Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Molecular Design and Photovoltaic Performances of Organic Dyes Containing Triphenylamine for Dye-Sensitized Solar Cell

Mi Ran Jung [a], Hyo Jeong Jo [b], Hyun Sik Yang [a], Hyojeong Kim [b], Jin Kyu Kang [b], Dae Hwan Kim [b], Kwang-Soon Ahn [a] & Jae Hong Kim [a]

[a] School of Display and Chemical Engineering, Yeungnam University, Gyeongsan, Gyeongbuk, Republic of Korea

[b] Senior Research Engineer Division of Nano & Bio Technology, Daegu-Gyeonbuk Institute of Science & Technology (DGIST), Republic of Korea

Version of record first published: 16 May 2011

To cite this article: Mi Ran Jung, Hyo Jeong Jo, Hyun Sik Yang, Hyojeong Kim, Jin Kyu Kang, Dae Hwan Kim, Kwang-Soon Ahn & Jae Hong Kim (2011): Molecular Design and Photovoltaic Performances of Organic Dyes Containing Triphenylamine for Dye-Sensitized Solar Cell, Molecular Crystals and Liquid Crystals, 538:1, 278-284

To link to this article: http://dx.doi.org/10.1080/15421406.2011.564102

Mol. Cryst. Liq. Cryst., Vol. 538: pp. 278–284, 2011

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2011.564102

Molecular Design and Photovoltaic Performances of Organic Dyes Containing Triphenylamine for Dye-Sensitized Solar Cell

MI RAN JUNG,[1] HYO JEONG JO,[2] HYUN SIK YANG,[1] HYOJEONG KIM,[2] JIN KYU KANG,[2] DAE HWAN KIM,[2] KWANG-SOON AHN,[1] AND JAE HONG KIM[1]

[1]School of Display and Chemical Engineering, Yeungnam University, Gyeongsan, Gyeongbuk, Republic of Korea
[2]Senior Research Engineer Division of Nano & Bio Technology, Daegu-Gyeonbuk Institute of Science & Technology (DGIST), Republic of Korea

Organic dyes containing multi-acceptors/anchors in a chromophore were synthesized for use in a dye-sensitized solar cell. The photovoltaic properties of organic dyes composed of different acceptor in their chromophores were measured to identify the effects on the DSSC performance. The organic dye, ***4*** *containing multi-cyanoacrylic acid as the electron acceptor showed a power conversion efficiency of 4.7% under AM 1.5 illumination (100 mW cm^{-2}) in an photo active area of 0.24 cm^2, short circuit current density of 12.9 mA cm^{-2}, open circuit photo voltage of 0.62 V and a fill-factor of 60%. The retarded recombination kinetics from TiO_2 electrode to electrolyte enhanced the electron life time of organic dye,* ***4*** *in the photo-anode in DSSC that was well confirmed with the impedance analysis.*

Keywords Dye-sensitized solar cells; organic photosensitizers; photovoltaic performances; triphenylamine chromophores

Introduction

Since the photons were converted into an electric current by charge injection from excited dye molecules into a chlorophyll sensitized zinc oxide (ZnO) electrode [1], the introduction of nanoporous TiO_2 electrodes enhanced the light harvesting efficiency dramatically about 7% [2]. This triggered a boom in research activities and recently, the photon energy-to-electricity conversion efficiency of the

J. H. Kim and J. K. Kang contributed equally to this work as the corresponding authors.
Address correspondence to Prof. Jae Hong Kim, School of Display and Chemical Engineering, Yeungham University, 214-1 Dae-dong, Gyeongsan, Gyeonbuk 712-749, S. Korea (ROK). Tel.: (+82)53-810-2521; Fax: (+82)53-810-4631; E-mail: jaehkim@ynu.ac.kr or Jin Kyu Kang, Senior Research Engineer Division of Nano & Bio Technology, Daegu-Gyeonbuk Institute of Science & Technology (DGIST), Republic of Korea. Tel.: (+82)53-430-8688; Fax: (+82)53-430-8475; E-mail: apollon@dgist.ac.kr

dye-sensitized solar cells (DSSCs) have achieved above 11.2% [3]. Moreover, DSSCs have attracted much attention due to their easy manufacturing process [4–5].

The mechanism of DSSC is based on the injection of an electron from photo-excited dyes (Ru-complexes such as N3 and N719) into the conduction band of nanocrystalline TiO_2. Thus, the electronic structures, HOMO, LUMO, and HOMO-LUMO gap, of dye molecule in DSSC play an important role due to the electron transfer by photo-excitation and redox potential [6–7].

On the other hand, organic dyes which have many advantages such as large absorption coefficients, customized molecular design for desired photophysical and photochemical properties, inexpensiveness and environment-friendliness, are suitable as photosensitizers for DSSC. But the efficiency of DSSC based on organic dye is much lower than that of Ru-dye which may limit the practical use of organic dyes in DSSCs. Recently, the performance of DSSC based on organic dye has been remarkably improved by several groups [8–11].

We have developed novel organic dyes which have triphenylamine moieties as an electron donor with various acceptors in their charge-transfer chromophoric system for application in DSSCs. In the previous article, we reported that organic dyes containing multi-electron acceptors are promising photosensitizers for DSSCs compared to dyes with a single-electron acceptor, due to the increased electron extraction paths from electron donor and the higher molar extinction coefficients [10(a)]. In this article, we designed and synthesized triphenylamine derivatives containing multi-acceptors/anchors in a molecule for DSSCs. The photovoltaic performance and the incident photon-to-current (IPCE) of DSSC composed of organic chromophores were measured and evaluated by comparison with that of pristine ruthenium dye.

Experimental

Materials and Synthesis

All commercially available starting materials and solvents were purchased from Aldrich, TCI, and ACROS Co., and used without further purification unless otherwise stated. HPLC grade toluene and tetrahydrofuran (THF) were purchased from Samchun chemical and distilled from CaH_2 immediately before use. The synthetic procedures were followed as the known method [11]. Structural analysis was conducted with ^{1}H NMR spectra were recorded on Bruker Advance NMR 300 Hz spectrometer using $CDCl_3$ and DMSO-d_6. The redox properties of three dyes were examined using cyclic voltammetry (Model:CV-BAS-Epsilon). The electrolyte solution employed was 0.10 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) in freshly dried acetonitrile. The Ag/AgCl and Pt wire (0.5 mm in diameter) electrodes were utilized as reference and counter electrodes, respectively. The scan rate was at 100 mV/s.

(2) [11]. The product was obtained as the light yellow powder. Yield: 1.2 g (59%), ^{1}H NMR (300 MHz, DMSO-d_6): δ 7.339 (d, $J = 8.7$ Hz, 6H), 7.195 (d, $J = 5.1$ Hz, 3H), 7.152 (d, $J = 5.1$ Hz, 3H), 6.804–6.860 (m, 9H).

(3) [11]. The product was obtained as orange powder. Yield: 0.86 g (49%), ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.889 (s, 3H), 7.754 (d, $J = 5.4$ Hz, 3H), 7.624 (d, $J = 8.4$ Hz, 6H), 7.373 (d, $J = 5.4$ Hz, 3H), 7.103 (d, $J = 8.4$ Hz, 6H).

TPA3TCN (4) *[11].* The product was obtained as dark red powder. Yield: 0.5 g (72.4%), ^{1}H NMR (300 MHz, DMSO-d_6): δ 8.388 (s, 3H), 7.945 (d, $J = 3.9$ Hz, 3H), 7.762 (d, $J = 2.7$ Hz, 6H), 7.661 (d, $J = 3.9$ Hz, 3H), 7.186 (d, $J = 2.7$ Hz, 6H).

TPA3TRO (5). The organic dye **5** was synthesized using the same procedure for **4**. The product was obtained as dark red powder. Yield: 0.5 g (72.4%), ^{1}H NMR (300 MHz, DMSO-d_6): δ 8.12 (s, 3H), 7.82–7.80 (m, 9H), 7.73 (d, $J = 3.9$ Hz, 3H), 7.18 (d, $J = 8.7$ Hz, 6H).

TPA3TOX (6). The organic dye **6** was synthesized using the same procedure for **4**. The product was obtained as dark red powder. Yield : 0.5 g (72.4%), ^{1}H NMR (300 MHz, DMSO-d_6): δ 8.84 (s, 3H), 8.27 (d, $J = 3.6$ Hz, 3H), 7.94–7.88 (m, 12H), 7.84 (d, $J = 3.9$ Hz, 3H), 7.50 (t, $J = 8$ Hz, 6H), 7.28 (t, $J = 8.1$ Hz, 3H), 7.25 (d, $J = 8.1$ Hz, 6H).

Assembly and Characterization of DSSCs

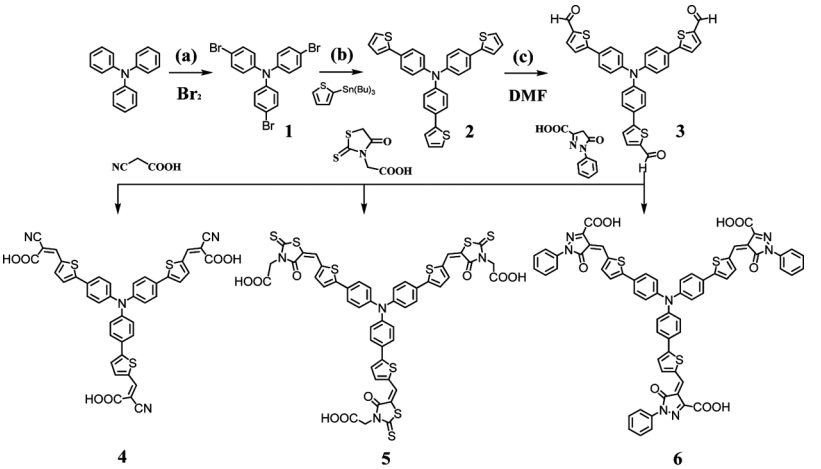
The TiO_2 paste was coated on the pre-cleaned FTO (TEC8, Pilkington, 8 Ω/cm^2, Thickness of 2.3 mm) coated glass substrate using doctor-blade, and sintered at 500°C for 30 min. The scattering TiO_2 paste was re-coated over the sintered layer using ca. 250 nm size of TiO_2 particle, and then sintered again at 500°C for 30 min. The prepared TiO_2 film was dipped in 0.04 M of $TiCl_4$ aqueous solution at 70°C for 30 min. For dye adsorption, the annealed TiO_2 electrodes were immersed in dye solution (0.5 mM of dye in DMF; TPA series, N3/N719) at 50°C for 3 hours. The dye-adsorbed TiO_2 electrode and Pt counter electrode were assembled using 60 μm-thick Surlyn (Dupont 1702) as a bonding agent. A liquid electrolyte was introduced through a pre-punctured hole on the counter electrode.

Results and Discussion

Usually, organic dyes have the push–pull chromophoric system in a molecule. Upon light irradiation, intramolecular charge transfer from the electron donor to the acceptor is induced and a subsequent electron transfer to TiO_2 via the anchoring group takes place. We designed and synthesized a series of triphenylamine derivatives containing multi-acceptors/anchors in a molecule with moderate yields as shown in experimental section and Scheme 1. The resultant multi-anchored organic dyes **4, 5**, and **6** contain different acceptors in their chromophores, respectively.

Figure 1 shows the UV-Vis absorption spectra of the organic dyes in DMF solution (A) and on the TiO_2 film state (B). The maximum absorption wavelength (λ_{max}) corresponding to the π-π^* transitions of dye **4** appeared around 430 nm with relatively high molar extinction coefficient (ε_{max}) in 6.8×10^4 M^{-1} cm^{-1}, as shown in Figure 1. The small red-shift and blue-shift in absorption peak of **TPA3TOX** (**6**) and **TPA3TCN** (**4**) in the TiO_2 film state may be caused by the formation of aggregates of organic dyes on the TiO_2 surface, respectively [12].

We found that organic dyes containing multi-anchors/acceptors were not desorbed from the TiO_2 surface, even in a strong NaOH basic aqueous solution, indicating that the multi-anchoring groups of the dyes may strengthen the adsorption properties of the dye onto the TiO_2 surface. However, we can say that adsorption



Scheme 1. Synthesis of organic dyes containing multi-anchors/acceptors.

ability of dye **4** on the TiO_2 surface was higher than those of others in same condition, which could affect the photovoltaic properties in DSSCs.

The photovoltaic properties of the DSSCs based on **TPA3TCN** (**4**), **TPA3TRO** (**5**), and **TPA3TOX** (**6**) were measured and compared to those of N3 dye, as shown in Table 1 and Figure 2. The highest efficiency of the 4.7% value was attained using organic dye (**4**) containing cyanoacrylic acid as the electron acceptor which may be due to the high molar extinction coefficient to compare with those of other organic dyes. It was also known that the cyanoacrylic acid moiety of the organic dye exhibited a strong electron-withdrawing capability and abundant electronic coupling at the interface of the TiO_2 particles, leading to efficient electron injection from the LUMO level of the dye to the conduction band of the TiO_2 [13]. The DSSC with the **TPA3TCN** (**4**) exhibited a slightly higher open-circuit voltage (Voc) than the DSSCs with **TPA3TRO** (**5**) and **TPA3TOX** (**6**) which might be due to the higher dye adsorption properties of **TPA3TCN** (**4**) in DSSC.

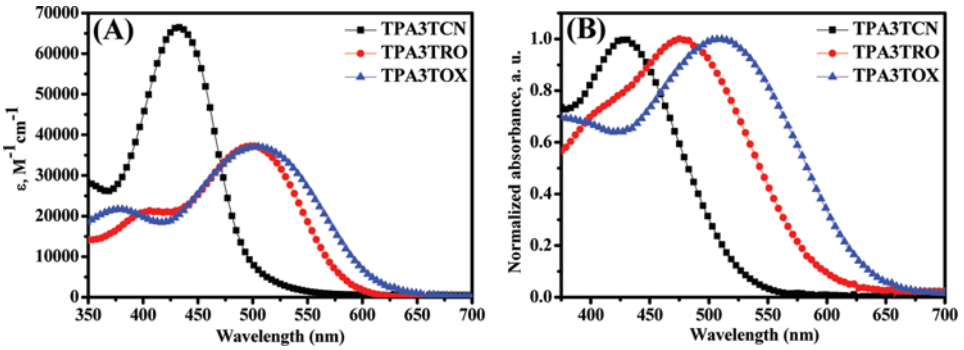


Figure 1. (A) Absorption spectra of the organic dyes in the DMF solution. (B) Normalized absorption spectra of the organic dyes that were adsorbed on to the TiO_2 films.

Table 1. Photovoltaic Performance of DSSCs composed of N3/Organic dye and the electron transport properties in their photoanodes determined by impedance analysis. (Cell areas: 0.24 cm^2.)

Dyes	J_{sc}/ mA cm^{-2}	V_{oc}/ V	FF	η/%	R1 (Ω)[a]	R2 (Ω)[b]	C1	R3 (Ω)[c]	C2	τ^d (ms)
N3	17.6	0.68	0.59	7.4	17.28	5.09	0.000023	14.2	0.00145	27.57
TPA3TCN	12.9	0.62	0.60	4.7	19.39	6.25	0.000010	12.8	0.00068	13.89
TPA3TRO	5.2	0.54	0.67	1.9	15.83	7.41	0.000014	26.1	0.00008	4.00
TPA3TOX	3.2	0.53	0.66	1.1	28.40	10.68	0.000013	40.0	0.00006	1.92

The impedance spectra were observed in open circuit voltage condition under illumination (AM 1.5, 100 mW/cm^2).

[a]R1 is FTO Interface resistance.

[b]R2 is due to the resistance at the interface between the counter electrode and the electrolyte.

[c]R3 is possibly originated from the backward charge transfer from TiO_2 to the electrolyte and the electron conduction in porous TiO_2 film.

[d]τ is life time of an electron in DSSC.

Figure 2 also shows the incident photon-to-current efficiency (IPCE) spectra of the DSSCs containing different organic dyes which revealed that the integrated IPCE values were consistent with the J_{sc} values of **TPA3TCN** (**4**), **TPA3TRO** (**5**), and **TPA3TOX** (**6**) shown in Table 1.

The solar response of the device using **TPA3TCN** (**4**) (300–650 nm), and its quantum efficiency was high, i.e., approximately 60% at 500 nm ; however, the quantum efficiency of the device with **TPA3TRO** (**5**) and **TPA3TOX** (**6**) were only 20% and 10% at 500 nm.

We also observed and evaluated the performance of DSSCs containing organic dyes by measuring their impedance spectra (IS) under light illumination condition as shown in Figure 3 and the results are summarized in Table 1. There are two well defined semi-circles in high frequency region and middle frequency region.

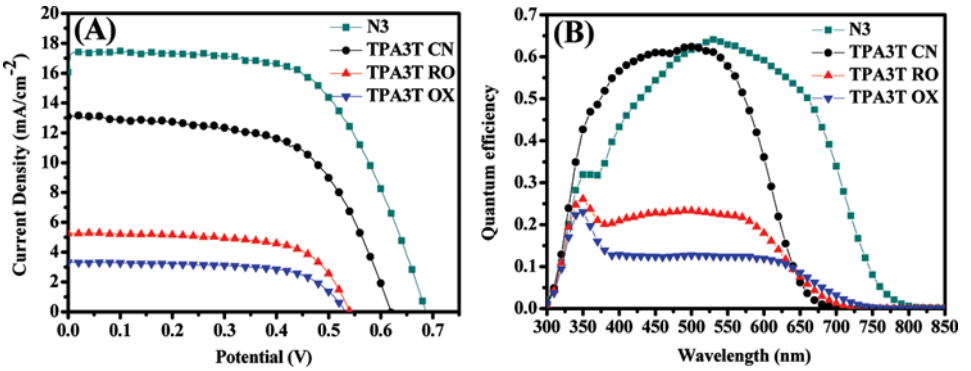


Figure 2. (A) Current density-voltage characteristics for DSSCs containing organic dyes under illumination of simulated solar light (AM 1.5, 100 mW/cm^2). (B) IPCE curves for DSSCs based on organic dyes. *Sample condition : Blocking layer, TiO_2 paste : B32, Organic Dye 0.5 mM – PMII(0.7 M) + LiI (0.2 M) + I_2 (0.05 M) + TBP (0.5 M) in ACN/VN = 85:15 – Pt electrode solution (7 mM), 60 μm surlyn, Dr.blade(2 T).

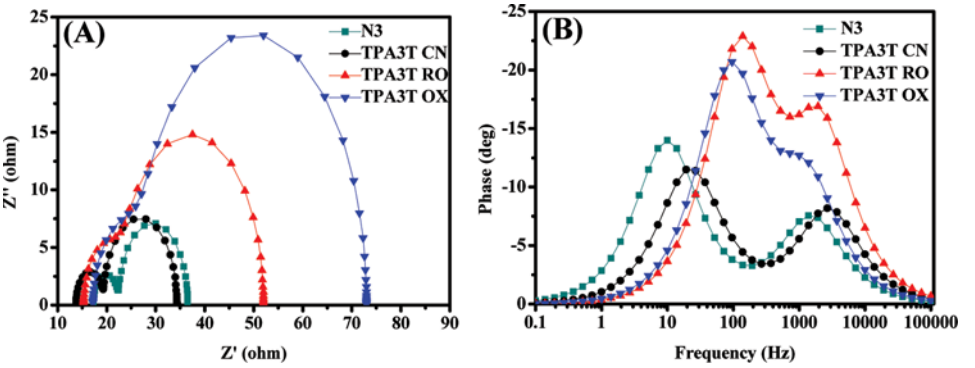


Figure 3. (A) Measured impedance spectrum of DSSC at forward bias applied condition under dark. Fitted curve calculated using circuit shown in the inset. (B) Displays of Bode-phase for DSSC cell.

The R3 value is originated from the backward charge transfer from TiO_2 to the electrolyte and the electron conduction in porous TiO_2 film. The Bode-phase spectra for DSSCs are also shown in Figure 3 (B) to calculate the electron life time in DSSC containing different organic dyes respectively, and are also compared in Table 1.

The observed electron life time of **TPA3TCN** (**4**) shows the longest value to compare with those of other dyes which can explain the highest V_{oc} value of **TPA3TCN** (**4**) in DSSC. The shorter electron life time of DSSC composed of **TPA3TRO** (**5**) and **TPA3TOX** (**6**) could be explained with the lower dye loading contents on TiO_2 surface to compare with that of **4**. Thus, the recombination kinetics from TiO_2 surface to the electrolyte in DSSC containing **TPA3TCN** (**4**) was retarded to compare with other dyes in DSSC.

Conclusions

We prepared metal-free organic dyes composed of multi-acceptors/anchors chromophores containing triphenylamine as an electron donor with various multi-electron acceptors in their intramolecular charge-transfer chromophoric system. The judicious choice/design of the donor and acceptors permits the relatively high power conversion efficiency of 4.7% in organic dye (**4**) containing cyanoacrylic acid as the electron acceptor which was confirmed with the photovoltaic- and IPCE-measurement, and impedance analysis, precisely.

Acknowledgment

This research was supported by a grant from the Fundamental R&D Program for Core Technology of Materials (10037239) funded by the Ministry of Knowledge Economy, Republic of Korea.

References

[1] Tributsch, H. (1971). *Photochem. Photobiol.*, *14*, 95.
[2] O'Regan, B., & Gratzel, M. (1991). *Nature*, *353*, 737.

[3] Nazeeruddin, M. K., De Angelis, F., Fantacci, S., Selloni, A., Viscardi, G., Liska, P., Ito, S., Takeru, B., & Gratzel, M. (2005). *J. Am. chem. Soc.*, *127*, 16835.
[4] Baxter, J. B., & Aydil, E. S. (2005). *Appl. Phys. Lett.*, *86*, 053114.
[5] Nazeeruddin, M. K., Kay, A., Rodicio, I., Humphry-Baker, R., Mueller, E., Liska, P., Valchopoulos, N., & Gratzel, M. (1993). *J. Am. Chem. Soc.*, *115*, 6382.
[6] Hagfeldt, A., & Gratzel, M. (2000). *Acc. Chem. Res.*, *33*, 269.
[7] Hara, K., Sato, T., Katoh, R., Furube, A., Yoshihara, T., Murai, M., Kurashige, M., Ito, S., Shinpo, A., Suga, S., & Arakawa, H. *Adv. Funct. Mater.*, *15*(2), 246.
[8] (a) Thomas, K. R. J., Lin, J. T., Hsu, Y.-C., & Ho, K.-C. (2005). *Chem. Comm.*, 4098; (b) Velusamy, M., Thomas, K. R. J., Lin, J. T., Hsu, Y.-C., & Ho, K.-C. (2005). *Org. Lett.*, *7*, 1899.
[9] (a) Hwang, S., Lee, J. H., Park, C., Lee, H., Kim, C., Park, C., Lee, M.-H., Lee, W., Park, J., Kim, K., Park, N.-G., & Kim, C. (2007). *Chem. Comm.*, 4887; (b) Qin, H., Wenger, S., Xu, M., Gao, F., Jing, X., Wang, P., Zakeeruddin, S. M., & Gartzel, M. (2008). *J. Amer. Chem. Soc.*, *130*, 9202.
[10] (a) Park, S. S., Won, Y. S., Choi, Y. C., & Kim, J. H. (2009). *Energy & Fuels*, *23*, 3732; (b) Tian, H., Yang, X., Cong, J., Chen, R., Liu, J., Hao, Y., Hagfeldt, A., & Sun, L. (2009). *Chem. Comm.*, 6288.
[11] Yang, Y. S., Ryu, J. H., Kim, K. K., Ahn, K.-S., & Kim, J. H. (2010). *Dyes and Pigments*, submitted.
[12] William, F. M., Patti, E. B., John, C. R., Silvia, B. C., Lee, G. P., & David, G. W. (1984). *J. Am. Chem. Soc.*, *106*, 5659.
[13] Won, Y. S., Yang, Y. S., Kim, J. H., Ryu, J.-H., Kim, K. K., & Park, S. S. (2010). *Energy & Fuels*, *24*, 3676–3681.