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PAPER

Bright-yellow to orange-red thermochromic luminescence of an Ag$^I_6$–Zn$^{II}_2$ heterometallic aggregate†

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A novel octanuclear Ag$^I_6$–Zn$^{II}_2$ heterometallic aggregate, (NH$_4$)$_2${[Zn$_2$(phen)$_2$(H$_2$O)$_4$][Ag$_6$(mna)$_6$]}·2H$_2$O·2CH$_3$CH$_2$OH (**1**, H$_2$mna = 2-mercaptonicotinic acid, phen = 1,10-phenanthroline), was stepwisely obtained based on a hexanuclear silver(I) metalloligand using a liquid–liquid diffusion method. It is an exceedingly rare example that exhibits interesting temperature dependent photoluminescence behaviors, including gradual changes in energy and intensity upon cooling.

Introduction

Current interest in luminescent compounds has been energetically pursued in the past few decades due to their numerous potential applications in light emitting devices.[1] The d^{10} coinage metal compounds are known to present a great variety of structural forms associated with rich photophysical properties.[2] Among these luminescent compounds, stimulated luminescence phenomena captured special attention, owing to their potential applications in luminescent switches and optical recording devices.[3] The polynuclear coinage metal clusters, especially Ag(I) clusters, with auxiliary organic chromophores are well-established candidates for the fabrication of luminescent materials.[4] On the other hand, controlling or modulating the luminescence properties of these compounds by external stimuli (such as mechanical grinding and thermal treatment) is particularly attractive in order to obtain photofunctional devices, such as luminescent molecular thermometer.[5] Recently, Prodi group reported a cluster-based fluorescence thermometry, trizwitterionic dicationic Cu$_5$ clusters, which exhibit excellent thermochromic luminescence performance in the range between −45 and +80 °C with the high sensitivity and the high temporal (sub-millisecond) and spatial (sub-micrometer) resolution.[6] Anyway, despite some sporadic reports on thermochromic phosphors, dyes, and coordination compounds,[7] these kinds of smart molecules are still in their infancy. Based on our previous work[8] and inspired by the

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†Electronic supplementary information (ESI) available: Powder X-ray diffraction (PXRD) patterns, IR spectrum, EDS, TGA for **1**. X-ray crystallographic data. CCDC 864085. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2dt32375c

Scheme 1 Schematic presentation of stepwise synthesis of **1** based on a hexanuclear silver(I) metalloligand.

exploration of thermochromic luminescent materials,[9] we used the liquid–liquid diffusion method to assemble a heterometallic Ag$^I_6$–Zn$^{II}_2$ aggregate based on a [Ag$_6$(mna)$_6$]$^{6-}$ metalloligand (hereafter, [Ag$_6$(mna)$_6$]$^{6-}$ is abbreviated as L$_{Ag}$),[10] namely, (NH$_4$)$_2${[Zn$_2$(phen)$_2$(H$_2$O)$_4$][Ag$_6$(mna)$_6$]}·2H$_2$O·2CH$_3$-CH$_2$OH (**1**, H$_2$mna = 2-mercaptonicotinic acid, phen = 1,10-phenanthroline), and its temperature-dependent emissive behaviors were firstly investigated (Scheme 1).

Experimental

Materials and methods

All chemicals and solvents used in the syntheses were of analytical grade and used without further purification. IR spectra were recorded on a Nicolet AVATAT FT-IR360 spectrometer as KBr pellets in the frequency range of 4000–400 cm^{-1}. The elemental analyses (C, H, N contents) were performed using a CE instruments EA 1110 analyzer. UV-Vis measurements (diffuse-reflectance mode) were carried out on a Varian Cary5000 UV-VIS-NIR spectrophotometer equipped with an integrating sphere at 298 K. Powder X-ray

diffraction (PXRD) data were collected on a Philips X'Pert Pro MPD X-ray diffractometer with Cu K$_\alpha$ radiation equipped with an X'Celerator detector. TG curves were measured from 25 to 800 °C on an SDT Q600 instrument at a heating rate of 5 °C min^{-1} under the N$_2$ atmosphere (100 mL min^{-1}). Energy dispersive X-ray spectra were obtained on a HITACHI S-4800 scanning electron microscope, which is equipped with a HORIBA EDS unit. The solid-state photoluminescence measurements were carried out on an Edinburgh Analytical Instruments FLSP920 spectrofluorimeter.

Synthesis of (NH$_4$)$_2$\{[Zn$_2$(phen)$_2$(H$_2$O)$_4$][Ag$_6$(mna)$_6$]\}· 2H$_2$O·2CH$_3$CH$_2$OH (1). First step: preparation of a solution of [Ag$_6$(mna)$_6$]$^{6-}$ metalloligand (solution A): a mixture of AgNO$_3$ (167 mg, 1 mmol) and H$_2$mna (155 mg, 1 mmol) was added to water (6 mL) in a conical flask under ultrasonic treatment (160 W, 40 kHz) for 20 min at room temperature. The precipitate was dissolved by dropwise addition of an aqueous solution of NH$_3$ (25%, 8 drops) to give a clear yellow solution.

Second step: preparation of a solution of a cationic metalloligand containing Zn(II) ions (solution B): a mixture of Zn-(OAc)$_2$·2H$_2$O (220 mg, 1 mmol) and phen (180 mg, 1 mmol) was added to water–ethanol (8 mL, v/v = 2 : 1) in a conical flask under ultrasonic treatment (160 W, 40 kHz) for 20 min at room temperature to give a clear colorless solution.

Third step: the solution B was carefully layered on the top of solution A in the tube (15 cm). After the solution was allowed to stand for about four days, pale yellow crystals 1 were formed. The crystals were filtered off and washed with ethanol and dried in air. Yield: *ca.* 75% based on Ag. Elemental analysis: Anal. Calc. for C$_{64}$H$_{66}$N$_{12}$O$_{20}$S$_6$Zn$_2$Ag$_6$: C 33.51, H 2.90, N 7.33%. Found: C 33.89, H 3.08, N 7.23%. Selected IR peaks (cm^{-1}): 3430 (s), 1579 (s), 1515 (w), 1427 (m), 1381 (s), 1225 (w), 1161 (w), 1122 (w), 1076 (m), 857 (m), 771 (w), 725 (m).

X-ray crystallography

Single crystal of the complex 1 was mounted on a glass fiber for data collection. Data were collected on a Rigaku R-AXIS RAPID Image Plate single-crystal diffractometer (Mo Kα radiation, λ = 0.71073 Å) equipped with an Oxford Cryostream low-temperature apparatus operating at 50 kV and 90 mA in ω scan mode for 1. Absorption correction was applied by correction of symmetry-equivalent reflections using the ABSCOR program.[11] The structure was solved by direct methods using SHELXS-97[12] and refined on F^2 by full-matrix least-squares procedures with SHELXL-97.[13] Hydrogen atoms were placed in calculated positions and included as riding atoms with isotropic displacement parameters 1.2–1.5 times U_{eq} of the attached C atoms. The hydrogen atoms attached to oxygen were refined with O–H = 0.85 Å, and U_{iso}(H) = 1.2U_{eq}(O). The structure was examined using the Addsym subroutine of PLATON[14] to assure that no additional symmetry could be applied to the models. Pertinent crystallographic data collection and refinement parameters are collated in Table 1. Selected bond lengths and angles are collated in Table S1 in ESI.† The hydrogen bond geometries for 1 are shown in Table S2 in ESI.†

Table 1 Crystal data for **1**

Empirical formula	C$_{64}$H$_{66}$N$_{12}$O$_{20}$S$_6$Zn$_2$Ag$_6$
Formula weight	2293.61
Temperature/K	173
Crystal system	Triclinic
Space group	$P\bar{1}$
a/Å	12.6846(4)
b/Å	12.8260(4)
c/Å	13.7071(5)
α/°	94.7760(10)
β/°	108.0400(10)
γ/°	115.4130(10)
Volume/Å^3	1853.59(11)
Z	1
ρ_{calc}/mg mm^{-3}	2.055
μ/mm^{-1}	2.435
F(000)	1132.0
Reflns collected/unique	16 091/7251
R_{int}	0.0629
Data/restraints/parameters	7251/0/401
Goodness-of-fit on F^2	1.064
Final R indexes [$I > 2\sigma(I)$]	R_1 = 0.0490, wR_2 = 0.1065
Final R indexes [all data]	R_1 = 0.0940, wR_2 = 0.1629
Largest diff. peak/hole/e Å^{-3}	1.62/−1.54

Result and discussion

General characterization

Phase purity of **1** is sustained by the powder X-ray diffraction pattern (Fig. S1 in ESI†). Thermogravimetry curves indicate (Fig. S3 in ESI†) that **1** has a gradual weight loss between 30 to 200 °C, corresponding to the release of uncoordinated solvents (observed, 6.78%; calculated, 5.59%), and then **1** started to decompose from 200 °C along with the loss of organic ligands. Energy dispersive X-ray spectroscopy proves the kinds of elements in **1** (Fig. S4 in ESI†). These results are in good agreement with solid state crystal structures.

Structure description. (NH$_4$)$_2$\{[Zn$_2$(phen)$_2$(H$_2$O)$_4$][Ag$_6$-(mna)$_6$]\}·2H$_2$O·2CH$_3$CH$_2$OH (1). The molecular structure of **1** determined from single crystal X-ray diffraction data is illustrated in Fig. 1a. Aggregate **1** is a discrete molecule containing one L$_{Ag}$ and two [Zn(phen)(H$_2$O)$_2$]$^{2+}$. The asymmetric unit of **1** consists of half L$_{Ag}$ located on an inversion center, one [Zn-(phen)(H$_2$O)$_2$]$^{2+}$, one NH$_4^+$, one ethanol and one lattice water molecule. The geometry, bond lengths and angles of L$_{Ag}$ are very similar to \{Na$_4$[Ag(mna)$_6$][(HOCH$_2$)$_3$CNH$_3$]$_2$·10H$_2$O\}.[10a] Only two of six carboxyl groups participate in linking Zn(II) centers which may be due to the combined requirements of steric hindrance and charge neutrality, that is to say, (i) six carboxyl groups are too crowded to fully bind metal centers, (ii) L$_{Ag}$ bears six negative charges which only can be neutralized by at most three Zn(II) ions. The L$_{Ag}$ adopts a μ_2-η^1:η^1 mode to link two [Zn(phen)(H$_2$O)$_2$]$^{2+}$ units to complete the whole octa-nuclear heterometallic aggregate in which Zn(II) is coordinated to two water molecules, two nitrogen atoms of one chelating phen ligand and one oxygen atom of mba (Zn1–O6 = 1.997(6), Zn1–O1W = 2.069(9), Zn1–O2W = 2.156(7), Zn1–N4 = 2.164(9) and Zn1–N5 = 2.087(7) Å) resulting in a distorted trigonal-bipyramidal geometry with the τ_5 parameter of 0.57 (for ideal trigonal-bipyramidal, τ_5 = 1).[15]
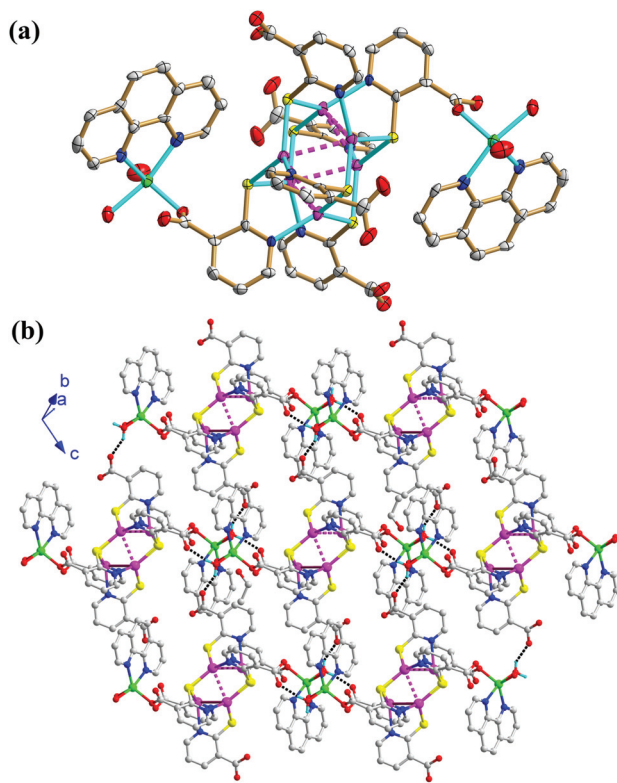
Fig. 1 (a) ORTEP drawing of the anionic part of **1** showing 30% thermal ellipsoids. Hydrogen atoms, NH_4^+, ethanol and water molecule are omitted for clarity. (b) The 2D layer formed by the packing of aggregates through hydrogen bonds (black dashed lines). Violet, Ag; green, Zn; yellow, S; blue, N; red, O; grey, C.
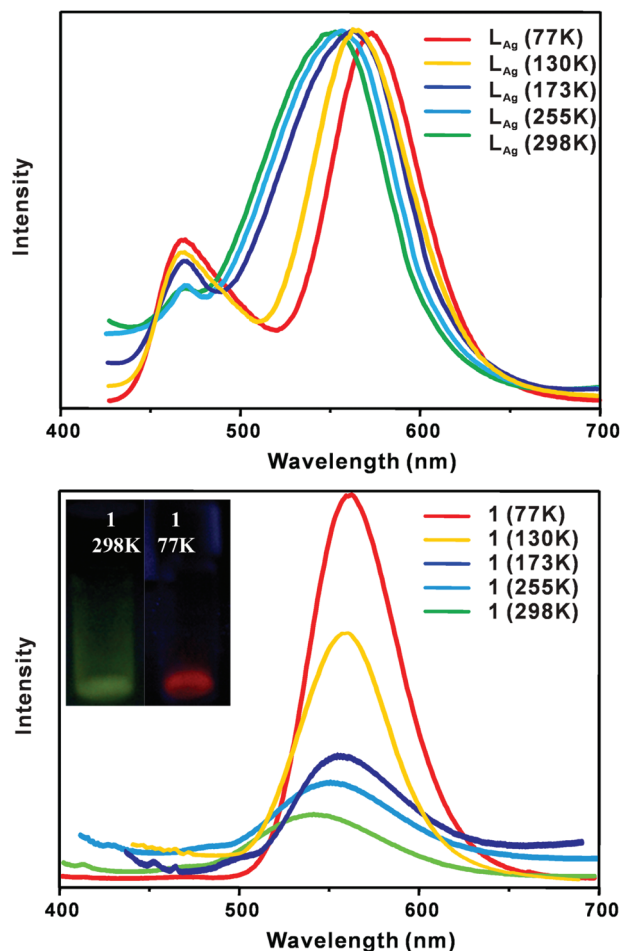

Fig. 2 Emission spectra of L_{Ag} and **1** in solid state at different temperatures under 365 nm excitation. Inset: photographs of the emission from **1** in the solid state at 77 K (right) and 298 K (left) under 365 nm excitation.

As shown in Fig. 1b, the Ag^I_6–Zn^{II}_2 aggregate packs as 2D layers in the crystal through inter-aggregate $O2W\cdots O_{carboxyl}$ hydrogen bonds ($O2W$–$H2WA\cdots O4^{iv}$ = 2.720(10) and $O2W$–$H2WB\cdots O2^{iii}$ = 2.766(9) Å, Table S2 in ESI†). The O7 atom on an ethanol molecule acts as both a hydrogen bond acceptor and donor to be fixed in the void of the crystal structure. Additionally, the $\pi\cdots\pi$ interactions between adjacent phen ligands ranging from 3.585(6) to 3.797(6) Å and C–H$\cdots\pi$ interactions contribute to the stability of the crystal packing (symmetry codes: (iii) $-x, -y, -z + 1$; (iv) $x - 1, y - 1, z - 1$).

UV-Vis absorption and temperature-dependent emissions

The absorption spectrum of yellow powder sample **1** was measured in solid state at room temperature. As shown in Fig. S5,† the intense broad absorption band for **1** in the range of 260–380 nm should be the transition of the ligand involving π orbitals of the aromatic ring of the mna moiety.

The temperature-dependent photoluminescence of metalloligand L_{Ag} and complex **1** was recorded in solid state at 298, 255, 173, 130 and 77 K (Fig. 2 and Table S3†). Under 365 nm excitation at 298 K, the L_{Ag} emission is at 551 nm accompanying a shoulder peak at 469 nm. Considering the emission of free H_2mna (λ_{em} = 470 nm, λ_{ex} = 300 nm, Fig. S6 in ESI†), the peaks at 469 and 551 nm can be attributed to π–$\pi^\star$ intraligand (IL) transitions of the mna ligand and ligand-to-metal charge

transfer (LMCT), mixed with cluster-centered (CC) transitions, respectively.[16] This assignment is consistent with the previous reports on the related Ag–S luminescent cluster.[4a] When cooling from 298 to 77 K, the high energy emission band of L_{Ag} was still kept at 469 nm with the stepwise increase of intensity, whereas the low energy emission band was gradually red-shifted from 551 nm to longer wavelength and reached 571 nm at 77 K, accompanying the negligible change in intensity. This result indicates that luminescence thermochromism in d^{10} metal complexes arises likely from interconversion between LMCT and CC or LLCT transition.[17] As we know, Ag$\cdots$Ag interactions largely contributed to the LMCT transition, so when cooling from 298 to 77 K, thermal compression of Ag$\cdots$Ag distance occurs in compounds, which is responsible for the red-shift of LMCT transition, suggesting that cluster-centered emission was strengthened at lower temperature.[18]

At 298 K, complex **1** shows blue-shifted (Δ = 7 nm) photoluminescence at 544 nm (λ_{ex} = 365 nm) with respect to L_{Ag} at 298 K. When cooling from 298 to 77 K, the emission band of complex **1** not only gradually red-shifts to 565 nm, but also has the dramatic enhancement in intensity. We tentatively assign

these temperature-dependent changes to be a synergistic effect of thermal relaxation between different emitting states and different Ag⋯Ag interactions at cryogenic temperature.[19] It is also noteworthy that all the emission properties are reversible in the temperature-dependent measurements. The emissive dissimilarities between L_{Ag} and **1** indicate that the energy level of LMCT excited state of L_{Ag} is essentially changed by incorporation of Zn(II)–phen units. Notably, low energy emission bands of both L_{Ag} and **1** show dramatic red-shifts (Δ = 20 nm) at 77 K compared to those at 298 K, which may be attributed to both the variation of the Ag⋯Ag interactions and enhanced intermolecular interaction such as hydrogen bond and π⋯π stacking at lower temperature.[20]

Conclusions

We have stepwisely assembled and characterized a heterometallic Ag^{I}_{6}–Zn^{II}_{2} aggregate based on a hexanuclear silver cluster metalloligand. We have firstly demonstrated that this heterometallic aggregate not only has intensive yellow photoluminescence at room temperature but also has a unique temperature-responsive photoluminescence in energy and intensity. The comparable results indicate that the incorporation of Zn(II) into the L_{Ag} has an important effect on the emission behaviors. This highly luminescent heterometallic aggregate whose emission properties vary with the temperature has thus great potential for light-emitting materials and sensor for temperatures.

Acknowledgements

References

1 (*a*) T. Jüstel, H. Nikol and C. Ronda, *Angew. Chem., Int. Ed.*, 1998, **37**, 3084; (*b*) A.-L. Pénard, T. Gacoin and J.-P. Boilot, *Acc. Chem. Res.*, 2007, **40**, 895; (*c*) G. Yuan, C. Zhu, Y. Liu, Y. Fang and Y. Cui, *Chem. Commun.*, 2010, **46**, 2307; (*d*) X. Liu, K.-L. Huang, G.-M. Liang, M.-S. Wang and G.-C. Guo, *CrystEngComm*, 2009, **11**, 1615; (*e*) R. B. Zhang, J. Zhang, Z. J. Li, J. K. Cheng, Y. Y. Qin and Y. G. Yao, *Cryst. Growth Des.*, 2008, **8**, 3735; (*f*) C. Seward, W. L. Jia, R. Y. Wang, G. D. Enright and S. N. Wang, *Angew. Chem., Int. Ed.*, 2004, **43**, 2933.

2 (*a*) P. C. Ford, E. Cariati and J. Bourasssa, *Chem. Rev.*, 1999, **99**, 3625; (*b*) G. F. Manbeck, W. W. Brennessel and R. Eisenberg, *Inorg. Chem.*, 2011, **50**, 3431; (*c*) M. G. Crestani, G. F. Manbeck, W. W. Brennessel, T. M. McCormick and R. Eisenberg, *Inorg. Chem.*, 2011, **50**, 7172; (*d*) M. Saitoh, A. L. Balch, J. Yuasa and T. Kawai, *Inorg. Chem.*, 2010, **49**, 7129; (*e*) G. F. Manbeck, W. W. Brennessel, C. M. Evans and R. Eisenberg, *Inorg. Chem.*, 2010, **49**, 2834; (*f*) G. F. Manbeck, W. W. Brennessel, R. A. Stockland Jr. and R. Eisenberg, *J. Am. Chem. Soc.*, 2010, **132**, 12307; (*g*) F. L. Jiang, C. F. Yan, Q. H. Chen, L. A. Chen, R. Feng, X. C. Shan and M. C. Hong, *Aust. J. Chem.*, 2011, **64**, 104; (*h*) S. B. Ren, X. L. Yang, J. Zhang, Y. Z. Li, Y. X. Zheng, H. B. Du and X. Z. You, *CrystEngComm*, 2009, **11**, 246; (*i*) C.-P. Li, J. Chen, Q. Yu and M. Du, *Cryst. Growth Des.*, 2010, **10**, 1623; (*j*) J. S. Hu, Y. J. Shang, X. Q. Yao, L. Qin, Y. Z. Li, Z. J. Guo, H. G. Zheng and Z. L. Xue, *Cryst. Growth Des.*, 2010, **10**, 4135; (*k*) C. Seward, J. L. Chan, D. T. Song and S. N. Wang, *Inorg. Chem.*, 2003, **42**, 1112; (*l*) C.-L. Chen, H.-Y. Tan, J.-H. Yao, Y.-Q. Wan and C.-Y. Su, *Inorg. Chem.*, 2005, **44**, 8510.

3 (*a*) M. Irie, T. Fukaminato, T. Sasaki, N. Tamai and T. Kawai, *Nature*, 2002, **420**, 759; (*b*) T. J. Wadas, Q.-M. Wang, Y.-J. Kim, C. Flaschenrein, T. N. Blanton and R. Eisenberg, *J. Am. Chem. Soc.*, 2004, **126**, 16841; (*c*) M. M. Olmstead, F. L. Jiang, S. Attar and A. L. Balch, *J. Am. Chem. Soc.*, 2001, **123**, 3260; (*d*) S. H. Lim, M. M. Olmstead and A. L. Balch, *J. Am. Chem. Soc.*, 2011, **133**, 10229; (*e*) E. Cariati, X. H. Bu and P. C. Ford, *Chem. Mater.*, 2000, **12**, 3385.

4 (*a*) G. Li, Z. Lei and Q.-M. Wang, *J. Am. Chem. Soc.*, 2010, **132**, 17678; (*b*) D. Sun, F.-J. Liu, R.-B. Huang and L.-S. Zheng, *Inorg. Chem.*, 2011, **50**, 12393; (*c*) Q.-M. Wang, Y.-A. Lee, O. Crespo, J. Deaton, C. Tang, H. J. Gysling, M. C. Gimeno, C. Larraz, M. D. Villacampa, A. Laguna and R. Eisenberg, *J. Am. Chem. Soc.*, 2004, **126**, 9488; (*d*) K. Zhou, C. Qin, H. B. Li, L. K. Yan, X. L. Wang, G. G. Shan, Z. M. Su, C. Xu and X. L. Wang, *Chem. Commun.*, 2012, **48**, 5844; (*e*) K. Zhou, X. L. Wang, C. Qin, H. N. Wang, G. S. Yang, Y. Q. Jiao, P. Huang, K. Z. Shao and Z. M. Su, *Dalton Trans.*, 2013, **42**, DOI: 10.1039/c2dt32145a; (*f*) Z. H. Chen, L. Y. Zhang and Z. N. Chen, *Organometallics*, 2012, **31**, 256; (*g*) I. O. Koshevoy, C.-L. Lin, A. J. Karttunen, M. Haukka, C.-W. Shih, P.-T. Chou, S. P. Tunik and T. A. Pakkanen, *Chem. Commun.*, 2011, **47**, 5533; (*h*) I. O. Koshevoy, Y.-C. Lin, A. J. Karttunen, P.-T. Chou, P. Vainiotalo, S. P. Tunik, M. Haukka and T. A. Pakkanen, *Inorg. Chem.*, 2009, **48**, 2094; (*i*) I. O. Koshevoy, Y.-C. Lin, A. J. Karttunen, M. Haukka, P.-T. Chou, S. P. Tunik and T. A. Pakkanen, *Chem. Commun.*, 2009, 2860.

5 (*a*) S. Uchiyama, N. Kawai, A. P. de Silva and K. Iwai, *J. Am. Chem. Soc.*, 2004, **126**, 3032; (*b*) Y. Cui, H. Xu, Y. Yue, Z. Guo, J. Yu, Z. Chen, J. Gao, Y. Yang, G. Qian and B. Chen, *J. Am. Chem. Soc.*, 2012, **134**, 3979; (*c*) E. J. McLaurin, V. A. Vlaskin and D. R. Gamelin, *J. Am. Chem. Soc.*, 2011, **133**, 149780.

6 D. Cauzzi, R. Pattacini, M. Delferro, F. Dini, C. Di Natale, R. Paolesse, S. Bonacchi, M. Montalti, N. Zaccheroni,

M. Calvaresi, F. Zerbetto and L. Prodi, *Angew. Chem., Int. Ed.*, 2012, **51**, 9662.

7 (*a*) J. Feng, K. Tian, D. Hu, S. Wang, S. Li, Y. Zeng, Y. Li and G. Yang, *Angew. Chem., Int. Ed.*, 2011, **50**, 8072; (*b*) H. S. Peng, M. I. J. Stich, J. B. Yu, L. N. Sun, L. H. Fischer and O. S. Wolfbeis, *Adv. Mater.*, 2010, **22**, 716; (*c*) F. H. C. Wong, D. S. Banks, A. Abu-Arish and C. Fradin, *J. Am. Chem. Soc.*, 2007, **129**, 10302; (*d*) C. D. S. Brites, P. P. Lima, N. J. O. Silva, A. Millán, V. S. Amaral, F. Palacio and L. D. Carlos, *Adv. Mater.*, 2010, **22**, 4499; (*e*) N. Tian, A. Thiessen, R. Schiewek, O. J. Schmitz, D. Hertel, K. Meerholz and E. Holder, *J. Org. Chem.*, 2009, **74**, 2718.

8 (*a*) D. Sun, L. Zhang, Z. Yan and D. Sun, *Chem.–Asian J.*, 2012, **7**, 1558; (*b*) D. Sun, D.-F. Wang, X.-G. Han, N. Zhang, R.-B. Huang and L.-S. Zheng, *Chem. Commun.*, 2011, **47**, 746; (*c*) D. Sun, G.-G. Luo, N. Zhang, R.-B. Huang and L.-S. Zheng, *Chem. Commun.*, 2011, **47**, 1461; (*d*) D. Sun, C.-F. Yang, H.-R. Xu, H.-X. Zhao, Z.-H. Wei, N. Zhang, L.-J. Yu, R.-B. Huang and L.-S. Zheng, *Chem. Commun.*, 2010, **46**, 8168; (*e*) D. Sun, D.-F. Wang, N. Zhang, F.-J. Liu, H.-J. Hao, R.-B. Huang and L.-S. Zheng, *Dalton Trans.*, 2011, **40**, 5677.

9 H. V. R. Dias, H. V. K. Diyabalanage, M. G. Eldabaja, O. Elbjeirami, M. A. Rawashdeh-Omary and M. A. Omary, *J. Am. Chem. Soc.*, 2005, **127**, 7489.

10 (*a*) I. Tsyba, B. B. K. Mui, R. Bau, R. Noguchi and K. Nomiya, *Inorg. Chem.*, 2003, **42**, 8028; (*b*) K. Nomiya, S. Takahashi and R. Noguchi, *J. Chem. Soc., Dalton Trans.*, 2000, 2091.

11 T. Higashi, *ABSCOR, Empirical Absorption Correction based on Fourier Series Approximation*, Rigaku Corporation, Tokyo, 1995.

12 G. M. Sheldrick, *SHELXS-97, Program for X-ray Crystal Structure Determination*, University of Gottingen, Germany, 1997.

13 G. M. Sheldrick, *SHELXL-97, Program for X-ray Crystal Structure Refinement*, University of Gottingen, Germany, 1997.

14 A. L. Spek, *Implemented as the PLATON Procedure, a Multipurpose Crystallographic Tool*, Utrecht University, Utrecht, The Netherlands, 1998.

15 A. W. Addison, T. N. Rao, J. Reedijk, J. Van Rijn and G. C. Verschoor, *J. Chem. Soc., Dalton Trans.*, 1984, 1349.

16 V. W.-W. Yam and K. K.-W. Lo, *Chem. Soc. Rev.*, 1999, **28**, 323.

17 (*a*) S. Perruchas, X. F. Le Goff, S. Maron, I. Maurin, F. Guillen, A. Garcia, T. Gacoin and J. P. Boilot, *J. Am. Chem. Soc.*, 2010, **132**, 10967; (*b*) H. Bouas-Laurent and H. Dürr, *Pure Appl. Chem.*, 2001, **73**, 639; (*c*) P. C. Ford, E. Cariati and J. Bourasssa, *Chem. Rev.*, 1999, **99**, 3625.

18 Q. Zhu, C. Shen, C. Tan, T. Sheng, S. Hu and X. Wu, *Chem. Commun.*, 2012, **48**, 531.

19 C.-M. Che, M.-C. Tse, M. C. W. Chan, K.-K. Cheung, D. L. Phillips and K.-H. Leung, *J. Am. Chem. Soc.*, 2000, **122**, 2464.

20 (*a*) P. D. Beer and P. A. Gale, *Angew. Chem., Int. Ed.*, 2001, **40**, 486; (*b*) R. L. White-Morris, M. M. Olmstead, F. Jiang, D. S. Tintia and A. L. Balch, *J. Am. Chem. Soc.*, 2002, **124**, 2327; (*c*) M. A. Mansour, W. B. Connick, R. J. Lachicotte, H. J. Gysling and R. Eisenberg, *J. Am. Chem. Soc.*, 1998, **120**, 1329.