1-Alkyl-1*H*-imidazole-Based Dipolar Organic Compounds for Dye-Sensitized Solar Cells

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Abstract: A series of donor– π –acceptor-type organic dyes based on 1-alkyl-1*H*-imidazole spacers **1–5** have been developed and characterized. The two electron donors are at positions 4 and 5 of the imidazole, while the electron-accepting cyanoacrylic acid is incorporated at position 2 by a spacer-containing heteroaromatic rings, such as thiophene and thiazole. Detailed investigation on the relationship between the structure,

Introduction

Inorganic semiconductor photovoltaic cells have been developed for over two decades; nevertheless, research in this area has never ceased because solar energy is readily available and environmentally friendly. To counteract the deficit of energy and the increasing decline of natural resources, organic compounds have also attracted considerable interest after Grätzel's^[1] and Heeger's^[2] seminal works on ruthenium complex-based dye-sensitized solar cells (DSSCs) and polymer-based photovoltaic cells. DSSCs with high conversion efficiency (~11%) approaching that of amorphous-silicabased photovoltaic cells have been achieved by using cis-di(thiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylate)ruthenium(II) (N3) and analogues as the sensitizer.^[3] Though there is still room for improvement of the efficiency of rutheniumbased DSSCs,^[4] prototype ruthenium sensitizers are nevertheless costly and normally have absorption coefficients at $\sim 20000 \,\mathrm{m}^{-1} \mathrm{cm}^{-1}$ or below. In comparison, metal-free sensi-

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spectral and electrochemical properties, and performance of DSSC is described here. Dye-sensitized solar cells (DSSCs) using dyes as the sensitizers exhibit good efficiencies, ranging from 3.06 to 6.35 %, which reached 42–87 %

Keywords: charge transfer • donoracceptor systems • dyes • photophysics • sensitizers with respect to that of N719-based device (7.33%) fabricated and measured under similar conditions. Timedependent density functional theory (TDDFT) calculations have been performed on the dyes, and the results show that both electron donors can contribute to electron injection upon photo-excitation, either directly or indirectly by internal conversion to the lowest excited state.

tizers are relatively cheaper, and molecules with high molar extinction coefficients are easily attained. Therefore, there is also tremendous progress in metal-free sensitizer-based DSSCs in recent years, and efficiencies exceeding 9% have been reached,^[5] using sensitizers which have very high molar extinction coefficients in the visible region.

The metal-to-ligand charge-transfer (MLCT) transition plays an important role in light-harvesting processes for ruthenium-based sensitizers. In contrast, typical metal-free organic dyes consist of the electron donor, the electron acceptor with an anchoring group (such as carboxylic acid), and a conjugated spacer to facilitate charge transfer from the donor to the acceptor. Various metal-free organic sensitizers including coumarin-,^[6] indoline-,^[7] cyanine-,^[8] hemicyanine-,^[9] merocyanine-,^[10] perylene,^[11] xanthene-,^[12] triarylamine-,^[13] oligoene-,^[14] and thiophene-based^[6b,15] dyes have been reported for DSSCs. Choice of the donor and the acceptor for the sensitizer is somewhat limited, and aryl- (or alkyl-) amine and 2-cyano-acrylic acid appear to be the most popular donor and acceptor, respectively. Tuning of the charge-transfer absorption for better light harvesting can be practiced by variation of the spacer.

We have been interested in metal-free sensitizers for DSSCs application. Previously, we reported several series of arylamine-based sensitizers with various heteroaromatic rings in the spacers, and achieved high-performance DSSCs using these sensitizers.^[15a,b,16] Among these, 1*H*-phenanthro-

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[9,10-d]imidazole^[16a] and 2,3-disubstituted thiophenebased^[16b] dyes with two terminal arylamines appear to be interesting. Recombination of the injected electrons with the oxidized dyes was retarded through a cascade of charge separation in the former, and recombination of the injected electrons with the oxidized electrolytes was suppressed in both cases because of the presence of an extra hydrophobic arylamine-containing segment. In continuation of our studies on organic sensitizers for DSSCs, 1-alkyl-1H-imidazolyl unit was used in the spacer based on the following reasons: 1) it is relatively easy to introduce electron donors at positions 2 and 4, and an electron acceptor at position 5 of 1alkyl-1H-imidazoles to form conjugated dipolar compounds;^[17] 2) through appropriate modification of the conjugated chain, it is possible to tune the charge-transfer transition of dipolar molecules; 3) charge recombination after electron injection may be retarded because of decreasing positive charge density at the donor by electronic delocalization of the two substituents at positions 4 and 5 of the imidazolyl ring; 4) cascade energy/electron transfer or panchromatic absorption may be possible with two different substituents at positions 4 and 5. In this paper, we report the synthesis and characterization of new dipolar dyes containing a 1-alkyl-1H-imidazole moiety. DSSCs using these dyes as the sensitizers are also discussed.

Results and Discussion

Synthesis and Characterization

The synthetic procedures of the compounds **1–5** are shown in Scheme 1. The structures of the new dyes are illustrated in Figure 1. The first step of the synthesis of compounds **1–5** was condensation of the corresponding diketone derivatives with aldehydes in the presence of ammonium acetate in acetic acid, followed by *N*-alkylation to form 1,2,4,5-tetrasubstituted imidazoles in good yields.^[17] Formylation of the







imidazolyl intermediate was performed with nBuLi and N-formylpiperidine in THF. The final target compounds were synthesized by treatment with cyanoacetic acid in refluxing acetic acid in the presence of a catalytic amount of ammonium acetate. The structures of all synthesized compounds were characterized by NMR, MS, and elemental analysis.

Photophysical Properties

The optical absorption spectra of the dyes in THF are displayed in Figure 2 and the data are collected in Table 1. The absorption band at <400 nm is attributed to the π - π * transition. The broad band at >400 nm stems from the chargetransfer transition from the donors at positions 4 and 5 of the imidazole to the acceptor, 2-cyanoacrylic acid (see below).^[17b,c] The charge-transfer characteristic of the low energy band is supported by the following observations: 1) this band disappears in compounds **na** (n=1-5); 2) replacement of the 2-cyanoacrylic acid in n (n=1-5) by a weaker acceptor, aldehyde nb (n=1-5) leads to a blue-shift of λ_{max} (434 vs 405 nm for 2 and 458 vs 444 nm for 5); 3) the wavelength of the charge-transfer band increases in the order of 1 < 2 < 3, which is consistent with the order of increasing electron-donating strength of the capping segment, $OMe < Ph_2N < Me_2N$. Although the diarylamino moiety is considered to be a much stronger electron-donating group than the methoxy moiety,^[18] the small difference in the λ_{max} value (16 nm) between 1 and 2 indicates that the charge transfer is only of moderate strength. Similarly, replacement of the 2-cyanoacrylic acid in 5 by a weaker acceptor, an aldehyde, leads to blue-shift of λ_{max} by only 14 nm (458 nm vs 444 nm). Similar to our previous observations,^[16c, d] replacement of the *p*-phenylene unit in **2** by a fluorene unit only leads to a small change in the absorption wavelength of the charge-transfer band. Interestingly, incorporation of an electron-deficient thiazole ring in the spacer, results in both a bathochromic shift and hyperchromic effect of the chargetransfer band, that is, 2 versus 5. The extinction coefficients of the charge-transfer bands in these compounds are only moderate, ranging from ~ 10000 to $\sim 27000 \text{ m}^{-1} \text{ cm}^{-1}$. This may be attributed to the twist of the donor at position 5 of the imidazole from co-planarity with the imidazole ring, which hampers the effective conjugation between the two. In this series of compounds, the two donor groups (aryl amine or methoxyphenyl) are attached at two different positions: position 5, which allows a resonance with electrons to flow from the donor through the imidazolyl group, whereas position 4 does not allow such a resonance. For the excitations involving position 5, we expect that the resonance allows a stronger interaction between the donor and the rest of the molecule, leading to a more delocalized transition, and therefore larger oscillator strength. On the contrary, excitations involving position 4 are expected to be more localized and thus have smaller oscillator strength, as the donor is more isolated from the rest of the molecule. However, there exists steric hindrance that increases the dihedral angles between the phenyl group in the donor and the imi-

O N N S CN CN



3



Figure 1. The structure of the dyes.



Figure 2. Absorption spectra of the dyes recorded in THF.

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dazole moiety, and therefore decreases electronic interaction between them. From our calculated results detailed below, the dihedral angle (angle A) between the phenyl group at position 4 and the imidazole ring, ranges from ~2.5 to 28° (see computation section). In comparison, the dihedral angle (angle B) between the phenyl group at position 5 and the imidazole ring is significantly larger, ranging from ~56 to 88°. Apparently, the donor at position 5 of the imidazole is more sterically crowded than that at position 4 because of the presence of the N-alkyl group in addition to the steric interaction between the two donors. Similar phenomenon was observed in other 1,2,4,5-tetra-substituted imidazolyl congeners.^[17a,c]

соон

соон

ĊN

COOH

соон

с'n

ĊN

1"

ĊN

2

A blue-shift of the chargetransfer band in more polar solvent, that is, negative solvatochromism, was recognized in these compounds. For example, the absorption wavelength increases in the order of DMF (2, 422 nm; 4, 418 nm) < THF (2, 438 nm; 4, 428 nm) < toluene (2, 447 nm; 4, 447 nm). This may be attributed to the strong interaction of polar solvent molecules with the sensitizer, which weakens the O-H bond of the carboxylic acid and consequently decreases the electron-withdrawing nature of the

COOH group. Additional support for this argument comes from the blue-shift of λ_{max} upon NEt₃ treatment of the THF solution of the dye, in which complete deprotonation of the COOH group is expected to occur. The MLCT band of the black dye^[19] and the charge-transfer band of some metalfree organic dye^[15c, 16b-d] were reported to behave similarly. No noticeable changes of λ_{max} values or band broadening were observed in these dyes upon adsorption on the TiO₂ nanoparticles (Figure 3) except for 4 and 5. The red tailing of the absorption bands for 4 and 5 adsorbed on TiO_2 is mostly likely caused by the J-aggregation of the dyes.[15d,20] Additional absorption in the shorter wavelength region for 4 on the TiO₂ nanoparticles compared to that in the solution may stem from H-aggregation of the dye molecules.^[15d,21] Though the absorption band of 3 has much weaker intensity than that of 2 in the solution, the two dyes adsorbed on the

Table 1. Electrooptical parameters of the dyes.^[a]

	1 1	2			
Dye	$\begin{array}{l} \lambda_{abs}[nm] \\ [\epsilon \times 10^{-4}\text{m}^{-1}\text{cm}^{-1}] \end{array}$	E _{1/2} (ox) [mV]	HOMO/LUMO [eV]	$E_{0-0}\left[\mathrm{eV} ight]$	$E_{0-0}^*\left[\mathbf{V} ight]$
1	418 (2.00), 276 (1.56)	577	5.38/2.88	2.50	-1.22
2	434 (1.94), 339 (3.04), 307 (3.99)	370, 512	5.17/2.74	2.43	-1.36
3	446 (1.08), 300 (1.58), 268 (1.94)	120, 259	4.92/2.61	2.31	-1.49
4	430 (2.30), 370 (5.81), 312 (3.59)	330, 448	5.13/2.60	2.53	-1.50
5	458 (2.70), 339 (3.14), 306 (4.14)	344, 502	5.14/2.85	2.29	-1.25

[a] Absorption data and electrochemical data were collected in DCM solutions. Scan rate, 100 mV s⁻¹; electrolyte, $(n-C_4H_9)_4NPF_6$; potentials are quoted in reference to the internal ferrocene standard $(E_{1/2} = +212 \text{ mV vs} \text{ Ag/AgNO}_3)$.



Figure 3. Absorption spectra of the dyes adsorbed on TiO₂ films.

 TiO_2 nanoparticles have comparable absorption intensity because of the higher adsorbed dye density of **3** than **2** (see below). The compound are emissive in THF, and the emission wavelength is in the order of **4** (535 nm) < **1** (558 nm) < **2** (590 nm) < **3** (595 nm) < **5** (602 nm), which is roughly parallel to the trend of the absorption wavelength.

Electrochemical Properties

The electrochemical properties of the compounds were studied by cyclic voltammetry, and all data are listed in Table 1. Representative cyclic voltammograms are shown in Figure 4. A quasireversible one-electron oxidation wave observed for 1 is attributed to the oxidation of the imidazolebased conjugated spacer. For compounds 2-5, the one-electron redox wave observed at lower potential is attributed to the oxidization of one of the amines, and the two-electron redox wave occurring at a higher potential is caused by the unresolvable waves from the oxidation of the second amine and the imidazole-based conjugated spacer. As expected, the N,N-dimethylamine in 3 is oxidized at a significantly lower potential^[16d] compared to the triarylamine in 2-5. The energy levels of the HOMOs of these materials were calculated with reference to ferrocene (4.8 eV) and ranged from 4.92 to 5.38 eV. The optical edge was utilized to derive the band gap and the LUMO energies. The excited-state poten-





Figure 4. Cyclic voltammograms of compounds 1 and 5 in DCM.

-1.50 V vs NHE, see Table 1) compared to the conductionband-edge energy level of the TiO₂ electrode (-0.5 V vs NHE).^[21] The first oxidation potentials of the dyes ($0.82 \sim$ 1.28 V vs NHE) are more positive than the I^-/I_3^- redox couple (0.4 V vs NHE),^[15e,22] therefore, dye regeneration should also be energetically favorable.

$$E_{0-0}^{*} = E_{0x} - E_{0-0} \tag{1}$$

Photocurrent–Voltage Characteristics

Compounds 1–5 were used as the sensitizers for dye-sensitized nanocrystalline anatase TiO₂ (20 nm particles, film ~ 18 µm thick) solar cells (DSSCs). The cells with an effective area of 0.25 cm² were fabricated with an electrolyte composed of $0.05 \text{ M I}_2/0.5 \text{ M Lil}/0.5 \text{ M tert-butyl}$ pyridine in acetonitrile solution. The device performance of solar cells under AM 1.5 illumination are summarized in Table 2. Figure 5 shows the photocurrent–voltage (*J*–*V*) curves of the cells. The action spectra of incident photon-to-current conversion efficiency (IPCE) for the cells are plotted in Figure 6. The efficiencies of the DSSCs are in the order of 2 (6.35%)>1 (5.41%)>4 (4.87%) ≈ 5 (4.76%)>3 (3.06%). The efficiencies

Table 2. Performance parameters of DSSCs constructed using the dyes.^[a]

Cell	$J_{\rm sc}[{ m mAcm^{-2}}]$	$V_{ m oc}\left[{ m V} ight]$	FF	h [%]
1	12.76	0.66	0.64	5.41
2	15.00	0.67	0.64	6.35
3	7.24	0.61	0.69	3.06
4	10.01	0.69	0.71	4.87
5	11.55	0.63	0.65	4.76
N719	16.15	0.72	0.63	7.33

[a] Experiments were conducted using TiO₂ photoelectrodes with approximately 18 μ m thickness and 0.25 cm² working area on the FTO (15 Ω /sq.) substrates.



Figure 5. J-V curves of DSSCs based on the dyes.



Figure 6. IPCE plots for the DSSCs.

cy of **2**-based device reaches 87% of the standard ruthenium dye N719-based cell (conversion efficiency = 7.33%) fabricated and measured under similar conditions. Interestingly, **1**-based device also has an efficiency reaching > 70% of the N719-based cell^[23] even though **1** has a much weaker electron donor (methoxophenyl) than **2** (diphenylamino). The higher efficiency (and therefore, higher short-circuit current) of the **2**-based device than the **1**-based device can be rationalized by the red-shift of the absorption spectra of **2** compared to **1**, that is, better light-harvesting efficiency of **2**. The device from **3** has the lowest efficiency (<50% of the

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standard ruthenium dye N719-based cell), and the lowest short-circuit current (J_{sc}) and open-circuit voltage (V_{oc}) . In view of the high dye density (1, 6.02×10^{-7} ; 2, 4.50×10^{-7} ; 3, 7.48×10^{-7} ; 4, 3.74×10^{-7} ; 5, 3.84×10^{-7} mol cm⁻²) of 3 on the TiO₂ surface, such an outcome can be rationalized by the following reasons: 1) 3 has a relatively small molar extinction coefficient of the charge-transfer band; 2) the high HOMO energy level of 3 results in slower regeneration of the oxidized sensitizer after electron injection. Consequently, more facile charge recombination between the conduction-band electrons and dye cations leads to lower J_{sc} and $V_{\rm oc}$ values. The lower efficiencies of the devices based on 4 and 5 compared to 1 can be attributed to the lower dye densities of 4 and 5 on TiO_2 arising from the larger sizes of the molecules. The device based on 5 has a performance inferior to those of 1 and 2 despite the broader and intense absorption band of 5 compared to 1 and 2. Apparently, the chargetransfer band overlaps with the delocalized π - π * transition, which does not contribute to the electron injection (see computation section). The recombination lifetime (τ_R) of the photoinjected electron with the oxidized dye was measured by transient photovoltage^[24] at open circuit. To avoid dark current, I2 was omitted and the electrolyte used was LiI in CH₃CN. The τ_R values are 3.9, 2.6, 1.0, 5.2, 1.6, and 8.9 ms for the cells based on 1-5 and N719, respectively. The rather short $\tau_{\rm R}$ value (1.0 ms) of the 3-based cell, attributed to the relatively slower regeneration of the oxidized sensitizer (see above), is consistent with its low efficiency. The longer lifetime for 4 may be caused by the longer distance between the donor and the anchoring group. Though the distance between the donor and the anchoring group in 5 is also large among the five compounds, surprisingly, the device based on 5 has a much smaller τ_R value when compared to that of **4**.

The cell stability for **2** was checked briefly by measuring the efficiency after a period of 24 h. The cell was exposed to the light source only during the measurements for the first 96 h. After 96 h, the cell was irradiated for 1 h before measurement. A 4% drop in efficiency was observed after 96 h, and a ~15% drop was noticed after 192 h. The decrease in the efficiency was mainly caused by the decrease in J_{sc} . Both leakage of the solvent and degradation of the sensitizer may contribute to the decline in the efficiency.

Theoretical Approach

To gain further insight into the correlation between structure and the physical properties as well as the device performance, quantum chemistry computation was conducted. Model compounds in which the substituent at position 4 (compounds, n', n=1-5) or 5 (compounds n'', n=1-5) of the imidazole was replaced by a hydrogen atom, were also calculated for comparison. Representative structures for 1' and 1" are illustrated in Figure 1. The molecules were divided into five to six segments: the arylamine group in the same side with the *N*-methyl (or *N*-ethyl) group (D_R), another arylamine group (D_{NR}), the imidazole ring next to D_R and D_{NR} (B1), the thiophene ring next to B1 (B2), the thiazole ring next to B2 (B3), and 2-cyanoacrylic acid (Acid). The results for the theoretical approach are included in Table 3 and Figure S1 of the Supporting Information, respectively.

Table 3. Calculated low-lying transition for the dyes.[a]

Dye	State	Excitation ^[a]	$\lambda_{cal}\left[eV\right]$	<i>f</i> ^[b]
1	S_1	H→L (99%)	2.34	0.505
	S_2	H1→L (94%)	3.18	0.410
	S ₃	H2 \rightarrow L (92%)	3.57	0.208
2	S_1	$H \rightarrow L (100\%)$	2.01	0.201
	S_2	H1 \rightarrow L (99%)	2.42	0.127
	S ₃	H2 \rightarrow L (97%)	2.90	0.761
3	\mathbf{S}_1	H→L (99%)	1.99	0.268
	S_2	H1→L (97%)	2.72	0.086
	S ₃	H2 \rightarrow L (95%)	3.04	0.726
4	\mathbf{S}_1	$H \rightarrow L (100\%)$	1.91	0.115
	S_2	$H1 \rightarrow L (100\%)$	2.28	0.000
	S ₃	H2 \rightarrow L (98%)	2.58	0.577
5	S_1	$H \rightarrow L (100\%)$	1.75	0.226
	S_2	H1→L (100%)	2.19	0.177
	S ₃	$H2 \rightarrow L (99\%)$	2.54	0.794

[a] H=HOMO, L=LUMO, H1=The next highest occupied molecular orbital, or HOMO-1, H2=HOMO-2. In the parentheses is the population of a pair of MO excitations. [b] Oscillator strength.

Mulliken charges for the S_1 , S_2 , and S_3 states were also calculated as a projection from the time-dependent DFT (TDDFT) results. Differences in the Mulliken charges in the excited state and ground state were calculated and grouped into the same segments in the molecules to estimate the extent of charge separation upon excitation (Figure 7).

As discussed above, in this series of compounds, the two donor groups (aryl amine or methoxyphenyl) play different roles in the photophysics: the one attached at position 5 (D_R), which allows a resonance with electrons, flows from the donor through the imidazolyl group, while position 4 (D_{NR}) does not allow such a resonance. For the former, the



Figure 7. Plot of difference in Mulliken charge between ground state and excited state for 1-5.

resonance allows a stronger interaction between the donor and the rest of the molecule, leading to higher oscillator strength and smaller charge separation, whereas for the latter, lower oscillator strength and larger charge separation are expected. The calculated results for model compounds n' and n'' are consistent with this expectation. The lowest energy transition ($S_0 \rightarrow S_1$; >98 % HOMO \rightarrow LUMO) in both n' and n'' has significant charge transfer from any amine (or methoxyphenyl). This transition has very different characteristics between n' and n'': 1) the energy of the transition is lower by ~0.3–0.5 eV for compound n'' (donor attached at position 4); 2) the oscillator strength (f) of the transition in n' (donor attached at position 5) is two-fold larger than that in n''; 3) compound n'' has better charge separation between the donor and Acid than compound n', and the Mulliken charge difference ranges from 1.02 to 1.42 |e| for n'', which reduces to 0.69–1.37 |e| for n'. Charge transfer is more facile from the donor at position 4 of the imidazole to the acceptor because of the smaller twist angle between the donor and the imidazole ring (Figure S2 of the Supporting Information).

The S_1 and S_2 states of our experimentally studied molecules n are mainly composed of excitations originating from electrons in one of the donors at positions 4 and 5, respectively (except for 1). The lowest energy transition $(S_0 \rightarrow S_1;$ >99% HOMO \rightarrow LUMO) is mainly from D_{NR} (position 4) to Acid, and significant charge transfer from D_R (position 5) to Acid is observed at higher energy transition, $S_0 \rightarrow S_2$ (> 97% HOMO-1 \rightarrow LUMO) for **2–5** and $S_0 \rightarrow S_3$ (>92%) HOMO-2 \rightarrow LUMO) for 1 and 2. For 1, excitation from the same D_{NR} contributes to the first two excitations, with a small mix from the excitation originated from D_{R} (Table S3 and Figure S1 in the Supporting Information). Therefore, it is believed that $S_0 \rightarrow S_2$ and $S_0 \rightarrow S_3$ transitions can also inject electrons directly to the conduction band of TiO₂, or indirectly through internal conversion to $S_0 \rightarrow S_1$. The contributions of the $S_0 \rightarrow S_2$ and $S_0 \rightarrow S_3$ transitions support the high

> conversion efficiency of 2-based DSSC. Though $S_0 \rightarrow S_2$ and $S_0 \rightarrow$ S_3 transitions in **1** have higher energies are not likely to contribute to electron injection, the rather high f value of $S_0 \rightarrow S_1$ may be responsible for its high efficiency conversion even though the methoxy unit is only a weak electron donor. The high dye density of 1 on the TiO₂ surface may also contribute to good conversion efficiency.

> The combination of several excited states is favorable in the design of sensitizing dyes for DSSCs. While the lower excited state offers a good charge separation, higher excited state can

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be optically active and helps in harvesting photons. The two distinct characters of donor positions appear to follow such an advantageous design for molecules studied in the present work: the donor attached at the 4-position offers charge separation, whereas the one at the 5-position, in which resonance is allowed, can help increase absorption, as indicated by the computational results for the model compounds n' and n''.

However, the oscillator strengths and charge separation for the molecules n did not quite follow those for n' and n''(Tables S2–S3 and Figure S3 in the Supporting Information). The oscillator strength values for S₁ are larger than those for S_2 in all compounds in the *n* series. In **3** and **4**, charge separations for the S_2 states are larger than those of the S_1 state. We believe, it is mainly occurring from the large dihedral angles between the donor and the imidazolyl moieties caused by the steric hindrance. As shown in Figure S1 in the Supporting Information, the effect of the N-alkyl group is evident by comparison of the dihedral angles when the substituent at position 4 (compounds 1'-5') or 5 (compounds 1''-5'') is replaced by a hydrogen atom. The dihedral angles between the donor and the imidazole ring are significantly larger in n' than in n" in all isomeric pairs: 1'/1", 44 to 9°; 2'/ 2", 54 to 4°; 3'/3", 54 to 2°; 4'/4", 45 to 2°; 5'/5", 56 to 1°. The dihedral angles for n are even larger in the D_R branch. The large dihedral angles for D_R pose an adverse effect to the electron resonance, reducing the interaction between the donor and the attached imidazole. This result indicates that even though in theory molecules n have a good potential for offering a good charge separation while absorbing light efficiently using its dual donor design, the desirable effect may be compromised by the final molecular structure. Unlike the previously reported cases^[16a,c,d] in this series of compounds, we see less correspondence between the extent of charge separation and the final DSSC performance. It is possible that the theoretical predictions for some of the important parameters, such as the dihedral angles between the donors and the imidazolyl group, do not reflect the actual situation. The twisting forces are expected to be weak, and the molecules could have a typical environment on the TiO₂ particle surface that may affect the structure of the dye molecules. Nevertheless, the computational results indicate the importance of controlling the electronic interaction between neighboring groups, which should be useful in the future design of organic DSSC dyes.

Conclusions

In summary, we have synthesized dipolar 1,2,4,5-tetra-substituted imidazole derivatives, in which, two electron-donating units are incorporated at positions 4 and 5 of 1-alkyl-1*H*-imidazole, and electron-accepting cyanoacetic acid is incorporated at position 2 of the imidazole ring by a conjugated spacer. DSSCs using these compounds exhibit efficiencies ranging from 5.41–6.35% under AM 1.5 illumination. The best performance of the device reaches 87% of N719-based DSSC (7.33%) fabricated and measured under similar conditions. Theoretical investigations indicate that both donors at positions 4 and 5 can contribute to electron injection into TiO_2 upon photo-excitation, either directly or indirectly by internal conversion to the lowest excited state.

Experimental Section

General Information

Unless otherwise specified, all the reactions and solvent distillations were performed under nitrogen atmosphere using standard Schlenk techniques. THF was distilled from sodium and benzophenone. DMF was distilled from CaH₂. Dichloromethane for spectroscopic measurements were distilled from calcium hydride. ¹H NMR spectra were recorded on a Bruker 400 MHz spectrometer operating at 400.135 MHz. Absorption spectra were recorded on a Cary 50 probe UV/Vis spectrophotometer. All chromatographic separations were carried out on silica gel (60M, 230–400 mesh). Mass spectra (FAB) were recorded on a VG70–250S mass spectrometer. Elemental analyses were performed on a Perkin–Elmer 2400 CHN analyzer.

Syntheses

The starting materials (1a-5a) were prepared by adopting literature procedures.^[17] 4,5-Bis(4-methoxyphenyl)-1-methyl-2-(thiophen-2-yl)-1*H*-imidazole (1a) and 5-(4,5-bis(4-methoxyphenyl)-1-methyl-1*H*-imidazol-2-yl) thiophene-2-carbaldehyde (1b) were synthesized according to the literature procedures.^[17b,25] Compounds 2b-5b were synthesized by similar procedures, and only the preparation of 3b is described in detail. The target compounds (1–5) were obtained by essentially following a similar procedure, and an illustrative example is given below for 1.

benzenamine) (2a): Colorless solid (90%); ¹H NMR (CDCl₃): δ = 1.21 (t, J = 7.2 Hz, 3H), 4.03 (q, J = 7.2 Hz, 2H), 6.93–6.97 (m, 4H), 7.04–7.08 (m, 7H), 7.09–7.11 (m, 2H), 7.12–7.15 (m, 4H), 7.18–7.21 (m, 6H), 7.25–7.29 (m, 4H), 7.37 (d, J = 4.8 Hz, 2H), 7.46 ppm (d, J = 8.7 Hz, 2H); HRMS (APCI): m/z (%) calcd for C₄₅H₃₇N₄S₁: 665.2739 [M⁺+H]; found: 665.2735.

4,4'-(1-Ethyl-2-(thiophen-2-yl)-1*H*-imidazole-4,5-diyl)bis(*N*,*N*-dimethylbenzenamine) (3a): Yellow solid (70%); ¹H NMR (CDCl₃): δ =1.16 (t, *J*=7.2 Hz, 3H), 2.86 (s, 6H), 3.01 (s, 6H), 3.96 (q, *J*=7.2 Hz, 2H), 6.58 (d, *J*=9.0 Hz, 2H), 6.76 (d, *J*=8.8 Hz, 2H), 7.09 (dd, *J*=3.6 Hz, 1H), 7.22 (d, *J*=9.5 Hz, 2H), 7.34–7.36 (m, 2H), 7.43 ppm (d, *J*=9.0 Hz, 2H); HRMS (APCI): *m*/*z* (%) calcd for C₂₅H₂₉N₄S: 417.2113 [*M*⁺+H]; found: 417.2114.

7,7'-(1-Ethyl-2-(thiophen-2-yl)-1*H***-imidazole-4,5-diyl)bis(9,9-diethyl-***N***,***N***-diphenyl-9***H***-fluoren-2-amine) (4a): Pale yellow solid (70%); ¹H NMR (CDCl₃): \delta=0.23 (t,** *J***=7.3 Hz, 6H), 0.39 (t,** *J***=7.3 Hz, 6H), 1.19 (t,** *J***=7.2 Hz, 3H), 1.72–1.74 (m, 4H), 1.88–1.92 (m, 4H), 4.05 (q,** *J***=7.2 Hz, 2H), 6.93–7.0 (m, 5H), 7.02–7.04 (m, 1H), 7.05–7.14 (m, 10H), 7.17–7.27 (m, 8H), 7.27–7.36 (m, 1H), 7.36–7.52 (m, 7H), 7.58 (d,** *J***=7.7 Hz, 1H), 7.52–7.69 (m, 1H), 7.68 ppm (d,** *J***=7.7 Hz, 1H); MS (FAB):** *m/z* **(%): 953.46 [***M***⁺+H].**

4,4'-(1-Ethyl-2-(5-(thiazol-2-yl)thiophen-2-yl)-1*H***-imidazole-4,5-diyl)-bis(***N*,*N***-diphenylbenzenamine)** (5a): Yellow solid (68%); ¹H NMR (CDCl₃): δ =1.26 (t, *J*=7.2 Hz, 3H), 4.1 (q, *J*=7.2 Hz, 2H), 6.93–6.98 (m, 4H), 7.04–7.08 (m, 8H), 7.10–7.15 (m, 4H), 7.18–7.22 (m, 6H), 7.25–7.29 (m, 5H), 7.44–7.47 (m, 3H), 7.52 (d, *J*=4.0 Hz, 1H), 7.77 ppm (d, *J*=3.2 Hz, 1H); HRMS (APCI): *m/z* (%) calcd for C₄₈H₃₈N₅S₂: 748.2569 [*M*⁺+H]; found: 748.2582.

5-(4,5-Bis(4-(diphenylamino)phenyl)-1-ethyl-1*H*-imidazol-2-yl)thio-

phene-2-carbaldehyde (2b): Orange solid (78%); ¹H NMR (CDCl₃): δ = 1.25 (t, *J*=7.2 Hz, 3 H), 4.11 (q, *J*=7.2 Hz, 2 H), 6.94–6.96 (m, 4 H), 7.05–7.13 (m, 8 H), 7.15–7.17 (m, 4 H), 7.19–7.21 (m, 6 H), 7.25–7.29 (m, 4 H), 7.44 (d, *J*=8.7 Hz, 2 H), 7.60 (d, *J*=4.0 Hz, 1 H), 7.75 (d, *J*=4.0 Hz, 1 H),

9.91 ppm (s, 1H); HRMS (APCI): m/z (%) calcd for $C_{46}H_{37}N_4O_1S_1$: 693.2688 [M^+ +H]; found: 693.2692.

5-(4,5-Bis(4-(dimethylamino)phenyl)-1-ethyl-1*H*-imidazol-2-yl)thio-

phene-2-carbaldehyde (3b): Compound 3a (1.66 g, 4 mmol) dissolved in THF (50 mL) was cooled to -78 °C under nitrogen atmosphere. n-Butyllithium (2.8 mL, 1.6 m in hexane, 4.4 mmol) was added dropwise with vigorous stirring. It was brought to 0°C during 1 h, and kept at this temperature for additional 30 min. Again, the mixture was cooled to -78 °C and dry dimethylformamide (2 mL) was added at once. The solution was brought to room temperature and stirred overnight. The reaction was quenched by the addition of dilute HCl (2 mL) in water (40 mL) and extracted with diethyl ether. The organic extract was dried over anhydrous MgSO4 and filtered. The filtrate was evaporated to yield the crude product as dark yellow solid. It was purified by column chromatography on silica gel using hexane/dichloromethane mixture (1:1) as eluent, to afford orange solid (80%). ¹H NMR (CDCl₃): $\delta = 1.23$ (t, J = 7.2 Hz, 3H), 2.87 (s, 6H), 3.02 (s, 6H), 4.05 (q, J=7.2 Hz, 2H), 6.59 (d, J=6.9 Hz, 2H), 6.76 (d, J=6.8 Hz, 2H), 7.21 (d, J=6.8 Hz, 2H), 7.41 (d, J=6.9 Hz, 2H), 7.57 (d, J=4.0 Hz, 1H), 7.73 (d, J=4.0 Hz, 1H), 9.90 ppm (s, 1H); HRMS (APCI): m/z (%) calcd for C₂₆H₂₉N₄O₁S₁: 445.2062 [M^+ +H]; found: 445.2055.

5-(4,5-Bis(7-(diphenylamino)-9,9-diethyl-9*H*-fluoren-2-yl)-1-ethyl-1*H*imidazol-2-yl)thiophene-2-carbaldehyde (4b): Yellow solid (75%); ¹H NMR (CDCl₃): $\delta = 0.24$ (t, J = 7.3 Hz, 6H), 0.39 (t, J = 7.2 Hz, 6H), 1.25 (t, J = 7.20 Hz, 3H), 1.71–1.76 (m, 4H), 1.89–1.92 (m, 4H), 4.12 (q, J = 7.2 Hz, 2H), 6.93–7.01 (m, 5H), 7.03–7.18 (m, 11H), 7.18–7.31 (m, 9H), 7.34–7.52 (m, 5H), 7.58–7.70 (m, 3H), 7.78 (d, J = 3.4 Hz, 1H) 9.94 ppm (s, 1H); MS (FAB): m/z (%): 981.45 [M^+ +H].

2-(5-(4,5-Bis(4-(diphenylamino)phenyl)-1-ethyl-1*H*-imidazol-2-yl)thio-

phen-2-yl)thiazole-5-carbaldehyde (5b): Red solid (75%); ¹H NMR (CDCl₃): δ =1.29 (t, J=7.2 Hz, 3H), 4.10 (q, J=7.0 Hz, 2H), 6.94–6.99 (m, 4H), 7.05–7.09 (m, 8H), 7.10–7.15 (m, 4H), 7.18–7.23 (m, 6H), 7.25–7.30 (m, 4H), 7.44 (d, J=8.7 Hz, 2H), 7.48 (d, J=4.0 Hz, 1H), 7.67 (d, J=4.0 Hz, 1H), 8.33 (s, 1H), 10.0 ppm (s, 1H); HRMS (APCI): *m/z* (%) calcd for C₄₉H₃₈N₅O₁S₂: 776.2518 [*M*⁺+H]; found: 776.2523.

(E)-3-(5-(4,5-Bis(4-methoxyphenyl)-1-methyl-1H-imidazol-2-yl)thiophen-2-yl)-2-cyanoacrylic acid (1): A mixture of 1b (0.404 g, 1 mmol) and cyanoacetic acid (0.102 g, 1.2 mmol), ammonium acetate (16 mg, 0.2 mmol), and acetic acid (20 m) were heated to reflux for 8 h. After cooling, the precipitate formed was filtered and thoroughly washed with water and cold methanol. After drying in air, the crude product was purified by column chromatography on silica gel with dichloromethane/methanol mixture as eluent to afford a red solid (70%). ¹H NMR ([D₆]DMSO): $\delta = 3.57$ (s, 3 H), 3.69 (s, 3 H), 3.82 (s, 3 H), 6.80 (d, J = 8.5 Hz, 2 H), 7.07 (d, J=8.4 Hz, 2H), 7.29-7.33 (m, 4H), 7.58 (d, J=3.7 Hz, 1H), 7.75 (d, J = 3.7 Hz, 1H), 8.22 ppm (s, 1H); ¹³C NMR ([D₆]DMSO): $\delta = 32.90$, 55.04, 55.25, 108.44, 113.69, 114.64, 118.96, 121.92, 125.48, 126.76, 127.53, 130.82, 132.21, 136.48, 136.55, 137.30, 138.59, 140.08, 141.60, 158.05, 159.62, 164.52 ppm; HRMS (ESI): m/z (%) calcd for $C_{26}H_{22}N_3O_4S_1$: 472.1331 [M⁺+H]; found: 472.1320; elemental analysis: calcd (%) for C₂₆H₂₁N₃O₄S: C 66.23, H 4.49, N 8.91; found: C 66.10, H 4.47, N 8.87.

(*E*)-3-(5-(4,5-Bis(4-(diphenylamino)phenyl)-1-ethyl-1*H*-imidazol-2-yl)thiophen-2-yl)-2-cyanoacrylic acid (2): Red solid (65%); ¹H NMR ([D₆]DMSO): δ =1.19 (t, *J*=7.2 Hz, 3H), 4.05 (q, *J*=6.8 Hz, 2H), 6.88 (d, *J*=8.7 Hz, 2H), 6.98 (d, *J*=7.6 Hz, 2H), 7.02–7.04 (m, 6H), 7.09–7.13 (m, 6H), 7.26–7.33 (m, 9H), 7.35–7.39 (m, 3H), 7.55 (d, *J*=4.0 Hz, 1H), 7.77 (d, *J*=4.0 Hz, 1H), 8.14 ppm (s, 1H); ¹³C NMR ([D₆]DMSO): δ =15.58, 40.08, 108.73, 118.80, 121.45, 122.58, 122.84, 123.20, 123.71, 123.90, 124.95, 126.94, 128.61, 129.43, 129.68, 130.53, 131.88, 136.26, 136.61, 137.18, 138.11, 139.05, 141.05, 145.52, 146.56, 147.06, 147.93, 163.79 ppm; HRMS (APCI): *m/z* (%) calcd for C₄₉H₃₈N₅O₂S₁: 760.2746 [*M*++H]; found: 760.2728; elemental analysis: calcd (%) for C₄₉H₃₇N₅O₂S: C 77.45, H 4.91, N 9.22; found: C 77.32, H 4.84, N 9.10.

(*E*)-3-(5-(4,5-Bis(4-(dimethylamino)phenyl)-1-ethyl-1*H*-imidazol-2-yl)thiophen-2-yl)-2-cyanoacrylic acid (3): Red solid (70%); ¹H NMR ([D₆]DMSO): δ =1.13, (t, *J*=7.2 Hz, 3H), 2.83 (s, 6H), 2.98 (s, 6H), 4.0 (q, *J*=6.8 Hz, 2H), 6.57 (d, *J*=9.0 Hz, 2H), 6.82 (d, *J*=8.7 Hz, 2H), 7.19 (d, *J*=8.7 Hz, 2H), 7.26 (d, *J*=8.9 Hz, 2H), 7.50 (d, *J*=4.0 Hz, 1H), 7.73 (d, J=4.0 Hz, 1 H), 8.13 ppm (s, 1 H); ¹³C NMR ([D₆]DMSO): δ =15.69, 26.97, 40.08, 108.54, 112.03, 112.24, 116.94, 118.44, 119.00, 122.54, 124.43, 126.70, 126.85, 130.28, 131.66, 136.26, 136.45, 138.09, 138.42, 138.80, 141.24, 149.03, 150.25, 164.25, 165.59 ppm; HRMS (APCI): m/z (%) calcd for C₂₉H₃₀N₅O₂S₁: 512.2120 [M^+ +H]; found: 512.2114; elemental analysis: calcd (%) for C₂₉H₂₉N₅O₂S: C 68.08, H 5.71, N 13.69; found: C 67.95, H 5.64, N 13.48.

(*E*)-3-(5-(4,5-Bis(7-(diphenylamino)-9,9-diethyl-9*H*-fluoren-2-yl)-1-ethyl-1*H*-imidazol-2-yl)thiophen-2-yl)-2-cyanoacrylic acid (4): Red solid (65%); ¹H NMR ([D₆]DMSO): δ =0.14 (*t*, *J*=7.3 Hz, 6H), 0.31 (*t*, *J*= 7.3 Hz, 6H), 1.20 (*t*, *J*=7.2 Hz, 3H), 1.51–1.69 (m, 4H), 1.84–2.30 (m, 4H), 4.06 (q, *J*=7.2 Hz, 2H), 6.88–6.90 (m, 1H), 6.97–7.10 (m, 15H), 7.24–7.35 (m, 10H), 7.55 (s, 1H), 7.57–7.64 (m, 4H), 7.29–7.85 (m, 3H), 8.19 ppm (s, 1H); ¹³C NMR ([D₆]DMSO): δ =8.26, 8.32, 15.42, 31.65, 40.08, 55.15, 55.83, 118.58, 118.67, 119.02, 119.83, 120.32, 120.60, 121.22, 122.54, 122.80, 123.17, 123.45, 125.27, 125.35, 128.11, 129.33, 129.43, 131.84, 132.29, 135.45, 136.11, 136.67, 138.06, 138.32, 139.02, 139.27, 141.55, 146.34, 147.19, 147.33, 147.35, 148.93, 150.19, 150.83, 151.22, 163.26 ppm; HRMS (APCI): *m*/*z* (%) calcd for C₇₁H₆₂N₅O₂S: 1048.4624 [*M*++H]; found: 1048.4629; elemental analysis: calcd (%) for C₇₁H₆₁N₅O₂S: C 81.34, H 5.86, N 6.68; found: C 81.20, H 5.72, N 6.63.

$(E) \hbox{-} 3 \hbox{-} (2 \hbox{-} (5 \hbox{-} (4, 5 \hbox{-} bis(4 \hbox{-} (diphenylamino)phenyl) \hbox{-} 1 \hbox{-} ethyl \hbox{-} 1 H \hbox{-} imidazol \hbox{-} 2 \hbox{-} 2 \hbox{-} 2 \hbox{-} (2 \hbox{-} (5 \hbox{-} (4, 5 \hbox{-} bis(4 \hbox{-} (diphenylamino)phenyl) \hbox{-} 1 \hbox{-} ethyl \hbox{-} 1 H \hbox{-} imidazol \hbox{-} 2 \hbox{-} 2$

yl)thiophen-2-yl)thiazol-5-yl)-2-cyanoacrylic acid (5): Red solid (70%); ¹H NMR ([D₆]DMSO): $\delta = 1.18$ (t, J = 7.2 Hz, 3H), 4.06 (q, J = 7.2 Hz, 2H), 6.86 (d, J = 8.7 Hz, 2H), 6.96–7.00 (m, 4H), 7.02–7.03 (m, 4H), 7.08–7.11 (m, 6H), 7.25–7.30 (m, 7H), 7.32–7.37 (m, 3H), 7.38 (d, J =6.8 Hz, 2H), 7.52 (d, J = 4.1 Hz, 1H), 7.82 (d, J = 4.0 Hz, 1H), 8.22 (s, 1H), 8.36 ppm (s, 1H); ¹³C NMR ([D₆]DMSO): $\delta = 15.62$, 40.08, 111.09, 118.45, 121.50, 122.62, 122.86, 123.24, 123.74, 123.91, 124.97, 125.62, 126.87, 128.64, 129.46, 129.70, 130.37, 131.90, 132.02, 135.34, 136.94, 137.05, 138.95, 145.51, 146.58, 147.10, 147.95, 151.40, 163.06, 163.79 ppm; HRMS (APCI): m/z (%) calcd for $C_{52}H_{39}N_6O_2S_2$: 843.2576 [M^+ +H]; found: 843.2579; elemental analysis: calcd (%) for $C_{52}H_{38}N_6O_2S_2$: C 74.08, H 4.54, N 9.97; found: C 73.72, H 4.49, N 9.85.

Assembly and Characterization of DSSCs

The photoanode used was the TiO2 thin film coated on FTO glass substrate^[26] with a dimension of 0.5×0.5 cm², and a platinized FTO was used as a counter electrode. The active area was controlled at a dimension of $0.6 \times 0.6 \text{ cm}^2$ by adhered polyester tape (3 M) with a thickness of 60 μ m on the Pt electrode. After heating the TiO₂ film to 80 °C, the film was taken out from the oven and dipped into the THF solution containing dye sensitizers $(3 \times 10^{-4} \text{ M})$ for at least 12 h. After rinsing with THF, the photoanode was placed on top of the counter electrode and tightly clipped together to form a cell. A 0.6×0.6 cm² cardboard mask was clipped onto the device to constrain the illumination area. Electrolyte was then injected into the space, and the cell was sealed with Torr Seal cement (Varian, MA. USA). The electrolyte was composed of lithium iodide (LiI, 0.5 m). iodine (I2, 0.05 M), and 4-tert-butylpyridine (TBP, 0.5 M) dissolved in acetonitrile. The photoelectrochemical characterizations on the solar cells were carried out using a modified light source, 300 W Xe lamp (Oriel 6258) equipped with a water-based IR filter and AM 1.5 filter (Oriel 81088). Photocurrent-voltage characteristics of the DSSCs were recorded with a potentiostat/galvanostat (CHI650B, CH Instruments, Inc., USA) at a light intensity of 100 mW cm⁻² measured by a thermopile probe (Oriel 71964). The light intensity was further calibrated by an Oriel reference solar cell (Oriel 91150) and adjusted to be 1.0 sun. The monochromatic quantum efficiency was recorded through a monochromator (Oriel 74100) at short circuit condition.

Measurement of Recombination Time Constant by Transient Photovoltage

The photovoltage transients of assembled devices were recorded with a digital oscilloscope (LeCroy, WaveSurfer 24Xs). Pulsed laser excitation was applied by a Q-switched Nd:YAG laser (Continuum, model Minilite II) with 1 Hz repetition rate at 532 nm and a 5 ns pulse width at half-height. The beam size was slightly larger than 0.5×0.5 cm² to cover the area of the device with an incident energy of 1 mJ cm⁻². The recombination lifetime of photoinjected electrons with oxidized dyes was measured

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by transient photovoltage at open circuit with the presence of LiI electrolyte (0.5 m). The average electron lifetime can be estimated approximately by fitting a decay of the open circuit voltage transient with $\exp(-t/\tau_{\rm R})$, in which, *t* is time and $\tau_{\rm R}$ is an average time constant before recombination.

Quantum Chemistry Computation

The predicted structures of the molecules were optimized by using B3LYP hybrid functional and 6-31G* basis sets. For each of the molecules, a number of conformational isomers were examined and the one with the lowest energy was used. For the excited states, we have employed the time-dependent density functional theory (TDDFT) with the B3LYP functional. All of the analyses were performed using Q-Chem 3.0 software.^[27] There exist a number of previous works that employed TDDFT to characterize excited states with charge-transfer character.^[28] In some cases, underestimation of the excitation energies was seen.^[29] Therefore, in the present work, we use TDDFT to characterize the extent of charge-shift, and avoid drawing conclusions from the excitation energy.

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- [1] a) B. O'Regan, M. Grätzel, *Nature* 1991, 353, 737; b) M. Grätzel, *Nature* 2001, 414, 338.
- [2] a) G. Yu, A. J. Heeger, J. Appl. Phys. 1995, 78, 4510; b) G. Yu, J. Gao, J. C. Hummelen, F. Wudl, A. J. Heeger, Science 1995, 270, 1789.
- [3] a) M. K. Nazeeruddin, A. Kay, L. Rodicio, R. Humphry-Baker, E. Müller, P. Liska, N. Vlachopoulos, M. Grätzel, J. Am. Chem. Soc. 1993, 115, 6382; b) M. Grätzel, J. Photochem. Photobiol. A 2004, 164, 3.
- [4] a) C.-Y. Chen, S.-J. Wu, C.-G. Wu, J.-G. Chen, K.-C. Ho, Angew. Chem. 2006, 118, 5954; Angew. Chem. Int. Ed. 2006, 45, 5822; b) C.-Y. Chen, S.-J. Wu, J.-Y. Li, C.-G. Wu, J.-G. Chen, K.-C. Ho, Adv. Mater. 2007, 19, 3888; c) F. Gao, Y. Wang, J. Zhang, D. Shi, M. Wang, R. Humphry-Baker, P. Wang, S. M. Zakeeruddin, M. Grätzel, Chem. Commun. 2008, 2635; d) C.-Y. Chen, J.-G. Chen, S.-J. Wu, J.-Y. Li, C.-G. Wu, K.-C. Ho, Angew. Chem. 2008, 120, 7452; Angew. Chem. Int. Ed. 2008, 47, 7342.
- [5] a) S. Ito, M. Zakeeruddin, R. Hummphrey-Baker, P. Liska, R. Charvet, P. Comte, M. K. Nazeeruddin, P. Péchy, M. Takata, H. Miura, S. Uchida, M. Grätzel, *Adv. Mater.* 2006, *18*, 1202; b) G. Zhang, H. Bala, Y. Cheng, D. Shi, X. Lv, Q. Yu, P. Wang, *Chem. Commun.* 2009, 2198.
- [6] a) K. Hara, K. Sayama, Y. Ohga, A. Shinpo, S. Suga, H. Arakawa, *Chem. Commun.* 2001, 569; b) K. Hara, M. Kurashige, Y. Dan-oh, C. Kasada, A. Shinpo, S. Suga, K. Sayama, H. Arakawa, *New J. Chem.* 2003, 27, 783.
- [7] a) T. Horiuchi, H. Miura, S. Uchida, *Chem. Commun.* 2003, 3036;
 b) T. Horiuchi, H. Miura, S. Uchida, *J. Photochem. Photobiol. A* 2004, *164*, 29; c) T. Horiuchi, H. Miura, K. Sumioka, S. Uchida, *J. Am. Chem. Soc.* 2004, *126*, 12218.
- [8] A. Ehret, L. Stuhl, M. T. Spitler, J. Phys. Chem. B 2001, 105, 9960.
- [9] a) Z.-S. Wang, F.-Y. Li, C.-H. Huang, *Chem. Commun.* 2000, 2063;
 b) Q.-H. Yao, F.-S. Meng, F.-Y. Li, H. Tian, C.-H. Huang, *J. Mater. Chem.* 2003, 13, 1048.
- [10] a) A. C. Khazraji, S. Hotchandani, S. Das, P. V. Kamat, J. Phys. Chem. B 1999, 103, 4693; b) K. Sayama, K. Hara, N. Mori, M. Satsuki, S. Suga, S. Tsukagoshi, Y. Abe, H. Sughara, H. Arakawa, Chem. Commun. 2000, 1173; c) K. Sayama, S. Tsukagoshi, T. Mori, K. Hara, Y. Ohga, A. Shinpou, Y. Abe, S. Suga, H. Arakawa, Sol. Energy Mater. Sol. Cells 2003, 80, 47.

- [11] a) S. Ferrere, A. Zaben, B. A. Gregg, J. Phys. Chem. B 1997, 101, 4490; b) S. Ferrere, B. A. Gregg, New J. Chem. B 2002, 26, 1155.
- [12] K. Hara, T. Horiguchi, T. Kinoshita, K. Sayama, H. Sugihara, H. Arakawa, *Chem. Lett.* 2000, 29, 316.
- [13] M. Liang, W. Wu, F. Cai, P. Chen, B. Peng, J. Chen, Z. Li, J. Phys. Chem. C 2007, 111, 4465.
- [14] a) T. Kitamura, M. Ikeda, K. Shigaki, T. Inoue, N. A. Anderson, X. Ai, T. Lian, S. Yanagida, *Chem. Mater.* 2004, *16*, 1806; b) K. Hara, T. Sato, R. Katoh, A. Furube, T. Yashihara, M. Murai, M. Kurashige, S. Ito, A. Shinpo, S. Suga, H. Arakawa, *Adv. Funct. Mater.* 2005, *15*, 246.
- [15] a) M. Velusamy, K. R. J. Thomas, J. T. Lin, Y.-C. Hsu, K.-C. Ho, Org. Lett. 2005, 7, 1899; b) K. R. J. Thomas, J. T. Lin, Y.-C. Hsu, K.-C. Ho, Chem. Commun. 2005, 4098; c) D. P. Hagberg, T. Edvinsson, T. Marinado, G. Boschloo, A. Hagfeldt, L. Sun, Chem. Commun. 2006, 2245; d) S.-L. Li, K.-J. Jiang, K.-F. Shao, L.-M. Yang, Chem. Commun. 2006, 2792; e) N. Koumura, Z.-S. Wang, S. Mori, M. Miyashita, E. Suzuki, K. Hara, J. Am. Chem. Soc. 2006, 128, 14256; f) S. Kim, J. K. Lee, S. O. Kang, J. Ko, J.-H. Yum, S. Fantacci, F. De Angelis, D. Di Censo, M. K. Nazeeruddin, M. Grätzel, J. Am. Chem. Soc. 2006, 128, 16701.
- [16] a) M.-S. Tsai, Y.-C. Hsu, J. T. Lin, H.-C. Chen, C.-P. Hsu, J. Phys. Chem. C 2007, 111, 18785; b) K. R. J. Thomas, Y.-C. Hsu, J. T. Lin, K.-M. Lee, K.-C. Ho, C.-H. Lai, Y.-M. Cheng, P.-T. Chou, Chem. Mater. 2008, 20, 1830; c) Y.-S. Yen, Y.-C. Hsu, J. T. Lin, C.-W. Chang, C.-P. Hsu, D.-J. Yin, J. Phys. Chem. C 2008, 112, 12557; d) S.-T. Huang, Y.-C. Hsu, Y.-S. Yen, H. H. Chou, J. T. Lin, C.-W. Chang, C.-P. Hsu, C. Chiitang Tsai, D.-J. Yin, J. Phys. Chem. C 2008, 112, 19739; e) J. T. Lin, P.-C. Chen, Y.-S. Yen, Y.-C. Hsu, H.-H. Chou, M.-C. P. Yeh, Org. Lett. 2009, 11, 97.
- [17] a) X. R. Bu, H. Li, E. A. Mintz, *Tetrahedron Lett.* **1996**, *37*, 7331;
 b) J. Santos, E. A. Mintz, O. Zehnder, C. Bosshard, X. R. Bu, P. Günter, *Tetrahedron Lett.* **2001**, *42*, 805; c) K. Feng, L. De Boni, L. Misoguti, C. R. Mendonça, M. Meador, F.-L. Hsu, X. R. Bu, *Chem. Commun.* **2004**, 1178.
- [18] a) L.-T. Cheng, W. Tam, S. H. Stevenson, G. R. Meredith, G. Rikken, S. R. Marder, J. Phys. Chem. 1991, 95, 10631; b) L.-T. Cheng, W. Tam, S. R. Marder, A. E. Stiegman, G. Rikken, C. W. Spangler, J. Phys. Chem. 1991, 95, 10643.
- [19] M. K. Nazeeruddin, P. Péchy, T. Renouard, S. M. Zakeeruddin, R. Humphrey-Baker, P. Comte, P. Liska, L. Cevey, E. Costa, V. Shklover, L. Spiccia, G. B. Deacon, C. A. Bignozzi, M. Grätzel, J. Am. Chem. Soc. 2001, 123, 1613.
- [20] Z. E. Wang, K. Hara, Y. Dan-oh, C. Kasada, A. Shinpo, S. Suga, H. Arakawa, H. Sugihara, J. Phys. Chem. B 2005, 109, 3907.
- [21] K. Hara, T. Sato, R. Katoh, A. Furube, Y. Ohga, A. Shinpo, S. Suga, K. Sayama, H. Sugihara, H. Arakawa, J. Phys. Chem. B 2003, 107, 597.
- [22] A. Hagfeldt, M. Grätzel, Chem. Rev. 1995, 95, 49.
- [23] M. K. Nazeeruddin, S. M. Zakeeruddin, R. Humphry-Baker, M. Jirousek, P. Liska, N. Vlachopoulos, V. Shklover, C. H. Fisher, M. Grätzel, *Inorg. Chem.* **1999**, *38*, 6298.
- [24] N. Kopidakis, K. D. Benkstein, J. van de Lagemaat, A. J. Frank, J. Phys. Chem. B 2003, 107, 11307.
- [25] J. G. Lombardino, E. H. Wiseman, J. Med. Chem. 1974, 17, 1182.
- [26] a) C. Y. Huang, Y.-C. Hsu, J. G. Chen, V. Suryanarayanan, K. M. Lee, K.-C. Ho, *Sol. Energy Mater. Sol. Cells* **2006**, *90*, 2391; b) K. M. Lee, V. Suryanarayanan, K.-C. Ho, *Sol. Energy Mater. Sol. Cells* **2006**, *90*, 2398.
- [27] a) N. Hirata, J.-J. Lagref, E. J. Palomares, J. R. Durrant, M. K. Nazeeruddin, M. Grätzel, D. Di Censo, *Chem. Eur. J.* 2004, *10*, 595; b) J. R. Durrant, S. A. Haque, E. Palomares, *Chem. Commun.* 2006, 3279; c) Y. Shao, L. F. Molnar, Y. Jung, J. Kussmann, C. Ochsenfeld, S. T. Brown, A. T. B. Gilbert, L. V. Slipchenko, S. V. Levchenko, D. P. O'Neill, R. A. DiStasio Jr., R. C. Lochan, T. Wang, G. J. O. Beran, N. A. Besley, J. M. Herbert, C. Y. Lin, T. V. Voorhis, S. H. Chien, A. Sodt, R. P. Steele, V. A. Rassolov, P. E. Maslen, P. P. Korambath, R. D. Adamson, B. Austin, J. Baker, E. F. C. Byrd, H. Dachsel, R. J. Doerksen, A. Dreuw, B. D. Dunietz, A. D. Dutoi,

T. R. Furlani, S. R. Gwaltney, A. Heyden, S. Hirata, C.-P. Hsu, G. Kedziora, R. Z. Khalliulin, P. Klunzinger, A. M. Lee, M. S. Lee, W. Z. Liang, I. Lotan, N. Nair, B. Peters, E. I. Proynov, P. A. Pieniazek, Y. M. Rhee, J. Ritchie, E. Rosta, C. D. Sherrill, A. C. Simmonett, J. E. Subotnik, H. L. Woodcock, III., W. Zhang, A. T. Bell, A. K. Chakraborty, Phys. Chem. Chem. Phys. **2006**, *8*, 3172.

[28] a) H. M. Vaswani, C.-P. Hsu, M. Head-Gordon, G. R. Fleming, J. Phys. Chem. B 2003, 107, 7940; b) Y. Kurashige, T. Nakajima, S. Kurashige, K. Hirao, Y. Nishikitani, J. Phys. Chem. A 2007, 111, 5544.

[29] A. Dreuw, M. Head-Gordon, J. Am. Chem. Soc. 2004, 126, 4007.

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