ChemComm

Controlling intermolecular aurophilicity in emissive dinuclear Au(I) materials and their luminescent response to ammonia vapour

Journal Name

Controlling Intermolecular Aurophilicity in Emissive Dinuclear Au(I) Materials and their Luminescent Response to Ammonia Vapour†

Ryan J. Roberts, Debbie Le, and Daniel B. Leznoff[a]

The concept that hydrogen bonding cations can reduce the coulombic repulsion inherent to anionic gold species and thereby trigger aurophilicity is realized with three new photoluminescent compounds of the form [Q]$_2$[Au$_2$(*i*-mnt)$_2$] (*i*-mnt = (CN)$_2$C=CS$_2$$^{2-}$, Q = 3,5-dimethylpyrazolium, piperidinium). These compounds illustrate unprecedented supramolecular aurophilicity between the anions, the emission of which is significantly red-shifted compared to zero-dimensional analogues, a direct result of the aurophilic network. The piperidinium salt exhibits a vapochromic/luminescent response to ammonia, inducing a change in colour of the reflectance and emission from red to yellow. These results demonstrate the ability to rationally control the formation of supramolecular metallophilic networks via the incorporation of hydrogen bonding cations.

Gold(I) containing materials are of considerable fundamental and practical interest in part due to their luminescent properties, which arise from short Au(I)-Au(I) contacts; this phenomenon is referred to as aurophilicity.[1–3] This luminescence is sensitive to the Au-Au distance[4–6] and has been harnessed in chemosensing where potential analytes directly or indirectly distort the aurophilic network, changing the emission intensity or frequency.[7] At the heart of developing Au(I) based materials lies the challenge of controlling the presence or absence of aurophilic interac-

tions; materials based on other metallophilic interactions (*e.g.* d^8 Pt(II)) face a similar imperative.[8] The formation of intramolecular aurophilicity has been encouraged by using bridging bidentate ligands with tight bite angles[9–11] to form dinuclear compounds sporting Au-Au bonds or the formation of Au(I)-containing clusters.[12,13]

Inducing *inter*molecular aurophilic interactions is a greater challenge. From a theoretical standpoint incorporating soft donors (*e.g.* S, Br, I) on Au(I) encourages aurophilicity.[2] Placing sterically non-demanding ligands on Au(I) reduces the steric barrier to aggregation.[8,14] More impressively, despite coulombic repulsion, Au(I)-containing anions can aggregate in certain cases. For example, the simple [Au(CN)$_2$]$^-$ anion only aggregates in the solid-state via aurophilic interactions when the accompanying cation exhibits hydrogen-bonding capabilities.[4] This has been rationalized in that hydrogen bonding between the cation (*e.g.* ammonium type) and the N-cyano termini in [Au(CN)$_2$]$^-$ decreases the coulombic repulsion between [Au(CN)$_2$]$^-$ units enough to allow the formation of aurophilic networks to form.[4]

In order to test the more general hypothesis that hydrogen bonding cations can induce aurophilicity, we targeted the more challenging dianionic, bis(*iso*-maleonitriledithiolate)digold(I), [Au$_2$(*i*-mnt)$_2$]$^{2-}$, which contains an intramolecular Au-Au bond,[10,15–18] but no intermolecular aggregation; reported structures all contain weakly coordinating cations which do little to reduce the substantial electrostatic repulsions between the 2- anions. Switching the prototypical [^{n}Bu$_4$N]$^+$ cation[15] with hydrogen-bond capable units, specifically [DMPzH]$^+$ (DMPz = 3,5-dimethylpyrazole), and [PipH]$^+$ (Pip = piperidine), we sought to rationally induce intermolecular aurophilic arrays of [Au$_2$(*i*-mnt)$_2$]$^{2-}$, and determine the impact on the photoluminescent properties. The success of this approach is outlined herein.

The DMPzH salt was synthesized by adding DMPzHCl to a yellow solution of K$_2$[Au$_2$(*i*-mnt)$_2$], resulting in *orange* **[DMPzH]$_2$[Au$_2$(*i*-mnt)$_2$]** which is starkly different *vs.* the yel-

a Department of Chemistry, Simon Fraser University, 8888 University Drive, Burnaby, British Columbia, V5A 1S6, Canada. Tel: +1-778-782-4887. E-mail: dleznoff@sfu.ca

low $[^nBu_4N]_2[Au_2(i\text{-mnt})_2]$ (Figure S1). The crystal structure of **[DMPzH]$_2$[Au$_2$(i-mnt)$_2$]** shows an $[Au_2(i\text{-mnt})_2]^{2-}$ unit with a typical gold(I) dinuclear core (Figure S2) and an intramolecular Au(I)-Au(I) distance of 2.7998(8) Å, comparable to the 2.796(1) Å in the prototypical $[^nBu_4N]^+$ analogue.[15] However, unlike the $[^nBu_4N]^+$ salt, the N-H protons of the DMPzH cation interact with the anion by forming hydrogen bonds with the nitriles of i-mnt.

Indeed, in support of the hypothesis that hydrogen-bonding cations could induce aurophilicity, the $[Au_2(i\text{-mnt})_2]^{2-}$ units aggregate to form a one-dimensional aurophilic chain of dimers (Figure 1), with interdimer Au(1′)-Au(1″) interactions of 2.9840(9) Å (Table S1), (versus 8.735 Å in the $[^nBu_4N]^+$ analogue). This represents the first aurophilic network incorporating dianionic $[Au_2(i\text{-mnt})_2]^{2-}$ units. The DMPzH$\cdots$N≡C hydrogen bonding likely reduces the repulsion between the dianions sufficiently for the attractive aurophilic interactions to manifest, as was postulated for the aggregation of $[Au(CN)_2]^-$.[4]

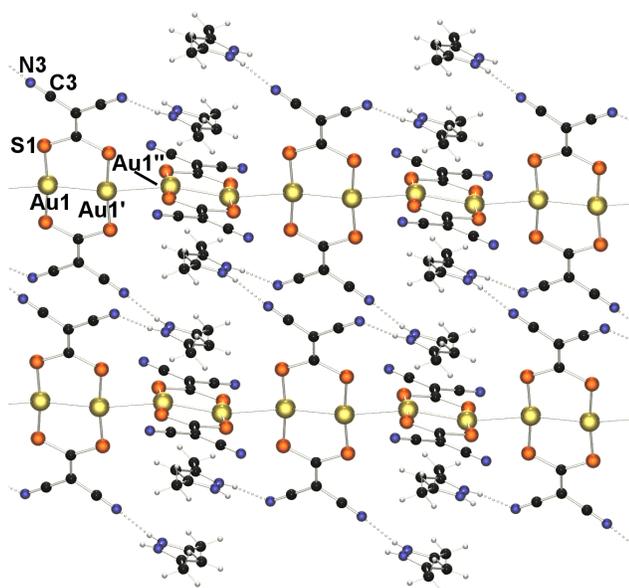**Fig. 1** The 1-D aurophilic chain of $[Au_2(i\text{-mnt})_2]^{2-}$ units (alternating face and edge on view), and DMPzH cations bridging *inter*chain $[Au_2(i\text{-mnt})_2]^{2-}$ chains in two directions. Au1-Au1′$_{intra}$ = 2.7998(8) Å, Au1′-Au1″$_{inter}$ = 2.9840(9) Å. Colour code; Au: gold, S: orange, C: black, N: blue, H: white.

Similarly, by adding PipHCl to **K$_2$[Au$_2$(i-mnt)$_2$]** the *red* **[PipH]$_2$[Au$_2$(i-mnt)$_2$]** was generated (Table S2). The crystal structure of **[PipH]$_2$[Au$_2$(i-mnt)$_2$]** (Figure 2) shows an $[Au_2(i\text{-mnt})_2]^{2-}$ unit with an intramolecular Au(1)-Au(2) distance of 2.7998(8) Å (Table S2) and an aurophilic 1-D chain of $[Au_2(i\text{-mnt})_2]^{2-}$ units with intermolecular Au(2)-Au(1′) contacts of 2.9115(6) Å, slightly shorter than in the DMPzH analogue (Table S2). As above, the nitriles of i-mnt hydrogen bond to the N-H protons of piperidinium. The piperidinium cations bridge chains of $[Au_2(i\text{-mnt})_2]^{2-}$ via hydrogen bonding (Figure S3) but also bridge in an *intra*chain fashion (Figure 2), to form an overall 2-D network.

Materials containing aurophilic interactions are often highly emissive;[1,3] indeed, the non-aggregated $[Au_2(i\text{-mnt})_2]^{2-}$ salts

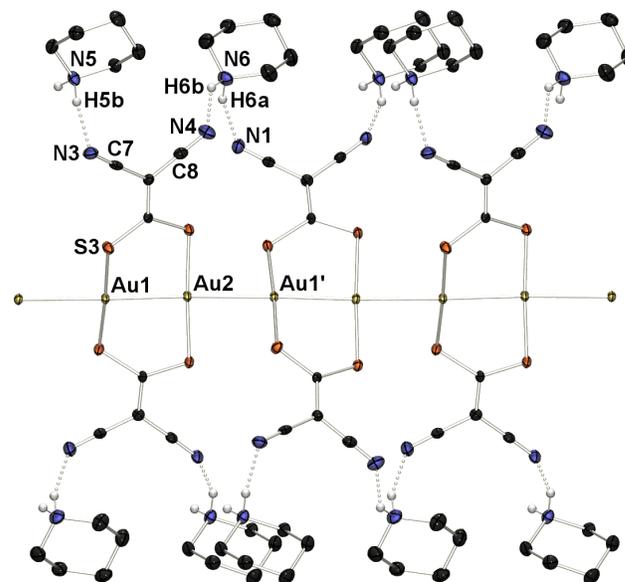**Fig. 2** Crystal structure of **[PipH]$_2$[Au$_2$(i-mnt)$_2$]** illustrating the aurophilic 1-D network of $[Au_2(i\text{-mnt})_2]^{2-}$ and the hydrogen bonded piperidinium units bridging *intra*chain $[Au_2(i\text{-mnt})_2]^{2-}$ units. Au1-Au2$_{intra}$ = 2.7792(6) Å, Au2-Au1′$_{inter}$ = 2.9115(6) Å.

emit green (λ_{max} = 515 nm,[10] Figure 3 and Table 1). In comparison, the DMPzH and PipH salts, with their 1-D chains of gold(I) centres, emit a orange to red colour. Luminescence data for both salts at 77 and 293 K and the $[^nBu_4N]^+$ analogue (Table 1) are described below.

Table 1 Summary of Luminescence Data at 77 and 293 K

$[Q]_2[Au_2(i\text{-mnt})_2]$	Excitation λ_{max} (nm)	Emission λ_{max} 77 K (nm)	Emission λ_{max} 293 K (nm)
$[^nBu_4N]$ [10]	398	524	515
[DMPzH]	520	596	582
[PipH]	550-560	696	642
$[PipH]\cdot(NH_3)_2(H_2O)$	500-505	584	556

[DMPzH]$_2$[Au$_2$(i-mnt)$_2$] displays an excitation band at 520 nm (Figure 3). The corresponding emission spectrum shows a single feature at 596 nm at 77 K (Figure 3). **[PipH]$_2$[Au$_2$(i-mnt)$_2$]** is similar, showing broad excitation bands from ≈ 400 to 600 nm (the most prominent band is at 550 nm) and emission at λ_{max} = 642 nm at 293 K. Clearly, the emission maxima of both **[DMPzH]$_2$[Au$_2$(i-mnt)$_2$]** and **[PipH]$_2$[Au$_2$(i-mnt)$_2$]** are significantly red-shifted compared to zero-dimensional, isolated $[Au_2(i\text{-mnt})_2]^{2-}$ systems.[10] This shift is likely attributable to the generation of a 1-D aurophilic chain, lowering the energy of emission, consistent with other studies on the role of dimensionality and Au-Au distance in $[Au(CN)_2]^-$ and other Au(I) systems.[6]

The excitation band of **[PipH]$_2$[Au$_2$(i-mnt)$_2$]** changes little between 293 and 77 K. However, the emission spectrum is more temperature dependant, with the λ_{max} shifting to 696 nm at 77 K. This corresponds to a red-shift of ≈ 1200 cm^{-1} or 5.6 cm^{-1}/K over this temperature range. The origin of this red-shift upon cooling is likely a contraction of Au(I)-Au(I) distances resulting in a lowering of the emission energy.[19]
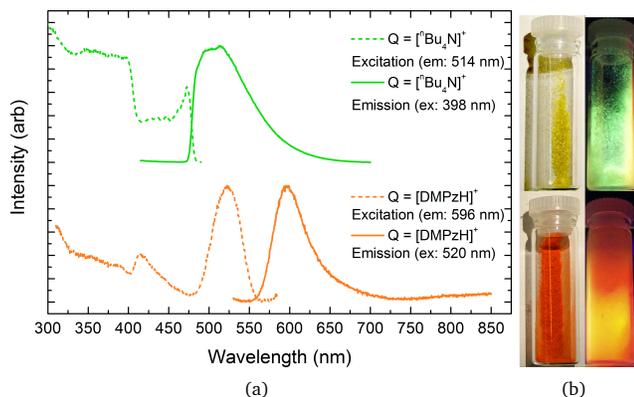
(a) (b)

Fig. 3 (a) Corrected excitation (dotted line) and emission (solid line) spectra 77 K of **[DMPzH]$_2$[Au$_2$(*i*-mnt)$_2$]** (orange) and **[^{n}Bu$_4$N]$_2$[Au$_2$(*i*-mnt)$_2$]** (green) (b) yellow and orange powders of **[^{n}Bu$_4$N]$_2$[Au$_2$(*i*-mnt)$_2$]** and **[DMPzH]$_2$[Au$_2$(*i*-mnt)$_2$]** emit green and orange respectively.
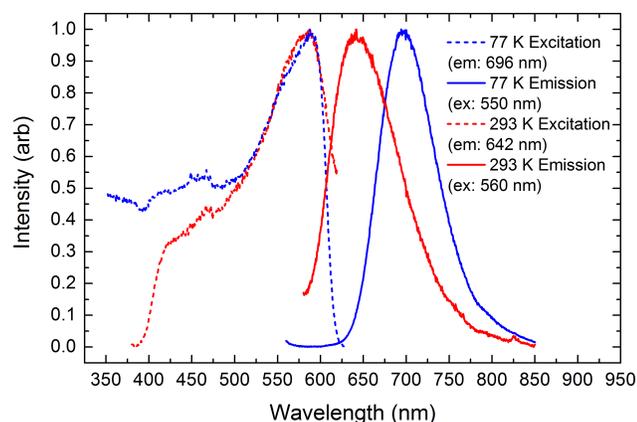

Fig. 4 Corrected excitation (dotted line) and emission (solid line) spectra at 293 (red) and 77 K (blue) of **[PipH]$_2$[Au$_2$(*i*-mnt)$_2$]**.

Metallophilic systems containing Au(I) and Pt(II) can react with volatile analytes, inducing a change in reflectance and/or emission colour as a direct or indirect result of perturbation of the metallophilic network.[20] For example, Zn[Au(CN)$_2$]$_2$ reacts with NH$_3$ vapour in the solid state, inducing a visible colour change from white to yellow and a shift in emission λ_{max} from 480 to 500 nm.[7] Even though the salts reported here lack a transition metal binding site for NH$_3$, exposing solid **[PipH]$_2$[Au$_2$(*i*-mnt)$_2$]** to NH$_3$ vapour generated a yellow powder from the red starting material. Crystallization of **[PipH]$_2$[Au$_2$(*i*-mnt)$_2$]** from concentrated aqueous NH$_3$ resulted in yellow crystals, which desolvate upon removal from NH$_3$ within seconds via a single-crystal to single-crystal transformation back to the starting material.

Using flash-freezing techniques, the structure of this NH$_3$ adduct was revealed to be **[PipH]$_2$[Au$_2$(*i*-mnt)$_2$]·(NH$_3$)$_2$(H$_2$O)** The 1-D chain of [Au$_2$(*i*-mnt)$_2$]$^{2-}$ units in the parent **[PipH]$_2$[Au$_2$(*i*-mnt)$_2$]** is maintained (Figure S4), but the nitriles of the [Au$_2$(*i*-mnt)$_2$]$^{2-}$ units hydrogen-bond mostly to captured NH$_3$ and H$_2$O molecules. An extensive hydrogen bonding network bridges chains of aurophilic [Au$_2$(*i*-mnt)$_2$]$^{2-}$ through H$_2$O, NH$_3$, and [PipH]$^+$, forming a 2-D network (Figure

S4). The *intra*- and *inter*molecular Au-Au distances of 2.8260(5) and 3.0305(5) Å respectively are substantially expanded by ΔAu-Au$_{intra}$ = 0.0468(11) and ΔAu-Au$_{inter}$ = 0.119(11) Å versus the parent **[PipH]$_2$[Au$_2$(*i*-mnt)$_2$]**. This adduct is particularly unusual since the putative ammonia ligand is not bound to a metal but is captured exclusively by hydrogen bonding sites. Note that wet samples (or those exposed to humid air) of [Q][Au$_2$(*i*-mnt)$_2$] do not uptake water in these hydrogen-bonding sites and thus H$_2$O itself has no impact on the emission properties of these materials.

Consistent with the observed changes in the aurophilic chain, a significant shift in both the reflectance (Figure S1) and emission of **[PipH]$_2$[Au$_2$(*i*-mnt)$_2$]** are observed upon exposure to NH$_3$ (Figure 5). Specifically, **[PipH]$_2$[Au$_2$(*i*-mnt)$_2$]·(NH$_3$)$_2$(H$_2$O)** shows broad excitations at 400 through 525 nm with a peak at 500 nm (Figure 6). The emission spectrum at 293 K has λ_{max} = 556 nm, a significant shift from the parent material (642 nm). At 77 K this emission band undergoes a red-shift to 584 nm (Figure 6), which is likely also attributable to a shortening of Au(I)-Au(I) contacts between dimers in the chain. This corresponds to a shift of $\approx$ 2400 and 2750 cm^{-1} at 293 and 77 K respectively upon addition of NH$_3$ to the parent material.
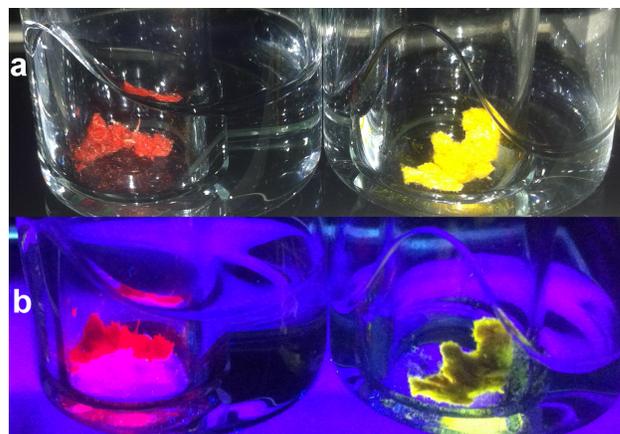

Fig. 5 Powders of **[PipH]$_2$[Au$_2$(*i*-mnt)$_2$]** (left) and **[PipH]$_2$[Au$_2$(*i*-mnt)$_2$]·(NH$_3$)$_2$(H$_2$O)** (right) at room temperature in (a) ambient light and (b) illuminated by a long wavelength UV-lamp.

The large blue-shift in emission energy upon the addition of NH$_3$ can be rationalized in terms of the lengthened aurophilic interactions versus the parent material **[PipH]$_2$[Au$_2$(*i*-mnt)$_2$]**, which is attributable to the differences in hydrogen bonding networks. In **[PipH]$_2$[Au$_2$(*i*-mnt)$_2$]·(NH$_3$)$_2$(H$_2$O)** the [Au$_2$(*i*-mnt)$_2$]$^{2-}$ anions hydrogen-bond primarily to neutral H$_2$O and NH$_3$ molecules, versus exclusively cationic [PipH]$^+$ in the parent. This increase in the relative coulombic repulsion between [Au$_2$(*i*-mnt)$_2$]$^{2-}$ units in the adduct, yielding weaker interdimer aurophilic interactions, results in a higher energy emission relative to **[PipH]$_2$[Au$_2$(*i*-mnt)$_2$]**.

In summary, the use of hydrogen-bonding cations [DMPzH]$^+$ and [PipH]$^+$ with [Au$_2$(*i*-mnt)$_2$]$^{2-}$ generate 1-D aurophilic chains which result in significantly red-shifted emission compared to zero dimensional [Au$_2$(*i*-mnt)$_2$]$^{2-}$ structures. **[PipH]$_2$-**
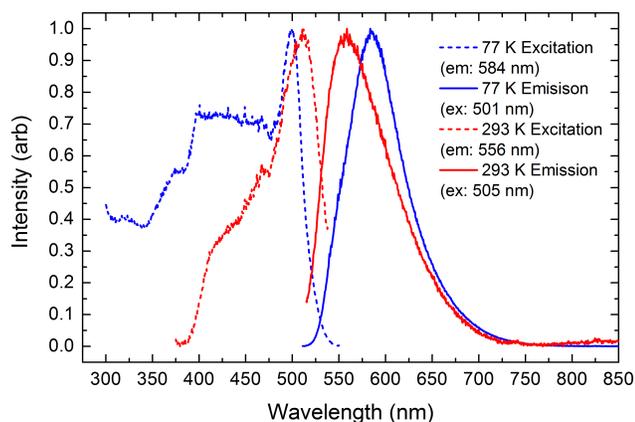
Fig. 6 Corrected excitation (dotted lines) and emission (solid lines) spectra at 293 (red) and 77 K (blue) of **[PipH]$_2$[Au$_2$(i-mnt)$_2$]·(NH$_3$)$_2$(H$_2$O)**.

[Au$_2$(i-mnt)$_2$] exhibited a vapochromic response to NH$_3$ vapour, wherein the reflectance and emission colour were significantly changed from red to yellow, illustrating that [Au$_2$(i-mnt)$_2$]$^{2-}$ can act as a chemosensing material. More generally, the ability to induce supramolecular metallophilic networks by incorporating hydrogen-bonding cations is promising for the continued development of these materials for a variety of applications.

References

1 H. Schmidbaur and A. Schier, *Chem. Soc. Rev.*, 2008, **37**, 1931–51.

2 J. Muñiz, C. Wang and P. Pyykkö, *Chem. Eur. J.*, 2011, **17**, 368–377.

3 A. L. Balch, *Struct. Bond.*, 2007, **123**, 1–40.

4 M. Stender, M. Olmstead, A. Balch, D. Rios and S. Attar, *Dalton Trans.*, 2003, 4282–4287.

5 X. He and V. W.-W. Yam, *Coord. Chem. Rev.*, 2011, **255**, 2111 – 2123.

6 M. Rawashdeh-Omary, M. Omary and H. Patterson, *J. Am. Chem. Soc.*, 2000, **122**, 10371–10380.

7 M. J. Katz, T. Ramnial, H. Z. Yu and D. B. Leznoff, *J. Am. Chem. Soc.*, 2008, **130**, 10662.

8 M. J. Katz, K. Sakai and D. B. Leznoff, *Chem. Soc. Rev.*, 2008, **37**, 1884–95.

9 R. Narayanaswamy, M. A. Young, E. Parkhurst, M. Ouellette, M. E. Kerr, D. M. Ho, R. C. Elder, A. E. Bruce and M. R. M. Bruce, *Inorg. Chem.*, 1993, **32**, 2506–2517.

10 C. King, J. C. Wang, M. N. I. Khan and J. P. Fackler, Jr., *Inorg. Chem.*, 1989, **28**, 2145–2149.

11 M.-R. Azani, O. Castillo, M. L. Gallego, T. Parella, G. Aullón, O. Crespo, A. Laguna, S. Alvarez, R. Mas-Ballesté and F. Zamora, *Chem. Eur. J.*, 2012, **18**, 9965–76.

12 V. W.-W. Yam, K. K.-W. Lo, W. K.-M. Fung and C.-R. Wang, *Coord. Chem. Rev.*, 1998, **171**, 17 – 41.

13 Q.-M. Wang, Y.-A. Lee, O. Crespo, J. Deaton, C. Tang, H. J. Gysling, M. Concepción Gimeno, C. Larraz, M. D. Villacampa, A. Laguna and R. Eisenberg, *J. Am. Chem. Soc.*, 2004, **126**, 9488–9489.

14 H. Ecken, M. M. Olmstead, B. C. Noll, S. Attar, B. Schlyer and A. L. Balch, *J. Chem. Soc., Dalton Trans.*, 1998, 3715–3720.

15 M. N. I. Khan, J. P. Fackler, Jr., C. King, J. C. Wang and S. Wang, *Inorg. Chem.*, 1988, **27**, 1672–1673.

16 M. A. Mansour, W. B. Connick, R. J. Lachicotte, H. J. Gysling and R. Eisenberg, *J. Am. Chem. Soc.*, 1998, **120**, 1329–1330.

17 A. A. Mohamed, I. Kani, A. O. Ramirez and J. P. Fackler, Jr., *Inorg. Chem.*, 2004, **43**, 3833–3839.

18 X.-F. Jiang, F. K.-W. Hau, Q.-F. Sun, S.-Y. Yu and V. W.-W. Yam, *J. Am. Chem. Soc.*, 2014, **136**, 10921–10929.

19 R. J. Roberts, N. Belanger-Desmarais, C. Reber and D. B. Leznoff, *Chem. Commun.*, 2014, **50**, 3148–3150.

20 O. S. Wenger, *Chem. Rev.*, 2013, **113**, 3686–3733.