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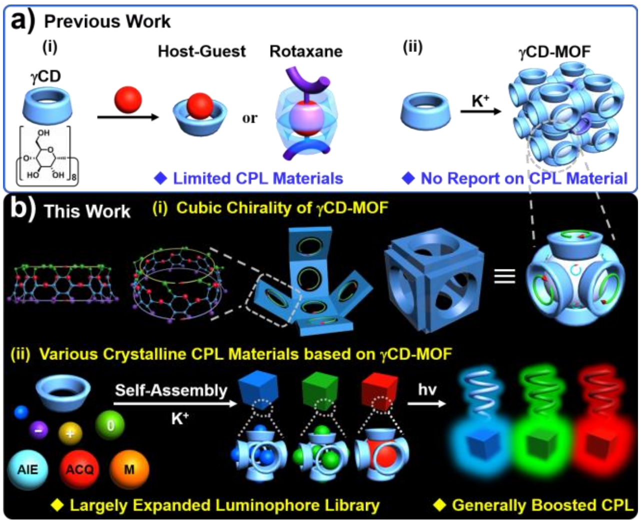
Emerging Cubic Chirality in γCD-MOF for Fabricating Circularly Polarized Luminescent Crystalline Materials and Size Effect

Liangyu Hu, Kun Li, Weili Shang, Xuefeng Zhu,* and Minghua Liu*

Abstract: *As an important chiral MOFs, the chiral feature of γCD-MOF, especially the emergent cubic void was not unveiled so far. Herein, through the host-guest interaction between γCD-MOF and achiral luminophores with different charges and sizes, we revealed the unique cubic chirality of the emerging void in γCD-MOF as well as a size effect on CPL induction for the first time. Numerous achiral luminophores could be integrated into γCD-MOF and emitted significantly boosted circularly polarized luminescence. While the small sized luminophores preferred to be loaded into the intrinsic void of γCD, the large ones were selectively encapsulated into the cubic void. Interestingly, when the size of the guest luminophores was close to the cubic size, it showed determined and strong negative CPL. Otherwise, either positive or negative CPL was induced. This work not only showed an insightful understanding of the emergent cubic chirality of γCD-MOF, but also provided a general platform for the preparation of crystalline CPL materials.*

Chirality is of essential importance in biological system, pharmaceutical industry and material science.[1] Molecular chirality concerns on a chiral molecule non-superimposable with its mirror image. When chiral molecules connected each other like cyclodextrins (CDs), including α-, β-, and γCD, they could lead to chiral voids (Scheme 1a).[2] Such covalent chiral voids have been extensively utilized to induce the supramolecular chirality of achiral molecules.[2a] Recently, γCD was self-assembled into metal-organic framework (MOF)[3] with alkali metal ions, pioneered by J. F. Stoddart et al.[4] In γCD-MOF, a newly supramolecular cubic box is formed by the self-assembly of six γCDs with a size of 1.7 nm, which is much larger than the intrinsic void of γCD (0.95 nm). Furthermore, in contrast to the ordinary cube which is symmetrical and achiral, the cubic void of the γCD-MOF is surrounded by six-γCD faces and expeted to be chiral. We can denote this novel kind of supramolecular chirality as "cubic chirality" (Scheme 1b). Unfortunately, while the γCD-MOF was extensively invesitgated as platforms for various functional materials,[5] the chiral features of this brandnew cubic box were scarcely reported. Here, through the study of the host-guest interaction between γCD-MOF and achiral luminophores, we have invesitgated induced circularly polarized luminescence (CPL)[6] by γCD-MOF and unveiled the chiral feature of the unique cubic void.

Circularly polarized luminescence (CPL) defines the differential emission of left- and right-circularly polarized light from chiral systems.[6] It reflects the chiral properties of the excited state and has potentially enchanting photonic applications including true 3D displays, advanced information storage and processing, smart sensing.[7] Generally, the fabrication of CPL materials needs the molecules to contain both chiral and luminescent units.[6,8] However, a combination of the achiral luminophore with the chiral voids can sense the chirality of the voids and simultaneously provides a general way for the fabrication of CPL materials.[9] We have found that numerous achiral luminophores, covering neutrally, positively and negatively charged, aggregation-caused quenching (ACQ) and aggregation-induced emission (AIE) molecules, with the size ranged from 0.5 to 2.1 nm, could be integrated into γCD-MOF (lum@γCD-MOF) and emitted significantly boosted CPL. Remarkably, the chiral cubic void showed an unprecedented size effect and induction ability. Small sized luminophores preferred to be loaded into the intrinsic void of γCD, while the large ones selectively into the cubic void. When the size of the guest luminophores is close to the cubic size, it showed strong negative CPL. Moreover, either single AIEgens or ACQ luminophores could emit strong CPL in chiral cubic void due to space confinement. This work unveiled the unique feature of the cubic chirality of γCD-MOF for the first time and provided a versatile platform for fabricating crystalline CPL materials from a vast number of achiral luminophores.



Scheme 1. (a) Previous work: (i) two typical kinds of CPL materials based on CDs and (ii) the preparation of γCD-MOF. (b) This work: (i) illustration of the cubic chirality of γCD-MOF and (ii) various crystalline CPL materials based on γCD-MOF and achiral luminophores with generally boosted CPL.

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The preparation of the lum@γCD-MOF was through an in-situ encapsulation strategy reported in the literature.[4a, 5e] Briefly, under ambient condition, the methanol vapor slowly diffused into the aqueous solution of the mixtures of γCD, KOH and luminophores, transparent crystals were acquired after several days. The powder X-ray diffraction (XRD) of the crystals has the same pattern as reported, indicating the formation of the cubic framework (Figure S1).[4a, 5e] The emerging of the larger cubic void of γCD-MOF was expected to greatly expand the encapsulation capability of γCD. To demonstrate this, two Ru complexes with sizes larger than γCD (0.95 nm) were selected (Figure 1a). Both complexes could not be encapsulated into γCD-MOF by immersing the blank γCD-MOF into their methanolic solution (*i.e.* the post-synthetic encapsulation strategy, Supporting Information, Figure S2), indicating that they could not be shipped through the γCD windows of the cube. That is, γCD could not encapsulate the two Ru complexes. However, the *in-situ* encapsulation strategy could afford deep-orange (Ru-BPy) and light-yellow (Ru-BPhen) colored crystals respectively, which suggested that the two Ru complexes were encapsulated into the crystal grains of γCD-MOF. The XRD characterization of the lum@γCD-MOF crystals revealed the preservation of the cubic frameworks after the luminophores encapsulation (Figure S1).[4a, 5e] Furthermore, when such crystals were dipped into methanol overnight, no leak of Ru complexes was observed. These experiments clearly demonstrated that the two complexes were undoubtedly encapsulated into the cubic void instead of the void of γCD during the cube formation.

Similar absorption bands of metal-to-ligand charge transfer (MLCT) at 375-475 nm were observed for both Ru complexes (Figure 1b,c and Figure S3,S4).[5b, 10] After the encapsulation into γCD-MOF, the MLCT bands remained unchanged. Meanwhile, strong emission typical of Ru-polypyridine complex at 611 nm[10] was shown for both Ru complexes based γCD-MOF (Figure 1f,g). These spectral results suggested that both Ru complexes were molecularly segregated in the cubic void of γCD-MOF.

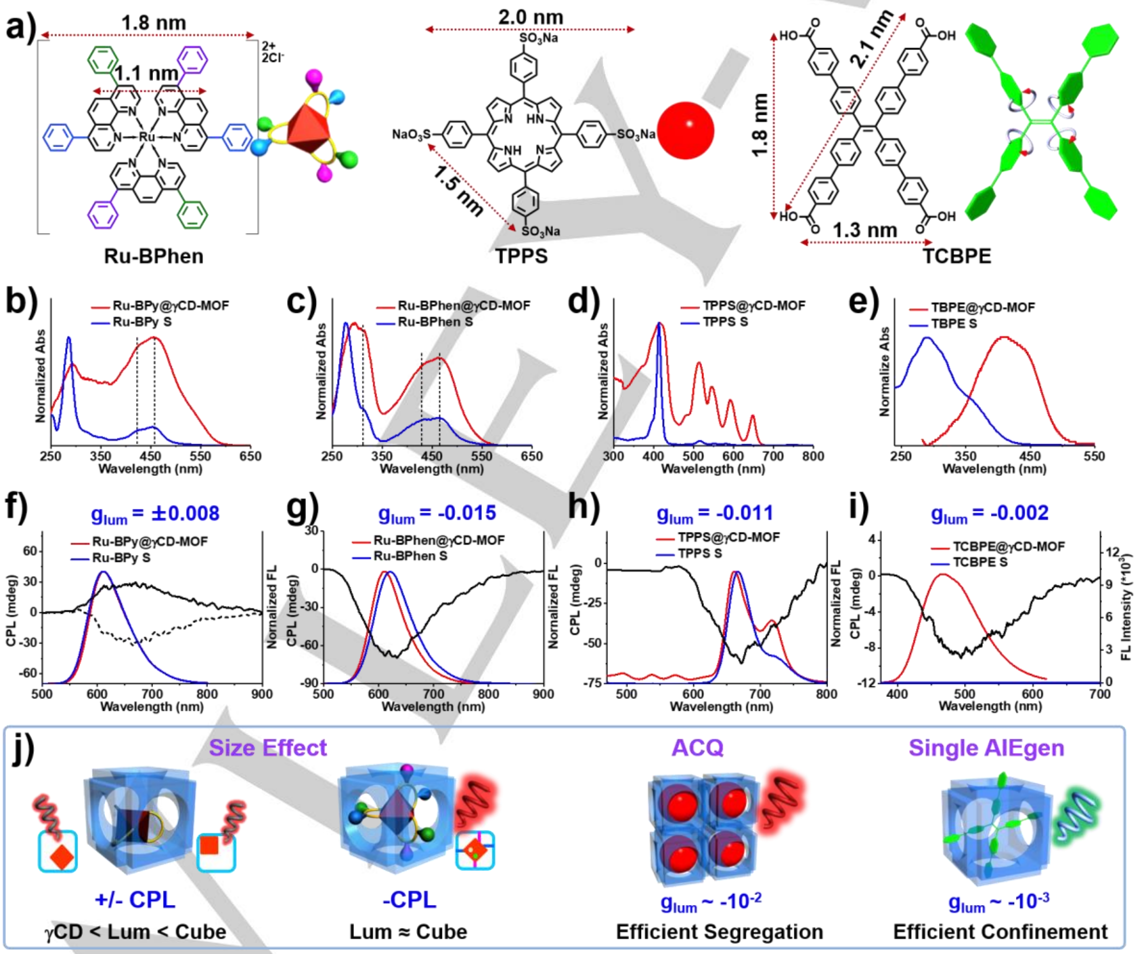

Figure 1. CPL rule in chiral cube of γCD-MOF. (a) Molecular structures, (b-e) UV-Vis, (f-i) CPL and FL (black lines for CPL and others for FL) spectra of Ru complexes, represented ACQ (PDITS) and AIE (TCBPE) molecules. (j) Illustration of the size effect and the mechanism of CPL induction of ACQ and single AIEgen based on cubic chirality.

Remarkably, strong orange-red CPL signals were observed for the two Ru complexes based γCD-MOF crystals. Interestingly, either positive or negative CPL signals could be observed for Ru-BPy@γCD-MOF, while a strong negative CPL signal was

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exclusively obtained for Ru-BPhen@γCD-MOF (Figure 1f,g and Figure S5,S6). Clearly, the CPL sign of the Ru-BPy@γCD-MOF was uncontrollable, while that of the Ru-BPhen@γCD-MOF was determined. Fluorescence spectra showed that the emission band of Ru-BPy@γCD-MOF was the same as that of the aqueous solution of Ru-BPy (Figure 1f). In contrast, the emission band of Ru-BPhen@γCD MOF has a 9 nm shift to 611 nm, compared to that of the aqueous solution of Ru-BPhen (620 nm) (Figure 1g). This suggests that the interaction between Ru-BPhen and γCD-MOF was stronger than that of Ru-BPy and γCD-MOF. This induction was further supported by the absorption spectra: the absorption band of the ligand of Ru-BPy shifted only 6 nm to 292 nm in γCD-MOF compared to the aqueous solution. However, the ligand absorption of Ru-BPhen shifted 17 nm from 277 nm in aqueous solution to 294 nm in γCD-MOF, and the absorption intensity of 321 nm was obviously enhanced in γCD-MOF. The core of the molecular structure of Ru-BPhen was comparable to that of Ru-BPy (Figure S2), whose size (1.15 nm) was much smaller than the cubic void (1.7 nm). Nevertheless, Ru-BPhen was composed of a periphery of six benzene rings, which extended its size to 1.8 nm, a little larger than the cubic void. The unique molecular structure of Ru-BPhen fitted well to the cubic void with six-γCD windows (Figure 1j). Consequently, Ru-BPhen was well constricted in the confined space of the cubic void and the strong negative CPL was exclusively induced. On the contrary, there were much free space of the cubic void for Ru-BPy, and it would distribute at different position of the cubic void, which might be contributed to the either positive or negative CPL induction. Meanwhile, the dissymmetry factor g_{lum} of Ru-BPhen (-0.015) was almost twice that of Ru-BPy (0.008), further indicating that the confinement effect of Ru-BPhen than Ru-BPy in the cubic void of γCD-MOF.

Obviously, there was a size match effect on CPL induction in the cubic void of γCD-MOF. That is, when the size of the luminophores was close to the size of the cubic void, the luminophores could be well confined in the cubic void and consequently strong negative CPL signals were exclusively induced. Otherwise, when the size of the luminophores was smaller than that of the cubic void, the interaction between the luminophore and the cubic void of γCD-MOF was not strong enough to control the sign of the induced CPL. This is an unprecedented phenomenon on CPL induction. Another three pairs of luminophores were also carefully investigated (Figure S7). Similar results were obtained, strongly supporting that the size effect on the excited-state chiroptical induction is a general rule for such cubic chirality. It is worthy of note that while both positive and negative ECD and CPL signals were observed for achiral middle-sized guests, positive ECD signals were always observed for Ru-BPy@γCD-MOF, although its CPL signals were still uncontrollable (Figure S8). It seemed that there was a certain enantiomeric excess of Ru-BPy in γCD-MOF during in-situ encapsulation, but the CPL was dominated by the chiral cube of γCD-MOF (for detail see Supporting Information).

We further introduced large ACQ molecules into γCD-MOF to investigate the cubic chirality. TPPS, a typical ACQ luminophore, was in-situ encapsulated into γCD-MOF (Figure 1a and Figure S9). UV-Vis spectra (Figure 1d) showed that the Soret B-band of TPPS@γCD-MOF was located at 413 nm, which was typical of TPPS monomer absorption and manifested the molecular distribution of TPPS in γCD-MOF.[11] Meanwhile, the Q-bands of TPPS@γCD-MOF were located at 514, 546, 592, and 648 nm and dramatically enhanced, which might be contributed to the restriction of the phenyl groups by the γCD-MOF.[11b] The results suggested that TPPS were well confined in the cubic void of γCD-MOF. As a result, the aggregation of TPPS was completely suppressed and TPPS@γCD-MOF was strongly luminescent. FL spectra (Figure 1h) showed that there was no apparent difference on the main emission peaks between the aqueous solution of TPPS and TPPS@γCD-MOF, which further suggested that TPPS was well segregated with each other by the cubic void of γCD-MOF. Significantly, both strong ECD (Figure S9) and intense CPL (Figure 1h) signals were observed for TPPS@γCD-MOF. Impressively, the dissymmetry factor g_{lum} was up to -0.011, which is the highest g_{lum} value of porphyrin compounds reported to date,[12] demonstrating the excellent chiral induction ability of the cubic void of γCD-MOF. Another large ACQ luminophore, PDITS, was also investigated (Figure S10). The absorption and emission behaviors were similar to that of the molecular state and were independent of different environmental solvents (Figure S11), indicating a molecular compartmentalization of PDITS in γCD-MOF. Strong negative CPL signal was also observed and the dissymmetry factor g_{lum} was up to -0.019, which is comparable to the highest g_{lum} (0.02) of covalent chiral systems based on perylene diimide (PDI) molecules.[13] Apparently, γCD-MOF is an efficient platform for the fabrication of CPL crystalline materials with high dissymmetry factors utilizing achiral ACQ luminophores.

Aggregation-induced emission (AIE)[14] is a phenomenon that the luminogens which are non-emissive at a molecular state, are induced to show strong emission under aggregation. The aggregation induced CPL (AICPL)[9d, 9e, 15] of the AIEgens has been well investigated. However, the CPL of segregated AIEgens was rarely reported.[9f] Here, the large AIEgen, TCBPE, was encapsulated into γCD-MOF (Figure 1a and Figure S12-S14). Compared to the basic aqueous solution of TCBPE, the absorption of the crystalline TCBPE@γCD-MOF was obviously red-shifted and the emissive intensity was greatly enhanced (Figure 1e,i), suggesting that the intramolecular rotation was restricted to some extent by the cubic framework of γCD-MOF. Significantly, the negative CPL was exclusively obtained, which indicated that the achiral AIEgens could be simultaneously endowed with both the emissive property and chirality through the restriction of intramolecular rotation[14] by the chiral framework of the chiral cube. The results demonstrated an insightful understanding of the chiral luminescence of the segregated AIEgens. It should be noted that for these segregated single molecular luminophores in γCD-MOF, while the fluorescence quantum yield (QY) of ACQ molecules was moderate, the QY of AIEgen, however, could be up to 69% (*i.e.*TCBPE@γCD-MOF, Table S1). This further indicated that γCD-MOF was a new kind of platform for efficient CPL materials produced from non-aggregated AIEgens.

In addition to large luminophores, small luminophores with the size smaller than the void of γCD (0.95 nm) could also be integrated into γCD-MOF (Figure 2 and Figure S15-19). Achiral luminophores with neutral, positive or negative charges could be encapsulated into γCD-MOF to emit from violet to red, and various crystalline CPL materials were therefore constructed covering the full-colored region (Figure 2). As mentioned above, the large luminophores were selectively encapsulated into the cubic void through the in-situ strategy. In principle, small luminophores could be encapsulated into the cubic void as well as the void of γCD. For the in-situ encapsulation of small luminophores, there was a strong host-guest interaction between the luminophores and γCD in aqueous solution. Consequently, the small luminophores could be selectively encapsulate into the void of γCD in γCD-MOF. This was well supported by the fact that the exclusively negative CPL signals were acquired from all small luminophores integrated γCD-MOFs, because there would be the size effect with either positive or negative CPL, if the small luminophores were encapsulated into the cubic void.

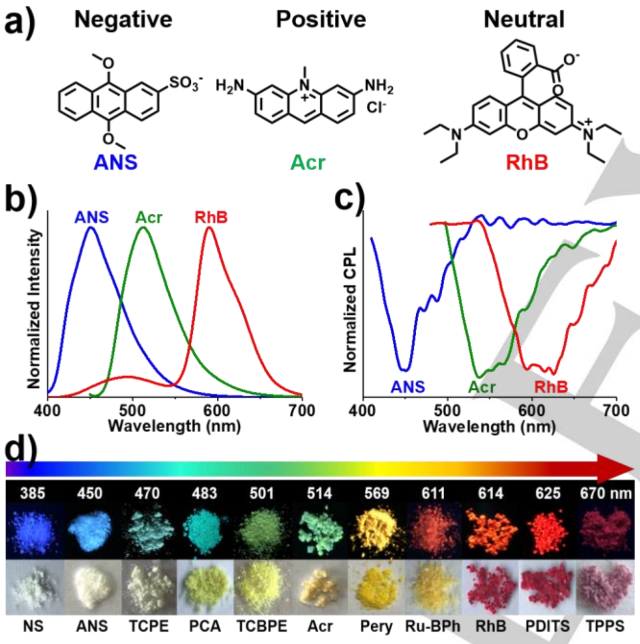

Figure 2. (a) Molecular structures, (b) FL and (c) CPL spectra of represented luminophores with negative, positive and neutral charges. For the spectra of other dyes, see Supporting Information. (d) Photographs of various CPL crystals of lum@γCD-MOF under the irradiation of 365 nm (upper) and visible light (lower).

We have also investigated the post-synthetic strategy, that is, to ship the small sized dye into γCD-MOF through dipping of the γCD-MOF into the solution containing dyes. Because the interior interface of γCD-MOF was wetted by the organic solvent in advance, the host-guest interaction of the luminophores and γCD was destroyed and the luminophores could be shipped into the cubic void of γCD-MOF by the organic solvent. In this case, the small dye molecules could randomly distribute in the cubic and uncontrollable CPL was obtained (Figure S20). This further supported that the in-situ fabrication method could lead to the small sized dyes fixed in the intrinsic γCD and exhibited negative CPL. It should be noted that for solid-state samples, there may be potential artifacts to chiroptical measurements, especially the linear dichroism (LD).[16] Therefore, the ECD, LD and CPL spectra have been carefully carried out to evaluate the contribution of the linear dichroism using the reported methods (for detail see Supporting Information).[16] It was confirmed that the chiral properties including CPL in γCD-MOF were reliable (Figure S21-23), and that the LD contribution to ECD was negligible, which mainly due to the low loading of the luminophore in γCD-MOFs (Figure S24).

The search of efficient methods to improve g_{lum} of CPL materials is one of the most important issues in developing CPL materials. It remains a great challenge to generally obtain high g_{lum} CPL materials via a versatile strategy. By means of the systematical investigation of the CPL spectra and the comparison of the dissymmetry factor g_{lum} values (Figure S25), we evaluated the chiroptical induction ability of different composites of the luminophores and γCD and γCD-MOF. It was found that γCD could hardly induced CPL in aqueous solution, and weak CPL in the amorphous powders of luminophores and γCD (lum@γCD). In contrast, all the tested luminophores could emit remarkably strong CPL in lum@γCD-MOF crystals (Figure S3,4,9,10,13-18). As shown in Figure 3a, γCD-MOF has dramatically boosted the CPL emission compared to other combinations. The results indicated that crystalline γCD-MOF is much more efficient for CPL induction.

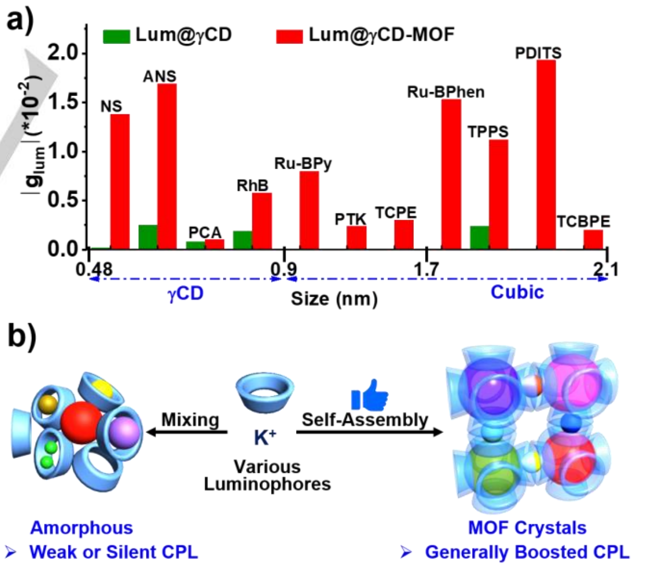

Figure 3. (a) The comparison of the absolute g_{lum} values of the amorphous lum@γCD powder and crystalline lum@γCD-MOF. (b) The mechanism of boosted CPL from lum@γCD-MOF. The disordered packing of γCDs and loss host-guest interaction between the luminophores and γCDs are responsible for the weak or silent CPL in the amorphous lum@γCD powders. In the crystalline γCD-MOF, the very ordered immobilization of γCDs and compact confinement of the luminophores in the chiral cubic void and the void of two γCDs with a rotaxane-like fashion are contributed to strong boosted CPL.

The mechanism of the boosted CPL by γCD-MOF from achiral luminophores could be illustrated in Figure 3b. The host-guest interaction contributed to the CPL induction.[17] For the ordinary composites of γCD and luminophores, like the amorphous powders, γCDs were loosely packed together with no order and there was no new void formed. The host-guest interaction between the luminophores and γCD was weak and limited to the intrinsic size of the void of γCD. Therefore, the weak or silent CPL was induced in lum@γCD powders. When γCD was self-assembled into γCD-MOF, however, not only was the ordering tremendously improved due to the crystalline packing of γCD, but also a new larger chiral cubic void was emerging, which greatly improved the encapsulation ability of γCD-MOF, and the library of the luminophores expanded from 0.5 to 2.1 nm in size. The larger luminophores could be selectively and orderly immobilized into the cubic void of γCD-MOF. The smaller ones could be selectively and tightly restricted into the void of γCDs to form rotaxane-like composite structures.[17c] Therefore, the CPL signal was generally and significantly boosted.

In summary, we unveiled the chiral features of the emerging cubic void of γCD-MOF for the first time by investigating the CPL properties of the luminophores integrated γCD-MOF. We have further developed various crystalline CPL materials utilizing a large family of economic achiral luminophores. The present work deepens the understanding of the induced excited-state chirality, and provided a versatile platform for the preparation of crystalline CPL materials with generally improved and high dissymmetry factor.

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Keywords: circularly polarized luminescence • metal-organic frameworks • cyclodextrin • chirality • host-guest

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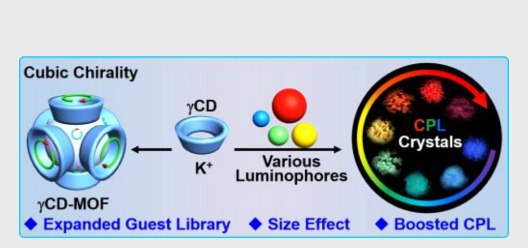

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