

Research Article

***N*-Aryl Arenedicarboximides as Tunable Panchromatic Dyes for Molecular Solar Cells**

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Three organic dyes designed as molecular dyads were prepared that feature a common naphthalimide acceptor and *N*-aryl donors. One of these incorporated an additional cyanoacrylic acid linker and conjugated thiophene bridge inserted between donor and acceptor groups. Electrochemical and photochemical characterizations have been carried out on nanocrystalline TiO₂ dye-sensitized solar cells which were fabricated with these dyes as the sensitizing component. HOMO and LUMO energies were also calculated using TDDFT methods and validated by the cyclic voltammetry method. A key finding from this study indicates that computational methods can provide energy values in close agreement to experimental for the *N*-aryl-naphthalimide system. Relative to HOMO/LUMO energy levels of **N719**, the dyes based on naphthalimide chromophore are promising candidates for metal-free DSSCs.

1. Introduction

Among the PV technologies, dye-sensitized solar cells (DSSCs) represent a promising one because of both their high performance as unconventional solar cells and possibility for low-cost production. Studies into such devices have been given added impetus by concerns that the high capital cost and long energy payback times of photovoltaic cells based upon crystalline silicon may limit the practicality of PV for large-scale renewable energy production [1–7]. As one of the most important components for harvesting the solar radiation and converting it to electric current, the sensitizers are currently attracting considerable research interests [8–15]. So far, the most successful charge transfer sensitizers employed are ruthenium polypyridyl complexes, yielding 9–11% solar-to-electric power conversion efficiencies under AM 1.5 [16–18]. Although the metal-complex dyes exhibited high efficiency and stability, they are quite expensive and hard to purify compared to the metal-free organic dyes [19–24]. Several groups are investigating metal-free organic dyes because of their lower cost, wide variety of structures, easy modification, and high molar absorptivity [25–28].

Nevertheless, many organic dyes have often presented low conversion efficiency and low operation stability compared to metal complexed dyes. Two major factors contribute to the low conversion efficiency of many organic dyes in the DSSCs: (1) formation of dye aggregates on the semiconductor surface; (2) formation of unstable radical species during redox reaction cycles is responsible for the low stability of many organic dyes [1, 19, 20]. To achieve a higher sunlight conversion efficiency, it is a basic requirement that short-circuit photocurrent (I_{sc}) and open-circuit potential (V_{oc}) of solar cells have to be optimized. Therefore, for optimal V_{oc} , it is critical that the sensitizer dye is of a higher conduction band than that of TiO₂ [29, 30]. Then, the injection of electrons from the sensitizer conduction band to that of TiO₂ leads to efficient charge separation, thus minimizing the electron-hole recombination.

By noticing these concerns, a key design concept that has been recently discovered is the use of donor/acceptor systems that promote the asymmetric induction of electrons resulting from photoexcited states toward the titanium oxide surface for enhanced PV efficiency [31]. Naphthalimide (N.I.) has long been treated as useful fluorescent

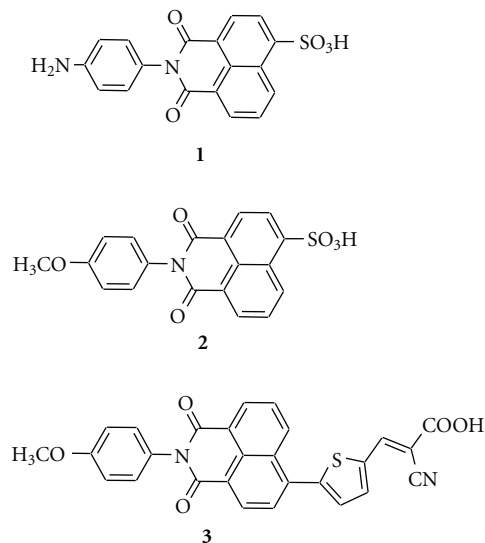


FIGURE 1: Structures of chromophores of 1–3.

labels for biomolecular investigation [32–36]. Until very recent, the photoinduced electron transfers of a series of triphenylamine-naphthalimide dyads have been studied [31]. Arenedicarboximides such as pyromellitic anhydride and 1,4,5,8-naphthalene tetracarboxylic diimide show relatively good affinity for electrons, $E_{\text{red}} = -0.55$ V and -0.695 V, respectively [37]. These electron reduction values are only slightly lower than that of the well-know electron acceptor benzoquinone ($E_{\text{red}} = -0.51$ V) [38]. By comparison, naphthalene monoimides are better electron donors than their tetracarboxylic derivatives, such as the case of 1,8-naphthalenedicarboxylic imide, at -1.31 V [39]. Hattori et al. recently reported BODIPY dyes for DSSC applications with E_{red} values of -1.11 V [40], while for N-[(3- and 4-Diarylamino) phenyl]-1,8-Naphthalimide Dyads, the E_{red} values are more negative, between the range of -1.7 V and -1.8 V [31]. This redox potential falls within the preferred voltage required for efficient electron transfer from dye to metal oxide, because it is lower than that of the conduction band of TiO_2 at -0.5 V. Our aim in the design and synthesis of new DSSCs is to promote the donor/acceptor features of the sensitizer dye and consequently enhancing asymmetric induction of electron injection by employing arenedicarboximides as molecular dyads for increased PV response. Based on our previous work with the arenedicarboximides, novel design approaches are proposed that investigate this unexplored class of dyes as a promising set of fluorophores for DSSCs applications.

In this paper, we report three novel organic dyes with structures shown in Figure 1: (1) containing naphthalimide ring as electron acceptor and methoxyphenyl moiety as electron donor connected to each other without linker; (2) containing naphthalimide ring as electron acceptor and aminophenyl moiety as electron donor connected to each other without linker; (3) containing naphthalimide ring as the electron donor and cyanoacrylic acid as the electron acceptor bridged by a thiophene unit to form a more

conjugated system with higher stability. Photochemical, electrochemical characterizations, UV-vis spectra as well as fluorescence spectra have been carried out upon these dyes. Dyes 1 and 2 were anchored to TiO_2 in a less common way, specifically through a sulfate group. To gain an insight into the nature of the excited states of N.I dyes, we performed TDDFT calculations on our models.

2. Experimental

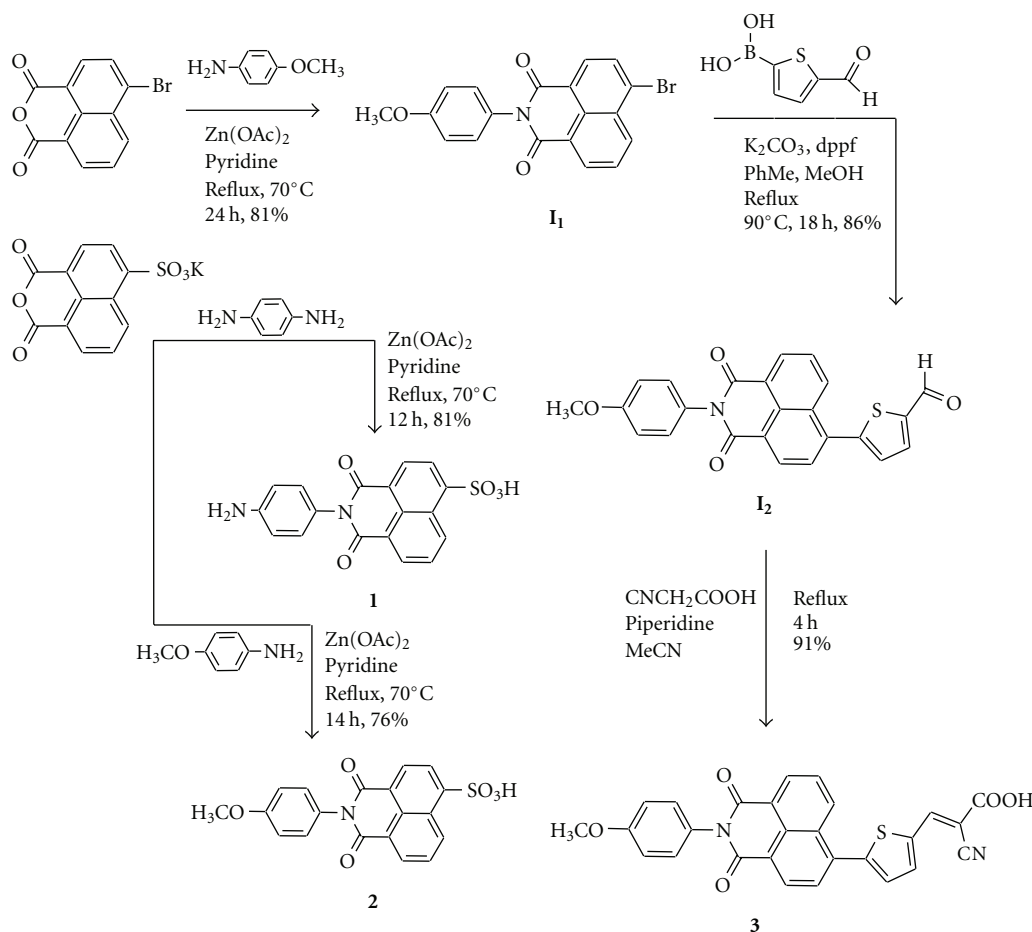
2.1. Materials. 4-Sulfo-1,8-naphthalic anhydride, 4-bromo-1,8-naphthalic anhydride, *p*-anisidine, *p*-phenylenediamine, and 5-formyl-2-thiopheneboronic acid were purchased from Aldrich. All solvents were of spectroscopic grade and used without further purification.

2.2. Materials Characterization. The UV-Vis absorption spectra of synthesized dyes 1–3 were recorded in a Cary 50 spectrophotometer. Concentrations were arranged to 2×10^{-5} molar in order to avoid aggregation or reabsorption effects for absorption measurements. Cyclic voltammetry measurements of the putative dyes were taken by using a Gamry Instrument 600 model Potentiostat.

2.3. Synthesis and Characterization of Dyes 1–3. The synthetic route to sensitizers 1–3 is provided in Scheme 1. Linker free sensitizers 1 and 2 were synthesized through simple imide coupling reaction based on 4-sulfo-1,8-naphthalic anhydride. Reaction of 4-sulfo-1,8-naphthalic anhydride with 1,4-phenylenediamine offered dye 1, while dye 2 was generated by a similar reaction when it reacted with *p*-anisidine. Dye 3 initially required 4-bromo-1,8-naphthalic anhydride and *p*-anisidine to form the arene imide intermediate I_1 . This substrate was then treated to Suzuki coupling conditions with unprotected 5-formyl-2-thiophene-boronic acid to yield the precursor aldehyde I_2 . Condensation of this aldehyde with cyanoacetic acid by the Knoevenagel reaction in the presence of piperidine offered the final sensitizer 3 with thiophene linker [8–10, 13, 19, 20, 22, 27].

4-Sulfo-N-(4'-aminophenyl)-1,8-naphthalimide (1). 1 mmol (316 mgs) of the 4-sulfo-1,8-naphthalic anhydride, potassium salt was combined with 1.1 mmol (118.9 mg) of the 1,4-phenylenediamine. The reactants were heated in 4 mL pyridine for a period of 12 hr in the presence of 0.027 mmol (5 mg) zinc acetate at 70°C . Pyridine was removed in the fume hood via stream of air, and the residue was filtered using a plug of silica gel with 2 : 8 ethyl acetate and hexane mixture. Recrystallization from ethanol solution offered a purple powder (yield 78%) m.p. $269\text{--}272^\circ\text{C}$ (Lit. [41–43] m.p. $269\text{--}272^\circ\text{C}$).

^1H NMR ($\text{DMSO}-d_6$): δ 9.35 (d, $J = 8.6$ Hz, 1H), 8.48 (dd, $J = 8.0$ Hz, 2H), 8.26 (d, $J = 7.4$ Hz, 1H), 7.93 (t, $J = 7.4$, 1H), 7.48 (d, $J = 8.8$ Hz, 2H), 7.38 (d, $J = 8.6$ Hz, 2H); ^{13}C NMR ($\text{DMSO}-d_6$): δ 164.4, 164.3, 150.9, 135.1, 135.0, 131.1, 131.0, 130.8, 130.7, 129.2, 128.5, 127.3, 125.6, 123.7, 123.0, 122.8; IR (cm^{-1}): $\nu = 1161, 1514, 1242, 1167, 1032, 751, 657$.



SCHEME 1: Synthesis of three chromophores.

4-Sulfo-N-(4'-methoxyphenyl)-1,8-naphthalimide (2). 1 mmol (316 mg) of the 4-sulfo-1,8-naphthalic anhydride, potassium salt was combined with 1.1 mmol (135.5 mg) of the *p*-anisidine. The reactants were heated in 4 mL pyridine for a period of 12 hr in the presence of 0.027 mmol (5 mg) zinc acetate at 70°C. Pyridine was removed in the fume hood via stream of air, and the residue was filtered using a plug of silica gel with 2:8 ethyl acetate and hexane mixture. Recrystallization from ethanol solution afforded a tan powder (yield 76%), mp 288–290°C (Lit. [41–43] mp 288–290°C).

$^1\text{H NMR}$ (DMSO- d_6): δ 9.31 (d, J = 8.9 Hz, 1H), 8.48 (dd, J = 8.0 Hz, 2H), 8.26 (d, J = 6.9 Hz, 1H), 7.90 (t, J = 7.4 Hz, 1H), 7.31 (d, J = 14 Hz, 2H), 7.07 (d, J = 14 Hz, 2H), 3.83 (s, 3H); $^{13}\text{C NMR}$ (DMSO- d_6): δ 164.6, 164.1, 159.5, 150.5, 134.8, 131.0, 130.7, 129.1, 129.0, 128.2, 127.3, 125.6, 123.9, 123.1, 115.6, 115.0, 114.6, 56.0; IR (cm^{-1}): ν = 1658, 1514, 1243, 1262, 1196, 1070, 1032, 785, 754.

4-Bromo-N-(4'-methoxyphenyl)-1,8-naphthalimide (I₁).

1 mmol (277 mg) of the 4-bromo-1,8-naphthalic anhydride was dissolved in 15 mL pyridine and treated with 1.1 mmol (135.5 mg) *p*-Anisidine. The reactants were heated in pyridine for a period of 24 hr in the presence of zinc

acetate at 70°C. Pyridine was removed in the fume hood via stream of air, and the residue was filtered by silica gel chromatography using 1:9 ethyl acetate and hexane mixture. Recrystallization from ethanol solution afforded a tan powder (yield 81%).

$^1\text{H NMR}$ (DMSO- d_6): δ 8.68 (d, J = 8.6 Hz, 1H), 8.60 (d, J = 8.6 Hz, 1H), 8.44 (d, J = 7.4 Hz, 1H), 8.06 (d, J = 7.4, 1H), 7.87 (t, J = 8.8 Hz, 1H), 7.24 (d, J = 8.6 Hz, 2H), 7.05 (d, J = 8.6 Hz, 2H), 3.83 (s, 3H); $^{13}\text{C NMR}$ (DMSO- d_6): δ 164.1, 159.7, 133.7, 132.5, 131.7, 131.3, 130.9, 130.7, 129.6, 128.3, 127.6, 123.4, 122.5, 114.9, 55.6; m.p. 281°C; HRMS for $\text{C}_{19}\text{H}_{13}\text{NBrO}_3$: expected m/z , 382.0079. Found: m/z , 382.0083.

5-[4'-(Methoxyphenyl)-1,8-naphthoyl]thiophene-2-carbaldehyde (I₂). 0.617 mmol (235.7 mg) of the 4-bromo-N-(4'-methoxyphenyl)-1,8-naphthalimide (I₁) and PdCl₂ (dppf) (51 mg, 0.06 mmol) dissolved in 10 mL dry toluene was added to a solution of 5-formylthiophene-2-yl-2-boronic acid (192 mg, 1.23 mmol) and K₂CO₃ (426 mg, 3.10 mmol) in 10 mL dry methanol. The mixture was refluxed at 90°C for 18 hr. The residue was extracted with ethyl acetate (3 × 30 mL), dried over anhydrous Na₂SO₄, and further filtered by silica gel chromatography with 1:9 ethyl acetate

and hexane mixture. Recrystallization from ethanol solution offered a brown powder (yield 86%).

^1H NMR (DMSO- d_6): δ 10.02 (s, 1H), 8.71 (d, J = 7.4 Hz, 1H), 8.68 (d, J = 7.4 Hz, 1H), 8.58 (d, J = 7.4, 1H), 7.92–7.86 (m, J = 8.8 Hz, 2H), 7.47 (d, J = 8.6 Hz, 1H), 7.26 (d, J = 8.6 Hz, 2H), 7.09 (d, J = 8.6 Hz, 2H), 3.83 (s, 3H); ^{13}C NMR (DMSO- d_6): δ 182.9, 163.9, 163.8, 159.8, 149.3, 145.2, 137.8, 136.5, 132.2, 131.9, 131.0, 130.0, 129.6, 129.2, 129.1, 128.0, 127.7, 123.5, 114.9, 55.6; m.p. 290°C; HRMS for $\text{C}_{24}\text{H}_{16}\text{SNO}_4$: expected m/z , 414.0800. Found: m/z , 414.0801.

5-[4'-(Methoxyphenyl)-1,8-naphthoyl]thiophene-2-cyanoacrylic Acid (3). A 5 mL acetonitrile solution of the 5-[4'-(methoxyphenyl)-1,8-naphthoyl]thiophene-2-carbaldehyde (I_2) (86.4 mg, 0.18 mmol), cyanoacetic acid (30 mg, 0.4 mmol), and piperidine (1.7 mg, 0.02 mmol) was heated to reflux temperature for 4 h under nitrogen atmosphere. Residue was extracted by petroleum ether and aq HCl (0.1 M) and further recrystallized in ethanol solution, offering a dark red powder (yield 91%).

^1H NMR (DMSO- d_6): δ 8.71 (d, J = 8.6 Hz, 1H), 8.56 (m, J = 8.6 Hz, 2H), 8.14 (s, 1H), 8.03 (m, J = 7.4 Hz, 2H), 7.89 (d, J = 7.4, 1H), 7.65 (d, J = 8.8 Hz, 1H), 7.34 (d, J = 8.6 Hz, 2H), 7.08 (d, J = 8.6 Hz, 2H), 3.83 (s, 3H); ^{13}C NMR (DMSO- d_6): δ 164.4, 164.2, 163.5, 159.6, 143.8, 140.2, 139.8, 137.6, 135.8, 131.8, 131.4, 130.9, 130.8, 130.6, 129.5, 129.4, 128.8, 128.7, 127.5, 127.3, 119.8, 114.7, 79.6, 56.0; m.p. 308°C; HRMS for $\text{C}_{27}\text{H}_{16}\text{SN}_2\text{O}_5$: expected m/z , 480.1480. Found: m/z , 480.1478.

3. Results and Discussion

3.1. UV-Vis Absorption Spectra. The UV-Vis absorption spectra of all three compounds as well as **N719** in dilute solution of ethanol are shown in Figure 2. Compounds 1 and 2 both exhibit two major bands at 350 and 450 nm, which are due to the localized aromatic π - π^* transitions. Similar phenomenon was observed on **N719** which presents the first absorption band at 380 nm and followed absorption band at 518 nm. Introduction of a thiophene into the organic framework expanded the conjugation resulting in a wide absorption in the visible region; compound 3 exhibits extended broad red-shifted absorption peaks at 439 nm and 672 nm, respectively. The short wave absorption band corresponds to the π - π^* transition and the long wave band to an intramolecular charge-transfer (ICT) transition between the aryl donor group and the N.I. acceptor block. The broad absorption and red shift of absorption maximum in the visible region is desirable for light harvesting for solar energy.

Compounds 1–3 have been analyzed by cyclic voltammetry in DMF in the presence of tetrabutylammonium hexafluorophosphate 0.10 M as supporting electrolyte. The examined stable reduction potentials of all three dyes as well as the lowest unoccupied molecular orbital (LUMO) energies are listed in Table 1. According to Gillman's method [45], there is a quantitative relationship between reduction potential E_{red} and E_{LUMO} , $E_{\text{LUMO}} = -4.42 - E_{\text{Red}}$

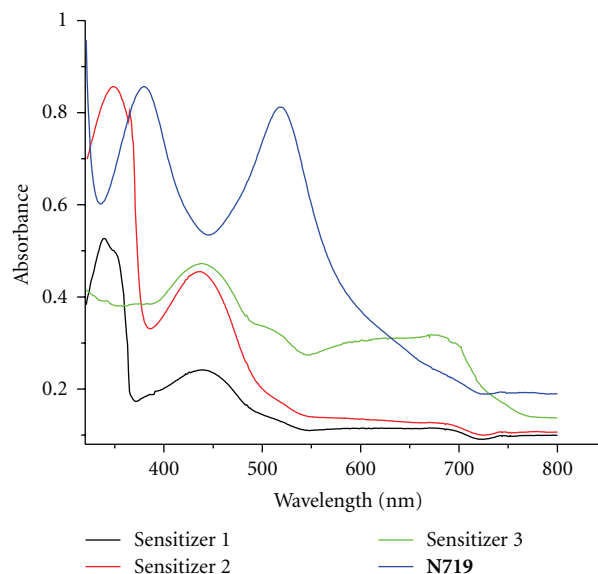


FIGURE 2: Absorption spectra of dyes 1, 2, and 3 in ($\text{C}_2\text{H}_5\text{OH} = 1 \times 10^{-5} \text{ M}$).

(V, versus Ag/AgCl). It becomes evident that the excited state energy levels are much higher than the conduction band of TiO_2 (-4.3 eV), indicating that the electron injection process from the excited sensitizer to TiO_2 conduction band is energetically favorable. Any dye with a LUMO energy level below the conduction band edge of TiO_2 would be incompatible for electron transfer and thus may not be useful for solar energy conversion.

3.2. Computational Study. Equilibrium structures for the three dyes have been calculated by using density functional theory (DFT) at B3LYP/6–21 level. The lowest excited states were computed on time-dependent DFT (TDDFT) at same level. All calculations were performed with Gaussian 03 software [46]. In each case, the ground state geometries of the phenyl plane and naphthalene ring are almost perpendicular to each other. The TDDFT calculations indicate that in all three dyes the lowest excitation is a charge-transfer transition of predominantly π - π^* character. Calculated HOMO and LUMO orbitals of the three dyes are listed in Figure 3. For dye 1, the HOMO orbital is of π -character and is delocalized over the amino phenyl group, whereas the HOMO orbital in dye 2 also shows that a π -character is delocalized over the methoxyl phenyl group. In the LUMO orbital, which has π^* -character, there is essentially no contribution from the amino phenyl/methoxyl phenyl group, and the electron density has been shifted toward the naphthalene end of the molecule. This indicates that the dipole moment should be considerably larger in the first excited state in comparison with the ground state [8, 10]. Electron density for the lowest unoccupied molecular orbital of all three sensitizers is localized near the anchoring groups (sulfo- for sensitizers 1 and 2, carboxylic for sensitizer 3) and above the conduction band edge of TiO_2 electrode. Furthermore, the HOMO energies of three dyes lie below the level of the redox

TABLE 1: UV-Vis absorption data (in ethanol) and cyclic voltammetry data (in 0.1 M Bu₄NPF₆/DMF, scan rate 100 mVs⁻¹, reference electrode Ag/AgCl) from compounds 1–3.

Dye	λ π - π^* (nm)	λ ICT (nm)	ϵ M ⁻¹ cm ⁻¹	$E_{\max}\lambda_{\max}$ (V)	E_{red} (V)	E_{HOMO} (V)	E_{LUMO} (V)
1	350/450	—	28,500/10,600	2.76	-0.83	-6.35	-3.59 ^a
2	350/450	—	42,700/21,250	2.76	-0.75	-6.43	-3.67 ^a
3	450	672	22,350/18,750	2.82	-1.23	-6.01	-3.19 ^a

^aaccording to Gillman's method [45]: $-E_{\text{LUMO}} = -4.42 - E_{\text{Red}}$ (V, versus Ag/AgCl), $E_{\max} = 1240/\lambda_{\max(\text{nm})}$ $E_{\text{HOMO}} = E_{\text{LUMO}} - E_{\max}$.

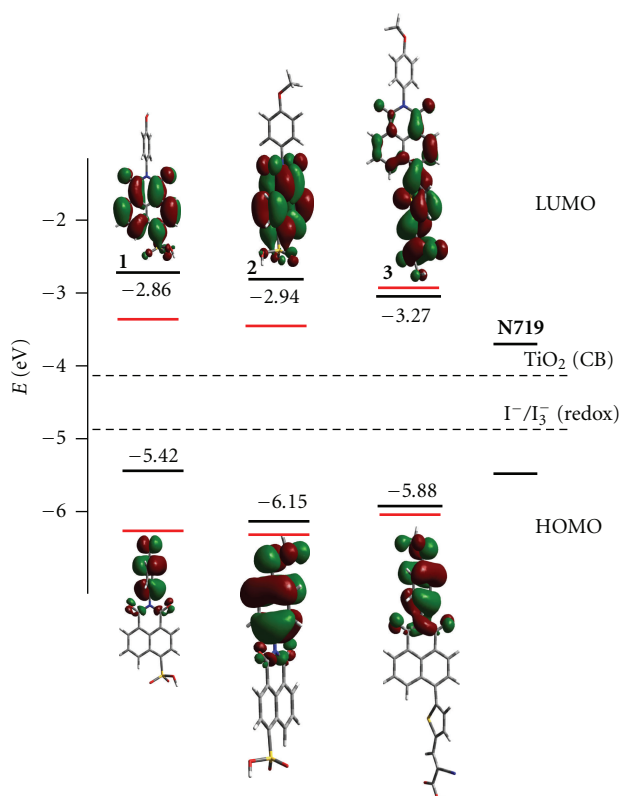


FIGURE 3: Energy diagram of TDDFT calculation indicates HOMO and LUMO orbitals of three sensitizers, adapted from [44].

mediator indicates that regeneration of the oxidized dyes is favorable.

3.3. Comparison between UV-Vis/Cyclic Voltammetry Analysis and Computational Study. As indicated in Figure 3, energies obtained by TDDFT calculations are marked in black, whereas comparison energies marked in red are taken from the data of Table 1. An important distinction should be made in that the computational parameters for TDDFT were carried out in gas phase. Despite this critical difference in surrounding matrix, all three dyes show similar trends between experimental values versus computational; agreement between these two approaches to HOMO/LUMO energy levels are best found in dye 3. We attribute the disparities in values for dyes 1 and 2 to the ionic sulfogroup attached to the naphthalimide ring. These charged groups involving sulfonate anion and potassium cation proved difficult to minimize in both geometry optimization mode for Gaussian

03 as well as molecular orbital calculations. Dye 3 proved to be easier to minimize without any charges present but rather with the carboxylic acid in the protonated form. Aside from the discrepancy observed between experimentally obtained HOMO/LUMO values and computational values for 1 and 2, the larger dye system 3 provided the best agreement.

4. Conclusion

This paper has demonstrated that, by virtue of their HOMO/LUMO energy values along with their optical molar absorptivities, the three organic dyes containing naphthalimide moiety are promising dyes for future DSSCs applications. Sensitizers 1 and 2 were synthesized in one step via straightforward imide coupling reactions and readily applied for solar cells study. As these dyes were obtained from readily available and inexpensive starting materials, they show promise as potential core structures for solar cell applications. By extending the thiophene linker to naphthalimide, a large red shift was observed on absorption spectra of sensitizer 3, indicating a capability for an increased light-harvesting ability. HOMO and LUMO energies were also calculated using TDDFT methods and validated by the cyclic voltammetry method. A key finding from this study indicates that computational methods can provide energy values in close agreement to experimental for the *N*-aryl-naphthalimide system. The values obtained were at appropriate energies for sensitizing the conduction band of TiO₂ as well as for regeneration of the ground state dye with respect to the KI/KI₃ redox couple. We believe that these findings point to an important use of computational studies of dyes *a priori* relative to synthesis and experimental determination of their HOMO/LUMO values. Such strategies may cut down in the time required to screen new metal-free systems for dye-sensitized solar cells.

Additional Data

NMR results for sensitizers 1, 2, and 3 as well as intermediates formed during the synthesis of 3 are shown in Supplementary Material available online at doi:10.1155/2010/264643. This material is available free of charge via the Internet at <http://pubs.acs.org/>.

Acknowledgments

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References

- [1] A. Mishra, M. K. R. Fischer, and P. Büuerle, "Metal-free organic dyes for dye-sensitized solar cells: from structure: property relationships to design rules," *Angewandte Chemie*, vol. 48, no. 14, pp. 2474–2499, 2009.
- [2] B. O'Regan and M. Grätzel, "A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO₂ films," *Nature*, vol. 353, no. 6346, pp. 737–740, 1991.
- [3] M. Grätzel, "Photoelectrochemical cells," *Nature*, vol. 414, no. 6861, pp. 338–344, 2001.
- [4] M. Grätzel, "Conversion of sunlight to electric power by nanocrystalline dye-sensitized solar cells," *Journal of Photochemistry and Photobiology A*, vol. 163, no. 1–3, pp. 3–14, 2004.
- [5] P. Xie and F. Guo, "Molecular engineering of ruthenium sensitizers in dye-sensitized solar cells," *Current Organic Chemistry*, vol. 11, no. 14, pp. 1272–1286, 2007.
- [6] N. Robertson, "Optimizing dyes for dye-sensitized solar cells," *Angewandte Chemie*, vol. 45, no. 15, pp. 2338–2345, 2006.
- [7] D. P. Hagberg, J. H. Yum, H. Lee et al., "Molecular engineering of organic sensitizers for dye-sensitized solar cell applications," *Journal of the American Chemical Society*, vol. 130, no. 19, pp. 6259–6266, 2008.
- [8] D. P. Hagberg, T. Marinado, K. M. Karlsson et al., "Tuning the HOMO and LUMO energy levels of organic chromophores for dye sensitized solar cells," *Journal of Organic Chemistry*, vol. 72, no. 25, pp. 9550–9556, 2007.
- [9] C. Kim, H. Choi, S. Kim et al., "Molecular engineering of organic sensitizers containing p-phenylene vinylene unit for dye-sensitized solar cells," *Journal of Organic Chemistry*, vol. 73, no. 18, pp. 7072–7079, 2008.
- [10] S. Erten-Ela, M. D. Yilmaz, B. Icli, Y. Dede, S. Icli, and E. U. Akkaya, "A panchromatic boradiazaindacene (BODIPY) sensitizer for dye-sensitized solar cells," *Organic Letters*, vol. 10, no. 15, pp. 3299–3302, 2008.
- [11] K. Hara, K. Sayama, Y. Ohga, A. Shinpo, S. Suga, and H. Arakawa, "A coumarin-derivative dye sensitized nanocrystalline TiO₂ solar cell having a high solar-energy conversion efficiency up to 5.6%," *Chemical Communications*, no. 6, pp. 569–570, 2001.
- [12] T. Horiuchi, H. Miura, K. Sumioka, and S. Uchida, "High efficiency of dye-sensitized solar cells based on metal-free indoline dyes," *Journal of the American Chemical Society*, vol. 126, no. 39, pp. 12218–12219, 2004.
- [13] N. Koumura, Z. S. Wang, S. Mori, M. Miyashita, E. Suzuki, and K. Hara, "Alkyl-functionalized organic dyes for efficient molecular photovoltaics," *Journal of the American Chemical Society*, vol. 128, no. 44, pp. 14256–14257, 2006.
- [14] T. Kitamura, M. Ikeda, K. Shigaki et al., "Phenyl-conjugated oligoene sensitizers for TiO₂ solar cells," *Chemistry of Materials*, vol. 16, no. 9, pp. 1806–1812, 2004.
- [15] K. Sayama, K. Hara, N. Mori et al., "Photosensitization of a porous TiO₂ electrode with merocyanine dyes containing a carboxyl group and a long alkyl chain," *Chemical Communications*, no. 13, pp. 1173–1174, 2000.
- [16] M. K. Nazeeruddin, P. Péchy, T. Renouard et al., "Engineering of efficient panchromatic sensitizers for nanocrystalline TiO₂-based solar cells," *Journal of the American Chemical Society*, vol. 123, no. 8, pp. 1613–1624, 2001.
- [17] M. K. Nazeeruddin, F. De Angelis, S. Fantacci et al., "Combined experimental and DFT-TDDFT computational study of photoelectrochemical cell ruthenium sensitizers," *Journal of the American Chemical Society*, vol. 127, no. 48, pp. 16835–16847, 2005.
- [18] M. K. Nazeeruddin, A. Kay, I. Rodicio et al., "Conversion of light to electricity by cis-Xbis(2,2'-bipyridyl-4,4'-dicarboxylate)ruthenium(II) charge-transfer sensitizers (X = Cl, Br, I, CN, and SCN) on nanocrystalline TiO₂ electrodes," *Journal of the American Chemical Society*, vol. 115, no. 14, pp. 6382–6390, 1993.
- [19] I. Jung, K. L. Jae, H. S. Kyu, K. Song, O. K. Sang, and J. Ko, "Synthesis and photovoltaic properties of efficient organic dyes containing the benzo[b]furan moiety for solar cells," *Journal of Organic Chemistry*, vol. 72, no. 10, pp. 3652–3658, 2007.
- [20] Z. Ning, Q. Zhang, W. Wu, H. Pei, BO. Liu, and HE. Tian, "Starburst triarylamine based dyes for efficient dye-sensitized solar cells," *Journal of Organic Chemistry*, vol. 73, no. 10, pp. 3791–3797, 2008.
- [21] P. Leriche, P. Frère, A. Cravino, O. Alévêque, and J. Roncali, "Molecular engineering of the internal charge transfer in thiophene-triphenylamine hybrid π -conjugated systems," *Journal of Organic Chemistry*, vol. 72, no. 22, pp. 8332–8336, 2007.
- [22] J. T. Lin, P.-C. Chen, Y.-S. Yen, Y.-C. Hsu, H.-H. Chou, and M.-C.P. Yeh, "Organic dyes containing furan moiety for high-performance dye-sensitized solar cells," *Organic Letters*, vol. 11, no. 1, pp. 97–100, 2009.
- [23] K.-F. Chen, Y.-C. Hsu, Q. Wu, M.-C.P. Yen, and S.-S. Sun, "Structurally simple dipolar organic dyes featuring 1,3-cyclohexadiene conjugated unit for dye-sensitized solar cells," *Organic Letters*, vol. 11, no. 2, pp. 377–380, 2009.
- [24] Y. Shibano, T. Umeyama, Y. Matano, and H. Imahori, "Electron-donating perylene tetracarboxylic acids for dye-sensitized solar cells," *Organic Letters*, vol. 9, no. 10, pp. 1971–1974, 2007.
- [25] T. Horiuchi, H. Miura, K. Sumioka, and S. Uchida, "High efficiency of dye-sensitized solar cells based on metal-free indoline dyes," *Journal of the American Chemical Society*, vol. 126, no. 39, pp. 12218–12219, 2004.
- [26] T. Kitamura, M. Ikeda, K. Shigaki et al., "Phenyl-Conjugated Oligoene Sensitizers for TiO₂ Solar Cells," *Chemistry of Materials*, vol. 16, no. 9, pp. 1806–1812, 2004.
- [27] N. Koumura, Z. S. Wang, S. Mori, M. Miyashita, E. Suzuki, and K. Hara, "Alkyl-functionalized organic dyes for efficient molecular photovoltaics," *Journal of the American Chemical Society*, vol. 128, no. 44, pp. 14256–14257, 2006.
- [28] S. Kim, J. K. Lee, S. O. Kang et al., "Molecular engineering of organic sensitizers for solar cell applications," *Journal of the American Chemical Society*, vol. 128, no. 51, pp. 16701–16707, 2006.
- [29] C. Y. Chen, S. J. Wu, C. G. Wu, J. G. Chen, and K. C. Ho, "A ruthenium complex with superhigh light-harvesting capacity for dye-sensitized solar cells," *Angewandte Chemie*, vol. 45, no. 35, pp. 5822–5825, 2006.
- [30] S. Stoyanov, G. Yordanov, and C. Dushkin, "Enhanced photocatalytic activity of thin TiO₂ films dotted with ZnS nanoparticles," *Reaction Kinetics and Catalysis Letters*, vol. 94, no. 2, pp. 227–232, 2008.
- [31] S. Takahashi, K. Nozaki, M. Kozaki et al., "Photoinduced electron transfer of N-[(3-and 4-diarylamino)phenyl]-1,8-naphthalimide dyads: Orbital-orthogonal approach in

- a short-linked D-A system,” *The Journal of Physical Chemistry A*, vol. 112, p. 15463, 2008.
- [32] Z. Cao, P. Nandhikonda, and M. D. Heagy, “Highly water-soluble monoboronic acid probes that show optical sensitivity to glucose based on 4-Sulfo-1,8-naphthalic anhydride,” *Journal of Organic Chemistry*, vol. 74, no. 9, pp. 3544–3546, 2009.
- [33] H. Cao, D. I. Diaz, N. DiCesare, J. R. Lakowicz, and M. D. Heagy, “Monoboronic acid sensor that displays anomalous fluorescence sensitivity to glucose,” *Organic Letters*, vol. 4, no. 9, pp. 1503–1505, 2002.
- [34] D. P. Adhikiri and M. D. Heagy, “Fluorescent chemosensor for carbohydrates which shows large change in chelation-enhanced quenching,” *Tetrahedron Letters*, vol. 40, no. 45, pp. 7893–7896, 1999.
- [35] H. Cao, V. Chang, R. Hernandez, and M. D. Heagy, “Matrix screening of substituted N-aryl-1,8-naphthalimides reveals new dual fluorescent dyes and unusually bright pyridine derivatives,” *Journal of Organic Chemistry*, vol. 70, no. 13, pp. 4929–4934, 2005.
- [36] H. Cao, T. McGill, and M. D. Heagy, “Substituent effects on monoboronic acid sensors for saccharides based on N-phenyl-1,8-naphthalenedicarboximides,” *Journal of Organic Chemistry*, vol. 69, no. 9, pp. 2959–2966, 2004.
- [37] B. M. Aveline, S. Matsugo, and R. W. Redmond, “Photochemical mechanisms responsible for the versatile application of naphthalimides and naphthalindiimides in biological systems,” *Journal of the American Chemical Society*, vol. 119, no. 49, pp. 11785–11795, 1997.
- [38] J. A. Cowan and J. K. M. Sanders, “Pyromellitimide-bridged porphyrins as model photosynthetic systems. 1. Synthesis and steady state fluorescence properties,” *Journal of the Chemical Society, Perkin Transactions*, vol. 1, pp. 2435–2437, 1985.
- [39] A. Samanta and G. Saroja, “Steady state and time-resolved studies on the redox behaviour of 1,8-naphthalimide in the excited state,” *Journal of Photochemistry and Photobiology A*, vol. 84, no. 1, pp. 19–26, 1994.
- [40] S. Hattori, K. Ohkubo, Y. Urano et al., “Charge separation in a nonfluorescent donor-acceptor dyad derived from boron dipyrromethene dye, leading to photocurrent generation,” *Journal of Physical Chemistry B*, vol. 109, no. 32, pp. 15368–15375, 2005.
- [41] Z. S. Wang, Y. Cui, Y. Dan-oh, C. Kasada, A. Shinpo, and K. Hara, “Thiophene-functionalized coumarin dye for efficient dye-sensitized solar cells: electron lifetime improved by coadsorption of deoxycholic acid,” *Journal of Physical Chemistry C*, vol. 111, no. 19, pp. 7224–7230, 2007.
- [42] M. Liang, W. Xu, F. Cai et al., “New triphenylamine-based organic dyes for efficient dye-sensitized solar cells,” *Journal of Physical Chemistry C*, vol. 111, no. 11, pp. 4465–4472, 2007.
- [43] G. Boschloo, L. Häggman, and A. Hagfeldt, “Quantification of the effect of 4-tert-butylpyridine addition to I /I redox electrolytes in dye-sensitized nanostructured TiO₂ solar cells,” *Journal of Physical Chemistry B*, vol. 110, no. 26, pp. 13144–13150, 2006.
- [44] R. Mosurkal, J. A. He, K. Yang, L. A. Samuelson, and J. Kumar, “Organic photosensitizers with catechol groups for dye-sensitized photovoltaics,” *Journal of Photochemistry and Photobiology A-Chemistry*, vol. 168, no. 3, pp. 191–196, 2004.
- [45] P. B. Gilman Jr., “use of spectral sensitizing dyes to estimate effective energy levels of silver halide substrates,” *Photographic Science and Engineerin*, vol. 18, no. 5, pp. 475–485, 1974.
- [46] M. J. Frisch, G. W. Trucks, H. B. Schlegel et al., Gaussian 03; Gaussian, Inc.: Pittsburgh, Pa, USA, 2003.



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