SYNTHESES, SPECTROSCOPIC PROPERTIES, AND CU(I) COMPLEXES OF ALL POSSIBLE SYMMETRIC BI-1,10-PHENANTHROLINES

**Shinji Toyota,* Akito Goto, Keiko Kaneko, and Takumi Umetani**

Department of Chemistry, Faculty of Science, Okayama University of Science, 1-1 Ridaicho, Okayama, 700-0005, Japan. E-mail: stoyo@chem.ous.ac.jp

Abstract – All possible symmetric bi-1,10-phenanthrolines (biphens) were synthesized by Ni-catalyzed coupling of corresponding halo-1,10-phenanthrolines. Their absorption and emission spectra were compared with those of phenanthroline as the reference compound. The spectral feature is explained by the molecular conformation, namely, coplanar 2,2'- and 3,3'-biphens and nearly bisected 4,4'- and 5,5'-biphens. The effects of additives, H^+ or Zn^{2+}, on the electronic spectra varied depending on the biphen ligand. The 2,2'-ligand formed a helical complex with Cu^+ ions in a 2:2 ratio as revealed by spectroscopic titration and X-Ray analysis.

INTRODUCTION

Multitopic ligands consisting of *N*-heterocyclic units have been widely used for the construction of molecular architecture by self-assembly *via* coordination with metal ions.[1,2] For example, oligomers of 2,2'-bipyridine and 2,2':6',2"-terpyridine subunits are useful components of molecular grids,[3] ladders,[4] and helicates,[5] owing to their rigid structures. There are also a number of applications of 1,10-phenanthroline (phen) based multitopic ligands in supramolecular chemistry[5a,6] as highlighted by the knot synthesis.[7] In most cases, however, phen moieties are separated by suitable chains or spacers, and the directly assembled oligomeric structures are less popular because of synthetic limitations. Bi-1,10-phenanthrolines (biphens) (**1–4**) are the simplest analogues of such oligomeric ligands. After the first synthesis by Case in 1964 of 2,2'-biphen (**1**) and 5,5'-biphen (**4**) by Ullmann coupling or Skraup reaction,[8] few studies of this type of ligands followed.[9] It was only recently that the practical syntheses of 2,2'-biphen (**1**) and 3,3'-biphen (**2**) by Ni-catalyzed coupling were again reported, and the synthetic access has made it possible to study the complexation and other properties in detail.[10–13] Furthermore, these

heteroaryls (extended π systems) are attracting attentions as building blocks of potentially useful electroluminescence[14] and conducting materials.[15] Therefore, we synthesized all possible symmetric biphens including known compounds as basic ditopic ligands, and examined their interactions with acid or metal ions (Zn^{2+} and Cu^+) by spectroscopic methods.
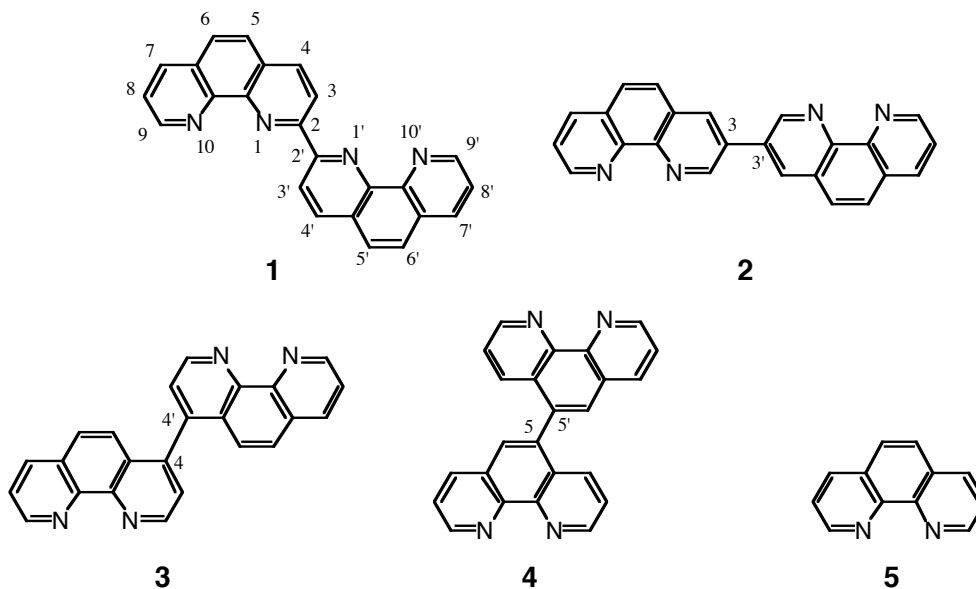
RESULTS AND DISCUSSION

Synthesis

Compounds (**1**) and (**2**) were prepared by the Ni-catalyzed coupling[16] of 2-Cl-phen and 3-Br-phen, respectively, according to the literature.[10,11] 4,4'-Biphen (**3**) was similarly synthesized from 4-Cl-phen in 66% yield: this new compound was satisfactorily characterized based on analytical and spectroscopic data. As for 5,5'-biphen (**4**), it was reported that the Ni- or Cu-catalyzed reactions of the corresponding chloride or bromide afforded none of the desired coupling product.[8] However, we successfully obtained (**4**) from 5-Cl-phen using the same procedure as that applied to the other isomers.

Structure and conformational analysis

The molecular structures of biphen ligands (**1–4**) were calculated using the PM3 method. The energy minimum structures are shown in Figure 1. Compound (**1**) preferred to take a planar conformation where N1 and N1' were *anti* along the C2–C2' axis. This result was almost consistent with the X-Ray data (dihedral angle: 10.0°).[10] As the torsion angle of N1–C2–C2'–N1' was changed from 180° to 0°, the energy was increased monotonically: the *anti* coplanar form was the only energy minimum among the possible conformations. For **2**, two coplanar conformations were obtained as the optimized structures, where the *anti* form was slightly more stable than the *syn* form (energy difference *ca*. 1 kJ/mol). The rotational barrier was only 5 kJ/mol *via* the nearly bisected conformation as the transition state. In contrast, the two phen moieties were nearly bisected in the optimized structures of **3** and **4**, the dihedral

angles being 90.2° and 92.6°, respectively. The coplanar conformations were considerably unstable because of the steric interactions between the aromatic protons around the C–C axis. Although the estimation of the rotational barriers of **3** and **4** by calculation was unsuccessful, we considered that their barriers were as high as that in 1,1'-binaphthyl (94 kJ/mol),[17] which could be regarded as a steric model.
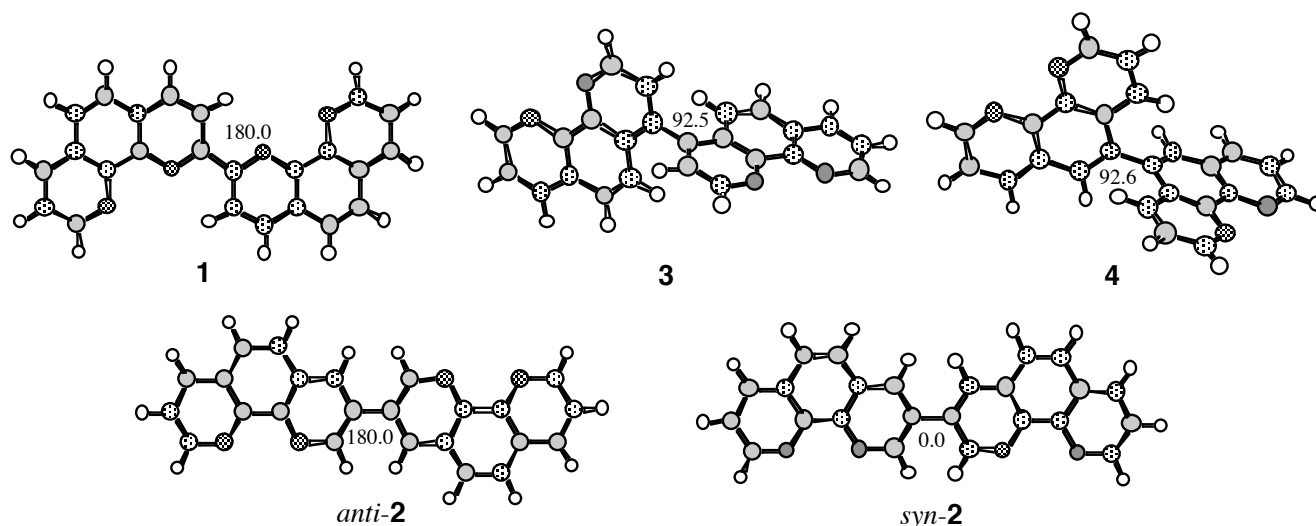

Figure 1. Optimized structures of **1**–**4** by PM3 method. Values indicate dihedral angles between two phen moieties.

Table 1. ^{1}H NMR chemical shifts and multiplicity of biphens (**1**–**4**) and phen (**5**) ligands, and the Cu(I) complex of **1**. [a]

Compd	2,2'-H	3,3'-H	4,4'-H	5,5'-H	6,6'-H	7,7'-H	8,8'-H	9,9'-H
1	—	9.46 d	8.50 d	7.92 d	7.85 d	8.31 dd	7.69 dd	9.29 dd
1$_2$·Cu$^+_2$	—	8.33, 8.34 AB[b]		7.65, 7.71 AB[b]		8.28 dd	7.54 dd	8.18 dd
2	9.60 d	—	8.65 d	7.99 d	7.92 d	8.32 dd	7.70 dd	9.26 dd
3	9.38 d	7.69 d	—	7.34 d	7.67 d	8.26 dd	7.70 dd	9.29 dd
4	9.24 dd	7.49 dd	7.78 dd	—	7.96 s	8.33 dd	7.75 dd	9.31 dd
5	9.21 dd	7.65 dd	8.27 dd	7.81 s	7.81 s	8.27 dd	7.65 dd	9.21 dd

[a]The signals were assigned by the decoupling and NOE experiments. Multiplicity, s: singlet, d: doublet, dd: double doublet, AB: AB quartet. [b]Not fully assigned.

The above structural features were reflected by the ^{1}H NMR chemical shifts listed in Table 1. The proton signal due to the 3,3'-H protons in **1** (δ 9.46) was shifted downfield by *ca.* 2 ppm relative to the corresponding signal in free phen (**5**) (δ 7.65). The downfield shift was attributed to the ring current effect of the attached aromatic rings as well as to the neighboring effect of the nitrogen atoms in the *anti*

coplanar conformation. In contrast, the 5,5'-H signal in **3** (δ 7.34) and the 4,4'-H signal in **4** (δ 7.78) were shifted upfield relative to the reference. These protons were found in the shielding region of the attached aromatic rings in the bisected conformation.

UV and fluorescence spectra

The absorption and emission spectra of this series of biphens were measured in acetonitrile. The emission spectra were recorded upon excitation at 305 nm. The absorption spectra of **1–5** are shown in Figure 2. These data are compiled in Table 2.
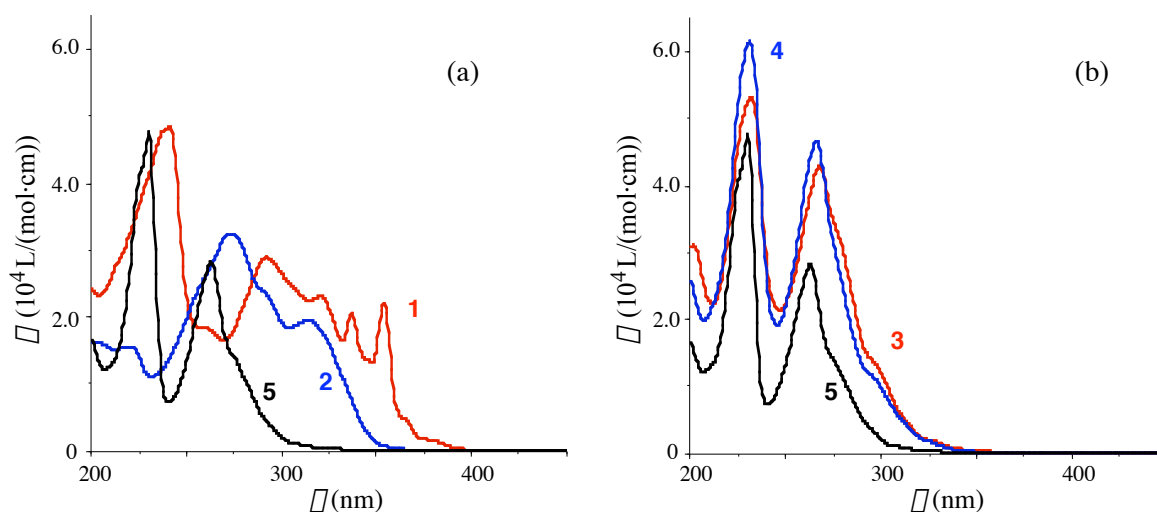

Figure 2. Absorption spectra of **1–5** in MeCN.

Table 2. Absorption (λ_{max}) and emission (λ_{em}) wavelengths and fluorescence quantum yield (Φ_f) of free, protonated and metallated biphen (**1–4**) and phen (**5**) ligands measured in acetonitrile. [a]

Compd	free			+ H^{+} [b]			+ ZnCl$_2$ [c]		
	λ_{max} (nm)	λ_{em} (nm)	Φ_f[d]	λ_{max} (nm)	λ_{em} (nm)	Φ_f[d]	λ_{max} (nm)	λ_{em} (nm)	Φ_f[d]
1	354, 337, 321, 292	390	0.22	346, 308, 247	434	0.14	380, 364, 304, 264	414	0.030
2	314, 273	366, 383	0.055	340, 289, 237	409	0.18	323, 281	384	0.018
3	268, 232	384	0.039	280, 221	439	0.14	277, 229	419	0.19
4	266, 231	378	0.061	277, 224	430	0.27	275, 233	404	0.082
5	263, 230	388, 376	0.031	303, 275, 272, 220	423	0.055	293, 272, 226	370, 387	0.050

[a]Shoulder bands are not listed here. [b]In the presence of excess methanesulfonic acid. [c]In the presence of excess ZnCl$_2$. [d]Quantum yield was measured relative to a solution of quinine sulfate in sulfuric acid.

Compounds (**3**) and (**4**) afforded two intense absorption bands at *ca.* 230 and 265 nm due to π-π* transitions (Figure 2(b)). This spectral pattern was quite similar to that of the parent phen ligand (**5**), and indicated that the two phen groups approximately behaved as independent chromophores.[18,19] This finding was rationally explained by the nearly bisected conformation mentioned above. In contrast, the absorption bands of **1** and **2** were broad and red-shifted compared with those of the other compounds, as have been already pointed out in the literature.[11] Preference for the coplanar conformations facilitated the electronic interactions between the two phen moieties across the C–C axis.

The biphen ligands exhibited weak fluorescence with a maximum at around 380 nm, being slightly red-shifted relative to that of phen. Whereas the fluorescence quantum yields of **2**–**5** were low ($\Phi_f < 0.06$), that of **1** (Φ_f 0.22) was significantly high compared with those of the other ligands. Therefore, the coupling site is an important factor that contributes to the fluorescence efficiency in the biphen system.

Effect of acid and ZnCl$_2$ on electronic spectra

The electronic properties of the phen derivatives were modulated by the addition of acid or metal ions to form protonated or coordinated species. The UV and fluorescence spectra of **1**–**5** were recorded in the presence of excess methanesulfonic acid or ZnCl$_2$ (Table 2). There are several papers on the red-shifts of the absorption and emission bands of phen derivatives by exogenous materials.[19–21] Most of the biphen ligands follow this general tendency although there are a few exceptional cases.

The influence of additives on the absorption bands was most remarkable in **1** among the biphen ligands studied (Figure 3). The protonation changed the continuous bands in the range of 280–360 nm into a broad peak centered at 308 nm without any red-shift. The metallation with Zn^{2+} ions increased the intensities of the bands at 367 and 382 nm: this change was almost saturated when one equivalent of ZnCl$_2$ was added. As regards **2**–**4**, the absorptions at the longest wavelength were red-shifted by both additives. The degree of the red-shift was increased in the order of Zn$^{2+} <$ H$^+$ by the type of additive,
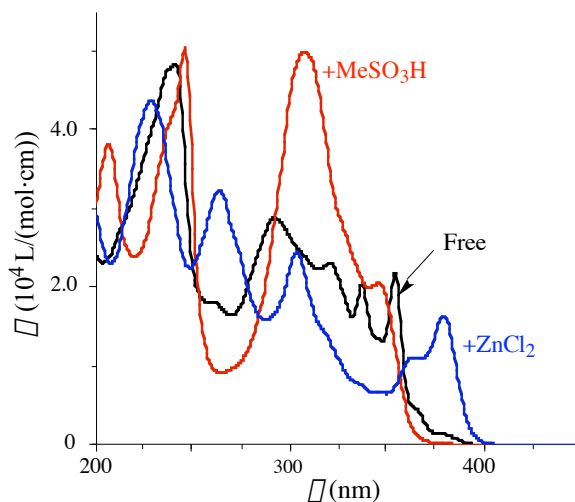

Figure 3. Absorption spectra of 2,2'-biphen (**1**) without additive, and in the presence of excess MeSO$_3$H and ZnCl$_2$ in MeCN.

and $4 < 3 < 2$ by the type of compound. The addition of H^+ or Zn^{2+} influenced both the fluorescence wavelength and intensity of each compound. The protonation of **1** resulted in a large red-shift of the emission band (Stokes shift: *ca.* 80 nm) with a decrease in Φ_f. The fluorescence was considerably quenched upon the addition of $ZnCl_2$ for **1**. A significant enhancement of the emission was observed for **2**–**4** by protonation, and only for **3** by metallation. These results contrasted those of **5** that showed only weak emission under any conditions. These effects are attributed to not only the modification of a single phen chromophore by the additives but also the structural change including conformation and aggregation.

Complexation with Cu(I) ion

We prepared the Cu(I) complexes of **1**–**4** by treating the ligand with $[Cu(CH_3CN)_4]PF_6$ in a 1:1 ratio in acetonitrile. In all cases, the complexation occurred immediately with color change from colorless to dark red. The Cu(I) complex of **1** was isolated as black crystals by concentrating the solution slowly. The complexes of the other ligands could not be isolated as stoichiometrically or structurally defined forms. The complexes of **3** and **4** decomposed upon standing for some time due to oxidation. On the other hand, the complex of **2** was stable for a long time in solution, but gradually became gel-like while maintaining the red color. These results indicated the formation of polymeric complexes, although we could not obtain any information on the degree of polymerization by spectroscopic measurements.

The properties and structures of the complex of **1** were further explored. In the ^{1}H NMR spectra, the aromatic signals, particularly the 3,3'-H and 9,9'-H signals, were shielded compared with those of the free ligand **1** (Table 1). This tendency is generally observed in the metal complexes of phen derivatives.[9d] An ORTEP drawing of the Cu(I) complex of **1** is shown in Figure 4. The structure consists of two biphen ligands and two tetrahedrally coordinated Cu ions that form a double helix along the metal centers.
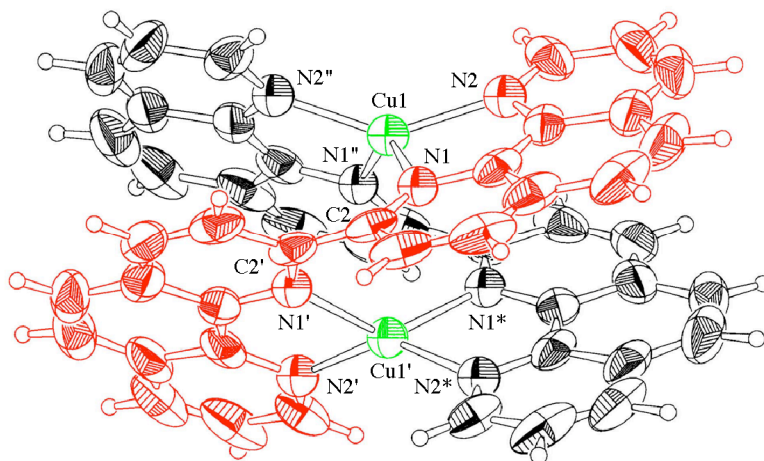

Figure 4. ORTEP drawing of $[Cu_2\mathbf{1}_2](PF_6)_2$. Counter anions are omitted for clarity. Four phen units are all related to symmetric operations.

The copper atom is unequally coordinated to the two types of N atoms, Cu–N1 2.081(5) and Cu–N2 2.013(6) Å. The bond angles are significantly small for N1–Cu–N2 (81.8(3)°) and large for N2–Cu–N2" (142.9(3)°) and N1–Cu–N1" (133.0(3)°) compared with 109.5°. This coordination mode is common to the Cu(I) complexes of 2,2'-biphen derivatives, [9c,d] and contrasts the 1:1 Ni(II) complex having a nearly square planar geometry.[10] The two phen moieties in each biphen ligand are twisted by 51° about the C2-C2' bond from the *syn* conformation and the distance between the two Cu atoms is 3.360(2) Å; these structural parameters are helpful in characterizing the helical geometry. The corresponding parameters are 31° and 2.92 Å for the Cu complex of **6**,[9d] and 64° and 3.59 Å for that of **7**[9c] in the reported X-Ray structures, which carry extra methylene chains across positions 3 and 3'. The helical pitch is increased in the order of the complexes of **6**, **1**, and **7**, reflecting the conformational mobility of the two phen moieties.
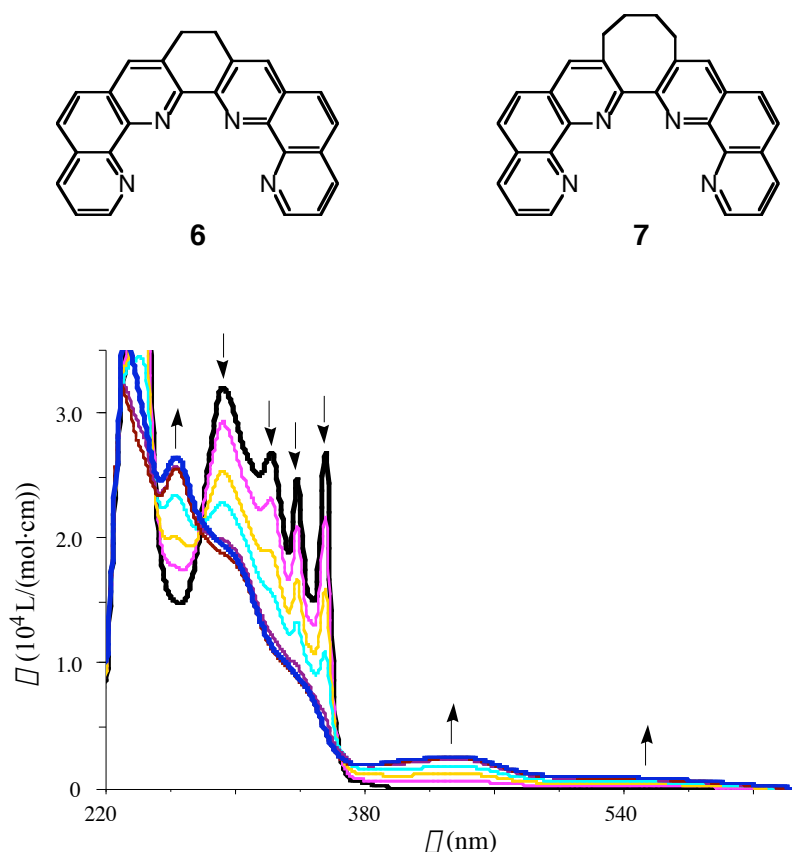

6   **7**

Figure 5. UV spectra of 2,2'-biphen (**1**) during titration with [Cu(MeCN)$_4$]PF$_6$ (0, 0.2, 0.4, 0.6, 0.8, 1.0, and 2.0 eq) in MeCN:CH$_2$Cl$_2$ (1:1). Arrows indicate increase or decrease in intensity of each peak.

The course of complexation of **1** with Cu$^+$ was monitored by UV titration experiments. As the Cu$^+$ reagent was added to a solution of **1** in acetonitrile, the absorptions at 290–360 nm were decreased and broad and weak bands appeared around 440 nm with a shoulder extending to 650 nm with some isosbestic points (Figure 5). The new absorption bands were attributed to metal-to-ligand charge transfer, and were typically observed around 450 nm for phen complexes. The spectrum remained unchanged when more

than one equivalent of metal reagent was added. These observations strongly support the hypothesis that **1** exclusively forms a Cu$^+$ complex in a 1:1 molar ratio under a simple equilibrium system. Although ligands (**2**–**4**) exhibited spectral changes upon Cu$^+$ addition accompanied by the appearance of new bands at longer wavelengths, there were no clear isosbestic points during the titration. This result suggests that several species exist in equilibrium even though Cu$^+$ ions are sufficiently present in the solution. This difference is related to the orientation of the two coordination sites in **2**–**4**, which can form not a dinuclear complex but a mixture of highly aggregated complexes because of the structural restriction.

In summary, all the symmetric bi-1,10-phenanthrolines were prepared by Ni-catalyzed coupling. Each compound possesses characteristic absorption and emission spectra depending on the structural or conformational circumstances, which are also modulated by acid or metal ions. These biphen ligands are expected to widen the scope of metal complex design in the field of supramolecular or functional molecular chemistry.

EXPERIMENTAL

^{1}H and ^{13}C NMR spectra were measured on a Gemini-300 at 300 and 75 MHz, respectively. HRMS were measured on a JEOL JMS-700 MStation spectrometer. Elemental analyses were performed with a Perkin-Elmer 2400-type analyzer. UV spectra were measured with a Hitachi U-3000 spectrophotometer with a 10 mm cell. Fluorescence spectra were measured with a JASCO FP-6500 spectrometer. Only selected physical and spectroscopic data are described for **1** and **2**. 5-Cl-phen was purchased from Aldrich Chemical Co. 4-Cl-phen was prepared according to the method in the literature.[22]

5,5'-Bi-1,10-phenanthroline (4). A solution of NiCl$_2$·6H$_2$O (266 mg, 1.12 mmol) and PPh$_3$ (977 mg, 3.72 mmol) in 10 mL of DMF was degassed by bubbling argon gas for 30 min. To the solution was added zinc powder (72 mg, 1.10 mmol), and the mixture was stirred for 3 h under argon. After the addition of tetraethylammonium iodide (240 mg, 0.935 mmol) and 5-Cl-phen (200 mg, 0.933 mmol), the whole mixture was heated at 55 °C for 14 h. The reaction mixture was poured into a solution of *ca.* 1 g of KCN in 30 mL of 10% aqueous ammonia, and stirred for 1 h at rt. The solid was collected by filtration and washed with hexane to remove PPh$_3$. The crude material was purified by chromatography on alumina using chloroform/hexane 1:3–1:1 as eluent. Recrystallization from chloroform afforded 118 mg (71%) of the pure product as pale yellow crystals. mp 367–369 °C (decomp, lit. 336–337 °C).[8] ^{1}H NMR (300 MHz, CDCl$_3$) δ (ppm): 7.49 (2H, dd, J = 4.3, 8.4 Hz), 7.75 (2H, dd, J = 4.4, 8.2 Hz), 7.78 (2H, dd, J = 1.7, 8.2 Hz), 7.96 (2H, s), 8.33 (2H, dd, J = 1.7, 8.1 Hz), 9.24 (2H, dd, J = 1.7, 4.2 Hz), 9.31 (2H, dd, J = 1.7, 4.4 Hz). ^{13}C NMR (75 MHz, CDCl$_3$) δ (ppm): 123.2, 123.6, 128.0, 128.1, 128.6, 134.5, 135.3, 136.1, 146.1, 146.2, 150.5, 150.9; UV (MeCN) λ_{max} (nm) (ε): 231 (61500), 266 (46500), 298 (10600), 325 (1850, sh).

HRMS (FAB): calcd for $C_{24}H_{14}N_4$: 359.1297 (MH$^+$), found: 359.1335. Anal. Calcd for $C_{24}H_{14}N_4 \cdot 1/2(CHCl_3)$: C, 70.38; H, 3.50; N, 13.40. Found: C, 70.06; H, 3.63; N, 13.53.

4,4'-Bi-1,10-phenanthroline (3). This compound was similarly prepared from 4-Cl-phen. The crude product was purified by chromatography on silica gel (Si-NH) with chloroform/hexane 1:1 as eluent. Recrystallization from chloroform afforded 66% of the desired compound as a white powder. mp 352–355 °C (decomp). ^{1}H NMR (300 MHz, CDCl$_3$) δ (ppm): 7.34 (2H, d, J = 9.2 Hz), 7.67 (2H, d, J = 9.2 Hz), 7.69 (2H, d, J = 4.5 Hz), 7.70 (2H, dd, J = 4.4, 8.1 Hz), 8.26 (2H, dd, J = 1.8, 8.1 Hz), 9.29 (2H, dd, J = 1.8, 4.4 Hz), 9.38 (2H, d, J = 4.5 Hz). ^{13}C NMR (75 MHz, CDCl$_3$) δ (ppm): 123.4, 123.5, 123.7, 126.8, 127.2, 128.4, 135.9, 144.1, 146.1, 146.4, 149.7, 150.7. UV (MeCN) λ_{max} (nm) (ε): 232 (53200), 268 (43000), 280 (30400), 299 (12500), 328 (1770, sh). HRMS (FAB): calcd for $C_{24}H_{14}N_4$: 359.1297 (MH$^+$), found: 359.1277. Anal. Calcd for $C_{24}H_{14}N_4 \cdot 1/2(H_2O)$: C, 78.46; H, 4.12; N, 15.25. Found: C, 78.82; H, 4.14; N, 15.41.

2,2'-Bi-1,10-phenanthroline (1). This compound was prepared from 2-Cl-phen in 71% yield. mp 364–366 °C (lit., 370 °C).[8] ^{1}H NMR (300 MHz, CDCl$_3$) δ (ppm): 7.69 (2H, dd, J = 4.4, 8.1 Hz), 7.85 and 7.92 (4H, ABq, J = 8.8 Hz), 8.31 (2H, dd, J = 1.7, 8.0 Hz), 8.50 (2H, d, J = 8.5 Hz), 9.29 (2H, dd, J = 1.7, 4.4 Hz), 9.46 (2H, d, J = 8.5 Hz). ^{13}C NMR (75 MHz, CDCl$_3$) δ (ppm): 122.4, 122.9, 126.7, 126.9, 129.0, 129.2, 136.3, 137.0, 145.7, 146.5, 150.5, 156.2; UV (MeCN) λ_{max} (nm) (ε): 241 (48300), 260 (18300), 292 (28800), 321 (23200), 337 (20500), 354 (22000), 367 (4350, sh), 382 (1310, sh).

3,3'-Bi-1,10-phenanthroline (2). This compound was prepared from 3-Br-phen in 62% yield; mp 365–366 °C (lit. >300 °C).[11] ^{1}H NMR (300 MHz, CDCl$_3$) δ (ppm): 7.70 (2H, dd, J = 8.0, 4.2 Hz), 7.92 and 7.99 (4H, ABq, J = 9.1 Hz), 8.32 (2H, dd, J = 1.6, 8.1 Hz), 8.65 (2H, d, J = 2.2 Hz), 9.26 (2H, dd, J = 1.4, 4.4 Hz), 9.60 (2H, d, J = 2.4 Hz). ^{13}C NMR (75 MHz, CDCl$_3$) δ (ppm): 123.3, 126.6, 127.5, 128.6, 129.1, 132.6, 134.0, 136.0, 146.0, 146.3, 149.2, 150.7. UV (MeCN) λ_{max} (nm) (ε): 216 (15300), 221 (15300), 273 (32300), 314 (19300).

Measurement of electronic spectra. All measurements were carried out with a 10 mm cell in spectroscopic grade solvents that were degassed before use. Sample was prepared by dissolving a ligand in acetonitrile to make a concentration of ca. 5×10^{-5} mol/L for UV measurement and 1–3×10^{-6} mol/L for fluorescence measurement. The spectra were first measured without an additive, and then with a large excess of methanesulfonic acid (10 μL per 10 ml of sample solution) or 10 molar amount of ZnCl$_2$. The emission spectra were measured upon excitation at 305 nm, and the quantum yield was determined with quinidine sulfate solution in 1.0 mol/L sulfuric acid as reference. For the titration experiment, each ligand was dissolved in dichloromethane/acetonitrile (1:1) to make a concentration of 1.0×10^{-4} mol/L because of poor solubility in acetonitrile. The spectra were measured repeatedly after each addition of a certain amount of [Cu(MeCN)$_4$]PF$_6$ solution in the same solvent.

Preparation of Cu(I) complex. To 10 mL of degassed acetonitrile were added $[Cu(MeCN)_4]PF_6$ (50 mg, 0.14 mmol) and 2,2'-biphen (**1**) (53 mg, 0.14 mmol) under argon. The solution became dark red immediately after the addition of the ligand. The solution was concentrated by slow evaporation to afford 64 mg (82%) of dark red crystals. mp > 300°C (decomp). ^{1}H NMR (300 MHz, CDCl$_3$) δ (ppm): 7.54 (2H, dd, J = 4.5, 7.9 Hz), 7.65 and 7.71 (4H, ABq, J = 9.0 Hz), 8.18 (2H, d, J = 4.5 Hz), 8.28 (2H, d, J = 7.9 Hz), 8.33 and 8.34 (4H, ABq, J = 8.3 Hz). UV (MeCN) λ_{max} (nm) (ε): 222 (41700), 261 (26900), 434 (3100), 555 (1400). Anal. Calcd for $C_{48}H_{28}N_8Cu_2F_{12}P_2$: C, 50.82; H, 2.49; N, 9.88. Found: C, 50.44; H, 2.39; N, 9.90. The other ligands were similarly treated with the Cu reagent to give red solutions from which the complexes could not be isolated in pure form.

Crystal Data of Cu(I) complex of 1. The data were collected on a Rigaku RAXIS-IV diffractometer. All intensity measurements were performed using graphite monochromated Mo-$K\alpha$ radiation (λ = 0.71073 Å). Single crystals of the Cu(I) complex of **1** were recrystallized from acetonitrile. Formula $C_{48}H_{28}N_8Cu_2F_{12}P_2$, MW = 1133.82, orthorhombic, space group Fddd (no. 70), a = 29.18(1), b = 38.10(2), c = 7.940(3) Å, V = 8826(6) Å^3, T = 296 K, Z = 8, D_{calcd} = 1.71 g/cm^3, μ = 11.35 cm^{-1}, 2274 reflections measured and used in all calculations. The final $R_1(F)$ = 0.054 , $wR_2(F^2)$ = 0.176, GOF 1.00. CCDC reference number 243741.

MO calculation. The PM3 calculations of **1**–**4** were performed using the MOPAC 2000 program on a personal computer. The molecular models in Fig. 1 were generated by the Chem3D Pro program (ver. 5.0).

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