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New Fluorescent Conjugates Displaying Solvatochromic Properties

Huijing Liu,[a] Rongrong Huang,[b] and Yu Fang*,[b]

[a] *Key Laboratory of Applied Surface and Colloid Chemistry (Ministry of Education), School of Materials Science and Engineering, Shaanxi Normal University, Xi'an, Shaanxi 710062, China*
[b] *School of Chemistry and Chemical Engineering, Shaanxi Normal University, Xi'an, Shaanxi 710062, China*

Four new fluorescent dyes based on bis(phenyl-ethynyl-)-2-naphthyl (BPEN) were designed and synthesized. To improve the solvatochromic property and enhance the brightness of the fluorescent BPEN, an electron-donating unit of azetidine and/or an electron deficient group of $-NO_2$ was introduced. The corresponding fluorophores are denoted as T1, T2, T3 and T4, respectively. Moreover, to facilitate derivatization of the probes, two ethoxy carbonyl residues were grafted onto the side positions of BPEN. Spectroscopic studies demonstrated that introduction of azetidine leads to superior solvatochromic properties and largely enhanced fluorescence quantum yields as evidenced by the fact that T3 shows more than 150 nm shift in its maximum emission when dissolved in solvents of very different polarities and displays high fluorescence quantum yields in the solvents studied. However, T2, which is the one bearing a $-NO_2$ group, is non-fluorescent. Theoretical analysis and Lippert-Mataga modeling revealed the intra-molecular charge transfer (ICT) nature of the solvatochromic behavior of the compounds. Further test reveals that the fluorophores, in particular T3, are sensitive to the presence of trace water in less polar solvents, such as THF and 1,4-dioxane. Moreover, it is believed that the new fluorophores may serve as building blocks for creating environment-sensitive fluorescent sensors.

Introduction

In the last few decades, various kinds of fluorescence probes have been developed and used as sensitive tools for the detection of physiologically or environmentally important analytes.[1] In particular, the probes displaying solvatochromic properties could show response to changes in their microenvironment induced by the conformational or structural changes of proteins, synthetic polymers, and assemblies of amphiphilic compounds, such as cell membranes.[2] Fast recognition of unknown liquids is another direct application of the solvatochromic probes.[3] In addition, the fluorophores as emphasized can also be utilized as emitting materials for optoelectronic devices.[4] It is of the reasons, a large number of solvatochromic probes have been developed during the last few years.[5] However, from the viewpoint of practical uses, there is still a big room for conducting research in this area. This is because as an ideal solvatochromic probe, the fluorophore needs to meet a few criterions, including but not limited to: (1) absorption in the visible region (＞400 nm), (2) high absorption coefficients (＞30000 $mol^{-1}•L•cm^{-1}$), (3) great fluorescence quantum yields, (4) good photochemical stability, (5) strong solvatochromism, and (6) adaptive to solvents of very different properties.[6]

As well known, a solvatochromic probe is structurally characterized by a conjugated π-system functionalized with an electron-withdrawing and/or an electron-donating unit. For example, 2-propionyl-6-dimethylaminonaphthalene (Prodan), one of the best-known polarity probes developed during the last few decades, takes a typical donor-π-acceptor structure, where the naphthalyl residue, the propionyl unit and dimethylamino group are the bridge, the electron-withdrawing and the electron-donating structures, respectively.[7] However, even for this widely recognized probe, it is still hard to meet all the requirements as mentioned since it absorbs at wavelengths shorter than 400 nm. Similar limitations occur for other reported probes. For example, the two well-known families of polarity probes, dansyl chloride and its derivatives as well as 4-(*N*,*N*-dimethylaminonaphthal)imide and its analogues, are generally showing low absorption coefficients.[8] Commercially available Nile Red (9-diethyl-amino-5*H*-benzo-[alpha]-phenoxazine-5-one), another fluorescent probe, is relatively weak in recognition of solvents of different polarities.[9] For anthracene and its analogues, their fluorescence quantum yields are usually low.[10] DNS (4-dimethylamino-4'-nitro-stilbene) and TNS (2-(*p*-toluidinyl)-

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* E-mail: yfang@snnu.edu.cn; Tel.: 0086-29-81530786. Fax: 0086-29-81530787
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In Memory of Professor Enze Min.

naphthalene-6-sulfonic acid), which are highly applicable for fluorescent imagine and probing studies, are also not satisfying due to their short wavelength absorptions and weak fluorescence in common solvents.[11]

Because of the shortcomings of the known probes and the increasing demand for them with specific characteristics, recent years were experienced by great progress in the development of new versatile solvatochromic probes. As examples, Brummond and co-workers reported a variety of Prodan-like fluorophores, and they appear promising since they overcome the drawbacks of the short wavelength absorptions of Prodan.[12] Another representative solvatochromic probes are push-pull substituted fluorene which have superior solvatochromic properties and have already been applied for labelling of biomolecules.[6a,13] Very recently, Marx,[14] Lavis and co-workers[15] reported that replacement of a general electron donation structure of *N*,*N*-dialkylamino groups in a fluorophore with four-membered azetidine ring not only improves the quantum yield of the compound, but also enhances its photochemical stability. Similar finding was also reported by Xu, Liu, and co-workers.[16]

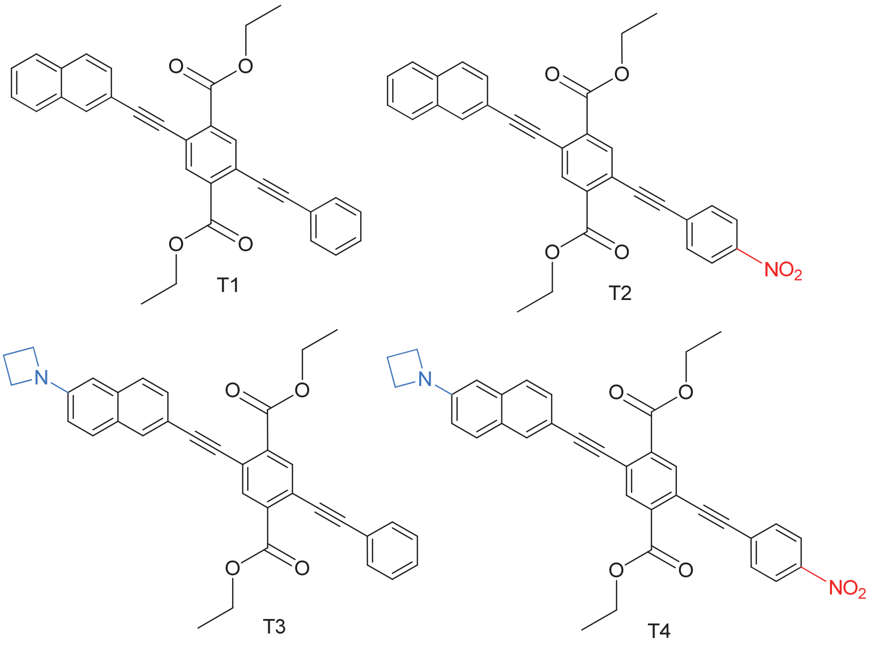
Recently, we focused on the studies of 1,4-bis(phenylethynyl)-benzene (BPEB) and bis(phenylethynyl)-2-naphthyl (BPEN)-based fluorophores.[17] Some of them show typical solvatochromic properties, of which different electron-withdrawing and electron-donating units were introduced. It was found that solvents with very similar structures or properties, such as methanol, ethanol, *n*-propanol, *n*-butanol, *n*-pentanol, *n*-hexanol, *n*-heptanol, *n*-octanol and *n*-decanol could be discriminated with no difficulty. Moreover, ethylbenzene and its isomers (*o*-xylenes, *m*-xylenes and *p*-xylenes), and even mono-alkyl-substituted benzenes can also be recognized. However, the probes as mentioned are hard to be derivatized due to lack of reactive groups, which may limit their practical applications. In addition, the probes as developed are poor to resist photochemical degradation. Accordingly, in the present work, two ethoxy carbonyl structures were introduced instead of *n*-hexadecyl residues which were taken as grafts in the earlier studies. Moreover, $-NO_2$ was employed as an electron-withdrawing group, and the well-known azetidine as an electron-donating structure. In this way, four new derivatives of BPEN with push-pull structures, T1, T2, T3 and T4 (Scheme 1), were designed, and their solvatochromic properties were studied. This paper reports the details.

Experimental

Synthetic procedure

All reagents were purchased from commercial suppliers and used directly unless otherwise noted. Prior to use, CH_2Cl_2, toluene, and diisopropylamine were purified by distillation from CaH_2. Reactions were conducted under a dry N_2 atmosphere using standard vacuum line techniques. Column chromatographic purification was performed with silica gel (300—400 mesh) as the stationary phase. ^1H NMR and ^{13}C NMR spectra were recorded on Bruker 600 MHz spectrometer in CD_2Cl_2 and $CDCl_3$ with tetramethylsilane (TMS) as an internal standard. Mass spectrometry measurements were performed on an AXIMA-CFR in MALDI-TOF mode by using α-cyano-4-hydroxycinnamic acid (CCA) as the matrixes.

Scheme 1 Molecular structures of T1, T2, T3 and T4



Photophysical characterization

UV-vis absorption spectra were recorded on an UV-vis spectrophotometer (U-3900, Hitachi), and the molar absorption coefficients for the compounds were calculated using the Lambert-beer law. Steady state fluorescence measurements were performed at room temperature on a time correlated single photon counting Edinburgh Instruments FLS 920 fluorescence spectrometer. All the solvents used for fluorescence measurements were freshly distilled prior to use. Absolute fluorescence quantum yields were determined on the same system equipped with an integral sphere at a concentration of 1.0×10^{-6} mol/L. With this instrument, the measured Φ_f values may be subject to an error of ±5%. Fluorescence lifetimes for the four compounds in different solvents were measured on the same system using a picosecond pulsed light emitting diode (EPLED-375, EPLED-405 or EPLED-445) as excitation source at a concentration of 5.0×10^{-6} mol/L.

Results and Discussion

UV-vis absorption

To understand the structure and structural differences of the four compounds as synthesized, their UV-vis absorption spectra in 1,4-dioxane were determined and the results are depicted in Figure 1. It is seen that all the spectra as obtained are characterized by two bands, which must be related to the transitions to different excited states. Further inspection of the spectra reveals that from T1 to T4 the absorption maxima of the low energy bands ($S_1\leftarrow S_0$) significantly red-shifted as evidenced by the value changing from 365 to 372, then to 404, and finally to 421 nm, respectively, suggesting the differences in the energy gaps between the Franck-Condon (FC) excited states and the ground states of the relevant compounds. However, for the maximum absorptions of the transitions to higher excited state, little shift is observed.

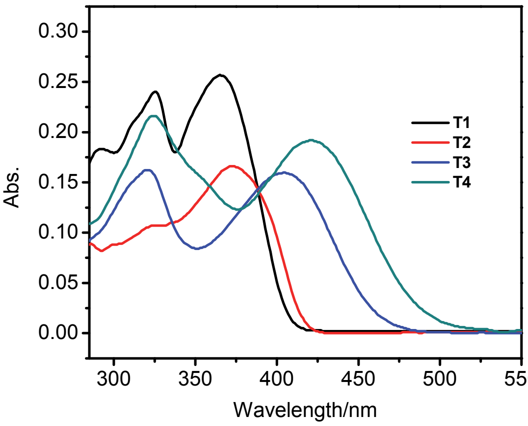


Figure 1 UV-vis absorption spectra of the 1,4-dioxane solutions of T1, T2, T3 and T4 recorded at a concentration of 5.0×10^{-6} mol/L and at 25 ℃.

The UV-vis absorption spectra of the compounds were also measured in other solvents of different polarities. The results are provided in Figure S-1 and the relevant parameters are listed in Table 1. It is seen that the positions of the absorption maxima of the compounds in the solvents vary from 364 to 429 nm depending on the exact structures of them. Further concentration-dependent absorption tests in the solvents revealed that the molar extinction coefficients (ε) ($S_1\leftarrow S_0$ transition) of the four compounds are greater than 3×10^4 $\text{mol}^{-1}\cdot\text{L}\cdot\text{cm}^{-1}$ (c.f. Table 1), which is favorable for them to be used as fluorescent probes. With reference to the two sets of the data shown in Table 1, it is seen that the absorption maxima and the extinction coefficients slightly change with increasing solvent polarity, but the change can not be simply correlated with their $E_T(30)$ values.[18] Careful examination of the data shown in the Table and the spectra depicted in Figure S-1 demonstrates that the spectra of the compounds in toluene are slightly red-shifted if compared to the absorptions recorded in other solvents, which could be a result of stabilization of the excited state due to specific π-π interaction between the solvent and the compounds.[19]

Fluorescence properties

The fluorescence emission spectra of the 1,4-dioxane solutions of T1, T2, T3 and T4 are, respectively, shown in Figure 2d. In accordance with the absorption spectra, the emission maximum exhibits great red-shift with the compound being changed from T1 to T3, and then to T4. Specifically, T1 is around 417 nm, T3 and T4 are around 551 and 599 nm, respectively. But the fluorescence quantum yields of them decrease in the solvent in the same order. In particular, T2 is almost non-fluorescent, which is the reason why it is not listed in the Table. Actually, for most of the nitro-aromatics, the aromatic rings are lacking electronic density because of the electron withdrawing effect of the nitro-groups, which must change the electronic structures of the compounds, resulting in decreased fluorescence quantum yields. Introduction of azetidine (T3), however, enhances the emission of the mother compound, and co-existence of the two structures also favors the emission of the compound as evidenced by the high fluorescence quantum yield of T4.

Fluorescence lifetime (τ_f) and quantum yield (Φ_f) are fundamental properties of fluorophores, and therefore the parameters for the three compounds as obtained were measured in different solvents. The results are also shown in Table 1. It is to be noted that all the fluorescence decays as recorded could be fitted quite well with a mono-exponential function (as examples, see Figure S-2). Based upon the lifetimes and the quantum yields as measured, the radiative decay rate constants (k_r) for each compound in different solvents can be calculated by using $k_r=\Phi_f/\tau_f$, and moreover, the relevant non-radiative decay rate constants (k_{nr}) by $k_{nr}=(1/\Phi_f-1)k_r$.

Table 1 Photophysical data for T1, T3 and T4 in selected solvents: solvent polarity parameter $E_T(30)$, molar absorption coefficient (ε), maximum absorption wavelength (λ_{abs}) and emission wavelength (λ_{em}), Stokes shifts ($\Delta\nu$), fluorescence quantum yield (Φ_f), lifetimes (τ_f), radiative decay rate constant (k_r) and non-radiative decay rate constant (k_{nr}) for the four compounds recorded in different solvents. For fluorescence quantum yield measurements, the probe's concentration was kept at 1.0 μmol/L. For other fluorescence measurements, the concentrations were set at 5.0 μmol/L

Fluorescent probe	Solvent	$E_T(30)$	ε/ (mol^{-1}•L•cm^{-1})	λ_{abs}/ nm	λ_{em}/ nm	$\triangle\nu$/ cm^{-1}	Φ_f/ %	τ_f/ ns	k_r/ MHz	k_{nr}/ MHz
T1	Hexane	31.0	36725	365	405	2706	99	1.24	798	8
	Toluene	33.9	37520	370	418	3104	97	1.43	678	21
	1,4-Dioxane	36.0	46510	365	417	3416	90	1.42	634	70
	THF	37.4	48020	367	421	3495	77	1.43	538	161
	$CHCl_3$	39.1	45806	370	426	3553	92	1.10	836	73
	CH_2Cl_2	40.7	38265	367	427	3829	73	1.30	562	208
	DMSO	45.1	39765	368	446	4752	58	1.38	413	312
	MeOH	55.4	46510	364	442	4849	57	1.27	449	339
T3	Hexane	31.0	31068	398	467	3712	66	1.51	437	225
	Toluene	33.9	32675	411	529	5427	90	2.91	309	34
	1,4-Dioxane	36.0	34256	405	551	6604	69	3.16	219	98
	THF	37.4	34927	408	618	8329	11	1.65	66	539
	EA	38.1	35153	404	613	8439	23	1.76	131	438
	$CHCl_3$	39.1	33586	409	596	7671	19	1.37	139	591
	CH_2Cl_2	40.7	34595	409	622	8373	69	1.53	451	203
	OOH	48.1	35658	408	548	6262	16	1.36	118	618
T4	Hexane	31.0	32561	418	492	3598	96	1.80	533	22
	Toluene	33.9	31680	429	522	4153	68	2.20	309	145
	CCl_4	32.4	32489	426	577	6143	45	0.50	900	1100
	1,4-Dioxane	36.0	38326	421	599	7086	15	2.64	57	322

Clearly, similar with the BPEN-based fluorophores reported earlier,[17d,17e] the fluorescence quantum yields of the three compounds as synthesized in the present study are generally high in less polar solvents, and low in polar solvents.

The photo-chemical stability of the three compounds was also studied as it is often a key factor affecting the practical applications of fluorescent probes.[20] An example result is shown in Figure S-3. It was shown that two-hour continuous illumination with a xenon lamp (450 W) as the light source did not result in any significant deduction in the fluorescence emission, indicating that the compounds under study possess exceptional photochemical stability.

Solvatochromic properties

The fluorescence emission spectra of T1, T3 and T4 were recorded in solvents of different polarities, and the results are shown in Figure 2. Entirely different from the absorption spectra, the emission positions of the three compounds studied are highly dependent upon the nature, in particular the polarity of the solvents tested. Further inspection of the spectra shows that the emission profiles of them are structured in *n*-hexane. With increasing the polarity of the solvents, however, the spectra become less structured or even structure-less.

Further interrogating of the spectra shown in Figure 2, and the data depicted in Table 1, it is also seen that the three compounds display different solvatochromic properties. Specifically, for T1, its emission maximum appeared around 405 nm in apolar *n*-hexane, but the emission shifted to 427 nm when the solvent was changed to a slightly polar solvent of CH_2Cl_2, a 22 nm shift due to the polarity increase, which is a typical positive solvatochromic behavior as expected from the weak push-pull structure of the fluorophore (naphthyl structure to the phenyl residue). With introduction of azetidine structure at the sixth position of the naphthyl residue of the core structure, both the solvatochromic property of the compound is significantly improved. For example, the emission maximum of T3 appeared at ~467 nm in *n*-hexane, but shifted to 622 nm in CH_2Cl_2, a 155 nm shift due to the same polarity increase, demonstrating the effectiveness of the structural modification. Further introduction of $-NO_2$ group also enhances the solvatochromic properties of the relevant compounds as evidenced by their increased emission maximum shift from *n*-hexane to dioxane, which is 30, 85, and 107 nm, respectively. However, it is to be noted that introduction of nitro-group significantly inhibits

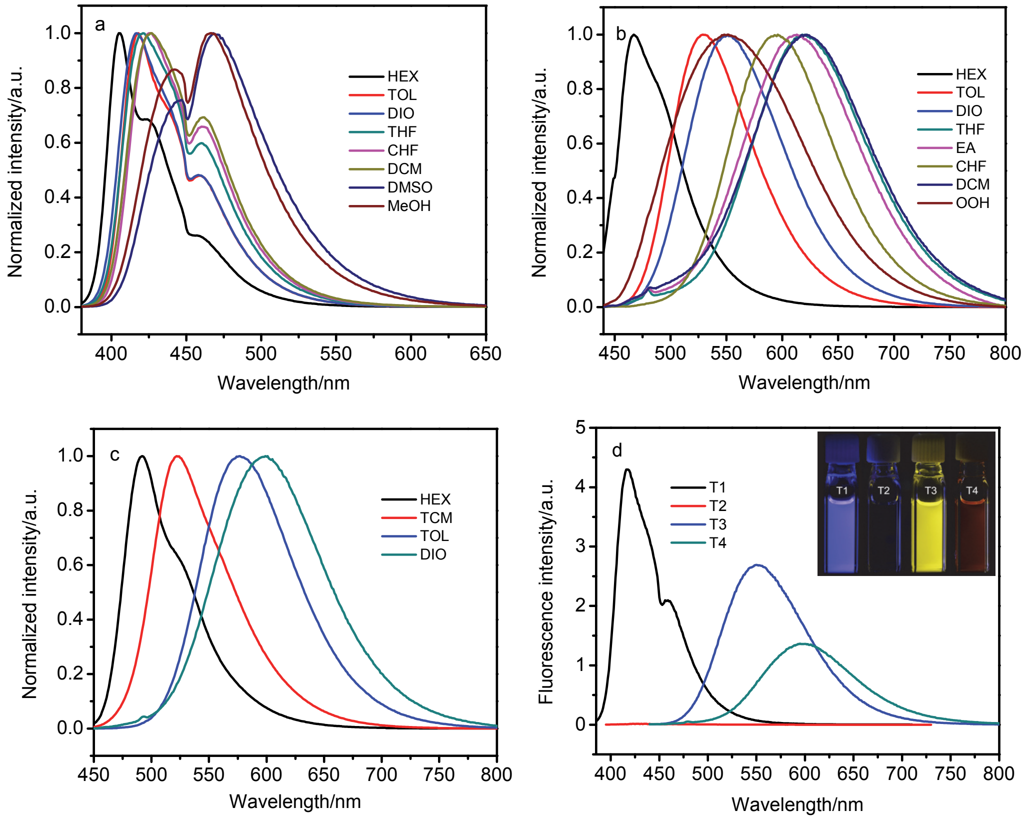


Figure 2 Normalized fluorescence emission spectra of T1 (a), T3 (b) and T4 (c) recorded at a concentration of 5.0×10^{-6} mol/L in different solvents with 365, 420 and 430 nm as the excitation wavelength of the respective compound, and comparison of the fluorescence emission spectra of the 1,4-dioxane solutions of T1, T2, T3 and T4 (d). The inset of d is the fluorescence pictures of the four compounds in 1,4-dioxane under UV light illumination (365 nm). All spectroscopic measurements were conducted at 25 ℃. HEX: hexane, TCM: carbon tetrachloride, TOL: toluene, DIO: dioxane, THF: tetrahydrofuran, DCM: dichloromethane, CHF: chloroform, and OOH: *o*-octanol.

the fluorescence emission of the relevant compounds as demonstrated by the fact that the fluorescence quantum yield of T4 in dioxane is only 16%, but the values for T1 and T3 in the same solvent are 90% and 69%, respectively. Moreover, nitro-containing T2 is non-fluorescent as indicated earlier. Introduction of the group also decreases the solubility of the compound in the solvents studied, which makes T4 less adaptive to solvents of different polarities. However, the negative effect induced by nitro-group does not mean that the compound, T4, can not find uses in solvent discrimination.

The emission positions and the remarkable shifts in the emission maxima of the fluorophores, in particular T3 and T4, as developed imply that they have the potential to be used for visualization discrimination of some organic solvents. Figure 3 compares the solvatochromic performances of T1 and T3. It is seen clearly that structural modification endows the core structure, T1, exceptional solvatochromic properties. Based on the findings, it is anticipated that T3 and possibly T4 as developed may find uses in the discrimination of solvents/liquids with similar properties and in the determination of trace water in organic liquids.

Theoretical calculations

Several quantum chemical methods were used to study the molecular structures and their photophysical properties relevant to the ground- and excited-dynamics. The ground-state structures of T1 to T4 were first optimized in the gas-phase using the CAM-B3LYP/6-31g* level of theory (Figure 4). From the results as depicted, it can be seen that for the four compounds as obtained the π-π conjugate, BPEN, takes a flat and rigid structure.

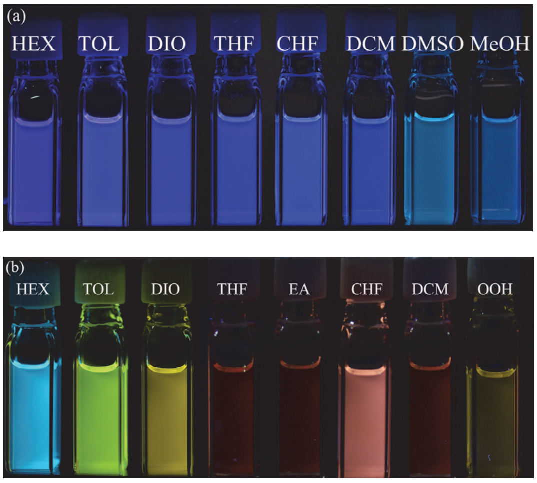


Figure 3 The fluorescence images of T1 (a) and T3 (b) in different solvents (5.0×10^{-6} mol/L), which were taken under the illumination of UV light (365 nm) and at room temperature.

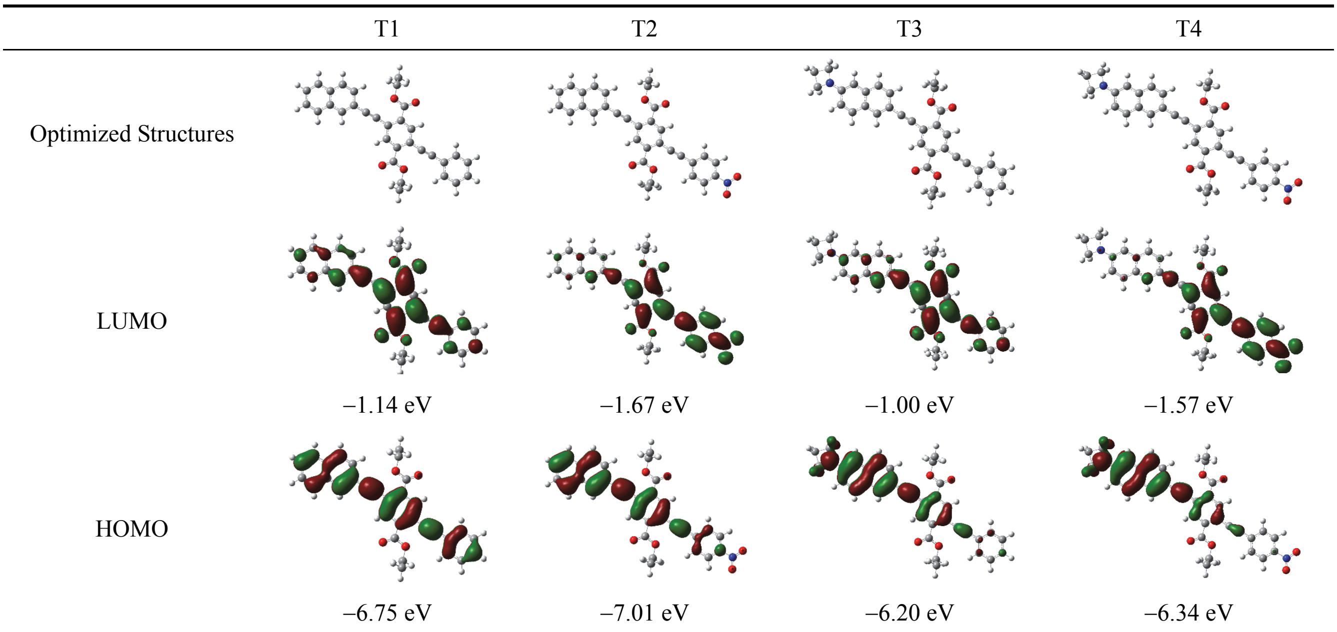


Figure 4 Molecular orbital energies and iso-density surface plots of HOMO and LUMO for T1, T2, T3 and T4 depicted in different columns.

In addition, for T3 and T4, the azetidine is almost in the co-planar position with BPEN. The molecular orbital diagrams of the compounds as generated from TD-DFT calculations are in support of the statement. For the highest occupied molecular orbitals (HOMOs) of the compounds, the electron densities are largely localized on the azetidine-(naphthalene ethynyl)-benzene part of the molecules. In contrast, the electron densities of the LUMO orbitals of the four compounds gradually move to another end with the fluorophore changing from T1 to T4. The change in the electron density distribution from the HOMO orbital to the LUMO orbital must be the origin of the difference between the ground and the excited state dipole moments ($\Delta\mu$) of the compounds as studied. The results from the calculations are listed in Table 2, which are 1.6, 7.8, 9.0 and 16.4 D, respectively, for the four compounds under study. In addition, Table 2 also shows the absorption maxima ($\lambda_{\max}$), the main orbital transitions, and the oscillator strengths (f) of the compounds from the calculations. It is seen that the theoretical $\lambda_{\max}$ values are in good agreement with the experimental results considering the fact that solvent effect was not considered during the calculations.

Rationalization based on experimental interrogation

From the experimental results shown in Table 1, it is seen that the emission position of T4 is more sensitive to the change of solvent polarity if compared to that of T3 and T1, and similarly, T3 is more sensitive than T1, which is a result in accordance with the change in dipole moment between the ground and excited states as depicted in Table 2. To further validate the nature of the solvatochromic characteristics of the fluorophores as created, Lippert-Mataga theory was employed to conduct further experimental studies.[21] The difference in dipole moment between the two states ($\Delta\mu$) was estimated by using the famous Lippert-Mataga equation (eq 1):

$$\Delta\nu = \nu_A - \nu_F = \frac{2\Delta f}{hca^3}(\Delta\mu)^2 + constant \qquad (1)$$

In the equation, ν_A and ν_F are the wavenumbers of the relevant absorption and emission maxima, respectively. h is the Planck's constant, c is the light velocity, a is the

Table 2 TD-DFT calculations at the long-range corrected CAM-B3LYP function and experimentally obtained absorption properties

Compound	Transition	$\lambda_{\max}{}^a$/nm	Main orbital transition	f	$\lambda_{\max}{}^b$/nm	(μ_e–μ_g)/Debye
T1	$S_1 \leftarrow S_0$	353	HOMO→LUMO	1.45	365	1.52
	$S_2 \leftarrow S_0$	298	HOMO→LUMO+1	0.18	327	1.36
T2	$S_1 \leftarrow S_0$	361	HOMO→LUMO	1.74	370	7.73
T3	$S_1 \leftarrow S_0$	369	HOMO→LUMO	1.67	405	8.94
T4	$S_1 \leftarrow S_0$	383	HOMO→LUMO	1.85	421	16.38
	$S_2 \leftarrow S_0$	309	HOMO→LUMO+1	0.06	323	14.12

[a] Calculated absorption maximum; [b] Observed absorption maximum in 1,4-dioxane.

radius of the cavity in which the fluorophore resides, and Δf is the orientation polarizability of the solvent system defined as follows (Eq. 2):

$$\Delta f = \frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{2n^2 + 1} \tag{2}$$

where ε and n are the dielectric constant and refractive index of the solvent. Specifically, *n*-hexane/1,4-dioxane was chosen as a class of typical solvent mixtures to adjust the orientation polarizabilities (Δf) of the mixture solvents through regular variation of their compositions. The emission spectra of T1, T3 and T4 in the mixtures were acquired and the results are shown in Figure S-4a, Figure 5a, and Figure 5b, respectively. The plots of the relevant compound's Stokes shift Δv vs. Δf were shown in Figure S-4b, Figure 5c and Figure 5d, respectively. With reference to the Figures, it can be observed that the linear correlations between the Stokes shifts of the compounds in the mixtures and the solvent orientation polarizabilities are perfect. In addition, the slops of the plots are positive, suggesting that the compounds as studied possess the ability to discriminate solvents of different polarities.

It is to be noted, however, that the Lippert equation was derived on the basis of many assumptions, and it is only an approximation of real situations. For example, in the development of the equation, the molecule of a fluorophore is considered to exist within a cavity with an ideal spherical shape. But for the compounds under study, the situation is different and in fact they take a linear shape. Accordingly, it should be better to modify the model into an ellipsoidal one. Moreover, the cavity radius is further supposed to be 40% of its long axis. In this way, the Onsager radii of T1, T3 and T4 can be calculated, and the results are 6.21, 6.35 and 6.51 Å, respectively. Based on the modified model and the Lippert-Mataga plots, the dipole moment changes ($\Delta\mu$) of the three probes were calculated, and the results are 14, 37 and 39 D, respectively. Obviously, these values are much larger than those estimated from theoretical calculations (Table 2), suggesting that there might be some specific interactions between the probes and the solvents, which did not take into account during the theoretical calculations. Anyway, the orders of the solvatochromic abilities of the relevant compounds predicated from the two methods are the same, and fit with the experimental observations.

Detection of water

As predicted in the discussions, the fluorescence emission of T3 and/or T4 should be sensitive to the presence of water in organic solvents. Accordingly, the fluorescence emission spectra of T3 in two example organic solvents, 1,4-dioxane and THF, with the pres-

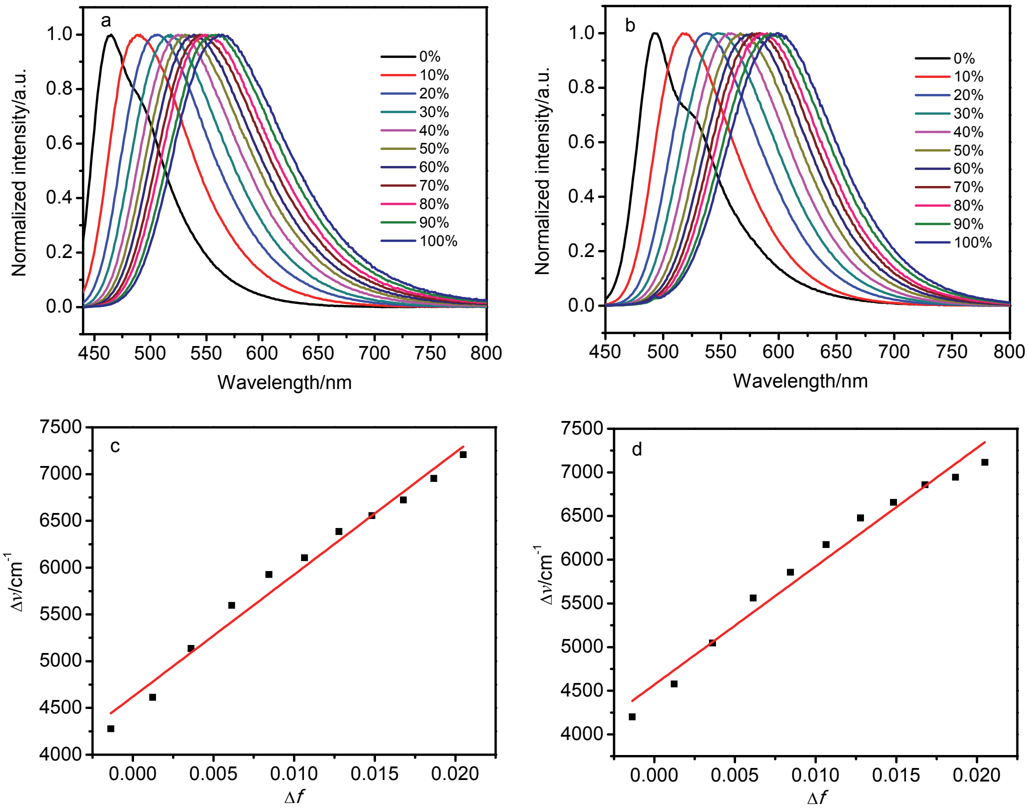


Figure 5 Fluorescence emission spectra of T3 (a) and T4 (b) in mixture solvents of *n*-hexane and DIO of different ratios at a concentration of 5.0×10^{-6} mol/L and at 25 ℃, of which excitation wavelength is 420 nm. Lippert plots for T3 (c) and T4 (d) in the set of mixture solvents.

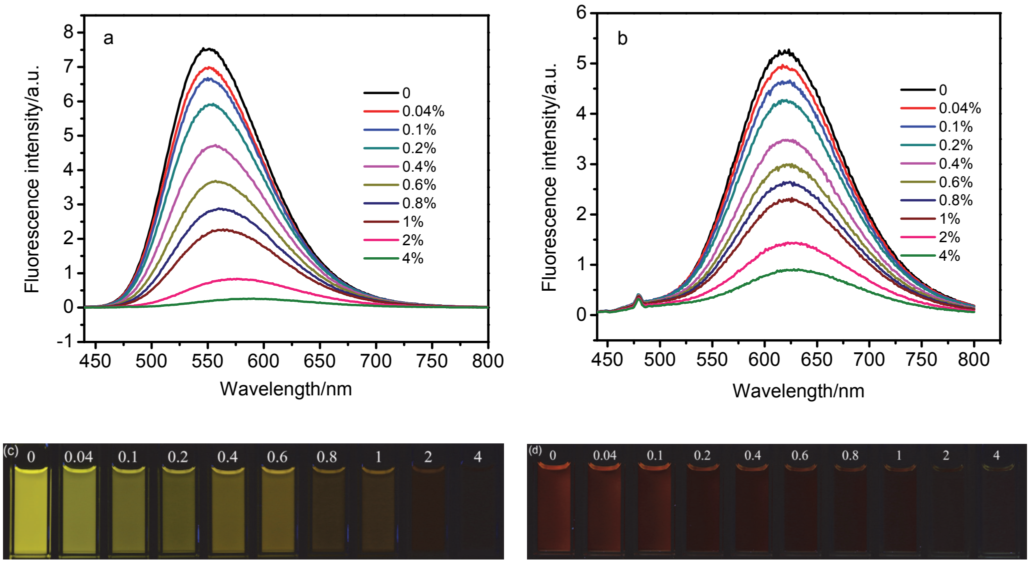


Figure 6 Fluorescence emission spectra of T3 in 1,4-dioxane-water (a) and THF-water (b) mixtures with different water contents (vol.%) recorded at a concentration of 5.0×10^{-6} mol/L and at 25 ℃, of which excitation wavelength is 420 nm. The pictures shown in (c) and (d) are the fluorescence images of T3 in the two sets of solvents under UV light illumination (365 nm).

ence of different amount of water were recorded, and the results are shown in Figure 6a and Figure 6b, respectively. With reference to the spectra, it is clearly seen that water shows significant quenching effect upon the fluorescence emission of the compound in the solvents (Figures 6c and 6d), and the quenching efficiencies are linearly related to the concentration of water in the systems. Quantitative analysis of the data (Supporting Information) shows that detection limits for water in the two solvents could be lower than 0.015% and 0.019% (*V*/*V*), respectively.

The Stern-Volmer plots of the data shown in Figure S-5 are up-curved, which is an indication of the complex nature of the quenching process. As an example, Figure S-6 shows one of the two plots (1,4-dioxane). To reveal the nature of the quenching, fluorescence lifetime measurements were conducted for the T3/1,4-dioxane system. The results are also presented in Figure S-6. It is clearly seen that the quenching is a combined static and dynamic process, and the contributions from them are 1 to 1.

Conclusions

In conclusion, four fluorescent conjugates with potential solvatochromic properties were designed and synthesized. In the design, an extended and rigid π system of bis(phenyl-ethynyl-)-2-naphthyl (BPEN) was taken as the core structure, a newly reported structure, azetidine, was chosen as an electron-donating group, and $-NO_2$ as an electron-withdrawing unit. In addition, two ethoxy carbonyl moieties were grafted onto the side positions of the core structure in order to endow the as to be developed fluorophores reactivity, which lays foundation for them to be grafted or labelled onto other structures. Spectroscopic studies demonstrated that the compounds (T3, T4) bearing an azetidine structure are superior than others in the discrimination of solvents of different polarities. But T4 is poor than T3 considering the facts (1) it is hard to be dissolved in most of common organic solvents, and (2) its fluorescence quantum yields in some polar solvents are significantly lower than that of T3. T2 behaviors very differently from others as it is fluorescence inactive in nature. The possible reason behind is the introduction of $-NO_2$ group. To our luck, the fluorophores are all stable under long time light illumination. Theoretical calculations and Lippert-Mataga model-based experimental studies revealed that the nature of the solvatochromic properties originates from the excitation related intra-molecular charge transfer (ICT) of their BPEN-based push-pull structures. Considering the long wavelength absorption (>400 nm), large molar absorption coefficient ($>32\ 000\ \text{cm}^{-1}\bullet\text{mol}^{-1}\bullet\text{L}$), great color change (400—620 nm), and exceptional photochemical stability of T3 and T4, it is believed that the two compounds as developed are attractive as they may find important applications due to their superior solvatochromic properties. As an example, trace amount of water in aprotic solvents could be determined with no difficulty.

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