6-Amino-2,2′-bipyridine as a new fluorescent organic compound

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6,6′-Diamino-2,2′-bipyridine (1a) has been found to exhibit a strong fluorescence in the near-UV region. Some amino and/or chloro substituted bipyridines (bpys) have been synthesized and studied to show that only 6-amino-substituted derivatives exhibited a strong emission. The emission of 6-amino-6′-chloro-bpy (3a) was the strongest (λ_{max} = 429.0 nm; Φ = 0.78 in ethanol) among them. On the other hand, little or no emission was observed for monochloro-, dichloro- and 4-amino- derivatives.

The application of fluorescent organic compounds to optical devices and photo-functionalized materials is a topic of current interest.[1] For these uses, the chemical and thermal stability of the compounds are essential factors in addition to their colour and higher emission efficiency. But because of limitations in the modification of existing fluorophores to meet the conditions mentioned above, new series of fluorophores are actively studied.

We have been studying the properties and functionality of 6,6′-diamino-2,2′-bipyridine (**1a**) and its derivatives,[2–4] and we recently found that **1a** displayed a relatively strong emission in the near-UV region. 2,2′-Bipyridine (bpy) is a π-electron deficient compound and needs much more drastic conditions than pyridine for both electrophilic and nucleophilic substitution. Though synthesis of its derivatives is rather complicated, the derivatives are inactive for ring-directed reactions and are thermally stable in general.

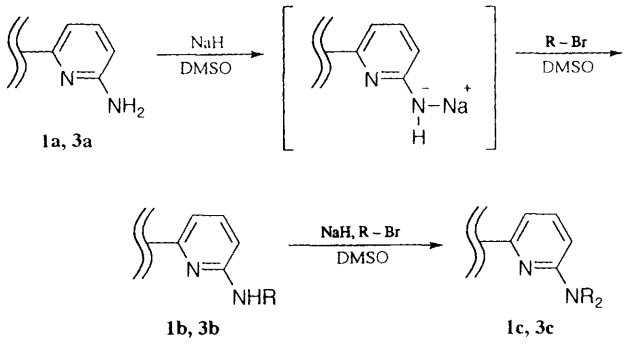
However, relatively little has been known about the fluorescent property of bpy and its derivatives. The bpy derivatives are generally non-fluorescent,[5] though 3,3′-dimethyl[6] and 3,3′-dihydroxy[7] bpys have been reported to show fluorescence.

In this report, we describe the fluorescent property of a series of amino- and chloro-substituted bpys at 4- and/or 6-position(s). Among the bpys tested in this study, asymmetrically substituted 6-amino-6′-chloro-bpy (**3a**) was found to exhibit a remarkably strong emission.

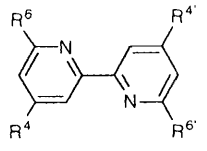
Results and discussion

Syntheses of 2,2′-bipyridine derivatives

6,6′-Dibromo-bpy obtained by the coupling of 2,6-dibromopyridine was converted to 6,6′-diamino-bpy (**1a**) with liquid ammonia according to the method previously reported.[3] A small amount of 6-amino-6′-bromo-bpy (**4**) was also obtained in this reaction. Similar treatment of 6,6′-dichloro-bpy (**12**) gave 6-amino-6′-chloro-bpy (**3a**). 6-Amino- (**2**), 4-amino- (**5**), 4,4′-diamino- (**6**) and 4-amino-6′-chloro-substituted (**8**) bpys were synthesized from corresponding chloro derivatives with ammonia gas in phenol/acetamide solution.[8] An attempt to prepare 6,6′-diamino (**1a**) and 6-amino-6′-chloro- (**3a**) derivatives from 6,6′-dichloro-bpy (**12**) by the same procedure was unsuccessful; 6,6′-diphenoxide and 6-amino-6′-phenoxide were obtained instead. 4,6′-Diamino- and 6-amino-4′-chloro-derivatives were not obtained because of the lower reactivity of chlorine at the 6-position than that at the 4-position. 4-Amino-4′-chloro-bpy (**7**) was prepared from 4-chloro-bpy (**9**) *via* *N*′-



Scheme 1 *N*-Alkylation of aminobipyridine



	R^4	R^6	$R^{4'}$	$R^{6'}$
6-Amino-				
1a	H	NH_2	H	NH_2
2	H	NH_2	H	H
3a	H	NH_2	H	Cl
4	H	NH_2	H	Br
4-Amino-				
5	NH_2	H	H	H
6	NH_2	H	NH_2	H
7	NH_2	H	Cl	H
8	NH_2	H	H	Cl
Monochloro-				
9	Cl	H	H	H
10	H	Cl	H	H
Dichloro-				
11	Cl	H	Cl	H
12	H	Cl	H	Cl
6-Alkylamino-				
1b	H	NH(Hx)	H	NH(Hx)
1c	H	NPr_2	H	NPr_2
3b	H	NHPr	H	Cl
3c	H	NPr_2	H	Cl

Hx = 1-Hexyl

Table 1 Absorption and emission maxima of substituted 2,2′-bipyridines at 20 °C

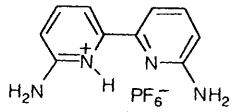
Compd.	Mp/°C	pK_a	Ethanol			Cyclohexane		
			λ_{abs}/nm (log ε)	λ_{em}/nm (Φ)	$\Delta\nu/10^3$ cm^{-1}	λ_{abs}/nm (log ε)	λ_{em}/nm (Φ)	$\Delta\nu/10^3$ cm^{-1}
1a	185–186	6.7	335.0 (4.123)	404.0 (0.45)	5.1	327.0 (4.224)	364.5 (0.49)	3.1
1d	—		372.0 (4.145)	470.5 (0.50)	5.6	—[a]	—[a]	
2	92.1–92.8	5.8	325.5 (3.900)	413.5 (0.42)	6.6	319.5 (3.972)	364.5 (0.46)	3.9
3a	103.5–104.4	5.7	331.0 (3.951)	431.0 (0.78)	7.0	324.5 (4.029)	372.5 (0.79)	4.0
4	115.5–116.0	5.6	331.0 (3.937)	431.5 (0.48)	7.0	326.0 (4.032)	375.5 (0.27)	4.0
5	126.5–127.5	8.1	277.5 (3.955)	397.0 (~ 10^{-2})		279.0 (4.053)	— (0)	
6	276–277	8.8	295.0sh[b]	— (0)		—[a]	—[a]	
7	155–157	7.4	279.5 (3.978)	— (0)		283.0 (3.995)	— (0)	
8	137.0–138.5	7.7	319.0 (4.253)	384.0 (0.05)		300.0 (4.212)	353.0 (~ 10^{-2})	
9	71.4–72.2	3.8	281.5 (4.170)	— (0)		282.0 (4.178)	— (0)	
10	60.0–60.4	3.7	289.0 (4.175)	— (0)		289.5 (4.205)	— (0)	
11	129–130	—[c]	281.0 (4.100)	— (0)		281.0 (4.163)	— (0)	
12	220–221	—[c]	291.5 (4.163)	— (0)		293.0 (4.275)	— (0)	
2-Aminopyridine	59–60	6.9	295.0 (3.621)	347.5 (0.37)	5.1	291.5 (3.561)	322.5 (0.20)	3.3

[a] Insoluble. [b] sh: shoulder peak. [c] Insoluble in water.

Table 2 Absorption and emission maxima of 6-alkylamino-2,2′-bipyridine at 20 °C

Compd.	Mp/°C	Ethanol		Cyclohexane	
		λ_{abs}/nm (log ε)	λ_{em}/nm (Φ)	λ_{abs}/nm (log ε)	λ_{em}/nm (Φ)
1a	185–186	335.0 (4.123)	404.0 (0.45)	327.0 (4.224)	364.5 (0.49)
1b	57–58	347.5 (4.098)	416.0 (0.26)	340.5 (4.136)	384.5 (0.35)
1c	86.1–86.4	354.0 (4.052)	415.5 (0.23)	352.5 (4.096)	398.5 (0.45)
3a	103.5–104.4	331.0 (3.951)	431.0 (0.78)	324.5 (4.029)	372.5 (0.79)
3b	liquid	349.5 (3.865)	444.0 (0.49)	344.0 (3.925)	396.0 (0.62)
3c	liquid	362.5 (3.830)	450.0 (0.34)	363.5 (3.765)	419.5 (0.45)

oxidation, introduction of the nitro group at the 4′-position and finally reduction of the 4′-nitro group to the amino group. 6,6′-Diamino-2,2′-bipyridinium hexafluorophosphate (**1d**) was prepared by addition of sodium hexafluorophosphate to **1a** in dilute hydrochloric acid.



1d

The 6-amino group of **1a** and **3a** is not readily reactive, and alkylbromides did not react with the 6-amino group under common experimental conditions. It required prior metallation of the amino nitrogen with sodium hydride in dimethylsulfoxide (DMSO), and subsequent addition of alkylbromide gave the corresponding *N*-alkylated derivateves (Scheme 1).[9]

Melting points of bpys are generally high (100 ~ 300 °C), except for some mono-substituted and *N*-alkylated derivatives (Tables 1 and 2). The pK_as of **1a**–**10** were determined from absorption spectral titrations in aqueous solutions,[2] and are included in Table 1. The pK_a values represent basicity of the ring nitrogen of the bpys, and the basicity increased by introduction of the electron-donating amino-substituent.

Emission spectra of 6,6′-diamino-2,2′-bipyridine 1a

An ethanolic solution of **1a** showed purple fluorescence upon irradiation in UV light. Absorption and fluorescence spectra of **1a** were measured in ethanol and in cyclohexane at 20 °C (Fig. 1). The emission maximum of **1a** was at 364.5 nm in cyclohexane and at 404.0 nm in ethanol with a relatively high quantum yield (Table 1). The shape of the excitation spectrum was essentially the same as that of the absorption spectrum. Therefore excitation at any points of the absorption band leads to the efficient conversion into the lower-lying emitting state. As the absorption and emission intensity of **1a** increased linearly with concentration, the observed emission was obviously from the monomeric species but not from the dimer or excimer. A freeze–thaw deaeration cycle of the solution did not increase the relative quantum yield, showing that the emission of **1a** was little affected by oxygen dissolved in the solution.

First protonation to **1a** occurs at the ring nitrogen as previously reported.[3] Both absorption and emission spectra of the protonated-form **1d** appeared at longer wavelength (Table 1), and the colour of the emission became bright blue. The molar absorption coefficient and the quantum yield of **1d** (log ε = 4.15; Φ = 0.50) were practically the same as those of **1a** (log ε = 4.11; Φ = 0.45). This indicates that the band at 372.0 is a π–π^* transition, since the protonation to the ring nitrogen would decrease the n–π^* transition considerably.[10] The results of MO calculations also support this assignment. A simulated absorption spectrum of **1a** by ZINDO (Cl = 8) agreed with the observed spectrum, and the lowest energy transition was ascribed to the transition from the ground state ^1B_g (the highest π orbital) to the excited state ^1A_u (the lowest π^* orbital).

2-Aminopyridine shows emission at the UV region in moderate yield (Table 1),[11] and has been used as a fluorescent label.[11] Compared to 2-aminopyridine, both the absorption and the emission bands of **1a** and **1d** appeared at longer wavelength showing purple to blue emission, and the quantum yields are higher (Table 1). It has been well demonstrated in previous studies that bpy and its derivatives have high thermal and chemical stability.[5] The amino groups of **1a** are not readily oxidized,[4] and their derivatives are proven to be stable enough under oxidative conditions.[12] Therefore, the fluorescent bpy derivative **1a** has suitable properties as a fluorophore.

Amino- and chloro-substituted bpys

Contrary to 6,6′-diamino-bpy **1a**, 4,4′-diamino-bpy **6** did not show any emission at all. Other 4-amino-bpys **5**, **7**, **8** also showed no or only a weak emission (Φ ~ 10^{-2}, Table 1). It is

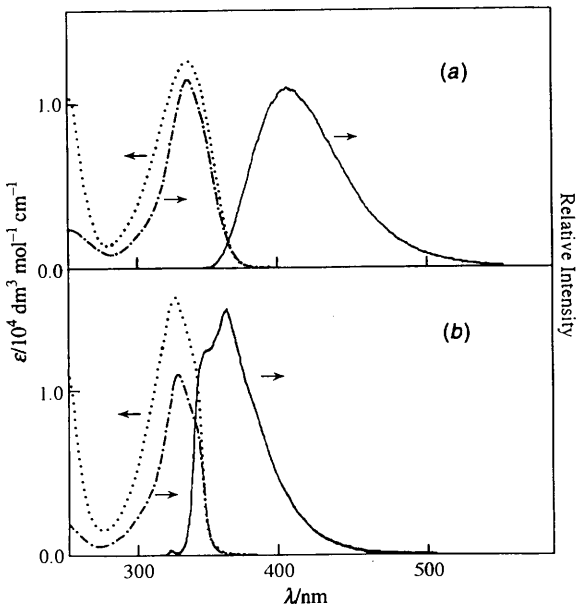


Fig. 1 Absorption (· · ·), emission (——) and excitation (– · – · –) spectra of 6,6′-diamino-2,2′-bpy (**1a**); (*a*) in ethanol, (*b*) in cyclohexane at 20 °C. Excitation at 285 nm.

worth noting that 4-aminopyridine showed only a weak emission (λ_{em} = 319.0 nm; $\Phi < 10^{-3}$, in ethanol), though 2-aminopyridine exhibited an emission of moderate strength. The substitution position of the amino group is an important factor for the fluorescent property. Monochloro derivatives **9**, **10** and dichloro derivatives **11**, **12** showed no emission regardless of the position of substitution. Deaeration by the freeze–thaw method of the solution of **5**–**12** did not improve the quantum yields. These results indicate that amino-substitution at the 6-position is essential for bpy to exhibit an efficient emission.

Other 6-amino-substituted bpys **2**, **3a** and **4** also showed an effective emission in the near-UV region. The emission of 6-amino-bpy **2** was in the same region as **1a** in moderate yield ($\Phi > 0.4$, Table 1). Bearing one amino group is sufficient for bpy to be fluorescent. 6-Amino-6′-chloro-bpy **3a** exhibited a remarkably strong fluorescence ($\Phi \sim 0.8$) which was about twice as strong as other 6-amino-derivatives, though 6-chloro-bpy **10** showed no fluorescence. The electronic absorption and emission spectra of another 6-amino-6′-halo-bpy **4** were observed in the same area as **3a**. The lower values of the fluorescence quantum yield may be due to the heavy atom effect of 6′-bromine.

The emission maxima of 6-amino-bpys **1a**, **2**, **3a** and **4** are solvent-dependent, though their absorption maxima are not. The difference between the absorption and emission maxima in cm^{-1} unit, $\Delta\nu$, is much larger in ethanol than in cyclohexane. These indicate considerable stabilization of the excited emitting state (S_1) in ethanol, and suggest that the S_1 state has a polar nature. The $\Delta\nu$ values of the asymmetrically substituted bpys **2**, **3a** and **4** are relatively large compared to that of **1a**. The compounds **1a** and **3a** showed a single-exponential emission-decay curve in ethanol, and the emission life time was 2.6 and 9.1 ns, respectively. The asymmetrically substituted **3a** has a remarkably longer life time than **1a**. Therefore, the intramolecular charge transfer process between two pyridine rings may be involved in the excited state of **3a**,[13] and the resultant highly polar excited state should be stabilized with ethanol.

6-Alkylamino-bpys

As it has been shown that the 6-amino substitution is essential for bpy to be fluorescent, the effects of amino-*N*-alkylation on **1a** and **3a** was examined. Introduction of alkyl groups reduced melting points of the bpys, and **3b** and **3c** were obtained as viscous liquids. Alkylation of the amino group increases the electron donating ability of the substituent. The pK_a value of **1b** increased from 6.4 of **1a** to 6.8 in water–dioxane (50:50) solution, confirming that the electron density of the bipyridine ring was increased by *N*-alkylation. 6-Alkylamino-bpys **1b**,**c** and **3b**,**c** also showed relatively strong emission, and they exhibited the bathochromic shift of both absorption and emission bands (Table 2). Therefore *N*-alkylation can be a convenient method to tune the colour of the emission without deterioration of the emission properties of 6-amino-bpys. However, slight reduction of $\Delta\nu$ was observed in this case, suggesting that the difference in the electron affinity of two substituents is not the decisive factor in the large value of $\Delta\nu$.

Conclusions

6-Amino-derivatives of bpy have good properties as a fluorescent organic compound such as the large value of $\Delta\nu$, efficient short-VIS fluorescence and high thermal and chemical stability. Among the 6-amino-substituted bpys, the asymmetrically substituted **3a** exhibited the remarkably strong fluorescence with a large $\Delta\nu$ (7.0×10^3 cm^{-1}, in this case 100 nm) in ethanol, though it is not yet clear what enhances the radiative process and what are the factors for large $\Delta\nu$. Until now, only a little has been known about the fluorescent properties of bpys. It is worth noting that the 6-amino-bpys also display a strong blue emission in the solid state. This report has demonstrated that the 6-amino-substituted bpys can be a new series of useful fluorophores. Since the bpy derivatives are well known to have a variety of functionalities,[14] fluorescent properties of 6-amino-substituted bpys may contribute further to their high functionality.

Experimental

Methods

The UV–VIS absorption spectra were measured with a JASCO Ubest-50 spectrophotometer and emission spectra were obtained with a JASCO FP-770 spectrofluorometer at 20 °C. ^{1}H NMR spectra were recorded on a JEOL GX-270, EX-270 or JNM-FX90Q spectrometer in chloroform-d or DMSO-d_6 with tetramethylsilane as an internal standard. Infrared spectra were measured on a JASCO IR-810. Mass spectra were obtained on a HITACHI M-80B or a JEOL JMS-D-300 spectrometer by the EI method. Relative quantum yields were calculated using 2-aminopyridine in ethanol as a standard (excitation at 285.0 nm, $\Phi = 0.37$). The emission life time was investigated by exciting the sample with a nitrogen laser pulse (337 nm). The emission was then dispersed with a HAMAMATSU Photonics C-2830 disperser and monitored on a HAMAMATSU Photonics M-2548 streak camera. MO calculations were performed with CAChe system on an Apple Macintosh Centris 650. The molecular structure was optimized by MOPAC PM3 and the absorption spectrum was simulated by ZINDO (CI = 8).

Materials

Spectrophotometric grade ethanol and cyclohexane were purchased from DOJIN Chem. Co. and used as received. Other chemicals were also obtained commercially. Dimethylsulfoxide (DMSO) was dried over calcium hydride and then distilled under reduced pressure. The following bpys were synthesized according to the literature method and their structures were confirmed by ^{1}H NMR, IR and mass spectrometry: 2,2′-bipyridine *N*-oxide,[15] 6,6′-diamino-2,2′-bipyridine (**1a**),[3] mp 185–186 °C (lit.,[3] 185–186 °C), 4,4′-dichloro-2,2′-bipyridine (**11**),[16] mp 129–130 °C (lit.,[16] 133–134 °C), 6,6′-dichloro-2,2′-bipyridine (**12**),[17] mp 220–221 °C (lit.,[17] 218–219 °C).

6,6′-Bis(hexylamino)-2,2′-bipyridine 1b. A suspension of sodium hydride (6 mmol) in dry (DMSO, 10 ml) was stirred

under nitrogen for 20 min at room temperature, then for 40 min at 70 °C to generate dimethylsulfinylcarbanion [$CH_3S(O)CH_2^-Na^+$], which was added dropwise to a solution of **1a** (0.50 g, 2.7 mmol) in dry DMSO (5 ml) at room temperature. To the resulting red solution was then added 1-bromohexane (1.07 g, 6.5 mmol) and stirred for 5 min. After 10 ml of water was added, the reaction mixture was extracted with 3 × 30 ml of dichloromethane. The solution was dried over sodium sulfate and evaporated to a small volume. It was then applied to a silica gel chromatography column and eluted with a mixture of dichloromethane–ethyl acetate (2:1 v/v). The solution was evaporated to give yellow solid (0.37 g, 39%), mp 57–58 °C (Found: C, 74.75; H, 9.8; N, 16.05. Calc. for $C_{22}H_{34}N_4$: C, 74.5; H, 9.7; N, 15.8%); δ(270 MHz, $CDCl_3$) 0.90 (6 H, t, CH_3), 1.32–1.68 (16 H, m, $NCH_2[CH_2]_4$), 3.30 (4 H, q, NCH_2), 4.55 (2 H, br, NH), 6.38 (2 H, d, 5,5′-H), 7.52 (2 H, t, 4,4′-H) and 7.57 (2 H, d, 3,3′-H).

6,6′-Bis(dipropylamino)-2,2′-bipyridine 1c. Essentially the same procedure as **1b**, except that metallation and subsequent alkylation reactions were repeated five times with ten equiv. of both sodium hydride and 1-bromopropane. Eluted with benzene. Recrystallized from methanol as yellow plates (30%), mp 86.1–86.4 °C (Found: C, 74.5; H, 10.0; N, 15.7. Calc. for $C_{22}H_{34}N_4$: C, 74.5; H, 9.7; N, 15.8%); δ(270 MHz, $CDCl_3$) 0.84 (12 H, t, CH_3), 1.68 (8 H, m, CH_2CH_3), 3.45 (8 H, t, NCH_2), 6.42 (2 H, d, 5,5′-H), 7.50 (2 H, t, 4,4′-H) and 7.59 (2 H, d, 3,3′-H).

6-Amino-6′-chloro-2,2′-bipyridine 3a. The reaction conditions were the same as for **1a**.[3] Mp 103.5–104.4 °C (Found: C, 58.4; H, 4.0; N, 20.2. $C_{10}H_8ClN_3$ requires C, 58.4; H, 3.9; N, 20.4%); δ(90 MHz, $CDCl_3$) 4.53 (2 H, br, NH), 6.54 (1 H, dd, 5-H), 7.28 (1 H, dd, 5′-H), 7.54 (1 H, dd, 4-H), 7.67 (1 H, d, 3-H), 7.72 (1 H, t, 4′-H) and 8.22 (1 H, d, 3′-H).

6-Propylamino-6′-chloro-2,2′-bipyridine 3b and 6-dipropylamino-6′-chloro-2,2′-bipyridine 3c. Essentially the same procedure as **1b**, except that six equiv. of both sodium hydride and 1-bromopropane were reacted. The mixture of **3b** and **3c** was obtained after three metallation and subsequent alkylation cycles. It was placed on a silica gel column and eluted with benzene–hexane (1:1 v/v) to give **3c**, then with benzene to give **3b**. **3b**: Yellow liquid (27.5%) (Found: C, 63.1; H, 6.0; N, 16.9. Calc. for $C_{13}H_{14}ClN_3$: C, 63.0; H, 5.7; N, 17.0%); δ(270 MHz, $CDCl_3$) 1.00 (3 H, t, CH_3), 1.69 (2 H, m, CH_2CH_3), 3.32 (2 H, q, NCH_2), 4.57 (1 H, br, NH), 6.45 (1 H, d, 5-H), 7.55 (1 H, t, 4-H), 7.67–7.75 (2 H, m, 3-H, 4′-H) and 8.26 (1 H, dd, 3′-H). **3c**: Yellow liquid (32.8%) (Found: C, 66.2; H, 7.3; N, 14.8. Calc. for $C_{16}H_{20}ClN_3$: C, 66.3; H, 7.0; N, 14.5%); δ(270 MHz, $CDCl_3$) 0.99 (6 H, t, CH_3), 1.68 (4 H, m, CH_2CH_3), 3.47 (4 H, t, NCH_2), 6.50 (1 H, d, 5-H), 7.27 (1 H, d, 5′-H), 7.52 (1 H, t, 4-H), 7.63 (1 H, d, 3-H); 7.72 (2 H, t, 4′-H) and 8.27 (1 H, d, 3′-H).

6-Amino-6′-bromo-2,2′-bipyridine 4. The crude product of **1a** was chromatographed on a silica gel column and eluted with ethyl acetate to give a small amount of **4** (recrystallized from benzene–hexane). Mp 115.5–116.0 °C; δ(270 MHz, $CDCl_3$) 4.49 (2 H, br, NH), 6.56 (1 H, d, 5-H), 7.44 (1 H, d, 5′-H), 7.54–7.65 (2 H, m, 4,4′-H), 7.76 (1 H, d, 3-H) and 8.26 (1 H, d, 3′-H) (Found: $M^+ + 2$, 250.9857; M^+, 248.9874. Calc. for $C_{10}H_8BrN_3$, M, 248.9894).

6,6′-Diamino-2,2′-bipyridinium hexafluorophosphate ($[H_2NC_5H_3N\text{-}C_5H_3N^+(H)NH_2]PF_6^-$) 1d. To a solution of **1a** (10 mg) in dilute hydrochloric acid (pH 3–4) was added saturated aqueous ammonium hexafluorophosphate to give a white solid precipitate. The precipitate was collected, washed with dilute hydrochloric acid and dried *in vacuo*; recrystallized from ethanol to afford **1d** as yellow needles (11.6 mg, 65%); sublimed (Found: C, 36.0; H, 3.7; N, 16.6. Calc. for $C_{10}H_{11}F_6N_4P$: C, 36.2; H, 3.3; N, 16.9%).

6-Amino-2,2′-bipyridine 2. Typical reaction conditions for converting the chloro group of bpy into an amino group are as follows: into a mixture of corresponding chloro-bpy (**10**; 0.5 g), acetamide (1.5 g) and phenol (4.0 g) was bubbled ammonia gas and maintained at 160 °C for 24 h. Aqueous sodium hydroxide was added to basify the cooled reaction mixture and extracted with dichloromethane which was then washed with dilute aqueous sodium hydroxide. After being dried over magnesium sulfate, the solvent was evaporated and residue was placed on a silica gel column. The first fraction eluted by dichloromethane gave 6-phenoxy-bpy, and a subsequent fraction eluted by ethyl acetate yielded **2** (0.098 g, 17%). Mp 92.1–92.8 °C (lit.,[18] 89 °C).

4-Amino-2,2′-bipyridine 5. Compound **5** was prepared as described for **2** from **9**. The first fraction eluted by ethyl acetate gave **5** (62%). Formation of 4-phenoxide was not observed. Mp 126.5–127.5 °C (lit.,[19] 124–125 °C).

4,4′-Diamino-2,2′-bipyridine 6. Prepared in the same reaction conditions as **2** from **11**. Addition of aqueous sodium hydroxide to the reaction mixture afforded the product as a precipitate, 87%, mp 276–277 °C (lit.,[20] 277–278 °C).

4-Amino-6′-chloro-2,2′-bipyridine 8. Similar amination of 4,6′-dichloro-2,2′-bpy (1.0 g),[16] and elution by chloroform yielded **8** (0.15 g, 18%). Mp 137.0–138.8 °C (Found: C, 58.3; H, 3.8; N, 20.0. Calc. for $C_{10}H_8ClN_3$: C, 58.4; H, 3.9; N, 20.4%); δ(90 MHz, $CDCl_3$) 6.27 (2 H, br, NH), 6.57 (1 H, dd, 5-H), 7.49 (1 H, dd, 5′-H), 7.55 (1 H, d, 3-H), 7.93 (1 H, t, 4′-H), 8.11 (1 H, d, 6-H) and 8.30 (1 H, dd, 3′-H).

4-Amino-4′-chloro-2,2′-bipyridine 7. To a solution of 4-chloro-bpy (**9**; 1.0 g) in chloroform (4 ml) was added dropwise a solution of *m*-chloroperbenzoic acid (0.9 g) in chloroform below 0 °C. The reaction mixture was stirred at 0 °C for 30 min, then at room temperature for 14 h. It was washed with 5% aqueous sodium carbonate and dried over magnesium sulfate. After the solvent was evaporated, the residue was applied to a silica gel chromatrography column and eluted with dichloromethane to give 4-chloro-bpy *N*′-oxide as the second band, whose structure was confirmed from the characteristic infrared absorption band of *N*′-oxide (1240 cm^{-1}) and mass spectrometry (M^+, 206). Then a mixture of 4-chloro-bpy *N*′-oxide (1.0 g), 98% sulfuric acid (2 ml), fuming sulfuric acid (1 ml) and fuming nitric acid (2 ml) was heated at 100 °C for 4 h. It was poured into crushed ice and stirred for 30 min. Sodium carbohydrate was added to give a yellow precipitate, which was confirmed as 4-chloro-4′-nitro-bpy *N*′-oxide from the infrared absorption band of the 4′-nitro group (1350 cm^{-1}) and mass spectrometry (M^+, 251). The precipitate (0.5 g) and tin chloride dihydrate (4.0 g) in concentrated hydrochloric acid (7 ml) was heated at 100 °C for 2 h. After cooling, the mixture was neutralized with aqueous sodium carbohydrate and then extracted with dichloromethane. The extract was dried ($MgSO_4$) and evaporated to afford **7** (0.14 g, 35%). Mp 155–157 °C (Found: C, 58.2; H, 4.0; N, 20.3. Calc. for $C_{10}H_8ClN_3$: C, 58.4; H, 3.9; N, 20.4%); δ(90 MHz, DMSO-d_6) 6.25 (2 H, br, NH), 6.57 (1 H, dd, 5-H), 7.50 (1 H, dd, 5′-H), 7.64 (1 H, d, 3-H), 8.12 (1 H, d, 6-H), 8.33 (1 H, d, 3′-H) and 8.60 (1 H, d, 6′-H).

4-Chloro-2,2′-bipyridine 9, 6-chloro-2,2′-bipyridine 10. To ice-cooled phosphoryl oxychloride (15 ml) was added 2,2′-bipyridine *N*-oxide[15] (1.0 g) in portions and the mixture was then refluxed for 5 h. Excessive phosphoryl oxychloride was evaporated and the residue was basified with an icy concentrated solution of sodium hydroxide to precipitate some solid. The collected solid was chromatographed with light petroleum to give **10** (0.44 g, 40%) and then with chloroform to give **9** (0.40 g, 36%). **9**: Mp 71.4–72.2 °C (lit.,[21] 70–71 °C); δ(90 MHz, $CDCl_3$) 7.25–7.40 (2 H, m, 5,5′-H), 7.82 (1 H, t, 4′-H), 8.40 (1 H, d, 3′-H), 8.44 (1 H, dd, 3-H), 8.55 (1 H, d, 6′-H) and 8.67 (1 H, d, 6-H). **10**: Mp 60.0–60.4 °C (lit.,[22] 61–62 °C); δ(90 MHz, $CDCl_3$) 6.27 (2 H, br, NH), 7.30 (1 H, d, 5′-H), 7.38 (1 H, d, 5-H), 7.77 (1 H, t, 4′-H), 7.82 (1 H, t, 4-H), 8.36 (1 H, d, 3′-H), 8.42 (1 H, dd, 3-H) and 8.65 (1 H, d, 6′-H).

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References

1 (*a*) R. A. Hann, *Mol. Cryst. Liq. Cryst.*, 1993, **236**, 65; (*b*) S. A. Soper, L. B. McGown and I. M. Warner, *Anal. Chem.*, 1994, **66**, 428R.
2 (*a*) M. Yamada, K. Araki and S. Shiraishi, *Bull. Chem. Soc. Jpn.*, 1988, **61**, 2208; (*b*) K. Araki, M. Fuse, N. Kishii and S. Shiraishi, *Bull. Chem. Soc. Jpn.*, 1990, **63**, 1299.
3 N. Kishii, K. Araki and S. Shiraishi, *Bull. Chem. Soc. Jpn.*, 1984, **57**, 2121.
4 K. Araki, M. Fuse, N. Kishii and S. Shiraishi, *Bull. Chem. Soc. Jpn.*, 1992, **65**, 1220.
5 L. A. Summers, *Adv. Heterocycl. Chem.*, 1984, **35**, 281.
6 H. Bulska and J. Kotlicka, *Pol. J. Chem.*, 1979, **53**, 2103.
7 (*a*) L. H. Vogt and J. G. Wirth, *J. Am. Chem. Soc.*, 1971, **93**, 5402; (*b*) H. Bulska, *Chem. Phys. Lett.*, 1983, **98**, 398; (*c*) H. Langhals and S. Pust, *Chem. Ber.*, 1985, **118**, 4674; (*d*) J. Sepiol, H. Bulska and A. Grabowska, *Chem. Phys. Lett.*, 1987, **140**, 607.
8 S. Ogawa and N. Goto, *Kogyo Kagaku Zasshi*, 1970, **74**, 83.
9 S.-H. Noh, K. Araki and M. Seno, *J. Mater. Chem.*, 1993, **3**, 755.
10 J. G. Calvert and J. N. Pitts, Jr., *Photochemistry*, Wiley, New York, 1967, p. 261.
11 A. Weisstuch and A. C. Testa, *J. Phys. Chem.*, 1968, **72**, 1982.
12 M. Yamada, S. Ochi, H. Suzuki, A. Hisazumi, S. Kuroda, I. Shimao and K. Araki, *J. Mol. Cat.*, 1994, **87**, 195.
13 G. J. Kavarnos and N. J. Turro, *Chem. Rev.*, 1986, **86**, 401.
14 (*a*) D. S. Lawrence, T. Jiang and M. Levett, *Chem. Rev.*, 1995, **95**, 2229; (*b*) F. C. J. M. van Veggel, W. Verboom and D. M. Reinhoudt, *Chem. Rev.*, 1994, **94**, 279; (*c*) G. Denti, S. Serroni, S. Campagna, A. Juris and V. Balzani, *Mol. Cryst. Liq. Cryst.*, 1993, **234**, 79.
15 D. Wenkert and R. B. Woodward, *J. Org. Chem.*, 1983, **48**, 283.
16 E. C. Constable and K. R. Seddon, *Tetrahedron*, 1983, **39**, 291.
17 S. Ogawa and S. Shiraishi, *J. Chem. Soc., Perkin Trans. 1*, 1980, 2527.
18 F. H. Burstall, *J. Chem. Soc.*, 1938, 1662.
19 M. J. Cook, A. R. Katritzky and S. Nadji, *J. Chem. Soc., Perkin Trans. 2*, 1978, 1215.
20 G. Maerker and F. H. Case, *J. Am. Chem. Soc.*, 1958, **80**, 2745.
21 M. J. Cook, A. P. Lewis, G. S. G. McAuliffe, V. Skarda and A. J. Thomson, *J. Chem. Soc., Perkin Trans. 2*, 1984, 1293.
22 F. H. Case, *J. Org. Chem.*, 1966, **31**, 2398.

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