



Structure–property relationships: Steric effect in ancillary ligand and how it influences photocurrent and photovoltage in dye-sensitized solar cells



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ABSTRACT

Here we report structure–property relationships of naphthalene-based ancillary ligands for DSCs employing Ru (II) bipyridyl complexes containing methoxy at 4,7-positions (**HL-41**) and ethoxy at 2-position (**HL-42**) on the naphthalene moiety respectively. 2-ethoxy naphthalene stilbazole-based ligand was strategically chosen as an ancillary ligand to ascertain the influence of steric effect of alkoxy group *ortho* to the spacer group (CH=CH) of stilbazole on the photovoltaic properties. It was found that under similar conditions photocurrent response was in the following order **HL-41** > **HL-42** > **N719**. Both **HL-41** and **HL-42** showed similar redox potential. The overall conversion efficiency for devices employing **HL-41**, **HL-42** and **N719** were 7.8%, 7.6% and 7.6%, respectively. DFT calculations showed that the torsion angles between the naphthyl moiety and CH=CH spacer was 34.81° and 39° for **HL-41** and **HL-42**, respectively. Thus, for **HL-42** ethoxy *ortho* to CH=CH produces more twisted naphthyl which precludes efficient charge transfer from the ancillary ligand to the metal.

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1. Introduction

Dye sensitized solar cells (DSCs) have been recognized as an efficient, stable and cheap alternative to conventional silicon solar cells [1–6]. In a study done by Texas Instruments [7], authors compared the organic (DSC, organic PV) and inorganic thin film (amorphous silicon) solar cells to identify the most efficient PV, specifically for indoor applications such as laptops, cell phones and other similar gadgets. The analysis concluded that DSCs showed higher power density in indoor conditions relative to a-Si and OPV solar cells because of the independence of the former on incident light angle. Owing to their superior indoor performance, consumer electronic products can be a huge market for DSC as seen by recent examples of flexible keyboard and a cell phone charger [8].

Since the first report of adsorbing ruthenium complex on wide band TiO₂ nanocrystalline semiconductor by O' Regan and Grätzel [9], huge efforts have resulted in highly efficient DSC materials [10–16]. DSCs with efficiency high as 13% (η) [17] has been achieved by Zn-porphyrin complex. Additionally, perovskite-sensitized solid

state dye solar cells have reached record high efficiency of 15.9% [18] whereas efficiency of 17.9% has also been recorded [19]. Sensitizer is one of the most critical functional components in a DSC. Sensitizer determines the spectral response and plays a crucial role at the interface of redox shuttle and TiO₂ [20–23] in determining electron injection, dye regeneration and charge recombination. Ruthenium (II) polypyridyl complexes with low energy metal-to-ligand charge transfer (MLCT) transitions [3], compatibility with diverse electrolyte compositions [24,25], long term stability [2,26] and ease of tuning the redox properties [26,27] have surpassed all other type of dyes in DSCs. In this regard, **N719** (η , 11.18%) is a popular benchmark [3,28] and other alternatives have been explored in order to improve light harvesting efficiency and long term stability. The strategies of adding new chromophores with high molar absorptivity [10,22,29,30], long alkyl chains for long term stability [2,31,32], thiocyanate-free Ru (II) sensitizers for high efficiency and long term stability [33–38] and sensitizers with spin-forbidden singlet-to-triplet transition for NIR response [5,39,40] have been the focus of research during last two decades. The strategy of adding new chromophores with high molar absorptivity and broader spectral response will lead to reduction of TiO₂ thickness, resulting in shortening of electron transport distance thus minimizing the underlying electron losses, which will

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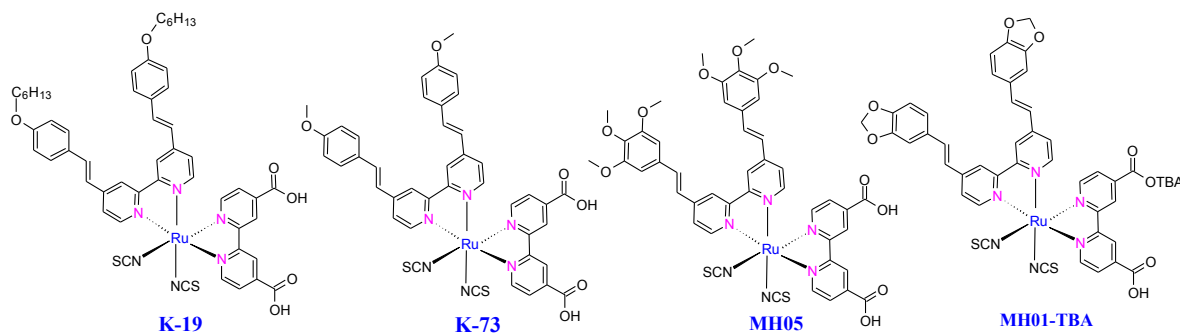


Fig. 1. Molecular structures of complexes K-19, K-73, MH05 and MH01-TBA.

translates into higher overall device efficiencies [26,27,41,42]. Oxygen containing electron donor cyclic and acyclic alkoxy groups (Fig. 1) have been investigated and recognized as alternatives for N719 [30,43–46]. Acyclic alkoxy groups were introduced in the beginning [30,43–46] (e.g. K-19 and K-73) in order to increase the molar extinction coefficient owing to increased conjugation and favorable alignment of the p-orbital (lone pairs) of electron donors with the conjugated system. Recently, El-Shafei et al. [22,30] in a detailed comparative study of cyclic vs. acyclic oxygen containing groups showed that cyclic oxygen containing donating groups perform better than acyclic electron donors.

With the aforementioned in mind, in this paper, we report the synthesis, spectral, electrochemical and photovoltaic characterizations of two novel sensitizers based on naphthalene with alkoxy electron donating groups at different positions on the naphthalene ring as shown in (Fig. 2). Electron donating groups based on naphthalene were expected to offer better photon harvesting owing to enhanced conjugation of fused benzene rings along with oxygen-containing electron donor groups of methoxy and ethoxy. In this study, fluorescence, UV–Vis spectroscopy, and cyclic voltammetry were employed for photophysical and photoelectrochemical characterizations. Dye/TiO₂ interface was characterized by impedance spectroscopy to qualitatively determine charge recombination resistance and electron life time in TiO₂ conduction band (CB). Photovoltaic characterizations such as IPCE and I–V graph for dye solar cells made with HL-41, HL-42 and N719 were measured and compared under similar conditions. Photovoltaic performance of sensitizer HL-41 outperformed N719 and HL-42 in photocurrent and total power conversion efficiency. However, the V_{oc} of devices based on the three dyes was in the following order: N719 > HL-42 > HL-41. Higher V_{oc} of HL-42 can be attributed to the presence of more twisted naphthyl due to the location of ethoxy group at the

ortho position with respect to the CH=CH spacer, which may play a key role in minimizing dye aggregations.

2. Experimental section

2.1. Materials and equipment

The solvents and chemicals were purchased from Sigma–Aldrich, Fisher Scientific or TCI-America and used as received. Sephadex LH-20 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 Heated Electrospray Ionization (HESI). Samples were dissolved in methanol and sonicated for 15 min. They were then diluted 1:1 with 20 mM ammonium acetate and analyzed via syringe injection into the mass spectrometer at a flow rate of 10 μL/min. The mass spectrometer was operated in negative ion mode. FT-IR (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. Fluorescence and emission decay were recorded at room temperature on a Fluorolog-3 spectrofluorometer (HORIBA Jobin Yvon Inc.). ¹H NMR spectra were recorded in a Bruker 500 MHz or Varian 400 MHz spectrometer.

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

The synthesis of proposed sensitizers HL-41 and HL-42 was carried out in typical three step one pot method as depicted in Scheme 2 of Supplementary Information (SI). The synthesis of sensitizers was completed following the synthesis of corresponding ancillary ligands L-41 and L-42 (Scheme 1, Fig. 3). The ligands were

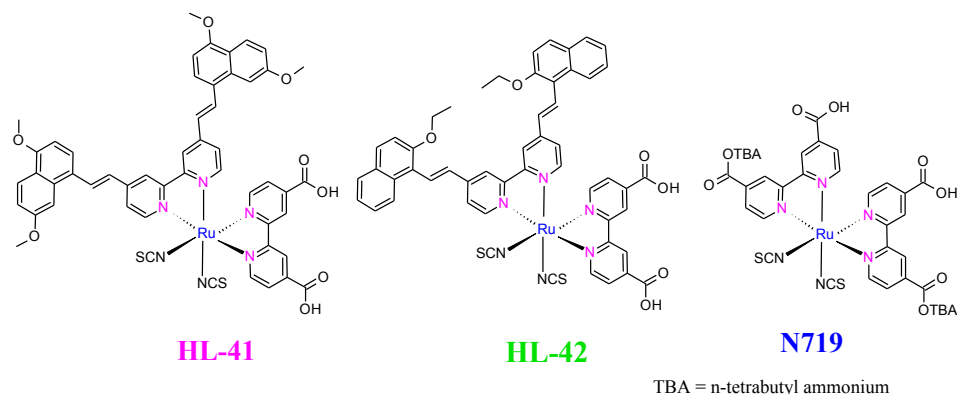


Fig. 2. Molecular structures of complexes HL-41, HL-42, and N719.

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