ORIGINAL PAPER



Synthesis of new dyes containing double tetrazole groups for sensitization of TiO₂ nanoparticles in dye-sensitized solar cells

Zahra Jafari Chermahini¹ · Alireza Najafi Chermahini¹ · Hossein A. Dabbagh¹ · Behzad Rezaei¹ · Neda Irannejad¹

Received: 24 December 2016 / Accepted: 13 March 2017 © Iranian Chemical Society 2017

Abstract Di(1*H*-tetrazol-5-yl)methane is employed as a new electron acceptor group in the synthesis of two metalfree organic dyes containing triphenylamine donor group. Dye-sensitized nanocrystalline TiO₂ solar cell (DSSC) applying these novel dyes is constructed for consideration of their photovoltaic properties. The electronic properties of the dyes are also considered with the aid of theoretical calculations. The DSSC constructed from 4-(2,2-di(1H-tetrazol-5-yl)vinyl)-N,N-diphenylaniline (T1) shows a shortcircuit photocurrent density of 13.38 mA cm⁻², an open circuit voltage of 578 mV, and a fill factor of 0.54, with a resulted solar energy-to-electricity conversion efficiency of 4.18% under simulated 1 sun irradiation (100 mW cm⁻²). This result reveals that the dye with the di(1H-tetrazol-5-yl)methane anchoring group injects more electrons to the conduction band of TiO₂ in comparison with its analogs with single tetrazole ring in their anchoring group. It is found that in spite of a red-shift of the absorption spectrum resulted from the lengthening of the molecule, the dye with two di(1H-tetrazol-5-yl)methane groups gives lower performance than the dye with a single electron acceptor.

Keywords DSSC · Dye · Electron acceptor · Sensitization · Tetrazole

Electronic supplementary material The online version of this article (doi:10.1007/s13738-017-1096-y) contains supplementary material, which is available to authorized users.

Alireza Najafi Chermahini anajafi@cc.iut.ac.ir; najafy@gmail.com

Introduction

There is wide interest in dye-sensitized solar cells (DSSCs) in the field of conversion of sunlight to electricity [1]. The solar cell efficiency is mainly affected by the properties of the sensitizer (dve) [2]. High molar absorption coefficient. constitution diversity, and easy synthesis method are the reasons for development of metal-free organic sensitizers for DSSCs in comparison with the ruthenium complexes that are the best dyes for DSSCs [3]. The electron donor, linker, and electron acceptor groups are the parts of a usual organic photosensitizer [4]. The electrons from the dye oxidation should inject to the semiconductor through channels being the acceptor groups that connect the dyes to the semiconductor surface [5]. The most universally applied acceptor group for the dyes is carboxyl group (-COOH) [6]. However, many alternative anchoring groups such as the nitro group [7], 2-(1,1-dicyanomethylene)rhodanine [8], pyridine [9], aldehyde [10], benzothienopyridine [11], and 8-hydroxyquinoline [12] have been considered. Recently, tetrazole ring has been used as a novel anchoring group in organic photosensitizers [13]. There are similar physical properties between tetrazoles and carboxylic acids that cause tetrazoles to act as the carboxylic acid isostere in active molecules in biology, and further they are resistant to many metabolic degradation conditions [14]. In addition to be useful in different scientific aspects, involving explosives, devices for information recording, and photography, tetrazoles are polydentate ligands in relation to the metals in coordination chemistry [15–17]. Recently, we have reported the synthesis of photosensitizers with anchoring groups based on the tetrazole ring [18]. The ethyl 2-(1H-tetrazol-5-yl) acetate, (2H-tetrazol-5-yl) acrylonitrile, and 1H-tetrazole-5-acetic acid compounds were

¹ Department of Chemistry, Isfahan University of Technology, Isfahan 84154-83111, Iran

applied as anchoring group in the reported dyes. These anchoring groups include single tetrazole ring. Herein, we discuss the synthesis and application of new sensitizers with double tetrazole in their anchoring group (Fig. 1).

Experimental

General information

All reactions were preceded using commercially available solvents and chemical reagents without extra purification. Triphenylamine was prepared from Merck, and other used chemical reagents and solvents were obtained from Sigma-Aldrich. A 5973 Network Mass Selective Detector [Agilent Technology (HP)] apparatus and a Bruker 400 MHz spectrometers were applied for recording the mass analyses and ¹H and ¹³C nuclear magnetic resonance (NMR) spectra, respectively. Fourier transform infrared (FTIR) absorption spectral data of the dyes using KBr pellets were taken on an FTIR Jasco 680 plus spectrometer. The absorption spectra of two dyes in solution and adsorbed on TiO₂ films were obtained by using a Jasco-570 UV/Vis spectrophotometer.

A SAMA 500 electroanalyser system, SAMA Research Center, Iran, with Pt working and counter electrodes, and an Ag/AgCl reference electrode was used for cyclic voltammetry experiments. The 0.1 M Bu_4NPF_6 and ferrocene as the salt support and the internal standard, respectively, in a scan rate of 0.1 V/s at room temperature were also applied, respectively. The precursors **1**, **2**, and di(1*H*-tetrazol-5-yl) methane were synthesized according to the methods mentioned in the studies [19–21] (see Scheme 1).

Fabrication of dye-sensitized solar cells

A 40-mM aqueous TiCl₄ solution was used for coating fluorine-doped tin oxide (FTO) glass substrates with a blocking layer at 70 °C for 30 min. Then, the substrates were applied for fabrication of anode films using TiO₂ pastes (Sharif Solar [22]) and doctor blade method [23, 24]. The TiO₂ pastes were deposited on the substrates as two layers. The first layer was composed of 20-nm TiO₂ particle with thickness of 7 μ m, and the second layer was included of 400-nm TiO₂ particle with a thickness of 5 μ m. These films were heated at 375 °C (10 min), 450 °C (15 min), and 500 °C (30 min). The films were again



Scheme 1 Synthesis process of the dyes with double tetrazole anchoring group: *i* POCl₃, DMF, 95–100 °C, 20 h, *ii* Di(1*H*-tetrazol-5-yl)methane, NH(Et)₂, CH₃CN, reflux, 24 h, *iii* POCl₃, DMF, 80 °C, 48 h, *iv* Di(1*H*-tetrazol-5-yl)methane, NH(Et)₂, CH₃CN, reflux, 48 h

soaked in the 40-mM aqueous TiCl₄ solution at 70 °C for 30 min and rinsed with water and heated at 500 °C for another 30 min. The obtained electrodes were dipped into dye solutions (0.4 mM in C₂H₅OH) for 20 h in the room temperature and then washed. For preparing the cathode, the FTO glasses were coated with Pt. The obtained cathodes were put on the anodes, and the iodine-based electrolyte was introduced into the space between two electrodes. Two cells were constructed with the active area of 0.25 cm². The spectra of incident photon-to-current conversion efficiency (IPCE) were taken on an IPCE instrument (Sharif Solar, IPCE-015 [25]) with a 100-W halogen lamp. Photocurrent-voltage data were gained with the aid of a Bio-Logic SAS model SP-300 apparatus without mask. The irradiance of 100 mW/cm² was provided by an AM 1.5G solar simulator (Sharif Solar, SIM-1000 [25]). Electrochemical impedance spectra were taken on an impedance analyzer (EIS-25H, Sharif Solar [25]) at a constant voltage.

General method for synthesis of the dyes T1 and T2

The synthesis process included the following steps: mixing the intermediate compounds (1 mmol), di(1*H*-tetrazol-5-yl)methane, diethylamine (20 mmol), and acetonitrile (5 mL), refluxing and evaporating the solvent of mixture, keeping in room environment for cooling, acidifying with hydrochloric acid (5 M), filtering the resulted residue, and drying and purifying the residue by column chromatography.

4-(2,2-di(1H-tetrazol-5-yl)vinyl)-N,N-diphenylaniline (T1)

The dye T1 was prepared as said by the general method from 1 (273 mg, 1 mmol), di(1H-tetrazol-5-yl)methane (228 mg, 1.5 mmol), and diethylamine (2 mL, 20 mmol) in CH₃CN (5 mL). Yield: 90%. Red solid. IR (KBr, cm^{-1}): v = 461 (w), 622 (s), 650 (s), 699 (m), 748 (w), 825 (w), 888 (w), 922 (m), 964 (m), 1006 (m), 1048 (m), 1076 (m), 1187 (w), 1585 (w), 1446 (s), 1578 (s), 2855 (s), 2925 (s), 2960 (s), 3406 (w, br). ¹H NMR (400 MHz, DMSO- d_6 , ppm): $\delta = 8.92$ (d, J = 8.8 Hz, 2H), 7.21 (m, 6H), 7.42 (t, J = 8.0 Hz, 4H), 7.89 (d, J = 9.2 Hz, 2H), 8.19 (s, 1H). ¹³C NMR (400 MHz, DMSO-*d*₆, ppm): $\delta = 118.78, 123.94, 125.04, 125.37, 125.89, 126.17,$ 129.88, 129.98, 131.79, 132.43, 145.43, 147.05. MS: m/z = 53.1, 69.1 (base peak), 91.1, 109.1, 129.1, 149.0, 165.1, 183.1, 207.1, 225.2, 241.2, 259.1, 275.2, 295.1, 310.1, 326.2, 341.2, 368.3, 386.3, 407.5 (M⁺). Anal. Calcd for C₂₂H₁₇N₉: C, 59.01; H, 3.71; N, 37.28; Found: C, 58.96; H, 3.70; N, 37.26.

4-(2,2-di(1H-tetrazol-5-yl) vinyl)-N-(4-(2,2-di(1H-tetrazol-5-yl)vinyl) phenyl)-N-phenylaniline

The dye T2 was prepared as said by the general method from 2 (301 mg, 1 mmol), di(1H-tetrazol-5-yl)methane (380 mg, 2.5 mmol) and diethylamine (2 mL, 20 mmol) in CH₂CN (5 mL). Yield: 90%. Dark red solid. IR (KBr, cm⁻¹): $\nu = 525$ (w), 692 (m), 804 (s), 916 (w), 1054 (s), 1159 (s), 1215 (w), 1285 (m), 1327 (s), 1390 (s), 1453 (s), 1502 (s), 1585 (s), 1627 (s), 1669 (s), 1850 (w), 2820 (s, br). ¹H NMR (400 MHz, DMSO- d_6 , ppm): $\delta = 7.02$ (d, J = 8.4 Hz, 4H), 7.08 (d, J = 8.4 Hz, 2H), 7.28 (t, J = 8.8 Hz, 1H), 7.46 (t, J = 8.0 Hz, 2H), 7.94 (d, J = 8.4 Hz, 4H), 8.03 (s, 2H). ¹³C NMR (400 MHz, DMSO- d_6 , ppm): $\delta = 119.07$, 123.77, 124.99, 125.61, 126.22, 129.42, 129.63, 132.49, 145.18, 146.73. MS: m/z = 57.1 (base peak), 83.1, 111.1, 149.0, 178.1, 210.2, 238.2, 261.2, 293.2, 337.4, 365.4, 400.4, 430.4, 472.4, 500.8, 530.5, 569.7 (M⁺). Anal. Calcd for C₂₆H₁₉N₁₇: C, 54.83; H, 3.36; N, 41.81; Found: C, 54.82; H, 3.33; N, 41.80.

Computational

The computational considerations were done through Gaussian [26] program. The optimized minima structures demonstrated by no imaginary frequency were obtained at the Becke-3-parameter-Lee–Yang–Parr (B3LYP) [27] level using 6-31 + G(d) basis set. TD-DFT (time-dependent density functional theory) calculations were carried out at B3LYP/6-31 + G(d) method for calculating the theoretical absorption spectra in ethanol solvent using the polarizable continuum model (PCM) [28] solvation model.

Results and discussion

Synthesis

A two-step route including the Vilsmeier–Haack formylation at the first step and the Knoevenagel condensation at the second step was applied for the synthesis of **T1** and **T2**. The synthesis process of the dyes is shown in Scheme 1.

Optical properties of the dyes

By looking to the recorded UV–Vis (ultraviolet–visible) absorption spectra of the dyes in ethanol in Fig. 2, we can recognize two separate peaks at 190–325 and 380–375 nm regions. The π – π * transitions and the intramolecular charge-transfer (ICT) transition from the triphenylamine electron donor to the di(1*H*-tetrazol-5-yl)methane electron



Fig. 2 Absorption spectra of the dyes in $C_2 H_5 OH$ solution $(2\times 10^{-5}\,M)$

acceptor moiety cause the appearance of peaks at these regions, respectively [3]. As seen in Table 1, the molar extinction coefficient of **T2** (29,640 $\text{LM}^{-1}\text{cm}^{-1}$) is more than that of **T1** (27,300 $\text{LM}^{-1}\text{cm}^{-1}$). The existence of two electron acceptor groups in the **T2** molecule enlarges the molecule; therefore, **T2** is also red-shifted by 15 nm compared to **T1**.

The absorption spectra of the dyes adsorbed on the TiO_2 surface illustrated in Fig. S1 in the supporting information seem to be broader than the spectrum in ethanol solution. It is also obvious that the adsorption on the surface shifts the absorption peaks to the higher wavelengths that can be a sign of the formation J-type aggregation [31].

Electrochemical properties

The oxidation and the reduction potentials of a molecule are a criterion of the HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) levels in that molecule. Therefore, the onset potentials of oxidation obtained from the cyclic voltammogram (Fig. S2) and the reduction potential calculated from the onset potentials of oxidation and the absorption onset are summarized in Table 1. The reduction of the oxidized dyes by the electrolyte is verified by having more positive oxidation potentials than the I^-/I_3^- redox couple [0.45 V vs NHE (normal hydrogen electrode)] [32], and the successful electron injection from the dyes to the semiconductor is proved by more negative reduction potentials than the conduction band edge of TiO₂ (-0.5 V vs NHE) [33]. We can also see a positive shift of both oxidation (0.04 V) and reduction (0.14 V) potentials of **T2** in comparison with those of **T1** due to the electron withdrawing effect of the second electron acceptor group. The lengthening of **T2** also decreases the band gap. The energy levels of the dyes are shown in Fig. 3.

Photovoltaic properties

The incident photo-to-current conversion efficiency (IPCE) images of **T1** and **T2** in Fig. 4 show expansive spectra. The maximum IPCE for **T1** occurs at 595 nm with the value of 67%. Obviously, **T1** shows the IPCE value of 55% in the range 465-625 nm. The maximum IPCE of 59% is also obtained at 525 nm for the DSSC based on the dye **T2**.



Fig. 3 Energy levels of the dyes T1 and T2

Table 1 Optical and electrochemical properties of the dyes in solutions and adsorbed on TiO_2

Dye	λ_{\max}^{a} (nm)	\mathcal{E}_{\max}^{a} (LM ⁻¹ cm ⁻¹)	$\lambda_{max}^{b}\left(nm\right)$	$E_{0-0}^{c} (eV)$	$E_{onset}^{ox d}(V)$	$E_{0-0}^{*e}(V)$	$HOMO_{exp}^{f}$ (calc) (eV)	$LUMO_{exp}^{g}$ (calc) (eV)
T1	370	27,300	426	2.67	0.78	-1.89	-4.98 (-5.60)	-2.31 (-2.62)
T2	385	29,640	430	2.57	0.82	-1.75	-5.02 (-5.71)	-2.45 (-2.88)

 a Absorption peak maximum and extinction coefficient at λ_{max} in C_2H_5OH solutions (2 \times 10 $^{-5}$ M at 298 K)

^b Absorption peak maximum on TiO₂

^c The band gap, E_{0-0} , was calculated approximately from the optical edge

^d Onset potentials of oxidation measured in CH_2Cl_2 containing 0.1 M Bu_4NPF_6 as supporting electrolyte, Ag/AgCl as a reference electrode, Pt as working and counter electrodes. Potentials were expressed as normal hydrogen electrode (NHE) by the addition of +0.63 V [29]

^e E_{0-0}^* : The excited-state oxidation potential versus NHE

^f HOMO = $-(E_{onset}^{ox} + 4.2)$ [30]

 g LUMO = E_{0-0} + HOMO



Fig. 4 Photocurrent action spectra of the DSSCs based on the dyes T1 and T2



Fig. 5 Current-voltage characteristics of DSSCs using T1 and T2

Table 2 Photovoltaic performance of DSSCs sensitized with the dyes T1 and T2

Dye	$J_{sc} (mA cm^{-2})$	V _{oc} [mV]	ff (%)	η (%)	Dye loading ^a ($\times 10^7$ mol cm ⁻²)
T1	13.38	578	54	4.18	3.52
T2	12.05	470	50	2.83	1.70

 $^{\rm a}$ Dye adsorption on TiO₂ was measured from the subtraction of the UV–Vis absorption spectra of dye solution before and after dipping of the cathode

The IPCE of the dye **T1** is broader than that of the dyes previously reported with the ethyl 2-(1*H*-tetrazol-5-yl) acetate, (2*H*-tetrazol-5-yl) acrylonitrile, or 1*H*-tetrazole-5-acetic acid moieties as anchoring group [18]. The DSSCs based on these dyes were constructed under the same conditions. The IPCE spectrum of **T1** is higher than that of the dyes with ethyl 2-(1*H*-tetrazol-5-yl) acetate (22%) and 1*H*-tetrazole-5-acetic acid (25%) anchoring groups, while the dye with (2*H*-tetrazol-5-yl) acrylonitrile (80%) shows higher IPCE than **T1**.

The current–voltage features of solar cells constructed of the **T1** and **T2** dyes are depicted in Fig. 5, and the cell performance parameters (J_{sc} (short-circuit current),



Fig. 6 Nyquist plots for DSSCs sensitized with T1 and T2 measured at 10 mV ac bias in the dark



Fig. 7 Nyquist plots of the DSSCs fabricated using the dyes T1 and T2

 V_{ac} (open circuit potential), ff (fill factor), and η (overall power conversion efficiency)) are summarized in Table 2. For the **T1**-based cell, a J_{sc} of 13.38 mA/cm², V_{oc} of 578 mV, and ff of 0.54 with a η of 4.18% were observed. The values of both J_{sc} and V_{oc} of the **T2**-based cell are lower than those for T1, resulting in a η of 2.83%. Although the **T2** dye has a longer π -conjugation system and red-shifted absorption spectrum, it shows a lower J_{sc} value. To find the reason for lower J_{sc} value of T2, the dye loading values were determined for T1 and T2 because in addition to the dye quality, the dye quantity on the TiO₂ surface influences the photovoltaic properties of DSSCs [13]. The obtained dye loading value for T2 $(1.70 \times 10^{-7} \text{ mol cm}^{-2})$ is lower than that for T1 $(3.52 \times 10^{-7} \text{ mol cm}^{-2})$; therefore, **T2**-based cell produces a lower J_{sc} value.

As seen, the V_{oc} value of the **T1**-based DSSC is higher than that of the **T2**-based DSSC. To explain the correlation between the V_{oc} values and the dyes, the electrochemical impedance spectroscopy (EIS) of DSSCs was measured in the dark (Fig. 6). As we can see in the picture, there is a large semicircle in the Nyquist plots of two DSSCs related to the charge-transfer resistance at the TiO₂/dye/electrolyte interface [4]. The radius of this semicircle is higher for the **T1** in comparison with that for **T2**, implying that the electron recombination resistance is high for the **T1**-based DSSC. Therefore, the V_{oc} value of DSSC constructed with **T1** is improved by the prevention of electron recombination between the electrolyte and the injected electrons.

In order to consider the electron transport in the DSSCs, the EIS of DSSCs was also measured under illumination. The Nyquist plots presented in Fig. 7 are recorded at the bias voltage with ac amplitude of 10 mV with frequency range of 0.1 Hz–100 kHz. In these plots, the larger semicircle is related to the charge-transfer processes at the $TiO_2/dye/electrolyte$ [4]. Obviously, the radius of larger semicircle for **T2** is higher than that for **T1**, implying that more charge transport occurs in the **T1**-based DSSC.

It is demonstrated that the dipole moment of the dye molecule with upward shifting of the conduction band of TiO₂ affects the V_{oc} value [34]. The calculated dipole moments for the dyes **T1** and **T2** are 10.09 and 8.83 D, respectively. According to these data, a larger dipole moment can also improve the V_{oc} value of **T1**.

In comparison with DSSCs based on the dyes with ethyl 2-(1*H*-tetrazol-5-yl) acetate, (2*H*-tetrazol-5-yl) acrylonitrile, and 1*H*-tetrazole-5-acetic acid anchoring groups, the cell based on **T1** exhibits the higher η value due to the highest short-circuit photocurrent density, which can be explained by its high IPCE value. The effects of the anchoring group on the overall power conversion efficiency are ranked di(1*H*-tetrazol-5-yl)methane > (2*H*-tetrazol-5-yl) acrylonitrile > ethyl 2-(1*H*-tetrazol-5-yl) acetate ~ 1*H*-tetrazole-5-acetic acid. The di(1*H*-tetrazol-5-yl) methane anchoring group has two tetrazole rings, while other anchoring groups include one tetrazole ring. It seems that the dye with two tetrazole units in its anchoring group is able to interact strongly with the TiO₂ surface and provides two charge transfer channels, which increases the

Table 3 Computed maximum absorption wavelengths (eV) and oscillator strengths (f) of the dyes T1 and T2 in C_2H_5OH

Dyes	λ_{\max} (nm)	Composition (%)	E(eV)	f	
T1	467	$H \rightarrow L (70.4)$	2.65	1.04	
T2	512	$\mathrm{H} \rightarrow \mathrm{L}~(70.4)$	2.42	1.29	

electron injection. The higher electron injection leads to the higher IPCE.

The study by Massin et al. [13] has shown that the photovoltaic properties of tetrazole-based dye with an enhanced photovoltage rival those of carboxylic acid-based dye. In addition, both tetrazole- and carboxylic acid-based dyes show similar stability under the same conditions. Based on these results, their study has demonstrated that tetrazole group is an effective alternative to common carboxyl group. As mentioned above, the dye with two tetrazole rings in its anchoring group (T1) shows the higher overall efficiency in comparison with the dyes with single tetrazole ring, revealing more efficient adsorption of the dye on the TiO₂ surface. Therefore, ditetrazole anchoring group (di(1H-tetrazol-5-yl)methane) may be a useful substitute for carboxyl group in sensitizers of solar cells and may lead to the higher efficiency of the dye bearing this anchoring group.

Theoretical approach

DFT calculations are applied for the study of the frontier orbitals of the dyes. The images of the frontier orbitals of these dyes in Fig. 8 appear that the HOMO of these dyes is distributed allover the molecule and the LUMO being on



Fig. 8 Isodensity surface plots of frontier orbitals (a: HOMO, b: LUMO) of the dyes T1 and T2



Fig. 9 Calculated absorption spectra of the dyes in C_2H_5OH calculated at TD/DFT 6-31 + G(d)

the acceptor group along with the phenyl ring connected to it.

The TD-DFT calculations are useful to understand the electronic transitions in these molecules. These calculations show that, in two dyes, the first singlet-singlet excitation occurs from the HOMO to the LUMO level with energy of 2.65 and 2.42 eV for T1 and T2, respectively. The data obtained from these calculations are presented in Table 3, and the absorption spectra are shown in Fig. 9. Although the theoretical spectra are red-shifted in comparison with the experimental spectra due to the self-interaction error in TD-DFT caused by the electron transfer in the extended charge-transfer state [34, 35], the spectroscopic behaviors are similar for both the theory and experiment. The absorption maxima of T1 and T2 are 467 and 512 nm, respectively. The extra electron acceptor group in T2 causes a decrease in the HOMO-LUMO gap, leading to the red-shift of its absorption spectrum.

Conclusions

In this paper, we discussed the properties of organic sensitizers with novel anchoring group including two tetrazole rings that will be applicable in DSSCs. The overall conversion efficiencies of the DSSCs based on **T1** and **T2** were obtained 4.18 and 2.83%, respectively. The dye **T2** with having two electron acceptor groups showed the lower J_{sc} and V_{oc} values due to the lower dye loading and electron recombination resistance and the smaller dipole moment. The DSSC based on **T1** with the di(1*H*-tetrazol-5-yl) methane electron acceptor was more efficient compared to those based on the sensitizers with single tetrazole ring in their anchoring group. The dye with double tetrazole in its anchoring group interacts stronger with the TiO₂ surface. This dye also transfers more electrons to the TiO₂ electrode, increasing the J_{sc} value. Acknowledgements We thank the Isfahan University of Technology for the financial support of this work. We gratefully acknowledge the Sheikh Bahaei National High Performance Computing Center (SBNHPCC) for the computational support.

References

- Z. Ning, Q. Zhang, W. Wu, H. Pei, B. Liu, H. Tian, J. Org. Chem. 73, 3791 (2008)
- K. Hara, Z.-S. Wang, T. Sato, A. Furube, R. Katoh, H. Sugihara, Y. Dan-oh, C. Kasada, A. Shinpo, S. Suga, J. Phys. Chem. B 109, 15476 (2005)
- M. Liang, W. Xu, F. Cai, P. Chen, B. Peng, J. Chen, Z. Li, J. Phys. Chem. C 111, 4465 (2007)
- S.P. Singh, M.S. Roy, K.R. Justin Thomas, S. Balaiah, K. Bhanuprakash, G.D. Sharma, J. Phys. Chem. C 116, 5941 (2012)
- J. Feng, Y. Jiao, W. Ma, MdK Nazeeruddin, M. Grätzel, S. Meng, J. Phys. Chem. C 117, 3772 (2013)
- A. Hagfeldt, G. Boschloo, L. Sun, L. Kloo, H. Pettersson, Chem. Rev. 110, 6595 (2010)
- J. Cong, X. Yang, J. Liu, J. Zhao, Y. Hao, Y. Wang, L. Sun, Chem. Commun. 48, 6663 (2012)
- J. Mao, N. He, Z. Ning, Q. Zhang, F. Guo, L. Chen, W. Wu, J. Hua, H. Tian, Angew. Chem. Int. Ed. 51, 9873 (2012)
- 9. Y. Ooyama, Y. Hagiwara, T. Mizumo, Y. Harima, J. Ohshita, New J. Chem. **37**, 2479 (2013)
- Y. Ooyama, Y. Hagiwara, Y. Oda, T. Mizumo, Y. Harima, J. Ohshita, New J. Chem. 37, 2336 (2013)
- Y. Ooyama, T. Sato, Y. Harima, J. Ohshita, J. Mater. Chem. A 2, 3293 (2014)
- 12. H. He, A. Gurung, L. Si, Chem. Commun. 48, 5910 (2012)
- J. Massin, L. Ducasse, T. Toupance, C. Olivier, J. Phys. Chem. C 118, 10677 (2014)
- 14. R.J. Herr, Bioorg. Med. Chem. 10, 3379 (2002)
- 15. Y. Zhou, C. Yao, R. Ni, G. Yang, Synth. Commun. 40, 2624 (2010)
- G. Wu, R. Kaneko, Y. Zhang, Y. Shinozaki, K. Sugawa, A. Islam, L. Han, I. Bedja, R.K. Gupta, Q. Shen, J. Otsuki, J. Power Sources 307, 416 (2016)
- Q. Liu, L.Y. Zhao, Y.M. Lu, Q.Y. Yue, F.F. Zhang, B. Wei, Q.Y. Li, G.W. Yang, J. Inorg. Gen. Chem. 642, 311 (2016)
- Z. Jafari Chermahini, A. Najafi Chermahini, H.A. Dabbagh, A. Teimouri, J. Energy Chem. 24, 770 (2015)
- 19. G. Lai, X.R. Bu, J. Santos, E.A. Mintz, Synlett 1275 (1997)
- 20. H.J. Lee, J. Sohn, J. Hwang, S.Y. Park, Chem. Mater. 16, 456 (2004)
- 21. M.A.A. El Remaily, S.K. Mohamed, Tetrahedron **70**, 270 (2014)
- 22. <http://sharifsolar.ir/product-category/mat/paste>
- G.N. Howatt, R.G. Breckenridge, J.M. Brownlow, J. Am. Ceram. Soc. 30, 237 (1947)
- A. Berni, M. Mennig, H. Schmidt, in *Sol-Gel Technologies for Glass Producers and Users*, ed. by M. Aegerter (Springer, New York, 2004), p. 88
- 25. <http://sharifsolar.ir/product-category/equ>
- M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G.A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H.P. Hratchian, A.F. Izmaylov, J. Bloino, G. Zheng, J.L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J.A. Montgomery Jr., J.E. Peralta, F. Ogliaro, M. Bearpark, J.J. Heyd, E. Brothers, K.N. Kudin, V.N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J.C. Burant, S.S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J.M. Millam, M. Klene, J.E. Knox,

J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, R.L. Martin, K. Morokuma, V.G. Zakrzewski, G.A. Voth, P. Salvador, J.J. Dannenberg, S. Dapprich, A.D. Daniels, O. Farkas, J.B. Foresman, J.V. Ortiz, J. Cioslowski, D.J. Fox, Gaussian 09, Revision A.01 (Gaussian Inc., Wallingford, 2009)

- 27. C. Lee, W. Yang, R.G. Parr, Phys. Rev. B 37, 785 (1988)
- 28. E. Cancès, B. Mennucci, J. Tomasi, J. Chem. Phys. **107**, 3032 (1997)
- T.-H. Kwon, V. Armel, A. Nattestad, D.R. MacFarlane, U. Bach, S.J. Lind, K.C. Gordon, W. Tang, D.J. Jones, A.B. Holmes, J. Org. Chem. **76**, 4088 (2011)

- 30. A.J. Bard, L.A. Faulkner, *Electrochemical Methods, Fundamentals and Applications* (Wiley, New York, 1984)
- 31. W. Xu, B. Peng, J. Chen, M. Liang, F. Cai, J. Phys. Chem. C 112, 874 (2008)
- 32. A. Hagfeldt, M. Grätzel, Chem. Rev. 95, 49 (1995)
- P. Chen, J.H. Yum, F.D. Angelis, E. Mosconi, S. Fantacci, S.-J. Moon, R. Humphry-Baker, J. Ko, M.K. Nazeeruddin, M. Grätzel, Nano Lett. 9, 2487 (2009)
- W. Cheng-Long, W. Jian, B. Fu-Quan, C. Jie, Z. Hong-Xing, Int. J. Quantum Chem. 114, 560 (2014)
- Z. Tian, M. Huang, B. Zhao, H. Huang, X. Feng, Y. Nie, P. Shen, S. Tan, Dyes Pigment. 87, 181 (2010)