

Tuning the Spectroscopic, Electrochemical, and Photovoltaic Properties of Triaryl Amine Based Sensitizers through Ring-Fused Thiophene Bridges

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Abstract: The ring-fused thiophene derivatives benzo[c]thiophene and its precursor bicyclo[2.2.2]octadiene (BCOD) have been introduced as π -conjugated spacers for organic push-pull sensitizers with dihexyloxy-substituted triphenylamine as donor and cyanoacrylic acid as acceptor (**OL1–OL6**). The effects of the fused ring on the spectroscopic and electrochemical properties

of these sensitizers and their photovoltaic performance in dye-sensitized solar cells have been evaluated. Introduction of a binary benzo[c]thiophene

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and ethylenedioxy thiophene as π bridge caused a significant red shift of the characteristic intramolecular charge-transfer band to 642 nm. It is found that the sensitizer **OL3**, which contains one benzo[c]thiophene unit as π linker, gives the highest overall conversion efficiency of 5.03 % among all these dyes.

Introduction

As a kind of renewable, green, and clean energy source, the solar cell has been explored as one of the candidates to meet the needs of increasing demands for decades. Since Grätzel's group first reported a notable power conversion efficiency of about 7 % based on a ruthenium complex,^[1] dye-sensitized solar cells (DSSCs) have attracted great attention in recent years. In light of the limited availability of ruthenium and its toxicity, metal-free organic dyes are considered to be promising candidates due to their high molar extinction coefficients, structural diversity, easy design and synthesis, low cost, environmental friendliness, and so

forth.^[2] Recently, significant achievements have been made based on various organic dyes as sensitizers for DSSCs.^[3] Donor– π –acceptor or donor–acceptor– π –acceptor^[4] structures are commonly adopted for the design of these dyes, since intramolecular charge separation is easily achieved. Triaryl amines have good electron-donating and -transporting capabilities and are usually used as the donor;^[5] long alkyl chains have been introduced to improve device performance.^[6] Oligothiophene and its derivatives, such as 3,4-ethylenedioxythiophene (EDOT), thienothiophene (TT), dithienothiophene (DTT), 2,2'-bithiophene (BT), and thiazole have been employed as π bridges,^[7] affording a conjugated pathway for charge transfer and extending the absorption spectra of dyes. Most of the thiophene-bridged sensitizers have exhibited superior photoelectronic properties, and some of them showed high thermostability and produced an overall light-to-power conversion of over 10 %^[8] which approaches the performance of ruthenium-based sensitizers.

Although polyisothianaphthene (PITN) has been synthesized and investigated for decades,^[9] to our knowledge, its monomer isothianaphthene, namely benzo[c]thiophene and its derivatives have not been applied in DSSCs. Recently Swager and co-workers reported a series of push-pull compounds utilizing benzo[c]thiophene and benzo[c]furan to furnish near-infrared fluorophores.^[10] Previously, Ono's group has reported a facile synthesis of isothianaphthene oligomers using bicyclo[2.2.2]octadiene (BCOD) thiophene as a synthon.^[11] The π -electron delocalization in the oligoisothianaphthenes were significantly enhanced. The UV/Vis absorption spectra of oligoisothianaphthene derivatives exhibited considerable bathochromic shift compared to the cases of other oligothiophene analogues, and cyclic voltammetry measurement showed narrowed HOMO–LUMO

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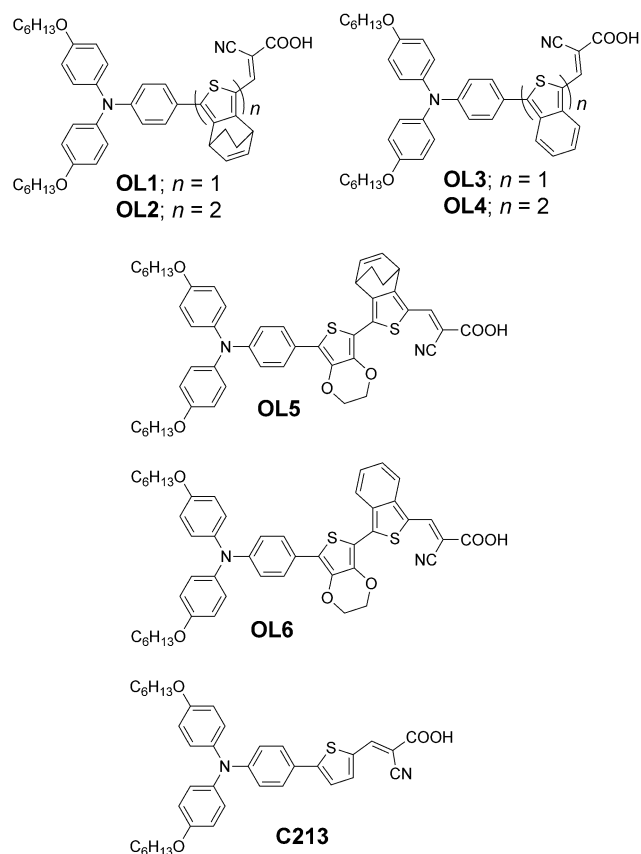
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gaps. Herein, we incorporate isothianaphthene as a bridge and EDOT as a binary bridge into the sensitizer containing dihexyloxy-substituted triphenylamine as the donor and cyanoacrylic acid as the acceptor (Scheme 1). Their absorption and emission spectra, electrochemical and photovoltaic properties have been measured to investigate the effect of fused-ring on the thiophene bridged push-pull dyes.



Scheme 1. Ring-fused thiophene-bridged triaryl amine based push-pull sensitizers.

Results and Discussions

Synthesis of the Ring-Fused Thiophene-Bridged Triaryl Amine Based Push-Pull Dyes

The syntheses of these dyes are shown in Scheme 2. For dyes **OL1** and **OL2**, BCOD-thiophene was attached to the triaryl amine donor through Suzuki coupling reaction, then the corresponding aldehydes were obtained by Vilsmeier reaction, and these condensed with 2-cyanoacetic acid to give the final product. The intermediate aldehydes of BCOD-thiophenes, **6** and **7**, were converted into the aldehydes of benzo[*c*]thiophene (**8** and **9**) by retro-Diels–Alder reaction under heat and vacuum. Aldehydes **8** and **9** condense with 2-cyanoacetic acid to afford **OL3** and **OL4**, respectively. Dyes **OL5** and **OL6** are prepared using a similar method as mentioned above, but with a binary EDOT linker combined with BCOD-thiophene or benzo[*c*]thiophene, respectively.

Spectroscopic Properties

To examine the effect of the fused ring on thiophene moiety on the spectroscopic properties of these dyes, their absorption spectra were measured in dichloromethane. All the dyes showed characteristic intramolecular charge-transfer bands in the visible region, peaking in the range from 485 to 642 nm (Figure 1).^[12] The transformation of BCOD-thio-

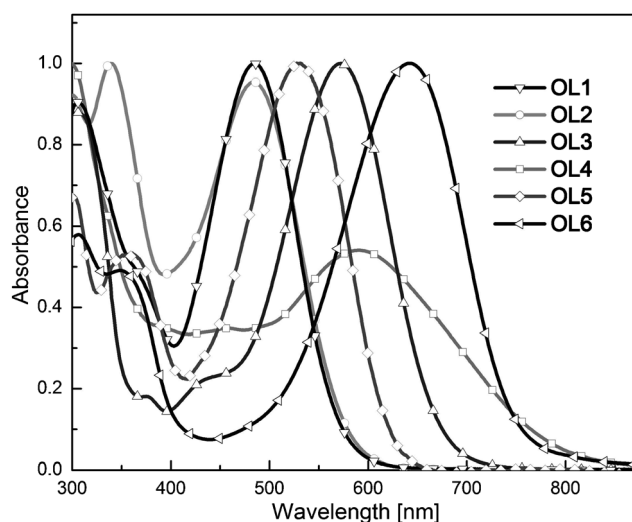


Figure 1. Normalized electronic absorption spectra of six dyes in CH_2Cl_2 .

phene into benzo[*c*]thiophene extended the π conjugation and led to a bathochromic shift in the absorption spectra.^[11] Dyes **OL3**, **OL4**, and **OL6** bearing one or two benzo[*c*]thiophene unit, or one benzo[*c*]thiophene and a binary EDOT spacer, exhibited peaks that are red-shifted by 88, 105, and 114 nm compared to the corresponding BCOD-fused precursors **OL1**, **OL2**, and **OL5**, respectively. As the number of thiophene units increased, the bathochromic shift become larger. Among the six dyes, **OL6** exhibited the highest absorption coefficient and the longest-wavelength charge-transfer absorption band, which may favor light harvesting and hence photocurrent generation in DSSCs.

Electrochemical Properties

The oxidation potentials of the dyes adsorbed on TiO_2 nanocrystalline film on FTO (fluorine-doped tin oxide, 15 ohm per square, transmittance of 90%, Nippon Sheet Glass, Japan) were measured using cyclic voltammetry (see Table 1). The results revealed that the HOMO level of I_3^-/I^- electrolyte (-4.85 eV vs. vacuum)^[2c] is higher than that of all the dyes and that this system is able to regenerate the dyes from electron donation on DSSCs. The LUMO levels of these dyes were higher than the conduction band edge of the TiO_2 electrode (-4.00 eV vs. vacuum).^[13] However, to induce a sufficient electron injection, an energy gap of approximately 0.2 eV between the LUMO of the dye and the conduction band edge of TiO_2 must be a necessary driving

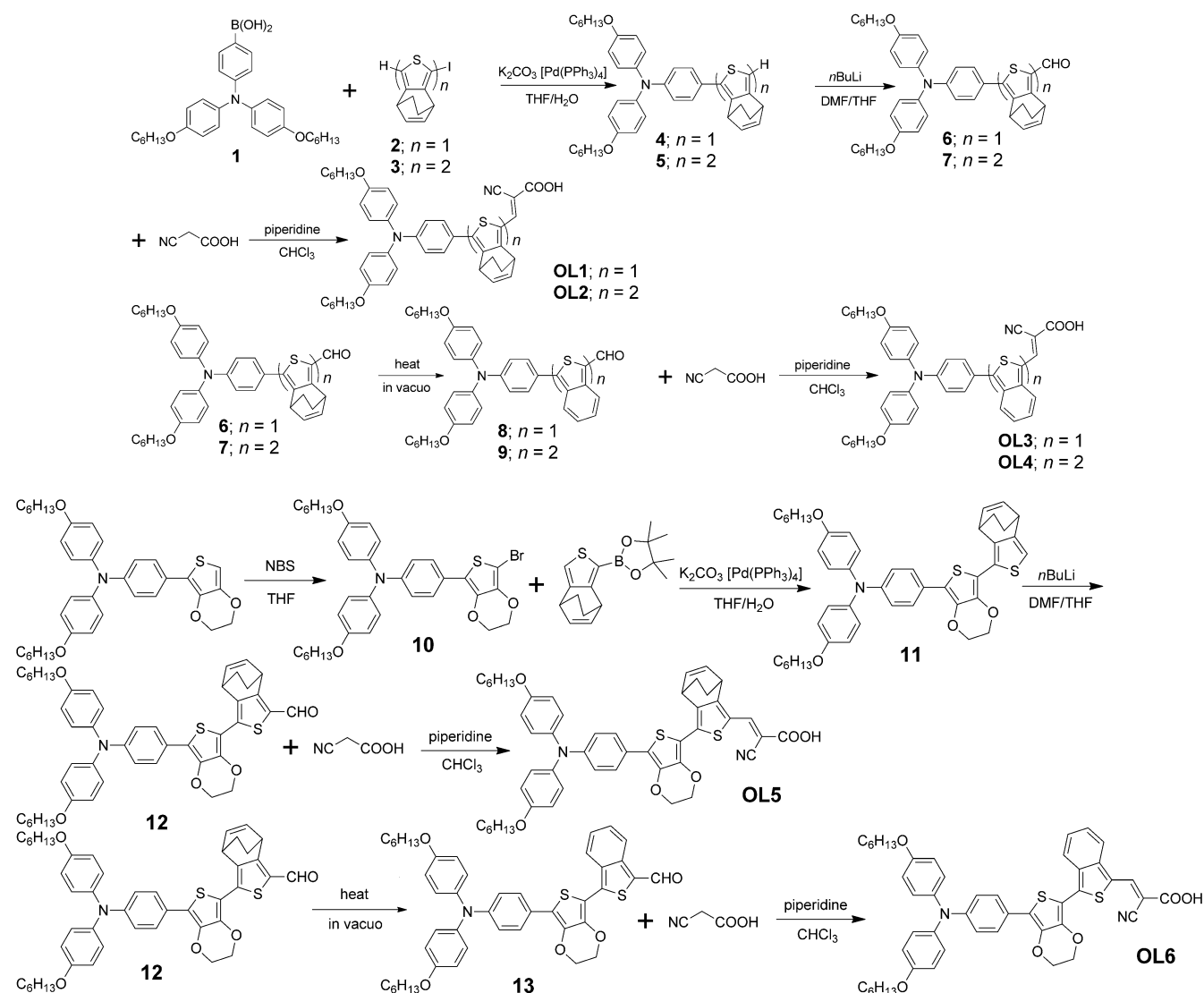
Scheme 2. Synthetic route to the ring-fused thiophene-bridged triaryl amine based push-pull dyes. NBS = *N*-bromosuccinimide.

Table 1. Electrooptical and electrochemical properties of the dyes.

| Dye | λ_{max} [nm] | (log ϵ) ^[a] | E_{HOMO} [eV] ^[b] | E_{0-0} [eV] ^[c] | E_{LUMO} [eV] ^[d] |
|------------|-----------------------------|----------------------------------|---------------------------------------|-------------------------------|---------------------------------------|
| OL1 | 485 (4.42) | | −5.526 | 2.262 | −3.264 |
| OL2 | 485 (4.38) | | −5.435 | 2.246 | −3.189 |
| OL3 | 573 (4.47) | | −5.518 | 1.914 | −3.604 |
| OL4 | 590 (4.21) | | −5.431 | 1.590 | −3.841 |
| OL5 | 528 (4.47) | | −5.279 | 1.987 | −3.292 |
| OL6 | 642 (4.53) | | −5.350 | 1.610 | −3.740 |

[a] The absorption spectra were measured in CH_2Cl_2 . [b] Energy levels for the highest occupied molecular orbitals (HOMOs) were measured from dye-loaded films. [c] The gap was derived from the onset wavelength at which the absorbance is 10 % of the maximum from the UV/Vis absorption spectra of the dye-loaded film. [d] The energy levels of the lowest unoccupied molecular orbitals (LUMOs) were estimated from the equation $E_{\text{LUMO}} = E_{\text{HOMO}} + E_{0-0}$.

force.^[14] Therefore except for **OL4**, the other five dyes allow effective electron injection into the TiO_2 electrode. Comparing the HOMO and LUMO levels of these dyes, the intro-

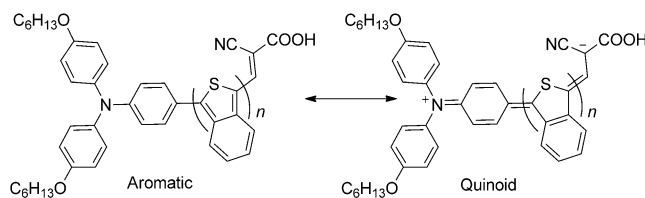
duction of benzo[*c*]thiophene significantly stabilized the LUMO energy level rather than destabilizing the HOMO (ΔLUMO values were 0.340, 0.652, and 0.448 eV from **OL1** to **OL3**, **OL2** to **OL4**, and **OL5** to **OL6**, respectively; ΔHOMO values were −0.008, −0.004, and 0.071 eV from **OL1** to **OL3**, **OL2** to **OL4**, and **OL5** to **OL6**, respectively). The introduction of a binary electron-rich EDOT unit in **OL5** and **OL6** further lifted the HOMO and lowered the LUMO energy levels and narrowed the energy gap.^[11] These results are in accordance with the trend observed in their electronic absorption spectra.

Molecular Orbital Calculations

MO calculations were performed for these sensitizers using the Gaussian03 program package^[15] at the B3LYP/6-31G(d) level of theory (Figure 2). It can be seen that when the π bridges change from BCOD-thiophene to benzo[*c*]thio-

phene, the HOMOs of the sensitizers are delocalized over the whole molecule. This transformation also leads to an obvious stabilization of the LUMOs, while there is little effect on the HOMOs and finally a smaller energy gap between the two. In the push-pull dyes, the contribution of charge separated quinoid resonance structure can be further stabilized by introducing fused benzene ring on the thiophene bridge^[10] (Scheme 3). As the LUMO is mainly located on the thiophene bridge and the acceptor part, the extension of

the π conjugation by fusion with benzene ring on the thiophene bridge thus stabilized the LUMO significantly compared to its contribution to the HOMO. These results are in accordance with the trend observed in their electrochemical properties.



Scheme 3. Aromatic and quinoid resonance structures of the sensitizers.

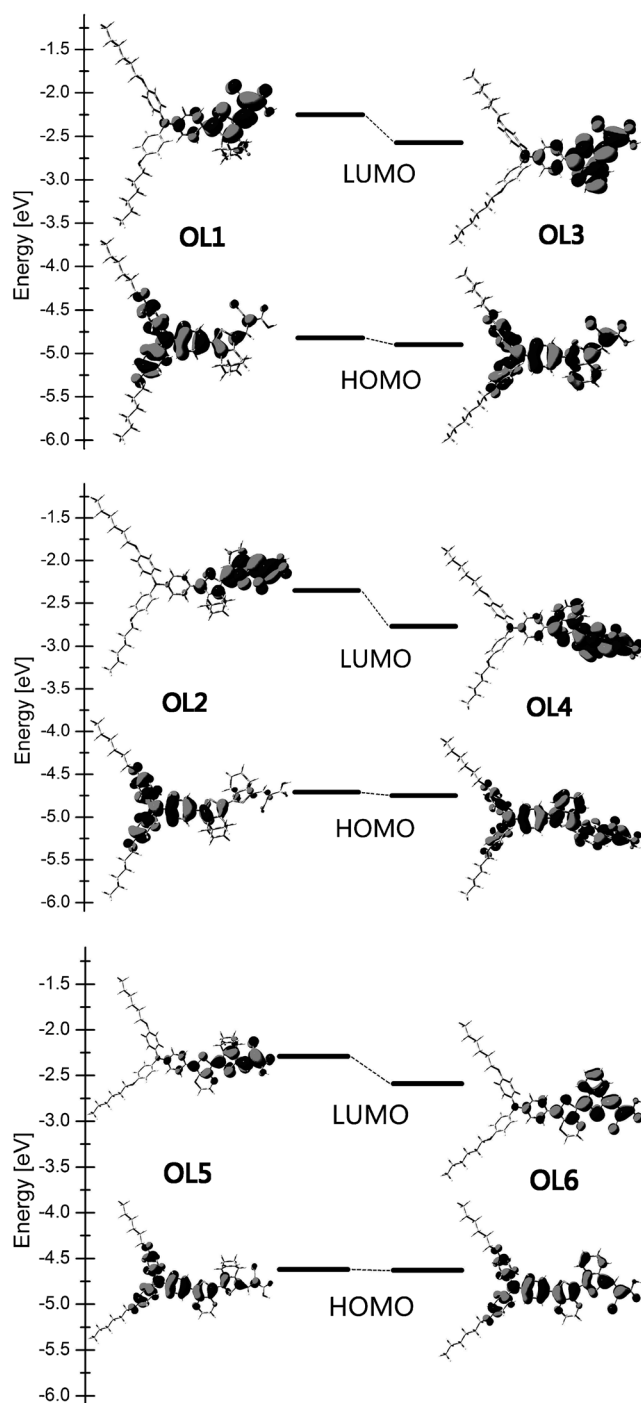


Figure 2. Calculated MOs of OL1–OL6.

Photovoltaic Performance

The dye-sensitized solar cells fabricated with these dyes and the reference dyes such as **C213**^[12] and **N719** were tested, and their photovoltaic performances are listed in Table 2. It should be noted that the solar-cell performance for the new and reference dyes were compared under the same but not optimal conditions, and the efficiencies for **C213** and **N719** listed in Table 2 were much lower than the reported highest values, as they were not optimized in this work. Figure 3 shows that compared with **C213**, which consists of the same donor and acceptor units linked with a simple thiophene, **OL1** bearing one BCOD-fused thiophene linker exhibited higher short-circuit photocurrent density (J_{sc}) but lower open-circuit photovoltage (V_{oc}). Overall, the loss in V_{oc} canceled the enhanced J_{sc} and led to a relatively lower power conversion efficiency (η) for **OL1**. Introducing two BCOD-fused thiophene units as linker in **OL2** also increased both the J_{sc} and V_{oc} values, and the η value for the cell using **OL2** was slightly higher than for that with **C213**. Sensitizer **OL5** possess one BCOD-fused thiophene unit and a binary EDOT showed slightly higher J_{sc} and V_{oc} values and better energy conversion efficiency than **OL2**. However, the J_{sc} value and the overall power conversion efficiency for **OL4**, which contains two benzo[*c*]thiophene units, were almost

Table 2. Photovoltaic performance of dyes OL1–OL6 and C213.^[a]

| Dye | V_{oc} [mV] | J_{sc} [mA cm ⁻²] | FF | η [%] |
|----------------------------|---------------|---------------------------------|------|------------|
| OL1 | 534 | 9.21 | 0.72 | 3.54 |
| OL2 | 680 | 8.11 | 0.74 | 4.08 |
| OL3 | 640 | 11.23 | 0.70 | 5.03 |
| OL4 | 405 | 0.67 | 0.58 | 0.16 |
| OL5 | 674 | 8.47 | 0.73 | 4.16 |
| OL6 | 514 | 4.05 | 0.70 | 1.45 |
| C213 | 680 | 7.87 | 0.69 | 3.69 |
| N719 ^[b] | 720 | 14.80 | 0.76 | 8.00 |

[a] Experiments were carried out with 0.2304 cm² working area of the cell under the illumination intensity of 100 mW cm⁻² at 1.5 AM sunlight condition. FF=fill factor. [b] The efficiency was obtained with 12 μ m transparent TiO₂. The efficiency was raised to 9.77% (J_{sc} =17.24 mA cm⁻², V_{oc} =765 mV, FF=0.741) with 4 μ m scattering layer on the transparent layer.

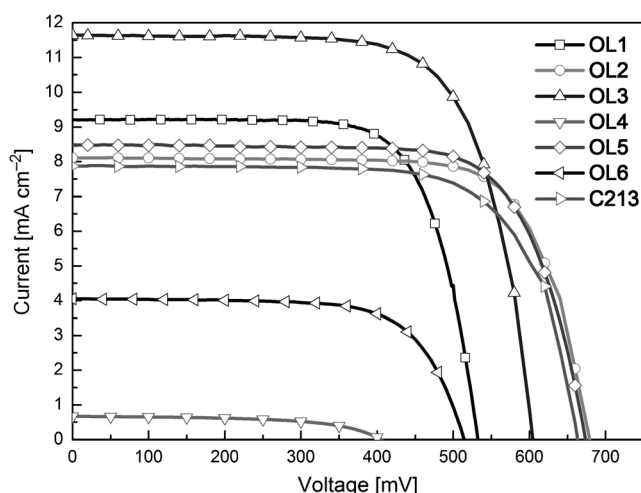


Figure 3. Current–voltage curves of DSSCs based on **OL1–OL6** and **C213** under irradiation of 100 mW cm^{-2} at 1.5AM sunlight condition.

negligible. The small short-circuit photocurrent for **OL4** might be mainly due to the fact that its LUMO does not match well with the conduction band of TiO_2 , which prevents sufficient electron injection into the TiO_2 electrode. To confirm this point, a higher concentration of LiI in the electrolyte, which is able to down-shift the conduction band edge for TiO_2 , was used for **OL4**. The value of J_{sc} increased remarkably, due to the enlarged driving force for electron injection, but remained much lower than for the other dyes. Similar results were found in the case of **OL6**. Among the six dyes, **OL3** with one benzo[c]thiophene linker produced the highest η (5.03 %), with $J_{\text{sc}} = 11.23 \text{ mA cm}^{-2}$, $V_{\text{oc}} = 640 \text{ mV}$, and $\text{FF} = 0.70$. Dyes **OL2**, **OL3**, and **OL5** generated similar V_{oc} values as the reference dye **C213**, but the other dyes generated much lower V_{oc} values. It seems that the higher the LUMO, the higher the V_{oc} , except for **OL1**. The low V_{oc} values for some of these dyes may be ascribed to the lower LUMO, recombination losses, non-optimal dye packing, or other factors, which will be investigated in detail in the future.

The incident-photon-to-current conversion efficiency (IPCE) spectra (Figure 4) of these dyes showed that **OL1** and **OL2** bearing one or two BCOD ring-fused thiophene units have very similar spectral responses and maintain over 50 % conversion efficiency in the region of 400–500 nm. The reference dye **C213** possesses about 70 % efficiency in the range of 400–550 nm and cutoff at 700 nm. Compared with **C213** dye, **OL5** and **OL3** exhibited the response of 60 % from 500 to 750 and 800 nm, respectively. Unlike other analogues, the spectral intensities of **OL4** and **OL6** were very low. In particular, the IPCE value of dye **OL4** is lower than 10 % in the whole visible region. Although the highest IPCE value of **OL6** is just 20 % at about 550 nm, it was notable that the response of **OL6** extended to about 850 nm, which is the farthest among all these dyes.

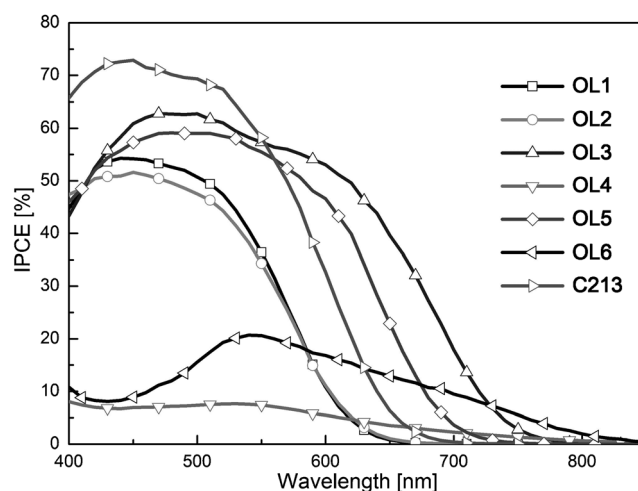


Figure 4. The incident photon-to-current conversion efficiency spectra for DSSCs based on **OL1–OL6** and **C213**.

Conclusions

In summary, we have introduced benzo[c]thiophene and its precursor as π bridges into a series of organic push–pull dyes for application in DSSCs for the first time. Fusion with a benzene ring on the thiophene bridge significantly stabilized the LUMO level of the sensitizer and narrowed the energy gap, which prominently bathochromically shifted the absorption spectra. Dye-sensitized solar cells fabricated with one benzo[c]thiophene bridged sensitizer produced the highest η value of 5.03 %, which is higher than that of **C213** measured under the same conditions, mainly due to the larger short-circuit photocurrent density resulted from extending the π conjugation. Further efforts to fine tune the frontier MOs thus improving the photovoltaic performance in other D– π –A dyes are currently underway.

Experimental Section

Materials and Reagents

All reagents were obtained from commercial suppliers and used without further purification unless otherwise indicated. Dry solvents were prepared using standard techniques. LiI, I_2 , acetonitrile, and 4-*tert*-butylpyridine (TBP) were obtained from Acros. 1,2-dimethyl-3-*n*-propylimidazolium iodide (DMPII) was obtained from Tomiyama Pure Chemical Industries Ltd., Japan. N719 was obtained from Solaronix SA. F-doped SnO_2 conductive glass (FTO, resistance 15Ω per square, transmittance 80 %) was purchased from Nippon Sheet Glass Co., Japan and ultrasonically rinsed in acetone and in water before use. 4-bromo-*N,N*-bis(4-(hexyloxy)phenyl)aniline,^[7d] 2-[4-[*N,N*-bis(4-hexyloxyphenyl)amino]phenyl]-3,4-(ethylenedioxy)thiophene,^[3a] 2-(4,7-dihydro-4,7-ethanobenzo[c]thiophen-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane,^[11] and 4,7-dihydro-4,7-ethanobenzo[c]thiophene and its dimer^[11] were prepared according to the literature. NMR spectra were recorded on a JEOL JNM-AL 400 spectrometer or Bruker DRX500 spectrometer and referenced to the residual proton signals of the solvent. Mass spectra were measured on a Bruker Daltonics Autoflex IITM MALDI TOF spectrometer or a Voyager DEPro (Applied Biosystems) spectrometer. Elemental analyses were recorded on a Vario MICRO analyzer.

Fabrication and Evaluation of DSSCs

TiO₂ films (12 µm thick) were coated on FTO glass using a screen-printing method with a paste consisting of TiO₂ nanoparticles (ca. 20 nm diameter) prepared according to a published method.^[16] TiO₂ films were colored by soaking them overnight in the dye solution (0.3 mM). The dye-loaded TiO₂ film as the working electrode and the Pt-coated conductive glass as the counter electrode were separated by a hot-melt Surlyn film (30 µm thick) and sealed together by hot-pressing. The redox electrolyte (0.1 M LiI, 0.05 M I₂, 0.6 M 1,2-dimethyl-3-*n*-propylimidazolium iodide, and 0.3 M TBP using anhydrous acetonitrile as a solvent) was injected into the interspace between the photoanode and counter electrode through a pre-drilled hole. Finally, the hole was sealed with a Surlyn film covered with a thin glass slide under heat. The DSSCs were evaluated by recording *I*–*V* curves with a Keithley 2400 Source Meter under illumination of simulated AM1.5G solar light coming from a solar simulator (Oriel-91193 equipped with a 1000 W Xe lamp and an AM1.5 filter). The light intensity was calibrated using a reference Si solar cell (Oriel-91150) and adjusted with appropriate neutral density filters. IPCE spectra were measured with an Oriel-74125 system (Oriel Instruments, USA), where intensity of monochromatic light was measured with a Si detector (Oriel-71640).

Synthesis

(4-(Bis(4-(hexyloxy)phenyl)amino)phenyl)boronic acid (**1**): 4-bromo-*N,N*-bis(4-(hexyloxy)phenyl)aniline (0.9374 g, 1.79 mmol) was dissolved in 20 mL anhydrous THF and protected with argon. The solution was cooled to –78°C. *n*BuLi (1.6 M in hexane, 1.67 mL, 2.68 mmol) was added slowly, and then the reaction mixture was stirred for 1 h. B(OMe)₃ (0.32 mL, 2.68 mmol) was added through a syringe. After addition was completed, the reaction mixture was gradually warmed to room temperature and stirred overnight. Water was added to quench the reaction, 6 N HCl was used to acidify until the pH of the mixture is less than 7, and then stirred for 15 min. The mixture was extracted with CH₂Cl₂ (3 × 50 mL). The combined organic layers were washed with water and brine and dried with Na₂SO₄. The product was purified by silica gel column chromatography using CH₂Cl₂/EtOAc (v/v = 5:1) as eluent. A pale green solid (441 mg) was obtained after removal of volatiles under reduced pressure, yield 50%. ¹H NMR (400 MHz, CDCl₃): δ = 7.93 (d, *J* = 8.5 Hz, 2H), 7.09 (d, *J* = 8.9 Hz, 4H), 6.92 (d, *J* = 8.6 Hz, 2H), 6.84 (d, *J* = 8.9 Hz, 4H), 3.94 (t, *J* = 6.5 Hz, 4H), 1.84–1.72 (m, 4H), 1.51–1.41 (m, 4H), 1.34 (dd, *J* = 8.8, 5.3 Hz, 8H), 0.91 ppm (t, *J* = 6.9 Hz, 6H). MS calcd: *m/z* 489.31 ([*M*⁺]), TOF-MS found 445.63 ([*M*⁺–B(OH)₂]).

1-Iodo-4,7-dihydro-4,7-ethanobenzo[c]thiophene (**2**): 4,7-dihydro-4,7-ethanobenzo[c]thiophene (205 mg, 1.25 mmol) was dissolved in anhydrous THF (20 mL) and protected with argon. The solution was cooled to –78°C, and *n*BuLi (1.6 M in hexane, 0.80 mL, 1.25 mmol) was added dropwise. After addition was completed, the reaction mixture was gradually returned to room temperature and stirred for 1 h. Then it was cooled to –78°C again, and a solution of iodine in anhydrous THF (369 mg, 1.4375 mmol, 20 mL) was added through a syringe. The reaction mixture was warmed to room temperature slowly and stirred for 1 h. Saturated Na₂SO₃ solution was used to quench the reaction, and the product was with CH₂Cl₂ (3 × 50 mL). The combined organic layers were washed with water and brine and dried with Na₂SO₄. The product was purified by silica gel column chromatography using hexane as eluent and was obtained as a white solid (286 mg) after removal of volatiles under reduced pressure, yield 79%. ¹H NMR (400 MHz, CDCl₃): δ = 6.83 (s, 1H), 6.53–6.41 (m, 2H), 3.88 (d, *J* = 4.7 Hz, 1H), 3.73 (d, *J* = 4.8 Hz, 1H), 1.63–1.44 ppm (m, 4H).

3-Iodo-5,5',8,8',10,10',11,11'-octahydro-1,1'-bi(4,7-ethano-benzo[c]thiophene) (**3**): The procedure was similar to that described in synthesis of **2**. The product was obtained as a white or light yellow solid, yield 91%. ¹H NMR (400 MHz, CDCl₃): δ = 6.72 (s, 1H), 6.57–6.44 (m, 4H), 4.09 (s, 1H), 4.05 (d, *J* = 6.2 Hz, 1H), 3.85 (d, *J* = 5.7 Hz, 1H), 3.74 (d, *J* = 6.0 Hz, 1H), 1.59 ppm (d, *J* = 2.7 Hz, 8H).

4-(4,7-Dihydro-4,7-ethanobenzo[c]thiophen-1-yl)-*N,N*-bis(4-(hexyloxy)phenyl) aniline (**4**): Compounds **1** (286 mg, 1 mmol) and **2** (492 mg, 1 mmol) were dissolved in THF (10 mL), 2 N K₂CO₃ solution (1 mL) was added, and the mixture was degassed using the freeze–pump–thaw technique

and then protected with argon. Tetrakis(triphenylphosphine)palladium (90 mg) was added in one portion. The reaction mixture was heated at reflux for two days. CHCl₃ and water were added, and the aqueous layer was extracted with CHCl₃. The combined organic layers were washed with water and brine and dried with Na₂SO₄. The product was purified by silica gel column chromatography using CH₂Cl₂/hexane (v/v = 1:1) as eluent to obtain the product as an orange oily solid (339 mg) after removal of volatiles under reduced pressure, yield 56%. ¹H NMR (400 MHz, CDCl₃): δ = 7.25 (d, *J* = 8.5 Hz, 2H), 7.12–6.99 (m, 4H), 6.95–6.89 (m, 2H), 6.85–6.79 (m, 4H), 6.63 (s, 1H), 6.56–6.42 (m, 2H), 4.11 (d, *J* = 6.0 Hz, 1H), 3.92 (dd, *J* = 9.0, 4.0 Hz, 4H), 3.82 (d, *J* = 5.5 Hz, 1H), 1.77 (dd, *J* = 9.2, 5.7 Hz, 4H), 1.60 (m, 4H), 1.52–1.40 (m, 4H), 1.34 (dt, *J* = 10.5, 5.1 Hz, 8H), 0.98–0.88 ppm (m, 6H). MS calcd: *m/z* 605.33 ([*M*⁺]), TOF-MS found 605.63 ([*M*⁺]).

4-(Hexyloxy)-*N*-(4-(hexyloxy)phenyl)-*N*-(4-(5,5',8,8',10,10',11,11'-octahydro-1,1'-bi(4,7-ethanobenzo[c]thiophen)-3'-yl)phenyl)aniline (**5**): The procedure was similar to that described in synthesis of **4**. Orange-brown solid, yield 64%. ¹H NMR (400 MHz, CDCl₃): δ = 7.27 (d, *J* = 8.7 Hz, 2H), 7.10–7.05 (m, 4H), 6.93 (d, *J* = 8.6 Hz, 2H), 6.86–6.80 (m, 4H), 6.70 (s, 1H), 6.58–6.48 (m, 4H), 4.14 (s, 2H), 4.09 (s, 1H), 3.93 (t, *J* = 6.5 Hz, 4H), 3.85 (s, 1H), 1.82–1.72 (m, 4H), 1.60 (d, *J* = 4.9 Hz, 8H), 1.52–1.41 (m, 4H), 1.34 (td, *J* = 7.0, 3.4 Hz, 8H), 0.97–0.87 ppm (m, 6H). MS calcd: *m/z* 765.37 ([*M*⁺]), TOF-MS found: 765.62 ([*M*⁺]).

3-(4-(Bis(4-(hexyloxy)phenyl)amino)phenyl)-4,7-dihydro-4,7-ethanobenzo[c]thiophene-1-carbaldehyde (**6**): Compound **4** (339 mg, 0.56 mmol) was dissolved in anhydrous THF (20 mL), protected with argon, and cooled to –78°C. *n*BuLi (1.6 M in hexane, 0.40 mL, 0.64 mmol) was added through a syringe. When addition was finished, the solution was maintained at this temperature and stirred for 30 min. Freshly distilled DMF (0.10 mL, excess) was added dropwise. The mixture was slowly warmed to ambient temperature and stirred overnight. HCl (0.5 N, 30 mL) was added to stop the reaction. The aqueous layer was extracted with CHCl₃. The combined organic layers were washed with water and brine and dried with Na₂SO₄. The product was purified by silica gel column chromatography using CH₂Cl₂/hexane (v/v = 1:1) as eluent to give the product as orange solid (147 mg) after removal of volatiles under reduced pressure, yield 41%. ¹H NMR (400 MHz, CDCl₃): δ = 9.96 (s, 1H), 7.33–7.27 (m, 2H), 7.15–7.06 (m, 4H), 6.92 (d, *J* = 8.7 Hz, 2H), 6.89–6.80 (m, 4H), 6.61–6.45 (m, 2H), 4.46 (d, *J* = 5.4 Hz, 1H), 4.20 (s, 1H), 3.94 (t, *J* = 6.5 Hz, 4H), 1.84–1.73 (m, 4H), 1.64 (m, 4H), 1.52–1.41 (m, 4H), 1.35 (td, *J* = 6.8, 3.4 Hz, 8H), 0.91 ppm (t, *J* = 6.9 Hz, 6H). MS calcd: *m/z* 633.33 ([*M*⁺]), TOF-MS found 633.55 ([*M*⁺]).

3'-(4-(Bis(4-(hexyloxy)phenyl)amino)phenyl)-5,5',8,8',10,10',11,11'-octahydro-1,1'-bi(4,7-ethanobenzo[c]thiophene)-3-carbaldehyde (**7**): The procedure was similar to that described in the synthesis of **6**. Orange solid, yield 92%. ¹H NMR (400 MHz, CDCl₃): δ = 9.98 (s, 1H), 7.27 (d, *J* = 8.6 Hz, 2H), 7.08 (t, *J* = 6.1 Hz, 4H), 6.94 (d, *J* = 8.6 Hz, 2H), 6.83 (t, *J* = 6.1 Hz, 4H), 6.66–6.46 (m, 4H), 4.46 (d, *J* = 5.8 Hz, 1H), 4.33 (t, *J* = 7.0 Hz, 1H), 4.26 (d, *J* = 9.8 Hz, 1H), 4.14 (s, 1H), 3.93 (t, *J* = 6.5 Hz, 4H), 1.85–1.73 (m, 4H), 1.72–1.60 (m, 8H), 1.45 (dd, *J* = 14.7, 7.1 Hz, 4H), 1.41–1.28 (m, 8H), 0.91 ppm (t, *J* = 7.0 Hz, 6H). MS calcd: *m/z* 793.36 ([*M*⁺]), TOF-MS found: 793.31 ([*M*⁺]).

OLI: Compound **6** (127 mg, 0.20 mmol), 2-cyanoacetic acid (55 mg, 0.60 mmol), and piperidine (120 mg, 1.40 mmol) were dissolved in CHCl₃ (20 mL). The reaction mixture was heated to reflux overnight. The mixture was cooled to room temperature, CHCl₃ and water were added, and the aqueous layer was extracted with CHCl₃. The combined organic layer was washed with 1 N HCl, water, and brine and dried with Na₂SO₄. The product was purified by silica gel column chromatography using CHCl₃/CH₃OH (v/v = 9:1) as eluent to give product as dark red solid (68 mg) after removal of volatiles under reduced pressure, yield 48%. ¹H NMR (400 MHz, CDCl₃): δ = 8.46 (s, 1H), 7.34 (d, *J* = 8.5 Hz, 2H), 7.08 (d, *J* = 8.8 Hz, 4H), 6.91 (d, *J* = 8.6 Hz, 2H), 6.85 (d, *J* = 8.8 Hz, 4H), 6.54 (m, 2H), 4.26 (s, 2H), 3.94 (t, *J* = 6.5 Hz, 4H), 1.86–1.72 (m, 4H), 1.61 (s, 4H), 1.46 (dd, *J* = 14.3, 7.0 Hz, 4H), 1.41–1.28 (m, 8H), 0.91 ppm (t, *J* = 6.9 Hz, 6H). MS calcd: *m/z* 701.3368 ([*M*⁺]), HRMS found: 701.3394 ([*M*⁺]). Elemental anal. calcd for C₄₄H₄₈N₂O₄S: C 75.40, H 6.90, N 4.00; found: C 75.31, H 6.81, N 3.99.

OL2: The procedure was similar to that described in the synthesis of **OL1**. Dark red solid, yield 76%. ¹H NMR (400 MHz, CDCl₃): δ = 8.46 (s, 1H), 7.28 (d, *J* = 8.7 Hz, 2H), 7.09 (dd, *J* = 9.5, 2.7 Hz, 4H), 6.94 (d, *J* = 8.7 Hz, 2H), 6.89–6.79 (m, 4H), 6.67–6.45 (m, 4H), 4.46–4.36 (m, 1H), 4.29 (dd, *J* = 17.4, 5.7 Hz, 2H), 4.16 (dd, *J* = 3.9 Hz, 1H), 3.94 (t, *J* = 6.5 Hz, 4H), 1.85–1.74 (m, 4H), 1.63 (d, *J* = 23.2 Hz, 8H), 1.46 (dd, *J* = 14.7, 7.1 Hz, 4H), 1.40–1.29 (m, 8H), 0.91 ppm (t, *J* = 7.0 Hz, 6H). MS calcd: *m/z* 861.3715 ([*M*⁺]), HRMS found: 861.3748 ([*M*⁺]). Elemental anal. calcd for C₃₄H₅₆N₂O₄S₂: C 75.31, H 6.55, N 3.25; found: C 75.24, H 6.68, N 3.26.

3-(4-(Bis(4-(hexyloxy)phenyl)amino)phenyl)benzo[c]thiophene-1-carbaldehyde (**8**): In a glass tube oven, **6** (62 mg) was heated under vacuum at 270°C for 30 min. Then it was cooled to room temperature. A dark red solid (58 mg) was obtained in quantitative yield. ¹H NMR (400 MHz, CDCl₃): δ = 10.25 (s, 1H), 8.30 (d, *J* = 8.4 Hz, 1H), 7.91 (d, *J* = 8.7 Hz, 1H), 7.50 (d, *J* = 8.6 Hz, 2H), 7.40 (dd, *J* = 8.7, 6.6 Hz, 1H), 7.25–7.19 (m, 1H), 7.13 (d, *J* = 8.8 Hz, 4H), 6.99 (d, *J* = 8.6 Hz, 2H), 6.87 (d, *J* = 8.8 Hz, 4H), 3.95 (t, *J* = 6.5 Hz, 4H), 1.86–1.70 (m, 4H), 1.47 (dt, *J* = 14.5, 7.1 Hz, 4H), 1.35 (td, *J* = 6.7, 3.3 Hz, 8H), 0.91 ppm (t, *J* = 6.8 Hz, 6H). MS calcd: *m/z* 605.30 ([*M*⁺]), TOF-MS found: 605.61 ([*M*⁺]).

3'-(4-(Bis(4-(hexyloxy)phenyl)amino)phenyl)-[1,1'-bibenzo[c]thio-phenyl]-3-carbaldehyde (**9**): The procedure was similar to that described in the synthesis of **8**. Purple solid. Quantitative yield. ¹H NMR (400 MHz, CDCl₃): δ = 10.26 (s, 1H), 8.28 (d, *J* = 8.5 Hz, 1H), 8.08 (dd, *J* = 8.8, 0.8 Hz, 1H), 8.03–7.96 (m, 1H), 7.86 (d, *J* = 8.8 Hz, 1H), 7.45 (d, *J* = 8.6 Hz, 2H), 7.43–7.35 (m, 1H), 7.21 (dt, *J* = 22.9, 4.9 Hz, 2H), 7.15–7.07 (m, 5H), 7.00 (d, *J* = 8.6 Hz, 2H), 6.85 (d, *J* = 8.7 Hz, 4H), 3.93 (t, *J* = 6.5 Hz, 4H), 1.77 (dd, *J* = 14.7, 6.7 Hz, 4H), 1.54–1.41 (m, 4H), 1.40–1.30 (m, 9H), 0.91 ppm (q, *J* = 6.6 Hz, 7H). MS calcd: *m/z* 737.30 ([*M*⁺]), TOF-MS found: 737.47 ([*M*⁺]).

OL3: The procedure was similar to that described in the synthesis of **OL1**, purple solid (26 mg), yield 48%. ¹H NMR (400 MHz, [D₆]acetone): δ = 8.68 (s, 1H), 7.90 (d, *J* = 6.7 Hz, 1H), 7.80 (d, *J* = 6.8 Hz, 1H), 7.44 (d, *J* = 6.3 Hz, 2H), 7.31 (s, 1H), 7.17 (s, 1H), 7.01 (d, *J* = 8.4 Hz, 4H), 6.81 (d, *J* = 8.6 Hz, 6H), 3.85 (t, *J* = 6.4 Hz, 4H), 1.72–1.54 (m, 4H), 1.33 (dd, *J* = 14.6, 7.1 Hz, 5H), 1.27–1.18 (m, 8H), 0.84–0.65 ppm (m, 6H). MS calcd: *m/z* 673.3055 ([*M*⁺]), HRMS found: 673.3100 ([*M*⁺]). Elemental Anal. calcd for C₄₂H₄₄N₂O₄S: C 74.97, H 6.59, N 4.16; found: C 75.01, H 6.51, N 4.10

OL4: The procedure was similar to that described in the synthesis of **OL1**, dark blue solid, yield 45%. ¹H NMR (400 MHz, CDCl₃): δ = 8.83 (d, *J* = 11.3 Hz, 1H), 8.19 (dt, *J* = 17.4, 9.5 Hz, 2H), 7.92 (dt, *J* = 16.3, 8.9 Hz, 2H), 7.52–7.42 (m, 2H), 7.31 (s, 2H), 7.19 (d, *J* = 8.0 Hz, 1H), 7.12 (d, *J* = 6.7 Hz, 4H), 7.00 (dd, *J* = 7.9, 2.4 Hz, 2H), 6.87 (d, *J* = 8.3 Hz, 4H), 6.78 (s, 1H), 3.95 (t, *J* = 6.5 Hz, 4H), 1.78 (dd, *J* = 14.7, 6.7 Hz, 4H), 1.53–1.43 (m, 4H), 1.35 (dt, *J* = 10.6, 3.5 Hz, 8H), 0.92 ppm (t, *J* = 7.0 Hz, 6H). MS calcd: *m/z* 805.3089 ([*M*⁺]), HRMS found: 805.3128 ([*M*⁺]). Elemental anal. calcd for C₅₀H₄₈N₂O₄S₂: C 74.60, H 6.01, N 3.48; found: C 74.42, H 6.14, N 3.40

4-(7-Bromo-2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-*N,N*-bis(4-(hexyloxy)phenyl)aniline (**10**): 2-[4-[*N,N*-bis(4-hexyloxyphenyl)amino]phenyl]-3,4-(ethylenedioxy)thiophene (602 mg, 1.03 mmol) was dissolved in anhydrous THF (20 mL), protected under argon, and cooled to 0°C. NBS, 215 mg, 1.21 mmol) was added in one portion. The reaction mixture was stirred for 3 h. Saturated sodium hyposulfite solution was added to stop the reaction. CHCl₃ and water were added, the phases were separated, and the aqueous layer was extracted with CHCl₃. The combined organic layer was washed with brine and dried with Na₂SO₄. The product was purified by silica gel column chromatography using EtOAc/hexane (*v/v* = 1:8) as eluent to give the product as dark green oil (667 mg) after removal of volatiles under reduced pressure, yield 98%. ¹H NMR (500 MHz, [D₆]acetone): δ = 7.45 (d, *J* = 8.8 Hz, 2H), 7.08–7.01 (m, 4H), 6.94–6.89 (m, 4H), 6.84 (d, *J* = 8.8 Hz, 2H), 4.34 (s, 4H), 3.98 (t, *J* = 6.5 Hz, 4H), 1.84–1.71 (m, 7H), 1.48 (m, 5H), 1.41–1.31 (m, 8H), 0.91 ppm (t, *J* = 6.9 Hz, 6H). MS calcd: *m/z* 663.20 ([*M*⁺]), MALDI-TOF found: 663.38 ([*M*⁺]).

3-(7-(4-(Bis(4-(hexyloxy)phenyl)amino)phenyl)-2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-4,7-dihydro-4,7-ethanobenzo[c]thiophene-1-carbaldehyde

(**12**): Compound **10** (667 mg, 1 mmol) and 2-(4,7-dihydro-4,7-ethanobenzo[c]thiophen-1-yl)-4,4,5,5-tetra-methyl-1,3,2-dioxaborolane (424 mg, 1.47 mmol) were dissolved in THF (20 mL). K₂CO₃ solution (2N, 10 mL) was added, and the mixture was degassed using the freeze-pump-thaw technique and then protected with argon. Tetrakis(triphenylphosphine)-palladium (120 mg) was added in one portion. The reaction mixture was heated at reflux for two days. CHCl₃ and water were added, the phases were separated, and the aqueous layer was extracted with CHCl₃. The combined organic layers were washed with water and brine and dried with Na₂SO₄. Silica gel column chromatography using CHCl₃/petroleum ether (*v/v* = 1:4) as eluent gave the crude product (400 mg), with polarity-closed debrominated starting material as byproduct. The crude product (400 mg) was dissolved in anhydrous THF (30 mL), protected with argon, and cooled to –78°C. *n*BuLi (1.6M in hexane, 0.40 mL, 0.64 mmol) was added through a syringe. While addition was finished, the solution was maintained at this temperature and stirred for 30 min. Freshly distilled DMF (0.30 mL, excess) was added dropwise. The mixture was slowly warmed to ambient temperature and was stirred overnight. HCl (0.5N, 60 mL) was added to stop the reaction. The aqueous layer was extracted with CHCl₃. The combined organic layers were washed with water and brine and dried with Na₂SO₄. Silica gel column chromatography using CHCl₃/petroleum ether (*v/v* = 1:1) as eluent gave the product as an orange solid (300 mg) after removal of volatiles under reduced pressure, yield 39%. ¹H NMR (500 MHz, CDCl₃): δ = 10.07 (s, 1H), 7.61 (d, *J* = 8.8 Hz, 2H), 7.08 (t, *J* = 8.9 Hz, 4H), 6.95 (t, *J* = 7.9 Hz, 4H), 6.89 (d, *J* = 8.8 Hz, 2H), 6.64 (t, *J* = 6.9 Hz, 1H), 6.57 (t, *J* = 6.6 Hz, 1H), 4.62 (d, *J* = 6.3 Hz, 1H), 4.54 (d, *J* = 6.0 Hz, 1H), 4.47 (m, 4H), 4.01 (t, *J* = 5.8 Hz, 4H), 1.84–1.73 (m, 4H), 1.67 (dd, *J* = 25.5, 11.2 Hz, 2H), 1.50 (m, 4H), 1.43–1.32 (m, 8H), 0.93 ppm (d, *J* = 6.1 Hz, 6H). MS calcd: *m/z* 773.32 ([*M*⁺]), MALDI-TOF found: 773.34 ([*M*⁺]).

OL5: The procedure was similar to that described in the synthesis of **OL1**. Dark purple-red solid, yield 78%. ¹H NMR (500 MHz, [D₆]acetone): δ = 8.44 (s, 1H), 7.62 (d, *J* = 8.6, 2H), 7.08 (d, *J* = 8.7, 4H), 6.93 (d, *J* = 8.7, 4H), 6.88 (d, *J* = 8.6, 2H), 6.63 (t, *J* = 6.8, 1H), 6.57 (t, *J* = 6.7, 1H), 4.58 (d, *J* = 5.7, 1H), 4.49 (d, *J* = 4.7, 2H), 4.45 (d, *J* = 4.4, 2H), 4.41 (d, *J* = 4.9, 1H), 3.99 (t, *J* = 6.4, 4H), 1.82–1.73 (m, 4H), 1.73–1.54 (m, 4H), 1.48 (m, 4H), 1.42–1.32 (m, 8H), 0.91 ppm (t, *J* = 6.6, 6H). MS calcd: *m/z* 840.33 ([*M*⁺]), MALDI-TOF found: 812.58 ([*M*⁺–C₂H₄]). Elemental anal. calcd for C₅₀H₅₂N₂O₆S₂: C 71.40, H 6.23, N 3.33; found: C 71.45, H 6.24, N 3.30

3-(7-(4-(Bis(4-(hexyloxy)phenyl)amino)phenyl)-2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)benzo[c]thiophene-1-carbaldehyde (**13**): The procedure was similar to that described in the synthesis of **8**, purple solid, quantitative yield. ¹H NMR (500 MHz, [D₆]acetone): δ = 10.37 (s, 1H), 8.41 (d, *J* = 8.6 Hz, 1H), 8.36 (d, *J* = 8.9 Hz, 1H), 7.69 (d, *J* = 8.8 Hz, 2H), 7.54–7.45 (m, 1H), 7.42–7.32 (m, 1H), 7.10 (d, *J* = 8.9 Hz, 4H), 6.95 (d, *J* = 8.9 Hz, 4H), 6.90 (d, *J* = 8.8 Hz, 2H), 4.65 (dd, *J* = 5.0, 2.8 Hz, 2H), 4.54 (dd, *J* = 4.9, 2.8 Hz, 2H), 4.00 (t, *J* = 6.5 Hz, 4H), 1.84–1.72 (m, 4H), 1.55–1.45 (m, 4H), 1.42–1.32 (m, 8H), 0.92 ppm (t, *J* = 6.8 Hz, 6H). MS calcd: *m/z* 745.29 ([*M*⁺]), MALDI-TOF found: 745.47 ([*M*⁺]).

OL6: The procedure was similar as that described in the synthesis of **OL1**, dark blue solid, yield 38%. ¹H NMR (500 MHz, [D₆]DMSO) δ = 8.78 (s, 1H), 8.32 (d, *J* = 8.7 Hz, 1H), 8.13 (d, *J* = 8.7 Hz, 1H), 7.65 (d, *J* = 8.8 Hz, 2H), 7.56–7.50 (m, 1H), 7.50–7.41 (m, 1H), 7.05 (d, *J* = 8.9 Hz, 4H), 6.93 (d, *J* = 8.9 Hz, 4H), 6.80 (d, *J* = 8.8 Hz, 2H), 4.60 (d, *J* = 2.4 Hz, 2H), 4.47 (d, *J* = 1.9 Hz, 2H), 3.95 (t, *J* = 6.4 Hz, 4H), 1.76–1.66 (m, 4H), 1.47–1.37 (m, 4H), 1.31 (dd, *J* = 7.0, 3.3 Hz, 8H), 0.89 ppm (t, *J* = 6.9 Hz, 6H). MS calcd: *m/z* 812.30 ([*M*⁺]), MALDI-TOF found: 812.44 ([*M*⁺]). Elemental anal. calcd for C₄₈H₄₈N₂O₆S₂: C 70.91, H 5.95, N 3.45; found: C 70.82, H 6.05, N 3.26

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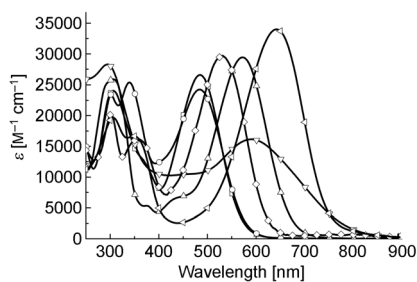
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Dyes

Q. Liu, Q.-Y. Feng, H. Yamada,
Z.-S. Wang,* N. Ono, X.-Z. You,
Z. Shen**



Tuning the Spectroscopic, Electrochemical, and Photovoltaic Properties of Triaryl Amine Based Sensitizers through Ring-Fused Thiophene Bridges

