

## Supporting Information

### Coronene-Embedded 'Super' Coumarins

Nitisha, Prabhakar Chetti, and Parthasarathy Venkatakrishnan

*Department of Chemistry, Indian Institute of Technology Madras, Chennai - 600036,  
Tamil Nadu, INDIA*

*Department of Chemistry, National Institute of Technology, Kurukshetra – 136119,  
Haryana, INDIA*

[pvenkat@iitm.ac.in](mailto:pvenkat@iitm.ac.in)

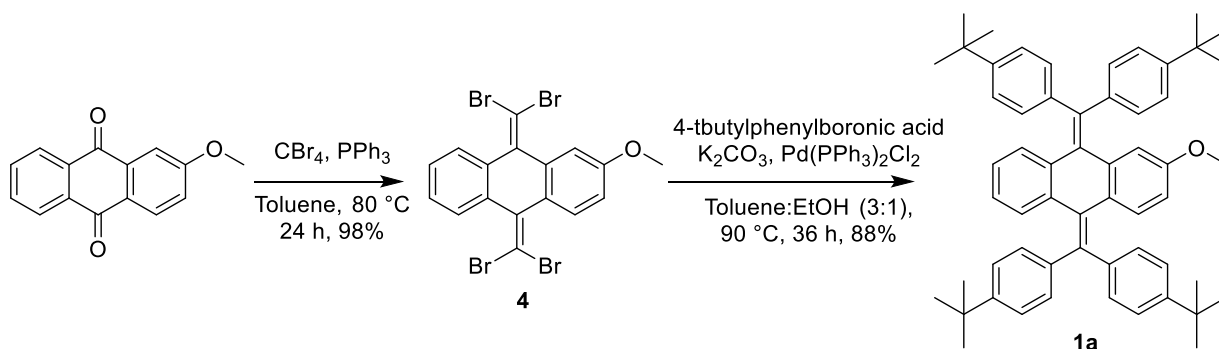
---

### Table of contents

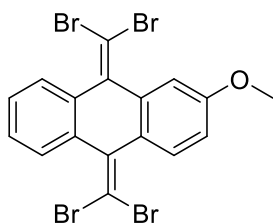
S. No.	Title	Page No.
1.	General Information	S2
2.	Experimental section	S2
3.	NMR Scans	S9
4.	X-ray Crystal Structure Characterization Details	S22
5.	Variable temperature <sup>1</sup> H NMR spectrum of TTBBCC-CN	S24
6.	Concentration dependent <sup>1</sup> H NMR spectrum of TTBBCC	S25
7.	Photophysical characterization details	S26
8.	DFT Calculations	S27
9.	Time-Resolved fluorescence measurements	S32
10.	Dipole moment calculations	S35
11.	Electrochemical properties	S43
12.	Comparison table	S44
13.	References	S47

**General Information.** All the reagents were purchased commercially and used without any further purification. The starting materials were prepared in the laboratory as reported in the literature.<sup>1, 2, 3</sup> The required solvents were dried and distilled prior to use for the reactions. Column chromatography was performed on 100- 200 silica gel mesh, and thin layer chromatography (TLC) was performed to check the progress of the reaction. The newly synthesized products were analyzed by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy, recorded by a Bruker Avance 400 spectrophotometer and the chemical shifts (in ppm) referenced relative to residual protic solvent peak (CDCl<sub>3</sub> in particular). High resolution Q-ToF mass spectrometer was used to obtain the High-resolution mass spectra.

## Experimental Section

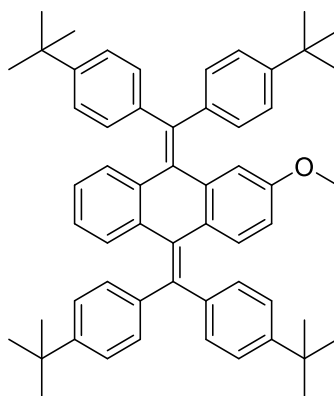


**Synthesis of 9,10-bis(dibromomethylene)-2-methoxy-9,10-dihydroanthracene (4).** To a mixture of 2-methoxy-9,10-anthraquinone (0.70 g, 2.94 mmol), carbon tetrabromide (3.12g, 9.41 mmol) and triphenylphosphine (5.39 g, 20.58 mmol), was added 10 ml dry toluene in a 100 ml two-necked round bottom flask. The reaction mixture was kept for stirring and heated at 80 °C temperature for 24 hours under nitrogen atmosphere. The progress of the reaction was monitored by thin layer chromatography. After the completion of the reaction, the reaction mixture was passed through the celite and washed with hexane. The collected filtrate was then concentrated by evaporating the solvent on rotary evaporator. The crude thus obtained was directly passed through the column chromatography to afford the purified product in 98% yield.



Yield: 1.5 g, 98%; white solid; Mp: 120-124 °C;  $R_f$  = 0.48 (in hexane); IR (KBr,  $\text{cm}^{-1}$ ): 3063, 3008, 2955, 2835, 1603, 1565, 1470, 1306, 1229, 1180, 1158, 1103, 1037, 980, 938, 881, 820, 761, 696, 664, 613, 571, 544;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.87-7.80 (m, 2H), 7.76 (d,  $J$  = 8.4 Hz, 1H), 7.37 (s, 1H), 7.26-7.30 (m, 2H), 6.82 (d,  $J$  = 8.8 Hz, 1H), 3.83 (s, 3H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  158.3, 139.7, 139.2, 137.4, 136.2, 136.0, 129.0, 128.5, 127.8, 127.7, 127.1, 127.0, 113.3, 112.9, 90.6, 89.4, 55.7; HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd. for  $\text{C}_{17}\text{H}_{11}\text{Br}_4\text{O}$ , 546.7543; found, 546.7545.

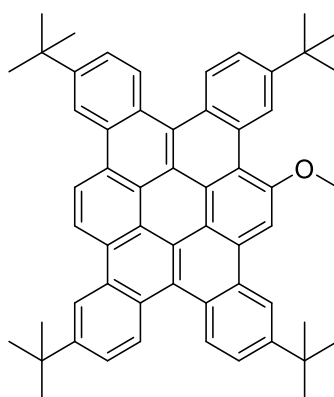
**Synthesis of 9,10-bis(bis(4-(*tert*-butyl)phenyl)methylene)-2-methoxy-9,10-dihydroanthracene (1a).** To the two-necked round bottom flask, compound **4** (0.60 g, 1.09 mmol), *tert*-butylphenyl boronic acid (1.16 g, 6.54 mmol), and potassium carbonate (0.75 g, 5.45 mmol) were added. The contents were dissolved in toluene-ethanol (3:1 = v/v) mixture of solvents. After the solution was purged with nitrogen for 10 minutes,  $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$  (0.11 g, 0.15 mmol) was added into it. The reaction mixture was kept stirring in oil bath for overnight at 90 °C. The completion of the reaction was estimated by TLC. Upon completion of the reaction, the organic layer was separated by using ethyl acetate (3  $\times$  10 ml) and washed with brine water. The collected organic layer was dried over anhydrous sodium sulphate and then concentrated by applying vacuum on rotary evaporator to afford the crude product. The crude was further purified by column chromatography to obtain the pure product in 88% yield.



Yield: 0.731 g, 88%; dull white solid; Mp: 221-225 °C;  $R_f$  = 0.31 (10% chloroform in hexane); IR (KBr,  $\text{cm}^{-1}$ ): 3077, 3027, 2861, 2904, 2868, 1603, 1506, 1466, 1398, 1363, 1301, 1271, 1236, 1110, 1027, 858, 827, 800, 759, 717, 637, 585;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.38-7.27 (m, 16H), 7.03-6.94 (m, 2H), 6.85 (d,  $J$  = 8.8 Hz, 1H), 6.73-6.64 (m, 2H), 6.47 (d,  $J$  = 2.0 Hz, 1H), 6.25 (dd,  $J$  = 2.0 Hz,  $J$  = 8.4 Hz, 1H), 3.27 (s, 3H), 1.33-1.28

(m, 36 H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  156.5, 149.3, 149.2, 149.12, 149.07, 140.1, 139.93, 139.89, 139.5, 139.0, 138.6, 138.3, 137.7, 135.2, 134.4, 130.6, 129.35, 129.31, 129.2, 128.2, 128.1, 125.2, 125.1, 125.0, 124.8, 124.7, 113.2, 111.3, 54.7, 34.4, 31.4; HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd. for  $\text{C}_{57}\text{H}_{63}\text{O}$ , 763.4879; found, 763.4825.

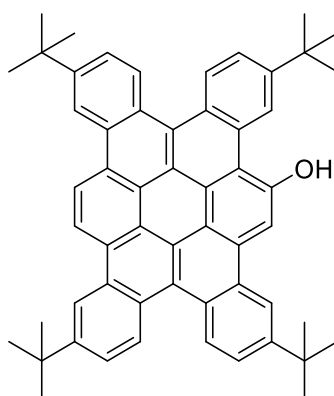
**Synthesis of 2,7,12,17-tetra-*tert*-butyl-9-methoxytetrabenzo[*a,d,j,m*]coronene (1).** To a (100 ml) quartz tube, were added compound **1a** (0.070 g, 0.09 mmol), iodine (0.033 g, 0.26 mmol), and propylene oxide (2 ml), and dissolved in 75 ml toluene. The solution was kept for stirring at room temperature in a Luzchem photoreactor (16 lamps,  $\lambda = 350$  nm) for 36 hours. The progress of the reaction was checked by TLC. After completion of the starting material, the reaction was stopped. The solvent was evaporated under vacuum on rotary evaporator. The organic contents were then extracted into chloroform ( $3 \times 5$  ml) and washed with hypo solution followed by brine solution. The organic layers were combined, dried over anhydrous sodium sulphate, filtered and evaporated on a rotary evaporator to dryness. The partially cyclized crude product obtained was dissolved in 10 ml dichloromethane, to which  $\text{FeCl}_3$  (0.117 g, 0.72 mmol) was added and kept for stirring at room temperature for 1 hour. After the completion of the reaction monitored by TLC, methanol was added to quench the reaction followed by evaporating the solvent. The compound was further extracted by chloroform ( $3 \times 5$  ml), washed with brine, dried over anhydrous sodium sulphate and evaporated to dryness. The isolated crude product was then passed through column chromatography to afford the pure product in 70% yield.



Yield: 0.048g, 70%; yellow solid; Mp:  $>330$  °C;  $R_f = 0.34$  (10% Chloroform in hexane); IR (KBr,  $\text{cm}^{-1}$ ): 2957, 2863, 1715, 1609, 1465, 1392, 1362, 1261, 1224, 1126, 1007, 835, 781, 757, 702, 617;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) ( $\delta$  10.12 (s, 1H), 9.45 (s, 2H), 9.26–9.12 (m, 6H), 9.10 (s, 1H), 8.89 (s, 1H), 7.95–7.86 (m, 4H), 4.57 (s, 3H), 1.67 (s, 9H), 1.66 (s, 18H), 1.63

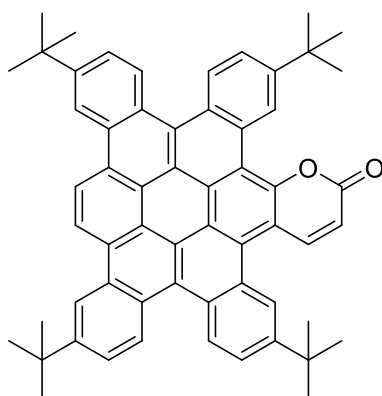
(s, 9H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  157.2, 149.5, 149.0, 148.8, 148.6, 130.3, 129.9, 129.7, 129.5, 129.4, 129.2, 128.5, 127.7, 127.5, 127.2, 127.03, 126.99, 126.7, 126.4, 125.3, 124.4, 124.3, 124.2, 124.1, 123.7, 122.62, 122.57, 122.4, 121.7, 121.6, 119.5, 119.3, 119.2, 119.1, 119.0, 103.6, 56.7, 35.5, 35.4, 31.8; HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{Na}]^+$  Calcd. for  $\text{C}_{57}\text{H}_{54}\text{NaO}$ , 777.4072; found, 777.4069.

**2,7,12,17-Tetra-*tert*-butyltetrabenzo[*a,d,j,m*]coronen-9-ol (2a).** To a two-necked round bottom flask, compound **1** (0.20 g, 0.26 mmol) was dissolved in 20 ml dichloromethane. The solution was cooled to 0 °C and boron tribromide (15  $\mu\text{l}$ , 0.32 mmol) was added and stirred at room temperature for 2 hours. The progress of the reaction was monitored by TLC. After completion of the reaction, the reaction was quenched by addition of water. The organic components were extracted into chloroform (3  $\times$  5 ml) and washed with brine and dried over anhydrous sodium sulphate. After filtration, the solvent was evaporated to dryness on a rotary evaporator to afford the crude product. The crude product was further passed through column chromatography to afford the purified dark yellow product in 78% yield.



Yield: 0.150 g, 78%; dark yellow solid; Mp: >330 °C;  $R_f$  = 0.39 (30% Chloroform in hexane); IR (KBr,  $\text{cm}^{-1}$ ): 3448, 2954, 2866, 1629, 1619, 1568, 1519, 1477, 1396, 1357, 1260, 1197, 1098, 875, 834, 786, 756, 712, 618;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.05 (s, 1H), 9.45 (s, 2H), 9.24–9.13 (m, 6H), 9.03 (s, 1H), 8.79 (s, 1H), 7.94–7.87 (m, 4H), 6.39 (s, 1H), 1.66 (s, 27H), 1.62 (s, 9H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  152.7, 149.4, 149.0, 148.9, 148.8, 130.2, 129.8, 129.6, 129.4, 128.9, 128.5, 127.6, 127.5, 127.2, 127.0, 126.9, 126.3, 125.2, 124.4, 124.3, 124.2, 123.9, 123.6, 123.1, 122.5, 121.6, 119.2, 118.0, 107.8, 35.5, 35.4, 31.8, 31.7; HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd. for  $\text{C}_{56}\text{H}_{53}\text{O}$ , 741.4096; found, 741.4037.

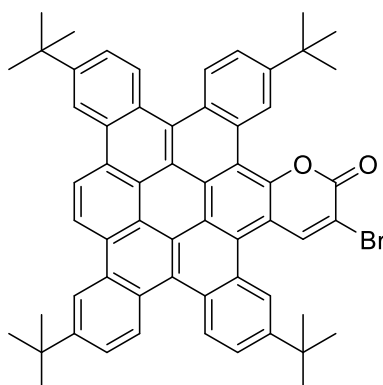
**6,11,16,21-Tetra-*tert*-butyl-2*H*-piceno[5',6',7',8':5,6,7,8]pentapheno[13,14-*fgh*]chromen-2-one (2).** A 50 ml round bottom flask was charged with compound **2a** (0.050 g, 0.06 mmol), ethyl propiolate (9  $\mu$ l, 0.076 mmol) and 2 ml methanesulphonic acid. The reaction mixture was stirred at 90 °C in oil bath for 50 minutes under nitrogen atmosphere. The reaction progress was monitored by TLC, and on completion the reaction was quenched by addition of water. The organic layer was extracted by ethyl acetate (3  $\times$  5 ml) and dried over anhydrous sodium sulphate. The crude product was then concentrated on vacuum using a rotary evaporator. Crude product was further purified by column chromatography using 30% chloroform in hexane as an eluent to yield 57% of pure product.



Yield: 0.030 g, 57%; orange red solid; Mp >330 °C;  $R_f$  = 0.29 (5% ethyl acetate in hexane); IR (KBr,  $\text{cm}^{-1}$ ): 2927, 2864, 1728, 1657, 1615, 1568, 1461, 1390, 1243, 1095, 1061, 924, 829, 748, 712, 614;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.76 (s, 1H), 9.04-8.96 (m, 3H), 8.87-8.76 (m, 3H), 8.72 (d,  $J$  = 8.0 Hz, 1H), 8.53–8.38 (m, 2H), 8.36 (s, 1H), 7.93–7.83 (m, 2H), 7.73 (d,  $J$  = 8.0 Hz, 1H), 7.67 (d,  $J$  = 8.0 Hz, 1H), 6.49 (d,  $J$  = 8.0 Hz, 1H), 1.80 (s, 9H), 1.78 (s, 9H), 1.66 (s, 9H), 1.55 (s, 9H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  160.1, 152.3, 149.8, 149.6, 149.1, 148.9, 145.1, 130.4, 129.6, 129.4, 129.2, 128.9, 127.8, 127.4, 127.3, 126.9, 126.7, 126.5, 125.7, 125.5, 124.9, 124.6, 124.4, 123.9, 123.5, 121.9, 120.4, 120.1, 118.9, 118.7, 115.0, 113.1, 111.6, 35.64, 35.58, 35.4, 31.9, 31.8, 31.6; HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd. for  $\text{C}_{59}\text{H}_{53}\text{O}_2$ , 793.4046; found, 793.3983.

**3-Bromo-6,11,16,21-tetra-*tert*-butyl-2*H*-piceno[5',6',7',8':5,6,7,8]pentapheno[13,14-*fgh*]chromen-2-one (3a).** To a 50 mL round bottom flask equipped with magnetic bar, oxone (0.010 mg, 0.068 mmol) was added to a solution of compound **2** (0.045 g, 0.06 mmol) in dichloromethane (1 mL). To this, 48% HBr (7  $\mu$ L, 0.12 mmol) dissolved in 0.1 ml of  $\text{H}_2\text{O}$ , was added dropwise. The reaction mixture was allowed to stir at room temperature for

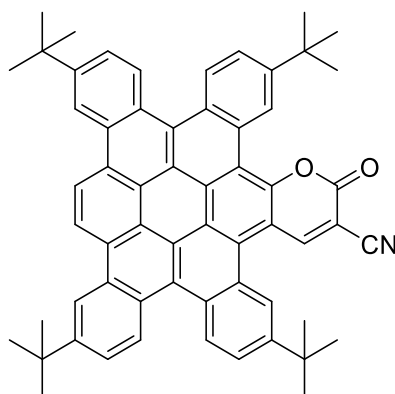
6 h. The progress of the reaction was monitored by TLC. Then Et<sub>3</sub>N (0.05 mL) was added into the reaction mixture and the reaction was stirred overnight at room temperature. On completion, the reaction was diluted by addition of water and extracted into chloroform (3×5ml). The collected organic layer was dried over anhydrous sodium sulphate. The crude product was then concentrated on high vacuum using rotary evaporator. The compound was purified by column chromatography using 15% chloroform in hexane as an eluent to yield 65% of pure product.



Yield: 0.032 g, 65%; dark red solid; Mp >330 °C; R<sub>f</sub> = 0.37 (30% Chloroform in hexane); IR (KBr, cm<sup>-1</sup>): 2958, 2927, 2866, 1743, 1654, 1613, 1566, 1547, 1527, 1471, 1463, 1362, 1261, 1109, 982, 890, 835, 790, 610; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.76 (s, 1H), 9.44 (s, 1H), 9.08 (d, *J* = 8.4 Hz, 1H), 8.99 (d, *J* = 6.0 Hz, 1H), 8.94–8.88 (m, 3H), 8.79 (s, 1H), 8.75–8.57 (m, 2H), 8.41 (s, 1H), 7.96–7.88 (m, 2H), 7.77 (s, 1H), 7.75 (s, 1H), 1.78 (s, 9H), 1.76 (s, 9H), 1.64 (s, 9H), 1.58 (s, 9H); <sup>13</sup>C NMR signals were not observed due to signal broadness even at 10 mg per 0.5 mL of concentration and 15000 scans in 500 MHz Bruker NMR; HRMS (ESI-TOF) *m/z*: [M + Na]<sup>+</sup> Calcd. for C<sub>59</sub>H<sub>51</sub>BrNaO<sub>2</sub>, 893.2970; found, 893.2954.

**6,11,16,21-Tetra-*tert*-butyl-2-oxo-2H-piceno[5',6',7',8':5,6,7,8]pentapheno[13,14-*fgh*]chromene-3-carbonitrile (3).** To the solution of **3a** (0.016 g, 0.018 mmol) in *N*-methyl-2-pyrrolidone (0.2 mL) in a 10 mL round bottom flask, was added CuCN (0.003 g, 0.037 mmol) and kept for stirring at 180 °C for 50 minutes. Using TLC, the reaction progress was monitored and upon completion, reaction mixture was allowed to attain room temperature and diluted with cold water. The organic components were extracted into ethyl acetate (3 × 2 ml). The organic layer was combined and dried over anhydrous sodium sulphate and filtered. The solvent was evaporated on high vacuum using rotary evaporator to afford the

crude product. The purified product in 80% yield was obtained by passing the crude product through column chromatography.



Yield: 0.012 g, 80%; dark red solid; Mp >330 °C;  $R_f$  = 0.33 (5% ethyl acetate in hexane); IR (KBr,  $\text{cm}^{-1}$ ): 2960, 2909, 2868, 2226, 1747, 1610, 1565, 1548, 1525, 1464, 1395, 1361, 1262, 1173, 1028, 976, 835, 791, 754, 612;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.69 (s, 1H), 9.41 (s, 1H), 9.09 (d,  $J$  = 6.4 Hz, 1H), 8.91-9.02 (m, 3H), 8.87 (s, 1H), 8.79 (d,  $J$  = 6.4 Hz, 1H), 8.53-8.71 (m, 2H), 8.24 (s, 1H), 8.02 (d,  $J$  = 6.4 Hz, 1H), 7.87 (d,  $J$  = 6.4 Hz, 1H), 7.78-7.85 (m, 2H), 1.80 (s, 9H), 1.78 (s, 9H), 1.66 (s, 9H), 1.59 (s, 9H);  $^{13}\text{C}$  NMR signals were not observed due to signal broadness even at 10 mg per 0.5 mL of concentration and 15000 scans in 500 MHz Bruker NMR; HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{Na}]^+$  Calcd. for  $\text{C}_{60}\text{H}_{51}\text{NNaO}_2$ , 840.3817; found, 840.3826.



## **NMR Scans**

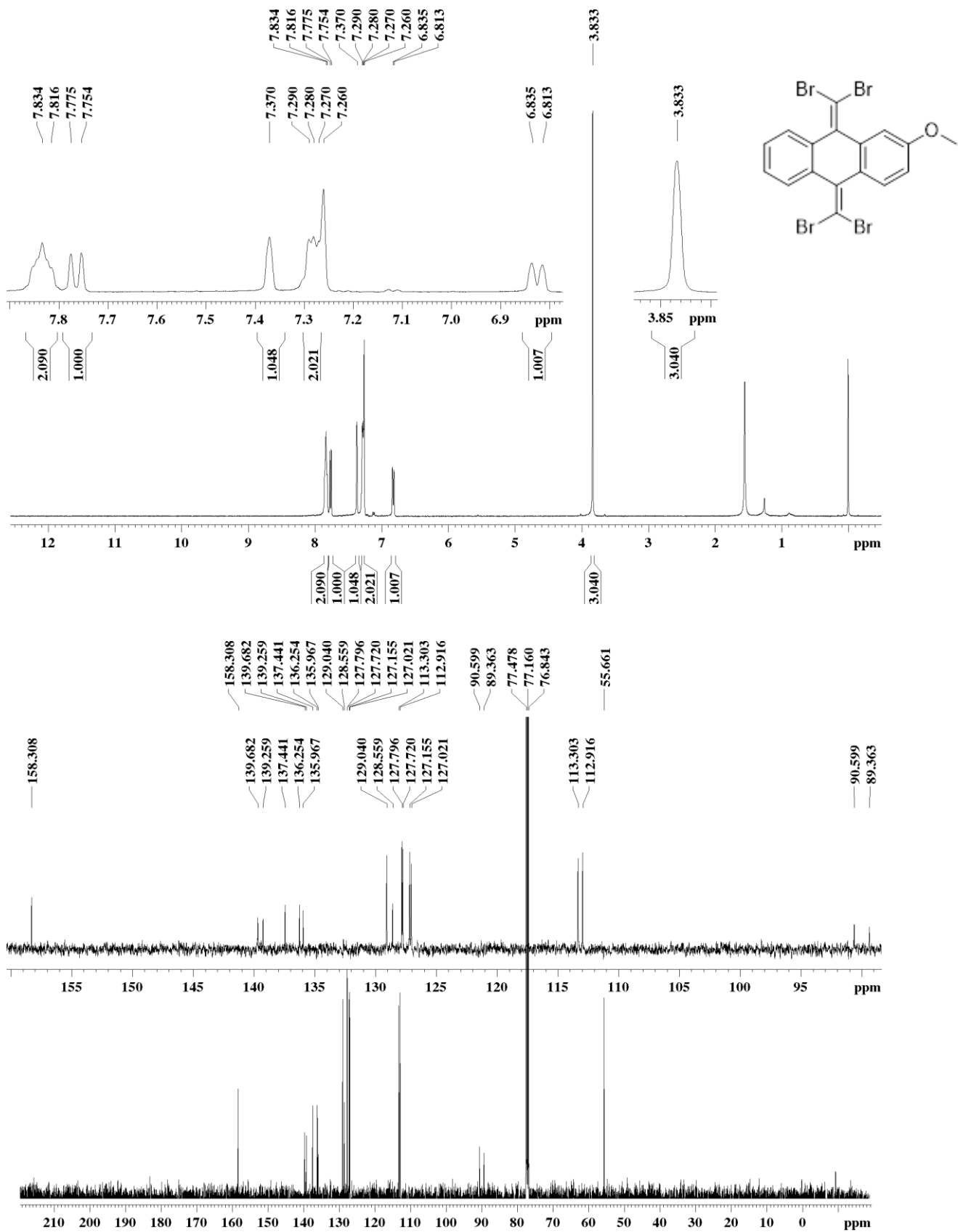


Figure S1. <sup>1</sup>H and <sup>13</sup>C NMR spectra of 4.

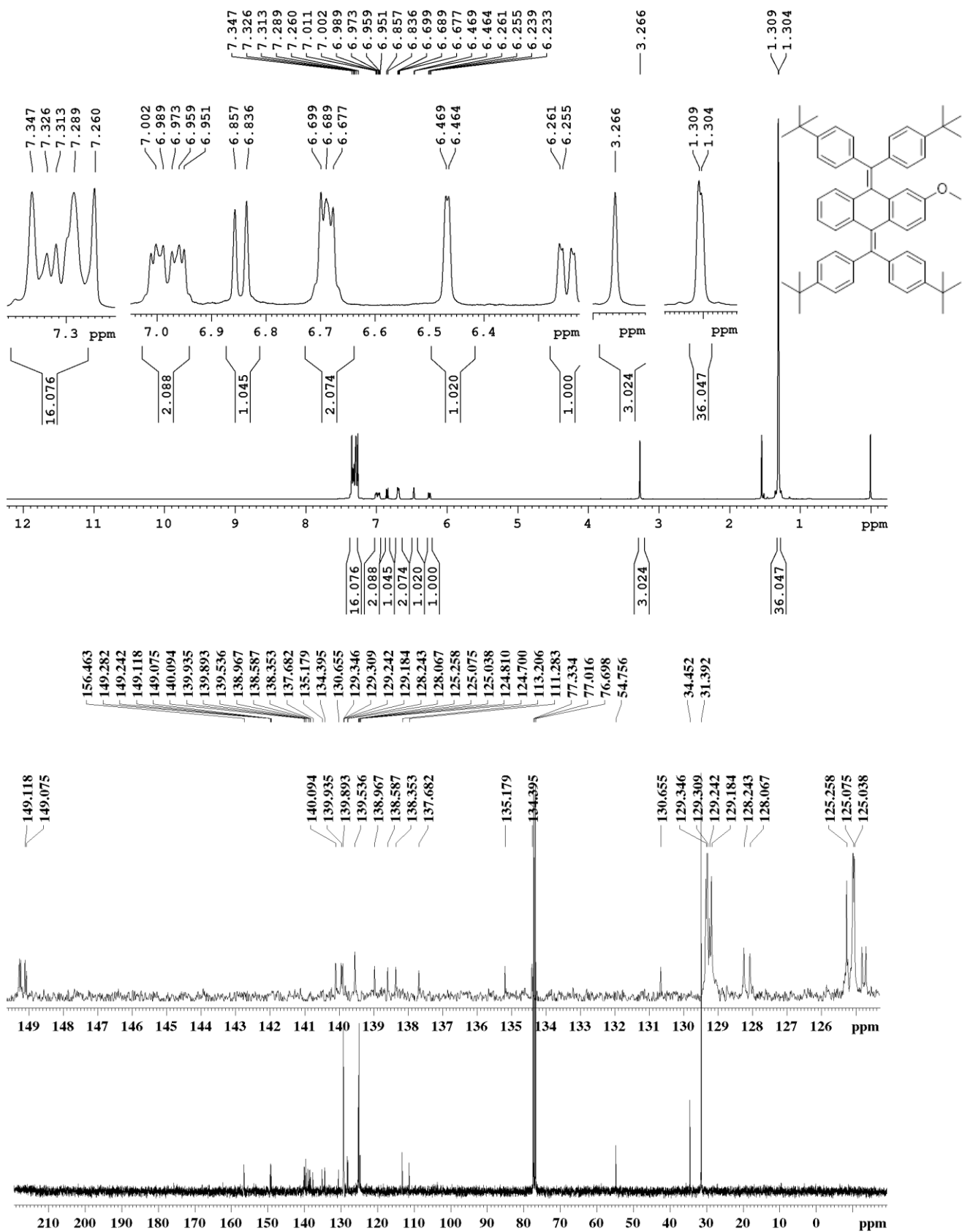
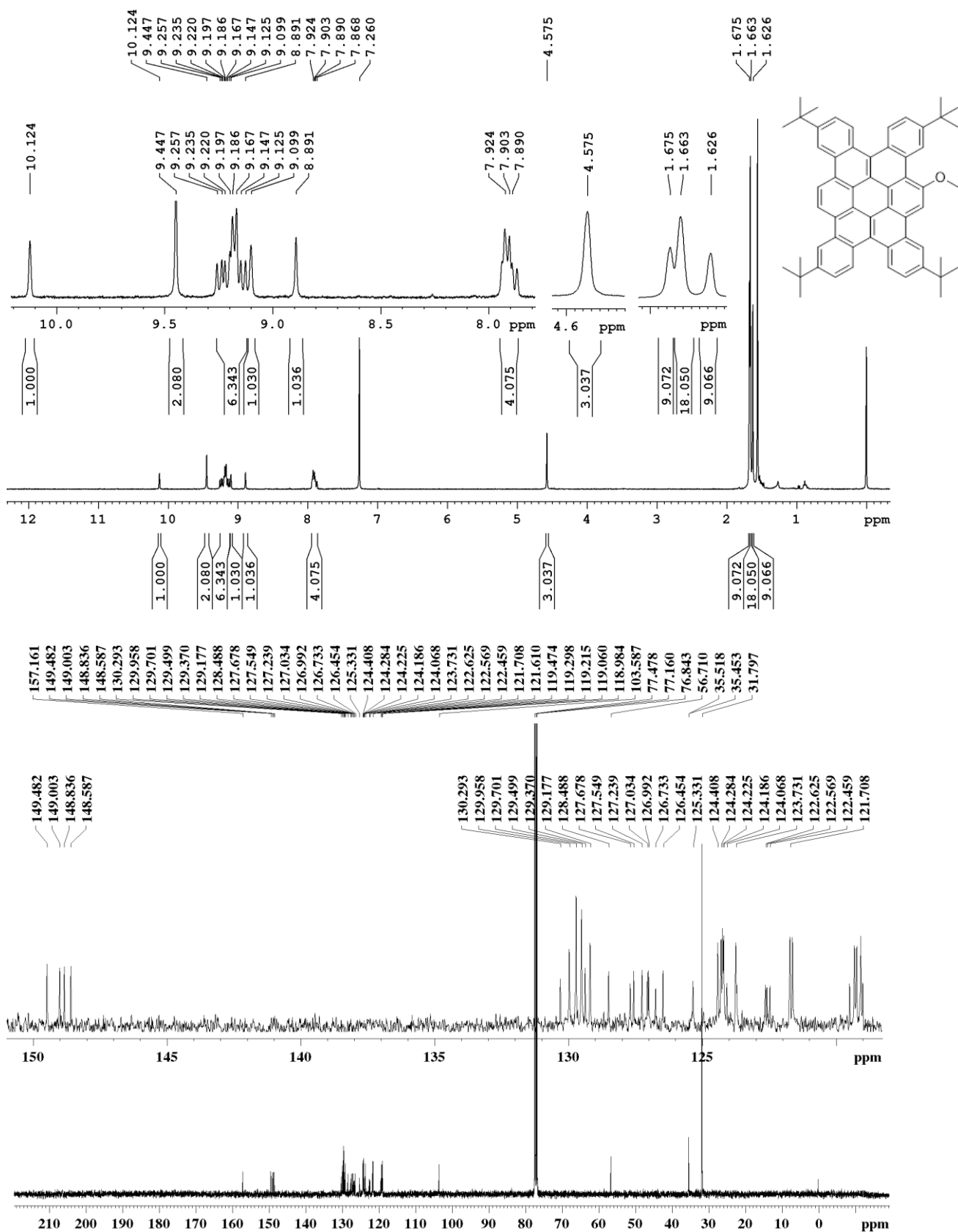
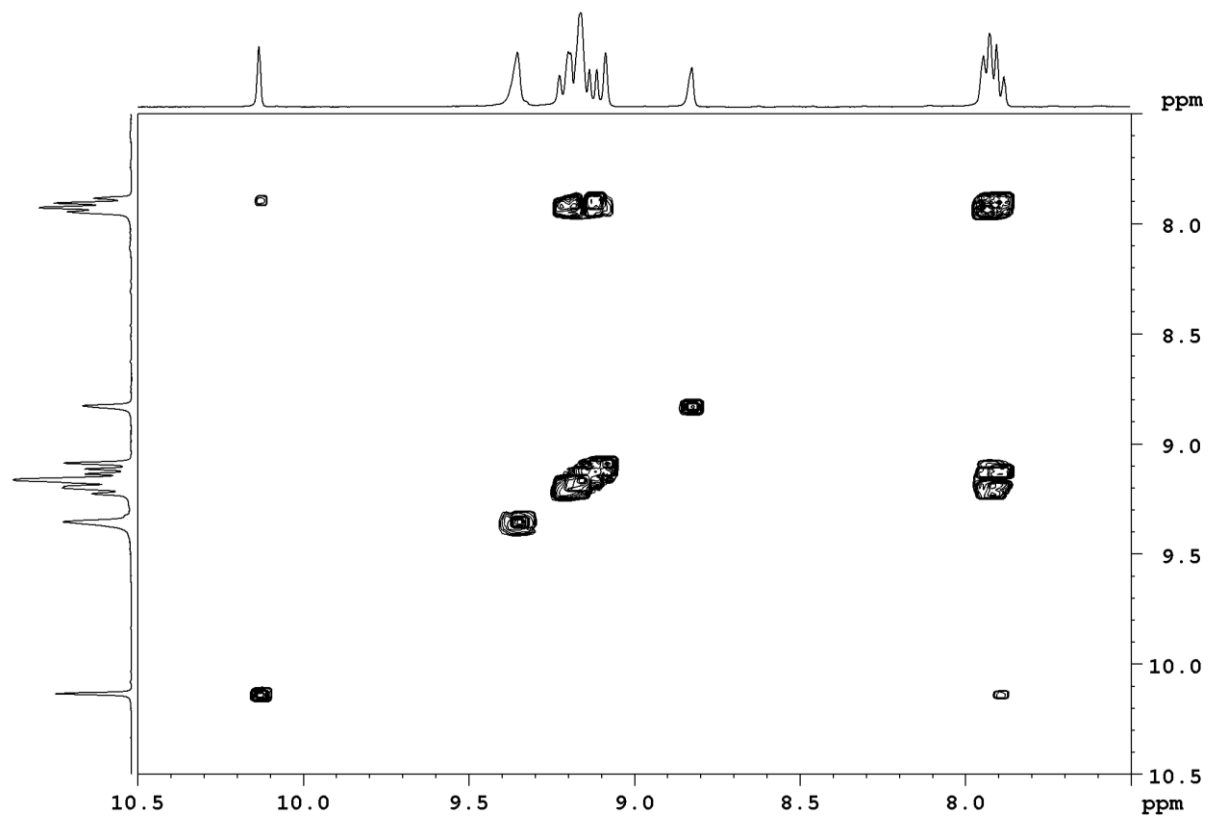


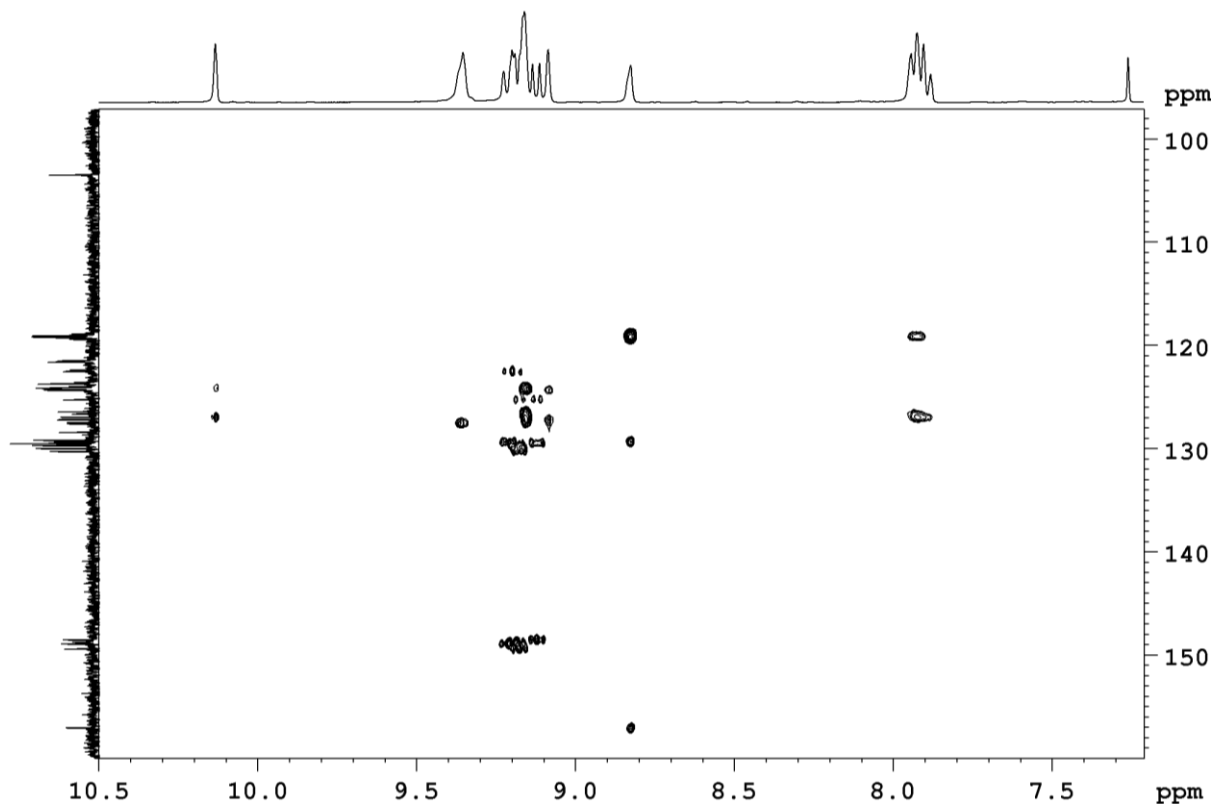
Figure S2. <sup>1</sup>H and <sup>13</sup>C NMR spectra of 1a.



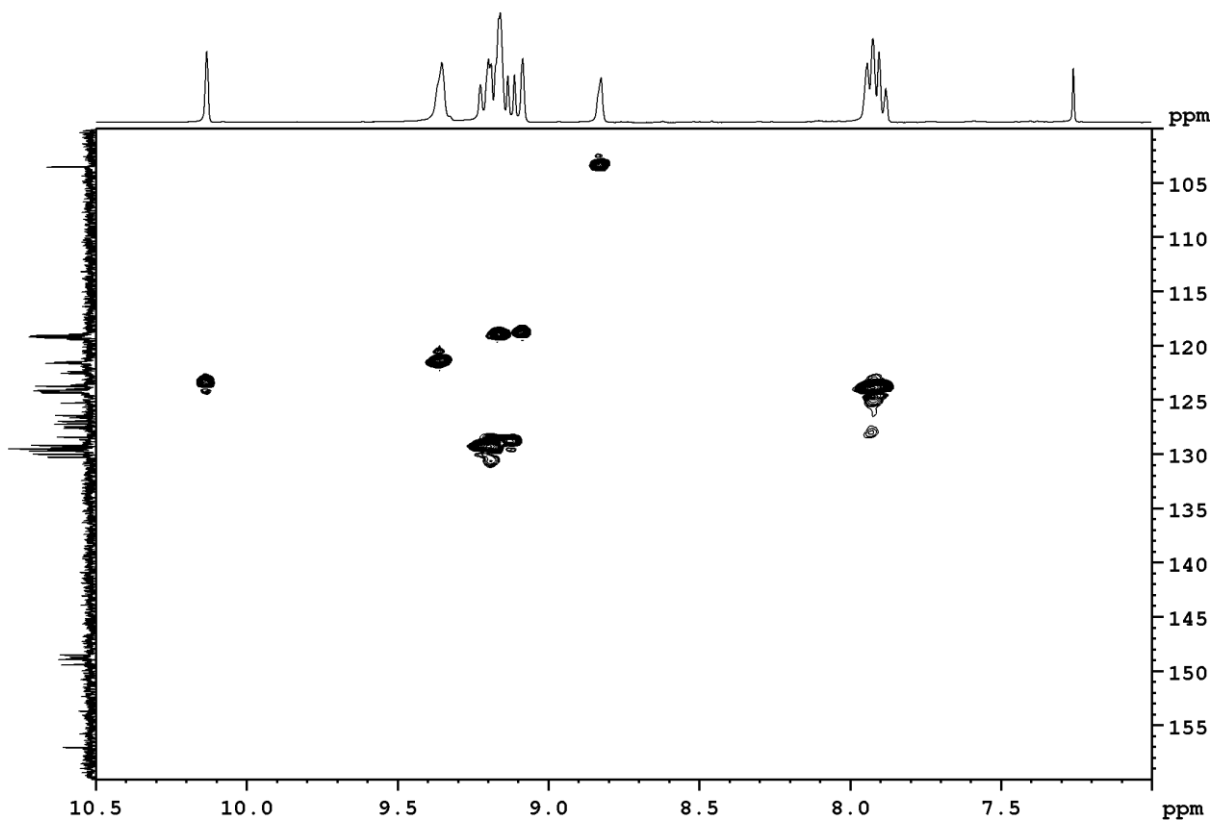
**Figure S3.** <sup>1</sup>H and <sup>13</sup>C NMR spectra of **1**.



**Figure S4.** COSY NMR spectrum of **1**.



**Figure S5.** HMBC NMR spectrum of **1**.



**Figure S6.** HSQC NMR spectrum of **1**.

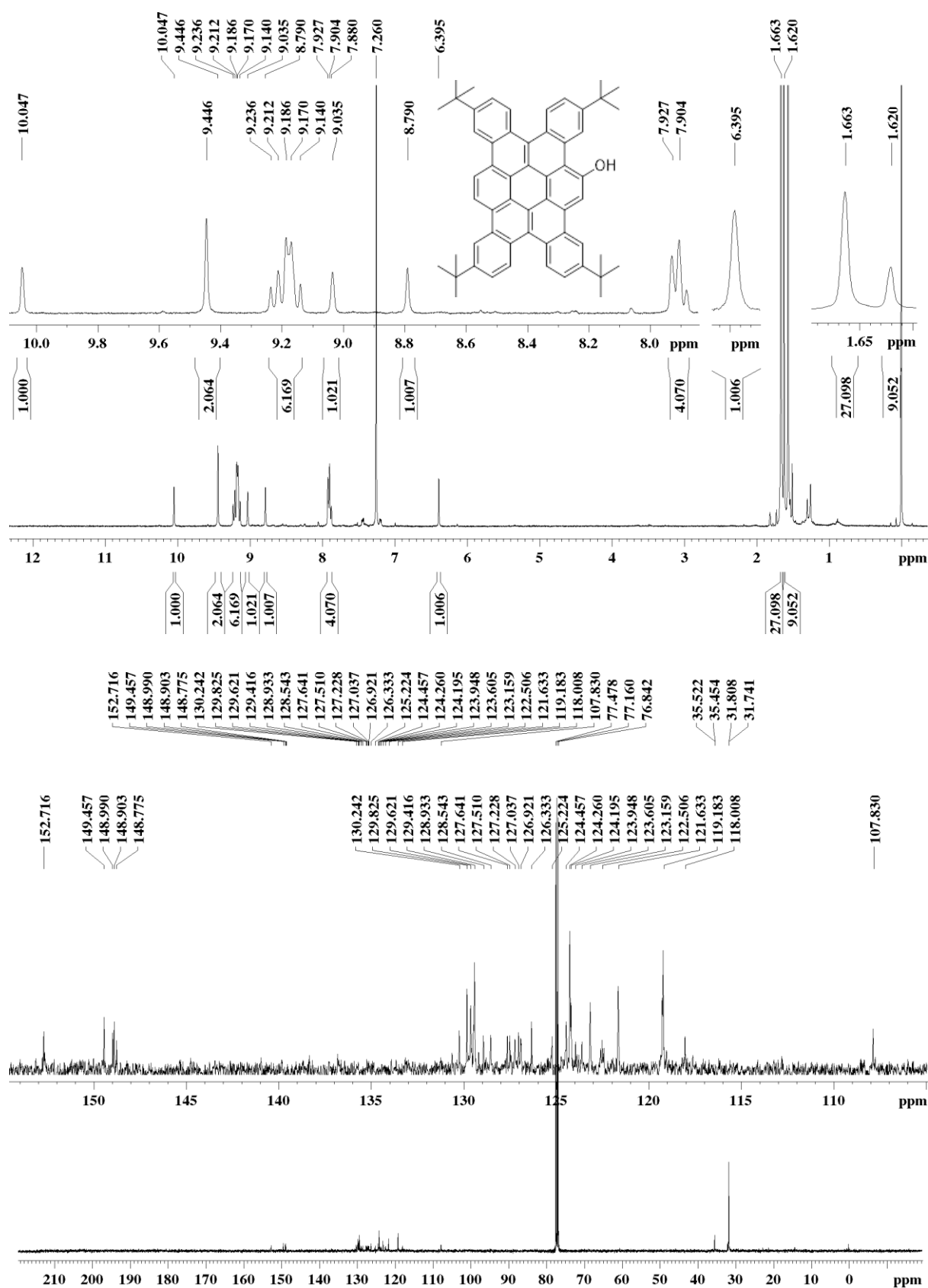


Figure S7. <sup>1</sup>H and <sup>13</sup>C NMR spectra of **2a**.

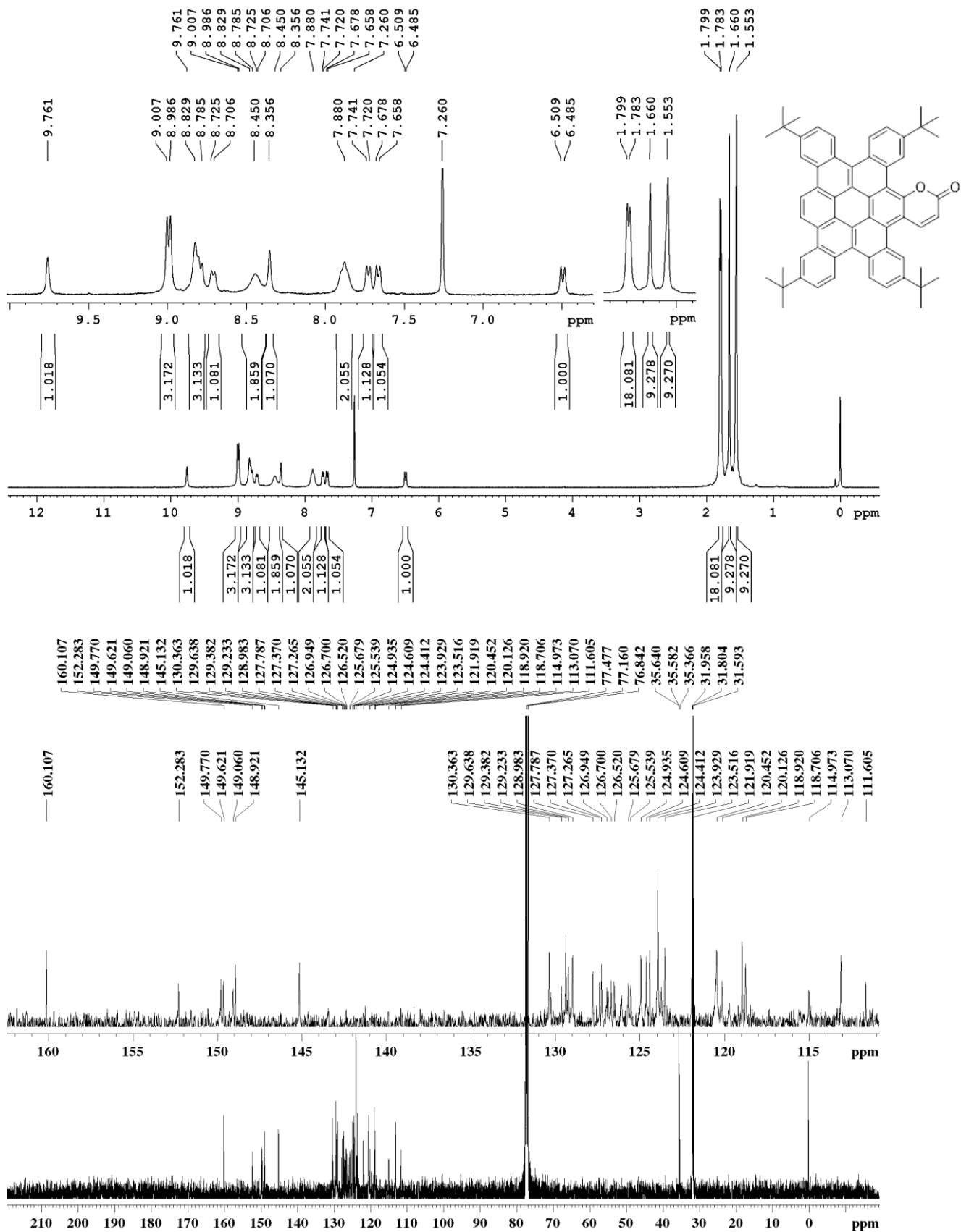
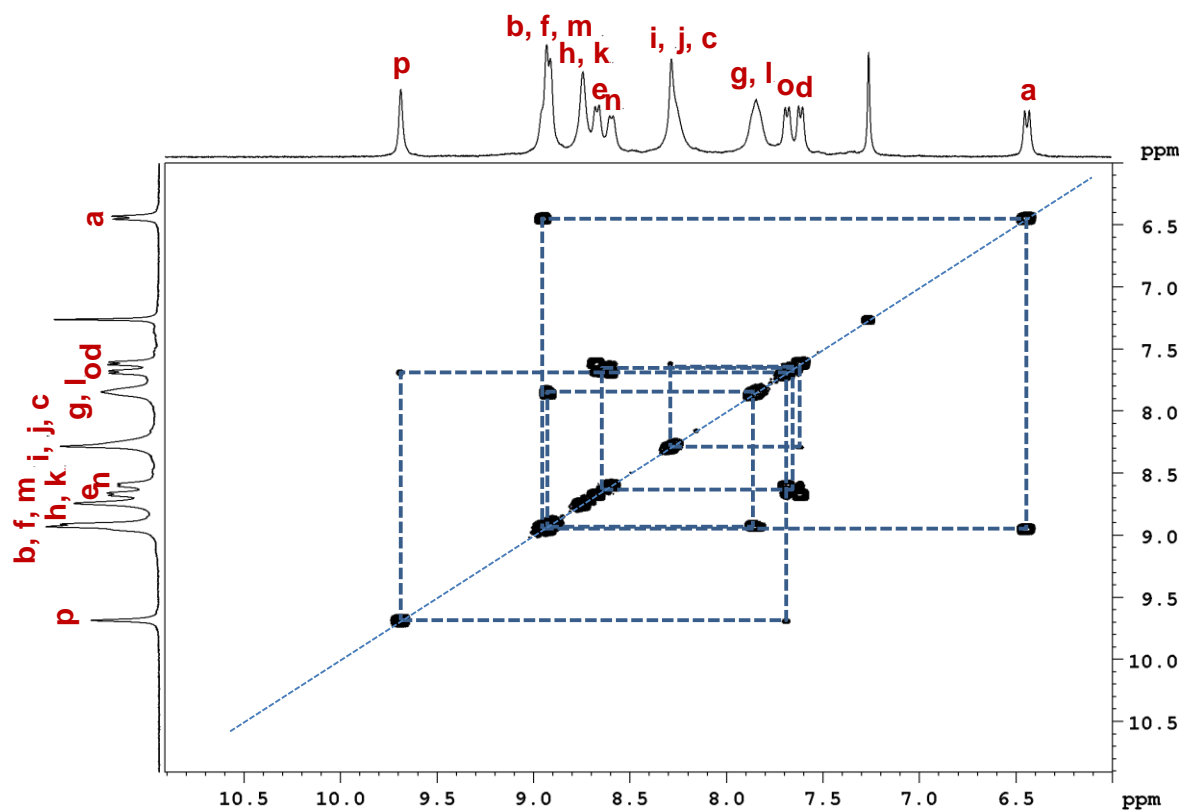
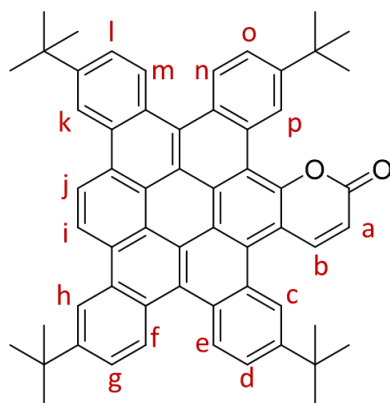


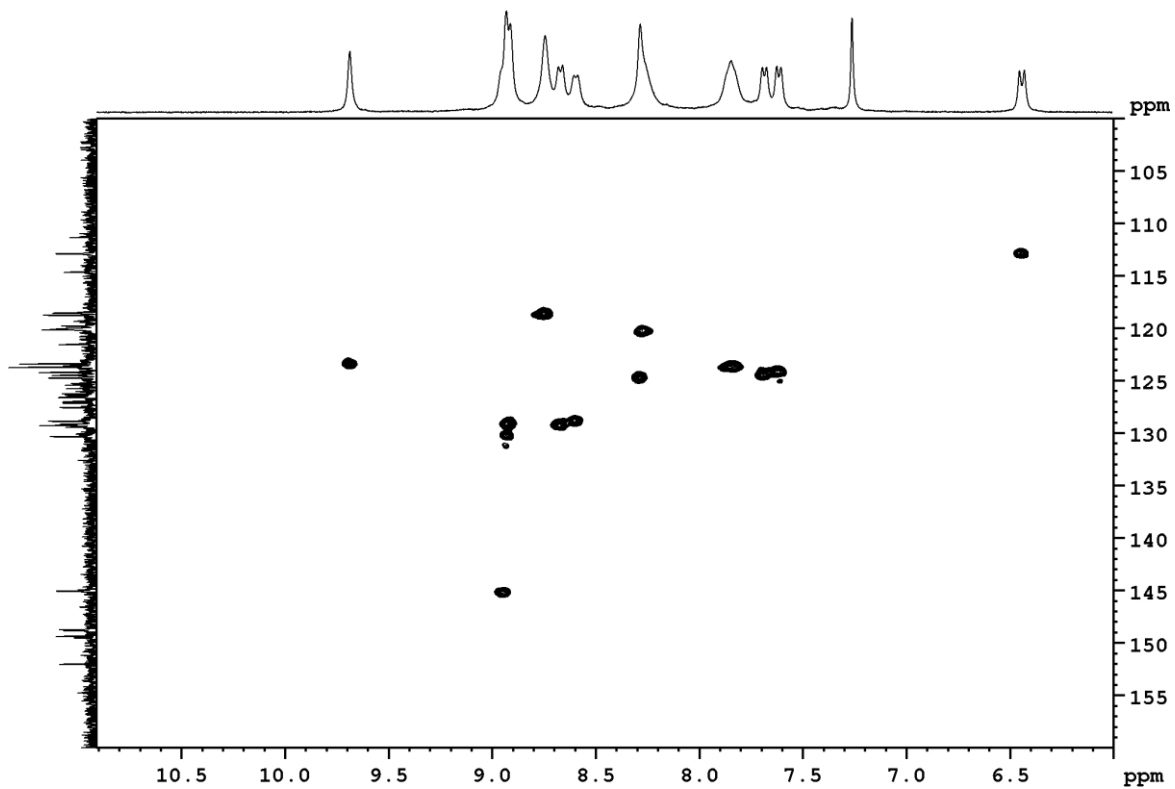
Figure S8. <sup>1</sup>H and <sup>13</sup>C NMR spectra of 2.



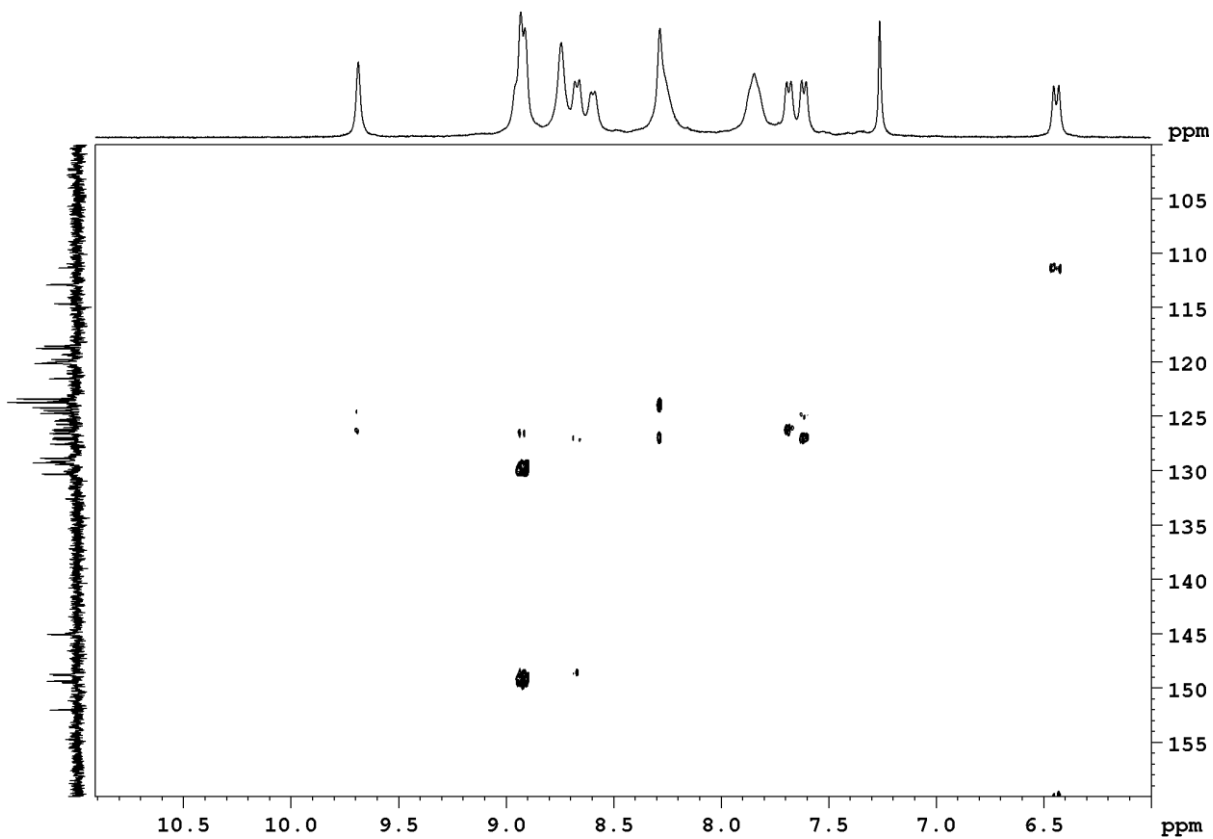


**Figure S9.** COSY NMR spectrum of **2**.





**Figure S10.** HSQC NMR spectrum of **2**.



**Figure S11.** HMBC NMR spectrum of **2**.

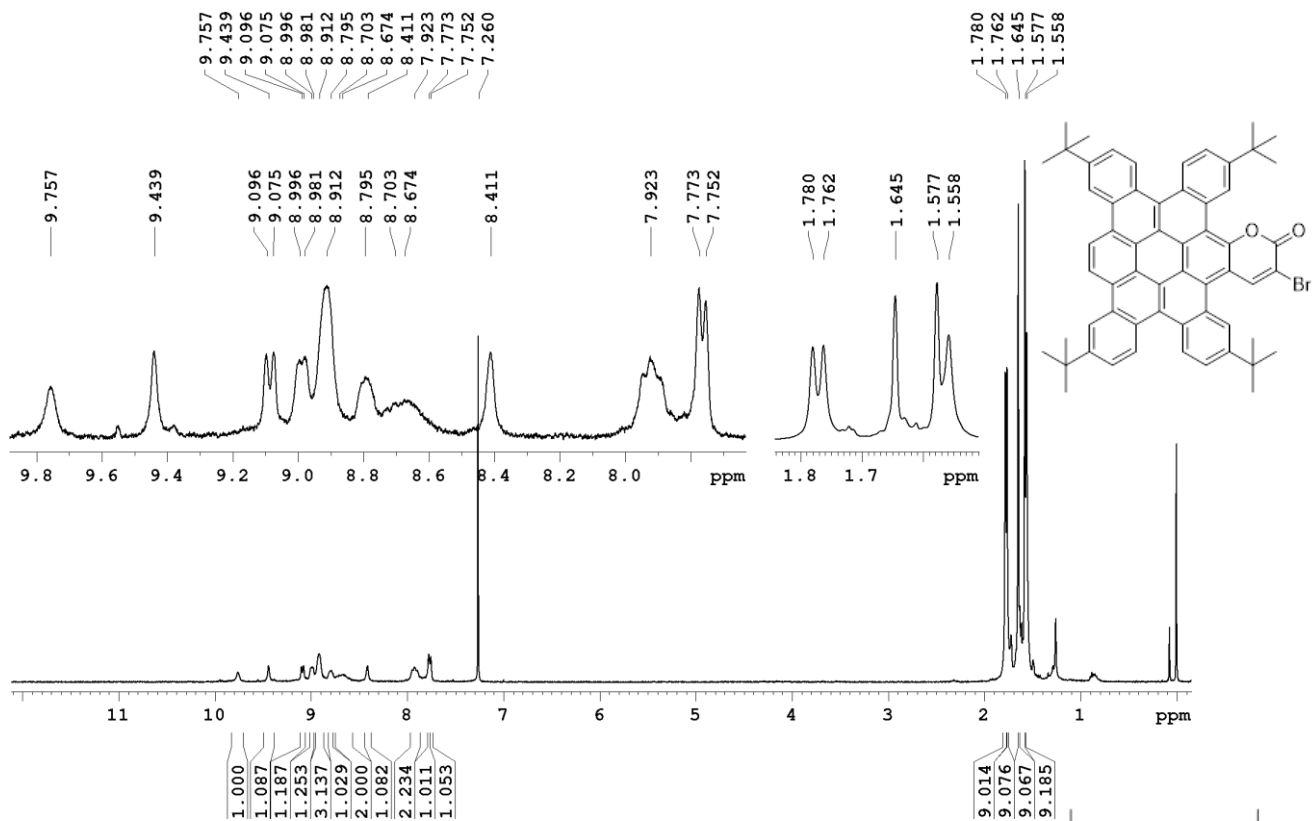


Figure S12.  $^1\text{H}$  NMR spectrum of 3a.

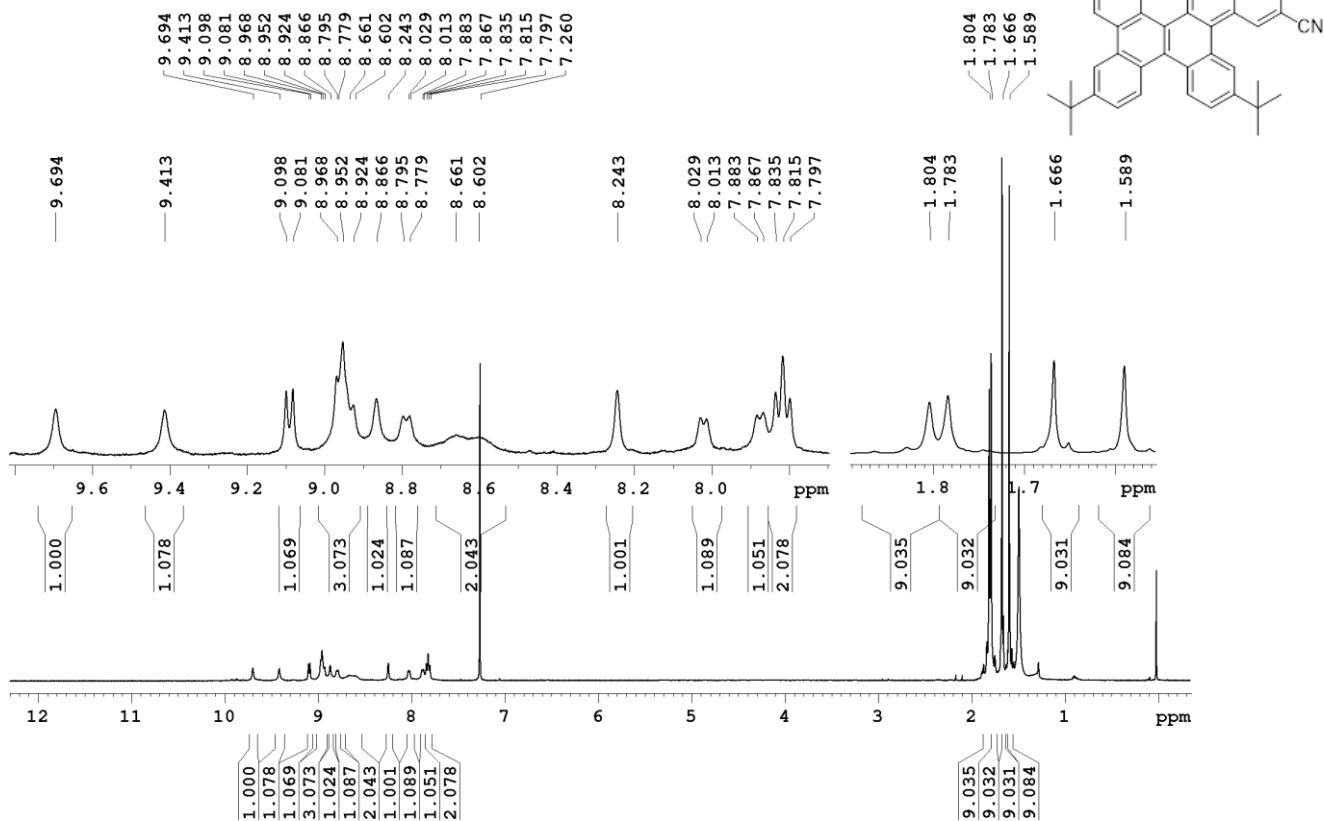


Figure S13.  $^1\text{H}$  NMR spectrum (500 MHz,  $\text{CDCl}_3$ , 328 K) of 3.

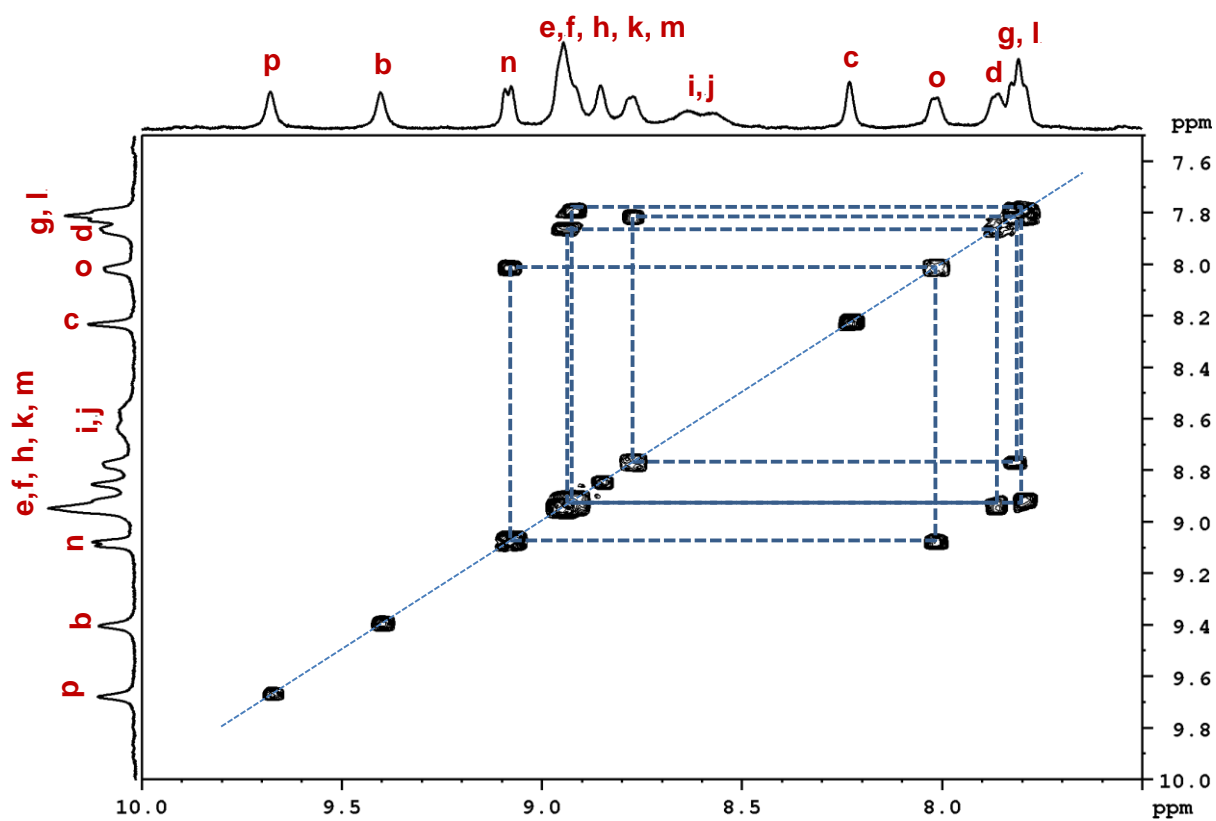
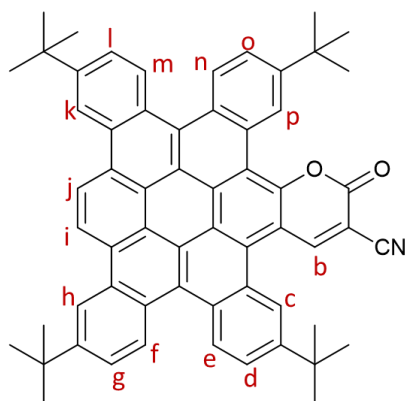


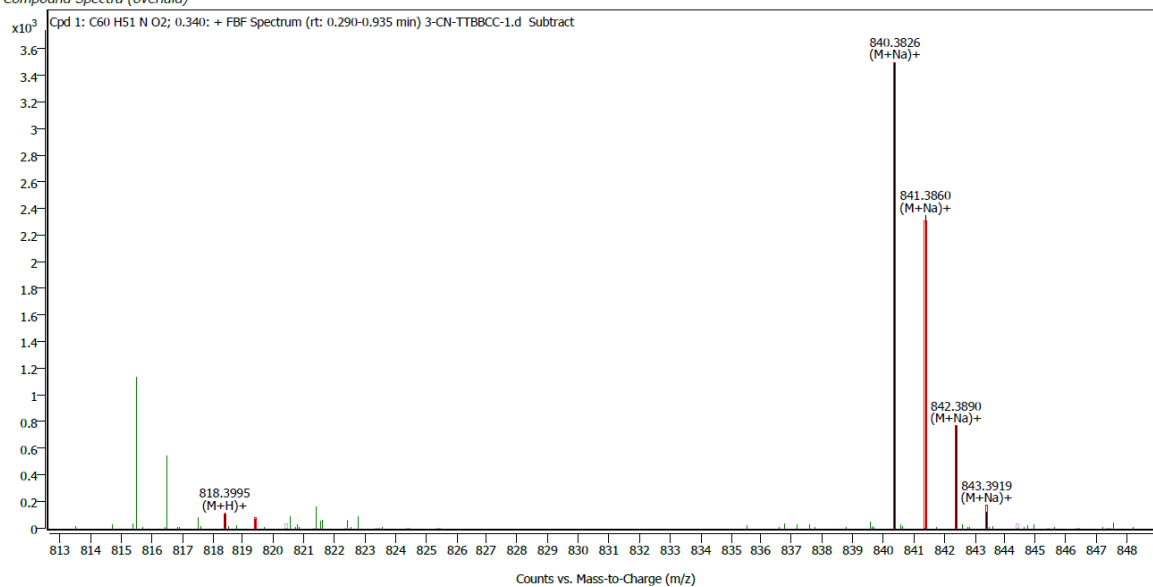
Figure S14. COSY NMR spectrum of 3.



### Compound Details

Cpd. 1: C<sub>60</sub>H<sub>51</sub>N O<sub>2</sub>

Compound Spectra (overlaid)



Compound ID Table

Cpd	Formula	Mass (Tgt)	Calc. Mass	Mass	Species	Diff (Tgt, ppm)	mDa
1	C <sub>60</sub> H <sub>51</sub> N O <sub>2</sub>	817.3920	817.3934	818.3995 840.3826	(M+H) <sup>+</sup> (M+Na) <sup>+</sup>	1.68	1.37

Figure S15. ESI-HRMS spectra of 3.

## X-ray Crystal Structure Characterization Details of **2**

The single crystals of **2** suitable for X-ray determination were grown by slow evaporation of the solution of Toluene. The transparent crystal was chosen and mounted along its longest dimension. The X-ray intensity data for **2** was collected on Bruker AXS (Kappa Apex 2) CCD diffractometer equipped with a graphite monochromated MoK $\alpha$  ( $\lambda = 0.7107 \text{ \AA}$ ) radiation source at 297 K. The multi-scan absorption correction was applied to the dataset using the program SADABS.<sup>4</sup> The structures were solved by direct method and was refined on F<sup>2</sup> by a full-matrix least squares technique using SHELXL-2014.

**Table S1.** Crystal data and structure refinement for **2**.

Identification code	shelx ( <b>TTBBCC</b> , CCDC 2102035)	
Empirical formula	C <sub>66</sub> H <sub>60</sub> O <sub>2</sub>	
Formula weight	885.14	
Temperature	297(2) K	
Wavelength	0.71073 $\text{\AA}$	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 11.778(9) $\text{\AA}$	$\alpha = 96.26(4)^\circ$ .
	b = 13.919(12) $\text{\AA}$	$\beta = 108.02(4)^\circ$ .
	c = 16.801(15) $\text{\AA}$	$\gamma = 105.66(4)^\circ$ .
Volume	2466(4) $\text{\AA}^3$	
Z	2	
Density (calculated)	1.192 Mg/m <sup>3</sup>	
Absorption coefficient	0.070 mm <sup>-1</sup>	
F(000)	944	
Crystal size	0.200 x 0.180 x 0.150 mm <sup>3</sup>	
Theta range for data collection	2.609 to 25.000 $^\circ$ .	
Index ranges	-13 $\leq$ h $\leq$ 13, -16 $\leq$ k $\leq$ 16, -19 $\leq$ l $\leq$ 19	
Reflections collected	87820	
Independent reflections	8677 [R(int) = 0.1064]	
Completeness to theta = 25.000 $^\circ$	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7461 and 0.6385	
Refinement method	Full-matrix least-squares on F <sup>2</sup>	
Data / restraints / parameters	8677 / 666 / 726	
Goodness-of-fit on F <sup>2</sup>	1.056	

Final R indices [ $I > 2\sigma(I)$ ]

$R_1 = 0.0793$ ,  $wR_2 = 0.2083$

R indices (all data)

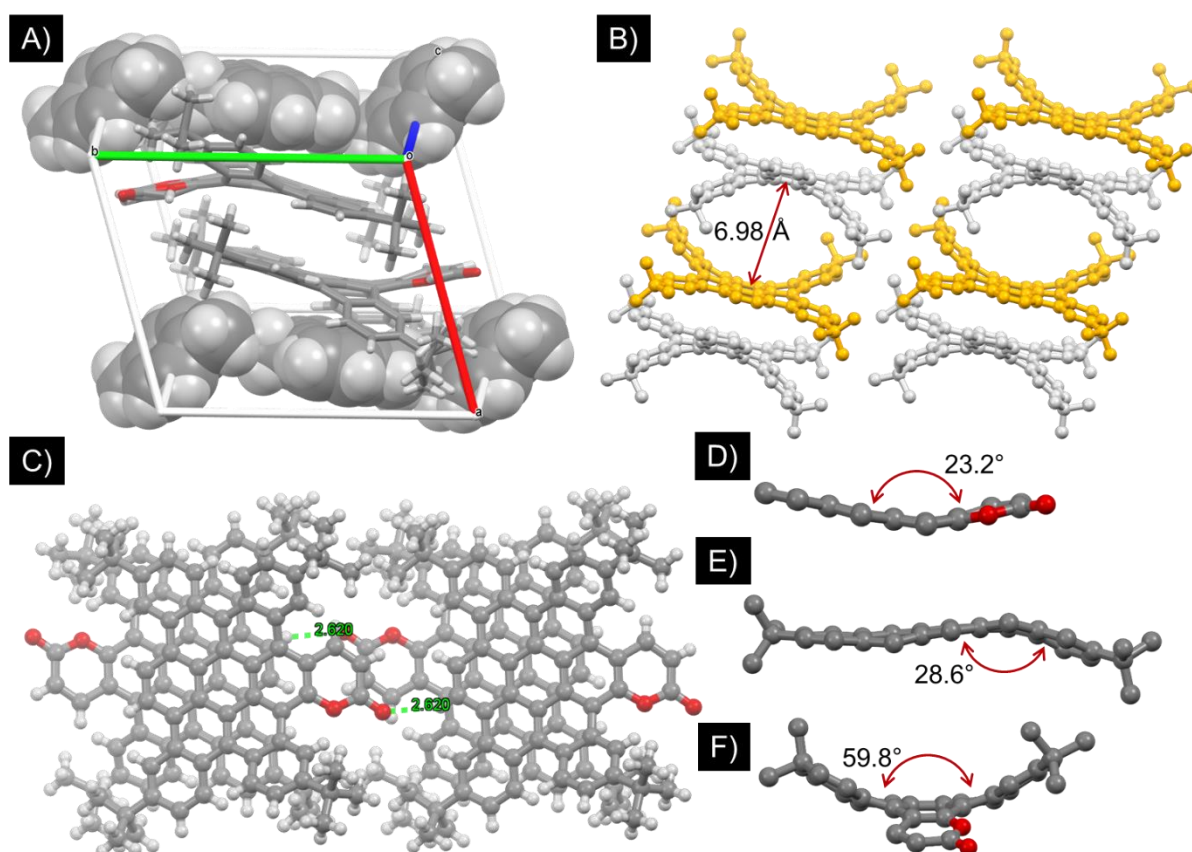
$R_1 = 0.1434$ ,  $wR_2 = 0.2752$

Extinction coefficient

n/a

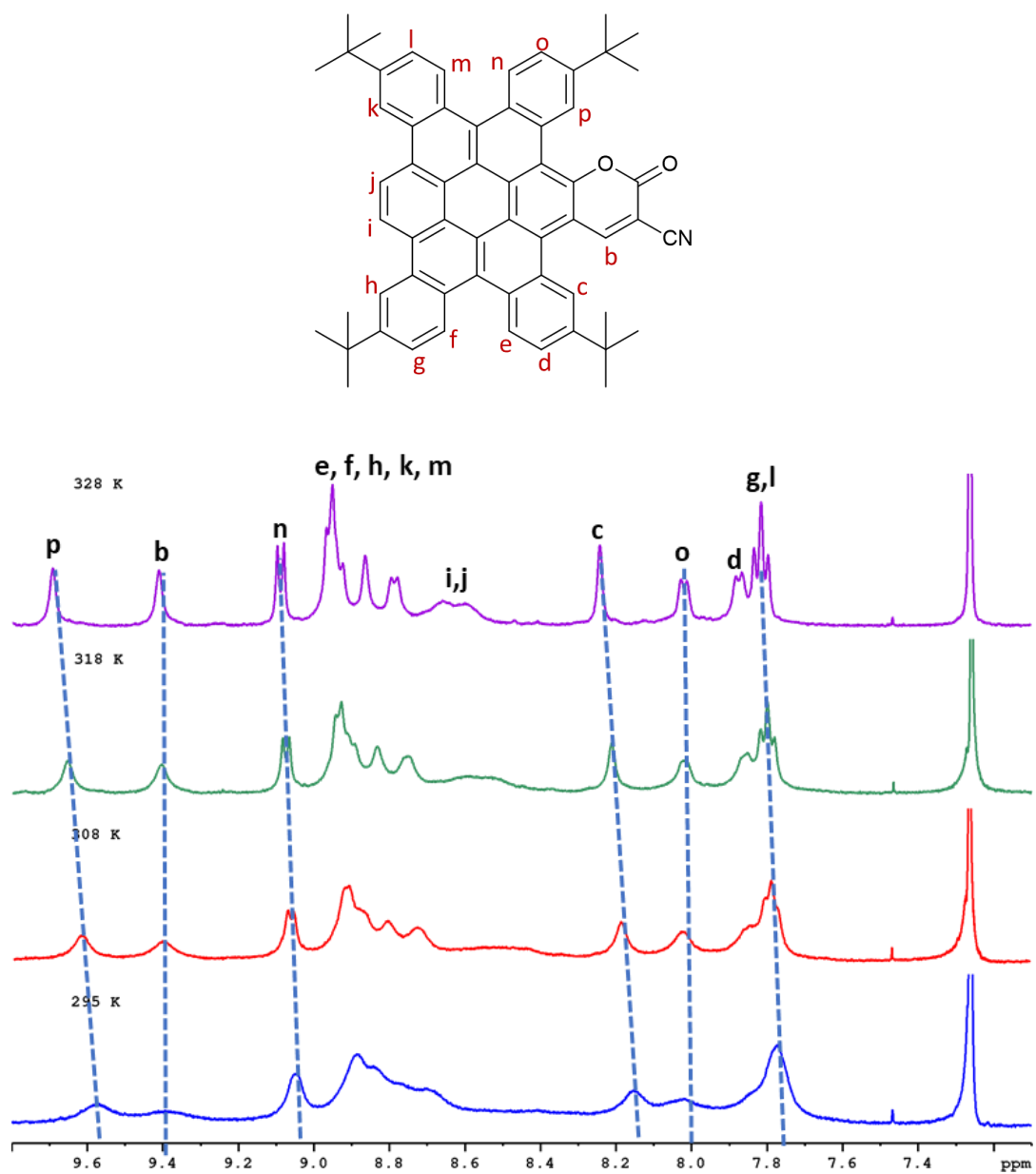
Largest diff. peak and hole

0.470 and  $-0.252 \text{ e.}\text{\AA}^{-3}$



**Figure S16.** A) Unit cell packing diagram of **2** (CCDC 2102035) with six toluene solvent molecules (shown by space-filling model). B) Each close-stacked enantiomeric pairs (yellow and white) are separated by 6.98 Å. C) Adjacent stacks of coronenocoumarins are interconnected by C-H...O interactions. D) Central naphthacoumarin unit is 23.2° bent. E) Pentacene units running diagonally are 28.6° bent. F) The chrysenes unit on one side of the tetrabenzocoronene is curved making an angle 59.8°.

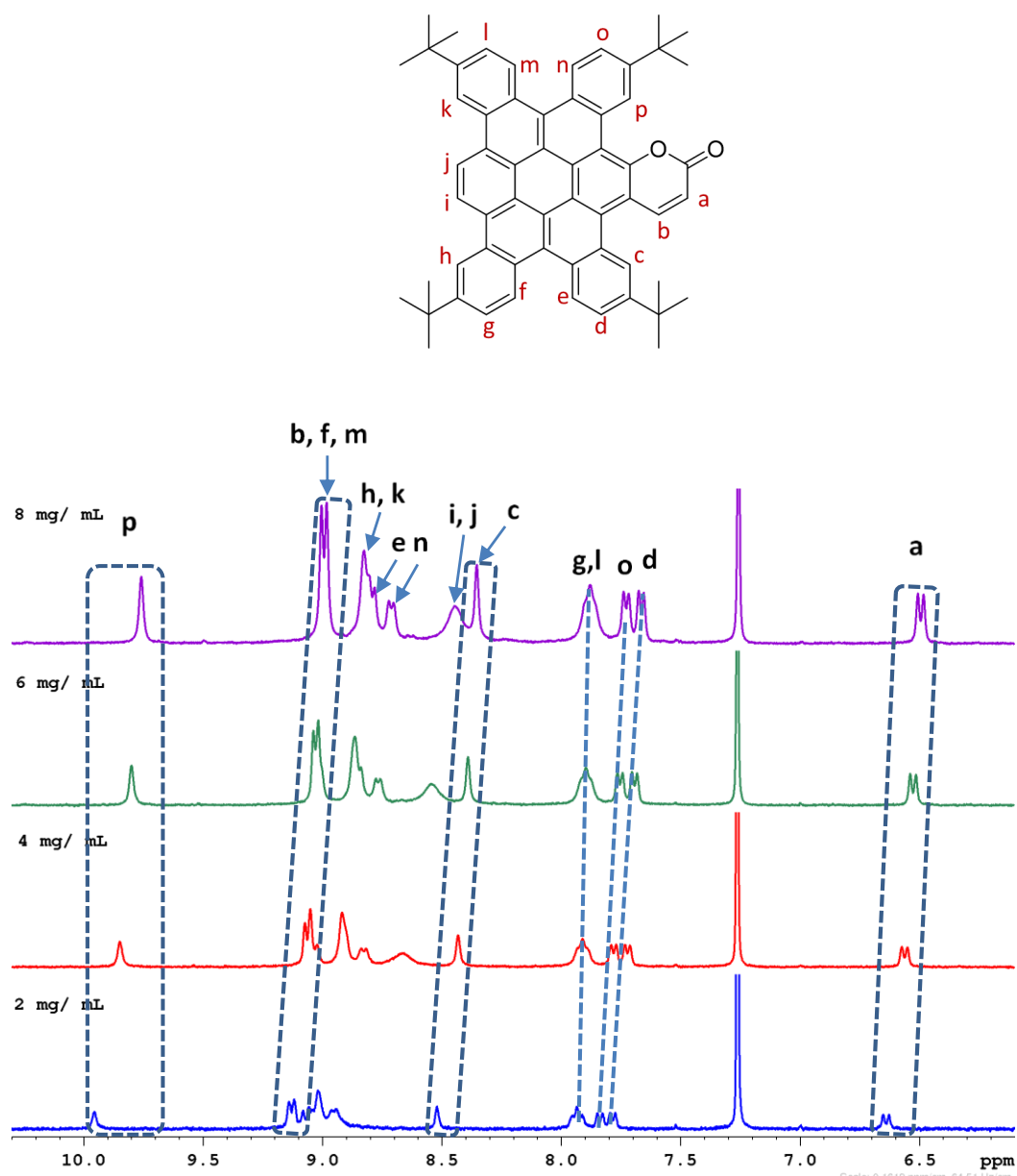
### Variable temperature $^1\text{H}$ NMR spectrum of **3**



**Figure S17.** Temperature-dependent partial  $^1\text{H}$  NMR spectra of **3** in  $\text{CDCl}_3$ .



## Concentration dependent $^1\text{H}$ NMR spectrum of **2**

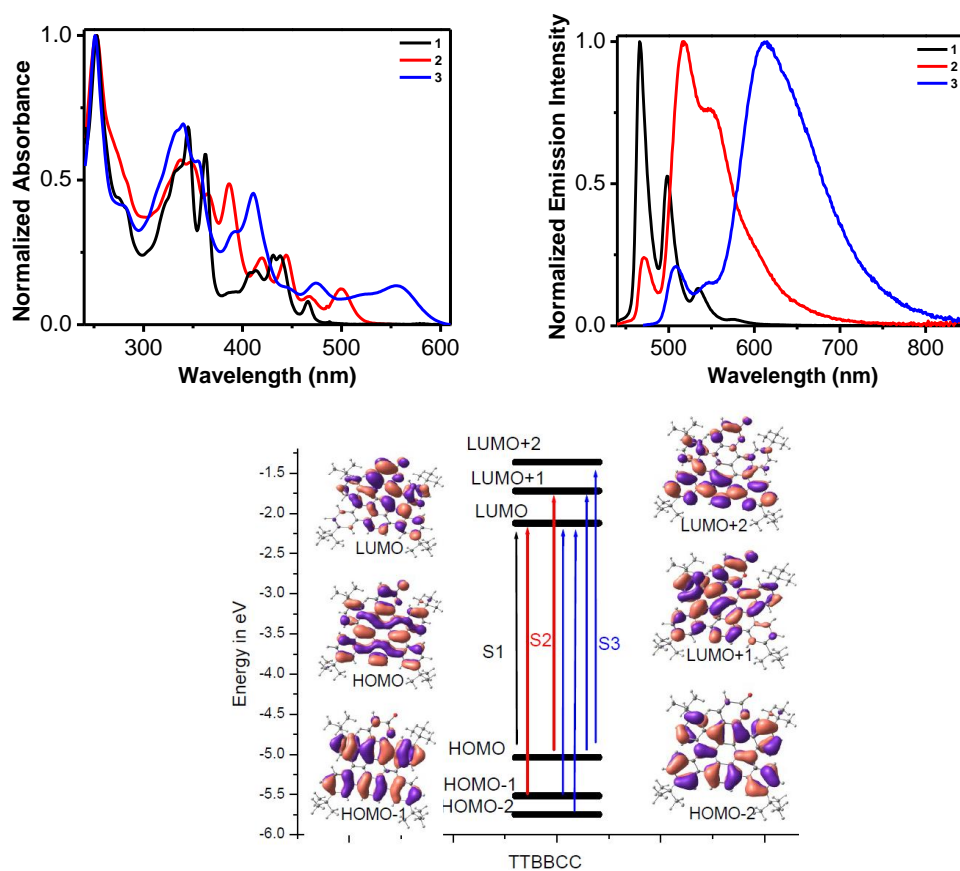


**Figure S18.**  $^1\text{H}$  NMR (partial) spectral changes upon increasing the concentration of **2** in  $\text{CDCl}_3$  (from bottom to top: 2 mg/mL:  $2.4 \times 10^{-3}$  M, 4 mg/mL:  $4.8 \times 10^{-3}$  M, 6 mg/mL:  $7.2 \times 10^{-3}$  M and 8 mg/mL:  $9.6 \times 10^{-3}$  M).

## Photophysical Characterization Details

**Steady state Absorption Measurements.** The absorption spectra of compounds were recorded on Agilent Technologies Cary 8454 spectrophotometer in (ca.  $1.0 \times 10^{-6}$  M) solutions at room temperature using cuvette of path-length 1.0 cm. The molar extinction coefficient of these compounds was obtained by three different absorbance readings of three solutions of each compound and calculated the average of these three readings. Further Beer-Lambert law was used to verify the consistency of molar extinction coefficient ( $\epsilon$ ).

**Steady State Fluorescence Measurements.** The emission spectra of these compounds were recorded in chloroform dilute (ca.  $1.0 \times 10^{-6}$  M) solutions on Horiba Fluoromax-4 choosing excitation wavelength  $\lambda_{\text{exc}} = 425$  nm. For measuring the relative fluorescence quantum yields of the compounds **1** and **2**, 9,10-bis(phenylethynyl)anthracene was chosen as a fluorescence quantum yield standard having fluorescence quantum yield unity in cyclohexane.<sup>6</sup> The relative fluorescence quantum yield of **3** was measured using Nile red dissolved in dioxane as a quantum yield standard, having fluorescence quantum yield of 0.7 and the excitation wavelength was chosen to be  $\lambda_{\text{exc}} = 460$  nm for this compound.



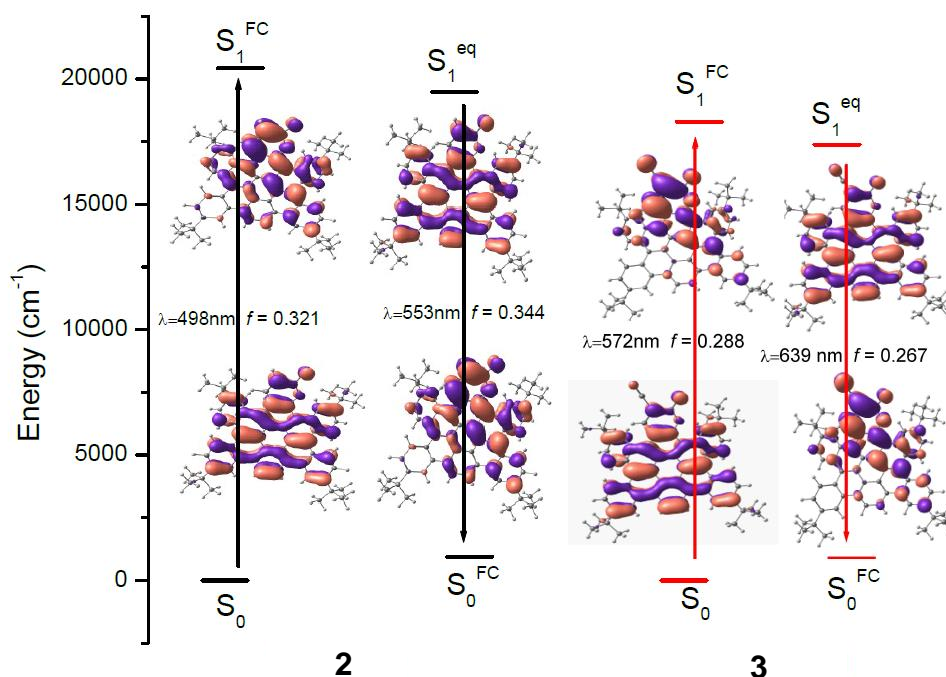
**Figure S19.** Normalized absorption (top left) and emission spectra (top right) of coronene derivative s in chloroform. Calculated FMOs and major transitions for **2** (bottom).

**Table S2.** Optical properties of **1-3** in dilute CHCl<sub>3</sub> solution.

Entry	$\lambda_{\text{abs}} (\epsilon)^{[a]}$ (nm) (M <sup>-1</sup> cm <sup>-1</sup> )	$\lambda_{\text{em}}^{[a]}$ (nm)	$\Delta\nu$ (cm <sup>-1</sup> )	$\Phi_f^{[b]}$ (%)	$\tau_f$ (ns)
<b>1</b>	345 (93000), 363 (81500), 440 (32700), 466 (9800)	466, 498, 534	--	36	7.16
<b>2</b>	348 (86800), 365 (71000), 387 (79900), 444 (38200), 500 (20250)	472, 517, 546	660	17	1.89, 8.94
<b>3</b>	340 (53200), 411 (35200), 474 (12600), 555 (11700)	509, 546, 615	1760	30	3.48, 8.39

[a] Optical measurements were performed using dilute solutions (ca. 10<sup>-6</sup> M) contained in 1 cm quartz cuvettes at room temperature. [b] Fluorescence quantum yields for **1** and **2** were measured using 9,10-bis(phenylethynyl)anthracene in cyclohexane as the standard, and  $\lambda_{\text{ex}} = 425$  nm. For **3**, Nile-red dissolved in dioxane was used as the fluorescence quantum yield standard, and  $\lambda_{\text{ex}} = 460$  nm.

**DFT Calculations.** All the calculations were carried out using ab-initio software Gaussian 16W program.<sup>4</sup> The electronic ground- and excited-state geometries are fully optimized in gas phase without any symmetric considerations by using the density functional theory (DFT) and time-dependent density functional theory (TDDFT) methods, respectively. Becke's three-parameter hybrid exchange functional and the Lee-Yang-Parr correlation functional (B3LYP) were utilized in the calculation<sup>5</sup> with 6-31 G (d, p) basis set. Vibrational frequencies were evaluated for the optimized geometries at the same level to ensure that the structure obtained was a minimum on the potential energy. To predict the absorption maxima vertical excitation energies were calculated at the ground-state geometries with time-dependent DFT (TDDFT) method at the B3LYP/6-31G (d, p) level. Similarly to get emission spectra, excitation energies were calculated at the excited state geometries with same level of theory.

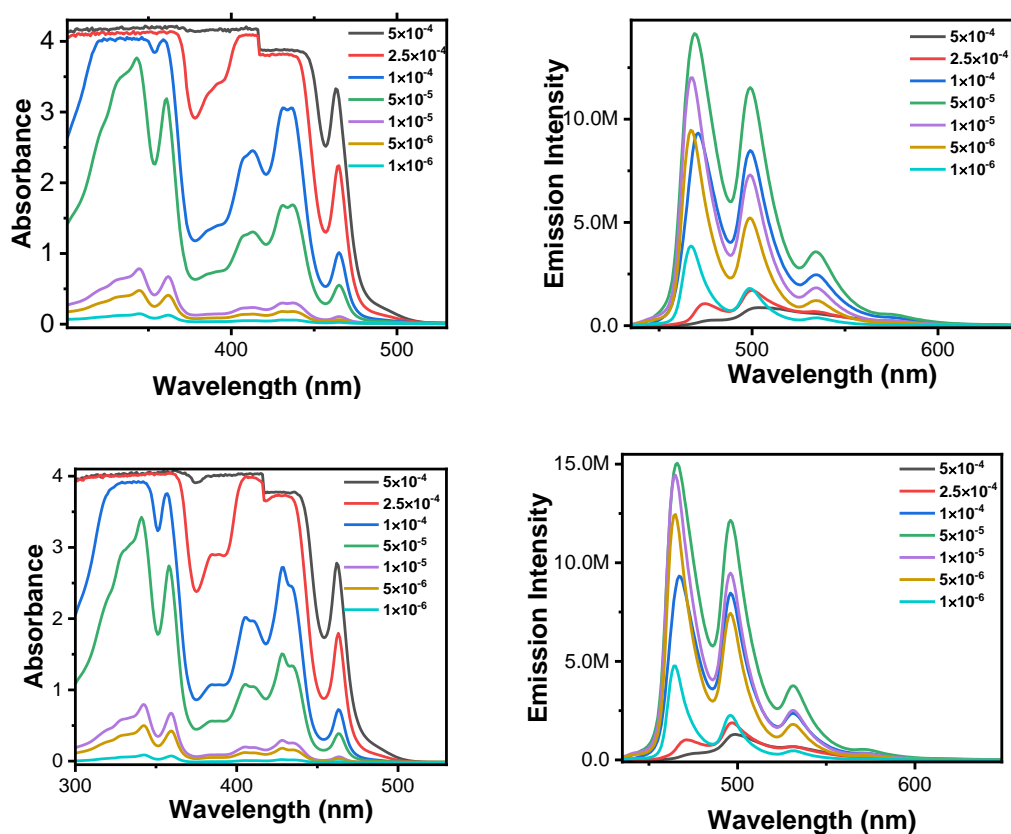


**Figure S20.** Major transitions and states involved with absorption and emission for **2** and **3** at TD-B3LYP/6-31g\*\* in chloroform solvent. The electron density changes in HOMO and LUMO upon photoexcitation and after relaxation to ground state suggest a charge transfer phenomenon in the excited state.

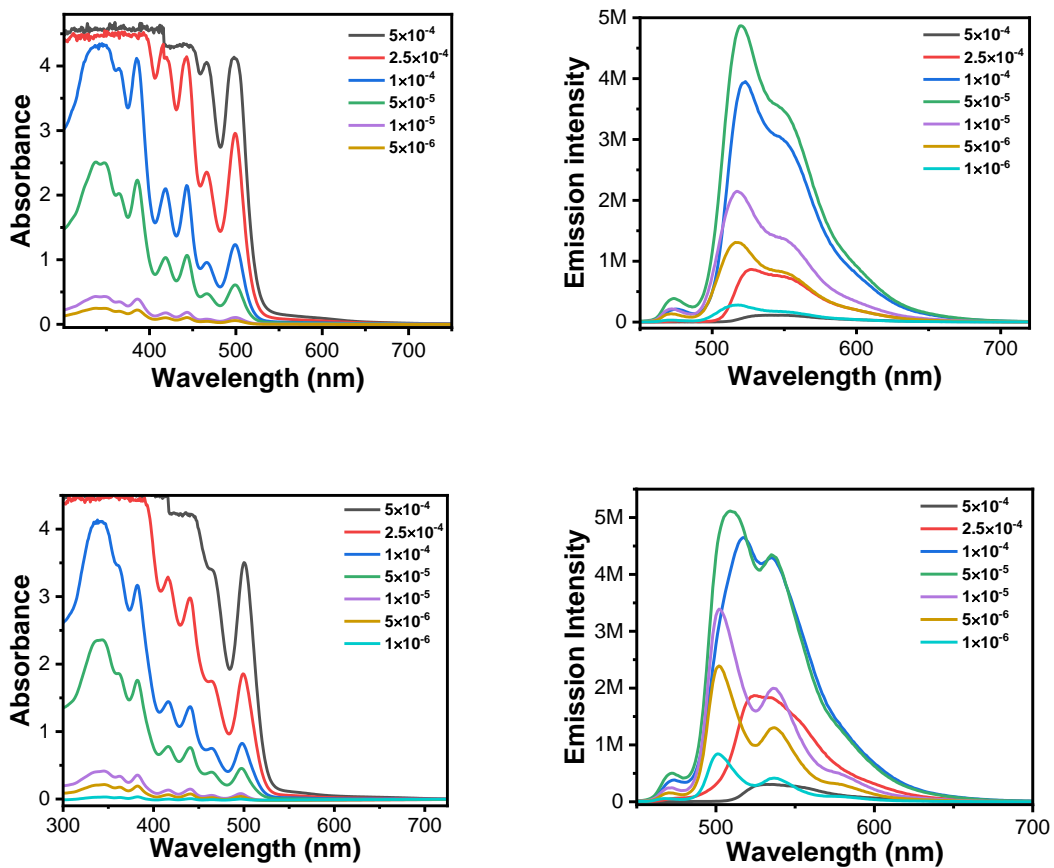
**Table S3.** Absorption energies ( $\lambda_{\max}$  in nm), oscillator strength ( $f$ ), major transitions ( $M_T$ ) and weight in percentage (%Ci) obtained at TD-B3LYP/6-31g\*\* level in chloroform solvent.

Entry	State	$\lambda_{\max}$ (nm)	$f$	$M_T$	(%Ci)
<b>1</b>	S <sub>1</sub>	457	0.557	H -> L	95
	S <sub>2</sub>	430	0.040	H-1 -> L	31
				H -> L+1	67
				H-2 -> L	13
	S <sub>3</sub>	398	0.004	H -> L+2	83
<b>2</b>	S <sub>1</sub>	498	0.321	H -> L	93
	S <sub>2</sub>	450	0.070	H-1 -> L	45
				H -> L+1	48
				H-2 -> L	13
	S <sub>3</sub>	410	0.513	H-1 -> L	33
				H -> L+1	36
				H -> L+2	14
<b>3</b>	S <sub>1</sub>	572	0.288	H -> L	97
	S <sub>2</sub>	489	0.098	H-1 -> L	89
	S <sub>3</sub>	448	0.064	H-2 -> L	91

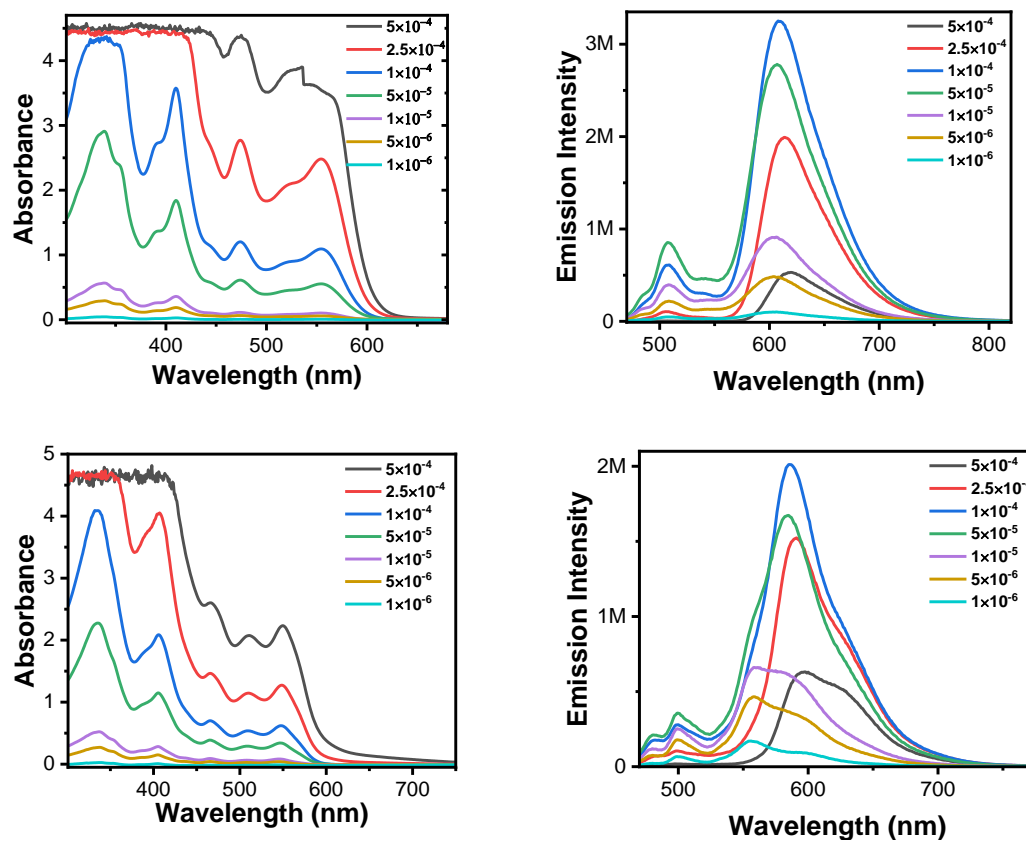
**Concentration dependent absorption and emission spectra.** The absorption spectra were recorded using Shimadzu UV-2600 spectrometer and the emission spectra were recorded on Horiba Jobin-Yvon FluoroMax-4 spectrofluorometer, with a 150 W xenon lamp as light source. Absorption and emission measurements were performed by preparing stock solutions of various concentrations ( $10^{-6}$  to  $10^{-4}$  M) in two solvents cyclohexane and chloroform.



**Figure S21.** Absorption spectra (left) and normalized emission spectra (right) of **1** compound in chloroform (top) and in cyclohexane (bottom).



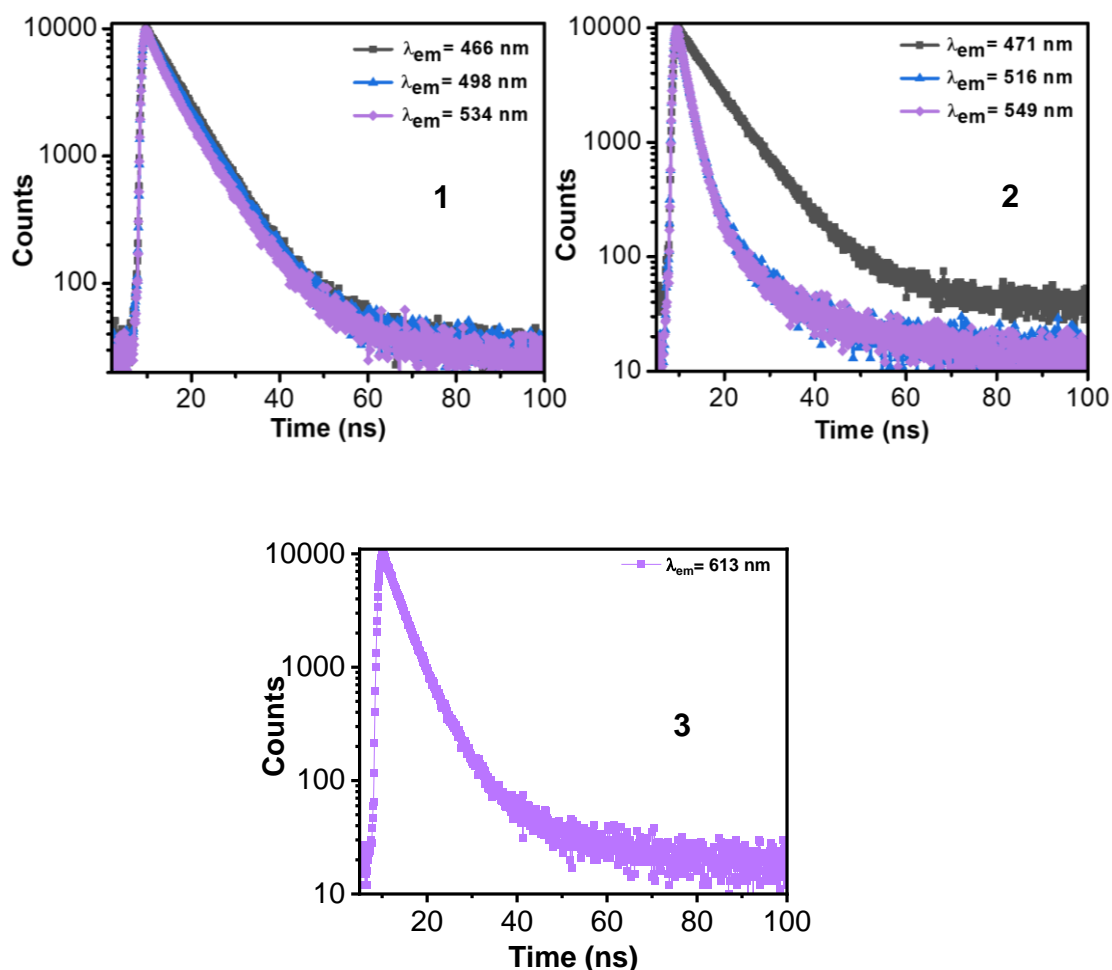
**Figure S22.** Absorption spectra (left) and normalized emission spectra (right) of **2** compound in chloroform (top) and in cyclohexane (bottom).



**Figure S23.** Absorption spectra (left) and normalized emission spectra (right) of **3** compound in chloroform (top) and in cyclohexane (bottom).

## Time-Resolved Fluorescence Measurements

Time resolved fluorescence lifetime experiment was performed using a time correlated single photon counting spectrometer, Edinburgh Instruments FLS 980 model (UK) having pulsed diode excitation source. For experiments, the nano-LEDs of 445 nm was used as light source for the compounds **1** and **2** and 510 nm was used as light source for the compound **3**. The pulse repetition rate was set to 1.0 MHz and the detector response was around 800 ps. The instrument response function was collected using a scatterer (Ludox AS40 colloidal silica). The decay data were analysed using IBH software. A value of  $\chi^2$ ,  $0.99 \leq \chi^2 \leq 1.3$  was considered as a good fit which was further verified by the symmetrical distribution of the residuals. Fluorescence lifetime of compounds (ca.  $10^{-6}$  M) was recorded in chloroform.

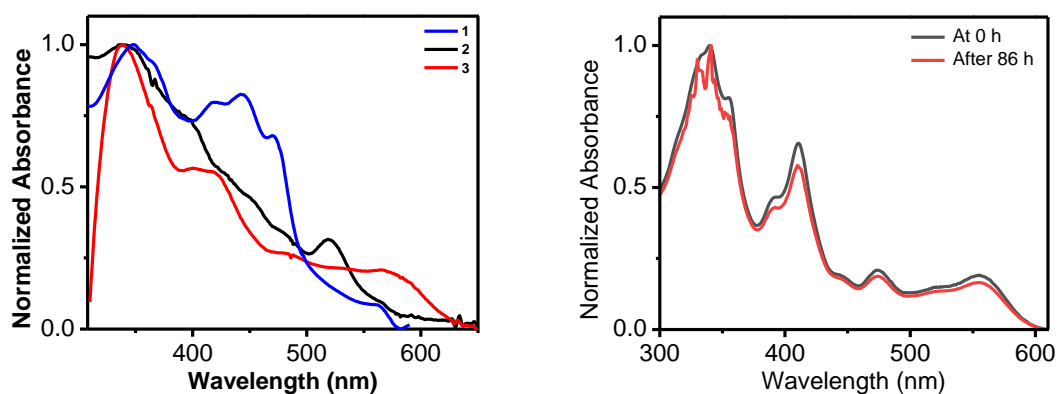


**Figure S24.** Fluorescence lifetime decays of coumarin **1**, **2** and **3** at different emission wavelengths.



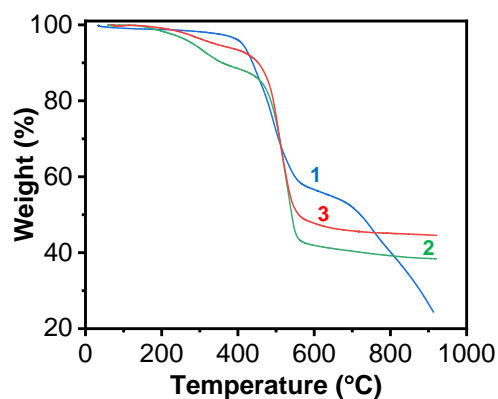
**Table S4.** Fluorescence lifetime (ns) data of **1**, **2** and **3** in chloroform, and calculated emission energies (in nm), oscillator strength ( $f$ ) obtained at the TD-B3LYP/6-31g\*\* solvent (chloroform) on TD-B3LYP/ 6-31g\*\* optimized geometries.

Entry	Solvent $\lambda_{em}$ , nm	Chloroform	$\chi^2$	$\lambda_{em}$ (Cal), nm	$f$
<b>1</b>	466	$\tau_1 (\alpha_1) = 7.2$ ns (100)	1.2	507	0.6765
	498	$\tau_1 (\alpha_1) = 3.7$ ns (25) $\tau_2 (\alpha_2) = 7.6$ ns (75)	1.1		
	534	$\tau_1 (\alpha_1) = 2.8$ (43) $\tau_2 (\alpha_2) = 7.7$ (57)	1.1		
<b>2</b>	471	$\tau_1 (\alpha_1) = 6.3$ ns (73) $\tau_2 (\alpha_2) = 9.8$ ns (27)	1.0	553	0.3444
	516	$\tau_1 (\alpha_1) = 1.9$ ns (97) $\tau_2 (\alpha_2) = 8.9$ ns (3)	1.2		
	549	$\tau_1 (\alpha_1) = 1.9$ ns (98) $\tau_2 (\alpha_2) = 10.3$ ns (2)	1.1		
<b>3</b>	613	$\tau_1 (\alpha_1) = 3.5$ ns (91) $\tau_2 (\alpha_2) = 8.4$ ns (9)	1.1	639	0.2671



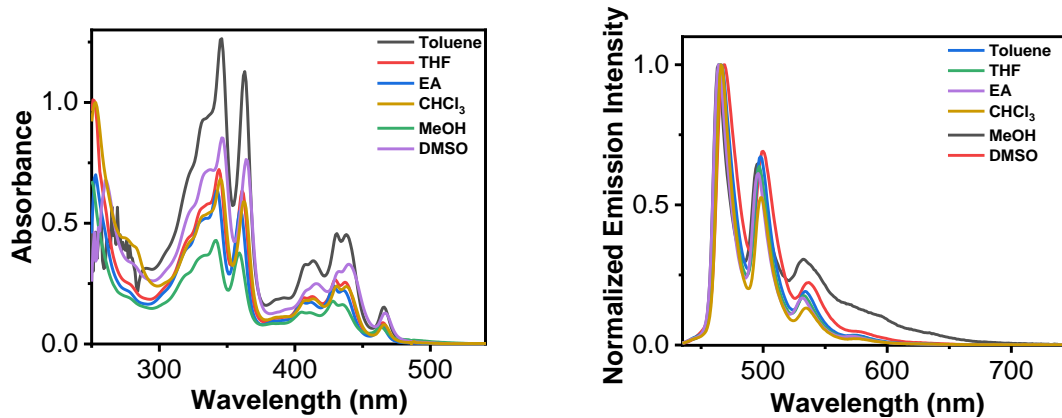
**Figure S25.** UV-vis absorption spectrum of thin films of **1**, **2** and **3** on a quartz substrates (left). UV-vis spectral monitoring of **3** in aerated  $\text{CHCl}_3$  solution before and after exposure to UV radiation under air for 86 h (right) reveals high photochemical and air stability. Intensity of the UV light ( $\lambda_{em} = 365$  nm) in the UV chamber during photoirradiation was measured to be  $3.28 \text{ mW/cm}^2$  during photostability measurements. The radiation intensity was measured with Newport 843-R optical power meter and the sample positioned at a distance of 15 cm from the UV lamp within the UV chamber.

**Thermogravimetric analysis.** Thermogravimetric analysis were recorded on TGA Q 500 V20.10 Build 36 under nitrogen gas atmosphere with an increment of 20 °C/min.



**Figure S26.** Thermogravimetric curves of **1-3**.

**Solvatochromic Studies.** These tetrabenzocoronene based compounds were examined for their solvatochromic behaviour in different solvents (toluene, tetrahydrofuran, ethyl acetate, chloroform, dimethylsulfoxide) varying from low polarity to high polarity.



**Figure S27.** Absorption (left) and normalized emission (right) solvatochromic behaviour of **1**.

### Experimental determination of ground and excited state dipole moment of 2 and 3.

Solvatochromism is one of the popular known methods for the determination of the experimental dipole moment of the molecule in the ground and excited states. It is mainly based on the effect of the electric field on the molecule in solution. It can be derived from the absorbance and the emission maximum of the molecule in different solvents.

**Table S5.** Solvent properties and polarity functions.

Solvent/Polarity function	$D^a$	$n^b$	$f_1(D, n)^c$	$f_2(D, n)^c$	$E_T^N$
Acetonitrile	37.5	1.342	0.864	0.665	0.460
Chloroform	4.8	1.444	0.371	0.486	0.259
DMSO	46.45	1.476	0.841	0.744	0.444
EA	6.02	1.370	0.489	0.498	0.228
Tetrahydrofuran	7.6	1.404	0.551	0.550	0.207
Toluene	2.38	1.494	0.031	0.349	0.099

Note: <sup>a</sup> Dielectric constant (D) at 25 °C. <sup>b</sup> Refractive index (n) at 25 °C. <sup>c</sup> Polarity functions  $f_1(D, n)$  and  $f_2(D, n)$ .

If  $N_B$  is the number of bonds,  $R_A$  is the number of aromatic rings, and  $R_{NA}$  is the number of non-aromatic rings, the Van der Waals volume ( $V_{vdW}$ ) can be calculated theoretically according to the formula given by Abraham et al., using the atomic and bond contributions of Van der Waals volume,<sup>7</sup>

$$V_{vdW} = \Sigma (\text{all atom contributions}) - 5.92 N_B - 14.7 R_A - 3.8 R_{NA} \quad \dots Eq. 1$$

The number of bonds  $N_B$  can be calculated from the formula:

$$N_B = N - 1 + R_A + R_{NA} \quad \dots Eq. 2$$

Where N represents the total number of atoms present in the molecule.

The values of  $V_{vdW}$  for atoms carbon, hydrogen, nitrogen and oxygen are calculated to be 20.58, 7.24, 15.60 and 14.71 Å<sup>3</sup> respectively. The molecular formula for **2** and **3** is C<sub>59</sub>H<sub>52</sub>O<sub>2</sub> and C<sub>60</sub>H<sub>51</sub>NO<sub>2</sub> respectively. The sum of all the atoms Van der Waals volume in the molecule is demonstrated as below.

For **2**,

$$\begin{aligned}\Sigma (\text{all atom contributions}) &= (59 \times 20.58) + (52 \times 7.24) + (14.71 \times 2) \\ &= 1214.22 + 376.48 + 29.42 \\ &= 1620.12.\end{aligned}$$

For **3**,

$$\begin{aligned}\Sigma (\text{all atom contributions}) &= (60 \times 20.58) + (51 \times 7.24) + (15.60 \times 1) + \\ &\quad (14.71 \times 2) \\ &= 1234.8 + 369.24 + 15.60 + 29.42 \\ &= 1649.06.\end{aligned}$$

So, the number of bonds present in the molecule are calculated for **2** and **3** using Eq. 2, and the values comes out to be 124 and 125 respectively. Using the values, the van der Waals volume are calculated.

For **2**,

$$\begin{aligned}V_{vdW} &= \Sigma (\text{all atom contributions}) - 5.92 N_B - 14.7 R_A - 3.8 R_{NA} \\ &= 1620.12 - (5.92 \times 124) - (14.7 \times 11) - (3.8 \times 1) \\ &= 1620.12 - 734.08 - 161.7 - 3.8 \\ &= 720.54\end{aligned}$$

For **3**,

$$\begin{aligned}V_{vdW} &= \Sigma (\text{all atom contributions}) - 5.92 N_B - 14.7 R_A - 3.8 R_{NA} \\ &= 1649.06 - (5.92 \times 125) - (14.7 \times 11) - (3.8 \times 1) \\ &= 1649.06 - 740 - 161.7 - 3.8 \\ &= 743.56\end{aligned}$$

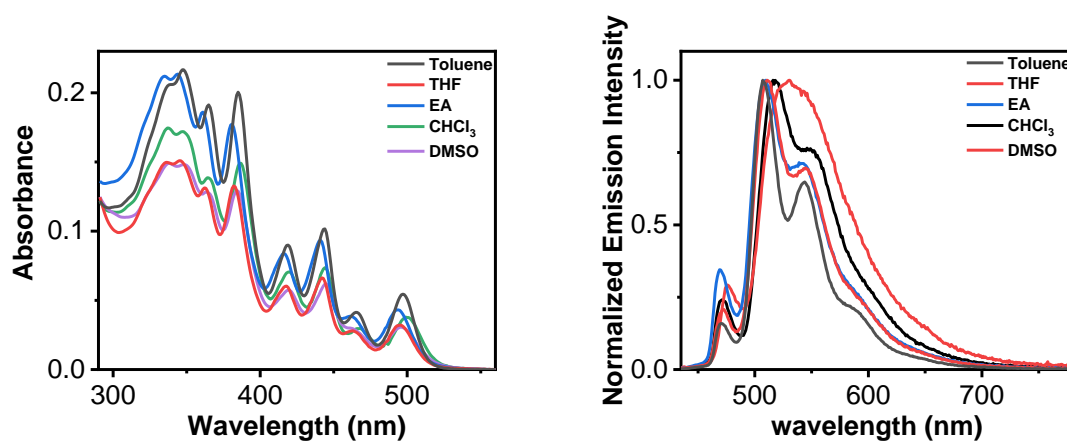
Further, assuming a spherical model, if the Onsager radius is considered to be 'a', then the Van der Waals volume can be represented as:

$$V_{vdW} = \frac{4}{3} \pi a^3 \quad \dots Eq. 3$$

Using this relation, the values for Onsager radius for **2** and **3** are calculated to be 5.56 Å and 5.62 Å respectively.

**Table S6.** Molecular data of compound **2** and **3**.

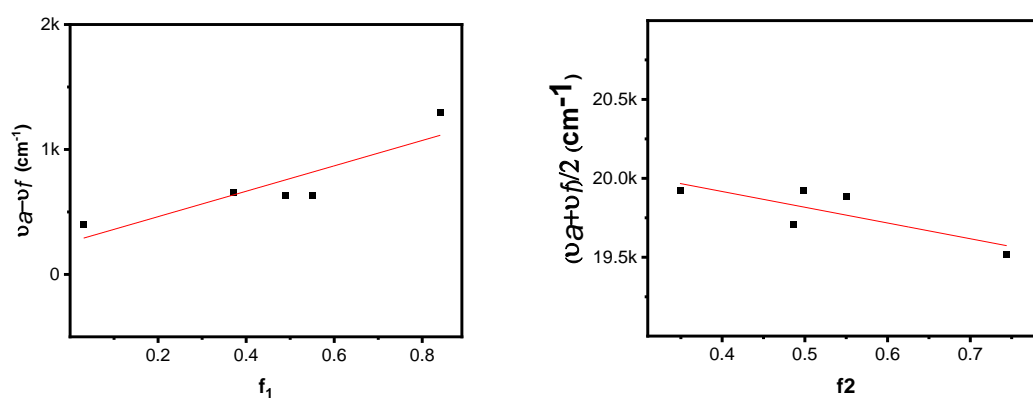
Entry	Molecular formulae	$\sum$ (all atom contributions)	Number of bonds $N_B$	Van der waals volume $V_{vdw}$ (Å <sup>3</sup> )	Onsagar cavity radius: $a$ (Å)
<b>2</b>	C <sub>59</sub> H <sub>52</sub> O <sub>2</sub>	1620.12	124	720.54	5.56
<b>3</b>	C <sub>60</sub> H <sub>51</sub> NO <sub>2</sub>	1649.06	125	743.56	5.62



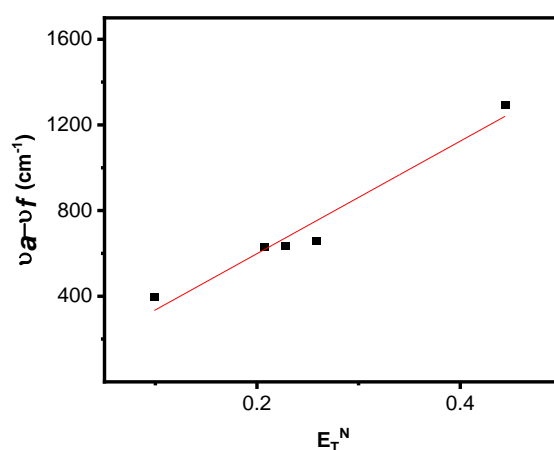
**Figure S28.** Absorption (left) and normalized emission (right) solvatochromic behaviour of **2**.

**Table S7.** Photophysical data of **2** in different solvents.

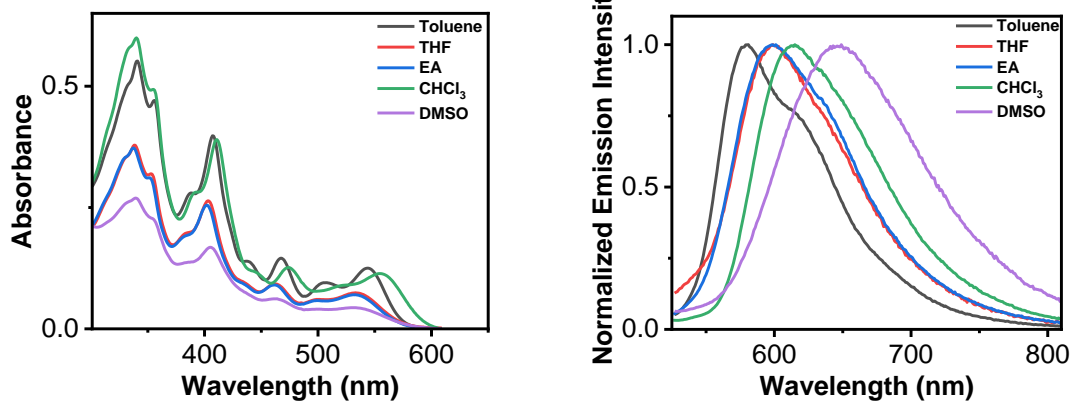
Solvent	$\lambda_{\max}$ (abs) nm	$\lambda_{\max}$ (em) nm	$\nu_a - \nu_f$ ( $\text{cm}^{-1}$ )	$\frac{\nu_a + \nu_f}{2}$ ( $\text{cm}^{-1}$ )	$\phi_f$ (%)
Toluene	497	507	397	19922	25
THF	495	511	632	19886	20
EA	494	510	635	19925	20
Chloroform	499	516	660	19710	17
DMSO	496	530	1293	19515	19



**Figure S29.** Plots of polarity functions  $f_1$  and  $f_2$  for different solvents versus solvent shift data.



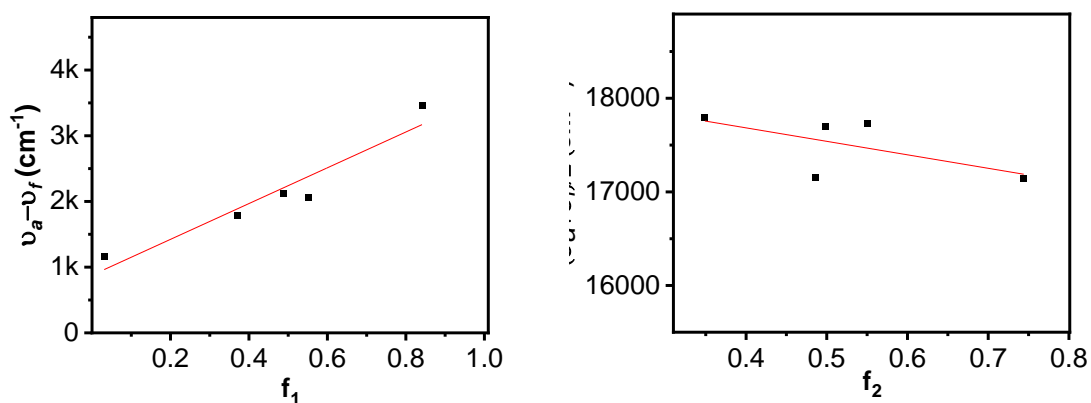
**Figure S30.** Plot of solvent parameter  $E_T^N$  versus Stokes shift of compound **2**.



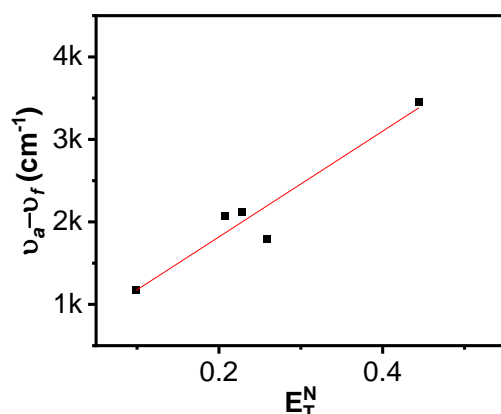
**Figure S31.** Absorption (left) and normalized emission (right) solvatochromic behaviour of **3**.

**Table S8.** Photophysical data of **3** in different solvents.

Solvent	$\lambda_{\max}(\text{abs})$ nm	$\lambda_{\max}(\text{em})$ nm	$\nu_a - \nu_f$ ( $\text{cm}^{-1}$ )	$\frac{\nu_a + \nu_f}{2}$ ( $\text{cm}^{-1}$ )	$\phi_f$ (%)
Toluene	544	581	1170	17797	18
THF	533	599	2067	17728	--
EA	533	601	2123	17700	--
Chloroform	554	615	1790	17155	30
DMSO	530	649	3460	17138	--



**Figure S32.** Plots of polarity functions  $f_1$  and  $f_2$  for different solvents versus solvent shift data of **3**.



**Figure S33.** Plot of solvent parameter  $E_T^N$  versus Stokes shift of compound **3**.

Here, initially, the ratio of excited state ( $\mu_e$ ) and ground state ( $\mu_g$ ) dipole moments was determined by utilizing the Bakshiev's equation and Chamma and Viallet equations.<sup>8</sup>

Bakshiev formulation,

$$\begin{aligned}\bar{\nu}_a - \bar{\nu}_f &= \frac{2(\mu_e - \mu_g)^2}{a^3 hc} f_1(D, n) + constant \\ &= S_1 f_1(D, n) + constant\end{aligned}$$

....Eq. 3

Where,  $S_1$  indicates the slope of the linear fit, which was obtained from the  $(\bar{\nu}_a - \bar{\nu}_f)$  versus  $f_1(D, n)$  and denoted as follows

$$S_1 = \frac{2(\mu_e - \mu_g)^2}{a^3 hc}$$

The Chamma and Viallet equations,

$$\begin{aligned}\frac{(\bar{\nu}_a + \bar{\nu}_f)}{2} &= -\frac{2(\mu_e^2 - \mu_g^2)}{a^3 hc} f_2(D, n) + constant \\ &= S_2 f_2(D, n) + constant\end{aligned}$$

....Eq. 4

Where,  $S_2$  is the slope of the linear fit, which was derived from the  $\frac{(\bar{\nu}_a + \bar{\nu}_f)}{2}$  versus  $f_2(D, n)$  and expressed as follows



$$S_2 = -\frac{2(\mu_e^2 - \mu_g^2)}{a^3 hc}$$

In the above equations,  $\bar{\nu}_a$  and  $\bar{\nu}_f$  are the absorption and fluorescence maxima respectively.  $n$ ,  $D$ ,  $a$ ,  $h$ ,  $c$  indicates refractive indices, dielectric constants of the solvents, Onsagar cavity radius, Planck's constant and velocity of light respectively.  $f$  indicates the function.

$$f_1(D, n) = \left[ \frac{D-1}{D+2} - \frac{n^2-1}{n^2+2} \right] \left( \frac{2n^2+1}{n^2+2} \right) \quad \dots \text{Eq. 5}$$

$$f_1(D, n) = \frac{1}{2} f_1(D, n) + \frac{3}{2} \frac{(n^4-1)}{(n^2+2)^2}$$

$$\frac{\mu_e}{\mu_g} = \frac{|S_1 - S_2|}{|S_1 + S_2|}$$

Radhakrishnan and co-workers

$$\begin{aligned} \bar{\nu}_a - \bar{\nu}_f &= 11307.6 \left[ \left( \frac{\Delta\mu_C}{\Delta\mu_B} \right)^2 \left( \frac{a_B}{a_C} \right)^3 \right] E_T^N + \text{constant} \\ &= m E_T^N + \text{constant} \end{aligned}$$

....Eq. 7

Where,  $m$  is the slope and obtained from the linear fit of the  $(\bar{\nu}_a - \bar{\nu}_f)$  versus  $E_T^N$ . It is expressed as follows.

$$m = 11307.6 \left[ \left( \frac{\Delta\mu_C}{\Delta\mu_B} \right)^2 \left( \frac{a_B}{a_C} \right)^3 \right]$$

Here,  $\Delta\mu_B$  and  $a_B$  are the change in the dipole moment and the Onsagar cavity radius for the betaine dye respectively. And the values are  $\Delta\mu_B = 9$  D and  $a_B = 6.2$  Å. Similarly,  $\Delta\mu_C$  and  $a_C$  denotes the dipole moment change and the Onsagar cavity radius of the compound **1**. Here,  $a_C$  is 5.56 Å.

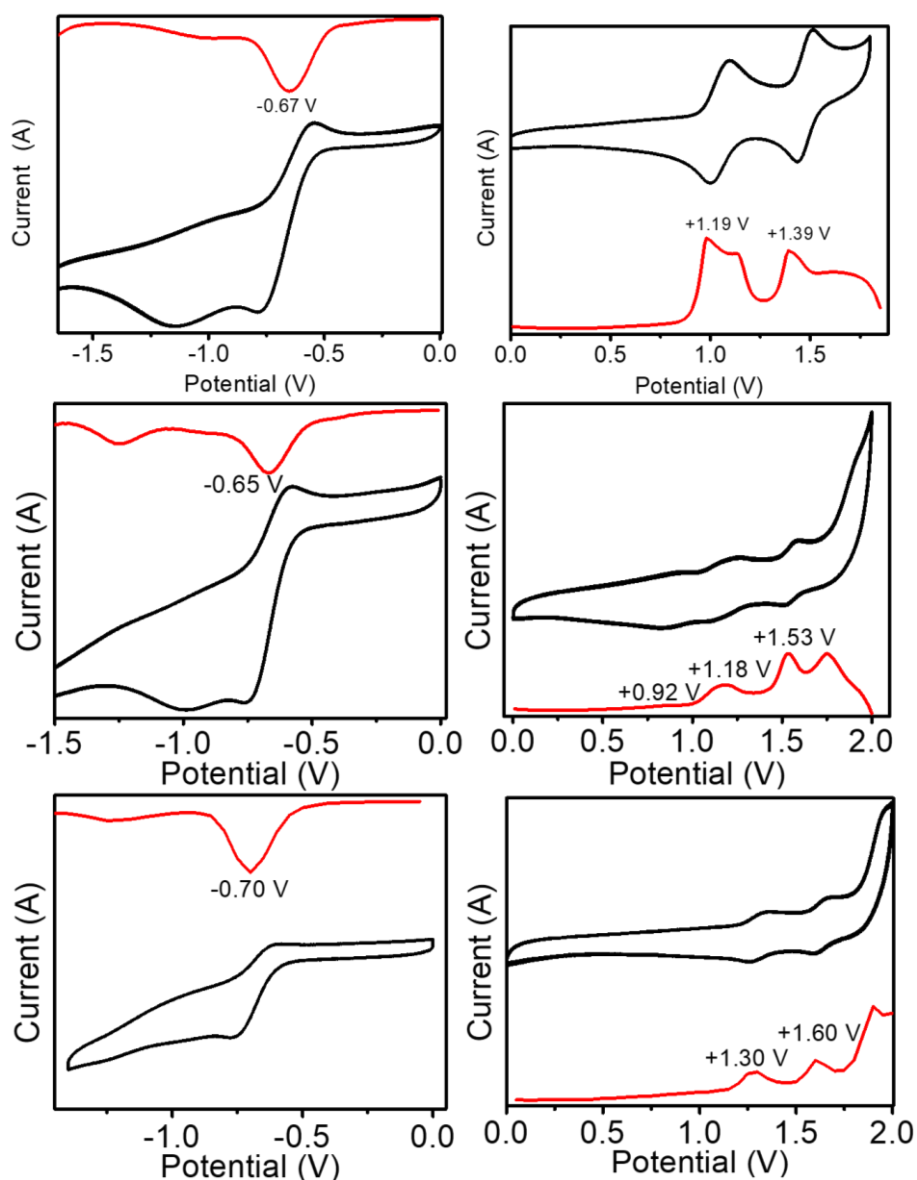
$$\Delta\mu = (\mu_e - \mu_g) = \sqrt{\frac{m \times 81}{11307.6 \left( \frac{6.2}{a} \right)^3}}$$

From the above, dipole moment ratio  $\left( \frac{\mu_e}{\mu_g} \right)$  and difference  $(\mu_e - \mu_g)$ , the experimental values of ground and excited state dipole moments can be calculated.

**Table S9.** Experimentally determined ground and excited state dipole moment values of compound **1**.

Property	S <sub>1</sub>	S <sub>2</sub>	$\frac{\mu_e}{\mu_g} = \frac{ S_1 - S_2 }{ S_1 + S_2 }$	M	$(\mu_e - \mu_g)$ (D)	$\mu_e$ (D)	$\mu_g$ (D)
<b>2</b>	1016	-997	105.95	2628	7.59	8.31	0.72
<b>3</b>	2723	-1439	3.24	6410	5.85	8.46	2.61

**Electrochemical properties.** Electrochemical properties were measured at a scan rate of 0.1 V/s using 0.1 M of tetra-*n*-butylammonium hexafluorophosphate (TBAPF<sub>6</sub>) as supporting electrolyte dissolved in nitrogen-purged dry dichloromethane with a CH Instruments 660A potentiostat using a glassy carbon as working electrode and an Ag/Ag<sup>+</sup> (0.01 M) as reference electrode at room temperature. The measurements were calibrated using ferrocene as an external standard. The formula used for HOMO-LUMO calculation from CV are  $E_{HOMO} = [E_{ox} - E_{1/2}(Fc) + 4.8]$  eV,  $E_{LUMO} = [E_{red} - E_{1/2}(Fc) + 4.8]$  eV and  $E_g = [E_{HOMO} - E_{LUMO}]$  eV and the  $E_{LUMO}(opt)$  was calculated from  $E_g = 1240/\lambda_{onset}$



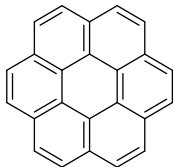
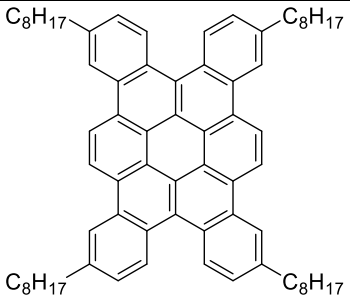
**Figure S34.** Cyclic voltammograms of **1** (top row), **2** (middle row) and **3** (bottom row) in dichloromethane.

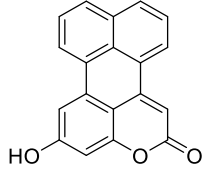
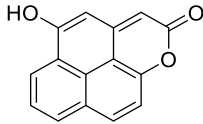
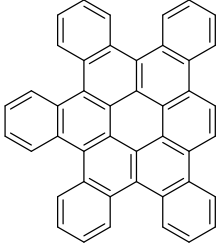
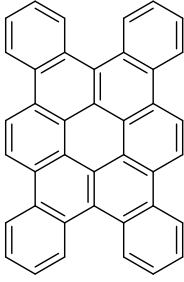
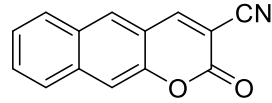
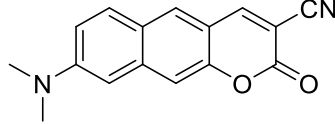
**Table S10.** Electrochemical properties of **1-3** in DCM, and DFT calculated HOMO and LUMO energy levels.

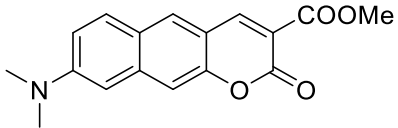
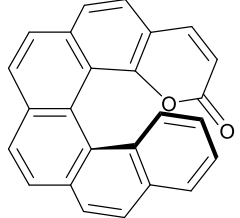
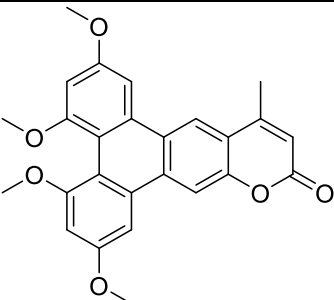
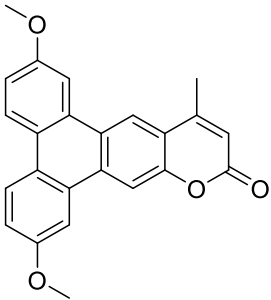
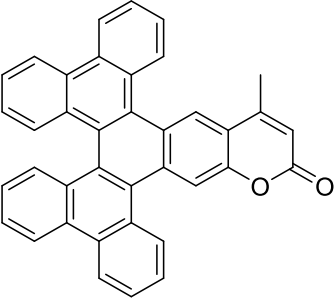
Entry	$E_{\text{ox}}^1$ / $E_{\text{red}}^1$ (eV)	$E_{\text{HOMO}}$ / $E_{\text{LUMO}}^{[a]}$ (V)	$E_{\text{HOMO}}$ / $E_{\text{LUMO}}^{[b]}$ (V)	$E_g$ (opt) <sup>[a]</sup> / $E_g$ (CV) (eV)	$E_g^{[b]}$ (eV)
<b>1</b>	1.19	-5.42	-4.73	2.62/1.76	3.10
	/-0.67	/-3.66	/-1.63		
<b>2</b>	0.98	-5.21	-5.04	2.38/1.53	2.92
	/-0.65	/-3.68	/-2.12		
<b>3</b>	1.3	-5.53	-5.27	2.08/2.00	2.63
	/-0.7	/-3.53	/-2.63		

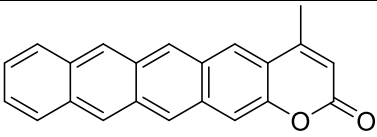
[a] from CV experiments; [b] from theoretical calculations

**Table S11.**  $\lambda_{\text{abs}}$ ,  $\lambda_{\text{em}}$ ,  $\Phi_f$ ,  $E_{\text{HOMO}}/E_{\text{LUMO}}$  and  $E_g$  values of reported compounds for comparison.

	Compound	$\lambda_{\text{abs}}$ nm	$\lambda_{\text{em}}$ Nm	$\Phi_f$ %	$E_{\text{HOMO}}$ eV	$E_{\text{LUMO}}$ eV	$E_g$ , eV /Ref. no.
1.	 Coronene in THF	290, 301 (max), 323, 340	425, 432, 443, 453, 472, 482	1	na	na	na/ <sup>9</sup>
2.	 TBC-C8 in CHCl <sub>3</sub>	431 (max), 462 ( $\alpha$ )	462, 493, 529	na	5.10	na	na/ <sup>10</sup>

3.	 <p>11-Hydroxy-1-oxaperylene-2-one in THF</p>	418	460	19	na	na	na/ <sup>11</sup>
4.	 <p>5-Hydroxy-naphtho[2,1,8-d,e,f]coumarin in 2-MeTHF</p>	440, 469	472, 508	35	na	na	2.65 (Toluene) / <sup>12</sup>
5.	 <p><b>PBC</b> in DCM</p>	375	na	na	5.52	2.98	2.54/ <sup>13</sup>
6.	 <p><b>TBC</b> in DCB</p>	340, 356, 360, 426	na	na	5.23	na	na/ <sup>3</sup>
7.	 <p>3-cyano-benzo[g]coumarin IN CH<sub>3</sub>CN</p>	335	533	na	na	na	na/ <sup>14</sup>
8.	 <p>3-Cyano-8-dimethylamino- benzo[g]coumarin in DMSO</p>	471	609	40	na	na	na/ <sup>15</sup>

9.	 <p>3-Methoxycarbonyl-8-dimethylamino-benzo[g]coumarin in H<sub>2</sub>O</p>	456	626	11	na	na	na/ <sup>15</sup>
10.	 <p>6-<i>in</i>-hexahelical coumarin in methanol</p>	415	486	14	na	na	na/ <sup>16</sup>
11.	 <p>7,9,10,12-Tetramethoxy-4-methyl-phenanthro[9,10-<i>g</i>]-2<i>H</i>-chromen-2-one in CHCl<sub>3</sub></p>	329, 344, 390	538, 585	10	na	na	na/ <sup>17</sup>
12.	 <p>7,12-Dimethoxy-4-methyl-phenanthro[9,10-<i>g</i>]-2<i>H</i>-chromen-2-one in CHCl<sub>3</sub></p>	318, 333, 365	475	17	na	na	na/ <sup>17</sup>
13.		332, 343, 393	415, 478	12	na	na	na/ <sup>17</sup>

	4-Methyl-tetrabenzo[1,2:3,4:5,6:7,8]phenanthro[9,10-g]-2H-chromen-2-one in CHCl <sub>3</sub>						
14.	 2H-anthra-[2,3-g]-chromen-2-one in CHCl <sub>3</sub>	397, 422, 502	518, 570, 609	19	-5.34	-3.01	2.33/ <sup>18</sup>

na: not available

## References

1. E. Rochlin, Z. Rappoport *J. Org. Chem.* 2003, **68**, 2, 216–226.
2. X.-H. Tian, X. Hao, T.-L. Liang, C.-F. Chen, *Chem. Commun.*, 2009, 6771-6773.
3. S. Pola, C.-H. Kuo, W.-T. Peng, M. M. Islam, I. Chao, Y.-T. Tao, *Chem. Mater.* 2012, **24**, 2566–2571.
4. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, Jr J. A. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts; R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, *Gaussian 16*, Revision B.01; Gaussian, Inc.: Wallingford, CT, 2016.
5. (a) A. D. Becke. *J. Chem. Phys.* 1993, **98**, 5648-5652; (b) C. Lee, W. Yang, R. G. Parr *Phys. Rev. B.* 1988, **37**, 785-789.
6. J. M. Dixon, M. Taniguchi, J. S. Lindsey, PhotochemCAD 2. A Refined Program with Accompanying Spectral Databases for Photochemical Calculations, *Photochem. Photobiol.*, 2005, **81**, 212-213.
7. Y. H. Zhao, M. H. Abraham and A. M. Zissimos, *J. Org. Chem.*, 2003, **68**, 7368.

8. (a) N. G. Bakshiev, *Opt. Spektosk. (USSR)*, 1964, **16**, 821. (b) A. Chamma and P. Viallet, *CR. Hebd. Seanc. Acad. Sci. Ser.*, 1970, **270**, 1901. (c) K. Chandrasekhar, L. R. Naik, H. M. Suresh Kumar and N. N. Math, *Ind. J. Pure Appl. Phys.*, 2006, **44**, 292. (d) M. Ravi, A. Samanta and T. P. Radhakrishan, *J. Phys. Chem.*, 1994, **98**, 9133. (e) M. Ravi, T. Soujanya, A. Samanta and T. P. Radhakrishan, *J. Chem. Soc. Faraday Trans.*, 1995, **91**, 2739.
9. (a) J. W. Patterson, *J. Am. Chem. Soc.*, **1942**, *64*, 1485; (b) B. Nickel, M. T. Wick, *Chem. Phys.*, 1992, **168**, 111; (c) N. Nijegorodov, R. Mabbs, and W. S. Downey, *Spectrochim. Acta*, Part A, 2001, **57**, 2673. (d) J. Xiao, H. Yang, Z. Yin, J. Guo, F. Boey, H. Zhang and Q. Zhang *J. Mater. Chem.*, 2011, **21**, 1423-1427.
10. X. Zhang, X. Jiang, K. Zhang, L. Mao, J. Luo, C. Chi, H. S. O. Chan, and J. Wu, *J. Org. Chem.* 2010, **75**, 8069–8077.
11. M. Tasiór, I. Deperasińska, K. Morawska, M. Banasiewicz, O. Vakuliuk, B. Kozankiewicz, and D. T. Gryko, *Phys. Chem. Chem. Phys.*, 2014, **16**, 18268-18275.
12. R. Nazir, A. J. Stasyuk, and D. T. Gryko, *J. Org. Chem.* 2016, **81**, 11104–11114.
13. Y.-T. Tao, S. Pola, S. Kumar, and M. M. Islam, *J. Org. Chem.* 2017, **82**, 8067–8071.
14. C. Murata, T. Masuda, Y. Kamochi, K. Todoroki, H. Yoshida, H. Nohta, M. Yamaguchi and A. Takadate, *Chem. Pharm. Bull.* 2005, **53**, 750–758.
15. D. Kim, Q.-P. Xuan, H. Moon, Y.-W. Jun and K. H. Ahn, *Asian Journal of Organic Chemistry*, 2014, **3**, 1089–1096.
16. A. Mukhopadhyay, T. Hossen, I. Ghosh, W. M. Nau, K. Sahu and J. N. Moorthy, *Chemistry – A European Journal* 2017, **23**, 14797-14805.
17. Nitisha and P. Venkatakrishnan, *J. Org. Chem.* 2019, **84**, 10679–10689.
18. A. Kumar, A. Rajpoot, F. Imroze, S. Maddala, S. Dutta and P. Venkatakrishnan, *Eur. J. Org. Chem.*, 2020, **45**, 6976–6980.