Supporting Information for
Construction of Transient Supramolecular Polymers Controlled by Mass Transfer in Biphasic System

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1 Instrument and Materials

All chemicals were commercially available and used without further purification unless otherwise noted. Column chromatography was conducted using basic Al_2O_3 or silica gel (200 - 300 mesh). ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AVIII-500 spectrometer (500 MHz and 125 MHz, respectively) or Bruker AVIII-850 spectrometer at 298 K (850 MHz and 213 MHz, respectively). (Variable temperature) UV-Vis spectra were recorded with a SHIMADZU UV-2550 spectrometer. Luminescence measurements were performed with a HITACHI F-4500 fluorescence spectrophotometer. Dynamic light scattering (DLS) measurements were performed by the Brookhaven173Plus DLS instrument. Transmission electron microscopy (TEM) images were recorded by a JEM-1400 microscope. Scanning electron microscopy (SEM) images were recorded by a Hitachi S-4800 microscope.

A list of abbreviations:

r.t.: room temperature

DCM: dichloromethane

PE: petrol ether

THF: tetrahydrofuran

NMR: nuclear magnetic resonance

COSY: correlation spectroscopy

NOESY: nuclear Overhauser enhancement spectroscopy

DLS: dynamic light scattering

TEM: transmission electron microscopy

SEM: scanning electron microscopy

2 Experimental Section

TEM and SEM

Samples were prepared by drop-casting the solution (in transient measurements, the same solution at different time intervals) on the square grids (300 mesh, ultra-thin, carbon-coated Cu) (EMS) and allowing to adsorb for 30 s. The samples were dried for a few hours at room temperature before TEM imaging. After the TEM investigation, the same samples were used for SEM imaging. Before performing the SEM measurements, the samples were coated with a thin layer of Pt to increase the contrast.

Determination of water content in the organic solvent

The water content in organic solvent was determined by Karl Fischer titrations on a ZDY-504(lei-ci) Coulometric KF Titrator with KF-1A and KF-1B reagents (purchased from Shanghai INESA Scientific instrument Co., Ltd.). The experiments were carried out on the benchtop.

Synthesis of ligands T-3tpy and T-1tpy.

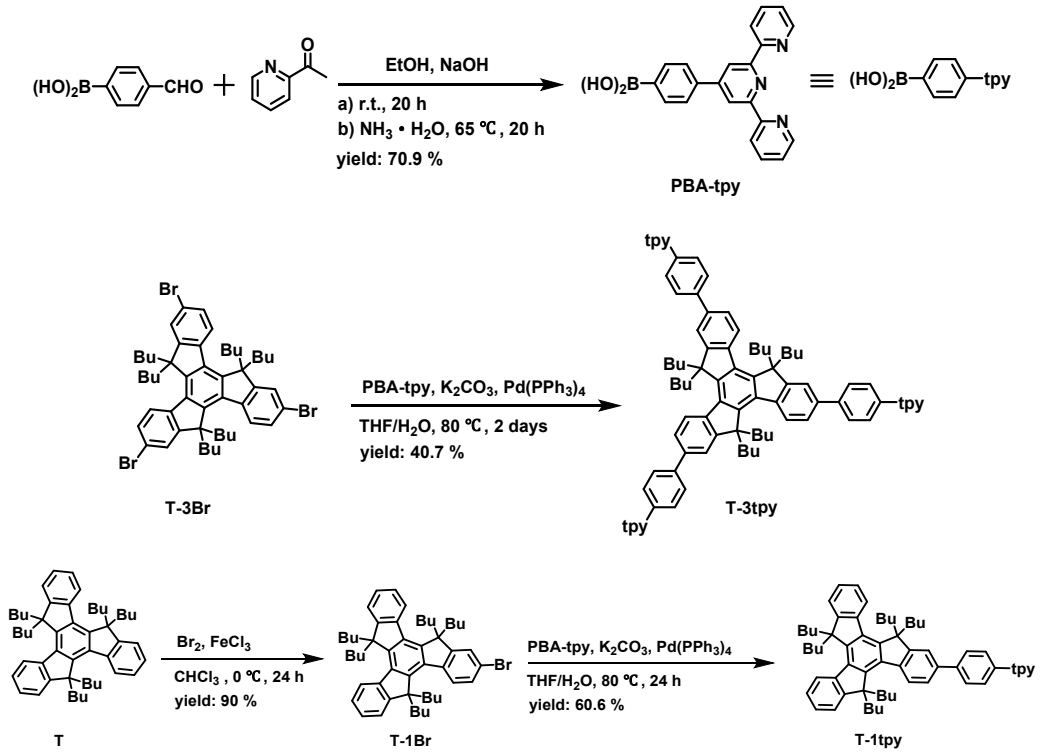

Figure S1. Representative procedures for the syntheses of ligands **T-3tpy** and **T-1tpy**.

Synthesis of PBA-tpy. This compound was synthesized according to the reported method[1]. 4-Formylphenylboronic acid (3.02 g, 20 mmol) and 2-acetylpyridine (4.92 mL, 44 mmol) was added to a solution of NaOH powder (4.84 g, 120 mmol) in EtOH (150 mL). The mixture was stirred at room temperature for 20 h, then aqueous $NH_3•H_2O$ (28%, 80 mL) was added. The resulting mixture was refluxed for 20 h. After cooling to room temperature, the solid was collected by filtration and was washed with $CHCl_3$ to give the product a pale purple solid (5.01 g, 70.9%). ^{1}H NMR (500 MHz, CD_3OD, ppm): δ 8.69 (d, J = 4.8 Hz, 2H), 8.66 (s, 2H), 8.63 (d, J = 8.0 Hz, 2H), 7.99 (td, J = 7.8 Hz, 1.7 Hz, 2H), 7.78 – 7.73 (m, 4H), 7.48 – 7.46 (m, 2H).

Compound **T** and compound **T-3Br** were synthesized as previously reported by our group[2].

Synthesis of T-3tpy. **T-3Br** (0.202 g, 0.221 mmol), **PBA-tpy** (0.467 g, 1.323 mmol), potassium carbonate (0.244 g, 1.768 mmol) and $Pd(PPh_3)_4$ (0.038 g, 0.033 mmol) were added into a 100 mL Schlenk flask. 24 mL THF, and 12 mL H_2O were added under N_2. The mixture was stirred at 80 °C for 2 days. After cooling to room temperature, the mixture was extracted with DCM. The combined organic layer was washed with brine, then dried over anhydrous Na_2SO_4. The solvent was removed by evaporating in vacuum, and the crude product was purified by column chromatography on Al_2O_3 with DCM/PE (v/v = 3/1) as eluent to afford the product as a pale white solid (0.144 g, 40.7%). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 8.86 (s, 6H), 8.78 (d, J = 3.9 Hz, 6H), 8.72 (d, J = 7.9 Hz, 6H), 8.53 (d, J = 8.2 Hz, 3H), 8.10 (d, J = 8.2 Hz, 6H), 7.95 (d, J = 8.2 Hz, 6H), 7.91 (td, J = 7.8 Hz, 1.7 Hz, 6H), 7.81 (s, 3H), 7.80 (d, J = 8.2 Hz, 3H), 7.40 – 7.38 (m, 6H), 3.12 – 3.08 (m, 6H), 2.30 – 2.25 (m, 6H), 1.04-0.93 (m, 12H), 0.72 – 0.65 (m, 6H), 0.64 – 0.57 (m, 6H), 0.52 (t, J = 7.3 Hz, 18H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.49, 156.18, 154.62, 150.01, 149.33, 145.74, 142.07, 140.19, 138.42, 138.31, 137.30, 137.07, 127.94, 127.71, 125.39, 125.24, 124.02, 121.59, 120.74, 118.86, 56.01, 37.01, 26.81, 23.10, 14.07.

Synthesis of T-1Br. Under N_2, compound **T** (1.005 g, 1.473 mmol), anhydrous $FeCl_3$ (10 mg), and chloroform (40 mL) were added to a round bottom flask, then the mixture was stirred until dissolved. The mixture was cooled to 0 °C and bromine (0.075 mL, 1.473 mmol) in chloroform (8 mL) was added slowly. After 24 hours, saturated sodium thiosulfate aqueous solution (30 mL) was added to quench the reaction. The organic layer was washed with saturated sodium chloride solution and

deionized water, then dried over anhydrous sodium sulfate. The solvent was removed by evaporating in vacuum, then the solid was recrystallized from methanol to give a white powder which was used in the next step directly.

Synthesis of T-1tpy. **T-1Br** (1.50 g, 1.983 mmol), **PBA-tpy** (0.911 g, 2.578 mmol), potassium carbonate (0.547 g, 3.966 mmol) and $Pd(PPh_3)_4$ (0.138 g, 0.119 mmol) were added into a 100 mL Schlenk flask. 30 mL THF, and 15 mL H_2O were added under N_2. The mixture was stirred at 80 ^oC for 24 hours. After cooling to room temperature, the mixture was extracted with DCM. The combined organic layer was washed with brine, then dried over anhydrous Na_2SO_4. The solvent was removed by evaporating in vacuum, and the crude product was purified by column chromatography on Al_2O_3 with DCM as eluent to afford the product as a pale white solid (0.144 g, 60.6%). ^1H NMR (500 MHz, $CDCl_3$, ppm): δ 8.84 (s, 2H), 8.78 (d, J = 3.9 Hz, 2H), 8.72 (d, J = 7.9 Hz, 2H), 8.48 (d, J = 8.2 Hz, 1H), 8.41 (t, J = 8.4 Hz, 2H), 8.09 (d, J = 8.2 Hz, 2H), 7.91 (t, J = 9.4 Hz, 4H), 7.77 (s, 1H), 7.75 (d, J = 8.1 Hz, 1H), 7.49 (t, J = 6.0 Hz, 2H), 7.44 – 7.37 (m, 6H), 3.08 – 2.98 (m, 6H), 2.23 – 2.09 (m, 6H), 0.93 – 0.83 (m, 12H), 0.67 – 0.49 (m, 12H), 0.48 – 0.44 (m, 18H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.48, 156.16, 154.65, 153.79, 153.77, 150.00, 149.32, 145.42, 145.30, 145.20, 142.09, 140.47, 140.43, 140.26, 138.68, 138.64, 138.28, 138.11, 137.26, 137.07, 127.91, 127.68, 126.56, 126.17, 126.15, 125.27, 125.17, 124.88, 124.85, 124.01, 122.43, 121.58, 120.68, 118.84, 55.91, 55.74, 36.89, 36.85, 36.80, 26.74, 26.70, 26.66, 23.06, 23.02, 14.03, 13.98.

3 NMR Spectra

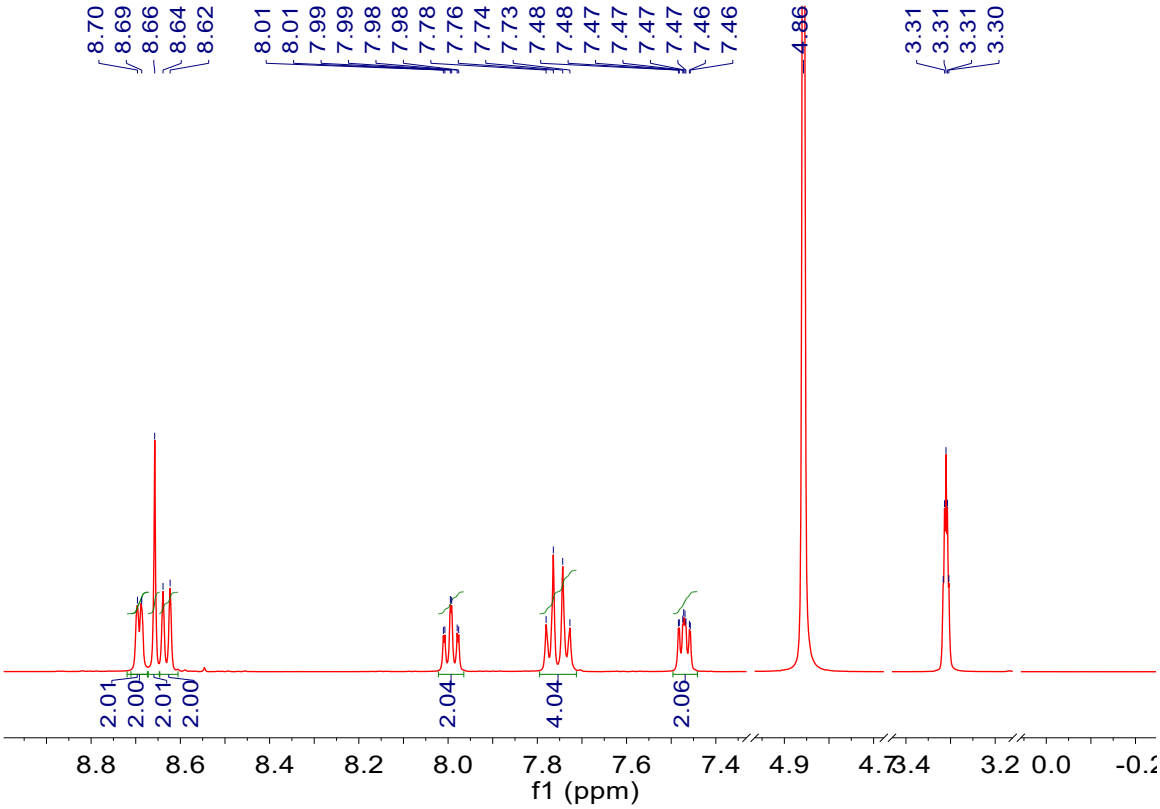

Figure S2. ^{1}H NMR (500 MHz, CD_3OD) spectrum of compound **PBA-tpy**.

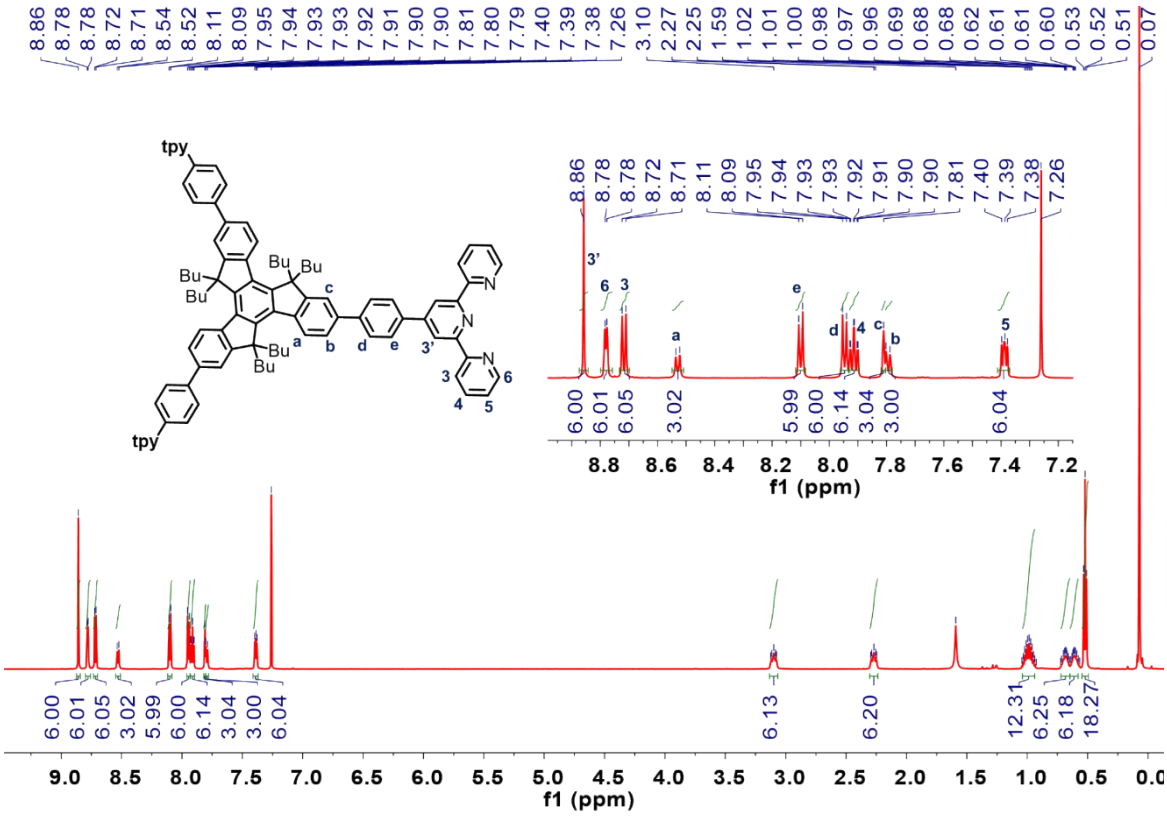

Figure S3. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of ligand **T-3tpy**.

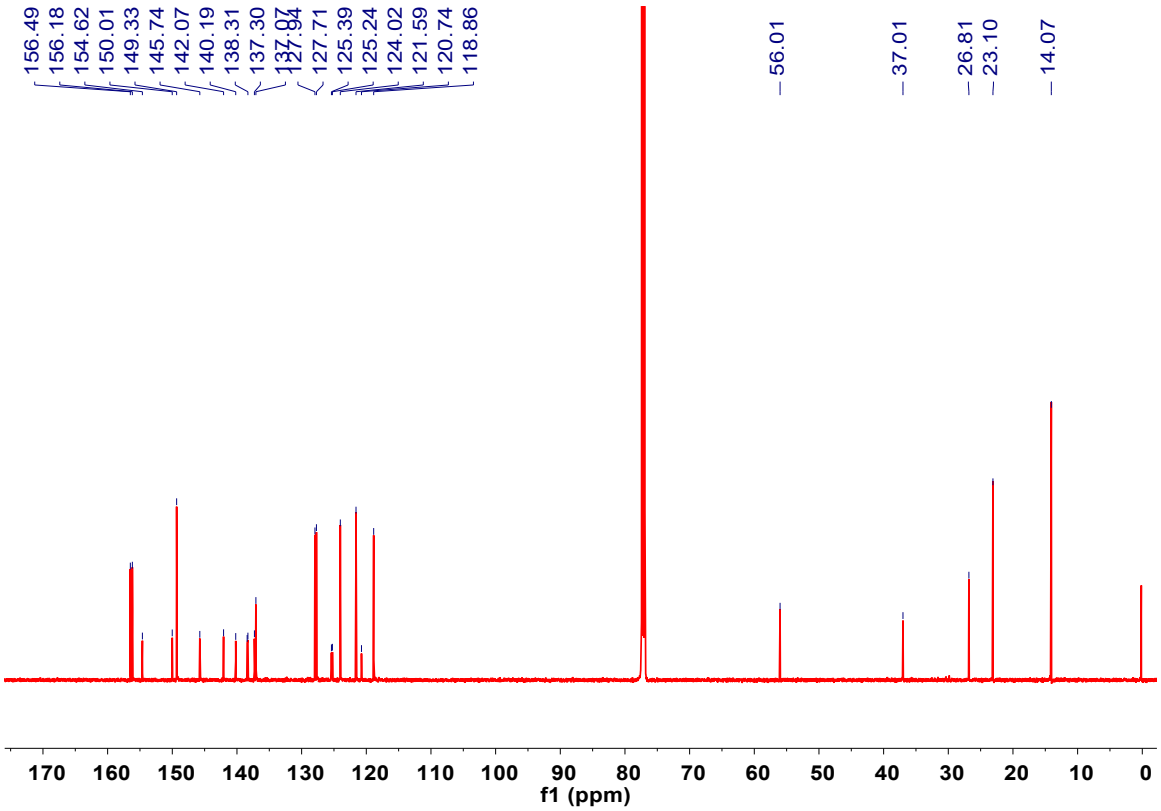

Figure S4. ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of ligand **T-3tpy**.

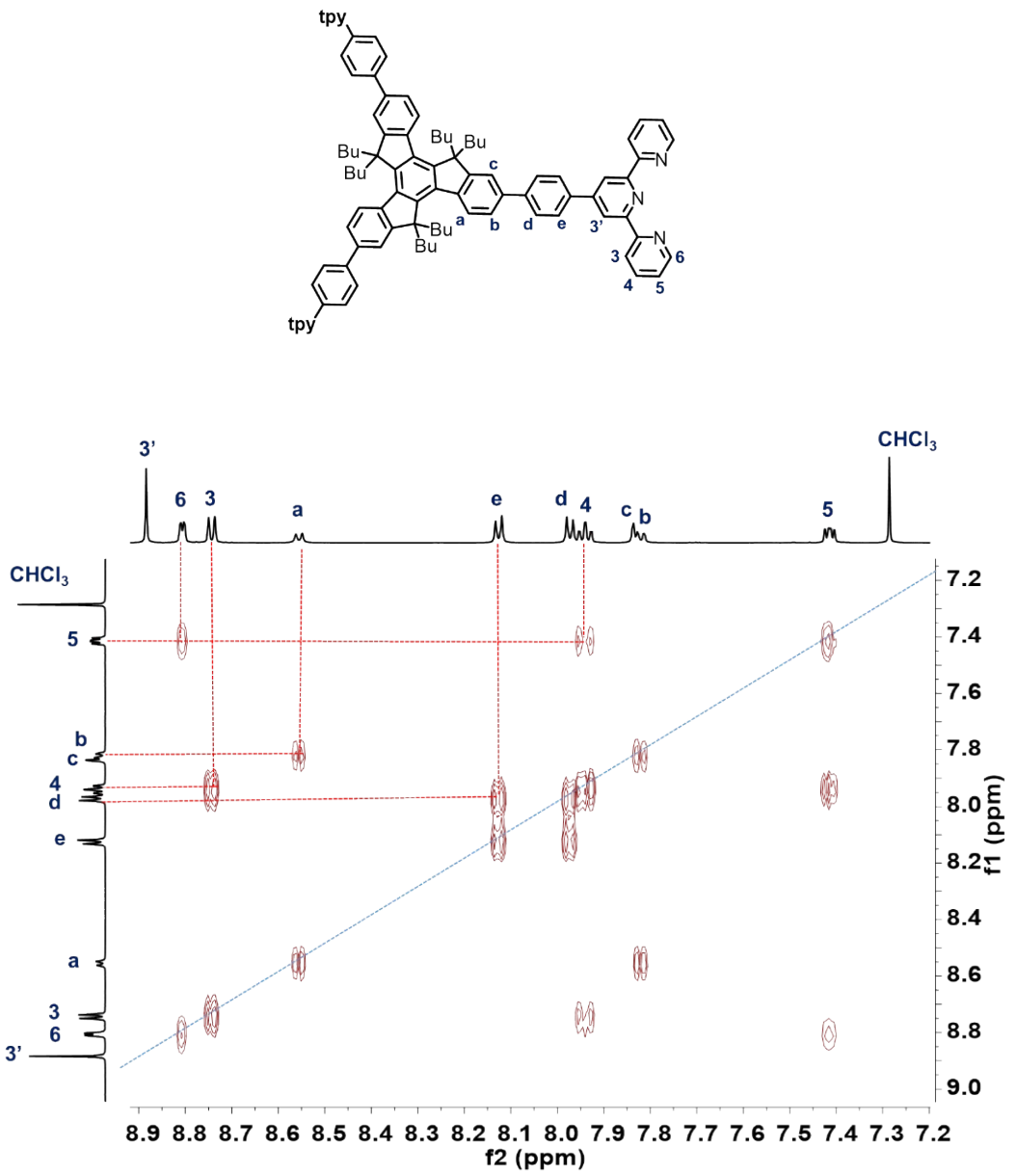

Figure S5. H-H COSY spectrum of ligand **T-3tpy** (aromatic region).

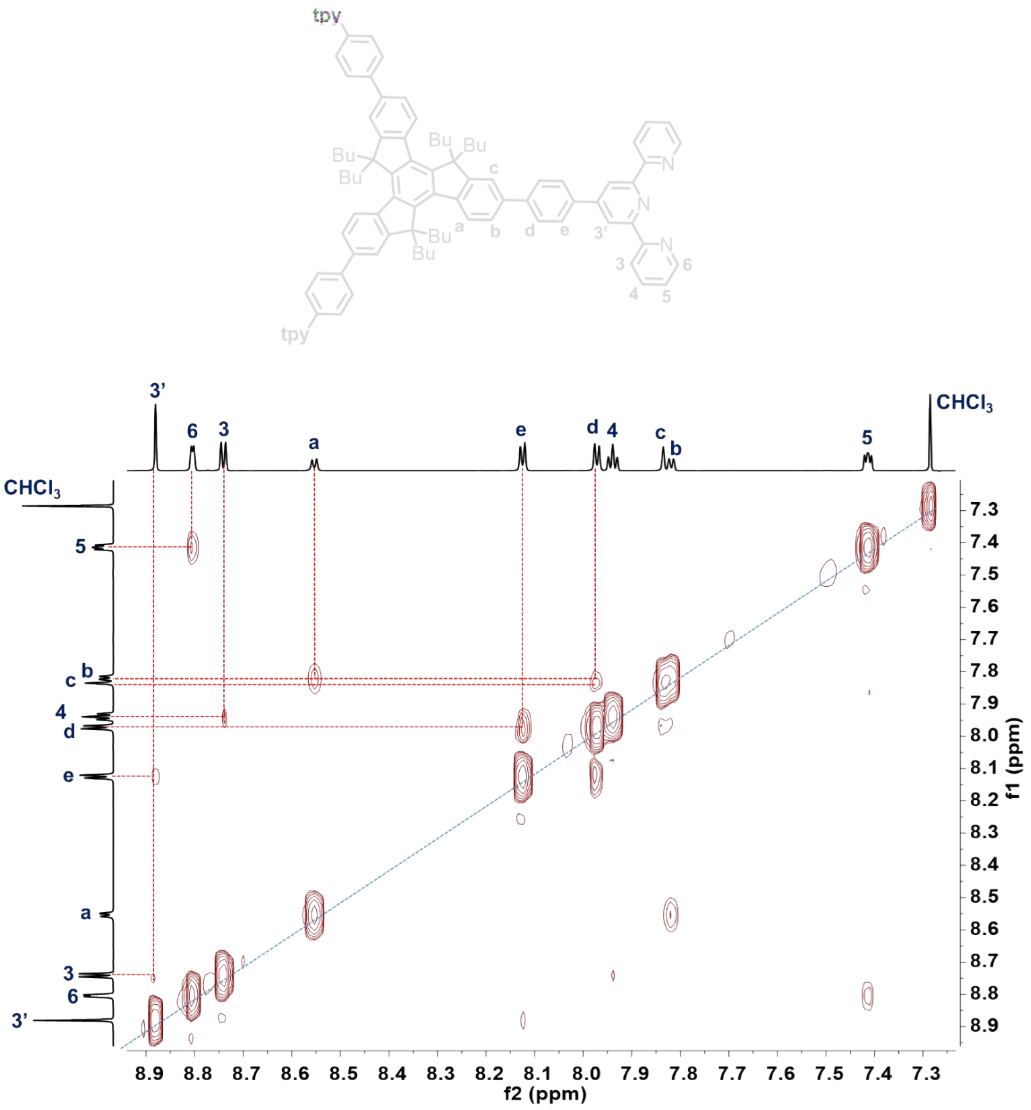

Figure S6. NOESY spectrum of ligand **T-3tpy** (aromatic region).

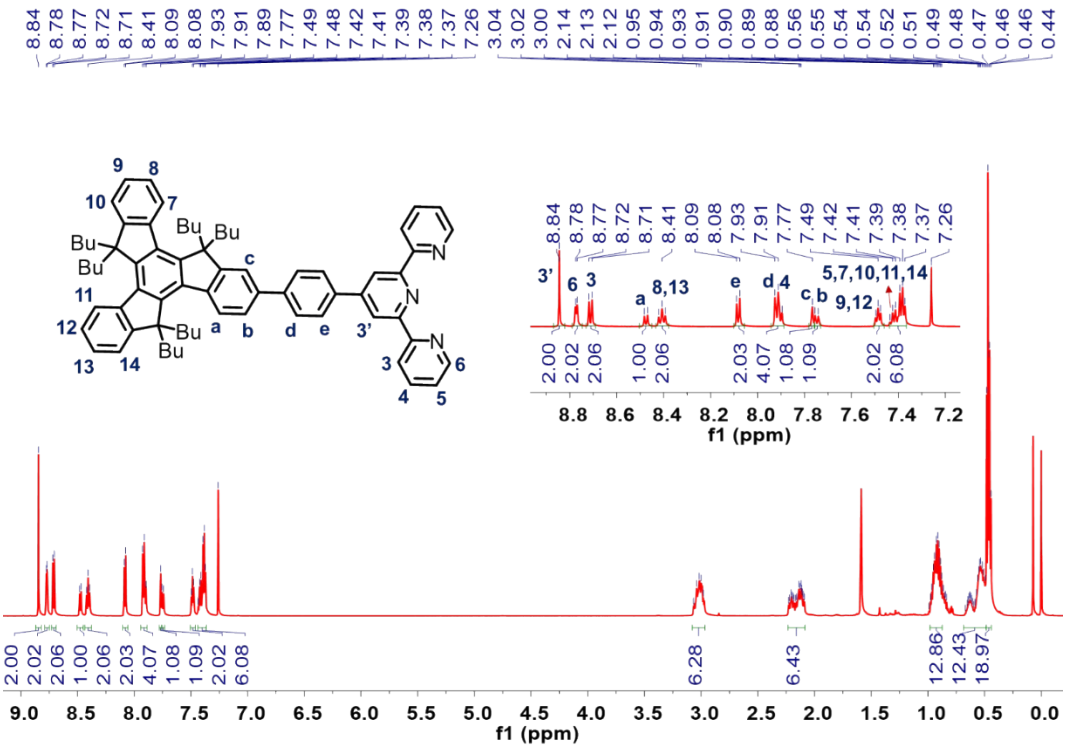

Figure S7. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of ligand **T-1tpy**.

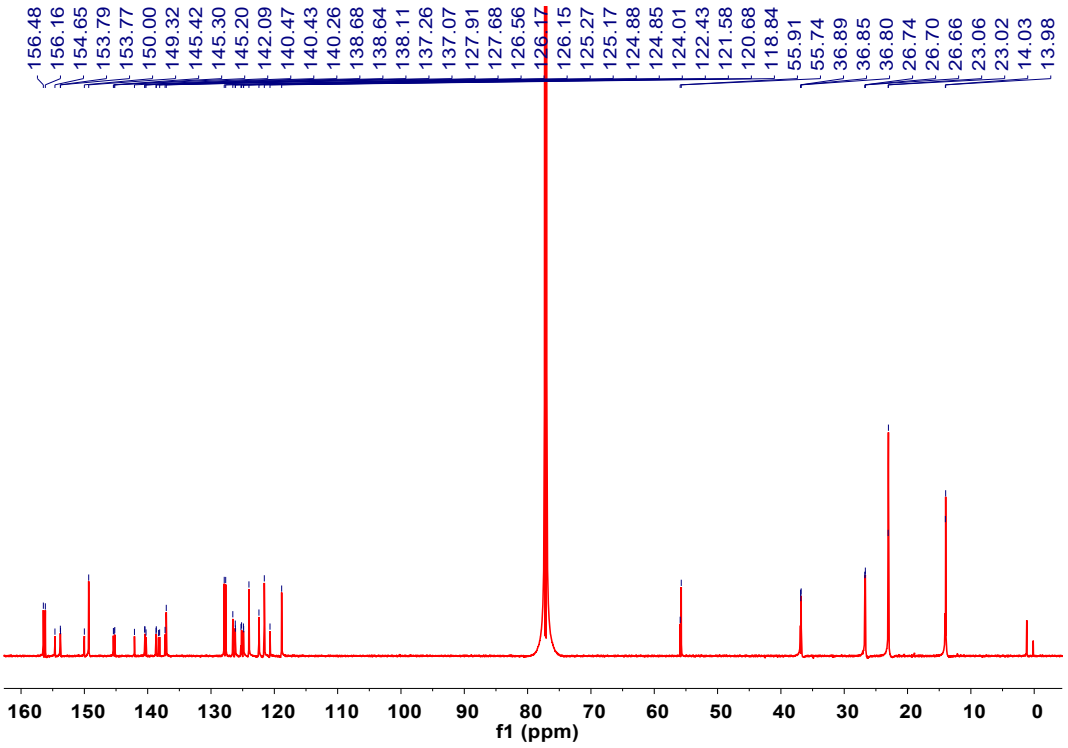

Figure S8. ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of ligand **T-1tpy**.

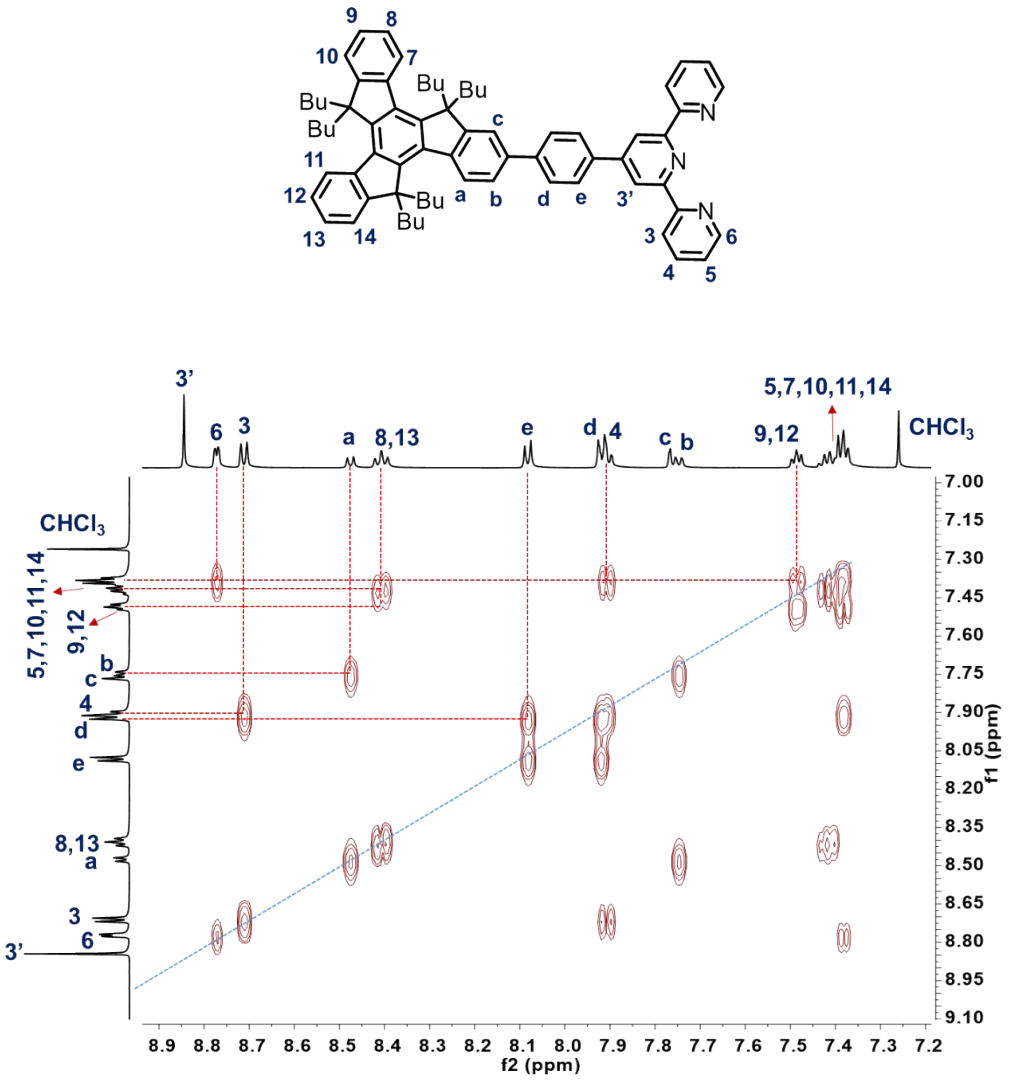

Figure S9. H-H COSY spectrum of ligand **T-1tpy** (aromatic region).

4 Supplementary Figures

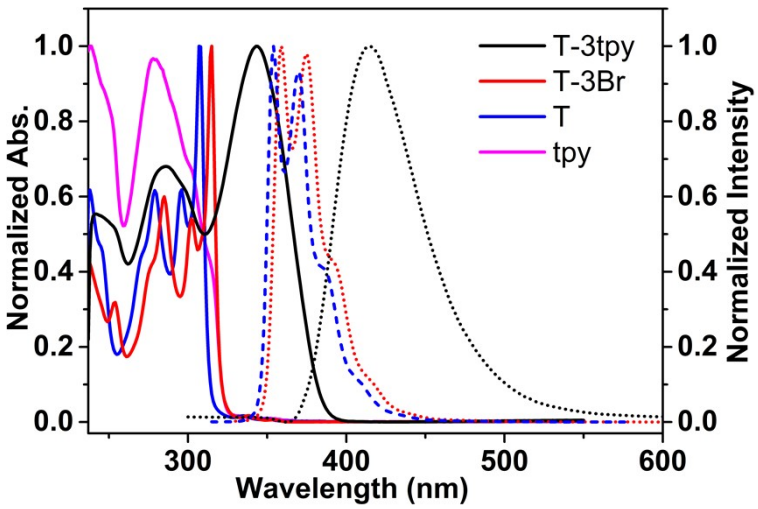

Figure S10. UV-Vis absorption (left, solid line) and emission spectrum (right, dotted line) of **T-3tpy** (black), **T-3Br** (red), **T** (blue) and **tpy** (pink).

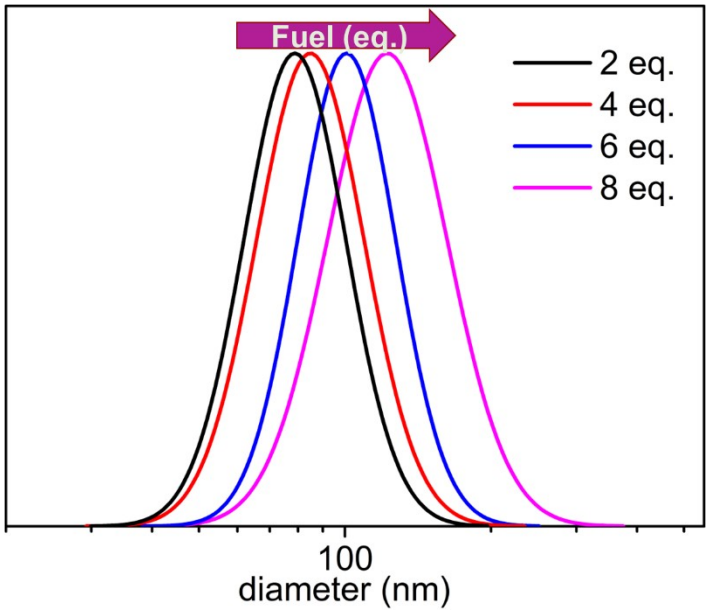

Figure S11. The effect of the equivalent of fuel on the size of **MSP**. (**T-3tpy** 11 μM, 25 ℃).

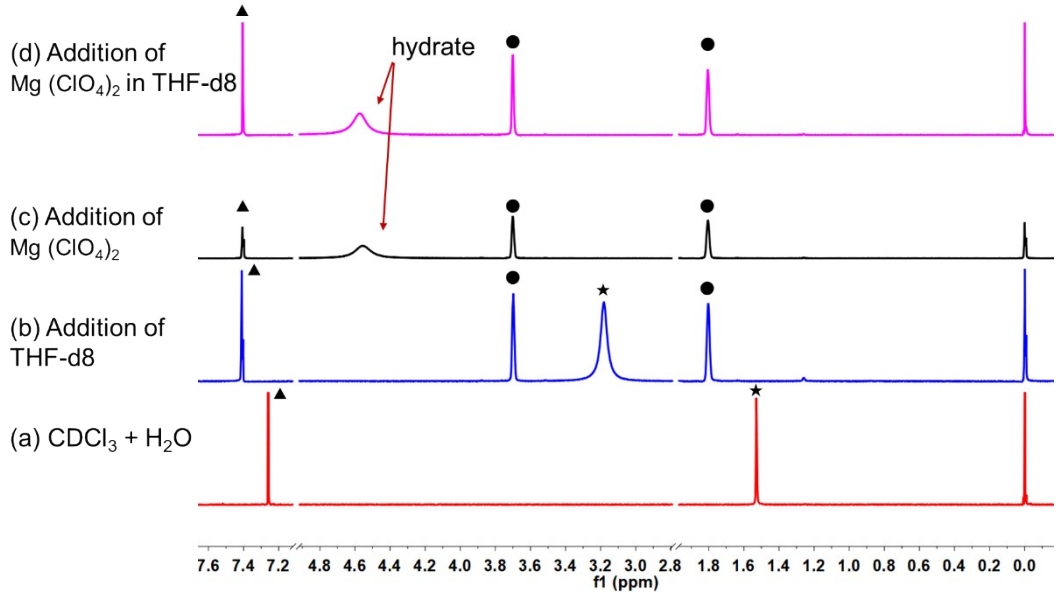

Figure S12. ^{1}H NMR spectra of control experiments. (a) $CDCl_3$ (0.5 mL) with pure H_2O (2.5 μL), (b) Addition of THF-d8 (100 μL) to (a). The peak of water shifted from 1.54 to 3.28 ppm, while the peak of $CHCl_3$ shifted from 7.26 to 7.47 ppm. (c) Addition of $Mg(ClO_4)_2$ solid to (b). The peak at 3.28 ppm disappeared, instead of a new peak at 4.63 ppm, corresponding to the protons of hydrating water. (d) Addition of $Mg(ClO_4)_2$ in THF-d8 to (a). The spectrum was alike to (c), indicating the peak at 4.63 ppm results from the hydration of Mg^{2+}. Marked signals are assigned to protons: ●, THF; ▲, $CHCl_3$; ★, and H_2O in the solvent.

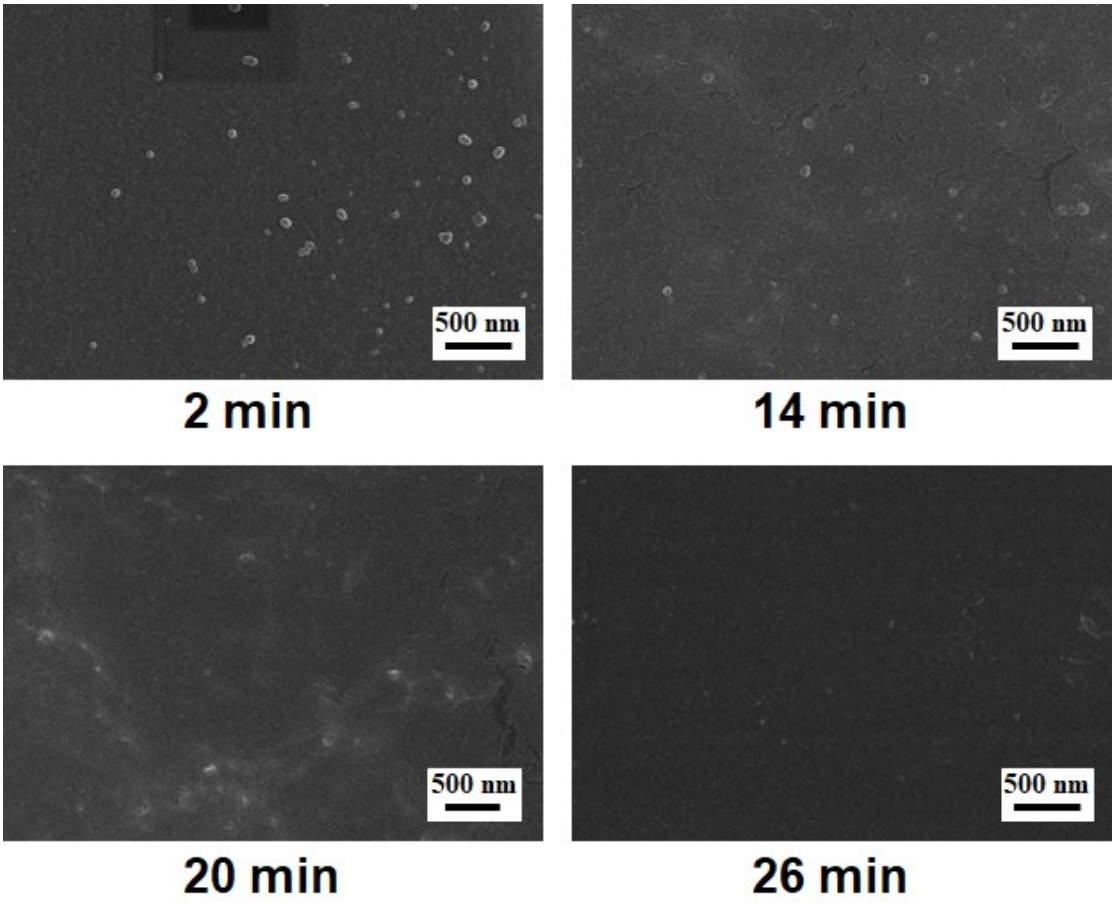

Figure S13. SEM images of transient **MSP** at 2 min, 14 min, 20min and 26 min. (**T-3tpy** 11 μM, $Mg(ClO_4)_2$ 22 μM, H_2O 10 μL, stirring rate 300 rpm, 25 ℃).

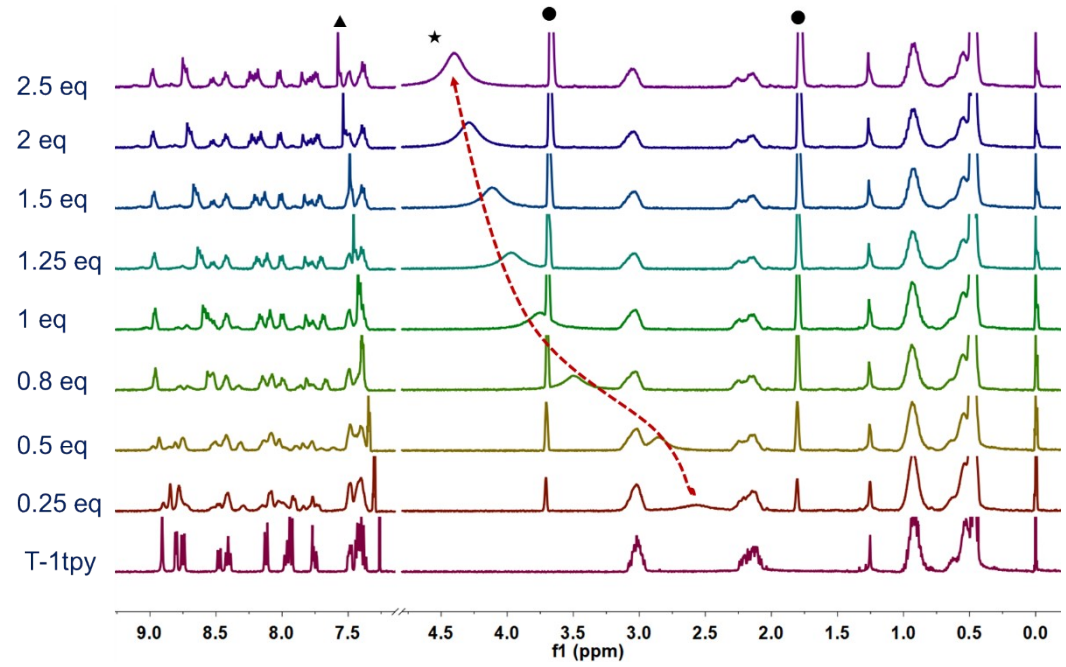

Figure S14. ^{1}H NMR titration of **T-1tpy** (5 mM, THF-d8) with $Mg(ClO_4)_2$ (15 mM, THF-d8). Marked signals are assigned to protons: ●, THF; ▲, $CHCl_3$; ★, and H_2O in the solvent. The dashed line serves to guide the eye for the shift of the water peak.

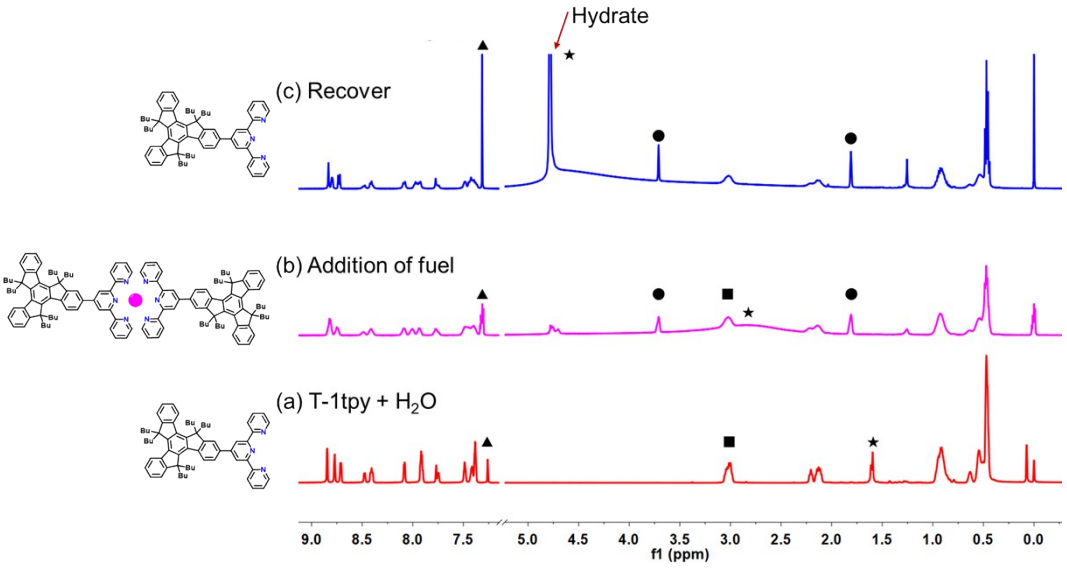

Figure S15. ^{1}H NMR monitoring of a solution containing ligand **T-1tpy** before (trace a,) and after (trace b and c) the addition of chemical fuel. Marked signals are assigned to protons: ●, THF; ▲, $CHCl_3$; ★, H_2O in the solvent; ■, -CH_2-.

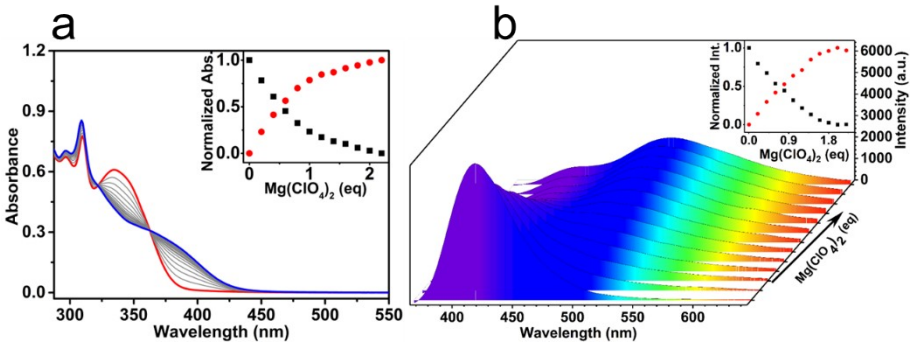

Figure S16. (a) Changes in the UV–Vis absorbance of ligand **T-1tpy** in $CHCl_3$ (10 μM) upon titration with $Mg(ClO_4)_2$ in THF (1 mM), red line: spectra before $Mg(ClO_4)_2$ addition; blue line: spectra after 2.2 equivalents of $Mg(ClO_4)_2$ were added; Inset: Normalized absorbance changes of ligand **T-1tpy** at 334 nm (black) and 386 nm (red) as a function of the molar ratio of $Mg(ClO_4)_2$. (b) Changes in the fluorescence spectra upon the addition of $Mg(ClO_4)_2$ (0 – 2.2 eq.) under the same condition as that in UV–Vis titration. Inset: Normalized intensity changes of ligand **T-1tpy** at 416 nm and 496 nm as a function of the molar ratio of $Mg(ClO_4)_2$.

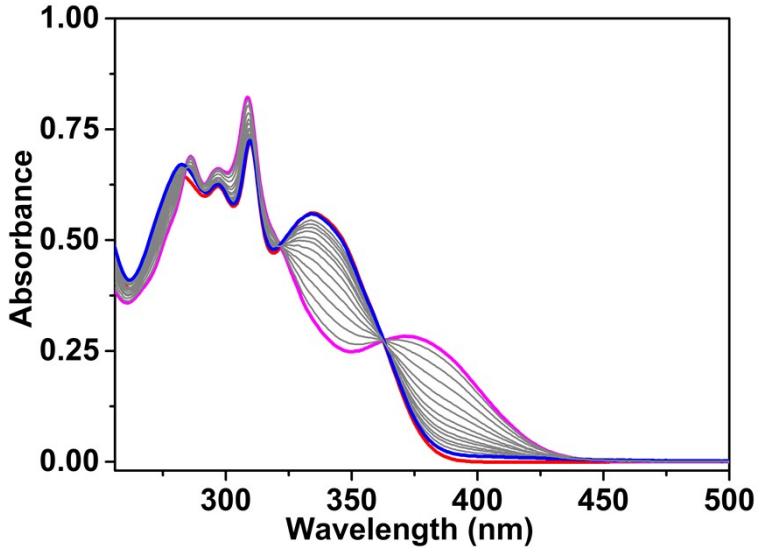

Figure S17. UV-Vis spectrum of **T-1tpy** (red) after the addition of fuel $Mg(ClO_4)_2$. The pink line shows the formation of a dimer. Then the absorbance returns to the starting point (blue) over ca. 19 min (adding $Mg(ClO_4)_2$ (2 eq.) to the solution of **T-1tpy** in $CHCl_3$ containing 1 μL pure water).

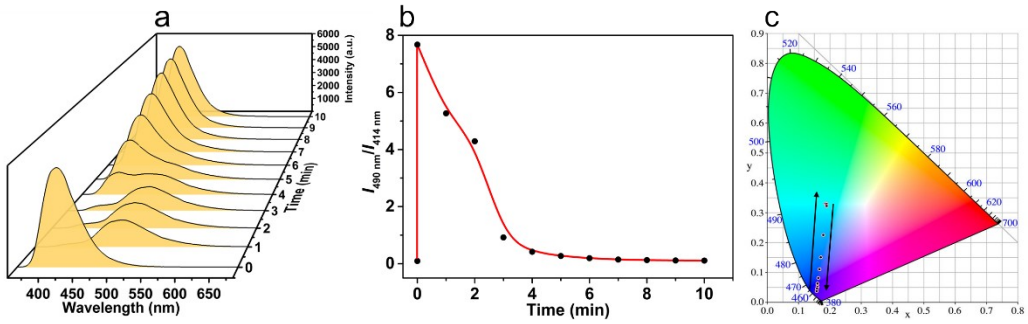

Figure S18. The transition process of luminescence of **T-1tpy**/$Mg(ClO_4)_2$ system over time. (a) Time-dependent fluorescence spectra (**T-1tpy** 10 μM, H_2O 10 μL, $Mg(ClO_4)_2$ 20 μM). (b) Time-dependent relative fluorescence intensity. (c) Time-dependent CIE coordinate diagram corresponding to b, showing the trajectory of the emission color change.

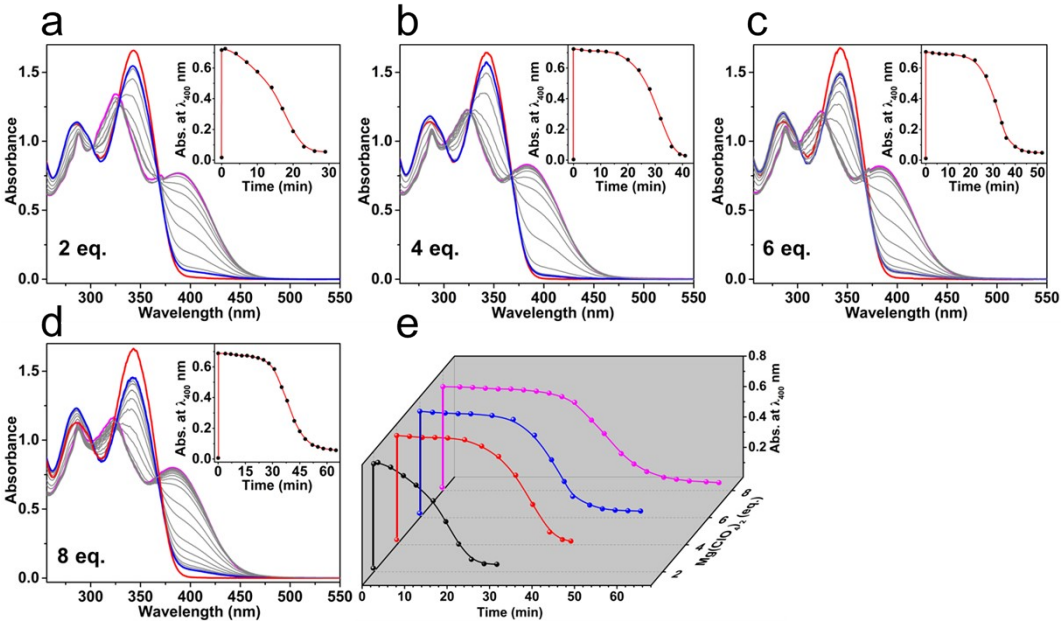

Figure S19. The lifetime of transient **MSP** regulated by the content of chemical fuel.

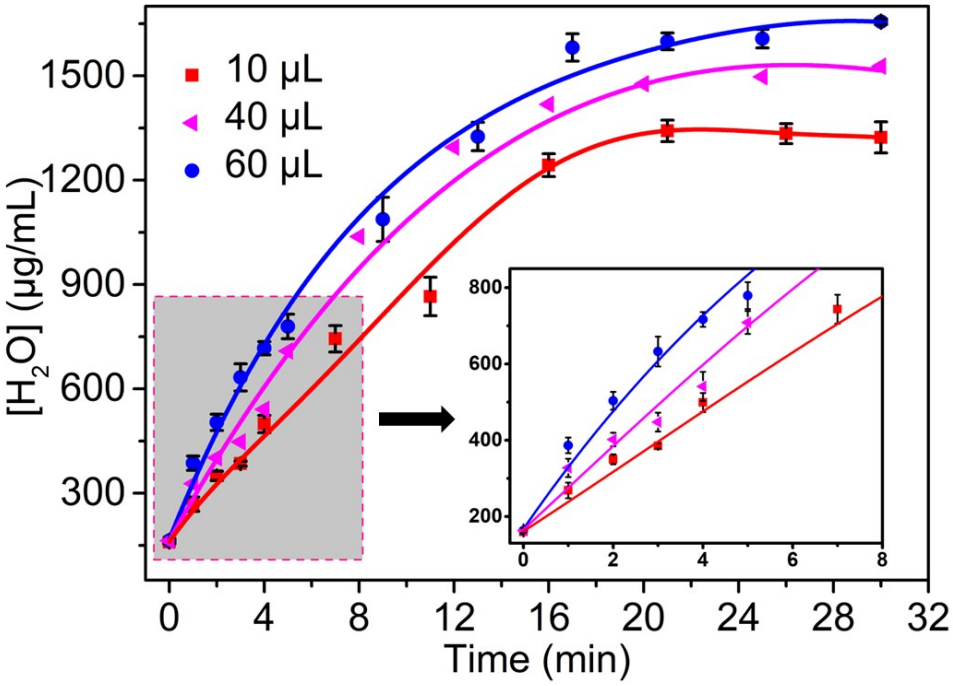

Figure S20. Time-dependent water content that diffused into $CHCl_3$.

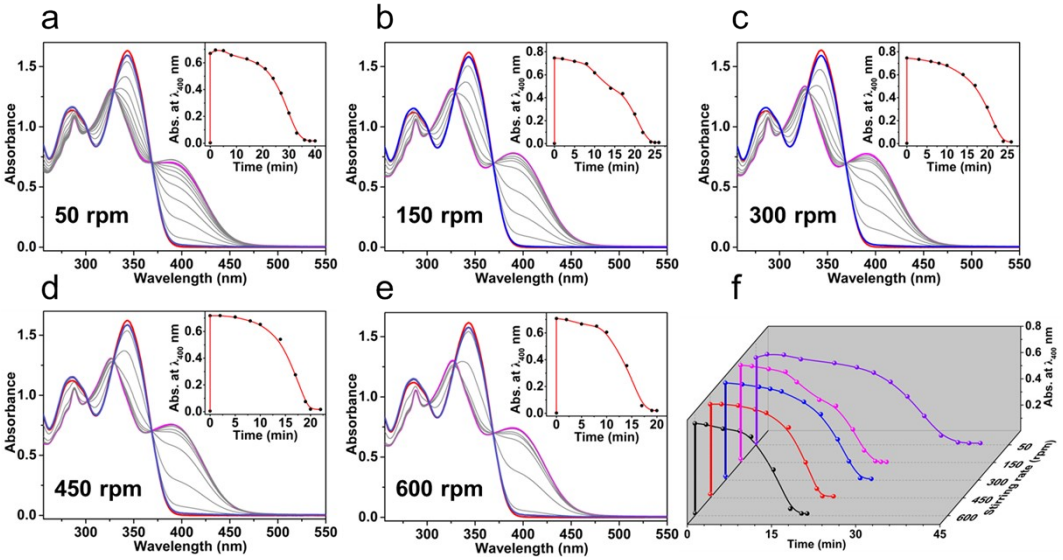

Figure S21. The effect of the stirring ra ıe lifetime of **MSP**.

Figure S22. An inhomogeneous oil phase was obtained without stirring. When exposed to 365 nm light, the **MSPs** only near the oil-water interface were decomposed (blue

layer) while the **MSPs** in oil bulk remained stable (green layer). (**T-3tpy** 11 μM, $Mg(ClO_4)_2$ 2 eq. H_2O 10 μL, 25 ℃)

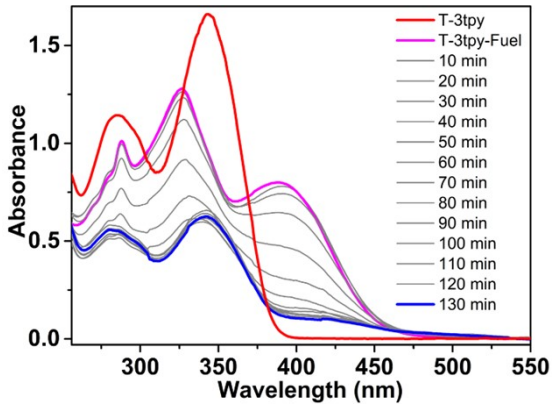

Figure S23. The **MSP** were partially degraded in the oil-air biphasic system. (**T-3tpy** 10 μM, $Mg(ClO_4)_2$ 20 μM, H_2O 10 μL, stirring rate 300 rpm, 25 ℃)

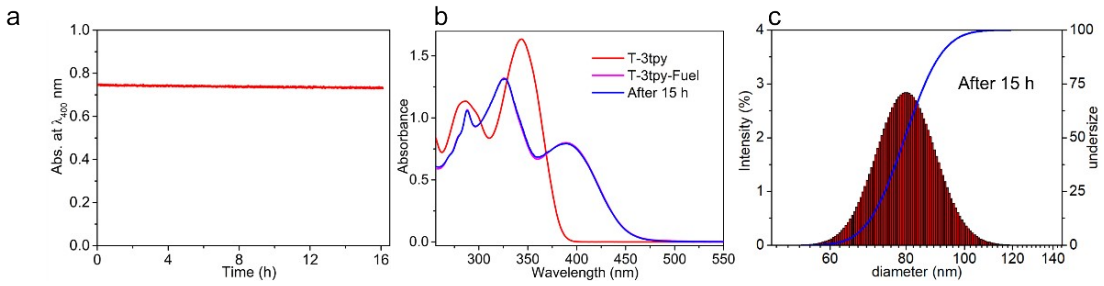

Figure S24. The **MSP** can exist for a long time in the sealed oil phase. (**T-3tpy** 10 μM, $Mg(ClO_4)_2$ 20 μM, 25 ℃) (a) Time-dependence of absorption of the **MSP** at 400 nm (b) UV-Vis spectra of **T-3tpy**, as prepared **MSP** and **MSP** after 15 h. (c) The size of **MSP** after 15 h determined by DLS.

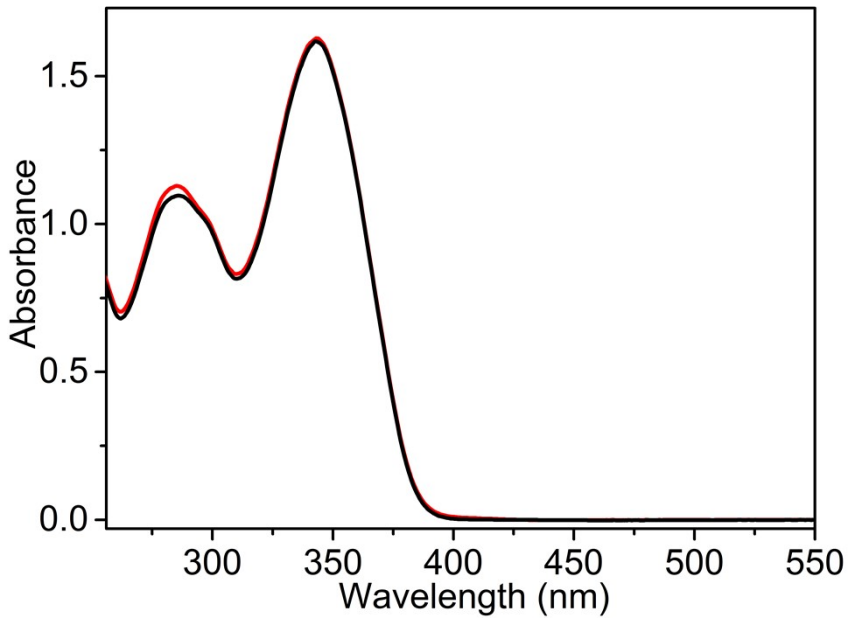

Figure S25. Changes in the UV-Vis absorbance of ligand **T-3tpy** (10 μM) in $CHCl_3$ ($[H_2O]$ = 1278 μg/mL) upon titration with $Mg(ClO_4)_2$ in THF (20 μM), red line: spectra before $Mg(ClO_4)_2$ addition; black line: spectra after 2 equivalents of $Mg(ClO_4)_2$ were added.

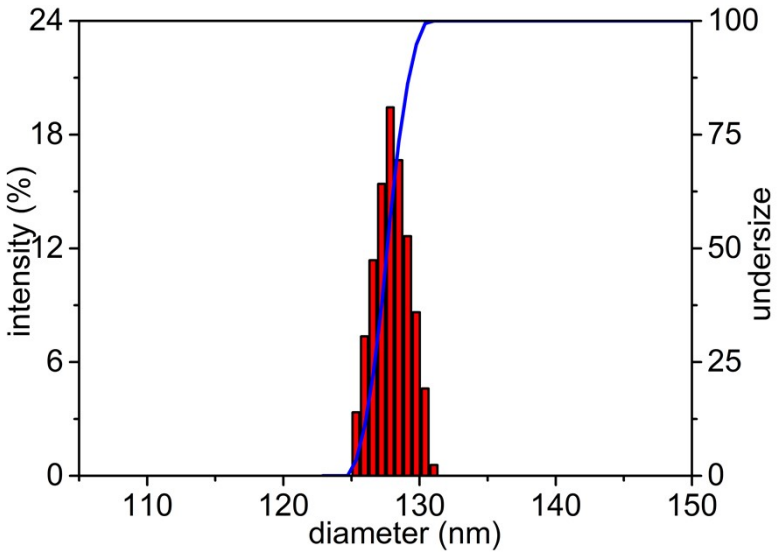

Figure S26. Size distribution of supramolecular polymers characterized by DLS when adding $Mg(ClO_4)_2$ into the solution of **T-3tpy** (**T-3tpy**: 10^{-4} M, $Mg(ClO_4)_2$: 2 eq.). The blue line refers to the cumulative frequency distribution of the size of the supramolecular polymers.

5 Movies

Movie S1

Formation and dynamics of supramolecular polymers. This time-lapse movie shows the formation of **MSP** after the addition of the fuel $Mg(ClO_4)_2$ and the recovery to the original state eventually. Conditions: room temperature, **T-3tpy** (11 μM) in chloroform (2 mL) containing water (10 μL); $Mg(ClO_4)_2$ (22 μM, 2 eq.). The solution was under exposure to a 365 nm light. The movie was captured by the camera (Canon). The total experiment time was ca. 20 min, and the movie plays at 44x speedup.

Movie S2

Formation and dynamics of MSP in high concentration. Conditions: room temperature, **T-3tpy** (0.1 mM) in chloroform (2 mL) containing water (10 μL); $Mg(ClO_4)_2$ (0.2 mM, 2 eq.). The solution was under exposure to a 365 nm light. The movie was captured by the mobile phone. The total experiment time was ca. 30 min, and the movie plays at 44x speedup. This time-lapse movie shows the formation of **MSP** after the addition of the fuel $Mg(ClO_4)_2$ and the recovery to the original state eventually.

6 References

1. Z. Zhang, H. Wang, X. Wang, Y. Li, B. Song, O. Bolarinwa, R. A. Reese, T. Zhang, X. Q. Wang, J. Cai, B. Xu, M. Wang, C. Liu, H. B. Yang and X. Li, *J. Am. Chem. Soc.*, 2017, **139**, 8174.
2. X. Wang, Y. Wang, H. Yang, H. Fang, R. Chen, Y. Sun, N. Zheng, K. Tan, X. Lu, Z. Tian and X. Cao, *Nat. Commun.*, 2016, **7**, 12469.