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## COMMUNICATION

# Pyrazino-[2,3-f][1,10]phenanthroline as a new anchoring group of organic dyes for dye-sensitized solar cells

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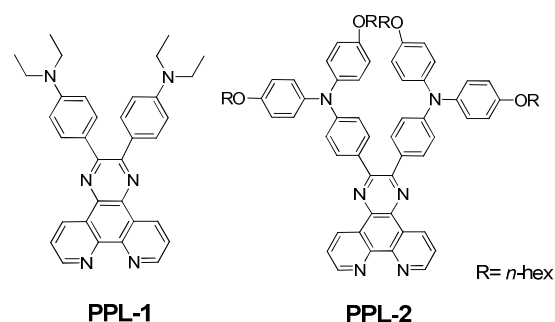
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**Two novel donor-acceptor organic dyes (PPL-1 and PPL-2) with pyrazino-[2,3-f][1,10]phenanthroline as an electron-withdrawing anchoring group were designed and synthesized for dye-sensitized solar cells, achieving a promising power conversion efficiency of 4.04% under standard AM 1.5 conditions.**

Dye-sensitized solar cells (DSCs) have emerged alongside conventional p-n junction solar cells as a mode to converting sun-light to electricity, and attracted intense attention due to their potentially low-cost production and high conversion efficiencies.<sup>1</sup> In a typical DSC, dye-coated mesoporous oxide film electrodes (usually TiO<sub>2</sub>), counter-electrodes (usually Pt), and electrolytes (usually I-/I<sub>3</sub>-) are "sandwiched", where the dye is considered to play a key role in maintaining performance and stability of the DSC.<sup>2,3</sup> Among the dyes utilized, organic dyes have been extensively investigated because of the diversity of molecular structures, high molar extinction coefficients, ease of synthesis, as well as low cost and environmental friendliness. Organic dyes are commonly based on a D-π-A molecular system to narrow optical band gap and improve light induced charge transfer, most of which utilize the carboxylic acid moiety as both acceptor and anchoring group.<sup>4</sup> The carboxylic acid can well bind to the TiO<sub>2</sub> surface through forming a stronger ester linkage with the TiO<sub>2</sub>. This contributes to effective photo-excited electron transfer from the dye to TiO<sub>2</sub>, allowing the DSCs to achieve high efficiencies and long-term stability. Although the carboxylic acid group shows remarkable performances in DSCs, an ongoing quest for alternatives is still desirable for various reasons. Typically, for example, carboxylic acid-containing dyes may cause the conduction-band potential of the TiO<sub>2</sub> to positively shift owing to proton intercalation into the TiO<sub>2</sub> in the dye adsorption process, thus lowering open-circuit voltages of the DSC device.<sup>5</sup>

Accordingly, carboxylic acid-free dyes for DSCs became the subject of intense research in recent years. In 2011, Harima et al. reported new organic dyes with the pyridine group as both electron acceptor and

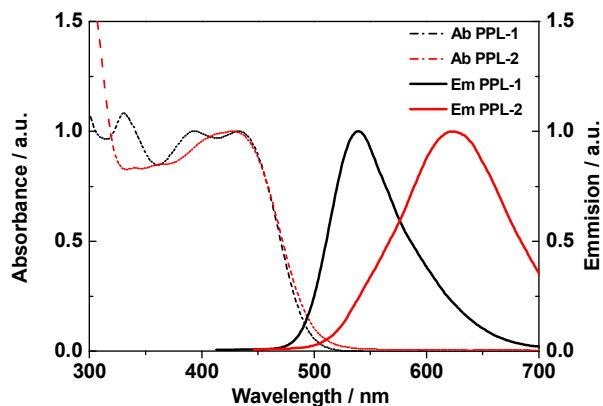
anchoring group.<sup>6a</sup> These dyes are attached onto the surface of the TiO<sub>2</sub> through a coordination bond formed between the pyridine N atom and TiO<sub>2</sub>. Inspired by the work, several dye variants based on the pyridine anchoring group were synthesized and characterized by the Wang group.<sup>6b,6c</sup> Subsequently, various other types of anchoring groups, such as 2-hydroxybenzointrile<sup>7</sup>, nitro group<sup>8</sup>, phosphinic acid<sup>9</sup>, rhodanine<sup>10</sup> and 8-hydroxylquinoline<sup>11</sup>, were successfully introduced into organic dye's molecules. These efforts undoubtedly enriches the content of sensitizers and provides new topics about dyes for DSCs, although current efficiencies of the non-carboxylic acid dye-based devices are far lower than those of the carboxylic acid counterpart-based ones.



**Scheme 1** Chemical structures of phenanthroline-based organic dyes **PPL-1** and **PPL-2**.

Pyrazino-[2,3-f][1,10]phenanthroline (PPL) is an interesting structural framework extensively used in organic catalysis<sup>12</sup> and organic optoelectronic materials<sup>13</sup>. As a bidentate ligand, it chelates various metal ions to form very stable complexes.<sup>14,15</sup> And its electron-withdrawing nature helps extend the spectral absorption range of the molecule. Therefore, PPL might likely be one of promising candidate motifs replacing the conventional carboxylic acid group in the development of new organic dyes for DSCs.

In this paper, two new organic dyes, featuring pyrazino[2,3-*f*]-1,10-phenanthroline as an electron-withdrawing anchoring group, were designed and synthesized, where the donor moiety, *N,N*-diethylbenzamine or 4-(hexyloxy)-*N*-(4-(hexyloxy)phenyl)-*N*-phenylaniline was attached at 2 and 3 positions of PPL. The two dyes were coded as **PPL-1** and **PPL-2**, as shown in Scheme 1. **PPL-1** and **PPL-2** were easily available by a simple two-step procedure (cf. Scheme S1): the Friedel–Crafts reaction of *N,N*-diethylbenzamine (or triarylamine) with oxalyl chloride produces the corresponding diones, followed by the condensation with 5,6-diamine-1,10-phenanthroline to afford the target dyes.



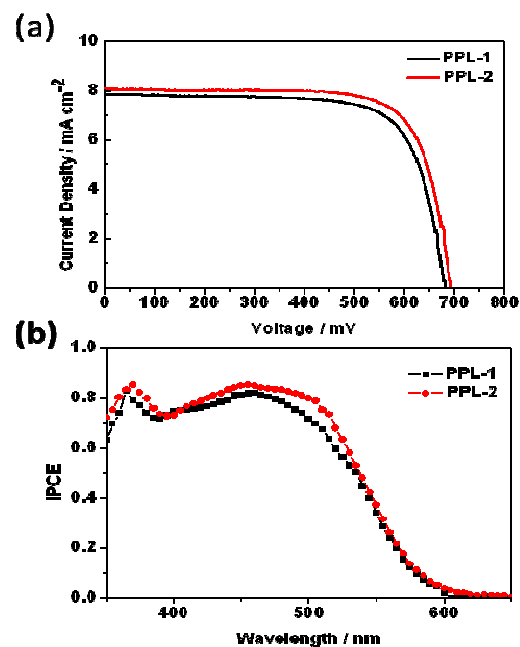
**Figure 1** Normalized absorption and emission spectra of **PPL-1** and **PPL-2** in dilute  $\text{CH}_2\text{Cl}_2$  solution.

Figure 1 shows the UV-vis absorption and emission spectra of **PPL-1** and **PPL-2** in diluted dichloromethane. Both the dyes exhibited similar absorption characteristics having two absorption bands with the maximum extinction coefficient is  $4.5 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$  at 433 nm for **PPL-1** and  $5.8 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$  at 427 nm for **PPL-2**. The band between 350 nm to 500 nm would be assigned to a  $\pi$ - $\pi^*$  transition and the intramolecular charge transfer (ICT) excitation from the donor to the acceptor. The luminescence is found with a maximum at 540 and 627 nm for **PPL-1** and **PPL-2**, respectively. Interestingly, **PPL-2** shows a larger Stokes shift compared with **PPL-1**, indicating its larger structural difference between ground and excited states and leading to the formation of more efficient charge-transfer states, which is favorable for the electron injection from a D- $\pi$ -A type dye to  $\text{TiO}_2$ . The optical bandgap is 2.52 and 2.42 eV for **PPL-1** and **PPL-2**, respectively, estimated from the intersection of the normalized absorption and emission spectra. The dye loading was measured to be  $1.65 \times 10^{-7} \text{ mol/cm}^2$  for **PPL-1** and  $1.43 \times 10^{-7} \text{ mol/cm}^2$  for **PPL-2**. Interestingly, the values are slightly higher than those for the dyes employing carboxylic acid anchoring group,<sup>16</sup> indicating that pyrazino-[2,3-*f*][1,10]phenanthroline (PPL) is a better anchoring group of the dye loading on the  $\text{TiO}_2$  film. To confirm the difference between the two types of anchoring groups (i.e., PPL and carboxylic acid), a desorption experiment was carried out. As demonstrated in the experiment (see the SI section and Figure S1), the carboxylic acid-containing dye N719 was desorbed completely from the  $\text{TiO}_2$  film within about 20 seconds, while the dyes **PPL-1** and **PPL-2** were only slightly lost after being

immersed into an aqueous NaOH solution (0.3 w/w%) for 12 h, indicating that the binding force of PPL dyes onto the  $\text{TiO}_2$  surface is far stronger than that of the carboxylic acid-containing dye.

To investigate the molecular energy levels, cyclic voltammetry measurements (Figure S2) were performed in a 0.1 M dichloromethane solution of tetra-*n*-butylammonium hexafluorophosphate using ferrocene as an internal standard. The first oxidation potentials ( $E_{\text{ox}}$ ) of **PPL-1** and **PPL-2** were observed to be 1.03 and 0.82 eV vs. NHE, respectively, indicating stronger donor ability of the triarylamine. Both the potential values are substantially more positive than that of the iodide/triiodide couple redox (0.4 V vs. NHE),<sup>17</sup> ensuring the regeneration of the ground-state sensitizer for both the dyes. The excited-state redox potentials,  $E_{\text{ox}}$ , determined by subtracting  $E_{\text{ox}}$  from  $E_{\text{ox}}$  were -1.49 eV for **PPL-1** and -1.62 eV for **PPL-2**. Both the values are negative enough to allow their excited-state electron transfer into the  $\text{TiO}_2$  conduction band (-0.5 V vs. NHE).<sup>18</sup>

For preparation of the DSC devices (For detailed information, see supporting information), a double  $\text{TiO}_2$  electrode was prepared by the screen printing method, where a 6  $\mu\text{m}$  transparent layer and a 4  $\mu\text{m}$  scattering layer were employed. The sintered  $\text{TiO}_2$  electrodes were stained in the dye solution of 0.2 mM **PPL-1** or **PPL-2** in chloromethane. In the solutions, 2 mM 3 $\alpha$ ,7 $\alpha$ -dihydroxy-5 $\beta$ -cholic acid (chenodeoxycholic acid) was added as a co-adsorbent to prevent dye aggregation on the  $\text{TiO}_2$  surface. The final devices were prepared in a sandwich-type fashion, where the dyed  $\text{TiO}_2$  electrode and a Pt-counter electrode were sealed using a hot-melt film, and filled with an  $\text{I}^-/\text{I}_3^-$  electrolyte comprising 0.68 M dimethyl imidazolium iodide, 0.03 M iodine, 0.10 M LiI, 0.05 M guanidinium thiocyanate, and 0.40 M *tert*-butylpyridine in the mixture of acetonitrile and valeronitrile (85:15, v/v).



**Figure 2** Photocurrent density-Voltage ( $J$ - $V$ ) curves (a), and incident photon-to-current conversion efficiency (IPCE) (b) spectra of DSCs for **PPL-1** and **PPL-2**.

**Table 1** Photoelectrochemical properties of dyes **PPL-1** and **PPL-2**, and their photovoltaic parameters of solar cells measured under AM 1.5 irradiation (100 mW cm<sup>-2</sup>).

Dye	$\lambda_{\max}^{ab}$ [nm]	E [M <sup>-1</sup> cm <sup>-1</sup> ]	$\lambda_{\text{em(max)}}$ [nm]	$E_{\text{S}+/}$ [V] <sup>b</sup>	$E_{\text{S}+/}$ [V]	$E_{0-0}$ [eV]	$J_{\text{SC}}$ [mA/ cm <sup>2</sup> ]	$V_{\text{oc}}$ [mV]	FF	PCE [%] <sup>c</sup>	dye loading [mol/cm <sup>2</sup> ]
<b>PPL-1</b>	433	45000	540	1.03	-1.49	2.52	<b>7.83</b>	<b>682</b>	<b>0.70</b>	<b>3.74</b>	$1.65 \times 10^{-7}$
							7.72	678	0.69	3.61	
<b>PPL-2</b>	427	58000	627	0.82	-1.62	2.42	<b>8.08</b>	<b>694</b>	<b>0.72</b>	<b>4.04</b>	$1.43 \times 10^{-7}$
							7.88	685	0.71	3.83	

<sup>a</sup> Measured in CH<sub>2</sub>Cl<sub>2</sub> solutions (1×10<sup>-5</sup>M) at room temperature. <sup>b</sup> Oxidation potentials of the dyes were measured in CH<sub>2</sub>Cl<sub>2</sub> solutions with tetrabutylammoniumhexafluorophosphate (TBAPF<sub>6</sub>, 0.1 M) as electrolyte, Pt wires as working and counter electrode, Ag/Ag<sup>+</sup> as reference electrode; calibrated with ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) as an internal reference and converted to N.H.E by addition of 630 mV. <sup>c</sup>  $E_{0-0}$  values were estimated from the intersection of the absorption and emission spectra. <sup>c</sup> Data in italics are the average of 6 cells, data in bold are the best results.

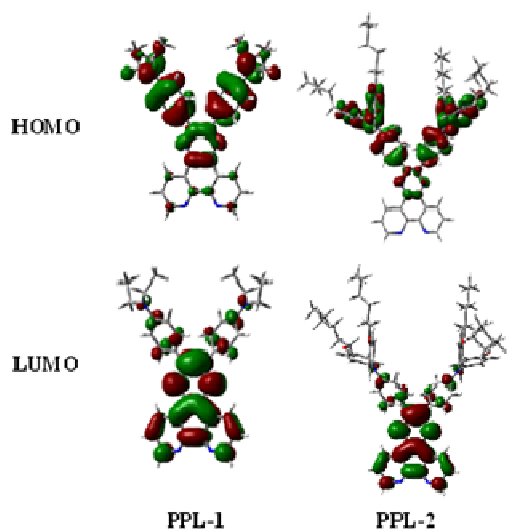
**Figure 3** HOMO–LUMO frontier molecular orbitals of **PPL-1** and **PPL-2**, calculated by DFT at a B3LYP/6-31G (d) level (isodensity = 0.02 au).

Figure 2a shows the I–V performance for DSCs sensitized by **PPL-1** and **PPL-2** under AM 1.5 G simulated solar light at a light intensity of 100 mW cm<sup>-2</sup>, and the photovoltaic parameters are listed in Table 1. The best device for **PPL-1** gave a short circuit photocurrent density ( $J_{\text{sc}}$ ) of 7.83 mA cm<sup>-2</sup>, an open circuit voltage ( $V_{\text{oc}}$ ) of 682 mV, and a fill factor ( $FF$ ) of 0.70, corresponding to a  $PCE$  of 3.74% with an average value of 3.61% for 6 samples. For **PPL-2**, the best device gave a  $PCE$  of 4.04% with an average value of 3.83%, which are slightly higher than those for **PPL-1**. The monochromatic incident photon-to-current conversion efficiencies (IPCEs) were recorded for both the dye-sensitized devices, as shown in Figure 2b. Both the dyes show strong response in the region between 350 and 600 nm with the highest values of about 80%.

In order to gain insight into the geometrical configuration and electron distribution of the frontier orbitals of the two dyes, density functional theory (DFT) calculations were made at a B3LYP/6-31G level, as shown in Figure 3. In the case of **PPL-1**, the electron distribution of the HOMO is homogeneously delocalized over both the donor groups, further extending to the PPL ring; the electron distribution of the LUMO is mainly located on the PPL unit, slightly

extending to both the donors. For **PPL-2**, the distribution of the HOMO is mainly delocalized on both the donor groups, slightly extending to the adjacent PPL ring; the distribution of the LUMO is located on whole molecule except for alkyl chains. According to these observations, the electron communication is favorable between the donor and the acceptor for both the dyes, allowing an efficient electron transfer from the dye to the TiO<sub>2</sub> electrode under light irradiation.

In conclusion, two novel donor-acceptor organic dyes using pyrazino-[2,3-f][1,10]phenanthroline (PPL) as anchoring group were synthesized. Both the dyes can be efficiently adsorbed on the TiO<sub>2</sub> surface through the anchoring group, and the dye-sensitized solar cells showed a highest power conversion efficiency of 4.04%, indicating that PPL is a promising building block as both acceptor and anchoring group for carboxylic acid-free organic dyes for DSCs. Further molecularly engineering of this type of dyes, as well as optimization of the DSC devices are under investigation in our group.

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## Notes and references

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