

Highly Efficient N-Heterocyclic Carbene/Pyridine-Based Ruthenium Sensitizers: Complexes for Dye-Sensitized Solar Cells**

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Dye-sensitized solar cells (DSSCs) are being investigated extensively for their use in renewable energy technologies because of their low cost and high light-to-electrical energy conversion efficiency.^[1] Since their initial report in 1991 by O'Regan and Grätzel, DSSCs have attracted much attention from researchers, resulting in the preparation of thousands of ruthenium polypyridine complexes, non-ruthenium organo-metallic dyes, and metal-free organic sensitizers.^[2,3] Organic dyes exhibiting high molar absorption coefficients and presenting a variety of specific functional groups, allowing fine tuning of the absorption spectra, have provided respectable incident photon-to-current conversion efficiencies (IPCEs).^[2] Coordination complexes of ruthenium, including N3,^[4,5] N719,^[6,7] and black dyes,^[8–10] have also received significant attention because their photophysical and photochemical properties provide DSSCs with excellent photoelectric conversion efficiencies. The most common inorganic dyes exploited in DSSCs are typically ruthenium(II) polypyridine complexes.^[3] Several attempts have been made to enhance the efficiency and long-term stability of the dyes, including increasing the conjugation length of the anchoring or ancillary ligand using thiophene,^[11,12] carbazole,^[13] or other^[14–17] substituents. Long-term stability can be achieved by modifying the architecture of amphiphilic bis(bipyridyl) Ru^{II} dyes featuring alkyl,^[18–20] alkoxy,^[16] or other^[21] substituent groups. Grätzel and co-workers replaced the NCS ligand of a ruthenium polypyridine complex with an anionic carbon atom as an alternative approach to structural modification.^[22,23] Herein, we report a set of N-heterocyclic carbene (NHC)/pyridine ruthenium complexes, in which one of the nitrogen atoms in the traditional bipyridine framework has

been replaced by a carbon atom, for use in DSSCs exhibiting enhanced solar cell performance.

Although there is much research on the preparation of metal-carbene complexes and their roles as catalytic reagents and luminescent emitters, their photovoltaic characteristics remain relatively unknown. NHC-pyridine-based ligands, with their unique set of electronic properties, are an exceptional class of donors; therefore, we expected them to make excellent ancillary ligands. The essential requirement of a dye that provides a DSSC with high efficiency is for the energy level of the lowest unoccupied molecular orbital (LUMO) of the sensitizer to be sufficiently high for efficient charge injection into the TiO₂ electrode, while the energy level of the highest occupied molecular orbital (HOMO) must be sufficiently low for efficient regeneration of the oxidized dye by the hole-transport material. Several methods have been reported to lower the HOMO energy level through tuning of the ancillary ligands and their substituents.^[3,11,13] The use of ruthenium complexes bearing ancillary ligands functionalized with NHC-pyridine units might be an alternative approach toward tuning the frontier orbitals of the dyes. Sensitizers using benzimidazole-based carbenes,^[24,25] rather than imidazole-based carbenes,^[26,27] should stabilize the HOMO energy levels while leaving the LUMO energy levels favorable for the injection of electrons into the conduction band of the TiO₂ electrode. In this study, we developed two photosensitizers (**1a** and **1b**), functionalized with electronically unsymmetrical benzimidazole-pyridine-based carbene units, which exhibited excellent photoelectric conversion efficiencies (η).

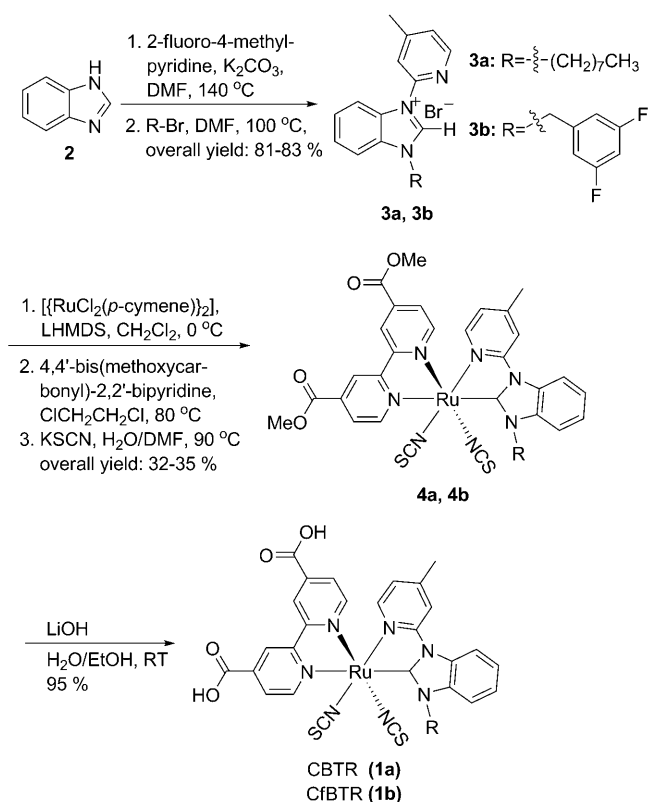
Scheme 1 illustrates the stepwise synthetic protocol toward the ruthenium(II) NHC-pyridine complexes CBTR (**1a**) and CFBTR (**1b**). The ligands **3a** and **3b** for the synthesis of these ruthenium complexes were obtained through treatment of benzimidazole (**2**) with 2-fluoro-4-methylpyridine, followed by alkylation with 1-bromooctane and 3,5-difluorobenzyl bromide, respectively.^[28] Treating the benzimidazole salts **3a** and **3b** with $[\{\text{RuCl}_2(p\text{-cymene})\}_2]$ in the presence of lithium bis(trimethylsilyl)amide (LHMDS) in CH₂Cl₂ and then with 4,4'-bis(methoxycarbonyl)-2,2'-bipyridine afforded the corresponding ruthenium-chloride complexes.^[29] The chloride ligands were replaced with NCS units at 90 °C in a mixture of H₂O and DMF, thereby yielding the corresponding ruthenium-thiocyanide complexes **4a** and **4b**.^[11,16] The molecular geometry of the ester **4b** was confirmed unequivocally through single-crystal structural analysis. Dark red crystals were obtained after slow evaporation of a solution of the ester **4b** in CH₂Cl₂. The molecular structure (see Figure S1 and Table S1 in the Supporting Information) revealed that the coordination geometry around the ruthenium atom could be

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Scheme 1. Synthesis of the NHC-pyridine-based ruthenium sensitizers CBTR (**1a**) and CbBTR (**1b**).

rationalized as a slightly distorted octahedron. The Ru–C_{carbene} bond [Ru(1)–C(26)] of the ester **4b** is located *trans* to one of pyridine nitrogen atoms (N2) of the 4,4'-dicarboxylic acid-2,2'-bipyridine (dc bpy) anchoring ligand. The Ru–C_{carbene} distance [1.973(3) Å] indicates that this bond is a single bond featuring back-donation; it is shorter than those reported for typical Ru–NHC complexes.^[26,27,29] Accordingly, in complex **4b**, the Ru–N_{pyridine} bond [Ru(1)–N(2), 2.119(2) Å] that is positioned *trans* to the NHC carbon atom is longer than that [Ru(1)–N(1), 2.038(2) Å] positioned *trans* to the NCS ligand. It is the longest Ru–N bond in the entire complex because of the strong *trans* influence of the carbene carbon atom. Hydrolysis of the esters **4a** and **4b** with LiOH in $H_2O/EtOH$ yielded the desired acids CBTR (**1a**) and CbBTR (**1b**), respectively.

To predict the behavior of the interfacial molecules when used in devices, the optical properties of CBTR, CbBTR, and N719 were investigated using UV/Vis absorption spectroscopy. Figure 1 displays the UV/Vis spectra of the dyes in various solvents and adsorbed onto TiO_2 films. The absorption spectra of CBTR solutions (Figure 1a) in CH_3CN , $CH_3CN/tBuOH$, and DMF (8.0×10^{-5} M) reveal that the maximum absorptions were dependent on the solvent used. The absorption spectrum of CBTR in CH_3CN features two bands centered at 442 nm (molar absorption coefficient $\epsilon = 1.1 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) and 535 nm ($\epsilon = 9.0 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$) and a distinct shoulder at around 630 nm extending to 750 nm; these signals are all characteristic of metal-to-ligand charge-transfer (MLCT) transitions. We observed a significant

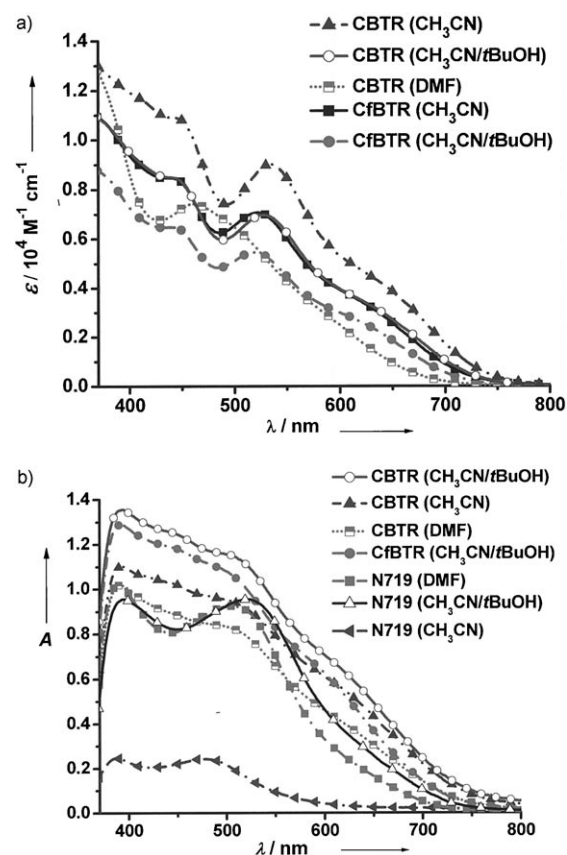


Figure 1. Absorption spectra of a) 8.0×10^{-5} M solutions of CBTR (**1a**) in CH_3CN , $CH_3CN/tBuOH$, and DMF and CbBTR (**1b**) in CH_3CN and $CH_3CN/tBuOH$ and b) transparent TiO_2 films (thickness: 10 μm) coated with 8.0×10^{-5} M solutions of CBTR in $CH_3CN/tBuOH$, CH_3CN , and DMF, CbBTR in $CH_3CN/tBuOH$, and N719 in DMF, $CH_3CN/tBuOH$, and CH_3CN .

decrease in the molar extinction coefficient of CBTR, which bears a strong σ donor, relative to that of N719 (535 nm; $\epsilon = 1.5 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ in C_2H_5OH or DMF).^[30,31] The absorption spectra revealed negative solvatochromism (i.e., a blue shift from 535 nm in CH_3CN to 469 nm in DMF) of the charge-transfer bands of CBTR in more-polar aprotic solvents (DMF). For example, the absorption maxima (λ_{max}) of CBTR (**1a**) in CH_3CN , $CH_3CN/tBuOH$, and DMF are 535, 529, and 469 nm, respectively.^[10,32,33] In contrast, in the case of N719, which features tetrabutylammonium units as counteranions, we observed only a slight blue shift.^[30,34,35] The absorption spectra of CBTR and N719 anchored onto TiO_2 nanocrystalline electrodes from various solutions featured broadened MLCT bands (Figure 1b) relative to those present in the solution spectra. Such broadening has also been reported for several other organic sensitizers deposited onto TiO_2 electrodes.^[36,37] These changes could be ascribed to aggregation or coordination of the dye molecules on the TiO_2 surface or to hydrogen-bonding interactions between the carboxylate groups of CBTR (**1a**) and the TiO_2 surface.^[38] Comparing the absorption spectra of CBTR in solution and on the film, the TiO_2 film that had been immersed in $CH_3CN/tBuOH$ exhibited wider absorption bands with higher absorption intensity over the region from 400 to 750 nm than those

Table 1: Physical and performance data of CBTR-, CfbTR- and N719-sensitized cells.

Sensitizer	$E_{\text{ox}}^{[a]}$ of $\text{Ru}^{\text{III/II}}$ [V vs. Fc/Fc^+]	$E_{\text{HOMO}}^{[b]}$ [eV]	$E_{\text{LUMO}}^{[c]}$ [eV]	$E_{0-0}^{[c]}$ [eV]	$E_{\text{LUMO}}^{[d]}$ [eV]	$E_{0-0}^{[d]}$ [eV]	J_{sc} [mA cm^{-2}]	Cell performance V_{oc} [mV]	FF	η [%]
CBTR	0.34	5.14	3.39	1.75	3.53 ^[e]	1.61	20.0	730	0.664	9.69
CfbTR	0.36	5.16	3.39	1.77	3.55	1.61	19.2	710	0.663	9.04
N719	0.31	5.11	3.46	1.65	3.48	1.63	18.6	700	0.690	8.98

[a] The Ag/AgNO_3 reference electrode was calibrated with a ferrocene/ferrocinium (Fc/Fc^+) redox couple. The same value for E_{ox} of $\text{Ru}^{\text{III/II}}$ was obtained when the electrochemical experiments were performed using 0.1 M $[\text{nBu}_4\text{N}]\text{PF}_6$ in DMF or $\text{CH}_3\text{CN}/t\text{BuOH}$ (1:1). [b] $E_{\text{HOMO}} = E_{\text{ox}} - E_{\text{Fc}/\text{Fc}^+} + 4.8$ eV [c] $E_{\text{LUMO}} = E_{\text{HOMO}} - E_{0-0}$. The band gap E_{0-0} was estimated from the onset of the absorption spectrum measured in DMF. [d] Obtained in $\text{CH}_3\text{CN}/t\text{BuOH}$ (1:1). [e] The LUMO energy level of CBTR was estimated to be 3.54 eV from the reduction potential (E_{red}) observed in the cyclic voltammetry (CV) measurements.

obtained from CH_3CN , presumably because more dye molecules had adsorbed. Unlike that of CBTR, the absorption spectra of N719 adsorbed on the film from various solvents featured distinct absorption bands, except from CH_3CN because of poor solubility. In comparison with that of N719, the absorption spectrum of CBTR adsorbed onto the TiO_2 film from $\text{CH}_3\text{CN}/t\text{BuOH}$ was broader—an advantageous spectral property for light harvesting of the solar spectrum.

The energy levels of the frontier orbitals of the sensitizer play a crucial role in affecting the dye-regeneration and electron-transfer processes in DSSCs. Prior to making the solar devices, we determined the HOMO and LUMO energy levels of CBTR and CfbTR from their UV/Vis absorption spectra and their cyclic voltammograms to ensure that they were suitable for injecting electrons and for regeneration after electron donation. Table 1 reveals that the difference between the HOMO energy level of CBTR (or CfbTR) and the I^-/I_3^- redox potential was greater than that of N719 dye. The oxidation potentials of CBTR and CfbTR are shifted by 0.03 and 0.05 eV, respectively, relative to that of N719 dye, indicating that the HOMO energy levels of both sensitizers are stabilized by their ancillary ligands—presumably their NHC moieties. The energy difference between the LUMO of CBTR (or CfbTR) and the TiO_2 film, measured in DMF, was larger than that of N719 dye. Stabilization of the LUMO was observed, however, when the measurements were performed in $\text{CH}_3\text{CN}/t\text{BuOH}$. The band gaps of the newly prepared sensitizers were greater than that of N719 dye in DMF, but similar to the value in $\text{CH}_3\text{CN}/t\text{BuOH}$. Nevertheless, the LUMO energy level of CBTR (or CfbTR) in solution was higher than that of the TiO_2 film, suggesting that it should be possible to inject electrons into the conduction band of the TiO_2 electrode.

To gain further insight into the frontier orbital profiles, the locations of the HOMOs and LUMOs of CBTR (**1a**) were calculated using a semiempirical computation method. The HOMO, HOMO–1, HOMO–2, and HOMO–3 of CBTR (see Figure S2 in the Supporting Information) feature significant contributions from the NCS ligands. It is noteworthy that the HOMO–4 of CBTR features contributions from the NHC–pyridine–carbene ligand, the NCS ligand, and the ruthenium center. The electrons on LUMO and LUMO + 1 are localized homogeneously on the 4,4′-dicarboxylic acid-

2,2′-bipyridine anchoring ligand, thereby favoring efficient electron injection into the TiO_2 electrode. The components of the HOMO and HOMO–1 and of the LUMO and LUMO + 1 of the CBTR are similar to those reported for N719 dye.^[6]

Figure 2 presents the photocurrent density–voltage (I – V) curves and IPCE spectra of DSSCs assembled with multiple layered TiO_2 films, anchored with CBTR, CfbTR, and N719 sensitizers. Table 1 summarizes the corresponding short-circuit photocurrent densities (J_{sc}), open-circuit voltages (V_{oc}), fill factors (FFs), and solar-to-electricity conversion efficiencies (η). The CBTR- and CfbTR-sensitized DSSCs exhibited slightly higher open-circuit voltages (730 and 710 mV, respectively) than that of N719 dye (700 mV) under the same fabrication conditions. A possible explanation for these results is that carbene sensitizers have an effect similar to that of N719 dye on the Fermi level of TiO_2 when they bind to the conduction band of the TiO_2 electrode. The DSSC based on the CBTR sensitizer achieved a cell efficiency of 9.69%, which is approximately 8% higher than that (8.98%) of the N719-sensitized DSSC prepared using the same cell fabrication technique. The higher value of η of the CBTR-sensitized cell (relative to that of the N719 cell) arose from its higher value of J_{sc} , which we attribute to the presence of the NHC ligand (a strong σ donor). The cell efficiency (9.04%) of the CfbTR-sensitized DSSC, however, was only slightly higher than that of the N719-sensitized DSSC. The values of J_{sc} of the CBTR- and N719-containing cells are consistent with the IPCE data (inset to Figure 2). The onsets in the IPCE spectra of the DSSCs sensitized with the CBTR and N719 dyes were equal (reaching 800 nm). The IPCE curves for the CBTR-, CfbTR-, and N719-containing DSSCs exhibited common broad characteristics that covered almost the entire visible spectrum (from 350 to 800 nm), with

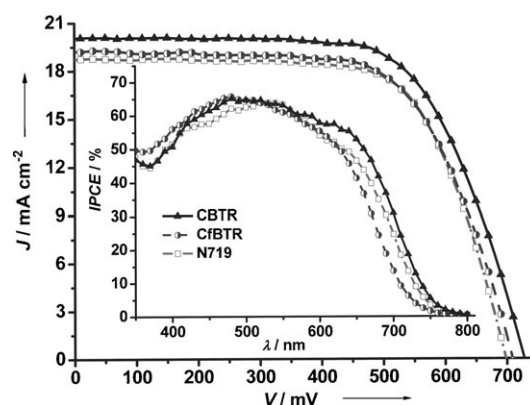


Figure 2. Current density–voltage characteristics of photovoltaic devices incorporating CBTR, CfbTR, and N719 as sensitizers under illumination with AM 1.5 simulated sunlight (100 mW cm^{-2}). Inset: Monochromatic IPCE spectra of the photovoltaic devices (TiO_2 thickness: $16 \mu\text{m}$; cell active area tested with a mask: 0.16 cm^2).

maxima at 65.1, 65.8, and 64.1 %, respectively. The enhanced IPCE spectrum of CBTR suggests that this new sensitizer might act as a more efficient electron donor to the conduction band of the TiO₂ film upon photoexcitation. Our results suggest that NHC–pyridine-based ruthenium complexes have promising applications and indicate the importance of molecular design for tuning sensitizers to produce high-efficiency DSSCs. A more thorough evaluation of the cell performance and further studies of the systematic optimization of these dyes are currently underway in our laboratories.

In conclusion, incorporation of novel NHC–pyridine ruthenium sensitizers results in DSSCs exhibiting excellent performance and sensitizing capability. We obtained these complexes by using simple, convergent, and short synthetic methods and inexpensive purification techniques, which are amenable to large-scale production. Using these new sensitizers represents a different molecular engineering approach: replacing the traditional bipyridine unit of ruthenium polypyridine complexes; therefore, we suspect that such supersensitizers might complement or be substitutes for [Ru(bpy)₂(NCS)₂] in dye design and DSSC applications. Relative to the DSSC incorporating the most common standard dye, N719, the DSSC incorporating the CBTR complex featuring an NHC–pyridine ancillary ligand exhibited superior values of J_{sc} , V_{oc} , and η . The absorption profile of the CBTR sensitizer indicates that red-shifted absorption properties can be enriched by increasing the conjugation length of the ancillary ligand to increase the light-harvesting ability. The introduction of carbene as an anchoring ligand by incorporating carboxylate groups on the NHC–pyridine ligand is currently in progress.

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