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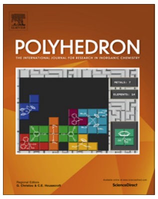

# Refining the anchor: Optimizing the performance of cyclometallated ruthenium(II) dyes in p-type dye sensitized solar cells

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ABSTRACT

A comparison of the performances of p-type dye sensitized solar cells (DSCs) sensitized by three cyclometallated ruthenium(II) dyes differing in their anchoring domains is presented. The dyes are $[Ru(bpy)_2(H\mathbf{1})]$ ($H_3\mathbf{1}$ = (4-(2-phenylpyridin-4-yl)phenyl)phosphonic acid) and the salts $[^nBu_4N][Ru(bpy)_2(\mathbf{1})]$ and $[Ru(bpy)_2(H\mathbf{2})][PF_6]$ ($H_2\mathbf{2}$ = (4-(2-phenylpyridin-4-yl)phenyl)carboxylic acid). DSCs were fabricated with FTO/NiO working electrodes and either an $I^-/I_3^-$/MeCN or $I^-/I_3^-$/MeCN:EtCN (3:1 by volume) electrolyte. The results confirm the higher performance of dyes with a phosphonate versus carboxylic acid anchor, and reveal that $[Ru(bpy)_2(H\mathbf{1})]$ ($J_{SC}$ = 3.24 mA cm$^{-2}$ and $\eta$ = 0.116%) performs better than $[Ru(bpy)_2(\mathbf{1})]^-$. Electrochemical impedance spectroscopy (EIS) shows that a DSC with $[Ru(bpy)_2(H\mathbf{1})]$ offers the lowest transport and recombination resistances and the shortest hole lifetime and diffusion length.

## 1. Introduction

There is significant interest in the use of cyclometallated ruthenium(II) complexes as sensitizers in dye-sensitized solar cells (DSCs) [1–4]. The special attraction of $[Ru(N\text{^}N)_2(C\text{^}N)]^+$ complexes (N^N = bidentate *N,N'*-ligand, C^N = cyclometallated *C,N*-ligand) as dyes originates in the orbital characteristics of the frontier molecular orbitals (HOMO and LUMO). The HOMO is localized on the Ru/C^N domain while the LUMO possesses N^N character [5] and therefore, the electronic properties of the complex can be modulated through functionalization of the C^N and C^N ligands. The discrete partitioning of N^N and $\{(C\text{^}N)_2Ir\}$ orbital character between the HOMO and LUMO in $[Ir(C\text{^}N)_2(N\text{^}N)]^+$ complexes has been exploited for the optimization of cyclometallated iridium(III) dyes in p-type DSCs [6]. Structurally, sensitizers for DSCs are characterized by the anchoring group (commonly a carboxylic or phosphonic acid) which binds the dye to the semiconductor surface [7] and ancillary groups which optimize electron transfer across the dye. Moving the anchor from the N^N to the C^N ligand in a $[Ru(N\text{^}N)_2(C\text{^}N)]^+$ cation converts the complex from being a sensitizer for an n-type to a p-type DSC [8–13]. A related p-type DSC sensitizer containing an $\{Ru^{II}(N\text{^}N\text{^}N)(C\text{^}N\text{^}N)\}$ core in which the cyclometallated ligand bears an anchoring carboxylic acid has also been reported [14].

Although cyclometallated ruthenium dyes (both for n-type and p-type DSCs) typically contain a carboxylic acid anchor [1,3,8–18] we have focused on the use of a phosphonic acids, based on the superior performance with respect to carboxylic acid anchors in n-type copper-sensitized DSCs [19]. Our initial investigations of p-type DSCs have used the zwitterionic dye $[Ru(bpy)_2(H\mathbf{1})]$ (Scheme 1). Even though the structure of this dye has not been optimized, p-type DSCs containing FTO/NiO photocathodes sensitized with $[Ru(bpy)_2(H\mathbf{1})]$ combined with an $I^-/I_3^-$/MeCN electrolyte show short-circuit current densities ($J_{SC}$) of between 3.38 and 4.13 mA cm$^{-2}$ and photoconversion efficiencies ($\eta$) of between 0.116 and 0.139% [12, 20]. This sensitizer outperforms the reference dye P1 [12,21] (Scheme 2). The long-term stability of the DSC can be enhanced by changing the electrolyte solvent composition to a mixture of MeCN and EtCN (3:1 volume ratio), although at the expense of $J_{SC}$ and $\eta$ [20]. The performances of DSCs with $[Ru(bpy)_2(H\mathbf{1})]$ are comparable to that of a DSC containing the more sophisticated dye shown in Scheme 3 ($J_{SC}$ = 3.43 mA cm$^{-2}$ and $\eta$ = 0.104%) which is currently one of the best-performing cyclometallated ruthenium(II) dyes in p-type DSCs [8]. We now compare the performances of DSCs sensitized with $[Ru(bpy)_2(H\mathbf{1})]$ with those containing the carboxylic acid anchored dye $[Ru(bpy)_2(H\mathbf{2})][PF_6]$ (Scheme 1) and also investigate the effects of deprotonating $[Ru(bpy)_2(H\mathbf{1})]$ and using $[^nBu_4N][Ru(bpy)_2(\mathbf{1})]$ (Scheme 1) as the dye.

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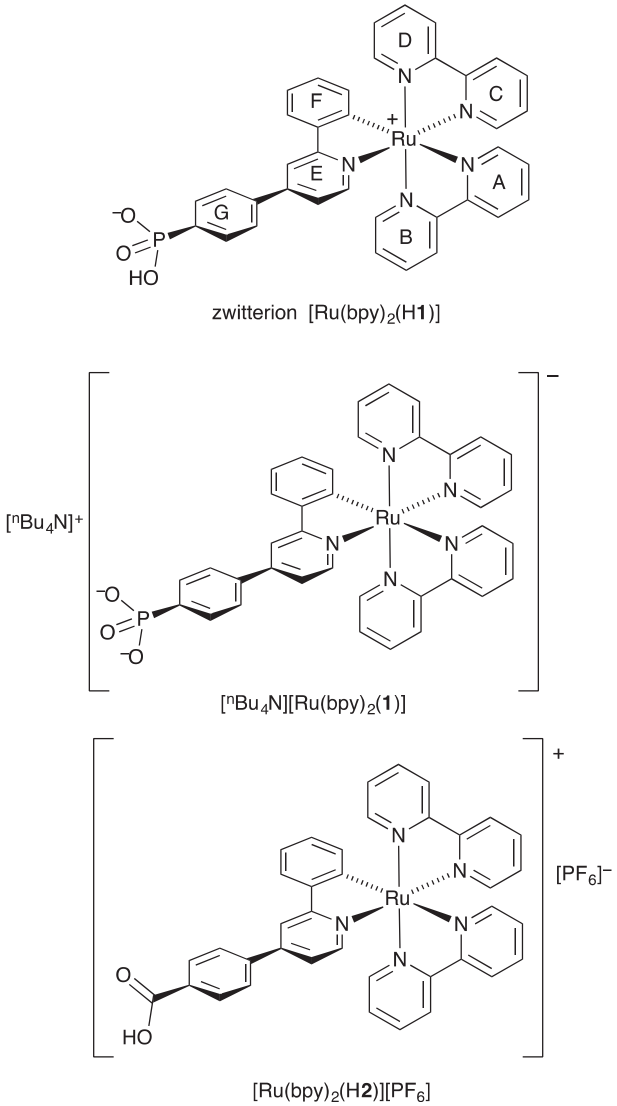
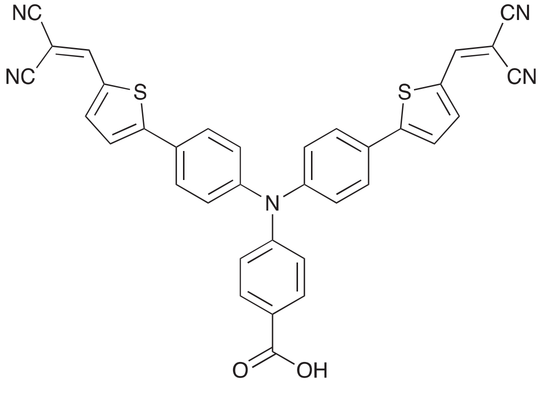


zwitterion [Ru(bpy)$_2$(H**1**)]

[$^{n}$Bu$_4$N][Ru(bpy)$_2$(**1**)]

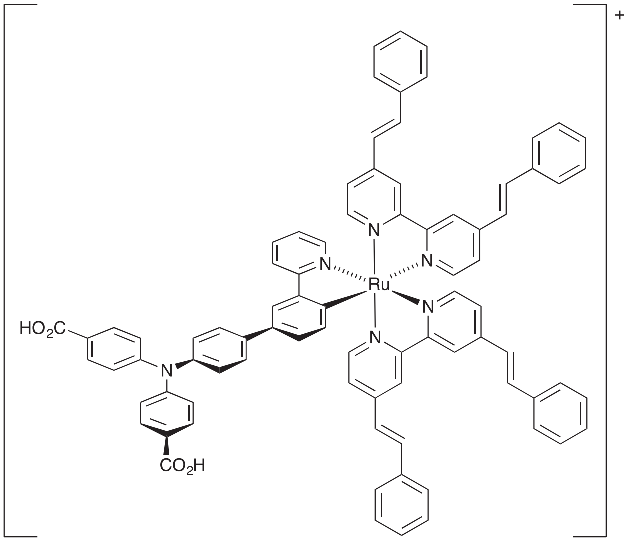
[Ru(bpy)$_2$(H**2**)][PF$_6$]

**Scheme 1.** Structures of the three dyes in this investigation.



**P1**

**Scheme 2.** The structure of the reference p-type sensitizer P1.



**Scheme 3.** A state-of-the-art p-type cyclometallated ruthenium(II) dye reported by Wu and coworkers [8].

## 2. Experimental

### 2.1. General

$^{1}$H and $^{31}$P NMR spectra were recorded on a Bruker Avance III-500 spectrometer at 295 K. The $^{1}$H chemical shifts were referenced with respect to residual solvent peaks ($\delta$TMS = 0), $^{11}$B with respect to $BF_3{\cdot}Et_2O$, and $^{31}$P with respect to 85% aqueous $H_3PO_4$. Mass spectra (LC–ESI-MS) were measured using a combination of Shimadzu (LC) and Bruker AmaZon X instruments.

[Ru(bpy)$_2$(H**1**)] and [Ru(bpy)$_2$(H**2**)][PF$_6$] were prepared as previously reported [12].

### 2.2. [$^{n}$Bu$_4$N][Ru(bpy)$_2$(**1**)]

[Ru(bpy)$_2$(H**1**)] (5.00 mg, 6.92 μmol, 1.0 eq.) was dissolved in MeOH (5.0 mL) and $^{n}$Bu$_4$NOH (4.49 mg, 17.3 μmol, 2.5 eq.) was added as a 0.1 M solution in MeOH. The solution was stirred at room temperature for 2 h, after which the solvent was removed under vacuum to leave [$^{n}$Bu$_4$N][Ru(bpy)$_2$(**1**)] with excess $^{n}$Bu$_4$NOH. Attempts to remove the latter were unsuccessful (see text). $^{1}$H NMR (500 MHz, $CD_3OD$) $^{1}$H NMR (500 MHz, $CD_3OD$) $\delta$/ppm 8.63 (dt, $J$ = 8.3, 1.0 Hz, 1H, H$^{A3}$), 8.54 (m, 1H, H$^{B3}$), 8.47 (m, 1H, H$^{C3}$), 8.44 (m, 1H, H$^{D3}$), 8.31 (d, $J$ = 2.0 Hz, 1H, H$^{E3}$), 8.17 (ddd, $J$ = 5.7, 1.6, 0.7 Hz, 1H, H$^{B6}$), 8.07–7.97 (overlapping m, 4H, H$^{A4+F3+\text{ two of } C4/B4/D4/C6}$), 7.92 (overlapping m, 2H, H$^{D6+A6}$), 7.86 (m, 2H, H$^{G2}$), 7.79 (overlapping m, 2H, H$^{\text{two of } C4/B4/D4/C6}$), 7.71 (m, 2H, H$^{G3}$), 7.59 (dd, $J$ = 6.0, 0.7 Hz, 1H, H$^{E6}$), 7.49 (ddd, $J$ = 7.6, 5.4, 1.2 Hz, 1H, H$^{A5}$), 7.30–7.22 (overlapping m, 4H, H$^{B5+C5+D5+E5}$), 6.92 (ddd, $J$ = 7.8, 7.2, 1.3 Hz, 1H, H$^{F4}$), 6.82 (td, $J$ = 7.3, 1.3 Hz, 1H, H$^{F5}$), 6.45 (m, 2H, H$^{F6}$). $^{31}$P{$^{1}$H} NMR (162 MHz, $CD_3OD$) $\delta$/ppm + 10.2. LC–ESI-MS *m*/*z*: 242.3 [$^{n}$Bu$_4$N]$^+$ (calc. 242.3), 724.2 [M+2H]$^+$ (calc. 724.1). Satisfactory elemental analysis could not be obtained: see text.

### 2.3. DSCs

Working NiO electrodes were prepared in–house. An FTO glass plate (Solaronix TCO22-7, 2.2 mm thickness, sheet resistance = 7 Ω square$^{-1}$) was cleaned by sonicating in surfactant (2% in milliQ water), and rinsed with milliQ water and EtOH. The surface was activated in a UV-$O_3$ system (Model 256–220, Jelight Company Inc) for 20 min. The plate was then dipped five times into a solution of [Ni(acac)$_2$] (ACROS) in MeCN (0.5 mM) and air dried after each dipping. A layer of NiO paste (Ni-Nanoxide N/SP, Solaronix) was screen-printed (90 T, Serilith AG, Switzerland) onto the