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Organic Dyes Containing a Coplanar Indacenodithiophene Bridge for High-Performance Dye-Sensitized Solar Cells

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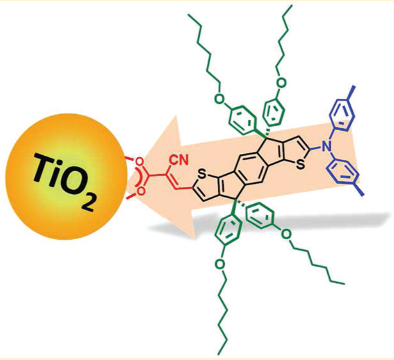
Supporting Information

ABSTRACT: A series of new organic dyes exploiting coplanar indacenodithiophene as the central π-spacer of the classical donor−(π-spacer)−acceptor configuration were synthesized and characterized for dye-sensitized solar cells. The coplanarity of the indacenodithiophene core facilitates efficient donor to acceptor charge transfer, imparting the new organic dyes significant bathochromic shifts and remarkable power conversion efficiencies of up to 6.7% (**DTInDT**) under AM 1.5G radiation.



Dye-sensitized solar cells (DSSCs), greatly improved by Grätzel since 1991,[1] are currently one of the most promising next-generation photovoltaic technologies because of their high efficiency, simplicity of device structures, and cost-effective production. In addition to the more costly ruthenium-based sensitizers,[2] metal-free organic dyes are also being exploited in DSSCs for their relatively lower cost and flexibility in tailoring molecular structures for manipulation of electronic and photophysical characteristics.[3] Among molecular designs of organic dyes for efficient DSSCs, donor−(π-spacer)−acceptor (D−π−A) structures stemming from the push−pull concept of the photoinduced intramolecular charge transfer are mostly employed to tune the molecular absorption to match solar radiation for efficient light harvesting.[4] In this context, in addition to the common adoption of a π-electron donor such as diarylamine and a π-electron acceptor such as cyanoacrylic acid bearing an anchoring group toward the TiO_2 surface, the modification on the π-spacer is also essential and substantial in the manipulation of the electronic structures and properties of the organic dyes. As such, various chromophores previously utilized in organic optoelectronic devices had been introduced as effective π-spacers for DSSC dyes, including oligoene,[5] coumarin,[6] oligothiophene,[7] fluorene,[8] spirobifluorene,[9] and phenoxazine.[10] Recently, organic dyes making use of varied intrinsic electronic characteristics of the π-spacers were also reported. The introduction of heteroarenes such as furan,[11] selenophene,[12] pyrrole,[13] quinoline,[14] pyrimidine,[15] isoxazole,[16] and thiazole[17] into the π-spacers was shown to enhance bathochromic shifts and thus to yield panchromatic light harvesting.

On the other hand, instead of the endless search for innumerable heteroarenes for use in DSSC dyes, better π-conjugation can also be readily achieved by increasing the coplanarity of bridged π-systems.[18] For instance, indacenodithiophene, comprising alternate thiophene-phenylene-thiophene aromatics through sp^3−carbon bridges, showed a great improvement in terms of both coplanarity and π-conjugation[19] and also had been widely exploited as a crucial building block for polymer solar cells.[20] Therefore, we envision that the utilization of the indacenodithiophene core as a π-spacer of D−π−A systems may yield new organic dyes for efficient DSSCs. We report a series of organic D−π−A dyes with diarylamino as the donor, cyanoacrylic acid as the acceptor, and coplanar indacenodithiophene as the bridging spacer (Figure 1). The modulation of the donor units allows us to tailor the molecular energy levels and the absorption edge. In addition, the central indacenodithiophene π-spacer is functionalized with 4-(n-hexoxy)phenyl groups on the sp^3−carbon bridges, which not only retains the brilliant photophysical properties of the core but also can potentially suppress undesirable aggregation of dyes and charge recombination between the electrolyte and the TiO_2 electrode. These new organic D−π−A dyes,

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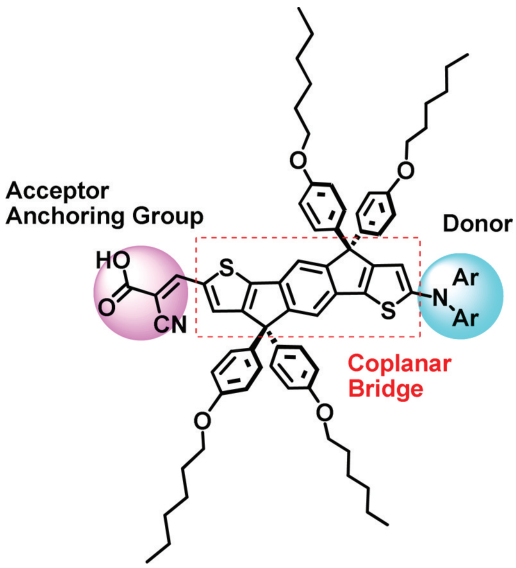


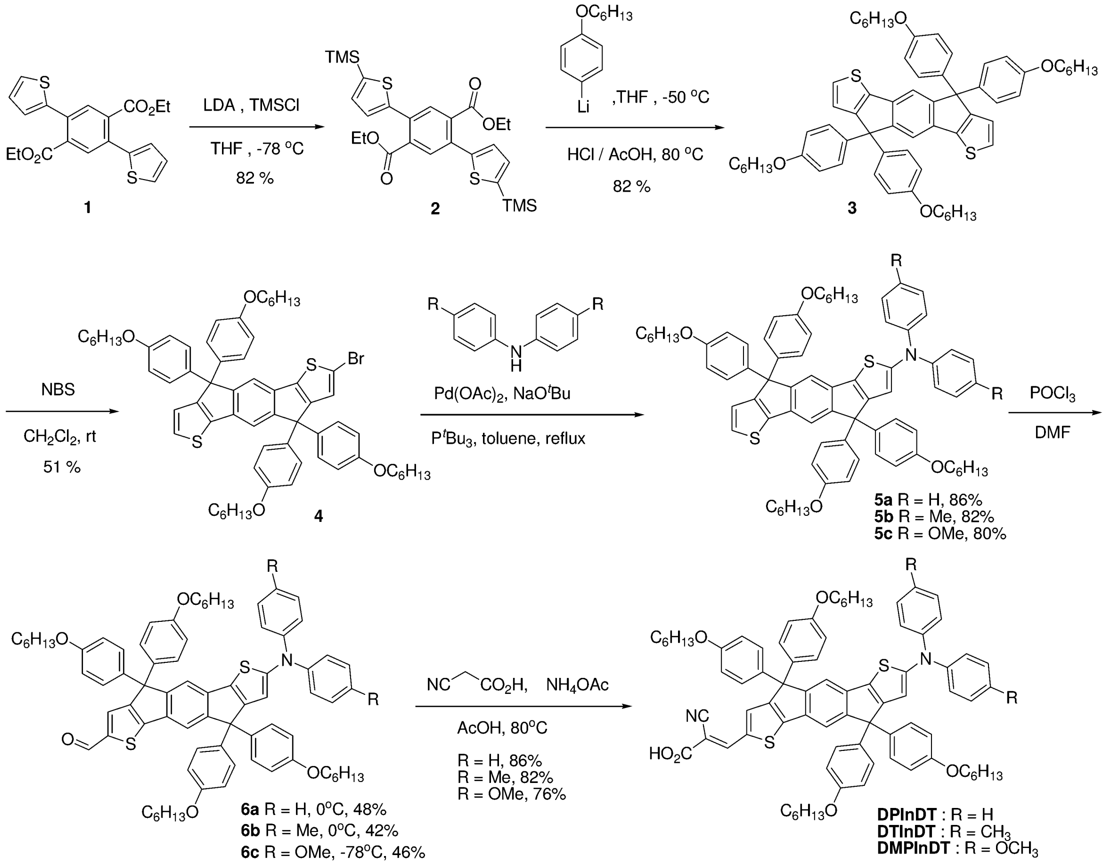
Figure 1. Structure of the indacenodithiophene-bridged organic dye.

combining essential characteristics of a DSSC dye, are thought to be useful for highly efficient organic photovoltaics.

Scheme 1 depicts the synthetic route for the new organic dyes. The synthesis of the coplanar indacenodithiophene core structure was generally based on our previously established method.[19a] With a starting compound of diethyl 1,4-bis(thiophen-2-yl)-2,5-benzenedicarbonate **1**, the trimethylsilyl (TMS) group was introduced onto the α-thienyl positions by LDA deprotonation, followed by the subsequent quenching with chlorotrimethylsilane to give 1,4-bis(5-trimethylsilylthiophen-2-yl)-2,5-benzenedicarbonate **2**. The TMS groups are intentionally introduced to facilitate the later intramolecular cyclization reactions. The addition of an excess of aryllithium, which was prepared in advance from the corresponding aryl bromide with *n*-BuLi, to the ester groups of **2** gave the corresponding triaryl alcohol intermediate, which was directly subjected to acid-catalyzed intramolecular annulation without further purification to afford the coplanar indacenodithiophene **3** in an 82% yield in two steps. The selective bromination of **3** with *N*-bromosuccinimide (NBS) in CH_2Cl_2 furnished monobrominated intermediate **4** in a moderate yield. The installation of an electronic donor on the indacenodithiophene core was achieved by palladium-catalyzed C−N bond formation of **4** with various diaryl amines, giving amine derivatives **5a−c** in high yields. Compounds **5a−c** were readily converted into their corresponding carbaldehydes, **6a−c**, respectively, via Vilsmeier−Haack reaction. In the final step, aldehydes **6a−c** underwent Knöevenagel condensation with cyanoacetic acid in refluxing acetic acid in the presence of ammonium acetate, giving the corresponding target DSSC sensitizers **DPInDT**, **DTInDT**, and **DMPInDT**, respectively.

The UV−vis absorption and photoluminescence spectra of the organic dyes in THF are depicted in Figure 2, and the corresponding photophysical data are summarized in Table 1. In the electronic absorption spectra, all three dyes exhibit a single prominent band with the absorption maximum around 490−520 nm and an extinction coefficient higher than 2.5 × 10^4 M^{-1} cm^{-1}. Such absorption characteristics can be ascribed

Scheme 1. Synthesis of Organic Dyes DPInDT, DTInDT, and DMPInDT



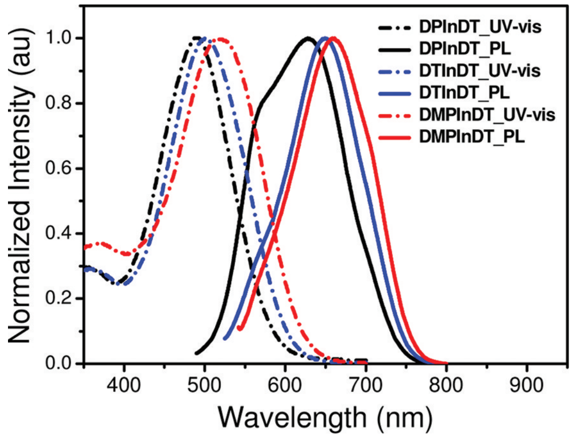


Figure 2. Normalized UV−vis absorption (−·−) and photoluminescence (—) spectra of organic dyes **DPInDT**, **DTInDT**, and **DMPInDT** in THF at 25 °C.

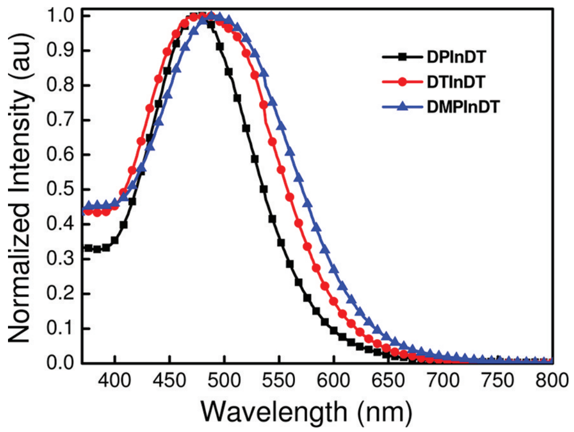


Figure 3. Absorption spectra of dyes **DPInDT**, **DTInDT**, and **DMPInDT** anchored to a 7 μm porous TiO_2 nanoparticle film.

to the $\pi-\pi^*$ transition of the whole D−π−A conjugation backbone. Apparently, the absorption spectra of **DTInDT** (λ_{max} = 500 nm) and **DMPInDT** (λ_{max} = 520 nm) show considerable bathochromic shifts as compared with that of **DPInDT** (λ_{max} = 490 nm). This result clearly indicates that the modulation of the optical band-gaps and energy levels of D−π−A dyes can be feasibly achieved by altering the electronic nature of diarylamino donors. Similarly, the charge transfer emission maximum shifts from 628 nm for **DPInDT** to 660 nm for **DMPInDT**. Besides the major emission peak, a shoulder around 550 nm, which is assigned as emission from the local excited state, was also detected for three dyes, yet with a much higher intensity in **DPInDT** than in **DTInDT** and **DMPInDT**. This result suggests that **DTInDT** and **DMPInDT**, the dyes incorporating stronger donors, possess stronger photoinduced intramolecular charge transfer ability over the π-conjugation backbone, leading to larger red shifts in absorption and emission. Figure 3 depicts the absorption spectra of the organic dyes once they are anchored to the 7 μm porous TiO_2 nanoparticle film. The absorption maxima of these three dyes were slightly blue-shifted compared to those observed in the THF solution. It is mainly that the deprotonation of carboxylic acid upon anchoring to the TiO_2 surface leads to the consequent carboxylate−TiO_2 unit which is in general a weaker acceptor compared to the corresponding carboxylic acid.[21] On the other hand, no peak broadening effect was observed in the film absorption, indicating that the intermolecular aggregation between dyes can be significantly suppressed by the pendant side chains on sp^3−carbon bridges, which is advantageous for constructing a highly efficient organic DSSC dye.

The frontier molecular orbitals of these new dyes were calculated with density functional theory (DFT) (Figure S1 of the Supporting Information). HOMOs are mainly populated from the diarylamino donor to the indacenodithiophene π-spacer, whereas LUMOs are mainly populated from the π-spacer to the cyanoacetic acid moiety. This result suggests an effective intramolecular charge transfer between the diarylamino donor and the cyanoacetic acid acceptor would occur during electronic transitions of these dyes. Such electronic population can facilitate injection of the electron from photoexcited dyes to the TiO_2 electrode. The calculation also reveals the coplanarity of the indacenodithiophene core as well as the contribution of methyl and methoxy groups to the HOMO distributions in **DTInDT** and **DMPInDT**, which is consistent with their stronger electron-donating nature and the observed red-shifted absorption.

Cyclic voltammetry (CV) was used to probe the electrochemical properties of **DPInDT**, **DTInDT**, and **DMPInDT**. Two oxidation waves were observed on the voltammograms. The first oxidation waves at lower oxidation potentials were generally from the contribution of diarylamine, whereas the second ones, with higher oxidation potentials and quasi-reversible behaviors, were from the indacenodithiophene π-spacer. Meanwhile, the lower oxidation potentials of **DTInDT** and **DMPInDT** as compared to that of **DPInDT** clearly indicate the HOMO raising effect upon the introduction of stronger donors in **DTInDT** and **DMPInDT**, which is in accord with the calculation showing the methyl and methoxy groups' significant contribution to the HOMO distributions (Figure S1 of the Supporting Information). On the other hand, for the reduction waves, these three dyes showed one quasi-reversible peak. The reduction potentials did not vary significantly with the variation of the donor moieties, which is also consistent with the calculations, in which the LUMOs are less influenced by the diarylamino donors. The zero−zero

Table 1. Physical Properties of Organic Dyes DPInDT, DTInDT, and DMPInDT

dye	$\lambda_{abs}{}^{a}$ (nm)	ε^{a} (M^{-1} cm^{-1})	$\lambda_{em}{}^{a}$ (nm)	$E_{ox}{}^{b}$ (V)	$E_{0-0}{}^{c}$ (V)	$E_{ox}{}^{*d}$ (V)
DPInDT	490	29622	628	0.82	2.28	−1.46
DTInDT	500	27866	648	0.77	2.17	−1.40
DMPInDT	520	25268	660	0.71	2.11	−1.40

[a] The absorption spectra were measured in a THF solution (10^{-5} M). [b] The oxidation potentials of the dyes were measured in CH_2Cl_2 with 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF6) as the electrolyte [working electrode, glassy carbon; reference electrode, Ag/Ag^+; calibrated with ferrocene/ferrocenium (Fc/Fc^+) as an internal reference and converted to NHE by addition of 630 mV,[22] counter electrode, Pt]. [c] E_{0-0} was determined from the intersection of the absorption and emission spectra in THF. [d] E_{ox}* was calculated as $E_{ox} - E_{0-0}$.

excitation energy (E_{0-0}) estimated from the onset of the absorption spectra together with the ground-state oxidation potential (E_{ox}) was used to calculate the excited-state oxidation potential [$E_{ox}^* = E_{ox} - E_{0-0}$ (Table 1)]. The thus obtained E_{ox}^* values for three dyes are more negative than the conduction band edge of TiO_2 (−0.5 V vs NHE),[23] indicating injection of the electron from excited-state dyes onto the TiO_2 electrode would be energetically favorable. These dyes also exhibit more positive ground-state oxidation potentials to ensure facile dye regeneration through the iodide/triiodide coupled electrolyte (0.4 V vs NHE) and to prevent the undesirable charge recombination between the oxidized dyes and photoinjected electrons on the TiO_2 electrode.

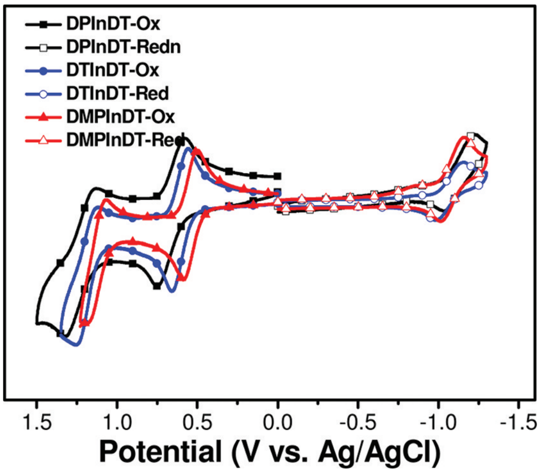


Figure 4. Cyclic voltammograms of **DPInDT** (black), **DTInDT** (blue), and **DMPInDT** (red). $TBAPF_6$ (0.1 M) (oxidation) in CH_2Cl_2 and TBAP (0.1 M) (reduction) in THF were used as supporting electrolytes. A glassy carbon electrode was used as the working electrode.

The photovoltaic characteristics of **DPInDT**, **DTInDT**, and **DMPInDT** as the sensitizers for DSSCs were evaluated using a sandwich-type DSSC cell comprising 0.6 M 1-butyl-3-methylimidazolium iodide (BMII), 0.05 M LiI, 0.03 M I_2, 0.5 M 4-*tert*-butylpyridine, and 0.1 M guanidinium thiocyanate in a mixture of acetonitrile and valeronitrile (85/15, v/v), as the redox electrolyte. Also, considering the spatial interruption between dyes provided by the pendant side chains on sp^3−carbon bridges, no co-absorbent was required in the fabrication of the devices (details of the preparation and characterization of the device are given in Experimental Section). The incident monochromatic photon-to-current conversion efficiency (IPCE) spectra of the DSSCs are shown in Figure 5. The IPCE of the device using the **DPInDT** sensitizer exceeds 70% in the spectral region ranging from 400 to 554 nm and reaches a maximum of 87% at 476 nm, whereas **DTInDT** and **DMPInDT**, bearing stronger π-electron donors, have shown IPCE values exceeding 70% in a more red-shifted region from 400−439 to 590 nm and maxima of 86% at 500 nm and 83% at 509 nm, respectively. Such broader spectral responses of **DTInDT** and **DMPInDT** are consistent with the trend in the absorption spectra, implying their better light harvesting ability for longer-wavelength visible lights. Intriguingly, though the IPCE of **DMPInDT** extends to wavelengths of nearly 700 nm, this broadened absorption does not reflect higher J_{SC} values (vs **DTInDT**) (Figure 6). This perhaps is associated with its intrinsically smaller extinction coefficient compared to those of the other two. Via integration of IPCE spectra with the AM 1.5G solar spectrum, indeed **DTInDT** gives the highest value, confirming that the **DTInDT** dye with both a broader absorption spectrum (vs **DPInDT**) and a higher extinction coefficient (vs **DMPInDT**) would give the highest short-circuit current density (J_{SC}) as shown in Figure 6.

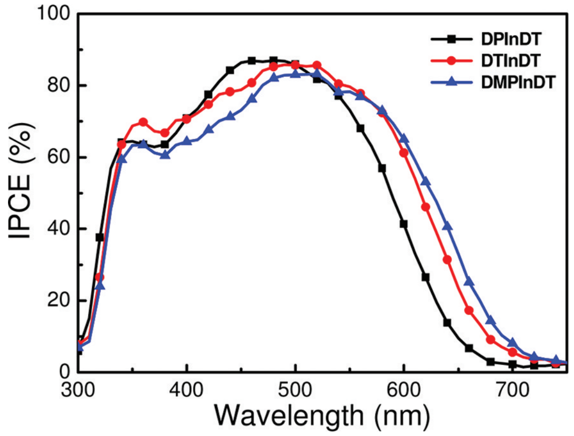


Figure 5. IPCE spectra of DSSCs based on organic dyes **DPInDT**, **DTInDT**, and **DMPInDT**.

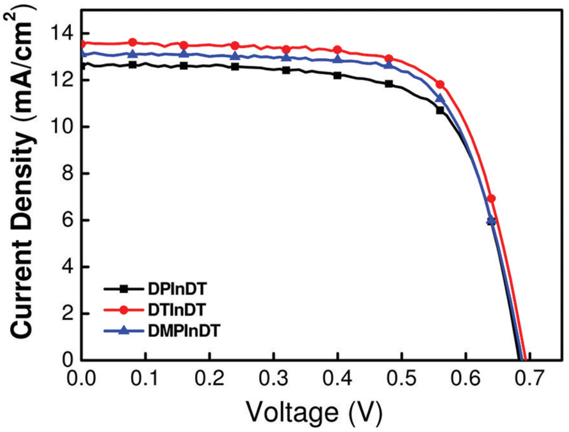


Figure 6. Photocurrent density vs voltage for DSSCs based on **DPInDT**, **DTInDT**, and **DMPInDT** organic dyes under AM 1.5G simulated solar light (100 mW/cm^2).

Figure 6 shows the current−voltage (J−V) curves of the DSSCs under standard global AM 1.5G solar irradiation. The DSSCs based on **DPInDT**, **DTInDT**, and **DMPInDT** dyes showed similar open-circuit voltage and fill factors. The short-circuit photocurrent density and overall conversion efficiency of the three dyes were in the following order: **DTInDT** > **DMPInDT** > **DPInDT**. The **DTInDT**-based cell exhibited the highest J_{SC} value, which is consistent with the better sunlight harvesting ability of **DTInDT** as discussed above. For the solar cell based on **DTInDT**, the short-circuit photocurrent density (J_{SC}) was 13.54 mA/cm^2, the open-circuit voltage (V_{OC}) was 0.69 V, and the fill factor (FF) was 0.71, yielding an overall conversion efficiency (η) of 6.67%. With relatively lower J_{SC} values, devices based on **DPInDT** and **DMPInDT** show inferior conversion efficiencies of 6.04 and 6.33%, respectively (see Table 2). For a fair comparison, the **N719**-sensitized DSSC was also fabricated under the same conditions. The

Table 2. DSSC Performance Parameters Based on DPInDT, DTInDT, DMPInDT, and N719 Dyes[a]

dye	J_{SC} (mA/cm^2)	V_{OC} (V)	FF	η (%)
DPInDT	12.59	0.68	0.71	6.04
DTInDT	13.54	0.69	0.71	6.67
DMPInDT	13.12	0.68	0.71	6.33
N719	15.59	0.75	0.70	8.16

[a] Performances of DSSCs were measured with a 0.125 cm^2 working area. Irradiating light was AM 1.5G light (100 mW/cm^2).

efficiency of the **DTInDT** cell reached 82% of that of the **N719** cell.

Electrochemical impedance spectroscopy (EIS) is a useful tool for characterizing important interfacial charge transfer processes in DSSCs, such as the charge recombination at the TiO_2–dye–electrolyte interface, electron transport in the TiO_2 electrode, electron transfer at the counter electrode, and I_3^- transport in the electrolyte. In this study, impedance spectroscopy of the cells based on **DPInDT**, **DTInDT**, and **DMPInDT** dyes was used to investigate mechanisms at the internal interfaces of the DSSCs. This examination was conducted by subjecting the cells to constant AM 1.5G 100 mW/cm^2 illumination and to bias at the open-circuit voltage (V_{OC}) of the cells (namely, under the condition of no dc electric current).

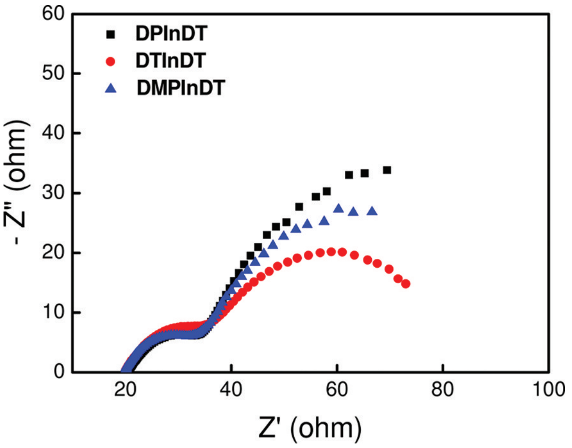


Figure 7. Electrochemical impedance spectroscopy Nyquist plots for DSSCs based on **DPInDT**, **DTInDT**, and **DMPInDT** organic dyes.

Figure 7 shows the EIS Nyquist plots (i.e., minus the imaginary part of the impedance, $-Z''$, vs the real part of the impedance, Z', when sweeping the frequency) for DSSCs based on **DPInDT**, **DTInDT**, and **DMPInDT** dyes. For the frequency range investigated (20 Hz to 1 MHz), a larger semicircle occurs in the lower-frequency range (~20 Hz to 1 kHz) and a smaller semicircle occurs in the higher-frequency range. With the bias illumination and voltage applied, the larger semicircle at lower frequencies corresponded to the charge transfer processes at the TiO_2–dye–electrolyte interface, while the smaller semicircle at higher frequencies corresponded to the charge transfer processes at the Pt–electrolyte interface. The three cells showed minimal differences in the smaller semicircles at higher frequencies; however, the difference between the cells in the larger semicircles at lower frequencies was significant. The width of the lower-frequency semicircle (corresponding to charge transfer resistance at the TiO_2–dye–electrolyte interface) in the Nyquist plot decreased in the following order: **DPInDT** > **DMPInDT** > **DTInDT**. The decrease in the lower-frequency semicircle width with the increase in DSSC efficiency and the smallest width observed in the highest-efficiency **DTInDT** cell indicate the most efficient electron generation and thus larger electron population at its TiO_2–dye–electrolyte interface.[7d] Thus, the EIS results are in good agreement with results of the short-circuit currents and the overall power conversion efficiencies of the DSSCs.

In summary, we successfully synthesized a series of metal-free organic DSSC sensitizers by exploiting indacenodithiophene as an essential π-spacer in the D–π–A structure. Their physical properties and device performances were examined and evaluated. Via incorporation of the conventional diarylamine donor and cyanoacetic acid acceptor, and the indacenodithiophene π-spacer with its remarkable coplanar conformation and charge transfer ability, these new dyes were able to extend the absorption maxima over 500 nm and exhibited IPCE values of >80%. Furthermore, the peripheral *n*-hexoxyphenyl side chains on the sp^3–carbon bridge of the core could serve as a spatial hindrance to mitigate undesirable dye aggregation. With the proper adjustment of the electron donating power of the π-donors, the level of the bathochromic shift could be enhanced. As the result, all the dyes in this series gave promising DSSC efficiencies of >6%. Among them, **DTInDT**, the dye with the relatively broader absorption and higher extinction coefficient, showed the highest J_{SC} of 13.54 mA/cm^2 and highest conversion efficiency of 6.67%, which is ~82% of the efficiency of the ruthenium dye **N719**-based reference cell under the same condition. We believe these results are sufficiently indicative for the further development of highly efficient metal-free organic dyes.

■ EXPERIMENTAL SECTION

Diethyl 1,4-Bis(5-trimethylsilylthiophen-2-yl)-2,5-benzenedicarbonate (2). To a solution of dry diisopropylamine (9.5 mL, 67.4 mmol) in THF (100 mL) at −78 °C was added *n*-BuLi (1.6 M solution in *n*-hexane, 40.4 mL, 64.7 mmol). The reaction mixture was kept at −78 °C for 1 h, and the solution of diethyl 1,4-bis(thiophen-2-yl)-2,5-benzenedicarboxylate (10 g, 25.9 mmol) in THF (100 mL) was added dropwise via an addition funnel. The resulting mixture was stirred at −78 °C for 1 h, and then chlorotrimethylsilane (8.4 mL, 68.0 mmol) was added dropwise via a syringe. The mixture was warmed to room temperature and stirred for 1 h. Then, it was poured into water and extracted with diethyl ether. The combined extracts were dried over anhydrous magnesium sulfate and filtered, and the solvent was evaporated. The resulting crude solid was washed with ethanol to afford **2** as a white solid (11.2 g, 82%): mp 96–97 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.81 (s, 2H), 7.18 (d, J = 3.6 Hz, 2H), 7.14 (d, J = 3.6 Hz, 2H), 4.21 (q, J = 7.2 Hz, 4H), 1.14 (t, J = 7.0 Hz, 6H), 0.35 (s, 18H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 167.6, 145.5, 141.7, 134.0, 133.6, 133.2, 131.5, 128.0, 61.6, 13.9, 0.1; IR (KBr) ν 3049, 2957, 1717, 1379, 1230, 841 cm^{-1}.

4,9-Dihydro-4,4,9,9-(*p*-hexoxyphenyl)-*s*-indaceno[1,2-*b*:5,6-*b*′]dithiophene (3). To a solution of 1-bromo-4-(*n*-hexoxy)benzene (23.0 g, 90.0 mmol) in THF (30 mL) at −78 °C was added *n*-BuLi (1.6 M solution in *n*-hexane, 56.0 mL, 90.0 mmol). The mixture was warmed to −50 °C and stirred for 1 h, and then a solution of **2** (5.3 g, 10.0 mmol) in THF (20 mL) was added dropwise via an addition funnel. The mixture was warmed to room temperature and stirred for 12 h, and the reaction was quenched with deionized water and the mixture extracted with dichloromethane. The combined organic extracts were dried over anhydrous magnesium sulfate and filtered, and the solvent was evaporated. The resulting solid was washed with hexanes to afford a white solid crude intermediate. The white intermediate was then directly dissolved in acetic acid and heated to 80

°C, and 1 mL of concentrated hydrochloric acid was added to the solution. The mixture was stirred at 80 °C for 2 h, and a solid precipitated. The suspension was cooled, and the solid was filtered out. The resulting solid was washed consecutively with water (2 × 50 mL), an aqueous sodium carbonate solution, and methanol (30 mL) to afford **3** as a white solid (7.9 g, 82%): mp 165 °C (DSC); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.39 (s, 2H), 7.24 (d, J = 5.2 Hz, 2H), 7.15 (d, d, J = 6.8 Hz, 8H), 6.97 (d, J = 4.8 Hz, 2H), 6.76 (d, J = 6.8 Hz, 8H), 3.90 (t, J = 6.6 Hz, 8H), 1.75 (m, 8H), 1.44 (m, 8H), 1.34–1.30 (m, 16H), 0.90 (t, J = 6.4 Hz, 12H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 157.7, 155.9, 153.5, 140.8, 136.5, 134.8, 128.8, 127.4, 122.8, 117.1, 114.0, 67.9, 61.9, 31.7, 29.3, 25.9, 22.7, 14.2; IR (KBr) ν 3031, 2932, 2858, 1606, 1507, 1467, 1245, 1175, 821 cm^{-1}; HRMS (m/z, FAB$^+$) calcd for $C_{64}H_{74}O_4S_2$ 970.5029, found 970.5012.

2-Bromo-4,9-dihydro-4,4,9,9-(*p*-hexoxyphenyl)-*s*-indaceno[1,2-*b*:5,6-*b*′]dithiophene (4). To a solution of **3** (2 g, 2.05 mmol) dissolved in dichloromethane (15 mL) was added dropwise a solution of NBS (0.47 g, 2.67 mmol) dissolved in dichloromethane (80 mL). The mixture was stirred at room temperature for 2 h and extracted with dichloromethane and water. The combined organic extracts were dried over anhydrous magnesium sulfate and filtered, and the solvent was evaporated. The resultant compound was purified by column chromatography on silica gel with dichloromethane and hexane as the eluent (v/v, 1/5) to afford **4** as a yellow oil (1.1 g, 51%): ^{1}H NMR (CD_2Cl_2, 400 MHz) δ 7.40 (s, 1H), 7.36 (s, 1H), 7.28 (d, J = 4.8 Hz, 1H), 7.13–7.10 (m, 8H), 7.00 (s, 1H), 6.97 (d, J = 4.8 Hz, 1H), 6.77–6.74 (m, 8H), 3.89 (q, J = 4.1 Hz, 8H), 1.75–1.70 (m, 8H), 1.43–1.31 (m, 24H), 0.88 (t, J = 6.6 Hz, 12H); ^{13}C NMR (CD_2Cl_2, 100 MHz) δ 158.4, 158.3, 156.6, 155.1, 154.1, 152.9, 141.4, 140.9, 136.5, 136.0, 135.4, 134.6, 129.0, 128.9, 128.3, 126.1, 123.0, 117.4, 114.5, 114.4, 113.8, 68.3, 63.1, 62.3, 32.0, 29.6, 26.1, 23.0, 14.3; IR (KBr) ν 3043, 2933, 2858, 1606, 1507, 1467, 1246, 1175, 822 cm^{-1}; HRMS (m/z, FAB$^+$) calcd for $C_{64}H_{73}Br^{79}O_4S_2$ 1048.4134, found 1048.4132; HRMS (m/z, FAB$^+$) calcd for $C_{64}H_{73}Br^{81}O_4S_2$ 1050.4113, found 1050.4119.

2-(*N,N*-Diphenylamino)-4,9-dihydro-4,4,9,9-(*p*-hexoxyphenyl)-*s*-indaceno[1,2-*b*:5,6-*b*′]dithiophene (5a). A mixture of **4** (1.2 g, 1.14 mmol), diphenylamine (0.252 g, 1.48 mmol), palladium(II) acetate (13 mg, 0.057 mmol), sodium *tert*-butoxide (0.73 g, 7.6 mmol), and tri-*tert*-butylphosphine (0.05 M in toluene, 0.24 mL, 0.012 mmol) in toluene (15 mL) was stirred under reflux for 10 h. The mixture was cooled to room temperature and extracted with dichloromethane and water. The combined organic extracts were dried over anhydrous magnesium sulfate and filtered, and the solvent was evaporated. The resulting crude product was purified by column chromatography on silica gel (washed with 1% triethylamine) with dichloromethane and hexane (v/v, 1/4) as the eluent to afford **5b** as a yellow solid (1.12 g, 86%): mp 66 °C (DSC); ^{1}H NMR (CD_2Cl_2, 400 MHz) δ 7.39 (s, 1H), 7.27–7.22 (m, 6H), 7.13–7.08 (m, 12H), 7.03–6.97 (m, 2H), 6.96 (d, J = 4.8 Hz, 1H), 6.74 (t, J = 9.6 Hz, 8H), 6.65 (s, 1H), 3.88 (q, J = 6.8 Hz, 8H), 1.74–1.67 (m, 8H), 1.404 (m, 8H), 1.32–1.30 (m, 16H), 0.89–0.86 (m, 12H); ^{13}C NMR (CD_2Cl_2, 100 MHz) δ 158.2, 156.2, 154.1, 154.0, 153.8, 152.7, 147.8, 141.1, 136.7, 136.6, 135.8, 134.6, 134.5, 129.3, 129.1, 129.0, 127.8, 123.4, 123.0, 122.8, 117.3, 117.2, 116.6, 114.4, 68.3, 63.2, 62.2, 32.0, 29.7, 26.1, 23.1, 14.3; IR (KBr) ν 3034, 2951, 2927, 1856, 1607, 1506, 1493, 1425, 1245, 1177, 823, 751, 695, 655 cm^{-1}; TOF MS (m/z, ESI$^+$) 1138; HRMS (m/z, FAB$^+$) calcd for $C_{76}H_{83}NO_4S_2$ 1137.5764, found 1137.5793.

2-[*N,N*-Bis(*p*-tolyl)amino]-4,9-dihydro-4,4,9,9-(*p*-hexoxyphenyl)-*s*-indaceno[1,2-*b*:5,6-*b*′]dithiophene (5b). A mixture of **4** (1.05 g, 1.01 mmol), di-*p*-tolylamine (0.26 g, 1.31 mmol), palladium(II) acetate (0.011 g, 0.048 mmol), sodium *tert*-butoxide (0.77 g, 7.99 mmol), and tri-*tert*-butylphosphine (0.05 M in toluene, 0.20 mL, 0.010 mmol) in toluene (15 mL) was stirred under reflux for 12 h. The mixture was cooled to room temperature and extracted with dichloromethane and water. The combined organic extracts were dried over anhydrous magnesium sulfate, filtered, and evaporated. The resulting crude product was purified by column chromatography on silica gel (washed with 1% triethylamine) with dichloromethane and hexane (v/v, 1/4) as the eluent to afford **5b** as a yellow-brown solid (0.96 g, 82%): mp 76–78 °C; ^{1}H NMR (CD_2Cl_2, 400 MHz) δ 7.41 (s, 1H), 7.30 (d, J = 4.9 Hz, 1H), 7.26 (s, 1H), 6.92–7.18 (m, 17H), 6.75–6.82 (m, 8H), 6.58 (s, 1H), 3.86–3.96 (m, 8H), 2.32 (s, 6H), 1.76–1.82 (m, 8H), 1.31–1.52 (m, 24H), 0.88–0.98 (m, 12H); ^{13}C NMR (CD_2Cl_2, 100 MHz) δ 158.2, 155.9, 155.2, 153.9, 152.6, 145.4, 141.1, 136.7, 136.6, 135.9, 134.1, 133.1, 133.0, 129.8, 128.9, 128.8, 127.5, 122.9, 116.9, 116.2, 115.1, 114.2, 68.0, 62.9, 62.0, 31.6, 29.3, 15.7, 22.6, 20.5, 13.9; IR (KBr) ν 2948, 2926, 2855, 1642, 1607, 1507, 1246, 1177, 823 cm^{-1}; MS (m/z, FAB$^+$) 808 (6), 986 (13), 1166 (7); HRMS (m/z, FAB$^+$) calcd for $C_{78}H_{87}NO_4S_2$ 1165.6077, found 1165.6072.

2-[*N,N*-Bis(*p*-methoxyphenyl)amino]-4,9-dihydro-4,4,9,9-(*p*-hexoxyphenyl)-*s*-indaceno[1,2-*b*:5,6-*b*′]dithiophene (5c). A mixture of **4** (1.05 g, 1.01 mmol), bis(4-methoxyphenyl)amine (0.30 g, 1.31 mmol), palladium(II) acetate (0.011 g, 0.048 mmol), sodium *tert*-butoxide (0.77 g, 7.99 mmol), and tri-*tert*-butylphosphine (0.05 M in toluene, 0.20 mL, 0.010 mmol) in toluene (30 mL) was stirred under reflux for 12 h. After that, the mixture was cooled to room temperature and extracted with dichloromethane and water. The combined organic extracts were dried over anhydrous magnesium sulfate, filtered, and evaporated. The resulting crude product was purified by column chromatography on silica gel (washed with 1% triethylamine) with dichloromethane and hexane (v/v, 1/4) as the eluent to afford **5c** as a yellow-brown solid (0.97 g, 80%): mp 81 °C (DSC); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.36 (s, 1H), 7.26 (d, J = 5.2 Hz, 1H), 7.19 (s, 1H), 7.13–706 (m, 12H), 6.83–6.72 (m, 12H), 6.43 (s, 1H), 3.95–3.89 (m, 8H), 3.80 (s, 6H), 1.80–1.47 (m, 8H), 1.46–1.43 (m, 8H), 1.37–1.32 (m, 16), 0.95–0.91 (m, 12H); ^{13}C NMR (CD_2Cl_2, 100 MHz) δ 157.9, 156.0, 155.8, 155.6, 154.0, 153.7, 152.2, 141.4, 141.3, 136.9, 136.8, 136.0, 133.9, 131.9, 129.1, 129.0, 127.1, 124.6, 122.9, 117.0, 116.1, 114.6, 114.2, 113.0, 68.1, 68.0, 63.0, 62.1, 55.7, 31.9, 29.6, 29.5, 26.1, 22.9, 14.4; IR (KBr) ν 3034, 2948, 2929, 2857, 1607, 1580, 1507, 1460, 1291, 1244, 1177, 1034, 826, 655 cm^{-1}; HRMS (m/z, FAB$^+$) calcd for $C_{78}H_{87}NO_6S_2$ 1197.5975, found 1197.5963.

2-(*N,N*-Diphenylamino)-4,9-dihydro-4,4,9,9-(*p*-hexoxyphenyl)-7-formyl-*s*-indaceno[1,2-*b*:5,6-*b*′]dithiophene (6a). To a solution of **5a** (0.33 g, 0.29 mmol) in dry DMF (6 mL) was added phosphorus oxychloride (0.05 mL, 0.62 mmol) dropwise at 0 °C, and the mixture was stirred at 0 °C for 1 h. The mixture was warmed to room temperature and heated at 80 °C for 4 h. The mixture was cooled to room temperature, and an aqueous sodium acetate solution was added to quench the reaction. The mixture was then extracted with diethyl acetate and water. The organic solution was washed with a saturated brine solution, dried over anhydrous magnesium sulfate, filtered, and evaporated. The resulting crude solid was purified by gradient column chromatography on silica gel (washed with 1% triethylamine) with dichloromethane and hexane as the eluent (v/v, from 1/3 to 1/1) to afford **6a** as an orange solid: mp 69 °C (DSC); ^{1}H NMR (CD_2Cl_2, 400 MHz) δ 9.77 (s, 1H), 7.62 (s, 1H), 7.53 (s, 1H), 7.29–7.24 (m, 5H), 7.15–7.10 (m, 12H), 7.06–7.03 (m, 2H), 6.78–6.75 (m, 8H), 6.40 (s, 1H), 3.91 (q, J = 6.4 Hz, 8H), 1.75–1.69 (m, 8H), 1.42–1.31 (m, 24H), 0.88 (m, 12H); ^{13}C NMR (CD_2Cl_2, 100 MHz) δ 182.7, 158.5, 158.3, 156.2, 155.8, 155.4, 155.4, 153.2, 151.2, 147.6, 145.5, 138.6, 136.1, 135.7, 133.2, 132.5, 132.0, 129.4, 129.0, 128.9, 123.7, 123.1, 118.7, 116.5, 116.1, 114.5, 114.4, 68.3, 63.2, 62.5, 32.0, 30.1, 29.6, 26.1, 23.0, 14.3; IR (KBr) ν 3065, 3035, 2948, 2929, 2857, 2768, 1661, 1606, 1507, 1467, 1426, 1246, 1177, 1138, 1028, 826, 753, 695, 657, 526 cm^{-1}; TOF MS (m/z, ESI$^+$) 1166; HRMS (m/z, FAB$^+$) calcd for $C_{77}H_{83}NO_5S_2$ 1165.5713, found 1165.5692.

2-[*N,N*-Bis(*p*-tolyl)amino]-4,9-dihydro-4,4,9,9-(*p*-hexoxyphenyl)-7-formyl-*s*-indaceno[1,2-*b*:5,6-*b*′]dithiophene (6b). To a solution of **5b** (0.37 g, 0.22 mmol) in dry DMF (10 mL) was added phosphorus oxychloride (0.043 mL, 0.46 mmol) dropwise at 0 °C, and the mixture was stirred at 0 °C for 1 h. The mixture was warmed to room temperature and heated to 70 °C for 4 h. The mixture was cooled to room temperature; an aqueous sodium acetate solution was added to quench the reaction, and a solid appeared and precipitated after the addition. The solid was collected, washed with water, dissolved in dichloromethane, and washed with water. The combined extracts were collected, dried over anhydrous magnesium sulfate, filtered, and evaporated. The resulting crude solid was purified by gradient column chromatography on silica gel (washed with 1% triethylamine) with dichloromethane and hexane as the eluent (v/v, from 1/3 to 1/1) to afford **6b** as an orange solid (0.15 g, 42%): mp 80−82 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.78 (s, 1H), 7.69 (s, 1H), 7.46 (s, 1H), 7.18 (s, 1H), 7.02−7.15 (m, 16H), 6.72−6.82 (m, 8H), 6.54 (s, 1H), 3.91 (q, *J* = 6.9 Hz, 8H), 2.31 (s, 6H), 1.69−1.82 (m, 8H), 1.25−1.51 (m, 24H), 0.86−0.95 (m, 12H); ^{13}C NMR (CD_2Cl_2, 100 MHz) δ 182.5, 158.4, 158.2, 157.0, 153.0, 145.2, 145.1, 136.1, 135.6, 133.5, 131.5, 129.8, 128.9, 128.7, 123.2, 118.4, 116.0, 114.3, 114.2, 113.6, 68.1, 62.9, 62.1, 31.9, 31.6, 30.1, 29.7, 29.3, 29.2, 29.1, 25.7, 25.6, 22.7, 22.6, 20.5, 13.9, 13.8; IR (KBr) ν 3040, 2952, 2927, 2856, 1662, 1507, 1247, 1177, 826 cm^{-1}; MS (*m*/*z*, FAB$^+$) 1015 (22), 1111 (13), 1194 (91); HRMS (*m*/*z*, FAB$^+$) calcd for $C_{79}H_{87}NO_5S_2$ 1193.6026, found 1193.6018.

2-[*N*,*N*-Bis(*p*-methoxyphenyl)amino]-4,9-dihydro-4,4,9,9-(*p*-hexoxyphenyl)-7-formyl-*s*-indaceno[1,2-*b*:5,6-*b*′]-ithiophene (6c). To a solution of **5c** (0.35 g, 0.29 mmol) in dry DMF (10 mL) was added phosphorus oxychloride (0.043 mL, 0.46 mmol) dropwise at −78 °C. The mixture was warmed to room temperature and heated at 50 °C. After 3 h, the mixture was cooled to room temperature, and 10% hydrochloric acid was added to quench the reaction. The mixture was extracted with ethyl ether and water; the combined organic extracts were collected, washed with a saturated brine solution, dried over anhydrous magnesium sulfate, and filtered, and the solvent was evaporated. The resulting crude solid was purified by gradient column chromatography on silica gel (basified with 1% triethylamine) with dichloromethane and hexane as the eluent (v/v, from 1/3 to 1/1) to afford **6c** as an orange solid (0.16 g, 46%): mp 89 °C (DSC); ^{1}H NMR (CD_2Cl_2, 400 MHz) δ 9.77 (s, 1H), 7.49 (s, 1H), 7.14−7.09 (m, 12H), 6.85−6.82 (m, 4H), 6.82−6.75 (m, 8H), 6.38 (s, 1H), 3.91 (q, *J* = 6.53 Hz, 8H), 3.78 (s, 6H), 1.79−1.71 (m, 8H), 1.47−1.40 (m, 8H), 1.40−1.28 (m, 16H), 0.93−0.87 (m, 12H); ^{13}C NMR (CD_2Cl_2, 100 MHz) δ 182.5, 158.6, 158.4, 156.4, 156.0, 155.9, 155.4, 152.8, 151.3, 145.2, 140.9, 138.9, 136.2, 135.8, 131.9, 131.7, 129.7, 129.0, 128.9, 125.4, 118.4, 115.8, 114.7, 114.5, 114.4, 110.4, 68.3, 63.1, 62.4, 31.9, 29.6, 29.6, 26.07, 26.05, 23.0, 14.2; IR (KBr) ν 3031, 2929, 2857, 1659, 1603, 1505, 1430, 1243, 1177, 1033, 827 cm^{-1}; TOF MS (*m*/*z*, ESI$^+$) 1126. Anal. Calcd: C, 77.35; H, 7.15; S, 5.23. Found: C, 77.61; H, 7.17; S, 5.21.

2-(N,N-diphenylamino)-4,9-dihydro-4,4,9,9-(p-hexoxyphenyl)-*s*-indaceno[1,2-b:5,6-b′]-dithiophen-7-yl-2-cyanoacrylic acid (DPInDT). A mixture of **6a** (0.14 g, 0.12 mmol), cyanoacetic acid (0.03 g, 0.59 mmol), and ammonium acetate (0.02 g, 0.26 mmol) in glacial acetic acid (5 mL) was stirred at 80 °C for 4 h. After the mixture had been cooled to room temperature, deionized water was added to quench the reaction, and a black solid precipitated. The solid was filtered out, washed with water, dissolved in dichloromethane, and washed with water. The organic extracts were collected, dried over anhydrous magnesium sulfate, filtered, and evaporated to afford **DPInDT** as a black solid (0.14 g, 96%): mp 135−137 °C; ^{1}H NMR (CD_2Cl_2, 400 MHz) δ 8.30 (s, 1H), 7.61 (s, 1H), 7.58 (s, 1H), 7.29−7.25 (m, 5H), 7.17−7.05 (m, 14H), 6.79−6.75 (m, 8H), 6.64 (s, 1H), 3.91 (q, *J* = 7.06 Hz, 8H), 1.77−1.70 (m, 8H), 1.44−1.27 (m, 24H), 0.92−0.89 (m, 12H); ^{13}C NMR (CD_2Cl_2, 100 MHz) δ 158.5, 158.3, 156.6, 156.4, 155.9, 154.6, 153.5, 153.3, 148.3, 148.3, 147.5, 139.4, 138.1, 136.0, 135.8, 135.4, 134.3, 132.8, 132.1, 129.4, 128.9, 128.8, 123.8, 123.6, 119.0, 116.5, 116.4, 115.5, 114.5, 114.4, 94.2, 68.3, 63.2, 62.4, 32.0, 30.1, 29.6, 29.5, 26.1, 23.0, 14.2; IR (KBr) ν 3444, 2926, 2855, 2211, 1692, 1606, 1579, 1507, 1493, 1419, 1177, 1153, 1030, 824, 696 cm^{-1}; HRMS (*m*/*z*, FAB$^+$) calcd for $C_{80}H_{84}N_2O_6S_2$ 1232.5771, found 1232.5740.

2-[*N*,*N*-Bis(*p*-tolyl)amino]-4,9-dihydro-4,4,9,9-(*p*-hexoxyphenyl)-*s*-indaceno[1,2-*b*:5,6-*b*′]dithiophen-7-yl-2-cyanoacrylic Acid (DTInDT). A mixture of **6b** (0.1 g, 0.081 mmol), cyanoacetic acid (0.02 g, 0.39 mmol), and ammonium acetate (0.02 g, 0.26 mmol) in glacial acetic acid (5 mL) was stirred at 80 °C for 10 h. After the mixture had been cooled to room temperature, deionized water was added to quench the reaction, and a black solid precipitated. The solid was filtered out, washed with water, dissolved in dichloromethane, and then washed with water. The organic extracts were collected, dried over anhydrous magnesium sulfate, filtered, and evaporated. The resulting crude solid was purified by column chromatography on silica gel with dichloromethane and THF as the eluent (v/v, from 1/0 to 0/1) to afford **DTInDT** as a black solid (84 mg, 82%): mp 134−136 °C; ^{1}H NMR (CD_2Cl_2, 400 MHz) δ 8.33 (s, 1H), 7.64 (s, 1H), 7.59 (s, 1H), 7.25 (s, 1H), 7.01−7.18 (m, 16H), 6.71−6.86 (m, 8H), 6.54 (1H), 3.93 (q, *J* = 7.1 Hz, 8H), 2.33 (s, 6H), 1.65−1.82 (m, 8H), 1.18−1.52 (m, 24H), 0.82−0.96 (m, 12H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 158.3, 158.1, 145.1, 136.0, 135.5, 133.4, 131.4, 129.9, 128.9, 128.8, 123.3, 114.4, 114.3, 67.9, 62.8, 62.1, 31.6, 30.3, 29.2, 25.7, 22.6, 20.8, 14.0; IR (KBr) ν 3412, 2952, 2925, 2853, 2214, 1646, 1506, 1454, 1359, 1246, 1177, 1011 cm^{-1}; MS (*m*/*z*, FAB$^+$) 1082 (4), 1178 (4), 1261 (24); HRMS (*m*/*z*, FAB$^+$) calcd for $C_{82}H_{88}N_2O_6S_2$ 1260.6084, found 1260.6083.

2-[*N*,*N*-Bis(*p*-methoxyphenyl)amino]-4,9-dihydro-4,4,9,9-(*p*-hexoxyphenyl)-*s*-indaceno[1,2-*b*:5,6-*b*′]dithiophen-7-yl-2-cyanoacrylic Acid (DMPInDT). A mixture of **6c** (0.1 g, 0.081 mmol), cyanoacetic acid (0.02 g, 0.39 mmol), and ammonium acetate (0.02 g, 0.26 mmol) in glacial acetic acid (5 mL) was stirred at 80 °C for 10 h. After the mixture had been cooled to room temperature, deionized water was added to quench the reaction, and a black solid precipitated. The solid was filtered out, washed with water, dissolved in dichloromethane, and washed with water. The organic extracts were collected, dried over anhydrous magnesium sulfate, filtered, and evaporated. The resulting crude solid was purified by column chromatography on silica gel with dichloromethane and THF as the eluent (v/v, from 1/0 to 0/1) to afford **DMPInDT** as a black solid (80 mg, 76%): mp 136−138 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.26 (s, 1H), 7.56 (s, 1H), 7.45 (s, 1H), 7.05−7.20 (m, 12H), 6.98 (s, 1H), 6.71−6.86 (m, 12H), 6.40 (s, 1H), 3.90 (t, *J* = 7.1 Hz, 8H), 3.79 (s, 6H), 1.68−1.82 (m, 8H), 1.21−1.52 (m, 24H), 0.81−0.98 (m, 12H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 158.2, 158.1, 156.3, 140.9, 136.1, 135.5, 128.9, 128.8, 125.5, 125.2, 114.6, 114.4, 114.3, 67.9, 62.7, 62.0, 55.5, 31.6, 31.5, 30.3, 29.7, 29.3, 29.2, 25.7, 22.6, 22.5, 21.2, 14.0; IR (KBr) ν 3392, 2958, 2924, 2853, 2217, 1606, 1528, 1350, 1259, 1024, 801, 732 cm^{-1}; HRMS (*m*/*z*, FAB$^+$) calcd for $C_{82}H_{89}N_2O_8S_2$ (M + H$^+$) 1293.6060, found 1293.6097.

Measurement of Absorption Spectra of Dye-Loaded Nanoporous TiO_2 Films. A 7 μm thick transparent porous TiO_2 nanoparticle layer (adopting 20 nm anatase TiO_2 nanoparticles) was coated on a glass plate by the doctor-blade method. After being sintered at 500 °C for 30 min, the TiO_2 film was immersed into 0.5 mM dye solutions in acetonitrile and *tert*-butanol (1/1 volume ratio) at room temperature for 24 h. The UV−vis absorption spectrum of the dye-loaded TiO_2 film was then recorded on a spectrophotometer.

Fabrication of Dye-Sensitized Solar Cells. To prepare the DSSC working electrodes, the FTO glass plates were first cleaned in a detergent solution using an ultrasonic bath for 15 min and then rinsed with water and ethanol. A layer of 20 nm anatase TiO_2 nanoparticles for the transparent nanocrystalline layer was first coated on the FTO glass plates by the doctor-blade method. After the film was dried at 120 °C, another layer of 400 nm anatase TiO_2 nanoparticles was then deposited as the light-scattering layer of the DSSC. The resulting working electrode was composed of a 12 μm thick transparent TiO_2 nanoparticle layer (particle size of 20 nm) and a 4 μm thick TiO_2 scattering layer (particle size of 400 nm). The nanoporous TiO_2 electrodes were then sequentially heated at 150 °C for 10 min, 300 °C for 10 min, 400 °C for 10 min, and finally 500 °C for 30 min. After the solutions had cooled, the nanoporous TiO_2 electrodes were immersed in the 0.5 mM dye solutions in acetonitrile and *tert*-butanol (1/1 volume ratio) at room temperature for 24 h. Counter electrodes of the DSSC were prepared by depositing 40 nm thick Pt films on the FTO glass plates by e-beam evaporation. The dye-adsorbed TiO_2 working electrode and a counter electrode were then assembled into a sealed DSSC cell with a sealant spacer between the two electrode plates. A drop of electrolyte solution [0.6 M 1-butyl-3-methylimidazolium iodide (BMII), 0.05 M LiI, 0.03 M I_2, 0.5 M 4-*tert*-butylpyridine, and 0.1 M guanidinium thiocyanate in a mixture of acetonitrile and valeronitrile (85/15, v/v)] was injected into the cell through a drilled hole. Finally, the hole was sealed using the sealant and a cover glass. An antireflection coating film was adhered to the DSSC. A mask with an aperture area of 0.125 cm^2 was covered on a testing cell during photocurrent−voltage and incident photon-to-current conversion efficiency measurements.

Photocurrent−Voltage Measurement. The photocurrent−voltage characteristics of the DSSCs were measured under illumination with AM 1.5G solar light from a 300 W xenon lamp solar simulator. The incident light intensity was calibrated as 100 mW/cm^2. Photocurrent−voltage curves were obtained by applying an external bias voltage to the cell and measuring the generated photocurrent.

Incident Monochromatic Photon-to-Current Conversion Efficiency Measurement. The incident monochromatic photon-to-current conversion efficiency (IPCE) spectra were recorded by using a 75 W xenon lamp as the light source coupled to a monochromator. The IPCE data were taken by illuminating monochromatic light on the solar cells (with a wavelength sampling interval of 10 nm from 300 to 750 nm) and measuring the short-circuit current of the solar cells. The IPCE measurement was performed with a lock-in amplifier, a low-speed chopper, and a bias light source under full computer control.

Electrochemical Impedance Spectroscopy Measurement. The electrochemical impedance of the cells was measured by using an impedance analyzer with a frequency range of 20 Hz to 1 MHz. In this study, during the impedance measurement, the cell was under constant AM 1.5G 100 mW/cm^2 illumination. The impedance of the cell (throughout the frequency range of 20 Hz to 1 MHz) was then measured by applying a bias at the open-circuit voltage (V_{OC}) of the cell and by using an ac amplitude of 10 mV.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^{1}H and ^{13}C NMR spectra for all new compounds and theoretical calculation with DFT. This material is available free of charge via the Internet at http://pubs.acs.org.

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