## **Supporting Information**

## Electrosynthesis and electrochromic properties of poly(amidetriarylamine)s containing triptycene units

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## Monomer synthesis and characterization data

The synthesis of **T-TPA-C** was used as an example to illustrate the general synthetic route used to produce the triptycene bis(amide-triarylamine) monomers. A mixture of 0.328 g (0.7 mmol) of triptycene-bis(ether amine) **3**, 0.463 g (1.6 mmol) of 4-carboxytriphenylamine **(6)**, 0.05 g of calcium chloride, 0.7 mL of triphenyl phosphite, 0.2 mL of pyridine, and 0.7 mL of NMP was heated with stirring at 120 °C for 3 h. The resulting solution was poured slowly with stirring into 50 mL of methanol, giving rise to a powdery precipitate. The precipitated product was collected by filtration, washed repeatedly with methanol and hot water, and dried to afford monomer **T-TPA-C** as a pale yellow solid (yield = 92%); mp 263–264 °C. The IR spectrum of **T-TPA-C** exhibited characteristic amide absorption bands at 3300 cm<sup>-1</sup> (N–H stretch) and 1650 cm<sup>-1</sup> (C=O stretch). <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>,  $\delta$ , ppm): 5.82 (s, 2H, H<sub>b</sub>), 6.68 (s, 2H, H<sub>a</sub>), 6.90 (d, *J* = 9.0 Hz, 4H, H<sub>e</sub>), 6.98 (d, *J* = 8.5 Hz, 4H, H<sub>h</sub>), 7.02 (dd, *J* = 5.0 and 3.0 Hz, 4H, H<sub>c</sub>), 7.12 (d, *J* = 7.5 Hz, 8H, H<sub>i</sub>), 7.17 (t, *J* = 7.5 Hz, 4H, H<sub>k</sub>), 7.38 (m, 12H, H<sub>d</sub> + H<sub>j</sub>), 7.75 (d, *J* = 9.0 Hz, 4H, H<sub>f</sub>), 7.87 (d, *J* = 9.0 Hz, 4H, H<sub>g</sub>), 10.10 (amide proton). <sup>13</sup>C NMR (125 MHz, DMSO-*d*<sub>6</sub>,  $\delta$ , ppm): 47.04 (C<sup>4</sup>), 117.52 (C<sup>3</sup>), 117.78 (C<sup>1</sup>), 120.06 (C<sup>14</sup>), 121.90 (C<sup>10</sup>), 123.88 (C<sup>7</sup>), 124.20 (C<sup>19</sup>), 125.11 (C<sup>17</sup>), 125.18 (C<sup>6</sup>), 129.02 (C<sup>13</sup>), 129.26 (C<sup>12</sup>), 129.70 (C<sup>18</sup>), 134.59 (C<sup>11</sup>), 138.10 (C<sup>3</sup>), 144.49 (C<sup>5</sup>), 146.33 (C<sup>16</sup>), 146.97 (C<sup>2</sup>), 150.14 (C<sup>15</sup>), 157.21 (C<sup>8</sup>), 164.63 (amide carbon).



**T-CBZ-C** was synthesized from the condensation of triptycene-bis(ether amine) **3** with *N*-(4-carboxyphenyl)carbazole (**7**) by a similar synthetic procedure as that of **T-TPA-C**. The yield of **T-CBZ-C** was 90%; mp 146–147 °C. The IR spectrum of **T-CBZ-C** exhibited characteristic amide absorption bands at 3300 cm<sup>-1</sup> (N–H stretch) and 1643 cm<sup>-1</sup> (C=O stretch). <sup>1</sup>H NMR (500 MHz, DMSO- $d_6$ ,  $\delta$ , ppm): 5.87 (s, 2H, H<sub>b</sub>), 6.73 (s, 2H, H<sub>a</sub>), 7.00 (d, *J* = 9.0 Hz, 4H, H<sub>e</sub>), 7.04 (dd, *J* = 5 and 3.5 Hz, 4H, H<sub>c</sub>), 7.33 (t, *J* = 8.0 Hz, 4H, H<sub>k</sub>), 7.39 (dd, *J* = 5 and 3.5 Hz, 4H, H<sub>d</sub>), 7.46–7.51 (m, 8H, H<sub>i</sub> + H<sub>j</sub>), 7.83 (d, *J* = 8.5 Hz, 4H, H<sub>h</sub>), 7.86 (d, *J* 

= 9.0 Hz, 4H, H<sub>f</sub>), 8.28 (d, *J* = 8.0 Hz, 4H, H<sub>l</sub>), 8.30 (d, *J* = 8.5 Hz, 4H, H<sub>g</sub>), 10.49 (amide proton). <sup>13</sup>C NMR (125 MHz, DMSO-*d*<sub>6</sub>, *δ*, ppm): 47.63 (C<sup>4</sup>), 110.15 (C<sup>18</sup>), 118.12 (C<sup>9</sup>), 118.45 (C<sup>1</sup>), 120.90 (C<sup>19</sup>), 121.06 (C<sup>20</sup>), 122.67 (C<sup>10</sup>), 123.48 (C<sup>21</sup>), 124.44 (C<sup>7</sup>), 125.75 (C<sup>6</sup>), 126.70 (C<sup>14</sup>), 126.87 (C<sup>17</sup>), 130.10 (C<sup>13</sup>), 134.05 (C<sup>12</sup>), 134.88 (C<sup>11</sup>), 138.75 (C<sup>3</sup>), 140.13 (C<sup>15</sup>), 140.23 (C<sup>16</sup>), 145.04 (C<sup>5</sup>), 147.51 (C<sup>2</sup>), 157.77 (C<sup>8</sup>), 165.05 (amide carbon).



Similarly, **T-TPA-N** was prepared from the condensation of triptycene-bis(ether carboxylic acid) **5** with two equivalent amount of 4-aminotriphenylamine **(8)** in 93% yield with a melting point of 262-263 °C. IR: 3300 cm<sup>-1</sup> (N–H stretch) and 1650 cm<sup>-1</sup> (C=O stretch). <sup>1</sup>H NMR (500 MHz, DMSO- $d_6$ ,  $\delta$ , ppm): 5.76 (s, 2H, H<sub>b</sub>), 6.86 (s, 2H, H<sub>a</sub>), 7.02 (m, 20H, H<sub>e</sub>+ H<sub>c</sub>+ H<sub>i</sub> + H<sub>k</sub>), 7.04 (d, *J* = 9.0 Hz, 4H, H<sub>h</sub>), 7.28 (t, *J* = 7.5 Hz, 8H, H<sub>j</sub>), 7.32 (dd, *J* = 5.5 and 3.0 Hz, 4H, H<sub>d</sub>), 7.75 (d, *J* = 9.0 Hz, 4H, H<sub>g</sub>), 8.01 (d, *J* = 9.0 Hz, 4H, H<sub>f</sub>), 10.20 (amide proton). <sup>13</sup>C NMR (125 MHz, DMSO- $d_6$ ,  $\delta$ , ppm): 47.11 (C<sup>4</sup>), 116.33 (C<sup>9</sup>), 119.22 (C<sup>1</sup>), 121.65 (C<sup>13</sup>), 122.32 (C<sup>19</sup>), 122.94 (C<sup>17</sup>), 123.92 (C<sup>7</sup>), 124.89 (C<sup>14</sup>), 125.34 (C<sup>6</sup>), 129.18 (C<sup>11</sup>), 129.32 (C<sup>18</sup>), 129.82 (C<sup>10</sup>), 134.86 (C<sup>12</sup>), 139.10 (C<sup>3</sup>), 142.64 (C<sup>5</sup>), 144.15 (C<sup>15</sup>), 146.25 (C<sup>2</sup>), 147.32 (C<sup>16</sup>), 160.37 (C<sup>8</sup>), 164.35 (amide carbon).



**T-CBZ-N** was prepared from the condensation of triptycene-bis(ether carboxylic acid) **5** with two equivalent amount of *N*-(4-aminophenyl)carbazole (**9**) in 90% yield with a melting point of 146-147 °C. IR: 3300 cm<sup>-1</sup> (N–H stretch) and 1643 cm<sup>-1</sup> (C=O stretch). <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>, *δ*, ppm): 5.79 (s, 2H, H<sub>b</sub>), 6.90 (s, 2H, H<sub>a</sub>), 7.06 (dd, *J* = 5.0 and 3.5 Hz, 4H, H<sub>c</sub>), 7.07 (d, *J* = 8.5 Hz, 4H, H<sub>e</sub>), 7.29 (t, *J* = 7.5 Hz, 4H, H<sub>k</sub>), 7.36 (dd, *J* = 5.0 and 3.5 Hz, 4H, H<sub>d</sub>), 7.38 (d, *J* = 8.5 Hz, 4H, H<sub>i</sub>), 7.44 (t, *J* = 8.0 Hz, 4H, H<sub>j</sub>), 7.61 (d, *J* = 9.0 Hz, 4H, H<sub>h</sub>), 8.09 (d, *J* = 9.0 Hz, 4H, H<sub>g</sub>), 8.10 (d, *J* = 8.5 Hz, 4H, H<sub>f</sub>), 8.25 (d, *J* = 8.0 Hz, 4H, H<sub>1</sub>), 10.49 (amide proton). <sup>13</sup>C NMR (125 MHz, DMSO-*d*<sub>6</sub>, *δ*, ppm): 47.12 (C<sup>4</sup>), 109.52 (C<sup>17</sup>), 116.43 (C<sup>9</sup>), 119.28 (C<sup>1</sup>), 119.82 (C<sup>19</sup>), 120.40 (C<sup>20</sup>), 121.56 (C<sup>13</sup>), 122.50 (C<sup>21</sup>), 123.96 (C<sup>7</sup>), 125.38 (C<sup>6</sup>), 126.12 (C<sup>18</sup>), 127.00 (C<sup>14</sup>),

129.07 (C<sup>11</sup>), 130.01 (C<sup>10</sup>), 131.88 (C<sup>12</sup>), 138.54 (C<sup>3</sup>), 139.15 (C<sup>15</sup>), 140.26 (C<sup>16</sup>), 144.17 (C<sup>5</sup>), 146.26 (C<sup>2</sup>), 160.55 (C<sup>8</sup>), 164.83 (amide carbon).



Fig. S1 IR spectra of monomers: (a) T-TPA-C and T-TPA-N; (b) T-CBZ-C and T-CBZ-N.



Fig. S2 (a) <sup>1</sup>H, (b) <sup>13</sup>C, (c) H-H COSY, and (d) C-H HSQC NMR spectra of monomer T-TPA-C in DMSO-d<sub>6</sub>.



Fig. S3 (a) <sup>1</sup>H, (b) <sup>13</sup>C, (c) H-H COSY, and (d) C-H HSQC NMR spectra of monomer T-TPA-N in DMSO-d<sub>6</sub>.



Fig. S4 (a) <sup>1</sup>H, (b) <sup>13</sup>C, (c) H-H COSY, and (d) C-H HSQC NMR spectra of monomer T-CBZ-C in DMSO-d<sub>6</sub>.



Fig. S5 (a) <sup>1</sup>H, (b) <sup>13</sup>C, (c) H-H COSY, and (d) C-H HSQC NMR spectra of monomer T-CBZ-N in DMSO-d<sub>6</sub>.