APPLIED ORGANOMETALLIC CHEMISTRY
Appl. Organometal. Chem. 2006; **20**: 835–839
DOI:10.1002/aoc.1122

Luminescent lanthanide molecular-based hybrid materials bridged through novel urethane linkages

Bing Yan*, Bing Zhou and Qian-Ming Wang

Department of Chemistry, Tongji University, Siping Road 1239, Shanghai 200092, People's Republic of China

Received 15 February 2006; Accepted 13 May 2006

Novel organosilicates with covalently linked functional modified aromatic acid have been synthesized from 3-aminopropyl triethoxysilane (APS) grafted 4-ethoxy benzoic acid (EB-Si) and terbium ions via a simple low-temperature route. The existence of covalent bonds between EB-Si and silica matrices was shown by the hydrolysis and polycondensation processes of ethoxysilyl groups. Luminescence spectra were used to characterize the photophysical properties of the obtained hybrid material and the above spectroscopic data reveal that the triplet energy of modified *para* ethoxy benzoic acid in this favorable hybrid system matches the emissive energy level of RE^{3+}. Copyright © 2006 John Wiley & Sons, Ltd.

KEYWORDS: molecular-based hybrid materials; luminescence; 3-aminopropyl triethoxysilane

INTRODUCTION

Hybrid materials formed by the combination of inorganic and organic components are attractive for the purpose of creating high-performance or high-functional composites in lighting and displays, optical amplifiers and lasers.[1,2] In particular, inorganic matrices doped with emitting centers like lanthanide organic complexes have already been found to show superior emission intensities, and organic components are treated as efficient sensitizers for the luminescence of rare earth ions, namely, the antenna effect. In addition, anchored lanthanide complexes with different ligands in a sol–gel derived matrix have been studied in much research[3–5] and the microstructure, the external shape or the degree of combination between the two phases, can be tuned by changing the sol–gel reaction conditions.[6] The fine control of the coupling between the hosts and the guest molecule can be used for the assembly of hybrid materials, especially for specific applications. For example, a common doping approach seems difficult for solution of the problem of the quenching effect of luminescent centers because of the high-energy vibration by the surrounding hydroxyl groups and because only weak interactions (such as hydrogen bonding, van der waals force or weak static effect) function between organic and inorganic parts.[7] The concept of molecular-level mixing between the two phases has been provided by Sanchez *et al*. and the complexation of the rare earth ions using ligands that are covalently fixed to the hybrid networks has emerged. Until recently, little work on the covalently bonded hybrids with increasing chemical stability have appeared and the as-derived molecular-based materials exhibit a monophasic appearance even at a high concentration of rare earth complexes.[8–22] Franville *et al*. have produced complexes of lanthanide–pyridine–dicarboxylic acid or their derivatives and the feasibility of a dicarboxylic acid system has been proved.[8] Zhang and co-workers utilized modified 1,10-phenanthroline and di-pyridine in order to prepare the determined high-efficiency molecular-level hybrid materials.[9–13] Our research team recently put more emphasis on rare earth coordination behavior and have now developed modified *ortho, meta*-aminobenzoic acid as a 'molecular bridge' that can not only develop chelating effects that can bind to rare earth ions, but also anchor a silica matrix with an aminoalkoxysilane group.[14–19] The idea is to restrict the degrees of freedom of the active molecule so as to decrease the contribution of librational movements to optical dephasing. Carlos *et al*. pointed out that amino-functional hybrids lacking metal ions could be divided into two major parts (di-ureasils and di-urethanesils) and the Eu^{3+} coordination shell involves the carbonyl-type oxygen atoms of the urea bridges.[18,19] For the sake of restricting the phase separation between organic molecules and the rigid inorganic network, and to increase the concentration of dopant, in this work, we attempted to modify 4-ethoxy benzoic acid by APS bearing tri-alkoxysilyl group as a functionalized organic

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*Correspondence to: Bing Yan, Department of Chemistry, Tongji University, Siping Road 1239, Shanghai 200092, People's Republic of China.
E-mail: byan@tongji.edu.cn
Contract/grant sponsor: National Natural Science Foundation of China; Contract/grant number: 20301013.

ligand (EB-Si). Then we designed a covalently bonded hybrid inorganic–organic system that incorporated terbium nitrate to EB-Si. The reaction processes for the hybridization formula EB-Si may be described as follows: the first step involves the individual hydrolysis of EB-Si and tetraethoxysilane (TEOS). The second process includes the polycondensation reactions between the above two composites, which produce the sol. Hence, condensation of the tri-alkoxysilyl chromophores in the presence of lanthanides salts leads to the formation of novel structured hybrid materials consisting of efficiently sequestered lanthanide species linked to powerful modified EB-Si grafted to the inorganic hosts. After drying in air at 60 °C, the gel turns into solid transparent material known as xerogel. In this experiment, the glass like characteristics sample were grounded as powders and the first results on luminescence are promising that the molecular-based hybrids bearing the RE–O coordination bond and Si–O covalent bond can exhibit green luminescence of Tb^{3+}.

EXPERIMENTAL

Chemicals and procedures

3-Aminopropyl triethoxysilane was provided by Lancaster Synthesis Ltd. The solvents used were purified by common methods. Other starting reagents were used as received. A typical procedure for the preparation of EB-Si was as follows: 4-ethoxy benzoic acid was first converted to acyl chloride by refluxing in excess $SOCl_2$ under argon for 5 h. After isolation, the acyl chlorides were directly reacted with APS in ethyl ether in presence of triethylamine. The detailed process, especially the corresponding conditions, were according to the literature. ^1H NMR ($CDCl_3$) $C_{18}H_{31}O_5NSi$: δ 8.09(2H,t), 8.06(1H,d), 6.97(4H,m), 4.13(3H,m), 3.59(2H,d), 3.57(9H,m), 3.47(2H,m), 2.79(2H,s), 1.71(2H,m), 1.46(4H,m). ^{13}C NMR ($CDCl_3$): δ 165.9(C_7), 133.9 (C_1), 132.7–131.5 (C_2–C_6), 127.1 (C_4), 114.6–114.5 (C_3–C_5), 73.5–71.3 (C_8–C_9), 64.1 [CH_2(OEt)], 50.8 (C_{10}), 50.4 (C_{11}), 22.7–14.5 [CH_3(OEt)], 5.23 (C_{12}). The sol–gel derived hybrid containing rare earth ions was prepared as follows: EB-Si was dissolved in dimethylformamide (DMF) with stirring. A stoichiometric amount of $RE(NO_3)_3{\cdot}6H_2O$ (Tb, Dy and Sm) was added to the solution. Then one drop of diluted hydrochloric acid was put into it to promote hydrolysis. The mole ratio of $RE(NO_3)_3 \cdot 6H_2O$–EB-Si–TEOS–H_2O was 1 : 3 : 6 : 12. The mixture was agitated magnetically to achieve a single phase in a covered Teflon beaker, then it was aged at 60 °C until the onset of gelation, which occurred within 3 days. The gels were collected as monolithic bulks and ground as powder materials for the photophysical studies (see Fig. 1).

Measurements

All measurements were completed under room temperature except that phosphorescence spectra (5×10^{-4} mol l^{-1} Acetone solution) were measured under 77 K. ^1H NMR spectra were recorded in $CDCl_3$ on a Bruker Avance-500 spectrometer with tetramethylsilane (TMS) as internal reference. Ultraviolet absorption spectra of these powder samples (5×10^{-4} mol l^{-1} acetone solution) were recorded with an Agilent 8453 spectrophotometer. Fluorescence excitation and emission spectrums were obtained on a Perkin-Elmer LS-55 spectrophotometer: excitation slit width = 10 nm, emission slit width = 5 nm. The scanning electronic microscope (SEM) was a JSM-6360LV.

RESULTS AND DISCUSSION

Figure 2 provides ultraviolet absorption spectra of (A) 4-ethoxy benzoic acid, (B) EB-Si and (C) EB-Si with excess Sm^{3+} ions. From the spectra, it is observed that a red shift (A → B) of the major $\pi - \pi^*$ electronic transitions (from 253 to 262 nm) occurs and it is estimated that, during the grafting reaction of 4-ethoxy benzoic acid, the diverse ligand may enhance the conjugating effect of double bonds and reduce the energy difference levels among electron transitions. In terms of B and C, the complexation between rare earth ions and EB-Si increase the energy levels of the corresponding transitions and exhibits an obvious blue shift from 262 to 234 nm (B → C).

Figure 3 gives the phosphorescence spectra of (A) 4-ethoxy benzoic acid and (B) EB-Si. Phosphorescence spectrum substantiates the character of the organic molecular ligands and a 23 nm red shift was observed between A and B (from 404 to 427 nm). From the phosphorescence emission, the maximum phosphorescence wavelengths of B located at 427 nm is due to the characteristic transitions of EB-Si and the triplet state energy can be determined to be 23420 cm^{-1}. According to Sato's result[23] and other reports,[24–30] the intramolecular energy migration efficiency from organic ligands to the central Ln^{3+} is the most important factor influencing the luminescence properties of rare earth complexes, which depends on the energy match (exactly the energy difference) between the triplet state energy of ligands and the resonant emissive energy level of lanthanide ions. Therefore, it can be estimated that the energy differences between bridging EB-Si and the emissive energy level of terbium (20 500 cm^{-1}), samarium (16 750 cm^{-1}) and dysprosium ions (21 000 cm^{-1}) are about 2920, 6770 and 2420 cm^{-1}). The energy difference between EB-Si and Sm^{3+} is too large (6770 cm^{-1}) to achieve the suitable energy match for the luminescence and there also exist some internal emissive levels ($^6F_{11/2}$, $^6F_{9/2,\ldots,}$ $^6H_{11/2}$, etc) between the first excited state $^4G_{5/2}$ and ground state $^6H_{9/2}$ of Sm^{3+}. The non-radiative energy transfer process takes place easily to lose the excited energy of the EB–Si ligand. Therefore, it can be predicted that the Sm^{3+} hybrid system exhibits the weaker luminescence. While the luminescence for both Tb^{3+} and Dy^{3+} hybrid systems can be expected to present the stronger luminescence for the more suitable energy match between EB-Si and Tb^{3+} (and Dy^{3+}).

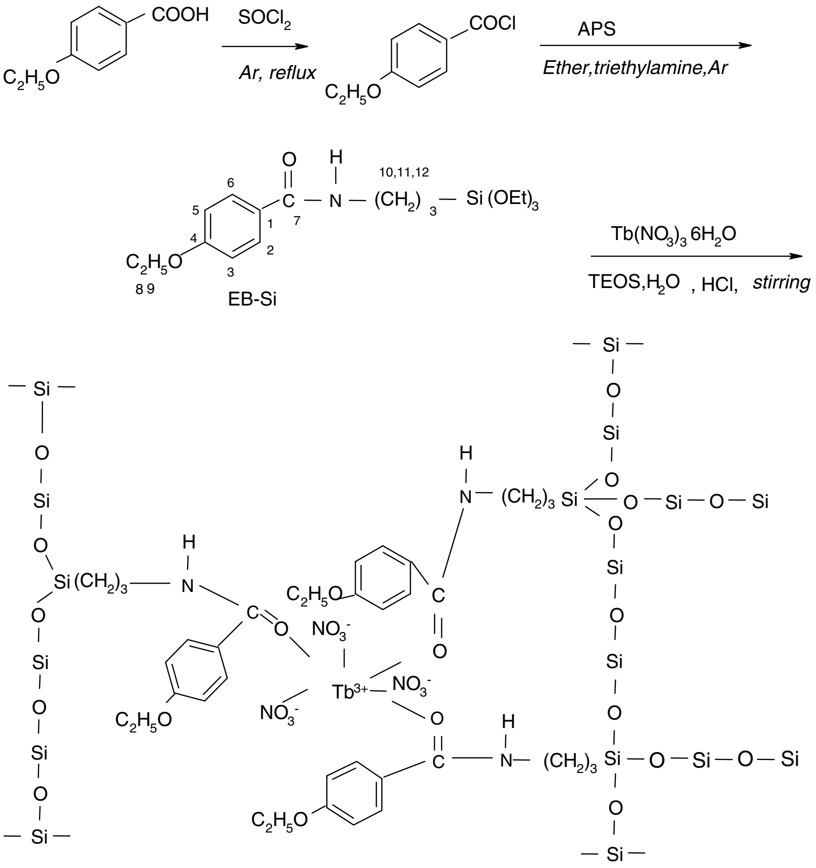

Figure 1. Scheme of the synthesis process of EB-Si and predicted structure of hybrid materials.

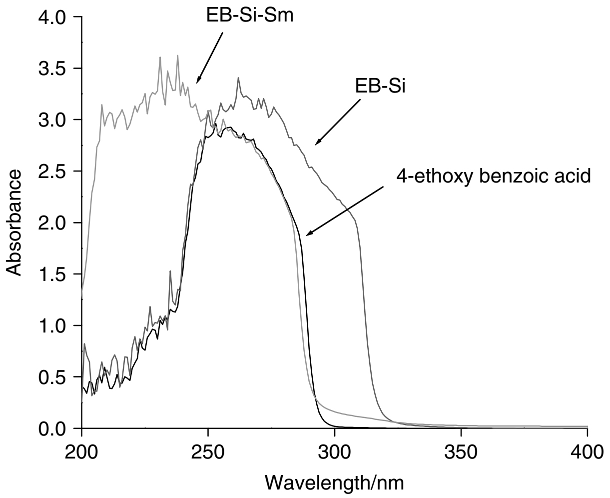

Figure 2. Ultraviolet absorption spectra of (A) 4-ethoxy benzoic acid, (B) EB-Si and (C) EB-Si with excess Sm^{3+} ions.

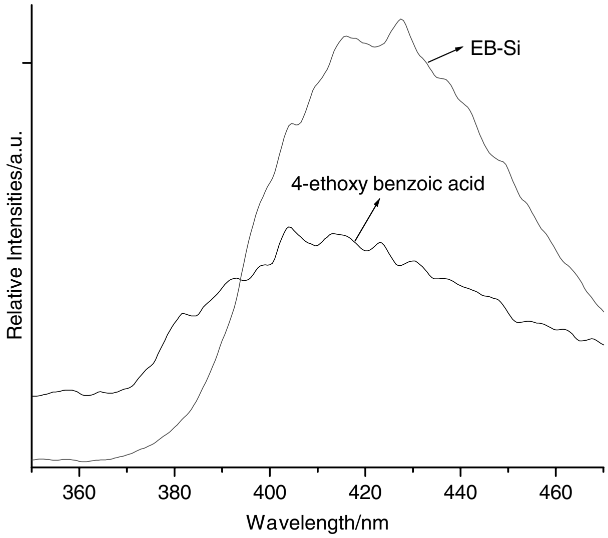

Figure 3. Phosphorescence spectra of (A) 4-ethoxy benzoic acid and (B) EB-Si.

The excitation and emission spectra of the resulting hybrid materials are shown in Figs. 4–6. The excitation spectra was obtained by monitoring the emission of Tb^{3+}, Dy^{3+} and Sm^{3+} ions at 545, 484 and 597 nm dominated by distinguished bands centered at 297, 225 and 244 nm. As a result, the emission lines of the hybrid material were assigned to the transitions from the $^5D_4 \rightarrow {}^7F_J$ ($J = 6, 5, 4, 3$) transitions at 490, 544, 587 and

DOI: 10.1002/aoc

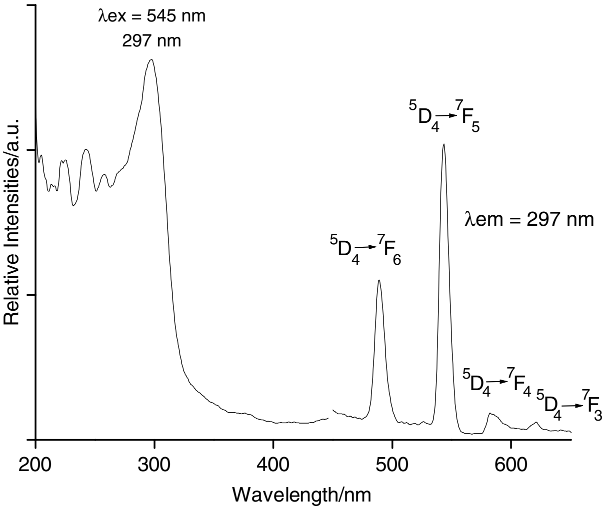

Figure 4. The excitation and emission spectra of the terbium resulting hybrid material.

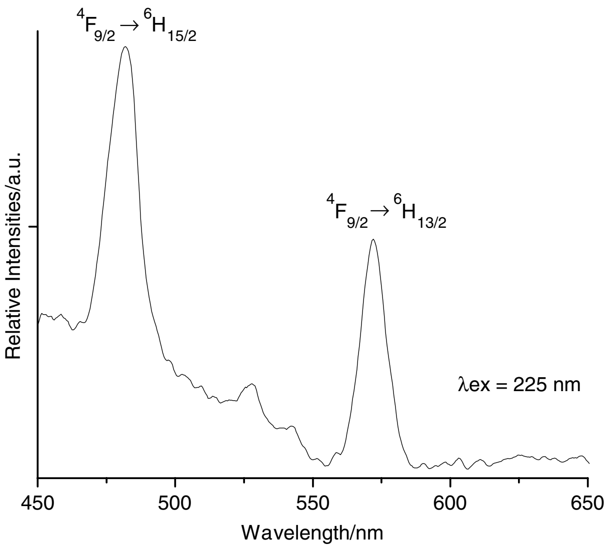

Figure 5. Emission spectra of Dy^{3+} containing molecular-based hybrids.

620 nm for terbium, $^4F_{9/2} \rightarrow {}^6H_J$ ($J = 15/2, 13/2$) transitions at 481 and 574 nm corresponding to Dy^{3+} and $^4G_{5/2} \rightarrow {}^6H_{7/2}$ transition at 597 nm for samarium. We still could not exclude other factors such as the relatively rigid structure of silica gel, which prohibits the vibration of ligand of RE^{3+} and limits non-radiative transitions. Hence, we may expect that, in this efficient way, leaching of the light-emitting molecules can be avoided; a higher concentration of metal ions is reached and clustering of the emitting centers may be changed. In addition, the Tb^{3+} and Dy^{3+} hybrid systems have stronger luminescence than that of Sm^{3+}, which agrees with the prediction from the energy match and intramolecular energy transfer.

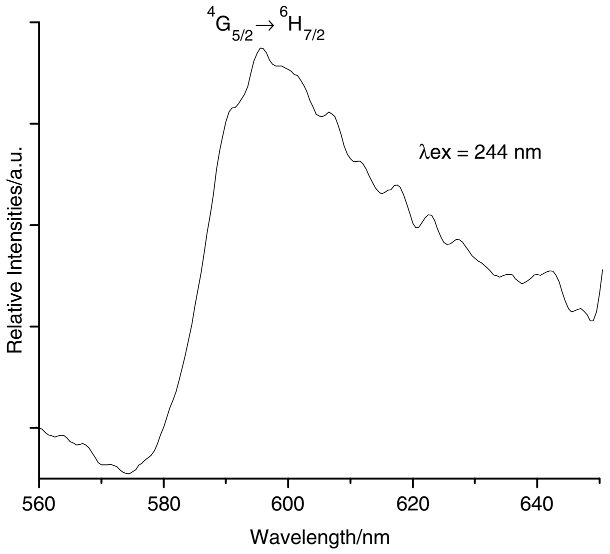

Figure 6. Emission spectra of Sm^{3+} containing molecular-based hybrids.

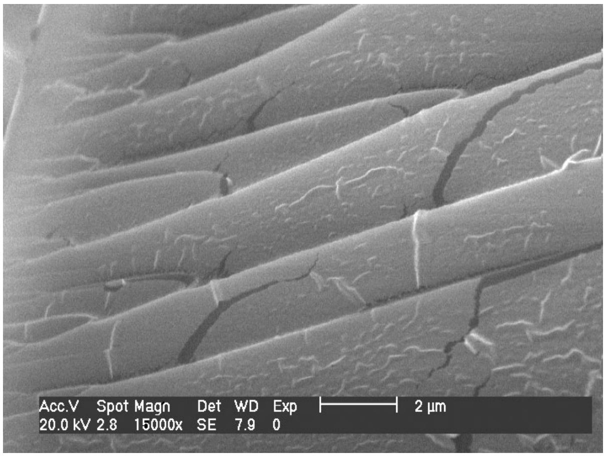

Figure 7. SEM graphs of Tb resulting molecular-based hybrid material.

The scanning electron micrographs for terbium containing hybrids are given in Fig. 7. It is worth pointing out that in Fig. 7 we observed some attracting regular micronmeter chains (approximately 2 µm) which were controlled by co-condensation reactions between Sal-Si and TEOS monomers. To our knowledge, it is less common to form such interesting structures and it is estimated that the complex of RE-4-ethoxy benzoic acid has the tendency of growing into infinite poly-chains[31] from a microstructure view and it retains the coordinated positions in corresponding bulk materials.

CONCLUSIONS

To investigate the coordination behavior between acylamide groups and rare earth ions, we designed three novel molecular-based hybrid materials. 4-Ethoxy benzoic acid was modified with 3-aminopropyl triethoxysilane and acted as a crosslinking monomer which plays a double role. On the one hand, it can coordinate to lanthanide ions through carbonyl groups; on the other, the hydrolysis and polycondensation reactions among triethoxysilyls of EB-Si and TEOS are ascribed to the formation of Si–O–Si network structures for the same ethoxy group. Meanwhile, strong green, blue or red luminescent systems with novel and homogeneous microstructures were achieved. In addition, the resulting hybrids could be shaped as monoliths or as transparent films with desired luminescence efficiency. We predicted that the novel structured organically modified silicate materials could prevent ions aggregation and be applied in the optical or opto-electronic fields.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (20301013).

REFERENCES

1. Avnir D, Levy D, Reisfeld R. *J. Phys. Chem.* 1984; **88**: 5956.
2. Avnir D. *Acc. Chem. Res.* 1995; **28**: 328.
3. Leu CM, Wu ZW, Wei KH. *Chem. Mater.* 2002; **14**: 3016.
4. Nandi M, Conklin JA, Salvati L, Sen A. *Chem. Mater.* 1990; **2**: 772.
5. Tanner PA, Yan B, Zhang HJ. *J. Mater. Sci.* 2000; **35**: 4325.
6. Koslova NI, Viana B, Sanchez C. *J. Mater. Chem.* 1993; **3**: 111.
7. Sanchez C, Lebeau B. *Mater. Res. Soc. Bull.* 2001; **26**: 377.
8. Franville AC, Zambon D, Mahiou R. *Chem. Mater.* 2000; **12**: 428.
9. Li HR, Lin J, Zhang HJ, Fu LS, Meng QG, Wang SB. *Chem. Commun.* 2001; 1212.
10. Li HR, Fu LS, Liu FY, Wang SB, Zhang HJ. *New J. Chem.* 2002; **26**: 674.
11. Li HR, Fu LS, Lin J, Zhang HJ. *Thin Solid Films* 2002; **416**: 197.
12. Li HR, Lin J, Zhang HJ, Li HC, Fu LS, Meng QG. *Chem. Mater.* 2002; **14**: 3651.
13. Li HR, Yu JB, Liu FY, Zhang HJ, Fu LS, Meng QG, Peng CY, Lin J. *New J. Chem.* 2004; **28**: 1137.
14. Wang QM, Yan B. *Inorg. Chem. Commun.* 2004; **7**: 747.
15. Wang QM, Yan B. *Inorg. Chem. Commun.* 2004; **7**: 1124.
16. Wang QM, Yan B. *J. Mater. Chem.* 2004; **14**: 2450.
17. Wang QM, Yan B. *Cryst. Growth Design* 2005; **5**: 497.
18. Wang QM, Yan B. *J. Mater. Res.* 2005; **20**: 592.
19. Yan B, Zhao LM. *Mater. Lett.* 2005; **59**: 795.
20. Binnemans K, Lenaerts P, Driesen K, Gorller-Walrand C. *J. Mater. Chem.* 2004; **14**: 291.
21. Carlos LD, Sa Ferreira RA, Pereira RN, Assuncao M, de Zea Bermudez V. *J. Phys. Chem. B* 2004; **108**: 14924.
22. Carlos LD, Sa. Ferreira RA, Rainho JP, de Zea Bermudez V. *Adv. Funct. Mater.* 2002; **12**: 819.
23. Sato S, Wada M. *Bull. Chem. Soc. Japan.* 1970; **43**: 1955.
24. Wu SL, Wu YL, Yang YS. *J. Alloys Compds.* 1994; **180**: 399.
25. Brown TD, Shepherd TM. *J. Chem. Soc. Dalton Trans.* 1973; 336.
26. Dexter DL. *J. Chem. Phys.* 1953; **21**: 836.
27. Yan B, Zhang HJ, Wang SB, Ni JZ. *Monafsh. Chem.* 1998; **129**: 151.
28. Yan B, Zhang HJ, Wang SB, Ni JZ. *J. Mater. Res. Bull.* 1998; **33**: 1517.
29. Zhang HJ, Yan B, Wang SB, Ni JZ. *J. Photochem. Photobiol. A.* 1997; **109**: 223.
30. Yan B, Zhang HJ, Wang SB, Ni JZ. *Spectrom. Lett.* 1998; **33**: 603.
31. Ma JF, Jin ZS, Ni JZ. *Chin. J. Inorg. Chem.* 1993; **9**: 160.