## SUPPORTING INFORMATION

## Switchable Electrochromic Devices based on disubstituted bipyridinium derivatives.

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## **Bipyridinium salts**

**[(C<sub>10</sub>)<sub>2</sub>bpy]I<sub>2</sub>** - red solid mp = 290°C (dec.). <sup>1</sup>H NMR (400.13 MHz, MeOD, 25°C)  $\delta$  = 9.29 (d, J = 5.7 Hz, 4H), 8.69 (d, J = 5.2 Hz, 4H), 4.75 (t, J = 7.4 Hz, 4H), 2.15-2.03 (m, 4H), 1.51-1.22 (m, 28H), 0.88 ppm (t, J = 6.8 Hz, 3H). <sup>13</sup>C NMR (100.61 MHz, MeOD, 25°C)  $\delta$  = 151.23, 147.27, 128.29, 128.29, 63.33, 33.03, 32.57, 30.61, 30.52, 30.41, 30.15, 27.24, 23.72, 14.44 ppm. FTIR (KBr) 3011, 2920, 2853, 1634, 1555, 1454, 1371, 1230, 1175, 831, 723 cm<sup>-1</sup>.

**[(C<sub>10</sub>)<sub>2</sub>bpy][NTf<sub>2</sub>]<sub>2</sub> -** pale yellow solid (0.344 g, 95%). mp = 161°C. <sup>1</sup>H NMR (400.13 MHz, DMSO, 25°C)  $\delta$  = 9.37 (d, J = 6.8 Hz, 4H), 8.76 (d, J = 6.8 Hz, 4H), 4.67 (t, J = 7.3 Hz, 4H), 2.04-1.90 (m, 4H), 1.38-1.14 (m, 28H), 0.84 ppm (t, J = 6.7 Hz, 6H); <sup>13</sup>C NMR (100.61 MHz, MeOD, 25°C)  $\delta$  = 148.61, 145.72, 126.57, 124.25, 60.94, 31.24, 30.72, 28.85, 28.77, 28.62, 28.37, 25.40, 22.06, 13.89 ppm; <sup>19</sup>F NMR (376.50 MHz, DMSO, 25°C)  $\delta$  = -78.76 ppm (s). IR(KBr) 3138, 3076, 2928, 2860, 1645, 1570, 1510, 1460, 1352, 1190, 1134, 1053, 837, 795, 735 cm<sup>-1</sup>. Elemental analysis calcd (%) for C<sub>34</sub>H<sub>50</sub>F<sub>12</sub>N<sub>4</sub>O<sub>8</sub>S<sub>4</sub>: C 40.88, H 5.04, N 5.61; found C 41.42, H 4.45, N 5.58.

 $[(C_5O_2)_2bpy]I_2$  - orange solid (1.154 g, 50%). mp = 248 °C. <sup>1</sup>H NMR (400.13 MHz, D<sub>2</sub>O, 25°C)  $\delta$  = 9.03 (d, J = 5.6 Hz, 4H), 8.48 (d, J = 5.6 Hz, 4H), 4.90-4.80 (m, 4H), 4.01-3.89 (m, 4H), 3.31 (s, 6H) ppm.<sup>13</sup>C NMR (100.61 MHz, D<sub>2</sub>O, 25°C)  $\delta$  = 150.34, 145.91, 126.90, 69.98, 61.17, 58.46 ppm. FTIR (KBr) 3130, 3084, 3009, 2893, 1637, 1556, 1502, 1443, 1377, 1223, 1115, 1074, 1015, 820, 710 cm<sup>-1</sup>.

**[(C<sub>5</sub>O<sub>2</sub>)<sub>2</sub>bpy][NTf<sub>2</sub>]<sub>2</sub> -** white solid (0.688 g, 89%). mp = 99.73°C. T<sub>g</sub> = -27.37 °C. <sup>1</sup>H NMR (400.13 MHz, DMSO, 25°C)  $\delta$  = 9.30 (d, J = 6.4 Hz, 4H), 8.78 (d, J = 6.2 Hz, 4H), 4.93-4.83 (m, 4H), 4.02-3.92 (m, 4H), 3.62-3.52 (m, 4H), 3.42-3.34 (m, 4H), 3.16 (s, 6H) ppm. <sup>19</sup>F NMR (376.50 MHz, DMSO, 25°C)  $\delta$  = -78.72 ppm. <sup>13</sup>C NMR (100.61 MHz, DMSO, 25°C)  $\delta$  = 149.37, 146.68, 126.74, 121.55, 118.35, 71.51, 69.92, 69.05, 60.96, 58.55 ppm. FTIR (KBr) 3140, 3102, 3070, 2990, 2938, 2898, 1640, 1450, 1354, 1208, 1144, 1060, 834, 790, 740 cm<sup>-1</sup>. Elemental analysis calcd (%) for C<sub>24</sub>H<sub>30</sub>F<sub>12</sub>N<sub>4</sub>O<sub>12</sub>S<sub>4</sub>: C 31.24, H 3.28, N 6.07; found. C 30.93, H 3.23, N 5.99.

## **Electrochemical Data**



**Figure S1** – Cyclic voltammetry of  $[(C_{10})_2 bpy][NTf_2]_2$  dissolved in adequate electrolyte (ca. 0.07 M) between two equal conducting PET surfaces (electrochromic device).



**Figure S2** – Cyclic voltammetry of  $[(C_5O_2)_2 bpy]I_2$  dissolved in adequate electrolyte (ca. 0.07 M) between two equal conducting PET surfaces (electrochromic device).



**Figure S3** – Cyclic voltammetry of  $[(C_5O_2)_2bpy][NTf_2]_2$  dissolved in adequate electrolyte (ca. 0.07 M) between two equal conducting PET surfaces (electrochromic device).



**Spectroelectrochemistry Data** 

**Figure S4** – Spectroelectrochemistry of  $[(C_{10})_2 bpy]I_2$ .



Figure S5 – Spectroelectrochemistry of [(C<sub>5</sub>O<sub>2</sub>)<sub>2</sub>bpy]I<sub>2</sub>.



Figure S6 – Spectroelectrochemistry of  $[(C_{10})_2 bpy][NTf_2]_2$ .



Figure S7 – Spectroelectrochemistry of  $[(C_5O_2)_2bpy][NTf_2]_2$ .



Preliminary cycling studies

**Figure S8** – Preliminary cycling studies of  $[(C_5O_2)_2bpy][NTf_2]_2$  at 605 nm, potential of 2V/0 V for 70 cycles.



**Figure S9** – Preliminary cycling studies of  $[(C_{10})_2 bpy]I_2$  at 550 nm, potential of 1.8V/0V for 100 cycles.