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## COMMUNICATION

## A Push-Pull Thienoquinoidal Chromophore for Highly Efficient P-Type Dye-Sensitized Solar Cells

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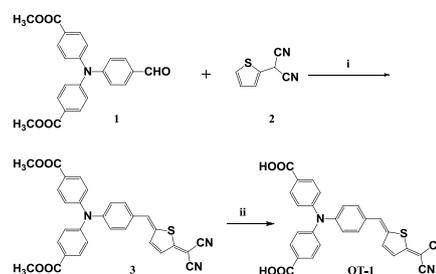
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**A push-pull thienoquinoidal chromophore, 4,4'-((4-((5-(dicyanomethylene)thiophen-2(5H)-ylidene) methyl)phenyl)azanediyl) dibenzoic acid (QT-1), was synthesized and used as a sensitizer in a p-DSC, giving a short-circuit photocurrent density of 8.2 mA/cm<sup>2</sup> under the standard AM 1.5 condition.**

Dye-sensitized solar cells (DSCs) have been intensively investigated as one of the most promising alternatives to conventional silicon-based devices owing to their potential low production costs and high conversion efficiencies.<sup>1</sup> In a typical DSC, n-type semiconductor electrode (usually, TiO<sub>2</sub>) is sensitized as an active photoanode in combination with a passive platinized cathode. In this n-DSC, light-induced electron is injected from the excited sensitizer into the conduction band of TiO<sub>2</sub>, followed by hole injection into an electrolyte (usually containing an I/I<sub>3</sub><sup>-</sup> based redox couple), where the photovoltage is defined by the difference in chemical potential between the TiO<sub>2</sub> photoanode and the electrolyte. As for a p-DSC using a p-type semiconductor (such as NiO), an inverse mode occurs, that is, dye-excitation is followed by rapid electron transfer from the p-type semiconductor to the sensitizer, where the photovoltage is decided by the difference in chemical potential between the NiO photocathode and the electrolyte.<sup>2</sup> Thus, it is expected that a tandem solar cell can be constructed using both the active electrodes in a single device (np-DSC),<sup>3</sup> leading to a high open-circuit voltage, namely a sum of the photovoltages obtained in the corresponding p and n devices, and thus potentially enhancing the power conversion efficiency (PCE). So far, however, high efficiencies have not been obtained as expected in such tandem DSCs, mainly due to the poor performance from p-DSCs.<sup>2,3</sup>

In an np-DSC with the given electrodes, in principle, the maximum possible open-circuit voltage ( $V_{oc}$ ) that can be delivered is directly related to the energy difference of conduction band for n-type semiconductor and valence band for

p-type counterpart. Thus, maximizing short-circuit photocurrent density ( $J_{sc}$ ) is a main means to an end through developing highly efficient sensitizers. In the past few years, great attention has been paid to the development of p-DSCs, including semiconductor electrodes,<sup>4</sup> electrolytes<sup>5</sup> and sensitizers.<sup>6</sup> In spite of high  $J_{sc}$ s up to 21 mA/cm<sup>2</sup> achieved in n-DSCs,<sup>7</sup> the photocurrent obtainable from a p-type-DSC is much lower, partly due to lack of the rational design of sensitizers. Considering the different working mechanism from the n-DSC, a series of sensitizers have been specifically designed and synthesized for p-DSCs.<sup>6</sup> In 2008, Sun and co-workers firstly developed an electron push-pull dye (P1) featuring anchoring group on triphenylamine moiety. In the P1-based p-DSC, a maximum incident-photon-to-current-conversion efficiency (IPCE) of 18% was initially reported with a 1.52 mA/cm<sup>2</sup> of  $J_{sc}$ .<sup>8</sup> Furthermore, about 2.5 mA/cm<sup>2</sup> of  $J_{sc}$  was achieved for **P1** and **P4** with optimized NiO films.<sup>9</sup> Recently, large and heavy perylene dyes were developed, where a long oligothiophene unit was used a linker to separate a triphenylamine unit and an perylene moiety, leading to long-lived charge-separated state.<sup>10,11</sup> Still, it is a challenge to develop highly efficient p-DSC sensitizers which can combine structural simplicity, broad spectral response and high efficiency.



Scheme 1 Synthetic route to **QT-1**. (i) Acetic anhydride, 100 °C, 6 h, stirring (yield: 62%). (ii) THF, aqueous NaOH, 40 °C, 2h, stirring (yield: 67%).

In this paper, a quinoidal thiophene based organic dye (**QT-1**) with a D- $\pi$ -A structure was designed and synthesized for a p-DSCs. In **QT-1**, quinoidal thiophene is used as a bridge to connect a triphenylamine donor and a malononitrile acceptor. The dye was designed with the following structural characteristics: (i) the incorporation of quinoid thiophene as a  $\pi$ -linker in the D- $\pi$ -A system can enable the construction of a rigid and planar  $\pi$ -system, favoring photo-induced intramolecular charge transfer and separation from the donor to the acceptor; (ii) two cyano groups attached to quinoidal thiophene by a C-C double bond can stabilize the lowest unoccupied molecular orbital (LUMO) and lower the energy level, resulting in a relatively narrow optical band gap, which is particularly attractive for light harvesting at longer wavelengths; (iii) the quinoid sensitizer is simple in structure, and can be readily prepared using a short synthetic route.

The synthesis of **QT-1** is described in Scheme 1. Dimethyl 4,4'-((4-formylphenyl)azanediy)l)dibenzoate (**1**) was synthesized according to the previous report,<sup>12</sup> and 2-(thiophen-2-yl)malononitrile (**2**) was synthesized by the Gompper coupling reaction of 2-iodothiophene with malononitrile according to the method reported by Takahashi and Tarutani.<sup>13</sup> The compound **3** was prepared by Knoevenagel condensation reaction of **1** and **2** in acetic anhydride. Finally, the methyl ester was hydrolyzed using hydrochloric acid to afford the target compound **QT-1** (see Supporting Information).

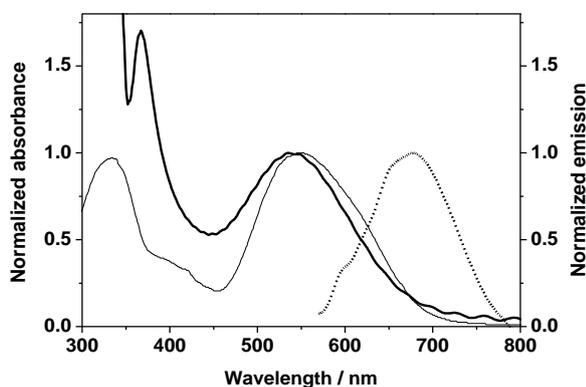


Fig. 1 Normalized absorption (solid lines) and emission (dotted lines) spectra of **QT-1** in methanol (thin lines) and adsorbed on NiO (thick lines). The absorption and emission maxima in methanol are 550 nm and 677 nm respectively, giving a zeroth-zeroth transition  $\Delta E_{0-0} = 1.98$  eV.

The UV-vis absorption and emission spectra of **QT-1** in methanol are shown in Fig. 1. The absorption spectrum has two bands with peaks at 333 and 550 nm covering the entire visible region from 300 to 750 nm. The first band comes from the donor TPA, and the second band is attributed to the  $\pi$ - $\pi^*$  electron transition and charge transfer transition from the TPA moiety to the dicyanovinyl unit.<sup>6f,14</sup> The maximum extinction coefficient is  $5.8 \times 10^4$  M<sup>-1</sup>·cm<sup>-1</sup> at 550 nm. With the dye loading on NiO film, the absorption spectrum was slightly blue-shifted, being attributed to the deprotonation of the carboxylic

group and/or the H-aggregation of the dye molecule on the semiconductor. When **QT-1** is excited within the  $\pi$ - $\pi^*$  band, luminescence can be found with a maximum at 678 nm. The large Stokes shift in methanol indicates large structural difference between ground and excited states, suggesting the possibility of the formation of the charge-transfer state, which is preferable for the hole injection from a D- $\pi$ -A type dye to a NiO valence band. The optical bandgap is 1.98 eV, estimated from the intersection of the normalized absorption and emission spectra.

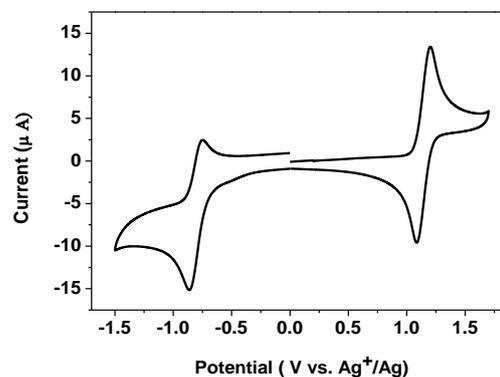


Fig. 2 Cyclic voltammograms of **QT-1** recorded in N,N-dimethylformamide (DMF) containing 0.1 M TBAPF<sub>6</sub> with scan rate of 100 mV/s.

The electrochemistry of **QT-1** was measured in N,N-dimethylformamide (DMF) solution by cyclic voltammetry (CV) as shown in Fig. 2. On the oxidation side, **QT-1** shows a reversible oxidation wave at 0.66 V vs Fc/Fc<sup>+</sup> (1290 mV vs NHE), which is assigned to the TPA moiety. On the reduction side, **QT-1** shows a reversible wave at -1.26 V vs Fc/Fc<sup>+</sup> (-630 mV vs NHE), corresponding to one-electron reduction of the dicyanomethylene unit. The energy levels of both the LUMO and HOMO are inward-shifted about 200 mV respectively in comparison with the thiophene-bridged dye reported previously,<sup>14</sup> resulting in relatively lower bandgap of 1.92 eV, in reasonable agreement with the optical band gap calculated above. The energy diagram in the p-type DSC is shown in Fig. 3. The HOMO level (1.29 eV) of **QT-1** is well below the energy level (0.54 eV) of the top of the valence band,<sup>9</sup> and the LUMO level (-0.63 eV) is above the potential of the redox I/I<sub>3</sub><sup>-</sup> system (0.40 eV). Thermodynamically, it is possible for hole transfer from the HOMO energy level of the dye to the valence band of NiO and electron transfer from the reduced dye molecule to the oxidized species (I/I<sub>3</sub><sup>-</sup>) in the electrolyte after the dye is excited by the light.

Density functional theory (DFT) calculations in Gaussian 03 at the B3LYP/6-31+G(d) level were performed for **QT-1** to study its optimized structure and electron density distribution profiles of frontier molecular orbitals. As shown in Fig. 4, the HOMO is delocalized over the entire molecular skeleton with some distribution from the anchoring groups on the TPA, and the LUMO level, on the other hand, is mainly localized on the quinoidal thiophene and cyano units with partial extension on

the adjacent phenyl group. The results indicate that light-induced excitation on **QT-1** could effectively move the electron distribution from the anchoring groups to the opposite acceptor moiety, and thus favor the interfacial electron transfer from the valence band of NiO to the anchoring groups and further to the acceptor moiety of the dye.

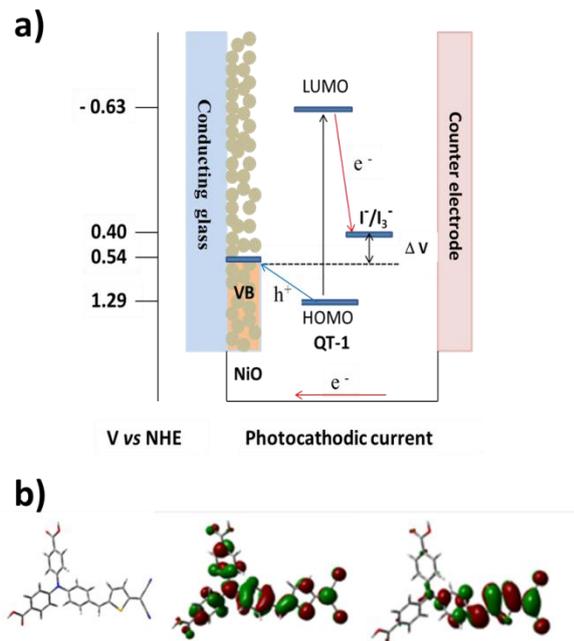


Fig. 3 (a) Schematic energy diagram for p-type DSSC based on **QT-1**; (b) The optimized structure (left) of **QT-1**, the frontier molecular orbitals of the HOMO (middle) and LUMO (right) calculated with DFT at the B3LYP/6-31+G(d) level. Cyclic voltammograms of **QT-1** recorded in N,N-dimethylformamide (DMF) containing 0.1 M TBAPF<sub>6</sub> with scan rate of 100 mV/s.

For the fabrication of p-type DSC, a nanostructured NiO film is employed as p-type-electrode for the adsorption of **QT-1**. The film was prepared on a FTO glass substrate by doctor blading method according to the previous method.<sup>4b</sup> The paste was prepared using a basic aqueous solution containing NiCl<sub>2</sub> and a polymer template. The prepared NiO electrodes (1.5 μm thick) were immersed in a 0.3 mM dye solution in ethanol overnight. The active photocathode and a Pt counter electrode were sandwiched for the p-type DSC using an I<sup>-</sup>/I<sub>3</sub><sup>-</sup> or Co<sup>2+</sup>/Co<sup>3+</sup> based liquid electrolyte. The I<sup>-</sup>/I<sub>3</sub><sup>-</sup> based electrolyte (**EL1**) is composed of 0.68 M dimethyl imidiazolium 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). In addition, the Co<sup>2+</sup>/Co<sup>3+</sup> based liquid electrolyte (**EL2**) was also used, which contains 0.1 M [Co(L)<sub>3</sub>](PF<sub>6</sub>)<sub>3</sub> and 0.1 M [Co(L)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub> in acetonitrile, where L represents 2-(1H-pyrazol-1-yl)pyridine).

**Fig. 4a** shows the *J-V* curves of the **QT-1** sensitized p-type DSCs with the I<sup>-</sup>/I<sub>3</sub><sup>-</sup> based electrolyte **EL1** and the Co<sup>2+</sup>/Co<sup>3+</sup> based electrolyte **EL2**. With **EL1**, the best device showed a *J*<sub>sc</sub> of 8.2 mA/cm<sup>2</sup>, *V*<sub>oc</sub> of 120 mV, and a fill factor (*FF*) of 0.34, resulting in an overall efficiency (*η*) of 0.33%. The *J*<sub>sc</sub> is the highest value achieved in p-type DSCs, which is essential to

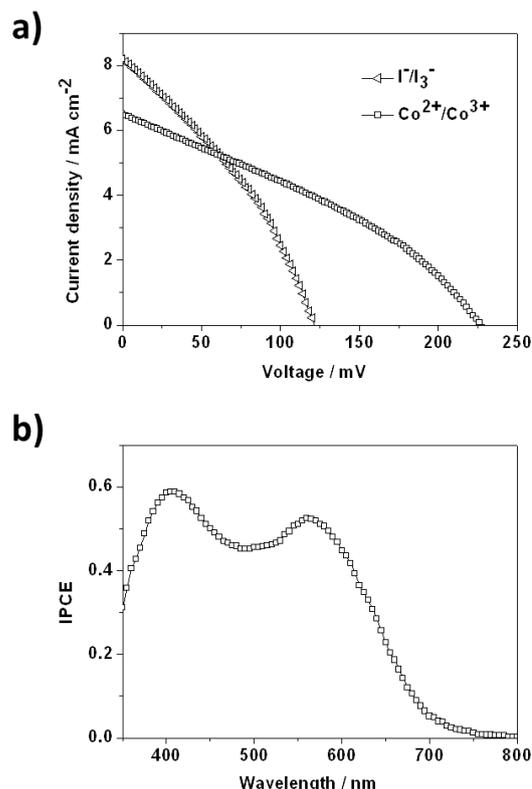


Fig. 4 (a) *J-V* curves of two **QT-1** sensitized p-type DSCs with the I<sup>-</sup>/I<sub>3</sub><sup>-</sup> based electrolyte (**EL1**) and the Co<sup>2+</sup>/Co<sup>3+</sup> based electrolyte (**EL2**) measured under AM 1.5 (100 mW cm<sup>-2</sup>) illumination. (b) IPCE spectrum of the **QT-1** sensitized p-type DSC with I<sup>-</sup>/I<sub>3</sub><sup>-</sup> based electrolyte (**EL1**).

construct high efficient np-DSCs as mentioned above. The high *J*<sub>sc</sub> is clearly ascribed to the broad light absorption of **QT-1** in the visible region as shown in **Fig. 1**. In addition, the surface coverage of **QT-1** on the NiO film was measured to be 8.5 × 10<sup>-8</sup> mol·cm<sup>-2</sup>, which is about 3 to 4 times higher than those reported with large and bulky perylene dyes.<sup>11</sup> Thus, the small molecule **QT-1** is more easy to assemble on the film with high surface coverage, which, on one hand, improve light harvesting ability and thus photocurrent, on the other hand, reduce charge recombination between the injected hole and the electrolyte. For most of p-DSCs, the charge recombination between the injected hole and the reduced dye were reported to be very fast, causing significant loss of the photocurrent. In **QT-1**, dicyanomethylene capped quinoid thiophene can stabilize the LUMO energy, and would reduce charge recombination between the reduced **QT-1** and the injected holes on NiO. With **EL2**, the best device showed a *J*<sub>sc</sub> of 6.5 mA/cm<sup>2</sup>, *V*<sub>oc</sub> of 226 mV, and a fill factor (*FF*) of 0.34, giving an overall efficiency (*η*) of 0.50%. the high *V*<sub>oc</sub> (226 mV) is due to the relatively large difference in chemical potential between the NiO photocathode and the Co<sup>2+</sup>/Co<sup>3+</sup> based electrolyte **EL2** as compared with that (120 mV) using I<sup>-</sup>/I<sub>3</sub><sup>-</sup> based electrolyte **EL1**. **Fig. 4b** shows the incident photon to electron conversion efficiency (IPCE) spectrum of the p-DSCs using **EL1**. Two peaks were observed with the values of 60% at 400 nm and

57% at 550 nm, which is among the highest reported efficiencies for p-DSCs.

In conclusion, a quinoid thiophene unit was firstly employed as a  $\pi$ -conjugated linker in a push-pull dye **QT-1** used as sensitizer for p-DSCs. The introduction of the quinoid thiophene unit greatly enhances intramolecular charge transfer in the D- $\pi$ -A system, yielding high molar absorptivity and a relatively narrow band-gap. The small molecular weight **QT-1** can be readily prepared using a short synthetic route with high yield. In the **QT-1** sensitized p-DSC, a high short-circuit photocurrent density of 8.2 mA/cm<sup>2</sup> was achieved under the standard AM 1.5 condition, which is the highest value achieved in the p-DSCs. Our results demonstrate that quinoid-based dyes would represent new and efficient organic semiconductor sensitizers used in p-DSCs and other organic optoelectronic devices.

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### Notes and references

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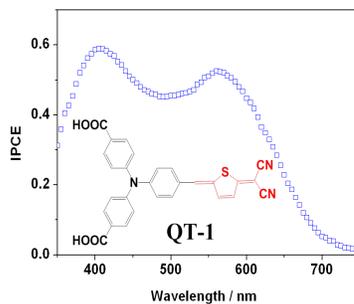
Electronic Supplementary Information (ESI) available: Experimental details and additional experimental data. See DOI: 10.1039/c000000x/

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## Entry for the Table of Contents

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A push-pull thienoquinoidal dye (**QT-1**), was synthesized as a sensitizer in a p-DSC, giving a high short-circuit photocurrent density of 8.2 mA/cm<sup>2</sup>. The result would pave a new way for the development of simple and efficient organic semiconductor sensitizers used in p-DSCs and other organic optoelectronic devices.



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