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A new ruthenium black dye design with improved optical properties for transparent dye sensitized solar devices.

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We report here on the preparation and on the electronic properties of a panchromatic Ru(II) sensitizer based on a new ligand which allows for higher molar extinction coefficient in the visible and performances with respect to the conventional “black dye” on transparent DSSC.

Introduction of a tris-thiocyanato–ruthenium(II) terpyridyl complex where the terpyridyl ligand was substituted by three carboxylic groups in 4,4',4'' position has led to significant advances in the efficient sensitization of nanocrystalline TiO₂ solar cells over the whole visible range, extending into the near-IR region up to 920 nm.^{1,2} Several studies have been carried out in order to improve the performances of the almost black absorber, addressing theoretically³ or experimentally the effect of changes at the non-chromophoric or at chromophoric polypyridine ligand.⁴ The panchromatic sensitization was also successfully extended beyond 1000 nm by substituting the ruthenium center with osmium. The x 3 higher spin-orbit coupling constant of Os with respect to Ru⁵ allowed direct access to spin forbidden Metal-to-Ligand Charge Transfer, ³MLCT, states which are responsible of intense absorption in the NIR spectral region and of efficient charge injection to the conduction band of titanium dioxide.⁶⁻⁸ Although the recent application of lead iodide perovskites has increased both red sensitivity and efficiency, up to reach the record conversion of 20 %, the use of transparent dye sensitized solar devices in window systems still represents one of the most interesting and unique applications for DSSCs technology. For integration in building facades, in fact, both power conversion efficiency and transparency should be considered since transparency, other than aesthetic, clearly affects lightning energy consumption.

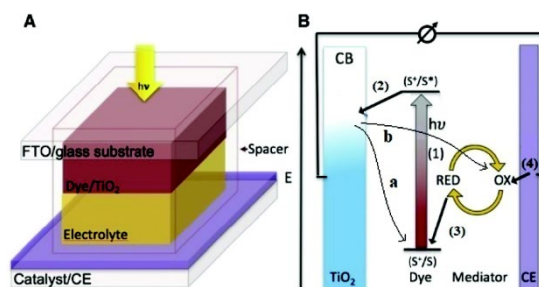
The major drawback of the typical black dye design is the moderate extinction coefficient which forces to use extremely thick and opaque TiO₂ films (15-40 μm) in order to extract high efficiencies.⁹⁻¹²

This type of TiO₂ films are clearly unsuitable for transparent applications, thus lacking one of the most attractive features of DSSCs for building integration

In order to increase the light harvesting efficiency of transparent devices we have now devised a new black absorber where the molar extinction coefficient of the relevant MLCT band of the tris-thiocyanate ruthenium complex is increased by modifying the chromophoric tris-carboxy terpyridine ligand with the introduction of π conjugating spacers between the terpyridine ligand and the anchoring carboxylic groups (**NBD** Fig.1).

Herein we report a comparison of spectroscopic and photo-electrochemical properties with the original black dye (**BD**, [Ru(II)[HTcTerpy]NCS₃](TBA)₃)(JACS 2001), showing improved cell performances when transparent DSSCs are assembled with the last synthesized **NBD**.

The preparation of the new 4,4',4''-([2,2':6',2''-terpyridine]-4,4',4''-trilyltris(ethyne-2,1-diyl)tribenzoic acid ligand,**5** (**NBDL** Fig.1), is shown in Scheme 1 and detailed in S1 of the supplementary information. The desired ligand has been obtained through a Sonogashira reaction on 4-substituted pyridines, followed by a Stille reaction to build up the terpyridine structure. In the chosen synthetic pathway the first step has been a trans- esterification of the methyl ester with isobutanol, in order to achieve an improved solubility of each intermediate in organic solvents. Functionalization of the terpyridine ring has been carried on through a selective Sonogashira reaction at low temperature.



Scheme 1. Scheme 1 (A) Schematic illustration of dye-sensitized solar cell. (B) Working principle of a typical DSSC. Upon illumination (1) electrons are injected from the photoexcited dye into TiO₂ (2) and collected at the FTO substrate, while the electrolyte (RED) reduces the oxidized dye (3) and transports the positive charges to the catalytic counter electrode where regeneration occurs (4). The difference between the quasi-Fermi level of the semiconductor and the redox potential of the relay gives the open circuit photovoltage generated by the cell. Recombinative losses are indicated by thin arrows (a, b).

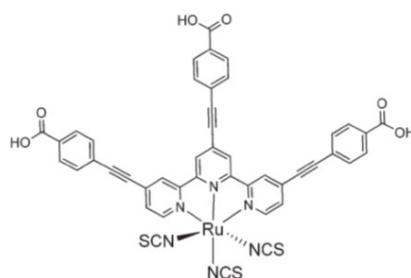
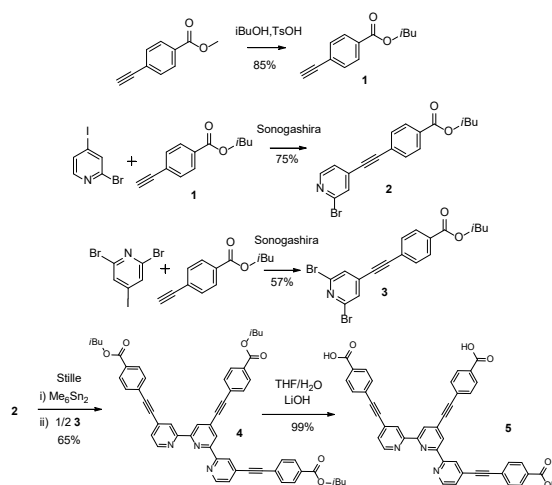


Fig. 1 4,4',4''-([2,2':6',2''-terpyridine]-4,4',4''-trilytris(ethyne-2,1-diyl))-tribenzoic acid ruthenium tris thiocyanate complex (NBD).



Scheme 2. Preparation of the new 4,4',4''-([2,2':6',2''-terpyridine]-4,4',4''-trilytris(ethyne-2,1-diyl)tribenzoic acid ligand (5).

Kinetic control allowed to obtain a selective reaction on iodine, leaving bromine group available for the subsequent terpyridine assembling by microwave assisted Stille coupling reaction.¹³ Finally isobutyl esters has been cleaved by alkaline treatment providing the desired ligand. NBD was prepared by stoichiometrically reacting Ru(II) dichloro *p*-cymene dimer with NBDL in DMF under microwave (MW) irradiation for 20 minutes (160 °C), followed by addition of excess NH₄NCS and MW heating for further 15 minutes. Evaporation of the solvent afforded the crude product which was purified by precipitation and gel permeation chromatography in DMF and methanol. Synthetic details (S2) and structural characterization are given in the ESI. Due to the insertion of the benzyl acetylene spacer between each pyridine ring and the carboxylic group, the absorption spectrum of NBD shows more intense transitions when compared to BD: the Ligand Centered (LC) π - π^* band at 340 nm is

increased by a factor of 3 and is followed, in the visible region, by two main bands, a sharper one at 448 nm and a broader one peaking at 636 nm (Table S1 ESI[†] and Fig. 2), which are both red shifted (by ca. 50 nm and 20 nm respectively) and more intense (by $\times 2$ and $\times 1.2$ respectively) with respect to the conventional BD. TDDFT calculations¹⁶ carried out at the B3LYP/LANL2DZ in ethanol (PCM) indicate that these bands are composed by a manifold of electronic excitations (Fig. S1 ESI) having a mixed MLCT-LLCT (Ligand to Ligand Charge Transfer) character, involving charge transfer from orbitals having a mixed Ru(II)/NCS composition to π^* orbitals belonging to the conjugated terpyridine.

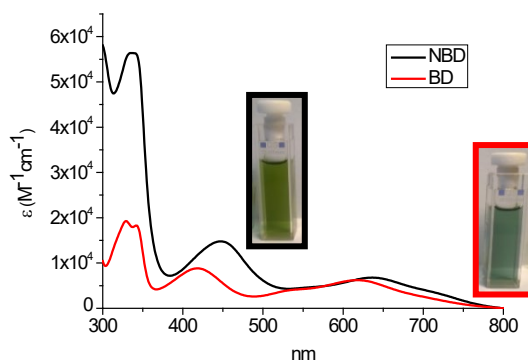


Fig. 2 Absorption spectra of NBD vs. BD in EtOH.

The relative intensity of the computed vertical transitions allows to reproduce well the shape of the absorption spectrum, once corrected for the systematic red shift (0.5 eV) originated by TDDFT when treating long range CT.¹⁵⁻¹⁷ The Electron Density Difference Maps (Figure S2 ESI) indicate that conjugation is well extended to the carboxylic anchoring group, thanks to the planarity of NBDL, establishing a good electronic coupling between the CT states and TiO₂. EDDMS clearly confirm that the increased optical extinction of NBD arises from the elongation of the electric dipole moment of the optical transitions (Figure S2). The energy of the frontier orbitals (Figure S3 ESI) are in reasonable agreement with the electrochemical data (Table 1) taken at 100 mV/s in DMF for solubility reasons. While the oxidation is quasi-reversible at 0.64 V vs SCE, the reduction is irreversible with a poly-electronic wave showing a shoulder at -1.26 V vs SCE and a well-defined diffusional peak at -1.56 V SCE (Figure S4). The frontier energy levels are thus suitably positioned to establish efficient charge transfer to TiO₂ and to the redox electrolyte (I⁻/I₃⁻ at ca. 0.2 V vs SCE). Consistent with experimental results (1.90 eV) (Figure S3) the computed HOMO-LUMO energy gap of NBD (2.16 eV) is only slightly lower than that of BD (2.18 eV). Indeed both NBD and BD show a similar absorption onset at ca. 800 nm. It should be recalled that the low energy absorption tail of these Ru(II) complexes bear the contribution of excitations to triplet states that are not considered in the computation nor observed in electrochemistry. Indeed NBD is weakly emitting at RT with the onset of the 3MLCT emission in ethanol at 720 nm and an undetected maximum extending into the NIR spectral region (Figure S5). From the crossing of the normalized absorption and emission spectra an E₀₀ = 1.7 V was estimated for NBD. If we neglect differences in outer sphere solvent interaction, a triplet excited state oxidation potential of ca. -1 V vs SCE can be estimated for **NBD**, safely suggesting the occurrence of activationless electron injection from the excited triplet state to the conduction band of TiO₂ in non-aqueous solvents as well.¹⁸

Table 1 Electrochemical data compared to computed energy levels.

	Ru(II)/(III)	L/L ⁻
BD Calculated	0.65 V (SCE)	-1.5 V (SCE)
BD Experimental	0.62 V (SCE)	-1.64 V (SCE)
NBD Calculated	0.5 V (SCE)	-1.64 V (SCE)
NBD Experimental	0.64 V (SCE)	-1.26 V, -1.56 V(SCE)

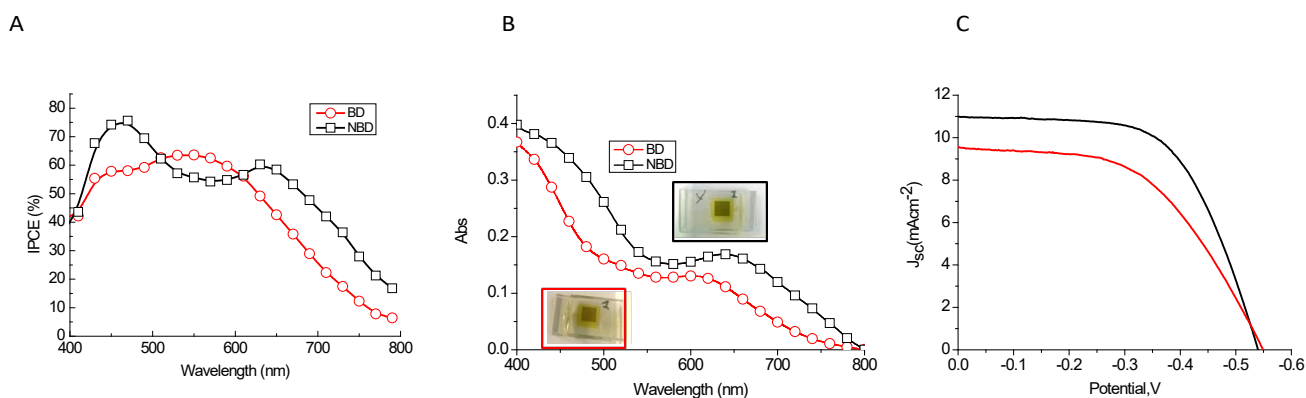


Fig. 3 Photovoltaic and optical characteristics of NBD (black) and BD (red) on ca. 6 μm transparent TiO_2 films. (A) Photoaction spectra with the electrolyte formulation (b); (B) absorption spectra; (C) J–V curves with the electrolyte formulation (b)

Table 2. J–V characterization of the DSCs

Dye	Layer	Electrolyte	J_{sc} (mA cm^{-2})	V_{oc} (V)	FF (%)	PCE (%)
BD	18NR-T	a	8.28	0.49	62	2.52
NBD	18NR-T	a	9.19	0.51	60	2.80
BD	18NR-T + TiCl_4 0.4 M	b	9.53	0.55	52	2.73
NBD	18NR-T + TiCl_4 0.4 M	b	11.0	0.54	60	3.60
BD	18NR-AO + TiCl_4 0.4 M	b	19.08	0.39	40	2.97
NBD	18NR-AO + TiCl_4 0.4 M	b	19.35	0.46	47	4.25
BD	18NR-AO + TiCl_4 0.4 M	c	10.68	0.72	63	4.85
NBD	18NR-AO + TiCl_4 0.4 M	c	2.56	0.68	80	1.39

Electrolyte: a 0.1 M I₂ – 0.1 M LiI – 0.1 M GuNCS – 0.6 M PMII in ACN. b 0.1 M I₂ – 0.1 M MgI₂ – 0.15 M GuNCS – 0.6 M PMII in ACN. c 0.1 M I₂ – 0.05 M MgI₂ – 0.15 M GuNCS – 0.6 M PMII – 0.4 M BzIm in ACN.

In these conditions **NBD** delivered on ca 6 μm transparent TiO_2 a J_{sc} of 11 mA/cm^2 (ca. 15 % more than **BD**) with a relative efficiency enhancement of 32% (Fig. 3C). On 6 μm opaque TiO_2 (Dyesol 18NR AO) the photocurrents for both **NBD** and **BD** are quite levelled, consistent with the better harvesting of light scattering TiO_2 substrates. Nevertheless, **NBD** maintains an edge over **BD** in both photocurrent and, more significantly, in photovoltage resulting in 4.25 % vs ca. 3% efficiency.

We have observed however that **NBD** suffers from low photocurrents (a ca. $8 \times$ drop, Table 2) when 4-tert-butylpyridine or benzimidazole are added to the electrolyte formulation with the aim of improving cell photovoltage. Such an effect is still under investigation. The introduction of a kinetic barrier for charge injection to TiO_2 due to upward shift of the semiconductor states²¹ may partly explain such observation, although **BD**, with similar energetics, exhibits, under identical conditions, a much smaller drop in photocurrent (ca 50%) which is compensated by a significant gain in photovoltage and Fill Factor, leading to overall improved efficiency (up to 4.85%, Table 2) when basic additives are present. Other recombination mechanisms possibly mediated through super exchange effects by the highly delocalized chromophoric ligand may become more active in **NBD**, in the presence of a negative shift of the TiO_2 Fermi level. This possibility is currently under investigation.

In conclusion, we have reported here the preparation of a new ligand which can serve as a flexible building block for the preparation of complexes having improved optical and electronic properties while maintaining good ground and excited state energetics for photoinduced charge separation. The incorporation of this ligand in a new “black” dye design resulted indeed in significant advantages over $[\text{Ru}(\text{II})[\text{HTcTerpy}]\text{NCS}_3](\text{TBA})_3$ on transparent TiO_2 , coupling a pleasant intense dark green coloration to increased conversion efficiency.

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