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Influence of brominated-TPA-stilbazole based ancillary ligand on the photocurrent and photovoltage in dye-sensitized solar cells

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ABSTRACT

Two novel heteroleptic brominated-TPA-stilbazole based Ru (II)-sensitizers denoted as SD-11 and SD-11 mono were designed, synthesized and characterized for dye-sensitized solar cells (DSCs) in comparison to benchmarked dye N719. The molecular structures of SD-11 and SD-11 mono were confirmed using FTIR, ^{1}H-NMR and mass spectrometry. The aim was to systematically study the effect of mono (SD-11 mono) *versus* bis-brominated-TPA moiety (SD-11) on molar absorptivity, ground and excited state oxidation potentials, light harvesting efficiency (LHE), incident-photon-to-current conversion efficiency (IPCE), short-circuit photocurrent density (*J*sc), and total solar-to-electric conversion efficiency (η) for DSCs. Optical results revealed that SD-11 and SD-11 mono have higher molar extinction coefficients, narrower HOMO – LUMO gaps compared to N719. Hence, it was found that SD-11 exhibited remarkably greater *J*sc than SD-11 mono and interestingly showed comparable extinction coefficients. However, in optimized conditions, SD-11 showed a higher *J*sc of 22.1 mA cm^{-2}, *V*oc of 0.68 V with (% η) of 8.7 compared to *J*sc of 14.4 mA cm^{-2}, *V*oc of 0.63 V and with (% η) of 5.8 for SD-11 mono whereas N719 attained a *J*sc of 15.9 mA cm^{-2}, *V*oc of 0.74 V with (% η) of 7.6 under the same experimental device conditions. It was concluded that SD-11 outperformed SD-11 mono in photovoltaic performance when anchored on TiO_2, owing to better light-harvesting ability. These results clearly demonstrated that the enhancement of the photovoltaic performance in SD-11 can be attributed to the presence of more number of –Br group.

1. Introduction

Dye-sensitized solar cells (DSCs) have enchanted significant attention in recent years after the first report by O'Regan and Gräetzel in 1991 [1] due to their low-cost, high incident solar light-to-energy conversion efficiency, low-energy manufacturing process and environment friendly nature, superior price to performance ratio, mechanically robust, able to work at wider angles and in low light [2–8]. Since then huge efforts have been devoted into this area and dyes as photosensitizers for high efficient DSCs have been widely studied and optimized [9]. To date the maximum efficiency achieved for DSCs was 13.0% by Zinc porphyrin complex [10]. Besides, solid state perovskite solar cells, which have achieved much attention recently with small exciton binding energy and ambipolar charge mobility, have reached efficiency as high as 22.1% [11].

High efficiency in DSCs is dependent on the optimization of the device components including a dye (sensitizer), TiO_2 and an electrolyte. Sensitizer is one of the key components in DSCs. Ru(II) polypyridyl complexes were proven to be very effective in achieving high solar-to-electric conversion efficiency due to their strong metal-to-ligand charge transfer (MLCT) properties, rich fluorescence behavior, stable ground and excited state potentials, compatibility with diverse electrolyte compositions and long excited state lifetime [12]. Triphenyl amine (TPA) based sensitizers are being used as electron-donor ancillary ligands for dye-sensitized solar cell applications and they are considered as potential energy harvesters [13–15]. There are few metal-free dyes reported in literature with TPA linkage as a good donor such as TC1–TC4 dyes with triphenylamine (TPA) moieties with reported efficiency ranging from 2.4 to 4.7% [16]. Similarly, TPA linkage was used in Ru(II) based sensitizers such as HMP-9 (see Fig. 1) [17]. It has two TPA linked moieties with –*Ohex* at *para* position of *phenyl* group in the ancillary ligand complexed to ruthenium with the current density (J_{SC}) of 16.7 mA/cm^2 with 5.3% of overall efficiency. Mono-ancillary ligand was synthesized using TPA moiety linked to stilbazole linkage denoted as Ru-TP1 (see Fig. 1) with *J*sc 9.39 mA/cm^2 with efficiency of 3.21% [18]. The discussed literature emphasized the importance of TPA moiety and urged us to rationalize its use in DSCs as sensitizer. Therefore, we functionalized the phenyl group in TPA with –Br atoms

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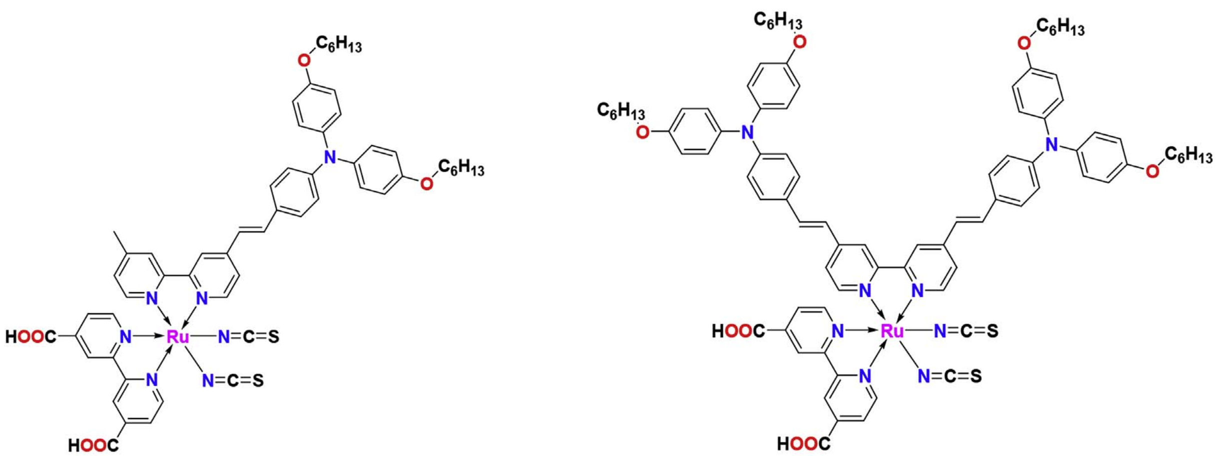


Ru-TP1 HMP-9

Fig. 1. Chemical structure of Ru(II) dyes [17,18].

and used these new ancillary ligands in Ru(II) dyes.

Keeping in view the importance of TPA moiety in DSC applications, we report two novel sensitizers based on brominated-TPA-stilbazole based electron-donor ancillary ligands as shown in Fig. 2. We have examined and compared the influence of mono (SD-11 mono) *versus* bis-ancillary ligands (SD-11) in contrast to benchmark dye N719 in terms of light harvesting efficiency, optical, electrochemical, dye/TiO_2 interface characteristics and photovoltaic performance. To best of our knowledge, this is first ever study carried out on effect of brominated-TPA-stilbazole based ancillary ligand in dye-sensitized solar cells.

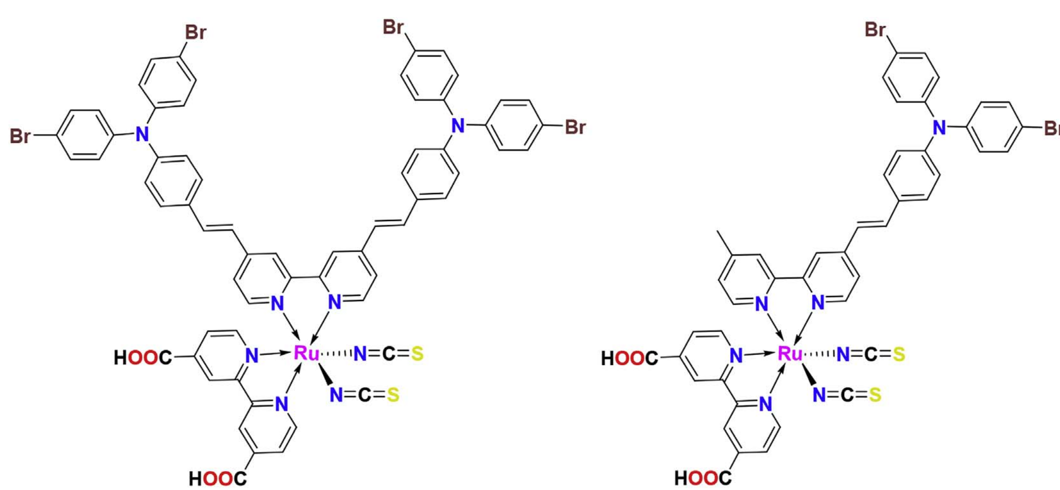
2. Experimental

2.1. Materials and equipment

The solvents and chemicals were purchased from Sigma-Aldrich, Fisher Scientific or TCI-America and used as received. Silica (230-400 mesh, Grade 60) for column chromatography was purchased from Fisher Scientific. The mass spectrometry analysis was carried out on a high resolution mass spectrometer – the Thermo Fisher Scientific Exactive Plus MS, a benchtop full-scan Orbitrap™ mass spectrometer using electrospray ionization (ESI). Fourier transform infrared spectroscopy (FTIR-ATR) spectra were recorded on a Nicolet Nexus 470 FT-IR spectrometer (Thermo Scientific, USA) and UV–Visible spectra were measured by using Cary 300 spectrophotometer. Emission was recorded at room temperature on a Fluorolog-3 spectro fluorometer (HORIBA Jobin Yvon Inc.). ^{1}HNMR spectra were recorded using a Bruker 500 MHz spectrometer.

2.2. Synthesis of ancillary ligands and Ru(II) sensitizers

For the synthesis of the proposed sensitizers, SD-11 and SD-11 mono, the corresponding ancillary ligands were synthesized according to the reported procedures with modifications [19,20]. The corresponding aromatic aldehydes and 4,4′-dimethyl-2,2′-bipyridyl were reacted in a pressure tube in the presence of chlorotrimethylsilane to produce the corresponding mono and bis-stilbazole in Knoevenagel condensation type reactions. The exact synthetic procedure can be found in the Supporting Information (Scheme 1). The proposed Ru(II) sensitizers were then synthesized in a typical one-pot three-steps synthetic scheme, as given in the Supporting Information (Scheme 2). The yield of the crude products was in the range of 75–80%, which was purified through a Silica column two times to obtain the highly pure product in 55–60% yield.



SD-11 SD-11 mono

Fig. 2. Chemical structure of synthesized Ru(II) dyes.