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ARTICLE

Photoluminescent calcium azolium carboxylates with diversified calcium coordination geometry and thermal stability

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Despite the popularity and versatility of transition-metal-azolium carboxylate coordination polymers, there are very few examples of group 2 complexes supported by azolium carboxylate ligands in the literature, and there are none featuring the luminescent calcium azolium carboxylates. New ionic calcium coordination networks, $\{[\text{Ca}_2(\text{L}^1)_2(\text{H}_2\text{O})_4](\text{Br})_{4.6}\text{H}_2\text{O}\}_\infty$ (**1**), $\{[(\text{L}^3)_2\text{Ca}(\text{H}_2\text{O})_2](\text{Br})_2\}_\infty$ (**3**), $\{[(\text{L}^4)_2\text{Ca}(\text{H}_2\text{O})_2](\text{Br})_2\}_\infty$ (**4**), and $\{[(\text{L}^5)_2\text{Ca}_3(\text{Na})(\text{H}_2\text{O})_9](\text{Cl})(\text{Br})_{6.2}\text{H}_2\text{O}\}_\infty$ (**5**) along with dimers, $\{[\text{Ca}_2(\text{L}^2)_2(\text{H}_2\text{O})_9](\text{Br})_{4.4}\text{H}_2\text{O}\}$ (**2**), and $\{[(\text{L}^6)_2\text{Ca}_3(\text{H}_2\text{O})_9](\text{Br})_6\}$ (**6**) were isolated from the reaction between corresponding azolium carboxylates and calcium carbonate in aqueous solution. **1-6** were characterized by FT-IR, NMR TGA, UV-vis, fluorescence and single crystal X-ray diffraction techniques. Interestingly, first tetra cationic binuclear calcium **2** was isolated using $\text{L}^2\text{H}_2\text{Br}_2$ and hexa cationic trinuclear calcium **6** was isolated using $\text{L}^6\text{H}_3\text{Br}_3$. The 3D coordination polymers **1** and **4** were derived with the help of $\text{L}^1\text{H}_2\text{Br}_2$ and $\text{L}^4\text{H}_2\text{Br}_2$, respectively, through $\text{Br}\cdots\text{H}$ hydrogen bonding. The 3D MOF **3** with rhomboidal channel was constructed using $\text{L}^3\text{H}_2\text{Br}_2$, where the channel size is about 4.8×2.9 nm. **5** was isolated as a rare 1D coordination polymer. The choice of azolium carboxylates in these solids not only changes the topology of the network but also affects the chemistry exhibited by the network. Calcium azolium carboxylate assemblies **1-4** and **6** exhibit interesting solid-state photoluminescent properties, driven by azolium carboxylate ligands. Variation of the bridging chromophore produced significant effects on the fluorescent properties. **1-4** and **6** represents a first example of luminescent calcium azolium carboxylate complexes. As can be seen in the six metal-organic assemblies presented in this report, a combination of carboxylate groups and steric hindrance affect the topology and physical properties of the resultant solids.

Introduction

The key strategy to design the functional porous coordination polymers (PCPs) or metal-organic frameworks (MOFs) for the specific application has been well documented, which allows better understanding on their structural-physicochemical relationships.^{1,2} Most of the PCPs/MOFs are constructed using multidentate rigid aromatic bridging ligands such as aromatic multicarboxylate ligands.³⁻⁶ Of the late, the azolium carboxylate linkers with flexible back bone have been widely used in construction of coordination frameworks,⁷⁻⁸ owing to their versatility in both structural and $[\text{C}-\text{H}]^{\delta+}$ functional aspects. The first azolium carboxylate coordination polymer was reported by Dyson *et al.* in 2005 using ionic imidazolium carboxylate linker.⁸ The bio-inspired supramolecular network

of one-dimensional water chain (comparable to the water chain present in aquaporin channels) was trapped by helical channels of zinc zwitterionic tubular coordination polymer $[(\text{ZnBr}(\text{H}_2\text{O})_4(\text{BCI}))(\text{H}_2\text{O})]_\infty$, **BCI** = 1,3-bis(carboxymethyl)-imidazolium, derived from reaction between N,N'-diacetic acid imidazolium bromide and zinc. Later, the high proton conductivity of zinc-**BCPI** MOF, **BCPI** = 1,3-bis(4-carboxyphenyl)imidazolium Chloride was demonstrated, where the methylene protons of imidazolium group played an important role to conduct protons.⁹ Recently, we have reported the first photoluminescent ionic zinc and copper imidazolium carboxylate coordination polymers using luminescent imidazolium carboxylate ligand.¹⁰

Collective efforts by a number of groups have expanded the metal-azolium carboxylate chemistry to provide a variety of routes toward desired PCPs/MOFs. Nevertheless, the imidazolium carboxylate supported coordination assemblies constructed from lighter alkaline-earth metals have been understudied¹¹⁻¹³ in comparison to the plethora of examples of d-block-based imidazolium carboxylate assemblies,^{7-10,14-16} perhaps due to their unpredictable geometries, coordination numbers and limited reactivity.

The first *s*-block coordination chemistry of imidazolium carboxylate was explored by Dyson *et al.* in 2005.¹¹ The two-dimensional strontium-imidazolium carboxylate polymer, $\{[\text{Sr}(\text{BCI}')_2(\text{H}_2\text{O})_4]\}_\infty$, $\text{BCI}' =$ zwitterionic 1,3-bis(carboxymethyl)imidazolium, derived from BCI' salt and SrCO_3 , where the polymeric sheet is separated by water sheets in which the water molecules form near-planar hexagons. Later, coordination polymers containing calcium, strontium, barium and cesium metal ions connected via BCI ligand were reported with different structural motifs of water molecules in the structural framework.¹² Recently, the structural properties of $\text{Mg}(\text{BCBI})_2(\text{H}_2\text{O})_4 \cdot 2\text{H}_2\text{O}$, $[\text{Ca}(\text{BCBI})_2(\text{H}_2\text{O})_4] \cdot 2\text{H}_2\text{O}$ and $[\text{Ba}(\text{BCBI})_2(\text{H}_2\text{O})_2 \cdot 2\text{H}_2\text{O}]_m$, $\text{BCBI} =$ 1,3-bis(carboxymethyl)benzimidazolium, were studied.¹³ Notably, only two structurally characterized calcium coordination complexes such as three-dimensional calcium- BCI supported coordination network and monomeric calcium- BCBI were reported using BCI or BCBI salts. As shown in chart 1, the structural motifs of known calcium-imidazolium carboxylates were tuned up by two flexible “methyl” arms and steric hindrance bestowed by BCI and BCBI ligands. In particular, the ionic calcium complexes derived from imidazolium or benzimidazolium carboxylate ligands bearing more than two flexible nodes are not known.

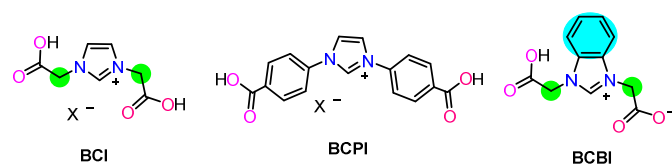


Chart 1 The structure of 1,3-bis(carboxymethyl)imidazolium (BCI) and 1,3-bis(carboxymethyl)benzimidazolium (BCBI) salts.

Continuing our efforts on photoluminescent ionic metal-azolium carboxylates,¹⁰ herein we report the synthesis and isolation of ionic calcium dimers and extended networks supported by bis- (with four flexible nodes) and tris- (with six flexible nodes)azolium carboxylic acid ligands. The first structurally authenticated calcium azolium carboxylate complexes with diversified calcium coordination geometry and photoluminescent property are described.

Experimental

Materials and methods

The solvents were purchased from commercial sources and purified according to standard procedures.¹⁷ Unless otherwise stated, the chemicals were purchased from commercial sources. Imidazolium carboxylates were prepared as reported.¹⁰ FT-IR measurement (neat) was carried out on a Bruker Alpha-P Fourier Transform spectrometer. NMR spectra were recorded on Bruker Ultrashield-400 spectrometers at 25 °C unless otherwise stated. Chemical shifts are given relative to TMS and were referenced to the solvent resonances as internal standards. Elemental analyses were performed by the Euro Vector EA-300 elemental analyzer. The UV-vis spectra were measured on a T90+ UV-visible spectrophotometer using ultrapure water with resistivity 18.2 M cm, obtained through the Millipore Direct-Q 3 UV system. The fluorescent emission spectra were measured on a Horiba Scientific fluorescence spectrophotometer using ultrapure water with resistivity 18.2 M cm, obtained through the Millipore Direct-Q 3 UV system. The excitation and emission slit width in fluorescence study is 5 nm for all the compounds and recorded at room temperature. The thermogravimetric analysis (TGA) was performed using a TA-SDT Q600, Tzeropress.

Synthesis of $\{[\text{Ca}_2(\text{L}^1)_2(\text{H}_2\text{O})_4](\text{Br})_4 \cdot 6\text{H}_2\text{O}\}_\infty$ (**1**)

The solution of $\text{L}^1\text{H}_2\text{Br}_2$ (0.100 g, 0.179 mmol) in water (10 mL) was added into a suspension of CaCO_3 (0.018 g, 0.180 mmol) in water (5 mL), stirred at ambient temperature for 24 h. The resultant cloudy solution was filtered and washed with water (10 mL). The crystals were formed through slow evaporation of filtered solution. Yield: 42% (based on CaCO_3). Anal. Calcd. (%) for $\text{C}_{21}\text{H}_{34}\text{N}_4\text{O}_9\text{Br}_2\text{Ca}$ (686.42): C, 36.75; H, 4.99; N, 8.16; found: C, 36.8; H, 5.1; N, 8.3. ^1H NMR (400 MHz, D_2O): $\delta = 7.43$ (d, 2H, ImH), 7.35 (s, 2H, ImH), 7.24 (s, 1H, ArH), 5.50 (s, 4H, CH_2), 4.73 (s, 4H, CH_2), 2.33 (s, 6H, 2 x CH_3), 2.12 (s, 3H, CH_3) ppm. ^{13}C NMR (100 MHz, D_2O): $\delta = 172.2$ (C=O), 140.8, 139.2, 131.4, 127.7 (ArC), 123.7, 121.5 (ImC), 52.0 (CH_2), 47.7 (CH_2), 18.9 (2 x CH_3), 14.7 (CH_3) ppm. FT-IR (neat): $\bar{\nu} = 3355$ (br), 3138 (w), 3045 (w), 2967 (w), 1590 (s), 1444 (m), 1404 (s), 1322 (s), 1212 (w), 1150 (s), 1104 (w), 1036 (w), 981 (w) cm^{-1} .

Synthesis of $\{[\text{Ca}_2(\text{L}^2)_2(\text{H}_2\text{O})_9](\text{Br})_4 \cdot 4\text{H}_2\text{O}\}_\infty$ (**2**)

2 was prepared as described for **1**, using $\text{L}^2\text{H}_2\text{Br}_2$ (0.100 g, 0.152 mmol) and CaCO_3 (0.016 g, 0.160 mmol). Yield: 41% (based on CaCO_3). Anal. Calcd. (%) for $\text{C}_{58}\text{H}_{82}\text{N}_8\text{O}_{21}\text{Br}_4\text{Ca}_2$ (1609.07): C, 42.81; H, 5.08; N, 6.89; found: C, 44.1; H, 5.0; N, 7.3. FT-IR (neat): $\bar{\nu} = 3333$ (br), 2972 (m), 2839 (w), 2775 (m), 1604 (s), 1565 (w), 1433 (w), 1397 (s), 1343 (w), 1309 (m), 1265 (w), 1190 (m), 1136 (w), 1020 (m), 986 (w) cm^{-1} . ^1H and ^{13}C NMR spectra of **2** were not clear due to dissociative nature of **2** in D_2O (See supporting information figure S5 and S6).

Synthesis of $\{[(\text{L}^3)_2\text{Ca}(\text{H}_2\text{O})_2]_2(\text{Br})_2\}_\infty$ (**3**)

3 was prepared as described for **1**, using $L^3H_2Br_2$ (0.100 g, 0.194 mmol) and $CaCO_3$ (0.019 g, 0.194 mmol). Yield: 39% (based on $CaCO_3$). Anal. Calcd. (%) for $C_{18}H_{22}N_4O_6CaBr$ (510.38): C, 42.36; H, 4.34; N, 10.98; found: C, 42.4; H, 4.33; N, 10.9. 1H NMR (400 MHz, D_2O): δ = 7.46-7.48 (m, 8H, *ArH* and *ImH*), 5.44 (s, 4H, CH_2), 4.80 (s, 4H, CH_2) ppm. ^{13}C NMR (100 MHz, D_2O): δ = 172.2 (C=O), 134.4, 129.4 (*ArC*), 123.8, 122.0 (*ImC*), 52.4 (CH_2), 52.0 (CH_2) ppm. FT-IR (neat): $\bar{\nu}$ = 3370 (br), 3034 (w), 2980 (w), 2941 (w), 1600 (s), 1555 (w), 1487 (w), 1441 (m), 1398 (s), 1306 (m), 1189 (w), 1156 (s), 1104 (w), 1024 (w), 979 (w) cm^{-1} .

Synthesis of $\{(L^4)_2Ca(H_2O)_2(Br)_2\}_x$ (**4**)

4 was prepared as described for **1**, using $L^4H_2Br_2$ (0.100 g, 0.162 mmol) and $CaCO_3$ (0.016 g, 0.162 mmol). Yellow crystals were formed through slow evaporation of yellow filtrate solution. Yield: 36% (based on $CaCO_3$). Anal. Calcd. (%) for $C_{26}H_{26}N_4O_6BrCa$ (610.50): C, 51.15; H, 4.29; N, 9.18; found: C, 51.2; H, 4.2; N, 9.2. 1H NMR (400 MHz, D_2O): δ = 8.25 (s, 2H, *ImH*), 8.11-8.08 (dd, 4H, *ArH*), 7.73-7.70 (dd, 4H, *ArH*), 7.31-7.30 (m, 2H, *ImH*), 7.25-7.24 (m, 2H, *ImH*), 5.83 (s, 4H, CH_2), 4.55 (s, 4H, CH_2) ppm. ^{13}C NMR (100 MHz, D_2O): δ = 171.9 (C=O), 135.9 (*ImC*), 129.9, 128.0, 125.3, 123.7 (*ArC*), 123.6, 121.7 (*ImC*), 51.9 (CH_2), 44.7 (CH_2) ppm. FT-IR (neat): $\bar{\nu}$ = 3342 (br), 3152 (w), 3091 (w), 3039 (w), 2992 (w), 1605 (s), 1481 (w), 1442 (m), 1397 (s), 1311 (m), 1180 (w), 1154 (s), 1103 (w) cm^{-1} .

Synthesis of $\{(L^5)_2Ca_3(Na)(H_2O)_9(Cl)](Br)_6 \cdot 2H_2O\}_x$ (**5**)

5 was prepared as described for **1**, using $L^5H_3Br_3$ (0.100 g, 0.128 mmol) and $CaCO_3$ (0.013 g, 0.128 mmol). Yield: 33% (based on $CaCO_3$). Anal. Calcd. (%) for $C_{54}H_{82}Br_6Ca_3ClN_{12}NaO_{23}$ (1925.40): C, 33.69; H, 4.29; N, 8.73; found: C, 36.4; H, 4.2; N, 9.8. 1H NMR (400 MHz, D_2O): δ = 8.58 (s, 3H, *ImH*), 7.49 (s, 3H, *ImH*), 7.41 (s, 3H, *ImH*), 5.63 (s, 6H, CH_2), 4.74 (s, 6H, CH_2), 2.37 (s, 9H, CH_3) ppm. ^{13}C NMR (100 MHz, D_2O): δ = 172.2 (C=O), 141.7 (*ArC*), 136.0 (*ImC*), 129.1 (*ArC*), 124.0 (*ArC*), 123.9 (*ArC*), 121.6 (*ImC*), 121.6, (*ImC*), 52.1 (CH_2), 48.2 (CH_2), 15.7 (CH_3) ppm. IR (neat): $\bar{\nu}$ = 3365 (br), 3090 (w), 1601 (s), 1445 (w), 1399 (s), 1308 (m), 1154 (s), 1104 (w), 1018 (w), 978 (w), 931 (w) cm^{-1} .

Synthesis of $\{(L^6)_2Ca_3(H_2O)_9(Br)_6\}$ (**6**)

6 was prepared as described for **1**, using $L^6H_3Br_3$ (0.100 g, 0.108 mmol) and $CaCO_3$ (0.011 g, 0.108 mmol). Yield: 41% (based on $CaCO_3$). Anal. Calcd. (%) for $C_{78}H_{90}Br_6Ca_3N_{12}O_{21}$ (2122.29): C, 43.96; H, 4.26; N, 7.89; found: C, 44.2; H, 4.4; N, 7.7. 1H NMR (400 MHz, D_2O): δ = 8.93 (s, 3H, *ImH* H/D exchange), 7.96-7.94 (m, 3H, *ArH*), 7.77-7.68 (m, 9H, *ArH*), 5.86 (s, 6H, CH_2), 5.01 (s, 6H, CH_2), 2.36 (s, 9H, CH_3) ppm. ^{13}C NMR (100 MHz, D_2O): δ = 171.8 (C=O), 142.2, 132.1, 131.2, 128.8, 127.5, 127.2, 113.2 (*ArC*), 49.6 (CH_2), 46.2 (CH_2), 15.9 (CH_3) ppm. FT-IR (neat): $\bar{\nu}$ = 3310 (br), 3020 (w), 1605 (s), 1565 (m), 1481 (w), 1429 (w), 1397 (s), 1345 (w),

1307 (m), 1271 (w), 1194 (m), 1133 (w), 1020 (m), 985 (w), 930 (w) cm^{-1} .

Crystallography

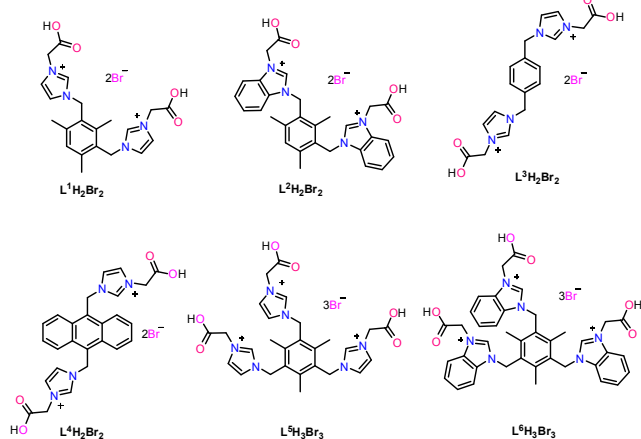
The crystal structures of **1-6** were measured on an Oxford Xcalibur 2 diffractometer. A suitable crystal was selected and mounted on a SuperNova, Dual, Cu at zero, Eos diffractometer. Data were collected at 150 K or 298 K. Using Olex2,¹⁸ the structures **1-6** were solved with the olex2.solve structure solution program using Charge Flipping and refined with the olex2.refine refinement package using Gauss-Newton minimization. The reported six crystals were crystallized using water as a solvent. In molecule **6**, approximately 31% (1710 Å³) of the unit cell volume comprises heavily disordered solvent molecules, which could not be modelled as discrete atomic sites, were “squeezed” out with the program PLATON. The estimated total count of 114 electrons per unit cell was removed as disordered solvents.

CCDC 1024405-1024410 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk

Results and discussion

Synthesis of **1-6**

The bis-azolium carboxylates ($L^1H_2Br_2$, $L^2H_2Br_2$, $L^3H_2Br_2$ and $L^4H_2Br_2$) and tris-azolium carboxylates ($L^5H_2Br_2$ and $L^6H_2Br_2$) ligands were synthesized as reported in good yield (Scheme 1) [10]. The compounds **1-6** were synthesized from the reaction of corresponding azolium carboxylic acid with calcium carbonate in aqueous solution. Compounds **1-6** are soluble only in water and characterized by FT-IR, multinuclear (1H and ^{13}C) NMR, TGA, UV-vis and fluorescent spectroscopy techniques. The FT-IR spectra of **1-6** showed a characteristic peak for asymmetric stretching frequency at 1590-1605 cm^{-1} and symmetric stretching frequency at 1397-1404 cm^{-1} . The ^{13}C NMR spectra of **1-6** showed the diagnostic peak for C=O carbon at 170-173 ppm. UV-visible absorption spectra of **1-6** were measured in water at room temperature and displayed a nearly comparable pattern with corresponding azolium carboxylic acids. The solid-state UV-visible absorption spectra of **1-6** were significantly different from that of solution. The solid UV-visible absorption spectra of **1-6** are nearly comparable with corresponding azolium carboxylic acids (See supporting information, Figures S19 and S20).



Scheme 1. Molecular structure of bis-imidazolium carboxylates ($L^1H_2Br_2$, $L^2H_2Br_2$, $L^3H_2Br_2$ and $L^4H_2Br_2$) and tris-imidazolium carboxylates ($L^5H_3Br_3$ and $L^6H_3Br_3$).

The solid state fluorescent emission spectra of **1-6** were measured at excitation wave length of 370 nm (Fig. 1). The emission wavelength (440 nm) of **1**, **3**, **5** and **6** are comparable. The emission wavelength intensity for **1**, **3** and **6** are enhanced compared to their corresponding ligands, $L^1H_2Br_2$ (444 nm), $L^3H_2Br_2$ (440 nm), $L^6H_3Br_3$ (440 nm), respectively. The emission wavelength of **2** (445 nm) and **4** (447 nm) are slightly shifted towards higher wavelengths compared to **1**, **3**, **5** and **6**. Moreover, the emission intensity of **2** is comparable with $L^2H_2Br_2$ (447 nm), while the emission intensity of **4** is enhanced compared to $L^4H_2Br_2$ (447 nm) (Fig. 1).

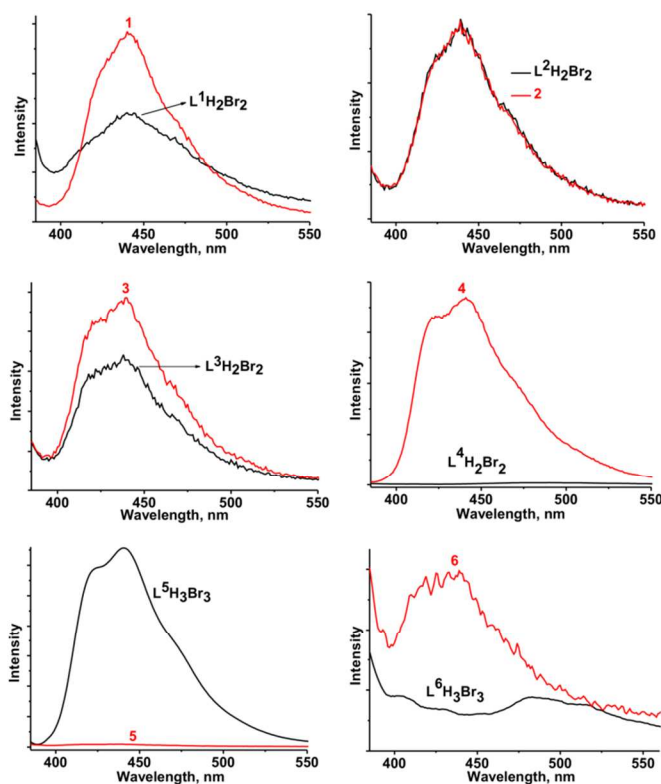


Fig. 1. The solid-state fluorescent spectra of **1-6** and corresponding organic spacers ($L^1H_2Br_2$, $L^2H_2Br_2$, $L^3H_2Br_2$, $L^4H_2Br_2$, $L^5H_3Br_3$ and $L^6H_3Br_3$) (Excitation wave length of 370 nm).

The fluorescent emission spectra of **1-6** were measured in water at an excitation wavelength of 370 nm, in which compound **1**, **2**, **3**, **5** and **6** shows similar emission wavelengths at 400 and 424 nm, whereas intensity of **1**, **2**, **3** and **5** are decreases compared to corresponding azolium carboxylic acids. The intensity of **6** is increased compared to corresponding azolium carboxylic acids (See supporting information, Figure S21). Molecule **4** shows emission wavelengths at 412, 441 and 462 nm, which are nearly comparable to corresponding azolium carboxylic acid (412, 441 and 468 nm) where the intensity increases with respect to azolium carboxylic acid. Since the luminescent property of **4** is much stronger than **1-3**, **5** and **6**, the fluorescent quantum yield (Φ_f) of **4** and $L^4H_2Br_2$ is measured in water (6.4×10^{-6} M) compared with that of anthracene in cyclohexane (6.4×10^{-6} M). The quantum yield of **4** ($\Phi_f = 0.434$) exhibits slightly higher than $L^4H_2Br_2$ ($\Phi_f = 0.414$), while significantly higher than anthracene ($\Phi_f = 0.36$).¹⁹

Furthermore, the solid state structures of **1-6** were unambiguously determined by single crystal X-ray diffraction technique. Data collection parameters are listed in Table 1 and 2.

Single crystal X-ray structure of **1**

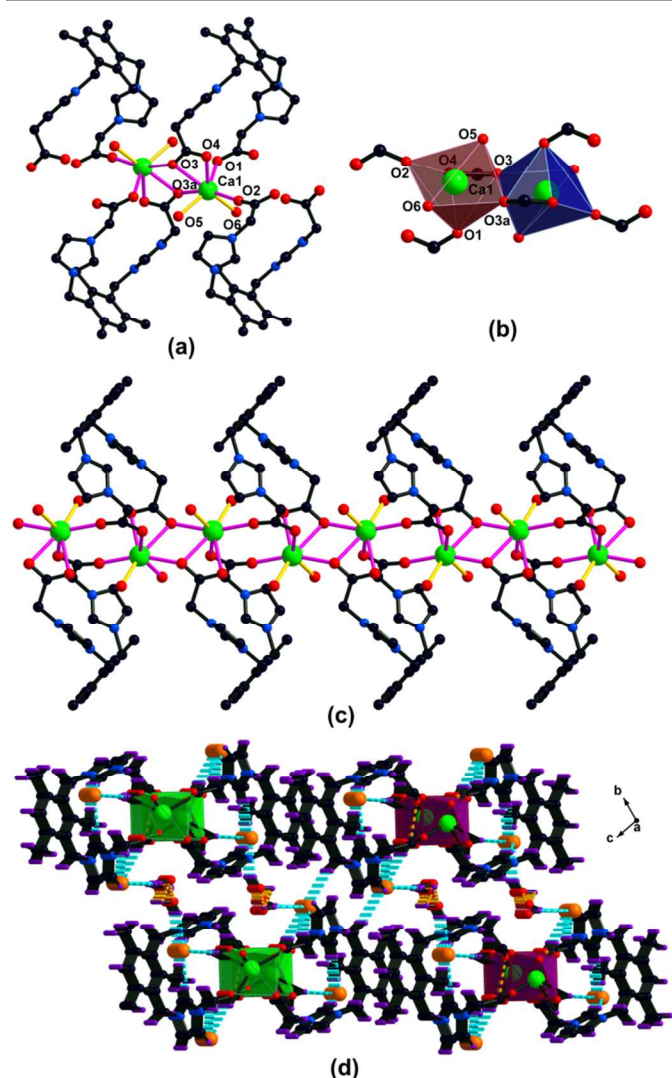


Fig. 2 (a) Coordination environment of Ca(II) centers in **1**. The hydrogen atoms have been omitted for clarity. (b) View of edge shared polyhedrons in **1**. (c) View of 1D coordination polymer. (d) 3D supramolecular network through O–H⋯Br and C–H⋯Br hydrogen bonds.

Complex **1** is a 3D supramolecular network connected through hydrogen bonding in the triclinic space group, $P\bar{1}$ (Figure 2). The molecular structure of **1** is depicted in Fig. 2a. The calcium(II) coordination number is seven and the geometry is distorted square-face monocapped trigonal-prismatic. The coordination environment of calcium is fulfilled by five oxygen atoms of carboxylates and two oxygen atoms of water molecules (Fig. 2b). Each organic spacer is connecting the three calcium centers through bridging coordination mode. One of the bridging carboxylate group is in $\mu_2\text{-}\eta^1\text{:}\eta^1$ COO bridging mode, while the second carboxylate group is in $\mu_2\text{-}\eta^1\text{:}\eta^2$ COO bridging mode. Two seven coordinated calcium polyhedrons are fused through edge sharing (Fig. 1b). The similar such dimers are bridged by carboxylate group to result a 1D coordination polymer. The cationic 1D calcium coordination polymer charge is balanced by bromine anions, where the

calcium centers are alternatively connected by $\mu_2\text{-}\eta^1\text{:}\eta^2$ and $\mu_2\text{-}\eta^1\text{:}\eta^1$ bridging mode of carboxylate groups (Fig. 2c).

As shown in Fig. 1d, the 1D polymer chains are further connected through C–H⋯Br and O–H⋯Br hydrogen bonding to form a 3D supramolecular network. In supramolecular network, two sets of bromine interactions are observed, namely (i) (NCHN)C–H⋯Br, (coordinated H₂O)O–H⋯Br and (lattice H₂O)O–H⋯Br; (ii) (CH₂)C–H⋯Br, (coordinated H₂O)O–H⋯Br and (lattice H₂O)O–H⋯Br. The different Ca–O_{COO} bond distances are observed in the range from 2.324(3) to 2.552(3) Å. Similarly, the Ca–O_{water} bond lengths are different (2.396(3) and 2.409(3) Å). The O_{COO}–Ca–O_{COO} angles vary from 52.18(9)° to 160.58(11)°.

Table 1 Selected crystallographic data and structure refinement results for **1**–**3**.

Parameters	1	2	3
Empirical formula	C ₂₁ H ₃₄ N ₄ O ₉ CaBr	C ₅₈ H _{80.4} N ₅ O _{23.97}	C ₁₈ H ₂₂ N ₄ O ₆ CaBr
Formula weight	686.42	1673.02	510.38
Temperature (K)	150	150	150
Crystal system	triclinic	triclinic	monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2/c$
<i>a</i> /Å	8.2450(6)	14.1675(7)	11.8051(15)
<i>b</i> /Å	11.6571(9)	16.5118(9)	14.1508(16)
<i>c</i> /Å	15.3212(13)	17.3328(8)	7.6915(5)
α /°	100.778(7)	94.247(4)	90.00
β /°	99.668(7)	109.921(4)	91.038(9)
γ /°	91.324(6)	110.838(5)	90.00
Volume (Å ³)	1423.8(2)	3473.6(3)	1284.7(2)
<i>Z</i>	2	2	2
ρ_{calc} /mg mm ⁻³	1.601	1.600	1.319
Absorption coefficient (mm ⁻¹)	5.652	4.821	4.242
<i>F</i> (000)	700.0	1712.0	522.0
Data collected	10212	26432	2326
Unique data	5338	13074	2326
GOF on <i>F</i> ²	1.041	1.023	0.952
<i>R</i> ₁ (<i>I</i> > 2 σ (<i>I</i>))	0.0490	0.0652	0.0697
w <i>R</i> ₂ (<i>I</i> > 2 σ (<i>I</i>))	0.1229	0.1920	0.1975
<i>R</i> ₁ values (all data)	0.0647	0.0816	0.0963
w <i>R</i> ₂ values (all data)	0.1345	0.2107	0.2293

Single crystal X-ray structure of **2**

The molecule **2** is a discrete tetracationic calcium dimer (Fig. 3). As shown in figure 3b, each organic spacer is coordinated to two calcium centers, where one carboxylate group is coordinated to calcium in $\mu_1\text{-}\eta^0\text{:}\eta^1$ mode, while the other carboxylate group is coordinated to two calcium centers in $\mu_2\text{-}\eta^1\text{:}\eta^2$ COO bridging mode. The geometry of calcium (II) centers are different, which are distorted square-face bicapped trigonal-prismatic and square-face tricapped trigonal-prismatic (Fig. 3b). The coordination environment of Ca1 is satisfied by four oxygen atoms of carboxylates and four water molecules,

while Ca2 center is satisfied by four oxygen atoms of carboxylates and five water molecules. The tetracationic charge is fulfilled by four bromine anions. The Ca and Ca separation distance is 4.068(13) Å. The Ca(1)–O_{COO} bond lengths (2.413(4) Å to 2.579(4) Å) around Ca(1) are different from that of Ca(2)–O_{COO} bond lengths (2.412(3) Å to 2.462(4) Å) around Ca(2). Similarly, the Ca(1)–O_{water} bond lengths (2.365(4) to 2.633(12) Å) are different from that of Ca(2)–O_{water} (2.386(4) to 2.454(4) Å).

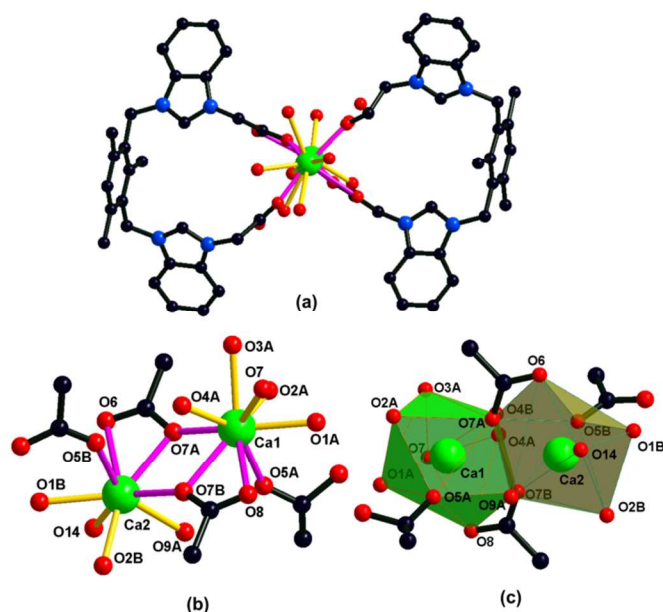


Fig. 3 (a) Coordination environment of the Ca(II) centers in **2**. The hydrogen atoms have been omitted for clarity. (b) Core unit of molecule **2**. (c) Polyhedron view of Ca(II) centers.

Single crystal X-ray structure of **3**

The molecule **3** is a three dimensional metal organic framework (Fig. 4). As shown in Fig. 4c, CaO₈ polyhedrons are edge shared by two carboxylate oxygen atoms and create inorganic motifs in the form of zigzag 1D chains running along the *c* axis. These chains are linked together by **L**³ organic spacer in rhomboidal channels. The channel size is about 4.8 x 2.9 nm (Fig. 4d and 4e). The Ca(II) ion is eight-coordinated by six oxygen atoms of carboxylate groups associated to four organic spacers and two oxygen atoms of coordinated water molecules (Fig. 4b). The calcium(II) coordination geometry is distorted square-face bicapped trigonal-prismatic geometry. The different Ca–O_{COO} bond distances are observed in the range from 2.327(5) to 2.540(5) Å. The Ca–O_{water} bond length is 2.405(8) and 2.56(2) Å. The Ca and Ca separation distance is 3.95(7) Å. The O_{COO}–Ca–O_{COO} angles fall in the range from 51.23(15)° to 159.3(4)°.

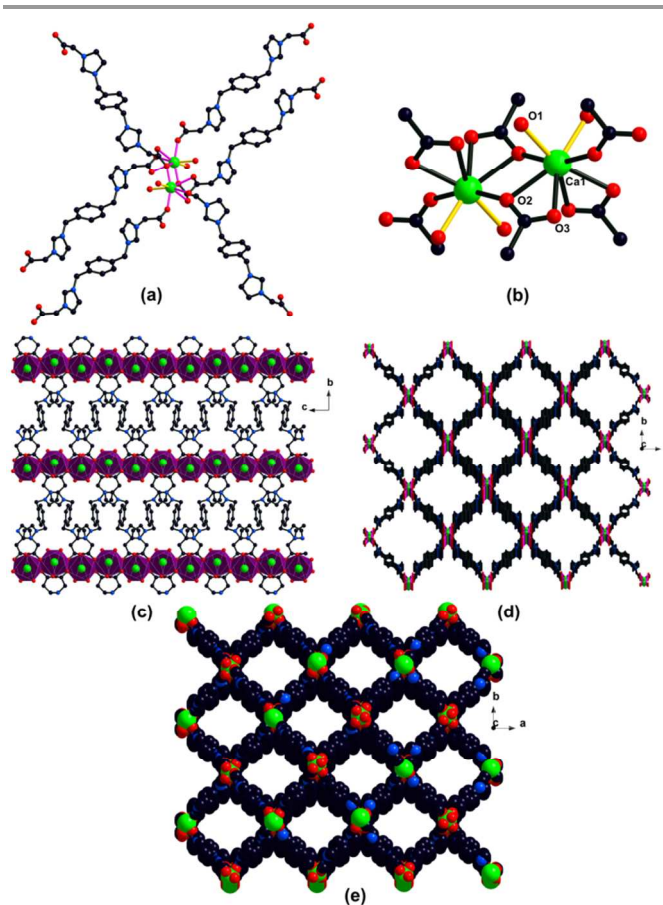


Fig. 4 (a) Coordination environment of the Ca(II) centers in **3**. The hydrogen atoms and bromine ions have been omitted for clarity. (b) Core unit of molecule **3**. (c) View of zig-zag arrangement of Ca(II) centers. (d) View of molecule **3** in the direction *c* axis. (e) Space filling model of **3** (Views along *c* axis).

Single crystal X-ray structure of **4**

The solid state structure of **4** was further confirmed by the single crystal X-ray diffraction study (Fig. 5). Molecule **4** crystallized in the triclinic space group, *P*₁. The asymmetric unit of **4** is composed of one calcium atom, a half anthracene imidazolium carboxylate anion of **L**⁴ and a bromide ion. The coordination environment of Ca is distorted octahedron and the coordination sites are satisfied by four carboxylate oxygen atoms of four **L**⁴ and the oxygen atoms of two water molecules (Fig. 5a). The anthracene imidazolium carboxylate ligand in **4** acts as μ_4 -bridge with bis-monodentate bridge mode to link four calcium atoms, in which each deprotonated carboxylic group bridges between two calcium atoms. The O_{COO}–Ca–O_{COO} angles fall in the range from 85.26(15)° to 180.00(0)°. The calcium and carboxylate oxygen bond distances are nearly comparable and the Ca(1)–O(2) (2.335(4) Å) bond distance is slightly longer than that of Ca(1)–O(1) (2.311(4) Å), which implies the nearly a symmetric coordination mode of carboxylate group. The calcium and oxygen atom of water (Ca(1)–O(3)) bond distance is 2.294(6) Å, which is considerably shorter than that of found in calcium N,N'-diacetic

acid imidazolium bromide network (2.390(5) Å). As shown in Fig. 5c, the extended network of calcium anthracene imidazolium carboxylate forms a two dimensional layer structure, in which the neighboring layers slipped with respect to each other. The bromide anion occupies in the inner layer site by which the layers are connected through (NCHN and two H₂CN groups) C–H⋯Br hydrogen bonding (HC–H⋯Br, 2.850 and 2.859 Å; NNCH⋯Br, 2.701 Å).

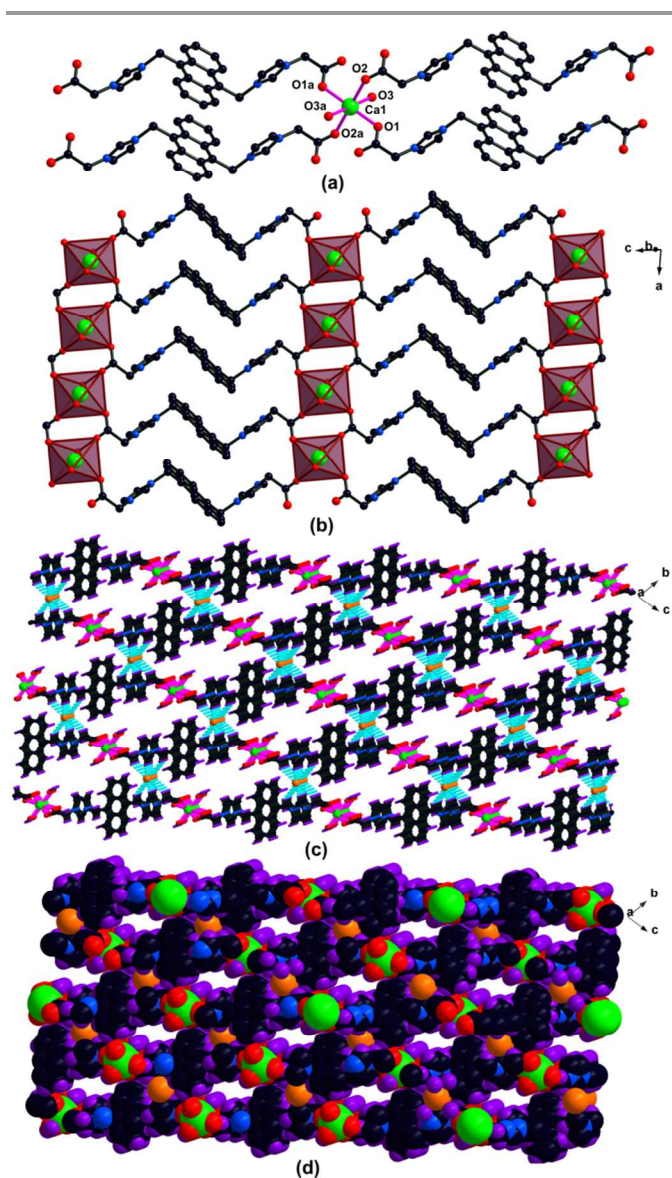


Fig. 5 (a) Coordination environment of the Ca(II) center in **4**. The hydrogen atoms and bromine ions have been omitted for clarity. (b) The polyhedron arrangement in two-dimensional layer of **4**. (c) Three-dimensional network through Br⋯H hydrogen bonding. (d) Space filling model of 3D network of **4**.

Table 2 Selected crystallographic data and structure refinement results for **4**–**6**.

Parameters	4	5	6
Empirical formula	C ₁₃ H ₁₃ N ₂ O ₃ Ca 0.5Br _{0.5}	C ₅₄ H _{72.5} N ₁₂ O _{21.7} 5Ca _{2.5} Cl _{0.85} NaBr 5.65	C ₇₈ H ₈₈ N ₁₂ O ₂₀ Br ₆ Ca _{2.5}
Formula weight	305.25	1842.55	2093.26
Temperature (K)	150	150	150
Crystal system	triclinic	triclinic	triclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> /Å	4.6746(12)	14.4574(8)	14.3416(7)
<i>b</i> /Å	11.632(3)	15.3803(6)	20.7798(8)
<i>c</i> /Å	13.537(3)	19.4570(11)	21.1629(8)
α /°	76.891(18)	103.011(4)	89.717(3)
β /°	84.108(19)	107.177(5)	74.471(4)
γ /°	85.173(19)	99.571(4)	75.245(4)
Volume (Å ³)	711.7(3)	3899.4(4)	5862.7(5)
<i>Z</i>	2	1	2
ρ_{calc} /mg mm ⁻³	1.424	1.569	1.186
Absorption coefficient (mm ⁻¹)	3.930	5.896	3.898
<i>F</i> (000)	313.0	1855.0	2120.0
Data collected	2562	27821	21809
Unique data	2562	13719	21809
GOF on <i>F</i> ²	1.027	1.023	1.036
<i>R</i> ₁ (<i>I</i> > 2 σ (<i>I</i>))	0.0787	0.0837	0.0975
w <i>R</i> ₂ (<i>I</i> > 2 σ (<i>I</i>))	0.1897	0.2304	0.2682
<i>R</i> ₁ values (all data)	0.0954	0.0983	0.1176
w <i>R</i> ₂ values (all data)	0.2054	0.2523	0.2916

Single crystal X-ray structure of **5**

Molecule **5** is a rare 1D coordination polymer constructed by a trinuclear Ca(II) and Na(I) carboxylate cluster (Fig. 6). The coordination environment of Ca(1) is fulfilled by six oxygen atoms of carboxylates, chlorine anion (with occupancy of 85%) and bromine anion (with occupancy of 15%), while Ca(3) is surrounded by seven oxygen atoms of carboxylates and Ca(4) center is satisfied by three oxygen atoms of carboxylates and four oxygen atoms of water molecules. The Na(2) center is fulfilled by two oxygen atoms of carboxylates and five oxygen atoms of water molecules. The Ca and Ca separation distances are not comparable (Ca(1)⋯Ca(3) 4.265(2) Å, Ca(1)⋯Ca(4) 3.907(4) Å, and Ca(1)⋯Ca(1¹) 4.108(2) Å). The Ca(1)–O_{COO} (2.297(5) Å–2.575(5) Å), Ca(3)–O_{COO} (2.333(10) Å–2.682(7) Å) and Ca(4)–O_{COO} (2.570(7) Å–2.652(6) Å) bond lengths are different. The Ca(1)–Cl distance is 2.719(7) Å and Ca(1)–Br distance is 2.953(2) Å. As shown in Fig. 5c, the inorganic zig-zag chain contains alternative orientation of trinuclear Ca(II) and Na(I) polyhedron units.

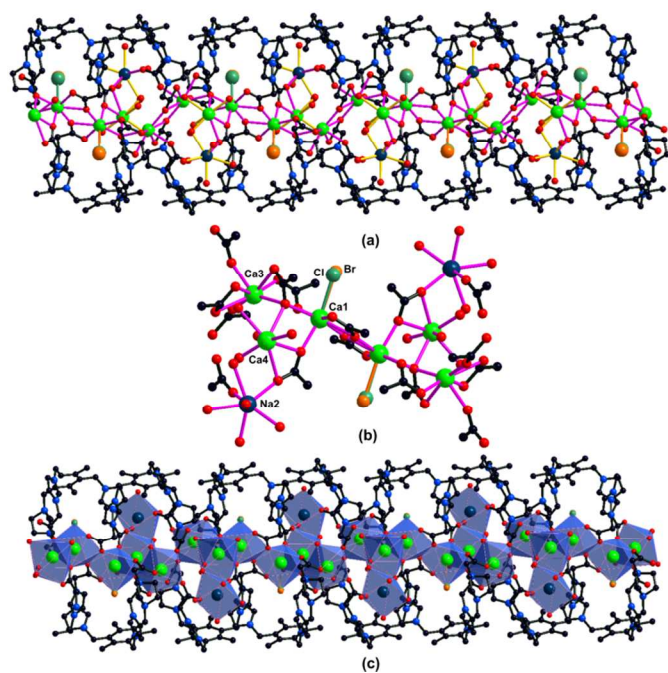


Fig. 6 (a) One-dimensional coordination polymer of **5**. The hydrogen atoms and counter ions have been omitted for clarity. (b) Repeating unit of molecule **5**. (c) Polyhedron view of Ca(II) centers in molecule **5**.

Single crystal X-ray structure of **6**

Compound **6** crystallized in the triclinic space group, $P\bar{1}$. The molecular structure of **6** is depicted in Fig. 7. Molecule **6** is a rare calcium trimer (Fig. 7a). **6** consisting of three different Ca geometry centers, where one calcium(II) center is in distorted square-face monocapped trigonal-prismatic, the second calcium(II) center is in distorted square-face bicapped trigonal-prismatic and third calcium center is in inverted tetrahedral geometry (Fig. 7b). The coordination environment around Ca(0A) center is fulfilled by five oxygen atoms of carboxylates and two water molecules. The geometry of Ca(2) center is satisfied by three oxygen atoms of carboxylates and five water molecules. The Ca(1B) center contented by two oxygen atoms of carboxylate group and two water molecules (Fig. 7b). The Ca and Ca separation distances are 4.008(16) and 4.655(27) Å. One organic spacer is coordinated to two calcium centers, where one carboxylate group is coordinated to calcium in $\mu_1\text{-}\eta^0\text{:}\eta^1$ mode and other carboxylate group is coordinated to two calcium centers in $\mu_2\text{-}\eta^1\text{:}\eta^2$ bridging mode. Second organic spacer is coordinated to three calcium centers, where one carboxylate group is coordinated to two calcium centers in $\mu_1\text{-}\eta^1\text{:}\eta^2$ mode and other carboxylate group is also coordinated to two calcium centers in $\mu_2\text{-}\eta^1\text{:}\eta^2$ bridging mode. The Ca(0A)–O_{COO} (Ca(0A)–O(2) 2.305(4) Å, Ca(0A)–O(1) 2.698(5) Å, Ca(0A)–O(2A) 2.318(5) Å, Ca(0A)–O(3) 2.453(4) Å and Ca(0A)–O(5) 2.353(4) Å), Ca(2)–O_{COO} (Ca(2)–O(2) 2.538(5) Å, Ca(2)–O(1) 2.371(5) Å and Ca(2)–O(4) 2.530(4) Å) and Ca(1B)–O_{COO} (Ca(1B)–O(5) 2.672(5) Å and Ca(1B)–O(14) 2.356(5) Å) bond lengths are different. Similarly, the Ca(0A)–O_{water} (2.368(5) and 2.436(5) Å),

Ca(2)–O_{water} (2.354(6) Å to 2.470(6) Å) and Ca(1B)–O_{water} (2.379(9) and 2.469(11) Å). The charge of Ca(II) centers are balanced by carboxylate anions, while the benziimidazol cations are balanced by bromine anions.

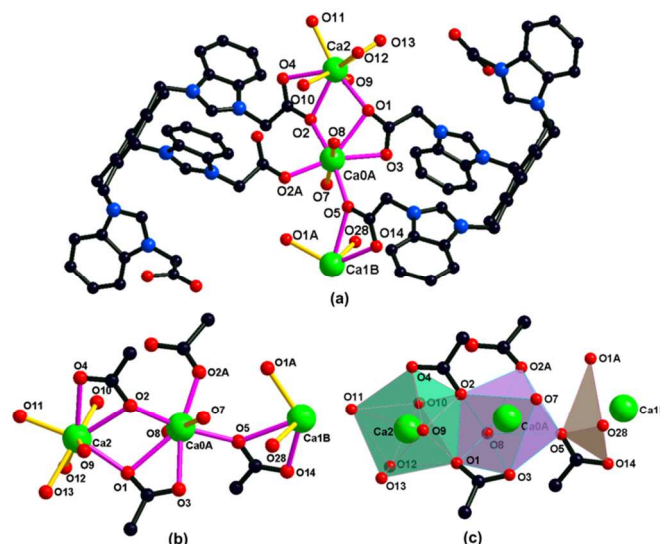


Fig. 7 (a) Coordination environment of the Ca(II) centers in **6**. The hydrogen atoms and bromine ions have been omitted for clarity. (b) Core unit of molecule **6**. (c) Polyhedron view of Ca(II) centers.

Comparison of solid state structures of 1-6

The coordination geometry of calcium centres in **1-6** are compared with known calcium imidazolium carboxylates, $\{[\text{Ca}_2(\text{BCI})_3(\text{Br})](\text{H}_2\text{O})_5\}_\infty$ ¹² and $[\text{Ca}(\text{BCBI})_2(\text{H}_2\text{O})_4]\cdot 2\text{H}_2\text{O}$ ¹³ in figure 8. The highly diversified and flexible coordination number and geometry are observed for the calcium centres in **1-6**. The geometry of calcium(II) in known calcium imidazolium carboxylates, $\{[\text{Ca}_2(\text{BCI})_3(\text{Br})](\text{H}_2\text{O})_5\}_\infty$ ¹² and $[\text{Ca}(\text{BCBI})_2(\text{H}_2\text{O})_4]\cdot 2\text{H}_2\text{O}$ ¹³ is distorted octahedron. The molecules **1** and **4** are isolated as a 3D supramolecular network through Br \cdots H hydrogen bonding. However the geometry of calcium centres in **1** is distorted square-face monocapped trigonal-prismatic (CN = 7) and geometry of **4** is distorted octahedron. The Ca–O_{COO} bond lengths of **4** are comparable with that of reported molecules. The molecules **2** and **6** are discrete binuclear and trinuclear calcium molecules, respectively. The geometry of calcium centers in **2** is distorted square-face bicapped trigonal-prismatic (CN = 8) and distorted square-face tricapped trigonal-prismatic (CN = 9), while **6** exhibits three different geometries (distorted square-face monocapped trigonal-prismatic (CN = 7), distorted square-face bicapped trigonal-prismatic (CN = 8) and inverted tetrahedral geometry (CN = 4)). The molecule **5** is a complicated 1D coordination polymer, where the molecule exists in three different calcium coordination environments with hexacoordinated sodium ions. The molecule **3** is constructed as three-dimensional metal-organic framework with distorted square-face bicapped trigonal-prismatic (CN = 8). Among all, the geometry of calcium center in **4** is comparable with known Ca imidazolium carboxylate complexes. In **1-3**, **5** and **6** the

calcium centers are in distorted square-face monocapped trigonal-prismatic and/or distorted square-face bicapped trigonal-prismatic geometry (besides the third calcium center in **6** shows inverted tetrahedral geometry (CN = 4) and in compound **2**, calcium centers exist in distorted square-face bicapped trigonal-prismatic and square-face tricapped trigonal-prismatic geometries, where the Ca–O_{COO} bond lengths are slightly larger than Ca–O_{COO} bond lengths found in **4**.

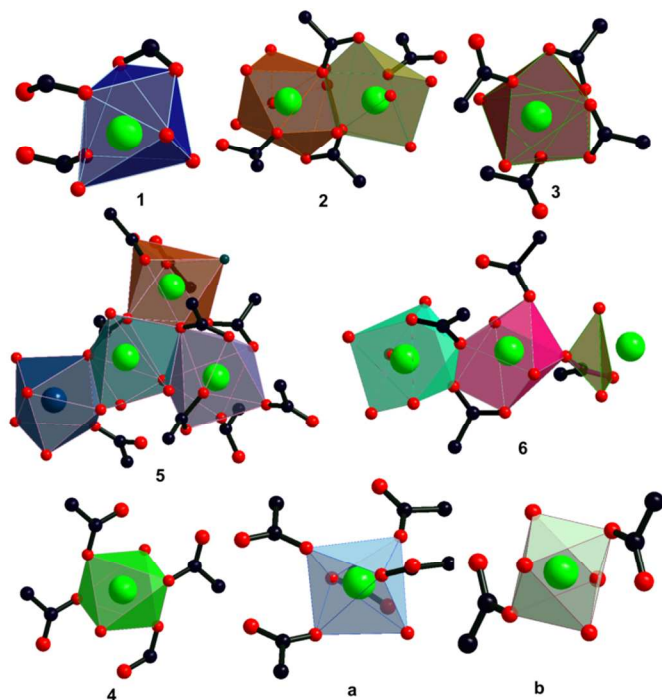


Fig. 8 Polyhedron of Ca coordination compounds **1-6** and reported Ca molecules based on imidazolium carboxylates; a = $\{[Ca_2(BCI)_3(Br)](H_2O)_5\}_\infty$ and b = $[Ca(BCBI)_2(H_2O)_4] \cdot 2H_2O$

TGA analysis

In order to understand the thermal decomposition pathway of **1-6**, thermogravimetric analysis (TGA) (10 °C/min, 30-1000 °C under N₂ atmosphere) was carried out on **1-6** (Fig. 9). The initial weight loss (11.6%) observed upto 170 °C in **1** can be attributed to the loss of lattice water and coordinated water molecules. Framework **1** showed the stability till 320 °C. Subsequently two major weight loss stages are observed (due to loss of organic part and Br anions). In the first stage (320-490 °C), about 33% weight loss was observed, and in the second stage (550-770 °C) about 25% of weight loss was observed. Compound **2** exhibited the initial weight loss of 10% till 224 °C, which may be due to the loss of coordinated and lattice water molecules. Then the molecule **2** slowly degraded in two stages, from 224-460 °C with 52% and from 461-840 °C with 19%. Furthermore, the weight loss was constant till 940 °C. Compound **3** displayed the first weight loss of 7% till 140 °C, which can be assigned to the loss of coordinated and lattice water molecules. Then the framework was stable upto 280 °C. Later the framework was slowly disturbed. Then sudden weight

loss was observed from 280-460 °C with weight loss of 36% and then slow weight loss was observed from 460-970 °C with weight loss of 35%. A small weight loss about 10% was observed for **4** in the initial stage (< 150 °C), attributable to the loss of moisture. From 150 to 320 °C, the compound was almost stable with 7% weight loss. Later, three stages of weight losses were occurred between 320-420 °C with 21%, 490-830 °C with 37% and 840-920 °C with 11% (due to evacuation of the Br⁻ and organic part). 1D coordination polymer **5** displayed the first weight loss of 15% till 127 °C, which can be assigned to the loss of coordinated and lattice water molecules. Then the framework was stable upto 326 °C. Later the framework was slowly disturbed. Subsequently, the sudden weight loss was observed from 326-680 °C with weight loss of 50 % and then further weight loss was observed from 780-923 °C with weight loss of 17.4%. **6** was stable upto 145 °C with loss of 5%, which may be due to the loss of water molecules. Later the framework was stable till 306 °C. Then the framework got degraded in different stages, 310-470 °C with 28%, 500-750 °C with 26%, 760-970 °C with 8%.

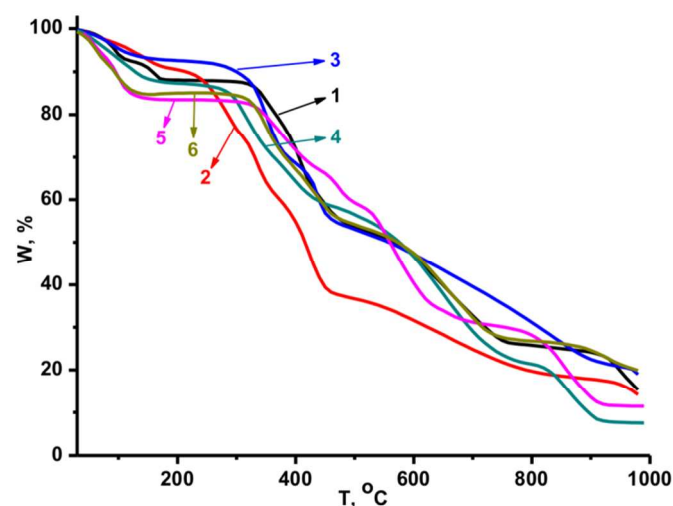


Fig. 9 The TGA profile of **1-6** (10 °C/min, 30-1000 °C under N₂ atmosphere).

Conclusions

Azolium carboxylate ligands featuring flexible bis- and tris-carboxylic acid groups have been used to assemble the first cationic calcium binuclear (**2**), trinuclear (**6**), one dimensional coordination polymer (**5**) and three dimensional calcium coordination networks (**1**, **3** and **4**) via carbonic acid elimination reactions. The flexible carboxylic acid groups in these ligands facilitated the isolation of calcium complexes persisting unusual coordination environments. The solid state structures of **2** and **6** reveals tetra cationic binuclear and hexa cationic trinuclear calcium molecules, respectively, which are rare examples of cationic calcium complexes supported by imidazolium carboxylate ligands. Complex **5** is the one-dimensional coordination polymer consists of three different calcium coordination environments. Elusive changes in the

position of imidazolium carboxylate group at aryl spacer (substitution at 1,3- or 1,4- positions of aryl spacer) yields three dimensional calcium coordination networks (**1**, **3** and **4**), which does not feature any structural resemblance. Changing the aryl spacer between azolium carboxylates in these solids not only changes the topology of the network but also affects the thermal and luminescent properties exhibited by the network. These calcium azolium carboxylate assemblies (except **5**) exhibit interesting solid-state photoluminescent behaviors, driven by imidazolium carboxylate ligand. Variation of the bridging chromophore produced significant effects on the fluorescent behaviors. Moreover **1-4** and **6** represents a first luminescent calcium complex derived using azolium carboxylate ligand. These results show that azolium carboxylate ligands can be used as potential functional spacers for the isolation of discrete molecules to three dimensional calcium complexes. We are currently exploring the chemistry of heavier main group imidazolium carboxylates, which will be reported in due course.

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Notes and references

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Electronic Supplementary Information (ESI) available: FT-IR, NMR, UV-vis and fluorescent spectra for **1-6**. See DOI: 10.1039/b000000x/

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Six new luminescent calcium coordination assemblies were successfully synthesized and characterized using bis- and tris-azolium carboxylic acid ligands.

Luminescent Ca(II) CP's

