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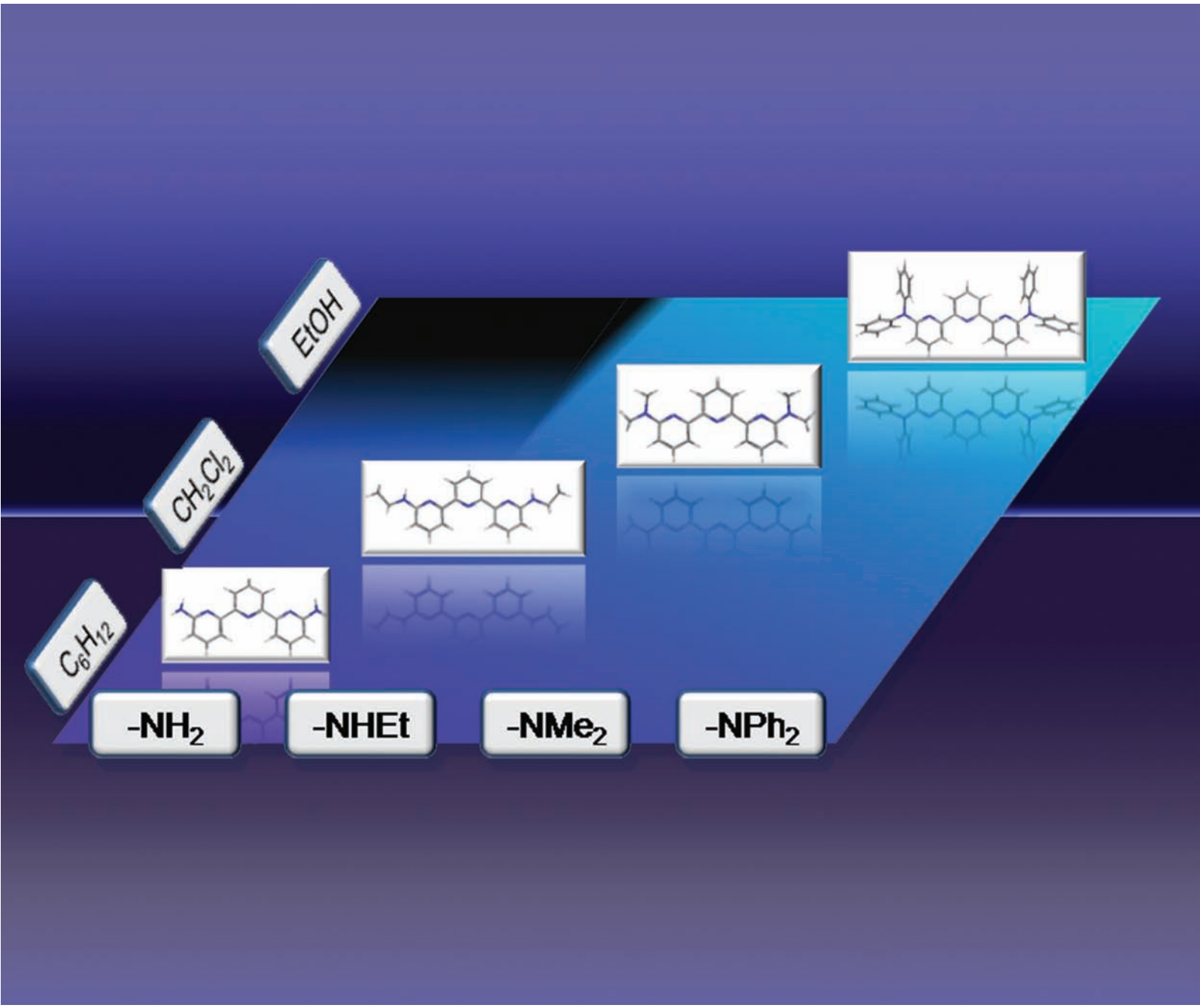

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Tuning of fluorescence properties of aminoterpyridine fluorophores by *N*-substitution†

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Several *N*-alkyl and *N*-phenyl derivatives of 6-amino- (**1**) and 6,6′-diamino-2,2′:6′,2″-terpyridine (**6**) were synthesized, and their fluorescence properties were studied. A successive red-shift was observed as the number of the *N*-substituted groups increased. It was also shown that the susceptivity of the fluorophores to a solvent varied considerably according to the mode of the *N*-substitution. While the monoamino-tpys **1–5** (tpy: 2,2′:6′,2″-terpyridine) suffered almost complete quenching of their fluorescence in ethanol, the fully *N*-alkylated diamino-tpys **8** and **9** retained their fluorescence. The results show that *N*-substitution is a useful way to tune both the radiation energy and solvent susceptivity of the fluorescence of the amino-tpys.

Introduction

Fluorescent compounds have found a wide range of applications, such as OLEDs,[1] probes[2] and markers,[3] plus phototherapeutic reagents,[4] and their uses are still expanding. Accordingly, there has been an increasing demand for fluorescent compounds with specific functions, and a variety of new fluorescent compounds have been developed so far. For these fluorophores, fine-tuning of their fluorescence colour is frequently required for better performance of photofunctional systems such as Förster-type energy-transfer systems, multiple fluorescent staining of cell tissues and multi-colour luminescent devices. Thus, tuning and switching of fluorophoric properties by modification of the electronic state is one of the major topics in developing fluorescent compounds. However, it is generally difficult to tune known fluorophores to desirable photophysical properties by chemical modification, since slight structural alteration frequently impairs their fluorescence properties.

2,2′:6′,2″-Terpyridine (tpy) is a chemically and thermally stable compound, and is well known to serve as an excellent chelate owing to its suitably arranged three ring nitrogens. A wide variety of transition metal complexes with tpy ligands have been synthesized and their unique photophysical properties, including luminescence, have been studied extensively.[5] However, tpy and its derivatives are generally non-fluorescent, and relatively few fluorescent derivatives, either in solution[6–10] or in the solid state,[11] have been reported. The non-fluorescent nature of tpy is ascribed to the relatively close-lying π–π* and n–π* singlet excited states, through which very rapid inter-system crossing and/or internal conversion proceeds. It is known as the 'proximity effect' of electronic states,[12] which is often observed in aza-aromatics. We previously reported[7] that 6-amino-tpy **1** exhibited a strong blue fluorescence in organic solutions. The key for the dominant radiative decay process is that the 'allowed' π–π* transition band lies much lower than the n–π* transition band, and is the lowest energy excitation, which has been shown by a molecular orbital calculation.

There is a wide variety of fluorescent nitrogen-, oxygen- and other heteroaromatics with highly electronegative atoms. The major drawback of these compounds is that their fluorescent nature is prone to impairment in protic solvents due to a solute–solvent hydrogen-bonding interaction, though this feature can be used for fluorescence sensing.[13] Except for 4′-[*p*-(*N*,*N*-diphenylamino)phenyl]-tpy, reported by Goodall *et al.*,[8] 6-amino-tpys[7] and 4′-phenyl-tpys[9] also fall into this category and their fluorescence quantum yields decrease dramatically in protic solvents, which limits their availability as novel and useful fluorophores. We previously showed[14] that amino-tpys and a series of *N*-substituted amino-tpys could be synthesized conveniently in good yields (65–90%) by Pd-catalyzed amination of bromo-tpys with the corresponding amines (Buchwald–Hartwig reaction[15]).

In this report, we describe the fluorescence properties of a series of *N*-substituted 6-amino- and 6,6″-diamino-tpys, and demonstrate the effectiveness of *N*-substitution for the fluorescence tuning of these novel fluorophores. It is to be emphasized that, unlike the parent amino-tpys (**1** and **6**) and monoamino derivatives (**2–5**), fully *N*-alkylated diamino-tpys **8** and **9** display efficient fluorescence even in a protic solvent, ethanol, thus extending the application of tpy-based fluorophores to protic media.

Results

Absorption and fluorescence properties in organic solution

The molecular structures of the parent 6-amino- (**1**) and 6,6″-diamino-tpys (**6**) and their *N*-substituted derivatives are shown in Fig. 1. The absorption and fluorescence maxima of 6-amino-tpys **1–5** and 6,6″-diamino-tpys **6–10** in cyclohexane, dichloromethane and ethanol are tabulated in Table 1. The lowest energy absorption band of **1** appeared at around 320 nm ($\log\varepsilon \sim 4$), which is presumably due to the π–π* transition. The first *N*-substitution of the amino group with an alkyl or phenyl group (**2** and **4**) caused a red-shift to about 340 nm, and the second *N*-substitution

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Table 1 Absorption and fluorescence maxima of *N*-substituted 6-amino and 6,6″-diamino-tpys in various of solution at 20 °C

	Cyclohexane		Dichloromethane		Ethanol	
Compound	λ_{abs}/nm (log ε)	λ_{fl}/nm (Φ^a)	λ_{abs}/nm (log ε)	λ_{fl}/nm (Φ^a)	λ_{abs}/nm (log ε)	λ_{fl}/nm (Φ^a)
1	320 (4.13)	366 (0.56)	319 (4.17)	386 (0.70)	324 (4.07)	402 (0.01)
2	336 (3.97)	383 (0.54)	339 (3.96)	407 (0.41)	341 (3.91)	421 (0.03)
3	349 (3.87)	388 (0.39)	350 (3.85)	428 (0.57)	349 (3.85)	436 (0.02)
4	339 (3.88)	388 (0.19)	341 (3.92)	443 (0.14)	350 (3.84)	453 (0.04)
5	355 (3.79)	400 (0.10)	353 (3.77)	455 (0.17)	355 (3.76)	466 (0.09)
6	324 (—[b])	364 (0.30)	327 (4.31)	386 (0.48)	330 (4.27)	408 (0.07)
7	337 (4.27)	381 (0.58)	341 (4.24)	404 (0.50)	342 (4.22)	423 (0.19)
8	348 (4.17)	386 (0.45)	352 (4.15)	422 (0.57)	352 (4.07)	434 (0.38)
9	353 (4.18)	387 (0.54)	359 (4.14)	428 (0.61)	355 (4.16)	433 (0.40)
10	357 (3.94)	397 (0.14)	357 (4.14)	453 (0.20)	358 (—[b])	462 (0.11)

[a] Relative quantum yields were determined by using 2-aminopyridine (Φ = 0.37, excitation at 285 nm, in ethanol) as the standard compound. [b] Not determined due to low solubility.

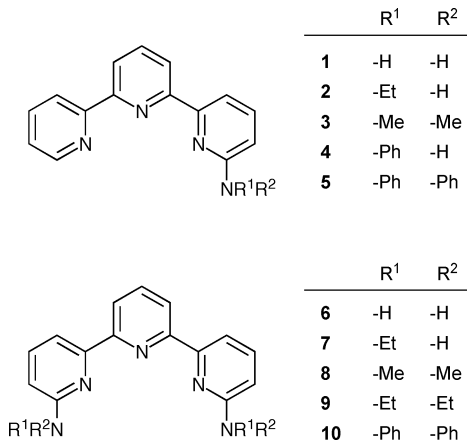

Fig. 1 Molecular structure of the monoamino-tpys (**1–5**) and diamino-tpys (**6–10**).

(**3** and **5**) further shifted the absorption to around 355 nm. The phenyl-substitution caused a large red-shift compared to the alkyl-substitution. Similar to monoamino-tpys **1–5**, diamino-tpys **6–10** showed a red-shift in the absorption band upon *N*-substitution with alkyl or phenyl groups. The absorption maxima of the diamino-tpys are essentially the same as those of the corresponding monoamino-tpys. Thus, the type and the number of substituent(s) in the amino group(s) is critical to the position of the lowest energy absorption band, but the number of amino groups in the tpy core hardly affects the absorption maximum. It is remarkable that the absorption maximum was essentially the same in cyclohexane, dichloromethane and ethanol, showing that the lowest energy absorption band was not sensitive to the solvent.

Upon excitation at 285 nm, all compounds (**1–10**) in the cyclohexane and dichloromethane solutions exhibited a purple-to-blue fluorescence (366–455 nm) with moderate to high quantum yields. The shapes of the excitation spectra of these compounds were similar to their absorption spectra (Fig. S1†), indicating that the emitting state was the lowest excited state and efficient internal conversion to this state took place within these compounds. The fluorescence band showed a successive red-shift as the number of *N*-substituted groups increased (Table 1). Fluorescence of the phenyl-substituted derivatives appeared in a lower-energy region compared to the alkyl-substituted derivatives (Fig. 2). The results

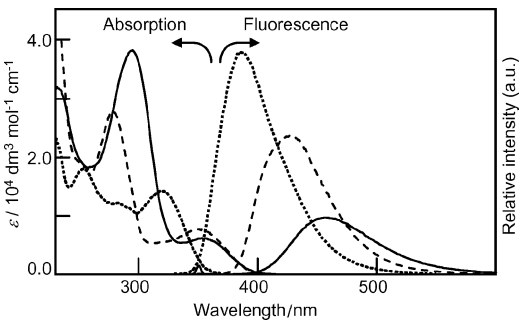

Fig. 2 Absorption and fluorescence spectra of **1** (dotted line), **3** (dashed line) and **5** (solid line) in dichloromethane solution.

demonstrate that fine-tuning of the fluorescence colour of amino-tpys can be achieved simply by *N*-substitution of the amino group without impairment of its fluorescent nature. There was no marked difference in the fluorescence maximum wavelength between the monoamino-tpys and the corresponding diamino-tpys.

Unlike the absorption spectra, considerable changes in the fluorescence spectra were observed in solvents of varying polarities. The fluorescence maxima of these compounds red-shifted as the polarity of the solvent increased from cyclohexane to ethanol, suggesting that the photoexcited state of these compounds has a relatively polar nature. Furthermore, the fluorescence of parent compound **1** was almost completely quenched in ethanol. Regardless of the type and number of the substituent, monoamino-tpys **2–5** showed a drastic decrease in their fluorescence quantum yield. The fluorescence lifetime of **3** became much shorter in ethanol (0.8 ns) compared to that in dichloromethane (10.4 ns), indicating the presence of an efficient non-radiative decay process from the emitting excited state in ethanol. In contrast, fully *N*-alkylated diamino-tpys **8** and **9** retained their fluorescence properties even in a protic solvent (Φ = 0.38–0.40). Partially *N*-alkylated diamino-tpy **7**, bearing N-H protons, showed a moderate decrease in its fluorescence, and parent diamino-tpy **6** suffered a much larger fluorescence quenching. Since the fluorescence quantum yields of monoamino-tpys **2** and **3** and diamino-tpys **7** and **8** were sufficiently large and comparable to each other in acetonitrile (an aprotic polar solvent), the observed fluorescence quenching in ethanol was not due to the polarity of the solvent and, therefore, the hydrogen bonding interaction has to be taken in to account.

Thus, the solvent effect on the fluorophore can also be tuned by the *N*-substitution; in particular, the fully *N*-substituted diamino-tpys are shown to be good fluorophores, even in protic solvents.

Discussion

Effect of *N*-substitution

Chemical alteration of a fluorophore frequently imparts undesirable perturbation to its emissive electronic state and results in impairment of its fluorescence properties. In the case of amino-tpys **1–10**, however, *N*-substitution of the amino group(s) successfully altered the fluorescence wavelength by ~20 nm steps in dichloromethane with reasonable fluorescence efficiency ($\Phi >$ 0.1), allowing fine-tuning of the fluorescence colour. Since *N*-substituted tpys can be easily prepared in one step from varieties of commercially available amines in good yield, *N*-substitution is a simple and useful method for fine-tuning the fluorescence of amino-tpys (ranging from 385 to 455 nm) without damaging the fluorescent nature of parent compounds **1** and **6**.

To understand the effect of *N*-substitution further, the electronic state of monoamino-tpys **1–5** was studied by molecular orbital calculation. The geometry optimized by HF/6-31G(d) calculation was applied to the time-dependent density functional theory (TD-DFT) using the B3LYP/6-31G(d) basis set. The tpy core of the optimized molecular structures showed a nearly planar *s-trans* conformation. The lowest and the second-lowest transition bands of **1–5** were HOMO→LUMO and HOMO→LUMO + 1, respectively. The electronic configurations of the HOMO, and that of the LUMO and LUMO + 1 as well, were practically identical for **1–5**. The HOMO orbital located significantly on the amino nitrogen, while LUMO and LUMO + 1 did not (Fig. 3, Fig. S3). The energy levels of the LUMO and LUMO + 1 were only slightly affected by the *N*-substitution, probably due to the negligibly small

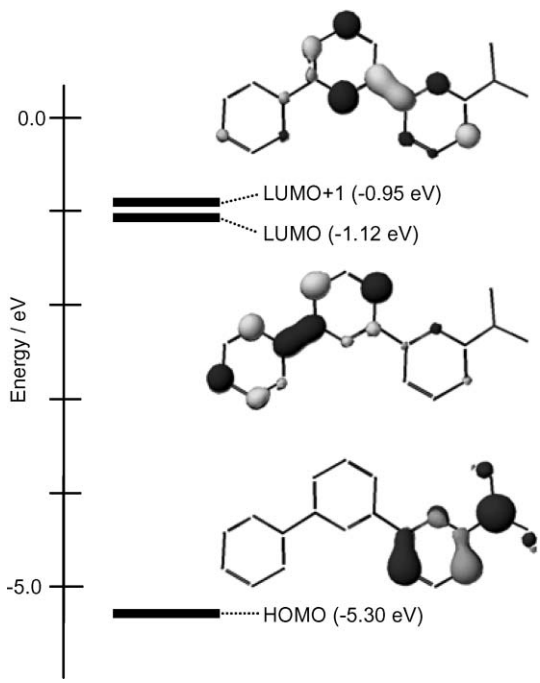

Fig. 3 Electronic state of **3** simulated by TD-DFT calculation.

electron density of these orbitals in the amino group. On the other hand, a successive rise in the HOMO energy level was indicated as the number of *N*-substitutions increased. Therefore, the effect of *N*-substitution was observed mostly at the HOMO level, and the red-shift of the fluorescence upon *N*-substitution can be explained by the decreased HOMO–LUMO gap.

The lowest energy absorption bands of **1–5**, estimated by TD-DFT, were plotted against the observed absorption bands in cyclohexane (Fig. 4a). Though the calculated transition energy was somewhat higher (850–1400 cm^{-1}) than the observed energy, they showed reasonably good linear correlation ($R = 0.96$), and the observed absorption spectra were qualitatively reproduced by simulation.

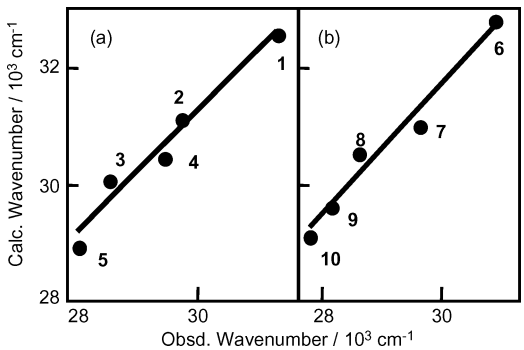

Fig. 4 Plot of the calculated against the measured lowest absorption energy of the monoamino-tpys (a) and diamino-tpys (b).

The TD-DFT calculation for the diamino-tpys **6–10** gave similar results for both the electronic state (Fig. S3) and the lowest absorption energy (Fig. 4b).

Effect of solvent

Though the solvent effect on the lowest energy absorption bands of **1–10** was negligibly small, a notable red-shift of the fluorescence band was observed in polar solvents (Table 1). Consideration of the solvent effect in the TD-DFT calculation using the polarizable continuum model (PCM)[16] gave only a slight difference in the electronic states and the lowest energy absorption bands, coinciding with the experimental results. Therefore, the excited state is thought to have a considerable charge-transfer (CT) character. To examine the CT character of the excited state, the difference between the excited and ground state dipole moment ($\Delta\mu$) was estimated for monoamino-tpy **3** and diamino-tpy **8** by the Lippert–Mataga equation (eqn (1)):[17]

$$\Delta\nu_{st} = \frac{2(\Delta\mu)^2}{hca^3}\Delta f + \text{constant}, \quad (1)$$

where Δf is Lippert's solvent polarity parameter:

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

ε and n are the relative permittivity and the optical refractive index of solvents, respectively, and a is the effective radius of the Onsager cavity[18] of a compound. The plots of the Stokes shift ($\Delta\nu_{st}$) of **3** and **8** against Δf were reasonably fitted linearly (Fig. S2). Assuming the value of a as 0.5 nm, $\Delta\mu$ for **3** and **8** was determined to be 11.2 and 10.5 Debye, respectively, indicating a moderate

Table 2 The rate constants of the radiative and non-radiative decay processes

	Dichloromethane				Acetonitrile				Ethanol			
Compound	λ_{fl}/nm (Φ)	τ/ns	$k_r/10^7\ s^{-1}$	$k_{nr}/10^7\ s^{-1}$	λ_{fl}/nm (Φ)	τ/ns	$k_r/10^7\ s^{-1}$	$k_{nr}/10^7\ s^{-1}$	λ_{fl}/nm (Φ)	τ/ns	$k_r/10^7\ s^{-1}$	$k_{nr}/10^7\ s^{-1}$
3	428 (0.57)	10.4	5.5	4.1	439 (0.30)	8.1	3.7	8.6	436 (0.02)	0.8	2.5	1.2×10^2
8	422 (0.57)	9.6	5.9	4.5	433 (0.38)	8.0	4.7	7.8	434 (0.38)	10.7	3.6	5.8

CT character. Thus, it is suggested that the more polar excited state is stabilized by reorganization of the polar solvent molecules, inducing the red-shift in the fluorescence. Because of this CT character, the choice of solvent can also be an effective tool for fine-tuning of the fluorescence colour. For example, the fluorescence maximum of **8** shifted from 386 nm in non-polar cyclohexane to 434 nm in polar ethanol.

In a protic ethanol solvent, fluorescence of the monoamino-tpys **1–5** showed a drastic decrease regardless of the mode of *N*-substitution, but fully *N*-alkylated diamino-tpys **8** and **9** retained their fluorescence properties ($\Phi \sim 0.4$). This pronounced difference in fluorescence quenching between the monoamino- and diamino-tpys in the protic solvent is of remarkable interest, and we further analyzed the photophysical properties of **3** and **8**. The rate constants of radiative (k_r) and non-radiative (k_{nr}) decay processes were calculated from the fluorescence quantum yield and the fluorescence lifetime (Table 2). In dichloromethane, the values of k_r and k_{nr} were of the same order of magnitude ($10^7\ s^{-1}$), typical of efficient fluorescence of organic compounds. Both rate constants showed no substantial difference between **3** and **8**. In ethanol, while the k_r values of **3** and **8**, and k_{nr} of **8**, were similar to those in dichloromethane, the k_{nr} value of **3** significantly increased. Therefore, the pronounced fluorescence quenching of **3** was mainly due to acceleration of the non-radiative decay process from the excited state.

It is well documented that fluorescence is prone to be quenched in protic solvents due to the formation of solute–solvent hydrogen bonds,[19] and this could be the reason for the observed acceleration of the non-radiative decay of **3** in ethanol. It has to be pointed out that this discussion does not give any reason for the strong fluorescence of diamino-tpy **8** in ethanol. Diamino-tpy **8** and monoamino-tpy **3** have the same dialkylamino and pyridyl nitrogens as the hydrogen-bond acceptors, but **8** does not suffer fluorescence quenching at all in ethanol. Therefore, the effect of the protic solvent is not so simple, and has to be studied further.

Conclusion

In this report, the effect of *N*-substitution on the fluorescence properties of 6-amino-tpy (**1**) and 6,6″-diamino-tpy (**6**) were studied. The fluorescence band showed a successive red-shift as the number of *N*-substituted groups increased. The *N*-phenyl substitution resulted in a larger red-shift compared to that of the *N*-alkyl substitution. It was also shown that the susceptivity of the fluorescence to the solvent varied considerably according to the mode of *N*-substitution. Of particular interest, we obtained *N*-substituted derivatives **8** and **9** that exhibited an efficient fluorescence even in ethanol. While the mechanism still needs to be studied, this finding will lead to new tpy derivatives that are capable of exhibiting strong emission even in protic media, and also make tpy a useful fluorophore in a wider range of applications. The results show that *N*-substitution is a useful way to tune both the radiation energy and solvent susceptivity of the fluorescence of amino-tpys.

Experimental

Syntheses of aminoterpyridines **1**,[7] **2–5**,[14] **6**,[7] and **7–10**[14] are described elsewhere. The purity of **1–10** was checked by elemental analysis and the melting point. Spectrophotometric-grade cyclohexane, dichloromethane, acetonitrile and ethanol were obtained commercially.

UV-Vis absorption and fluorescence spectra in the organic solutions were measured with a Shimadzu UV-2500PC spectrophotometer and a Shimadzu RF-5300PC spectrofluorometer, respectively, at 20 °C. The fluorescence quantum yield was calculated using 2-aminopyridine (excitation 285 nm; $\Phi = 0.37$; ethanol) as the standard. Time-resolved emission decay was measured by exciting sample solutions with a nitrogen laser pulse (337 nm). The emission was dispersed with a Hamamatsu Photonics C-2830 disperser and monitored on a Hamamasu Photonics M-2548 streak camera. The rate constants of the radiative (k_r) and non-radiative (k_{nr}) decay were calculated from the following equations, $\tau = (k_r + k_{nr})^{-1}$, $\Phi = k_r/(k_r + k_{nr})$, where τ and Φ are the fluorescence lifetime and the fluorescence quantum yield, respectively.

The ground-state energies of **1–10** were calculated by the DFT method after geometry optimization (B3LYP/6-31G(d)//HF/6-31G(d)).[20] The absorption bands were simulated by the time-dependent DFT method (B3LYP/6-31G(d)//HF/6-31G(d)). The solvation effect was introduced using the polarizable continuum model (PCM)[16] with the solvent parameter of ethanol, ε_r, set at 24.55. These calculations were performed on a Gaussian 03W package,[21] and the results were processed on a Fujitsu CAChe WorkSystem (version 5.5).

Acknowledgements

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