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Supporting Information

Platinum(II) Metallacycles as Highly Affinitive Hosts for Dendritic Amino Acid with Tunable Circularly Polarized Luminescence

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Experimental Section: All reagents and solvents were purchased from commercial sources and used as supplied without further purification. Solvents were dried and distilled prior to use according to standard procedures. ^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectra were recorded on Bruker 400 MHz Spectrometer and Bruker 500 MHz Spectrometer at 298 K. The ^{1}H and ^{13}C NMR chemical shifts are reported relative to residual solvent signals and ^{31}P NMR resonances are referenced to an external unlocked sample of 85% H_3PO_4 (δ 0.0). Coupling constants (J) are denoted in Hz and

chemical shifts (d) in ppm. Multiplicities are denoted as follows: s= singlet, d= doublet, m= multiplet. The fluorescence spectra of the samples were measured with a Hitachi F-7000 fluorescence spectrophotometer using a monochromated Xe lamo as an excitation source. Samples for emission measurements were contained in 1 cm*cm cuvette, all the tests were carried out in the room temperature if not mentioned. Electrospray ionization (ESI) mass spectral analyses were performed using an AgilentQ-TOF6510. High resolution mass spectrum (HRMS) were performed using Ultra-Performance liquid chromatography coupled to quadrupole time-of-flight spectrometer. Circular dichroism (CD) and circularly polarized luminescence (CPL) spectra were measured with an Applied Photophysics Chirascan V100. CD spectroscopy was carried out in solution state and CPL samples were centrifuged and drop-casted in cuvette plates before testing. DLS was measured on a Malvern with laser wavelength at 632.5 nm (NanoZS model, UK). The AFM sample was dropped on the mica wafer and air-dried. Transmission electron microscope (TEM) images were measured by a HITACHI JEM-100CX II electron microscope (Japan). The samples for TEM detection were dropped in the copper grid and air-dried.

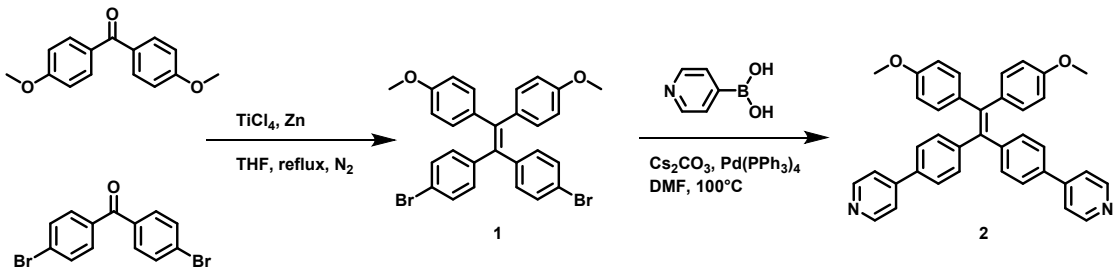
Determination of binding constant

Determination of binding constant between host and guest was based on the following equation:

$$\Delta I = \Delta I + (I_D - I_{MD})\frac{\left([D]_0 - [M]_0 - \frac{1}{K}\right) - \sqrt{b\left([D]_0 - [M]_0 - \frac{1}{K}\right)^2 - 4[D]_0[M]_0}}{2[D]_0}$$

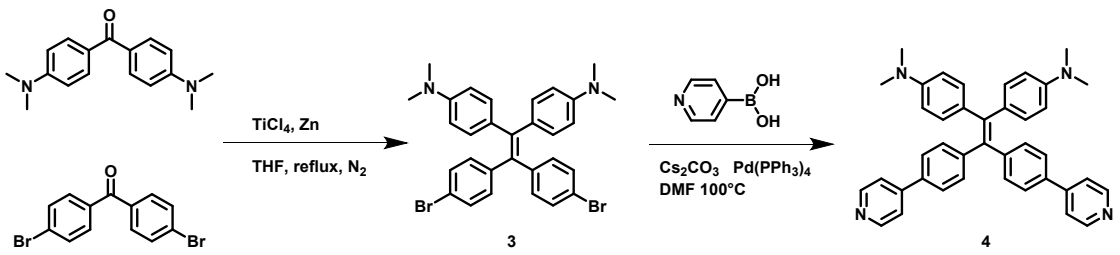
Here, $[D]_0$ is a constant number, [M] is the concentration of cycles, and ΔI is the change of fluorescence intensity of macrocycles when the guests were added. For fitting, the fluorescence intensity change was plotted against the total of the guest to obtain the binding constant K.

Scheme 1: The synthesis route of compound **2**.



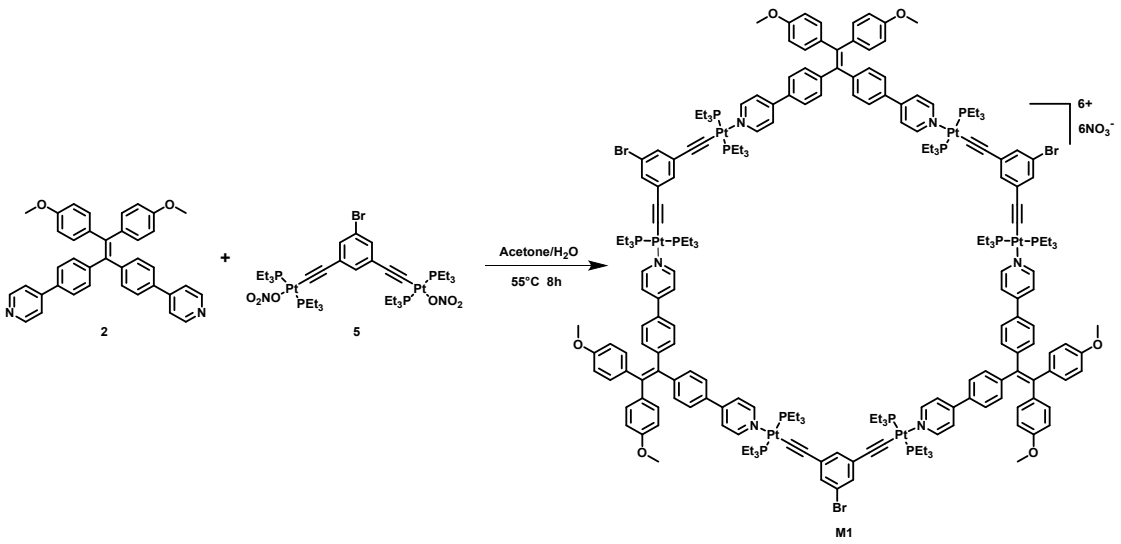
Synthesis of 2: Compound **1** was synthesized according to previous report[1]. **1** (500 mg, 0.908 mmol) and Pyridine-4-boronic acid (335 mg, 2.72 mmol), catalyst Pd $(PPh_3)_4$ (104.92 mg, 0.0908 mmol) and CsCO3 (591.68 mg, 1.82 mmol) were added to the three-necked flask under nitrogen atmosphere. Then 30 ml of dried DMF was added to the system to dissolve the mixture. The reaction system was allowed to stir for 48 hours at 100 ℃. The solvent was removed under vacuum. The product was extracted with dichloromethane and water, the organic phase was washed with water and dried with anhydrous sodium sulfate and concentrated. Then the crude product was purified by column chromatography, with DCM: MeOH = 40:1, get the yellow solid product **2** (376 mg, 75.7%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.63-8.61 (d, J=8.0 Hz, 4H), 7.48-7.47 (d, J=4.0 Hz, 4H), 7.45-7.43 (d, J=8.0 Hz, 4H), 7.17-7.15 (d, J=8.0 Hz, 4H), 7.00-6.97 (d, J=12.0 Hz, 4H), 6.68-6.66 (d, J=8.0 Hz, 4H), 3.75(s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): 158.60, 150.36, 147.86, 145.32, 142.04, 137.54, 135.99, 135.59, 132.79, 132.33, 126.45, 121.38, 113.35, 55.27. MS (ESI-MS): calculated for $[M+H]^+$: 547.3407; found: 547.2307

Scheme 2: The synthesis route of compound **4**.



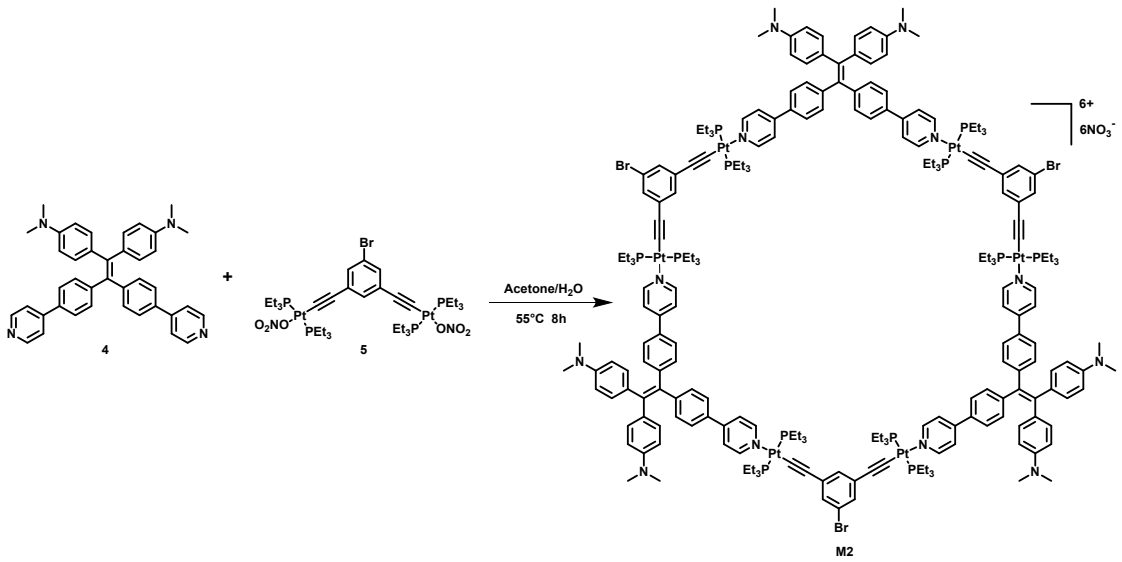
Synthesis of 4: Compound **3** was synthesized according to previous report[2]. **3** (500 mg, 0.867 mmol) and Pyridine-4-boronic acid (319.7 mg, 2.6 mmol), catalyst Pd $(PPh_3)_4$ (100.19 mg, 0.0867 mmol) and CsCO3 (564.97 mg, 1.73 mmol) were added to the three-necked flask under nitrogen atmosphere. Then 30 ml of dried DMF was added to the system to dissolve the mixture. The reaction system was allowed to stir for 48 hours at 100 ℃. The solvent was removed under vacuum. The product was extracted with dichloromethane and water, the organic phase was washed with water and dried with anhydrous sodium sulfate and concentrated. Then the crude product was purified by column chromatography, with DCM: MeOH = 30:1, get the orange product **4** (339.3 mg, 68.4%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.62-8.60 (d, J=8.0 Hz, 4H), 7.49-7.48 (d, J=4.0 Hz, 4H), 7.45-7.43 (d, J=8.0 Hz, 4H), 7.19-7.17 (d, J=8.0 Hz, 4H), 6.95-6.93 (d, J=8.0 Hz, 4H), 6.48-6.46 (d, J=8.0 Hz, 4H), 2.91(s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): 150.32, 149.27, 148.04, 146.48, 143.41, 134.99, 134.88, 132.83, 132.51, 131.81, 126.30, 121.32, 111.47, 40.46. MS (ESI-MS): calculated for $[M+H]^+$: 573.2940; found: 573.3006.

Scheme 3: The synthesis route of **M1**.



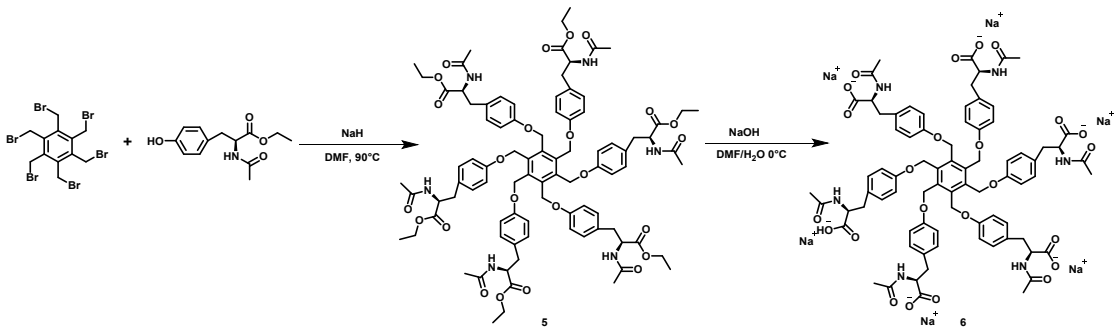
Synthesis of M1: The dipyridyl donor ligand **2** (12.9 mg, 0.023 mmol) and the 120° diplatinum acceptor **5** (28.07 mg, 0.023 mmol) were weighed into a glass vial. To the vial was added 2.0 ml acetone and 0.5 ml water. The reaction solution was then stirred at 55 ℃ for 12 h. The solvent was then evaporated under pressure to afford metallacycle **M1** (40.9 mg, >99%) as a yellow solid. ^{1}H NMR (400 MHz, acetone-d_6): δ 8.83-8.81 (d, J=8.0 Hz, 12H), 8.03-8.02 (d, 4.0 Hz, 12H), 7.76-7.74 (d, J=8.0 Hz, 12H), 7.22-7.21 (d, J=4.0 Hz, 12H), 7.20 (d, J=4.0 Hz, 6H), 7.06 (s, 3H), 6.97-6.94 (d, J=12 Hz, 8H), 6.71-6.68 (d, J=12 Hz, 8H), 3.69 (s, 18H), 1.90-1.82 (m, 72H), 1.18-1.10 (m, 108H); ^{31}P NMR (162 MHz, acetone-d_6): δ 15.80 ($^{1}J_{Pt\text{-}P}$= 2308.5 Hz). MS (HR-MS): calculated for $[M\text{-}6NO_3]^{6+}$: 806.2331, found: 806.2121; calculated for $[M\text{-}5NO_3]^{5+}$: 979.8774, found: 979.8518; calculated for $[M\text{-}4NO_3]^{4+}$: 1240.3438, found: 1240.3128.

Scheme 4: The synthesis route of **M2**.



Synthesis of M2: The dipyridyl donor ligand **4** (17.7 mg, 0.0309 mmol) and the 120° diplatinum acceptor **5** (36.76 mg, 0.0309 mmol) were weighed into a glass vial. To the vial was added 2.0 ml acetone and 0.5 ml water. The reaction solution was then stirred at 55 ℃ for 12 h. The solvent was then evaporated under pressure to afford metallacycle **M2** (51.2 mg, >99%) as an orange solid. ^{1}H NMR (400 MHz, acetone-d_6): δ 8.84-8.82 (d, J=8.0 Hz, 12H), 8.04-8.03 (d, 4.0 Hz, 12H), 7.76-7.74 (d, J=8.0 Hz, 12H), 7.20-7.19 (d, J=4.0 Hz, 12H), 7.23 (d, J=4.0 Hz, 6H), 7.07 (s, 3H), 6.87-6.84 (d, J=12 Hz, 8H), 6.49-6.47 (d, J=8 Hz, 8H), 2.84 (s, 36H), 1.89-1.84 (m, 72H), 1.19-1.11 (m, 108H); ^{31}P NMR (162 MHz, acetone-d_6): δ 15.76 ($^{1}J_{Pt\text{-}P}$= 2311.74 Hz). MS (HR-MS): calculated for $[M\text{-}6NO_3]^{6+}$: 819.2647, found: 819.2361; calculated for $[M\text{-}5NO_3]^{5+}$: 995.5154, found: 995.4814; calculated for $[M\text{-}4NO_3]^{4+}$: 1259.8913, found: 1259.8511.

Scheme 5: The synthesis route of compound **5** and **6.**

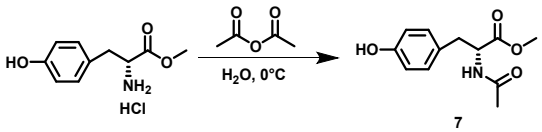


Synthesis of 5: A solution of sodium hydride (75.36 mg, 3.14 mmol) in DMF (2 ml) was added dropwise to a solution of ethyl N-acetyl-L-tyrosinate hydrate (845.57 mg, 3.14 mmol) in DMF (10 ml) at room temperature. Then the solution was heated to 90 ℃ and it turned to deep green. After 30 min, 1,2,3,4,5,6-hexa(bromomethyl)benzene (200 mg, 0.314 mmol) was added, and the solution was stirred at 90 ℃ for 12 h. After cooling to room temperature, the solution was diluted with 100 ml of water, and a lot of white precipitate was produced. The precipitate was extracted with dichloromethane and water, the organic phase was dried with anhydrous sodium sulfate and concentrated. Then the crude product was purified by column chromatography, with DCM: MeOH = 8:1, get the white solid. The solid was washed with acetone, then get the product **5** (150 mg, 28.8%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.98-6.96 (d, J=8.0 Hz, 12H), 6.81-6.79 (d, J=12.0 Hz), 5.14 (s, 12H), 4.82-4.77 (q, J=8.0 Hz, 6H), 4.19-4.12 (m, 12H), 3.10-2.98 (m, 12H), 1.96 (s, 18H), 1.24-1.21 (t, J=8.0 Hz, 18H); ^{13}C NMR (100 MHz, $CDCl_3$): 171.77, 169.69, 157.60, 137.96, 130.57, 128.97, 114.78, 63.63, 61.63, 53.36, 37.15, 23.29, 14.27; MS (ESI-MS): m/z calculated for $[M+2H]^{2+}$: 829.3707; found: 829.8698.

Synthesis of 6: A solution of NaOH (13.04 mg, 0.326 mmol) in H_2O (1 ml) was added to a solution of **5** (90 mg, 0.054 mmol) in DMF (10 ml) at 0 ℃. The solution was stirred at 0 ℃ for 2h and a lot

of white precipitate was produced. The precipitate was obtained by centrifugation and was washed with dichloromethane, get the white solid **6** (40 mg, 45.6%). ^{1}H NMR (400 MHz, D_2O): δ 7.07-7.05 (d, J=8.0 Hz, 12H), 6.82-6.80 (d, J=8.0 Hz, 12H), 5.26 (s, 12H), 4.34-4.31 (dd, J_1=8.0 Hz, J_2=4.0 Hz, 6H), 3.10-2.73 (m, 12H), 1.80 (s, 18H); ^{13}C NMR (100 MHz, D_2O): δ 178.35, 173.09, 156.49, 137.89, 131.08, 130.22, 114.94, 64.42, 56.39, 36.73, 21.74. MS (ESI-MS): m/z calculated for [M-6Na+8H]$^{2+}$: 745.2841; found: 745.3016.

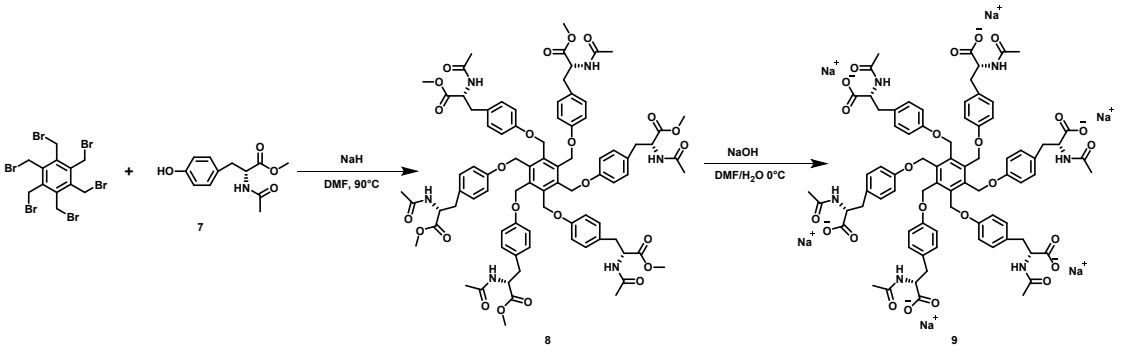
Scheme 6: The synthesis route of compound **7**



7

Synthesis of 7: A solution of the H-D-Tyr-OMe hydrochloride (500 mg, 2.16 mmol) in water (3 ml) was cooled to 0 ℃ before the addition of 5 M sodium acetate solution (20 ml). Acetic anhydride (3 ml) was added and the solution was stirred for 20 min. The resulting precipitate was washed with water and dried to yield the white solid **7** (370 mg, 72.5%). ^{1}H NMR (400 MHz, acetone-d_6): δ 7.27 (s, 1H), 7.04-7.02 (d, J=8.0 Hz, 2H), 6.75-6.73 (d, J=8.0 Hz, 2H), 3.63 (s, 3H), 3.01-2.84 (m, 2H), 1.87 (s, 3H); ^{13}C NMR (100 MHz, acetone-d_6): 173.01, 170.05, 157.16, 131.05, 128.52, 116.02, 54.81, 52.11, 37.59, 22.61. MS (ESI-MS): m/z calculated for [M+H]$^{+}$: 237.1001; found: 238.1082.

Scheme 7: The synthesis route of compound **8** and **9.**



Synthesis of 8: A solution of sodium hydride (75.36 mg, 3.14 mmol) in DMF (2 ml) was added dropwise to a solution of compound **7** (744.99 mg, 3.14 mmol) in DMF (10 ml) at room temperature. Then the solution was heated to 90 ℃ and it turned to deep green. After 30 min, 1,2,3,4,5,6-hexa(bromomethyl)benzene (200 mg, 0.314 mmol) was added, and the solution was stirred at 90 ℃ for 12 h. After cooling to room temperature, the solution was diluted with 100 ml of water, and a lot of white precipitate was produced. The precipitate was extracted with dichloromethane and water, the organic phase was dried with anhydrous sodium sulfate and concentrated. Then the crude product was purified by column chromatography, with DCM: MeOH = 8:1, get the white solid. The solid was washed with acetone, then get the compound **8** (143 mg, 28.9%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.97-6.95 (d, J=8.0 Hz, 12H), 6.81-6.79 (d, J=12.0 Hz), 5.14 (s, 12H), 4.85-4.80 (q, J=8.0 Hz, 6H), 3.70 (s, 18H), 3.10-2.97 (m, 12H), 1.96 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$): 172.22, 169.72, 157.52, 137.97, 130.51, 128.89, 114.87, 63.63, 53.34, 52.49, 37.11, 23.30. MS (HR-MS): m/z calculated for $[M+2H]^{2+}$: 787.3238; found: 787.3214.

Synthesis of 9: A solution of NaOH (15.26 mg, 0.38 mmol) in H_2O (1 ml) was added to a solution of **8** (100 mg, 0.063 mmol) in DMF (10 ml) at 0 ℃. The solution was stirred at 0 ℃ for 2h and a lot of white precipitate was produced. The precipitate was obtained by centrifugation and was

washed with dichloromethane, get the white solid **9** (43 mg, 42.1%). ^{1}H NMR (400 MHz, D_2O): δ 7.11-7.09 (d, J=8.0 Hz, 12H), 6.87-6.85 (d, J=8.0 Hz, 12H), 5.31 (s, 12H), 4.36-4.33 (dd, J_1=8.0 Hz, J_2=4.0 Hz, 6H), 3.12-2.74 (m, 12H), 1.83 (s, 18H); ^{13}C NMR (100 MHz, D_2O): δ 178.35, 173.08, 156.50, 137.89, 131.08, 130.22, 114.94, 64.43, 56.40, 36.73, 21.74. MS (ESI-MS): m/z calculated for $[M-6Na+8H]^{2+}$: 745.2841; found: 745.2688.

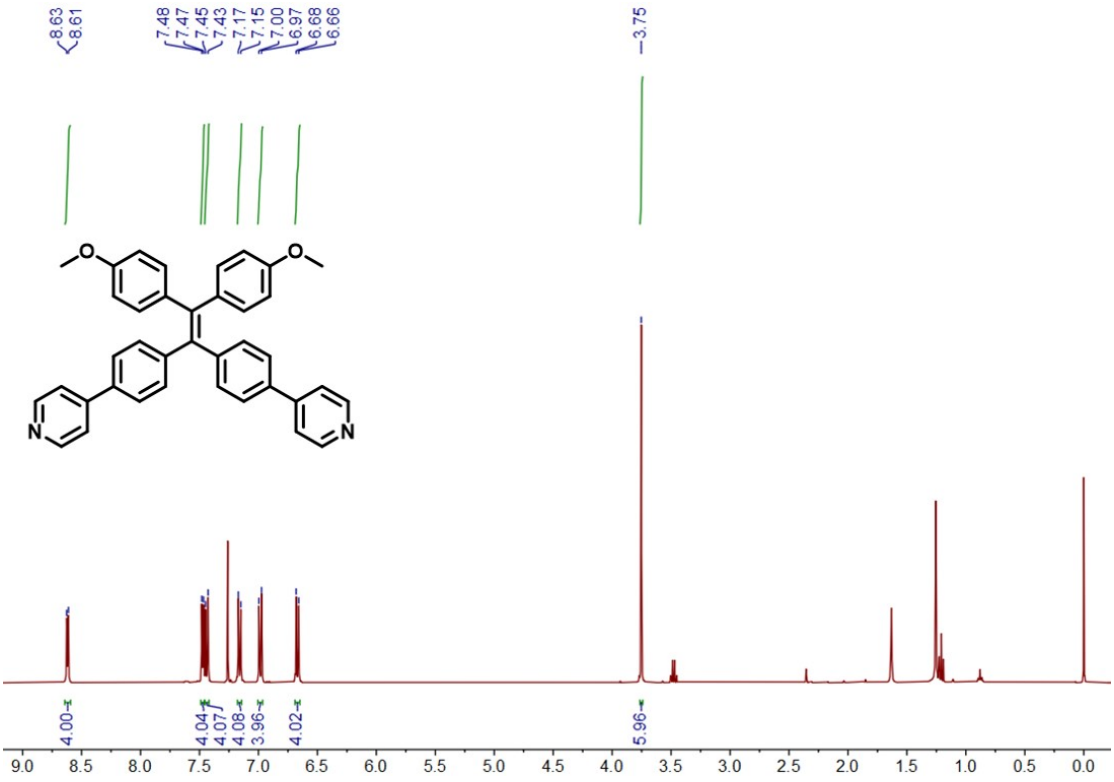


Figure S1. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of compound **2**.

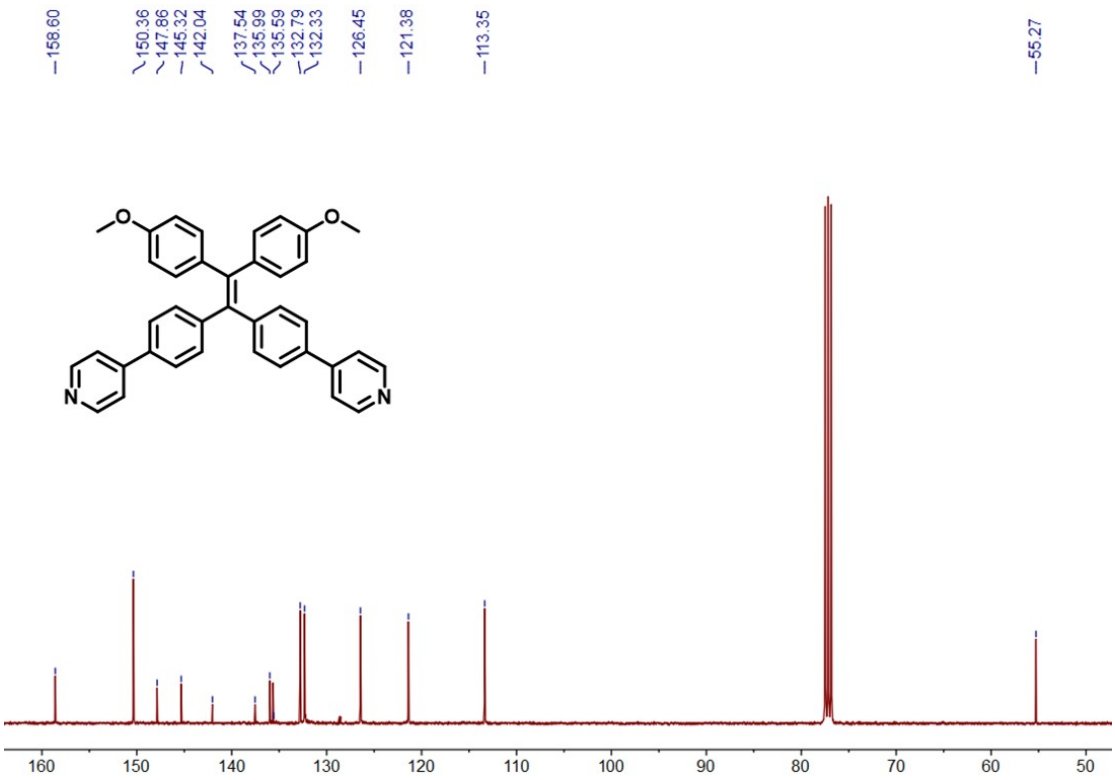


Figure S2. ^{13}C NMR spectrum (100 MHz, $CDCl_3$, 298 K) of compound **2**.

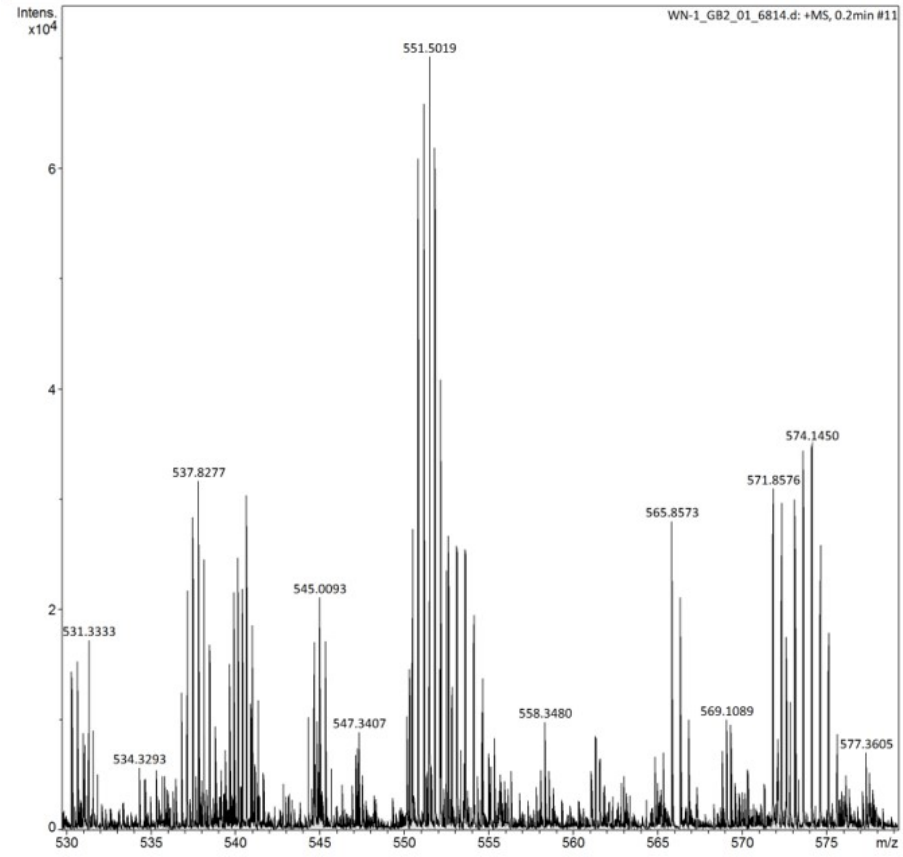


Figure S3. ESI-MS spectra of compound **2**.

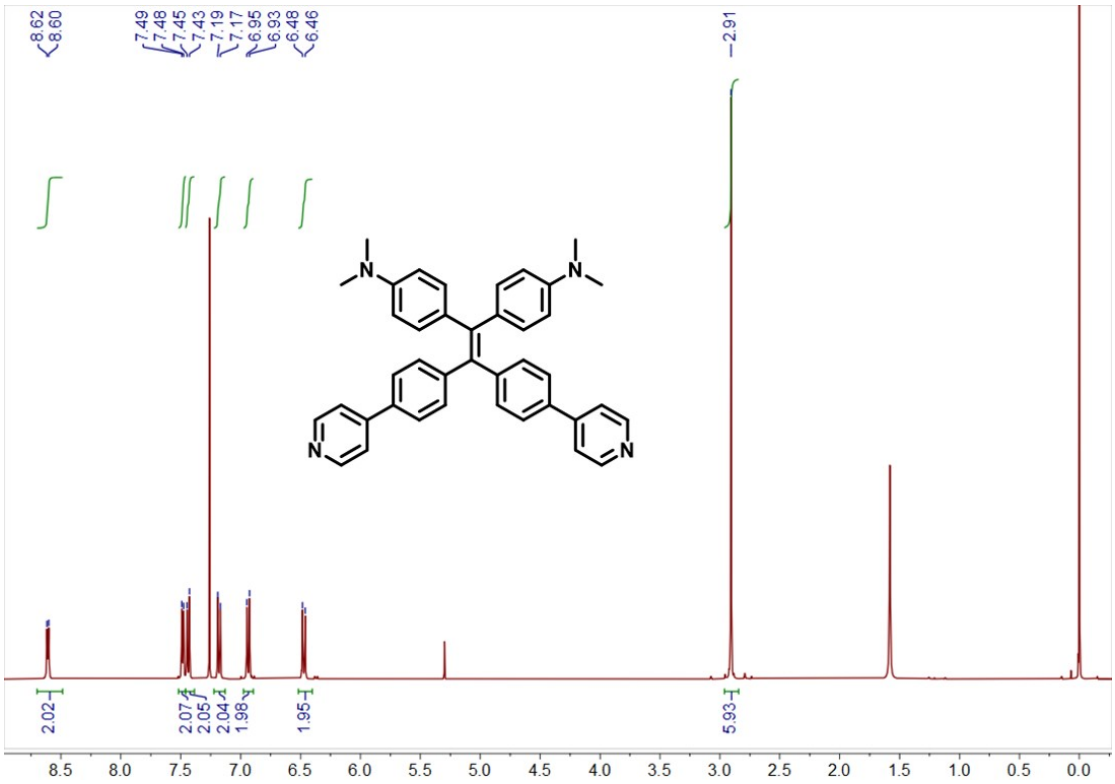


Figure S4. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of compound **4**.

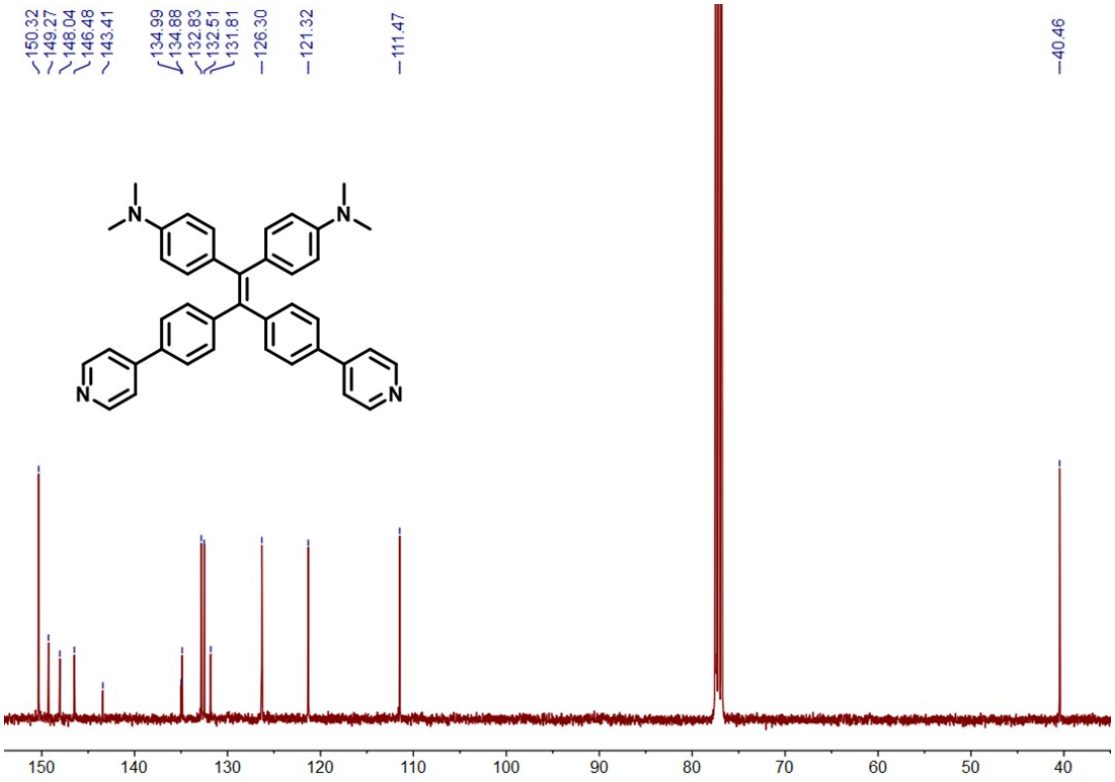


Figure S5. ^{13}C NMR spectrum (100 MHz, $CDCl_3$, 298 K) of compound **4**.

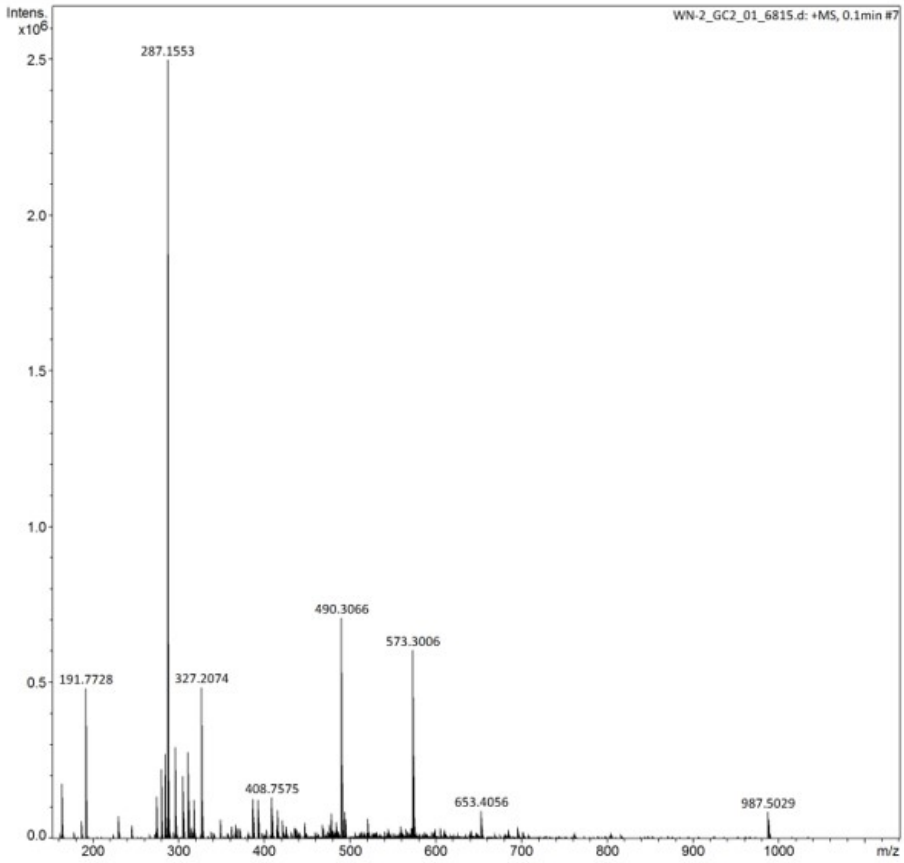


Figure S6. ESI-MS spectra of compound **4**.

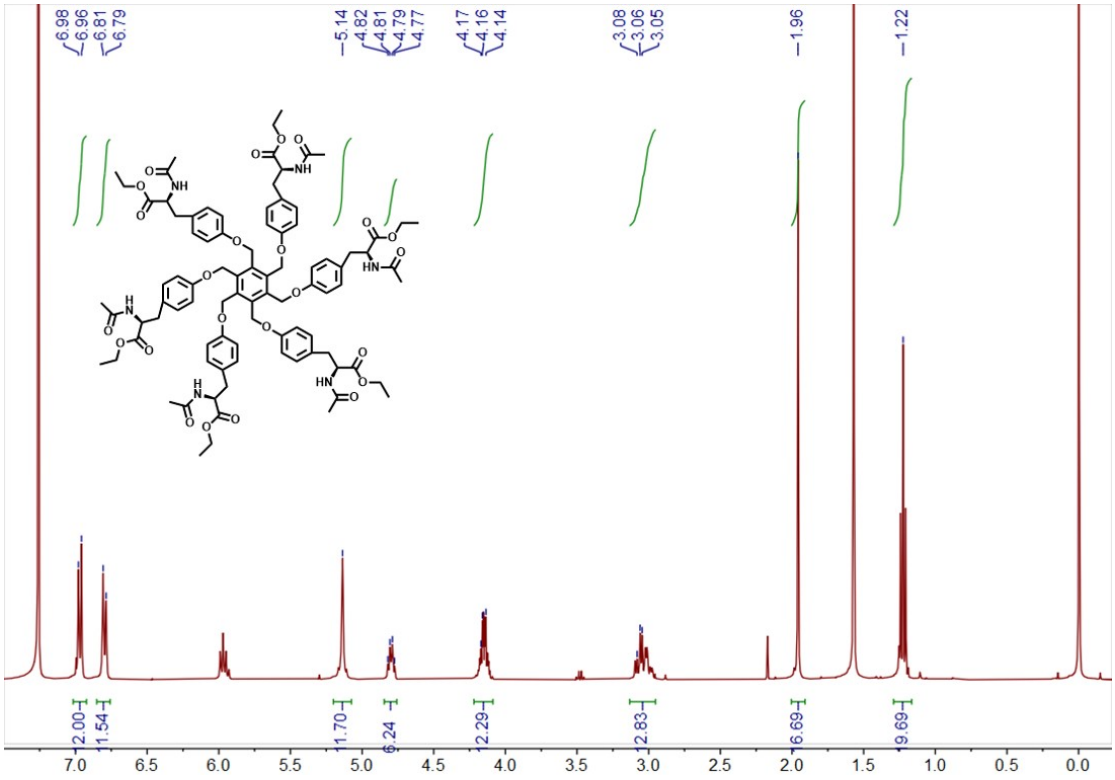


Figure S7. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of compound **5**.

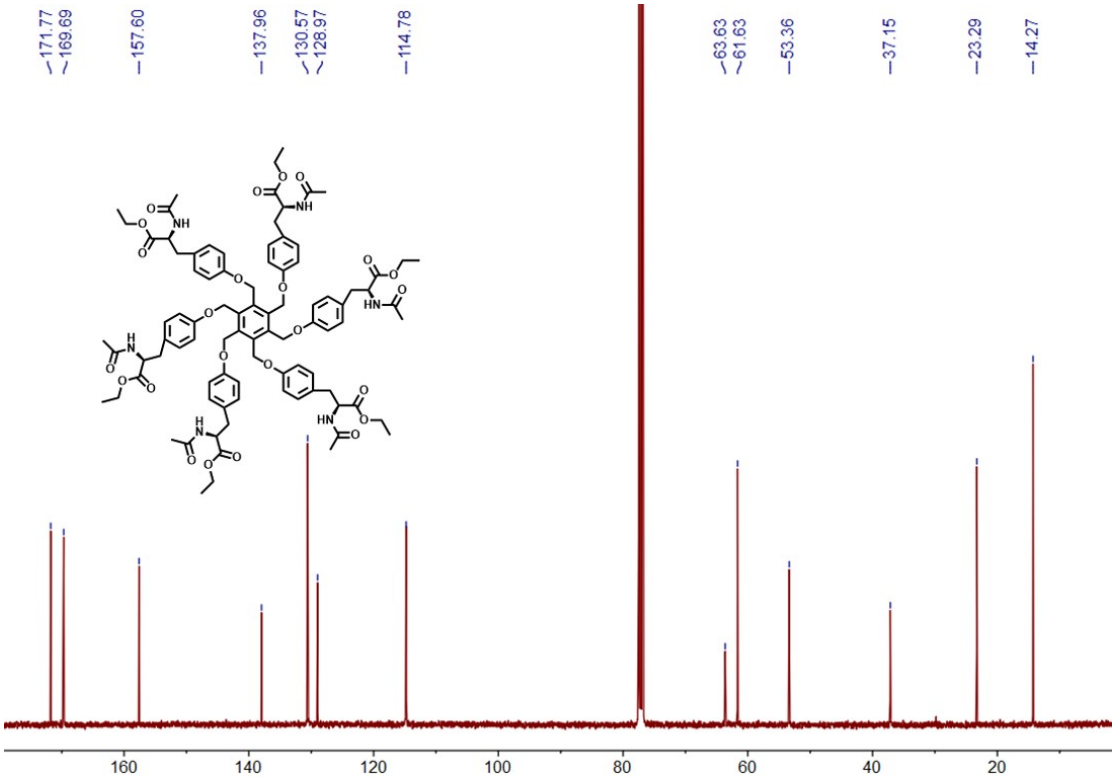


Figure S8. ^{13}C NMR spectrum (100 MHz, $CDCl_3$, 298 K) of compound **5**.

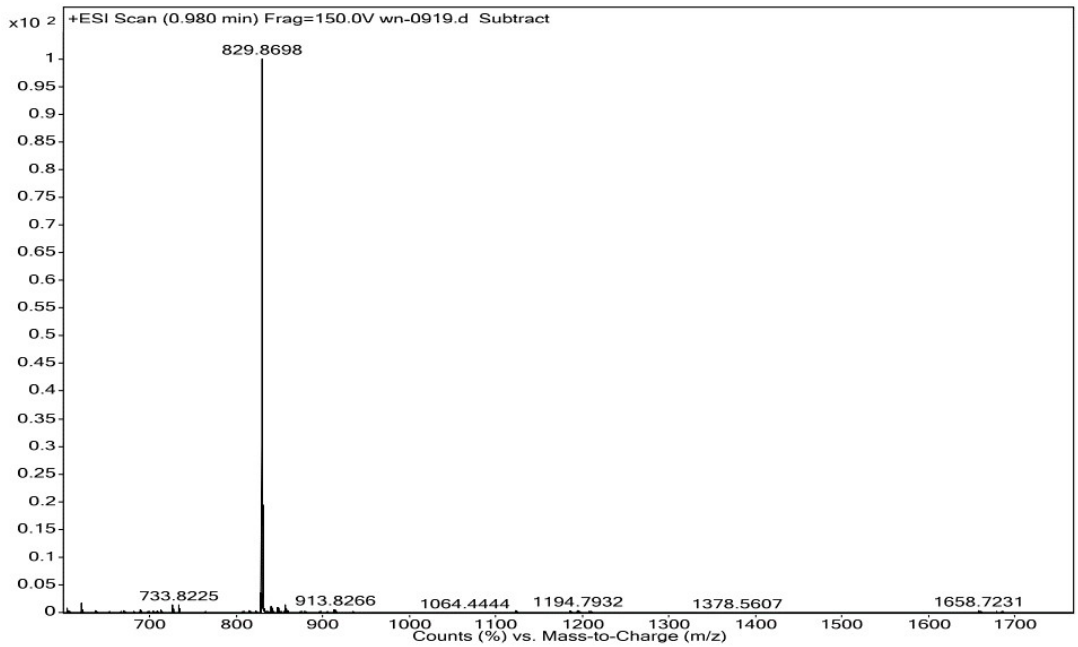


Figure S9. ESI-MS spectra of compound **5**.

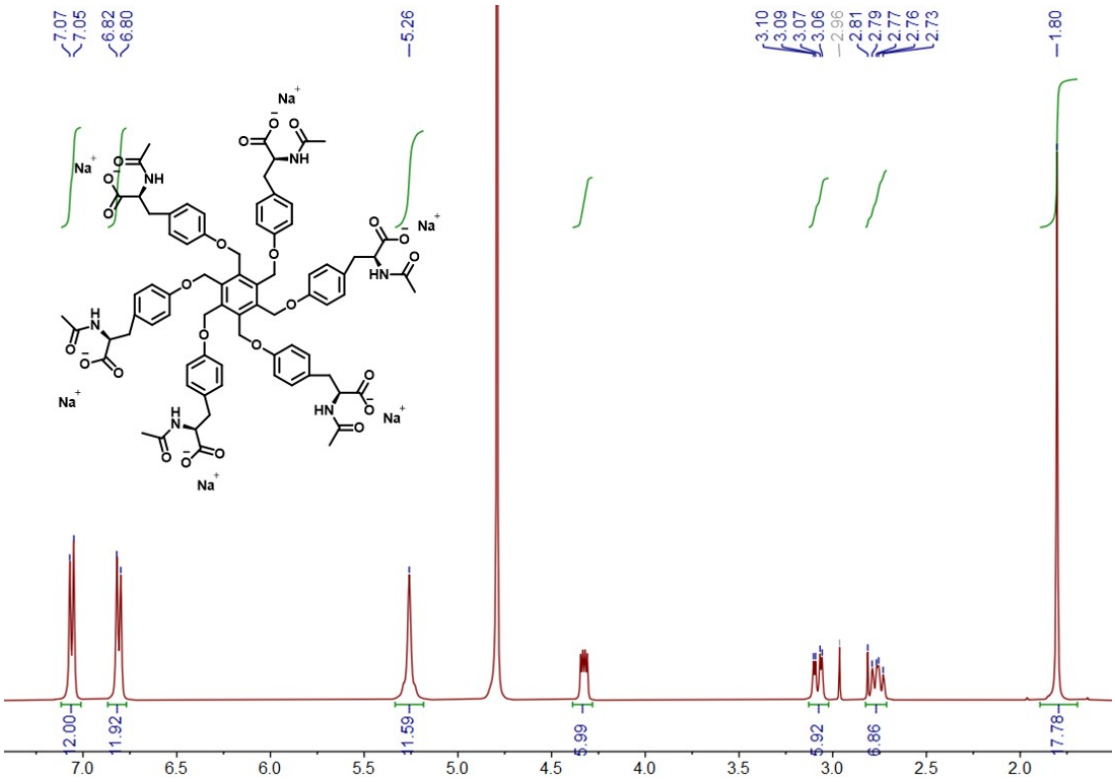


Figure S10. ^{1}H NMR spectrum (400 MHz, D_2O, 298 K) of compound **6**.

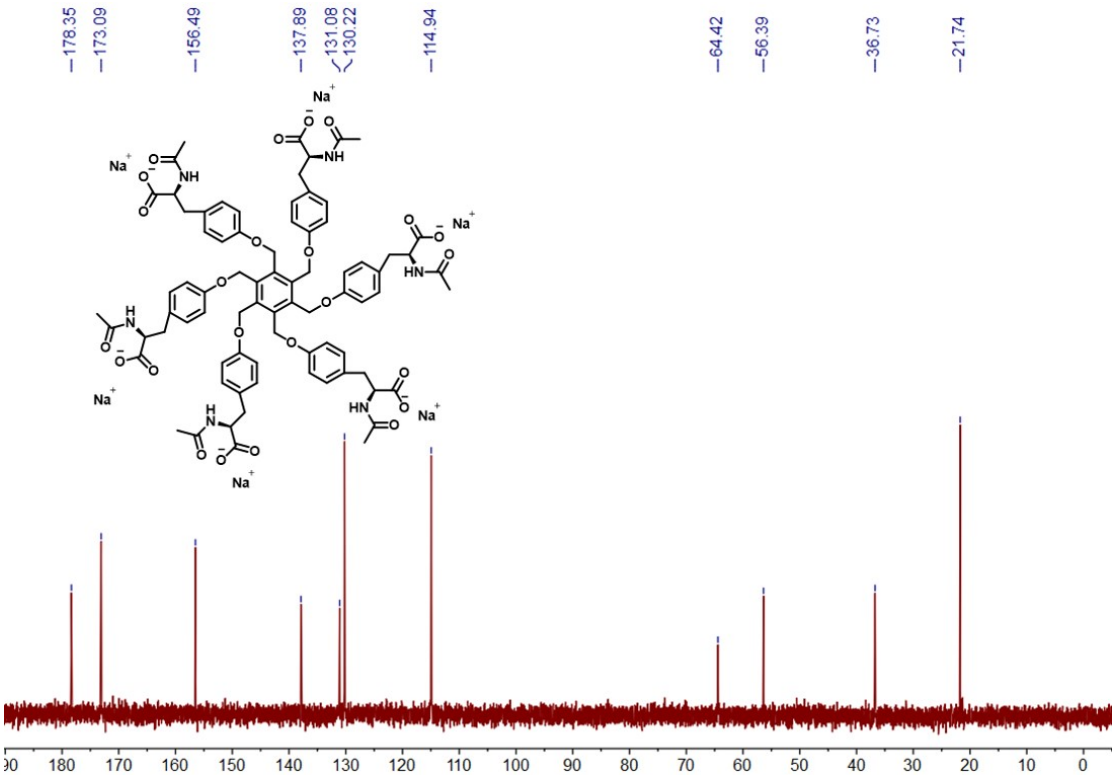


Figure S11. ^{13}C NMR spectrum (100 MHz, D_2O, 298 K) of compound **6**.

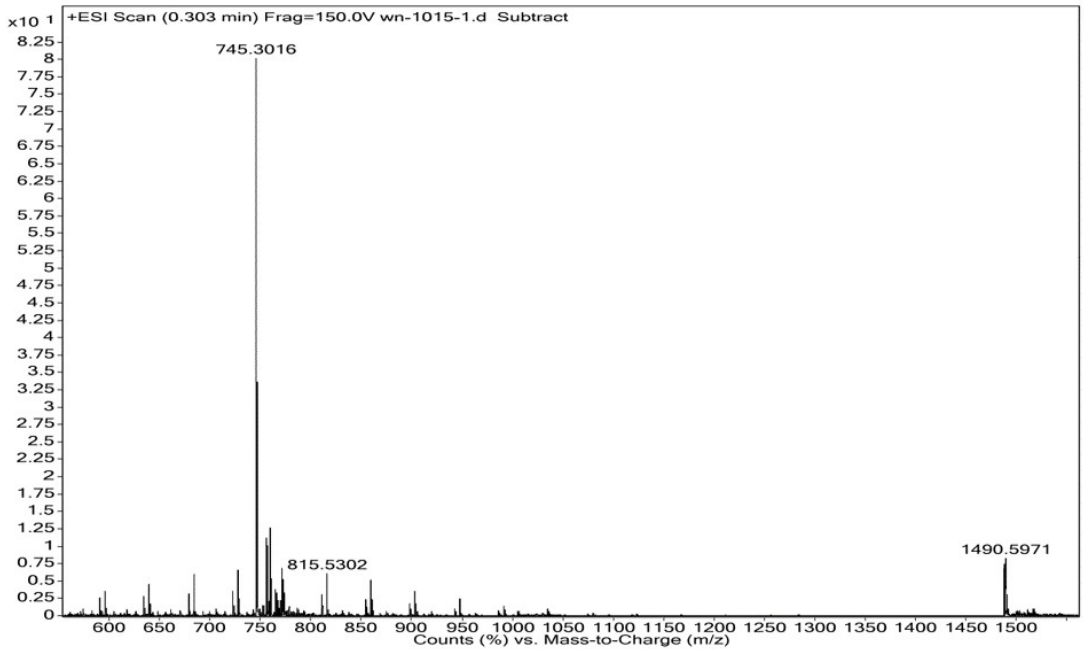


Figure S12. ESI-MS spectra of compound **6**.

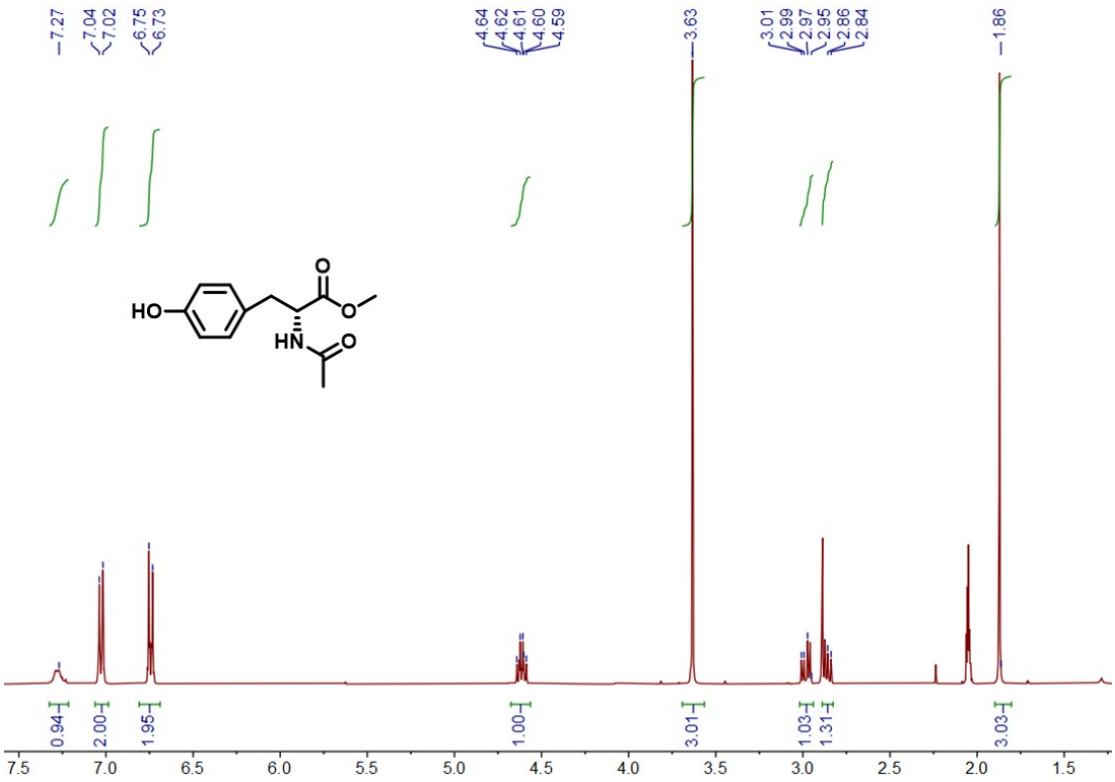


Figure S13. ^{1}H NMR spectrum (400 MHz, acetone-d_6, 298 K) of compound **7**.

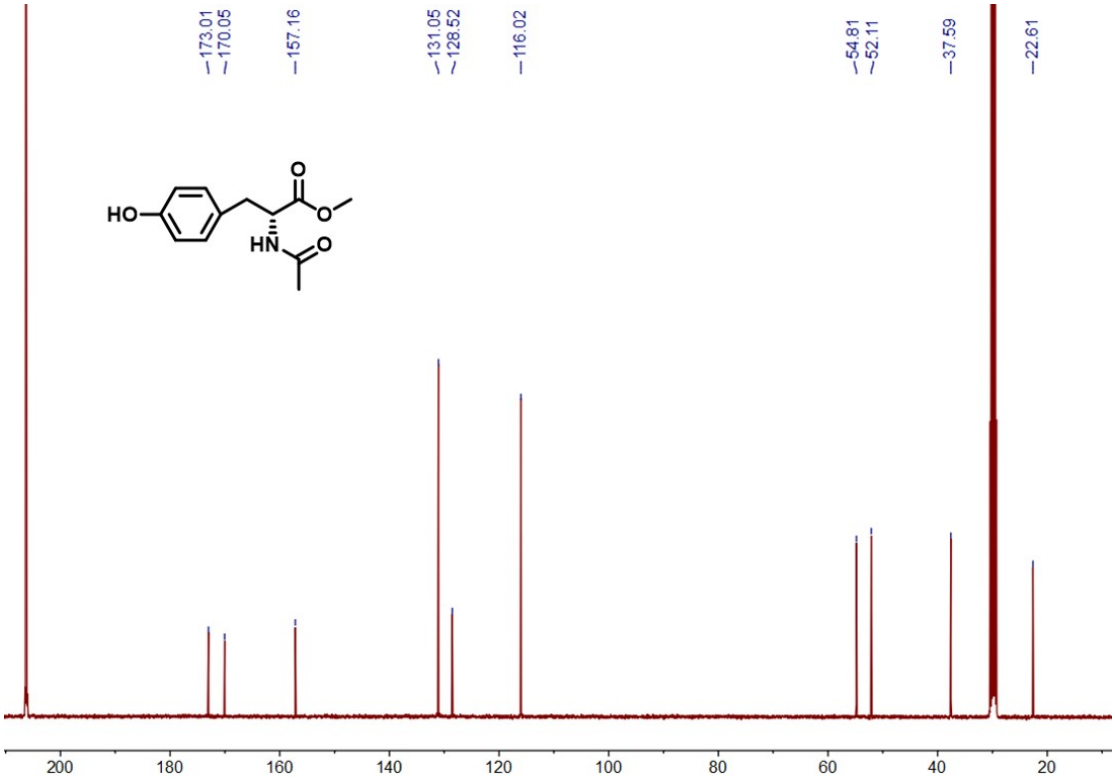


Figure S14. ^{13}C NMR spectrum (100 MHz, acetone-d_6, 298 K) of compound **7**.

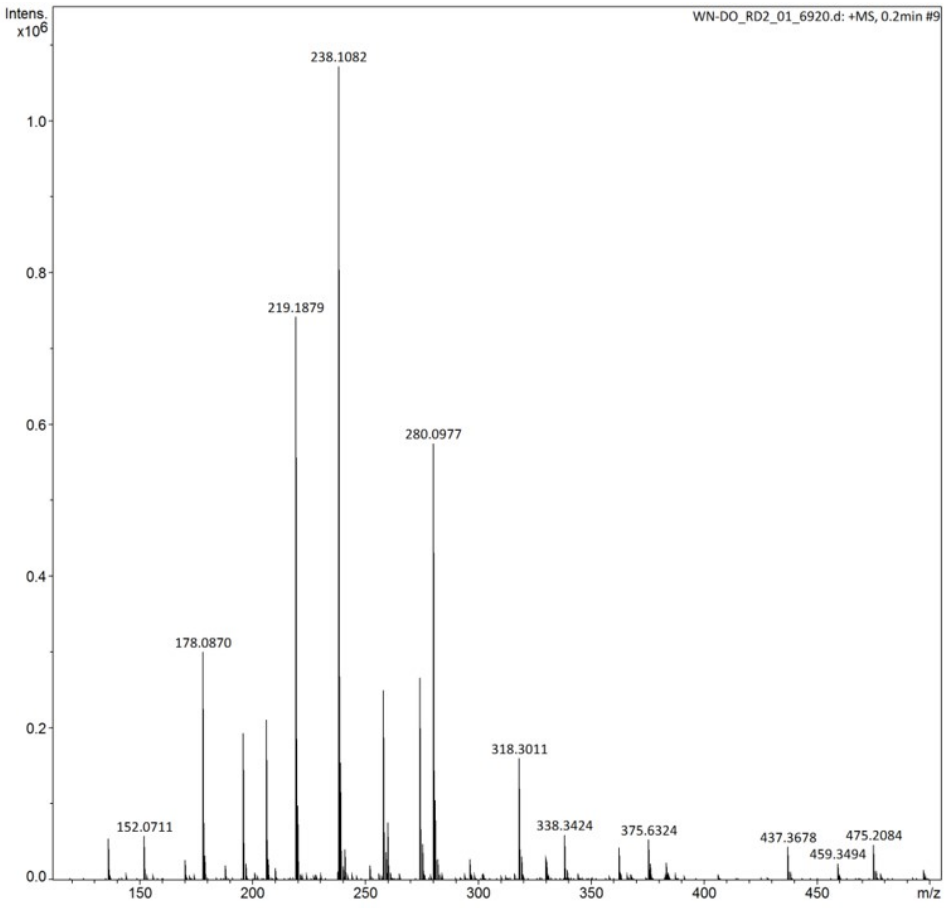


Figure S15. ESI-MS spectra of compound **7**.

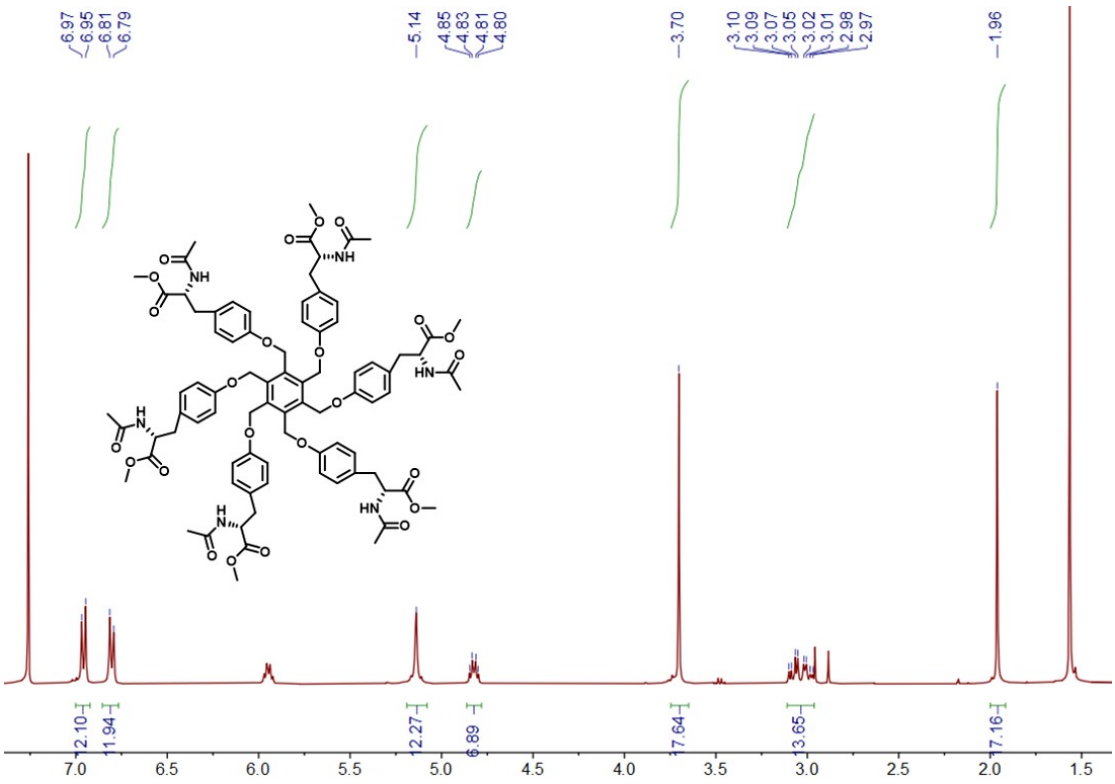


Figure S16. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of compound **8**.

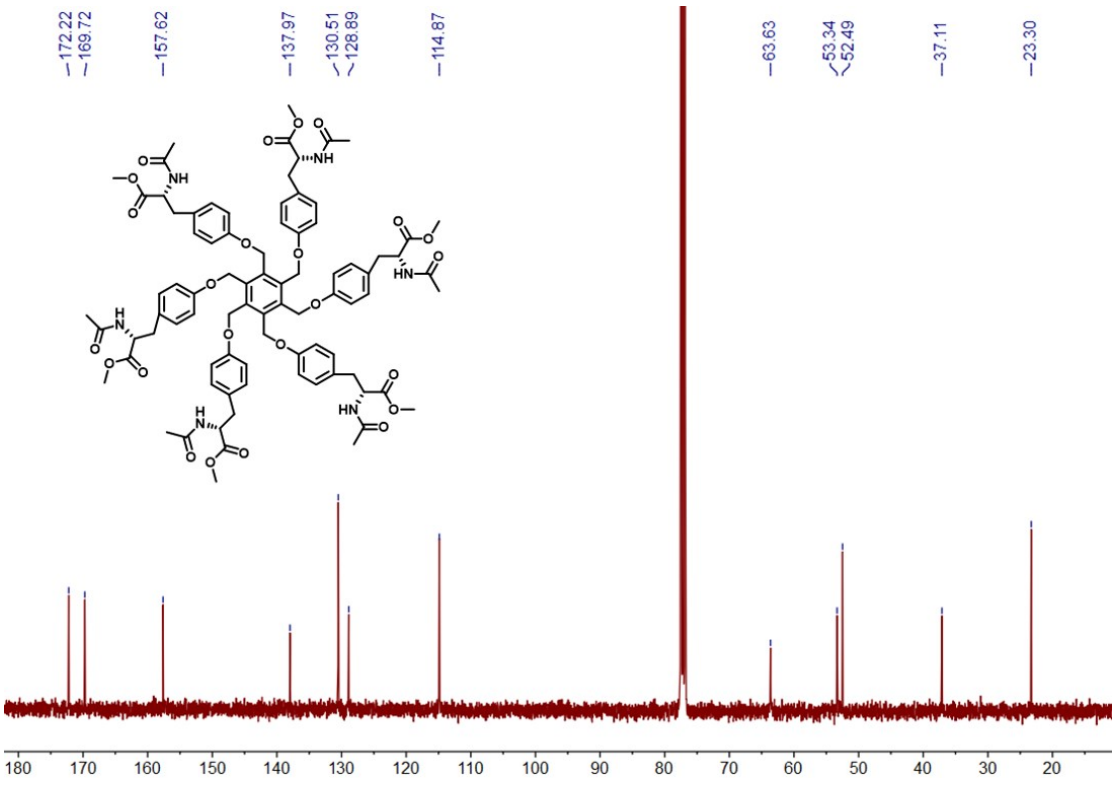


Figure S17. ^{13}C NMR spectrum (100 MHz, $CDCl_3$, 298 K) of compound **8**.

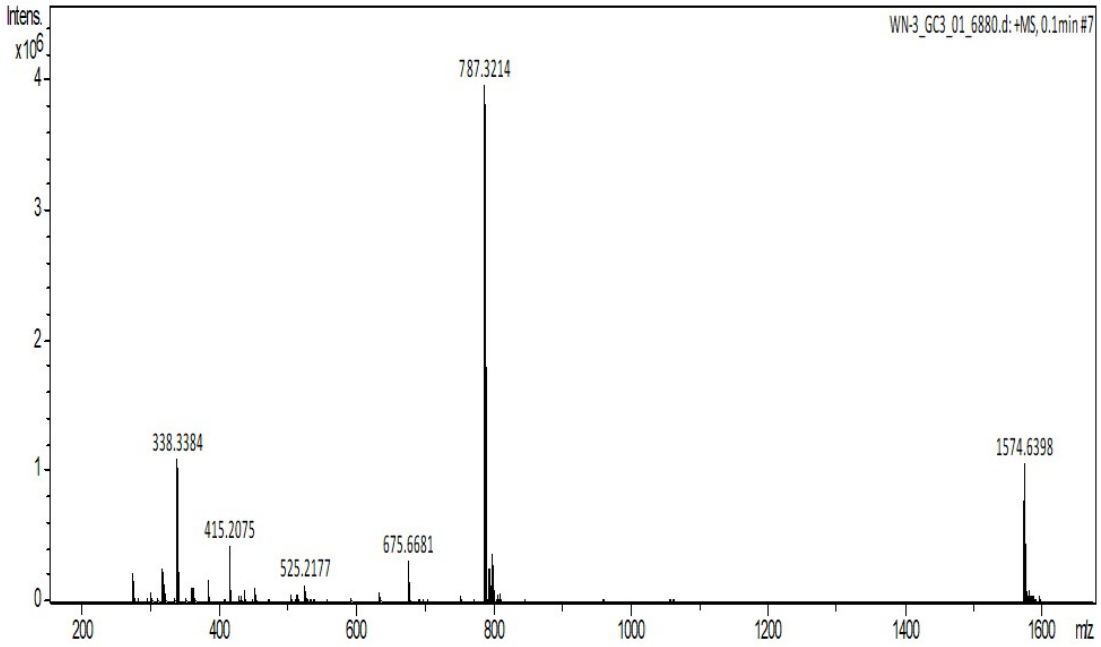


Figure S18. HR-MS spectra of compound **8**.

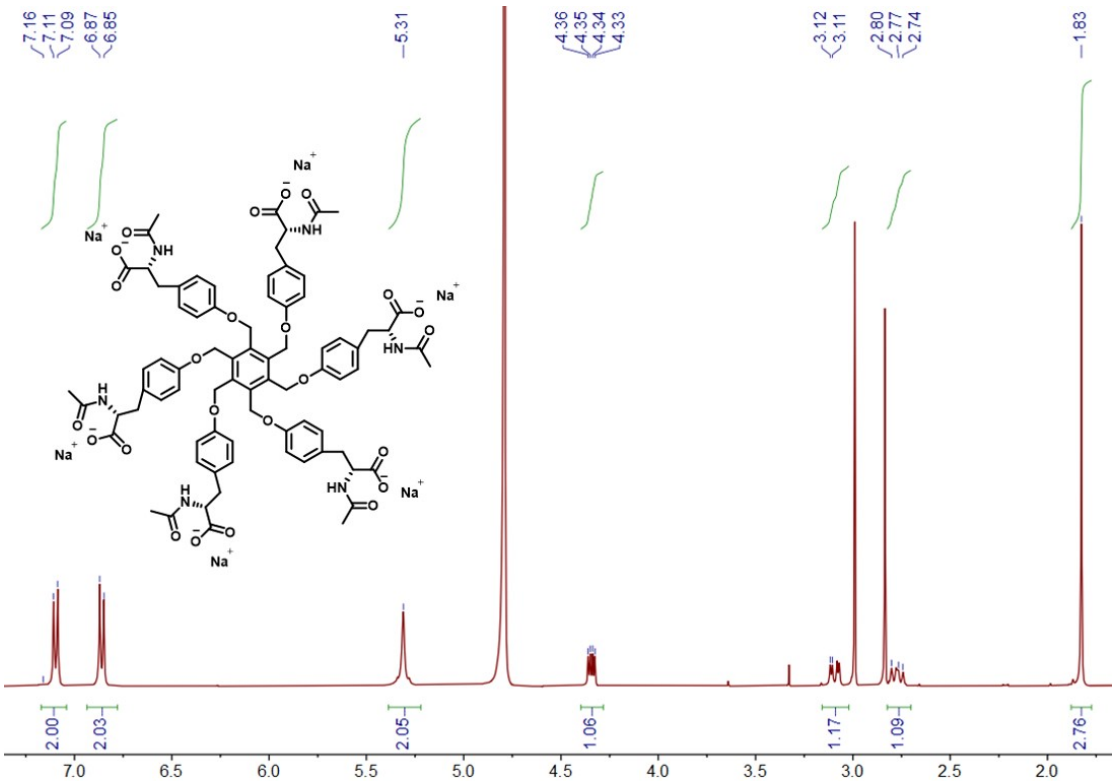


Figure S19. ^{1}H NMR spectrum (400 MHz, D_2O, 298 K) of compound **9**.

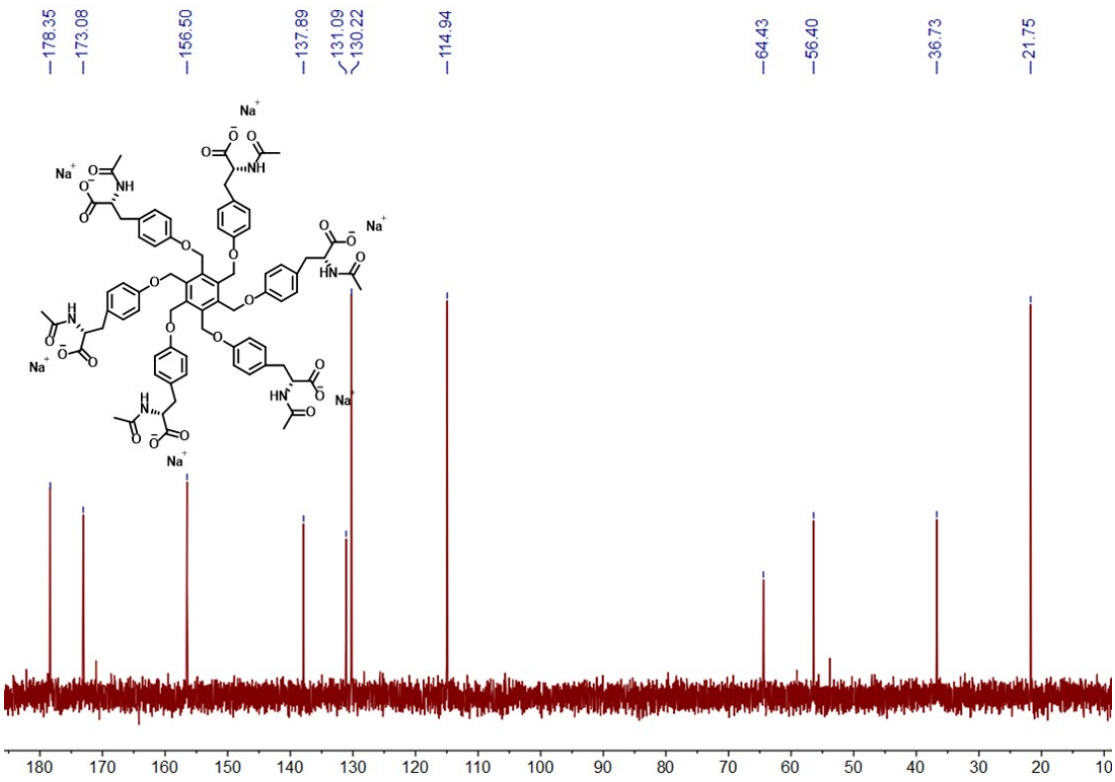


Figure S20. ^{13}C NMR spectrum (100 MHz, D_2O, 298 K) of compound **9**.

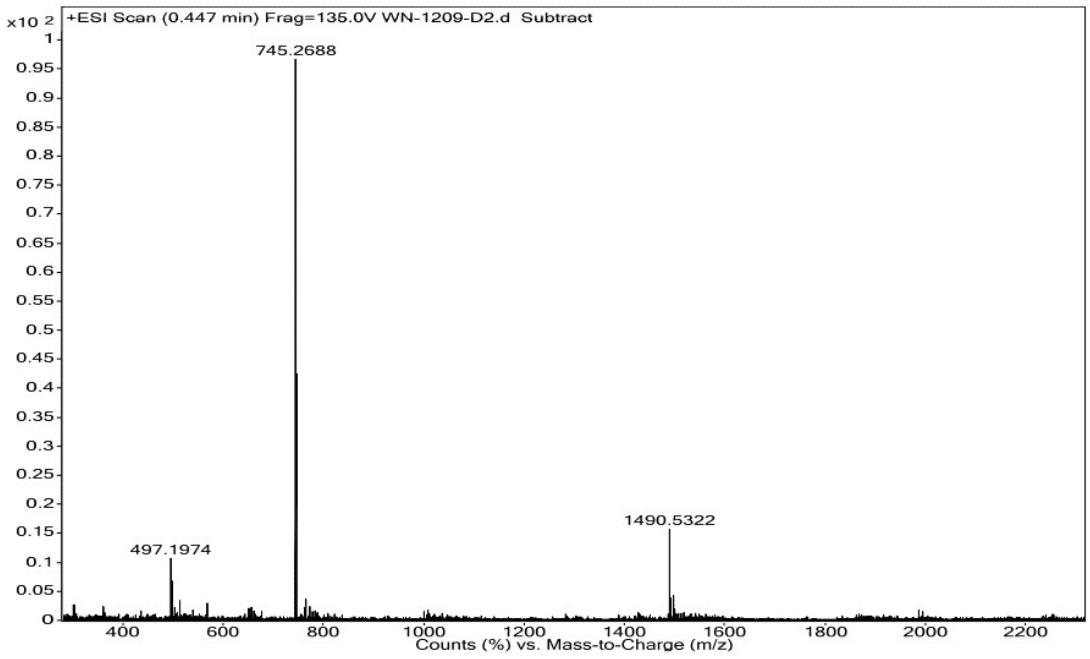


Figure S21. ESI-MS spectra of compound **9**.

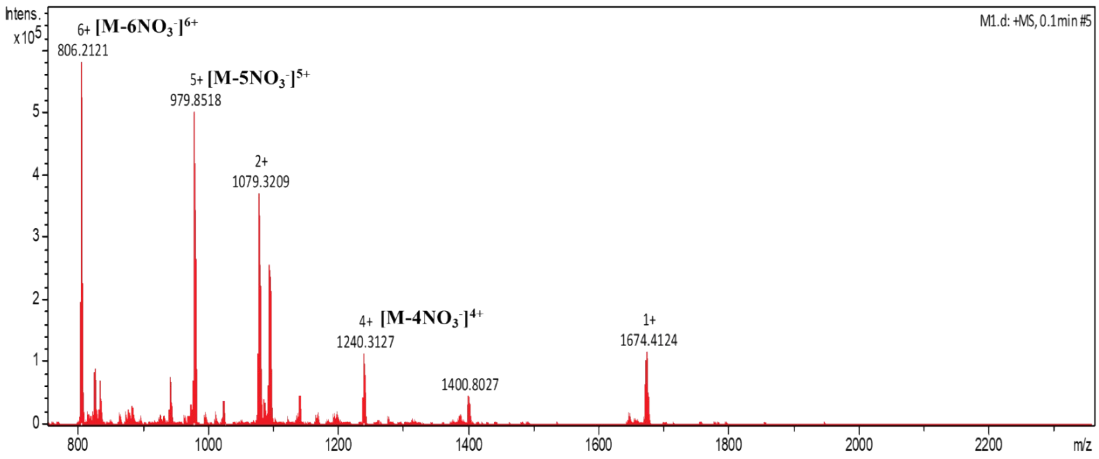


Figure S22. Full HR-MS spectra of metallacycle **M1**.

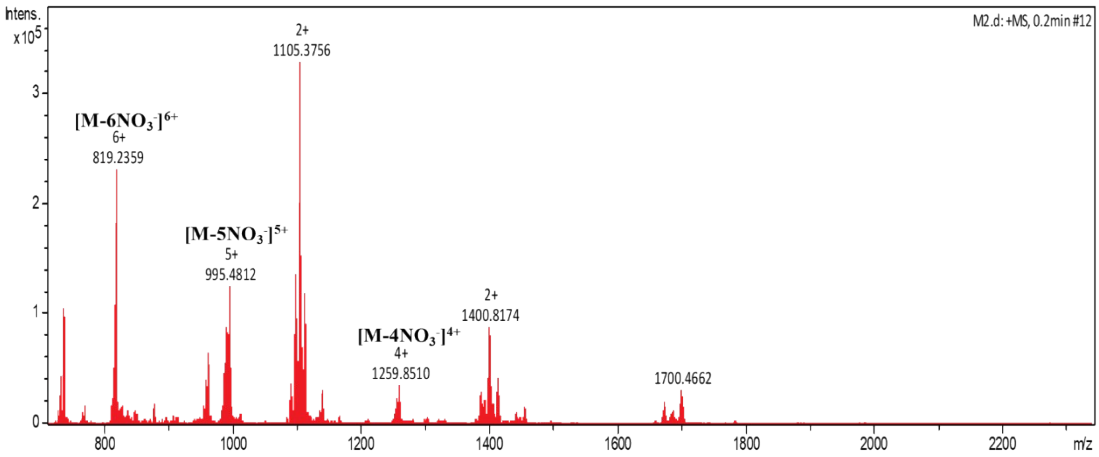


Figure S23. Full HR-MS spectra of metallacycle **M2**.

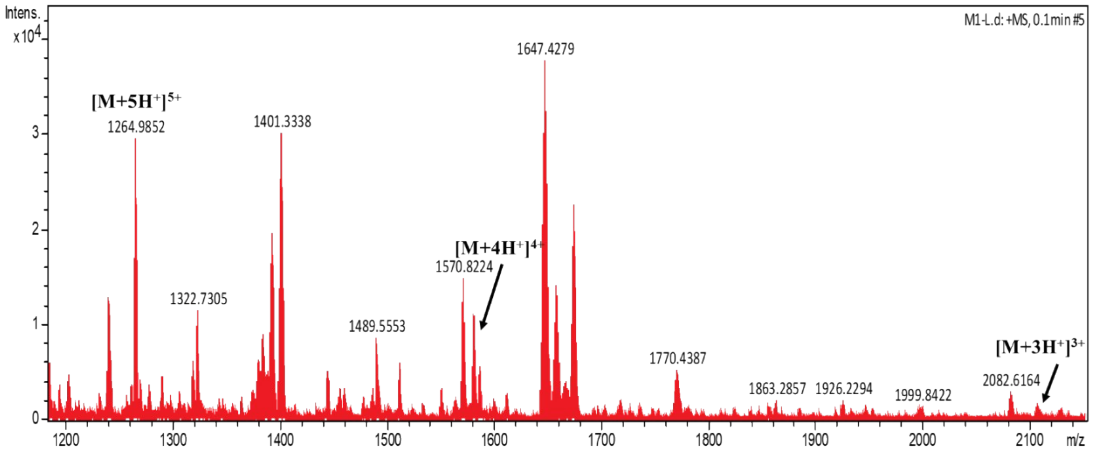


Figure S24. Full HR-MS spectra of metallacycle **M1+L**.

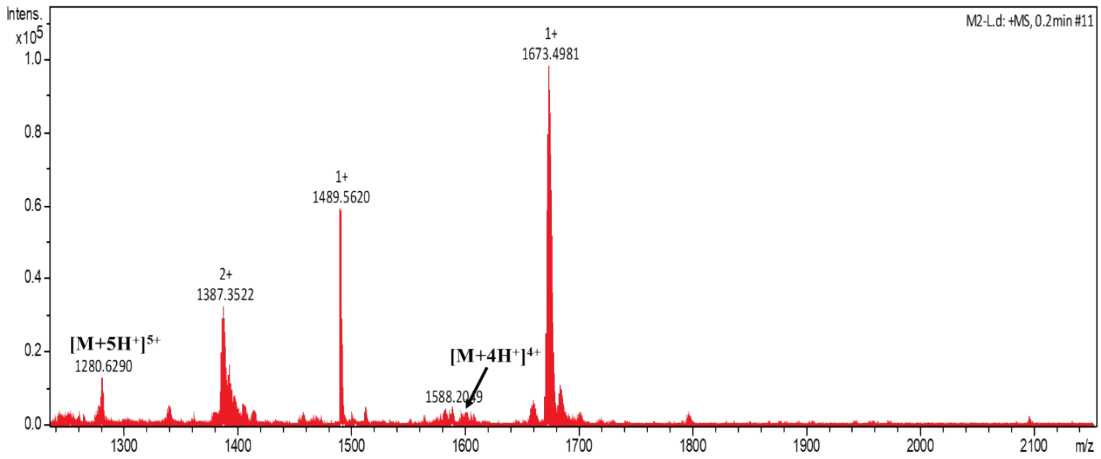


Figure S25. Full HR-MS spectra of metallacycle **M2+L**.

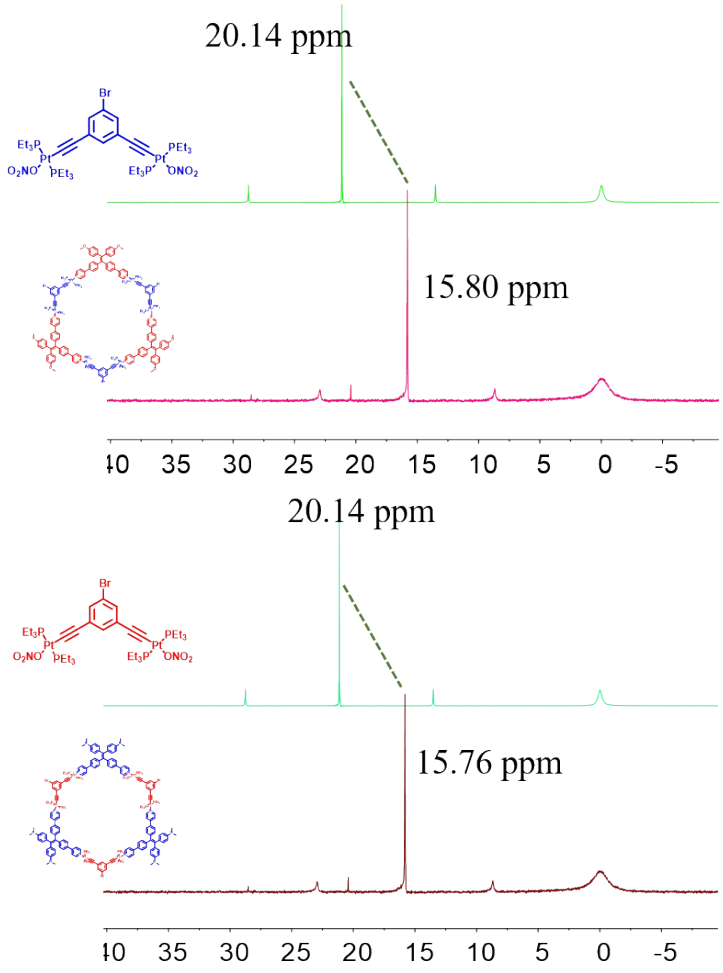


Figure S26. ^{31}P NMR spectra of metallacycle**s**.

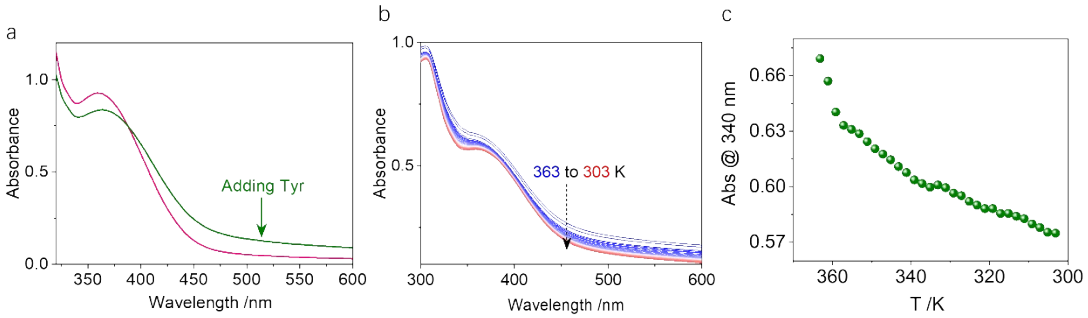


Figure S27. a) Absorption spectra comparison of **Cycle$_1$** (0.1 mM) by the addition of *L*-Tyr (0.5 mM). b,c) Temperature-variable absorbance spectra of **Cycle$_1$**/*L*-Tyr mixture (0.1 mM : 0.3 mM) in water.

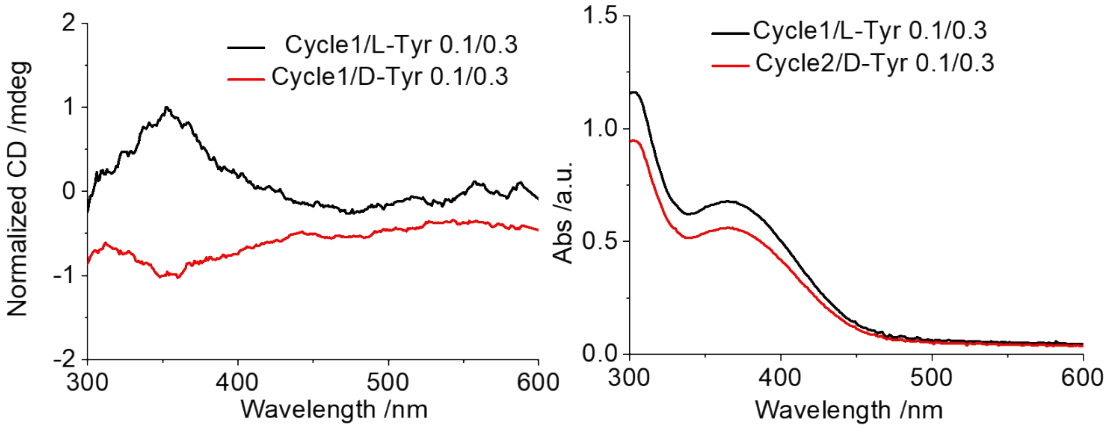


Figure S28. ECD spectra and the corresponding absorption spectra of **Cycle$_1$**/Tyr coassembly at a concentration of 0.1:0.3 mM. ECD spectra were quite small, and only small Cotton effects were observed at the maximum absorbance at around 370 nm. However, the ECD spectra of Cycle2/Tyr were unable to collect. The chirality transfer at ground state is not profound compared to the CPL spectra. In the revision, we have mentioned it in the ESI.

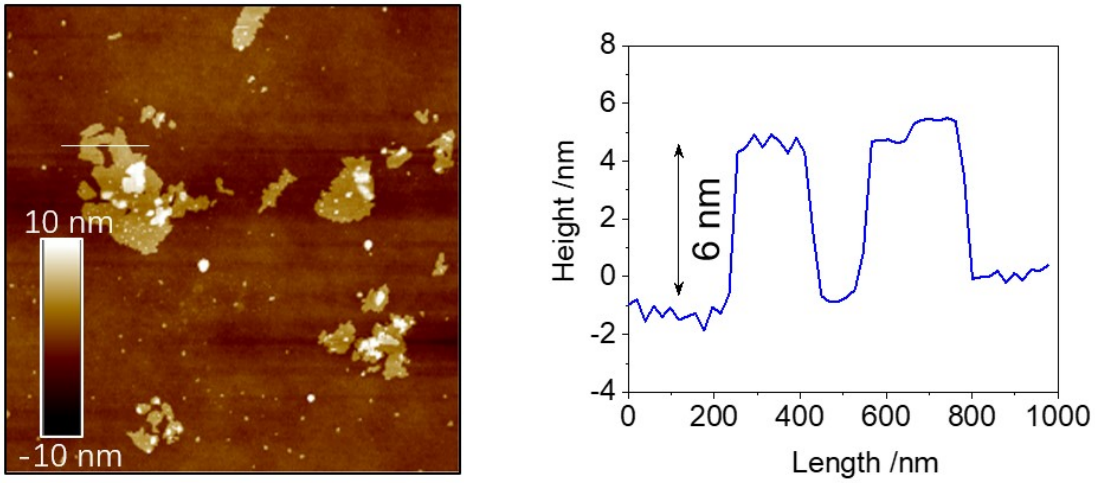


Figure S29. AFM image (5 × 5 μm) and the height profile of the **Cycle$_1$**/Tyr coassembly.

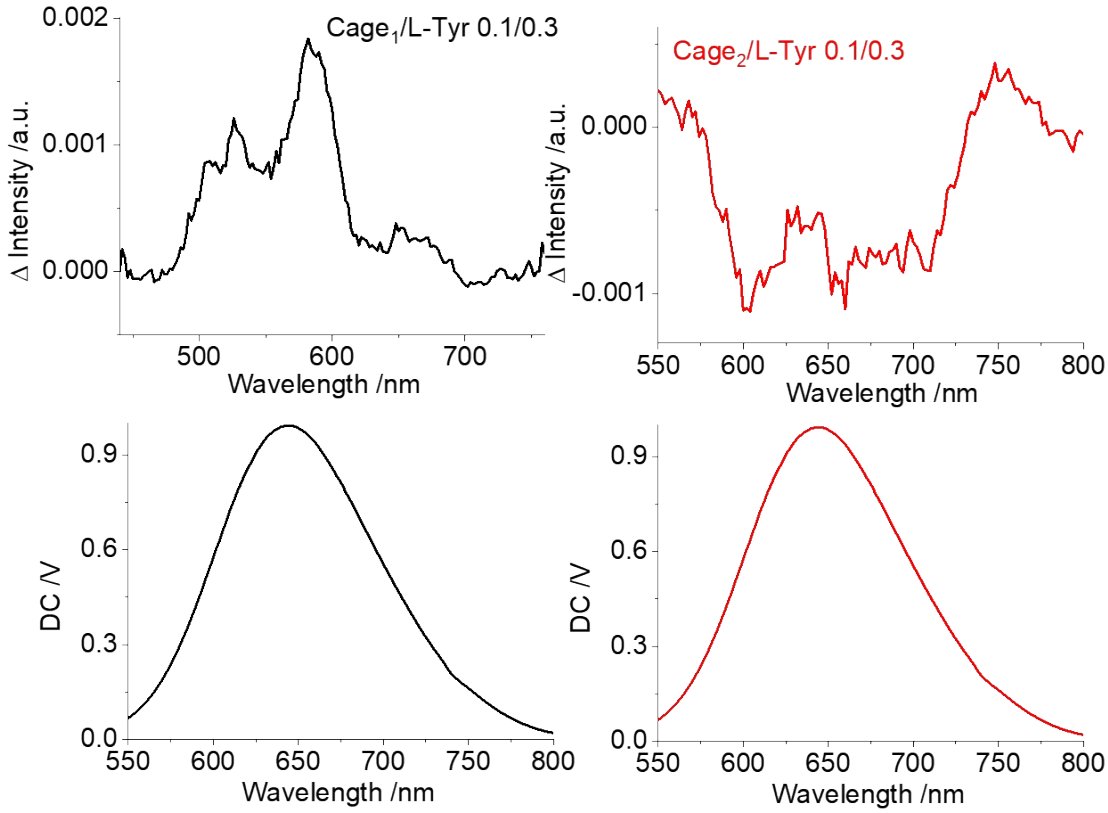


Figure 30. Additional CPL spectra of Cycle/L-Tyr coassemblies. (0.1 mM : 0.3 mM).

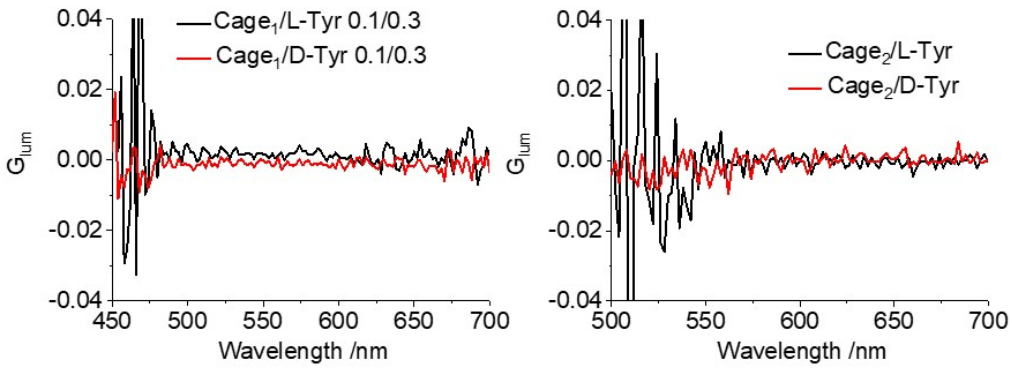


Figure S31. G_{lum} profiles of Cycle/Tyr coassemblies.

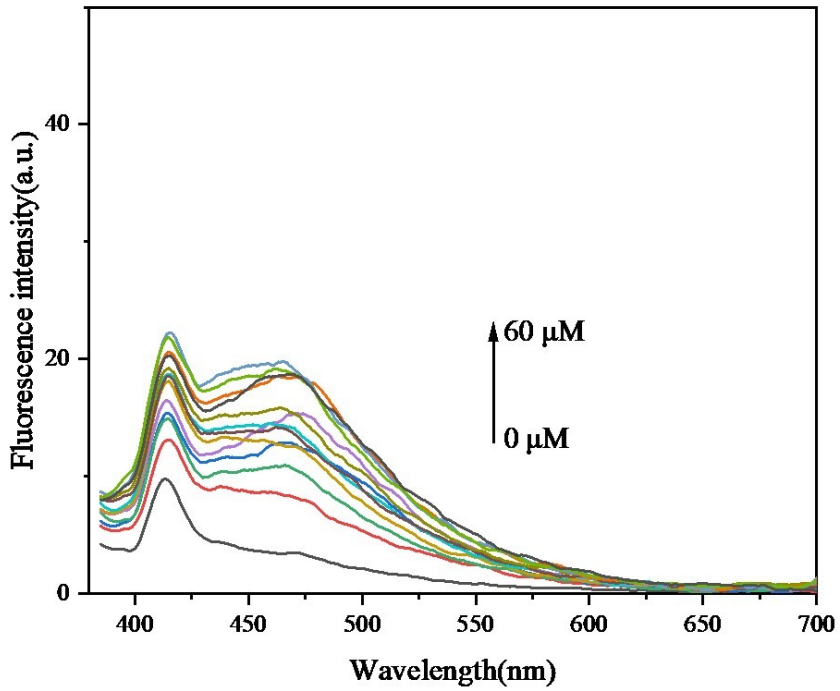


Figure S32. The emission spectra of Tyr with different concentrations in the acetone/water mixtures (f_w = 60 vol%), Ex. = 365 nm.

References

[1] Liu Y., F. X. Lin, Y. Feng, X. Liu, L. Wang, Z. Q. Yu, B. Z. Tang, *ACS Appl Mater Interfaces* **2019**, *11*, 34232-34240.

[2] Zhang F., Y. Di, Y. Li, Q. Qi, J. Qian, X. Fu, B. Xu, W. Tian, *Dyes and Pigments*

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