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Effect of terthiophene spacer position in Ru(II) bipyridyl complexes on the photocurrent and photovoltage for high efficiency dye-sensitized solar cells

Mohamed R. Elmorsy[a,b], Rui Su[a], Ahmed A. Fadda[b], H.A. Etman[b], Eman H. Tawfik[b], Ahmed El-Shafei[a,*]

[a] Polymer and Color Chemistry Program, North Carolina State University, Raleigh, NC 27695, United States
[b] Department of Chemistry, Faculty of Science, Mansoura University, El-Gomhoria Street, 35516 Mansoura, Egypt

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ABSTRACT

Two novel ruthenium complexes, MR-1 and MR-2 were synthesized for use in dye-sensitized solar cells (DSSCs). Under similar fabrication conditions, the photovoltaic performances of these dyes were evaluated and compared to the standard ruthenium complex N719. MR-1 and MR-2 showed the efficiencies of 8.19% and 5.32%, respectively, while N719 achieved 7.66%. MR-1 also displayed higher V_{OC} than MR-2, which is due to the larger molecular size and higher molar extinction coefficient of the former, which translates into less dye aggregation on a thinner film of TiO_2. Incorporation of terthiophene as a linker reduces the band gap of MR-1 when compared to that of MR-2. The influence of π-conjugated bridge on optical and electrochemical properties was investigated. Results demonstrated that the absorption band of MR-1 displayed higher extinction coefficient with a broader absorption compared to MR-2 and the benchmark Ru(II) dye, N719, due to the enhancement of electron donating ability of π-conjugated bridge.

1. Introduction

Clean and sustainable power sources are consistently getting more attention worldwide because of environmental contamination and the risk of climate change caused by traditional energy utilization [1]. Dye-sensitized solar cells (DSSCs) based on nano-porous TiO_2 photoelectrode with dye photosensitizers sensitized to visible light have been extensively studied because of the low cost of production and their high-power conversion efficiency (PCE) compared to traditional silicon-based solar cells. Huge progress has been made in their performance and stability since the major work of O'Regan and Grätzel in 1991 [2]. The main constituents of DSSCs were photosensitizers (dyes), semiconductor metal oxides and electrolyte [3,4]. The sensitizer plays an important role in enhancing the PCE. An ideal sensitizer should have a broad absorption range in both visible and NIR region as well as a high molar extinction coefficient [5]; furthermore, sensitizers should have suitable anchoring groups so as to be bound with semiconductor surface. Among all the transition metal complexes, Ru(II) complex-based DSSCs have been widely researched with the achieved PCE(η) over 10% as published [6]. The co-sensitization method between small organic co-sensitizer and main Ru(II) sensitizer were also concerned in many studies to further increase the overall efficiencies [7–10]. There are several ways to design Ru(II) sensitizers on the molecular level, such as the modification of ancillary ligands and thiocyanate moieties with other strong electron donor moieties, heterocycle introduction and long alkyl chain substitution, and modification of the anchoring species [11–13]. For new advances in achieving higher PCEs, the evolution of the π-bridge unit is essential in the molecular engineering of sensitizers, which should be inserted as planar-type building blocks of fused heterocycles instead of twisted structures [4,14,15]. Many fused heterocycles such as thienothiophene [16], dithienothiophene [17] and benzo [2,1-b:3,4-b']dithiophene [18] have been incorporated into the π-bridge with broad and intense spectral absorption in the visible-light region. Furthermore, introduction of the π-bridge spacer enhancement of the photocurrent for efficient charge transfer [19]. Our group has developed many attractive ruthenium sensitizers that exhibit higher conversion efficiency than N719 such as MH-1, NSCU-10, HD-8 and MH-8 [20–25].

The combination of thiophene spacer and the electron donor is one of the strategies for designing more efficient Ru(II) photosensitizers due to the enhancement of the molar extinction coefficient for both the $\pi \rightarrow \pi^*$ and $4d \rightarrow \pi^*$ transitions [26–29]. In this way, investigations of the molecular engineering of favorable Ru(II) sensitizers with trimethoxy benzene as a donor incorporated with terthiophene as π-spacer is intriguing. Herein, two novel ruthenium sensitizers, MR-1 and MR-2, are structurally modified with the aim of increasing the molar extinction

* Corresponding author.
E-mail address: Ahmed_El-Shafei@ncsu.edu (A. El-Shafei).

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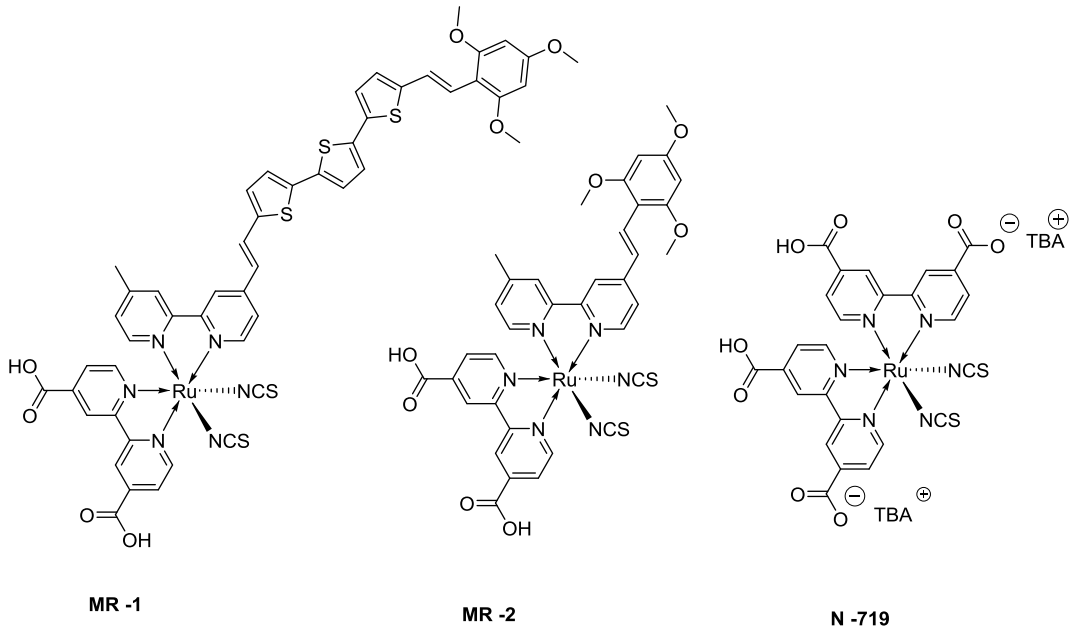


Fig. 1. Molecular structures of MR-1, MR-2 and N719.

coefficient compared to N719. For MR-1 terthiophene spacer, which linked to trimethoxy benzene donor, was further attached to a bipyridyl to study the influence of the thiophene-π-bridged on absorption properties and photovoltaic performances. Our attempts to synthesize the bis-electron donor ancillary ligand for MR-1 wasn't successful, due to the bulky structure of the dye molecule. The molecular structures of MR-1 and MR-2 are displayed in Fig. 1.

2. Experimental section

2.1. Synthesis of Ru(II) bipyridyl complexes

The solvents and chemicals were purchased from Fisher Scientific, Sigma-Aldrich, or TCI America and used as received. Sephadex LH-20 was obtained from Sigma-Aldrich. The synthesis of all ligands and complexes are shown in Schemes 1 and 2, respectively. Details of synthesis are provided in the ESI.

2.2. Cyclic voltammetry measurements

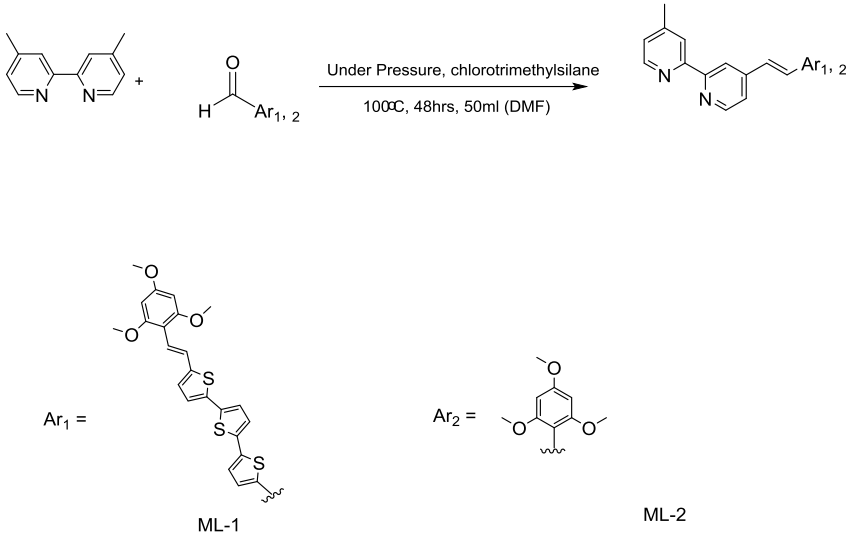
Cyclic voltammetry (CV) was measured in dimethylformamide with 0.1 M [TBA][PF_6] as an electrolyte at a scan rate of 50 mV s^{-1}. The working electrode (WE) represented by Glassy carbon, the counter electrode is Pt wire and Ag/Ag^+ in acetonitrile was used as the reference electrode. Fc/Fc^+ was used as a reference, Addition of 0.63 V to convert voltage measured to NHE. Figs. 5S and 6S (Supplementary Information) show the cyclic voltammetry shapes of sensitizers.

2.3. TiO_2 electrode preparation and device fabrication

TiO_2 electrode preparation and DSSC devices fabrications with the detailed procedure are provided in the supplementary information.

2.4. Photovoltaic measurements

Photovoltaic parameters of sealed cells can be measured by illuminating the cell through the conductive glass from the anode side with a



Scheme 1. Synthesis route of ligands ML-1 and ML-2.