Supporting Information

The influence of the intramolecular 2D interactions on the physicochemical properties of hexasubstituted benzene derivatives

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1. Materials

All chemicals and starting materials were commercially available and were used without further purification. Solvents were distilled as per the standard methods and purged with nitrogen before use. All reactions were carried out under argon atmosphere unless otherwise indicated. Column chromatography was carried out on Merck silica gel. Thin layer chromatography (TLC) was performed on silica gel (Merck TLC Silica Gel 60). 5-Iodo-2,2'-bithiophene, (2,2'-bithiophen-5-yl)-ethynyltrimethylsilane and 5-ethynyl-2,2'-bithiophene was prepared according to the method described in our previously published paper [31 - manuscript].
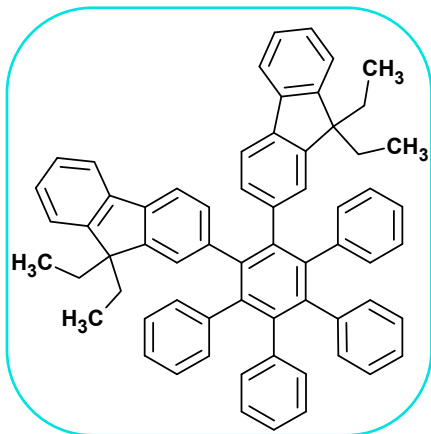
2. General methods - measurements

NMR spectra were recorded with a Bruker Avance 400 MHz instrument by using $CDCl_3$ as a solvent. U.V./Vis spectra were recorded with a Biosens model UV 5600 UV/Vis spectrophotometer in dichloromethane solution. Photoluminescence emission spectra were acquired using Hitachi Fluorescence Spectrophotometer F-7100. Electrochemical measurements were carried out with an Eco Chemie Autolab PGSTAT128n potentiostat using glassy carbon (with diam. 2 mm) or Indium tin oxide (ITO, with 10 Ω per square) as the working electrode. Platinum coil and silver wire were used as auxiliary and reference electrodes, respectively. Potentials are referenced with respect to ferrocene (Fc), which was used as the internal standard. Cyclic and differential pulse voltammetry experiments were conducted in a standard one-compartment cell, in CH_2Cl_2 (Carlo Erba, HPLC grade), under argon. Bu_4NPF_6 (Aldrich; 0.2 M, 99%) was used as the supporting electrolyte. UV-Vis spectroelectrochemical measurements were performed on Indium Tin Oxide (ITO) glass working electrode coated with polymers. Polymeric layers were synthesized on an ITO electrode under conditions similar to those of cyclic voltammetry measurement. The quantum theoretical calculations were performed with use of density functional theory (DFT), with an exchange-correlation hybrid functional B3LYP and the basis 6-311+G for all atoms. The calculations were carried out with use of Gaussian 09 program.

3. Synthesis

A mixture of 1.20 mmol (0.46g) tetraphenylcyclopentadienone, 1.00 mmol appropriate alkyne and 13.15 mmol (2.40g) benzophenone was heated at 300°C under argon atmosphere. The progress of the reaction was monitored by TLC chromatography. The time of each reaction depended on the alkyne used and ranged from 2h to 4h (**M1** - 4h, **M2** -3h, **M3** - 2h). After this time the reaction mixture was cooled to room temperature. Crude product was purified using column chromatography.

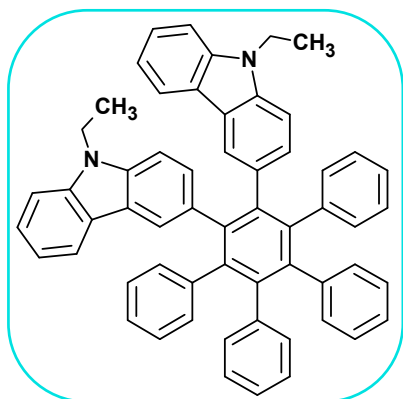## 1,2-bis(9,9-diethyl-9H-fluoren-2-yl)-3,4,5,6-tetraphenylbenzene (M1)

0.47g (1 mmol) of 1,2-bis(9,9-diethyl-9H-fluoren-2-yl)acetylene was used for the synthesis. The product was isolated with silica gel column chromatography (hexane : dichloromethane, 1:3). **M1** was obtained as beige solid with 34% yield. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.49 – 7.34 (m, 4H), 7.14 (m, 6H), 7.01 – 6.74 (m, 24H), 1.82 (q, J = 7.3 Hz, 4H), 1.65 (q, J = 7.3 Hz, 4H), 0.42 (t, J = 7.5 Hz, 6H), 0.32 (t, J = 7.5 Hz, 6H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 150.1, 149.8, 149.8, 148.5, 148.3, 148.1, 141.8, 141.1, 140.8, 140.7, 140.3, 139.9, 138.9, 138.7, 131.9, 131.6, 131.4, 126.8, 126.7, 126.6, 126.5, 125.4, 125.3, 122.6, 119.5, 118.2, 117.9, 55.8, 33.2, 32.9, 8.3, 8.2.
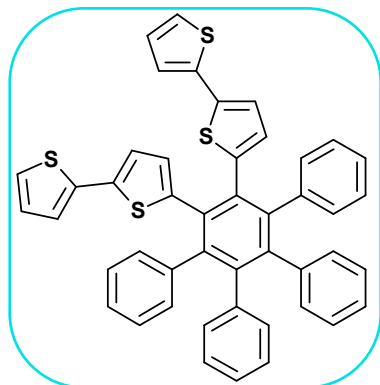
1,2-bis(N-ethyl-9H-carbazol-3-yl)-3,4,5,6-tetraphenylbenzene (M2)

0.41g (1 mmol) of 1,2-bis(N-ethyl-9H-carbazol-3-yl)acetylene was used for the synthesis. The product was isolated with silica gel column chromatography (hexane : dichloromethane, 1:5). **M2** was obtained as beige solid with 47% yield. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.78 (d, J = 7.6 Hz, 2H), 7.61 (s, 2H), 7.32 (t, J = 7.5 Hz, 2H), 7.24 – 7.16 (m, 2H), 7.08 (t, J = 7.4 Hz, 2H), 7.01 – 6.82 (m, 16H), 6.81 – 6.68 (m, 8H), 4.07 (q, J = 7.1 Hz, 4H), 1.16 (t, J = 6.9 Hz, 6H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 141.3, 141.2, 140.2, 139.9, 137.9, 131.8, 131.7, 131.5, 129.8, 129.2, 127.3, 126.7, 125.2, 125.1, 124.9, 123.9, 123.8, 123.4, 120.1, 118.3, 110.4, 108.3, 106.7, 37.4, 13.6.
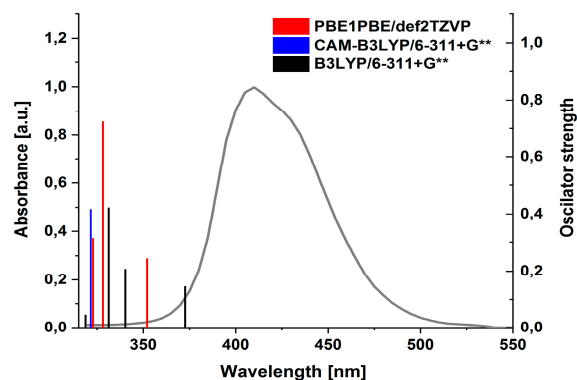
1,2-bis(2,2'-bithiophene-5-yl)-3,4,5,6-tetraphenylbenzene (M3)

0.35g (1 mmol) of 1,2-bis(2,2'-bithiophene-5-yl)acetylene was used for the synthesis. The product was isolated with silica gel column chromatography (hexane : dichloromethane, 1:1). **M3** was obtained as beige solid with 56% yield. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.08 (d, J = 4.9 Hz, 2H), 6.99 – 6.92 (m, 12H), 6.91 – 6.88 (m, 2H), 6.87 – 6.79 (m, 10H), 6.71 (d, J = 3.6 Hz, 2H), 6.41 (d, J = 3.6 Hz, 2H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 142.1, 141.8, 140.8, 140.3, 140.2, 138.0, 137.9, 134.0, 131.3, 130.9, 130.1, 127.7, 127.1, 126.8, 125.9, 125.6, 123.9, 123.3, 122.8.
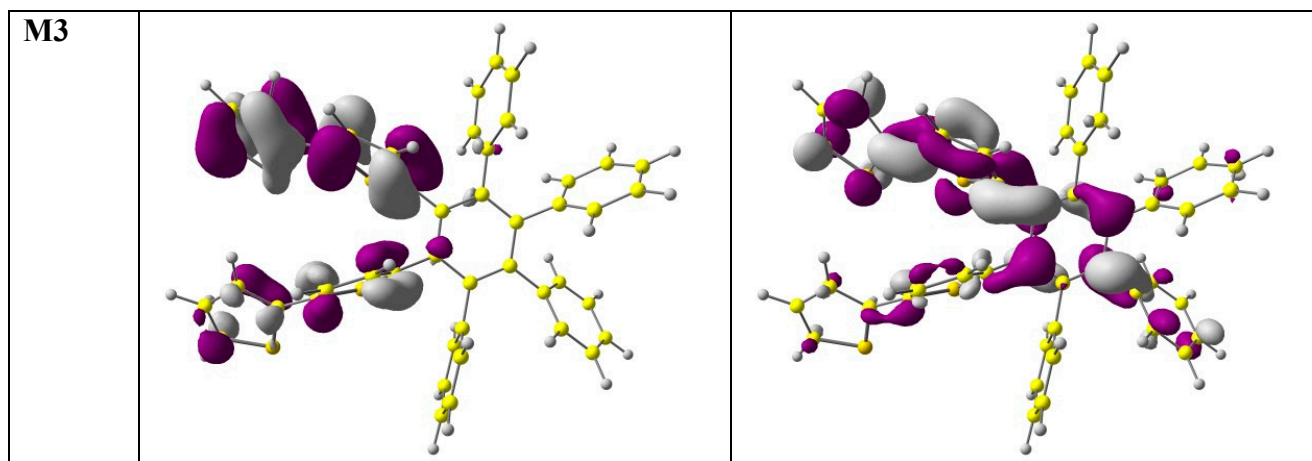
4.DFT calculations

Figure S1. Experimental (gray line) absorption spectra and calculated transitions of **M3** in dichloromethane at B3LYP/6-311+G**, CAM-B3LYP/6-311+G** and PBE1PBE/def2TZVP.
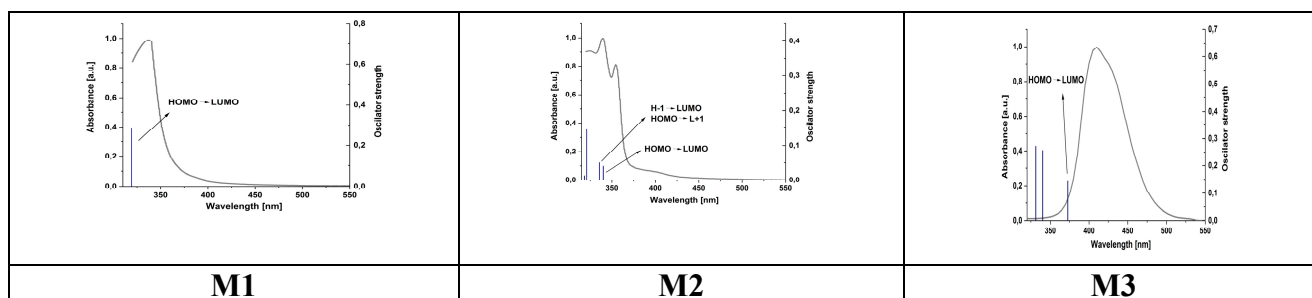
Table S1. The HOMO and LUMO levels.

Code	HOMO	LUMO
M1		
M2		

M3	

Table S2. The energies and characters of the selected spin-allowed electronic transitions for **M1, M2** and **M3** calculated with the B3LYP/6-311+G** method, together with assignment to the experimental absorption bands.

Experimental absorption λ [nm]	Calculated transitions			
	Major contribution (%)	E[eV]	λ [nm]	Oscillator strength
M1				
337	H→L (98%)	3.88	319.2	0.2871
M2				
354	H→L (89%)	3.64	340.0	0.0403
	H-1→L (27%) H→L+1 (65%)	3.69	335.6	0.0505
M3				
409	H→L (98%)	3.32	372.7	0.1458

Table S3. The energies and characters of the selected spin-allowed electronic transitions for **M1, M2** and **M3** calculated with the B3LYP/6-311+G** method, together with assignment to the experimental absorption bands.

Figure S2. Experimental (blue line) absorption spectra and calculated transitions (black) of M1-M3 in dichloromethane (at B3LYP/6-311+G level).

5.NMR spectra (¹H, ¹³C, COSY, HMQC, HMBC)

Figure S3. ¹H NMR of M3
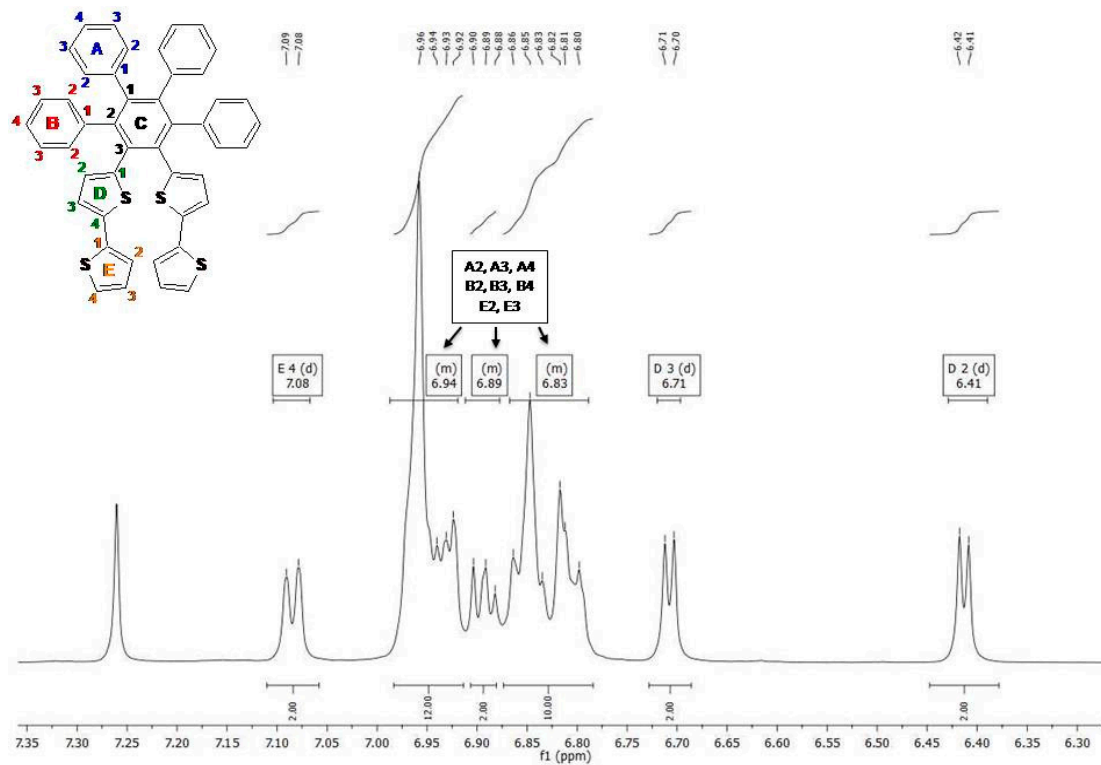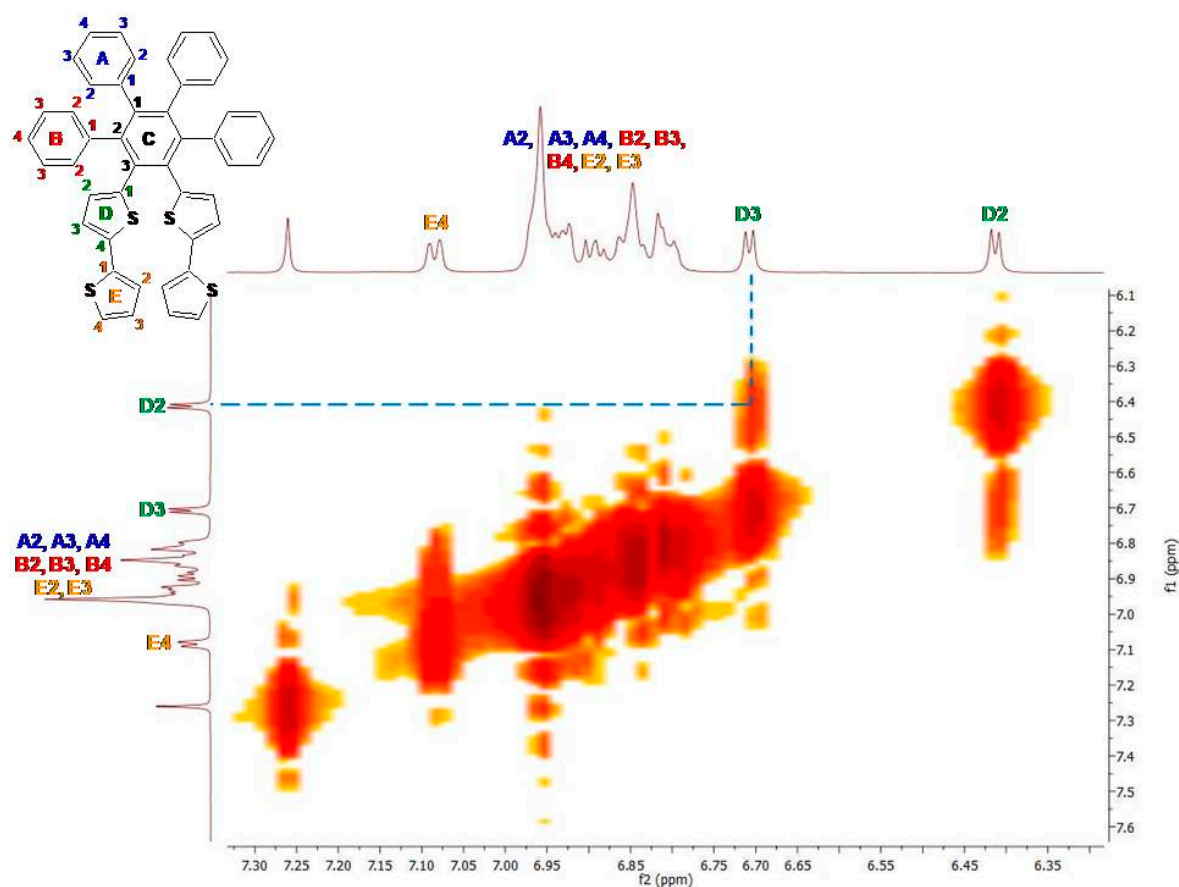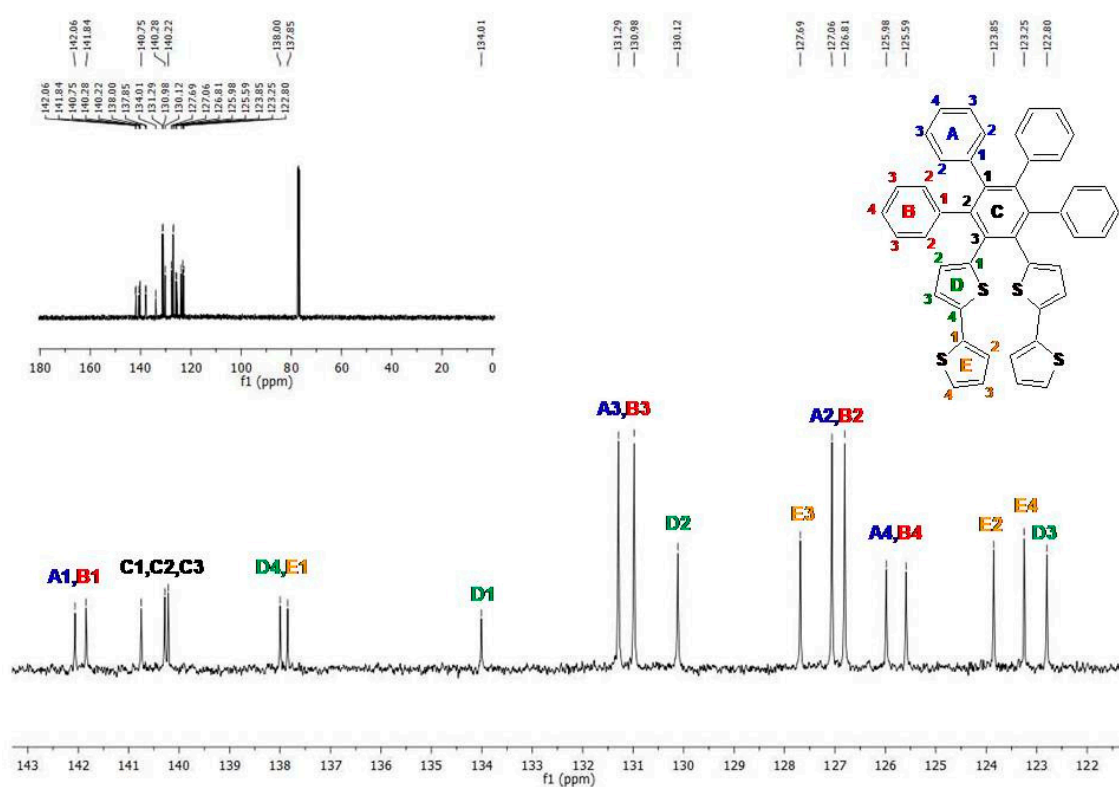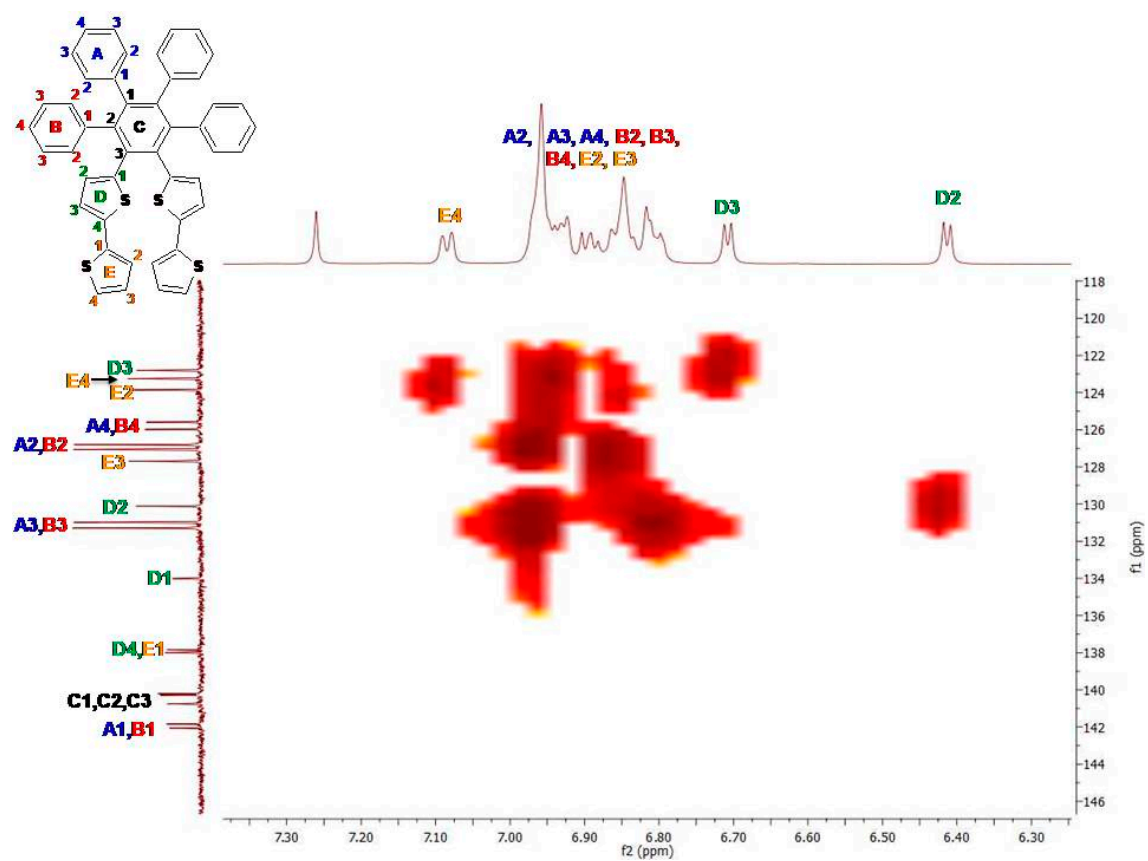
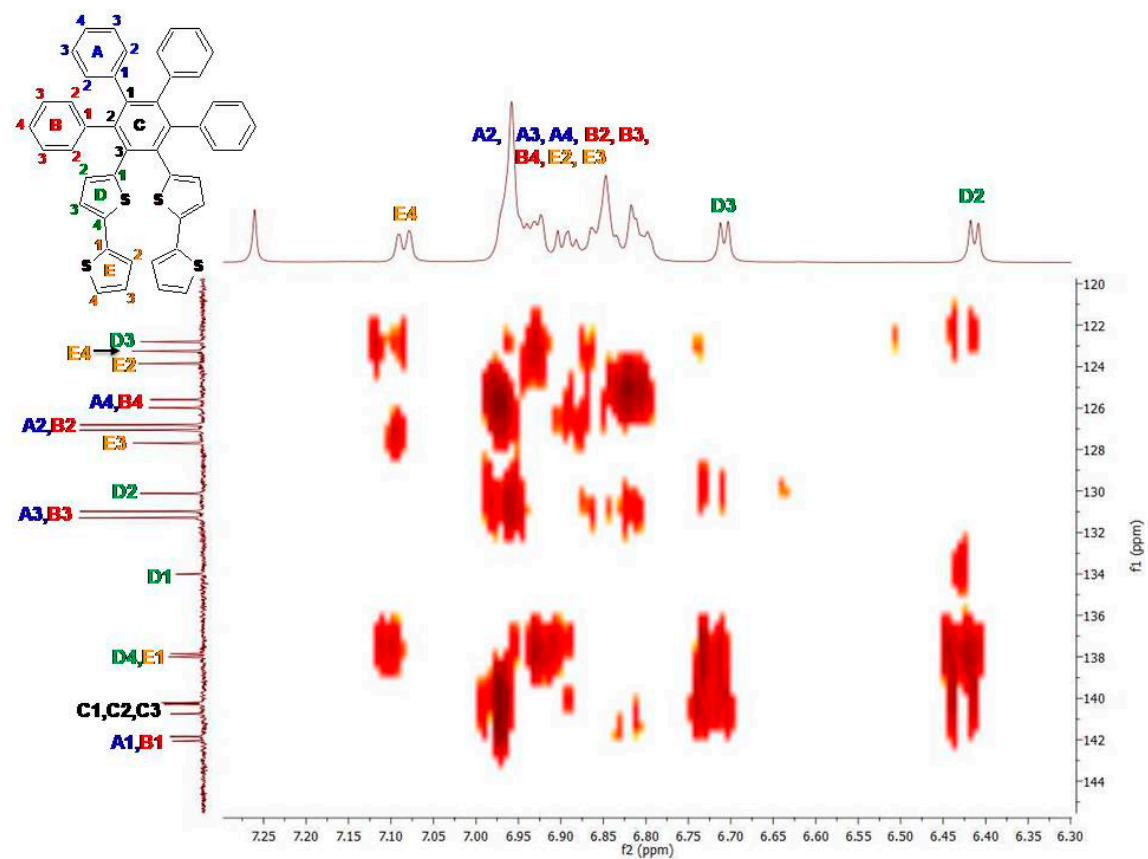**Figure S4. H-H COSY of M3**

Figure S5. ¹³C NMR of M3

Figure S6. H-C HMQC of M3

Figure S7. H-C HMBC of M3