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Studies of the isomerization and photophysical properties of a novel 2,2':6',2''-terpyridine-based ligand and its complexes[†]

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A novel 2,2':6',2"-terpyridine-based ligand L and its complexes $[ML_2](ClO_4)_2 \cdot CH_2Cl_2$ (M = Cd 1, Zn 2, Cu 4, Mn 5), $[CoL_2](ClO_4)_2$ 3, CdLI₂ 6 and CdL(SCN)₂ 7 were synthesized and fully characterized. The crystal structures of 1–6 were solved by single crystal X-ray diffraction analysis. The linear absorption and emission properties, and third-order nonlinear optical (NLO) properties of all the complexes were systematically investigated. The equilibrium of the *trans-* and *cis-* isomers of L was studied both experimentally and theoretically. The configurations and photophysical properties of the complexes display a large dependence on the choice of metal ions and anions.

Introduction

Since the 1990s, increasing attention has been devoted to twophoton absorption (2PA) materials because of their applications in photonic and biophotonic areas, such as three-dimensional optical data storage and microfabrication,1 power limiting,2 upconversion lasing,3 three-dimensional fluorescence imaging,4 and photodynamic therapy.⁵ For this reason, extensive efforts have been concentrated on the synthesis of various materials with large 2PA cross-sections (σ), such as polymers,⁶ small organic molecules,7 semiconductors or metal nanoparticles8 and coordination compounds.9 Recently, material design directed towards 2PA optimization has had extensive research for certain applications.¹⁰ Additionally, good physical and chemical stabilities are important to a novel material as an applicable material and must be addressed in parallel to continuing efforts to enhance the effective σ values. In contrast with organic molecules, coordination compounds can be easily synthesized in high yield and are expected to show better physical and chemical stability, in which the metal ions can serve either as a multidimensional template for increasing the molecular

number density of two-photon active components (*i.e.*, ligands), or as an important structural control in the intramolecular charge-transfer process, leading to an enhanced σ value.

The control of the molecular geometry as well as the electronic structure, which are interconnected, is of crucial importance to optimize physical properties of the coordination compounds. The architectures of them rest on several factors, but herein, we mainly discuss the influences from the ligand, metal centers and anions. Firstly, the design of ligands is a useful way of manipulating the structures. For example, 2, 2':6',2"-terpyridine (tpy) derivatives are important tridentate ligands, which can be incorporated into various supramolecular structures, such as for the preparation of wire-type components, helicates, molecular cycles, wheels and scorpionates.¹¹ The three conformations observed in the tpy ligand are well documented (Scheme 1a).12 Although a large number of tpys and their metal complexes have been synthesized,^{11,13} the studies of the third-order nonlinear optical (NLO) properties and structure-property relationships of them are scarcely reported. Based on our interest in searching for the optimized 2PA molecules having large σ value, we selected the tpy unit as a strong acceptor (A) group with three pyridine rings preferring a planar geometry to achieve maximum conjugation, which is helpful for the π electron delocalization. Phenothiazine (PTZ) was chosen as the donor group (D) as PTZs are well-known dyes, antioxidants, and pharmaceuticals.¹⁴ Compared with the coplanar molecules, the nonplanar PTZ ring is a stronger electron donor and shows better 2PA properties.^{7d,9c} Here we use a styryl moiety as the π -bridge to build a novel ligand 10-ethyl-3-[4-(2, 2':6',2"-terpyridinyl-4'yl) styryl] phenolthiazine (L), in which the vinyl double bond can adopt cis or trans configurations (Scheme 1b); the tpy unit, tridentate ligand, can easily coordinate to various metal ions. The metal-ion binds to the acceptor, forming a D- π -A motif ligand, rather than a donor site, it should yield an increase rather than decrease of intraligand charge transfer (ICT) upon

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Scheme 1 (a) Three conformations of the terpyridine unit, (b) *trans* and *cis* tautomerization of the ligand L.

excitation. Consequently, metal-ion binding is expected to result in an increased σ and enhanced fluorescence brightness.^{15,16}

Secondly, different metal ions can influence the structures and photophysical properties of resulting complexes to a large extent. Therefore, in the present work, a series of metal complexes were synthesized based on the designed ligand above. The isomerization and photophysical properties of L and its complexes were investigated, along with time-dependent density functional theory (TD-DFT) computational studies to elucidate the electronic structures of the ground and excited states of the two isomers of L.

Experimental section

1 General procedures

All chemicals were purchased as reagent grade and used without further purification. The solvents were dried and distilled according to standard procedures. The synthetic routes towards L and its complexes are described in Scheme 2.



Scheme 2 Synthetic routes to L and its complexes.

All of the reactions were monitored by TLC (silica gel plates, GF254). Silica gel 60 (100–200 mesh) was used for column chromatography. Elemental analyses were carried out on a Perkin–Elmer 240 analyzer. IR spectra were recorded on a Nicolet FT-IR-instrument with KBr discs in the 4000 ~ 400 cm⁻¹ range. ¹H-NMR spectra were performed on a Bruker 400 Hz Ultrashield spectrometer and were reported as parts per million (ppm) from TMS (δ). The linear absorption spectra were measured on a UV-265 spectrophotometer. The linear emission spectra and fluorescence quantum yields were performed using F-2500 fluorescence spectrophotometer. The concentration of the sample solution was 1.0×10^{-5} M. NLO measurements were investigated with 532 nm laser pulses of 18 ns duration in 1.5×10^{-4} M DMF solution.

2 X-ray crystallography and structure solution

Single crystal X-ray diffraction measurements were carried out on a Siemens Smart 1000 CCD diffractmeter equipped with a graphite crystal monochromator situated in the incident beam for data collection at room temperature. The determinations of unit cell parameters and data collections were performed with Mo-K α radiation. Unit cell dimensions were obtained with leastsquares refinements, and all structures were solved by direct methods with SHELXS–97 and refined with SHEXLX–97. All the non-hydrogen atoms were located in successive difference Fourier syntheses. The final refinement was performed by fullmatrix 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.

3 Synthesis of 10-ethyl-3-[4-(2,2':6',2"-terpyridinyl-4'-yl) styryl]phenothiazine L

t-BuOK (1.3 g, 12.3 mmol), 4-(2,2':6',2"-terpyridinyl-4'-yl)benzyltriphenyl-phosphonium bromide a^{17} (2.0 g, 3.0 mmol) and 10-ethylphenothiazine-3-carbaldehyde b¹⁸ (0.8 g, 3.1 mmol) were added to a dry mortar and milled vigorously for about 35 min. And then the mixture was washed with water and extracted with 3×100 mL CH₂Cl₂. The crude product was purified by chromatography on a silica gel with CH₂Cl₂/methanol mixture (20:1 v/v) as the eluent. Yellow solid was collected, yield: 0.71 g (42%). Mp: 386 °C. Anal. Calcd for C₃₇H₂₈N₄S (560.7): C 79.26, H 5.04, N 9.99, S 5.71; found: C 79.04, H 5.20, N 9.88, S 5.88. IR (KBr): v = 1583 (vs), 1564 (s), 1467 (vs), 1443 (m), 1385 (s), 1250 (m), 791 (m), 749 (m), 620 (w). ¹H NMR (400 MHz, d_6 -DMSO): δ 1.29 (t, 3H, J = 6.78, 6.78 Hz), 3.90 (q, 2H, J = 6.27, 6.78, 6.27 Hz), 6.93 (t, 1H, J = 7.53, 7.53 Hz), 6.99 (d, 2H, J = 8.78 Hz), 7.14 (d, 1H, J = 7.53 Hz), 7.17–7.26 (m, 3H), 7.42 (t, 2H, J = 5.27, 5.27 Hz), 7.51 (t, 2H, J = 5.78, 5.53 Hz), 7.72 (d, 2H, J = 8.03 Hz), 7.89 (d, 2H, J = 8.03 Hz), 8.02 (t, 2H, J = 7.53, 7.53 Hz), 8.65 (d, 2H, J = 7.78 Hz), 8.71 (s, 2H), 8.76 (d, 2H, J = 4.02 Hz). MS: m/z =560. ¹³C NMR (100 MHz, d_6 -DMSO): δ 13.06, 41.69, 115.90, 118.02, 118.19, 121.43, 122.79, 122.97, 123.56, 124.99, 125.14, 126.40, 126.92, 127.50, 127.64, 128.16, 128.82, 131.84, 136.39, 137.95, 139.02, 144.32, 149.40, 149.80, 155.45, 156.15, 162.775.

4 Synthesis of the complexes

L (56.0 mg, 0.1 mmol) in 10 mL of CH_2Cl_2 was added into a 50 mL colorimeter tube, layered with 18 mL of methanol, and then $M(ClO_4)_2 \cdot nH_2O$ (M = Cd 1, Zn 2, Co 3, Cu 4, Mn 5) (0.05 mmol)

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or $CdX_2 \cdot nH_2O$ (X = I for 6, SCN for 7) (0.1 mmol) in 10 mL of methanol was added. The solution was left for slow evaporation and a lot of red crystals were collected for each case in two weeks.

[CdL₂](ClO₄)₂·CH₂Cl₂ 1. Yield: 91%. Anal. Calcd for C₇₅H₅₈Cl₄N₈O₈S₂Cd (1517.65): C 59.35, H 3.85, O 8.43, N 7.38, S 4.23; found: C 59.23, H 3.90, O 8.33, N 7.48, S 4.31. IR (KBr): v = 1597 (vs), 1572 (s), 1465 (s), 1385 (m), 1249 (m), 1090 (vs), 1016 (m), 791 (m), 729 (m), 620 (m).¹H NMR (400 MHz, d_6 -DMSO): δ 1.34 (t, 6H, J = 6.78, 7.03 Hz), 3.96 (q, 4H, J = 7.03, 7.03, 7.03 Hz), 6.96 (t, 2H, J = 7.53, 7.28 Hz), 7.04 (d, 4H, J = 8.53 Hz), 7.16 (d, 2H, J = 7.78 Hz), 7.22 (t, 2H, J = 7.78, 7.53 Hz), 7.28 (d, 2H, J = 16.31 Hz), 7.36 (d, 2H, J = 16.31 Hz), 7.48 (m, 4H), 7.61 (m, 4H), 7.83 (d, 4H, J = 7.53 Hz), 8.17 (m, 8H), 8.79 (m, 12H). TGA: The first stage of weight loss occurred at 220 °C corresponding to the lost of CH₂Cl₂ molecules. The second stage started at 410 °C is attributed to the lost of anions ClO₄⁻. The main structure decomposed at 500 °C exhibiting high thermal stability.

[ZnL₂](ClO₄)₂·CH₂Cl₂ 2. Yield: 92%. Anal. Calcd for C₇₅H₅₈Cl₄N₈O₈S₂Zn (1470.64): C 61.25, H 3.98, O 8.70, N 7.62, S 4.36; found: C 61.38, H 3.82, O 8.71, N 7.50, S 4.47. IR (KBr): v = 1598 (vs), 1572 (vs), 1547 (m), 1469 (vs), 1404 (m), 1252 (m), 1091 (vs), 1017 (m), 793 (m), 732 (m), 620 (m). ¹H NMR (400 MHz, d_6 -DMSO): δ 1.35 (t, 6H, J = 7.03, 6.78 Hz), 3.97 (q, 4H, J = 7.03, 7.03, 6.78 Hz), 6.98 (t, 2H, J = 7.28, 7.28 Hz), 7.07 (t, 4H, J = 8.53, 7.53 Hz), 7.17 (d, 2H, J = 7.78 Hz), 7.23 (t, 2H, J = 8.03, 7.53 Hz), 7.35 (d, 2H, J = 16.06 Hz), 7.50 (m, 10H), 7.97 (m, 8H), 8.30 (t, 4H, J = 7.28, 7.53 Hz), 8.50 (d, 4H, J = 8.03 Hz), 9.18 (d, 4H, J = 8.03 Hz), 9.42 (s, 4H). TGA: The first stage of weight loss occurred at 220 °C attributed to the lost of CH₂Cl₂ molecules. The second stage started at 395 °C is attributed to the lost of anions ClO₄⁻. The main structure decomposed at 480 °C.

[CoL_](ClO_4)₂ **3.** Yield: 95%. Anal. Calcd for $C_{74}H_{56}Cl_2N_8O_8S_2Co$ (1379.23): C 64.44, H 4.09, O 9.28, N 7.63, S 4.37; found: C 64.48, H 4.15, O 9.10, N 7.50, S 4.28. IR (KBr): v = 1615 (vs), 1570 (m), 1470 (s), 1401 (vs), 1249 (m), 1085 (s), 793 (m), 751 (m), 620 (m). TGA: The first stage of weight loss occurred at 390 °C is attributed to the lost of anions ClO_4^- . The main structure decomposed at 480 °C.

[CuL₂](ClO₄)₂·CH₂Cl₂ 4. Yield: 87%. Anal. Calcd for $C_{75}H_{58}Cl_4N_8O_8S_2Cu$ (1468.75): C 61.33, H 3.98, O 8.71, N 7.63, S 4.37; found: C 61.45, H 4.05, O 8.84, N 7.78, S 4.46. IR (KBr): v = 1618 (vs), 1597 (s), 1471 (m), 1383 (s), 1249 (m), 1085 (s), 791 (w), 745 (w), 620 (m). TGA: The first stage of weight loss occurred at 190 °C corresponding to the lost of CH₂Cl₂ molecules. The second stage started at 360 °C is attributed to the lost of anions ClO₄⁻. The main structure decomposed at 450 °C.

[MnL₂](ClO₄)₂·CH₂Cl₂ 5. Yield: 85%. Anal. Calcd for C₇₅H₅₈Cl₄N₈O₈S₂ Mn (1460.16): C 61.69, H 4.00, O 8.77, N 7.67, S 4.39; found: C 61.65, H 3.92, O 8.69, N 7.83, S 4.50. IR (KBr): v = 1598 (vs), 1571 (vs), 1472 (vs), 1401 (s), 1249 (m), 1087 (vs), 790 (m), 733 (m), 620 (m). TGA: The first stage of weight loss occurred at 220 °C corresponding to the lost of CH₂Cl₂ molecules. The second stage started at 390 °C is attributed to the lost of anions ClO₄⁻. The main structure decomposed at 500 °C.

CdLl₂ 6. Yield: 93%. Anal. Calcd for $C_{37}H_{28}N_4I_2SCd$ (926.93): C 47.94, H 3.04, N 6.04, S 3.46; found: C 47.86, H 3.15, N 5.95, S 3.63. IR (KBr): v = 1592 (vs), 1572 (s), 1467 (vs), 1401 (s), 1360 (s), 1248 (s), 1012 (m), 787 (m), 732 (m). ¹H NMR (400 MHz, d_6 -DMSO): δ 1.33 (t, 3H, J = 6.58, 6.88 Hz), 3.95 (q, 2H, J = 6.88, 7.18, 6.58 Hz), 6.96 (t, 1H, J = 7.48, 7.48 Hz), 7.04 (d, 2H, J =8.98 Hz), 7.16 (d, 1H, J = 7.78 Hz), 7.22 (t, 1H, J = 7.78, 7.78 Hz), 7.29 (d, 1H, J = 16.16 Hz), 7.39 (d, 1H, J = 16.16 Hz), 7.49 (m, 2H), 7.84 (d, 2H, J = 8.08 Hz), 7.92 (s, 2H), 8.33 (d, 4H, J = 25.13 Hz), 8.83 (d, 2H, J = 4.49 Hz), 9.05 (d, 4H, J = 18.55 Hz). TGA: The main structure decomposed at 470 °C.

CdL(SCN)₂ **7.** Yield: 90%. Anal. Calcd for C₃₉H₂₈N₆S₃Cd (789.29): C 59.35, H 3.58, N 10.65, S 12.19; found: C 59.47, H 3.65, N 10.76, S 12.08. IR (KBr): v = 1594 (vs), 1570 (vs), 1461 (vs), 1401 (vs), 1360 (s), 1249 (s), 1013 (m), 785 (s), 751 (s). TGA: The first stage of weight loss occurred at 390 °C attributed to the lost of two SCN⁻, respectively. The main structure decomposed at 600 °C.

Results and discussion

1 Synthesis and characterization

Through the solvent-free Wittig reaction, L was afforded as a yellow solid in moderate yield (42%) (Scheme 2 and Fig. S1[†]). ¹H NMR spectra of L in d⁶-DMSO and CDCl₃ show that the signals of the vinyl and aromatic protons are overlapped, consequently, the course of cis-trans isomerization of the free ligand can not be followed through this way. ¹H NMR spectrum of 6 measured immediately after its dissolution in d^6 -DMSO shows that the vinyl protons of the *trans*- isomer of L in 6 exhibit doublets at δ 7.39 (J = 16 Hz) and 7.29 (J = 16 Hz) (Fig. S1[†]), respectively. After 6 h irradiation, ¹H NMR spectrum of **6** shows that vinyl protons of *cis*- isomer was shifted to δ 7.34 (J = 7 Hz) and 7.31 (J = 7 Hz) (Fig. S2[†]). It is also distinguished that the downfield shifts of the CH₂ and CH₃ protons in *trans vs. cis* δ = 3.96 and 1.33 *vs.* 4.47 and 1.47 ppm were observed, respectively. The dissolution of 6 in d^6 -DMSO for 6 h results in the formation of a 7 : 8 *cis/trans* ratio. The methyl proton regions of the ¹H NMR spectra of **2** are shown in Fig. S3.[†] The chemical shift at δ 1.35 was observed for the CH₃ protons of the Trans-Trans isomers of 2. After 6 h (Fig. S3, † inset), a new triplet at δ 1.49 shall be assigned to the methyl protons of the Trans-Cis or Cis-Cis, or both of them (shown in Scheme 3).



Scheme 3 Representations of three configurations of the complexes 1-5.

 Table 1
 Conformational Parameters for complexes 1–6
 1 2 3 4 5 6 4 93 $P_{3,1}^{a}$ 7.95 7.92 7.77 7.24 8.73 $\mathbf{P}_{3,2}$ 2.97 2.67 2.93 5.23 2.62 3.25 $\mathbf{P}_{3,4}$ 18.56 21.50 8.79 19.82 20.58 9.88 P_{5,4} 17.58 20.37 24.48 20.98 18.89 16.73 P_{5,6} 53.56 53.88 13.69 53.84 54.03 27.56 9.08 $P_{9,7}$ 7.04 8.91 8.03 8.96 ${\bf P}_{9,8}$ 10.22 9.51 11.52 12.83 9.90 $P_{9,10}$ 28.37 29.28 28.75 33.10 29.09 $P_{10,11}$ 10.30 10.20 26.14 9.61 10.80 26.62 25.49 13.43 26.76 P_{11,12} 26.88 ^{*a*} P_{3,1} represent the dihedral angles between P3 and P1, and so on.

No evidence was available for the co-existence of the three configurations of **2**, but at least two of them are presented. The constitution of the *cis*- isomer of **L** in **6** is much larger than that in **2** after they are kept in the same solvent prolonging the same time. The study as to whether this isomerization is induced photochemically or not is in progress. For the IR spectra of **1–5**, v of ClO₄⁻ at *ca*. 1090 cm⁻¹ shows strong signals. The thermogravimetric analysis (TGA) shows that the decompositions of the main structures of all complexes occurred above 450 °C. It is obvious that the thermal stability of the complexes is higher than that of the free ligand **L**. (Mp: 386 °C).

2 Crystallographic results

Crystallographic data, selected bond lengths and angles for **1–6** are summarized in Table S1 and S2.† The non-covalent interactions in the complexes **1–5** are shown in Table S3.† In order to illustrate the conformation of the ligand, the parameters P1–P12 are presented in Table 1. The crystal structures of **1–5** are very similar, and the molecular structure of **1** is shown in Fig. 1 as an example.

Comparison of crystal structures of 1-5.

Similarities of their structures. (i) Each $M(ClO_4)_2 \cdot nH_2O$ reacted with two equiv of L; (ii) all the complexes 1-5 crystallize in the triclinic Pi space group (Table S1[†]); (iii) the M(II) atoms are all coordinated by six N atoms from two tpy groups of the two different L with the slightly distorted octahedral coordination environments and the tpy units in ${M(tpy)_2}^{2+}$ adopted the *cis,cis* conformation (Fig. 1a); (iv) the ligands in the complex molecules are all in the trans configuration, consequently, the complexes exist in a Trans-Trans configuration in the solid state; (v) the conformations of the two ligand units in each complex molecule are different. For example, in the molecular structure of 1, the PTZ unit on the left side is folded about the S-N axis with a dihedral angle of 126.44° (Fig. 1a and Table 1). The dihedral angles formed by P3 with the two pyridine rings P1 and P2 are 7.95° and 2.67°, respectively. The dihedral angles formed by P4 with P3 and P5 are 18.56° and 17.58°, respectively. On the right side, the PTZ unit is folded about the S-N axis with a dihedral angle of 143.38°. The dihedral angles formed by P9 with the two pyridine rings P8 and P7 are 7.04° and 10.22° , respectively. The dihedral angles formed by P10 with P9 and P11 are 29.28° and 10.30°, respectively. (vi) There exists not only the electrical attraction between $[ML_2]^{2+}$ and ClO_4^{-} , but also the strong H-bonds, where the H-bonding acceptor is from one oxygen atom of the perchlorate anion. (vii) In each



Fig. 1 (a) ORTEP plot of **I** showing the conformational parameters P1–P12 with the 50% probability ellipsoids. Inset (right bottom corner): Coordination geometry around the metal ion. (b) Packing diagram of **I** shows the 3D structure, view down *b*-axis. Solvent molecules and anions were omitted for clarity. (c) C–H··· π interactions in **I** indicated by dashed lines, as an example.

complex, molecules interacted with each other to form a 2D layer extending along the *b*-axis (Fig. 1b). The 2D layers were further organized to form a 3D supramolecular structure through non-covalent interactions, such as H–bonds and C–H $\cdots \pi$ interactions (Fig. 1c).

Differences between the crystal structures of 1–5. (i) The ligands show different conformations in 1–5. The dihedral angles of the investigated planes P1–P12 were summarized in Table 1. When the dihedral angles are close to 0 or 180° , it means that the planes in one ligand are close to being coplanar. (ii) The number and type of the H–bonds are very different in 1–5 (Table S3†). (iii) The separations of the C–H $\cdots \pi$ interactions for 1–5 are different, and the shortest one was found in the crystal structure of 2.

Comparison of crystal structures of 1 and 6.

Differences between the crystal structures of 1 and 6. (i) Each Cd(II) ion in 6, shown in Fig. 2, is five-coordinate with three N atoms from one tpy unit and two I atoms, while Cd(II) ion is six-coordinate in 1. (ii) The conformations of L in the two complexes are different (Fig. 2a and Table 1). It is clear that the dihedral angles in 6 are smaller than that in 1. The planarity of L in 6 is coplanar, which will facilitate the π -electron delocalization in the complex. (iii) In the crystal structure of 6, the complex molecules interacted with each other to form a 2D layer extending along the *b*-axis, which were further linked to give a 3D supramolecular structure through C-H…I and $\pi \dots \pi$ interactions (Fig. 2b and c). I…H(C) distances of the two types of H–bonds a and b are 3.083 and 3.096 Å, while C-H…I angles are 154.79 and 157.36°, respectively. The separation of the $\pi \dots \pi$ interaction between one





Fig. 3 Linear absorption (a) and emission (b) spectra of L in six solvents.

Fig. 2 (a) ORTEP plot of **6** showing the conformational parameters P1–P6 with the 50% probability ellipsoids. Inset: Coordination geometries around the metal ions. (b) Representation of hydrogen bonds. (c) Packing diagram shows the 3D structure, view down *b*-axis.

pyridine ring and phenyl ring of PTZ unit from another molecule is 3.362 Å.

To summarize, the different metal centers in 1-5 with similar coordination geometries have large influences on the conformations of the ligands and the non-covalent interactions in the complex molecules in solid state. While the coordination geometries of the Cd(II) centers vary a lot with different anions in 1 and 6. In the solid state, L in all the complexes adopts the *trans*- configuration.

3 Linear absorption and emission spectra

The photophysical data of all the compounds were summarized in Table 2. The linear absorption and emission spectra of L in six organic solvents are shown in Fig. 3, while those of all the compounds in DMF are depicted in Figs. 5 and 6, respectively.

Solvatochromism. Generally, the linear absorption spectra of L feature an intense absorption band at 293–306 nm and a moderately intense absorption in the 378–394 nm range in all the solvents (Fig. 3a). The low-energy band originating from a HOMO (H) \rightarrow LUMO (L) transition was assigned to intraligand charge transfer (ICT) transitions, while the high-energy band was assigned to a H–1 \rightarrow L transition (ICT) and mixed with H–1 \rightarrow L+5 transition due to the π - π * transitions of the tpy. It was further corroborated by calculations. As shown in Fig. 3a and Table 2, weak solvatochromism was observed in the ICT absorption bands, indicating the L molecule with fairly small dipole moments and the difference in dipoles between ground and excited state.¹⁹

The linear emission spectra of **L** exhibit dual emissions, which show strong solvatochromism. With increasing polarity of the solvent, their emission maxima (λ_{max}^{em}) show remarkable bathochromic shifts. As shown in Fig. 3b, the dual emission wavelengths in hexane are located at 449 and 503 nm, whereas in DMF red-shifted to 496 and 561 nm, respectively. These results suggest that the molecular polarity of the excited state of **L** must be larger than that of the ground state, as the enhanced dipole–dipole interactions caused by increasing the polarity of solute and/or solvent will lead to decreasing energy level significantly for the excited state.

The ratio of the intensities of the dual emission bands varies with different excitation wavelengths, L in hexane as an example shown in Fig. 4a (Fig. S4[†] shows those of L in THF and DMF). In such cases, it is generally taken as an evidence for a heterogeneous sample with more than one absorbing and emitting species. The bands at 449-496 nm and 503-561 nm were tentatively assigned to the emissions of *trans* and *cis* originating from the ICT transitions, respectively. It was supported by the fact that the both emission bands show strong solvatochromism. The hypothesis of different absorbers can be checked readily by recording fluorescence excitation spectra with observation wavelengths of the fluorescence bands relevant to the cis and trans configuration of the molecule, respectively (Fig. 4b). The similarity in the overall appearance of the excitation spectra is in accordance with the assumption that the two absorbing species are different configurations of the same molecular species, which exhibit slightly different absorption characteristics. When the detection wavelength was chosen at 450 nm rather than 505 nm, all the maxima in the excitation spectra shifted toward longer wavelengths, indicating that the trans absorbs at a lower energy region than the *cis*. The assignments above were further corroborated by theoretical calculations.

L	Solvent	$\lambda_{\max}{}^a$	$\lambda_{\max}{}^{b}$	ϕ^c	eta^{d}	$ au^e$	σ^{f}
	Hexane	293, 378	449, 503				
	Benzene	294, 386	451, 528				
	CH_2Cl_2	300, 388	454, 535				
	THF	302, 390	457, 539				
	CHCl ₃	~, 391	461, 553				
	DMF	306, 394	491, 561	0.62/0.44	14	1.4/1.2	5.8
	Solid		530				
1	DMF	310, 396	492, 564	0.67/0.42	49	1.6/1.2	20
	Solid		602				
2	DMF	315, 397	494, 562	0.47/0.28	51	1.7/1.5	21
	Solid		623				
3	DMF	326, 401	496, 564	0.27/0.18	45	1.6/1.2	19
	Solid		604				
4	DMF	308, 396	499, 572	0.18/0.24	38	1.6/1.4	15
	Solid		595				
5	DMF	311, 397	495, 572	0.16/0.23	34	1.5/1.2	14
	Solid		583				
6	DMF	320, 301	491, 571	0.33/0.31	47	1.8/1.4	19
	Solid		648				
7	DMF	320, 400	491, 570	0.42/0.45	43	1.6/1.2	18
	Solid		626				

^{*a*} Linear absorption maxima (nm). ^{*b*} Linear emission maxima (in nm, under the excitation wavelength of 310 nm). ^{*c*} x/y represent quantum yields obtained by comparison of emission of RHB ethanol solution with that of *trans/cis* under identical experimental conditions. ^{*d*} Nonlinear absorption coefficient (10⁻³ cm GW⁻¹). ^{*e*} Fluorescence lifetime (ns). ^{*f*} 2PA cross-section in 10³ GM (1 GM = 10⁻⁵⁰ cm⁴ s·photon⁻¹).



 Table 2
 Photophysical data of all the compounds

Fig. 4 Fluorescence emission (a) and excitation (b) spectra of **L** in hexane at room temperature. Inset: the excitation wavelengths.

Comparison of the complexes with the ligand. The observation of similar absorption bands for the complexes and L suggested their assignments as the metal-perturbed ICT (Table 2 and Fig. 5). The absorption maxima (λ_{max}^{ab}) of the complexes show a small red shift compared to that of the ligand, indicating a little increase of the ICT in the complex. In 1–5 with the same anions, λ_{max}^{ab} of 3 exhibits the largest red shift of all the complexes. In complexes

Fig. 5 Linear absorption spectra of all the compounds in DMF.

1, 6 and 7 with the same metal ions, the red shifts of 6 and 7 are slightly larger than that of 1.

The linear emission spectra of all the compounds exhibit similar emission characteristics (Fig. 6), which give the evidence again that at least two configurations of each complex (1–5) are co-existing in DMF. As shown in Fig. 6a, under the same excitation wavelength (λ^{ex}) of 287 nm, the ratio of the intensities of the dual emission bands varies from different compounds with different metal ions or anions.

To summarize, in the solvent, the configuration of ligand in the complexes varies with either different metal centers or anions, leading to the changes in photophysical properties of the complexes.

Linear emission spectra of all the compounds in solid state. All the compounds exhibit one emission band at 530–648 nm in the solid state at ambient temperature (Table 2), corresponding to the results of single crystal X-ray diffraction analysis that the ligands in the complexes exist in *trans* in solid state. In 1–5, the emission peaks (λ_{max}) show the order of 5 < 4 < 3 < 1 < 2. While λ_{max} of the complexes 1, 6 and 7 exhibit the sequence of 1 < 7 < 6.



Fig. 6 Linear emission spectra of all the compounds (L, 1–7) in DMF (a) $\lambda^{ex} = 287 \text{ nm}$, (b) $\lambda^{ex} = 368 \text{ nm}$.

The stronger non-covalent interactions between molecules in 2 and 6 may be in responsible for the larger red shifts of the solidstate emission bands compared to their respective counterparts in solution. Table 2 also shows that the fluorescence lifetimes (τ) of the complexes are a little longer than that of the ligand when they are all under the excitation wavelength of 370 nm. The quantum yields of *trans* in each compound show the sequence of 1 > L >2 > 7 > 6 > 3 > 4 > 5, while those of *cis* follow the order of 7 > L > 1 > 6 > 2 > 4 > 5 > 3. Obviously, 3, 4 and 5 show much lower quantum yields of both *trans* and *cis* compared to those of the other complexes.

4 Computational studies

The initialized geometry of *cis* and *trans* pre-optimized by AM1 was obtained by further geometry optimization in vacuum (B3LYP (6-31G(d)) for S_0 , CIS (6-31G(d)) for S_1). Then TDDFT (B3LYP (6-31G(d,p)) calculations were performed on the optimized structure. All the calculations including optimizations and TDDFT were conducted using G03 software. In the calculation of the optical absorption spectrum, the 25 lowest spin-allowed singlet-singlet transitions, up to an energy of ~5 eV, were taken into account. Moreover, the lowest 25 singlet and singlet excited states were calculated for each calculated optimized geometry.

For the sake of reducing the computational cost, *trans'* and *cis'* were used instead of *trans* and *cis*, in which the ethyl groups on the PTZ moieties were replaced by a methyl group.²⁰

The selected singlet-singlet excitations of the two isomers of L in the range detected in the absorption spectra are listed in Table 3. The nature of the orbitals involved in the excitation is also shown in Fig. 7a. The frontier filled orbitals H of *trans'* and *cis'* are mainly localized on the PTZ (D) and vinyl units. H–1 of the two



Fig. 7 Molecular orbital plots of (a) the ground state, (b) the excited state, left: *cis'*; right: *trans'*. The molecular structures of the species studied were calculated at TDDFT level of theory.

isomers is localized on the D and π -bridge groups. The unoccupied molecular obitals L and L+2 are localized on the A and π -bridge groups. From the calculation results, two transitions in the lower energy region resemble those observed in the experimental linear absorption spectra. The transitions at *ca*. 420 nm (f = 0.27) and 330 nm (f = 0.53) originating from H \rightarrow L and H–1 \rightarrow L transitions are assigned as the ICT transitions of cis', respectively. The transitions at 427 nm (f = 0.73) and 341 nm (f = 1.01) originating from H \rightarrow L and $H-1 \rightarrow L$ transitions are all assigned as the ICT transitions of *trans'*, respectively. The transitions at 318 nm (f = 0.16 and 0.33) of cis' and trans' both originating from $H-1 \rightarrow L+5$ transitions are assigned as the π - π * transitions of the terpyridine. The most difference in the absorption spectra of the two isomers is that the oscillator strengths of the two ICT absorption bands of trans' are 2-fold larger than those of cis'. This suggests that there is a factor of 2 higher probabilities for the two ICT transitions in *trans'*, which is a result of better electronic coupling between the PTZ donor and tpy acceptor moieties in trans' compared to that in cis'. A better coplanarity between the D/A units can result in superior D/A coupling in the ground state of *trans*'. It is reaffirmed that the ICT transitions of trans' are red-shifted compared to those of cis'. Basically, the calculated singlet-singlet transitions in L are in reasonable agreement with the experimental λ_{max}^{ab} in the two major absorption bands observed in the experimental spectra, except the two closely overlapping transitions, $H-1 \rightarrow L$ and $H-1 \rightarrow L+5$ transitions, that may only exhibit one high energy band in the experimental result.

Table 3	Selected Low-Lying Singlet (S _n) Excited States Computed by TDDFT method, with the Orbitals Involved (OI) in the Excitations. Tr	ransition
coefficien	nt (Tc), Excitation eneries (eV and nm), and Oscillator Strengths (f) in cis' and trans'	

Isomer	\mathbf{S}_n	C^a	OI	Tc ^b	$E_{\mathrm{ex}}{}^{c}$	f^d
cis'	S,	ICT	H→L⁄	0.68	2.95/420.04	0.27
	S ₄	ICT	$H-1 \rightarrow L$	0.66	3.76/329.50	0.53
	S5	π – $\pi^*(D)^e$	$H-1 \rightarrow L+5$	0.54	3.90/317.92	0.16
	S15	ICT	$H-1 \rightarrow L+2$	0.44	4.35/285.15	0.21
trans'	S ₁	ICT	$H \rightarrow L$	0.67	2.91/426.53	0.73
	$\dot{S_4}$	ICT	$H-1 \rightarrow L$	0.61	3.63/341.37	1.01
	S_6	$\pi - \pi^*(D)$	$H-1 \rightarrow L+5$	0.57	3.89/318.34	0.33
	\mathbf{S}_{12}	ICT	$H-1 \rightarrow L+2$	0.49	4.26/292.01	0.12

^{*a*} C: Character of the transitions. ^{*b*} The excitations with transition coefficients less than 0.4 were not shown. ^{*c*} Excitation energy in eV nm⁻¹. ^{*d*} Only the singlet excited stated with f > 0.1 were listed. ^{*e*} $\pi - \pi^*$ transition of PTZ(D) unit. ^{*f*} H(HOMO) and L(LUMO).

In order to study the nature of the emitting singlet states and the structural changes from the corresponding ground states, CIS (6-31G(d)) method was used to optimize the low-lying singlet states in *trans'* and *cis'* (Fig. 7b). The calculated emission maxima of the ICT transitions, corresponding to 540 and 474 nm for *cis'* and *trans'*, are correlated well with the experimental emissions in the range of 503–561 nm and 449–491 nm for *cis* and *trans*.

5 Nonlinear optical properties (NLO)

The third-order NLO properties of all the compounds in DMF were studied using the Z-scan method. Fig. 8 shows the typical Z-scan measurement of **2** in DMF. The nonlinear absorption component was evaluated under an open aperture. The filled squares represent the experimental data measured under this condition. It is clearly illustrated that the absorption increases as the incident light irradiance rises. The solid line in Fig. 8 is the theoretical curve from the eq $1.^{21}$

$$T(z) = \frac{1}{q(z)\sqrt{\pi}} \int_{-\infty}^{+\infty} \ln\left[1 + q(z)\right] \exp(-\tau^2) d\tau$$
(1)

$$q(z) = \beta I_0 L_{\rm eff} / (1 + z^2 / z_0^2)$$
⁽²⁾

$$L_{\rm eff} = (1 - e^{-\alpha L})/\alpha \tag{3}$$

where I_0 is the input intensity at the focus z = 0, L is the sample length, α is the linear absorption coefficient and β is the 2PA coefficient. $z_0 = \pi \omega_0^2 / \lambda$ is the Rayleigh diffraction length, ω_0 is the radius of beam at focus. Thus, once an open-aperture Zscan is performed, the nonlinear absorption coefficient β can be unambiguously deduced.²² The open-aperture transmittance is symmetric with respect to the focus (z = 0), where it has a minimum transmittance. The intensity dependent transmittance indicates the nonlinear absorption for **2**. No linear absorption above 500 nm was observed in the linear absorption spectrum of **2** in DMF, we attribute the nonlinear absorption to the 2PA effect.

Using the above equation, we can get the nonlinear absorption coefficient β (in units of cm GW⁻¹). In addition, the molecular 2PA cross-section σ (in units of cm⁴ s·photon⁻¹) can be determined by the following expression:

$$\sigma = h \nu \beta / N_A d \times 10^{-3}$$



Fig. 8 Z-scan data for 2 in DMF, obtained under an open aperture configuration. The black dots are the experimental data and the solid curve is the theoretical fit.

where hv is the energy of the incident photon. N_A is the Avogadro constant. d is the concentration of the 2PA compound in mol cm⁻³ units.²³

The nonlinear absorption coefficient β and the 2PA crosssection σ of all the compounds were listed in Table 2. σ of L was 5.8×10^3 GM. Considering the molecular weight difference between the complexes and free ligand, the 2PA cross-section values for all the complexes are approximately 2.4- to 3.6-fold larger than that for L. Generally, the different metal centers are responsible for the different 2PA properties of the complexes. The detailed experimental information is given in Table 2, and further explanations are listed as follows. (i) The σ values of the complexes 1–5 exhibit the order of 5 < 3 < 4 < 1 < 2. (ii) The configurations of L in 1-5 vary with the different metal centers, e.g. the ratio of trans of L in 1, 2 and 3 are much larger than that in 4 and 5, which may be a potential reason for the enhanced NLO properties of 1, 2 and 3. (iii) Another factor for the larger σ of 1 and 2 compared to those of 3, 4 and 5 is attributed to the closed-shell d¹⁰-metal centers being non-detrimental to fluorescence. (iv) Considering each complex molecule of 1 contains two ligand molecules, it is slightly surprising that 1 (with two ligands L) has such similar values to 6 and 7 (one ligand L).

Although bis(tpy) complexes 1–5 are bound to be linear 1D, different from metallo-octupolar D_3 ter(bipyridine) complexes that showing enhanced 2PA response. Functionalized TPY ligands give rise to octahedral and pyramidal metal complexes, showing high 2PA response.²⁴ Large enhanced 2PA response in **6** and

7 may arise from an extended π -electron delocalization after complexation and an increase of intramolecular charge transfer (ICT) upon excitation. The σ values of the complexes are larger than those of most transition metal complexes.²⁵ In conclusion, the results indicate that the novel type ligand combined terpy with PTZ offers a new opportunity to enhance the nonlinear optical properties in different aspects.

Conclusions

A novel 2,2':6',2"-terpyridine-based ligand L and its complexes 1-7 have been synthesized and fully characterized. The equilibrium of the trans- and cis- isomers of L was investigated both experimentally and theoretically. All the complexes were easily obtained in high yield and show better thermal stability than that of L, which exhibit good one- and two-photon excited fluorescence properties. Compared with those of L, the larger 2PA cross-section values and longer fluorescence lifetimes of the complexes were obtained. The molecular structures and photophysical properties of the complexes display large dependence on the choice of the metal ions and anions. The joint theoretical and experimental study gives reasonable interpretation for their photophysical properties based on sufficient crystallographic data from the series of the compounds. The results show that terpy group and PTZ are linked by a π -conjugated system to form a novel two-photon absorbing ligand. Its metal complexes (M = Zn, Cd) with the closed-shell d^{10} configuration and anions (X = SCN, I) possess the larger 2PA cross-section values. Consequently, simple and efficient preparation of these complexes for enhanced 2PA properties may be a better alternative to those organic compounds obtained by significant skill.

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