

Supplementary Information

Electrochemical current rectification with cross reaction at a TEMPO/viologen-substituted polymer thin-layer heterojunction

H. Tokue, K. Kakitani, H. Nishide and K. Oyaizu**

Department of Applied Chemistry, Waseda University, Tokyo 169-8555, Japan.

Synthesis of 1,3,5-tris(4-cyanopyridinio)mesitylene (TPM) bromide salts

4-Cyanopyridine (3.54 g, 34.0 mmol), 1,3,5-tris(bromomethyl)benzene (1.00 g, 2.80 mmol) were refluxed in acetonitrile (13.4 ml) for 24 h under nitrogen atmosphere. The reaction mixture was cooled to room temperature. The yellow-colored precipitation was recovered by filtration and washed with acetonitrile followed by recrystallization in methanol/ethanol to give TPM bromide salt (1.3 g, 71%) as a needle-like yellow solid. ¹H NMR (500 MHz, D₂O, 25 °C, Me₄Si): δ = 9.42 (6 H, d, *J* = 4 Hz, α-H of pyridinium), 8.52 (6 H, d, *J* = 5 Hz, β-H of pyridinium), 7.95 (3 H, s, ph), 6.04 ppm (6 H, s, CH₂); ¹³C-NMR (500 MHz, D₂O, 25 °C, Me₄Si): δ = 146.2, 134.6, 132.4, 131.7, 128.9, 114.2, 64.4 ppm; FAB-MS (*m/z*): 223.1 (M⁺, calcd), 220.1 (found).

Calculation of I_{LIM}

The average values of diffusion coefficient were employed for the calculation. They were obtained from five measurements with different PTAm-A modified electrodes and the previous literature²⁹ for the PTAm-A and the PTPM layer, respectively. Film thickness is represented as an average value from three measurements at different points in a modified electrode.

I_{LIM} was calculated using equation (S1):

$$I_{LIM} = \frac{\omega^0 n F A D_e C_T}{d} \quad (S1)$$

where ω^0 , n , F , A , D_e , C_T and d are the correction factor, the number of electrons, the Faraday constant, the electrode area, the diffusion coefficient, the concentration of the redox site and the polymer thickness, respectively.

C_T was calculated using equation (S2):

$$C_T = \frac{\rho}{M_T} \quad (S2)$$

where ρ and M_T are the polymer density and the molecular weight per redox site.

I_{LIM} for each device in the paper were calculated as follows:

The PTAm-A layer in the single-layer device

$$I_{LIM} A = \frac{1.50 \times 1 \times 96500 \text{ s A mol}^{-1} \times 1 \text{ cm}^2 \times 2.2 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1} \times 1 \text{ g cm}^{-3} \times \frac{83}{225.3 \times 83 + 72.1 \times 17} \text{ mol g}^{-1}}{120 \times 10^{-7} \text{ cm}}$$

$$= 11.1 \times 10^{-3} \text{ A}$$

The PTPM layer in the single-layer and bilayer device (first redox reaction)

$$I_{LIM} A = \frac{1.11 \times 1 \times 96500 \text{ s A mol}^{-1} \times 1 \text{ cm}^2 \times 1.9 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1} \times 1 \text{ g cm}^{-3} \times \frac{1.5}{460.8} \text{ mol g}^{-1}}{110 \times 10^{-7} \text{ cm}}$$

$$= 6.0 \times 10^{-3} \text{ A}$$

The PTPM layer in the single-layer and bilayer device (second redox reaction)

$$I_{LIM} A = \frac{1.50 \times 1 \times 96500 \text{ s A mol}^{-1} \times 1 \text{ cm}^2 \times 8.1 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1} \times 1 \text{ g cm}^{-3} \times \frac{1.5}{460.8} \text{ mol g}^{-1}}{110 \times 10^{-7} \text{ cm}}$$

$$= 34.7 \times 10^{-3} \text{ A}$$

The PTAm-A layer in the bilayer device

$$I_{LIM} A = \frac{1.50 \times 1 \times 96500 \text{ s A mol}^{-1} \times 1 \text{ cm}^2 \times 2.2 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1} \times 1 \text{ g cm}^{-3} \times \frac{83}{225.3 \times 83 + 72.1 \times 17} \text{ mol g}^{-1}}{130 \times 10^{-7} \text{ cm}}$$

$$= 10.2 \times 10^{-3} \text{ A}$$

Calculation of the saturated amount of charge

The saturated amount of charge was calculated using equation (S3):

$$\text{Saturated amount of charge} = AdC_T F \quad (S3)$$

where A , d , C_T and F are the electrode area, the polymer thickness, the concentration of the redox site and the Faraday constant, respectively. The concentration of the redox site was calculated using equation (S2) and the saturated amounts of charge for each device were calculated as follows.

The PTAm-A layer on the electrode in Fig. 4a

$$\text{Saturated amount of charge C} = \frac{3 \text{ cm}^2 \times 110 \times 10^{-7} \text{ cm} \times 1 \text{ g cm}^{-3} \times 96500 \text{ C mol}^{-1}}{\frac{225.3 \times 83 + 72.1 \times 17}{83} \text{ g mol}^{-1}}$$

$$= 13.3 \times 10^{-3} \text{ C}$$

The PTAm-A layer in the bilayer device in Fig. 5

$$\text{Saturated amount of charge C} = \frac{1 \text{ cm}^2 \times 130 \times 10^{-7} \text{ cm} \times 1 \text{ g cm}^{-3} \times 96500 \text{ C mol}^{-1}}{\frac{225.3 \times 83 + 72.1 \times 17}{83} \text{ g mol}^{-1}}$$

$$= 5.2 \times 10^{-3} \text{ C}$$

The PTPM layer in the bilayer device in Fig. 5

$$\text{Saturated amount of charge C} = \frac{1 \text{ cm}^2 \times 160 \times 10^{-7} \text{ cm} \times 1 \text{ g cm}^{-3} \times 96500 \text{ C mol}^{-1}}{\frac{460.8}{3} \text{ g mol}^{-1}}$$

$$= 10.1 \times 10^{-3} \text{ C}$$

Table S1 Thickness of the polymer layers

Figure	Device or electrode	Polymer	Thickness/nm
2	Modified electrode	P(TAm-A)	130
3a	Modified electrode	P(TAm-A)	110
3a	Single-layer device	P(TAm-A)	120
3a	Single-layer device	P(Cam-A)	130
3b	Modified electrode	PTPM	60
3b	Single-layer device	PTPM	110
4a	Modified electrode	P(TAm-A)	110
4a	Single-layer device	P(TAm-A)	110
4b	Modified electrode	PTPM	180
4b	Single-layer device	PTPM	110
5	Single-layer device	P(TAm-A)	50
5	Single-layer device	PTPM	180
5	Bilayer device for CV	P(TAm-A)	130
5	Bilayer device for CV	PTPM	110
5	Bilayer device for CC	P(TAm-A)	130
5	Bilayer device for CC	PTPM	160
S1	Modified electrode	P(TAm-A)	190
S5	Bilayer device	P(TAm-A)	130
S5	Bilayer device	PTPM	160
S6	Bilayer device	P(TAm-A)	130
S6	Bilayer device	PTPM	110

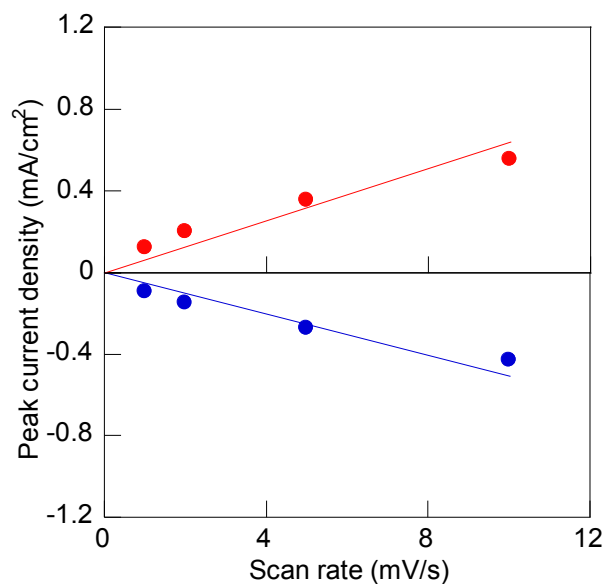


Fig. S1 Plots of anodic (red closed circle) and cathodic (blue closed circle) peak current densities versus the potential scan rate obtained from cyclic voltammograms of the layer of PTAm-A on a GC substrate in a 0.1 M NaCl aqueous solution. The electrode area was 3 cm².

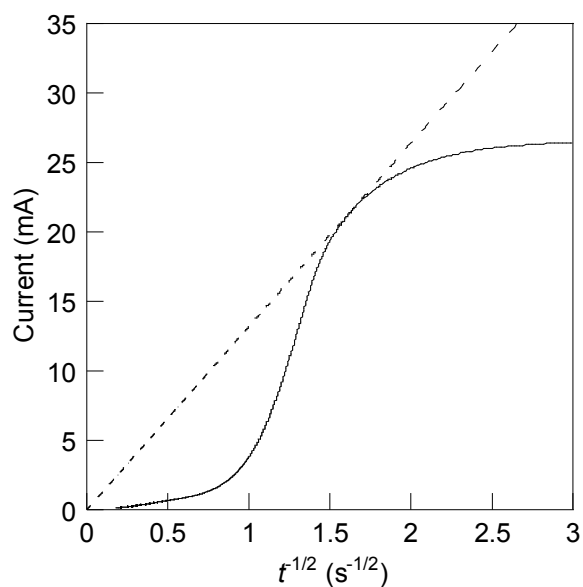


Fig. S2 Cottrell curve for chronoamperometry of the PTAm-A modified GC electrode in a 0.1 M NaCl aqueous solution. The potential was stepped from 0 to 1.1 V vs. Ag/AgCl. The electrode area of the modified electrode was 4 cm².

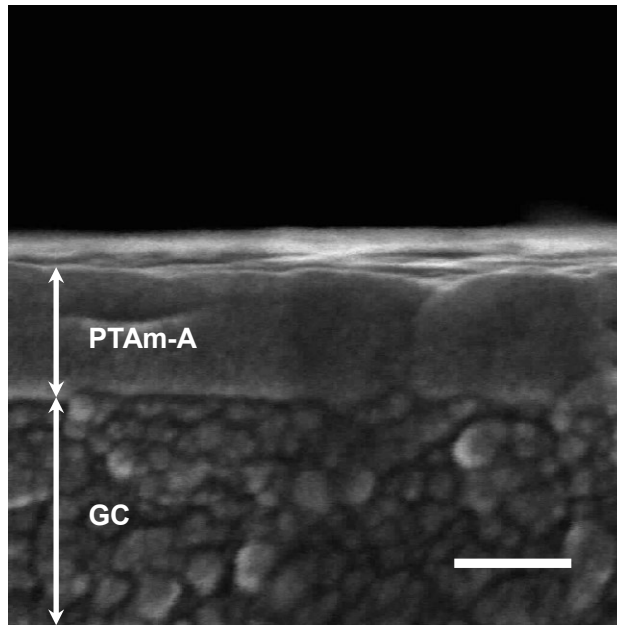


Fig. S3 SEM image of the cross section of the PTAm-A layer on a GC substrate. Scale bar = 100 nm.

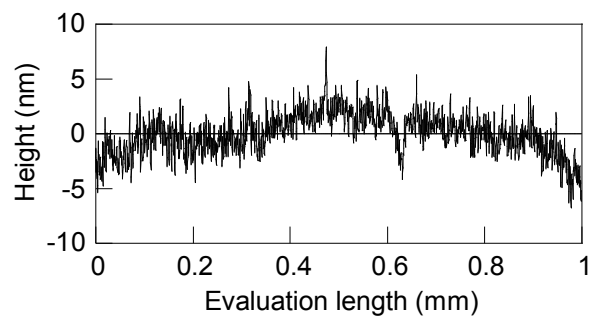


Fig. S4 Contact stylus profilometer height profiles of the PTAm-A layer. Thickness of the polymer layer was 120 nm.

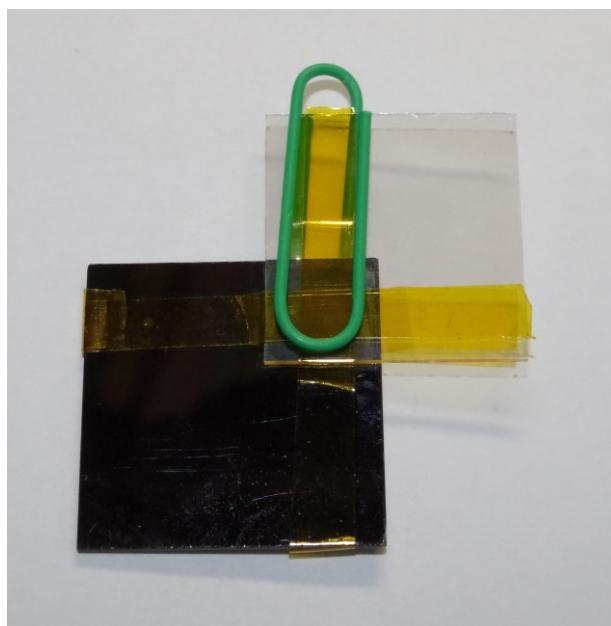


Fig. S5 General view of the bilayer device in Fig. 5, composed of PTAm-A and PTPM. A spin-coated PTAm-A/GC and electropolymerized PTPM/FTO were fixed with each other using kapton tapes and a paper clip.

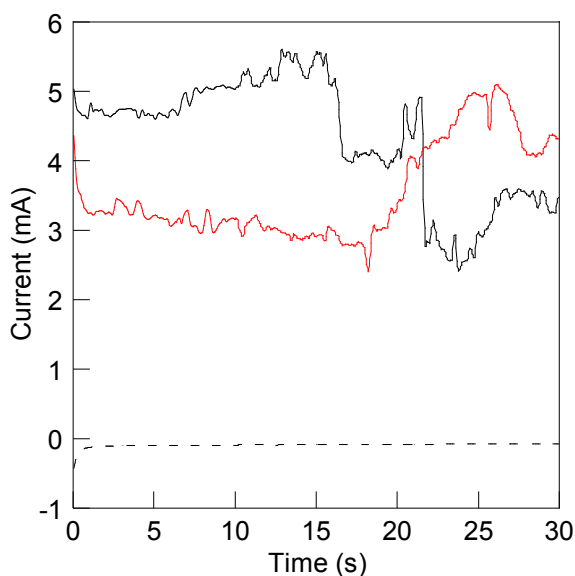


Fig. S6 Current vs. time obtained for the bilayer device composed of PTAm-A and PTPM in a 0.1 M NaCl aqueous solution. The voltage was stepped from 0 to +1.8 V (black solid curve) and then stepped from 0 to -1.8 V (black dashed curve). After that, the voltage was stepped from 0 to +1.8 V again (red solid line). The electrode area was 1 cm².

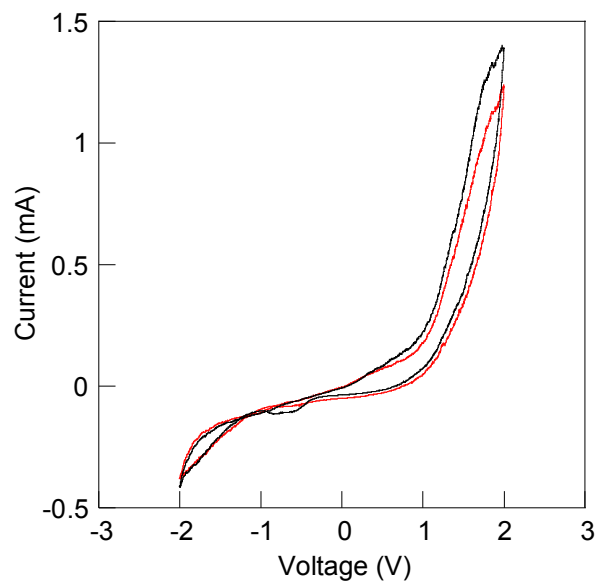


Fig. S7 Two-electrode cyclic voltammograms obtained for the bilayer device composed of PTAm-A and PTPM before (black solid curve) and after (red solid curve) 30 times applications of negative bias of -1.8 V for 10 seconds in a 0.1 M NaCl aqueous solution at a scan rate of $\nu = 50 \text{ mV s}^{-1}$. The electrode area was 1 cm^2 .

References

See References in main text.