Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Influence of Thermal and Solvent Annealing on the Morphology and Photovoltaic Performance of the Solution Processed, D-A-D type Small Molecules- Based Bulk Heterojunction Solar Cells

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Content

1. Experimental Section

1.1 Materials and instrumentation

The starting materials and reagents, thiophene carbonitrile, di-n-ethylsuccinate, *tert*-BuOK, *tert* amyl alcohol, 2-ethyl hexyl bromide, mesitylboronic acid, (4-isopropoxy-2-methylphenyl)boronic acid, (2,3,4-trimethoxyphenyl)boronic acid, (3,5-di-tert-butylphenyl)boronic acid and *N*-bromosuccinimide were purchased from Sigma-Aldrich. The solvents were purified by standard procedures and purged with nitrogen before use. All other chemicals used in this work were analytical grade and were used without further purification, and all reactions were performed under argon atmosphere unless and otherwise mentioned. Chromatographic separations were carried out on silica gel (60–120 mesh). ^{1}HNMR spectra were recorded on Bruker 300 MHz spectrometer using TMS as an internal standard. Mass spectra were recorded on Shimadzu LCMS- 2010 EV model with ESI probe. Absorption spectra were recorded on a Shimadzu UV-Vis to near IR region 3600 spectrometer. Electrochemical data were obtained from cyclic voltammetry using a conventional three-electrode cell and a BAS100 electrochemical analyzer. C, H, N, S data was recorded on Elementar (variomicrotube) instrument.

1.2 Synthesis of 3,6-Dithiophen-2-yl-2,5-dihydro-pyrrolo[3,4-c]pyrrole-1,4-dione (1)

3,6-Dithiophen-2-yl-2,5-dihydro-pyrrolo[3,4-c]pyrrole-1,4-dione was synthesized according to a reported procedure.[1-3]

1.3 Synthesis of 2,5-bis(2-ethylhexyl)-3,6-dithiophen-2-yl-pyrrolo[3,4-c]pyrrole-1,4-dione (2)

In a three-necked, oven-dried 250 mL round-bottom flask, compound **1** (3.00 g, 10.0 mmol) and anhydrous K_2CO_3 (4.15 g, 30.0 mmol) were dissolved in 100 mL of anhydrous *N*,*N*-dimethylformamide (DMF) and heated to 120 °C under argon for 1 h. 2-ethylhexyl bromide (4.80 mL, 25.0 mmol) was then added dropwise, and the reaction mixture was further stirred and heated overnight at 130 °C. The reaction mixture was allowed to cool down to room temperature; after that it was poured into 400 mL of distilled water, and the resulting suspension was stirred at room temperature for 1 h. The solid was collected by vacuum filtration, washed with several portions of distilled water, methanol, and then air-dried. The crude product was purified by flash chromatography using chloroform as eluent, and the solvent was removed in vacuo to obtain a brown color solid (Yield: 75%). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 8.90 (d, 2H), 7.64 (d, 2H), 7.29

(t, 2H), 4.08-3.98 (m, 4H), 1.88-1.83 (m, 2H), 1.40-1.20 (m, 16H), 0.90 (m, 12H); ^{13}C NMR (125 MHz, $CDCl_3$, δ):161.72, 140.39, 135.23, 130.48, 129.80, 128.38, 107.90, 45.83, 39.05, 30.18, 29.67, 28.33, 23.52, 13.99, 10.46; FT-IR (KBr), cm^{-1}: 3095, 2956, 2928, 2857, 1672, 1567, 1503, 1450, 1403, 1325, 1273, 1230, 1168, 1097, 1065, 1027.

1.4 Synthesis of 3,6-Bis-(5-bromo-thiophen-2-yl)-2,5-bis(2-ethylhexyl)-pyrrolo[3,4-c]-pyrrole-1,4-dione (3)

In a three-necked, oven-dried, 150 mL round-bottom flask, compound **2** (1 g, 1.908 mmol) was dissolved in 40 mL of anhydrous $CHCl_3$, covered with aluminum foil, and stirred at room temperature under argon for 15 min. *N*-bromosuccinimide (0.781 g, 4.389 mmol) was then added, and the reaction mixture was kept at room temperature with stirring for 12 h. The reaction mixture was poured into 100 mL of methanol, and the resulting suspension was stirred at room temperature for 1 h. The solid was then collected by vacuum filtration and washed with several portions of hot distilled water and hot methanol to obtain brown color solid (65%). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 8.84 (d, 2H), 7.62 (d, 2H), 4.08-3.98 (m, 4H), 1.90-1.80 (m, 2H), 1.40-1.20 (m, 16H), 0.90 (m, 12H);); ^{13}C NMR (125 MHz, $CDCl_3$, δ):161.37, 139.38, 135.35, 131.43, 131.13, 118.99, 107.98, 45.99, 39.14, 29.68, 28.29, 23.53, 13.99, 10.43; FT-IR (KBr), cm^{-1}: 3084, 2956, 2925, 2855, 1745, 1657, 1554, 1502, 1450, 1405, 1307, 1260, 1233, 1163, 1101, 1073, 1025. ESI-MS: m/z $(M+4H)^+$: 685.

1.5 General procedure for the synthesis of CSDPP9-CSDPP12

A 50 mL of Schlenk tube was charged with compound **3** (0.500 g, 0.729 mmol), $Pd(PPh_3)_4$ (0.062 g, 0.054 mmol). Dimethoxy ethane (8 mL) and 2M aqueous sodium carbonate (2 mL) were added, and the tube was purged with argon gas with 5 evacuate/refill cycles. The aryl boronic acid (1.534 mmol) was subsequently added as a neat liquid. The tube was sealed and heated at 90 °C vigorously for 18 h. Upon cooling to ambient temperature, the organics were extracted into dichloromethane (3×30 mL) from 30 mL water. The combined organics were washed with water (1×30 mL) and brine (1×30 mL), dried over Na_2SO_4, filtered and the solvent was removed under reduced pressure to give **CSDPP9-CSDPP12.**

1.5.1 2,5-bis(2-ethylhexyl)-3,6-bis(5-mesitylthiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (CSDPP9) (Reddish pink solid, 48%). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 9.02 (d, 2H), 7.00 (d, 2H), 6.98-6.96 (brs, 4H), 4.11-3.96 (m, 4H), 2.34 (s, 6H), 2.17 (s, 12H), 1.88-1.82 (m, 2H),

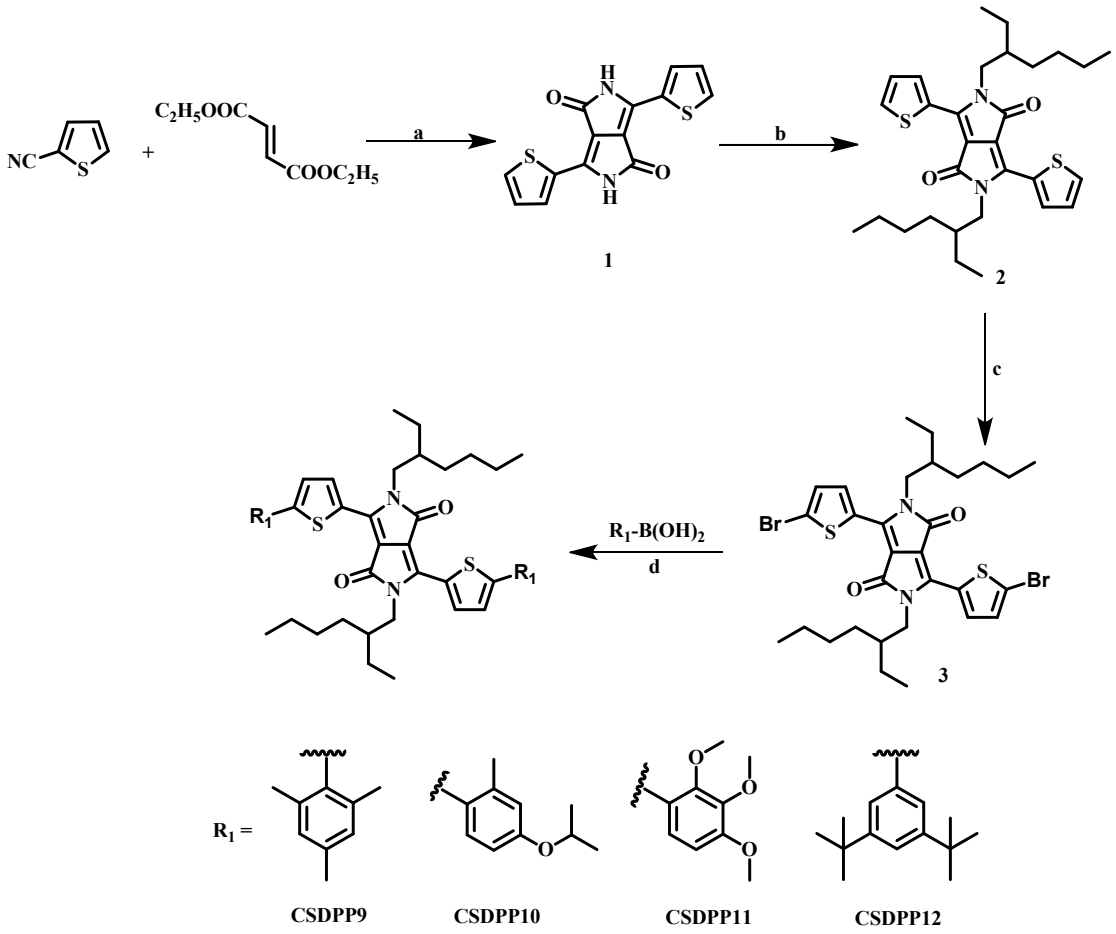
144-1.22 (m, 16H), 0.90-0.80 (m, 12H); ^{13}C NMR (125 MHz, $CDCl_3$, δ):161.79, 147.67, 140.21, 138.67, 137.94, 136.13, 129.95, 129.53, 128.44, 128.31, 107.68, 45.98, 39.16, 30.12, 29.68, 28.36, 23.39, 23.04, 21.10, 20.72, 13.99, 10.43; FT-IR (KBr), cm^{-1}: 3081, 2955, 2923, 2856, 1666, 1567, 1450, 1392, 1306, 1221, 1161, 1094, 1063, 1023. ESI-MS: m/z $[M+H]^+$: 762. Anal. Cal.: $C_{48}H_{60}N_2O_2S_2$. C: 75.74, H: 7.95, N: 3.68, S: 8.43 Found- C: 75.94, H: 7.79, N:3.51, S: 8.33.

1.5.2 2,5-bis(2-ethylhexyl)-3,6-bis(5-(4-isopropoxy-2-methylphenyl)thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (CSDPP10) (dark brownish solid, 52%). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 8.97 (d, 2H), 7.37 (d, 2H), 7.17 (d, 2H), 6.85-6.82 (m, 2H), 6.81-6.76 (m, 2H), 4.65-4.56 (m, 2H), 4.10-4.03 (m, 4H), 2.46 (s, 6H), 1.99-1.90 (m. 2H), 145-1.22 (m, 28H), 0.90-0.80 (m, 12H); ^{13}C NMR (125 MHz, $CDCl_3$, δ):161.79, 158.22, 149.18, 140.03, 137.68, 135.98, 131.49, 128.79, 127.42, 125.15, 118.35, 107.74, 69.86, 45.98, 39.22, 30.27, 28.48, 2.356, 22.04, 21.54, 14.04, 10.52; FT-IR (KBr), cm^{-1}: 2960, 2925, 2860, 1743, 1662, 1599, 1553, 1490, 1437, 1405, 1307, 1236, 1171, 1109, 1021. ESI-MS: m/z $[M+H]^+$: 822. Anal. Cal.: $C_{50}H_{64}N_2O_4S_2$. C: 73.13, H: 7.86, N: 3.41, S: 7.81 Found- C: 73.50, H: 7.89, N:3.39, S: 7.76.

1.5.3 2,5-bis(2-ethylhexyl)-3,6-bis(5-(2,3,4-trimethoxyphenyl)thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (CSDPP11) (light greenish solid, 54%).^{1}H NMR (300 MHz, $CDCl_3$, δ): 9.04 (d, 2H), 7.54 (d, 2H), 7.45 (d, 2H), 6.76 (d, 2H), 4.15-4.10 (m, 4H), 3.97 (s, 6H), 3.94-3.90 (m, 12H), 2.04-1.94 (m, 2H), 145-1.25 (m, 16H), 0.94-0.82 (m, 12H); ^{13}C NMR (125 MHz, $CDCl_3$, δ):161.86, 154.01, 150.76, 144.61, 142.71, 140.18, 135.77, 129.27, 125.14, 122.42, 120.31, 107.96, 60.64, 56.12, 46.15, 39.19, 30.24, 29.68, 28.41, 23.16, 14.04, 10.50; FT-IR (KBr), cm^{-1}: 3078, 2926, 2857, 1663, 1590, 1549, 1485, 1434, 1403, 1326, 1290, 1247, 1173,

1097, 1062, 1020. ESI-MS: m/z $[M+H]^+$: 858. Anal. Cal.: $C_{48}H_{60}N_2O_8S_2$. C: 67.26, H: 7.06, N: 3.27, S: 7.48 Found- C: 68.21, H: 7.01, N:3.43, S: 7.56.

1.5.4 3,6-bis(5-(3,5-di-tert-butylphenyl)thiophen-2-yl)-2,5-bis(2-ethylhexyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (CSDPP12) (dark purple solid, 58%). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 9.03 (d, 2H), 7.53-7.50 (m, 4H), 7.46-7.43 (m, 4H), 4.16-4.05 (m, 4H), 2.01-1.94 (m, 2H), 141-1.35 (m, 44H), 1.30-1.24 (m, 8H), 0.96-0.84 (m, 12H); ^{13}C NMR (125 MHz, $CDCl_3$, δ):161.79, 151.76, 151.10, 139.90, 136.97, 132.51, 128.40, 124.27, 123.32, 120.65, 107.98, 45.90, 39.35, 34.94, 31.37, 30.48, 29.68, 23.70, 23.11, 14.00, 10.68; FT-IR (KBr), cm^{-1}: 3073, 2959, 2928, 2859, 1667, 1592, 1556, 1516, 1459, 1400, 1362, 1297, 1233, 1205, 1140, 1080, 1045. ESI-MS: m/z $[M+H]^+$: 902. Anal. Cal.: $C_{50}H_{80}N_2O_2S_2$. C: 77.28, H: 8.95, N: 3.11, S: 7.11 Found- C: 78.23, H: 9.21, N:3.41, S: 7.02.



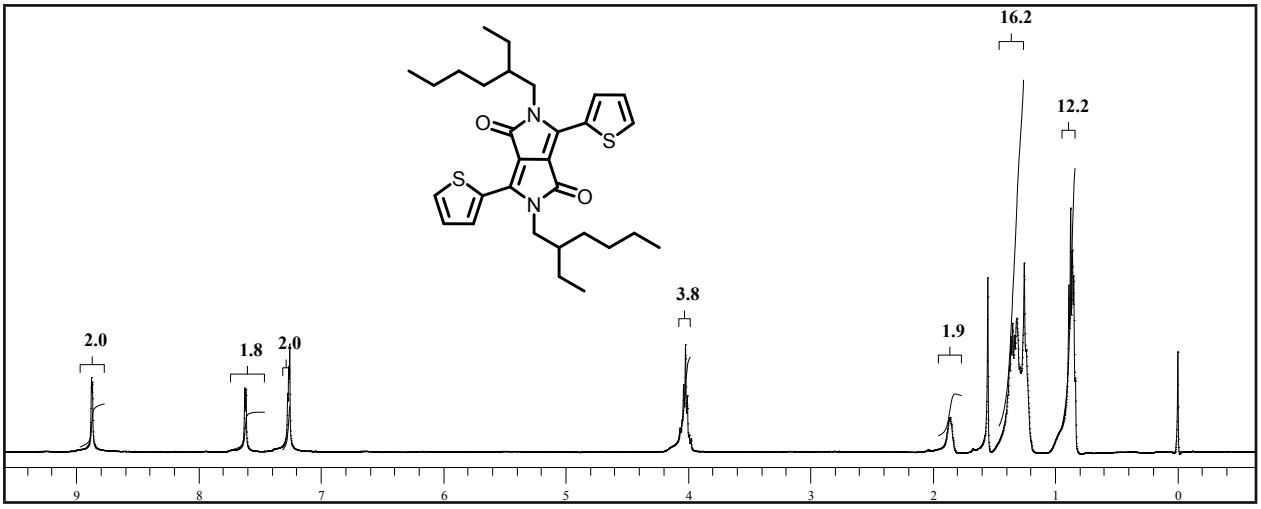
Reagents and conditions: a) 0.5 eq. di-n-ethylsuccinate, *tert*-BuOK, *tert*-amyl alcohol 120 °C, under Ar, 24 h; b) 2.5 eq 2-ethyl hexyl bromide, K_2CO_3, DMF, 130 °C, under Ar, 24 h; c) 2.05 eq. N-bromosuccinimide, $CHCl_3$, dark, under Ar, 12 h; d) $Pd(PPh_3)_4$, 2 M Na_2CO_3, DME , 90 °C, under Ar, 18 h.

1.6 Scheme 1 Synthetic route of **CSDPP9**, **CSDPP10**, **CSDDP11** and **CSDPP12.**

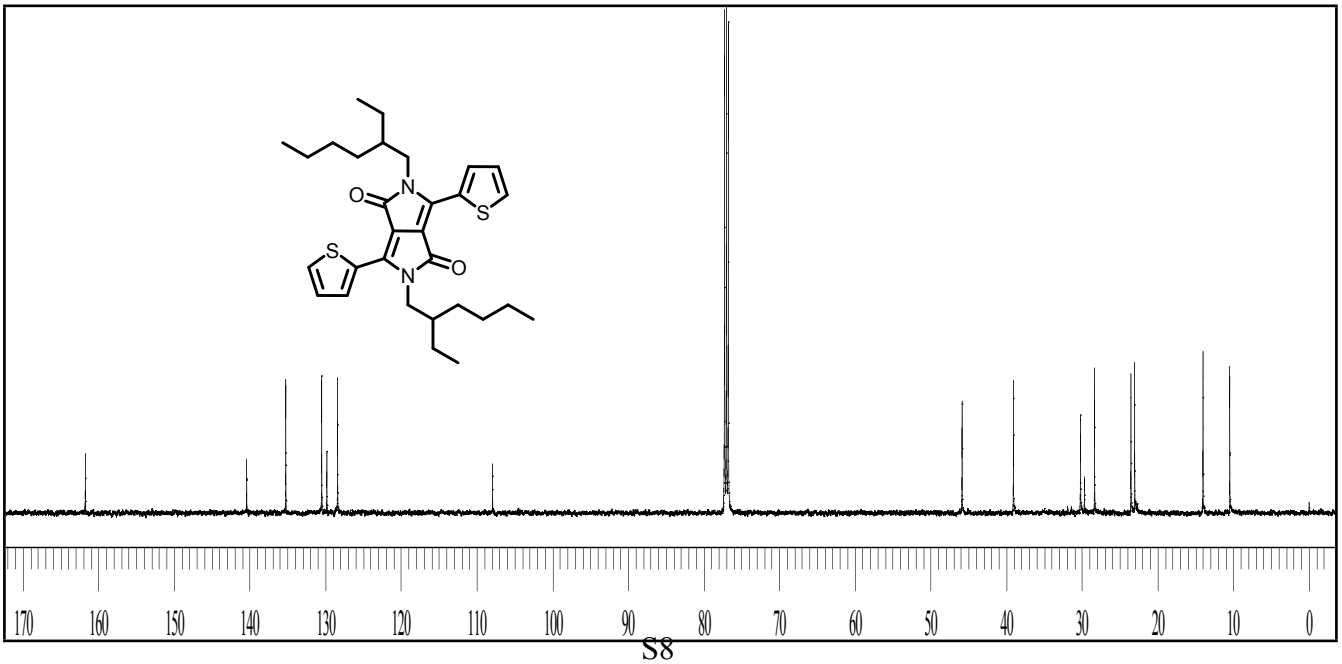
1.7. ^{1}H and ^{13}C NMR Spcetra:

1.7.1. ^{1}H NMR and 13C NMR spectra of **2,5-bis(2-ethylhexyl)-3,6-dithiophen-2-yl-pyrrolo[3,4-c]pyrrole-1,4-dione (2)**

^{1}H NMR Spectrum of 2,5-bis(2-ethylhexyl)-3,6-dithiophen-2-yl-pyrrolo[3,4-c]pyrrole-1,4-dione (2)

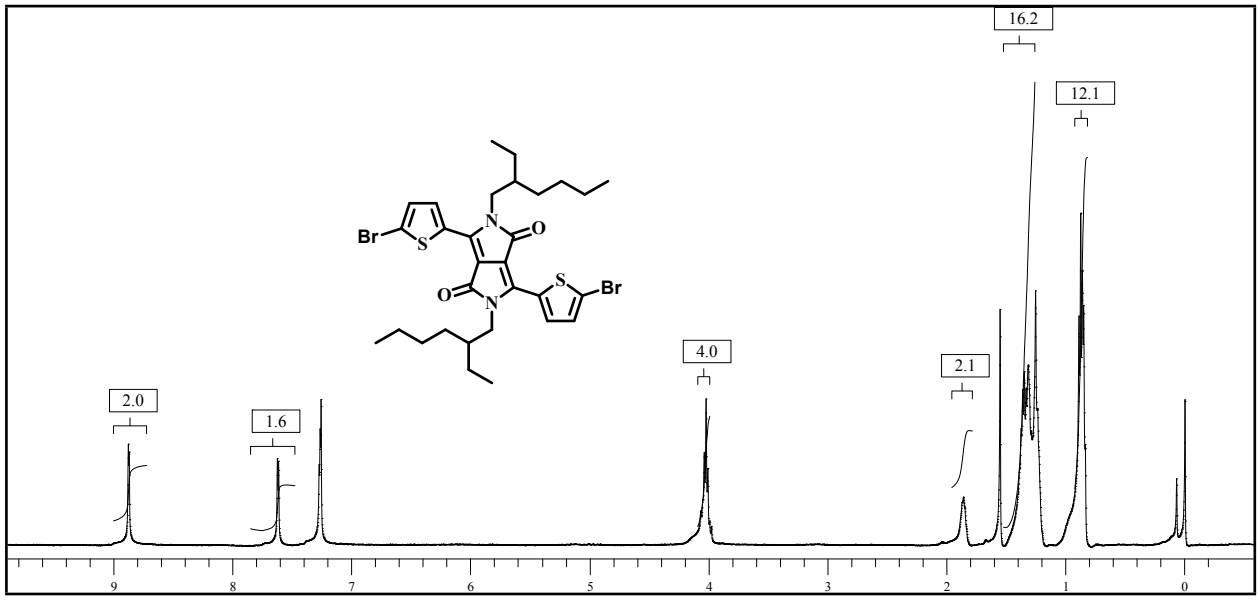


^{13}C NMR Spectrum of 2,5-bis(2-ethylhexyl)-3,6-dithiophen-2-yl-pyrrolo[3,4-c]pyrrole-1,4-dione (2)

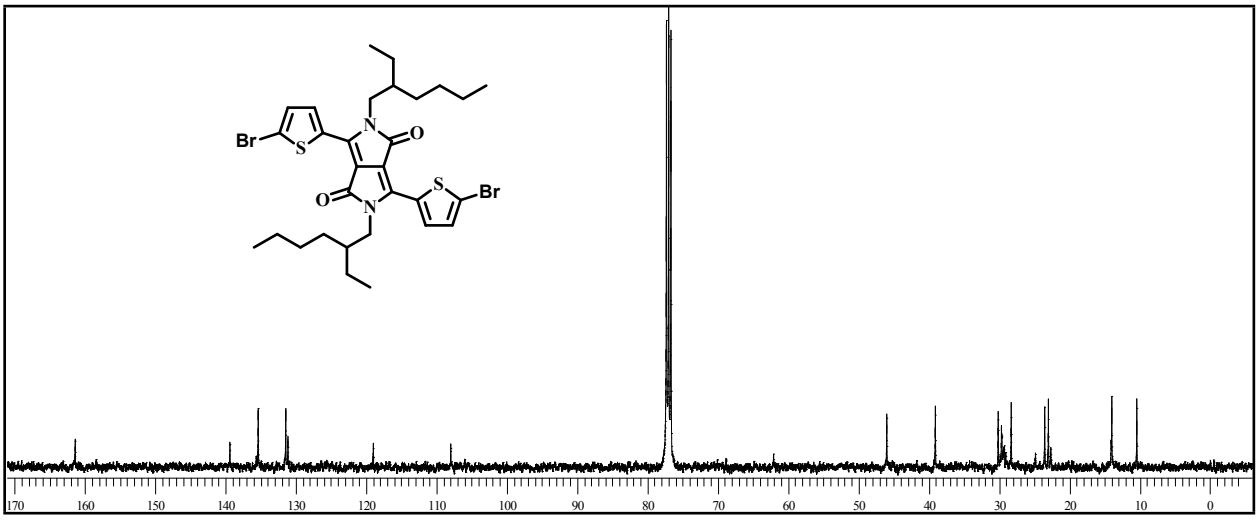


1.7.2. ^{1}H NMR and ^{13}C NMR spectra of **3,6-Bis-(5-bromo-thiophen-2-yl)-2,5-bis(2-ethylhexyl)-pyrrolo[3,4-c]-pyrrole-1,4-dione (3)**

^{1}H NMR spectrum of **3,6-Bis-(5-bromo-thiophen-2-yl)-2,5-bis(2-ethylhexyl)-pyrrolo[3,4-c]-pyrrole-1,4-dione (3)**

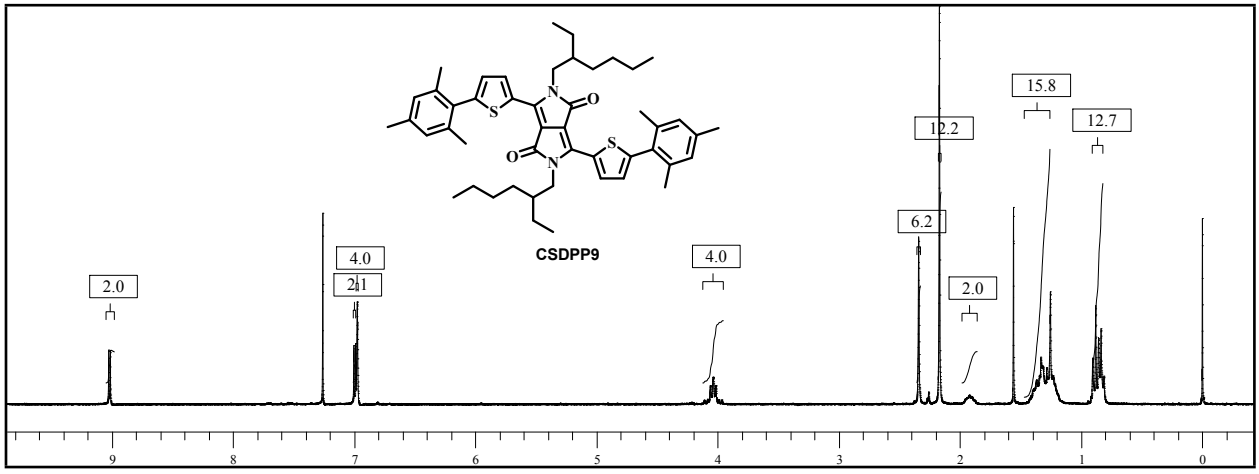


^{13}CNMR spectrum of **3,6-Bis-(5-bromo-thiophen-2-yl)-2,5-bis(2-ethylhexyl)-pyrrolo[3,4-c]-pyrrole-1,4-dione (3)**

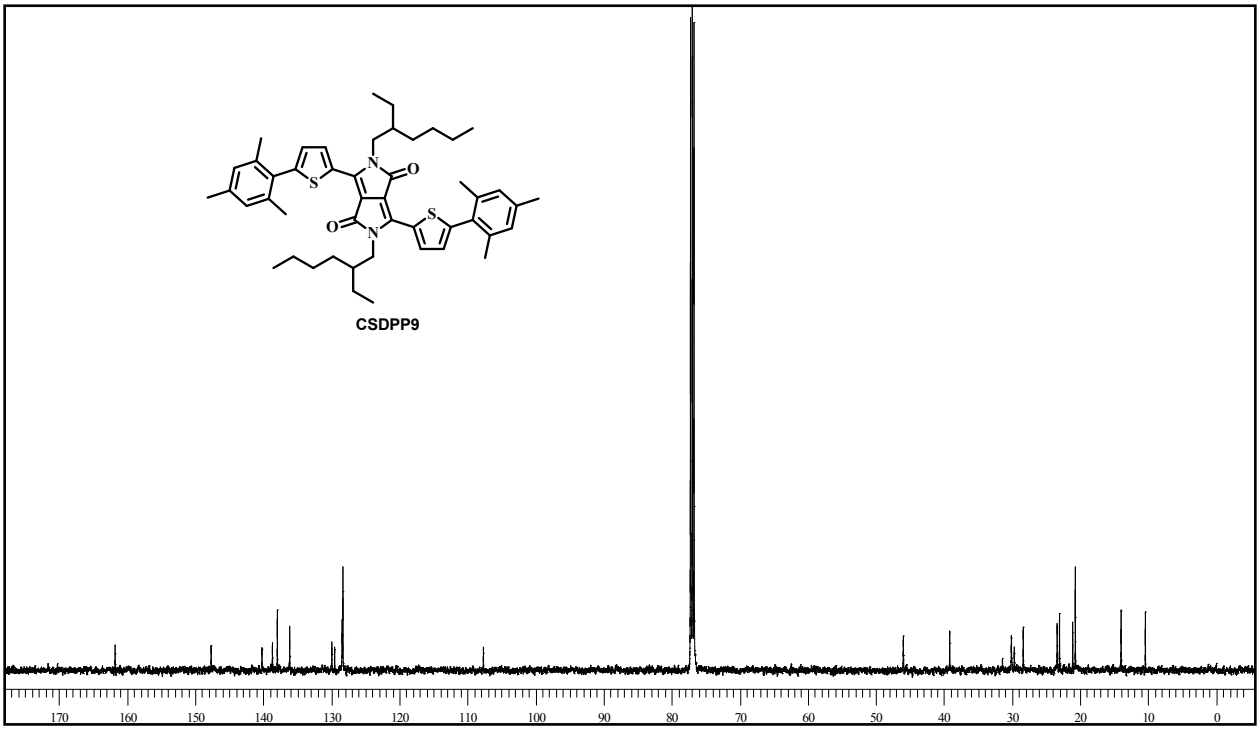


1.7.3. ^{1}H NMR and 13C NMR spectra of CSDPP9

^{1}H NMR spectrum of **CSDPP9:**

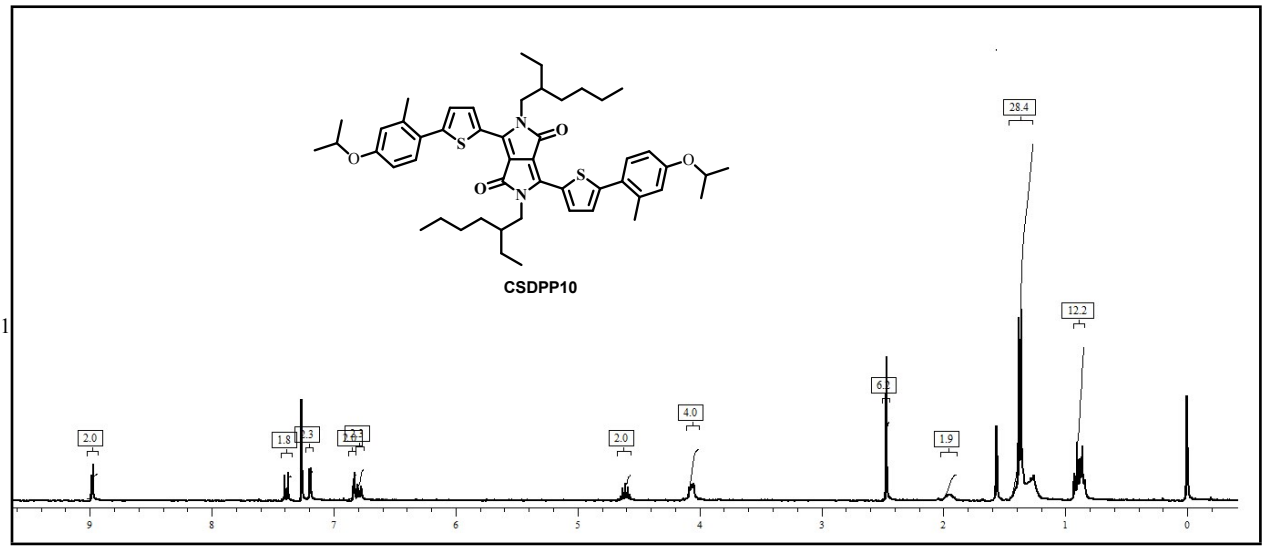


^{13}C NMR spectrum of **CSDPP9:**

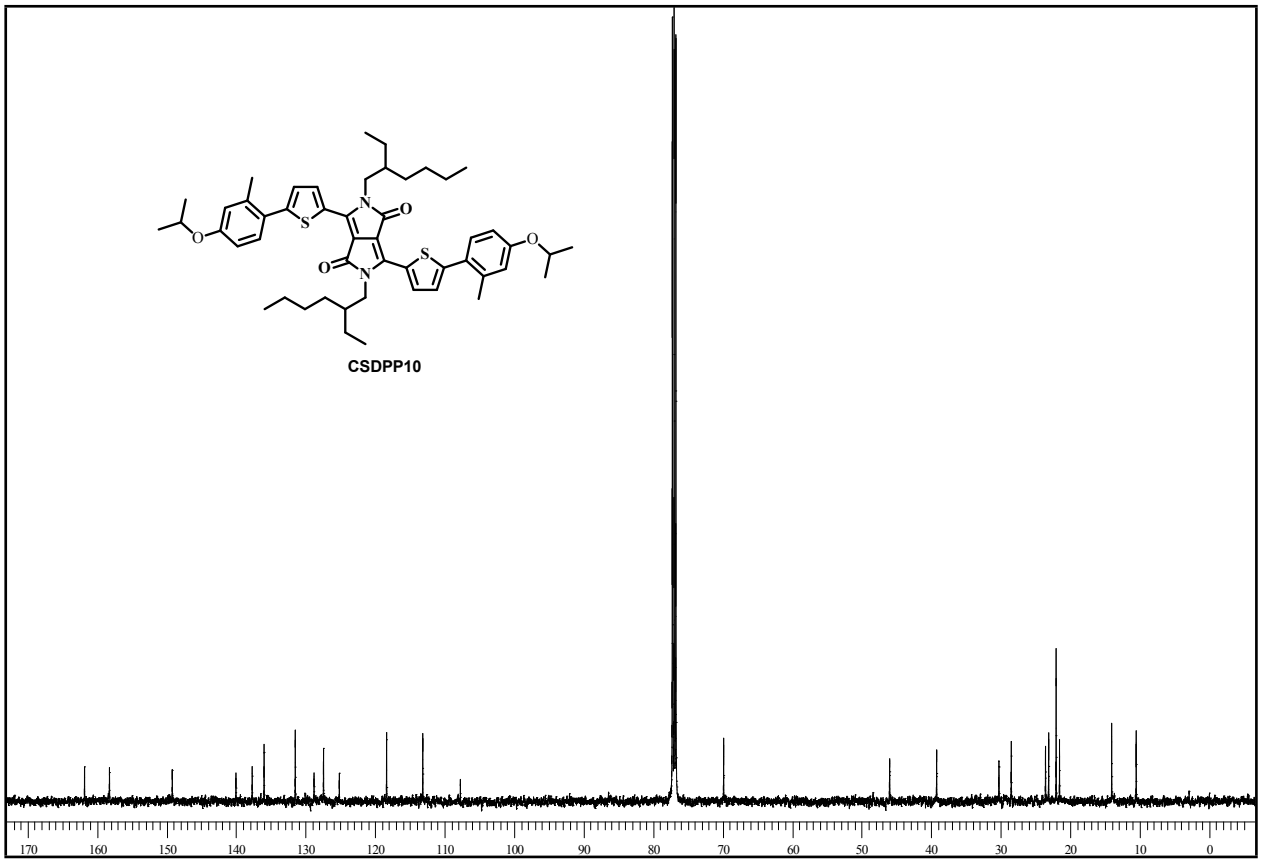


1.7.4. ^{1}H NMR and ^{13}C NMR spectra of **CSDPP10:**

^{1}H NMR spectrum of **CSDPP10:**

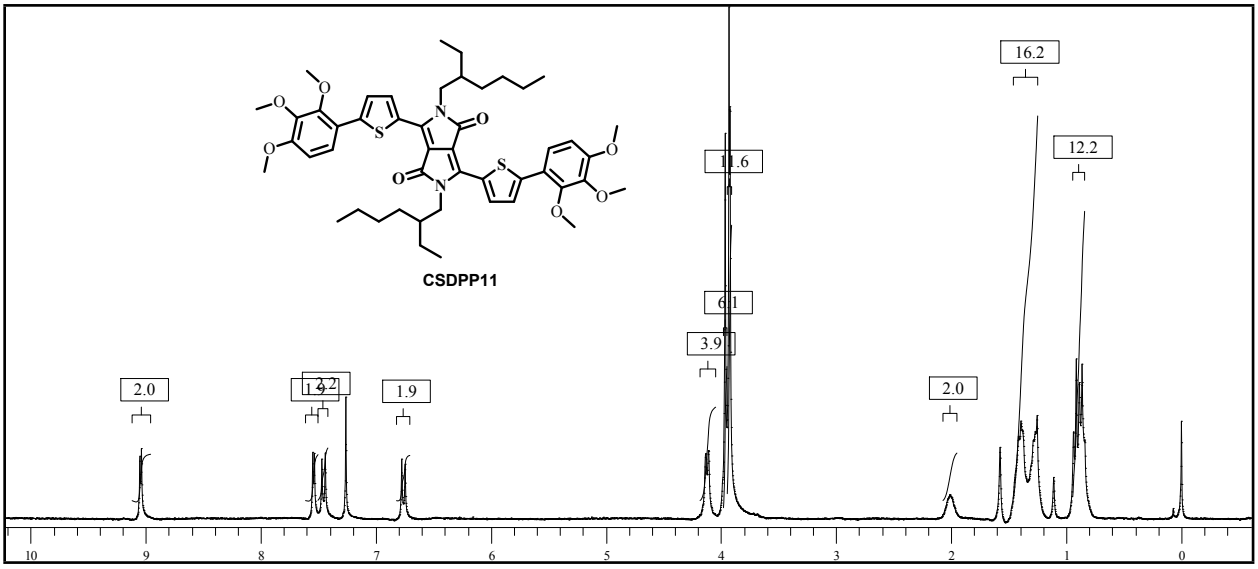


^{13}C NMR spectrum of **CSDPP10**:

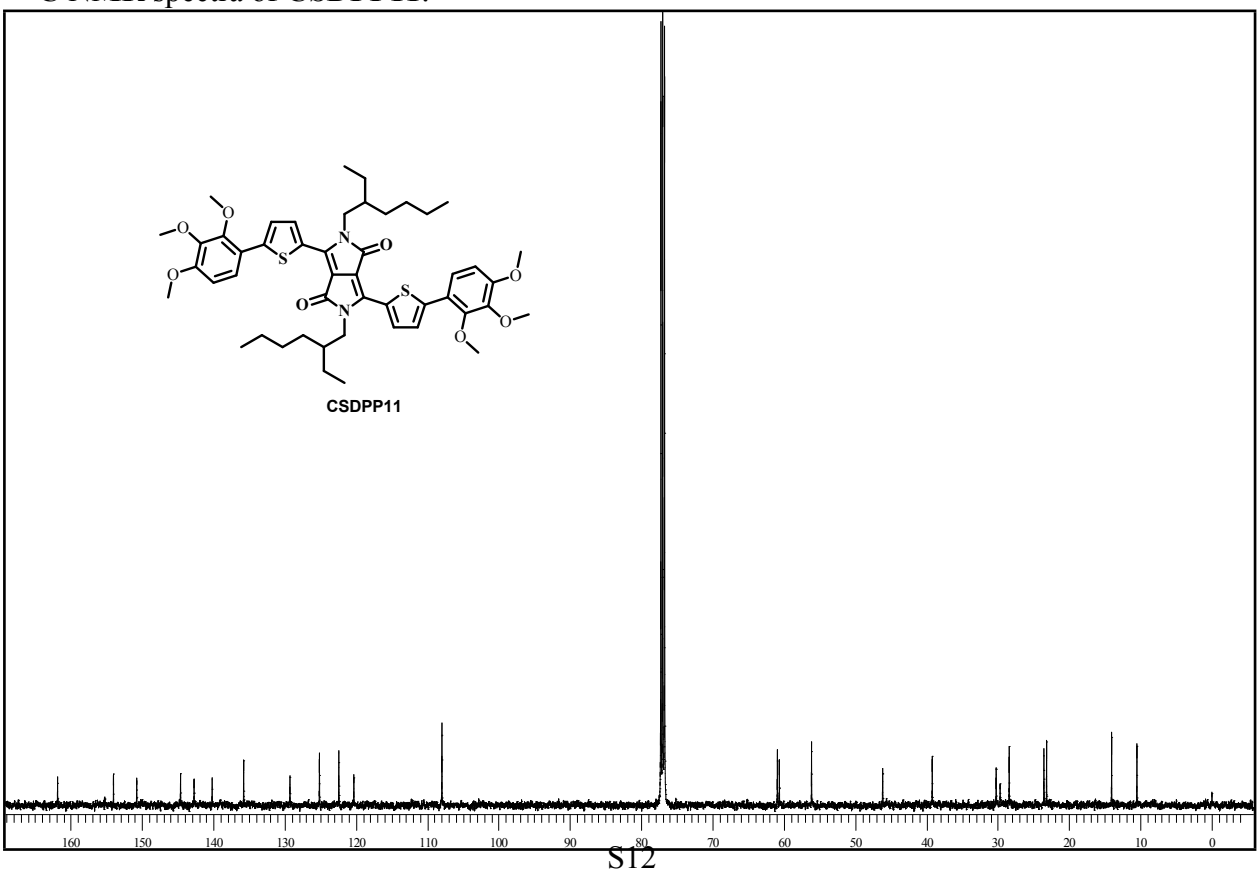


1.7.5. [1]H NMR and 13C NMR spectra of CSDPP11

[1]H NMR spectrum of **CSDPP11:**

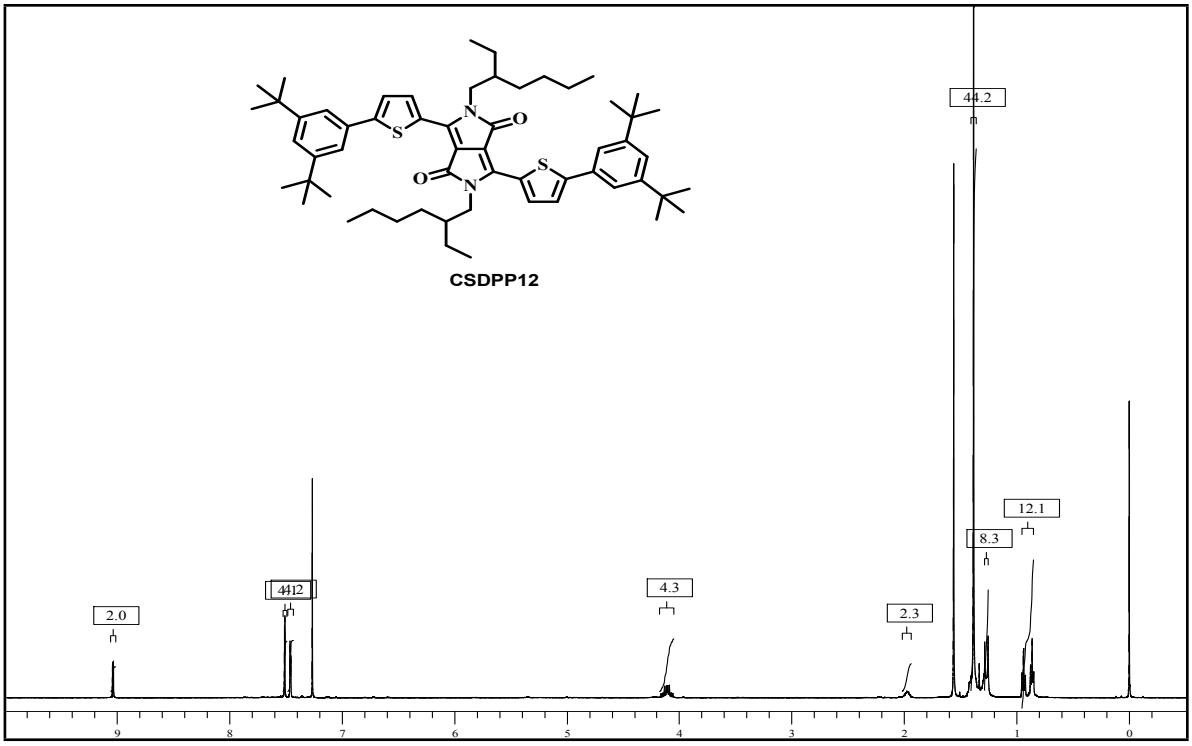


[13]C NMR spectra of **CSDPP11**:



1.7.5. [I]H NMR and 13C NMR spectra of **CSDPP12:**

[I]H NMR spectrum of **CSDPP12**



[13]C NMR spectrum of **CSDPP12:**

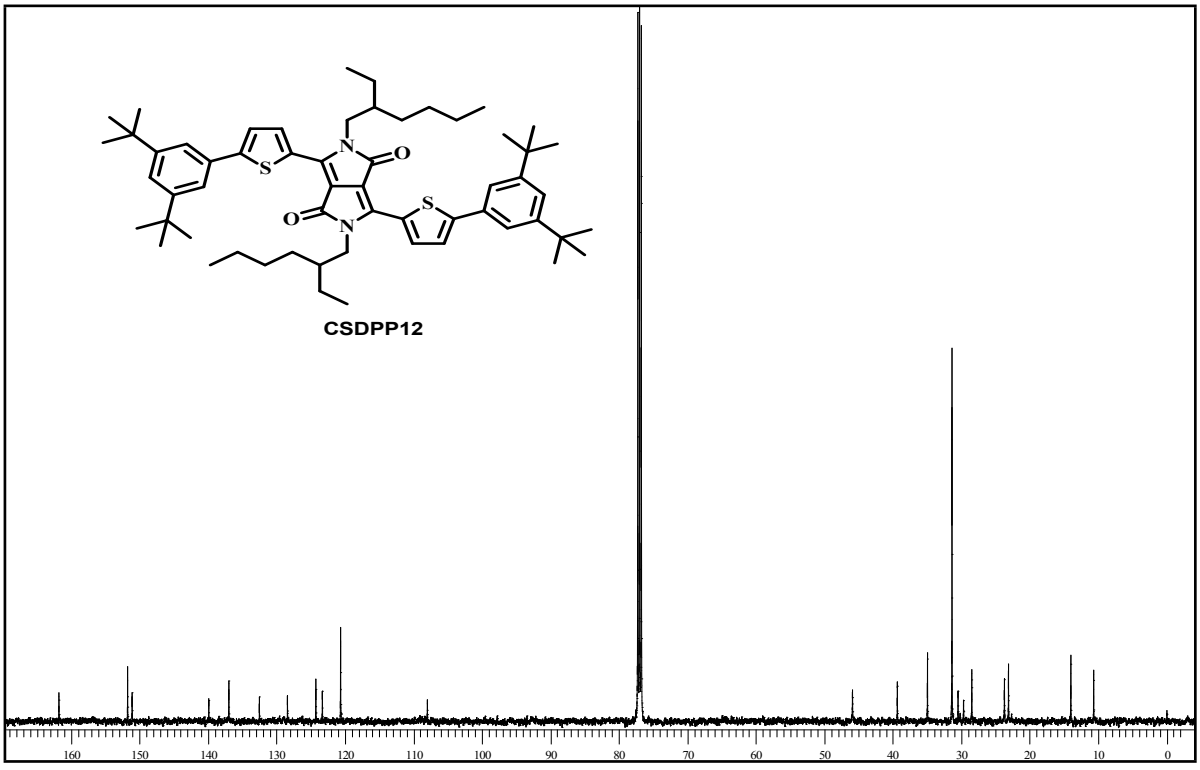
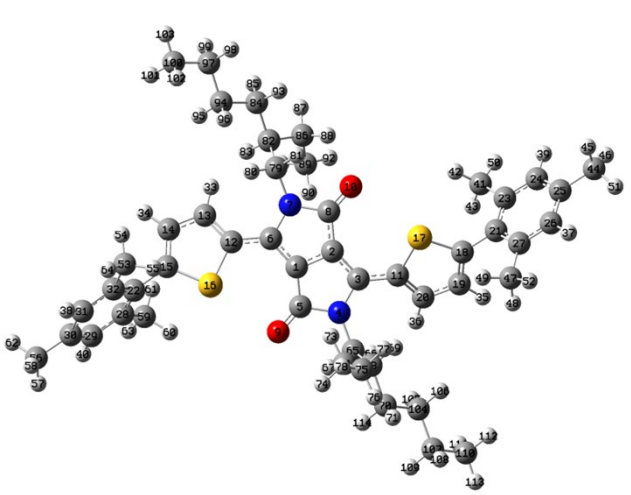
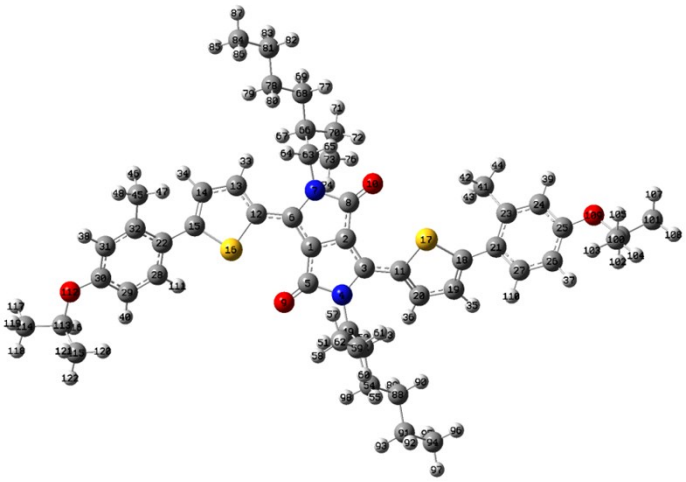


Table S1 Optimized geometry parameters of **CSDPP9-CSDPP12** calculated at B3LYP/6-311 G(d,p) level theory.

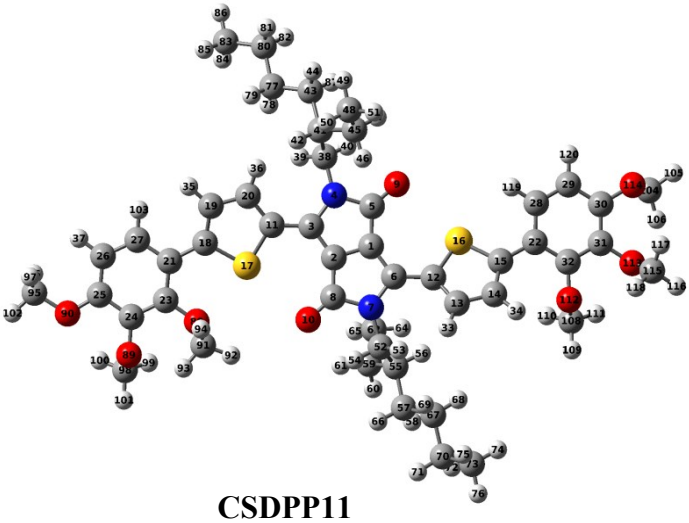
CSDPP9		**CSDPP10**		**CSDPP11**		**CSDPP12**	
Bond lengths (°A)							
C_6-C_{12}	1.44	C_6-C_{12}	1.44	C_3-C_{11}	1.44	C_6-C_{13}	1.44
C_5-C_{22}	1.48	C_{15}-C_{22}	1.48	C_{18}-C_{21}	1.47	C_{15}-C_{22}	1.47
C_3-C_{11}	1.44	C_3-C_{11}	1.44	C_6-C_{12}	1.44	C_3-C_{11}	1.44
C_{18}-C_{21}	1.48	C_{18}-C_{21}	1.48	C_{15}-C_{22}	1.47	C_{18}-C_{21}	1.47
Dihedral angles (°)							
S_{16}-C_{12}-C_6-C_1	17.18	S_{16}-C_{12}-C_6-C_1	15.27	S_{17}-C_{11}-C_3-C_2	-17.43	S_{16}-C_{12}-C_6-C_1	9.20
S_{16}-C_{12}-C_6-N_7	-162.30	S_{16}-C_{12}-C_6-N_7	-164.03	S_{17}-C_{11}-C_3-N_4	161.12	S_{16}-C_{12}-C_6-N_7	-169.97
C_{13}-C_{12}-C_6-N_7	17.78	C_{13}-C_{12}-C_6-N_7	15.40	C_{20}-C_{11}-C_3-N_4	-19.72	C_{13}-C_{12}-C_6-N_7	9.16
C_{13}-C_{12}-C_6-C_1	-162.74	C_{13}-C_{12}-C_6-C_1	-165.29	C_{20}-C_{11}-C_3-C_2	161.72	C_{13}-C_{12}-C_6-C_1	-171.68
S_{16}-C_{15}-C_{22}-C_{28}	-79.31	S_{16}-C_{15}-C_{22}-C_{28}	-40.68	C_{23}-C_{21}-C_{18}-S_{17}	12.35	S_{16}-C_{15}-C_{22}-C_{28}	-29.07
C_{32}-C_{22}-C_{15}-S_{16}	100.82	S_{16}-C_{15}-C_{22}-C_{32}	38.33	C_{23}-C_{21}-C_{18}-C_{19}	-167.61	S_{16}-C_{15}-C_{22}-C_{32}	151.09
C_{32}-C_{22}-C_{15}-C_{14}	-79.67	S_{17}-C_{11}-C_3-C_2	22.05	C_1-C_6-C_{12}-S_{16}	-19.74	C_{32}-C_{22}-C_{15}-C_{14}	-29.66
N_4-C_3-C_{11}-S_{17}	-158.08	S_{17}-C_{11}-C_3-N_4	-160.77	C_1-C_6-C_{12}-C_{13}	159.49	N_4-C_3-C_{11}-C_{20}	18.42
N_4-C_3-C_{11}-C_{20}	24.29	S_{17}-C_{18}-C_{21}-C_{23}	-51.56	N_7-C_6-C_{12}-C_{13}	-19.05	N_4-C_3-C_{11}-S_{17}	-163.23
C_2-C_3-C_{11}-S_{17}	24.83	S_{17}-C_{18}-C_{21}-C_{27}	129.77	N_7-C_6-C_{12}-S_{16}	161.72	C_2-C_3-C_{11}-S_{17}	19.49
C_2-C_3-C_{11}-C_{20}	-152.79	C_{19}-C_{18}-C_{21}-C_{27}	-46.62	S_{16}-C_{15}-C_{22}-C_{28}	27.85	C_2-C_3-C_{11}-C_{20}	-158.85
S_{17}-C_{18}-C_{21}-C_{23}	79.68	C_{19}-C_{18}-C_{21}-C_{23}	132.04	S_{16}-C_{15}-C_{22}-C_{32}	-151.94	S_{17}-C_{18}-C_{21}-C_{23}	-29.45



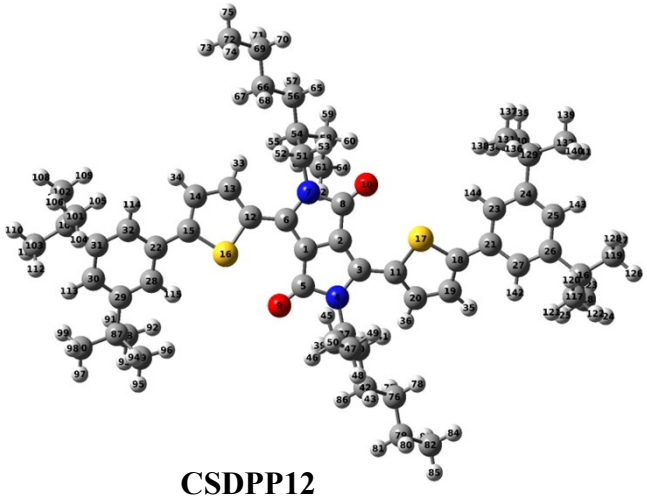
CSDPP9



CSDPP10



CSDPP11



CSDPP12

Figure S1. Structures of optimized geometries of **CSDPP9-CSDPP12** at B3LYP/6-311 G(d,p) level theory.

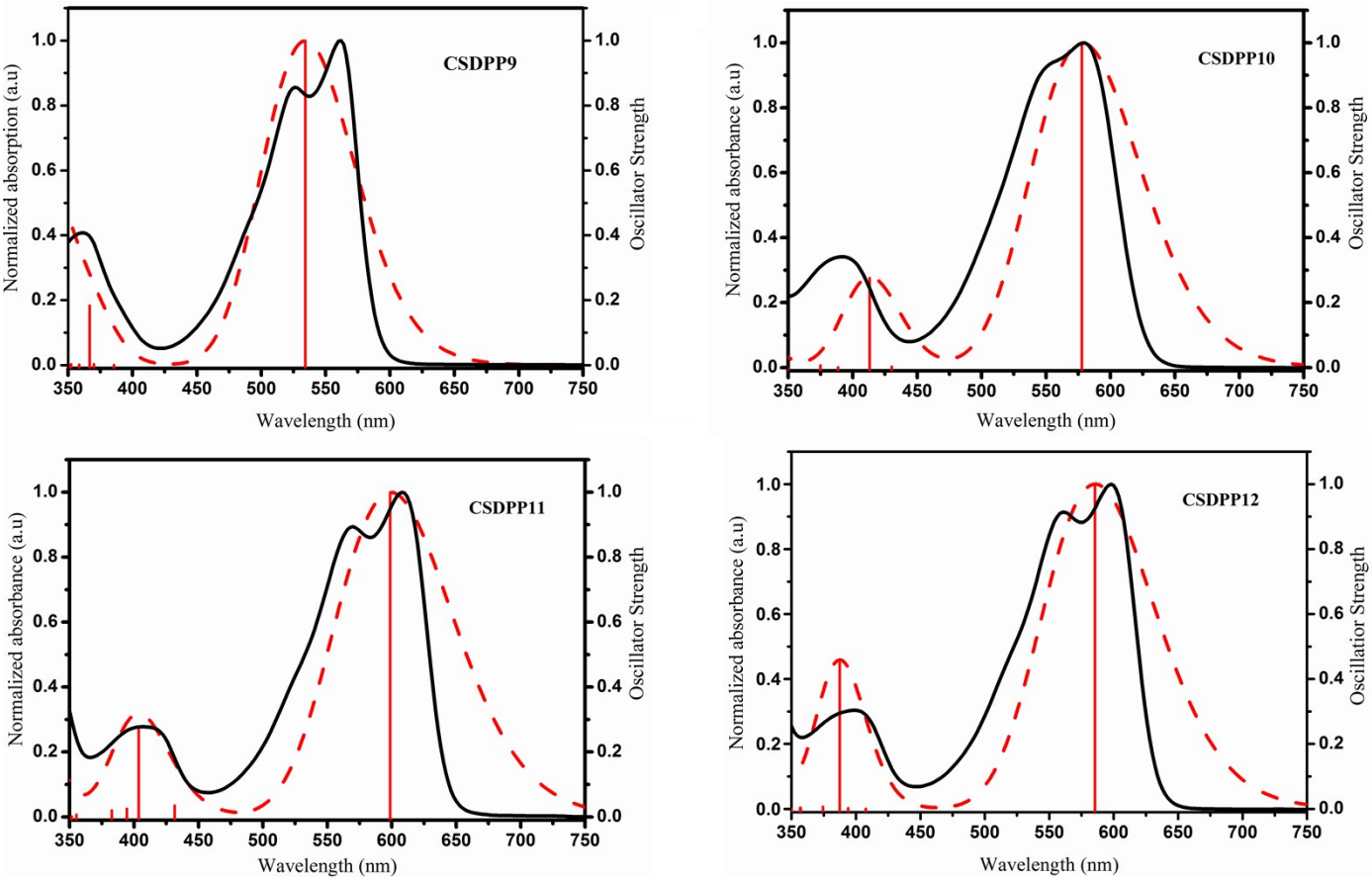


Figure S2. Comparison between experimental (black lines) and calculated (red lines) UV-Vis absorption spectra of the **CSDPP** dyes in DCM solution. Red vertical lines represent the calculated singlet excitation energies in GaussSum 2.2.5.

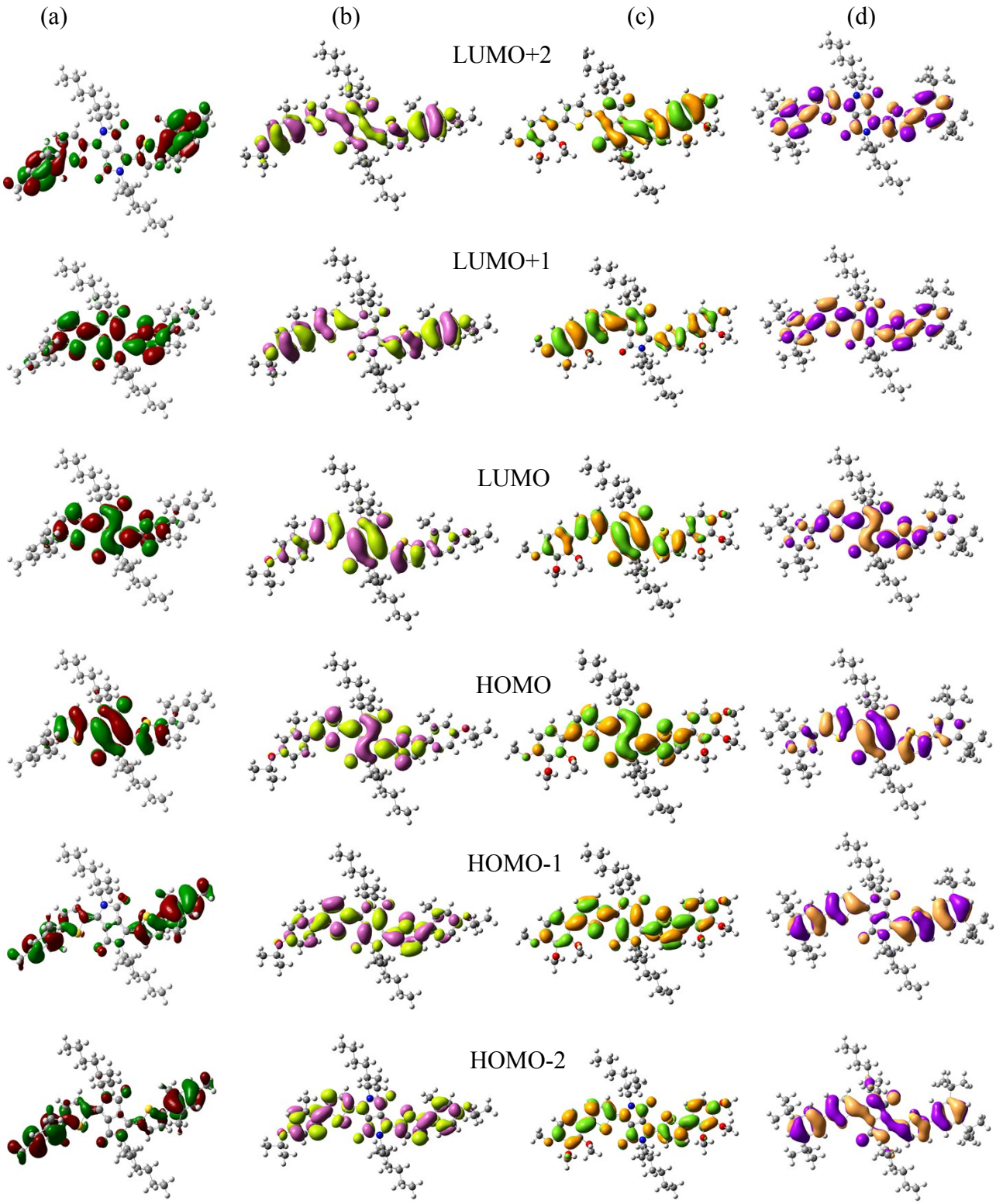


Figure S3. Molecular orbitals of (a) **CSDPP9**, (b) **CSDPP10**, (c) **CSDPP11**, and (d) **CSDPP12** in B3LYP functional, involved in transitions that contribute to the first excitation and to the next high absorbance excitation.

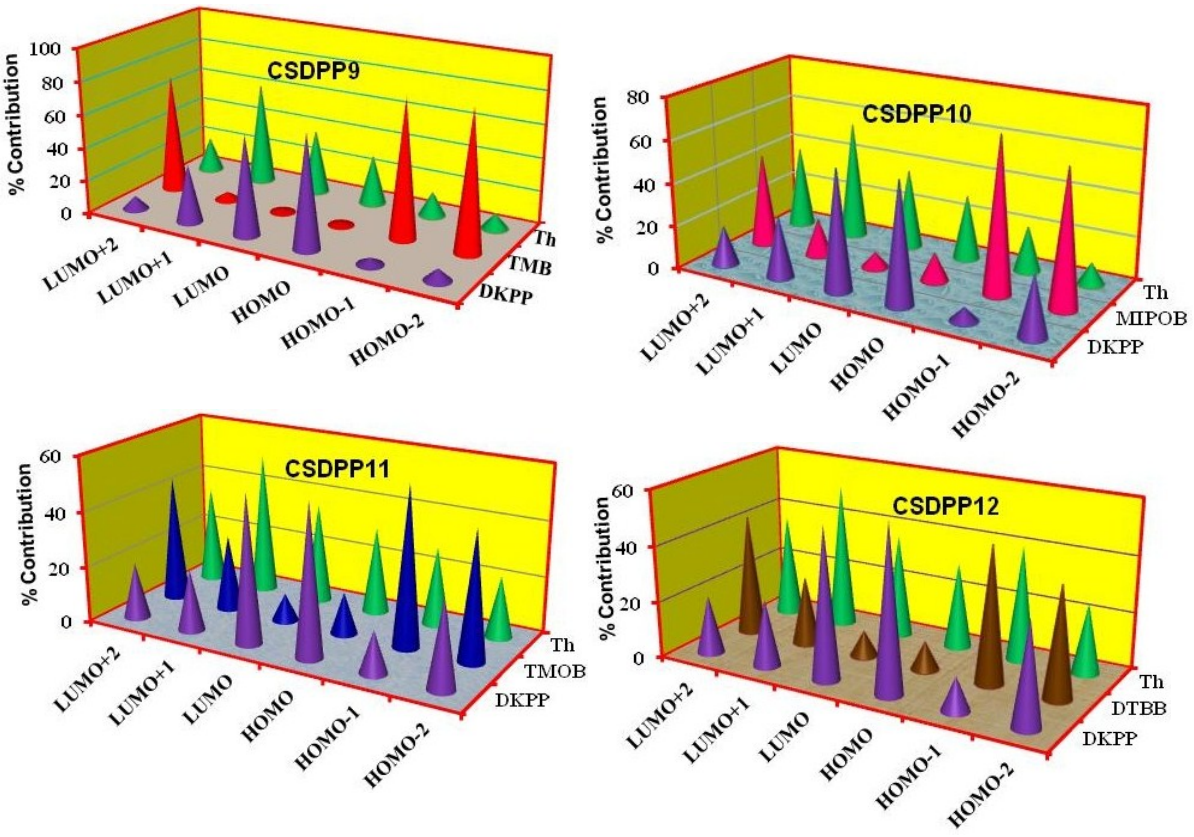


Figure S4. Percentage contributions of the orbital density of the individual groups in HOMO-2, HOMO-1, HOMO, LUMO, LUMO+1 and LUMO+2 of the **CSDPP** dyes.

2. References

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