# Electronic Supplementary Information

Carbazole-functionalized Polyphenylene-decorated solid state emissive D-A-D molecules: Reduced Donor-Acceptor interaction and enhanced emission in solid state

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Experimental Section

General Information

All reagents were purchased from Aldrich and were used without further purification. CH$_2$Cl$_2$ was distilled from CaH$_2$. Mass spectra were recorded on Bruker MicroToff/QII. Differential scanning colorimetry (DSC), and thermal gravimetric analysis (TGA) was recorded on EXSTAR TG/DTA 6300. HPLC analyses were performed on Shimadzu LC-20AD using silica column. The TEM mages was recorded from Transmission Electron Microscope (TEM) - JEOL 2100F. The dynamic light scattering (DLS) data were recorded with MALVERN Instruments (Nano-ZS). The X-ray powder diffraction (XRPD) measurements were recorded on a Rigaku miniflex X ray diffractometer with Cu Ka radiation in the range of $\theta = 0^\circ$ to 100$^\circ$. Elemental analysis was carried out on Elementar vario EL cube. The Time resolved fluorescence spectra were recorded with a HORIBA Time Resolved Fluorescence Spectrometer. UV-vis spectra were recorded on SHIMADZU UV-2450 spectrophotometer, with a quartz cuvette (path length, 1 cm). The cell holder was thermostatted at 25 °C. The fluorescence spectra were recorded with a SHIMADZU 5301 PC spectrofluorimeter. For fluorescence measurements, each time 3 mL respective solution of 1-3 (10 μM) was filled in a quartz cuvette (path length, 1 cm) and excitation was provided at their respective absorption maxima. $^1$H and $^{13}$C were recorded on JOEL-FT NMR–AL 300 MHz spectrophotometer and BRUKER-AVANCE-II FT-NMR-AL 500 MHz spectrophotometer using CDCl$_3$ as solvent and TMS as internal standard. Data is reported as follows: chemical shifts in ppm (δ), multiplicity (s = singlet, d = doublet, m = multiplet), coupling constant $J$ (Hz), integration, and interpretation. Silica gel 60–120 mesh was used for column chromatography.

Quantum yield calculation

Fluorescence quantum yield was determined using optically matching solutions of diphenylanthracene (Φ$_F$ = 0.9 in cyclohexane) as standard and quantum yield was calculated using the equation:

$$\Phi_{Fs} = \Phi_{Fr} \frac{1-10^{A_{r}L_{r}}}{1-10^{A_{s}L_{s}}} \times \frac{N_{s}^{2}}{N_{r}^{2}} \times \frac{D_{s}}{D_{r}}$$

Φ$_{Fs}$ and Φ$_{Fr}$ are the radiative quantum yields of sample and the reference respectively, $A_s$ and $A_r$ are the absorbance of the sample and the reference respectively, $D_s$ and $D_r$ the respective areas of emission for sample and reference. $L_s$ and $L_r$ are the lengths of the absorption cells of
sample and reference respectively. \( N_s \) and \( N_r \) are the refractive indices of the sample and reference solutions.

**Electrochemical studies**

Electrochemical studies were carried out on CH Instruments CH1660D in DCM solution with 0.1M tetrabutylammonium perchlorate as electrolyte. Glassy carbon electrode was used as working electrode, Ag/AgNO\(_3\) as reference electrode and platinum wire as counter electrode. Experiments were calibrated with standard ferrocenium redox system. The cell was purged with nitrogen prior to each scan and the scans were performed at the rate of 50mV/sec. at room temperature.

**Experimental section**

Compound \( 4,^1 5^2 \) and \( 6^3 \) were synthesised according to previous reported procedures in literature while compound 7 and 11 were commercially available and used as such.

**Synthesis**

**Synthesis of 2,5-bis(4-((9-hexyl-9H-carbazol-3-yl)ethynyl)phenyl)-1,3,4-oxadiazole (8)**

In a flame dried two necked round bottomed flask, precursor 5 (0.62 g, 1.3 mmol), Cul (0.49 g, 0.26 mmol), and Pd(PPh\(_3\))\(_4\) catalyst (0.2 g, 0.13 mmol) was stirred in toluene (10 ml) and triphenylamine (5 ml) under nitrogen for 20 min. Alkyne 4 (0.83 g, 3.01 mmol) in toluene (5 ml) was added dropwise. The resulting mixture was stirred at 55 °C for 24 h. After cooling to room temperature, a saturated solution of NH\(_4\)Cl was added and the mixture was extracted with DCM twice. The organic layer was washed with brine and dried over Na\(_2\)SO\(_4\). The solvent was evaporated to dryness and the crude was purified by column chromatography in hexane–Ethyl acetate (9: 1) to afford 0.45 g of a yellow solid in 45% yield.\(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 8.33 (s, 2H), 8.12 (t, \( J = 7.3 \) Hz, 6H), 7.68 (dd, \( J = 20.3, 8.3 \) Hz, 6H), 7.50 (t, \( J = 7.6 \) Hz, 2H), 7.40 (dd, \( J = 12.2, 8.4 \) Hz, 4H), 7.28 (d, \( J = 7.4 \) Hz, 2H), 4.30 (t, \( J = 7.2 \) Hz, 4H), 1.93 – 1.79 (m, 4H), 1.41 – 1.25 (m, 12H), 0.87 (t, \( J = 6.7 \) Hz, 6H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \( \delta \) 164.31, 140.78, 140.34, 131.91, 129.30, 127.58, 126.79, 126.20, 124.28, 122.87, 122.50, 122.35, 120.51, 119.44, 112.42, 108.98, 108.82, 94.33, 87.02, 43.21, 31.53,


28.91, 26.93, 22.53, 14.00. HPLC analysis, 100% (silica column, \( \lambda = 308 \) nm, \( i \)-PrOH : hexane = 05 : 95, flow rate = 1.0 mL/min, \( T_R = 3.456 \) min.) MALDI-TOF MS m/z calcd. for \( C_{54}H_{48}N_4O \) (M+): 768.38. Found: 768.38.

**Synthesis of 3,7-bis((9-hexyl-9H-carbazol-3-yl)ethynyl)dibenzo[b,d]thiophene 5,5-dioxide (9).** The same procedure as described for 3 was followed. Precursor 6 (0.47 g, 1.25 mmol), CuI (43 mg, 0.22 mmol), and Pd(PPh$_3$)$_2$Cl$_2$ catalyst (93 mg, 0.13 mmol), Alkyne 4 (0.76 g, 2.76 mmol). The product was purified by column chromatography in hexane–Ethyl acetate (9: 1). Yield: 60% (0.57g). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 8.31 (s, 2H), 8.11 (d, $J = 7.5$ Hz, 2H), 7.99 (s, 2H), 7.80 – 7.70 (m, 4H), 7.64 (d, $J = 7.3$ Hz, 2H), 7.44 (ddd, $J = 40.6$, 18.7, 11.7 Hz, 8H), 4.29 (t, $J = 6.6$ Hz, 4H), 1.89 (dd, $J = 14.6$, 9.4 Hz, 4H), 1.32 (s, 12H), 0.87 (s, 6H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 140.91, 140.60, 137.76, 137.04, 136.71, 129.43, 129.17, 127.16, 125.54, 124.94, 124.47, 123.01, 122.39, 121.53, 120.62, 119.61, 111.95, 109.07, 108.94, 95.53, 85.94, 43.18, 31.45, 28.83, 26.85, 22.43, 13.89. HPLC analysis, 100% (silica column, \( \lambda = 297 \) nm, \( i \)-PrOH : hexane = 05 : 95, flow rate = 1.0 mL/min, \( T_R = 3.462 \) min.) MALDI-TOF MS m/z calcd. for \( C_{52}H_{46}N_2O_2S \) (M+): 762.33. Found: 762.51.

**Synthesis of 4,7-bis((9-hexyl-9H-carbazol-3-yl)ethynyl)benzo[c][1,2,5]thiadiazole (10)**

The same procedure as described for 3 was followed. Precursor 7 (0.26 g, 0.88 mmol), CuI (33 mg, 0.17 mmol), and Pd(PPh$_3$)$_2$Cl$_2$ catalyst (61mg, 0.08 mmol), Alkyne 4 (0.584 g, 2.12 mmol). The product was purified by column chromatography in hexane–Ethyl acetate (9: 1). Yield: 42% (0.195 g, orange red solid). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 8.45 (s, 2H), 8.13 (d, $J = 7.7$ Hz, 2H), 7.84 – 7.75 (m, 4H), 7.54 – 7.39 (m, 6H), 7.29 (d, $J = 7.4$ Hz, 2H), 4.31 (t, $J = 7.2$ Hz, 4H), 1.87 (dd, $J = 14.5$, 7.2 Hz, 4H), 1.39 – 1.21 (m, 12H), 0.87 (t, $J = 6.8$ Hz, 6H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 154.67, 140.93, 140.65, 132.09, 129.69, 126.28, 124.71, 122.99, 122.54, 120.70, 119.57, 117.22, 112.48, 109.04, 108.95, 99.39, 84.10, 43.21, 31.46, 28.84, 26.86, 22.44, 13.88. HPLC analysis, 100% (silica column, \( \lambda = 301 \) nm, \( i \)-PrOH : hexane = 05 : 95, flow rate = 1.0 mL/min, \( T_R = 3.267 \) min.) MALDI-TOF MS m/z calcd. for \( C_{46}H_{46}N_2O_2S \) (M+): 682.3. Found: 683.34.

**Synthesis of 2,5-bis(6'-(9-hexyl-9H-carbazol-3-yl)-3',4',5'-triphenyl-[1,1':2',1''-terphenyl]-4-yl)-1,3,4-oxadiazole (1).**

Compound 9 (0.16 g, 0.2 mmol) and compound 11 (0.16 g, 0.4 mmol) were refluxed in diphenyl ether for 48 hours under nitrogen atmosphere. Reaction mixture was cooled and methanol was added. Resulting crude solid product was purified by column chromatography.
using hexane–Ethyl acetate (9: 1) as eluent to get 77 mg of white solid in 25 % yield. H NMR (500 MHz, CDCl$_3$) δ 7.74 (d, J = 7.7 Hz, 2H), 7.53 (s, 2H), 7.44 (d, J = 7.5 Hz, 2H), 7.33 (dd, J = 18.1, 9.5 Hz, 4H), 7.23 (d, J = 7.5 Hz, 2H), 7.07 (t, J = 7.4 Hz, 2H), 6.95 (d, J = 8.1 Hz, 4H), 6.89 – 6.69 (m, 44H), 4.05 (t, J = 7.2 Hz, 4H), 1.67 (brs, 4H), 1.16 (s, 12H), 0.74 (brs, 6H). 13C NMR (126 MHz, CDCl$_3$) δ 164.05, 144.96, 141.07, 140.81, 140.74, 140.64, 140.53, 140.48, 140.28, 140.15, 140.08, 139.77, 138.53, 132.05, 131.96, 131.47, 131.38, 131.29, 130.53, 129.14, 126.74, 126.58, 126.49, 125.43, 125.22, 125.01, 123.33, 122.93, 121.59, 120.34, 119.97, 118.27, 108.46, 106.97, 42.90, 31.38, 28.69, 26.77, 22.44, 13.90. HPLC analysis, 100% (silica column, λ = 290 nm, i-PrOH : hexane = 05 : 95, flow rate = 1.0 mL/min, T$_R$ = 3.453 min.) MALDI-TOF MS m/z calcd. for C$_{110}$H$_{88}$N$_4$O (M+1): 1480.70. Found: 1481.68. Elemental analysis: Calculated for C$_{110}$H$_{88}$N$_4$O: C 89.15; H 5.99; N 3.78; Found: C 89.39%; H 6.17%; N 3.54%.

**Synthesis of 3,7-bis(4'-(9-hexyl-9H-carbazol-3-yl)-5',6'-diphenyl-[1,1':2',1''-terphenyl]-3'-yl)dibenzo[b,d]thiophene 5,5-dioxide (2).**

50mg of compound 9 (0.25 g, 0.32 mmol) and 11 (0.302 g, 0.78 mmol) were refluxed in diphenyl ether for 48 hours under nitrogen atmosphere. Reaction mixture was cooled and methanol was added. Resulting crude solid product was purified by column chromatography using hexane–Ethyl acetate (9: 1) as eluent to get 170 mg of creamish white solid in 39 % yield. H NMR (300 MHz, CDCL$_3$) δ 7.76 (d, J = 7.3 Hz, 2H), 7.51 (t, J = 7.5 Hz, 2H), 7.34 (dd, J = 17.0, 9.5 Hz, 4H), 7.24 – 7.03 (m, 6H), 6.94 – 6.70 (m, 46H), 4.10 (brs, 4H), 1.71 (brs, 24), 1.22 (brs, 12H), 0.81 (brs, 6H). 13C NMR (126 MHz, CDCl$_3$) δ 143.19, 141.32, 141.15, 140.86, 140.68, 140.50, 140.35, 140.18, 139.87, 139.83, 138.64, 138.49, 138.39, 136.72, 136.63, 136.27, 131.50, 131.31, 131.23, 131.14, 130.88, 130.73, 130.25, 129.29, 129.16, 127.99, 127.20, 127.13, 126.76, 126.64, 126.51, 125.70, 125.63, 125.25, 125.21, 125.08, 124.91, 124.75, 123.59, 123.10, 122.84, 121.91, 121.56, 120.46, 119.85, 119.42, 118.59, 118.19, 108.56, 108.25, 107.64, 106.95, 42.95, 31.44, 28.63, 26.78, 22.50, 14.00. HPLC analysis, 100% (silica column, λ = 291 nm, i-PrOH : hexane = 05 : 95, flow rate = 1.0 mL/min, T$_R$ = 3.414 min.) MALDI-TOF MS m/z calcd. for C$_{108}$H$_{86}$N$_4$O$_2$S (M+1): 1474.64. Found: 1475.58. Elemental analysis: Calculated for C$_{108}$H$_{86}$N$_4$O$_2$S: C 87.89; H 5.87; N 1.90; S 2.17; Found: C 87.60%; H 5.98%; N 1.76%; S 2.05%.
Synthesis of 4,7-bis(4’-(9-hexyl-9H-carbazol-3-yl)-5’,6’-diphenyl-[1,1’:2’,1”-terphenyl]3’-yl)benzo[c][1,2,5]thiadiazole (3).

50mg of compound 10 (0.22 g, 0.322 mmol) and 11 (0.247 g, 0.644 mmol) were refluxed in diphenyl ether for 48 hours under nitrogen atmosphere. Reaction mixture was cooled and methanol was added. Resulting crude solid product was purified by column chromatography using hexane–Ethyl acetate (9: 1) as eluent to get 166 mg of light green solid in 37 % yield.

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.85 (dd, $J = 18.6$, 7.5 Hz, 2H), 7.77 – 7.48 (m, 6H), 7.41 – 7.31 (m, 4H), 7.21 – 7.02 (m, 4H), 6.94 – 6.53 (m, 40H), 4.14 (brs, 4H), 1.73 (brs, 4H), 1.24 (brs, 12H), 0.85 (brs, 6H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 153.70, 141.77, 141.58, 140.91, 140.83, 140.68, 140.55, 140.29, 140.25, 139.98, 139.57, 138.58, 135.55, 132.80, 131.44, 131.34, 131.27, 131.15, 131.01, 130.84, 130.04, 129.94, 129.84, 128.48, 128.25, 126.47, 126.34, 126.20, 126.15, 125.60, 125.38, 125.21, 125.02, 124.91, 124.71, 124.59, 123.34, 122.48, 122.26, 121.62, 120.25, 118.37, 118.29, 108.43, 106.70, 106.39, 42.91, 31.56, 28.82, 26.85, 22.51, 14.00. HPLC analysis, 100% (silica column, $\lambda = 298$ nm, i-PrOH : hexane = 05 : 95, flow rate = 1.0 mL/min, $T_R = 3.265$ min.). MALDI-TOF MS m/z calcd. for C$_{102}$H$_{82}$N$_4$S (M+1): 1394.63. Found: 1395.64. Elemental analysis: Calculated for C$_{102}$H$_{82}$N$_4$S: C 87.77; H 5.92; N 4.01; S 2.30; Found: C 87.66%; H 5.81%; N 3.88%; S 2.19%.
Figure S1. DSC measurements of derivative 1, 2 and 3 recorded at 10°Cmin⁻¹

Figure S2. Repeated Cyclic voltammograms of 1 (5 cycles) at scan rate of 50 mV/s in DCM
Figure S3. Repeated Cyclic voltammograms of 2 (5 cycles) at scan rate of 50 mV/s in DCM

Figure S4. Repeated Cyclic voltammograms of 3 (5 cycles) at scan rate of 50 mV/s in DCM
Figure S5. UV-visible spectrum of derivative 1 in different fractions of THF/Water [conc. - 10μM, λ<sub>ex</sub> = 355 nm]

Figure S6. UV-visible spectrum of derivative 2 in different fractions of THF/Water [conc. - 10μM, λ<sub>ex</sub> = 355 nm]
Figure S7. UV-visible spectrum of derivative 3 in different fractions of THF/Water [conc. - 10μM, λ<sub>ex</sub> = 352 nm]

Figure S8. Powder XRD patterns of derivative 1
Figure S9. Powder XRD patterns of derivative 2

Figure S10. Powder XRD patterns of derivative 3
Figure S11. TEM images (a and b) and ED spectra (c) of derivative 1 in 60% water

Figure S12. TEM images (a and b) and ED spectra (c) of derivative 1 in 90% water
Figure S13. TEM images (a and b) and ED spectra (c) of derivative 2 in 60% water

Figure S14. TEM images (a and b) and ED spectra (c) of derivative 2 in 90% water
**Figure S15.** TEM images (a and b) and ED spectra (c) of derivative 3 in 60% water

**Figure S16.** TEM images (a and b) and ED spectra (c) of derivative 3 in 90% water
**Figure S17.** Differential Light Scattering (DLS) results of derivative 1 showing particle size diameter in 90% water.

**Figure S18.** Differential Light Scattering (DLS) results of derivative 1 showing particle size diameter in 90% water.
**Figure S19.** Differential Light Scattering (DLS) results of derivative 2 showing particle size diameter in 90% water.

**Figure S20.** Differential Light Scattering (DLS) results of derivative 2 showing particle size diameter in 90% water.
Figure S21. Differential Light Scattering (DLS) results of derivative 3 showing particle size diameter in 90% water.

Figure S22. Differential Light Scattering (DLS) results of derivative 3 showing particle size diameter in 90% water.
Figure S23. $^1$H NMR of derivative 1 (CDCl$_3$, 300 MHz)
Figure S24. $^1$H NMR of derivative 2 (CDCl$_3$, 300 MHz)
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Figure S42. HPLC data of derivative 2
Figure S43. HPLC data of derivative 3

Figure S44. HPLC data of derivative 8
**Figure S45.** HPLC data of derivative 9

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**Figure S46.** HPLC data of derivative 10

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