Taylor & Francis
Taylor & Francis Group

Molecular Crystals and Liquid Crystals

ISSN: 1542-1406 (Print) 1563-5287 (Online) Journal homepage: http://www.tandfonline.com/loi/gmcl20

Z-scan measurements and TDDFT study of the two-photon absorption properties of diaqua-bis(4-hydroxy-3-methoxybenzaldehyde)-cobalt(II)

Tingbin Li, Yali Hu, Chunlin Ma, Shenglai Wang & Dong Xu

To cite this article: Tingbin Li, Yali Hu, Chunlin Ma, Shenglai Wang & Dong Xu (2016) Z-scan measurements and TDDFT study of the two-photon absorption properties of diaqua-bis(4-hydroxy-3-methoxybenzaldehyde)-cobalt(II), Molecular Crystals and Liquid Crystals, 641:1, 71-77, DOI: 10.1080/15421406.2016.1246352

To link to this article: http://dx.doi.org/10.1080/15421406.2016.1246352

Published online: 15 Dec 2016.

MOLECULAR CRYSTALS AND LIQUID CRYSTALS
2016, VOL. 641, 71–77
http://dx.doi.org/10.1080/15421406.2016.1246352

Taylor & Francis
Taylor & Francis Group

Z-scan measurements and TDDFT study of the two-photon absorption properties of diaqua-bis(4-hydroxy-3-methoxybenzaldehyde)-cobalt(II)

Tingbin Li[a], Yali Hu[a], Chunlin Ma[b], Shenglai Wang[c], and Dong Xu[c]

[a]Department of Chemistry, Taishan University, Taian City, Shandong Province, People's Republic of China; [b]Department of Chemistry, Liaocheng University, Liaocheng City, Shandong Province, People's Republic of China; [c]State Key Lab of Crystal Materials, Shandong University, Jinan City, Shandong Province, People's Republic of China

ABSTRACT

A cobalt complex constructed by the ligand(L): 4-hydroxy-3-methoxybenzaldehyde $[Co(C_8H_7O_3)_2(H_2O)_2]$ has been synthesized and characterized by X-ray single crystal diffraction. The cobalt(II) atom is six-coordinate in a distorted octahedral geometry, intermolecular O-H•••O hydrogen bonds lead to the formation of a two-dimensional supramolecular network along ab plane. Its thermal stability was determined by TGA/DSC. Its two-photon absorption (TPA) cross-section σ_2 value and second hyperpolarizability γ value were determined to be 1.59×10^{-53} ($m^4 \cdot s$/photon $\cdot$ molecule) and 1.06×10^{-56} ($C \cdot m^4/V^3$) by Z-scan technique with 20 picosecond (ps) pulses at wavelength 1064 nm. The γ value is about six times larger than the time-dependent density-functional theory (TDDFT) calculation results.

KEYWORDS

chemical synthesis; crystal structure; differential scanning calorimetry (DSC); optical materials

Introduction

The prospect of applying the molecular level control inherent in organic and organometallic syntheses has motivated many chemists to pursue the development of new complex as new TPA materials, and many molecular organic and organometallic compounds are currently being studied intensively in an effort to identify materials with large TPA cross-sections for various optical limiting, fluorescence excitation microscopy and imaging, three-dimensional optical data storage and lithographic microfabrication, etc., applications [1,2]. Aromatic aldehydes-based complexes are highly π-conjugated molecules [3], to explore the TPA properties of this kind complexes, we synthesized and determined the single crystal structure of a cobalt(II) complex constructed by an aromatic aldehyde: diaqua-bis(4-hydroxy-3-methoxybenzaldehyde). Using Z-scan technique with 20 ps pulses at wavelength 1064 nm we studied its TPA properties and determined its γ value. Using TDDFT method we also theoretically calculated its γ value and reported in this letter.

CONTACT Tingbin Li tscltb@163.com Department of Chemistry, Taishan University, Taian City, Shandong Province 271021, People's Republic of China.

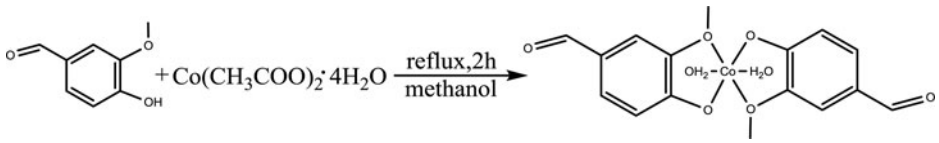
Color versions of one or more of the figures in the article can be found online at www.tandfonline.com/gmcl.

Experimental

All reagents and solvents were obtained commercially and used as supplied. The IR spectrum was recorded with Nicolet 6700 spectrometer in the region of 400–4000 cm^{-1} with KBr pellet technique. The linear absorption spectra in its methanol solution at the concentration of 1.21 $\times$ 10^{-5} mol/L was recorded at 20 °C with Helios Alpha spectrometer. TGA/DSC were performed on a Mettler-Toledo TGA/DSC/1100 instrument in the range 30–478 °C at a heating rate of 20 °C/min under continuous nitrogen purge.

Synthesis and recrystallization

$[Co(C_8H_7O_3)_2(H_2O)_2]$ was obtained by condensation of vanillin ($C_8H_8O_3$) and cobalt(II) acetate tetrahydrate ($Co(CH_3COO)_2{\cdot}4H_2O$) in methanol solution. Stoichiometric amounts of $C_8H_8O_3$ and $Co(CH_3COO)_2{\cdot}4H_2O$ are added to 20 mL of refluxing reagent grade methanol. After refluxing for 2 hr, the methanol was removed by distillation. The resulting red crystals are dried in vacuo. After chromatographic purification $[Co(C_8H_7O_3)_2(H_2O)_2]$ was obtained in 70% yield (Scheme 1). IR (cm^{-1}): $\tilde{\nu}$ = 3184.9, 3020.8, 1622.7, 1570.6, 1505.3, 1348.5, 1305.1, 1253.5, 1184.6, 1113.1, 1030.9, 985.3, 884.4, 836.2, 758.0, 656.5, 609.5.



Scheme 1. Synthesis of $[Co(C_8H_7O_3)_2(H_2O)_2]$.

X-ray crystallographic study

All measurements were made with a BRUKER SMART APEX II CCD X-ray diffractometer equipped with a graphite-monochromatic Mo-Kα radiation (λ = 0.71073 Å). All data were collected at 293 K using the ω-2θ scan technique. A total of 4701 reflections including 1815 independent ones (R_{int} = 0.0292, R_{sigma} = 0.0369) were collected in the range of 3.26 $\leq \theta \leq$ 25.54°, of which 1566 were observed with $I > 2\sigma(I)$ and used in the succeeding structure determination and refinements. Absorption corrections were applied using the SADABS program [4]. The structure was solved by direct methods and refined by full-matrix least-squares calculations for 116 parameters. All the calculations were carried out with SHELXL-97 program [5] with anisotropic thermal parameters for the non-hydrogen atoms. All hydrogen atoms were placed in the calculated positions and refined isotropically using a riding model. The final R = 0.037, ωR = 0.1217 ($\omega = 1/[\sigma^2(F_0^2) + (0.1000P)^2 + 0.00P]$ where $P = (F_0^2 + 2F_c^2)/3$) and $(\Delta/\sigma)_{max}$ = 0.001, $(\Delta\rho)_{max}$ = 0.29 and $(\Delta\rho)_{min}$ = −0.32 e/Å^3. CCDC-1402096 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html.

Nonlinear absorption properties measurements

The nonlinear absorption properties measurements were performed using single beam open aperture Z-scan technique [6]. The light source is a mode-locked Nd:YAG laser (Continuum Leopard D-10, 20 ps, 10 Hz, 1064 nm). The focal-length of the positive lens is f =

25 cm. The transmitted energy was measured with Molectron J3S-10 energy sensor in combination with EPM2000 2-Channel laser power and energy meter (Coherent Corp.) in the far field and a transmission of the sample is calculated by averaging 10 pulses. The concentration of the $[Co(C_8H_7O_3)_2(H_2O)_2]$'s methanol solution for the Z-scan measurements is 5.63×10^{-4} mol/L.

Computation details

The theoretical calculations of γ were performed with the Gaussian09 [7] package and Multiwfn [8]. The input file for Gaussian09 calculations was generated from the title compound's cif file by GaussView program. TDDFT with the B3LYP functional was used [9,10]. The basis set LanL2DZ associated with the effective core potentials were employed [11], and the nstates was designated as 150. The geometry was optimized at the B3LYP levels. The solvation effects were neglected. The optimized geometry was then used to carry out the TDDFT/B3LYP calculations. The output file of Gaussian09 calculation results was used by Multiwfn program to calculate the title compound's γ value.

Results and discussion

Crystal structure

Crystal data: Monoclinic, space group C2/c, $a = 22.321(3)$, $b = 10.4374(12)$, $c = 7.7958(9)$ Å, $\beta = 107.3728(18)°$, V = 1733.4(3) Å^3, $z = 4$, $F(000) = 820$. Fig. 1 shows $[Co(C_8H_7O_3)_2(H_2O)_2]$ molecule structure. The Co^{2+} cation is nearly octahedrally coordinated by four oxygen atoms from the methoxy and hydroxy groups of vanillinate anions and two oxygen atoms of water molecules. The Co-$O_{hydroxy}$, Co-$O_{methoxy}$ and Co-O_{water} bond distances are 1.9955(16), 2.2697(16) and 2.0468(16) Å, which are in the common range [12,13]. Fig. 2 shows its crystal packing diagram that viewed from the *c* axis. Hydrogen bonds calculations were carried out by PLATON program [14], as the results shown that there are two kinds of hydrogen bonds of type O4-H···O2 (2.736(3) Å) and O4-H···O1 (2.720(3) Å). These pairs formed a two-dimensional supramolecular network along ab plane.

Computed molecular orbitals and linear absorption spectra

Figure 3 shows the frontier molecular orbitals contours. The excitation of $[Co(C_8H_7O_3)_2(H_2O)_2]$ from HOMO (MO 58) to LUMO (MO 59) is 2.7998 eV. Fig. 4

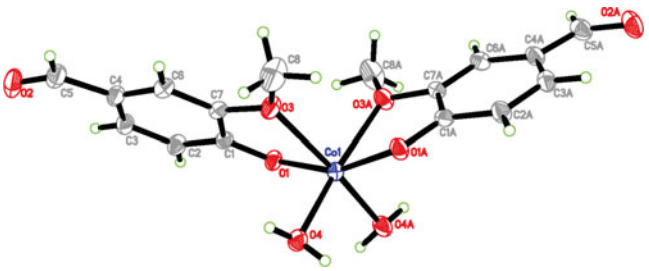


Figure 1. Molecule structure of $[Co(C_8H_7O_3)_2(H_2O)_2]$.

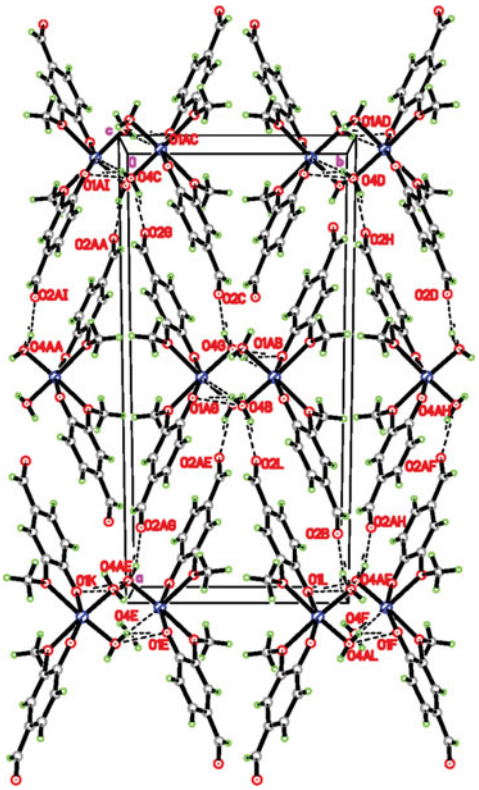


Figure 2. Crystal packing, viewed from the *c* axis. The $[Co(C_8H_7O_3)_2(H_2O)_2]$ molecules are connected by hydrogen bonds of type O4-H···O2 (2.736(3) Å) and O4-H···O1 (2.720(3) Å) into a two-dimensional supramolecular network along ab plane.

shows the linear absorption spectra, the λ_{max} is located around 418 nm, which is blue-shifted about 24.83 nm compared with TDDFT calculation results ($\lambda_{max} = 442.83$ nm).

Thermogravimetric analysis

Figure 5 shows its TGA-DSC curves. The overall weight loss is 76% in the TGA curves. The decrease in the TGA curves and exotherms in the DSC curves in the region of 194–243 °C may be due to its decomposition. TGA curve indicates that it decomposed in one step without

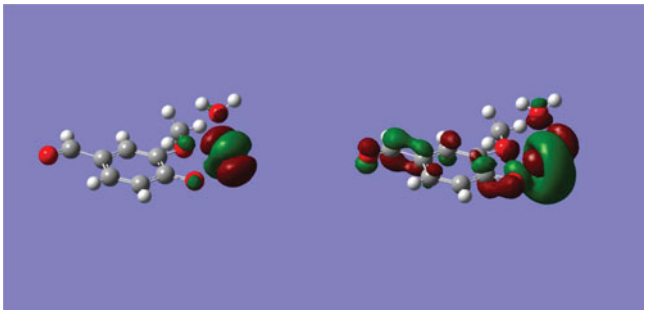


Figure 3. HOMO (left) and LUMO (right) contours (isovalue surface 0.02 a.u.) calculated at B3LYP/LanL2DZ level.

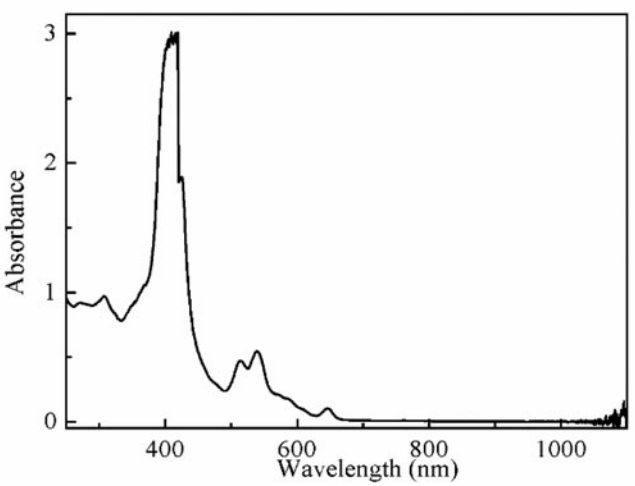


Figure 4. The linear absorption spectra of $[Co(C_8H_7O_3)_2(H_2O)_2]$ (methanol solution, 1.21×10^{-5} mol/L).

formation of stable intermediates. The endothermic peak around 158 °C in the DSC curve corresponds to the melting point.

Nonlinear absorption properties at 1064 nm

Figure 6(a) shows the intensity-dependent open aperture Z-scan study of the $[Co(C_8H_7O_3)_2(H_2O)_2]$'s solution in methanol, and the theoretical fitted results were shown in Fig. 6(b). The analysis methods were same as our previously reported methods [15,16]. The inset picture of Fig. 6(b) depicted the β as a function of focal intensity. From the plot, it can be seen that the β decreased linearly as the incident laser irradiance increased, this indicating that the nonlinear absorption process was not simply the results of a TPA process. Instead, it appears more likely that the nonlinear absorption was the results of a TPA process combined with saturable absorption (SA) process. A fit to the data gives an intercept of 2.88 cm/GW. This corresponds to the strictly TPA coefficient for $[Co(C_8H_7O_3)_2(H_2O)_2]$. Using this value, the TPA cross-section σ_2 for $[Co(C_8H_7O_3)_2(H_2O)_2]$ was determined to be 1.59×10^{-53} ($m^4 \cdot s$/photon × molecule) according equation: $\sigma_2 = \hbar\omega\beta/N$ ($m^4 \cdot s$/photon × *molecule*) where $\hbar\omega = 1.87 \times 10^{-19}$ J = 1.1652 eV is incident photon energy, N is the molecular number of the solute per unit volume (m^{-3}). The imaginary part of the third-order nonlinear susceptibility $\chi^{(3)}$ was determined to be 1.53×10^{-20} (SI) according equation: $\chi_I^{(3)} = (\varepsilon_0 n_0^2 c\lambda/3\pi)\beta$ (SI) where $\varepsilon_0 = 8.85 \times 10^{-12}$ $c^2/N \times m^2$ is the electric permittivity

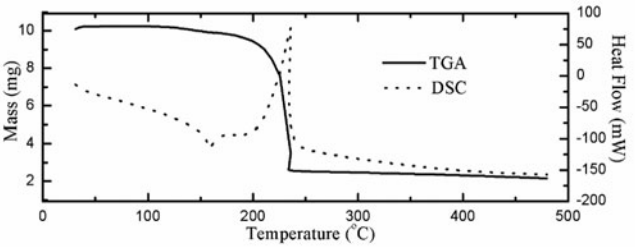


Figure 5. TGA-DSC curve of $[Co(C_8H_7O_3)_2(H_2O)_2]$.

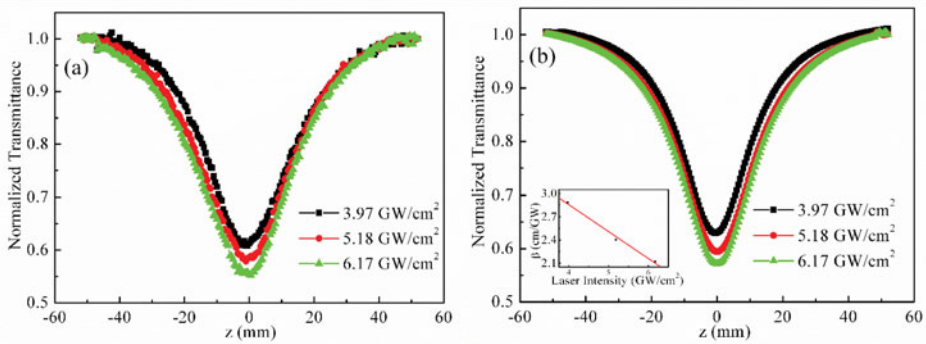


Figure 6. The normalized open aperture Z-scan of $[Co(C_8H_7O_3)_2(H_2O)_2]$'s methanol solution in a 1-mm cuvette as a function of on-axis incident intensity for 20 ps 1064 nm laser pulses, (a) is the experimental results, (b) is the theoretical fitted results. Inset picture shows the nonlinear absorption coefficients versus focal intensity, intensity dependence is observed.

of free space, n_0 is the linear refractive index, c is the speed of light in free space and λ is the wavelength. In our case, no obvious nonlinear refraction were observed in closed aperture Z-scan measurements, so the third-order nonlinear susceptibility $\chi^{(3)} \approx \chi_I^{(3)}$. The molecular second hyperpolarizability γ was calculated to be 1.06×10^{-56} C · m^4/V^3 through equation $\gamma(m^4C/V^3) = (\varepsilon_0/f^4N) \cdot \chi^{(3)}$ (m^2/V^2), where $f = (n_0^2 + 2)/3$ is the local field factor. The titled complex clearly shows better TPA properties in comparison with other previously reported complexes. Such as M. Cha et. al have reported the β value of di-alkyl-amino-nitro-stilbene side-chain polymer is 5.5 cm/GW [17], V. Chandrasekhar et. al have reported the σ_2 values of the phosphorus-based tris-hydrazone ligand and its metal complexes are in the range 3213–3516 GM (1 GM = 10^{-50} (cm^4 · s/photon × molecule)) [18], and S. Das et. al have reported the σ_2 values of zinc and copper complexes constructed by bis-cinnamaldiminato Schiff base are in the range 1700–10736 GM [19], etc. This implies the titled complex may have promising applications in the fields of optical limiting, etc.

TDDFT study

The γ value was calculated by Multiwfn program using the sum-overstates (SOS) [20] expression:

$$\gamma_{ijkl}(-\omega_\sigma;\omega_1,\omega_2,\omega_3) = \frac{4\pi^3}{3h^3}\mathrm{P}(i,j,k,l;-\omega_\sigma;\omega_1,\omega_2,\omega_3)\left(\gamma^{(I)}-\gamma^{(II)}\right)$$

$$\gamma^{(I)} = \sum_{m\neq 0}\sum_{n\neq 0}\sum_{p\neq 0}\frac{o|\mu_i|mm|\bar{\mu}_j|nn|\bar{\mu}_k|pp|\mu_l|o}{(\omega_{mo}-\omega_\sigma-\mathrm{i}\Gamma_{mo})(\omega_{no}-\omega_2-\omega_3-\mathrm{i}\Gamma_{no})(\omega_{po}-\omega_3-\mathrm{i}\Gamma_{po})}$$

$$\gamma^{(II)} = \sum_{m\neq 0}\sum_{n\neq 0}\frac{o|\mu_i|mm|\mu_j|oo|\mu_k|nn|\mu_l|o}{(\omega_{mo}-\omega_\sigma-\mathrm{i}\Gamma_{mo})(\omega_{no}-\omega_3-\mathrm{i}\Gamma_{no})(\omega_{no}-\omega_2-\mathrm{i}\Gamma_{no})}$$

where $\mathrm{P}(i,j,k,l;-\omega_\sigma;\omega_1,\omega_2,\omega_3)$ is a permutation operator defined in such a way that for any permutation of (i,j,k,l), an equivalent permutation of $(-\omega_\sigma;\omega_1,\omega_2,\omega_3)$ is made simultaneously; $\omega_\sigma = \omega_1 + \omega_2 + \omega_3$ is the polarization response frequency; $\omega_1, \omega_2, \omega_3$ indicate the frequencies of the perturbing radiation fields (considering the degenerate TPA, $\omega_1 = \omega_2 = \omega$

and $\omega_3 = -\omega$); m, n and p denote excited states and o, the ground state; μ_j is the j(x,y,z)th component of the dipole operator; $m|\bar{\mu}_j|n$ is the transition energy between the m and o states and Γ_{mo} is the damping factor of excited state m. And the calculated γ value was 2.55×10^7 a.u. (1.59×10^{-57} Cm^4/V^3), which is about six times smaller than the experimental results (1.06×10^{-56} $C \cdot m^4/V^3$).

Conclusions

In conclusion a cobalt(II) complex has been synthesized and its crystal structure has been determined by means of X-ray single crystal diffraction, its two-photon absorption properties have been studied using Z-scan technique. As the results shown, it possesses good TPA properties and implies its promising applications in optical limiting, fluorescence excitation microscopy and imaging, three-dimensional optical data storage and lithographic microfabrication etc. fields. The theoretical calculations of its second hyperpolarizability γ value has been performed also, as the results shown that the calculated value is about six times smaller than the experimental value. This is because only gas-phase calculations have been developed to a reliable level so far, and the relationship between gas phase and condensed-phase behavior for a particular class of compounds is determined experimentally, so the theoretical calculation results should be scaled accordingly.

Acknowledgments

The authors thank for financial support of China Postdoctoral Science Foundation (No. 2013M541908).

References

[1] Hu, Y. L., & Li, T. B. (2010). *Mol. Cryst. Liq. Cryst.*, *533*, 172.
[2] Piant, S., Specht, A., Zemelman, B., Losonczy, A., & Bolze, F. (2016). *Mol. Cryst. Liq. Cryst.*, *627*, 56.
[3] Amrutha Kala, A. L., Harohally, N. V., Naveen, S., Ramegowda, M., & Lokanath, N. K. (2016). *Mol. Cryst. Liq. Cryst.*, *629*, 146.
[4] Sheldrick, G. M. (1996). *SADABS*, University of Göttingen: Göttingen, Germany.
[5] Sheldrick, G. M. (1997). *SHELXT 97, Program for Crystal Structure Refinement*, University of Göttingen: Göttingen, Germany.
[6] Sheik-Bahae, M., Said, A. A., Wei, T. H., Hagan, D. J., & Van-Stryland, E. W. (1990). *IEEE J. Quantum Electron.*, *26*, 760.
[7] Frisch, M. J., et al. (2009). *Gaussian 09, Revision A. 02*, Gaussian, Inc., Wallingford, CT.
[8] Lu, T., & Chen, F. (2012). *J. Comput. Chem.*, *33*, 580.
[9] Lee, C. T., Yang, W. T., & Parr, R. G. (1988). *Phys. Rev. B.*, *37*, 785.
[10] Becke, A. D. (1993) *J. Chem. Phys.*, *98*, 5648.
[11] Hay, P. J., & Wadt, W. R. (1985) *J. Chem. Phys.*, *82*, 270.
[12] Oka, Y., Kumagai, H., Inoue, K. & Kurmoo, M. (2002). *Mol. Cryst. Liq. Cryst.*, *379*, 265.
[13] Lin, D. D., & Xu, D. J. (2005). *Acta Cryst. E61*, m1821.
[14] Spek, A. L. (1999) *PLATON: A Multipurpose Crystallographic Tool*, Utrecht University: Utrecht, The Netherlands.
[15] Li, T. B., et al. (2013). *Mater. Chem. Phys.*, *141*, 22.
[16] Li, Z., Hu, Y. L., & Li, T. B. (2014). *Mol. Cryst. Liquid. Cryst.*, *605*, 135.
[17] Cha, M., Torruellas, W. E., Stegeman, G. I., Horsthuis, W. H., & Mohlmann, G. R. (1994). *Appl. Phys. Lett.*, *65*, 2648.
[18] Chandrasekhar, V., et al. (2010). *Inorg. Chem.*, *49*, 4008.
[19] Das, S., Nag, A., Goswami, D., & Bharadwaj, P. K. (2006). *J. Am. Chem. Soc.*, *128*, 402.
[20] Dirk, C. W., Cheng, L. T., & Kuzyk, M. G. (1992). *Int. J. Quantum. Chem.*, *43*, 27.