NJC

Accepted Manuscript

This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the **Information for Authors**.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard **Terms & Conditions** and the **Ethical guidelines** still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

ARTICLE TYPE

Halide-modulated bistate and tristate fluorescence switching for Cu(I) and Ag(I) complexes

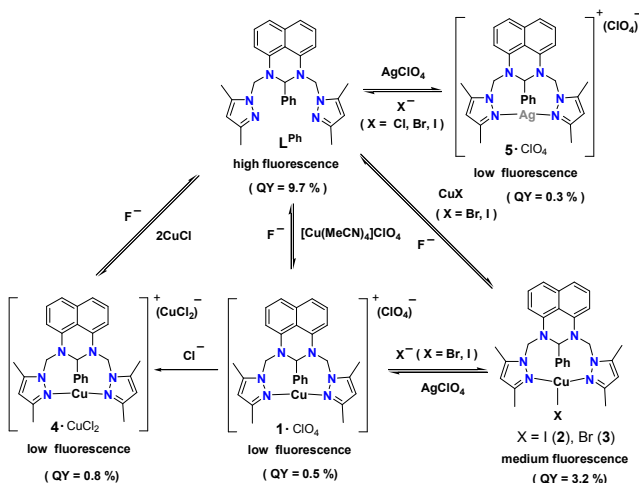**Chang-Chuan Chou,* Hsueh-Ju Liu, Lucas Hung-Chieh Chao and Chia-Chi Yang**

The reaction of a fluorescent trans-chelating ligand L^{Ph} (where L^{Ph} = 1,3-bis-(3,5-dimethyl-pyrazol-1-ylmethyl)-2-phenyl-2,3-dihydro-1*H*-perimidine, QY = 9.7 %) with $MClO_4$ (M = Cu, Ag) can lead to two-coordinate complexes $[M(L^{Ph})](ClO_4)$ (M = Cu (**1·**ClO_4) and Ag (**5·**ClO_4)). When L^{Ph} is treated with CuX (X = Cl, Br or I), however, this may lead either to two-coordinate linear complex $[Cu(L^{Ph})](CuCl_2)$
10 (**4·**$CuCl_2$) or to three-coordinate T-shaped complexes $[Cu(L^{Ph})X]$ (X = Br (**2**), I (**3**)). Moreover, while complex **1·**ClO_4 shows a ligand substitution for Cl^- to form **4·**$CuCl_2$, it displays anion coordination for both Br^- and I^- to give **2** and **3**, respectively. All of the copper(I) derivatives can readily liberate ligand L^{Ph} upon reacting with F^-. As such, a cyclic tristate molecular switching system "$L^{Ph} \leftrightarrow$ **1·**$ClO_4 \leftrightarrow$ **2** or **3** $\leftrightarrow L^{Ph}$" can be accomplished. For complex **5·**ClO_4, the addition of halides X^- (X = Cl, Br, I) results in an
15 abstraction of the silver ions and a release of the ligand L^{Ph}. A simple "$L^{Ph} \leftrightarrow$ **5·**ClO_4" bistate molecular interconversion may also be constructed. Above all, the complexation of either $MClO_4$ or CuX with L^{Ph} can be signalled through different quenching effects: QY = 0.5% for **1·**ClO_4, 3.1% for **2**, 3.2% for **3**, 0.8% for **4·**$CuCl_2$, and 0.3% for **5·**ClO_4, to realize facile bistate and tristate fluorescence switching operations.

Introduction

20 The construction of a molecular or supramolecular system that has two or more controllable optical states is of great interest for its potential application in molecular devices such as sensors, switches or logic gates.[1,4] Accordingly, we have begun to develop a proton-controlled fluorescent switch for copper(II) complexes[2]
25 and an Iodide-controlled fluorescent switch for copper(I) complexes[3] by taking advantage of the flexible coordination

numbers of copper ions: C. N. = 2, 3 or 4 for Cu(I); and, C. N.= 4, 5 or 6 for Cu(II). Recently, an ion-triggered multistate molecular switching device based on regioselective coordination-controlled
30 ion binding was reported in which a four-state molecular switching system involving copper(I) and znic(II) binding/releasing process was set up.[4] This inspired us to further develop a simple two-state fluorescence switching system for Ag(I) and a three-state fluorescence switching system for Cu(I)
35 based on a fluorescent ligand L^{Ph}, shown in Scheme 1. The design concept of the reversible chemical process and fluorescence switching are shown in Fig. 1, where the ligand L^{Ph}, complex **1·**ClO_4 and complex **2** are referred to as state 1, state 2, and state 3, respectively, and the Cu(I) ion, halide ions X (bromide or
40 iodide) and CuX are referred to as stimulus 1, 2 and 3, respectively.

The perimidine-based bis(pyrazole) ligand L^{Ph} was a semi-flexible ligand featuring a trans-chelating mode toward copper(I) center. Moreover, upon interacting with either the Cu(I) ion or

Scheme 1 Reversibility of ligand L^{Ph} and its copper(I) and silver(I) derivatives.
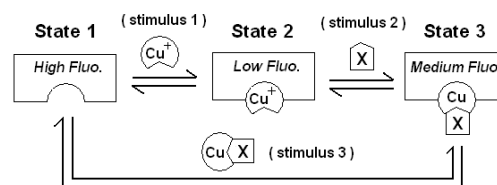

Fig. 1 Design concept of the molecular operations. State 1 (ligand), high fluorescence intensity; State 2 (complex 1), low fluorescence intensity; State 3 (complex 2), medium fluorescence intensity.
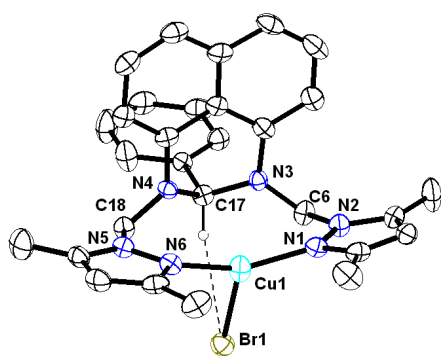
Fig. 2 Molecular structure of **3** with partial labelling showing 50% probability ellipsoids. Selected bond lengths (Å) and angles (°): Cu1–N1 1.939 (4), Cu1–N6 1.944 (4), Cu1...N3 3.032 (5), Cu1...N4 2.922 (4), Cu1–Br1 2.544 (1), N1–Cu1–N6 149.2 (2), N6–Cu1–Br1 102.7 (1), N1–Cu1–Br1 107.8 (1), H17...Br1 .2.875 (1).

CuI, different extents of fluorescence quenching were remarkable due to the influence of a different degree of N(amine)…Cu(I) interaction.[5] Therefore, the discrimination between **1·ClO₄** and **2** can be accomplished through fluorescence emissive spectra. By
5 iodide addition↔abstraction, a controllable reaction signalled a structural transformation "**1·ClO₄** ↔**2**".[3] As far as we could ascertain, a conversion of nonemissive two-coordinate copper(I) complex to an emissive one by means of additional halide binding has not been accomplished to date.[6] Therefore, we further
10 surveyed other halides and completed simple three-state fluorescence switching operations "L^Ph ↔ **1·ClO₄** ↔ **2** or **3** ↔ L^Ph" for copper(I) complexes as well as an ON↔OFF two-state fluorescence switching "L^Ph ↔ **5·ClO₄**" for a silver(I) complex, as shown in Scheme 1. The structural characterizations, reactions,
15 and photophysical properties of the presented complexes are described in the text.

Results and Discussion

Synthesis and characterization of the complexes

Copper(I) complexes **3** and **4·CuCl₂** were synthesized from the
20 reaction of the L^Ph ligand with CuCl and CuBr, respectively, in molar ratios of 1:2 and 1:1 in yields of 87 and 91%. A silver (I) complex **5·ClO₄** was prepared from the reaction of the ligand L^Ph with AgClO₄ in an 90 % yield. The elemental analyses and ESI-MS agreed with the proposed formulas. The ¹H and ¹³C NMR
25 spectra in CD₂Cl₂ exhibited only one set of ligand resonance under room temperature, indicating a symmetrical structure for **3** – **5·ClO₄**, which was in agreement with the solid state structures. Previous studies showed that the resonances of the methylene protons of the coordinated L^Ph ligand can determine the presence,
30 or lack, of a dynamic molecular nature.[3] Complex **1·ClO₄** displayed only singlet absorption at δ 5.96 ppm for the methylene protons, and the variable-temperature ¹H NMR spectra demonstrated that **1·ClO₄** was indeed stereochemically nonrigid. As for **2**, the AB pattern resonance (δ 5.93, 5.78 ppm) for the two
35 diastereotopic methylene groups indicated that the structure of **2** was stereochemically rigid. It was surprising that both complexes **4·CuCl₂** and **5·ClO₄** were rigid in a CH₂Cl₂ solution, as shown in the ¹H NMR spectra, despite a similar appearance for the
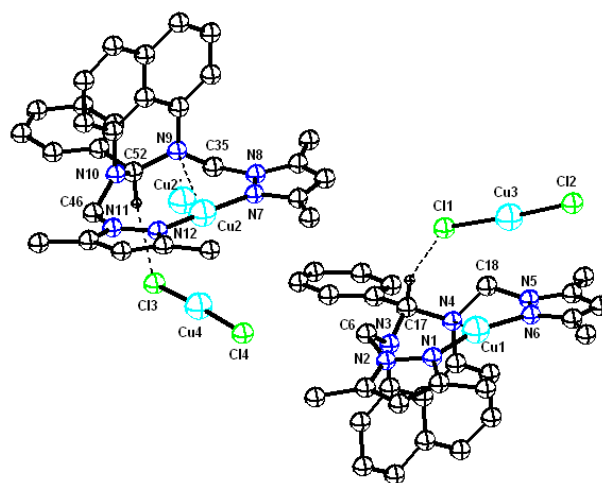

Fig. 3 Molecular structure of **4·CuCl₂** with partial labelling showing 50% probability ellipsoids. Selected bond lengths (Å) and angles (°): Cu1–N1 1.872(7), Cu1–N6 1.921 (6), Cu1...N3 2.970 (7), Cu1...N4 2.846 (7), H17…Cl1 2.697 (3), Cu1…Cu3 3.630 (2), Cu1…Cl1 3.161 (3), Cu3–Cl1 2.110 (4), Cu3–Cl2 2.0770 (4); N1–Cu1–N6 164.3(3), Cl1–Cu3–Cl2 177.5 (2). Cu2–N7 1.878(7), Cu2–N12 1.873 (7), Cu2...N9 2.855 (7), Cu2...N10 2.883 (8), H52..Cl3 2.500(3), Cu2…Cu4 3.137 (2), Cu2…Cl3 3.910 (3), Cu4–Cl3 2.082 (3), Cu4–Cl4 2.081 (4); N7–Cu2–N12 169.1 (3), Cl3–Cu4–Cl4 175.7 (2).

structures of cations **1⁺**, **4⁺** and **5⁺**. The diastereotopic natures of
40 the methylene groups in **4·CuCl₂** and **5·ClO₄** were indeed exhibited as AB pattern resonances at δ 6.14, 5.94 ppm and 5.96, 5.85 ppm, respectively, which suggested decreased conformational flexibility for the cation portions of **4·CuCl₂** and **5·ClO₄**. Although the fluxional process for **1·ClO₄** remained
45 inexplicable, the significant difference in ¹H NMR spectra was very beneficial for differentiating the structural change between **1·ClO₄** and either the other related complexes or a free ligand L^Ph. As in the case of **2**, complex **3** showed two sets of doublets (δ 6.13 and 5.92 ppm) for its methylene groups. Obviously, the
50 fluxionality of the complex cation [Cu(L^Ph)]⁺ was significantly susceptible to the third coligand.

X-Ray crystallography

The crystals were grown from CH₂Cl₂/Et₂O and their structures were confirmed by X-ray diffraction analyses. The structures of
55 complexes **3**, **4·CuCl₂** and complex cation **5** (**5⁺**) are shown in Figures 1, 2 and 3, respectively. As expected, the coordinated L^Ph in **3**, **4⁺** and **5⁺** behaved as a trans-chelating ligand with two coordinated pyrazoles trans-located. On the whole, these complexes have approximately C₂ᵥ-symmetric geometries,
60 analogous to complexes **1·ClO₄** or **2**.
For complex **3** (Fig. 2), the N(Pz')–Cu–N(Pz') bond angle of 149.2 (2)° severely deviated from linearity because of the bromide binding, which gave rise to a 10.0 (1)° increment in the dihedral angle of the coordinated pyrazole rings when compared
65 to **1·ClO₄**. The Cu(I)–N(heterocycle) three- and four-coordination bond lengths were reported to be 1.89 ~ 1 .92 Å and 1.98 ~ 2.04 Å, respectively.[7] The Cu(I)–N(Pz') bond distances of 1.939 (4) and 1.944 (4) Å that were between the three and four coordinate copper(I) complexes were comparable to those of the related
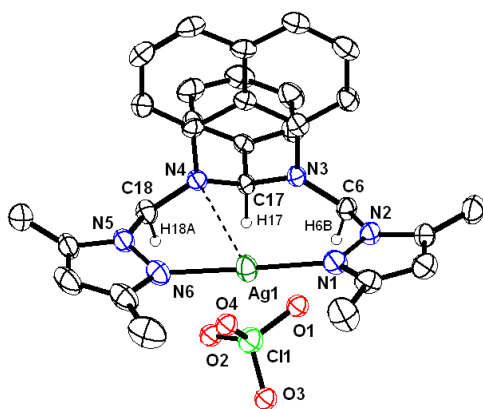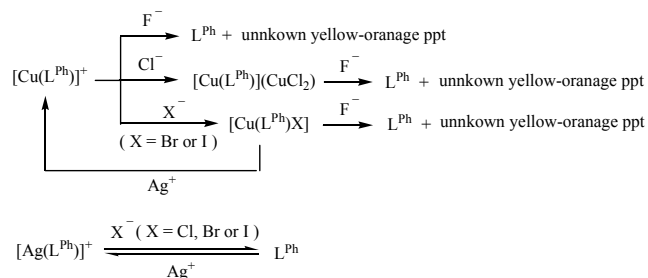
Fig. 4 Molecular structure of cation **5**$^+$ with partial labelling showing 50% probability ellipsoids. Selected bond lengths (Å) and angles (°): Ag1–N1 2.097 (4), Ag1–N6 2.093 (4), Ag1...N3 2.965 (4), Ag1...N4 2.877 (4), Ag1...O4 2.971 (6), O1...H6B 2.453 (5), O4...H17 2.434 (7), O4...H18A 2.567 (7); N1–Ag1–N6 171.65 (13).

complex **2** (1.942 (5) and 1.955 (5) Å), suggesting an electron neutralization effect of the bromide anion on the copper(I) ion. While the terminal Cu(I)–Br bond distance of 2.544 (1) Å in **3** was within the upper limits of the Cu(I)–Br(terminal) lengths of 2.5152 (2) Å for tetrahedral anion CuBr$_4^{3-}$,[8] it was evidently longer than that of the 2.365 (3) Å seen in trigonal planar anion CuBr$_3^{2-}$,[9] which showed T-shaped characteristics.[10] The distance of the bromo ligand Br1 to the benzylic hydrogen atom amounted to 2.875 (1) Å, which was within the sum of the van der Waals radii for hydrogen and bromine (3.05 Å), suggesting a weak intramolecular C17–H...Br hydrogen bonding. To the best of our knowledge, complex **3** was the second example of a structurally characterized, T-shaped copper(I) halide complex with a N-donor chelating ligand.

For complex **4**·CuCl$_2$ (Fig. 3), two slightly different conformations were exhibited in the unit cell. Unfortunately, one of the two copper centers in the complex cations was disordered over two positions (93:7 ratio), and the asymmetry in the Cu–N bonds in another molecule seemed to be due to a crystal packing effect, although the structures unambiguously showed atomic connectivities within this molecule that were comparable to cation **1**$^+$. The formation of the CuCl$_2^-$ counter anion was certain, which seemed to suggest that the transient species [Cu(L^{Ph})Cl] was promptly transfomed into [Cu(L^{Ph})]$^+$(Cl$^-$) followed by a reaction with CuCl to form a CuCl$_2^-$ anion. It was noteworthy that a Cu1...Cu3 distance of 3.6300(19) Å precluded the Cu(I)...Cu(I) interaction. However, either a Cu2...Cu4 distance of 3.1369 (17) Å or a Cu2'...Cu4 distance of 3.2222 (123) Å was short enough to reveal a probable unsupported Cu(I)...Cu(I) ligand interaction.[11] Moreover, the existence of C17–H...Cl1 and C52–H...Cl3 hydrogen bonds may help to promote cation and anion attraction to one another and a restraint of structural flexibility. Therefore, although the fluxional behavior of cation **1**$^+$ was expected for cation **4**$^+$, it did not happen.

The structure of complex cation **5**$^+$ (Fig. 4) generally is similar to that of **1**$^+$ with the exception of the metal center. The silver(I) ion was coordinated by two pyrazole nitrogen atoms of the L^{Ph} with a N(Pz')–Ag–N(Pz') bond angle of 171.65 (13)° toward C17. The

Scheme 2 The reaction of Cu(I) and Ag(I) derivatives with halides.

Ag(I)–N(Pz') distances of 2.093 (4) and 2.097 (4) Å were similar to the related two-coordinate silver(I)-pyrazole complexes (~ 2.1 Å).[12] The contacts of Ag(I)···N(amine) were 2.877 (4) and 2.965 (4) Å, indicating probable weak N(amine)…Ag(I) interactions. It was interesting that, unlike **1**$^+$, complex cation **5**$^+$ was a rigid molecular in CH$_2$Cl$_2$, suggesting a probable influence arising from counter anion like **4**·CuCl$_2$ and/or a stronger Ag(I)···N(amine) interaction due to the size of Ag(I) (1.16 Å), which was larger than that of Cu(I) (0.74 Å). Inspection of the closest ClO$_4$ anion contact to the H6B, H17, H18A and Ag1, respectively, showed weak interactions indeed, which could lead to a restraint of structural flexibility in solution.

Reactions of 1·ClO$_4$ with *n*-Bu$_4$NX (X = F, Cl, Br)

We previously confirmed a "2+1" bonding mode for the formation of T-shaped complex **2**.[13] Herein, the other halides binding to the copper(I) and silver(I) derivatives were examined using *n*-Bu$_4$NX (X = F, Cl, Br), as shown in scheme 2.

As in the case of **1**$^+$ and **2**, the interconvertable reaction of **1**$^+$ and **3** can be performed and investigated via ^{1}H NMR spectra. When complex **1**·ClO$_4$ reacted stoichiometrically with n-Bu$_4$NBr, neutral complex **3** was generated nearly quantitatively. On the other hand, when complex **3** reacted stoichiometrically with Ag(ClO$_4$) to eliminate the coordinated bromide, complex **1**·ClO$_4$ was regenerated. If complex **1**·ClO$_4$ first reacted with a stoichiometric amount of *n*-Bu$_4$NBr and then a stoichiometric amount of Ag(ClO$_4$) was introduced, only the peaks of **1**$^+$ and the n-butyl group were observed in the ^{1}H NMR solution spectrum (S7), which manifested the reversibility between **1**$^+$ and **3**.

The reaction of **1**$^+$ and *n*-Bu$_4$NCl was carried out at a molar ratio of 1:1 in CH$_2$Cl$_2$ solution. Crystal growth from the resultant solution gave the 1:1 co-crystals of {**1**·ClO$_4$ + **4**·CuCl$_2$} (S8). Despite the poor quality of the crystals, a CuCl$_2^-$ anion was produced, which was indicative of a partial ligand substitution by Cl$^-$. The attempt to synthesize the [Cu(L^{Ph})Cl] adduct by using CuCl and L^{Ph} in a molar ratio of 1:1 proceeded. However, the isolated product was solely **4**·CuCl$_2$, which indicated the instability of [Cu(L^{Ph})Cl]. A strong complexation of Cu (I) by chloride ions resulted in a favorable CuCl$_2^-$ anion.

The reaction of **1**·ClO$_4$, **2**, **3** or **4**·CuCl$_2$ with *n*-Bu$_4$NF quickly yielded unknown yellow-orange precipitates. The precipitates were insoluble in water and in most organic solvents such as MeOH, CH$_3$CN, DMSO, DMF, Et$_2$O, EA, or hexane. Also, none of the absorption peaks for L^{Ph} were observed in the IR spectrum. Thus, the precipitates were tentatively assigned as copper(I)
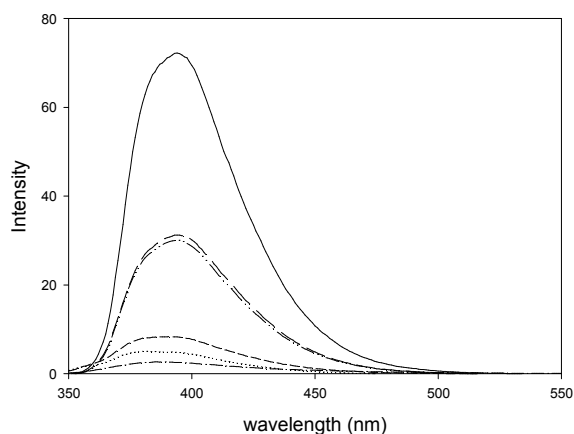
Fig. 5 Fluorescence spectra of ligand L^{Ph} (solid line) and complexes **1**·ClO_4 (dotted line), **2** (dash-dot-dot line), **3** (long dash line), **4**·$CuCl_2$ (medium dash line) and **5**·ClO_4 (dash-dot line) in CH_2Cl_2 excited at 340nm at room temperature.
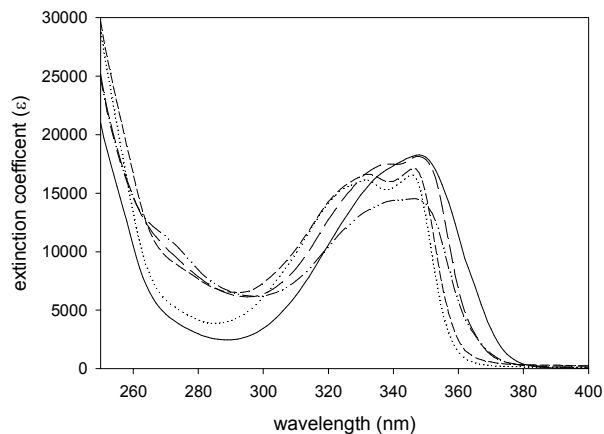
Fig. 6 UV-vis spectra of ligand L^{Ph} (solid line) and complexes **1**·ClO_4 (dotted line), **2** (dash-dot-dot line), **3** (long dash line) and **4**·$CuCl_2$ (medium dash line) in CH_2Cl_2.

halocuprates. These species are known to have various molecular assemblies and diverse polymeric extended systems.[14] This made the analysis of these species very difficult. Nonetheless, inspection of the colorless filtrate from the reactions for **1**·ClO_4, **2**

5 and **3** by NMR showed only a free ligand L^{Ph} and (*n*-Bu_4N)(ClO_4) salt. For the reaction of **4**·$CuCl_2$, the filtrate color turned green. However, it continued to display a strong emission comparable to that of L^{Ph}. Evidently, L^{Ph} were released. Upon further removal of the green species via the addition of hexane, most of the L^{Ph} was

10 recovered. Therefore, by using only the halides, an interconvertable tristate switching system "$L^{Ph} \leftrightarrow$ **1**·$ClO_4 \leftrightarrow$ **2** or **3** $\leftrightarrow L^{Ph}$" was constructed, as shown in scheme 1.

On the other hand, treatment of **5**·ClO_4 with *n*-Bu_4NX (X= Cl, Br, I) gave readily the AgX precipitates and the released ligand L^{Ph}.

15 Then, the L^{Ph} can react with the additional Ag(I) again to reform **5**·ClO_4, showing a simple "$L^{Ph} \leftrightarrow$ **5**·ClO_4" bistate switching system.

Photophysical properties

The fluorescent emission profiles originating from the ligand-

20 centered $\pi-\pi^*$ transitions of the perimidine moiety are compared in Figure 5. The fluorescent properties of complexes **3** (λ_{max} = 394 nm, Φ_f = 0.032), **4**·$CuCl_2$ (λ_{max} = 388 nm, Φ_f = 0.008), and **5**·ClO_4 (λ_{max} = 385 nm, Φ_f = 0.003) in CH_2Cl_2 were examined when excited at λ = 340 nm. Besides, fluorescence enhancement

Table 1 Comparison of rigidity and quantum yield.

Compound	Quantum Yield	Rigidity
Free ligand L^{Ph}	0.097	Rigid
Complex **1**·ClO_4	0.005	Nonrigid
Complex **2**	0.031	Rigid
Complex **3**	0.032	Rigid
Complex **4**·$CuCl_2$	0.008	Rigid
Complex **5**·ClO_4	0.003	Rrigid

25 took place when Br^- was introduced to **1**$^+$ (S9), indicating that **1**$^+$ changed from a bromide-unbound two-coordinated species to a bromide-bound three-coordinated species **3**, as in the case of **2**. By monitoring the change in fluorescent spectra, the interconversion of **1**$^+$ and **3** was reversible in the presence (ON)

30 and absence (OFF) of Br^-, giving an ON↔OFF emission switch. The fluorescence quenching was considered to be a result of both the fluxional behavior[15] and the electronic factor from **1**·ClO_4, whereas the electronic factor was predominately taken into account for the rigid complexes. The rigidity and quantum yield

35 are compared in Table 1. It was evident that the influence of fluxionality on the quenching effect for **1**·ClO_4 was small when **1**·ClO_4 was compared with **4**·$CuCl_2$ for their high similarity in a cationic structure. A similar situation was found for complex **2** when it was compared with a related T-shaped nonrigid complex

40 [$Cu(L^H)I$] (QY = 0.034).[16] Thus, the major reason for quenching was ascribed mostly to the extent of the electronic perturbation of the perimidine fluorophore upon complexation of Cu(I), Ag(I) or CuX by L^{Ph}, as observed by the UV-vis spectra.

The absorption spectra of the ligand L^{Ph} and its copper(I) and

45 silver(I) derivatives are shown in Figures 6 and S10. The prominent absorption peaks for the ligand and its copper(I) derivatives were indeed different and were characterized by a blue-shift spectra that is known to be relative to the presence of a free ligand,[3] indicating that the vibronic $\pi-\pi^*$ transtions of the

50 perimidine nucleus in these complexes were really affected. The absorption envelope in the range of $\pi-\pi^*$ transition of the perimidine nucleus between **1**·ClO_4 and **4**·$CuCl_2$ was similar due to the structural similarity in the cationic portion whereas the difference in the range of 260-300 nm appeared to suggest the

55 influence of the attraction of the $CuCl_2^-$ anion. As in the case of complex **2**, complex **3** had a broad shoulder at ~ 273 nm, which can be assigned to the Cu(I) to pyrazole MLCT transition ($d\sigma^* \rightarrow \pi^*$).[17] The absorption envelope of the $\pi-\pi^*$ transition of the perimidine nucleus of **3** changed back to that of a free ligand

60 to a large extent because the perturbation of the $\pi-\pi^*$ transition was lessened by the bromide coordination, which was consistent

with the emission spectra. For complex **5·ClO₄**, the absorption envelope of the π–π* transition of the perimidine nucleus was similar to that of **1·ClO₄**, showing a blue shift of the absorption spectrum despite its lower extinction coefficient (S10). A strikingly quenching effect for **5·ClO₄** was therefore displayed in spite that the involvement of a heavy atom effect could also be instrumental in fluorescence quenching.

Conclusions

This study marks the first implementation of a controllable interconversion among free ligands and linear two-coordinate, as well as T-shaped three-coordinate, copper(I) complexes. This accomplishment could result in a facile tristate fluorescent switching system when halides are used only as the modulators for copper(I) complexes. Also, a simple ON↔OFF bistate fluorescence switching between a free ligand and a two-coordinate silver(I) complex can be easily achieved by the addition/abstraction of the silver(I) ion. The examination of other metal centres using the presented and modified ligand systems for the development of intriguing functional molecules or catalysts[18] is now in progress.

Acknowledgements

Experimental Section

General information and materials

All manipulations were carried out using standard Schlenk lines or glove-box techniques under an atmosphere of dinitrogen. Acetonitrile and dichloromethane were distilled from calcium hydride before use. Diethyl ether was dried by distillation from sodium benzophenone prior to use. *n*-Bu₄NF (1.0M in THF) and *n*-Bu₄NX (X = Cl, Br, I) were obtained from commercial sources and used as received without further purification. The starting materials CuX (X = Cl, Br, I) and AgClO₄ are purchased and used as received. The ligand L^Ph, complex **1·ClO₄** and **2** were prepared according to literature procedures.[3] **Warning**: *Perchlorate compounds are potentially explosive! Extreme care must be taken when working with perchlorate complexes, and only small quantities should be handled.*

Physical measurements

Infrared spectra were recorded on a Bruker Alpha-T FTIR spectrometer as Nujol mulls. Variable-temperature 1H-NMR spectra were obtained on Bruker Avance 400.13 or 500.13 MHz NMR spectrometer. Data were recorded in CD₂Cl₂ at room temperature. ¹³C NMR spectra were recorded on Bruker Avance 125.77 or 150.04 MHz spectrometer. Mass spectra were acquired on a Finnigan TSQ 700 spectrometer. Elemental analyses were performed on a HERAEUS CHN-O-S-Rapid elemental analyzer by Instruments Center, National Chung Hsin University, and a HERAEUS VarioEL- Ⅲ Analyzer by Advanced Instrument Center, National Taiwan University. Fluorescence emission spectra were recorded at ambient on a Hitachi F-7000 fluorescence spectrophotometer. Ultraviolet- Visible spectra were recorded on a JASCO V-650 Ultraviolet/Visible Absorption Spectrometer. Fluorescence quantum yields (Φ_f) were determined using degassed dichloromethane solution at room temperature. The complex and the reference dye, coumarine 151 (QY = 0.49 in dichloromethane), were excited at same wavelength, maintaining

Table 2 Selected X-ray crystallographic data for complexes **3·CH₂Cl₂ – 5·ClO₄**

	3·CH₂Cl₂	**4·CuCl₂·CH₂Cl₂**	**5·ClO₄**
Empirical formula	$C_{30}H_{32}BrCl_2CuN_6$	$C_{30}H_{32}Cl_4Cu_2N_6$	$C_{29}H_{30}AgClN_6O_4$
M	690.97	745.50	669.91
T/K	200(2)	200(2)	200(2)
λ/Å	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1$/c	$P2_1$/c	$P\bar{1}$
a /Å	13.3142(3)	25.9994(17)	10.2448(9)
b /Å	15.6092(3)	15.1102(10)	12.5810(11)
c /Å	14.3394(4)	17.1561(11)	13.3336(11)
α /°	90	90	71.022(2)
β /°	98.7790(10)	107.436(3)	86.393(2)
γ /°	90	90	66.479(2)
V /Å³	2945.16(12)	6430.2(7)	1485.7(2)
Z	4	8	2
D_{calcd} /g cm⁻¹	1.558	1.540	1.498
μ /mm⁻¹	2.311	1.686	0.813
θ range for data collection/°	2.34 – 25.04	1.58 – 25.03	2.23 – 25.02
No. reflns. collected	19154	44655	14245
No. indep. reflns. [$I > 2\sigma(I)$]	5197 (R_{int} = 0.0916)	11342 (R_{int} = 0.0725)	5171 (R_{int} = 0.0424)
No. param.	361	756	370
R_1	0.0610	0.0920	0.0474
wR_2	0.1627	0.2418	0.1193
GOF on F^2	1.086	1.020	1.031
CCDC No.	1024054	1024055	1024056

nearly equal absorbance, and the emission spectra were recorded. Fluorescence quantum yields were taken as the average of three separate determinations and were reproducible to within 10%.

X-Ray crystallography

Crystal data collection and processing parameters are given in Table 2. Diffraction data were carried out on a Bruker Kappa (**3**) and Bruker APEX II (**4**·CuCl$_2$·CH$_2$Cl$_2$ and **5**·ClO$_4$) CCD diffractometers with graphite monochromated Mo-Kα radiation (λ = 0.7107 Å). The structures **3**·CH$_2$Cl$_2$, **4**·CuCl$_2$·CH$_2$Cl$_2$ and **5**·ClO$_4$ were solved by direct methods and refined by full-matrix least-squares procedures using the SHELXL-97 program.[19] The higher but acceptable R values for **4**·CuCl$_2$·CH$_2$Cl$_2$ (9.2%) was due to the slightly poor quality of the crystals. In the lattice, part of the copper atoms in the cationic **4**$^+$ was disordered over two positions (93:7 ratio). Complex **5**·ClO$_4$ was squeeze half CH$_2$Cl$_2$ using the SQUEEZE option of PLATON. All of the non-hydrogen atoms were refined with anisotropic temperature factors. All hydrogen atoms were located geometrically and refined in the riding mode. Additional crystallographic data as CIF files are available as Supporting Information.

Synthesis of complex 3

Method 1: The reaction of CuBr (72 mg, 0.50 mmol) and L^{Ph} (232 mg, 0.50 mmol) was carried out following a procedure similar to that of described for the synthesis of complex **2** in a 87% yield (263 mg). Single crystals of **3**·CH$_2$Cl$_2$ were grown from CH$_2$Cl$_2$/Et$_2$O. ^{1}H NMR (CD$_2$Cl$_2$, 500.13 MHz): δ 7.54 (s, 1H, C*H*), 7.29~7.13 (m, 9H, C*H* of naphthalene and phenyl), 6.65 (d, 2H, C*H* of phenyl), 6.13 (d, 2H, $^2J_{HH}$ = 13.8 Hz, C*H*$_2$), 5.97 (s, 2H, C*H* of pyrazole), 5.92 (d, 2H, $^2J_{HH}$ = 13.7 Hz, C*H*$_2$), 2.54 (s, 6H, C*H*$_3$), 2.35 (s, 6H, C*H*$_3$) ppm. ^{13}C NMR (CD$_2$Cl$_2$, 125.77 MHz): δ149.63, 141.91, 141.34, 138.49, 135.38, 129.10, 128.48, 127.33, 126.98, 120.21, 117.91, 107.50, 107.15, 76.38, 63.80, 15.23, 12.24 ppm. Positive ESI-MS: 525.3 ([M-Br]$^+$, 100%). UV-Vis (CH$_2$Cl$_2$) λmax, nm (ε, M^{-1}cm^{-1}): 339 (17487), 348 (18140). Anal. Calcd for C$_{29}$H$_{30}$BrCuN$_6$ (**3**): C,57.47; H, 4.99; N, 13.87. Found: C, 56.95.10; H, 4.96; N, 13.97. **Method 2**: To a stirred solution of complex **1**·ClO$_4$ (31 mg, 0.05mmol) in 10 CH$_2$Cl$_2$ was added a solution of *n*-Bu$_4$NBr (16 mg, 0.05mmol) in 5ml CH$_2$Cl$_2$. After reaction for 20 min at room temperature, the resulting solution was dried under vacuum. The solid was analyzed by ^{1}H NMR in CD$_2$Cl$_2$ and the yield of **3** is nearly quantitative. ^{1}H NMR (CD$_2$Cl$_2$, 400.13 MHz): δ 7.34 (s, 1H, C*H*), 7.32~7.15 (m, 9H, C*H* of naphthalene and phenyl), 6.73 (d, 2H, C*H* of phenyl), 6.08 (d, 2H, $^2J_{HH}$ = 13.8 Hz, C*H*$_2$), 5.99 (s, 2H, C*H* of pyrazole), 5.95 (d, 2H, $^2J_{HH}$ = 13.8 Hz, C*H*$_2$), 3.23~3.19 (m, 8H, C*H*$_2$ of *n*-butyl), 2.55 (s, 6H, C*H*$_3$), 2.37 (s, 6H, C*H*$_3$), 1.70~1.64 (m, 8H, C*H*$_2$ of *n*-butyl), 1.50~1.44 (m, 8H, C*H*$_2$ of *n*-butyl), 1.06 (t, 12H, C*H*$_3$ of *n*-butyl) ppm.

Synthesis of complex 4·CuCl$_2$

A 10ml CH$_2$Cl$_2$ solution of CuCl (100 mg, 1.00 mmol) and L^{Ph} (235mg, 0.51 mmol) was stirred at room temperature for 0.5 hr under N$_2$. After the addition of 10 ml Et$_2$O, the white precipitates formed was filtered off and washed by 5 ml Et$_2$O for two times. The resulting white solid was dried under vacuum to yield 301 mg (91 %) of **4**·CuCl$_2$. Single crystals of **4**·CuCl$_2$·CH$_2$Cl$_2$ were grown from CH$_2$Cl$_2$/Et$_2$O. ^{1}H NMR (CD$_2$Cl$_2$, 500.13 MHz): δ 7.42 (s, 1H, C*H*), 7.27~7.15 (m, 9H, C*H* of naphthalene and phenyl), 6.44 (d, 2H, C*H* of phenyl), 6.05 (s, 2H, C*H* of pyrazole), 6.13 (d, 2H, $^2J_{HH}$ = 13.5 Hz, C*H*$_2$), 5.94 (d, 2H, $^2J_{HH}$ = 13.5 Hz, C*H*$_2$), 2.57 (s, 6H, C*H*$_3$), 2.43 (s, 6H, C*H*$_3$) ppm. ^{13}C NMR (CD$_2$Cl$_2$, 125.77 MHz): δ 151.82, 143.05, 140.49, 137.42, 135.47, 129.38, 128.95, 127.50, 126.84, 120.45, 117.06, 107.93, 106.25, 78.04, 63.64, 15.75, 12.17 ppm. Positive ESI-MS: 525.3 ([M-CuCl$_2$]$^+$, 100%). UV-Vis (CH$_2$Cl$_2$) λmax, nm (ε, M^{-1}cm^{-1}): 332 (16613), 346 (17117). Anal. Calcd for C$_{29}$H$_{30}$Cl$_2$Cu$_2$N$_6$ (**4**·CuCl$_2$): C, 52.73; H, 4.58; N, 12.72. Found: C, 52.96; H, 4.51; N, 12.88.

Synthesis of complex 5·ClO$_4$

A 8 ml CH$_2$Cl$_2$ solution of AgClO$_4$ (103 mg, 0.50 mmol) and L^{Ph} (240 mg, 0.52 mmol) was stirred at 0 °C for 1 hr in the dark. Then the solution was filtered. Addition of 10ml hexane results in the precipitate of white solid, which was separated by filtration and washed by 10ml hexane for two times. The resulting white solid was dried under vacuum to yield 301 mg (90 %) of **5**·ClO$_4$. Single crystals of **5**·ClO$_4$ were obtained from CH$_2$Cl$_2$/Et$_2$O in the dark. IR (KBr): $ν_{CO4}$- 1096 cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$, 500.13 MHz): δ 7.28~7.19 (m, 9H, C*H* of naphthalene and phenyl), 6.95 (s, 1H, C*H*), 6.36 (dd, 2H, C*H* of phenyl), 6.10 (s, 2H, C*H* of pyrazole), 5.95 (d, 2H, $^2J_{HH}$ = 13.5 Hz, C*H*$_2$), 5.85 (d, 2H, $^2J_{HH}$ = 13.4 Hz, C*H*$_2$), 2.59 (s, 6H, C*H*$_3$), 2.29 (s, 6H, C*H*$_3$) ppm. ^{13}C NMR (CD$_2$Cl$_2$, 150.04 MHz): δ 151.06, 143.43, 139.68, 137.62, 135.48, 129.49, 1298.19, 127.67, 126.80, 120.21, 116.21, 107.49, 105.23, 78.01, 63.26, 15.76, 12.01 ppm. Positive ESI-MS: 569.0 ([M-ClO$_4$]$^+$, 100%). UV-Vis (CH$_2$Cl$_2$) λmax, nm (ε, M^{-1}cm^{-1}): 322 (10681), 327 (11017), 342 (11660). Anal. Calcd for C$_{29}$H$_{30}$N$_6$AgClO$_4$ (**5**·ClO$_4$): C, 51.99; H, 4.51; N, 12.55. Found: C, 52.32; H, 4.53; N, 12.78.

General procedure for the reactions of copper(I) derivatives, 1·ClO$_4$, 2, 3 or 4 ·ClO$_4$, with *n*-Bu$_4$NF

To a stirred solution of complex **1**·ClO$_4$ (40 mg, 0.064 mmol) in 10ml CH$_2$Cl$_2$ was added a solution of *n*-Bu$_4$NF in THF (0.064 ml, 0.064 mmol). The orange-yellow precipitates were formed in 5 minutes at room temperature under N$_2$. The solution was filtered and the resulting solution was dried under vacuum. The solid was analyzed by ^{1}H NMR in CD$_2$Cl$_2$ to firm the liberation of L^{Ph}.

Reactions of 5·ClO$_4$ with *n*-Bu$_4$NX (X = Cl, Br, I)

To a stirred solution of complex **5**·ClO$_4$ (40 mg, 0.064 mmol) in 5 ml CH$_2$Cl$_2$ was added a solution of *n*-Bu$_4$NX (X = Cl, Br, I) in 5 ml CH$_2$Cl$_2$. The white (AgCl) or yellow (AgBr, AgI) precipitates were formed immediately. The solution was filtered and the resulting solution was dried under vacuum. The solid was analyzed by ^{1}H NMR in CD$_2$Cl$_2$ to firm the liberation of L^{Ph}.

Notes and references

Center for General Education, Chang Gung University of Science and Technology, Tao-Yuan, 333, Taiwan, R.O.C. E-mail: Fax: +886-3-2118866; Tel: +886-3-2118999 ext. 5583; E-mail: ccchou@mail.cgust.edu.tw

† Electronic Supplementary Information (ESI) available: ^{1}H&^{13}C NMR spectra, absorption and emission spectra, crystal structures CCDC 1024054–1024056. See DOI: 10.1039/b000000x/

1   J. M. Lehn, *Supramolecular Chemistry: Concepts and Perspectives,* VCH, Weinheim, 1995; V. Balzani and F. Scandola,

    Supramolecular Photochemistry, Ellis Horwood, Chichester, 1991; A. P. de Silva, H. Q. N. Gunaratne and C. P. Mccoy, *Nature* 1993, **364**, 42; A. P. de Silva, H. Q. N. Gunaratne, T. Gunnlaugsson, A. J. M. Huxley, C. P. McCoy, J. T. Rademacher, and T. E. Rice,

5   1997, **97**, 1515; D. Margulies, G. Melman, C. E. Felder, R. Arad-Yellin and A. Shanzer, *J. Am. Chem. Soc.* 2004, **126**, 15400; Q. Zou, X. Li, J. Zhang, J. Zhou, B. Sun, H. Tian, *Chem. Commun.* 2012, **48**, 2095; Y.-P. Li, H.-R. Yang, Q. Zhao, W.-C. Song, J. Han and X.-H. Bu. *Inorg. Chem.* 2012, **51**, 9642; S. Karmakar, D. Maity, S.

10   Mardanya and S. Baitalik, *J. Phys. Chem. A,* 2014, **118**, 9397.

2   H.-J. Liu, Y.-H. Hung, C.-C. Chou and C.-C. Su, *Chem. Commun.*, 2007, 4958.

3   C.-C. Chou, H.-J. Liu and L. H.-C. Chao, *Chem. Commun.*, 2009, 6382. A.

15 4   A. Petitjean, N. Kyritsakas, and J.-M. Lehn, *Chem. Eur. J.* 2005, **11**, 6818.

5   The related perimidine-based bis(phosphine) trans-chelating ligands, N,N′-bis(phoshinomethyl)-dihydroperimidines, have been recently repored for the complexation with Rh(I) and revealed that the

20   N(amine) atom in the perimidine nucleus can bond to the metal center. A. F. Hill and C. M. A. McQueen, *Organometallics*, 2014, **33**, 1909.

6   Examples for a conversion of nonemissive two-coordinate Ag(I) or Au(I) complexes to an emissive one by additional ligand binding:

25   F.-B. Xu, L.-H. Weng, L.-J. Sun and Z.-Z. Zhang, *Organometallics*, 2000,**19**, 2658; W.-H. Chan, Thomas C.W. Mak and C.-M. Che, *Dalton Trans.*, 1998, 2275.

7   T. N. Sorrell, M. R. Malachowski and D. L. Jameson, *Inorg. Chem.*, 1982, **21**, 3250.

30 8   S.-H. Liu, J.-D. Chen, L.-S. Liou and J.-C. Wang, *Inorg. Chem.*, 2001, **40**, 6499.

9   S. Andersson and S. Jager, *Acta Chem. Scand.*, 1987, **A41**, 230.

10   M. Munakata, M. Maekawa, S Kitagawa, S. Matsuyama. and H. Masuda, *Inorg. Chem.*, 1989, **28**, 4300.

35 11   U. Siemeling, U. Vorfeld, B. Neumann and H.-G. Stammler, *Chem. Commun.*, 1997, 1723; K. Singh, J. R. Long, and P. Stavropoulos, *J. Am. Chem. Soc.* 1997**, 119***, 2942.

12   M. L. Gallego, P. Ovejero, M. Cano, J. V. Heras, J. A. Campo, E. Pinilla and M. R. Torres, *Eur. J. Inorg. Chem.*, 2004, 3089; A. A.

40   Mohamed and J. P. Fackler Jr., *Acta Crystallogr., C* 2002, **58**, m228; I. Boldog, E. B. Rusanov, A. N. Chernega, J. Sieler and K. V. Domasevitch, *Polyhedron* 2001, **20**, 887; M. L. Gallego, M. Cano, J. A. Campo, J. V. Heras, E. Pinilla and M. R. Torres, Helv. Chim. Acta 2005, 88, 2433.

45 13   Linear two-coordinate copper(I)-imidazole complexes had proven to be the precursors of their ensuing T-shaped, three-coordinate, copper(I) derivatives. R. A. Himes, G. Y. Park, A. N. Barry, N. J. Blackburn and K. D. Karlin, *J. Am. Chem. Soc.* 2007**, 129***, 5352.

14   L. Subramanian and R. Hoffmann, *Inorg. Chem.*, 1992, **31**, 1021.

50 15   J. Shao, Y.-H. Qiao, H. Lin and H.-K. Lin, J. Inclusion Phenom. *Macrocyclic Chem.*, 2008, 62, 99.

16   C.-C. Chou, H.-J. Liu, L. H.-C. Chao, H.-B. Syu, T.-S Kuo, *Polyhedron*, 2012, **37**, 60.

17   T. N. Sorrell and A. S. Borovik, *Inorg. Chem.*, 1987, 26, 1957.

55 18   C.-C. Chou, C.-C. Yang, H.-B. Syu and T.-S Kuo, *J. Organomet. Chem.*, 2013, **745-746**, 387.

19   G. M. Sheldrick, *Acta Crystallogr., Sect.*, 2008, **A64**, 112.