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

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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 of converting sun-light to electricity, and have attracted intense attention due to their potentially low-cost production and high conversion efficiencies.[1] In a typical DSC, dye-coated mesoporous oxide film electrodes (usually TiO_2), counter-electrodes (usually Pt), and electrolytes (usually I^-/I_3^-) are "sandwiched", where the dye is considered to play a key role in maintaining the performance and stability of the DSC.[2,3] 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.[4] The carboxylic acid can well bind to the TiO_2 surface through forming a stronger ester linkage with the TiO_2. This contributes to effective photo-excited electron transfer from the dye to TiO_2, 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_2 to positively shift owing to proton intercalation into the TiO_2 in the dye adsorption process, thus lowering open-circuit voltages of the DSC device.[5]

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.[6a] These dyes are attached onto the surface of the TiO_2 through a coordination bond formed between the pyridine N atom and TiO_2. Inspired by the work, several dye variants based on the pyridine anchoring group were synthesized and characterized by the Wang group.[6b,c] Subsequently, various other types of anchoring groups, such as 2-hydroxybenzonitrile,[7] nitro group,[8] phosphinic acid,[9] rhodanine[10] and 8-hydroxylquinoline,[11] 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.

Pyrazino-[2,3-*f*][1,10]phenanthroline (PPL) is an interesting structural framework extensively used in organic catalysis[12] and organic optoelectronic materials.[13] As a bidentate ligand, it chelates various metal ions to form very stable complexes.[14,15] 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*-diethylbenzenamine 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*-diethylbenzenamine (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.

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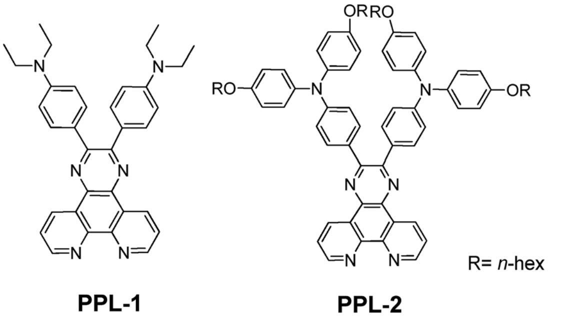

Scheme 1 Chemical structures of phenanthroline-based organic dyes PPL-1 and PPL-2.

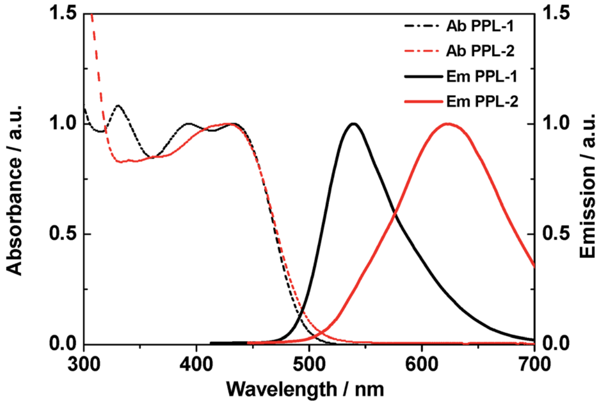

Fig. 1 Normalized absorption and emission spectra of PPL-1 and PPL-2 in dilute CH_2Cl_2 solution.

Fig. 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 4.5×10^4 M^{-1} cm^{-1} at 433 nm for **PPL-1** and 5.8×10^4 M^{-1} cm^{-1} at 427 nm for **PPL-2**. The band between 350 nm to 500 nm would be assigned to a π–π* 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–π–A type dye to 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 1.65×10^{-7} mol cm^{-2} for **PPL-1** and 1.43×10^{-7} mol cm^{-2} **PPL-2**. Interestingly, the values are slightly higher than those for the dyes employing carboxylic acid anchoring group,[16] indicating that pyrazino-[2,3-*f*][1,10]phenanthroline (PPL) is a better anchoring group of the dye loading on the 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 ESI section and Fig. S1†), the carboxyl acid-containing dye N719 was desorbed completely from the 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 TiO_2 surface is far stronger than that of the carboxyl acid-containing dye.

To investigate the molecular energy levels, cyclic voltammetry measurements (Fig. 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 ($E_{s/+}$) 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),[17] ensuring the regeneration of the ground-state sensitizer for both the dyes. The excited-state redox potentials, $E_{+/*}$, determined by subtracting E_{0-0} from $E_{+/0}$, 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 TiO_2 conduction band (−0.5 V *vs.* NHE).[18]

For preparation of the DSC devices (For detailed information, see ESI†), a double TiO_2 electrode was prepared by the screen printing method, where a 6 μm transparent layer and a 4 μm scattering layer were employed. The sintered 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*a*,7*a*-dihydroxy-5*b*-cholic acid (chenodeoxycholic acid) was added as a co-adsorbent to prevent dye aggregation on the TiO_2 surface. The final devices were prepared in a sandwich-type fashion, where the dyed TiO_2 electrode and a Pt-counter electrode were sealed

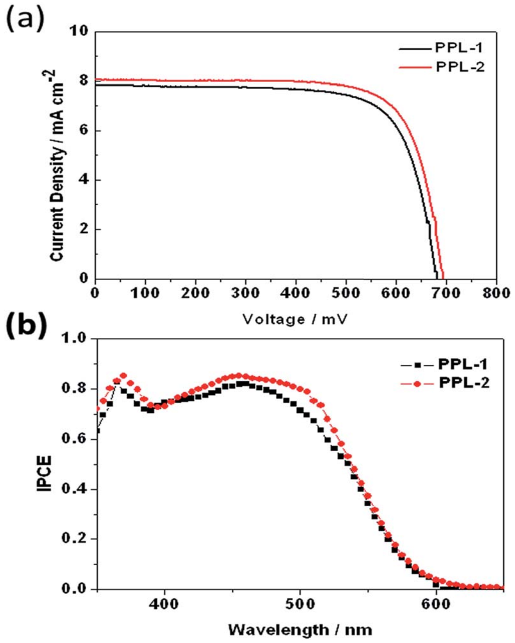

Fig. 2 Photocurrent density–voltage (*J*–*V*) curves (a), and incident photon-to-current conversion efficiency (IPCE) (b) spectra of DSCs for PPL-1 and PPL-2.

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^{-2})

Dye	λ_{max}[a] [nm]	E [M^{-1} cm^{-1}]	$\lambda_{em(max)}$ [nm]	$E_{s/+}$ [V][b]	$E_{s+/*}$ [V]	E_{0-0}[c] [eV]	J_{SC} [mA cm^{-2}]	V_{oc} [mV]	FF	PCE[d] [%]	Dye loading [mol cm^{-2}]
PPL-1	433	45 000	540	1.03	−1.49	2.52	**7.83**	**682**	**0.70**	**3.74**	1.65×10^{-7}
							7.72	*678*	*0.69*	*3.61*	
PPL-2	427	58 000	627	0.82	−1.62	2.42	**8.08**	**694**	**0.72**	**4.04**	1.43×10^{-7}
							7.88	*685*	*0.71*	*3.83*	

[a] Measured in CH_2Cl_2 solutions (1×10^{-5} M) at room temperature. [b] Oxidation potentials of the dyes were measured in CH_2Cl_2 solutions with tetrabutylammoniumhexafluorophosphate ($TBAPF_6$, 0.1 M) as electrolyte, Pt wires as working and counter electrode, Ag/Ag$^+$ as reference electrode; calibrated with ferrocene/ferrocenium (Fc/Fc$^+$) as an internal reference and converted to NHE by addition of 630 mV. [c] E_{0-0} values were estimated from the intersection of the absorption and emission spectra. [d] Data in italics are the average of 6 cells, data in bold are the best results.

using a hot-melt film, and filled with an I^-/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).

Fig. 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^{-2}, and the photovoltaic parameters are listed in Table 1. The best device for **PPL-1** gave a short circuit photocurrent density (J_{sc}) of 7.83 mA cm^{-2}, an open circuit voltage (V_{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 Fig. 2b. Both the dyes show strong response in the region between 350 and 600 nm with the highest values of about 80%.

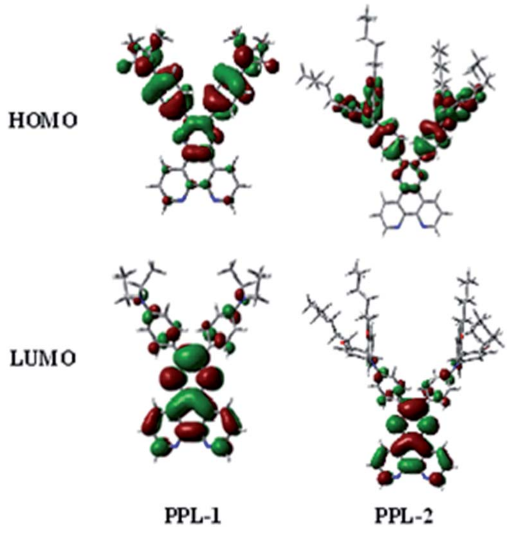

Fig. 3 HOMO–LUMO frontier molecular orbitals of **PPL-1** and **PPL-2**, calculated by DFT at a B3LYP/6-31G (d) level (isodensity = 0.02 au).

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 Fig. 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_2 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_2 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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