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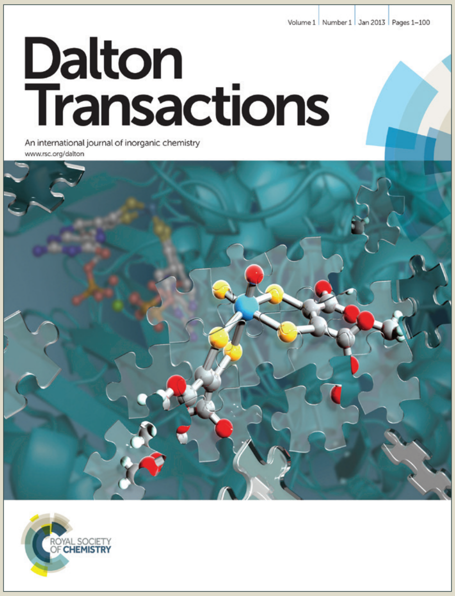

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ARTICLE TYPE

Studies on the one-photon and two-photon properties of two water-soluble terpyridines and their zinc complexes

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Two water soluble 2,2':6',2''-terpyridine derivatives (TPYOH and O3TPY) with di(hydroxyethyl)amino or long (2-(2-methoxyethoxy)ethoxy)benzyl group respectively were designed and synthesized. The two terpyridine ligands and their Zn(II) complexes display strong one-photon fluorescence. An unusually large solvatechromism effect in ethanol and water was found, which was ascribed to their interactions with the solvent through hydrogen bonds. All the four compounds show evident two-photon absorption ability when evaluated by Z-scan technology. The free ligands could give distinct two-photon excited fluorescence, and the emission of O3TPY could respond linearly with Zn^{2+} under the excitation of 780nm femtosecond laser. Only the complex ZnO3TPY, which possesses large π conjugation system and suitable election-donating groups, displayed emission maxima at 595nm when excited by 680~880nm laser.

Introduction

Due to the important role of Zn^{2+} in biological and life science, much attention were focused on the sensitive and quantitative measurement of trace Zn^{2+} in vivo.[1] Considering the large red-shift in emission when terpyridine derivatives coordinating to Zn^{2+}, some novel terpyridines have been designed to act as Zn(II) fluorescence probes, which could preferentially respond to Zn2+ and even map the cellular Zn^{2+} distribution by means of confocal microscopy.[2] Meanwhile, some Zn-terpyridine complexes have been found to selectively recognize ATP (adenosine triphosphate) and PPi (pyrophosphate) ions, which are crucial in various metabolic processes by participation in enzymatic reactions.[3] Many published optical analysis on Zn(II) and relevant researches were performed based on UV-Vis absorption spectra and single-photon excited fluorescence.[4] Two-photon confocal microscopy can be a superior alternative to single-photon microscopy due to its near-infrared excitation wavelength, deeper tissue penetration, efficient light detection, suppressed background signals and reduced phototoxicity.[5] With the help of two-photon excitation microscopy it is possible to image the cellular zinc and phosphates with ideal resolution. So two-photon active Zn^{2+}-selective fluorophores are of particular interest and a large numbers of molecules have been screened for cellular Zn(II) bioimaging based on two-photon confocal microscopy.[6] Fortunately, some Zn-terpyridine complexes have been reported to show marked two-photon absorption properties recently.[7] Furthermore, some Zn-terpyridine complexes have been reported to display notable in vitro cytotoxicity and interact distinctly with DNA or protein.[8] It's very meaningful to investigate the two-photon ability of the cytotoxic Zn-terpyridine complexes, which will help to reveal their accurate bio-targets and true antitumor mechanism.

With the aim to obtain terpyridines applicable for biological system, di(hydroxyethyl)amino and (2-(2-meth-oxyethoxy)-ethoxy)benzyl groups were chose to combine with 2, 2':6',2''-terpyridine and two novel terpyridines (O3TPY and TPYOH) behaving good water-solubility were obtained.[9] Among them, the electron-donors and the terpyridine moiety were bridged by vinyl group in the O3TPY in order to improve the two-photon absorption cross-section (δ) values. The one-photon and two-photon properties of the two terpyridines and their Zn(II) complexes (ZnO3TPY and ZnTPYOH) were investigated, the structure-property relationship was generally discussed in this paper.

Experimental section

1. General procedures

All the reagents were obtained commercially and used as supplied. Products were dried overnight in a vacuum desicator ($CaSO_4$) prior to characterization. The chemical structure of the terpyridine ligands and their Zn(II) complexes are described in scheme 1. The ^1H NMR and ^{13}C NMR data were obtained with a 400 MHz Bruker DMX spectrometer and all shifts were quoted with respect to TMS. Electrospray Mass spectra were measured on a Micromass Platform II spectrometer. MAIDI-TOF data were acquired on Bruker Autoflex spectrometer. Elemental analysis was carried out on Heraeus CHN-O Rapid analytical instrument.

2. Single Crystal Structure Analysis:

X-ray crystallography data were collected on a Bruker APEX CCD X-ray diffractometer using Mo Ka radiation (k = 0.71073 Å), and the data were processed using the Bruker SAINT and SADABS software packages. The structures were solved by direct methods using SHELXS-97, and refined by full-matrix least-squares on all F_0^2 data using SHELXL-97. All nonhydrogen atoms were refined anisotropically and hydrogen atoms were included in idealised positions using the riding model. CCDC: 855404[10], 1020953, 1020945 and 1020946, for the four compounds contained the supplementary crystallographic data (These data can be obtained free of charge from the Cambridge Crystallographic Data Centre).

3. Quantum Chemical Calculations:

Density functional theory (DFT) calculations were carried out using the Gaussian 09 suite of programs. The B3LYP functional was employed in conjunction with the all-electron 6-31G(d) basis set for all atoms. Calculated molecular geometry obtained from X-ray diffraction crystallographic data.

4. Two-Photon Excited Fluorescence Spectra Measurement:

The two-photon excited fluorescence (TPEF) spectra were measured using a mode-locked Ti:sapphire laser (Coherent Mira900F) as the pump source with a pulse duration of 200 fs, a repetition rate of 76 MHz, and a single-scan streak camera (Hamamastu Model C5680-01) together with a monochromator as the recorder. The sample was dissolved in H_2O/acenonitrile (4:1) with a concentration of 1.0×10^{-3} mol·L^{-1}.

5. Measurement of Two-Photon Absorption Cross Section:

The two-photon absorption cross section (δ) was determined on the open-aperture Z-scan setup. All the optical studies were done using a femtosecond laser with pulse duration of 140 fs and 80 MHz repetition rate. The thermal heating of the sample with high repetition rate (HRR) laser pulse was removed by the use of a mechanical chopper running at 1 kHz. The nonlinear absorption component was evaluated under an open aperture. The measured experimental data was fitted according to equation (1) to obtain the value of the two-photon absorption coefficient (β). Furthermore, δ could be determined by equation (4).

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

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

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

$$\delta = h\beta\gamma/N_A\, C \times 10^{-3} \qquad (4)$$

Here, I_0 is the input intensity at the focus z = 0, L is the sample length, α is the linear absorption coefficient. $z_0 = \pi\omega_0^2/\lambda$ is the Rayleigh diffraction length, ω_0 is the radius of beam at focus. h is the Planck’s constant, γ is the frequency of input intensity, N_A is the Avogadro constant, and C is the concentration of the sample.

6. Synthesis of the terpyridines and Zn(II) complexes

4’-p-N,N-bis(2-hydroxyethyl)benzyl-2,2’:6’,2’’-terpyridine (TPYOH): A mixture of 10.5 g (0.05mol) of *p-N,N*-bis(2-hydroxyethyl)amino benzaldehyde, 14.5 g (0.12 mol) of 2-acetylpyridine, 20mL of 10 mol/L NaOH and 100 mL of ethanol were stirred vigorously at room temperature for 3 h, then cooled down to -4^{o}C for 1h. The supernatant solution was decanted and the solid residue was dissolved in 200 mL of ethanol. 10 g of NaOH solid was added to the deep red solution and then 100 mL of $NH_3\cdot H_2O$ (25%) was added dropwise. After the mixture had been refluxed for 4h, the solvent was evaporated under high vacuum to obtain the crude product as a thick paste. 400 mL solution of ethanol and diethyl ester (v:v = 1:15) was added to produce a yellow precipitate. The yellow solid was collected by filtration and dried in vacuum. Yield: 46%. ^{1}H NMR (d_6-DMSO): δ(ppm): 3.52 (t, 4H, -CH_2O-), 3.61 (t, 4H, -NCH_2-), 4.85 (s, 2H, -OH), 6.87 (d, 2H, phenyl-H), 7.52 (m, 2H, $C^{5,5''}$-H), 7.78 (d, 2H, phenyl-H), 8.02 (m, 2H, $C^{4,4''}$-H), 8.65 (m, 4H, $C^{3',5'+6,\ 6''}$-H), 8.76 (d, 2H, $C^{3,3''}$-H). ^{13}C NMR (d_6-DMSO): δ(ppm): 53.80 (-NCH2-), 58.74 (-CH2O-), 112.43 (phenyl-C), 116.84 (-$C^{3'5'}$-), 121.49 (-$C^{3,5,3'',5''}$-), 123.83 (phenyl-C link to $C^{4'}$), 124.95 (phenyl-C), 128.27 (-$C^{4,4''}$-), 137.98 (-N-phenyl-C), 149.79 (-$C^{4'}$-), 149.91 (-$C^{6,6''}$-), 155.98 (-$C^{2',6'}$-), 156.00 (-$C^{2,2''}$-). ESI-MS(+p): *m*/*z*=413.1 could be assigned as $[TPYOH+H]^+$ (calc. m/z=413.1). Elemental analysis for C25H24N4O2: Calc.: C, 72.80%; H, 5.86; N, 13.58; Found: C, 72.56%; H, 5.62; N, 13.69.

4’-p-[(β-(β’-methoxyethoxy)ethoxy)]vinyl-2,2’:6’,2’’-terpyridine (O3TPY): 4 mmol of the sodium methoxide and 1.8 mmol of the 4’-p-triphenylphosphine methylphenyl-2,2’:6’,2’’-terpyridine bromide were dissolved in 15 mL of methanol, and then 2.0 mmol of 4-(2-(2-methoxyethoxy) ethoxy)benzaldehyde was added. The clear mixture was refluxed for 1 h and then the white precipitation of O3TPY was obtained. The solid was collected by filtration and washed with ethanol, diethyl ether, then dried in vacuum. Yield: 42%. ^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm): 3.41(s, 3H, -CH3), 3.59(t, 2H, ethyl-H), 3.74(t, 2H,ethyl-H), 3.89(t, 2H, -ethyl-O-CH2-C-), 4.19(t, 2H, -CH2-O-phenyl-), 6.94(d, 2H, -O-phenyl-H), 7.01(d, 1H, -vinyl-H), 7.14(d, 1H, -vinyl-H), 7.38(m, 2H, $C^{5,5''}$-H), 7.49(d, 2H, -O-phenyl-H), 7.64(d, 2H, central phenyl-H), 7.92(q, 4H, $C^{4,4''}$-H plus central phenyl-H), 8.70(d, 2H, $C^{6,6''}$-H), 8.76(t, 4H, $C^{3,3',3'',5'}$-H). ^{13}C NMR(d_6-DMSO): δ(ppm): 58.74 (methyl-C), 67.84 (C-O-phenyl), 69.56 (ethyl-C), 70.31 (ethyl-C), 71.94 (C-O-Met), 115.32 (-O-phenyl-C), 118.09 (-$C^{3',5'}$-), 121.61 (-$C^{3,3''}$-), 125.11 (-$C^{5,5''}$-), 125.88 (central phenyl-C), 127.76 (vinyl-C), 127.84 (vinyl-C), 128.719 (central phenyl-C), 129.93 (-O-phenyl-C), 130.23 (-O-phenyl-C), 136.44 (central phenyl-C), 137.88 (-$C^{4,4''}$-), 139.38 (central phenyl-C), 149.61 (-$C^{4'}$-), 150.52 (-$C^{6,6''}$-), 155.64(-$C^{2',6'}$-), 156.19 (-$C^{2,2''}$-), 159.08 (phenyl-C linked to O atom). ESI-MS (+p): m/z=530.6 could be assigned as $[O3TPY+H]^+$ (calc. m/z=530.6). Elemental analysis for $C_{34}H_{31}N_3O_3$, Calc.: C, 77.10; H, 5.90; N, 7.93%. Found: C, 77.25; H, 5.98; N, 7.86%.

General synthetic procedure for the Zinc(II) complexes: A mixture of 1 mmol of $Zn(BF_4)_2$ and 2.2 mmol of the terpyridine ligands in 10 mL $CHCl_3$ and 10mL CH_3OH was refluxed with stirring for 4h. Yellow precipitate was collected by filtration, washed with ethanol and ethyl ether, then dried in vacuum. Crystals suitable for X-ray crystallography diffraction were obtained by slow diffusion of diethyl ether into the acetonitrile solution. ^{1}H NMR for ZnTPYOH (d_3-CD_3CN): δ(ppm): 3.34 (t, 4H, OH), 3.72 (t, 8H, -CH_2O-), 3.84 (q, 8H, -NCH_2-), 7.09 (d, 4H, phenyl-H), 7.40 (m, 4H, $C^{5,5''}$-H), 7.84 (d, 4H, phenyl-H), 8.17 (m, 8H, $C^{3,3'',4,4''}$-H), 8.73 (d, 4H, $C^{6,\ 6''}$-H), 8.89 (s, 4H, $C^{3',5'}$-H). ^{13}CNMR for ZnTPYOH (d_3-CD_3CN): δ(ppm): 53.79 (-NCH_2-), 59.25(-CH2O-), 112.73 (phenyl-C), 119.03 (phenyl-C linked to $C^{4'}$), 121.77(-$C^{3,3''}$-), 123.07 (-$C^{5,5''}$-), 127.37 (phenyl-C), 129.29 (-$C^{4,4''}$-), 141.22 (-$C^{3',5'}$-), 147.92 (phenyl-C linked to N atom), 148.53 (-$C^{4'}$-), 149.59(-$C^{6,6''}$-), 151.40(-$C^{2,2''}$-), 155.87 (-$C^{2',6'}$-). MALDI-TOF: m/z=889.7 and 495.7 were assigned to $[ZnTPYOH]^+$ (calc. m/z=888.3) and $[ZnTPYOH+BF_4+H_2O]^{2+}$

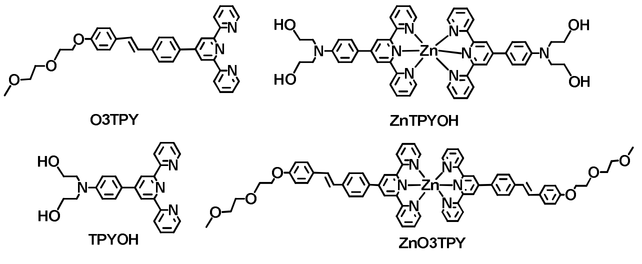
(calc. m/z=496.5), respectively. Elemental analysis of $C_{50}H_{48}N_8O_4B_2F_8Zn$: C, 56.44, H, 4.55, N, 10.53%. Found: C, 56.28, H, 4.35, N, 10.46%. ^{1}H NMR for ZnO3TPY (d_3-CD_3CN): δ(ppm): 3.35(s, 6H, -CH3), 3.54(m, 4H, ethyl-H), 3.67(m, 4H, ethyl-H), 3.83(m, 4H, -ethyl-O-CH2-C-), 4.19(m, 4H, -CH2-O-phenyl-), 7.05(d, 4H, -O-phenyl-H), 7.30(d, 2H, vinyl-H), 7.44(m, 6H, C$^{5,5''}$-H plus vinyl-H), 7.63(d, 4H, -O-phenyl-H), 7.87(d, 4H, central phenyl-H), 7.94 (d, 4H, central phenyl-H), 8.22 (m, 8H, C$^{4,4'',6,6''}$-H), 8.77 (d, 4H, C$^{3',3''}$-H), 9.03 (s, 4H, C$^{3',5'}$-H). ^{13}CNMR for ZnO3TPY (d_3-CD_3CN): δ(ppm): 58.13 (methyl-C), 67.76 (C-O-phenyl), 69.43 (ethyl-C), 70.41 (ethyl-C), 71.82 (C-O-Met), 115.06 (-O-phenyl-C), 121.21(vinyl-C), 123.38 (central phenyl-C), 125.29 (central phenyl-C), 127.40 (-C$^{3,3''}$-), 127.69 (-C$^{5,5''}$-), 128.41 (-O-phenyl-C), 128.67 (-O-phenyl-C linked to C=C), 130.02 (-C$^{4,4''}$-), 130.77(-C$^{3',5'}$-), 134.34 (central phenyl-C linked to C=C), 141.12 (central phenyl-C linked to C$^{4'}$), 141.44 (-C$^{4'}$-), 148.16 (-C$^{6,6''}$-), 150.01 (-C$^{2,2''}$-), 155.93 (-C$^{2',6'}$-), 159.34(phenyl-C linked to O atom). MALDI-TOF m/z=1122.3 was assigned as ZnO3TPY$^+$ (calc. m/z=1122.4), 612.5 and 1247.7 were assigned to $[ZnO3TPY+BF_4+H_2O]^{2+}$ (calc. m/z=613.7), and $[ZnO3TPY +BF_4+2H_2O]^+$ (calc. m/z=1246.7), respectively.

Results and discussion

1. Synthesis and characterization

O3TPY was afforded by Wittig-reaction in methanol solution and the target molecule was readily precipitated with high purity and good yield without further purification. The two signals at 7.06 and 7.14ppm (J=16.0Hz) in ^{1}H NMR spectra (Fig. S3) indicated the formation of *trans*-vinyl group. TPYOH was obtained by "one pot" method. Excess of aqueous NH_3 was used and the overall yield was higher than using ammonium acetate.

Zinc tetrafluoroborate was selected as the starting Zn(II) salt in the synthesis of the Zn(II) complexes of TPYOH and O3TPY, considering both the water-solubility and the purification effort. If the $Zn(NO_3)_2$ was used, the complexes need complicated purification processes although the cationic ions were readily to be dissolved in water.



Scheme 1. The chemical structure of the terpyridine ligands and their Zn(II) complexes

2. Crystallographic results

Experimental details for the structural determinations of TPYOH, O3TPY and their Zn(II) complexes are summarized in Table 1, while the selected bond lengths, angles are presented in Table S1(supporting information). The crystal structures of the terpyridines and their Zn(II) complexes are shown in Fig. 1. Both Zn(II) complexes present a $[Zn(terpyridine)_2]^{2+}$ cationic core. Two terpyridines act as equatorial ligands in a double-tridentate mode. The {N, N, N} coordination planes are nearly perpendicular to each other with the dihedral angles of about 88.76° and 81.51° for ZnTPYOH and ZnO3TPY, respectively. The coordination distance of Zn–N$_{lateral}$ (2.16~2.21Å in ZnTPYOH and 2.17~2.21 Å in ZnO3TPY) is slightly longer than that of Zn–N$_{central}$ (2.06～2.07 Å in ZnTPYOH and 2.07~2.10 Å in ZnO3TPY), which is comparable with those found in similar zinc(II) terpyridine complexes.[8-11]

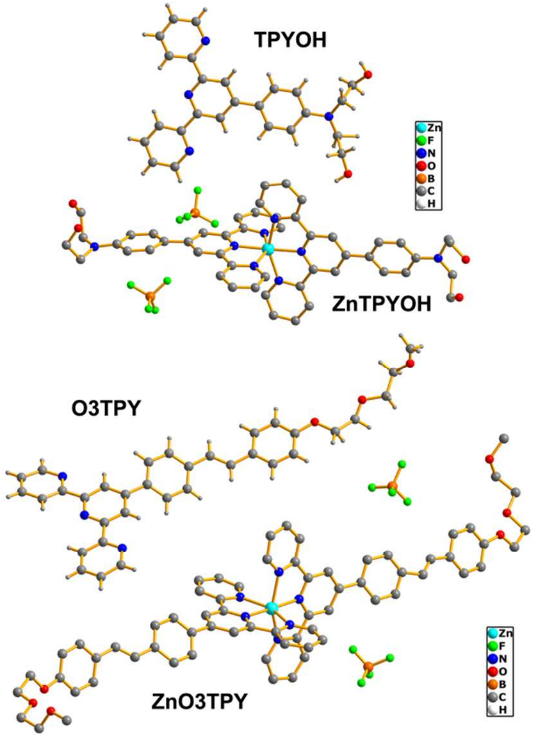


Fig. 1. Crystal structure of O3TPY, ZnO3TPY, TPYOH and ZnTPYOH. Hydrogen atoms are omitted in zinc complexes for clarity.

There exists strong hydrogen-bonding (C-H···O) between the oxygen atoms and the C-H on the pyridine ring in both the TPYOH and O3TPY (Fig S13). Intense H-bonds between the coordination cations and BF_4^- were found in both the ZnTPYOH and ZnO3TPY. As shown in Fig. 2, the two BF_4^- play crucial roles in connecting the cations into 3D networks and all fluorin atoms act as H-bonding acceptors. The H-bonding donors are the C-H from adjacent pyridine rings, benzene rings, and the hydroxyethyl groups (ZnTPYOH) or the methyl groups (ZnO3TPY). Compared with their ligands, however, no oxygen atoms were found to participate in the formation of hydrogen bonds in both the Zn complexes.

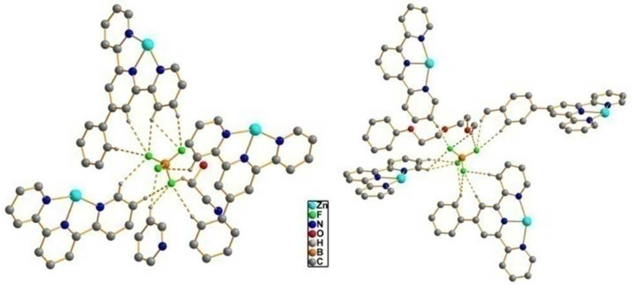


Fig. 2. Diagrams of hydrogen bonding between the BF_4^- and C-H groups in the terpyridines. ZnTPYOH(left) and ZnO3TPY(right).

Compound	TPYOH	O3TPY	ZnTPYOH	ZnO3TPY
empirical formula	$C_{25}H_{24}N_4O_2$	$C_{34}H_{31}N_3O_3$	$C_{51}H_{52}B_2F_8N_8O_5Zn$	$C_{68}H_{62}B_2F_8N_6O_6Zn$
formula weight	412.48	529.62	1096.00	1296.81
T [K]	296(2)	293(2)	293(2)	293(2) K
crystal system	Tetragonal	Monoclinic	Triclinic	Triclinic
space group	I4(1) cd	P2(1)/c	P-1	P-1
a [Å]	11.9604(9)	21.569(2)	12.1579(9)	15.4795(7)
b [Å]	11.9604(9)	11.9264(13)	14.2028(15)	15.7780(7)
c [Å]	29.871(4)	11.1252(9)	15.1132(16)	16.7889(8)
α [°]	90	90	89.697(9)	102.259(4)
β [°]	90	100.590(10)	82.362(8)	111.596(4)
γ [°]	90	90	71.041(8)	107.951(4)
V / Å3	4273.0(8)	2813.1(5)	2444.2(4)	3372.1(3)
Z	8	4	2	2
D calcd/ $(g \cdot cm^{-3})$	1.282	1.251	1.489	1.339
F(000)	1744	1120	1132	1410
absorption coefficient	0.083 mm^{-1}	0.081 mm^{-1}	0.591 mm^{-1}	0.444 mm^{-1}
θ range	2.73~25.02	3.35~28.94	3.04~25.02	3.07~25.04
reflections collected	10051	9985	12172	19317
ndependen reflections	1887	6268	8573	11805
GOF on F^2	1.025	1.033	1.047	1.049
R_1 [I>2σ(I)]	0.0640	0.1220	0.0764	0.0901
R_2 [I>2σ(I	0.1813	0.3143	0.1714	0.2532

Table 1 Crystallographic Parameters for the four compounds

3. Single-photon absorption and emission

The UV-Vis absorption properties of the two terpyridines and their Zn(II) complexes were investigated in H_2O solution (Fig. 3 and Table 2). The spectra of TPYOH and O3TPY exhibited three major bands in the region of 220-400 nm. The Zn(II) complexes have more complicate absorption profiles yet similar to each other. Interestingly, their absorption bands are remarkably red-shifted in comparison to the respective absorption bands of ligands, indicating a decrease in the band gap energy after Zn(II) coordination.

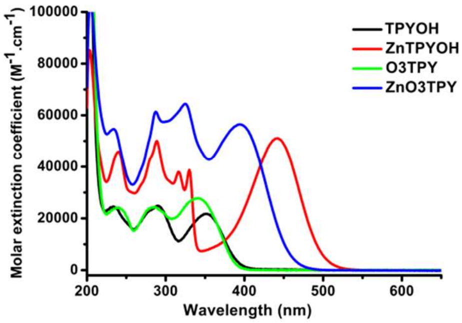


Fig. 3. UV-vis absorption spectra for two terpyridines and their Zn(II) complexes in H_2O solution (1.0×10^{-5} M).

To gain insight into the electronic transitions of terpyridine ligands and their Zn(II) complexes, TD-DFT calculations on the ground state (S_0) optimized structures were performed with the B3LYP functional and 6-31G(d) basis sets. The calculation results are in accordance with the experimentally observed absorption bands. The molecular orbitals of the TPYOH and ZnTPYOH are shown in Fig. 4 as an example. Notably, the HOMOs of TPYOH are mainly located on the di(hydroxyethyl)amino group, phenyl and the central pyridine ring of terpyridine moieties, while the LUMOs have confined contributions from all the three pyridines. The lowest energy absorption in the TPYOH can be assigned to a π(tpy)→π*(tpy) intramolecular charge transfer (ICT) transition with p(bishydroxylamino)→π(Ar) CT character. The absorption spectrum of ZnTPYOH displayed pronounced ligand-centered (LC) transitions.

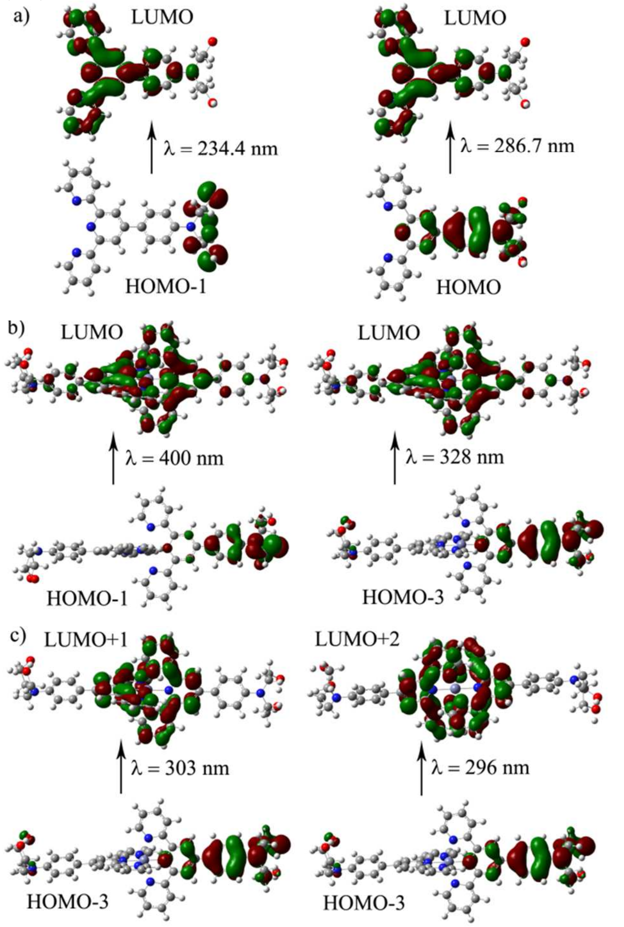


Fig. 4. Molecular orbitals for TPYOH (a) and ZnTPYOH (b and c) at their ground state (S_0) optimized geometries from TD-DFT calculations. Transition energies (in nm) were calculated using the TD-B3LYP method with 6-31G(d) basis sets.

Compounds	Exp^a	$Calc^b$	Transitions assignment
TPYOH	350(21.7) 290(24.7) 234(24.5)	 286.7(4.32) 234.4(5.29)	 HOMO→LUMO HOMO-1→LUMO
ZnTPYOH	441(51.0) 330(38.3) 316(37.7) 288(49.8) 240(45.6)	400(3.10) 328(3.78) 303(4.09) 296(4.18) 247(5.02)	HOMO-1→LUMO HOMO-3→LUMO HOMO-3→LUMO+1 HOMO-3→LUMO+2 HOMO-3→LUMO+3
O3TPY	340(28.2) 285(24.3)	317(3.91) 285(4.34)	HOMO→LUMO HOMO-1→LUMO

	240(24.3)	244(5.07)	HOMO-2→LUMO
ZnO3TPY	394(56.5); 324(64.4); 287(61.2); 234(54.5);	375(3.30) 331(3.74) 283(4.38) 256(4.84)	HOMO-1→LUMO HOMO-1→LUMO+1 HOMO-3→LUMO+1 HOMO-4→LUMO+3

Table 2. UV-vis absorption data for the compounds. [a] Experimental absorption wavelength (nm) and the molar extinction coefficient ($\varepsilon\times10^{-3}$/M^{-1}cm^{-1}) [b] Calculated absorption maximum (nm) and excitation energies (eV).

The fluorescence spectra of the terpyridines and their Zn(II) complexes displayed strong broad emission bands (Fig. 5). The trends of redshift in emission were consistent with the absorption features, when compared with the emission spectra of TPYOH and O3TPY in H_2O, ZnTPYOH and ZnO3TPY showed a redshift of 63nm and 81nm, respectively. The effect of solvent on the emission spectra was further examined and the recorded fluorescence spectra clearly displayed positive solvatechromism, indicating the polar excited states of the terpyridine ligands and Zn(II) complexes. This result also indicated that emission is CT transition in nature. [12] It's worthy to note that the emission maximum for all the four compounds is much longer in ethanol and H_2O than that in other polar solvents. When compared with that in DMF, the emission maximum of ZnO3TPY and ZnTPYOH in H_2O showed a redshift of 87nm and 70nm, respectively. The major cause for the redshift is attributed to the hydrogen-bonding effect between the complexes and the solvents. Since the derivative groups of N, N-(dihydroxyethyl)amino and (2-(2-methoxyethoxy)ethoxy)-benzene could interact evidently with the water or ethanol through hydrogen bonds, which will decrease the energy of the lowest excitation state and thus the emission wavelength red-shift.

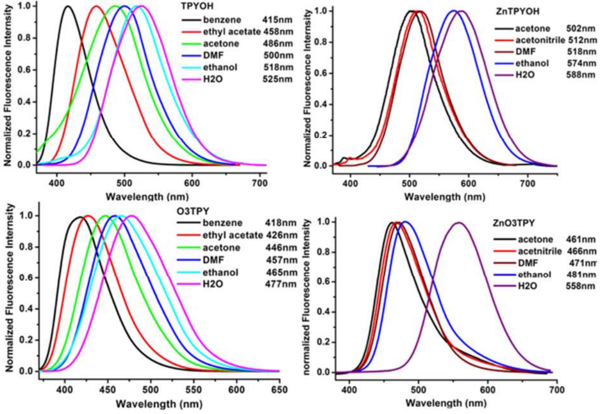


Fig. 5 The normallized one-photon excited fluorescence of the four compounds in different solvents. The concentrations were 1.0×10^{-5} M.

4. Two-photon absorption and emission

The TPA cross-section values (δ) of the terpyridines were evaluated by Z-scan technology using 750 nm femtosecond laser. TPYOH and O3TPY behaved strong two-photon absorption ability (Fig. 6), which were remarkably higher (515 and 148 GM for TPYOH and O3TPY, respectively) than that of similar terpyridine derivatives.[7] It's interesting to note that the δ value of TPYOH was much higher than that of O3TPY, which was differed from the common expectation that the increase of the conjugation length leads to an increase of the TPA activity.[13] Since the electron donating ability of di(hydroxyethyl)amino was stronger than that of the (2-(2-methoxy- ethoxy)ethoxy)benzyl group, it's more effective to improve the TPA ability of terpyridine derivatives by connecting strong electron-donating group than prolonging the π conjugation length. For verification reason, the 4'-p-9-anthracenevinyl-2,2':6',2''-terpyridine (antpy) that possessing a large π conjugation system but without electron-donating group was chose as a reference, whose δ value was tested to be only 115GM.

Differed from our previous report on enhanced TPA ability of Cd(II), Zn(II) coordination complexes when compared with their terpyridine ligand,[14] coordination to Zn(II) center here leads to a decrease of the TPA response, with the δ of 140 and 110 GM for ZnTPYOH and ZnO3TPY, respectively.

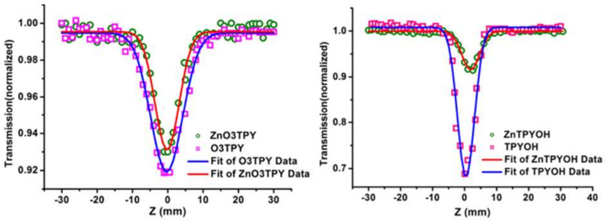


Fig. 6 Open-aperture Z-scan experimental data and fitting curves for four compounds in H_2O:acetonitrile(4:1) under 750nm laser beam. The concentration were 1.0×10^{-3} M.

The two terpydines display evident two-photon excited fluorescence (TPEF) under 700~940nm femtosecond laser (Fig. S16), with the emission maxima around 507 and 480 nm for TPYOH and O3TPY in mixed H_2O: acetontrile (v:v=4:1) solution, respectively. Since much higher concentration used in the measurement of TPEF, the TPEF spectra showed distinct redshift when compared with the one-photon excited fluorescence in the same solvent, due to the fluorescence reabsorption effect. Unexpectedly, the ZnO3TPY could display TPEF in H_2O/acetontrile (v:v=4:1) solution while no two-photon excited emission could be recorded for the ZnTPYOH under the same condition. Since the two-photon absorption spectrum of ZnO3TPY showed a broad band at 740~800nm (Fig. 7, left), the TPEF of ZnO3TPY was recorded under 700-940nm femtosecond laser and showed a strong emission maxima at 595nm when excited by 780 nm laser (Fig. 7, right). When compared with the redshift (81nm) in the one-photon emission, the TPEF emission band of ZnO3TPY showed an unusually large redshift of 130nm against that of O3TPY, which will bring great advantages in the future bioimaging of celluar Zn^{2+} using two-photon confocal microscopy, such as reduced background fluorescence interference and decreased photobleaching.

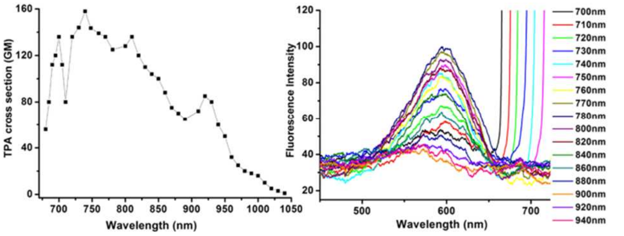


Fig. 7 Two-photon absorption spectrum (left) and two-photon excited fluorescence of ZnO3TPY in H_2O:acetonitrile=4:1

solution under different laser beam. The TPA spectrum was recorded using Z-scan technology and the concentration was 1.0×10^{-3} M.

To examine the Zn(II) sensing ability of O3TPY using TPEF, zinc titration experiment was carried out under 780nm laser (Fig.8). The TPEF of O3TPY was quenched gradually with the concentration increase of Zn^{2+} while the TPEF for ZnO3TPY increased, and the equivalent point appeared at 558nm. Since the required concentration of the sample for TPEF was much higher than that for one-photon excited fluorescence and the two photon absorption effect at high concentration cannot be ignored, the O3TPY can respond linearly with the zinc concentration ranging from 2×10^{-6} to 3.5×10^{-4}mol/L, and the linear correlation coefficient R=0.99818.

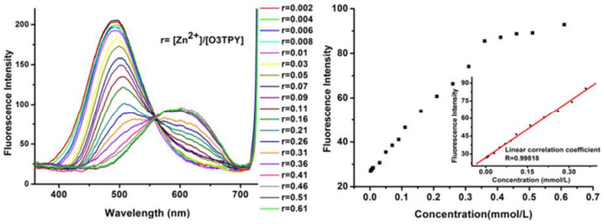


Fig. 8. (left) The TPEF spectra of O3TPY in the absence and presence of Zn^{2+}.(right) The plot of TPEF intensity of the O3TPY-Zn^{2+}system *vs* Zn^{2+} concentrations (inserted is the linear fit of the data).

Conclusions

Herein, we designed two terpyridines with good water solubility and reported the facile synthesis procedures. The structure of the terpyridine ligands and their Zn(II) complexes were fully characterized by ^{1}H NMR, ^{13}CNMR, ESI-MS, MALDI-TOF, elemental analysis and X-ray crystallography. The one-photon absorption of the four compounds was analyzed experimentally and theoretically. The absorption bands can be assigned to a π(tpy)→π*(tpy) ICT transition with p(nitrogen or oxygen)→π(Ar) CT character. The four compounds could display strong one-photon fluorescence, and the di(hydroxyethyl)amino and the (2-(2-methoxy- ethoxy)ethoxy) benzyl groups played important roles in the solvatechromism effect on the emission spectra. The evaluation on the two-photon properties of the compounds demonstrated that the free terpyridines could behave good two-photon absorption properties, while the two-photon ability were weakened for their Zn(II) complexes. The two terpyridine ligands could display good two photon excited fluorescence (TPEF). Although TPYOH presented the highest TPA cross section values, its TPEF was fully quenched by the Zn(II) coordination. Only ZnO3TPY that possessing large π-conjugation system together with suitable electon-donating group could give an emission maxima at 595nm when excited by 680~880nm femtosecond laser. The TPEF titration experiment revealed that O3TPY could respond linearly with the Zn^{2+} concentration. The high water solubility and two-photon emissive ability of ZnO3TPY provides an excellent starting point for the development of cellular zinc two-photon fluorescent probes. The current results form an important base for future design of terpyridine based Zn(II) complexes with large TPA cross-section values and are important for the future Zn(II)-bioimaging using two-photon confocal microscopy.

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Notes and references

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† Electronic Supplementary Information (ESI) available: [^{1}H NMR, ^{13}CNMR, ESI-MS and MALDI-TOF data for the four compounds; Selected bond lengthes and angels for the compounds; ORTEP drawing of the compounds; Molecular orbitals for O3TPY and ZnO3TPY based on TD-DFT calculations; TPEF spectra for TPYOH and O3TPY, etc.].

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Studies on the one-photon and two-photon properties of two water-soluble terpyridines and their zinc complexes

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The terpyridines and its Zn(II) complex processing suitable conjugation system and electron donors display strong two-photon excited fluorescence.