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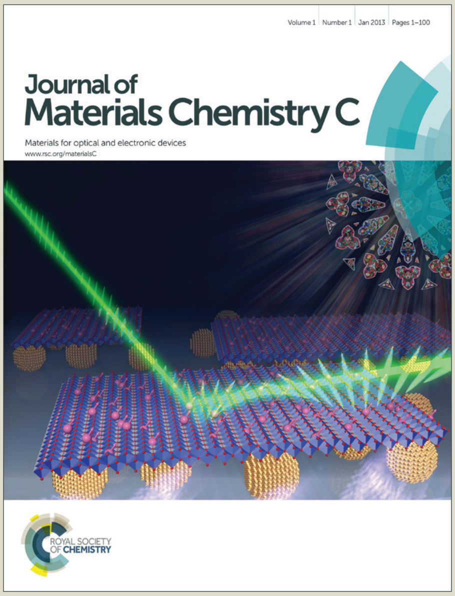

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BINOL-based chiral aggregation-induced emission luminogens and application for detecting copper (II) ion in aqueous media

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Two novel chiral luminogens BINOM-CN and BINOP-CN derived from (*R*)-1,1'-binaphthol (BINOL) with aggregation-induced emission (AIE) characteristics were designed and synthesized. Dicyanomethylene and substituent of hydroxyl group have been found to be the key structural element for this unique AIE effect. Meanwhile, these two chiral AIE luminogens exhibit abnormal aggregation-induced annihilation of circular dichroism (CD) signal, which is ascribed to the decrease of the dihedral angle between adjacent naphthalene rings in aggregation state. With the assistant of pyridine unit, BINOP-CN can serve as an excellent sensor for Cu^{2+}. In the presence of Cu^{2+}, the fluorescence intensity and CD signals of BINOP-CN both decreased observably due to its ideal coordination with Cu^{2+}, which further confirmed by the X-ray crystallography. Moreover, addition of Cu^{2+} can induce the self-assembly of BINOP-CN.

Introduction

Fluorescent materials, especially those with advanced properties, are of great importance due to their widely application in the fields of optoelectronic devices, environmental sensors, biological science and become indispensable tool in physics, chemistry and biology etc.[1] Despite their intense fluorescence in solution, but, most of the traditional fluorophores suffer from the aggregation-caused quenching (ACQ) effect, which prevent their application in most concentrated state or aqueous media.[1a] In 2001, Tang's group firstly discovered an intriguing aggregation-induced emission (AIE) phenomenon for some propeller shaped molecules: they show weak emission or even non-emission when dissolved in solution state, but became intense emitters after formed molecular aggregation.[2] AIE phenomenon is precisely opposite to ACQ and provides a new strategy to broaden the application of organic fluorophores in the fields which require them to be concentrated or aggregated. As a result, much effort has been put to explore novel AIE system[3] and their application in the areas of organic light-emitting diodes,[4] sensors,[5] cell stains,[6] drug delivery[7] and so on.

On the other hand, chiral luminogens have attracted considerable attention as they show great potential applications in both bio-sensing and imaging process.[8] Recently, chiral AIE luminogens have been successfully synthesized through melding of chiral elements such as sugars or amino acids with typical AIE luminogens, and impressive property of aggregation-induced circularly polarized luminescence (CPL), self-assembly as well as enantio-selective recognition have been obtained.[9] Nevertheless, the poor thermal stability and difficult wavelength tunability troubled their further development. Binaphthol (BINOL), a well-known versatile chiral fluorophore, attracts great interest due to its structure diversity and excellent luminescence, and provides a wide application from asymmetric catalysis to optical-based molecular detection.[10] However, BINOL suffers from notorious ACQ effect, limiting its practical application in some fields.[11a] To overcome this undesirable nature, the chiral AIE-active polymers and luminongens based on BINOL were developed by Zhu and Tang's group through attaching outstanding AIE unit-tetraphenylethene (TPE) to BINOL moieties.[11] Despite these elegant examples, a straightforward protocol to generate chiral AIE-active BINOL derivatives remains a long-standing challenge.

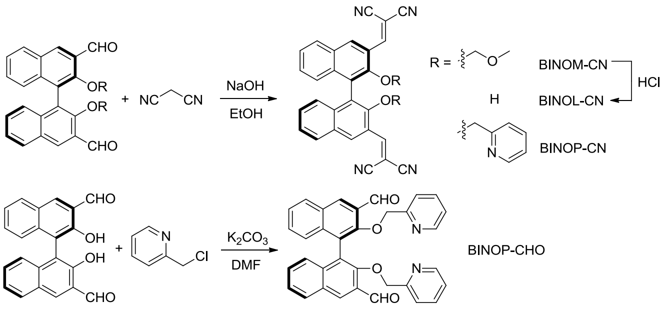
In addition, Cu^{2+}, the third most abundant transition metal ion in the body, plays a crucial role in numerous enzyme functions.[12] Incorrect regulation of Cu^{2+} always links with some disease such as Parkinson's, Wilson's and Alzheimer's disease.[13] Therefore, the development of sensor for Cu^{2+} is crucial in early stage diagnostics and therapeutics for various diseases, and large amount of fluorescent sensor for Cu^{2+} have been successfully developed.[14] Nonetheless, the detection of Cu^{2+} based on chiral AIE luminogens via both channel of fluorescence and CD signals have rarely been reported.

With those in mind, herein, we designed and synthesized two compounds BINOM-CN and BINOP-CN based on chiral BINOL skeleton. Both of them are weakly emissive in solution but give enhanced emission in aggregate state, displaying a specific AIE phenomenon. Through detailed emission behavior analysis for control luminogens BINOL-CN and BINOP-CHO, it was found that functional group dicyanomethylene and substituents of hydroxyl groups serve as determining moieties for this unique AIE feature, and restriction of intramolecular free motion should be responsible for the AIE phenomenon. Interestingly, both chiral AIE luminogens exhibit abnormal aggregation induced annihilation of CD signal, which attributed to the decrease of the dihedral angle between adjacent naphthalene rings in aggregation state. With the assistant of pyridine unit in molecular structure of BINOP-CN,[15] it can detect Cu^{2+} in aggregate state with high selectivity and sensitivity. After added Cu^{2+} into the solution of BINOP-CN, the obvious decrease of the fluorescence and CD signals were observed, which caused by the coordination between BINOP-CN and Cu^{2+}, and further confirmed by the X-ray crystallography. Interestingly, introducing Cu^{2+} into the solution of BINOP-CN can induce the morphological transition from nano-polyhedra into micro-branches.

Results and Discussions

Synthesis and optical properties

The compounds BINOM-CN and BINOP-CN were simply synthesized by a one-step condensation reaction between the appropriate aldehydes based on BINOL with malononitrile in ethanol. The control compounds BINOL-CN and BINOP-CHO were synthesized by de-protection of BINOM-CN using hydrochloric acid and the etherification between dialdehyde modified BINOL and 2-chloromethyl-pyridine, respectively (Scheme 1). Their structures were determined by ^1H NMR, ^{13}C NMR and high resolution mass spectroscopy from which satisfactory results corresponding to its structure were obtained (Supporting Information). All of them were soluble in common organic solvent such as tetrahydrofuran (THF), dichloromethane and dimethylsulfoxide (DMSO), but insoluble in water.



Scheme 1. Chemical structures of BINOL derivatives and their synthetic routes.

The UV-vis spectrum of BINOM-CN in diluted DMSO solution exhibits a characteristic absorption band at 339 nm (Table 1, Fig. S1), corresponding to the intramolecular charge transfer (ICT) transition from the electron-donating BINOL to the electron-accepting dicyanomethylene unit. When its diluted solution was photoexcited, BINOM-CN emitted weak emission at 548 nm with a fluorescence quantum yield (Φ_F) of 0.4%. As water is poor solvent for BINOM-CN, the emission behavior was then studied in DMSO-water mixture with various ratios. As shown in Fig. 1A, while increasing of the water fraction (f_w) in DMSO solution, the emission intensity was decreased when the f_w was less than 60%, which presumably due to the ICT effect. In contrast, further addition of water led to enhancement of emission intensity with the blue shift in emission peak at 511 nm which might be caused by the decrease of polarity inside the aggregates. When the f_w was up to 99%, the fluorescence intensity boosted sharply (Φ_F = 2.7%) and showed about 16 times higher than that in pure DMSO solution (Fig. 1B) as well as a bright green color. Clearly, BINOM-CN is a typical AIE luminogens. In order to further functionalize this novel BINOL based AIE system, the compound BINOP-CN was obtained through the replacement of methoxymethylene (MOM) group by 2-methylene pyridine. Interestingly, increasing of f_w can also light up the emission of BINOP-CN as described in Fig. 1C and 1D, meanwhile the Φ_F value was increased from 0.5% to 2.2% when the f_w is altered from 0 to 99%, suggestive of the intrinsic AIE nature of BINOP-CN.

Table 1. Optical properties of BINOL derivatives.

Compound	λ_{ab}/nm	λ_{em}/nm		Φ_F/%[c]	
	sol[a]	sol[a]	aggr[b]	sol[a]	aggr[b]
BINOM-CN	339	548	498	0.4	2.7
BINOP-CN	342	549	509	0.5	2.2
BINOL-CN	342	514	509	1.0	1.2
BINOP-CHO	360	433	441	0.8	0.4

[a] Measured in DMSO (10 μM); [b] Measured in DMSO-H_2O (99:1) (10 μM); [c] Quantum yield was measured using quinine sulfate in 0.1 N sulfuric acid as standard.

Mechanistic study

To understand the relationship between the molecular structure and AIE property, two control compounds BINOL-CN and BINOP-CHO were designed and synthesized. They are either lack of protecting group on phenolic hydroxyl group or dicyanomethylene group compared to BINOM-CN and BINOP-CN, respectively. As showed in Table 1 and Fig. S1, BINOL-CN absorbed at 342 nm which was close to that of BINOM-CN, however, displayed an emission peak at 514 nm in DMSO solution with Φ_F value about 1.0%. Upon addition of water into its DMSO solution, the changing of emission intensity was almost irregular (Fig. S2). At the same time, the emission intensity did not enhance markedly in mixture while f_w values was 99%, suggested BINOL-CN was non-AIE active. On the other hand, due to lack of electron withdrawing dicyanomethylene unit, BINOP-CHO showed a blue-shifted emission peaked at 441 nm with a lower Φ_F (0.8%) in DMSO solution. Similarly, its luminescence was not activated even when the f_w was up to 99%, which explains BINOP-CHO did not process AIE property (Fig. S3).

From above investigation, we deduced that both dicyanomethylene and substituents of hydroxyl group at BINOL backbone act as the determining moieties for specific AIE feature. Based on the AIE mechanism proposed by Tang's group,[2] it's likely that drastic motion of these two important group results in faint emission in solution state. But, the free motion of them is restricted once molecular aggregation is formed, and thus results in intense fluorescence.

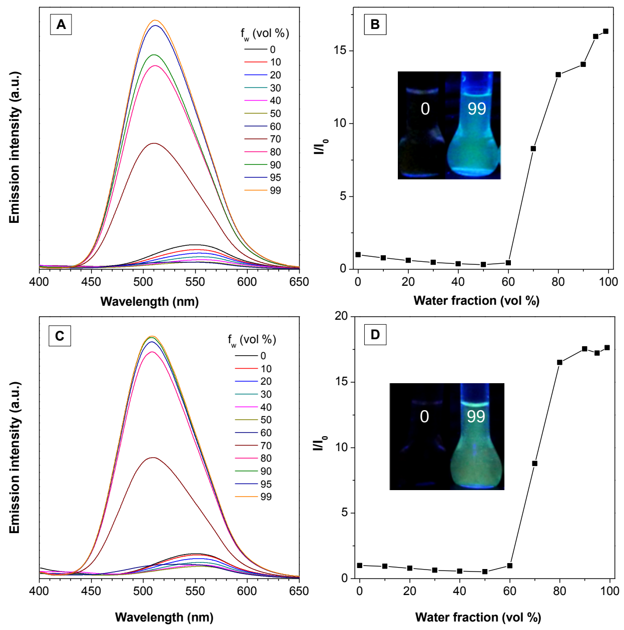


Fig. 1 (A) Emission spectra of BINOM-CN (A) and BINOP-CN (C) (10 μM) in DMSO and DMSO-water mixtures with different water fractions (f_w). Plots of emission intensity versus the composition of the aqueous mixtures of BINOM-CN (B) and BINOP-CN (D). Inset: Photo of BINOM-CN (B) and BINOP-CN (D) in DMSO and DMSO-water mixtures with f_w values of 0 and 99 vol% under 365 nm UV lamp illumination.

Aggregation induced annihilation of CD signals

It's well-known that the BINOL possesses CD signal because of its chiral nature. Meanwhile, the aggregation induced enhancement or annihilation of CD signal was observed for AIE luminogens bearing chirality. With chiral AIE-active luminogens in hand, we checked whether the aggregation can give same CD enhancement or annihilation performance. The CD spectra in THF-water mixtures with different f_w were measured. As shown in Fig. 2, both BINOP-CN and BINOM-CN exhibited slightly CD signals enhancement when a small amount of water was added. In comparison, after the f_w was more than 80%, the CD signals were sharply weakened. Increasing the f_w up to 99%, the CD signals showed the lowest value with a wavelength red-shifted. The results manifested that BINOM-CN and BINOP-CN display extraordinary abnormal aggregation-annihilation CD phenomenon, which should be attributed to the decrease of the adjacent naphthalene rings in aggregation state based on the previous report.[11a]

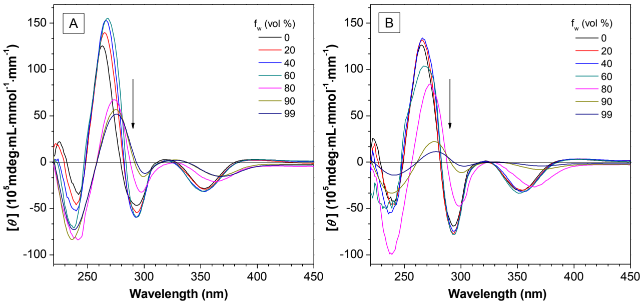


Fig. 2 CD spectra of (A) BINOM-CN, (B) BINOP-CN (100 μM) in THF-water mixtures with different f_w.

Optical response of BINOP-CN for Cu^{2+}

Based on the molecular structure, BINOP-CN may serve as an ideal fluorescent probe for Cu^{2+} as it possess O and N atoms which show great affinity to Cu^{2+}. To conduct the detection process, we examined the optical sensing behavior toward Cu^{2+} in DMSO/ phosphate buffer (20 : 80 v/v, pH 7.4) by UV-vis and emission spectra. Upon gradual addition of Cu^{2+} into the solution of BINOP-CN, the absorbance peak at 350 nm was decreased (Fig. S4), which suggested that the new species was generated between BINOP-CN and Cu^{2+}. Correspondingly, the emission intensity of BINOP-CN was weakened after addition of Cu^{2+} (Fig. 3A). When the concentration of Cu^{2+} was as high as 200 μM, the fluorescence of BINOP-CN was almost totally quenched, meanwhile the green emission color also faded away after incubation with Cu^{2+} under 365 nm UV illumination (Fig. 3 inset). Above results verified BINOP-CN can serve as a fluorescent sensor for Cu^{2+} in aqueous solution. The detection limit of Cu^{2+} using BINOP-CN was found as 1.48 x 10^{-7} M (Fig. S6). It's noteworthy that the maximum allowable level of Cu^{2+} in drinking water is 2.0 x 10^{-5} M based on the U.S. Environmental Protection Agency (EPA). The time-course quenching effect of BINOP-CN by Cu^{2+} was also investigated. In the presence of 200 μM Cu^{2+}, the emission intensity was decreased and totally quenched after ca. 25 minutes (Fig. S7), indicating the quick optical response of BINOP-CN toward Cu^{2+}.

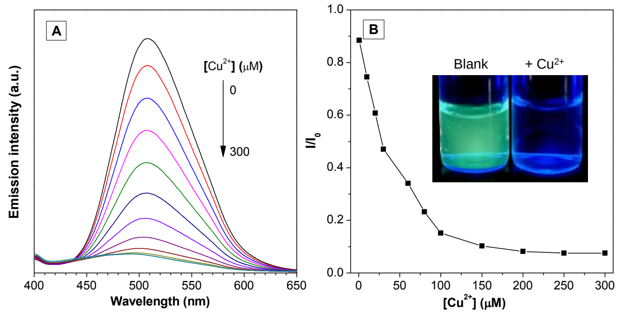


Fig. 3 (A) Emission spectra of BINOP-CN (10 μM) in DMSO/PBS buffer (20 : 80 v/v, pH 7.4) with different concentration of Cu^{2+} (0–300 μM). (B) Plots of emission intensity at 509 nm *versus* the concentration of Cu^{2+}. Inset: photographs of BINOP-CN without and with Cu^{2+} (200 μM).

Subsequently, the optical response of BINOP-CN to various metal ions including Ag^{+}, Ba^{2+}, Ca^{2+}, Cd^{2+}, Co^{2+}, Hg^{2+}, Li^{+}, Mg^{2+}, Mn^{2+}, Ni^{2+} and Zn^{2+} were carried out under the same conditions. As described in Fig. S8, other metal ions did not generate remarkable decrease of absorbance at 350 nm after added into BINOP-CN solution except Cu^{2+}. Correspondingly, only Cu^{2+} gave a sharp decrease of emission up to 10 fold while a little change of emission intensity was detected for other metal ions (Fig. S9, Fig. 4). As a result, BINOP-CN shows higher selectivity to Cu^{2+}. The interference of various metal ions to the sensing process was also tested. Even the solutions contained the same amount of other metal ions, an efficiently quench of emission was observed after adding Cu^{2+}, thus verifying the high anti-interference of the BINOP-CN for Cu^{2+} (Fig. 4).

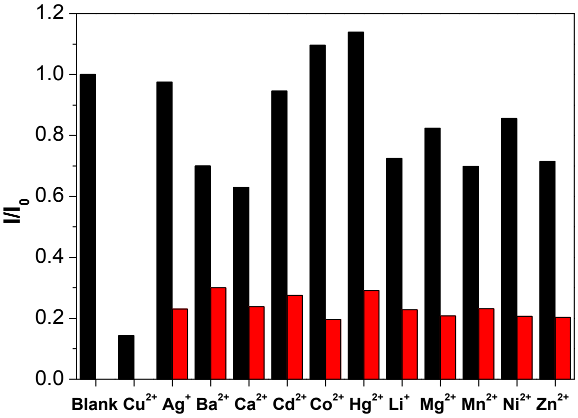


Fig. 4 Fluorescence response of BINOP-CN towards various metal ions. Black bars represent the addition of different metal ions (200 μM) to the solution of BINOP-CN, whereas the red bars represent the subsequent addition of Cu^{2+} (200 μM) to the solution containing a specific metal ion.

Since BINOP-CN shows CD signal, we also carried out the detection of Cu^{2+} using CD spectroscopy in THF solution with f_w value of 80%. Fig. 5 described the time–dependent CD spectra for BINOP-CN in the presence of 20 equiv. Cu^{2+}. With extending of incubation time, the CD signals were decreased gradually. This result implies that BINOP-CN may serve as a promising chiral sensor for Cu^{2+}.

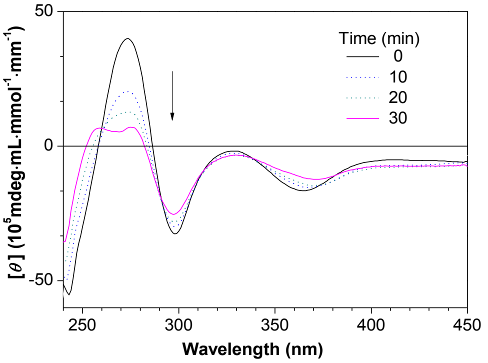


Fig. 5 The time–dependent CD spectra for BINOP-CN (100 μM) with 20 equiv. Cu^{2+}.

In order to further investigate the sensing process of BINOP-CN to Cu^{2+}, scanning electron microscopy (SEM) was employed to examine the morphological transition of BINOP-CN in DMSO/water mixture with f_w values of 80% after treated with Cu^{2+}. As shown in Fig. 6A and 6B, the SEM images reveal BINOP-CN can aggregate into irregular nano-polyhedra in mixture with large amount of water. Conversely, large pieces of micro-branched structure were observed after added Cu^{2+} into the solution of BINOP-CN (Fig. 6C). At high magnification, the micro-branch was constituted by lots of nano-polyhedra and they were arranged one-by-one in a cluster way that presents a growing tendency for micro-branch (Fig. 6D). Clearly, the observations demonstrate that addition of Cu^{2+} lead to the self-assembly of BINOP-CN.

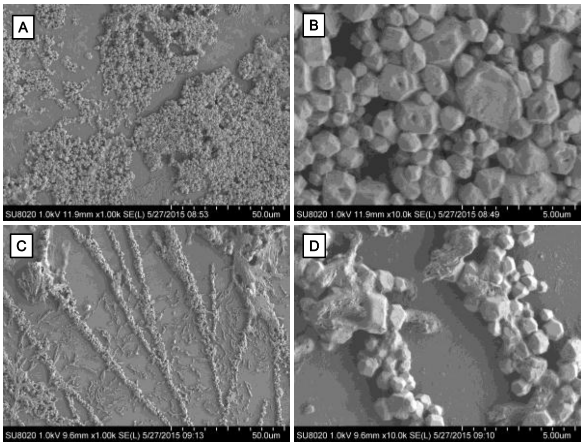


Fig. 6 SEM image of BINOP-CN (10 μM) in the absence (A, B) or presence of Cu^{2+} (200 μM) (C, D) in DMSO-water (20 : 80 v/v).

To further understand the interactions between the BINOP-CN and Cu^{2+} as well as the mechanism of how Cu^{2+} quench the fluorescence and CD signals, the single crystal of complex between BINOP-CN and Cu^{2+} was obtained by slowly evaporating their ethanol solution. The structure of complex was successfully characterized by X-ray crystallography as depicted in Scheme S1. Complex BINOP-CN-Cu exhibited a mononuclear structure with the Cu coordinated by two pyridine nitrogen atoms, two naphthol oxygen atoms and two chlorine atoms in distorted octahedron geometry. The bond lengths of Cu-O and Cu-N are 2.374 Å, 2.287 Å and 2.023Å, 2.022Å, respectively. Due to above stable binding pattern, we speculate that strong ligand-to-metal charge transfer (LMCT) from BINOP-CN to Cu occurs and gives rise to the effective quenching of fluorescence. Meanwhile, the adjacent naphthalene rings in crystal was calculated as 65.15° (Fig. 7B), which extremely decreased compared to BINOL,[11] Therefore, the CD annihilation effect of BINOP-CN for Cu^{2+} was given. In addition, multiple intermolecular interactions including C-H···N, C-H···Cl and C-H···π exist in crystal structure (Fig. 7A), which may facilitate molecules stacking and further self-assemble into micro-branched structures.

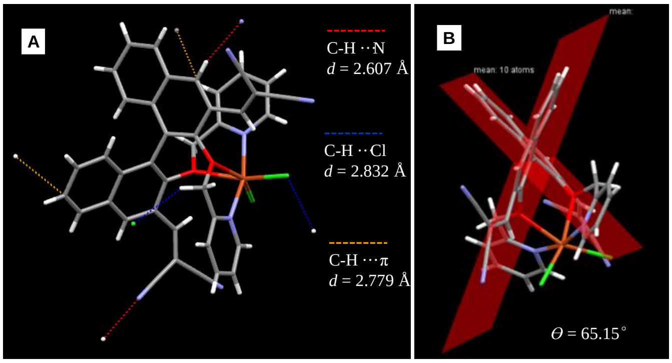


Fig. 7 (A) Molecular structure of BINOP-CN-Cu and intermolecular interaction. (B) The dihedral angle between naphthalene rings in crystal structure

Conclusions

In conclusion, we have constructed two novel chiral AIE luminogens BINOM-CN and BINOP-CN based on (*R*)-1,1'-binaphthol. It was found that the functional groups dicyanomethylene and substituents of hydroxyl units play a vital role for the unique AIE feature of BINOL derivatives. Meanwhile, the decrease of dihedral angle between adjacent naphthalene rings during the aggregating process lead to these luminogens present abnormal aggregation induced annihilation of CD signal. Furthermore, BINOP-CN displays superior optical response to Cu^{2+} over other metal ions. The drastic quenching of both fluorescence and CD signals for BINOP-CN was observed in the case of Cu^{2+}, which contributed to the coordination of BINOP-CN with Cu^{2+} according to the X-ray crystallography. SEM images reveal that BINOP-CN can form nano-polyhedra in aggregate state, but self-assemble into micro-branches after added Cu^{2+}. Undoubtedly, this work provides a simple and powerful method to building chiral AIE system based on BINOL backbone and opens new perspectives for the construction of chiral fluorescent sensors.

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Notes and references

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Electronic Supplementary Information (ESI) available: NMR and high resolution mass; supplementary figures. See DOI: 10.1039/b000000x/

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TOC: In this work, two novel chiral luminogens BINOM-CN and BINOP-CN based on BINOL platform have been reported. They exhibit specific aggregation induced emission and annihilation of CD performance. In the presence of Cu^{2+}, both fluorescence and CD signal of BINOP-CN are quenched, making it as an ideal chiral fluorescent sensor for Cu^{2+}.