Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Solvent-Controlled Assembly of Pillar[5]arene-Based Supramolecular Networks via π-π Interactions for White Light Modulation

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Electronic Supplementary Information (11 pages)

1. Materials and methods

All reagents and solvents were commercially available and used as supplied without further purification.

Solution-state NMR, 2D NOESY NMR and Diffusion Coefficient *D*. Solution-state ^{1}H NMR, ^{13}C NMR spectra, 2D NOESY spectra and Diffusion Coefficient *D* (DOSY) were recorded on a Bruker Avance III 500 spectrophotometer with use of the deuterated solvent as the lock and the residual solvent or TMS as the internal reference.

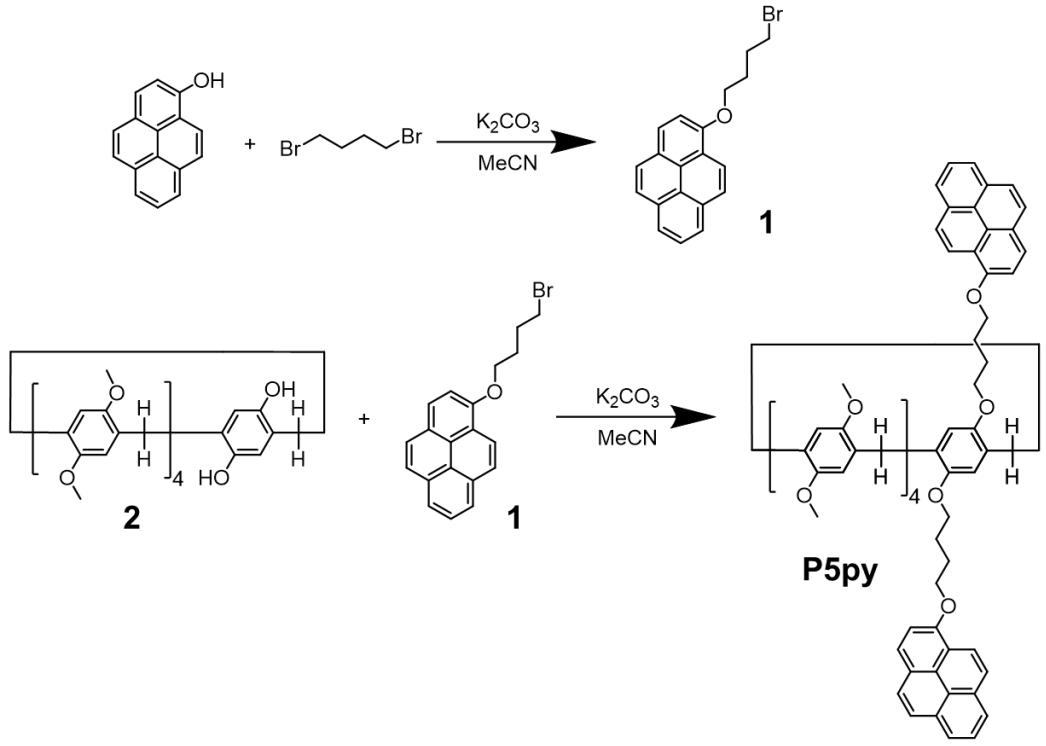
Fluorescence Spectrascopy. Fluorescence spectra of solid and solution samples were obtained on an RF-5301 spectrofluorophotometer (Shimadzu Corporation, Japan).

Single-Crystal X-ray Diffraction. Single-crystal X-ray data of **P5py** was measured on a Bruker D8 Venture diffractometer (Ga-Kα radiation, λ = 1.34139 Å)

UV-Vis Adsorption Spectroscopy. UV-Vis spectra of solution samples were obtained on a Shimadzu UV-2550 instrument at room temperature.

Scanning electron microscopy (SEM). SEM experiments were carried out on a JEOL 6390LV instrument. SEM samples were prepared by dissolving **P5py** (0.1 mM) in $CHCl_3$/methanol 1:1 mixed solvent and drop minute amount of the solution on a monocrystalline silicon piece and then remove the solvent under vacuum and low temperature (258.15K) .

*2. Synthesis of **P5py***



***Scheme S1*.** Synthetic route to **P5py**.

Synthesis of **1**[S1]: 1-Hydroxypyrene (1.5 g, 6.9 mmol, 1.0 eq), 1,4-dibromobutane (3.0 g, 14 mmol, 2.0 eq) and K_2CO_3 (5.0 g, 36 mmol, 5.0 eq) were dissolved in CH_3CN (80 mL) and the mixture was refluxed overnight. After cooling to room temperature, undissolved solid was filtered off. The filtrate was concentrated to obtain the crude product, and then purified by column chromatography using hexane : dichloromethane = 10 : 1 as the eluent to give pure compound **1** as white solid (1.5 g, 60 %). ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ (ppm): 8.44 (d, J = 10 Hz, 1H), 8.10 (dd, J_1 = 5 Hz, J_2 = 15 Hz, 3H), 8.04 (d, J = 10 Hz, 1H), 7.96 (dd, J_1 = 5 Hz, J_2 = 15 Hz, 2H), 7.89 (d, J = 10 Hz, 1H), 7.53 (d, J = 10 Hz, 1H), 4.37 (t, J = 10 Hz, 2H), 3.59 (t, J = 15 Hz, 2H), 2.22 (m, 4H).

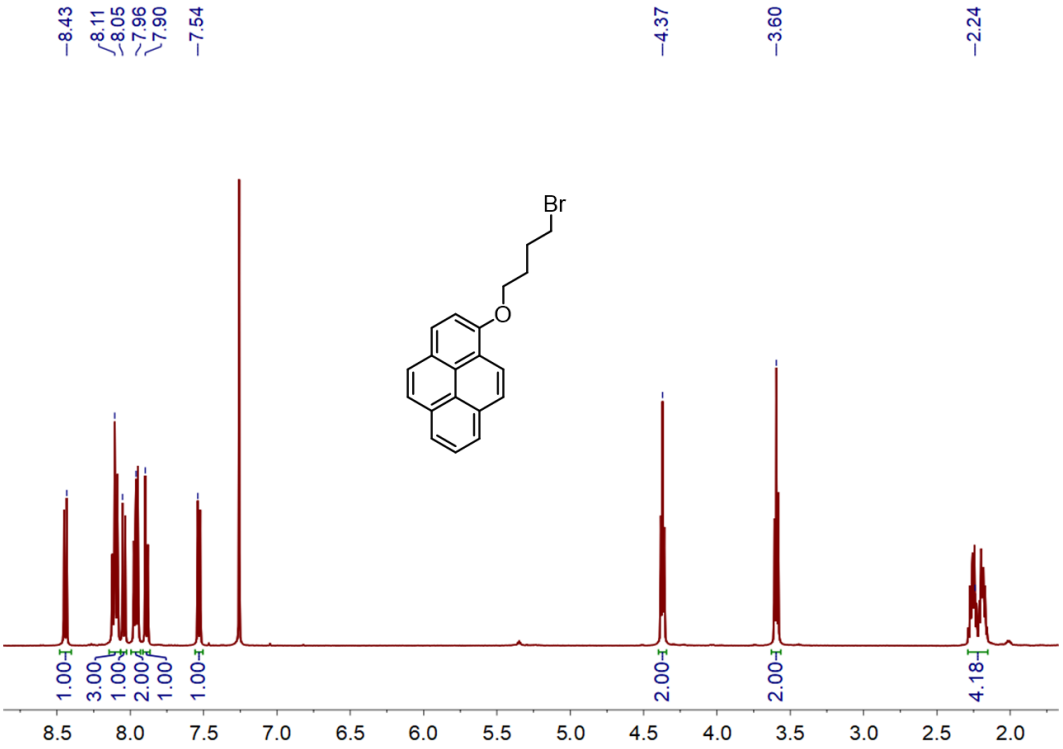


Fig. S1 ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298 K) of **1**.

Synthesis of **P5py**: Hydroxy-pillar[5]arene **2** (0.5 g, 0.7 mmol, 1.0 eq), pure compound **1** (1.0 g, 2.8 mmol, 4.0 eq) and K_2CO_3 (10.0 g, 70 mmol, 10.0 eq) were dissolved in CH_3CN (80 mL) and the mixture was refluxed for 48 h. After cooling to room temperature, undissolved solid was filtered off. The filtrate was concentrated to obtain the crude product, and then purified by column chromatography using hexane : dichloromethane = 3 : 1 as the eluent to give pure **P5py** as white solid (0.5 g, 56 %), mp 118−122 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ (ppm): 8.46 (d, J = 15 Hz, 2H), 8.10 (m, 6H), 8.03 (d, J = 10 Hz, 2H), 7.96 (dd, J_1 = 5 Hz, J_2 = 10 Hz, 4H), 7.89 (d, J = 10 Hz, 2H), 7.54 (d, J = 5 Hz, 2H), 6.85 (s, 2H), 6.81 (s, 2H), 6.76 (d, J = 10 Hz, 6H), 4.40 (t, J = 10 Hz, 4H), 4.00 (t, J = 10 Hz, 4H), 3.92 (d, J = 15 Hz, 2H), 3.75 (m, 8H), 3.61 (m, 24H), 2.20 (m, 8H). ^{13}C NMR (125 MHz, $CDCl_3$, 298 K) δ (ppm): 132.7, 132.6, 129.4, 129.3, 129.2, 129.0, 128.2, 127.3, 127.1, 126.8, 126.2, 126.0, 125.2, 125.1, 122.1, 121.3, 115.9, 115.1, 115.0, 114.8, 109.9, 69.4, 69.0, 56.7, 30.7, 27.6, 27.5. MALDI-TOF: *m*/*z* calcd for

$[C_{83}H_{80}O_{12}]^+$ 1268.56, found 1268.27; Elemental analysis calcd (%) for $C_{83}H_{80}O_{12}$: C 78.53, H 6.35, found: C 78.36, H 6.41.

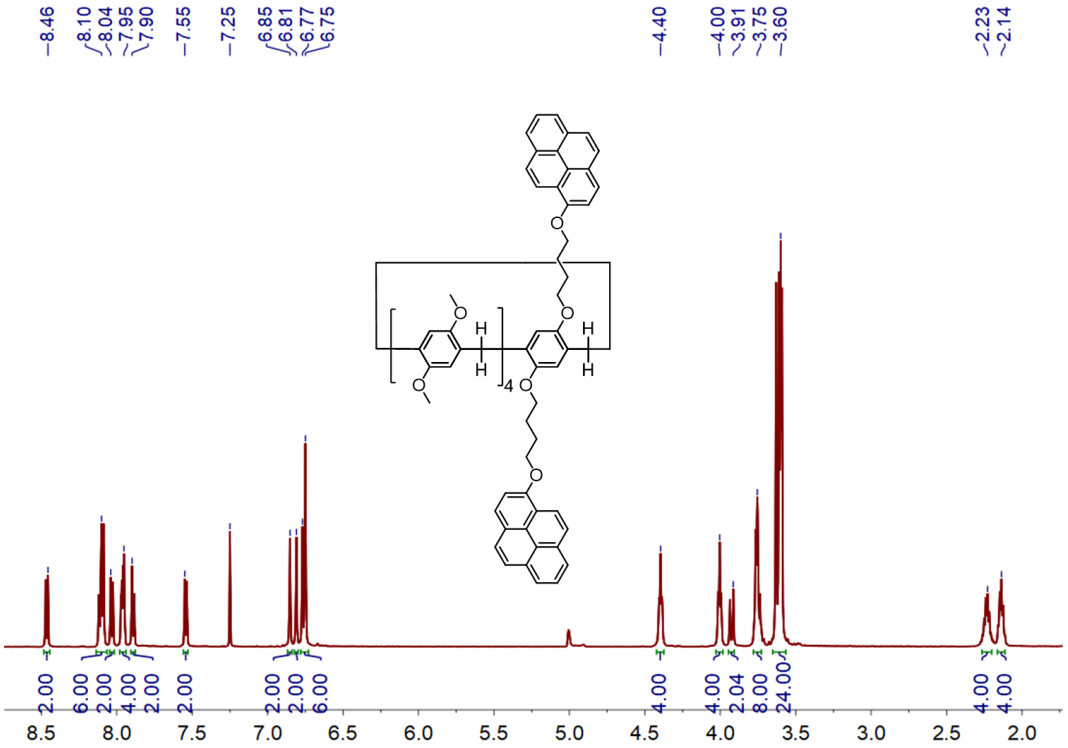


Fig. S2 ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298 K) of **P5py**.

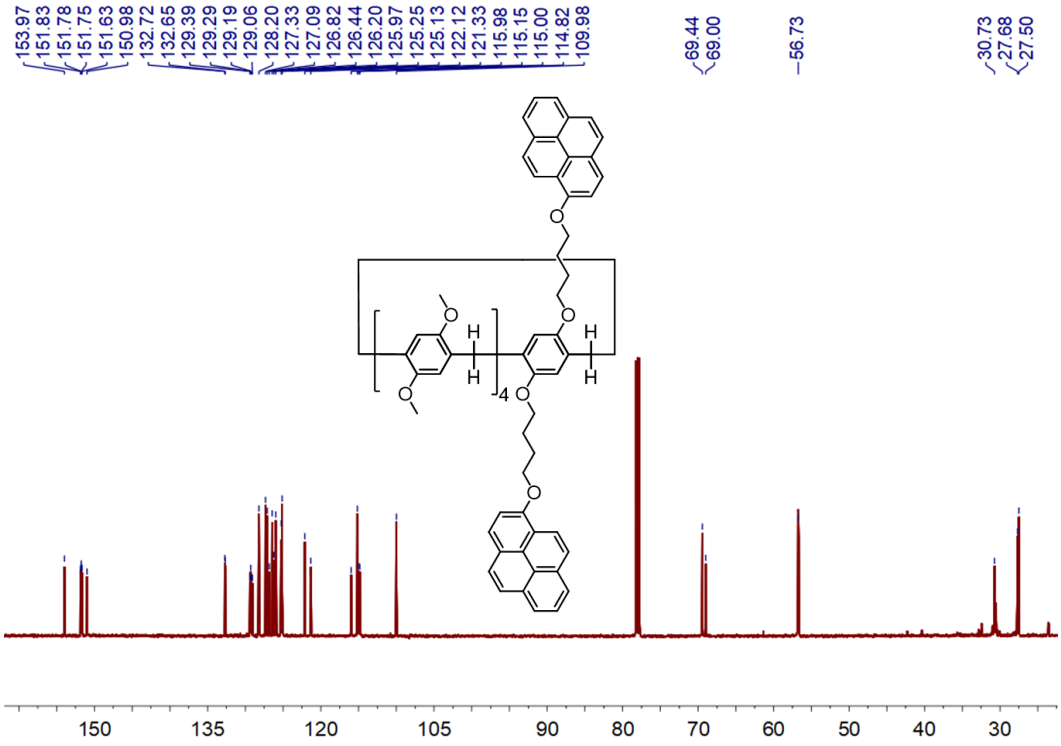


Fig. S3 ^{13}C NMR spectrum (125 MHz, $CDCl_3$, 298 K) of **P5py**.

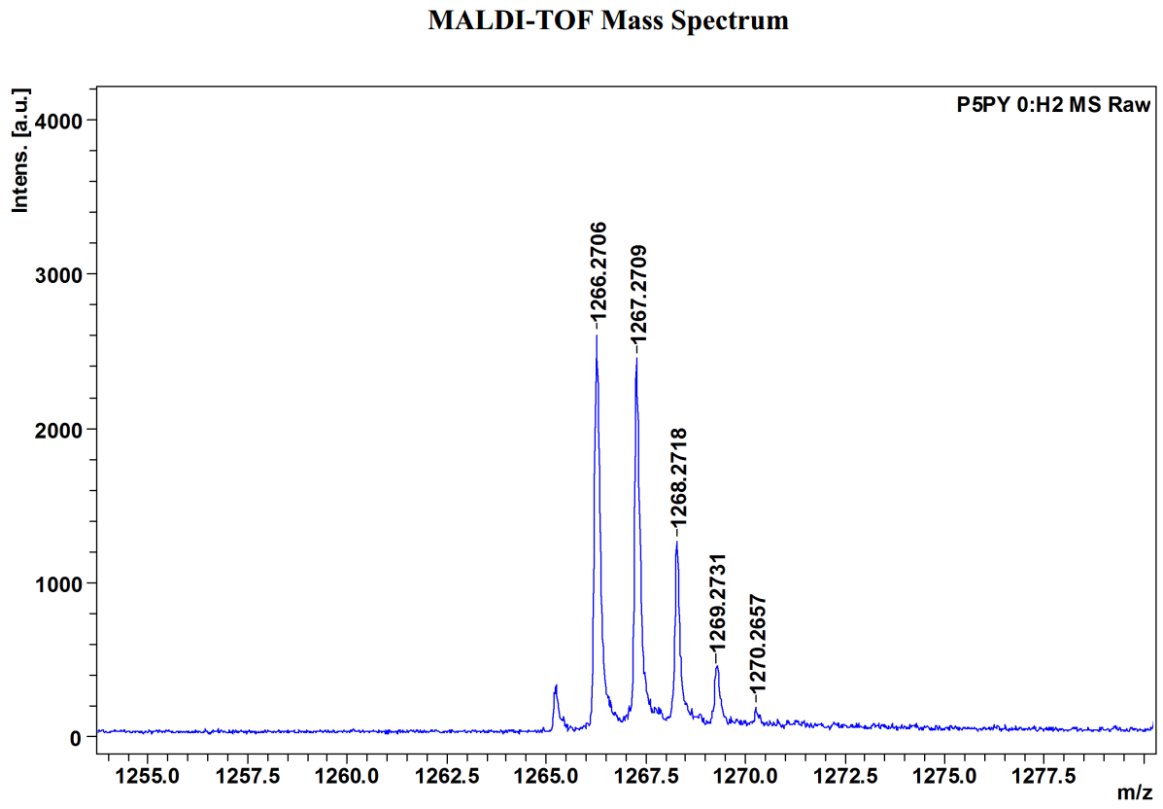
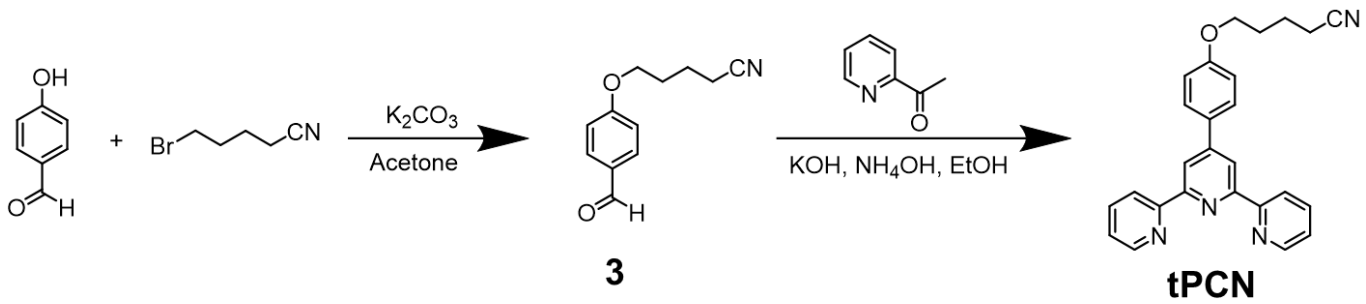


Fig. S4 MALDI-TOF mass spectrum of **P5py**.

*3. Synthesis of **EuCN***



Scheme S2. Synthetic route to **3PYCN**.

Synthesis of **3**[S2]: In a 150 mL three-necked flask equipped with a stirring bar and condenser pipe, 4-hydroxybenzaldehyde (2.0 g, 16 mmol, 1.0 eq), 5-bromopentanenitrile (5.7 mL, 33 mmol, 2.0 eq) and K_2CO_3 (11 g, 80 mmol, 5.0 eq) were dissolved in acetone (100 mL) and the mixture was refluxed overnight. After cooling to room temperature, undissolved solid was filtered off. The filtrate was concentrated to obtain the crude product, and

then purified by column chromatography using hexane : dichloromethane = 1 : 10 as the eluent to give pure compound **3** as colorless oil (2.6 g, 80 %). ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ (ppm): 9.88 (s, 1H), 7.83 (d, J = 10 Hz, 2H), 6.99 (d, J = 10 Hz, 2H), 4.10 (t, J = 10 Hz, 2H), 2.47 (t, J = 15 Hz, 1H), 1.95 (m, 4H).

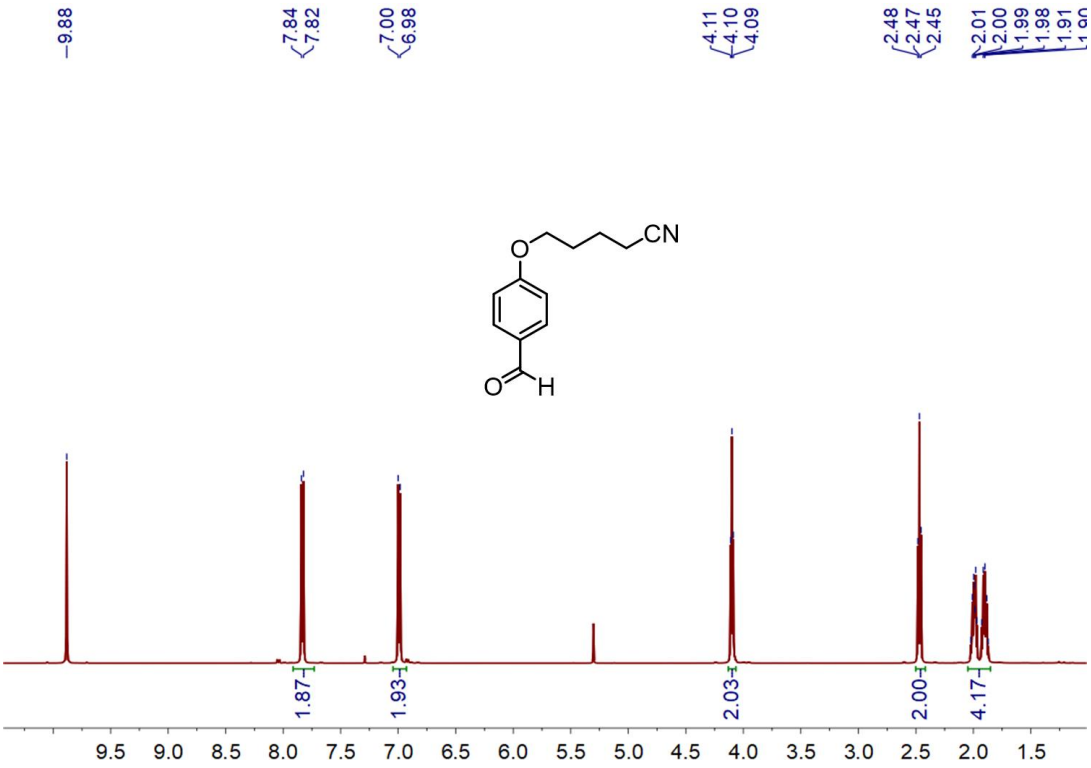


Fig. S5 ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298 K) of **3**.

Synthesis of **tPCN**[S3]: 2-Acetylpyridine (1.8 mL, 15 mmol, 2.0 eq) was added into a solution of pure compound **3** (1.5 g, 7.5 mmol, 1.0 eq) in EtOH (80 mL). KOH (0.85 g, 15 mmol, 2.0 eq) and aq NH_3 (30 mL, 29.3%) were then added to the solution. The solution was stirred at room temperature for 4 h. The off-white solid was collected by filtration and washed with EtOH (3 × 10 mL). Recrystallization from $CHCl_3$–MeOH afforded white crystalline solid **tPCN** (1.8 g, 60%), mp 175−178 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ (ppm): 8.73 (m, 2H), 8.71 (s, 2H), 8.67 (d, J = 10 Hz, 2H), 7.88 (m, 4H), 7.35 (m, 2H), 7.00 (m, 2H), 4.07 (t, J = 15 Hz, 2H), 2.47 (t, J = 15 Hz, 2H), 1.95 (m, 4H). HRMS: m/z calcd for $[C_{26}H_{22}N_4O + H]^+$ 407.1794, found 407.1877, error: 20 ppm m/z calcd for $[C_{26}H_{22}N_4O + Na]^+$ 429.1691, found 429.1669 error: −5.1 ppm; Elemental analysis calcd (%) for $C_{26}H_{22}N_4O$: C 76.83, H 5.46, N 13.78, found: C 76.85, H 5.43, N 13.74.

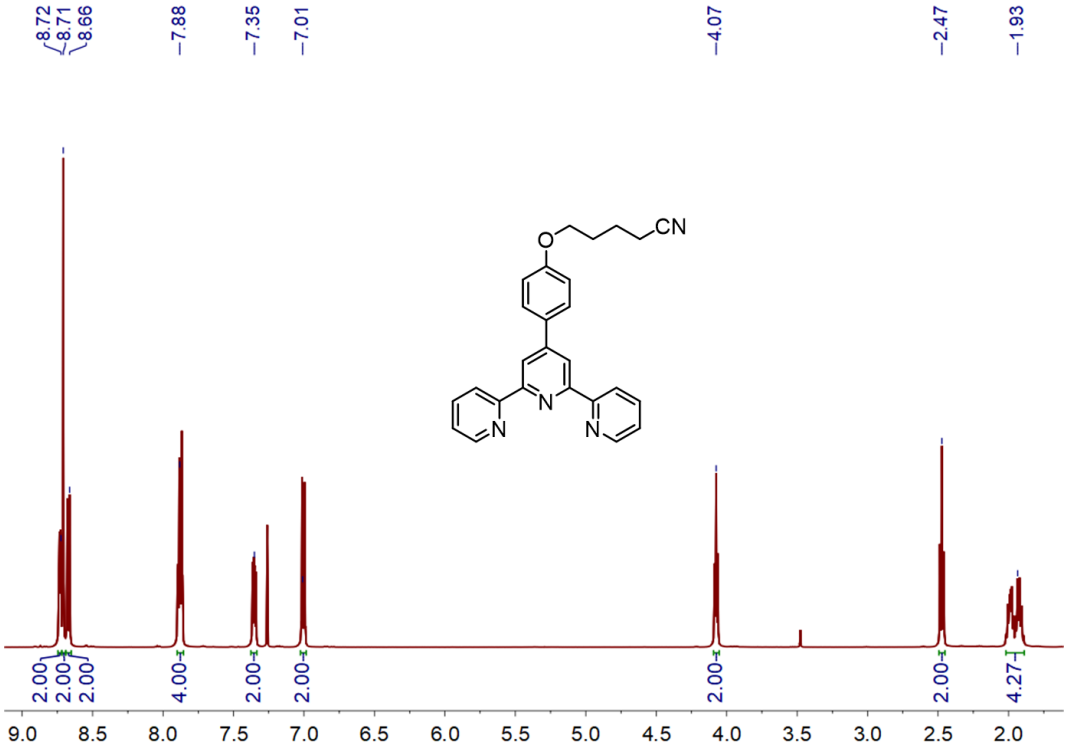


Fig. S6 ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298 K) of **tPCN**.

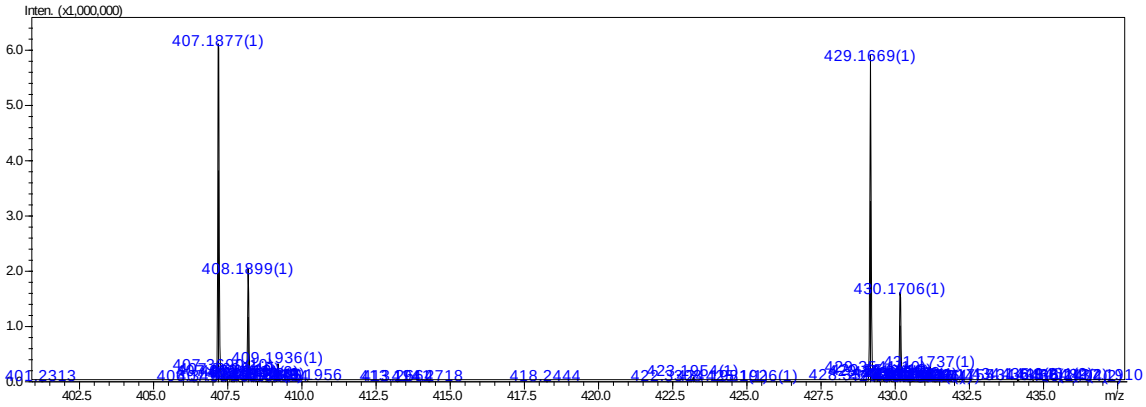


Figure S7. HRMS spectrum of **tPCN**.

*4. Crystallography Data of single crystals of **P5py***

Table S1. Crystal data and structure refinement for single crystals of **P5py**

Formula	**P5py**
Crystallization Solvent	chloroform+methanol
Formula	1.5($C_2H_2Cl_{16}$), $C_{83}H_{78}O_{12}$
Formula weight	1625.55
Collection Temperature /K	170(2)
Crystal system	monoclinic
Space group	C2/c
a /Å	26.7768(15)
b /Å	21.9422(14)
c /Å	14.8133(11)
α /°	90
β /°	107.915(4)
γ /°	90
Volume /$Å^3$	8281.4(10)
Z	4
ρ_{calc} g/cm^3	1.304
μ /mm^{-1}	2.164
F(000)	3384
Crystal size /mm^3	0.1 × 0.05 × 0.03
Radiation	Ga-Kα (λ = 1.34139)
2Θ range for data collection /°	6.038 to 108.698
Index ranges	-32 ≤ *h* ≤ 32, -26 ≤ *k* ≤ 26, -16 ≤ *l* ≤ 18
Reflections collected	38266
Independent reflections, R_{int}	7813,0.0804
Data/restraints/parameters	7813/50/523
Goodness-of-fit on F^2	1.033
Final R_1 indexes [I>=2σ (I)]	0.0955
Final R_1 indexes [all data]	0.1453
Final wR(F_2) indexes [all data]	0.2959
Largest diff. peak/hole / e $Å^{-3}$	0.910/-0.592

5. *SEM image of **P5py** in $CHCl_3$/methanol 1:1 mixed solvent*

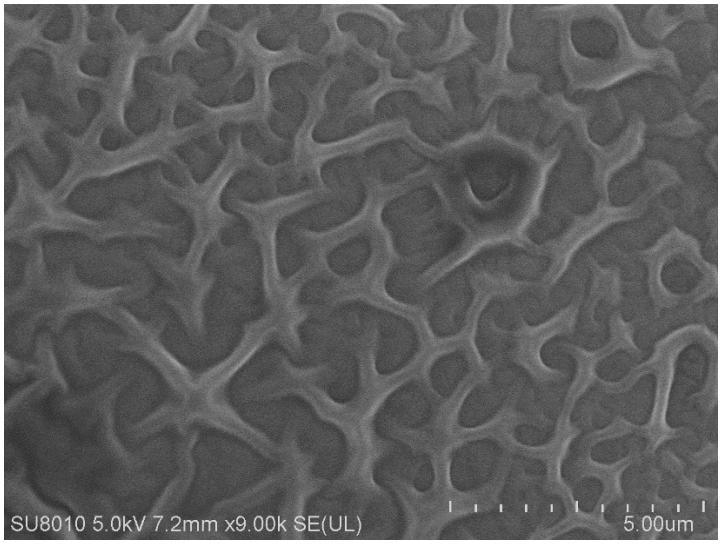


Fig. S8 SEM image of **P5py** (0.1 mM) in $CHCl_3$/methanol (1/1, v/v) mixed solvents.

6. *Photos of **P5py** in $CHCl_3$ at different concentrations under UV light*

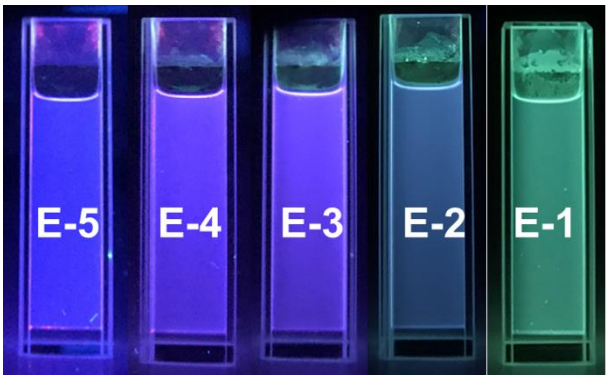


Fig. S9 Photos of **P5py** in $CHCl_3$ at different concentrations under UV light. (concentration from left to right: 0.01 mM, 0.1 mM, 1.0 mM, 10 mM, 100 mM)

7. *^{1}H NMR spectra of MeP5 **tPCN** host-guest complex in $CDCl_3$/MeOD mixed solvent*

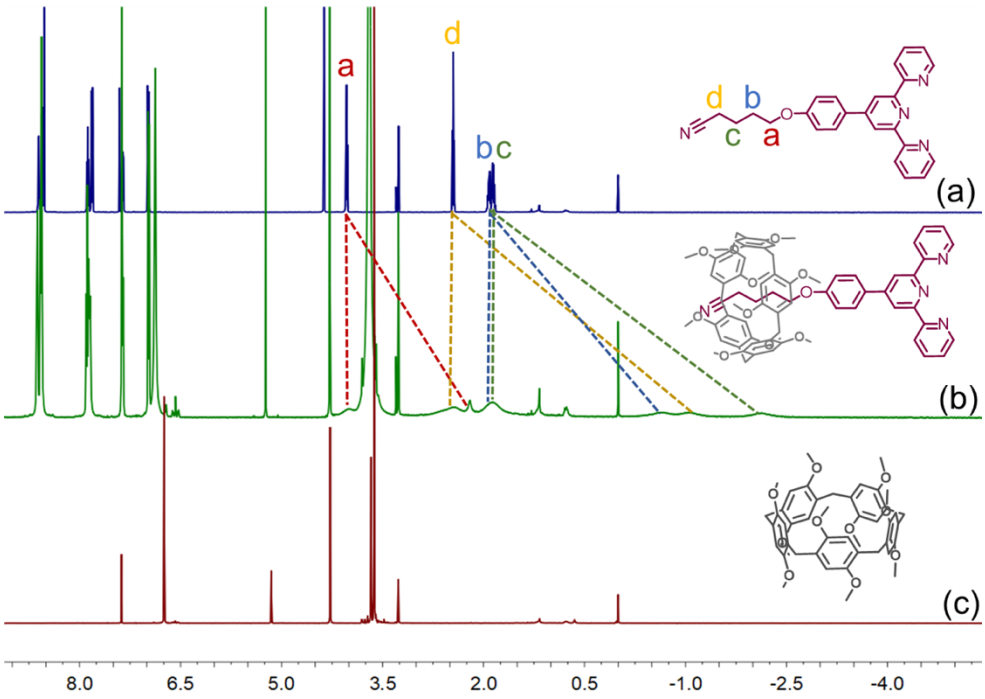


Fig. S10 ^{1}H NMR spectra (500 MHz, 298 K) in 50% $CDCl_3$ + 50% MeOD of (a) **tPCN** (5.0 mM), (b) **MeP5** + **tPCN** 1:1 mixture (5.0 mM) and (c) **MeP5** (5.0 mM).

*8. NOESY NMR spectrum of **MeP5 tPCN** host–guest complex in $CDCl_3$/MeOD mixed solvent*

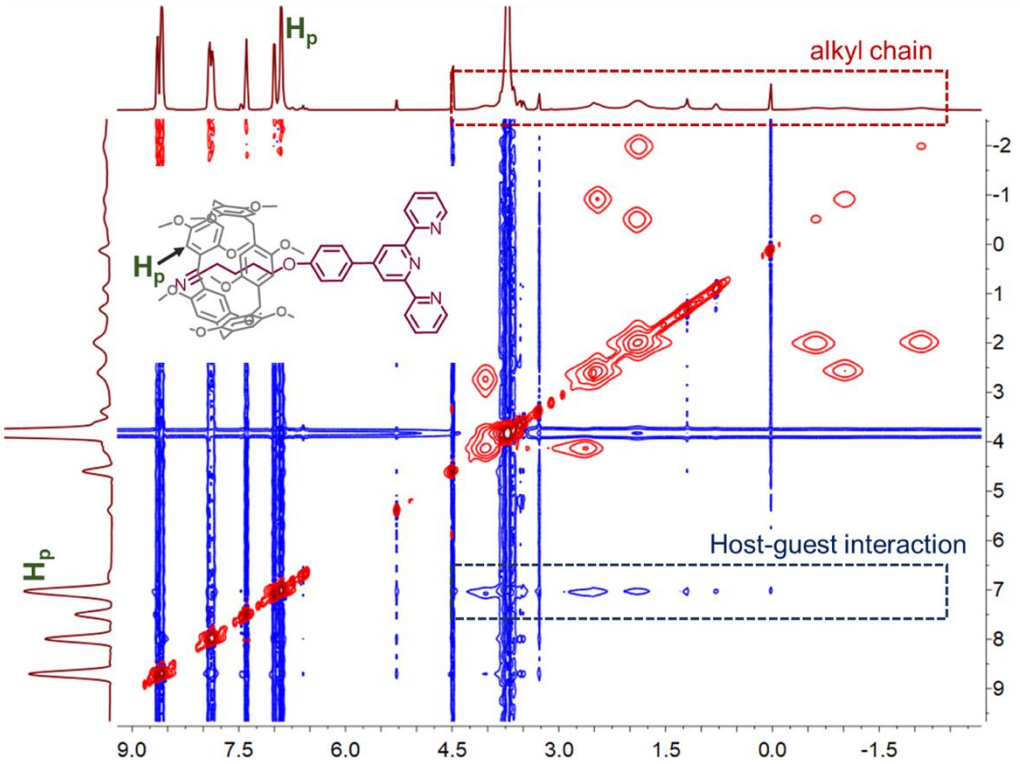


Fig. S11 NOESY NMR spectrum of **MeP5 tPCN** host–guest complex in $CDCl_3$/MeOD mixed solvent

9. References

S1. Shi, B.; Liu, Y.; Zhu, H.; Vanderlinden, R. T.; Shangguan, L.; Ni, R.; Acharyya, K.; Tang, J.-H.; Zhou, Z.; Li, X.; Huang, F.; Stang, P. J. Spontaneous Formation of a Cross-Linked Supramolecular Polymer Both in the Solid State and in Solution, Driven by Platinum(II) Metallacycle-Based Host–Guest Interactions. *J. Am. Chem. Soc.* **2019**, *141*, 6494−6498.

S2. Fan, C.; Wu, W.; Chruma, J. J.; Zhao, J.; Yang, C. Enhanced Triplet–Triplet Energy Transfer and Upconversion Fluorescence through Host–Guest Complexation. *J. Am. Chem. Soc.* **2016**, *138*, 15405−15412.

S3. Wang, J.; Hanan, G. S. A Facile Route to Sterically Hindered and Non-Hindered 4'-Aryl-2,2':6',2''-Terpyridines. *Synlett* **2005**, *8*, 1251–1254.