Synthesis of a new copper(I) complex, $[Cu(tmdcbpy)_2]^+$ (tmdcbpy = 4,4′,6,6′-tetramethyl-2,2′-bipyridine-5,5′-dicarboxylic acid), and its application to solar cells†

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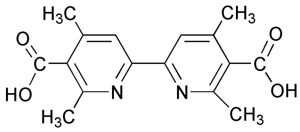
A newly synthesized copper(I) complex, $[Cu(tmdcbpy)_2]^+$ (tmdcbpy = 4,4′,6,6′-tetramethyl-2,2′-bipyridine-5,5′-dicarboxylic acid), was applied to a solar cell with TiO_2, which provided successful results, a photocurrent of about 4 mA cm^{-2}, photovoltage of 630 mV and an IPCE (incident monochromatic photon-to-current conversion efficiency) value of 30%, under visible light irradiation from a AM 1.5G sunlight simulator (100 mW cm^{-2}).

Grätzel and co-workers proposed a very efficient solar cell with TiO_2 and ruthenium(II) complexes.[1] In the Grätzel cell, excellent results have been presented with ruthenium(II) complexes such as $[Ru(NCS)_2(dc\text{-}bpy)_2]$ (dc-bpy = 2,2′-bipyridine-4,4′-dicarboxylic acid),[1] while, to the best of our knowledge, other transition metal photo-sensitizers have been relatively ineffective. In several pioneering works, the copper(I) complex of a 1,10-phenanthroline derivative, $[Cu(dcp\text{-}phen)_2]^-$ [H(dcp-phen) = 2,9-di(*p*-carboxyphenyl)-1,10-phenanthroline], and the iron(II) complex of a 2,2′-bipyridine derivative, *cis*-$[Fe(CN)_2(dc\text{-}bpy)_2]$, were applied to the TiO_2 solar cell.[2,3] However, the reported photocurrents (600 and 360 mV, respectively) and photovoltages (0.6 and 0.29 mA cm^{-2}, respectively) were much smaller than those of the Grätzel cell. In $[Cu(dcp\text{-}phen)_2]^-$, carboxylic acids were not directly introduced into the 1,10-phenanthroline framework but into the phenyl substituent of 1,10-phenanthroline.[2] This structure is considered unfavorable for injection of the excited electron into the conduction band of TiO_2. In *cis*-$[Fe(CN)_2(dc\text{-}bpy)_2]$, two carboxylic acids were introduced directly into the 2,2′-bipyridine framework, but the MLCT excited state was too short-lived (25 ps).[3] This is also unfavorable for the photo-induced electron transfer reaction, even though an excited electron can be rapidly injected into the conduction band of TiO_2 from the photo-excited transition metal complex in a few femtoseconds with a quantum yield approaching unity.[1c,4,5]

In copper(I) complexes of such conjugated ligands as 2,2′-bipyridine, 1,10-phenanthroline, and their derivatives, the triplet MLCT excited state is their lowest excited state the same as for ruthenium(II) 2,2′-bipyridine complexes.[6] As a result, their photoreactivities are similar to those of ruthenium(II) complexes; photo-isomerization of *trans*-stilbene[7] and photoreduction of methylviologen[8–10] were successfully carried out with the copper(I) complexes. Considering the photoreactivities, the long lifetime and the considerably negative redox potential (about −1.2 V *vs.* SCE) of the excited state of these copper(I) complexes,[11] we can expect to construct an efficient solar cell with a copper(I) complex if the carboxylic acids are directly introduced into the 2,2′-bipyridine framework like in $[Ru(NCS)_2(dc\text{-}bpy)_2]$.

In this communication, we wish to report the synthesis of a new copper(I) complex, $[Cu(tmdcbpy)_2]^+$ **1** (tmdcbpy = 4,4′,6,6′-tetramethyl-2,2′-bipyridine-5,5′-dicarboxylic acid; see Scheme 1),‡ and its successful application to Grätzel-type solar cells. Our intention is to obtain a complex useful for a solar cell through the introduction of two carboxylic acids (which are expected to play a key role in the rapid injection of an excited electron into the conduction band of TiO_2) and two methyl groups (necessary for a long-lived excited state) at the 5,5′- and 6,6′-positions of 2,2′-bipyridine, respectively.[13]



Scheme 1 4,4′,6,6′-Tetramethyl-2,2′-bipyridine-5,5′-dicarboxylic acid (tmdcbpy).

Complex **1** exhibits a large MLCT absorption band around 450 nm [molar extinction coefficient (ε) = 6400 M^{-1} cm^{-1}], as shown in Fig. 1. However, an emission spectrum could not be observed, probably because **1** is not soluble in aprotic solvents such as dichloromethane and chloroform. It is worth noting that the similar copper(I) complex, $[Cu(NN)_2]^+$ (NN = 1,10-phenanthroline derivatives), is not emissive in ethanol and methanol but emissive in chloroform and dichloromethane.[14]

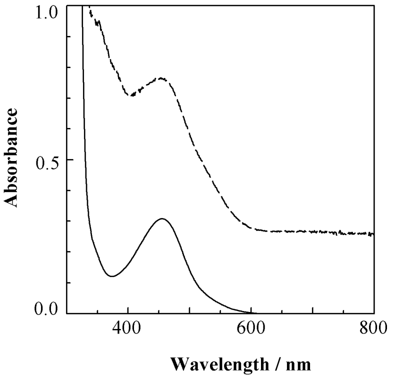


Fig. 1 Solid line: absorption spectrum of $[Cu(tmdcbpy)_2]Cl$ in methanol (4.8 × 10^{-5} mol dm^{-3}). Dashed line: reflectance spectrum of $[Cu(tmdcbpy)_2]Cl$ adsorbed on TiO_2 (prior to heating).

A solar cell was prepared from **1** and TiO_2 (P25),§ according to the method of Grätzel *et al.*[1c] As shown by the photocurrent–photovoltage curve of Fig. 2, the open-circuit photovoltage is about 630 mV and the short-circuit photocurrent is 2.9 mA cm^{-2}, where a sunlight simulator (AM 1.5G,

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† Electronic supplementary information (ESI) available: dependences of photocurrent and photovoltage on concentrations of KI, I_2, and 4-*tert*-butylpyridine (one table), effects of sintering temperature and sintering time (two tables) and persistency test of the solar cell (one figure). See http://www.rsc.org/suppdata/dt/b1/b109518h/

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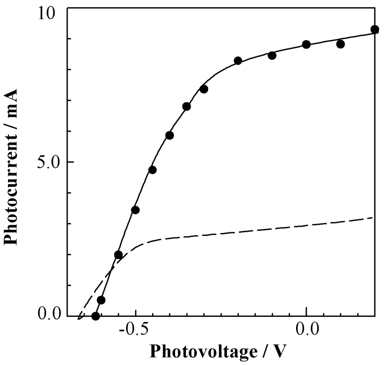

Fig. 2 Photocurrent–photovoltage relation of the TiO_2 solar cell alone (dashed line) and coated with [Cu(tmdcbpy)$_2$]Cl (solid line). Conditions: TiO_2 (P25) area, 2.9 cm^2; [Cu(tmdcbpy)$_2$]Cl, 1.0×10^{-3} mol dm^{-3}; electrolyte: KI, 0.04 mol dm^{-3}, I_2, 0.05 mol dm^{-3}, and 4-*tert*-butylpyridine, 1.0 mol dm^{-3} in propylenecarbonate–acetonitrile (11 : 1, v/v); sintering temperature, 450 °C.

100 mW cm^{-2})¶ was employed (see the caption of Fig. 2 for more detailed experimental conditions).

TiO_2 coated with **1** displays a large absorption around 450 nm in the reflectance spectrum, as shown in Fig. 1. This spectrum is almost the same as that of the methanol solution of **1**. The incident monochromatic photon-to-current conversion efficiency (IPCE) is plotted as a function of excitation wavelength, as shown in Fig. 3. Its maximum value is about 30%.

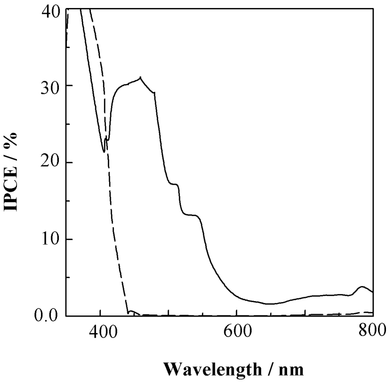

Fig. 3 Incident monochromatic photon-to-current conversion efficiency (IPCE) curve of the TiO_2 solar cell alone (dashed line) and coated with [Cu(tmdcbpy)$_2$]Cl (solid line). See the caption of Fig. 2 for more detailed conditions.

This spectrum agrees well with the absorption spectrum of **1**. These results clearly indicate that **1** is adsorbed onto the TiO_2 surface and plays the role of photo-sensitizer for the solar cell.

We also prepared the solar cell with a similar copper(I) complex, $[Cu(dmdp\text{-}phen)_2]^+$ (dmdp-phen = 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline) **2**, since **2** exhibits a larger MLCT absorption than does **1** and the analogous copper(I) complex, $[Cu(dm\text{-}phen)_2]^+$ (dm-phen = 2,9-dimethyl-1,10-phenanthroline), was successfully applied to the photo-reduction of various cobalt(III) complexes under visible-light irradiation.[13,15] However, the solar cell with **2** was inactive. Consistent with this result, no absorption band was observed in the UV-VIS reflectance spectrum of TiO_2 coated with **2**, indicating that **2** could not be adsorbed onto the TiO_2 surface. From this result, it should be concluded that the carboxylic acid moiety in **1** plays a key role in the adsorption of the Cu(I) complex onto TiO_2.

In the solar cell with **1**, we investigated effects of the concentrations of I_2, KI, and 4-*tert*-butylpyridine (4-^{t}BuPy) (see ESI, Table S1). Though the photocurrent and photovoltage were not very sensitive to the concentrations of I_2 and KI, the best result (2.9 mA cm^{-2} and 640 mV) was observed when the I_2 and KI concentrations were 0.40 mol dm^{-3} and 0.05 mol dm^{-3}, respectively, in the presence of 4-^{t}BuPy (1.0 mol dm^{-3}). In the absence of 4-^{t}BuPy, the photocurrent and photovoltage decreased to 1.98 mA cm^{-2} and 430 mV, respectively. The improvement by 4-^{t}BuPy could be interpreted in terms of suppression of back-electron transfer from TiO_2 to the Cu(II) complex, like that observed in the TiO_2 cell with the well-known photo-sensitizer, $[Ru(SCN)_2(dc\text{-}bpy)_2]$.[1c]

In the above-described solar cells, the first and the second sintering processes were carried out at 450 °C for 0.5 h. Here, we optimized the sintering time and the sintering temperature of TiO_2. The best result was observed when the first and second sintering processes were carried out at 500 °C for 0.5 h (see ESI, Tables S2 and S3); the photocurrent and photovoltage were 3.9 mA cm^{-2} and 630 mV, respectively, and the energy conversion efficiency was 2.5%, where propylenecarbonate–acetonitrile (11 : 1 v/v) including KI (0.40 mol dm^{-3}), I_2 (0.05 mol dm^{-3}) and 4-^{t}BuPy (1.0 mol dm^{-3}) was used as the electrolyte solution. These values are smaller than the best values of Grätzel *et al.*[1d] but much larger than those of the previously reported solar cells with $[Cu(dcp\text{-}phen)_2]^-$ and $[Fe(CN)_2(dc\text{-}bpy)_2]^+$.[2,3]

Finally, we examined the longevity of this solar cell, since the photocurrent decreased to almost zero after several hours in the previously prepared solar cell with $[Cu(dcp\text{-}phen)_2]^-$.[2] In our cell, the photovoltage decreased to about 500 mV within 24 h, while it decreased little after that and the photovoltage of 500 mV was maintained even after 15 days (see ESI, Fig. S1).‖ Also, the photocurrent gradually decreased to 2.5 mA cm^{-2} from 2.9 mA cm^{-2} in 15 days but it was still about 2.5 mA cm^{-2} even after 15 days. Thus, the present solar cell can work well for a longer time than the previously prepared cell with $[Cu(dcp\text{-}phen)_2]^-$.[2] This is probably because the carboxylic acid groups introduced into the 2,2′-bipyridine framework are effective for adsorption of the copper(I) complex onto the TiO_2 surface.

To the best of our knowledge, this is the first report of a solar cell that provides a considerable photocurrent and photovoltage using a transition metal photo-sensitizer other than ruthenium. This report is expected to accelerate the development of new TiO_2 solar cells with copper(I) complexes.

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Notes and references

‡ Preparation of 4,4′,6,6′-tetramethyl-2,2′-bipyridine-5,5′-dicarboxylic acid (tmdcbpy). 4,4′,6,6′-Tetramethyl-5,5′-ethoxycarbonyl-2,2′-bipyridine (tmetbpy, synthesized according to our previously reported method)[12] was hydrolysed in aqueous sodium hydroxide (1.4 M).

Preparation of $[Cu(tmdcbpy)_2]^+$. A method similar to that for the synthesis of $[Cu(2,9\text{-dimethyl-}1,10\text{-phenanthroline})_2]^+$ was used.[13] tmdcbpy (0.33 mmol) in water (2 ml) was warmed to 70 °C, and then 15 drops of NaOH solution (1 M) were added. To this solution, copper sulfate [$Cu(SO_4)\cdot 5H_2O$, 0.17 mmol] in water (2 ml) was added, followed by further addition of 20 drops of NaOH solution (1 M). Ascorbic acid (0.25 mmol) in water (0.3 ml) was added to this solution. After the solution became red-brown, the solution pH was adjusted to 2 by addition of HCl (1 M), to afford red-brown precipitates. The crude precipitates were re-crystallized from ethanol–chloroform. Yield 74 mg, 62%. Anal. for [Cu(tmdcbpy)$_2$]Cl, $CuC_{32}H_{32}N_4O_8Cl$. Calc. (%): C, 54.94, H, 4.61, N, 8.01. Found: C, 54.40, H, 4.80, N, 7.86. ^1H NMR (methanol-d4): δ 2.30 (6,6′-CH_3, 6H), 2.54 (4,4′-CH_3, 6H), and 8.34 (3,3′-H of pyridine ring, 2H).

§ Preparation of the solar cell. TiO_2 (3 g, P25, a gift from Aerozil Ltd.) was mixed well with acetylacetone (0.1 ml) and water (1 ml) until it became sticky. The TiO_2 suspension was further stirred with water (4 ml) and TritonX-100 (0.05 ml) and then coated onto a U-type TCO plate (a gift from Asahi-Glass Ltd.). The TiO_2-coated plate was heated in an oven at 450 °C (or 500 °C) for 0.5 h. After cooling, $TiCl_4$ in water (0.2 M) was dropped onto the plate, which was washed with water after standing for one night and again heated in an oven at 450 °C (or 500 °C) for 0.5 h. This plate was dipped into a methanol solution of the copper(I) complex (5.0×10^{-4} M) for 12 h. Pt-coated glass was used as a counter electrode, the distance between the two plates being controlled by use of Scotch tape (63 μm thick) on one side, and the electrolyte solution [KI and I_2 in propylenecarbonate and acetonitrile, 11 : 1 (v/v)] was poured between them.

¶ AM1.5G is an air mass filter for a solar simulator which provides a spectrum when the sun is at a zenith angle of 48.2° (ASTME891).

|| The sintering processes were carried out at 450 °C for 0.5 h in this solar cell.

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