Supporting Information

Fabrication of Both Photoactive Layer and Electrode by Electrochemical Assembly: Towards Fully Solution-Processable Device

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1. Materials

TBAPF₆ (tetrabutylammonium hexafluorophosphate), indium tin oxide (ITO) (8-12 Ω/\Box), dichlorobenzene and acetonitrile were purchased from Aldrich Chemical Co.

2. General techniques

¹H and ¹³C NMR spectra were obtained at 298 K (unless otherwise stated) using a JEOL AL300 BX spectrometer. Electronic absorption spectra were measured using a Shimadzu UV-3600 UV/Vis/NIR spectrophotometer. AFM images were obtained with a commercial AFM unit (SPA400-SPI4000, Seiko Instruments Inc., Chiba, Japan). Fluorescence measurements are carried out with Perkin-Elmer LS55 luminescence spectrometer. FEG-SEM images were obtained using a FEI COMPANY XL-30 scanning electron microscope operating at an accelerating voltage of 25 kV. TEM images were obtained using a JEOL-JEM2100 operating at 200 kV. The switching photocurrent-time (I-t) characteristics were measured using a two-point probe method in air using an Arbitrary Waveform Generator (Agilent 33250A) and a Sourcemeter (Keithley 2400). Monochromatic light of 360 nm (1 mV/cm²) was obtained from a monochromatic LED.

3. Electrochemical experiments

For electrochemical experiments, the supporting electrolyte TBAPF₆ (tetrabutylammonium hexafluorophosphate) was dried for 24 h at 80°C under vacuum before use. Cyclic voltammetry (CV) experiments were performed using a typical one-compartment, three-electrode electrochemical cell driven by a CHI Model 630B electrochemical analyzer. In all cases, Ag/0.01M AgNO₃ ($E_{1/2} = 0.26$ Vvs Fc/Fc⁺) was used as reference. Indium tin oxide (ITO) (8-12 Ω/\Box , Aldrich) (deposition area: ~ 1.0 cm²) was used as the working electrode; The counter electrode was a gold foil (area: ~ 2.0 cm²). After electrochemical processes, the resulting films were rinsed with CH₂Cl₂ to remove any unreacted precursors.



Fig. S1 (A) TEM image of monodispersed **Au-Cz**; (B) UV-vis spectra of **Au-Cz** in CH₂Cl₂ solution, and **Au-Cz** LbL film (photo) and dipped film.

The absorption peaks at 420-450 nm (Figure S1 and Figure 1A) of **Au-Cz** ECC-LbL films can probably be attributed to the formation of the plenty of dicarbazyl radical cations^{S1}, which absorption intensity can be controlled by potential^{S2} and different peripheral carbazyl ligands.^{S3,S4}



Fig. S2 I-V curve of device ITO/Au-Cz(~150 nm)/Al. The conductivity has been calculated to be 1.2×10^2 S·cm⁻¹.



Fig. S3 AFM images of F-Cz film by 0 (A), 4 (B), 10 (C) and 20 (D) cycles prepared Au-Cz

film covered, and their fluorescence spectra (F) respectively.



Fig. S4 (A) Cyclic voltammogram of **F-Cz** and **Au-Cz** as the 5th layer and 6th layer respectively. (B) AFM image of 20th layer of **F-Cz/Au-Cz** multilayer.

4. Gold Nanoparticles (AuNPs) Preparation

4.1 Synthesis of carbazyl thiol capped AuNPs

The synthesis of AuNPs was according to a reported method^{S5}, but herein the different thiol compound 6-(9*H*-carbazol-9-yl)hexane-1-thiol was specially designed and synthesized for ECC-LbL assembly. At room temperature, 0.017 g (0.05 mmol) of Et₃PAuCl was dissolved in 100 mL of toluene. The solution was stirred for 5 min and then 0.17 g (0.5 mmol) was added into solution, and stirring was continued for another 30 min and cooled down with ice water. After that, 0.2 mL (0.5 M) 9-BBN in THF was added followed by immediate injection of 0.005 mL (0.01 mmol) of trioctylamine (TOA). The color of the solution gradually changed to purple 1 h after the reaction was stopped. The solution was centrifuged at 7000 rpm for 10 min to remove any large aggregates of nanoparticles and one drop of the centrifuged solution was dipped onto a copper grid for TEM measurement. The final solution was washed by ethyl acetate and hexane for 3 times respectively to remove any unreactive thiol compound and the solvent was evaporated, and the black solid product was dried in vacuum oven for overnight.

4.2Synthesis route and characterization of 6-(9H-carbazol-9-yl)hexane-1-thiol



9-(6-Iodohexyl)-9H-carbazole

To a mixture of carbazole (2.06 g, 5.98 mmol) in THF, NaH (0.148 g, 6.17 mmol) was slowly

added. The mixture was stirred for 1 h to give a solution. The resulting solution was introduced under nitrogen in a dropping funnel and slowly added in 10 min to a solution of 1,6-diiodohexane (25 g, 74.0 mmol). The reaction mixture was stirred for 12 h at room temperature, quenched with water and THF was evaporated under reduced pressure. The mixture was extracted with ethyl ether (3×50 mL) and the organic phases were collected and combined, dried over Na₂SO₄ and evaporated under reduced pressure. The crude product was purified by chromatography (from hexane: CH₂Cl₂ 10:1). Yield: 2.32 g, 50%. ¹H-NMR (ppm, CD₂Cl₂, 300 MHz): $\delta = 8.09$ (d, 2H, Ar-*H*), 7.50-7.41 (m, 4H, Ar-*H*), 7.25-7.18 (m, 2H, Ar-*H*), 4.32 (t, 2H, NCH₂), 3.16 (t, 2H, *CH*₂I), 1.94-1.72 (m, 4H, *CH*₂), 1.49-1.35 (m, 4H, *CH*₂). ¹³C-NMR (ppm, CD₂Cl₂, 300 MHz): $\delta = 140.70$, 125.91, 122.98, 120.53, 119.01, 109.05, 43.16, 33.73, 30.56, 29.07, 26.51, 7.51. MALDI-TOF-MS: calcd. for C₁₈H₂₀IN: 377.06, found 376.88. Elemental analysis: calcd. for C₁₈H₂₀IN: C 57.31 H 5.34 N 3.71, found C 57.49 H 5.55 N 3.69.

S-6-(9H-carbazol-9-yl)hexyl ethanethioate

The compound obtained in the preceding step, 9-(6-iodohexyl)-9H-carbazole (3.43 g, 9.10 mmol), was dissolved in DMF (100 mL) and then potassium thioacetate (1.5 g, 13.2 mmol) was added. The mixture was stirred at room temperature overnight. The reaction was quenched by adding dichloromethane/acidic water (0.5 M HCl) to the reaction mixture, which was then washed twice with acidic water. The organic phases were then dried over Na₂SO₄ and evaporated under reduced pressure. The crude product was purified by chromatography (from hexane: CH₂Cl₂ 10:1). Yield: 2.81 g, 95%.

¹H-NMR (ppm, CD₂Cl₂, 300 MHz): $\delta = 8.11-8.07$ (d, 2H, Ar-*H*), 7.50-7.40 (m, 4H, Ar-*H*),

7.25-7.18 (m, 2H, Ar-*H*), 4.31 (t, 2H, NC*H*₂), 2.82 (t, 2H, *CH*₂S), 2.29 (s, 3H, *CH*₃), 1.94-1.80 (m, 2H, *CH*₂), 1.57-1.48 (m, 2H, *CH*₂), 1.47-1.33 (m, 4H, *CH*₂). ¹³C-NMR (ppm, CD₂Cl₂, 300 MHz): $\delta = 195.76$, 140.76, 125.93, 123.04, 120.55, 119.04, 109.09, 43.19, 30.78, 29.79, 29.26, 29.10, 28.85, 27.08. MALDI-TOF-MS: calcd. for C₂₀H₂₃NOS 325.15, found 324.87. Elemental analysis: calcd. for C₂₀H₂₃NOS C 73.81 H 7.12 N 4.30, found C 73.97 H 7.32 N 4.32.

6-(9H-carbazol-9-yl)hexane-1-thiol

S-6-(*9H*-carbazol-9-yl)hexyl ethanethioate (2.11 g, 6.48 mmol) was dissolved in isopropyl alcohol/THF/H₂O 2.5:6:1.5 and subsequently the mixture was carefully degassed through a freez/thaw cycle. Solid KOH (6.50 g, 116 mmol) was then added and the mixture was stirred at 60°C for 5 hours, after which it was quenched with 0.5 M HCl until pH was neutral. The mixture was extracted with ethyl ether (3×50 mL) and the organic phases were collected and combined, dried over Na₂SO₄ and evaporated under reduced pressure. The crude product was washed with water and purified by chromatography (from hexane: dichloromethane 3:2). Yield: 1.47 g, 80%. ¹H-NMR (ppm, CD₂Cl₂, 300 MHz): $\delta = 8.10$ (d, 2H, Ar-*H*), 7.51-7.40 (m, 4H, Ar-*H*), 7.26-7.18 (m, 2H, Ar-*H*), 4.32 (t, 2H, NC*H*₂), 2.47 (q, 2H, *CH*₂), 1.95-1.82 (m, 2H, *CH*₂), 1.63-1.50 (m, 2H, *CH*₂), 1.49-1.29 (m, 4H, *CH*₂). ¹³C-NMR (ppm, CD₂Cl₂, 300 MHz): $\delta = 140.80$, 125.94, 123.06, 120.55, 119.05, 109.10, 43.28, 34.29, 29.18, 28.46, 27.09, 24.78. HRMS: calcd. for C₁₈H₂₁NS 283.14, found 282.77. Elemental analysis: calcd. for C₁₈H₂₁NS C 76.28 H 7.47 N 4.94, found C 76.28 H 7.43 N 4.93.

¹H-NMR spectrum of 9-(6-iodohexyl)-9*H*-carbazole



¹³C-NMR spectrum of 9-(6-iodohexyl)-9H-carbazole



¹H-NMR spectrum of *S*-6-(*9H*-carbazol-9-yl)hexyl ethanethioate



¹³C-NMR spectrum of *S*-6-(*9H*-carbazol-9-yl)hexyl ethanethioate



¹H-NMR spectrum of 6-(9*H*-carbazol-9-yl)hexane-1-thiol



¹³C-NMR spectrum of 6-(9H-carbazol-9-yl)hexane-1-thiol



2.3 Synthesis and characterization of F4C

F4C was synthesized as described in our previous paper.^{S6}

Reference:

[S1] (a) J. F. Ambrose, L. L. Carpenter, R. F. Nelson, *J. Electrochem. Soc.*, 1975, 122, 876; (b)
M. C. Tria, K. S. Liao, N. Alley, S. Curran, R. Advincula, *J. Mater. Chem.*, 2011, 21, 10261.
[S2] F. Tran-Van, T. Henri, C. Chevrot, *Electrochimica Acta*, 2002, 47, 2927.

[S3] C. Danda, R. Ponnapati, P. Dutta, P. Taranekar, G. Patterson, R. C. Advincula, *Macromol. Chem. Phys.*, 2011, **212**, 1600.

[S4] Polycarbazole linked in the 3,6-positions chemically synthesized showed an absorption peak at 318 nm with absorption onset below 380 nm, that also demonstrates herein the absorption peaks at 420-450 nm do not belong to carbazoles polymer formation. J. Ostrauskaite, P. Strohriegl, *Macromol. Chem. Phys.*, 2003, **204**, 1713.

[S5] R.Sardar, J. S. Shumaker-Parry, J. Am. Chem. Soc., 2011, 133, 8179.

[S6] M. Li, S. Tang, F. Shen, M. Liu, W. Xie, H. Xia, L. Liu, L. Tian, Z. Xie, P. Lu, M. Hanif, D. Lu, G. Cheng, Y. G. Ma, *Chem. Commun.*, 2006, 3393.