Organic Dyes Containing Fluorene Decorated with Imidazole Units for Dye-Sensitized Solar Cells

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Supporting Information

ABSTRACT: New organic dyes containing fluorene functionalized with two imidazole chromophores as donors and cyanoacrylic acid acceptors have been synthesized and successfully demonstrated as sensitizers in nanocrystalline TiO_2 -based dye-sensitized solar cells (DSSCs). The monoimidazole analogues were also synthesized for comparison. The Sommelet reaction of bromomethylated 2-bromo-9,9-diethyl-9H-fluorene produced the key precursor 7-bromo-9,9-diethyl-9H-fluorene-2,4-dicarbaldehyde required for the preparation of imidazole-functionalized fluorenes. Since the dyes possess weak donor segment, the electronrichness of the conjugation pathway dictated the optical, electrochemical, and photovoltaic properties of the dyes. The dyes served as sensitizers in DSSC and exhibited moderate efficiency up to 3.44%. The additional imidazole present on the fluorene has been found to retard the electron



recombination due to the bulkier hydrophobic environment and led to high open-circuit voltage in the devices.

INTRODUCTION

Organic dyes suitable for application as sensitizers in dyesensitized solar cells $(DSSCs)^{\dagger}$ and as donors or acceptors in bulk heterojunction solar cells² have been intensively searched in recent years owing to the demand for renewable energy technologies. The molecular composition of the organic dyes plays an important role in the performance of DSSCs. The structural components of organic sensitizers suitable for DSSCs can be divided into three categories: donor (D), π -linker, and acceptor with an anchoring (A) group. A large number of organic dyes containing nitrogenous electron donors such as triphenylamine,³ carbazole,⁴ phenothiazine,⁵ amine-substituted coumarin,⁶ indoline,⁷ thienoindole,⁸ and fluoreneamine⁹ have been used with great success in DSSCs. The π -conjugated linker in a D- π -linker-A system besides being a part of the light absorbing chromophore functions as a molecular wire for electron transfer from the donor to acceptor. Various aromatic/ heteroaromatic units such as naphthalene,¹⁰ dihydrophenan-threne,¹¹ fluorene,¹² spirobifluorene,¹³ anthracene,¹⁴ oligothio-phene,¹⁵ thienothiophene,¹⁶ dithienothiophene,¹⁷ carbazole,¹⁸ phenoxazine,¹⁹ phenothiazine,²⁰ benzothiadiazole,²¹ and benzotriazole²² have been explored as π -linkers between the electron donor and electron acceptor for tuning the absorption, electrochemical, and other characteristics required for DSSC performance. Triarylamine-containing imidazoles²³ or fused aromatic imidazoles such as phenanthromidazole²⁴ and pyrenoimidazole²⁵ have also been found to serve as promising donors when connected with oligothiophene units.

Fluorene-derived compounds are well documented in the literature as promising electro-optical materials due to their

striking photophysical and electrochemical properties as well as their admirable hole-transporting abilities.²⁶ Due to their high molar extinction coefficients and efficient light harvesting properties, fluorene-based compounds, especially thienylfluorene-bridged dyes, exhibited significant power conversion efficiencies in DSSCs.²⁷ Though the 2,7-disubstituted fluorene derivatives have been explored widely as constituents for electronic applications, the use of 2,4,7-trisubstituted fluorene derivatives is limited.²⁸ Also, to the best of our knowledge, fluorenes tethered to multiple imidazole chromophores have not been utilized as donors in the design of organic dyes suitable for DSSCs. In this paper, we present new organic dyes developed on a fluorene core featuring two imidazole units (Figure 1). For comparison, we have also synthesized dyes containing one imidazole unit (IF1 and IF2). The substituents on the imidazole nucleus were varied from phenyl to fluorene. Additional imidazole on the C4 of fluorene drastically affects the absorption and, consequently, the photovoltaic performance. It is presumed that the slight nonplanarity induced in the fluorene unit due to crowded functionalization is responsible for the blue-shifted absorption. However, the presence of bithiophene unit in the conjugation pathway has been found to supplement the donor-acceptor interactions with its electron richness.

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Figure 1. Structures of the organic sensitizers.





RESULTS AND DISCUSSION

Synthesis and Characterization. For the synthesis of the dyes we required the aldehyde 2a and the diketone 4 (Scheme 1). The diketone 4 was synthesized by a two-step synthetic sequence involving Sonogashira coupling²⁹ and iodine-mediated oxidation in dimethyl sulfoxide.³⁰ The dialdehyde 2a was obtained by the exhaustive bromomethylation followed by Sommelet reaction.³¹ In addition to the required dialdehyde 2a, the monoaldehyde 2b and the trialdehyde 2c were also obtained in trace amounts from this reaction sequence. The target dyes IF1-IF6 were synthesized by a four-step synthetic protocol shown in Scheme 2. First, the imidazole-tethered fluorene fragment was constructed from 7-bromo-9,9-diethyl-9H-fluorene-2,4-dicarbaldehyde or 7-bromo-9,9-diethyl-9H-fluorene-2-carbaldehyde and the corresponding diketone in a multicomponent reaction in the presence of ammonium acetate. The -NH imidazoles (5 and 8) were then alkylated to increase the solubility either by using phase-transfer catalysis or using K₂CO₃ in DMF. The aldehyde functionality was introduced by a Stille coupling³² reaction of the bromides **6** and 9 with the tin derivative of the protected thiophene and bithiophene aldehydes followed by acidic hydrolysis. Finally, these aldehydes were converted to the desired cyanoacrylic acid derivatives IF1-IF6 by Knoevenagel reaction.³³ All the new compounds were well characterized by IR, NMR, and highresolution mass spectral analysis. The spectral data were

consistent with the proposed structures. The dyes are reasonably soluble in common organic solvents such as dichloromethane, tetrahydrofuran, acetonitrile, dimethylformamide, etc.

Photophysical Properties. The absorption spectra recorded for the dyes in tetrahydrofuran are displayed in Figure 2 and relevant data summarized in Table 1. All the dyes exhibited two or three prominent absorptions. The absorption bands at the higher energy side of the profile are attributed to the localized $\pi - \pi^*$ transitions. The longer wavelength absorption peak appearing in the range 420-460 nm for the dyes is primarily arising from the charge transfer (CT) from the imidazole donor to the cyanoacrylic acid acceptor (vide infra). Increasing the conjugation pathway by the insertion of additional thiophene has been found to be beneficial for shifting the CT absorption to the longer wavelength region. For the 4,5-diphenylimidazole-functionalized dyes (IF1, IF2, IF3, and IF4), the intensity of the CT transition diminished on elongation of conjugation. A similar effect was observed on increasing the number of imidazole units on a fluorene nucleus (compare IF2 and IF4). However, for the dyes containing a 4,5-difluorenylimidazole unit, elongation of conjugation in the bridge increased the molar extinction coefficient for the CT transition. We have recently observed that the polysubstitution on the fluorene core affects the planarity of the fluorene ring.³⁴ It is probable that incorporation of the additional imidazole on

Scheme 2. Synthesis of the Dyes





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

the fluorene core disturbs the planarity of the fluorene ring and affects the electronic interaction between the donor and

acceptor fragments. Such an effect is more severely manifested for the much bulkier 4,5-difluorenylimidazole group. However, on elongation of conjugation by the insertion of bithiophene between the fluorene and cyanoacrylic acid units in IF6 a reversal in the trend is observed. It is more likely due to the increased electron-richness in the conjugation bridge which facilitates the donor-acceptor interactions. Additionally, the dyes containing 4,5-difluorenylimidazole possessed intense absorption peaks in the shorter wavelength region due to the fluorene localized $\pi - \pi^*$ electronic transitions, but the CT transition did not show wavelength variations attributable to the changes in the imidazole chromophore (compare, for instance, IF2, IF4, and IF6).

The charge-transfer character of the longer wavelength absorption was established by the solvatochromism and theoretical calculations (vide infra). All the dyes showed redshifted CT peak for the nonpolar solvents such as toluene, DCM, etc. and blue-shifted peak for the solvents such as ACN, DMF, and methanol (Figure 3, Table 2). The blue-shift may be explained by considering a relatively effective solvation by the

Table	1.	Optical	and	Electrochemical	Pro	perties	of	the	Dy	yes	in	THF	
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		$\lambda_{\rm abs}$, nm ($\varepsilon \times 10^3$,						
dye	THF	THF + TFA	THF + TEA	TiO ₂	$\lambda_{ m em} \ (nm)$	$\begin{array}{c} E_{\mathrm{ox}}{}^{a} \\ \mathrm{(V)} \end{array}$	${{E_{ox}}^{*}}^{b}$ (V)	$\frac{E_{\rm HOMO}}{({\rm eV})} \frac{E_{\rm LUMO}}{c}$
IF1	425 (78.3), 291 (40.5)	415 (82.8), 293 (32.6), 276 (32.3)	410 (73.6), 287 (37.8)	471	558	0.99	-0.81	5.79/3.22
IF2	458 (56.8), 356 (35.6)	452 (59.4), 354 (35.0), 279 (29.2)	436 (55.1), 363 (33.7), 274 (29.9)	533	562	1.02	-0.61	5.82/3.42
IF3	424 (45.3), 366 (38.9)	413 (48.9)	408 (43.9), 376 (45.3)	466	543	0.94	-0.91	5.74/3.12
IF4	457 (32.1), 362 (18.5)	451 (34.2), 358 (15.7)	431 (32.9), 275 (26.2)	509	558	0.97	-0.68	5.77/3.35
IF5	425 (15.5), 334 (56.1)	411 (19.2), 320 (56.3)	334 (55.4), 308 (50.1)	461	530	0.95	-0.98	5.75/3.05
IF6	459 (37.9), 333 (58.0)	451 (40.3)	442 (36.4), 333 (56.9)	512	562	0.96	-0.68	5.76/3.35

^{*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 E_{0-0} (band gap) is derived from the optical edge and reported vs NHE. ^{*c*}Deduced from the equation $E_{HOMO} = E_{ox} + 4.8$ and $E_{LUMO} = E_{HOMO} - E_{0-0}$.



Figure 3. Absorption spectra of (a) IF1 and (b) IF3 recorded in different solvents.

Table 2. Absorption and Emission Spectral Data for the Dyes Recorded in Different Solver
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	λ_{abs} (nm)							$\lambda_{\rm em}$ (nm)						
dye	Tol	DCM	CHCl ₃	THF	DMF	ACN	MeOH	Tol	DCM	CHCl_3	THF	DMF	ACN	MeOH
IF1	426, 337	428, 292	432, 294	425, 291	395, 281	391, 282	397, 282	536	545	562	558	502	505	492
IF2	459, 368	464, 355, 277	470, 356, 277	458, 356	419	427, 355, 272	427, 348, 271	544	568	569	562	521	515	543
IF3	410, 380	410, 364, 283, 261	413, 364, 284	424, 366, 287	380, 275	373	395, 374	495	509	512	543	492	498	487
IF4	445	458, 366, 273	464, 363, 273	457, 362	427	425, 264	426, 260	532	564	566	558	505	507	523
IF5	421, ^a 333, 309	428, ^a 333, 310	429, ^a 332, 310, 281	425, ^a 334, 309, 280	395, ^a 335, 309, 280	380, ^a 331, 308, 279	409, ^a 323, 309, 279	489	518	510	530	497	491	492
IF6	453, 329, 309	449, 329, 309, 280	463, 329 310, 281	459, 333, 308, 280	428, 330, 309, 280	422, 327, 308, 279	430, 321, 309, 278	545	553	566	562	506	497	536
^a Shou	lder.													

polar solvents or a zwitterionic character. It has been well established that the $D-\pi-A$ organic sensitizers exist in deprotonated form in solution, particularly in polar solvents.³⁵ In the present dyes, since the imidazole nitrogen can be easily protonated, the dyes may assume a zwitterionic structure with a protonated imidazole and deprotonated carboxylate sites. Such a configuration may also result in a blue shift in the absorption (vide supra). Unusual red-shifted absorption observed in dichloromethane and chloroform when compared to toluene may be originating from the stabilization due to the fast

rearrangement of polarizable electrons during electronic excitation.³⁶ Interestingly, the dyes containing one imidazole chromophore (IF1 and IF2) displayed similar absorption profiles in toluene and THF, but the dyes containing two imidazole chromophores (IF3–IF6) displayed hypsochromic absorption in toluene when compared to that of THF. The ineffective solvation of the bulkier bis-imidazoles by the toluene may be the reason for such deviation. Additionally, the donor–acceptor interactions could be attenuated by the addition of trifluoroacetic acid (TFA) or triethylamine (TEA) to the dye

solutions. Addition of TFA or TEA resulted in a blue-shifted absorption, but the magnitude of shift is larger for TEA (Figure 4). Triethylamine deprotonates the carboxylic acid unit while



Figure 4. Absorption spectra of IF4 recorded in THF on addition of TFA/TEA.

the TFA protonates the imidazole unit. Deprotonation of the carboxylic acid will reduce the acceptor strength while the protonation of imidazole will diminish the donor strength. In both cases, donor-acceptor interaction in the dye is decreased substantially which manifests as a blue shift in the absorption spectrum.

All the dyes showed red-shifted absorption profile (Figure 5) when adsorbed on TiO_2 as compared to the corresponding



Figure 5. Absorption spectra for the dyes anchored on the TiO₂ film.

spectra recorded in solution. The red-shifted absorption may be originating from the aggregation of the dyes at the TiO_2 surface or due to the use of thicker TiO_2 layer,³⁷ which is opposite to the blue-shift observed for most of the organic dyes because of partial deprotonation of the carboxylic acid unit due to the dye– TiO_2 interaction.³⁸ The fluorenylbithiophene-bridged dyes (IF2, IF4 ,and IF6) showed more stacking as evidenced by broader and more red-shifted absorption on TiO_2 film than the fluorenyl-thiophene-bridged dyes (IF1, IF3, and IF6). Despite the presence of nonplanar moieties in the donor side, the existence of intermolecular dye interactions suggest the

requirement of twisted π -bridge to deter the aggregation at the surface of the TiO₂.

All the compounds displayed a weak emission with characteristic colors ranging from green to orange (Figure 6).



Figure 6. Emission spectra of the dyes recorded in THF.

Similar to the absorption, insertion of a thiophene unit led to red-shifted emission. However, the results are more pronounced for bis-imidazoles (IF3-IF6) than that of mono-imidazoles (IF1 and IF2). Further, the negative solvatochrom-ism observed in the fluorescence also confirmed the charge-transfer nature of the excited state (Table 2).

Electrochemical Properties. In the present dyes, there are no easily oxidizable chromophores. Thus, the electron removal must be difficult and highly dependent on the nature of the conjugation backbone which altered the donor-acceptor interactions and the oxidation potentials. As expected, all the dyes displayed an irreversible oxidation wave (Table 1). The bithiophene derivatives (IF2, IF4, and IF6) possessed a slightly more positive oxidation waves when compared to the corresponding thiophene derivatives (IF1, IF3, and IF5) (Table 1). If the electron-richness alone is considered then the bithiophene derivatives are expected to display more facile oxidation. However, the contradictory observation suggests a strong donor-acceptor interaction in the bithiophene derivatives which in turn could make the molecule difficult to undergo oxidation. This behavior is consistent with the optical properties of the dyes where the bithiophene derivatives showed pronounced donor-acceptor interactions. In addition, the oxidation potentials of the dyes containing two imidazoles (IF1-IF6) were found to be cathodically shifted compared to those observed for the comparable monoimidazoles (IF1 and IF2). This could be attributed to the slight conjugation extension arising from the additional imidazole unit. The excited-state oxidation potentials (E_{ox}^*) of the dyes are more negative (-0.61 to -0.91 V versus NHE) than the conduction band edge of TiO₂ (-0.5 V versus NHE),³⁹ which ensures an energetically favorable electron injection from the excited dye to TiO_2 (Figure 7). The ground-state oxidation potentials of the dyes are more positive (1.71-1.79 V versus NHE) than that of the I^-/I_3^- redox couple (0.4 V versus NHE),⁴⁰ which suggests a thermodynamically favorable dye regeneration by the electrolyte. Moreover, the bithiophene-containing dyes (IF2, IF4, and IF6), having closer excited-state oxidation potential with the TiO₂ conduction band, would ensure better electron



Figure 7. Comparison of the ground- and excited-state oxidation potentials for the dyes.

collection, higher photocurrent, and better efficiency (vide infra).

Theoretical Calculations. To gain more insight into the electronic properties of the compounds, density functional theoretical (DFT) calculations were performed for the dyes containing phenyl substituents (IF1-IF4) on the imidazole nucleus with the Gaussian 09 program package.⁴¹ The structures were optimized using the B3LYP functional and 6-31G(d,p) basis set. Since the B3LYP functional was not suitable for the charge-transfer excitations in the donor–acceptor compounds, we have used the range-separated hybrid functional LC-BLYP to compute the vertical excitation energies and their orbital contributions (Table 3). The electron density

Table 3. Computed Vertical Excitation Wavelengths and Their Orbital Contribution for the Dyes IF1–IF4 Using LC-BLYP/6-31G(d,p) for THF with IEFPCM Model

dye	λ_{abs} (nm)	oscillator strength	assignment
IF1	368.5	1.4711	HOMO \rightarrow LUMO (32%)
			HOMO-1 \rightarrow LUMO (47%)
	279.7	0.4041	HOMO \rightarrow LUMO+1 (44%)
			HOMO-2 \rightarrow LUMO (16%)
IF2	405.1	1.8017	HOMO \rightarrow LUMO (44%)
			HOMO-1 \rightarrow LUMO (34%)
	299.9	0.4750	HOMO \rightarrow LUMO+1 (49%)
			HOMO-2 \rightarrow LUMO (17%)
IF3	369.6	1.5152	HOMO \rightarrow LUMO (34%)
			HOMO-1 \rightarrow LUMO (46%)
	286.6	0.5626	HOMO \rightarrow LUMO+1 (45%)
			HOMO-3 \rightarrow LUMO (16%)
IF4	405.1	1.8136	HOMO \rightarrow LUMO (48%)
			HOMO-1 \rightarrow LUMO (22%)
	300.4	0.4300	HOMO \rightarrow LUMO+1 (50%)
			HOMO-3 \rightarrow LUMO (17%)

distribution in HOMO is primarily located at the imidazole at C2 and spread over the fluorene and thiophene linker (Figure 8). In the case of **IF3** and **IF4**, the auxiliary imidazole unit at C4 is considerably tilted from the fluorene core $(65-70^\circ)$ (Figure 9), and it contributed to the construction of HOMO-1. In the case of monoimidazole derivatives, the HOMO-1 is also contributed by the C2 imidazole and the conjugation framework. The electron density of the LUMO is delocalized

on the anchoring group and the π -bridge. Thus, the absorption leading to the electronic excitation from the HOMO or HOMO-1 to the LUMO orbital can constitute to the charge transfer from the imidazole-donor unit to the cyanoacrylic acid acceptor. This favorable condition may ensure the charge separation in the molecule on light absorption and subsequent electron injection into the conduction band of TiO₂ for the monoimidazole derivatives IF1 and IF2. However, for the diimidazole dyes (IF3 and IF4) the major contribution for the charge-transfer transition arises from the HOMO-1 to LUMO excitation. Since the HOMO-1 is located on the nonconjugated imidazole segment in these dyes, the corresponding excitation may not produce the desirable charge migration. In addition, the tilting between the fluorene and thiophene units explains the blue-shifted absorption observed for the dyes IF1, IF3, and IF5, but the bithiophene unit assumes near-planar arrangement.

The theoretical predictions about the absorption peaks and their orbital contributions are listed in Table 3. From the computational results, the longer wavelength absorption originates from the HOMO to LUMO electronic excitation which involves the charge migration from the imidazole unit to the cyanoacrylic acid acceptor. The trends observed in the solution absorption wavelengths are consistent with the theoretical predictions. The bithiophene dyes (IF2 and IF4) possessed the red-shifted absorption when compared to their thiophene analogues (IF1 and IF3). However, the molar extinction coefficients observed for the bithiophene derivatives (IF2 and IF4) are not complying with the theoretical predictions. The relatively low extinction coefficients observed for the bithiophene derivatives (IF2 and IF4) when compared to their corresponding thiophene analogues (IF1 and IF3) may originate from their poor solubility. It is interesting to note that the fluorene derivatives IF5 and IF6 show molar extinction coefficients in keeping with the expectations. The fluorene dyes are highly soluble due to the presence of solubilizing alkyl groups on the fluorene nucleus.

Photovoltaic Properties. The performance of DSSCs with the new dyes (IF1-IF6) as sensitizers was evaluated under standard conditions and the relevant parameters listed in Table 4. In general, the bithiophene-containing dyes (IF2, IF4, and IF6) exhibited higher device efficiencies than their thiophene analogues (IF1, IF3, and IF5) (Figure 10). This difference originated mainly from the variation in the photocurrent density. The higher J_{SC} and IPCE values observed for the bithiophene dyes are consistent with their absorption properties.⁴² The overall power conversion efficiency of the devices fall in the range 1.39-3.44%. In addition, the additional imidazole on the C4 position of the fluorene led to reduced photocurrent density (for instance compare IF1 with IF3). This is probably attributable to the larger size of the dyes due to the additional imidazole unit which may reduce the dye-loading on the surface of TiO₂ and consequently the light-harvesting propensity. The low photocurrent density may arise due to poor interaction between the dye and TiO₂ because of the larger bulkiness of the dyes containing two imidazole units.

Though the bithiophene dyes exhibited comparatively large photocurrent density when compared to their thiophene analogues, the trends in the V_{OC} values were found to be dependent on the nature of the substituents on the imidazole unit. For the dyes containing 4,5-diphenylimidazole units (IF1–IF4), the V_{OC} values for the thiophene derivatives (IF1 and IF3) are larger than those of the corresponding bithiophene derivatives (IF2 and IF4), but the dyes containing

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Figure 8. Electronic distribution in the selected molecular orbitals of the dyes IF1and IF3.



Figure 9. Calculated interplanar angles (deg) between various aromatic segments and cyanoacrylic acid plane in the optimized geometries of the dyes IF1, IF2, IF3, and IF4.

 Table 4. Photovoltaic Parameters of the DSSCs Fabricated

 Using the Dyes^a

dye	η (%)	V _{OC} (V)	$\int_{\rm SC} (\rm mA~cm^{-2})$	ff	$\stackrel{b,c}{(\Omega)}$	$\stackrel{R_{ ext{ct2}}{(\Omega)}^{c}}{R_{ ext{ct2}}}$	$ au_{e}^{c}$ (ms)
IF1	2.42	0.61	5.78	0.68	16.00	34.35	8.41
IF2	3.44	0.57	9.25	0.66	10.20	23.13	1.16
IF3	1.67	0.60	4.16	0.68	9.49	46.02	4.63
IF4	2.75	0.58	7.13	0.67	14.00	28.13	2.09
IF5	1.39	0.57	3.76	0.65	5.55	55.03	2.55
IF6	3.27	0.63	7.88	0.66	21.60	27.81	4.63
^a Meas	ured ur	ider an	irradiation	of 100	mW cm	⁻² (AM	1.5 G

simulated sunlight) at room temperature. ^bMeasured in the dark. ^cEstimated with the aid of electrochemical impedance spectroscopy (EIS) measurements.

4,5-difluoreneylimidazole units exhibited a reverse trend. Among them, the bithiophene dye (IF6) displayed larger $V_{\rm OC}$ in the device than the thiophene analogue (IF5). In order to probe these differences, the electrochemical impedance spectral measurements were performed for the dyes. The Nyquist plots observed for the devices under illumination and dark conditions are shown in Figure 11. Under dark conditions, as there is no photocurrent generation, the resistance of the electron recombination can be estimated from the interfacial kinetic parameters. The Nyquist plot measured under dark condition (Figure 11a) exhibited three semicircles corresponding to the TiO₂/dye/electrolyte interfacial electron recombination kinetics. The prominent semicircle observed at the midfrequency is attributed to the electron recombination resistance at the TiO₂/electrolyte interface. The larger the radius of the semicircle, the smaller is the rate for electron recombination at the interface. The resistance of the recombination $(R_{\rm rec})$ at the TiO_2 /electrolyte assumed the order for the similar dyes as IF1 > IF2, IF3 < IF4, and IF5 < IF6. The enhanced electron recombination rate is attributed to the dye characteristics such as aggregation propensity and complex formation with iodide in the electrolyte. Factors that retard aggregation between the dyes and complex formation with iodide will reduce the electron recombination rate. Smaller recombination resistance observed for IF2, IF3, and IF5 indicated a pronounced electron recombination rate for them when compared to the structurally similar dyes IF1, IF4, and IF6 respectively. On this basis, one would expect comparatively high V_{OC} for the dyes IF1, IF4, and IF6. This is in agreement with the dye pairs IF1/IF2 and IF5/ IF6, but the order is reversed for the dye pair IF3/IF4. The relatively large amount of electrons in the conduction band of TiO_2 could also give rise to high V_{OC} . The electron density in the conduction band of TiO_2 may be a result of better charge collection efficiency in the corresponding device. In order to probe the relative charge collection rate in the devices, electrochemical impedance spectra were measured under illumination conditions (Figure 11b). The charge transport



Figure 10. (a) I-V and (b) IPCE plots for the DSSCs using the dyes 7a-d, 11a, and 11b.



Figure 11. Nyquist plots for the DSSCs under (a) dark and (b) illumination conditions.

resistance (R_{ct2}) is small for the bithiophene dyes (IF2, IF4, and IF6) relative to the thiophene analogues (IF1, IF3, and IF5) (Figure 11b). This suggests an effective electron collection for the bithiophene dyes. This observation is in agreement with the larger J_{SC} values observed for the bithiophene dyes. Interestingly, the bithiophene dyes possessed comparatively low lying E_{ox}^* , which probably led to an effective electronic coupling between the excited dyes and the TiO₂ and facilitated electron injection.

Additionally, the electron lifetimes (τ_e) of the DSSCs were large for the dyes IF1, IF3, and IF6 when compared to the analogous dyes IF2, IF4, and IF5, respectively (Figure 12). The larger electron lifetime observed for the former dyes is consistent with their superior $V_{\rm OC}$ values. On the basis of the EIS studies, the better performance of the bithiophene derivatives IF2 and IF6 is attributed to their comparatively good light-harvesting properties, the favorable electron injection, and the effective retardation of electron recombination.

CONCLUSIONS

In summary, we have synthesized new organic dyes containing imidazole and fluorene units. The D $-\pi$ -A configuration of the dyes was fulfilled by the thienylfluorene π -linker and cyanoacrylic acid acceptor. The photophysical and photovoltaic properties were investigated after structural variation from



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Figure 12. Bode phase plots of the DSSCs under the illumination of 100 mW cm⁻².

linear dyes to branched dyes featuring bis-donors. The synthesis of branched dyes could be achieved from novel 7-bromo-9,9-diethyl-9*H*-fluorene-2,4-dicarbaldehyde, which was synthesized by convenient Sommelet reaction along with 7-bromo-9,9-diethyl-9*H*-fluorene-2,4,5-tricarbaldehyde. These intermediates have vast synthetic utility and can become

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benchmarks to construct a variety of electronic materials. All the dyes displayed moderate absorption properties with molar extinction coefficients higher than the most successful ruthenium dyes. The performance of DSSCs with these dyes as the sensitizers exhibited efficiencies ranging from 1.39% to 3.44% under one sun illumination. Although bisimidazoles exhibited slightly lower efficiencies than monoimidazoles, because of poor dye-loading, further introduction of more electron-rich segments led to improvement. The maximum power conversion efficiency of 3.44% was achieved from IF2, a monoimidazole dye featuring 4,5-diphenyl and bithiophene conjugation segment, which was dropped to 2.75% for bisimidazole analogue (IF4). When the phenyl units were replaced by fluorene, the efficiency improved to 3.27% with the highest open-circuit voltage in the series. The results concluded the importance of the bulkier bis-structure which is able to control the electrolyte interactions and thus charge recombination. The present design is promising, and further structural optimization can be customized to attain the improved photovoltaic properties. Encouraged by these studies, we are further exploring the possibility of developing electronrich thiophene fused imidazoles as donors for DSSC dyes in our laboratory.

EXPERIMENTAL SECTION

Material and Methods. Chemicals were purchased from commercial sources and used as received. Solvents were dried and distilled immediately prior to use by standard procedures. Column chromatography purification was performed with the use of silica gel (230-400 mesh) as the stationary phase in a column with 40 cm long and 3.0 cm diameter. ¹H NMR and ¹³C NMR were recorded in acetone- d_{60} CDCl₃₀ or DMSO- d_6 on an FT-NMR spectrometer operating at 500.13 and 125.77 MHz, respectively. High-resolution mass spectrometric measurements were carried out using a FAB mass spectrometer. Absorption spectra were recorded at room temperature in quartz cuvettes using a UV-vis spectrophotometer. The cyclic voltammetry (CV) and differential pulse voltammetry (DPV) measurements were carried out on an electrochemical analyzer in tetrahydrofuran by using 0.1 M tetrabutylammonium perchlorate as supporting electrolyte. The experiments were performed at room temperature in nitrogen atmosphere with a three-electrode cell consisting of a platinum wire as auxiliary electrode, a nonaqueous Ag/AgNO₃ reference electrode, and a glassy carbon working electrode. The highest occupied molecular orbital (HOMO) energy levels of organic materials were measured from the oxidation potential obtained from cyclic voltammetry, and lowest unoccupied molecular orbital (LUMO) energy levels were determined from the HOMO energy levels and optical band gap estimated from the intersection of absorption and emission. The IR spectra were recorded on FT-IR spectrometer.

Computational Methods. All the computations were performed with the Gaussian 09 program package⁴¹ on a computer workstation. The ground-state geometries were fully optimized without symmetry constraints with Becke's⁴³ three parameters hybrid functional and Lee, Yang, and Parr's correlational functional (B3LYP)⁴⁴ using 6-31G(d, p) basis set on all atoms. The default parameters for the convergence criteria were used. Vibrational analyses on the optimized structures were performed to confirm the structure. The excitation energies and oscillator strengths for the lowest 10 singlet–singlet transitions at the optimized geometry in the ground state were obtained by TD-DFT calculations using the same basis set as for the geometry minimization but with the range separated hybrid functional LC-BLYP.

DSSC Fabrication and Characterization. For the TiO_2 colloid solution, the TiO_2 precursor was prepared by the sol-gel method as described below. Titanium(IV) tetraisopropoxide (72 mL) was added to 430 mL of a 0.1 M nitric acid aqueous solution with constant stirring and heated to 85 °C simultaneously for 8 h. When the mixture

was cooled down to room temperature, the resultant colloid was transferred to an autoclave and then heated in at 240 °C for 12 h in order to allow the TiO₂ particles to grow uniformly (ca. 20 nm). Consequently, the TiO₂ colloid was concentrated to 10 wt % (with respect to the TiO₂). The first type of TiO₂ paste (for transparent layer) was prepared by the addition 25 wt % (with respect to the TiO₂) of PEG to the above solution in order to control the pore diameters and to prevent the film from cracking during drying. For the second one (for scattering layer), the first type of TiO₂ paste incorporated with 50 wt % of light scattering TiO₂ particles (PT-501A, 15 m² g⁻¹, 100 nm, 99.74%) (with respect to the 20 nm TiO₂) for reducing the light loss by back scattering.

A fluorine-doped SnO₂ conducting glass (FTO, 7 Ω sq.⁻¹, transmittance ~80%) was first cleaned with a neutral cleaner and then washed with DI water, acetone, and IPA, sequentially. The conducting surface of the FTO was treated with a solution of TTIP (1 g) in 2-methoxyethanol (99.5%, 3 g) for obtaining a good mechanical contact between the conducting glass and TiO2 film, as well as to isolate the conducting glass surface from the electrolyte. TiO₂ pastes were coated onto the treated conducting glass by using the doctor blade technique. For each coating TiO₂ layer, the dried TiO₂ film was gradually heated to 450 °C in an oxygen atmosphere and subsequently sintered at that temperature for 30 min. The TiO₂ photoanodes of the DSSCs employed in the experiments were composed of a 14 μ m thick transparent TiO₂ layer and with a scattering layer of 4.5 μ m thickness. After sintering at 450 °C and cooling to 80 °C, the TiO₂ film was immersed in a 3×10^{-4} M solution of dye at room temperature for 24 h. N719 was dissolved in ACN and tert-butylamine (volume ratio of 1:1) to obtain a standard dye solution. Various organic dye solutions were prepared in a mixing solvent containing ACN, tert-butylamine, and DMSO (volume ratio of 1:1:3). The thus-prepared TiO_2/dye electrode was placed on a platinum-sputtered conducting glass electrode (ITO, 7 Ω sq.⁻¹), keeping the two electrodes separated by a 25 μ m-thick Surlyn (SX1170-25). The two electrodes were then sealed by heating. A mixture of 0.1 M LiI, 0.6 M DMPII, 0.05 M I₂, and 0.5 M TBP in 3-methoxypropionitrile (MPN)/ACN (volume ratio of 1:1) was used as the electrolyte. The electrolyte was injected into the gap between the electrodes by capillarity; the electrolyteinjecting hole was previously made in the counter electrode with a drilling machine, and the hole was sealed with hot-melt glue after the injection of the electrolyte.

The surface of the DSSC was covered by a mask with a lightilluminated area of 0.16 cm² and then illuminated by a class-A quality solar simulator (AM1.5G). Incident light intensity (100 mW cm⁻²) was calibrated with a standard Si Cell (PECSI01). Photocurrentvoltage curves of the DSSCs were obtained with a potentiostat/ galvanostat. Cross-sectional image of the TiO2 film was observed in scanning electron microscopic images (SEM). For UV-absorption spectra, dye molecules were coated on the TiO2 films, and the corresponding spectra were obtained using an UV-vis spectrophotometer equipped with an equipment of total integrating sphere. Electrochemical impedance spectra (EIS) were obtained by the abovementioned potentiostat/galvanostat, equipped with an FRA2 module, under a constant light illumination of 100 mW cm⁻² or dark at a potential of -0.55 V at room temperature. The frequency range explored was 10 mHz to 65 kHz. The applied bias voltage was set at the open-circuit voltage of the DSSC, between the counter electrode and the FTO-TiO2-dye working electrode, starting from the shortcircuit condition; the corresponding ac amplitude was 10 mV. The impedance spectra were analyzed using an equivalent circuit model. Incident photo-to-current conversion efficiency (IPCE) curves were obtained at short-circuit condition. The light source was a class A quality solar simulator (AM1.5G); light was focused through a monochromator onto the photovoltaic cell. The monochromator was incremented through the visible spectrum to generate the IPCE (λ) as defined by IPCE (λ) = 1240 ($J_{SC}/\lambda\varphi$), where λ is the wavelength, J_{SC} is short-circuit photocurrent (mA cm⁻²) recorded with a potentiostat/ galvanostat, and φ is the incident radiative flux (W m⁻²) measured with an optical detector and power meter.

Synthesis. The precursor compounds 2-bromo-9,9-diethyl-9*H*-fluorene (1),⁴⁵ 9,9-diethyl-2-ethynyl-9*H*-fluorene,⁴⁶ 2,2'-bithiophene-5-carbaldehyde,⁴⁷ (5-(1,3-dioxolan-2-yl)thiophene-2-yl)-tributylstannane,⁴⁸ and (5'-(1,3-dioxolan-2-yl)-2,2'-bithiophene-5-yl)-tributylstannane⁴⁹ were synthesized by following reported procedures.

Synthesis of 2a-2c. A mixture of 2-bromo-9,9-diethyl-9Hfluorene (3 g, 10 mmol) and paraformaldehyde (1.5 g, 50 mmol) in 20 mL of HBr (33% solution in acetic acid) was taken in a sealed tube. The tube was closed and heated at 110 °C for 48 h. After completion of the reaction, the reaction mixture was cooled, poured into water, and extracted with dichloromethane. The organic layer was thoroughly washed with brine solution, collected, and dried over anhydrous Na₂SO₄. The solvent was evaporated and residue dissolved in 50 mL of chloroform. Hexamethylenetetramine (4.2 g, 30 mmol) was added, and the resultant mixture was refluxed for 12 h. The solvent was removed and residual salt washed with chloroform two to three times. It was dried and dissolved in 20 mL of acetic acid/water mixture (1:1). The mixture was again refluxed for 4 h. It was cooled and neutralized with aq sodium bicarbonate and extracted with dichloromethane. The organic layer was washed with brine solution liberally, collected, and dried over anhydrous Na2SO4. The solvent was evaporated and the residue purified by column chromatography on silica gel by using dichloromethane/ethyl acetate mixture as eluent. The compounds 2b, 2a, and 2c were obtained, in that order, from the column in pure form.

7-Bromo-9,9-diethyl-9H-fluorene-2,4-dicarbaldehyde (**2***a*): white solid; yield 1.14 g, 32%; mp 48–50 °C; IR (KBr, cm⁻¹) 1696 ($\nu_{C=0}$); ¹H NMR (CDCl₃, 500.13 MHz) δ 10.57 (s, 1 H), 10.15 (s, 1 H), 8.57 (d, *J* = 8.5 Hz, 1 H), 8.36 (d, *J* = 1.0 Hz, 1 H), 8.07 (d, *J* = 1.5 Hz, 1 H), 7.56–7.58 (m, 2 H), 2.06–2.17 (m, 4 H), 0.26 (t, *J* = 7.5 Hz, 6 H); ¹³C NMR (CDCl₃, 125.77 MHz) δ 191.2, 191.0, 154.7, 153.1, 146.9, 138.0, 135.4, 135.0, 132.3, 131.0, 128.3, 126.6, 126.3, 125.1, 56.3, 32.8, 8.3; HRMS (ESI) *m/z* calcd for C₁₉H₁₈BrO₂ (M + H) 357.0485, found 357.0494.

7-Bromo-9,9-diethyl-9H-fluorene-2-carbaldehyde (**2b**).⁵⁰ white solid; yield 0.23 g, 7%; mp 122–124 °C; IR (KBr, cm⁻¹) 1690 ($\nu_{C=O}$); ¹H NMR (CDCl₃, 500.13 MHz) δ 10.06 (s, 1 H), 7.86–7.88 (m, 2 H), 7.82 (d, J = 7.5 Hz, 1 H), 7.64–7.65 (m, 1 H), 7.51–7.53 (m, 2 H), 2.03–2.13 (m, 4 H), 0.30 (t, J = 7.5 Hz, 6 H). The compound can also be synthesized by the reaction of 2,7-dibromo-9,9-diethyl-9H-fluorene with *n*-BuLi/DMF in THF as reported in literature.⁵⁰

7-Bromo-9,9-diethyl-9H-fluorene-2,4,5-tricarbaldehyde (2c): white solid; yield 77 mg, 2%; mp 55–58 °C; IR (KBr, cm⁻¹) 1702 ($\nu_{C=O}$); ¹H NMR (CDCl₃, 500.13 MHz) δ 10.66 (s, 1 H), 10.45 (s, 1 H), 10.17 (m, 1 H), 9.18 (s, 1 H), 8.41 (d, *J* = 1.5 Hz, 1 H), 8.09 (d, *J* = 1.5 Hz, 1 H), 7.70 (s, 1 H), 2.11 (m, 4 H), 0.28 (t, *J* = 7.5 Hz, 6 H); ¹³C NMR (CDCl₃, 125.77 MHz) δ 191.3, 190.8, 190.5, 159.9, 152.9, 145.4, 139.1, 135.8, 135.0, 133.2, 132.9, 128.9, 128.5, 128.2, 126.6, 56.8, 32.9, 8.4; HRMS (ESI) *m*/*z* calcd for C₂₀H₁₈BrO₃ (M + H) 385.0434, found 385.0441.

1,2-Bis(9,9-diethyl-9H-fluoren-2-yl)ethyne (3). A mixture of 1 (3 g, 10 mmol), 9,9-diethyl-2-ethynyl-9H-fluorene (2.71 g, 11 mmol), Pd(PPh₃)₂Cl₂ (70 mg, 0.1 mmol), PPh₃ (52 mg, 0.2 mmol), and CuI (20 mg, 0.1 mmol) in 50 mL of triethylamine was degassed with nitrogen. The mixture was stirred and refluxed under nitrogen for 12 h and then cooled to room temperature. It was poured into water and extracted with ethyl acetate. The organic layer was washed with brine for several times, separated, and dried over anhydrous Na₂SO₄. The solvent was removed, and crude product purified by column chromatography on silica gel (hexane/dichloromethane): white solid; yield 3.03 g, 65%; mp 120 °C; IR (KBr, cm⁻¹) 2202 ($\nu_{C=C}$); ¹H NMR (CDCl₃, 500.13 MHz) δ 7.70–7.73 (m, 4 H), 7.56–7.58 (m, 4 H), 7.33-7.36 (m, 6 H), 2.06 (q, J = 7.5 Hz, 8 H), 0.33 (t, J = 7.5 Hz, 12 H); ¹³C NMR (CDCl₃, 125.77 MHz) δ 150.2, 150.0, 141.8, 140.9, 130.6, 127.5, 127.0, 126.1, 123.0, 121.6, 120.0, 119.7, 90.5, 56.2, 32.8, 8.5; HRMS (ESI) m/z calcd for C₃₆H₃₅ (M + H) 467.2733, found 467.2742.

1,2-Bis(9,9-diethyl-9H-fluoren-2-yl)ethane-1,2-dione (4). A mixture of 3 (2.33 g, 5 mmol) and iodine (1.27 g, 5 mmol) was dissolved in DMSO. The resulting solution was heated at 140 $^{\circ}$ C for 12 h and then treated with 10% aq sodium thiosulfate solution followed by extraction with ethyl acetate. The extract was dried over anhydrous Na₂SO₄. The solvent was evaporated and residue chromatographed on a silica gel column (hexane/dichloromethane) to obtain the pure product: light orange solid; yield 2.29 g, 92%; mp 130–132 °C; IR (KBr, cm⁻¹) 1663 ($\nu_{C=0}$); ¹H NMR (CDCl₃, 500.13 MHz) δ 8.08 (s, 2 H), 7.96 (dd, *J* = 8 Hz, 1 Hz, 2 H), 7.98 (t, *J* = 7.5 Hz, 4 H), 7.37–7.43 (m, 6 H), 2.09 (m, 8 H), 0.32 (t, *J* = 7.5 Hz, 12 H); ¹³C NMR (CDCl₃, 125.77 MHz) δ 195.1, 151.5, 150.8, 148.4, 139.8, 131.9, 130.6, 129.1, 127.3, 123.7, 123.3, 121.1, 119.9, 56.5, 32.6, 8.5; HRMS (ESI) *m*/*z* calcd for C₃₆H₃₅O₂ (M + H) 499.2632, found 499.2635.

General Procedure for the Synthesis of 5a and 5b. A mixture of 7-bromo-9,9-diethyl-9H-fluorene-2,4-dicarbaldehyde (2a) (0.71 g, 2 mmol), diketone benzil or 4 (4 mmol), and ammonium acetate (1.54 g, 20 mmol) in 10 mL of acetic acid was refluxed for 24 h. The reaction mixture was cooled and poured into water to obtain a solid precipitate. The solid was washed thoroughly with water, dried, and recrystallized from DCM/methanol mixture

2,2'-(7-Bromo-9,9-diethyl-9H-fluorene-2,4-diyl)bis(4,5-diphenyl-1H-imidazole) (**5a**): cream-colored solid; yield 2.12 g, 72%; mp 256–258 °C; ¹H NMR (acetone- d_6 , 500.13 MHz) δ 12.12 (s, 1 H), 12.03 (s, 1 H), 8.41 (d, *J* = 1.5 Hz, 1 H), 8.22 (s, 1 H), 7.77 (d, *J* = 7.0 Hz, 2 H), 7.58–7.65 (m, 5 H), 7.36–7.43 (m, 10 H), 7.29–7.32 (m, 4 H), 7.24 (t, *J* = 7.5 Hz, 2 H), 2.17 (q, *J* = 7.5 Hz, 4 H), 0.33 (t, *J* = 7.5 Hz, 6 H); ¹³C NMR (CDCl₃ + TFA, 125.77 MHz) δ 153.8, 153.5, 143.5, 141.8, 136.0, 131.1, 130.5, 130.2, 130.1, 130.0, 129.6, 129.5, 129.3, 129.2, 127.2, 126.2, 126.0, 125.9, 125.6, 124.9, 122.7, 121.3, 57.1, 32.4, 7.8; HRMS (FAB) *m*/*z* calcd for C₄₇H₃₈BrN₄ (M + H) 737.2274, found 737.2282.

2,2'-(7-Bromo-9,9-diethyl-9H-fluorene-2,4-diyl)bis(4,5-bis(9,9-diethyl-9H-fluoren-2-yl)-1H-imidazole) (**5b**): yellow solid; yield 3.99 g, 76%; mp 190–192 °C; ¹H NMR (acetone- d_{67} 500.13 MHz) δ 12.74 (s, 1 H), 12.30 (s, 1 H), 8.53 (s, 1 H), 8.32 (s, 1 H), 7.63–7.87 (m, 17 H), 7.32–7.43 (m, 14 H), 1.90–2.01 (m, 20 H), 0.27–0.34 (m, 30 H), ¹³C NMR (CDCl₃ + TFA, 125.77 MHz) δ 153.7, 153.6, 151.5, 151.3, 150.4, 144.2, 144.0, 143.9, 143.0, 141.2, 140.3, 140.2, 135.9, 131.3, 130.9, 130.5, 129.4, 128.3, 128.2, 127.3, 127.23, 127.19, 127.16, 127.0, 125.5, 125.2, 124.4, 124.1, 123.14, 123.10, 122.7, 122.6, 122.5, 121.5, 120.5, 120.4, 120.3, 116.8, 57.3, 56.6, 56.5, 32.5, 8.21, 8.19, 7.7; HRMS (ESI) *m*/*z* calcd for C₉₁H₈₆BrN₄ (M + H) 1313.6030, found 1313.6041.

2,2'-(7-Bromo-9,9-diethyl-9H-fluorene-2,4-diyl)bis(1-ethyl-4,5-diphenyl-1H-imidazole) (6a). A mixture of 5a (0.74 g, 1 mmol) and K₂CO₃ (0.55 g, 4 mmol) in 10 mL of dry DMF was degassed with nitrogen and heated at 50 °C. After 1 h, bromoethane (0.32 g, 3 mmol) was added to the reaction mixture slowly and heating continued for additional 48 h. The reaction mixture was poured into water and extracted with dichloromethane. The organic layer was washed with brine solution several times, collected, and dried over anhydrous Na₂SO₄. The solvent was evaporated and crude product purified by column chromatography on silica gel by using dichloromethane/ethyl acetate mixture as eluent: light-yellow solid; yield 0.56 g, 70%; mp 100–102 °C; ¹H NMR (CDCl₃, 500.13 MHz) δ 8.02 (s, 1 H), 7.85-7.87 (m, 2 H), 7.58-7.60 (m, 2 H), 7.43-7.54 (m, 12 H), 7.35 (dd, J = 8.5 Hz, 2.0 Hz, 1 H), 7.20-7.25 (m, 4 H), 7.13-7.18 (m, 2 H), 6.69 (d, I = 8.0 Hz, 1 H), 4.04–4.06 (m, 2 H), 3.62 (s, 2 H), 2.07–2.20 (m, 4 H), 1.02 (t, *J* = 7.0 Hz, 3 H), 0.76 (t, *J* = 7.0 Hz, 3 H), 0.38 (t, J = 7.5 Hz, 6 H); ¹³C NMR (CDCl₃, 125.77 MHz) δ 152.92, 150.86, 147.0, 144.9, 141.0, 139.2, 138.2, 137.7, 134.6, 131.4, 131.3, 131.1, 131.0, 130.6, 130.5, 130.4, 130.0, 129.31, 129.26, 129.2, 128.9, 128.8, 128.21, 128.15, 126.9, 126.8, 126.43, 126.37, 126.2, 125.4, 124.9, 123.3, 122.3, 56.7, 40.1, 39.6, 33.0, 16.3, 16.1, 8.6; HRMS (ESI) m/z calcd for C₅₁H₄₆BrN₄ (M + H) 793.2900, found 793.2911.

2,2'-(7-Bromo-9,9-diethyl-9H-fluorene-2,4-diyl)bis(4,5-bis(9,9-diethyl-9H-fluoren-2-yl)-1-ethyl-1H-imidazole) (**6b**). A mixture of **5b** (1.31 g, 1 mmol), bromoethane (0.32 g, 3 mmol), BTEAC (0.10 g), 10 mL of 50% aq NaOH, and 5 mL of benzene was refluxed for 12 h. After a clear organic layer formed, the reaction mixture was poured into hot water and allowed to sit overnight in the hood. The residual mass was extracted with dichloromethane and the extract dried over

anhydrous Na2SO4. The compound was purified by column chromatography on silica gel by using dichloromethane/ethyl acetate as eluent: light-yellow solid; yield 1.05 g, 77%; mp 140-142 °C; ¹H NMR (CDCl₃, 500.13 MHz) δ 7.94 (dd, J = 13.0 Hz, 1.5 Hz, 2 H), 7.78-7.84 (m, 4 H), 7.67 (d, I = 1.5 Hz, 1 H), 7.60-7.62 (m, 3 H), 7.56-7.58 (m, 2 H), 7.50-7.54 (m, 3 H), 7.47-7.48 (m, 2 H), 7.43-7.46 (m, 2 H), 7.38–7.41 (m, 8 H), 7.23–7.25 (m, 5 H), 6.88 (d, J = 8.5 Hz, 1 H), 4.14-4.19 (m, 2 H), 3.70 (s, 2 H), 2.11-2.24 (m, 4 H), 2.04-2.09 (m, 8 H), 1.82-1.89 (m, 8 H), 1.09 (t, J = 7.0 Hz, 3 H), 0.82 (t, J = 7.0 Hz, 3 H), 0.38–0.45 (m, 18 H), 0.20–0.26 (m, 12 H); ¹³C NMR (CDCl₂, 125.77 MHz) δ 153.0, 151.0, 150.9, 150.7, 150.2, 150.12, 150.07, 149.9, 149.8, 147.1, 145.0, 142.3, 142.2, 141.7, 141.6, 140.92, 140.87, 140.0, 139.9, 139.3, 138.9, 138.4, 133.6, 130.8, 130.7, 130.6, 130.1, 130.03, 129.98, 129.9, 127.8, 127.7, 127.2, 126.8, 126.7, 126.3, 125.9, 125.7, 125.6, 125.5, 125.0, 123.5, 123.0, 122.82, 122.79, 122.4, 121.6, 121.3, 120.5, 120.4, 120.1, 120.0, 119. 5, 119.3, 56.7, 56.40, 56.37, 56.12, 56.07, 40.3, 39.7, 32.9, 32.70, 32.65, 16.4, 16.1, 8.8, 8.63, 8.58; HRMS (ESI) m/z calcd for $C_{95}H_{94}BrN_4$ (M + H) 1370.6689, found 1370.6697.

5-(9.9-Diethyl-5.7-bis(1-ethyl-4.5-diphenyl-1H-imidazol-2-yl)-9Hfluoren-2-yl)thiophene-2-carbaldehyde (7a). A mixture of 6a (0.397 g, 0.5 mmol) and (5-(1,3-dioxolan-2-yl)thiophene-2-yl)tributylstannane (0.245 g, 0.55 mmol) in 5 mL of DMF was degassed with nitrogen followed by the addition of $Pd(PPh_3)_2Cl_2$ (3.5 mg, 5 × 10⁻³ mmol). The reaction mixture was heated at 80 °C for 36 h under nitrogen. It was cooled, poured into water, and extracted with dichloromethane. The solvent was evaporated and the solid residue suspended in glacial acetic acid (5 mL). The acetic acid solution was warmed to dissolve the solids and water (1 mL) added. It was stirred for 1 h at 50 °C and then extracted with dichloromethane. The organic layer was washed liberally with water and dried over anhydrous Na₂SO₄. After removal of solvent, the residue obtained was purified by column chromatography on silica gel (dichloromethane/ethyl acetate): yellow solid; yield 0.23 g, 55%; mp 112-114 °C; IR (KBr, cm⁻¹) 1658 ($\nu_{C=0}$); ¹H NMR (CDCl₃, 500.13 MHz) δ 9.90 (s, 1 H), 7.90 (dd, J = 13.0 Hz, 1.5 Hz, 2 H), 7.76 (d, J = 4.0 Hz, 1 H), 7.65 (d, J = 1.5 Hz, 1 H), 7.60-7.62 (m, 2 H), 7.57 (dd, J = 8.5 Hz, 1.5 Hz, 1 H), 7.55 (d, J = 1.5 Hz, 1 H), 7.49–7.53 (m, 9 H), 7.47 (d, J = 4.0 Hz, 1 H), 7.45 (dd, J = 7.5 Hz, 1.5 Hz, 2 H), 7.20–7.24 (m, 4 H), 7.15– 7.19 (m, 2 H), 6.89 (d, J = 8.5 Hz, 1 H), 4.06-4.08 (m, 2 H), 3.66 (s, 2 H), 2.17–2.23 (m, 4 H), 1.04 (t, J = 7.0 Hz, 3 H), 0.79 (t, J = 7.0 Hz, 3 H), 0.42 (t, J = 7.5 Hz, 6 H); ¹³C NMR (CDCl₃, 125.77 MHz) δ 182.8, 154.5, 151.8, 151.7, 146.9, 144.9, 142.3, 141.6, 141.1, 138.1, 137.7, 137.6, 134.5, 134.4, 132.6, 131.3, 131.2, 131.1, 131.0, 130.6, 130.4, 130.1, 129.4, 129.3, 129.2, 129.1, 129.0, 128.8, 128.24, 128.17, 127.0, 126.8, 126.49, 126.45, 126.0, 125.6, 125.0, 124.3, 122.6, 120.5, 56.6, 40.1, 39.6, 33.0, 16.3, 16.1, 8.7; HRMS (ESI) m/z calcd for C₅₆H₄₉N₄OS (M + H) 825.3622, found 825.3629.

5'-(9,9-Diethyl-5,7-bis(1-ethyl-4,5-diphenyl-1H-imidazol-2-yl)-9H-fluoren-2-yl)-2,2'-bithiophene-5-carbaldehyde (7b). Compound 7b was obtained by following the procedure described above for 7a using 6a and (5'-(1,3-dioxolan-2-yl)-2,2'-bithiophene-5-yl)tributylstannane: dark-yellow solid; yield 0.18 g, 39%; mp 88-90 °C; IR (KBr, cm⁻¹) 1654 ($\nu_{C=0}$); ¹H NMR (CDCl₃, 500.13 MHz) δ 9.87 (s, 1 H), 7.89 (dd, J = 10.5 Hz, 1.5 Hz, 2 H), 7.69 (d, J = 4.0 Hz, 1 H), 7.61 (d, J = 7.5 Hz, 2 H), 7.58 (d, J = 1.5 Hz, 1 H), 7.48-7.55 (m, 11 H), 7.45 (dd, J = 7.5 Hz, 2.0 Hz, 2 H), 7.35–7.37 (m, 2 H), 7.28 (d, J = 3.5 Hz, 1 H), 7.22–7.25 (m, 3 H), 7.13–7.21 (m, 3 H), 6.85 (d, J = 8.0 Hz, 1 H), 4.07-4.08 (m, 2 H), 3.66 (s, 2 H), 2.15-2.25 (m, 4 H), 1.04 (t, J = 7.0 Hz, 3 H), 0.79 (t, J = 7.0 Hz, 3 H), 0.42 (t, J = 7.0 Hz, 6 H); ¹³C NMR (CDCl₃, 125.77 MHz) δ 182.4, 151.6, 151.3, 145.0, 146.9, 146.2, 144.9, 141.4, 141.2, 140.3, 138.0, 137.5, 137.4, 134.9, 134.5, 134.4, 132.9, 131.22, 131.15, 130.93, 130.87, 130.23, 130.18, 129.9, 129.2, 129.1, 129.0, 128.8, 128.6, 128.1, 128.0, 127.1, 126.8, 126.6, 126.3, 126.2, 125.2, 125.1, 124.8, 124.3, 123.9, 122.4, 119.6, 56.4, 39.9, 39.5, 32.9, 16.2, 15.9, 8.6; HRMS (ESI) m/z calcd for C₆₀H₅₁N₄OS₂ (M + H) 907.3499, found 907.3508.

5-(5,7-Bis(4,5-bis(9,9-diethyl-9H-fluoren-2-yl)-1-ethyl-1H-imidazol-2-yl)-9,9-diethyl-9H-fluoren-2-yl)thiophene-2-carbaldehyde(**7c**). Compound**7c**was obtained by following the procedure describe above for 7a using 6b in place of 6a: yellow solid; yield 0.29 g, 41%; mp 138–140 °C; IR (KBr, cm⁻¹) 1655 ($\nu_{C=O}$); ¹H NMR (CDCl₃, 500.13 MHz) δ 9.91 (s, 1 H), 7.98 (dd, J = 10.0 Hz, 1.5 Hz, 2 H), 7.85 (d, J = 7.5 Hz, 1 H), 7.77–7.82 (m, 4 H), 7.57–7.70 (m, 9 H), 7.48– 7.53 (m, 6 H), 7.38–7.43 (m, 7 H), 7.27–7.28 (m, 1 H), 7.23–7.25 (m, 4 H), 7.09 (d, J = 8.0 Hz, 1 H), 4.18-4.19 (m, 2 H), 3.74 (s, 2 H),2.21-2.28 (m, 4 H), 2.06-2.09 (m, 8 H), 1.83-1.91 (m, 8 H), 1.11 (t, J = 7.0 Hz, 3 H), 0.85 (t, J = 7.0 Hz, 3 H), 0.48 (t, J = 7.0 Hz, 6 H), 0.40 (t, J = 7.5 Hz, 12 H), 0.21–0.28 (m, 12 H); ¹³C NMR (CDCl₃, 125.77 MHz) δ 182.8, 154.6, 151.9, 151.8, 150.9, 150.7, 150.2, 150.1, 150.0, 149.9, 149.7, 147.1, 145.0, 142.3, 142.2, 141.7, 141.64, 141.59, 140.1, 140.8, 139.93, 139.89, 138.9, 138.4, 137.5, 133.5, 132.6, 130.9, 130.8, 130.7, 130.04, 129.97, 129.9, 127.73, 127.67, 127.1, 126.7, 126.6, 126.0, 125.8, 125.7, 125.4, 125.0, 124.2, 123.0, 122.80, 122.76, 121.5, 121.3, 120.6, 120.5, 120.4, 120.01, 119.97, 119.4, 119.3, 56.6, 56.37, 56.35, 56.1, 56.0, 40.3, 39.7, 32.8, 32.7, 32.6, 16.4, 16.1, 8.8, 8.6, 8.5; HRMS (ESI) m/z calcd for $C_{100}H_{97}N_4OS$ (M + H) 1402.7410, found 1402.7419.

5'-(5.7-Bis(4,5-bis(9,9-diethyl-9H-fluoren-2-yl)-1-ethyl-1H-imidazol-2-yl)-9,9-diethyl-9H-fluoren-2-yl)-2,2'-bithiophene-5-carbaldehyde (7d). Compound 7d was obtained by following the procedure described above for 7a using 6b and (5'-(1,3-dioxolan-2-yl)-2,2'bithiophene-5-yl)tributylstannane: dark-yellow solid; yield 0.22 g, 30%; mp 130–132 °C; IR (KBr, cm⁻¹) 1653 ($\nu_{C=0}$); ¹H NMR $(CDCl_3, 500.13 \text{ MHz}) \delta 9.88 \text{ (s, 1 H)}, 7.97 \text{ (dd, } J = 8.5 \text{ Hz}, 1.5 \text{ Hz}, 2$ H), 7.85 (d, J = 7.5 Hz, 1 H), 7.77–7.82 (m, 3 H), 7.70–7.71 (m, 2 H), 7.57–7.65 (m, 7 H), 7.48–7.53 (m, 5 H), 7.38–7.43 (m, 9 H), 7.28-7.30 (m, 2 H), 7.23-7.25 (m, 5 H), 7.05 (d, J = 8.0 Hz, 1 H), 4.18-4.19 (m, 2 H), 3.74 (s, 2 H), 2.20-2.29 (m, 4 H), 2.06-2.09 (m, 8 H), 1.83–1.90 (m, 8 H), 1.11 (t, J = 7.0 Hz, 3 H), 0.85 (t, J = 7.0 Hz, 3 H), 0.48 (t, J = 7.5 Hz, 6 H), 0.40 (t, J = 7.5 Hz, 12 H), 0.21–0.28 (m, 12 H); ¹³C NMR (CDCl₃, 125.77 MHz) δ 182.3, 151.6, 151.4, 150.7, 150.5, 150.0, 149.93, 149.87, 149.7, 149.5, 147.0, 146.3, 145.0, 142.1, 142.0, 141.5, 141.44, 141.41, 141.0, 140.74, 140.68, 140.4, 139.72, 139.69, 138.7, 138.2, 137.4, 135.0, 133.39, 133.35, 132.9, 130.6, 130.43, 130.35, 129.9, 129.81, 129.76, 129.7, 127.6, 127.5, 127.1, 127.0, 126.5, 126.4, 125.7, 125.5, 125.4, 125.30, 125.25, 125.1, 124.8, 124.2, 123.9, 122.8, 122.63, 122.59, 121.4, 121.1, 120.3, 120.2, 119.8, 119.7, 119.2, 119.1, 56.4, 56.20, 56.17, 55.92, 55.87, 40.1, 39.6, 32.7, 32.49, 32.45, 16.2, 15.9, 8.7, 8.42, 8.37; HRMS (ESI) m/z calcd for $C_{104}H_{99}N_4OS_2$ (M + H) 1484.7287, found 1484.7298.

(E)-2-Cyano-3-(5-(9,9-diethyl-5,7-bis(1-ethyl-4,5-diphenyl-1Himidazol-2-yl)-9H-fluoren-2-yl)thiophene-2-yl)acrylic Acid (IF3). A mixture of the aldehyde 7a (0.20 g, 0.24 mmol), 2-cyanoacetic acid (25 mg, 0.29 mmol), and a catalytic amount of ammonium acetate in acetic acid (5 mL) was refluxed for 12 h. After cooling, it was poured into water and the resulting solid collected by filtration. The solid formed was thoroughly washed with water and dried. It was crystallized by using a dichloromethane/hexane mixture to obtain analytically pure compound: yellow solid; yield 0.17 g, 81%; mp 166-168 °C; IR (KBr, cm⁻¹) 2208 ($\nu_{C=N}$), 1700, 1582; ¹H NMR (DMSO- d_{6t} 500.13 MHz) δ 8.30 (s, 1 H), 8.02–8.05 (m, 1 H), 7.90–7.94 (m, 2 H), 7.83 (d, J = 4.0 Hz, 1 H), 7.74-7.78 (m, 1 H), 7.44-7.60 (m, 15 H), 7.20-7.25 (m, 4 H), 7.13-7.17 (m, 2 H), 6.68-6.77 (m, 1 H), 4.05-4.06 (m, 2 H), 3.59 (s, 2 H), 2.24–2.29 (m, 4 H), 1.00 (t, J = 7.0 Hz, 3 H), 0.77 (t, J = 7.0 Hz, 3 H), 0.33 (s, 6 H); ¹³C NMR (DMSO- d_6 +TFA, 125.77 MHz) δ 163.5, 152.4, 152.3, 152.2, 152.0, 146.5, 143.2, 143.04, 142.98, 141.3, 141.2, 141.1, 138.3, 135.3, 133.7, 131.2, 131.1, 131.0, 130.7, 130.63, 130.58, 130.5, 130.4, 129.6, 129.5, 129.2, 129.14, 129.09, 128.9, 128.83, 128.78, 127.9, 127.64, 127.60, 127.3, 127.1, 127.0, 126.8, 126.5, 126.4, 126.1, 122.7, 122.3, 120.9, 118.1, 117.7, 56.9, 41.3, 41.1, 31.9, 14.53, 14.49, 8.4; HRMS (FAB) m/z calcd for C₅₉H₄₈N₅O₂S (M-H) 890.3534, found 890.3553; *m/z* calcd for $C_{59}H_{49}N_5NaO_2S$ (M + Na) 914.3510, found 914.3515.

(E)-2-Cyano-3-(5'-(9,9-diethyl-5,7-bis(1-ethyl-4,5-diphenyl-1*H*-imidazol-2-yl)-9*H*-fluoren-2-yl)-2,2'-bithiophene-5-yl)-acrylic Acid (IF4). Compound IF4 was obtained from 7b by following a procedure described above for IF3: orange solid; yield 0.21 g, 88%; mp >300 °C; IR (KBr, cm⁻¹) 2204 ($\nu_{C\equiv N}$), 1709, 1585; ¹H

NMR (DMSO- d_6 , 500.13 MHz) δ 8.39 (s, 1 H), 8.03 (d, J = 1.0 Hz, 1 H), 7.91–7.92 (m, 3 H), 7.74 (d, J = 4.0 Hz, 2 H), 7.67 (d, J = 3.5 Hz, 1 H), 7.55–7.61 (m, 9 H), 7.50–7.52 (m, 4 H), 7.44 (d, J = 7.0 Hz, 2 H), 7.20–7.26 (m, 4 H), 7.13–7.17 (m, 2 H), 6.70 (d, J = 8.0 Hz, 1 H), 4.04–4.06 (m, 2 H), 3.58 (s, 2 H), 2.27–2.28 (m, 4 H), 0.99 (t, J = 7.0 Hz, 3 H), 0.77 (t, J = 7.0 Hz, 3 H), 0.32–0.34 (m, 6 H); ¹³C NMR (CDCl₃+TFA, 125.77 MHz) δ 154.0, 153.1, 148.8, 145.8, 144.9, 142.6, 141.4, 140.9, 136.6, 135.8, 134.1, 131.7, 131.5, 131.3, 131.1, 131.0, 130.7, 130.6, 130.5, 130.3, 130.22, 130.16, 130.1, 130.0, 129.4, 129.3, 129.2, 128.7, 128.4, 127.3, 127.2, 127.0, 126.0, 125.4, 125.31, 145.8, 8.0; HRMS (FAB) m/z calcd for $C_{63}H_{50}N_5O_2S_2$ (M – H) 972.3411, found 972.3414; m/z calcd for $C_{63}H_{51}N_5NaO_2S_2$ (M + Na) 996.3387, found 996.3378.

(E)-3-(5-(5,7-Bis(4,5-bis(9,9-diethyl-9H-fluoren-2-yl)-1-ethyl-1Himidazol-2-yl)-9,9-diethyl-9H-fluoren-2-yl)thiophene-2-yl)-2-cyanoacrylic Acid (IF5). Compound IF5 was obtained from 7c by following a procedure described above for IF3: yellow solid; yield 0.30 g, 84%; mp >300 °C; IR (KBr, cm⁻¹) 2207 ($\nu_{C=N}$), 1699, 1582; ¹H NMR (DMSO-d₆, 500.13 MHz) δ 8.02-8.08 (m, 2 H), 7.90-7.98 (m, 5 H), 7.82-7.84 (m, 1 H), 7.70-7.76 (m, 5 H), 7.55-7.65 (m, 7 H), 7.49-7.51 (m, 2 H), 7.40 (s, 6 H), 7.21-7.34 (m, 7 H), 6.88-6.96 (m, 1 H), 4.15 (s, 2 H), 3.62-3.66 (m, 2 H), 2.27-2.36 (m, 4 H), 2.06-2.15 (m, 8 H), 1.82-1.91 (m, 4 H), 1.65-1.75 (m, 4 H), 1.05 (t, J = 7.0 Hz, 3 H), 0.85 (t, J = 7.0 Hz, 3 H), 0.23–0.37 (m, 18 H), 0.13–0.18 (m, 12 H); ¹³C NMR (DMSO- d_6 + TFA, 125.77 MHz) δ 163.5, 152.7, 152.4, 152.3, 151.8, 150.6, 150.5, 149.8, 149.74, 149.70, 149.52, 149.49, 146.4, 143.4, 143.2, 142.8, 142.7, 142.2, 142.1, 141.1, 140.8, 140.6, 139.8, 138.1, 135.3, 133.9, 131.5, 131.04, 130.97, 130.9, 130.7, 130.6, 130.0, 129.7, 128.2, 127.9, 127.2, 127.0, 126.6, 126.3, 126.0, 125.5, 125.3, 125.2, 124.7, 124.6, 122.9, 122.8, 122.5, 122.2, 121.7, 120.8, 120.4, 120.3, 120.19, 120.15, 120.1, 120.0, 118.0, 116.9, 56.0, 55.9, 55.59, 55.56, 41.4, 41.3, 31.7, 31.5, 31.2, 14.3, 14.2, 8.4, 8.08, 8.05, 7.9, 7.8; HRMS (FAB) m/z calcd for C₁₀₃H₉₆N₅O₂S (M -H) 1466.7279, found 1466.7286.

(E)-3-(5'-(5,7-Bis(4,5-bis(9,9-diethyl-9H-fluoren-2-yl)-1-ethyl-1Himidazol-2-yl)-9,9-diethyl-9H-fluoren-2-yl)-2,2'-bithiophene-5-yl)-2cyanoacrylic Acid (IF6). Compound IF6 was obtained from 7d by following a procedure described above for IF3: orange solid; yield 0.32 g, 85%; mp >300 °C; IR (KBr, cm⁻¹) 2205 ($\nu_{C\equiv N}$), 1699, 1585; ¹H NMR (DMSO- d_{6} , 500.13 MHz) δ 8.38 (s, 1 H), 8.03–8.08 (m, 2 H), 7.90-7.98 (m, 6 H), 7.81 (d, J = 9.5 Hz, 1 H), 7.70-7.76 (m, 5 H),7.66-7.68 (m, 4 H), 7.55-7.63 (m, 4 H), 7.49-7.51 (m, 2 H), 7.39-7.41 (m, 6 H), 7.33 (t, J = 7.5 Hz, 2 H), 7.25-7.30 (m, 4 H), 6.90 (d, J = 8.0 Hz, 1 H), 4.14-4.16 (m, 2 H), 3.66 (s, 2 H), 2.31-2.36 (m, 4 H), 2.04-2.14 (m, 8 H), 1.82-1.89 (m, 4 H), 1.65-1.75 (m, 4 H), 1.06 (t, J = 7.5 Hz, 3 H), 0.85 (t, J = 7.0 Hz, 3 H), 0.30-0.38 (m, 18 H), 0.11–0.18 (m, 12 H); ¹³C NMR (DMSO-*d*₆ + TFA, 125.77 MHz) δ 163.5, 152.6, 152.4, 150.6, 150.5, 149.9, 149.7, 149.5, 146.2, 145.2, 144.5, 143.4, 143.2, 142.7, 142.2, 142.1, 141.2, 140.7, 139.8, 137.0, 135.1, 134.5, 134.2, 131.4, 131.1, 131.0, 130.7, 130.0, 129.7, 128.4, 128.2, 127.8, 127.2, 127.0, 126.6, 126.4, 126.3, 125.9, 125.4, 125.3, 124.9, 124.7, 122.8, 122.2, 121.7, 120.8, 120.6, 120.3, 120.1, 120.0, 116.5, 116.4, 56.8, 56.0, 55.9, 55.6, 41.3, 31.7, 31.5, 31.2, 14.3, 13.5, 8.4, 8.0, 7.9; HRMS (FAB) m/z calcd for $C_{107}H_{98}N_5O_2S_2$ (M – H) 1548.7156, found 1548.7162.

2-(7-Bromo-9,9-diethyl-9H-fluoren-2-yl)-4,5-diphenyl-1H-imidazole (8). Compound 8 was synthesized following the general procedure as described for the synthesis of 5a and 5b by using 7bromo-9,9-diethyl-9H-fluorene-2-carbaldehyde (2b) (0.66 g, 2 mmol) and benzil (0.42 g, 2 mmol): cream-colored solid; yield 0.78 g, 75%; mp >300 °C; ¹H NMR (acetone- d_{6} , 500.13 MHz) δ 11.79 (s, 1 H), 8.21 (s, 1 H), 8.19 (dd, J = 8.0 Hz, 1.5 Hz, 1 H), 7.92 (d, J = 8.0 Hz, 1 H), 7.81 (d, J = 8.0 Hz, 1 H), 7.69–7.70 (m, 2 H), 7.66 (d, J = 1.5 Hz, 1 H), 7.32 (t, J = 7.5 Hz, 2 H), 7.44 (t, J = 7.5 Hz, 2 H), 7.36–7.39 (m, 1 H), 7.32 (t, J = 7.5 Hz, 2 H), 7.24 (t, J = 7.5 Hz, 1 H), 2.16 (q, J = 7.5Hz, 4 H), 0.33 (t, J = 7.5 Hz, 6 H); ¹³C NMR (CDCl₃+TFA, 125.77 MHz) δ 152.9, 151.5, 145.6, 144.8, 144.7, 138.5, 130.7, 130.3, 129.5, 129.3, 128.1, 126.6, 126.0, 125.8, 123.4, 122.1, 121.2, 121.0, 119.9, 57.0, 32.4, 8.0; HRMS (ESI) m/z calcd for $C_{32}H_{28}BrN_2$ (M + H) 521.1415, found 521.1426.

2-(7-Bromo-9,9-diethyl-9H-fluoren-2-yl)-1-ethyl-4,5-diphenyl-1Himidazole (9). Compound 9 was synthesized following the procedure as described for the synthesis of **6a**, by using 8 (52 g, 1 mmol) and bromoethane (0.16 g, 2 mmol): light-yellow solid; yield 0.47 g, 78%; mp 183–185 °C; ¹H NMR (CDCl₃, 500.13 MHz) δ 7.79 (d, *J* = 8.0 Hz, 1 H), 7.67–7.70 (m, 2 H), 7.60–7.62 (m, 1 H), 7.43–7.54 (m, 9 H), 7.21 (t, *J* = 7.5 Hz, 2 H), 7.14 (tt, *J* = 7.5 Hz, 1.5 Hz, 1 H), 3.96 (q, *J* = 7.0 Hz, 2 H), 2.02–2.11 (m, 4 H), 1.01 (t, *J* = 7.0 Hz, 3 H), 0.35 (t, *J* = 7.5 Hz, 6 H); ¹³C NMR (CDCl₃, 125.77 MHz) δ 152.5, 149.8, 147.7, 141.1, 140.0, 137.9, 134.6, 131.6, 131.1, 130.5, 130.2, 129.6, 129.1, 128.7, 128.3, 128.1, 126.9, 126.4, 126.3, 123.8, 121.6, 121.4, 119.9, 56.7, 39.8, 32.8, 16.1, 8.6; HRMS (ESI) *m*/*z* calcd for C₃₄H₃₂BrN₂ (M + H) 549.1729, found 549.1739.

5-(9,9-Diethyl-7-(1-ethyl-4,5-diphenyl-1H-imidazol-2-yl)-9H-fluoren-2-yl)thiophene-2-carbaldehyde (10a). Compound 10a was obtained by following the procedure as described for the synthesis of 7a by using 9 in place of 6a: yellow solid; yield 0.18 g, 63%; mp 214–216 °C; IR (KBr, cm⁻¹) 1655 ($\nu_{C=0}$); ¹H NMR (CDCl₃, 500.13 MHz) δ 9.90 (s, 1 H), 7.85 (d, *J* = 8.0 Hz, 1 H), 7.76–7.80 (m, 2 H), 7.70–7.73 (m, 3 H), 7.66 (d, *J* = 1.5 Hz, 1 H), 7.43–7.54 (m, 8 H), 7.22 (t, *J* = 7.5 Hz, 2 H), 7.15 (tt, *J* = 7.5 Hz, 1.0 Hz, 1 H), 3.99 (q, *J* = 7.0 Hz, 2 H), 2.12–2.16 (m, 4 H), 1.03 (t, *J* = 7.0 Hz, 3 H), 0.40 (t, *J* = 7.5 Hz, 6 H); ¹³C NMR (CDCl₃, 125.77 MHz) δ 182.8, 155.0, 151.4, 150.7, 147.6, 142.5, 142.1, 141.3, 137.8, 137.6, 134.3, 132.3, 131.3, 131.1, 130.3, 129.7, 129.1, 128.8, 128.3, 128.1, 127.0, 126.4, 125.8, 124.04, 123.96, 120.8, 120.7, 120.3, 56.7, 39.9, 32.8, 16.1, 8.6; HRMS (ESI) *m/z* calcd for C₃₉H₃₅N₂OS (M + H) 579.2465, found 579.2472.

5'-(9,9-Diethyl-7-(1-ethyl-4,5-diphenyl-1H-imidazol-2-yl)-9H-fluoren-2-yl)-2,2'-bithiophene-5-carbaldehyde (10b). Compound 10b was obtained by following the procedure as described for the synthesis of 7a by using 9 and (5'-(1,3-dioxolan-2-yl)-2,2'-bithiophene-5yl)tributylstannane: light-brown solid; yield 0.22 g, 68%; mp 160-162 °C; IR (KBr, cm⁻¹) 1653 ($\nu_{C=0}$); ¹H NMR (CDCl₃, 500.13) MHz) δ 9.88 (s, 1 H), 7.83 (d, J = 7.5 Hz, 1 H), 7.77 (d, J = 8.0 Hz, 1 H), 7.69–7.73 (m, 3 H), 7.64 (dd, J = 8.0 Hz, 1.5 Hz, 1 H), 7.58 (d, J = 1.5 Hz, 1 H), 7.54–7.55 (m, 2 H), 7.48–7.51 (m, 3 H), 7.44–7.46 (m, 2 H), 7.37 (q, J = 4.0 Hz, 2 H), 7.29 (d, J = 4.0 Hz, 1 H), 7.21 (t, J = 7.5 Hz, 2 H), 7.14 (tt, J = 7.5 Hz, 1.5 Hz, 1 H), 3.98 (q, J = 7.0 Hz, 2 H), 2.13 (q, J = 7.5 Hz, 4 H), 1.03 (t, J = 7.0 Hz, 3 H), 0.40 (t, J = 7.5 Hz, 6 H); ¹³C NMR (CDCl₃, 125.77 MHz) δ 182.4, 151.2, 150.3, 147.6, 147.1, 146.6, 141.4, 141.3, 141.2, 137.7, 137.4, 134.7, 134.5, 132.5, 131.4, 131.0, 130.2, 129.5, 129.0, 128.6, 128.1, 128.0, 127.1, 126.7, 126.1, 124.9, 124.0, 123.9, 123.6, 120.5, 120.0, 119.9, 56.4, 39.7, 32.7, 16.0, 8.5; HRMS (ESI) m/z calcd for $C_{43}H_{37}N_2OS_2$ (M + H) 661.2342, found 661.2354.

(E)-2-Cyano-3-(5-(9,9-diethyl-7-(1-ethyl-4,5-diphenyl-1H-imidazol-2-yl)-9H-fluoren-2-yl)thiophene-2-yl)acrylic acid (IF1). Compound IF1 was obtained from 10a by following a procedure described for **IF3**: yellow solid; yield 0.13 g, 82%; mp 204–206 °C; IR (KBr, cm⁻¹) 2206 ($\nu_{C\equiv N}$), 1698, 1582; ¹H NMR (DMSO- d_6 , 500.13 MHz) δ 8.51 (s, 1 H), 8.02-8.06 (m, 3 H), 7.90-7.93 (m, 2 H), 7.82-7.85 (m, 2 H), 7.74 (dd, J = 7.5 Hz, 1.5 Hz, 1 H), 7.54–7.59 (m, 3 H), 7.48–7.50 (m, 2 H), 7.42–7.43 (m, 2 H), 7.21 (t, J = 7.5 Hz, 2 H), 7.13 (tt, J = 7.0 Hz, 1.5 Hz, 1 H), 3.96 (q, J = 7.0 Hz, 2 H), 2.18 (q, J = 7.5 Hz, 4 H), 0.95 (t, J = 7.0 Hz, 3 H), 0.30 (t, J = 7.5 Hz, 6 H); ^{13}C NMR (DMSO-d₆ + TFA, 125.77 MHz) δ 163.5, 152.9, 151.4, 150.7, 146.5, 144.3, 143.8, 141.0, 140.9, 134.7, 132.7, 130.9, 130.5, 130.2, 129.5, 129.4, 129.2, 129.0, 128.7, 128.0, 127.6, 126.7, 126.2, 125.9, 125.5, 124.6, 121.8, 121.6, 121.0, 120.6, 116.4, 56.5, 41.2, 31.5, 14.3, 8.2; HRMS (FAB) m/z calcd for C₄₂H₃₄N₃O₂S (M-H) 644.2377, found 644.2389; m/z calcd for C₄₂H₃₅N₃NaO₂S (M + Na) 668.2353, found 668.2366.

(E)-2-Cyano-3-(5'-(9,9-diethyl-7-(1-ethyl-4,5-diphenyl-1H-imidazol-2-yl)-9H-fluoren-2-yl)-2,2'-bithiophene-5-yl)acrylic Acid (IF2). Compound IF2 was obtained from 10b by following a procedure described for IF3: orange solid; yield 0.15 g, 86%; mp 168–170 °C; IR (KBr, cm⁻¹) 2203 ($\nu_{C=N}$), 1708, 1585; ¹H NMR (DMSO- d_{6} , 500.13 MHz) δ 8.51 (s, 1 H), 7.96–8.03 (m, 3 H), 7.88 (s, 1 H), 7.76–7.80 (m, 3 H), 7.71–7.73 (m, 2 H), 7.66 (d, J = 4.0 Hz, 1 H), 7.54–7.59 (m, 3 H), 7.49 (d, J = 7.5 Hz, 2 H), 7.42 (d, J = 7.5 Hz, 2 H), 7.21 (t, J = 7.5 Hz, 2 H), 7.13 (t, J = 7.5 Hz, 1 H), 3.94–3.98 (m, 2 H), 2.14–2.22 (m, 4 H), 0.95 (t, J = 7.0 Hz, 3 H), 0.30 (t, J = 7.5 Hz, 6 H); ¹³C NMR (DMSO- d_6 +TFA, 125.77 MHz) δ 163.6, 151.3, 150.6, 146.2, 145.53, 145.46, 144.4, 144.0, 141.2, 139.7, 134.3, 133.9, 133.2, 130.9, 130.4, 130.2, 129.5, 129.4, 129.2, 128.9, 128.7, 128.1, 127.6, 126.7, 126.2, 125.7, 124.9, 124.7, 124.4, 121.6, 121.2, 121.0, 120.6, 119.8, 116.4, 56.4, 41.2, 31.5, 14.3, 8.2; HRMS (FAB) m/z calcd for C₄₆H₃₆N₃O₂S₂ (M – H) 726.2254, found 726.2262; m/z calcd for C₄₆H₃₇N₃NaO₂S₂ (M + Na) 750.2230, found 750.2232.

ASSOCIATED CONTENT

S Supporting Information

Copies of ¹H and ¹³C NMR spectra, solvatochromic plots, and 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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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Mishra, A.; Fischer, M. K. R.; Bäuerle, P. Angew. Chem., Int. Ed. 2009, 48, 2474–2499.

(2) Mishra, A.; Bäuerle, P. Angew. Chem., Int. Ed. 2012, 51, 2020–2067.

(3) (a) Li, H.; Hou, Y.; Yang, Y.; Tang, R.; Chen, J.; Wang, H.; Han, H.; Peng, T.; Li, Q.; Li, Z. *ACS Appl. Mater. Interfaces* **2013**, *5*, 12469–12477. (b) Wang, Z.; Liang, M.; Wang, L.; Hao, Y.; Wang, C.; Sun, Z.; Xue, S. *Chem. Commun.* **2013**, *49*, 5748–5750. (c) Chen, J.; Liang, M. *Chem. Soc. Rev.* **2013**, *42*, 3453–3488.

(4) (a) Gupta, K. S. V.; Suresh, T.; Singh, S. P.; Islam, A.; Han, L.; Chandrasekharam, M. Org. Electron. 2014, 15, 266–275. (b) Venkateswararao, A.; Thomas, K. R. J.; Lee, C. P.; Li, C. T.; Ho, K. C. ACS Appl. Mater. Interfaces 2014, 6, 2528–2539.

(5) (a) Cao, D.; Peng, J.; Hong, Y.; Fang, X.; Wang, L.; Meier, H. *Org. Lett.* **2011**, *13*, 1610–1613. (b) Marszalek, M.; Nagane, S.; Ichake, A.; Baker, R. H.; Paul, V.; Zakeeruddin, S. M.; Grätzel, M. *RSC Adv.* **2013**, *3*, 7921–7927.

(6) Wang, Z. S.; Cui, Y.; Hara, K.; Dan-oh, Y.; Kasada, C.; Shinpo, A. *Adv. Mater.* **2007**, *19*, 1138–1141.

(7) (a) Liu, B.; Wang, B.; Wang, R.; Gao, L.; Huo, S.; Liu, Q.; Li, X.; Zhu, W. J. Mater. Chem. A **2014**, *2*, 804–812. (b) Chai, Q.; Li, W.; Zhu, S.; Zhang, Q.; Zhu, W. ACS Sustainable Chem. Eng. **2014**, *2*, 239– 247.

(8) Zhang, X. H.; Cui, Y.; Katoh, R.; Koumura, N.; Hara, K. J. Phys. Chem. C 2010, 114, 18283-18290.

(9) (a) Yu, L.; Xi, J.; Chan, H. T.; Su, T.; Antrobus, L. C.; Tong, B.; Dong, Y.; Chan, W. K.; Phillips, D. L. *J. Phys. Chem. C* **2013**, *117*, 2041–2052. (b) Yella, A.; Baker, R. H.; Curchod, B. F. E.; Astani, N. A.; Teuscher, J.; Polander, L. E.; Mathew, S.; Moser, J. E.; Tavernelli, I.; Rothlisberger, U.; Grätzel, M.; Nazeeruddin, M. K.; Frey, J. *Chem. Mater.* **2013**, *25*, 2733–2739.

(10) Chen, Y. C.; Chen, Y. H.; Chou, H. H.; Chaurasia, S.; Wen, Y. S.; Lin, J. T.; Yao, C. F. *Chem.—Asian J.* **2012**, *7*, 1074–1084.

(11) Lin, R. Y. Y.; Yen, Y. S.; Cheng, Y. T.; Lee, C. P.; Hsu, Y. C.; Chou, H. H.; Hsu, C. Y.; Chen, Y. C.; Lin, J. T.; Ho, K. C.; Tsai, C. Org. Lett. **2012**, *14*, 3612–3615.

(12) (a) Marzari, G.; Durantini, J.; Minudri, D.; Gervaldo, M.; Otrero, L.; Fungo, F.; Pozzi, G.; Cavazzini, M.; Orlandi, S.; Quici, S. J. *Phys. Chem. C* **2012**, *116*, 21190–21200. (b) Ci, Z.; Yu, X.; Wang, C.; Ma, T.; Bao, M. Dyes Pigm. **2014**, *104*, 8–14.

(13) (a) Heredia, D.; Natera, J.; Gervaldo, M.; Otero, L.; Fungo, F.; Lin, C. Y.; Wong, K. T. *Org. Lett.* **2010**, *12*, 12–15. (b) Macor, L.; Gervaldo, M.; Fungo, F.; Otero, L.; Dittrich, T.; Lin, C. Y.; Chi, L. C.; Fang, F. C.; Lii, S. W.; Wong, K. T.; Tsai, C. H.; Wu, C. C. *RSC Adv.* **2012**, *2*, 4869–4878.

(14) (a) Lin, R. Y. Y.; Lin, H. W.; Yen, Y. S.; Chang, C. H.; Chou, H. H.; Chen, P. W.; Hsu, C. Y.; Chen, Y. C.; Lin, J. T.; Ho, K. C. *Energy Environ. Sci.* **2013**, *6*, 2477–2486. (b) Lin, Y. Z.; Huang, C. H.; Chang, Y. J.; Yeh, C. W.; Chin, T. M.; Chi, K. M.; Chou, P. T.; Watanabe, M.; Chow, T. J. *Tetrahedron* **2014**, *70*, 262–269.

(15) (a) Liu, J.; Li, R.; Si, X.; Zhou, D.; Shi, Y.; Wang, Y.; Jing, X.; Wang, P. *Energy Environ. Sci.* **2010**, *3*, 1924–1928. (b) Fischer, M. K. R; Wenger, S.; Wang, M.; Mishra, A.; Zakeeruddin, S. M.; Grätzel, M.; Bäuerle, P. *Chem. Mater.* **2010**, *22*, 1836–1845. (c) Feng, Q.; Zhang, Q.; Lu, X.; Wang, H.; Zhou, G.; Wang, Z. S. *ACS Appl. Mater. Interfaces* **2013**, *5*, 8982–8990.

(16) (a) Choi, H.; Raabe, I.; Kim, D.; Teocoli, F.; Kim, C.; Song, K.; Yum, J. H.; Ko, J.; Nazeeruddin, M. K.; Grätzel, M. *Chem.—Eur. J.* **2010**, *16*, 1193–1201. (b) Chen, C. Y.; Pootrakulchote, N.; Hung, T. H.; Tan, C. J.; Tsai, H. H.; Zakeeruddin, S. M.; Wu, C. G.; Grätzel, M. *J. Phys. Chem. C* **2011**, *115*, 20043–20050.

(17) Kwon, T. H.; Armel, V.; Nattestad, A.; MacFarlane, D. R.; Bach, U.; Lind, S. J.; Gordon, K. C.; Tang, W.; Jones, D. J.; Holmes, A. B. *J. Org. Chem.* **2011**, *76*, 4088–4093.

(18) (a) Venkateswararao, A.; Thomas, K. R. J.; Lee, C. P.; Ho, K. C. *Tetrahedron Lett.* **2013**, *54*, 3985–3989. (b) Sudyoadsuk, T.; Pansay, S.; Morada, S.; Rattanawan, R.; Namuangruk, S.; Kaewin, T.; Jungsuttiwong, S.; Promarak, V. *Eur. J. Org. Chem.* **2013**, 5051–5063. (19) Hong, Y.; Liao, J. Y.; Cao, D.; Zang, X.; Kuang, D. B.; Wang, L.; Meier, H.; Su, C. Y. *J. Org. Chem.* **2011**, *76*, 8015–8021. (b) Lee, W.; Yuk, S. B.; Choi, J.; Kim, H. J.; Kim, H. W.; Kim, S. H.; Kim, B.; Ko, M. J.; Kim, J. P. *Dyes Pigm.* **2014**, *102*, 13–21.

(20) (a) Hua, Y.; Chang, S.; Huang, D.; Zhou, X.; Zhu, X.; Zhao, J.; Chen, T.; Wong, W. Y.; Wong, W. K. *Chem. Mater.* **2013**, *25*, 2146– 2153. (b) Chen, C.; Yang, X.; Cheng, M.; Zhang, F.; Zhao, J.; Sun, L. *ACS Appl. Mater. Interfaces* **2013**, *5*, 10960–10965.

(21) (a) Velusamy, M.; Thomas, K. R. J.; Lin, J. T.; Hsu, Y. C.; Ho, K. C. Org. Lett. 2005, 7, 1899–1902. (b) Haid, S.; Marszalek, M.; Mishra, A.; Wielopolski, M.; Teuscher, J.; Moser, J. E.; Baker, R. H.; Zakeeruddin, S. M.; Grätzel, M.; Bäuerle, P. Adv. Funct. Mater. 2012, 22, 1291–1302. (c) Zhang, M.; Wang, Y.; Xu, M.; Ma, W.; Li, R.; Wang, P. Energy Environ. Sci. 2013, 6, 2944–2949.

(22) (a) Cui, Y.; Wu, Y.; Lu, X.; Zhang, X.; Zhou, G.; Miapeh, F. B.; Zhu, W.; Wang, Z. S. *Chem. Mater.* **2011**, *23*, 4394–4401. (b) Yen, Y. S.; Lee, C. T.; Hsu, C. Y.; Chou, H. H.; Chen, Y. C.; Lin, J. T. *Chem.*— *Asian J.* **2013**, *8*, 809–816.

(23) (a) Velusamy, M.; Hsu, Y. C.; Lin, J. T.; Chang, C. W.; Hsu, C.
P. *Chem.*—*Asian J.* 2010, *5*, 87–96. (b) Zhou, L.; Jia, C.; Wan, Z.; Li,
Z.; Bai, J.; Zhang, L.; Zhang, J.; Yao, X. *Dyes Pigm.* 2012, *95*, 743–750.
(c) Zhou, L.; Jia, C.; Wan, Z.; Chen, X.; Yao, X. *Org. Electron.* 2013, *14*, 1755–1762.

(24) (a) Mao, M.; Wang, J. B.; Xiao, Z. F.; Dai, S. Y.; Song, Q. H. *Dyes Pigm.* **2012**, *94*, 224–232. (b) Lee, W.; Yang, Y.; Cho, N.; Ko, J.; Hong, J. I. *Tetrahedron* **2012**, *68*, 5590–5598.

(25) (a) Kumar, D.; Thomas, K. R. J.; Lee, C. P.; Ho, K. C. Org. Lett. 2011, 13, 2622–2625. (b) Chang, J.; Lee, C. P.; Kumar, D.; Chen, P. W.; Lin, L. Y.; Thomas, K. R. J.; Ho, K. C. J. Power Sources 2013, 240, 779–785.

(26) (a) Peng, Z.; Tao, S.; Zhang, X.; Tang, J.; Lee, C. S.; Lee, S. T. J. Phys. Chem. C 2008, 112, 2165–2169. (b) Jiang, Z.; Liu, Z.; Yang, C.; Zhong, C.; Qin, J.; Yu, G.; Liu, Y. Adv. Funct. Mater. 2009, 19, 3987–3995. (c) Zhu, M.; Ye, T.; Li, C. G.; Cao, X.; Zhong, C.; Ma, D.; Qin, J.; Yang, C. J. Phys. Chem. C 2011, 115, 17965–17972.

(27) (a) Thomas, K. R. J.; Lin, J. T.; Hsu, Y. C.; Ho, K. C. Chem. Commun. 2005, 4098–4100. (b) Li, W.; Wu, Y.; Li, X.; Xie, Y.; Zhu, W. Energy Environ. Sci. 2011, 4, 1830–1837. (c) Nguyen, W. H.; Bailie,

The Journal of Organic Chemistry

C. D.; Burschka, J.; Moehl, T.; Grätzel, M.; McGehee, M. D.; Sellinger, A. Chem. Mater. 2013, 25, 1519–1525.

(28) (a) Yao, S.; Belfield, K. D. J. Org. Chem. 2005, 70, 5126-5132.
(b) Kumar, D.; Thomas, K. R. J.; Chen, Y. L.; Jou, Y. C.; Jou, J. H. Tetrahedron 2013, 69, 2594-2602.

(29) Sonogashira, K.; Tohda, Y.; Hagihara, N. Tetrahedron Lett. 1975, 16, 4467–4470.

(30) Yusybov, M. S.; Filimonov, V. D. Synthesis 1991, 2, 131-132.

(31) Sommelet, M. Compt. Rend. 1913, 157, 852-854.

(32) Stille, J. K. Angew. Chem., Int. Ed. Engl. 1986, 25, 508-524.

(33) Knoevenagel, E. Dtsch. Chem. Ges. 1896, 29, 172-174.

(34) Kumar, S.; Karthik, D.; Thomas, K. R. J.; Hundal, M. S. *Tetrahedron Lett.* **2014**, 55, 1931–1935.

(35) (a) Baheti, A.; Tyagi, P.; Thomas, K. R. J.; Hsu, Y.-C.; Lin, J. T. J. Phys. Chem. C 2009, 113, 8541–8547. (b) Baheti, A.; Thomas, K. R. J.; Lee, C.-P.; Ho, K.-C. Chem.—Asian. J. 2012, 7, 2942–2954. (c) Baheti, A.; Thomas, K. R. J.; Lee, C.-P.; Ho, K.-C. Org. Electron. 2013, 14, 3267–3276.

(36) (a) Berg, O. V. D.; Jager, W. F. J. Org. Chem. 2006, 71, 2666–2676. (b) Granzhan, A.; Ihmels, H.; Viola, G. J. Am. Chem. Soc. 2007, 129, 1254–1267.

(37) Cheng, H. M.; Hsieh, W. F. Energy Environ. Sci. 2010, 3, 442–447.

(38) (a) Hagberg, D. P.; Edvinsson, T.; Marinado, T.; Boschloo, G.; Hagfeldt, A.; Sun, L. *Chem. Commun.* **2006**, 2245–2247. (b) Thomas, K. R. J.; Hsu, Y. C.; Lin, J. T.; Lee, K. M.; Ho, K. C.; Lai, C. H.; Cheng, Y. M.; Chou, P. T. *Chem. Mater.* **2008**, *20*, 1830–1840.

(39) Hagfeldt, A.; Grätzel, M. Chem. Rev. **1995**, 95, 49–68.

(40) Grätzel, M. Nature 2001, 414, 338-344.

(41) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N; Staroverov, V. N; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian 09, revision A.02; Gaussian, Inc.: Wallingford, CT, 2009.

(42) (a) Kim, S.; Lee, J. K.; Kang, S. O.; Ko, J.; Yum, J. H.; Fantacci, S.; Angelis, F. D.; Censo, D. D.; Nazeeruddin, M. K.; Grätzel, M. *J. Am. Chem. Soc.* **2006**, *128*, 16701–16707. (b) O'Rourke, C.; Bowler, D. R. J. Phys. Chem. C **2010**, *114*, 20240–20248.

(43) Becke, A. D. J. Chem. Phys. 1993, 98, 1372-1377.

(44) Lee, C.; Yang, W.; Parr, R. G. Phys. Rev. B 1988, 37, 785-789.

(45) Kannan, R.; He, G. S.; Yuan, L.; Xu, F.; Prasad, P. N.; Dombroskie, A. G.; Reinhardt, B. A.; Baur, J. W.; Vaia, R. A.; Tan, L. S. *Chem. Mater.* **2001**, *13*, 1896–1904.

(46) (a) Lee, S. H.; Nakamura, T.; Tsutsui, T. Org. Lett. 2001, 3, 2005–2007. (b) Liu, L.; Wong, W. Y.; Lam, Y. W.; Tam, W. Y. Inorg. Chim. Acta 2007, 360, 109–121.

(47) (a) Wei, Y.; Y. Yang, Y.; Yeh, J. M. *Chem. Mater.* **1996**, *8*, 2659–2666. (b) Raimundo, J. M.; Blanchard, P.; Planas, N. G.; Mercier, N.;

Rak, I. L.; Hierle, R.; Roncali, J. J. Org. Chem. 2002, 67, 205–218.

(48) Chen, H.; Huang, H.; Huang, X.; Clifford, J. N.; Forneli, A.; Palomares, E.; Zheng, X.; Zheng, L.; Wang, X.; Shen, P.; Zhao, B.; Tan, S. J. Phys. Chem. C **2010**, 114, 3280–3286.

(49) Wang, E.; Meng, Q.; Wang, C.; Li, L.; Li, H.; Hu, W. Synth. Met. **2009**, 159, 1298–1301.

(50) Tan, L. S.; Kannan, R., US 7319151 B1, 2008.

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