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Novel Pyrenoimidazole-Based Organic Dyes for Dye-Sensitized Solar Cells

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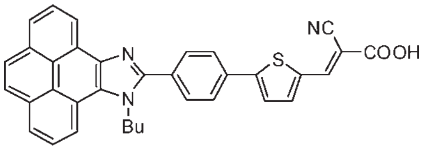
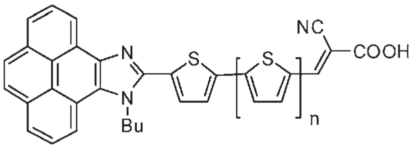
ABSTRACT



5a



5b: n = 1
5c: n = 2

A novel class of organic dyes containing pyrenoimidazole donors, cyanoacrylic acid acceptors, and oligothiophene π-linkers has been synthesized and characterized. The electro-optical properties of these dyes can be tuned by changing the conjugation length of the π-linkers. A dye containing terthiophene in the conjugation pathway exhibited a solar energy-to-electricity conversion efficiency of 5.65%.

There has been considerable interest for the synthesis and characterization of novel organic and organometallic dyes suitable for application in nanocrystalline TiO_2-based dye-sensitized solar cells (DSSCs) due to the demand for the alternative energy sources.[1] These photoelectrochemical cells were first reported by Grätzel using ruthenium complexes as sensitizers and demonstrated solar energy-to-electricity conversion efficiency up to 11% under 100 mW cm^{-2} irradiation (AM 1.5 G simulated sunlight).[2] The metal-to-ligand charge transfer (MLCT) transition present in the ruthenium complex plays an important role in the light-harvesting process. Similarly, the organic dyes derived with a donor-π-acceptor architecture show charge migration from the donor to the acceptor through the π-bridge. The charge transfer transition of the organic dyes generally exhibits a higher molar extinction coefficient in the visible region than the MLCT transition of the ruthenium complexes. Also, the position and intensity of the charge transfer transition in organic dyes can be tuned by simple structural modifications such as variation of donor strength and nature of the conjugation pathway.[3] Due to these advantages, many chromophores such as coumarin, indoline, cyanine, hemicyanine, merocyanine, perylene, xanthene, triarylamine, oligothiophene, thienothiophene, indolothiophene, benzothiadiazole, and imidazole have been used for the development of organic dyes suitable for DSSCs.[4]

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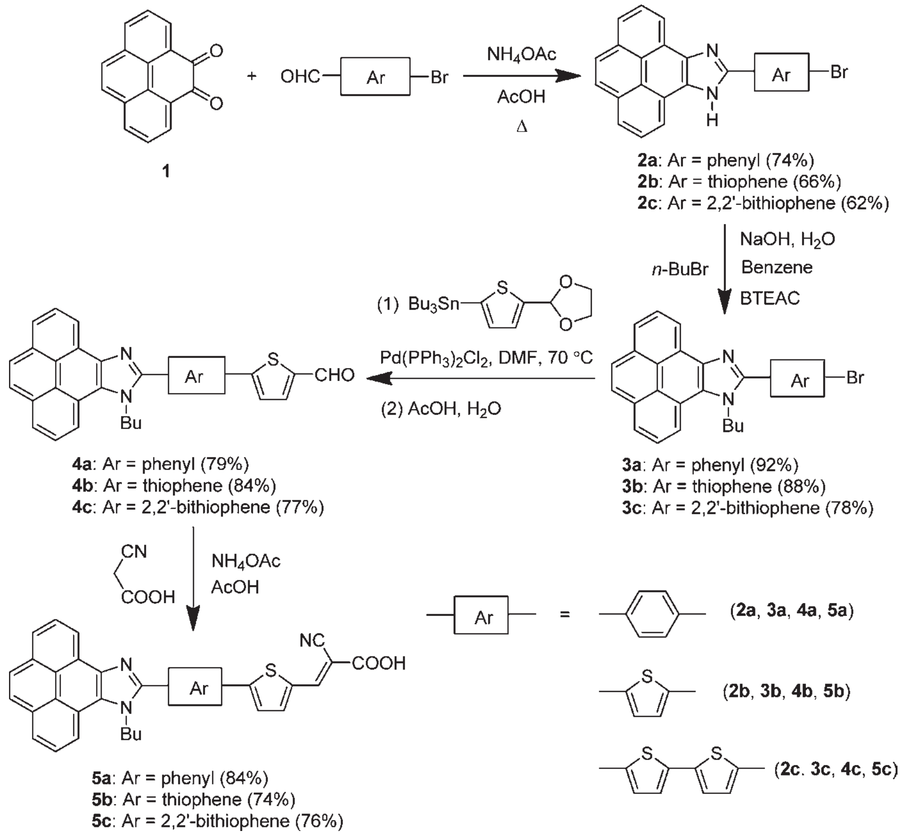
Scheme 1. Synthetic Sequence Employed to Obtain the Dyes **5a**−**c**



Recombination of electrons injected to the conduction band of TiO_2 with the oxidized dyes or electrolyte constituents (I_3^-) were identified as detrimental for the overall efficiency of the DSSCs.[5] To retard these side processes, selected chromophores were incorporated in the structure of the organic dyes. The probability of the recombination of the ejected electron back with the oxidized dye may be diminished by the addition of groups that are capable of dissipating the positive charge via electronic delocalization. The direct recombination of injected electrons with the I_3^- may be reduced by the inclusion of hydrophobic substituents.[6] Triarylamines or fused amine segments were invariably used in most of the organic dyes to achieve a push−pull structure and resonance stabilization of oxidized dyes.[7] Triarylamine-free organic dyes suitable for DSSC are scarce and often lead to inferior performance.[8,9] In this communication, we report three new dyes **5a**−**c** containing pyrenoimidazole donors and cyanoacrylic acid acceptors. They are linked via a π-bridge constituted by oligothiophene. It is hypothesized that on oxidation the cation radical generated at either imidazole and/or the oligothiophene segment will be resonance stabilized by the pyrene moiety and will disfavor the back electron transfer. In an earlier work, imidazole unit has been demonstrated as a two-way π-linker for the triarylamine donors and cyanoacrylic acid acceptor.[9] They have observed that triarylamine donors are mandatory to obtain decent efficiency from the DSSCs. In this work, we demonstrate that due to the enhanced donor ability of pyrenoimidazole and oligothiophene linker the electro-optical properties show significant improvements which manifests in the overall efficiency for the DSSCs.

The pyrenoimidazole-based organic dyes were conveniently obtained from pyrenodione in four steps involving imidazole construction with a suitable aldehyde, phase-transfer catalyzed *N*-alkylation, Stille coupling[10] reaction followed by acid hydrolysis to liberate the aldehyde and Knoevenagel condensation[11] with cyanoacetic acid as illustrated in Scheme 1.

The absorption and electrochemical properties of the dyes are presented in Table 1. Figure 1 shows the absorption

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Table 1. Electro-Optical Properties of the Pyrenoimidazole Based Dyes

	λ_{abs}, nm (ε, $\times 10^3$ M^{-1} cm^{-1})						
dye	thf	dmf	TiO$_2$	λ_{em}, nm	E$_{ox}$, V^a	E$_{ox}$*, eV^b	HOMO/LUMO, eV^c
5a	405 (31.7), 354 (31.3), 289 (48.8)	389 (35.7), 364 (37.3), 290 (29.9)	485	597	0.80	−0.97	5.60/3.06
5b	452 (32.4), 384 (18.7), 354 (23.5), 287 (30.5)	423 (35.5), 380 (24.6), 289 (25.9)	544	626	0.63	−0.83	5.43/3.20
5c	464 (44.9), 358 (24.2), 290 (31.7)	442 (45.1), 357 (20.5), 290 (27.9)	580	624	0.54	−0.87	5.34/3.16

[a] Oxidation potentials with reference to the ferrocene which was used as an internal standard. [b] Computed from the formula $E_{ox}* = E_{ox} - E_{0-0}$ where the band gap was derived from the optical edge [c] From HOMO $= 4.8 + E_{ox}$ and LUMO $=$ HOMO $- E_{0-0}$ where E_{0-0} was estimated from optical edge.

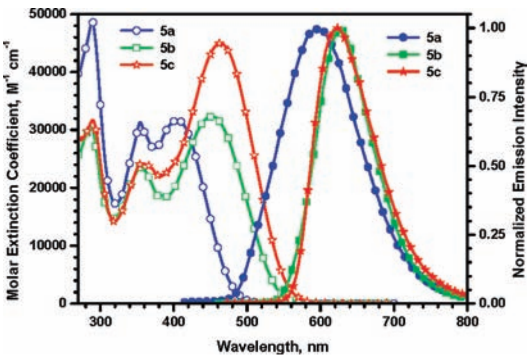

Figure 1. Absorption and emission spectra of the dyes **5a**−**c** recorded in tetrahydrofuran.

spectra of the dyes recorded in THF solutions. All the dyes possess three absorption peaks at around 280, 350 and >400 nm. The two bands in the ultraviolet region are present in all the dyes and are probably originating from the electronic transitions localized within the pyrenoimidazole segment. The third absorption occurring in the visible region is sensitive to the nature of the conjugation pathway and red-shifts on progressive addition of thiophene units.[12] The dye **5c** bearing terthiophene as linker shows a significant red-shift and enhancement in extinction coefficient in the longer-wavelength band when compared with that of the dyes **5a** and **5b**. Also, the peak position of the charge transfer transition for **5a** is much shorter when compared with the other two dyes, probably due to the electron-deficiency of the benzene linker relative to the thiophene unit.[13] All the dyes when adsorbed on TiO$_2$ exhibits red-shifted absorption profile (Figure S5, SI) in comparison to that measured in solution. The red-shifted absorption may be attributed to the intermolecular interactions at the TiO$_2$ surface which is likely to happen due to the planar pyrenoimidazole π-system or to the thicker TiO$_2$ layer.[14] This is contrary to the blue-shift observed for most the organic dyes generally originating from the dye-TiO$_2$ interaction leading to a partial deprotonation of the carboxylic acid unit.[15] However, in more basic solvents such as dimethyl formamide and in the presence of triethylamine they showed a slight blue-shift for the charge transfer transition (Figures S1−S4, SI) typical of the presence of deprotonated species.

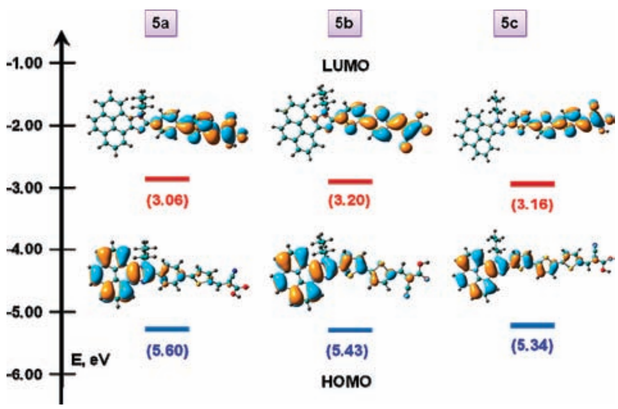

Figure 2. Computed orbital energies (observed solution data shown in parentheses) and electronic distribution in the dyes.

To get further insight into the molecular structure and electron distribution of dyes, the geometries of the dyes were optimized by density functional theory (DFT) calculations at the B3LYP/6-31G (d, p) level. Figure 2 shows the relative energies and electron distributions of the HOMO and LUMO of the dyes **5a**−**c**. The HOMO is delocalized over the pyrenoimidazole π system with the highest electron density located at the two nitrogen atoms of the imidazole moiety, while the LUMO is located in the anchoring group through the π bridge constituted by the benzene and/or thiophene moieties. Thus, the HOMO−LUMO excitation induced by light irradiation could move the electron distribution from the pyrenoimidazole segment to the anchoring unit through the conjugation pathway.

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Table 2. Performance Parameters of the DSSCs Fabricated Using the Dyes[a]

dye	J_{SC}, mA cm^{-2}	V_{OC}, mV	*ff*	η, %	τ_e, ms[b]
5a	8.8	545	0.71	3.41	2.55
5b	11.4	524	0.63	3.75	1.41
5c	15.5	543	0.67	5.65	3.80
N719	18.6	665	0.70	8.62	1.48

[a] Measured under irradiation of 100 mW cm^{-2} (AM 1.5 G simulated sunlight) at room temperature. [b] Estimated with the aid of electrochemical impedance spectroscopy (EIS) measurements.

The oxidation potentials of the dyes fall in the range of 1.31 (**5c**) and 1.57 (**5a**) vs NHE and are more positive than the oxidation potential of the I^-/I_3^- redox couple (0.4 V vs NHE).[16] This indicates the existence of fair driving force for the regeneration of the oxidized dye by the I^- ions. The excited state oxidation potentials of the dyes are more negative (−0.83 to −0.97 V vs NHE) than the conduction band of TiO_2, which ensures facile electron injection from the dyes into the conduction band of TiO_2.

The performances of the DSSCs fabricated using these dyes are presented in Table 2 and the I−V curves plotted in Figure 3. The terthiophene bridged dye, **5c** showed promising efficiency of 5.65% when compared to the dyes containing bithiophene (**5b**) and phenylthiophene (**5a**) linkers. The higher efficiency observed for **5c** mainly originates due to the relatively larger short-circuit photocurrent density which is consistent with the intense red-shifted charge transfer transition realized for this dye.[17] For the dye **5c**, highest IPCE (~85%) was observed from 420 to 500 nm while the dyes **5a** and **5b** gave moderate IPCE response (Figure S6, SI) in line with the trend in molar extinction coefficients of these dyes (Figure 1). The lower open-circuit photovoltage of **5b** is attributed to the relatively shorter recombination time estimated for this device from electrochemical impedance measurements (Figures S7 and S8, SI).

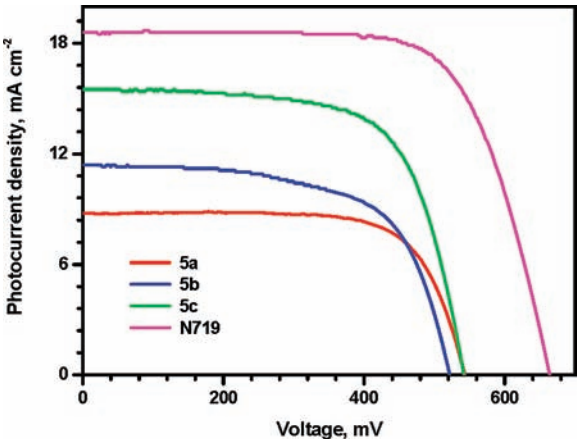

Figure 3. I−V characteristics of the DSSCs fabricated using the dyes.

In summary, we have developed new pyrenoimidazole-based organic dyes yielding up to 5.65% power conversion efficiency in a conventional DSSC. The promising performance of these dyes as sensitizers is intriguing as they do not possess triarylamine-based donors. Our studies open avenues for the development of organic dyes featuring polyaromatic fused heterocycles as electron donors. By appropriate structural modifications, electron-rich polyaromatic fused heterocycles can be developed, which may serve as an efficient donor.

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Supporting Information Available. Experimental details, characterization data of the compounds, copies of ^{1}H, and ^{13}C NMR spectra for new compounds, and the Cartesian coordinates of the optimized structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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