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Synthesis and spectroscopic properties of ring-fused thiophene bridged push–pull dyes and their application in dye-sensitized solar cells

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ABSTRACT

Bisdimethylfluorenylamino-based push–pull dyes bearing one or two benzo[*c*]thiophene and its precursor bicyclo[2.2.2]octadiene (BCOD) fused thiophene as π bridge have been synthesized. The effect of fused-ring on thiophene bridge for the spectroscopic and electrochemical properties of these dyes has been investigated. Dye-sensitized solar cells fabricated with these dyes show moderate photovoltaic properties.

Introduction

Dye-sensitized solar cells (DSSCs) have attracted considerable research interest in the past decades due to its advantages such as low cost and easy fabrication.[1] As one of the key components of DSSC, Ru complex based sensitizers encountered the problems of limited resource and high toxicity, although they hold the highest power conversion for a long time.[2] The search for alternative dyes is now ongoing. Metal-free organic dyes with the structure of donor–π–acceptor are considered to be the promising candidate because of their high molar extinction coefficient, easy modification on structure, low cost, and clean to environment.[3–5] In the past 10 years, great progresses have been achieved on organic dye based DSSC.[6–10] Some organic dyes exhibit good conversion efficiency of about 10%[11–14] and even higher.[15,16] Triarylamine and cyanoacrylic acid are most commonly employed as donor and acceptor, respectively, in the design of donor–π–acceptor structure while thiophene and its derivatives are served as π bridge to provide conjugation and enhance light absorbance.

Among the triarylamine derivatives, dimethylfluoreaniline (or bisdimethylfluorenylamino group) was first introduced into DSSC by Ko's group which brought the combination of high conversion efficiency with excellent light and thermostability.[17] A series of novel dyes derived from dimethylfluoreaniline donor part were hence developed.[8,18–23] Recently we reported a series of push–pull sensitizers in which benzo[*c*]thiophene and its precursor bicyclo[2.2.2]octadiene (BCOD) ring-fused thiophene have been introduced as π-conjugated spacers, containing dihexyloxy-substituted triphenylamine as the donor and cyanoacrylic acid as the acceptor.[24] It was the first time that benzo[*c*]thiophene and its precursor were applied as π bridge in dyes for DSSC and we found that appropriate extension in π conjugation significantly red-shifted the absorption spectra and enhanced their performance in DSSC. Since dimethyl-fluoreaniline exhibited excellent performance as donor part of DSSC dyes, it motivated us to design and synthesis new dyes in combination of dimethylfluoreaniline and ring-fused thiophene, with the aim of enriching the alterations of dyes and finding robust and efficient organic dyes for DSSC.

Experiment

The organic dyes **OL7**–**OL10** were prepared following the synthetic procedure illustrated in Scheme 1. **1** was prepared through Ullmann reaction by aniline coupled with 2-iodo-dimethylfluorene in moderate yield. Compound **3** was achieved by reacting **1** with NBS and then with trimethyl borate. Since benzo[*c*]thiophene is very unstable, its introduction is achieved

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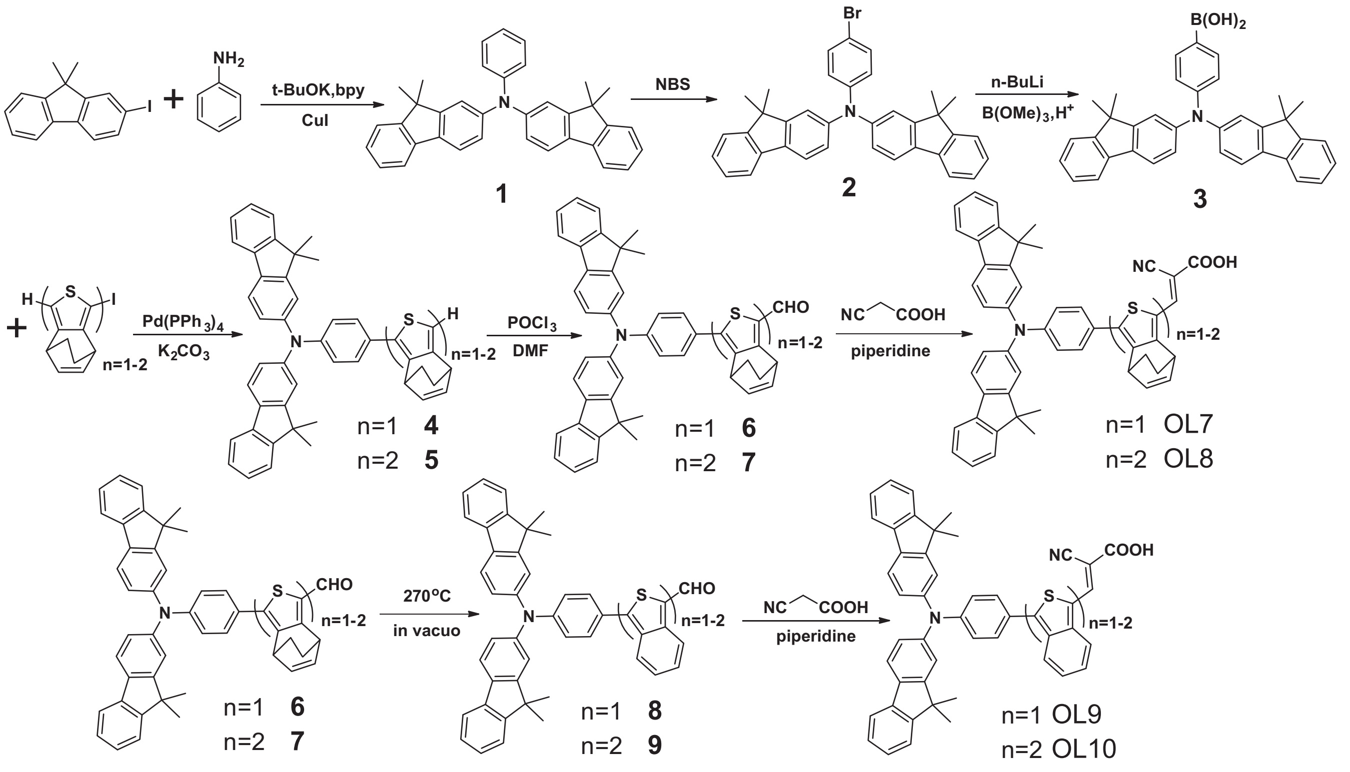

Scheme 1. Synthetic procedure for dyes **OL7**–**OL10**.

through the transformation of appropriate precursor. Previously, Ono's group has reported the facile synthesis of isothianaphthene oligomers using BCOD-thiophene as a precursor.[25] Here we follow this protocol and connect one or two BCOD-thiophene to the donor part through Suzuki coupling reaction to obtain **4** and **5**, respectively. Target compounds **OL7** and **OL8** were synthesized through Knoevenagel reaction from aldehydes **6** and **7** which were prepared by Vilsmeyer reaction with **4** and **5**, respectively. The transformation of BCOD-thiophene precursor into benzo[*c*]thiophene analog was carried out at the aldehyde stage to prevent potential decarboxylation of the final product at 270 °C. **OL9** and **OL10** were obtained in a way similar to **OL7** and **OL8** after the transformation.

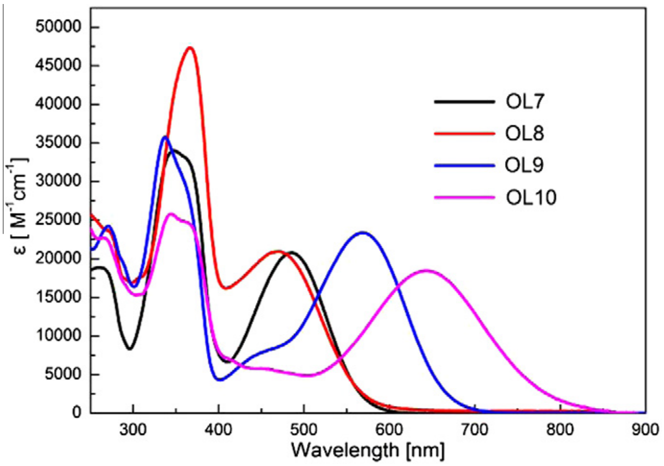

Figure 1. UV–vis absorption spectra of dyes **OL7**–**OL10** measured in CH_2Cl_2.

Table 1
Electrooptical and electrochemical properties of the dyes

Dye	λ_{max} (nm)/log ε	E_{HOMO} (eV)	E_{0-0} (eV)	E_{LUMO} (eV)
OL7	485/4.32, 347/4.53	−5.56	2.28	−3.28
OL8	472/4.32, 367/4.68	−5.50	2.42	−3.08
OL9	569/4.37, 337/4.55	−5.61	2.01	−3.60
OL10	645/4.27, 345/4.41	−5.50	1.67	−3.83

Results and discussions

Spectroscopic properties of the ring-fused thiophene bridged bisdimethylfluorenylamino-based push–pull organic dyes

To inspect the effect of fused ring on thiophene for the spectroscopic properties of these dyes, the electronic absorption spectra of dyes **OL7**–**OL10** were measured in dichloromethane, as shown in Figure 1 and the detailed data were listed in Table 1. All dyes exhibited two peaks with maximum absorption bands mainly located at around 340–370 nm and ranging from 470 to 640 nm, respectively, and the latter could be attributed to the intrinsic charge transfer transition from HOMO to LUMO. The absorption spectra are very similar to their dihexyloxy-substitute triphenylamine analog,[24] except for **OL10** with λ_{max} further redshift to 645 nm. Comparing the absorption spectra of **OL7** and **OL8**, the additional BCOD thiophene moiety has little effect on the charge transfer band but enhancing the absorption in the ultraviolet region. The transformation of BCOD thiophene into benzo[*c*]thiophene leading to the expansion of the π-conjugation pathway, which notably bathchromic shifted the absorption maximum in the visible region. From **OL7** to **OL9** and **OL8** to **OL10**, the maximum absorption peak red-shifted for 84 and 73 nm, respectively. In addition from **OL9** to **OL10**, a red shift of 76 nm was observed. Among the four dyes, **OL9** shows the highest absorption coefficient ($\varepsilon = 23341\ M^{-1}\ cm^{-1}$) in the visible region. The absorption spectrum of **OL10** is broadened with the tailed off at 850 nm. Such strong and broadening absorption in the visible and even near infrared region indicates that the light harvesting of device fabricated with these dyes may be improved and hence enhance the generation of photocurrent.

Electrochemical properties of the ring-fused thiophene bridged bisdimethylfluorenylamino-based push–pull dyes

The electrochemical properties of these dyes were studied by cyclic voltammetry (CV) in CH_2Cl_2 solution containing tetrabutylammonium hexafluorophosphate (0.1 M) as a supporting electrolyte with a scan rate of 100 mV/s and ferrocene was taken as reference. Comparing with the HOMO level of electrolyte I_3^-/I^- redox couple (−4.85 eV vs vacuum),[3] it can be found that all the dyes could meet the requirements of regeneration after the photoinduced electron injection. Beside **OL10**, the LUMO level of **OL7**–**OL9** is higher enough than the conduction band edge of TiO_2 (−4.00 eV vs vacuum),[26] as an offset of ca. 0.2 eV is required for the driving force of electron injecting.[27] Comparing with their dihexyloxy-substitute triphenylamine analog,[24] it can be found that their LUMO level is almost the same (except for OL3 and OL9, ΔLUMO is 0.11 eV), while HOMO level of dimethylfluoreaniline derivatives maintains somewhat lower (ranging from −0.03 to −0.09 eV). This may be attributed to the fluorene moiety which disperses the electron density distribution and thus stabilized the HOMO. To evaluate the effect of introducing benzo[*c*]thiophene as a π bridge, we compared the HOMO and LUMO levels of the dyes. From **OL7** and **OL8** to **OL9** and **OL10** the change in energy level ΔHOMO is −0.05 and 0 eV, respectively, and ΔLUMO is −0.32 and −0.75 eV, respectively, indicating that fused benzo[*c*]thiophene can stabilize the LUMO level remarkably while has little affect on the HOMO level. This character may be applicable for fine tuning the energy level of organic push–pull dyes to match the conduction band edge of TiO_2 and the sunlight spectra for better performance in DSSC.

X-Ray analysis of OL7

For further understanding the relationship between the structure and performance of the designed dyes, we tried to obtain single crystals of these dyes, but unfortunately only the single crystal of **OL7** was obtained by slow evaporation of a mixed solution of CH_2Cl_2 and hexane. Its structure was subjected to X-ray analysis.

OL7 belongs to triclinic space group P-1 and its structure is shown in Figure 2. The two fluorene moieties are highly coplanar, respectively (mean deviation from plane is 0.0206 Å of C1–C13 and 0.0294 Å of C16–C28). The dihedral angle between C16–C28 and C1–C13 rings is 62°. The dihedral angles between the benzene ring and two fluorene planes are 64.3° and 64.5°, respectively. Also the thiophene ring is distorted with the benzene ring in 34.5°. It is noteworthy that thiophene and cyanoacrylic acid group are not coplanar, torsion angle between C44 and C47 is 13.4°, and carboxylate group plane twist 2.9° from the cyano group. Due to the existence of carboxylate group, there is hydrogen bonding between the neighboring molecules in the crystal lattice in a head-to-tail fashion.

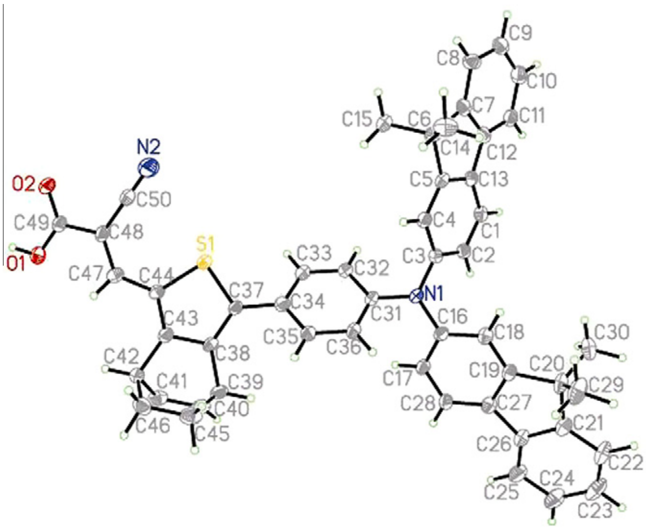

Figure 2. ORTEP plot of **OL7** with thermal ellipsoids shown at 50%. Disordered ethano group and CH_2Cl_2 are omitted for clarity.

Table 2
Photovoltaic performance of dyes **OL7**–**OL9** and **N719**

Dye	V_{oc}/mV	J_{sc}/mA cm^{-2}	FF	η/%
OL7	465 ± 5	14.32 ± 0.08	0.66 ± 0.01	4.37 ± 0.06
OL8	500 ± 0	13.08 ± 0.04	0.69 ± 0.00	4.54 ± 0.01
OL9	405 ± 5	11.86 ± 0.06	0.65 ± 0.01	3.13 ± 0.06
N719	535 ± 15	19.38 ± 0.54	0.61 ± 0.01	6.22 ± 0.04

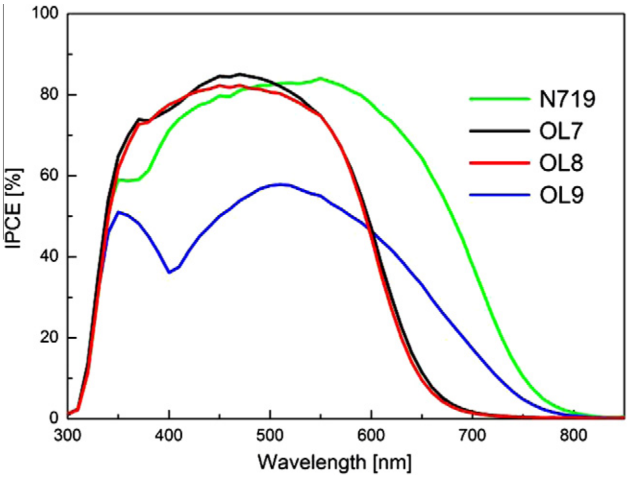

Figure 3. The incident photon-to-current conversion efficiency spectra for DSSCs based on **OL7–OL9** and **N719**.

Photovoltaic performance of the ring-fused thiophene bridged bisdimethylfluorenylamino-based push–pull dyes

The dye-sensitized solar cells fabricated with these dyes and **N719** as a reference were measured and their photovoltaic performance are listed in Table 2. It should be noted that the solar cell performance for the new and reference dyes was compared under the same but not optimal conditions and the efficiency for **N719** listed in Table 2 was much lower than the reported highest value, as it was not optimized in this work. Among all the dyes, **OL8** exhibited the highest light to power conversion efficiency of 4.54% (V_{oc} = 500 mV, J_{sc} = 13.08 mA cm^{-2}, FF = 0.69), while **OL7** had a maximum short circuit current density of 14.32 mA cm^{-2}. Although **OL9** exhibited broader and stronger absorption in the visible region, its conversion efficiency was 3.13% with less short circuit current density and open circuit voltage, which was lower than **OL7** and **OL8**. Under the same condition, **N719** sensitized DSSC showed a conversion efficiency of 6.22%. Since **OL10** was unstable in solution and gradually decomposed with color fading from original blue to yellow, we could not obtain reliable photovoltaic data under the same condition of other dyes.

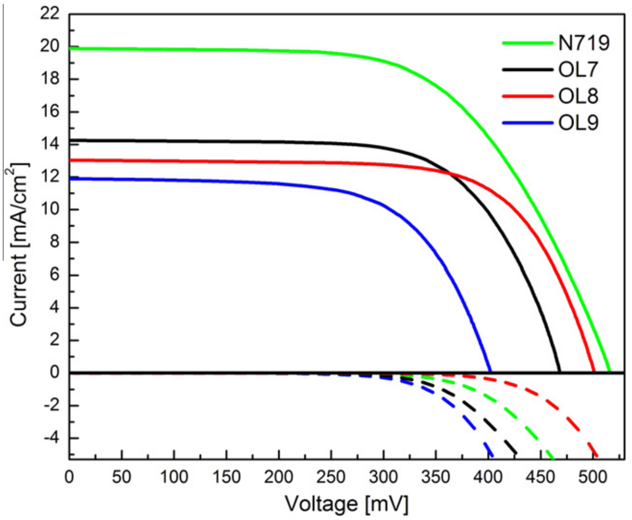

Figure 4. *J–V* curves of DSSCs based on **OL7–OL9** and **N719** under irradiation of 100 mW/cm^2 at 1.5AM sunlight condition.

In the incident photo-to-current conversion efficiency (IPCE) spectra of these dyes (Fig. 3), **OL7** and **OL8** showed very similar spectrum response with highest IPCE value of 85% and 82%, respectively. Their IPCE values were over 70% at the wavelength between 400 and 550 nm and cut off at 700 nm. As a comparison, **OL9** has highest value of 58% and above 50% between 450 and 600 nm. But it is interesting that the spectrum response of **OL9** was extended to 800 nm, which is similar to that of **N719**.

The *J–V* curves of these dyes are shown in Figure 4. From the dark current we could find that the charge recombination trend follows the order of **OL9** > **OL7** > **OL8** in these DSSCs. This may explain the relative poor performance of **OL9**. Another reason for the lower performance may be the poor solubility.[28] Considering the good planarity and π conjugation of fluorene and benzo[*c*]thiophene, it is possible that the poor solubility is caused by the π–π stacking which prevents the efficient electron injection from the dye into the TiO_2 conducting band. Structural modification with more space hindrance group or using co-adsorbents may improve the performance of **OL9** and the corresponding work is now undergoing.

Conclusions

In summary, we have introduced benzo[*c*]thiophene and its precursor as π bridge to bisdimethylfluorenylamino-based push–pull organic dyes; their spectroscopic and electrochemical properties have been studied. Fusion with benzene ring on thiophene bridge significantly expands π-conjugation thus red-shift the spectrum response and greatly stabilized the LUMO level of dyes. Dye-sensitized solar cells fabricated with these dyes are measured and moderate power conversion is obtained compared with that of **N719**, suggesting that these dyes may be good candidate for sensitizers. Further modifications of the dye structure and device optimization to improve the performance of these dyes are now in progress.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2012.04.052.

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