

Electronic Supplementary Information

Optoelectronic properties of ambipolar transport triphenylene- perylene donor-acceptor discotic liquid crystals

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1. Materials, measurement, characterization syntheses and molecular schemes

(1) Materials

All chemicals were purchased from Aldrich, and all solvents from Aladdin. All chemicals and solvents were used without further purification unless stated otherwise.

(2) Measurement and characterization

1) Measurement of chemical structure

¹H-NMR spectra were recorded in CDCl₃ on Bruker NMR spectrometers (DMX 300 and 400 MHz), chemical shifts were given in parts per million (δ) and were referenced from tetramethylsilane (TMS). Multiplicities of the peaks were given as s=singlet, d=doublet, t=triplet and m=multiplet. ¹³C NMR spectra were recorded on a Bruker Ascend™ spectrometer at room temperature (600 MHz_z) using CDCl₃ as the solvent and tetramethylsilane (TMS) as the internal standard. Fourier transform infrared spectroscopy (FT-IR) was carried out on a Shimadzu FTIR-8400 spectrometer using KBr pellets. Mass spectra were performed on a MALDI-TOF mass spectrometer (5800 Proteomic analyzer, Applied Biosystems). Elemental analysis was performed with an Elementar Vireo EL instrument.

2) Measurement of Mesomorphic property

The thermal gravimetric analysis (TGA) was measured on a NETZSCH TG 209F3 instrument with heating rate of 10 °C min⁻¹ in nitrogen atmosphere. Differential scanning calorimetry (DSC) was performed on a Netzsch DSC 200. Sealed about 5 mg sample in aluminum crucibles and scanned by 5°C min⁻¹ in nitrogen atmosphere. Polarizing optical microscopy (POM) was carried out on a Leica DM4500P microscope equipped with a Linkam TMS94 hot stage. One-dimensional wide-angle X-ray diffraction (1D WAXD) test experiments were conducted on a Buler D8 Advance diffractometer equipped with a temperature controller by 5 °C min⁻¹. The powder samples were placed on aluminium foil and acquired data were processed on relevant

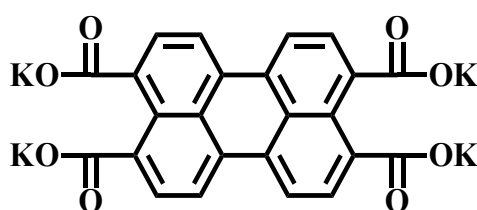
software. Small angle X-ray scattering (SAXS) experiments were carried on with a high flux SAXS instrument (SAXSess, Anton Paar) equipped with Kratky block-collimation system. Two-dimensional wide-angle X-ray diffraction (2D WAXD) experiments were performed on a Bruker Axs D8 Discover diffractometer fitted with a 40KV FL tube as X-ray source (Cu K α) and a VANTEC 500 detector.

3) Measurement of Steady-state spectroscopy

Photophysical properties of the series of 5D10An compounds were investigated in dilute CH₂Cl₂(dichloromethane) solution and thin-film state. For photophysical measurements, thin films of 5D10A4, 5D10A5, 5D10A6, 5D10A7 and 5D10A8 were prepared onto pre-cleaned quartz glass substrates by spin coating from chloroform solutions and annealing of 5D10A4, 5D10A5, 5D10A6, 5D10A7 and 5D10A8 was performed by annealing the samples at 5°C below clearing point for a whole night. For the concentration dependence of the absorption, HAT5, 5D10A4, 5D10A5, 5D10A6, 5D10A7, 5D10A8 and PEAC4, PEAC5, PEAC6, PEAC7, PEAC8 diluted solutions were prepared in CH₂Cl₂ at various concentrations ranging from 1.0 \times 10⁻⁶ to 1.6 \times 10⁻⁵ M and held in a quartz cuvette at ambient temperature, and for the concentration dependence of steady-state fluorescence spectra, were prepared in dichloromethane at various concentrations ranging from 1.0 \times 10⁻⁴ to 1.0 \times 10⁻³ M and held in a quartz cuvette at ambient temperature. UV/vis absorption spectra of the solutions and thin films were recorded on an Agilent Cary 300 UV/vis Spectrophotometer. Steady state fluorescence spectra of the solutions and thin films were obtained using a Hitachi F-4700 Fluorescence Spectrophotometer.

(3) Syntheses and molecular schemes

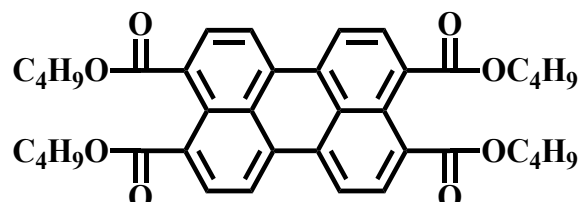
Potassium salt of 3, 4, 9, 10-perylene tetracarboxylic acid (1)



A mixture of 3,4,9,10-perylene tetracarboxylic acid dianhydride (7.84 g, 20 mmol),

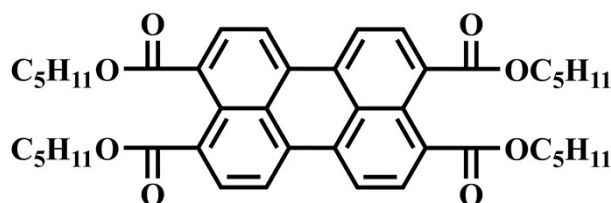
potassium hydroxide (6 g, 106 mmol) in 100 mL aqueous solution was stirred at reflux temperature for 4 h. The cooled aqueous solution was gradually added to methanol (500 mL). The precipitate was collected by filtration and dried in vacuum. A yellow solid was obtained (11.5 g, 99%).

3, 4, 9, 10-tetra -(4-alkoxycarbonyl)perylene (2-1)

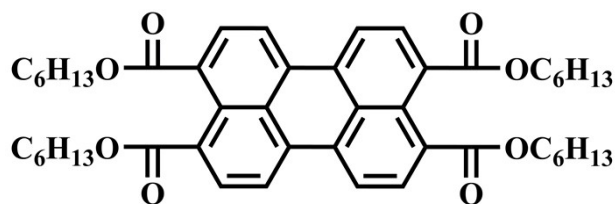


The mixture of **1** (5 g, 8.61 mmol), 1-bromobutane (9.44 g, 68.88 mmol), potassium carbonate (10 g, 72.35 mmol), ALIQUAT 336 (1.05 g, 2.59 mmol) and catalyzed KI (0.29 g, 1.72 mmol) was vigorously stirred in deionized water (70 mL) and heated at reflux for 24 h. The mixture was cooled to room temperature and extracted with CHCl_2 . Washed with water, the CH_2Cl_2 solution was dried with Na_2SO_4 overnight. Removing the solvent, a golden yellow solid was recrystallized from ethanol (5 g, 89%). ^1H NMR δ_{H} (ppm) (300 MHz, CDCl_3): 8.37-8.34 (d, 4H), 8.09-8.07 (d, 4H), 4.35-4.31 (t, 8H), 1.77-1.75 (m, 8H), 1.56-1.44 (m, 8H), 1.01-0.96 (m, 12H). According to the same method, other 3,4,9,10-tetra-(n-alkoxycarbonyl) perylene derivatives were successfully synthesized.

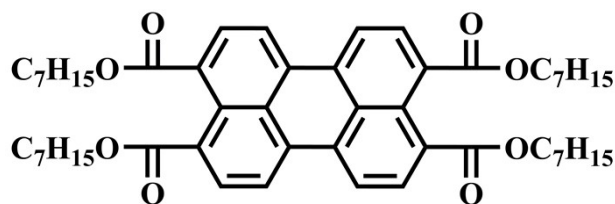
3, 4, 9, 10-tetra -(5-alkoxycarbonyl)perylene (2-2): yield=90%, ^1H NMR δ_{H} (ppm) (300 MHz, CDCl_3): 8.34-8.31 (d, 4H), 8.07-8.05 (d, 4H), 4.34-4.30 (t, 8H), 1.79-1.77 (m, 8H), 1.56-1.41 (m, 16H), 0.93 (m, 12H).



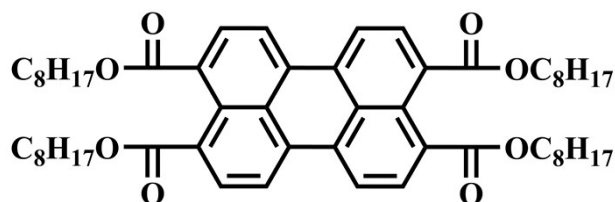
3, 4, 9, 10-tetra -(6-alkoxycarbonyl)perylene (2-3): yield=91%, ^1H NMR δ_{H} (ppm) (300 MHz, CDCl_3): 8.37-8.34 (d, 4H), 8.09-8.06 (d, 4H), 4.32-4.30 (t, 8H), 1.78-1.76 (m, 8H), 1.56-1.34 (m, 24H), 0.90 (m, 12H).



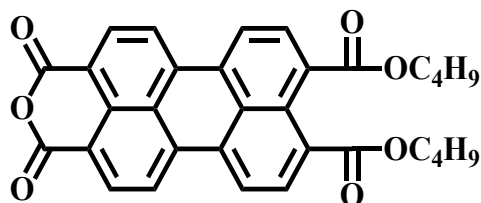
3, 4, 9, 10-tetra -(7-alkoxycarbonyl)perylene (2-4): yield=90%, $^1\text{H NMR } \delta_{\text{H}}$ (ppm) (300 MHz, CDCl_3): 8.36-8.33 (d, 4H), 8.08-8.06 (d, 4H), 4.34-4.29 (t, 8H), 1.80-1.76 (m, 8H), 1.58-1.31 (m, 32H), 0.89 (m, 12H).



3, 4, 9, 10-tetra -(8-alkoxycarbonyl)perylene (2-5): yield=89%, $^1\text{H NMR } \delta_{\text{H}}$ (ppm) (300 MHz, CDCl_3): 8.34-8.32 (d, 4H), 8.08-8.05 (d, 4H), 4.34-4.29 (t, 8H), 1.78-1.76 (m, 8H), 1.57-1.28 (m, 40H), 0.88 (m, 12H).



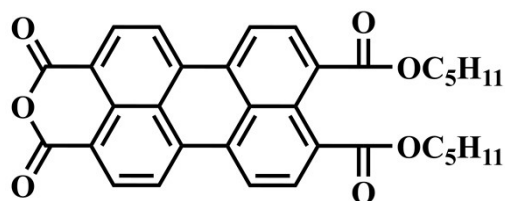
Perylene-3, 4-anhydride-9, 10-di-(butoxycarbonyl) (3-1)



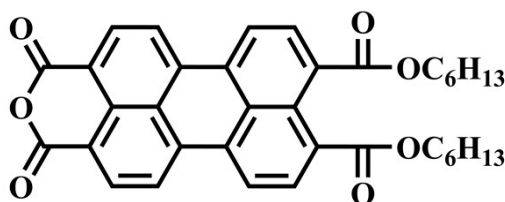
2-1 (2 g, 3.06 mmol) was added into toluene (0.8 mL) and *n*-dodecane (4 mL) before being heated to 95 °C. After the yellow powder **2-1** was all dissolved, *p*-toluenesulfonic acid monohydrate ($\text{TsOH}\cdot\text{H}_2\text{O}$) (0.58 g, 3.06 mmol) was added to the solution and the solution was stirred at 95 °C for 5 h. Then the dark red mixture was dissolved in hot CH_2Cl_2 (30 mL) and precipitated dropwise in ethanol (300 mL). The resulting residue was collected by filtration and purified by column chromatography (silica gel, chloroform/Methanol 100:1) to give a dark red solid (1.12 g, 70%). $^1\text{H NMR}$

δ_H (ppm) (300 MHz, $CDCl_3$): 8.65 (d, 2H), 8.53 (d, 4H), 8.15 (d, 2H), 4.36 (t, 4H), 1.78 (m, 4H), 1.35-1.26 (m, 4H), 1.00-0.88 (m, 6H). According to the same method, other PEA derivatives were successfully synthesized.

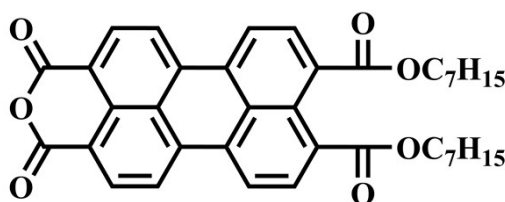
Perylene-3, 4-anhydride-9, 10-di-(pentyloxycarbonyl) (3-2): yield=73%, 1H NMR δ_H (ppm) (300 MHz, $CDCl_3$): 8.64 (d, 2H), 8.53 (d, 4H), 8.15 (d, 2H), 4.34 (t, 4H), 1.81 (m, 4H), 1.57-1.25 (m, 8H), 0.94 (m, 6H).



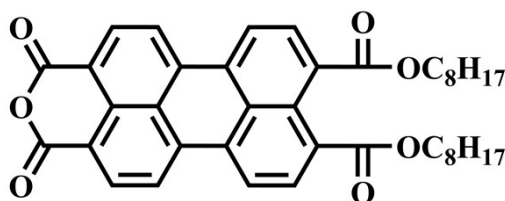
Perylene-3, 4-anhydride-9, 10-di-(hexyloxycarbonyl) (3-3): yield=72%, 1H NMR δ_H (ppm) (300 MHz, $CDCl_3$): 8.66 (d, 2H), 8.55 (d, 4H), 8.17 (d, 2H), 4.34 (t, 4H), 1.80 (m, 4H), 1.56-1.25 (m, 12H), 0.90 (m, 6H).



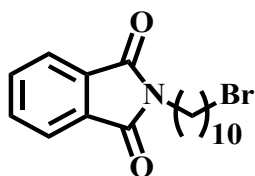
Perylene-3, 4-anhydride-9, 10-di-(heptoxycarbonyl) (3-4): yield=71%, 1H NMR δ_H (ppm) (300 MHz, $CDCl_3$): 8.65-8.62 (d, 2H), 8.52-8.48 (d, 4H), 8.14-8.12 (d, 2H), 4.37-4.32 (t, 4H), 2.02 (m, 4H), 1.56-1.30 (m, 16H), 0.78-0.75 (m, 6H).



Perylene-3, 4-anhydride-9, 10-di-(capryloxycarbonyl) (3-5): yield=73%, 1H NMR δ_H (ppm) (300 MHz, $CDCl_3$): 8.66 (d, 2H), 8.57 (d, 4H), 8.17 (d, 2H), 4.36-4.34 (t, 4H), 1.80 (m, 4H), 1.57-1.26 (m, 20H), 0.88 (m, 6H).

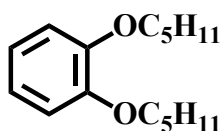


N-(10-bromodecyl) phthalimide (5)



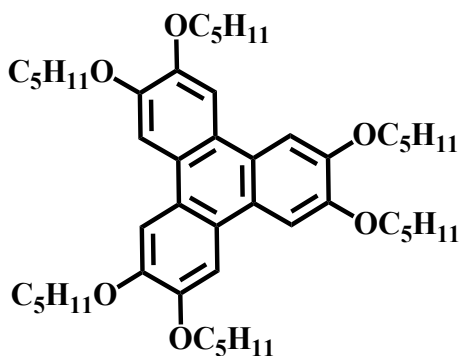
The mixture of potassium phthalimide (10 g, 53.99 mmol) and 1,10-dibromodecane (81 g, 220 mmol) was stirred in DMF (125 mL) and heated at 100 °C for 12 h. The distillation was set by condenser, and the excess 1,10-dibromodecane and DMF were distilled off under reduced pressure. The crude product was purified by column chromatography (silica gel, light petroleum/dichloromethane 4:1) and afforded a white solid (16.02 g, 86%). $^1\text{H NMR } \delta_{\text{H}}$ (ppm) (300MHz, CDCl_3): 7.84 (m, 2H), 7.71 (m, 2H), 3.67 (t, 2H), 3.40 (t, 2H), 1.83 (m, 2H), 1.66 (m, 2H), 1.28 (m, 12H).

1, 2-dipentyloxybenzene (6)



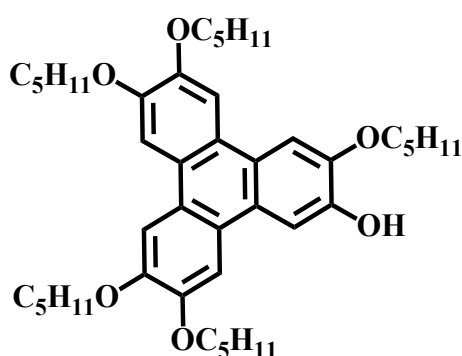
The mixture of catechol (66 g, 599.4 mmol), 1-bromopentane (271.61 g, 1800 mmol), potassium carbonate (248.52 g, 1800 mmol), potassium iodide (15 g, 90 mmol) was stirred in ethanol (300 mL) and heated at reflux for 24 h under nitrogen atmosphere. Organic layer was filtered and distilled off to give crude product. The crude product was purified by column chromatography (silica gel, light petroleum/dichloromethane 4:1) and afforded pale yellow oil (142.57 g, 95%). $^1\text{H NMR } \delta_{\text{H}}$ (ppm) (300 MHz, CDCl_3): 6.99-6.81(m, 4H), 4.11-3.99 (m, 4H), 1.89-1.80 (m, 4H), 1.71-1.35 (m, 8H), 1.28-0.72 (m, 6H); FT-IR (cm^{-1}): 1260 (C-O-C).

2, 3, 6, 7, 10, 11-hexapentyloxytriphenylene (7)



1,2-dipentyloxybenzene (20 g, 79.88 mmol) was added to a well-stirred suspension of Iron (III) trichloride (39 g, 239.64 mmol) in anhydrous dichloromethane (80 mL) under nitrogen atmosphere. The reaction was continuously accompanied with 3 mL H₂SO₄ for catalysis at room temperature for 3 h. The mixture was added to Methanol (500 mL) to quench the reaction. The mixture was filtered and purified by column chromatography (silica gel, light petroleum/dichloromethane 2:1) and afforded white solid (14.88 g, 75%). ¹H NMR δ_H (ppm) (300 MHz, CDCl₃): 7.85 (s, 6H), 4.25 (t, 12H), 1.99-1.92 (m, 12H), 1.67-1.42 (m, 24H), 0.99 (t, 18H); FT-IR (cm⁻¹): 1253 (C-O-C).

2-hydroxy-3, 6, 7, 10, 11-pentapentyloxytriphenylene (8)

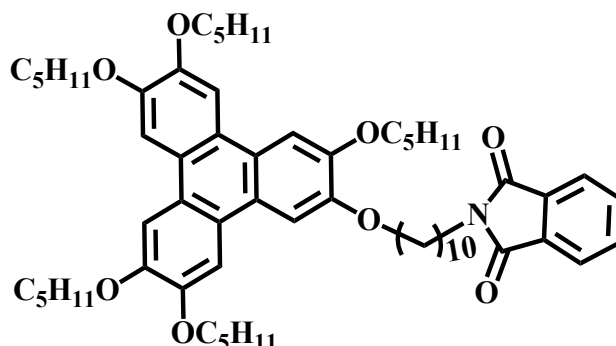


BBr₃ (28.6 g, 110 mmol) was added dropwise to a well-stirred suspension of catechol (11 g, 110 mmol) in anhydrous dichloromethane (70 mL) until the initially suspension became yellow solution at 0 °C. The reaction continued for 3 h at room temperature. The solvent was removed, and the product was distilled under vacuum to give B-Bromocatecholboronane (**4**) as white solid (15 g, 75%). The solid was then used to make a 0.5 M solution by mixing with CH₂Cl₂ (150 mL) and this was used for next ether cleavage reactions.

A solution of **7** (14.9 g, 20 mmol) was dissolved in anhydrous CH₂Cl₂ (140 mL) and cooled to 0 °C. B-Bromocatecholboronane (**4**) solution in CH₂Cl₂ (48 mL, 24 mmol) was added under nitrogen atmosphere and the mixture was stirred at room temperature for 24 h. The mixture was poured over ice-water and extracted with CH₂Cl₂, the combined extract was dried with anhydrous Na₂SO₄ overnight, solvent was removed under vacuum and the crude product was purified by column chromatography (silica gel, light petroleum/dichloromethane 4:3) and afforded white solid (5.4 g, 40%) which was recrystallized from ethanol. ¹H NMR δ_H (ppm) (300 MHz, CDCl₃): 7.96-7.77 (m,

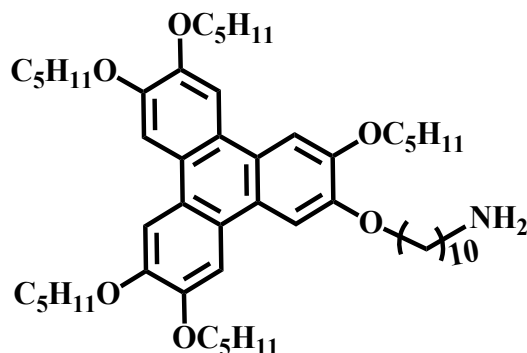
6H), 5.91 (s, 1H), 4.29-4.21 (m, 10H), 1.95 (m, 10H), 1.56-1.47 (m, 20H), 0.97 (t, 15H); FT-IR (cm⁻¹): 3456 (O-H), 1255 (C-O-C).

3, 6, 7, 10, 11-penta (pentylloxy-2-(10-phthalimidodecyloxy)-triphenylene (9)



A mixture of **8** (2.628 g, 3.9 mmol), **5** (2.86 g, 7.8 mmol), potassium carbonate (3.23 g, 23.4mmol) and KI (cata) in acetonitrile (30 mL) was heated under reflux for 12 h. After cooling to room temperature, organic layer was filtered, and the solvent was removed under reduced pressure. The resulting residue was purified by column chromatography (silica gel, light petroleum/dichloromethane 4:3) to give a pale yellow solid (3.40 g, 90.7%). ¹H NMR δ_H (ppm) (300 MHz, CDCl₃): 7.83 (m, 8H), 7.1-7.70 (m, 2H), 4.3 (m, 12H), 3.67 (t, 2H), 1.95-1.93 (m, 14H), 1.67-1.26 (m, 32H), 1-0.95 (m, 15H).

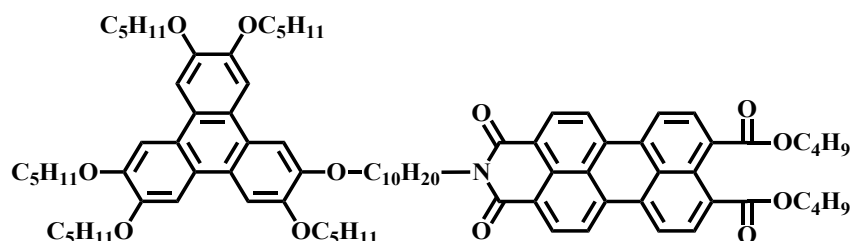
2-(10-aminodecyloxy)-3, 6, 7, 10, 11-penta (pentylloxy)triphenylene (10)



9 (2 g, 2.08 mmol) was dissolved in hot ethanol (30 mL) and the mixture was refluxed. Hydrazine hydrate (3 mL, 80%) was added to the mixture, and the reaction mixture was refluxed for 5 h. The reaction mixture was allowed to cool and subsequently washed with 5 wt% aqueous NaOH. The product was extracted with CH₂Cl₂, dried with anhydrous Na₂SO₄ and concentrated under reduced pressure. The crude product was purified by column chromatography (silica gel, dichloromethane/ Methanol 5:1) and afforded white solid (1.38g, 80%). ¹H NMR δ_H (ppm) (300 MHz, CDCl₃): 7.83 (s, 6H),

4.23-4.21 (t, 12H), 2.68-2.66 (t, 2H), 1.95-1.93 (m, 12H), 1.55-1.31 (m, 36H), 1.00-0.95 (t, 15H).

Dyad **5D10A4**

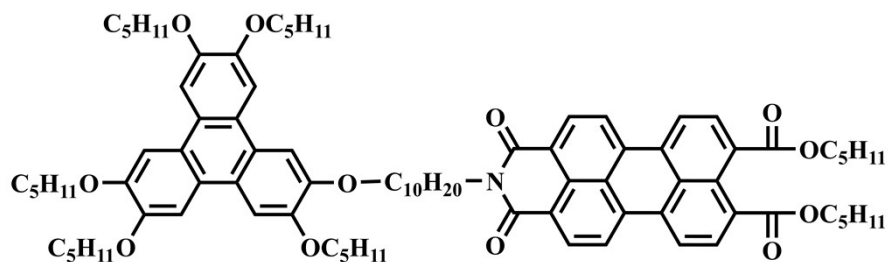


The mixture of **10** (0.4 g, 0.48 mmol), **3-1** (0.25 g, 0.48 mmol) and zinc acetate (0.09 g, 0.48 mmol) was stirred in N-Methyl pyrrolidone (NMP) (10 mL) and heated at 160 °C for 5 h under nitrogen atmosphere. The reaction mixture precipitated in ethanol (100 mL) and the precipitate was filtered off and purified by column chromatography (silica gel, dichloromethane/ethyl acetate 100:1) and recrystallized from dichloromethane and ethanol to give **5D10A4** (0.4 g, 62.2%) as a dark red solid.

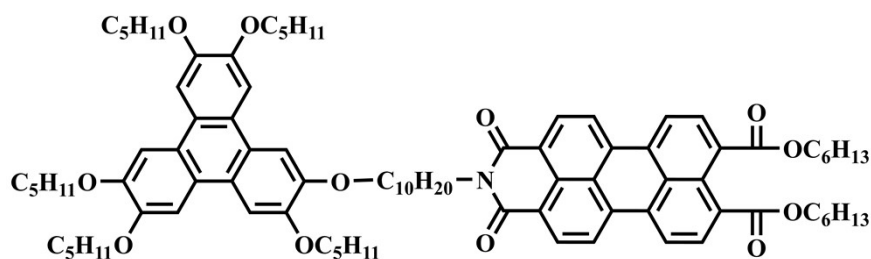
^1H NMR δ_{H} (ppm) (300 MHz, CDCl_3): 8.49 (d, 2H), 8.45 (m, 4H), 8.08 (d, 2H), 7.69 (s, 4H), 7.56 (s, 2H), 4.35 (t, 4H), 4.21 (m, 8H), 4.11 (m, 6H), 1.94-1.79 (m, 18H), 1.56-1.25 (m, 36H), 0.98 (m, 21H); ^{13}C NMR δ_{C} (ppm) (600 MHz, CDCl_3): 168.22, 163.36, 148.70, 135.05, 132.00, 131.58, 130.91, 130.12, 123.26, 122.25, 121.91, 121.48, 106.92, 69.57, 69.40, 69.35, 69.23, 65.45, 40.38, 30.58, 29.08, 29.82, 28.34, 28.30, 25.72, 22.53, 19.21, 14.07, 14.05, 13.75; FT-IR (cm^{-1}): 2952 (C-H), 2862 (C-H), 1720 (C=O), 1691 (C=O), 1259 (C=O); MALDI-TOF-MS: calcd. for $\text{C}_{85}\text{H}_{107}\text{NO}_{12}\text{Na}^+$ 1356.78, found 1356.55; Elemental Analysis: calcd. for $\text{C}_{85}\text{H}_{107}\text{NO}_{12}$ C, 76.49; H, 8.08; N, 1.05; found: C, 76.69; H, 8.23; N, 1.23.

According to the same method, other dyads derivatives were successfully synthesized.

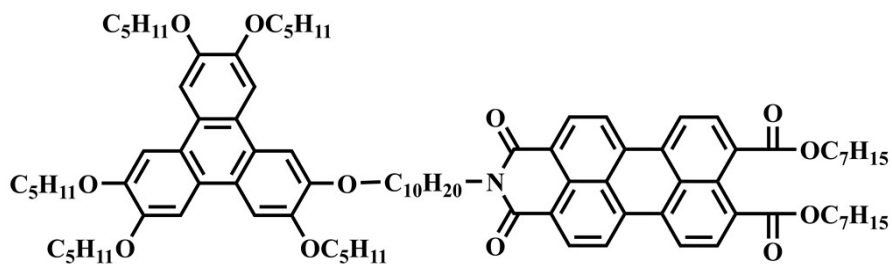
Dyad 5D10A5: (yield=66%) ^1H NMR δ_{H} (ppm) (300 MHz, CDCl_3): 8.48 (d, 2H), 8.32 (m, 4H), 8.06 (d, 2H), 7.68 (s, 4H), 7.56 (s, 2H), 4.33 (t, 4H), 4.20-4.11 (m, 14H), 1.93-1.81 (m, 18H), 1.55-1.43 (m, 40H), 0.96 (m, 21H); FT-IR (cm^{-1}): 2948 (C-H), 2852 (C-H), 1716 (C=O), 1693 (C=O), 1261 (C=O); MALDI-TOF-MS: calcd. for $\text{C}_{87}\text{H}_{111}\text{NO}_{12}\text{Na}^+$ 1384.81, found 1384.71; Elemental Analysis: calcd. for $\text{C}_{87}\text{H}_{111}\text{NO}_{12}$ C, 76.67; H, 8.21; N, 1.03; found: C, 76.69; H, 8.13; N, 1.23.



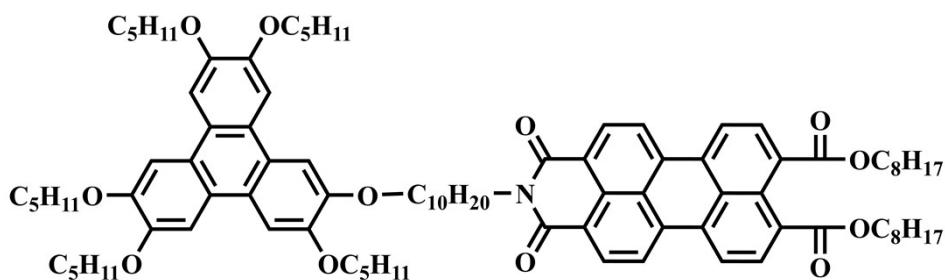
Dyad 5D10A6: (yield=73%) ^1H NMR δ_{H} (ppm) (300 MHz, CDCl_3): 8.46 (d, 2H), 8.30 (m, 4H), 8.05 (d, 2H), 7.68 (s, 4H), 7.55 (s, 2H), 4.33 (t, 4H), 4.20 (m, 8H), 4.11 (m, 6H), 1.94-1.80 (m, 18H), 1.56-1.45 (m, 44H), 0.97 (m, 21H); FT-IR (cm^{-1}): 2948 (C-H), 2860 (C-H), 1718 (C=O), 1691 (C=O), 1263 (C=O); MALDI-TOF-MS: calcd. for $\text{C}_{89}\text{H}_{115}\text{NO}_{12}\text{H}^+$ 1389.84, found 1389.74; Elemental Analysis: calcd. for $\text{C}_{89}\text{H}_{115}\text{NO}_{12}$ C, 76.86; H, 8.33; N, 1.01; found: C, 76.76; H, 8.43; N, 1.23.



Dyad 5D10A7: (yield=71%) ^1H NMR δ_{H} (ppm) (300 MHz, CDCl_3): 8.51-8.48 (d, 2H), 8.35-8.33 (m, 4H), 8.08-8.05 (d, 2H), 7.73-7.67 (m, 4H), 7.55 (s, 2H), 4.36-4.33 (t, 4H), 4.22-4.20 (m, 8H), 4.12-4.10 (m, 6H), 1.94-1.79 (m, 18H), 1.56-1.25 (m, 48H), 0.97-0.90 (m, 21H); FT-IR (cm^{-1}): 2948 (C-H), 2850 (C-H), 1718 (C=O), 1691 (C=O), 1261 (C=O); MALDI-TOF-MS: calcd. for $\text{C}_{91}\text{H}_{119}\text{NO}_{12} \text{Na}^+$ 1441.88, found 1440.75; Elemental Analysis: calcd. for $\text{C}_{91}\text{H}_{119}\text{NO}_{12}$ C, 77.03; H, 8.45; N, 0.99; found: C, 77.09; H, 8.35; N, 1.12.



Dyad 5D10A8: (yield=74%) ^1H NMR δ_{H} (ppm) (300 MHz, CDCl_3): 8.52-8.50 (d, 2H), 8.37-8.35 (m, 4H), 8.09-8.06 (d, 2H), 7.74-7.68 (m, 4H), 7.56 (s, 2H), 4.33-4.31 (t, 4H), 4.20 (m, 8H), 4.12-4.10 (m, 6H), 1.94-1.78 (m, 18H), 1.56-1.29 (m, 52H), 0.97-0.89 (m, 21H) ; FT-IR (cm^{-1}): 2948 (C-H), 2850 (C-H), 1716 (C=O), 1689 (C=O), 1261 (C=O); MALDI-TOF- MS: calcd. for $\text{C}_{93}\text{H}_{123}\text{NO}_{12}\text{Na}^+$ 1469.91, found 1468.77; Elemental Analysis: calcd. for $\text{C}_{93}\text{H}_{123}\text{NO}_{12}$ C, 77.20; H, 8.57; N, 0.97; found: C, 77.13; H, 8.72; N, 1.16.



2. ^1H NMR, FT-IR spectra and MALDI-TOF mass spectra

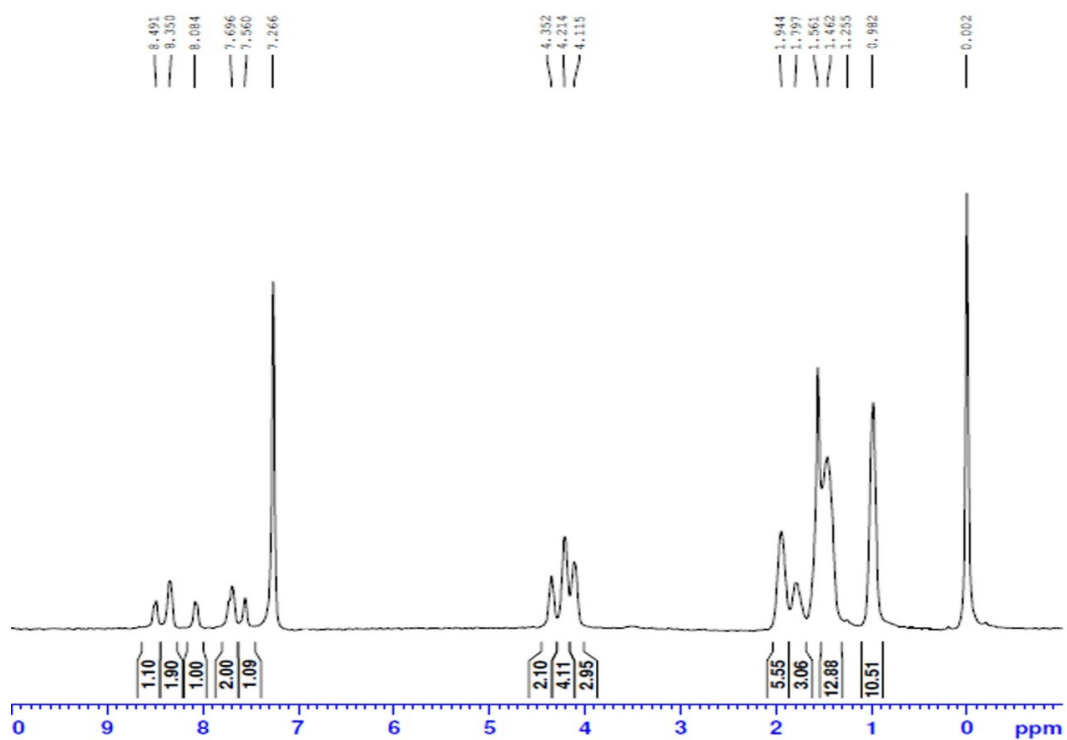


Fig.S1 ^1H NMR spectrum of compound **5D10A4**

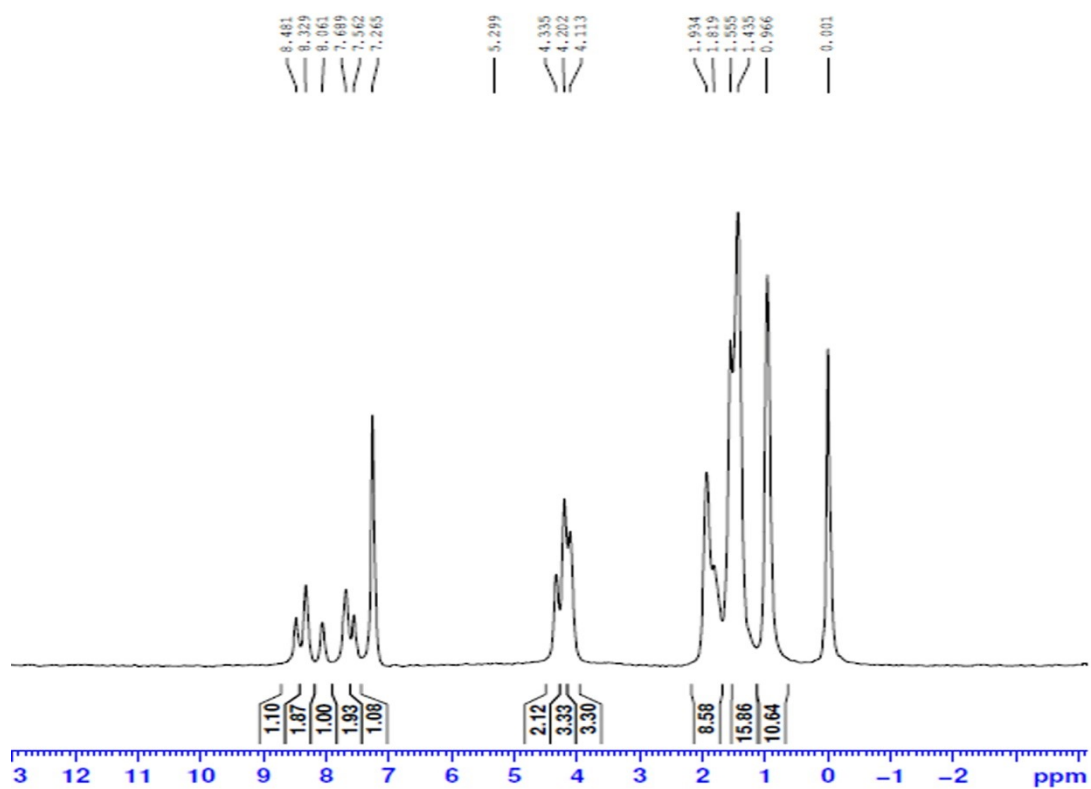


Fig.S2 ^1H NMR spectrum of compound **5D10A5**

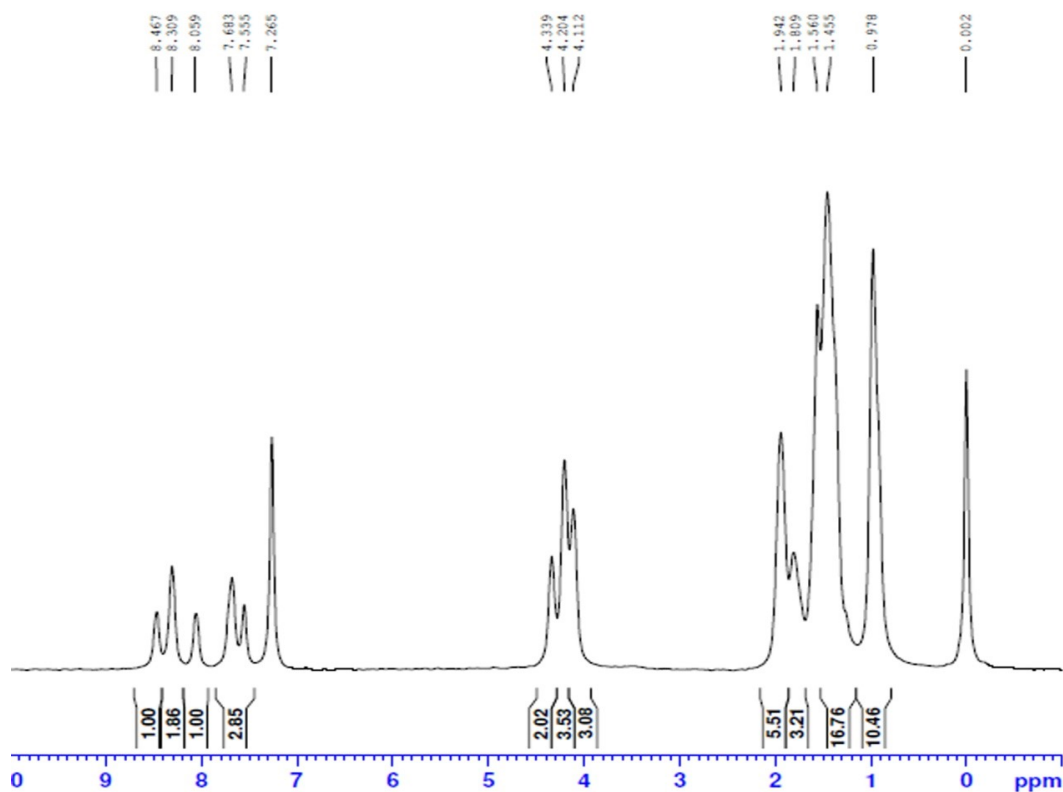


Fig.S3 ^1H NMR spectrum of compound **5D10A6**

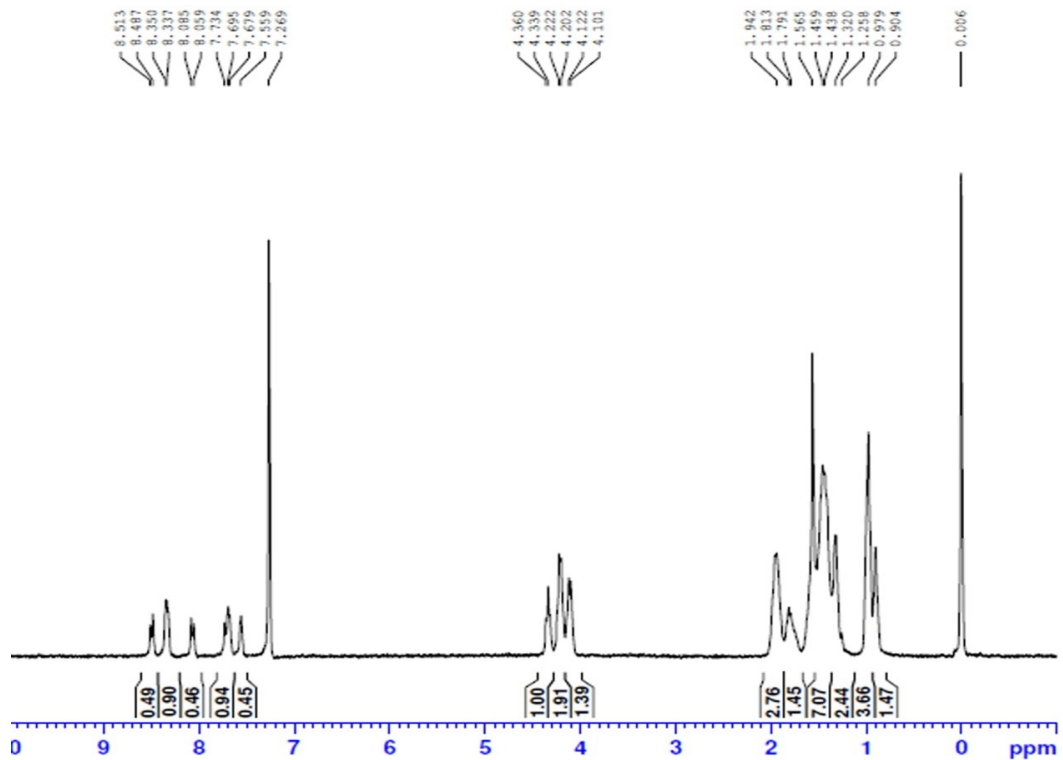


Fig.S4 ^1H NMR spectrum of compound **5D10A7**

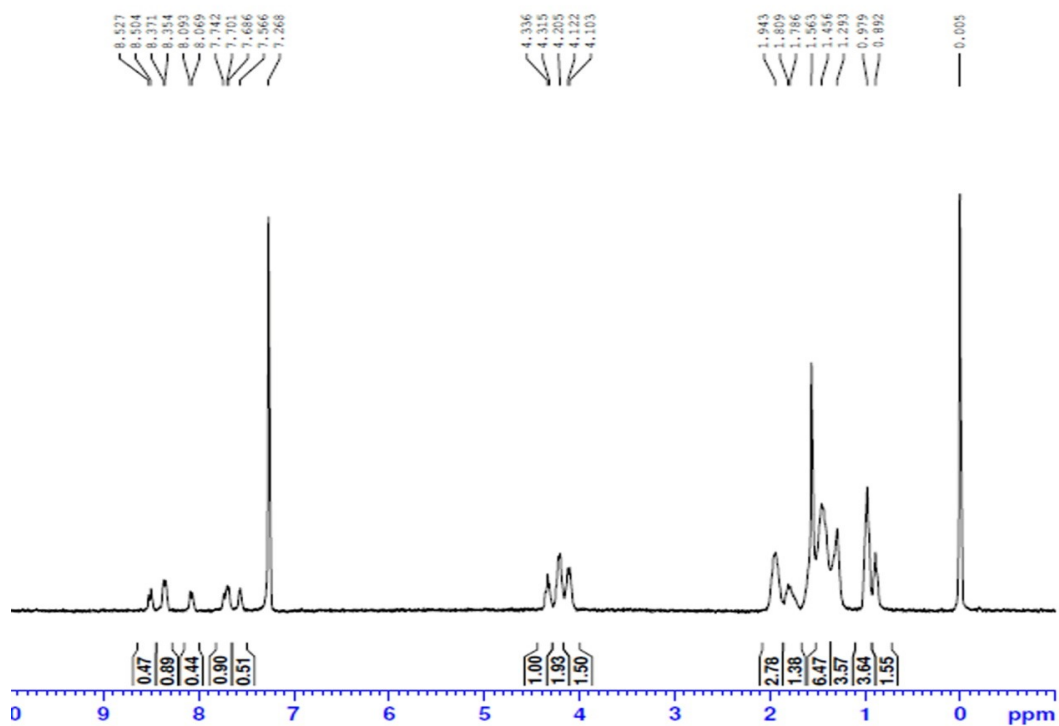


Fig.S5¹H NMR spectrum of compound **5D10A8**

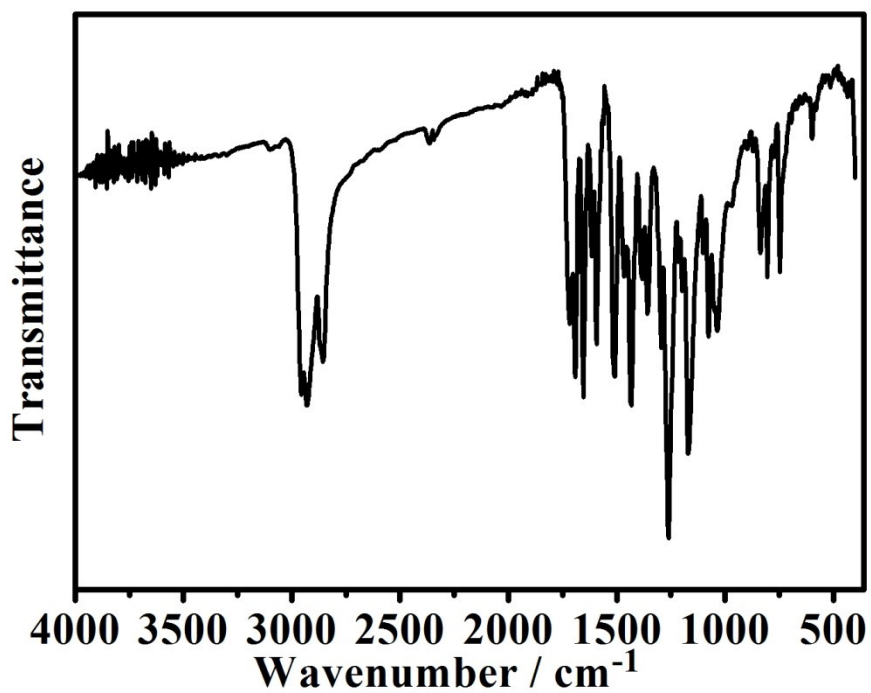


Fig.S6 FT-IR spectrum of compound **5D10A4**

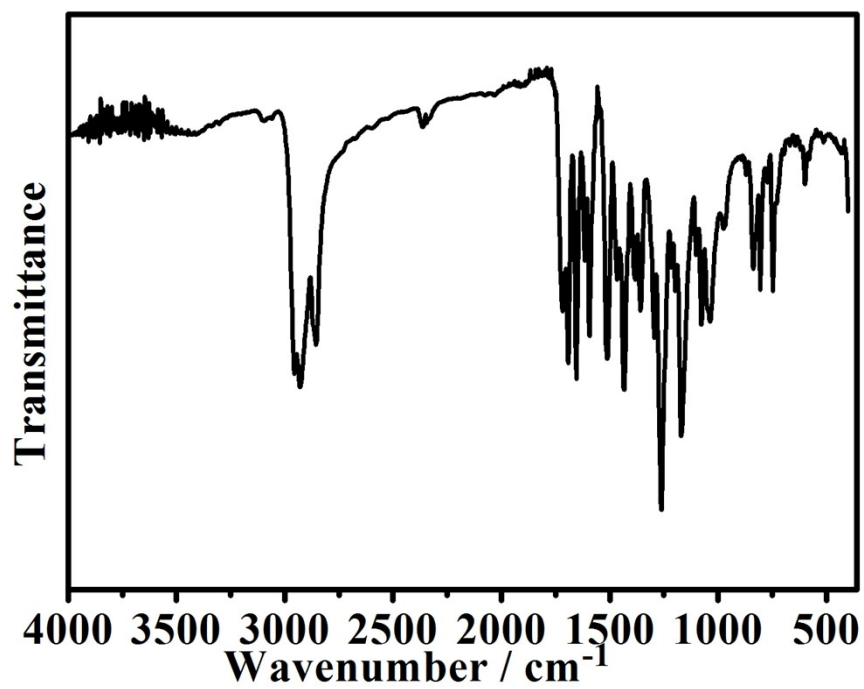


Fig.S7 FT-IR spectrum of compound 5D10A5

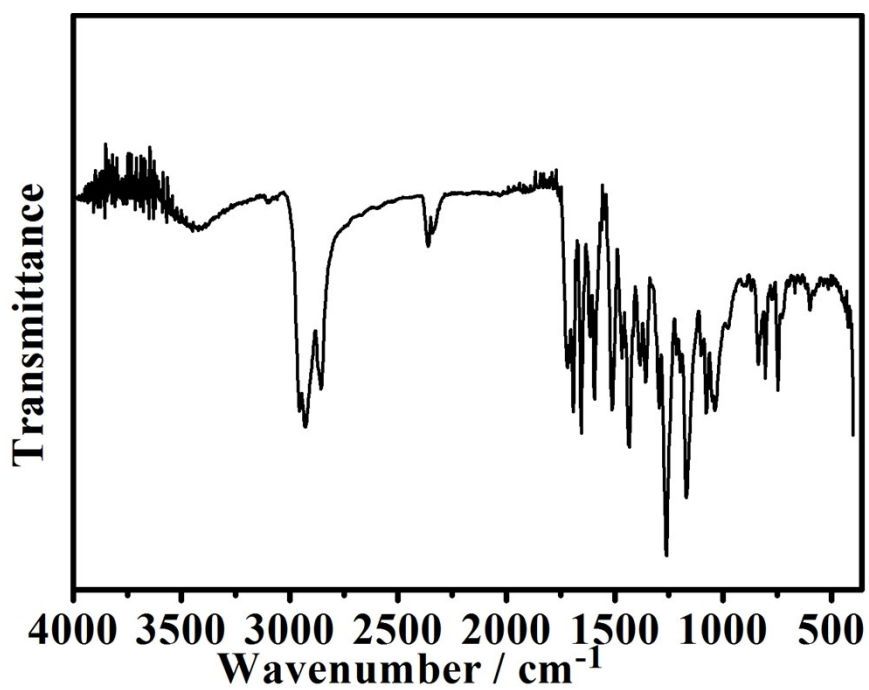


Fig.S8 FT-IR spectrum of compound 5D10A6

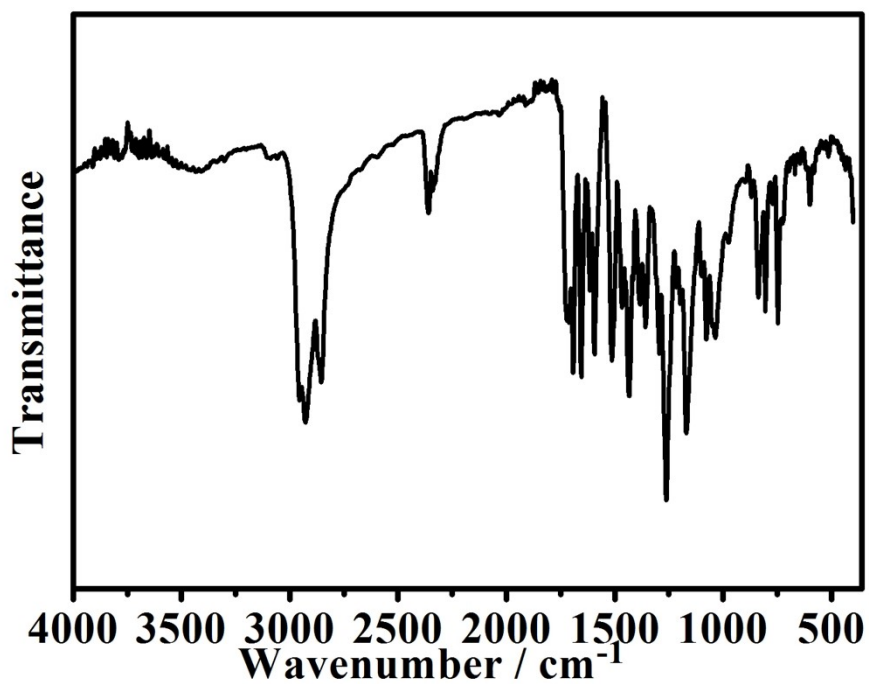


Fig.S9 FT-IR spectrum of compound 5D10A7

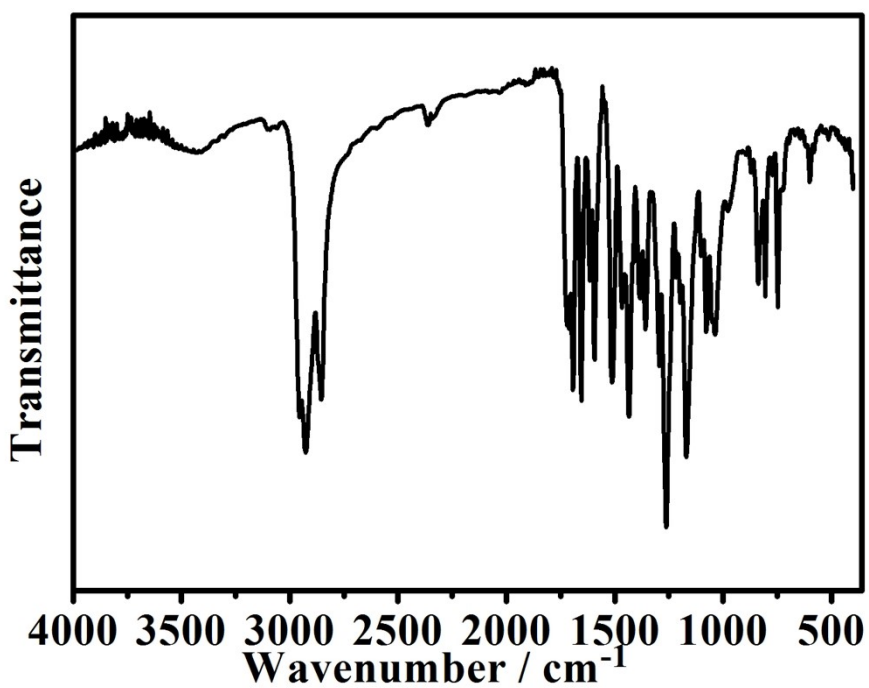


Fig.S10 FT-IR spectrum of compound 5D10A8

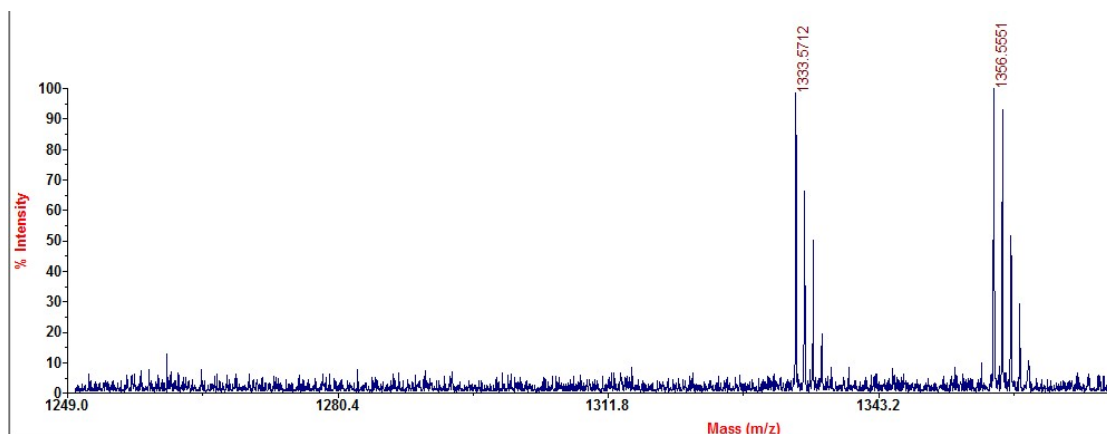


Fig.S11 MALDI-TOF mass spectra of compound 5D10A4

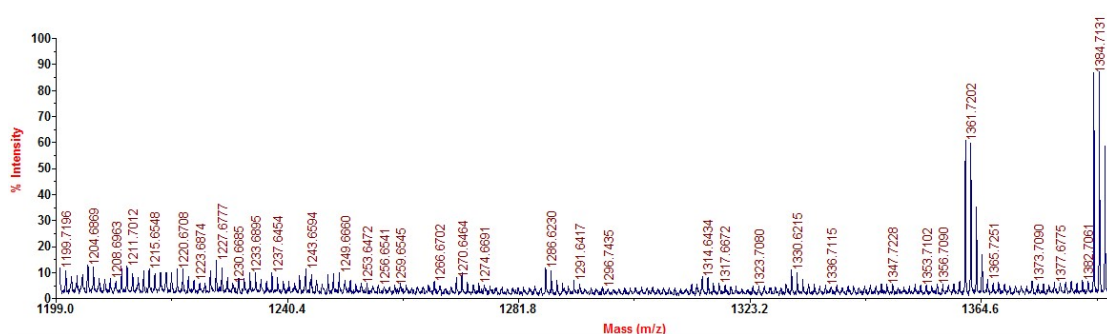


Fig.S12 MALDI-TOF mass spectra of compound 5D10A5

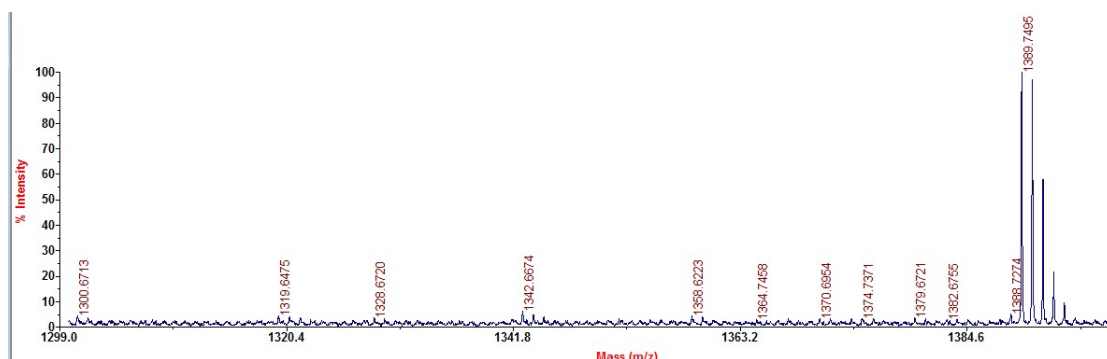


Fig.S13 MALDI-TOF mass spectra of compound 5D10A6

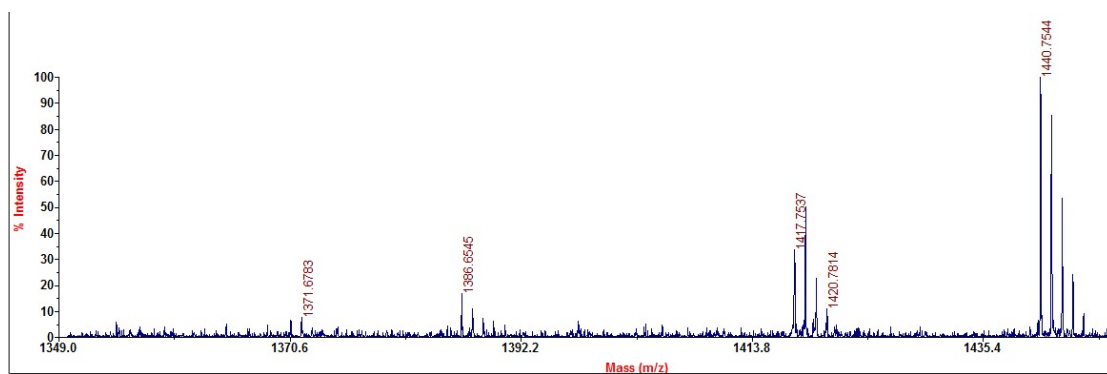


Fig.S14 MALDI-TOF mass spectra of compound 5D10A7

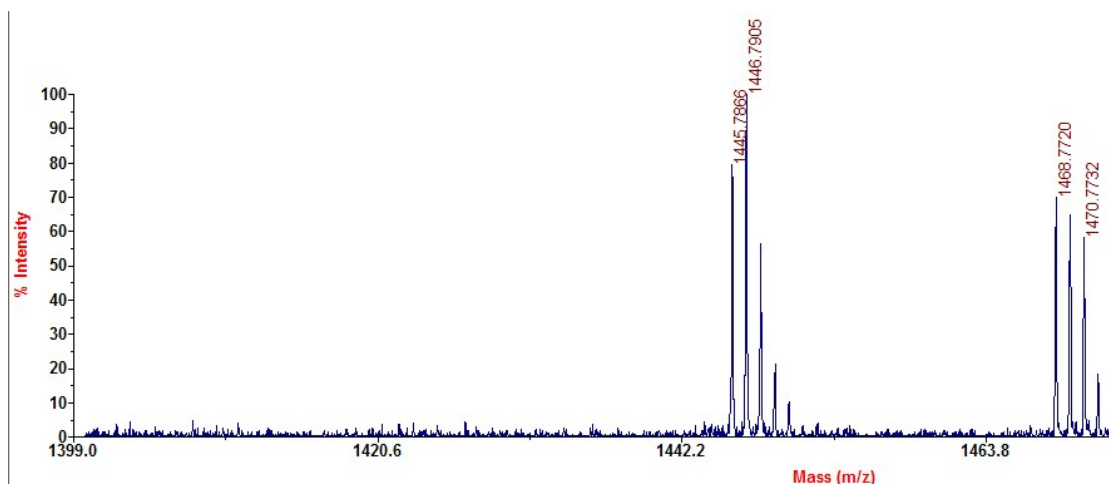


Fig.S15 MALDI-TOF mass spectra of compound 5D10A8

3. TGA diagrams

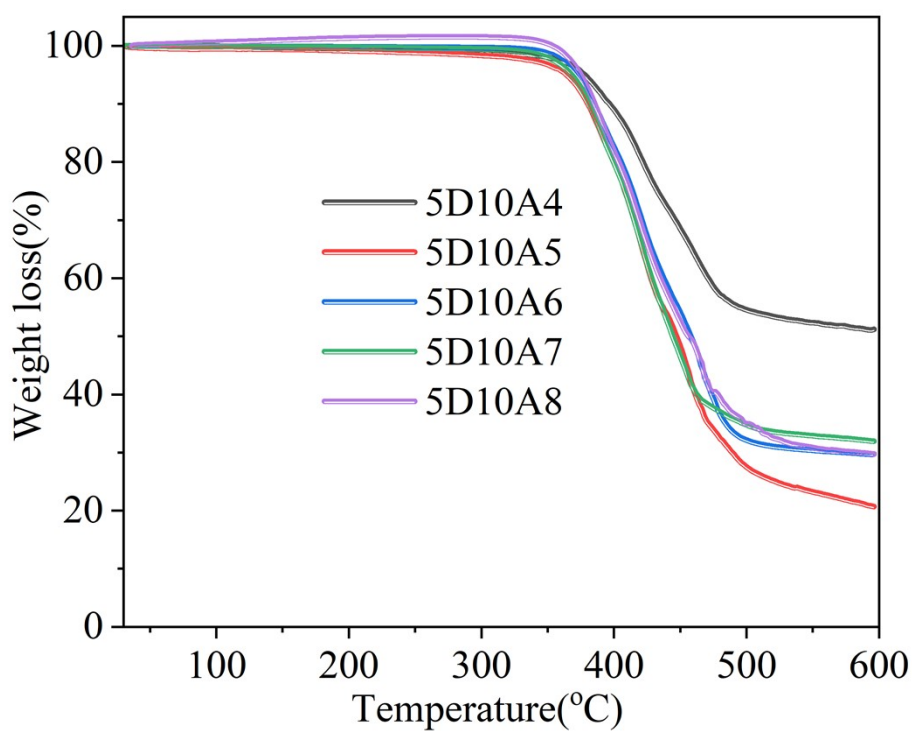


Fig.S16 TGA curve of compound 5D10A4(black line), 5D10A5(red line), 5D10A6(blue line), 5D10A7(green line), 5D10A8(purple line).

4. 1D WAXD,2D WAXD and SAXS patterns

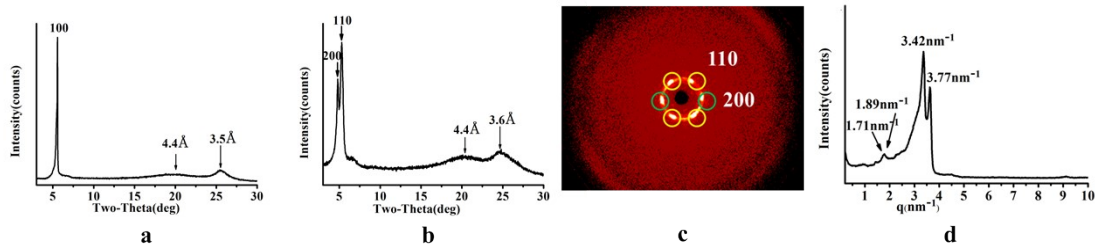


Fig.S17 1D WAXD in 90°C (a) and 30°C (b), 2D WAXD (c) in RT and SAXS(d) patterns in RT of 5D10A5

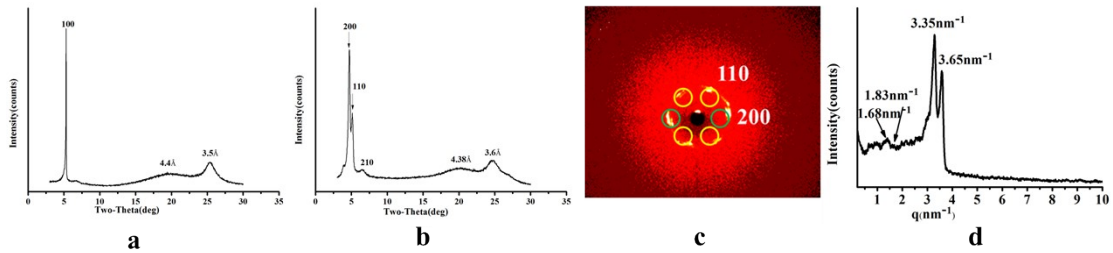


Fig.S18 1D WAXD in 90°C (a) and 30°C (b), 2D WAXD in RT (c) and SAXS(d) patterns in RT of 5D10A6

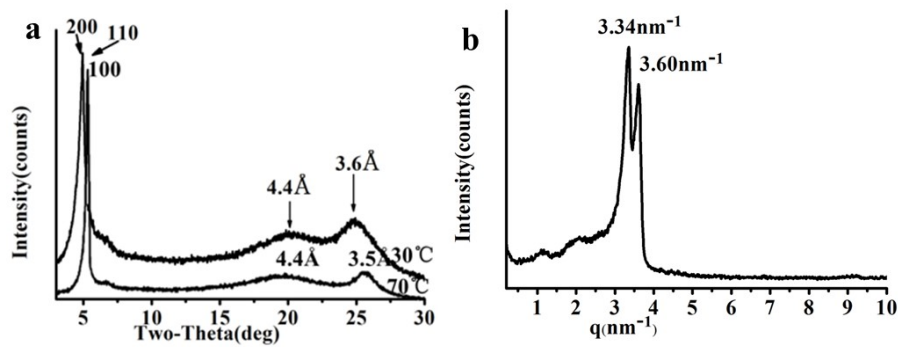


Fig.S19 1D WAXD in 70°C and 30°C (a) and SAXS(b) patterns in RT of 5D10A7

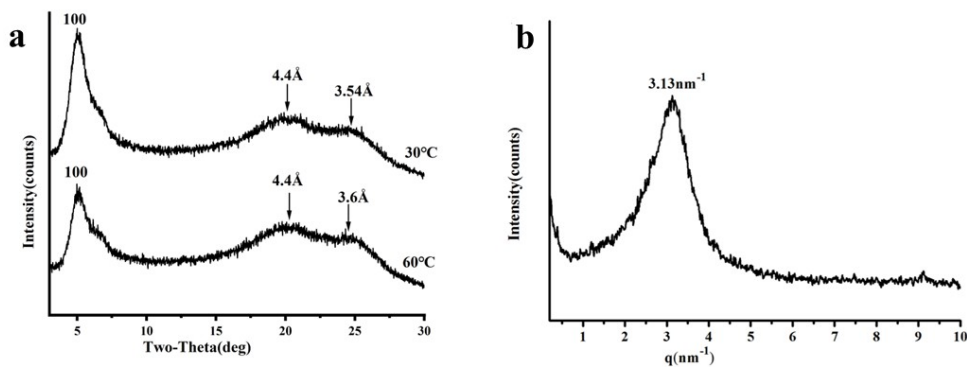


Fig.S20 1D WAXD in 60°C and 30°C (a) and SAXS(b) patterns in RT of 5D10A8

5. UV/Vis absorption spectra

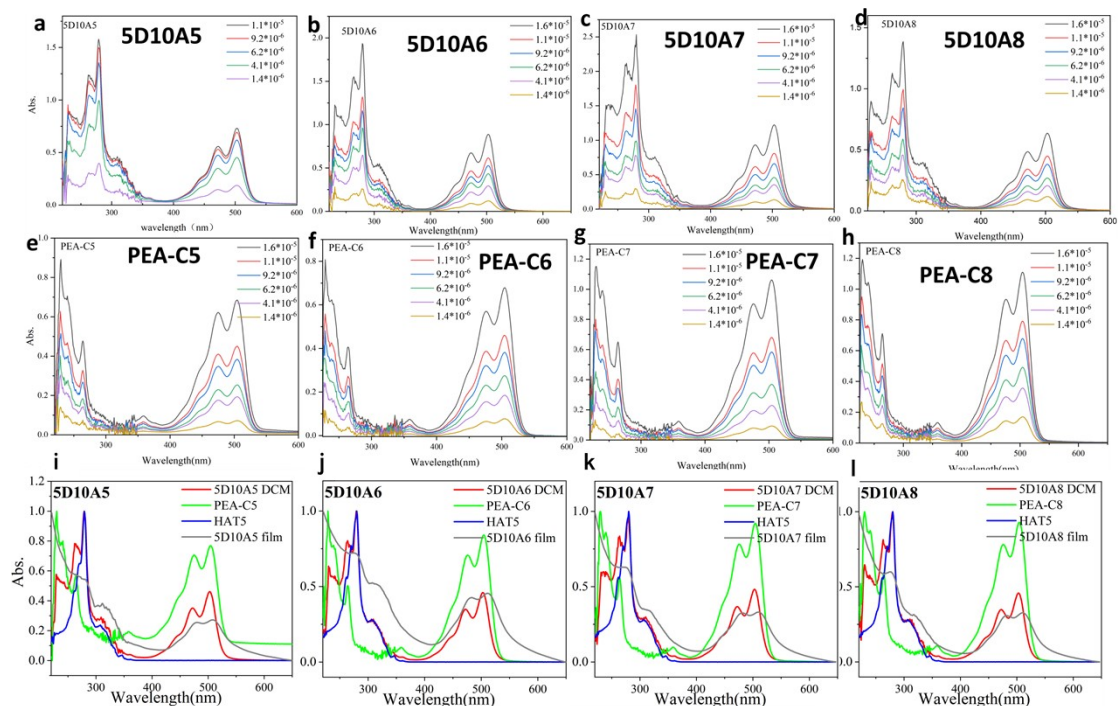


Fig.S21 Concentration-dependent absorption spectra of 5D10A5(a), 5D10A6(b), 5D10A7(c), 5D10A8(d), PEA-C5(e), PEA-C6(f), PEA-C7(g), PEA-C8(h), and film absorption spectra of 5D10A5(i), 5D10A6(j), 5D10A7(k), 5D10A8(l).

6. Fluorescence emission spectra

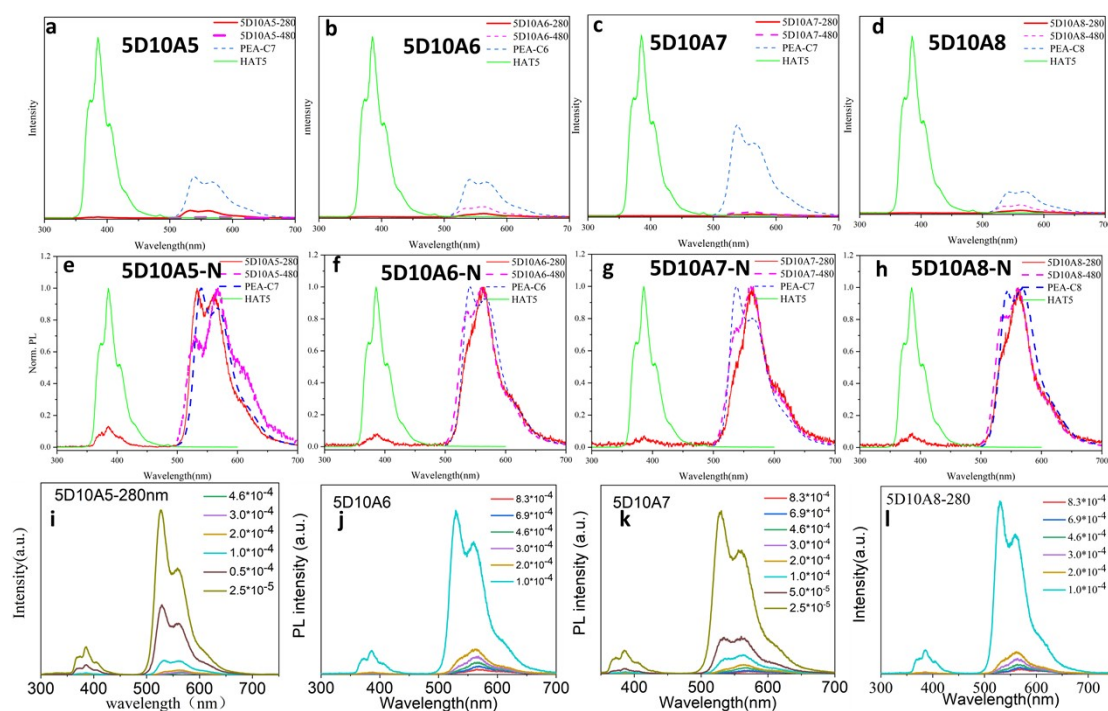


Fig. S22 PL spectra of (a) 5D10A5 with λ_{ex} = 280 and 480 nm, PEA-C5, (b) 5D10A6 with λ_{ex} = 280 and 480 nm, PEA-C6, (c) 5D10A7 with λ_{ex} = 280 and 480 nm, PEA-C7, (d) 5D10A8 with λ_{ex} = 280 and 480 nm, PEA-C8, The normalization of PL spectra of (e) 5D10A5 with λ_{ex} = 280 and 480 nm, PEA-C5, (f) 5D10A6 with λ_{ex} = 280 and 480 nm, PEA-C6, (g) 5D10A7 with λ_{ex} = 280 and 480 nm, PEA-C7, (h) 5D10A8 with λ_{ex} = 280 and 480 nm, PEA-C8, Concentration-dependent PL spectra of 5D10A5(i), 5D10A6(j), 5D10A7(k), 5D10A8(l).

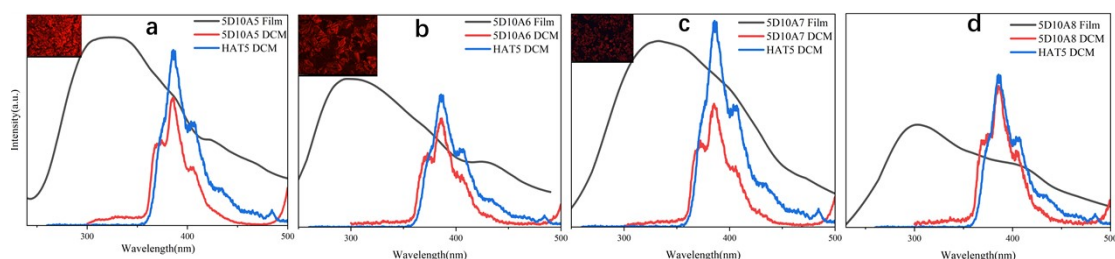


Fig. S23 (a) PL spectra for HAT5 in CH_2Cl_2 , 5D10A5 in CH_2Cl_2 , and 5D10A5 thin film exciting at 240 nm, respectively. (b) PL spectra for HAT5 in CH_2Cl_2 , 5D10A6 in CH_2Cl_2 , and 5D10A6 thin film exciting at 240 nm, respectively. (c) PL spectra for HAT5 in CH_2Cl_2 , 5D10A7 in CH_2Cl_2 , and 5D10A7 thin film exciting at 240 nm, respectively. (d) PL spectra for HAT5 in CH_2Cl_2 , 5D10A8 in CH_2Cl_2 , and 5D10A8 thin film excited at 240 nm, respectively.

7. Cyclic Voltammetry (CV) and E_g^{opt}

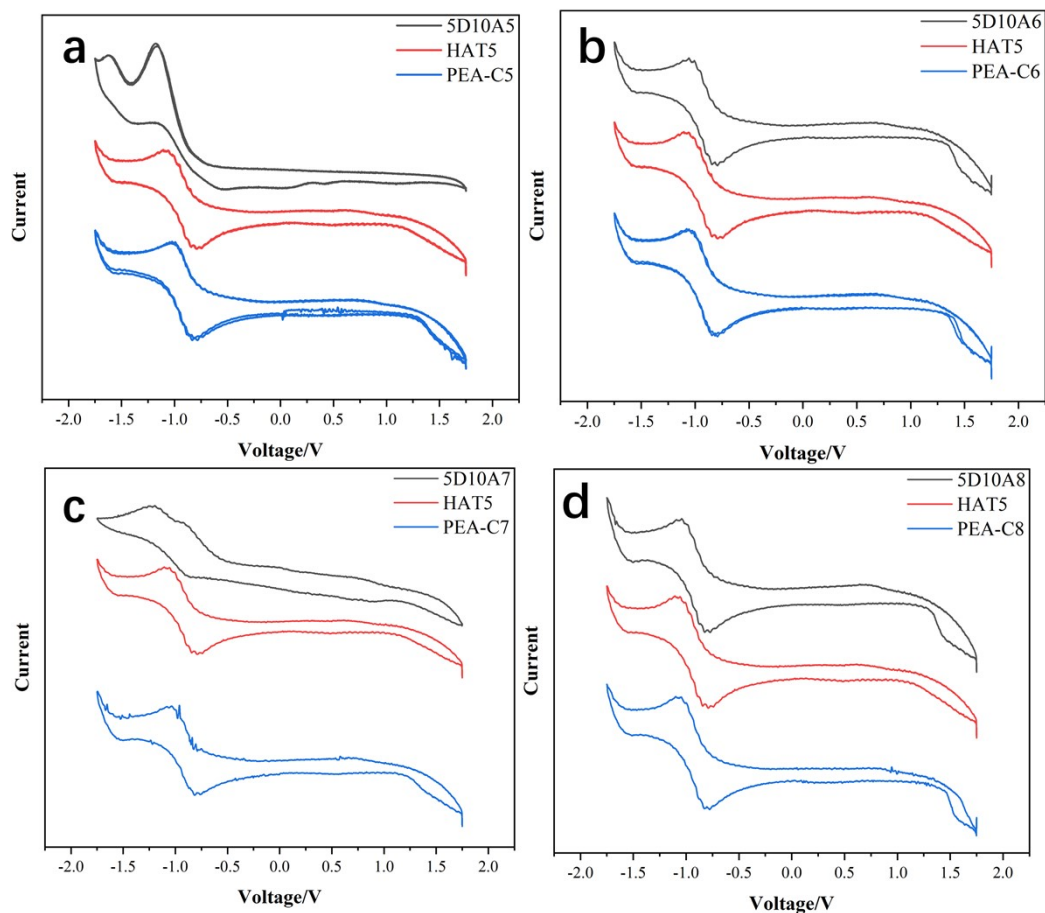


Fig. S24 (a)Cyclic voltammograms of compounds of 5D10A5, HAT5, PEA-C5. (b) Cyclic voltammograms of compounds of 5D10A6, HAT5, PEA-C6. (c) Cyclic voltammograms of compounds of 5D10A7, HAT5, PEA-C7. (d) Cyclic voltammograms of compounds of 5D10A8, HAT5, PEA-C8.

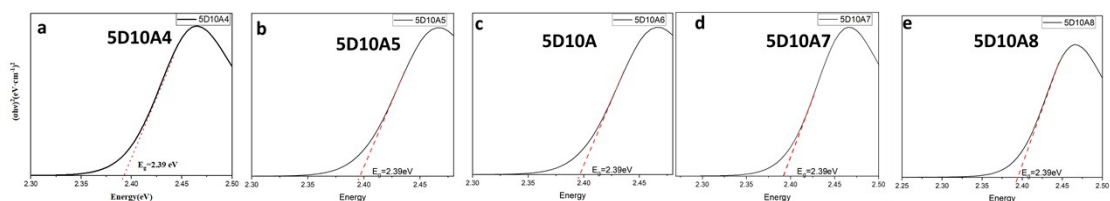


Fig. S25 the determination of the Kubelka-Monk function, $F(R_\infty)$, which was extracted from the UV/vis of (a)5D10A4, (b) 5D10A5, (c) 5D10A6, (d) 5D10A7 and (d) 5D10A8 diffuse reflectance absorbance.

8. Ultraviolet photoelectron spectroscopy (UPS)

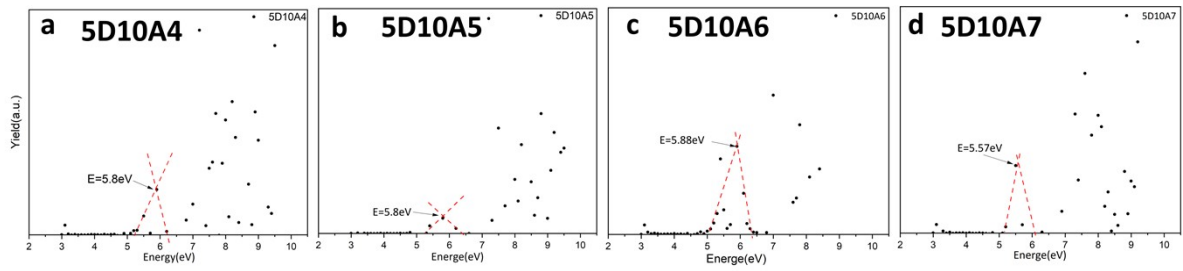


Fig. S26 UPS measurement of (a)5D10A4, (b)5D10A5, (c)5D10A6 and (d)5D10A7

9. gaussian09

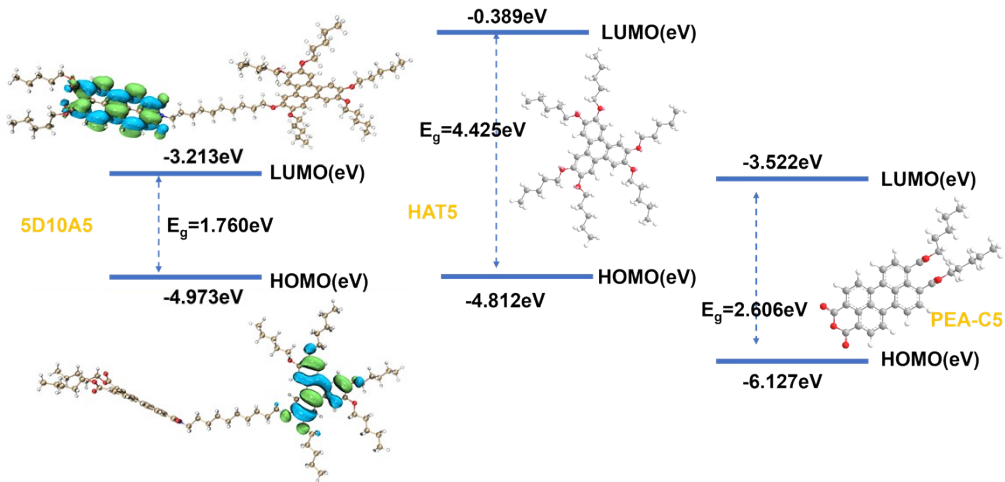


Fig. S27 Results from Gaussian 09 software simulations of 5D10A5, HAT5 and PEA-C5

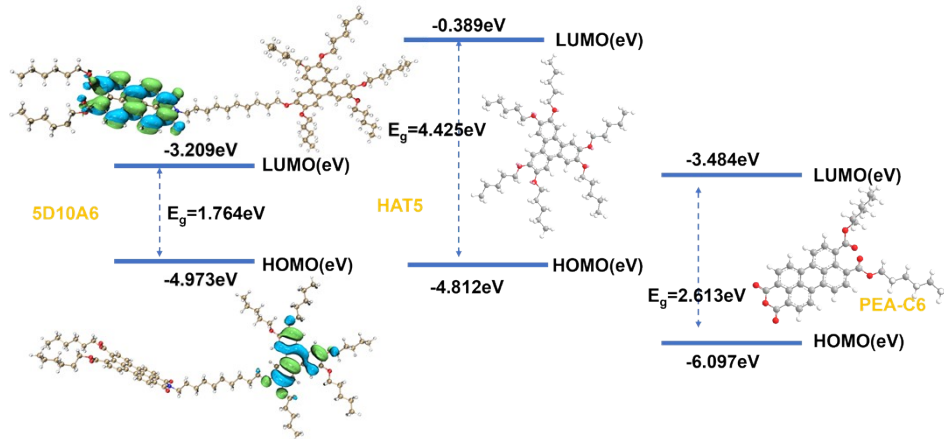


Fig. S28 Results from Gaussian 09 software simulations of 5D10A6, HAT5 and PEA-C6

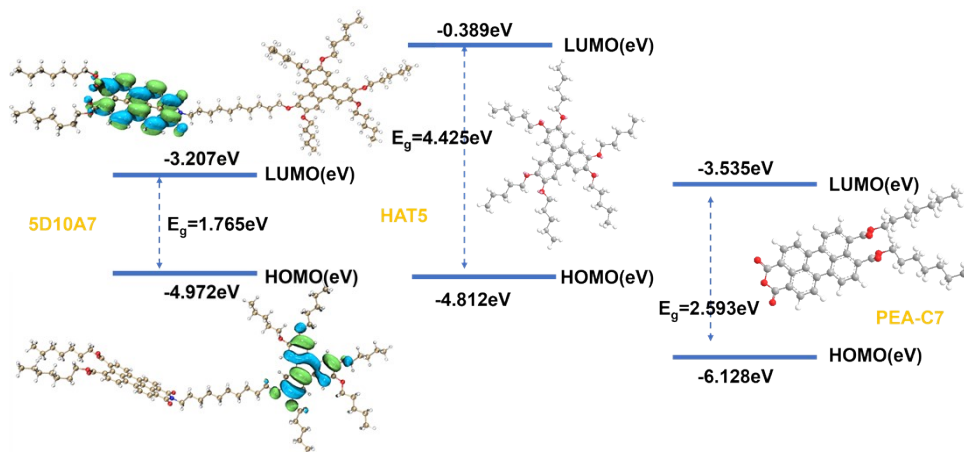


Fig. S29 Results from Gaussian 09 software simulations of 5D10A7, HAT5 and PEA-C7

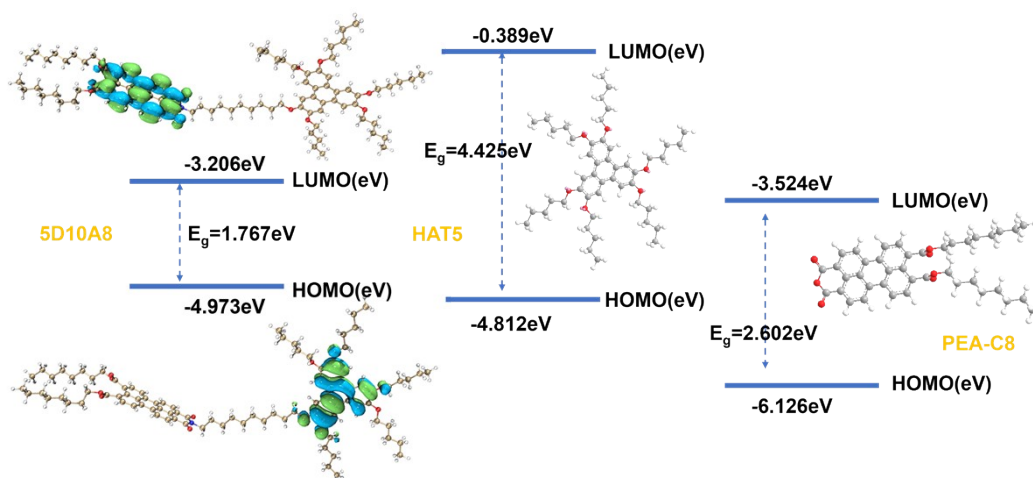


Fig. S30 Results from Gaussian 09 software simulations of 5D10A8, HAT5 and PEA-C8

10. Time of flight (TOF)

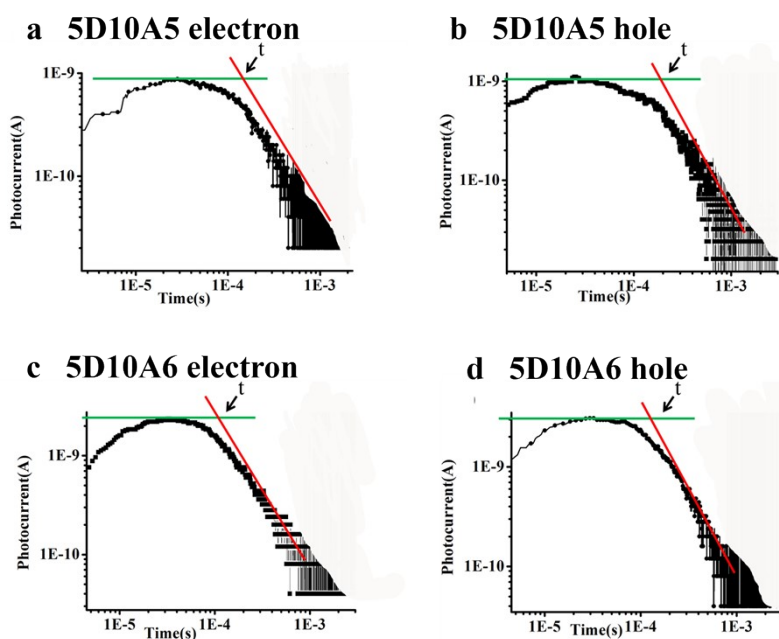


Fig. S31 Plot of raw data from TOF measurement for 5D10A5 electron(a), 5D10A5 hole(b), 5D10A6 electron(c) and 5D10A6 hole(d).

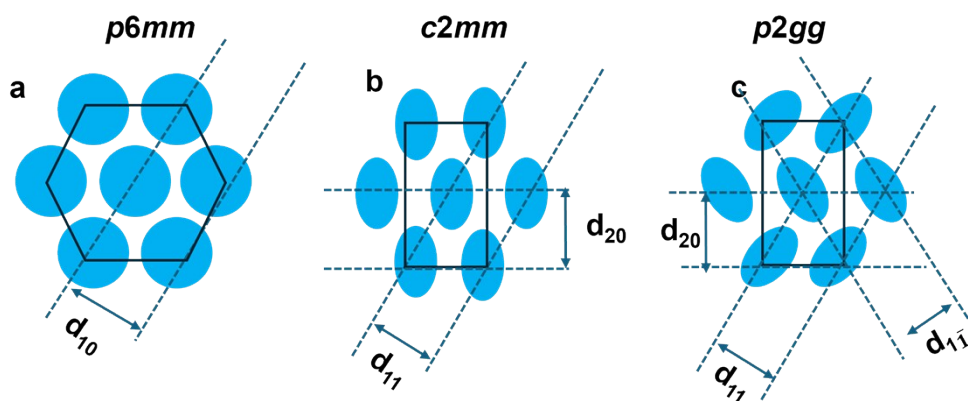


Fig. S32 Representation of the arrangement of the columns in the (a) $p6mm$, (b) $c2mm$, and (c) $p2gg$ plane group.

Table S1

parameters of the compounds

| Compds(30°C) | phase | a/Å | b/Å | A/Å ² | h_{π} /Å | Z | ξ /Å |
|--------------|------------------|-------|-------|------------------|--------------|---|----------|
| 5D10A4 | Col _r | 36.34 | 19.16 | 696.27 | 3.56 | 2 | 60 |
| 5D10A5 | Col _r | 36.72 | 18.72 | 687.40 | 3.6 | 2 | 60 |
| 5D10A6 | Col _r | 37.5 | 19.38 | 726.75 | 3.6 | 2 | 55 |
| 5D10A7 | Col _r | 37.62 | 19.77 | 743.75 | 3.6 | 2 | 78 |
| 5D10A8 | Col _h | 20.62 | / | 490.96 | 3.6 | 1 | 66 |

All parameters of the compounds were obtained at 30°C; a and b: 2-dimensional lattice parameters; A: lattice area; h_{π} and ξ : π -stacking distance from the scattering maximum and correlation length (Scherrer); V_{mol} : Molecular volume (Å³) calculated by additivity of partial elementary volumes; Z: number of columns per lattice; h_{mol} : =molecular slice thickness.