6-Amino-2,2′:6′,2″-terpyridines as highly fluorescent compounds—effect of the number of pyridine rings on fluorescence properties

Toshiki Mutai, Jin-Dong Cheon, Gaku Tsuchiya and Koji Araki *

Institute of Industrial Science, University of Tokyo, 4-6-1, Komaba, Meguro-ku, Tokyo 153-8505, Japan

Received (in Cambridge, UK) 22nd February 2002, Accepted 8th March 2002
First published as an Advance Article on the web 5th April 2002

2,2′:6′,2″-Terpyridine (tpy) was found to exhibit remarkably efficient fluorescence in organic solutions when substituted by 6-amino (**2**, λ_{fl} = 384 nm, Φ = 0.70, dichloromethane) and 6,6″-diamino (**3**, λ_{fl} = 386 nm, Φ = 0.48, dichloromethane) groups. The fluorescence maxima of 6-amino tpys were shifted to longer wavelengths as the solvent polarity increased, whereas the absorption maxima were little affected. In protic solvents, the fluorescence was largely quenched. The absorption and fluorescence bands of **2** and **3** were observed in the same region as those of 6-amino-2,2′-bipyridine, but at much longer wavelengths compared to 2-aminopyridine. These results and detailed analysis of the absorption and fluorescence spectra reveal that the photophysical properties of tpys could be interpreted as resulting from a contribution of the two bipyridyl units within the tpy structures that share the center pyridyl ring; the 6-aminobipyridyl unit appeared to be the fluorescent chromophore of **2** and **3**. Semi-empirical molecular orbital calculations supported the above conclusion.

Introduction

Fluorescent compounds have been utilized in various fields,[1] and there are increasing demands for those having new and multi-functionalities. We have been studying fluorescent oligopyridines as a new series of fluorescent compounds and have evaluated their functionalities. 2,2′:6′,2″-Terpyridine (tpy) is well known for its good coordination ability due to its suitably arranged ring nitrogens. A variety of tpy derivatives have been reported to date,[2] and their transition metal complexes have been extensively examined as photo-excited donor or acceptor[3] units or as components for supramolecular assemblies.[4]

On the other hand, fluorescence properties of tpy derivatives have been much less studied, as they generally show little or no fluorescence. Although there have been some reports on the fluorescence of the protonated species[5,6] and luminescence of zinc(II)[4b,6,7] or cadmium(II)[4b] complexes, only a few free-base tpys have been reported to show noticeable fluorescence. A few exceptional tpys are 4′-(9-anthryl)-tpy[6] with moderate quantum yield (Φ = 0.5) and 5,5″-bis(4-methoxy-2,6-dimethylphenyl)-tpy[8] with markedly strong (Φ = 0.85) blue fluorescence. We also reported[9] the fluorescence properties of 4′-phenyl-tpy derivatives showing moderate quantum yields (Φ = 0.2–0.4) and fluorescence tuning by the intramolecular charge transfer process.

2-Aminopyridine has been known[10] to exhibit strong fluorescence, and in our previous report,[11] introduction of an amino group at the *o*-position of the ring nitrogen of 2,2′-bipyridine (bpy) was effective in obtaining fluorescent bpy derivatives. We extended this strategy to the tpy derivatives, and synthesized a series of amino-substituted tpys.

In the study reported here, the fluorescence properties of amino substituted tpys were examined. The effects of *o*-amino substitution on the photoelectronic properties of tpys were examined by comparing with those of the aminopyridines and amino-bpys.

Results

The molecular structures of tpys used in this study are presented in Fig. 1. Compounds **2**–**5** were prepared by converting the corresponding halo-tpys, which were synthesized by ring forming reactions of Mannich base and pyridinium ketone for **2**, **3**, and **5**,[12] or acetylpyridine and acetone for **4**.[9] Reaction of **2** with propionyl chloride gave **6**.

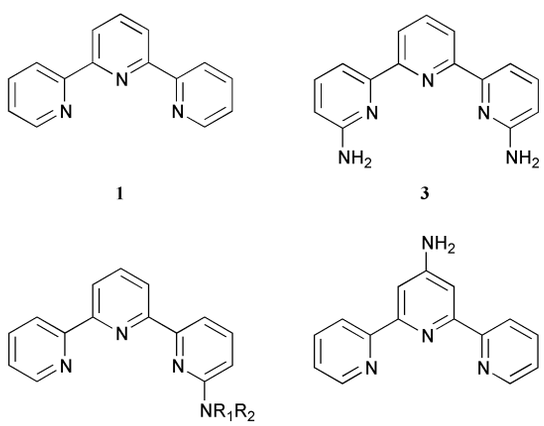

Fig. 1 Molecular structure of 2,2′:6′,2″-terpyridine (tpy) derivatives **1**–**6**.

Fig. 2 shows the absorption and fluorescence spectra of **1**–**3** measured in dichloromethane solutions at 20 °C. The lowest energy absorption band of tpy **1** was shown at 280 nm. As one amino group was introduced at the 6-position of the parent compound **1**, the absorption band at around 325 nm (band-I) appeared with concomitant decrease of the band at around 280 nm (band-II). Introduction of an additional amino group at the 6″-position resulted in an increase of band-I and the disappearance of band-II. These results suggest that band-I and -II might be related to the amino-substituted part and the non-substituted part, respectively, of compounds **1**–**3**. On the other hand, 4′-substitution (**4**) did not affect the absorption spectrum of the parent compound (Table 1).

When the 6-amino group was further modified to dimethyl-

 DOI: 10.1039/b201911f

Table 1 Absorption and fluorescence maxima of tpy derivatives at 20 °C

Compd.	Cyclohexane		Dichloromethane		Ethanol	
	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	279(4.30)	335(<0.01)	280(4.30)	337(<0.01)	280(4.28)	337(<0.01)
2	284,[b] 320(4.13)	366(0.56)	284,[b] 319(4.17)	384(0.70)	283,[b] 324(4.07)	398(0.01)
3	324[c]	364(0.30)	327(4.31)	386(0.48)	330(4.27)	408(0.07)
4	277[c]	347(0.02)	278(4.46)	368(0.02)	278(4.40)	386(<0.01)
5	275(4.41), 348(3.88)	396(0.54)	278(4.41), 354(3.85)	427(0.57)	276(4.39), 346(3.85)	438(0.01)
6	284,[b] 305(4.32)	340(0.05)	289,[b] 306(4.35)	345(0.05)	286,[b] 304(4.30)	350(0.06)

[a] Relative quantum yields were determined by using 2-aminopyridine (Φ = 0.37, excitation at 285 nm, in ethanol) as the standard compound. [b] Shoulder peak. [c] Because of low solubility, the absorption coefficient could not be determined.

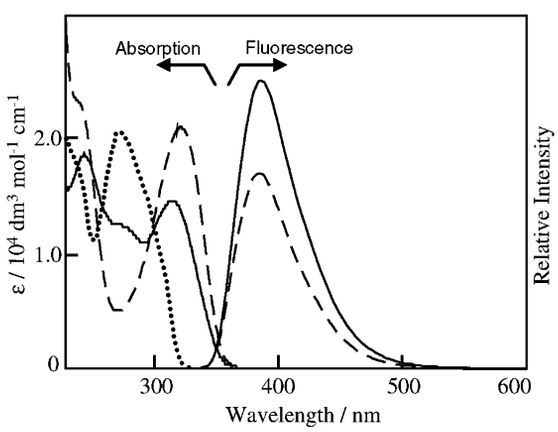

Fig. 2 Absorption and fluorescence spectra of **1** (···), **2** (—) and **3** (- - -) in dichloromethane at 20 °C. The excitation wavelength is 285 nm.

amino (**5**) and amide (**6**), the lowest energy absorption (band-I) of **5** and **6** appeared at longer and shorter wavelengths respectively compared to those of **2**, though the absorption band at around 285 nm (band-II) of **2**, **5**, and **6** was little affected.

Fluorescence maxima of **1**–**6** in dichloromethane are also collected in Table 1. 6-Amino-tpy **2** exhibited remarkably efficient blue fluorescence. The fluorescence quantum yield (Φ) of 0.70 is quite a large value for the free base tpy derivatives. In contrast, 4′-amino-tpy **4** has poor fluorescence ability, indicating that substitution at the 6-position is essential for obtaining the fluorescent amino tpys. Fluorescence of diamino tpy **3** was observed at the same wavelength as **2**, with a rather reduced fluorescence quantum yield. Methylation of the amino group of **2** shifted the fluorescence band more than 40 nm to a longer wavelength. The fluorescence quantum yield became smaller, but still retained a large value (Φ = 0.57). However, conversion of the amino group of **2** to amide **6** largely impaired the fluorescence properties.

The fluorescence intensity of **2**, **3** and **5** increased proportionally to their concentration between 10^{-8} and 10^{-6} mol dm^{-3}, and the excitation spectra were all identical to the corresponding absorption spectra. These results indicated that the fluorescence of 6-amino-tpys was due to monomeric emissions from the lowest excited state (S_1).

In cyclohexane, dichloromethane and ethanol, the absorption maxima of each compound showed little solvent dependence appearing at almost the same position. On the other hand, the fluorescence maxima of **2**–**6** shifted to longer wavelengths as the solvent polarity increased. In addition, the fluorescence of **2** and **3** almost disappeared in ethanol.

Discussion

Photophysical properties of amino tpys

The relation between the number of pyridine rings and the absorption spectrum was examined for several oligopyridine compounds. Table 2 shows the absorption and fluorescence maxima of *o*-amino substituted pyridine (py) and bpy derivatives.

Table 2 Absorption and fluorescence maxima of oligopyridine derivatives in dichloromethane at 20 °C

Compound	λ_{abs}/nm (log ε)	λ_{fl}/nm (Φ^a)
Bpy	283 (3.89)	—(0)
1	280(4.30)	337(<0.01)
2-Amino-py	291 (3.58)	338 (0.33)
6-Amino-bpy	320 (3.97)	385 (0.65)
2	284,[b] 319(4.17)	384(0.70)

[a] Relative quantum yields were determined by using 2-aminopyridine (Φ = 0.37, excitation at 285 nm, in ethanol) as the standard compound. [b] Shoulder peak.

6-Amino-bpy had an absorption band 30 nm longer in wavelength compared to 2-amino-py, which was due to the expansion of the π-electronic system caused by connecting two pyridine rings. On the other hand, the lowest energy absorption band of **2** and **3** (band-I) appeared in the same region as that of the amino bpys, indicating that the third pyridyl ring did not affect the lowest transition energy. Similarly, the absorption bands of both **1** (band-II) and bpy appeared in the same region. It is also to be noted that *o*-amino substitution of bpy and tpy induced a nearly equal red shift (40–50 nm) of their absorption band.

The similarity of the electronic properties of bpys and tpys reveals that bipyridyl or 6-aminobipyridyl domains would be regarded as the units responsible for the lowest energy transition bands of **1**–**3**. Detailed examination of the absorption spectra of **1**–**3** supported this assumption. While **1** and **3** exhibited only band-II and -I, respectively, both bands were found in the absorption spectrum of **2** with a reduced molar absorptivity. It could be explained that **1** and **3** have two bipyridyl units and two 6-aminobipyridyl units respectively, with the center pyridyl ring being shared in each case, while **2** has one of each.

The fluorescence spectra of the *o*-amino substituted oligopyridines had a similar dependence on the number of pyridine rings as the absorption spectra: the fluorescence of 6-amino-bpy was observed at about a 50 nm longer wavelength than that of 2-amino-py, whereas fluorescence of **2** and **3** appeared in the same region as for 6-amino-bpy. The result again showed the small effect of the third pyridyl ring on the lowest transition energy of 6-amino-bpy and -tpys, and therefore, it is concluded that the 6-aminobipyridyl unit could be considered as the fluorescent chromophore of the 6-amino-tpys.

The excitation spectra of **2** showed marked intensity at around 280 nm, indicating that the excitation of band-II emitted strong fluorescence. This is a result of the internal conversion process from the excited bipyridyl to the emitting level (S_1), and it confirms that efficient electronic communication exists between the bipyridyl and 6-aminobipyridyl units within **2**.

Though **2** and **3** were shown to have very similar fluorescence properties to those of 6-amino-bpy, their fluorescent response

to the protic solvents was different. In ethanol, fluorescence of **2** and **3** almost completely disappeared, though that of the 6-amino bpy[11] remained strong (Φ = 0.42). Fluorescence quenching by alcohol molecules has been discussed[13] for various compounds, and some mechanisms have been presented. In the case of **2** and **3**, the vibrational coupling between the amino tpys and ethanol molecules might enhance the radiationless deactivation process, since the strong fluorescence reappeared in solid solutions at 77 K.

Modification of the amino group of 2

Modification of the 6-amino group of **2** caused a large shift of band-I and in contrast, almost had no effect on band-II. This clear difference reveals that the effect of the 6-substituent is limited to the band-I, and supports the idea that the photophysical properties of tpys can be attributed to the combination of the two bipyridyl units.

The fluorescence properties of **5** and **6** were further studied in order to identify the reasons for the reduced fluorescence quantum yields. At 77 K in dichloromethane, weak but clear (**5**) and strong (**6**) yellow–green phosphorescence was observed, whereas phosphorescence from **2** was not detected. A similar result was reported[12] in which 2-dimethylamino py exhibited weak fluorescence and strong phosphorescence compared to 2- amino py at 77 K. These results indicate that the reduced fluorescence quantum yields of **5** (Φ = 0.57) and **6** (Φ = 0.05) are partly due to the enhancement of the intersystem crossing process from the singlet excited state to the triplet excited state.[14]

MO calculation of the amino tpys

Photophysical properties of oligopyridines were further studied using a molecular orbital (MO) calculation. Fig. 3 shows the energy levels and electronic states of the HOMO (π) and the LUMO (π*) of oligopyridines calculated by the MOPAC/PM3 method.

The HOMO–LUMO energy gap (ΔE_{HL}), which corresponds to the lowest energy absorption band of 6-amino-bpy was noticeably smaller than for 2-amino-py, whereas ΔE_{HL} of 6-amino-tpy **2** was the same as that for 6-amino-bpy. These results were consistent with the observed absorption spectra.

Among the tpys, the HOMOs of **2** and **3** were shown to have higher energy levels compared to their parent compound **1**, whereas their LUMO energy levels remained unchanged. Their smaller ΔE_{HL} values well reproduced the experimental results in which band-I appeared on the lower energy side.

Furthermore, the HOMOs of **2** and **3** were localized on the aminopyridyl unit(s), which were very similar to the calculated HOMO of 6-amino-bpy. In addition the configurations of the LUMOs of **2** and **3** were not very different from that of 6-amino-bpy. It should be noted that the LUMO does not directly represent the lowest excited state (S_1), however, these results support the 6-amino-bpy as the chromophoric unit of **2** and **3**.

It is worth noting that similar energy levels and electronic states were obtained for the HOMO-1 of **2** and the HOMO of bpy. Therefore, the HOMO-1 of **2** would be involved in band-II, representing essentially the bipyridyl-localized transition. Thus, the MO calculation well reproduced the lowest energy absorption band of the oligopyridines and supported the interpretation based on the experimental data.

Conclusion

o-Amino substitution endowed tpy with remarkable fluorescence ability. Comparison of the absorption and fluorescence spectra of oligopyridines showed that the 6-aminobipyridyl unit was the key structure in determining the photophysical properties of 6-amino-tpys. Modification of the 6-amino group and the computational MO calculation also supported this conclusion.

As we previously reported,[11] 6-amino-bpy and its derivatives generally exhibited efficient fluorescence, and are chemically and thermally stable compounds. The finding that the excellent properties of 6-amino-bpy are almost totally preserved in 6-amino-tpys may lead to a new strategy of designing pyridine-based fluorescent functional compounds.

Experimental

Methods

The UV–Vis absorption spectra (230–600 nm) were measured with a Shimadzu UV-2500PC spectrophotometer and the luminescence spectra (285–700 nm) were obtained with a Shimadzu RF-5300PC spectrofluorimeter at 20 °C. Relative quantum yields were calculated using 2-aminopyridine in ethanol as a standard (excitation at 285.0 nm, Φ = 0.37). ^{1}H-NMR spectra were recorded on a JEOL JMN-AL500 or a JEOL AL-400 spectrometer in chloroform-*d* with tetramethylsilane as an internal standard. Infra red spectra were measured on a Perkin-Elmer FT-1600. Mass spectra were obtained on a JEOL JMS-D-300 spectrometer by the FAB method. Molecular orbital calculations were performed by MOPAC/PM3 on a CAChe system.

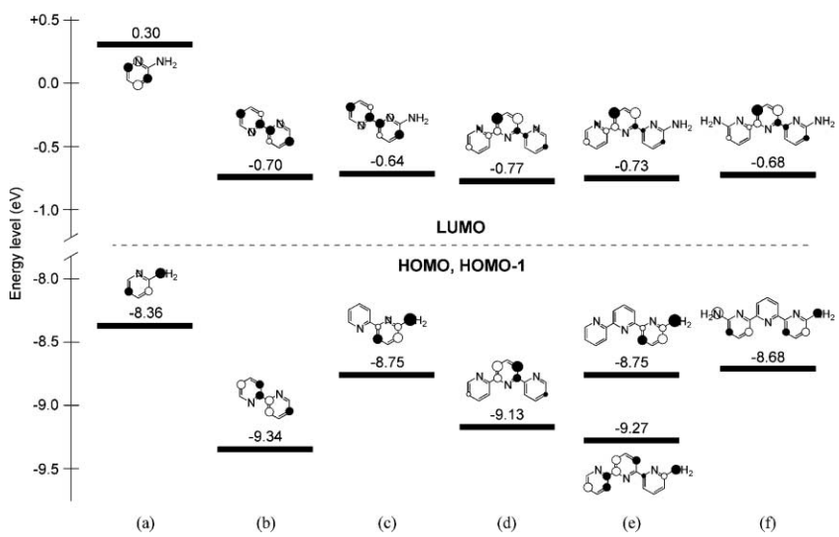

Fig. 3 Calculated LUMO, HOMO, and HOMO-1 of the oligopyridines. (a) 2-Amino-py, (b) bpy, (c) 6-amino-bpy, (d) **1**, (e) **2**, and (f) **3**.

Materials

Spectrophotometric grade ethanol and dichloromethane were purchased from DOJIN Chem. Co. and used as received. Spectrophotometric grade 2-aminopyridine and tpy **1** were obtained commercially. 4′-Amino-tpy **4**[9] and 6-bromo-tpy[12] were prepared according to the literature methods. Syntheses of 6-amino and 6,6′-diamino-bpy are described in our previous report.[11]

6-Amino-2,2′:6′,2″-terpyridine (2). 6-Amino-tpy and 6,6″-diamino-tpy were synthesized by amination of the corresponding bromo derivatives. The typical reaction is as follows: 6-bromo-tpy (0.5 g), was treated with liquid ammonia (60 ml) in an autoclave at 175 °C, 150 atm for 48 h. After the removal of ammonia, residual solid was triturated in hydrochloric acid (1.0 mol dm^{-3}, 100 ml) and insoluble solid was filtered off. The filtrate was basified and extracted with dichloromethane. Recrystallization from hexane gave a yellow powder (65%). Mp 113.1–114.1 °C. Found: C, 72.43; H, 4.85; N, 22.66. Calc. for $C_{15}H_{12}N_4$: C, 72.56; H, 4.87; N, 22.57%. δ_H (400 MHz, $CDCl_3$) 4.54 (2H, br, NH_2), 6.58 (1H, d, 5-H), 7.26 (1H, t, 5″-H), 7.63 (1H, t, 4-H), 7.85 (1H, t, 4′-H), 7.92 (1H, t, 4″-H), 7.98 (1H, d, 3-H), 8.34 (1H, d, 3′-H), 8.41 (1H, d, 5′-H), 8.63 (1H, d, 3″-H), 8.70 (1H, d, 6″-H).

6,6″-Diamino-2,2':6′,2″-terpyridine (3). Yield: 62%. Mp 191.0–192.0 °C. Found: C, 68.57; H, 5.03; N, 26.35. Calc. for $C_{15}H_{13}N_5$: C, 68.42; H, 4.98; N, 26.60%. δ_H (400 MHz, $CDCl_3$) 4.49 (2H, br, NH_2), 6.56 (2H, d, 5,5″-H), 7.60 (2H, t, 4,4″-H), 7.87 (1H, t, 4′-H), 7.97 (2H, d, 3,3″-H), 8.30 (2H, d, 3′,5′-H).

6-Dimethylamino-2,2':6′,2″-terpyridine (5). 6-Bromo-tpy (0.1 g, 0.32 mmol) was treated with hexamethylphosphoramide (3 ml) at 150 °C for 17 h. After cooling to room temperature, water (30 ml) was added, and the mixture was extracted with dichloromethane. The organic layer was washed with water, dried with sodium sulfate, and evaporated to dryness. Recrystallization from hexane gave yellow crystals (65%). Mp 127.2–127.8 °C. Found: C, 73.58; H, 5.76; N, 19.85. Calc. for $C_{17}H_{16}N_4$: C, 73.89; H, 5.84; N, 20.27%. δ_H (400 MHz, $CDCl_3$) 3.20 (6H, s, $N(CH_3)_2$), 6.60 (1H, d, 5-H), 7.25 (1H, t, 5″-H), 7.31 (1H, t, 4-H), 7.64 (1H, t, 4′-H), 7.83–7.94 (2H, m, 3,4″-H), 8.39 (1H, d, 3′-H), 8.46 (1H, d, 5′-H), 8.64 (1H, d, 3″-H), 8.69 (1H, d, 6″-H). FAB-MS: $[M + H]^+$ 277.12.

6-Propionylamino-2,2':6′,2″-terpyridine (6). To a stirring solution of 6-amino-tpy **2** (290 mg, 1.2 mmol) in anhydrous pyridine (1.4 ml) was slowly added propionyl chloride (0.3 ml) at 0 °C under a nitrogen atmosphere. After stirring for 4.5 h, methanol (*ca*. 10 ml) was added and the reaction mixture was poured into an aqueous solution of sodium hydrogencarbonate (0.1 mol dm^{-3}, 100 ml). The yellow precipitate was collected by filtration and purified by column chromatography (aluminum oxide, chloroform). Recrystallization from ethanol–water gave a white solid (70%) mp 161.3–163.1 °C. δ_H (400 MHz, $CDCl_3$) 1.28 (3H, t), 2.47 (2H, q), 7.33 (1H, ddd), 7.85 (1H, ddd), 7.87 (1H, dd), 7.92 (1H, dd), 8.00 (1H, s), 8.26 (1H, d), 8.30 (1H, dd), 8.30 (1H, d), 8.45 (1H, dd), 8.61 (1H, d), 8.70 (1H, m). HRMS (FAB) $[M + H]^+$, 305.1402. Calc. for $C_{18}H_{17}N_4O$, ($M + H$), 305.1402).

Acknowledgements

This work was partly supported by a Grant-in-Aid for Scientific Research (No. 10450339) from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

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