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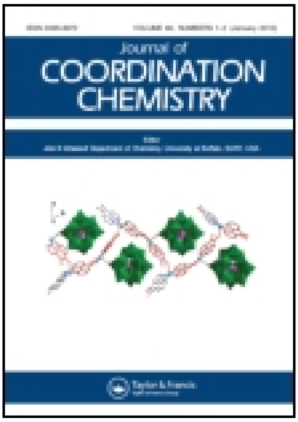

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Rotaxane based on terpyridyl bimetal ruthenium complexes and β-cyclodextrin as organic sensitizer for dye-sensitized solar cells

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[2]Rotaxane based on terpyridyl bimetal ruthenium complexes and *β*-cyclodextrin as organic sensitizer for dye-sensitized solar cells

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The conjugated carboxy-functionalized terpyridyl bimetal ruthenium complex [(tdctpy)Ru(dctpy-(ph)$_4$-dctpy)Ru(tdctpy)][PF$_6$]$_4$ and [2]rotaxane by self-assembly of [(tdctpy)Ru(dctpy-(ph)$_4$-dctpy)Ru(tdctpy)][PF$_6$]$_4$ with β-cyclodextrin are reported as sensitizer for dye-sensitized solar cells (DSSCs), where tdctpy = 4′-*p*-tolyl-4,4″-dicarboxy-2,2′ : 6,2″-terpyridine, dctpy = 4,4″-dicarboxy-2,2′ : 6,2″-terpyridine and dctpy-(ph)$_4$-dctpy represents a bridging ligand where two 4,4″-dicarboxy-2,2′ : 6′,2″-terpyridine units are connected through four phenyl spacers in the 4′-position. The DSSCs fabricated utilizing these materials give typical electric power conversion efficiency of 0.013–0.523% under air mass (AM) 1.5, 100 mW cm^{-2} irradiation at room temperature. The terpyridyl bimetal ruthenium complex [(tdctpy)Ru(dctpy-(ph)$_4$-dctpy)Ru(tdctpy)][PF$_6$]$_4$ with conjugated-bridge chains displayed much higher conversion efficiency compared with the carboxy-functionalized terpyridyl monometal ruthenium complex [tdctpy-Ru-(idctpy)][PF$_6$]$_2$, where idctpy = 4′-*p*-iodophenyl-4,4″-dicarboxy-2,2′ : 6,2″-terpyridine. [2]Rotaxane displayed the highest electric power conversion efficiency of 0.523% when β-cyclodextrin was introduced into the conjugated terpyridyl bimetal ruthenium complex and formed [2]rotaxane.

Keywords: Dye-sensitized solar cells; Bimetal ruthenium complexes; β-Cyclodextrin; Rotaxane

1. Introduction

Dye-sensitized solar cells (DSSCs) are an important subject in the field of optical materials for low-cost solar energy conversion [1–6]. DSSCs based on bipyridine and terpyridine mono ruthenium complexes are excellent sensitizers, showing high conversion efficiency [7–13]. For example, ([(C$_4$H$_9$)$_4$N]$_2$[Ru(dcbpyH)$_2$(NCS)$_2$]) and ([(C$_4$H$_9$)$_4$N]$_4$[Ru(dcbpy)$_2$(NCS)$_2$]) displayed very high conversion efficiency [14–16]. Some groups have reported many bimetal ruthenium complexes with terpyridine

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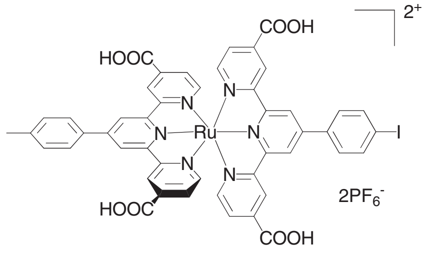
ligands [17–22]. However, there are few reports of terpyridine bimetal ruthenium complexes with conjugated-bridge chains as sensitizers for DSSCs [17]. Recently we reported the terpyridyl bimetal ruthenium complex **2** with conjugated oligophenyl units and [2]rotaxane derivative **3** by self-assembly of **2** with *β*-cyclodextrin, and investigated the basic optical properties such as the UV/Vis absorption and fluorescence spectra [23]. However, there are few reports of terpyridyl biruthenium complexes as sensitizers for DSSCs [17]. Introduction of *β*-cyclodextrin which is efficient in intramolecular charge and energy transfer from the linked dye molecule and peripheral hydroxy-groups of *β*-cyclodextrin enhances attachment with TiO_2 [8, 24, 25], improving the electric power conversion efficiency. Based on the above considerations, herein, we investigate electric power conversion efficiencies as sensitizers for DSSCs. The results indicated that: (1) the terpyridyl biruthenium complex **2** with conjugated chains displayed much higher conversion efficiency than **1**, (2) the [2]rotaxane by self-assembly of **2** with *β*-cyclodextrin showed the highest conversion efficiency of 0.523%. Peripheral hydroxy-groups of *β*-cyclodextrin in **3** enhance the ability of attachment with TiO_2 and degrade energy levels of the LUMO.



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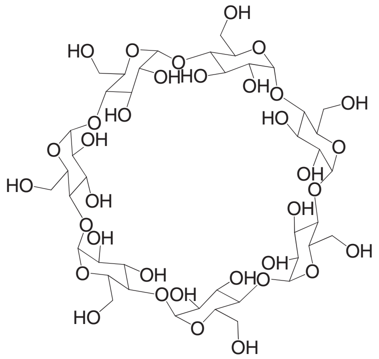
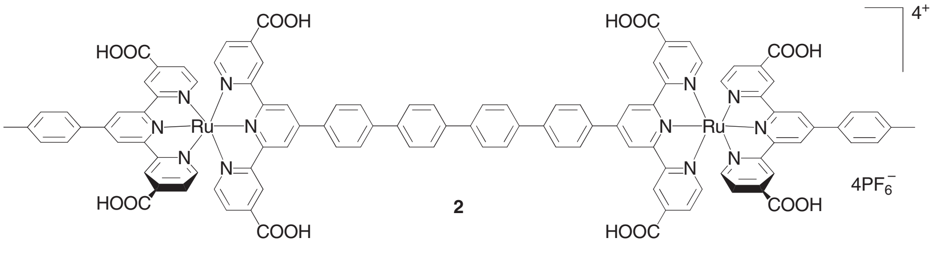


β-Cyclodextrin



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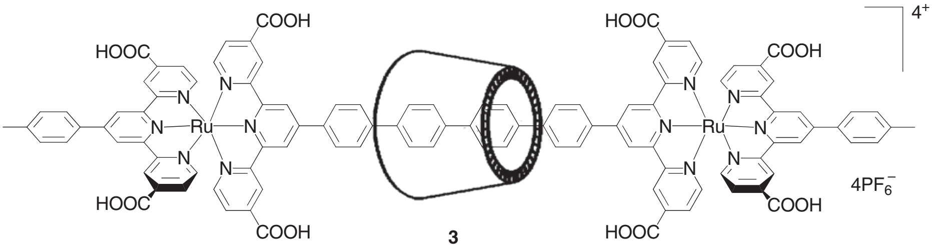

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2. Experimental

The three compounds were prepared according to previous methods [23, 26–34]. UV/Vis absorption spectra were performed on a Hitachi U-3310. Luminescence data were recorded on a Hitachi Model F-4500. Cyclic voltammograms were measured using a CHI 660C electrochemical analyzer in acetonitrile containing 0.1 mol dm^{-3} n-Bu$_4$NPF$_6$ using a glassy-carbon working electrode and a platinum-wire counter electrode. All potential values were referenced to the saturated calomel electrode (SCE). An argon atmosphere was continuously maintained above the solution while the experiments were in progress. The glassy-carbon working electrode surface was polished with 0.03 mm alumina, sonicated in distilled water, and air-dried immediately before use. The film was dried at 100°C for 15 min and then sintered at 450°C for 30 min to remove the organics and to form a mesoporous film structure. The thickness of the film was about 12 μm. Photovoltaic performances of DSSC samples with an active area of 0.08 cm^2 were performed by using an electrolyte 0.03 M I$_2$, 0.3 M LiI in propylene carbonate under standard illumination (100 mW cm^{-2}, AM 1.5, 25°C). The photocurrent–voltage (*I*–*V*) curves were obtained over a potential range of 0.0 V to 0.6 V using a Keithley M 236 source measure unit. A 300 W Xe arc lamp (Oriel) with an AM 1.5 solar simulating filter for spectral correction was used to illuminate the working electrode (from back side). The light intensity was adjusted to 100 mW cm^{-2} using a Si solar cell.

3. Results and discussion

3.1. *UV/Vis absorption spectra and electrochemical properties*

UV/Visible absorption spectra of **1**, **2**, and **3** have been investigated at room temperature, as shown in figure 1. In the visible region, **2** and **3** display more intense absorption than **1**, possibly because **2** and **3** have more intense metal-to-ligand

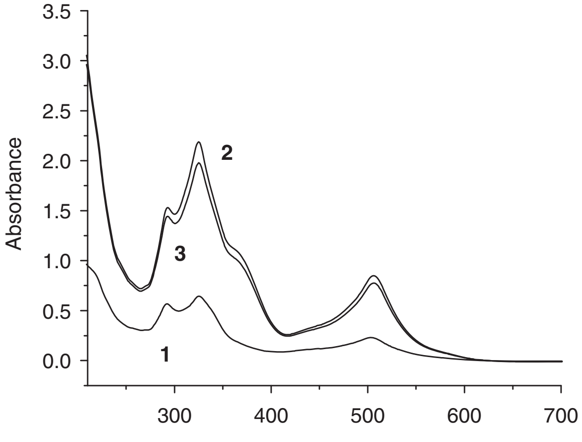

Figure 1. Absorption spectra of **1**, dumbbell **2** and rotaxane **3** in 10 μM methanol solution.

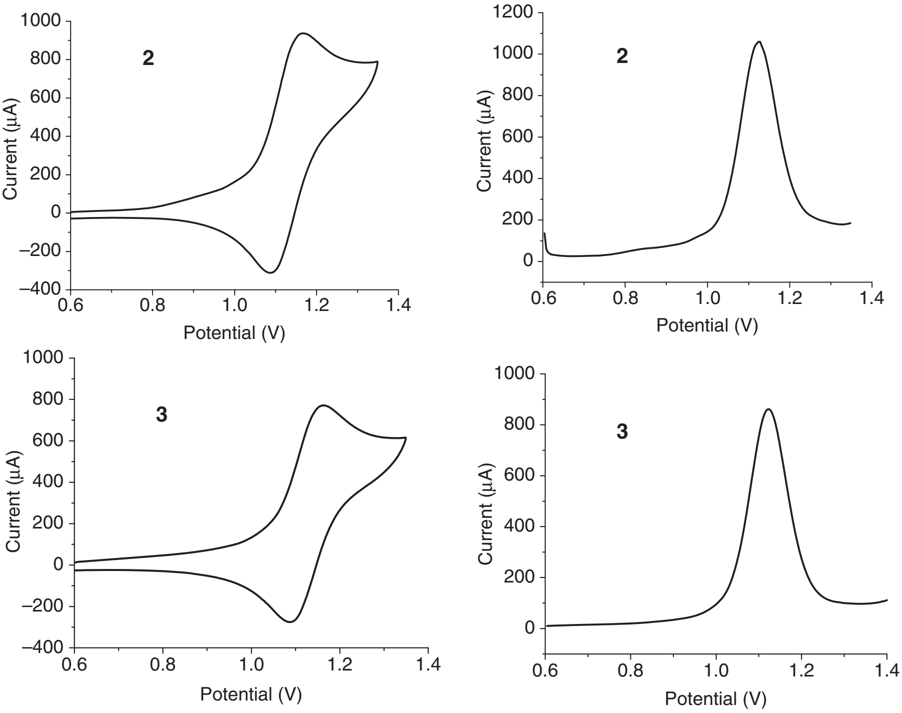

Figure 2. Cyclic voltammetry (left) and square-wave voltammograms (right) of **2** and **3** in 10 μM acetonitrile solution at a scan rate of $100\,\mathrm{mV\,s^{-1}}$.

charge-transfer (MLCT) than **1** [35]. Absorption intensity of rotaxane **3** was similar to the dumbbell **2**. Electrochemical properties of **2** and **3** were measured in 10 μM acetonitrile solution at room temperature. The solubility of **2** and **3** is not good in acetonitrile and several drops of trifluoroacetic acid (TFA) was added to improve the solubility. As shown in figure 2, **2** and **3** display the similar oxidation potential.

3.2. *Photovoltaic properties*

The photovoltaic experiments were performed under irradiation from the back of the core-shell film to the Pt film with an Oriel 91192 AM 1.5 solar simulator as a light source. I/V characteristics of DSSCs (dye-sensitisers for solar cells) sensitized by **1**, **2**, and **3** using a liquid electrolyte are described in figure 3. Photovoltaic performances of DSSC samples with an active area of $0.08\,\mathrm{cm^2}$ using 0.03 M I_2, 0.3 M LiI electrolyte in propylene carbonate under standard illumination ($100\,\mathrm{mW\,cm^{-2}}$, AM 1.5, 25°C) are listed in table 1. Terpyridine–ruthenium complexes were attached to TiO_2 as sensitizers for DSSCs. The presence of carboxylic functions is needed to obtain a stable absorption and high electronic coupling between the metal centre and the nanocrystals that leads to efficient charge injection. We have tested the photocurrent action of **1**, **2**, and **3** under the same liquid electrolyte device geometry (table 1), in which **2** with the conjugated-bridge chains displayed much higher conversion efficiency compared with **1**, while **3**

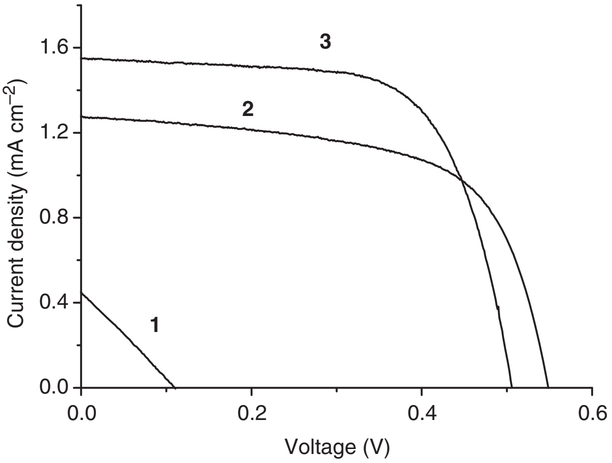

Figure 3. The I/V characteristics of **1**, dumbbell **2** and rotaxane **3**.

Table 1. Photovoltaic performances of **1**–**3**.

Materials	I_{sc} (mA cm^{-2})[a]	V_{oc} (mV)[b]	P_{max} (mW)[c]	FF (%)[d]	Efficiency (%)[e]
1	0.446	110	0.001	26.3	0.013
2	1.277	547	0.035	62.8	0.438
3	1.511	506	0.042	66.7	0.523

[a] Short-circuit current.
[b] Open-circuit voltage.
[c] The maximum power.
[d] Fill factor.
[e] Electric power conversion efficiency.

displayed the highest electric power conversion efficiency of 0.523% when the β-cyclodextrin was introduced into **2** and formed the [2]rotaxane which possibly attributed to the addition of β-cyclodextrin.

4. Conclusions

The conjugated terpyridyl bimetal ruthenium complexes are sensitizers for DSSCs. According to typical electric power conversion efficiencies, we found that **2** with the conjugated-bridge chains displayed much higher conversion efficiency than **1**. Furthermore, introduction of β-cyclodextrin, in which an inclusion [2]rotaxane was formed, improves the conversion efficiency of DSSCs. Perhaps peripheral hydroxy-groups of β-cyclodextrin in **3** enhance the attachment with TiO_2 and decrease energy levels of the LUMO. The performance is relatively low, compared with reported dinuclear Ru(II) dyes, probably due to the length and conjugation of the bridging ligand. Next work will focus on inclusion to improve the conversion efficiency.

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