Alkoxy-Substituted Triphenylamine based Chromophores for Dye-Sensitized Solar Cells

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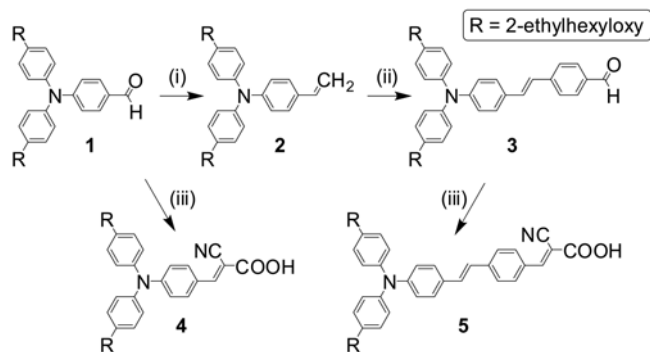[‡]*Department of Chemistry, Kunsan National University, Kunsan 573-701, Korea. *E-mail: dhkim@kunsan.ac.kr*

Dye-sensitized solar cells (DSSCs) have been classified as one of the most promising candidates for widespread solar energy utilization owing to their low cost and relatively high photon to electric current conversion efficiencies (η).[1] The performances of these devices depend mainly on the properties of the functionalized organic photosensitizers present. Among photosensitizers, metal-free organic dyes – whose efficiencies have been markedly improved over the years – have many advantages compared to ruthenium-based dyes. These advantages include their wide selection of compounds that can be easily modified to suit the absorption profile, be more environmentally-friendly and have lower production costs.[2]

One major flaw of organic dyes is the interaction of the iodine electrolyte with the TiO_2 semiconductor, resulting decreasing the efficiency of the cell. This can be prevented by introducing a bulky hydrophobic group at the periphery of the donor moieties.[3] In our research, we attached 2-ethylhexyloxy groups at the triphenylamine moieties in order to minimize the electrolyte-TiO_2 interaction that in turn enhances the electron donating capacity of the donor group and increases the highest occupied molecular orbital energy level for better charge injection.[4] The electronic and photovoltaic performances of two alkoxy substituted dyes with varying conjugation length (Scheme 1) are presented in this paper.

The synthesis of chromophores 4[5] and 5[6] were achieved from intermediates derived from Wittig,[7] Heck-Mizoroki coupling,[8] and Knoevenagel condensation[9] reactions. During the Knoevenagel reaction, it was observed that the purification of the product was hard to achieve when using catalytic amounts of piperidine. However, when stoichiometric amounts of piperidine were used, the product precipitated upon cooling and it could be easily filtered off.

The UV-visible spectra of the chromophores in ethanol solution produced a typical red-shift of about 25 nm after styrene was introduced to chromophore **5** (429 nm), compared to chromophore **4** (404 nm) as shown in Figure 1. The red-shift of the absorption spectra in chromophore **5** was due to the increased separation of the donor and acceptor groups brought about by the extension of the π-conjugated moiety. This resulted in better charge-transfer
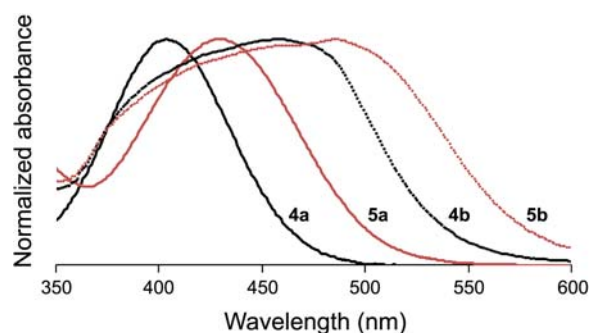
Figure 1. Absorption spectra of chromophores **4** (black) and **5** (red) in ethanol solution (**a**, solid line) and in TiO_2 film (**b**, dotted lines).
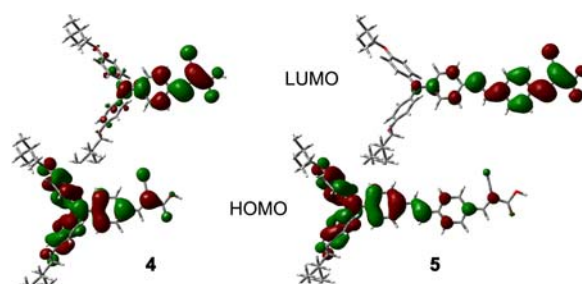
Scheme 1. Syntheses of chromophores **4** and **5**. (i) CH_3PPh_3Br, *n*-BuLi, THF, –20-25 °C, 3 H; (ii) 4-BrPhCHO, Na_2CO_3, 2,6-di-tert-butyl cresol, Pd(II), dimethylacetamide, 130 °C, 24 H; (iii) $CH_2(CN)CO_2H$, piperidine, CH_3CN, 90 °C, 24 H.

Figure 2. HOMO-LUMO isodensity plots of chromophores **4** and **5** calculated using B3LYP/6-31G(d) in a gas phase. Calculations were performed using Gaussian 03[10] software.

Table 1. Photovoltaic performance of chromophores **4** and **5**[a]

| Chromophores	J_{sc} (mA cm^{-2})	V_{oc} (mV)	*FF* (%)	η (%)
4	10.3	738	71.8	5.47
5	9.7	656	68.4	4.30

[a]Data obtained using a sealed cell under illumination of AM 1.5 (100 mW cm^{-2}) with a 0.159 cm^2 masking area using Oriel Sol3A class AAA solar simulator. The electrolyte consists of 0.7 M BMII, 0.05 M I$_2$, 0.25 M LiI, 0.5 M tBP in 1:1 acetonitrile/3-methoxyprionitrile. Fabrication of the DSSCs was based on the doctor blade technique[11]. TiO$_2$ electrodes were immersed in 0.5 mM ethanol solutions for 2 h.

characteristics than chromophore **4** based on the HOMO and LUMO isodensity plots shown in Figure 2.

Contrary to expectations, the photovoltaic performance of chromophore **5** is 21% lower than chromophore **4** as shown in Table 1. The lower efficiency observed in chromophore **5** is due to the increase in dye aggregation at the semiconductor surface. This can be seen by looking at the amount of absorbed dye, chromophore **5** (100 nmol cm^{-2}) was almost 3 times more absorbed compared to chromophore **4** (34 nmol cm^{-2}). The aggregation effect was further confirmed by the absorption spectra of the film (Fig. 1), where the chromophores produced a much broader absorption profile that indicates the presence of aggregation at the semiconductor surface. The full width at half maximum (FWHM) difference between chromophores **4** and **5** was 30 nm in film compared to only a 19 nm difference observed in solution. This indicates that chromophore **5** undergoes more aggregation at the semiconductor surface than chromophore **4**.

Figure 3 shows the representative external quantum efficiency (EQE) or incident photon to current conversion efficiency (IPCE) spectrum for a sandwich cell using chromophores **4** and **5**. Although chromophore **5** produced a much broader IPCE spectrum, chromophore **4** has a higher maximum IPCE value of 62% at 420 nm compared to chromophore **5**'s IPCE value of 56% at 440 nm. The differences in the IPCE values are consistent with the J_{sc} values presented in Table 1.

In conclusion, these results demonstrate that the extension of the π-conjugation typically produces a red-shift in the absorption spectra and increases charge transfer properties,
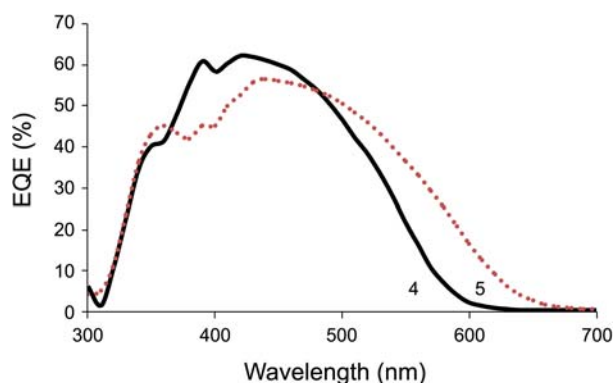
but can also result in serious dye aggregation due to the planarity of the styrene moiety. This information could help in the design of an organic dye that not only blocks the iodine-TiO$_2$ interaction but also attaches bulky groups or uses a coadsorbent that could prevent aggregation of the dye. Based on these results, we are currently designing highly efficient sensitizers for DSSCs.

References and Notes

1. (a) O'Regan, B.; Grätzel, M. *Nature* **1991**, *353*, 737. (b) Grätzel, M. *Nature* **2001**, *414*, 338. (c) Grätzel, M. *Journal of Photochemistry and Photobiology A: Chemistry* **2004**, *164*, 3. (d) Nazeeruddin, M. K.; Baranoff, E.; Grätzel, M. *Solar Energy* **2011**, *85*, 1172.
2. Mishra, A.; Fischer, M. K. R.; Bäuerle, P. *Angewandte Chemie International Edition* **2009**, *48*, 2474.
3. (a) Schmidt-Mende, L.; Kroeze, J. E.; Durrant, J. R.; Nazeeruddin, M. K.; Grätzel, M. *Nano Letters* **2005**, *5*, 1315. (b) Xu, M.; Li, R.; Pootrakulchote, N.; Shi, D.; Guo, J. *et al. The Journal of Physical Chemistry C* **2008**, *112*, 19770.
4. Hwang, S.; Lee, J. H.; Park, C.; Lee, H.; Kim, C. *et al. Chemical Communications* **2007**, 4887.
5. ^{1}H NMR (400 MHz, DMSO-d_6) δ 0.89 (12H, t, *J* = 7.3 Hz, -CH$_3$), 1.20-1.54 (16H, m, -CH$_2$-), 1.63-1.72 (2H, m, -CH-), 3.84 (4H, d, *J* = 5.8 Hz, -CH$_2$-O-), 6.68 (2H, d, *J* = 8.8 Hz, ArH), 6.95 (4H, d, *J* = 8.8 Hz, ArH), 7.11 (4H, d, *J* = 8.8 Hz, ArH), 7.71 (2H, d, *J* = 8.3(8) Hz, ArH), 7.88 (1H, bs, =CH-); ^{13}C NMR (CDCl$_3$, ppm) δ 10.81, 13.79, 22.49, 28.46, 29.94, 30.47, 48.44, 48.56, 54.59, 70.12, 78.51, 78.84, 79.05, 115.52, 116.65, 127.69, 130.99, 138.46, 156.39. MS (*m/z*) 597(29) (M+1)$^+$, 529 (100), 501 (73), 437 (14), 344 (10), 325 (23), 283 (16), 261 (30), 239 (17), 217 (35).
6. ^{1}H NMR (400 MHz, DMSO-d_6) δ 0.84 (12H, t, *J* = 7.3 Hz, -CH$_3$), 1.10-1.52 (16H, m, -CH$_2$-), 1.54-1.72 (2H, m, -CH-), 3.71 (4H, d, *J* = 5.5 Hz, -CH$_2$-O-), 4.80 (1H, bs), 6.70 (4H, d, *J* = 8.5 Hz, ArH), 6.75 (2H, d, *J* = 8.0 Hz, ArH), 6.90 (4H, d, *J* = 8.5 Hz, ArH), 7.13 (2H, d, *J* = 8.0 Hz, ArH), 7.24 (2H, bs), 7.64 (2H, bs), 8.03 (1H, bs, =CH-); ^{13}C NMR (CDCl$_3$, ppm) δ 11.12, 14.09, 23.04, 23.83, 29.09, 30.50, 39.44, 70.64, 115.23, 119.00, 119.76, 124.49, 126.29, 126.78, 127.62, 128.48, 130.65, 130.93, 131.07, 138.46, 140.13, 141.55, 148.84, 151.87, 155.89, 175.88. MS (*m/z*) 698 (29) (M$^+$), 575 (25), 529 (24), 501 (6), 413 (12), 367 (21), 287 (19), 261 (9), 240 (17), 183 (100), 129 (51).
7. Wittig, G.; Schöllkopf, U. *Chemische Berichte* **1954**, *87*, 1318.
8. (a) Wang, A.-E.; Xie, J.-H.; Wang, L.-X.; Zhou, Q.-L. *Tetrahedron* **2005**, *61*, 259. (b) Kantchev, E. A. B.; Peh, G.-R.; Zhang, C.; Ying, J. Y. *Organic Letters* **2008**, *10*, 3949.
9. (a) Jessup, P. J.; Petty, C. B.; Roos, J.; Overman, L. E. *Organic Syntheses Collective Volume* **1988**, *6*, 95. (b) Jones, G. *Organic Reactions* **1967**, *15*, 204.
10. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A. *et al. Gaussian 03*, Revision D.01; Gaussian, Inc., Wallingford CT: 2004.
11. Paek, S.; Choi, H.; Kim, C.; Cho, N.; So, S. *et al. Chemical Communications* **2011**, *47*, 2874.

Figure 3. External quantum efficiencies (EQE) of DSSCs based alkoxy-substituted triphenylamine dyes taken using Oriel IQE-200 quantum efficiency measurement with a white bias light.