Impact of strength and size of donors on the optoelectronic properties of D-π-A sensitizers

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Figure S1: Comparison of carbazole aldehydes with phenyl donor based carbazole sensitizers by using absorption spectra.
Figure S2: Normalised absorption spectrum of TBR, TMR, OMR and PR dyes in CHCl₃ solution and on TiO₂ films
Synthetic pathways for the preparation of intermediate compounds.

**9-Octyl-9H-carbazole (CB)**

Carbazole (1 mol ratio) was added to a suspension of sodium hydroxide (1.2 mol ratio) in DMSO (13V) under nitrogen atmosphere. The mixture was stirred for 30 min and then 1-bromo octane (1.1 mol ratio) was added. After completion of the reaction, the mixture was extracted with CHCl$_3$ and dried over sodium sulphate and evaporated to afford CB. Product: brown liquid. Yield: 90 %. $^1$H NMR, (400MHz, CDCl$_3$-d): $\delta$ = 8.10-8.07 (m, 2 H), 7.46-7.42 (m, 2 H), 7.38 (d, $J = 8$ Hz, 2 H), 7.23-7.19 (m, 2 H), 4.26 (t, $J = 7.2$ Hz, 2 H), 1.84 (p, $J = 7.3$ Hz, 2 H), 1.39-1.23 (m, 10H), 0.85 (t, $J = 7.2$ Hz, 3 H) ppm. $^{13}$C NMR, (100MHz, CDCl$_3$-d): $\delta$ = 140.52, 125.64, 122.90, 120.42, 118.77, 108.73, 43.13, 34.14, 31.90, 29.48, 29.28, 29.06, 27.41, 22.71, 14.18 ppm. HRMS (ESI) $m/z$: calculated for C$_{20}$H$_{25}$N [M+H]$^+$: 279.20, Found : 280.17.

**9-Octyl-9H-carbazole-3-carbaldehyde (CBA)**

A round bottom flask was charged with a solution of DMF (2.01 mol ratio) and 1, 2-dichloroethane (3ml) at 0°C. POCl$_3$ (1.25 mol ratio) was slowly added to the mixture. Then, CB (1 mol ratio) in 1, 2-dichloroethane (3ml) was added dropwise to the mixture. The mixture was stirred for 12h at 90°C. Next, it was poured into ice water and the compound was filtered and dried to give CBA. Product: yellow solid, Yield: 88 %. $^1$H NMR, (400MHz, CDCl$_3$-d): $\delta$ = 10.09 (s, 1 H), 8.62 (s, 1 H), 8.16 (d, $J = 8$ Hz, 1 H), 8.01 (dd, $J = 8.8$, 1.2 Hz, 1 H), 7.55-7.51 (m, 1 H), 7.47 (t, $J = 8.4$ Hz, 2 H), 7.34-7.30 (m, 1 H), 4.34 (t, $J = 7.2$ Hz, 2 H), 1.89 (p, $J = 7.4$ Hz, 2 H), 1.41-1.23 (m, 10 H), 0.86 (t, $J = 6.8$ Hz, 3 H) ppm. $^{13}$C NMR, (100MHz, CDCl$_3$-d): $\delta$ = 191.77, 144.08, 141.18, 128.50, 127.14, 126.70, 123.99, 123.07, 123.00, 120.74, 120.29, 109.40, 108.94, 43.44, 31.76, 29.32, 28.93, 27.26, 22.59, 14.06 ppm.
**6-Iodo-9-octyl-9H-carbazole-3-carbaldehyde (CBAI)**

To a two neck RB flask, CBA (1mol ratio) was dissolved in glacial acetic acid (16V) and then KI (0.67 mol ratio) and KIO₃ (0.4 mol ratio) were added. The mixture was stirred at 80°C until iodine was fully consumed, then the mixture was cooled to room temperature, a pale brown colour solid appeared and filter the solid and then poured into 5% NaHSO₃ to remove KIO₃. After 1 hr stirring, the mixture was filtered off and dried to get CBAI. Product: pale brown colour solid, yield: 68 %. ¹H NMR, (400MHz, CDCl₃-d): δ = 10.08 (s, 1 H), 8.54 (s, 1 H), 8.46 (s, 1 H), 8.03 (dd, J = 8.4, 1.6 Hz, 1 H), 7.77 (dd, J = 8.8, 1.6 Hz, 1 H), 7.47 (d, J = 8.4 Hz, 1 H), 7.24 (d, J = 8.4 Hz, 1 H), 4.30 (t, J = 7.2 Hz, 2 H), 1.86 (p, J = 7.3 Hz, 2 H), 1.37-1.23 (m, 10 H), 0.86 (t, J = 6.8 Hz, 3 H) ppm. ¹³C NMR, (100MHz, CDCl₃-d): δ = 191.50, 143.87, 140.32, 134.94, 129.59, 128.94, 127.43, 125.38, 124.32, 121.72, 111.38, 109.22, 82.89, 43.53, 31.73, 29.27, 29.11, 28.87, 27.20, 22.57, 14.05 ppm.

**6-(4-tert-Butyl-phenyl)-9-octyl-9H-carbazole-3-carbaldehyde (CTB)**

Tetrahydrofuran (50V) and water (10V) was charged with a dried 100 ml two neck RB flask under nitrogen atmosphere for 10 min. 4-tert-butyl phenyl boronic acid (1 mol ratio) and CBAI (1.2 mol ratio) and K₂CO₃ (3 mol ratio) was added to the above mixture and stirrered for 5 min. Then Pd(PPh₃)₄ (0.05 mol ratio) was added and heat at 75°C for 12 hr. After completion of the reaction, the mixture was extracted with DCM and dried over anhydrous sodium sulphate. The residue was purifed by column chromatography (100-200 mesh, silica gel) with hexane/ethylacetate as the eluent to afford CTB. Product: light yellow solid, yield: 91 %. ¹H NMR, (400MHz, CDCl₃-d): δ = 10.11 (s, 1 H), 8.65 (s, 1 H), 8.36 (s, 1 H), 8.02 (dd, J = 8.8, 1.2 Hz, 1 H), 7.77 (dd, J = 8.4, 1.6 Hz, 1 H), 7.65 (d, J = 8.4 Hz, 2 H), 7.53-7.47 (m, 4 H), 4.35 (t, J = 7.2 Hz, 2 H), 1.91 (p, J = 7.3 Hz, 2 H), 1.39 (s, 9 H), 1.36-1.25 (m, 10 H), 0.86 (t, J = 6.4 Hz,
3 H) ppm. $^{13}$C NMR, (100MHz, CDCl$_3$-d): δ = 191.77, 149.82, 144.47, 140.49, 138.67, 133.75, 128.91, 128.56, 127.33, 127.20, 126.94, 126.17, 125.87, 124.12, 123.51, 123.23, 119.00, 109.61, 109.09, 43.57, 34.56, 31.78, 31.45, 29.74, 29.34, 29.17, 29.00, 27.29, 22.62, 14.16, 14.09 ppm.

HRMS (ESI-TOF) m/z: calculated for C$_{31}$H$_{37}$NO [M+H]$^+$: 439.29, Found : 440.3097.

**9-Octyl-6-(2,4,6-trimethyl-phenyl)-9H-carbazole-3-carbaldehyde (CTM)**

Product: pale brown colour, yield: 78 %. $^1$H NMR, (400MHz, CDCl$_3$-d): δ = 10.08 (s, 1 H), 8.55 (s, 1 H), 8.02 (dd, $J = 8.8, 1.6$ Hz, 1 H), 7.92 (s, 1 H), 7.49 (d, $J = 8$Hz, 2 H), 7.30 (dd, $J = 8.4, 1.2$ Hz, 1 H), 6.99 (s, 2 H), 4.36 (t, $J = 7.2$ Hz, 2 H), 2.36 (s, 3 H), 2.04 (s, 6 H), 1.94 (p, $J = 7.4$ Hz, 2 H), 1.46-1.20 (m, 10 H), 0.86 (t, $J = 6.8$ Hz, 3 H) ppm. $^{13}$C NMR, (100MHz, CDCl$_3$-d): δ = 191.72, 144.35, 140.03, 139.18, 136.60, 136.54, 133.28, 128.50, 128.26, 128.15, 126.99, 124.26, 123.16, 123.09, 121.27, 109.33, 109.05, 43.62, 31.79, 29.35, 29.19, 29.04, 27.35, 22.63, 21.09, 21.00, 14.09 ppm. HRMS (ESI-TOF) m/z: calculated for C$_{30}$H$_{35}$NO [M+H]$^+$: 425.27, Found : 426.2767.

**6-(4-Methoxy-phenyl)-9-octyl-9H-carbazole-3-carbaldehyde (COMe)**

Product: yellow colour, yield: 68 %. $^1$H NMR, (400MHz, CDCl$_3$-d): δ = 10.11 (s, 1 H), 8.65 (s, 1 H), 8.32 (s, 1 H), 8.02 (d, $J = 8.4$ Hz, 1 H), 7.73 (d, $J = 8.4$ Hz, 1 H), 7.64 (d, $J = 8.4$ Hz, 2 H), 7.49 (dd, $J = 8.4, 3.6$ Hz, 2 H), 7.04 (d, $J = 8.4$ Hz, 2 H), 4.35 (t, $J = 7.2$ Hz, 2 H), 3.88 (s, 3 H), 1.91 (p, $J = 7.3$ Hz, 2 H), 1.43-1.20 (m, 10 H), 0.86 (t, $J = 6.4$ Hz, 3 H) ppm. $^{13}$C NMR, (100MHz, CDCl$_3$-d): δ = 191.70, 158.88, 144.43, 140.26, 134.18, 133.55, 128.54, 128.27, 127.13, 125.92, 124.11, 123.51, 123.17, 118.66, 114.37, 109.61, 109.06, 55.40, 43.51, 31.78, 29.74, 29.34, 29.17, 28.98, 27.27, 22.62, 14.09 ppm. HRMS (ESI-TOF) m/z: calculated for C$_{28}$H$_{31}$NO$_2$ [M+H]$^+$: 413.24, Found : 414.2444.
**9-Octyl-6-phenyl-9H-carbazole-3-carbaldehyde (CPB)**

Product: yellow colour solid, yield: 47 \% \(^1\)H NMR, (400MHz, CDCl\(_3\)-d): \(\delta = 10.11\) (s, 1 H), 8.66 (s, 1 H), 8.37 (s, 1 H), 8.03 (dd, \(J = 8.4, 1.2\) Hz, 1 H), 7.78 (dd, \(J = 8.4, 1.6\) Hz, 1 H), 7.71 (d, \(J = 7.6\) Hz, 2 H), 7.52-7.47 (m, 4 H), 7.36 (t, \(J = 7.2\) Hz, 1 H), 4.36 (t, \(J = 7.2\) Hz, 2 H), 1.91 (p, \(J = 7.3\) Hz, 2 H), 1.42-1.21 (m, 10 H), 0.86 (t, \(J = 6.4\) Hz, 3 H) ppm. \(^{13}\)C NMR, (100MHz, CDCl\(_3\)-d): \(\delta = 191.69, 144.44, 141.58, 140.61, 133.81, 128.93, 128.61, 127.30, 127.17, 126.84, 126.19, 124.11, 123.52, 123.18, 119.14, 109.67, 109.11, 43.51, 31.81, 29.35, 29.19, 28.99, 27.28, 22.65, 14.13\) ppm.

**General procedure for the preparation of amine donor aldehydes**

CBAI (0.0006 mol), amine donors (Bis-(4-methoxy-phenyl)-amine, Bis-(4-Hexyloxy-phenyl)-amine, Bis(2’,4’-bis(hexyloxy)-[1,1’-biphenyl]-4-yl)amine) (0.0006 mol) and sodium tertiary butoxide (0.0008 mol) were dissolved in toluene (6 ml). This solution was degassed under nitrogen for 20 min and then Pd[P(t-Bu)_3]_2 was added to the reaction mixture. The reaction was then brought to 80 °C and stirred for 12 hours. The reaction mixture was cooled to room temperature and plugged through a thin pad of NaSO\(_4\) with DCM. The crude product was adsorbed in silica gel and purified by column chromatography to get the corresponding compounds.

**6-[Bis-(4-methoxy-phenyl)-amino]-9-octyl-9H-carbazole-3-carbaldehyde (COMN)**

Yield: 35.7 \%. \(^1\)H NMR (400 MHz, Chloroform-d) \(\delta = 10.04\) (s, 1H), 8.45 (d, \(J = 1.3\) Hz, 1H), 7.99 (dd, \(J = 8.6, 1.5\) Hz, 1H), 7.78 (d, \(J = 1.8\) Hz, 1H), 7.45 (d, \(J = 8.6\) Hz, 1H), 7.32 (s, 2H), 7.07 (d, \(J = 9.0\) Hz, 4H), 6.84 (d, \(J = 9.0\) Hz, 4H), 4.31 (s, 2H), 3.83 (s, 6H), 1.93 – 1.86 (m, 2H), 1.27 (s, 10H), 0.88 (d, \(J = 7.0\) Hz, 3H).
6-[Bis-(4-hexyloxy-phenyl)-amino]-9-octyl-9H-carbazole-3-carbaldehyde (CCN)

Yield: 25.7 %. $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 10.04 (s, 1H), 8.45 (s, 1H), 7.99 (dd, $J$ = 8.6, 1.2 Hz, 1H), 7.83 – 7.76 (m, 1H), 7.45 (s, 1H), 7.30 (dd, $J$ = 5.5, 3.6 Hz, 2H), 7.05 (d, $J$ = 8.9 Hz, 4H), 6.84 (d, $J$ = 8.9 Hz, 4H), 4.31 (s, 2H), 3.96 (t, $J$ = 6.6 Hz, 4H), 1.92 – 1.88 (m, 2H), 1.81 (s, 2H), 1.49 (s, 2H), 1.37 – 1.28 (m, 22H), 0.94 – 0.90 (m, 9H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ = 191.68, 154.67, 144.42, 143.34, 142.67, 142.07, 136.86, 135.22, 130.52, 128.98, 128.40, 128.16, 126.78, 125.41, 125.08, 124.54, 123.77, 123.74, 122.74, 115.21, 109.86, 108.95, 77.35, 77.23, 77.03, 76.71, 68.31, 59.53, 43.54, 38.16, 31.95, 31.86, 31.64, 31.26, 29.72, 29.68, 29.52, 29.49, 29.39, 29.37, 29.27, 29.04, 27.28, 25.80, 25.04, 24.90, 24.59, 22.72, 22.67, 22.64, 14.15, 14.13, 14.08.

6-[Bis(20,40-bis(hexyloxy)-[1,10-biphenyl]-4-yl)amino]-9-octyl-9H-carbazole-3-carbaldehyde (CHN)

Yield: 18.6 %. $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 10.06 (s, 1H), 8.50 (d, $J$ = 1.3 Hz, 1H), 8.03 (dd, $J$ = 8.3, 1.7 Hz, 2H), 7.51 – 7.38 (m, 8H), 7.31 (s, 1H), 7.19 – 7.15 (m, 4H), 6.56 (dd, $J$ = 6.1, 2.3 Hz, 4H), 4.35 (s, 2H), 4.02 – 3.97 (m, 8H), 1.97 – 1.91 (m, 2H), 1.84 – 1.76 (m, 8H), 1.48 – 1.28 (m, 34H), 0.96 – 0.85 (m, 15H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ = 191.64, 159.44, 156.96, 146.67, 144.46, 141.31, 137.91, 132.01, 130.82, 130.10, 128.42, 126.08, 123.94, 123.10, 122.74, 122.40, 118.34, 110.11, 109.13, 105.27, 100.41, 77.35, 77.24, 77.03, 76.72, 68.39, 68.12, 43.62, 31.87, 31.64, 31.46, 29.54, 29.51, 29.39, 29.34, 29.28, 29.08, 27.32, 25.79, 25.77, 22.67, 22.65, 22.57, 14.13, 14.08, 14.03.
Figure S3A: Frontier molecular orbitals of carbazole based sensitizers

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Figure S3B:
Figure S3C:

HOMO

OMC

OMR

LUMO

OMC

OMR
Figure S3D:

HOMO

LUMO

PC

PR

PC

PR
Figure S3E:
Figure S3F:
Table S1: HOMO and LUMO values of carbazole based sensitizers obtained from DFT calculations

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