Electronic Supplementary Material (ESI) for Chemical Communications

Supporting information:

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

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I. Physical measurements

All the reagents and solvents employed were commercially available and used as received without further purification. The C, H and N analyses were carried out with a Vario EL III elemental analyzer. ^{31}P NMR data were recorded on a Bruker Avance II spectrometer (400MHz) using H_3PO_4 (85%) as external standards. Emission spectra were taken with F4500 Fluorescence Spectrofluorometer manufactured by HITACHI, Japan. Lifetimes were measured by Horiba JobinYvon HJY-FM4P-TCSPC fluorometer. The thermogravimetric analysis (TGA) were recorded under nitrogen atmosphere in the range 30-1000℃ with a NETZSCH TG-209F1 instrument. Solid-state ^{31}P Mas NMR spectra were recorded on a Bruker AVANCE Ⅲ400 spectrometer at 10KHz, and chemical shifts for ^{31}P NMR spectra were referenced to ADP (adenosine diphosphate) by means of a coaxial tube.

X-ray experimental

The X-ray intensity data were collected on a standard Bruker-AXS SMART CCD area detector system at 197K. Frames were integrated with the Bruker-AXS SAINT program. Data were corrected for absorption with the SADABS program. The structures were solved by direct methods using SHELXS-97 and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for the non-H atoms. Hydrogen atoms were calculated in ideal positions with isotropic displacement parameters set to 1.2 x Ueq of the attached atom (1.5 x Ueq for methyl hydrogen atoms).

II. Synthesis

$[Cu_2(\mu\text{-dppy})_3(MeCN)][BF_4]_2$ (1) "head to tail" configuration

A modified method was used to prepare **1**.[1] A mixture of $[Cu(MeCN)_4]BF_4$ and Diphenyl-2-pyridylphosphine (dppy) (in a molar ratio of 2 : 3) was refluxed in acetonitrile under nitrogen atmosphere for 1h. After cooled down to room temperature, the solution was filtered. The filtrate was concentrated under reduced pressure and diethyl ether (20 ml) was added to give **1** as a white solid. Slow evaporation of **1** in $MeCN/Et_2O$ afforded colorless crystals in 55% yield.

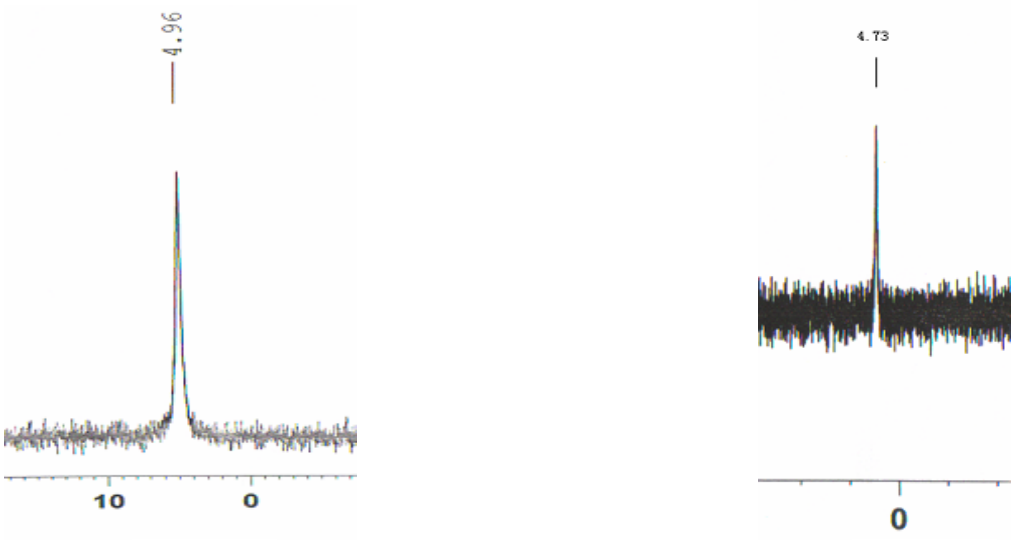
$[Cu_2(\mu\text{-dppy})_3(MeCN)][BF_4]_2$·MeOH (2·MeOH) "head to head" configuration

Slow evaporation of a mixture of CH_2Cl_2-MeOH (2:1) containing **1** (0.0868 g, 0.077 mmol) afforded yellow crystals (0.0675g, 0.060mmol) in 78% yield. Anal. Calcd for $Cu_2C_{54}H_{49}N_4P_3OB_2F_8O$: C, 55.74; H, 4.244; N, 4.815. Found: C, 55.56; H, 4.434; N, 4.742.

Ref:

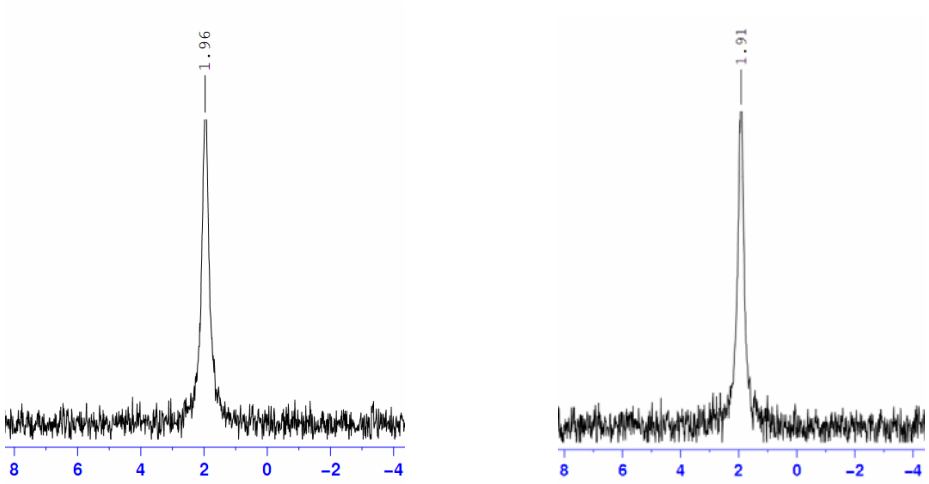
1 Elena Lastra, M. Pilar Gamasa, José Gimeno, Maurizio Lanfranchi, Antonio Tiripicchio, *J. Chem. Soc., Dalton Trans.*, **1989**, (8), 1499-1506.

Ⅲ. Characterization



(**1**) (**2**)

Fig. S1. ^{31}PNMR spectra (400MHz) of two isomers in $CDCl_3$ at 25℃.



(**1**) (**2**)

Fig. S2. ^{31}PNMR spectra (400MHz) of two isomers in MeOH at 25℃.

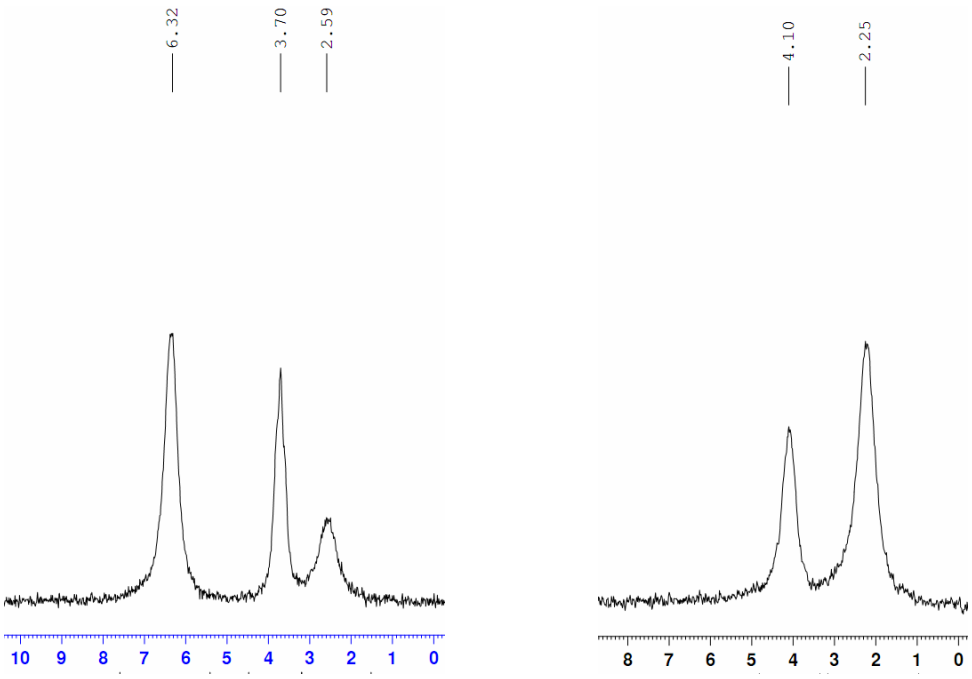


Fig. S3. ^{31}P NMR spectra (400MHz) of **1** at -80℃.

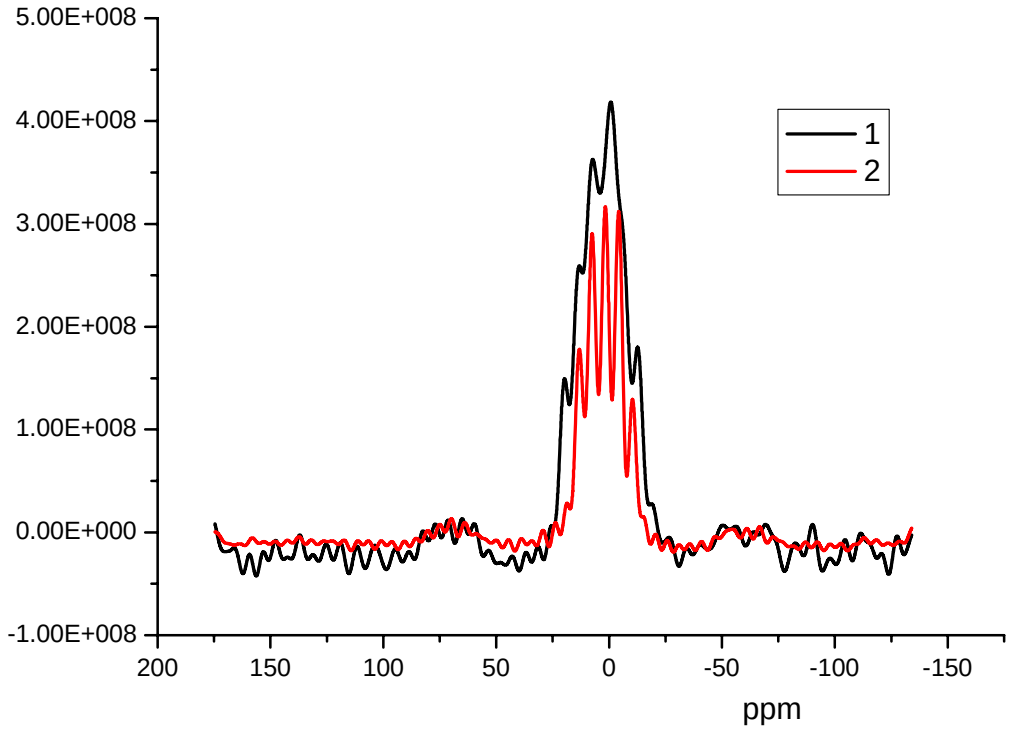


Fig. S4. Solid state ^{31}P NMR spectra.

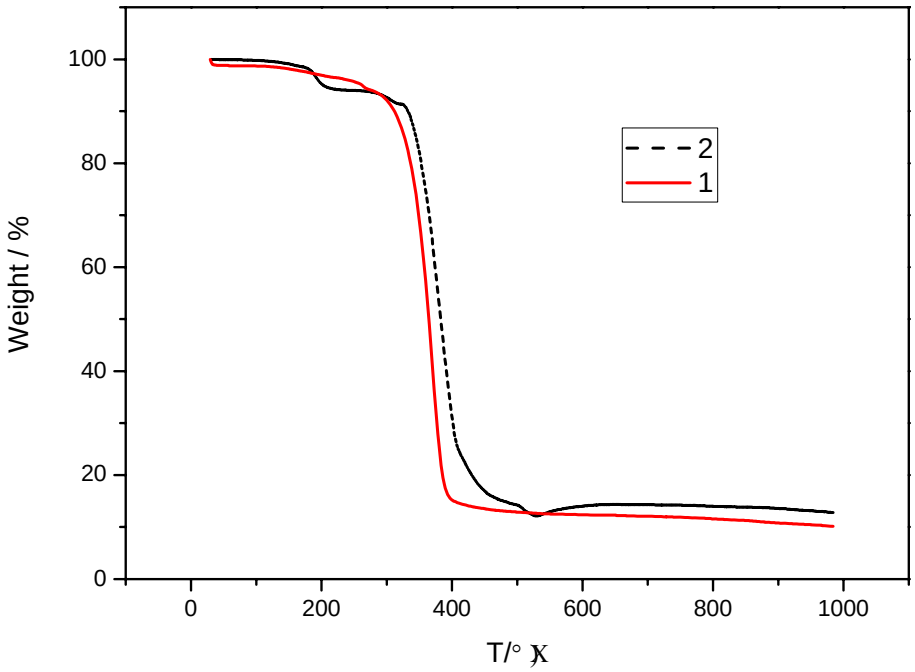
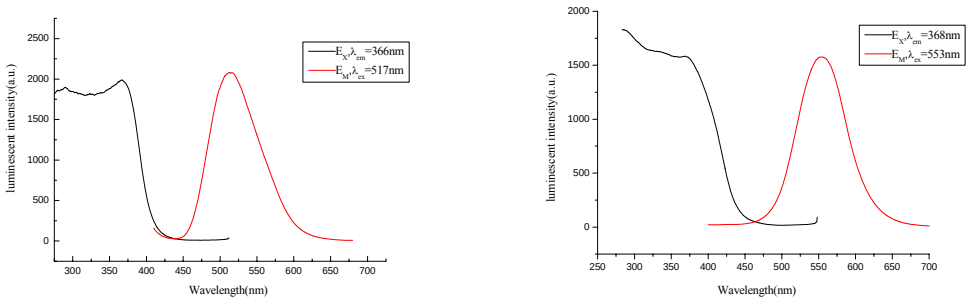
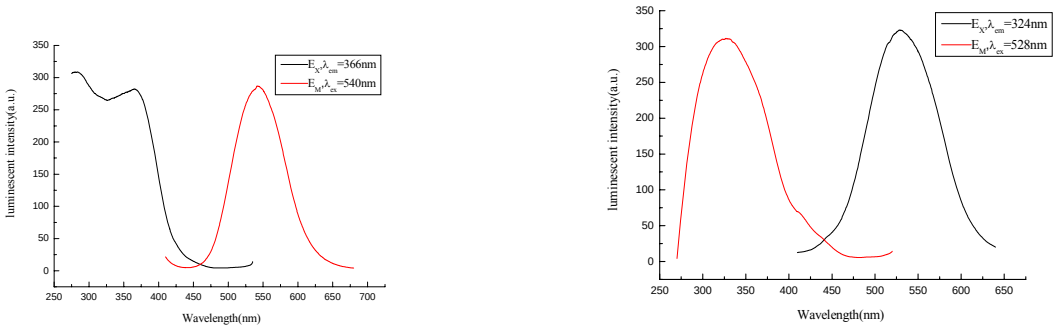


Fig. S5. TGA data for **1** and **2**.



1 **2**

Fig. S6. Emission and excitation spectra of **1** and **2** in the solid state at 77K.



1 **2**

Fig. S7. Emission and excitation spectra of **1** (in MeCN) and **2** (in MeOH) as frozen glasses at 77K.

IV. DFT calculations

All calculations are performed using Gaussian 03 program package.

M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, 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, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, *GAUSSIAN 03*, Revision D.01; Gaussian, Inc., Wallingford CT (2004).

Table S1. The Calculated Energies of HOMO, LUMO Orbitals and HOMO-LUMO Gap (HLG) at B3LYP/6-31G* Level, and the Calculated Vertical Excitation Energy of the Low-lying Excited States at TDB3LYP/6-31G* Level.

6-31G*	**2**			**1**		
HOMO	-0.36919			-0.37311		
LUMO	-0.22868			-0.23377		
HLG	0.14051; 3.82eV			0.13934; 3.79eV		
	character	ΔE(eV/nm)	f	character	ΔE(eV/nm)	f
S_1	246→247	2.91/425.86	0.0198	246→247	3.03/409.55	0.0076
S_2	246→249	3.00/412.73	0.0038	245→247	3.17/391.03	0.0084
S_3	246→248	3.03/409.64	0.0092	246→248	3.23/384.23	0.0090
T_1	246→247 246→248	2.67/464.95	0.0000	246→247	2.85/434.44	0.0000
T_2	246→247 246→248 246→249	2.75/451.08	0.0000	245→247 246→248	3.01/412.11	0.0000
T_3	246→249 246→247	2.88/431.14	0.0000	246→248	3.12/397.06	0.0000
Emission(exp.)		2.38eV/520nm			2.54eV/489nm	
Phosphorescence(cal.)		2.18eV/569nm			2.48eV/542nm	

[a] Method: TD-B3LYP. Basis sets: 6-31G(d) for P, C, N, H; Couty-Hall-modified Lanl2DZ for Cu

Table S2. The Calculated Energies of HOMO, LUMO Orbitals and HOMO-LUMO Gap (HLG) at B3LYP/TZVP Level, and the Calculated Vertical Excitation Energy of the Low-lying Excited States at TDB3LYP/TZVP Level.

TZVP	**2**			**1**		
HOMO	-0.39077			-0.39033		
LUMO	-0.23858			-0.24336		
HLG	0.15219;4.14eV			0.14697;4.00eV		
	character	ΔE(eV/nm)	f	character	ΔE(eV/nm)	f
S_1	246→247	3.25/380.84	0.0145	246→247	3.28/377.79	0.0044
S_2	246→249	3.34/371.56	0.0062	246→248	3.48/356.36	0.0100
S_3	246→248 246→249	3.36/369.22	0.0065	245→247	3.54/349.95	0.0036
T_1	246→247 246→248	3.07/404.04	0.0000	246→247	3.15/393.28	0.0000
T_2	246→248	3.15/393.36	0.0000	246→248	3.33/371.83	0.0000
T_3	246→249	3.20/387.02	0.0000	244→247 246→248	3.42/362.17	0.0000