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Highly Emissive Copper(I) Complexes Bearing Diimine and Bis(diphenylphosphinomethyl)-2,2-dimethyl-1,3-dioxolane

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A highly emissive copper(I) complex bearing (4R, 5R)-(-)-4,5-bis(diphenylphosphinomethyl)-2,2-dimethyl-1,3-dioxolane (diop) and 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (dmpp), [Cu(dmpp)(diop)]PF₆ (1·PF₆), was newly synthesized. The quantum yield of the luminescence of 1·PF₆ in degassed dichloromethane is 0.38, which is one of the highest values among all copper(I) complexes bearing two bidentate ligands, diimine and diphosphine, under the same condition. The long lifetime (26 µs) and high intensity of the emission come from the small non-radiative decay rate of the excited states. TD-DFT study indicates that the charge transfer transition from both copper and diphosphine to diimine orbitals plays an important role for the photophysical properties. Photophysics of [Cu(dmp)(diop)]PF₆ (2·PF₆, dmp = 2,9-dimethyl-1,10-phenanthroline) was also studied in order to reveal the effects of the introduction of the phenyl group at 4- and 7-positions of phenanthroline.

Introduction

Charge transfer (CT) excited state of metal complexes is one of the key features for photocatalysts and light-emitting devices due to their unique photochemical and photophysical properties. Copper(I) complexes bearing two bidentate ligands are one of the promising candidates for these photofunctional materials.1-6

Up to now, bis(2-diphenylphosphinophenyl)ether (DPEPhos) has been often used for the development of the photofunctional copper(I) complexes bearing diimine (NN) and diphosphine (PP) ligands due to their long lifetime and high quantum efficiency of the luminescence.7-20 Diimine ligands, such as 2,9-dimethyl-1,10-phenanthroline (dmp) derivatives, are useful for the enhancement of the luminescence properties, because the methyl groups, which are close to the copper centre, effectively inhibit the structural rearrangement in the photoexcited states. Additionally, photophysics of the copper(I) complexes bearing 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (dmpp) and DPEphos has been reported;20 the substitution of the phenyl groups at 4- and 7-positions of the phenanthroline (Ph₂NN) moiety has been found to increase the quantum yield and the lifetime of the luminescence.

Diop ((4R, 5R)-(-)-4,5-bis(diphenylphosphinomethyl)-2,2-dimethyl-1,3-dioxolane) had been widely used in the catalyst for asymmetric catalysis.21 A few copper(I) complexes bearing diop, such as dinuclear copper(I) complex bridged by chloride anion, have been reported.22 However, the number of reports about heteroleptic metal complexes bearing diimine and diop as well as their photophysical properties is limited.23
enables us to elucidate the ligand effects of diop moiety which drastically enhances the luminescence.

Experimental

Materials and Methods

(4R, 5R)-(−)-4,5-Bis(diphenylphosphinomethyl)-2,2-dimethyl-1,3-dioxolane (diop) was purchased from Strem Chemical Inc., 4,7-Diphenyl-2,9-dimethyl-1,10-phenanthroline (bathocuproine, dmp) was purchased from Tokyo Chemical Industry CO., LTD. Tetrais(acetonitrile)coppper(I) hexafluorophosphate ([Cu(MeCN)]PF6)37a, [Cu(dmpp)]PF637b and [Cu(dmpp)]PF637b were synthesized according to the method described in the literature. 1H-NMR, 13C-NMR, and 31P-NMR spectra in acetone-d6 were recorded on a JEOL Delta-500 spectrometer using tetramethylsilane (δ = 0.00 ppm, 1H) and solvent residual signals (δ = 29.84 ppm, 13C) as an internal standard. Absorption and emission spectra were obtained in a solvent degassed by at least five freeze-pump-thaw cycles using a quartz cell fitted with a Teflon vacuum stop cock. Absorption spectra were measured on a Shimadzu UV-3100 spectrometer. Emission spectra and emission lifetimes were collected on a laboratory-made apparatus. For the steady state emission spectra, a degassed sample solution was excited through a quartz fiber and fed into a spectrometer equipped with a cooled CCD sensor (Ocean Optics model QE65000). Emission quantum yields were obtained using [Ru(bpy)3]Cl2 as a standard (ϕ = 0.94% in acetonitrile). For the measurement of emission decay, the sample was excited by a Nd:YAG laser (Usho, KEN-1520), and the emission was focused on a 20 cm monochromator (Jovin Yvon H-20). The emission light was detected by a photomultiplier tube, Hamamatsu R928, and the signal was digitized by an oscilloscope (Tektronix TDS5034).

Synthesis

[Cu(dmpp)(diop)]PF6 (1-PF6). Under an argon atmosphere, [Cu(MeCN)]PF6 (35 mg, 0.094 mmol) was added to diop (47 mg, 0.094 mmol) in a 5 mL tetrahydrofuran solvent. Then, dmpp (36 mg, 0.094 mmol) was added. The reaction mixture was stirred for 90 min. At room temperature. Diethyl ether was added to the solution to precipitate the product as a yellow solid, which was filtered, washed with diethyl ether, and dried in vacuo: yield, 53 mg (0.050 mmol, 53%). 1H NMR (500 MHz, acetone-d6) δ 8.01 (s, 2H, phen), 7.66 (m, 12H, 7.52 (m, 4H), 7.44 (t, 2H, J = 8 Hz), 7.37 (t, 2H, J = 8 Hz), 7.28 (t, 2H, J = 8 Hz), 7.22 (m, 4H), 7.13 (m, 4H), 4.67 (m, 2H), 3.52 (m, 2H), 3.19 (m, 2H), 2.36 (s, 6H), 1.53 (s, 6H). 13C NMR (126 MHz, acetone-d6) δ 159.9, 151.3, 144.9, 137.6, 134.6, 134.4, 132.7 (t, J = 7 Hz), 131.9 (t, J = 7 Hz), 131.2, 130.7, 130.3, 130.2, 130.0 (t, J = 5 Hz), 129.9, 129.5 (t, J = 5 Hz), 126.8, 126.6, 124.8, 109.5, 81.0 (t, J = 10 Hz), 32.0 (t, J = 10 Hz), 28.1, 27.2. 31P[1H] NMR (202 MHz, acetone-d6) δ −21.0 (s, br, phosphine), −143.6 (septet, PF6). Anal. Found: C, 64.12; H, 4.67; N, 2.71%. Calcd for C57H54N4O22PF3PF6 Cu: C, 64.13; H, 4.91; N, 2.62.

[Cu(dmp)(diop)]PF6 (2-PF6). Synthesis of 2-ClO4 has been mentioned in the literature. 2-PF6 was synthesized according to a similar procedure to that of 1-PF6 with a modification of the solvent from tetrahydrofuran to CH2Cl2. 1H NMR (500 MHz, acetone-d6) δ 8.70 (d, 2H, J = 8 Hz, phen), 8.24 (s, 2H, phen), 7.73 (d, 2H, J = 8 Hz, phen), 7.42 (m, 6H, Ph), 7.31 (t, J = 8 Hz, 4H, Ph), 7.24 (t, J = 8 Hz, 2H, Ph), 7.15 (m, 4H, Ph), 7.06 (t, J = 8 Hz, 4H, Ph), 4.66 (m, 2H), 3.51 (m, 2H), 3.15 (m, 2H), 2.25 (s, 6H), 1.53 (s, 6H). 13C NMR (126 MHz, acetone-d6) δ 160.4, 144.0, 139.3, 134.5, 134.4, 132.5 (t, J = 7 Hz), 131.8 (t, J = 7 Hz), 131.1, 130.7, 129.9 (t, J = 4 Hz), 129.5 (t, J = 4 Hz), 129.1, 127.3, 126.4, 109.8, 81.0 (t, J = 10 Hz), 32.0 (t, J = 10 Hz), 27.8, 132.3. 31P[1H] NMR (202 MHz, acetone-d6) δ 21.7 (s, br, phosphine), −143.6 (septet, PF6). Anal. Found: C, 58.88; H, 4.62; N, 3.47%. Calcd for 2-PF6C65H52N6O42F6P2PF6 Cu: C, 59.05; H, 4.85; N, 3.06.

Crystallography

X-ray crystallographic measurements of 1-PF6-2THF and 2-PF6-CH2Cl2 were made on a Rigaku Saturn 70 CCD area detector with graphite-monochromated MoKα radiation. Images were collected and the data were processed using CrystalClear. The structures were solved by direct methods SIR-92 and refined by full matrix least squares procedures (SHELXL-97). All calculations were performed by using the WinGX crystallographic software package. Crystallographic data have been deposited with Cambridge Crystallographic Data Centre: Deposition number CCDC-1020906 for 1-PF6-2THF and CCDC-1020905 for 2-PF6-CH2Cl2. Copies of this data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html. Single crystals suitable for analysis were obtained by slow diffusion of hexane in tetrahydrofuran or dichloromethane solution of 1-PF6 or 2-PF6, respectively. Crystal data for 1-PF6-2THF: C65H62N6O42P3PF6Cu, M = 1187.56, yellow crystal, orthorhombic, space group P212121, a = 11.3979(7) Å, b = 21.3866(11) Å, c = 51.6198(16) Å, α = β = γ = 90°, V = 6172.7(6) Å3, Z = 4, T = 123 K, Dc = 1.278 g cm−3, µ = 0.494 mm−1, R = 0.0737 for 27281 reflections with I > 2σ(I), Rw = 0.2188 GOF = 1.06. Flack parameter 0.001(14); Crystal data of 2-PF6-CH2Cl2: C65H52N6O42P3PF6Cl2Cu, M = 1000.2, yellow crystal, triclinic, space group P1, a = 9.927(9) Å, b = 11.073(10) Å, c = 11.197(11) Å, α = 90.23(3)°, β = 90.84(3)°, γ = 112.89(3)°, V = 1133.6(18) Å3, Z = 1, T = 123 K, Dc = 1.465 g cm−3, µ = 0.771 mm−1, R = 0.0558 for 5952 reflections with I > 2σ(I), Rw = 0.138 GOF = 1.032 Flack parameter 0.014(16).

DFT calculation

Calculation was performed using Gaussian 03W software44 with the B3LYP53-57 method using the atomic coordinates determined by X-ray as the initial coordinates in the optimization. TDDFT was used to calculate singlet and triplet excited state energies. Basis sets were as follows: copper 6-311G with Wachters’s 4p functions,48 phosphorus, oxygen, and nitrogen 6-31G*, carbon 6-31G*, and hydrogen 6-31G. Population analysis was carried out by AOMIX software.49 The pictures of the orbitals have been depicted with MOLKEL software.50

Discussion and Results

1-PF6 was newly synthesized by a reaction of diop, dmp, and tetrais(acetonitrile)coppper(I) hexafluorophosphate ([Cu(MeCN)]PF6) in tetrahydrofuran at room temperature. The compound was characterized by 1H NMR, elemental analysis, and single-crystal X-ray structural analysis. Crystal structures of 1 and 2 are shown in Fig. 1. The structures of heteroleptic mononuclear copper(I) complexes

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bearing two bidentate ligands, diimine and diphosphine, with tetrahedral coordination geometry were confirmed in both 1\(^+\) and 2\(^+\). The bond lengths, angles, and dihedral angles of these complexes were comparable to those in a family of copper(I) complexes bearing diimine and diphosphines (Table S1). The P-Cu-P angles of 1\(^+\) and 2\(^+\) are 116.25(4)\(^\circ\) and 114.71(4)\(^\circ\), respectively. The P-Cu-P angle of 2\(^+\) is larger than that of [Cu(dmpp)(dppp)]\(^+\) (105.42(3)\(^\circ\) and 105.31(3)\(^\circ\)), and is similar to that of [Cu(dmpp)(DPEPhos)]\(^+\) (116.44(4)\(^\circ\)). The dihedral angle between N-Cu-N and P-Cu-P planes of 1\(^+\) (81.00\(^\circ\)) is smaller than those of 2\(^+\) (84.7\(^\circ\)), indicating that the introduction of PbNS increases the distortion of four-coordinated copper(I) complexes from regular tetrahedral geometry. The dihedral angle is also smaller than that observed in [Cu(dmpp)(dppe)]\(^+\) (89.5\(^\circ\), 87.2\(^\circ\)), and [Cu(dmpp)(dppp)]\(^+\) (86.2\(^\circ\), 83.8\(^\circ\)). The dihedral angles between PbNS and phenanthroline planes in 1\(^+\) are 52\(^\circ\) and 49\(^\circ\), suggesting that the \(\pi\)-conjugation of the phenanthroline moiety is not apparently extended to the PbNS groups.

\(^1\)H NMR spectra of both 1\(^+\) and 2\(^+\) in acetone-\(d_6\) at room temperature suggest that the heteroleptic structures are kept in the solution state. Other species, such as [Cu(dmpp)]\(PF_6\) (\(\delta = 8.16\) and 8.00 ppm in acetone-\(d_6\)) and [Cu(dmpp)]\(PF_6\) (\(\delta = 8.76\), 8.23, and 7.98 ppm in acetone-\(d_6\)), are negligible, since only one set of aromatic signals of phenanthroline moieties is observed in the \(^1\)H NMR spectra of both 1\(^+\) (\(\delta = 8.01\) and 7.66 ppm) and 2\(^+\) (\(\delta = 8.70\), 8.24 and 7.73 ppm) (Fig. 2 and Supplementary Information Fig. S1-S6). The chemical shifts in the ligand moieties, such as alkyld chain of diop, in \(^1\)H NMR spectra of both 1\(^+\) and 2\(^+\) are shifted downfield from those of the free ligand, diop, because of the decrease of the electron density caused by coordination (Table S2). The downfield shifts of chemical shifts are also observed in \(^31\)P NMR spectra (\(-21.0\) ppm for 1\(^+\), -21.7 ppm for 2\(^+\), and -22.4 ppm for diop). Moreover, the ratios of signal integrations of diop and diimine moieties are also consistent with the heteroleptic compounds. \(^1\)H NMR signals did not change after several days in air at room temperature excited by UV light. (Fig. S7). Additionally, \(^1\)H NMR spectrum of 1\(^+\) in dimethylsulfoxide-\(d_6\)/D\(_2\)O (v/v 10:1) after heating at 353 K for 2 hours under air is essentially the same as that before heating, suggesting that 1\(^+\) has sufficient stability even in the presence of water and highly coordinative solvent (Fig. S8). Heating 1\(^+\) in dimethylsulfoxide-

Fig. 1. The crystal structures of the complex cations of 1\(^+\) (left) and 2\(^+\) (right). Hydrogens, counter ions, and solvent molecules are omitted for clarity. Important bond length (Å) and angles (\(^\circ\)) for 1\(^+\): Cu1–N1, 2.060(3); Cu1–N2, 2.080(4); Cu1–P1, 2.2279(12); Cu1–P2, 2.2449(11); N1–Cu1–N2, 80.97(13); P1–Cu1–P2, 116.25(4). For 2\(^+\): Cu1–N1, 2.075(5); Cu1–N2, 2.084(5); Cu1–P1, 2.228(2); Cu1–P2, 2.258(2); N1–Cu1–N2, 81.3(2); P1–Cu1–P2, 114.71(8).

Fig. 2. Partial \(^1\)H NMR spectra of 1\(PF_6\) (a) and 2\(PF_6\) (b) in acetone-\(d_6\) at room temperature.

Fig. 3. (a) Absorption spectra of 1\(PF_6\) (blue, solid line) and 2\(PF_6\) (red, dashed line) in dichloromethane at room temperature. (b) Emission spectra of (blue, solid line) and 2\(PF_6\) (red, dashed line) in degassed dichloromethane at room temperature. Excitation wavelength is 370 nm. (c) Emission decay curve of 1\(PF_6\) (blue) and 2\(PF_6\) (red) in degassed dichloromethane at room temperature observed at 580 nm. (d) Photograph of the emission of (left) [Ru(bpy)]\(Cl_3\) in degassed acetonitrile, (middle) 1\(PF_6\) in degassed dichloromethane, and (right) 2\(PF_6\) in degassed dichloromethane at room temperature excited by UV light.
be due to the large P9Cu9P angles. An absorption shoulder both 

$[Cu(dmp)(dppe)]PF_6$ complexes bearing diimine and diphosphine. 

The apparent radiative rate constant, $k_r$, of $1^{+}$ is much longer than those of $[Cu(dmp)(dppp)]^+$ (0.14,5,29) and $[Cu(dmp)(DPEphos)]^+$ (0.15,14) indicating that the dip ligand is effective to enhance the luminescence.

Table 2. Population analysis of the DFT calculations based on the singlet optimized structures.

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<tr>
<th>K-S orbital</th>
<th>Energy/eV</th>
<th>Cu$^{a}$</th>
<th>PP$^{b}$</th>
<th>NN$^{c}$</th>
<th>Phos$^{d}$</th>
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<tr>
<td>$1^{+}$</td>
<td>LUMO+1</td>
<td>-4.05</td>
<td>0</td>
<td>1</td>
<td>90</td>
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<td></td>
<td>LUMO</td>
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<td>1</td>
<td>89</td>
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<td>34</td>
<td>9</td>
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<tr>
<td></td>
<td>HOMO-1</td>
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<td>78</td>
<td>4</td>
<td>17</td>
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<tr>
<td></td>
<td>HOMO-2</td>
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<td>76</td>
<td>16</td>
<td>8</td>
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<td>56</td>
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<td>-8.98</td>
<td>2</td>
<td>27</td>
<td>70</td>
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Table 1. Photophysical properties of the copper(II) complexes. All data were obtained in degassed dichloromethane at room temperature.

<table>
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<tr>
<th>$\lambda_{abs,max}$/nm</th>
<th>$\lambda_{em,max}$/nm</th>
<th>$\tau$/µs</th>
<th>$\Phi$</th>
<th>$k_r$/$10^4$</th>
<th>$k_n$/$10^4$</th>
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<tr>
<td>1-PF$_6$</td>
<td>286, 382</td>
<td>570</td>
<td>26.1</td>
<td>0.38</td>
<td>1.4</td>
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<tr>
<td>2-PF$_6$</td>
<td>274, 374</td>
<td>560</td>
<td>17.7</td>
<td>0.30</td>
<td>1.7</td>
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<table>
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<tr>
<th>$\lambda_{em}$/nm</th>
<th>$\Phi_c$/%</th>
<th>$\tau_c$/µs</th>
<th>$k_{c}$/$10^4$</th>
<th>$k_{nc}$/$10^4$</th>
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<tr>
<td>$1^{+}$</td>
<td>570</td>
<td>560</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>$2^{+}$</td>
<td>600</td>
<td>565</td>
<td>130</td>
<td>130</td>
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</table>

The emission spectra of both $1^{+}$ and $2^{+}$ show broad luminescence bands due to the CT excited state, which is characteristic of a family of $[Cu(NN)(PP)]^+$ complexes (Fig. 3b). The wavelength at the emission maximum, $\lambda_{em}$, of $1^{+}$ and $2^{+}$ are

\[ \lambda_{em} = 570 \text{ nm} \] and \[ \lambda_{em} = 560 \text{ nm} \] respectively. Furthermore, the difference in the Stokes shift of $1^{+}$ (8700 cm$^{-1}$) and $2^{+}$ (8800 cm$^{-1}$) is very small (100 cm$^{-1}$). The result can be explained by the small difference in the structural rearrangement in the photoexcited states between $1^{+}$ and $2^{+}$. The maximum wavelength of the CT luminescence of $2^{+}$ is blue-shifted from that of $[Cu(dmp)(dppe)]PF_6$, $[Cu(dmp)(dppp)]PF_6$ ($\lambda_{em} = 594$ nm), \[ [Cu(dmp)(DPEphos)]^+ \] ($\lambda_{em} = 600$ nm), and $[Cu(dmp)(DPEphos)]BF_4$ ($\lambda_{em} = 565$ nm) in dichloromethane at room temperature. In the solid state, strong emissions are observed for complexes $1^{+}$ and $2^{+}$. The wavelength at the emission maximum of $1^{+}$ in the solid state under air at room temperature is red-shifted from that of $2^{+}$ (Fig. S10). The difference in the emission maxima could be caused by the difference between the two crystal structures. $1^{+}$ has more distorted tetrahedral geometry than $2^{+}$ as mentioned above.

The quantum yield, $\Phi_c$ of the CT luminescence of $1^{+}$ in degassed dichloromethane at room temperature is 0.38, which is one of the highest values for copper(II) complexes bearing diphosphine and diimine ligands. The value is slightly larger than that of $2^{+}$ (0.30) under the same condition, suggesting that the introduction of Ph$_2$N contributes to the enhancement of the quantum yield. The value of $2^{+}$ is much longer than those of $[Cu(dmp)(dppp)]^+$ (0.04), and $[Cu(dmp)(DPEphos)]^+$ (0.15), indicating that $2^{+}$ is effective to enhance the luminescence.

The emission decay curves of $1^{+}$ and $2^{+}$ in degassed dichloromethane are best fit to a single-exponential function (Fig. 3c). The lifetimes of the emission, $\tau$, of $1^{+}$ and $2^{+}$ in degassed dichloromethane are 26.1 µs and 17.7 µs, respectively, suggesting that the Ph$_2$N substitution extends the lifetime of the luminescence. The long lifetime of both $1^{+}$ and $2^{+}$ compared to normal organic fluorescence attributes to the fact that the emission of $[Cu(NN)(PP)]^+$ is often derived from delayed fluorescence. The value of $2^{+}$ is much longer than those of $[Cu(dmp)(dppe)]^+$ (1.3 µs) and $[Cu(dmp)(dppp)]$ (5.4 µs), and is comparable with that of $[Cu(dmp)(DPEphos)]^+$ (14.3 µs).

The apparent radiative rate constant, $k_r$, of $1^{+}$ ($1.4 \times 10^4$ s$^{-1}$) is similar to that of $2^{+}$ ($1.7 \times 10^4$ s$^{-1}$); $k_r$ includes two radiative processes from both the excited singlet and triplet
The luminescence was found to be strongly air-sensitive; the long-lived photoexcited states of 1' and 2' are efficiently quenched by dioxygen molecules (Fig. 4a and Fig. S11). The quantum yields of the emission of 1' and 2' in air-saturated dichloromethane are 0.004 and 0.002, respectively, which are one hundredth of those in degassed one. The lifetimes of 1' and 2' in air-saturated dichloromethane are 0.3 µs and 0.2 µs, respectively, which are also one hundredth of those in degassed one. The values of $k_{nr}$ of 1' and 2' in air-saturated dichloromethane are $2.4 \times 10^4$ s$^{-1}$ and $4.0 \times 10^4$ s$^{-1}$, respectively, which are not so different from those in degassed one. The decrease in $k_{nr}$ could be explained by the energy-gap law and the steric effects of rigid diop ligand in the excited states: the inhibition of the structural rearrangement and the inhibition of the solvent quenching. These two factors are often used to explain the photophysics of copper(I) complexes bearing diimine.$^{9,31}$

Fig. 5. Kohn-Sham orbitals of 1' and 2'. Orbitals calculated based on the optimized structure in the $S_0$ (singlet ground) states (contour value 0.02).
The values of $k_t$ at 253 K and 213 K are much smaller than that at 298 K, because the contribution of the thermally-activated-fluorescence at lower temperature is reduced than that at higher temperature (Table S3). The values of $k_{nr}$ at 253 K and 213 K are also smaller than that at 298 K, but the decrease in $k_t$ at low temperature is more remarkable than that in $k_{nr}$. Therefore the emission intensities at lower temperature are weaker than those at higher temperature.

DFT calculations for $1^\ast$ and $2^\ast$ were performed in order to examine the photophysics of the complexes. The results are tabulated in Table 2 and Table 3, and the Kohn-Sham orbitals are displayed in Fig. 5. Details of the results of the calculations are tabulated in Table S4, S5, S6, and S7. The optimized structures in the singlet ground state ($S_0$) of both $1^\ast$ and $2^\ast$ were used in the population analysis and TD-DFT calculations.

The HOMO, HOMO-1, and HOMO-2 of $1^\ast$ mainly consist of the copper (54% for HOMO, 78% for HOMO-1, 76% for HOMO-2) atom orbitals with minor contribution of the phosphorus atoms as well as phenyl groups in diimopyridine (Table 2, Table S4, and Table S5). In contrast, LUMO and LUMO+1 of $1^\ast$ have major components of the $\pi^*$ orbitals of the phenanthroline moiety. The contributions of Ph$_{NN}$ in LUMO and LUMO+1 are small but not negligible, and those in HOMO-3 and HOMO-4 are significant (31% for HOMO-3 and 62% for HOMO-4). This result suggests that the phenyl groups, Ph$_{NN}$, which are not parallel to the phenanthroline plane, can significantly affect the photophysics of the complexes. The population for these orbitals of $2^\ast$ is basically similar to that of $1^\ast$, except for the orbitals related to the phenyl groups on the phenanthroline moiety.

TD-DFT calculation for $1^\ast$ indicates that the largest component of the transition from ground ($S_0$) to singlet lowest-lying excited ($S_1$) states ($S_0\rightarrow S_1$) is HOMO$\rightarrow$LUMO, which can be represented as a CT transition from an orbital consist of copper and phosphorus atomic orbitals to the $\pi^*$ orbital of diimine moiety (Table 3, Table S3 and Table S4). The component of HOMO-1$\rightarrow$LUMO also contributes to the CT transition mentioned above. The calculated energy of the wavelength of $1^\ast$ is 427 nm, which is close to the experimental value obtained from lowest-energy, suggesting that the absorption is assigned as the CT transition, which is characteristic of a family of [Cu(NN)(PP)]$^{\ast}$.

Other calculated transitions, shown in Table 3, from ground to upper excited states are related to the components of the CT transition, such as HOMO$\rightarrow$LUMO+1, or the $\pi\pi^*$ transitions of the phenanthroline moiety, such as HOMO-3$\rightarrow$LUMO and HOMO-4$\rightarrow$LUMO+1.

The character of the transition of $2^\ast$ is similar to that of $1^\ast$. For example, the $S_0\rightarrow S_1$ transition has a major component of HOMO$\rightarrow$LUMO, which is assigned as the CT transition mentioned above. The calculated energy of the $S_0\rightarrow S_1$ transition of $2^\ast$ (432 nm) is red-shifted from that of $1^\ast$ (427 nm), whereas experimental absorption of $2^\ast$ (374 nm) in dichloromethane is blue-shifted from that of $1^\ast$ (382 nm). The value of $\lambda_f$ of $1^\ast$ is approximately twice as large as that of $2^\ast$. The increase of the value of $\lambda_f$ can be caused by the effects of the introduction of Ph$_{NN}$. The contribution of the Ph$_{NN}$ moieties to the LUMO, LUMO+1, HOMO-3 and HOMO-4 as described above should be the main reason why almost all oscillator strength values of $1^\ast$ are large than that of $2^\ast$.

The largest component among the transitions from ground to triplet excited ($T_1$) states ($S_0\rightarrow T_1$) of $1^\ast$ is HOMO$\rightarrow$LUMO+1, which is also represented as the CT transition from an orbital, which consists of copper and phosphorus atomic orbitals, to the $\pi^*$ orbital of phenanthroline moiety. The energy of the $S_0\rightarrow T_1$ transition of $1^\ast$ is 476 nm, which is shorter than the experimental emission spectra (570 nm) in the solution state. The difference between calculated and experimental values is due to the fact that the structural relaxation in the excited state of [Cu(NN)(PP)]$^{\ast}$ is generally large. The difference in the calculated energy between $S_0\rightarrow S_1$ (23400 cm$^{-1}$) and $S_0\rightarrow T_1$ (21000 cm$^{-1}$) transitions is small (2400 cm$^{-1}$) compared to normal organic compounds. The calculation is consistent with the fact that the observed emission at room temperature is derived from delayed fluorescence which is characteristic of the luminescence of [Cu(NN)$_2$]$^{\ast}$ and a family of [Cu(NN)(PP)].

The experimental results of the temperature dependence of the emission spectra also support the mechanism. The trend in the $S_0\rightarrow T_1$ transition of $2^\ast$ is basically similar to that of $1^\ast$. It should be noted that the calculated $S_0\rightarrow T_1$ transition of $1^\ast$ has the contribution of the orbitals HOMO-3, HOMO-4, HOMO-11, HOMO-13, and HOMO-21, which show significant amplitude at the Ph$_{NN}$ groups in the phenanthroline moiety. These contributions should be one of the origins of the remarkable photophysical properties of $1^\ast$.

Conclusion

A highly emissive copper(I) complex bearing dmp and diop, 1-PF$_6$, was newly synthesized, and the photophysics of 1-PF$_6$ and its dmp analogue, 2-PF$_6$, were examined in detail. The diop ligand is very effective to increase the quantum yield and the lifetime of the luminescence. One of the important reasons for the enhancement is the decrease of the apparent non-radiative constant. These emission properties are found to be enhanced by the introduction of Ph$_{NN}$, the phenyl groups at 4- and 7-positions of phenanthroline. The nature of the luminescence is charge transfer from both copper and phosphorus atom orbitals to $\pi^*$ orbitals of diimine moieties. This finding is important for development of photofunctional materials and utilization of light energy.

Acknowledgements

This work was financially supported by Grants-in-Aid from MEXT of Japan (26410077), the Promotion and Mutual Aid Corporation for Private Schools of Japan, and Grant from Seikei University.

Notes and references

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51 Apparent radiative and non-radiative constants are defined as $k_r = \Phi / \tau$ and $k_{nr} = (1 - \Phi) / \tau$, respectively.

52 The quantum yield for [Cu(dmp)(DPEphos)]$^+$ was reported to 0.15 based on the standard value ($\Phi = 0.042$ for [Ru(bpy)$_3$]$^{2+}$ in deoxygenated water). If the recently reported value of 0.06 (Reference 39) is employed for the standard, the value for [Cu(dmp)(DPEphos)]$^+$ should be 0.23. In this case, $k_r$ and $k_{nr}$ of [Cu(dmp)(DPEphos)]$^+$ are calculated to be $1.6 \times 10^4$ s$^{-1}$ and $5.4 \times 10^3$ s$^{-1}$, respectively. Even if these values are correct, the $k_{nr}$ of 2$^+$ is significantly lower than that of the DPEphos complex.
Highly Emissive Copper(I) Complexes Bearing Diimine and Bis(diphenylphosphinomethyl)-2,2-dimethyl-1,3-dioxolane

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TOC graphic

Highly emissive copper(I) complexes bearing 4,5-bis(diphenylphosphinomethyl)-2,2-dimethyl-1,3-dioxolane and 1,10-phenanthroline derivative were newly synthesized. The quantum yields of the photoluminescence are up to 0.38.