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Organization of luminescent molecular-scale hybrids with double strong chemical bonds from modification of a functional bridge

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2-chlorobenzoic acid was modified by (3-aminopropyl)triethoxysilane to behave as a intermediate and prepared their corresponding organic-inorganic molecular-based hybrid material with the two components equipped with covalent bonds . The critical point is that the derivative of chlorobenzoic acid which is not confined only to coordinate to Tb^{3+} but is capable of undergoing hydrolysis and polymerization or cross-linking reactions with two ethoxy groups (both CBA-Si and TEOS) by Si-O bonds. According to the Judd-Ofelt theory, covalency increases with increasing reciprocal energy difference between the $4f^N$ and $4f^{N-1}5d^1$configurations. Ultraviolet absorption, phosphorescence spectra, and luminescence spectra were applied to provide supplementary information about the photophysical properties of the obtained hybrid material and the above spectroscopic data reveal that the triplet energy of modified chlorobenzoic acid matches with the emissive energy level of Tb^{3+}. Accordingly, the intramolecular energy transfer mechanism runs smoothly within these molecular-based hybrids and strong green emission of Tb^{3+} has been achieved.

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1. Introduction

Hybrid organic-inorganic materials are currently applied for various functional purposes with their extraordinary properties in many fields as they combine the mutual advantages of both organic and inorganic networks [1, 2]. Recently, Hybrids of lanthanide organic complexes introduced in silica gel have already been found to display characteristic emission intensities compared with simple metal ions in inorganic hosts. Organic components are regarded to be efficient sensitizers for the luminescence of rare earth ions, namely, the antenna effect. Anchored lanthanide complexes by aromatic carboxylic acids, β-diketones or heterocyclic ligands in a sol-gel derived matrix have been discussed in many latest studies [3-13]. However, the two networks remain as individual domains connected only via mechanical mixture and it seems impossible to solve the problem of clustering of emitting centers because only weak interactions (such as hydrogen bonding, van der waals force or weak static effect) present between organic and inorganic components. In addition, inhomogeneous dispersion of two phases and leaching of the photoactive molecules frequently occur in this kind of hybrid system for which the concentration of complexes is also prohibited. Following the classification by Sanchez et al., [14] class II is called the one which has the structure properties of true connections, through covalent bonding, between the organic and inorganic moieties. Lately, a few researches concerning the covalently bonded hybrids have emerged and the as-derived molecular-based materials exhibit monophasic appearance even at a high concentration of rare earth complexes [15-23]. Compared with diverse synthetic approaches, sol-gel method which is founded on hydrolysis/polycondensation reactions of metal alkoxides exhibits its unique features viz convenience, low temperature, versatility [3-6], which can be further realized by altering the sol-gel processing conditions to the control of the microstructure, the external shape or the degree of combination between the two phases. At present, the crucial step to prepare such materials is to synthesize a new monomer as a covalent bridge which can not only develop chelating effects that can bind to rare earth ions but also act as precursors of inorganic network [15-17]. Some previous researches have been done on complexes of rare earth-pyridine-dicarboxylic acid or their derivatives and the feasibility of dicarboxylic acid system has been firmly proved [22]. In this paper, we firstly use 2-chlorobenzoic acid as organic ligand, then we designed a covalently bonded hybrid inorganic-organic system that incorporated modified chlorobenzoic acid, tetraethoxysilane (TEOS) and H_2O. The reaction model for the hybridization formula of TEOS and CBA-Si may be described in Fig. 1. At the beginning of the reaction, as shown in Fig. 1 (Step I), the individual hydrolysis of CBA-Si and TEOS are predominant. The Step II, however, is related to the polycondensation reactions between hydroxyl groups of both CBA-Si and TEOS. After these treatments, the molecular-based hybrids bearing the Tb-O coordination bond and Si-O covalent bond can exhibit the strong green luminescence of Tb^{3+}.

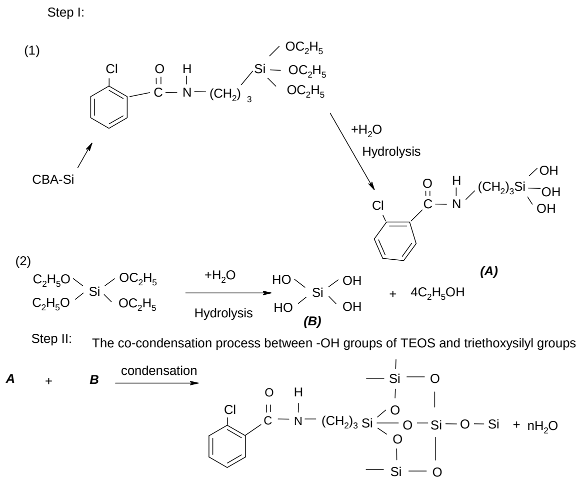


Fig. 1. Scheme of hydrolysis and polycondensation processes between CBA-Si and TEOS.

2. Experimental section

2.1 Chemicals and procedures

2-chloribenzoic acid was provided by Lancaster Synthesis Ltd. (3-aminopropyl)triethoxysilane (APS) was purchased from shanghai YaoHua chemical plant. Other starting reagents were used as received. A typical procedure for the preparation of CBA-Si was as follows: 2-chlorobenzoic acid was first converted to acyl chloride by refluxing in excess $SOCl_2$ under argon for 5 hours. After isolation, the acyl chlorides were directly reacted with APS in ethyl ether in presence of triethylamine. The resulting solution was stirred under argon for 5 hours at room temperature. After the filtration of the precipitates, a clear oil CBA-Si was furnished and dried on a vacuum line. CBA-Si: $C_{27}H_{51}O_8N_3Si_2$: IR (KBr): –CONH– (1648 cm^{-1}, 1569 cm^{-1}), C-Si (1198 cm^{-1}). ^1H NMR ($CDCl_3$): δ 7.73 (1H,t), 7.65 (1H,s), 7.58 (1H,d), 7.50 (1H,t), 3.87 (1H,s), 3.46 (9H,m), 3.18 (1H,s), 3.06 (2H,t), 2.71 (1H,s), 1.58 (2H,d), 1.18 (4H,m), 0.58 (2H,m) . ^{13}C NMR ($CDCl_3$): δ 166.9 (C_7), 132.9 (C_1), 131.9 (C_2), 131.2 (C_6), 130.7 (C_3), 127.3 (C_4), 127.0 (C_5), 72.5-71.4 (C_8-C_9), 71.0 (C_{10}), 49.9 ($CH_2(OEt)$), 18.4 ($CH_3(OEt)$). The sol-gel derived hybrid containing terbium was prepared as follows: CBA-Si was dissolved in ethanol, and TEOS, H_2O were added while stirring, then one drop of diluted hydrochloric acid was put into it to promote hydrolysis. A stoichiometric amount of $Tb(NO_3)_3{\cdot}6H_2O$ was added to the final stirring mixture. The mole ratio of $Tb(NO_3)_3{\cdot}6H_2O$ /CBA-Si/TEOS/H_2O was 1: 3: 6: 24. After the treatment of hydrolysis, 2 ml DMF (dimethylformamide) and appropriate amount of hexamethylene-tetramine were added to adjust the pH value of 6 ~ 7. The mixture was agitated magnetically to achieve a single phase and thermal treatment was performed at 60 °C until the sample solidified (see Fig. 2).

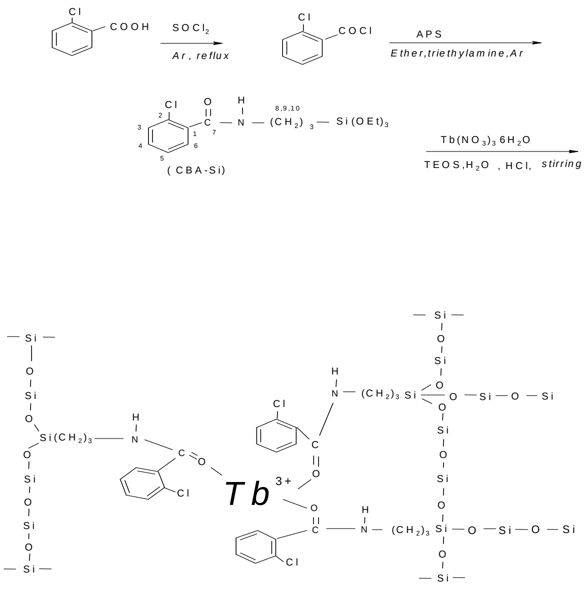


Fig. 2. Scheme of the synthesis process of CBA-Si and predicted structure of hybrid materials.

2.2 Measurements

All measurements were completed under room temperature. ^1H NMR spectra was recorded in DMSO 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} chloroform ($CHCl_3$) solution) were recorded with an Agilent 8453 spectrophotometer. Phosphorescence spectra (5×10^{-4} mol·L^{-1} $CHCl_3$ solution) and 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 microstructure was estimated by scanning electronic microscope (SEM, Philps XL-30).

3. Results and discussion

As for the phosphorescence spectra of 2-chlorobenzoic acid (A), CBA-Si (B) and CBA-Si with Tb^{3+} (Fig. 3). Phosphorescence spectrum belongs to character of the organic molecular ligands and different phosphorescence bands correspond to different ligand molecules, so a blue shift occurs between A and B in terms of modification of amino group (from 450 nm to 434 nm $A \rightarrow B$). There is no shift between B and C except the difference of intensities because they represent the same organic groups with the distinction that C can sensitize terbium ions and transfer part of energy. It can be indicated that the maximum phosphorescence band (B) is located at 434 nm and the triplet state energy of CBA-Si can be determined to be 23041 cm^{-1}. According to the energy transfer and intramolecular energy mechanism [24-29], it can be predicted that the triplet state energy of CBA-Si is quite suitable for the luminescence of terbium ion (20500 cm^{-1}) especially compared with 2-chlorobenzoic acid because the optimal energy match between CBA-Si and the resonant emissive energy level of the central Tb^{3+} ions is around 4000 ± 500 cm^{-1}.

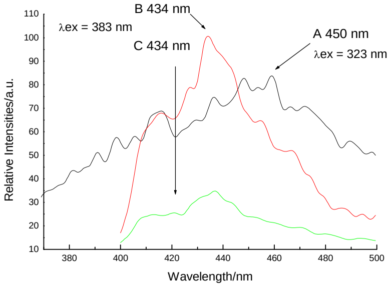


Fig. 3. Phosphorescence spectra of 2-chlorobenzoic acid (A), CBA-Si (B), and CBA-Si with Tb^{3+} ions (C).

The excitation spectrum of hybrid material (A) and the absorption spectrum of CBA-Si (B) are shown in Fig. 4 simultaneously. The corresponding overlap between these two spectra exhibits the effective sensitization of the Tb^{3+} by the organic ligand, thus makes sure that Tb^{3+} ions are bonded with CBA-Si.

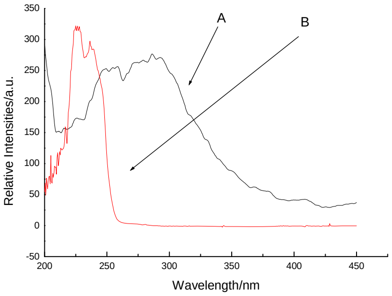


Fig. 4. The excitation spectrum of Hybrid material (A) and the absorption spectrum of CBA-Si (B).

Fig. 5 shows the Tb^{3+} 4f-5d absorption spectra of TEOS sol-gel materials doping directly with Tb^{3+} ions (A), TEOS hybrid materials doping with Tb-chlorobenzoic acid complex (B) and molecular-based hybrids (C). The different spectra correspond to diverse peak wavelengths (A 241 nm; B 251 nm; C 257 nm) which exhibit the difference in the covalency of terbium ions sites. In terms of Judd-Ofelt theory [30, 31] and much previous work 32-34 concerning relationship among hosts, bonding forms of RE ions and the transition properties of these metal ions, it has been reported that along with the increase of the peak wavelength, a corresponding degree of covalency between rare earth ions and ligands will be increased. As for A, most non-covalent interactions existed within Tb^{3+} ions and the surrounding environments. However, B and C that containing Tb-O covalent bonds exhibit obvious red shift compared with A (241 → 251 nm; 240 → 257 nm) which are caused by nephelauxetic effects and sensitivity to hosts. In terms of change between B and C, we may deduce that through the functionalization of strong covalent bonds like Si-O-Si, the molecular-based materials decrease the energy difference between $4f^8 \rightarrow 4f^7 5d^1$ or increase the polarizability of oxygen ions which result in a large overlap between lanthanide and ligand orbitals and a higher degree of covalency (Tb-O) was well established.

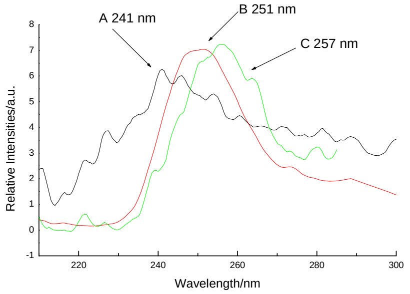


Fig. 5. The absorption spectra of TEOS sol-gel materials doping directly with Tb^{3+} ions (A), TEOS hybrid materials doping with Tb-chlorobenzoic acid complex (B) and molecular-based hybrids (C).

The excitation and emission spectra of the resulting Hybrid materials are shown in Fig. 6. The excitation spectra was obtained by monitoring the emission of Tb^{3+} ions at 545 nm and dominated by a broad band centered at 287 nm in the ultra-violet region which is the characteristic absorption of the lanthanide complexes arising from the efficient transition based on the conjugated double bonds of the aromatic benzoate ligand. 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 622 nm, respectively. Among these emission peaks, the most striking green luminescence ($^5D_4 \rightarrow {}^7F_5$) was observed in their emission spectra which indicated that the effective energy transfer took place between the CBA-Si and the chelated Tb^{3+} ions. Other factors still can not be excluded such as relatively rigid structure of silica gel which limits the vibration of ligand of Tb^{3+} and prohibits non-radiative transitions. Accordingly, we may expect that through this efficient way, leaching of the photoactive molecules can be avoided; higher concentration of metal ions is reached and clustering of the emitting centers may be prevented. Moreover, we have measured decay curves of the covalently bonded hybrid material and Tb-2-chlorobenzoic complex (Figs not presented, lifetimes were given in Table 1) and the corresponding curves can be described to be single exponential, showing that all the Tb^{3+} ions lie in the same chemical environment. The lifetime of covalently bonded silicate was greatly increased in contrast to pure complexes because rigid silica network restrict the vibration of CBA-Si ligands considerably and so improve the respective emission efficiency.

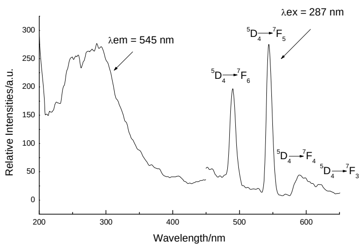
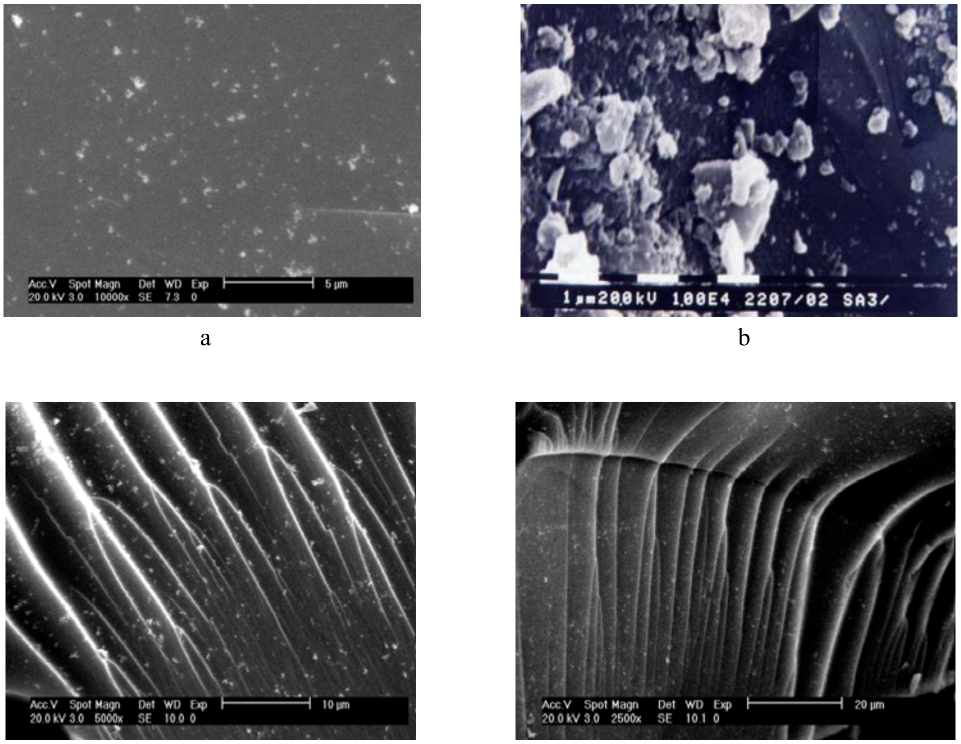


Fig. 6. Excitation and emission spectra of covalently bonded hybrid materials.

Table 1. The luminescent lifetimes for two different hybrid materials.

Compounds	Transition	Wavelength (nm)	τ(μs)
Covalently bonded hybrids	$^5D_4 \rightarrow {}^7F_5$	545	1232.7
2-chlorobenzoic complex	$^5D_4 \rightarrow {}^7F_5$	545	577.2

In contrast to the hybrid materials from conventional doping ways (Fig. 7b), this molecular-based materials was present demonstrated by the scanning electron micrographs that terbium complexes were dispersed in silica homogeneously through strong covalent bonds tied with the two moieties and they composed uniformly so two phases can exhibit their distinct properties together and no phase separation was observed (Fig. 7a). Especially, what arouse our interest were the chains like structures of the molecular-based hybrid materials, which seem as the trunk of pine trees (Fig. 7b-c). According to reference [35], the crystal structure of complex [Tb(o-ClC$_6$H$_4$CO$_2$)$_3$·H$_2$O]n reveals that each terbium ion coordinates to eight oxygen atoms from five carboxylate groups and one water molecule, the coordination number is considered to be nine. There are two types of coordination modes of 2-chlorobenzoic acid anions existing in the molecular structure of terbium 1-D coordination polymer: 1) bidentates chelating,, all the oxygen atoms participate into the coordination to one terbium ion; 2) tetradentates bridging, two of the whole five carboxylate groups take part in coordinating to two adjacent terbium ions, connecting Tb^{3+} ions to form the polymeric chain-like structure through such binding mode. Therefore, it is estimated that the complex of CBA-Si-Tb has the appealing tendency of growing into infinite chains from the microstructure view and it retains the coordinated positions in corresponding bulk materials.



a b

c d

Fig. 7. SEM graph of molecular-based hybrid materials.

4. Conclusions

In summary, because the organic monomers attached to the hosts must carry a functional organic group like triethoxysilyl capable of forming covalent bonds with tetraethoxysilane, we have modified 2-chlorobenzoic acid with functional (3-aminopropyl)triethoxysilane (APS) as a crosslinking molecule. Since the hydrolysis and polycondensation reactions between triethoxysilyl of CBA-Si and tetraethoxysilane lead to the formation of Si-O-Si network structures for the same ethoxy group of them, a novel luminescent molecular-based hybrid material was firstly achieved using CBA-Si derivative coordinated to Tb^{3+}. Hence, this homogeneous hybrid material with strong covalent bond within its molecule and chains like macrostructure is anticipated to probe its utilization in optical or electronic applications.

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References

[1] T. Suratwala, Z. Gardlund, K. Davidson, D. R. Uhlmann, Chem. Mater. **10**, 190 (1998).
[2] C. Molina, K. Dahmouche, C. V. Santilli, Chem. Mater. **13**, 2818 (2001).
[3] L. R. Matthews, E. T. Knobbe, Chem. Mater. **5**, 1697 (1993).
[4] M. Casalboni, R. Senesi, P. Prospositio, Appl. Phys. Lett. **30**, 2969 (1997).
[5] B. Lebeau, C. E. Fowler, S. R. Hall, J. Mater. Chem. **9**, 2279 (1999).
[6] P. Innocenzi, H. Kozuka, T. J. Yoko, J. Phys. Chem. B. **101**, 2285 (1997).
[7] K. Mstsui, F. Momose, Chem. Mater. **9**, 2588 (1997).
[8] K. Maruszewski, D. Andrzejewski, W. Strke, J. Lumin. **72-4**, 226 (1997).
[9] M. T. Murtagh, H. C. Kwon, M. R. Shahriari, J. Mater. Res. **13**, 3326 (1998).
[10] P. A. Tanner, B. Yan, H. J. Zhang, J. Mater. Sci. **35**, 4325 (2000).
[11] H. J. Zhang, L. S. Fu, S. B. Wang, Q. G. Meng, K. Y. Yang, J. Z. Ni, Mater. Lett. **38**, 260 (1999).
[12] J. Gracia, M. A. Mondragon, C. Tellez, Mater. Chem. Phys. **41**, 15 (1995).
[13] B. Yan, H. J. Zhang, S. B. Wang, J. Z. Ni, Mater. Chem. Phys. **51**, 92 (1997).
[14] C. Sanchez, F. Ribot, New. J. Chem. **18**, 1007 (1994).
[15] H. R. Li, J. Lin, H. J. Zhang, L. S. Fu, Chem. Mater. **14**, 3651 (2002).
[16] H. R. Li, J. Lin, H. J. Zhang, L. S. Fu, Chem. Commun. 1212 (2001).
[17] D. W. Dong, S .C. Jiang, Y. F. Men, X. L. Ji, B. Z. Jiang, Adv. Mater. **12**, 646 (2002).
[18] H. R. Li, L. S. Fu, H. J. Zhang, Thin Solid. Films **416**, 197 (2002).
[19] H. R. Li, J. Lin, L. S. Fu, J. F. Guo, Q. G. Meng, F. Y. Liu, H. J. Zhang, Microporous Mesoporous Mater. **55**, 103 (2002).
[20] F. Y. Liu, L. S. Fu, J. Wang, Z. Liu, H. R. Li, H. J. Zhang, Thin Solid Films. **419**, 178 (2002).
[21] K. Binnemans, P. Lenaerts, K. Driesen, W. C. Gorller, J. Mater. Chem. **14**, 291 (2004).
[22] A. C. Franville, D. Zambon, R. Mahiou, Chem. Mater. **12**, 428 (2000).
[23] F. Y. Liu, L. S. Fu, H. J. Zhang, New J. Chem. **27**, 233 (2003).
[24] S. Sato, M. Wada, Bull. Chem. Soc. Jap. 1970, 43, 1955.
[25] M. J. Kleinerman, J. Chem. Phys. **52**, 2370 (1969).
[26] B. Yan, H. J. Zhang, S. B. Wang, J. Z. Ni, Monafsh. Chem. Chem. Monthly **129**, 151 (1998).
[27] B. Yan, H. J. Zhang, S. B. Wang, J. Z. Ni, Mater. Res. Bull. **33**, 1517 (1998).
[28] H. J. Zhang, B. Yan, S. B. Wang, J. Z. Ni, J. Photochem. Photobiol. A. **109**, 223 (1997).
[29] B. Yan, H. J. Zhang, S. B. Wang, J. Z. Ni, Spectro. Lett. **33**, 603 (1998).
[30] B. R. Judd, Phys. Rev. **127**, 750 (1962).
[31] G. S. Ofelt, J. Chem. Phys. **37**, 511 (1962).
[32] H. H. Ebendorff, J. Non-Cryst. Solids. **248**, 247 (1999).
[33] S. Q. Xu, Z. M. Yang, S. X. Dai, J. H. Yang, L. L. Hu, Z. H. Jiang, J. Alloys Compds. **361**, 313 (2003).
[34] Y. L. Huang, Z. Feng, H. Xu, G. J. Zhao, G. S. Huang, S. G. Li, Solid State Commun. **127**, 1 (2003).
[35] J. F. Ma, Z. S. Jin, J. Z. Ni, Acta Chim. Sin. **51**, 784 (1993).

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