DOI: 10.1002/cphc.201100885

## Evidence for Two-Photon Absorption-Induced ESIPT of Chromophores Containing Hydroxyl and Imino Groups\*\*

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This paper presents experimental and theoretical investigations into excited-state intramolecular proton transfer (ESIPT) in new chromophores with hydroxyl and imino groups under oneand two-photon excitation. The results show that internal hydrogen bonding exhibits a remarkable influence on the maximum absorption wavelength of 2-[(4'-N,N-diethylaminodiphenylethylene-4-ylimino)methyl]phenol (C1) and 2-[(4'-methoxyldiphenylethylene-4-ylimino)methyl]phenol (C3). Compounds C1 and C3 exhibit well-separated dual fluorescence emission bands under one- and two-photon excitation. The second fluorescence peaks of C1 and C3 are characterized by much larger Stokes shift than the first normal peaks (ca. 140 vs. 30 nm). 4-[(4'-N,N-Diethylaminodiphenylethylene-4-ylimino)methyl]phenol (C2) and 4-[(4'-methoxyldiphenylethylene-4-ylimino)methyl]phenol (C4) display single emission bands with small Stokes shifts (ca. 30 nm) in various solvents under one- and two-photon excitation. Furthermore, the first emission maxima of C1 and C3 are almost identical to the maximum fluorescence emission wavelengths of C2 and C4, respectively. These results show that C1 and C3 can undergo ESIPT via a reasonable six-membered ring, while there is no ESIPT in C2 and C4 under one- and two-photon excitation. Compounds C1 and C2 have larger two-photon absorption cross-sections under various near-infrared laser frequencies tuned from 700 to 880 nm. Molecular geometry optimization of the phototautomers (enol and keto) was performed to analyze the experimental results. The possibility of using these chromophores for metal ions as chemosensors of was thoroughly investigated. In DMF C3 exhibits excellent sensing responses to Zn<sup>2+</sup> and Fe<sup>3+</sup> ions through a greatly increased greatly and a largely reduced emission, respectively. In methanol disappearance of ESIPT emission with added Zn<sup>2+</sup> ions confirms its existence. The binding constants of C3 with Zn<sup>2+</sup> and Fe<sup>3+</sup> ions in DMF are also estimated.

## 1. Introduction

Excited-state intramolecular proton transfer (ESIPT) has received considerable experimental and theoretical attention because it is regarded as a significantly important phenomenon in chemical and biological systems.<sup>[1-6]</sup> ESIPT is achieved by an ultrafast femtosecond photoinduced enol-keto tautomerization process as the intramolecular hydrogen-bonded molecule is excited; this represents a four-level cyclic reaction occurring via five- or quasi-six-membered ring, and even in rare cases seven-membered rings.<sup>[7-9]</sup> Such definite conformational changes are caused by the stable enol form (E) in the ground state and the stable keto form (K) in the excited state, resulting in absorption from  $E{\rightarrow}E^*$  and emission from  $K^*{\rightarrow}K,$  and thus, dual, well-separated emission bands and exceptionally and abnormally large Stokes shift without self-absorption; this has been found in a range of applications, including photochromic materials,<sup>[10]</sup> fluorescence probes,<sup>[11]</sup> and electroluminescent materials.<sup>[12]</sup> Most reported ESIPT compounds are small, which could be favorable for a barrierless or negligible energy barrier  $E{\rightarrow}K$  transition in the excited state. It is necessary to develop new ESIPT molecules with larger chemical structures. One of the main concerns is whether ESIPT could be inhibited by increased size, so it is quite difficult to look for an enlarged ESIPT molecule with a finite and well-defined barrier, although this is important to gain detailed insights into the reaction potential energy surfaces.<sup>[7,8]</sup> Few such ESIPT molecules have been reported due to the great challenge.<sup>[13]</sup> To the best of our knowledge, no strong evidence has been observed to demonstrate two-photon absorption (TPA)-induced ESIPT so far.

An efficient strategy could be to develop enlarged TPA ESIPT molecules if the ESIPT moiety were attached to chromophore groups through covalent bonds. ESIPT in salicylidene methylamine makes it an attractive target for constructing larger molecules.<sup>[11d, 14]</sup> Molecular geometry optimization showed that new chromophores, 2-[(4'-N,N-diethylaminodiphenylethylene-4-ylimino)methyl]phenol (C1) and 2-[(4'-methoxyl-diphenylethylene-4-ylimino)methyl]phenol (C3), were likely to show ESIPT with a finite and well-defined barrier through a guasi-sixmembered ring (Scheme 1),<sup>[15]</sup> in which a hydroxyl group is in the ortho position. Strong experimental evidence of ESIPT under one- and two-photon excitation was obtained for both chromophores. Furthermore, the  $S_0$  and  $S_1$  electronic states of 2-[(4'-methoxyldiphenylethylene-4-ylimino)methyl]phenol (C2) and 4-[(4'-methoxyldiphenylethylene-4-ylimino)methyl]phenol

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**1	ESIPT—excited-state intramolecular proton transfer

[\*\*] ESIPT = excited-state intramolecular proton transfer.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/cphc.201100885.

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#### Scheme 1.

(C4), with a hydroxyl group at the *para* position, were surveyed experimentally and theoretically. The ground electronic state ( $S_0$ ) was modeled with the Hartree–Fock (HF) method and at the DFT level using the B3LYP method, whereas configuration interaction singlet excitation (CIS) was employed to optimize the geometries of the first singlet excited state ( $S_1$ ) of the phototautomers.

Owing to the presence of heteroatoms, ESIPT molecules could be used as chemosensors for specific metal ions, such as Na<sup>+</sup>, Zn<sup>2+</sup>, Mg<sup>2+</sup>, Fe<sup>3+</sup>, and Ni<sup>2+</sup>, which play significant roles in biology and the environment. We also fully evaluated the possibility of using these chromophores as chemosensors for specific metal ions.

## **Experimental Section**

#### **Reagents and Materials**

Chromphores C1, C2, C3, and C4 were synthesized in our laboratory (Scheme 1). Organic solvents were obtained from Chongqing Medical and Chemical Corporation. Other chemicals and reagents were purchased from Aldrich, unless otherwise specified. Organic solvents were purified and dried by using well-known standard laboratory techniques before use.<sup>[16]</sup> Others compounds were further purified by distillation or recrystallization before use. Zn-(OOCCH<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O, Mg(OOCCH<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O, KOOCCH<sub>3</sub>, NaOOCCH<sub>3</sub>·3·H<sub>2</sub>O, LiCl, Ca(OOCCH<sub>3</sub>)<sub>2</sub>·H<sub>2</sub>O, Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, Cu(OOCCH<sub>3</sub>)<sub>2</sub>·H<sub>2</sub>O, and NiCl<sub>2</sub>·6H<sub>2</sub>O were used as received from Aldrich.

#### Calculation Methods

The calculations were performed with the Gaussian 03 program package. All calculations were carried out with the 6-31G\*\* basis set. The geometry optimizations of enol and keto forms of **C2** and **C4** for the ground electronic state ( $S_0$ ) were carried out with the HF method at the DFT level using the B3LYP method,<sup>(17-19)</sup> whereas CIS was employed to optimize the geometries of the first singlet excited state ( $S_1$ ) of the phototautomers.

Although the CIS method produces reliable geometries and force fields, it predicts excitation energies that are too high (ca. 1 eV).<sup>[17]</sup> To correct the errors and introduce the dynamic electron correlation, DFT and time-dependent DFT (TD-DFT) were performed to predict energies at HF- and CIS-optimized geometries of S<sub>0</sub> and S<sub>1</sub> states, respectively, such as DFT//HF or TDDFT//CIS (denoted as single-point calculation//optimization method).<sup>[20]</sup>

#### **Characterization of Compounds**

NMR spectroscopy (<sup>1</sup>H and <sup>13</sup>C) was performed at room temperature on a Bruker 500 MHz spectrometer with tetramethylsilane (TMS) as an internal standard. Elemental analysis was performed on a CE440 elemental analysis meter from Exeter Analytical. Melting points was determined by using a Beijing Fukai melting point apparatus.

### **One- and Two- Photon Optical Measurements**

UV/Vis absorption spectra  $(1 \times 10^{-5} \text{ mol L}^{-1})$  were recorded with a Cintra spectrophotometer. Emission spectra  $(1 \times 10^{-6} - 1 \times 10^{-5} \text{ mol L}^{-1})$  were recorded with a Shimadzu RF-531PC spectro-fluorophotonmeter. Rhodamine 6G in ethanol ( $\Phi = 0.94$ ) and quinine sulfate in  $0.5 \text{ m H}_2\text{SO}_4$  ( $\Phi = 0.546$ )<sup>[21]</sup> were used as references to determine the fluorescence quantum yields of the compounds reported herein. To avoid self-quenching of the fluorescence emission, a low concentration of the compounds was used to determine the fluorescence quantum yields, according to Equation (1):<sup>[22]</sup>

$$\Phi_{\rm f} = \Phi_{\rm f}^0 \frac{n_0^2 A^0 \int I_{\rm f}(\lambda_{\rm f}) d\lambda_{\rm f}}{n^2 A \int I_{\rm f}^0(\lambda_{\rm f}) d\lambda_{\rm f}} \tag{1}$$

in which  $n_0$  and n are the refractive indices of the solvents,  $A^0$  and A are the optical densities at the excitation wavelength,  $\Phi_f$  and  $\Phi_f^0$  are the quantum yields, and the integrals denote the area of the fluorescence bands for the reference and sample, respectively.

Two-photon excited fluorescence spectra, pumped by a Ti:sapphire femtosecond laser (Spectra-Physics, Tsunami mode-locked, 80 MHz, <130 fs, average power  $\leq$ 700 mW) tuned by steps of 20 nm in the range 700–880 nm were recorded with an Ocean Optics USB2000 CCD camera with a detecting range of 180–880 nm. TPA cross-sections ( $\sigma$ ) were determined by an up-conversion fluorescence method using fluorescein ( $5 \times 10^{-4} \text{ mol L}^{-1}$ ) in a solution of NaOH (0.1 mol L<sup>-1</sup>) as a reference sample.<sup>[23]</sup> The samples were bubbled with N<sub>2</sub> for 15 min to eliminate O<sub>2</sub> before detection. TPA cross-sections of the compounds were determined by Equations (2) and (3):<sup>[24]</sup>

$$\sigma = \frac{\sigma^{\text{TPE}}}{\Phi_{\text{E}}} \tag{2}$$

$$\sigma^{\text{TPE}} = \sigma_{\text{cal}}^{\text{TPE}} \frac{c_{\text{cal}}}{c} \frac{n_{\text{cal}}}{n} \frac{S}{S_{\text{cal}}}$$
(3)

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in which  $\sigma$  is the TPA cross-section,  $\sigma^{\text{TPE}}$  is the two-photon excited cross-section, c is the concentration of reference ( $c_{cal}$ ) and sample molecules, n is the refractive index of the solvent, and S is the two-photon up-conversion fluorescence intensity, cal represents a reference.

## **Calculation of the Binding Constants**

The binding constant, *K*, was determined by the fluorescence spectra changes using the Benesi–Hildebrand equation,<sup>[25]</sup> which could describe 1:1 complex as shown in Equation (4):

$$\frac{F_{0}}{F_{0}-F} = \frac{F_{0}}{F_{0}-F_{\text{complex}}} + \frac{F_{0}}{F_{0}-F_{\text{complex}}} \frac{1}{K} \frac{1}{[M]}$$
(4)

in which K is the binding constant,  $F_0$  is the integrated fluorescence intensity of free ligand, F is the observed integrated fluorescence intensity,  $F_{\text{complex}}$  is the emission of the ligand-metal complex, and [M] is the concentration of added metal. The binding constants are given by the ratio intercept/slope from the plot of  $F_0/F_0-F$  versus 1/[M].

#### **Titration Procedures**

Metal ion stock solution (a few  $\mu$ L,  $5 \times 10^{-3}$  to 1 mol L<sup>-1</sup>) was added to the corresponding ligand solution (3 mL,  $1 \times 10^{-5}$  mol L<sup>-1</sup>) in hydrophilic solvents. The total volume added was less than 10  $\mu$ L. The blank experiments were performed by using the same procedure without metal ions to check the effects of additional water on the optical properties. Upon each addition, the solution was stirred rapidly for 30 min to reach equilibrium, and UV/Vis spectra and fluorescence spectra were subsequently recorded. No clear influence on either the UV/Vis spectra or the emission spectra was found for the additional water.

#### **Synthesis**

*p*-N,N-Diethylamino-*p*'-aminostilbene: *p*-N,N-Diethylamino-*p*'-nitrostilbene, which was prepared according to a well-known method,<sup>[26]</sup> was dissolved in anhydrous ethanol. Under an argon atmosphere, stannous chloride dehydrate was added slowly into the solution in ethanol. The mixture was heated at reflux for 24 h and then concentrated in vacuum. The solid was dissolved in an aqueous solution of NaOH (3 mol L<sup>-1</sup>) and the pH was adjusted to 8-9 with dilute HCl. A brown solid was obtained after filtration and was then was washed with distilled water three times. Further purification by column chromatography using cyclohexane and dichloromethane (v/v 1:1) as the eluent gave p-N,N-diethylamino-p'aminostilbene as a dark red solid (63%). M.p. 95.6-96.8°C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz, TMS):  $\delta = 1.17$  (t, J = 7.0 Hz, 6H; -(CH<sub>3</sub>)<sub>2</sub>), 3.37 (m, 4H; -CH<sub>2</sub>-), 6.66 (d, J=8.5 Hz, 4H; Ar-H), 6.82 (d, J=10.0 Hz, 2H; Ar-CH = CH-Ar), 7.29 (d, J = 8.5 Hz, 2H; Ar-H), 7.34 ppm (d, J = 8.5 Hz, 2 H; Ar-H); elemental analysis calcd (%) for C<sub>18</sub>H<sub>22</sub>N<sub>2</sub>: C 81.16, H 8.32, N 10.52; found: C 81.32, H 8.23, N 10.63.

**2-[(4'-N,N-Diethylaminostilbene-4-ylimino)methyl]phenol (C1):** *p*-*N*,*N*-Diethylamino-*p*'-aminostilbene (0.300 g, 1.127 mmol) was dissolved in absolute ethanol (30 mL). *o*-Hydroxybenzaldehyde (0.206 g, 0.173 mmol) was added to the mixture slowly under an argon atmosphere. The solution was heated at reflux for 3 h. After cooling, a yellow solid was precipitated and was filtered and washed with anhydrous alcohol three times. The product was obtained as a red solid after being recrystallization from ethanol twice (0.257 g 61.5%). M.p. 192–193 °C; <sup>1</sup>H NMR ([D<sub>6</sub>]DMSO,

500 MHz, TMS):  $\delta = 1.09$  (t, J = 7.0, Hz, 6H; -CH<sub>3</sub>), 3.35 (t, J = 7.0 Hz, 4H; -CH<sub>2</sub>-), 6.65 (d, J = 8.5 Hz, 2H; Ar-H), 6.95 (d, J = 8.0 Hz, 2H; -CH=CH-), 6.97 (d, J = 7.5 Hz, 1H; Ar-H), 7.13 (d, J = 16.5 Hz, 1H; Ar-H), 7.40 (m, 5H; Ar-H), 7.59 (d, J = 8.0 Hz, 2H; Ar-H), 7.63 (t, J = 3.75 Hz, 1H; Ar-H), 8.99 (s, 1H; -CH=N-), 13.22 ppm (s, 1H; Ar-OH); <sup>13</sup>C NMR([D<sub>6</sub>]DMSO, 125 MHz):  $\delta = 13.0$ , 44.1, 111.9, 117.0, 119.6, 119.9, 122.3, 122.6, 127.2, 128.4, 129.6, 133.0, 133.6, 137.6, 146.3, 147.7, 160.8, 162.6 ppm; elemental analysis calcd (%) for C<sub>25</sub>H<sub>26</sub>N<sub>2</sub>O: C 81.05, H 7.07, N 7.56; found: C 80.98, H 7.13, N 7.48.

**4-[(4'-N,N-Diethylaminostilbene-4-ylimino)methyl]phenol (C2):** A similar experimental procedure to that used for **C1** gave **C2** as a brown solid (62.8%). M.p. 218–219°C; <sup>1</sup>H NMR([D<sub>6</sub>]DMSO, 500 MHz, TMS):  $\delta$  = 1.10 (t, *J* = 7.0 Hz, 6H; -CH<sub>3</sub>), 3.34 (t, *J* = 6.75 Hz, 4H; -CH<sub>2</sub>-), 3.37 (s, 1H; Ar-OH), 6.65 (d, *J* = 9.0 Hz, 2H; Ar-H), 6.87 (d, *J* = 8.5 Hz, 2H; Ar-H), 6.94 (d, *J* = 16.5 Hz, 1H; -CH=CH-), 7.08 (d, *J* = 16.5 Hz, 1H; -CH=CH-), 7.21 (d, *J*=8.5 Hz, 2H; Ar-H), 7.39 (d, *J* = 9.0 Hz, 2H; Ar-H), 7.53 (d, *J*=8.5 Hz, 2H; Ar-H), 7.77 (d, *J*=8.5 Hz, 2H; Ar-H), 8.50 ppm (s, 1H; -CH=N-); <sup>13</sup>C NMR([D<sub>6</sub>]DMSO, 125 MHz):  $\delta$  = 12.9, 44.1, 111.9, 116.2, 121.9, 123.0, 124.4, 127.0, 127.9, 128.3, 28.6, 131.1, 135.9, 147.5, 150.4, 159.5, 161.2 ppm; elemental analysis calcd (%) for C<sub>25</sub>H<sub>26</sub>N<sub>2</sub>O: C 81.05, H 7.07, N 7.56; found: C 81.11, H 7.13, N 7.47.

*p*-Methoxy-*p*'-aminostilbene: The title compound was prepared as a brown yellow solid by a similar procedure to that used for *p*-*N*,*N*-diethylamino-*p*'-aminostilbene (59%). M.p. 158.2–159.6 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz, TMS):  $\delta$  = 3.80 (s, 3 H; -OCH<sub>3</sub>), 6.96 (d, *J* = 9.0 Hz, 2 H; Ar-H),7.26 (d, *J* = 16.5 Hz, 1 H; Ar-CH = CH-Ar), 7.48 (d, *J* = 16.5 Hz, 1 H; Ar-CH = CH-Ar), 7.62 (d, *J* = 8.5 Hz, 2 H; Ar-H), 7.81 (d, *J* = 9.0 Hz, 2 H; Ar-H), 8.21 ppm (d, *J* = 8.5 Hz, 2 H; Ar-H); elemental analysis calcd (%) for C<sub>15</sub>H<sub>15</sub>NO: C 79.97, H 6.71, N 7.10; found: C 79.76, H 6.54, N 7.32.

Synthesis of C3 and C4: Compounds C3 and C4 were obtained by using a similar procedure to that for C1 and C2. C3: Pale-yellow solid; yield: 55.1%; m.p. 208-210°C; <sup>1</sup>H NMR ([D<sub>6</sub>]DMSO, 500 MHz, TMS):  $\delta = 3.79$  (s, 3H; Ar-OCH<sub>3</sub>), 7.03 (m, 4H; Ar-H), 7.15 (d, J =15.0 Hz, 2 H; -CH = CH-), 7.24 (s, 1 H; Ar-H), 7.50 (m, 3 H; Ar-H), 7.78 (m, 4H; Ar-H), 9.02 (s, 1H; -CH = N-), 13.18 ppm (s, 1H; Ar-OH); elemental analysis calcd (%) for C<sub>22</sub>H<sub>19</sub>NO<sub>2</sub>: C 80.22, H 5.81, N 4.25; found: C 80.31, H 5.74, N 4.31. C4: Yellow solid; yield: 54.3%; m.p. 252–254 °C; <sup>1</sup>H NMR ([D<sub>6</sub>]DMSO, 500 MHz, TMS):  $\delta = 3.78$  (s, 3H; -OCH<sub>3</sub>), 6.89 (d, J=8.5 Hz, 2H; Ar-H), 6.95 (d, J=8.5 Hz, 2H; Ar-H), 7.11 (d, J=16.5 Hz, 1H; Ar-CH=CH-Ar), 7.18 (d, J=16.5 Hz, 1H; Ar-CH=CH-Ar), 7.23 (d, J=8 Hz, 2H; Ar-H), 7.54 (d, J=8.5 Hz, 2H; Ar-H), 7.58 (d, J=8.5 Hz, 2H; Ar-H), 7.78 (d, J=8.5 Hz, 2H; Ar-H), 8.51 (s, 1H; -CH = N-), 10.13 ppm (s, 1H; -OH); <sup>13</sup>C NMR ([D<sub>6</sub>]DMSO, 125 MHz):  $\delta = 55.6$ , 114.7, 116.6, 121.9, 126.2, 127.5, 127.8, 128.1, 128.2, 130.3, 131.1, 135.3, 151.1, 159.4, 159.8, 161.1 ppm; elemental analysis calcd (%) for  $C_{22}H_{19}NO_2 {:}\ C$  80.22, H 5.81, N 4.25; found: C 80.27, H 5.73, N 4.18.

## 2. Results and Discussion

## 2.1. ESIPT under One-Photon Excitation

## 2.1.1. Absorption Spectroscopy

Typical actual and normalized absorption spectra of these derivatives in benzene and THF are presented in Figure 1. The absorption maxima and the molar extinction coefficients of the compounds in various solvents are shown in Table 1. The absorption maxima of **C1** are clearly redshifted with respect to those of **C2** (ca. 15 nm, Table 1). Similar phenomena were ob-



Figure 1. UV/Vis absorption spectra of derivatives C1–C4 in benzene (a) and THF (b);  $c(C1) = c(C2) = c(C3) = c(C4) = 1 \times 10^{-5} \text{ mol } L^{-1}$ .

served for C3 and C4 (ca. 13 nm, Table 1). This reflects the internal hydrogen-bonding effect on the absorption spectra of C1 and C3. As shown in Scheme 1, compounds C1 and C3 are characterized by internal hydrogen bonds, whereas there are no internal hydrogen bonds in C2 and C4. The maximal absorption wavelengths of C1 and C2 are redshifted compared with those of C3 and C4, respectively (ca. 30 nm, Table 1), whereas the absorption maxima of all compounds are less sensitive to solvent polarity (Figure 1 and Table 1). These results indicate that the absorption could be ascribed to a  $\pi \rightarrow \pi^*$  transition of the entire molecule with weak intramolecular charge transfer in the ground state.<sup>[27]</sup>

## 2.2. One-Photon Fluorescence Spectroscopy

Compounds C1 and C3 could undergo ESIPT due to an intramolecular hydrogen-bonding effect, whereas C2 and C4 could not due to a lack of internal hydrogen bonds. Figure 2 shows that C1 and C3 exhibit well-separated dual emission bands in benzene and THF, whereas C2 and C4 display only single emission bands. The first emission bands of C1 and C3 are almost identical to the emission bands of C2 and C4, respectively. They are effectively the same as the  $S_0 \rightarrow S_1$  absorption spectral feature, which demonstrates that both emission bands originate from similar ground-state precursors. On the other hand, the second emission bands of C1 and C3 redshift greatly with respect to the first ones. The emission maxima and the fluorescence quantum yields of the compounds in various solvents are also presented in Table 1. The emission maxima of C2 and C4 show small Stokes shifts (ca. 30 nm, Table 1) and the first maximal emission peaks of C1 and C3 also exhibit small Stokes shifts (ca. 30 nm, Table 1), whereas in contrast the second maximal fluorescence peaks of C1 and C3 show quite large Stokes shifts (ca. 140 nm, Table 1).

The results indicate that the second emission bands of **C1** and **C3** could be assigned to ESIPT. The ESIPT emission intensity of **C1** and **C3** is much lower than the normal emission intensity in benzene. The intensity ratios of the emission bands,  $I_{E^*}/I_{N^*}$  (wherein  $I_{E^*}$  is the representative of the intensity of ESIPT emission intensity;  $I_{N^*}$  refers to the normal emission intensity), are approximate 0.25 for **C1** and 0.1 for **C3** in benzene. The fact that the normal emission prevails indicates the existence of an appreciable energy barrier associated with ESIPT; therefore, the S<sub>1</sub> $\rightarrow$ S<sub>0</sub> decay of enol emission becomes a competitive pathway,<sup>[7]</sup> which is in accordance with our theoretical calculation.<sup>[15]</sup> On the other hand,  $I_{E^*}/I_{N^*}$  ratios for **C1** and **C3** are smaller in THF than those in benzene (**C1**: 0.17, **C3**: 0.07 in THF). The ESIPT emission of **C1** and **C3** diminishes further or even

Table 1. The maximum absorption wavelengths, molar extinction coefficients, emission maxima, and fluorescence quantum yields of C1–C4 in various solvents.  $^{\rm [a]}$ 

Solvents		C1	C2	C3	C4	
	$\lambda_{a'max}$ [nm]	405.6	390.4	372.8	360.0	
hanzana	ε	0.448	0.442	0.397	0.433	
benzene	$\lambda_{\text{frmax}}$ [nm]	426, 542	428	423, 527	422	
	$\Phi$	0.0224	0.0291	0.0109	0.0162	
	$\lambda_{a,max}$ [nm]	403.2	388	370.4	358.4	
1.4 diavana	ε	0.435	0.458	0.439	0.439	
1,4-010xane	$\lambda_{fmax}$ [nm]	405,425, 543	406,429	423, 523	423	
	$\Phi$	0.0249	0.0278	0.00988	0.0128	
	$\lambda_{a'max}$ [nm]	403.2	386.4	371.2	359.2	
тыс	ε	0.450	0.461	0.351	0.293	
	$\lambda_{\text{frmax}}$ [nm]	427, 551	430	426, 524	421	
	$\Phi$	0.0304	0.0672	0.0143	0.0329	
	$\lambda_{a'max}$ [nm]	402.4	388	367.2	356	
acatona	ε	0.443	0.478	0.473	0.441	
acetone	$\lambda_{f'max}$ [nm]	423, 581	431	434	434	
	$\Phi$	0.0122	0.00895	0.00791	0.0107	
	$\lambda_{a'max}$ [nm]	400.8	387.2	365.6	354.4	
acotonitrilo	ε	0.446	0.437	0.463	0.448	
acetonitine	$\lambda_{f'max}$ [nm]	434	432	438	438	
	$\Phi$	0.00393	0.00600	0.00675	0.00886	
	$\lambda_{a'max}$ [nm]	408.3	394.7	373.3	363.1	
DME	ε	0.380	0.424	0.257	0343	
Divil	$\lambda_{f'max}$ [nm]	434	438	438	440	
	$\Phi$	0.0634	0.0172	0.0183	0.0149	
	$\lambda_{a'max}$ [nm]	399.8	379.3	367.4	342.5	
methanol	ε	0.446	0.277	0.335	0.374	
methanoi	$\lambda_{fmax}$ [nm]	434	430	435, 523	429	
	$\Phi$	0.0172	0.0872	0.00301	0.00709	
[a] $\varepsilon$ : 1×10 <sup>5</sup> Lmol <sup>-1</sup> cm <sup>-1</sup> , $\lambda_{armax}$ : the maximal absorption wavelength, $\lambda_{frmax}$ : the emission maxima. The measurement errors of fluorescence quantum yields do not exceed ±10%.						

completely disappears in strong, aprotic polar solvents, such as acetone and acetonitrile (see the Supporting Information). This could be caused by twisted intramolecular charge transfer, which could be the major competitive deactivation approach in the excited singlet state of the enol forms of **C1** and **C3** in strong, polar solvents; therefore, the ESIPT emission could be restricted.<sup>[28]</sup> Although photoinduced *cis-trans* isomerization of stilbene and its derivatives is often a rapid process (several hundred fs to ps),<sup>[29]</sup> it is still much slower than the ESIPT process (less than one hundred fs).<sup>[1c]]</sup> Hence, *cis-trans* isomerization of **C1** and **C3** may not be a competitive photochemical decay channel to ESIPT. The above results demonstrate that **C1** and **C3** could undergo ESIPT under one-photon excitation via a reasonable six-membered ring in the excited states (Scheme 1), while it is hard to process ESIPTs for **C2** and **C4**.

It is interesting that **C1** does not exhibit ESIPT emission in protic methanol solvent, whereas **C3** does present an ESIPT emission in methanol (see the Supporting Information). Calculations show that the hydrogen atom of the hydroxyl group in **C1** has a more positive charge than that in **C3**, which could be caused by larger intramolecular charge transfer in **C1** due to a stronger electron-donating effect of the diethylamino group, inducing a greater hydrogen-bond effect with protic methanol. Consequently, internal proton transfer in the excited state of **C1** could be inhibited in methanol. This means that excitedstate deprotonation instead of ESIPT occurs in protic solvents for **C1**.<sup>[30]</sup> On the other hand, the more positively charged hydrogen atom of the hydroxyl group in **C1** could be favorable for internal proton transfer in the excited state in aprotic solvents, and thus, the  $I_{E^*}/I_{N^*}$  ratio of **C1** is larger than that of **C3**.

It is accepted generally that ESIPT could diminish the emission; hence, compounds C2 and C4 have larger fluorescence quantum yields than C1 and C3, respectively (Table 1). On the other hand, the emission of all compounds is low in various solvents, even if C2 and C4 do not undergo ESIPT. It was demonstrated that efficient conical intersections in the twisted geometries could give rise to dramatic nonradiative deactivation of the excited singlet state to the ground state of different isomers for some Schiff base compounds.<sup>[31]</sup> A large dihedral angle exists between the imino group and C=C band of these analogues (C1: 30.378°, C2:35.507°, C3: 31.780°, C4: 36.791°). This indicates that conical intersections as an efficient internal conversion decay pathway could play a dominant role on the deactivation of singlet states of these compounds. Consequently, the emission of C1-C4 is reduced remarkably. In particular, such as in strong, polar solvents, non-luminescent decay of twisted intramolecular charge transfer could further quench the emission greatly.[32]

#### 2.3 ESIPT under Two-Photon Excitation

We utilized a Ti:sapphire femtosecond laser to determine the TPA-induced emission of the compounds. Compounds C1 and C2 exhibit remarkable TPA emissions in benzene, and C3 and C4 display clear TPA emissions in THF under 740 nm laser excitation. As seen in Figure 3a, compound C1 exhibits dual TPA emission bands in benzene, whereas C2 shows a single TPA emission band. Furthermore, the maximal emission wavelength of the first TPA emission band of C1 is almost identical to that of C2. The maximal emission wavelength of the second TPA emission band of C1 is much larger than that of the first emission band. Furthermore, the maximal emission wavelength of the second TPA emission band of C1 is close to that of the one-photon ESIPT emission of C1. As a result, the first TPA emission band of C1 could be normal TPA emission and the second TPA emission band of C1 could be assigned to the ESIPT TPA emission. The C3/C4 pair exhibits similar contrasting TPA optical properties to those of C1/C2 (as shown in Figure 3 b). The experimental results suggest that C1 and C3 could undergo ESIPT under two-photon excitation, whereas C2 and C4 do not process ESIPTs under the same conditions.

The maximal TPA ESIPT emission wavelengths of **C1** and **C3** are almost identical to the maximal one-photon ESIPT emission wavelength (one-photon ESIPT **C1**: 542 nm in benzene, **C3**: 527 nm in THF; two-photon ESIPT: **C1**: 544 nm in benzene, **C3**: ca. 531 nm in THF), which indicates that ESIPT could occur through the same or similar excited states for one- and two-photon process. However, the  $I_{\text{E*}}/I_{\text{N*}}$  ratio in the two-photon process is much larger than that in the one-photon emission process (**C1**: ca. 1.40 in benzene; **C3**: ca. 1.0 in THF). At present, we do not fully understand why ESIPT becomes predomi-



Figure 2. Actual and normalized fluorescence spectra of derivatives C1–C4 in benzene (a) and THF (b) under the same excitation condition;  $c(C1) = c(C2) = c(C3) = c(C4) = 1 \times 10^{-5} \text{ mol } L^{-1}$ .

nant in the two-photon process. It is generally accepted that the two-photon excitation process of a compound is different from one-photo excitation.<sup>[33]</sup> During two-photon excitation, the excited molecule could reach the excited state  $S_2$  or  $S_n$  first and then decay to  $S_1$  by a radiationless transition and vibration relaxation, alternatively the excited molecule could reach  $S_1$ first through excitation by one photon. Therefore, because **C1** and **C3** are excited by two photons, we suppose that phototautomerization could take place in higher excited states of enols of **C1** and **C3**,<sup>[34]</sup> and thus, the energy barrier could be reduced and easily overcome. Furthermore, a femtosecond laser and the E–K phototautomerization process have wonderful timescale matches. As a result, two-photon excitation could be favorable for ESIPT.

As in low polarity solvents, the maximal (normal and ESIPT) emission maxima of **C1** redshift in comparison with those of **C3** under one- and two-photon excitation, as observed in the absorption spectra, which indicates that phototautomers E and K of **C1** could have larger dipole moment changes between the excited and ground states than those of **C3**. The phototautomers E and K of **C1** exhibit larger dipole moment differences between the excited and ground states than those of **C3**,<sup>[15]</sup> while HOMO–LUMO gaps of E and K of **C1** are lower than those of **C3**.<sup>[15]</sup> This could be the fundamental reason why **C1** 

displays larger TPA cross-sections than **C3** under various near-IR laser frequencies (Table 2).

### 2.4. Calculations

Calculations demonstrate that C1 and C3 have a high possibility of undergoing ESIPT;<sup>[15]</sup> this was verified by the above experimental observations. We performed further various calculations, including bond lengths, energies, dipole moments, and frontier orbitals, to give an in-depth analysis of why C2 and C4 could not undergo ESIPT. We expected that, unlike C1 and C3, the transition states from E to K were not possible for the ground and excited states of C2 and C4, which indicated that proton transfer occurred less in the ground and excited states of C2 and C4.

#### 2.5. Bond Length

The internal hydrogen-bonding effect is dependent on bond length. The most important bond lengths of the E and K forms of the compounds associated with ESIPT in  $S_0$  and  $S_1$  are shown in Table 3. The data show that the H–N distances in the E forms of **C2** and **C4** are much longer than **C1** and **C3** in  $S_0$  and  $S_1$ , even up to about 6.7 Å. The H–O distances in the K



Figure 3. Actual and normalized TPA emission spectra of C1–C4 in benzene (a) and THF (b) under 740 nm laser excitation;  $c(C1) = c(C2) = c(C3) = c(C4) = 5 \times 10^{-4} \text{ mol L}^{-1}$ .

Laser frequencies		ر <sup>[a]</sup> [	CVV]*			
[nm]	C1	C2	<b>C3</b>	C4		
700	163	54	-	-		
720	74	29	15	-		
740	64	22	6	5		
760	67	22	-	10		
780	72	19	12	5		
800	107	22	13	-		
820	106	25	6	2		
840	104	22	-	-		
860	60	11	-	-		
880	59	13	-	-		
[a] Two-photon cross-section $(1GM = 10^{-50} \text{ cm s}^{-1} \text{ photon}^{-1})$ ; the errors do not exceed 15%; C1 and C2 were recorded in benzene, whereas C3 and C4 were recorded in THF.						

forms of **C2** and **C4** are also much longer in  $S_0$  and  $S_1$  (ca. 6.2 Å) than those of **C1** and **C3**. It is well known that hydrogen bonds are short distance effects in essence; hence, intramolecular hydrogen-bonding forces between H and N in the E form and between H and O in the K form should be quite weak for

**C2** and **C4** in S<sub>0</sub> and S<sub>1</sub>. Furthermore, owing to a weak stretching effect of N for H, the H–O distances in the E forms of **C2** and **C4** are shorter than those of **C1** and **C3** in S<sub>0</sub> and S<sub>1</sub>. The data in Table 3 also show that the H–N distances in the K form of **C2** and **C4** are shorter than those of **C1** and **C3** in S<sub>0</sub> and S<sub>1</sub>. The due to the lack of a strong pulling effect of O for H. This means that it is hard for H to leave O in the E forms and to leave N in the K forms of **C2** and **C4**. The bond length suggests that it is hard for the ground and excited states of **C2** and **C4** to undergo internal proton transfer.

#### 2.6. Energies

As shown in Table 4, compounds C2 and C4 have approximately twice the energy differences between E and K in ground state ( $\Delta E$ ) than those of C1 and C3. Furthermore, the energy differences in the excited state are much larger than those of C1 and C3 (> 20 times). This indicates that the occurrence of internal proton transfer in the ground and excited states of C2 and C4 is much less likely than that of C1 and C3, particularly in the excited state. This could be the fundamental reason that C2 and C4 do not show ESIPT.

Table 3. The most important bond lengths associated with ESIPT obtained at DFT and HF (in bracket) level and excited state at CIS level.

Structural		Groun	Ground State				
parameters		E	К	E*	K*		
	R <sub>O-H</sub>	0.9988 (0.9548)	1.6306 (1.8678)	0.9566	1.7925		
C1 <sup>[15]</sup>	$R_{H-N}$	1.7171 (1.8876)	1.0542 (1.0056)	1.8543	1.0129		
	R <sub>O-N</sub>	2.6202 (2.7116)	2.5565 (2.6569)	2.6912	2.6365		
	R <sub>O-H</sub>	0.9665 (0.9429)	6.2667 (6.2455)	0.9430	6.1935		
C2	$R_{H-N}$	6.7039 (6.6815)	1.0108 (0.9928)	6.6657	0.9948		
	R <sub>O-N</sub>	6.4396 (6.3949)	6.4433 (6.3834)	6.3861	6.3893		
	R <sub>O-H</sub>	0.9982 (0.9546)	1.6287 (1.8666)	0.9570	1.8078		
C3 <sup>[15]</sup>	$R_{H-N}$	1.7203 (1.8887)	1.0544 (1.0055)	1.8500	1.0118		
	R <sub>O-N</sub>	2.6218 (2.7121)	2.5550 (2.6561)	2.6872	2.6461		
	R <sub>O-H</sub>	0.9665 (0.9429)	6.2651 (6.2433)	0.9431	6.1816		
C4	$R_{\rm H-N}$	6.7053 (6.6817)	1.0107 (0.9928)	6.6633	0.9952		
	R <sub>O-N</sub>	6.4398 (6.3947)	6.4420 (6.3823)	6.3826	6.3869		

**Table 4.** Calculated relative energy difference between E and K for the ground and excited states and all the energies of E as a reference point at the corresponding methods ( $E_{\varepsilon}$ =0).

States	Method	$\Delta E$ [kcal mol <sup>-</sup>	1]		
		C1 <sup>[15]</sup>	C2	<b>C3</b> <sup>[15]</sup>	C4
around	DFT//DFT	4.703	8.364	4.762	8.508
ground	DFT//HF	5.431	9.093	5.436	9.220
excited	TD-DFT//CIS	0.246	5.883	0.143	6.758

## 2.7. Dipole Moment and Frontier Orbitals

As seen from Table 5, the dipole moment differences between the phototautomers E and K of **C2** and **C4** are much greater C4 suggests that charge transfer does occur from the electron donor part to the imino moiety during the HOMO $\rightarrow$ LUMO transition and C2 exhibits a larger charge transfer than C4.



Figure 4. Calculated qualitative shapes of the frontier molecular orbits of C2 and C4 in the ground and excited states.

than those of C1 and C3 in the ground and excited states ( $\Delta \mu_{F-K}$ in the ground state: C1: 1.875, C2: 9.844, C3: 1.877, C4: 8.265; in the excited state for C1: 1.174, C2: 9.252, C3: 1.635, C4: 8.702). This means that if internal proton transfer occurs in the ground and excited states, compounds C2 and C4 would have to undergo much larger charge transfer between E and K than that in C1 and C3, which in turn indicates that the possibility of undergoing internal proton transfer would be negligible for C2 and C4.

The electron distribution of the frontier orbitals reflects the electron transition characteristics. Figure 4 shows that the HOMO and LUMO of **C2** and **C4** are characterized with excellent  $\pi$ -type symmetry. Furthermore, the electron density distribution of the frontier orbitals of **C2** and

Table 5.	The dipole	moment	of	each	phototau	tomer	in	the	ground	and
excited s	states.									

States	Phototautomers	Compo			
		C1 <sup>[15]</sup>	C2	C3 <sup>[15]</sup>	C4
	μ <sub>E</sub> [D]	5.446	1.784	3.882	1.192
ground	$\mu_{K}$ [D]	7.321	11.628	5.559	9.457
	$\Delta \mu_{\text{E-K}}$ [D]	1.875	9.844	1.677	8.265
	$\mu_{E^*}$ [D]	6.370	3.466	4.072	0.983
excited	μ <sub>K*</sub> [D]	7.544	12.718	5.707	9.685
	$\Delta\!\mu_{E^*\!-\!K^*}$ [D]	1.174	9.252	1.635	8.702

Hence, the HOMO $\rightarrow$ LUMO transition could be ascribed to  $\pi \rightarrow \pi^*$  excitation with internal charge-transfer character.

The calculated absorption and normal fluorescence maxima of C2 and C4, which equal the corresponding frontier orbital transition energy difference (namely, singlet-singlet transition energies,  $\Delta E$ ), are shown in Table 6. Herein, the values of the absorption refer to the vertical transition from  $S_0$  states to the Franck–Condon S<sub>1</sub> states, while the values from S<sub>1</sub> states to the corresponding Franck–Condon So states are assigned to emissions that are redshifted with respect to the absorption. The  $H \rightarrow L$  transitions of C2 and C4 show the largest f values for absorption (f: C2: 0.9506, C4: 1.0919) and fluorescence spectroscopy (f : C2: 1.8163, C4: 1.7476) and the biggest weighting (C2: 91%, C4: 87% for the absorption spectroscopy, C2: 78%, C4: 76% the fluorescence spectroscopy). This further demonstrates that the absorption spectra of C2 and C4 are characterized by  $\pi \rightarrow \pi^*$  excitations. The calculated absorption maxima of C2 and C4 are in good agreement with experimental measurements; this suggests the weak dependence of the absorption maxima on the polarity of the media. Furthermore, the calculated maximal absorption maxima of C2 and C4 are blueshifted approximately 10 nm with respect to those of C1 and C3, as also determined experimentally. Tables 5 and 6 show that C2 exhibits larger dipole moment changes between the excited state and the ground state than C4 ( $E \rightarrow E^*$ ), and smaller HOMO-LUMO gaps, which could cause larger absorption and emission maxima and higher TPA cross-sections for C2 (Table 2).

## 2.8. Sensing Properties

Owing to the presence of adjacent heteroatoms, some ESIPT compounds could be used as efficient chemosensors for specific metal ions through the inhibition of ESIPT. We performed sensing response experiments with these chromophores for metal ions in DMF. As expected, compounds **C2** and **C4** do not exhibit clear responses due to their structural characteristics,



Figure 5. UV/Vis (a) and fluorescence spectra (b) of C3  $(1 \times 10^{-5} \text{ mol } L^{-1})$  in DMF at room temperature as a function of the addition of various aqueous stock solutions of Zn(OAc)<sub>2</sub>  $(5 \times 10^{-3} \text{ to } 1 \text{ mol } L^{-1})$ .

Table 6. Calculated energy difference of frontier orbital transitions (in eV), absorption and fluorescence peak wavelengths (in nm), oscillator strengths (f), and the weighting of the most important microstates (H: HOMO, L: LUMO) in the anterior excited states for C2 and C4 at the TDDFT//HF and TDDFT//CIS levels.

Spectra	$\Delta E$ [eV]	λ [nm]	f	Transition		
		1	3.10	399.7	0.9506	H-0→L+0:91%
	C2	2	3.90	317.8	0.8651	H-0 $\rightarrow$ L+1: 47%; H-1 $\rightarrow$ L+0: 45%
absorption		3	3.97	312.2	0.0649	H-0 $\rightarrow$ L+1: 37%; H-1 $\rightarrow$ L+0: 33%
absorption		1	3.40	365.2	1.0919	$H-0 \rightarrow L+0:87\%$
	C4	2	4.15	298.9	0.6223	$H-0 \rightarrow L+1:62\%$ ; $H-1 \rightarrow L+0:31\%$
		3	4.23	293.2	0.0423	$H-2 \rightarrow L+0:36\%; H-1 \rightarrow L+0:33\%$
		1	2.55	485.4	1.8163	$H-0 \rightarrow L+0:78\%$
	C2	2	3.39	366.2	0.4246	H-1 $\rightarrow$ L:+0: 55%; H-0 $\rightarrow$ L+1: 40%
normal fluoroscon co		3	3.71	334.5	0.0443	$H-3 \rightarrow L+0: 38\%; H-2 \rightarrow L+0: 21\%$
normal nuorescence		1	2.71	458.2	1.7476	$H-0 \rightarrow L+0:76\%$
	C4	2	3.50	353.9	0.2244	H-1 $\rightarrow$ L:+0: 54%; H-0 $\rightarrow$ L+1: 44%
		3	3.70	335.3	0.0917	H-2 $\rightarrow$ L+0: 60%; H-3 $\rightarrow$ L+0: 12%

whereas, as shown in Figure 5, compound **C3** shows a remarkable sensing response to  $Zn^{2+}$  ions in DMF that is much better than that of **C1**. Continuous titration with an aqueous solution of  $Zn^{2+}$  ions in DMF causes a gradual redshift and a single isosbestic point in the absorption spectra of **C3**. Figure 5 also shows a gradual increase, which finally reaches an approximate constant, of the emission intensity with a slight redshift as the aqueous solution of  $Zn^{2+}$  ions is

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added. These phenomena indicate an equilibrium of zinc complex. Compared with C3, the absorption and emission spectra of C1 are much less sensitive to  $Zn^{2+}$  concentration (see the Supporting Information). This could be ascribed to stronger internal hydrogen bonding in C1, so that the hydrogen atom of the OH group in C1 does not leave as easily to allow the formation of a complex with  $Zn^{2+}$ .

We investigated further the sensing nature of C3 for other metal ions. Figure 6 shows the fluorescence response and the photoluminescence of C3 to metal ions at equilibrium. Com-



**Figure 6.** a) Sensing nature of **C3** to various metal ions. The concentration of  $Zn^{2+}$  ions added is  $5 \times 10^{-5} \text{ mol } L^{-1}$ ; the concentrations of other metal ions are  $5 \times 10^{-4}$  mol  $L^{-1}$ . All surveys were performed at equilibrium. b) Photoluminescence of **C3** in DMF containing metal ions under excitation at 365 nm; from left to right: K<sup>+</sup>, Ca<sup>2+</sup>, Na<sup>+</sup>, Mg<sup>2+</sup>, Li<sup>+</sup>, Zn<sup>2+</sup>, Cu<sup>2+</sup>, Ni<sup>2+</sup>, Fe<sup>3+</sup>, and blank solution.

pound **C3** could recognize  $Zn^{2+}$  ions to bring about a large fluorescence enhancement and was sensitive to  $Fe^{3+}$  ions with a remarkable decrease in emission intensity. Only slight or negligible changes were observed for the addition of other aqueous solutions of metal ions, including significant physiological metal ions (such as  $K^+$ ,  $Na^+$ ,  $Mg^{2+}$ ,  $Ca^{2+}$ ) and heavy metal ions (such as  $Fe^{3+}$ ,  $Cu^{2+}$  and  $Ni^{2+}$  ions) in DMF (see the Supporting Information), except for  $Zn^{2+}$  and  $Fe^{3+}$  ions. The emission intensity of **C3** in DMF reduced gradually with continuous titration of an aqueous solution of  $Fe^{3+}$  ions, while the optical density in the absorption spectra increased gradually (see the Supporting Information).

Consequently, compound C3 shows unique sensing responses to  $Zn^{2+}$  and  $Fe^{3+}$  ions; this demonstrates that C3 could be an effective chemosensor for  $Zn^{2+}$  and  $Fe^{3+}$  ions. Fitting of the

fluorescence intensity curve of **C3** against the reciprocal of the  $Zn^{2+}$  and Fe<sup>3+</sup> concentration (Figure 7), the Benesi–Hildebrand plot, gives linear fit characteristics for 1:1 complexation behavior from which the association constants are estimated to be  $0.5 \times 10^4$  (Zn<sup>2+</sup>) and  $0.45 \times 10^4$  Lmol<sup>-1</sup> (Fe<sup>3+</sup>).



Figure 7. Benesi–Hildebrand plot of the fluorescence intensity of C3 against the reciprocal of the  $Zn^{2+}$  (a) and  $Fe^{3+}$  (b) concentrations.

We also performed a survey of the **C3** sensing response to various metal ions in other hydrophilic solvents. Compound **C3** displays a much weaker sensing response to metal ions in THF, acetonitrile, and DMSO (see the Supporting Information), while in methanol it shows some sensitivity to  $Zn^{2+}$  ions (Figure 8). Furthermore, the ESIPT emission band of **C3** disappeared with the addition of  $Zn^{2+}$  ions in methanol, which demonstrated that the adjacent O and N heteroatoms participated in the formation of the complex (Figure 8).

## 3. Conclusions

We fully investigated the linear absorption, emission, and twophoto properties of new chromophores containing hydroxyl and imino groups, with the hydroxyl group being in the *ortho* or *para* positions of the aromatic ring. One- and two-photon optical properties of these compounds had a strong relationship with their molecular structures. There was strong evidence that **C1** and **C3** were able to undergo ESIPT under one- and two-photon excitation, whereas **C2** and **C4** could not. Furthermore, ESIPT becomes competitive under two-photon excita-



**Figure 8.** Sensing nature of **C3** to various metal ions. The concentration of  $Zn^{2+}$  ions added is  $5 \times 10^{-5}$  mol L<sup>-1</sup>; the concentrations of other metal ions are  $5 \times 10^{-4}$  mol L<sup>-1</sup>. The structure of the complex is also shown; L is solvent or water.

tion. Calculations demonstrated that E forms of **C1** and **C2** had larger dipole moment differences between the ground and excited states than those of **C3** and **C4** due to greater internal charge-transfer character from the *N*,*N*-diethylamino group. As a result, TPA cross-sections of **C1** and **C2** were larger than those of **C3** and **C4**. The bond lengths, energies, and dipole moments of phototautomers of **C2** and **C4** in S<sub>0</sub> and S<sub>1</sub> were not favorable for ESIPT. Compound **C3** in DMF displayed excellent sensing properties for Zn<sup>2+</sup> and Fe<sup>3+</sup> ions with a large enhancement or significant decrease in fluorescence emission, respectively. Disappearance of the ESIPT emission band of **C3** in methanol demonstrated that the hydroxyl and imino groups played key roles in the formation of complexes with the metal ions. The results presented herein will benefit the development of new larger ESIPT molecules.

## Acknowledgements

We thank encouragement from the National Science Foundations of China and the Key Laboratory of Functional Crystals and Laser Technology, Technical Institute of Physics and Chemistry, Chinese Academy of Sciences. We appreciate financial support from the Fundamental Research Funds for the Central Universities (no. CDJZR10220006). **Keywords:** charge transfer • density functional theory • photochemistry • sensors • synthesis design

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Received: November 5, 2011 Published online on February 16, 2012