Unprecedented cationic copper(I)–iodide aggregates trapped in "click" formation of anionic-tetrazolate-based coordination polymers†

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A series of unprecedented cationic copper(I)–iodide aggregates, $(Cu_4I_2)^{2+}$, $(Cu_6I_2)^{4+}$ and $(Cu_{10}I_4)^{6+}$, are trapped in the *in situ* formation of anionic-tetrazolate-based coordination polymers, namely $[Cu_2(\mu_3\text{-}I)(\mu_5\text{-}Cpta)]_n$ (1), $[Cu_5(\mu_4\text{-}I)(\mu_4\text{-}Mtta)_3(CN)]_n$ (2) and $[Cu_5(\mu_6\text{-}I)(\mu_2\text{-}I)(\mu_4\text{-}Mtta)_3]_n$ (3) [Cpta = 5-(3-cyanophenyl)tetrazolate, Mtta = 5-methyltetrazolate], which exhibit structure-related green, cyan and blue luminescence, respectively.

In the historical research realm of polynuclear d^{10} transition metal complexes,[1,2] the prominent copper(I)–iodide aggregates have attracted considerable attention, both in experimental[2a,b] and theoretical[2c] aspects. Recent focus has transferred from isolated clusters to functional copper(I)–iodide-based coordination polymers,[3–5] on the basis that the structural diversity and photophysical properties of copper(I)–iodide aggregates can be propagated to coordination polymers *via* proper bridging ligands. The structural variation in the $[(Cu_xI_y)^{x-y}]_n$ species is basically caused by the ligating versatility of the iodine anion, constructing diverse neutral ($x = y$), anionic ($x < y$) and cationic ($x > y$) aggregates.[3–6] In contrast to the extensively investigated neutral[3,4] and anionic species,[6] the structural and luminescent aspects of cationic copper(I)–iodide aggregates[5] remain unexplored due to synthetic and calculating difficulties.

The zinc-catalyzed "click" reaction for synthesizing 5-substituted 1*H*-tetrazoles, coined by Sharpless *et al.*,[7] was utilized in the preparation of functional tetrazolate coordination polymers, firstly by Xiong *et al.*,[8] and lately has been extended to copper- and silver-catalyzed hydro(solvo)thermal *in situ* reactions by our group.[9] Herein, we report three copper(I)–iodide–tetrazolate coordination polymers, namely $[Cu_2(\mu_3\text{-}I)(\mu_5\text{-}Cpta)]_n$ (**1**), $[Cu_5(\mu_4\text{-}I)(\mu_4\text{-}Mtta)_3(CN)]_n$ (**2**) and $[Cu_5(\mu_6\text{-}I)(\mu_2\text{-}I)(\mu_4\text{-}Mtta)_3]_n$ (**3**), which exhibit structure-related green, cyan and blue fluorescence, respectively.

In appropriate solvothermal conditions, we introduced cuprous iodide salt to the tetrazole cycloaddition precursors,[7b] sodium azide and isophthalonitrile (or acetonitrile), yielding complexes **1**, **2** and **3** (Chart S1 and Scheme S1, ESI).†‡ The cuprous iodide in these reactions serves not only as the metal catalyst for the *in situ* tetrazole cycloaddition, but also as the source of the copper(I)–iodide aggregates. X-Ray crystallographic analyses confirm the *in situ* formation of the deprotonated anionic tetrazolate groups, all of which act as μ_4 bridging ligands. Interestingly, in the "click" reactions forming anionic tetrazolates, we have trapped a series of unusual cationic copper(I)–iodide aggregates, $(Cu_4I_2)^{2+}$ (in **1**), $(Cu_6I_2)^{4+}$ (in **2**) and $(Cu_{10}I_4)^{6+}$ (in **3**), as shown in Fig. 1.

Complex **1** is a 3D coordination polymer constructed from repeating self-penetrated-macrocycle subunits (Fig. 2). There are two kinds of tetrahedral copper(I) atoms (Fig. S1, ESI†), ligated by the μ_3-centered iodine atoms, and which construct the cationic $(Cu_4I_2)^{2+}$ aggregates (Fig. 1 top left, Cu2···Cu2 2.721 Å, Cu1–N 1.984–2.104 Å, Cu1–I 2.672 Å, Cu2–N 2.053–2.113 Å, Cu2–I 2.627–2.665 Å). The Cpta ligand is generated *in situ* from the dicyano-precursor isophthalonitrile, in which only one cyano-group undergoes cycloaddition to generate the tetrazolate group.[8c,10] Two inverse Cpta ligands are linked through Cu1–I–Cu2 linkages to construct the macrocycle subunit, and two adjacent parallel macrocycles are connected by sharing a $(Cu_4I_2)^{2+}$ aggregate, generating a double-chain ribbon fragment (Fig. 2, left). These ribbons extend along the *a*-direction or the [110] direction in an inclined fashion. Each macrocycle subunit is penetrated by two others from adjacent inclined ribbons, and two adjacent inclined macrocycles are connected *via* two sets of Cu1–N bonds, accomplishing a rare 1D → 3D self-penetrating network (Fig. 2, right).[11] Notably, this structure represents an example of genuine self-penetrating entanglement entirely sustained by the coordinative bonds of the spacer ligands,[11f] unlike those derived from interpenetrated sets of independent networks that are cross-linked *via* counterion bridges, aurophilic metal-to-metal linkages or other weak interactions.[11c]

Complex **2** is a 3D coordination polymer constructed from fascinating crown-like macrocycle subunits and cyanide linkers (Fig. 3). There exist three crystallographically

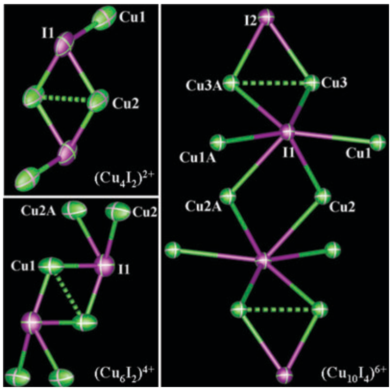

Fig. 1 A series of cationic copper(I)–iodide aggregates trapped in the *in situ* anionic tetrazolate formation. $(Cu_4I_2)^{2+}$ in **1**, $(Cu_6I_2)^{4+}$ in **2**, $(Cu_{10}I_4)^{6+}$ in **3** (Cu: green, I: purple).

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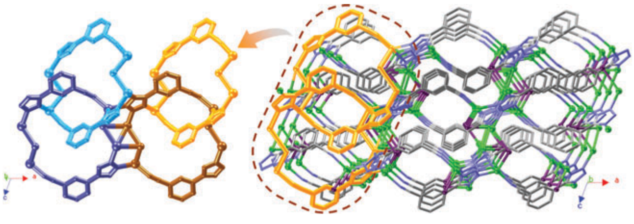

Fig. 2 Complex **1**: the overall 3D framework (right, Cu: green, I: purple, N: blue, C: grey, H omitted), showing the self-penetrating rings highlighted in orange, and the illustrated penetrated macrocycles (left, in different colours) that are linked together.

independent copper(I) atoms (Fig. S2, ESI†), two of which are tetrahedral and construct the cationic $(Cu_6I_2)^{4+}$ aggregates along with μ_4-centered iodine atoms (Fig. 1 bottom left, Cu1···Cu1 2.982 Å, Cu2–N 1.971–2.097 Å, Cu2–I 2.951 Å, Cu1–N 2.048 Å, Cu1–I 2.636–2.718 Å), and the other one is a trigonal copper(I) linking the cyanide group (Cu3···Cu3A 2.856 Å, Cu3–N 1.929–2.028 Å). The cyanide ligand was generated *in situ via* C–C bond cleavage in acetonitrile under the solvothermal conditions.[12] The building subunit is a 16-copper-membered crown-like macrocycle, in which all six μ_4-Mtta ligands are linked to copper(I) atoms (Fig. 3 right, bottom). Adjacent macrocycles along the *b*-direction are connected by sharing $(Cu_6I_2)^{4+}$ aggregates, constructing 1D double-ribbon fragments. Adjacent 1D fragments parallel along the *a*-direction are further connected *via* Cu2–N bonds in an ABAB fashion, generating a crossbedded layer fragment (Fig. 3 right, top). The overall 3D framework is accomplished by the connections of parallel 2D layers *via* Cu3–CN–Cu3 linkages, stabilized by aurophilic-like Cu3···Cu3A interactions (Fig. 3 left).

Complex **3** is a 2D bi-layered coordination polymer containing novel cationic $(Cu_{10}I_4)^{6+}$ building blocks (Fig. 4). All three types of the tetrahedral copper(I) atoms (Fig. S3†), ligated by the rare μ_6-centered and μ_2-bridged iodine atoms, are observed in the Z-ribbon-shape $(Cu_{10}I_4)^{6+}$ aggregates (Fig. 1 right, Cu3···Cu3 2.670 Å, Cu1–N 1.959–2.009 Å, Cu1–I 2.922 Å, Cu2–N 1.927 Å, Cu2–I 2.929 Å, Cu3–N 2.045–2.079 Å, Cu3–I 2.553–2.762 Å). Note that there are only two other examples of high-connected iodine atoms in copper(I)–iodide aggregates, one with μ_6 and the other with μ_8 bridging modes.[5b,13]

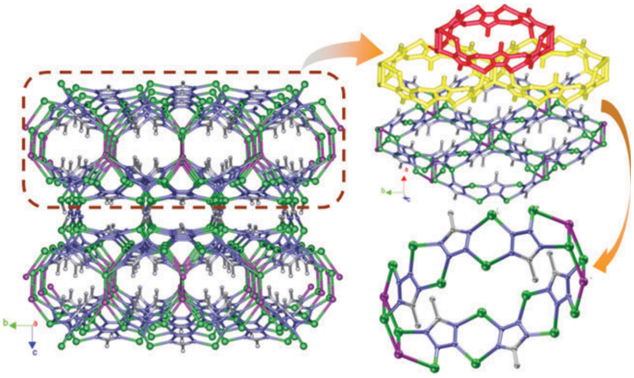

Fig. 3 Complex **2**: the overall 3D framework (left, Cu: green, I: purple, N: blue, C: grey, H omitted), and the 2D layer fragment (top right), showing the crown-like macrocycle subunits (bottom right) highlighted in red and yellow.

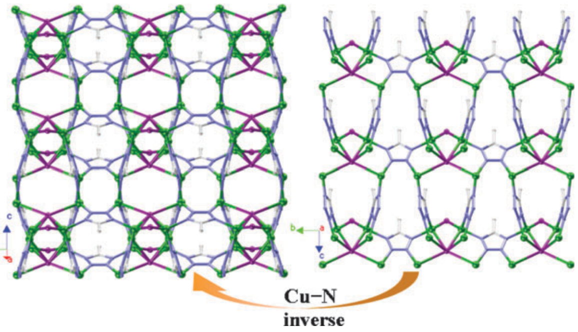

Fig. 4 Complex **3**: the overall 2D bi-layered framework (left, Cu: green, I: purple, N: blue, C: grey, H omitted) constructed from two inverse single layers (right).

The 2D bi-layered structure (Fig. 4 left) is constructed from two inverse parallel single layers (Fig. 4 right) linked *via* the Cu1–N bonds, and each layer contains one half of the $(Cu_{10}I_4)^{6+}$ aggregate, which connects six surrounding μ_4-Mtta ligands.

It is noteworthy that the observation of this series of cationic copper(I)–iodide aggregates is unexpected and unprecedented, according to the latest version of the Cambridge Structural Database (CSD).[14] The $[Cu_4I_2]$ linkage is commonly observed but mostly as a part of the neutral cubane-like Cu_4I_4 cluster, whereas the $[Cu_6I_2]$ linkage is sporadically observed in the construction of certain complicated $[Cu_xI_y]$ aggregates,[5b,15] and the $[Cu_{10}I_4]$ linkage has never been observed. The versatile iodine anions, with μ_3, μ_4 or μ_6 bridging modes, play dominant roles in generating diverse trigonal, tetrahedral or trigonal prismatic centers, and hence lead to distinct bond lengths and angles, especially the Cu···Cu distances (2.721 Å in **1**, 2.982 Å in **2**, 2.670 Å in **3**) in the different cationic aggregates, respectively. A prominent cationic $(Cu_{24}I_{10})^{14+}$ cluster, sustained by highly symmetrical anionic-polyoxometalate-based frameworks, was recently communicated.[5b]

At room temperature, solid-state **1**, **2** and **3** show distinct strong photoluminescence with maxima (λ_{max}^{em}) at 525 nm, 479 nm and 445 nm upon excitation at 393 nm, 355 nm and 338 nm, exhibiting green, cyan and blue emissions, respectively (Fig. 5). According to previous research and our investigation on copper(I)–tetrazolate compounds,[1,9] the emissions of these complexes are tentatively attributed to a [Cu →

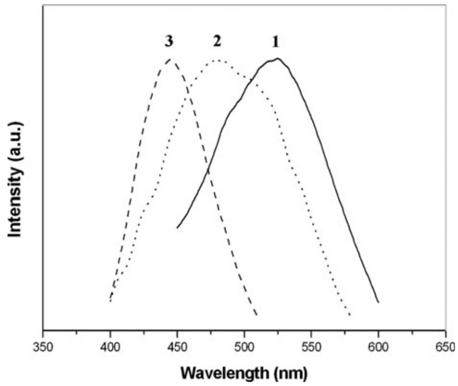

Fig. 5 Solid-state fluorescent emission spectra of **1** (solid line), **2** (dot line) and **3** (dashed line) at room temperature.

π*(tetrazolate)] metal-to-ligand charge transfer (MLCT), probably involved with Cu···Cu [3d → 4s] cluster-centered (CC) excited states. Although the explanation of luminescence remains controversial in the current level of science, we have found some valuable phenomena in this system: (i) the red shift of the bands in the spectrum of **1** compared to those of **2** and **3**, probably because the phenyl group (compared to methyl group) increases the electron-accepting character of the ligand, which lowers the excited-state energy level of Cpta, and hence a smaller energy gap in the MLCT and a higher wavelength emission occurs;[10,16*a*] (ii) the red shift of the bands in the spectrum of **2** (with mixed trigonal–tetrahedral copper(I) atoms) compared to that of **3** (with only tetrahedral copper(I) atoms) may be due to the higher d* energy level of trigonal copper(I) compared to that of tetrahedral copper(I), accordingly a smaller energy gap in the MLCT and a higher wavelength;[5*a*,9*b*] (iii) there may exist CC excited states because of the vibronic progression in the spectra and the short Cu···Cu distances in the structures,[2*c*] but it is still uncertain in light of Cotton's work through DFT calculations, which points out that short Cu···Cu separation does not guarantee a metal–metal bond, and related bonds and angles with the bridging ligands should be taken into account.[16*b*]

In conclusion, we have unprecedentedly trapped a series of cationic copper(I)–iodide aggregates, by taking advantage of Sharpless's "click" reaction for the formation of anionic-tetrazolate-based coordination polymers, which possess structure-related fluorescent properties. This work is significant not only for producing a novel type of halogenocuprate aggregate through utilizing a simple synthetic route, but also for exemplifying the correlation between crystal structures and luminescent properties in copper(I) compounds. To further clarify the structure–luminescence relationship, theoretical calculations, as well as luminescent thermochromism, should be investigated in the future.

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Notes and references

‡ Crystal data for **1**: monoclinic, space group $C2/c$, M = 424.14, a = 20.7315(16) Å, b = 8.8557(7) Å, c = 12.0833(10) Å, β = 110.7310(10)°, V = 2074.8(3) Å^3, Z = 8, ρ_{calcd} = 2.716 g cm^{-3}, T = 298(2) K, 12 414 reflections collected, 2368 unique with R_{int} = 0.0228, $R1$ [$I > 2\sigma(I)$] = 0.0292, $R1$ = 0.0307, w$R2$ = 0.0704, GOF = 1.114 for all data. Crystal data for **2**: monoclinic, space group $C2/m$, M = 719.87, a = 8.8201(17) Å, b = 14.300(3) Å, c = 13.556(3) Å, β = 92.241(3)°, V = 1708.5(6) Å^3, Z = 4, ρ_{calcd} = 2.799 g cm^{-3}, T = 298(2) K, 4572 reflections collected, 1570 unique with R_{int} = 0.0430, $R1$ [$I > 2\sigma(I)$] = 0.0360, $R1$ = 0.0399, w$R2$ = 0.0951, GOF = 1.063 for all data. Crystal data for **3**: monoclinic, space group $C2/m$, M = 820.75, a = 26.193(2) Å, b = 8.5613(7) Å, c = 8.2997(7) Å, β = 104.008(2)°, V = 1805.8(3) Å^3, Z = 4, ρ_{calcd} = 3.019 g cm^{-3}, T = 298(2) K, 5944 reflections collected, 2275 unique with R_{int} = 0.0301, $R1$ [$I > 2\sigma(I)$] = 0.0453, $R1$ = 0.0506, w$R2$ = 0.1402, GOF = 1.072 for all data. Data collection was performed on a Bruker Smart Apex CCD diffractometer (Mo Kα, λ = 0.710 73 Å).

1. For reviews: (*a*) P. C. Ford and A. Vogler, *Acc. Chem. Res.*, 1993, **26**, 220; (*b*) P. C. Ford, E. Cariati and J. Bourassa, *Chem. Rev.*, 1999, **99**, 3625; (*c*) V. W.-W. Yam and K. K.-W. Lo, *Chem. Soc. Rev.*, 1999, **28**, 323; (*d*) M. Vitale and P. C. Ford, *Coord. Chem. Rev.*, 2001, **219–221**, 3; (*e*) N. Armaroli, G. Accorsi, F. Cardinali and A. Listorti, *Top. Curr. Chem.*, 2007, **280**, 69.
2. (*a*) C.-M. Che, Z. Mao, V. M. Miskowski, M.-C. Tse, C.-K. Chan, K.-K. Cheung, D. L. Phillips and K.-H. Leung, *Angew. Chem., Int. Ed.*, 2000, **39**, 4084; (*b*) W.-F. Fu, X. Gan, C.-M. Che, Q.-Y. Cao, Z.-Y. Zhou and N. N.-Y. Zhu, *Chem.–Eur. J.*, 2004, **10**, 2228; (*c*) F. D. Angelis, S. Fantacci, A. Sgamellotti, E. Cariati, R. Ugo and P. C. Ford, *Inorg. Chem.*, 2006, **45**, 10576.
3. For examples: (*a*) A. J. Blake, N. R. Brooks, N. R. Champness, L. R. Hanton, P. Hubberstey and M. Schröder, *Pure Appl. Chem.*, 1998, **70**, 2351; (*b*) J. Y. Lu, *Coord. Chem. Rev.*, 2003, **246**, 327; (*c*) X. Xue, X.-S. Wang, R.-G. Xiong, X.-Z. You, B. F. Abrahams, C.-M. Che and H.-X. Ju, *Angew. Chem., Int. Ed.*, 2002, **41**, 2944; (*d*) S. Hu, J.-C. Chen, M.-L. Tong, B. Wang, Y.-X. Yan and S. R. Batten, *Angew. Chem., Int. Ed.*, 2005, **44**, 5471; (*e*) T. H. Kim, Y. W. Shin, J. H. Jung, J. S. Kim and J. Kim, *Angew. Chem., Int. Ed.*, 2008, **47**, 685.
4. (*a*) T. Wu, D. Li and S. W. Ng, *CrystEngComm*, 2005, **7**, 514; (*b*) R. Peng, T. Wu and D. Li, *CrystEngComm*, 2005, **7**, 595; (*c*) R. Peng, D. Li, T. Wu, X.-P. Zhou and S. W. Ng, *Inorg. Chem.*, 2006, **45**, 4035; (*d*) T. Wu, M. Li, D. Li and X.-C. Huang, *Cryst. Growth Des.*, 2008, **8**, 568.
5. (*a*) J.-P. Zhang, Y.-Y. Lin, X.-C. Huang and X.-M. Chen, *J. Am. Chem. Soc.*, 2005, **127**, 5495; (*b*) X.-L. Wang, C. Qin, E.-B. Wang, Z.-M. Su, Y.-G. Li and L. Xu, *Angew. Chem., Int. Ed.*, 2006, **45**, 7411.
6. C. H. Arnby, S. Jagner and I. Dance, *CrystEngComm*, 2004, **6**, 257.
7. (*a*) H. C. Kolb, M. G. Finn and K. B. Sharpless, *Angew. Chem., Int. Ed.*, 2001, **40**, 2004; (*b*) Z. P. Demko and K. B. Sharpless, *J. Org. Chem.*, 2001, **66**, 7945. "Click" chemistry was first defined by the Sharpless Lab as "a set of powerful, virtually 100% reliable, selective reactions for the rapid synthesis of new compounds *via* heteroatom links (C–X–C)", and this concept has been widely spread into many research fields, including coordination chemistry.
8. (*a*) R.-G. Xiong, X. Xue, H. Zhao, X.-Z. You, B. F. Abrahams and Z.-L. Xue, *Angew. Chem., Int. Ed.*, 2002, **41**, 3800; (*b*) Q. Ye, Y.-M. Song, G.-X. Wang, K. Chen, D.-W. Fu, P. W. H. Chan, J.-S. Zhu, S. D. Huang and R.-G. Xiong, *J. Am. Chem. Soc.*, 2006, **128**, 6554; (*c*) H. Zhao, Z.-R. Qu, H.-Y. Ye and R.-G. Xiong, *Chem. Soc. Rev.*, 2008, **37**, 84.
9. (*a*) T. Wu, B.-H. Yi and D. Li, *Inorg. Chem.*, 2005, **44**, 4130; (*b*) T. Wu, M. Chen and D. Li, *Eur. J. Inorg. Chem.*, 2006, 2132; (*c*) T. Wu, R. Zhou and D. Li, *Inorg. Chem. Commun.*, 2006, **9**, 341; (*d*) Z. Li, M. Li, X.-P. Zhou, T. Wu, D. Li and S. W. Ng, *Cryst. Growth Des.*, 2007, **7**, 1992; (*e*) Z. Li, M. Li, S.-Z. Zhan, X.-C. Huang, S. W. Ng and D. Li, *CrystEngComm*, 2008, DOI: 10.1039/b806768f.
10. X.-H. Huang, T.-L. Sheng, S.-C. Xiang, R.-B. Fu, S.-M. Hu, Y.-M. Li and X.-T. Wu, *Inorg. Chem. Commun.*, 2006, **9**, 1304.
11. (*a*) S. R. Batten and R. Robson, *Angew. Chem., Int. Ed.*, 1998, **37**, 1460; (*b*) S. R. Batten, *CrystEngComm*, 2001, **3**, 67; (*c*) L. Carlucci, G. Ciani and D. M. Proserpio, *Coord. Chem. Rev.*, 2003, **246**, 247; (*d*) S. Kitagawa, R. Kitaura and S.-i. Noro, *Angew. Chem., Int. Ed.*, 2004, **43**, 2334; (*e*) A. Y. Robin and K. M. Fromm, *Coord. Chem. Rev.*, 2006, **250**, 2127; (*f*) J. L. Sagué and K. M. Fromm, *Cryst. Growth Des.*, 2006, **6**, 1566.
12. (*a*) X.-M. Zhang, *Coord. Chem. Rev.*, 2005, **249**, 1201; (*b*) X.-M. Chen and M.-L. Tong, *Acc. Chem. Res.*, 2007, **40**, 162.
13. N. P. Rath and E. M. Holt, *J. Chem. Soc., Chem. Commun.*, 1985, 665.
14. F. H. Allen, *Acta Crystallogr., Sect. B: Struct. Sci.*, 2002, **B58**, 380. Searching in ConQuest Version 1.10 (CSD version 5.29, November 2007) resulted in 113 analyzable hits for [Cu_4I_2] aggregates (61 of which are cubane-like Cu_4I_2 clusters), and only 4 hits for [Cu_6I_2] aggregates, while no hits were found for [$Cu_{10}I_4$] aggregates. Note that cationic $(Cu_4I_2)^{2+}$, $(Cu_6I_2)^{4+}$ and $(Cu_{10}I_4)^{6+}$ aggregates are all unprecedented.
15. (*a*) H. Hartl and I. Brudgam, *Z. Naturforsch., B: Chem. Sci.*, 1989, **44**, 936; (*b*) B. E. Cariati, R. Ugo, F. Cariati, D. Roberto, N. Masciocchi, S. Galli and A. Sironi, *Adv. Mater.*, 2001, **13**, 1665; (*c*) S. Mishra, L. G. H. Pfalzgraf, E. Jeanneau and H. Chermette, *Dalton Trans.*, 2007, 410.
16. (*a*) H. Araki, K. Tsuge, Y. Sasaki, S. Ishizaka and N. Kitamura, *Inorg. Chem.*, 2005, **44**, 9667; (*b*) F. A. Cotton, X. Feng and D. J. Timmons, *Inorg. Chem.*, 1998, **37**, 4066.