NJC

PAPER

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Cite this: DOI: 10.1039/c8nj00505b

Substituent regulated photoluminescent thermochromism in a rare type of octahedral Cu₄I₄ clusters[†]

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A series of Cu₄I₄ clusters (**1**–**5**) supported by two pyrazolate-type zwitterionic ligands *N*-methyl-[4-(5-R-pyrazolyl)]pyridinium (**1**: R = *tert*-butyl; **2**: R = trifluoromethyl; **3**, **4**, **5**: R = phenyl) have been prepared and fully characterized. These compounds all exhibit a distorted "octahedral" geometry and their luminescence behavior is quite distinct from those of previously reported tetranuclear copper halide clusters. The crystalline powders of all five clusters only show a single broad low-energy (LE) emission band from 300 to 80 K. Cluster **1** shows temperature-independent orange phosphorescence despite a slight blue-shift of the low-energy flank upon cooling. Intriguingly, for clusters **2–5**, a hypsochromic phenomenon is clearly observed by decreasing the temperature. Using DFT/TDDFT calculations, we find that the nature of the electronic transitions responsible for the LE emission is dominated by the steric demand and/or electronic characteristics of the substituents on the pyrazolyl moiety. Specially, contribution of cuprophilic interactions in the lowest triplet excited states is ruled out by the rigid ligands. The single LE emission of **1** and **2** is attributed to pure ³ILCT and ³(M + X)LCT transition with different proportions.

Received 29th January 2018, Accepted 19th March 2018

DOI: 10.1039/c8nj00505b

rsc.li/njc

1. Introduction

Multinuclear copper(1) halide clusters possessing diverse structural and rich photophysical properties^{1–5} have been of great interest for decades due to their wide range of potential applications, including stimuli-responsive luminescent materials,^{6–14} whitelight emitters,¹⁵ and organic light-emitting diodes (OLEDS).^{16–20} In particular, tetranuclear Cu₄X₄L_n (X = Cl, Br, and I) clusters have been extensively investigated because of their original luminescence behavior. The Cu₄X₄ cores often adopt cubane, octahedral, or stair-step structures with four copper atoms forming a Cu₄ tetrahedron, a square plane, or a zigzag chain, respectively (Fig. 1a). The cubane-like clusters are the most widely studied structural motifs, which are well-known for their thermochromic luminescence properties.^{6–9,21,22} They usually display two distinct emission bands from two different triplet

Guangdong 515063, China. E-mail: xchuang@stu.edu.cn; Fax: (+86)-0754-82902767 † Electronic supplementary information (ESI) available: The X-ray crystallographic file (CIF), tabulated structural parameters, supplemental theoretical and experimental spectra, and other characterization data are provided. CCDC 1525210–1525215 and 1525981–1525983. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c8nj00505b



Fig. 1 Illustrations of (a) structural motifs of the Cu_4X_4 cores (redrawn from the structural data, Cu, yellow; X, purple), (b) bidentate ligands used in the "octahedral" clusters, (c) the zwitterionic ligands used in this work, (d) the chemical structure of one of the title compound.

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excited states with relative intensities that vary sharply with temperature. The low-energy band (around 550–600 nm) originating from triplet cluster-centered (³CC) charge transfer transitions dominates at room temperature (RT), in which the wavelength is closely related to cuprophilic interactions, the shorter the Cu–Cu distances, the longer is the wavelength. While at low temperatures, the high-energy band (around 400–450 nm) originating from halide-to-ligand charge transfer excited states (³XLCT) (sometimes mixed with metal-to-ligand charge transfer, ³MLCT) becomes more prominent. Distinct from the cubane-type copper halide clusters, the stair-step clusters exhibit phosphorescence only from the ³XLCT/³MLCT excited states due to very weak cuprophilic interactions.^{8,23}

Octahedral $Cu_4X_4L_2$ motifs are less-studied compared to cubane analogues presumably due to the difficulty in synthesis.^{24–40} According to the theoretical calculations by Thompson *et al.* the bare octahedral Cu_4I_4 cores are energetically unfavorable relative to the cubane Cu_4 array.²⁹ In the limited reports of octahedral $Cu_4X_4L_2$ compounds, two copper atoms are bridged by phosphine-based bidentate ligands bearing small bite angles, such as P^N donors (I–IV), P^P ligands (V–VIII), and P^C carbene IX (Fig. 1b). Among these reports, the synthesis and structural characterization are the majority and only scarce photophysical studies are available.^{25–31}

On the basis of these studies on octahedral Cu₄X₄L₂ complexes, the rigidity and steric demands of the ligands play a significant role on the optical properties of the clusters. In the example with ligand I, Thompson and co-workers synthesized a series of octahedral copper iodide complexes formulated as Cu₄I₄PR₂, which exhibit dual temperature-dependent ³XLCT and ³CC emission similar to copper cubanes when the ligand contains phenyl, cyclohexyl, or ethyl groups. However, the bulky tert-butyl or iso-propyl substituent on ligand I imparts the clusters with only one high energy band from the ³XLCT excited states. The authors reasoned that the structural relaxation of the ³CC excited state is limited by the bulky ligands, impeding the development of the LE emission band.²⁹ With the more rigid ligand II in which the CH₂ spacer linking the organophosphine moiety and the pyridine ring is missing compared to ligand I, Catalano and co-workers have also prepared several octahedral $Cu_4X_4L_2$ (X = Cl or Br) clusters showing only one single temperature-independent LE emission band at around 520 nm assigned to (M + X)LCT. Despite the appreciable cuprophilic interactions in these complexes, such an optical phenomenon is in stark contrast to copper cubanes or other octahedral Cu₄I₄L₂ clusters, however, resembling the stair-step copper halide clusters.²⁸ Employing ligand III (R = H or CH_3) which introduces a phospholane unit to replace the PPh2 moiety in ligand II, Musina obtained two octahedral Cu₄I₄L₂ compounds with photophysical properties in analogy with the cubane structures through both experimental and theoretical methods.²⁶ From these studies, the emissions observed seem to have different origins defined by the ligands. Therefore, the influence of the properties of the ligands, such as rigidity, steric hindrance and electronic characteristics, on the luminescence behavior of the octahedral Cu₄I₄L₂ clusters has yet not been addressed.

To better comprehend the optical properties of the octahedral copper halide clusters and explore the impact of the ligands on the origin of the electronic transitions, we have both experimentally and theoretically investigated several copper iodide clusters bearing pyrazolate-type zwitterionic ligands. Pyrazolate ligands have been widely investigated in cyclic trinuclear copper(1) complexes.⁴¹⁻⁴⁵ Pyridinium derivatives are strongly electron deficient and have been reported to exhibit thermochromic phenomena in the solid state upon hydration and dehydration.⁴⁶ The combination of pyrazole and pyridinium with different substituents on the pyrazolyl moiety gives rise to three proligands with iodide as the counterion (HL₁·I, HL₂·I, and HL₃·I), which convert into neutral but chargeseparated zwitterionic ligands after losing a molecule of HI (Fig. 1c). The chemical structure of one of the title compound is presented in Fig. 1d. These ligands without the bridging atoms between the two N-donors are expected to be more rigid than previously reported phosphine-based chelating ligands and possess a charged organic surface which is likely to exhibit intriguing luminescence properties. tert-Butyl, trifluoromethyl, and phenyl are expected to finely tune and modulate the emission properties of the clusters.

Herein, we report the synthesis, structural characterization, photophysical properties, and theoretical study of five octahedral copper iodide clusters $[Cu_4I_4(L_1)_2] \cdot CH_3CN(1), [Cu_4I_4(L_2)_2]$ (2), $[Cu_4I_4(L_3)_2] \cdot CH_3 CN$ (3), $[Cu_4I_4(L_3)_2]$ (4), and $[Cu_4I_4(L_3)_2] \cdot CH_3 CN$ 2C13H10O (5, C13H10O denotes benzophenone). Thermochromic behavior was observed for these clusters in the solid state in which the LE emission bands are blue-shifted upon lowering the temperature. This unique hypsochromic phenomenon differs from previous reports on traditional cubane-type clusters and other octahedral analogues. To rationalize these interesting optical properties in the solid state, the nature of the excited state involved in the absorption and emission spectra for clusters 1-4 has been investigated using density functional theory (DFT) and time dependent DFT (TDDFT) calculations. There is no convincing evidence which shows that these clusters maintain integrity in solution. Therefore, the photophysical properties in acetonitrile solution of clusters 1-4 were not investigated in detail.

2. Results and discussion

2.1 Synthesis and structural characterization of the clusters

The pyrazolate-type zwitterionic ligands were synthesized by a Claisen condensation reaction giving rise to diketones, followed by treatment with hydrazine hydrate and iodomethane (Scheme S1, ESI[†]). The IR and ¹H NMR spectra of the three ligands are shown in Fig. S1–S4 (ESI[†]). Clusters 1–3 and 5 were synthesized by slowly vaporizing the solutions while complex 4 was prepared by solvothermal reactions. The five clusters are merely moderately soluble in acetonitrile. All of these compounds were characterized by elemental analyses, IR (Fig. S1, ESI[†]), ¹H NMR (Fig. S5–S9, ESI[†]), ESI-MS (Fig. S10–S17, ESI[†]) spectroscopies and PXRD analysis (Fig. S18, ESI[†]). More details

about the synthesis and characterization are found in the ESI.† In PXRD analysis, the peaks of the powdered sample correspond to those calculated from the data of the single crystal diffraction measurements, which confirms its purity.

These five copper iodide clusters are also characterized by single crystal X-ray analysis at RT. For compounds 2-5, the data were also collected at 100 K. The X-ray crystallographic data of the clusters are provided in Table S1 (ESI[†]). As shown in Fig. 2, these clusters possess a rare "octahedral" geometry that differs significantly from the cubane or the stair-step configurations. Except for cluster 3, the four copper atoms are arranged in a parallelogram with obtuse angles ranging from 93.14° to 110.80°. In particular, the Cu_4 array forms a trapezoid with an obtuse angle of 91.72° for cluster 3. The planar Cu₄ array is axially capped by two μ_3 -iodides forming a distorted octahedron and two additional μ_2 -iodides bound on the each short side of the Cu₄ array. There is a long nonbonding interaction between the iodide ions and the copper atoms. The zwitterionic ligands are coordinated to the copper atoms on the opposing long sides of the Cu₄ array in a "head-to-tail" arrangement for 1, 2, 4 and 5, while in a "head-to-head" manner for 3. For the first time, to our knowledge, two dissymmetric chelating ligands are arranged in a "head-to-head" manner in octahedral clusters. Complex 1 contains two independent clusters in the asymmetric unit (1a and 1b). The tetranuclear copper core adopts a more skewed parallelogram geometry in 1a than in 1b with obtuse angles of 110.80° and 100.81° , respectively. The three analogous complexes 3–5 are composed of the same Cu_4I_4 cores and ligands, showing significantly different emissions in the solid state (*vide infra*). Compounds 3 and 4 could be treated as *cis-trans* isomers, while compound 5 additionally contains cocrystallized benzophenone molecules compared to 4.

The Cu–N bond lengths of the five clusters fall between 1.896 and 2.028 Å (average = 1.967(8) Å) similar to the values of the reported octahedral clusters with P^N donors.²⁹ The average distance between Cu and μ_2 -bound iodide (2.568(1) Å) is greatly shorter than that between Cu and μ_3 -bridging iodide (2.936(2) Å). The Cu–Cu bond distances at the short sides of the Cu₄ array range from 2.466(4) to 2.637(5) Å (average = 2.547(5) Å) and vary from 2.834(4) to 2.918(9) Å (average = 2.882(9) Å) at the long sides of the array, which are comparable with those in previously reported octahedral clusters. The Cu–Cu distances for 2–5 between 293 K and 100 K are almost identical within the experimental error (Tables 1–5). This is in stark contrast to the cubane-like clusters in which the Cu–Cu distances always become shorter when lowing the temperature.²¹

2.2 Luminescence properties in the solid state

Clusters 1–5 are yellow or brown crystalline powers under ambient light. At RT, 2, 3 and 5 display a bright red emission, while 1 and 4 emit orange and yellow light, respectively. The thermochromic luminescence properties of the clusters are revealed by dipping the samples into liquid nitrogen. Under the same UV irradiation, all the five clusters exhibit intense



Fig. 2 Molecular structure of clusters 1–5 (H atoms are omitted for clarity. 1a and 1b are the two independent clusters in the asymmetric unit for 1).

Table 1 Selected bond distances (Å) and angles (deg) of 1 at 293 K

1a		1b	
Cu1-Cu2	2.834(4)	Cu3–Cu4a	2.891(4)
Cu1–Cu2a	2.549(4)	Cu3–Cu4	2.544(4)
Cu1–I1	2.696(4)	Cu3–I3	2.607(3)
Cu1–I2a	2.700(3)	Cu3–I4a	2.665(4)
Cu1–I1a	2.964(4)	Cu3–I4	2.993(4)
Cu2–I2	2.473(4)	Cu4–I3	2.499(3)
Cu2–I1a	2.684(4)	Cu4–I4	3.028(4)
Cu2–I1	3.739(4)	Cu4–I4a	3.107(4)
Cu1-N2	2.028(15)	Cu3-N5	1.974(15)
Cu2-N3	1.942(16)	Cu4–N6a	1.896(16)
Cu2a-Cu1-Cu2	110.80(14)	Cu4-Cu3-Cu4a	100.81(13)
Cu1a-Cu2-Cu1	69.20(14)	Cu3–Cu4–Cu3a	79.19(13)
Cu2a-Cu1-Cu2-Cu1a	0.0	Cu4a-Cu3-Cu4-Cu3a	0.0
N2-Cu1-Cu2-N3	-7.2(8)	N5-Cu3-Cu4-N6a	-30(3)

Table 2 Selected bond distances (Å) and angles (deg) of ${\bf 2}$ at 293 K and 100 K

2 (293 K)		2 (100 K)	
Cu1-Cu2	2.918(9)	Cu1-Cu2	2.920(15)
Cu1–Cu2a	2.520(8)	Cu1–Cu2a	2.515(13)
Cu1–I2	2.572(7)	Cu1–I2	2.589(11)
Cu1–I1a	2.782(8)	Cu1–I1a	2.765(11)
Cu1–I1	2.935(9)	Cu1-I1	2.854(13)
Cu2–I2a	2.514(7)	Cu2–I2a	2.506(11)
Cu2–I1	2.727(9)	Cu2-I1	2.679(13)
Cu2–I1a	3.262(9)	Cu2–I1a	3.331(13)
Cu1-N1	1.972(3)	Cu1-N1	1.980(6)
Cu2-N2	1.947(3)	Cu2-N2	1.951(6)
Cu2a-Cu1-Cu2	96.71(3)	Cu2a-Cu1-Cu2	99.74(4)
Cu1a-Cu2-Cu1	83.29(3)	Cu1a-Cu2-Cu1	80.26(4)
Cu2a-Cu1-Cu2-Cu1a	0.0	Cu2a-Cu1-Cu2-Cu1a	0.0
N1-Cu1-Cu2-N2	2.81(18)	N1-Cu1-Cu2-N2	3.0(3)

Table 3 Selected bond distances (Å) and angles (deg) of ${\bf 3}$ at 293 K and 100 K

3 (293 K)		3 (100 K)	
Cu1-Cu2	2.852(4)	Cu1-Cu2	2.841(14)
Cu1–Cu1a	2.637(5)	Cu1–Cu1a	2.651(19)
Cu2–Cu2a	2.466(4)	Cu2–Cu2a	2.474(17)
Cu1–I1	2.741(3)	Cu1–I1	2.725(11)
Cu1–I4	2.540(3)	Cu1–I4	2.547(11)
Cu1–I3	3.242(3)	Cu1–I3	3.210(11)
Cu2–I2	2.615(3)	Cu2–I2	2.618(10)
Cu2–I3	2.703(3)	Cu2–I3	2.706(10)
Cu2–I1	3.010(3)	Cu2–I1	2.958(10)
Cu1–N1	1.993(12)	Cu1-N1	1.981(5)
Cu2-N2	1.947(13)	Cu2-N2	1.972(5)
Cu1a-Cu1-Cu2	88.28(6)	Cu1a-Cu1-Cu2	88.22(2)
Cu2a-Cu2-Cu1	91.72(6)	Cu2a-Cu2-Cu1	91.78(2)
N1-Cu1-Cu2-N2	2.4(6)	N1-Cu1-Cu2-N2	1.9(2)
Cu1a-Cu1-Cu2-Cu2a	0.0	Cu1a-Cu1-Cu2-Cu2a	0.0

yellow emission (Fig. 3 inset). The original emission colors are recovered when the samples gradually warm up to RT again, indicating a reversible thermochromism for the clusters.

Solid-state emission spectra were recorded for clusters 1–5 from 300 to 80 K (Fig. 3 for normalized emission and excitation spectra of 1–5 and Fig. S19 (ESI[†]) for original emission spectra

 Table 4
 Selected bond distances (Å) and angles (deg) of 4 at 293 K and

4 (293 K)		4 (100 K)	
Cu1-Cu2a	2.906(11)	Cu1–Cu2a	2.915(11)
Cu1-Cu2	2.572(9)	Cu1-Cu2	2.575(9)
Cu1-I2	2.597(8)	Cu1-I2	2.612(8)
Cu1–I1a	2.795(8)	Cu1–I1a	2.747(8)
Cu1-I1	2.907(9)	Cu1-I1	2.885(9)
Cu2-I2	2.528(8)	Cu2-I2	2.527(8)
Cu2-I1	2.732(9)	Cu2-I1	2.696(8)
Cu2–I1a	3.207(9)	Cu2-I1a	3.288(8)
Cu1-N1	1.978(4)	Cu1-N1	1.994(4)
Cu2-N2a	1.949(3)	Cu2-N2a	1.952(4)
Cu2-Cu1-Cu2a	95.70(3)	Cu2-Cu1-Cu2a	98.49(3)
Cu1-Cu2-Cu1a	84.30(3)	Cu1-Cu2-Cu1a	81.51(3)
N1-Cu1-Cu2-N2a	-50.1(4)	N1-Cu1-Cu2-N2a	-61.6(4)
Cu2a-Cu1-Cu2-Cu1a	0.0	Cu2a-Cu1-Cu2-Cu1a	0.0

100 K

Table 5 Selected bond distances (Å) and angles (deg) of ${\bf 5}$ at 293 K and 100 K

5 (293 K)		5 (100 K)	
Cu1-Cu2a	2.895(16)	Cu1-Cu2a	2.892(10)
Cu1–Cu2	2.544(14)	Cu1–Cu2	2.545(10)
Cu1–I2	2.594(11)	Cu1–I2	2.591(8)
Cu1–I1	2.807(14)	Cu1–I1	2.791(8)
Cu1–I1a	3.036(14)	Cu1–I1a	2.997(8)
Cu2–I2	2.576(11)	Cu2–I2	2.575(7)
Cu2–I1	2.732(12)	Cu2–I1	2.707(7)
Cu2–I1a	2.971(13)	Cu2–I1a	2.947(7)
Cu1-N2	1.986(5)	Cu1-N2	1.979(4)
Cu2–N1a	1.993(5)	Cu2–N1a	1.990(4)
Cu2-Cu1-Cu2a	86.86(5)	Cu2-Cu1-Cu2a	87.04(3)
Cu1-Cu2-Cu1a	93.14(5)	Cu1-Cu2-Cu1a	92.96(3)
N2-Cu1-Cu2-N1a	-6.1(7)	N2-Cu1-Cu2-N1a	-8.6(4)
Cu2a-Cu1-Cu2-Cu1a	0.0	Cu2a-Cu1-Cu2-Cu1a	0.0

of 1–5), and the corresponding photophysical data are provided in Table S2 (ESI[†]). At 300 K, the emission spectra all display a single featureless broad low-energy emission band centered at 640 nm for 1, at 650 nm for 2, at 655 nm for 3, at 615 nm for 4, and at 695 nm for 5 in agreement with the corresponding emission color observed at RT. The different excitation wavelengths have no influence on the emission maxima (see Fig. S20, ESI[†]). The broad excitation and emission spectra indicate the charge transfer (CT) nature of the involved excited states.⁴⁷

By lowering the temperature down to 80 K, a significant blue-shift of the emission from 650 to 597 nm (\approx 1366 cm⁻¹) for 2, from 655 to 607 nm (\approx 1207 cm⁻¹) for 3, from 615 to 577 nm (\approx 1071 cm⁻¹) for 4, and from 695 to 644 nm (\approx 1139 cm⁻¹) for 5 were observed with a concomitant increase of the intensity. The luminescent behavior of 1 is very different from those of 2–5. Indeed, despite a slight blue-shift of the low energy flank observed on cooling, the emission position is almost unchanged with maxima at 640 nm at 300 K and 633 nm at 80 K. In addition, the emission lifetimes of the five clusters are around 5 µs at 300 K and become slightly longer at 80 K, suggesting that they are all phosphorescence stemming from triplet states. A striking feature is that the three analogues 3–5 exhibit distinct luminescence, in particular, the *cis-trans*

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Fig. 3 Normalized temperature dependence of solid-state luminescence spectra of cluster **1–5** from 300 to 80 K (λ_{ex} = 330 nm for **1** and λ_{ex} = 340 nm for **2–5**) and corresponding excitation spectra (yellow lines), corresponding λ_{em} 640 nm for **1**, 650 nm for **2**, 640 nm for **3**, 600 nm for **4**, 685 nm for **5**. The photos of **1–5** under UV irradiation at 365 nm (UV lamp) at RT and in the liquid nitrogen (77 K) are presented in the inset.

isomers 3 and 4 display red and yellow emission at RT, respectively.

2.3 Investigation of the luminescence properties in solution

Because the octahedral clusters $Cu_4X_4(PPh_2py)_2$ (X = Br, Cl, PPh₂py = 2-(diphenylphosphino)pyridine) were reported to be dynamic in solution,²⁸ the stability of clusters **1–4** in acetonitrile solution was investigated. Fig. S21 (ESI[†]) shows the concentration dependence of the UV-vis absorption spectra of clusters **1–4** in CH₃CN at RT. As exemplified in the inset of Fig. S21 (ESI[†]), a linear Beer's law plot of concentration-dependent absorbance for **1** and **2** was observed, suggesting a single species or a collection of species of identical composition existing in CH₃CN solution. However, only fragments of the parent clusters like [Cu₃I₂(L₁)₂]⁺ or [Cu₃I₂(L₂)₂]⁺ were found in the MALDI-TOF-MS spectra (Fig. S22, ESI[†]), which implies that **1** and **2** probably do not maintain integrity in acetonitrile and undergo fragmentation to species of lower nuclearities. The obvious non-linear relationships of **3** and **4** indicate that they dissociate in CH₃CN solution.

The emission spectra of the proligands in acetonitrile solution at RT are provided in Fig. S23 (ESI[†]). The luminescence spectra of clusters **1–4** in dry acetonitrile solution at RT and at 77 K are shown in Fig. S24 (ESI[†]). Distinct from the low energy (LE) phosphorescence in the solid state, these clusters display high energy (HE) emission in acetonitrile solution at RT. When the temperature is decreased to 77 K, an intense LE emission band is observed in the glassy CH₃CN matrix for all **1–4** from 655 to 670 nm which is in agreement with the red light observed.

2.4 Exploration of the photophysical properties for complexes 1–4 in the solid state

2.4.1 Computed bond distances. To gain insight into the photophysical properties, combined DFT and TDDFT calculations were performed for clusters **1–4** using coordinates obtained from the X-ray data. The results reported below merely concern optimized geometries of isolated clusters unless otherwise stated. The geometries of the singlet ground state (S_0) and of the lowest triplet state (T_1) under spin-unrestricted calculations (UDFT) were fully optimized for **1–4**. Geometry optimization of the T_1 with the TDDFT approach was only successful for **2** and **3**. We found that the PBE0 and M06-2X functional will severely underestimate the emission energy $T_1 \rightarrow S_0$ for **2**, thus the more suitable range-separated ω B97X-D functional was used throughout except the geometry optimization calculations (Table S3, ESI⁺).

Relevant computed bond distances for 1–4 (S_0 , T_1^{UDFT} , and T_1^{TDDFT}) are compared to the experimental metrical values (exp) in Table S4 (ESI†). The computed values for the ground state are in fair agreement with the X-ray experimental data, despite a small overestimation of the bond distances that can be probably traced back to the neglect of the solid-state packing effects. For 2–4, it is worth noting that the Cu–Cu separations from T_1 optimized geometries are longer and the Cu–I bond lengths become shorter than those at S_0 optimized structures, whereas it is reversed in 1.

2.4.2 Molecular orbitals. A schematic representation and isodensity surface plots of the frontier molecular orbitals



Fig. 4 Schematic representation and isosurface plots (isovalue 0.0005) of the frontier molecular orbitals for the singlet ground state calculated at the S₀ optimized geometries. The orbital compositions (in brackets), HOMO and LUMO energies (in green), and the HOMO–LUMO energy gaps (in red) are also listed.

calculated at the S_0 geometries for 1-4 are shown in Fig. 4. Isosurface plots of other selected molecular orbitals (HOMO-1/ HOMO-4, LUMO+1/LUMO+8) are shown in Fig. S25-S28 (ESI[†]). The four clusters have similar frontier orbitals. As shown in the figure, the highest occupied molecular orbitals (HOMOs) of these clusters are combinations of copper d and iodine p orbitals (>95%), while the unoccupied molecular orbitals (LUMOs) are mainly located on the pyrazolyl groups and N-methyl pyridinium moieties of the ligands (>97%). The LUMO+4 for 1-2 and LUMO+6 for 3-4 represent a combination of the copper and iodine s-p state, which have a bonding character among the Cu₄ array and the antibonding characteristic between all the Cu and I atoms. Such molecular orbital compositions are similar to a previous study for the cubanetype and other reported octahedral clusters.^{21,29} Although the compositions of the frontier orbitals are not impacted by the substituent groups, the energy levels of the orbitals and HOMO-LUMO energy gaps of these clusters are significantly affected by them. For instance, the electron-withdrawing CF₃ group in 2 will stabilize the frontier orbitals relative to the bulky butyl group in 1 or the π -conjugated phenyl group in 3 and 4. Notably, the symmetry of the molecules has a significant influence on the HOMO-LUMO gaps. As described in Fig. 6,

the energy gaps of **3** bearing two "head-to-head" ligands and of **4** possessing two "head-to-tail" ligands are 5.28 eV and 5.72 eV, respectively.

2.4.3 Optical absorption spectra. The solid-state absorption spectra of clusters **1–4** are shown in Fig. 5. The computed data *in vacuo* are also shown in Fig. 5, their height being proportional to their oscillator strength (f). The calculated TDDFT singlet-singlet of the first 10 and most intense (f > 0.03) transitions and of the 10 lowest singlet-triplet transitions with transition assignments in terms of electron density difference (EDD) maps at the S₀ optimized geometry in the gas state for all **1–4** are listed in Tables S5–S12 (ESI[†]).

As depicted in Fig. 5, the solid-state absorption spectra contain three absorption regions: (1) the first region, a high energy band originating from 200–260 nm for all 1-4; (2) the second region, a broad absorption band from 260–325 nm centered at 280 nm for 1, 3, 4 and from 250–300 centered at 270 nm for 2; (3) the third region, a low energy band from 325 nm tailing to 550 nm centered at 370 nm for 1, 3, 4, and from 300–550 centered at *ca.* 360 nm for 2. The calculated wavelength and oscillator strength nicely correlate with the presence of mainly three absorption regions in the experimental spectra. The intense transitions of sizable intensity



Fig. 5 Experimental solid-state absorption spectra of 1-4 (black lines) and calculated transitions *in vacuo* at the S₀ optimized geometries with bar heights proportional to the oscillator strengths (vertical red lines).

(f > 0.1) correspond well to the three absorption regions respectively (Table S13, ESI†). Generally, it is shown in vacuo that the low energy absorption (ca. > 370 nm) is dominated by pure ${}^{1}(X + M)LCT$ transitions with a low oscillator strength, the ¹ILCT (intraligand charge transfer) starts to manifest itself in the region of ca. 250-370 nm showing a high oscillator strength with the ${}^{1}(X + M)LCT$ character still being the majority, and the cluster-centered transition (1CC) is only observed at the high energy absorption zone (ca. <250 nm). Another interesting finding is that transitions with a high oscillator strength bearing the prominent ILCT character are not found in the spin-allowed singlet-singlet transitions, however, observed in the first two lowest spin-restricted singlet-triplet transitions at ca. 525 nm for 1, at 470 nm for 2, at 566 nm for 3, and at 520 nm for 4. These spin-restricted transitions may be the origin of the very weak tails displayed in the solid-state absorption spectra.

2.4.4 Investigation into the emission properties in the solid state. As far as the luminescence behavior of the title

compound is in the solid state, it seems that the characteristics of the ligands, such as rigidity, steric demands, and electronic properties, are operative in modifying the photophysical character of the octahedral copper iodide clusters. On one hand, only a single emission band is observed upon cooling in all five compounds similar to the octahedral clusters with rigid ligand II in ref. 28. On the other hand, the evident blueshift of the LE phosphorescence in clusters 2-5 by lowering the temperature had not been observed in copper cubanes or other octahedral Cu₄X₄L₂ clusters in which the LE emission band is apt to show the bathochromic shift due to the shortening of Cu-Cu distances upon cooling. Notably, the blue-shift behavior of the luminescence stemming from the ³XLCT excited state of tetranuclear clusters [Cu₄I₄(PPh₃)₄] with a stair-step configuration or a simple dimeric compound [Cu₂I₂(PPh₃)₃] has been reported.^{12,23} These observations indicate that the emission properties of these clusters are not controlled by the Cu-Cu interactions in spite of the short Cu-Cu distances falling within the range found for ³CC transitions.

The electron density difference maps presented in Fig. 6 provide insights into the origin of the excited states responsible for LE phosphorescence. Intriguingly, the emission of complex **1** is dominated by pure ³ILCT (intraligand charge transfer) transitions while the emission of complex 2 is dominated by ${}^{3}(X + M)LCT$ transitions. The luminescence of complexes 3 and 4 is assigned to the emission from the mixed ${}^{3}(X + M)LCT/{}^{3}ILCT$ excited states with different proportions. In complex 3, the ³ILCT transitions are the major contribution while in complex 4 the ${}^{3}(X + M)LCT$ transitions are the major contribution. The considerable influence of the substituents on the origin of the electronic transitions involved in the LE emission arise from the zwitterionic character of the ligands. The pyridinium part of the ligand is highly electron-deficient, which could be affected by the characteristics of the substituent on the pyrazolyl moiety. For instance, the electron-withdrawing CF₃ group in 2 presumably inhibits the charge transfer from the pyrazolyl part to the pyridinium part, resulting in the absence of ³ILCT in 2 which is observed for 1 and 3-4 in the lowest triplet excited states. No ³CC transition in the lowest triplet excited state which is



Fig. 6 The density difference plots (isovalue 0.0005) for the lowest triplet excitation of complex **1–4** *in vacuo*, calculated at the UDFT optimized T_1 geometry. Blue and purple represent zones of depletion and augmentation of electron density in the T_1 excited state *versus* the S₀ ground state. The calculated $T_1 \rightarrow S_0$ emission wavelengths together with the experimental ones at 300 K are also listed for the sake of comparison.

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typical for the classic cubane-like copper clusters and some previously reported octahedral clusters is found in our calculations. The assignments of the emission for 2 and 3 calculated at the UDFT optimized T₁ geometry are consistent with those calculated at the TDDFT optimized T₁ geometry (see Fig. S29, ESI†). The calculated emission energies at the UDFT optimized T₁ geometry are overestimated relative to the experimental values at 300 K; however, at the TDDFT optimized T₁ geometry the energy is underestimated for 2 and is in fair agreement with the experimental one for 3. Generally, the calculated T₁ \rightarrow S₀ emission wavelengths are in rather good agreement with the corresponding experimental ones, especially the trend observed in the emission energies of 2–4 follows the experimental trend (4 > 2 > 3).

From these theoretical results, the emission origin of copper iodide clusters is closely related to the properties of the ligands as we supposed. Both experimental and theoretical studies of the cubane or some octahedral clusters reveal that structural relaxation is required to shorten the Cu-Cu distances to produce the LE emission from the ³CC excited state.^{21,29} For cubane clusters, concerns about how the rigidity/steric demands of the ligands would influence the contraction of the Cu-Cu separations in the excited state can almost be neglected because monodentate ligands, such as the pyridine-derivatives and phosphine-based molecules, are employed which show less influence on the LE emission band. However, when it comes to octahedral clusters, the rigidity/steric hindrance of the ligands must be considered since bidentate ligands are generally required to obtain the planar Cu4 arrangement. If the bidentate ligands are too rigid or bulky, the contraction of the Cu-Cu distances in the excited state may be severely restricted. Such an assumption is consistent with the reported studies on the octahedral clusters in which emission from the ³CC excited state will be blocked by very rigid bidentate ligands or ligands with very bulky substituents in spite of the short Cu-Cu bond lengths.²⁹ The crystallographic data that the Cu-Cu distances of 2-5 at 293 K and 100 K are basically the same supported that the rigid pyrazolate-type ligand employed in this work hinders the shortening of Cu-Cu separations upon cooling. Therefore, the studies described here confirm that the emission from the ³CC excited state in octahedral copper iodide clusters will be blocked by the rigid bidentate pyrazolate-type though strong cuprophilic interactions existed.

It is commonly known that the energy of emission controlled by ³ILCT transitions is not liable to be affected by varying the temperature. Therefore, the slight blue-shift of the low-energy flank observed upon cooling for cluster **1** may be explained by freezing energetically higher lying emissions from an inhomogeneously broadened distribution in the powder sample.⁵ On the basis of the current experimental results or computational data, we cannot elucidate the molecular details of the hypsochromic shift for **2–5**. Considering the great difference of the emission energies of the two pseudopolymorphs **4** and **5**, one possible explanation is that the slight distortion of the structures upon cooling results in such a considerable blue shift.

3. Conclusions

A rare family of tetranuclear copper(1) iodide clusters with a rare octahedral configuration supported by charge-separated zwitterionic ligands have been synthesized and fully characterized. The photophysical properties of these complexes in the solid state at varying temperatures have been systematically investigated. The results of the DFT/TDDFT calculations have provided a fundamental understanding and deep insights into the nature and origin of the excited states involved in the absorption spectra and those responsible for the single LE emission bands for the clusters described here.

Upon cooling in the solid state, the position of the single LE emission band is considerably blue-shifted for clusters 2-5 in contrast to that of cubane or other octahedral clusters. However, for complex 1 with bulky tert-butyl groups, the single LE emission band hardly moves when lowering the temperature. According to TDDFT calculations, the emission of complex 1 originates from ³ILCT and complex 2 is dominated by pure ${}^{3}(X + M)LCT$ transitions. The luminescence of complexes 3 and 4 arises from the mixed ${}^{3}(X + M)LCT/{}^{3}ILCT$ excited states. ${}^{3}CC$ states are not involved in the luminescence. Although these complexes contain short Cu-Cu contacts less than or close to 2.8 Å (the van der Waals radius of Cu is 1.4 Å), our results suggest that the rigid pyrazolate-type ligands will block the ³CC emission probably by restricting the structural relaxation in the excited state. Furthermore, via modifying the characteristic of the substituents, the origin of the electronic transitions involved in the emission can be tuned. In addition, a pair of cis-trans isomers (3 and 4) displaying distinct luminescence behavior have been reported for the first time in the family of octahedral copper halide clusters.

To conclude, the unique photophysical properties of this class of clusters lead to the development of new luminophores. The detailed DFT and TDDFT calculations reported here provide a significantly enhanced understanding of the role of ligands in the luminescence of the copper cluster family.

4. Experimental

4.1 Materials

Reagents and solvents employed were commercially available and used as received. Spectroscopically pure solvents for photophysical measurements were additionally dried over molecular sieves or sodium.

4.2 Synthesis of the ligands

4-(5-(tert-Butyl)-1H-pyrazol-3-yl)-1-methylpyridin-1-ium iodide (**HL**₁-**I**). **HL**₁-I was prepared using a literature method with a slight modification.⁴⁸ Firstly, 3,3-dimethyl-2-butanone (11.2 mL, 90 mmol) was added to a suspension of potassium *tert*-butoxide (11.2 g, 100 mmol) in dry THF (100 mL). The mixture was stirred at RT for about 30 min. Methyl isonicotinate (10 mL, 85 mmol) was slowly added to the mixture. After stirring for 12 h, dilute acetic acid (10 mL acetic acid in 30 mL H₂O) was added to the solution and further stirred for 10 min. The aqueous solution was extracted with diethyl ether (3 \times 20 mL). The combined organic phase was washed with brine, and then the diethyl ether solvent was removed under vacuum to yield the crude 1,3-dione. Secondly, this 1,3-dione was dissolved in ethanol (200 mL) and the resulting ethanol solution was treated with an excess of hydrazine (80%, 15 mL) and then refluxed for 12 h. The ethanol solvent was removed under reduced pressure and the crude product was recrystallized from methanol and H₂O (v/v 1:1). A white solid was obtained (8.04 g, yield: 44%). Thirdly, the product (2.01 g, 10 mmol) from the last step was dissolved in acetonitrile (200 mL) and treated with excess iodomethane (15 mL). The mixture was stirred for 24 hours at RT. Then the solvent was removed under reduced pressure and the crude product was recrystallized from ethanol and H₂O (v/v 1:1). A pale yellow solid was obtained (3.0 g, yield: 90%). IR (KBr pellet, cm⁻¹): 3480 (b), 3184 (s), 3184 (s), 3134 (m), 3101 (m), 3033 (w), 2964 (s), 2867 (w), 1643 (vs), 1579 (w), 1538 (s), 1479 (m), 1401 (m), 1364 (w), 1332 (w), 1285 (w), 1249 (w), 1209 (s), 1137 (m), 1174 (w), 1000 (m), 963 (m), 853 (s), 811 (m), 710 (w), 684 (w), 647 (w), 525 (w), 511 (w), 442 (m). ¹H NMR (400 MHz, CD_3CN δ 11.70 (s, 1H), 8.51 (d, I = 6.7 Hz, 2H), 8.26 (d, I = 6.7 Hz, 2H), 6.85 (s, 1H), 4.22 (s, 3H), 1.37 (s, 9H).

1-Methyl-4-(5-(trifluoromethyl)-1H-pyrazol-3-yl) pyridin-1-ium iodide (HL_2 ·I). The synthesis procedure of HL_2 ·I is similar to that of HL1-I. Firstly, 4-acetylpyridine (5.6 mL, 50 mmol) was added to a suspension of potassium tert-butoxide (6.72 g, 60 mmol) in dry THF (100 mL). The mixture was stirred at RT for about 30 min. Ethyl trifluoroacetate (6.5 mL, 55 mmol) was slowly added to the mixture. After stirring for 24 h, dilute acetic acid (10 mL acetic acid in 30 mL H₂O) was added to the solution and further stirred for 10 min. The aqueous solution was extracted with diethyl ether (3 \times 20 mL). The combined organic phase was washed with brine; the diethyl ether solvent was removed under vacuum to yield the crude 1,3-dione. Secondly, this 1,3-dione was dissolved in ethanol (60 mL) and the resulting ethanol solution was treated with an excess of hydrazine (80%, 15 mL) and then refluxed for 12 h. After then, the ethanol solvent was removed in a vacuum and the residue was re-dissolved in 50 mL of ethanol along with 1 mL of conc. HCl. The solution was refluxed for an additional 5 h. The ethanol was evaporated again under vacuum and the resulting solid was recrystallized from CH₂Cl₂ and n-hexane (v/v 1:1). A white solid was obtained (4.26 g, yield: 40%). The next step is similar to that of HL₁·I, and a brown solid was obtained (3.2 g, yield: 90%). IR (KBr pellet, cm^{-1}): 3440 (b), 3105 (m), 3052 (m), 2824 (b), 1639 (s), 1615 (s), 1587 (w), 1575 (w), 1522 (m), 1490 (m), 1452 (w), 1417 (s), 1341 (w), 1284 (s), 1260 (vs), 1222 (s), 1159 (vs), 1126 (vs), 1063 (w), 1005 (m), 973 (vs), 897 (w), 820 (s), 746 (s), 717 (w), 694 (m), 667 (w), 618 (w), 560 (w), 517 (w), 431 (w). ¹H NMR (400 MHz, CD₃CN) δ 8.65 (d, J = 6.8 Hz, 2H), 8.32 (d, J = 6.7 Hz, 2H), 7.48 (s, 1H), 4.24 (s, 3H).

1-Methyl-4-(3-phenyl-1H-pyrazol-5-yl)pyridin-1-ium iodide (HL₃·I). The synthesis process of HL₃·I is almost the same as that of HL₁·I except that 3,3-dimethyl-2-butanone is replaced by acetophenone in the first step. Finally, a white solid was obtained (3.26 g, yield: 90%). IR (KBr pellet, cm⁻¹): 3456 (b), 3127 (b), 3041 (w), 1639 (vs), 1571 (w), 1539 (s), 1480 (s), 1395 (m),

1332 (w), 1265 (w), 1217 (m), 1186 (s), 1056 (w), 964 (s), 859 (w), 841 (w), 807 (m), 771 (vs), 724 (w), 691 (m), 663 (w), 527 (w), 507 (w), 490 (w), 438 (w). ¹H NMR (400 MHz, CD₃CN) δ 12.20 (s, 1H), 8.56 (d, *J* = 6.7 Hz, 2H), 8.35 (d, *J* = 6.4 Hz, 2H), 7.77 (d, *J* = 7.6 Hz, 2H), 7.54 (t, *J* = 7.5 Hz, 2H), 7.47 (t, *J* = 7.3 Hz, 1H), 7.39 (s, 1H), 4.24 (s, 3H).

4.3 Synthesis of the complexes

Synthesis of [Cu₄I₄(L₁)₂]·CH₃CN (1). First, HL₁·I (17.15 mg, 0.05 mmol) in 1 mL CH₃CN and CuI (28.5 mg, 0.15 mmol) in 1 mL CH₃CN were mixed together. Then, 3 mL of benzene was added to the solution. The solution was allowed to stand at RT for about a week to afford yellow crystals. Yield: 60% (based on CuI). IR (KBr pellet, cm⁻¹): 3457 (b), 3046 (w), 2955 (m), 1637 (vs), 1560 (w), 1540 (s), 1499 (w), 1476 (w), 1381 (w), 1333 (w), 1280 (w), 1249 (w), 1199 (m), 1181 (m), 1032 (w), 980 (w), 848 (w), 831 (w), 789 (m), 524 (w), 410 (w). ¹H NMR (400 MHz, CD_3CN) δ 8.47 (d, J = 6.2 Hz, 8H), 8.29 (d, J = 3.9 Hz, 8H), 6.83 (s, 2H), 4.17 (s, 6H), 1.38 (s, 18H). Anal. calcd for C₂₆H₃₄Cu₄I₄N₆: C, 26.19; H, 2.87; N, 7.05 and for C₂₆H₃₄Cu₄I₄N₆ + 1 (CH₃CN): C, 27.27; H, 3.02; N, 7.95. Found: C, 26.57; H, 2.71; N, 7.31. ESI-MS: the parent ion was not observed in either positive or negative ion mode. In the positive mode, the fragment corresponding to the ligand was found: m/z 216.15 $(HL_1)^+$. In the negative mode, fragments corresponding to various inorganic anions were found: m/z 1269.91 (Cu₆I₇)⁻, m/z 1078.08 (Cu₅I₆)⁻, m/z 888.24 (Cu₄I₅)⁻, m/z 698.41 (Cu₃I₄)⁻, *m*/*z* 506.58 (Cu₂I₃)⁻, *m*/*z* 380.72 (I₃)⁻, *m*/*z* 316.74 (CuI₂)⁻. MALDI-TOF-MS (trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile as the matrix, positive mode): m/z +874.9 $\{ [Cu_4I_4(L_1)_2] - CuI_2 \}^+.$

Synthesis of $[Cu_4I_4(L_2)_2]$ (2). First, $HL_2 \cdot I$ (35.5 mg, 0.1 mmol) in 0.5 mL CH₃CN and CuI (28.5 mg, 0.15 mmol) in 1 mL CH₃CN were mixed together. Then, 3 mL of 1,3-dimethoxybenzene was added to the solution. The solution was allowed to stand at RT for about a week to afford brown crystals. Yield: 65% (based on CuI). IR (KBr pellet, cm⁻¹): 3441 (b), 3127 (w), 3051 (w), 1637 (vs), 1566 (w), 1542 (s), 1524 (m), 1477 (w), 1402 (w), 1349 (w), 1281 (s), 1255 (vs), 1220 (w), 1197 (s), 1152 (vs), 1125 (vs), 1008 (s), 976 (w), 840 (w), 829 (m), 808 (s), 744 (w), 512 (w), 517 (w), 440 (w). ¹H NMR (400 MHz, CD₃CN) δ 8.63 (d, J = 6.5 Hz, 4H), 8.24 (s, 7H), 7.48 (s, 2H), 4.25 (s, 3H). Anal. calcd for C₂₀H₁₆Cu₄I₄F₆N₆: C, 19.75; H, 1.33; N, 6.91. Found: C, 20.04; H, 1.36; N, 6.94. ESI-MS: the parent ion was not observed in either the positive or negative ion mode. In the positive mode, the fragment corresponding to the ligand was found: m/z228.08 $(HL_2)^+$. In the negative mode, fragments corresponding to various inorganic anions were found: m/z 1269.91 (Cu₆I₇)⁻, m/z 1078.08 (Cu₅I₆)⁻, m/z 888.25 (Cu₄I₅)⁻, m/z 698.41 (Cu₃I₄)⁻, m/z 506.58 (Cu₂I₃)⁻, m/z 380.72 (I₃)⁻, m/z 316.74 (CuI₂)⁻. MALDI-TOF-MS (trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene] malononitrile as the matrix, positive mode): m/z +898.7 $\{ [Cu_4I_4(L_2)_2] - CuI_2 \}^+, +706.9 \{ [Cu_4I_4(L_2)_2] - Cu_2I_3 \}^+.$

Synthesis of $[Cu_4I_4(L_3)_2]$ ·CH₃CN (3). The HL₃·I (18.1 mg, 0.05 mmol) in mixed DMF/EtOH (v/v = 1:1, 2 mL) and CuI (19.0 mg, 0.1 mmol) in 1 mL CH₃CN were mixed together. The solution was allowed to stand at RT for about a week to

afford brown crystals. Yield: 65% (based on CuI). IR (KBr pellet, cm⁻¹): 3441 (b), 3113 (w), 3054 (w), 1672 (s), 1637 (vs), 1560 (w), 1542 (s), 1521 (w), 1478 (m), 1431 (w), 1385 (m), 1215 (w), 1196 (m), 1152 (w), 1094 (m), 990 (m), 840 (m), 798 (w), 769 (m), 723 (w), 694 (w), 667 (w), 530 (w), 507 (w), 493 (w), 444 (w). ¹H NMR (400 MHz, CD₃CN) δ 8.54 (d, J = 5.3 Hz, 4H), 8.34 (d, J = 6.8 Hz, 4H), 7.92 (s, 1.5H), 7.77 (d, J = 7.6 Hz, 4H), 7.57-7.48 (m, 4.5H), 7.46 (d, J = 6.9 Hz, 3H), 7.37 (s, 2H), 4.19 (s, 3H). Anal. calcd for C₃₂H₂₉Cu₄I₄N₇: C, 30.18; H, 2.30; N, 7.70. Found: C, 30.53; H, 2.48; N, 7.35. ESI-MS: the parent ion was not observed in either the positive or negative ion mode. In the positive mode, the fragment corresponding to the ligand was found: m/z 236.12 $(HL_3)^+$. In the negative mode, fragments corresponding to various inorganic anions were found: m/z 1269.93 (Cu₆I₇)⁻, m/z 1078.09 $(Cu_5I_6)^-$, m/z 888.25 $(Cu_4I_5)^-$, m/z 698.42 $(Cu_3I_4)^-$, m/z506.58 $(Cu_2I_3)^-$, m/z 380.72 $(I_3)^-$, m/z 316.74 $(CuI_2)^-$.

Synthesis of $[Cu_4I_4(L_3)_2]$ (4). The HL₃·I (18.1 mg, 0.05 mmol) in mixed DMF/EtOH (v/v = 1:1, 2 mL) and CuI (19.0 mg, 0.1 mmol) in 1 mL CH₃CN were mixed together and loaded into a 15 mL Teflon-lined reactor, and then heated to 120 °C in a programmable oven for 72 h, followed by slow cooling (3 $^{\circ}C$ h⁻¹) to RT. Yellow crystals were obtained. Yield: 55% (based on CuI). IR (KBr pellet, cm⁻¹): 3441 (b), 3113 (w), 3054 (w), 1637 (vs), 1560 (w), 1542 (s), 1521 (w), 1478 (m), 1431 (w), 1385 (m), 1215 (w), 1196 (m), 1152 (w), 1094 (m), 990 (m), 840 (m), 798 (w), 769 (m), 723 (w), 694 (w), 667 (w), 530 (w), 507 (w), 493 (w), 444 (w). ¹H NMR (400 MHz, CD_3CN) δ 8.55 (d, J = 6.7 Hz, 4H), 8.34 (d, J = 6.8 Hz, 4H), 7.76 (d, J = 7.4 Hz, 4H), 7.57-7.51 (m, 5H), 7.50-7.44 (m, 4H), 7.38 (s, 2H), 4.24 (s, 3H). Anal. calcd for C₃₀H₂₆Cu₄I₄ N₆: C, 29.24; H, 2.13; N, 6.82. Found: C, 29.10; H, 2.09; N, 6.75. ESI-MS: the parent ion was not observed in either the positive or negative ion mode. In the positive mode, the fragment corresponding to the ligand was found: m/z236.12 $(HL_3)^+$. In the negative mode, fragments corresponding to various inorganic anions were found: m/z 1269.93 (Cu₆I₇)⁻, m/z1078.09 $(Cu_5I_6)^-$, m/z 888.25 $(Cu_4I_5)^-$, m/z 698.41 $(Cu_3I_4)^-$, m/z506.58 $(Cu_2I_3)^-$, m/z 316.74 $(CuI_2)^-$.

Synthesis of [Cu₄I₄(L₃)₂]·2C₁₃H₁₀O (5, C₁₃H₁₀O denotes benzophenone). First, HL₃·I (9.0 mg, 0.025 mmol) in 1 mL CH₃CN and CuI (9.5 mg, 0.05 mmol) in 1 mL of CH₃CN were mixed together. Then, 0.45 g of benzophenone in 3 mL of CH₃CN was added to the solution. The solution was allowed to stand at RT for about a week to afford brown crystals. Yield: 45% (based on CuI). IR (KBr pellet, cm⁻¹): 3429 (b), 3113 (w), 3054 (w), 1656 (s), 1638 (vs), 1597 (w), 1542 (s), 1521 (w), 1476 (w), 1445 (w), 1380 (w), 1316 (m), 1278 (s), 1216 (w), 1196 (m), 1152 (w), 1096 (w), 1074 (w), 991 (w), 942 (w), 918 (w), 841 (m), 813 (w), 798 (w), 766 (s), 72w (w), 704 (s), 661 (w), 638 (m), 533 (w), 507 (w), 493 (w), 444 (w). ¹H NMR (400 MHz, CD₃CN) δ 8.55 (d, J = 6.7 Hz, 4H), 8.34 (d, J = 6.7 Hz, 4H), 7.77 (d, J = 7.1 Hz, 25H), 7.65 (t, J = 7.4 Hz, 14H), 7.54 (t, J = 7.6 Hz, 26H), 7.49-7.44 (m, 4H), 7.38 (s, 1H), 4.21 (s, 4H). Anal. calcd for C₅₆H₄₆Cu₄I₄N₆O₂: C, 42.12; H, 2.90; N, 5.26. Found: C, 42.26; H, 3.20; N, 5.03.

4.4 Crystal structure determination

Single crystals of clusters 1–5 suitable for X-ray analysis were obtained as described in the synthesis section. Crystals were

mounted on the top of fiberglass with glue. Data collection for 1-5 at 293 K and 2 at 100 K was performed using an Oxford Diffraction Gemini E (Enhance Mo X-ray source, K α , λ = 0.71073 Å) equipped with a graphite monochromator and an ATLAS CCD detector (CrysAlis CCD, Oxford Diffraction Ltd). Data collection for 3-5 at 100 K was performed using a Bruker APEX2 (Cu X-ray source, K α , λ = 1.54178 Å). Structures were solved by direct methods (SHELXTL-97) and refined on F^2 using full-matrix least-squares (SHELXTL-97).49 Restraints on bond lengths for the disordered t-butyl groups were employed for cluster 1 to obtain reasonable thermal displacement parameters. All non-hydrogen atoms were refined with anisotropic thermal parameters, and all hydrogen atoms were placed in geometrically calculated positions. PLATON/SQUEEZE⁵⁰ was used to correct the diffraction data for the contribution from disordered acetonitrile solvent molecules in complex 3.

4.5 Characterization

¹H NMR spectra were recorded on a Bruker Biospin Avance 400 MHz spectrometer and were referenced to the residual solvent signal (CH₃CN at 1.94 ppm). Elemental analyses (C, H, and N) were carried out using an Elementar Vario EL Cube instrument. Powder X-ray diffraction (PXRD) experiments were performed using a D8 Advance X-ray diffractometer with CuKa radiation. ESI-MS spectra were recorded on a Thermo Finnigan LCQ DECA XP quadrupole ion trap mass spectrometer using an electrospray ionization source with acetonitrile as the mobile phase and were acquired in both positive and negative ion mode. MALDI-TOF mass spectra were obtained on a 4800 Plus MALDI TOF Analyzer (ABI) spectrometer using trans-2-[3-(4*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) as the matrix. Solid UV-vis spectra were recorded on a Bio-Logic MOS-450/AF-CD spectrometer. Infrared spectra (KBr pellet) were recorded on a Nicolet Avatar 360 FTIR spectrometer in the range of 4000–400 cm^{-1} (abbreviations: w = weak, m = medium, b = broad, s = strong, and vs = very strong).

Steady-state luminescence spectra were recorded on a PTI QuantaMaster Model QM-TM scanning spectrofluorometer. The emission spectra were corrected for the detector response. Lifetime data were acquired using phosphorescence subsystem add-ons to the PTI instrument. A pulsed excitation source of 337 nm was generated from a nitrogen laser. A liquid-nitrogen cryostat (Janis Research Model VPF-100 System) was used to control the sample temperature. Microcrystalline samples were used for the photoluminescence measurements in the solid state.

4.6 Computational details

Density functional theory (DFT) and time-dependent DFT (TDDFT) have been carried out with the Gaussian09 software without symmetry constraints.⁵¹ The Lanl2dz⁵² effective core potential (ECP) was applied for Cu and I while the 6-31G** basis set⁵³ was used for C, N, O, F, and H atoms throughout. The hybrid PBE1PBE (PBE0)⁵⁴ functional was exerted for geometry optimizations while ω B97X-D was used for molecular orbitals (MOs) and vertical excitation energies calculations. Spin-unrestricted calculations were also performed in the case of

triplet states. Vibrational frequency calculations were only carried out on the optimized ground state (S₀) structures to ensure they are minima on the potential energy surface. In the calculation of UV-vis transitions, the 150 singlet–singlet or singlet–triplet transitions of lowest energy were computed. Note that we performed TDDFT calculations without including spin–orbit coupling, so that singlet–triplet excitations have zero oscillator strengths (*f*). The molecular orbital compositions were obtained by the Hirshfeld method⁵⁵ and using Multiwfn packages.⁵⁶ The electron density difference (EDD) maps were also generated from Multiwfn packages. More detailed computational results including coordinates of geometry optimized structures (Table S14) are given in the ESI.†

Conflicts of interest

The authors declare no competing financial interests.

Acknowledgements

We gratefully acknowledge financial support from the NSFC (No. 21571122), the National Basic Research Program of China (973 Program, 2013CB834803), and the Department of Education in Guangdong Province (No. 2014KCXTD012). We thank Dr Ji Zheng for his kind help with the theoretical calculations and Prof. Ming-Hua Zeng for the measurements of ESI-MS.

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