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Selective Anion Exchange and Tunable Luminescent Behaviors of Metal–Organic Framework Based Supramolecular Isomers

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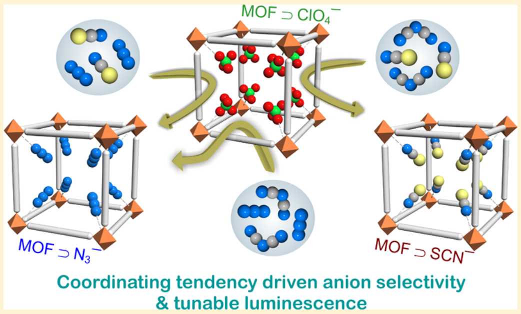
S *Supporting Information*

ABSTRACT: Owing to the conformational (cis or trans) flexibility of a N-donor ligand, the combinations of the same and $Cd(ClO_4)_2$ under variable solvent templates afforded two supramolecular isomers based on two-dimensional metal–organic frameworks. Both compounds contain weakly coordinating ClO_4^- anions attached to the metal centers. Both frameworks showed facile anion exchange behaviors with various kinds of foreign anions. Moreover, both frameworks showed anion-driven structural dynamism and exhibited the preferential uptake of strongly coordinating anions over others. Anion-regulated modulation in luminescent behaviors was also observed in both cases.



■ INTRODUCTION

The active participation of anions in certain biological and environmental processes imparts fundamental importance to the function of anion separation and removal.[1] Metal–organic frameworks[2] (MOFs) or metal–organic supramolecular architectures[3] can be conceived as potential candidates for this anion separation purpose. Particularly, cationic MOFs can provide a platform for anion encapsulation/separation or recognition.[4] Generally, combinations of neutral N-donor ligand and metal ion in the presence of some organic solvents (templates) render cationic MOFs, wherein extraframework anions reside in the porous channel or are weakly coordinated to the metal centers.[5] Often it has been observed that such organic solvent molecules remain in the pores of the cationic framework as free guests and regulate the overall structure of the framework.[6] Switching such organic templates along with the effect of conformation flexibility (cis or trans) of a N-donor ligand may produce cationic supramolecular isomers which possess the same chemical formula with different framework structures.[7] Weakly coordinated or free anions in such cationic MOFs can be exchanged with other anions of different properties.[8] Furthermore, exchanging such coordinated anions with other anions of variable nature may induce a flexible character to the framework. The degree of flexibility might depend on the shape, size, and coordinating tendencies of the foreign anions. Hence, strongly coordinating anions may be preferably captured over weakly coordinating anions by a cationic framework, which leads to the dynamic nature of the cationic framework.[4h,8a] Thus, an extrinsic dynamic nature of the cationic framework is observed due to the differential behavior of the anions, acting as chemical stimuli.[9] A luminescent N-donor ligand while anchored with a d^{10} metal ion generally builds up a luminescent cationic framework.[4g,10] Such luminescent behavior of the framework can be tuned by exchanging the host anions with other anions of different nature.[4h,5b] By incorporating all the above features into a single species, a unique material with multiple functionality can be developed.[11]It has been observed that the 4,4′-pyridyl functionality of a N-donor ligand often gives a luminescent cationic framework.[12] Hence, we chose 1,4-bis(4-pyridyl)-2,3-diaza-1,3-butadiene[13] as the ligand (L) and the Cd(II) ion to generate luminescent cationic frameworks. Here, we present two supramolecular isomers based on 2D MOFs arising due to a dual effect: conformation flexibility of the ligand used and different solvent templates (Scheme 1A). The MOFs are made of L (Figure 1A,B), Cd(II) ions, and ClO_4^- anions which are coordinated to the metal centers. Both frameworks showed facile anion exchange behaviors under ambient conditions with various types of external anions. Interestingly, the frameworks showed more affinity toward strongly coordinating anions than weakly coordinating anions (Scheme 1B). A noteworthy feature of the compounds is their anion-triggered structural dynamism. Moreover, both compounds exhibited an anion-switchable tunable luminescent property.

■ EXPERIMENTAL SECTION

Materials and Measurements. L was synthesized according to the literature procedure.[13] All other reagents and solvents were commercially available and used without further purification. The X-ray powder diffraction (XPRD) pattern was recorded on a Bruker D8 Advance X-ray diffractometer at room temperature (rt) using Cu Kα radiation (λ = 1.5406 Å). FT-IR spectra were measured on a Nicolet 6700 FT-IR spectrophotometer using KBr pellets. Thermogravimetric analysis (TGA) was performed in the temperature range of 30–800 °C on a PerkinElmer STA 6000 analyzer under a N_2 atmosphere at a heating rate of 10 °C min. Solid-state fluoroscence spectra were recorded on Fluorolog 3.

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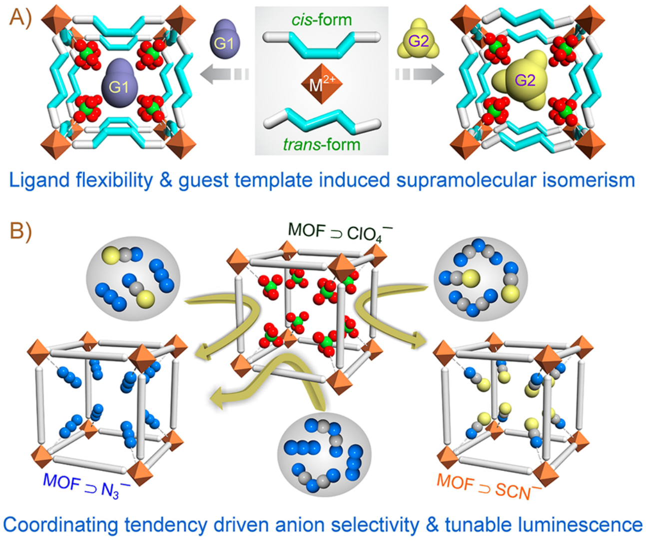
Scheme 1. Schematic Representation Showing (A) Ligand Flexibility and Guest-Template-Driven Supramolecular Isomers and (B) Coordinating-Tendency-Driven Guest Anion Affinity



Synthesis of 1$\supset\mathrm{ClO_4}^-$**.** A DCM solution of the ligand (21 mg, 1 mL) was taken into a glass tube. Toluene (1 mL) was poured onto the ligand followed by layering of a methanolic solution of $\mathrm{Cd(ClO_4)_2}$ (31 mg, 1 mL). Yellow crystals suitable for X-ray studies were obtained after 15 days in 70% yield. FT-IR (KBr pellet, $\mathrm{cm^{-1}}$): 3454.64 (m), 1952.58 (w), 1612.45 (s), 1549.93 (m), 1422.12 (m), 1317.68 (w), 1233.16 (s), 1100.22 (s), 813.22 (m), 728.81 (m), 683.46 (m), 620.93 (m), 513.05 (m). We were unable to locate highly disordered guest molecules crystallographically. From the SQUEEZE function of PLATON and CHN analysis the formula of compound **1**$\supset\mathrm{ClO_4}^-$ was found to be $[\{\mathrm{Cd(L)_2(ClO_4)_2}\}\cdot\text{toluene}\cdot\mathrm{MeOH}]_n$. Anal. Calcd for $[\{\mathrm{Cd(L)_2(ClO_4)_2}\}\cdot\text{toluene}\cdot\mathrm{MeOH}]$: C, 44.86; H, 3.76; N, 13.08. Found: C, 44.21; H, 3.92; N, 13.30.

Synthesis of 2$\supset\mathrm{ClO_4}^-$**.** A DCM solution of the ligand (21 mg, 1 mL) was taken into a glass tube. Mesitylene (1 mL) was poured onto the ligand followed by layering of a methanolic solution of $\mathrm{Cd(ClO)_4}$ (31 mg, 1 mL). Yellow crystals suitable for X-ray studies were obtained after 15 days in 75% yield. FT-IR (KBr pellet, $\mathrm{cm^{-1}}$): 3460.15 (m), 1947.05 (w), 1703.16 (w), 1612.45 (s), 1556.11 (w), 1420.06 (m), 1312.18 (m), 1233.16 (m), 1103.29(s), 824.32 (m), 683.46 (m), 631.92 (m), 518.55 (m). We were unable to locate highly disordered guest molecules in the structure crystallographically. CHN and TGA analysis of compound **2**$\supset\mathrm{ClO_4}^-$ also indicates the presence of three mesitylene molecules in its formula unit which are highly disordered. From the SQUEEZE function of PLATON and CHN and TGA analysis the formula of compound **2**$\supset\mathrm{ClO_4}^-$ was determined to be $[\{\mathrm{Cd_2(L)_4(ClO_4)_4}\}\cdot 3(\text{mesitylene})]_n$. Anal. Calcd for $[\{\mathrm{Cd_2(L)_4(ClO_4)_4}\}\cdot 3(\text{mesitylene})]$: C, 49.38; H, 4.14; N, 12.29. Found: C, 49.20; H, 3.95; N, 11.98.

Anion Exchange Study. Single crystals of **1**$\supset\mathrm{ClO_4}^-$ and **2**$\supset\mathrm{ClO_4}^-$ were separately dipped in methanolic solutions (1 mmol/10 mL of MeOH) of $\mathrm{NaN_3}$, KSCN, and $\mathrm{NaN(CN)_2}$ for about 6 days at rt, which yielded the anion-exchanged product. The products were characterized by FT-IR spectroscopy, XPRD, diffuse reflectance spectroscopy, solid-state emission spectroscopy, and scanning electron microscopy (SEM).

Anion Selectivity Study. *Separation of* N_3^- *and* SCN^-. Single crystals of **1**$\supset\mathrm{ClO_4}^-$ and **2**$\supset\mathrm{ClO_4}^-$ were separately dipped in a methanolic solution (10 mL) of equimolar $\mathrm{NaN_3}$ (1 mmol) and KSCN (1 mmol) for about 6 days at rt, giving rise to the anion exchange product, characterized by FT-IR spectroscopy and PXRD.

The same procedure was followed for $\mathrm{N_3}^-/\mathrm{N(CN)_2}^-$ and $\mathrm{SCN}^-/\mathrm{N(CN)_2}^-$ binary mixtures.

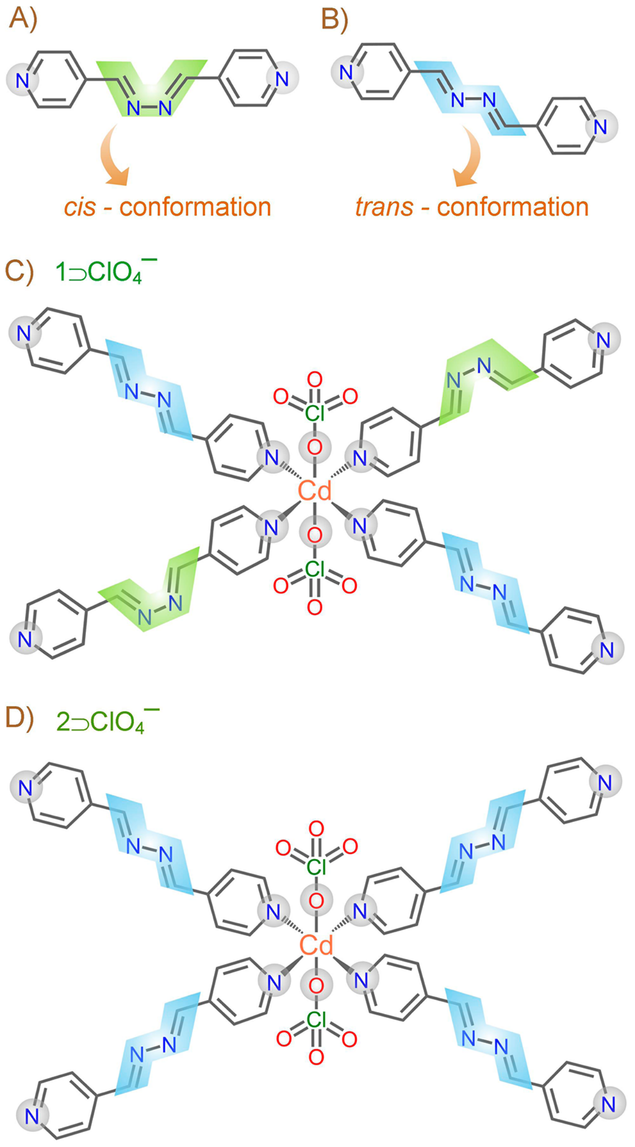


Figure 1. (A) Cis conformation of the ligand in **1**$\supset\mathrm{ClO_4}^-$. (B) Trans conformation of the ligand in **2**$\supset\mathrm{ClO_4}^-$. Chemical diagram of the coordination environment of the Cd(II) node in (C) **1**$\supset\mathrm{ClO_4}^-$ and (D) **2**$\supset\mathrm{ClO_4}^-$.

X-ray Structural Studies. Single-crystal X-ray data of compound **1**$\supset\mathrm{ClO_4}^-$ and compound **2**$\supset\mathrm{ClO_4}^-$ were collected at 150 K on a Bruker KAPPA APEX II charge-coupled devide (CCD) Duo diffractometer (operated at 1500 W power, 50 kV, 30 mA) using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The crystal was mounted on a nylon CryoLoop (Hampton Research) with Paraton-N (Hampton Research). The data integration and reduction were processed with SAINT[14] software. A multiscan absorption correction was applied to the collected reflections. The structure was solved by the direct method using SHELXTL[15] and was refined on F^2 by the full-matrix least-squares technique using the SHELXL-97[16] program package within the WinGX[17] program. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were located in successive difference Fourier maps, and they were treated as riding atoms using SHELXL default parameters. The structures were examined using the Adsym subroutine of PLATON[18] to ensure that no additional symmetry could be applied to the models.

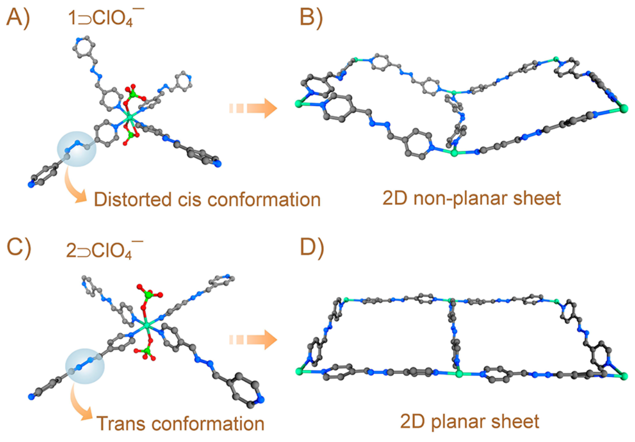


Figure 2. (A) Coordination environment of the Cd(II) node in $\mathbf{1}\supset\mathrm{ClO_4^-}$. (B) 2D nonplanar sheet in $\mathbf{1}\supset\mathrm{ClO_4^-}$. (C) Coordination environment of the Cd(II) node in $\mathbf{2}\supset\mathrm{ClO_4^-}$. (D) 2D planar sheet in $\mathbf{2}\supset\mathrm{ClO_4^-}$.

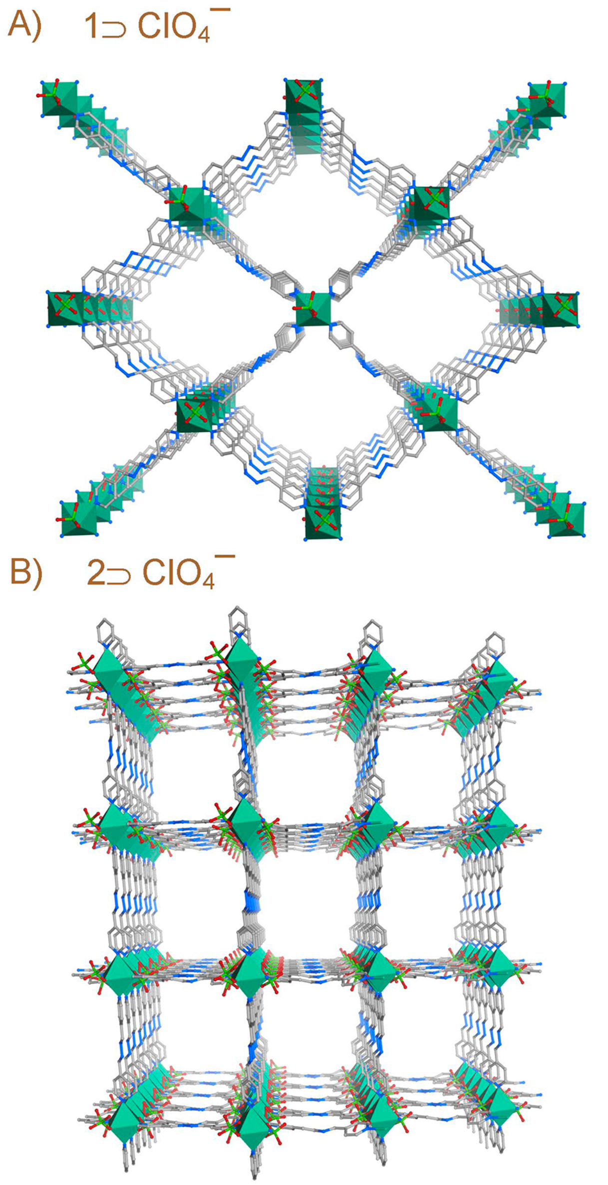


Figure 3. Perspective view of packing showing similar nets of (A) $\mathbf{1}\supset\mathrm{ClO_4^-}$ and (B) $\mathbf{2}\supset\mathrm{ClO_4^-}$ (metal shown as blue polyhedron).

■ RESULTS AND DISCUSSION

The reactions of L with $\mathrm{Cd(ClO_4)_2}$ in the solvent combination of $\mathrm{CH_2Cl_2}$/toluene/MeOH gave yellow single crystals of compound $\mathbf{1}\supset\mathrm{ClO_4^-}$ ($[\{\mathrm{Cd(L)_2(ClO_4)_2}\}\cdot\mathrm{toluene}\cdot\mathrm{MeOH}]_n$). Use of mesitylene in place of toluene while keeping the rest of the solvent system intact produced yellow crystals of compound $\mathbf{2}\supset\mathrm{ClO_4^-}$. Single-crystal analysis of compound $\mathbf{1}\supset\mathrm{ClO_4^-}$ revealed construction of a 2D nonplanar sheet like structure. These 2D sheets formed H-bonds with like sheets via coordinated anions and free solvent molecules, leading to a H-bond-based 3D structure. A single-crystal X-ray diffraction (SC-XRD) study of $\mathbf{1}\supset\mathrm{ClO_4^-}$ showed that the compound crystallized in the monoclinic system with space group $P2_1/c$.

The asymmetric unit contains one Cd(II) ion, two ligand molecules (wherein one is in the trans form and the other is in the cis geometry), two $\mathrm{ClO_4^-}$ ions, one toluene, and one guest molecule. Among the two perchlorate anions bound to the metal site, one was monodentately bound while the other was bidentately bound (Figure 2A). Coordination via terminal *N*-pyridyl donors extended the structure in a zigzag fashion to form a two-dimensional net (Figure 3). The nets were not planar owing to the cis geometry of one of the ligands (Figure 2B). Guest molecules were encapsulated in the voids between the two nets. C−H···π interactions were observed between the C−H of the cis ligand and the π cloud of toluene (Figure S11, Supporting Information). Various framework−anion noncovalent interactions were also observed in $\mathbf{1}\supset\mathrm{ClO_4^-}$ (Figure S12, Supporting Information). SC-XRD analysis showed that $\mathbf{2}\supset\mathrm{ClO_4^-}$ crystallized in the triclinic system, space group $P\bar{1}$. The asymmetric unit of the compound consisted of two metal sites coordinated to four ligand molecules, four perchlorate anions and mesitylene guest molecules denoted by $[\{\mathrm{Cd_2(L)_4(ClO_4)_4}\}\cdot 3(\mathrm{mesitylene})]_n$. One metal site was bound to four different ligands and two perchlorate anions in a monodentate fashion, leading to an octahedral geometry of the metal center (Figures 1D and 2C). The ligand was coordinated to the metal centers via the terminal nitrogens, thereby extending the framework to form a 2D net (Figure 3). The trans dispositions of each ligand in $\mathbf{2}\supset\mathrm{ClO_4^-}$ facilitate formation of 2D planar sheets (Figure 2D). Different kinds of noncovalent interactions of the framework-coordinated anions were also present in the compound (Figure S13, Supporting Information). Thus, the above-mentioned structural analysis for both compounds indicates that $\mathbf{1}\supset\mathrm{ClO_4^-}$ and $\mathbf{2}\supset\mathrm{ClO_4^-}$ possess the same chemical formula with different framework structures, exhibiting supramolecular isomerism. This supramolecular isomerism arises due to the combined effect of cis/trans conformations of the ligand and solvent templates used in the complexation. PXRD patterns of $\mathbf{1}\supset\mathrm{ClO_4^-}$ and $\mathbf{2}\supset\mathrm{ClO_4^-}$ showed that both frameworks are pure in their bulk phase and stable at room temperature (Figure S14, Supporting Information). As mentioned earlier, $\mathbf{1}\supset\mathrm{ClO_4^-}$ and $\mathbf{2}\supset\mathrm{ClO_4^-}$ had $\mathrm{ClO_4^-}$ anions coordinated to the metal centers. To investigate the anion-triggered structural dynamism of both frameworks, anion exchange studies were carried out. We took two types of anions: (A) strongly coordinating in nature (representative anions $\mathrm{N_3^-}$ and $\mathrm{SCN^-}$) and (B) weakly coordinating in nature (representative anions $\mathrm{N(CN)_2^-}$). In a typical experiment, crystals of $\mathbf{1}\supset\mathrm{ClO_4^-}$ and $\mathbf{2}\supset\mathrm{ClO_4^-}$ were separately immersed in methanolic solutions of $\mathrm{NaN_3}$, KSCN, and $\mathrm{NaN(CN)_2}$ for about ~6 days. The exchange process was

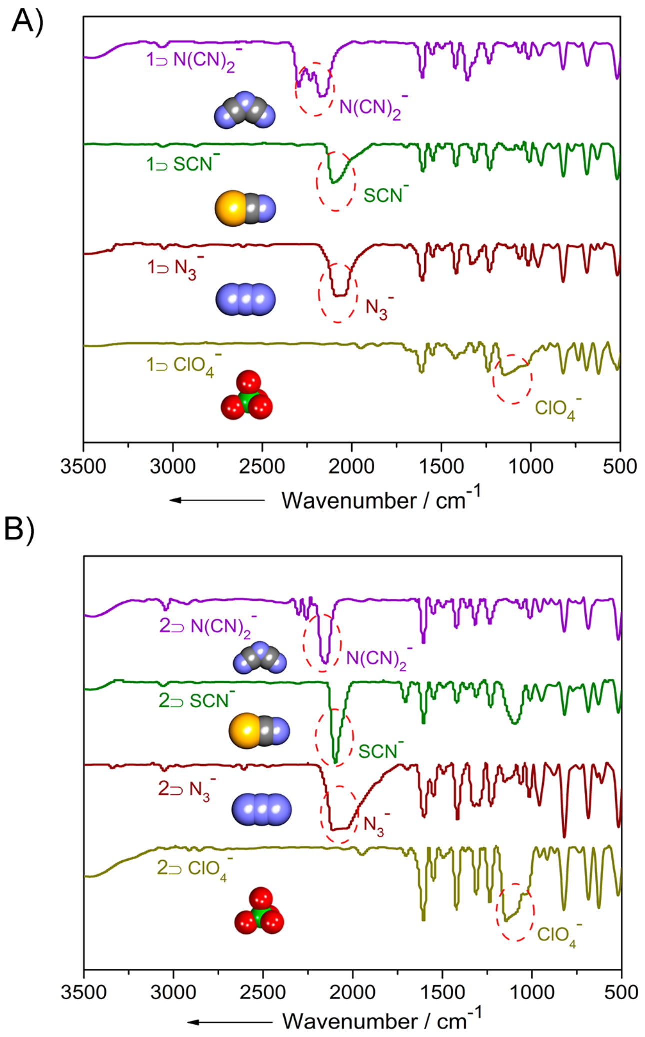


Figure 4. FT-IR spectra of (A) $\mathbf{1}\supset\mathrm{ClO_4}^-$ and its anion-exchanged products with highlighted bands of the corresponding anions and (B) $\mathbf{2}\supset\mathrm{ClO_4}^-$ and its anion-exchanged products with highlighted bands of the corresponding anions (anions are weakly coordinating (or noncoordinating) or strongly coordinating in nature).

monitored by FT- IR spectroscopy. Each product was separated and characterized using FT-IR spectroscopy and PXRD measurements. FT-IR spectra showed that strong bands associated with the exchanged anions were observed in each of the two cases.

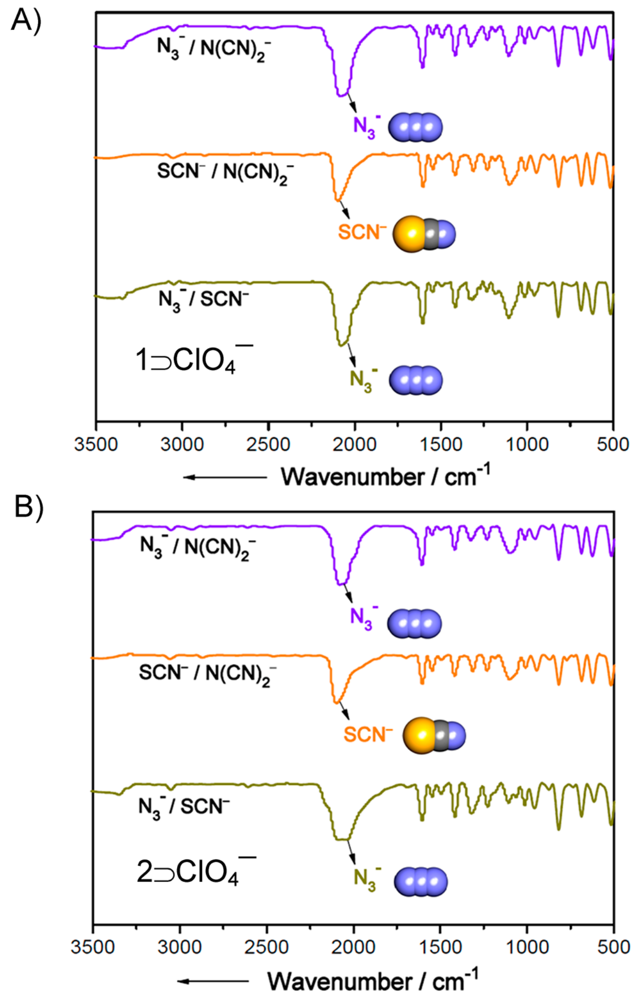


Figure 5. FT-IR spectra for different binary mixtures of (A) $\mathbf{1}\supset\mathrm{ClO_4}^-$ and (B) $\mathbf{2}\supset\mathrm{ClO_4}^-$.

The disappearance of bands related to $\mathrm{ClO_4}^-$ validated the process. Other peaks in the spectra remained virtually unchanged, which may suggest that the skeletal structure of the frameworks remained intact after the exchange process. The strong bands associated with $\mathrm{ClO_4}^-$ (~1100 cm^{-1}) were significantly weakened, indicating that $\mathrm{ClO_4}^-$ in $\mathbf{1}\supset\mathrm{ClO_4}^-$ and $\mathbf{2}\supset\mathrm{ClO_4}^-$ was exchanged by the incursive anions. Besides,the decrease of the $\mathrm{ClO_4}^-$ signal, new peaks were observed in both compounds at ~2035 cm^{-1}(characteristic of $\mathrm{N_3}^-$), ~2088 cm^{-1} (characteristic of SCN^-) and ~ 2150 cm^{-1} (characteristic of $\mathrm{N(CN)_2}^-$), which confirmed that anion exchange reactions have occurred (Figure 4). A UV−vis spectrophotometry experiment was also performed to check the extent of the anion exchange process by taking the supernatant solution of the exchange reaction mixtures. Unfortunately, we were unable to get the extent of this process as the absorption maxima of incursive anions almost coincide with the $\mathrm{ClO_4}^-$ absorption maxima (~200 nm) (Figure S34, Supporting Information). However, the progressiveness of the exchange process was confirmed by the appearance of a new absorption band ~281 nm with increasing absorbance at various time intervals (Figures S38−S41, Supporting Information). We tried to find the extent of anion exchange by performing inductively coupled plasma mass spectrometry (ICP-MS) analysis, but we could not get fruitful and conclusive data. Although CHN analysis of dried exchanged samples of both frameworks gave inconsistent data, ~80−90% exchange could be achieved for both cases. PXRD patterns of the anion-exchanged products of both compounds are quite different for different types of anions (Figures S15 and S16, Supporting Information). These variations in PXRD patterns arise because of the different coordinating tendencies, shapes, and sizes of various anions. SCN^- and $\mathrm{N_3}^-$ being strongly coordinating anions can easily replace the coordinated $\mathrm{ClO_4}^-$ anions from the respective parent frameworks and may induce structural changes after the exchange process, whereas $\mathrm{N(CN)_2}^-$ being a weakly coordinating anion may fit into the framework in such a way that the structural change will be less as compared to the SCN^- and $\mathrm{N_3}^-$ cases after the exchange process. Thus, here anions are playing the role of external chemical stimuli for the structural changes in the course of the exchange process. The above anion exchange process occurs in heterogeneous systems, and the

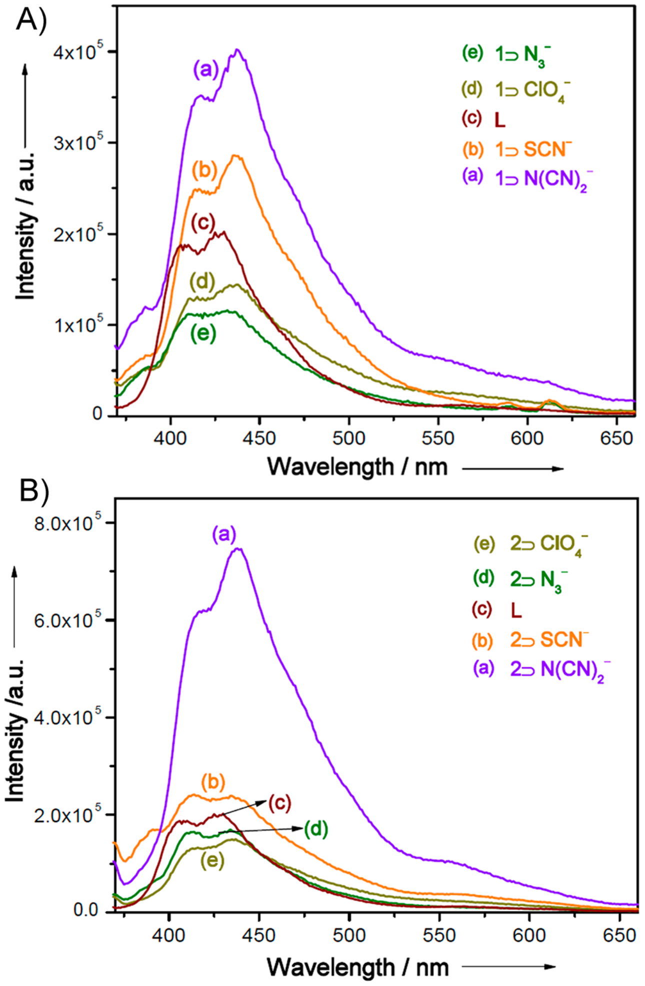


Figure 6. Solid-state luminescence spectra of (A) $\mathbf{1}\supset ClO_4^-$ and its various anion-exchanged products and (B) $\mathbf{2}\supset ClO_4^-$ and its various anion-exchanged products at rt.

experiments were done by taking single crystals of both compounds in methanolic solutions of various anions separately. The morphology of the parent and exchanged MOF particles were also analyzed by SEM (Figures S26−S32, Supporting Information). For both cases, the morphology remains almost same and slight changes in morphology may be ascribed to the structural changes after the exchange process as observed in the PXRD patterns. To compare the diffusion rate in the anion exchange process of both frameworks, in situ UV−vis spectrophotometry and FT-IR analysis were performed by taking the supernatant solution of the exchange reaction mixtures. UV−vis spectrophotometry and FT-IR analysis after a certain time revealed that $\mathbf{2}\supset ClO_4^-$ displayed more diffusion for all three anions as compared to $\mathbf{1}\supset ClO_4^-$(Figures S23 and S34−S37, Supporting Information). The higher diffusion rate in the anion exchange process of $\mathbf{2}\supset ClO_4^-$ may be ascribed to the larger void available in its structure compared to that of $\mathbf{1}\supset ClO_4^-$. The availability of bidentate coordinated ClO_4^- and the compact structure of $\mathbf{1}\supset ClO_4^-$ make it sluggish toward the anion exchange process. The reversibility of this anion exchange was checked with a methanolic solution of $NaClO_4$ (1 mM/10 mL). FT-IR spectra showed no uptake of ClO_4^- in any of these exchanged products, indicating reversibility could not be achieved in these cases.

Compared to anion exchange, anion selectivity, i.e., capturing specific anions in the presence of other anionic competitors, is more significant and challenging. The guest anion affinity of the frameworks was investigated by performing anion exchange experiments by taking various binary mixtures of anions: N_3^-/SCN^-, N_3^-/$N(CN)_2^-$, and SCN^-/$N(CN)_2^-$. In a typical experiment, crystals of $\mathbf{1}\supset ClO_4^-$ and $\mathbf{2}\supset ClO_4^-$ were separately immersed in a methanolic solution of mixed anions in equimolar concentration. The FT-IR spectroscopic tool was used to examine preferential exchange of the anion from the mixture. Careful analysis of the FT-IR spectra showed that all three combinations underwent preferential uptake. N_3^- was selectively taken from N_3^-/$N(CN)_2^-$, and with SCN^-/$N(CN)_2^-$, SCN^- was preferentially exchanged. However, when the experiment was conducted with N_3^- and SCN^-, N_3^- was preferred over SCN^-(Figure 5). Hence, the order of affinity of guest anions for the framework was $N_3^- > SCN^- > N(CN)_2^-$. PXRD patterns of binary anionic composites of both frameworks suggest very similar affinities for the frameworks (Figures S17 and S18, Supporting Information). These variations in the guest anion affinity of the frameworks may be due to the different coordinating abilities, sizes, and shapes of the guest anions.

TGA of compound $\mathbf{1}\supset ClO_4^-$ showed ~8% weight loss at ~185 °C corresponding to the loss of free guest molecules in the framework and thereafter showed no weight loss up to 280 °C (Figure S24, Supporting Information), whereas $\mathbf{2}\supset ClO_4^-$ showed a 20% weight loss around 175 °C which is consistent with the loss of guest molecules and then showed no weight loss up to 300 °C (Figure S25, Supporting Information). Both compounds $\mathbf{1}\supset ClO_4^-$ and $\mathbf{2}\supset ClO_4^-$ displayed anion-switchable luminescent behaviors. Diffuse reflectance spectra were recorded for $\mathbf{1}\supset ClO_4^-$, $\mathbf{2}\supset ClO_4^-$, and all the anion-exchanged compounds to determine the excitation wavelength. These reflectance spectra of the exchanged compounds were found to be similar to those of their parent compounds for both set of compounds. $\mathbf{1}\supset ClO_4^-$ and its anion-exchanged compounds showed minimum reflectance at a wavelength of ~355 nm (Figure S42, Supporting Information), whereas, in case of $\mathbf{2}\supset ClO_4^-$ and its corresponding anion-exchanged products, minimum reflectance was observed at a wavelength of ~350 nm (Figure S43, Supporting Information). Solid-state photoluminescence spectra of powder samples of the two batches which included the parent compounds and the anion-exchanged products were measured at room temperature. Upon photoexcitation at 355 nm, L displayed two emission bands at 408 and 427 nm. $\mathbf{1}\supset ClO_4^-$ showed an emission with a maximum at around 432 nm and a higher energy but less intense shoulder at 411 nm. All the other anion-exchanged products displayed emission bands with intensity maxima similar to that of compound $\mathbf{1}\supset ClO_4^-$. For $\mathbf{1}\supset N(CN)_2^-$, the band obtained was at around 437 nm with a less intense shoulder at 416 nm. In the case of $\mathbf{1}\supset SCN^-$, an intensity maximum at 436 nm and a higher energy shoulder at 415 nm were observed. However, for $\mathbf{1}\supset N_3^-$, two bands were located at 435 and 413 nm, the former being more intense. The anion-exchanged compounds exhibited different emission intensities compared to the parent compound $\mathbf{1}\supset ClO_4^-$. The highest enhancement in fluorescence was observed in the case of $\mathbf{1}\supset N(CN)_2^-$ followed by $\mathbf{1}\supset SCN^-$; however, $\mathbf{1}\supset N_3^-$ showed fluorescence quenching with respect to $\mathbf{1}\supset ClO_4^-$ (Figure 6A). π^*−n or π^*−π intraligand (IL) transitions are possible for the emissions of $\mathbf{1}\supset ClO_4^-$ and the exchanged compounds. The low-energy emissions in the 430−440 nm region may arise due to mixed events, IL and metal-to-ligand charge-transfer (MLCT) transition. Solid samples of $2\supset ClO_4^-$ showed an emission profile similar to that of $1\supset ClO_4^-$ upon photoexcitation at 350 nm at room temperature. The parent compound showed two emission bands at 413 and 434 nm, respectively. The anion-exchanged compounds, viz., $2\supset N(CN)_2^-$, $2\supset SCN^-$, and $2\supset N_3^-$ displayed emission bands with intensity maxima at 437, 435, and 434 nm and higher energy shoulders at 417, 414, and 412 nm, respectively. Similar to the trend observed in the case of **1**, $2\supset N(CN)_2^-$ showed the highest intensity profile, followed by $2\supset SCN^-$ and $2\supset N_3^-$ (Figure 6B). The plausible rationale to the variation in luminescence intensities can be attributed to the diverse electronic interactions of the respective anions with the framework and metal node, along with their characteristic coordinating tendencies, sizes, shapes, and geometries.

■ CONCLUSION

To conclude, use of cis/trans conformation based flexible N-donor ligands along with different solvent templates gave two supramolecular isomers based on MOFs. Both frameworks contain coordinated ClO_4^- anions which can be easily exchanged with two types of anions. Both compounds exhibit affinity of guest anions based their coordinating tendencies. The frameworks show anion-driven structural dynamism. Both compounds show anion-switchable tunable luminescence. Such anion-switchable tunable luminescent behavior can seek applications in the field of anion sensing and removal.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details, crystal structures, PXRD and TGA data, IR, UV, diffuse reflectance, and solid-state photoluminescence spectra, SEM images, and crystal structure data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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