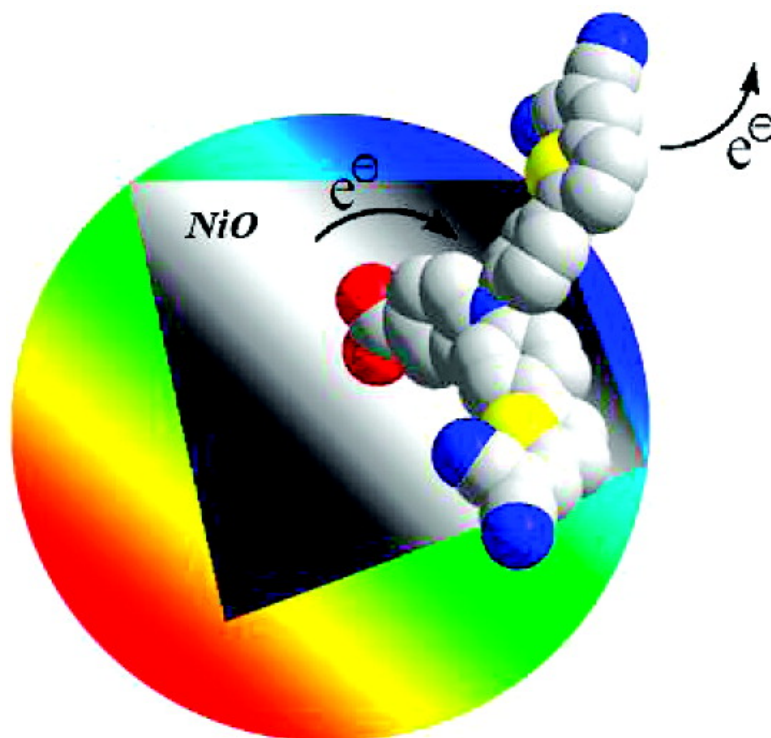## Communication

# Design of an Organic Chromophore for P-Type Dye-Sensitized Solar Cells

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# Design of an Organic Chromophore for P-Type Dye-Sensitized Solar Cells

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Dye-sensitized solar cells (DSSCs) have attracted a great deal of interest since the seminal paper of Grätzel and co-workers in 1991.[1] The majority of studies in this field are based on the sensitization of a n-type semiconductor. Normally this kind of solar cell consists of a photoactive anode and a passive cathode (n-type DSSCs). However, DSSCs in which the cathode is photoactive are also possible,[2–8] and the development of photocathodes can provide an entry to the preparation of a tandem solar cell,[7] in which both electrodes are photoactive. Until now, there have been very few studies on the sensitization of p-type semiconductors. Although attempts have been made to use some dyes as the sensitizer, their efficiencies are relatively low.[6–10]

In this paper, we report the design, synthesis, and characterization of a new organic dye, **P1**, together with its performance in a photovoltaic device based on NiO as the photocathode and a passive anode (p-type DSSCs). In **P1**, we use the triphenylamine moiety as the electron donor, malononitrile moiety as the electron acceptor, and a thiophene unit as the conjugated chain (Figure 1). The difference between **P1** and the normal organic dyes used in n-type DSSCs is that the attaching group is now on the electron donor part. By introducing two electron acceptor groups and having the anchoring group on the donor moiety, light excitation is associated with electron flow from the donor part of the dye to the acceptor part, providing an efficient electron transfer pathway from the dye to the electrolyte.

The synthesis of **P1** is conducted in four steps with moderate yields. Bromination of 4-(diphenylamino)benzaldehyde afforded 4-(bis(4-bromophenyl)amino)benzaldehyde, followed by oxidation using silver oxide as the oxidant, yielding 4-(bis(4-bromophenyl)amino)benzoic acid. The thiophene moiety was introduced by Suzuki coupling reaction and provided the intermediate 4-(bis(4-(5-formylthiophen-2-yl)phenyl)amino)benzoic acid. Finally, condensation of the aldehyde with malononitrile by the Knoevenagel reaction gave the target compound **P1** (see Supporting Information).

The p-type semiconductor, nanostructured NiO, was made by doctor-blading a $Ni(OH)_2$ gel on a fluorine-doped $SnO_2$ glass (Pilkington TEC8, sheet resistance 8 Ω/square) followed by sintering at 300 °C for 30 min. The $Ni(OH)_2$ gel was prepared using a procedure similar to that described in the literature.[11] The $Ni(OH)_2$ colloids were separated by washing with deionized water using a centrifuge, and the paste was made by dispersing $Ni(OH)_2$ colloids in EtOH with a weight concentration of ca. 20%. The prepared NiO electrodes (600 nm thick) were soaked in a 0.3 mM dye
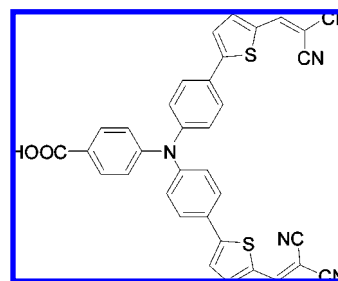


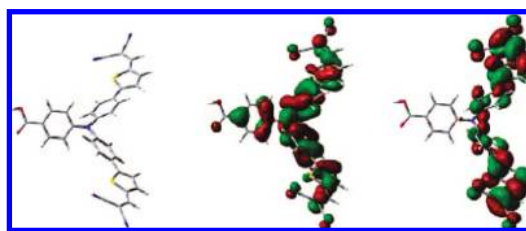**Figure 1.** The molecular structure of **P1**.



**Figure 2.** The optimized structure (left) of **P1**, the frontier molecular orbitals of the HOMO (middle) and LUMO (right) calculated with DFT at the B3LYP/6-31+G(d) level.

solution in ethanol for 16 h. The solar cells were assembled with a platinized conducting glass counter electrode using a 50 $\mu$m thick thermoplastic frame (Surlyn 1702) and had an active area of 0.32 $cm^2$. The electrolyte was composed of 0.5 M LiI and 0.1 M $I_2$ in propylene carbonate.

The UV–vis spectrum of **P1** has two absorption bands with peaks at 345 and 468 nm (Figure S1). The maximum extinction coefficient is $5.8 \times 10^4$ $M^{-1}$ $cm^{-1}$ at 468 nm. By adsorbing the dye on the NiO film, a broadening of the absorption band and a red shift of the spectrum were observed, being attributed to the coupling of the dye with the semiconductor.

Density functional theory (DFT) calculations were performed in Gaussian 03 at the B3LYP/6-31+G(d) level.[12] From the calculations, there are a multitude of excitations allowed in the UV region, while only HOMO → LUMO and the combined HOMO-1 → LUMO and HOMO → LUMO+1 are in the visible. The frontier molecular orbitals of the HOMO and LUMO included in the dominating transition ($f = 1.20$) are shown in Figure 2. The HOMO is delocalized on the full stretch of the molecule and partly localized close to the attachment group. The LUMO is mainly on the acceptor part, which is far away from the attaching group, beneficial for a p-type DSSC. The electronic redistribution between the HOMO and LUMO shows a pronounced intramolecular charge separation after excitation. A semitheoretical estimation of the maximum

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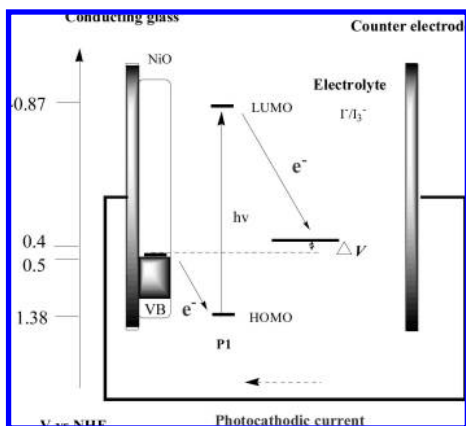§ Department of Materials Chemistry, Uppsala University.

**Figure 3.** Schematic energy diagram for p-type DSSC based on **P1**.

extinction coefficient for the visible band, taking the theoretical oscillator strengths and assuming Gaussian profiles for the transitions, gives $5.2 \times 10^4 \, M^{-1} \, cm^{-1}$ (with 0.67 eV broadening taken from the experimental full width at half-maximum of the band).

Cyclic voltammetry (CV) and square wave voltammetry (SWV) of **P1** were measured in dry MeCN (Figure S2). There were two oxidation peaks and one reduction peak. The first reversible one corresponds to the oxidation of the triphenylamine moiety, and the second one is the oxidation of the thiophene ring. The respective oxidation and reduction potentials of **P1** were 679 and −1463 mV vs Fc/Fc+ (1375 and −767 mV vs NHE). From these data, we can estimate the HOMO and LUMO energy levels of **P1** to be 1.38 and −0.87 V vs NHE, respectively. The HOMO level of **P1** is below the energy level of the top of the valence band, while the LUMO level is above the potential of the redox system ($I^-/I_3^-$) and far below the bottom of the conduction band of NiO. After the dye is excited by the light, there are two possible ways for the electron transfer (see Figure 3): (a) electron transfer from the valence band of NiO to the HOMO energy level of the dye, followed by electron transfer from the reduced dye molecule to the oxidized species ($I_3^-$) in the electrolyte, or (b) electron transfer first from the excited dye to the oxidized species in the electrolyte, followed by electron transfer from the valence band of the semiconductor to the oxidized dye. Ultrafast spectroscopy on similar systems suggests that the former mechanism is dominant.[8,9]

In comparison with previously reported p-type DSSCs, high incident photon-to-current conversion efficiency (IPCE) values were obtained. The highest value for **P1** was 18%, being, to the best of our knowledge, the highest reported IPCE efficiency for p-type DSSCs. Under the same conditions, two other dyes were examined: the coumarin dye C343[9] and N3[1] (*cis*-RuL₂-(NCS)₂, L = 2,2′-bipyidyl-4,4′-dicarboxylic acid); see Figure 4 and Table S1. N3, the state-of-the-art dye for n-type DSSCs, shows virtually no photocurrent at all. For C343, the IPCE values are significantly lower than those of **P1**. The calculated absorbed photon-to-current conversion efficiency (APCE) for **P1** was about 30%, which is a very high value for dye-sensitized NiO. Very recently, high APCE values (45%) of a dyad sensitizer was reported.[13]

Although a low photovoltage is expected for these p-type systems, due to the small difference between the quasi-Fermi level of the NiO electrode and the electrochemical potential of the $I^-/I_3^-$ redox system, we measured the current−voltage characteristics at 1000 W m$^{-2}$ under AM 1.5 irradiation. For **P1**, in these preliminary tests, the short-circuit current density was 1.52 mA cm$^{-2}$, the open-circuit voltage was 110 mV, and the fill factor was 0.31, giving an overall efficiency of 0.05%.
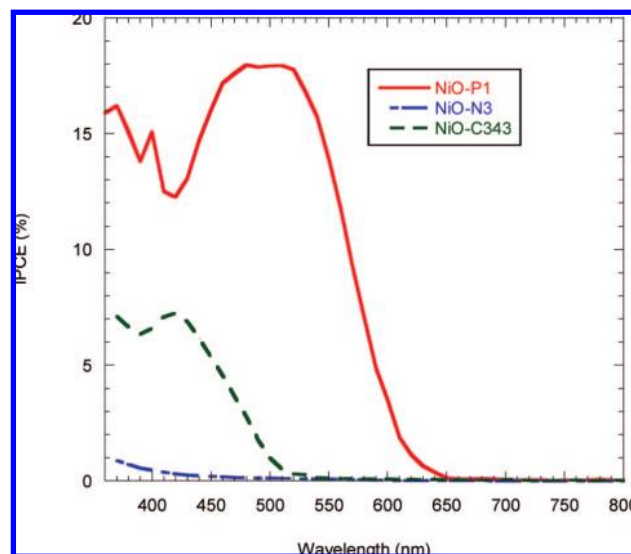


**Figure 4.** Comparison of IPCE spectra of N3, C343, and **P1** dye-sensitized NiO solar cells.

In conclusion, we have demonstrated a successful model for the design of efficient dyes for p-type DSSCs. We are now optimizing these systems by increasing the thickness of the semiconductor film (in the present study, a relatively thin film of 600 nm was used) and by optimizing the structure of the sensitizer. Furthermore, different redox couples with more negative redox potentials and alternative p-type semiconductors with more positive valence band energy levels should be developed.

**Supporting Information Available:** Synthetic procedures, characterization details for **P1**, and computed vertical excitation energies. This material is available free of charge via the Internet at http://pubs.acs.org.

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