Electronic Supporting Information (ESI) for

Bisindeno-annulated Pentacenes with Exceptionally High Photo-stability and Ordered Molecular Packing: Simple Synthesis by Regio-selective Scholl Reaction

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1. Experimental section

1.1. Materials

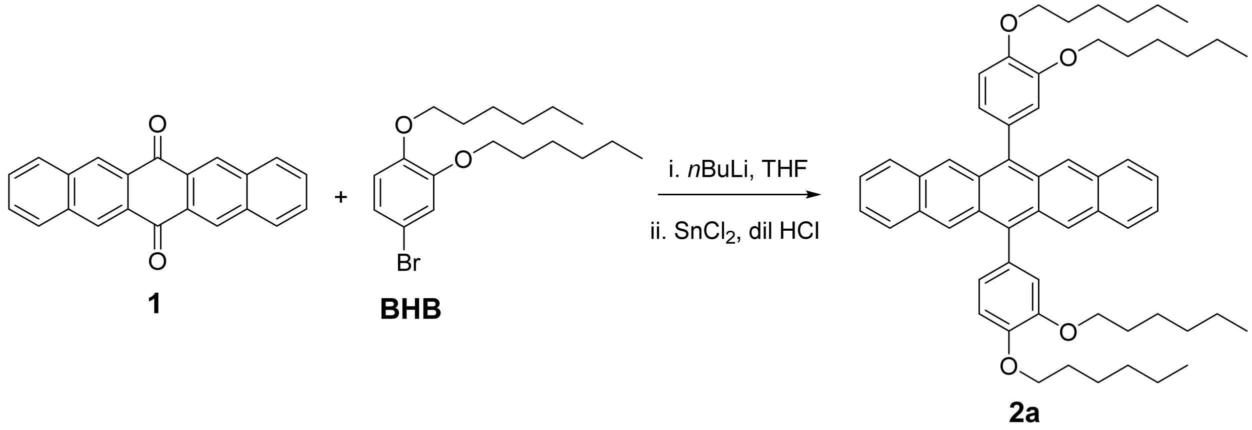
All the reagents were purchased from commercial sources without further purification. Anhydrous dichloromethane (DCM) was distilled from CaH_2. Anhydrous THF were distilled from sodium-benzophenone self-indicator drying process immediately prior to use.

1.2.General characterization method

^1H and ^{13}C NMR spectra were recorded using Bruker Advance 500 MHz spectrometer in $CDCl_3$ or 1,1,2,2 tetrachloroethane-d_2 with tetramethylsilane (TMS) as the internal standard. The chemical shift was recorded in ppm and the following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, m = multiplet, br = broad. Column chromatography was performed on silica gel 60 (Merck 40-60 nm, 230-400 mesh). ESI mass spectra were recorded on Agilent 5975C DIP/MS mass spectrometer and APCI mass was recorded with Bruker microTOF QII spectrometer. UV-vis absorption spectra were recorded on a Shimadzu UV-1700 spectrophotometer. Cyclic voltammetry and differential pulse voltammetry experiments were performed in anhydrous DCM on a CHI 620C electrochemical analyzer with a three-electrode cell, using 0.1M Bu_4NPF_6 as supporting electrolyte, AgCl/Ag as reference electrode, gold disk as working electrode, Pt wire as counter electrode, and scan rate at 50 mVs^{-1}. The potential was externally calibrated against the ferrocene/ferrocenium couple. The HOMO and LUMO energy levels were calculated using the following equations: HOMO = $-[E_{ox}^{onset} + 4.80]$ eV, LUMO = $-[E_{red}^{onset} + 4.80]$ eV, where E_{ox}^{onset} and E_{red}^{onset} are the onset of the first oxidation and reduction wave, respectively. Tapping-mode Atomic Force Microscopy (TM-AFM) was performed on a Nanoscope V microscope (Veeco Inc.). X-ray diffraction (XRD) patterns of the thin film were measured on a Bruker-AXS D8 DISCOVER with GADDS X-ray diffractometer. Copper K_α line was used as a radiation source with $\lambda = 1.5418$ Å.

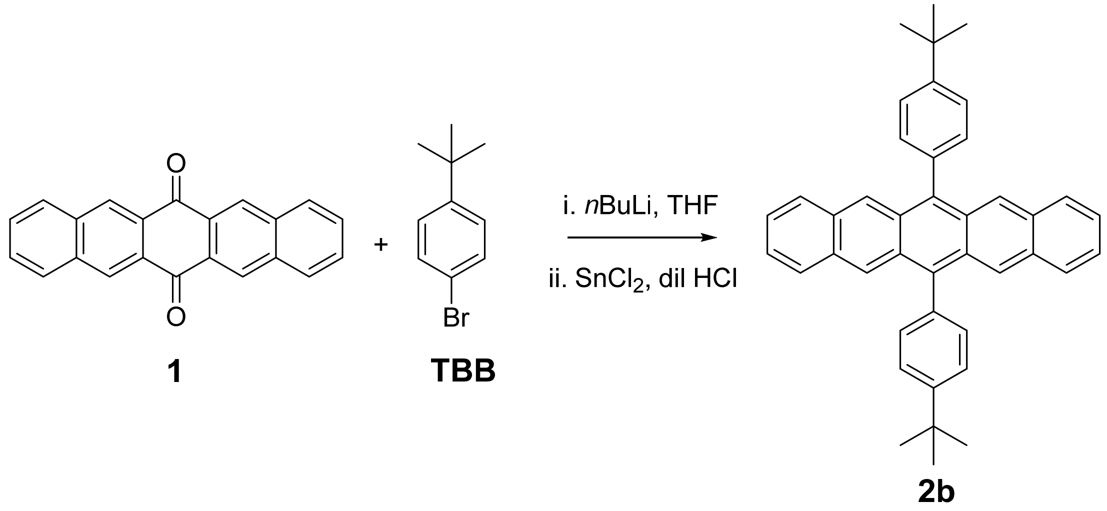
1.3. Synthetic procedures and characterization data

Preparation of 6,13-bis(3,4-bis(hexyloxy)phenyl)pentacene, ***2a***



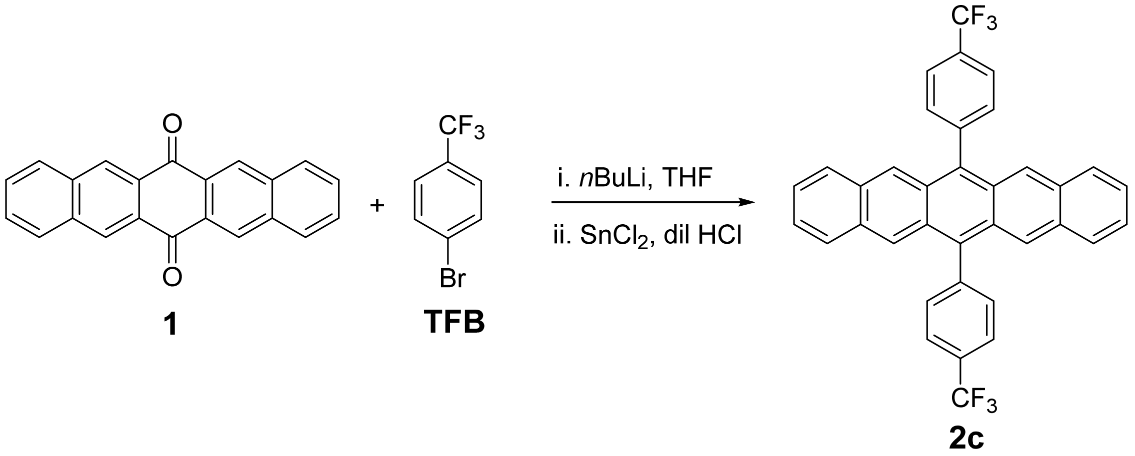
3.48 g (9.730 mmol) of 1-bromo-3,4-bis(hexyloxy)benzene (BHB) was dissolved in 10 mL of anhydrous THF in a dry round-bottom flask (RBF) that is evacuated and purged with argon beforehand and the solution was cooled down to -78 ^{o}C in a dry ice/acetone bath. 6.2 mL (9.892 mmol) of 1.6 M *n*-BuLi was added slowly into the stirring reaction mixture at -78 ^{o}C and the solution was allowed to gradually reach 0 ^{o}C over two hours. The reaction mass was cooled back to -78 ^{o}C and quickly charged with 0.5 g (1.6220 mmol) of compound **1** in one portion and stirred overnight, allowing it to reach room temperature. Reaction was quenched with 10 mL of 10% aqueous ammonium chloride solution and the intermediate *diol* was extracted with ethyl acetate (3x10mL). The organic layer was washed with water (30 ml) and dried over sodium sulphate and evaporated to dryness. The brownish yellow *diol* was then dissolved in 10 mL of THF and added 10 mL of saturated solution of $SnCl_2$ in 10% aq HCl. The mixture was stirred for 1 hour in dark and then diluted with 20 mL of water. The product was extracted using ethyl acetate (3x15 mL), washed with 30 mL of water, dried over sodium sulphate and evaporated the solvent under vacuum in dark. The crude mixture was eluted in silica gel column using 95:5 [hexane: ethylacetate] as eluent to collect the purple fraction, which was dried under vacuum in dark to give a purple liquid, **2a** in 60% yield (810 mg). HRMS (APCI): calcd for $C_{58}H_{70}O_4$ $(M+H)^+$, 831.5274; found, 831.5365 (error: -2.2 ppm). This compound is very sensitive to air and light due to its electron-rich character and the recorded NMR spectrum was very messy due to the rapid degradation during the measurement. The freshly prepared sample was used immediately for CV/DPV measurements under nitrogen and for next-step Scholl reaction.

Preparation of 6,13-bis(4-(tert-butyl)phenyl)pentacene, ***2b***



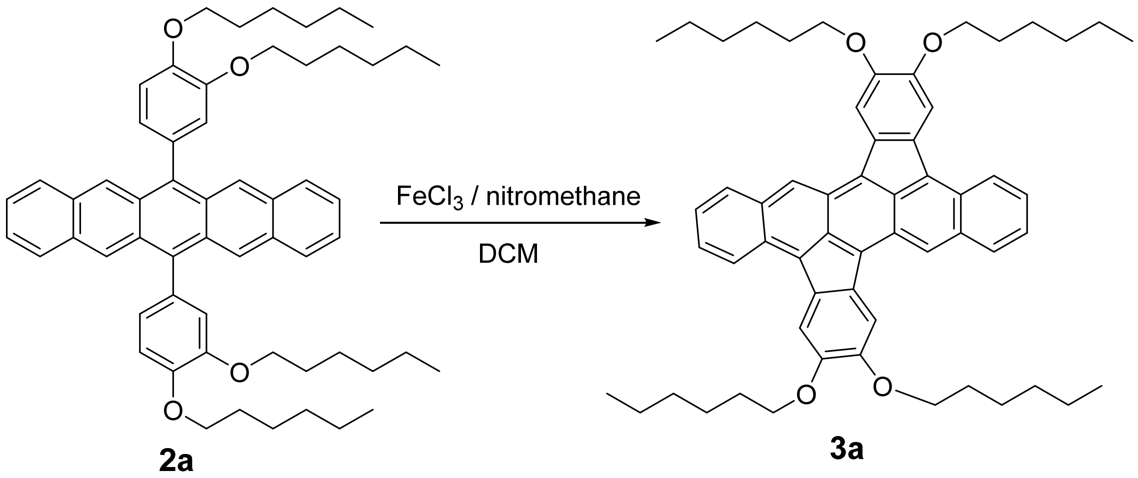
2.1 g (9.730 mmol) of 1-bromo-4-*tert*-butylbenzene (TBB) was dissolved in 10 mL of anhydrous THF in a dry RBF that is evacuated and purged with argon beforehand and the solution was cooled down to -78 °C in a dry ice/acetone bath. 6.2 mL (9.892 mmol) of 1.6 M *n*-BuLi was added slowly into the stirring reaction mixture at -78 °C and the solution was allowed to gradually reach 0 °C over two hours. The reaction mass was cooled back to -78 °C and quickly charged 0.5 g (1.6220 mmol) compound **1** in one portion and stirred overnight, allowing it to reach room temperature. Reaction was quenched with 10 mL of 10% aqueous ammonium chloride solution and the intermediate *diol* was extracted with ethyl acetate (3x10 mL). The organic layer was washed with water (30 mL) and dried over sodium sulphate and evaporated to dryness. The brownish yellow *diol* was then dissolved in 10 mL of THF and added 10 mL of saturated solution of $SnCl_2$ in 10% aq HCl. The mixture was stirred for 1 hour in dark and then diluted with 20 mL of water. The product was extracted using ethyl acetate (3x15 mL), washed with 30 mL of water, dried over sodium sulphate and evaporated the solvent under vacuum in dark. To the crude mixture obtained, 30 mL of anhydrous methanol was added and stirred well to precipitate out the dark purple solid which was later filtered using 20 mL of methanol. The crude solid was re-purified by dissolving in 3 mL of DCM and reprecipitating using 30 mL of anhydrous methanol and filtering to give the pure product **2b** in 64% yield (564 mg). HRMS (ESI): calcd for $C_{42}H_{38}$ (M^+), 542.2974; found, 542.2978 (error: -1.8 ppm). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): $\delta = 1.55$ (s, 18 H), aromatic peaks do not show up due to aggregation even it is soluble. ^{13}C NMR (125 MHz, $CDCl_3$, ppm): peaks do not show up due to aggregation. The high temperature ^{1}H NMR and ^{13}C NMR data are not available due to its poor stability at high temperature. The freshly prepared sample was used immediately for CV/DPV measurements under nitrogen and for next-step Scholl reaction.

Preparation of 6,13-bis(4-(trifluoromethyl)phenyl)pentacene, ***2c***



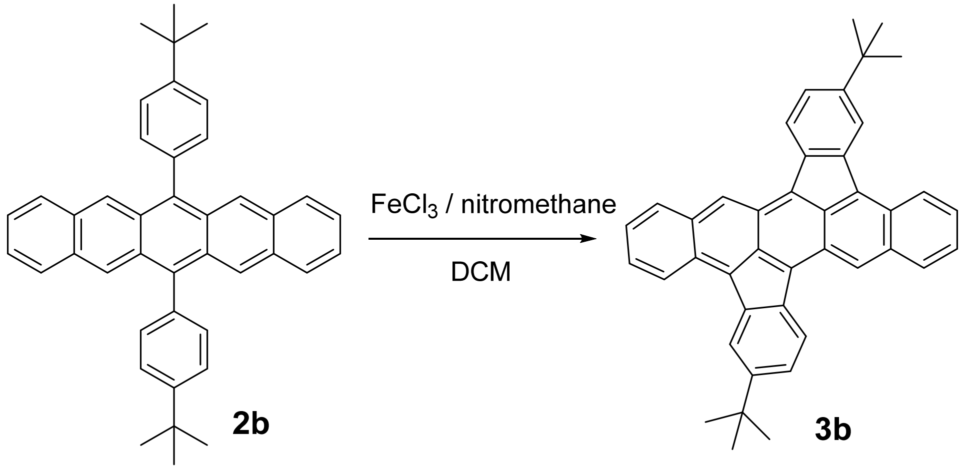
2.2 g (9.730 mmol) of 1-bromomo-4-trifluoromethylbenzene (TFB) was dissolved in 10 mL of anhydrous THF in a dry RBF that is evacuated and purged with argon beforehand and the solution was cooled down to -78 °C in a dry ice/acetone bath. 6.2 mL (9.892 mmol) of 1.6 M *n*-BuLi was added slowly into the stirring reaction mixture at -78 °C and the solution was allowed to gradually reach 0 °C over two hours. The reaction mass was cooled back to -78 °C and quickly charged 0.5 g (1.6220 mmol) **1** in one portion and stirred overnight, allowing it to reach room temperature. The reaction was quenched with 10 mL of 10% aqueous ammonium chloride solution and the intermediate *diol* was extracted with ethyl acetate (3x10 mL). The organic layer was washed with water (30 mL), dried over sodium sulphate and evaporated to dryness. The brownish yellow *diol* was then dissolved in 10 mL of THF and added 10 mL of saturated solution of $SnCl_2$ in 10% aq HCl. The mixture was stirred for 1 hour in dark and then diluted with 20 mL water. The product was extracted using ethyl acetate (3x15 mL), washed with 30 mL of water, dried over sodium sulphate and evaporated the solvent under vacuum in dark. To the crude mixture obtained, 30 mL of anhydrous methanol was added and stirred well to precipitate out the dark purple solid which was later filtered using 20 mL of methanol. The crude solid was re-purified by dissolving in 3 mL of DCM and reprecipitating using 30 mL of anhydrous methanol to give pure product **2c** in 81% yield (741 mg). HRMS (APCI): calcd for $C_{36}H_{20}F_6$ $(M+H)^+$, 567.1469; found, 567.1537 (error: 0.90 ppm). ^{1}H NMR and ^{13}C NMR ($CDCl_3$): peaks do not show up due to aggregation. The high temperature ^{1}H NMR and ^{13}C NMR data are not available due to its poor stability at high temperature. The freshly prepared sample was used immediately for next-step Scholl reaction.

Preparation of 6,7,15,16-tetrakis(hexyloxy)dibenzo[b,n]rubicene, ***3a***



300 mg (0.3610 mmol) of **2a** was dissolved in 300 mL of anhydrous DCM in a dry reaction flask. Argon gas was purged into the reaction mixture throughout the reaction. A solution of 468 mg (2.887 mmol) of anhydrous ferric chloride in 2 mL of nitromethane was charged into the reaction mixture through a syringe and stirred for 55 minutes at room temperature. Reaction was later quenched by 30 mL of methanol. Reaction mixture was later washed with 3x 100 mL of water and the dichloromethane layer was collected and evaporated to 10 mL. Addition of 60 mL of methanol precipitated the dark green solid which was filtered using 30 mL of methanol and re-precipitated using DCM / Acetonitrile to give pure product, **3a** in 54% yield (162 mg). ^{1}H NMR (500 MHz, 1,1,2,2-tetrachloroethane-d_2, ppm) at 100 ^{0}C: δ = 8.77 (br, 2H), 8.47 (br, 2H), 8.04 (br, 2H), 7.92 (br, 2H), 7.84 (br, 2H), 7.56 (br, 2H), 7.44 (br, 2H), 4.33 (t, 8H) , 2.03 (br, 8H), 1.72 (br, 8H), 1.54 (br, 16H), 1.06 (br, 12H). ^{13}C NMR (125 MHz, 1,1,2,2-tetrachloroethane-d_2, ppm): peaks do not show up even after overnight measurement due to aggregation. HRMS (APCI): calcd for $C_{58}H_{66}O_4$ (M^+), 826.4961; found, 826.5000 (error -4.7 ppm). Single crystal of this compound was obtained.

Preparation of 6,15-di-tert-butyldibenzo[b,n]rubicene, ***3b***



300 mg (0.5530 mmol) of **2b** was dissolved in 300 mL of anhydrous DCM in a dry reaction flask. Argon gas was purged into the reaction mixture throughout the reaction. A solution of 718 mg (4.4260 mmol) of anhydrous ferric chloride in 3 mL of nitromethane was charged into the reaction mixture through a syringe and stirred for 70 minutes at room temperature. The reaction was later quenched by 30 mL of methanol. Reaction mixture was later washed with 3x 100 mL of water and the dichloromethane layer was collected and evaporated to 10 mL. Addition of 60 mL of methanol precipitated the dark green solid which was filtered using 30 mL of methanol and reprecipitated using DCM / Acetonitrile to give pure product, **3b** with 72% yield (215 mg). ^{1}H NMR (500 MHz, 1,1,2,2-tetrachloroethane-d_2, ppm) at 100 ^{0}C: $\delta = 1.66$ (s, 18 H), broad aromatic peak is due to aggregation even it is soluble. ^{13}C NMR (125 MHz, 1,1,2,2-tetrachloroethane-d_2, ppm): peaks do not show up even after overnight measurement due to aggregation. HRMS (APCI): calcd for $C_{42}H_{34}$ $(M+H)^+$, 539.2661; found, 539.2731 (error: 0.5 ppm). Single crystal of this compound was obtained.

2. DFT calculation details

DFT calculations have been performed both at the B3LYP/6-31G*[1-5] level of theory, as implemented in the Gaussian 09 program package.[6]

Table S1. DFT (B3LYP/6-31G*) calculated energies levels of **2a**, **2b**, **3a** and **3b** (eV)

	2a (eV)	**2b** (eV)	**3a** (eV)	**3b** (eV)
LUMO+5	0.37	0.03	0.33	0.10
LUMO+4	0.36	0.00	0.07	-0.12
LUMO+3	0.19	-0.11	-0.20	-0.35
LUMO+2	-0.30	-0.40	-0.46	-0.65
LUMO+1	-0.75	-0.82	-1.12	-1.28
LUMO	-2.20	-2.28	-2.82	-2.95
HOMO	-4.35	-4.43	-4.60	-4.76
HOMO-1	-5.38	-5.73	-4.89	-5.47
HOMO-2	-5.40	-6.27	-4.98	-5.54
HOMO-3	-5.68	-6.40	-6.02	-6.48
HOMO-4	-6.19	-6.42	-6.37	-6.52
HOMO-5	-6.34	-6.73	-6.45	-6.77
HOMO-6	-6.35	-6.73	-6.50	-6.80
HOMO-7	-6.74	-6.83	-7.10	-7.46
HOMO-8	-7.26	-7.33	-7.50	-7.68
HOMO-9	-7.59	-7.67	-7.60	-8.10

Table S2. Selected TD-DFT (B3LYP/6-31G*) calculated wavelength, oscillator strength and compositions of major electronic transitions of **2a**.

Wavelength (nm)	Band gap (eV)	Ocilator Frequency (*f*)	Major contribution
663.0	1.87	0.1046	H-0->L+0(+101%)
302.4	4.10	0.2634	H-0->L+5(+82%) H-0->L+2(10%)
			H-4->L+0(6%)
297.3	4.17	0.2821	H-2->L+1(+66%) H-0->L+6(13%)
			H-0->L+2(7%) H-0->L+5(6%)
			H-4->L+0(6%)
295.7	4.19	0.4804	H-0->L+6(+46%) H-2>L+1(+31%)
			H-0->L+2(+12%) H-4->L+0(+7%)
286.8	4.32	1.5450	H-0->L+6(+36%) H-0->L+2(21%)
			H-4->L+0(19%) H-0->L+5(10%)
283.8	4.37	0.1385	H-8->L+0(+43%) H-3>L+2(+18%)
			H-0->L+8(+15%) H-4->L+1(+9%)
			H-1->L+2(+6%)

273.4	4.54	0.1046	H-3->L+1(+90%)
269.1	4.61	0.1017	H-1->L+2(+88%)

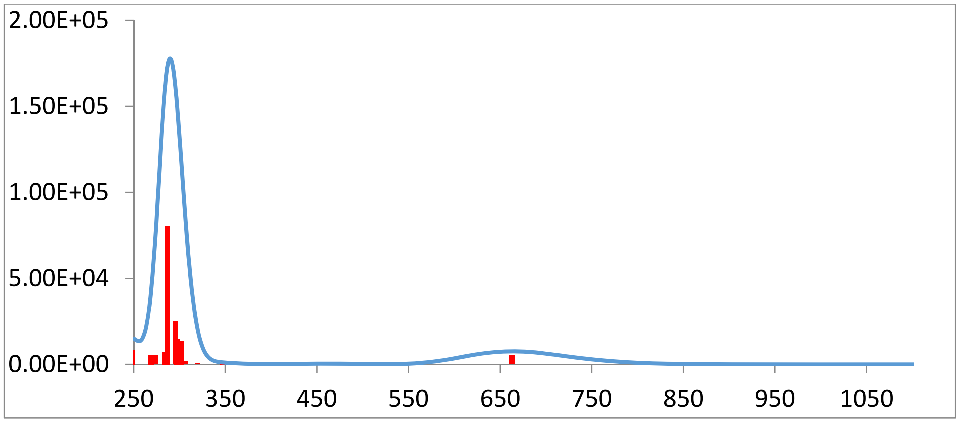


Fig. S1. Calculated (B3LYP/6-31G*) absorption spectrum of **2a**.

Table S3. Selected TD-DFT (B3LYP/6-31G**) calculated wavelength, oscillator strength and compositions of major electronic transitions of **2b**.

Wavelength (nm)	Band gap (eV)	Ocilator Frequency (*f*)	Major contribution
659.3	1.88	0.0984	H-0->L+0(+101%)
315.2	3.93	0.1178	H-0->L+6(+77%) H-0->L+2(10%) H-6 >L+0(7%)
288.0	4.31	2.6432	H-2->L+0(+39%) H-0->L+2(35%) H-0->L+6(20%)
274.1	4.52	0.1181	H-1->L+1(+90%)

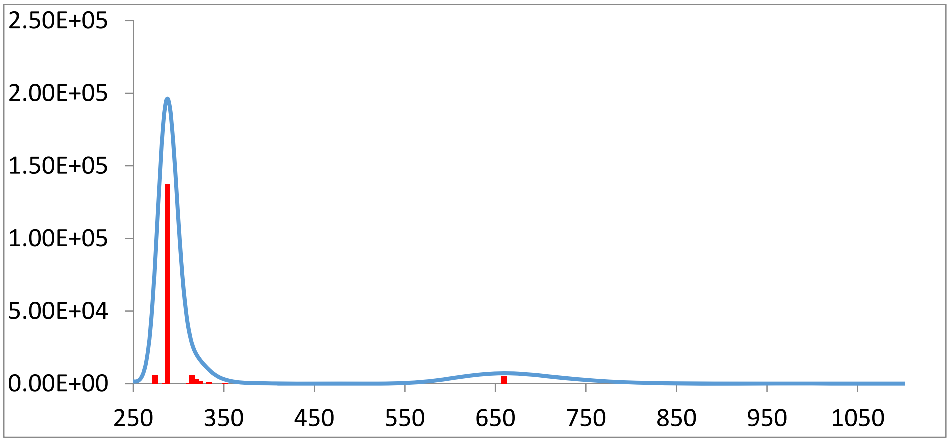


Fig. S2. Calculated (B3LYP/6-31G*) absorption spectrum of **2b**.

Table S4. Selected TD-DFT (B3LYP/6-31G*) calculated wavelength, oscillator strength and compositions of major electronic transitions of **3a**.

Wavelength (nm)	Band gap (eV)	Oscilator Frequency (*f*)	Major contributions
873.6	1.42	0.0659	H-1->L+0(+50%) H-0->L+0(+49%)
763.6	1.62	0.1179	H-0->L+0(+51%) H-1->L+0(49%)
408.7	3.03	0.1953	H-4->L+0(+75%) H-0->L+2(16%)
360.0	3.44	0.2174	H-2->L+1(+90%) H-0->L+3(6%)
332.4	3.73	0.2374	H-7->L+0(+59%) H-0->L+2(+26%)
323.9	3.83	0.5584	H-0->L+2(+43%) H-1->L+2(+36%) H-7->L+0(11%), H-4->L+0(+6%)
304.5	4.07	0.5334	H-1->L+2(+33%) H-0->L+3(27%) H-9->L+0(+10%) H-7->L+0(+6%) H-4->L+0(6%)
295.6	4.19	0.042	S H-9->L+0(+47%) H-1->L+3(+32%) H-0->L+5(14%)
290.1	4.27	0.3754	S H-1->L+3(+45%) H-9->L+0(35%)
281.7	4.4	0.2511	S H-0->L+5(+63%) H-1->L+3(+12%) H-3->L+1(11%) H-2->L+4(6%)
266.5	4.65	0.6829	S H-2->L+4(+64%) H-6->L+1(+10%) H-1->L+5(+5%)
263.3	4.71	0.2194	S H-1->L+5(+63%) H-2->L+4(16%) H-2->L+6(+11%)
252.7	4.91	0.3258	S H-6->L+1(+71%) H-1->L+5(12%) H-2->L+4(5%)

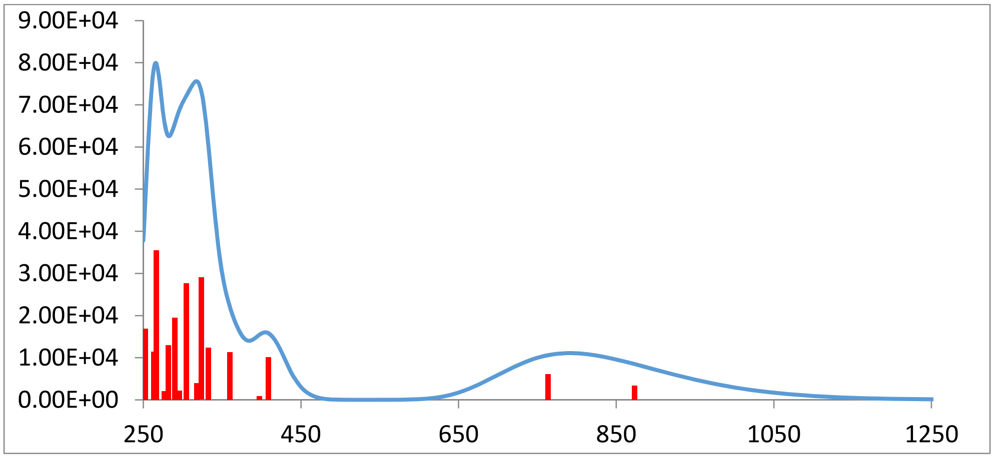


Fig. S3. Calculated (B3LYP/6-31G*) absorption spectrum of **3a**.

Table S5. Selected TD-DFT (B3LYP/6-31G*) calculated wavelength, oscillator strength and compositions of major electronic transitions of **3b**.

Wavelength (nm)	Bandgap (eV)	Ocilator Frequency (*f*)	Major contribution
776.1	1.60	0.1785	H-0->L+0(+101%)
409.1	3.03	0.1984	H-3->L+0(+76%) H-0->L+2(16%)
333.1	3.72	0.2109	H-0->L+2(+41%) H-2->L+1(31%) H-0>L+3(17%)
327.2	3.79	0.4135	H-1->L+1(+36%) H-2->L+1(+33%) H-0->L+2(+21%)
310.6	3.99	0.1531	H-7->L+0(+82%) H-0->L+2(+5%)
302.6	4.10	0.5873	H-0->L+3(+45%) H-7->L+0(11%) H-1->L+1(8%)
			H-3->L+0(+7%) H-2->L+2(6%)
289.2	4.29	0.3435	H-0->L+5(+70%) H-2->L+2(6%) H-1->L+2(+6%)
282.7	4.39	0.4413	H-2->L+2(+57%) H-0->L+5(+16%) H-1->L+2(8%)
265.2	4.68	0.4060	H-2->L+3(+65%) H-1->L+3(9%) H-10->L+0(8%)

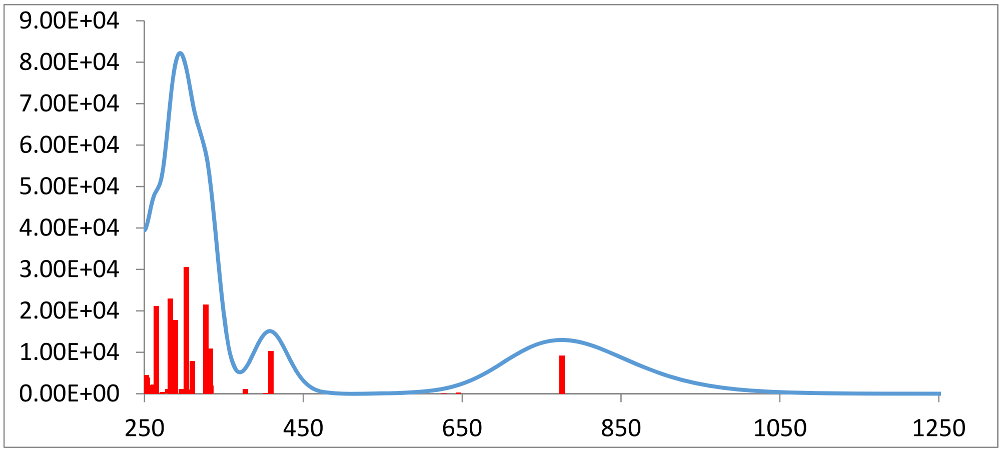


Fig. S4. Calculated (B3LYP/6-31G*) absorption spectrum of **3b**.

References

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A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J.; Gaussian, Inc., Wallingford CT, 2009.

3. Electrochemical analysis (CV and DPV)

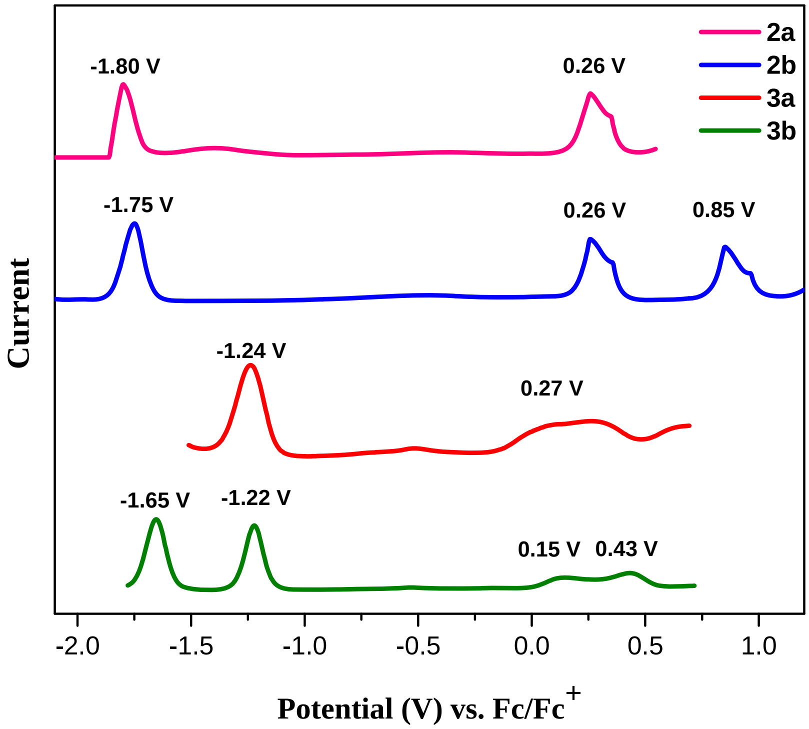


Fig. S5. Differential pulse voltammograms of **2a**, **2b**, **3a** and **3b** in dry dichloromethane with 0.1 M $n\mathrm{Bu_4NPF_6}$ as the supporting electrolyte, AgCl/Ag as reference electrode, Au as working electrode, Pt wire as counter electrode.

4. Photostability test

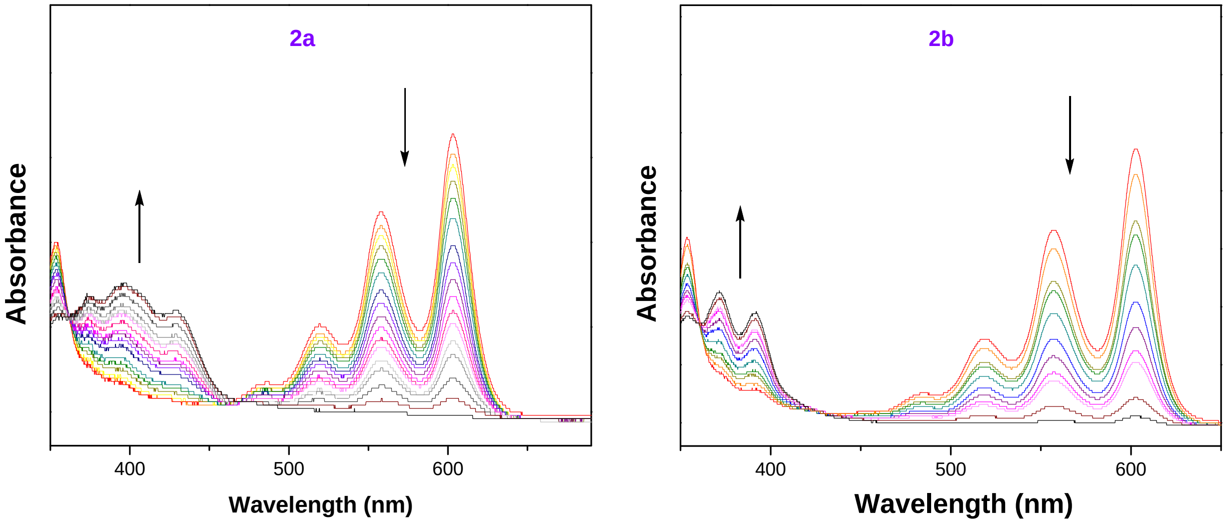
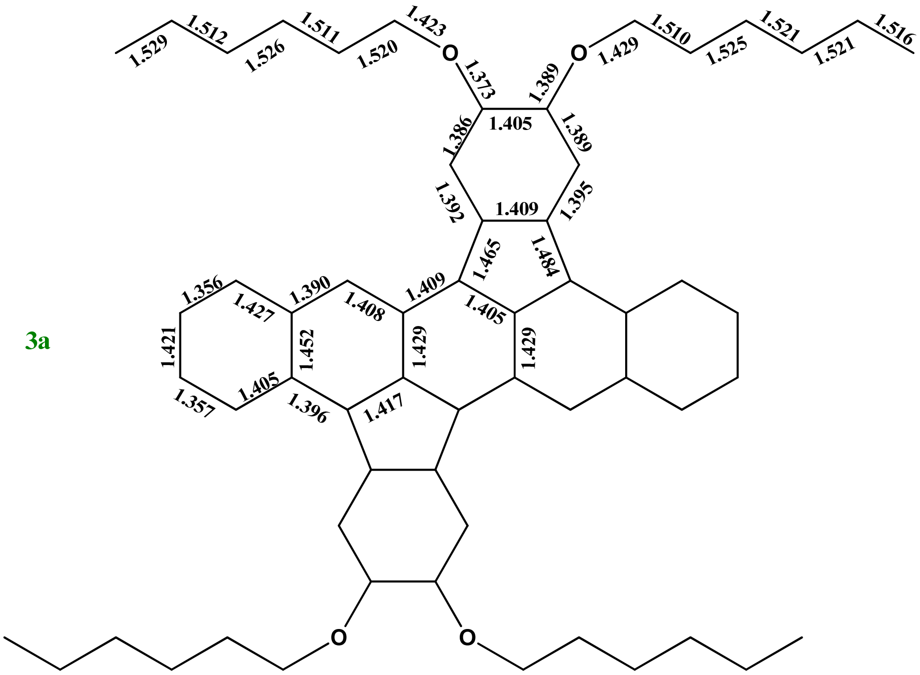


Fig. S6. Changes of the UV-vis absorption spectra of (a) **2a** and (b) **2b** in 10^{-5} M $CHCl_3$ solutions under ambient light and air conditions.

5. Crystallographic data of 3a and 3b

3a



3b

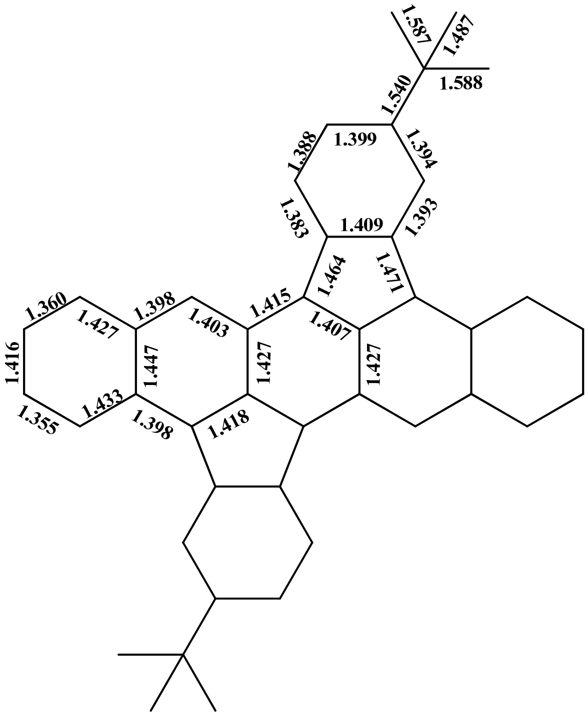


Fig. S7. Selected bond lengths of **3a** and **3b** (based on X-ray crystallographic structures).

Table S6. Crystal data and structure refinement for **3a**

Identification code	**3a**	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 4.6842(5) Å	α= 107.779(5)°.
	b = 14.8758(15) Å	β= 94.984(5)°.
	c = 17.8030(18) Å	γ = 91.886(5)°.
Volume	1174.5(2) Å^3	
Z	1	
Density (calculated)	1.215 Mg/m^3	
Absorption coefficient	0.585 mm^{-1}	
F(000)	464	
Crystal size	0.540 x 0.080 x 0.030 mm^3	
Theta range for data collection	2.620 to 66.583°.	
Index ranges	-5<=h<=5, -17<=k<=17, -21<=l<=21	
Reflections collected	14776	
Independent reflections	4108 [R(int) = 0.0388]	
Completeness to theta = 66.650°	98.4 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7528 and 0.6358	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4108 / 14 / 344	
Goodness-of-fit on F^2	1.037	
Final R indices [I>2sigma(I)]	R1 = 0.0512, wR2 = 0.1248	
R indices (all data)	R1 = 0.0702, wR2 = 0.1359	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.571 and -0.552 e.Å^{-3}	

Table S7. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for **3a**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1S)	2160(16)	9693(6)	4675(5)	33(1)
O(1S)	4925(13)	10264(5)	4828(4)	33(1)
C(2S)	3972(14)	9877(7)	4868(6)	33(1)
O(2S)	902(10)	9979(4)	4915(4)	33(1)
C(24)	2960(40)	1622(13)	6678(13)	40(2)
C(25)	2860(60)	871(18)	7095(11)	47(2)
C(26)	3010(20)	1121(9)	7987(9)	42(2)
C(27)	2525(18)	233(6)	8230(5)	48(2)
C(28)	2818(13)	440(4)	9120(3)	55(2)
C(29)	2410(20)	-466(5)	9344(5)	73(2)
C(30)	3300(40)	1702(15)	6797(15)	40(2)
C(31)	2540(60)	850(20)	7067(12)	47(2)
C(32)	4010(20)	1176(11)	7919(10)	50(3)
C(33)	3910(20)	401(8)	8334(7)	60(3)
C(34)	1014(16)	230(4)	8577(4)	55(2)
C(35)	926(19)	-623(5)	8908(5)	65(2)
O(1)	-2003(3)	3638(1)	7786(1)	26(1)
O(2)	1070(3)	2326(1)	7027(1)	30(1)
C(1)	-491(4)	3859(1)	7236(1)	24(1)
C(2)	-515(4)	4718(1)	7080(1)	24(1)
C(3)	1101(4)	4862(1)	6500(1)	23(1)
C(4)	2759(4)	4138(1)	6080(1)	23(1)
C(5)	2801(4)	3282(1)	6245(1)	24(1)
C(6)	1178(4)	3141(1)	6819(1)	25(1)
C(7)	1411(4)	5666(1)	6178(1)	22(1)
C(8)	3248(4)	5375(1)	5567(1)	22(1)
C(9)	4136(4)	4460(1)	5491(1)	22(1)
C(10)	287(4)	6555(1)	6339(1)	22(1)
C(11)	-1605(4)	6924(1)	6931(1)	26(1)
C(12)	-2641(4)	7792(2)	7049(1)	30(1)

C(13)	-1866(4)	8369(2)	6584(1)	31(1)
C(14)	-85(4)	8049(1)	6012(1)	28(1)
C(15)	1067(4)	7142(1)	5860(1)	24(1)
C(16)	5967(4)	4054(1)	4907(1)	22(1)
C(17)	7134(4)	3162(1)	4737(1)	24(1)
C(18)	-3567(4)	4369(1)	8265(1)	25(1)
C(19)	-5132(4)	3966(1)	8808(1)	25(1)
C(20)	-3153(4)	3674(2)	9408(1)	27(1)
C(21)	-4777(4)	3365(2)	10000(1)	26(1)
C(22)	-2850(5)	3144(2)	10645(1)	35(1)
C(23)	-4486(5)	2951(2)	11284(1)	41(1)

Table S8. Bond lengths [Å] and angles [°] for **3a**.

C(1S)-O(1S)	1.483(5)
C(1S)-H(1S1)	0.9800
C(1S)-H(1S2)	0.9800
C(1S)-H(1S3)	0.9800
O(1S)-H(1S)	0.8400
C(2S)-O(2S)	1.458(5)
C(2S)-H(2S1)	0.9800
C(2S)-H(2S2)	0.9800
C(2S)-H(2S3)	0.9800
O(2S)-H(2S)	0.8400
C(24)-O(2)	1.422(7)
C(24)-C(25)	1.519(14)
C(24)-H(24A)	0.9900
C(24)-H(24B)	0.9900
C(25)-C(26)	1.511(14)
C(25)-H(25A)	0.9900
C(25)-H(25B)	0.9900
C(26)-C(27)	1.526(11)
C(26)-H(26A)	0.9900
C(26)-H(26B)	0.9900

C(27)-C(28)	1.512(10)
C(27)-H(27A)	0.9900
C(27)-H(27B)	0.9900
C(28)-C(29)	1.529(7)
C(28)-H(28A)	0.9900
C(28)-H(28B)	0.9900
C(29)-H(29A)	0.9800
C(29)-H(29B)	0.9800
C(29)-H(29C)	0.9800
C(30)-O(2)	1.425(8)
C(30)-C(31)	1.524(16)
C(30)-H(30A)	0.9900
C(30)-H(30B)	0.9900
C(31)-C(32)	1.536(16)
C(31)-H(31A)	0.9900
C(31)-H(31B)	0.9900
C(32)-C(33)	1.548(13)
C(32)-H(32A)	0.9900
C(32)-H(32B)	0.9900
C(33)-C(34)	1.497(10)
C(33)-H(33A)	0.9900
C(33)-H(33B)	0.9900
C(34)-C(35)	1.554(8)
C(34)-H(34A)	0.9900
C(34)-H(34B)	0.9900
C(35)-H(35A)	0.9800
C(35)-H(35B)	0.9800
C(35)-H(35C)	0.9800
O(1)-C(1)	1.367(2)
O(1)-C(18)	1.429(2)
O(2)-C(6)	1.373(2)
C(1)-C(2)	1.389(3)
C(1)-C(6)	1.405(3)
C(2)-C(3)	1.395(3)
C(2)-H(2)	0.9500
C(3)-C(4)	1.409(3)

C(3)-C(7)	1.484(3)
C(4)-C(5)	1.393(3)
C(4)-C(9)	1.465(3)
C(5)-C(6)	1.386(3)
C(5)-H(5)	0.9500
C(7)-C(10)	1.396(3)
C(7)-C(8)	1.417(3)
C(8)-C(9)	1.407(3)
C(8)-C(16)#1	1.429(3)
C(9)-C(16)	1.410(3)
C(10)-C(11)	1.429(3)
C(10)-C(15)	1.452(3)
C(11)-C(12)	1.357(3)
C(11)-H(11)	0.9500
C(12)-C(13)	1.421(3)
C(12)-H(12)	0.9500
C(13)-C(14)	1.356(3)
C(13)-H(13)	0.9500
C(14)-C(15)	1.427(3)
C(14)-H(14)	0.9500
C(15)-C(17)#1	1.390(3)
C(16)-C(17)	1.408(3)
C(16)-C(8)#1	1.429(3)
C(17)-C(15)#1	1.390(3)
C(17)-H(17)	0.9500
C(18)-C(19)	1.511(3)
C(18)-H(18A)	0.9900
C(18)-H(18B)	0.9900
C(19)-C(20)	1.525(3)
C(19)-H(19A)	0.9900
C(19)-H(19B)	0.9900
C(20)-C(21)	1.520(3)
C(20)-H(20A)	0.9900
C(20)-H(20B)	0.9900
C(21)-C(22)	1.521(3)
C(21)-H(21A)	0.9900

C(21)-H(21B)	0.9900
C(22)-C(23)	1.516(3)
C(22)-H(22A)	0.9900
C(22)-H(22B)	0.9900
C(23)-H(23A)	0.9800
C(23)-H(23B)	0.9800
C(23)-H(23C)	0.9800

O(1S)-C(1S)-H(1S1)	109.5
O(1S)-C(1S)-H(1S2)	109.5
H(1S1)-C(1S)-H(1S2)	109.5
O(1S)-C(1S)-H(1S3)	109.5
H(1S1)-C(1S)-H(1S3)	109.5
H(1S2)-C(1S)-H(1S3)	109.5
C(1S)-O(1S)-H(1S)	109.5
O(2S)-C(2S)-H(2S1)	109.5
O(2S)-C(2S)-H(2S2)	109.5
H(2S1)-C(2S)-H(2S2)	109.5
O(2S)-C(2S)-H(2S3)	109.5
H(2S1)-C(2S)-H(2S3)	109.5
H(2S2)-C(2S)-H(2S3)	109.5
C(2S)-O(2S)-H(2S)	109.5
O(2)-C(24)-C(25)	107.9(17)
O(2)-C(24)-H(24A)	110.1
C(25)-C(24)-H(24A)	110.1
O(2)-C(24)-H(24B)	110.1
C(25)-C(24)-H(24B)	110.1
H(24A)-C(24)-H(24B)	108.4
C(26)-C(25)-C(24)	122.2(18)
C(26)-C(25)-H(25A)	106.8
C(24)-C(25)-H(25A)	106.8
C(26)-C(25)-H(25B)	106.8
C(24)-C(25)-H(25B)	106.8
H(25A)-C(25)-H(25B)	106.6
C(25)-C(26)-C(27)	110.4(13)
C(25)-C(26)-H(26A)	109.6

C(27)-C(26)-H(26A)	109.6
C(25)-C(26)-H(26B)	109.6
C(27)-C(26)-H(26B)	109.6
H(26A)-C(26)-H(26B)	108.1
C(28)-C(27)-C(26)	112.4(8)
C(28)-C(27)-H(27A)	109.1
C(26)-C(27)-H(27A)	109.1
C(28)-C(27)-H(27B)	109.1
C(26)-C(27)-H(27B)	109.1
H(27A)-C(27)-H(27B)	107.9
C(27)-C(28)-C(29)	111.2(5)
C(27)-C(28)-H(28A)	109.4
C(29)-C(28)-H(28A)	109.4
C(27)-C(28)-H(28B)	109.4
C(29)-C(28)-H(28B)	109.4
H(28A)-C(28)-H(28B)	108.0
C(28)-C(29)-H(29A)	109.5
C(28)-C(29)-H(29B)	109.5
H(29A)-C(29)-H(29B)	109.5
C(28)-C(29)-H(29C)	109.5
H(29A)-C(29)-H(29C)	109.5
H(29B)-C(29)-H(29C)	109.5
O(2)-C(30)-C(31)	105(2)
O(2)-C(30)-H(30A)	110.8
C(31)-C(30)-H(30A)	110.8
O(2)-C(30)-H(30B)	110.8
C(31)-C(30)-H(30B)	110.8
H(30A)-C(30)-H(30B)	108.9
C(30)-C(31)-C(32)	100.9(19)
C(30)-C(31)-H(31A)	111.6
C(32)-C(31)-H(31A)	111.6
C(30)-C(31)-H(31B)	111.6
C(32)-C(31)-H(31B)	111.6
H(31A)-C(31)-H(31B)	109.4
C(31)-C(32)-C(33)	113.5(15)
C(31)-C(32)-H(32A)	108.9

C(33)-C(32)-H(32A)	108.9
C(31)-C(32)-H(32B)	108.9
C(33)-C(32)-H(32B)	108.9
H(32A)-C(32)-H(32B)	107.7
C(34)-C(33)-C(32)	113.4(7)
C(34)-C(33)-H(33A)	108.9
C(32)-C(33)-H(33A)	108.9
C(34)-C(33)-H(33B)	108.9
C(32)-C(33)-H(33B)	108.9
H(33A)-C(33)-H(33B)	107.7
C(33)-C(34)-C(35)	111.7(6)
C(33)-C(34)-H(34A)	109.3
C(35)-C(34)-H(34A)	109.3
C(33)-C(34)-H(34B)	109.3
C(35)-C(34)-H(34B)	109.3
H(34A)-C(34)-H(34B)	107.9
C(34)-C(35)-H(35A)	109.5
C(34)-C(35)-H(35B)	109.5
H(35A)-C(35)-H(35B)	109.5
C(34)-C(35)-H(35C)	109.5
H(35A)-C(35)-H(35C)	109.5
H(35B)-C(35)-H(35C)	109.5
C(1)-O(1)-C(18)	117.06(15)
C(6)-O(2)-C(24)	117.0(10)
C(6)-O(2)-C(30)	116.7(12)
O(1)-C(1)-C(2)	124.68(18)
O(1)-C(1)-C(6)	115.08(17)
C(2)-C(1)-C(6)	120.24(17)
C(1)-C(2)-C(3)	119.65(18)
C(1)-C(2)-H(2)	120.2
C(3)-C(2)-H(2)	120.2
C(2)-C(3)-C(4)	119.88(18)
C(2)-C(3)-C(7)	132.28(18)
C(4)-C(3)-C(7)	107.79(16)
C(5)-C(4)-C(3)	120.24(17)
C(5)-C(4)-C(9)	131.16(18)

C(3)-C(4)-C(9)	108.57(16)
C(6)-C(5)-C(4)	119.63(18)
C(6)-C(5)-H(5)	120.2
C(4)-C(5)-H(5)	120.2
O(2)-C(6)-C(5)	124.28(18)
O(2)-C(6)-C(1)	115.35(16)
C(5)-C(6)-C(1)	120.36(18)
C(10)-C(7)-C(8)	119.54(17)
C(10)-C(7)-C(3)	134.52(17)
C(8)-C(7)-C(3)	105.93(16)
C(9)-C(8)-C(7)	111.11(16)
C(9)-C(8)-C(16)#1	125.42(17)
C(7)-C(8)-C(16)#1	123.47(18)
C(8)-C(9)-C(16)	118.80(17)
C(8)-C(9)-C(4)	106.60(16)
C(16)-C(9)-C(4)	134.58(18)
C(7)-C(10)-C(11)	124.85(17)
C(7)-C(10)-C(15)	117.56(17)
C(11)-C(10)-C(15)	117.59(17)
C(12)-C(11)-C(10)	121.67(18)
C(12)-C(11)-H(11)	119.2
C(10)-C(11)-H(11)	119.2
C(11)-C(12)-C(13)	120.73(19)
C(11)-C(12)-H(12)	119.6
C(13)-C(12)-H(12)	119.6
C(14)-C(13)-C(12)	119.91(19)
C(14)-C(13)-H(13)	120.0
C(12)-C(13)-H(13)	120.0
C(13)-C(14)-C(15)	121.82(19)
C(13)-C(14)-H(14)	119.1
C(15)-C(14)-H(14)	119.1
C(17)#1-C(15)-C(14)	120.01(18)
C(17)#1-C(15)-C(10)	121.71(18)
C(14)-C(15)-C(10)	118.28(17)
C(17)-C(16)-C(9)	128.17(17)
C(17)-C(16)-C(8)#1	116.04(17)

C(9)-C(16)-C(8)#1	115.78(17)
C(15)#1-C(17)-C(16)	121.67(17)
C(15)#1-C(17)-H(17)	119.2
C(16)-C(17)-H(17)	119.2
O(1)-C(18)-C(19)	108.18(15)
O(1)-C(18)-H(18A)	110.1
C(19)-C(18)-H(18A)	110.1
O(1)-C(18)-H(18B)	110.1
C(19)-C(18)-H(18B)	110.1
H(18A)-C(18)-H(18B)	108.4
C(18)-C(19)-C(20)	113.95(16)
C(18)-C(19)-H(19A)	108.8
C(20)-C(19)-H(19A)	108.8
C(18)-C(19)-H(19B)	108.8
C(20)-C(19)-H(19B)	108.8
H(19A)-C(19)-H(19B)	107.7
C(21)-C(20)-C(19)	112.77(16)
C(21)-C(20)-H(20A)	109.0
C(19)-C(20)-H(20A)	109.0
C(21)-C(20)-H(20B)	109.0
C(19)-C(20)-H(20B)	109.0
H(20A)-C(20)-H(20B)	107.8
C(20)-C(21)-C(22)	114.01(16)
C(20)-C(21)-H(21A)	108.7
C(22)-C(21)-H(21A)	108.7
C(20)-C(21)-H(21B)	108.7
C(22)-C(21)-H(21B)	108.7
H(21A)-C(21)-H(21B)	107.6
C(23)-C(22)-C(21)	113.28(18)
C(23)-C(22)-H(22A)	108.9
C(21)-C(22)-H(22A)	108.9
C(23)-C(22)-H(22B)	108.9
C(21)-C(22)-H(22B)	108.9
H(22A)-C(22)-H(22B)	107.7
C(22)-C(23)-H(23A)	109.5
C(22)-C(23)-H(23B)	109.5

H(23A)-C(23)-H(23B)	109.5
C(22)-C(23)-H(23C)	109.5
H(23A)-C(23)-H(23C)	109.5
H(23B)-C(23)-H(23C)	109.5

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y+1,-z+1

Table S9. Anisotropic displacement parameters ($Å^2$x 10^3) for **3a**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(24)	59(4)	26(3)	40(5)	12(3)	26(3)	9(3)
C(25)	70(4)	27(1)	52(2)	18(1)	30(2)	11(3)
C(26)	47(5)	37(3)	53(4)	27(3)	10(4)	3(4)
C(27)	63(6)	40(4)	47(4)	21(3)	11(5)	9(4)
C(28)	76(4)	49(3)	46(3)	26(3)	-1(3)	7(3)
C(29)	106(6)	63(4)	66(4)	45(4)	-4(4)	1(4)
C(30)	59(4)	26(3)	40(5)	12(3)	26(3)	9(3)
C(31)	70(4)	27(1)	52(2)	18(1)	30(2)	11(3)
C(32)	59(7)	44(4)	62(5)	36(4)	15(6)	12(6)
C(33)	72(7)	57(6)	64(6)	36(5)	12(5)	20(5)
C(34)	65(5)	59(4)	46(4)	23(3)	10(4)	10(3)
C(35)	77(5)	64(4)	60(5)	28(4)	6(4)	-6(4)
O(1)	24(1)	35(1)	26(1)	18(1)	8(1)	5(1)
O(2)	30(1)	34(1)	34(1)	21(1)	9(1)	4(1)
C(1)	17(1)	37(1)	21(1)	16(1)	1(1)	0(1)
C(2)	19(1)	34(1)	22(1)	14(1)	0(1)	2(1)
C(3)	18(1)	33(1)	20(1)	14(1)	-2(1)	0(1)
C(4)	18(1)	33(1)	19(1)	12(1)	-1(1)	-1(1)
C(5)	22(1)	30(1)	21(1)	10(1)	2(1)	2(1)
C(6)	22(1)	31(1)	24(1)	15(1)	-2(1)	-1(1)
C(7)	18(1)	32(1)	19(1)	12(1)	-2(1)	-2(1)
C(8)	18(1)	31(1)	18(1)	11(1)	-1(1)	-1(1)
C(9)	19(1)	30(1)	18(1)	10(1)	-1(1)	-1(1)

C(10)	19(1)	30(1)	20(1)	11(1)	-2(1)	-2(1)
C(11)	25(1)	34(1)	22(1)	13(1)	3(1)	0(1)
C(12)	30(1)	34(1)	26(1)	9(1)	6(1)	3(1)
C(13)	32(1)	30(1)	33(1)	13(1)	6(1)	5(1)
C(14)	29(1)	31(1)	29(1)	15(1)	4(1)	2(1)
C(15)	20(1)	30(1)	22(1)	11(1)	-2(1)	-1(1)
C(16)	19(1)	30(1)	19(1)	11(1)	-2(1)	-2(1)
C(17)	22(1)	32(1)	22(1)	15(1)	1(1)	-1(1)
C(18)	22(1)	32(1)	25(1)	13(1)	3(1)	4(1)
C(19)	22(1)	31(1)	25(1)	13(1)	6(1)	2(1)
C(20)	23(1)	37(1)	24(1)	14(1)	4(1)	3(1)
C(21)	24(1)	34(1)	25(1)	13(1)	4(1)	2(1)
C(22)	31(1)	48(1)	31(1)	22(1)	1(1)	0(1)
C(23)	43(1)	58(2)	33(1)	28(1)	7(1)	9(1)

Table S10. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **3a**.

	x	y	z	U(eq)
H(1S1)	2412	9135	4852	49
H(1S2)	1531	9490	4106	49
H(1S3)	709	10075	4965	49
H(1S)	4777	10695	4616	49
H(2S1)	5044	10432	5245	49
H(2S2)	4425	9822	4330	49
H(2S3)	4510	9307	4999	49
H(2S)	-5	9468	4650	49
H(24A)	4937	1907	6740	48
H(24B)	2345	1336	6105	48
H(25A)	1057	475	6879	56
H(25B)	4456	461	6925	56
H(26A)	1537	1570	8188	51
H(26B)	4921	1433	8226	51

H(27A)	579	-58	8010	58
H(27B)	3932	-229	7999	58
H(28A)	1369	885	9352	66
H(28B)	4744	746	9344	66
H(29A)	456	-749	9151	110
H(29B)	2692	-316	9922	110
H(29C)	3803	-914	9102	110
H(30A)	5192	2009	7060	48
H(30B)	3370	1507	6216	48
H(31A)	3326	270	6739	56
H(31B)	434	748	7056	56
H(32A)	3072	1733	8235	60
H(32B)	6043	1375	7910	60
H(33A)	4492	-198	7969	72
H(33B)	5325	587	8810	72
H(34A)	-440	106	8113	66
H(34B)	519	804	8987	66
H(35A)	2284	-486	9386	98
H(35B)	1456	-1190	8507	98
H(35C)	-1017	-729	9041	98
H(2)	-1627	5206	7367	29
H(5)	3936	2797	5966	28
H(11)	-2152	6552	7250	31
H(12)	-3898	8017	7448	36
H(13)	-2596	8977	6674	37
H(14)	410	8441	5703	34
H(17)	6680	2758	5039	29
H(18A)	-4958	4598	7925	30
H(18B)	-2233	4908	8581	30
H(19A)	-6372	3407	8482	30
H(19B)	-6396	4444	9099	30
H(20A)	-2034	3147	9120	32
H(20B)	-1780	4213	9699	32
H(21A)	-6037	2795	9709	32
H(21B)	-6023	3873	10252	32
H(22A)	-1777	2584	10400	42

H(22B)	-1433	3685	10894	42
H(23A)	-5537	3505	11534	62
H(23B)	-3133	2821	11684	62
H(23C)	-5847	2402	11045	62

Table S11. Crystal data and structure refinement for **3b**

Identification code	**3b**	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal size	0.100 x 0.260 x 0.360 mm	
Crystal system	monoclinic	
Space group	C 1 2/c 1	
Unit cell dimensions	a = 27.2227(14) Å	α = 90°
	b = 16.4194(8) Å	β = 101.7790(18)°
	c = 6.9476(4) Å	γ = 90°
Volume	3040.0(3) Å^3	
Z	4	
Density (calculated)	1.256 g/cm^3	
Absorption coefficient	0.074 mm^{-1}	
F(000)	1216	
Theta range for data collection	2.48 to 25.03°	
Index ranges	-32<=h<=32, -19<=k<=19, -8<=l<=8	
Reflections collected	35647	
Independent reflections	2694 [R(int) = 0.0597]	
Max. and min. transmission	0.7457 and 0.6662	
Structure solution technique	direct methods	
Structure solution program	SHELXS-97 (Sheldrick 2008)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2014 (Sheldrick, 2014)	
Function minimized	Σ w(F$_o^2$ - F$_c^2$)^2	
Data / restraints / parameters	2694 / 55 / 247	
Goodness-of-fit on F^2	1.037	
Δ/σ_{max}	0.001	
Final R indices	2243 data; I>2σ(I) R1 = 0.0549, wR2 = 0.1467	

	all data	R1 = 0.0665, wR2 = 0.1564
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0767P)^2+4.6491P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	0.456 and -0.364 eÅ^{-3}	
R.M.S. deviation from mean	0.048 eÅ^{-3}	

Table S12. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for **3b.**

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	**y/b**	**z/c**	**U(eq)**
O1S	0.4555(2)	0.0867(4)	0.6028(8)	0.1063(18)
C1S	0.4793(4)	0.0294(7)	0.4813(18)	0.146(4)
O1W	0.5	0.0325(9)	0.75	0.179(5)
C19	0.67533(13)	0.15824(19)	0.2847(5)	0.0456(7)
C20	0.69168(13)	0.1572(2)	0.6526(5)	0.0452(8)
C21	0.62928(12)	0.06314(18)	0.4611(5)	0.0428(7)
C19A	0.7106(3)	0.1960(5)	0.4724(14)	0.0439(12)
C20A	0.6627(4)	0.1134(6)	0.6719(14)	0.0461(12)
C21A	0.6430(4)	0.1052(5)	0.3053(14)	0.0466(12)
C1	0.62224(7)	0.59257(12)	0.4642(2)	0.0233(4)
C2	0.66100(7)	0.65021(13)	0.4559(3)	0.0295(5)
C3	0.70789(7)	0.62601(14)	0.4417(3)	0.0333(5)
C4	0.71881(7)	0.54197(13)	0.4323(3)	0.0317(5)
C5	0.68339(7)	0.48456(13)	0.4380(3)	0.0266(5)
C6	0.63357(6)	0.50668(12)	0.4557(2)	0.0219(4)
C7	0.59524(7)	0.45123(11)	0.4660(2)	0.0207(4)
C8	0.54743(6)	0.48095(11)	0.4831(2)	0.0190(4)
C9	0.53566(6)	0.56545(11)	0.4900(2)	0.0191(4)
C10	0.57464(7)	0.62015(12)	0.4798(2)	0.0222(4)
C11	0.51402(6)	0.41634(11)	0.4924(2)	0.0194(4)
C12	0.54190(7)	0.34072(11)	0.4828(2)	0.0222(4)
C13	0.52865(7)	0.25957(12)	0.4875(3)	0.0284(5)
C14	0.56391(8)	0.19928(13)	0.4794(3)	0.0334(5)
C15	0.61324(8)	0.21840(13)	0.4666(3)	0.0315(5)
C16	0.62640(7)	0.30025(12)	0.4596(3)	0.0277(5)
C17	0.59164(7)	0.36182(11)	0.4670(2)	0.0220(4)
C18	0.65303(9)	0.15160(13)	0.4679(3)	0.0386(6)

Table S13. Bond lengths (Å) for **3b.**

O1S-C1S	1.498(11)	C19-C18	1.522(4)
C20-C18	1.487(4)	C21-C18	1.587(4)
C19A-C18	1.723(9)	C20A-C18	1.523(9)
C21A-C18	1.343(9)	C1-C10	1.398(3)
C1-C2	1.427(3)	C1-C6	1.447(3)
C2-C3	1.360(3)	C3-C4	1.416(3)
C4-C5	1.355(3)	C5-C6	1.433(2)
C6-C7	1.398(3)	C7-C8	1.417(2)
C7-C17	1.471(3)	C8-C11	1.407(3)
C8-C9	1.427(2)	C9-C10	1.403(3)
C9-C11	1.415(2)	C11-C9	1.415(2)
C11-C12	1.464(2)	C12-C13	1.383(3)
C12-C17	1.424(3)	C13-C14	1.388(3)
C14-C15	1.400(3)	C15-C16	1.394(3)
C15-C18	1.540(3)	C16-C17	1.393(3)
C10-C1-C2	119.54(18)	C10-C1-C6	121.84(17)
C2-C1-C6	118.62(17)	C3-C2-C1	121.5(2)
C2-C3-C4	119.82(19)	C5-C4-C3	121.29(18)
C4-C5-C6	121.18(19)	C7-C6-C5	124.67(18)
C7-C6-C1	117.71(16)	C5-C6-C1	117.63(17)
C6-C7-C8	119.21(17)	C6-C7-C17	134.52(16)
C8-C7-C17	106.26(16)	C11-C8-C7	110.95(16)
C11-C8-C9	125.43(16)	C7-C8-C9	123.63(17)
C10-C9-C11	127.98(17)	C10-C9-C8	116.33(16)
C11-C9-C8	115.69(17)	C1-C10-C9	121.28(17)
C8-C11-C9	118.88(16)	C8-C11-C12	106.94(15)
C9-C11-C12	134.18(17)	C13-C12-C17	119.55(17)
C13-C12-C11	132.56(17)	C17-C12-C11	107.89(16)
C12-C13-C14	120.04(19)	C13-C14-C15	121.5(2)
C16-C15-C14	118.37(17)	C16-C15-C18	120.08(19)
C14-C15-C18	121.51(19)	C17-C16-C15	121.13(19)
C16-C17-C12	119.36(18)	C16-C17-C7	132.66(18)
C12-C17-C7	107.96(15)	C20-C18-C19	112.6(3)
C21A-C18-C20A	121.0(6)	C21A-C18-C15	112.1(4)
C20-C18-C15	109.5(2)	C19-C18-C15	110.13(19)

C20A-C18-C15	106.7(3)	C20-C18-C21	107.2(2)
C19-C18-C21	105.7(2)	C15-C18-C21	111.7(2)
C21A-C18-C19A	106.4(5)	C20A-C18-C19A	100.0(5)
C15-C18-C19A	109.6(3)		

Table S14.Anisotropic atomic displacement parameters (Å^2) for **3b.**
The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	**U_{22}**	**U_{33}**	**U_{23}**	**U_{13}**	**U_{12}**
O1S	0.116(3)	0.128(4)	0.094(3)	-0.037(3)	0.063(3)	-0.044(3)
C1S	0.137(6)	0.142(6)	0.156(6)	-0.003(4)	0.024(4)	-0.006(4)
O1W	0.178(6)	0.195(6)	0.177(6)	0	0.068(5)	0
C19	0.0554(17)	0.0331(14)	0.0570(17)	0.0049(13)	0.0319(14)	0.0192(13)
C20	0.0432(16)	0.0377(15)	0.0548(17)	0.0038(13)	0.0101(14)	0.0224(13)
C21	0.0505(16)	0.0286(13)	0.0545(17)	0.0062(12)	0.0225(14)	0.0189(12)
C19A	0.045(2)	0.034(2)	0.058(2)	0.006(2)	0.021(2)	0.020(2)
C20A	0.048(2)	0.035(2)	0.058(2)	0.008(2)	0.017(2)	0.021(2)
C21A	0.053(2)	0.034(2)	0.059(2)	0.002(2)	0.025(2)	0.017(2)
C1	0.0205(9)	0.0351(11)	0.0140(8)	0.0046(7)	0.0032(7)	0.0041(8)
C2	0.0254(10)	0.0366(11)	0.0263(10)	0.0063(8)	0.0048(8)	0.0021(8)
C3	0.0216(10)	0.0471(13)	0.0314(11)	0.0102(9)	0.0056(8)	-0.0013(9)
C4	0.0193(9)	0.0501(13)	0.0268(10)	0.0094(9)	0.0072(8)	0.0086(9)
C5	0.0207(9)	0.0398(11)	0.0201(9)	0.0053(8)	0.0061(7)	0.0095(8)
C6	0.0196(9)	0.0347(10)	0.0115(8)	0.0036(7)	0.0031(7)	0.0077(8)
C7	0.0197(9)	0.0313(10)	0.0113(8)	0.0014(7)	0.0033(7)	0.0084(7)
C8	0.0190(9)	0.0276(10)	0.0102(8)	0.0006(7)	0.0027(6)	0.0074(7)
C9	0.0190(9)	0.0274(10)	0.0103(8)	0.0005(7)	0.0015(6)	0.0071(7)
C10	0.0230(9)	0.0275(9)	0.0159(9)	0.0018(7)	0.0031(7)	0.0055(8)
C11	0.0199(9)	0.0267(9)	0.0113(8)	0.0001(7)	0.0022(7)	0.0071(7)
C12	0.0228(9)	0.0288(10)	0.0144(9)	0.0006(7)	0.0024(7)	0.0092(8)
C13	0.0256(10)	0.0291(10)	0.0301(11)	0.0008(8)	0.0049(8)	0.0061(8)
C14	0.0378(12)	0.0271(10)	0.0356(12)	0.0011(9)	0.0079(9)	0.0119(9)
C15	0.0377(12)	0.0338(11)	0.0242(10)	0.0043(8)	0.0089(8)	0.0181(9)
C16	0.0260(10)	0.0373(11)	0.0212(10)	0.0048(8)	0.0085(8)	0.0155(8)
C17	0.0231(9)	0.0301(10)	0.0128(8)	0.0011(7)	0.0035(7)	0.0097(8)
C18	0.0426(13)	0.0350(12)	0.0427(13)	0.0072(10)	0.0189(10)	0.0214(10)

Table S15. Hydrogen atomic coordinates and isotropic atomic displacement parameters (Å^2) for **3b**.

	x/a	**y/b**	**z/c**	**U(eq)**
H19A	0.7015	0.1169	0.2896	0.068
H19B	0.6899	0.2125	0.2789	0.068
H19C	0.6489	0.1495	0.1676	0.068
H20A	0.7177	0.1161	0.6511	0.068
H20B	0.6760	0.1478	0.7656	0.068
H20C	0.7069	0.2116	0.6629	0.068
H21A	0.6028	0.0578	0.3429	0.064
H21B	0.6150	0.0547	0.5781	0.064
H21C	0.6554	0.0224	0.4579	0.064
H19D	0.7360	0.1534	0.4765	0.066
H19E	0.7196	0.2306	0.5892	0.066
H19F	0.7089	0.2292	0.3540	0.066
H20D	0.6326	0.0843	0.6906	0.069
H20E	0.6710	0.1561	0.7716	0.069
H20F	0.6908	0.0750	0.6848	0.069
H21D	0.6702	0.0659	0.3081	0.07
H21E	0.6401	0.1400	0.1888	0.07
H21F	0.6114	0.0760	0.3004	0.07
H2	0.6539	0.7067	0.4603	0.035
H3	0.7333	0.6654	0.4381	0.04
H4	0.7516	0.5255	0.4219	0.038
H5	0.6917	0.4286	0.4302	0.032
H10	0.5686	0.6770	0.4837	0.027
H13	0.4954	0.2451	0.4962	0.034
H14	0.5543	0.1437	0.4826	0.04
H16	0.6596	0.3143	0.4496	0.033

6. OFET fabrication and characterizations

Organic field effect transistors (OFETs) of **3a** and **3b** were fabricated on n^{+}-Si/SiO$_2$ substrates using a bottom-gate top-contact device structure. The SiO$_2$ dielectric was treated with octadecyltrichlorosilane (ODTS) or hexamethyldisilazane (HMDS), and the thin film was spin-coated from CHCl$_3$ solution onto the substrates, then thermal annealed at selective temperatures for 20 min. Finally, Au source/drain electrodes (80 nm) were patterned onto the organic layer through a shadow mask to fabricate the devices. All devices were characterized in N$_2$ atmosphere.

Table S16. The device characteristics of thin film **3a** and **3b**.

Sample	Surface treatment	Annealing temp [^{0}C]	μ (cm^{2}V^{-1}s^{-1})	V$_{T\ [V]}$	On/Off
3a	OTS	As spun	0.06	-1	10^{5}
	OTS	A100	$3*10^{-4}$	-5	10^{3}
	ODTS	As spun	$6.5*10^{-3}$	-3	10^{3}
	ODTS	A100	$1.2*10^{-5}$	-2	10^{2}
	HMDS	As spun	$3.2*10^{-5}$	-2	10^{2}
	HMDS	A100	$1.0*10^{-5}$	-1	10^{2}
3b	OTS-C8	RT	$1.9*10^{-5}$	-5	10^{3}
	OTS-C8	80	$1.2*10^{-6}$	-1.3	10^{2}
	OTS-C18	RT	$6.3*10^{-6}$	-1.4	10^{2}
	OTS-C18	80	$5.0*10^{-5}$	-4.1	10^{2}

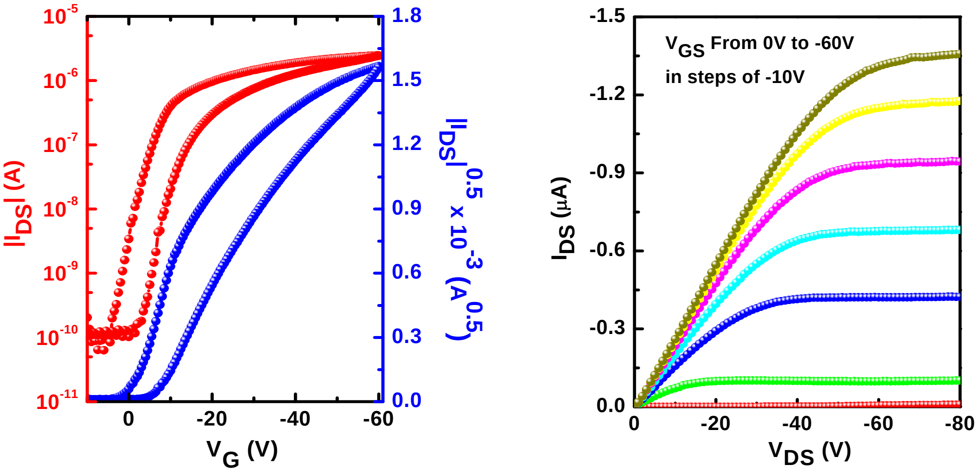


Fig. S8. Transfer and output characteristics of **3a** on OTS-modified substrates.

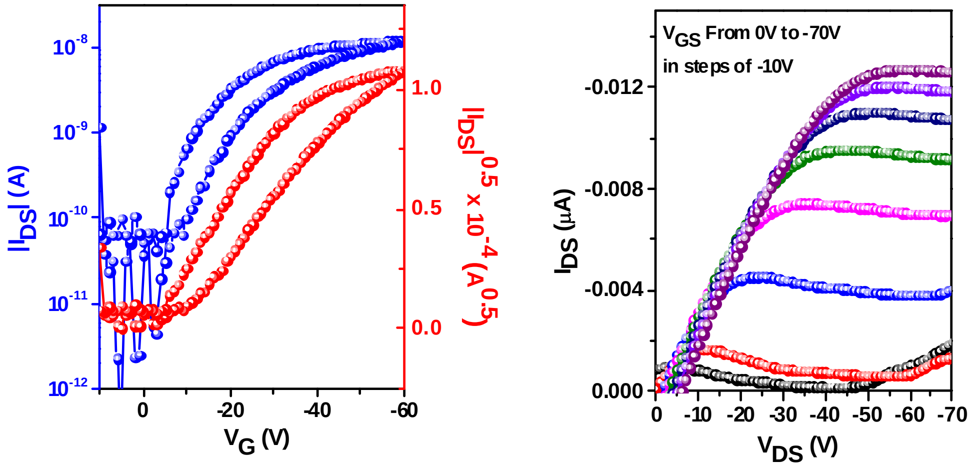


Fig. S9. Transfer and output characteristics of **3b** on OTS-modified substrates**.**

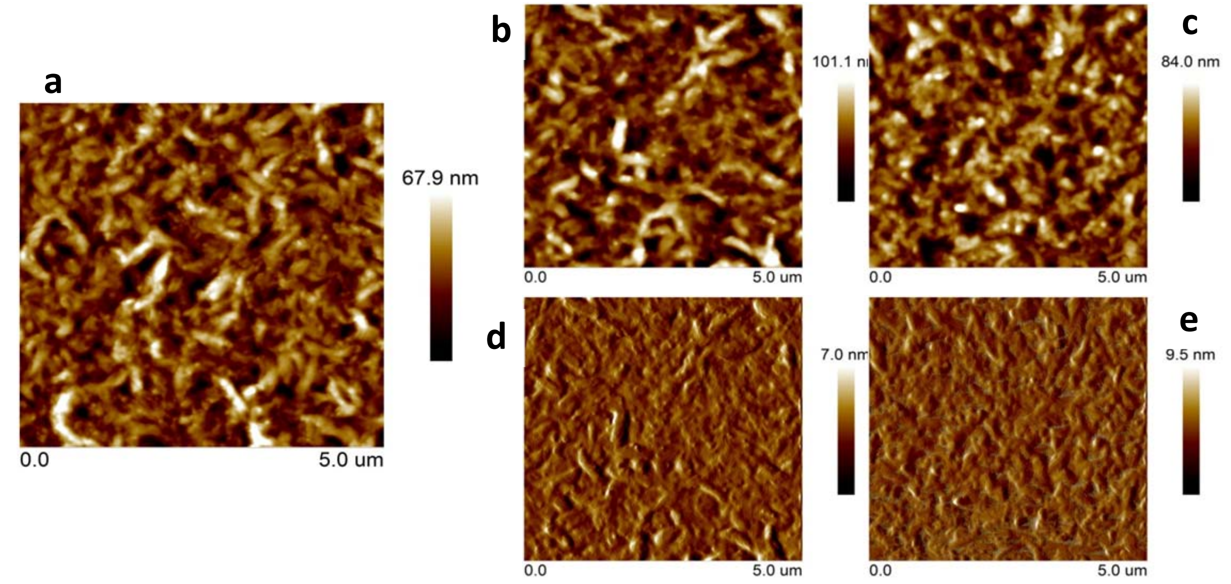


Fig. S10. The AFM images of the thin film **3a** spin coated from $CHCl_3$ solution onto a) HMDS, b) OTS as spun, c) OTS annealing at 100 ^{0}C, and the corresponding phase images of d) OTS, and e) OTS at 100 ^{0}C.

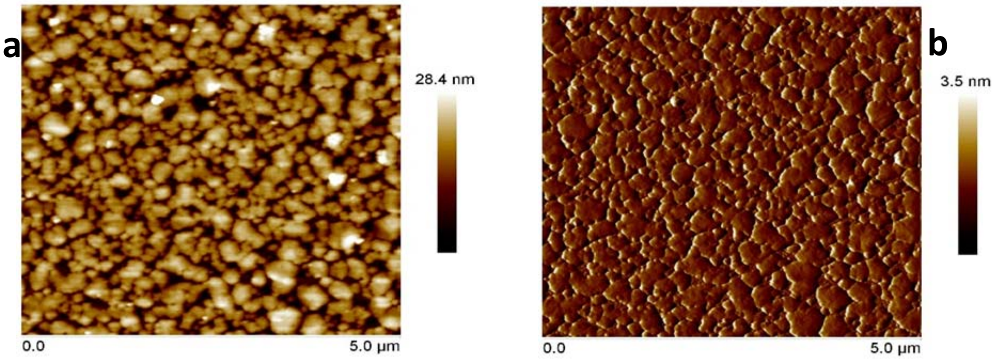


Fig. S11. The AFM images of the thin film **3b** spin coated from $CHCl_3$ solution onto a) OTS surface and the corresponding b) phase image of OTS surface.

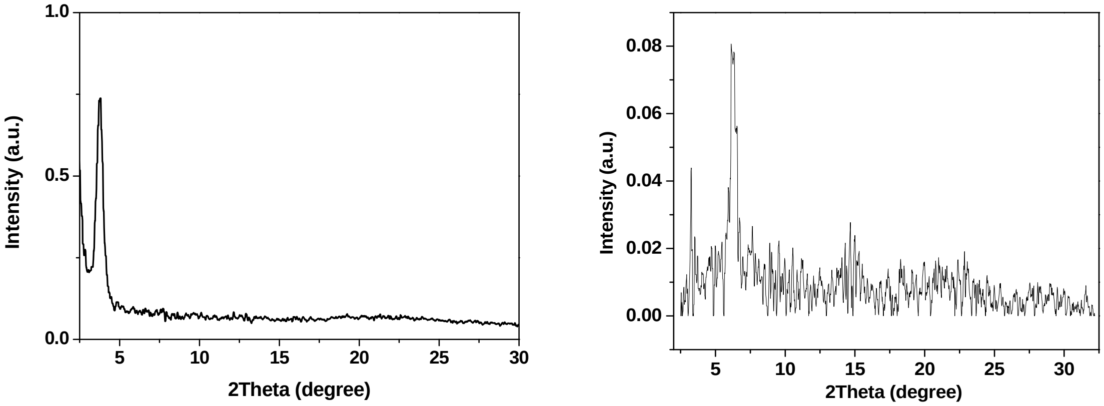


Fig. S12. XRD patterns of **3a** (a) and **3b** (b) thin films on OTS-modified substrates.

7. Mass and NMR spectra of the newly synthesized compounds

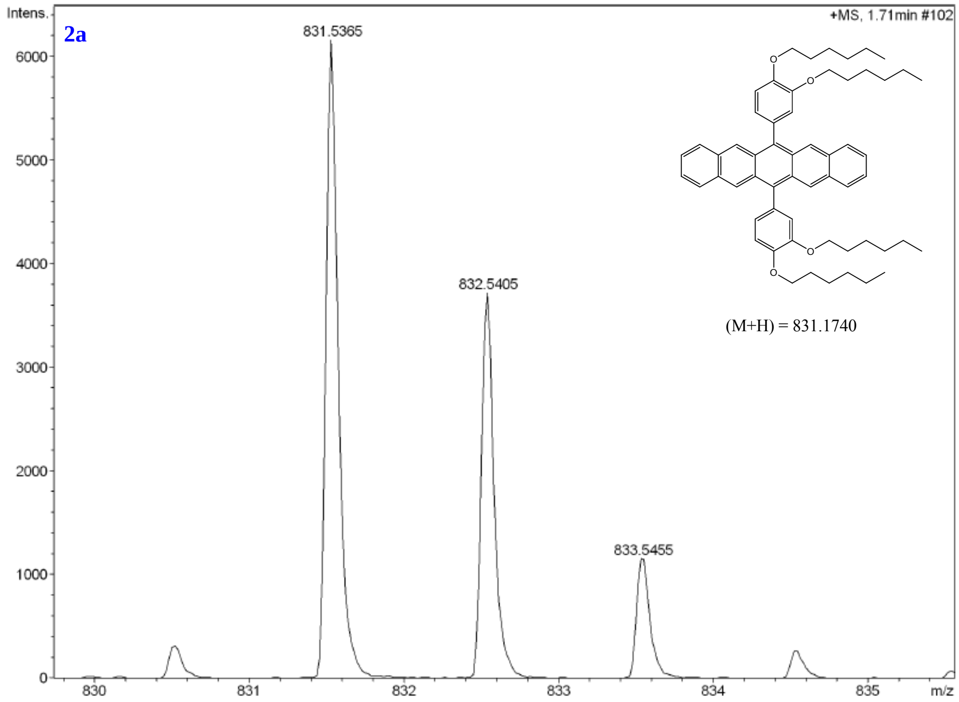


Fig. S13. APCI high resoulution mass spectrum of compound **2a**.

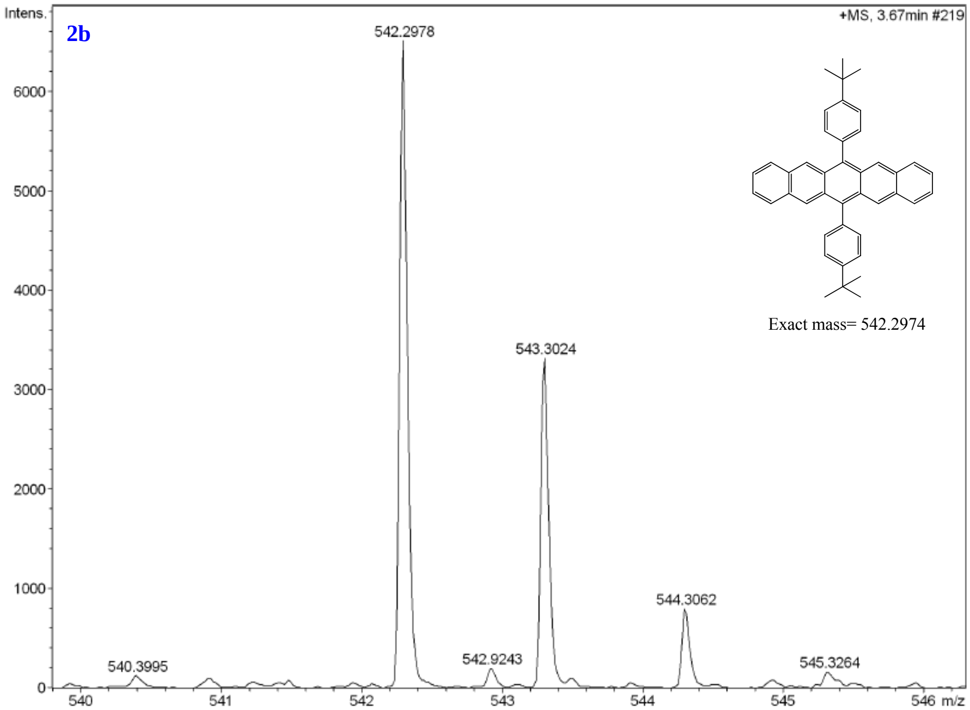


Fig. S14. ESI high resolution mass spectrum of compound **2b**.

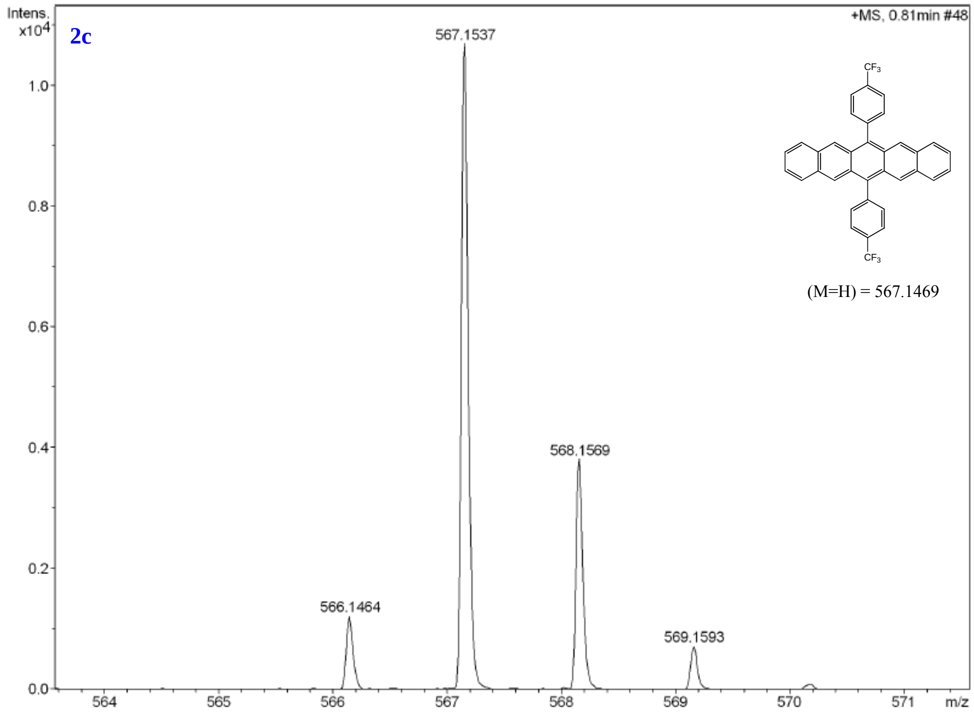


Fig. S15. APCI high resolution mass spectrum of compound **2c**.

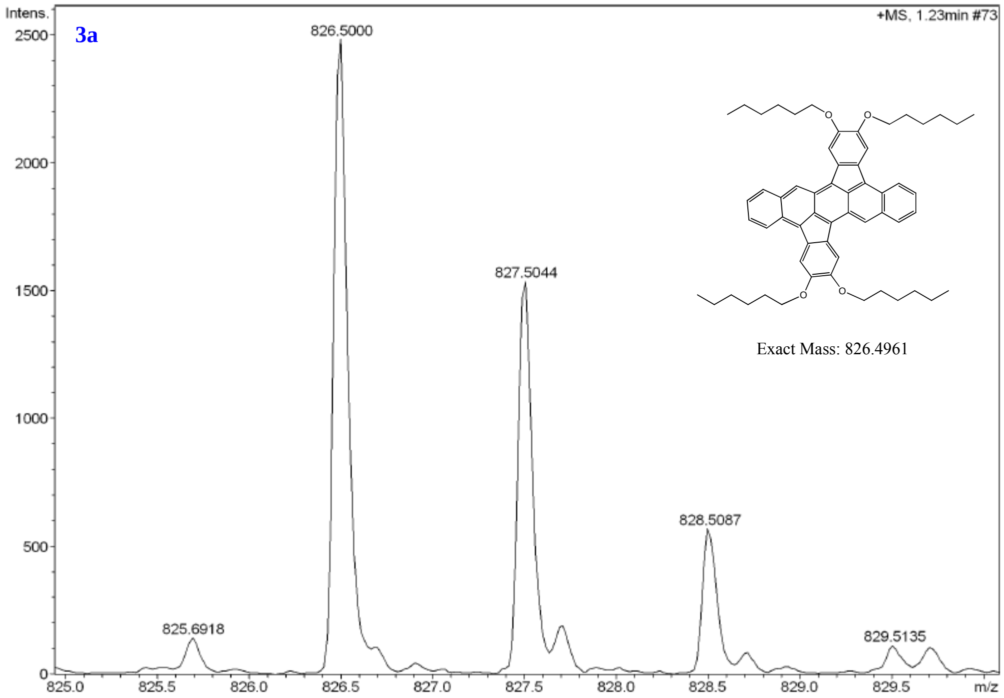


Fig. S16. ESI high resolution mass spectrum of compound **3a**.

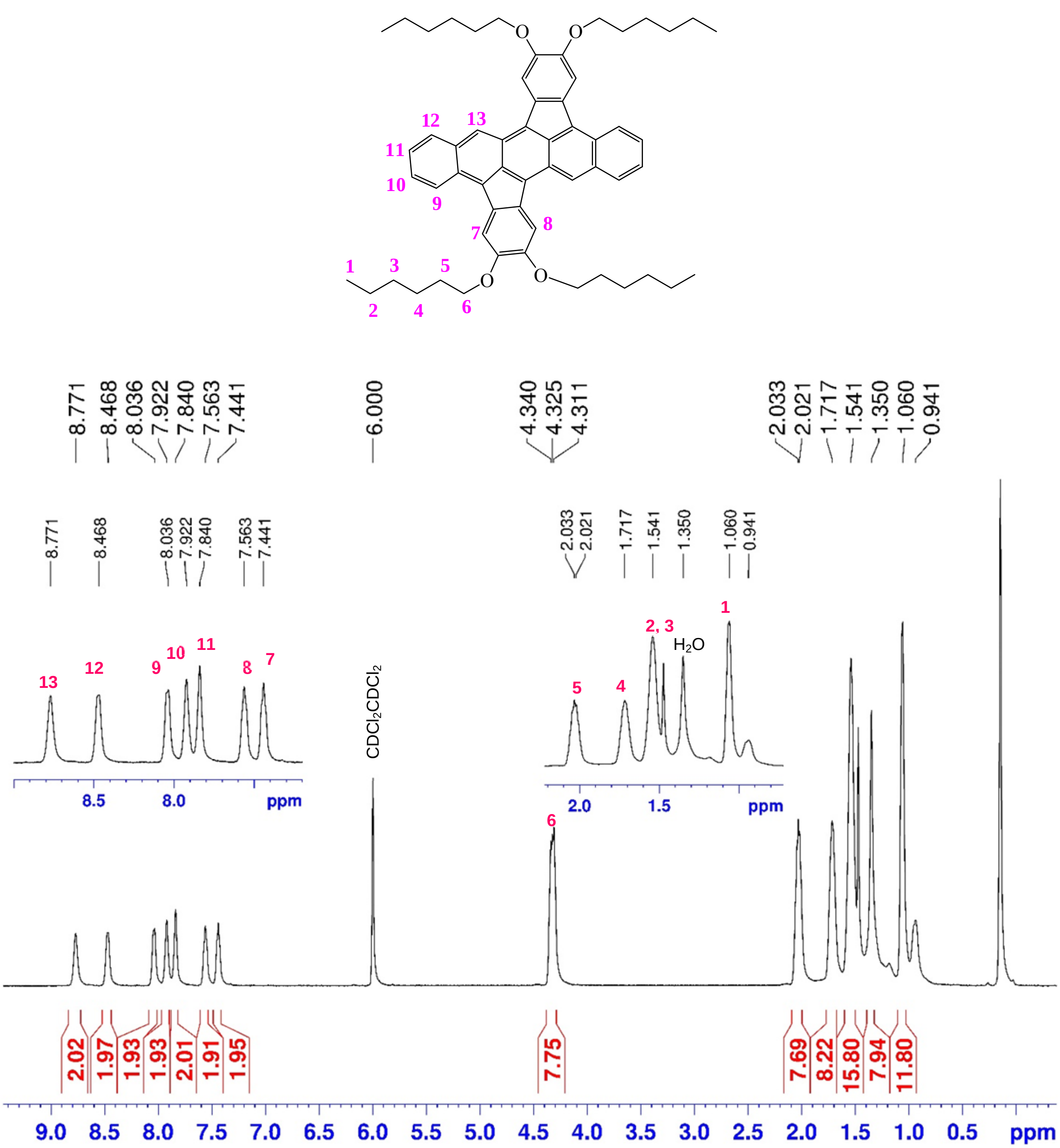


Fig. S17. ^{1}H NMR (500 MHz) spectrum of the compound **3a** in 1,1,2,2-tetrachloroethane-d_2 at 100 ^{0}C**.**

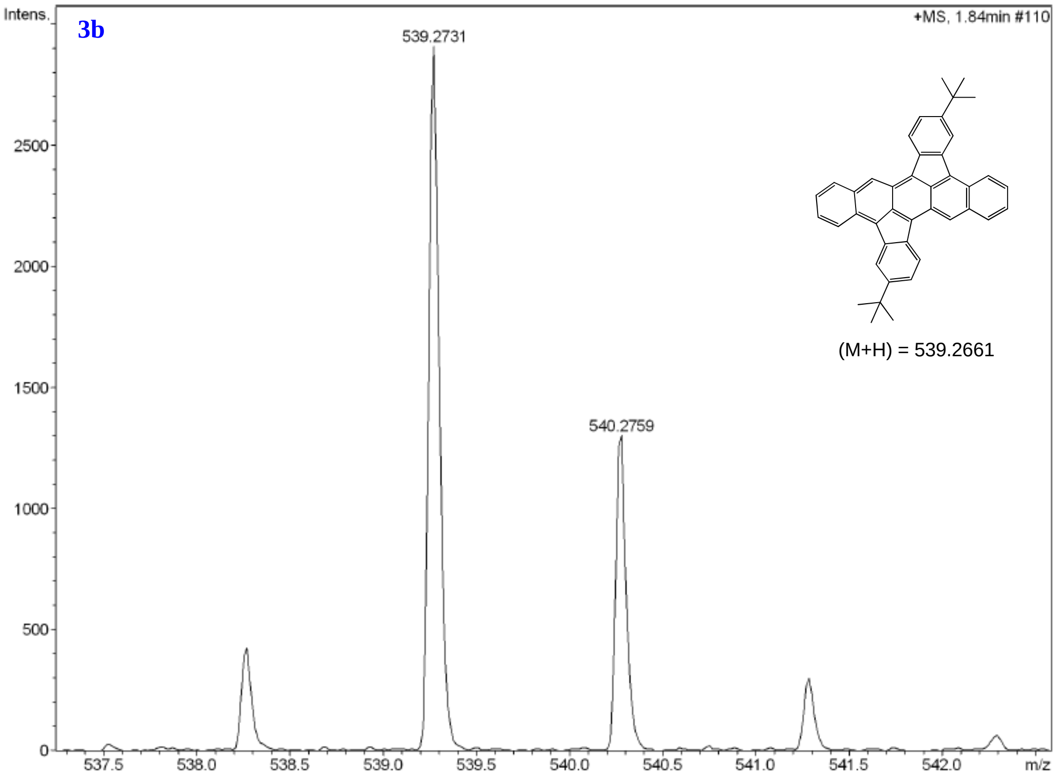


Fig. S18. APCI high resolution mass spectrum of compound **3b**.

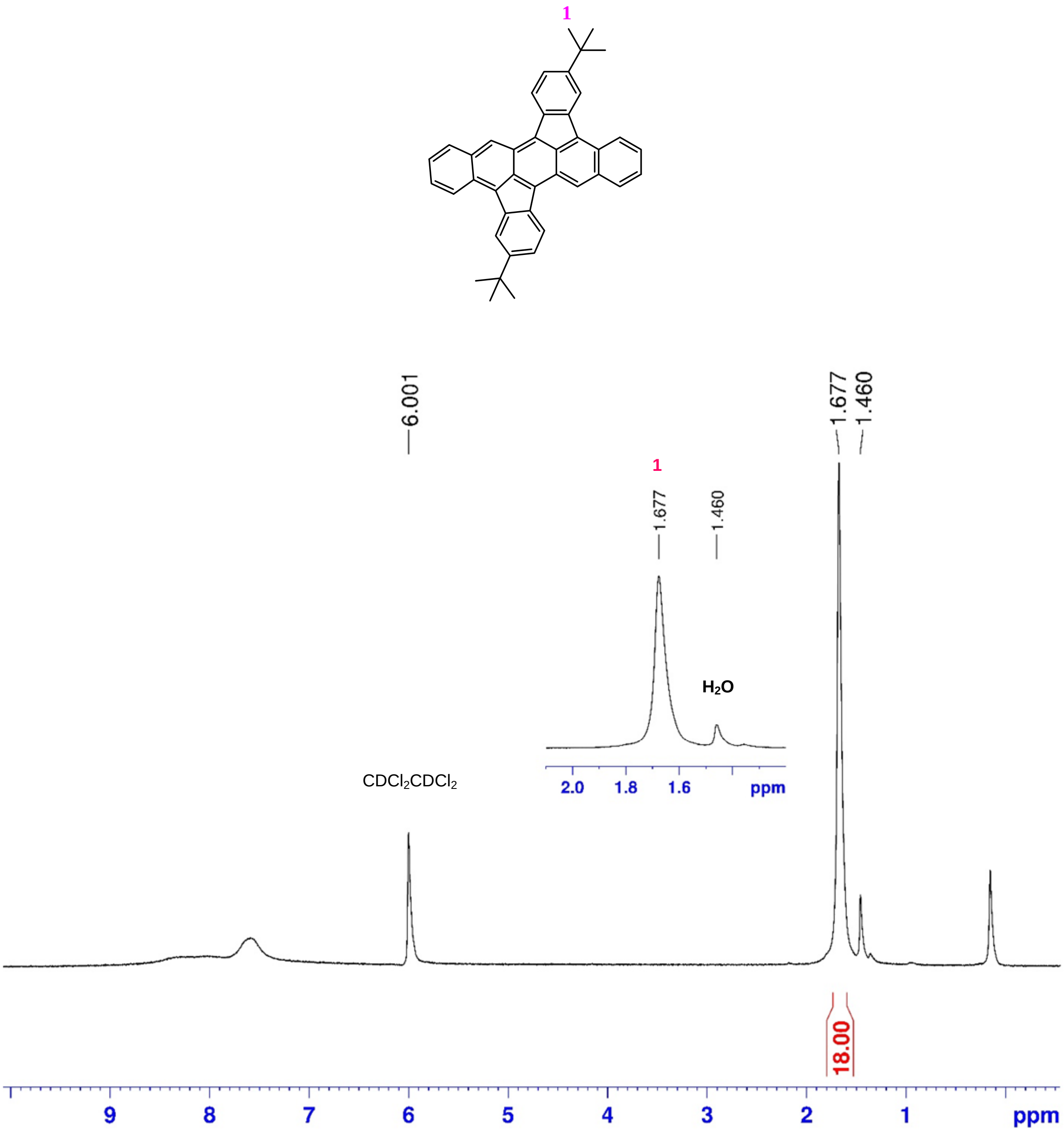


Fig. S19. ^{1}H NMR (500 MHz) spectrum of compound **3b** in 1,1,2,2-tetrachloroethane-d$_2$ at 100 ^{0}C**.** The broad aromatic peak is due to aggregation even it is soluble in CDCl$_2$CDCl$_2$.