Phenyl-substituted 2,2′:6′,2″-terpyridine as a new series of fluorescent compounds—their photophysical properties and fluorescence tuning

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Several phenyl-substituted 2,2′:6′,2″-terpyridines (tpy) were synthesized and it was found that 4′-phenyl tpy (ptp, **3**) exhibited the most effective fluorescence, whose quantum yield was up to 0.64 in cyclohexane. For further study on tuning the fluorescence properties of ptp, different substituents were introduced into the *p*-position of the phenyl group. While Br- **10**, Cl- **11**, and CH_3-ptp **12** showed their absorption and fluorescence in the same region as **3**, those of NH_2- **14** and Me_2N-ptp **15** were observed at much longer wavelengths. In addition, fluorescence maxima of **14** and **15** showed large (>130 nm) solvent dependence. The difference between ground and excited state dipole moment ($\Delta\mu$) for **15** was estimated to be 15.2 D by the Lippert–Mataga equation, indicating the intramolecular charge transfer (ICT) process. Semi-empirical MO calculation (MOPAC/AM1) demonstrated that the HOMO-1, HOMO and LUMO of **3**, **10**–**12** were mainly localized on the phenyl (π_{ph}), tpy (π_{tpy}) and tpy (π^*_{tpy}) part, respectively, indicating that the lowest energy absorption band of **3**, **10**–**12** was the local excitation (π_{tpy}–π^*_{tpy}). In the case of **14** and **15**, which have an electron-donating substituent, π_{ph} instead of π_{tpy} became the HOMO. Thus, the lowest energy absorption of **14** and **15** was an ICT transition (π_{ph}–π^*_{tpy}), and a large red shift of the fluorescence occurred. In these compounds, the energy level of π_{ph} is controlled without affecting that of π_{tpy} and π^*_{tpy}, suggesting a novel approach for tuning the color of fluorescence.

Introduction

Though photofunctional fluorescent compounds have already been utilized in various fields,[1] increasing demand for those having superior and multi-functionality is attracting further research interest. A common method of molecular design of these compounds is to connect the functional molecule with a known fluorophore.[2] However, there are limitations to this method because of attenuation of the emission from the fluorophore by substitution or difficulty in constructing sufficient communication between the functional part and the signalling part (fluorophore). Thus, the development of a new series of fluorescent compounds having better functionality is required.

We have been studying the molecular design of photofunctional fluorescent compounds based on a novel strategy. The essence of our approach is designing a conjugated system displaying both fluorescence and the desired function. In such a system, highly efficient signal transduction can be realized.[3]

Oligopyridyl compounds have ring nitrogens serving as multiple interaction sites, and form stable coordination and hydrogen-bonded complexes with various metal ions and molecules. They have been widely used as ligands for transition metal cations and building blocks in supramolecular chemistry.[4] In addition, they are generally thermally and chemically stable. Among these oligopyridyl compounds, 2,2′-bipyridine (bpy) has been most extensively studied as a chelating compound. Since its ruthenium and osmium complexes have a unique metal-to-ligand charge transfer triplet excited state, the photophysical properties and energy transfer processes of these complexes have been intensively investigated[5] for decades.

Recently, 2,2′:6′,2″-terpyridine (tpy) complexes of Ru(II) and Os(II) have attracted increasing interest due to the structural advantage[6] in designing photofunctional supramolecular assemblies. The synthesis of tpy derivatives has been actively studied by Constable and his group, and a variety of substituted tpys have been reported.[7] However, tpy and its derivatives are poorly fluorescent in general. Though several reports have mentioned the fluorescence of tpys, for example, 4′-(9-anthryl)-tpy and protonated tpy,[8] there has been no systematic research on emissive tpy derivatives. According to Maestri *et al.*,[9] the Ru(II) complex of 4′-phenyl-substituted tpy exhibited much more efficient luminescence than the corresponding tpy complex at room temperature. 4′-Phenyl substitution might give 'favorable' photophysical properties to tpy.

We synthesized a series of phenyl-substituted tpy derivatives and evaluated their fluorescence properties, and found some of the derivatives to be novel fluorescent compounds. In addition, their fluorescence color can be tuned by controlling the orbital energy level. Introduction of fluorescence properties to the tpy derivatives might open the way for further application as a new series of photofunctional compounds.

Results and discussion

Synthesis of tpy derivatives

Molecular structures of tpy derivatives are shown in Fig. 1. 4-Phenyl tpy **2**, 4,4″-diphenyl **4** and 6,6″-diphenyl **6** tpy were synthesized by formation of the side pyridine rings of tpy. 6-Phenyl tpy **5** was obtained from 6-bromo tpy and 2-bromopyridine using trimethyltin chloride.

A series of *p*-substituted ptps were synthesized through two different routes (Table 2). Method A[10] is a step-by-step reaction, through which **9**, **10**, and **11** were obtained. 2′-Azachalcone, prepared from 2-acetylpyridine and *p*-substituted benzaldehyde, was coupled with a mole equivalent of pyridinium ketone to give only 2,2′:6′,2″-terpyridine isomer in satisfactory yield. Bromo ptp **10** was converted to amino ptp **14** using liquid ammonia. Compounds **12**, **13**, and **15** were

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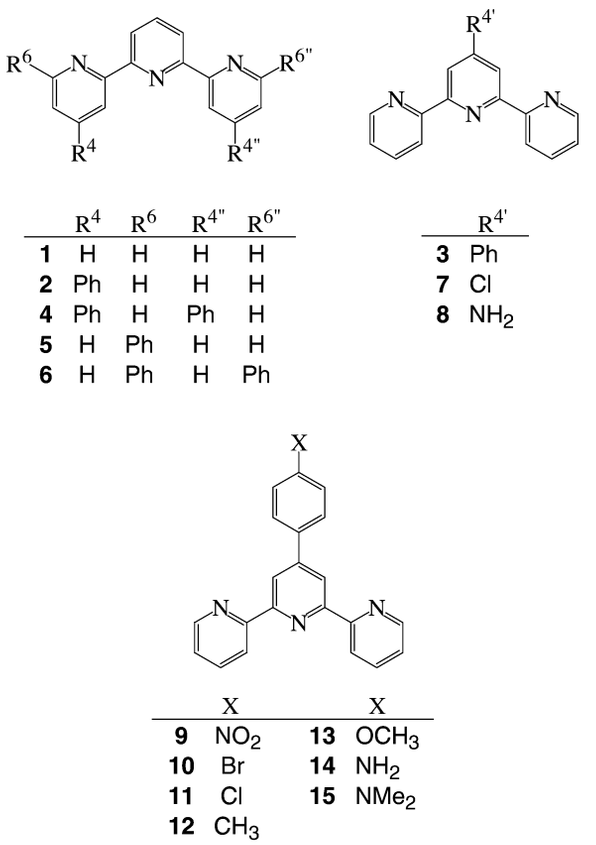
Table 1 Absorption and fluorescence maxima of tpy derivatives in dichloromethane at 20 °C

Compound	λ_{abs}/nm (log ε)	λ_{fl}/nm (Φ^a)
1	279.5 (4.30)	337 (0.02)
2	262 (4.16), 307 (3.95)	344 (0.02)
3	278 (4.52)	340 (0.33)
4	301 (4.23)	342 (0.05)
5	278 (4.55)	341 (0.07)
6	306 (4.38)	344 (0.16)
7	278.5 (4.32)	335 (<0.01)
8	277.0 (4.46)	368 (0.02)

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



	R^4	R^6	$R^{4''}$	$R^{6''}$
1	H	H	H	H
2	Ph	H	H	H
4	Ph	H	Ph	H
5	H	Ph	H	H
6	H	Ph	H	Ph

	$R^{4'}$
3	Ph
7	Cl
8	NH_2

	X		X
9	NO_2	**13**	OCH_3
10	Br	**14**	NH_2
11	Cl	**15**	NMe_2
12	CH_3		

Fig. 1 Molecular structures of tpy derivatives.

prepared in one step by coupling two moles of 2-acetylpyridine and one mole of the corresponding *p*-substituted benzaldehyde (method B).[11] However, yields of the desired products were generally low (~20%), since considerable amounts of isomeric 2,2′:4′,2″-terpyridine derivatives were also formed.

Absorption and fluorescence spectra of phenyl tpys

Table 1 shows the absorption and fluorescence maxima of the phenyl-substituted tpys **2**–**6** measured in dichloromethane solution at 20 °C. The lowest energy absorption bands of these compounds appeared below 310 nm, not much different from that of the parent compound **1**.

Fluorescence of **2**–**6** was observed at around 340 nm regardless of the substitution position and the number of the phenyl groups (Fig. 2). The excitation spectra monitored at any point in between 330 and 400 nm were identical to the corresponding absorption spectra, showing that the excitation of the lowest-energy absorption of **2**–**6** led to the emitting state. However, the fluorescence quantum yields (Φ) of these compounds were greatly affected by the substitution position. While 4-, 6- and 4,4″-substitution resulted in only a weak fluorescence

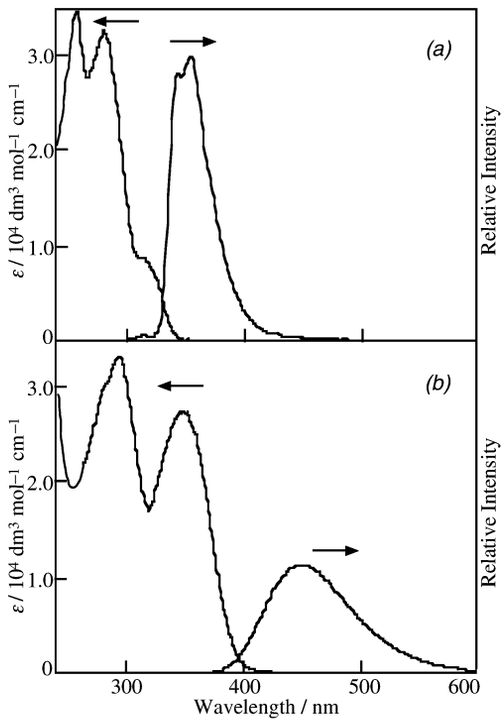


Fig. 2 Absorption and fluorescence spectra of 4′-phenyl tpy **3** (*a*), and 4′-(*p*-dimethylaminophenyl) tpy **15** (*b*) in dichloromethane.

(Φ < 0.07), 4′- (**3**) and 6,6″-substitution (**6**) markedly improved the quantum yields to 0.33 and 0.17, respectively. Moreover, the quantum yield of **3** was as high as 0.64 in cyclohexane. Fluorescence intensities of **3** and **6** increased linearly with the concentration of the solutes, indicating the unimolecular fluorescence of **3** and **6**. It should be noted that 4′-substitution with chloro- **7** or amino- **8** group was not effective.

Semi-empirical molecular orbital calculations (MOPAC/AM1) were carried out on 4′-phenyl tpy (ptp; **3**). The results showed that both HOMO and LUMO having π character were localized exclusively on the tpy part, and can be denoted as π_{tpy} and π^*_{tpy}, respectively (Fig. 3). It was also shown that the lowest energy absorption band of **3** was mainly composed of a HOMO (π_{tpy})–LUMO (π^*_{tpy}) transition. The second HOMO (HOMO-1) orbital was localized mostly on the phenyl unit (denoted as π_{ph}), and the second lowest energy transition band (π_{ph}–π^*_{tpy}) was suggested to have the intramolecular charge transfer (ICT) character.

Effect of *p*-substitution in the 4′-phenyl part on the absorption and fluorescence spectra of ptp

To further examine and tune the fluorescence properties of 4′-phenyl tpy (ptp, **3**), several substituents having different electron donating or withdrawing properties were introduced into the *p*-position of the 4′-phenyl unit. Absorption and fluorescence maxima of the *p*-substituted ptps **9**–**15** are collected in Table 2.

The lowest energy π–π* absorption bands of **9**–**13** were practically the same as that of the parent ptp, shifting less than 15 nm. However, those of the amino **14** and dimethylamino **15** ptp appeared at 50–70 nm longer wavelength. Similar results were obtained for the fluorescence properties of these compounds. Substitution of relatively weak electron donating or withdrawing groups, such as bromo- **10**, chloro- **11**, methyl- **12**, and methoxy- **13** showed only a small effect on the fluorescence maxima and quantum yield of **3**. On the other hand, fluorescence of **14** and **15** appeared at more than 90 nm longer wavelength compared to that of **3**, though the fluorescence quantum yields decreased to some extent. As shown in Table 3, the fluorescence maxima of **14** and **15** were

Table 2 Absorption and fluorescence maxima of *p*-substituted ptps in dichloromethane at 20 °C

Compound	Method[a]	Mp/°C	λ_{abs}/nm (log ε)	λ_{fl}/nm (Φ^b)
9	A	210–211	283 (4.57)	[d] (0)
10	A	158–160	278 (4.61)	355 (0.22)
11	A	170–172	278 (4.58)	356 (0.40)
12	B	166–167	279 (4.60)	352 (0.33)
13	B	171–172	285 (4.62)	373 (0.28)
14	[c]	253–254	288 (4.53), 325 (4.30)	450 (0.13)
15	B	205–207	291 (4.46), 348 (4.37)	469 (0.23)

[a] Synthetic method for each compound (see text). [b] Relative quantum yields were determined by using 2-aminopyridine ($\Phi = 0.37$, excitation at 285 nm, in ethanol) as the standard compound. [c] Compound **14** was obtained by amination of **10** which was synthesized by method A. [d] Not detected.

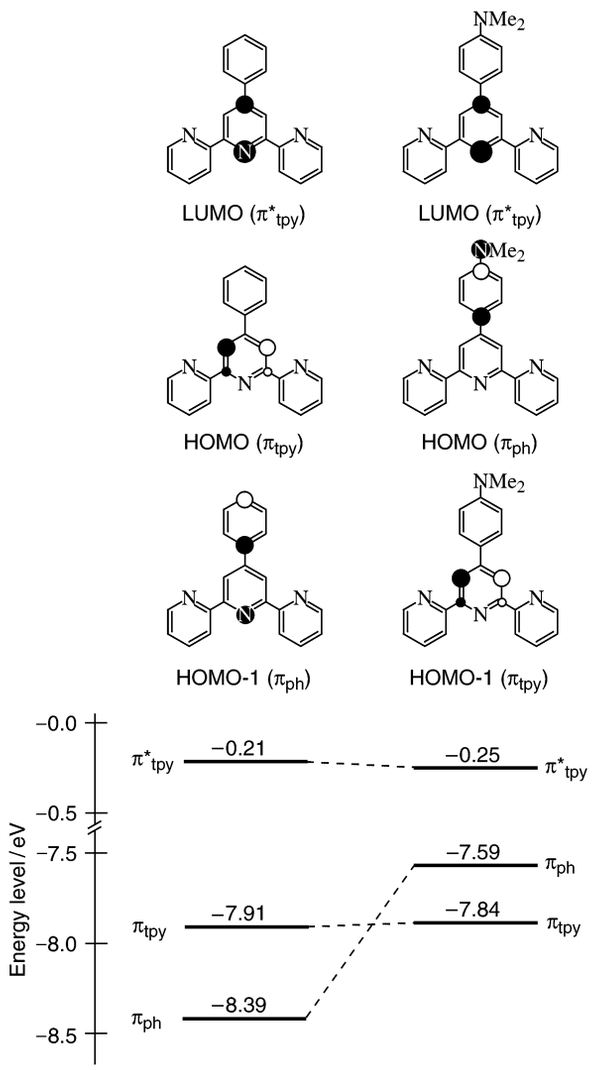


Fig. 3 Calculated electronic state and energy level diagram of HOMO, HOMO-1 and LUMO in **3** (left) and **15** (right).

found to show considerable solvent-dependence. They appeared at more than 130 nm longer wavelength in ethanol compared to those in cyclohexane. Therefore, an intramolecular charge transfer (ICT) process should be involved in the excited states of **14** and **15**. It is well known that fluorescence from the ICT state suffers a large solvent effect because of the contribution of solvent reorientation energy.[12]

Excitation process of ptps

Fig. 3 presents the electronic states of the HOMO-1 (π_{ph}), HOMO (π_{tpy}) and LUMO (π^*_{tpy}) of **3** and **15** calculated by the MOPAC/AM1 method. As discussed before, the lowest energy excitation band of **3** was a local excitation (LE) transition (π_{tpy}–π^*_{tpy}). The same results were obtained for **10**–**13**. In the

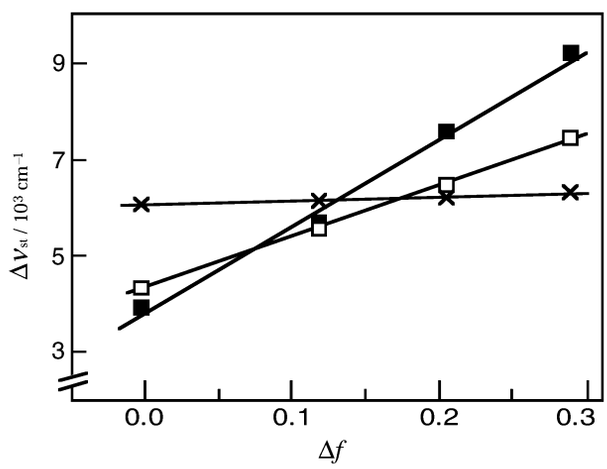


Fig. 4 Plot of difference between absorption and fluorescence wavenumber ($\Delta\nu_{st}$) *vs.* solvent polarity parameter (Δf) of **3** (×), **13** (□) and **15** (■) in cyclohexene (0.00), dipropyl ether (0.12), dichloromethane (0.21) and ethanol (0.29). Values in parentheses are Δf of each solvent.

case of **15** (and also **14**), the energy level of the π_{ph} became higher than that of π_{tpy}, though the energy level of π_{tpy} was not much different from those in other ptps. As a result, π_{ph} instead of π_{tpy} became HOMO, and therefore, the lowest energy excitation band shifted from the LE transition to the ICT transition (π_{ph}–π^*_{tpy}). It is worth noting that the π_{tpy} and π^*_{tpy} orbitals were little affected by the substituents at the *p*-position of the phenyl unit.

To examine the photo-excitation and relaxation processes of **10**–**15**, the difference between the excited and ground state dipole moment, $\Delta\mu$, was calculated using the Lippert–Mataga equation [eqn. (1)],[13] where Δf is Lippert's solvent polarity

$$\Delta\nu_{st} = \nu_{abs} - \nu_{fluo} = \frac{2(\Delta\mu)^2}{hca^3}\Delta f + \text{Const}$$
$$\Delta f = \frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{2n^2 + 1} \quad (1)$$

parameter, ε and n are the relative permittivity and the optical refractive index of solvents, respectively, and a is an effective radius of the Onsager cavity[14] of a compound.

Fig. 4 plots the Stokes shift ($\Delta\nu_{st}$) of **3**, **13** and **15** against Δf. Whereas $\Delta\nu_{st}$ of **3** was almost insensitive to the solvent, **13** and **15**, having a moderately and a strongly electron donating substituent, respectively, presented a much steeper line giving large $\Delta\mu$. Assuming the effective radius of the Onsager cavity a as 0.5 nm, $\Delta\mu$ for **3**, **13** and **15** were calculated to be 2.1, 10.4 and 15.2 D, respectively. The reported values of $\Delta\mu$ for the compounds showing an ICT excited state such as 4-(dimethylamino)stilbene,[15] 4-(dimethylamino)-4′-cyanostilbene[16] and 1-(4-cyanophenyl)-3-[4-(dimethylamino)phenyl]propane-1,3-dione[17] were in the range 14–15 D, and therefore, the

Table 3 Absorption and fluorescence maxima of **3**, **14** and **15** in organic solutions at 20 °C

	3		**14**		**15**	
Solvent	λ_{abs}/nm	λ_{fl}/nm	λ_{abs}/nm	λ_{fl}/nm	λ_{abs}/nm	λ_{fl}/nm
Cyclohexane	276	338	286	367	290.5, 334.5	383
Dipropyl ether	277.5	339	290, 327.5	420	290, 337	417
Dichloromethane	278	340	288. 325	450	291, 348	469
Ethanol	277	340	288. 326	506	289, 348	511

emitting levels of **14** and **15** were concluded to be the ICT excited states. Thus, introduction of strongly electron donating groups at the *p*-position of the phenyl unit altered the emitting state from the LE to the ICT state by increasing the π_{ph} level, which caused a large red shift of the fluorescence.

Introduction of substituents often alters the energy levels of both HOMO and LUMO, and impairs the fluorescent properties. In the case of **14** and **15**, the substitutions affected only π_{ph} and not π_{tpy} and π^*_{tpy} (LUMO). Since alteration of the emitting state from the LE to the ICT state by substitution can cause a large fluorescence color change, this may offer a novel way of tuning the fluorescence of organic fluorophores.

Conclusion

Several phenyl-substituted tpys were prepared and their fluorescence properties were examined. 4′-Phenyl tpy **3** exhibited highly effective fluorescence ($\Phi = 0.33$ in dichloromethane, and 0.64 in cyclohexane). The results also confirmed that fluorescence of ptp is tunable by introduction of substituents having different electron affinity into the *p*-position of the phenyl part. Amino- **14** and dimethylamino- **15** substitution switched the lowest transition energy band from an LE transition to an ICT transition by elevating the π_{ph} energy level, which caused a large red shift of the fluorescence.

There have been a large number of studies on tuning the color of fluorescence, however, the relationship between the substituents and their effect on the orbital energy level has not been fully discussed. Tuning the fluorescence color by controlling the LE and ICT transition energies could be a novel strategy for the molecular design of fluorophores.

Experimental

Methods

The UV-VIS absorption spectra were measured with a Shimadzu UV-2500PC spectrophotometer and emission spectra were obtained with a Shimadzu RF-5300PC spectrofluorometer at 20 °C. ^{1}H-NMR spectra were recorded on a JEOL JMN-AL500 or a JEOL AL-400 spectrometer in chloroform-*d* or DMSO-d_6 with tetramethylsilane as an internal standard. Infrared spectra were measured on a Perkin-Elmer FT-1600. Mass spectra were obtained on a Hitachi M-80B or a JEOL JMS-D-300 spectrometer by an EI or FAB method. Relative quantum yields were calculated using 2-aminopyridine in ethanol as a standard (excitation at 285.0 nm, $\Phi = 0.37$). Molecular orbital (MO) calculations and structure optimizations were performed by MOPAC/AM1 on a CAChe system. The effective radii of the Onsager cavities of tpy derivatives were estimated from their rotational volume in the optimized structures.

Spectrophotometric grade ethanol, dichloromethane and cyclohexane were purchased from DOJIN Chem. Co. and used as received. Guaranteed reagent grade dipropyl ether obtained from TCI (Tokyo Chemical Industry) was purified with sodium wire and used for the spectral measurements. 2,2′:6′,2″-Terpyridine **1**, 2-acetylpyridine, 2,6-diacetylpyridine, and 4-substituted benzaldehydes were obtained commercially. The following compounds were prepared by published methods. 4′-Phenyl tpy **3**;[18] mp 206–207 °C, found: C, 81.53; H, 4.84; N, 13.51; calc. for $C_{21}H_{15}N_3$: C, 81.53; H, 4.89; N, 13.58%; 4′-chloro tpy **7**;[19] mp 150–152 °C (lit.,[19] 149–152 °C); 1-[2-oxo-2-(2-pyridyl)ethyl]pyridinium iodide **16**;[20] 1-(2-oxo-2-phenylethyl)pyridinium iodide **17**;[21] pyridine-2,6-bis(*N*,*N*-dimethyl-3-oxopropanamine) hydrochloride **18**;[22] and 2-oxo-4-phenylbut-3-enoic acid **19**.[23]

4,4″-Diphenyl-2,2′:6′,2″-terpyridine 4

To a warm solution of iodine (1.75 g, 6.5 mmol) in freshly distilled pyridine (15 ml) was added a pyridine solution of 2,6-diacetylpyridine (0.52 g, 3.2 mmol) dropwise with stirring. The mixture was refluxed for 2 h and then cooled to −20 °C in a freezer. The precipitated product was collected. As for the pyridine layer, the remaining slurry after evaporation was partitioned between water and dichloromethane. The organic layer was separated, and the aqueous phase extracted with several additional portions of dichloromethane. The combined organic extracts were dried (sodium sulfate) and evaporated to give the second crop of the product, which was recrystallized from ethanol (48%; mp 169–171.5 °C). The obtained pyridine-2,6-diylbis[(1-pyridyl)acetyl] diiodide (0.31 g, 0.54 mmol), **19** (0.19 g, 1.07 mmol), and ammonium acetate (1.24 g, 16.0 mmol) were dissolved in 5 ml of glacial acetic acid and refluxed for 3 h. After cooling, the gray solid, 4,4″-diphenyl-2,2′:6′,2″-terpyridine-6,6″-ammonium carboxylate, precipitated (63%; mp 280–280.5 °C). The collected gray solid was then heated at 220 °C until liquified. After cooling, it was triturated in chloroform and insoluble solid was filtered off. Evaporation of chloroform gave the product. Recrystallization from ethanol gave the product (65%), mp 214.5–215 °C. ν_{max}(KBr)/cm^{-1} 3108, 1546, 1410, 766 and 690; δ_H(400 MHz, $CDCl_3$) 7.47–7.56 (6H, m, phenyl 3,4,5-H), 7.58 (2H, dd, 5,5″-H), 7.81 (4H, d, phenyl 2,6-H), 8.01 (1H, t, 4′-H), 8.51 (2H, d, 3′,5′-H), 8.76 (2H, d, 6,6″-H), 8.90 (2H, sd, 3,3″-H); HRMS(FAB): found *m*/*z* 386.1662 ([M + H]$^+$); calc. for $C_{27}H_{19}N_3$ + H: 386.1657.

(Trimethylstannyl)benzene ($PhSnMe_3$)

To a solution of bromobenzene (2.1 ml, 20 mmol) in anhydrous ether (30 ml) was added dropwise a hexane solution of butyllithium (1.6 mol dm^{-3}, 13 ml) below −70 °C and reaction was allowed to take place for 1 h under a nitrogen atmosphere. After dropwise addition of trimethyltin chloride in THF (1 mol dm^{-3}, 20 ml), the reaction mixture was stirred for 4 h at −75 °C, and then at room temperature overnight to give a white precipitate. Water (40 ml) was poured in and the organic layer was separated. The aqueous layer was extracted with ether, and the combined organic layer was dried over sodium sulfate. After evaporation, the brown liquid was distilled (117 °C, 4 mmHg) to give phenyltrimethyltin as a colorless liquid (3.7 g, 77%).

6-Phenyl-2,2′:6′,2″-terpyridine 5

6-Bromo tpy (115 mg), (trimethylstannyl)benzene (830 mg), bis(triphenylphosphine)palladium(II) dichloride (30 mg), and lithium chloride (54 mg) were dissolved in anhydrous toluene

and maintained at 120 °C for 16 h. After filtration, the filtrate was evaporated and the obtained crude product was recrystallized from ethanol. Yield 18%, mp 160.5–161.5 °C. δ_H(400 MHz, $CDCl_3$) 7.34 (1H, ddd, 5″-H), 7.45 (1H, t, phenyl 4-H), 7.53 (2H, t, phenyl 3,5-H), 7.81 (1H, dd, 5-H), 7.88 (1H, td, 4″-H), 7.94 (1H, t, 4-H), 7.99 (1H, t, 4-H), 8.18 (2H, d, phenyl 2,6-H), 8.47 (1H, dd, 5′-H), 8.60 (1H, dd, 3″-H), 8.65–8.70 (2H, m, 3,3′-H), 8.72 (1H, dd, 6″-H); HRMS(FAB): found *m*/*z* 310.1366 ($[M + H]^+$); calc. for $C_{21}H_{15}N_3$ + H: 310.1344.

4-Phenyl-2,2′:6′,2″-terpyridine 2

2-(Trimethylstannyl)pyridine (6.0 g), prepared from 2-bromopyridine analogously to (trimethylstannyl)benzene, 2-acetyl-6-bromopyridine (555 mg), bis(triphenylphosphine)palladium(II) dichloride (220 mg), and lithium chloride (413 mg) were dissolved in anhydrous toluene and refluxed for 16 h. After filtration, the filtrate was evaporated to give 6-acetyl-2,2′-bipyridine (41%, crude). The subsequent procedure was the same as for **4**, replacing 2,6-diacetylpyridine with 6-acetyl-2,2′-bipyridine. Mp 176–176.5 °C. ν_{max}(KBr)/cm^{-1} 3107, 1543, 1482, 1410, 761 and 687; δ_H(400 MHz, $CDCl_3$) 7.33 (1H, ddd, 5″-H), 7.43–7.55 (3H, m, phenyl 3,4,5-H), 7.60 (1H, dd, 5-H), 7.80 (2H, d, phenyl 2,6-H), 7.88 (1H, t, 4″-H), 7.98 (1H, t, 4′-H), 8.48 (1H, dd, 5′-H), 8.60 (1H, dd, 3″-H), 8.65 (1H, dd, 3′-H), 8.70–8.79 (2H, m, 6,6″-H), 8.90 (1H, sd, 3-H); HRMS(FAB): found *m*/*z* 310.1308 ($[M + H]^+$); calc. for $C_{21}H_{15}N_3$ + H: 310.1344.

6,6″-Diphenyl-2,2′:6′,2″-terpyridine 6

A mixture of **18** (0.21 g, 0.6 mmol), **17** (0.39 g, 1.2 mmol), and ammonium acetate (0.27 g, 3.5 mmol) in methanol was heated to reflux for 8 h. After cooling, water was added dropwise to the solution until a yellow solid precipitated. After filtration, washing with water and drying *in vacuo*, the crude material was purified by column chromatography on silica with chloroform. The product was the first to elute from the column. Recrystallization by slow evaporation from a dichloromethane–ethanol mixture gave white needles (0.16 g, 71%). Mp 206–207 °C. Found: C, 84.10; H, 5.05; N, 10.78; calc. for $C_{27}H_{19}N_3$: C, 84.13; H, 4.97; N, 10.90%. δ_H(500 MHz, $CDCl_3$) 7.46 (2H, t, phenyl 4-H), 7.53 (4H, t, phenyl 3,5-H), 7.81 (2H, d, 5,5″-H), 7.95 (2H, t, 4,4″-H), 8.03 (1H, t, 4′-H), 8.19 (4H, phenyl 2,6-H), 8.63–8.71 (4H, m, 3,3′,3″,5′-H).

4′-Amino-2,2′:6′,2″-terpyridine 8

Ammonia gas was bubbled into acetamide (5 g)–phenol (13.6 g) solution and the mixture was kept at 100 °C for 30 min. After chloro-tpy (**7**; 3.7 g, 14 mmol) was added, the reaction mixture was heated up to 160 °C over 10 min and maintained for 5 h with continuous bubbling of the ammonia gas. After cooling, the reaction mixture was separated between aqueous sodium hydroxide (6 mol dm^{-3}, 30 ml) and chloroform (30 ml). The aqueous layer was washed with further portions of chloroform (5 × 30 ml). The combined organic layer was dried over magnesium sulfate, and then the solvent was evaporated. The product was recrystallized from benzene. Yield 63%, mp 222–226 °C. Found: C, 72.40; H, 4.87; N, 22.46; calc. for $C_{15}H_{12}N_4$: C, 72.56; H, 4.87; N, 22.57%. δ_H(400 MHz, $CDCl_3$) 7.31 (2H, ddd, 5,5″-H), 7.74 (2H, s, 3′,5′-H), 7.84 (2H, ddd, 4,4″-H), 8.60 (2H, d, 3,3″-H), 8.67 (2H, ddd, 6,6″-H).

Method A[10]

Compounds **9**, **10** and **11** were synthesized by the following procedure represented by the preparation of **10**. Starting from an appropriate 4-substituted benzaldehyde gave the corresponding compound.

To a solution of 4-bromobenzaldehyde (3.7 g, 20 mmol) in methanol (45 ml) and aqueous sodium hydroxide (1 mol dm^{-3}, 15 ml) was added 2-acetylpyridine (2.5 g, 21 mmol) and the mixture was stirred for 30 min. The resulting precipitate was filtered off, dissolved in dichloromethane and washed once with water. The organic phase was dried over sodium sulfate and evaporated to dryness.

Recrystallization from ethanol gave 4-bromo-2′-azachalcone as a light yellow solid (81%). 4-Bromo-2′-azachalcone (0.58 g, 2.0 mmol), **16** (0.62 g, 2.0 mmol), and ammonium acetate (4.0 g, 51 mmol) were dissolved in 4 ml of glacial acetic acid and the mixture was refluxed for 7 h. After cooling, the reaction mixture was basified with 7 ml of aqueous sodium hydroxide (10 mol dm^{-3}), and then extracted with dichloromethane. The combined organic phases were dried over sodium hydroxide. The evaporated residue was applied to a flash chromatography column (activated alumina) and eluted with hexane–dichloromethane–ethyl acetate (8 : 2 : 1–3 : 6 : 2) to give 4′-(*p*-bromophenyl)-2,2′:6′,2″-terpyridine **10** (86%). Mp 158–160 °C. Found: C, 64.95; H, 3.52; N, 10.81; calc. for $C_{21}H_{14}BrN_3$: C, 64.96; H, 3.63; N, 10.82%. δ_H(500 MHz, $CDCl_3$) 7.35 (2H, td, 5,5″-H), 7.62 (2H, d, phenyl 3,5-H), 7.76 (2H, d, phenyl 2,6-H), 7.87 (2H, td, 4,4″-H), 8.65 (2H, 3,3″-H), 8.67 (2H, s, 3′,5′-H), 8.71 (2H, d, 6,6″-H).

4′-(*p*-Nitrophenyl)-2,2′:6′,2″-terpyridine 9. Yield: 80%, mp 210–211 °C. IR (KBr) 1512, 1352 cm^{-1} (NO_2). HRMS: 355.1189 (M^+); calc. for $C_{21}H_{14}N_4O_2$: *M*, 355.1194. δ_H(500 MHz, $CDCl_3$) 7.56 (2H, ddd, 5,5″-H), 8.07 (2H, td, 4,4″-H), 8.25 (2H, d, phenyl 3,5-H), 8.42 (2H, d, phenyl 2,6-H), 8.70 (2H, 3,3″-H), 8.78–8.80 (4H, m, 6,3′,5′,6″-H).

4′-(*p*-Chlorophenyl)-2,2′:6′,2″-terpyridine 11. Yield: 85%, mp 171–172 °C. Found: C, 73.08; H, 3.96; N, 12.05; calc. for $C_{21}H_{14}ClN_3$: C, 73.36; H, 4.10; N, 12.22%. δ_H(500 MHz, $CDCl_3$) 7.34 (2H, ddd, 5,5″-H), 7.47 (2H, d, phenyl 3,5-H), 7.83 (2H, d, phenyl 2,6-H), 7.87 (2H, d, 4,4″-H), 8.65 (2H, 3,3″-H), 8.69 (2H, s, 3′,5′-H), 8.71 (2H, d, 6,6″-H).

4′-(*p*-Aminophenyl)-2,2′:6′,2″-terpyridine 14. 4′-(*p*-Bromophenyl) tpy **10** (0.5 g) was treated with liquid ammonia (60 ml) in an autoclave at 175 °C, 150 atm for 48 h. After removal of ammonia, residual brown solid was applied on an alumina column and eluted with ethyl acetate (56%). Mp 253–254 °C. HRMS: 324.1378 (M^+); calc. for $C_{21}H_{20}N_4$: *M*, 324.1375. δ_H(500 MHz, $CDCl_3$) 6.81 (2H, d, 3‴,5‴-H), 7.35 (2H, td, 5,5″-H), 7.79 (2H, d, 2‴,6″-H), 7.88 (2H, td, 4,4″-H), 8.66 (2H, 3,3″-H), 8.69 (2H, s, 3′,5′-H), 8.73 (2H, d, 6,6″-H).

Method B[11]

Compounds **12**, **13** and **15** were prepared by the following synthetic method represented by the preparation of **12**.

A mixture of acetamide (26.6 g, 450 mmol), ammonium acetate (17.3 g, 2.25 mmol), *p*-tolualdehyde (1.80 g, 15 mmol), and 2-acetylpyridine (3.7 g, 30 mmoL) was refluxed for 2 h and cooled to 120 °C, and aqueous sodium hydroxide (13.1 g in 30 ml of water) was added. After further standing at 120 °C for 2 h without stirring, the solution was cooled to room temperature. A brown solid was separated, washed with water, and dissolved in acetic acid (9 ml). The hydrobromide salt was precipitated with 47% hydrobromic acid (9 ml), filtered off, and dissolved in water (30 ml). The solution was basified with aqueous potassium hydroxide (4 mol dm^{-3}), and the obtained suspension was extracted with dichloromethane. After evaporation of the solvent, the residue was recrystallized from ethanol to give yellow needles (1.34 g), which were dissolved in an ethanol–dichloromethane mixture (60 ml). Addition of a Mohr salt aqueous solution (0.73 g in 15 ml) immediately gave a purple solution. After evaporation of dichloromethane, aqueous potassium hexafluorophosphate (0.68 g in 10 ml) was added, and the collected precipitate, $[Fe(\mathbf{12})_2][PF_6]_2$, was

dissolved in acetonitrile, then washed with toluene. The isolated precipitate (1.88 g) was redissolved in acetonitrile–water (1 : 1; 30 ml), into which was poured aqueous potassium hydroxide (1.83 g, in 10 ml) followed by the dropwise addition of hydrogen peroxide solution (35%) until the purple color had been discharged. The suspension was filtered to remove iron oxide, and the filtrate extracted with chloroform. The extract was concentrated and chromatographed (alumina, chloroform) and recrystallized from ethanol to give **12** (19%). Mp 166–167 °C. Found: C, 81.44; H, 5.23; N, 13.14; calc. for $C_{22}H_{17}N_3$: C, 81.71; H, 5.30; N, 12.99%. δ_H(500 MHz, $CDCl_3$) 2.42 (3H, s, CH_3), 7.30 (2H, d, phenyl 3,5-H), 7.33 (2H, ddd, 5,5″-H), 7.80 (2H, d, phenyl 2,6-H), 7.86 (2H, td, 4,4″-H), 8.65 (2H, 3,3″-H), 8.70–8.72 (4H, m, 6,3′,5′,6″-H).

4′-(*p*-Methoxyphenyl)-2,2′:6′,2″-terpyridine 13. Yield: 20%, mp 171–172 °C. Found: C, 77.59; H, 5.09; N, 12.67; calc. for $C_{22}H_{17}N_3O$: C, 77.86; H, 5.05; N, 12.38%. δ_H(500 MHz, $CDCl_3$) 3.87 (3H, s, OCH_3), 7.01 (2H, d, phenyl 3,5-H), 7.33 (2H, t, 5,5″-H), 7.84–7.87 (4H, m, 4,4″- and phenyl 2,6-H), 8.65 (2H, 3,3″-H), 8.69 (2H, s, 3′,5′-H), 8.71 (2H, d, 6,6″-H).

4′-(*p*-Dimethylaminophenyl)-2,2′:6′,2″-terpyridine 15. Yield: 17%, mp 205–207 °C. Found: C, 78.14; H, 5.73; N, 15.90; calc. for $C_{23}H_{20}N_4$: C, 78.38; H, 5.72; N, 15.90%. ν_{max}(KBr)/cm^{-1} 3102, 2815, 1582, 1524, 1363, 1197 and 793; δ_H(500 MHz, $CDCl_3$) 3.05 (6H, s, $N(CH_3)_2$), 6.82 (2H, d, phenyl 3,5-H), 7.35 (2H, td, 5,5″-H), 7.86–7.89 (4H, m, 4,4″- and phenyl 2,6-H), 8.66 (2H, 3,3″-H), 8.71 (2H, s, 3′,5′-H), 8.74 (2H, d, 6,6″-H).

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