

# Photocurrent amplification by an energy/electron transfer cascade in polymer Langmuir–Blodgett films

Jinfeng Chen, Masaya Mitsuishi, Atsushi Aoki and Tokuji Miyashita\*

*Institute of Multidisciplinary Research for Advanced Materials (IMRAM), Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan. E-mail: miya@tagen.tohoku.ac.jp*

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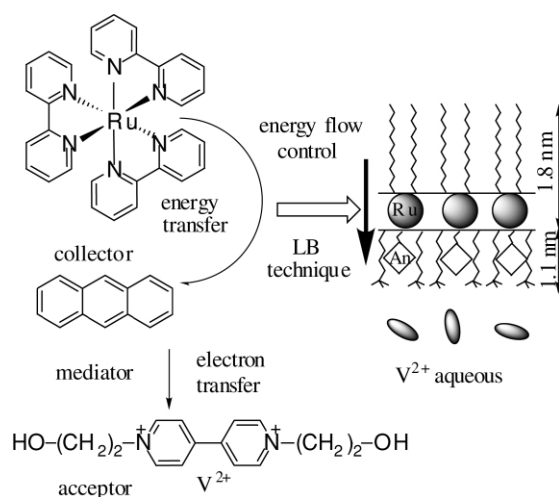
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Effective photocurrent generation by visible light irradiation on hetero-deposited polymer Langmuir–Blodgett (LB) films containing tris(bipyridine) ruthenium(II) ( $\text{Ru}(\text{bpy})_3^{2+}$ ) and anthracene derivatives was observed. The photocurrent amplification was found to be assisted by the photoinduced energy/electron transfer cascade, which consists of the interlayer triplet–triplet energy transfer process from photoexcited  $\text{Ru}(\text{bpy})_3^{2+}$  to anthracene, and then electron transfer processes from the triplet anthracene to a viologen acceptor, from  $\text{Ru}(\text{bpy})_3^{2+}$  to the oxidized anthracene and from the electrode to  $\text{Ru}(\text{bpy})_3^{3+}$ .

Photoinduced charge separation and light harvesting effects with high quantum efficiency play a crucial role in natural photosynthesis, light-energy conversion systems,<sup>1</sup> resulting in oxidation of water, reduction of  $\text{NADP}^+$ , and synthesis of ATP. Many approaches for mimicking the photosynthesis system are based on the simplification of these processes, *i.e.*, photoinduced charge separation<sup>2</sup> and energy transfer processes.<sup>3</sup> So far, much effort has been devoted to synthesizing supramolecular assemblies showing an effective photoinduced electron transfer.<sup>4</sup> However, a variety of fascinating features of these supramolecules have been limited in solution.<sup>5</sup> It is necessary to assemble these materials onto a solid substrate for fabrication of devices.

Recently, organization of molecular assemblies using molecular architecture techniques, such as the Langmuir–Blodgett (LB) technique, self-assembled monolayers (SAM), and the layer-by-layer alternate adsorption method has received much attention.<sup>6</sup> These ‘bottom up’ approaches are expected to be good candidates for construction of artificial molecular nano-devices.<sup>7</sup> In a previous paper, we have demonstrated effective vectorial photoinduced electron transfer in hetero-deposited LB films composed of the monolayers containing  $\text{Ru}(\text{bpy})_3^{2+}$  and the monolayer containing ferrocene derivatives.<sup>8</sup> Here we expand this concept to the photoinduced energy/electron transfer cascade system, which consists of triplet–triplet energy transfer and electron transfer processes in a hetero-deposited LB film containing the polymer LB films with  $\text{Ru}(\text{bpy})_3^{2+}$  as an inner layer and with anthracene chromophore as an outer layer on the electrode, and focus on the photocurrent generation due to the photoinduced energy/electron transfer cascade system in the hetero-deposited LB film contacted with an aqueous solution of viologen derivative as a sacrificial acceptor. Since the triplet lifetimes are longer than the singlet ones, efficient triplet–triplet energy transfer as well as electron transfer are expected in the hetero-deposited LB film system. Consequently, photocurrent enhancement was achieved in the hetero-deposited layer system *via* the energy/electron transfer cascade compared with the single layer system of  $\text{Ru}(\text{bpy})_3^{2+}$  *via* the electron transfer process (Scheme 1).

The synthesis of poly(*N*-dodecylacrylamide-*co*-(4-(acryloyl-ethyl)-4'-methyl-2,2'-bipyridine)ruthenium) (p(DDA/Ru)) is described in the previous paper.<sup>8</sup> Anthracene-labeled copolymers (An) with 5 (An5), 10 (An10), and 20 (An20) mol% anthracene content were prepared with copolymerization of *N*-neopentyl methacrylamide (nPMA) and 9-anthrylmethyl methacrylamide (AMMA) (Fig. 1). The mole



Scheme 1 Control of energy transfer by LB technique.

fraction of  $\text{Ru}(\text{bpy})_3^{2+}$  was determined to be 11 mol% with UV spectroscopy. Bis(2-hydroxyethyl)-*N,N'*-4,4'-bipyridinium cation ( $\text{V}^{2+}$ ) was prepared according to the literature,<sup>9</sup> and recrystallized three times from methanol before use. Quartz and indium tin oxide (ITO) substrates were used as solid supports. The surface was cleaned by a UV- $\text{O}_3$  cleaner (NL-UV253, Nippon Laser Electronics), and then the quartz substrate was made hydrophobic with octyltrichlorosilane.

It has previously been reported that these copolymers spread onto a water surface form stable monolayers.<sup>10,11</sup> The monolayers were transferred onto solid substrates by the vertical dipping method as Y-type LB films with a transfer ratio of almost unity. Monolayer thickness of p(DDA/Ru) and An10 LB films were determined to be 1.8 and 1.1 nm, respectively, from XRD measurement.

Quenching of the emission of  $\text{Ru}(\text{bpy})_3^{2+}$  by anthracene was examined in the hetero-deposited LB films constructed by successive deposition of the polymer monolayers with

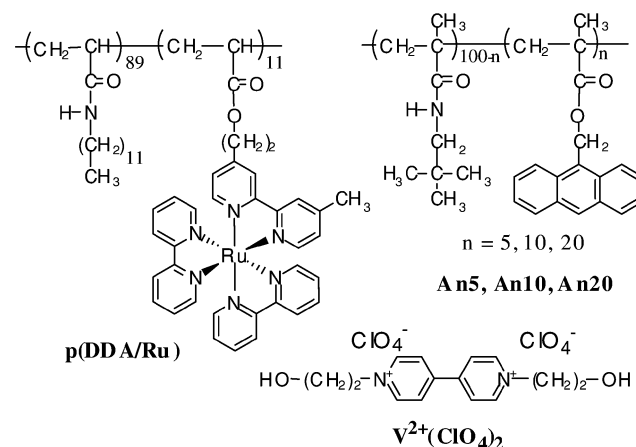
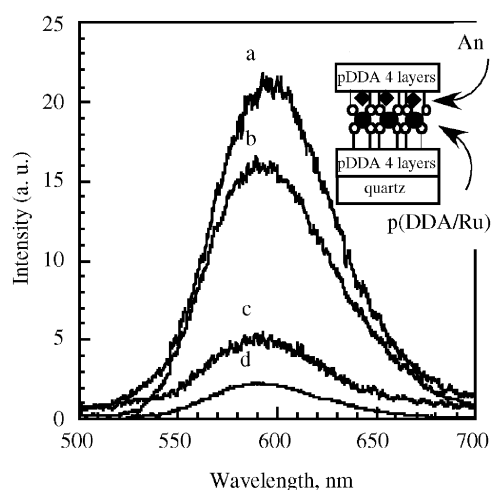


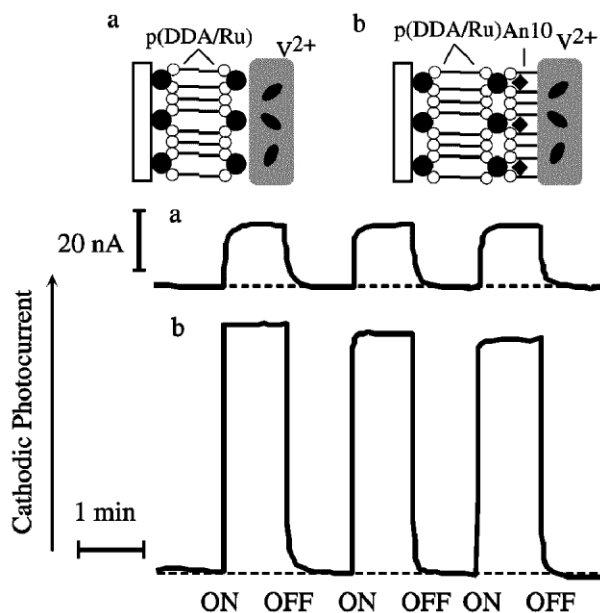
Fig. 1 Chemical structure of p(DDA/Ru), An and  $\text{V}^{2+}$ .

Ru(bpy)<sub>3</sub><sup>2+</sup> and anthracene on the quartz substrate, which has a head-to-head structure (Fig. 2, inset). Poly(*N*-dodecylacrylamide) (pDDA) LB film with 4 layers were deposited as pre- and post-coating layers to avoid substrate and oxygen quenching. The emission intensity at 600 nm is apparently quenched by the anthracene layer and, moreover, the intensity decreases with increasing anthracene contents in the LB film. Triplet-triplet energy transfer from excited Ru(bpy)<sub>3</sub><sup>2+</sup> to anthracene is possible because the energy level of the Ru(bpy)<sub>3</sub><sup>2+</sup> triplet is higher than that of the anthracene triplet, whereas, electron transfer from the excited Ru(bpy)<sub>3</sub><sup>2+</sup> to anthracene is impossible, demonstrated by thermodynamic data which shows that the oxidation potential of excited Ru(bpy)<sub>3</sub><sup>2+</sup> (−0.8 V vs. SCE) is lower than the reduction potential of anthracene (−2.2 V vs. SCE).<sup>12</sup> It is well-known that the lifetime of the anthracene triplet is longer than that of the excited ruthenium complex, and also that the anthracene triplet acts as a good electron donor.<sup>13</sup> Therefore, it is expected that photoinduced charge separation between Ru(bpy)<sub>3</sub><sup>2+</sup> and V<sup>2+</sup> is enhanced by the presence of the anthracene layer as a mediator. Photocurrent measurement for the LB film of Ru(bpy)<sub>3</sub><sup>2+</sup> with or without An10 LB monolayer in an aqueous solution of V<sup>2+</sup> was carried out (Fig. 3). Cathodic photocurrent, caused by electron transfer to V<sup>2+</sup> from the LB films, was measured under visible light irradiation (λ > 430 nm). Apparently, the photocurrent from the hetero-deposited LB film with Ru(bpy)<sub>3</sub><sup>2+</sup> and anthracene layer was enhanced, compared with the case of single LB film with Ru(bpy)<sub>3</sub><sup>2+</sup> (Fig. 3(a) and (b)). In other words, the photoinduced electron transfer efficiency from Ru(bpy)<sub>3</sub><sup>2+</sup> to V<sup>2+</sup> increases with introducing the anthracene layer between Ru(bpy)<sub>3</sub><sup>2+</sup> and V<sup>2+</sup>. Therefore, we suppose the photocurrent generation mechanism in this system to be as follows: the triplet-triplet energy transfer from excited Ru(bpy)<sub>3</sub><sup>2+</sup> to anthracene, and then the electron transfer processes from the anthracene triplet to V<sup>2+</sup>, from Ru(bpy)<sub>3</sub><sup>2+</sup> to oxidized anthracene and from the electrode to Ru(bpy)<sub>3</sub><sup>3+</sup> took place efficiently. An effective relay system based on triplet-triplet energy transfer and electron transfer processes is achieved in the hetero-deposited LB films with Ru(bpy)<sub>3</sub><sup>2+</sup> and anthracene. Detailed understanding of mechanism and quantitative analysis for this system is now in progress.

In conclusion, photoinduced energy/electron transfer cascade system of Ru(bpy)<sub>3</sub><sup>2+</sup> and anthracene was fabricated by the LB



**Fig. 2** Steady-state fluorescence emission spectra ( $\lambda_{\text{ex}} = 460 \text{ nm}$ ) for (a) p(DDA/Ru) LB films only, (b) p(DDA/Ru)/An5, (c) p(DDA/Ru)/An10, and (d) p(DDA/Ru)/An20; (Inset) the layer structure for p(DDA/Ru)/An.



**Fig. 3** Photocurrent response for p(DDA/Ru)/ITO (a) and p(DDA/Ru)/An10/ITO (b) in 20 mM V<sup>2+</sup> and 0.1 M NaClO<sub>4</sub> solution. Conditions: applied potential, 0.0 V vs SCE; light intensity, 75 mW cm<sup>−2</sup>.

technique. Emission of Ru(bpy)<sub>3</sub><sup>2+</sup> was efficiently quenched by anthracene through interlayer triplet-triplet energy transfer in the polymer LB film. Spatial miniaturization of energy relay parts, An LB monolayer, gave photocurrent amplification between Ru(bpy)<sub>3</sub><sup>2+</sup> and V<sup>2+</sup>. In other words, the An LB film not only acts as an intervening energy relay part, but also electron donor to V<sup>2+</sup>.

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