Visual synapse based on reconfigurable organic photovoltaic cell

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1. Synthesis of polymers.

All drugs are analytically pure (AR), purchased from Shanghai Aladdin Bio-Chem Technology Co., LTD. and indium tin oxide (ITO) conductive glass: Huanan Xiangcheng Technology Co., LTD. with a square resistance of ≤ 6 Ω. All organic solvents are dried before use, and all other chemicals are used directly after purchase without special treatment unless otherwise specified.

Synthesis of PM6:

The PM6 synthesis route is show in Fig. S1 below:

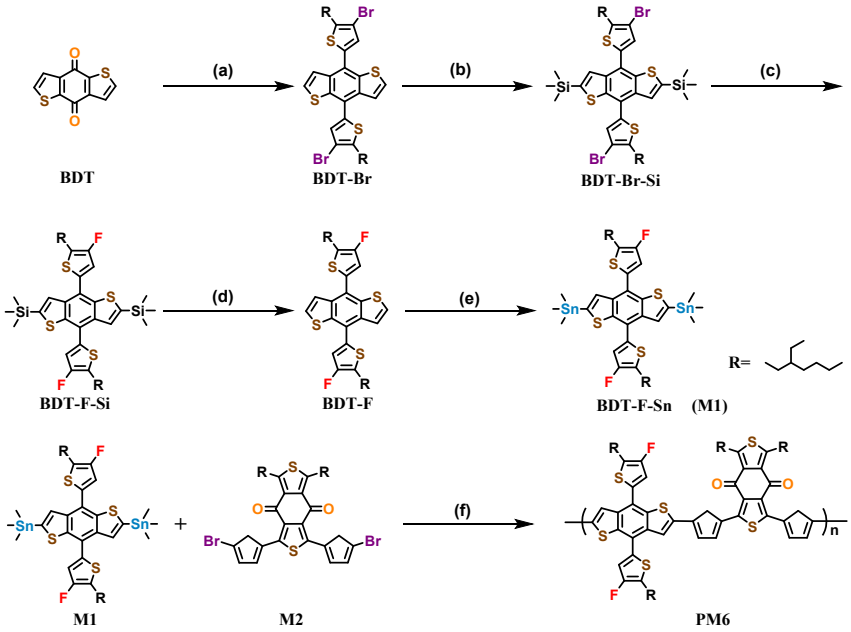

Fig. S1. Synthetic routes for PM6. (a) 3-bromo-2-(2-ethylhexyl)-thiophene, THF, LDA, −78 °C, 1 h; benzo[1,2- b :4,5- b ′]dithiophen-4,8-dione, 50 °C, 2 h; then, SnCl2·2H2O, HCl, 50 °C, overnight. (b) LDA, −78 °C, 1 h; Si(CH3)3Cl, rt, 2 h. (c) n-BuLi, THF, −78 °C; PhSO2NF, rt, overnight. (d) CF3COOH/CHCl3, rt, 5 h; (e) LDA, THF, −78 °C, 1 h; Sn(CH3)3Cl, rt, 2 h. (f) Pd(PPh3)4 , toluene/DMF, 110 °C

BDT-Br: LDA (12 mL, 2M) was slowly added to 30 mL of a THF solution of 3-bromo-2-(2-ethylhexyl)-thiophene (6.6 g, 24 mmol) at −78 °C under argon protection, kept at -78 °C for about 1 h, and then slowly warmed to room temperature. Benzo[1,2- b :4,5- b ′]dithiophen-4,8-dione (BDT) (1.76 g, 8 mmol) was added and the mixture was stirred at 50 °C for 2 h. After cooling to room temperature, a 10% HCl (25 mL) solution of SnCl2-2H2O (12.6 g, 56 mmol) was added, and the mixture was stirred at 50 °C for overnight. The mixture was stirred overnight at 50 °C. The mixed solution was cooled to room temperature and poured into ice water, the mixture was extracted with ether two to three times, the organic phases were combined and concentrated. The mixture was further purified by silica gel column chromatography (dry sampling) using pure petroleum ether as eluent to give pure BDT-Br as a light yellow solid (3.6 g, 61%).MS (MALDI-TOF): m/z 735.7 (M+). 1H NMR (400 MHz, CDCl3),δ (ppm): 7.60 (d, 2H),7.50 (d, 2H),7.21 (s, 2H),2.84 (d, 4 H),1.76 (m,

2H),1.42-1.27 (m, 16H),0.89 (m, 12H).13C NMR (400 MHz,CDCl3),δ (ppm): 139.91, 138.61, 136.59, 136.09, 129.85, 127.60, 122.74, 122.56, 109.05, 40.51, 33.26, 32.09, 28.40, 25.41, 13.73, 10.48.

BDT-Br-Si: LDA (3.5 mL, 2M) was slowly added to a THF (30 mL) solution of BDT-Br (2.2 g, 3 mmol) at −78 °C. The mixture was kept at −78 °C for 1 h. Chlorotrimethylsilane (2 mL) was added dropwise. After addition, the solution was kept at -78 °C for 1 h. Trimethylchlorosilane (2 mL) was added dropwise. The mixed solution was then stirred at room temperature for 2 h and quenched with water. The mixture was extracted twice with ether, dried with MgSO4, the solvent was removed and purified by silica gel column chromatography using pure petroleum ether as eluent to give BDT-Br-Si (2.1 g, 80%) as a light yellow solid. MS (MALDI-TOF): m/z 880.1(M+).1H NMR (400 MHz,CDCl3),δ (ppm): 7.66 (s,2H),7.28 (s,2H), 2.84 (d, 4 H),1.79 (m, 2H),1.42-1.27 (m, 16H),0.89 (m,12H),0.34 (t,18H).13C NMR (400 MHz,CDCl3),δ (ppm): 144.39, 142.18, 139.71, 137.43, 136.93, 129.64, 129.01, 121.90, 40.39, 33.27, 32.04, 28.36, 25.45, 22.55, 13.66, 10.46, -0.91.

BDT-F-Si: n-BuLi (2 mL, 2.5 M) was slowly added to a THF (30 mL) solution of BDT-Br-Si (1.76 g, 2 mmol) at -78 °C. After addition, the mixture was kept at -78 °C for 1 h. A THF solution of N-fluorobenzenesulfonimide (1.89 g, 6 mmol) in 20 mL was added dropwise. After addition, the mixture was kept at -78 °C for 1 h. N-BuLi (2 mL, 2.5 M) was added dropwise to 20 mL of N-fluorobenzenesulfonimide in THF (1.89 g, 6 mmol). The mixed solution was then stirred overnight at room temperature and quenched with 50 mL of water. The mixture was extracted twice with ether, dried over MgSO4, the solvent removed, and purified by silica gel column chromatography using pure petroleum ether as eluent to give BDT-F-Si (0.99 g, 65%) as a light yellow solid. MS (MALDI-TOF): m/z 758.2 (M+).1H NMR (400 MHz, CDCl3),δ (ppm): 7.71 (s, 2H), 7.15 (s, 2H), 2.84 (d, 4 H), 1.67 (m, 2H), 1.42-1.27 (m, 16H), 0.93 (m, 12H), 0.34 (t, 18H).13C NMR (400 MHz, CDCl3),δ (ppm): 155.09, 152.53, 144.35, 142.09, 137.34, 134.14, 129.13, 122.42, 121.64, 121.46, 117.48, 117.21, 40.44, 32.09, 28.77, 28.44, 25.46, 22.57, 13.68, 10.46, -0.88.

BDT-F: Trifluoroacetic acid (10 mL) was added dropwise to a chloroform (10 mL) solution of BDT-F-Si (1.52 g, 2 mmol) and stirred for 5 h. The mixture was extracted with chloroform two to three times and the organics were combined. The solvent was purified by fast column chromatography using dichloromethane as eluent to give BDT-F (1.1 g, 89%) as a light yellow solid. MS (MALDI-TOF): m / z 614.1 (M+). 1H NMR (400 MHz,CDCl3), δ (ppm): 7.64 (d, 2H), 7.50 (d, 2H), 7.14 (s, 2H), 2.79 (d, 4 H), 1.67 (m, 2H), 1.40 (m, 16H), 0.93 (m, 12H). 13C NMR (400 MHz, CDCl3), δ (ppm): 155.11, 152.57, 138.55, 135.99, 133.75, 127.57, 123.22, 122.59, 121.83, 117.59, 40.48, 32.10, 28.72, 28.44, 25.40, 22.58, 13.69, 10.43.

BDT-F-Sn (M1): To a THF (20 mL) solution of **BDT-F** (1.23 g, 2 mmol) was slowly added n-BuLi (2 mL, 2.5 M) at -78 °C. After addition, the mixture was kept at −78 °C for 1 h. A THF solution of trimethyltin chloride (7.34 mL, 1.0 M) was added. After addition, the mixed solution was kept at −78 °C for 1 h. A solution of trimethyltin chloride in THF (7.34 mL, 1.0 M) was added. The solution was then stirred at room temperature for 2 h and quenched with 50 mL of water. The mixture

was extracted twice with ether and then dried with MgSO4, the solvent was removed and the residue was recrystallized in isopropanol to give the compound BDT-F-Sn (M1) (1.41 g, 75%). MS (MALDI-TOF): m/z 940.1 (M+).1H NMR (400 MHz, CDCl3), δ (ppm): 7.67 (s, 2H), 7.16 (s, 2H), 2.85 (d, 4H), 1.66 (m, 2H), 1.41 (m, 16H), 0.94 (m, 12H),0.41 (t, 18H). 13C NMR (300 MHz, CDCl3), δ (ppm): 143.38, 143.28, 140.0, 137.76, 137.34, 130.59, 130.01, 121.45, 109.32, 40.88, 33.75, 32.53, 28.85, 25.91, 23.05, 14.17, 10.95, −8.28.

PM6: M1 (450 mg, 0.5 mmol) and **M2** (383 mg, 0.5 mmol) were added to a 50 mL pre-dried two-necked round-bottomed flask followed by 12 mL of redistilled toluene. Pd(PPh3)4 (25 mg) was added under argon after being purged with argon using a long needle for 30 min to remove oxygen and then frozen and evacuated with liquid nitrogen - dissolved 3 times. After rinsing with argon for another 20 min, the reactants were heated and refluxed for more than 12 h. After cooling to room temperature, the reactants were poured into a water bath. After cooling to room temperature, it was poured into 200 mL of methanol and then filtered through a Soxhlet tip, followed by Soxhlet extraction with methanol, hexane, acetone and chloroform in that order. The polymer chloroform fraction was recovered by methanol precipitation to obtain a solid. The solid was dried under vacuum. Collection rate: 493 mg (81%).GPC:Mn=4.3 K,PDI=2.0. Calculated values for elemental analysis of C65H78O2S8 (%): C, 66.95; H, 6.28. Actual value (%): C, 66.90; H, 6.23.

Y6 and monomer M2 were purchased from Shanghai Aladdin Bio-Chem Technology Co., LTD.

2. AFM and SEM images.

We characterized the structure of the device and the spin-coated thin film using atomic force microscopy (AFM) and cross-sectional scanning electron microscopy (SEM), as shown in Fig. S2(a) and Fig. S2(b). Since PM6 and Y6 are both organic compounds, they exhibit excellent solubility in chloroform solution. Consequently, the thin film demonstrated good uniformity and smoothness in the AFM test, with an average roughness of 2.08 nm in a 5 μm × 5 μm scanning area (Fig. S2(a)). A lower roughness implies a smoother film surface, which is beneficial for the binding of the electrode to the film surface and the transfer of charge carriers on the film. The cross-sectional SEM (Fig. S2(b)) revealed the clear layered structure of the device, with the ITO layer thickness being approximately 195.31 nm and the active layer thickness being about 84.82 nm. A moderate thickness of the active layer is advantageous for the electrical performance testing of the device: at such a thickness, the device is not easily punctured by a large current, nor does it fail to undergo resistive switching due to excessive thickness. Good film uniformity and moderate thickness are the prerequisites for the resistive switching effect in the ITO/PM6 : Y6/Au device. Based on these conditions, we conducted the resistive switching performance test of the device.

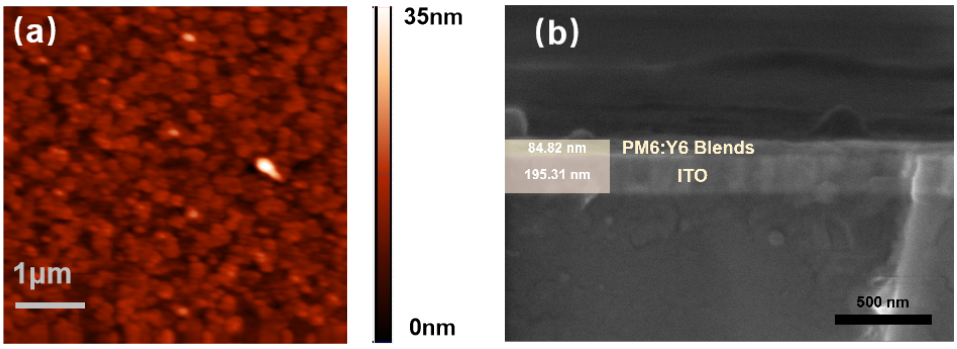

Fig. S2. (a) AFM images of blends films with mass ratio of ITO/PM6 : Y6/Au device; (b) SEM image of the section of the device (thickness of active layer is 84.82 nm, thickness of ITO electrode is 195.31 nm).

3. KPFM spectra of ITO/PM6:Y6/Au device

In KPFM testing, a Pt/Ir cantilever probe is commonly used for measurements. The good electrical conductivity allows us to effectively inject charge into the surface through the probe to observe the behavior of the material in capturing and retaining charge carriers at the microscale. Using KPFM in contact mode, a 2 μm × 2 μm square area on the sample surface (ITO substrate) was scanned, and the initial surface potential distribution map was obtained, as shown in Fig. S(3).

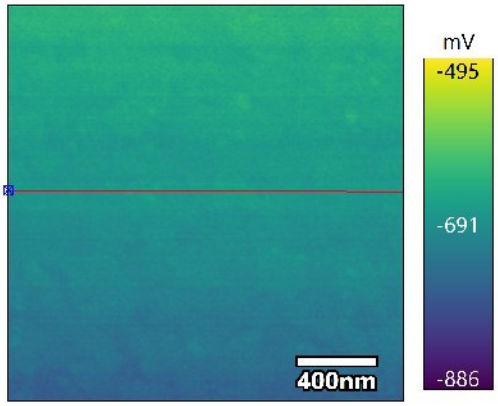

Fig. S3. Uncharged film surface potential diagram

4. Photocurrent response capability.

After understanding the effect of different light intensities on the device, we tested the regulatory ability of the device's photodetection by applying different pulse voltage stimulation times. In Fig. S(4), we used a 1V pulse voltage to stimulate for 10 s, 20 s, and 30 s (using the read program) and then tested the photocurrent of the device with a 20-intensity light pulse. The results showed that compared to 10 s, there was a significant increase in the photocurrent of the device after continuous stimulation with a 20 s pulse voltage. However, when the pulse voltage stimulation time was further increased to 30 s, the photocurrent of the device did not increase significantly and tended to saturate. Therefore, to balance the experimental results and efficiency, we used a 30 s bias stimulation time in subsequent experiments to regulate

the photocurrent response of the device.

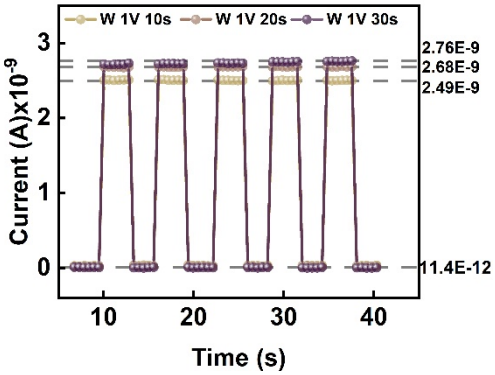

Fig. S4. The influence of different bias stimulation times on the photocurrent of the device under the same light intensity and white light

4. Photocurrent was trend.

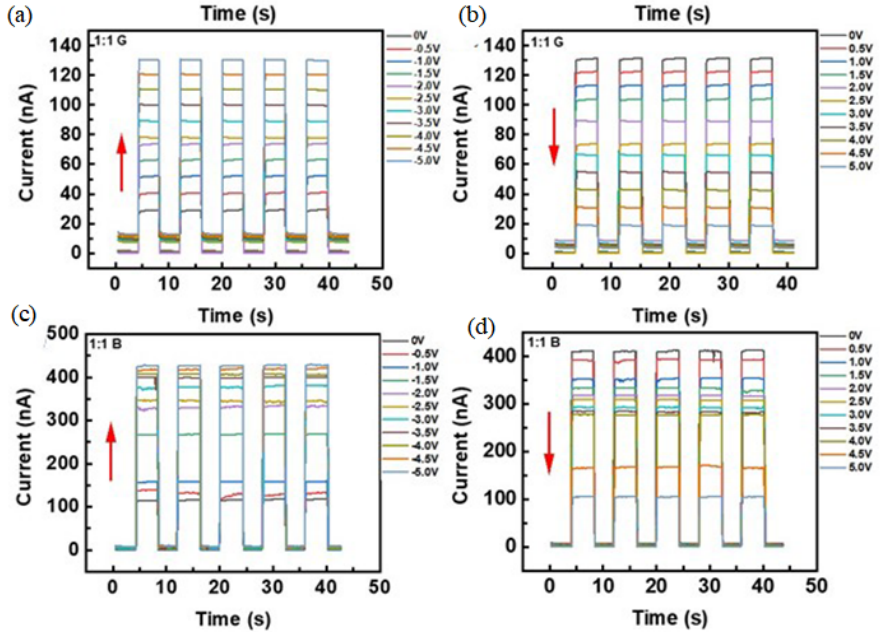

Fig. S5. ITO/PM6 : Y6/Au device under maximum light intensity of green light (a) and blue light (c) (level 255 light intensity), The I-t curve of the device was stimulated by increasing negative bias voltage (0 V, −0.5 V, −1 V, −1.5 V, −2 V, −2.5 V, −3 V, −3.5 V, −4 V, −4.5 V, −5 V), and the optical pulse current showed a stepwise rising trend. PM6:Y6=1:1 devices at both ends are exposed to the maximum light intensity of green light (b) and blue light (d) (level 255 light intensity), and the *I*−*t* curve of the device is stimulated by gradually increasing forward bias voltage (0 V, 0.5 V, 1 V, 1.5 V, 2 V, 2.5 V, 3 V, 3.5 V, 4 V, 4.5 V, 5 V). The optical pulse current shows a step-down trend (Note: since there is no current in the device at 0 V, we used 0.01 V instead of 0 V in the experiment to represent the initial state of the device).