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A new bis(salicylaldiminato)Zn(II) Schiff-base complex BTZn, derived from benzo[c][1,2,5]thiadiazole-5,6-diamine has been designed and synthesized. It exhibited unique mechanical force induced luminescence change characteristic. Upon mechanical grinding, as-prepared BTZn solid crystalized from ethanol/dichloromethane solution displayed a high-contrast emission-colour variation from yellow (emission maximum λ_{em} = 545 nm) to red (λ_{em} = 645 nm) and such emission variation can be erased through solvent vapour treatment. The reversible emission colour alteration between yellow and red can be repeatedly performed. The thermal annealing of as-prepared BTZn solid resulted in a more ordered orange phase with emission maximum of 575 nm. The multi-stimuli-responsive luminescence mechanism has been investigated by the SEM, powder X-ray diffraction (XRD) and thermal analyses. It was demonstrated that the mechanical force can induce the morphology transformation from crystalline to amorphous phase, which was accompanied by the change of BTZn molecualr packing modes. The BTZn based solids have molecular packing dependent emission characteristic. XRD experimental results revealed that for yellow emissive as-prepared BTZn solid molecualr columnar square arrangement was adopted. On the other hand, BTZn complex exhibited the ability to organize into organic luminescent gels that were constructed by one dimensional BTZn molecualr nanofibrils. The BTZn xerogels also displayed mechanochromic property. Accordingly, BTZn based solids may be the potential candidates for the development of new stimuli-responsive materials.

Introduction

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Luminescent materials that respond to external stimuli are of scientific and technological interest owing to their wide potential applications in the fields of various sensors, optoelectronic and medical devices.¹ For stimuli-responsive materials, mechanochromic luminescent materials, which change their emission colours based on the response to external mechanical forces (such as grinding, crushing, shearing and rubbing) and can subsequently revert to their original emission states by another external stimulus, have attracted much attention. This is due to that the property can be used to develop memory-recording devices, motion or damage sensors, and security inks.² Although a number of pressure-sensitive luminescent transition-metal complexes have been reported,³ the amount of metal complexes with mechanochromic luminescence feature is still limited compared with the organic compounds that have responsive property to mechanical force stimuli.⁴ So far, most of the reported mechanochromic metal complexes are gold and platinum based complexes. 5, 6 In addition, some copper and silver complexes exhibited

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The mechanochromism behaviours were often attributed to the molecular packing changes within metal complex or organic compound solids. Generally, the intermolecular interactions such as $\pi \cdots \pi$ stacking, hydrogen bonding, weak coordination bonding and metal---metal interactions dominate the molecular packing modes. The intermolecular interactions have dramatic influence on the emissive properties of molecules based solids.¹⁰ On the other hand, the mechanical force induced phase transformations are frequently accompanied by the changes of intermolecular interactions and sequentially lead to the emission.11 alteration of Therefore. to achieve mechanochromism, developing the strategies that can efficiently regulate the intermolecular interactions should be focused on. It is worth to note that most of luminescent mechanochromism compounds can only show a single phase transformation process that are accompanied by the alternation of two emission colours. The metal complex or

⁺ Electronic Supplementary Information (ESI) available: supplementary figures and tables. See DOI: 10.1039/x0xx00000x

ARTICLE



organic molecule based solids with multiple colour luminescence change property is still a challenge.¹² Recently, bis(salicylaldiminato)zinc(II) Schiff-base complexes have drawn a lot of attention due to their multifunctional characteristics, such as, non-linear optical materials, supramolecular assembly, fluorescent molecular probes and active materials for organic optoelectronics.¹³ However, there is only a few examples of Schiff-base zinc(II) complexes exhibiting thermochromic, vapochromism and mechanochromism behaviors.^{14,9} It is noteworthv that, Zn(II) complexes often adopt pentacoordination structures with relatively weak axial binding contact of Zn…donor interactions. It was demonstrated that the axial intermolecular Zn…O interactions can result in the formation of dimeric or oligomeric Schiff-base zinc(II) complexes.¹⁵ Generally, the weak axial Zn…O interactions are sensitive to external stimuli resulting in different aggregation states, ¹⁶ which may be employed to develop smart materials.

In this paper, a new Zn(II) Schiff base complex BTZn (Scheme 1) with mutil-color mechanochromism luminescent property is reported. BTZn based solid exhibited luminescence changes upon mechanical, organic solvent and thermal stimuli. To the best of our knowledge, BTZn represents the largest mechanochromic luminescence shift (around 100 nm) for zinc complexes. To understand the intriguing emission colour alternation behaviour of BTZn solids, comprehensive investigations on structural, photophysical and morphological properties were performed. Furthermore, the BTZn complex displays gelation characteristic in some organic solutions and the xerogel of BTZn also exhibits mechanochromic luminescence feature.

Results and discussion

Synthesis

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Zinc(II) complex BTZn was synthesized with benzothiadiazolecontaining salicylaldiminato Schiff base ligand through a facile and straightforward procedure (Scheme 1). In ethanol solution, zinc acetate dihydrate, 4-(hexyloxy)-2-hydroxybenzaldehyde heated at reflux temperature for 3 h. The complex was isolated as yellow solid with good yield and confirmed by NMR, mass and elemental analysis spectroscopies. The synthetic details of the intermediates and target product are presented in Experimental Section. In MALDI-TOF mass spectrum of BTZn complex the dominant peak was attributed to the parent molecular ion and a peak corresponding to molecular dimer species (Fig. S1) was also recorded, which was often observed for Zn(II) Schiff base complexes and generated base on intermolecular Zn···O interactions.17 Therefore, in the BTZn solid the molecular dimers really exist. The presence of lateral alkyl chains that attach to the salicylidene rings of the Schiff base makes complex BTZn moderately soluble in common organic solvents. This property is essential for the investigations of photophysical and assembly properties in solutions. On the other hand, the lateral alkyl chains also have dramatic effect on supramolecular assembly properties.¹⁸ In this study the Schiff base ligand was modified by 1,3,4-thiadiazole with the electron withdrawing property, and the benzothiadiazole-containing salicylaldiminato moiety and hydroxybenzyl are electron acceptor (A) and donor (D), respectively. The introduction of 1,3,4-thiadiazole moiety not only extended the π -conjugated area of ligand, but also established a donor-acceptor-donor (D–A–D) type molecule with intramolecular charge transfer (ICT) feature. Generally, the large planar π -conjugated ligand based assembly complexes have abundant emission, and mechanochromism properties.

and benzo[c][1,2,5]thiadiazole-5,6-diamine were stirred and

Photophysical Properties in Solution

The UV-vis absorption and photoluminescent (PL) spectra of BTZn complex in different solvents are shown in Fig. 1. The absorption spectra of BTZn in noncoordinating solvents of toluene and DCM display identical profile with two intense bands at around 330 and 450 nm, respectively. However, in coordinating solvents of THF and DMSO, two defined absorption bands were recorded in the region from 300 to 400 nm and a slight red-shift (around 10 nm) of absorption was observed. Similar results were obtained for the reported Zn(II)

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Schiff bases complexes. This phenomena was attributed to that aggregates are always formed in noncoordinating solvents, while monomeric species exist in coordinating solvents due to the axial coordination of the solvent to the Zn(II) metal center.¹⁵ It was demonstrated that BTZn exhibited remarkable solvent-dependent emission property (Fig. 1b). Upon increasing solvent polarity obvious red-shift of emission was observed suggesting the ICT excited sate characteristic of BTZn complex. Due to the fully filled d shell of the central Zn(II) ion, the observed fluorescence emission of the complex should originate from the ligand-centred excited state.¹⁹



Fig. 1 Normalized UV-vis absorption and fluoroscence spectra of BTZn in different solutions (1.0 \times 10 5 M).

1.0 0.8 0.6

mechanochromic phenomenon (Fig. 2b). When_{vit}he_{rti}ground powder was exposed to organic ^Dିଏହି/୦୫୨/୦୫୨/୦୫୨

dichloromethane (DCM), tetrahydrofuran (THF) and toluene,

the emission rapidly recovered to the initially yellow colour (Fig.

2a-iii). However, heating the ground sample at 125 °C for 2 min

resulted in an orange luminescent solid with emission maximum

at 575 nm (Fig. 2a-iv). Under grinding-fuming and grinding-

heating stimuli the luminescence alternation processes can be

mechanochromic behaviour of BTZn solid (Fig. 2c). Interestingly,

some marks can be easily written by using a stick on the as-cast

circles,

indicating

the



Mechanochromic Property

The as-prepared BTZn solid crystallized from ethanol/dichloromethane solution displayed yellow emission under UV (365 nm) illumination (Fig. 2a-i). Upon simply grinding with a mortar and pestle, the as-prepared BTZn solid changed into a red emissive powder (Fig. 2a-ii). The PL maximum of asprepared solid is similar to that of toluene solution of BTZn, this phenomenon may be attributed to that aggregates are often formed in noncoordinating solvents. In toluene solution BTZn molecules should adopt aggregated state. The PL spectra indicated that the grinding treatment has induced a remarkable spectral red-shift by 100 nm and the emission maximum underwent a shift from 545 to 645 nm suggesting a typical

Fig. 2 (a) Photo images recorded under UV light (λ_{ex} = 365 nm) for BTZn solids with different phases: (i) as-prepared solid, (ii) ground powder, (iii) sample fumed with DCM vapour, and (iv) solid annealed at 125 °C. (b) Normalized PL spectra of BTZn solids with different phases. (c) Emission switching characteristics of BTZn solids upon repeating grinding-fuming and grinding-heating processes.

dichloromethane solution on the quartz slides (Fig. 3a). Once the film was treated with a small drop of DCM, the red marks could be erased. The reversible and sensitive luminescence switching based on BTZn complex may have potential applications in sensing, ambient monitoring and security inking.

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Journal Name

We demonstrated that the mechanochromic behaviour of BTZn can be characterized by absorption spectra. The UV-vis spectra of the film in different states were compared in Fig. 3b. The absorption maximum of the yellow emissive as-casting film located at 450 nm with a shoulder at around 470 nm. Grinding treatment induced a broad absorption spectrum, suggesting that the molecular packing mode has changed under grinding treatment. Upon fuming the ground film with DCM vapour for 2 min, the absorption spectrum exhibited blue-shifted and almost recovered into the initial profile of as-casting film, indicating that the molecular aggregate restored into the original mode. In contrast, thermal annealing resulted in a significant red-shift of the absorption maximum. The longer wavelength absorption feature implied a J-aggregate



Fig. 3 (a) Photo images recorded for stimuli-responsive property. (b) Normalized UV-vis spectra of BTZn thin films with different phases.

state may be adopted in annealed film. Accordingly, in ascasting film, BTZn molecules may adopt an H-like aggregate.

The morphologies of different phases were recorded by fluorescence microscopy and scanning electron microscopy (SEM) images (Fig. 4). The as-prepared solid crystallized from ethanol/dichloromethane solution showed a one-dimensional (1D) morphology feature and is composed of green emissive fibrillar network (Fig. 4a and b). It was demonstrated that some salphen complexes exhibited similar 1D nano-assembly property, 13b, 13f which are similar to the nature of BTZn in this study. After mechanical shearing, BTZn solid changed into a red emissive film (Fig. 4c and d), indicating the amorphous characteristic. The DCM vapour treated sample showed Irregular green emissive aggregates on the substrate surface, which may suggest the tendency of phase transformation from amorphous to ordered phase (Fig. 4e and f). Heating treatment leaded to the formation of block-like crystalline aggregates, demonstrating that more ordered structure was achieved (Fig. 4g and h). Above experiment results provided valuable information for understanding the different morphologies induced by various external stimuli.

To understand the mechanochromism mechanism repeated X-ray diffraction measurements (Fig. 5) were too ducted, which provided direct information on molecular packing modes of different phases based on BTZn. The as-prepared solid showed multiple intense diffraction pattern with several split peaks. Therefore, the as-prepared solid with thin nano-fiber structure feature should adopt a polycrystalline state and composed of a mixture of BTZn samples with different phase due to that the as-prepared solid was prepared by rapid recrystallization process. For the as-prepared solid sample, 125 °C heating treatment for 5 min has not resulted in phase transformation, while further higher temperature treatment (165 °C and 2 min) leaded to the generation of orange emissive crystals with highly ordered lamellar structure feature and a sharp diffraction peak at $2\theta = 4.27^\circ$, and a series of peaks at $2\theta =$



Fig. 4 Fluorescence microscopy and SEM images for BTZn in different states: (a, b) asprepared solid, (c, d) ground film, (e, f) solid fumed with DCM vapour, and (g, h) solid thermally annealed at 125 °C for 2 min.

8.60, 12.83, and 17.14 were recorded. These peaks corresponding to *d*-spacing of 20.68, 10.27, 6.89 and 5.17 Å, respectively, with a ratio of 1:1/2:1/3:1/4, suggesting a perfect layered structure. (Fig. 5a).

In contrast, the ground solid sample displayed only ambiguous diffuse halo suggesting the formation of amorphous phase. After fuming with DCM vapour for 2 min, the diffraction pattern showed a set of strong diffraction peaks, which are different from that of as-prepared solid (Fig. 5b). It is worthy to

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note that the diffraction peaks in the low angle region of the solvent vapour fumed sample displayed 2ϑ values of 3.24, 4.58, 6.48, 7.22, and 9.73°, corresponding to *d*-spacings of 27.25, 19.28, 13.63, 12.24, and 9.08 Å, respectively, with a ratio of almost $1:1/\sqrt{2}:1/\sqrt{4}:1/\sqrt{5}:1/\sqrt{9}$. This diffraction pattern is consistent with a high-symmetry 2D (two-dimensional) columnar square arrangement with a lattice constant of 27.25 Å. Based on solvent vapour treatment the amorphous ground powder has changed into crystalline columnar phase with a higher symmetry. For the ground amorphous sample, 125 and 165 °C heating treatment leaded to the formation of crystalline phase with intensity diffraction peaks (Fig. 5b), in which except the peak at 10.2° all of the other peaks are identical to that observed for the sample of as-prepared solid that was heated at 165 °C for 2 min (Fig. S2).



Fig. 5 (a) X-ray powder diffraction of as-prepared BTZn solid before and after heating at 125 °C and 165 °C. (b) X-ray powder diffraction of the as-prepared solid upon grinding, and the ground sample upon DCM vapour fuming and heating at 125 °C and 165 °C.

Therefore, for the ground sample the heating treatment resulted in the formation of layered phase accompanied by another phase, which showed diffraction peak at 10.2°with *d*-spacing of 8.66 Å. For the amorphous BTZn sample, heating treatment induced the generation of mixture crystalline phases. When the as-prepared solid was heated at 165 °C for 2 min and

then ground into amorphous red phase, which is was clinally heated at 125 °C for 2 min, the obtained or ingelery stalline solid displayed identical X-Ray patterns to that of the sample prepared by grinding the as-prepared solid and then heating at 125 °C for 2 min (Fig. S2). These XRD results revealed that the mechanochromic process of BTZn solid was accompanied by the transformation between crystalline and amorphous phases. The crystalline structure of solvent vapour fumed sample is different from that of the thermally treated sample.

Thermodynamic properties of the BTZn based samples with different phases were checked by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) measurements to check the phase transformation processes (Fig. S3). BTZn complex was stable up to 300 °C, and displayed a melting point at around 340 °C with concurrent decomposition. For the as-prepared sample, there was an endothermic peak at around 165 °C. While a small exothermic peak at 125 °C and a weak broad endothermic peak at around 135 °C were observed for the ground sample. Solvent vapour fuming treatment to the ground sample resulted in the solid with identical thermal property to that of as prepared solid. It is proposed that the phase transitions induced by fuming and heating treatments are most likely relevant to the solvent molecules adsorption and release process, since a significant weight loss (around 5.5wt %) occurs within the temperature range from 130 to 180 °C for the initial as-prepared and fumed samples. The grinding treatment resulted in a small amount release of solvent molecules. On the other hand, the heating treatment (125 °C) generated the sample that does not show any discernible thermic peak or weight loss before decomposition temperature. Therefore, for the heated sample solvent molecules have been completely eliminated. In the ¹H-NMR spectrum of as-prepared solid sample an additional peak at δ 3.30 ppm, which is associated with the existence of water molecules, was observed, and this signal nearly disappeared after the sample was heated at 165 °C for 2 min (Fig. S4 and S5). Therefore, the as-prepared solid should have the position of BTZn·2H₂O due to that upon heating the weight loss of 5.5% is close to the water content (5.3%) of the BTZn·2H₂O complex. For the CH₂Cl₂ vapour fumed sample, the ¹H-NMR spectrum (Fig. S6) presented a peak at δ 5.76 ppm, which was assigned to CH₂Cl₂. For the samples that were heated no solvent or water signal was observed in the ¹H-NMR spectra.

To figure out the mechanochromic mechanism of BTZn solid, a possible supramolecular structure transformation process is presented in Fig. 6a. The DFT optimized results demonstrated that BTZn molecule adopts a equilateral triangle like structure feature and the molecular dimension is about 20 Å (Fig. 6b). The as-prepared yellow emissive solid crystallized from ethanol/dichloromethane solution may be composed of onedimensional molecular columns. Although the accurate molecular stacking mode is unavailable, it is presumed that the BTZn molecules should aggregate into dimers with antiparallel mode (Fig. 6c), which then assemble into columns based weak interdimer π ... π stacking interactions. It is well known that in solid state some Zn(II) Schiff-base complex molecules often aggregate into solids based on intermolecular Zn…O interactions in absence of axial coordinating ligand.¹⁴ Since the

Journal Name

ARTICLE

lattice constant of 27.25 Å is obviously larger than the dimension of the BTZn molecule, solvent molecules should exist in the as-prepared sample. The side alkyl chains on the salicylidene rings could provide Van der Waals interactions between molecular columns, leading to the formation of 2D columnar square structure. This class molecular columnar structures were commonly observed in Zn(II) Schiff-base complexes.²⁰

Upon mechanical grinding, the well-organized <u>AD</u> columnar arrangement should be destroyed and the molecular dimens form disordered aggregate resulting in amorphous phase. Under solvent vapour atmosphere the BTZn molecular dimers can spontaneously arrange themselves into ordered crystalline phases with high-symmetry columnar square structure feature.



Fig. 6 (a) Schematic presentation of the BTZn molecular packing transformation process induced by multi-stimuli. (b) The theoretically estimated BTZn molecular structure. (c) BTZn molecular dimer based on Zn…O interactions.

Under thermal annealing condition, the complex dimers prefer to arrange into a well-defined and more condensed lamellar packing structure with layer period distance of 20.68 Å, in which J-aggregates stabilized by $\pi \cdots \pi$ stacking interactions between the benzothiadiazole rings may be adopted. The thermal treatment induced orange solid of BTZn complex with a close packing lamellar arrangement is the thermodynamically stable phase.

Gelation Property

The 1D fibrillar structure feature prompt us to check the gellization property of BTZn complex. The organic gel formation ability of BTZn was tested in various solvents by means of the "stable to inversion of a test tube" method.²¹ The results are listed in Table S1. Notably, the complex easily forms gels in aromatic solvents, such as toluene, p-xylene and odichlorobenzene. For the selected solvents the low critical gelation concentration of complex BTZn was 1 mg/mL, suggesting the strong gellization characteristic. Timedependent fluorescence emission spectra showed slightly blueshifted and the emission intensity gradually decreased upon cooling the hot solutions $(2 \times 10^{-3} \text{ M})$ to room temperature, suggesting that H-like aggregates formed in the gel phase (Fig. 7a). The gels still exhibited strong luminescence with emission maxima at around 542 nm, which is similar to that of the asprepared solid. Transmission electron microscopy (TEM) of the xerogels revealed that BTZn molecules formed 1D nanofibers

with small diameter of several tens nanometers. The xerogel obtained from toluene showed a rope-type morphology formed by the assembly of numerous bundled and slender fibers (Fig. 7b). In *o*-dichlorobenzene solution BTZn molecules can form 3D nano-network based on thin fibrils (Fig. S7). The XRD pattern of xerogel exhibited two obvious diffraction peaks corresponding to *d*-spacings of 37.6 and 18.8 Å, respectively, which were in a ratio of 1:1/2, indicating that a lamellar-like assembly structure with an interlayer distance of 37.6 Å was adopt in BTZn xerogel (Fig. S8). The period length is approximately twice dimension of BTZn molecule, suggesting that in gel BTZn molecules aggregated into different supramolecular structure.

The BTZn xerogel also exhibited mechanochromic characteristic. As shown in Fig. 7c, upon grinding a part of the xerogel by a spatula, sharp emission contrast between yellow and red was achieved. Upon solvent (such as toluene or DCM) vapour fuming, the ground sample recovered into original yellow emission. Heating treatment at 125 °C for 2 min only resulted in the luminescent change of ground xerogel, while the emitting colour of unground xerogel gradually changed into orange based on a longer heating time (30 min). We deduced that the mechanofluorochromic mechanism of the as-prepared solid could be applied to the xerogel. The solvent molecules can be fixed in the nanonetwork during the gel

ARTICLE



Fig. 7 (a) Time-dependent photoluminescence spectra upon cooling the hot solutions in toluene (2×10⁻³ M). Inset: Photograph of BTZn gel from toluene under normal and UV-light. (b)TEM images of BTZn xerogel obtained from toluene gel. (c) Photographs of the xerogel recorded under UV light (λ_{ex} = 365 nm) and the responsive properties to the stimuli of grinding, fuming and heating.

formation and grinding could result in part of solvents release. The ground xerogel is more sensitive to thermal stimuli than the unground one suggesting that the latter should be more stable than the former.

Conclusions

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In summary, a bis(salicylaldiminato Zn(II) Schiff-base complex BTZn with unique mechanochromic property was prepared and characterized. BTZn based solid is a new class mechanochromic materials. Detail photophysical, SEM, X-ray diffraction characterizations of the different phases provided deep insights into the mechanochromism phenomena. The mechanochromic and solvent or thermal annealing processes were accompanied by the ordered molecular columns disassembly and reassembly behaviours, respectively. The assembly molecular packing changes resulted in the emission alterations of BTZn samples with different phases. The thermal treatment resulted in the formation of solvent-free and well defined lamellar structure. Moreover, in some organic solution BTZn complex displayed excellent gellization ability and assembled into nanofiber network. The BTZn based xerogel also exhibited mechanochromic characteristic, which was similar to that shown by as-prepared BTZn solid. The 1D supramolecular selfassembly property endows BTZn based solids or xerogel with mechanochromic feature. The BTZn based 1D nano-structure is generated based on the weak interdimer interactions that can be easily destroyed by mechanical forces leading to disorder aggregation structure and emission change. The multicolour emission alteration property of BTZn solids or xerogel implies that this complex may be employed to develop multifunctional chromic materials.

Experimental Section

General Information

NMR was measured on Bruker Avance 500 MHz spectrometer at room temperature with tetramethylsilane (TMS) as internal standard. Gas chromatography-mass spectrometry (GC-MS) were recorded on a Thermo Fisher ITQ1100 mass spectrometer. Matrix-assisted laser desorption/ionizatioh0.1(WALDA)TOWERE obtained on a Bruker Autoflex speed TOF/TOF (TOF = time-offlight) spectrometer, samples were dissolved in chloroform before analysis. Elemental analyses were performed on a Vario Micro (Elementar) spectrometer. UV-vis absorption spectra were recorded by a Shimadzu UV-2550 spectrophotometer and PL emission spectra were recorded by a Shimadzu RF-5301 PC spectrometer. TGA and DSC was carried out on TA Q500 and TA Q20 thermogravimeter at a heating rate of 10 °C min⁻¹ under a nitrogen atmosphere, respectively. FESEM images were performed on a JSM 6700F field emission scanning electronic TEM (transmission electron microscopy) microscope. characterization was performed with a JEOL JEM-2100F microscope operated at 200 KV. Power X-ray diffraction data were recorded by a PANalytical B.V. Empyrean diffractometer with Cu-K α radiation (λ = 1.5418 Å), operating at 40 kV and 40 mA.

Preparation of Materials

CHCl₃ and triethylamine (Et₃N) used for organic synthesis were freshly distilled over CaH₂ under a nitrogen atmosphere. Thionyl chloride (SOCl₂) in high-performance liquid chromatography (HPLC)-grade was purchased from Aladdin (Shanghai, China). All the other chemicals and reagents were used as received from commercial sources without further purification. Compounds benzo[c][1,2,5]thiadiazole-5,6-diamine²² and 4-(hexyloxy)-2hydroxybenzaldehyde²³ were synthesized based on a slightly modified method reported earlier. All reactions were performed under nitrogen atmospheres.

Synthesis of 5,6-dinitrobenzo[c][1,2,5]thiadiazole To a 250 mL flask, 4,5-dinitrobenzene-1,2-diamine (1.1 g, 5.6 mmol), CHCl₃ (80 mL) and Et₃N 2.3 mL, 22.7 mmol) were added. The solution was stirred until total dissolution of the diamine. SOCl₂ (0.9 mL, 11.4 mmol) was slowly added dropwise under ice-cooled condition, and the reaction mixture was then heated at reflux with stirring for 5 h. The solvent was then removed with a rotatory evaporator and water (150 mL) was added. Concentrated hydrochloric acid was added to the water solution and the pH value of water solution was controlled at around 2. The mixture was extracted with dichloromethane and the combined organic layer was dried over anhydrous MgSO4 and concentrated. The crude product was purified by column chromatography using а mixture of dichloromethane/petroleum (1:1) as the eluent to afford pale yellow solids (845 mg, 67 %). ¹H NMR (500 MHz, CDCl₃): δ 8.67 (s, 2H). GC-MS m/z: 225.98 [M]⁺ (calcd: 225.84).

Synthesis of benzo[c][1,2,5]thiadiazole-5,6-diamine 5,6-dinitrobenzo[c][1,2,5]thiadiazole (678 mg, 3.0 mmol) and iron powder (3.36 g, 60.0 mmol) were suspended in acetic acid (60 ml) and the mixture was stirred at 65 °C for 7 h under N₂. After cooling down to room temperature, the resulting mixture was poured into 5% NaOH aqueous, and extracted with diethyl ether (3 × 100 mL). The organic layer was collected, dried over anhydrous MgSO₄ and followed by purification by column chromatography using a mixture of dichloromethane/ethyl acetate (10:1) as the eluent, affording a white solid of 224 mg

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(45% yield). ¹H NMR (500 MHz, DMSO): δ 6.74 (s, 2H), 5.81 (s, 4H). GC-MS m/z: 166.03 [M]⁺ (calcd: 166.14).

Synthesis of 4-(hexyloxy)-2-hydroxybenzaldehyde 2,4dihydroxybenzaldehyde (2 g, 14.5 mmol), 1-bromohexane (2.6 g, 16 mmol), KHCO $_3$ (2.2 g, 21.7 mmol) and catalytic amount of KI (0.1 g) were mixed in dry acetone (100 mL) and the mixture was refluxed for 48 h. It was then filtered to remove the insoluble solid. The warm solution was neutralized with dilute hydrochloric acid and extracted twice with CH₂Cl₂ (100 mL). The combined extracts were concentrated to give a purple solid. The product was purified by column chromatography using silica gel (200-300 mesh) eluting with a mixture of dichloromethane and petroleum (v/v=1:1) followed by evaporation of solvent to yield colourless oily product (2.5 g, 78%). ¹H NMR (500 MHz, CDCl3): δ 11.47 (s, 1H), 9.70 (s, 1H), 7.41 (d, J = 8.7 Hz, 1H), 6.53 (d, J = 8.7 Hz, 1H), 6.41 (s, 1H), 4.00 (t, J = 6.5 Hz, 2H), 1.86 - 1.73 (m, 2H), 1.51 – 1.30 (m, 6H), 0.91 (t, J = 6.3 Hz, 3H). GC-MS m/z: 222.13 [M]⁺ (calcd: 222.19).

Synthesis of [N,N-Bis(4-hexyloxy-2-hydroxybenzylidene)-5,6benzo[c][1,2,5]thiadiazole-diaminato]ZnII (BTZn) A mixture of 4-(hexyloxy)-2-hydroxybenzaldehyde (444 mg, 2.0 mmol), benzo[c][1,2,5]thiadiazole-5,6-diamine (166 mg, 1.0 mmol), and zinc acetate dihydrate (220 mg, 1.0 mmol) in ethanol (40 mL) was heated at reflux with stirring for 3 h under a nitrogen atmosphere. After cooling to room temperature, the resulting precipitates were collected by filtration and then crystallized from ethanol/dichloromethane (v/v=3:1). The yellow crystalline powder was dried in vacuum (80 °C, 10⁻² Torr) for 5 h and finally heated at 165 $\,^\circ\!\mathrm{C}$ for 10 min in air to offer orange solid product (572 mg, 90%). ¹H NMR (500 MHz, DMSO-d₆): δ 9.04 (s, 2H), 8.34 (s, 2H), 7.35 (d, J = 9.4 Hz, 2H), 6.21 – 6.18 (m, 4H), 4.00 (t, J = 6.5 Hz, 4H), 1.77 – 1.69 (m, 4H), 1.47 – 1.39 (m, 4H), 1.37 – 1.29 (m, 8H), 0.90 (t, J = 6.9 Hz, 6H). ¹³C NMR (125 MHz, DMSO- d_6): δ 175.97, 165.77, 164.01, 153.68, 145.03, 138.48, 114.93, 105.64, 105.26, 104.97, 67.81, 31.49, 29.01, 25.68, 22.55, 14.40. GC-MS m/z: 635.90 [M]⁺ (calcd: 636.17). MOLDI-TOF-MS m/z: 636.66 [M]⁺, 1272.34 [(M)₂]⁺. Elemental analysis calculated for $C_{32}H_{36}N_4O_4SZn$): C, 60.23; H, 5.69; N, 8.78; S, 5.02; Found: C, 59.79; H, 5.65; N, 8.53; S, 4.78.

DFT Calculations

The ground state geometries were fully optimized by the density functional theory (DFT)²⁴ method with Becke three-parameter hybrid exchange and the Lee–Yang–Parr correlation functional²⁵ (B3LYP) using the Gaussian 09 software package.²⁶ The 6-311++G(d,p)²⁷ basis set for C, H, N, and O atoms and LANL2DZ²⁸ basis set for Zn atom were employed. This basis set was adopted as it was widely used for calculating geometries and frontier orbital distributions of organometallic complexes and it provided reliable results.²⁹

Organogelation

The suspensions of certain amount of the complex in various organic solvents were heated in a screw-cap vial until the solid dissolved. After cooling to room temperature, gelation was considered successful if no flow was observed upon inverting the vial.

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