SENSITIZATION OF Yb(III), Er(III), AND Nd(III) LUMINESCENCE BY LIGANDS BASED ON 3-FORMYL-4-HYDROXYBENZOIC ACID AND TRANSITION METALS

F. F. Dang [1*], Q. Zhang [1], C. Zhu [1], Zh. Ju [2]

[1] School of Chemistry and Chemical Engineering at Xi'an University of Architecture and Technology, Xi'an Shanxi Province 710055, China; e-mail: dff516@163.com
[2] College of Chemistry and Chemical Engineering at Lanzhou University, Lan'zhou Gansu Province China

The syntheses of 3-formyl-4-hydroxybenzoic acid-derived ligands from ethylenediamine, diethylenetriamine, and triethylenetetramine are described. These ligands can further form hetero-binuclear complexes with transition metal ions (M^{2+} = Zn^{2+}, Fe^{2+}, Ni^{2+}, Mn^{2+}) and lanthanide ions (Ln^{3+} = Nd^{3+}, Er^{3+}, Yb^{3+}). The spectroscopic properties were studied using near infrared (NIR) luminescence emission spectra, fluorescence lifetime, and quantum yield. These hetero-nuclear complexes exhibited the characteristic lanthanide near-infrared luminescence in the solid state through energy-transfer from the chromophore to lanthanide ions. The d-block emission bands of transition metal ions in the solid state overlapped with f-f absorption bands of Yb(III), Er(III), or Nd(III), sensitizing the near-infrared luminescence of these hetero-binuclear complexes.

Keywords: *lanthanide ions, hetero-binuclear complexes, sensitization, NIR luminescence.*

СЕНСИБИЛИЗАЦИЯ Yb(III), Er(III) И Nd(III)-ЛЮМИНЕСЦЕНЦИИ ЛИГАНДАМИ НА ОСНОВЕ 3-ФОРМИЛ-4-ГИДРОКСИБЕНЗОЙНОЙ КИСЛОТЫ И ПЕРЕХОДНЫХ МЕТАЛЛОВ

F. F. Dang [1*], Q. Zhang [1], C. Zhu [1], Zh. Ju [2]

УДК 535.37

[1] Сианьский университет архитектуры и технологий, Сиань, провинция Шаньси, 710055, Китай; e-mail: dff516@163.com
[2] Колледж химии и химической инженерии университета Ланьчжоу, Ланьчжоу, провинция Ганьсу, Китай

(Поступила 4 февраля 2020)

Описан синтез лигандов на основе 3-формил-4-гидроксибензойной кислоты и этилендиамина, диэтилентриамина и триэтилентетрамина. Эти лиганды могут дополнительно образовывать гетеробиядерные комплексы с ионами переходных металлов (M^{2+} = Zn^{2+}, Fe^{2+}, Ni^{2+}, Mn^{2+}) и ионами лантанидов (Ln^{3+} = Nd^{3+}, Er^{3+}, Yb^{3+}). Исследованы спектры люминесценции в ближней ИК-области, время жизни флуоресценции и квантовый выход. Гетероядерные комплексы проявляют характерную люминесценцию лантаноидов в ближней ИК-области в твердом состоянии за счет передачи энергии от хромофора к ионам лантаноидов. Полосы излучения d-блока ионов переходных металлов в твердом состоянии перекрываются с полосами поглощения f-f Yb(III), Er(III) или Nd(III), сенсибилизируя люминесценцию этих гетеробиядерных комплексов в ближнем ИК-диапазоне.

Ключевые слова: *ионы лантаноидов, гетеробиядерные комплексы, сенсибилизация, люминесценция в ближней инфракрасной области.*

Introduction. Owing to their unique electronic configuration, the lanthanide cations have linear emission spectrum, high color purity, and long fluorescence lifetime, which makes them appropriate for several applications [1–5]. Among them, the lanthanide ions with near infrared luminescence such as Er(III), Nd(III), and Yb(III) receive special attention. They are widely employed in laser, optical fiber communica-

tion, and near infrared light diagnosis because of their large penetration depth, small background interference, high sensitivity, good thermal effects, etc. [6]. However, due to symmetry-forbidden *f-f* transitions, the near-infrared luminescence of the above ions has to be sensitized by the chromophores that can absorb shorter wavelengths. As the cells and tissues can be damaged in the UV area [7, 8], it limits their use in biological imaging [9].

To address these issues, in recent years, scientists have proposed to use *d*-block metal organic chromophore as a sensitizer to obtain lanthanide near infrared luminescence via *d-f* energy transfer [10, 11]. These chromophores have a strong absorption in the visible region, where the biological tissues can be safe. Also, they have other advantages such as a high triplet quantum efficiency, long-life triple excited state, etc. [12]. Hence, it is a promising route for the development of lanthanide-based near-infrared luminescence. To obtain *d-f* hetero-nuclear compounds, the *d-f* energy transfer from the transition metal organic chromophores to the lanthanide luminescent mass has to be achieved. This can be attained by employing suitable organic bridging ligands, which have "soft" coordination atoms such as P, S, C, and N that can coordinate with *d*-block transition metal ions, and the "hard" coordination atoms such as O that can coordinate with the *f*-block lanthanide metal ions [13–16].

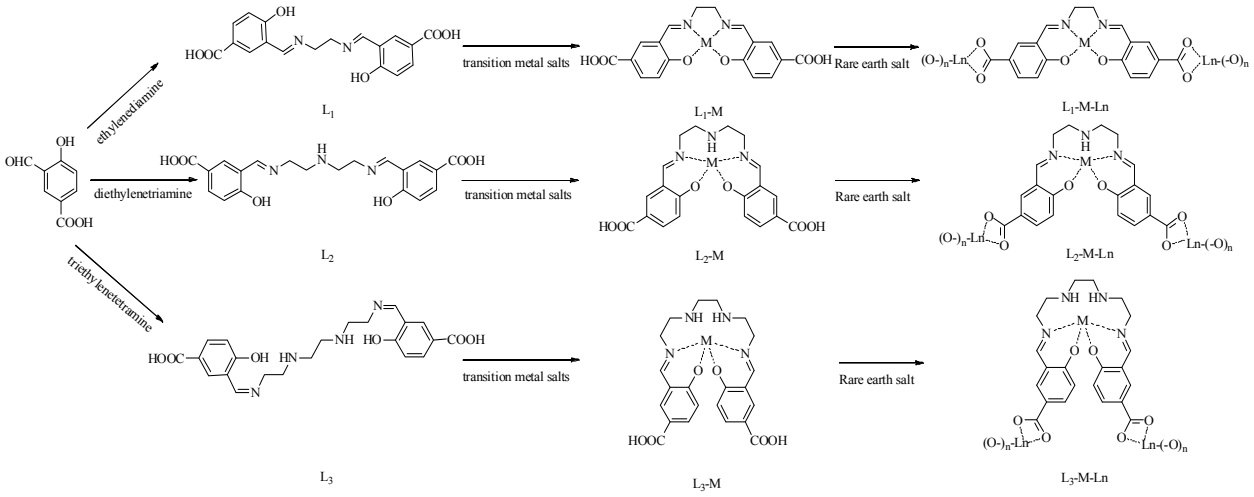
Therefore, herein, a series of carboxylic salicylaldehyde Schiff base organic ligands and their *d-f* complexes were synthesized. The obtained compounds were characterized using the IR spectra, UV-vis spectra, and near-IR luminescence spectra.

Experimental. 3-formyl-4-hydroxybenzoic acid was prepared according to the literature [17] with slight modifications.

Preparation of Schiff base ligands. First, a solution of 3-formyl-4-hydroxybenzoic acid (14.96 g, 90 mmol) in ethanol was added to a stirred solution of ethylenediamine (2.67 mL, 40 mmol) in ethanol (200 mL). Then the stirred reaction mixture was refluxed for 3 h and the mixture was concentrated by vacuum filtration. The desired product (L_1, 9.39 g, 72.0% yield) was recrystallized twice from ethanol [18]. L_2 and L_3 were prepared by the same method using diethylenetriamine and triethylenetetramine, respectively, as the starting material.

Preparation of the complexes. L_1 (5.7 g, 16.0 mmol) was completely dissolved in deionized water, and the pH was carefully adjusted to ~7.0 with dilute ammonia water. A solution of $Zn(CH_3COO)_2 \cdot 2H_2O$ (3.4 g, 15.5 mmol) in deionized water was added to the aqueous solution of ligands. The mixture was then stirred at room temperature for 4 h. The precipitate was obtained by centrifugation, which was separated and washed three times with deionized water. A yellow product was obtained (L_1-Zn, 5.6 g) [19]. The other mononuclear transition metal compounds were prepared by the same method using L_1, L_2, and L_3 with $Mn(CH_3COO)_2 \cdot 4H_2O$, $NiCl_2 \cdot 6H_2O$, or $Fe(NO_3)_3 \cdot 6H_2O$ separately.

The synthesis process of *d-f* hetero-nuclear metal compounds was the same as that mentioned above. Extremely light yellows products were obtained, and the synthesis paths are presented in Scheme 1.



Scheme 1. Synthesis of Schiff base ligands and their complexes (M^{2+} = Zn^{2+}, Fe^{2+}, Ni^{2+}, and Mn^{2+}; Ln^{3+} = Nd^{3+}, Er^{3+}, and Yb^{3+}).

Results and discussion. *IR spectra.* The vital IR assignments in the spectra of the ligands and their complexes are listed in Table 1 [20]. The IR spectra of L_1, L_1-Fe, and L_1-Fe-Er are good examples to describe the L_1 coordination. The IR band at 1637 cm^{-1} was due to the presence of the C=N group. The bands at 3417 and 1123 cm^{-1} were assigned to the C-O group and O-H group, respectively, indicating the presence of phenol hydroxyl. The IR band around 1397 cm^{-1} is related to the COO^- group. Regarding the complexes with transition metal, the corresponding bands $\nu_{(O-H)}$ of phenol hydroxyl and $\nu_{(C=N)}$ were red shifted. It is shown that the transition metal was coordinated with the N atom of the imines group of L_1 and the O atom of the phenol hydroxyl group [21]; $\nu_{(COO-)}$ was not shifted, suggesting that the carboxyl group did not coordinate with the transition metal, which is due to the steric hindrance and the "hard" coordination atoms. For example, "O" can hardly coordinate with transition metal ions [13–15]. These results coincide with our initial design. When the hetero-nuclear complexes were further formed with the lanthanides ions, $\nu_{(COO-)}$ were clearly blue-shifted and $\nu_{(C=N)}$ were shifted to higher wave number, which indicates that there are two coordination modes between the lanthanide metals and carboxyl group [22]. This is because when the carboxy coordinates with the lanthanide ions, the unshared pair electrons on the carboxylic oxygen shift from the benzene ring, which leads to the stability of the conjugated system of the benzene ring and the carboxyl group are reduced. The conjugation stability of the benzene ring and C=N is further affected, and the polarity of the C=N double bond is enhanced [22]. The characteristic peaks of other hetero-nuclear complexes are similar, indicating they have the same structure. The IR bands at 3120 cm^{-1} of L_2 and 3114 cm^{-1} of L_3 were due to the presence of the N-H group. $\nu_{(N-H)}$ were not shifted, indicating that the N atom of the NH group in L_2 and L_3 was not coordinated with the lanthanide metal ions and transition metal ions [23].

TABLE 1. IR Spectral Data (KBr) (cm^{-1})

Complex	$\nu_{(O-H)}$	$\nu_{(C-O)}$	$\nu_{(C=N)}$	$\nu_{(COO-)}$	$\nu_{(N-H)}$
L_1	3432	1109	1625	1392	–
L_1-Fe	3418	1123	1612	1396	–
L_1-Fe-Er	3452	–	1638	1412	–
L_2	3450	1121	1640	1401	3120
L_2-Mn	3422	1114	1626	1396	3119
L_2-Mn-Nd	3452	–	1630	1412	3127
L_3	3432	1116	1630	1398	3114
L_3-Ni	3424	1117	1610	1399	3114
L_3-Ni-Nd	3459	–	1631	1414	3118

UV-Vis spectra. The absorption spectra in aqueous solution ($c = 1\times10^{-4}$ mol/L, pH 7–8) were investigated at room temperature using UV-Vis spectrophotometer NicoIet Evolution 300 (Thermo Fisher Scientific). As shown in Fig. 1a, the absorption spectra of the three ligands were similar, displaying three bands at 208, 230, and 255 nm, belonging to the π-π* electron transitions of the conjugated large π bond system of the benzene ring. The other one at 348 nm is attributed to the *n*–π* transitions in C=N groups [24]. L_1 had stronger UV-vis absorption than L_2 or L_3 because L_1 Schiff base imines can form a large π bond conjugate system containing two aromatic rings. The spectra of their transition metal complex and *d-f* hetero-binuclear ones were also similar. Therefore, L_1, L_1-Fe, and L_1-Fe-Er are used as examples to discuss the absorption spectra. Comparing Fig. 1a with b, the absorption spectra of the complexes were similar to those of the ligands, implying that the lanthanide ions had no significant impact on the energy of 1ππ* state. As the metal ions themselves have weak absorption in the ultraviolet region, the UV absorption of the hetero-nuclear complex came from L_1, which is substantially independent of the central ion [25]. When the ligand L_1 coordinated with Fe^{2+} ions, the characteristic absorption peak became sharp and blue-shifted. As the electron-withdrawing group, the Fe atoms became the central ions after π-electron cloud density decreased and transition energy increased, resulting in blue-shift phenomenon [26]. However, compared with the complex L_1-Fe, the characteristic absorption peaks of the hetero-nuclear complex L_1-Fe-Er displayed a red-shift (π-π* transition, 227→246 nm) and a blue-shift (*n*-π* transition, 320→310 nm), which further suggests that a stable complex structure was formed between the L_1-Fe and lanthanide metal ion [26].

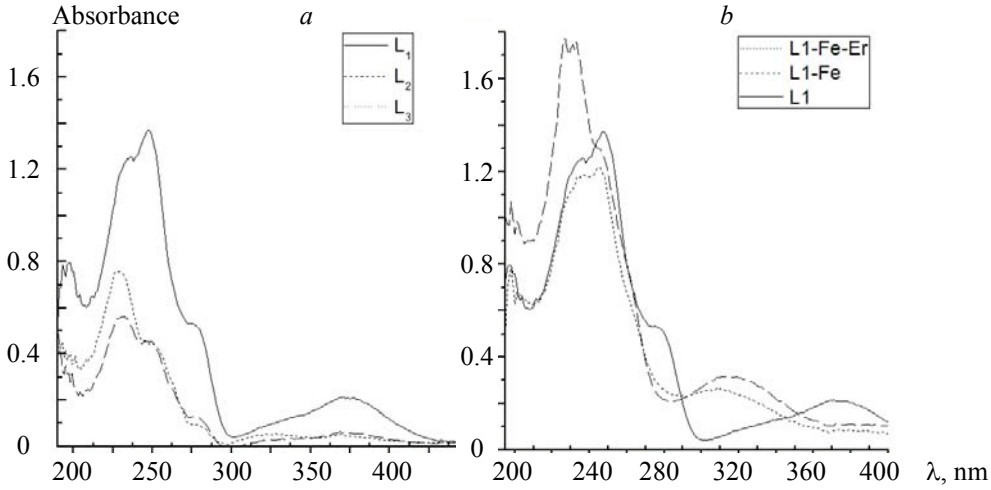


Fig. 1. (a) UV-vis spectra of L_1, L_2, and L_3; (b) L_1, L_1-Fe, and L_1-Fe-Er.

NIR Spectra. The NIR-emission spectra in solid were investigated at room temperature using FLS 920 (UK Edinburgh Instruments Co.). As shown in Fig. 2a, the NIR-emission spectra of Yb(III) ion were characterized by only one intra-configurational manifold of transition $^2F_{5/2}\rightarrow{}^2F_{7/2}$ around λ_{em} = 980 nm under the excitation of 608 nm, which is significantly more intense for L_1 complexes than for L_2 or L_3 ones. This result signifies more effective sensitization (or energy-transfer overlap) in L_1 complexes to the $^2F_{7/2}$ excited state of Yb(III) than in L_2 and L_3 ones.

As per Fig. 2b, upon excitation at 584 nm, the emission spectra of Nd(III) complexes displayed main characteristic emission lines corresponding to $^4F_{3/2}\rightarrow{}^4I_{11/2}$ (1060 nm) transition, which is potentially suitable for application in laser emission [27]. The peaks of L_1-Ni-Nd were higher than the ones for L_3-Ni-Nd, and for the other Nd(III) complexes, no prominent or only feeble NIR emission attributable to Nd^{3+} ion was observed under the experimental conditions. Hence, although the Nd^{3+} ion has several electronic excited states that are appropriate for accepting energy from a sensitizer, its NIR emission may have been quenched by N-H vibrations from the ligands L_2 and L_3 [28]. As per Fig. 2c, the emission spectra of Er(III) complexes were composed of typical Er(III) emission, corresponding to $^4I_{13/2}\rightarrow{}^4I_{15/2}$ (1532 nm) transition at 715 nm excitation (position of the ligand absorption band). As shown in Fig. 2b, all the complexes of L_1, such as L_1-Fe-Er, L_1-Ni-Nd, and L_1-Zn-Yb, had higher luminescence intensity than the ones of L_2 and L_3.

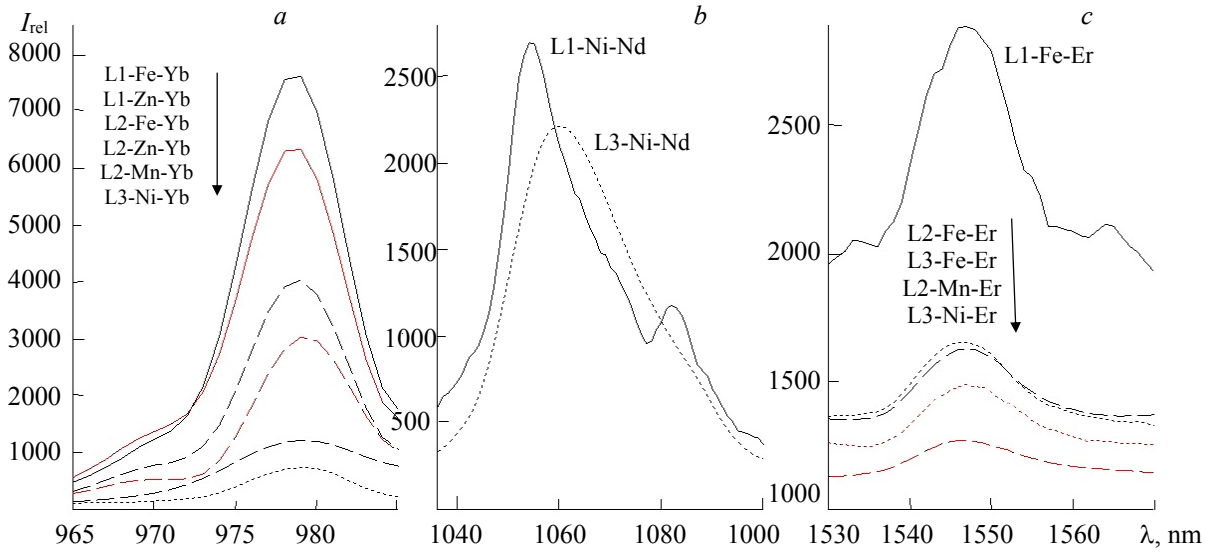


Fig. 2. Near-IR luminescent emission spectrum.

Lifetime and quantum yields. The lifetime and calculated quantum yield are summarized in Table 2. The decay process is double-exponential decay. The quantum yield for metal-based emission processes in solid is determined from the formula, $\Phi = \tau_{obs}/\tau_0$, where τ_{obs} is the observed emission lifetime and τ_0 is the "natural" lifetime, viz. 8.0, 0.25, and 2 ms for Er^{3+}, Nd^{3+}, and Yb^{3+}, respectively [29]. Notably, only the Yb(III) compounds displayed long fluorescence lifetime and good quantum yield, while for the Er(III) and Nd(III) compounds, the lifetime was too short for calculation of quantum yield. The Er(III) and Nd(III) compounds probably experienced some other phenomenon, such as more effective C-H vibration quenching [30].

TABLE 2. Near-IR Luminescence Data

Complex	λ_{max}, nm (I_{rel})	τ_1, τ_2, μs	Φ, %
L_1-Fe-Yb	979 (8524)	1.9792 (10.40%), 9.9765 (89.60%)	0.499
L_1-Zn-Yb	979 (7063)	0.8703 (30.36%), 8.6042 (69.64%)	0.430
L_2-Fe-Yb	979 (4586)	1.9105 (23.78%), 9.0404 (76.22%)	0.452
L_2-Zn-Yb	979 (3431)	0.8183 (31.94%), 9.4219 (68.06%)	0.471
L_2-Mn-Yb	979(1244)	1.4377(24.65%), 8.2650(75.35%)	0.413
L_3-Ni-Yb	978 (807)	2.2597 (25.64%), 10.2544 (74.37%)	0.513

Conclusions. Herein, novel transition-lanthanide (*d-f*) complexes have been developed based on derivatives of 3-formyl-4-hydroxybenzoic acid. Their Infrared, UV-vis, and near-infrared luminescence spectra have been studied. It is concluded that the *d*-block transition metal complexes can be used as chromophore to sensitize the near-infrared luminescence of Yb(III), Er(III), or Nd(III) ions.

Acknowledgments. The authors acknowledge China Scholarship Fund for support.

REFERENCES

1. Y. Cui, Y. Yue, G. Qian, *Chem. Rev.*, **112**, No. 2, 1126–1162 (2012).
2. T. L. Mako, J. M. Racicot, M. Levine, *Chem. Rev*., **119**, No. 1, 322–477 (2019).
3. K. Y. Zhang, Q. Yu, H. J. Wei, S. J. Liu, Q. Zhao, W. Huang, *Chem. Rev.*, **118**, No. 4, 1770–1839 (2018).
4. H. Terraschke, C. Wickleder, *Chem. Rev.*, **115**, No. 20, 11352–11378 (2015).
5. M. C. Heffern, L. M. Matosziuk, T. J. Meade, *Chem. Rev.*, **114**, No. 8, 4496–4539 (2014).
6. L. J. Li, L. Wondraczek, L. H. Li, Y. Zhang, Y. Zhu, M. Y. Peng, C. B. Mao, *ACS Appl. Mater. Interfaces,* **10**, No. 17, 14509–14516 (2018).
7. Q. Zhan, J. Qian, H. Liang, *ACS Nano*, **5**, No. 5, 3744–3757 (2011).
8. X. Li, R. Wang, F. Zhang, *Sci. Rep.*, **3**, 3536–3543 (2013).
9. S. Faulkner, J. I. Matthews, *Application of Coordination Complexes in Comprehensive Coordination Chemistry*, 2nd ed., Vol. 9, Ed. M. D. Ward, Elsevier, Amsterdam, The Netherlands (2003).
10. L. J. Xu, G. T. Xu, Z. N. Chen, *Coord. Chem. Rev.*, **273-274**, 47–62 (2014).
11. X. Qin, X. W. Liu, W. Huang, M. Bettinelli, X. G. Liu, *Chem. Rev*., **117**, No. 5, 4488–4527 (2017).
12. X. Feng, Y. Q. Feng, J. J. Chen, S. W. Ng, L. Y. Wang, J. Z. Guo, *Dalton Trans*., **44**, 804–816 (2015).
13. M. Andruh, *Dalton Trans.*, **44**, 16633–16653 (2015).
14. K. Liu, W. Shi, P. Cheng, *Coord. Chem. Rev.*, **289-290**, 74–122 (2015).
15. A. Thevenon, J. A. Garden, A. J. P. White, *Inorg. Chem*., **54**, No. 24, 11906–11915 (2015).
16. Y. J. Dong, J. C. Ma, L. C. Zhu, et al., *Coord. Chem. Rev*, **70**, 103–115 (2017).
17. M. Komiyama, H. Hirai, *Macromol. Chem. Rapid Commun.*, **2**, 759–760 (1981).
18. J. R. Buchwald, S. Kal, M. R. Civic, I. M. DeJoode, A. S. Filatov, P. H. Dinolfo, *J. Coord. Chem.*, **69**, No. 11-13, 1695–1708 (2016).
19. M. Y. Khuhawar, et al., *Eur. Polym. J.*, **40**, No. 4, 805–809 (2004).
20. S. P. Wong, Y. Z. Xu, *Fourier Transform Infrared Spectrometer*, 3rd ed., Chemical Industry Press, Beijing, China (2016).
21. K. Liu, X. Liu, Q. Zeng, *ACS nano*, **6**, No. 5, 4054–4062 (2012).
22. B. W. Fei, P. F. Yan, T. Q. Liu, F. Yang, G. M. Li, *J. Lumin.*, **177**, 380–386 (2016).
23. W. X. Li, Y. S. Zheng, X. J. Sun, *J. Lumin.*, **130**, 1455–1462 (2010).

24. Z. Zhang, W. X. Feng, P. Y. Su, H. Liu, Y. Zhang, Z. Wang, T. Z. Miao, X. Q. Lü, D. D. Fan, W. K. Wong, R. A. Jones, *Spectrochim. Acta A*, **116**, 102–110 (2013).
25. X. Zou, P. Yan, J. Zhang, *Dalton Trans.*, **42**, 13190–13199 (2013).
26. W. Feng, Y. Zhang, X. Q. Lü, Y. N. Hui, G. X. Shi, D. Zou, J. R. Song, D. D. Fan, W. K. Wong, R. A. Jones, *CrystEngComm.*, **14**, 3456–3463 (2012).
27. X. P. Yang, D. Schipper, R. A. Jones, L. A. Lytwak, B. J. Holliday, S. M. Huang, *J. Am. Chem. Soc.*, **135**, No. 23, 8468–8471 (2013).
28. Y. Liu, K. Ai, J. Liu, Q. Yuan, Y. He, L. Lu, *Angew. Chem., Int. Ed*, **51**, No. 12, 1437–1442 (2012).
29. L. Liu, Z. Zhang, W. X. Feng,C. Yu, X. Q. Lv, W. L. Wong, R. A. Jones, *Inorg. Chem. Comm.*, **49**, 124–126 (2014).
30. S. I. Klink, L. Grave, D. N. Reinhoudt, F. G. J. M. v. Veggel, *J. Phys. Chem. A*, **104**, 5457–5468 (2000).