

Showcasing research from Professor Sudipta Roy's laboratory, Department of Chemistry, Indian Institute of Science Education and Research (IISER) Tirupati, Andhra Pradesh, India.

Isolation of mixed valence charge-neutral  $Ag_{12}$ , and dicationic  $Ag_{10}$  nano-clusters stabilized by carbene-phosphaalkenides

Cyclic alkyl(amino) carbene-supported phosphaalkenides were employed as ligands for isolation of two atomically precise mixed-valence nanoclusters (NCs) with  $Ag_{12}^{/0}Cl_3$ , and  $Ag_{10}^{/0}$  cores. The characteristic EPR signals exhibited by the NCs suggested coupling of unpaired electrons with <sup>35,37</sup>Cl, <sup>31</sup>P and <sup>107,109</sup>Ag nuclei.

The cover image was prepared using components from © Natalia Dobrovolska | Dreamstime.com.



As featured in:



See Sudipta Roy *et al.*, *Chem. Commun.*, 2025, **61**, 1379.





# ChemComm



**View Article Online** 

View Journal | View Issue

COMMUNICATION

Check for updates

Cite this: Chem. Commun., 2025, 61, 1379

Received 23rd October 2024, Accepted 11th December 2024

DOI: 10.1039/d4cc05628k

rsc.li/chemcomm

## Isolation of mixed valence charge-neutral Ag<sub>12</sub>, and dicationic Ag<sub>10</sub> nano-clusters stabilized by carbene-phosphaalkenides<sup>†</sup>

Maria Francis, (D) ‡<sup>a</sup> Asutosh Patra, (D) ‡<sup>a</sup> Farsana Abdul Salam, (D)<sup>a</sup> Siriyara Jagannatha Prathapa<sup>b</sup> and Sudipta Roy (D) \*<sup>a</sup>

Cyclic alkyl(amino) carbene (cAAC)-supported phosphaalkenides  $(cAAC = P)^{-}$  have been employed as ligands for the isolation of two atomically precise mixed valence paramagnetic  $Ag_{12}^{I/0}Cl_3$ , and  $Ag_{10}^{I/0}$ , nano-clusters  $[(Me_2-cAAC = P)_6Ag_{12}Cl_3]$  (2), and  $[(Me_2-cAAC = P)_6Ag_{10}](NTf_2)_2$  (4). 2 and 4 have been structurally characterized by single-crystal X-ray diffraction revealing the presence of three  $Ag^0$  atoms, nine  $Ag^1$  ions (2); and two  $Ag^0$  atoms, eight  $Ag^1$  ions (4), respectively. The clustering inorganic unit  $Ag_{12}Cl_3$  in 2 has been found to be surrounded by six mono-anionic  $\mu_3$ -cAAC = P moieties having 3-bar symmetry. 2 and 4 have been studied by cyclic voltammetry, UV-vis, ESI-MS, XPS, EPR spectroscopy, and DFT calculations.

Silver nanoclusters (NCs) are known to exhibit unique electronic, and optical properties, such as strong photoluminescence, and various catalytic activities.<sup>1</sup> They are utilised as attractive luminescent probes for sensing and bioimaging.<sup>2</sup> Structurally well-defined NCs possessing Ag<sup>0</sup> atoms are highly reactive, and easier to oxidize compared to their heavier Au analogues, which makes their synthesis challenging. Metallic silver is nonmagnetic in its bulk form. However, Pereiro et al. theoretically predicted that the small nuclearity silver NCs,  $Ag_n$ , could be magnetic with variation of the magnetic moment depending on the value of n [n = 2-22].<sup>3</sup> Liu *et al.* reported the isolation of the chiral open-shell Ag<sub>23</sub> NC with five Ag<sup>0</sup> atoms, which was structurally characterized by single-crystal X-ray diffraction.<sup>4</sup> The open-shell behaviour of this Ag<sub>23</sub> NC was confirmed by a weak electron paramagnetic resonance (EPR) signal, characteristic of s = 1/2, with g = 1.959 and 1.955.<sup>4</sup> The first atomically precise mixed valence Ag<sub>22</sub><sup>0/I</sup> NC displaying thermally activated delayed fluorescence (TADF) was reported in 2022 by Sun and

co-workers.<sup>5</sup> In the same year, two other mixed valence NCs Ag<sub>8</sub><sup>0/I</sup> and Ag<sub>29</sub><sup>0/I</sup> exhibiting strong EPR signals were reported.<sup>6</sup> The heavily Ag<sup>0</sup>-doped KCl:AgCl crystals in different chemical defect positions [cationic and anionic holes] were studied by EPR spectroscopy.<sup>7*a*</sup> The generation of  $Ag_4^{3^+}$ , and  $Ag_6^+$  clusters was also reported under different chemical conditions.<sup>7b,c</sup> However, the mixed valence silver NCs are rarely reported.8 The first closed-shell mixed valence  $Ag_2^{I/III} [Ag \cdots Ag 7.4 Å]$  containing  $N_8$ donor macrocyclic ligand was isolated by Qin-Hui et al. in 1994.<sup>9a</sup> The 1D zig-zag chain of  $Ag_2^{I/II}$  (ref. 9b) stabilized by the cyclic alkyl(amino) carbene (cAAC)-supported mono-anion of the inversely polarized phosphaalkene, viz., the phosphaalkenide<sup>10</sup> was reported by Roy and co-workers. N-heterocyclic carbene (NHC), and P-SiMe<sub>3</sub> ligated diamagnetic Ag<sup>I</sup><sub>12</sub>, and Ag<sup>I</sup><sub>26</sub> clusters were reported by Corrigan et al.11 A plethora of other Ag<sup>I</sup> clusters have been synthesized, and characterized employing alkyne, thiolate, sulfide, selenide, phosphine, perchlorate, etc. as ligands.<sup>12</sup> Moreover, clusters with Ag-H moieties have also been isolated, and further studied by mass spectrometry.<sup>13</sup> However, isolation of stable silver NCs introducing carbenephosphaalkenides as ligands is still scarce. Herein, we report on the solid-state isolation, and structural characterization of two novel structurally well-defined mixed valence paramagnetic silver NCs with Ag<sup>I/0</sup><sub>12</sub>Cl<sub>3</sub>, and Ag<sup>I/0</sup><sub>10</sub> metallic cores.

The dark red crystals of Me<sub>2</sub>-cAAC=P-K (1)<sup>14</sup> (Me<sub>2</sub>-cAAC= C(*N*-2,6<sup>-i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)(CMe<sub>2</sub>)<sub>2</sub>(CH<sub>2</sub>)) were reacted with AgNTf<sub>2</sub> in a 3:2 molar ratio in toluene at 0 °C to room temperature (rt) for 12 h to obtain a dark brown-red reaction mixture. Upon drying, the resultant crystalline solid obtained was dissolved in freshly distilled DCM, and stored for crystallization upon concentration to ~1 mL in a freezer at -40 °C. After one-week, dark red blocks of [(Me<sub>2</sub>-cAAC=P)<sub>6</sub>(Ag)<sub>12</sub>(Cl)<sub>3</sub>] (2) were isolated in 40% yield (Scheme 1). The presence of the three chloride ions in 2 can be attributed to the decomposition of DCM, the usage of which is found to be crucial for the isolation of 2. A different mixed valence dicationic cluster [(Me<sub>2</sub>-cAAC=P)<sub>6</sub>(Ag)<sub>10</sub>](NTf<sub>2</sub>)<sub>2</sub> (4) was isolated in 60% yield as yellow blocks when [Me<sub>2</sub>cAAC=P-B(N(<sup>i</sup>Pr)<sub>2</sub>)<sub>2</sub>] (3)<sup>9b</sup> was reacted with AgNTf<sub>2</sub> in 2:1

<sup>&</sup>lt;sup>a</sup> Department of Chemistry, Indian Institute of Science Education and Research (IISER) Tirupati, Tirupati 517619, India. E-mail: roy.sudipta@iisertirupati.ac.in

<sup>&</sup>lt;sup>b</sup> Bruker India Scientific Pvt. Ltd, India

<sup>†</sup> Electronic supplementary information (ESI) available. CCDC 2242239 (2), 2194453 (4). For ESI and crystallographic data in CIF or other electronic format see DOI: https://doi.org/10.1039/d4cc05628k

<sup>‡</sup> Both authors contributed equally.



molar ratio in toluene at rt for 12 h, followed by crystallization of the resultant precipitate from concentrated DCM solution, stored at 0 °C in a refrigerator (Scheme 2). The (cAAC=P)<sup>-</sup> ligands are found to be redox non-innocent, and undergo oxidation to produce the corresponding radical followed by dimerization, resulting in the formation of (Me<sub>2</sub>-cAAC)<sub>2</sub>P<sub>2</sub> with a subsequent reduction of Ag<sup>I</sup> to Ag<sup>0</sup> in solution affording the mixed valence Ag-NCs 2 and 4.<sup>6</sup> The presence of Ag<sup>0</sup> and Ag<sup>I</sup> centres in 2 and 4 is supported by XPS spectroscopy (see ESI†). The formation of (Me<sub>2</sub>-cAAC)<sub>2</sub>P<sub>2</sub> in the reaction mixture is confirmed by <sup>31</sup>P NMR spectroscopy ( $\delta$  = 55.1 ppm).

The red/yellow blocks of 2/4 are found to be stable under an argon atmosphere for six months inside a glove box at rt. The powders of 2 and 4 decompose above 205 and 165 °C, respectively. 2 and 4 are found to be NMR silent, and EPR active.

2 and 4 have been structurally characterized by single-crystal X-ray diffraction. The dodeca-nuclear Ag-NC  $[(Me_2-cAAC=P)_6-(Ag)_{12}(Cl)_3]$  (2) crystallizes in the trigonal  $R\bar{3}$  space group (Fig. 1). 2 comprises six  $(Me_2-cAAC=P)^-$  ligands, three chloride ions, and twelve Ag-atoms/ions. Fig. 2 shows that the asymmetric unit of 2 starting at position-1, generates six different symmetry equiv. points (1–6). Positions 1, 3 and 5 are non-inverted, while positions 2, 4 and 6 are three inverted-symmetry equiv. positions. There are three  $Ag^0$  atoms in 2, which is

Scheme 2 Synthesis of mixed-valence dicationic NC [(Me\_2-cAAC=P)\_6Ag\_{10}]-(NTf\_2)\_2 (4).



Fig. 1 Molecular structure of NC [ $(Me_2-cAAC = P)_6(Ag)_{12}(Cl_3)$ ] (2). Hydrogen atoms are omitted for clarity.



Fig. 2 Structural topology and symmetry [3-bar] in NC 2.

suggested from charge balance consideration, since there are a total of nine mono-anionic ligands present.

The space filling model of 2 has been shown in Fig. 3 (left), which represents how the central Ag<sub>12</sub> metallic core is well protected by the surrounding cAAC-supported phosphaalkenide ligands. The natural bond orbital (NBO) analyses of NCs 2 and 4 at neutral doublet, and dicationic triplet states, respectively, were performed at the UBP86-D3(BJ)/Def2-SVP level of theory (see ESI† for details). The NBO analysis of 2 revealed that the  $\alpha$ -LUMO+1,  $\alpha$ -LUMO, and  $\alpha$ -SOMO are very close in energy ( $\Delta E = 0.01-0.05$  eV) suggesting that the unpaired electron in 2 can span all these three orbitals involving the C—N–P unit, Cl and Ag atoms (see ESI†). This is also reflected in the Mulliken  $\alpha$ -spin densities of 2 showing delocalization of spin densities due to the unpaired electron (Fig. 3 (right), see ESI†).

The Ag–Ag distances of charge-neutral NC 2 are found to be 2.883(1), and 3.024(2) Å, which are significantly shorter than



Fig. 3 Space filling model (left), and Mulliken  $\alpha\text{-spin}$  densities (right) of [(Me\_2-cAAC=P)\_6Ag\_{12}Cl\_3] (2).

8

those of the previously isolated tri-cationic closed-shell Ag NC  $2^{3+}(\text{OTf}^{-})_3$  (2.9593(14), 2.9174 (12), 3.2026(15), 3.1541(13) Å).<sup>6</sup> The Ag-P distances of 2 are 2.379(4), 2.401(3), and 2.455(2) Å, which are close to those of  $2^{3+}(OTf^{-})_3$  (Ag-P 2.393(4)-2.431(4) Å).<sup>6</sup> The C-P bond in 2 is 1.75(1) Å, which is slightly shorter than those of  $2^{3+}(OTf^{-})_3$  (1.780(11)–1.801(11) Å).<sup>6</sup> The Ag–Cl distances in 2 are found to be 2.4530(14), and 2.572(7) Å, which are either very similar in value or significantly smaller than those of  $2^{3+}$ (2.475(9), 2.705(5), 2.638 (4), 2.7143(11), 2.732(4), 2.8254(10) Å).<sup>6</sup> The diameter of the outer/peripheral Ag<sub>6</sub> ring of 2 having a threefold symmetry is 8.37 Å, which is very close to those of  $2^{3+}$  with two-fold symmetry (8.26, 8.36, 8.48 Å).6 The Cl-Cl distance between the two extreme Cl-ions in 2 is 5.8 Å, which is shorter than that of  $2^{3+}$  (6.5 Å).<sup>6</sup> The P–P distance in 2 is 9.02 Å, which is slightly greater than the average value of  $2^{3+}$  (8.46 Å; 8.26, 8.36, 4.48, 8.88, 9.22 Å).<sup>6</sup> 2 represents the first example of an  $Ag^{I/0}$ based mixed valence NC, which has been structurally characterized in two different charged  $(0(2) vs. +3(2^{3+})]$ , and spin states [doublet (2) vs. singlet  $(2^{3+})$ ).<sup>6</sup>

The dicationic deca-nuclear Ag NC [(Me<sub>2</sub>-cAAC=P)<sub>6</sub>Ag<sub>10</sub>]- $(NTf_2)_2$  (4) crystallizes in triclinic space group  $P\overline{1}$  (Fig. 4). The entire molecule of 4 appears in the crystallographic asymmetric unit, which possesses six mono-anionic ligands (Me<sub>2</sub>-cAAC=P)<sup>-</sup>, and ten Ag-atoms/ions. There are two non-coordinating/free mono-anionic NTf<sub>2</sub><sup>-</sup> anions present for the electrical charge balance. The charge balance consideration suggests that there are two Ag<sup>0</sup> atoms in 4. The four arms of the central Ag<sub>4</sub> unit of 4 have been bridged by four P-atoms of mono-anionic Me<sub>2</sub>cAAC=P<sup>-</sup> ligands producing a (Me<sub>2</sub>-cAAC=P)<sub>4</sub>Ag<sub>4</sub> unit. Two Ag<sub>2</sub> units have been placed in anti-fashion above and below the irregular square-like Ag<sub>4</sub> unit (Fig. 4 and 5).

An additional Ag-atom is present above the Ag<sub>2</sub> unit (Fig. 4 and 5), while another Ag atom is bridged by a  $\mu_3$ -P atom (right, Fig. 5). The Ag-Ag distances of the central four-membered Ag<sub>4</sub> ring in 4 are 2.90, 3.0, and 3.20 Å, which are longer than those  $(\sim 2.96 \text{ Å})$  of the Ag<sub>8</sub><sup>0/I</sup> complex.<sup>6</sup>

The Ag<sub>2</sub> unit, which is situated on the top of the central Ag<sub>4</sub> unit, possesses the Ag-Ag distance of 2.91 Å, which is



Fig. 4 Molecular structure of NC [(Me2-cAAC=P)6Ag10](NTf2)2 (4). Hydrogen atoms are omitted for clarity. Two triflimide anions [N(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub><sup>-</sup>] are omitted for clarity



Fig. 5 Core topology of [(Me<sub>2</sub>-cAAC=P)<sub>6</sub>Ag<sub>10</sub>](NTf<sub>2</sub>)<sub>2</sub> (4). Two Ag<sub>6</sub> square prisms sharing the blue colored pseudo-Aq<sub>4</sub>-square with a 4-bar symmetry operation

significantly shorter than that of the Ag<sub>3</sub> triangle of 4 (3.04 Å). The corresponding Ag-Ag distance in previously reported  $Ag_8^{0/I}$  complexes is 3.07 Å.<sup>6</sup> Notably, the distal Ag atom (Ag9) (Ag7-Ag9, Ag8-Ag9; 2.472(3), 2.458(3) Å) is significantly closer to the Ag<sub>2</sub> arm (Ag8-Ag9), which is situated above the central Ag<sub>4</sub> unit of 4. The Ag–P bond lengths of NC  $Ag_{10}^{0/I}$  (4) range from 2.23 Å to 2.48 Å, and are significantly different than those of the neutral Ag<sub>8</sub> cluster (2.404(5)–2.417(4) Å).<sup>6</sup> The space filling diagram of a ten Ag atoms/ions unit of 4 has been shown in Fig. 6 (left). The Ag atom placed above the Ag<sub>2</sub> unit is situated in between the two aromatic rings of the Dipp ligands. The NBO, and Mulliken spin density analyses of 4 (Fig. 6 (right)) showed the major spin densities on the C=N-P unit with very small values on the Ag-atoms except for one Ag-atom (5.6%) and thus typical EPR features of Ag-P systems were not observed<sup>6</sup> in the experimental EPR spectrum of 4.

The EPR spectra of 2 and 4 (in DCM) are shown in Fig. 7 and 8. The EPR simulation/fitting of 2 considering coupling of the unpaired electron with the nuclei of <sup>107,109</sup>Ag, <sup>31</sup>P and <sup>35,37</sup>Cl atoms is quite satisfactory (Fig. 7). Three board lines near g =2.0033 were observed for the previously reported  $Ag_8^{0/I}$  cluster containing four Ag<sup>0</sup> atoms.<sup>6,9b</sup> However, the EPR spectrum of 2 shows three sets of multiple hyperfine lines, which have been simulated with EasySpin.

The coupling constants of one <sup>107,109</sup>Ag<sup>0</sup>, two <sup>31</sup>P and one <sup>35,37</sup>Cl nuclei are 9.43, 111.79/111.75, and 9.81 MHz, respectively, with a slight rhombic nature of g  $[g_x = 2.00766,$  $g_v = 2.00885$ ,  $g_z = 1.99959$ ]. The EPR spectrum of 4 appears as unsymmetrical showing two resonances around  $g \approx 2 [g_x =$ 2.00165,  $g_y = 2.00006$ ,  $g_z = 1.99703$ ] (Fig. 8). The coupling constant of Ag<sup>0</sup> is 2.51 MHz, which is significantly smaller than that of 2 (9.43 MHz). The ESI-MS studies show that 2 (see ESI<sup>†</sup>) and 4 can fly as dications. The ESI-MS spectrum of  $4^{2+}$  corroborates the loss of two isopropyl groups with the intake of a sodium ion as [(Me<sub>2</sub>cAACP)<sub>6</sub>Ag<sub>10</sub> + Na-2C<sub>3</sub>H<sub>7</sub>-H]<sup>2+</sup>. The cyclic



Fig. 6 Space filling model of total molecule (left), and Mulliken  $\alpha$ -spin densities (right) of [(Me2-cAAC=P)6Ag10](NTf2)2 (4).





**Fig. 7** Experimental (black), and simulated (red) X-band EPR spectra of  $[(Me_2-cAAC = P)_6(Ag)_{12}(Cl_3)]$  (2) in DCM at 293 K. EasySpin, simulated parameters: one <sup>107,109</sup>Ag(0) [A = 9.43 MHz], two <sup>31</sup>P [A = 111.79, 111.75 MHz], one <sup>35,37</sup>Cl [A = 9.81 MHz],  $g_x = 2.00766$ ,  $g_y = 2.00885$ ,  $g_z = 1.99959$ , LW1 = 0.016 mT, LW2 = 0.166 mT. Experimental frequency = 9.436369 GHz.



**Fig. 8** X-band EPR spectrum of the NC  $[(Me_2-cAAC = P)_6(Ag)_{10}](NTf_2)$  (**4**) in DCM at 293 K. Black line represents the experimental spectrum, and the red line represents the simulated spectrum using the EasySpin program  $[g_x = 2.00165, g_y = 2.00006, g_z = 1.99703, LWPP_1 = 0.0678384 mT, LWPP_2 = 0.0817786 mT, A_{Ag} = 2.51891 MHz].$ 

voltammetry studies of 2 and 4 suggest the possible oxidation (see ESI<sup>†</sup>). The UV-vis spectra (in THF at 298 K) of 2 and 4 exhibited the absorption maxima ( $\lambda_{max}$ ) at 365 and 367 nm, respectively (see ESI<sup>†</sup>). 2 and 4 were observed to be non-emissive.

In conclusion, two novel mixed valence Ag-NCs (Ag<sub>10</sub>, 2; Ag<sub>12</sub>, 4) were isolated as red/yellow blocks. 2 and 4 have been structurally characterized by X-ray single-crystal diffraction. The Ag<sub>10</sub>, and Ag<sub>12</sub> NCs possess three and two Ag<sup>0</sup> atoms, respectively. The NMR silent NCs 2 and 4 were found to be EPR active. The unpaired electrons couple with the <sup>35,37</sup>Cl, <sup>31</sup>P and <sup>107,109</sup>Ag nuclei. The strongest coupling constant was obtained for <sup>31</sup>P-nuclei (111.75 MHz) in 2. The coupling constant of <sup>107,109</sup>Ag of 2 (9.43 MHz) is four times stronger than that of 4 (2.51 MHz). The distributions of electron densities in 2 and 4 were estimated by computation of the Mulliken spin densities, and further correlated with ERP simulation.

SR gratefully acknowledges STARS-IISC, MoE (MoE-STARS/ STARS-2/2023-0666), IISERT, CSIR for the generous financial support. We thank Dr S. S. Sen (NCL-Pune), and KB for the XPS measurements.

## Data availability

The data supporting this article (experimental details, UV-vis, HRMS, EPR, XPS, single-crystal X-ray data, and computational details) have been included as part of the ESI.† Crystallographic data for 2 and 4 have been deposited at the CCDC (2242239, 2194453†), and can be obtained from https://www.ccdc.cam.ac.uk/.

### Conflicts of interest

There are no conflicts to declare.

#### Notes and references

- 1 (a) C. M. Aikens, *J. Phys. Chem. Lett.*, 2011, **2**, 99; (b) Y. Du, H. Sheng, D. Astruc and M. Zhu, *Chem. Rev.*, 2020, **120**, 526.
- 2 (a) T. Udayabhaskararao and T. Pradeep, J. Phys. Chem. Lett., 2013, 4, 1553; (b) K. Zheng, X. Yuan, N. Goswami, Q. Zhang and J. Xie, RSC Adv., 2014, 4, 60581.
- 3 M. Pereiro, D. Baldomir and J. E. Arias, Phys. Rev. A, 2007, 75, 063204.
- 4 C. Liu, T. Li, H. Abroshan, Z. Li, C. Zhang, H. J. Kim, G. Li and R. Jin, *Nat. Commun.*, 2018, 9, 744.
- 5 Z.-R. Yuan, Z. Wang, B.-L. Han, C.-K. Zhang, S.-S. Zhang, Z.-Y. Zhu, J.-H. Yu, T.-D. Li, Y.-Z. Li, C.-H. Tung and D. Sun, *Angew. Chem., Int. Ed.*, 2022, **61**, e202211628.
- 6 E. Nag, S. Battuluri, K. C. Mondal and S. Roy, *Chem. Eur. J.*, 2022, **28**, e202202324.
- 7 (a) P. G. Baranov, N. G. Romanov, V. A. Khramtsov and V. S. Vikhnin, J. Phys.: Condens. Matter, 2001, 13, 2651; (b) J. Sadło, J. Michalik and L. Kevan, EPR and ESEEM study of silver clusters in ZK-4 molecular sieves, Nukleonika, 2006, 51, 49; (c) A. Baldansuren, R. Eichel and E. Roduner, Phys. Chem. Chem. Phys., 2009, 11, 6664.
- 8 H. Hirai, S. Ito, S. Takano, K. Koyasu and T. Tsukuda, *Chem. Sci.*, 2020, **11**, 12233.
- 9 (a) Y. Shu-Yan, L. Qin-Hui and S. Meng-Chang, *Inorg. Chem.*, 1994,
  33, 1251; (b) E. Nag, S. Battuluri, B. B. Sinu and S. Roy, *Inorg. Chem.*,
  2022, 61, 3007.
- 10 L. Weber, U. Lassahn, H.-G. Stammler and B. Neumann, *Eur. J. Inorg. Chem.*, 2005, 4590.
- 11 B. K. Najafabadi and J. F. Corrigan, Chem. Commun., 2014, 51, 665.
- 12 (a) D. Fenske and F. Simon, Angew. Chem., Int. Ed. Engl., 1997, 36, 230; (b) X. He, H.-X. Liu and L. Zhao, Chem. Commun., 2016, 52, 5682; (c) X.-J. Wang, T. Langetepe, C. Persau, B.-S. Kang, G. M. Sheldrick and D. Fenske, Angew. Chem., Int. Ed., 2002, 41, 3818; (d) D. Fenske, C. Persau, S. Dehnen and C. E. Anson, Angew. Chem., Int. Ed., 2004, 43, 305; (e) M. Ueda, Z. L. Goo, K. Minami, N. Yoshinari and T. Konno, Angew. Chem., Int. Ed., 2019, 58, 14673; (f) Z.-A. Nan, Y. Wang, Z.-X. Chen, S.-F. Yuan, Z.-Q. Tian and Q.-M. Wang, Chem. Commun., 2018, 1, 1; (g) J.-W. Liu, H.-F. Su, Z. Wang, Y.-A. Li, Q.-Q. Zhao, X.-P. Wang, C.-H. Tung, D. Sun and L.-S. Zheng, Chem. Commun., 2018, 54, 4461; (h) L. G. AbdulHalim, M. S. Bootharaju, Q. Tang, S. Del Gobbo, R. G. AbdulHalim, M. Eddaoudi, D.-E. Jiang and O. M. Bakr, J. Am. Chem. Soc., 2015, 137, 11970; (i) S.-F. Yuan, Z.-J. Guan, W.-D. Liu and Q.-M. Wang, Nat. Commun., 2019, 10, 1; (j) C. Sun, B. K. Teo, C. Deng, J. Lin, G.-G. Luo, C.-H. Tung and D. Sun, Coord. Chem. Rev., 2021, 427, 213576; (k) M. S. Bootharaju, R. Dey, L. E. Gevers, M. N. Hedhili, J.-M. Basset and O. M. Bakr, J. Am. Chem. Soc., 2016, 138, 13770.
- 13 M. Jash, A. C. Reber, A. Ghosh, D. Sarkar, M. Bodiuzzaman, P. Basuri, A. Baksi, S. N. Khanna and T. Pradeep, *Nanoscale*, 2018, 10, 15714.
- 14 A. Kulkarni, S. Arumugam, M. Francis, P. G. Reddy, E. Nag, S. M. N. V. T. Gorantla, K. C. Mondal and S. Roy, *Chem. – Eur. J.*, 2021, 27, 200.