Supporting Information

NIR Electrochemical Fluorescence Switching from Polymethine Dyes

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1. Calibration of Ag wire reference electrode

The electrochemical analysis was demonstrated with Ag wire as a reference electrode, which is not a stable reference electrode. CVs can be calibrated using ferrocene as an external reference. (Figure S1) $E_0(Fc/Fc^+) = 0.28$ V.

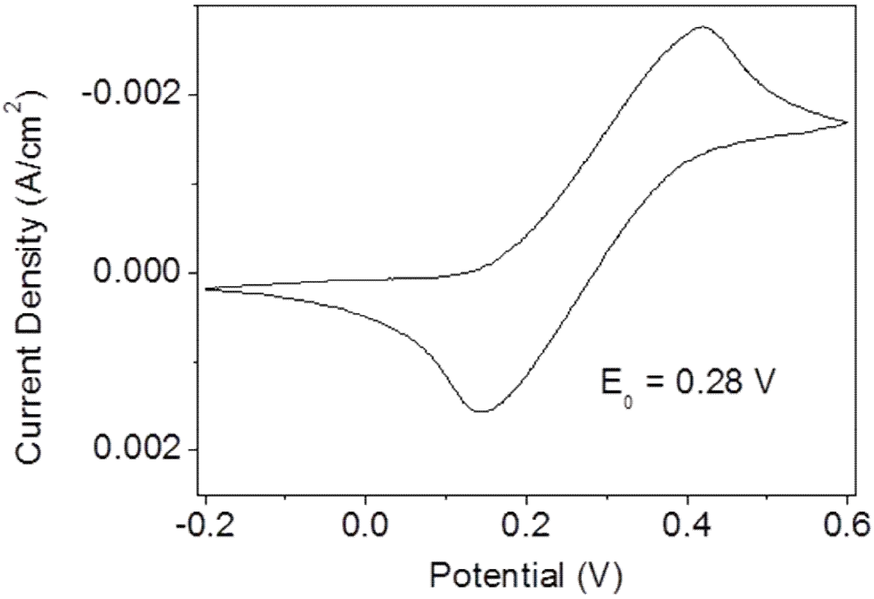

Figure S1. Cyclic voltammogram of ferrocene was measured in same condition with CVs of polymethine dyes, to check electrochemical system, with a scan rate of 100 mV/s in 3-electrode switching cell with an Ag wire reference.

2. Cyclability of the electrochemical fluorescence switching device containing PM1

The cyclability of the electrochemical fluorescence switching device containing PM1 was tested within working potential window (1.1 V /-0.5 V), with a step duration time of 10 s. The fluorescence intensity was normalized by the intensity of the pristine state. The reversible switching continued for over 100 cycles, but a contrast loss ~ 30 % was observed.

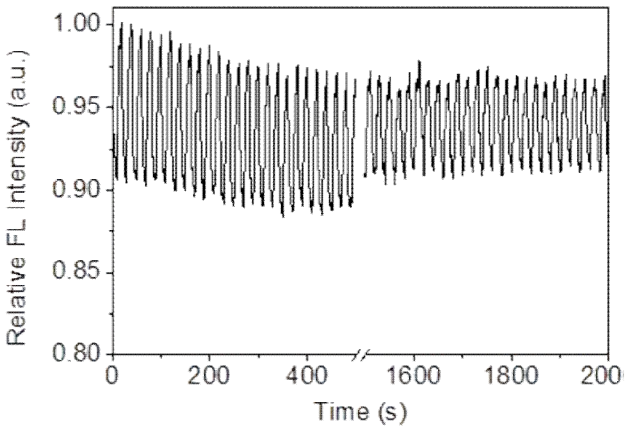

Figure S2. Cyclability of the electrochemical fluorescence switching device containing PM1 at the potentials between 1.1 V and -0.5 V, with a step duration time of 10 s at each potential and monitoring at 820 nm. (λ_{exc} = 733 nm).

3. Quantitative calculation of the switching charge

The percentage of the oxidized fluorophore in OFF state was determined from the following equation: R(%) = [Q / Q_{Total}] x 100(%), where Q is injected/ejected charge through the switching, and Q_{Total} is the total amount of charge that is required to one-electron oxidize all the polymethine dye in the device. Q_{Total} was calculated by multiplying the concentration of the dye (10^{-2}M) by the volume of the switching cell, using the equation: Q_{Total} = F * C * V, where F is faraday constant (96485 C/mol), C is concentration of the dye, V is the volume of the switching cell (13 mm x 18 mm x 0.24 mm, for PM1; 15 mm x 14 mm x 0.024 mm, for PM2). As a result, Q_{Total} of PM1 was calculated as 54.2 mC, and R was calculated as 11 %, with a step potential of 1.1 V to -0.5 V with a step duration time for 20s (**Figure S3a**). The injected/ejected charge was balanced with a linear shift, because of electric leakage current or ion diffusion. This current leakage was hardly related with decomposition of PM1, because the fluorescence intensity was maintained over 100 cycles.

With similar calculation, Q_{Total} of PM2 was calculated as 48.6 mC, and R was calculated as 24 %, with a step potential of 0.95 V to -1.1 V with a step duration time for 20s (**Figure S3b**). The electrochemical fluorescence switching efficiency (E_{EF}) can be derived by the similar method to calculation the coloration efficiency in electrochromic reaction,[1] using the following equation:

$$E_{EF} = \boldsymbol{r}_{ON/OFF} / C$$

, where $\boldsymbol{r}_{ON/OFF}$ represents the ON/OFF ration, and C represents the injected/ejected charge per unit. Based on this equation, E_{EF} of PM1 was calculated as 557 cm^2/C. E_{EF} of PM2 was 507 cm^2/C, which was approximately calculated using the first step of the ON/OFF intensity, and injected/ejected charge.

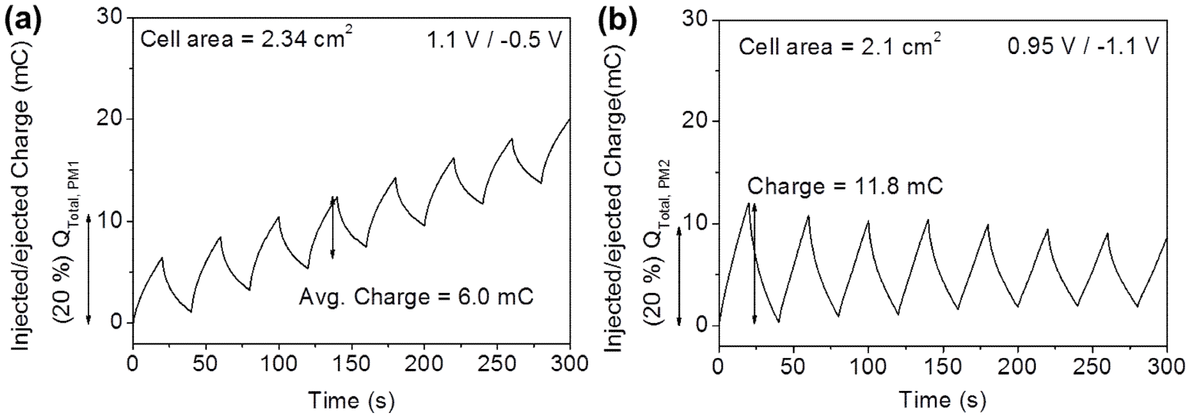

Figure S3. Injected/ejected charges were recorded for the switching device containing (a) PM1 and (b) PM2, within a proper working potential window (1.1 V/-0.5V for PM1; 0.95 V/-1.1 V for PM2). $Q_{Total, PM1}$ and $Q_{Total, PM2}$ represents the amount of charge that is required to oxidize the total amount of the fluorophore in the unit cell. The cell area represents the area of the working electrode.

4. Electrochemical fluorescence switching of PM2

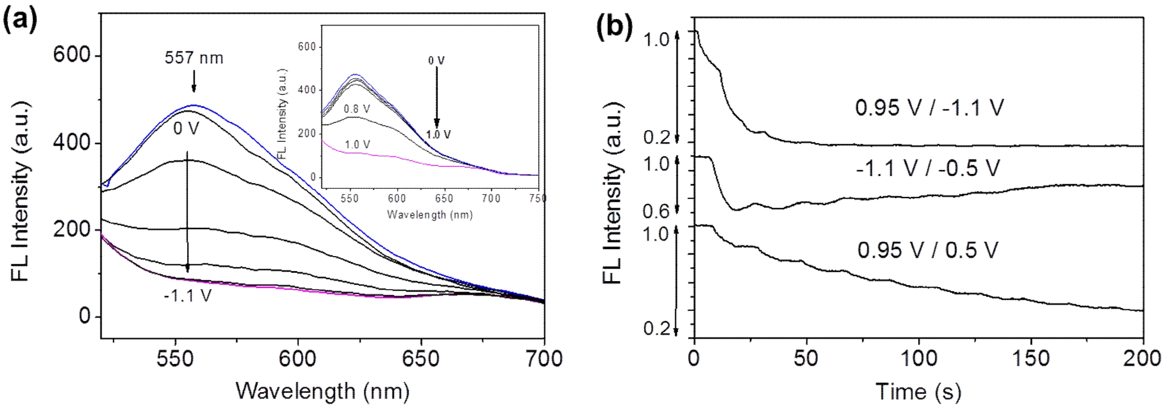

Figure S4. (a) Fluorescence changes in the switching device containing PM2 at different applied potentials, ranging from 0 V (top) to -1.1 V (bottom), with a decrease of 0.2 V at each step. Inset shows fluorescence change with potential change from 0V (top) to 1.0 V (bottom) (λ_{exc} = 495 nm). Each spectrum was obtained after applying the target potential for 10 s to obtain fluorescence spectra at an equilibrated state. (b) The Fluorescence switching responses of the device with PM2 at different switching potentials. (0.95 V/-1.1 V, -1.1 V/-0.5 V, and 0.95 V/0.5 V) with 10 s step duration time.

5. NIR electrochemical fluorescence imaging system

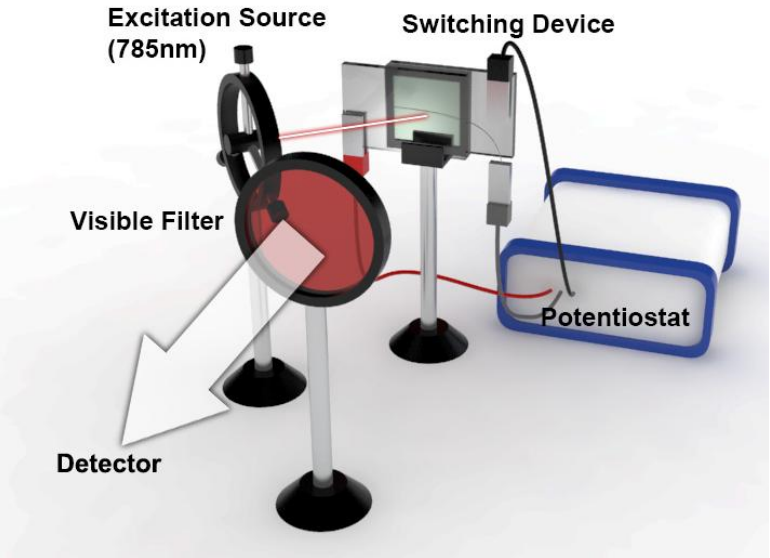

Figure S5. The schematic diagram of the electrochemical fluorescence switching system, which consists of the excitation source, switching device, visible cut-off filter, and the detector.

As a detector, the conventional digital camera was used after removal of inner band-pass filter to obtain NIR images. The NIR imaging system was designed to extract NIR signal from the detectable light of CCD. With a <720 nm cut-off, CCD achieved the optical signal beyond 720 nm wavelength. Especially, PM1 solution took blue color in Figure 1c, because of its absorption band at 795 nm. The NIR images are the processed image, which is white-balanced using a white background. Therefore, the long wavelength region (near 800 nm) would be presented as yellow or red and the wavelength region near 720 nm would be processed as blue, in this NIR detecting system. On the other hand, with a <830 nm cut-off, the detectable wavelength region was so narrow, so the processed image presented only gray scale images. (Figure 1c) Because the absorption of PM1 was not detected with this region, the solution would show bright white emission.

References

[1] H. Shin, Y. Kim, T. Bhuvana, J. Lee, X. Yang, C. Park, E. Kim, *ACS Appl. Mater. Interfaces* **2011**, *4*, 185-191.