Preparation and Photoelectrochemical Properties of a Self-Assembled Monolayer of a Ruthenium Tris(2,2'-bipyridine)-viologen 1:2 Linked Compound

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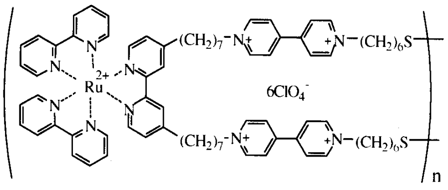
A ruthenium tris(2,2'-bipyridine)-viologen 1:2 linked disulfide was prepared. A gold electrode modified with this compound showed a higher efficiency of photocurrent as compared with a corresponding 1:1 linked compound.

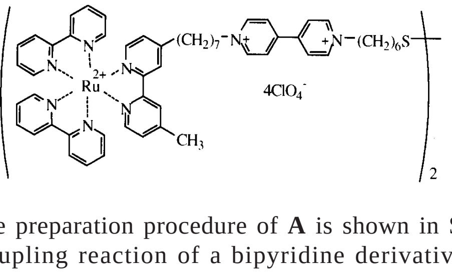
Fabrication of organized molecular assemblies in which a photoredox pair is elaborately arranged on the electrode surface is promising to achieve highly-efficient photoelectric conversion.[1] Recently, novel electron donor-acceptor linked sulfur compounds have been prepared and photo-electrochemical properties of their self-assembled monolayers (SAMs)[2] on gold surfaces have been investigated.[3-11]

A ruthenium tris(2,2'-bipyridine)-viologen (Ru^{2+}-V^{2+}) couple is a typical photoredox pair for generating charge-separated states.[12-14] We previously reported the photocurrent responses from gold electrodes modified with Ru^{2+}-V^{2+} (1:1) linked disulfides.[5,9] It was also suggested that the photocurrent induced by electron-transfer from photoexcited Ru^{2+}($^*Ru^{2+}$) to V^{2+} was suppressed by the reverse electron-transfer reaction.[9] Highly-efficient charge-separation in the SAMs is primarily important to obtain larger photocurrents.

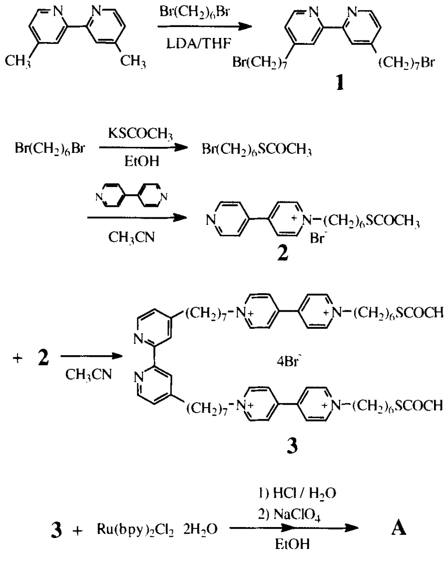
Early studies using organized V^{2+} assemblies as electron accepting sites achieved highly-efficient charge-separated states, ascribing to electron migration among the V^{2+} assemblies.[15] From these viewpoints, we have prepared a Ru^{2+}-V^{2+} 1:2 linked complex **A**, intending for achieving efficient charge-separation in the SAM. The **A**-modified gold electrode gave a higher efficiency of photocurrent as compared with a Ru^{2+}-V^{2+} 1:1 linked complex **B** in terms of the identical coverage.



A



B



Scheme 1.

The preparation procedure of **A** is shown in Scheme 1. The coupling reaction of a bipyridine derivative **1** and a monopyridinium thioacetate **2** in CH_3CN under reflux gave a bisviologen-linked bipyridine ligand **3** in 9% yield. The final product was obtained in 29% yield by the reaction of $Ru(bpy)_2Cl_2 \cdot 2H_2O$ and **3**, followed by hydrolysis and oxidation. The formation of **A** was confirmed from the ^1H-NMR.[16] The Ru^{2+} moiety shows a characteristic absorption band at the ~400–~500 nm region based on metal-to-ligand charge-transfer transition. They were essentially identical in **A** and **B**, indicating no appreciable interactions between Ru^{2+} and V^{2+} moieties at the ground states. Redox potentials of **A** (1.20, -0.38, -0.83, -1.30 V vs. Ag/AgCl (sat. KCl)) in CH_3CN using 0.1 mol dm^{-3} $(C_4H_9)_4NClO_4$ as a supporting electrolyte were almost identical to the corresponding values of **B** (1.20, -0.39, -0.82, -1.31 V vs. Ag/AgCl (sat. KCl)).

However, the luminescence intensity of **A** was substantially smaller than that of **B**, as shown in Figure 1. Since the spacer-chain lengths between the Ru^{2+} and the V^{2+} moieties are identical in **A** and **B**, the result of Figure 1 strongly suggests that the efficient electron-transfer quenching of $^*Ru^{2+}$ by the V^{2+} moieties is occurring in **A** as compared with **B**.

The gold electrode was prepared by vacuum deposition of gold onto a mica plate (30×10×1 mm) (roughness factor 2.7). It has a polycrystalline surface from cyclic voltammetric measurements in aqueous H_2SO_4. It was immersed into a CH_3CN solution containing **A** or **B** (1×10^{-3} mol dm^{-3} = M as monomer unit) for one day. After soaking with CH_3CN and methanol, the **A**-(or **B**-) modified electrode was dried with a stream of nitrogen gas.

Formation of the SAM was confirmed from XPS and cyclic voltammetric measurements.[9] XPS results indicated the formation of S–Au bonding (161.7 eV : $S(2p_{1/2})$) and no significant peaks due to free –SH and –SS– groups were detected.

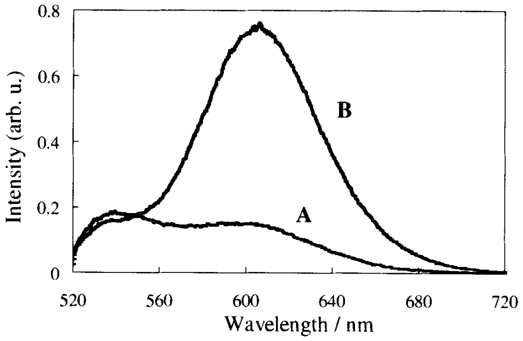


Figure 1. Luminescence spectra of **A** (ε_{470} = 9.39×10^3) and **B** (ε_{470} = 9.36×10^3) in CH_3CN (1×10^{-5} M: monomer unit).

From the analysis of broad and reversible redox-peaks for one-electron reduction of the V^{2+} moieties (**A**-modified electrode: -0.49V, **B**-modified electrode: -0.44V vs. Ag/AgCl (sat. KCl)), fractional coverages of **A** and **B** were evaluated to be 3.6×10^{-11} and 2.0×10^{-10} mol cm^{-2}, respectively. A considerably lower coverage for **A** may be at least in part due to increased intramolecular and intermolecular electrostatic repulsion among the positively charged Ru^{2+} and V^{2+} moieties in the SAM, as compared with the case of **B**.

Photocurrent measurements for the modified electrodes were taken in aqueous solutions containing triethanolamine (5×10^{-2} M) as a sacrificial reductant and $NaClO_4$ (0.1 M). Figure 2 shows a photocurrent action spectrum for the **A**-modified electrode at 0 V vs. Ag/AgCl (sat.KCl). The photocurrent was observed in the anodic direction. The spectrum showed a broad band, almost overlapping with the absorption band in solution. The **B**-modified electrode also showed similar photocurrent results as reported previously.[9]

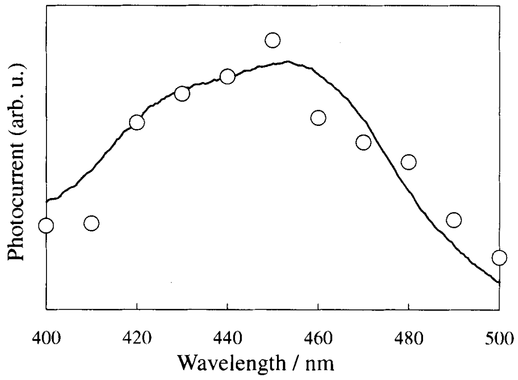


Figure 2. Photocurrent action spectrum of **A**-modified electrode (○) and the absorption spectrum of **A** in CH_3CN (—). Conditions for photocurrent measurements: *E*=0 V vs. Ag/AgCl, λ_{ex}=470±16 nm, [TEOA]=5×10^{-2} M, [$NaClO_4$]=0.1 M

Potential dependencies of photocurrents under illumination at 470 ± 40 nm (4.1 mW cm^{-2}) were compared between the two modified electrodes. Larger photocurrents were observed from the **B**-modified electrode because of the higher coverage as compared with the **A**-modified electrode. However, the efficiency of photocurrent is roughly twice higher in the **A**-modified electrode, if the comparison is made in terms of the identical coverage as shown in Figure 3.

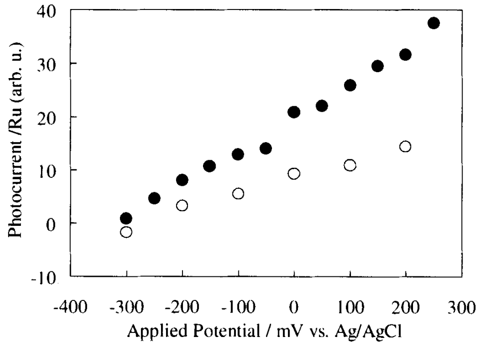


Figure 3. Applied potential dependencies on the photocurrent intensities of modified electrodes with **A** (●) and **B** (○) calculated at the identical coverage. λ_{ex} = 470 ± 40 nm. Other conditions are same as those in Figure 2.

There can be two pathways for the photoinduced electron-transfer from the $^*Ru^{2+}$ to the V^{2+} moieties in **A**. In fact, the efficiency of photoinduced electron-transfer from $^*Ru^{2+}$ to V^{2+} became substantially higher by linking the two V^{2+} moieties. Obviously, this is one of the requirements for improving the photocurrent efficiency. However, it is not clear at this stage how effectively the two V^{2+} moieties cooperate to retard the reverse electron-transfer. Structural differences between the SAMs of **A** and **B** also should be considered. Absorption spectral measurements after controlled potential reduction of **A** may be helpful to elucidate the role of the V^{2+} moieties, and the work is in progress along this line.

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References and Notes

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16 The product tends to polymerize via intermolecular disulfide bonding, causing poor solubility. ^{1}H-NMR (400 MHz, CD_3CN) δ = 1.15, 1.30, and 1.60 (m, 36H), 2.75 (m, 8H), 4.60 (t, *J* = 7.9 Hz, 8H), 7.23 (brs, 2H), 7.38 (dd, *J* = 6.7 Hz, 8.6Hz, 4H), 7.55 (d, *J* = 6.3 Hz, 2H), 7.73 (dd, *J* = 6.3 Hz, 8.6 Hz, 4H), 8.03 (m, 4H), 8.44 (d, *J* = 5.5 Hz, 8H), 8.51 (d, *J* = 6.3 Hz, 6H), 8.95 ppm (m, 8H).