RSC Advances

RSC Advances

www.rsc.org/advances

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/advances

Table of Content

ARTICLE TYPE

A hexanuclear Cu(I) cluster supported by cuprophilic interaction: Effects of aromatics on luminescence properties

Anindita Chakraborty,[a#] Ramachandran Krishna Kumar,[a#] Sharma SRKC Yamijala,[b] Swapan K. Pati [b] and Tapas K. Maji*[a]

[5]

#These authors contributed equally

A hexanuclear Cu(I) cluster $\{Cu_3(L)_2\}_2$ (**1**) based on a novel
[10] tripodal linker (**L**) has been synthesized. **1** shows intense
emission (λ_{max} = 560 nm) with lifetime $<\tau>$ = 224 μS and
quantum yield = 27.6%. The emission is highly sensitive
towards different electron rich and electron deficient
aromatics. DFT calculations were performed to understand
[15] the origin of emission and sensing properties.

Design and study of polynuclear coordination clusters is of
paramount importance as these ensembles are potential
candidates for catalysis,[1] trapping molecules,[2] sensing[3] and
specific guest encapsulation.[4] Particularly, polynuclear Cu(I)
[20] compounds demand special attention because of their rich
photoluminescent (PL) properties[5a-d] and possible applications as
solar energy sensors.[5f] Cu(I) coordination compounds have also
established their importance in biological processes.[5e] However,
synthesis of such complexes remains as a great challenge because
[25] of the intrinsic instability of the Cu(I) state leading to facile
oxidation to Cu(II).[6] Cu(I) cluster based on chalcogenide, halide
and pseudohalide[7,8] have been widely studied, but studies
pertaining to Cu(I) carboxylate complexes are still limited.[9a-d]
The inadequate literature relates to the hardness of oxygen in
[30] carboxylate ligand, unlike halides or chalcogenides which can
easily stabilize soft Cu(I) centre. Despite the synthetic challenges,
study of Cu(I) carboxylate compound remains a fascinating
research aspiration because excellent optoelectronic devices can
be furnished. The 'syn-syn' carboxylate binding can render a
[35] close proximity between metal centres and such arrangement
leads to interactions between closed d^{10} shells[10] which eventually
ensue cuprophilic interaction. Such metal-metal interactions
usher interesting PL behaviour,[10c] which can be further exploited
for fast sensing of specific molecules. Specially, fluorescence-
[40] quenching based detection of nitroaromatics has become very
important due to its significant applications in environmental
cleaning, defence and security.[11] Our group have been working
on the fabrication of novel Cu(I)-coordination compounds.[9c-e] In
present work, we focused on synthesis of Cu(I) cluster with
[45] interesting photophysical properties, fast sensing capability and
investigate the underlying mechanism for the luminescence. To
achieve desired Cu(I) cluster, it is necessary to conceive a rational

Fig. 1 Synthesis and structure of a hexanuclear complex $\{Cu_3(L)_2\}_2$ (**1**) using a novel tripodal carboxylate linker.

[50] approach based on the ligand binding mode. Here we have
synthesized a new carboxylate based ligand 4,4′,4″-[1,3,5-phenyl-
tri(methoxy)]-tris-benzoic acid] (**L**) [Fig. 1] and envisioned that
flexible backbone of **L** allows the formation of a novel complex
based on its diverse binding mode. Here in this communication,
[55] we report synthesis and structural characterization of an unusual
hexanuclear Cu(I) cluster $\{Cu_3(L)_2\}_2$ (**1**), which shows intense
yellow emission (λ_{max}= 560 nm) with considerably high lifetime.
The emission properties of **1** are further explored to sense
electron rich and deficient solvent vapours including
[60] nitroaromatics. Cuprophilic interaction plays a crucial role for the
luminescence behaviour, whereas sensing of different analyte
vapours has been correlated with the electronic structures and the
interactions in excited state which are further supported by
density functional theory (DFT) based calculations.
[65] Reaction between $Cu(NO_3)_2\cdot2.5H_2O$ and **L** in DMF at
solvothermal condition [see supporting information (SI)] yields
colourless crystal of **1** by *in situ* reduction of Cu(II) to Cu(I)
during the reaction process. Single-crystal X-ray crystallographic
studies (see SI) revealed that a hexanuclear Cu(I) cluster is
[70] bridged by the tripodal ligand **L** (Fig. 1). In the asymmetric unit,
there are three crystallographically independent Cu(I) centres and
one **L** ligand. Each ligand binds six Cu(I) centres while each
carboxylate group binds two Cu(I) centres in a bridging bidentate
syn-syn fashion. Cu1, Cu2 and Cu3 are connected to O1, O3; O2,
[75] O6 and O4 and O5, respectively. The carboxylate groups control
the Cu---Cu inter-ionic distance which eventually results the
cuprophilic interactions. In the hexanuclear core, the nearest
neighbouring Cu(I) centers Cu1---Cu2, Cu2--Cu3, and Cu1---Cu3

are separated by distances 2.801 Å, 2.718 Å, and 2.696 Å respectively, which are in the required range for cuprophilic interaction (<2.8Å)[10]. There is additional short Cu---Cu contact between the non-bridged metal centers, Cu1-Cu2 of 2.895 Å, Cu2-Cu2 of 2.994 Å and a longest distance of 4.793 Å between Cu2-Cu3. Cu(I) shows versatile coordination geometries because of the relatively small energy differences between various geometries like distorted trigonal pyramid, tetragonally elongated octahedral and see-saw geometries.[12] For **1**, Cu1 and Cu3 show see-saw coordination while Cu2 exhibits a square planar geometry (considering only adjacent Cu(I) metal centers). The tripodal ligand is flexible based on -O-ϕ-CO2 linkage to the benzoic acid part (ϕ) and all the three benzene carboxylate groups are oriented towards the same directions driven by the Cu(I) geometries. This leads to the formation of a unique hexanuclear cluster. Each cluster undergoes π-π interaction operating between the parallel faces of two clusters with a cg-cg distance of 3.677Å. This helps in stacking the clusters in one-dimension (Fig. S4, SI). The emission spectra were recorded on solid crystalline sample at room temperature and it shows intense yellow emission with maximum at 560 nm when excited at 360 nm (Fig. 2). The ligand shows luminescence maxima at 380 nm (Fig. S6, SI); hence the large stokes shifted emission can't be explained only in terms of metal to ligand charge transfer (MLCT) or ligand to metal charge transfer (LMCT). Time-resolved single-photon counting experiments (Fig. S9, SI) showed a long-lived bi-exponential decay [τ_1=272 μs τ_2=21μs, τ_{avg}=224μs] for **1**. The quantum yield (Φ) of **1** is 27.6% and hence **1** can be suitable for fabricating organic light emitting diode etc.[5c,f] Neutral Cu(I) compounds can potentially show high quantum yield (Φ>20%) and complexes with pyridyl-tetrazolate and phosphine ligands have been reported showing strong emission (Φ=89%) from mixed MLCT and intraligand CT states.[5c]

Though there are few reports on the PL study on Cu(I) carboxylate,[9a,b] to the best of our knowledge, there is no systematic study discussing the origin of PL and its dependence on the structural type. We have done DFT calculations (see SI) to get insight of the PL properties of **1**.
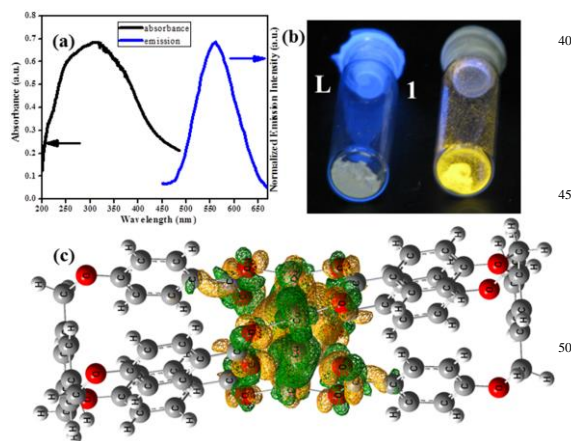
Fig. 2 (a) The UV-Vis (black) and emission (blue) spectra of **1** (λ_{em}= 560 nm, λ_{ex}= 360 nm). (b) The images of ligand L and **1** under UV light. (c) Electron density difference map between T and S states (at T state optimized geometry). Electron transferred from green region to orange region

From the calculated UV-Vis spectrum of **1**, we observed transitions having higher oscillator strengths (OS) (Table S2, SI) are mainly of hybrid character [mixture of LMCT, metal to metal charge transfer (MMCT) and ligand to ligand charge transfer (LLCT)]. To understand PL property precisely, we have optimized the H-atom positions of the experimental structure and found it to exist in a singlet ground state. We then optimized the structure considering triplet (T1) state as the initial state and found another single state (S1) at a lower energy in the same geometry of T1 state (see SI for details). In fact, we find a number of singlet and other magnetic states, forming almost a band of energy spectrum, all with almost the same energy. Although we find a large band gap value, the emission occurs from one of such low-lying singlet sate. The energy difference[13] between these states is ~ 588 nm (Table S3, SI), which is close to the experimental λ_{max} value. The optical excitation once reaches the excited singlet state, juggles around the continuum of states including long lived triplet state, before emitting from an excited singlet state which has large OS. The experimental observations of high life time is probably due to the continuum of states together with large OS of excited single state and thus may be called as delayed fluorescence. Electron density difference map (EDDM) between the T1 and S1 states (Fig. 2c) clearly shows that the map is mainly cluster centred. As shown in the map, the electron transfer has occurred within the metal atoms and the COO groups suggesting the nature of emission as hybrid of LMCT and MMCT character, where the latter may be seen as cuprophilic interaction. Thus our results show that the luminescence of such clusters may have originated from cuprophilic interaction.
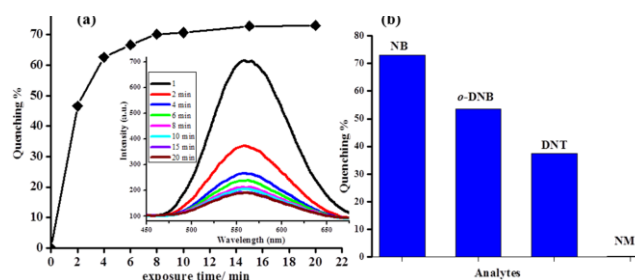

Fig. 3 (a) Time dependent fluorescence quenching upon the exposure of NB vapour. (b) Reduction in fluorescence intensity observed upon the addition of different analytes.

The effects of electron rich and electron donating aromatics on emission properties of **1** were further studied. Indeed, the study revealed that vapours of compounds containing electron deficient groups like nitrobenzene (NB), *o*-dinitrobenzene (*o*-DNB) and 2, 4-dinitrotoluene (DNT) quench the emission of **1** (Fig. 3, S10-S12, SI), while that of having electron donating groups like toluene, *o*-xylene and *p*-xylene show an enhancing ability (Fig. S13-16, SI). The capability of the complex to detect both the electron deficient and electron rich aromatic compounds is moderately fast, for e.g., the maximum quenching by NB is achieved within 15 minutes (Fig. 3a). The order of quenching efficiency is NB > o-DNB > DNT (Fig. 3b). Two factors such as electron availability and vapour pressure of the solvent affect the quenching or enhancement. The strongest quenching effect

exhibited by NB is due to the strong electron withdrawing –NO$_2$ group and the high vapor pressure (Table S1, SI). Again DNT contains two strongly electron-withdrawing -NO$_2$ groups, but because of its low vapor pressures at room temperature, its
5 quenching ability is less than that of NB. Among the electron donating analytes, highest enhancement ability is shown by toluene (Fig. S16, SI), which is attributed to its higher vapour pressure. Furthermore, we measured the lifetime of the NB and toluene vapour exposed samples, which come out to be 0.09 and
10 29.98% respectively, further proving the quenching and enhancement mechanism.

The observed trend can be explained by the donor-acceptor electron transfer mechanism. In the case of an electron-withdrawing analyte, the lowest unoccupied MO (LUMO) is a
15 low-lying π*-type orbital and its energy is below the LUMO of **1**, while the LUMO of the electron donating analytes is above the LUMO of **1**, as suggested by the DFT calculation (Fig. S17, SI). Upon excitation, for the electron-withdrawing analytes, electrons are transferred from the LUMO of **1** to the LUMO of analyte
20 resulting quenching effect. In the other case, electron can flow from LUMO of analytes to the LUMO of complex which results in emission enhancement (Scheme 1). This mechanism is well established for conjugated polymers[14] and has been observed in a recently reported Zn metal-organic framework[15]. The proposed
25 mechanism is consistent with the relative orbital energy levels of the cluster and analyte as obtained from DFT calculations. Interestingly, the quenching is negligible for nitromethane (Fig. S12, SI), an aliphatic nitro containing compound. This reflects the selectivity of **1** towards aromatic nitro aromatics, which is
30 attributed to the better interaction of **1** with the π orbitals with the aromatics, rather than the σ orbitals of aliphatic compounds.[15]
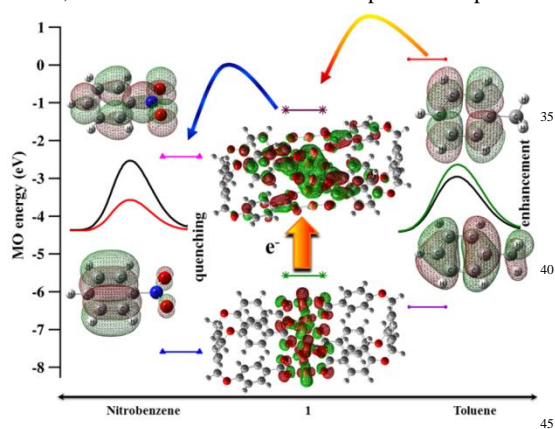
Scheme 1 Excited state electron migration mechanism (calculated energy levels for **1**, NB and toluene are shown; for details see SI).

Conclusions

We have synthesized a novel hexanuclear Cu(I) cluster, which
50 shows interesting cluster-centred emission properties with unique sensing properties. Formation of such rare polynuclear cluster driven by metallophilic interaction can be achieved by judicious ligand design. We believe that cuprophilic interaction plays a pivotal role to usher novel PL properties of such compounds. So
55 far such compounds are rarely investigated and they indeed demand detailed experimental and theoretical investigations. Hence, a library of such compounds has to be furnished and studied thoroughly, which we are pursuing in our lab.
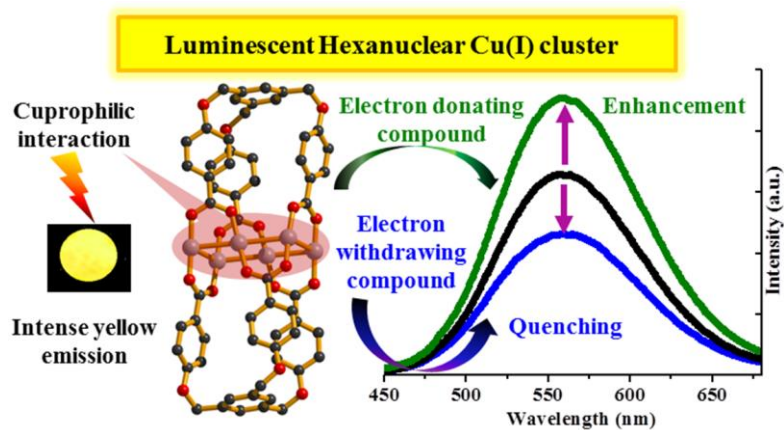
Notes and references

60 ^{a} *Molecular Materials Laboratory, Chemistry and Physics of Materials Unit, Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur, Bangalore – 560 064, India; E-mail: tmaji@jncasr.ac.in*
^{b} *Theoretical Science Unit, Jawaharlal Nehru Centre for Advanced Scientific research, , Jakkur, Bangalore – 560 064, India.*

1 D. Fiedler, R. G. Bergman and K. N. Raymond, *Angew. Chem., Int. Ed.*, 2004, **43**, 6748.
75 2 A. Mueller, S. K. Das, S. Talismanov, S. Roy, E. Beckmann, H. Boegge, M. Schmidtmann, A. Merca, A. Berkle, L. Allouche, Y. Zhou and L. Zhang, *Angew. Chem., Int. Ed.*, 2003, **42**, 5039.
3 M.-L. Lehaire, R. Scopelliti, H. Piotrowski and K. Severin, *Angew. Chem., Int. Ed.*, 2002, **41**, 1419.
80 4 S. Freye, R. Michel, D. Stalke, M. Pawliczek, H. Frauendorf and G.H. Clever, *J. Am. Chem. Soc.*, 2013, **135**, 8476.
5 (*a*) E. Cariati, X. Bu and P. C. Ford, *Chem. Mater.*, 2000, **12**, 3385; (*b*) T. Wen, D.-Xi. Zhang, J. Liu, R. Lin and J. Zhang, *Chem. Commun.*, 2013, **49**, 5660; (c) L. Bergmann, J. Friedrichs, M. Mydlak, T.
85 Baumann, M. Nieger and S.Bräse, *Chem. Commun.*, 2013, **49**, 6501; (*d*) Q. Zhang, Q. Zhou, Y. Cheng, L. Wang, D. Ma, X. Jing, F. Wang, *Adv. Mater*, 2004, **16**, 432; (*e*) E. A. Lewis and W.B. Tolman, *Chem. Rev.*, 2004, **104**, 1047; (*f*) C.W. Rogers and M. O. wolf, *Coord. Chem. Rev.* 2002, **233-234**, 341.
90 6 W. Klaui, B. Lenders, B. Hessner and K. Evertz, *Organometallics* 1988, **7**, 1357.
7 (*a*) V. W.-W. Yam, C. H. Lam, W. K. M. Fung and K. K. Cheung, *Inorg. Chem.*, 2001, **40**, 3435; (*b*) V. W.-W. Yam, C. H. Lam, Cheung and K. K. Cheung, *Chem. Commun.*, 2001, 545.
95 8 E. Cariati, D. Roberto, R. Ugo, P. C. Ford, S. Galli and A. Sironi, *Inorg. Chem.* 2005, **44**, 4077.
9 (*a*) Y. Sevryugina and M. A. Petrukhina, *Eur. J. Inorg. Chem.* 2008, 219; (*b*) Y. Sevryugina, A. Yu. Rogachev and M. A. Petrukhina, *Inorg. Chem.* 2007, **46**, 7870; (*c*) S. Mohapatra and T. K. Maji,
100 *Dalton Trans.*, 2010, **39**, 3412; (*d*) S. Mohapatra, H. Sato, R. Matsuda, S. Kitagawa and T. K. Maji, *CrystEngComm.*, 2012, **14**, 4153; (*e*) T.K. Maji, D. Ghoshal, E. Zangrando, J. Ribas and N.R. Chaudhuri, *CrystEngComm.*, 2004, **6**, 623.
10 (*a*) W.-F. Fu, X. Gan, C.-M. Che, Q.-Y. Cao, Z.-Y. Zhou and N. N.-Y.
105 Zhu, *Chem. Eur. J.* 2004, **10**, 2228; (*b*) S. Tashiro, J. Tanihira, M. Yamada and M. Shionoya, *Sensors*, 2013, **13**, 5671; (*c*) D. Braga, L. Maini, P. P. Mazzeo and B. Ventura, *Chem. Eur. J.* 2010, **16**, 1553.
11 (*a*) A. Rose, Z. Zhu, C. F. Madigan, T. M. Swager and V. Bulovic, *Nature* 2005, **434**, 876; (*b*) B. Gole, A. K. Bar and P. S. Mukherjee,
110 *Chem. Commun.* 2011, **47**, 12137.
12 (*a*) Y. Sevryugina, A. Y. Rogachev and M. A. Petrukhina, *Inorg. Chem.*, 2007, **46**, 7870; (*b*) Y. Sevryugina, O. Hietsoi and M. A. Petrukhina, *Chem Comm.*, 2007, 3853.
13 S. Perruchas, C. Tard, X. F. Le Goff, A. Fargues, A. Garcia, S. Kahlal,
115 J.-Y.Saillard, T. Gacoin, and J.-P. Boilot, *Inorg. Chem.*, 2011, **50**, 10682.
14 (*a*) S. J. Toal, J. C. Sanchez, R. E. Dugan and W. C. Trogler, *J. Forensic Sci.*, 2007, **52**, 79; (*b*) S. J. Toal and W. C. Trogler, *J. Mater. Chem.*, 2006, **16**, 2871.
120 15 S. Pramanik, C. Zheng, X. Zhang, T. J. Emge and J. Li, *J. Am. Chem. Soc.*, 2011, **133**, 4153.

125

RSC Advances Accepted Manuscript

5

Table of Content

10

15