DOI: 10.1002/cjoc.201300924

SalenZn-bridged D-π-A Dyes For Dye-Sensitized Solar Cells

Yongjian Jia,[a] Faliang Gou,[a] Ran Fang,[a] Huanwang Jing,*,[a,b] and Zhenping Zhu[b]

[a] *State Key Laboratory of Applied Organic Chemistry and College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou, Gansu 730000, China*

[b] *State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan, Shanxi 030001, China*

A series of SalenZn based dyes with triphenylamine derivatives as the donor, benzoic acid as the acceptor, and coplanar Salen complexes as the spacer have been designed and synthesized for dye-sensitized solar cells. The absorption, electrochemical, and photovoltaic properties for all sensitizers have been systematically investigated. When the tail length of the alkyl substituents is increased from C-0 to C-8 on the donor part, the efficiency of its DSSC augments evidently. It is found that the incorporation of bis-carboxyl groups instead of the single carboxyl group as anchoring groups induces a remarkable enhancement of the electron injection efficiency from the excited dyes to the TiO_2 semiconductor and generates higher electron density and voltage.

Keywords dye-sensitized solar cells, SalenZn complexes, salicylic acid, anchoring group

Introduction

Along with the increasing energy demand in the world, sustainable energy, especially the solar energy, has received widespread attention in various research fileds. Dye-sensitized solar cells (DSSCs) improved by Grätzel since 1991,[1] are regarded as prospective alternative for renewable clean energy sources in virtue of their versatility, short energy payback time and low cost of manufacture compared with conventional silicon-based solar cells and thin-film photovoltaic technologies.[2] A characteristic solar cell makes up of three components: (i) a sensitized photoanode, which is typically a monolayer of molecular dye sensitized nanocrystalline TiO_2 film with anatase phases on a transparent fluorine doped tin oxide (FTO) conducting glass; (ii) an electrolyte solution embracing iodide anion/triiodide anion or Co (II/III) tris(bipyridyl)-based as a redox couple; and (iii) a cathode platinized on a FTO conducting glass or a carbon film as a flexible counter electrode.[3]

Although many factors affect the photovoltaic performance of the DSSCs, the role of dye is obviously a crucial one. To approach high photovoltaic performance, numerous focuses are centered on designing and synthesizing new photosensitizers with a panchromatic light response. DSSC devices with Ru complexes (N719) as photosensitizers keep the record of validated efficiency of over 11%.[4] Recently, more cheaper dyes of zinc porphyrin chromophores are also hopeful candidates.[5] The metal-free organic sensitizers[6] have also gained considerable light-to-electron conversion efficiency in spite of their less stabilities.[7] So far, one of zinc porphyrin dyes (YD-*o*-C-8) based DSSCs in conjunction with an organic dye as co-sensitizer and a Co (II/III)-based redox has gained superior photovoltaic performance (12.3%)[5a] under full sun illumination, which might overcome the limit resources of ruthenium on the Earth.

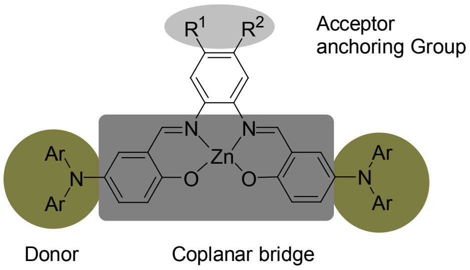
Generally, the designs of metal-based dyes for high performance DSSCs obey donor-(π-spacer)-acceptor (D-π-A) structure principle springing from the push-pull concept of the photo-induced intramolecular charge transfer, which adjusts the molecular absorption to match solar radiation for competent light harvesting.[8]

Salen metal complexes as mimic metalloporphyrins, in addition to broadly employing in the field of homogeneous catalysis,[9] have been paid much less attention to the sensitizers.[9c] Typical and promising salen metal complexes-based materials have recently emerged including molecular sensors,[10] and useful supramolecular structures.[11] Along with the syntheses of metallosallens are widely accessible, relatively and increasingly mature, they become good alternatives of metalloporphyrins due to their planar structures.

Herein, we report a new series of dyes with D (triphenylamine)-π (SalenZn complexes)-A (benzoic acids) structure (Figure 1). The detailed investigations of the performances of their DSSC devices were achieved in comparison with those of DSSCs of N719.

---

* E-mail: hwjing@lzu.edu.cn; Tel.: 0086-0931-8912585; Fax: 0086-0931-8912582
Received December 31, 2013; accepted March 20, 2014; published online April 22, 2014.
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/cjoc.201300924 or from the author.



SLa:	Ar = Ph	R^1 = H; R^2 = COOH
SLb:	Ar = *m*-xylene	R^1 = H; R^2 = COOH
SLc:	Ar = 4-*tert*-butylbenzene	R^1 = H; R^2 = COOH
SLd:	Ar = 4-pentylbenzene	R^1 = H; R^2 = COOH
SLe:	Ar = 4-octylbenze	R^1 = H; R^2 = COOH
SLf:	Ar = Ph	R^1= R^2 = COOH

Figure 1 Structure of the SalenZn-bridged D-π-A dyes.

Experimental

Materials

All reagents and solvents were purchased from commercial resources and used without further purification unless otherwise noted. CH_2Cl_2 was dried over CaH_2 and freshly distilled prior to use. THF, ether, toluene and triethylamine were dried over sodium/benzophenone and freshly distilled before use. 1,2-Dimethyl-3-propylimidazolium iodide (DMPII, Aldrich), iodine (I_2, Aldrich), 4-*tert*-butylpyridine (TBP, Aldrich) were used as received. The N719 dye (*cis*-diisothiocyanato-bis(2,2-bipyridyl-4,4'-dicarboxylato) ruthenium(II) bis(tetrabutylammonium)) was purchased from Solaronix. All other chemicals were of analytical grade. FTO glass was purchased from Nippon Sheet Glass Co. Ltd. (15/sq). ^{1}H NMR and ^{13}C NMR spectra were measured by using Varian 300 MHz spectrometer. The UV-vis absorption spectra were determined by an UV-3600 spectrophotometer in THF at room temperature.

General preparation of compound 3

To a stirred solution of *p*-methoxyaniline (4 mmol), CuI (0.08 mmol), KO^{t}Bu (12 mmol) and 1,10-phenanthroline (0.08 mmol) in toluene was added aryl halide (12 mmol) under argon. The reaction mixture was then stirred and refluxed for 14 h. After cooling to room temperature, the mixture was filtered to remove the base precipitate. The solution was concentrated to obtain the crude product, which was chromatographed to get the pure product.

3a Colorless solid (60%); ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 3.78 (s, 3H), 6.81—6.83 (m, 2H), 6.84—6.95 (m, 2H), 7.04—7.08 (m, 6H), 7.16—7.22 (m, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 55.4, 114.7, 121.8, 122.8, 127.3, 129.0, 140.7, 148.1, 156.1; ESI-HRMS *m*/*z*: $[M+H]^+$ calcd for $C_{19}H_{17}NO$: 276.1383, found 276.1378.

3b Colorless solid (60%); ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 2.20 (s, 12H), 3.80 (s, 3H), 6.60 (d, J=12.3 Hz, 5H), 6.80 (d, J=8.7 Hz, 2H), 7.01 (d, J=8.7 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 21.3, 55.4, 114.5, 121.7, 123.7, 127.1, 138.5, 141.2, 148.3, 155.8. ESI-HRMS *m*/*z*: $[M+H]^+$ calcd for $C_{23}H_{25}NO$: 332.2009, found 332.2011.

3c Colorless solid (49%); ^{1}H NMR ($CDCl_3$, 300 MHz) δ: (s, 18H), 3.78 (s, 3H), 6.82 (d, J=8.7 Hz, 2H), 6.95 (d, J=8.4 Hz, 4H), 7.07 (d, J=8.7 Hz, 2H), 7.21 (d, J=9 Hz, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 31.4, 34.1, 55.4, 114.6, 122.3, 125.8, 126.9, 141.1, 144.3, 145.6, 155.7.

3d Colorless oil (55%); ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 0.94—0.98 (m, 6H), 1.37—1.41 (m, 8H), 1.63—1.68 (m, 4H), 2.56 (t, J=8.1Hz, 4H), 3.83 (s, 3H), 6.84—6.86 (m, 2H), 7.00 (d, J=8.1 Hz, 4H), 7.09—7.11 (m, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 14.1, 22.6, 31.3, 31.6, 35.2, 55.4, 114.5, 122.8, 126.6, 128.9, 136.3, 141.2, 146.0, 155.6. ESI-HRMS *m*/*z*: $[M+H]^+$ calcd for $C_{29}H_{37}NO$: 415.29, found 416.2947.

3e Colorless oil (50%); ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 0.88 (t, J=6.9 Hz, 6H), 1.29—1.39 (m, 20H), 1.56—1.63 (m, 4H), 2.52 (t, J=7.8 Hz, 4H), 3.78 (s, 3H), 6.81 (d, J=2.1 Hz, 2H), 6.84 (d, J=2.4 Hz, 4H), 6.97—7.08 (m, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 14.1, 22.7, 29.5, 29.7, 30.3, 31.6, 31.9, 35.2, 55.4, 113.6, 122.2, 126.6, 128.9, 136.3, 141.3, 146.0, 155.6; ESI-MS $[M+H]^+$ calcd for $C_{35}H_{50}NO$: 499, found 500.6.

General preparation of compound 4

To a solution of compound **3** (7.09 mmol) in dry dichloromethane (70 mL) was added boron tribromide (1.0 mol/L solution in dichloromethane) (10.64 mmol) at 0 ℃ and stirred for 30 min. The reaction mixture was stirred at room temperature for 24 h, poured into water and then extracted with dichloromethane (50 mL ×3). The extract was dried over Na_2SO_4, and evaporated. The residue was chromatographed on silica gel to give compound **4**.

4a Colorless solid (99%); ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 5.22 (br s, 1H), 6.73 (br s, 2H), 6.90—6.94 (m, 2H), 6.99 (d, J=7.5 Hz, 6H), 7.20 (d, J=8.1 Hz, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 116.22, 121.82, 122.83, 127.38, 129.04, 140.87, 147.94, 151.57; ESI-HRMS $[M+H]^+$ calcd for $C_{18}H_{15}NO$: 262.1226, found 262.1219.

4b Colorless solid (99%); MS $[M+H]^+$ calcd for $C_{22}H_{23}NO$ 317, found 317.

4c Colorless solid (98%); ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 1.21—1.29 (m 18H), 5.04 (br s, 1H), 6.76 (br s, 1H), 6.94—7.03 (m, 4H), 7.20—7.22 (m, 4H); ESI-HRMS $[M+H]^+$ calcd for $C_{19}H_{17}NO$: 374.2478, found 374.2470.

4d Colorless oil (97%); ESI-HRMS $[M+H]^+$ calcd for $C_{28}H_{35}NO$: 401.27, found 402.2786.

4e Colorless oil (99%); ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 0.858—0.903 (m, 6H), 1.27 (br s, 20H), 1.58 (br s, 4H), 2.50—2.54 (m, 4H), 4.70 (br s, 1H), 6.73 (dd, J=6.6, 2.4 Hz, 2H), 7.02 (d, J=8.4 Hz, 8H), 7.24 (d, J=8.1 Hz, 2H); ESI-MS *m*/*z*: $[M+H]^+$ calcd for $C_{35}H_{46}NO$: 486, found 486.6.

General preparation of compound 5

The compound **5** was performed referring to a literature procedure.[13a]

5a Yellow solid (90%); ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 6.92—7.05 (m, 8H), 7.22—7.38 (m, 3H), 9.74 (s, 1H), 10.85 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 118.8, 120.9, 122.6, 123.1, 129.3, 135.1, 140.2, 147.5, 157.8, 176.2; ESI-MS *m*/*z*: $[M+H]^+$ calcd for $C_{19}H_{15}NO_2$: 289, found 289.

5b Yellow solid (90%); ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 2.32 (s, 12H), 6.76 (s, 6H), 7.01 (d, *J*=8.7 Hz, 1H), 7.37—7.44 (m, 2H), 9.80 (s, 1H), 10.93 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 21.3, 118.5, 120.9, 121.2, 124.4, 129.1, 135.0, 140.7, 147.7, 157.5, 196.2.

5c Yellow solid (92%); ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 1.31 (d, *J*=1.2 Hz, 18H), 6.89—6.97 (m, 5H), 7.24 (d, *J*=7.2 Hz, 4H), 7.31—7.33 (m, 2H), 9.72 (s, 1H), 10.82 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 29.7, 31.2, 31.4, 34.2, 118.6, 120.9, 122.7, 126.1, 128.8, 134.8, 140.6, 144.9, 145.3, 157.5, 196.3.

5d Yellow oil (89%); ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 0.92 (t, *J*=6.6 Hz, 6H), 1.32—1.44 (m, 8H), 1.68 (d, *J*=7.2 Hz, 4H), 2.57 (t, *J*=8.1 Hz, 4H), 6.92—7.10 (m, 8H), 7.26—7.38 (m, 3H), 9.72 (s, 1H), 10.87 (br s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 14.0, 22.5, 32.2, 33.5, 35.2, 118.5, 120.8, 123.2, 128.4, 129.2, 134.3, 137.1, 140.7, 145.3, 157.3, 196.1.

5e Yellow oil (95%); ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 0.86—0.90 (m, 6H), 1.27—1.30 (m, 20H), 1.60—1.61 (m, 4H), 2.51 (t, *J*=8.1 Hz, 4H), 6.91 (d, *J*=2.7 Hz, 4H), 7.03 (d, *J*=8.4 Hz, 4H), 7.26 (d, *J*=3.9 Hz, 2H), 7.31 (d, *J*=2.4 Hz, 1H), 9.73 (s, 1H), 10.80 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 14.1, 22.7, 29.27, 29.40, 29.48, 31.54, 31.88, 35.3, 118.5, 120.8, 123.2, 128.5, 129.2, 134.3, 137.3, 140.8, 143.3, 145.3, 157.3, 196.1.

Preparation of dimethyl 4,5-diaminophthalate (12)

Compounds **9**, **10**, **11**, and **12** were synthesized following the literature procedures[13b] and characterized with NMR spectra that were consistent with the reported data.

A solution of dimethyl-4-amino-5-nitrophthalate (1.0 g) and 10% Pd/C (0.2 g) in methanol (30 mL) was placed into a hydrogenation apparatus for 1 d. The solvent was removed by evaporation and the product **12** was obtained. ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 3.57 (br s, 4H), 3.77 (s, 6H), 6.96 (s, 2H); ESI-MS *m*/*z*: $[M+H]^+$ calcd for $C_{19}H_{46}NO$: 224, found 225.3.

Preparation of the dyes SLa—SLe

Et_3N (2 mL) was added to a solution of salicylaldehyde (0.5 mmol), 3,4-diaminobenzoic acid (0.25 mmol) and $Zn(OAc)_2 \cdot 2H_2O$ (0.65 mmol) in ethanol (10 mL). The reaction mixture was heated to reflux for 5 h under argon. The mixture was filtrated under vacuum pump and washed with Et_2O to obtain **7**.

A solution of **7** in THF was dropped with 0.03 mol/L HCl (2 mL) at 0 ℃ and stirred for 4 h. The most solvent was removed by evaporation and the crude product was obtained, which was filtrated under vacuum pump and washed with H_2O.

SLa (60%); ^{1}H NMR (DMSO-d_6, 300 MHz) δ: 6.75 (dd, *J*=2.7, 6 Hz, 1H), 6.91—6.96 (m, 12H), 7.08—7.19 (m, 3H), 7.21—7.24 (m, 10H), 7.44 (s, 1H), 7.84 (s, 2H), 8.36 (s, 1H), 9.03 (s, 2H); MS (MALDI-TOF) *m*/*z*: $[M+Ag]^+$ calcd for $C_{45}H_{32}N_4O_4$-Zn 758.17, found 866.6.

SLb (63%); ^{1}H NMR (DMSO-d_6, 300 MHz) δ: 2.11—2.14 (m, 24H), 6.53—6.55 (m, 12H), 6.73—6.76 (m, 2H), 7.02—7.07 (m, 2H), 7.22 (s, 1H), 7.34 (s, 1H), 7.85 (s, 2H), 8.30 (s, 1H), 8.96 (d, *J*=8.4 Hz, 2H); MS (MALDI-TOF) *m*/*z*: $[M+Ag]^+$ calcd for $C_{53}H_{48}N_4O_4$-Zn 868.3, found 976.2.

SLc (64%); ^{1}H NMR (DMSO-d_6, 300 MHz) δ: 1.20 (d, *J*=12.9 Hz, 36H), 6.71—6.77 (m, 2H), 6.83 (t, *J*=8.7 Hz, 7H), 6.89 (t, *J*=8.7 Hz , 2H), 6.99—7.23 (m, 9H), 7.25 (s, 1H), 7.38 (s, 1H), 7.84 (s, 1H), 8.30 (s, 1H), 9.00 (s, 2H); MS (MALDI-TOF) *m*/*z*: $[M+H]^+$ calcd for $C_{61}H_{64}N_4O_4Zn$ 980.42, found 981.1.

SLd (61%); ^{1}H NMR (DMSO-d_6, 300 MHz) δ: 0.81—0.88 (m, 12H), 1.24—1.29 (m, 18H), 1.51—1.52 (m, 8H), 2.26—2.53 (m, 8H), 6.71—6.75 (m, 2H), 6.81 (t, *J*=7.6 Hz, 7H), 7.01—7.05 (m, 9H), 7.25 (s, 1H), 7.38 (s, 1H), 7.84 (s, 1H), 8.30 (s, 1H), 8.98 (s, 1H); MS (MALDI-TOF) *m*/*z*: $[M+Ag]^+$ calcd for $C_{65}H_{72}N_4O_4Zn$ 1036.48, found 1144.3.

SLe (63%); ^{1}H NMR (benzene-d_6, 300 MHz) δ: 0.59—0.64 (m, 12H), 0.97 (s, 48H), 1.32 (s, 8H), 2.23 (t, *J*=7.5, Hz, 8H), 6.47 (s, 8H), 6.60 (s, 6H), 6.97—6.95 (m, 14H), 7.15 (s, 2H), 7.43 (s, 1H); MS (MALDI-TOF) *m*/*z*: $[M]^+$ calcd for $C_{77}H_{96}N_4O_4Zn$ 1207, found 1207.4.

13 (62%); ^{1}H NMR (DMSO-d_6, 300 MHz) δ: 3.81 (s, 6H), 6.76 (d, *J*=9.3 Hz, 1H), 6.90—6.99 (m, 13H), 7.09—7.11 (m, 1H), 7.22 (t, *J*=8.1 Hz, 8H), 7.37 (s, 1H), 8.21 (s, 1H), 9.08 (s, 1H).

Preparation of the dye SLf

The compound **13** was prepared by using the method as the same as that of making SLa.

A solution of **13** (1 mmol) and NaOH (4 mmol) in water (5 mL) and THF (5 mL) was refluxed for 6 h. After cooling, the mixture was acidified with 0.012 mol/L HCl to get the precipitate, which was filtrated, washed with $CHCl_3$, and dried under vacuum oven.

SLf (61%); ^{1}H NMR (DMSO-d_6, 300 MHz) δ: 6.75 (d, *J*=2.7 Hz, 1H), 6.91—6.99 (m, 12H), 7.08—7.09 (m, 3H), 7.22—7.27 (m, 10), 7.30—7.44 (m, 2H), 7.84—7.91 (m, 2H), 8.36 (s, 1H), 9.03 (s, 1H), 9.08 (s, 1H); MS (MALDI-TOF) *m*/*z*: $[M]^+$ calcd for $C_{46}H_{32}N_4O_6Zn$ 800.16, found 800.00.

Fabrication of the DSSCs

Fabrication of the DSSCs was prepared following a modified procedure reported in the literature.[14] With a starting compound of titanium(IV) *n*-butoxide, TiO_2 nanoparticles were prepared *via* a hydrothermal synthesis. The practicable TiO_2 paste invloving polyethylene glycol (molecular weight 20000) in a proportion of 50% weight was coated on a commercial fluorine-tin-oxide (FTO) using vacuum spincoater method. The FTO glass supported TiO_2 film (thickness 15 μm and active area 0.16 cm^2) was then sintered at 500 ℃ for 1 h. The electrode was immerged immediately into the dye solution (SL series, 1 mmol/L, $V(EtOH)/V(THF)=1/1$, 12 h) when the oven temperature was cooled to 100 ℃. The TiO_2 electrode was then taken out, flushed with CH_3CN, and dried with nitrogen stream. The solar cell was prepared by agglutinating the platinum counter electrode and the TiO_2 electrode. Electrolyte was injected and penetrated to the TiO_2 film *via* vacuum perfusion. The electrolyte solution was constitutive of 0.6 mol/L DMPII, 0.05 mol/L I_2, and 0.5 mol/L TBP in a mixture solution of acetonitrile and valeronitrile (85 : 15, *V*/*V*). The solar cell was finally sealed by hot glue.

Photoelectrochemistry and electrochemistry

The working performance of DSSCs was examined *via* recording the photocurrent-voltage (*J-V)* curves with a Keithley Series 2601A System Source Meter under irradiating from a solar simulator (San-Ei XES-301S) giving AM 1.5 G illumination. The light intensity was 100 mW/cm^2 calibrated by a standard Si solar cell. The measurement of the incident photon-to-current conversion efficiency (IPCE) was carried out with a Crown instrument. Cyclic voltammetry curves were obtained by a CHI 660D electrochemical workstation with a traditional three-electrode system. The working electrode, reference electrode, and auxiliary electrode were a glassy carbon electrode, Ag/AgCl and Pt-wire electrode, respectively.

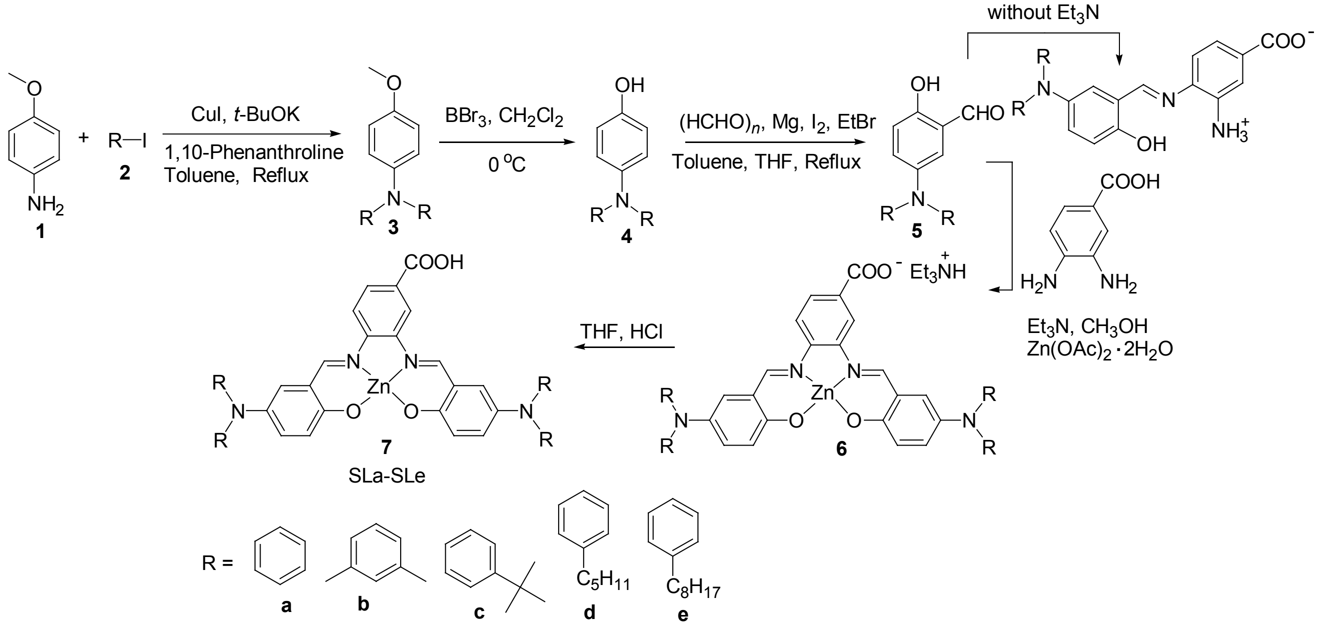
Results and Discussion

Synthesis of the target compounds

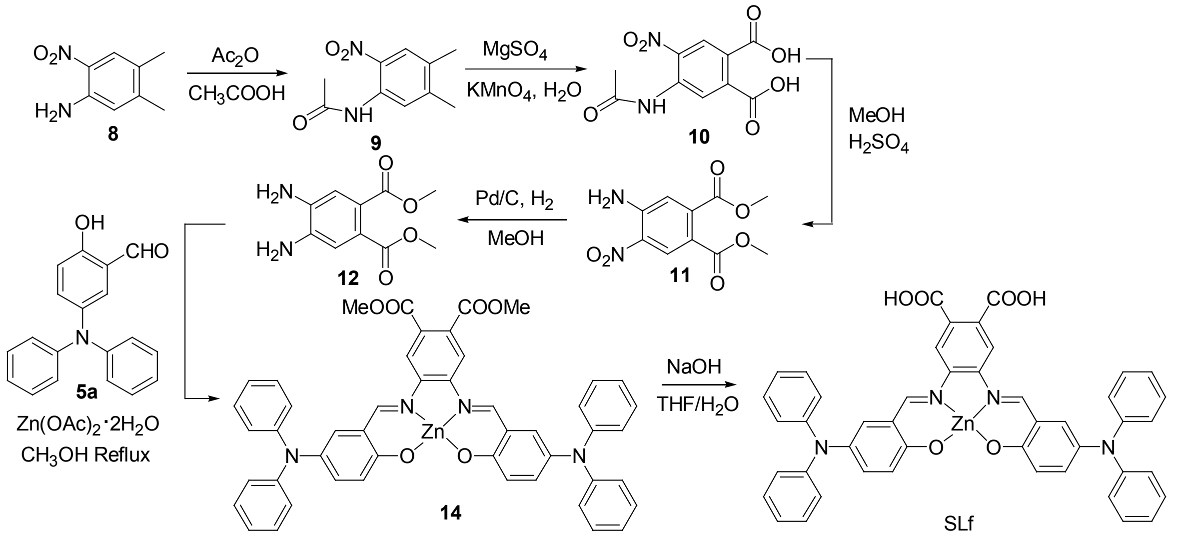
The synthetic route of the new dyes named SL is dipicted in Scheme 1. With a starting compound of 4-methoxyaniline **1** and various aryl iodides **2**, C—N bond formation was achieved *via* Ullmann reaction catalyzed by CuI, and gave 4-methoxy-*N*,*N*-diphenylaniline derivates **3**. By dint of BBr_3 removing the methoxy group, hydroxyl was exposed and the series compounds **4** were formed, which were readily converted into their corresponding salicylaldehydes **5** *via* Grignard reagent and paraformaldehyde, respectively. The addition of an excess of triethylamine protected the free carboxyl group from facilitating inner salt with amine group resulting in mono-Schiff base. In the presence of dilute aqueous solution of HCl, the triethylamine was removed to generate the target molecules SLa—SLe.

To enhance the efficiency of electron injection and increase effective contact area between TiO_2 film and dyes, the second carboxyl group was introduced into *ortho*-position of carboxyl group and *meta*-position of 3-amino-group (Scheme 2). Treatment of the intermediate **8** with acetic anhydride and CH_3COOH afforded amide **9** for protecting the free amine. The phthalic acid derivative **10** was oxidized with potassium permanganate. Reaction of **10** with CH_3OH *via* a one pot esterification and deprotection reaction gave dimethyl-4-amino-5-nitrophthalate **11**, which carried through hydrogenation reaction using H_2 and Pd/C to give the molecule **12**. The installation of backbone bond on dyes was disposed by template synthesis of the compound **12** with **5a**, and then Schiff-base metal complex **13** was formed, which underwent hydrolysis reaction with

Scheme 1 Synthetic route of the SL dyes



Seheme 2 Synthetic route of absorption group & SLf dye



NaOH to afford the desired dye SLf.

Photophysical and electrochemical properties

The UV-vis absorption spectra of SL series dyes are depicted in Figure 2a & Table 1. In THF solution, all of dyes reveal two obvious bands between 350—600 nm, which is fulfilling for solar light harvesting. The peak at a wavelength region (300—350 nm) and with a high molar absorption coefficient is ascribed to the triphenylamine (TPA) and 3,5-diaminobenzoic acid (Anchor), which have wavelength peaks at 297 nm and broad absorption from 270 to 400 nm respectively (see SI). The other peak at 400—650 nm is a characteristic absorption peak of SalenZn complex, which shows a significant bathochromic shift (*ca.* 50 nm) due to the elongation of the π-conjugation compared with SalenZn complex without diphenylamine as donor (CON). Upon adsorption onto TiO_2 (Figure 2b), most of dyes show different levels of hypsochromic effect compared with that measured in solution, and display wavelength peak at *ca.* 420 nm, which exihibts bathochromic shift compared to the absorption of nanocrystalline TiO_2 (380 nm). SLf based on TiO_2, of which the peak has a little change, gives a broader and higher absorption in comparison with other dyes.

The electrochemical properties of the dyes were measured by cyclic voltammetry and presented in Table 1. The lowest unoccupied molecular orbital (LUMO) of all dyes lies lower than that of N719 (–3.64 eV) and

Table 1 Absorption and electrochemical properties of SL series dyes

Dye	$\lambda_{\max}$[a]/nm $[\varepsilon/(10^4\ \text{L•mol}^{-1}\text{•cm}^{-1})]$	$E_{\text{ox}}/E_{\text{red}}$[b]	E_g[c]	HOMO[d]	LUMO[e]
SLa	303 (8), 470 (1.3)	0.67/–0.73	1.40	–4.91	–3.51
SLb	305 (7.7), 473 (1.4)	0.59/–0.72	1.33	–4.83	–3.50
SLc	303 (12), 470 (1.7)	0.66/–0.75	1.41	–4.90	–3.49
SLd	303 (14), 452 (1.6)	0.93/–0.82	1.75	–5.17	–3.15
SLe	292 (7.7), 470 (8.9)	0.62/–0.74	1.36	–4.86	–3.50
SLf	303 (11), 470 (1.8)	0.69/–0.83	1.52	–4.93	–3.41

[a] Absorption spectra were measured in THF solutions. [b] The oxidation and reduction potentials of dyes were measured in THF with 0.1 mol/L tetrabutylammonium hexafluorophosphate (TBA-PF_6) with a scan rate of 50 mV•s^{-1}. [c] Band gaps derived from the difference between onset potentials of oxidation and reduction. [d] HOMO$=-(E_{\text{ox}}+4.8-E_{\text{ox}}^{\text{Fe/Fe}^+})$. [e] LUMO$=$HOMO$+E_g$.

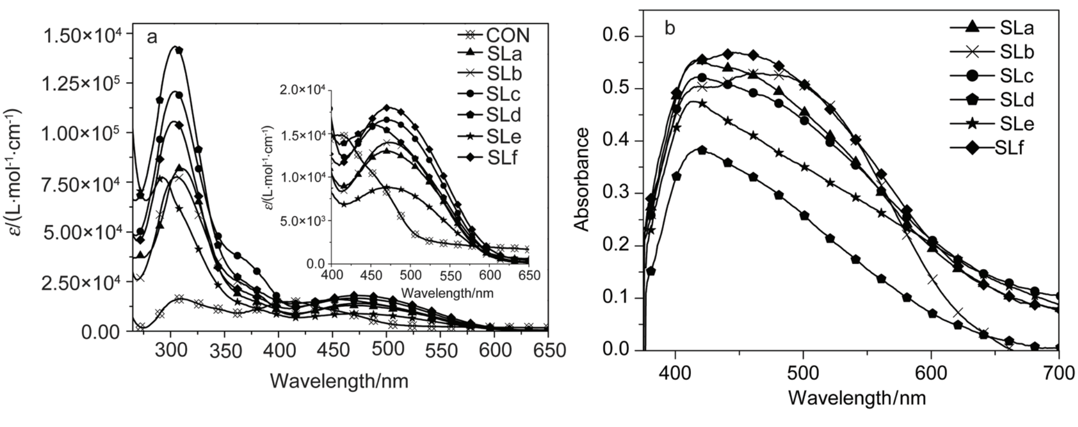


Figure 2 UV-vis absorption spectra of SL series dyes in THF (a) and on TiO_2 film (b).

above the conduction band minimum (CB) of TiO_2 (–4.26 eV). The highest occupied molecular orbital (HOMO) of the dyes is much higher than the valence band maximum (VB) of TiO_2 (–7.46 eV).

Photovoltaic performance of DSSCs

DSSCs with an effective area of 0.159 cm^2 were fabricated combined with a redox electrolyte composed of 0.6 mol/L 1-butyl-3-methylimidazolium iodide (BMII), 0.05 mol/L LiI, 0.03 mol/L I_2, 0.5 mol/L 4-*tert*-butylpyridine, and 0.1 mol/L guanidinium thiocyanate in a mixture of acetonitrile and valeronitrile (85/15, *V*/*V*). Photovoltaic characteristics of the DSSCs based on the six dyes as well as the standard N719 dye under standard global AM1.5G solar irradiation condition (100 mW/cm^2) are exhibited in Table 2.

Table 2 Photovoltaic performance of DSSCs based on SL dyes

Sensitizer	$V_{oc}{}^b$/V	J_{sc}/(mA•cm^{-2})	FF/%	η/%
SLa	0.55	0.91	56.5	0.28
SLb	0.52	0.55	67.5	0.19
SLc	0.58	1.08	61.5	0.39
SLd	0.60	1.32	62.4	0.50
SLe	0.56	1.52	70.4	0.60
SLf	0.62	1.85	70.5	0.81
N719	0.75	13.2	64.1	6.35

The incident photon to current conversion efficiency (IPCE) spectra of the devices based on each dye, which is directly related to the short-circuit current, reveals one obvious band in the spectral region ranging from 400 to 800 nm. Figure 3 indicated the IPCE spectra of SLa, SLe and SLf, among which SLa showed the worst result. When the substituted branch R group increased to C-8, the IPCE of cell sensitized by SLe enhanced almost double in all range of solar spectrum implying the less back current inhibited by the C-8 branches under the similar absorption spectra/light harvesting. And the alkyl groups regarded as spatial hindrance chains on the sp^3-carbon bridge of the core could mitigate undesirable dye aggregation. In contrast, the IPCE of cell sensitized by SLf was higher than that of SLa and lower than that of SLe in the range of visible light.

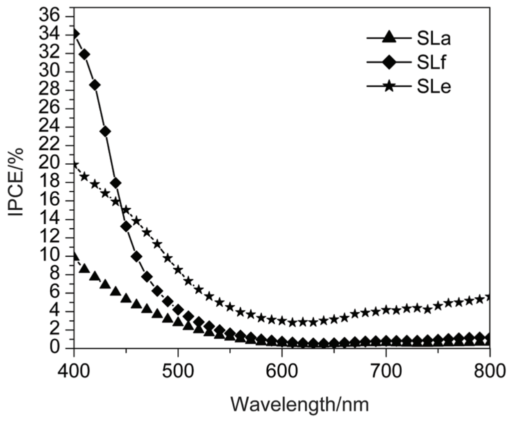


Figure 3 IPCE of DSSCs sensitized with SL series dyes.

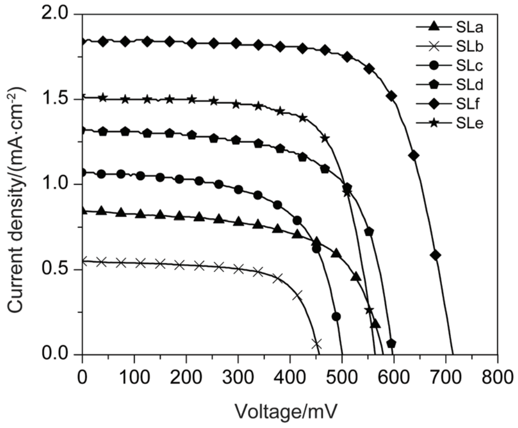


Figure 4 *J-V* curves of DSSCs sensitized with SL series dyes.

The short circuit photocurrent density and overall conversion efficiency of DSSCs sensitized by the five dyes were in the following order: SLe > SLd > SLc > SLa > SLb. These phenomena were attributed to their abilities of prohibition for the back current from TiO_2 to the HOMO of dye molecule. When increasing the length of the alkyl substituents attaching on the donor part, the back current of the DSSC device reduced. Strangely, the device sensitized by SLf exhibited the highest J_{SC} value (0.81%) under the lower IPCE in the range of visible light. This phenomenum was attributed to its good electron injection from LUMO of exited dye molecules to the VB of TiO_2 *via* tetradentates anchoring group (Figure 5) and consistent with our recent results of diazoporphyrinZn dyes.[5c]

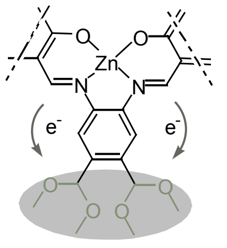


Figure 5 The sketch map of binding modes.

DFT calculations and energy levels

Geometries and energies of the stationary points found herein were fully optimized by hybrid density functional theory (DFT) utilizing the GAUSSIAN 09 program suite.[15] According to our calculations, the hybrid gradient corrected exchange functional of B3LYP was used.[16] The standardized 6-31G basis set was used together with the polarization (d) functions basis set[17] for all atoms except Zn that was depicted by the effective core potential LANL2DZ basis set.[18] The MO patterns of HOMO and LUMO of zinc Salen dyes were shown in Figure 6. Our DFT calculations demonstrated that the electrons staying in the frontier molecular orbital (HOMO) easily delocalized from the zinc Salen skeleton to the framework of benzene and the anchoring group of carboxylic acid (LUMO). Figure 7 displayed that the energy level of conduction band of TiO_2 was located between that of the LUMO and the HOMO of SalenZn dyes. These results confirmed that the electron injection from the LUMO of dyes to the conduction band of TiO_2 was quite available.

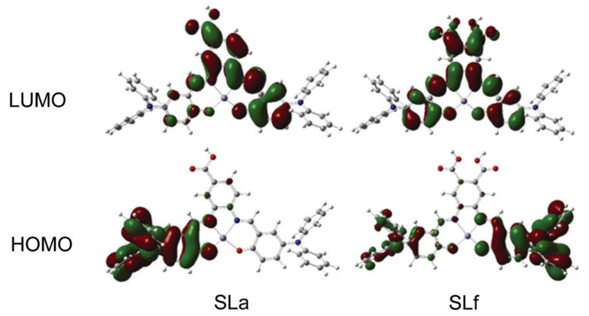


Figure 6 Molecular orbitals of SLa and SLf.

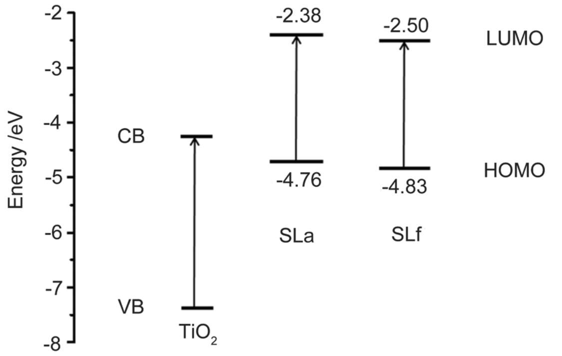


Figure 7 Energy-level diagram of dyes and anatase TiO_2.

Conclusions

In summary, we synthesized a class of sensitizers for DSSCs by developing Schiff-base zinc complexes as an essential π-spacer in the D-π-A structure. Their physical properties and device performances were tested and evaluated by means of integration of the conventional triarylamine derivatives as donor and benzoic acid as accepter, and the SalenZn complexes as π-spacer. Even though the photoelectric conversion efficiency of our devices of DSSCs was not satisfying, we found that when the second carboxyl group was introduced to the framework of SalenZn dyes, not only the electron injection efficiency increased, but also the open voltage of DSSC augmented. We believe these results are sufficiently indicative for the further development of these series metal-based dyes.

Acknowledgement

The authors acknowledge the financial support of this work from the National Natural Science Foundation of China (No. 21173106) and the Foundation of State Key Laboratory of Coal Conversion (No. J14-15-913-1).

References

[1] O'Regan, B.; Grätzel, M. *Nature* **1991**, *353*, 737.

[2] (a) Koumura, N.; Wang, Z.-S.; Mori, S.; Miyashita, M.; Suzuki, E.; Hara, K. *J. Am. Chem. Soc.* **2006**, *128*, 14256; (b) Nattestad, A.; Mozer, A. J.; Fischer, M. K. R.; Cheng, Y. B.; Mishra, A.; Bauerle, P.; Bach, U. *Nat. Mater.* **2010**, *9*, 31; (c) Clifford, J. N.; Martinez-Ferrero, E.; Viterisi, A.; Palomares, E. *Chem. Soc. Rev.* **2011**, *40*, 1635; (d) Bessho, T.; Zakeeruddin, S. M.; Yeh, C. Y.; Diau, E. W. G.; Grätzel, M. *Angew. Chem.*, *Int. Ed.* **2010**, *49*, 6646; (e) Wang, H.; Zhang, X.; Gong, F.; Zhou, G.; Wang, Z.-S. *Adv. Mater.* **2012**, *24*, 121; (f) Kimura, M.; Nomoto, H.; Masaki, N.; Shogo Mori, S. *Angew. Chem.*, *Int. Ed.* **2012**, *51*, 4371; (g) Wu, K. L.; Li, C.-H.; Chi, Y.; Clifford, J. N.; Cabau, L.; Palomares, E.; Cheng, Y.-M.; Pan, H. A.; Chou, P. T. *J. Am. Chem. Soc.* **2012**, *134*, 7488.; (h) Liu, Q. P.; Huang, H. J.; Zhou, Y.; Duan, Y. D.; Sun, Q. W.; Lin, Y. *Acta Phys.-Chim. Sin.* **2012**, *28*, 591; (i) Zhu, J.; Yu, X. C.; Wang, S. M.; Dong, W. W.; Hu, L. H.; Fang, X. D.; Dai, S. Y. *Acta Phys.-Chim. Sin.* **2013**, *29*, 533.

[3] Chen, J. Z.; Li, B.; Zheng, J. F.; Zhao, J. H.; Jing, H. W.; Zhu, Z. P. *Electrochim. Acta* **2011**, *56*, 4624.

[4] (a) Nazeeruddin, M. K.; De Angelis, F.; Fantacci, S.; Selloni, A.; Viscardi, G.; Liska, P.; Ito, S.; Takeru, B.; Grätzel, M. G. *J. Am. Chem. Soc.* **2005**, *127*, 16835; (b) Gao, F. F.; Wang, Y.; Shi, D.; Zhang, J.; Wang, M. K.; Jing, X. Y.; Baker, R. H.; Wang, P.; Zakeeruddin, S. M.; Grätzel, M. *J. Am. Chem. Soc.* **2008**, *130*, 10720.

[5] (a) Yella, A.; Lee, H. W.; Tsao, H. N.; Yi, C.; Chandiran, A. K.; Nazeeruddin, M. K.; Diau, E. W. G.; Yeh, C. Y.; Zakeeruddin, M. K.; Grätzel, M. *Science* **2011**, *334*, 629; (b) Wu, C. H.; Chen, M. C.; Su, P. C.; Kuo, H. H.; Wang, C. L.; Lu, C. Y.; Tsai, C. H.; Wu, C. C.; Lin, C. Y. *J. Mater. Chem. A*: *Mater. Energy Sustain.* **2014**, *4*, 991; (c) Zeng, Z.; Zhang, B.; Li, C. J.; Peng, X.; Liu, X. J.; Meng, S. X.; Feng, Y. Q. *Dyes Pigments* **2014**, *100*, 278; (d) Gou, F. L.; Jiang, X.; Li, B.; Jing, H. W.; Zhu, Z. P. *ACS Appl. Mater. Interfaces* **2013**, *5*, 12631.

[6] (a) Liu, X. S.; Cao, Z. C.; Huang, H. L.; Liu, X. X.; Tan, Y. Z.; Chen, H. J.; Pei, Y.; Tan, S. T. *J. Power Sources* **2014**, *248*, 400; (b) Alexis, T.; Vivek, D.; Alejandro, O.; Braulio, I.; Nazario, M.; Luis, E. *Solar Energy Mater. Solar Cells* **2014**, *121*, 61; (c) Ning, Z.; Zhang, Q.; Pei, H.; Luan, J.; Lu, C.; Cui, Y.; Tian, H. *J. Phys. Chem. C* **2009**, *113*, 10307; (d) Zeng, W.; Cao, Y.; Bai, Y.; Wang, Y.; Shi, Y.; Zhang, M.; Wang, F.; Pan, C.; Wang, P. *Chem. Mater.* **2010**, *22*, 1915.

[7] (a) Grätzel, M. *J. Photochem. Photobiol.* **2004**, *168*, 235; (b) Zhang, G. L.; Bala, H.; Cheng, M. Y.; Shi, D.; Lv, X. J.; Yu, Q. J.; Wang, P. *Chem. Commun.* **2009**, 2198.

[8] Chen, Z.; Li, F.; Huang, C. *Curr. Org. Chem.* **2007**, *11*, 124.

[9] (a) Lu, X. B.; Darensbourg, D. J. *Chem. Soc. Rev.* **2012**, *41*, 1462; (b) Yan, P.; Jing, H. W. *Adv. Synth. Catal.* **2009**, *351*, 1325; (c) Xia, J. B.; Yang, H.; Li, F. Y.; Huang, C. H. *Chem. J. Chin. Univ.* **2006**, *27*, 204 (in Chinese).

[10] (a) Germain, M. E.; Knapp, M. J. J. *J. Am. Chem. Soc.* **2008**, *130*, 5422; (b) Dalla, C. A.; Mandolini, L.; Pasquini, C.; Rissanen, K.; Russo, L.; Schiaffino, L. *New. J. Chem.* **2007**, *31*, 1633.

[11] Gianneschi, N. C.; Nguyen, S. T.; Mirkin, C. A. *J. Am. Chem. Soc.* **2005**, *127*, 1644.

[12] (a) Mizukami, S.; Houjou, H.; Nagawa, Y.; Kanesato, M. *Chem. Commun.* **2003**, 1148; (b) Kleij, A. W.; Kuil, M.; Tooke, D. M.; Spek, A. L.; Reek, J. N. H. *Inorg. Chem.* **2007**, *46*, 5829.

[13] (a) Tan, R.; Yin, D. H.; Yu, N. H.; Tao, L.; Fu, Z. H.; Yin, D. L. *J. Mol. Catal. A*: *Chem.* **2006**, *259*, 125; (b) Tucker, N. T. *Ph. D. Dissertation*, Universtiy of Washington, Washington, **2008**, p. 56.

[14] Barbe, C. J.; Arendse, F.; Comte, P.; Jirousek, M.; Lenzmann, F.; Shklover, V.; Grätzel, M. *J. Am. Ceram. Soc.* **1997**, *80*, 3157.

[15] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09*, Revision A. 01, Gaussian, Inc., Wallingford, CT, **2009**.

[16] (a) Becke, A. D. *J. Chem. Phys*. **1993**, *98*, 5648; (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

[17] (a) Rassolov, V. A.; Ratner, M. A.; Pople, J. A.; Redfern, P. C.; Curtiss, L. A. *J. Comp. Chem.* **2001**, *22*, 976; (b) Rassolov, V. A.; Pople, J. A.; Ratner, M. A.; Windus, T. L. *J. Chem. Phys*. **1998**, *109*, 1223.

[18] (a) Hay, P. J.; Wadt, W. R. *J. Chem. Phys*. **1985**, *82*, 270; (b) Wadt, W. R.; Hay, P. J. *J. Chem. Phys*. **1985**, *82*, 284; (c) Hay, P. J.; Wadt, W. R. *J. Chem. Phys*. **1985**, *82*, 29.

(Cheng, F.)