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Syntheses, crystal structures, nonlinear optical properties and cis-trans isomerization of functionalized sulfur-terminal [Zn(II) and Cd (II)] complexes based on phenothiazine-2,2':6',2"-terpyridine conjugated ligands

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enhanced compared to the free $D-\pi-A$ type ligand.

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ABSTRACT

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1. Introduction

Terpyridyl compounds have ring nitrogens serving as multiple interaction sites, and form stable coordination and hydrogenbonded complexes with various metal ions and molecules. They have been widely used as ligands for transition metal cations and building blocks in supramolecular chemistry [1]. In addition, they are generally thermally and chemically stable. Among these terpyridyl compounds, 2, 2':6', 2"-terpyridine (tpy) has been most extensively studied as a chelating compound. The coordination chemistry of terpyridine is attracting a current attention, due to coordinating with different metal ions and their photoluminescent properties [2–7], in particular those of platinum or ruthenium [8,9], zinc or cadmium [10,11]. The complexes can be of significance especially in coordination chemistry, bioinorganic chemistry, catalysis, supramolecular chemistry and molecular devices [12–14].

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One novel 2,2':6',2"-terpyridine ligand L and its complexes (Zn(S)₂L, Cd(S)₂L) were synthesized and

systematically characterized. There were cis-trans isomerization of the ethylene group in compounds of

 L_{1} Zn(S)₂L and Cd(S)₂L though some characterization. Finally it was found that the two-photon absorption

cross section values (σ) for the complexes in the near infrared region (~800 nm) were dramatically

Phenothiazines (PTZs) are a class of electron-rich tricylic nitrogen–sulfur hetrocycles with a low oxidation potential and a high propensity to form stable radical cations [15]. PTZs can exhibit relatively intense luminescence, high photoconductivities and undergo reversible oxidation processes. Besides, the nonplanar phenothiazine ring structure can restrict π -stacking aggregation, which prevents the detrimental pure singlet excitation recombination process [16]. Consequently, PTZs have been recently used as spectroscopic probes in supermolecular assembly for PET (photoinduced electron transfer) studies, and as electron donor components in the materials science [17,18].

In this article as our continuous work [19], the 2,2':6',2''-terpyridine ligand (L) and their complexes (Zn(S)₂L, Cd(S)₂L) were synthesized and characterized by elemental analysis, ¹H NMR, IR, MALDI-TOF spectroscopy, and single crystal X-ray diffraction. A







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facile synthesis route for a D $-\pi$ -A system ligand with PTZ as the electron donor, tpy group as an electron acceptor and styrene group as π -bridge [20], and its two sulfur-terminal metal complexes are presented. S⁻¹ valence state results from charge self-regulation behavior, which is novel and has been seldom reported before [19].

As we know, the terpyridyl ligand can easily coordinate to zinc or cadmium ions. The metal ion binds to the acceptor to form a $D-\pi-A$ type complex, thus it should yield an increase rather than a decrease of ICT (intramolecular charge transfer) upon excitation. Consequently, metal ion binding is expected to realize an increased 2 PA cross section [21–24]. And then, the properties of all the complexes were systematically investigated compared to the original ligand. Finally, we successfully found Cd(II) complex to be an efficient two photon absorption material with larger twophoton absorption cross section values ($\sigma = 1311.68$ GM).

In addition, the nonplanar phenothiazine ring structure results in cis- and trans-isomerization of the ethylene π -bridge (see Scheme 1). The single-photon fluorescence spectra are given, and a brief discussion on the structure-property relationship has been described.

2. Experiments

2.1. Materials and instruments

All chemicals were purchased as reagent grade and used without further purification. The solvents were dried and distilled according to standard procedures. Elemental analysis was performed with a Perkin–Elmer 240 analyzer. IR spectra (4000–400 cm⁻¹), in KBr pressed pellets, were recorded on a Nicolet FT-IR 170 SX spectrophotometer. Mass spectra were obtained on a Micromass GCT-MS spectrometer. ¹H NMR spectra were performed on a Bruker 500 Hz Ultrashield spectrometer and reported as parts per million (ppm) from TMS (δ). Coupling constants *J* are given in Hertz. Mass spectra were acquired on a Micromass GCT-MS (El source).

2.2. Optical measurements

UV-vis absorption spectra were measured on a UV-265 spectrophotometer. The fluorescence spectra in solid states and solution were performed with an F-4500 fluorescence spectrophotometer. The concentration of sample solution was 1.0×10^{-5} M. The fluorescence quantum yields (Φ) were determined relative to coumarin 307 using a standard method. Quantum yields were corrected as follows:

$$\Phi_{\rm S} = \Phi_r igg(rac{A_r \eta_{
m S}^2 D_{
m S}}{A_{
m S} \eta_r^2 D_r} igg)$$

where the s and r indices designate the sample and reference samples, respectively, A is the absorbance at λ_{exc} , η is the average refractive index of the appropriate solution, and D is the integrated area under the corrected emission spectrum. All measurements were carried out in air at room temperature.

2.3. Syntheses

2.3.1. Synthesis of 10-hexyl-phenothiazin 1

10-H-phenothiazine (10.0 g, 50 mmol), 1-bromohexane (8.5 mL, 60 mmol) and sodium hydroxide powder (8.0 g, 0.2 mol) were well mixed in 60 mL DMF solution and aliqiuat-336 was used as phase transfer catalyst. The reaction mixture was stirred at 120 °C for 24 h and then neutralized with 2.0 M HCl, extracted three times with 100 mL of dichloromethane. The combined organic layer was washed with aqueous brine and dried with anhydrous magnesium sulfate. After that, the solvent was evaporated using a rotary evaporator. The crude liquid product was then purified by flash column chromatography, eluting with petroleum ether to give colorless liquid (12.0 g, yield: 85%).

2.3.2. Synthesis of 10-hexyl-10H-phenothiazine-3-carbaldehyde 2

Put DMF (7.3 g, 0.1 mol) at 0 °C, phosphorus oxychloride (30.6 g, 0.2 mol) was added and the solution was allowed to warm to room temperature. Then, **1** (5.7 g, 0.02 mol) and distilled chloroform (60 mL) were added. The reaction mixture was heated to 80 °C and kept for 16 h. After that, the resulting solution was poured into icewater, neutralized with 20% sodium hydroxide. The mixture was stirred at room temperature for 1 h and then extracted with CH₂Cl₂, dried with anhydrous magnesium sulfate. Organic phase was filtered and concentrated. The residue was purified through column



Scheme 1. cis- and trans-isomerization of L.

chromatography on silica gel using petroleum ether-ethyl acetate (10:1) as eluent to give red oily liquid (5.0 g, yield: 80%).

2.3.3. Synthesis of 10-hexyl-3-[4-(2,6-di-(pyridine-2-yl)pyridine-4-yl)styryl]-10H- phenothiazine **L**

4-(2,2':6',2"-terpyridyl-4')-benzyl triphenyl phosphonium bromide 3 was synthesized [25]. t-BuOK (1.3 g, 12.3 mmol) was placed into a dry mortar and milled to very small particles, then 2 (1.0 g, 3.14 mmol) and **3** (2.0 g, 3.0 mmol) were added and mixed. The mixture was milled vigorously for 20 min. After completion of the reaction (monitored by TLC), the mixture was solved with 100 mL dichloromethane, washed three times with water, and dried with anhydrous magnesium sulfate. Then it was filtered and concentrated. The resulting solution was dispersed in 100 mL ethanol. The residual solid was filtered and recrystallized from dichloromethane/ethanol (1:1) to give pale yellow crystals of L (1.3 g, yield: 70%). Anal. Calcd. for C₄₁H₃₆N₄S: C, 79.87; H, 5.84; N, 9.09%. Found: C, 79.62; H, 5.76; N, 8.95%. IR (KBr, cm⁻¹): 3051 (w), 2925(m), 2853 (w), 1583 (s), 1600 (m), 1567 (m), 1470 (m), 1389 (m), 1335 (w), 1249 (m), 1189 (m), 962 (s), 792 (m), 745 (m). ¹H NMR (DMSO-d₆, 400 MHz) ppm: 0.84 (m, 3H), 1.27 (m, 4H), 1.38 (m, 2H), 1.70 (m, 2H), 3.90 (m, 2H), 6.96 (m, 1H), 7.04 (d, 2H, J = 9.54), 7.19 (m, 2H), 7.25 (d, 1H, I = 15.56), 7.31 (d, 1H, I = 16.06), 7.48 (d, 2H, I = 4.52), 7.55 (m, 2H), 7.78 (d, 2H, *I* = 8.78), 7.96 (d, 2H, *I* = 7.53), 8.06 (m, 2H) 8.69 (m, 2H), 8.85 (m, 2H), 8.90 (m, 2H). MS: *m*/*z* (%): 616 (M⁺), 545, 531.

2.3.4. Synthesis of ZnS/CdS nanocrystals

 $Zn(CH_3COO)_2 \cdot 2H_2O$ (0.44 g, 2.0 mmol), CH_3CSNH_2 (0.15 mg, 2.0 mmol) and cetyltrimethylammonium bromide (CTAB, 0.01 g) were dissolved in 80 mL of ethanol to form transparent solution. Then the mixture was refluxed with vigorous stirring for 3 h and a white turbid solution formed. Finally, the white powders of ZnS nanocrystals were obtained by subsequent centrifugation and followed by washing several times with water and ethanol.

In the same way, CdS nanocrystals were also prepared via $Cd(CH_3COO)_2 \cdot 2H_2O$ (0.50 g, 2.0 mmol) and CH_3CSNH_2 (0.15 g, 2.0 mmol) to afford pale yellow solid eventually.

2.3.5. Synthesis of $M(S)_2L$ complexes (M = Zn/Cd)

Zn(S)₂L complex: Ligand L (61.8 mg, 0.1 mmol), ZnS nanocrystals (9.7 mg, 0.1 mmol) and NaSCN (32.4 mg, 0.4 mmol) was solved in ethanol (14 mL) and DMSO (2 mL), the mixture was sealed in a 20 mL Teflon-lined reactor and heated at 130 °C for 24 h. After cooling to room temperature, red single crystals were obtained. Yield: 65%. Anal. Calcd. for C₄₁H₃₆N₄S₃Zn: C, 66.04; H, 4.83; N,7.52%. Found: C, 65.79; H, 4.74; N, 7.40%. IR (KBr, cm⁻¹): 3059 (w), 2922 (w), 2852 (w), 1596 (s), 1573 (m), 1469 (s), 1249 (m), 1188 (m), 1014 (m), 975 (s), 794 (m), 745 (m), 637 (w), 515 (w), 415 (w). ¹H NMR (DMSO-*d*₆, 400 MHz) ppm: 9.14 (s, 2H), 9.01 (d, 2H, *J* = 7.3), 8.86 (d, 2H), 8.37 (m, 4H), 7.89 (m, 4H), 7.50 (s, 2H), 7.39 (d, 1H, *J* = 16.00), 7.32 (d, 1H, *J* = 16.00), 7.23 (m, 2H), 7.05 (m, 2H), 6.96 (m, 1H), 3.91 (m, 2H), 1.41 (m, 2H), 1.22 (m, 6H), 0.85 (d, 3H).

The Cd(S)₂L complex was also prepared similarly to Zn(S)₂L via CdS nanocrystals, L and NaSCN to afford orange-red single crystals. Yield: 59%. Anal. Calcd. for $C_{41}H_{36}N_4S_3Cd$: C, 61.96; H, 4.53; N, 7.05%. Found: C, 62.07; H, 4.45; N, 6.93%. IR (KBr, cm⁻¹): 3059 (w), 2922 (w), 2851 (w), 1596 (s), 1574 (m), 1467 (s), 1402 (m), 1247 (m), 1189 (m), 1014 (m), 979 (s), 793 (m), 743 (m), 517 (w). ¹H NMR (DMSO- d_6 , 400 MHz) ppm: 9.08 (s, 3H), 8.78 (d, J = 4.2, 3H), 8.34 (s, 3H), 7.83 (d, 4H), 7.49 (s, 2H), 7.33 (d, 1H, J = 18), 7.31 (d, 2H, J = 14), 7.20 (m, 3H), 7.05 (m, 2H), 6.96 (m, 1H), 3.90 (m, 2H), 1.25 (m, 6H), 0.85 (m, 2H).

2.4. X-ray crystallography

X-ray diffraction data of single crystals of compound L, Zn(S)₂L and Cd(S)₂L were collected on a Siemens Smart 1000 CCD diffractometer. The determination of unit cell parameters and data collections were performed with MoK α radiation ($\lambda = 0.71073$ Å). Unit cell dimensions were solved by direct methods using SHELXS-97. The other non-hydrogen atoms were located in successive difference Fourier syntheses. The final refinement was performed by using full-matrix least-squares methods with anisotropic thermal parameters for non-hydrogen atoms on F^2 . The hydrogen atoms were added theoretically and riding on the concerned atoms.

2.5. Computational details

TD-DFT computational studies were performed to elucidate the electronic structures of the ground state of the compound. Optimizations were carried out with B3LYP [6-31G(d)] without any symmetry restraints, and the TD-DFT {B3LYP[6-31G(d)]} calculations were performed on the optimized structure. All calculations, including optimizations and TD-DFT, were performed with the G03 software [26]. In the calculation of the optical absorption spectrum, the 25 lowest spin-allowed singlet—singlet transitions, up to energy of about 5 eV, were taken into account.

3. Results and discussion

3.1. Preparation and spectroscopic characterization

The synthetic route of L is shown in Scheme 2. Compound L was synthesized by a solvent free Wittig reaction, which is a facile method to prepare oligomers with extended π -electron conjugations. ZnS nanocrystals were synthesized according to reported methods [19]. Zn(CH₃COO)₂·2H₂O was used to provide the zinc source, CH₃CSNH₂ provide the sulfur source and cetyl trimethy-lammonium bromide (CTAB) was added as surfactant. The M(S)₂L complex was synthesized by a solvothermal process and the MS nanocrystals were used as optimal precursor, which can simultaneously provide both metal and sulfur sources. Here, NaSCN is used as a mineralizer to improve the crystal quality.

Compound **L** was characterisized by EA, IR, ¹H NMR and Mass spectra. In the IR spectra, strong bands appear around 1249, 2925 and 2853 cm⁻¹, which can be assigned to vibrations of the 10-hexyl-PTZ moiety. The bands of 1583, 1470 and 1389 cm⁻¹ for **L**, can be assigned to vibrations of the terpyridyl moiety. Meanwhile, the composition of complex $M(S)_2L$ (M = Zn or Cd) was also confirmed. In IR spectra, the bond at 513 cm⁻¹ for Zn complex and 517 cm⁻¹ for Cd complex is attributed to the stretching vibrations of Zn–S and Cd–S bond, respectively. From ¹HNMR spectra of ligand **L**, it could be found that the double bond protons display integration corresponding to 2H, centered at 7.25 and 7.31 ppm with J = 15.56 and 16.06 Hz, respectively, which indicate that trans isomer would not isomerize to a cis isomer at room temperature even after a few days under visible light.

3.2. Crystal structure

The structure of L is shown in Fig. 1. Pale yellow single crystals suitable for X-ray diffraction analysis were obtained by slow evaporation of L solution (CH₂Cl₂ covered with ethanol) at room temperature after several days. Data collections and refinements were listed in Table S1, selected bond distances and angles were given in Table S2. The center pyridinyl plane (labeled P2) is arranged with two pyridine planes (P1 and P3) being 8.65° (P2 and P1) and 9.32° (P2 and P3). The result indicates that the terpyridyl



Scheme 2. Synthetic route for L and M(S)₂L.

group is barely coplanar. The dihedral angle between P2 and phenyl ring (labeled P4) is 41.57°. At the PTZ donor end, the dihedral angle of 33.37° between one phenyl ring (labeled P5) and P7, the dihedral angle of 31.34° between other phenyl ring (labeled P6) and P7, which indicate that there are some distortion between terpyridyl, PTZ and styrene. The C=C linkage between P4 and P5 exists in trans-isomer and was quite conjugated with bond lengths of C(24)–C(22): 1.484(1) Å, C(22)=C(23): 1.305(1) Å and C(23)–C(21): 1.550(1) Å. These structural features suggest that all nonhydrogen atoms between donor and acceptor are conjugated, leading to a π -bridge for the charge transfer from PTZ to terpyridyl. However, the whole molecule has a certain degree of distortion because of the intermolecular interaction in solid states.

The structures of two complexes are shown in Fig. 1. Data collections and refinements were also listed in Table S1, selected bond distances and angles were given in Table S2. The structures of $M(S)_2L$ (M = Zn, Cd) are similar. In each molecule, the center metal is in a distorted five-coordinated trigonal-bipyramidal geometry with the two apical sites occupied by two sulfur atoms, respectively. The S–M bond lengths are almost equal (2.290 and 2.310 Å for Zn; 2.446 and 2.437 Å for Cd), and the sulfur atoms are most likely to be identical S⁻¹ valence states as a result of charge self-regulation behavior. In the two complexes, it is observed that the N atom torsion angle of terpyridyl group (electron-acceptor) was changed owing to the highly versatile and adaptive coordination modes of the terpyridyl moiety. In complex Zn(S)₂L, the dihedral angles between P2 and P1, P2 and P3, P2 and P4, P4 and P5, P5 and P6 are 2.49°, 3.09°, 9.56°, 16.89° and 16.13°, respectively. In

complex Cd(S)₂L, the dihedral angles between P2 and P1, P2 and P3, P2 and P4, P4 and P5, P5 and P6 are 11.62°, 3.35°, 18.92°, 32.94° and 25.00°, respectively. These dihedral angles of two complexes are lower than that of the ligand L molecule. In two complexes, it is similar that the C=C linkage between P4 and P5 exists in transisomer and was quite conjugated with bonds of C(15)–C(13): 1.493(1)Å, C(13)=C(14): 1.229(1)Å and C(14)–C(17): 1.488(1)Å for Zn complex, and C(34)–C(36): 1.466(1)Å, C(34)=C(28): 1.338(1)Å and C(28)–C(2): 1.459(1)Å for Cd complex. The results indicate that the molecules of complexes have better planarity than the ligand L in spite of a degree of distortion to some extent. In addition, the planarity of Zn complex is better than that of Cd complex. These structure features provide a theoretical foundation for their optical properties.

3.3. The linear absorption spectra and TD-DFT studies

The photophysicle properties of Ligand L and its complexes in different solvents are collected in Table 1. The linear absorption spectra of the ligand L and its complexes were measured in THF, as shown in Fig. 2. The calculated frontier orbitals of L, $Zn(S)_2L$ and $Cd(S)_2L$ are shown in Fig. 3. In the spectra of ligand L, there are two absorption shoulder_s. One shoulder at ca. 383 nm can be assigned to ICT from PTZ to terpyridyl group, the shoulder originating from HOMO \rightarrow LUMO + 1 (calculated at 375.3 nm) (Table S3).

There are visible red-shifts from the peak positions of two complexes to those of L ligand in the same solvent. As shown in the molecular structures of two complexes, the metal (Zn/Cd) ions



Fig. 1. The molecular structures of L, Zn(S)₂L and Cd(S)₂L.

Table 1 Single-photon-related photophysical properties of L, $Zn(S)_2L$ and $Cd(S)_2L$.

Compound	Solvent	$\Lambda_{\max}{}^a$	ε	Λ_{\max}^{b}	Φ^{c}
L	Benzene	275, 324, 379	2.83, 1.18, 0.43	527	0.75
	CH_2Cl_2	280, 325, 375	2.92, 1.31, 0.54	556	0.54
	THF	282, 325, 379	3.01, 1.34, 0.481	545	0.63
	CH ₃ CN	279, 326, 380	3.05, 1.38, 0.56	563	0.28
	DMF	281, 324, 380	2.93, 1.16, 0.54	564	0.31
Zn(S) ₂ L	Benzene	327, 416	3.19, 1.43	513	0.09
	CH_2Cl_2	329, 424	3.56, 1.93	543	0.01
	THF	323, 404	3.28, 1.94	459, 538	0.31
	CH ₃ CN	322, 410	3.39, 2.07	473, 556	0.06
	DMF	320, 396	2.96, 2.00	474, 560	0.04
$Cd(S)_2L$	Benzene	324, 406	1.16, 0.48	432, 517	0.09
	CH_2Cl_2	325, 417	3.96, 2.14	539	0.06
	THF	322, 402	3.67, 2.15	462, 536	0.32
	CH₃CN	321, 408	3.91, 2.35	474	0.01
	DMF	315, 394	3.23, 2.32	487	0.15

^a Peak position of the absorption band.

^b Peak position of Single-photon fluorescence, excited at the absorption maximum.

^c Quantun yields determined by using fluorescein as standard.

coordinate with terpyridyl group of ligand L, which makes the molecule better planarity relative to the ligand, contributing to increase the intramolecular charge transfer degree and enhance molecular polarity, especially in the excited state [27]. The two peaks located at 405 nm for Zn(S)₂L and 399 nm for Zn(S)₂L can be assigned to MLCT, and the calculated frontier orbitals can also proved the band for Zn(S)₂L originating from HOMO \rightarrow LUMO + 3 (calculated at 403.8 nm) (Table S3), the band for Cd(S)₂L originating from HOMO-1 \rightarrow LUMO + 3 (calculated at 402.3 nm) (Table S3). Therefore, it can be concluded that the results of experiments are well consistent with the theoretical calculations.

The absorption spectra of L, Zn(S)₂L and Cd(S)₂L in four solvents after 3 h and 5 days are presented in Figs. S1 and S2. 5days later, the band of $\pi \rightarrow \pi^*$ red shifted along with the increase in trans structure, because trans structure being planar conjugate, cis structure being the not planar conjugated system [28].



Fig. 2. Linear absorption spectra of L, $Zn(S)_2L$ and $Cd(S)_2L$ in THF solution($c = 1.0 \times 10^{-5} \text{ mol} \cdot L^{-1}$).

- new 3000 1 h 2 h 3 h 2500 Fluorescence Intensity 5 h 6 h 5 d 2000 1500 1000 500 0 500 450 550 600 400 650 Wavelength (nm)

Fig. 4. Single-photon fluorescence spectra of L in THF solution at different times (c = 1.0×10^{-5} mol·L⁻¹).

3.4. The fluorescence property

The fluorescence spectra of L and its complexes were investigated and found to change along with time in weaker-polar solvent. For instance, there are two emission peaks in new THF solution of L (see Fig. 4): one at 454 nm with low-intensity and the other at 541 nm with high-intensity. The peak-intensity at 454 nm increased and that at 541 nm reduced along with the time. Finally, the fluorescence peak at 541 nm disappeared and the singleemission peak of L is at 454 nm. From ¹HNMR of L, Zn(S)2L and Cd(S)2L, the ligand and its two complexes all exist trans isomerization stably. The two emission peaks of L in weaker-polar solvent reflect body's tautomerization from cis isomer to trans isomer.

The luminescence behaviors of L are different in different solvent polarity. The fluorescence spectra of L in five solvents after 3 h

and 5 days are presented in Fig. 5. As shown, there are two emission peaks in weaker-polar solvent and one single-emission peak in stronger-polar solvent like DMF and acetonitrile at short wave after 3 h. However, there is only one emission peak at short wave in almost all solvents after 5 days. As shown in Fig. 6, the solid fluorescence spectra of L is also one emission peak and is red-shifted 40 nm compared with DMF solution. In the crystal structure of L, the styrene double bond of solid L exists with Trans structure. We can speculate that the short wave emission would be trans configuration and the long wave is induced by Cis structure. This suggests that styrene double bond can flip cis configuration in weaker-polar solvent, due to the smaller molecular forces between the solvent and solute. The weaker of polarity, the higher proportion of cis-lycopene. So in stronger-polar solvent and solid, L only exists as trans-lycopene. In addition, the emission peak position of



Fig. 3. Molecular orbital energy diagram for L, Zn(S)₂L, Cd(S)₂L.



Fig. 5. Single-photon fluorescence spectra of L in five solvents after 3 h (left) and five days (right) ($c = 1.0 \times 10^{-5} \text{ mol} \cdot L^{-1}$).

cis-trans isomerization increasing with the solvent polarity was positively solvatochromism. This explains that the two emission peaks would be assigned to ICT [29].

In Fig. 7, the fluorescence spectra of Zn complex is similar to L in THF, acetonitrile and DMF due to intramolecular charge transfer of the ligand. The metal coordinates with acceptor group of donor– π –acceptor (D– π –A) models which increased the charge transfer degree and the emission peaks showed slight red-shifting. Just start testing in the benzene and methylene chloride, fluorescence emission is given priority to short wave. This indicates that the introduction of the metal ions, planarity enhancement, more stable and trans configuration are afforded by complex formation. So, the transformation time of complex from cis to trans configuration is less than that of the ligand.

3.5. Infrared optical properties

According to the results of infrared test, L, Zn(S)₂L and Cd(S)₂L appear peaks at about 962 (s), 792 (m), 975 (s), 794 (m), 979 (s) and 793 (m) cm⁻¹, respectively. It is characterized as the trans and cis asymmetric deformation vibration $\delta = C-H$ (out-plane) of R₁CH = CHR₂, indicating that the samples contains both cis- and trans-structures, which has been examined by XRD. As shown in Fig. S3, there are some overlap between the sample and single crystal. It also proved the fluorescence test of the sample in solvent, excitation wave also cis structure is reduced and short wave



Fig. 6. Solid fluorescence spectra of L, Zn(S)₂L and Cd(S)₂L.

excitation also trans structure is increased, which provides an explanation for this interesting phenomenon.

3.6. Two-photon absorption (TPA) properties

The nonlinear properties of the compounds were studied by using an open aperture Z-scan technique under a femtosecond laser pulse and Ti: 95 sapphire system (680–1080 nm, 80 MHz, 140 fs). We chose the testing wavelengths from 700 nm to 900 nm, but only in some wavelengths were the TPA found which was shown in Fig. S4. The following experiment datas were measured under the optimum wavelengths. The experimental spectra, measured at 740 nm for L, 780 nm for $Zn(S)_2L$ and 790 nm for $Cd(S)_2L$ in DMF at a concentration of 1.00 mM, are shown in Fig. 8. The theoretical data were fitted using the following equations:

$$T(z,s=1) = \sum_{m=0}^{\infty} \frac{\left[-q_0(z)\right]^m}{(m+1)^{3/2}} \quad \text{for } |q_0| < 1$$
(1)

where $q_0(z) = \beta I_0 L_{eff} / (1 + x^2)$, $x = z/z_0$, $z_0 = \pi \omega_0^2 / \lambda$, β is the twophoton absorption (TPA) coefficient of the solution, I_0 is the intensity of laser beam at focus (z = 0), $L_{eff} = [1 - exp(-\alpha_0 L)] / \alpha_0$ is the effective length with α_0 the linear absorption coefficient, L is the sample length, $z_0 = \pi \omega_0^2 / \lambda$ is the diffraction length of the beam with ω_0 the spot size at focus, λ the wavelength of the beam and z is the sample position. Based on (1)*Eq.*, the molecular TPA coefficient β can be deduced. Furthermore, the TPA cross-section for a given sample is determinated by using the following relationship:

$$h\beta v = \sigma N_A d_0 \times 10^{-3} \tag{2}$$

here *h* is the Planck constant, *v* is the frequency of incident laser, N_A is the Avogadro number, and d_0 is the sample concentration. According to (2)*Eq.*, the TPA cross-section σ can be got [30].

From the linear absorption spectra (see Fig. 2), it is discovered that there is no linear absorption in the wavelength range 680-900 nm for all the chromophores. Therefore, any absorption at this wavelength range should be derived from multiphoton absorption process. In Fig. 8, the open-aperture transmittance was symmetric with respect to the focus (z = 0). The obvious minimum transmittance unambiguously indicated a biggish nonlinear absorption which was attributed to TPA effect.

It has been found that the two-photon absorption cross sections of coordination compounds $(Zn(S)_2L \text{ and } Cd(S)_2L)$ are remarkably enhanced compared with that of L. The behavior of TPA spectra can



Fig. 7. Single-photon fluorescence spectra of $Zn(S)_2L$ (upleft) and $Cd(S)_2L$ (upper right) in five different solvents after 3 h, $Zn(S)_2L$ and $Cd(S)_2L$ in THF after five days (down) (c = $1.0 \times 10^{-5} \text{ mol} \cdot L^{-1}$).



Fig. 8. Open aperture Z-scan curves of L, $Zn(S)_2L$ and $Cd(S)_2L$ in DMF (c = $1.0 \times 10^{-3} \text{ mol} \cdot L^{-1}$).

Table 2

Two-photo absorption coefficient β and cross section σ of L, Zn(S)₂L and Cd(S)₂L.

Compound	Best nonlinear absorption wavelength/nm	$\beta/(cm \cdot W^{-1})$	σ/GM ^a
L	740	0.012	535.19
$Zn(S)_2L$	780	0.023	973.20
$Cd(S)_2L$	790	0.031	1311.68
	50 1		

 $^a~1~\text{GM} = 1 \times 10^{-50}~\text{cm}^4$ s per photon.

be attributed to the extending conjugation after complexation of the ligand with Cd(II) or Zn(II) ions and a double bond added, in which the ICT states also play an important role for TPA sections of the coordination compounds [31]. The increased TPA values were observed from Zn(II) to Cd(II) complex due to a larger radius of Cd(II) compared with Zn(II) ion which possibly gives a more extended delocalization. The experimental results are also in accordance with those from TD-DFT calculations. The 2 PA spectra of all the compounds in DMF are presented in Table 2. It is shown that the σ for L, Zn(S)₂L and Cd(S)₂L are ca. 535.19 (740 nm), 973.20 (780 nm), 1311.67 (790 nm), respectively, which is consistent with experimental trend (σ (Cd(S)₂L) > σ (Zn(S)₂L) > L). This large TPA response comes from the marked core to periphery charge redistribution in Cd(S)₂L and Zn(S)₂L upon photoexcitation. Therefore, complexation with Zn(II) and Cd(II) enhances the electron-acceptor character of the central terpyridine group, which converts the ligand to a more strongly polarized D- π -A unit, making the complexes potential candidates for TPA response materials [32].

4. Conclusion

In this article, the compounds L, $Zn(S)_2L$ and $Cd(S)_2L$ have obvious cis-trans isomerization of the ethylene group. They were proved by single-photon fluorescence spectra, IR spectra and XRD. The transformation time of complex from cis into trans type is shorter than that of ligand, and the electronic delocalization is extended by metal ion in the coordination compounds. In addition, metal ions were coordinated with terpyridine ligand, which leads to dramatically enhanced two-photon absorption, especially for the complex Cd(S)₂L. In addition, the functionalized complexes can be used for excellent fluorogenic and potential applications due to a simple preparation. It provides a new idea and effective pathway to design and synthesize novel two-photon fluorescence materials.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.dyepig.2014.12.011.

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