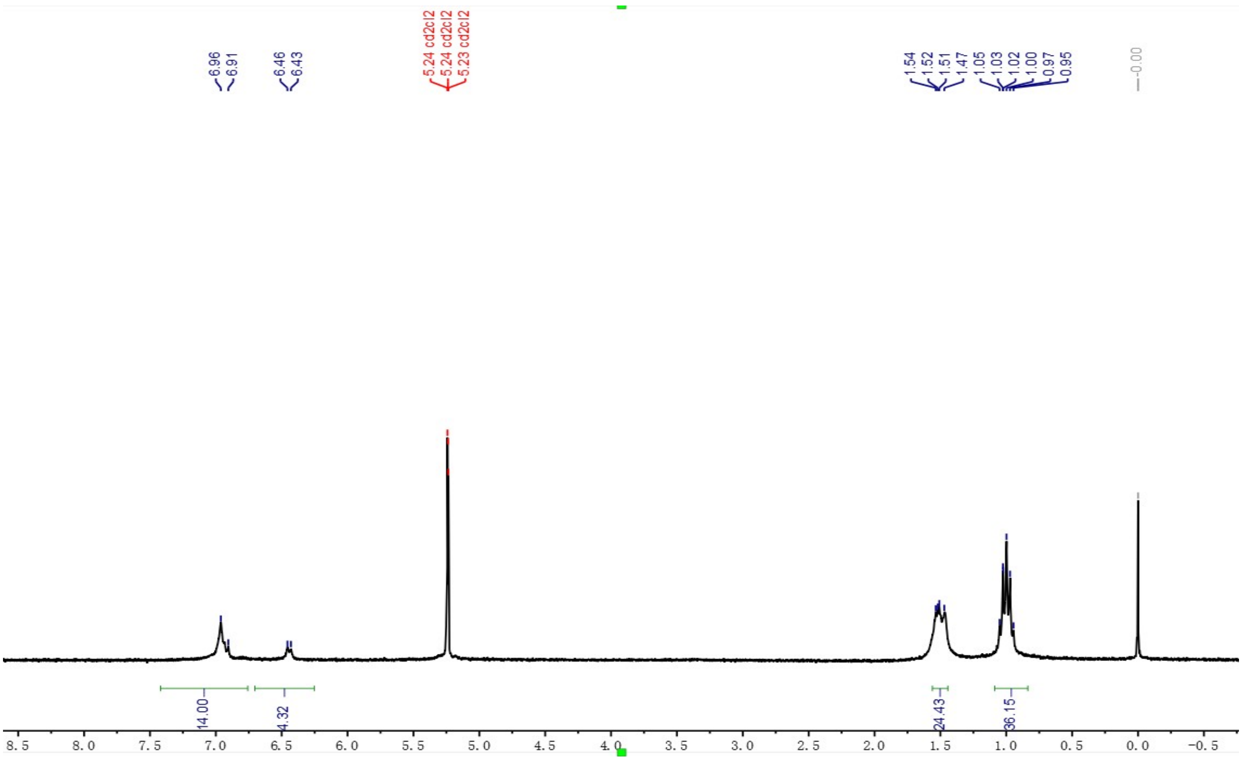


Figure S1. ^{1}H NMR spectrum (CD_2Cl_2, room temperature, 300 MHz) of **3**.

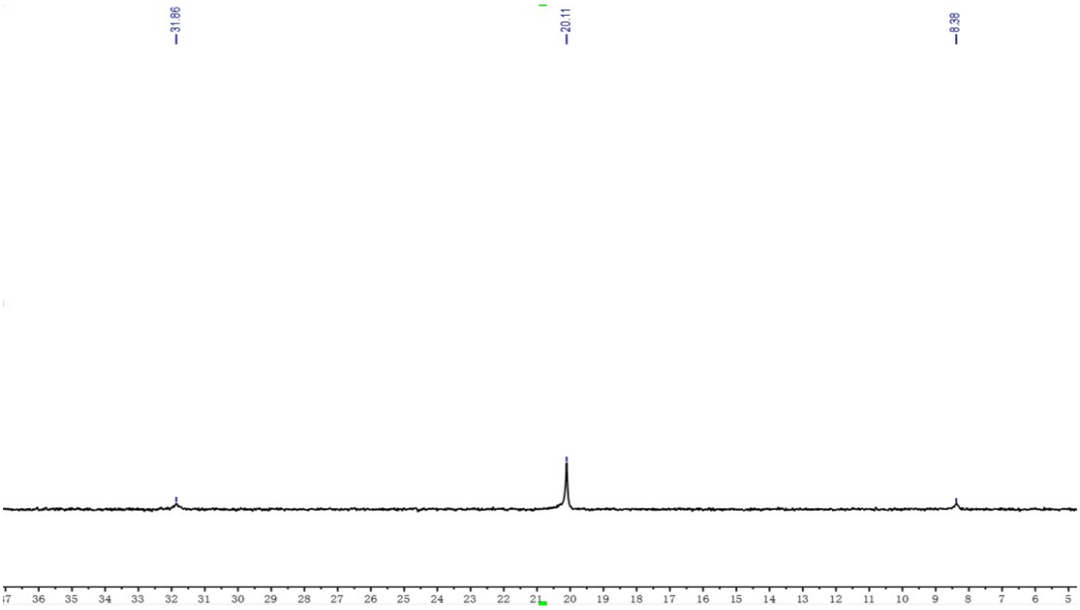
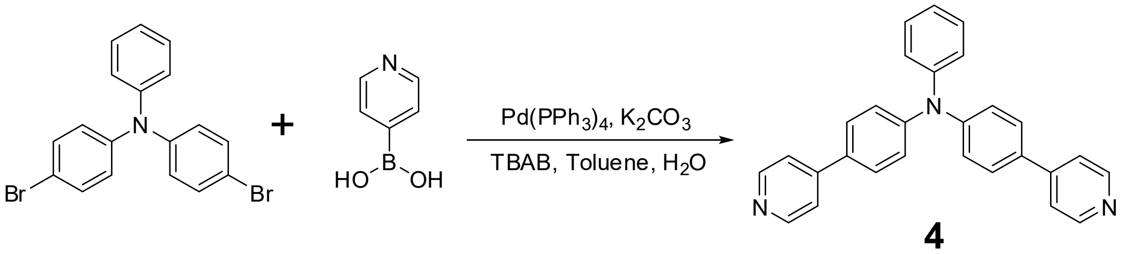


Figure S2. ^{31}P{^{1}H} NMR spectrum (CD_2Cl_2, room temperature, 121.4 MHz) of **3**.

3. *Synthesis of ligand **4***



Scheme S1

To 4,4'-dibromotriphenylamine (1.00 g, 2.48 mmol) and 4-pyridylboronic acid (1.53 g, 12.4 mmol) in toluene (55.0 mL), K_2CO_3 (2.68 g, 19.8 mmol) aqueous solution (15.0 mL) and TBAB (tetrabutylammonium hydrogen sulfate) (85.0 mg, 0.250 mmol) were added. Then the $Pd(PPh_3)_4$ (289 mg, 0.250 mmol) was added and the reaction mixture was stirred at 85 °C for 2 days under nitrogen atmosphere. After cooling to room temperature, the product was concentrated and purified by silica gel column chromatography with CH_2Cl_2:MeOH (100:1, *v*/*v*) as the eluant to afford ligand **4** (0.77 g, 78%) as yellow powder. M.P. 136.5–137.3 °C. The ^1H NMR spectrum of **4** is shown in Figure S3. ^1H NMR (CD_2Cl_2, room temperature, 300 MHz) δ (ppm): 8.62 (d, J = 6.3 Hz, 4H), 7.58–7.65 (m, 4H), 7.52 (d, J = 6.0 Hz, 4H), 7.32–7.40 (m, 2H), 7.25–7.13 (m, 7H). The ^{13}C NMR spectrum of **4** is shown in Figure S4. ^{13}C NMR (CD_2Cl_2, room temperature, 75.0 MHz) δ (ppm): 121.03, 124.10, 124.47, 125.76, 127.99, 129.80, 132.23, 147.08, 147.46, 148.56, 150.48. LRESIMS is shown in Figure S5: *m*/*z* 400.22 $[M + H]^+$. HRESIMS: *m*/*z* calcd for $[M + H]^+$ $C_{28}H_{22}N_3$, 400.1808; found 400.2203.

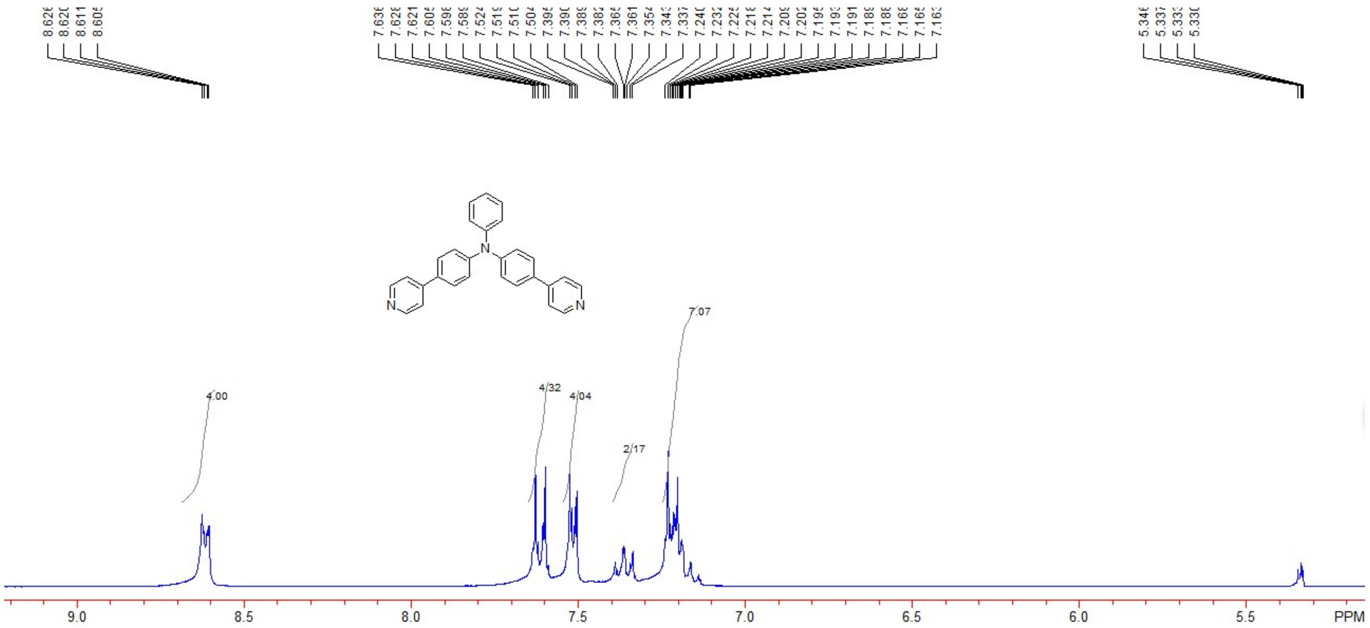


Figure S3. ^{1}H NMR spectrum (CD_2Cl_2, room temperature, 300 MHz) of **4**.

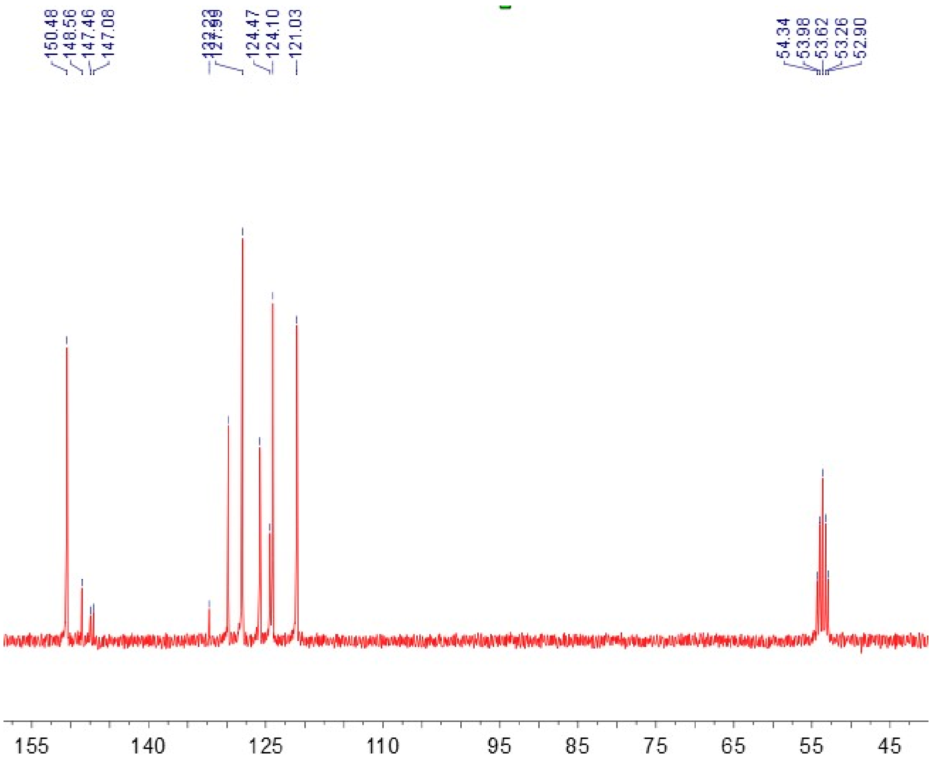


Figure S4. ^{13}C NMR spectrum (CD_2Cl_2, room temperature, 75.0 MHz) of **4**.

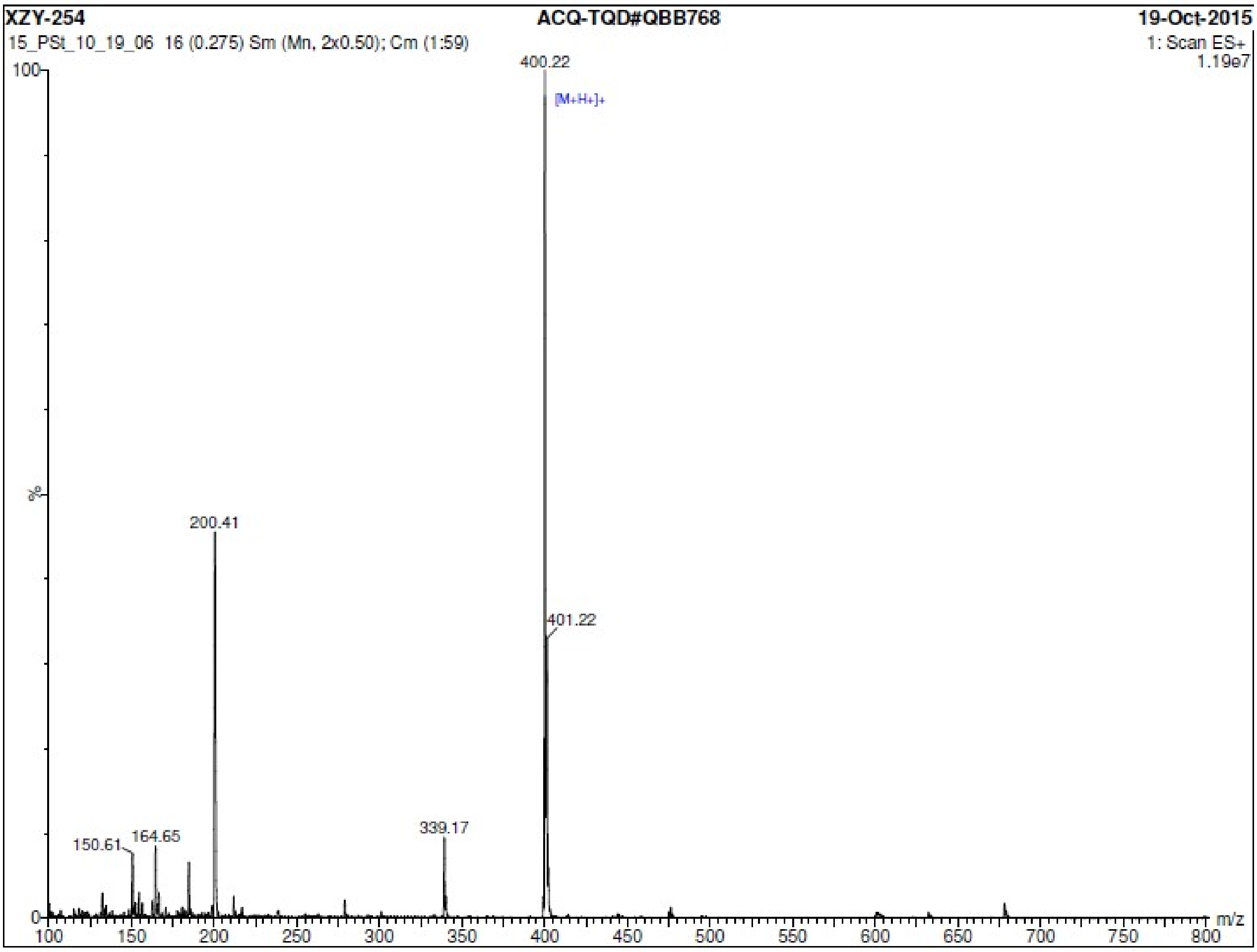
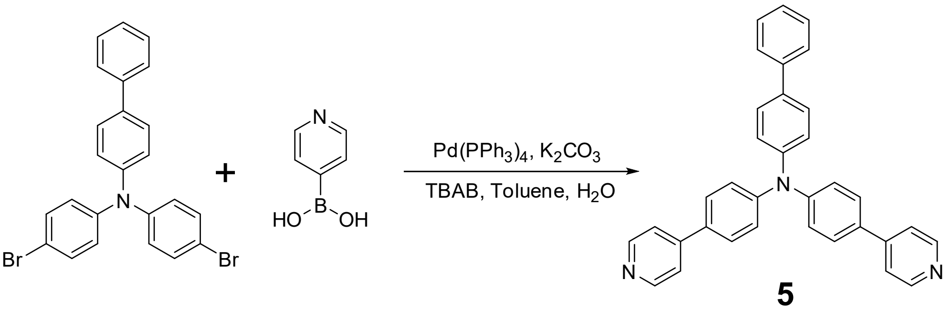


Figure S5. Electrospray ionization mass spectrum of **4**.

4. *Synthesis of ligand* **5**



Scheme S2

To 4,4'-dibromo-4-phenyltriphenylamine (1.00 g, 2.09 mmol) and 4-pyridylboronic acid (1.28 g, 10.4 mmol) in toluene (55.0 mL), K_2CO_3 (2.31 g, 16.7 mmol) aqueous solution (15.0 mL) and TBAB (tetrabutylammonium hydrogen sulfate) (71.0 mg, 0.210 mmol) were added. Then the $Pd(PPh_3)_4$ (243 mg, 0.210 mmol) was added and the reaction mixture was stirred at 85 °C for 2 days under nitrogen atmosphere. After cooling to room temperature, the product was concentrated and purified by silica gel column chromatography with CH_2Cl_2:MeOH (100:1, *v*/*v*) as the eluant to afford ligand **5** (0.80 g, 81%) as pale-yellow powder. M.P. 100.8–101.5 °C. The ^1H NMR spectrum of **5** is shown in Figure S6. ^1H NMR (CD_2Cl_2, room temperature, 300 MHz) δ (ppm): 8.62 (d, J = 6.3 Hz, 4H), 7.57–7.66 (m, 8H), 7.53 (d, J = 6.0 Hz, 4H), 7.42–7.49 (m, 2H), 7.31–7.38 (m, 1H), 7.23–7.29 (m, 6H). The ^{13}C NMR spectrum of **5** is shown in Figure S7. ^{13}C NMR ($CDCl_3$, room temperature, 75.0 MHz) δ (ppm): 121.22, 124.40, 125.64, 127.01, 128.16, 128.43, 129.08, 132.46, 137.10, 140.54, 146.27, 147.67, 148.41, 150.53. LRESIMS is shown in Figure S8: *m*/*z* 476.20 $[M + H]^+$. HRESIMS: *m*/*z* calcd for $[M + H]^+$ $C_{34}H_{26}N_3$, 476.2121; found 476.2049.

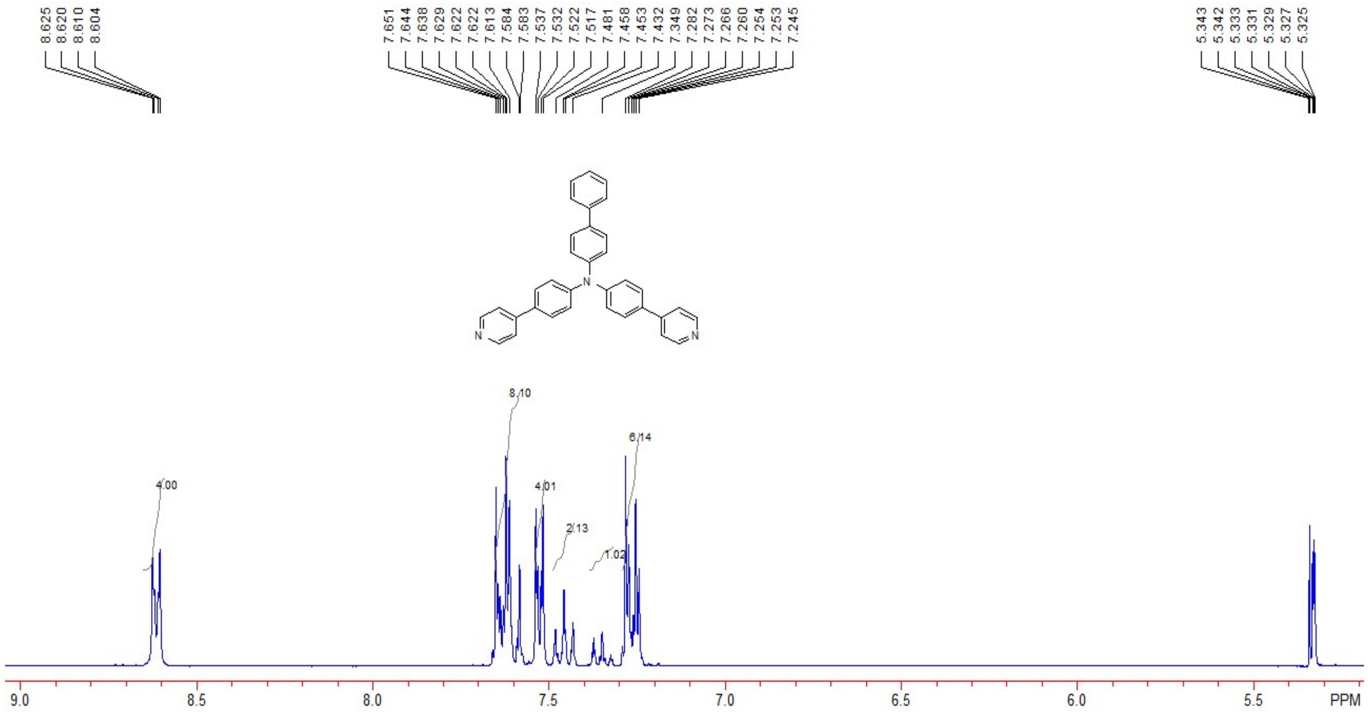


Figure S6. ^{1}H NMR spectrum (CD_2Cl_2, room temperature, 300 MHz) of **5**.

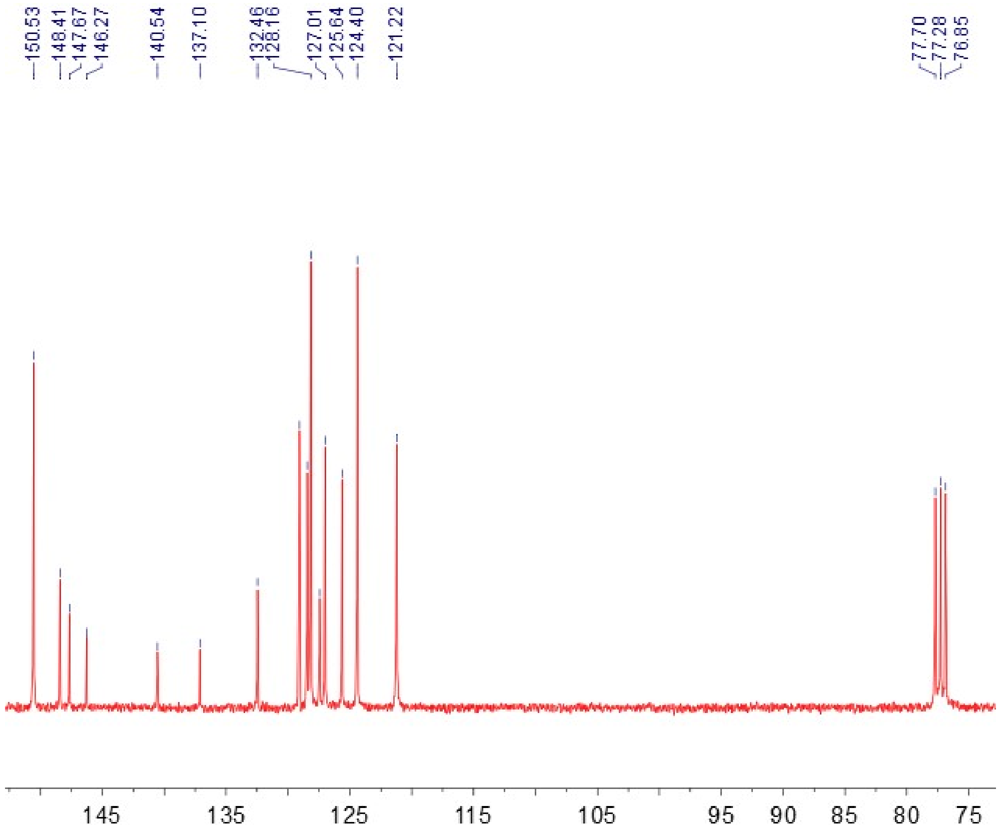


Figure S7. ^{13}C NMR spectrum ($CDCl_3$, room temperature, 75.0 MHz) of **5**.

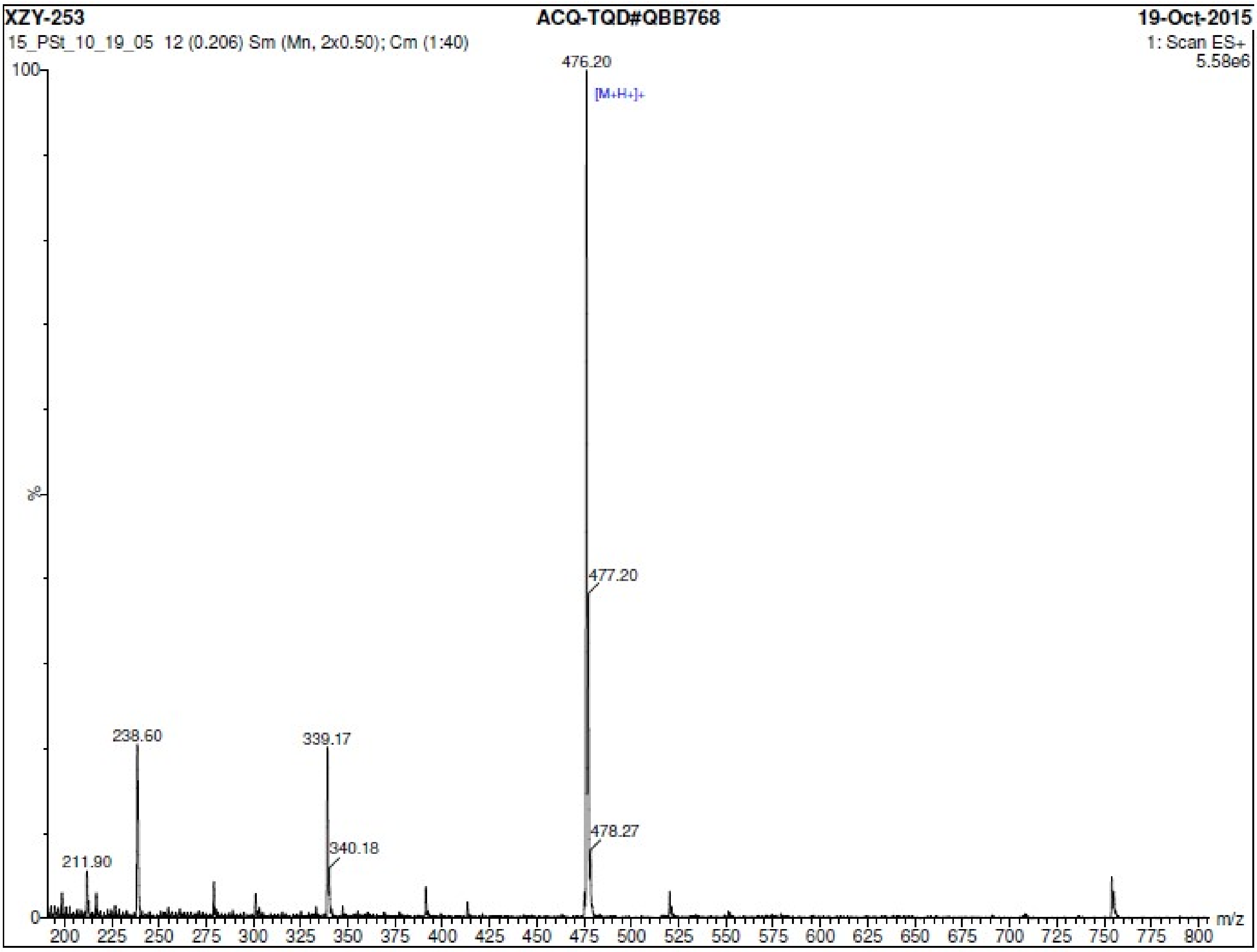
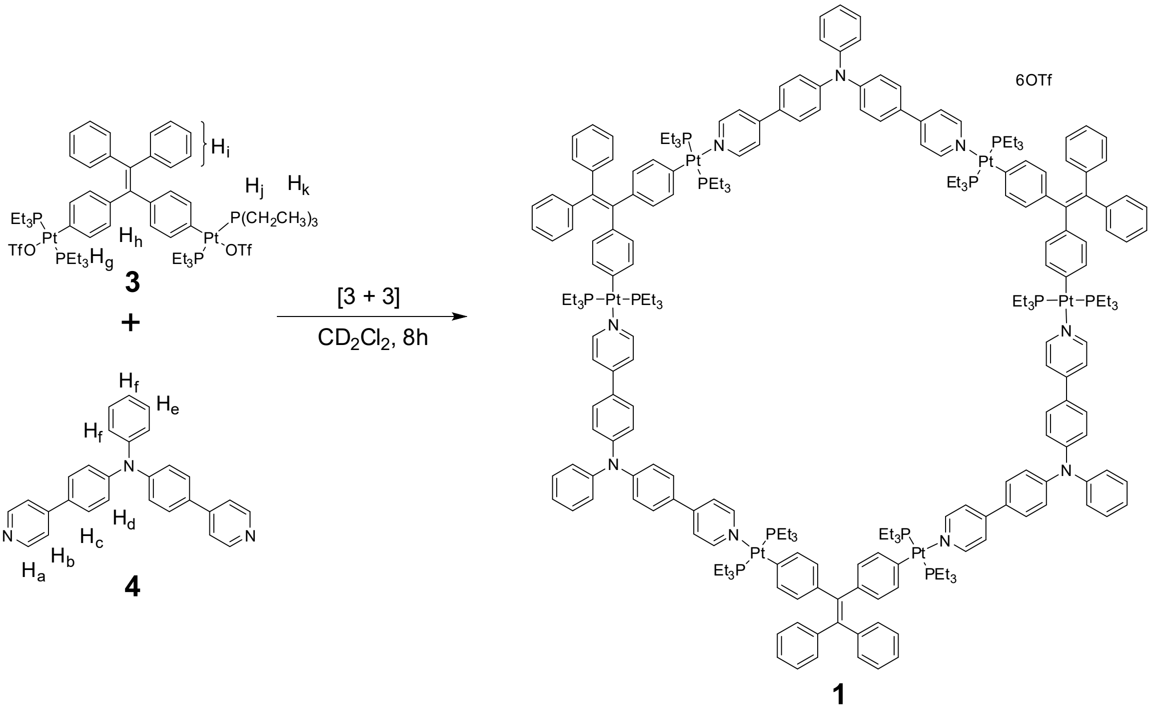


Figure S8. Electrospray ionization mass spectrum of **5**.

5. *Synthesis of hexagon **1***



In a 1:1 molar ratio, ligand **4** (1.20 mg, 0.003 mmol) and TPE-based diplatinum acceptor **3** (4.47 mg, 0.003 mmol) were dissolved in 0.50 mL of CH_2Cl_2 in a 2.00 mL vial. The reaction mixture was allowed to stir for 8 h at room temperature. To the resulting homogeneous solution, hexane was added to precipitate the product, which was then isolated and dried under reduced pressure and re-dissolved in CD_2Cl_2 for characterization. The ^{1}H NMR spectrum of **1** is shown in Figure S9. ^{1}H NMR (CD_2Cl_2, room temperature, 300 MHz) δ (ppm): 8.59 (d, J = 6.3 Hz, 12H), 7.91 (d, J = 6.3 Hz, 12H), 7.82 (d, J = 8.8 Hz, 12H), 7.42 (t, J = 7.6 Hz, 6H), 7.19–7.31 (m, 21H), 7.00–7.16 (m, 42H), 6.77 (d, J = 8.0 Hz, 12H), 1.24–1.44 (m, 72H), 1.00–1.18 (m, 108H). The ^{31}P{^{1}H} NMR spectrum of **1** is shown in Figure S10. ^{31}P{^{1}H} NMR (CD_2Cl_2, room temperature, 121.4 MHz) δ (ppm): 14.30 ppm (s, ^{195}Pt satellites, $^1J_{\text{Pt–P}}$ = 2702.3 Hz). ESI-TOF-MS is shown in Figure S11: m/z 796.6568 $[M - 6OTf]^{6+}$, 1268.9484 $[M - 4OTf]^{5+}$, and 1740.5327 $[M - 3OTf]^{3+}$.

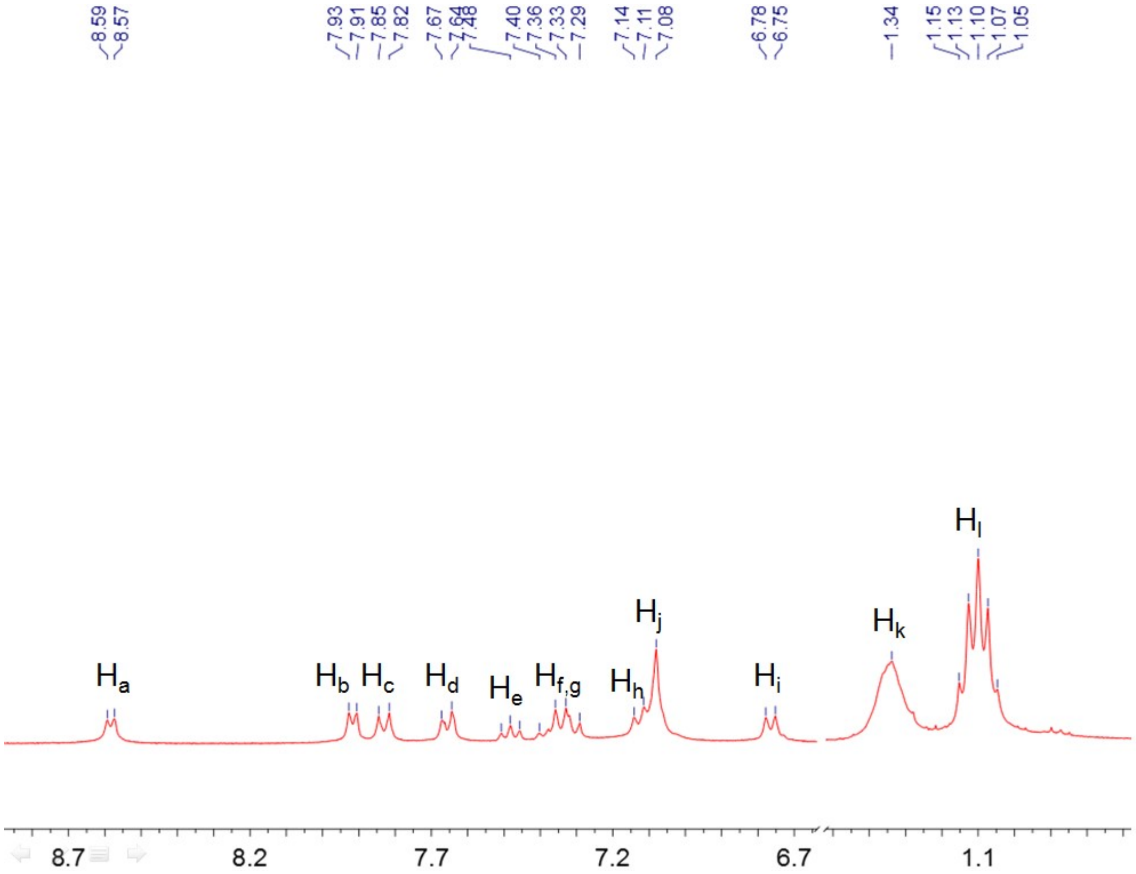


Figure S9. ^{1}H NMR spectrum (CD_2Cl_2, room temperature, 300 MHz) of **1**.

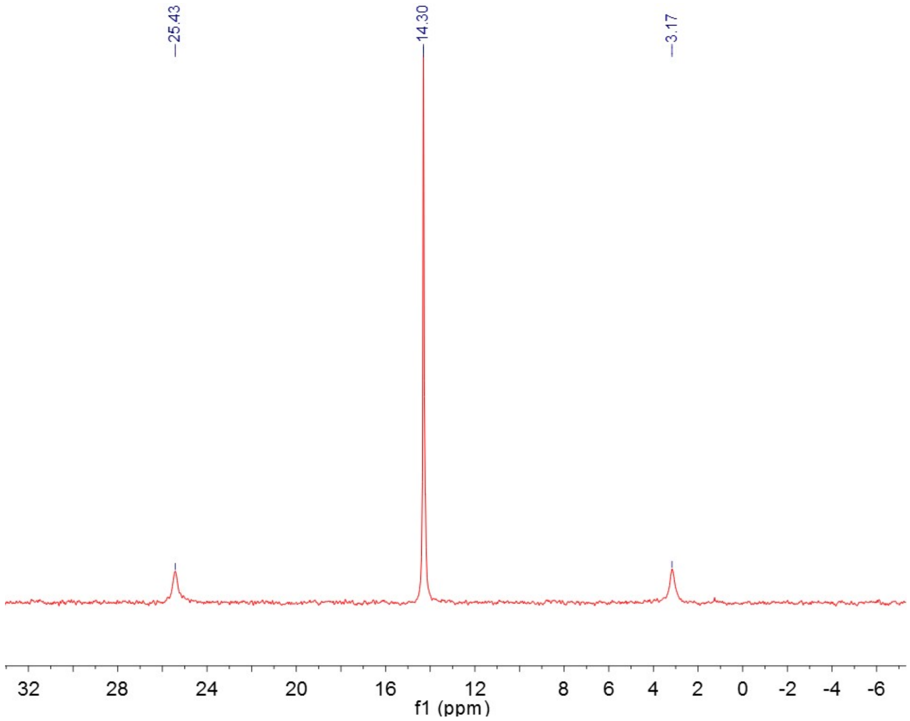


Figure S10. ^{31}P{^{1}H} NMR spectrum (CD_2Cl_2, room temperature, 121.4 MHz) of **1**.

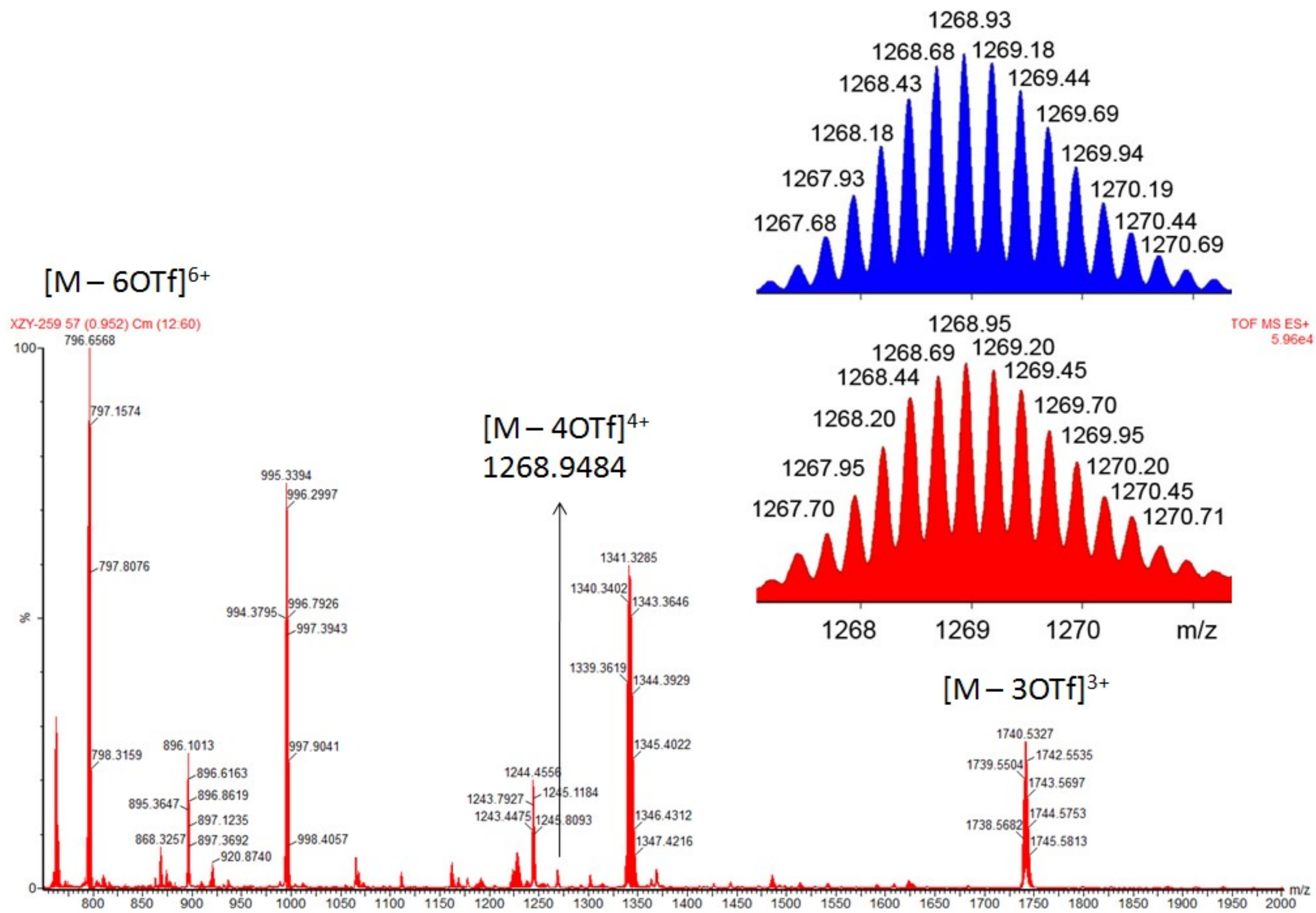
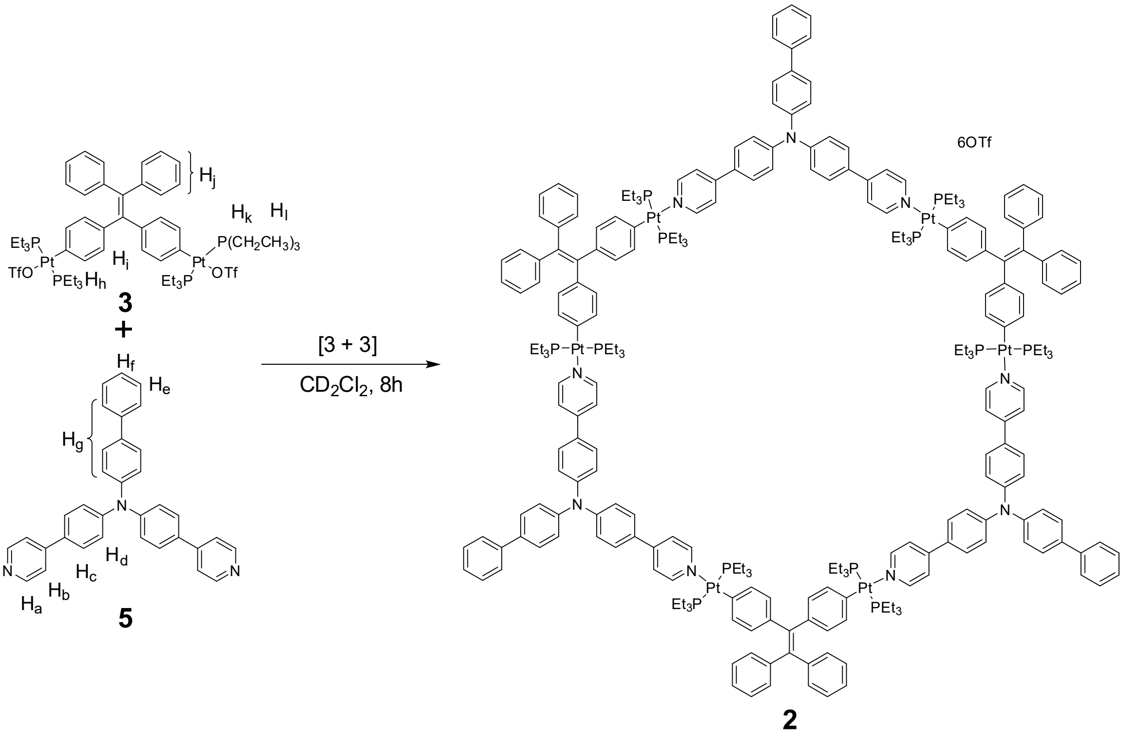


Figure S11. Experimental (red) and calculated (blue) electrospray ionization mass spectra of **1**.

6. Synthesis of hexagon **2**



In a 1:1 molar ratio, ligand **5** (1.43 mg, 0.003 mmol) and TPE-based diplatinum acceptor **3** (4.47 mg, 0.003 mmol) were dissolved in 0.50 mL of CH_2Cl_2 in a 2.00 mL vial. The reaction mixture was allowed to stir for 8 h at room temperature. To the resulting homogeneous solution, hexane was added to precipitate the product, which was then isolated and dried under reduced pressure and re-dissolved in CD_2Cl_2 for characterization. The ^{1}H NMR spectrum of **2** is shown in Figure S12. ^{1}H NMR (CD_2Cl_2, room temperature, 300 MHz) δ (ppm): 8.59 (d, J = 6.0 Hz, 12H), 7.93 (d, J = 6.0 Hz, 12H), 7.85 (d, J = 9.0 Hz, 12H), 7.67 (d, J = 9.0 Hz, 12H), 7.48 (t, J = 7.6 Hz, 6H), 7.26–7.41 (m, 21H), 7.00–7.16 (m, 42H), 6.78 (d, J = 9.0 Hz, 12H), 1.24–1.44 (m, 72H), 1.00–1.18 (m, 108H). The ^{31}P{^{1}H} NMR spectrum of **1** is shown in Figure S13. ^{31}P{^{1}H} NMR (CD_2Cl_2, room temperature, 121.4 MHz) δ (ppm): 14.31 ppm (s, ^{195}Pt satellites, $^1J_{\text{Pt–P}}$ = 2706.0 Hz). ESI-TOF-MS is shown in Figure S14: m/z 833.2850 $[M - 6OTf]^{6+}$, 1030.9836 $[M - 5OTf]^{5+}$, 1325.9727 $[M - 4OTf]^{4+}$, and 1816.5430 $[M - 3OTf]^{3+}$.

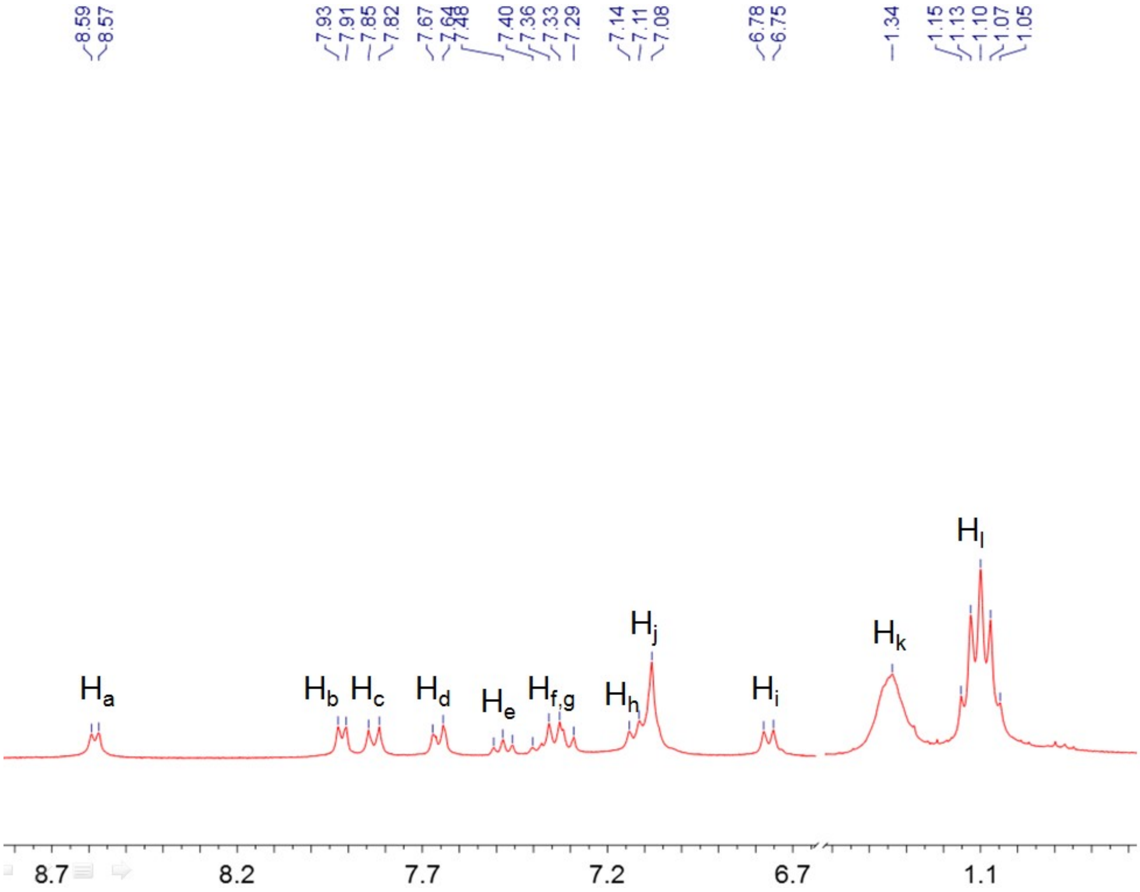


Figure S12. ^{1}H NMR spectrum (CD_2Cl_2, room temperature, 300 MHz) of **2**.

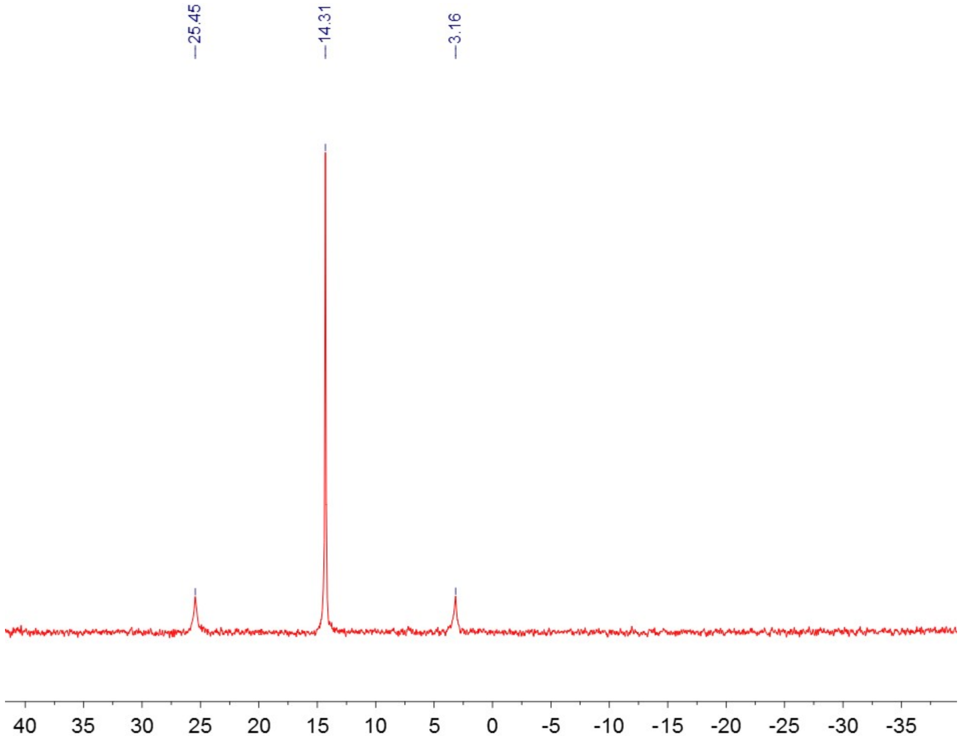


Figure S13. $^{31}P\{^1H\}$ NMR spectrum (CD_2Cl_2, room temperature, 121.4 MHz) of **2**.

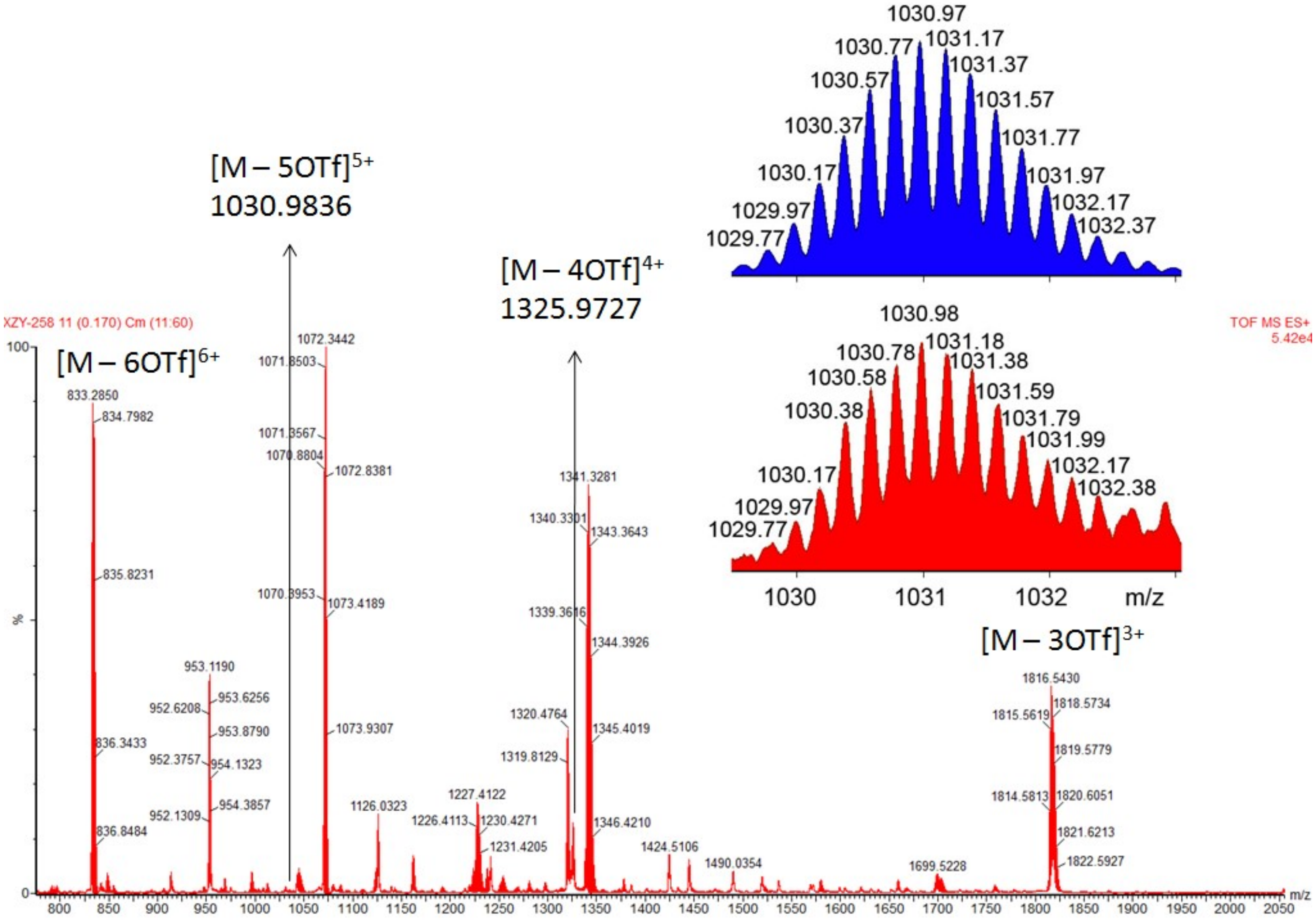


Figure S14. Experimental (red) and calculated (blue) electrospray ionization mass spectra of **2**.

7. Absorption spectra of metallacycles in CH_2Cl_2/hexane mixtures with different hexane contents

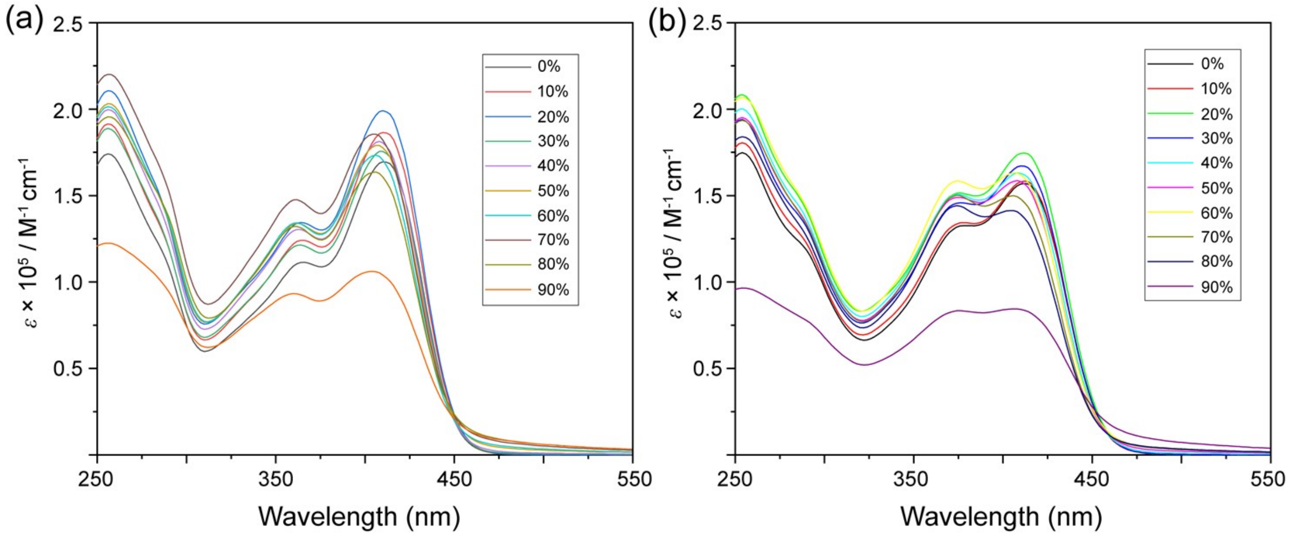


Figure S15. Absorption spectra of multi-TPA-TPE hexagon **1** (a) and multi-TPA-TPE hexagon **2** (b) in CH_2Cl_2/hexane mixtures with different hexane contents (c = 10.0 μM).

*8. Absorption spectra of multi-TPA-TPE hexagon **2** in different solvents*

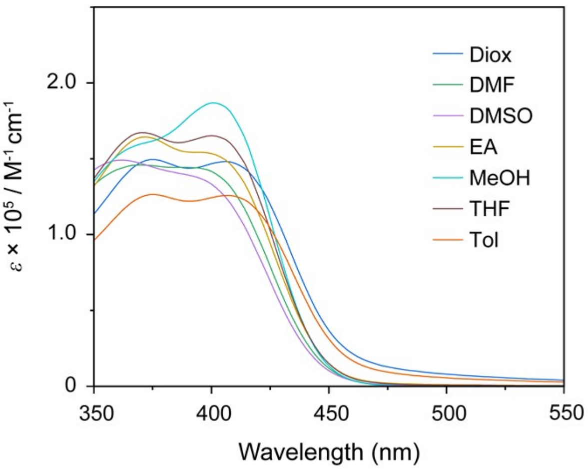


Figure S16. Absorption spectra of multi-TPA-TPE hexagon **2** in different solvents (*c* = 10.0 *μ*M). Dio, dioxane; DMF, dimethylformamide; DMSO, dimethyl sulfoxide; EA, ethyl acetate; MeOH, methanol; THF, tetrahydrofuran; Tol, toluene.

*9. Photographs of multi-TPA-TPE hexagon **2** in different solvents*

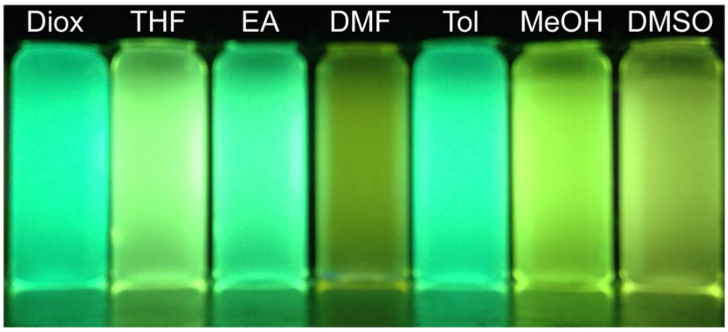


Figure S17. photographs of multi-TPA-TPE hexagon **2** in different solvents upon excitation at 365 nm using an UV lamp at 298 K (c = 10.0 μM). Dio, dioxane; DMF, dimethylformamide; DMSO, dimethyl sulfoxide; EA, ethyl acetate; MeOH, methanol; THF, tetrahydrofuran; Tol, toluene.

*10. Scanning Electron Microscopy images of metallacycle **2** in DCM/hexane mixture with varying solvent fraction*

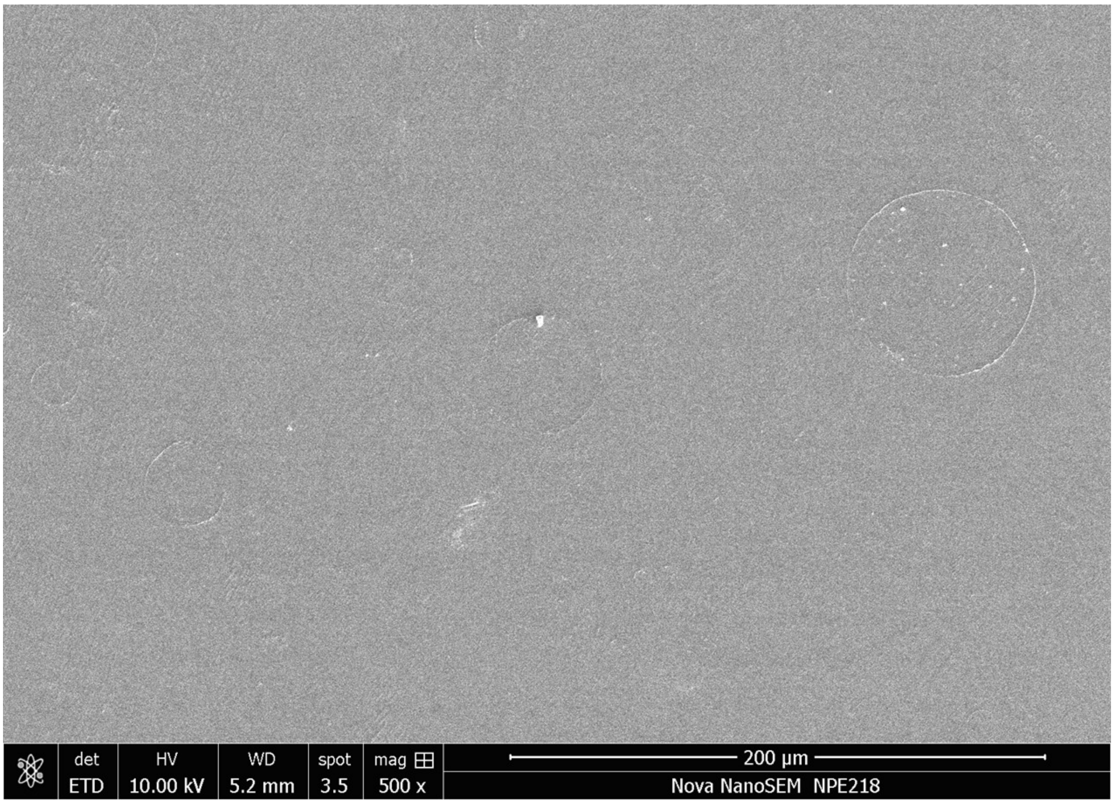


Figure S18. *SEM image of metallacycle **2** in DCM.*

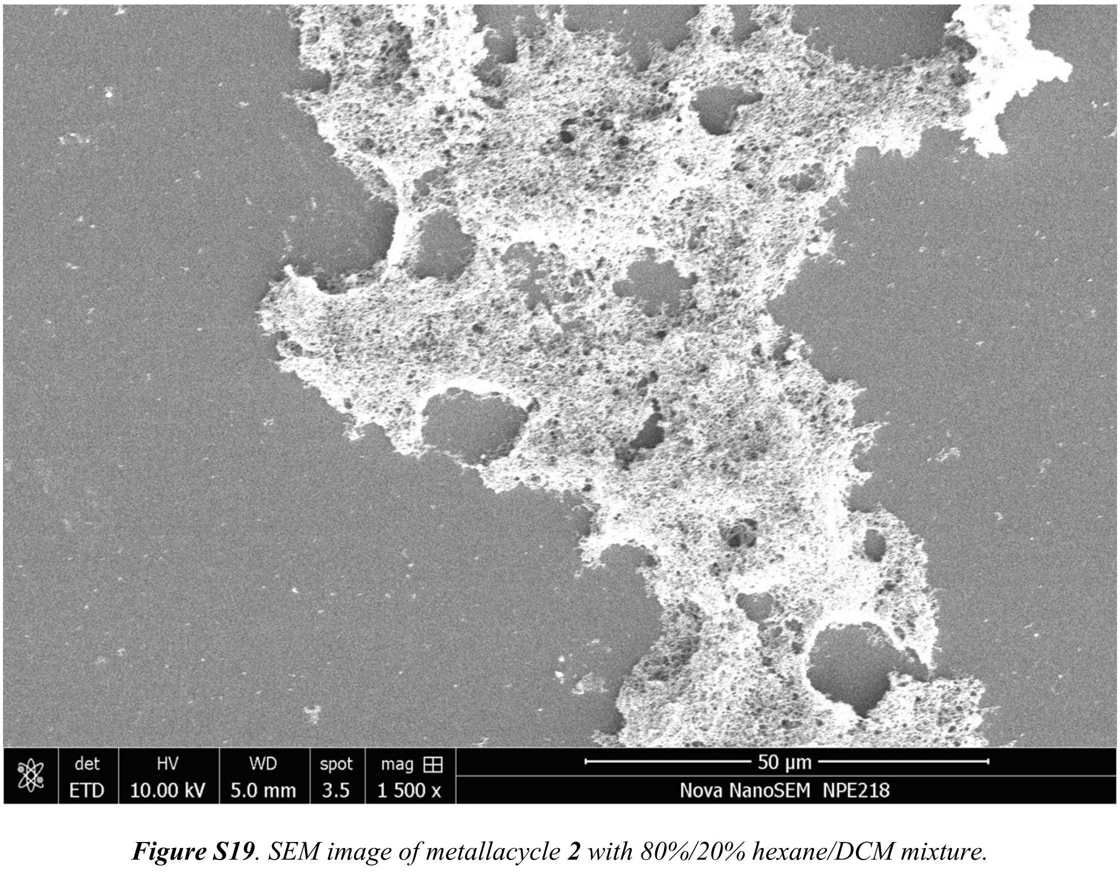


Figure S19. *SEM image of metallacycle **2** with 80%/20% hexane/DCM mixture.*

*11. Frontier orbital of ligands **4**, **5** and metallacycles **1**, **2***

DFT calculations were performed using the Gaussian09 (G09) program packageS2 to analyze the HOMOs and LUMOs of ligands and resultant metallacycles. The B3LYP hybrid functional with LANL2DZ effective core potentials (Pt) and 6-31 G* (C, H, N, F and O) basis set. Orbitals were visualized with an isovalue of 0.02. To minimize computational cost, we simplified the compound and replaced it with 1/3 of the compound. This result showed that electrons transferred from the aniline groups to the pyridine units when ligands as well as the resultant metallacycles was excited from the ground state to the first excited state.

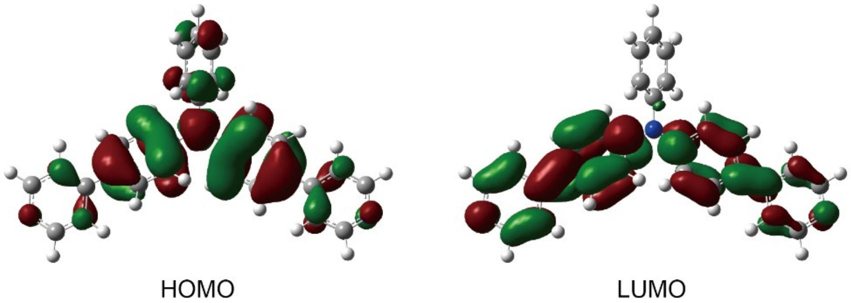


Figure S20. Frontier orbital of ligand **4**.

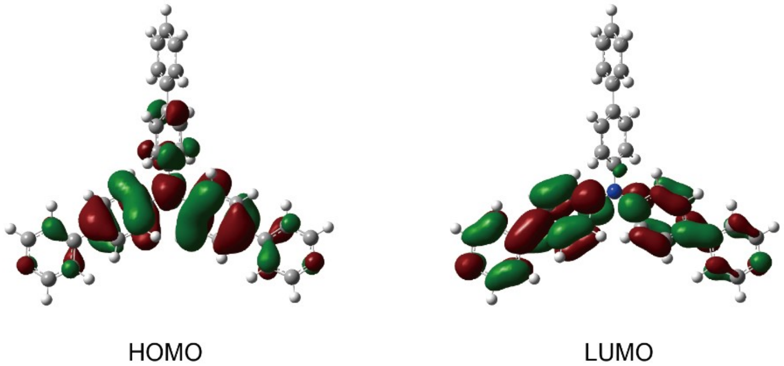


Figure S21. Frontier orbital of ligand **5**.

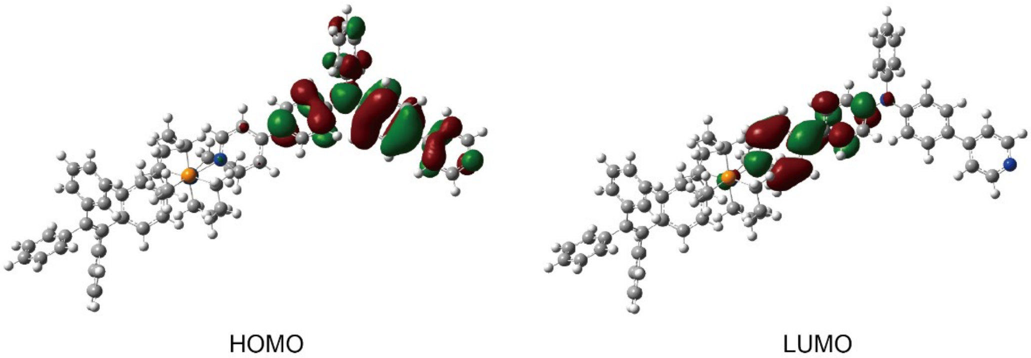
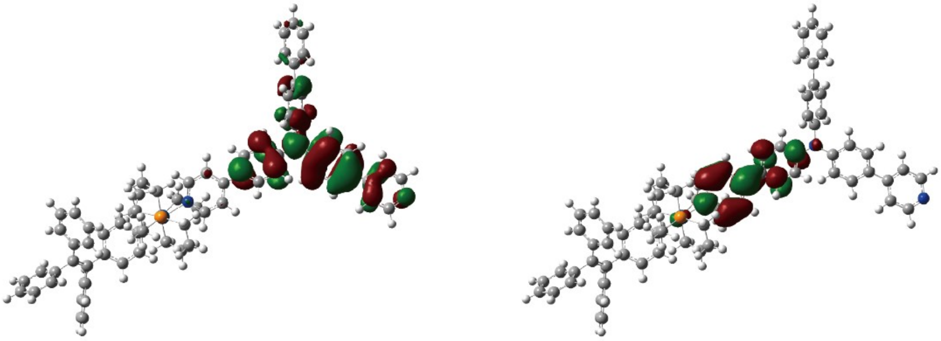


Figure S22. Frontier orbital of metallacycle **1** (1/3).



HOMO LUMO

Figure S23. Frontier orbital of metallacycle **2** (1/3).

References

S1. X. Yan, M. Wang, T. R. Cook, M. Zhang, M. L. Saha, Z. Zhou, X. Li, F. Huang, P. J. Stang, *J. Am. Chem. Soc.* 2016, **138**, 4580-4588.

S2. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, Williams, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman and D. J. Fox, Wallingford CT, 2013.