

Triphenylamine-Based Dyes Bearing Functionalized 3,4-Propylenedioxythiophene Linkers with Enhanced Performance for Dye-Sensitized Solar Cells

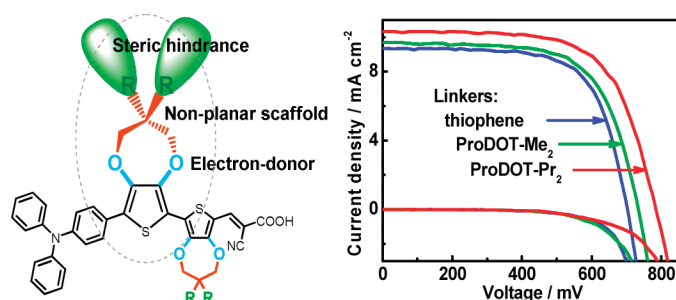
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ABSTRACT



Introduction of modified 3,4-propylenedioxythiophene units into triphenylamine-based dyes is found to enhance light capturing, suppress dye aggregation, and remarkably retard charge recombination in dye-sensitized solar cells. Open circuit voltages of the as-synthesized dyes (~800 mV) are much higher than that with a thiophene congener (720 mV) under similar conditions as a result of self-passivation benefiting from their three-dimensional branched structures.

Dye-sensitized solar cells (DSCs) are one of the most promising candidates for widespread solar energy utilization owing to their low cost and relatively high photoenergy-conversion efficiencies (η).¹ Although Ru-based complexes hold the record validated efficiency of over 11% under full sunlight,² they have encountered problems such as limited resources and elaborated purification. On the other hand, organic sensitizers with robust availability, ease of structural tuning, and generally high molar extinction coefficients have emerged as competitive alternatives to the Ru-based counterparts.³

Although encouraging efficiencies of near 10% have been reported,⁴ organic dyes need to overcome three major drawbacks before they can outperform Ru dyes, namely, (1) narrow photoresponse range resulting from their limited spectral coverage, (2) formation of aggregates on the TiO₂ surface that decreases electron injection,⁵ and, especially, (3) relatively fast charge recombination of the injected electrons in the TiO₂ with the redox species in the electrolyte.⁶ After making extensive studies on molecular modification based on the donor- π -acceptor configuration,³ effective strategies for fine-tuning the energy levels of dyes to better-

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match the solar spectrum are now available,⁷ and aggregation of the adsorbed dyes could be prevented by introducing bulky nonplanar structures.⁸ In contrast, few established strategies for retardation of interfacial charge recombination are known. Involvement of multiple long alkyl chains^{4b,9} and starburst structures^{7b,c,10} in dye backbones are found to improve open circuit voltage (V_{OC}) since these bulky “functions” or the thick dye aggregates formed can block the redox species, i.e. passivate the TiO_2 surface. However, construction of such complex structures is synthetically challenging, and the V_{OC} values of these dyes remain mostly lower than that of the Ru complex **N719**. More groundwork toward the reduction of charge recombination for organic dyes is in urgent need. Recent studies suggested that the generally low V_{OC} values for organic dyes were most likely suffered from complex formation between dye molecules and I_2 or I_3^- , or from indirect electrostatic attraction of I_3^- by negatively charged atoms in the dyes, whichever pathway increased the local concentration of electron acceptor species in the vicinity of TiO_2 surface.^{6,11} We therefore envisage the possibility that retardation of charge recombination could be effectively realized by introducing appropriate steric hindrance to the sensitizer backbone in order to alleviate the strong interaction between sensitizers and acceptor species in the electrolyte, that is, passivation of the sensitizers, rather than the entire TiO_2 surface.

Herein we report on the facile and expedient multifunctionalization of triphenylamine dyes by introducing rationally modified ProDOT building blocks to their π -conjugated systems (**OR** dyes, Figure 1). ProDOT shares attractive properties with 3,4-ethylenedioxythiophene (EDOT) such as high electron-richness and excellent coplanarity of their oligomers,¹² while sensitizers bearing EDOT have shown

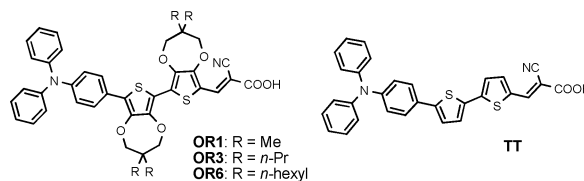
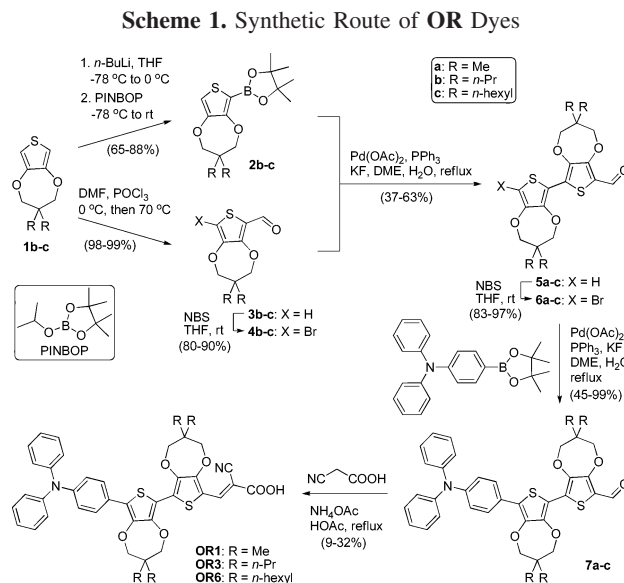


Figure 1. Molecular structures of sensitizers bearing bisProDOTs (**OR1**, **OR3**, and **OR6**) and bithiophene (**TT**).

impressive performances in DSCs.^{4a,7g} In addition, ProDOT have a tetrahedral central carbon in the propylene ring at which a variety of functional groups could be installed to form three-dimensional (3D) branched structures¹² which will not only disfavor π - π packing but also block other molecules (e.g., I_3^-) from approaching. On the basis of the above considerations, we could reasonably expect improved optical properties, suppressed dye aggregation, and, most hopefully, hindered charge recombination all by simply replacing the commonly employed thiophene linker by ProDOTs. Therefore, **OR** dyes containing dimeric dialkylated ProDOTs (bisProDOT- R_2) are engineered and tested in DSCs. In particular, the sizes of alkyl groups are systematically varied to examine the role they play in the dyes' photovoltaic performance. A bithiophene congener, coded **TT**,^{10,13} is also synthesized for a comparison.

The synthetic route of **OR** dyes is shown in Scheme 1. ProDOTs **1** were constructed by transesterification of commercially available 3,4-dimethoxythiophene with the corresponding 1,3-propanediols (Scheme S1, Supporting Information (SI)). They were transformed into aromatic boron derivatives **2b,c** and brominated aromatic aldehydes **4b,c**, respectively, which were cross-coupled under Suzuki conditions to give bisProDOT aldehydes **5** (aldehyde **5a** was prepared with a different method; see Scheme S2, SI).



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Subsequent bromination and coupling of **5** with an appropriate phenylborate afforded aldehydes **7**, which underwent Knoevenagel condensation with cyanoacetic acid to form the target dyes.

The optical and electrochemical properties of the four dyes are summarized in Table 1. In THF solutions (Figure 2a),

Table 1. Optical and Electrochemical Properties of the Four Dyes Shown in Figure 1

dye	$\lambda_{\text{abs}}^a/\text{nm}$	$\epsilon^a/\text{M}^{-1}\text{cm}^{-1}$	E_{ox}^b/V	$E_{\text{ox}}^{c}/\text{V}$
OR1	499	52800	1.03	−1.12
OR3	503	51700	0.97	−1.19
OR6	502	47500	0.96	−1.19
TT	472	42800	1.10	−1.23

^a The absorption spectra were measured in THF solutions (1×10^{-5} M). ^b First oxidation potentials (vs NHE) in CH_2Cl_2 internally calibrated with ferrocene (0.63 V vs NHE). ^c $E_{\text{ox}}^c = E_{\text{ox}} - E_{0-0}$. E_{0-0} values (zeroth–zeroth transition energies) were estimated from the intersections of normalized absorption and emission spectra in THF.

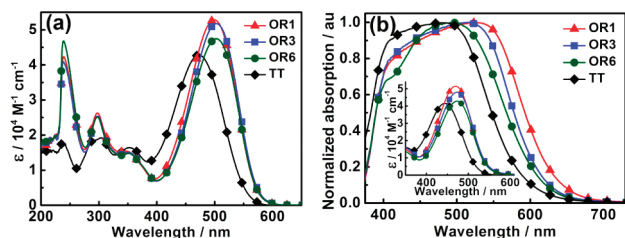


Figure 2. Absorption spectra of **OR** dyes and **TT** in THF (a) and on $4.6 \mu\text{m}$ TiO_2 films (b). The inset shows the absorption spectra of the deprotonated dyes in alkaline MeOH solutions.

they all exhibit strong absorption at 400–600 nm, which is attributed to intramolecular charge transitions (Figure S3, SI). Compared to **TT**, ca. 30 nm red-shifts in the absorption peaks together with increases in molar extinction coefficient (ϵ) are found for **OR** dyes. Theoretical calculation shows that replacement of bithiophene with bisProDOTs dramatically decreases the dihedral angle between the two thienyl rings from 13.3° to 0.4° while only slightly increases that between the phenyl and thienyl rings from 22.4° to 23.6° , thus resulting in a more planar conjugating system. The improved optical properties of **OR** dyes imply the merit of applying such electron-rich and highly planar linkers to sensitizer engineering. Upon adsorption onto TiO_2 , **TT** and **OR1**, which possess relatively planar structures, show significantly broadened and red-shifted absorption spectra compared with that measured in alkaline solutions (Figure

2b and inset), indicating the formation of *J*-aggregates.⁵ Interestingly, as the substituents at the ProDOT units become bulkier, i.e., from methyl (**OR1**) to *n*-propyl (**OR3**) to *n*-hexyl (**OR6**), the spectra become narrower and less red-shifted accordingly, reflecting systematically reduced intermolecular π – π interactions.

All four dyes exhibit two reversible oxidative waves in the cyclic voltammogram (Figure S1, SI). The first oxidation potentials of **OR** dyes (0.96–1.03 V vs NHE) are more negative than that of **TT** (1.10 V vs NHE) because of the presence of the electron-donating alkoxy substituents. They are all more positive than the Nernst potential of I^-/I_3^- redox couple (0.4 V vs NHE), ensuring regeneration of the oxidized dyes by I^- after electron injection. The excited state redox potentials of the four dyes (−1.23 to −1.12 V vs NHE) are sufficiently more negative than the fermi level of TiO_2 (−0.5 V vs NHE),^{1b} providing enough driving force for electron injection from the excited dyes to the conduction band of TiO_2 .

Table 2. DSC Performace Parameters of the Four Dyes Shown in Figure 1 with **N3** as a Reference.^a

dye	$J_{\text{SC}}/\text{mA cm}^{-2}$	V_{OC}/mV	fill factor	$\eta/\%$
OR1	9.54	756	0.62	4.45
OR3	10.33	797	0.64	5.30
OR6	9.45	793	0.67	5.04
TT	9.38	720	0.64	4.36
N3	9.32	745	0.67	4.65

^a The DSCs had an active area of $\sim 0.13 \text{ cm}^2$ and used an electrolyte composed of 0.6 M DMPImI, 0.1 M LiI, 0.05 M I_2 , and 0.5 M 4-*tert*-butylpyridine in acetonitrile.

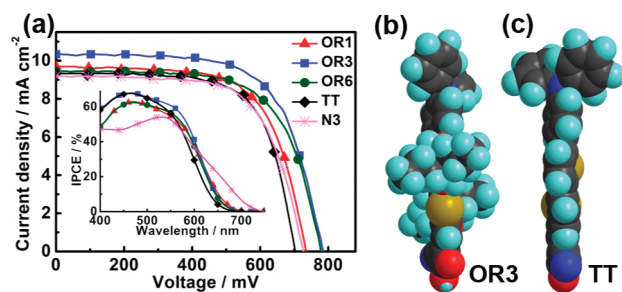


Figure 3. Photocurrent density–voltage (J – V) curves (a) and IPCE spectra (inset) of DSCs based on **OR** dyes, **TT**, and **N3**. Optimized 3D structures of **OR3** (b) and **TT** (c) are also shown.

Photovoltaic characteristics of the DSCs based on the four dyes as well as the standard **N3** dye under AM1.5G condition (100 mW cm^{-2}) are displayed in Table 2 and the J – V curves are plotted in Figure 3. To demonstrate the advantage of these highly absorptive sensitizers in thin-film devices, relatively thin TiO_2 films (ca. $4.6 \mu\text{m}$) were employed, which thickness

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is proposed to be optimal for future solid state DSCs.¹⁴ All three **OR** dyes exhibit higher short circuit current densities (J_{SC}) than **TT** owing to their enhanced incident photon-to-current conversion efficiency (IPCE) (Figure 3, inset) in the long-wavelength region. Although the adsorption amount of **TT** (17.2×10^{-8} mol cm⁻²) is ~ 1.5 -fold higher than that of **OR** dyes (7.1×10^{-8} mol cm⁻² for **OR1**,¹⁵ 7.8×10^{-8} mol cm⁻² for **OR3**, and 6.2×10^{-8} mol cm⁻² for **OR6**) and more intense light-absorption could be expected, the IPCE maximum of **TT** (68%) is just comparable to that of **OR** dyes (e.g., 68% for **OR3**), which is attributable to disadvantageous intermolecular energy transfer as a result of aggregate formation.⁵ Though all three **OR** dyes share similar broadness in their IPCE spectra, **OR1** and **OR6** display lower plateaus and thus lower J_{SC} values than **OR3** due to dye aggregation and poor dye uptake, respectively. The J_{SC} for **N3** is lower than the organic dyes because of insufficient light-harvesting in such thin film devices.

The open-circuit photovoltage (V_{OC}) values are in the sequence **TT** < **N3** $\approx$ **OR1** < **OR6** $\approx$ **OR3**. When the bithiophene bridge is displaced by bisProDOT-Me₂, the V_{OC} rises remarkably from 720 mV to 756 mV, a phenomenon that was also observed by other research groups where 3,4-dialkoxythiophenes were employed instead of thiophene.^{7g} For **OR3** incorporating a more branched ProDOT-Pr₂ unit, a significantly higher V_{OC} (797 mV) was achieved. Introduction of long alkyl chains to ProDOTs (**OR6**) does not lead to a further enhanced V_{OC} (793 mV) than **OR3**. The respectable increase of V_{OC} obtained by the delicate change in molecular structure (e.g., from **OR1** to **OR3**) is intriguing. To scrutinize the origin of the improvement in V_{OC} , measurement of the dark current–voltage characteristics is performed. From the dark J – V curves (Figure S4, SI), onsets of dark current of the five DSCs are derived as **TT** (639 mV) < **OR1** (660 mV) $\approx$ **N3** (664 mV) < **OR6** (706 mV) $\approx$ **OR3** (720 mV). This sequence is in good accordance with that of the V_{OC} values, indicating that the gradual increase

in V_{OC} from **TT** to **OR3** is closely associated with a gradually decreased tendency of the electron recombination in the TiO₂ with the I⁻/I₃⁻ redox couple in the electrolyte.^{9c} The slightly lower V_{OC} of **OR6** than **OR3** suggests that the presence of long alkyl chains itself is not responsible for the reduction of the interfacial charge recombination, which agrees with a previous study.¹⁶ The success of **OR** dyes might have originated from their 3D branched features, which effectively passivate the dyes by blocking the acceptor species from being attracted to the dye molecules (cf. Figure 3b,c). One exciting conclusion from our results is that as long as the scaffolds of organic dyes are rationally designed, very bulky structures are not indispensable for the achievement of high V_{OC} values. In fact, the four differently oriented alkyl chains in **OR6** lead to loose packing,¹⁷ leaving more voids between dye molecules, which might facilitate I₃⁻ to penetrate the chromophore layer and in turn aggravate charge recombination. The size of steric hindrance for passivating the dyes seems to require careful design in the future.

In summary, we have successfully multifunctionalized triphenylamine-based organic dyes through simple replacement of the thiophene linker with various ProDOT-R₂ building blocks. Besides their enhanced light-capturing abilities and controlled dye aggregation, the **OR** dyes have achieved respectably high V_{OC} values probably benefiting from their 3D branched structures. Our findings provide a novel strategy for multifunctionalization of organic dyes, as well as retardation of charge recombination in DSCs.

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Supporting Information Available: Experimental details, copies of ¹H and ¹³C NMR spectra of synthetic compounds, cyclic voltammogram, emission spectra, 3D structures, molecular orbitals, and dark J – V characteristics of the dyes. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(15) Although with a smaller molecular size, the slightly lower adsorption amount of **OR1** than that of **OR3** is understandable because the concentration of the optimized dye bath for **OR1** is about 70% lower than that for the other dyes in this study (see the SI).

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(17) For a graphical illustration of the relationship between the 3D structure of **OR** dyes and packing density, see Figure S5 in the SI.