ORGANIC
LETTERS

2010
Vol. 12, No. 6
1204−1207

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

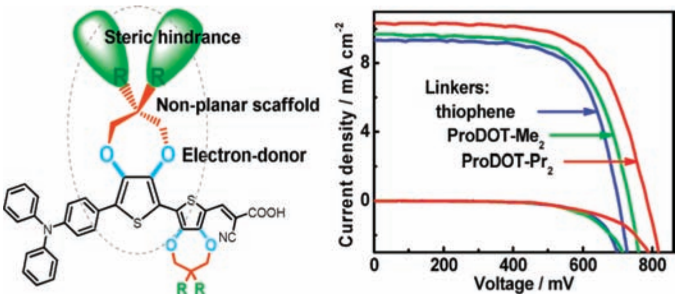
**Yanliang Liang, Bo Peng, Jing Liang, Zhanliang Tao, and Jun Chen***

*Institute of New Energy Material Chemistry and Key Laboratory of Advanced*
*Micro/Nanomaterials and Batteries/Cells (Ministry of Education), Chemistry College,*
*Nankai University, Tianjin 300071, People's Republic of China*

*chenabc@nankai.edu.cn*

**Received December 29, 2009**

## 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 ($\eta$).[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 $TiO_2$ surface that decreases electron injection,[5] and, especially, (3) relatively fast charge recombination of the injected electrons in the $TiO_2$ with the redox species in the electrolyte.[6] After making extensive studies on molecular modification based on the donor-$\pi$-acceptor configuration,[3] effective strategies for fine-tuning the energy levels of dyes to better-

---

(1) (a) O'Regan, B. C.; Grätzel, M. *Nature* **1991**, *353*, 737. (b) Grätzel, M. *Nature* **2001**, *414*, 338.

(2) Chiba, Y.; Islam, A.; Watanabe, Y.; Komiya, R.; Koide, N.; Han, L. Y. *Jpn. J. Appl. Phys., Part 2* **2006**, *45*, L638.

(3) Mishra, A.; Fischer, M. K. R.; Bäuerle, P. *Angew. Chem., Int. Ed.* **2009**, *48*, 2474.

(4) (a) Zhang, G. L.; Bala, H.; Cheng, Y. M.; Shi, D.; Lv, X. J.; Yu, Q. J.; Wang, P. *Chem. Commun.* **2009**, 2198. (b) Ito, S.; Miura, H.; Uchida, S.; Takata, M.; Sumioka, K.; Liska, P.; Comte, P.; Péchy, P.; Grätzel, M. *Chem. Commun.* **2008**, 5194.

(5) Wang, Z. S.; Hara, K.; Dan-Oh, Y.; Kasada, C.; Shinpo, A.; Suga, S.; Arakawa, H.; Sugihara, H. *J. Phys. Chem. B* **2005**, *109*, 3907.

10.1021/ol902973r

match the solar spectrum are now availble,[7] and aggregation of the adsorbed dyes could be prevented by introducing bulky nonplanar stuctures.[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 interation 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 $\pi$-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 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 structures[12] which will not only disfavor $\pi-\pi$ 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 performace. A bithiophene congener, coded **TT**,[10,13] is also synthesized for a comparison.

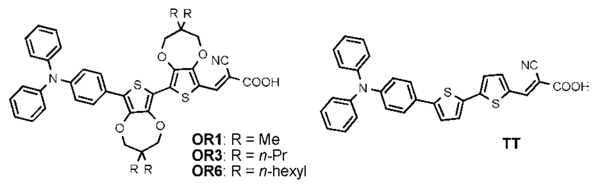
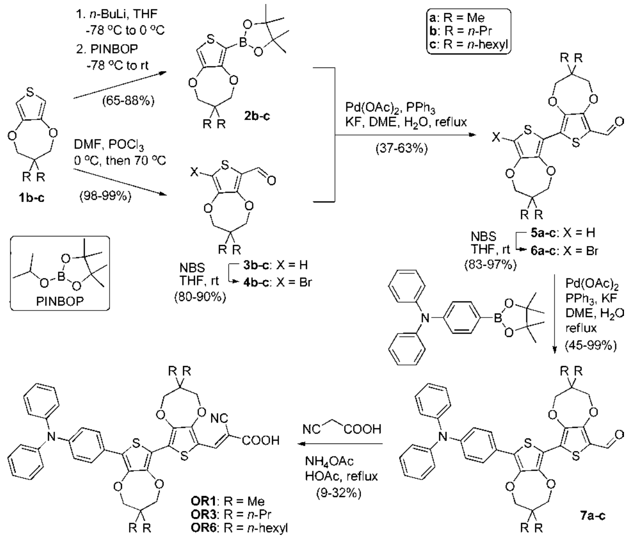


**Figure 1.** Molecular structures of sensitizers bearing bisProDOTs (**OR1**, **OR3**, and **OR6**) and bithiophene (**TT**).

The synthetic route of **OR** dyes is shown in Scheme 1. ProDOTs **1** were constructed by transetherification 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**, repectively, which were cross-coupled under Suzuki conditions to give bisProDOT aldehydes **5** (aldehyde **5a** was prepared with a different method; see Scheme S2, SI).

**Scheme 1.** Synthetic Route of **OR** Dyes



---

(6) (a) O'Regan, B. C.; López-Duarte, I.; Martínez-Díaz, M. V.; Forneli, A.; Albero, J.; Morandeira, A.; Palomares, E.; Torres, T.; Durrant, J. R. *J. Am. Chem. Soc.* **2008**, *130*, 2906. (b) Miyashita, M.; Sunahara, K.; Nishikawa, T.; Uemura, Y.; Koumura, N.; Hara, K.; Mori, A.; Abe, T.; Suzuki, E.; Mori, S. *J. Am. Chem. Soc.* **2008**, *130*, 17874.

(7) (a) Shibano, Y.; Umeyama, T.; Matano, Y.; Imahori, H. *Org. Lett.* **2007**, *9*, 1971. (b) Hagberg, D. P.; Yum, J.-H.; Lee, H.; De Angelis, F.; Marinado, T.; Karlsson, K. M.; Humphry-Baker, R.; Sun, L.; Hagfeldt, A.; Grätzel, M.; Nazeeruddin, M. K. *J. Am. Chem. Soc.* **2008**, *130*, 6259. (c) Ning, Z. J.; Zhang, Q.; Wu, W. J.; Pei, H. C.; Liu, B.; Tian, H. *J. Org. Chem.* **2008**, *73*, 3791. (d) Velusamy, M.; Justin Thomas, K. R.; Lin, J. T.; Hsu, Y. C.; Ho, K. C. *Org. Lett.* **2005**, *7*, 1899. (e) Erten-Ela, S.; Yilmaz, M. D.; Icli, B.; Dede, Y.; Icli, S.; Akkaya, E. U. *Org. Lett.* **2008**, *10*, 3299. (f) Lin, J. T.; Chen, P. C.; Yen, Y. S.; Hsu, Y. C.; Chou, H. H.; Yeh, M. C. P. *Org. Lett.* **2009**, *11*, 97. (g) Liu, W. H.; Wu, I. C.; Lai, C. H.; Chou, P. T.; Li, Y. T.; Chen, C. L.; Hsu, Y. Y.; Chi, Y. *Chem. Commun.* **2008**, 5152. (h) Qin, H.; Wenger, S.; Xu, M.; Gao, F.; Jing, X.; Wang, P.; Zakeeruddin, S. M.; Grätzel, M. *J. Am. Chem. Soc.* **2008**, *130*, 9202. (i) Wang, Z. S.; Cui, Y.; Hara, K.; Dan-Oh, Y.; Kasada, C.; Shinpo, A. *Adv. Mater.* **2007**, *19*, 1138. (j) Tian, H. N.; Yang, X. C.; Chen, R. K.; Hagfeldt, A.; Sun, L. C. *Energy Environ. Sci.* **2009**, *2*, 674. (k) Hao, Y.; Yang, X. C.; Cong, J. Y.; Tian, H. N.; Hagfeldt, A.; Sun, L. C. *Chem. Commun.* **2009**, 4031.

(8) (a) Kim, S.; Lee, J. K.; Kang, S. O.; Ko, J.; Yum, J. H.; Fantacci, S.; De Angelis, F.; Di Censo, D.; Nazeeruddin, M. K.; Grätzel, M. *J. Am. Chem. Soc.* **2006**, *128*, 16701. (b) Heredia, D.; Natera, J.; Gervaldo, M.; Otero, L.; Fungo, F.; Lin, C.-Y.; Wong, K.-T. *Org. Lett.* **2010**, *12*, 12.

(9) (a) Koumura, N.; Wang, Z. S.; Mori, S.; Miyashita, M.; Suzuki, E.; Hara, K. *J. Am. Chem. Soc.* **2006**, *128*, 14256. (b) Kim, S.; Kim, D.; Choi, H.; Kang, M. S.; Song, K.; Kang, S. O.; Ko, J. *Chem. Commun.* **2008**, 4951. (c) Ning, Z. J.; Zhang, Q.; Pei, H. C.; Luan, J. F.; Lu, C. G.; Cui, Y. P.; Tian, H. *J. Phys. Chem. C* **2009**, *113*, 10307.

(10) Justin Thomas, K. R.; Hsu, Y.-C.; Lin, J. T.; Lee, K.-M.; Ho, K.-C.; Lai, C.-H.; Cheng, Y.-M.; Chou, P.-T. *Chem. Mater.* **2008**, *20*, 1830.

(11) Marinado, T.; Nonomura, K.; Nissfolk, J.; Karlsson, K. M.; Hagberg, D. P.; Sun, L.; Mori, S.; Hagfeldt, A. *Langmuir* **2010**, *26*, 2592.

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

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

| dye | $\lambda_{abs}{}^{a}$/nm | $\varepsilon^{a}$/M$^{-1}$ cm$^{-1}$ | $E_{ox}{}^{b}$/V | $E_{ox*}{}^{c}$/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 ($1 \times 10^{-5}$ M). [b] First oxidation potentials (vs NHE) in $CH_2Cl_2$ internally calibrated with ferrocene (0.63 V vs NHE). [c] $E_{ox*} = E_{ox} - E_{0-0}$. $E_{0-0}$ values (zeroth−zeroth transition energies) were estimated from the intersections of normalized absorption and emission spectra in THF.

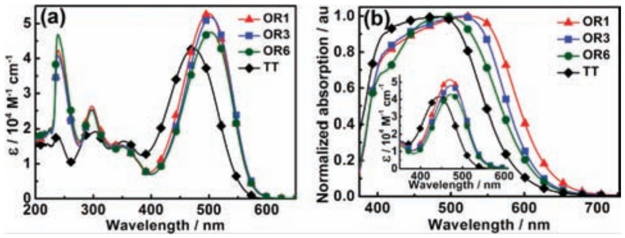


**Figure 2.** Absorption spectra of **OR** dyes and **TT** in THF (a) and on 4.6 $\mu$m $TiO_2$ films (b). The inset shows the absorption spectra of the deprotonated dyes in alkaline MeOH solutions.

The optical and electrochemical properties of the four dyes are summarized in Table 1. In THF solutions (Figure 2a), 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 ($\varepsilon$) are found for **OR** dyes. Theoritical 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 $\pi-\pi$ 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 | $J_{SC}$/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 ~0.13 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.

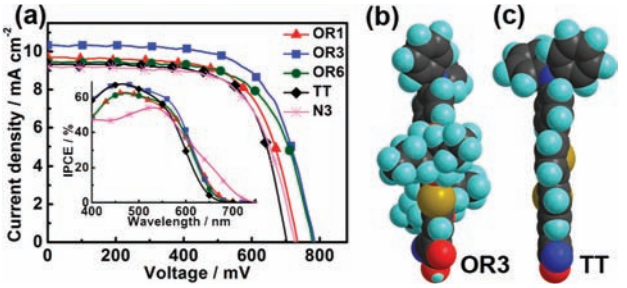


**Figure 3.** Photocurrent density−voltage (*J*−*V*) curves (a) and IPCE spectra (inset) of DSCs based on **OR** dyes, **TT**, and **N3**. Optimized 3D structures of **OR3** (b) and **TT** (c) are also shown.

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 $\mu$m) were employed, which thickness

---

(12) (a) Welsh, D. M.; Kumar, A.; Meijer, E. W.; Reynolds, J. R. *Adv. Mater.* **1999**, *11*, 1379. (b) Nielsen, C. B.; Bjørnholm, T. *Macromolecules* **2005**, *38*, 10379. (c) Hammond, S. R.; Clot, O.; Firestone, K. A.; Bale, D. H.; Lao, D.; Haller, M.; Phelan, G. D.; Carlson, B.; Jen, A. K. Y.; Reid, P. J.; Dalton, L. R. *Chem. Mater.* **2008**, *20*, 3425.

(13) Moon, S. J.; Yum, J. H.; Humphry-Baker, R.; Karlsson, K. M.; Hagberg, D. P.; Marinado, T.; Hagfeldt, A.; Sun, L. C.; Grätzel, M.; Nazeeruddin, M. K. *J. Phys. Chem. C* **2009**, *113*, 16816.

(14) Yum, J. H.; Chen, P.; Grätzel, M.; Nazeeruddin, M. K. *ChemSusChem* **2008**, *1*, 699.

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** ($17.2 \times 10^{-8}$ mol cm$^{-2}$) is ~1.5-fold higher than that of **OR** dyes ($7.1 \times 10^{-8}$ mol cm$^{-2}$ for **OR1**,[15] $7.8 \times 10^{-8}$ mol cm$^{-2}$ for **OR3**, and $6.2 \times 10^{-8}$ 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** ≈ **OR1** < **OR6** ≈ **OR3**. When the bithiophene bridge is displaced by bisProDOT-Me$_2$, 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-Pr$_2$ 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) ≈ **N3** (664 mV) < **OR6** (706 mV) ≈ **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 TiO$_2$ with the I$^-$/I$_3^-$ 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 I$_3^-$ 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-R$_2$ 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.

**Acknowledgment.** This work was supported by the Research Programs from National MOST (2005CB623607 and 2009AA05Z421). We thank Professor Jin Qu at Nankai University, China, for the help in compound characterization. We also acknowledge the computational support by NK-STARS provided by the Center of Theoretical and Computational Chemistry at Nankai University.

**Supporting Information Available:** Experimental details, copies of $^1$H and $^{13}$C 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.

OL902973R

---

(15) Alhough 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).

(16) Mori, S. N.; Kubo, W.; Kanzaki, T.; Masaki, N.; Wada, Y.; Yanagida, S. *J. Phys. Chem. C* **2007**, *111*, 3522.

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