# Rotational isomerization: Spontaneous structural transformation of a thermally activated delayed fluorescence binuclear copper(I) complex

Xiaowen Zhang,<sup>a,b,c‡</sup> Chun-Hua Huang,<sup>a,b‡</sup> Mingxue Yang<sup>a, b‡</sup>, Xu-Lin Chen<sup>\*a,b</sup>, and Can-Zhong Lu<sup>\*a,b,c</sup>

<sup>a</sup> State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian, 350002, China. Email: <u>xlchem@fjirsm.ac.cn</u>; <u>czlu@fjirsm.ac.cn</u> <sup>b</sup> Xiamen Key Laboratory of Rare Earth Photoelectric Functional Materials, Xiamen Institute of Rare Earth Materials, Haixi Institutes, Chinese Academy of Sciences, Xiamen, Fujian 361021, China <sup>c</sup> School of Physical Science and Technology, ShanghaiTech University, Shanghai 201210, China

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#### 1. Materials and Methods (General Information)

All commercially available starting materials were used without any purification. All reactions were performed under a nitrogen atmosphere. The crystal diffraction data were collected by single-crystal X-ray diffraction analysis with graphite monochromatized Mo  $K_{\alpha}$  radiation ( $\lambda$  = 0.71073 Å) on a Bruker D8 VENTRUE diffractometer. The structures were obtained by direct methods and refined by full-matrix least squares methods using the SHELXL-2018 program package.<sup>1</sup> The crystallographic data of three Cu(I) complexes have been deposited at the Cambridge Crystallographic Data Center. CCDC 2077313 (Cu-G) and 2077331 (Cu-Y). Elemental analyses of C, H, and N were carried out with an Elementar Vario El Cube elemental analyzer. UV-Vis absorption spectra were obtained on a Perkin-Elmer lambda 900 UV-Vis spectrometer. Luminescence spectra were carried out on an Edinburgh Instrument F980 fluorescent spectrometer. The luminescence quantum yields were recorded on a Hamamatsu Photonics C11347-11 absolute photoluminescence quantum yield spectrometer.<sup>2</sup> Configurational symmetry for single molecule of **Cu-G** is determined by Material Studio Software. All the calculations were carried out using the Gaussian 09 program package.<sup>3</sup> The density functional theory (DFT) calculations were used to optimize the ground state geometries of the investigated compounds.<sup>4</sup> A "double-ζ" quality basis set consisting of Hay and Wadt's effective core potentials (LANL2DZ) was employed for the C, N and H atoms, and a LANL08 basis set was employed for the Cu and P atoms. Time-dependent density functional theory (TD-DFT) calculations were performed at the 6-311G\* level using the optimized ground state geometries.<sup>5-6</sup> The total energy for simulating crystalline state was performed under ONIOM(MO:MM) method.<sup>7</sup> A matrix of 9 × 9 × 9 molecules were adopted, in which the innermost one molecule is selected to adopt high-level quantum mechanics (B3LYP) while the other molecules are treated by the efficient universal force field (UFF) method. The electron density diagrams of molecular orbitals were generated using Gauss View program. The partition orbital composition was analyzed by using the Multiwfn 2.7 program.<sup>8</sup> Cyclic voltammetry was performed on a BAS Epsilon Electrochemical Analyzer with a gastight single-compartment three-electrode cell. A glassy carbon disk and a platinum wire were used as working and auxiliary electrodes, respectively and the reference electrode was  $Ag/Ag^+$  (0.1 mol / L of AgNO<sub>3</sub> in CH<sub>2</sub>Cl<sub>2</sub>). The CV measurements were performed in anhydrous and nitrogensaturated dichloromethane solutions with 0.05 mol/L n-tetrabutylammonium perchlorate (TBAP) and 0.05 mmol/L cuprous complexes. The ferrocenium/ferrocene couple was used as an internal standard. The TGA test were performed on a Mettler Telodo synchronous thermal analyser with a 10°C/min heating rate at the flowing N<sub>2</sub> atmosphere. All of these samples prepared for experiment have been dried for 2 hours at 90°C.

#### 2. Synthesis of Materials

#### 2.1. Synthesis of 1-(diphenylphosphino)-9-(pyridin-2-yl)-9H-carbazole (N^P)

The source material 1-bromo-9-(2-pyridyl)-9*H*-carbazole was synthesized from previous report.<sup>2</sup> Under anhydrous and oxygen-free conditions, 1-bromo-9-(2-pyridyl)-9-hydrocarbazole2 (0.897 g, 3 mmol) and distilled dried tetrahydrofuran (10 mL) were added to a 100 mL Schlenk bottle. 2.5 M n-butyllithium solution (0.192 g, 3 mmol) was slowly added to the reaction system at -78°C to obtain a brown-yellow solution. After stirring for half an hour, a tetrahydrofuran solution (5 mL) of diphenylphosphine chloride (0.725 g, 3.3 mmol) was slowly added dropwise to the mixture. Stir overnight at room temperature, add a small amount of distilled water to the reaction solution to quench the reaction, and extract with  $CH_2Cl_2$  and saturated brine several times. The organic phase was separated and dried with anhydrous  $Na_2SO_4$ . The solvent was evaporated and then purified by column to obtain yellow powder (yield: 60%). <sup>1</sup>H NMR (500 MHz, Methylene Chloride- $d_2$ )  $\delta$  8.77 (s, 2H), 8.18 (dd, J=55.6, 7.6, 4H), 7.42 – 7.11 (m, 26H), 6.83 (s, 2H), 6.47 (dd, J=68.5, 37.2, 7H).

# 2.2. Synthesis of crystalline Cu(I)–DPPCz complex (Cu-G and Cu-Y):

The crystals were grown via diffusion method. In a typical procedure, the 0.25 mmol of CuI and DPPCz ligand were dissolved in 5 mL of acetonitrile and dichloromethane, respectively. Acetonitrile solution of CuI was carefully dripped into the solution of the ligand. Seal the cover and wait until the first crystals formed (**Cu-G**). The crystal turned to **Cu-Y** after 2 days. Besides, the powder yellow-emitting **Cu-Y** also precipitate with the stirring of the mixture.

Cu-G <sup>1</sup>H NMR (500 MHz, Methylene Chloride- $d_2$ )  $\delta$  = 9.00 (s, 2H), 8.36 – 8.12 (m, 5H), 7.78 (s, 1H), 7.55 – 7.41 (m, 4H), 7.39 – 7.12 (m, 20H), 7.10 – 6.96 (m, 4H), 6.93 – 6.56 (m, 6H). <sup>31</sup>P NMR (202 MHz, Methylene Chloride- $d_2$ )  $\delta$  32.91. Elemental analysis: calc for C<sub>58</sub>H<sub>42</sub>Cu<sub>2</sub>I<sub>2</sub>N<sub>4</sub>P<sub>2</sub> C, 56.28; H, 3.42; N, 4.53. Found: C, 55.73; H, 3.66; N, 4.51.

Cu-Y <sup>1</sup>H NMR (500 MHz, Methylene Chloride- $d_2$ )  $\delta$  = 9.03 (s, 2H), 8.38 – 8.15 (m, 5H), 7.49 – 7.18 (m, 31H), 7.02 – 6.62 (m, 4H). <sup>31</sup>P NMR (202 MHz, Methylene Chloride- $d_2$ )  $\delta$  32.69. Elemental analysis: calc for C<sub>58</sub>H<sub>42</sub>Cu<sub>2</sub>I<sub>2</sub>N<sub>4</sub>P<sub>2</sub> C, 56.28; H, 3.42; N, 4.53. Found: C, 56.23; H, 3.57; N, 4.55.

# 3. Crystal Parameters and Refinement Data

Table S1 Crystal parameters and refinement data of complexes Cu-G and Cu-Y

Complex reference	Cu-G	Cu-Y	
Chemical formula	$C_{58}H_{42}Cu_2I_2N_4P_2$	$C_{58}H_{42}Cu_2I_2N_4P_2$	
Formula weight	1237.77	1237.77	
Space group	P-1	P21/c	
Crystal system	Triclinic	Monoclinic	
<i>a</i> (Å)	10.67(5)	12.3773(3)	
<i>b</i> (Å)	13.79(6)	16.0279(4)	
<i>c</i> (Å)	23.49(10)	12.3747(3)	
α (°)	97.34(14)	90	
β (°)	101.29(2)	98.6740(10)	
γ (°)	112.57	90	
Volume (ų)	3051(24)	2426.84(10)	
Ζ	2	2	
Density (g· cm⁻¹)	1.347	1.694	
2ϑ (°)	4.09 to 54.206	5.656 to 55.022	
h	$-13 \le h \le 13$	-16 ≤ <i>h</i> ≤ 16	
k	$-17 \leq k \leq 17$	$-20 \le k \le 20$	
1	-30 ≤ <i>l</i> ≤ 30	-16 ≤ <i>l</i> ≤ 15	
F (000)	1224	1224	
Collection Num.	13476	43178	
Independent Num.	13476	5466	

Data / restraints / parameters	13772/0/613	5466 / 0 / 307
G. O. F.	1.067	1.047
$R_1, wR_2 [I > 2\sigma(I)]$	0.0510, 0.1333	0.0173, 0.0412
$R_1$ , $wR_2$ (all data)	0.0681, 0.1438	0.0200, 0.0428
$\Delta  ho_{max}$ , $\Delta  ho_{min}$ (e·Å <sup>-3</sup> )	3.10, -1.42	0.33, -0.25

 ${}^{a}R_{1}=\sum ||F_{o}| - |F_{c}|| / \sum |F_{o}| \cdot {}^{b}wR_{2}=[\sum w(F_{o}^{2} - F_{c}^{2})^{2} / \sum w(F_{o}^{2})]^{1/2}$ 

# 4. Selected Bond Distances and Angles

Table S2 Selected bond distances [Å] and angles [°] for complexes Cu-G and Cu-Y

	Cu-G	Cu-Y	
l(1)-Cu(2)	2.653(13)	2.7001(2)	
l(1)-Cu(1)	2.647(10)	2.6006(2)	
Cu(1)-P(1)	2.251(8)	2.2376(4)	
Cu(1)-N(1)	2.154(12)	2.0915(13)	
Cu(1)-Cu(2)	2.701(9)		
Cu(2)-P(2)	2.246(8)		
I(2)-Cu(2)	2.650(9)		
Cu(2)-N(4)	2.167(12)		
I(2)-Cu(1)	2.644(10)		
N(1)-Cu(1)-P(1)	92.5(2)	97.48(4)	
N(1)-Cu(1)-I(1)	108.0(2)	115.18(4)	
N(1)-Cu(1)-I(2)	113.1(3) 110.51(4)		
N(4)-Cu(2)-P(2)	91.4(3)		
N(4)-Cu(2)-I(1)	114.7(2)		
N(4)-Cu(2)-I(2)	108.5(3)		



Figure S1 Superimposed graph of symmetrized and crystalline molecular configuration of Cu-G.

	Cu-G	Cu-Y	
	(Unit: Hartree / Particle)	(Unit: Hartree / Particle)	
Zero-point correction	21.970438	21.960127	
Thermal correction to Energy	23.199035	23.198205	
Thermal correction to Enthalpy	23.199979	23.199149	
Thermal correction to Gibbs Free Energy	20.683190	20.692399	
Sum of electronic and zero-point Energies	-3495.510812	-3502.178788	
Sum of electronic and thermal Energies	-3494.282215	-3500.940710	
Sum of electronic and thermal Enthalpies	-3494.281271	-3500.939766	
Sum of electronic and thermal Free Energies	-3496.798060	-3503.446516	

# Table S3 Thermodynamic information of Cu-G and Cu-Y



Figure S2. The HOMO+1(blue) and LUMO-1(orange) orbital distribution of complex Cu-G and Cu-Y

Table S4 The orbital composition of	HOMO and LUMO orbits for Cu-G and Cu-Y
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Complex	Orbital	Cu	I	PPh <sub>2</sub>	9-pyCz
Cu-G	НОМО	46.46%	17.99%	27.40%	8.14%
	LUMO	6.34%	0.43%	8.91%	84.32%
Cu-Y	НОМО	38.54%	31.38%	23.06%	7.02%
	LUMO	4.43%	0.43%	10.86%	84.28%

 Table S5 Excited-state energy levels, oscillator strength (f) and the lowest energy state of frontier orbital analysis for Cu-G and Cu-Y

Complex	State	λ <sub>cal</sub> <sup>a</sup> (nm)	f <sup>b</sup>	Assignment <sup>c</sup>	MLCT	XLCT	ILCT
Cu-G	S <sub>1</sub>	525	0.015	H→L (98.34%)	35.41%	36.71%	12.91%
	S <sub>2</sub>	517	0.0019	H→L+1 (98.62%)	35.97%	36.80%	17.55%
	S <sub>3</sub>	451	0.0026	H-1→L (95.97%)	29.64%	66.30%	_
	T <sub>1</sub>	545	0	H→L (94.37%)	35.41%	36.80%	16.57%
Cu-Y	S <sub>1</sub>	502	0	H→L+1 (95.86%)	32.49%	43.28%	16.51%
	S <sub>2</sub>	501	0.0073	H→L (95.94%)	32.65%	43.36%	16.67%
	S <sub>3</sub>	436	0.0138	H-1→L (83.21%)	37.15%	55.78%	1.15%
	T <sub>1</sub>	515	0	H→L (86.43%)	34.63%	39.82%	17.35%

<sup>*a.*</sup> Calculated emission wavelength; <sup>*b.*</sup> oscillator strength; <sup>*c.*</sup> "H" stands for HOMO and "L" for LUMO.



Figure S3 TGA curves of Cu-G and Cu-Y. The purple dashed line marks 95% of the original sample weight.



# 7. NMR Spectra

Figure S4 <sup>1</sup>H-NMR spectrum of DPPCz.







Figure S6 <sup>1</sup>H-NMR spectrum of Cu-G.



Figure S7 Excitation spectra of Cu-G and Cu-Y.

# References

1. Sheldrick, G. M., A short history of SHELX. Acta Crystallogr. A 2008, 64, 112-122.

2. Qi, H.; Huang, Z.; Wang, M.; Yang, P.; Du, C.-X.; Chen, S.-W.; Li, Y., Bifunctional ligands for Pd-catalyzed selective alkoxycarbonylation of alkynes. *J. Catal.* **2018**, *363*, 63-68.

M. J. Frisch, G. W. T., H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone,
 B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G.
 Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y.
 Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd,
 E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant,
 S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo,
 J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L.
 Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels,
 Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox *Gaussian 09*, Revision D.01; Gaussian, Inc.:
 Wallingford CT, 2009.

4. Lee, C.; Yang, W.; Parr, R. G., Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. *Phys. Rev. B* **1988**, *37* (2), 785–789.

5. Casida, M. E.; Jamorski, C.; Casida, K. C.; Salahub, D. R., Molecular excitation energies to high-lying bound states from time-dependent density-functional response theory: Characterization and

correction of the time-dependent local density approximation ionization threshold. *J. Chem. Phys.* **1998,** *108* (11), 4439–4449.

6. Stratmann, R. E.; Scuseria, G. E.; Frisch, M. J., An efficient implementation of time-dependent densityfunctional theory for the calculation of excitation energies of large molecules. *J. Chem. Phys.* **1998**, *109* (19), 8218–8224.

7. Gao, Y.-J.; Chen, W.-K.; Wang, Z.-R.; Fang, W.-H.; Cui, G., QM and ONIOM studies on thermally activated delayed fluorescence of copper(I) complexes in gas phase, solution, and crystal. *Phys. Chem. Chem. Phys.* **2018**, *20* (38), 24955–24967.

8. Lu, T.; Chen, F., Multiwfn: A multifunctional wavefunction analyzer. J. Comput. Chem. 2012, 33 (5), 580–592.