

## Supporting Information

### Triplet Energy Confinement and Transfer in Organic Semiconducting Molecular Assemblies

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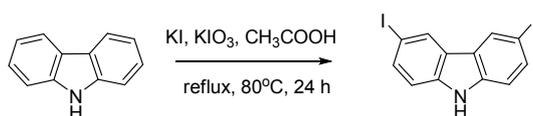
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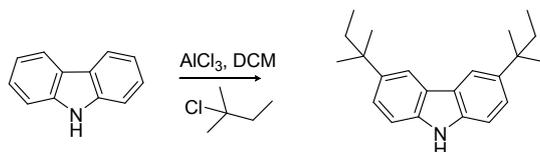
#### 1. Materials Synthesis.

##### 3,6-Diiodo-9H-carbazole (**2b**)<sup>1</sup>



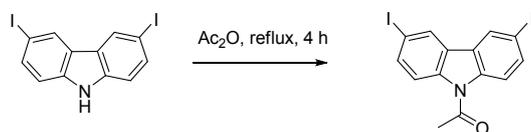
Carbazole (5.0 g, 29.94 mmol) was dissolved in acetic acid (50 ml) and then warmed to 80°C. Potassium iodide (6.51 g, 39.22 mmol) and potassium iodate (4.99 g, 23.35 mmol) was added to this solution and the mixture was refluxed for 24 hours. The crude product was diluted with water and filtered under vacuum. The brown precipitates were stirred in solution of sodium sulfite for 1 hour and filtered with vacuum. The product was recrystallized from dichloromethane to give brownish solid. (9.08 g, 72 %). **Mp** 145-150°C; **IR** ( $\nu_{\max}$ , cm<sup>-1</sup>): 3412, 1378; **<sup>1</sup>H NMR** (ppm, 400 Mhz, CDCl<sub>3</sub>)  $\delta_{\text{H}}$  : 8.32 (2H, s), 8.10 (1H, s, N-H), 7.69 (2H, dd,  $J = 1.08, 7.40$  Hz), 7.22 (2H, d,  $J = 8.48$  Hz); **<sup>13</sup>C NMR** (ppm, 100 Mhz, CDCl<sub>3</sub>)  $\delta_{\text{C}}$  : 138.51, 134.82, 129.39, 124.58, 112.69, 82.45; **MS (GC) [m/z]**: calcd for C<sub>12</sub>H<sub>7</sub>I<sub>2</sub>N, 418.87; found, 419.00.

### 3, 6-Di-*tert*-pentyl-9H-carbazole (3)



The mixture of carbazole (10.0 g, 59.88 mmol), anhydrous  $\text{AlCl}_3$  (7.98g, 58.88mmol) and  $\text{CH}_2\text{Cl}_2$  (200 ml) in a three-necked flask cooled to  $0^\circ\text{C}$  was added dropwise a solution of 2-chloro-2-methylbutane (14.75 ml, 119.76 mmol) in  $\text{CH}_2\text{Cl}_2$  (40 ml). After addition, the mixture was stirred for 10 min at the same temperature. Then the ice bath was removed and the reaction was stirred for 24 hours. The mixture poured into ice-water (500 ml) and extracted with dichloromethane. The combined organic phase was dried over  $\text{MgSO}_4$ . After filtered, the filtration was evaporated to give grey crude which was recrystallized from ethanol to afford white powder (9.33 g, 51%). **Mp** 215-220  $^\circ\text{C}$ ; **IR** ( $\nu_{\text{max}}$ ,  $\text{cm}^{-1}$ ): 3417; 2962;  **$^1\text{H}$  NMR** (ppm, 400 Mhz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$  : 8.01 (2H, s), 7.83 (1H, s, N-H), 7.39 (2H, d,  $J = 8.48$  Hz), 7.33 (2H, d,  $J = 8.52$  Hz), 1.76 (4H, q,  $J = 7.40, 7.44$  Hz), 1.41(12H, s), 0.71 (6H, t,  $J = 7.40$  Hz);  **$^{13}\text{C}$  NMR** (ppm, 100 Mhz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$  :140.41, 137.96, 124.03, 123.31, 117.06, 109.96, 37.90, 37.42, 29.15, 9.31; **MS (GC) [m/z]**: calcd for  $\text{C}_{22}\text{H}_{29}\text{N}$ , 307.23; found, 307.00.

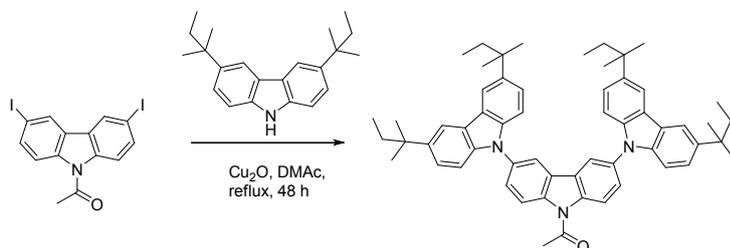
### *N*-(3, 6-diiodo-9H-carbazol-9-yl)ethanone (4)



3, 6-Diiodo-9H-carbazole (10 g, 23.87 mmol) was dissolved in acetic anhydride (50 ml). The mixture was refluxed for about 4 hours. The precipitates were filtered under vacuum and wash with water several times to afford white powder (8.76 g, 79 %). **Mp** 215-220 $^\circ\text{C}$ ; **IR** ( $\nu_{\text{max}}$ ,  $\text{cm}^{-1}$ ):3062, 1703;  **$^1\text{H}$  NMR** (ppm, 400 Mhz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$  : 8.25 (2H, s), 7.96 (2H, d,  $J = 8.80$  Hz), 7.78 (2H, d,  $J = 8.80$  Hz), 2.84 (3H, s);  **$^{13}\text{C}$  NMR** (ppm, 100 Mhz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$  : 137.95,

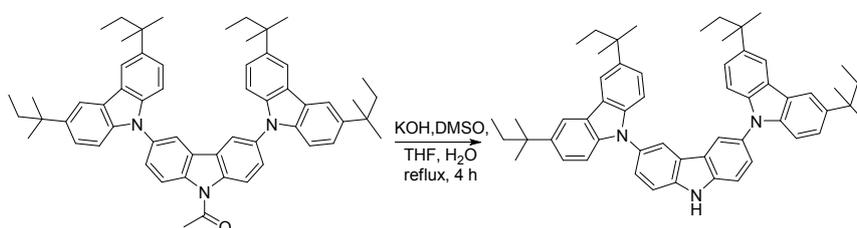
136.47, 128.99, 127.19, 118.01, 87.60, 27.68; **MS (GC) [m/z]:** calcd for C<sub>14</sub>H<sub>9</sub>I<sub>2</sub>NO, 460.88; found, 461.00.

### ***N*-(3,6-bis(3,6-di-*tert*-pentyl-carbazol-9-yl)carbazole)ethanone (5)**



To a solution of 1-(3,6-diiodo-9H-carbazol-9-yl)ethanone (2.0 g, 4.33 mmol) and 3,6-Di-*tert*-pentyl-9H-carbazole (2.67, 8.68 mmol) in *N,N*-dimethylacetamide (30 ml) was added copper oxide. The mixture was refluxed for 48 hours and cooled to room temperature and then diluted with water. The precipitates were filtered and recrystallized from ethanol to afford white powder (2.65 g, 74 %). **IR** ( $\nu_{\max}$ , cm<sup>-1</sup>): 2962, 1702; **<sup>1</sup>H NMR** (ppm, 400 Mhz, CDCl<sub>3</sub>)  $\delta_{\text{H}}$  : 8.49 (2H, d), 8.16 (2H, d), 8.08 (4H, s), 7.75 (2H, dd), 7.37 (8H, m), 3.05 (3H, s), 1.77 (8H, q), 1.42 (24H, s), 0.72 (12H, t); **<sup>13</sup>C NMR** (ppm, 100 Mhz, CDCl<sub>3</sub>)  $\delta_{\text{C}}$  :169.88, 141.17,139.46, 137.74, 134.38, 127.37, 126.71, 124.22, 123.35, 118.39, 117.56, 117.18, 108.92, 37.95, 37.36, 29.12, 27.79, 9.32. **MS (MALDI-TOF) [m/z]:** calcd for C<sub>58</sub>H<sub>65</sub>N<sub>3</sub>O, 819.51; found, 820.1171.

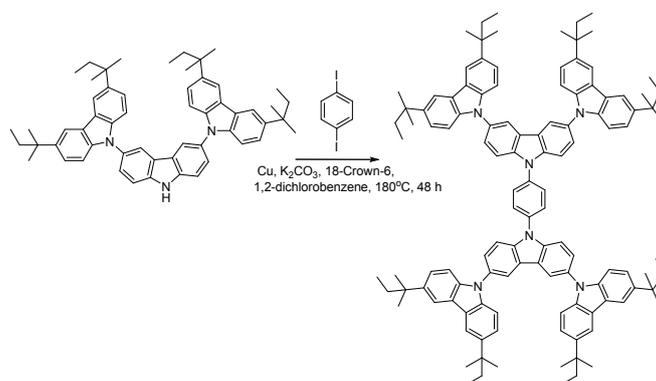
### **3,6-bis(3,6-di-*tert*-pentyl-carbazol-9-yl)carbazole (6)**



To a solution of *N*-(3,6-bis(3,6-di-*tert*-pentyl-carbazol-9-yl)carbazole)ethanone (2.0 g, 2.44 mmol) in THF (6.0 ml), DMSO (3.0 ml) and water (1.0) was added. The mixture was stirred for 10 min. KOH (1.2 g, 21.4 mmol) was added subsequently to the mixture and then

refluxed for 4 hours. The crude was diluted with water and neutralize with HCl solution (6 N). The crude was filtered and recrystallised from mixture of Hexane : Ethylacetate (1:1) to give white solid. (1.80 g, 95 %). **Mp** 285-290 °C; **IR** ( $\nu_{\max}$ ,  $\text{cm}^{-1}$ ): 3453, 2963, 1489;  **$^1\text{H NMR}$**  (ppm, 400 Mhz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$  : 8.41 (1H, s, N-H), 8.19 (2H, s), 8.08 (4H, s), 7.67 (4H, m), 7.36 (8H, m), 1.77 (8H, q,  $J = 7.32, 7.44$  Hz), 1.42 (24H, s), 0.72 (12H, t,  $J = 7.28$  Hz);  **$^{13}\text{C NMR}$**  (ppm, 100 Mhz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$  :140.66, 140.08, 139.01, 130.49, 125.95, 124.11, 124.02, 123.07, 119.42, 117.03, 111.81, 109.04, 37.92, 37.39, 29.15, 9.33; **MS (MALDI-TOF) [m/z]**: calcd for  $\text{C}_{56}\text{H}_{63}\text{N}_3$ , 777.50; found, 777.6461.

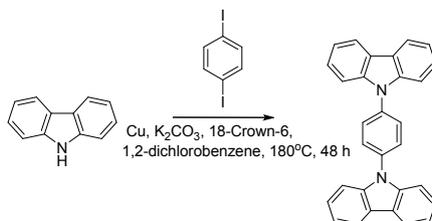
### 1,4-bis(3,6-bis(3,6-di-*tert*-pentyl-carbazol-9-yl)carbazol-9-yl)benzene (7)



Using a 50 ml two neck round bottom flask with a magnetic stir and a condenser topped with nitrogen inlet. All of the apparatus was purged with nitrogen gas. *O*-dichlorobenzene (10 ml), 3,6-bis(3,6-di-*tert*-pentyl-carbazol-9-yl)carbazole (0.51 g, 0.66 mmol), 1,4-diiodobenzene (0.10 g, 0.30 mmol),  $\text{K}_2\text{CO}_3$  (0.33 g, 2.40 mmol), Cu powder (0.04 g, 0.60 mmol) and 18-Crown-6 (0.02 g, 0.06 mmol) was added. The mixture was heated at 180°C using oil bath and maintained at that temperature for 48 hours. Cooled the crude mixture and filtered to remove inorganic solid. The filtrate was reduced under high vacuum pump and purify using column chromatography (Hexane: Ethyl acetate; 30:1) to give white powder (0.45 g, 90 %). **IR** ( $\nu_{\max}$ ,  $\text{cm}^{-1}$ ):2963, 1489;  **$^1\text{H NMR}$**  (ppm, 400 Mhz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$  : 8.32 (4H, d,  $J=1.28$  Hz), 8.12 (8H,s), 8.10(4H,s), 7.86 (4H, d,  $J=8.68$  Hz), 7.73 (4H, dd,  $J =1.52, 7.12$  Hz), 7.41 (8H, d,  $J =9.28$  Hz), 7.38 (8H, d,  $J=8.56$  Hz), 1.80 (16H, q,  $J=7.28, 7.40$  Hz), 1.43 (48H, s), 0.75 (24H, t,  $J=7.28$  Hz);  **$^{13}\text{C NMR}$**  (ppm, 100 Mhz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$  : 140.85, 140.20, 140.00, 136.88,

131.39, 128.80, 126.19, 124.32, 124.10, 123.16, 119.50, 117.14, 111.09, 109.01, 37.96, 37.40, 29.16, 9.35; **MS (MALDI-TOF) [m/z]**: calcd for C<sub>118</sub>H<sub>128</sub>N<sub>6</sub>, 1630.02; found, 1630.5803.

### 1, 4-Di (9H-carbazol-9-yl)benzene (8)<sup>2</sup>



Using a 50 ml two neck round bottom flask with a magnetic stir and a condenser topped with nitrogen inlet. All of the apparatus was purged with nitrogen gas. *O*-dichlorobenzene (5 ml), carbazole (0.22 g, 1.33 mmol), 1,4-diiodobenzene (0.2 g, 0.61 mmol), K<sub>2</sub>CO<sub>3</sub> (0.67 g, 4.85 mmol), Cu powder (0.08 g, 1.21 mmol) and 18-Crown-6 (0.032 g, 0.12 mmol) was added. The mixture was heated at 180°C using oil bath and maintained of that temperature for 8 hours. Cooled the crude mixture and filtered to remove inorganic solid. The filtrate was reduced under high vacuum pump and recrystallization using chloroform to afford a white powder (0.13 g, 59%). **Mp** 305-310°C; **IR** ( $\nu_{\max}$ , cm<sup>-1</sup>): 3056, 1595; **<sup>1</sup>H NMR** (ppm, 400 Mhz, CDCl<sub>3</sub>)  $\delta_{\text{H}}$  : 8.18 (4H, d, *J*=7.6 Hz), 7.81, 4(s, 4H), 7.56 (4H, d, *J*=8.4 Hz), 7.46 (4H, t, *J*=7.6, 7.2 Hz, 7.32 (4H, t, *J*= 7.6 Hz); **<sup>13</sup>C NMR** (ppm, 100 Mhz, CDCl<sub>3</sub>)  $\delta_{\text{C}}$  : 140.77, 136.69, 128.39, 126.13, 123.58, 120.46, 120.28, 109.76; **MS (MALDI-TOF) [m/z]**: calcd for C<sub>30</sub>H<sub>20</sub>N<sub>2</sub>, 408.16; found, 408.2013

### 3,6-Dibromocarbazole (2a)<sup>3</sup>

A two-neck round-bottom-flask with stir bar was sealed with rubber septum. Air was evacuated with vacuum pump. Nitrogen balloon was inserted. **1** (6.07 g, 36.3 mmol, 1 eq) was dissolved in dry toluene (70 ml) and injected into the reaction flask. A solution of NBS (13.63 g, 76.58 mmol, 2.1 eq) in DMF (35 ml) was injected dropwise into the reaction flask. The reaction was monitored with TLC. The reaction mixture was poured into cold water,

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stirred, and sealed until precipitation was observed. The white precipitate was filtered, washed with cold MeOH, and recrystallized with MeOH / Hexane (1:5) to give white needle (5.36 g, 46 % yield). Lit. yield = 92 %. m. p. 204-205 °C. Lit. m. p. 206-208 °C. <sup>1</sup>H NMR (400 MHz, Acetone-d<sub>6</sub>) δ 10.65 (1H, broad s, NH), 8.36 (2H, d, *J* = 1.28 Hz, H4 and H5), 7.55 (2H, dd, *J* = 5.74 and 1.30 Hz, H2 and H7), 7.51 (2H, d, *J* = 5.76 Hz, H1 and H8). <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>) δ 139.2, 128.9, 123.9, 123.2, 113.0, 111.6. <sup>1</sup>H NMR and <sup>13</sup>C NMR agree to reported values.<sup>4</sup>

### Diphenylphosphine oxide (10)

**9** (3.0 ml, 16.3 mmol, 1 eq), AR grade acetonitrile (50 ml), water (20 ml) was added to a 100 ml Xpress Plus vessel. The reaction mixture was irradiated with microwave to reach 90 °C in 15 min and the temperature was hold for another 15 min. The reaction mixture was allowed to cool to rt. Acetonitrile was removed with rotavap. Extraction with DCM (3 X 50 ml) and water (10 ml) was done. The collected organic layer was dried with MgSO<sub>4</sub> and concentrated. The crude product was purified with flash column (EtOAc/Hexane, 1:1) to give clear light yellow liquid (2.47 g, 74% yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 8.69 (s, 1H), 7.74-7.68 (m, 4H), 7.60-7.48 (m, 6H), <sup>1</sup>H NMR agrees to reported values.<sup>5</sup>

### 3,6-Bis-(diphenylphosphinyl)-9H-Carbazole (11)<sup>6</sup>

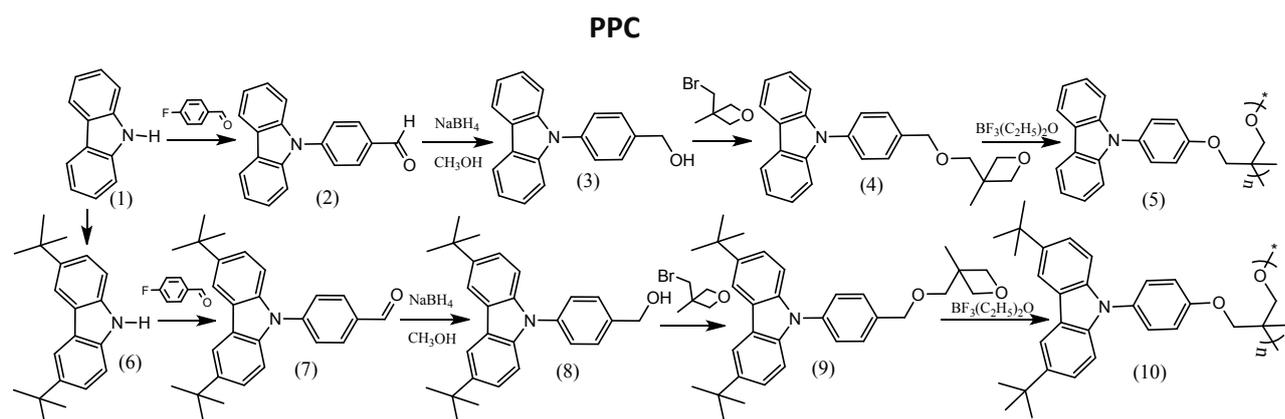
In a 50 ml round-bottom-flask, **2a** (1.28 g, 3.9 mmol, 1 eq), **10** (3.59 g, 17.7 mmol, 4.5 eq), nickel(II) chloride hexahydrate (467.7 mg, 1.97 mmol, 0.5 eq), Zinc dust (1.10 g, 16.8 mmol, 4.3 eq), bipyridine (311.6 mg, 2.0 mmol, 0.5 eq) and 99.5% ethanol (10 ml) were added. The reaction mixture was heated to 70 °C for 5 days. The reaction mixture was then concentrated with rotavap and diluted with DCM. Extraction was done with DCM (3 X 50 ml). The organic layers are dried with MgSO<sub>4</sub> and concentrated. Flash column was done. The product was eluted with 1:20 MeOH:EtOAc. Yield = 1.40 g, 63%. Lit. yield = 74%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 11.78 (br s, 1 H), 8.31 (d, *J* = 12.44, 2H) 7.68-7.58 (m, 10 H), 7.49-7.7.40 (m, 14 H). <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>) δ 142.9 (d, *J* = 2.2 Hz), 132.9 (d, *J* = 104.3 Hz), 132.1,

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132.0 129.3 (d,  $J = 11.7$  Hz), 128.6 (d,  $J = 11.7$  Hz), 125.3 (d,  $J = 11$  Hz), 122.7 (d,  $J = 14.6$  Hz), 121.3 (d,  $J = 109.3$  Hz), 111.0 (d,  $J = 13.8$  Hz).  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR agree to reported values.

### Synthesis of poly{3,6-di(*t*-butyl)-9-[4-(3-methyloxetan-3-ylmethoxy)phenyl]carbazole} (PtPC) and poly{9-[4-(3-methyloxetan-3-ylmethoxy)phenyl]carbazole} (PPC)

The monomers (**4** and **9**) used for preparation of the polymers **PtPC** and **PPC** were synthesized by a multi-step synthetic route as shown in Scheme 15. Carbazole-based aldehydes **2** and **7** were synthesized from 9H-carbazole (**1**) and 3,6-di-(*tert*-butyl)carbazole (**2**), correspondingly, according to the procedures outlined in literature<sup>7</sup>. The hydroxymethyl group containing compounds **3** and **8** were obtained by the reduction of the aldehydes (**2** and **7**) with sodium borohydride in methanol. The compounds **3** and **8** were then converted to the oxetane-based monomers **4** and **9** by their reactions with an excess of 3-bromomethyl-3-methyl-oxetane under basic conditions. The oxetanyl-functionalized monomers were used for the synthesis of polymers **PPC** (**5**) and **PtPC** (**10**) by cationic ring-opening polymerization. The monomers were subjected to polymerization in 1,2-dichloroethane solutions using  $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$  as an initiator. Low-molecular-weight fractions were removed from the products of polymerization by Soxhlet extraction with methanol.



## Scheme 1S

### Experimental details for the synthesis

9H-carbazole, 4-fluorobenzaldehyde, tetra-n-butylammonium hydrogen sulfate (TBAS), NaBH<sub>4</sub> and boron trifluoride diethyl etherate [BF<sub>3</sub>·O(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>] were purchased from Aldrich and used as received. 3-Bromomethyl-3-methyloxetane was bought from Chemada Fine Chemicals (Israel) and used without further purification.

4-(Carbazol-9-yl)benzaldehyde (**2**)<sup>7</sup>, 9-{4-(hidroxymethyl)phenyl-1-yl}carbazole (**3**)<sup>8</sup> and 3,6-di(tert-butyl)-9H-carbazole **6**<sup>9</sup> were synthesized according to the procedures outlined in literature.

#### **9-{4-(3-methyloxetan-3-ylmethyl oxymethyl)phenyl-1-yl}carbazole (4).**

9-{4-(hidroxymethyl)phenyl-1-yl}carbazole (**3**) (2 g, 7.3 mmol) was dissolved in 10 ml of acetone and 3-bromomethyl-3-methyl-oxetane (2.4 g, 14 mmol) was added. The mixture was heated to 60 °C and KOH (1.24 g, 22 mmol), K<sub>2</sub>CO<sub>3</sub> (0.96 g, 7.3 mmol) and a catalytic amount of TBAS were added to it by small portions. The reaction mixture was stirred at 60 °C for 2 h. When the reaction was finished (TLC control), the mixture was filtered off and the solvent was evaporated under reduced pressure. The crude product was purified by silica gel column chromatography using hexane/ethyl acetate (vol. ratio 4:1) as an eluent. Yield: 1.7 g (65 %) of material 4. M.p.: 95 °C (DSC). <sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>, δ, ppm): 8.14 (d, 2H, J = 7.6 Hz, Ar); 7.56 (d, 4H, J = 7.8 Hz, Ar); 7.42 - 7.40 (m, 4H, Ar); 7.31 - 7.27 (m, 2H, Ar); 4.69 (s, 2H, PhCH<sub>2</sub>); 4.59 (d, 2H, J = 5.6 Hz, CH<sub>2</sub> of oxetane ring); 4.43 (d, 2H, J = 6.2 Hz, CH<sub>2</sub> of oxetane ring); 3.64 (s, 2H, OCH<sub>2</sub>); 1.40 (s, 3H, CH<sub>3</sub>). IR (KBr, cm<sup>-1</sup>): 3048 (C-H, Ar); 2951, 2925, 2865 (C-H); 1624, 1594, 1573 (C=C Ar); 1516, 1478, 1452 (C=C, Ar and C-H); 1334, 1315, 1234 (C-N, Ar); 1106 (C-O-C, of oxetane ring); 1094, 980, 972 (C-O-C); 836, 824, 748, 724 (C-H Ar).

**Poly{9-[4-(3-methyloxetan-3-ylmethoxy)phenyl]carbazole} (PPC) (5).** 9-{4-(3-methyloxetan-3-ylmethyl oxymethyl)phenyl-1-yl}carbazole (**4**) (1.4 g, 3.9 mmol) was dissolved in 7.8 ml of dichloroethane under nitrogen. Then BF<sub>3</sub>·O(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub> (0.12 mmol, 14.5 μl) was added to the solution and the reaction mixture was stirred for 24 h at 60 °C under nitrogen. After the reaction the initiator was neutralized by ammonia solution (26%). Then

the solvent was removed by evaporation. The product was dissolved in a small amount of chloroform and precipitated into methanol. After Soxhlet extraction (24 h) by methanol and re-precipitation, the yield of polymer **5** was 1.3 g (93%).  $M_n = 22700$ ,  $M_w = 26400$ .  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{CDCl}_3$ ,  $\delta$ , ppm): 8.13 - 8.91 (m, 2H, Ar); 7.53 - 7.17 (m, 10H, Ar); 4.64 - 4.39 (m, 2H,  $\text{PhCH}_2$ ); 3.55 - 3.18 (m, 6H,  $\text{OCH}_2$ ); 1.10 - 0.85 (m, 3H,  $\text{CH}_3$ ). IR (KBr,  $\text{cm}^{-1}$ ): 3046 (C-H, Ar); 2961, 2854 (C-H); 1625, 1607, 1597 (C=C, Ar); 1516, 1479, 1452 (C=C, Ar and C-H); 1361, 1334, 1316 (C-N, Ar); 1094 (C-O-C); 748, 723 (C-H Ar).

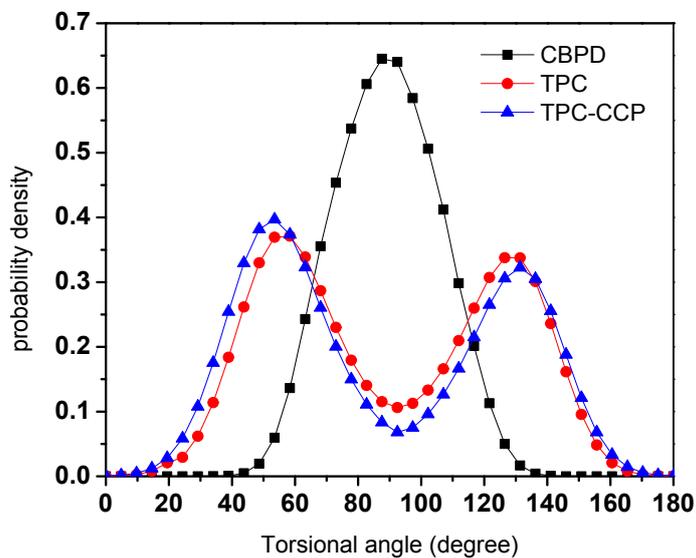
**4-(3,6-di-tert-butylcarbazol-9-yl)benzaldehyde (7)** To a stirred 3,6-di-tert-butylcarbazole (3.6 g, 12.9 mmol), potassium tert-butoxide (2.48 g, 25.8 mmol) in 15ml of anhydrous DMF, 4-fluorobenzaldehyde (2.78 ml, 19.3 mmol) was added slowly. The mixture was heated at 110 °C for 2 h. The resulting mixture was poured in ice-water. The mixture was filtered and evaporated. The crude product was purified by silica gel column chromatography using the mixture of ethyl acetate and hexane (vol. ratio 1:30) as an eluent. Yield: 2.2 g (44 %) of yellow solid.  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{CDCl}_3$ ,  $\delta$ , ppm): 10.1 (s, 1H, -CHO); 8.16 (s, 2H, Ar); 8.11 (d, 2H,  $J = 8,4$  Hz, Ar); 7.79 (d, 2H,  $J = 8,4$  Hz, Ar); 7.50 (dd, 2H,  $J_1 = 1.6$  Hz,  $J_2 = 8.4$  Hz, Ar); 7.46 (d, 2H,  $J = 8.8$  Hz, Ar); 1.48 (s, 18H,  $\text{CH}_3$ ). IR (KBr,  $\text{cm}^{-1}$ ): 2959, 2906, 2865 (C-H); 2827, 2734 (C-H, CHO gr); 1698 (C=O, CHO gr.); 1600 (C=C Ar); 1513, 1488, 1472, 1451 (C=C, Ar and C-H); 1368 (C-H,  $\text{C}(\text{CH}_3)_3$  gr.); 1325, 1297 (C-N, Ar); 875, 841, 818 (C-H Ar).

**9-(4-{hidroksimethyl}phenyl-1-yl)-3,6-di-tert-butylcarbazole (8)** was synthesized as follows. Compound **6** (0.9 g, 2.35 mmol) was dissolved in 9 ml methanol.  $\text{NaBH}_4$  (0.1 g, 2.65 mmol) was added to the solution. The resulting mixture was refluxed for 0.5 h. Then the reaction mixture was poured into ice-water. The product was extracted by chloroform. The combined extract was dried over anhydrous  $\text{Na}_2\text{SO}_4$ . The crude product was purified by silica gel column chromatography using the mixture of ethyl acetate and hexane (vol. ratio 1:4) as an eluent. Yield: 0.88 g (98 %) of material **8**.  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{CDCl}_3$ ,  $\delta$ , ppm): 8.14 (d, 2H,  $J = 1.6$  Hz, Ar); 7.58 (d, 2H,  $J = 8,8$  Hz, Ar); 7.55 (d, 2H,  $J = 8.8$  Hz, Ar); 7.46 (dd, 2H,  $J_1 = 2.0$  Hz,  $J_2 = 8.4$  Hz, Ar); 7.34 (d, 2H,  $J = 8.4$  Hz, Ar); 4.83 (s, 2H,  $\text{CH}_2$ ); 1.65 (s, 1H, OH), 1.47 (s, 18H,  $\text{CH}_3$ ). IR (KBr,  $\text{cm}^{-1}$ ): 3271 (O-H); 2953, 2901, 2865 (C-H); 1609 (C=C Ar); 1516, 1489, 1474 (C=C, Ar and C-H); 1369, 1364 (C-H,  $\text{C}(\text{CH}_3)_3$  gr.); 1295, 1263 (C-N, Ar); 880, 849, 811 (C-H Ar).

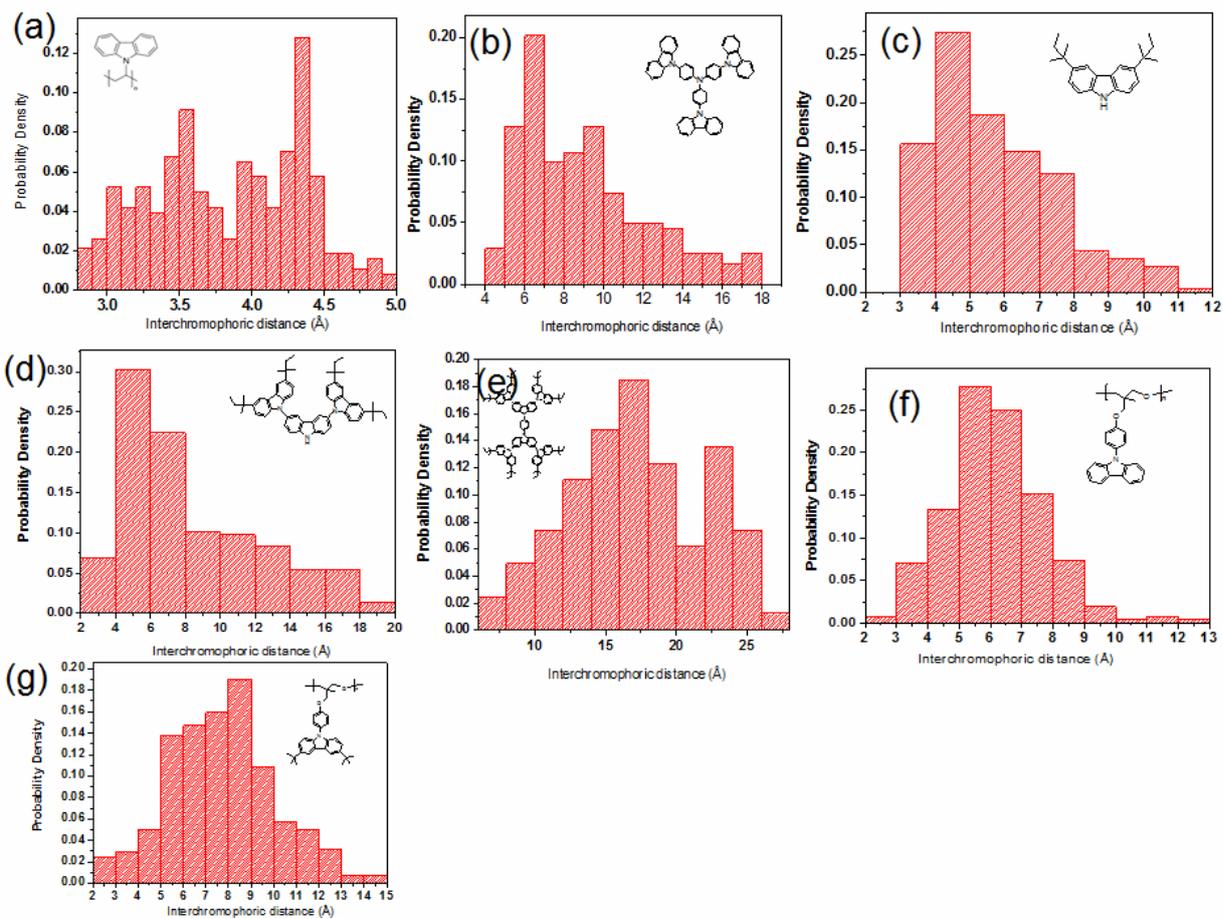
**3,6-Di(t-butyl)-9-[4-(3-methyloxetan-3-ylmethoxy)phenyl]carbazole (4).** 9-(4-(4-{hidroksimethyl}phenyl-1-yl)-3,6-di-tret-butylcarbazole (1.0 g, 2.6 mmol) was dissolved in 10 ml of acetone and 3-bromomethyl-3-methyl-oxetane (1.2 g, 7.3 mmol) was added. The mixture was heated to 60 °C and KOH (0.5 g, 8.9 mmol), K<sub>2</sub>CO<sub>3</sub> (0.4 g, 3.1 mmol) and a catalytic amount of TBAS were added to it by small portions. The reaction mixture was stirred at 60 °C for 2 h. When the reaction was finished (TLC control), the mixture was filtered off and the solvent was evaporated under reduced pressure. The product was crystallized from methanol. Yield: 1.1 g (66 %) of white crystals. M.p.: 127 °C (DSC). <sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>, δ, ppm): 8.18 (d, 2H, J = 1.6 Hz, Ar); 7.56 (s, 4H, Ar); 7.47 (dd, 2H, J<sub>1</sub> = 2.0 Hz, J<sub>2</sub> = 8.8 Hz, Ar); 7.37 (d, 2H, J = 8.8 Hz, Ar); 4.70 (s, 2H, PhCH<sub>2</sub>); 4.61 (d, 2H, J = 5.6 Hz, CH<sub>2</sub> of oxetane ring); 4.44 (d, 2H, J = 6.2 Hz, CH<sub>2</sub> of oxetane ring); 3.64 (s, 2H, OCH<sub>2</sub>); 1.48 (s, 18H, C(CH<sub>3</sub>)<sub>3</sub>); 1.41 (s, 3H, CH<sub>3</sub>). IR (KBr, cm<sup>-1</sup>): 3048 (C-H, Ar); 2959, 2905, 2869 (C-H); 1624 (C=C Ar); 1516, 1493, 1473 (C=C, Ar and C-H); 1370, 1363 (C-H, C(CH<sub>3</sub>)<sub>3</sub> gr.); 1298, 1265, 1239 (C-N, Ar); 1082, 977 (C-O-C); 847, 837, 712 (C-H, Ar).

**Poly{9-[4-(3-methyloxetan-3-ylmethoxy)phenyl]carbazole} (PPC, 10)** 9-(3-methyloxetan-3-ylmethyl)-3,6-di-tret-butylcarbazole (**4**) (0.7 g, 1.5 mmol) was dissolved in 3.0 ml of dichloroethane under nitrogen. Then BF<sub>3</sub>·O(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub> (0.04 mmol, 5.5 μl) was added to the solution and the reaction mixture was stirred for 24 h at 60 °C under nitrogen. After the reaction the initiator was neutralized by ammonia solution (26%). Then the solvent was removed by evaporation. The product was dissolved in a small amount of chloroform and precipitated into methanol. After Soxhlet extraction (24 h) by methanol and re-precipitation, the yield of polymer 10 was 0.54 g (78%). Mn = 14300, Mw = 21700. <sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>, δ, ppm): 8.14 - 8.04 (m, 2H, Ar); 7.55 - 7.15 (m, 8H, Ar); 4.65 - 4.42 (m, 2H, PhCH<sub>2</sub>); 3.52 - 3.16 (m, 6H, OCH<sub>2</sub>); 1.51 - 1.32 (m, 18H, C(CH<sub>3</sub>)<sub>3</sub>); 1.06 - 0.95 (m, 3H, CH<sub>3</sub>).

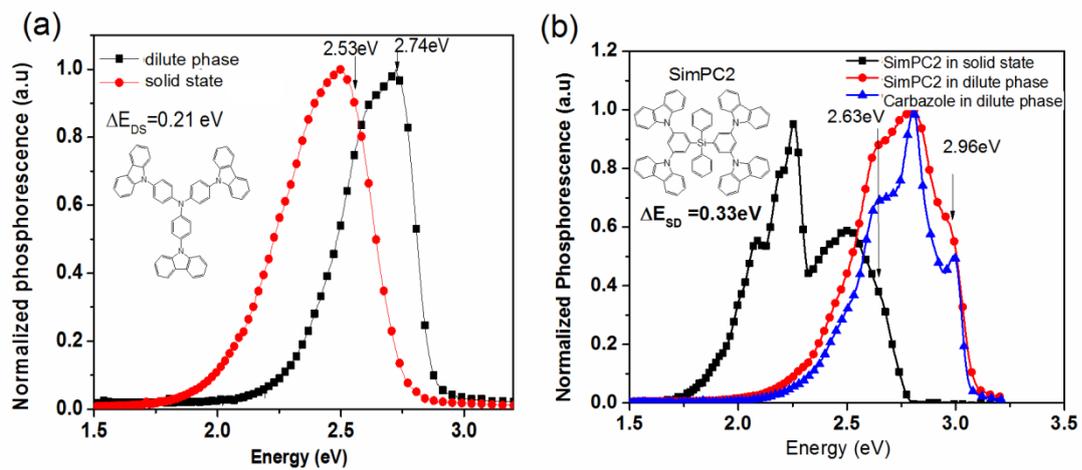
## 2. Supplementary Figures



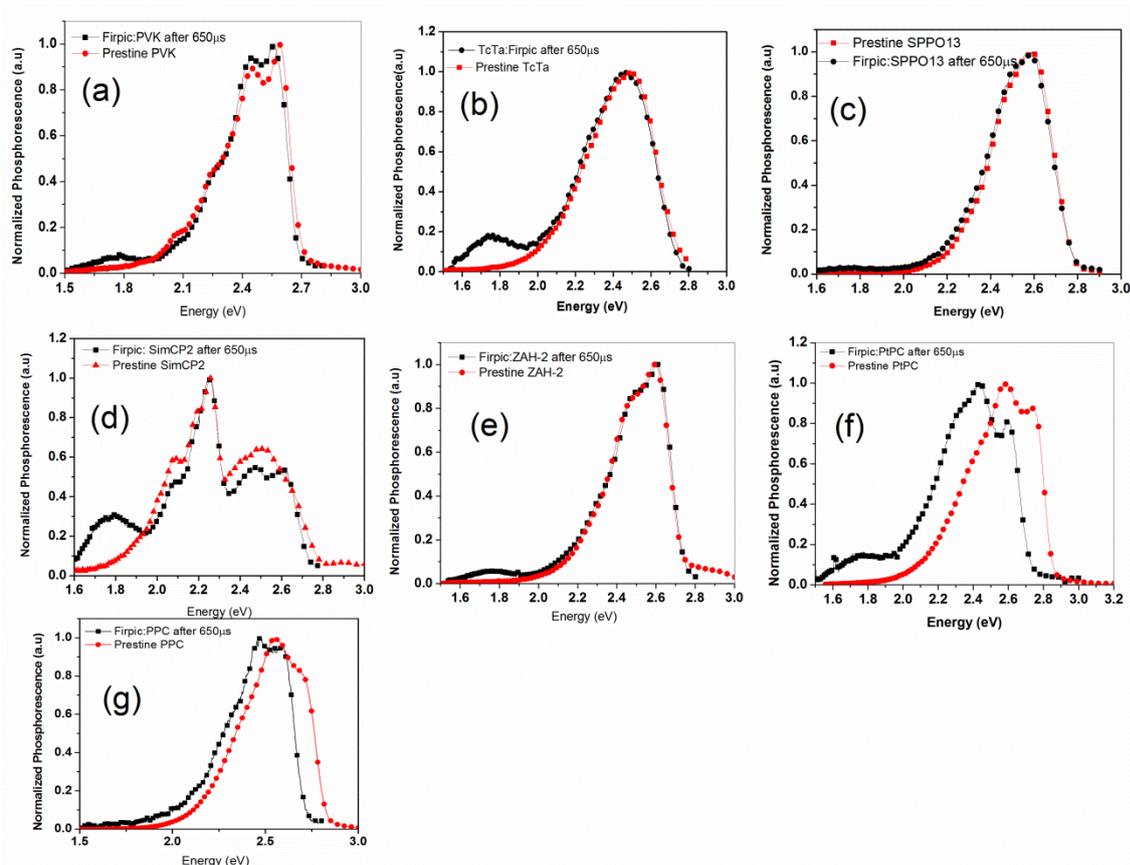
Supplementary Figure 1: Probability density distribution of torsional angle as predicted by Boltzmann distribution for free rotating unit. Less than 1% of TPC and TPC-CCP molecules have torsional angle less than  $20^\circ$ . This will increase the electronic wave function overlap between two chromophores separated by the torsional twist. For CBPD molecules, the torsional angle is highly confined in the range of  $40^\circ$  to  $130^\circ$ . This means that the carbazoles separated by the twist are effectively spectroscopically distinct.



Supplementary Figure 2: Probability density distribution of the interchromophoric distance. Note that most of the interchromophoric distances exhibit lognormal distributions.



Supplementary Figure 3: The phosphorescence spectra of (a) TcTa and (b) SimPC2.



Supplementary Figure 4: Phosphorescence of Firpic doped hosts. The emission is dominated by Firpic (not shown here) within time window of  $10\mu\text{s}$  after the pulse excitation at  $400\text{nm}$ . Phosphorescence of the host from the Firpic doped hosts can still be detected albeit very weak with a gate delay of  $650\mu\text{s}$ . (a)-(e) The phosphorescence are very similar to the host emission without Firpic except there is a peak observed at  $1.8\text{eV}$ . (f) and (g) the phosphorescence of the Firpic doped host is very different from the pristine host emission in terms of shift of spectra. No phosphorescence is observed above  $2.8\text{eV}$ .

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