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ARTICLE

Emission Properties and Cu(I)-Cu(I) Interaction in 2-Coordinate Dicopper(I)-bis(N-heterocyclic)carbene Complexes

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The synthesis, characterization, and emission properties of 2-coordinate dicopper(I) complexes bearing two trimethylene-bridged bis-NHC ligands, [Cu₂(L3Me)₂](PF₆)₂ (**1**), [Cu₂(L3Et)₂](PF₆)₂ (**2**), [Cu₂(L3Bu)₂](PF₆)₂ (**3**), [Cu₂(L3MeOPh)₂](PF₆)₂ (**4**) and [Cu₂(L3Mes)₂](PF₆)₂ (**5**), where L3R denotes trimethylene-bridged bis(N-heterocyclic)carbene (NHC) ligand substituted by two R groups at the nitrogen atoms of NHC, have been investigated. The quantum yield, Φ , and the lifetime, τ , of the emission of **2**, are 0.21 and 25 μ s, respectively in methanol, which is a well-known solvent for quenching the luminescence of many copper(I) complexes. The 8-shaped geometry of dicopper(I) complexes brings a considerable copper(I)-copper(I) interaction which affects the luminescent properties. Additionally, we find that methoxyphenyl and mesityl groups substituted at nitrogen atom of NHC moiety drastically stabilize the bis(NHC) copper(I) complexes even in air-saturated acetone-*d*₆.

Introduction

Photophysics of coordination compounds, such as ruthenium(II),¹ iridium(III)² and copper(I) complexes,³⁻¹⁷ are of much interest as photofunctional materials. N-heterocyclic carbene (NHC) is one of the important class of ligands for the development of catalysts^{18,19} as well as the photofunctional materials.²⁰⁻²³ Emission properties of heteroleptic 3-coordinate copper(I) complexes bearing a monodentate NHC ligand, such as 1,3-bis(2,6-diisopropylphenyl)imidazole-2-ylidene (IPr), and a diimine or pyridyl-azolate ligand have been investigated.²⁴⁻²⁶ Recently, we found that a dicopper(I) complex bearing a methylene-bridged NHC ligand, [Cu₂(L1Me)₂](PF₆)₂ (**1'**), where L1Me denotes 1,1-methanediylbis(3-methyl-1*H*-imidazol-1-yl-2(3*H*)-ylidene (Scheme 1), exhibits strong photoluminescence in the solid state.²⁷ Several dinuclear 2-coordinate bis(NHC) copper(I) complexes have been reported in the past decade.²⁸⁻³² For example, the reaction of a trimethylene bridged NHC ligand, [H₂L3Me]²⁺, and silver(I) oxide provides disilver(I) complex, [Ag₂(L3Me)₂](PF₆)₂^{32,33} followed by transmetalation using copper(I) iodide to give [Cu₂(L3Me)₂](PF₆)₂ (**1**)³²; L3R denotes L3Me denotes 1,3-propanediylbis(3-methyl-1*H*-imidazol-1-yl-2(3*H*)-ylidene. Catalysis mediated by **1** was studied in the work,³² but no photophysical properties of the complexes have been reported.

Metal-metal interaction using multinuclear metal

complexes, such as platinum(II)-platinum(II)³⁴ and gold(I)-gold(I)³⁵ interactions, plays a key role in enhancing the photophysical properties; for copper(I) complexes,¹²⁻¹⁷ notable effects of weak metal-metal interactions on the properties of complexes such as cubane-like tetranuclear copper(I) iodide complexes¹⁴⁻¹⁶ have also been known. However, there are only limited number of reports studying the effect of the metal-metal interactions on the photophysical properties of Cu(I) complexes in contrast to the gold(I) complexes. Here, we study the photophysical properties of dicopper(I) complexes bearing NHC ligands by employing **1** and newly synthesized [Cu₂(L3Et)₂](PF₆)₂ (**2**, L3Et = 1,3-propanediylbis(3-ethyl-1*H*-imidazol-1-yl-2(3*H*)-ylidene), [Cu₂(L3Bu)₂](PF₆)₂ (**3**, L3Bu = 1,3-propanediylbis(3-(*n*-butyl)-1*H*-imidazol-1-yl-2(3*H*)-ylidene), [Cu₂(L3MeOPh)₂](PF₆)₂ (**4**, L3Bu = 1,3-propanediylbis(3-(4-methoxyphenyl)-1*H*-imidazol-1-yl-2(3*H*)-ylidene) and [Cu₂(L3Mes)₂](PF₆)₂ (**5**, L3Bu = 1,3-propanediylbis(3-mesityl-1*H*-imidazol-1-yl-2(3*H*)-ylidene) (Scheme 1). We found that the dicopper(I) complexes, **1**, **2**, and **3** show intense photoluminescence in methanol at room temperature, whereas emission of copper(I) complexes bearing diimine ligand is often quenched by solvent coordination. These emission properties are related to the effects of copper(I)-copper(I) interactions.

Experimental

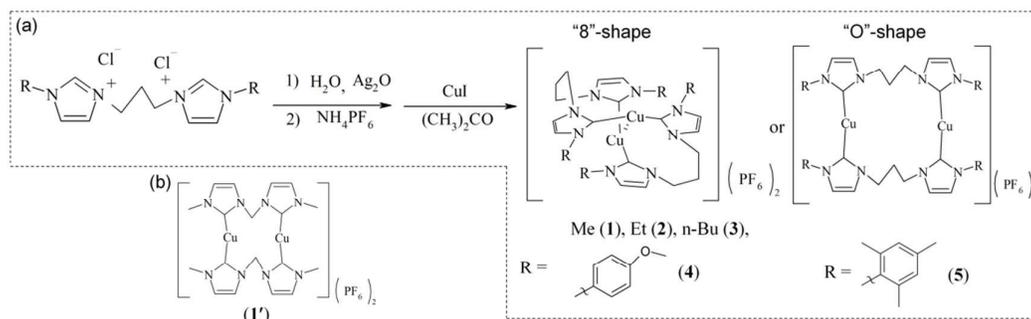
Materials and Methods

1,3-Dichloropropane, methylimidazole, ethylimidazole, and *n*-butylimidazole were purchased from Tokyo Chemical Industry CO., LTD. Silver(I) oxide, ammonium hexafluorophosphate, and copper iodide were purchased from

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*Electronic Supplementary Information (ESI) available: Crystallographic data for X-ray structural analysis, NMR spectra, emission spectra, and details of the DFT calculations. See DOI: 10.1039/x0xx00000x



Scheme 1. (a) Synthesis of **1**, **2**, **3**, **4**, and **5**. (b) Chemical structure of **1'**.²⁷

Wako Pure Chemicals Co., LTD. Methoxyphenylimidazole was purchased from Aldrich. Mesitylphenylimidazole was synthesized according to the method described in literature.⁴¹ The ligands, $[\text{H}_2\text{L3R}]\text{Cl}_2$, were obtained by the following modified methods described in the literature for $[\text{H}_2\text{L3Me}]\text{Cl}_2$. For example, for $[\text{H}_2\text{L3Bu}]\text{Cl}_2$, 1, 3-dichloropropane (0.13 mL, 1.4 mmol) and n-butylimidazole (0.36 mL, 2.8 mmol) were heated at 378 K for 2 days. The colorless solids precipitated were washed with tetrahydrofuran, dried in vacuum, and employed for preparation of silver(I) complexes without further purifications. ¹H-NMR were recorded on a JEOL Delta-500 spectrometer using tetramethylsilane ($\delta = 0.00$ ppm) and solvent residual signals ($\delta = 2.05$ ppm for acetone- d_6 , $\delta = 2.50$ ppm for DMSO- d_6) as references.⁴² 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. For these photophysical measurements, the solid sample is dissolved by the degassed solvent by using the homemade cell for freeze-pump-thaw handling, because the immediate chemical degradations, especially for **1**, **2**, and **3**, in air-saturated methanol are observed. Absorption spectra were measured on an Agilent 8453 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 by a monochromated Xe lamp (a 75 W lamp connected to an Oriol Cornerstone 130 monochromator) and the emission was collected 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 $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ as a standard ($\Phi = 0.094$ in acetonitrile).⁴³ For the measurement of emission decay, the sample was excited by a N_2 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). Elemental analysis was performed by A-Rabbit-Science Japan Co., Ltd.

Synthesis

Synthesis of $[\text{Cu}_2(\text{L3Me})_2](\text{PF}_6)_2$ (1**).** The known compound, **1**,³² was synthesized using a procedure similar to that described for **2**, described in the next paragraph, by using CuI

(62.9 mg, 0.33 mmol) and $[\text{Ag}_2(\text{L3Me})_2](\text{PF}_6)_2$ (99.5 mg, 0.11 mmol). The purity of the solid was checked by ¹H NMR and elemental analysis. White solids, yield 21 %. Elemental analysis. Found: C, 32.15; H, 4.01; N, 13.58. Calcd. For $\text{C}_{22}\text{H}_{32}\text{N}_8\text{P}_2\text{F}_{12}\text{Cu}_2$: C, 32.01; H, 3.91; N, 13.57.

Synthesis of $[\text{Cu}_2(\text{L3Et})_2](\text{PF}_6)_2$ (2**).** The compound, **2**, was synthesized by a modified method described in the literatures for **1**²⁷ and **1**.³² $[\text{H}_2\text{L3Et}]\text{Cl}_2$ (197 mg, 0.65 mmol) and Ag_2O (376 mg, 1.6 mmol) were added to 10 mL distilled water and stirred

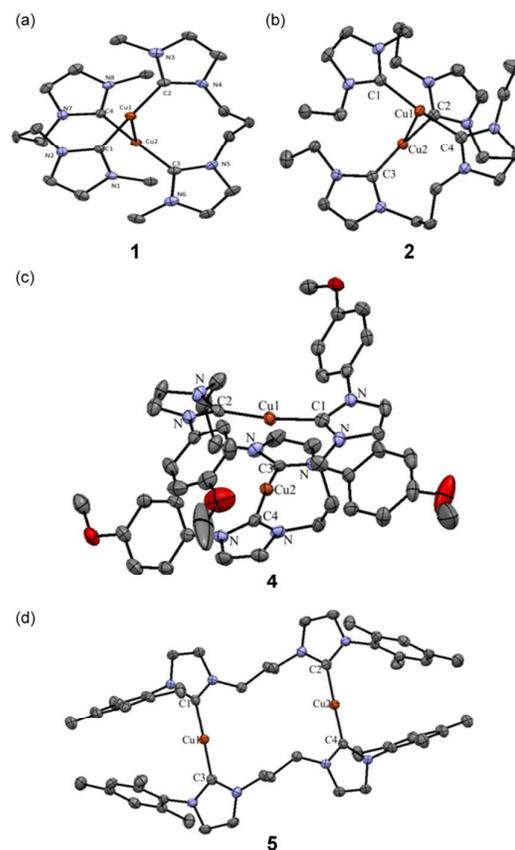


Fig. 1 The crystal structures of the copper(I) complexes of (a) **1**, (b) **2**, (c) **4** and (d) **5**. Hydrogens, counter ions, and solvent molecules are omitted for clarity. The displacement ellipsoids are drawn at the 50% probability level.

for 3 hours at room temperature. The solid was filtered off using Celite, and to the filtrate was added NH_4PF_6 (220 mg, 1.3 mmol) and kept in a refrigerator for several minutes. The formed precipitates were filtered and dried under vacuum. Molar ratio of Ag(I), L3Et, and PF_6^- of the solid is 1:1:1, confirmed by elemental analysis; Elemental analysis. Found: C, 31.49; H, 3.91; N, 11.42. Calculated for $\text{C}_{26}\text{H}_{40}\text{N}_8\text{P}_2\text{F}_{12}\text{Ag}_2 \cdot 0.5\text{H}_2\text{O}$: C, 31.89; H, 4.22; N, 11.44. The colorless solid of the silver(I) complex was employed for the next reaction without further purifications. Following synthetic procedures for the copper(I) complex were carried out under an argon atmosphere using the Schlenk technique. Copper iodide (CuI) powder (60.4 mg, 0.3 mmol) was added to a solution of the silver(I) complex (101.6 mg, 0.2 mmol for silver(I) ion) in acetone (15 mL). After stirring for 1 hour at room temperature, the yellow precipitates (AgI) were filtered off and the filtrate was added to diethyl ether to form white precipitates. After standing several minutes, the white precipitates were filtered off and dried in vacuum. White solids, yield 69 mg, 78 %. ^1H NMR (500 MHz, acetone- d_6) δ 7.670 (d, $J = 1.72$ Hz, 4H, NCHC), 7.643 (d, $J = 1.72$ Hz, 4H,

NCHC), 4.337(t, $J = 5.58$ Hz, 8H, NCH_2CH_2), 3.931 (q, $J = 7.30$ Hz, 8H, NCH_2CH_3), 2.707 (m, 4H, $\text{CH}_2\text{CH}_2\text{CH}_2$), 1.394 (t, $J = 7.30$ Hz, 12H, NCH_2CH_3). Elemental analysis. Found: C, 35.18; H, 4.57; N, 12.72. Calculated for $\text{C}_{26}\text{H}_{40}\text{N}_8\text{P}_2\text{F}_{12}\text{Cu}_2$: C, 35.42; H, 4.57; N, 12.71.

Synthesis of $[\text{Cu}_2(\text{L3Bu})_2](\text{PF}_6)_2$ (3). The compound, **3**, was synthesized according to a similar procedure to that of **2**. The silver(I) complex (Elemental analysis. Found: C, 37.57; H, 5.24; N, 10.48. Calculated for $\text{C}_{34}\text{H}_{56}\text{N}_8\text{P}_2\text{F}_{12}\text{Ag}_2$: C, 37.72; H, 5.21; N, 10.35.) was made by a reaction of $[\text{H}_2\text{L3Bu}]\text{Cl}_2$ (101 mg, 0.28 mmol), Ag_2O (184 mg, 0.8 mmol), 10 mL distilled water, and NH_4PF_6 (94.9 mg, 0.58 mmol). The copper complex, **3**, was prepared from silver(I) complex (101.2 mg, 0.19 mmol for silver(I) ion), CuI (56.3 mg, 0.3 mmol), and acetone (5 mL). Colorless solids, yield 76 mg, 85 %. ^1H NMR (500 MHz, acetone- d_6) δ 7.712 (br s, 4H, NCHC), 7.666 (br s, 4H, NCHC), 4.350(t, $J = 4.73$ Hz, 8H), 3.871 (t, $J = 7.16$ Hz, 8H), 2.741 (m, 4H), 1.780 (m, 8H), 1.246 (m, 8H), 0.830 (t, 7.16 Hz, 12H, CH_3). Elemental analysis. Found: C, 41.11; H, 5.73; N, 11.4. Calculated for $\text{C}_{34}\text{H}_{56}\text{N}_8\text{P}_2\text{F}_{12}\text{Cu}_2$: C, 41.09; H, 5.68; N, 11.27.

Table 2 Selected bond lengths and angles for **1**, **2**, **4** and **5**.

Complex	1	2 -acetone	4 -0.5acetone	5 -Et ₂ O
Cu(1)-C _{NHC} / Å	1.898(5)	1.888(3)	1.893(8)	1.902(3)
	1.901(6)	1.889(3)	1.904(8)	1.904(3)
Cu(2)-C _{NHC} / Å	^a	1.903(3)	^a	1.898(4)
	^a	1.907(3)	^a	1.903(4)
C _{NHC} -Cu(1)-C _{NHC} / °	174.4(2)	172.19(15)	171.0(3)	177.54(16)
C _{NHC} -Cu(2)-C _{NHC} / °	^a	173.45(15)	^a	177.95(14)
C _{NHC} -Cu(1)-Cu(2)-C _{NHC}	77.67	83.08	89.84	
	84.88	83.52	87.07	
Cu-Cu / Å	2.6941(17) ^b	2.6705(13) ^b	2.909(2) ^b	6.655, 6.163 ^c

^a The values are same as those of Cu(1), because one type of half of the complex cation is observed in asymmetric unit. ^b Cu(1)-Cu(2). ^c Cu(1)-Cu(1) and Cu(2)-Cu(2), because two types of half of the complex cation are observed in an asymmetric unit.

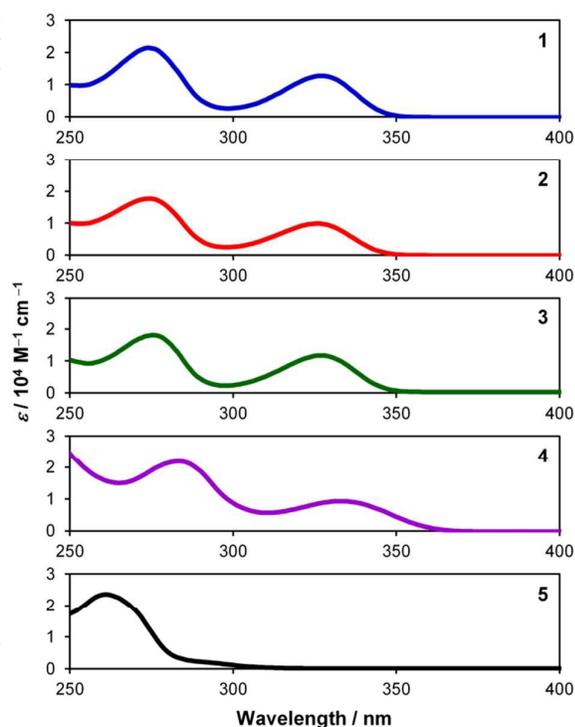


Fig. 2 Absorption spectra of **1**, **2**, **3**, **4** and **5** in degassed methanol at room temperature. There are large errors in the molar coefficients due to the air-sensitive nature of the complexes; the differences in the absorption spectra between **1**, **2**, and **3** are within errors.

Synthesis of [Cu₂(L3MeOPh)₂](PF₆)₂ (4**).** The compound, **4**, was synthesized according to a similar procedure to that of **2**. The silver(I) complex (Elemental analysis. Found: C, 42.42; H, 3.75; N, 8.57. Calculated for C₄₆H₄₈N₈O₄P₂F₁₂Ag₂·0.5H₂O: C, 42.51; H, 3.80; N, 8.62) was made by a reaction of [H₂L3MeOPh]Cl₂ (0.521 g, 1.1 mmol), Ag₂O (0.707 mg, 3 mmol), 20 mL distilled water, and NH₄PF₆ (0.423 mg, 2.6 mmol). The copper complex, **4**, was prepared from the silver complex (100.4 mg, 0.156 mmol for silver(I) ion), CuI (50.0 mg, 0.26 mmol), and acetone (10 mL). Colorless solids, yield 61 mg, 65%. ¹H NMR (500 MHz, acetone-*d*₆) δ 7.798 (d, *J* = 1.72 Hz, 4H, NCHC), 7.755 (d, *J* = 1.86 Hz, 4H, NCHC), 7.349(m, 8H, Ph), 7.013(m, 8H, Ph), 4.049(t, *J* = 5.44 Hz, 8H, NCH₂CH₂), 3.865 (s, 12H, OCH₃), 2.590(m, 4H, NCH₂CH₂). Elemental analysis. Found: C, 46.27; H, 4.12; N, 9.39. Calculated for C₄₆H₄₈N₈O₄P₂F₁₂Cu₂: C, 46.28; H, 4.05; N, 9.39.

Synthesis of [Cu₂(L3Mes)₂](PF₆)₂ (5**).** The compound, **5**, was synthesized according to a similar procedure to that of **2**. The silver(I) complex (Elemental analysis. Found: C, 47.22; H, 4.62; N, 8.22. Calculated for C₅₄H₆₄N₈P₂F₁₂Ag₂·2H₂O: C, 47.45; H, 5.01; N, 8.20), was made by a reaction of [H₂L3Mes]Cl₂ (104.9 mg, 0.22 mmol), Ag₂O (122.3 mg, 0.53 mmol), and NH₄PF₆ (69.5 mg, 0.43 mmol). The copper complex, **5**, was prepared from silver(I) complex (50 mg, 0.076 mmol for silver(I) ion), CuI (0.11 mmol, 20 mg), and acetone (15 mL). Colorless solids, yield 31 mg (66%). ¹H NMR (500 MHz, acetone-*d*₆) δ 7.717 (br

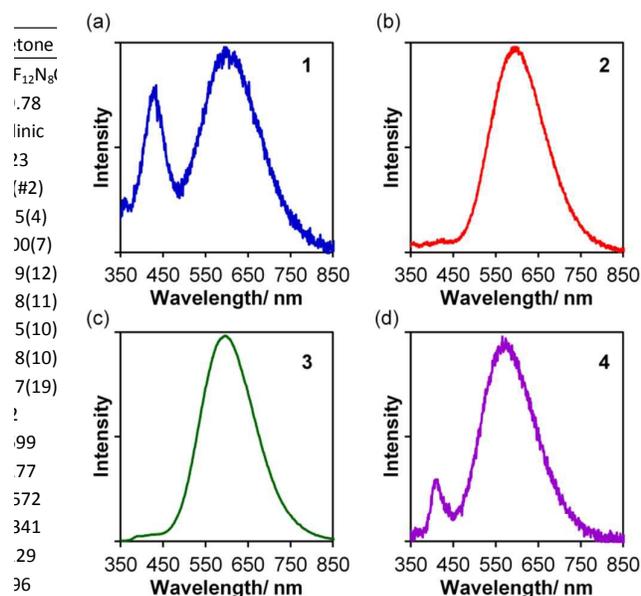


Fig. 3 Emission spectra of **1** (a), **2** (b), **3** (c), **4** (d) at room temperature in degassed methanol. Excitation wavelength is 330 nm.

s, 4H, NCHC), 7.338 (br s, 4H, NCHC), 7.003(s, 8H, Ph), 4.592(t, *J* = 7.45 Hz, 8H, NCH₂CH₂), 2.768(m, 4H, NCH₂CH₂), 2.433 (s, 12H, CH₃), 1.731(s, 24H, 2 CH₃). Elemental analysis. Found: C, 51.61; H, 5.08; N, 8.69. Calculated for C₅₄H₆₄N₈P₂F₁₂Cu₂·0.5H₂O: C, 51.84; H, 5.24; N, 8.96.

Crystallography

X-ray crystallographic measurements of **1**, **2**, **4** and **5** were made on a Rigaku Saturn 70 CCD area detector with graphite-monochromated MoK α radiation. Images were collected and the data were processed by using *CrystalClear*.⁴⁴ The structures were solved by direct methods *SIR-92*⁴⁵ and refined by full matrix least squares procedures (*SHELXL-97*).⁴⁶ All calculations were performed by using the *Wingx* crystallographic software package.⁴⁷ The asymmetric unit of **4** consists of a half of the dicopper(I) complex cation, a PF₆⁻ ion positioned in special position (0.5 occupancy), and another PF₆⁻ ion analyzed with 0.5 occupancy. A disordered methoxy group of **4** and a PF₆⁻ ion of **5** were analyzed with the PART option, and the ISOR option is used for PF₆⁻ ion of **4**. Crystallographic data have been deposited with Cambridge Crystallographic Data Centre: Deposition number CCDC-1434651 for **1**, CCDC-1434652 for **2**, CCDC-1434653 for **4** and CCDC-1434654 for **5**. Copies of the 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 vapor diffusion of diethylether in acetone solution of **1**, **2**, **4** and **5** under an argon atmosphere using the Schlenk technique. Checkcif alert C for large R and wR values of **4** is due to the low

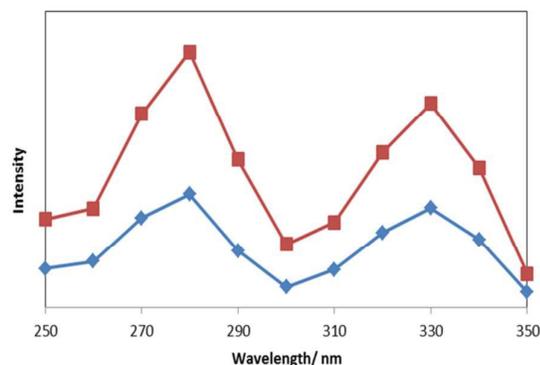


Fig. 4 Excitation spectra of **1** in degassed methanol at room temperature: $\lambda_{\text{obs}} = 430$ nm (blue rhombus) and 610 nm (red square).

quality of the crystals; the intensities of the diffractions are low. Crystallographic data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

DFT calculation

Calculation was performed using Gaussian 03W software⁴⁸ with the B3LYP⁴⁹⁻⁵¹ 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,⁵² phosphorus, oxygen, and nitrogen 6-31G*, carbon 6-31G*, and hydrogen 6-31G. Population analysis was carried out by AOMIX software.⁵³ The pictures of the orbitals have been depicted with Gaussview 5 software.

Results and discussion

The reaction of bisimidazolium salts, $[\text{H}_2\text{L3R}]\text{Cl}_2$ (R = methyl (Me),³⁶ ethyl (Et), *n*-butyl (Bu), *p*-methoxyphenyl (MeOPh),³⁷ and mesityl (Mes)³⁸), with 1 equiv of Ag_2O , followed by addition of NH_4PF_6 , gave the silver(I) NHC complexes.^{27, 31-33, 39,40} The copper(I)-bis(NHC) complexes, **1**,³² **2**, **3**, **4** and **5** were prepared by transmetalation of the corresponding silver(I) complexes as shown in Scheme 1, and characterized by elemental analysis and NMR. Single-crystal X-ray structural analysis for **1**, **2**, **4**, and **5** were also studied (Fig. 1 and Tables 1 and 2).

The crystal structure of the dinuclear silver(I)-bis(NHC) complex, $[\text{Ag}_2(\text{L3Me})_2](\text{PF}_6)_2$,³³ and the synthesis and the use of the corresponding copper(I) complex, **1**, as a catalyst³² were already known, but the crystal structure of **1** has not been reported. We successfully made single crystals of **1**, and the crystal structure of **1** is shown in Fig. 1. A half of the dicopper complex cation and a PF_6^- ion were observed in the asymmetric unit. The centre of inversion lies on the midpoint of two copper atoms, suggesting that both metal atoms are copper(I) states. 8-shaped geometry of the 16-membered ring

Table 3. Photophysical properties of the copper(I) complexes in degassed methanol.

	$\lambda_{\text{abs.max}}$ / nm	$\lambda_{\text{em.max}}$ / nm	τ^a / μs	ϕ
1	274, 327	430, 610	6.9 ^b	0.07
2	275, 326	600	25	0.21
3	275, 327	600	30	0.19
4	280, 335	410, 570	0.23 ^c	0.002
5	260, 280	650	- ^d	- ^d

^aThe emission lifetimes observed at the wavelength of $\lambda_{\text{em,max}}$ for LE. ^bThe values for HE are 4.9 μs . ^cThe value for HE is 0.20 μs . ^dThe values could not be determined because of very low absorption intensity at λ_{ex} .

made of the two copper atoms, two NHC, and two trimethylene moieties was observed in the crystal of **1**, as shown in Fig. 1. The conformation of the 16-membered ring of **1** is different from that of the corresponding silver(I) complex,³³ which shows a geometry with the intraligand π -stacking between two NHC rings. The structure of **1** is different from that of the previously reported bis(NHC)-copper(I) complex, **1'**,²⁷ where the 12-membered ring made of the two copper atoms, two NHC, and two methylene moieties forms the O-shaped geometry. There should be a metal-metal bonding interaction in the crystal of **1**, since the intramolecular bonding interaction between the two copper atoms (Cu-Cu) is 2.696(2) Å, which is smaller than the sum of the van der Waals radii of the two copper atoms, 2.8 Å. The bond lengths between the copper atom and the carbon atom in the NHC moiety (Cu-C_{NHC}) are 1.902(6) Å and 1.906(6) Å, which are in the range of Cu-C_{NHC} of other reported copper(I)-NHC complexes.^{27, 31} The C_{NHC}-Cu-C_{NHC} angle is 174.7(2)°, which is slightly distorted from the ideal linear geometry around the copper atom. Additionally, a weak interaction between one Cu atom and one nitrogen atom of NHC in the neighbouring cation (3.532 Å) is found in the crystal.

The 8-shaped geometry of the 16-membered ring is observed for **2** and **4** as well (Fig. 1). The bond lengths and bond angles of **2** and **4** are similar to those of **1**. The distance of Cu-Cu in **2** (2.671(2) Å) is very similar to that of **1**, and much shorter than those in **4** (2.909(2) Å) and in previously reported **1'** (2.9031(17) Å),²⁷ suggesting that the intramolecular Cu-Cu interactions in the single crystals of **1** and **2** are much stronger than those of **4** and **1'**. The close distances between the Cu atom and the NHC groups in the neighbouring molecular group are observed not only in **1** but also in **2**, where a carbon atom in the ethyl group (3.485 Å) and a nitrogen atom (3.916 Å) of NHC moiety are close to two copper ions, respectively. The corresponding intermolecular distance in **4** is 4.090 Å, which shows very weak interaction (see Fig. S1 in the ESI[†]). On the other hand, the shape of the 16-membered ring of **5** is more planar, and the distance of Cu-Cu of **5** (6.164 Å) is much larger than those of other complexes, indicating that there is no interaction between the two copper atoms in the cation.

The ¹H NMR spectrum of **2** in degassed acetone-*d*₆ shows one set of signals due to a single chemical species with high symmetry (see Fig. S2 in the ESI[†]), similar to that of **1**; NMR

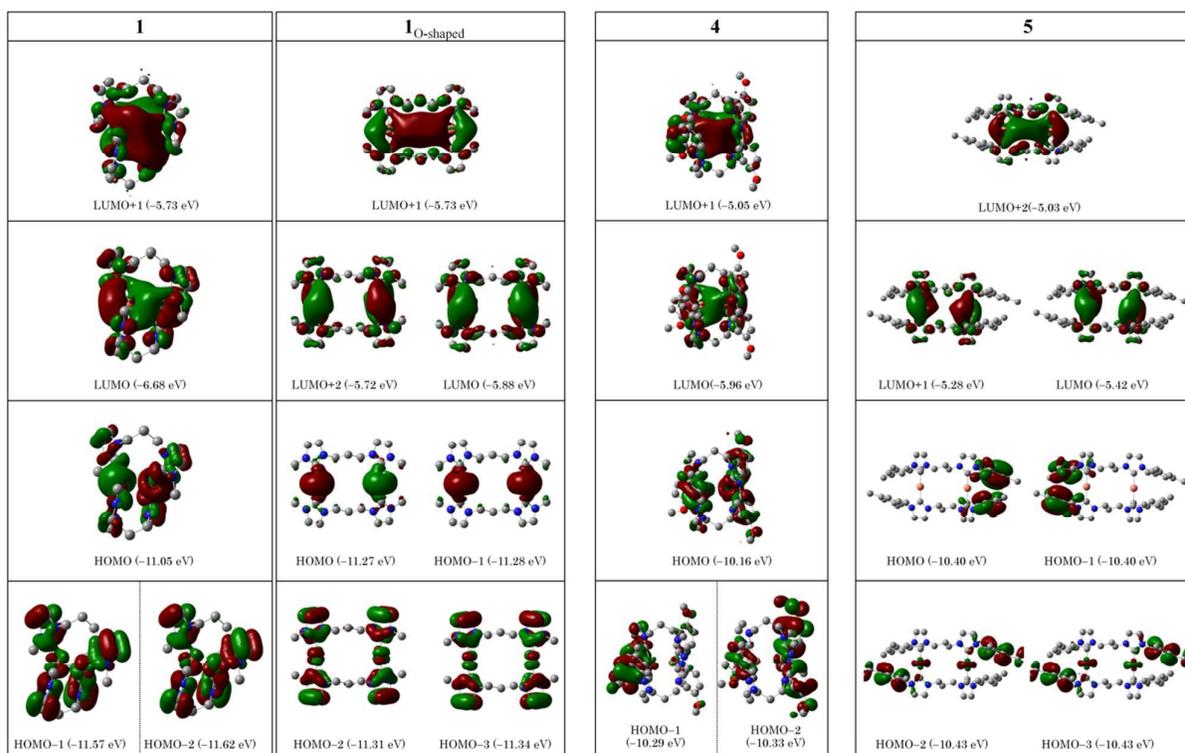


Fig. 5 Kohn-Sham orbitals of $[\text{Cu}_2(\text{L3Me})_2]^{2+}$ (**1**), hypothetical O-shaped geometry of $[\text{Cu}_2(\text{L3Me})_2]^{2+}$ (**1_{O-shaped}**), $[\text{Cu}_2(\text{L3MeOPh})_2]^{2+}$ (**4**) and $[\text{Cu}_2(\text{L3Mes})_2]^{2+}$ (**5**). Orbitals calculated based on the optimized structure in the S_0 (singlet ground) states (contour value 0.02). Hydrogen atoms are omitted for clarity.

data of **1** in dimethylsulfoxide- d_6 are described in the literature.³² The spectra may indicate that the geometry of the complexes, **1** and **2**, observed in the crystals is also kept in solution (Scheme 1). The ^1H NMR spectra of **3-5** are similar to that of **2** in acetone- d_6 , suggesting that the dinuclear structure of the bis(NHC) dicopper(I) complexes may be also maintained in acetone (see Fig. S3-S5 in the ESI[†]). The spectra of **1**, **4**, and **5** in methanol- d_4 are basically similar to those under the same conditions in acetone- d_6 , suggesting that even methanol, which has high-coordinating ability, does not induce crucial chemical degradation of the complexes (see Fig. S6-S8 in the ESI[†]). Air-bubbling into the solution of **1** in degassed acetone- d_6 immediately results in the precipitation of blue-green solids, and the NMR spectrum of the mixture shows several species due to chemical degradation (see Fig. S9 in the ESI[†]). On the other hand, the acetone solution of **4** has been kept transparent in air. For **4** and **5**, the ^1H NMR spectra measured at 2 hours after the dissolution in air-saturated solution at room temperature show negligible changes from those just after dissolution, indicating that the structures of both **4** and **5** are kept for at least several hours in acetone solution (see Fig. S10 and S11 in the ESI[†]). The four methoxyphenyl or mesityl groups substituted at the nitrogen atoms of NHC moieties can effectively prevent the chemical degradation.

The absorption spectra of the copper(I) complexes in degassed methanol at room temperature are displayed in Fig. 2. The absorption maxima, λ_{abs} , of the two bands of **1** (274,

327 nm) are similar to those of **2** (275, 326 nm) and **3** (275, 327 nm) (Table 3). The difference in the absorption spectra among **1**, **2**, and **3** is very small, supporting that the geometry of **3** can be assigned to 8-shaped structure. As shown in the TD-DFT results, the absorption band centred at 327 nm clearly indicates the presence of Cu-Cu interaction. The two bands of **4** (280, 335 nm) are slightly red-shifted from those of **1**, **2**, and **3**, because the NHC ligand in **4** includes the phenyl groups. The contribution of metal-to-ligand charge transfer (MLCT) transition from the copper to the NHC orbitals is decreased in **4** by introducing the π -conjugate moieties in the NHC ligand as described later. The values of λ_{abs} as well as the calculated wavelength of the singlet-singlet transitions of the complexes with the 8-shaped geometries **1**, **2**, **3** and **4** are much longer than those with O-shaped geometries of **1'** (261, 300 nm).²⁷ The values of **5** (260, 280 nm) are totally different from those of **1**, **2**, **3**, and **4**. This should be mainly due to the lack of Cu-Cu interaction in the O-shaped geometry of **5**. The steric interaction between the R groups in **5** can be much larger than those in **1**, **2**, **3**, and **4**, if they adopt the 8-shaped geometry. The steric interaction can play a key role for being the O-shaped geometry of **5**.

The bis(NHC) dicopper(I) complexes, **1**, **2** and **3**, in degassed methanol at room temperature show intense orange luminescence upon UV light excitation. The emission spectrum of **1** in degassed methanol shows two distinct emission bands centred at 430 nm and 610 nm; The higher-energy band and

Table 4 Population analysis of the DFT calculations based on the singlet optimized structures. See Table S1 for **2** and **3**.

K-S orbital	1			4			5			1_o-shaped		
	<i>E</i> / eV	Cu ^a	NHC ^b	<i>E</i> / eV	Cu ^a	NHC ^b	<i>E</i> / eV	Cu ^a	NHC ^b	<i>E</i> / eV	Cu ^a	NHC ^b
LUMO+2	-5.57	24	76	-4.95	13	87	-5.03	53	47	-5.72	47	53
LUMO+1	-5.89	53	47	-5.05	33	67	-5.28	42	58	-5.73	68	32
LUMO	-6.68	44	56	-5.96	41	59	-5.42	47	53	-5.88	47	53
HOMO	-11.05	75	25	-10.16	49	51	-10.40	0	100	-11.27	95	5
HOMO-1	-11.57	38	62	-10.29	4	96	-10.40	0	100	-11.28	97	3
HOMO-2	-11.62	35	65	-10.33	2	98	-10.43	17	83	-11.31	37	63
HOMO-3	-12.16	44	56	-10.36	1	99	-10.43	17	83	-11.34	35	65
HOMO-4	-12.25	31	69	-10.45	29	71	-10.49	9	91	-11.54	30	70

^a Components for copper moieties / %. ^b Components for NHC moieties / %.

the lower energy one are denoted as HE ($\lambda_{\text{em_HE}} = 430$ nm) and LE ($\lambda_{\text{em_LE}} = 610$ nm), respectively. The difference in the width of the two bands is small when the spectra are displayed on a scale in the energy unit (see Fig. S12 in the ESI[†]). The emission maximum of the LE band of both **2** and **3** is seen at 600 nm (Fig. 3 and Table 3). The similarity of the emission spectra of **2** and **3** supports the 8-shaped geometry of **3**. The shape of the spectrum of weakly emissive **4** at room temperature ($\lambda_{\text{em_HE}} = 410$ nm, $\lambda_{\text{em_LE}} = 570$ nm) is similar to those of **1**. The HE emission band of **1** is higher in intensity than that of **4**. One of the possibilities for the difference is that the molar ratios of one transient copper(I) complex which emit the HE band to another one emitting the LE band of **1** are larger than those of **4**; discussion for the species is described in next paragraph. It should be related to the fact that **4** has more bulky side groups than **1**. There is a very weak HE band also for **2** and **3**, indicating that two emission bands are generally observed in the present bis(NHC) dicopper(I) complexes. Additionally, the generality of two emission bands is also supported by the fact that the emission spectra of **3** at 220 K show both LE and HE bands in the solution state (Fig. S13). We repeated the synthetic study of the complexes to ensure the genuineness of the dual emission, then all experiments reproduce the results. The values of the Stokes-shifts of **1**, **2**, **3**, **4**, and **1'**, using the value of $\lambda_{\text{em_LE}}$, are in the range from 1.2×10^4 to 1.5×10^4 cm^{-1} . The $\lambda_{\text{em_LE}}$ of **1**, **2**, and **3** at room temperature is red-shifted from that of **1'** ($\lambda_{\text{em_LE}} = 542$ nm). The red-shift can be attributed to the strong copper(I)-copper(I) interactions of **1**, **2** and **3**, since the interaction can decrease the energy difference between ground and excited states.¹² $\lambda_{\text{em_LE}}$ of **4** is blue-shifted from $\lambda_{\text{em_LE}}$ of **1**. Since the Stokes-shift of **4** (1.2×10^4 cm^{-1}) is smaller than those of **1**, **2**, and **3** (1.4×10^4 cm^{-1}), the structural rearrangements, including the coordination of the solvent, of **4** in the excited state should be efficiently inhibited by the four methoxyphenyl groups, which are more bulky than methyl, ethyl, and butyl groups. The solution of **5** exhibits only a very weak emission band centred at $\lambda_{\text{em_LE}} = 650$ nm (see Fig. S12 in the ESI[†]).

The excitation spectra of **1** observed at 430 nm and 610 nm components in degassed methanol are shown in Fig. 4. The difference in the two spectra is negligible, and the maximum wavelength of the excitation spectra ($\lambda_{\text{max}} = 280, 330$ nm) is sufficiently similar to that of experimental absorption spectra,

indicating that one chemical species of the copper(I) complex causes both bands of the luminescence. One of the possible assumptions for the assignment of two emission bands is that two transient copper(I) species generated after light excitation have different nature of the emissive excited state; this assumption is similar to the reported model for cubane-like tetranuclear copper(I) iodide complexes in the view point that there are two species with different Cu-Cu distances, having cluster centred (shorter Cu-Cu) and halogen-to-ligand charge transfer (longer Cu-Cu) excited states.¹⁴⁻¹⁶ Another possible assumption is that the shorter and longer emission bands are derived from two temporal species, the dicopper(I) complex cation without coordinating solvent and that coordinated by solvent molecule; this assumption is similar to the report that the emission intensity of $[\text{Cu}_2(\text{dcpm})_2]^{2+}$ (dcpm = bis(dicyclohexylphosphino)methane) is enhanced by solvent coordination, and the two emission bands of $[\text{Au}_2(\text{dcpm})_2]^{2+}$ in the solid state are induced by the coordination of its counterion.^{12,13} Since Cu-Cu interaction could decrease the energy for the transitions and induce the red shift of the emission, the HE and LE emission bands could be assigned to the species with relatively weaker and stronger Cu-Cu interactions, respectively. The complexes with only LE emission band, such as **2** and **3**, show higher quantum yields and shorter lifetimes than those with both HE and LE bands, such as **1** and **4**, suggesting that the Cu-Cu interaction can enhance the emission properties of the dicopper(I) NHC complexes; the trends are observed not only in the solution state but also in the solid state, as described later. This may indicate that the HE emission band is observed in the case that there is a deactivation path from the initial excited state to generate a new transient species such as the one with long Cu-Cu distances. The quantum yield must be low when the deactivation occurs.

The lifetimes of the emission, τ , at room temperature of **1**, **2** and **3** in MeOH at $\lambda_{\text{em_max}}$ are 6.9, 25 and 30 μs , which are much longer than those of **4** (0.23 μs at $\lambda_{\text{em_LE}}$, 0.20 μs at $\lambda_{\text{em_HE}}$) and **1'** (0.69 μs)²⁷ (Table 3 and S14-S19 in the ESI[†]). These decays can be described as a single-exponential curve. All lifetime values observed for **1**, **2**, and **3** at room temperature are in the microsecond range, supporting that two bands are due to the emission of the copper(I) complexes and not due to ligand emission. The quantum yields of the

Table 5 TDDFT results of the complexes. Calculated transition wavelength, oscillator strength (f), and components of singlet and triplet excited states using the singlet optimized structures are shown. Details of the calculation results are shown in Tables S2, S3, and S4 in the ESI[†].

	Singlets calculated using singlet-optimized structures ^a				Triplets calculated using singlet-optimized structures ^a		
	λ / nm	f	Components	Coefficients	λ / nm	Components	Coefficients
1	341	0.2394	HOMO→LUMO	0.666	400	HOMO→LUMO	0.719
	309	0.0582	HOMO-1→LUMO	0.654	335	HOMO-1→LUMO	0.682
2	339	0.2372	HOMO→LUMO	0.667	393	HOMO→LUMO	0.717
	313	0.0503	HOMO-1→LUMO	0.654	339	HOMO-1→LUMO	0.679
3	341	0.2549	HOMO→LUMO	0.666	399	HOMO→LUMO	0.720
	306	0.0608	HOMO-1→LUMO	0.654	332	HOMO-1→LUMO	0.682
4	359	0.1956	HOMO→LUMO	0.65	411	HOMO→LUMO	0.64
	332	0.0455	HOMO-1→LUMO	0.65	356	HOMO-1→LUMO	0.46
5	293	0.0001	HOMO-3→LUMO	0.41	339	HOMO-4→LUMO+5	0.27
	293	0.0415	HOMO-2→LUMO	0.41	339	HOMO-5→LUMO+5	0.27
	281	0.0005	HOMO→LUMO	0.57	338	HOMO-3→LUMO+7	0.20
	281	0.0005	HOMO-1→LUMO	0.57	338	HOMO-1→LUMO+12	0.21
1_{O-shaped}	280	0.0000	HOMO→LUMO	0.512	311	HOMO→LUMO	0.526
	279	0.0567	HOMO-1→LUMO	0.506	311	HOMO-1→LUMO	0.529
	270	0.0552	HOMO→LUMO+1	0.509	304	HOMO-2→LUMO	0.486
	270	0.0052	HOMO-2→LUMO	0.509	304	HOMO-3→LUMO	0.480

^aSince the transitions are contributed by several components, only component with largest positive values of coefficients are shown in this table.

emission, Φ , of **1**, **2** and **3** in MeOH at room temperature show moderate values (7-20%), and those are much higher than those of **4** and **5**. One of the possible reasons for the larger values of both τ and Φ of **1**, **2**, and **3** compared to **4** is due to the increase in the contribution of MLCT, and the increase in the values of **1**, **2**, and **3** compared to those of **5** could be caused by the increase of Cu-Cu interaction as well as the structure of the NHC ligand; details are discussed in DFT calculation.

The powder samples of **1**, **2**, and **3** exhibit blue-green photoluminescence (See Fig. S20-S23 in the ESI[†]), while **4** and **5** show very weak luminescence. The photoluminescence of the LE band of **1** (1.4 (15%) and 12 (85%) μ s), **2** (35 μ s), and **3** (2.7 (17%) and 13 (83%) μ s) decays in several microseconds, supporting that two components are attributed to the luminescence of the copper(I) complexes. The value of $\lambda_{em,LE}$ of the blue-green emission bands of the complexes with 8-shaped geometries, **1** (525 nm), **2** (505 nm), and **3** (550 nm) are red-shifted from that of O-shaped one, **1'** (482 nm).²⁷

The results of DFT calculations for **1-5** are tabulated in Tables 4 and 5, and the Kohn-Sham orbitals are displayed in Fig. 5; details are shown in the ESI, Table S1-S4. The optimized structures in the singlet ground state (S_0) of the copper(I) complexes were used in the population analysis and TDDFT calculations. The geometries of the singlet-optimized structures of **1**, **2**, **4**, and **5** are slightly distorted from those of the corresponding crystal structures (See Table S2 in the ESI[†]). The optimized structures have shorter Cu-Cu distances than those of crystal structures. However, the results of TDDFT calculations by using singlet-optimized structures are essentially similar to those by using crystal structures (See Table S3 in the ESI[†]). Therefore, we discuss the electronic structures using the optimized-structures in this section. The Mayer bond order⁵³ of Cu-Cu in **1**, **2**, **3**, **4** are 0.352, 0.332,

0.322, 0.359, respectively, and that in **5** is less than 0, suggesting that the two copper atoms totally have bonding interaction in **1-4**.

The HOMO of **1** mainly consists of the two copper atomic orbitals, Cu, (75%) with minor contribution of NHC moieties, NHC, (25%) as shown in Table 4. The contribution of NHC moieties of the LUMO (Cu 44%, NHC 56%) is larger than that of the HOMO (Table 4). Additionally, significant overlap between the two copper atomic orbitals is observed especially in the LUMO in 8-shaped geometry. The electronic structure of a hypothetical complex cation with O-shaped geometry of **1** (**1_{O-shaped}**) was also calculated. Near degeneracy is observed in orbitals of **1_{O-shaped}** such as the HOMO and HOMO-1, and this is not observed in **1**. The shape of the LUMO around the two copper atoms in **1** is similar to that of LUMO+1 in **1_{O-shaped}**, but the energy of the LUMO of **1** is much deeper than that of **1_{O-shaped}**. Similarly, an increase in the energy caused by the Cu-Cu interaction is also observed in the HOMO of **1** compared to **1_{O-shaped}**. We can obviously see the anti-bonding nodes of two copper orbitals in the HOMO. These observation shows the Cu-Cu interactions are important to the nature of the frontier orbitals. TDDFT calculation for **1** indicates that the largest component of the transition from the ground (S_0) to the singlet lowest-lying excited (S_1) state ($S_0 \rightarrow S_1$) is HOMO (Cu: 75%, NHC: 25%) \rightarrow LUMO (Cu: 44%, NHC: 56%) (Table 5). The calculated energy of the wavelength, λ_{calc} , of the $S_0 \rightarrow S_1$ transition of **1** is 341 nm, which is distinctly red-shifted from that of **1_{O-shaped}** ($\lambda_{calc} = 279$ nm) because of the Cu-Cu interaction. The oscillator strength, f , of $S_0 \rightarrow S_1$ of **1** is much higher than those of **1_{O-shaped}**, indicating that copper(I)-copper(I) interactions can drastically enhance the absorption intensity. This may affect the luminescence properties, because the $T_1 \rightarrow S_0$ transition should borrow intensity from highly radiative spin-allowed transitions of $S_0 \rightarrow S_1$. The red-shift is also observed in the

calculated $S_0 \rightarrow T_1$ transition which is related to the luminescence.

Finally, we want to discuss the electronic structure of the complexes **2-5**. The components of the HOMO and LUMO of **2** and **3** are similar to those of **1** (Table S1). The calculated energy of the $S_0 \rightarrow S_1$ and $S_0 \rightarrow T_1$ transitions of **2** and **3** are very similar to those of **1**, indicating that the photophysical properties of the complexes may little depend on the alkyl substituents on the nitrogen atoms (Tables 4 and 5). On the other hand, the HOMO of **4** has a smaller component of Cu atom (49%) than that of **1** (75%). The $S_0 \rightarrow S_1$ transition of **4** is mainly HOMO (Cu: 49%, NHC: 51%) \rightarrow LUMO (Cu: 41%, NHC: 59%), and the wavelength is calculated to be 359 nm, which is longer than the calculated wavelengths for **1-3**. This result is in accordance with the absorption spectra of these complexes. The contribution of the Cu orbitals in the transition of **4** is smaller than those of **1, 2, and 3**; the methoxyphenyl moieties of **4** are significantly involved in the relevant orbitals. The effects lead to the reduced MLCT character in the excited state of **4**. The $S_0 \rightarrow S_1$ transition of **5** is mainly HOMO-2 (Cu: 17%, NHC: 83%) \rightarrow LUMO (Cu: 46%, NHC: 53%) and HOMO-3 \rightarrow LUMO. The HOMO-2 and HOMO-3 orbitals as well as the HOMO and HOMO-1 of **5** have very small components of the Cu orbitals, and the mesityl moieties of **5** are important for these orbitals. The results should be related to the fact that the Cu-Cu interaction is negligible.

Conclusions

We newly synthesized several dicopper(I) complexes bearing trimethylene-bridging NHC ligands, and investigated the properties of them. The photophysics of the complexes can be summarized as follows: (i) **1, 2** and **3** are considerably emissive based on the strong Cu-Cu interaction in 8-shaped geometries, (ii) **4** is weakly emissive due to the large contributions of methoxyphenyl groups and the reduced MLCT character in the transition, (iii) **5** has O-shaped geometries and shows totally different electronic structure from **1-4** because of the absence of the Cu-Cu interaction and the electronic effects of mesityl groups. These findings are important to the development of promising photofunctional materials based on the copper(I) complexes bearing NHCs.

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