



J. Serb. Chem. Soc. 76 (11) 1497–1504 (2011)
JSCS–4223

The synthesis, structure and photoluminescence property of a novel 3D supramolecular compound based on mixed ligands of 8-hydroxyquinoline-5-sulfonate and ethylenediamine

YING WANG^{1,2}, CHANGFU ZHUANG^{1*}, CHUNHUA WU¹, JIAYAN ZHANG¹, LI WANG², MINGHONG XIN², GUANGSHAN ZHU² and JIANING XU²

¹Southwest Forestry University, Kunming, 650224, and ²State Key Laboratory of Inorganic Synthesis and Preparation, Jilin University, Changchun, 130012, P. R. China

(Received 29 January, revised 29 September 2011)

Abstract: A new organic–inorganic hybrid coordination compound ZnQS(en)·2H₂O (**1**) in which two different organic ligands, ethylenediamine (en) and 8-hydroxyquinoline-5-sulfonic acid (H₂QS) coordinate with zinc ions, has been synthesized *via* the evaporation method and characterized by single crystal X-ray diffraction analysis, IR spectroscopy and thermogravimetric analysis (TGA). The structure solution showed that compound **1** displays a three-dimensional supramolecular network by synergic linkage of hydrogen and coordinated bonds. Moreover, compound **1** exhibits intense photoluminescence at 513 nm excited at 396 nm in the solid state at room temperature.

Keywords: organic–inorganic hybrid material; 8-hydroxyquinoline-5-sulfonic acid; photoluminescence property.

INTRODUCTION

Due to the potential applications of organic–inorganic hybrid materials in catalysis, gas storage, molecular recognition, optics and magnetic fields,^{1–10} the design and synthesis of organic–inorganic hybrid materials have been attracting tremendous attention. To date, much research has focused on constructing organic–inorganic hybrid materials by choosing versatile organic ligands. As functional organic ligands, 8-hydroxyquinoline and its substituted derivatives are attracting more and more attention from synthesis chemists because of their fantastic coordination properties and special photoelectric properties. Many organic–inorganic hybrid materials based on the derivatives of 8-hydroxyquinoline (q) have been synthesized,^{11–14} and most of them exhibit amazing optical properties, enabling their application as organic light-emitting devices (OLEDs).^{15–17} As organic

* Corresponding author. E-mail: cfzhuang_2008@yahoo.com.cn
doi: 10.2298/JSC110129127W

ligand, 8-hydroxyquinoline-5-sulfonate still remains largely unexplored, since sulfonate group is considered as poor ligand and bonds hardly to many metal cations. It is noted that there are only a few articles reporting about organic–inorganic hybrid materials containing the 8-hydroxyquinoline-5-sulfonate group.^{18–20} Here, 8-hydroxyquinoline-5-sulfonic acid (H₂QS) and ethylenediamine (en) were employed as reactants to obtain a novel zinc–organic hybrid ZnQS(en)·2H₂O (**1**) by the evaporation method. Interestingly, compound **1** displays a 3D supramolecular structure, which is built from $\pi\cdots\pi$ stacking interactions of binuclear complexes and hydrogen bonds interactions of the chelating ethylenediamine, mediated uncoordinated water molecules and QS. Herein, the synthesis, structure and photoluminescence property of compound **1** are reported.

EXPERIMENTAL

All chemicals of reagent quality were obtained from commercial sources and used without further purification. The elemental analysis was performed on a Perkin–Elmer 2400 elemental analyzer. The IR spectra were obtained from KBr pellets in the range of 400–4000 cm⁻¹ on a Nicolet Impact 410 FTIR spectrometer. Thermogravimetric analyses (TGA) were performed on a Perkin–Elmer TGA 7 thermogravimetric analyzer at a heating rate of 10 °C min⁻¹ in air up to 800 °C. Fluorescence spectra were recorded on a LS 55 fluorescence/phosphorescence spectrophotometer at room temperature.

Synthesis of ZnQS(en)·2H₂O (1)

A mixture of Zn(NO₃)₂·6H₂O (148 mg, 0.5 mmol) and H₂QS (24 mg, 0.1 mmol) was dissolved in *N,N*-dimethylformamide (DMF) (10 mL) at room temperature, and then about 0.1 mL ethylenediamine was added to this mixture under stirring. After the mixture became clear, the beaker was left undisturbed at room temperature for 24 h to give yellow crystals in a yield of 43 % (based on S).

Determination of the single-crystal structure

The intensity data was collected on a Smart CCD diffractometer with graphite-monochromated MoK α ($\lambda = 0.71073$ Å) radiation at room temperature in the ω – 2θ scan mode. An empirical absorption correction was applied to the data using the SADABS program.²¹ The structure was solved by direct methods. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms of the organic ligand were fixed at calculated positions and refined using a riding mode. The hydrogen atoms of the H₂O were located in the difference Fourier map. All calculations were performed using the SHELXTL program.²²

RESULTS AND DISCUSSION

Description of the structure

The crystallographic data are summarized in Table I, and selected bond lengths and bond angles of compound **1** are listed in Table II.

The zinc atom is five-coordinated in a square-pyramidal coordination environment, coordinating to two oxygen atoms (O1 and O2) and three nitrogen atoms (N1, N2 and N3). O1 and N3 are from the hydroxyl group and the quinoline ring of one ligand, respectively; O2 is from the sulfonate group of the

other QS ligand. N1 and N2 are from the same ethylenediamine molecule, *i.e.*, the ethylenediamine molecule as a bidentate chelate ligand is coordinated to the zinc atom. The O2 is in apical position with $d(\text{Zn}-\text{O}2) = 2.280(4) \text{ \AA}$ and the other four coordinated atoms are in bottom positions of the square-pyramid with $d(\text{Zn}-\text{O}1) = 2.062(4) \text{ \AA}$, $d(\text{Zn}-\text{N}1) = 2.102(5) \text{ \AA}$, $d(\text{Zn}-\text{N}2) = 2.087(5) \text{ \AA}$ and $d(\text{Zn}-\text{N}3) = 2.072(5) \text{ \AA}$. The distance of Zn–O2 is significantly longer than that of Zn–O1, but they are in normal range reported for zinc compounds.²³ The Zn–N distances range from 2.072(5) to 2.101(5) Å. These distances are comparable to those reported for other zinc compounds.²⁴

TABLE I. Crystal data and structure refinement for compound **1**

Molecular formula	$\text{C}_{11}\text{H}_{17}\text{N}_3\text{O}_6\text{SZn}$
Formula weight	384.71
T / K	293(2)
$\lambda / \text{Å}$	0.71073
Crystal system	Monoclinic
Space group	P2(1)/c
$a / \text{Å}$	7.0737(14)
$b / \text{Å}$	19.296(4)
$c / \text{Å}$	10.680(2)
$\beta / ^\circ$	100.599(4)
$V / \text{Å}^3$	1432.8(5)
Z	4
$D_{\text{calc}} / \text{kg m}^{-3}$	1783
μ / mm^{-1}	1.894
$F(000)$	792
Reflections collected	7434
Independent reflection (R_{int})	2521 (0.2316)
$R_1(I > 2\sigma(I))$	0.0715
wR_2	0.1629

TABLE II. Selected bond lengths and angles for compound **1**

Bond	Distance, Å		
Zn(1)–O(1)	2.062(4)		
Zn(1)–O(2)	2.280(4)		
Zn(1)–N(3)	2.072(5)		
Zn(1)–N(1)	2.101(5)		
Zn(1)–N(2)	2.087(5)		
Bonds	Angle, °	Bonds	Angle, °
O(1)–Zn(1)–N(3)	80.25(16)	N(1)–Zn(1)–O(2)	88.21(17)
O(1)–Zn(1)–N(2)	95.96(17)	N(2)–Zn(1)–O(2)	95.04(18)
O(1)–Zn(1)–N(1)	174.80(18)	N(2)–Zn(1)–N(1)	84.20(18)
O(1)–Zn(1)–O(2)	86.59(15)	N(3)–Zn(1)–N(1)	100.43(18)
N(3)–Zn(1)–N(2)	170.06(19)	N(3)–Zn(1)–O(2)	93.90(16)

Two crystallographically equivalent Zn atoms link to each other through the O2 and its symmetry equivalent at $-x, 1-y, 2-z$ to form a binuclear zinc secondary building unit, as shown in Fig. 1. Weak $\pi\cdots\pi$ stacking interactions exist between the two quinoline rings and the contact distance is 3.622 Å. These binuclear zinc secondary building units form a 3D supramolecular network due to the $\pi\cdots\pi$ stacking interactions and the complicated hydrogen bonds existing between uncoordinated H₂O molecules and ethylenediamine molecules as well as the QS ligands. There are strong hydrogen bonds between O1w and O1, O2, O4, N2, O2w, respectively. The distances of the hydrogen bonds are O1W–H2W \cdots O1, 2.718 Å, O1W–H1W \cdots O2, 3.240 Å, O1W–H1W \cdots O4, 2.955 Å, N2–H2B \cdots O1W, 3.079 Å and O2W–H3W \cdots O1W, 2.835 Å. Simultaneously, the hydrogen bonds between O2w and O3, N1 are also strong. The distances of the hydrogen bonds are O2W–H4W \cdots O3, 2.844 Å, N1–H1C \cdots O2w, 2.995 Å. Hydrogen bonds also exist between N1 and O3, N2 and O1. Moreover, there are weak hydrogen bonds between S and O1w, O2w, N1. The hydrogen-bond interactions are listed in Table III. The stacking networks based on the hydrogen bonds are shown in Fig. 2.

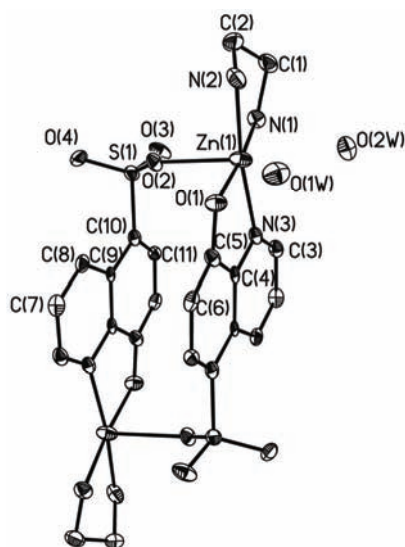


Fig. 1. The binuclear Zn unit of compound **1** showing the atom-labeling scheme (30 % thermal ellipsoids).

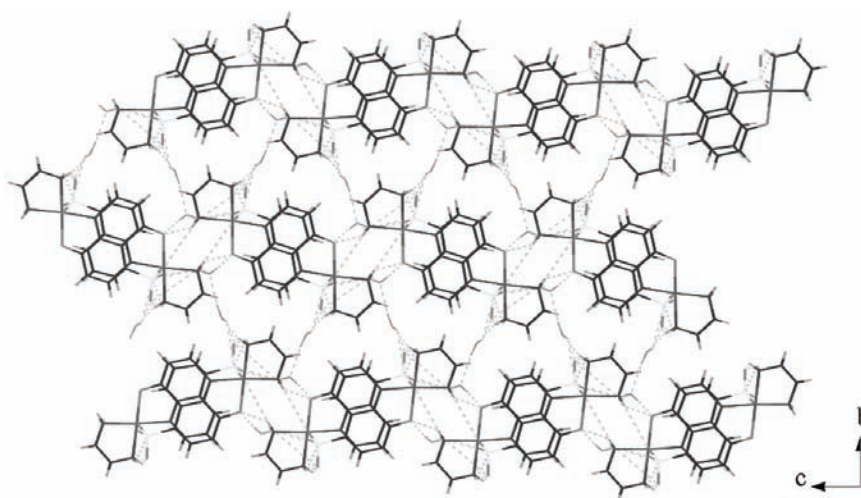
Although both compound **1** and the reported compound [Cu(L4)₂](H₂biim-4)·8H₂O¹⁹ are three-dimension supramolecular compounds with two different organic compounds and are both based on the 8-hydroxyquinoline-5-sulfonate organic ligand, there are obvious differences between them. In the latter compound, only the nitrogen atom and hydroxyl oxygen atom of the 8-hydroxyquinoline-5-sulfonate organic ligand coordinate to Cu(II) and none of the oxygen atoms of the sulfonate group, whereas in compound **1**, one oxygen atom of the sulfonate group coordinates to the metal center. Moreover, in compound **1**, besides the 8-hy-

droxyquinoline-5-sulfonate ligand, ethylenediamine adopts a bidentate chelating mode to coordinate to Zn(II), while in reported $[\text{Cu}(\text{L4})_2](\text{H}_2\text{biim-4})\cdot 8\text{H}_2\text{O}$, only 8-hydroxyquinoline-5-sulfonate coordinates to Cu(II). In compound **1**, two crystallographically equivalent Zn(II) link to each other through two bridging oxygen atoms to form a binuclear zinc secondary building unit, and these secondary building units form a 3D supramolecular network due to $\pi\cdots\pi$ stacking interactions and hydrogen bonds.

TABLE III. Hydrogen bond lengths and angles in compound **1**

D-H	D \cdots H / Å	H \cdots A / Å	D-H \cdots A / °	D \cdots A / Å	A
N1-H1C	0.900	2.112	166.89	2.995	O2W
N1-H1D	0.900	2.181	154.38	3.018	O3
N1-H1D	0.900	2.963	128.06	3.588	S1
N2-H1	0.899	2.414	148.35	3.214	O1 ^a
N2-H2	0.900	2.213	161.32	3.079	O1W ^a
O1W-H1W	0.874	2.352	126.38	2.955	O4 ^a
O1W-H1W	0.874	2.395	162.70	3.240	O2 ^a
O1W-H1W	0.874	2.799	146.55	3.561	S1 ^a
O1W-H2W	0.857	1.863	175.36	2.718	O1
O2W-H3W	0.853	1.990	170.44	2.835	O1W ^b
O2W-H4W	0.856	2.046	154.76	2.844	O3 ^c
O2W-H4W	0.856	3.011	130.39	3.626	S1 ^c

^a-x, -y+1, -z+1; ^b-x-1, y-1/2, -z-3/2; ^cx-1, y, z

Fig. 2. Stacking hydrogen-bonded network viewed down the *bc* plane.

Characterization

Anal. Calcd. for $\text{ZnO}_6\text{SN}_3\text{C}_{11}\text{H}_{17}$: C, 34.31; H, 4.42; N, 10.92%. Found: C, 35.02; H, 4.23; N, 10.85%.

In the IR spectrum, bands in the 1643–1394 cm^{-1} region can be assigned to the vibrations of C=C and C=N of the quinoline ring. The bands in the 1611–1391 cm^{-1} region are characteristic bands of the benzene ring and the bands in the 1354–1199 cm^{-1} region are assigned to the Ar–O. Broad bands due to $\nu(\text{N-H})$ are observed in the 3200–3500 cm^{-1} region, while the bending modes for the amine are observed in the range 1300–1650 cm^{-1} . The bands in the 1030–1250 cm^{-1} region are due to the vibration of S–O.^{25,26} The absorption bands at around 3303 cm^{-1} are due to the stretching of the hydroxyl groups (from the water molecules), which experience a shift to lower frequency compared with the O–H stretch in free water at 3600 cm^{-1} . This may be due to the formation of hydrogen bonds between the water and the ligands, as well as between the water molecules. In the low-frequency region, the bands are attributed to the lattice vibration of Zn–O and Zn–O–Zn.

To understand the thermal stability of compound **1**, thermogravimetric analysis was performed. There were two separate mass loss steps. The first mass loss of 8.9 % occurred between 50–150 °C, which corresponds to the loss of free H_2O molecules (calcd. 9.4 %) of crystallization. The second mass loss occurred between 300–640 °C, corresponding to the loss of the organic components, and shows that compound **1** may be stable up to 300 °C. The residual mass of about 24.0 % corresponds to ZnO (calcd. 23.3 %).

Photoluminescence

The fluorescence spectrum of compound **1**, measured in the solid state at room temperature, is shown in Fig. 3. The compound was excited at a wavelength of 396 nm. The emission peak at 513 nm is attributed to electron $\pi^*-\pi$ transitions of the intraligand.²⁰ The emission peak of compound **1** was blue shifted by ≈ 30 nm compared to that of Znq_2 (542 nm).²⁶ This blue-shift is connected to the elec-

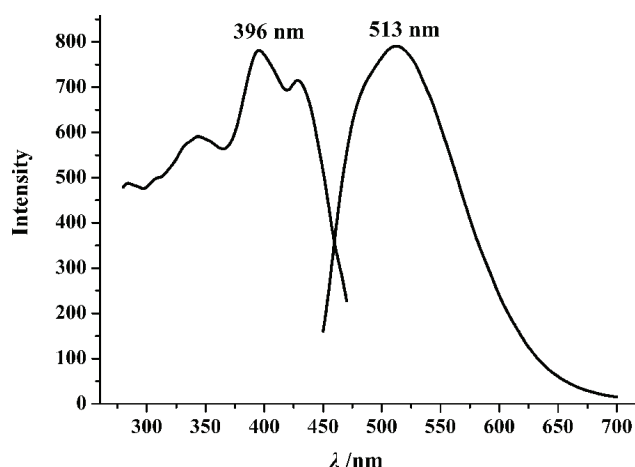


Fig. 3. Fluorescence spectra of compound **1**, excited at 396 nm; emission peak at 513 nm.

tron-withdrawing sulfonate group of the quinoline ring. The sulfonate group in the 5-position of the quinoline ring increases the energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO).^{27–29} This good fluorescence will have the significant usage property in the OLED devices.

CONCLUSIONS

In summary, a novel organic–inorganic hybrid material $\text{ZnQS(en)}\cdot 2\text{H}_2\text{O}$ based on 8-hydroxyquinoline-5-sulfonate and ethylenediamine mixed ligands was successfully synthesized and characterized. The compound, synthesized using the solvent evaporation method, displayed a three-dimensional supramolecular network based on multi-type hydrogen bond interactions and $\pi\cdots\pi$ stacking interactions. It is very interesting that this compound exhibited a ≈ 30 nm blue-shift in its emission band compared to that of Znq_2 . This good photoluminescence property has potential significance for its employment in electroluminescent and photoluminescent devices. Further synthesis and characterization studies of other metals with 8-hydroxyquinoline-5-sulfonate ligand are in progress.

Supplementary information. Crystallographic data (excluding structure factors) for the structure reported in this paper has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC608873. Copy of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk).

Acknowledgements. This work was supported by the Key Foundation of Southwest Forestry University (Grant No.111030), the National Natural Science Foundation of China (Grant No. 31060099) and the Key Program of the Ministry of Education of China (Grant No. 2010Z040).

ИЗВОД

СИНТЕЗА, СТРУКТУРА И ФОТОЛУМИНСЦЕНТНА КАРАКТЕРИСТИКА НОВОГ 3Д СУПРАМОЛЕКУЛАРНОГ ЈЕДИЊЕЊА ДОБИЈЕНОГ ИЗ СМЕШЕ 8-ХИДРОКСИ-ХИНОЛИН-5-СУЛФОНАТА И ЕТИЛЕНДИАМИНА КАО ЛИГАНДА

YING WANG^{1,2}, CHANGFU ZHUANG¹, CHUNHUA WU¹, LIJIAN ZHANG¹, LI WANG², MINGHONG XIN²,
GUANGSHAN ZHU² И JIANING XU²

¹Southwest Forestry University, Kunming, 650224 и ²State Key Lab of Inorganic Synthesis and Preparation, Jilin University, Changchun, 130012, P. R. China

Применом технике испаравања синтетизовано је ново органско-неорганско хибридно координационо једињење $\text{ZnQS(en)}\cdot 2\text{H}_2\text{O}$ (**1**) у којем су два различита органска лиганда, етилендиамин (en) и 8-хидрокси-хинолин-5-сулфонска киселина (H_2QS), координовани за јон цинка. За карактеризацију овог једињења употребљена је метода дифракције X-зрака са монокристала, као и IR и термогравиметријска анализа (TGA). Испитивање структуре **1** у раствору показује да ово једињење поседује тродимензионалну супрамолекуларну синергијску мрежу интеракција водоничних и координационих веза. Истовремено, једињење **1** показује интензивну луминисценцију на 513 nm, ексцитовану на 396 nm у чврстом стању на соб-

ној температури. Кристалографски подаци за једињење **1** су: монклична просторна група $P2_1/c$, $a = 7,0737(14) \text{ \AA}$, $b = 19,296(4) \text{ \AA}$, $c = 10,680(2) \text{ \AA}$, $\beta = 100,599(4)^\circ$, $V = 1432,8(5) \text{ \AA}^3$, $Z = 4$, $M_r = 384,71$, $D_{\text{calc}} = 1,783 \text{ g}\cdot\text{cm}^{-3}$, $\text{MoK}\alpha$, $R_1 = 0,0715$, $wR_2 = 0,1629$, $GOF = 1,038$.

(Примљено 29. јануара, ревидирано 29. септембра 2011)

REFERENCES

1. K. S. Min, M. P. Suh, *J. Am. Chem. Soc.* **122** (2000) 6834
2. H. Li, M. Eddaoudi, M. O'Keeffe, O. M. Yaghi, *Nature* **402** (1999) 276
3. W. T. Chen, X. N. Fang, Q. Y. Luo, Y. P. Xu, *J. Serb. Chem. Soc.* **74** (2009) 755
4. A. P. Mishra, R. K. Mishra, S. P. Shrivastava, *J. Serb. Chem. Soc.* **74** (2009) 523
5. B. Moulton, M. J. Zaworotko, *Chem. Rev.* **101** (2001) 1629
6. O. M. Yaghi, H. Li, *J. Am. Chem. Soc.* **118** (1996) 295
7. J. S. Seo, D. M. Whang, H. Y. Lee, S. I. Jun, J. H. Oh, Y. J. Jeon, K. M. Kim, *Nature* **404** (2000) 982
8. T. Sawaki, Y. Aoyama, *J. Am. Chem. Soc.* **121** (1999) 4793
9. S. R. Batten, R. Robson, *Angew. Chem. Int. Ed.* **37** (1998) 1460
10. P. J. Hagrman, D. Hagrman, J. Zubieta, *Angew. Chem. Int. Ed.* **38** (1999) 2638
11. J. Xie, L. Fan, J. Su, H. Tian, *Dyes Pigm.* **59** (2003) 153
12. M. Ghedini, M. L. Deda, I. Aiello, A. Grisolia, *Synth. Met.* **138** (2003) 189
13. M. Ghedini, M. L. Deda, I. Aiello, A. Grisolia, *J. Chem. Soc., Dalton Trans.* (2002) 3406
14. C. Bae, S. Lee, S. Choi, G. Kwag, *Inorg. Chem.* **44** (2005) 7911
15. P. Mark, W. Helfrich, *J. Appl. Phys.* **33** (1962) 205
16. M. Pope, H. P. Kallmann, P. J. Magnante, *J. Chem. Phys.* **38** (1963) 2042
17. W. Helfrich, W. G. Schneidere, *Phys. Rev. Lett.* **14** (1965) 229
18. H. Y. Rao, J. Tao, S. W. Ng, *Acta Cryst.* **E59** (2003) 859
19. W. L. Zhang, Y. Y. Liu, J. F. Ma, H. Jiang, J. Yang, G. J. Ping, *Cryst. Growth Des.* **8** (2008) 1250
20. Y. Wang, M. Xue, J. N. Xu, G. S. Zhu, S. L. Qiu, *Sci. China, Ser. B Chem.* **52** (2009) 1602
21. G. M. Sheldrick, *SADABS, Program for Empirical Absorption Correction for Area Detector Data*, University of Göttingen, Göttingen, Germany, 1996
22. G. M. Sheldrick, *SHELXTL, v. 5 Reference Manual*, Siemens Analytical X-Ray Systems, Madison, WI, USA, 1997
23. W. T. A. Harrison, Z. Bircsak, L. Hannooman, *J. Solid State Chem.* **134** (1997) 148
24. Y. R. Xie, R. G. Xiong, X. Xue, X. T. Chen, Z. I. Xue, X. Z. You, *Inorg. Chem.* **41** (2002) 3323
25. J. Selbin, L. H. Holmes, S. P. J. McGlynn, *Inorg. Nucl. Chem.* **25** (1963) 1359
26. K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, Wiley, New York, 1978
27. T. A. Hopkins, K. Meerholz, S. Shaheen, M. L. Anderson, A. Schmidt, B. Kippelen, A. B. Padias, H. K. Hall Jr., N. Peyghambarian, N. R. Armstrong, *Chem. Mater.* **8** (1996) 344, and references therein
28. T. A. Albright, J. K. Burdett, M. H. Whangbo, *Orbital Interactions in Chemistry*, Wiley, New York, 1985
29. C. A. Coulson, A. Streitwieser Jr., *Dictionary of pi-Electron Calculations*, Freeman, San Francisco, 1965.