COMMUNICATION

Methanol triggered ligand flip isomerization in a binuclear copper(I) complex and the luminescence response†‡

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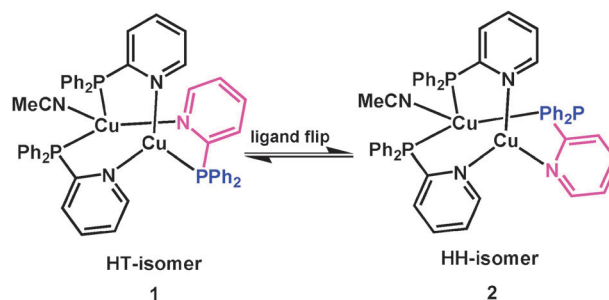
Methanol drives the blue emissive complex, [Cu$_2$(dppy)$_3$(MeCN)](BF$_4$)$_2$ (dppy = diphenylphosphino-pyridine), with a head-to-tail arrangement of the three bridging phosphine ligands to convert to its linkage isomer (head-to-head, green emissive) in the solid state, and the transformation could be reversibly realized through recrystallization in different solvents.

Photoluminescent d^{10} complexes have been of great interest due to their potential applications in devices, sensors and bioapplications.[1] Copper(I) luminophores have been studied as an inexpensive alternative to noble metal emitters.[2] Based on the fact that many Cu(I)–phosphine and Cu(I)–pyridine complexes display interesting photophysical properties,[3] we are interested in using the hemilabile ligand diphenylphosphino-pyridine (dppy) for the assembly of luminescent copper(I) complexes. Our studies revealed that a simple binuclear copper(I) complex displays intense blue luminescence, and a ligand flip isomerization could be triggered by methanol vapor in the solid state. Furthermore, the isomerization process can be controlled reversibly through recrystallization in different solvents, and each isomer displays distinct luminescence color. Herein, we report the synthesis, structural characterization, and emission properties of a pair of intensely luminescent dinuclear Cu(I) isomers, namely [Cu$_2$(dppy)$_3$(MeCN)](BF$_4$)$_2$ (**1**) and [Cu$_2$(dppy)$_3$(MeCN)](BF$_4$)$_2$·MeOH (**2**·MeOH).

It is known that **1** could be prepared easily by reacting [Cu(MeCN)$_4$]BF$_4$ with dppy in 2 : 3 ratio in acetonitrile.[4] Its molecular structure has a head-to-tail (HT) arrangement of the three bridging dppy ligands with two phosphorus donors located at one copper and the third phosphorus on the other one (Scheme 1, HT-isomer). We found that this compound emits bright blue light in the solid state at room temperature under UV (365 nm) irradiation. Interestingly, recrystallization of **1** from a mixed solvent of CH$_2$Cl$_2$–MeOH afforded complex

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† Dedicated to Prof. T. C. W. Mak on the occasion of his 75th birthday.
‡ Electronic supplementary information (ESI) available: Synthesis and characterization details. CCDC 826053 (**2**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1cc12857d

Scheme 1

2·MeOH, which is a linkage isomer of **1** and displays green light when exposed to UV light.

X-Ray single crystal structural analysis§ revealed that **2** has a structure similar to that of **1** (Fig. 1), but its two Cu(I) centers are triply bridged by dppy ligands with all three phosphorus donors on one copper(I) atom. This is the head-to-head configuration (Scheme 1, HH-isomer), which can be virtually derived from the head-to-tail configuration by flipping one of the three dppy ligands. Further investigation showed that solid samples of **1** could be transformed to **2** under methanol vapor,
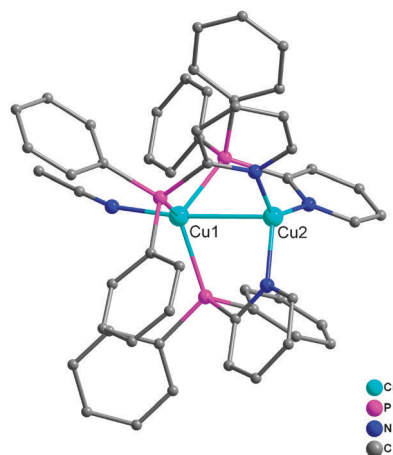

Fig. 1 Molecular structure of the cationic part of [Cu$_2$(dppy)$_3$(MeCN)](BF$_4$)$_2$·MeOH (**2**·MeOH). Selected bond distances [Å]: Cu(1)–Cu(2) 2.7961(4), Cu(1)–P(1) 2.3105(6), Cu(1)–P(2) 2.3094(6), Cu(1)–P(3) 2.2975(6), Cu(1)–N(4) 2.022(2), Cu(2)–N(1) 2.031(2), Cu(2)–N(2) 2.1.978(2), Cu(2)–N(3) 2.016(2).

and methanol was proved to be critical for the formation of **2**, as only **1** was recovered by similar preparation methods with other solvents in place of methanol.

The Cu···Cu separation in **2** is 2.7961(4) Å, which is significantly longer than that of 2.721(3) Å in **1**. The closest Cu–FBF$_3$ distance in **2** is 3.112 Å (a value of 2.755(6) Å was found for its linkage isomer, **1**), indicating a weak interaction of one of the BF$_4^-$ anions with the 3-coordinate Cu atom in this dimer. The Cu–N and Cu–P bond distances in **2** are shorter for the 3-coordinate Cu1 than for the 4-coordinate Cu2, which is similar to the case in **1**.

It was found that methanol is critical to the transformation. Recrystallization of **1** in CH$_2$Cl$_2$/EtOH still gave **1**, while **2** crystallized from the solution of **1** in CH$_2$Cl$_2$/MeOH. At −80 °C, the ^{31}P NMR profile of **2** in methanol is quite different from that in CH$_2$Cl$_2$ (Fig. S3, ESI‡), which indicated that solvents affected profoundly the ligand dissociation and association processes taking place in solution. Thus, different species (HH or HT isomers) could be obtained through crystallization from different solvents, and methanol favors the formation of HH isomer **2**. It is notable that linkage isomerism of bridging dppy has also been observed in the Pt(I)–Pd(I) dimer, [IPd(dppy)$_2$PtI], the HH isomer converts completely to the HT isomer on refluxing in CH$_2$Cl$_2$ solution.[5] Solid state ^{31}P NMR profile of **2** is symmetric while that of **1** is asymmetric (Fig. S4, ESI‡), which corresponds with the different structures.

The presence of MeOH in **2** was confirmed by thermogravimetric analysis (TGA). Complex **2** gradually loses its MeOH and MeCN content upon heating, and a total loss of 5.96% at 203 °C is close to the calculated value 6.27% (Fig. S5, ESI‡). Decomposition occurred when the temperature went up to 300 °C.

As shown in Fig. 2, **1** and **2** display distinct luminescence behavior in the solid state, and life time data were measured to be 63.7(3) μs for **1** and 39.9(2) μs for **2**, which suggests a triplet parentage of the transition. Complexes **1** and **2** can be converted to each other reversibly; recrystallization of **1** in CH$_2$Cl$_2$/MeOH affords **2** while recrystallization of **2** in MeCN/Et$_2$O gives **1**. Consequently, the emission changes with regard to different isomers. It is noteworthy that vapor-induced emission switching behavior has been found in metal complexes.[6,7]
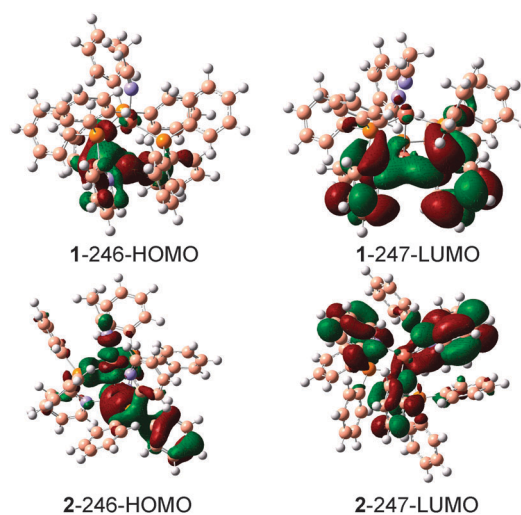
Fig. 3 HOMOs and LUMOs of **1** and **2**.

The electronic structures of **1** and **2** have been theoretically investigated on the basis of their single crystal structural data using the density functional theory. The hybrid functional B3LYP[8] and basis set 6-31G*[9] are used in calculations. As shown in Fig. 3, the basic components of the highest occupied molecular orbital (HOMO) in **1** are d orbitals of the two Cu atoms, p orbitals of the P and N atoms, and the π bonding orbital of one phenyl group. The lowest unoccupied molecular orbital (LUMO) of **1** comprises π orbitals primarily located on the two pyridyl groups. For **2**, the calculated HOMO mainly consists of the d orbital of the Cu atom coordinated by three pyridyl groups and p orbitals of pyridyl N atoms, while the LUMO is composed of π orbitals delocalized over the three pyridyl rings. The involvement of both copper centers in the HOMO of **1** is consistent with the shorter Cu(I)···Cu(I) separation in **1**, which demonstrates the importance of cuprophilicity.

The vertical transition energies of the three lowest singlet excited states and three lowest triplet excited states for **1** and **2** have been computed by the time-dependent density functional method (TDDFT)[10] with the B3LYP functional (hereafter: TDB3LYP) and the 6-31G* basis set. Table S1 (ESI‡) displays the calculated energies of HOMO, LUMO orbitals and the HOMO–LUMO gap (HLG) at the B3LYP/6-31G* level and the calculated vertical excitation energy of the low-lying excited states at the TDB3LYP/6-31G* level. The character of the low-lying excited states and the calculated oscillator strengths also are given in Table S1 (ESI‡). The HOMO and LUMO orbitals of **1** and **2** have been shown in Fig. 3. Although **2** has a little larger HLG than **1**, both the calculated S1 (the first excited singlet state) and T1 (the first excited triplet state) states of **2** have smaller vertical excitation energies than the corresponding those of **1**, which shows good agreement with the experimental emission spectra where **2** has a lower energy emission band than that of **1** (**2**: 520 nm, **1**: 489 nm).

We also used the larger basis set TZVP[11] to repeat these calculations, and the calculated results are given in Table S2 (ESI‡), and the calculations with TZVP basis set draw the same conclusion as that from 6-31G*.

It is found that π–π interactions profoundly influence the emission energy. Significant π–π contacts between phenyl and pyridyl planes are found in **2**, which lower the LUMO energy
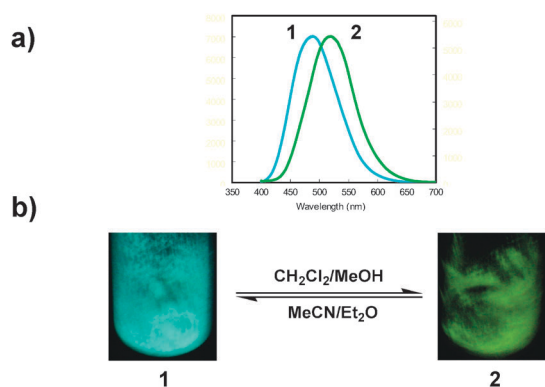

Fig. 2 (a) Normalized emission spectra of **1** and **2**. (b) Interconversion of **1** and **2** with photos of emissions from **1** and **2** in the solid state at room temperature (365 nm excitation).

level and result in a lower energy of the emission compared with **1**. Although the Cu(I)···Cu(I) interaction in **2** is weaker than that in **1**, the π–π interactions in **2** lead to a red-shifted emission relative to **1**.

In summary, a pair of phosphine stabilized dinuclear copper complexes could be interconverted through recrystallization in different solvents, and they emit blue or green light when irradiated with UV light depending on the ligand bridging orientation.

Notes and references

§ Crystal data for **2**·CH$_3$OH, C$_{53}$H$_{45}$B$_2$N$_4$F$_8$P$_3$Cu$_2$·CH$_3$OH, a = 11.4057(5), b = 12.5265(5), c = 20.1978(8) Å, α = 75.491(1), β = 89.626(1), γ = 66.936(1)°, V = 2556.8(2) Å^3, monoclinic space group $P\bar{1}$, Z = 2, T = 193(2) K, 35 916 reflections measured, 12 708 unique (R_{int} = 0.0196), final R_1 = 0.0476, wR_2 = 0.1300 for 11 105 observed reflections [$I > 2\sigma(I)$].

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