Supporting information for

A New Thiophene-Functionalized Pyrene, Peropyrene, and Teropyrene via a Two- or Four-fold Alkyne Annulation and Their Photophysical Properties

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1. General Experimental Section

All reactions dealing with air- or moisture-sensitive compounds were carried out in a dry reaction vessel under nitrogen. Anhydrous tetrahydrofuran (THF) and dichloromethane (CH_2Cl_2) were obtained by passing the solvent (HPLC grade) through an activated alumina column on a PureSolv MD 5 solvent drying system. ^1H and ^{13}C NMR spectra were recorded on Varian 400 MHz or Varian 500 MHz NMR Systems Spectrometers. Spectra were recorded in deuterated chloroform ($CDCl_3$). The residual protio-solvent peaks (7.26 ppm for ^1H and 77.16 ppm for ^{13}C, respectively) was used as an internal standard. Chemical shifts are reported in part per million (ppm) from low to high frequency and referenced to the residual solvent resonance. Coupling constants (*J*) are reported in Hz. The multiplicity of ^1H signals are indicated as: s = singlet, d = doublet, t = triplet, m = multiplet, br = broad. High resolution ESI mass spectrometry was recorded using an Agilent 6230 TOF MS and TFA was added to samples to promote ionization. MALDI-TOF mass spectra were recorded on a Bruker microflex MALDI-TOF spectrometer. TLC information was recorded on Silica gel 60 F254 glass plates. Purification of reaction products was carried out by flash chromatography using Silica Gel 60 (230-400 mesh).

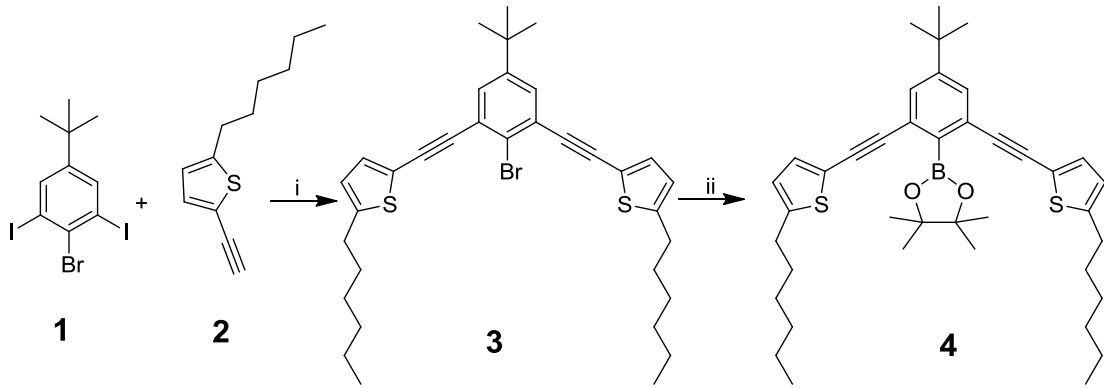
A suitable crystal was mounted on a glass fiber and placed in the low-temperature nitrogen stream. Data were collected on a Bruker SMART CCD area detector diffractometer equipped with a low-temperature device, using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) and a full sphere of data was collected. Cell parameters were retrieved using SMART[1] software and refined using SAINTPlus[2]on all observed reflections. Data reduction and correction for Lp and decay were performed using the SAINTPlus[2] software. Multi-scan absorption corrections were applied using SADABS,[3] unless otherwise indicated. The structures were solved by direct methods and refined by least square methods on F^2 using the SHELXTL[4] program package. All non-hydrogen atoms were refined anisotropically. The majority of the hydrogen atoms were added geometrically and their parameters constrained to the parent site.

2. Synthesis and Characterization

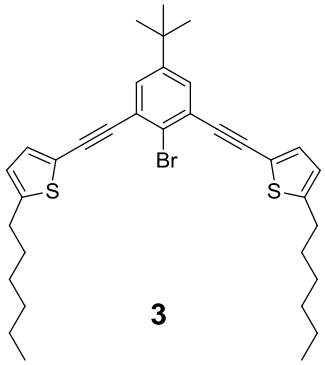
Compounds **1** was synthesized according to our previous report,[5] and compound **2** was synthesized according to the literature.[6]

Note: For ^{13}C NMR spectra of compounds **4** and **6**, one carbon signal was missed due to coincidental overlap.

2.1 Synthesis of compound 4



Scheme S1. Conditions: i) $Pd(PPh_3)_2Cl_2$, CuI, THF/Et_3N, r.t., 14 h; ii) (a) *n*-butyllithium (*n*-BuLi), THF, -78 °C, 30 min; (b) isopropoxyboronic acid pinacol ester, -78 °C to r.t.



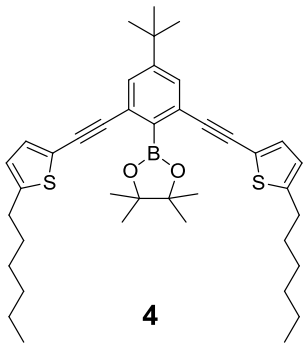
To the solution of 4-bromo-1-(*tert*-butyl)-3,5-diiodobenzene **1** (1.16 g, 2.50 mmol) and the terminal alkyne **2** (1.15 g, 6.00 mmol) in Et_3N (20 mL) and THF (40 mL), were added $Pd(PPh_3)_2Cl_2$ (70.2 mg, 0.100 mmol) and CuI (38.1 mg, 0.200 mmol). The resulting mixture was stirred under a N_2 atmosphere at room temperature for 14 h. The ammonium salt was then removed by filtration. The solvent was removed under reduced pressure and the residue was purified by column chromatography (silica gel, hexane) to yield **3** as a yellow oil (1.33 g, 90%). R_f = 0.20 (hexane).

FTIR (neat) 2954, 2925, 2854, 2204, 1565, 1465 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (s, 2H), 7.19 (d, *J* = 3.6 Hz, 2H), 6.71 (m, 2H), 2.82 (t, *J* = 7.6 Hz, 4H), 1.70 (m, 4H), 1.54 – 1.17 (m, 21H), 1.01 – 0.83 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 150.19, 149.22, 132.65, 129.85, 125.89, 124.60, 124.46, 120.09, 91.59, 87.46, 34.66, 31.66, 31.64, 31.09, 30.39, 28.84, 22.70, 14.21.

HRMS (ESI, positive) *m/z* calcd for $C_{34}H_{41}BrS_2$ $[M+H]^+$ 593.1911, found 593. 1902.



4

To a solution of **3** (5.94 g, 10.0 mmol) in THF (100 mL) at -78 °C was added a solution of *n*-butyllithium in hexanes (4.00 mL, 2.5 M, 10.0 mmol). After stirring for 30 min at -78 °C, isopropoxyboronic acid pinacol ester (1.86 g, 10.0 mmol) was added, the reaction removed from the cooling bath and allowed to warm. Upon reaching room temperature the reaction was quenched by the addition of H_2O, and then extracted with CH_2Cl_2. The extract was washed with water, dried with Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by flash column chromatography (silica gel, hexane:CH_2Cl_2 = 4:1, v/v) to yield **4** as light yellow oil (4.70 g, 73%). R_f = 0.20 (hexane/CH_2Cl_2 4:1).

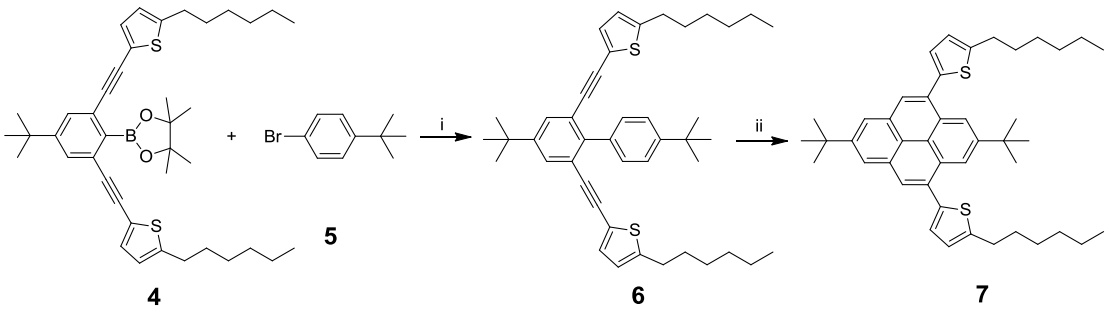
FTIR (neat) 2955, 2926, 2855, 2200, 1585, 1542, 1466 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (s, 2H), 7.10 (d, *J* = 3.6 Hz, 2H), 6.67 (d, *J* = 3.6 Hz, 2H), 2.80 (t, *J* = 7.5 Hz, 4H), 1.74 – 1.64 (m, 4H), 1.57 – 1.17 (m, 33H), 0.91 (t, *J* = 6.9 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 152.29, 148.21, 131.88, 128.75, 126.55, 124.19, 120.86, 93.05, 84.36, 83.89, 34.71, 31.61, 31.55, 31.03, 30.28, 28.76, 25.14(2), 22.65, 14.15.

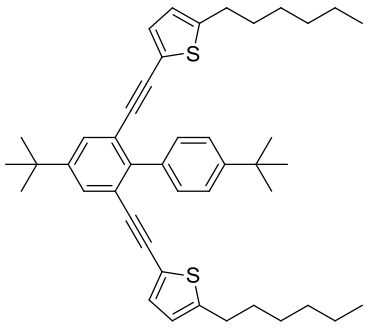
MALDI-TOFMS *m/z* calcd for $C_{40}H_{53}BO_2S_2$ $[M]^+$ 640.358, found 640.677.

2.2 Synthesis of compound 7



4 5 6 7

Scheme S2. Conditions. i) $Pd(PPh_3)_4$, K_2CO_3, THF/H_2O, 70 °C, 12 h; ii) TfOH, CH_2Cl_2, 0 °C.



6

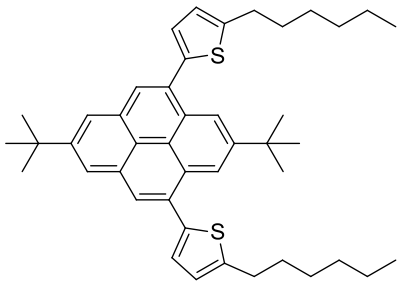
1-Bromo-4-*tert*-butylbenzene **5** (213 mg, 1.00 mmol), 2,6-diynylphenyl borate **4** (641 mg, 1.00 mmol) and K_2CO_3 (276 mg, 2.00 mmol) were dissolved in THF (60 mL) and water (10 mL) solution. $Pd(PPh_3)_4$ (58.0 mg, 0.0502 mmol) was added to the solution before degassing the mixture via bubbling nitrogen for 30 min. The resulting mixture was stirred under a N_2 atmosphere at 70 °C for 24 h. After the reaction was complete, the mixture was diluted with CH_2Cl_2, washed with H_2O and dried over Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by column chromatography (silica gel, hexane:CH_2Cl_2 = 15:1, v/v) to yield **6** as yellow oil (375 mg, 58%). R_f = 0.30 (hexane/CH_2Cl_2 10:1).

FTIR (neat) 2954, 2926, 2855, 2201, 1587, 1544, 1465 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$) δ 7.59 (s, 2H), 7.54 (m, 4H), 6.86 (d, J = 3.6 Hz, 2H), 6.62 (d, J = 3.6 Hz, 2H), 2.77 (t, J = 7.6 Hz, 4H), 1.71 – 1.59 (m, 4H), 1.57 – 1.18 (m, 30H), 0.92 (t, J = 6.8 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 150.18, 149.86, 148.45, 142.95, 135.78, 131.61, 130.07, 128.79, 124.43, 124.16, 122.87, 120.89, 92.97, 86.26, 34.79, 34.67, 31.67, 31.62(2), 31.28, 30.36, 28.82, 22.68, 14.22.

HRMS (ESI, positive) *m/z* calcd for $C_{44}H_{54}S_2$ $[M+H]^+$ 647.3740, found 647.3739.



7

A 100 mL flame-dried flask was charged with compound **6** (35.0 mg, 0.0541 mmol) and anhydrous CH_2Cl_2 (50 mL). A solution of triflic acid (3.00 mg, 0.0199 mmol) in anhydrous CH_2Cl_2 (3 mL) was then added slowly by syringe in 30 minutes. After stirring for 12 hours at room temperature, the reaction was quenched with saturated $NaHCO_3$ solution (5 mL). The solution was then washed with H_2O (2 x 30 mL) and dried (Na_2SO_4). After removal of the solvent under reduced pressure, the residue was purified by column chromatography (silica gel, hexane:CH_2Cl_2 = 10:1, v/v) to yield **7** as yellow oil (21.0 mg, 60%). R_f = 0.50 (hexane/CH_2Cl_2 7:1).

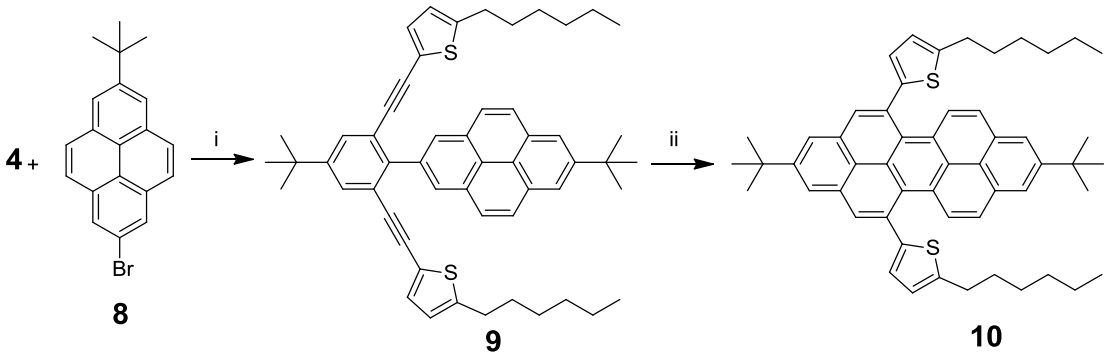
FTIR (neat) 2953, 2923, 2853, 1601, 1457 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.79 (s, 2H), 8.21 (s, 2H), 8.17 (s, 2H), 7.30 (d, *J* = 3.4 Hz, 2H), 6.96 (d, *J* = 3.4 Hz, 2H), 2.98 (t, *J* = 7.6 Hz, 4H), 1.83 (dd, *J* = 15.2, 7.6 Hz, 4H), 1.61 (s, 9H), 1.54 (s, 9H), 1.41 (m, 12H), 0.97 (t, *J* = 7.1 Hz, 6H).

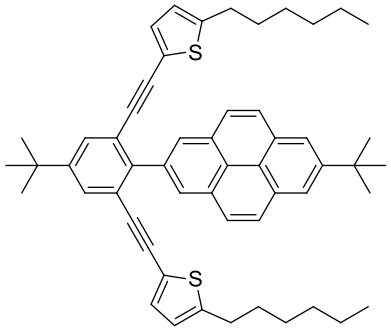
^{13}C NMR (101 MHz, $CDCl_3$) δ 149.27, 148.44, 146.35, 140.02, 132.58, 130.33, 130.12, 128.97, 127.06, 124.50, 123.82, 122.51, 122.12, 121.42, 35.80, 35.35, 32.05, 32.01, 31.92, 31.83, 30.45, 29.04, 22.81, 14.30.

HRMS (ESI, positive) *m/z* calcd for $C_{44}H_{54}S_2$ $[M]^+$ 646.3661, found 646.3651.

2.3 Synthesis of compound 10



Scheme S3. Conditions. i) $Pd(PPh_3)_4$, K_2CO_3, THF/H_2O, 70 °C, 24 h; ii) TfOH, CH_2Cl_2, 0 °C.



9

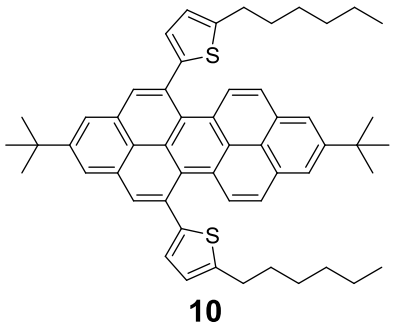
Compound **9** was prepared from 2,6-diynylphenyl borate **4** (320 mg, 0.499 mmol) and 2-bromo-7-(*tert*-butyl)pyrene **8** (168 mg, 0.498 mmol) according to the similar procedure to compound **6**. The resulting residue was purified by column chromatography (silica gel, hexane:CH_2Cl_2 = 15:1, v/v) to yield **9** as brown solid (169 mg, 49%). R_f = 0.30 (hexane/CH_2Cl_2 10:1).

FTIR (neat) 2955, 2928, 2856, 2202, 1606, 1587, 1557, 1466 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (s, 2H), 8.27 (s, 2H), 8.13 (m, 4H), 7.71 (s, 2H), 6.66 (d, *J* = 3.6 Hz, 2H), 6.46 (d, *J* = 3.6 Hz, 2H), 2.64 (t, *J* = 7.6 Hz, 4H), 1.64 (s, 9H), 1.36 (d, *J* = 83.2 Hz, 34H), 0.88 (t, *J* = 6.8 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 150.37, 149.04, 148.49, 142.51, 135.87, 131.87, 131.42, 130.37, 129.34, 127.97, 127.41, 127.35, 124.20, 124.15, 123.33, 123.16, 122.08, 120.41, 92.87, 86.35, 35.40, 34.79, 32.14, 31.61, 31.48, 31.32, 30.23, 28.74, 22.65, 14.19.

HRMS (ESI, positive) *m/z* calcd for $C_{54}H_{58}S_2$ $[M+H]^+$ 771.4053, found 771.4048.



10

Compound **10** was prepared from compound **9** (23.0 mg, 0.0298 mmol) according to the similar procedure to compound **7**. The resulting residue was purified by column chromatography (silica gel, hexane:CH_2Cl_2 = 10:1, v/v) to yield **10** as brown solid (16.6 mg, 72%). R_f = 0.50 (hexane/CH_2Cl_2 10:1).

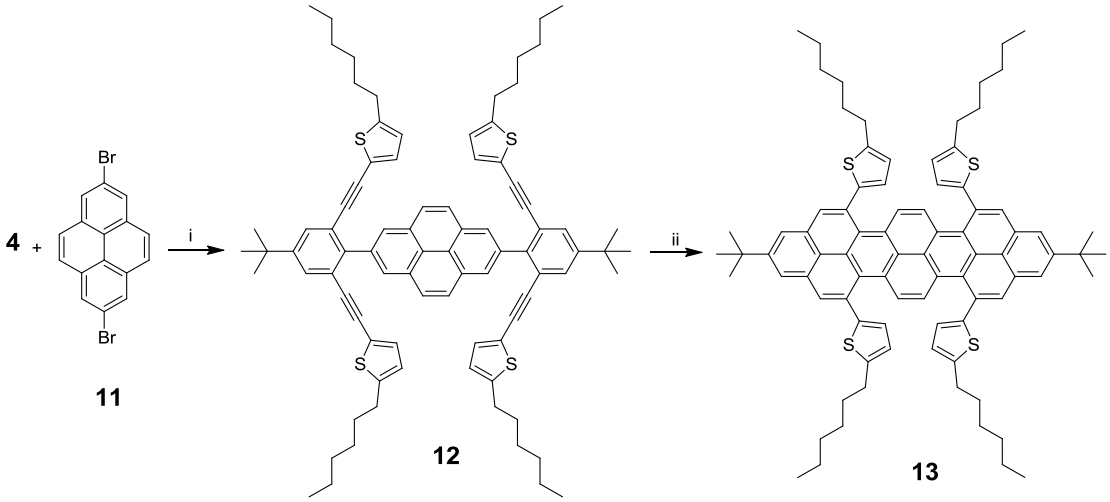
FTIR (neat) 2952, 2921, 2852, 1459 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (d, *J* = 9.4 Hz, 2H), 8.43 (s, 2H), 8.40 (s, 2H), 8.32 (s, 2H), 7.94 (d, *J* = 9.4 Hz, 2H), 7.06 (d, *J* = 3.4 Hz, 2H), 6.91 (d, *J* = 3.4 Hz, 2H), 2.98 (t, *J* = 7.4 Hz, 4H), 1.83 (m, 4H), 1.75 – 1.59 (m, 18H), 1.57 – 1.40 (m, 12H), 1.02 (t, *J* = 6.9 Hz, 6H).

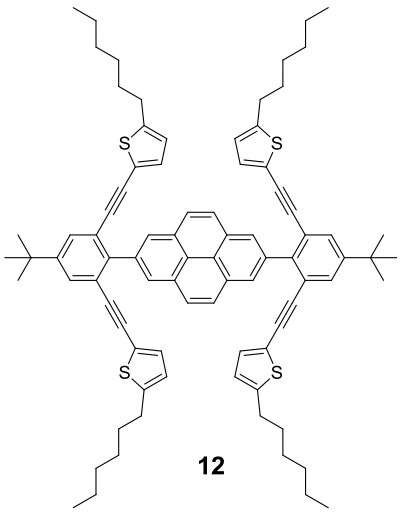
^{13}C NMR (100 MHz, $CDCl_3$) δ 149.81, 149.27, 146.50, 145.17, 132.39, 131.90, 130.98, 130.75, 127.65, 126.17, 125.85, 125.25, 125.01, 124.89, 124.65, 124.49, 123.07, 122.62, 122.58, 122.39, 35.33, 35.30, 32.07, 32.01, 31.97, 31.87, 30.46, 28.89, 22.88, 14.37.

HRMS (ESI, positive) *m/z* calcd for $C_{54}H_{58}S_2$ $[M]^+$ 770.3974, found 770.3966.

2.4 Synthesis of compound 13



Scheme S3. Conditions. i) $Pd(PPh_3)_4$, K_2CO_3, THF/H_2O, 70 °C, 48 h; ii) TfOH, CH_2Cl_2, 0 °C to r.t..



Compound **12** was prepared from 2,6-diynylphenyl borate **4** (641 mg, 1.00 mmol)

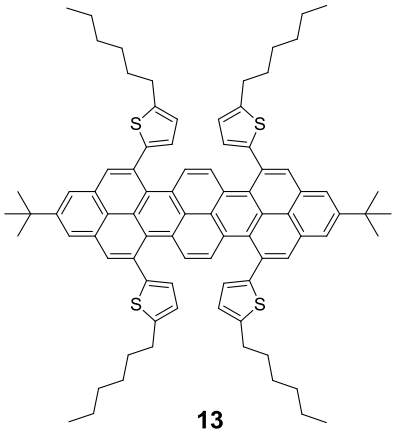
and 2,7-dibromopyrene **11** (180 mg, 0.500 mmol) according to the similar procedure to compound **6**. The resulting residue was purified by column chromatography (silica gel, hexane:CH_2Cl_2 = 7:1, v/v) to yield **12** as brown solid (171 mg, 28%). R_f = 0.20 (hexane/CH_2Cl_2 7:1).

FTIR (neat) 2953, 2924, 2853, 2199, 1587, 1554, 1464 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (s, 4H), 8.18 (s, 4H), 7.70 (s, 4H), 6.67 (d, *J* = 3.6 Hz, 4H), 6.43 (d, *J* = 3.6 Hz, 4H), 2.59 (t, *J* = 7.5 Hz, 8H), 1.46 (s, 18H), 1.24 (m, 32H), 0.87 – 0.80 (m, 12H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 150.39, 148.57, 142.42, 136.12, 131.95, 130.84, 129.37, 127.78, 127.33, 124.36, 124.17, 123.35, 120.39, 92.93, 86.47, 34.81, 31.62, 31.49, 31.34, 30.24, 28.79, 22.67, 14.17.

MALDI-TOFMS *m/z* calcd for $C_{84}H_{90}S_4$ $[M+H]^+$ 1227.600, found 1227.715.



13

Compound **13** was prepared from compound **12** (61.0 mg, 0.0497 mmol) with triflic acid (2 equiv.) according to the similar procedure to compound **7**. The resulting residue was purified by column chromatography (silica gel, hexane:CH_2Cl_2 = 8:1, v/v) to yield **13** as brown solid (34.2 mg, 56%). R_f = 0.20 (hexane/CH_2Cl_2 8:1).

FTIR (neat) 2955, 2925, 2853, 1465 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (s, 4H), 8.33 (s, 4H), 8.31 (s, 4H), 6.90 (d, *J* = 3.4 Hz, 4H), 6.81 (d, *J* = 3.4 Hz, 4H), 2.94 (t, *J* = 7.6 Hz, 8H), 1.81 – 1.75 (m, 8H), 1.64 – 1.61 (m, 18H), 1.50 – 1.37 (m, 24H), 0.91 (m, 12H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 149.95, 145.93, 144.68, 132.51, 132.00, 130.84, 126.21, 126.01, 125.50, 124.99, 124.87, 124.74, 124.45, 123.04, 122.09, 35.37, 32.01, 32.00, 31.83, 30.59, 29.06, 22.82, 14.30.

MALDI-TOFMS *m/z* calcd for $C_{84}H_{90}S_4$ $[M+H]^+$ 1227.600, found 1227.619.

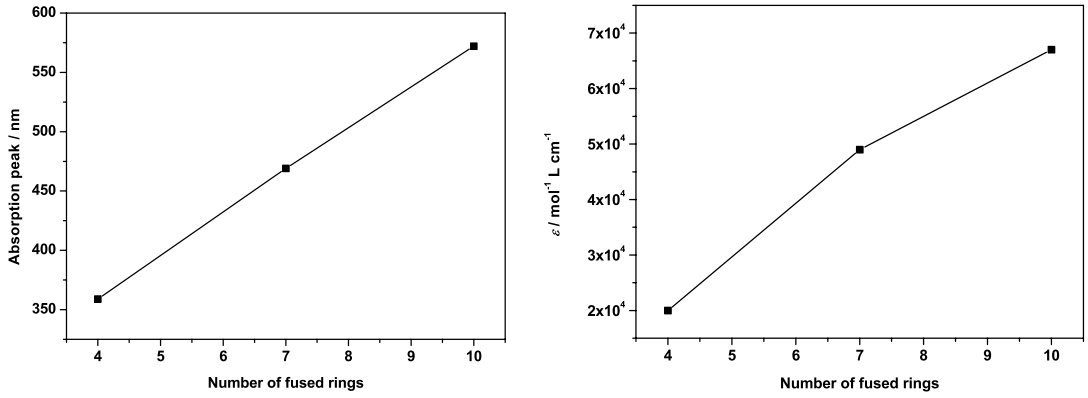
3. Photophysical characterization

Solutions with concentrations in the range $1x10^{-5}$ to $1x10^{-6}$ M in toluene were used to obtain the absorption, emission and excitation spectra. The absorption spectra were measured on a Perkin Elmer Lambda 35 spectrometer. The photoluminescence data were obtained in a Fluorolog-3 spectrofluorimeter (Horiba FL3-22-iHR550), with 1200 grooves/mm excitation monochromator gratings blazed at 330 nm and 1200 grooves/mm emission monochromator gratings blazed at 500 nm. An ozone-free xenon lamp of 450 W (Ushio) was used as the radiation source. The excitation spectra corrected for instrumental function were measured between 250 and 600 nm. The emission spectra were measured in the range 350-800 nm at right angle. All emission spectra were corrected for instrumental function. Standards for quantum yield measurements were quinine sulfate (ϕ ~ 55%, $5x10^{-6}$ M in aqueous 0.5 M H_2SO_4) [7, 8] for compounds pyrene **7** and peropyrene **10** and $[Ru(bpy)_3]Cl_2$ (ϕ ~ 2.8%, $1x10^{-5}$ M in water)[8, 9] for compound teropyrene **13**. Both samples and quantum yield standards were excited at the same wavelengths, which were chosen to ensure a linear relationship between the intensity of emitted light and the concentration of the absorbing/emitting species ($A \leq 0.05$). The quantum yield of the samples was determined by the dilution method using Equation 1.

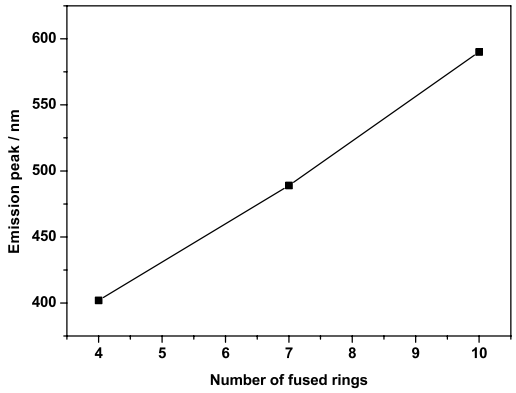
$$\Phi_x = \frac{Grad_x}{Grad_{std}} \times \frac{n_x^2}{n_{std}^2} \times \Phi_{std} \qquad (1)$$

Grad is the slope of the plot 'Emission area vs Absorbance', *n* is the refractive index of the solvent and Φ is the quantum yield for sample *x* and standard *std*.

The emission decay curves were obtained using a TCSPC system and a Horiba NanoLED model N-370 (peak wavelength = 370 ± 10 nm, ~4 pJ/pulse) as excitation source. Before all decay curves measurements a blank, using Ludox® solution, was obtained.

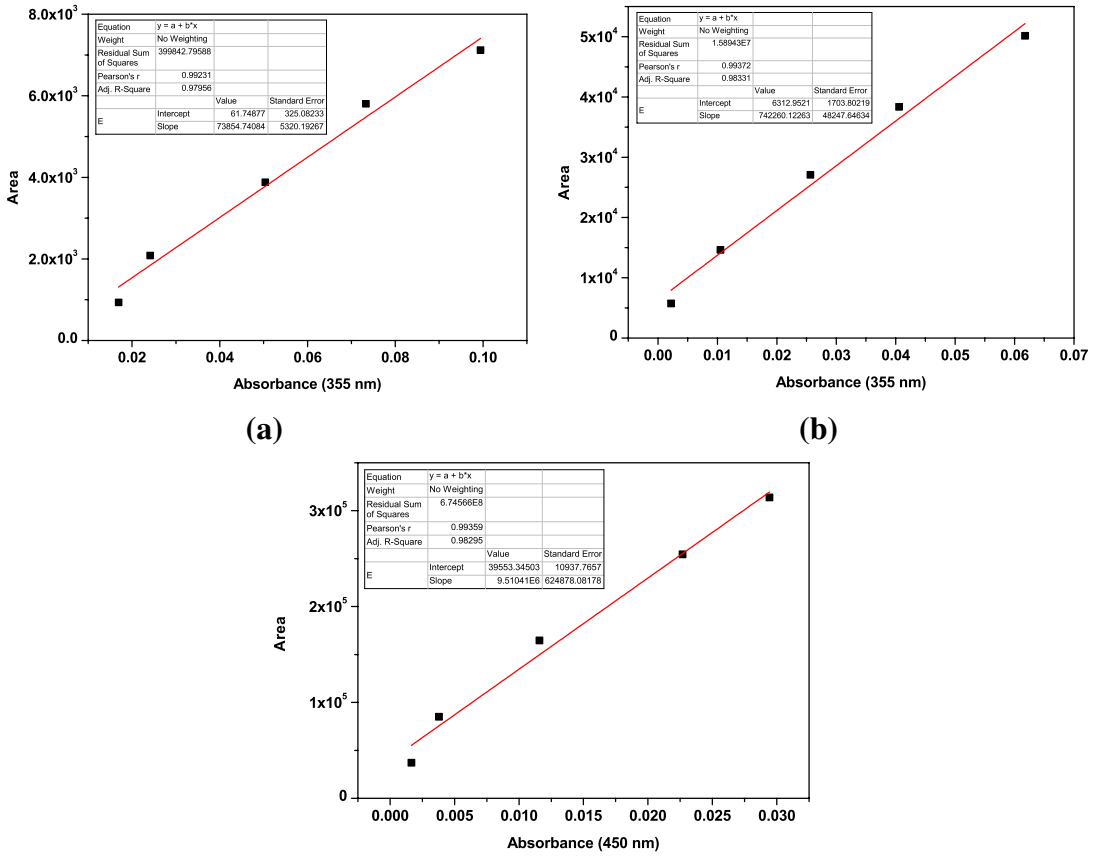


(a) **(b)**



(c)

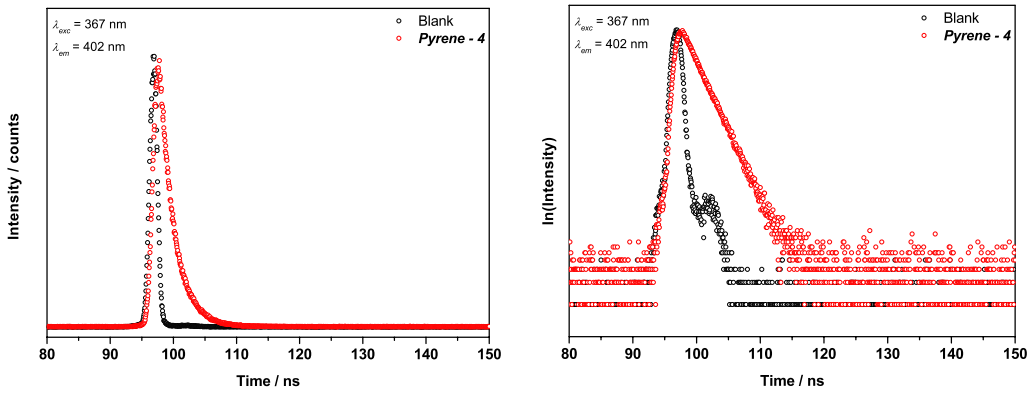
Figure S1. Correlation between (a) absorption peak, (b) molar absorptivity and (c) emission peak maximum and the number of fused rings.



(a) **(b)**

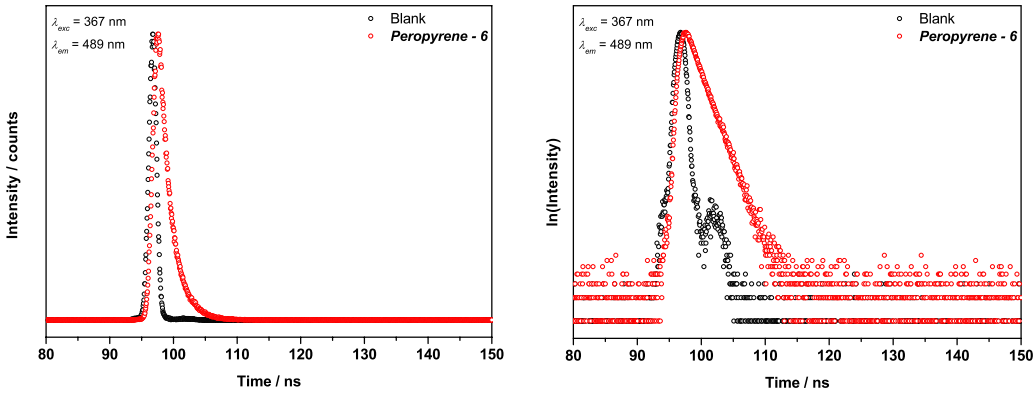
(c)

Figure S2. Plots of 'Emission area vs. Absorbance' for compounds (a) **7**, (b) **10** and (c) **13**. The concentrations of the solutions were in the range $1x10^{-5}$–$1x10^{-6}$ M in toluene. Inserts show linear regression analysis of the fit (red lines).



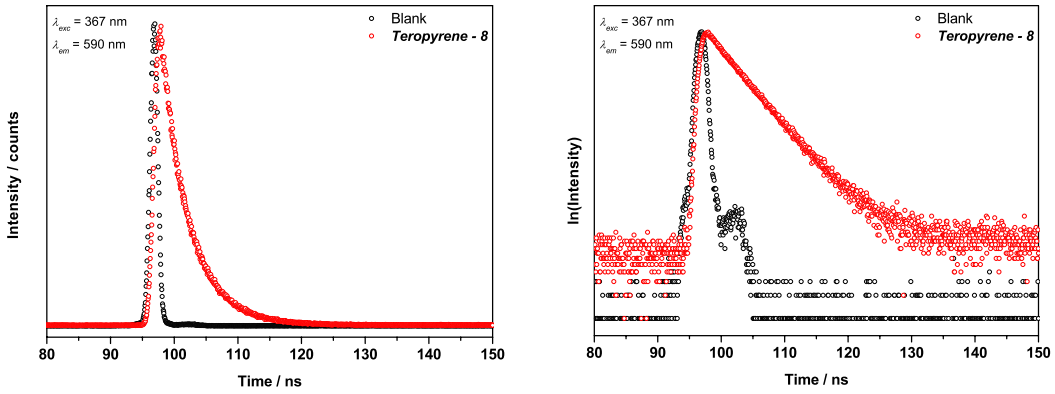
(a) **(b)**

Figure S3. Emission decay curves for **7**. (a) Exponential decay. (b) Linearization.



(a) **(b)**

Figure S4. Emission decay curves for **10**. (a) Exponential decay. (b) Linearization.

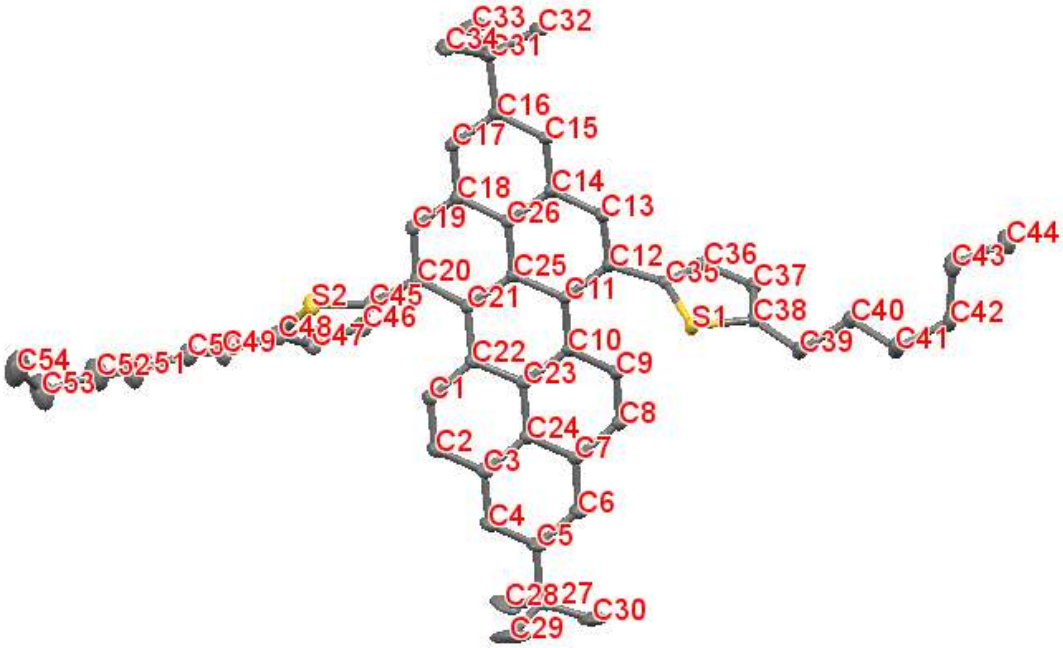


(a) **(b)**

Figure S5. Emission decay curves for **13**. (a) Exponential decay. (b) Linearization.

4. X-ray crystallographic analysis

Crystallographic data for **10**: $C_{54}H_{58}S_2$; *Mr*=771.12; crystal size= 0.715 x 0.135 x 0.100 mm^3; triclinic; space group *P-1*; *a*=11.8559(5), *b*=13.4824(6), *c*=14.0263(6) Å; α=70.6239(8) ° , β=88.9436(8) ° , γ=87.6922(8) ° ; *V*=2113.31(16) $Å^3$; *Z*=2, ρ_{calcd}=1.212 Mg/m^3; μ=0.163 mm^{-1}; λ=0.71073 Å; *T*=100(2) K; $2\theta_{max}$=60.00 ° ; reflections measured 52815, independent 12321 [*R(int)*=0.0432]; R_1=0.0646, wR_2=0.1831 (I>2σ(I)); residual electron density=1.417 and − 0.617 $eÅ^{-3}$. CCDC 1501742 (**10**) contains the supplementary crystallographic data for this paper. All these data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.



4.1 Crystal data and structure refinement for 10

Table S1 Crystal data and structure refinement for **10**.

Empirical formula	C54 H58 S2	
Formula weight	771.12	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 11.8559(5) Å	a= 70.6239(8)°.
	b = 13.4824(6) Å	b= 88.9436(8)°.
	c = 14.0263(6) Å	g = 87.6922(8)°.
Volume	2113.31(16) $Å^3$	
Z	2	

Density (calculated)	1.212 Mg/m^3
Absorption coefficient	0.163 mm^{-1}
F(000)	828
Crystal size	0.715 x 0.135 x 0.100 mm^3
Theta range for data collection	1.539 to 29.999°.
Index ranges	-16<=h<=16, -18<=k<=18, -19<=l<=19
Reflections collected	52815
Independent reflections	12321 [R(int) = 0.0432]
Completeness to theta = 25.242°	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7461 and 0.7140
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	12321 / 30 / 535
Goodness-of-fit on F^2	1.113
Final R indices [I>2sigma(I)]	R1 = 0.0646, wR2 = 0.1831
R indices (all data)	R1 = 0.0869, wR2 = 0.1962
Extinction coefficient	n/a
Largest diff. peak and hole	1.417 and -0.617 $e.Å^{-3}$

Table S2 Selected bond lengths [Å] for **10**.

C(1)-C(2)	1.355(3)	C(5)-C(6)	1.396(3)	C(9)-C(10)	1.447(2)
C(1)-C(22)	1.442(2)	C(5)-C(27)	1.531(3)	C(10)-C(23)	1.427(2)
C(2)-C(3)	1.428(3)	C(6)-C(7)	1.404(2)	C(10)-C(11)	1.429(2)
C(3)-C(4)	1.400(3)	C(7)-C(24)	1.412(2)	C(11)-C(25)	1.436(2)
C(3)-C(24)	1.420(2)	C(7)-C(8)	1.431(2)	C(11)-C(12)	1.454(2)
C(4)-C(5)	1.393(3)	C(8)-C(9)	1.357(2)		

Table S3 Selected bond angles [°] for **10**.

C(2)-C(1)-C(22)	121.84(17)	C(24)-C(7)-C(8)	118.08(16)
C(1)-C(2)-C(3)	121.18(17)	C(9)-C(8)-C(7)	121.34(17)
C(4)-C(3)-C(24)	119.70(17)	C(8)-C(9)-C(10)	122.19(17)
C(4)-C(3)-C(2)	121.90(17)	C(23)-C(10)-C(11)	118.92(15)
C(24)-C(3)-C(2)	118.39(16)	C(23)-C(10)-C(9)	116.97(15)
C(5)-C(4)-C(3)	122.28(18)	C(11)-C(10)-C(9)	124.06(16)
C(4)-C(5)-C(6)	117.56(17)	C(10)-C(11)-C(25)	117.99(15)
C(5)-C(6)-C(7)	122.13(18)	C(10)-C(11)-C(12)	124.29(16)
C(6)-C(7)-C(24)	119.76(17)	C(25)-C(11)-C(12)	117.70(15)
C(6)-C(7)-C(8)	122.15(17)		

Table S4 Selected torsion angles [°] for **10**.

C(22)-C(1)-C(2)-C(3)	-1.5(3)	C(6)-C(7)-C(8)-C(9)	-176.25(18)
C(1)-C(2)-C(3)-C(4)	-175.81(19)	C(24)-C(7)-C(8)-C(9)	4.9(3)

C(1)-C(2)-C(3)-C(24)	5.2(3)	C(7)-C(8)-C(9)-C(10)	-2.2(3)
C(24)-C(3)-C(4)-C(5)	-1.9(3)	C(8)-C(9)-C(10)-C(23)	-5.5(3)
C(2)-C(3)-C(4)-C(5)	179.10(19)	C(8)-C(9)-C(10)-C(11)	176.81(17)
C(3)-C(4)-C(5)-C(6)	0.2(3)	C(23)-C(10)-C(11)-C(25)	-16.0(2)
C(4)-C(5)-C(6)-C(7)	1.8(3)	C(9)-C(10)-C(11)-C(25)	161.61(17)
C(27)-C(5)-C(6)-C(7)	-179.2(2)	C(11)-C(12)-C(35)-S(1)	-72.2(2)
C(5)-C(6)-C(7)-C(24)	-2.2(3)	C(10)-C(11)-C(12)-C(35)	-3.1(3)
C(5)-C(6)-C(7)-C(8)	178.99(19)		

5. ^{1}H and ^{13}C NMR spectra for new compounds

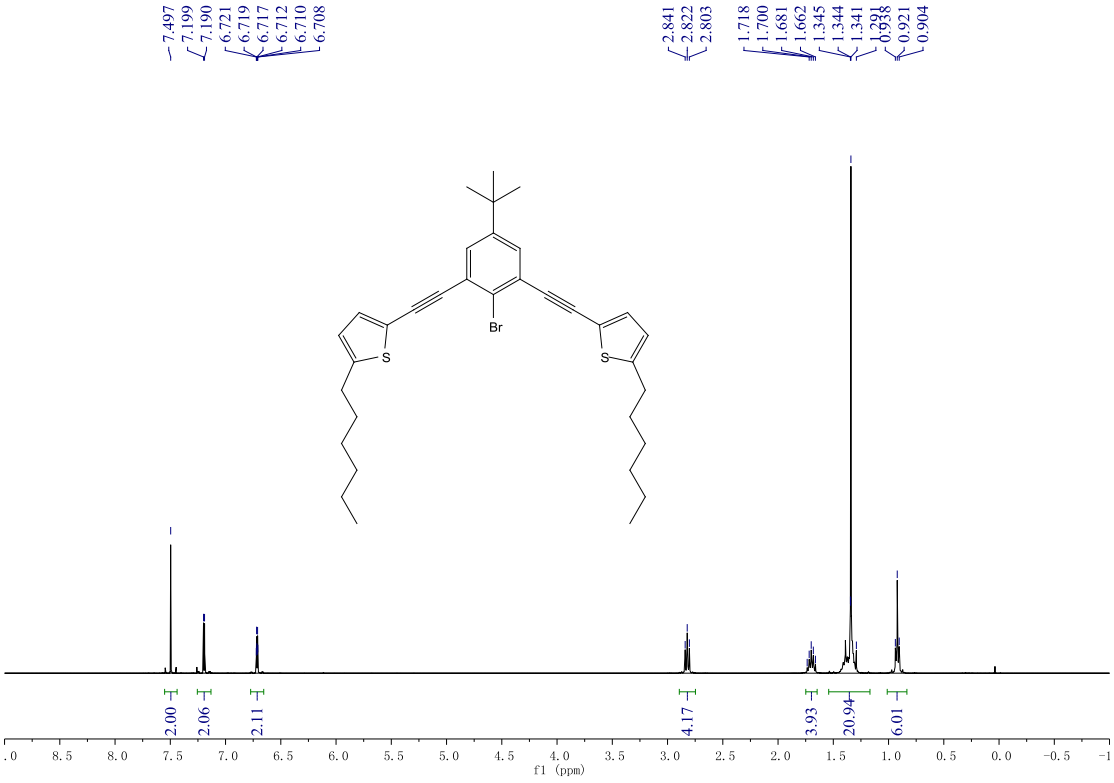


Figure S6. ^{1}H NMR spectrum for compound **3** in $CDCl_3$ at 298 K.

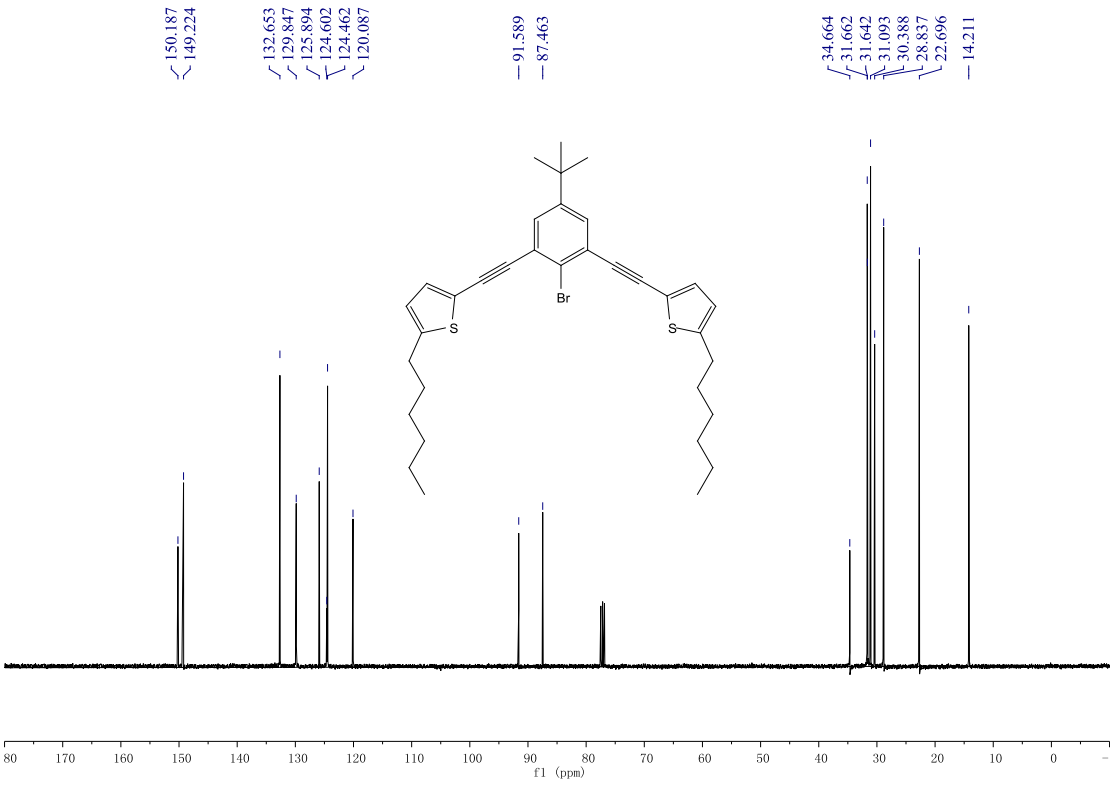


Figure S7. ^{13}C NMR spectrum for compound **3** in $CDCl_3$ at 298 K.

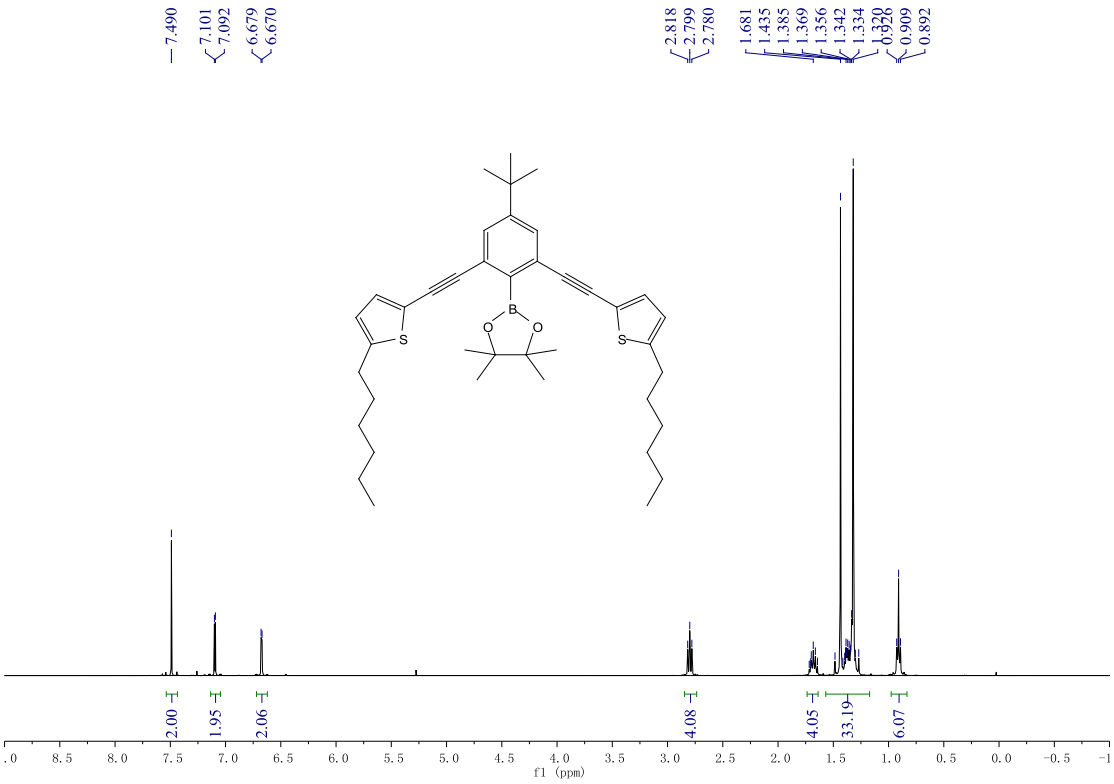


Figure S8. ^{1}H NMR spectrum for compound **4** in $CDCl_3$ at 298 K.

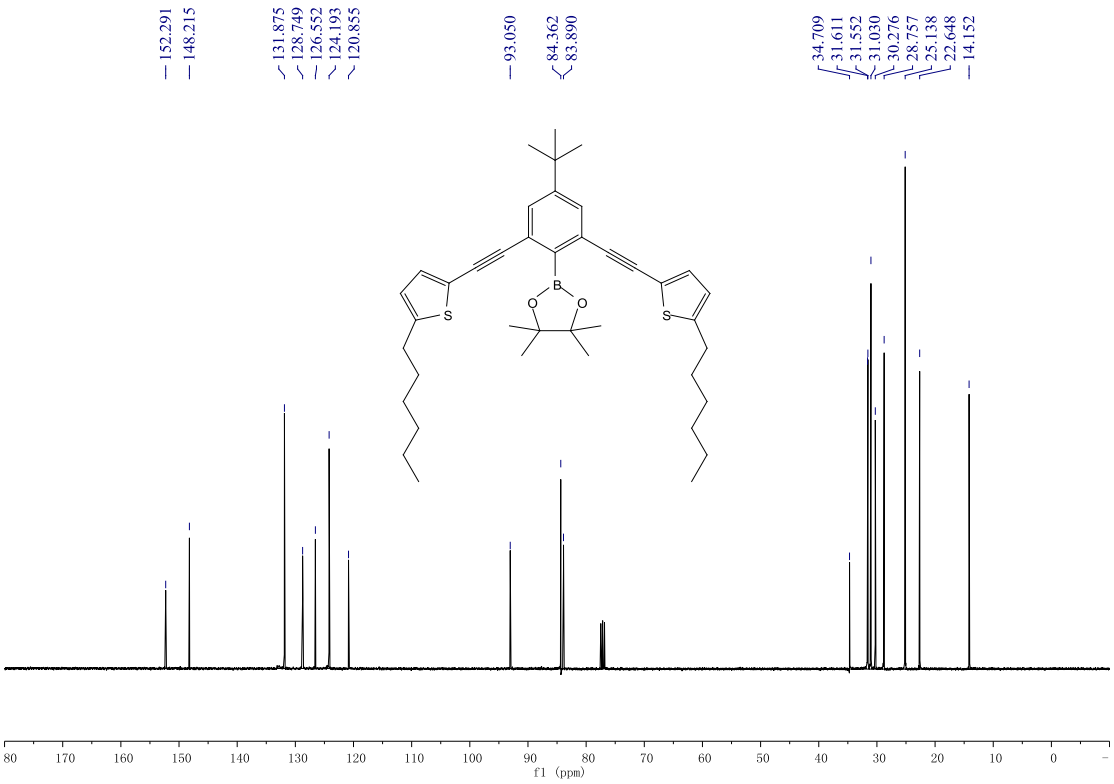


Figure S9. ^{13}C NMR spectrum for compound **4** in $CDCl_3$ at 298 K.

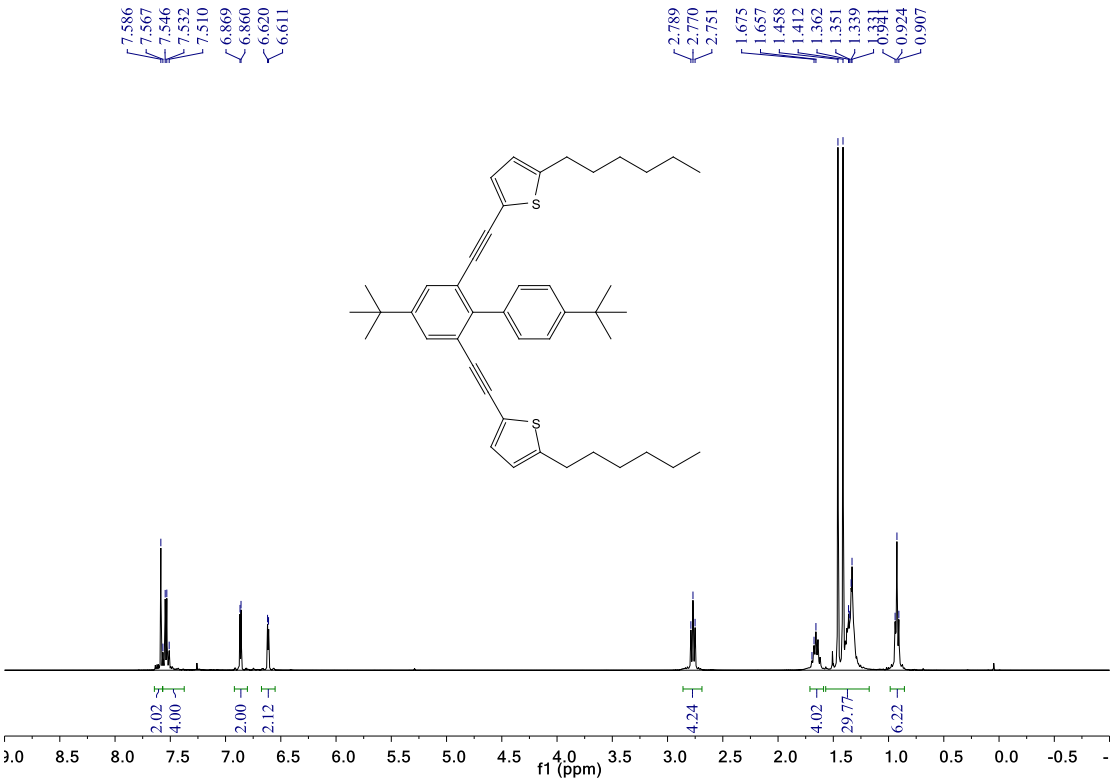


Figure S10. ^{1}H NMR spectrum for compound **6** in $CDCl_3$ at 298 K.

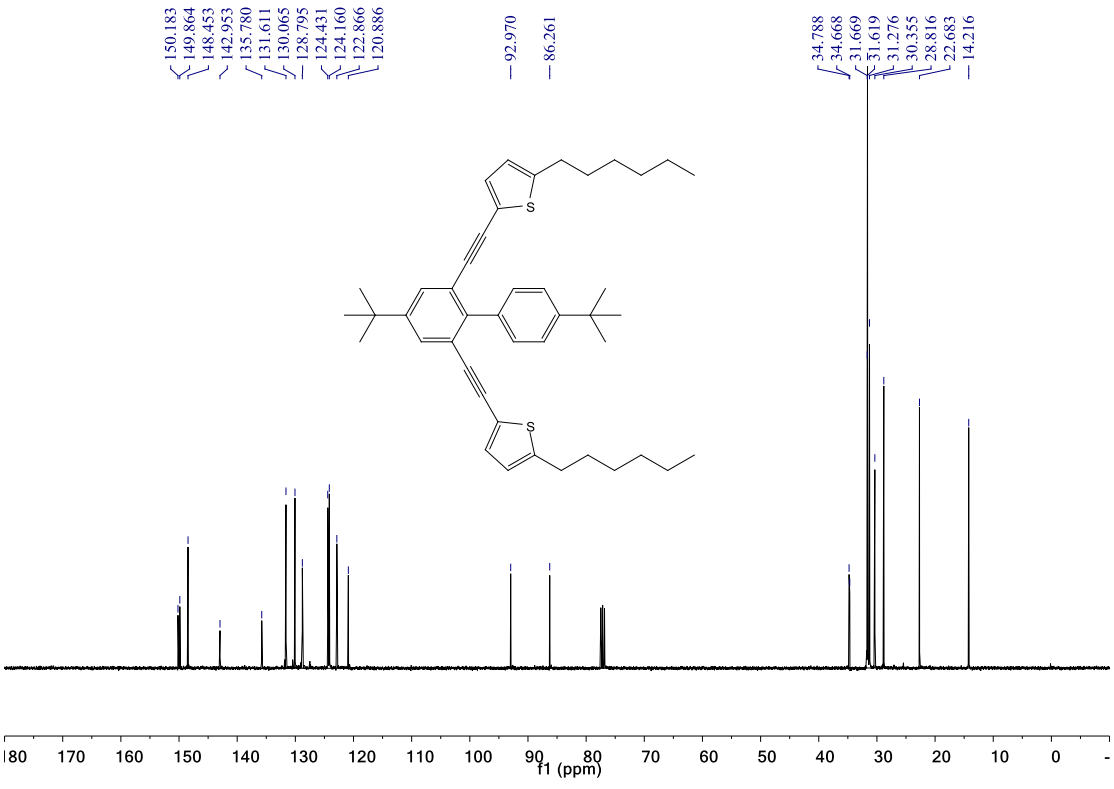


Figure S11. ^{13}C NMR spectrum for compound **6** in $CDCl_3$ at 298 K.

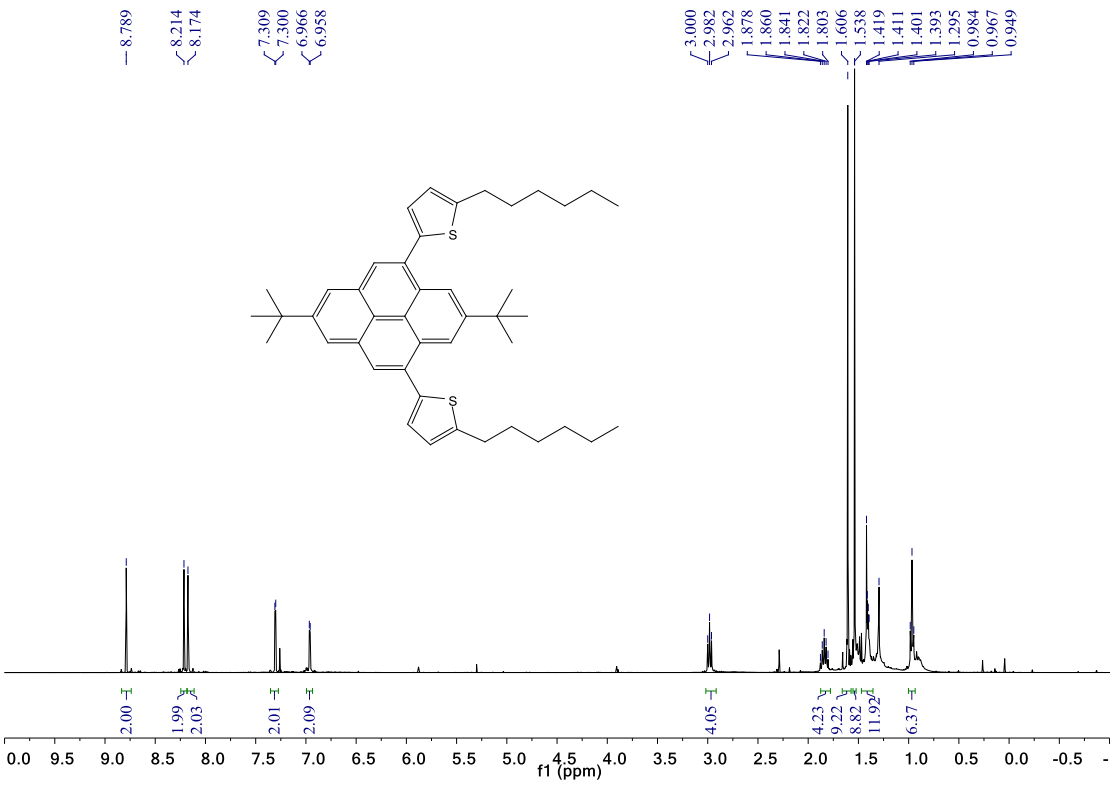


Figure S12. ^{1}H NMR spectrum for compound **7** in $CDCl_3$ at 298 K.

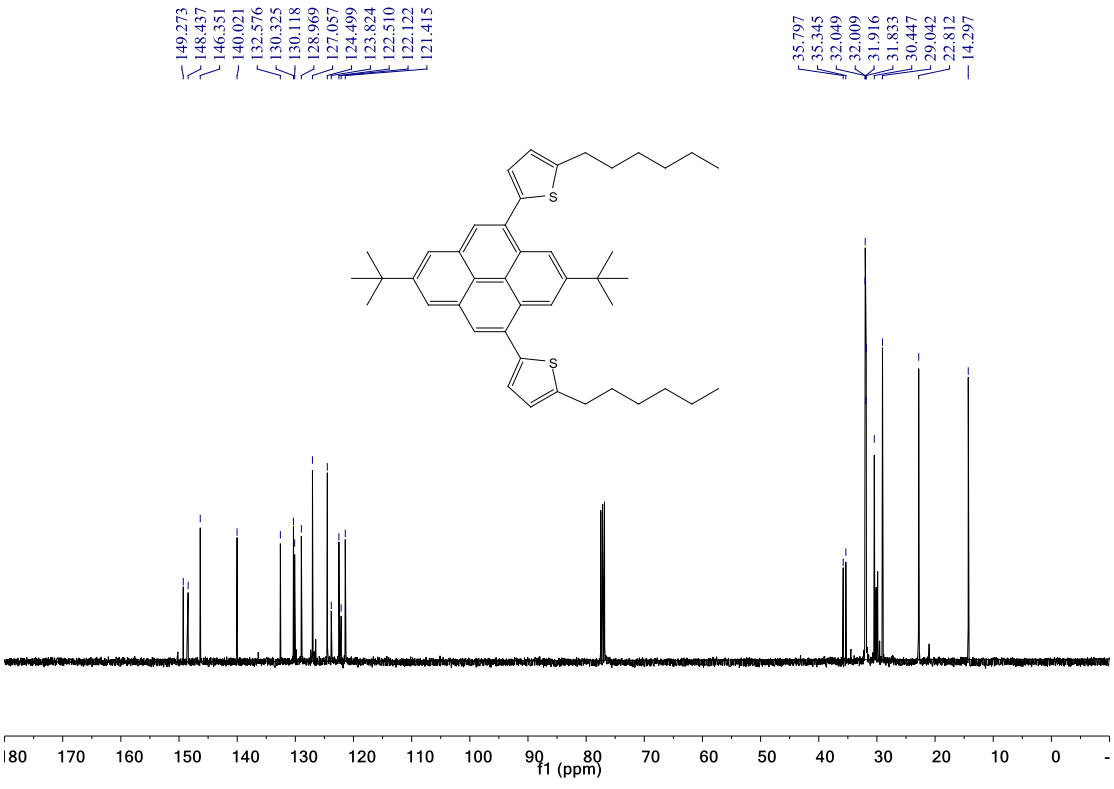


Figure S13. ^{13}C NMR spectrum for compound **7** in $CDCl_3$ at 298 K.

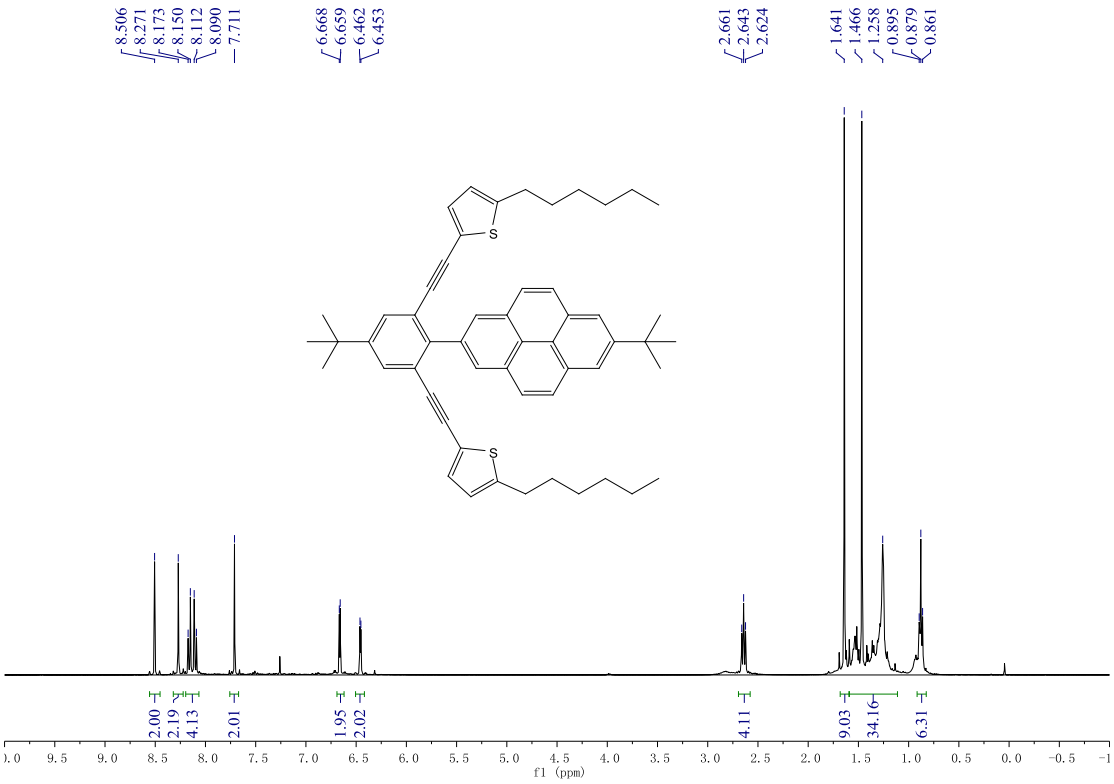


Figure S14. ^{1}H NMR spectrum for compound **9** in $CDCl_3$ at 298 K.

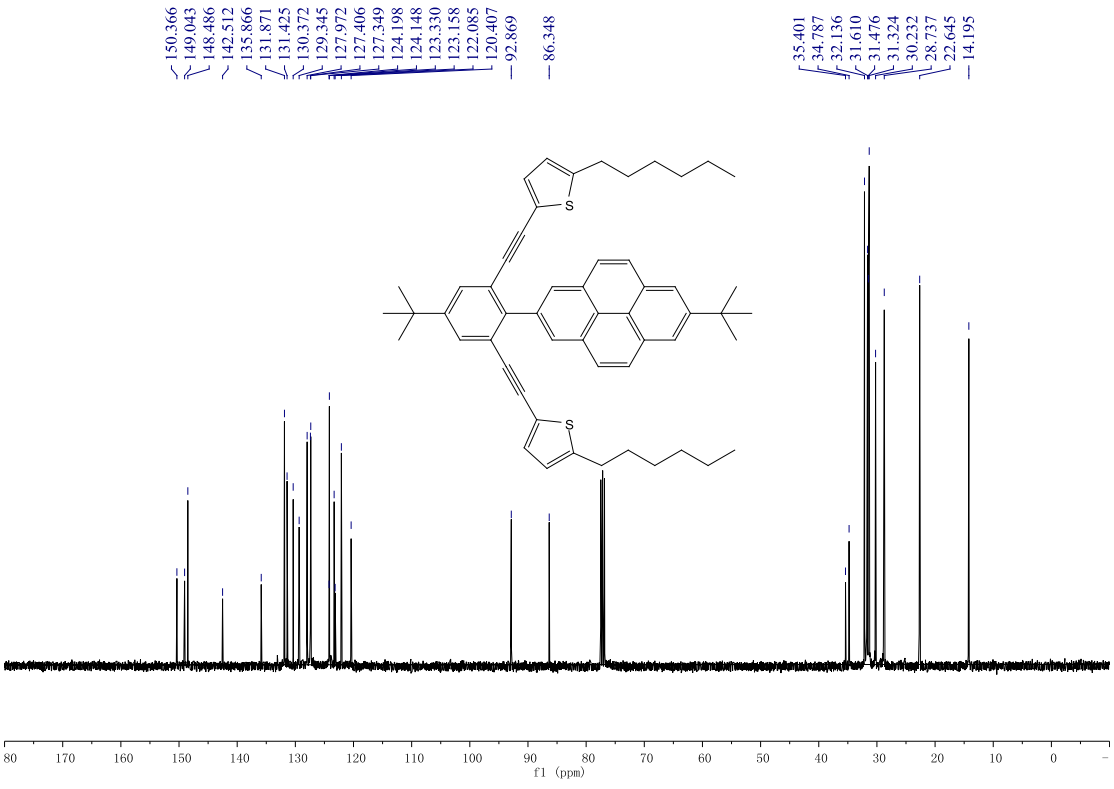


Figure S15. ^{13}C NMR spectrum for compound **9** in $CDCl_3$ at 298 K.

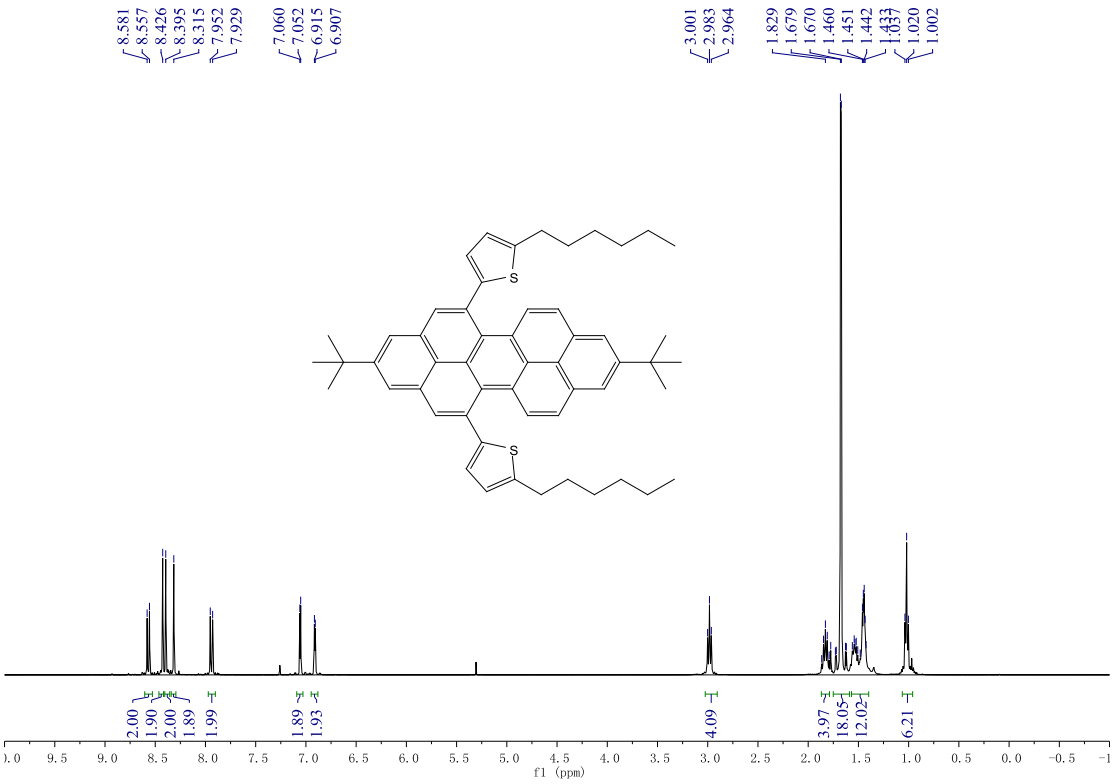


Figure S16. ^{1}H NMR spectrum for compound **10** in $CDCl_3$ at 298 K.

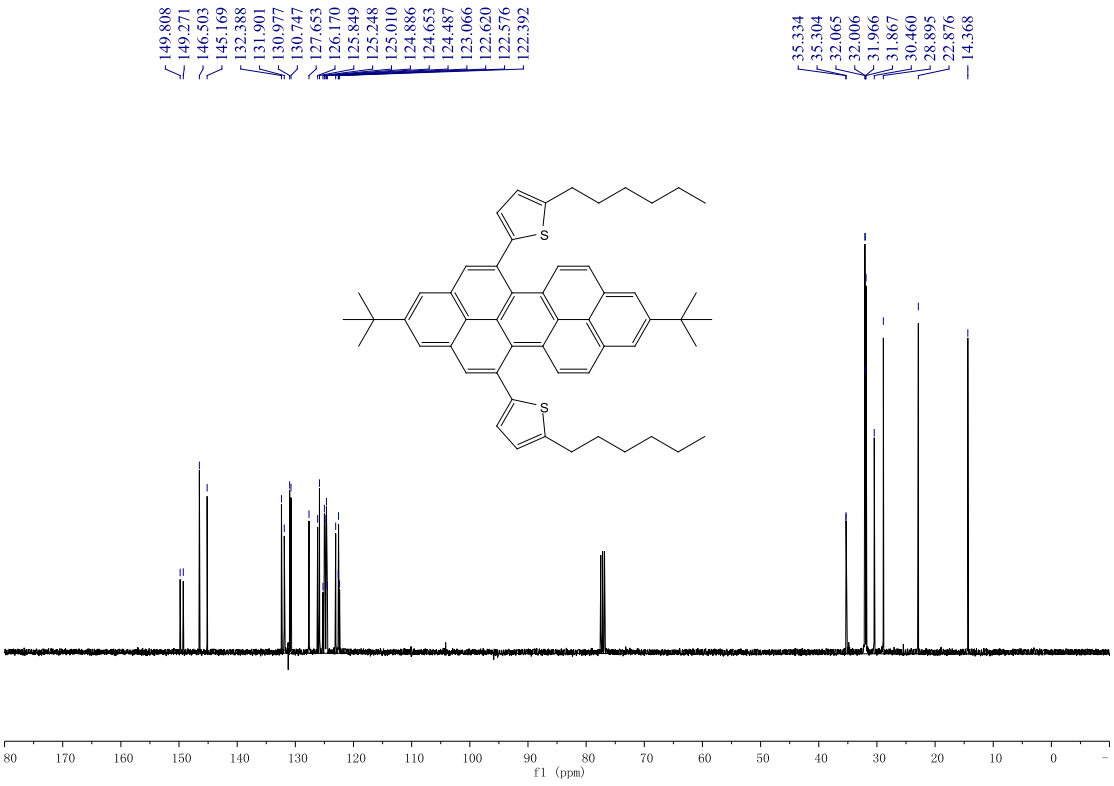


Figure S17. ^{13}C NMR spectrum for compound **10** in $CDCl_3$ at 298 K.

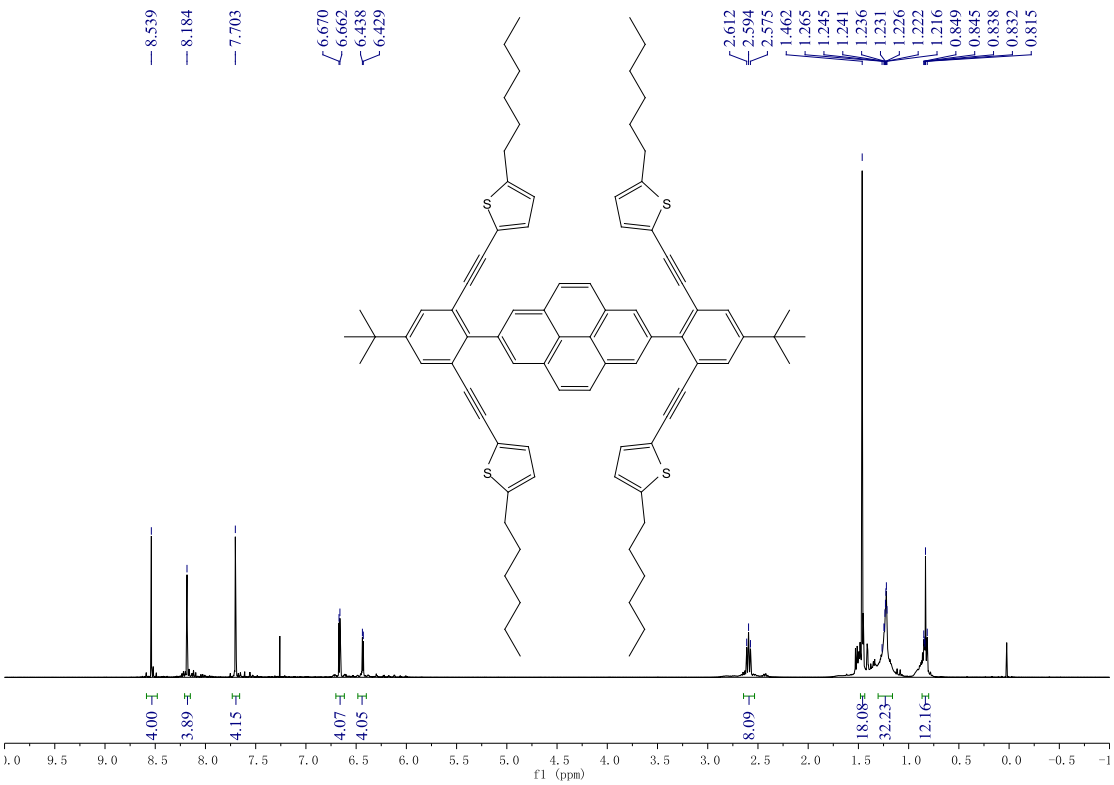


Figure S18. ^{1}H NMR spectrum for compound **12** in $CDCl_3$ at 298 K.

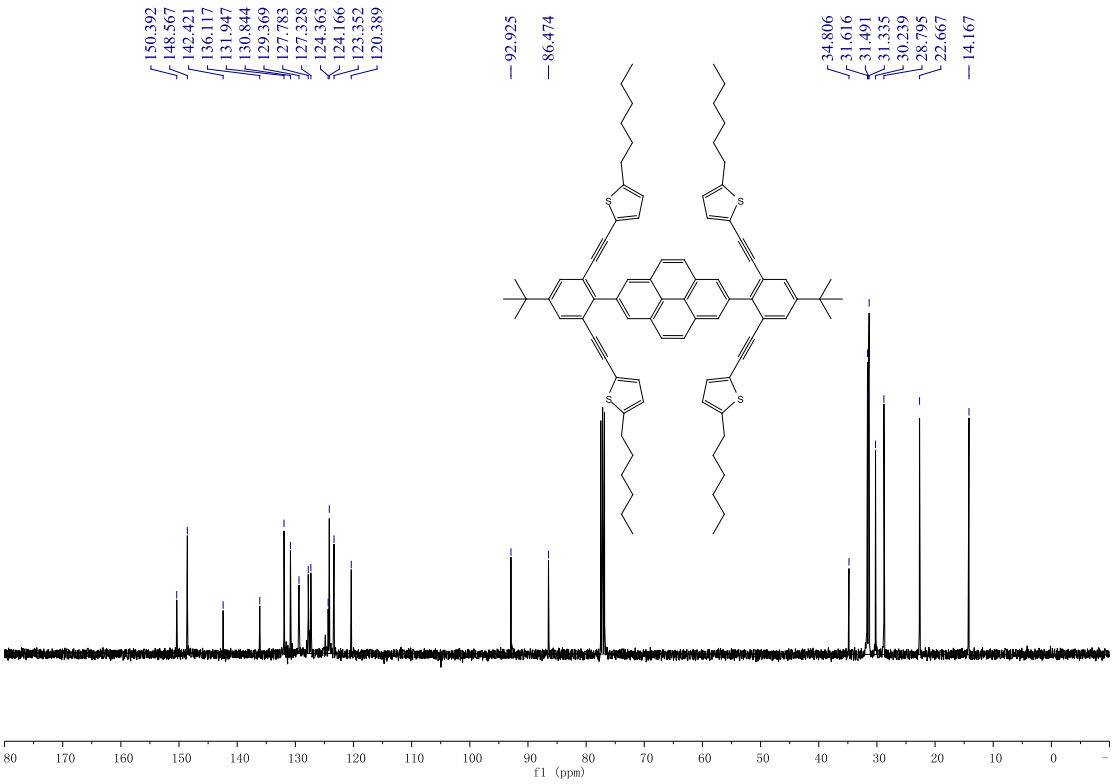


Figure S19. ^{13}C NMR spectrum for compound **12** in $CDCl_3$ at 298 K.

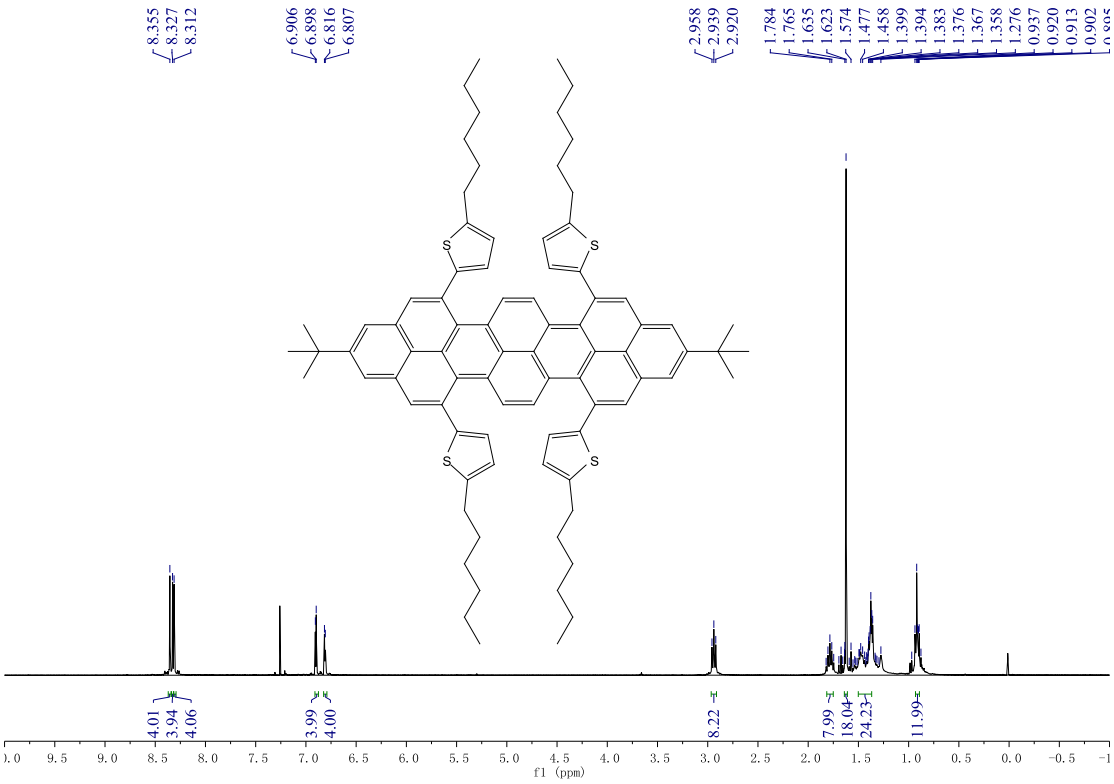


Figure S20. ^{1}H NMR spectrum for compound **13** in $CDCl_3$ at 298 K.

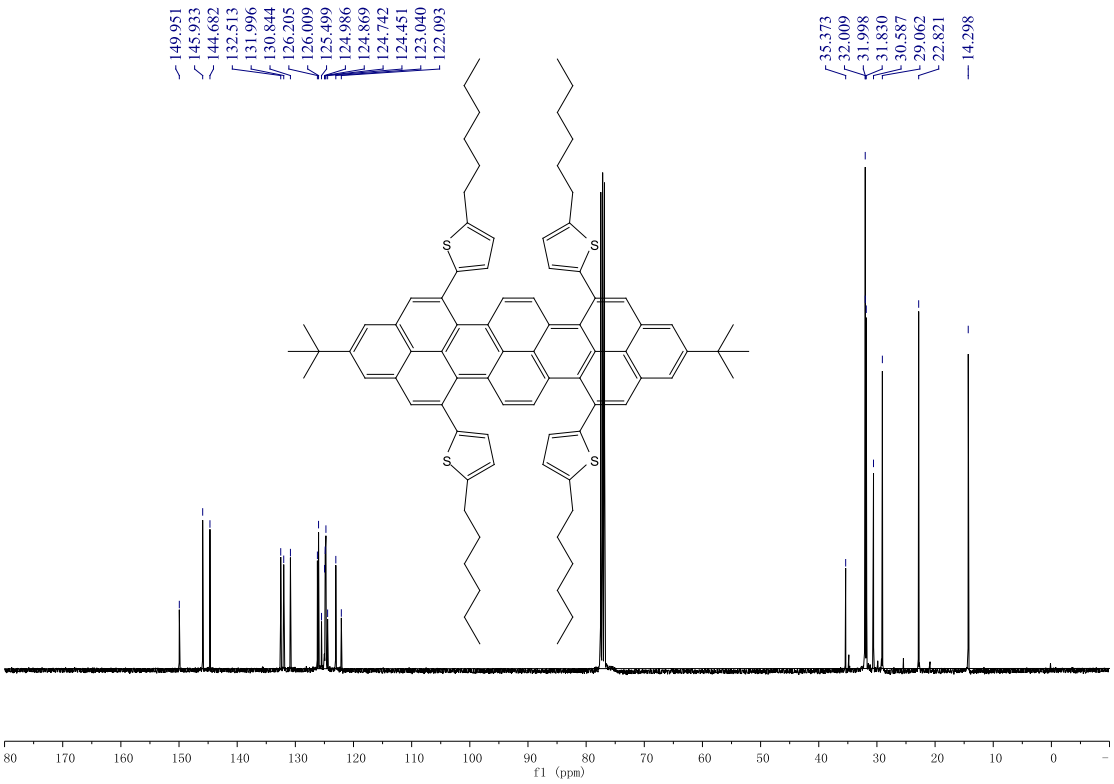


Figure S21. ^{13}C NMR spectrum for compound **13** in $CDCl_3$ at 298 K.

6. References:

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