Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information

A novel multifunctional C_3-symmetric triphenylamine discotic liquid crystal: synthesis, columnar self-assembly, organogel behavior, selectively detecting PA and application in Si solar cells

Lu Liu,‡[a] Jiayang Li,‡[b] He Zhu,[a] Hanyan Yang,[a] Xi Feng,[a] Daping Xiao,[a] Yu Yang,*[b] Hongfei Gao*[a]

[a] Key Laboratory of Medicinal Chemistry for Natural Resource, Ministry of Education; Yunnan Provincial Center for Research & Development of Natural Products; School of Pharmacy, Yunnan University, Kunming 650500, P. R. China. E-mail: ghfynu@126.com;

[b] National Center for International Research on Photoelectric and Energy, Materials School of Materials and Energy, Yunnan University, Kunming 650500, P. R. China. E-mail: yuyang@ynu.edu.cn

‡ Both authors contributed equally to this work.

Content

1. Material and methods

Reactions requiring an inert gas atmosphere were conducted under argon and the glassware was oven-dried (100 °C). Commercially available chemicals were used as received. ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker-DRX-400 spectrometers with tatramethysilane (TMS) as internal standard and $CDCl_3$ as solvent. Elemental analysis was performed using an ThermoFisher FlashsmartCHNS/OMVC elemental analyzer. Column chromatography was performed with merck silica gel 60 (230-400 mesh). High-resolution MS spectra were measured on a RapifleX MALDI-TOF/TOF MS. UV/vis spectra were recorded on a UNICO UV-4802S spectrometer. Fluorescence spectral data was recorded on a Hitachi F-4500 fluorescence spectrometer. FT-IR spectra were recorded on Nicoletis10 spectrometer. Cyclic voltammograms (CV) were recorded on a CHI 660E S4 Electrochemical Workstation from Shanghai Chenhua Instrument (Shanghai, China) and conducted using a three electrodes system, with the modified GCE as working electrode, a platinum wire as the counter electrode, a saturated calomel electrode (SCE) as the reference electrode with nitrogen-saturated solution of 0.1 mol/L tetra-n-butylammonium tetrafluoroborate (Bu_4NPF_6) in acetonitrile. XRD patterns were obtained using a RIGAKUTTRIII-18KW diffractometer using Ni-filtered Cu Kα radiation.

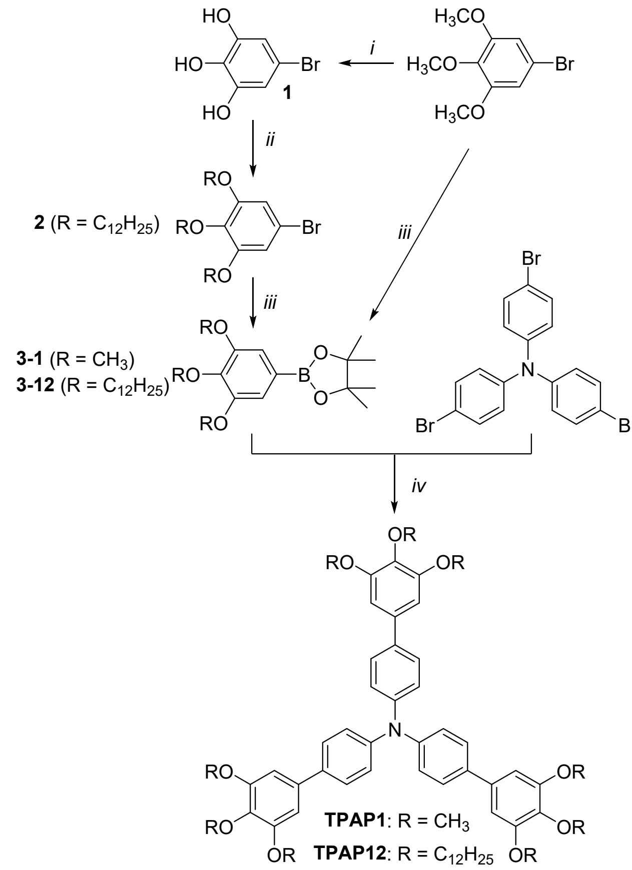
The fabrication of Planar Organic-Si Hybrid Solar Cell

At first, pure liquid crystal sample **TPAP12** was dissolved in anhydrous tetrahydrofuran to prepare a solution at a concentration of 100 mg/mL. Second, the precursor solution was formed by mixing 5 wt% dimethyl sulfoxide (DMSO, 99.9%) and 0.2 wt% Triton X-100 in PEDOT:PSS (PH1000, Clevios). The prepared **TPAP12** solution was dissolved in a precursor solution with doping ratios of 0, 0.2, 0.4, 0.6, and 0.8 vol%, respectively.

The ⟨100⟩ crystalline single-crystal Si substrate (n-type, 0.05–0.1 Ω cm, 300 ± 10 μm) was washed by sonication in acetone, deionized water, and isopropanol, and eventually immersed in 5% hydrofluoric acid (HF) for 1 min to remove natural oxides, then it was rinsed in the Millipore water. The prepared PEDOT:PSS+**TPAP12** solution was then covered on the H-terminated Si substrates with a speed of 3000 rpm for 60 s in a spinning manner. After the PEDOT:PSS+**TPAP12** was spin-coated, the sample was tempered on a heated plate at 130 °C for 20 min to form a uniform and conductive organic thin film of p-type in the Si substrate. Finally, 200 nm thick Ag grid was thermally vaporized on the device to the front electrode and an Al layer with a thickness of 60 nm was vaporized on the device to form the back electrode.

The *J–V* characteristics were measured by a solar IV measurement system (ZoliX SS150) at AM 1.5 G illumination. Optical transmission measurements of the film were measured by a spectrophotometer (Hitachi U-4100).

2. Synthesis and analytical data



Scheme S1 Synthesis of compounds **TPAP1** and **TPAP12**. *Reagents and conditions*: *i*) DCM, BBr_3, 0 °C, 0.5 h, RT, 12 h; *ii*) $C_{12}H_{25}Br$, DMF, K_2CO_3, 90 °C, 12 h; *iii*) AcOK, $PdCl_2(dppf)$, 1,4-Dioxane, 100 °C, 18 h; *iv*) THF, K_2CO_3, 70 °C, $Pd(PPh_3)_4$, 24 h.

1.1 General

Reactions requiring an inert gas atmosphere were conducted under argon and the glassware was oven-dried (120 °C). Commercially available chemicals were used as received. ^1H NMR and ^{13}C NMR spectra were recorded on Bruker–DRX-400 spectrometers. Elemental analysis was performed using an Elementar VARIO EL elemental analyzer. Column chromatography was performed with merck silica gel 60 (230-400 mesh). The analytical data correspond to those reported in the references.

1.2 Compound 1

To a 100 mL flask were added 1-bromo-3,4,5-trimethoxybenzene (1.52 g, 6.15 mmol) and 50 mL dry CH_2Cl_2. Then BBr_3 (1 M, 2.1 mL) was added carefully at 0 °C and the solution was stirred at room temperature for 12 h. After the reaction was compete (TLC), 5 mL of water was added carefully into the reaction mixture. The mixture was filtered and washed exhaustively with petroleum ether, and the obtained solid was extracted with absolute ethanol, and the organic layer was spin-dried to obtain the desired product **1** as brown solid. The obtained product was used directly for the next step.

1.3 Compound 2

To a 50 mL necked round bottom flask were added 1-Bromo-3,4,5-trihydroxybenzene (compound **1**) (500 mg, 2.44 mmol) and 3 mL of DMF. and K_2CO_3 (1.52 g, 10.98 mmol). The mixture was heated to 90 °C and stirred for 30 min. Add $C_{12}H_{25}Br$ (10.98 mmol) in the reaction system and continue to react for 24 h to obtain the desired product **2** as white solid. Yield: 81% (1.40 g, 1.97 mmol). ^{1}H NMR ($CDCl_3$; 400 MHz): δ = 6.67 (s, 2 H, 2 Ar**H**), 3.94-3.88 (m, 6 H, 3 OC**H**$_2$), 1.82-1.69 (m, 6 H, 3 OCH_2C**H**$_2$), 1.47-1.41 (m, 6 H, 3 OCH_2CH_2C**H**$_2$), 1.33-1.21 (m, 48 H, 24 C**H**$_2$), 0.88 (t, J = 6.6 Hz, 9 H, 3 C**H**$_3$).

1.4 Compound 3-12

To a mixture of **2** (986 umol), 4 Bis (pinacolato) diboron (625.93 mg, 2.46 mmol), AcOK (483.8 mg, 4.93 mmol), 10 ml dry 1,4-Dioxane and $PdCl_2$(dppf) (0.1 mmol) to a 50ml necked round bottom flask under argon. The reaction mixture was heated to reflux and this temperature was maintained for 18 h under intensive stirring. After being cooled to room temperature and 20 mL water was added, then the mixture was extracted with ethyl acetate (3 × 30 mL). The combined extracts were dried over anhydrous Na_2SO_4, and the solvent was removed in *vacuo*. The residue was purified by chromatography (eluent: petroleum ether/ethyl acetate = 20/1, V/V). White solid, yield: 94% (701.6 mg, 0.927 mmol). ^{1}H NMR ($CDCl_3$; 400 MHz): δ = 6.99 (s, 2 H, 2 Ar**H**), 4.02-3.95 (m, 6 H, 3 OC**H**$_2$), 1.83-1.70 (m, 6 H, 3 OCH_2C**H**$_2$), 1.46-1.43 (m, 6 H, 3 OCH_2CH_2C**H**$_2$), 1.33 (s, 12 H, 4 C**H**$_3$), 1.32-1.18 (m, 48 H, 24 C**H**$_2$), 0.88 (t, J = 6.6 Hz, 9 H, 3 CH_2C**H**$_3$).

1.5 Compound 3-1

Under argon gas, add a mixture of 1-bromo-3,4,5-trimethoxybenzene (1.00 g, 4.05 mmol), 4-bis (pinacolato) diborane (2.57 g, 10.12 mmol), AcOK (1.99 g, 20.24 mmol), 15 ml of dried 1,4-dioxane, and $PdCl_2$(dppf) (0.1 mmol) to a 50 ml neck round bottom bottle. Heat the reaction mixture to reflux and maintain this temperature for 12 hours under intense stirring. After cooling to room temperature and adding 20 mL of water, use ethyl acetate (3 × 30 mL) extraction mixture. Dry the combined extract with anhydrous Na_2SO_4 and remove the solvent in vacuum. The residue was purified by chromatography (eluent: petroleum ether/ethyl acetate = 10/1, V/V). Yellow solid, yield: 92% (1.09 g, 3.73 mmol) ^{1}H NMR ($CDCl_3$; 400 MHz): δ = 7.03 (s, 2 H, 2 Ar**H**), 3.90 (s, 6 H, 2 OC**H**$_3$), 3.87 (s, 3 H, 1 OC**H**$_3$), 1.34 (s, 12 H, 4 C**H**$_3$).

1.6 Compound TPAP1

To a mixture of **3-1** (1.00 g, 3.41 mmol), tris (4-bromophenyl) amine (470 mg, 0.98 mmol), and an aqueous solution of 2 M K_2CO_3 (2 mL) in dry THF (5 mL), $Pd(PPh_3)_4$ (115.6 mg, 0.1 mmol) (purged with N_2). Heat the reaction mixture to reflux and maintain this temperature for 14 hours under intense stirring. After cooling to room temperature and adding 20 mL of water. Using DCM (3 × 50 mL) extract the mixture. Dry the merged organic layer with anhydrous Na_2SO_4. After vacuum evaporation of the solvent, the residue was purified by DCM pure **TPAP1** (580 mg, 80%) as a yellow solid. ^{1}H NMR ($CDCl_3$; 400 MHz): δ = 7.48 (d, J = 8.4 Hz, 6 H, 6 Ar**H**), 7.23 (d, J = 8.8 Hz, 6 H, 6 N-Ar**H**), 6.77 (s, 6 H, 6 Ar**H**), 3.93 (s, 18 H, 6 OC**H**$_3$), 3.89 (s, 9 H, 3 OC**H**$_3$); ^{13}C NMR ($CDCl_3$; 100 MHz): 153.6 (6 C), 146.9 (3 C), 137.6 (3 C), 136.8 (3 C), 136.1 (3 C), 128.1 (6 C), 124.5 (6 C), 104.2 (6 C), 61.1 (3 C), 56.3 (6 C) 14.1(multicarbons in alkyl chains). The single crystal data was submitted to the Cambridge Crystallographic Data Centre (CCDC), and its corresponding number is 2312835.

1.7 The target compound TPAP12

To a mixture of **3-12** (1.0 g, 3.4 mmol), tris(4-bromophenyl)amine (50 mg, 103.7 umol), and an aqueous solution of 2 M K_2CO_3 (2 mL) in dry THF (5 mL), $Pd(PPh_3)_4$ (115.6 mg, 0.1 mmol) (purged with N_2) was added. The reaction mixture was heated to reflux and this temperature was maintained for 24 h under intensive stirring. After being cooled to room temperature and 20 mL water was added. The mixture was extracted with ethyl acetate (3 × 50 mL). The combined organic layer was dried over anhydrous Na_2SO_4. After evaporation of the solvent in *vacuo*, the residue was purified by chromatography (eluent: petroleum ether/ethyl acetate = 20/1, V/V) to yield pure **TPAP12** as a white solid (181.4 mg, 82%). ^{1}H NMR ($CDCl_3$; 400 MHz): δ = 7.45 (d, J = 8.8 Hz, 6 H, 6 Ar**H**), 7.19 (d, J = 8.8 Hz, 6 H, 6 Ar**H**), 6.74 (s, 6 H, 6 Ar**H**), 4.05-3.97 (m, 18 H, 9 ArOC**H**$_2$), 1.86-1.73 (m, 18 H, 9 ArOCH$_2$C**H**$_2$) 1.53-1.42 (m, 18 H, 9 ArOCH$_2$CH$_2$C**H**$_2$) .1.34-1.23 (m, 144 H, 72 C**H**$_2$) 0.87 (t, J = 6.8 Hz, 27 H, 9 C**H**$_3$); ^{13}C NMR ($CDCl_3$; 100 MHz): 153.5 (6 C), 146.8 (3 C), 137.9 (3 C), 136.12 (3 C), 136.08 (3 C), 127.9 (6 C), 124.4 (6 C), 105.8 (6 C), 73.7 (3 C), 69.4 (6 C), 32.1 (9 C), 30.5-29.5 (63 C), 26.3 (9 C),22.8 (9 C),14.3 (9 C) 14.1(multicarbons in alkyl chains); MALDI-TOF: *m*/*z* calculated for $C_{144}H_{243}NO_9$, $[M]^+$: 2131.8616, found 2131.8638; Elemental analysis calcd (%) for $C_{144}H_{243}NO_9$ (2132.53): C 81.10, H 11.49; Found: C 80.92, H 11.54.

1.8 NMR spectra

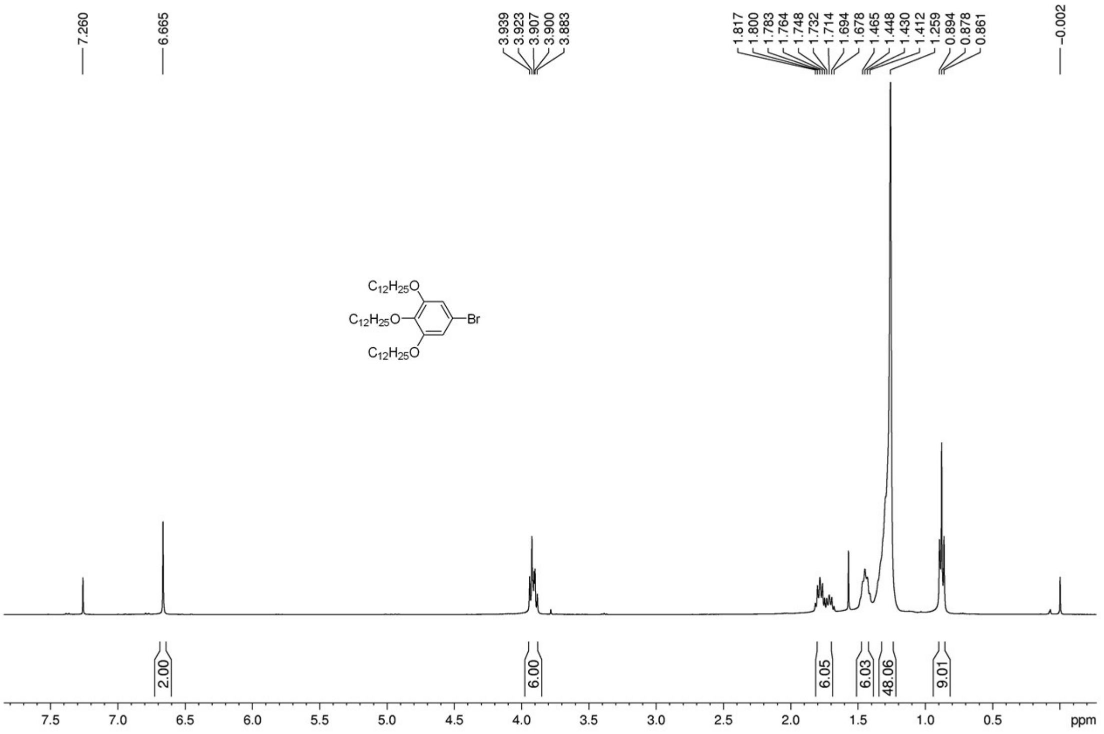


Fig. S1 ^{1}H NMR spectrum of compound **2** (400 MHz, in $CDCl_3$).

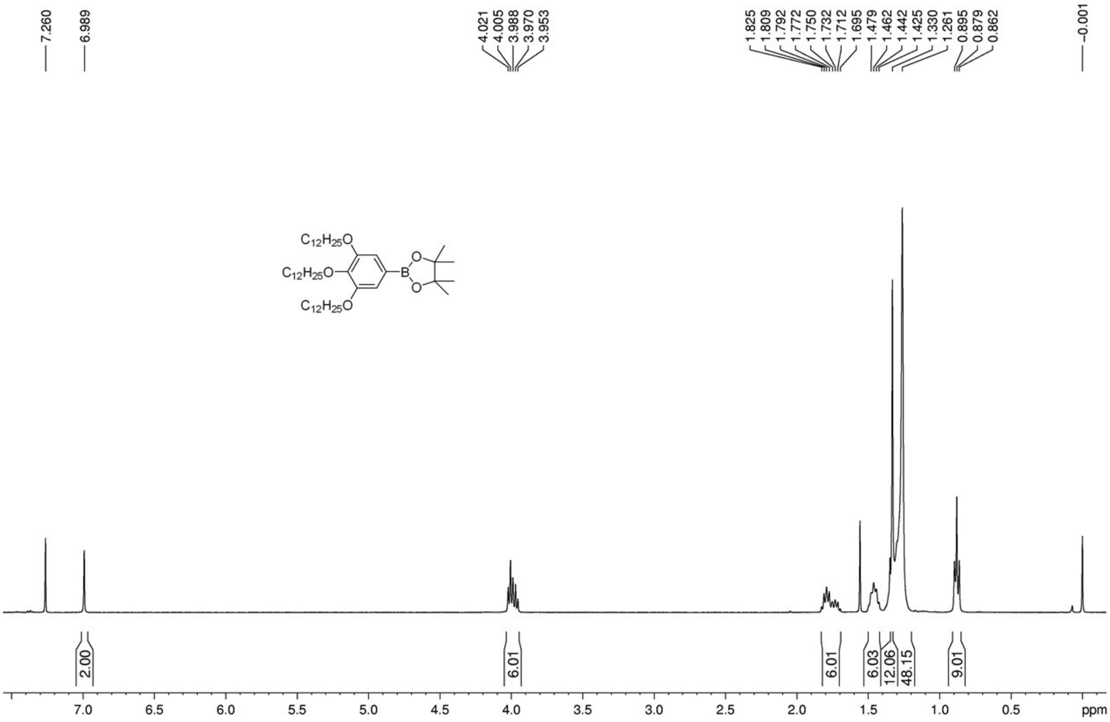


Fig. S2 ^{1}H NMR spectrum of compound **3-12** (400 MHz, in $CDCl_3$).

.

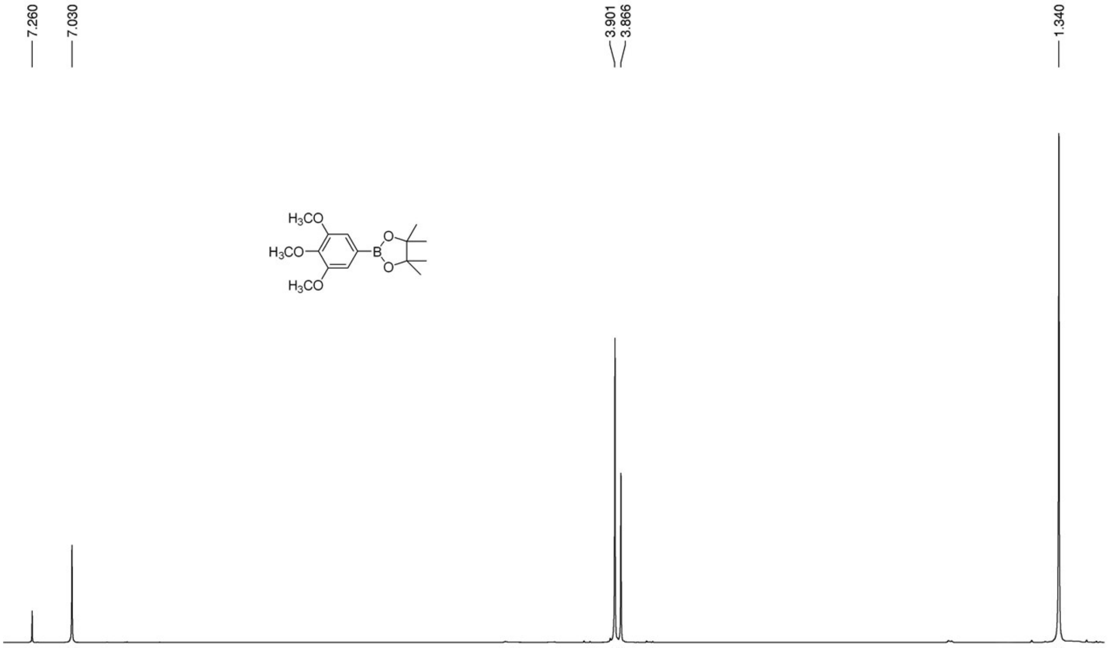


Fig. S3 ^{1}H NMR spectrum of compound **3-1** (400 MHz, in $CDCl_3$).

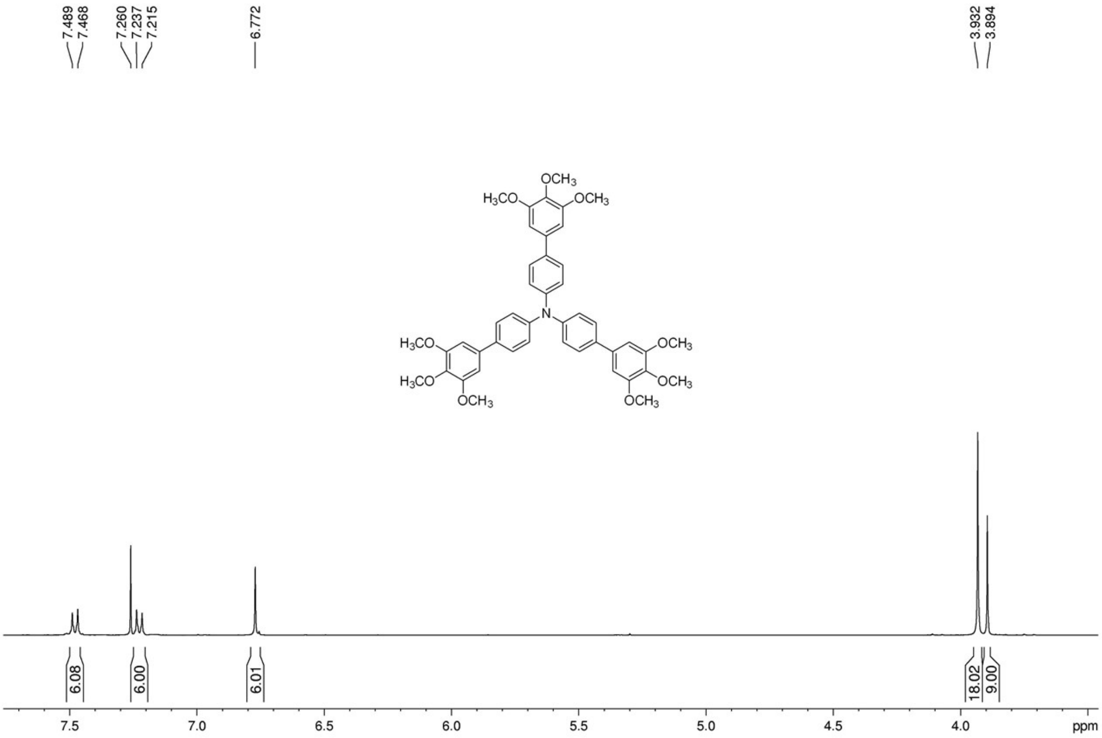


Fig. S4 ^{1}H NMR spectrum of compound **TPAP1** (400 MHz, in CDCl$_3$).

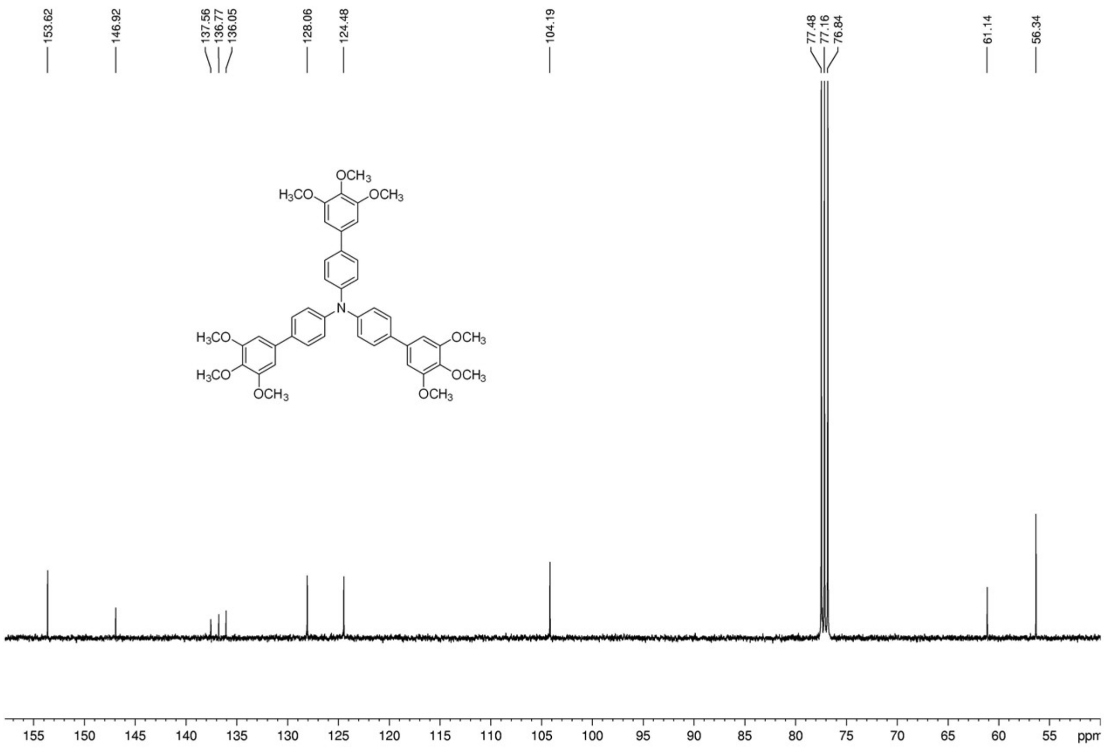


Fig. S5 ^{13}C NMR spectrum of compound **TPAP1** (100 MHz, in CDCl$_3$).

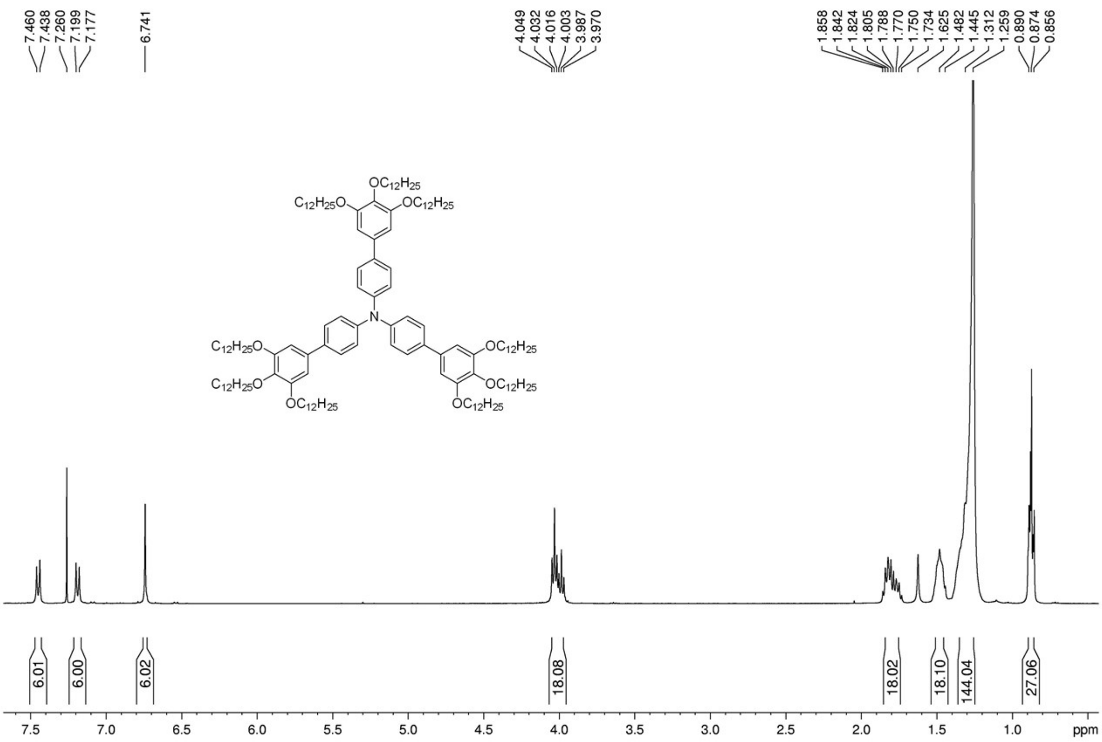


Fig. S6 ^{1}H NMR spectrum of compound **TPAP12** (400 MHz, in $CDCl_3$).

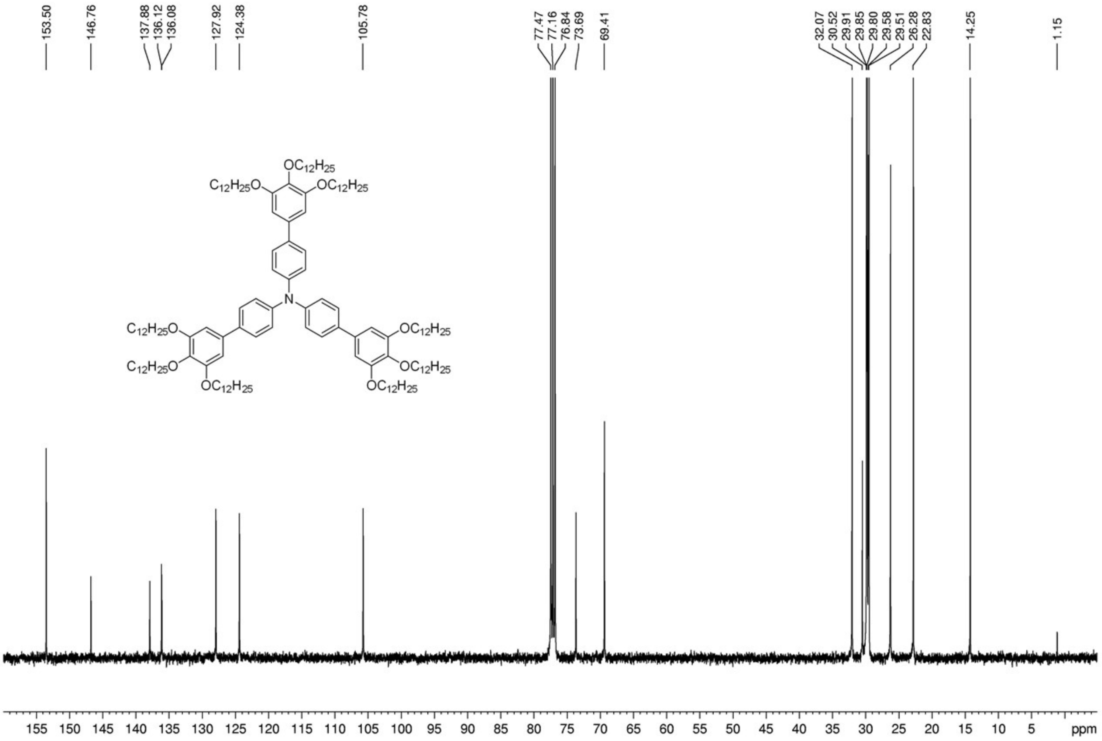


Fig. S7 ^{13}C NMR spectrum of compound **TPAP12** (100 MHz, in $CDCl_3$).

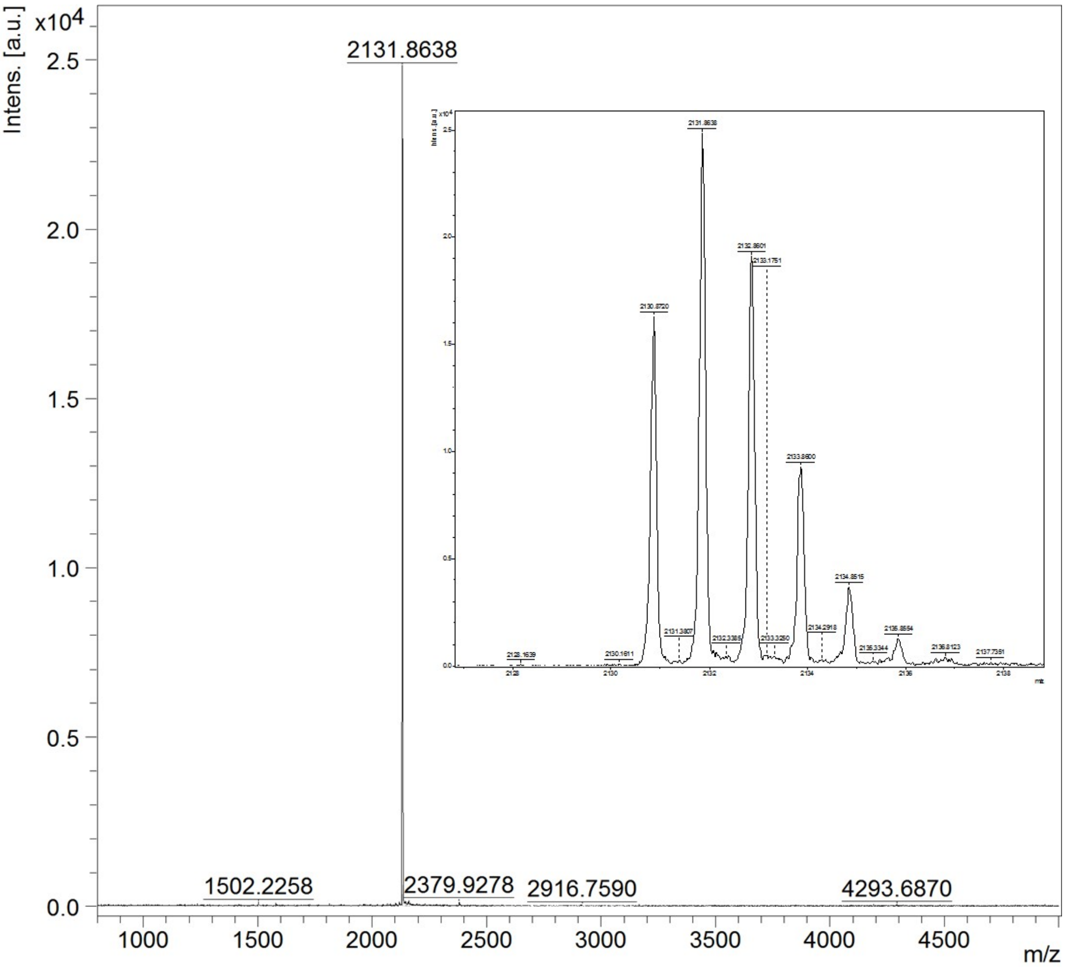


Fig. S8 MALDI-TOF-MS spectra of compound **TPAP12**. (MALDI-TOF: *m*/*z* calculated for $C_{144}H_{243}NO_9$, $[M]^+$: 2131.8616, found 2131.8638).

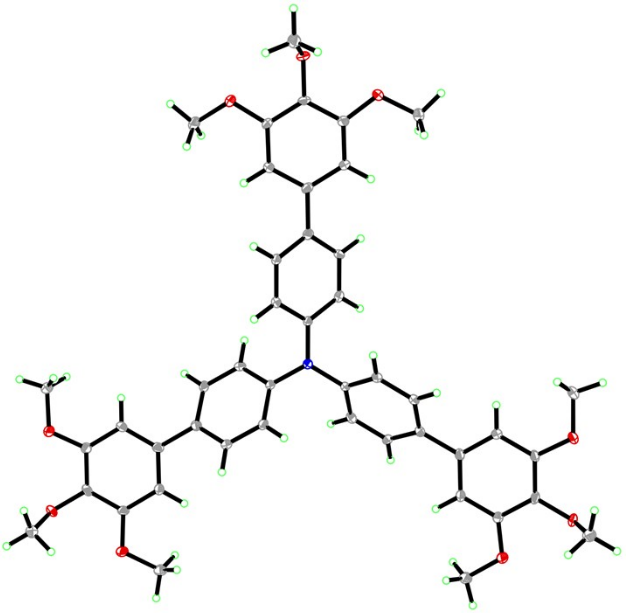


Fig. S9 The single crystal X-ray structure of **TPAP1**.

3. Additional POM texture

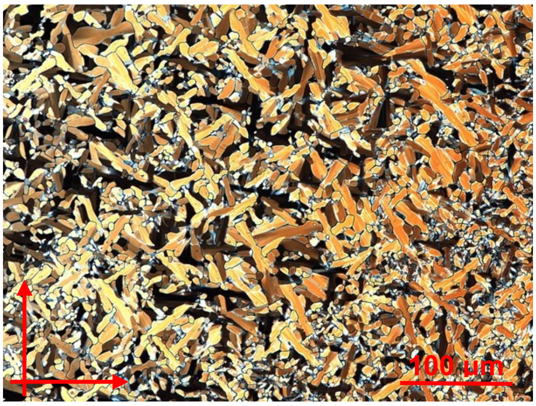


Fig. S10 The texture of the $\mathrm{Col_h}$ phase of **TPAP12** observed by POM at $T = 55$ °C on heating process.

4. Additional X-ray data

4.1 Experimental techniques

High-resolution small-angle powder diffraction experiments were recorded at the 1W2A SAXS beamline at Beijing Accelerator Laboratory [S1]. Samples were held in evacuated 1 mm capillaries. A modified Linkam hot stage with a thermal stability within 0.2 ºC was used, with a hole for the capillary drilled through the silver heating block and mica windows attached to it on each side. A MarCCD 165 detector was used. q calibration and linearization were verified using several orders of layer reflections from silver behemate.

For 2D structures $I(hk)$ and Eqn. (1) was used:

$$E(xy) = \Sigma_{hk}\ \mathrm{sqrt}[I(hk)]\ \exp[i2\pi(hx+ky) + \phi_{hk}] \qquad \text{(Eqn. 1)}$$

here m being the multiplicity, F the structure factor, which is proportional to the intensity and ϕ the phase of the reflex.

4.2 Molecular dynamics simulation

Annealing dynamics runs were carried out using the Universal Force Field (Material Studio, Accelrys). The structures in Fig. 6 were obtained with 2 molecules in a 60 degree rhombic prism box with the side equal to the unit cell length and a height of 0.9 nm, with 3D periodic boundary conditions. 30 temperature cycles of NVT dynamics were run between 300 and 700 K, with a total annealing time of 30 ps.

4.3 Additional X-ray data

Table S1 Experimental and calculated *d*-spacing of the observed SAXS reflection of the hexagonal columnar phase in **TPAP12** at cooling 25 ºC. All intensity values are Lorentz and multiplicity corrected.

(*hk*)	d_{obs}-spacing(Å)	d_{cal}-spacing(Å)	*intensity*	*phase*
(10)	31.5	31.5	100	0
(11)	18.2	18.2	0.05	0
(20)	15.8	15.8	0.13	π
		a_{hex} = 36.4 Å		

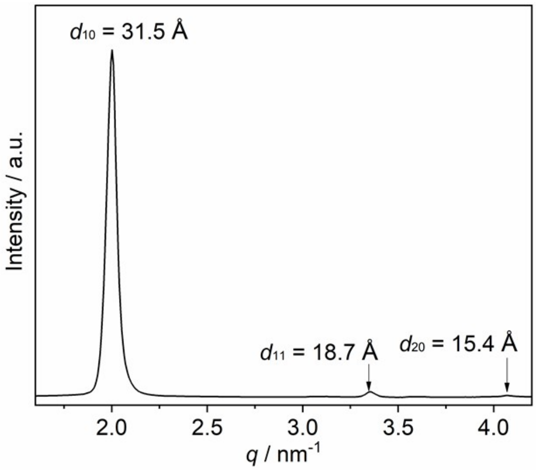


Fig. S11 X-ray diffraction pattern of the Col_h phase of compound **TPAP12** at T = 55 °C on heating process.

Table S2 Experimental and calculated *d*-spacing of the observed SAXS reflection of the hexagonal columnar phase in **TPAP12** at T = 55 ºC on heating process. All intensity values are Lorentz and multiplicity corrected.

(*hk*)	d_{obs}-spacing(Å)	d_{cal}-spacing(Å)	*intensity*	*phase*
(10)	31.4	31.5	100	0
(11)	18.7	18.2	1.06	0
(20)	15.4	15.8	0.19	π
		a_{hex} = 36.4 Å		

4. Additional molecular arrangement, CV, UV and PL spectra data

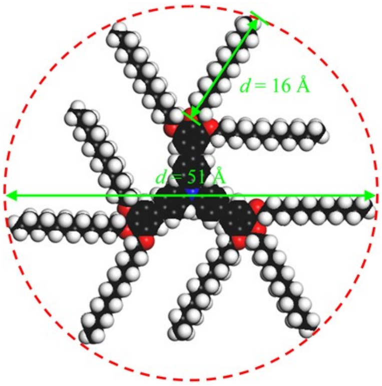


Fig. S12 CPK model of **TPAP12** calculated using Materials Studio software.

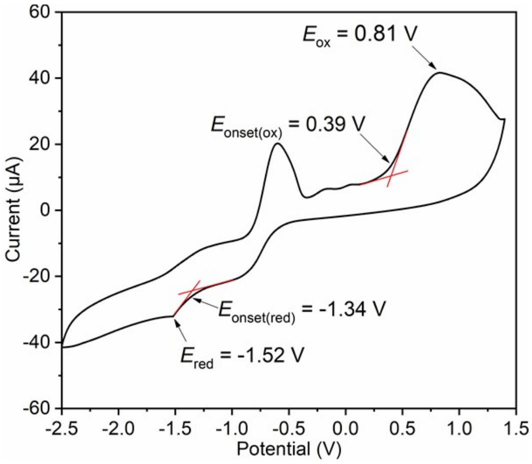


Fig. S13 Cyclic voltammogram of **TPAP12** film on glassy carbon electrode in 0.1 mol/L Bu_4NPF_6 in acetonitrile solution with a scan rate of 100 mVs^{-1}. Reference electrode: Ag/AgCl.

Table S3 Electrochemical properties of **TPAP12** in CH_3CN solution.

Comp.	E_{ox} (V)	E_{red} (V)	$E_{HOMO}{}^{a}$ (V)	$E_{LUMO}{}^{b}$ (V)	$E_g{}^{c}$ (V)
TPAP12	0.81	-1.52	-5.10	-3.37	1.73

[a] $E_{HOMO} = -E_{onset(ox)}$ - 4.71 eV; [b] $E_{LUMO} = -E_{onset(red)}$ - 4.71 eV; [c] $E_g = E_{LUMO} - E_{HOMO}$.

Table S4 Gelation properties of compound **TPAP12** in different solvents at room temperature.[a]

Solvent	**TPAP12**	Solvent	**TPAP12**
Chloroform	S	Cyclohexane	S
Ethyl acetate	S	Hexane	S
THF	S	*n*-Butanol	G
Methanol	IS	Toluene	S
Acetone	P	Dichloromethane	S
DMF	IS	Ethanol	IS
1,4-Dioxane	G	DMSO	IS
PE	S	Acetonitrile	IS

[a] S = solution, P = precipitation, G = gelation, PG = partial gelation, IS = insoluble; gelator concentration is 5.0 mg mL^{-1}; gels formed at room temperature.

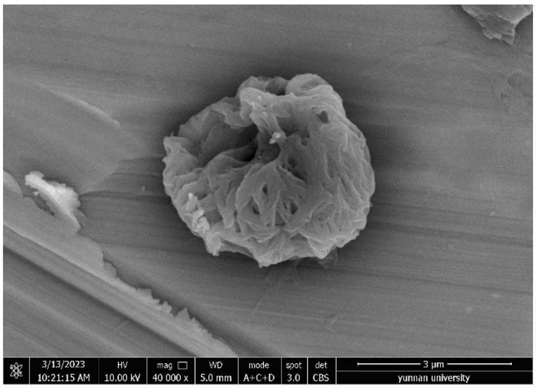


Fig. S14 SEM image of xerogel formed by **TPAP12** in *n*-butanol (scale bar is 3 μm).

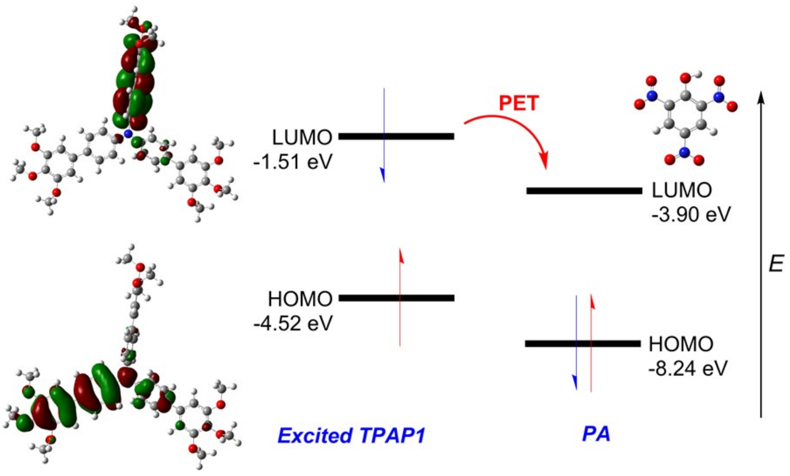


Fig. S15. Schematic illustration for photo-induced electron transfer process between **TPAP1** and PA.

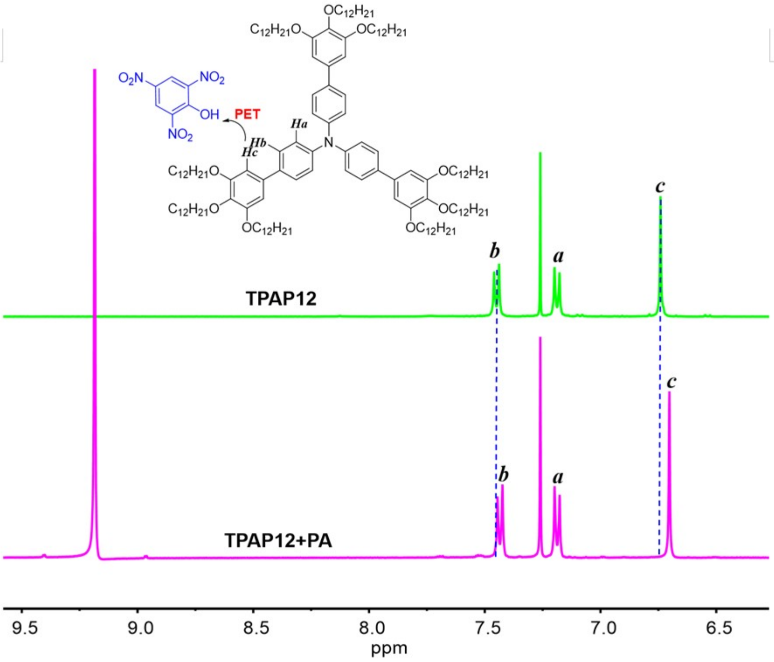


Fig. S16 ^{1}H NMR spectra of **TPAP12** with addition of 10 equiv. **PA** in CDCl$_3$.

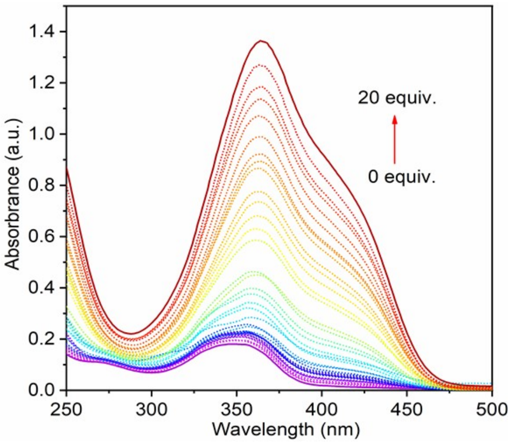
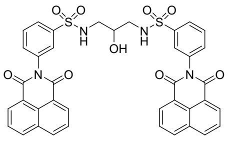
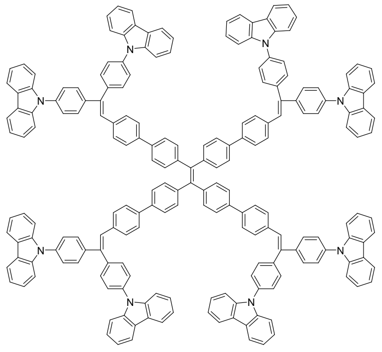
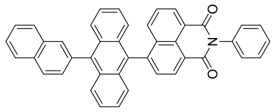
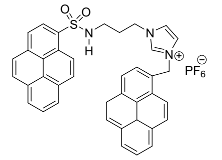
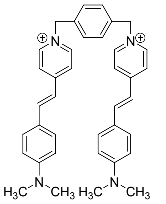
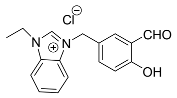
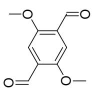
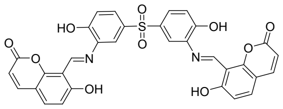
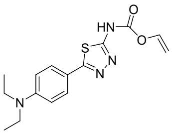
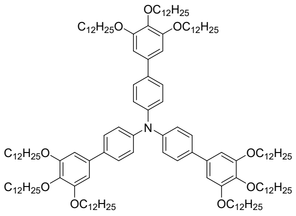
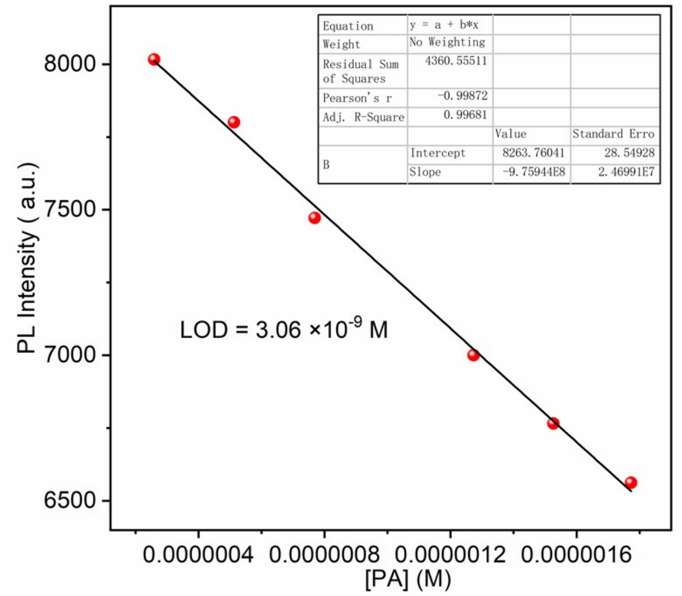


Fig. S17 UV-Vis absorption spectra of **TPAT12** (5.0 × 10^{-6} M) upon addition of PA from 0 to 20 equiv. in a mixed aqueous solution (H$_2$O : THF = 1 : 1, v/v).

Table S5 The comparison of probe **TPAT12** with some reported PA fluorescent probes.

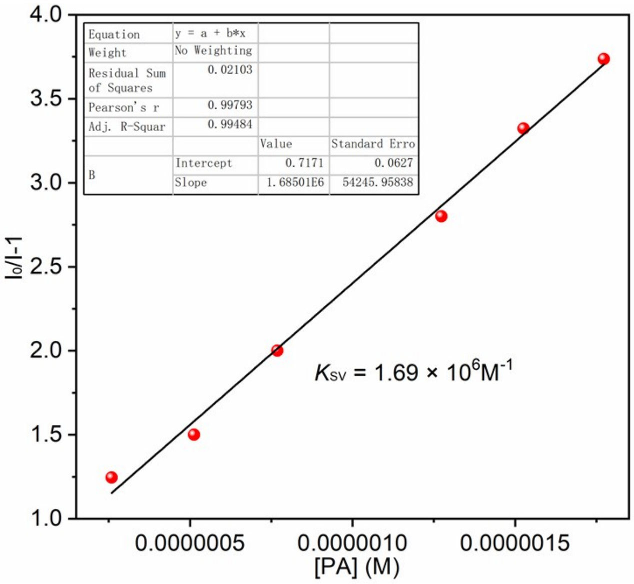
Entry	Structure	LOD(M)	*K*sv(M^{-1})	Time(s)	Solvent	Ref
1		3×10^{-9}	2.20×0^{7}	12h	PBS buffer (pH 7.4):DMSO (20:1)	S2
2		3.8×10^{-9}	1.63×10^{5}	180s	H_2O/THF (v/v, 8/2)	S3
3		4.7×10^{-7}	7.0×10^{4}		(water/THF=9/1	S4
4		1×10^{-8}	1.01×10^{6}		pH 7.4 PBS–DMSO (99.5:0.5 v/v))	S5
5		3×10^{-9}	-	-	HEPES buffer pH 7.2, 1% DMSO	S6
6		2.82×10^{-7}	2.32×10^{6}	-	aqueous solution	S7
7		1.2×10^{-7}	-	-	THF-H_2O	S8
8		2.15×10^{-7}	2.86×10^{4}		DMF/H_2O	S9
9		3.8×10^{-8}	4.575×10^{4}	-	DMSO	S10

10		3.06×10^{-9}	1.69×10^{6}	5	THF:H_2O=1:1	This work



Equation	y = a + b*x		
Weight	No Weighting		
Residual Sum of Squares	4360.55511		
Pearson's r	-0.99872		
Adj. R-Square	0.99681		
		Value	Standard Erro
B	Intercept	8263.76041	28.54928
	Slope	-9.75944E8	2.46991E7

Fig. S18 Fitted plot of lower limit of detection of compound **TPAT12** against PA.



Equation	y = a + b*x		
Weight	No Weighting		
Residual Sum of Squares	0.02103		
Pearson's r	0.99793		
Adj. R-Squar	0.99484		
		Value	Standard Erro
B	Intercept	0.7171	0.0627
	Slope	1.68501E6	54245.95838

Fig. S19 Stern-Volmer plot of compound **TPAT12** against PA.

Table S6 Photovoltaic parameters of Si/PEDOT:PSS HSCs with different concentration of **TPAP12**.

TPAP12 (vol %)	J_{SC} [mA cm^{-2}]	V_{OC}(V)	FF(%)	PCE(%)
0	32.89	0.615	51.66	10.46
0.2	33.16	0.632	57.38	12.03
0.4	32.76	0.637	59.75	12.5
0.6	32.8	0.638	59.35	12.42
0.8	32.12	0.633	47.22	9.61

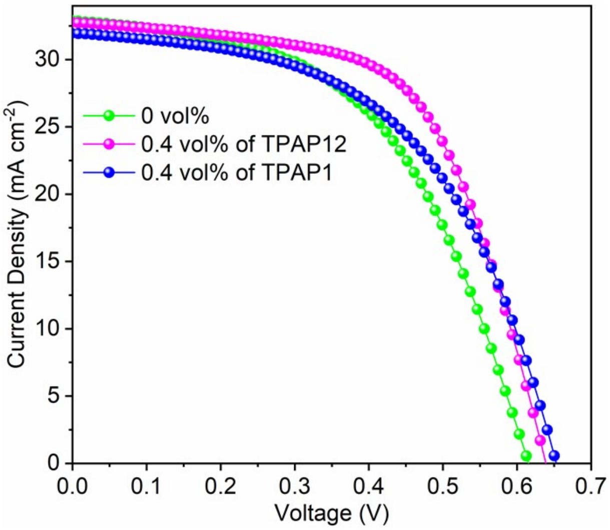


Fig. S20 *J–V* characteristics of organic-Si solar cells with the same doping concentration of **TPAP12** and **TPAP1** under AM 1.5G illumination.

Table S7 Photovoltaic parameters of Si/PEDOT:PSS HSCs with the same doping concentration of **TPAP12** and **TPAP1**.

Doping concentration	J_{sc} (mA/cm^{-2})	V_{oc} (V)	*FF* (%)	PCE (%)
0 vol%	32.89	0.615	51.66	10.46
0.4 vol% of **TPAP12**	32.76	0.637	59.75	12.50
0.4 vol% of **TPAP1**	31.94	0.653	52.69	10.99

5. References

S1 Z. H. Li, Z. H. Wu, G. Mo, X. Q. Xing and P. Liu, *Instrum. Sci. Technol.*, 2014, **42**, 128–141.

S2 A. Kumar and P. S. Chae, *Sensor Actuat. B*, 2007, **240**, 1–9.

S3 H. M. Hao, C. Xu, H. Y. Luo, J. L. Yang, C. Liu, B. j. Xu, G. Shi, X. B. Xing and Z. G. Chi, *Mater. Chem. Front.*, 2021, **5**, 492–499.

S4 H. W. Ma, C. Y. He, X. L. Li, O. Ablikim, S. Zhang and M. Zhang, *Sensor Actuat. B*, 2016, **230**, 746–752.

S5 A. Kumar, A. Pandith and H. S. Kim, *Sensor Actuat. B*, 2016, **231**, 293–301.

S6 S. Dhiman, G. Kumar, V. Luxami, P. Singh and S. Kumar, *New J. Chem.*, 2020, **44**, 10870–10877.

S7 J. Harathi and K. Thenmozhi, *Chemosphere*, 2022, **286**, 131825.

S8 H. Liu, Y. Y. Fu, W. Xu, Q. G. He, H. M. Cao , G. H. Liu and J. G. Cheng, *Sci. China Chem.*, 2018, **61**, 857–862.

S9 B. Wang, X. M. Ma, X. X. Zuo and J. Ma, *Phosphorus Sulfur Silicon Relat. Elem.*, 2021, **196**, 616–621.

S10 X. J. Li, Y. X. Hu,· W. J. Huang, W. R. Li, G. Gao, C. W. Lü and Y. An, *J. Fluoresc.*, 2022, **32**, 1601–1610.