Supporting Information

Radical-Induced Hierarchical Self-assembly Involving Supramolecular Coordination Complexes in Both Solution and Solid States

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# Table of content

1. Materials and Methods…………………………………………………………………………… S3
2. Experimental details for synthesis and characterization of new compounds…………… S4
   2.1 Synthesis and characterization of 120° dipyridyl donor D……………………………… S4
   2.2 Synthesis and characterization of functionalized metallacycles M…………………….. S6
3. Crystallographic data………………………………………………………………………… S18
4. Additional data of radical induced HAS…………………………………………………… S19
5. Additional data of molecular modeling…………………………………………………… S25
6. $^1$H, $^{13}$C NMR and MS spectra of other new compounds…………………………… S30
1. Materials and Methods

All reagents were of analytical purity and used without further treatment. TLC analyses were performed on silica-gel plates, and flash chromatography was conducted using silica-gel column packages. All solvents were dried according to standard procedures and all of them were degassed under N\textsubscript{2} for 30 minutes before use. Chloroform and dichloromethane were filtered over basic alumina before use in all of the experiments. In most cases, irradiation using a Philips halogen lamp (20 W, 12 V) placed 5 cm from the sample. \textsuperscript{1}H and \textsuperscript{31}P NMR spectra were recorded on Bruker 500 MHz Spectrometer (\textsuperscript{1}H: 500 MHz; \textsuperscript{31}P: 202.4 MHz) at 298 K. The \textsuperscript{1}H and \textsuperscript{13}C NMR chemical shifts are reported relative to the residual solvent signals, and \textsuperscript{31}P NMR resonances are referenced to an internal standard sample of 85\% H\textsubscript{3}PO\textsubscript{4} (\textdelta 0.0). Electrospray ionization (ESI) mass spectra were recorded with a Waters Synapt G2 mass spectrometer. The ESI-TOF-MS spectra were acquired using an AccuTOF CS mass spectrometer (JMS-T100CS, JEOL, Tokyo, Japan). UV–vis spectra were recorded in a quartz cell on a Cary 50Bio UV-Visible spectrophotometer. SEM images were obtained by using a S-4800 (Hitachi Ltd.) with an accelerating voltage of 3.0-10.0 kV. TEM images were recorded on a Tecnai G2 F30 (FEI Ltd.) and JEM-1011 (JEOL Ltd.). DLS measurements were performed under a Malvern Zetasizer Nano-ZS light scattering apparatus (Malvern Instruments, U. K.) with a He-Ne laser (633 nm, 4 mW). EPR measurements were performed on a Bruker EMX spectrometer operating at X-band. Pulsed EPR and relaxation time measurements were obtained on Bruker E580 pulse X-band spectrometers. Spin–spin relaxation time (T\textsubscript{2}) was measured by two-pulse electron spin echo decay. The relaxation time was calculated by fitting exponentials to the data using Bruker Xepr software. SQUID measurements were performed on a Quantum Design's MPMS 3. Quantitative EPR was performed by comparison of the integrated EPR spectra with the integration of the spectra of a Magic Blue standard. Thin matrix membranes were performed, 2 mg Metallacycle M\textsubscript{3} was dispersed in 0.5 mL acetone, and 106 mg of Polyvinylidene fluoride (PVDF) solution (7.5 wt\% in DMF) was then added to the metallacycle solution. The combined M\textsubscript{3}/PVDF was sonicated in an ultrasonic bath until evenly mixed. The viscous mixed liquid was cast with a glass rod by hand onto glass substrates. The coated films were formed after removing solvent (1 h in an isothermal oven set at 70 °C). Immersion in solvent (EtOH or MeOH) resulted in rapid delamination of the mixed matrix membranes (MMMs).
2. Experimental details for synthesis and characterization of new compounds

2.1 Synthesis and characterization of 120° dipyridyl donor D

The precursor compound 4, 5 and 6 were synthesized according to reported procedures.\textsuperscript{1,2}

Scheme S1. Synthesis of 120° dipyridyl donor D1, D2 and D3.

Synthesis of compound 3. A solution of 4-aminotriphenylamine 1 (200 mg, 0.77 mmol) and triethylamine (0.3 ml, 2.31 mmol) in DCM (10 ml) was added dropwise chloroacetyl chloride 2 (0.2 ml, 2.31 mmol) at 0 °C and then the reaction was stirred overnight at room temperature. The solvent was removed by evaporation on a rotary evaporator. The residue was purified by column chromatography on silica gel (dichloromethane/ethyl acetate = 1:1) to give 3 (168 mg, 68.22 %) as a beige solid. \(R_f = 0.35\) (dichloromethane/ethyl acetate = 1:1). M.p.260-261 °C. \(^1\text{H NMR (500 MHz, CDCl}_3\):} δ 8.17 (s, 1H), 7.42 (d, 2H, \(J = 5.0\) Hz), 7.24-7.23 (m, 4H), 7.09-7.06 (m, 6H), 7.01 (t, 2H, \(J = 5.0\) Hz), 4.19 (s, 2H); \(^{13}\text{C NMR (125 MHz, CDCl}_3\):} δ 163.7, 147.7, 145.2, 131.5, 129.4, 124.7, 124.1, 122.9, 121.5, 77.3, 42.9. MS: \textit{m/z} calculated for C\(_{20}\)H\(_{17}\)ClN\(_2\)O [M]+ 336.10, found 336.00.

Synthesis of compound D1. A suspension of compound 3 (450 mg, 1.34 mmol) and 6 (225 mg, 0.76 mmol) and potassium carbonate (525 mg, 3.8 mmol) in DMF (15 ml) was stirred at 100 °C for 24 h. After cooling down to room temperature, the solvent was removed under reduced pressure and then dissolved with dichloromethane (100 ml), washed with brine (50 ml) three times, dried over Na\(_2\)SO\(_4\) and concentrated under reduced pressure. The residue was separated by column chromatography on silica gel (dichloromethane/acetone = 4:1) to give desired product D1 (500 mg, 77.28 %) as a yellow solid. \(R_f = 0.54\) (dichloromethane/acetone = 4:1). M.p.205-206 °C. \(^1\text{H NMR (500 MHz, acetone-d\(_6\)):} δ 9.29 (s, 1H), 8.65 (d, 4H, \(J = 5.0\) Hz), 7.59 (d, 2H, \(J = 10.0\) Hz), 7.50 (d, 4H, \(J = 10.0\) Hz), 7.46 (s, 1H), 7.37 (d, 2H, \(J = 5.0\) Hz), 6.98 (d, 4H, \(J = 5.0\) Hz), 6.88-6.86 (m, 6H),
4.79 (s, 2H), 3.96 (t, 4H, J = 5.0 Hz), 1.79-1.74 (m, 4H), 1.51-1.45 (m, 4H), 1.39-1.32 (m, 16H), 0.90 (t, 6H, 15.0 Hz); 13C NMR (125 MHz, Acetone- $d_6$): $\delta$ 166.1, 158.8, 156.2, 150.9, 146.2, 141.9, 132.6, 131.2, 129.0, 126.8, 126.2, 124.7, 122.2, 121.9, 119.9, 116.1, 92.5, 88.2, 68.7, 68.4, 32.5, 30.1, 30.0, 26.8, 23.3, 14.37. MS: $m/z$ calculated for C$_{56}$H$_{60}$N$_4$O$_4$ [M]$^+$ 853.12, found 853.10.

**Synthesis of compound D2.** A suspension of compound 4 (450 mg, 0.94 mmol) and 6 (277 mg, 0.94 mmol) and potassium carbonate (649 mg, 4.7 mmol) in DMF (15 ml) was stirred at 100 °C for 24 h. After cooling down to room temperature, the solvent was removed under reduced pressure and then dissolved with dichloromethane (100 ml), washed with brine (50 ml) three times, dried over Na$_2$SO$_4$ and concentrated under reduced pressure. The residue was separated by column chromatography on silica gel (dichloromethane/acetone = 4:1) to give desired product D2 (495 mg, 71.12 %) as a yellow solid. R$_f$ = 0.48 (dichloromethane/acetone = 4:1). M.p.200-201 °C. 1H NMR (500 MHz, Acetone-$d_6$): $\delta$ 9.28 (s, 1H), 8.66 (d, 4H, J = 5.0 Hz), 7.59 (d, 2H, J = 10.0 Hz), 7.51 (d, 4H, J = 5.0 Hz), 7.48 (s, 1H), 7.39 (d, 2H, J = 5.0 Hz), 7.00 (d, 4H, J = 10.0 Hz), 6.89-6.88 (m, 6H), 4.81 (s, 2H), 3.98 (t, 4H, J = 5.0Hz), 1.78-1.73 (m, 4H), 1.55-1.47 (m, 4H), 0.98 (t, 6H, 5.0 Hz); 13C NMR (125 MHz, Acetone-$d_6$): $\delta$ 166.1, 158.8, 151.0, 148.8, 144.7, 131.1, 129.0, 126.7, 126.2, 124.6, 122.1, 121.9, 119.9, 116.1, 92.5, 88.2, 68.4, 32.1, 19.9, 14.1. MS: $m/z$ calculated for C$_{48}$H$_{44}$N$_4$O$_4$ [M]$^+$ 740.34, found 739.90.

**Synthesis of compound D3.** A suspension of compound 5 (450 mg, 0.76 mmol) and 6 (396 mg, 1.34 mmol) and potassium carbonate (926 mg, 6.7 mmol) in DMF (15 ml) was stirred at 100 °C for 24 h. After cooling down to room temperature, the solvent was removed under reduced pressure and then dissolved with dichloromethane (100 ml), washed with brine (50 ml) three times, dried over Na$_2$SO$_4$ and concentrated under reduced pressure. The residue was separated by column chromatography on silica gel (dichloromethane/acetone = 4:1) to give desired product D3 (551 mg, 69.02 %) as a yellow solid. R$_f$= 0.50 (dichloromethane/acetone = 4:1). M.p.198-199 °C. 1H NMR (500 MHz, Acetone-$d_6$): $\delta$ 9.39 (s, 1H), 8.65 (d, 4H, J = 5.0 Hz), 7.69 (d, 2H, J = 10.0 Hz), 7.50 (d, 4H, J = 5.0 Hz), 7.47 (s, 1H), 7.39 (d, 2H, J = 5.0 Hz), 7.29-7.26 (m, 4H), 7.04-6.99 (m, 8H), 4.82 (s, 2H); 13C NMR (125 MHz, Acetone-$d_6$): $\delta$ 166.1, 158.8, 151.0, 148.8, 144.7, 134.7, 131.1, 130.1,
129.0, 126.2, 125.8, 124.7, 124.4, 123.4, 122.0, 120.0, 92.5, 88.2, 68.7. MS: m/z calculated for C_{40}H_{28}N_{4}O_{2} [M]^{+} 596.22, found 597.10.

2.2 Synthesis and characterization of functionalized metallacycles M

Scheme S2. Self-assembly of functionalized metallacyle M1.

Self-assembly of functionalized metallacycle M1. The 120° dipyridyl donor D1 (11.16 mg, 18.71 μmol) and the 60° diplatinum (II) acceptor A (21.73 mg, 18.71 μmol) were weighed accurately into a glass vial. To the vial was added 5.0 mL acetone and 1.0 mL water. The reaction solution was then stirred at 50 °C for 12 h to yield a yellow solution. Then the KPF_{6} was added into the bottle to precipitate the yellow product. The reaction mixture was centrifuged, washed several times with water, and dried. The yellow product M1 (40.55 mg, 99.35 %) was collected and re-dissolved in mixed solvent of CDCl_{3} and CD_{2}Cl_{2} (V/V 2:1) for NMR analysis. ¹H NMR (500 MHz, CDCl_{3}:CD_{2}Cl_{2} = 1:2): δ 9.28 (d, 4H, J = 5.0 Hz), 8.86 (s, 4H), 8.68 (d, 4H, J = 5.0 Hz), 8.23 (s, 2H), 7.96 (d, 4H, J = 5.0 Hz), 7.84 (d, 4H, J = 10.0 Hz), 7.69 (s, 2H), 7.66-7.61 (m, 12H), 7.50-7.48 (m, 8H), 7.07 (d, 8H, J = 5.0 Hz), 6.98 (d, 4H, J = 10.0 Hz), 6.86 (d, 8H, J = 10.0 Hz), 4.78 (s, 4H), 3.97 (t, 8H, J = 5.0 Hz), 1.84-1.78 (m, 8H), 1.53-1.47 (m, 8H), 1.41-1.31 (m, 80H), 1.21-1.15 (m, 72H), 0.94 (t, 12H, J = 5.0 Hz); ³¹P NMR (202.4 MHz, CDCl_{3}:CD_{2}Cl_{2} = 1:2): δ 13.38 (s, J_{Pt-P} = 2710.0). ESI-TOF-MS of M1: calculated for C_{188}H_{256}F_{13}N_{8}O_{8}P_{10}Pt_{4} [M–2PF_{6}]^{2+}: 2036.7876, found: 2036.9146; calculated for C_{188}H_{256}F_{13}N_{8}O_{8}P_{9}Pt_{4} [M–3PF_{6}]^{3+}: 1309.5319, found: 1309.5248; calculated for C_{188}H_{256}N_{8}O_{8}P_{8}Pt_{4} [M–4PF_{6}]^{4+}: 945.9078, found: 945.8408.
**Figure S1.** The partial $^1$H NMR spectra (500 MHz, 298 K) of 60° diplatinum (II) acceptor A, 120° dipyridyl donor D1, and their corresponding self-assembled metallacycle M1 in CD$_2$Cl$_2$/CDCl$_3$ (2:1 v/v).

**Figure S2.** The partial $^{31}$P NMR spectra (202.4 MHz, 298 K) of 60° diplatinum (II) acceptor A and metallacycle M1 in CD$_2$Cl$_2$/CDCl$_3$ (2:1 v/v).
Figure S3. 2D COSY NMR (500 MHz, CD$_2$Cl$_2$/CDCl$_3$ 2:1 v/v, 298 K) spectrum of metallacycle M1.

Figure S4. 2D NOESY NMR (500 MHz, CD$_2$Cl$_2$/CDCl$_3$ 2:1 v/v, 298 K) spectrum of metallacycle M1.
Figure S5. 2D DOSY NMR (500 MHz, CD$_2$Cl$_2$/CDCl$_3$ 2:1 v/v, 298 K) spectrum of metallacycle M1.

Figure S6. ESI-TOF-MS spectrum of M1. Inset: Theoretical (top) and experimental (bottom) isotopic distribution.
Self-assembly of functionalized metallacycle M2. The 120° dipyridyl donor D2 (16.81 mg, 22.71 μmol) and the 60° diplatinum (II) acceptor A (26.37 mg, 22.71 μmol) were weighed accurately into a glass vial. To the vial was added 5.0 mL acetone and 1.0 mL water. The reaction solution was then stirred at 50 °C for 12 h to yield a yellow solution. Then the KPF$_6$ was added into the bottle to precipitate the yellow product. The reaction mixture was centrifuged, washed several times with water, and dried. The yellow product M2 (46.57 mg, 99.15%) was collected and re-dissolved in mixed solvent of CDCl$_3$ and CD$_2$Cl$_2$ (V/V 2:1) for NMR analysis. $^1$H NMR (500 MHz, CDCl$_3$:CD$_2$Cl$_2$ = 1:2): δ 9.25 (d, 4H, $J = 5.0$ Hz), 8.82 (s, 4H), 8.65 (d, 4H, $J = 5.0$ Hz), 8.20 (s, 2H), 7.92 (d, 4H, $J = 5.0$ Hz), 7.81 (d, 4H, $J = 10.0$ Hz), 7.65 (s, 2H), 7.62-7.57 (m, 12H), 7.47-7.44 (m, 8H), 7.02 (d, 8H, $J = 10.0$ Hz), 6.94 (d, 4H, $J = 10.0$ Hz), 6.82 (d, 8H, $J = 10.0$ Hz), 4.74 (s, 4H), 3.95 (t, 8H, $J = 5.0$ Hz), 1.79-1.73 (m, 8H), 1.52-1.48 (m, 8H), 1.39-1.35 (m, 48H), 1.17-1.11 (m, 72H), 0.99 (t, 12H, $J = 5.0$ Hz); $^{31}$P NMR (202.4 MHz, CDCl$_3$:CD$_2$Cl$_2$ = 1:2): δ 12.27 (s, $J_{Pt-P} = 2705.9$). ESI-TOF-MS of M2: calculated for C$_{172}$H$_{224}$F$_{6}$N$_{8}$O$_{8}$P$_{9}$Pt$_{4}$ [M–2PF$_6$]$^{2+}$: 1924.6624, found: 1924.7518; calculated for C$_{172}$H$_{224}$F$_{6}$N$_{8}$O$_{8}$P$_{9}$Pt$_{4}$ [M–3PF$_6$]$^{3+}$: 1234.7816, found: 1234.7532; calculated for C$_{172}$H$_{224}$N$_{8}$O$_{8}$P$_{9}$Pt$_{4}$ [M–4PF$_6$]$^{4+}$: 889.8452, found: 889.7576.
Figure S7. The partial $^1$H NMR spectra (500 MHz, 298 K) of 60° diplatinum (II) acceptor A, 120° dipyridyl donor D2, and their corresponding self-assembled metallacycle M2 in CD$_2$Cl$_2$/CDCl$_3$ (2:1 v/v).

Figure S8. The partial $^{31}$P NMR spectra (202.4 MHz, 298 K) of 60° diplatinum (II) acceptor A and metallacycle M2 in CD$_2$Cl$_2$/CDCl$_3$ (2:1 v/v).
Figure S9. 2D COSY NMR (500 MHz, CD$_2$Cl$_2$/CDCl$_3$ 2:1 v/v, 298 K) spectrum of metallacycle M2.

Figure S10. 2D NOESY NMR (500 MHz, CD$_2$Cl$_2$/CDCl$_3$ 2:1 v/v, 298 K) spectrum of metallacycle M2.
Figure S11. 2D DOSY NMR (500 MHz, CD₂Cl₂/CDCl₃ 2:1 v/v, 298 K) spectrum of metallacycle M₂.

Figure S12. ESI-TOF-MS spectrum of M₂. Inset: Theoretical (top) and experimental (bottom) isotopic distribution.
**Scheme S4.** Self-assembly of functionalized metallacycle M3.

Self-assembly of functionalized metallacycle M3. The 120° dipyridyl donor D3 (23.92 mg, 28.06 μmol) and the 60° diplatinum (II) acceptor A (32.59 mg, 28.06 μmol) were weighed accurately into a glass vial. To the vial was added 5.0 mL acetone and 1.0 mL water. The reaction solution was then stirred at 50 °C for 12 h to yield a yellow solution. Then the KPF₆ was added into the bottle to precipitate the yellow product. The reaction mixture was centrifuged, washed several times with water, and dried. The yellow product M3 (53.51 mg, 99.09 %) was collected and re-dissolved in mixed solvent of CDCl₃ and CD₂Cl₂ (V/V 2:1) for NMR analysis. $^1$H NMR (500 MHz, CDCl₃:CD₂Cl₂ = 1:2): δ 9.21 (d, 4H, J = 5.0 Hz), 8.77 (s, 4H), 8.59 (d, 4H, J = 5.0 Hz), 8.22 (s, 2H), 7.87 (d, 4H, J = 5.0 Hz), 7.77 (d, 4H, J = 5.0 Hz), 7.60 (s, 2H), 7.56-7.51 (m, 16H), 7.40 (s, 4H), 7.22-7.19 (m, 8H), 7.06-7.02 (m, 12H), 6.97 (t, 4H, J = 10.0 Hz), 4.71 (s, 4H), 1.34-1.32 (m, 48H), 1.12-1.06 (m, 72H); $^{31}$P NMR (202.4 MHz, CDCl₃:CD₂Cl₂ = 1:2): δ 11.68 (s, J Pt-P = 2715.8).

Figure S13. The partial $^1$H NMR spectra (500 MHz, 298 K) of 60° diplatinum (II) acceptor A, 120° dipyridyl donor D3, and their corresponding self-assembled metallacycle M3 in CD$_2$Cl$_2$/CDCl$_3$ (2:1 v/v).

Figure S14. The partial $^{31}$P NMR spectra (202.4 MHz, 298 K) of 60° diplatinum (II) acceptor A and metallacycle M3 in CD$_2$Cl$_2$/CDCl$_3$ (2:1 v/v).
Figure S15. 2D COSY NMR (500 MHz, CD$_2$Cl$_2$/CDCl$_3$ 2:1 v/v, 298 K) spectrum of metallacycle M3.

Figure S16. 2D NOESY NMR (500 MHz, CD$_2$Cl$_2$/CDCl$_3$ 2:1 v/v, 298 K) spectrum of metallacycle M3.
Figure S17. 2D DOSY NMR (500 MHz, CD$_2$Cl$_2$/CDCl$_3$ 2:1 v/v, 298 K) spectrum of metallacycle M3.

Figure S18. ESI-TOF-MS spectrum of M3. Inset: Theoretical (top) and experimental (bottom) isotopic distribution.
## 3. Crystallographic data

### Table S1. Crystallographic data and structure refinement for M2.

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### Table S2. Crystallographic data and structure refinement for M1.

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---|---
F (000) | 1924
Theta range for data collection | 1.885 to 72.716°
Index range | -13≤h≤13, -24≤k≤21, -29≤l≤29
Reflections collected | 19529
Absorption correction | multi-scan
Max. and min. transmission | 0.30 and 0.45
Data / restraints / parameters | /0/949
Goodness-of-fit on F² | 2.382
Final R indices [I>2σ(I)] | R1 = 0.1158, wR2 = 0.3203
R indices (all data) | R1 = 0.1061, wR2 = 0.3096
Largest diff. peak and hole | 3.256 and -1.056 e. Å⁻³

4. Additional data of radical induced HSA

Figure S19. (a) UV-vis spectra of Magic Blue in different concentrations; (b) UV-vis calibration curve of Magic Blue. Note: about 10 TPA radical units existed in 57 molecules of M₃.

Figure S20. UV-vis spectra obtained as a function of time on irradiation of M₃ in dichloromethane (a), in 1,1-dichloroethane (b), and in chloroform (c) solution with 0.02 mM concentration.
**Figure S21.** The partial $^{31}$P NMR spectra (202.4 MHz, 298 K) of metallacycle M3 in CD$_2$Cl$_2$/CDCl$_3$ (2:1 v/v) before irradiation (blue line) and after 30 min visible irradiation (red line).

**Figure S22.** Typical $^1$H NMR spectra (CD$_2$Cl$_2$/CDCl$_3$ 2:1 v/v) of M3 (a); after 30 min exposure to visible light, (b); and after subsequent heating 60 min at 60°C (c); [M3] = 3.0 mM.
Figure S23. (a) UV-vis spectra obtained as a function of time on irradiation of \( \text{M2} \) in chloroform solution with 0.02 mM concentration. (b) Irradiation kinetic experiment plotted from NIR absorption at 765 nm for 0.02 mM solutions of compounds \( \text{M2} \).

Figure S24. Single crystal of the oxidized Pt metal ligand obtained during the chemical oxidation of \( \text{M2} \) with triethylxonium hexachloroantimonate as oxidant. Noted: the Pt oxidation number here is +4. CCDC: 1950593.
Figure S25. EPR spectra of 2 mM solution of M1, M2 and M3 in CDCl3 after exposed to the white light. EPR data are all collected at 298 K.

![EPR spectra image]

Figure S26. (a) EPR spectra of 1 mM solution of tris(4-bromophenyl)ammoniumyl hexachloroantimonate (Magic Blue) in DCM. (b) The Magic Blue calibration curve. EPR data are all collected at 298 K.
Figure S27. EPR spectra of powder M1, M2 and M3 after exposed to the white light. EPR data are all collected at 298 K.

Figure 28. (a) Temperature dependence of magnetization of irradiated M3 (8.8 mg) obtained with an applied field of B = 10000 Oe; (b) Field-dependent magnetization of irradiated M3 (8.8 mg) measured under different temperatures.

Figure 29. (a) Echo-detected EPR spectrum at room temperature of M3; (b) Two-pulse electron spin echo decay as a function of the interpulse delay τ, measured at T = 298 K with long selective pulses and the superimposed exponential fit (red line).
**Figure S30.** Scanning electron micrograph image of compound M3 before irradiation (a) and irradiated solution of compound M3 (b) (prepared from a 0.1 mM solution in CHCl₃).

**Figure S31.** Hydrodynamic radius distributions observed for compound M3 ([M3] = 0.1 mM in CHCl₃ at T = 25°C) before irradiation (black line) and after 30 min visible irradiation (red line).
5. Additional data of molecular modeling

The coarse-grained (CG) molecular dynamics (MD) simulations were applied to investigate the underlying mechanism of the self-assembly of M3 molecules in different cases. Here, for the sake of simplicity, we constructed the CG ring with different size and topology using the different type of beads (Py, Bz, Pt, S, T1/T2 beads)\(^3\) to denote the M3 molecule in the simulations (see Figure S30a). In particular, to denote the radical effect in the self-assembly, two different CG rings were
constructed, where the ring containing T1 bead (orange) represented M3 without radicals and that containing T2 bead (red) represented M3 with radicals.

**Figure S34.** (a) Schematic illustration of the coarse-grained (CG) models for M3 with/without radicals in CG molecular dynamics simulation: Py bead (pyridine, green bead), Bz bead (benzene, blue bead), Pt bead (Et$_3$P-Pt-PEt$_3$, yellow bead), S bead (side chain, purple bead), T1 bead (TPA without radicals, orange bead), T2 bead (TPA with radicals, red bead). (b) The CGMD simulation system (128 M3 molecules were uniformly placed in the box at the beginning of the simulation)

Here, for the sake of simplicity, the metallacycle in M3 was treated as the rigid one in the simulations. To maintain the integrality of the side chains, the harmonic spring interaction $U_s = k_s (l_{i,i+1} - l_0)^2$ was applied between the connected beads in the site chains and the binding site of the metallacycle, where $k_s = 1000 \frac{k_B T}{r_0^2} l_0 = 0.46 r_0$. We also used a three-body bond angle potential $U_a = k_a (1 - \cos (\varphi - \varphi_0))$ to depict the rigidity of the side chain, where $k_a = 10 k_B T$, $\varphi_0 = 180^\circ$ or $120^\circ$. Additionally, to model the effective $\pi-\pi$ stacking between the pyridine and/or the benzene, a standard Lennard-Jones (LJ) potential (cut off at $1.5\sigma$) was used, where $\epsilon$ was chosen as $2.5 k_B T$, and $\sigma$ was set as 0.35 $r_0$. Of note, due to the steric effect, we did not consider the effective $\pi-\pi$ stacking between the benzene in the side chain and the pyridine/benzene in the main chain of the metallacycle. Besides, the same potential (i.e., standard LJ potential) was also used to model the strong TPA-TPA interaction between the T2 beads ($\epsilon_0 = 10 k_B T$, $\sigma = 0.35 r_0$). Moreover, due to the solvent effect, the strength $\epsilon$ of $\pi-\pi$ stacking between the pyridine and/or the benzene in the solution was weaker than that in the solid state, and here was chosen as $2.0 k_B T$. Further, a shifted LJ potential (i.e., Weeks-Chandler-Andersen potential), cut off at $2^{1/6} \sigma$, was used to model the repulsive interaction among the other beads, where $\epsilon$ was chosen as $1.0 k_B T$, and $\sigma$ was set as 0.35 $r_0$

At the beginning of the simulation, we randomly placed hundreds of M3 molecules in the system (see Figure S30b). The velocity-Verlet integration algorithm was used to update the coordination of each bead, with the integration time step $\Delta t = 0.005\tau$. During the simulation, the temperature was firstly coupled at 1.0 $T_0$ by using the Nose/Hoover thermostat. The size of the simulation box
was about $30 r_c \times 30 r_c \times 30 r_c$ and the periodic boundary conditions were adopted in all three directions. All simulations in this work were carried out by using the software package LAMMPS (5 Sep 2018)\textsuperscript{11}.

**Figure S35.** Time sequence of snapshots illustrating the self-assembly process of M3 molecules in case I (solid state, no light) in the simulation.

**Figure S36.** Time sequence of snapshots illustrating the self-assembly process of M3 molecules in case II (solid state, light) in the simulation. The percentage of radical-form of M3 molecules in this
The system is about 0.25.

**Figure S37.** Time evolution of interaction energy (including N-N interaction and π-π stacking) during the self-assembly process in Case I (a) and Case II (b) in the simulation.

**Figure S38.** Time sequence of snapshots illustrating the self-assembly process of M3 molecules in case III (solution state, no light) in the simulation.
Figure S39. Time evolution of interaction energy (including N-N interaction and \( \pi-\pi \) stacking) during the self-assembly process in Case III (a) and Case IV (b) in the simulation.

Figure S40. Time sequence of snapshots illustrating the self-assembly process of M3 molecules in case IV (solution state, light) in the simulation.
6. $^1$H, $^{13}$C NMR and MS spectra of other new compounds

Figure S41. $^1$H NMR spectrum (500 MHz, CDCl$_3$, 298 K) of compound 3.

Figure S42. $^{13}$C NMR spectrum (125 MHz, CDCl$_3$, 298 K) of compound 3.
Figure S43. MS for compound 3: $m/z$ calculated for C$_{30}$H$_{17}$ClN$_2$O $[M]^{+}$ 336.10, found 336.00.

Figure S44. $^1$H NMR spectrum (500 MHz, Acetone-$d_6$, 298 K) of compound D3.
Figure S45. $^{13}$C NMR spectrum (125 MHz, Acetone-$d_6$, 298 K) of compound D3.

Figure S46. MS for compound D3: $m/z$ calculated for C$_{56}$H$_{60}$N$_4$O$_4$ [M]$^+$ 853.12, found 853.10.
Figure S47. $^1$H NMR spectrum (500 MHz, Acetone-$d_6$, 298 K) of compound D2.

Figure S48. $^{13}$C NMR spectrum (125 MHz, Acetone-$d_6$, 298 K) of compound D2.
Figure S49. MS for compound D2: m/z calculated for C_{48}H_{44}N_{4}O_{4} [M]^+ 740.34, found 739.90.

Figure S50. ^1H NMR spectrum (500 MHz, Acetone-\textit{d}_6, 298 K) of compound D1.
Figure S51. $^{13}$C NMR spectrum (125 MHz, Acetone-$d_6$, 298 K) of compound D1.

Figure S52. MS for compound D1: $m/z$ calculated for $C_{40}H_{28}N_4O_2$ [M]$^+$ 596.22, found 597.10.
Figure S53. $^1$H NMR spectrum (500 MHz, CD$_2$Cl$_2$/CDCl$_3$ 2:1 v/v, 298 K) of compound M3.

Figure S54. $^1$H NMR spectrum (500 MHz, CD$_2$Cl$_2$/CDCl$_3$ 2:1 v/v, 298 K) of compound M2.
Figure S55. $^1$H NMR spectrum (500 MHz, CD$_2$Cl$_2$/CDCl$_3$ 2:1 v/v, 298 K) of compound M1.

References
