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Co-sensitized ruthenium(II) for dye-sensitized solar cells (DSSCs)

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Abstract

The co-sensitized dyesof the ruthenium complexes which are **P2**+**N719** and **YN07**+**N719** were synthesized and studied for dye-sensitized solar cells (DSSCs).The mixed solutions showed the complementary absorption spectra which gave a larger molar extinction coefficient and longer MLCT absorptions than the pure complexes. However,the DSSCs gave the low power conversion efficiency (PCE) at 2.37% and1.59%,compared with 5.17% of **N719**.The results concluded thatthe molecular size and unsuitable HOMO of the ruthenium complexes can be a responsible.

Keywords: Dye-sensitized solar cell (DSSC), Ruthenium complex, Co-sensitization, Co-dye

1. Introduction

The dye-sensitized solar cell (DSSC) has been proposed as a low-cost alternative to conventional solar cells in 1991 [1]. At present, an efficiency of more than 12% can be obtained for DSSC using the volatile solvents [2]. The important component of DSSC is the photosensitizer which absorbs light from the sun and transfers an electron from its excited state to the conduction band of TiO_2. The most common sensitizers are ruthenium(II) complexes such as **N3** and **N719**. However, limitations of these materials are a weak absorption in the red and IR regions. Co-sensitization is an effective approach which is a combination of two or more dyes adsorbs together to extend the light harvesting ability, to enhance the molar extinction coefficient of ruthenium dyes and enhance the performance [3]. Ranasinghe reported the co-sensitized system form **N719** and **Black dye**. The result shows higher absorption spectra more than pure dye which results to enhance both the short-circuit current density (J_{SC}) and the open circuit voltage (V_{OC}). More importantly, it improves the power conversion efficiency (PCE) of DSSCs [4]. In the same strategy, Ogura used **Black dye** and **D131** as a co-dye. The results showed that the combination found to exhibit remarkable performance with 11% [5].

In this paper, we study the co-sensitized dyes for DSSCs which arethe combination of **P2**, **YN07** and **N719**. The structures of (2-phenyl-5-(trifluoromethyl)pyrido)-bis(2,2'-bipyridine-4,4'-dicarboxylic acid) ruthenium(II) hexafluoro phosphate (**P2**), cis[bis(thiocyanato)bis(2,2'-bipyridine-4,4'-dicarboxylic acid) ruthenium(II)] tetrabutylammonium (**N719**) and cis[bis(thiocyanato)bis(2,2'- biquinoline- 4,4'-dicarboxylic acid (4-carboxy-2,2'-bipyridine-4'-caboxylate) ruthenium(II)] tetrabutylammonium (**YN07**) shows in Figure 1.

2. Materials and methods

2.1 Materials

The **P2** and **N719** dyes were synthesized following reported procedure [6-7]. The heteroleptic ruthenium complex (**YN07**) was synthesized similar as reported [8]. All the complexes were characterized by ^{1}H, ^{13}C NMR, FTIR and mass. The NMR spectra were recorded on a BrukerAvance 300 spectrometer. Chemical shifts are quoted downfield from internal standard TMS. IR spectra were measured on a Perkin-Elmer Spectrum RX.I one Fourier transform infrared spectrophotometer as attenuated total reflectance (ATR) technique using neat sample. Molecular weights were measured by the high resolution mass spectra with the time of flight (TOF) mode on a BrukerMicroTOF model by Electrospray Ionization techniques (ESI).UV-Visible spectra were measured in a 1 cm path length quartz cell using a UV-2600 spectrophotometer high. Cyclic voltammetry was conducted on aAutolabMetrohm PG11. The 1×10^{-3} M solutions of the corresponding complexes were prepared in DMF containing 0.1 M tetrabutylammoniumhexafluorophosphate (Bu_4NPF_6) as supporting electrolyte. The working electrode was a glassy carbon electrode. The auxiliary electrode was a Pt electrode and Ag^+/AgCl (3 M KCl) electrode was used as reference electrode.

2.2 Fabrication of DSSC

DSSC cells were fabricated and studied with a previously report [8]. The current density-voltage of DSSCs was measured by calibrated Newport sun simulator 96000

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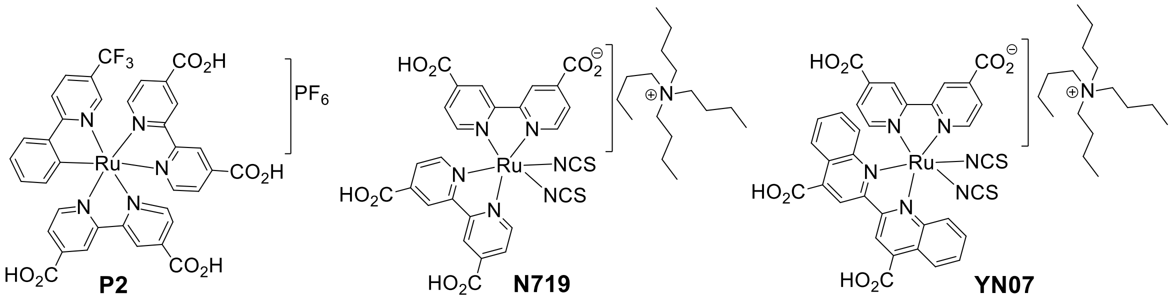

Figure 1 Structures of **P2**, **N719** and **YN07**

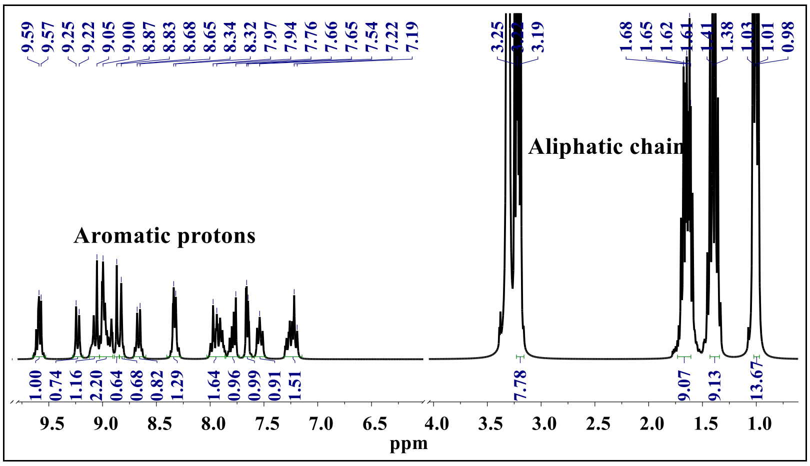

Figure 2 The ^{1}H NMR spectrum of **YN07** in CD_3OD solution

equipped with the device under an AM 1.5 G. The PCE is obtained *via* $\eta = J_{SC}V_{OC}FF/P_{in}$, where J_{SC} (mA/cm^2) is the current density measured at short circuit and V_{OC} (V) is the voltage measured at open circuit. P_{in} is 100 mW/cm^2 and FF is the fill factor.

3. Results and discussion

3.1 Characterization of ***YN07***

The new dye (**YN07**) was synthesized and characterized by ^{1}H NMR (Figure 2).The spectra exhibit the aromatic at9.59-7.19 ppm and aliphatic side chain at 3.23-0.98 ppm. Moreover, we found that the integration ratio of the aromatic proton and the aliphatic proton is 1: 8, confirming the present of one ammonium salts in the complex structures. The molecular weight of the complex was observed at 828.9761 m/z assigned to MW-$N(C_4H_9)_4$+H+Na.

3.2 Photophysical properties

The pictures of pure and co-dyes (1:1 molar ratios) in ethanol(4×10^{-5} M) show the solution colors vary from green to deep red.UV-Vis absorption spectra of pure and co-dyes are shown in Figure 3. We found that the main absorption peaks are π-π^* transition (below 400 nm) and metal-to-ligand charge transfer (MLCT) transition (400-650 nm). Interestingly, the co-dyes show a much higher extinction coefficient and also give larger MLCT absorptions range compared to that of pure **P2** and **YN07** dyes which was summerized in Table 1.

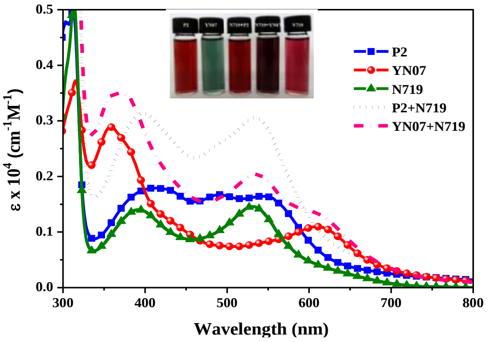

Figure 3 UV-Vis absorption spectra and the photographic of pure and co-dyes in ethanol

3.3 Electrochemical properties

The electrochemical properties of the ruthenium complexes were investigated with the cyclic voltammetry which can be determined (Figure 4, left). The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels of complexes were calculated from equation 1 and 2, respectively [9].

$$E_{HOMO} = -[E_{ox,\,onset} - E_{1/2,\,Fc,Fc^+} + 4.8]\ \text{eV} \quad \text{equation 1}$$

$$E_{LUMO} = -[E_{red,\,onset} - E_{1/2,\,Fc,Fc^+} + 4.8]\ \text{eV} \quad \text{equation 2}$$

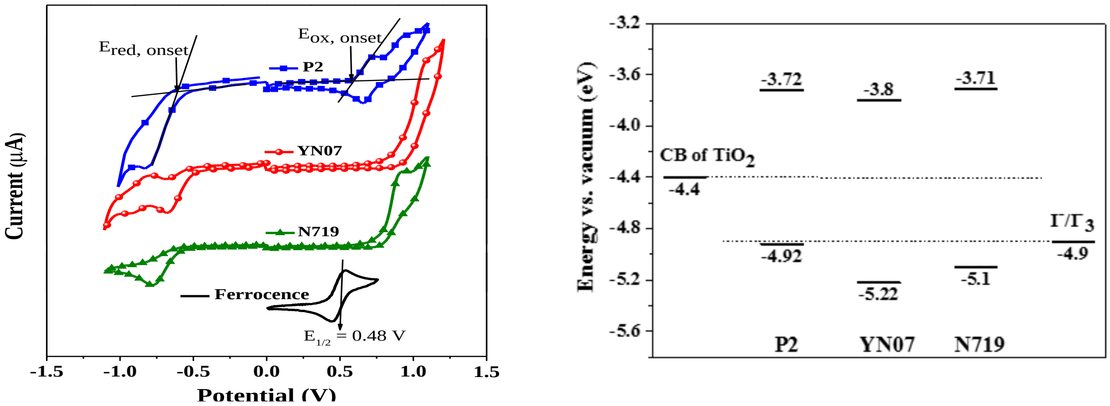

Figure 4 Cyclic voltammogramsof pure dyes (left) and energy levels of DSSCs (right)

Table 1 Photophysical and electrochemical properties of pure and co-dyes

Dye	λ^a/nm ($\varepsilon/10^4$ $M^{-1}cm^{-1}$)	$E_{ox,onset}$ (V)	$E_{red,\ onset}$ (V)	E_g^b (eV)	E_{HOMO} (eV)	E_{LUMO} (eV)
P2	411 (1.78), 490 (1.66), 584 (1.63)	0.60	-0.60	1.18	-4.92	-3.72
YN07	360 (2.87), 612 (1.10)	0.90	-0.52	1.40	-5.22	-3.80
N719	392 (1.40), 531 (1.47)	0.78	-0.61	2.00	-5.10	-3.71
P2+N719	397 (3.14), 533 (3.05)					
YN07+N719	382 (3.50), 548 (2.04), 624 (1.33)					

[a] Maximum absorption wavelength

[b] Energy gap (E_g) determined from E_{HOMO} - E_{LUMO}

Table 2 The photovoltaic parameters of DSSC devices from pure and co-dyes

Dye	J_{SC} (mA/cm^2)	V_{OC} (mA/cm^2)	FF	η (%)
P2	3.82	0.52	0.72	1.42
YN07	1.41	0.48	0.68	0.46
N719	12.02	0.60	0.71	5.17
P2+N719	5.84	0.56	0.73	2.37
YN07+N719	4.08	0.53	0.74	1.59

3.4 Photovoltaic performance

The DSSC performances were investigated with pure and co-dyes under standard AM 1.5 sun light. The current-voltage curve are shown in Figure 5 and summarized in Table 2.

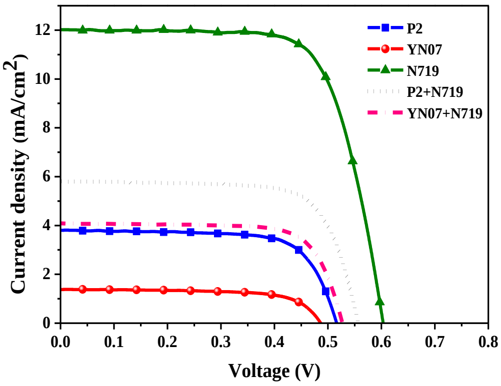

Figure 5 Current-voltage characteristics of pure and co-dyes under standard AM 1.5

We found that the PCE can be obtained at 2.37% (**P2+N719**) and 1.59% (**YN07+N719**), compared to **P2** (1.42%), **YN07** (0.46%) and **YN07** (5.17%).The result suggested that the co-synthesized dyes showed a lower performance than pure**N719.** We think that the bulky **YN07** prevent the **N719** absorption process on TiO_2 surface [10]. For **P2**, the unsuitable HOMO level affected to dye generation see in Figure 4 (right) [11] thus the resulting in lower power conversion efficiency.

4. Conclusions

We report the synthesis and characterization of ruthenium complex for using as sensitizers in DSSCs. The co-dyes show the higher extinction coefficient and larger MLCT absorptions range can be obtained. However, the molecular size and unsuitable HOMO can be a responsible with low power efficiencies at 2.37% and 1.59% compared with 5.17% of **N719**. This study could be a benefit DSSC development in a future.

5. Acknowledgements

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