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Water vapour induced reversible switching between a 1-D coordination polymer and a 0-D aqua complex†

Min Deng,^{‡a} Soumya Mukherjee,^{‡b} Yu-Jie Liang,^a Xiao-Dan Fang,^a Ai-Xin Zhu^{*a} and Michael J. Zaworotko^{*,b}

[Zn(3-tba)₂], 1, a 1-D coordination polymer synthesised as 1 DMA, 1 α , transformed to a nonporous form, 1 β , upon activation. 1 β underwent further transformation to the dimeric complex [Zn(3-tba)₂(H₂O)₂], 2, above 40% RH. The reverse transformations, 2 to 1 β and 1 β to 1 α , were accomplished by heating and exposure to DMA, respectively, and were single-crystal-to-single-crystal phase changes. Single crystal X-ray diffraction revealed that the second transformation resulted from Zn–carboxylate bond breakage and concomitant coordination of water molecules. Other solvent molecules did not induce a phase change.

Metal–organic materials (MOMs),¹ especially porous MOMs such as metal–organic frameworks (MOFs)² and porous coordination polymers (PCPs),³ have received considerable attention with respect to their gas and vapour adsorption properties.⁴ Whereas > 100 000 coordination networks have been deposited in the MOF subset of the Cambridge Structural Database (CSD),⁵ only a small proportion, < 100, are known to exhibit type F-IV isotherms with reversible transformations between nonporous (closed) and porous (open) phases.⁶ Such stepped isotherms are of topical interest because their “switching” between closed and open phases can result in relatively high uptake capacity and, perhaps counter-intuitively, stronger separation selectivity than rigid porous materials with similar pore size.^{7,8} Indeed, benchmark binding to C₂H₂ has been observed for a switching sorbent through an induced-fit mechanism reminiscent of enzyme–substrate binding.⁹

Single-crystal-to-single-crystal (SCSC) transformations in switching sorbents can provide insight into structure–property

relationships through single-crystal X-ray diffraction (SCXRD).¹⁰ SCSC transformations can typically be induced by external stimuli, e.g. gas/vapour uptake and/or removal,^{11,12} temperature change,¹³ pH change,¹⁴ light¹⁵ and cation or anion exchange.^{16,17} Water vapour sorption is of particular relevance as it can bind with open metal centres^{18,19} or physisorb, thereby being relevant to applications such as atmospheric water harvesting and dehumidification. Most MOMs exhibit type F-IV water vapour isotherms that result from pore filling (capillary condensation, Table S6 in ESI†).²⁰ Our literature survey revealed only 12 MOMs (Table S6, ESI†) that exhibit a type F-IV stepped isotherm caused by water-induced structural changes and, to our knowledge, water-induced 1D \rightarrow 0D SCSC structural phase changes with a single-step are unstudied. Such transformations have the potential to exhibit high selectivity for water over alcohols. Indeed, some examples display selective water uptake over alcohols attributed to structural transformations.^{19a,21}

Herein, we report that the new 1D coordination polymer [Zn(3-tba)₂]-DMA (1 α ; 3-Htba = 3-(4H-1,2,4-triazol-4-yl)benzoic acid; DMA = *N,N*-dimethylacetamide), 1 α , underwent SCSC transformation to 1 β , a nonporous phase, upon removal of DMA. 1 β in turn transformed to a discrete, binuclear complex, 2, upon exposure to water vapour. Insight into these reversible transformations comes from the results of SCXRD studies.

Solvothermal reaction of 3-Htba with Zn(NO₃)₂·6H₂O in DMA at 105 °C afforded diamond-shaped crystals of 1 α (synthetic details are available in ESI†). SCXRD revealed that 1 α crystallized in the triclinic space group *P* $\bar{1}$ and that it displays a 1D chain structure with spiro linkages (Fig. 1). Zn(II) cations adopt a tetrahedral coordination geometry through two oxygen atoms from different 3-tba ligands and two nitrogen atoms from two additional 3-tba ligands. Pairs of 3-tba ligands serve as V-shaped linkers between adjacent Zn(II) cations to form [Zn₂(3-tba)₂] rings that are further connected into a one-dimensional (1D) coordination polymer (Fig. 1). Adjacent chains are cross-linked by C–H \cdots O interactions (C \cdots O = 3.049(6)–3.097(6) Å, H \cdots O = 2.39–2.44 Å, C–H \cdots O = 127–128°) to form a supramolecular layer (Fig. S1, ESI†). π – π and C–H \cdots π

^a Faculty of Chemistry and Chemical Engineering, Yunnan Normal University, Kunming, 650500, China. E-mail: zaxchem@126.com

^b Department of Chemical Sciences, Bernal Institute, University of Limerick, Limerick, V94T9PX, Ireland. E-mail: xtal@ul.ie

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‡ These authors contributed equally to this work.





Fig. 1 Structural transformations in $[\text{Zn}(\text{3-tba})_2]$ involving **1α**, **1β** and **2** (unit cells are illustrated). Charge-assisted H-bonding (black broken lines) occurs between aqua ligands and free carboxylate moieties in **2**.

interactions between 1D chains also stabilise the supramolecular layer (Fig. S2, ESI[†]) which pack through C–H \cdots N interactions (C \cdots N = 3.486(6) Å, H \cdots N = 2.57 Å, C–H \cdots N = 168°) between layers (Fig. S3, ESI[†]). Along the *a*-axis, the crystal packing of **1α** results in 1D rhombic channels with an effective pore diameter of 4.9×7.3 Å² (Fig. 2 and Fig. S4, ESI[†]). Void volume in the channel (310.3 Å³) is *ca.* 27.4% of the crystal volume (1134.2 Å³) which is occupied by DMA guest molecules. Thermogravimetric analysis (TGA) revealed that as-synthesized **1α** loses guest molecules (obs. 16.11%, calc. 16.47%) from 78 °C to 180 °C and remains stable to 290 °C (Fig. S17, ESI[†]).

Heating **1α** under vacuum at 150 °C overnight resulted in SCSC transformation to **1β**. SCXRD revealed that the **1β** is a contorted version of **1α** with the same connectivity. **1β** also crystallized in triclinic space group *P* $\bar{1}$ but with 24.8% shrinkage of its unit-cell volume relative to **1α**. PLATON calculations indicated that **1β** contains no residual solvent-accessible void and so it is nonporous (Fig. 2). TGA and FT-IR data support the guest-free nature of **1β** (Fig. S17 and S19, ESI[†]). Transformation between **1α** and **1β** was accompanied by distortions of $[\text{Zn}_2(\text{3-tba})_2]$ rings and contraction of interstitial spaces (Fig. S5, ESI[†]). Meanwhile, rotation of the 3-tba ligand and a hinge-like motion associated with carboxylate coordination occurred (Table S2, ESI[†]). Aromatic π – π stacking interactions were found to be present in **1β** (Tables S4, S5 and Fig. S7, ESI[†]). The structural transformation associated with guest removal was found to be reversible as **1β** reverted to **1α** after soaking in DMA at room temperature for 1 day



Fig. 2 Space-filling diagrams of the reversible structural transformation between **1α** and **1β** (viewed along the *a*-axis, for more details see Fig. S5, ESI[†]).

(Fig. 3 and Fig. S9, ESI[†]). **1β** was observed to transform to a new phase, **2**, after exposure to humidity (Fig. S11 and S12, ESI[†]).

Single crystals of **2** were obtained after exposure of **1β** to water vapour (vial-in-vial method, details in the ESI[†]). Such SCSC transformations of low-dimensional coordination networks between multiple phases are relatively rare.²² SCXRD revealed that the formation of **2**, $[\text{Zn}(\text{3-tba})_2(\text{H}_2\text{O})_2]$, a discrete complex, involved the following: (a) change from 1-D to 0-D dimensionality; (b) cleavage of some Zn–carboxylate coordination bonds; (c) insertion of coordinated water molecules that form hydrogen bonds to the uncoordinated carboxylate moieties; (d) change of the Zn coordination geometry from tetrahedral to trigonal bipyramidal. As revealed by Fig. 1, **2** is composed of Zn(II) ions that adopt a distorted trigonal bipyramidal coordination geometry ($\tau = 0.77$) with two nitrogen atoms from two 3-tba ligands, one oxygen atom from another 3-tba ligand and two coordinated water molecules. Coordination of water molecules to Zn(II) in effect results in the insertion of water molecules into a Zn–carboxylate bond and formation of charge assisted hydrogen bonds (O \cdots O = 2.535 and 2.626 Å, Fig. 1). Furthermore, the other hydrogen atom from one of the coordinated water molecules formed H-bonds (O \cdots O = 2.737 Å) with uncoordinated O atoms of 3-tba ligands in adjacent complexes whereas the remaining hydrogen atom formed bifurcated H-bonds with two basic N atoms (O \cdots N = 3.146 and 3.254 Å, Fig. S8, ESI[†]). The FT-IR spectrum of **2** indicates that C=O (1600 cm^{−1}) and C–O (\sim 1051 cm^{−1}) vibrations are different from **1α** and **1β**, consistent with the respective coordination environments (Fig. S19, ESI[†]). In contrast to **1α** and



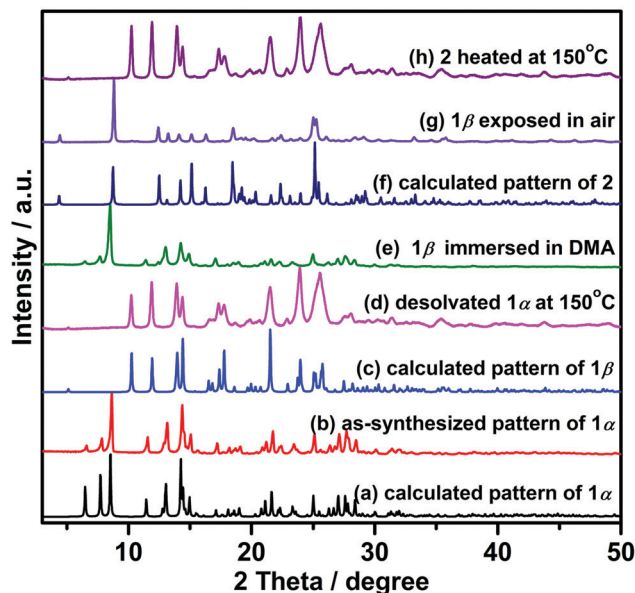


Fig. 3 PXRD patterns of (a) **1α** calculated from SCXRD data, (b) as-synthesized **1α** at room temperature, (c) **1β** calculated from SCXRD data, (d) desolvated **1α** at 150 °C, (e) **1β** immersed in DMA for 1 day, (f) calculated **2** from SCXRD data, (g) **1β** exposed to humid air (ca. 45% RH), and (h) dehydrated **2** at 150 °C.

1β, there are no aromatic π - π stacking interactions between triazole rings (Table S4, ESI†) but multiple O-H...O and O-H...N hydrogen bonds formed between aqua ligands and uncoordinated N or O atoms of 3-tba ligands (Table S3 and Fig. S8, ESI†). **2** was found to reversibly revert to **1β** *in vacuo* at 150 °C (Fig. S10, ESI†). Attempts to obtain **2** by direct routes were unsuccessful.

Gas sorption experiments for N₂ at 77 K and CO₂ at 195 K were performed on **1β**, which exhibited a type II nitrogen adsorption isotherm (Fig. S20, ESI†) characteristic of a non-porous solid. The BET surface area was determined to be 5.6 m² g⁻¹. The CO₂ adsorption isotherm collected at 195 K likewise indicated that **1β** is nonporous (Fig. S13 and S20, ESI†).

Vapour sorption isotherms of water, methanol and ethanol for **1β** were conducted at 298 K. As shown in Fig. 4, no water was adsorbed in the low humidity region but water uptake showed a sudden increase (step) at 46% RH. Such a profile is consistent with a structural transformation. The desorption isotherm exhibits large hysteresis, indicating strong sorbate-water interactions as would be expected from the crystal structure of **2**. To our knowledge, this is the first example of a water-induced 1D → 0D SCSC structural transformation with a one-step type F-IV adsorption isotherm (Table S6, ESI†). At 50% RH, the uptake reached 102 cm³ g⁻¹, corresponding to approximately 2.0 H₂O molecules per Zn cation, a value in accordance with the TGA measured for **1β** exposed to water vapour for one day (Fig. S18, ESI†). As revealed by Fig. 4, methanol and ethanol adsorption exhibited no uptake up to $P/P_0 = 0.96$. To the best of our knowledge, only one example of a sorbent that displays selective water uptake over alcohols has been observed for materials with type F-IV isotherms.^{21a}



Fig. 4 Water, methanol and ethanol vapour sorption isotherms of **1β** collected at 298 K (closed and open symbols denote adsorption and desorption, respectively).

In **1β**, one Zn-carboxylate bond in each formula unit deviates from the carboxylate group plane (20.6°, Table S2 and Fig. S5, ESI†). The structure of **2** indicates that two water molecules had in effect inserted into a Zn-carboxylate bond, in turn forming two charge assisted OH...carboxylate H-bonds (Fig. 1). Such a motif has been observed in molecular crystals as exemplified by DL-tartaric acid monohydrate²³ and there are ca. 1400 hits in the CSD database for this motif. The coordination of water molecules and charge assisted OH...carboxylate hydrogen bonds supports this water-induced phase transformation. It seems unlikely that the structure of **2** would exist with MeOH or EtOH molecules as there is also H-bonding to the adjacent chains (Fig. S5 and S8, ESI†), perhaps explaining why MeOH and EtOH were not adsorbed.

The sorption isotherms of **1β** for acetonitrile, acetone and benzene also indicated no uptake (Fig. S22, ESI†) and PXRD data revealed that crystals of **1β** were unaffected by exposure to methanol, ethanol, acetonitrile, acetone or benzene vapours in contrast to water vapour, which induced transformation from **1β** to **2** (Fig. S14 and S15, ESI†). Not only was **1β** selective for water, but it was found to retain its water uptake after 5 consecutive activation-uptake cycles (Fig. 5 and Fig. S16, ESI†), indicating that **1β** is recyclable.

In summary, we report a new 1D coordination polymer, [Zn(3-tba)₂] (**1α**), that transformed to **1β** upon removal of guests. **1β** further transformed to a 0D aqua complex [Zn(3-tba)₂(H₂O)₂], **2**, upon exposure to water vapour above 40% RH. Both transformations were verified by SCXRD studies and found to be reversible. Interestingly, **1β** exhibited a one-step type F-IV water adsorption isotherm concomitant with the 1D → 0D SCSC structural transformation. The coordination of two water molecules and self-assembly sustained by charge-assisted OH...carboxylate hydrogen bonds are likely key drivers for this switching event along with other H-bonds formed by the aqua ligands. The water-triggered transformation enabled selective and reversible adsorption of water vapour over other vapours such as methanol, ethanol, acetone, acetonitrile and

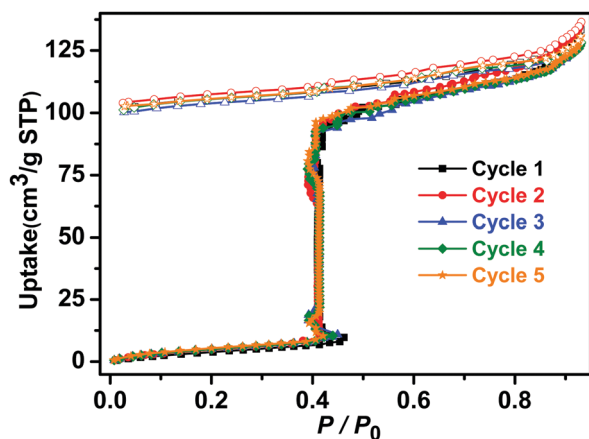


Fig. 5 Five consecutive activation–uptake cycles of water sorption isotherms of **1β** at 298 K (closed and open symbols denote adsorption and desorption, respectively).

benzene. Transformation between **1β** and **2** implies that there could be other low-dimensional MOMs or molecular compounds that might serve as switching water sorbents given that there are *ca.* 1400 crystal structures with diaqua-carboxylate motifs archived in the CSD.

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Conflicts of interest

There are no conflicts to declare.

Notes and references

- J. J. Perry IV, J. A. Perman and M. J. Zaworotko, *Chem. Soc. Rev.*, 2009, **38**, 1400–1417.
- L. R. MacGillivray, *Metal-organic frameworks: design and application*, John Wiley & Sons, 2010.
- (a) S. Kitagawa, R. Kitaura and S. Noro, *Angew. Chem., Int. Ed.*, 2004, **43**, 2334–2375; (b) S. R. Batten, S. M. Neville and D. R. Turner, *Coordination polymers: design, analysis and application Introduction*, Royal Society of Chemistry, London, 2009.
- (a) J.-R. Li, J. Sculley and H.-C. Zhou, *Chem. Rev.*, 2012, **112**, 869–893; (b) X. Han, S. Yang and M. Schröder, *Nat. Rev. Chem.*, 2019, **3**, 108–118; (c) S. Mukherjee, A. V. Desai and S. K. Ghosh, *Coord. Chem. Rev.*, 2018, **367**, 82–126; (d) Y. Wang, S. B. Peh and D. Zhao, *Small*, 2019, **15**, 1900058; (e) T. Wang, E. Lin, Y.-L. Peng, Y. Chen, P. Cheng and Z. Zhang, *Coord. Chem. Rev.*, 2020, **423**, 213485.
- P. Z. Moghadam, A. Li, X.-W. Liu, R. Bueno-Perez, S.-D. Wang, S. B. Wiggins, P. A. Wood and D. Fairen-Jimenez, *Chem. Sci.*, 2020, **11**, 8373–8387.
- (a) S.-Q. Wang, S. Mukherjee and M. J. Zaworotko, *Faraday Discuss.*, 2021, **231**, 9–50; (b) Q.-Y. Yang, P. Lama, S. Sen, M. Lusi, K.-J. Chen, W. Y. Gao, M. Shivanna, T. Pham, N. Hosono, S. Kusaka, J. Perry IV, S. Ma, B. Space, L. J. Barbour, S. Kitagawa and M. Zaworotko, *Angew. Chem., Int. Ed.*, 2018, **57**, 5684–5689.
- J. A. Mason, J. Oktawiec, M. K. Taylor, M. R. Hudson, J. Rodriguez, J. E. Bachman, M. I. Gonzalez, A. Cervellino, A. Guagliardi, C. M. Brown, P. L. Llewellyn, N. Masciocchi and J. R. Long, *Nature*, 2015, **527**, 357–361.
- (a) N. Nijem, H. Wu, P. Canepa, A. Marti, K. J. Balkus Jr., T. Thonhauser, J. Li and Y. J. Chabal, *J. Am. Chem. Soc.*, 2012, **134**, 15201–15204; (b) M. L. Foo, R. Matsuda, Y. Hijikata, R. Krishna, H. Sato, S. Horike, A. Hori, J. Duan, Y. Sato, Y. Kubota, M. Takata and S. Kitagawa, *J. Am. Chem. Soc.*, 2016, **138**, 3022–3030; (c) M. K. Taylor, T. Runčevski, J. Oktawiec, J. E. Bachman, R. L. Siegelman, H. Jiang, J. A. Mason, J. D. Tarver and J. R. Long, *J. Am. Chem. Soc.*, 2018, **140**, 10324–10331.
- M. Shivanna, K.-i. Otake, B.-Q. Song, L. M. van Wyk, Q.-Y. Yang, N. Kumar, W. K. Feldmann, T. Pham, S. Suepaul, B. Space, L. J. Barbour, S. Kitagawa and M. J. Zaworotko, *Angew. Chem., Int. Ed.*, 2021, **133**, 20546–20553.
- (a) G. K. Kole and J. J. Vittal, *Chem. Soc. Rev.*, 2013, **42**, 1755–1775; (b) J.-P. Zhang, P.-Q. Liao, H.-L. Zhou, R.-B. Lin and X.-M. Chen, *Chem. Soc. Rev.*, 2014, **43**, 5789–5814.
- (a) S. Horike, S. Shimomura and S. Kitagawa, *Nat. Chem.*, 2009, **1**, 695–704; (b) E. Fernandez-Bartolome, A. Martinez-Martinez, E. Resines-Urien, L. Piñeiro-Lopez and J. S. Costa, *Coord. Chem. Rev.*, 2022, **452**, 214281.
- (a) J. Liu, X.-P. Zhang, T. Wu, B.-B. Ma, T.-W. Wang, C.-H. Li, Y.-Z. Li and X.-Z. You, *Inorg. Chem.*, 2012, **51**, 8649–8651; (b) S. Sen, S. Neogi, K. Rissanen and P. K. Bharadwaj, *Chem. Commun.*, 2015, **51**, 3173–3176.
- (a) Z. Xie, L. Mei, Q. Wu, K. Hu, L. Xia, Z. Chai and W. Shi, *Dalton Trans.*, 2017, **46**, 7392–7396; (b) S. M. Mobin, A. K. Srivastava, P. Mathur and G. K. Lahiri, *Dalton Trans.*, 2010, **39**, 8698–8705.
- H.-C. Fang, J.-Q. Zhu, L.-J. Zhou, H.-Y. Jia, S.-S. Li, X. Gong, S.-B. Li, Y.-P. Cai, P. K. Thallapally, J. Liu and G. J. Exarhos, *Cryst. Growth Des.*, 2010, **10**(7), 3277–3284.
- (a) J.-M. Chen, Y.-X. Hou, Q.-K. Zhou, H. Zhang and D. Liu, *Dalton Trans.*, 2017, **46**, 9755–9759; (b) R. Medishetty, A. Husain, Z. Bai, T. Runčevski, R. E. Dinnebie, P. Naumov and J. J. Vittal, *Angew. Chem., Int. Ed.*, 2014, **53**, 5907–5911.
- (a) C. K. Brozek and M. Dincă, *Chem. Soc. Rev.*, 2014, **43**, 5456–5467; (b) E. Papazoi, A. Douvali, S. Rapti, E. Skliri, G. S. Armatas, G. S. Papaefstathiou, X. Wang, Z.-F. Huang, S. Kaziannis, C. Kosmidis, A. G. Hatzidimitriou, T. Lazarides and M. J. Manos, *Inorg. Chem. Front.*, 2017, **4**, 530–536.
- (a) J.-Y. Wu, Y.-C. Liu and T.-C. Chao, *Inorg. Chem.*, 2014, **53**, 5581–5588; (b) J. Fu, H. Li, Y. Mu, H. Hou and Y. Fan, *Chem. Commun.*, 2011, **47**, 5271–5273.
- S.-Y. Ke and C.-C. Wang, *CrystEngComm*, 2015, **17**, 8776–8785.
- (a) S. K. Ghosh, W. Kaneko, D. Kiriya, M. Ohba and S. Kitagawa, *Angew. Chem., Int. Ed.*, 2008, **47**, 8843–8847; (b) J. Albalad, J. Arinez-Soriano, J. Vidal-Gancedo, V. Lloveras, J. Juanhuix, I. Imaz, N. Aliaga-Alcalde and D. MasPOCH, *Chem. Commun.*, 2016, **52**, 13397–13400; (c) W.-B. Chen, Y.-C. Chen, M. Yang, M.-L. Tong and W. Dong, *Dalton Trans.*, 2018, **47**, 4307–4314.
- (a) N. C. Burtch, H. Jasuja and K. S. Walton, *Chem. Rev.*, 2014, **114**, 10575–10612; (b) J. Canivet, A. Fateeva, Y. Guo, B. Coasne and D. Farrusseng, *Chem. Soc. Rev.*, 2014, **43**, 5594–5617; (c) M. J. Kalmutzki, C. S. Diercks and O. M. Yaghi, *Adv. Mater.*, 2018, **30**, 1704304.
- (a) S. K. Ghosh, J.-P. Zhang and S. Kitagawa, *Angew. Chem., Int. Ed.*, 2007, **46**, 7965–7968; (b) A. K. Gupta, S. S. Nagarkar and R. Boomishankar, *Dalton Trans.*, 2013, **42**, 10964–10970; (c) S. S. Nagarkar and S. K. Ghosh, *J. Chem. Sci.*, 2015, **127**, 627–633.
- (a) A. Kondo, T. Nakagawa, H. Kajiro, A. Chinen, Y. Hattori, F. Okino, T. Ohba, K. Kaneko and H. Kanoh, *Inorg. Chem.*, 2010, **49**, 9247–9252; (b) A. V. Gavrikov, A. B. Ilyukhin and P. S. Koroteev, *CrystEngComm*, 2020, **22**, 2895–2899; (c) W.-B. Chen, Y.-C. Chen, G.-Z. Huang, J.-L. Liu, J.-H. Jia and M.-L. Tong, *Chem. Commun.*, 2018, **54**, 10886–10889; (d) C. D. Ene, C. Maxim, M. Rouzières, R. Clérac, N. Avarvari and M. Andruh, *Chem. – Eur. J.*, 2018, **24**, 8569–8576.
- T. Fukami, S. Tahara, C. Yasuda and K. Nakasone, *Int. J. Chem.*, 2016, **8**, 9–21.

