Supporting information

Organic Terpyridyl-Iron Polymer based Memristor for Synaptic Plasticity and Learning Behavior Simulation

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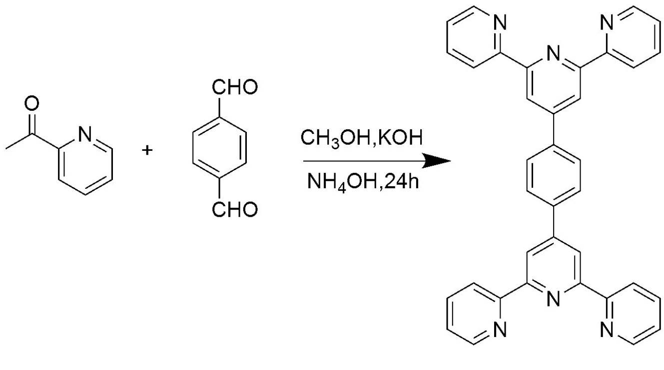
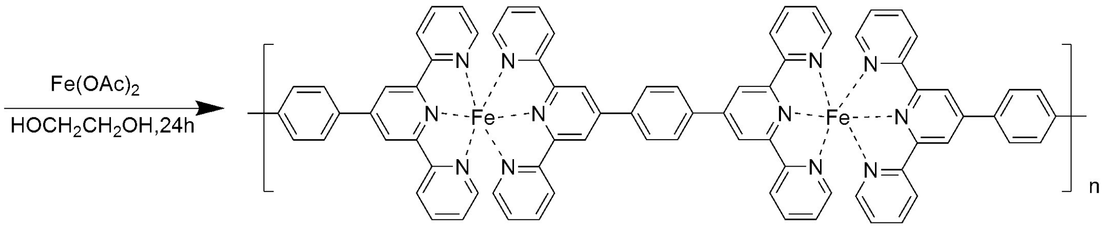


L1



TPy-Fe

Scheme S1. Synthetic routes of monomer L1 and polymer TPy-Fe.

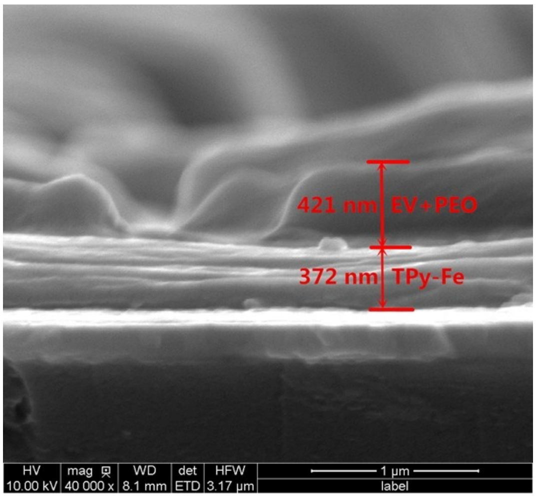


Figure S1. Cross-sectional scanning electron microscopic image of the EV+PEO/TPy-Fe bilayer structure deposited on ITO/Glass substrates.

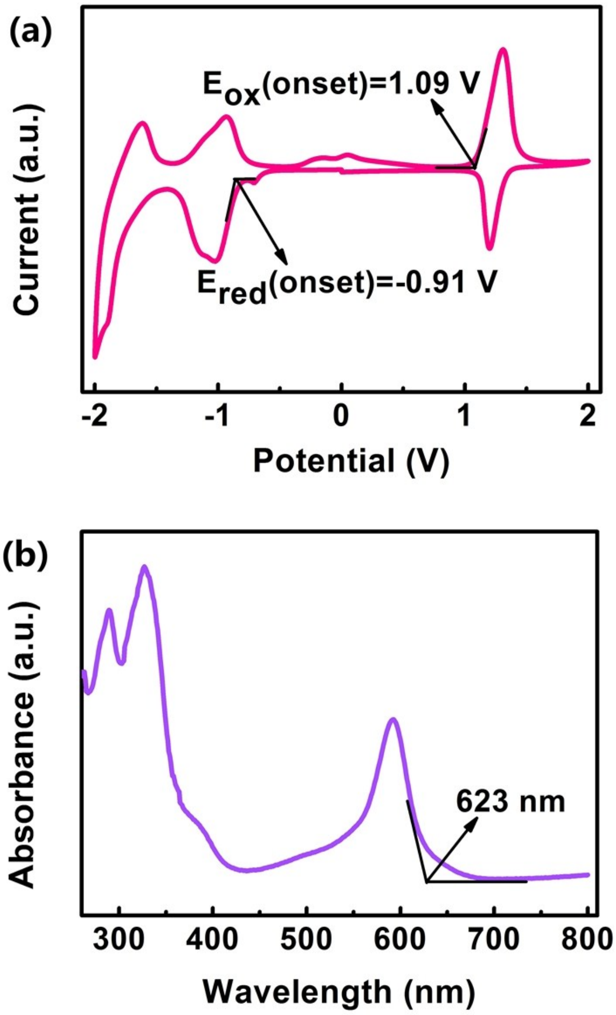


Figure S2. (a) The electrochemical redox behavior of the polymer TPy-Fe. (b) The UV-Visible absorption spectra and the absorption edge of the TPy-Fe in dilute solutions of DMF.

The highest occupied molecular orbital (HOMO) energy level and the lowest occupied molecular orbital (LUMO) energy level, energy bandgap, as well as the optical bandgap of the TPy-Fe polymer, are calculated by the following equations:

$$E_{HOMO} = - (E_{(ox)}onset+4.8-E_{FOC}) \quad (1)$$

$$E_{LUMO} = - (E_{(red)}onset+4.8-E_{FOC}) \quad (2)$$

$$E_g=-(E_{HOMO}-E_{LUMO}) \quad (3)$$

$$E_{op}=hc/\lambda_{\text{onset}} \quad (4)$$

where E_{HOMO} and E_{LUMO} correspond to the energy levels of HOMO and LUMO, $E_{ox}(onset)$ is the onset oxidation potential, $E_{red}(onset)$ is the onset reduction potential, 4.8 is the reference energy of ferrocene (FOC, 4.8 eV under the vacuum level), E_{FOC} is the potential of FOC/FOC$^+$ *versus* Ag/AgCl (0.38 eV, as measured by cyclic voltammetry), E_g is the energy bandgap while E_{op} is the optical bandgap of the TPy-Fe polymer, h is the Planck constant (6.63×10^{-34} m^{2}kg/s), c is the speed of light (3×10^8 m/s) and λ_{onset} is the absorption band edge (623 nm) of the TPy-Fe polymer. The onset oxidation potential and onset reduction potential of TPy-Fe, which corresponds to the reversible redox of the bivalent iron, are 1.09 V and -0.91 V, respectively (**Figure S2a**). According to the above equations, the calculated E_{HOMO}, E_{LUMO}, E_g, E_{op} are -5.51 eV, -3.51 eV, 2.00 V and 3.19 eV, respectively.

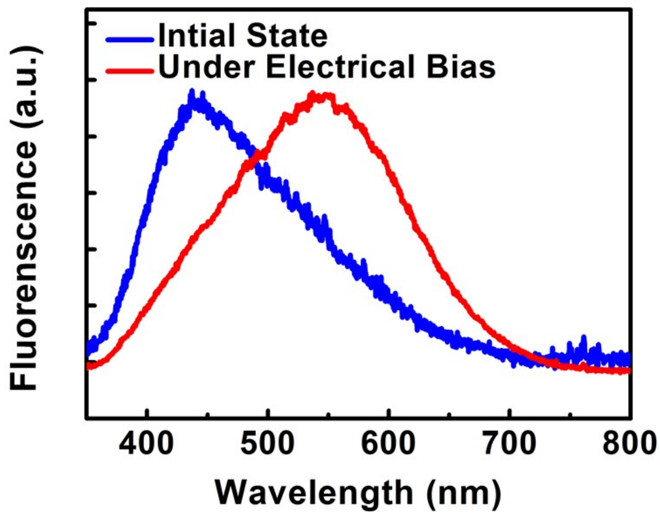


Figure S3. Fluorescence spectra of the $EV(ClO_4)_2$/TPy-Fe bilayer structure in the initial state and under electrical bias.

The original $EV(ClO_4)_2$/TPy-Fe bilayer structure shows an emission band at the wavelength range of 350 nm ~ 600 nm, with the emission maximum centered at ~ 440 nm. When electrical pulses are applied, it is obviously observed that red shift (~ 100 nm) of maximum excitation wavelength occurs, verifying that memristive behaviors of the device are accompanied by electrochemical redox reaction of the bilayer structure which modulates the energy bandgap and optical properties of the system.

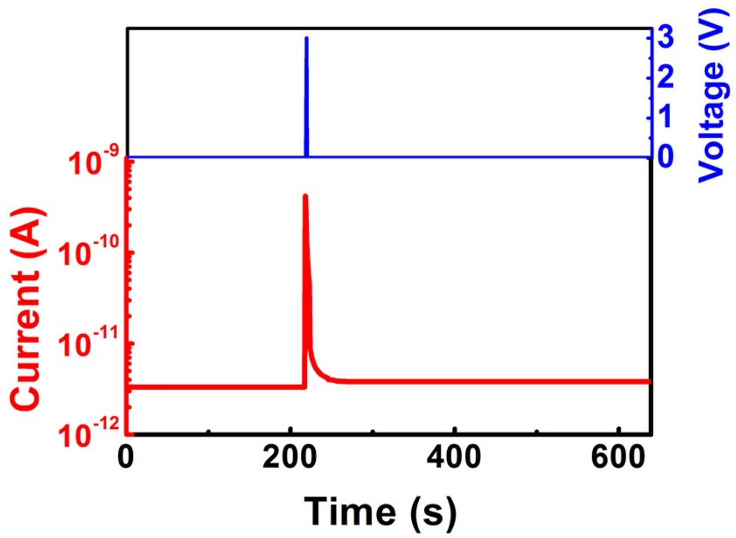


Figure S4. Evolution of an excitatory post-synaptic current (EPSC) stimulated by voltage pulse with the amplitude and duration of 3 V and 10 ms, respectively.

An action potential spike could cause an excitatory post-synaptic current (EPSC), which lasts for tens of milliseconds in a post-synaptic neuron.[1] EPSC indicates that after removing the stimulating pulse, the current would slowly fade to the initial value. In **Figure S4,** a pre-synaptic spike with the amplitude of 2 V and the duration of 10 ms applied on the TE of the memristor. After removing the spike, an EPSC appeared, which can last for ~ 200 ms. This result is similar to the behavior of EPSC in biological synapse, which may be ascribed to the inertial ion migration after removing the electric field. In addition, the lasting duration of the EPSC is even longer than duration of the stimulating spike. When multiple stimulations with the various pulse-to-pulse time intervals have been applied onto the memristor, the overlap between the current induced by voltage spiking and the EPSC may speed up the ionic flux and thus lead to a more effective potentiation in the conductivity of the device.

[1] G. Q. Bi and M. M. Poo, *J. Neurosci.*, 1998, **18**, 10464-10472.