Indolo[2,3-b]carbazole Synthesized from a Double-Intramolecular Buchwald−Hartwig Reaction: Its Application for a Dianchor DSSC Organic Dye

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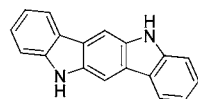[†]Department of Chemistry, National Taiwan University, Taipei 10617, Taiwan
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Ⓢ Supporting Information

ABSTRACT: A new synthetic strategy for indolo[2,3-b]carbazole via a double-intramolecular Buchwald−Hartwig reaction has been established. The N-alkylated indolo[2,3-b]carbazole then was adopted as the geometry-fixed core for the synthesis of a new molecule (**ICZDTA**) bearing two bithiophene π-bridged 2-cyanoacrylic acid groups as the bidentate anchor. The bidentate anchoring together with efficient HOMO (indolo[2,3-b]carbazole) → LUMO (TiO₂ nanocluster) electron transfer leads to the successful development of **ICZDTA**-based DSSC with a power conversion efficiency of 6.02%.
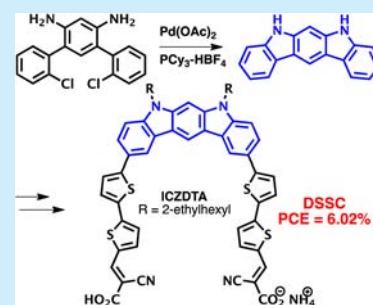
Indolocarbazole derivatives (ICZs) are alkaloids showing highly attractive biological properties such as antitumor and antibiotic activities in the field of pharmaceutical research.[1] The rigid and coplanar structural features give ICZs high HOMO levels and outstanding hole-transporting properties. Therefore, ICZs have been widely introduced as important electron-rich π-conjugated backbones in optoelectronic materials for applications such as OFET[2a−d] and OLED.[2e−g] In addition, ICZs exhibit a strong light extinction coefficient and versatile functionalizations that meet the crucial requirements in the development of efficient dyes for DSSC[2h,i] and OPV.[2j] Among the various isomeric ICZs, 5,11-dihydroindolo[3,2-b]carbazole (Figure 1) is the electron-rich core most widely used in
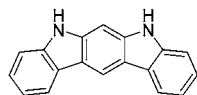
Figure 1. Chemical structures of indolocarbazoles.

optoelectronic materials due to its synthetic accessibility[3] and the flexibility on functionalizations. In contrast, the application of the isomeric indolo[2,3-b]carbazole remains relatively unexplored due to the lack of efficient synthetic method, particularly for the synthesis of 5,7-dihydroindolo[2,3-b]-carbazole. The typical indole−aldehyde condensation widely used for the synthesis of indolo[3,2-b]carbazoles failed to give the isomeric indolo[2,3-b]carbazole. This challenge was solved by a modified method reported by Bhuyan et al., rendering the synthesis of 6,12-disubstituted indolo[2,3-b]carbazoles feasi-

ble.[4a] However, this new method gave better yields for 6,12-diarylindolo[2,3-b]carbazoles, whereas the yields of 6,12-dialkylindolo[2,3-b]carbazoles were inferior. This synthetic method was further modified and improved by Dehaen et al.[4b] In addition to the condensation reaction, the addition of MeLi onto indolo[2,3-b]carbazole-6,12-dione followed by reductive aromatization gave N-benzyl-6,12-imethylindolo[2,3-b]carbazole.[5] Two interesting examples were reported for the synthesis of 6-substituted indolo[2,3-b]carbazoles: (1) the copper(II) triflate-catalyzed heteroannulation between 2-alkynylindole-3-aldehydes with indoles gave 6-benzoyl-5,7-dihydroindolo[2,3-b]carbazoles in moderate yields,[6] and (2) 6-carbonate indolo[2,3-b]carbazoles can be accessed by the cyclization of 3,3′-diindolylmethane.[7] Very recently, N,N′-bis(p-toluenesulfonyl)indolo[2,3-b]carbazole was synthesized in good yield with a double-intramolecular Pd-catalyzed oxidative C−H amination of N,N′-ditosyl-m-phenylenediamine.[8] So far, only a few literature sources have reported the efficient synthesis of parent 5,7-dihydroindolo[2,3-b]-carbazole, including metal-catalyzed high-temperature cyclodehydrogenation of N,N′-diphenyl-m-phenylenediamine,[9a] double-Cadogan cyclization of 1,3-dinitro-4,6-diphenylbenzene,[9b] and iron-mediated cyclization of 1,3-diaminophenylene precursor.[9c,d] To employ parent indolo[2,3-b]carbazole as a functional core for π-conjugated materials, we initially followed the double-Cadogan cyclization of 1,3-dinitro-4,6-diphenylbenzene to synthesize 5,7-dihydroindolo[2,3-b]carbazole.[9b] However, after various trials (solvents, reaction time and temper-

ature, and phosphine sources), and even with the assistance of microwave irradiation,[10] the best isolated yield of 5,7-dihydroindolo[2,3-b]carbazole was about 10%. Instead, we isolated a single-cyclized compound as the major product. Thus, a new synthesis toward 5,7-dihydroindolo[2,3-b]-carbazole was then explored. In this work, a new synthetic strategy incorporating a double-intramolecular Buchwald–Hartwig cyclization as the key step has been established for the efficient synthesis of 5,7-dihydroindolo[2,3-b]carbazoles.

We envisioned that the curved molecular skeleton of indolo[2,3-b]carbazole could be a promising core for developing a new C-shaped dianchor photosensitizer for DSSC. As compared to the linear molecules configured as donor (D)−π−acceptor (A), the rigid and curve architecture of the C-shaped molecule is regarded as a bidentate ligand that is able to strongly anchor onto the TiO$_2$ surface. For the carboxylate ion anchors, the most accessible distance of two neighboring active sites is about 10 Å.[11] A better matching distance between two anchoring groups and two active sites should lead to a stronger binding affinity.[12] In addition, the rigidity of the C-shaped molecule limits the possible molecular conformations, reducing the steric congestion while they are bound on the TiO$_2$ surface. As for the electron-donating core, the alkyl substitutions introduced on the two nitrogen atoms of indolo[2,3-b]carbazole serve as the steric groups for preventing dye aggregation as well as the blocking groups for suppressing the dark current caused by the electrolyte diffusion to the TiO$_2$ electrode. In this work, a new C-shaped A−π−D−π−A dianchor dye **ICZDTA** (Scheme 1), in which the bithiophene is introduced as the π-bridge between the electron-rich indolo-[2,3-b]carbazole core and the electron-deficient 2-cyanoacrylic acid, has been synthesized and characterized. We found that **ICZDTA** could strongly anchor to the TiO$_2$ surface, achieving a good DSSC performance with a PCE of up to 6.02%.

The new synthesis of 5,7-dihydroindolo[2,3-b]carbazole is depicted in Scheme 1, starting from the readily available 4,6-dibromo-1,3-phenylenediacetamide (**1**), which was coupled with 2-chlorophenylboronic acid (**2a**) under Suzuki coupling conditions and subsequently followed by the hydrolysis of acetamide to afford the m,m-terphenyl intermediate **3a**. Then compound **3a** underwent a double-intramolecular Buchwald–Hartwig amination, giving the desired indolo[2,3-b]carbazole (**4a**) as the single product with a 90% yield. This synthetic protocol can be generally applied for the other 5,7-dihydroindolo[2,3-b]carbazoles (**4c** and **4b**) with comparable isolated yields. Then, the alkylation of indolo[2,3-b]carbazole (**4a**) with 1-bromo-2-ethylhexane was smoothly achieved. The alkylated indolo[2,3-b]carbazole was then subjected to brominate with NBS at low temperature (−78 °C), affording the dibromo compound **5** in 55% yield after precipitation from a boiling acetone–methanol solution. Through metal–halogen exchange and stannylation, dibromo compound **5** was converted into the distannane intermediate, which was directly reacted with dithienyl acetal (**6**) under Stille coupling conditions, followed by the hydrolysis of the acetal group to give the dialdehyde **7**. The aldehyde group of **7** was then converted into 2-cyanoacrylic acid by Knoevenagel condensation with 2-cyanoacetic acid. The final target molecule **ICZDTA** was isolated in 77% yield as a monoammonium salt.

The electrochemical properties of C-shaped dye **ICZDTA** monoammonium salt were investigated with cyclic voltammetry (Figure S1, Supporting Information). This dye showed both irreversible oxidation and reduction behavior. The oxidation

Scheme 1. Synthesis of Indolo[2,3-b]carbazoles and New Dianchor Dye ICZDTA
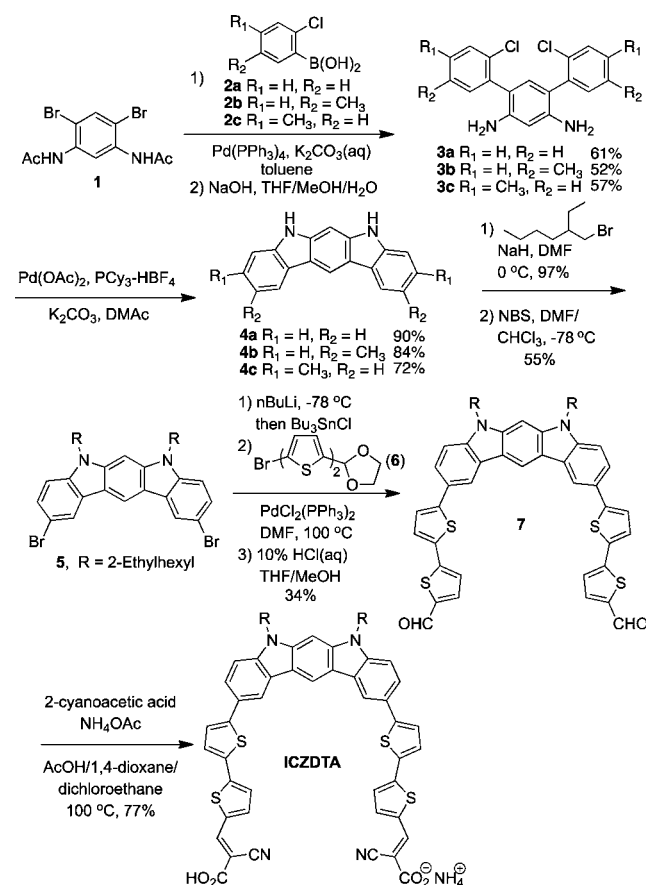
potential onset occurred at 0.74 V (vs Ag$^+$/AgCl). Referring to the redox couple of ferrocene/ferrocenium (Fc/Fc$^+$), the HOMO energy of **ICZDTA** was estimated to be −5.07 eV. The electronic absorption spectrum of **ICZDTA** (Figure 2a,
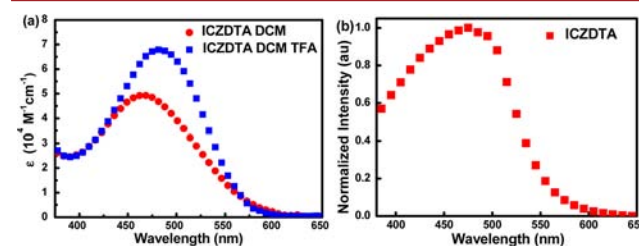

Figure 2. (a) Electronic absorption spectrum of **ICZDTA** measured in 10^{-6} M DCM solution (red) and acidified **ICZDTA** spectrum (blue). (b) Absorption spectra of **ICZDTA** anchoring on the 7 μm porous TiO$_2$ nanocrystalline film.

10^{-6} M in DCM solution) showed an intense intramolecular charge-transfer absorption centered at 467 nm, with a molar extinction coefficient as high as 4.93 × 10^4 M^{-1} cm^{-1}. To eliminate the absorption wavelength shift caused by the proton dissociation of the anchoring group, the original sample solution was acidified with trifluoroacetic acid. As shown in Figure 2a, a more intense and red-shifted absorption peak centered at 483 nm and having a much higher molar extinction coefficient (6.77 × 10^4 M^{-1} cm^{-1}) was observed. The optical band gap (2.16 eV) of **ICZDTA** was deduced from the onset (575 nm) of the absorption spectrum of acidified **ICZDTA**.

Accordingly, the LUMO energy level of **ICZDTA** was calculated to be −2.91 eV. Both HOMO and LUMO energy levels were suitable for dye regeneration and electron injection to the TiO$_2$ conduction band. The absorption spectrum of **ICZDTA** anchoring on a porous TiO$_2$ nanoparticle film (7 μm) exhibited an absorption maximum centered at 475 nm, which is blue-shifted by 8 nm relative to acidified **ICZDTA** (Figure 2b). The slight blue shift could possibly be attributed to the balance of dye deprotonation (blue shift)[13] and the interaction between the dye LUMO and TiO$_2$ conduction band (red shift).[14] In addition, the insignificant spectral broadening indicates that dye aggregation was negligible, as they were anchored onto the TiO$_2$ surface.

TD-DFT calculations were performed to investigate the electronic transitions in relation to their compositions in terms of molecular orbital contributions (Table S1, Supporting Information). The lowest energy excitation corresponded to a charge-transfer (CT) character stemming from the whole backbone-localized HOMO to LUMO that was mainly delocalized on the terminal anchoring groups (Figure S2, Supporting Information). A plausible model of a dye with two anchoring cites on the TiO$_2$ surface was proposed by Abbotto et al.[15] We further examined this intermolecular interaction of **ICZDTA** with an expanded (TiO$_2$)$_{70}$ nanocluster modified through our previous research.[16] The attainable distance between two carboxylic groups of a single **ICZDTA** molecule was calculated to be *ca.* 15.7 Å, while in a more confined **ICZDTA**/(TiO$_2$)$_{70}$ cluster, this value was 15.2 Å. The lowest singlet excitation of **ICZDTA**/(TiO$_2$)$_{70}$ turned out to be 100% HOMO → LUMO (Table S2, Supporting Information), and HOMO was mainly populated on the electron-rich indolo[2,3-*b*]carbazole backbone, whereas the LUMO was mainly localized on the (TiO$_2$)$_{70}$ nanocluster (Figure 3). This fully spatial separation of HOMO/LUMO with corresponding transition ensures efficient electron transfer and injection from **ICZDTA** into TiO$_2$.
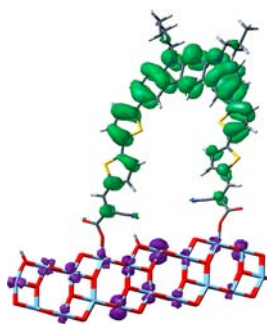
Figure 3. Contour plot for the lowest energy transition of **ICZDTA**/(TiO$_2$)$_{70}$, in which lime green symbolizes the holes and purple represents electrons.

The anchoring properties of the dyes and the interactions between carboxylic groups of **ICZDTA** and TiO$_2$ were characterized with FT-IR spectroscopy. Figure 4 depicts the FT-IR spectra of pristine **ICZDTA** and **ICZDTA** adsorbed TiO$_2$ film. Apparently, the characteristic band at 2210 cm^{-1} for the cyano group remained intact, revealing that cyano groups of **ICZDTA** are not involved in the anchoring functions. The intense absorption band of carboxylic acid at 1708 cm^{-1} in pristine **ICZDTA** disappeared as **ICZDTA** was loaded on the TiO$_2$ film. Instead, the **ICZDTA**-loaded TiO$_2$ film exhibited a
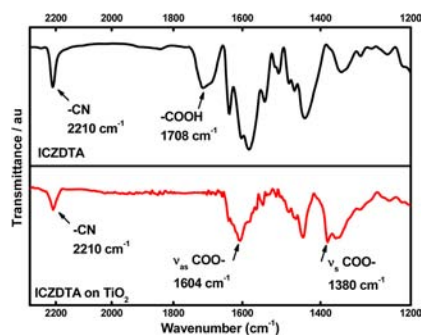
Figure 4. FT-IR spectra of pristine **ICZDTA** (top) and **ICZDTA**-adsorbed TiO$_2$ film (bottom).

carboxylate symmetric stretching absorption band (1380 cm^{-1}) as well as an asymmetric stretching absorption band (1604 cm^{-1}, which was partially overlapped with aromatic C=C bond stretching). The results clearly reveal that both carboxylic acids in **ICZDTA** were anchored on the TiO$_2$ film. Moreover, the calculated frequency difference of 224 cm^{-1} is consistent with the Deacon Philips rule[17] and is also in agreement with the other dianchor systems[18] and our previous report,[19] supporting that the two anchoring groups in **ICZDTA** are both adsorbed on the TiO$_2$ surface via a bidentate binding mode.

The photovoltaic characteristics of **ICZDTA** as a sensitizer for DSSCs were evaluated with a sandwich DSSC cell using 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−valeronitrile (85:15, v/v) as the redox electrolyte (see the experimental procedures, Supporting Information). The incident monochromatic photon-to-current conversion efficiency (IPCE) spectrum of the DSSC based on **ICZDTA** is shown in Figure 5a. The **ICZDTA**-based DSSC shows an IPCE of >70% from 360 to 540 nm and reaches a maximum of 88% around 450 nm.
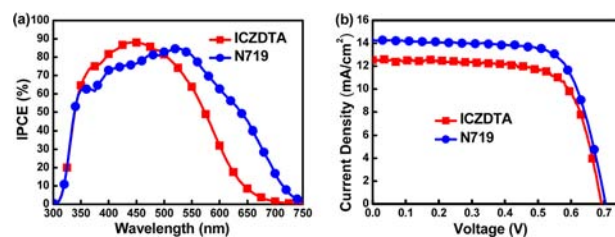
Figure 5. (a) IPCE spectra of DSSCs based on **ICZDTA** (red) and N719 (blue). (b) Current density−voltage curves for DSSCs sensitized by **ICZDTA** (red) and N719 (blue) under AM 1.5 G simulated sunlight.

Figure 5b shows the current density−voltage (J−V) curve of the DSSC under standard global AM 1.5G solar irradiation. The short-circuit photocurrent density (J_{SC}), open-circuit voltage (V_{OC}), and fill factor (FF) of the DSSC based on **ICZDTA** were 12.45 mA/cm^2, 0.69 V, and 0.70, respectively, yielding an overall power conversion efficiency of 6.02%. For comparison, the N719-sensitized DSSC was also fabricated and tested under similar conditions. The J_{SC}, V_{OC}, and FF of the DSSC based on N719 were 14.48 mA/cm^2, 0.70 V, and 0.70, respectively, yielding an overall PCE of 7.10%. The efficiency of the **ICZDTA**-sensitized cell reached ∼85% of the N719-based cell efficiency.

In conclusion, an efficient method has been established to synthesize 5,7-dihydroindolo[2,3-*b*]carbazole. This product was then adopted as a rigid/coplanar core to develop a new dye (**ICZDTA**) bearing two anchor groups via bithiophene bridges. The distance between two carboxylic anchoring groups of **ICZDTA** has been calculated to be ca. 15.2 Å in a virtual **ICZDTA**/(TiO$_2$)$_{70}$ cluster. The strong adsorption of C-shaped **ICZDTA** onto TiO$_2$ has been firmly verified via IR analyses. A computational approach also indicated that HOMO of **ICZDTA**/(TiO$_2$)$_{70}$ is mainly populated on the electron-rich indolo[2,3-*b*]carbazole backbone, whereas LUMO is localized on the (TiO$_2$)$_{70}$ nanocluster, allowing the lowest singlet excitation of **ICZDTA**/(TiO$_2$)$_{70}$ to be 100% HOMO → LUMO electron transfer/injection from **ICZDTA** to TiO$_2$. As a result, the **ICZDTA**−based DSSC delivers a power conversion efficiency of 6.02%.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Details of the experimental procedures; spectroscopic characterization; cyclic voltammogram of compound **ICZDTA**; theoretical calculations; ^{1}H, ^{13}C NMR spectra of new compounds. This materialis available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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