Dye-Sensitized Solar Cells

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Multifunctionalized Ruthenium-Based Supersensitizers for Highly Efficient Dye-Sensitized Solar Cells**

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Dye-sensitized solar cells (DSCs) have been explored for photovoltaic applications because of their low cost and impressive conversion efficiency.[1] A DSC with 10% efficiency was first demonstrated by Grätzel and co-workers using **N3** (*cis*-di(thiocyanato)bis(2,2′-bipyridyl-4,4-dicarboxylate) ruthenium(II)) as a sensitizer.[2] Progress in optimizing ruthenium-based sensitizers for DSCs has been focused primarily on enhancing the light-harvesting ability, and red-shifting the metal-to-ligand charge transfer (MLCT) band.[3–10] These results can be achieved by extending the conjugation length of the anchoring or ancillary ligand.[11–15] Furthermore, retaining the photoinduced interfacial charge separation between the dye molecules and TiO_2 is also a crucial strategy to enhance the performance of DSCs.[16] This strategy is beautifully demonstrated by adding a hole-transport segment on the dye molecule in all-solid-state DSCs.[17,18] However, this concept could not be applied to liquid-state DSCs,[19,20] probably because the ruthenium sensitizers have relatively low light-harvesting capacity and large molecular size.

We have shown[21,22] that thiophene-derived units are the good candidates for increasing the conjugation length of the ancillary ligand to increase the light-harvesting ability and red-shift the MLCT band of a ruthenium complex. Herein we reveal that thiophene-derived species can be functionalized easily with a alkyl-substituted hole-transport moiety, such as bis(heptyl)carbazole. Ruthenium complexes with ligands functionalized by thiophene, carbazole, and alkyl chains can be regarded as supersensitizers. The efficiency of a liquid-state DSC based on one of these supersensitizers is 9.72%, which is 1.2% higher than that (8.51%) of the N3-based cell at the same fabrication and efficiency measuring conditions. This is the first demonstration that a carbazole moiety in the dye can enhance the performance of a liquid-state DSC. Furthermore, the terminal alkyl chains on the ancillary ligand were also modulated to explore the impact of the sensitizer size on the cell performance in the DSC. In situ photoelectrochemical measurements were used for the first time to study the intramolecular electron-transfer processes of the oxidized dye.

The structures of the supersensitizers **CYC-B6S** and **CYC-B6L** are depicted in Figure 1. The electronic absorption spectra of these supersensitizers and **N3** measured in DMF are displayed in Figure 2, and the optical data are summarized in Table 1. The absorption spectra of the supersensitizers show that the band centered at around 550 nm (which is the characteristic metal-to-ligand charge-transfer (MLCT) transition) is stronger and more red-shifted than that for **N3**. These results indicate that the spectral response of ruthenium

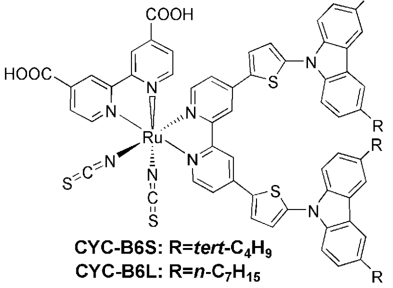

Figure 1. Molecular structures of two new supersensitizers.

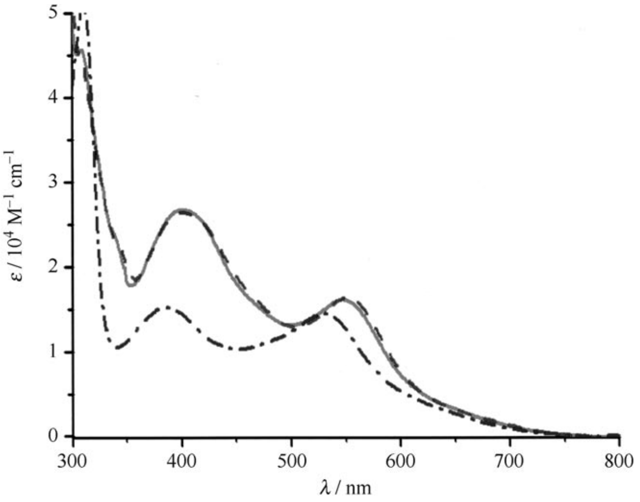

Figure 2. Electronic absorption spectra of **CYC-B6S** (solid line), **CYC-B6L** (dashed line), and **N3** (dash dotted line), measured in DMF.

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Table 1: Physical data of the dye molecules and the performance of their corresponding DSCs.

Sensitizer	ε [$10^4\,M^{-1}\,cm^{-1}$] (λ_{max} [nm])		E_{HOMO}[a]	E_{LUMO}[a]	Cell performance			
	π–π* or 4d–π*	4d–π*	[eV]	[eV]	J_{sc} [$mA\,cm^{-2}$]	V_{oc} [mV]	*FF*	η [%]
CYC-B6S	2.67 (401)	1.61 (548)	5.08	3.50	19.8	777	0.633	9.72
CYC-B6L	2.64 (400)	1.63 (551)	5.08	3.50	18.2	776	0.636	8.98
N3	1.52 (385)	1.45 (530)	5.15	3.47	16.9	784	0.642	8.51

[a] The energy levels of the HOMOs and LUMOs are calculated with the following formula: HOMO (eV) $= E_{ox} - E_{Fc/Fc^+} + 4.8$; LUMO (eV) $=$ HOMO$-E_g$. E_{ox} is determined by square-wave voltammetry. E_g is the absorption onset estimated from the electronic absorption spectra of the sensitizers.

sensitizers can be enriched by incorporating the carbazole-substituted thiophene moieties in the ancillary ligand. The absorption profile of **CYC-B6S** is similar to that of **CYC-B6L**, suggesting that the difference in the alkyl chain on carbazole will not affect prominently the light-absorption ability of dye molecules.

The energy levels of the frontier orbitals of dye molecule play an important role in the electron-transfer processes in a DSC cell.[23] The energy levels of HOMOs and LUMOs were derived from the oxidation potentials and the absorption onset of these dyes (Table 1). The data show that **CYC-B6L** and **CYC-B6S** have the same oxidation potential (which is cathodically shifted by 0.07 V relative to that of **N3**), indicating that the HOMOs of both supersensitizers are destabilized by the ancillary ligands, probably by the carbazole moiety. The energy levels of the LUMOs for two supersensitizers are also the same since they have close absorption onset (see Figure 2). Therefore, we may expect that the driving force for electron injection from the excited dye into TiO_2 conduction band for two supersensitizers is similar.

The photocurrent density–voltage curves and incident photon-to-current efficiency (IPCE) spectra of the cells based on these new supersensitizers and **N3** under the illumination of air mass (AM) 1.5 sunlight ($100\,mW\,cm^{-2}$) are shown in Figure 3. The photovoltaic parameters of the cells are also listed in Table 1. The DSC based on **CYC-B6S** achieves a conversion efficiency (η) of 9.72 %, which is 14 % higher than that (8.51 %) of the **N3**-sensitized solar cell under the same cell fabrication and efficiency measuring procedures. Interestingly, the efficiency (8.98 %) of the **CYC-B6L**-sensitized cell is slightly higher than that of the **N3**-sensitized cell. We reported previously[22] that the efficiency of a **CYC-B3** (its ancillary ligand is octylthiophene-substituted bipyridine) based cell is lower than that of the **N3**-based cell. The better photovoltaic performance of **CYC-B6L** compared with **CYC-B3** is due to that the ancillary ligand of the former has carbazole groups.

Surprisingly, we found that the efficiency of the **CYC-B6S**-based cell is higher than that of the cell based on **CYC-B6L**, even though their absorption profile and energy level of the frontier orbitals are almost the same. The result indicates that the performance of a sensitizer does not depend entirely on its absorption profile and energy level of the frontier orbitals; the size (and therefore the number of molecules adsorbed on TiO_2 electrode) of the sensitizer also plays a pivotal role. The quantity of the dyes adsorbed on TiO_2 was estimated by facilely desorbing the dye molecules from TiO_2 electrode. The amounts of **CYC-B6S**, **CYC-B6L**, and **N3** adsorbed on TiO_2 electrode (active area of $0.16\,cm^2$ and thickness of 15 μm) were calculated to be 1.30×10^{-8}, 1.15×10^{-8}, and 1.61×10^{-8} mol, respectively; more **CYC-B6S** adsorbed on the TiO_2 electrode than did **CYC-B6L**, which not only explains why the efficiency of the **CYC-B6S**-based cell is higher than that of the **CYC-B6L**-based cell, but also suggests that molecular engineering for high performance dyes for DSCs should pay particular attention to the molecular size.

The function of the hole-transport moiety in the dye molecule[18,19] is to provide the electron to the oxidized metal center (hole), which can retard the charge recombination between the electron in TiO_2 electrode and metal center.[19,20,24,25] Nevertheless, only careful molecular design can guaranteed an improvement in the efficiency. We used carbazole instead of phenothiazines[20] or triphenylamine[18,19,24,25] to reduce the size of the sensitizer. The carbazole moiety was bound covalently to thiophene-substituted bipyridine through its N atom. Therefore, the HOMO of the supersensitizer is located on the metal center (Figure 4), increasing the intensity of the MLCT band. The

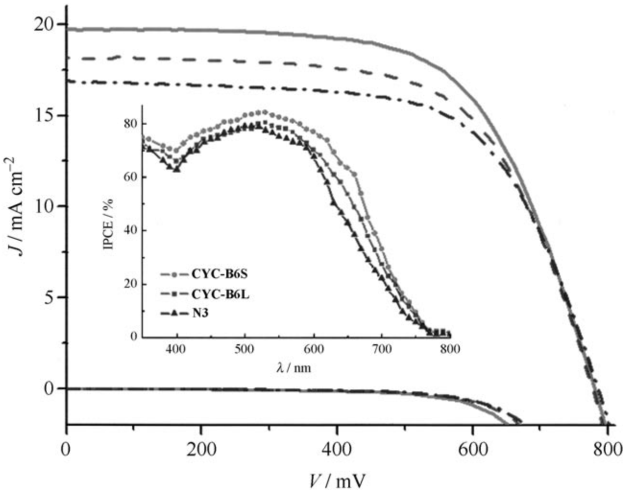

Figure 3. Photocurrent density–voltage curves of photovoltaic devices with **CYC-B6S** (solid line), **CYC-B6L** (dashed line), or **N3** (dash dotted line) as the sensitizer measured under AM 1.5 simulated sunlight illumination ($100\,mW\,cm^{-2}$; upper curves) and in the dark (lower curves). The inset shows the photon-to-current efficiency (IPCE) spectra of these photovoltaic devices (thickness of TiO_2: 15 μm; cell active area tested with a mask: $0.16\,cm^2$).

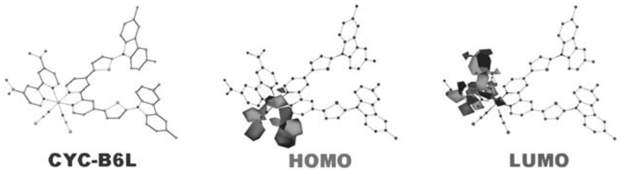

Figure 4. Frontier orbitals of **CYC-B6L**.

nonbonded electron on the N atom may have a chance to migrate from carbazole to the oxidized metal center. However, since the energy level of the HOMO for the carbazole-containing ancillary ligand is lower than that of the metal center, the ancillary ligand-to-metal charge-transfer (LMCT) transition occurs only by absorbing extra energy.

The efficiency of **CYC-B6L** is higher than that of **CYC-B3**, which we reported[22] previously. The absorption coefficients, λ_{max} values, and the energy levels of the frontier orbitals for both sensitizers are similar. The only difference is that the ancillary ligand of **CYC-B6L** contains a bis(heptyl)carbazole moiety instead of an octyl chain. In situ photoelectrochemical measurements[26] were performed to understand more about how the carbazole moiety affects the photovoltaic performance of the supersensitizer. The **CYC-B6S**-absorbed TiO_2 thin film displays two absorption bands centered at 526 and 410 nm (Figure 5; curve A). The absorption profile (Figure 5, curve B) of **CYC-B6S**-absorbed TiO_2 thin film changes significantly when a bias potential of 1.11 V (versus Ag/Ag^+) is applied on the electrode to oxidize **CYC-B6S**. To see the change in the absorption spectrum of **CYC-B6S** after electrochemical oxidation, curve A was subtracted from curve B to give curve C (Figure 5), which shows that the original MLCT band decreases and two new bands appear. The weak, broad peak at near-IR region is due to charge transfer from the NCS ligand to the oxidized metal center, as confirmed by ultrafast laser-pulsed transient absorption.[27,28] Another discernible absorption band (which was not observed in **N3**) with energy higher than that of the origin MLCT band grows. The origin of this high energy band (471 nm) is not yet clear; it may be attributed to another LMCT transition from the carbazole-functionalized ancillary ligand. Nevertheless, this LMCT transition in the supersensitizer may not occur in a practical environment since the peak is very weak and most visible light was absorbed by the sensitizers, as revealed by the IPCE data (the inset of Figure 3). Therefore, the carbazole moiety in the supersensitizers acts as a electron-donation group to red-shift the λ_{max} and increase the light-harvesting ability of the dye and may also reduce the tendency for electrons transfer from TiO_2 back to the oxidized dye because of its electron-donating nature.

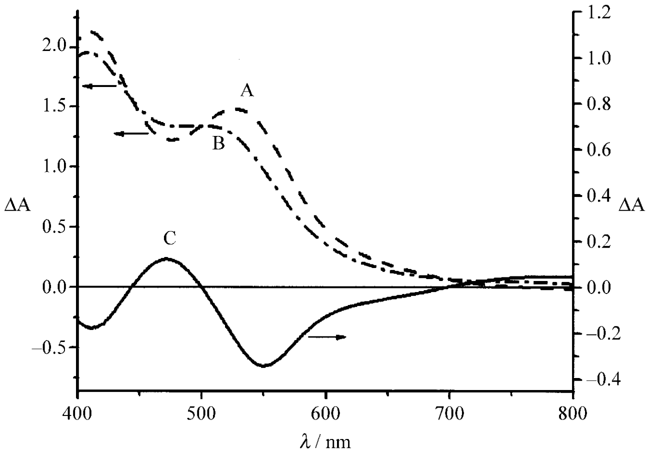

Figure 5. The absorption spectra of **CYC-B6S**-sensitized TiO_2 electrode (12 μm thick): before (A) and after (B) applying a potential of 1.11 V (versus Ag/Ag^+); C) absorption change after applying potential.

In summary, we prepared two new ruthenium based dyes (**CYC-B6S** and **CYC-B6L**) in which alkyl-substituted carbazole moieties were incorporated in the thiophene-substituted bipyridine ligand. Compared with the dicarboxylatebipyridyl (dcbpy) ligand in **N3** dye, the unique ancillary ligand in **CYC-B6S** was well-designed to enhance the light-harvesting capacity with thiophene unit to further enrich the spectral response by using a carbazole unit, and using saturated alkyl chains to create a hydrophobic environment. These multifunctional ruthenium-based supersensitizers are not only promising for liquid-state DSCs but also provide a new prospect for dye innovation.

Experimental Section

The detailed synthetic procedures and structure characterizations of these new supersensitizers, physicochemical studies, and DSCs device fabrication, as well as efficiency measurements can be found in the Supporting Information.

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