New Zinc(II) Dyes: Photophysical Properties and Enhanced Two-Photon Absorption

YUANLE CAO, DONGLING XU, MINGDI YANG, YANG WANG, FEIXIA ZHOU and HONGPING ZHOU[*]

College of Chemistry and Chemical Engineering, Anhui University and Key Laboratory of Functional Inorganic Materials Chemistry of Anhui Province, Hefei 230039, P.R. China

*Corresponding author: Fax: +86 551 5107342; Tel: +86 551 5108151; E-mail: zhpzhp@263.net

A series of zinc(II) complexes (**dyes 1-5**) based on 4'-(4-[4-(imidazole)styryl]phenyl)-2,2':6',2"-terpyridine have been synthesized and fully characterized. Linear and non-linear optical properties of them were investigated in detail. Experimental results reveal that the maximum two-photon absorption (TPA) cross-section of these five two-photon fluorescence complexes are 646, 367, 180, 456 and 246 GM for dyes 1-5 in DMF, respectively, which are extraordinary larger than that of ligand with the maximum values of 149 GM in the DMF. Besides, with the same metal cation, the two-photon absorption cross-section vary by the order of Cl > SCN > Br > ClO₄ > I, which suggests that the two-photon absorption cross-sections of complexes display a large dependence on the choice of anions.

Key Words: Terpyridine, Two-photon absorption cross-sections, Linear optical properties, Non-linear optical properties, Anions.

INTRODUCTION

Organic molecules with high two-photon absorption (TPA) properties have received increasing attention in the last decade. They have potential applications in three-dimensional microfabrication[1], optical limiting[2], biological imaging[3], 3-D optical date storage[4], photodynamic therapy[5], *etc*.

However, the generally small two-photon absorption cross section (δ) restrict the application of two-photon absorption materials. In particular, extended π-conjugated systems symmetrically substituted with electron-donating (D) and electron-accepting (A) functionalities have been revealed as efficient two-photon absorption molecules, which exhibited higher two-photon absorption cross sections than the corresponding unsubstituted molecules, indicating that the efficient intramolecular charge transfer (ICT) made by the donating or withdrawing abilities of the electron donor or acceptor played an important role in increasing their δ values[6]. Nonetheless, the increasing complexity of these donor and acceptor moieties is often paired with an equal increase of the difficulties associated with their synthesis.

Coordination compounds are expected to show better physical and chemical stability than uncoordinated ligands. The metal ions which serve as a powerful 3D templates, can assemble simple organic ligands in a variety of multipolar arrangements, showing interesting electronic and optical properties[7].

The metal ion binded to the ligand can form a D-π-A complex and it may induce a low-energy metal-ligand charge-transfer transition (MLCT)[8], leading to an enhanced two-photon absorption cross-section. Besides, intraligand charge-transfer (ILCT) transition caused by the introduction of metal ions may also affect the δ value[9].

Our synthetic strategy is based on self-assembly of inorganic metal ion and organic ligand with excellent optical performance. As the metal ion was bound to the acceptor, the π-conjugation structure was extended. The enhanced intramolecular charge transfer (ICT) caused by the extended π-conjugation afford these coordination compounds excellent optical property to serve as two-photon absorption materials. The hybridization of organic ligand and inorganic metal ion is expected to give an enhanced δ value[10].

In our previous work, we have used the D-π-A type ligand 4'-(4-[4-(imidazole)styryl]phenyl)-2,2':6',2"-terpyridine to coordinate with HgX₂ (X = Cl, Br, I) so as to afford a series of complexes. The linear and non-linear optical properties of the ligand and three dyes also have been studied. The experimental results reveal that the two-photon absorption cross sections of three dyes are extraordinary stronger than that of ligand[11]. Another triazole-based system we have researched also confirms that complexes have larger two-photon absorption cross sections than that of ligands. This phenomenon may be attributed to the longer delocalization of the electrons upon coordinating metal ions[12]. In order to further study how anions affect the two-photon absorption cross sections of complexes and finally perfect our work, we used the reported D-π-A type 4'-(4-[4-(imidazole)styryl]phenyl)-2,2':6',2"-terpyridine (Fig. 1) to coordinated with ZnX₂ (X = Cl, Br, I, SCN or ClO₄)
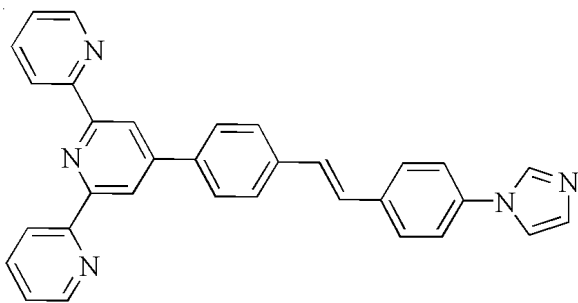
Fig. 1. Schematic drawing of the ligand (L)

to verify our inference and provide chemical and material researchers with a helpful reference (**Scheme-I**).

EXPERIMENTAL

All chemicals were available commercially from Acros Organics Company and Aladdin and the solvents were purified *via* distillation before use. The synthesis of 4'-(4-[4-(imidazole)-styryl]phenyl)-2,2':6',2''-terpyridine was described in our previous work[11].

Photophysical methods: IR spectra were recorded with a Nicolet FT-IR NEXUS 870 spectrometer (KBr discs). UV-visible absorption spectra were recorded on a UV-3100 spectrophotometer. Fluorescence measurements were carried out using an Edinburgh FLS920 fluorescence spectrometer equipped with a 450 W Xe lamp and a time-correlated single-photon counting (TCSPC) card. All solvents used in the test were chromatographically pure reagents. The two-photon excited fluorescence (TPEF) spectra were measured using a mira 900-D Ti: sapphire femtosecond laser with a pulsewidth of 200 fs and a repetition rate of 76 MHz. Two-photon absorption cross sections were measured using fluorescein as reference. Elemental analyses data were measured by a Perkin-Elmer 240B elemental analyzer.

ZnLCl$_2$ (dye 1): FT-IR (KBr, cm^{-1}): 3441 (m), 1597 (vs), 1571 (m), 1522 (s), 1473 (s), 1429 (m), 1404 (m), 1306 (m), 1248 (m), 1064 (m), 1013 (m), 964 (m), 838 (m), 791 (m), 748 (m). Anal. calcd. for C$_{32}$H$_{23}$N$_5$Cl$_2$Zn: C, 62.61; H, 3.78; N, 11.41 %. Found: C, 62.35; H, 3.77; N, 11.49 %.

ZnLBr$_2$ (dye 2): FT-IR (KBr, cm^{-1}): 3441 (m), 1598 (vs), 1571 (m), 1521 (s), 1473 (s), 1428 (m), 1404 (m), 1304 (m), 1249 (m), 1055 (m), 1015 (m), 963 (m), 837 (m), 792 (m), 731 (m). Anal. calcd. for C$_{32}$H$_{23}$N$_5$Br$_2$Zn: C, 54.69; H, 3.30; N, 9.97 %. Found: C, 54.55; H, 3.27; N, 9.89 %.

ZnLI$_2$ (dye 3): FT-IR (KBr, cm^{-1}): 3416 (m), 1597 (vs), 1571 (m), 1521 (s), 1473 (s), 1428 (m), 1403 (m), 1304 (m), 1248 (m), 1063 (m), 1013 (m), 963 (m), 836 (m), 792 (m), 730 (m). Anal. calcd. for C$_{32}$H$_{23}$N$_5$I$_2$Zn: C, 48.24; H, 2.91; N, 8.79 %. Found: C, 48.13; H, 2.92; N, 8.84 %.

ZnL(NCS)$_2$ (dye 4): FT-IR (KBr, cm^{-1}): 3437 (m), 2065 (vs), 1597 (vs), 1572 (m), 1521 (s), 1471 (s), 1426 (m), 1304 (m), 1247 (m), 1123 (m), 1062 (m), 1017 (m), 964 (m), 834 (m), 791 (m). Anal. calcd. for C$_{34}$H$_{23}$N$_7$S$_2$Zn: C, 61.95; H, 3.52; N, 14.88 %. Found: C, 61.79; H, 3.56; N, 14.86 %.

ZnL$_2$(ClO$_4$)$_2$ (dye 5): FT-IR (KBr, cm^{-1}): 3437 (m), 1599 (vs), 1572 (m), 1521 (s), 1473 (s), 1305 (m), 1250 (m), 1089 (vs), 1018 (m), 964 (m), 837 (m), 795 (m), 748 (m), 623 (m). Anal. calcd. for C$_{64}$H$_{46}$N$_{10}$O$_8$Cl$_2$Zn: C, 63.04; H, 3.80; N, 11.49 %. Found: C, 63.23; H, 3.81; N, 11.42 %. From the element analysis result and our former experience we can infer that the unit of dyes 1-4 may contain one ligand, while that of dye 5 may contain two ligands.

RESULTS AND DISCUSSION

Linear absorption properties: The linear photophysical data (absorption and fluorescence) of the complexes in five different solvents are summarized in Table-1 (including fluorescence quantum yields and Stokes' shift).

The linear absorption and SPEF spectra of L and complexes **1-5** in THF, ethyl acetate, ethanol, acetonitrile, DMF and methanol with a solution concentration of c = 1.0 × 10^{-5} mol/L are shown in Fig. 2, from which one can see that their absorption Linear spectra exhibits dual bands in the 279-348 nm range in all the solvents. The high energy band was assigned to the π→π* transition, while the low energy band was assigned to the intramolecular charge tranfer (ICT) between terpyridyl moiety and the whole molecular. One can see that the absorption profile and maxima of the five compounds are similar in
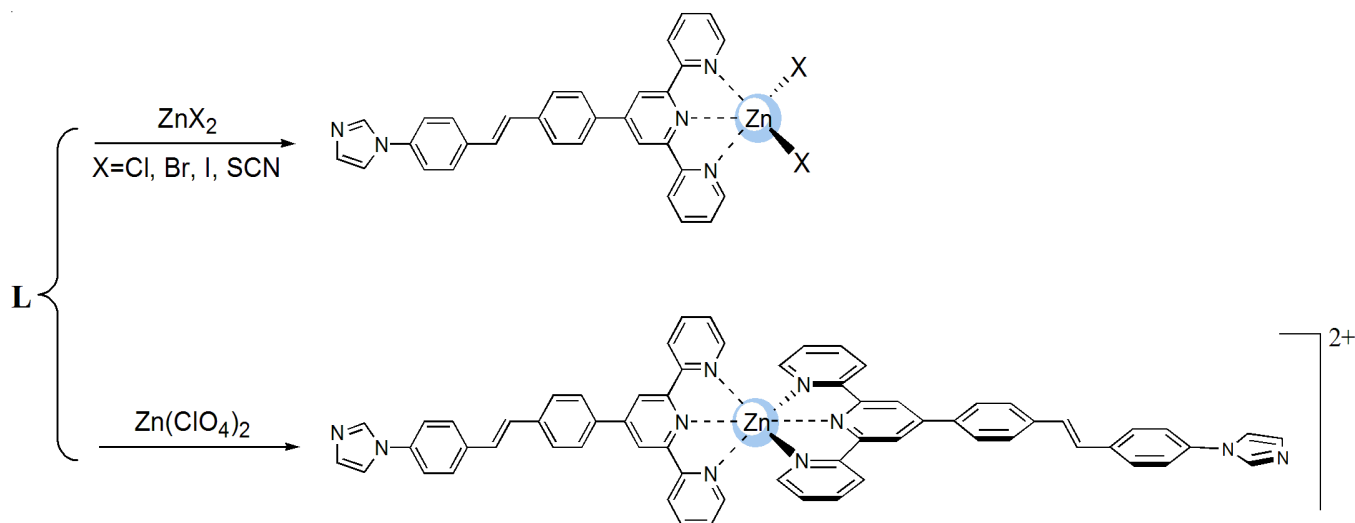
Scheme-I: Synthetic routes to dyes 1-5

TABLE-1
PHOTOPHYSICAL PROPERTIES OF COMPLEXES **1-5** IN DIFFERENT POLAR SOLVENTS

Compound	Solvents	$\lambda_{max}^{(1a)\ [a]}$	$\lambda_{max}^{(1f)\ [b]}$	$\Phi^{[c]}$	$\Delta\nu^{[d]}$
Dye 1	THF	282, 331	485	0.551	9593
	Ethyl acetate	286, 341	469	0.239	8004
	Ethanol	288, 348	462	0.137	7091
	Acetonitrile	287, 342	516	0.190	9860
	DMF	279, 336	432	0.530	6614
	Methanol	287, 344	516	0.099	9690
Dye 2	THF	289, 336	469, 491	0.527	9395
	Ethyl acetate	285, 343	461	0.138	7463
	Ethanol	290, 345	463	0.137	7387
	Acetonitrile	288, 340	517	0.177	10069
	DMF	279, 333	432	0.556	6882
	Methanol	287, 342	444, 502	0.147	9319
Dye 3	THF	282, 335	421, 460	0.526	8112
	Ethyl acetate	289, 337	411	0.418	5343
	Ethanol	290, 345	464	0.282	7434
	Acetonitrile	286, 341	516	0.150	9946
	DMF	279, 331	433	0.560	7117
	Methanol	288, 343	515	0.179	9737
Dye 4	THF	282, 334	490	0.633	9532
	Ethyl acetate	285, 345	415, 454	0.097	6959
	Ethanol	290, 345	463	0.209	7387
	Acetonitrile	286, 340	518	0.176	10107
	DMF	279, 333	432	0.525	6882
	Methanol	290, 346	518	0.146	9597
Dye 5	THF	285, 333	413	0.474	5817
	Ethyl acetate	285, 333	409	0.278	5580
	Ethanol	288, 343	462	0.259	7509
	Acetonitrile	286, 338	426	0.268	6112
	DMF	281, 333	433	0.547	6935
	Methanol	287, 339	435	0.226	6510

[a]Peak position of the longest absorption band. [b]Peak position of SPEF, excited at the absorption maximum. [c]Quantum yields determined by using quinine sulfate as standard. [d] Stokes' shift in cm^{-1}.

different solvent, which means that absorption spectra of **dyes 1-5** shows no sensibility on the polarity of solvent.

Single-photon exited fluorescence (SPEF): The single-photon fluorescence spectra of the series of complexes in six different solvents are collected in Fig. 3.

The single-photon excited fluorescence (SPEF) quantum yields (Φ) were measured by using a standard method under the same experimental conditions for all compounds. The data step is 1 nm, 400 mV excitation voltage, excitation slit width and emission slit widths were 5.0 nm. Quinine sulfate, which is dissolved in ethanol ($\Phi = 0.577$)[13] at the same concentration as other samples, is used as the reference. The single-photon excited fluorescence spectra were measured at the same concentration as that of the linear absorption spectra. With the increasing polarity of the solvent, the single-photon excited fluorescence spectra of L and its complexes show remarkable bathochromic shifts, except in DMF. For example, λ_{max} (SPEF) of **dye 1** is located at 469 nm in ethyl acetate and red-shifted to 516 nm in acetonitrile, which indicates that the enhanced dipolar-dipolar interactions caused by the increasing polarity of solvent lead to the decrease of energy level for the excited state[6]. The charge separation increases in the excited state, resulting in a larger dipolar moment than that in the ground state, explaining the sensitivity of the emission spectra of the dipolar dyes to solvent polarity.

The two peaks phenomenon of **dye 2** and **dye 3** in the minimum polar solvent of THF may be attributed to the twisted intramolecular charge transfer (TICT)[14]. Besides, the quantum yields (Φ) of **dyes 1-5** decrease regularly as the polarity of solvent reduce (except in DMF). As to the blue shift in DMF, the possible reason may be that **dyes 1-5** have better solubility in DMF to avoid aggregation[15].

Non-linear photophysical properties: Detailed experiments reveal that there is no linear absorption in the wavelength range 450-850 nm for all the dyes, which indicates that there are no molecular energy levels corresponding to an electron transition in the spectra range. The emission excited in this spectral range can be attributed to the nonlinear two-photon process. By tuning the pump wavelengths increments at 10 nm from 680 to 840 nm on condition that keeping the input power fixed and recording TPEF intensity, TPEF spectra of the compounds are obtained.

As shown in Fig. 4, the TPEF spectra of L and its complexes **1-5** are determined in DMF with a concentration of 1×10^{-3} mol/L. One can see that the TPEF peak position of Fig. 4 has no dependence relationship with excitation wavelength. However, there is strong dependence between two photon fluorescence intensity and excitation wavelength. The optimum excitation wavelength of **dyes 1-5** are located at 760, 760, 780, 760 and 750 nm, respectively.
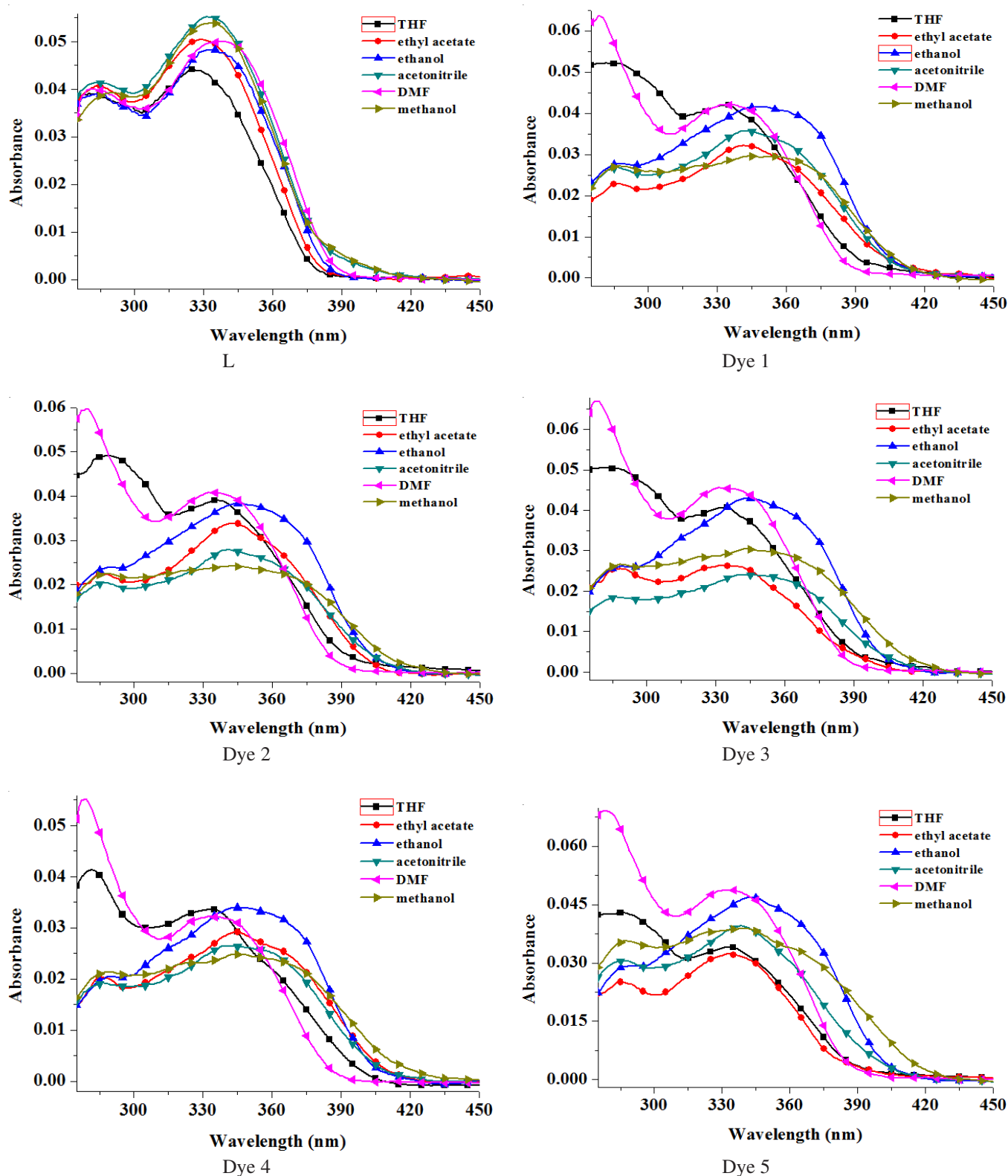
Fig. 2. Linear absorption spectra of L and the dyes 1-5 in variety solvent with different polarity

Two-photon absorption cross-section: The two-photon absorption cross sections (δ) are determined by comparing their TPEF to that of fluorescein in DMF, according to the following equation[16]:

$$\delta = \delta_{ref} \frac{\Phi_{ref}}{\Phi} \frac{c_{ref}}{c} \frac{n_{ref}}{n} \frac{F}{F_{ref}}$$

The subscripts ref. stands for the reference molecule. δ is the two-photon absorption cross-section value, c is the concentration of solution, n is the refractive index of the solution, F is the TPEF integral intensities of the solution emitted at the exciting wavelength and Φ is the fluorescence quantum yield. The δ_ref value of reference was taken from the literature[17].
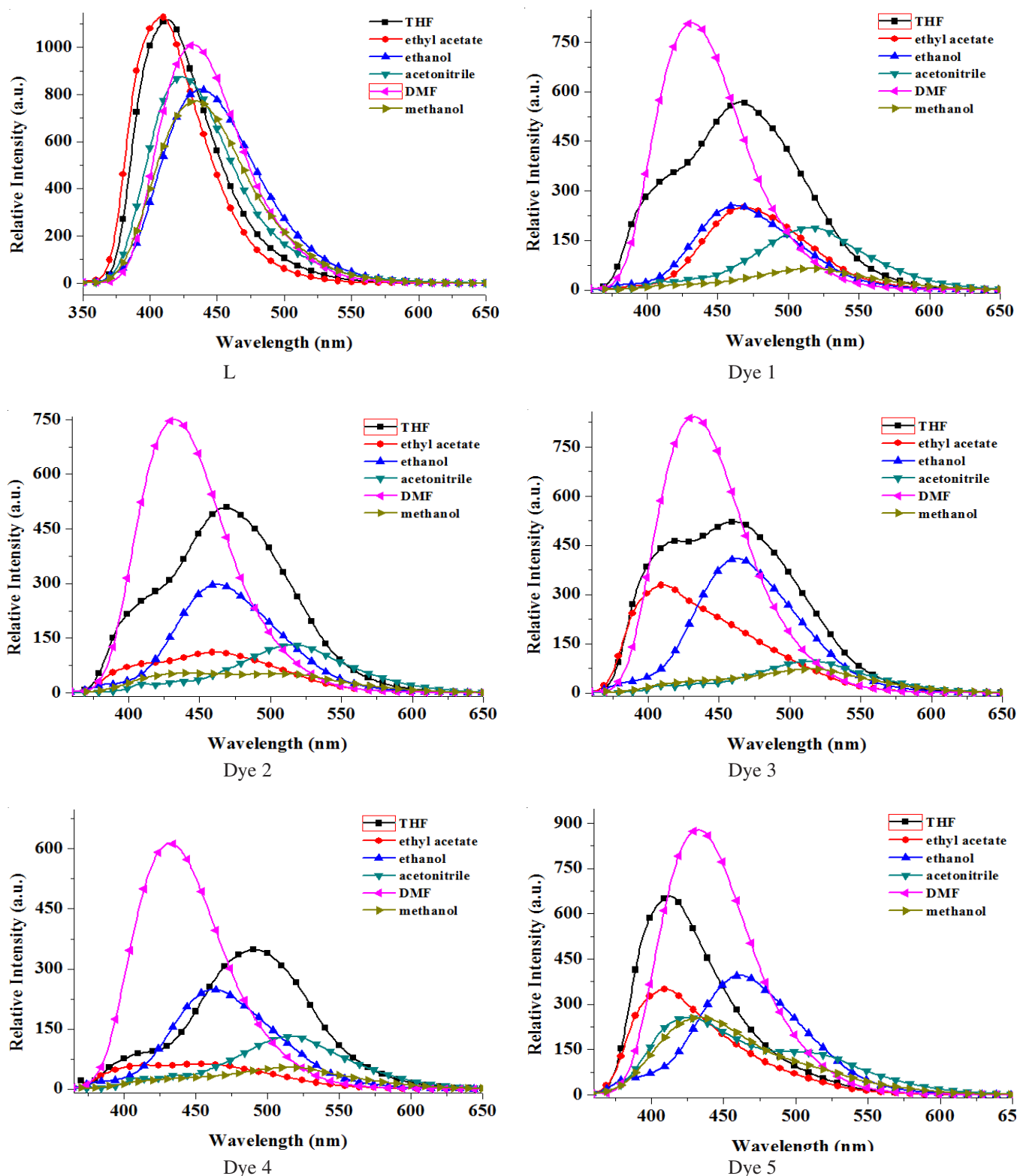
Fig. 3. One-photon fluorescence spectra of L and dyes 1-5

By referencing the two-photon absorption cross-section of fluorescein to be 19 GM (1GM = 10^{-50} cm^{-4} s photon^{-1})[18], we obtain the maximum two-photon absorption cross sections of L and **dyes 1-5**. From Fig. 5, we noted that the two-photon absorption cross-sections of these dyes vary significant and have an order as **dye 1** (646 GM) > **dye 4** (456 GM) > **dye 2** (367 GM) > **dye 5** (246 GM) > **dye 3** (180 GM) > L (149

GM). Obviously, the δ values of ligand L is lower than those of all complexes, probably due to the enlarged conjugation length upon Zn addition L. When L is coordinated with ZnX$_2$, the Zn^{2+} becomes the acceptor, which induces a larger delocalization of the electrons. The experiment results reveals that the enhancement of δ followed the order of Cl$^-$ > SCN$^-$ > Br$^-$ > ClO$_4^-$ > I$^-$ which was corresponded to our previous studies.
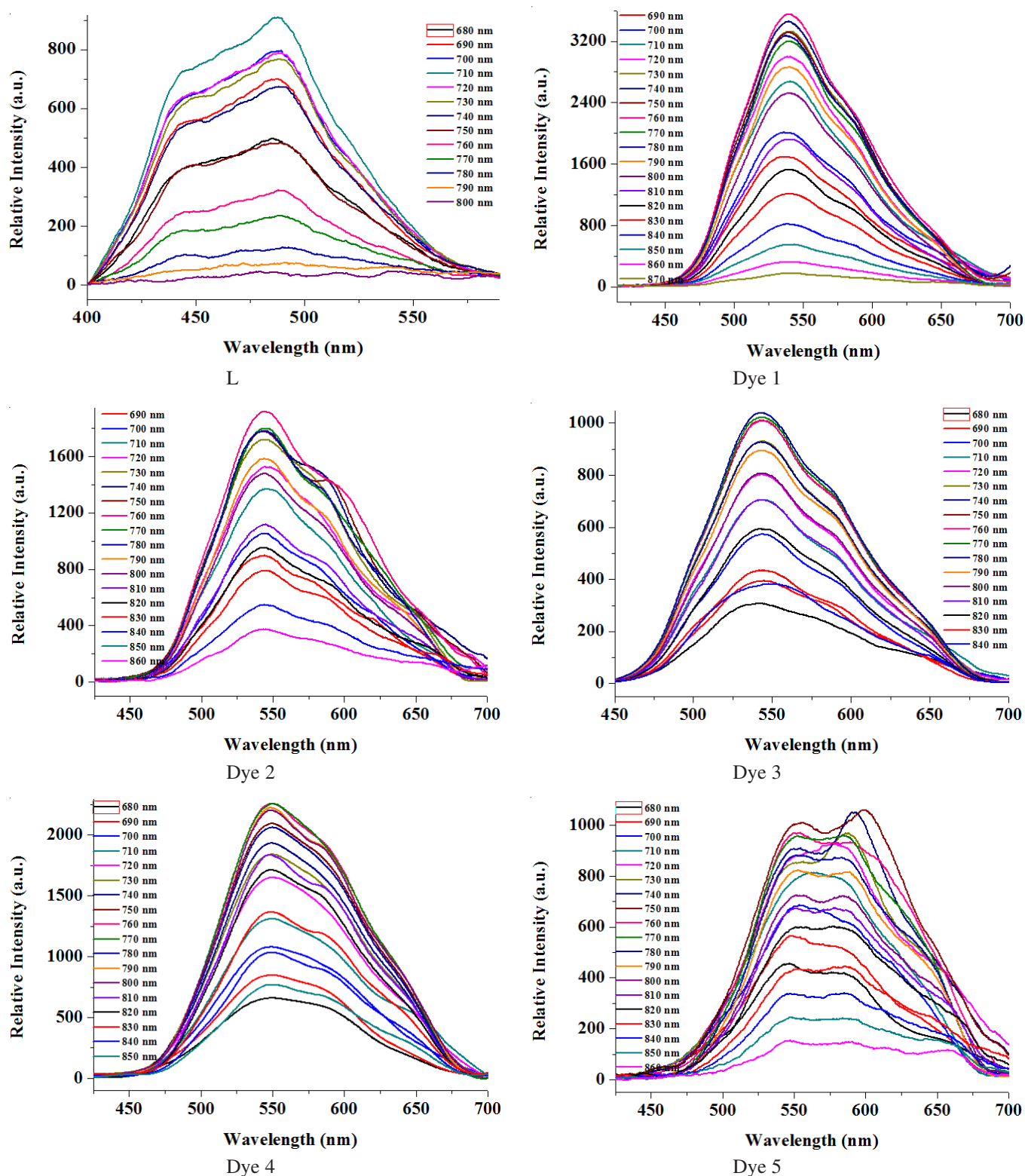
Fig. 4. Two-photon absorption spectra of L and dyes 1-5 in DMF under different exciting wavelengths (c = 1.0 × 10⁻³ mol/L)

It is probably because of the different degrees of electron de-localization, which was caused by electron inductive effect of corresponding anions.

Conclusion

In summary, a series of new coordination complexes (**dyes 1-5**) is obtained by self-assembly of the ligand 4'-(4-[4-(imidazole)-styryl]phenyl)-2,2':6',2"-terpyridine (L) with ZnX₂ (X= Cl, Br, I, SCN or ClO₄). One-photon absorption and emission spectra, two-photon excited fluorescence action have been systematically investigated. It's noteworthy that the two-photon absorption-induced fluorescence of these five dyes are obviously larger than that of L, which can be ascribed to the enlarged conjugation
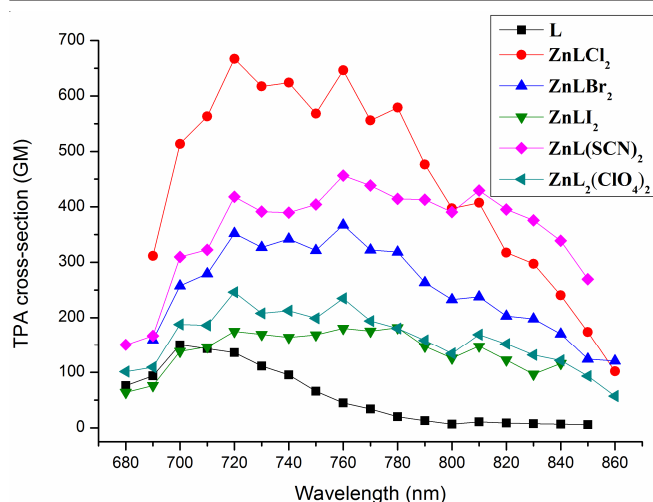
Fig. 5. Two-photon (from a 200 fs, 76 MHz, Ti: sapphire laser) absorption cross sections of L, **dyes 1-5** in DMF versus excitation wavelengths of identical energy of 0.100 w. (experimental uncertainties: 10 %)

length when Zn^{2+} become the acceptor. The two-photon absorption cross-section dependents on a number of factors, among which electronic delocazation and intramolecular charge-transfer phenomenon are of great significant. The electron inductive effect of anions may also enhance δ_{TPA}. The stronger the electron inductive effect is, the larger the two-photon absorption cross-section is.

REFERENCES

1. S.J. Jhaveri, J.D. McMullen, R. Sijbesma, L.S. Tan, W. Zipfel and C.K. Ober, *Chem. Mater.*, **21**, 2003 (2009).
2. (a) L.S. Li, J.Y. Wu, Tian, Y.W. Tang and M.H. Jiang, H.K. Fun and S. Chantrapromma, *Opt. Mater.*, **28**, 897 (2006); (b) B. Xu, H.H. Fang, F.P. Chen, H.G. Lu, J.T. He, YW. Li, Q.D. Chen, H.B. Sun and W.J. Tian, *New. J. Chem.*, **33**, 2457 (2009).
3. (a) J.H. Son, C.S. Lim, J.H. Han, I.A. Danish, H.M. Kim and B.R. Cho, *J. Org. Chem.*, **76**, 8113 (2011); (b) G.J. Kim, K. Lee, H. Kwon and H.J. Kim, *Org. Lett.*, **13**, 2799 (2011); (c) C.J. Zhang, L. Li, G.Y.J. Chen, Q.H. Xu and S.Q. Yao, *Org. Lett.*, **13**, 4160 (2011); (d) C.B. Huang, J.L. Qu, J. Qi, M. Yan and G. Xu, *Org. Lett.*, **13**, 1462 (2011).
4. (a) A.S. Dvornikov, E.P. Walker and P.M. Rentzepis, *J. Phys. Chem.*, **113**, 13633 (2009); (b) C.C. Corredor, Z.L. Huang, K.D. Belfield, A.R. Morales and M. Bondar, *Chem. Mater.*, **19**, 5165 (2007).
5. (a) K. Ogawa, H. Hasegawa, Y. Inaba, Y. Kobuke, H. Inouye, Y. Kanemitsu, E. Kohno, T. Hirano, S. Ogura and I. Okura, *J. Med. Chem.*, **49**, 2276 (2006); (b) M.K. Kuimova, H.A. Collins, M. Balaz, E. Dahlstedt, J.A. Levitt, N. Sergent, K. Suhling, M. Drobizhev, N.S. Makarov, A. Rebane, H.L. Anderson and D. Phillips, *Org. Biomol. Chem.*, **7**, 889 (2009).
6. (a) A. Bhaskar, G. Ramakrishna, Z.K. Lu, R. Twieg, J.M. Hales, D.J. Hagan, E. Van Stryland and T. Goodson 3rd, *J. Am. Chem. Soc.*, **128**, 11840 (2006); (b) H.M. Kim and B.R. Cho, *Chem. Commun.*, 153 (2009).
7. Y.P. Tian, L. Li, Y.H. Zhou, P. Wang, H.P. Zhou, J.Y. Wu, Z.J. Hu, J.-X. Yang, L. Kong, G.-B. Xu, X.-T. Tao and M.-H. Jiang, *Cryst. Growth. Des.*, **9**, 1499 (2009).
8. A. Vlcek and S. Zalis, *Coord. Chem. Rev.*, **251**, 258 (2007).
9. C. Feuvrie, O. Maury, H.L. Bozec, I. Ledoux, J.P. Morrall, G.T. Dalton, M. Samoc and M.G. Humphrey, *J. Phys. Chem. A*, **111**, 8980 (2007).
10. S.J. Das, A. Nag, D. Goswami and P.K. Bharadwaj, *J. Am. Chem. Soc.*, **128**, 402 (2006).
11. H.P. Zhou, F.X. Zhou, P. Wu, Z. Zheng, Z.P. Yu, Y.X. Chen, Y.L. Tu, L. Kong, J.Y. Wu and Y.P. Tian, *Dyes Pigments*, **91**, 237 (2011).
12. H.P. Zhou, J.Q. Wang, F.X. Zhou, D.L. Xu, Y.L. Cao, G. Liu, L. Kong, J.X. Yang, J.Y. Wu and Y.P. Tian, *Dyes Pigments*, **95**, 723 (2012).
13. Z.Y. Wang, Y.Y. Gong, S.M. Chen, Y.S. Xiao, J.W.Y. Lam, P. Lu, Y.W. Lu, Z.M. Wang, R.R. Hu, N. Xie, H.S. Kwok, Y.M. Zhang, J.Z. Sun, and B.Z. Tang, *Chem. Mater.*, **24**, 1518 (2012).
14. M. Drobizhev, A. Karotki, Y. Dzenis, A. Rebane, Z. Suo and C.W. Spangler, *J. Phys. Chem. B.*, **107**, 7540 (2003).
15. Y.Q. Wang, A.J. Zappas II, J.N. Wilson, I.B. Kim, K.M. Solntsev, L.M. Tolbert and U.H.F. Bunz, *Macromolecules*, **41**, 1112 (2008).
16. C. Xu and W.W. Webb, *J. Opt. Soc. Am. B*, **13**, 481 (1996).
17. O. Varnavski, T. Goodson, L. Sukhomlinova and R. Twieg, *J. Phys. Chem. B*, **108**, 10484 (2004).
18. M.A. Albota, C. Xu and W.W. Webb, *Appl. Opt.*, **37**, 7352 (1998).