

## Supplementary Material (ESI)

### **Covalent layer-by-layer thin films with charge-transfer chromophores: side chain engineering for the efficient Ag<sup>+</sup> ion recognition from aqueous solutions**

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## 1. Materials

All reagents were used without further purification. 1-Iodo-2-(2-(2-ethoxyethoxy)ethoxy)ethane<sup>S1</sup>, 4-ethynylstyrene<sup>S2</sup>, *N,N*-dihexyl-4-iodoaniline (**3**)<sup>S3</sup>, and TCNQ polyester (**P3**)<sup>S4</sup> ( $M_n$  (GPC, THF) 4600;  $M_w/M_n$  1.56;  $T_{d5\%}$  324 °C) were prepared according to the reported procedure.

## 2. Synthesis

### *N,N*-Bis(2-(2-(2-ethoxyethoxy)ethoxy)ethyl)-4-iodoaniline (**1**)

To a solution of 4-iodoaniline (1.42 g, 5.22 mmol) in dehydrated DMF (14 mL), 1-iodo-2-(2-(2-ethoxyethoxy)ethoxy)ethane (5.01 g, 17.4 mmol) and Na<sub>2</sub>CO<sub>3</sub> (1.03 g, 9.71 mmol) were added under nitrogen. The mixture was stirred at 95 °C for 20 h. After cooling to 20 °C, EtOAc was added to the mixture. The organic phase was washed with water and brine, and dried over Na<sub>2</sub>SO<sub>4</sub>. After filtration, the solvents were evaporated. Column chromatography (SiO<sub>2</sub>, hexane/EtOAc 1:1→EtOAc) afforded the desired product as yellow oil (915 mg, 32.5%). <sup>1</sup>H NMR (400 MHz; CDCl<sub>3</sub>, δ): 1.18 (t,  $J$  = 7.0 Hz, 6 H), 3.48-3.60 (m, 28 H), 6.46 (d,  $J$  = 9.2 Hz, 2 H), 7.37 (d,  $J$  = 9.2 Hz, 2 H); <sup>13</sup>C NMR (100 MHz; CDCl<sub>3</sub>, δ): 15.18, 50.85, 66.62, 68.26, 69.80, 70.60, 70.70, 76.50, 77.37, 114.10, 137.65, 147.36; IR (neat):  $\nu$  = 2971, 2865, 1586, 1495, 1454, 1382, 1349, 1322, 1283, 1231, 1193, 1105, 988, 944, 881, 843, 803, 747, 727, 705, 694, 685, 675, 668, 656, 648, 632, 618, 608 cm<sup>-1</sup>; MALDI-TOF MS (dithranol)  $m/z$ : [M]<sup>+</sup> calcd for C<sub>22</sub>H<sub>38</sub>INO<sub>6</sub>: 539.17; found 539.10.

### 4-[4'-*N,N*-Bis(2-(2-(2-ethoxyethoxy)ethoxy)ethyl)aminophenylethynyl]styrene (**2**)

To a degassed solution of 4-ethynylstyrene (215 mg, 1.68 mmol) and **4** (815 mg, 1.51 mmol) in diisopropylamine (23 mL), bis(triphenylphosphine)palladium(II) dichloride (32.3 mg, 0.0461 mmol) and cuprous iodide (8.7 mg, 0.046 mmol) were added under argon. The mixture was stirred at 20 °C for 21 h. After removal of the precipitated salt by filtration, evaporation and column chromatography (SiO<sub>2</sub>, hexane→hexane/EtOAc 5:1→EtOAc) followed by the purification using a preparative HPLC (chloroform) afforded the desired product (537 mg, 65.8 %) as yellow oil. <sup>1</sup>H NMR (400 MHz; CDCl<sub>3</sub>, δ): 1.21 (t,  $J$  = 7.0 Hz, 6 H), 3.50-3.66 (m, 28 H), 5.27 (d,  $J$  = 11.6 Hz, 1 H), 5.76 (d,  $J$  = 17.6 Hz, 1 H), 6.65-6.73 (m, 1+2 H), 7.36 (d,  $J$  = 8.8 Hz, 4 H), 7.44 (d,  $J$  = 8.4 Hz, 2 H); <sup>13</sup>C NMR (100 MHz; CDCl<sub>3</sub>, δ): 15.26, 50.90, 66.73, 68.45, 69.90, 70.71, 70.81, 77.37, 87.49, 91.38, 109.83, 111.48, 114.30, 123.80, 126.17, 131.46, 132.95, 136.44, 136.66, 147.76; IR (neat):  $\nu$  = 2971, 2865, 2206, 2165, 1608, 1597, 1521, 1485, 1471, 1454, 1392, 1350, 1325, 1282, 1272, 1239, 1199, 1106, 1032, 1016, 991, 942, 913, 882, 843, 815, 733, 703, 686, 677, 661, 646, 638, 625, 612 cm<sup>-1</sup>; MALDI-TOF MS (dithranol)  $m/z$ : [M]<sup>+</sup> calcd for C<sub>32</sub>H<sub>45</sub>NO<sub>6</sub>: 539.32; found 539.11.

### 4-(4'-*N,N*-Dihexylaminophenylethynyl)styrene (**4**)

To a degassed solution of 4-ethynylstyrene (4.00 g, 31.2 mmol) and *N,N*-dihexyl-4-iodoaniline (11.0 g, 28.3 mmol) in diisopropylamine (312 mL), bis(triphenylphosphine)palladium(II) dichloride (329.5 mg, 0.4694 mmol) and cuprous iodide (179.0 mg, 0.9399 mmol) were added under argon. The mixture was stirred at 20 °C for 18 h. After removal of the precipitated salt by filtration, evaporation and column chromatography (SiO<sub>2</sub>, hexane→hexane/EtOAc 5:1) followed by the purification using

a preparative HPLC (chloroform) afforded the desired product (9.06 g, 82.6 %) as a yellow solid.  $^1\text{H}$  NMR (400 MHz;  $\text{C}_6\text{D}_6$ ,  $\delta$ ): 0.89 (t,  $J = 6.0$  Hz, 6 H), 1.18 (m, 12 H), 1.39 (m, 4 H), 2.99 (t,  $J = 8.0$  Hz, 4 H), 5.05 (d,  $J = 12.0$  Hz, 1 H), 5.53 (d,  $J = 16.0$  Hz, 1 H), 6.47 (m, 1 H), 6.54 (d,  $J = 8.0$  Hz, 2 H), 7.09 (d,  $J = 8.0$  Hz, 2 H), 7.53 (d,  $J = 8.0$  Hz, 2 H), 7.65 (d,  $J = 12.0$  Hz, 2 H);  $^{13}\text{C}$  NMR (100 MHz;  $\text{C}_6\text{D}_6$ ,  $\delta$ ): 14.31, 23.08, 27.08, 27.54, 32.06, 51.08, 88.22, 92.73, 109.97, 111.89, 114.03, 124.48, 126.61, 131.86, 133.50, 136.79, 136.90, 148.35; IR (neat):  $\nu = 3088, 3040, 3004, 2953, 2926, 2855, 2206, 2164, 1909, 1871, 1820, 1714, 1608, 1598, 1520, 1465, 1421, 1401, 1367, 1316, 1294, 1254, 1227, 1196, 1178, 1135, 1110, 1027, 1014, 1004, 986, 950, 930, 904, 840, 811, 744, 725, 642, 615$   $\text{cm}^{-1}$ ; MALDI-TOF MS (dithranol)  $m/z$ :  $[\text{M}]^+$  calcd for  $\text{C}_{28}\text{H}_{37}\text{N}$ : 387.29; found 387.08.

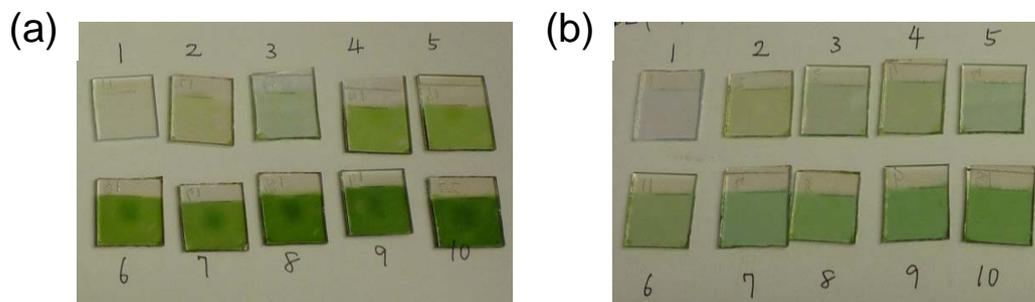
### P1

To an ampoule tube, **2** (196 mg, 0.363 mmol), a solution of 2,2'-azobis(isobutyronitrile) in benzene (0.0362 M, 0.10 mL), and benzene (0.81 mL) were added. The tube was attached to a vacuum line, freeze pump thaw 10 times, sealed off, and then heated to 60 °C for 60 h. After cooling to room temperature, a small amount of benzene was added to the mixture. The mixture was then poured into a large excess of hexane. The precipitate was dissolved in benzene and poured into hexane again. The precipitate was collected and passed through a preparative HPLC column (chloroform), affording the desired product (163 mg, 85.5%) as a yellow viscous solid.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 0.88 (t,  $J = 6.9$  Hz, 1n H), 1.16-1.26 (br m, (6+2)n H), 3.50-3.59 (br m, 28n H), 6.10-6.70 (br m, 4n H), 7.00-7.55 (br m, 4n H); IR (neat):  $\nu = 2971, 2924, 2865, 2208, 1773, 1722, 1677, 1604, 1521, 1451, 1392, 1351, 1324, 1278, 1241, 1193, 1105, 1036, 995, 942, 882, 817, 738, 715, 694, 645, 634, 613$   $\text{cm}^{-1}$ .

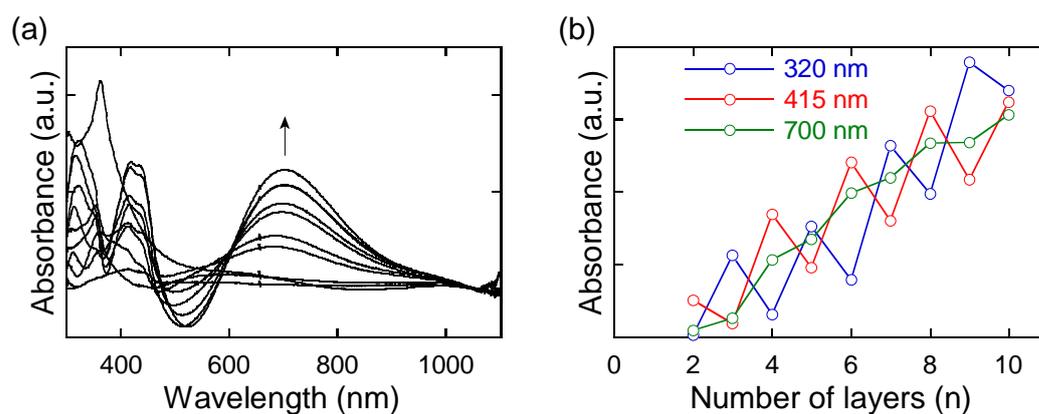
### P2

To an ampoule tube, **4** (1.708 g, 4.409 mmol), a solution of 2,2'-azobis(isobutyronitrile) in benzene (0.11 M, 0.40 mL), and benzene (4.41 mL) were added. The tube was attached to a vacuum line, freeze pump thaw 10 times, sealed off, and then heated to 60 °C for 60 h. After cooling to room temperature, the mixture was poured into a large excess of methanol. The precipitate was dissolved in dichloromethane (20 mL) and poured into methanol again. The precipitate was collected as a yellow solid (1.461 g, 85.5 %).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 0.87 (br m, 6n H), 1.27 (m, 14n H), 1.52 (m, 5n H), 3.20 (br m, 4n H), 6.48 (br s, 4n H), 7.34 (br s, 4n H); IR (neat):  $\nu = 2954, 2924, 2854, 2208, 2163, 1601, 1520, 1464, 1399, 1366, 1294, 1276, 1254, 1227, 1195, 1135, 1106, 1017, 984, 934, 889, 828, 811, 757, 677, 664, 644, 629, 617, 604$   $\text{cm}^{-1}$ .

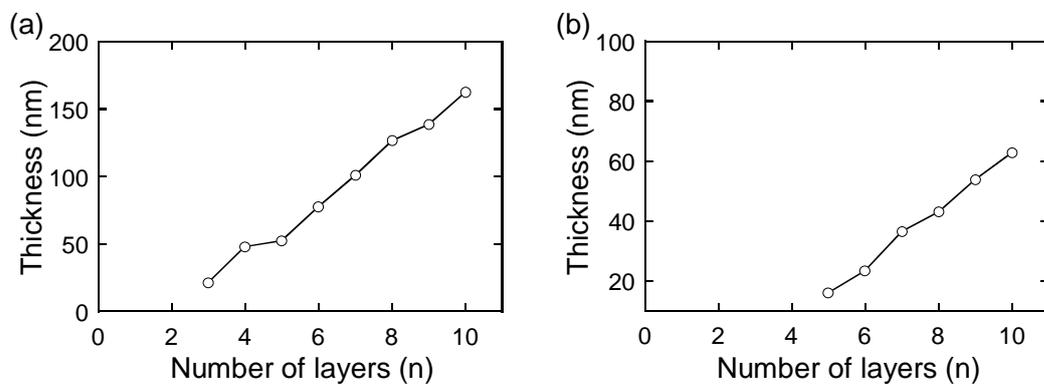
### 3. Supporting figures



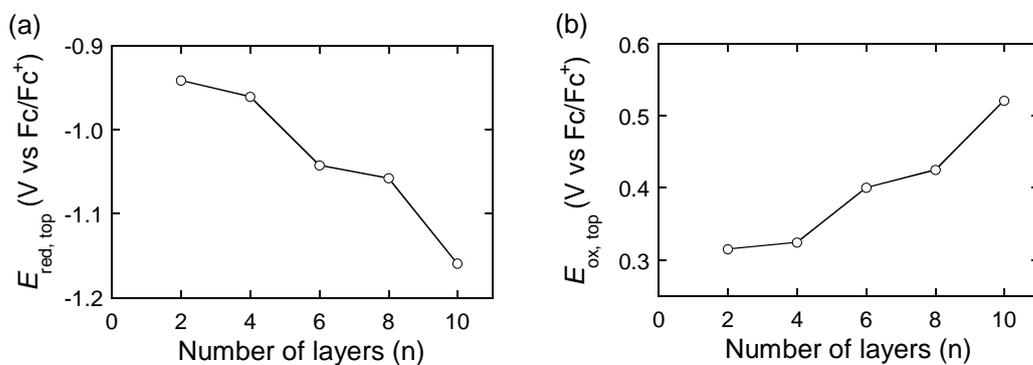
**Fig. S1** Images of multilayer films during LbL assembling process of (a) **P1** and **P3** and (b) **P2** and **P3**.



**Fig. S2** (a) UV-vis-near IR absorption spectra of multilayer films of **P2** and **P3** on the ITO substrate and (b) absorbance changes at 320, 415, and 700 nm during the LbL assembling process of **P2** and **P3**. (Absorbances of all spectra were adjusted at 1050 nm.)



**Fig. S3** Plots of thickness versus number of layers during the LbL assembling process of (a) **P1** and **P3** and (b) **P2** and **P3**.



**Fig. S4** (a)  $E_{\text{red,top}}$  and (b)  $E_{\text{ox,top}}$  values versus number of layers of the films constructed from **P2** and **P3** on the ITO electrode, measured in CH<sub>3</sub>CN with 0.1 M (nC<sub>4</sub>H<sub>9</sub>)<sub>4</sub>NClO<sub>4</sub> at 20 °C and the scan rate of 0.1 V s<sup>-1</sup>.

### References

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