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Achiral Fluorescence Guests | Very Important Paper

Circularly Polarized Luminescence of Achiral Metal–Organic Colloids and Guest Molecules in a Vortex Field

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Abstract: Recently, scientists have reported a range of chiral fluorescence materials or chiral composites that can emit circularly polarized luminescence. Herein, two achiral metal–organic colloidal solutions were studied, showing active circularly polarized luminescence, which is observed in vortex stirring. The absolute values for g_{lum} are 0.05 and 0.03 and the plus or minus sign of g_{lum} depends on the colloidal struc-

Introduction

Circularly polarized luminescence (CPL) has attracted much attention owing to the potential applications in optical storage,^[1] flat panel display,^[2] photoelectric devices,^[3] etc. In the application of CPL functional materials, the photoluminescence asymmetric factor g_{lum} is of key importance.^[3,4] Scientists have found that the g_{lum} value could be greatly improved by the help of supramolecular self-assembly,^[5] which is always constructed by chiral supramolecular aggregates as chiral "hosts" and achiral photoluminescence small molecules as fluorophore "guests".^[6] However, when the interaction between the chiral "host" and the achiral fluorophore "guest" is strong enough for chirality transfer, which is of benefit to boost the g_{lum} value, the quantum yield (Φ) may be suppressed.^[6a] In this context, we would like to find some chiral physical field that is strong enough for the chirality transfer, but does not introduce a chemical influence on the quantum yield.

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ture and stirring direction, which make the property easy to manipulate. Further, the host-guest interaction study suggests both electrostatic interactions and coordination bonding may influence the chiroptical property from the colloidal solution to the guest molecule. Rhodamine 6G and its carboxylic acid derivative exhibit good quantum yields and acceptable g_{lum} values in the colloidal solution.

The construction of chiral structures usually relies on chemical reactions, which is problematic for enantiomeric synthesis.^[7] If CPL materials could be obtained from achiral components, and further, possess convenient modulation of handedness, it would surely encourage the development of CPL applications. In this sense, chiral physical fields, such as vortex stirring,^[8] circular polarized light,^[9] etc. should be taken into consideration. Both vortex field and the circular polarized light field are found to influence and convert the handedness of certain objects, which are built from achiral nanoscale matter. In this paper, we would like to share our study based on vortex stirring as the chiral physical source.

Vortex stirring is a common process in chemical labs, which is believed to make the mixture homogeneous. It is hard to think about its influence on the construction of chiral matter because the chiral force in the vortex is too weak to function on chemical processes. In 1991, Kondepud et al. reported a spontaneous mirror symmetry-breaking system of NaClO₃ crystals by involving vortex stirring. The resulting crystalline product was homochiral but with unpredictable handedness.^[10] Later studies demonstrated that vortex stirring generated a grind effect, which greatly encourages chirality amplification with the help of enantioselective cooperation.^[11] In 2001, Ribó et al. observed that vortex stirring greatly influenced the chirality of J-aggregates composed of achiral TPPS₃ ((5,10,15tris(4-sulfonatophenyl)-20-phenylporphyrin)).^[8a] In recent years, chiral assemblies composed of achiral BTAC (tris(ethyl cinnamate) benzene-1,3,5-tricarboxamide) or TPPS₄ (tetra-(4-sulfonatophenyl) porphyrin) were prepared in the vortex flow generated in a microfluidic device, with vortex-responsive handedness.^[8c,e] The shear force generated in the vortex field was found to have a select effect on the chiral initial $nucleation.^{\scriptscriptstyle[8a-e]}$

Unlike these two kinds of vortex-responsive system, a third kind of system was reported by several labs, showing dynamic

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and switchable chiroptical properties and the ability to turn them ON/OFF by controlling the vortex stirring.^[8f-n] The third kind of vortex-responsive system always includes nanoscale assemblies that possess anisotropic morphologies, such as fibers. After decades of study, Ribó et al. pointed out that the chiroptical properties of those systems were generated by the dynamic chiral arrangement of nanoscale assemblies in the vortex flow.^[8],n] The limiting Curie groups were adopted for discussion.^[12] The achiral nanofibers in the stagnant state were found to be isotropous and belonged to the achiral $\infty/\infty m$ group. When the vortex field was generated by magnetic stirring at the bottom, the system including nanofibers was found to be of conical group ∞ , which allowed the existence of enantiomorphism, and consequently exhibited chiroptical properties. To date, the study of vortex-responsive matter has mainly centered around the chiroptical properties of their ground state. The CPL properties of such systems remain unknown. In 2011, Okano et al. demonstrated that achiral Rhodamine B could be endowed with CPL properties by adding it into a stirring supramolecular oligomer gel.^[13] However, the stirring gel system shows no CPL properties. Thus, we are curious about the potential CPL properties of nanoscale supramolecular systems in vortex.

As shown in Scheme 1, two long-shaped hydrazide compounds were selected because of their potential ability in coordination bonding. In the previous study, X-ray crystallographic structural resolution demonstrated the coordination bonding between hydrazide compounds and $M^{2+/3+}$ (M=Fe, Mn, Cu, Zn, etc.) was a chelating coordination mode, which makes the resultant complex stable in the solution.^[14] Our pervious study revealed the long-shaped and bi-functional groups of L1 can lead the coordination assembly with Zn^{\parallel} to form an anisotropic morphology that may easily respond to the vortex field.^[14d,e] Secondly, the coordination environment for $M^{2\,+/3\,+}$ in the hydrazide-based coordination compounds in the CCDC (Cambridge Crystallographic Data Centre) database suggests a general solvated effect. Scientists have found that the replacement of coordinated solvent could lead to secondary assembly,^[14b] which indicates abundant host-guest chemistry. In this work, two metal-organic colloids from achiral units are fabricated, and whose unidimensional morphology and flexibility endow them with the ability to respond to a vortex. Both colloids show CPL properties in the vortex field, and the guests doped in the colloid also exhibit strong CPL.



Scheme 1. Molecular structure of L1 and L2, and the preparation of Zn-L1 and Zn-L2.

Results and Discussion

Chiroptical study of Zn-L1 and Zn-L2

The preparation of Zn-L1 and Zn-L2 follows the process outlined in Scheme 1. The mixed colloidal solution should be aged for at least two months for uniformity and reproducibility. Atomic force microscopy (AFM, Figure 1a,e) and SEM (Figure S12 in the Supporting Information) microscopy suggest that both colloids adopt nanofiber structures with diameters of about several nanometers. The IR spectra (Figures S13 and 14 in the Supporting Information) and UV/Vis absorption spectra (Figure 1 b,f) indicate coordination interactions between Zn^{II} ions and L1/L2 possibly occur. It is assumed that the thin nanofiber nature may give the chance to respond to the vortex field. In addition, the remaining absorption peaks around 3000 cm⁻¹ in the IR spectra (Figures S13 and 14 in the Supporting Information) indicate potential active sites for host–guest chemistry.

In the following study, the chiral vortex was generated by in situ magnetic stirring in the cuvette, which was placed in the CD spectrometer, the direction of which was labeled as clockwise (CW) or counter clockwise (CCW). If the magnetic stirring is withdrawn, the recorded spectrum was labeled as STAY. As shown in Figure 1, when the Zn-L1 is in CW or CCW vortex, it shows a Cotton effect, which means it is CD active in its characteristic absorption band. A similar phenomenon was observed for Zn-L2. Further, the dependence of the CD signals on stirring speed and time was investigated, suggesting quite



Figure 1. From top to bottom: AFM images, UV/Vis absorption spectra, CD spectra, and LD spectra of Zn-L1 (a–d) and Zn-L2 (e–h). ([Zn-L1]= 1.25×10^{-4} M, [Zn-L2]= 6.25×10^{-5} M, stirring speed: 240 rpm).

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stable CD in the range of 240–960 rpm stirring speed and > 30 min stirring time (Figure S15 in the Supporting Information). As a contrast, the fresh Zn-L1, which was used without aging for months, is CD silent (Figure S16 in the Supporting Information). Thus, the nano fibrous structure of Zn-L1/L2 may be crucial to the active CD properties in the vortex.

Although the morphology for Zn-L1 and Zn-L2 is quite similar, the CD spectra for both systems are different, indicating the relationship with the intrinsic molecular structure. In the range 320-420 nm, there are a pair of peaks and valleys with same direction in the spectra of both Zn-L1 and Zn-L2. Whereas in the range 250-300 nm, the CD spectrum of Zn-L1 shows another pair of peaks and valleys, whereas the spectrum of Zn-L2 is almost silent. If we look at the absorption spectra of both systems, the absorption in the range 320-420 nm could be attributed to the ligand-to-metal charge transfer (LMCT) between the metal ion and the organic ligand; whereas the absorption in the range 250–300 nm should be attributed to the $n-\pi^*$ or π - π * transitions of the ligand. In this context, it is possible that the similar coordination interaction between Zn^{II} and L1/ L2 leads to a similar Cotton effect in the CD spectra, but the different molecular structures of L1 and L2 clearly influence the CD properties in the corresponding absorption band.

Considering the anisotropic appearance of the Zn-L1/L2 nano fibrous morphology, the linear dichroism (LD) properties were studied as well. As shown in Figure 1 d, the LD spectrum of Zn-L1 without vortex stirring shows an almost horizontal curve. Once the Zn-L1 was in vortex, the LD spectra of both CW and CCW direction exhibit the same peaks and valleys but with different intensities, which indicates the nanofibers of Zn-L1 might orderly orient in either direction in the vortex. A similar phenomenon was observed in the Zn-L2 system (Fig-

ure 1 h). In both cases, it is possible that the observed CD properties may be related to the LD property that are attributed to their natural anisotropic appearance.

In our study, Zn-L1 emits blue luminescence ($\lambda_{em} = 460$ nm, $\Phi = 3.2\%$; fluorescence lifetime $\tau = 0.20$ ns), and Zn-L2 emits yellow luminescence ($\lambda_{\rm em}$ = 525 nm, Φ = 4.4%; τ = 0.22 ns; Figures S17 and 18 in the Supporting Information). Both of them exhibit an excitation wavelength that depends on the concentration (Figure S17 in the Supporting Information). Take Zn-L1 for example: when the colloidal solution concentration is diluted from 1.25×10^{-2} M to 1.25×10^{-6} M, the emission spectra remain almost unchanged in emission wavelength but the intensity is altered. In contrast, the excitation spectra show different excitation wavelengths with significant blueshifts and multiple peaks, which indicate the excitation wavelength could range from 300-400 nm. According to the CPL test requirements, an excitation wavelength that close to the emission bands will greatly disturb the observation. Consequently, the CPL spectra study for both Zn-L1 and Zn-L2 adopts 350 nm as the excitation wavelength. As shown in Figure 2a-c, when using 350 nm light to excite the Zn-L1, there is no CPL response from the stagnant Zn-L1, which means the emission intensity of right-handed circularly polarized light (I1) and righthanded circularly polarized light $(I_{\rm R})$ are equal. When the Zn-L1 was in CCW vortex, there is a negative CPL (ΔI) peak at 430 nm, which demonstrates the Zn-L1 in CCW vortex emits weaker $I_{\rm L}$ rather than $I_{\rm R}$. The dissymmetry factor $(g_{\rm lum})$ is -0.05at 430 nm. For the Zn-L2, as shown in Figure 2 d-f, a positive CPL peak appeared when the Zn-L2 was in CCW vortex. The g_{lum} is +0.03 at 500 nm, which means the Zn-L2 in CCW vortex emits stronger $I_{\rm L}$ rather than $I_{\rm R}$.



Figure 2. CPL spectra for Zn-L1 (a-c) and Zn-L2 (d-f). ([Zn-L1]=[Zn-L2]=1.25×10⁻³ M, stirring speed: 1000 rpm).

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From host to guest: chiroptical transfer of CD properties

In our previous study, the Zn^{II}-based salicylhydrazide gel showed negative charge, and favored the adsorption of positively charged dye molecules.^[14e] In this work, several charged dye compounds were introduced into the Zn-L1 colloidal solution. When negatively charged dyes, such as Congo Red and Methyl Orange, were used, the resulting mixtures show no Cotton effect in their characteristic absorption band in the vortex stirring state, similarly with the neutral uncharged Alizarin Yellow R and Nile Red (Figure S19 in the Supporting Information). On the contrary, when positively charged dye compounds such as Crystal Violet (CV), Methylene Blue (MB), thioflavin T (ThT), and Perylene Diimide derivative (PDI) were introduced into the stirring Zn-L1, a new CD peak was detected in the characteristic absorption band of the dye compounds and the handedness of the Cotton effect is dependent on the vortex direction (Figure 3).

The molecular diameters for the guest molecules are 14× 13×3 Å for CV, $14 \times 5 \times 2$ Å for MB, $14 \times 5 \times 2$ Å for ThT, and 21×10^{-10} 7×4 Å for PDI. The small scale of the molecular structure and disordered thermal vibration in solution make them LD silent in solution. However, the LD spectra for those compounds embedded in the Zn-L1 colloidal solution exhibit LD peaks at their absorption band, which indicates an ordered arrangement of the dye molecules trapped in the stirring colloidal solution. In this way, the chiroptical property observed herein should be attributed to the ordered arrangement of those molecules in the vortex by the help of the Zn-L1 colloidal solution. It is noticed that the PDI molecule possesses two positive charges, which may lead to stronger interaction with the Zn-L1 host. That might be the reason for the quite high CD intensity in the recorded spectrum (Figure 3 d). How to understand the chiroptical properties for these dye compounds endowed by the stirring colloidal solution? What is the relationship with the normal molecular chirality? A popular positively charged chiral compound, tris(1,10-phenanthroline) ruthenium(II) cation (Δ / Λ -[Ru(phen)₃]²⁺) was selected. As shown in Figure 4a, there was a pair of peaks and valleys for the enantiomers in the range 400-600 nm, which should be attributed to the intrinsic



Figure 4. (a) CD spectra of the Δ/Λ -[Ru(phen)₃]²⁺ solution and Zn-L1 + Δ/Λ -[Ru(phen)₃]²⁺ in the STAY state. (b) CD spectra of Zn-L1 + Λ -[Ru(phen)₃]²⁺ in the stirring state. ([Zn-L1] = 1.25 × 10⁻³ M, concentration of Δ/Λ -[Ru(phen)₃]²⁺ and *rac*-[Ru(phen)₃]²⁺ are 1.0 × 10⁻⁴ M, stirring speed: 240 rpm).

chiral structure of Δ/Λ -[Ru(phen)₃]²⁺. When the Δ/Λ -[Ru(phen)₃]²⁺ was added into the stagnant Zn-L1 colloidal solution, the CD spectra remain almost unchanged (Figure 4a). However, when the mixture (labeled as ${\rm Zn-L1}+\Delta/\Lambda-$ [Ru(phen)₃]²⁺) was CCW stirring, the recorded CD spectrum changes and exhibits a single peak at the same absorption band (Figure 4b, Figure S20 in the Supporting Information). The CD spectra for either enantiomer or racemic [Ru(phen)₃]²⁺ in Zn-L1 are identical if under the same stirring treatment, which indicates the similar spatial arrangement of molecules in the CCW stirred Zn-L1 colloidal solution. In other words, the CD spectrum recorded in the vortex field offers information on the spatial arrangement of the particles in the dynamic movement. In this case, no matter the absolute configuration that the [Ru(phen)₃]²⁺ cations adopt, the dynamic spatial alignment for those cations was endowed by its electric static interaction with the Zn-L1 host and the stirring vortex field.

It is interesting that the intensities of the CD signals for the intrinsic molecular chirality and the dynamic spatial alignment are quite different. For the former, the peak value is 60 mdeg at the maximum; for the latter, the peak value is about 1200 mdeg, which is nearly 20 times larger than pure Δ/Λ -[Ru(phen)₃]²⁺. It is assumed that the orientation of fibers in the vortex will lead to macroscopic chiral anisotropy for the polarized light phenomena. The combined linear polarizations may result in stronger chirality than intrinsically molecular chirality.^[8h] The high value of CD intensity observed herein pushed



Figure 3. The absorption, CD, and LD spectra of (a) CV, (b) MB, (c) ThT, and (d) PDI in Zn-L1. ([Zn-L1] = 1.25×10^{-3} M, [CV] = [MB] = [PDI] = 3.0×10^{-5} M, [ThT] = 1.5×10^{-4} M, stirring speed: 240 rpm).

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us to study the performance of the CPL properties of these host-guests mixed colloidal solutions.

From host to guest: chiroptical transfer of CPL properties

ThT and PDI are fluorescence compounds in solution. However, the luminescence property is greatly quenched in the Zn-L1 colloidal solution, making the CPL study difficult. Thus, the Rhodamine family was chosen to study the potential CPL properties trigged by host–guest interactions and the vortex field.

Rhodamine 6G (Rh6G) is known for its high quantum yield that is close to 100%. When Rh6G is added into the Zn-L1 colloidal solution (labeled as Zn-L1 + Rh6G), the quantum yield for Rh6G remains at 83%, which is pretty good for a fluorescence material. Meanwhile, the CD spectroscopy study shows that Rh6G in the stirring Zn-L1 colloidal solution possesses both CD and LD properties in its characteristic absorption band (Figure 5c, Figure S21 in the Supporting Information). The CPL spectrum of Zn-L1 + Rh6G was taken by setting the excitation wavelength to 500 nm. As shown in Figure 5b, there is a negative emission peak, the position of which (563 nm) is close to the emission wavelength of Rh6G (573 nm). The g_{lum} of Zn-L1 + Rh6G at 563 nm is -0.02, which is almost half the value of Zn-L1.

It is assumed that the electrostatic interaction between Rh6G and Zn-L1 colloids leads the small molecules of Rh6G adopting a chiral arrangement in the vortex. If so, there is a chance to strengthen the supramolecular interaction between the Zn-L1 colloids and small guest molecules to improve the g_{lum} . In the study of PDI, a fluorescence compound shown in Figure 3d, the +2 charged nature of PDI may endow it with a stronger electrostatic interaction with Zn-L1 colloids. However, the photoluminescence of PDI is quenched greatly in the Zn-L1, although the CD intensity for PDI in the stirring Zn-L1 is quite high. It seems that the stronger electrostatic interaction may encourage the small molecules to arrange orderly according to the alignment of Zn-L1 colloids, but sacrifice the lumi-



Figure 5. The UV/Vis absorption and PL spectra of Zn-L1 + Rh6G (a) and Zn-L1 + Rh-COOH (b). The CD and CPL spectra of Zn-L1 + Rh6G (c) and Zn-L1 + Rh-COOH (d). ([Zn-L1]= 1.25×10^{-3} M, [Rh6G]=[Rh-COOH]= 3.0×10^{-5} M, stirring speed: 240 rpm for CD spectra, 1000 rpm for CPL spectra).

nescence. Thus, the coordination interaction was taken into consideration. Rh-COOH adopts a similar molecular structure to Rh6G. The major difference in structure is the function group 2-COOEt is replaced by 4-COOH. It is supposed that the -COOH group may adopt coordination bonding with the Zn^{II} in the Zn-L1 colloid, considering the popular coordination bonds observed between the -COO and Zn^{II} in reported coordination polymers or metal-organic frameworks (MOFs).^[15] It is surprising that the Zn-L1+Rh-COOH shows a strong Cotton effect with the intensity exceeding the limit of spectrometer at the characteristic absorption band of Rh-COOH (Figure 5 d, Figure S22 in the Supporting Information). The direction of the Cotton effect for Zn-L1+Rh-COOH at 550 nm is opposite that of Zn-L1+Rh6G with the same CCW stirring direction. Meanwhile, the CPL study of Zn-L1+Rh-COOH with stirring reveals a negative CPL peak centered at 570 nm under the excitation wavelength of 500 nm. The g_{lum} value at 570 nm is -0.046, which is more than twice the g_{lum} value of Zn-L1+Rh6G at 570 nm and close to that of Zn-L1. Rh-COOH possesses a quantum yield in solution of approximately 51%. When the Rh-COOH is added into the Zn-L1 colloidal solution, the quantum yield was maintained at 40%.

We wondered if the high value of g_{lum} for Rh-COOH in Zn-L1 colloidal solution is attributed to the coordination bonding. Thus, the functional group 4-COOH was esterified into 4-COOMe. The resulting Zn-L1 + Rh-COOMe is also CD active in its absorption band with in situ stirring (Figure S22 in the Supporting Information). But the CD intensity is much weaker than that of Zn-L1 + Rh-COOH. In the meantime, the direction of the Cotton effect is opposite to that of Zn-L1 + Rh-COOH with the same vortex direction (but the same as Zn-L1 + Rh-GO). It is assumed that the esterification for Rh-COOMe may weaken the molecular interaction with Zn-L1. The CPL study for Zn-L1 + Rh-COOMe suggests a negative emission difference band at 570 nm, with $g_{lum} = -0.03$ (Figure S22 in the Supporting Information). The lower g_{lum} value of Rh-COOMe compared with that of Rh-COOH confirms the coordination bonding plays a

key role in obtaining the high value of g_{lum} . In addition, the quantum yield maintenance for Rh-COOMe (84%) in Zn-L1 is close to that of Rh-COOH (78%), which indicates the presence of coordination bonding may not diminish the quantum yield to a great extent. On the other side of the coin, the fluorescence lifetime study shows equal lifetimes for Rh6G in Zn-L1 colloid or in solution (both 4.4 ns, Figure S23 in the Supporting Information). Similar phenomena were observed for Rh-COOH and Rh-COOMe, indicating the interaction between the dye molecules and Zn-L1 colloid may not greatly influence the fluorescence properties, which results in the high Φ maintenance.

In the previous study of CPL functional materials, it was found that the chiral photoluminescence compounds always possess poor g_{lum} but good quantum yields, whereas the composites of chiral supramolecular architectures and photoluminescent molecules may lead to improved g_{lum} but poor quantum yields.

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The typical examples include NK-1020^[6a] ($|g_{lum}| = 10^{-1}$, $\Phi = 7.5\%$) and the anthracene and pyrene derivatives^[6g] ($|g_{lum}| = 10^{-3}$, $\Phi = 48\%$). The interplay of both criteria may be related to the intrinsic structure involved with the electric transition moment and magnetic transition dipole moments.^[3,4] In this context, the colloids studied herein possesses $g_{lum} 10^{-2}$ in magnitude, with quantum yields maintained at about 40–80% for the Rhodamine family (Figure 6), which is a good candidate for CPL functional materials.



Figure 6. The quantum yield and $g_{\rm lum}$ of the colloidal solutions discussed in this paper.

Conclusion

Two metal-organic colloids based on achiral starting materials were prepared and characterized, including their optical spectroscopy properties and microscopic morphology. Both colloids show active CD and CPL properties in the vortex field generated by stirring. The dynamic chiroptical property could be delivered to small molecules by suitable electrostatic interactions and coordination bonding, which further indicates the ordered chiral arrangement of small molecules in the stirring colloidal solution. In this paper, the g_{lum} values are in the 10^{-2} magnitude range, and the quantum yields are low for the monocomponent colloids (3-4%) but high for the double-composites (40-83%). It is hoped that the study herein could offer a new possibility for CPL functional materials: the direction and ON/OFF state can be controlled by the vortex field physics, whereas the wavelength, Φ , and g_{lum} could be modulated by the molecular structure and host-quest interaction chemistry.

Experimental Section

General information

CV, MB, chiral $[Ru(phen)_3]^{2+}$ compounds, NR, ThT, and Rh6G were purchased from TCI Co., Ltd. All the solvents and reagents were analytically pure and used without further purification. L1, PDI, and Rh-COOH/Me were synthesized by referring to previous literature reports.^[14e, 16] Detailed information on the synthesis and characterization of the above compounds can be found in the Supporting Information.

Preparation of Zn-L1

To obtain the Zn-L1 colloid, an equal volume of DMSO solution of L1 $(2.5\times 10^{-2}\,M)$ and ZnAc_2+2H_2O $(5.0\times 10^{-2}\,M)$ was mixed, then ammonia water (10 $\mu L)$ was added into the mixture (10 mL). The mixture turned into an opaque colloidal solution when allowed to stand for at least two months.

Preparation of Zn-L2

The Zn-L2 colloid was synthesized by mixing equal volumes of DMSO solution of L2 $(2.5\times 10^{-2}\,M)$ and DMF solution of ZnAc_2+2H_2O (5.0\times 10^{-2}\,M). Then, the mixture was allowed to stand for at least two months.

SEM sample preparation

Zn-L1 or Zn-L2 $(1.25 \times 10^{-3} \text{ M})$ was dripped into liquid nitrogen to make a solid sample, which was freeze dried under vacuum.

AFM sample preparation

Zn-L1 or Zn-L2 (10 $\mu L,~1.25 \times 10^{-3}\,M)$ was diluted in DMSO (1 mL), and after being well mixed, 4 μL of the mixture was dropped onto clean mica. Then, the mica was vacuum dried.

Characterization

NMR spectra were taken with Bruker Advance III 400 and JNM-ECZ500R spectrometers. Mass spectra were taken with a Thermo Fisher Scientific Exactive Plus ultra-high-resolution liquid chromatography mass spectrometer, with ESI ion source in negative ion mode or positive ion mode. AFM experiments were taken with an Agilent 5500. SEM images were taken with the Nova Nano SEM 230. UV/Vis absorption spectra were taken with a Lambda 900 UV/ Vis/NIR spectrometer. The optical path length was 10 mm for Zn-L1 and Zn-L2, and 1 mm for the Zn-L1 + quest series. The IR spectra were taken with a Nicolet iS50. CD spectra were taken with a MOS-450 circular dichroism spectrometer. The length of the stirring bar was 7 mm. In situ stirred CD spectra were recorded with a MOS-450 circular dichroism spectrometer by adopting a genuine clockwise stirring device and home-made double stirring direction device. The CPL spectra were carried by using a Jasco CPL 300. The fluorescence spectra and lifetime were collected with a FL-980. The quantum yield tests were carried by using a Quantaurus-QY absolute quantum yield measuring instrument.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: achiral fluorescence guests • achiral metal–organic colloids • circularly polarized luminescence (CPL) • Rhodamine • supramolecular interactions • vortex stirring

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