

## Supporting Information

### Dendritic Donor-Acceptor Ensembles;

### Control over Energy and Electron Transduction

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### Synthesis of triphenylphosphonium salt and phosphonates.

#### 3,5-bis(triphenylphosphoniummethyl)benzonitrile dibromide (8)

A solution of 240 mg (0.83 mmol) of 3,5-di(bromomethyl)benzonitrile (**7a**)<sup>20</sup> and 435 mg (1.66 mmol) of triphenylphosphine in 7 mL of dry N,N-dimethylformamide was refluxed under argon atmosphere for 2 hours. Then, the solution was allowed to cool to room temperature and the precipitate formed was filtered and washed thoroughly with diethyl ether to yield 430 mg (64 %) of 3,5-bis(triphenylphosphoniummethyl)benzonitrile (**8**) as a white solid. M.p.: >300°C (diethyl oxide). <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 200 MHz):  $\delta$  7.72 (m, 33H), 5.41 (d, 4H, J= 15.1 Hz). FTIR (KBr, cm<sup>-1</sup>): 3051, 2989, 2962, 2854, 2231, 1585, 1437, 1111, 740, 717, 692 cm<sup>-1</sup>. MS m/z

(ESI): 732 ( $[M^+ + H - Br]^+$ ), 652 ( $[M^+ + H - 2Br]^+$ ). Anal. Calc. for  $C_{45}H_{37}Br_2NP_2$ : C: 66.44; H: 4.55; N: 1.72. Found: C: 65.59; H: 4.70; N: 1.80.

### 3,5-Bis(dimethyl phosphonatemethyl)benzonitrile (11a)

A solution of 150 mg (0.52 mmol) of 3,5-di(bromomethyl)benzonitrile (**7a**) in 10 mL of trimethylphosphite was refluxed under argon atmosphere for 8 hours. After this time, the reaction was allowed to reach room temperature and the excess trimethylphosphite was removed under vacuum. The residue obtained was chromatographed to yield 150 mg (84 %) of 3,5-bis(dimethyl phosphonate-methyl)benzonitrile (**11a**) as a white solid. M.p.: 94°C (dichloromethane/methanol).  $^1H$ -NMR ( $CDCl_3$ , 200 MHz):  $\delta$  7.42 (t, 3H,  $J = 2.4$  Hz), 3.68 (s, 6H), 3.62 (s, 6H), 3.10 (d, 4H,  $J = 22.0$  Hz).  $^{13}C$ -NMR ( $CDCl_3$ , 50 MHz)  $\delta$  135.6, 134.5, 133.7, 131.7, 113.2, 53.1, 52.9, 32.6. FTIR (KBr,  $cm^{-1}$ ): 2959, 2916, 2852, 2226, 1560, 1458, 1271, 1234, 1221, 1178, 1051, 1024, 970, 893, 831, 802, 712. MS  $m/z$  (EI) (%I): 347 ( $M^+$ , 61), 253 (100), 239 (48), 143 (28), 130 (61), 109 (57), 93 (31), 79 (30). Anal. Calc. for  $C_{13}H_{19}O_6NP_2$ : C: 44.95, H: 5.52, N: 4.03. Found C: 45.33, H: 5.92, N: 4.05.

### 3,5-Bis(dimethyl phosphonatemethyl)bromobenzene (11b)

A solution of 800 mg (3.04 mmol) of 3,5-di(bromomethyl)bromobenzene (**7b**) in 60 mL of trimethylphosphite was refluxed under argon atmosphere for 8 hours. After this time the reaction was allowed to reach room temperature and the excess trimethylphosphite was removed under vacuum. The residue obtained was chromatographed to yield 1.06 g (87 %) of 3,5-bis(dimethylphosphonate-methyl)bromobenzene (**11b**) as a white solid. M.p.: 142°C (dichloromethane/methanol).  $^1H$ -NMR ( $CDCl_3$ , 200 MHz)  $\delta$  7.45-7.42 (m, 3H), 3.82 (s, 6H),

3.77 (s, 6H), 3.20 (d, 4H,  $J = 22.0$  Hz).  $^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ , 50 MHz)  $\delta$  133.8, 131.4, 129.9, 122.7, 53.0, 52.8, 32.6. FTIR (KBr,  $\text{cm}^{-1}$ ) 2953, 2916, 2847, 1603, 1570, 1446, 1242, 1225, 1053, 1030, 864, 804. MS  $m/z$  (EI) (%I): 402 ( $[\text{M}^+ + \text{H}]^+$ , 54), 401 ( $\text{M}^+$ , 54), 321 ( $\text{M}^+ - \text{Br}$ , 32), 306 (100), 292 (35), 227 (35), 211 (17), 197 (40), 183 (56), 109 (62), 103 (59), 93 (84), 77 (46), 63 (32). Anal. Calc. for  $\text{C}_{12}\text{H}_{19}\text{BrO}_6\text{P}_2$ : C: 35.93, H: 4.77. Found C: 36.18, H: 4.78.

### First generation dendrons

#### 3,5-Bis[2'-4(dibutylaminophenyl)vinyl]benzonitrile (10a)

Via Wittig reaction: 1.84 mL (1.84 mmol) of a 1.0 M solution of lithium ethoxide in ethanol were added drop-wise to a refluxing solution of 750 mg (0.92 mL) 3,5-bis(triphenylphosphoniummethyl)benzonitrile (8) and 0.44 mL (429 mg, 1.84 mmol) of 4-(N,N-dibutylamino)benzaldehyde (9) under argon atmosphere. After 4 hours the crude reaction was allowed to cool to room temperature. The precipitate formed was filtered and suspended in 10 mL of p-xylene. The solution was heated at reflux temperature for 24 hours after the addition of a catalytic amount of iodine. The reaction was allowed to cool, the precipitate formed was filtered and purified by using flash chromatography (silica gel, hexane/dichloromethane 7:3) to yield 330 mg (64 %) of 10a as a yellow solid. M.p.: 74-76 °C (hexane/dichloromethane).  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ , 200 MHz)  $\delta$  7.62 (s, 2H), 7.46 (s, 1H), 7.33 (d, 4H,  $J = 8.6$  Hz), 7.03 (d, 2H,  $J_{\text{trans}} = 16.2$  Hz), 6.74 (d, 2H,  $J_{\text{trans}} = 16.2$  Hz), 6.57 (d, 4H,  $J = 8.6$  Hz), 3.23 (t, 8H), 1.52 (m, 8H), 1.28 (m, 8H), 0.89 (t, 12H).  $^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ , 50 MHz)  $\delta$  148.9, 140.4, 131.9, 128.8, 128.0, 127.4, 124.1, 121.8, 120.0, 113.5, 112.2, 51.4, 30.4, 30.1, 21.0, 14.7. FTIR (KBr,  $\text{cm}^{-1}$ ) 2955, 2926, 2860, 2226, 1607, 1581, 1520, 1369, 1186, 970, 840. MS  $m/z$  (EI) (%I): 561 ( $\text{M}^+$ , 64), 518

(100), 476 (20), 238 (20), 196 (26), 69 (32), 57 (53). Anal. Calc. for  $C_{39}H_{51}N_3$ : C: 83.37, H: 9.15, N: 7.48. Found C: 83.40, H: 9.18, N: 7.46.

*Via Wittig-Horner reaction:*

General procedure for Wittig-Horner reactions: Under argon atmosphere, 224 mg (2.0 mmol) of potassium tert-butoxide were added portion-wise to a solution of 1.0 mmol of the bisphosphonate and 2.0 mmol of the aldehyde in 20 mL of dry THF at 0 °C. The reaction was stirred for 10 minutes and after this time methanol and water were added. The two phases obtained were separated. The aqueous layer was extracted with chloroform and the combined organic layers were washed with water and dried with magnesium sulfate. The solvent was vacuum evaporated and the residue was chromatographed to yield the pure product.

Synthesis of **10a**: Following the above general procedure for Wittig-Horner reactions, 224 mg (2.0 mmol) of potassium tert-butoxide, 347 mg (1.0 mmol) of 3,5-bis(dimethylphosphonomethyl)benzonitrile (**11**) and 0.48 mL (466 mg, 2.0 mmol) of 4-(N,N-dibutylamino)benzaldehyde (**9**) were reacted. After chromatographic purification (silica gel, hexane / dichloromethane 7:3), 375 mg (67 %) of **10a** were obtained as a yellow solid.

**3,5-Bis[2'-4(dibutylaminophenyl)vinyl]benzaldehyde (5a)**

Via Wittig reaction: 6.15 mL (6.15 mmol) of a 1.0 M solution of lithium ethoxide in ethanol were added dropwise to a refluxing solution of 3.72 g (6.15 mmol) of N,N-dibutylamino-4-(triphenylphosphoniummethyl)benzene (**4**) and 557 mg (3.32 mmol) of 1,3,5-triformylbenzene (**3**) under argon atmosphere. After 4 hours the crude reaction was allowed to cool to room temperature. The precipitate formed was filtered and suspended in 30 mL of p-xylene. The

solution was heated at reflux temperature for 24 hours after the addition of a catalytic amount of iodine. The reaction was allowed to cool, the precipitate formed was filtered and purified by using flash chromatography (silica gel, hexane/dichloromethane 7:3) to yield 1.2 g (65 %) of **5a** as a yellow solid. M.p.: 60-63°C (hexane/dichloromethane).  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 200 MHz)  $\delta$  9.98 (s, 1H), 7.79 (s, 2H), 7.76 (s, 1H), 7.41 (d, 4H,  $J = 8.8$  Hz), 7.16 (d, 2H,  $J_{\text{trans}} = 16.4$  Hz), 6.91 (d, 2H,  $J_{\text{trans}} = 16.4$  Hz), 6.64 (d, 4H,  $J = 8.8$  Hz), 3.23 (t, 8H), 1.53 (m, 8H), 1.29 (m, 8H), 0.90 (t, 12H).  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ , 50 MHz)  $\delta$  192.7, 148.1, 139.5, 136.9, 130.5, 129.3, 127.9, 124.7, 123.8, 121.9, 111.5, 50.7, 29.4, 20.7, 13.9. FTIR (KBr,  $\text{cm}^{-1}$ ): 2954, 2927, 1697, 1606, 1583, 1517, 1186, 960, 802. MS  $m/z$  (EI) (%I): 564 ( $\text{M}^+$ , 100), 521 (97), 479 (36), 239 (33), 218 (33), 197 (35), 190 (25), 57 (32). Anal. Calc. for  $\text{C}_{39}\text{H}_{52}\text{N}_2\text{O}$ : C: 82.93; H: 9.28; N: 4.96. Found C: 80.17; H: 9.25; N: 4.62.

***Via DIBAL-H reduction:***

General procedure for DIBAL-H reductions: 0.34 mL (0.34 mmol) of a 1.0 M solution of diisobutylaluminum hydride in dichloromethane were added drop-wise under argon atmosphere to a refluxing solution of 0.34 mmol of the corresponding cyano-derivative in 25 mL of dry dichloromethane. After 5 hours the reaction was allowed to cool to room temperature and small amounts of concentrated hydrochloric acid were added until the white precipitate formed was fully redissolved. The two layers formed were separated and the aqueous layer was extracted with dichloromethane. The combined organic layers were washed with water, and dried with magnesium sulfate. After the solvent was vacuum evaporated, the residue was chromatographed to yield the pure product.

Synthesis of **5a**: Following the above general procedure for DIBAL-H reductions, 346 mg (0.62 mmol) of **10a** were reacted with 0.62 mL (0.62 mmol) of a 1.0 M solution of DIBAL-H in dichloromethane. After the chromatographic purification (silica gel, hexane / methylene chloride 6:4), 225 mg (73 %) of **5a** were obtained as a yellow solid.

### 3,5-Bis[2'-(6-dodecyloxy-2-naphthyl)vinyl]bromobenzene (**13**)

Following the above general procedure for Wittig-Horner reactions, 112 mg (1.0 mmol) of potassium tert-butoxide, 200 mg (0.5 mmol) of 3,5-bis(dimethylphosphonatemethyl)bromobenzene (**11b**) and 340 mg (1.0 mmol) of 2-dodecyloxy-6-formylnaphthalene (**12**) were reacted. After crystallization from chloroform/methanol, 325 mg (78 %) of **13** were obtained as a yellow solid. M.p.: 161-163 °C (chloroform/methanol). <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 200 MHz) δ 7.73 (s, 2H), 7.69 (s, 1H), 7.64 (s, 4H), 7.50 (s, 2H), 7.21 (d, 2H, J<sub>trans</sub> = 16.2 Hz), 7.12-7.10 (m, 2H), 7.06 (s, 4H), 7.03 (d, 2H, J<sub>trans</sub> = 16.2 Hz), 4.01 (t, 4H), 1.75 (m, 4H), 1.48-1.18 (m, 36H), 0.81 (t, 6H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 50 MHz) δ 157.6, 139.9, 134.5, 132.0, 130.6, 129.6, 128.9, 127.8, 127.2, 127.0, 126.2, 123.9, 123.3, 119.5, 106.7, 68.1, 31.9, 29.6, 29.4, 29.4, 29.3, 26.1, 22.7, 14.1. FTIR (KBr, cm<sup>-1</sup>) 2920, 2852, 1626, 1597, 1472, 1273, 1178, 1034, 957, 862, 843. MS m/z (ESI) 853 ([M<sup>+</sup>+23]).

### 3,5-Bis[2'-(6-dodecyloxy-2-naphthyl)vinyl] benzonitrile (**10b**)

A suspension of 1.34 g (1.6 mmol) of **13**, 241 mg (2.4 mmol) of copper cyanide and a catalytic amount of sodium iodide in 45 mL of N,N-dimethylformamide was refluxed under argon atmosphere for 72 hours. After this time the reaction was cooled to room temperature and then poured into a 15 % solution of ammonia in water. A solid precipitated and was filtered and

washed with another portion of ammonia solution and then with water. The solid was dried under vacuum and then chromatographed (silica gel, hexane / dichloromethane 6:4) to yield 740 mg (60 %) of **10b** as a white solid. M.p.: 94-97 °C (hexane/dichloromethane). <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 200 MHz) δ 7.79 (s, 2H), 7.76 (s, 2H), 7.71 (s, 1H), 7.66 (s, 4H), 7.61 (s, 2H), 7.27 (d, 2H, J<sub>trans</sub> = 16.3 Hz), 7.12 (s, 2H), 7.07 (s, 2H), 7.08 (d, 2H, J<sub>trans</sub> = 16.3 Hz), 4.01 (t, 4H), 1.79 (m, 4H), 1.20 (s, 36H), 0.81 (t, 6H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 50 MHz) δ 157.7, 139.2, 134.6, 131.6, 131.6, 129.5, 128.8, 128.0, 127.3, 127.2, 125.3, 123.8, 119.5, 118.8, 113.3, 106.7, 68.1, 31.8, 29.6, 29.5, 29.3, 29.3, 29.2, 26.0, 22.6, 14.0. FTIR (KBr, cm<sup>-1</sup>) 2920, 2852, 2235, 1626, 1599, 1472, 1273, 1180, 1034, 970, 862. MS m/z (ESI): 775 ([M<sup>+</sup>+H]<sup>+</sup>). Anal. Calc. for C<sub>55</sub>H<sub>69</sub>NO<sub>2</sub>: C: 85.10, H: 8.97, N: 1.81. Found C: 83.92, H: 8.98, N: 1.70.

### 3,5-Bis[2'-(6-dodecyloxy-2-naphthyl)vinyl] benzaldehyde (**5b**)

Following the above general procedure for DIBAL-H reduction, 140 mg (0.18 mmol) of **10a** were reacted with 0.18 mL (0.18 mmol) of a 1.0 M solution of DIBAL-H in dichloromethane. After the chromatographic purification (silica gel, hexane / methylene chloride 6:4), 100 mg (71 %) of **5a** were obtained as a yellowish solid. M.p.: 101-103 °C (hexane/dichloromethane). <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 200 MHz) δ 10.04 (s, 1H), 7.87 (s, 2H), 7.78 (s, 2H), 7.71 (s, 1H), 7.67 (s, 6H), 7.32 (d, 2H, J<sub>trans</sub> = 16.3 Hz), 7.12-7.07 (m, 6H), 4.02 (t, 4H), 1.79 (m, 4H), 1.20 (s, 36H), 0.81 (t, 6H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 50 MHz) δ 157.8, 139.1, 138.0, 137.4, 134.7, 132.5, 132.1, 131.0, 129.7, 129.1, 127.4, 127.2, 126.3, 124.0, 119.7, 106.9, 68.3, 32.1, 29.8, 29.8, 29.8, 29.6, 29.5, 29.4, 26.3, 22.8, 14.3. FTIR (KBr, cm<sup>-1</sup>) 2920, 2852, 1701, 1626, 1601, 1473, 1389, 1270, 1246, 1028, 959, 860. MS m/z (ESI): 801 ([M<sup>+</sup>+23]). Anal. Calc. for C<sub>55</sub>H<sub>70</sub>O<sub>3</sub>: C: 84.77, H: 9.06. Found C: 83.69, H: 9.06.

**Second generation dendrons****3,5-Bis{2'[3,5-bis[2'-(4-dibutylaminophenyl)vinyl]phenylvinyl]}benzonitrile (14a)**

Following the above general procedure for Wittig-Horner reactions, 200 mg (1.79 mmol) of potassium tert-butoxide, 312 mg (0.9 mmol) of 3,5-bis(dimethylphosphonatomethyl)benzonitrile (**11a**) and 1.01 g (1.79 mmol) of aldehyde **5a** were reacted. After chromatography (silica gel, hexane / dichloromethane 1:1) 865 mg (78 %) of **14a** were obtained as a yellow solid. M.p.: 108-110°C (hexane/dichloromethane). <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 200 MHz) δ 7.70 (s, 2H), 7.49 (s, 3H), 7.43 (d, 8H, J = 8.8 Hz), 7.23 (s, 2H), 7.20 (s, 2H), 7.14 (d, 6H, J<sub>trans</sub> = 16.4 Hz), 6.92 (d, 6H, J<sub>trans</sub> = 16.4 Hz), 6.66 (d, 8H, J = 8.8 Hz), 3.23 (t, 16H), 1.53 (m, 16H), 1.25 (m, 16H), 0.78 (t, 24H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 75 MHz) δ 147.9, 139.3, 139.0, 138.9, 137.2, 137.1, 130.9, 130.2, 129.3, 127.8, 127.0, 126.3, 124.3, 123.6, 123.3, 122.6, 114.0, 111.6, 50.8, 29.5, 20.3, 14.0. FTIR (KBr, cm<sup>-1</sup>) 2925, 2854, 2226, 1606, 1583, 1517, 1186, 959. EM m/z (ESI): 1225 ([M<sup>+</sup>+H]). Anal. Calc. for C<sub>87</sub>H<sub>109</sub>N<sub>5</sub>: C: 85.31; H: 8.97; N: 5.71. Found C: 85.45; H: 9.66; N: 4.76.

**3,5-Bis{2'[3,5-bis[2'-(6-dodecyloxy-2-naphthyl)vinyl]phenylvinyl]}benzo-nitrile (14b)**

Following the above general procedure for Wittig-Horner reactions, 12 mg (0.1 mmol) of potassium tert-butoxide, 18 mg (0.05 mmol) of 3,5-bis(dimethyl phosphonatemethyl)benzonitrile (**11**) and 80 mg (0.1 mmol) of aldehyde **5b** were reacted. After crystallization from chloroform / methanol, 75 mg (90 %) of **14b** were obtained as a yellow solid. M.p.: 76-79 °C (chloroform/methanol). <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 200 MHz) δ 7.74 (s, 4H), 7.68 (s, 2H), 7.65 (s, 8H), 7.59-7.56 (m, 6H), 7.50 (s, 4H), 7.30 (d, 6H, J<sub>trans</sub> = 16.1 Hz), 7.16 (s, 3H), 7.18-7.16 (m, 2H), 7.05 (s, 8H), 3.99 (t, 8H), 1.78 (m, 8H), 1.21 (s, 72H), 0.82 (t, 12H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 75 MHz)



$\delta$  157.5, 138.4, 137.0, 134.4, 132.3, 131.6, 129.7, 129.5, 128.9, 128.5, 127.2, 126.8, 123.9, 119.4, 106.8, 68.1, 31.9, 29.7, 29.5, 29.4, 29.3, 26.1, 22.7, 14.1. FTIR (KBr,  $\text{cm}^{-1}$ ) 2922, 2852, 2220, 1624, 1601, 1466, 1389, 1270, 1242, 1184, 960. MS  $m/z$  (APCI): 1654 ( $[\text{M}^+ + \text{H}]^+$ ). Anal. Calc. for  $\text{C}_{119}\text{H}_{145}\text{NO}_4$ : C: 86.44, H: 8.84, N: 0.85. Found C: 82.28, H: 9.00, N: 1.29.

### 3,5-Bis{2'[3,5-bis[2'-(4-dibutylaminophenyl)vinyl]phenylvinyl]}benzaldehyde (15a)

Following the above general procedure for DIBAL-H reduction, 200 mg (0.2 mmol) of **14a** were reacted with 0.2 mL (0.2 mmol) of a 1.0 M solution of DIBAL-H in dichloromethane. After the chromatographic purification (silica gel, hexane / methylene chloride 6:4), 165 mg (82 %) of **14a** were obtained as a yellow solid. M.p.: 111-114°C (hexane/dichloromethane).  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  10.04 (s, 1H), 7.88 (s, 2H), 7.44 (s, 3H), 7.36 (d, 8H,  $J = 8.7$  Hz), 7.23 (s, 2H), 7.21 (s, 2H), 7.07 (d, 6H,  $J_{\text{trans}} = 16.2$  Hz), 6.86 (d, 6H,  $J_{\text{trans}} = 16.2$  Hz), 6.58 (d, 8H,  $J = 8.7$  Hz), 3.24 (t, 16H), 1.56 (m, 16H), 1.22 (m, 16H), 0.76 (t, 24H).  $^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ , 50 MHz)  $\delta$  192.4, 148.0, 139.1, 138.9, 137.3, 137.2, 131.0, 130.25, 129.4, 127.9, 127.1, 126.4, 124.5, 123.7, 123.4, 122.6, 111.7, 50.8, 29.5, 20.4, 14.1. FTIR (KBr,  $\text{cm}^{-1}$ ) 3018, 2960, 2928, 1690, 1605, 1581, 1520, 1215, 1188, 962, 758. MS  $m/z$  (ESI): 1228 ( $[\text{M}^+ + \text{H}]^+$ ).

### 3,5-Bis{2'[3,5-bis[2'-(6-dodecyloxy-2-naphthyl)vinyl]phenylvinyl]}benz-aldehyde (15b)

Following the above general procedure for DIBAL-H reduction, 100 mg (0.06 mmol) of **14b** were reacted with 0.06 mL (0.06 mmol) of a 1.0 M solution of DIBAL-H in dichloromethane. After the chromatographic purification (silica gel, hexane / methylene chloride 6:4), 85 mg (86 %) of **15b** were obtained as a yellowish solid. M.p.: 96-99 °C (hexane/dichloromethane).  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  9.80 (s, 1H), 7.76 (s, 4H), 7.67 (s,

2H), 7.65 (s, 8H), 7.57-7.54 (m, 6H), 7.50 (s, 4H), 7.33 (d, 6H,  $J_{\text{trans}} = 16.1$  Hz), 7.17 (s, 3H), 7.14-7.10 (m, 4H), 7.03 (s, 8H), 4.01 (t, 8H), 1.78 (m, 8H), 1.23 (s, 72H), 0.81 (t, 12H).  $^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$  157.4, 138.6, 138.3, 137.3, 134.4, 132.4, 129.5, 129.0, 127.2, 126.7, 124.0, 119.4, 106.7, 68.0, 31.9, 29.6, 29.5, 29.3, 26.1, 22.6, 14.1. FTIR (KBr,  $\text{cm}^{-1}$ ) 2922, 2851, 1697, 1624, 1599, 1506, 1468, 1388, 1270, 1240, 1213, 1028, 957 1270. MS  $m/z$  (APCI): 1657 ( $[\text{M}^+ + \text{H}]^+$ ). Anal. Calc. for  $\text{C}_{119}\text{H}_{146}\text{O}_5$ : C: 86.29%, H: 8.88%. Found C: 84.26, H: 8.94.

### 1,3-Dipolar cycloaddition reactions

#### *Synthesis of dyads*

General procedure: 0.05 mmol of the corresponding aldehyde, 38 mg (0.05 mmol) of [60]fullerene and 0.25 mmol of N-methylglycine (sarcosine) were dissolved in 30 mL of toluene and the mixture was refluxed for 24 hours. After this time the reaction was allowed to reach room temperature, then the solvent was partially vacuum evaporated and then poured on a silica-gel column. The black solid obtained after chromatography (cyclohexane/toluene) was further purified by repetitive centrifugation using methanol and diethyl ether to yield the corresponding dyads as black solids.

#### **N-Methyl-2'-{3,5-bis[2'(4-dibutylaminophenyl)vinyl]phenyl}pyrrolidino[3',4':1,2]-[60]fullerene (1a):**

By following the above general procedure and using 100 mg (0.22 mmol) of aldehyde **5a**, 160 mg (0.22 mmol) of [60]fullerene and 99 mg (1.1 mmol) of N-methylglycine as reagents, 60 mg (26 %) of **1a** were obtained after chromatography (silica gel, cyclohexane / toluene 6:4) as a black solid.  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ , 200 MHz)  $\delta$  7.46 (s, 2H), 7.35, (s, 1H), 7.21 (d, 4H,  $J = 8.7$  Hz),

6.91 (d, 2H, d,  $J_{\text{trans}} = 16.2$  Hz), 6.73 (d, 2H,  $J_{\text{trans}} = 16.2$  Hz), 6.44 (d, 4H,  $J = 8.1$  Hz), 5.03 (d, 1H,  $J = 9.4$  Hz), 4.93 (s, 1H), 4.10 (d, 1H,  $J = 9.4$  Hz), 3.11 (t, 8H), 2.69 (s, 3H), 1.39 (m, 8H), 1.19 (m, 8H), 1.03 (t, 12H).  $^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  157.81, 155.74, 155.23, 155.16, 148.56, 148.00, 147.95, 147.57, 147.20, 147.02, 146.92, 146.90, 146.82, 146.80, 146.76, 146.62, 146.59, 146.51, 146.22, 146.18, 146.01, 145.97, 145.92, 145.85, 145.35, 145.11, 145.04, 143.81, 143.63, 143.34, 143.23, 143.21, 143.20, 142.99, 142.93, 142.82, 142.75, 142.71, 142.65, 142.58, 142.35, 142.29, 140.84, 140.79, 140.66, 140.33, 130.05, 128.53, 125.06, 124.35, 124.22, 124.19, 124.16, 112.31, 84.49, 77.90, 70.84, 69.79, 51.06, 40.96, 30.17, 21.04, 14.71. FTIR (KBr,  $\text{cm}^{-1}$ ) 2950, 2865, 1605, 1584, 1516, 1456, 1397, 1282, 1218, 1185, 156, 800, 526. MS  $m/z$  (ESI): 1311 ( $[\text{M}^+ + \text{H}]^+$ ). Anal. Calc. for  $\text{C}_{101}\text{H}_{57}\text{N}_3$ : C: 93.23; H: 3.36; N: 3.51. Found C: 93.20; H: 3.66; N: 3.15.

**N-Methyl-3,5-bis[2'-(6-dodecyloxy-2-naphthyl)vinyl]pyrrolidino[3',4':1,2]-[60]fullerene (1b):**

By following the above general procedure and using 60 mg (0.08 mmol) of aldehyde **5b**, 56 mg (0.08 mmol) of [60]fullerene and 34 mg (0.38 mmol) of N-methylglycine as reagents, 41 mg (35 %) of **1b** were obtained after chromatography (silica gel, cyclohexane / toluene 1:1) as a black solid.  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  7.73 (s, 3H), 7.67 (s, 1H), 7.63 (s, 6H), 7.31 (d, 2H,  $J_{\text{trans}} = 16.6$  Hz), 7.17 (s, 1H), 7.08 (s, 2H), 7.04 (s, 4H), 5.02 (d, 1H,  $J = 9.3$  Hz), 4.91 (s, 1H), 4.23 (d, 1H,  $J = 9.3$  Hz), 3.99 (t, 4H), 2.80 (s, 3H), 1.77 (m, 4H), 1.20 (s, 36H), 0.81 (t, 6H).  $^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  157.41, 156.12, 154.00, 153.41, 153.30, 147.30, 147.28, 146.74, 146.46, 146.33, 146.26, 146.21, 146.13, 146.09, 146.04, 145.93, 145.92, 145.79, 145.55, 145.52, 145.46, 145.35, 145.33, 145.30, 145.25, 145.22, 145.17, 144.68, 144.62, 144.38, 143.14, 142.98,

142.68, 142.55, 142.52, 142.29, 142.24, 142.14, 142.10, 142.05, 142.03, 142.02, 141.96, 141.86, 141.68, 141.60, 140.19, 140.16, 140.02, 139.65, 137.85, 136.72, 136.62, 135.88, 135.77, 134.35, 132.38, 129.64, 129.49, 128.96, 127.16, 126.73, 124.43, 124.00, 119.39, 106.70, 83.62, 77.04, 70.10, 69.10, 68.07, 31.91), 29.69, 29.63, 29.42, 29.34, 29.23, 26.10, 22.69, 14.12. FTIR (KBr,  $\text{cm}^{-1}$ ) 2920, 2849, 1599, 1463, 1388, 1182, 953, 526. MS  $m/z$  (ESI): 1548 ( $[\text{M}^+ + 23]$ ). Anal. Calc. for  $\text{C}_{117}\text{H}_{75}\text{NO}_2$ : C: 92.04, H: 4.95, N: 0.92. Found C: 91.28, H: 5.30, N: 1.01.

**N-Methyl-3,5-bis{2'-[3,5-bis(2'(4-dibutylaminophenyl)vinyl]phenylvinyl}-pyrrolidino[3',4':1,2]-[60]fullerene (2a):**

By following the above general procedure and using 90 mg (0.09 mmol) of aldehyde **15a**, 65 mg (0.09 mmol) of [60]fullerene and 40 mg (0.45 mmol) of N-methylglycine as reagents, 41 mg (35 %) of **2a** were obtained after chromatography (silica gel, cyclohexane / toluene 4:6) as a black solid.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 200 MHz)  $\delta$  7.58 (s, 2H), 7.38 (s, 2H), 7.33 (d, 8H,  $J = 8.8$  Hz), 7.13 (s, 5H), 7.04 (d, 6H,  $J_{\text{trans}} = 16.2$  Hz), 6.82 (d, 6H,  $J_{\text{trans}} = 16.2$  Hz), 6.56 (d, 8H,  $J = 8.8$  Hz), 4.95 (d, 1H,  $J = 9.5$  Hz), 4.91 (s, 1H), 4.22 (d, 1H,  $J = 9.5$  Hz), 3.23 (t, 16H), 2.83 (s, 3H), 1.52 (m, 12H), 1.20 (m, 32H), 0.89 (t, 24H).  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  156.82, 154.72, 154.12, 154.00, 148.53, 148.02, 147.96, 147.44, 147.17, 147.04, 146.95, 146.91, 146.84, 146.81, 146.77, 146.72, 146.63, 146.59, 146.52, 146.29, 146.23, 146.22, 146.16, 146.06, 146.02, 146.01, 145.99, 145.93, 145.88, 145.36, 145.12, 145.06, 143.85, 143.77, 143.66, 143.36, 143.26, 143.23, 143.22, 143.03, 142.95, 142.84, 142.82, 142.76, 142.75, 142.72, 142.70, 142.60, 142.35, 142.33, 140.86, 140.83, 140.77, 140.40, 139.55, 138.53, 138.52, 137.43, 137.37, 136.59, 136.50, 130.36, 130.35, 129.89, 128.54, 125.42, 125.18, 124.19, 123.99, 123.98, 123.26, 112.32, 84.27, 77.78, 70.82, 69.82, 51.49, 40.94, 30.19, 21.06, 14.72. FTIR (KBr,  $\text{cm}^{-1}$ ) 2922, 2853, 1604, 1579, 1515, 1326,

1184, 955, 526. EM m/z (APCI): 1976 ( $[M^+ + H]^+$ ), 721 ( $[C_{60}^+ + H]^+$ ). Anal. Calc. for  $C_{149}H_{115}N_5$ : C: 90.63; H: 5.83; N: 3.52. Found C: 88.16; H: 5.57; N: 3.38.

**N-Methyl-3,5-bis{2'-[bis(2'(6-dodecyloxy-2-naphthyl)vinyl)vinylphenyl]-pyrrolidino[3',4':1,2]-[60]fullerene (2b):**

By following the above general procedure and using 70 mg (0.042 mmol) of aldehyde **15b**, 30 mg (0.042 mmol) of [60]fullerene and 34 mg (0.38 mmol) of N-methylglycine as reagents, 30 mg (30 %) of **2b** were obtained after chromatography (silica gel, cyclohexane / toluene 7:3) as a black solid.  $^1H$ -NMR ( $CDCl_3$ , 300 MHz)  $\delta$  7.75 (s, 4H), 7.69 (s, 2H), 7.64 (s, 8H), 7.57-7.54 (m, 6H), 7.51 (s, 4H), 7.32 (d, 6H,  $J_{trans} = 16.6$  Hz), 7.20 (s, 3H), 7.14-7.10 (m, 4H), 7.03 (s, 8H), 4.80 (d, 1H,  $J = 9.6$  Hz), 4.88 (s, 1H), 4.12 (d, 1H,  $J = 9.6$  Hz), 3.97 (t, 8H), 2.76 (s, 3H), 1.75 (m, 8H), 1.48 (s, 8H), 1.20 (s, 64H), 0.81 (t, 12H).  $^{13}C$ -RMN ( $CDCl_3$ , 125 MHz)  $\delta$  152.59, 141.60, 140.94, 140.69, 140.51, 140.42, 140.32, 140.08, 139.87, 139.72, 139.68, 139.41, 139.34, 139.30, 138.43, 136.44, 136.09, 135.94, 135.83, 131.39, 131.31, 131.19, 127.39, 125.35, 122.31, 122.12, 121.94, 121.84, 121.80, 121.53, 120.01, 119.57, 119.12, 116.27, 116.10, 110.98, 97.16, 64.91, 54.89, 29.52, 29.34, 29.32, 26.30, 22.79, 14.15. FTIR (KBr,  $cm^{-1}$ ) 2926, 2854, 1600, 1467, 1268, 1244, 1183, 960, 526. MS m/z (APCI): 2405 ( $[M^+ + H]^+$ ). Anal. Calc. for  $C_{181}H_{151}NO_4$ : C: 90.42, H: 6.33, N: 0.58. Found C: 88.21, H: 6.32, N: 0.66.

**N-Methyl-2'(4-dibutylaminophenyl)pyrrolidino[3',4':1,2][60]fullerene (16)**

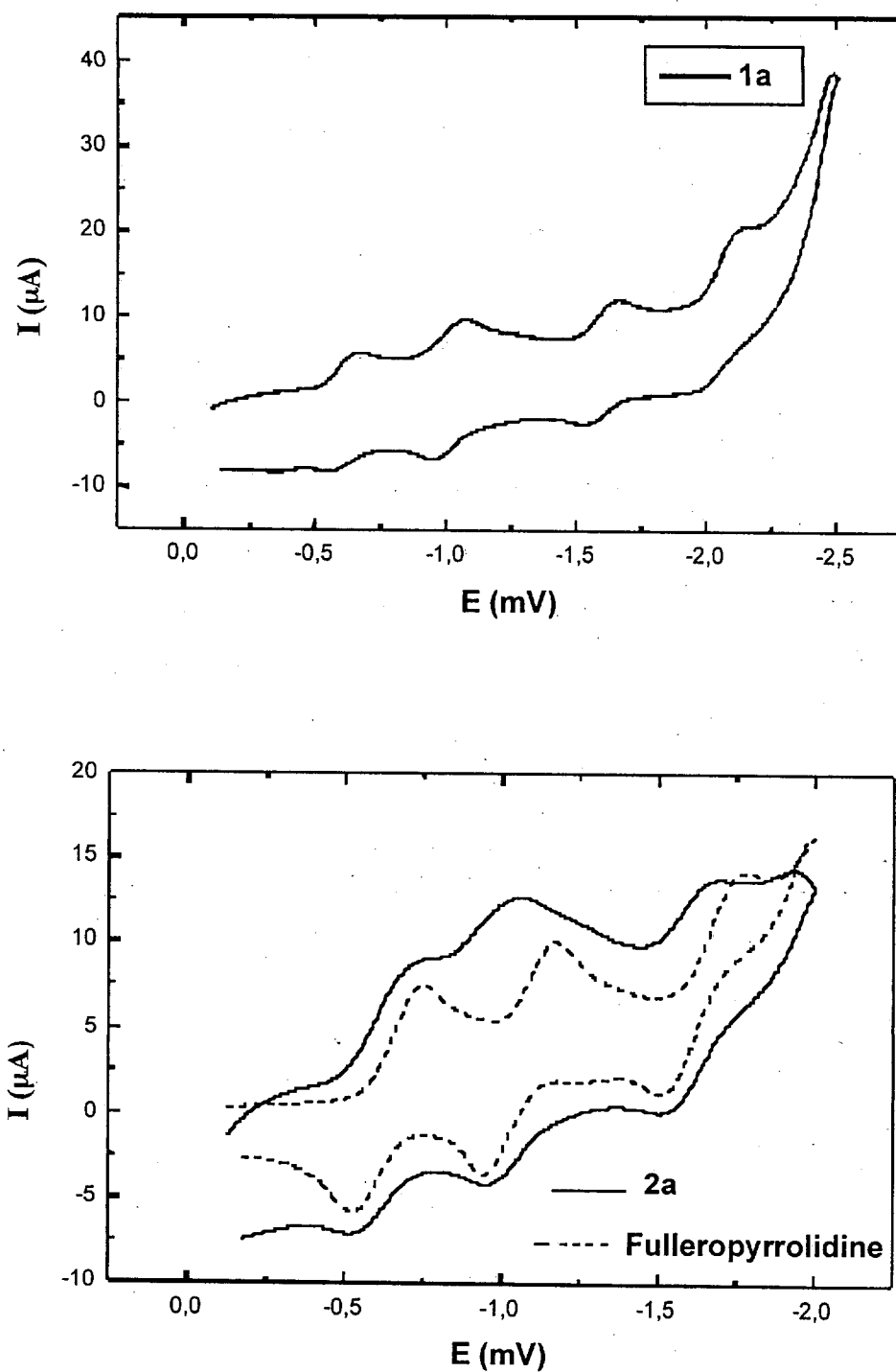
By following the above general procedure and using 0.19 mL (100 mg, 0.43 mmol) of 4-(N,N-dibutylamino)benzaldehyde (**9**), 310 mg (0.43 mmol) of [60]fullerene and 191 mg (2.15 mmol) of N-methylglycine as reagents, 160 mg (38 %) of **16** were obtained after

chromatography (silica gel, cyclohexane / toluene 1:1) as a black solid.  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  7.75 (d, 2H,  $J$ = 8.4 Hz), 6.82 (d, 2H,  $J$ = 8.4 Hz), 5.13 (d, 1H,  $J$ = 9.4 Hz), 4.98 (s, 1H), 4.38 (d, 1H,  $J$ = 9.4 Hz), 3.41 (t, 4H), 2.96 (s, 3H), 1.74 (m, 4H), 1.51-1.44 (m, 4H), 1.11 (t, 6H).  $^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$  144.22, 144.20, 143.22, 143.20, 143.14, 143.08, 143.04, 143.02, 142.84, 143.02, 142.83, 142.84, 142.72, 142.71, 142.48, 142.46, 142.38, 142.28, 142.23, 142.20, 142.16, 142.11, 142.09, 142.06, 141.63, 141.54, 141.32, 140.07, 140.04, 139.61, 139.52, 139.49, 139.21, 139.20, 139.19, 139.09, 139.07, 139.04, 139.02, 138.96, 138.92, 138.60, 138.50, 137.09, 137.03, 136.87, 132.70, 127.54, 127.50, 127.45, 127.42, 127.40, 127.36, 127.35, 137.33, 137.32, 137.30, 137.28, 137.26, 137.25, 137.25, 74.20, 66.90, 65.85, 36.99, 26.20, 17.31, 10.93, 10.96, 31.91, 29.69. FTIR (KBr,  $\text{cm}^{-1}$ ) 2956, 2866, 2775, 1618, 1512, 1461, 1183, 526. MS  $m/z$  (ESI): 981 ( $[\text{M}^+ + \text{H}]^+$ ). Anal. Calc. Anal. Calc. for  $\text{C}_{77}\text{H}_{29}\text{N}_2$ : C: 94.27, H: 2.88, N: 2.86. Found C: 93.87, H: 3.01, N: 2.90.

#### **N-Methyl-2'(6-dodecyloxy-2-naphthyl)pyrrolidino[3',4':1,2][60]fullerene (17)**

By following the above general procedure and using 100 mg (0.29 mmol) of 2-dodecyloxy-6-formylnaphthalene (12), 211 mg (0.29 mmol) of [60]fullerene and 129 mg (1.45 mmol) of N-methylglycine as reagents, 106 mg (34 %) of 17 were obtained after chromatography (silica gel, cyclohexane / toluene 6:4) as a black solid.  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  8.00 (m, 2H), 7.65 (d, 2H,  $J$ = 8.4 Hz), 7.04 (d, 1H,  $J$ = 2.4 Hz), 6.99 (s, 1H), 4.97 (s, 1H), 4.96 (d, 1H,  $J$ = 9.4 Hz), 4.21 (d, 1H,  $J$ = 9.4 Hz), 3.92 (t, 2H), 2.96 (s, 3H), 1.70 (q, 2H), 1.41 (s, 2H), 1.13 (s, 16H), 1.11 (t, 3H).  $^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$  158.72, 148.40, 148.38, 148.10, 147.42, 147.35, 147.31, 147.25, 147.23, 147.19, 147.03, 147.01, 146.88, 146.61, 146.47, 146.40, 146.35, 146.33, 146.27, 145.80, 145.65, 145.46, 144.22, 144.08, 143.78, 143.68, 143.66, 143.61,

143.34, 143.31, 143.26, 143.17, 143.15, 143.10, 143.07, 143.01, 142.94, 142.78, 142.59, 141.27, 141.25, 141.02, 140.69, 137.02, 136.82, 135.91, 130.69, 130.67, 130.64, 130.63, 130.62, 120.59, 107.58, 84.94, 78.35, 69.16, 41.25, 33.06, 30.77, 30.75, 30.56, 30.51, 30.35, 27.26, 23.86, 15.29. FTIR (KBr,  $\text{cm}^{-1}$ ) 2926, 2854, 2275, 1639, 1606, 1467, 1268, 1220, 1183, 526. MS  $m/z$  (ESI): 981 ( $[\text{M}^+ + \text{H}]^+$ ). Anal. Calc. Anal. Calc. for  $\text{C}_{85}\text{H}_{24}\text{NO}$ : C: 93.28, H: 3.43, N: 1.29. Found C: 93.87, H: 3.64, N: 1.30.



**Figure S1:** Cyclic voltammograms of dyads **1a** (upper part), **2a** and fulleropyrrolidine (lower part) in dichloromethane solution. Scan rate  $200 \text{ mVs}^{-1}$ .