

Supporting Information for
Significant effect of alkyl chain length on fluorescent
thermochromism of 9,10-bis(*p*-alkoxystyryl)anthracenes

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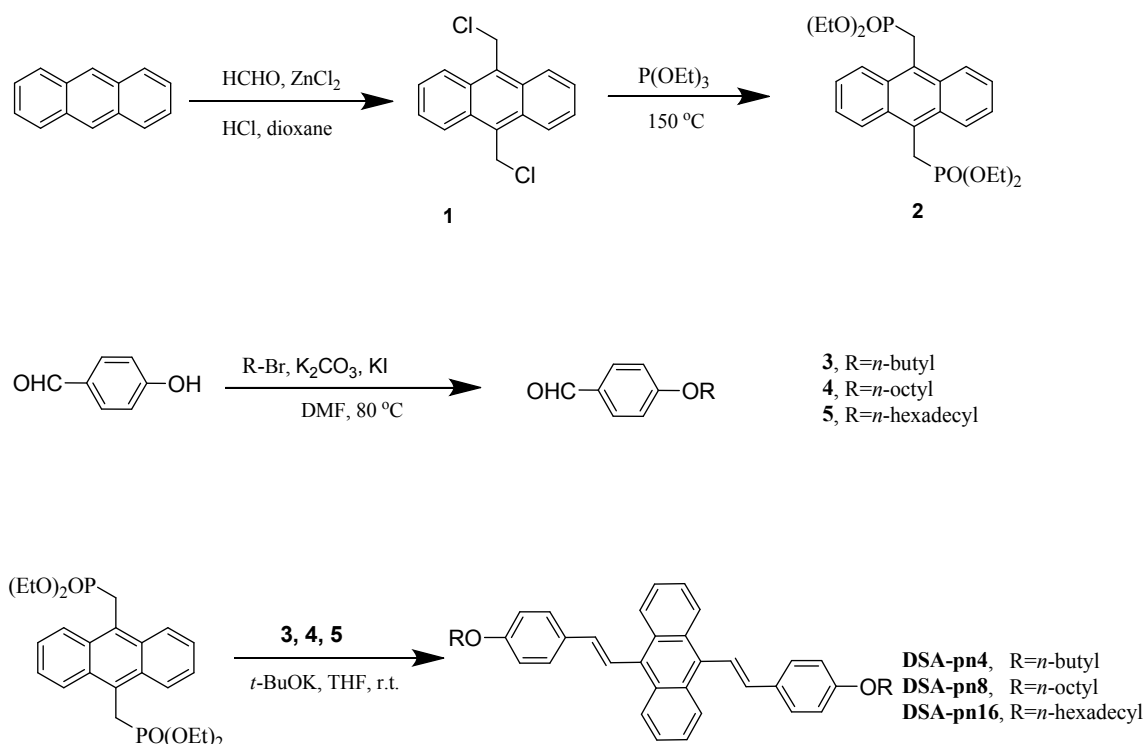
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1 Experimental section

Materials and measurements

Anthracene, paraformaldehyde, 4-hydroxybenzaldehyde, *n*-butyl bromide, *n*-octyl bromide and *n*-hexadecyl bromide were purchased from Tianjin Guangfu Fine Chemical Reagents Company (China) and used as received. Other common reagents and solvents were purchased as analytical grade from Tianjin Jiangtian Chemical technology Co., LTD (China) and used without further purification. Tetrahydrofuran (THF) was distilled from sodium/benzophenone before use. Deionized water was employed throughout this study. 9,10-Bis(chloromethyl) anthracene¹ (**1**), 9,10-bis(diethylphosphorylmethyl)anthracene² (**2**) and alkoxy-substituted benzaldehydes³ (**3**, **4** and **5**) were prepared according to the literature methods. 9,10-Bis(*p*-alkoxystyryl)anthracenes (**DSA-pn_n**, *n* = 4, 8, 16) were successfully synthesized by Wittig–Horner reactions of corresponding alkoxy-substituted benzaldehydes and 9,10-bis(diethoxyphosphorylmethyl)anthracene⁴, described in **Scheme 1**.

NMR spectra were recorded on a Bruker AVANCE III spectrometer (600 MHz for ¹H NMR and 150 MHz for ¹³C NMR) with CDCl₃ as solvent and tetramethylsilane (TMS) as the internal standard. High-resolution mass spectra (HRMS) were measured on a Bruker Daltonics micrOTOF-Q II instrument. Photoluminescence spectra (PL) were measured on an Edinburgh FLS920 spectrometer with a slit width of 1.0 nm for both excitation and emission. TGA (thermal gravimetric analysis) was recorded on an STA 409PC with a heating rate of 10 °C /min from room temperature to 800 °C in a stream of N₂ (40 mL/min). Quantitative analysis of **DSA-pn4**, **DSA-pn8** and **DSA-pn16** were conducted on a Baker Norton pharmaceuticals detector with a baseline C₁₈-column at 365 nm under 1 mL/min of mobile phase by gradient elution with the ratio (V:V) of methylene chloride and methanol as 80:20, 50:50, 30:70, data was collected and analyzed with N2000 chromatography data system. Differential scanning calorimetry (DSC) curves were obtained with a Perkin Elmer Diamond DSC at heating rate of 10 °C/min under N₂ atmosphere. Wide-angle X-ray diffraction (WAXD) measurements were performed by using a BRUKER X-ray diffractometer (D8 ADVANCE) at a scanning rate of 4°/min. THF aqueous solution of certain concentration was made up by addition of water into the THF solutions of samples under vigorous stirring at room temperature. The concentrations of all samples were adjusted to 1.0 × 10⁻⁵ μM by adding water. Thermochromic experiments: The powder sample placed on a microslide was heated by an electronic hot plate to the color-transition temperature, the fluorescence images under a 365 nm UV lamp were taken immediately. Then the heated sample was exposed in air and naturally cooled to room temperature.



Scheme 1 Synthesis and structures of **DSA-pn_n**

9,10-Bis(chloromethyl)anthracene (**1**)

To a mixture of anthracene (8.90 g, 50 mmol) and paraformaldehyde (7.50 g, 250 mmol) in dioxane (100 mL) was dropwise added concentrated hydrochloric acid (200 mL) at room temperature under N₂ atmosphere. Then the solution was heated and slowly stirred under gentle reflux for 3 h. After this, the reaction mixture was allowed to stand for 16 h. The crude product was obtained by filtration and washed with 1,4-dioxane and water until pH = 7. Finally, its recrystallization in toluene yields a yellow solid (8.44g, 60% yield). ¹H NMR (600MHz, CDCl₃, ppm): 8.40-8.38 (m, 4H), 7.67-7.66 (m, 4H), 5.61(s, 4H).

9,10-Bis(diethylphosphorylmethyl)anthracene (**2**)

A solution of compound **1** (7.80 g, 28 mmol) in triethyl phosphite (30 ml) was stirred vigorously at gentle reflux for 12 h. After cooling down to room temperature, it was purified by flash chromatography (ethyl acetate/petroleum ether, 1/1, v/v) to give 8.16 g compound **2** as a yellow solid (59% yield). ¹H NMR (600 MHz, CDCl₃, ppm): 8.38-8.37 (m, 4H), 7.58-7.56 (m, 4H), 4.21 (d, 4H, *J* = 19.8 Hz), 3.91-3.86 (m, 4H), 3.82-3.78(m, 4H), 1.06 (t, 12H, *J* = 7.2 Hz).

4-(*n*-Butoxy)benzaldehyde (**3**)

To a solution of 4-hydroxybenzaldehyde (3.00 g, 24 mmol) in dry DMF (30 mL), K₂CO₃ (3.18 g, 30 mmol) and KI (catalytic amount) were added. The mixture was stirred and heated to 80 °C, followed by slow addition of *n*-butyl bromide (2.4 ml, 27 mmol). The mixture was continually stirred for 8 h at this temperature. After cooling to room temperature, it was poured into brine (50 mL) and extracted with dichloromethane (3×30 mL). The organic phases were combined, washed by NaOH aqueous solutions (10%, 3×30mL) and deionized water (3×30mL). Then the organic

phases were dried over MgSO₄ and concentrated to afford a brownish liquid (3.30 g, 65 %).

4-(*n*-Octyl)benzaldehyde (**4**) and 4-(*n*-hexadecyl)benzaldehyde (**5**) were synthesized by the same method.

9,10-Bis(4-(*n*-butoxy)styryl)anthracenes (DSA-pn4)

To the solution of compounds **2** (0.60 g, 1.26 mmol) and **3** (0.40 g, 2.76 mmol) in 40 mL of dry THF, potassium *t*-butoxide (0.30 g, 2.76 mmol) was added. The obtained suspension was stirred at room temperature for 8 h. After removing the solvent under reduced pressure, the residue was recrystallized in THF/MeOH (1/10, v/v). The yellow solids were collected by filtration, washed with methanol, then purified by flash chromatography (petroleum ether/methylene chloride, 5/1, v/v) to afford 0.43 g

DSA-pn4 as a yellow-green solid in 76 % yield. m.p. 214-215 °C. ¹H NMR (600MHz, CDCl₃) δ (ppm): 8.41-8.40 (m, 4H), 7.78 (d, 2H, *J* = 16.2 Hz), 7.62 (d, 4H, *J* = 8.4 Hz), 7.47-7.45 (m, 4H), 6.99 (d, 4H, *J* = 8.4 Hz), 6.88 (d, 2H, *J* = 16.2 Hz), 4.05 (t, 4H, *J* = 6.6 Hz), 1.85-1.80 (m, 4H), 1.56-1.54 (m, 4H), 1.02 (t, 6H, *J* = 7.2 Hz); ¹³C NMR (150MHz, CDCl₃) δ (ppm): 159.34, 137.06, 132.95, 130.17, 129.79, 127.92, 126.69, 125.22, 122.91, 115.00, 68.01, 31.49, 19.42, 14.02. HRMS (APCI): calcd. for C₃₈H₃₈O₂H 527.2945 [M + H]⁺; found 527.2944. Purity: 96.95% (HPLC, *t*_R = 10.607 min).

DSA-pn8 and **DSA-pn16** were obtained by the same procedure.

DSA-pn8: Yield 67%, m.p. 145-147 °C. ¹H NMR (600MHz, CDCl₃) δ (ppm): 8.42-8.40 (m, 4H), 7.78 (d, 2H, *J* = 16.8 Hz), 7.62 (d, 4H, *J* = 8.4 Hz), 7.47-7.46 (m, 4H), 6.99 (d, 4H, *J* = 8.4 Hz), 6.88 (d, 2H, *J* = 16.8 Hz), 4.04 (t, 4H, *J* = 6.6 Hz), 1.86-1.82 (m, 4H), 1.52-1.48 (m, 4H), 1.40-1.33 (m, 16H), 0.93 (t, 6H, *J* = 6.6 Hz); ¹³C NMR (150MHz, CDCl₃) δ (ppm): 159.34, 137.06, 132.95, 130.16, 129.79, 127.91, 126.69, 125.21, 122.90, 114.99, 68.34, 31.99, 29.54, 29.44, 29.41, 26.22, 22.83, 14.26.

HRMS (APCI): calcd. for C₄₆H₅₄O₂H 639.4197 [M + H]⁺; found 639.4195. Purity: 99.03 % (HPLC, *t*_R = 12.557 min).

DSA-pn16: Yield 65%, m.p. 124-125 °C. ¹H NMR (600MHz, CDCl₃) δ(ppm): 8.41-8.40 (m, 4H), 7.78 (d, 2H, *J* = 16.2 Hz), 7.61 (d, 4H, *J* = 7.8 Hz), 7.47-7.45 (m, 4H), 6.99 (d, 4H, *J* = 7.8 Hz), 6.87 (d, 2H, *J* = 16.8 Hz), 4.03 (t, 4H, *J* = 6.6 Hz), 1.85-1.81 (m, 4H), 1.39-1.27 (m, 52H), 0.89 (t, 6H, *J* = 6.6 Hz); ¹³C NMR (150MHz, CDCl₃) δ (ppm): 159.22, 136.93, 132.83, 130.03, 129.66, 127.78, 126.56, 125.08, 122.77, 114.87, 68.22, 31.95, 29.72, 29.70, 29.68, 29.64, 29.62, 29.45, 29.38, 29.31, 26.08, 22.71, 14.13.

HRMS (ESI): calcd. for C₆₂H₈₆O₂H 863.6701 [M + H]⁺; found 863.6710. Purity: 96.11% (HPLC, *t*_R = 11.623 min).

2 References

1. W. Liu, *et al. Chem. Commun.*, 2013, **49**, 6042
2. H. Zhang, *et al. Chem. Mater.*, 2009, **21**, 5125.
3. C. Wang, *et al. Chem. Eur. J.*, 2011, **17**, 3322.
4. X. Zhang, *et al. Chem. Commun.*, 2012, **48**, 10895

3 Table S1, Figs. S1-S5

Table S1 Emission wavelength (nm) and intensity of **DSA-pn_n** from 298 K to 498 K

Temperature/K	DSA-pn4		DSA-pn8		DSA-pn16	
	Peak Wavelength/nm	Peak Intensity	Peak Wavelength/nm	Peak Intensity	Peak Wavelength/nm	Peak Intensity
298	520	403.8	521	12210.0	505	3934.0
308	522	386.5	522	12160.0	505	3890.0
318	521	372.0	523	11950.0	505	3852.0
328	521	398.6	523	11800.0	506	3767.0
338	521	411.3	522	11610.0	508	3757.0
348	522	407.0	524	11320.0	512	3627.0
358	521	413.0	529	11420.0	515	3613.0
368	519	405.5	527	11260.0	518	3574.0
378	519	388.4	518	10470.0	524	3360.0
388	515	356.4	520	9012.0	528	2667.0
398	515	324.6	517	8005.0	532	1226.0
408	518	294.3	517	7574.0	573	315.4
418	519	278.6	519	7781.0	570	271.2
428	520	302.4	518	7829.0	576	233.6
438	521	316.4	541	5094.0	576	212.1
448	524	303.6	562	302.5	575	198.8
458	523	288.1	568	273.6	574	171.9
468	524	269.0	568	246.0	577	163.8
478	522	255.1	569	221.4	576	156.7
488	567	33.6	569	200.2	577	148.9
498	566	20.8	569	177.7	577	140.6

Fig. S1 Maximum fluorescence intensity vs temperature of **DSA-pn_n** upon heating

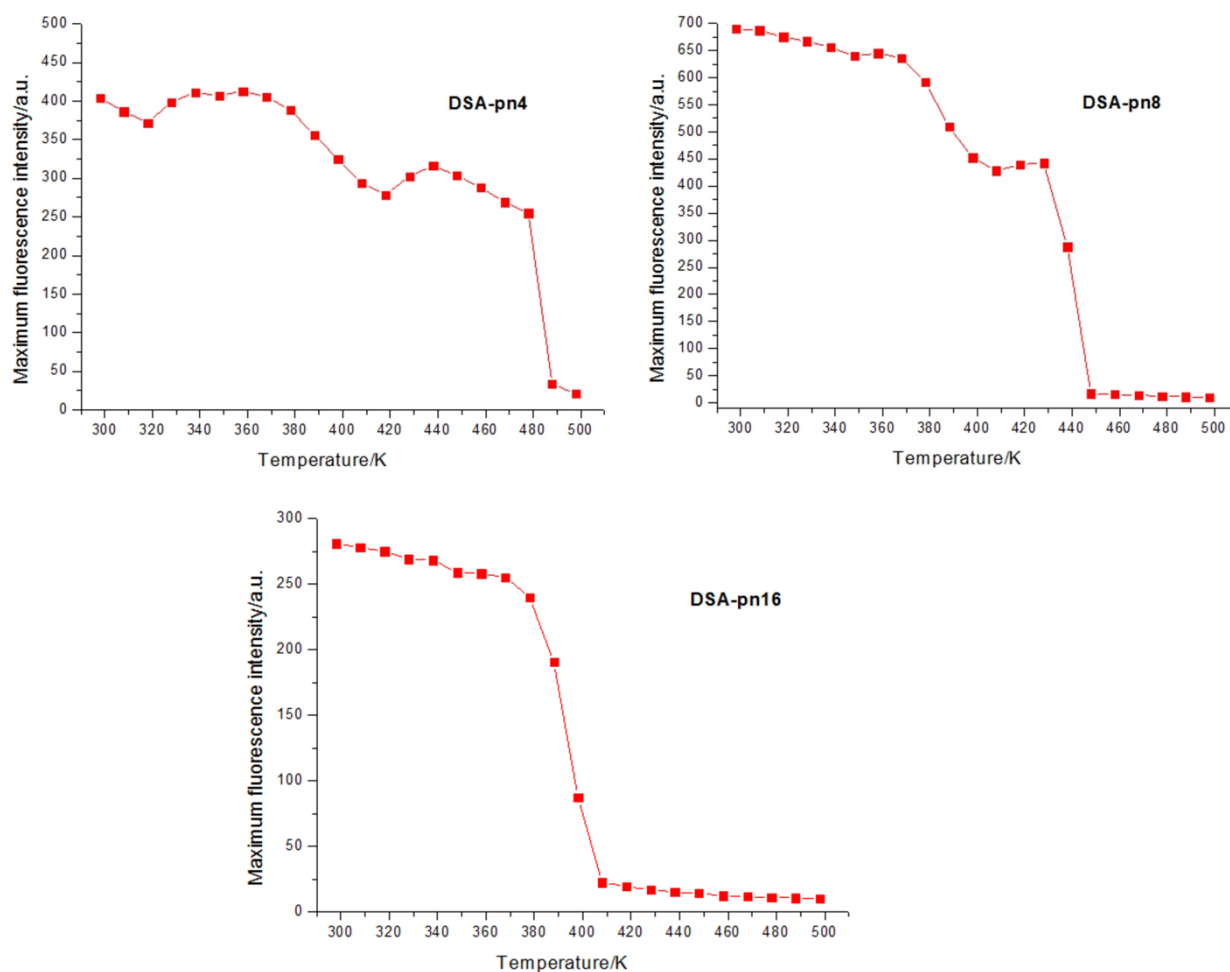


Fig. S2 DSC curves of **DSA-pn_n** pristine solids

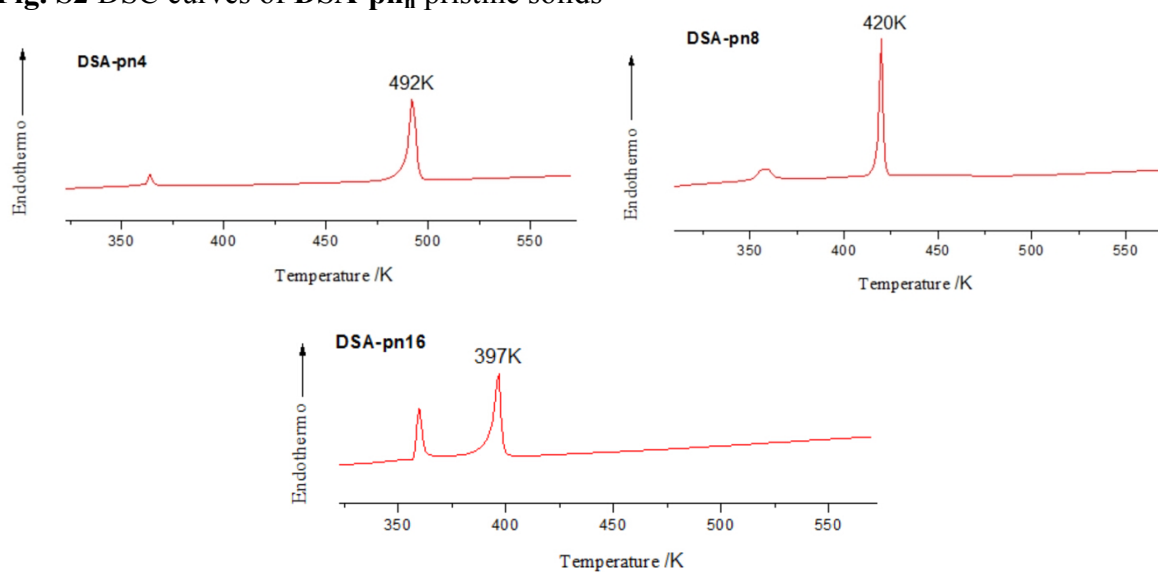


Fig. S3 Powder X-ray diffraction patterns of **DSA-pn_n** at room temperature and 478K for DSA-pn4, 428K for DSA-pn8, 398K for DSA-pn16

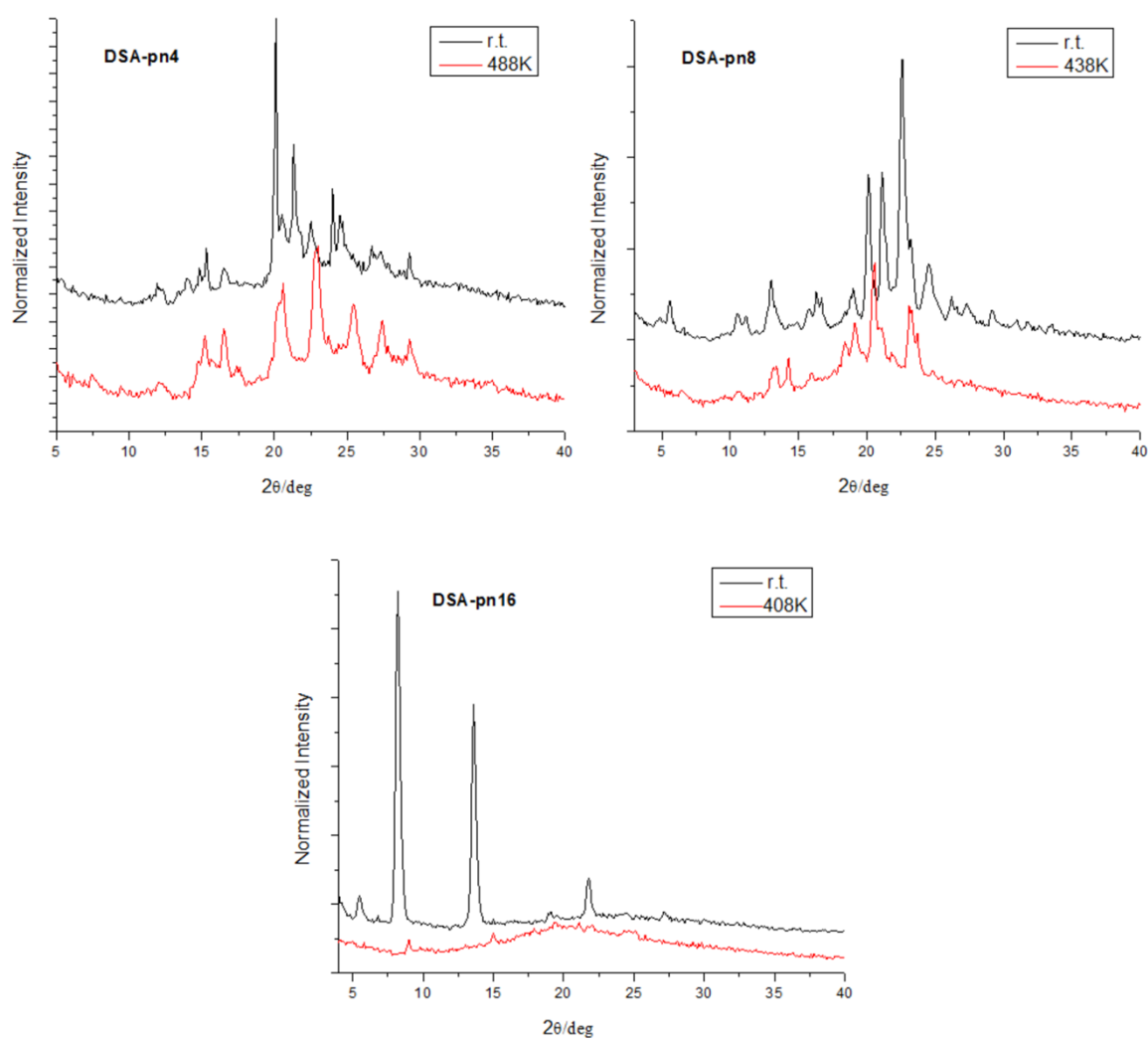


Fig. S4 TGA curves for **DSA-pn_n**

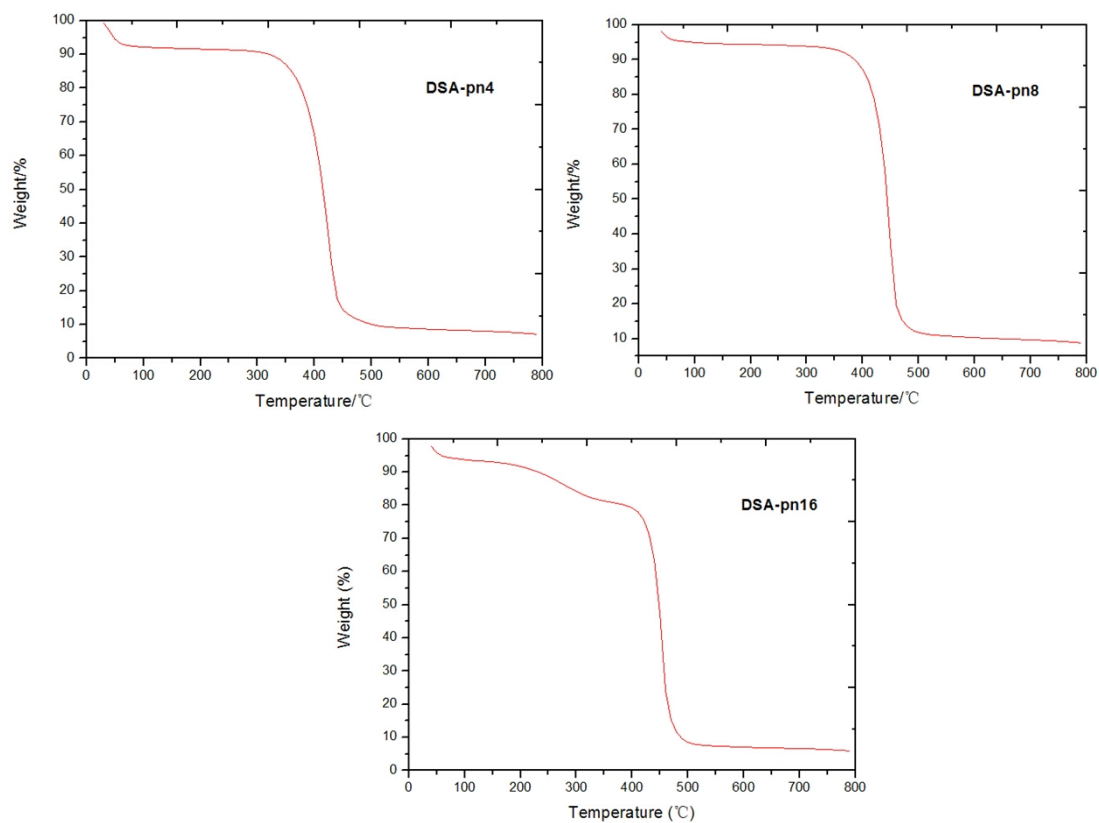
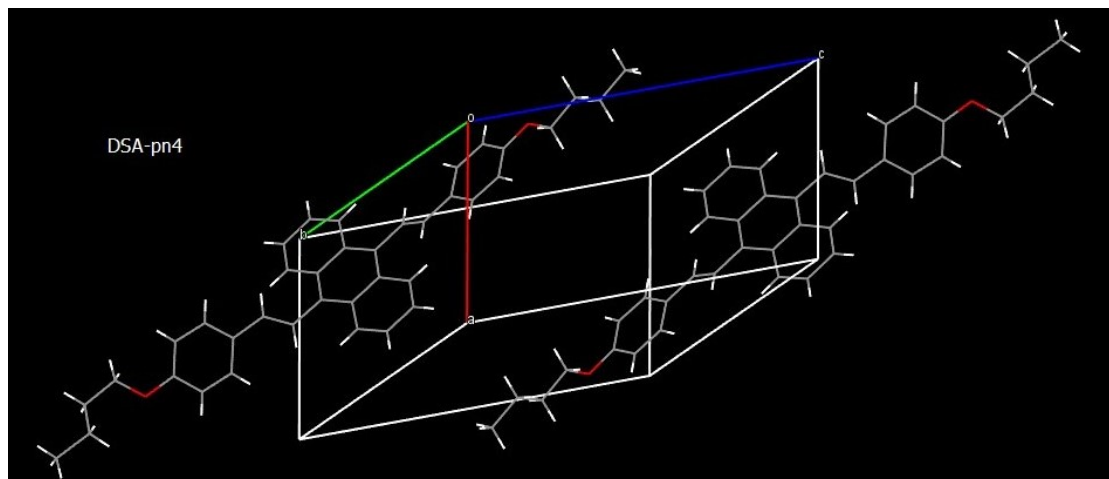
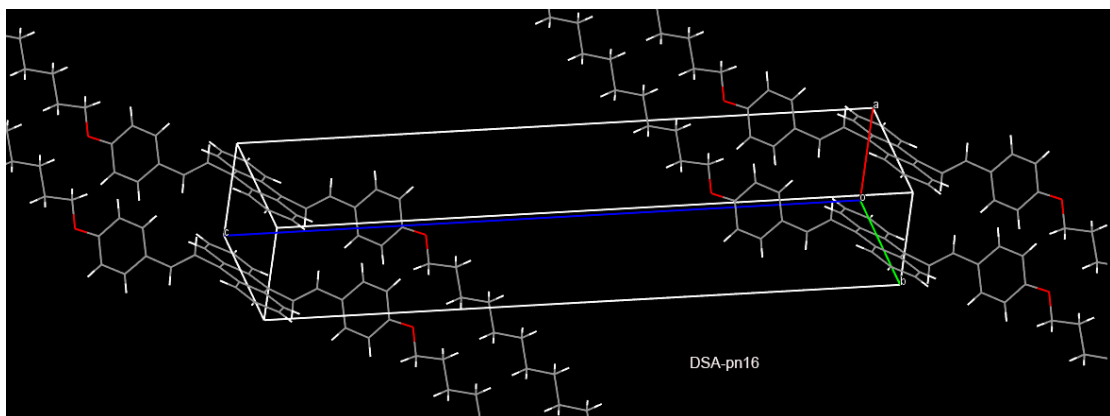
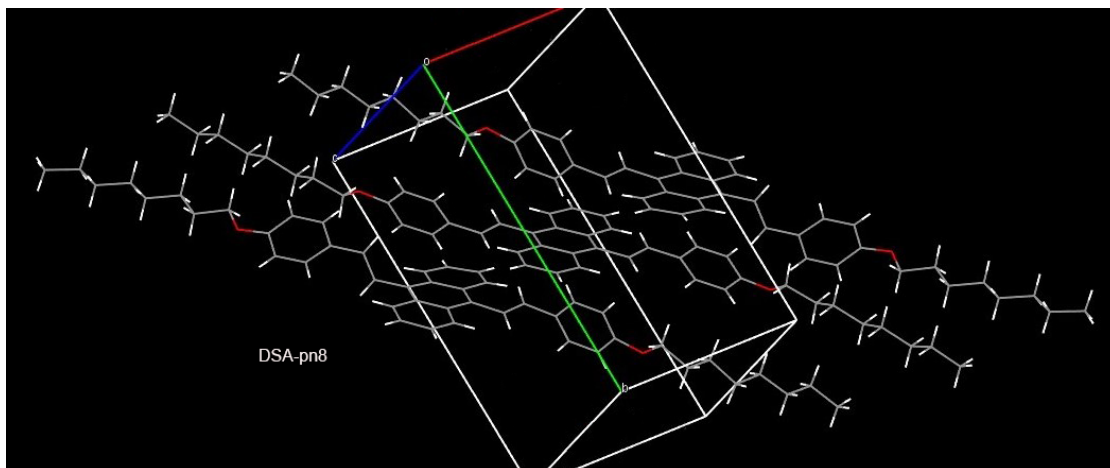


Fig. S5 Molecular stacking modes of **DSA-pn4**, **DSA-pn8** and **DSA-pn16** in crystals





4 ¹H NMR, ¹³C NMR, HRMS spectra and HPLC

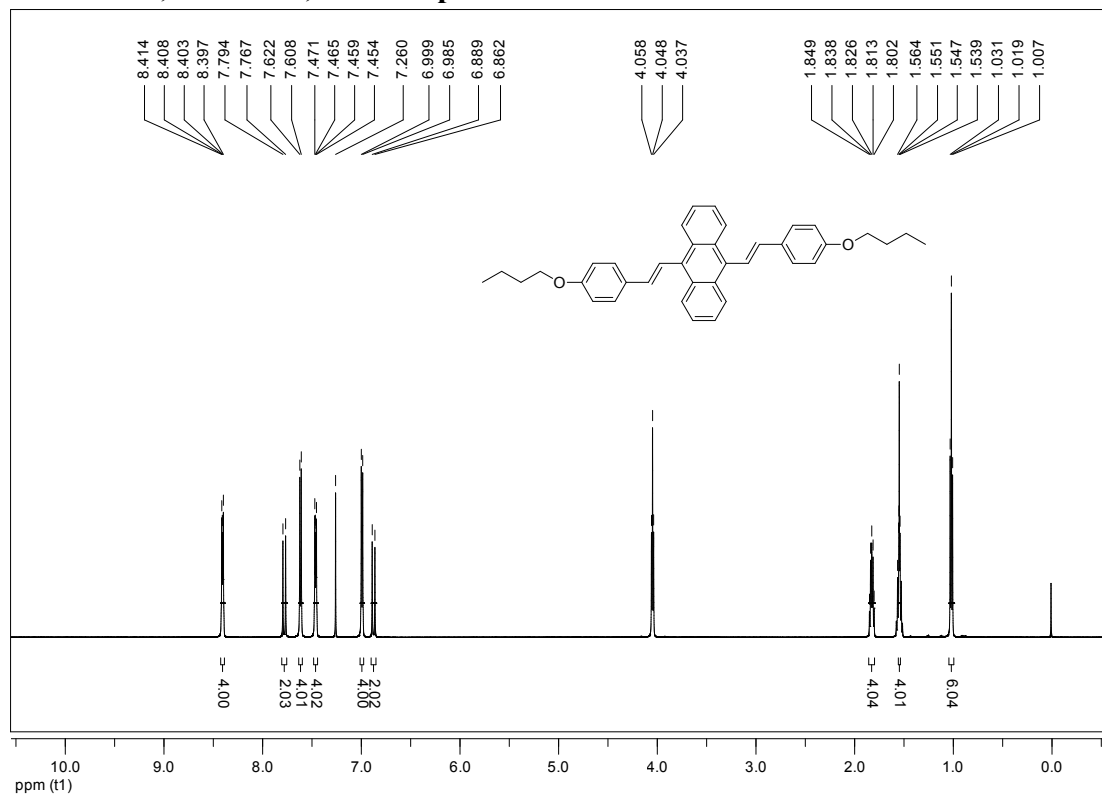


Fig. S6 ¹H NMR spectrum of DSA-pn4

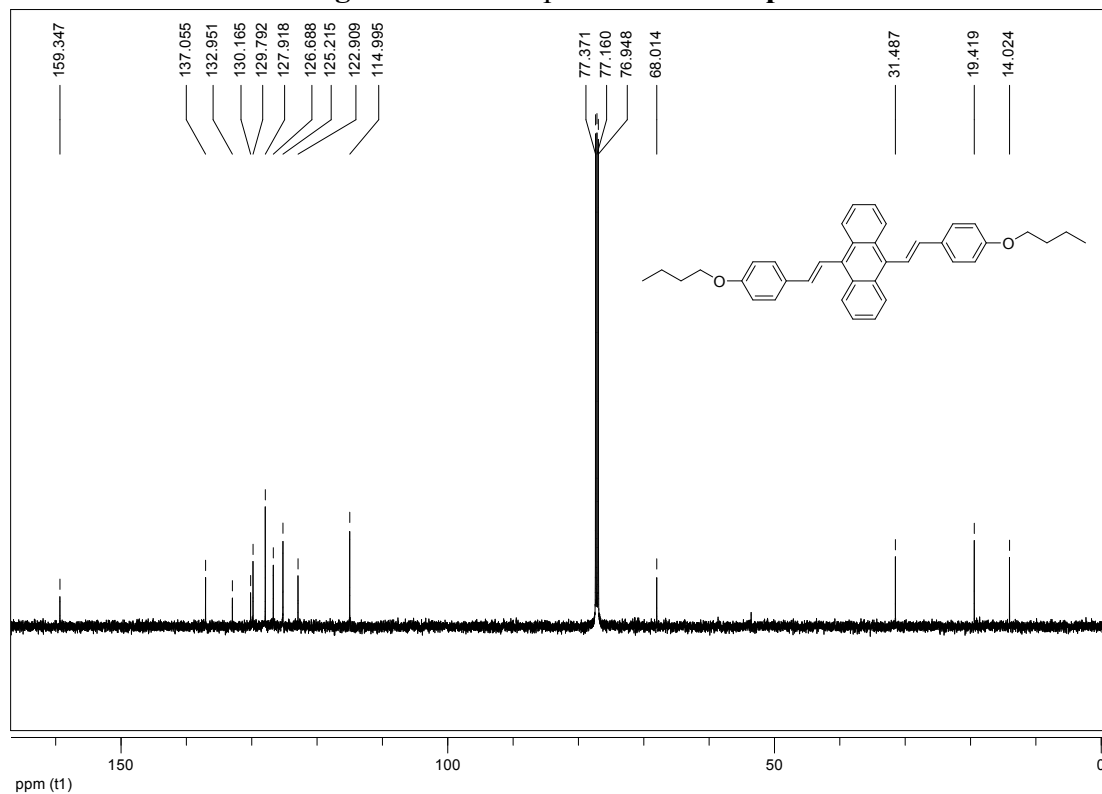
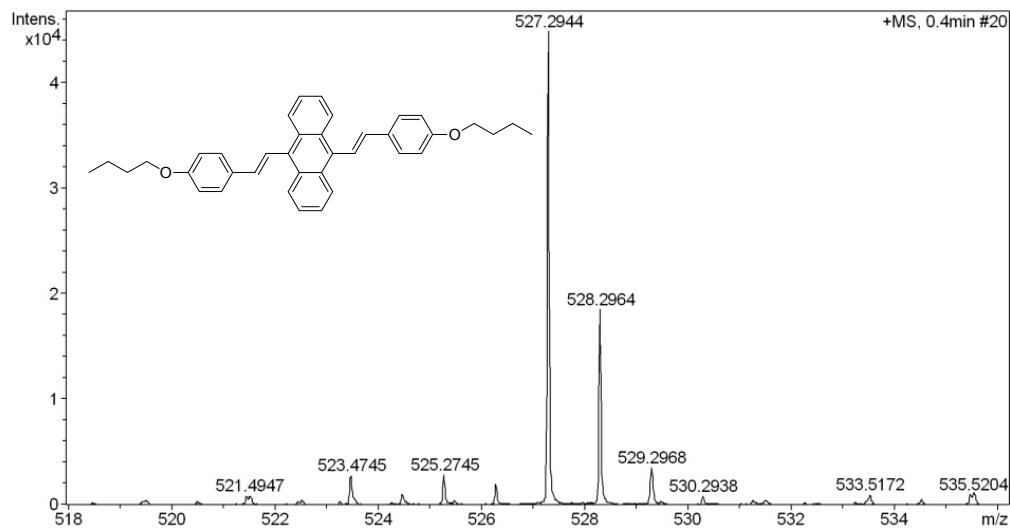
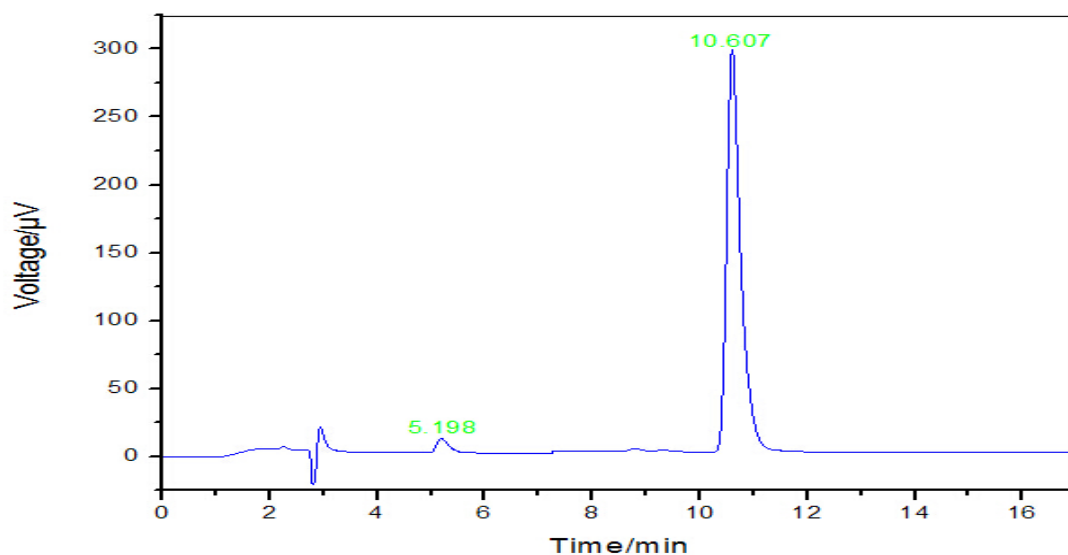


Fig. S7 ¹³C NMR spectrum of DSA-pn4

Acquisition Parameter

Source Type	APCI	Ion Polarity	Positive	Set Nebulizer	1.6 Bar
Focus	Active	Set Capillary	4000 V	Set Dry Heater	200 °C
Scan Begin	350 m/z	Set End Plate Offset	-500 V	Set Dry Gas	8.0 l/min
Scan End	2000 m/z	Set Collision Cell RF	600.0 Vpp	Set Divert Valve	Source

**Fig. S8 HRMS spectrum of DSA-pn4**

Peak	RT (min)	Height (µ V)	Area (µ V*Sec)	Area%
1	5.198	10.485	170825.857	3.05
2	10.607	295.756	5430554.000	96.95
Total		306.241	5601379.857	100.00

Fig. S9 HPLC spectrum of DSA-pn4

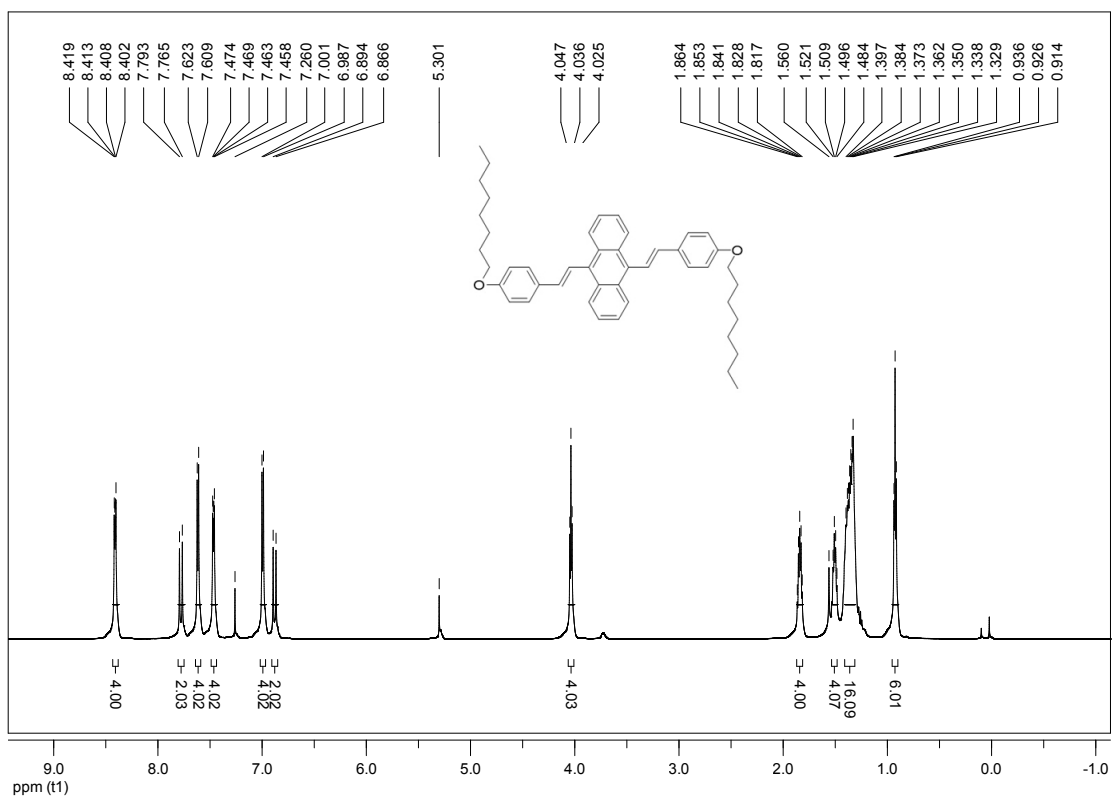


Fig. S10 ^1H NMR spectrum of DSA-pn8

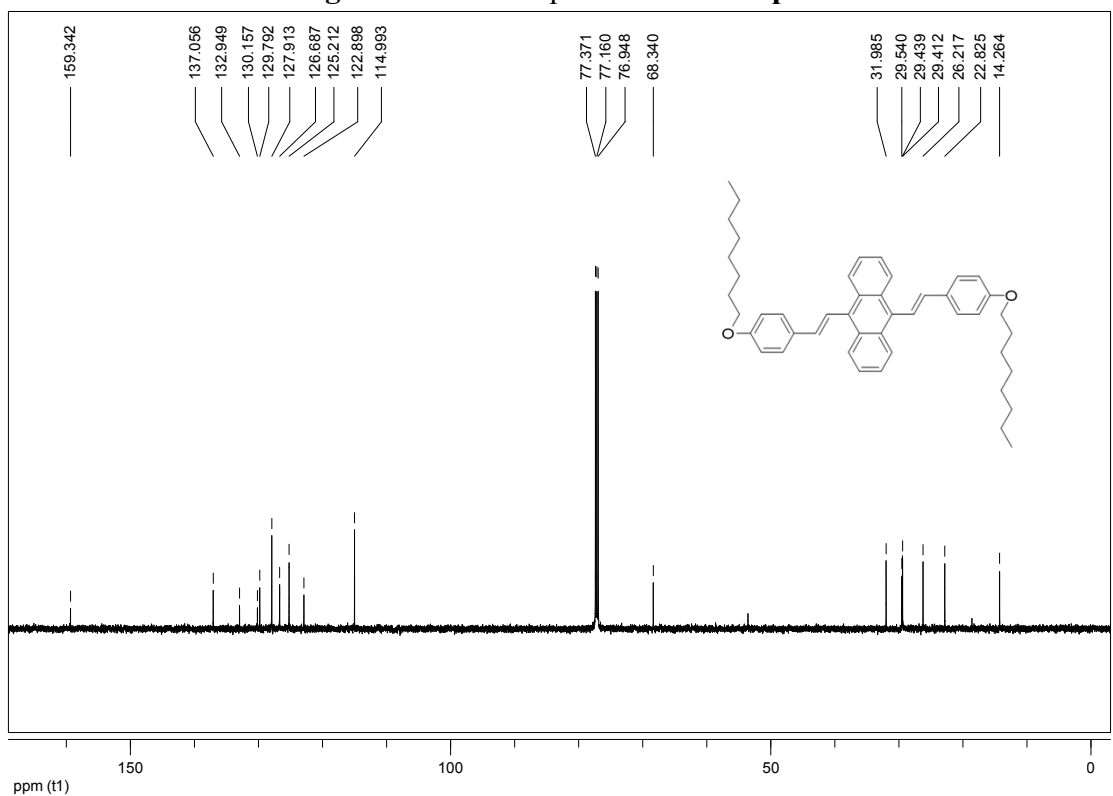
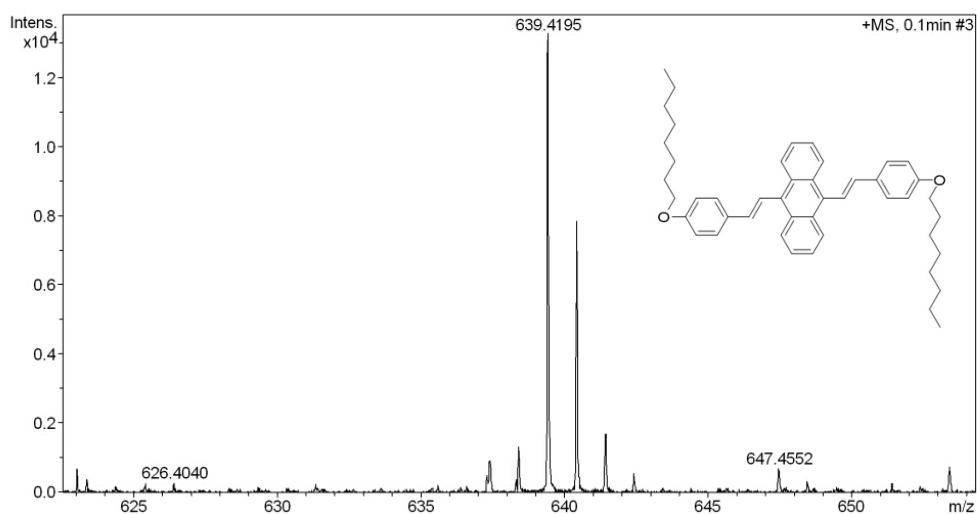
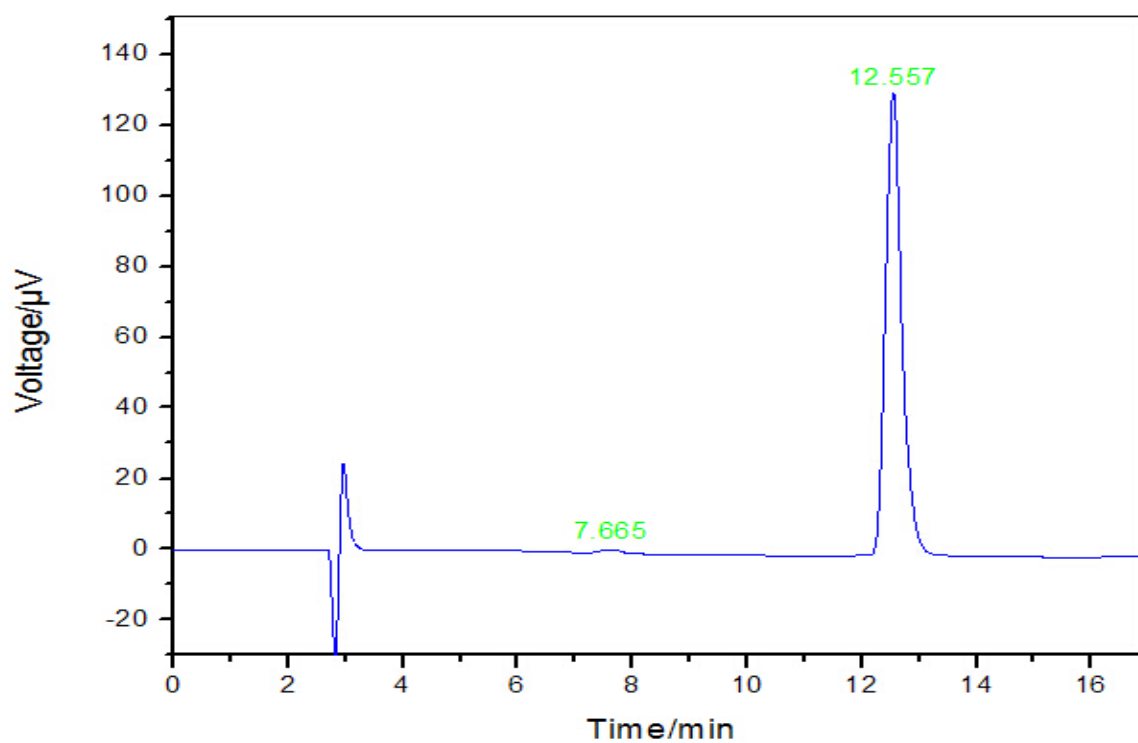


Fig. S11 ^{13}C NMR spectrum of DSA-pn8

Acquisition Parameter

Source Type	APCI	Ion Polarity	Positive	Set Nebulizer	1.6 Bar
Focus	Active	Set Capillary	4000 V	Set Dry Heater	200 °C
Scan Begin	350 m/z	Set End Plate Offset	-500 V	Set Dry Gas	8.0 l/min
Scan End	2000 m/z	Set Collision Cell RF	600.0 Vpp	Set Divert Valve	Source

**Fig. S12 HRMS spectrum of DSA-pn8**

Peak	RT (min)	Height (μV)	Area ($\mu\text{V}\cdot\text{min}$)	Area%
1	7.665	1.120	1607.200	0.97
2	12.557	130.566	2671387.250	99.03
Total		131.686	2672994.450	100.00

Fig. S13 HPLC spectrum of DSA-pn8

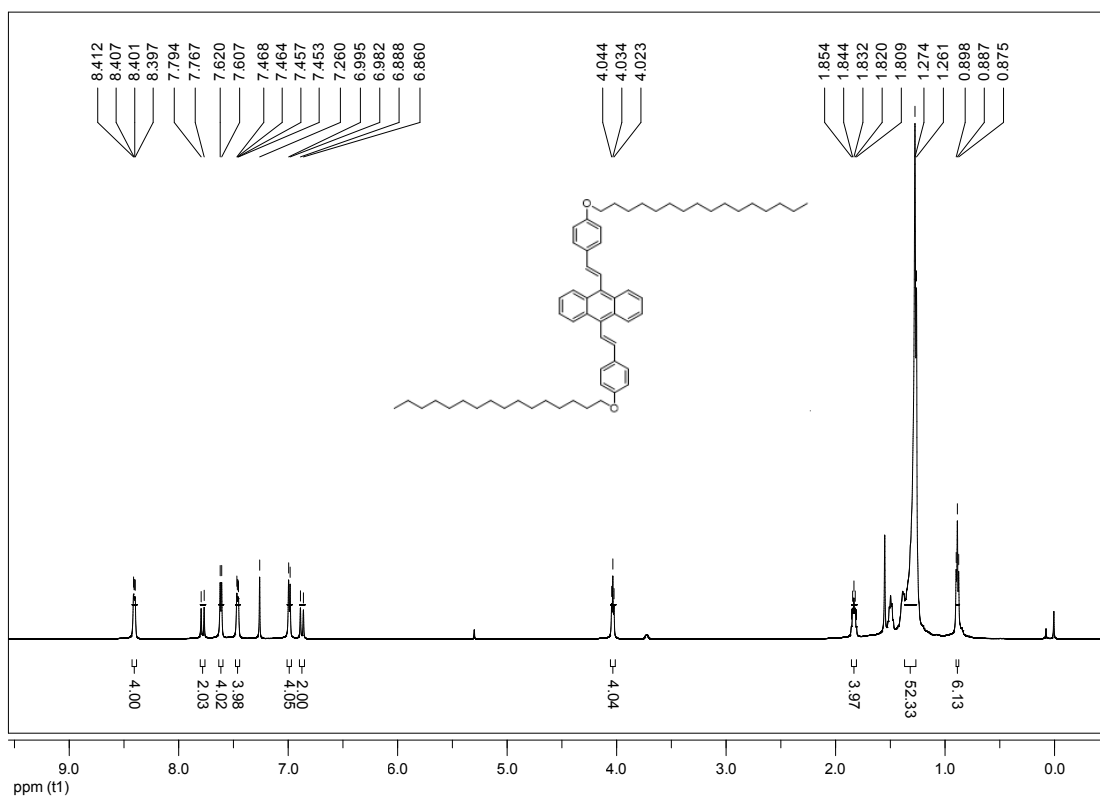


Fig. S14 ¹H NMR spectrum of DSA-pn16

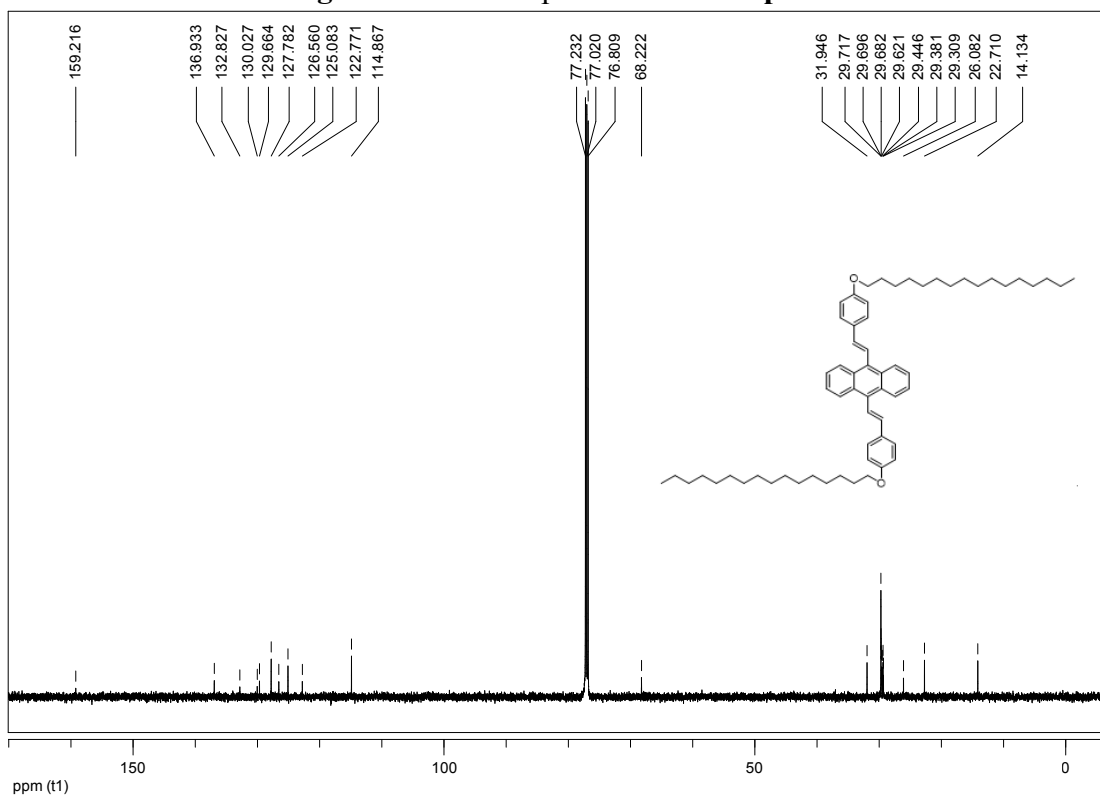


Fig. S15 ¹³C NMR spectrum of DSA-pn16

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	190 °C
Scan Begin	300 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1000 m/z	Set Collision Cell RF	150.0 Vpp	Set Divert Valve	Waste

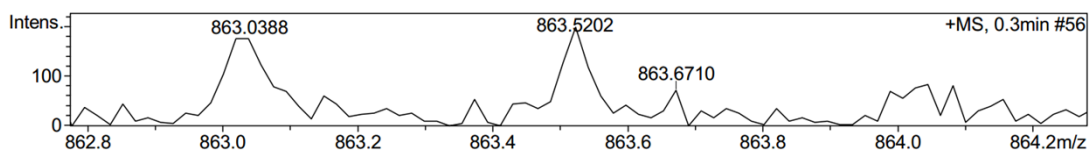
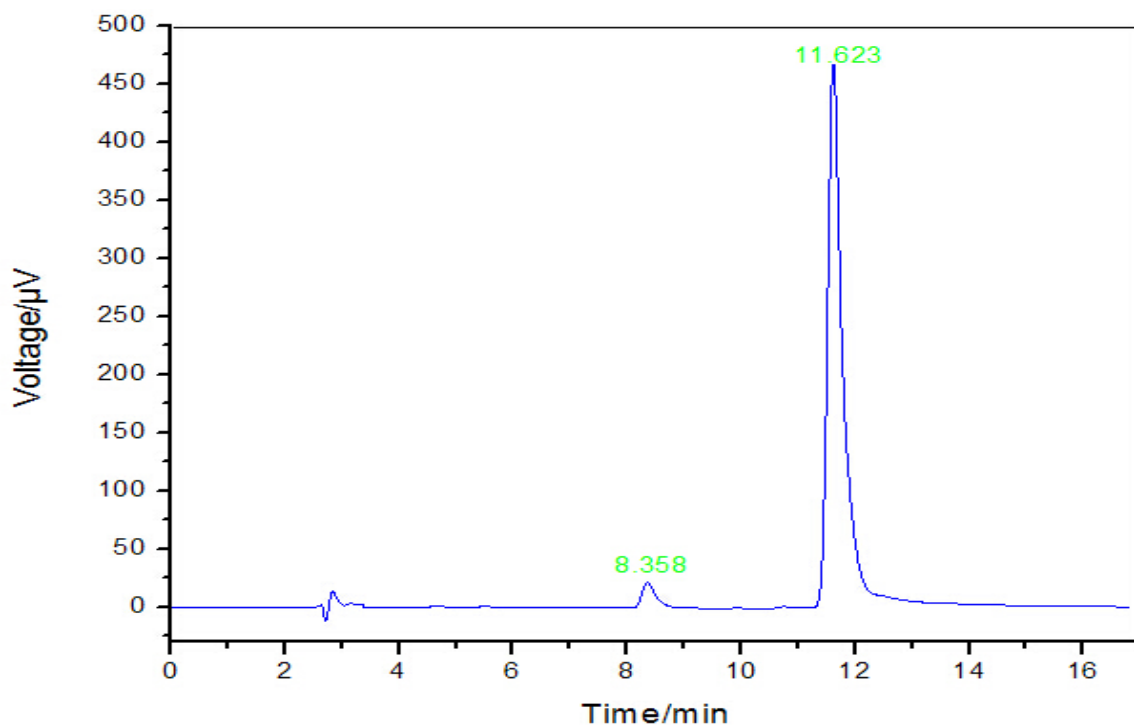


Fig. S16 HRMS spectrum of **DSA-pn16**



Peak	RT (min)	Height (μ V)	Area (μ V*min)	Area%
1	8.358	21.818	381709.938	3.89
2	11.623	468.182	9440492.000	96.11
Total		490.000	9822201.938	100.00

Fig. S17 HPLC spectrum of **DSA-pn16**

5 Crystallographic data

Table S2 Crystallographic data of **DSA-pn4**

Empirical formula	C ₃₈ H ₃₈ O ₂
Formula weight	526.68
Temperature	292.1(4) K
Wavelength	0.7107 Å
Crystal system, space group	Triclinic, P -1
Unit cell dimensions	a = 9.6115(5) Å alpha = 110.013(6) deg. b = 12.5777(8) Å beta = 107.490(5) deg. c = 14.3804(10) Å gamma = 99.474(5) deg.
Volume	1486.96(15) Å ³
Z, Calculated density	2, 1.150 Mg/m ³
Absorption coefficient	0.069 mm ⁻¹
F (000)	552
Crystal size	0.3900 x 0.2100 x 0.0700 mm
Theta range for data collection	3.00 to 26.37 deg.
Limiting indices	-11 ≤ h ≤ 12, -15 ≤ k ≤ 15, - 17 ≤ l ≤ 17
Reflections collected / unique	12303 / 6064 [R (int) = 0.0251]
Completeness to theta = 26.37	99.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.64979
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	6064 / 5 / 364
Goodness-of-fit on F ²	1.040
Final R indices [I > 2 sigma (I)]	R ₁ = 0.0674, wR ² = 0.1743
R indices (all data)	R ₁ = 0.1051, wR ² = 0.2033
Extinction coefficient	0.014(2)
Largest diff. peak and hole	0.429 and -0.311 e. Å ⁻³

Table S3 Crystallographic data of **DSA-pn8**

Empirical formula	C ₄₆ H ₅₄ O ₂
Formula weight	638.89
Temperature	293(2) K
Wavelength	1.54184 Å
Crystal system, space group	Triclinic, P -1
Unit cell dimensions	a = 9.0161(4) Å alpha = 78.313(4) deg. b = 16.5141(8) Å beta = 79.260(4) deg. c = 19.8096(9) Å gamma = 78.543(4) deg.
Volume	2797.8(2) Å ³
Z, Calculated density	2, 1.138 Mg/m ³
Absorption coefficient	0.512 mm ⁻¹

F(000)	1038
Crystal size	0.4800 x 0.1000 x 0.0800 mm
Theta range for data collection	3.29 to 67.08 deg.
Limiting indices	-9<=h<=10, -19<=k<=19, -21<=l<=23
Reflections collected / unique	18454 / 9928 [R(int) = 0.0316]
Completeness to theta = 67.08	99.3 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.58251
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	9928 / 2 / 736
Goodness-of-fit on F ²	1.077
Final R indices [I>2sigma(I)]	R1 = 0.0714, wR2 = 0.2035
R indices (all data)	R1 = 0.0944, wR2 = 0.2364
Extinction coefficient	0.0041(5)
Largest diff. peak and hole	0.684 and -0.338 e.A ⁻³

Table S4 Crystallographic data of **DSA-pn16**

Empirical formula	C ₆₂ H ₈₆ O ₂
Formula weight	863.30
Temperature	100.00(10) K
Wavelength	0.7107 Å
Crystal system, space group	Triclinic, P -1
Unit cell dimensions	a = 5.4009(2) Å alpha = 89.974(3) deg. b = 7.3944(3) Å beta = 89.926(3) deg. c = 31.9700(11) Å gamma = 88.837(3) deg.
Volume	1276.50(8) Å ³
Z, Calculated density	2, 1.123 Mg/m ³
Absorption coefficient	0.065 mm ⁻¹
F(000)	474
Crystal size	0.48 x 0.12 x 0.01 mm
Theta range for data collection	3.19 to 26.37 deg.
Limiting indices	-6<=h<=6, -9<=k<=9, -39<=l<=39
	1 / 5234 [R(int) = 0.0325]
Completeness to theta = 26.37	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.55454
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	5234 / 0 / 290
Goodness-of-fit on F ²	1.031
Final R indices [I>2sigma(I)]	R1 = 0.0509, wR2 = 0.1275
R indices (all data)	R1 = 0.0714, wR2 = 0.1406
Largest diff. peak and hole	0.221 and -0.238 e.A ⁻³
