

Research Article

Separation of Functionalized 5,6-Disubstituted-1,10-Phenanthroline for Dye-Sensitized Solar Cell Applications

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5,6-Epoxy-1,10-phenanthroline is used as a convenient starting material for 5-hydroxy-6-Aryl-1,10-phenanthroline ligands containing carboxylic and sulfonic groups useful for further anchoring of the sensitizer on TiO₂ for dye-sensitized solar cells (DSCs). Based on the crystal growth of the mixture of products, a convenient separation route for the extension of the p-system on 5,6-disubstituted-1,10-phenanthroline was used to develop a novel series of functionalized 1,10-phenanthroline ligands with electron-withdrawing end-capping group. Also, we report the epoxy opening of 5,6-epoxy-1,10-phenanthroline by aromatic amines stoichiometrically in refluxing water and ethanol in the absence of any catalyst. The dyes were characterized by ¹H-NMR, FT-IR, UV-Vis, and X-ray single crystal diffraction analyses. It crystallizes in the monoclinic space group *C* 2/c, *a* = 20.920(4) Å, *b* = 10.340(2) Å, *c* = 16.187(3) Å, β = 92.30(3)°, *V* = 3498.6(12) Å³, and *Z* = 8. The reaction details and features were described in detail.

1. Introduction

The dye-sensitized nanocrystalline solar cell (DSC) offers special opportunities in the realm of renewable energy sources primarily stemming from its use of low-cost materials and its lack of stringent conditions required for device manufacturing [1]. In a dye-sensitized cell, the immobilization of the sensitizer on the nanocrystalline TiO₂ surface allows efficient electronic communication between the light-harvesting center and the semiconductor substrate. The immobilization of the sensitizer is achieved by attaching anchoring groups (e.g., carboxylate [2, 3], sulfonate [4, 5], salicylate [6], phosphonate [7–9], carbonyl [10, 11], catechol [12], and acetyl acetate groups [13]) to the surfaces of the mesoporous TiO₂ nanoparticles [14]. To further increase the performances of dye-sensitized solar cell, it is of paramount importance to engineer ligands at a molecular level and thus to endow sensitizers with both panchromatic absorption and a relatively high molar extinction coefficient. Therefore, to

accelerate the discovery and improvement of better performing sensitizers, easily accessible strategies for the functionalization of 2,2-bipyridyl (bpy) or 1,10-phenanthroline (phen) derivatives are required [15]. A distinct property of this class of chelating agents, phen and bpy, in particular, is their π electron deficiency that makes them excellent π acceptors capable of stabilizing metal ions in lower oxidation states. Furthermore, due to the presence of low-energy π^* orbitals of the ligand, metal complexes can be characterized by strong metal-to-ligand charge-transfer (MLCT) absorption bands in the visible spectrum and red-shifted fluorescent emissions [13–17] which is indicated as suitable ligand for dye-sensitized solar cell application. Due to the combination in phen of these distinct structural and chemical properties, the increasing interest in the chemistry of phen derivatives has prompted the development of efficient synthetic procedures for the chemical fictionalization of the phen nucleus at the various ring positions [18]. The 5- and 6-positions of phen are the most susceptible to electrophilic

substitutions. Reaction with commercial bleach under phase-transfer conditions can afford, in good yield, 5,6-epoxy-1,10-phenanthroline which represents a good intermediate for functionalization of the 5-position of phen with different binding sites for analytes [18]. In this paper, we report such an efficient synthetic route for the preparation of a series of symmetrically 5,6-disubstituted-1,10-phenanthroline being end-capped by electron-withdrawing groups. This end-capping diversity will allow us to tune the photophysical properties of the corresponding Ru-based sensitizers in a rational manner.

2. Experimental

All chemicals and solvents were purchased from Merck & Aldrich and used without further purification. IR spectra were recorded on a Perkin-Elmer 597 spectrometer and ^1H -NMR spectra were recorded by using a Bruker 250 MHz spectrometer.

The X-ray diffraction measurements were made on a STOE IPDS-II diffractometer with graphite monochromated Mo-K α radiation. Cell constants and orientation matrices for data collection were obtained by least-squares refinement of diffraction data from 4711 unique reflections. Data were collected to a maximum 2θ value of 58.5° in a series of ω scans in 1° oscillations and integrated using the Stoe X-Area [19] software package. The data were corrected for Lorentz and Polarizing effects. The structures were solved by direct methods [20] and subsequent difference Fourier maps and then refined on F^2 by a full-matrix least-squares procedure using anisotropic displacement parameters [21]. All hydrogen attached to carbon atoms were added in idealized positions and hydrogen atoms of the water molecule, NH and NH $_2$ group were found in difference Fourier map. All refinements were performed using the X-STEP32 crystallographic software package [22]. A summary of crystal data, experimental details, and refinement results is given in Table 1.

For the synthesis of 5,6-epoxy-1,10-phenanthroline, 1 mmol (198 mg) of phenanthroline, dissolved in 20 mL of chloroform, is added to 250 mL of 0.6 M aqueous sodium hypochlorite (commercial bleach), the pH of which has been adjusted to 8.5 with concentrated HCl. Tetrabutylammonium hydrogen sulfate (0.2–1 equiv) is added and the mixture is stirred at room temperature until TLC indicates that all of the phenanthroline has reacted. The layers are separated and the organic layer is washed with a large excess of cold water, dried, and evaporated at room temperature. The crude epoxide was purified by recrystallization from a mixture of chloroform and hexanes (5:1) to give a product [23]. For synthesis of L_1 , the phenanthroline 5,6-epoxide (100 mg, 0.5 mmol) and 4-amino-benzenesulfonic acid (A) (88.53 mg, 0.5 mmol) were taken in a mixture of water and methanol (50 ml) and refluxed for 14 h. After evaporation at room temperature, orange and yellow crystals were appeared. For synthesis of L_2 1,10-phenanthroline-5,6-epoxide (L) (100 mg, 0.5 mmol) was dissolved in 30 ml of methanol which contained 109 mg (0.5 mmol) of 2-phenylamino-benzoic acid

TABLE 1: Crystal data and structure refinement for C $_{18}$ H $_{17}$ N $_3$ O $_4$ S (L_1) at 298 K.

Molecular formula	C $_{18}$ H $_{17}$ N $_3$ O $_4$ S
Molecular weight	371.42
Temperature (K)	298 (2)
Radiation λ (Å)	0.71073
Crystal system	Monoclinic
Space group	C 2/c
$a/\text{Å}$	20.920(4)
$b/\text{Å}$	10.340(2)
$c/\text{Å}$	16.187(3)
β ($^\circ$)	92.30(3)
$V/\text{Å}^3$	3498.6(12)
Z	8
D_{calc} (g cm $^{-3}$)	1.410
Crystal size (mm)	$0.25 \times 0.17 \times 0.15$
Crystal colour	Yellow
Absorption coefficient (mm $^{-1}$)	0.215
$F(000)$	1552
Reflections collected/unique	18828/4711
θ range ($^\circ$)	1.95–29.25
Number of parameters	253
Number of restraints	0
Goodness of fit on F^2	1.141
R_1, wR_2 [$I \geq 2\sigma(I)$]	0.0767, 0.1530
R_1, wR_2 (all data)	0.1314, 0.1775
Largest difference peak and hole	0.302, –0.238

(B). The reactants were refluxed for 14 h. Again, orange and white were yielded.

3. Results and Discussion

Reaction of 5,6-epoxy-1,10-phenanthroline with a variety of nucleophiles results in hydroxy-dihydro intermediates that upon dehydration can afford not only 5-substituted phen derivatives useful for further manipulations but also interesting ditopic ligands featuring the phen nucleus derivatized at the 5-position with chelating groups [18]. Based on experimental results, the opening of the strained three-membered epoxy ring usually occurs in nonaqueous media in presence of a Lewis acid catalyst like Al $_2$ O $_3$, Li $^+$, Mg $^{2+}$ [24]. Additionally often elevated temperature and excess of nucleophiles are required. There are a few reports where the use of a catalyst has not been necessary [25, 26]. For example, aminolysis of epoxide by an α -amino acid ester proceeds smoothly in refluxing trifluoroethanol [25]. The same reactions fail in water. Azizi and Saidi found that the aliphatic and aromatic amines cleave an epoxide ring in water at room temperature without any Lewis acid catalyst [26].

Herein, aminolysis of 5,6-epoxy-1,10-phenanthroline is potential in generating two products. We obtained phen as a minor product also in the reaction of epoxide with aniline group in the standard conditions for preparation of L_1 and

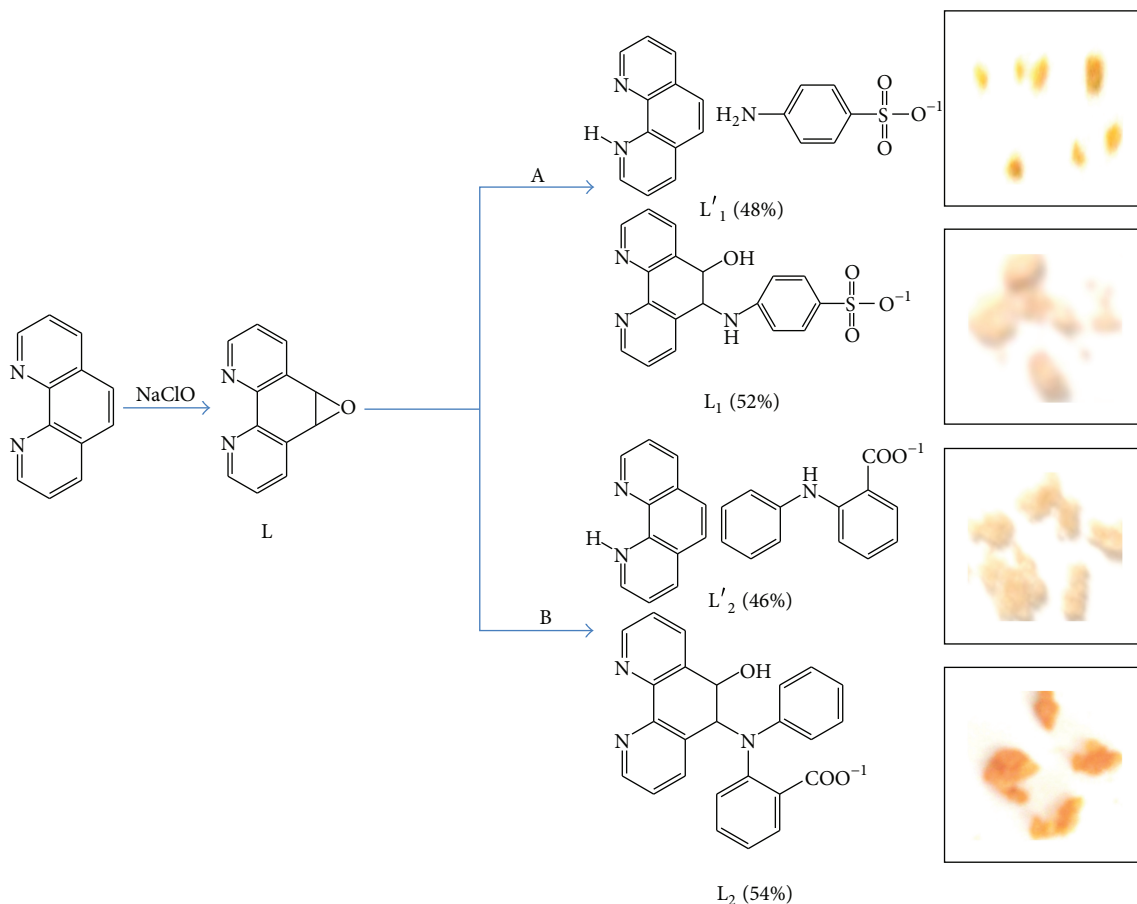


FIGURE 1: Molecular structure of the investigated ligands and the procedure of reactions.

L'_1 (Figure 1). A plausible mechanism for the deoxygenation may include formation and subsequent denitrogenation of L'_1 and L'_2 . The easy denitrogenation at room temperature that we found was apparently stimulated by the aromatization of the central ring as in the case of reactions. Apparently, aromatization of the central ring is a driving force for this elimination [27].

Also, the epoxide ring in 5,6-epoxy-1,10-phenanthroline opens up in its reaction with 4-sulfonfyl aniline and 2-[(6-hydroxy)-phenyl-amino]-benzoic acid in water and methanol without any Lewis acid catalyst to give a monohydrate of and 4-(6-hydroxy-5,6-dihydro-[1,10]phenanthro-lin-5-yl-amino)-benzenesulfonic(L_1) acid and 2-[(6-hydroxy-5,6-dihydro-[1,10]phenanthrolin-5-yl)-phenyl-amino]-benzoic acid(L_2), respectively (Figure 1).

As shown in Figures 2 and 3, the main absorption peaks in the IR spectra of compounds are determined. Generally, in the IR spectrum of the phen, strong bands were observed in frequency region between 1400 and 1650 cm^{-1} , the one band occurring at 1505 cm^{-1} , the second appearing at 1590 cm^{-1} , and the third band at 1423 cm^{-1} . In the present study, IR

spectra of L_1 and L_2 show $\nu(\text{C-N})$ band related to phen, at 1422 and 1420 cm^{-1} , respectively, indicating the partial double bond character. The ring frequencies associated with phen are observed at 1497 , 1601 cm^{-1} and 1509 , 1594 cm^{-1} , for L_1 and L_2 . The $\nu(\text{C-H})$ of phen bands appear at 2876 , 2946 , 2965 cm^{-1} and 2885 , 2941 , 2970 cm^{-1} , respectively. The (A) compound actually has the zwitterions structure that contains the $-\text{NH}_3^+$ and $-\text{SO}_3^-$ groups. In the IR spectrum of L_1 , there are a number of bands between 2735 cm^{-1} and 2735 cm^{-1} due to combination bands of the NH_3 group. The CH stretching vibration of anilinic ring is observed at 2883 , 2905 , and 2921 cm^{-1} [28]. The $\nu(\text{ph})$ vibrations are observed at 1601 , 1578 , 1547 , 1422 , and 1319 cm^{-1} . Bands at 1173 , 1037 , 684 , and 561 cm^{-1} derive from presence of SO_3 . The vibration band at 1037 is characteristics of the vibrations of the sulfur atoms linked to the aromatic cycle and of S=O symmetric [29]. The asymmetric S=O vibration is observed at 1173 cm^{-1} . It is important to note, the disappearance of $\nu(\text{NH}_2)$ stretching frequency of amine group and appearance of $\nu(\text{NH})$ stretching at 3445 cm^{-1} in the IR spectrum of L_1 reveals the formation of L_1 (Figure 2).

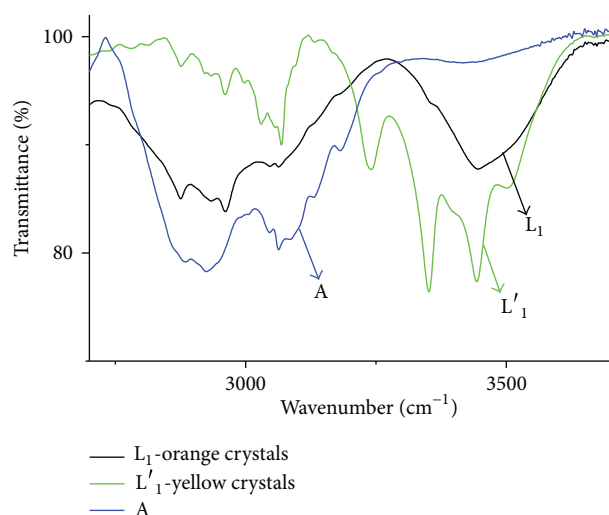


FIGURE 2: FT-IR spectra of L_1 , L'_1 , and (A) ligands.

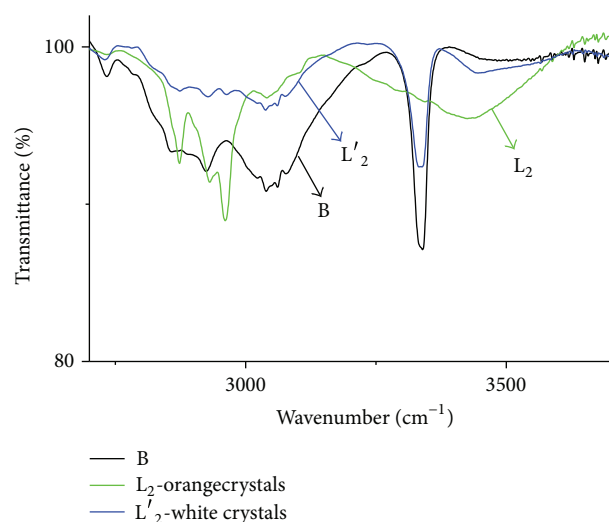


FIGURE 3: FT-IR spectra of L_2 , L'_2 , and (B) ligands.

Two significant vibrations at 1659 and 1262 occur in IR spectrum of L_2 . The band at 1659 cm^{-1} is attributed to the C=O stretching vibration of the carboxyl group and that 1259 cm^{-1} can be ascribed to the C-N stretching vibration. The N-H stretching vibration at 3339 cm^{-1} was removed. These results suggest that (B) was linked to L (Figure 3).

The UV-Vis absorption spectra of the compound in ethanol solution are given in Figures 4 and 5. Phen is characterized in aqueous solution by UV absorption at 229 and 265 nm, the latter attributed to π - π^* transition to the lowest-energy excited singlet state, π - π^* . The absorption band at 230 nm of L_1 and 229 nm of L'_1 are the characteristic of the phen. The absorption band of L_1 at 265 nm shows blue shift to 255, may be due to being overlapped with that of (A) at 249 nm.

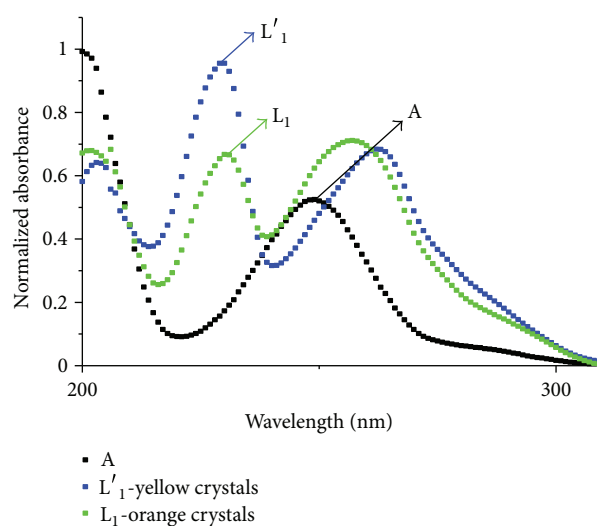


FIGURE 4: Normalized absorption spectra of L_1 , L'_1 , and (A) ligands.

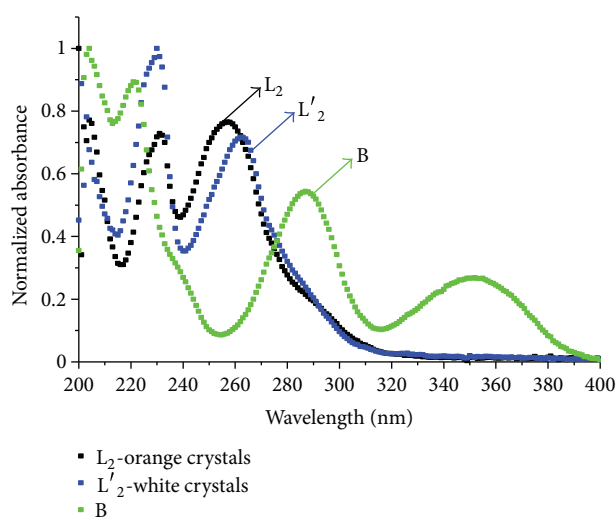


FIGURE 5: Normalized absorption spectra of L_2 , L'_2 , and (B) ligands.

In the UV-Vis spectra of L_2 and L'_2 , two absorption bands were observed at 230, 257 nm and 229, 262 nm, respectively. These bands are characterized to the π - π^* transition of the phen rings. But the band at 265 nm, due to the lowest-energy singlet state, shifts to 257 nm in spectrum of L_2 . These absorption bands are good evidence for presence of L in the product. In ^1H NMR spectra of L_1 , the protons of phen give signals at 8.06, 8.87, and 9.21 ppm which are slightly deshielded. The signal observed at 7.4 ppm is assigned to the H_f present in L_1 . Other proton of anilinc ring, H_e , is slightly shielded and is observed in the upfield region at 6.76 ppm. These observed changes show the formation of L_1 as shown in Figure 5.

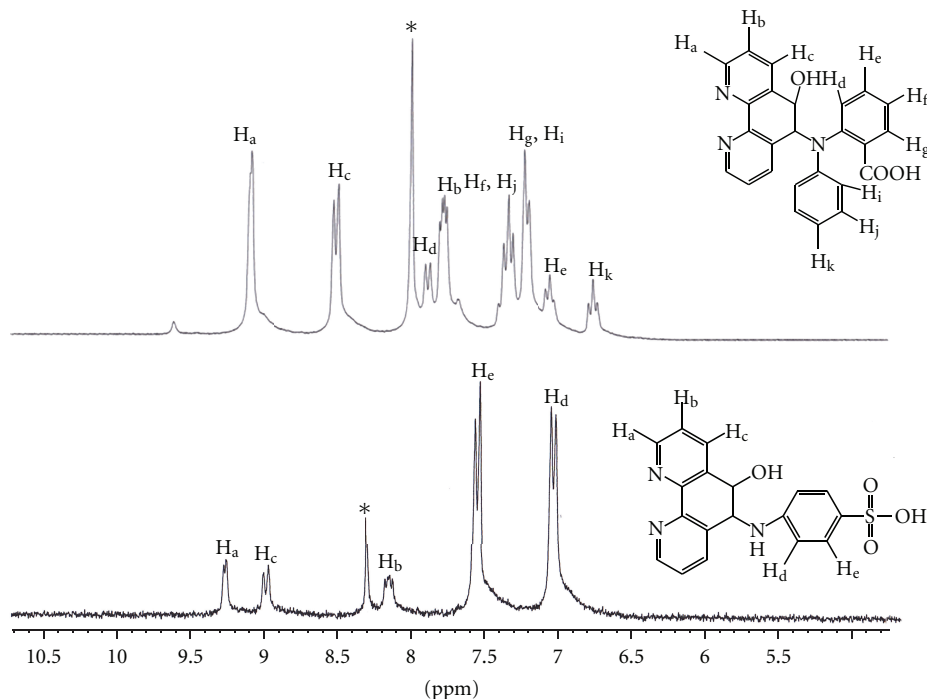


FIGURE 6: ^1H -NMR spectra of aromatic region of L_1 and L_2 dissolved in DMSO solvent at room temperature.

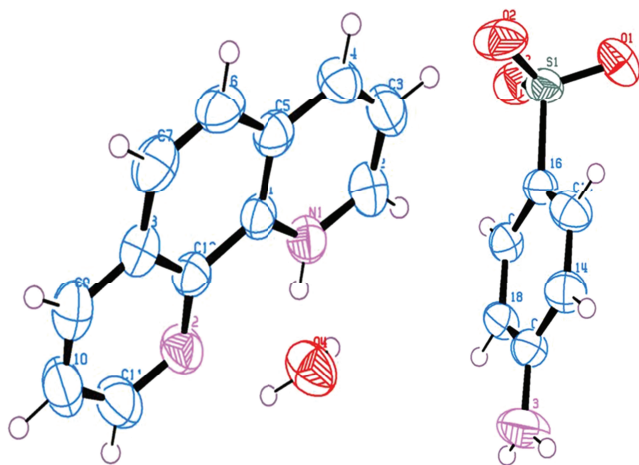


FIGURE 7: ORTEP of L_1' with the numbering scheme. Thermal ellipsoids are at the 50% probability level.

For L_2 , ^1H NMR signals around 7.77, 8.48, and 9.08 ppm arise from the phen protons (Figure 6). The signals of H_d are deshielded due to the SO_3 group and observed at 7.86 ppm. The proton signals of the H_g , H_i and H_f , H_j appear at 7.20 and 7.31 ppm, respectively. The signals at 6.75 and 7.05 ppm are associated to H_e and H_k . All of these signals indicate that the production of L_2 is occurred.

The molecular structure of L_1' and the atom-numbering scheme are shown in Figure 7.

There are $\text{C-H}\cdots\pi$ interactions and also different weak hydrogen bonds (Table 2), stabilizing the three-dimensional

crystal structure. Significant π - π interactions are found in the crystal structure.

To gain further insight into the electron density distribution within the frontier and other close lying orbitals, we performed quantum chemical calculations on the L_1 using density functional theory (DFT) as shown in Figure 8. The simulations have been performed with the Gaussian 09 program. The level of LAN L2DZ was carried out. In the dye-sensitized solar cells, the LUMO of the dye must be sufficiently high in energy to promote efficient charge injection into the semiconductor film and the HOMO should be sufficiently low in energy for efficient regeneration of the oxidized dye by the hole transport material. Figure 8 shows schematic representation of frontier orbitals of L_1 , along with isodensity plots of HOMO, HOMO^{-1} and LUMO, LUMO^{+1} orbitals. Here, the chemical structures of the phen and amino benzene sulfonic acid have an important effect on the electronic properties of the L_1 . The L_1 presents a HOMO-LUMO energy gap of 4.48 eV significantly larger than the gap calculated for many dye-sensitized solar cell. In the ground state, the electron density of L_1 for the highest occupied molecular orbital (HOMO) and HOMO^{-1} is shared by the phenyl moiety of phen and amino benzene sulfonic group. Whereas the LUMO resides on the phen for L_1 and shows no overlap with the amino benzene sulfonic group. The predicted effect is an increase of the HOMO-LUMO gap of L_1 , which is in good agreement with the experimental observations. As shown in the figures, these energy levels are able to inject energetic electrons into the conduction band of TiO_2 .

Further work on the photovoltaic performance of 5,6-functionalized 1,10-phenanthroline is in progress, and

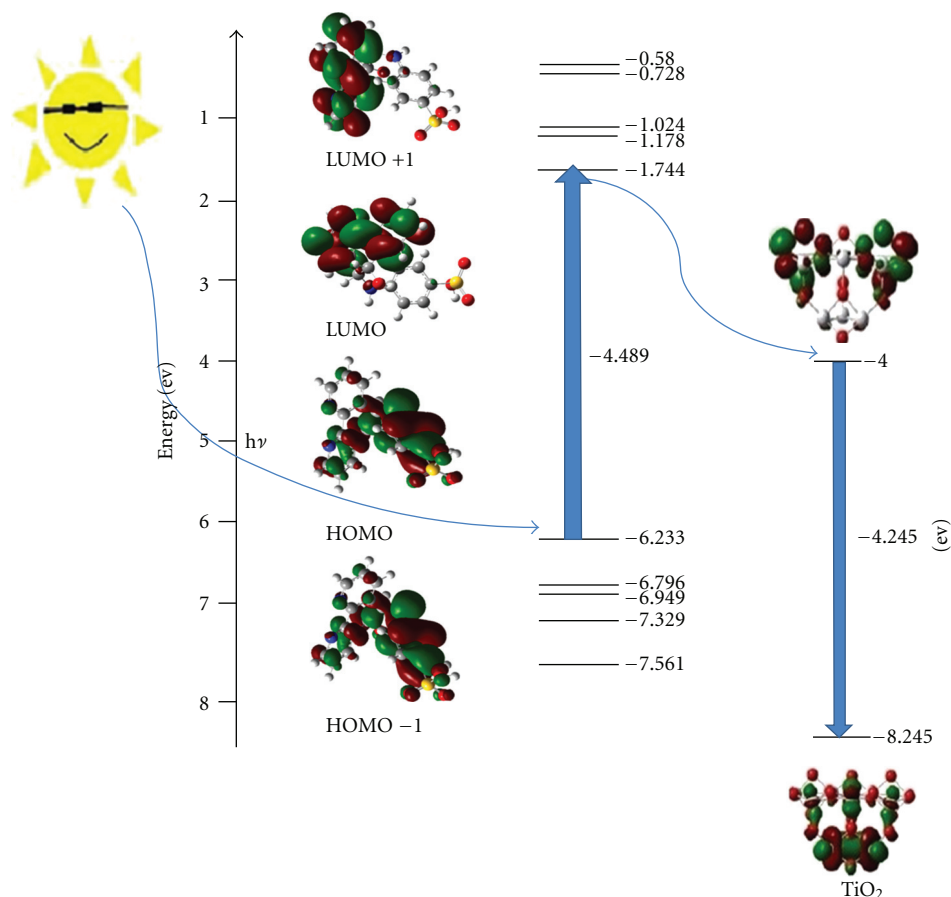


FIGURE 8: Schematic representation of frontier orbitals of L_1 , along with isodensity plots of HOMO, HOMO -1 and LUMO, LUMO +1 orbitals.

TABLE 2: Hydrogen bond parameters for L_1 [\AA and deg.].

D-H...A	$d(\text{D-H})$	$d(\text{H}\cdots\text{A})$	$d(\text{D}\cdots\text{A})$	$\angle(\text{DHA})$
N(1)-H(1A)...O(4)	0.89(3)	1.88(3)	2.721(4)	157(3)
N(3)-H(3A)...O(2)#1	0.76(4)	2.32(4)	2.939(4)	139(4)
N(3)-H(3B)...O(2)#2	0.93(7)	2.12(7)	3.027(5)	166(6)
O(4)-H(4A)...O(1)#3	0.90(6)	2.12(6)	2.929(4)	149(4)
O(4)-H(4B)...O(1)#4	0.79(5)	2.06(5)	2.848(4)	171(5)
C(2)-H(2)...O(3)#4	0.93	2.25	3.168(4)	169.3
C(4)-H(4)...O(2)#5	0.93	2.41	3.321(4)	165.4

Symmetry transformations used to generate equivalent atoms:

#1 $-x + 1/2, y - 1/2, -z + 1/2$; #2 $x, -y + 1, z + 1/2$; #3 $x - 1/2, y - 1/2, z$
 #4 $-x + 1/2, -y + 1/2, -z$; #5 $-x + 1/2, -y + 3/2, -z$.

we believe improvements can be achieved by a thorough optimization of ruthenium complexes with respect to, for example, other functionalized 5,6-functionalized 1,10-phenanthroline.

4. Conclusion

In summary, two new symmetrically 5,6-functionalized 1,10-phenanthroline bidentate ligands have been synthesized from

5,6-epoxy-1,10-phenanthroline and carboxyl and sulfonyl aryl ligands. This easy and convenient synthetic strategy allowed us to introduce either electron-withdrawing anchoring groups on the p-conjugated-phenanthroline core. Those ligands have potential for ruthenium sensitizer for dye-sensitized solar cells. ^1H NMR analysis revealed that all the new synthesized ligands were exclusively obtained. Synthesized dye can be relieved by disappeared amine group in FT-IR spectra. This simple synthetic approach is expected

to expedite the development of antenna-type ligands for ruthenium sensitizers.

Disclosure

Crystallographic data for the title compound has been deposited to the Cambridge Crystallographic Data Centre (CCDC no. 888674). Copies of available materials can be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge CB2 IEZ, UK.

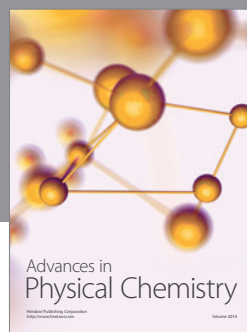
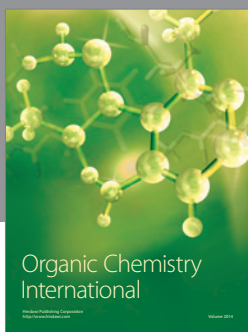
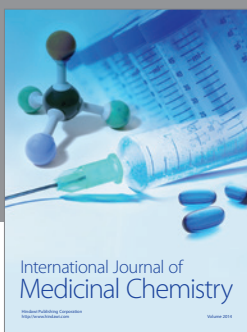
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