

## ***Supporting Information***

# **TADF-Emitting Copper(I) and Silver(I) Complexes Featuring Intra-Ligand Charge Transfer Based on a Donor- Acceptor-Donor Ligand**

Xinwei Wang,<sup>a</sup> Weijun Li,<sup>a</sup> Xiao Li,<sup>bc</sup> Chenlu Hou,<sup>bc</sup> Sanyue Wei<sup>b</sup>, Wenxin Lei<sup>bc</sup> and  
Xu-Lin Chen<sup>\*bc</sup>

<sup>a</sup> Fu Jian Police College, Fuzhou, Fujian 350007, China.

<sup>b</sup> State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the  
Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, China

<sup>c</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

E-mail: xlchem@fjirsm.ac.cn

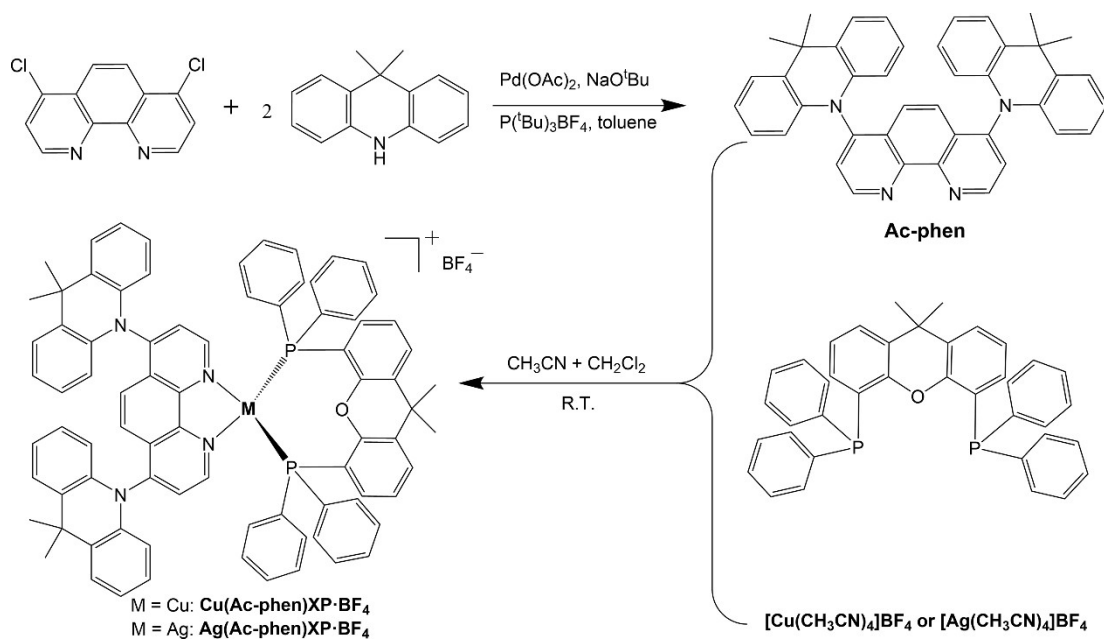
## **Table of Contents**

- 1 General Methods
- 2 Material Synthesis and Characterization
- 3 X-ray structure determination
- 4 Computational methodology and results
- 5 Thermogravimetric Analysis (TGA)
- 6 Cyclic Voltammetry
- 7 NMR Spectra
- 8 Reference

## 1. General Methods

The precursor complexes  $[\text{Cu}(\text{CH}_3\text{CN})_4][\text{BF}_4]$  and  $[\text{Ag}(\text{CH}_3\text{CN})_4][\text{BF}_4]$  were prepared according to a similar literature procedure.<sup>1</sup> Unless otherwise specified, starting materials used are commercially available and require no further purification. The reaction solvents are all commercial analytical pure reagents have been dried by molecular sieve (4 Å) before use. <sup>1</sup>H NMR were measured using a Bruker Avance III nuclear magnetic resonance spectrometer at a frequency of 500 Hz in deuterated chloroform ( $\text{CDCl}_3$ ). Thermogravimetric analysis (TGA) was performed on a METTLER TOLEDO system with a heating rate of 10 °C/min under nitrogen. Single crystal X-ray diffraction data were collected on a Bruker-D8 VENTRUE diffractometer with an X-ray source of Mo  $\alpha$ . Cyclic voltammetry (CV) was performed by CHI840D electrochemical analyzer. Cyclic voltammetry was performed at room temperature in anhydrous and argon-saturated dichloromethane solutions of 0.1 M tetrabutylammonium hexafluorophosphate and 1.0 mM investigated compounds with a CHI840D electrochemical analyzer. Glassy carbon, platinum wire and Ag/Ag<sup>+</sup> (0.01 M of AgNO<sub>3</sub> in acetonitrile) were selected as the working electrode, auxiliary electrode and reference electrode, respectively. The ferrocenium/ferrocene couple was used as an internal standard. The UV-VIS absorption spectra were recorded by Agilent Cary 5000 UV-VIS spectrophotometer under ambient conditions. The steady-state PL spectra were measured on an Edinburgh FLS980 using a Xenon lamp as an excitation light source. The absolute PLQYs were measured using an integrating sphere with a PL measurement unit (Quantaaurus-QY, C11347-11), measured in N<sub>2</sub>. The transient PL decay curves of samples were recorded in multichannel scanning mode at Edinburgh FLS980.

## 2. Material Synthesis and Characterization



**Scheme S1.** Synthetic route of the diimine ligand and the complexes.

### 2.1. Synthesis of the diimine ligand Ac-phen

Under nitrogen, to the flask was added 4,7-dichloro-1,10-phenanthroline (1.25 g, 5 mmol), 9,9-dimethyl-9,10-dihydroacridine (2.51 g, 12 mmol), tri-tert-butylphosphine tetrafluoroborate (0.44 g, 1.5 mmol), sodium tert-butoxide (2.88 g, 30 mmol), palladium acetate (112 mg, 0.5 mmol) and dry toluene, the mixture was refluxed at 110 °C for 24 h. After cooling to room temperature, the solvent was removed by vacuum-rotary evaporation. The mixture was extracted with dichloromethane (3 × 50 mL). Collecting organic phase, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, the solvent was removed to give the crude product. With petroleum ether and dichloromethane mixed solvent as eluent, using silica gel column separation and purification, vacuum drying to obtain orange solid (2.14 g, yield 72%). <sup>1</sup>H NMR (500 MHz, Chloroform-d) δ 9.52 (d, J = 4.6 Hz, 2H), 7.74 (d, J = 4.6 Hz, 2H), 7.61 (s, 2H), 7.48 (dd, J = 7.9, 1.6 Hz, 4H), 6.91 (td, J = 7.5, 1.3 Hz, 4H), 6.84 (ddd, J = 8.6, 7.2, 1.6 Hz, 4H), 5.99 (dd, J = 8.2, 1.2 Hz, 4H), 1.74 (s, 12H).

### 2.2. Synthesis of the Cu(I) complex

[Cu(CH<sub>3</sub>CN)<sub>4</sub>][BF<sub>4</sub>] (1 mmol, 0.314 g) and Xantphos (XP) (1 mmol, 0.578) were added to a mixture of CH<sub>2</sub>Cl<sub>2</sub> (2 mL) and CH<sub>3</sub>CN (2 mL). The mixture was sonicated for 2 minutes, after which the diimine ligand Ac-phen (1 mmol, 0.594 g) was added. Sonication was continued until the ligand was completely dissolved. The reaction mixture was stirred for another 1 hour. Single crystals of this complex suitable for X-ray diffraction measurements were obtained by diffusion of diethyl ether into the reaction solution (1.05 g, yield 77%). <sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 8.96 (d, *J* = 5.0 Hz, 2H), 7.82 (d, *J* = 5.0 Hz, 2H), 7.71 (d, *J* = 6.9 Hz, 4H), 7.50 (dd, *J* = 7.8, 1.5 Hz, 4H), 7.31 (t, *J* = 7.4 Hz, 4H), 7.23 – 7.16 (m, 10H), 7.07 – 7.02 (m, 8H), 6.96 (td, *J* = 7.6, 1.2 Hz, 4H), 6.84 (td, *J* = 7.8, 7.3, 1.5 Hz, 4H), 6.67 (qd, *J* = 4.5, 1.3 Hz, 2H), 5.75 – 5.70 (m, 4H), 1.79 (s, 6H), 1.73 (d, *J* = 13.2 Hz, 18H).

### 2.3. Synthesis of the Ag(I) complex

[Ag(CH<sub>3</sub>CN)<sub>4</sub>][BF<sub>4</sub>] (1 mmol, 0.358 g) and Xantphos (XP) (1 mmol, 0.578) were added to a mixture of CH<sub>2</sub>Cl<sub>2</sub> (2 mL) and CH<sub>3</sub>CN (2 mL). The mixture was sonicated for 2 minutes, after which the diimine ligand Ac-phen (1 mmol, 0.594 g) was added. Sonication was continued until the ligand was completely dissolved. The reaction mixture was stirred for another 1 hour. Single crystals of this complex suitable for X-ray diffraction measurements were obtained by diffusion of diethyl ether into the reaction solution (0.97g, yield 69%). <sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 9.16 (s, 2H), 7.83 (d, *J* = 4.9 Hz, 2H), 7.70 (d, *J* = 7.1 Hz, 4H), 7.49 (dd, *J* = 7.9, 1.5 Hz, 4H), 7.33 (t, *J* = 7.4 Hz, 4H), 7.19 (dt, *J* = 26.3, 7.0 Hz, 17H), 6.94 (td, *J* = 7.5, 1.2 Hz, 4H), 6.87 (d, *J* = 4.1 Hz, 1H), 6.82 (td, *J* = 7.9, 7.3, 1.6 Hz, 4H), 6.71 (dt, *J* = 8.4, 4.1 Hz, 2H), 5.76 (d, *J* = 8.3 Hz, 4H), 1.74 (d, *J* = 8.2 Hz, 18H).

### 3. X-ray structure determination

**Table S1** Crystal parameters and refinement data of the Cu(I) and Ag(I) complexes

Complex	Cu(Ac-phen)XP·BF <sub>4</sub> ·1.5(C <sub>4</sub> H <sub>10</sub> O)	Ag(Ac-phen)XP·BF <sub>4</sub> ·(C <sub>4</sub> H <sub>10</sub> O)
Empirical formula	C <sub>87</sub> H <sub>81</sub> CuBF <sub>4</sub> N <sub>4</sub> O <sub>2.5</sub> P <sub>2</sub>	C <sub>85</sub> H <sub>76</sub> AgBF <sub>4</sub> N <sub>4</sub> O <sub>2</sub> P <sub>2</sub>
Formula weight	1434.92	1442.12
Temperature/K	200.00	113(20)
Crystal system	monoclinic	triclinic
Space group	C2/c	P-1
a/Å	19.927(3)	19.2498(2)
b/Å	21.694(3)	25.6897(3)
c/Å	34.974(6)	31.4864(4)
α/°	90	77.9013(10)
β/°	104.466(5)	78.6755(10)
γ/°	90	89.8003(9)
Volume/Å <sup>3</sup>	14640(4)	14917.0(3)
Z	8	8
μ/mm <sup>-1</sup>	0.406	3.056
F(000)	5504.0	5981.0
Crystal size/mm <sup>3</sup>	0.15×0.13×0.12	0.242×0.168×0.108
Radiation	MoKα (λ = 0.71073)	CuKα (λ = 1.54184)
Θ /°	1.971 to 24.498	1.760 to 64.999
h	-23 ≤ h ≤ 23	-21 ≤ h ≤ 22
k	-25 ≤ k ≤ 25	-30 ≤ k ≤ 30
l	-40 ≤ l ≤ 40	-37 ≤ l ≤ 36
Reflections collected	91109	187272
Data/restraints/parameter	12127/ 220/736	50685/423/3513
Goodness-of-fit on F <sup>2</sup>	1.040	1.065
R <sub>1</sub> , wR <sub>2</sub> [I ≥ 2σ (I)]	0.0779, 0.2148	0.0696, 0.1899
R <sub>1</sub> , wR <sub>2</sub> [all data]	0.1146, 0.2459	0.0759, 0.1939
Δρ <sub>max</sub> , Δρ <sub>min</sub> / e Å <sup>-3</sup>	0.566/-0.936	2.558/-1.318

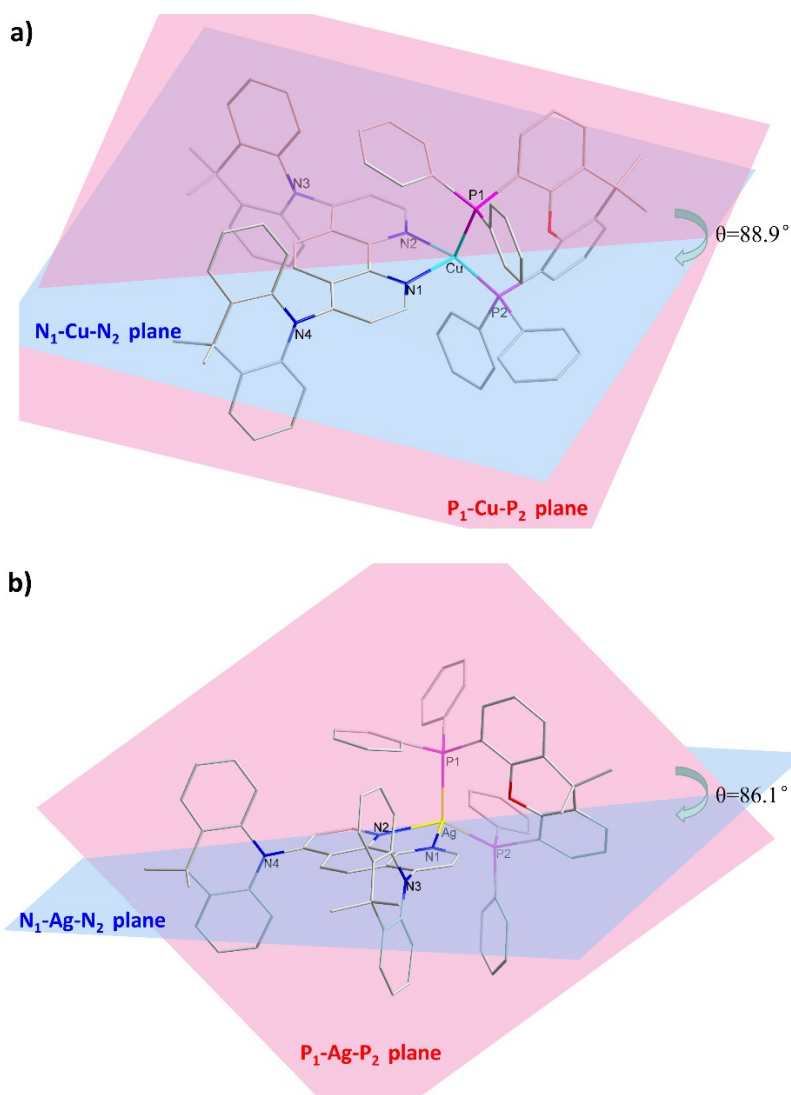
**Table S2** Selected bond length (Å) and bond angles (deg) of Cu(Ac-phen)XP·BF<sub>4</sub>

C <sub>81</sub> H <sub>66</sub> BCuF <sub>4</sub> N <sub>4</sub> OP <sub>2</sub>		
bond distances [Å]		
Cu-P1		2.2681(15)
Cu-P2		2.2302(13)
Cu-N1		2.099(4)
Cu-N2		2.047(5)
angles [°]		
P1-Cu-P2		121.48(5)
N1-Cu-P1		101.12(11)
N1-Cu-P2		119.69(12)
N1-Cu-N2		80.28(18)
N2-Cu-P1		118.57(13)
N2-Cu-P2		118.57(13)

**Table S3** Selected bond length (Å) and bond angles (deg) of Ag(Ac-phen)XP·BF<sub>4</sub>

Ag(Ac-phen)XP·BF <sub>4</sub>		
bond distances [Å]		
Ag-P1		2.4743(12)
Ag-P2		2.3678(12)
Ag-N1		2.348(4)
Ag-N2		2.327(4)
angles [°]		
P1-Ag-P2		118.22(4)
N1-Ag-P1		104.40(12)

N1-Ag-P2	121.13(11)
N1-Ag-N2	71.85(14)
N2-Ag-P1	98.92(10)
N2-Ag-P2	132.00(10)



**Figure S1** Dihedral angles between the N–Cu–N and P–Cu–P planes in a) Cu(Ac-phen)XP·BF<sub>4</sub> and b) Ag(Ac-phen)XP·BF<sub>4</sub>.

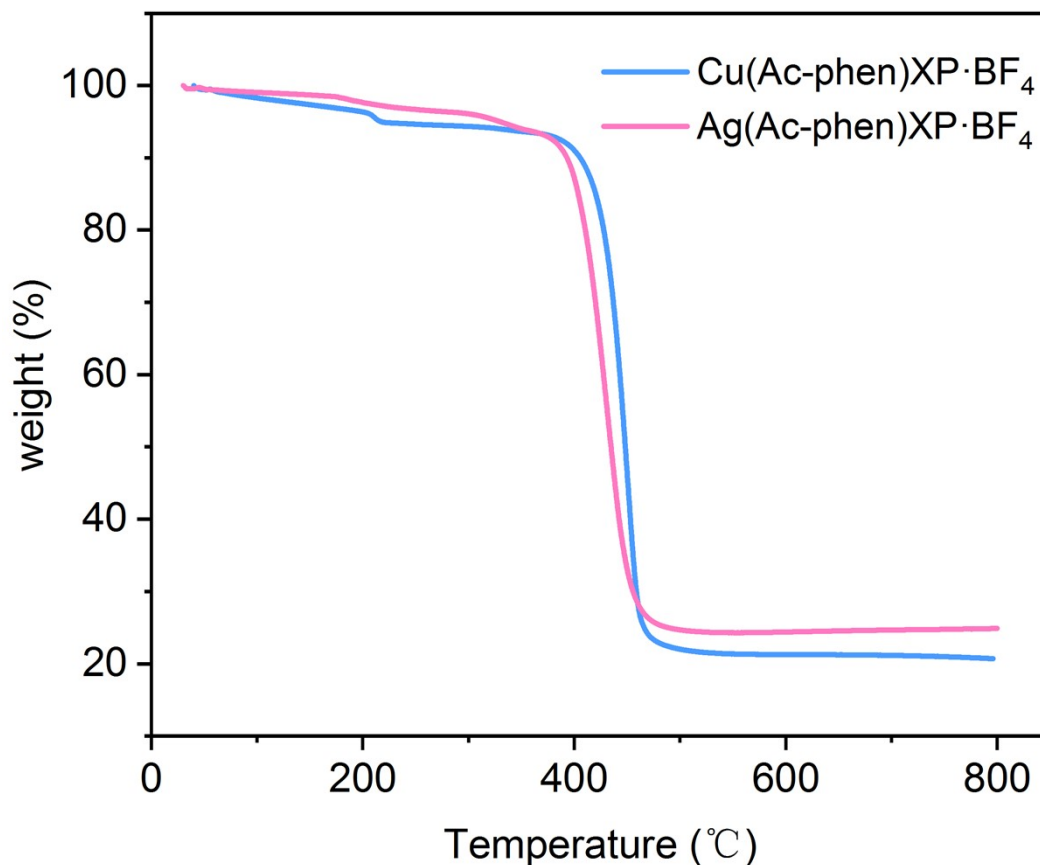
#### 4. Computational methodology and results

The density functional theory (DFT) and time-dependent DFT (TD-DFT) calculations were performed with the Gaussian 09 program package.<sup>2</sup> The density functional theory



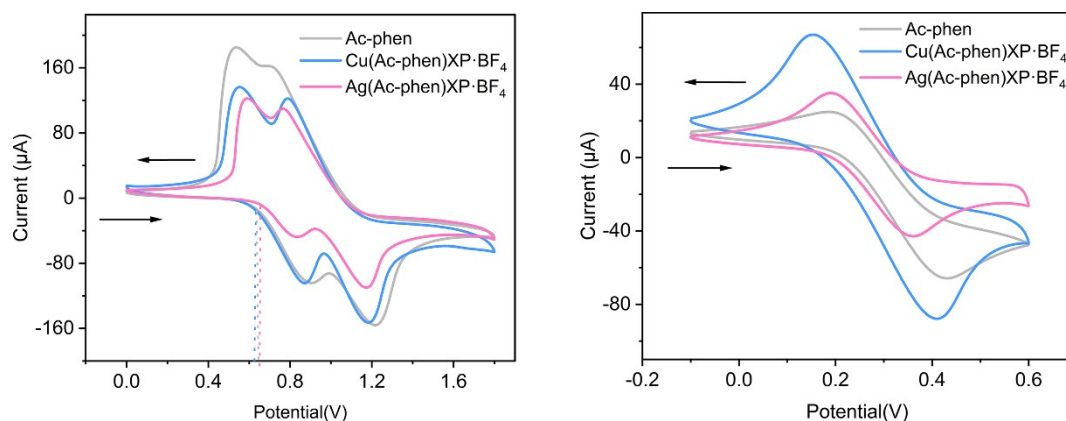
(DFT) calculations at the B3LYP/6-31G\* level was used to optimize the ground state geometries of the investigated compounds. Time-dependent density functional theory (TD-DFT) calculations was performed at the same level using the optimized ground state geometries. The electron density diagrams of molecular orbitals were generated using GaussView program.

### 5. Thermogravimetric Analysis (TGA)



**Figure S2** TGA curves of the complexes

### 6. Cyclic Voltammetry



**Figure S3** a) Cyclic voltammetry curves of the diimine ligand and the complexes in dichloromethane at room temperature; b) Cyclic voltammetry curves of ferrocene (internal standard).

**Table S4** Summary of CV data and energy levels

Compound	$E_{OX}^a$ [eV]	$E_{Fc/Fc+}^b$ [eV]	$E_g^c$ [eV]	$E_{HOMO}^d$ [eV]	$E_{LUMO}^e$ [eV]
Ac-phen	0.65	0.29	2.97	-5.16	-2.19
Cu(Ac-phen)XP·BF <sub>4</sub>	0.64	0.28	2.41	-5.16	-2.75
Ag(Ac-phen)XP·BF <sub>4</sub>	0.65	0.28	2.48	-5.17	-2.69

<sup>a</sup> The oxidation potentials ( $E_{OX}$ ) were acquired from the onset of first oxidation potentials in cyclic voltammograms; <sup>b</sup> ferrocenium/ferrocene couple was used as an internal standard; <sup>c</sup> calculated from the absorption edge  $\lambda_{onset}$  using equation:  $1240/\lambda_{onset}$ ; <sup>d</sup> calculated using the equation:  $E_{HOMO} = - [E_{OX} - E_{Fc/Fc+} + 4.8]$  eV; <sup>e</sup> calculated from  $E_g$  and  $E_{HOMO}$  using the equation:  $E_{LUMO} = (E_{HOMO} + E_g)$  (eV).

## 7. NMR Spectra

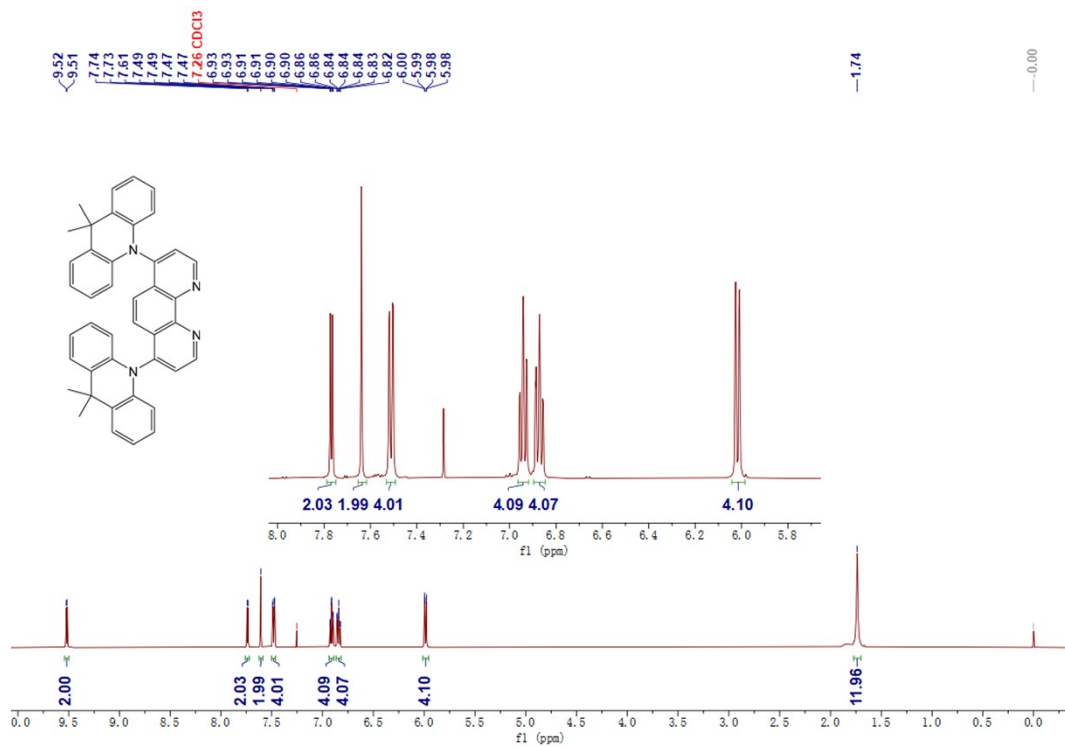


Figure S4 <sup>1</sup>H-NMR spectrum of Ac-phen in CDCl<sub>3</sub>.

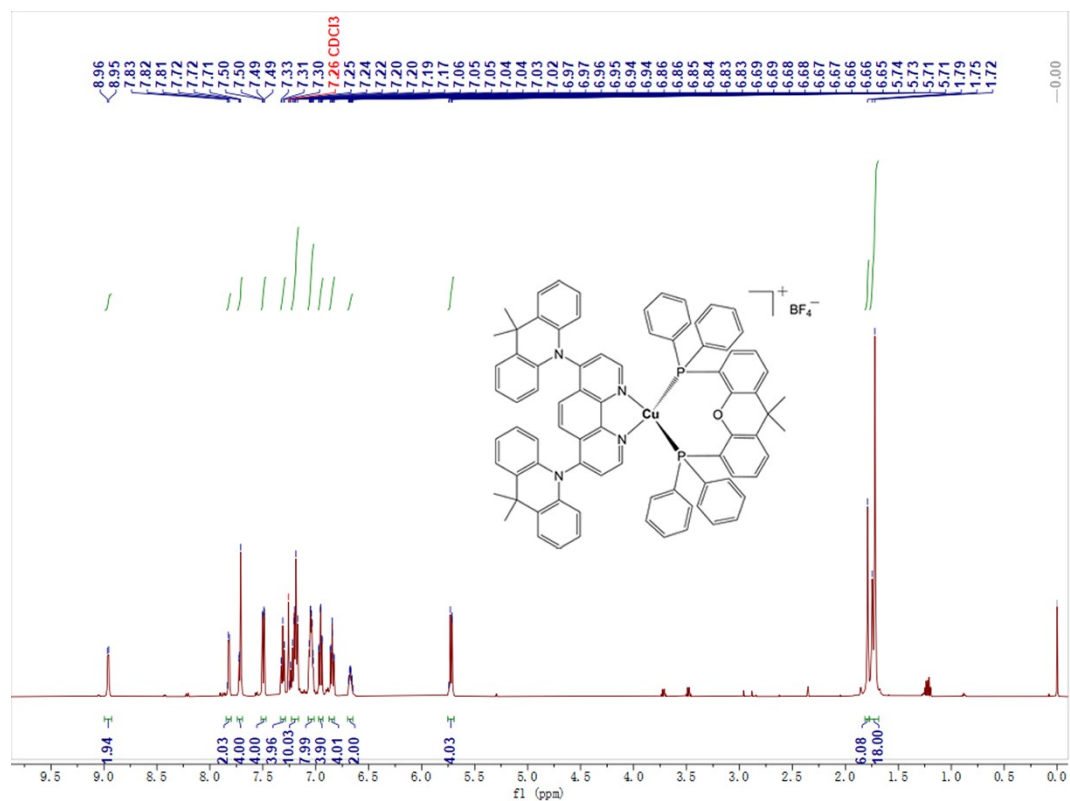
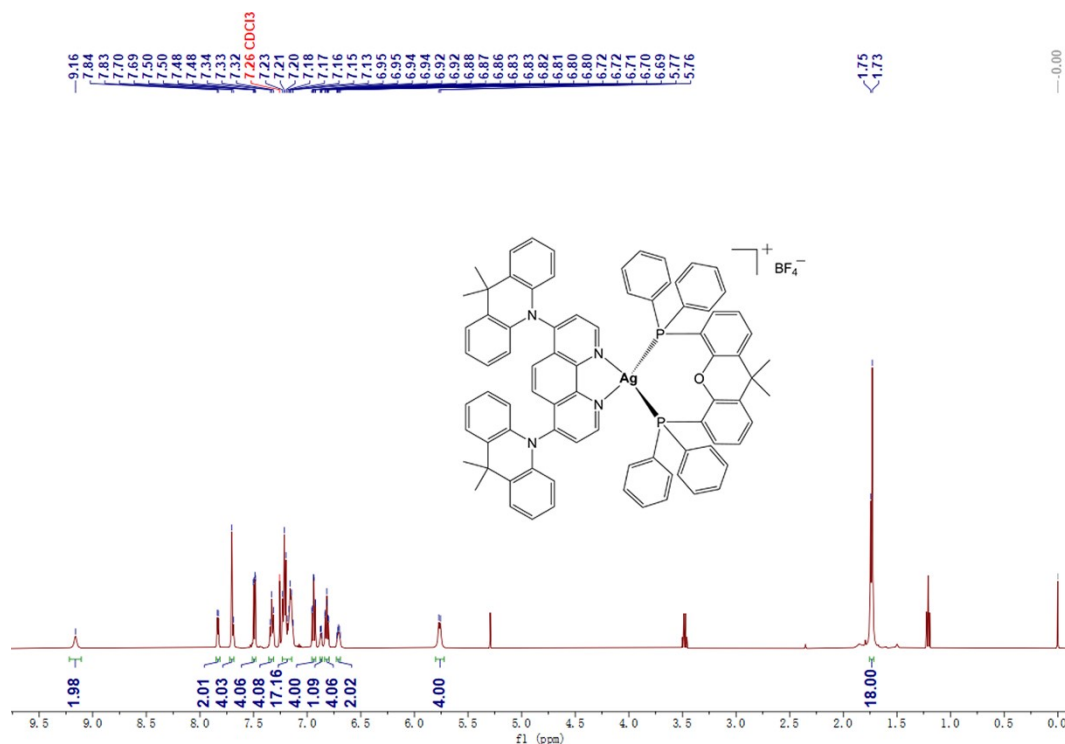


Figure S5 <sup>1</sup>H-NMR spectrum of Cu(Ac-phen)XP·BF<sub>4</sub> in CDCl<sub>3</sub>.



**Figure S6** <sup>1</sup>H-NMR spectrum of Ag(Ac-phen)XP·BF<sub>4</sub> in CDCl<sub>3</sub>.

## 8. Reference

1. G. J. Kubas, *Inorg. Synth.*, 1990, 28, 68.
2. G. W. T. M. J. Frisch, 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.