

Mechanochromic Properties in Mononuclear Cu(I) Complex without Cuprophilic Interaction

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General

Without special declaration, all the reactions were performed in inert gas atmosphere using standard Schlenk techniques or glovebox. All reagents and solvents were commercially available with analytical grade. Tetrahydrofuran (THF) and diethyl ether (DEE) were pretreated with Na/NaH prior to use. CuBr used in this experiment also needs to be pretreated. ^[1] The ¹H and ¹³C NMR spectra were measured by using Bruker ARX 400 MHz spectrometer and the ³¹P NMR spectra were measured by AVANCE III 500 MHz spectrometer. Elemental analyses were performed on a VARIO EL analyzer (GmbH, Hanau, Germany). ESI mass spectra were performed using Bruker Solarix XR FTMS. UV-vis absorption spectra were recorded with Shimadzu UV-3600. Photoluminescence spectra and the decay lifetimes were recorded on an Edinburgh FLS920 instrument. The PLQYs were measured on Hamamatsu C9920 system with xenon lamp as excitation source. The infrared spectra were measured by a Tensor 27 Fourier transform infrared spectrometer (Bruker). Powder X-ray diffraction (PXRD) was performed on X-Pert3 Powder X-ray diffractometer. Single-crystal X-ray diffraction (XRD) data were collected on a Rigaku XtaLAB AFC12 diffractometer equipped with Cu-K α radiation ($\lambda = 1.54184 \text{ \AA}$). The structures were resolved and refined using OLEX-2 ^[2] software integrated with Shelx2014 program. Theoretical simulations were performed using the Gaussian 09 ^[3] program packages and produced by CAM-B3LYP ^[4]. The model for calculation was extracted from single crystals.

Synthesis

Potassium bis(pyrazol-1-yl)borohydrate (Kpz₂BH₂) ^[5]

Under N₂ atmosphere, a mixture of pyrazole (20.0 g, 290 mmol) and potassium borohydride (4.0 g, 74 mmol) was heated at 110 °C with stirring in a 100 mL round-bottom flask connected with spherical condenser tube. After 10 hours, 50 mL toluene was added slowly to the melt. The precipitate was filtered, washed with hot toluene and hexane, and dried under vacuum at 70 °C for 3 hours. Then 7.6 g (41 mmol) white solid was obtained (yield, 55%). ¹H NMR (400 MHz, DMSO-*d*₆) $\delta = 7.34$ (d, 2H), 7.23 (d,

2H), 5.93 (t, 2H), 2.95-4.03 (br, 2H).

3,4-bis(diphenylphosphino)thiophene (3,4-dppTp) [6]

3,4-Dibromothiophene (5.00 g, 20.7 mmol) was stirred in diethyl ether (15 mL) and the mixture was cooled to -78 °C. Then n-BuLi (10 mL, 2.4 M in n-hexane) was slowly added and the yellow mixture was stirred for 3 hours at -78 °C. Then, chlorodiphenylphosphine (Ph₂PCL, 4.56 g, 20.7 mmol) was added dropwise and the mixture was stirred at -78 °C for 1 hour, naturally warmed to room temperature and stirred for another 4 hours. Then the mixture was cooled to -78 °C and n-BuLi (10 mL, 2.4 M in n-hexane) was slowly added again and the brown mixture was stirred for 3 hours at -78 °C. Then PPh₂Cl (4.56 g, 20.7 mmol) was added slowly and the mixture was stirred at -78 °C for 1 hour. After then, the mixture was naturally warmed up to room temperature and stirred overnight. On the second day, 20 mL distilled water was added to quench the reaction. The salts were removed by extraction with CH₂Cl₂ (3 × 60 mL) and the organic phase was concentrated under reduced pressure. The brown gelatinous was further purified by sublimation to obtain 4.56 g (10.1 mmol) yellow solid (yield, 49%). ¹H NMR (400 MHz, DMSO-*d*₆) δ = 7.24 (m, 20H), 7.10 (m, 2H); ¹³C NMR (101 MHz, CD₂Cl₂) δ=141.45, 137.09 (t, *J* = 3.7 Hz), 133.53 (t, *J* = 10.1 Hz), 132.53, 128.63, 128.34 (t, *J* = 3.6 Hz).

Cu₂Br₂(3,4-dppTp)₂ [7]

CuBr (0.34 g, 2.35 mmol) and 3,4-dppTp (1.09 g, 2.41 mmol) were added to 30 mL toluene and stirred for 10 hours at room temperature. The resulting yellow precipitate was filtered off, washed with toluene and acetonitrile, and dried under vacuum at 60 °C for 3 hours. Finally, 1.12 g (0.94 mmol) yellow solid was obtained (yield, 80%). ¹H NMR (400 MHz, DMSO-*d*₆) δ = 7.80 (s, 4H) 7.39 (m, 40H).

Cu[(3,4-dppTp)(pz₂BH₂)] (1)

Kpz₂BH₂ (0.20 g, 1.07 mmol) and Cu₂Br₂(3,4-dppTp)₂ (0.51 g, 0.43 mmol) were mixed and stirred in 35 mL THF at room temperature for 12 hours, and then the mixture was concentrated under reduced pressure. The resulting solid was dissolved in CH₂Cl₂

and passed through a short column with neutral aluminum oxide. The obtained yellow solution was concentrated to about 3 mL under reduced pressure and then was added 20 mL methanol. The resulting precipitate was collected and dried under reduced pressure to give 0.47 g (0.71 mmol, yield 83%) of the title complex as a white powder. ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ = 8.02 (t, 2H), 7.59 (d, 2H), 7.34 (m, 20H), 6.86 (d, 2H), 6.05 (t, 2H), 3.35-3.78 (br, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ = 139.05, 133.51, 133.48, 131.87, 131.78, 131.70, 131.25, 128.23, 127.44, 127.40, 127.35, 102.02, 76.23. ^{31}P NMR (202 MHz, CDCl_3), δ = -24.63. Anal. Calc. For $\text{C}_{34}\text{H}_{30}\text{BN}_4\text{P}_2\text{SCu}$: C, 61.59%, H, 4.56%, N, 8.45%. Found: C, 61.04%, H, 4.56%, N, 8.36%. MS (ESI): m/z calculated for $\text{C}_{34}\text{H}_{30}\text{BN}_4\text{P}_2\text{SCu}$: 663.0, found: 663.1.

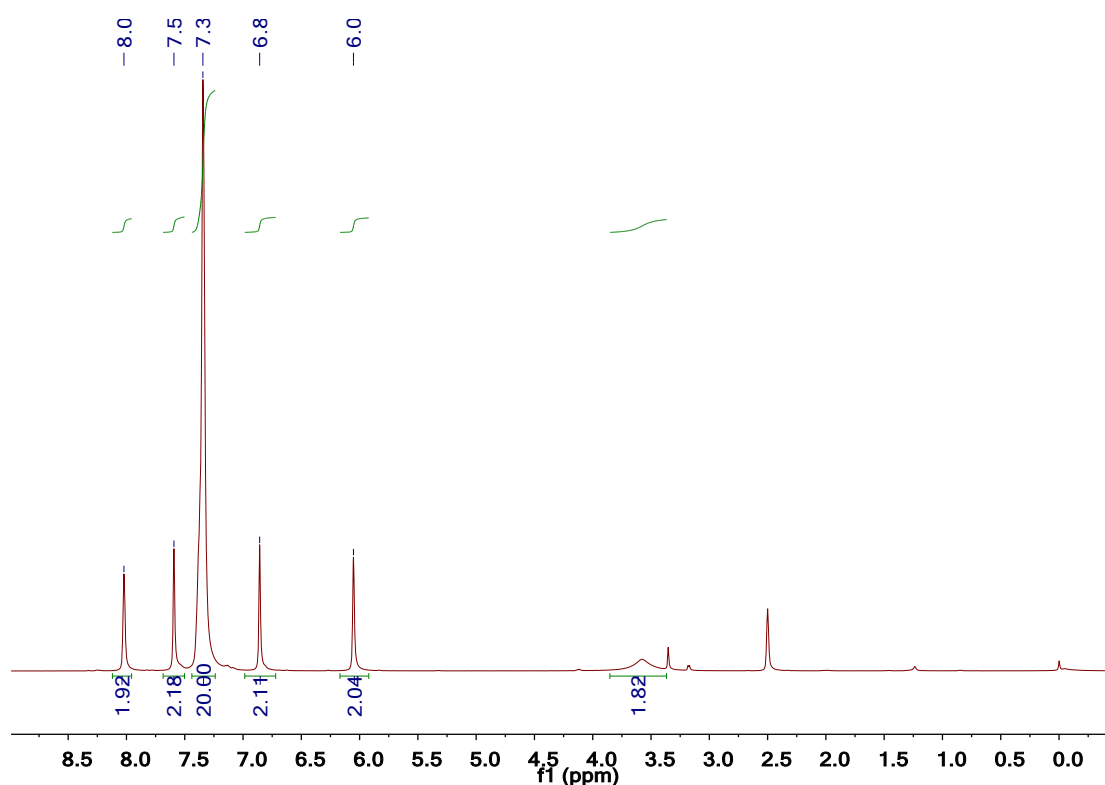


Fig. S1. ^1H NMR spectrum of $\text{Cu}[(3,4\text{-dppTp})(\text{pz}_2\text{BH}_2)]$ at room temperature.

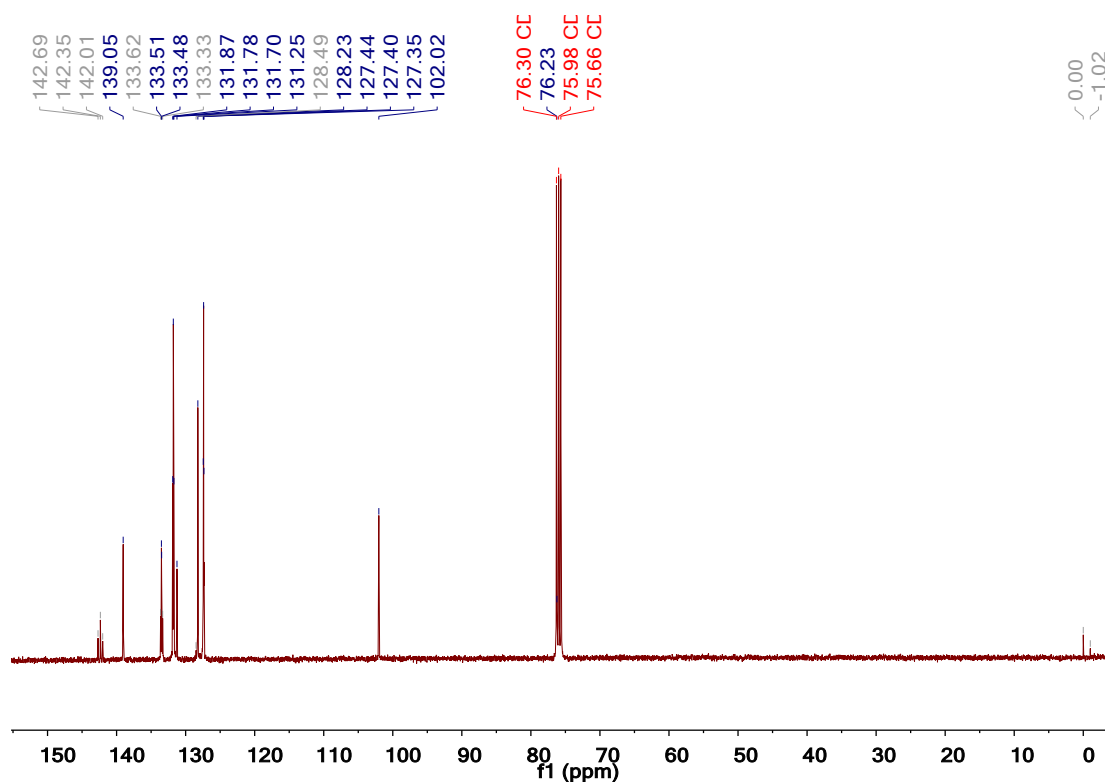


Fig. S2. ^{13}C NMR spectrum of $\text{Cu}[(3,4\text{-dppTp})(\text{pz}_2\text{BH}_2)]$ at room temperature.

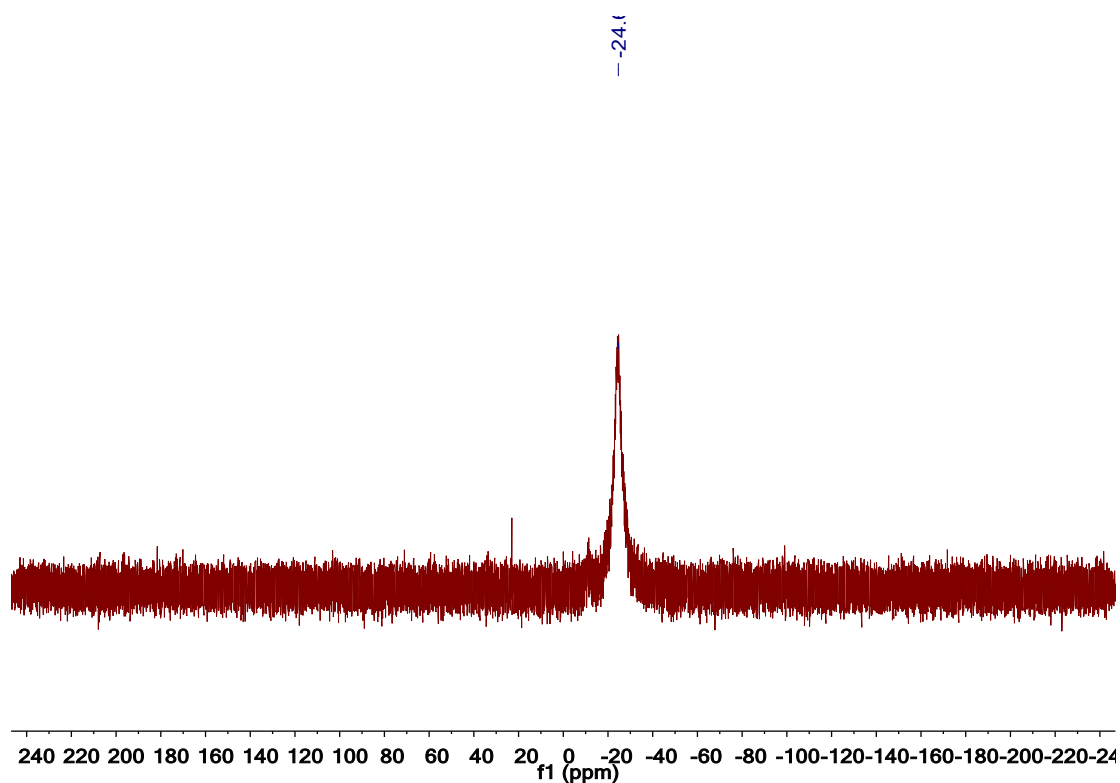


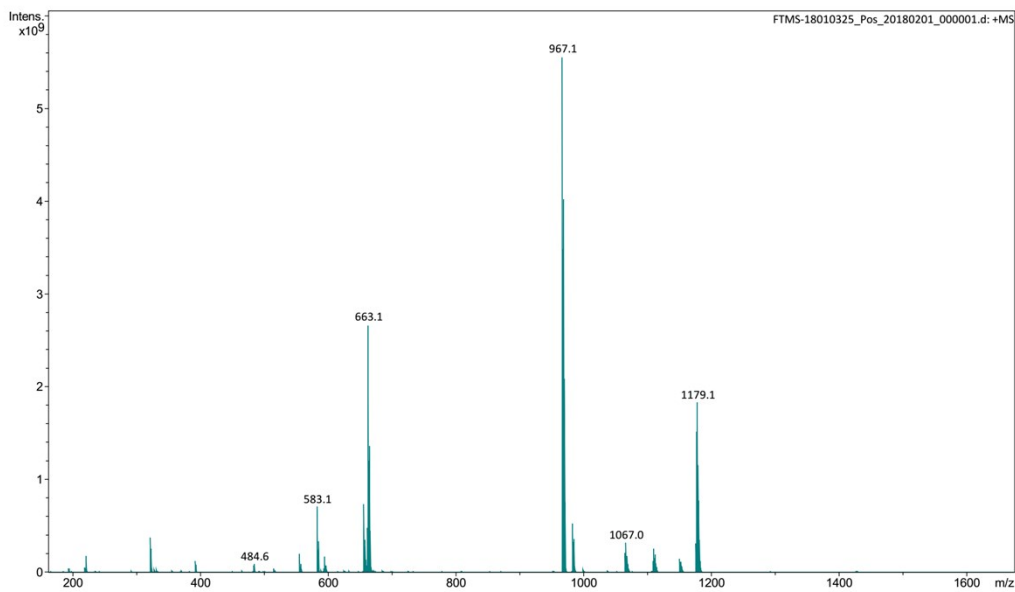
Fig. S3. ^{31}P NMR spectrum of $\text{Cu}[(3,4\text{-dppTp})(\text{pz}_2\text{BH}_2)]$ at room temperature.

Peking University Mass Spectrometry Analysis Report

Analysis Info

Analysis Name FTMS-18010325_Pos_20180201_000001.d
Sample 20180131-2
Comment

Acquisition Date 2/1/2018 9:34:48 AM
Instrument Bruker Solarix XR FTMS
Operator Peking University



Bruker Compass DataAnalysis 4.4

printed: 2/1/2018 9:35:12 AM

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Fig. S4. ESI mass spectra of complex **1**. The peak with m/z of 967.1 is a new complex $\text{Cu}(3,4\text{-dppTp})_2^+$ which is generated in the test.

Crystal Growth

Generally, Slow crystallization of **1** from the CH₃OH/CH₂Cl₂ (1:1) solution generated two colorless polymorphs with blue (**1B**) and yellow (**1Y**) luminescence under UV radiation.

Complex **1** (50 mg) was dissolved in 8 mL of CH₂Cl₂ in a vial and 8 mL of CH₃OH was added, Sonicate for 1 min, and then filtered it in a vial. After slowly volatilized for 5 days, **1B** and **1Y** obtained. They can be easily separated upon irradiation with a 365 nm lamp. In this way, pure **1B** and **1Y** crystals can be obtained for testing.

In addition, **1B** can selective formation by the following method. In a vial, 700 mg of complex **1** was dissolved in 7 mL of dichloromethane, and then 15 ml of methanol was added, sonicated for 1 min, a large amount of white precipitate would be precipitated, so that a large amount of **1B** could be obtained.

As shown in the Fig. S4, the PXRD diffraction peaks of the selectively formed **1B** sample are consistent with the **1B** sample obtained by slow crystallization.

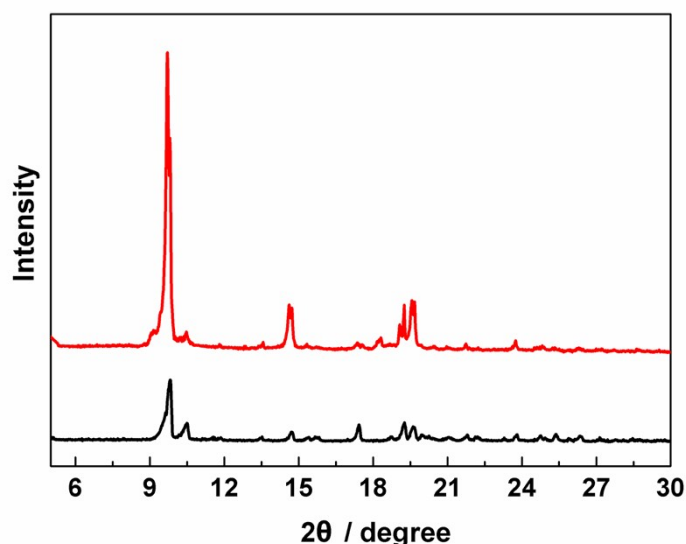


Fig. S5. PXRD patterns of selectively formed **1B** sample (black) and Slowly crystallized **1B** sample (red).

Mechanochromic Luminescence

The as-synthesized **1B** is colorless and transparent crystals (the selectively formed **1B** is white powder crystals). In a mortar, **1B** will become yellow powder **1G** after grinding. This transition will be completed in a short time, and UV lamps can be used to monitor whether **1B** has completely changed to **1G**.

After grinding, place the mortar containing the **1G** sample in a clean glass tank, and add a small amount of dichloromethane (or diethyl ether) to the tank. Cover the tank with a lid and let the dichloromethane (or diethyl ether) vapor fumigate the **1G** sample. After 5 minutes, open the lid, and the **1G** sample turned back to white powder. These white powders are samples of **1G-F1** (**1G-F2**).

Add a few drops of diethyl ether to the **1G** sample. After the diethyl ether evaporates, a white powder, **1G-S**, is obtained.

The preparation method of **1-Film** as follows: The solutions of complex **1** (10 mg/mL in chloroform) were spin-coated on ultrasonic cleaned quartz wafer at a speed of 2000 rpm for 60 s to form the neat film.

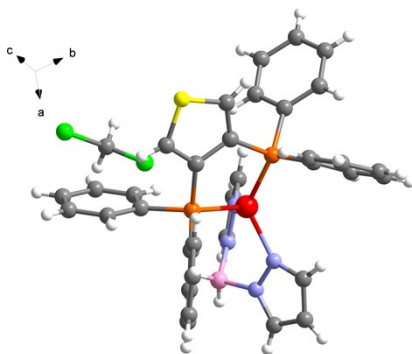


Fig. S6. Crystallographically derived molecular structures of **1B**. Color code: B (pink), C (grey), Cl (green), Cu (red), H (white), N (blue), P (orange), S (yellow).

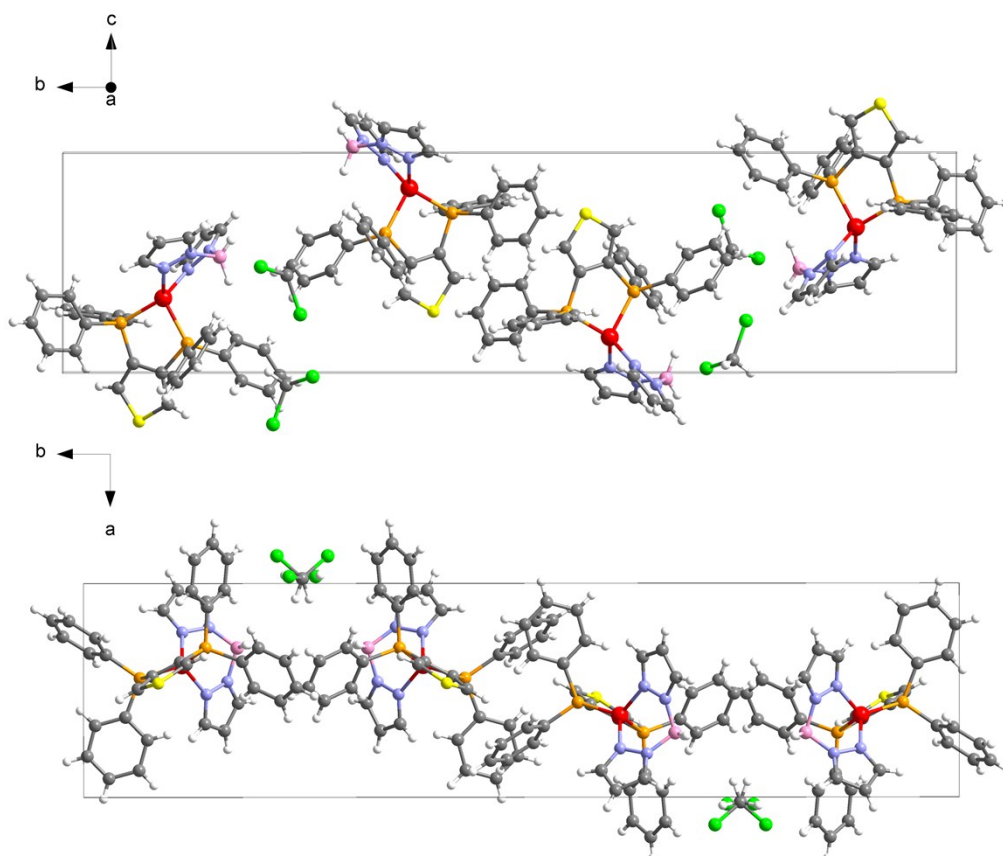


Fig. S7. Unit cell of **1B** shown along the a axis (top) and c axis (bottom).

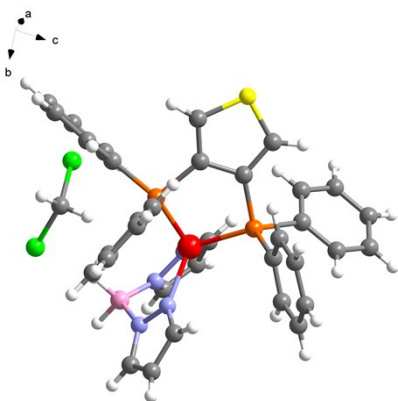


Fig. S8. Crystallographically derived molecular structures of **1Y**.

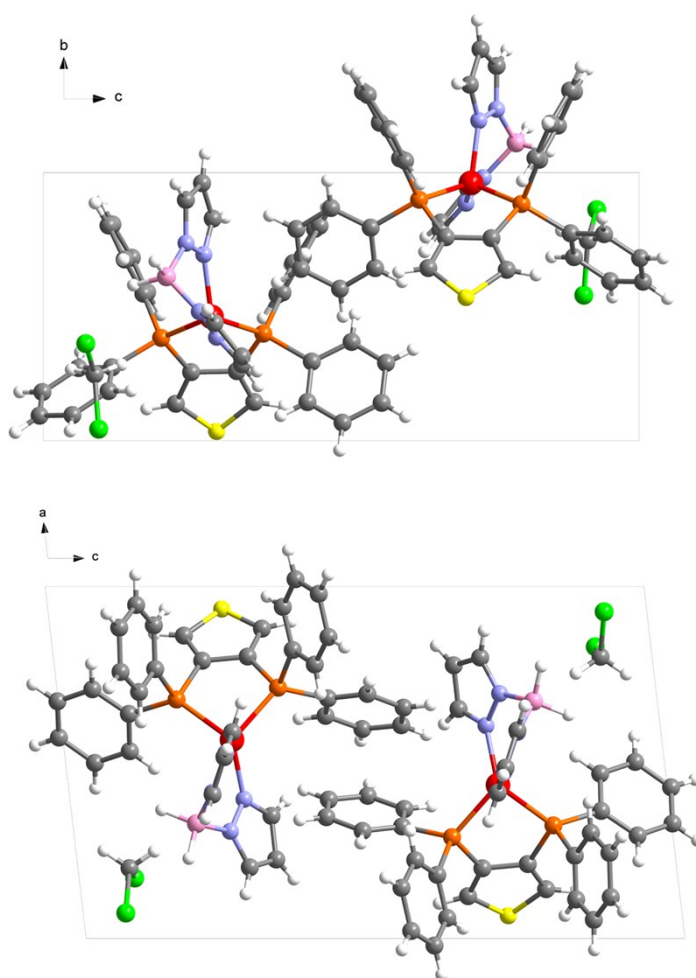


Fig. S9. Unit cell of **1Y** shown along the a axis (top) and b axis (bottom).

Table S1. Summary of crystallographic data of the two crystal forms.

identification code	1B	1Y
Empirical formula	$C_{35}H_{32}BCl_2CuN_4P_2S$	$C_{35}H_{32}BCl_2CuN_4P_2S$
Formula weight	747.89	747.89

Temperature/K	172.99(10)	173
Crystal system	monoclinic	monoclinic
Space group	P2 ₁ /c	P2 ₁
a/Å	9.4427(2)	11.20173(11)
b/Å	38.5575(6)	8.45092(9)
c/Å	9.5037(2)	18.9038(2)
α /°	90	90
β /°	94.951(2)	96.6573(10)
γ /°	90	90
Volume/Å ³	3447.26(12)	1777.46(3)
Z	4	2
ρ_{calc} /cm ³	1.441	1.397
μ /mm ⁻¹	4.013	3.891
F(000)	1536.0	768.0
Crystal size/mm ³	0.25 × 0.2 × 0.2	0.2 × 0.2 × 0.2
Radiation	CuK α (λ = 1.54184)	CuK α (λ = 1.54184)
2 θ range for data collection/°	9.174 to 147.306	7.946 to 147.356
Index ranges	-11 ≤ h ≤ 10, -45 ≤ k ≤ 46, -11 ≤ l ≤ 11	-13 ≤ h ≤ 13, -10 ≤ k ≤ 10, -22 ≤ l ≤ 23
Reflections collected	13817	11330
Independent reflections	6349 [R _{int} = 0.0411, R _{sigma} = 0.0420]	5841 [R _{int} = 0.0260, R _{sigma} = 0.0363]
Data/restraints/parameters	6349/19/423	5841/608/423
Goodness-of-fit on F ²	1.064	1.035
Final R indexes [I ≥ 2 σ (I)]	R ₁ = 0.0727, wR ₂ = 0.2125	R ₁ = 0.0509, wR ₂ = 0.1366
Final R indexes [all data]	R ₁ = 0.0765, wR ₂ = 0.2166	R ₁ = 0.0517, wR ₂ = 0.1377
Largest diff. peak/hole / e Å ⁻³	1.08/-1.84	0.62/-0.81
Flack parameter		0.02(3)

Table S2. The selected bond distances and angles around Cu atoms of two crystals.

	1B	1Y
Cu-P1 (Å)	2.2355(10)	2.2585(13)
Cu-P2 (Å)	2.2964(11)	2.2642(12)
Cu-N1 (Å)	2.035(3)	2.023(4)
Cu-N2 (Å)	2.020(3)	2.023(5)
P1-Cu-P2 (°)	92.18(4)	90.97(5)
N1-Cu-N2 (°)	93.15(14)	97.54(19)
P1-Cu-N1 (°)	122.79(10)	118.89(12)
P1-Cu-N2 (°)	124.33(9)	116.39(12)

P2-Cu-N1 (°)	109.55(10)	125.15(13)
P2-Cu-N2 (°)	115.89(10)	109.14(13)
Dihedral angle (°)	87.26(9)	84.36(10)

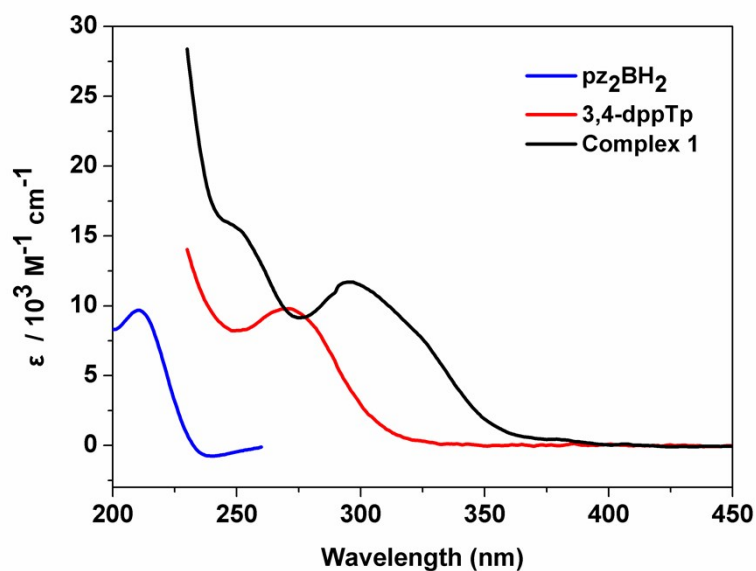


Fig. S10. Absorption spectra of the complex **1** and free ligands measured at ambient temperature. Spectra of **1** and the 3,4-dppTp ligand were recorded in dichloromethane ($c \approx 2 \times 10^{-5}$ M). Kpz_2BH_2 was measured in an acetonitrile solution.

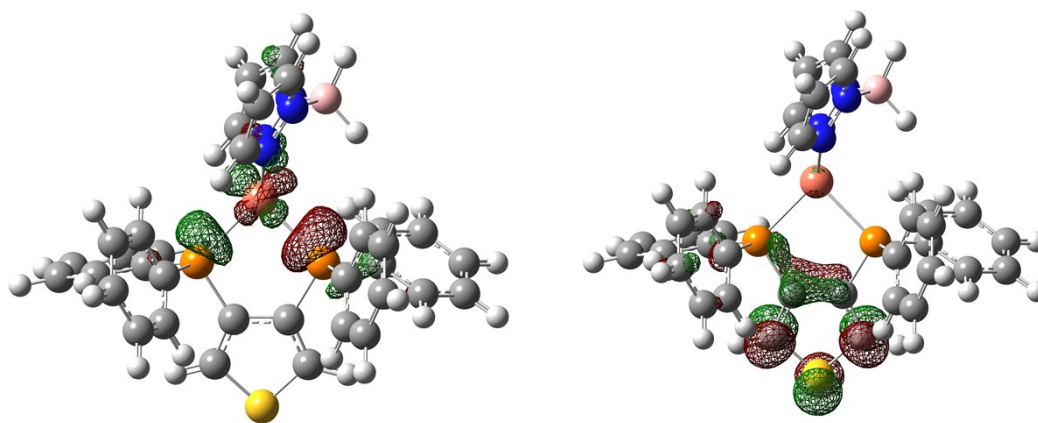


Fig. S11. DFT calculated HOMO (left) and LUMO (right) diagrams of the complex **1**.

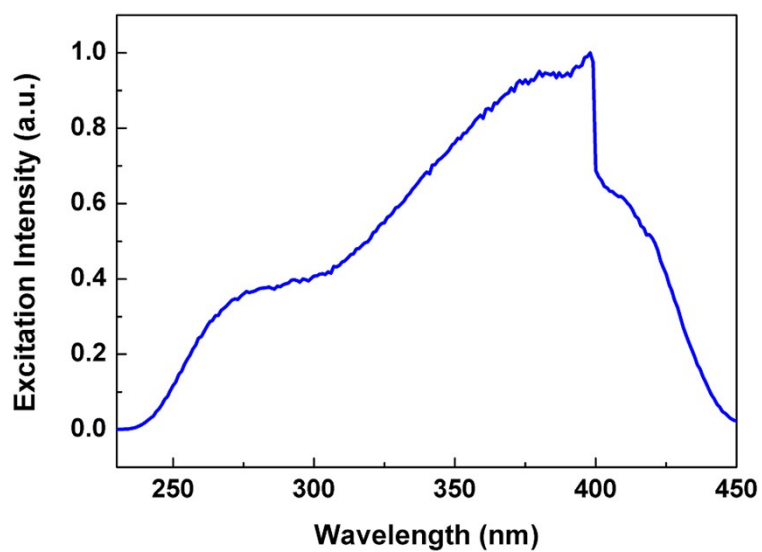


Fig. S12. Excitation of crystal **1B** at ambient temperature.

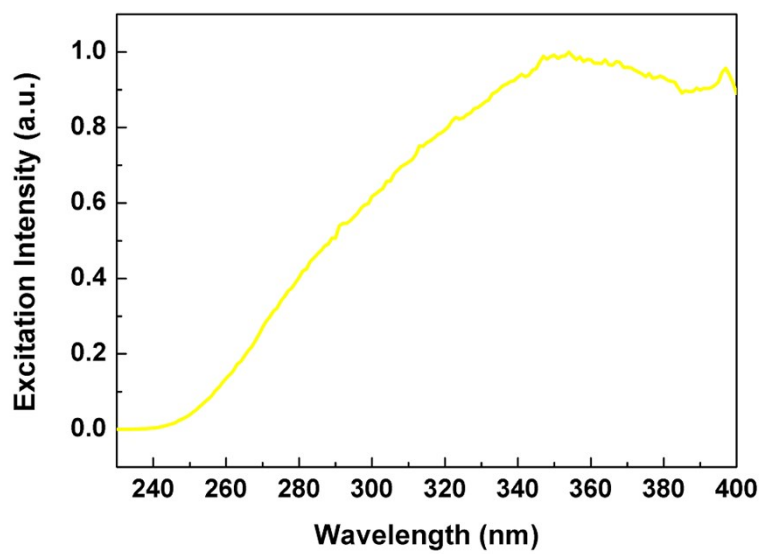


Fig. S13. Excitation of crystal **1Y** at ambient temperature.

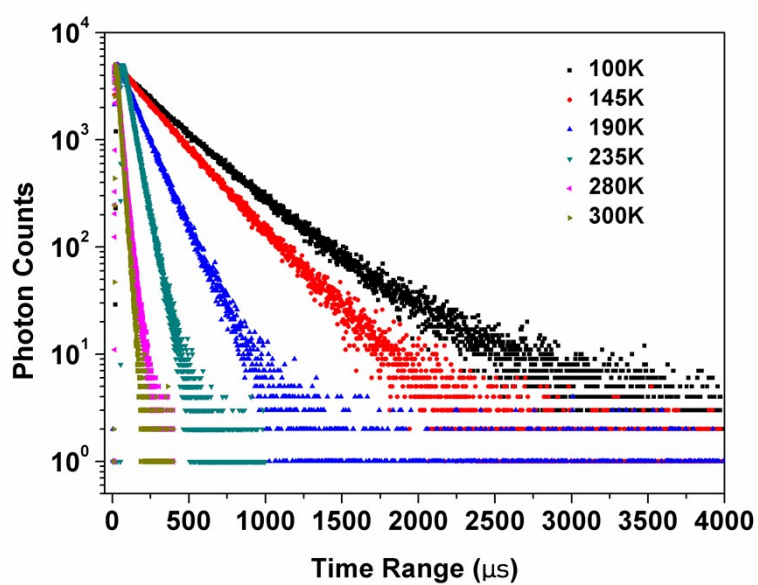


Fig. S14. Temperature dependent photoluminescence spectra of **1B**.

Table S3. Detailed temperature dependent excited state lifetime values of **1B** and **1Y** crystals.

	1B	1Y
77K	207.70	336.54
85K	207.84	371.72
100K	198.96	335.36
115K	191.93	333.99
130K	182.04	308.18
145K	157.60	298.07
160K	142.50	242.45
175K	130.24	175.98
190K	102.97	130.52
205K	73.19	92.07
220K	47.82	67.74
235K	42.86	49.35
250K	37.29	44.00
265K	33.63	33.56
280K	28.85	27.48
300K	23.09	21.59

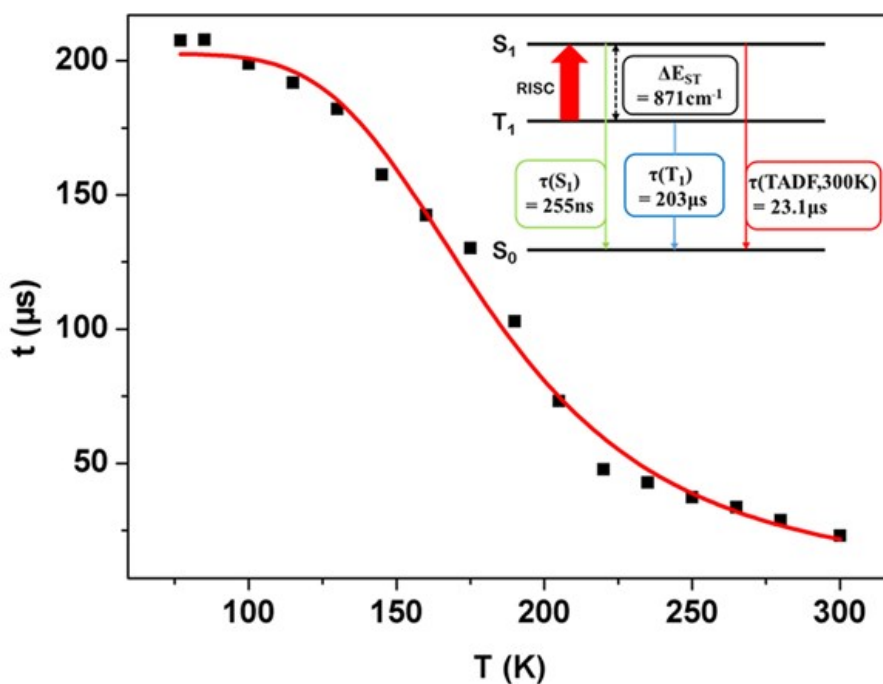


Fig. S15. Temperature-dependent emission lifetimes of **1B**. The solid line is a fit curve according to literature.⁸ Insert: Energy levels for ground state and lowest excited state of **1B**, in which $\tau(S_1)$, $\tau(T_1)$, $\tau(\text{TADF})$, RISC, and ΔE_{ST} represent prompt fluorescence decay time, phosphorescence decay time, delayed fluorescence decay time, reverse intersystem crossing, and the energy gap between the S_1 state and T_1 state.

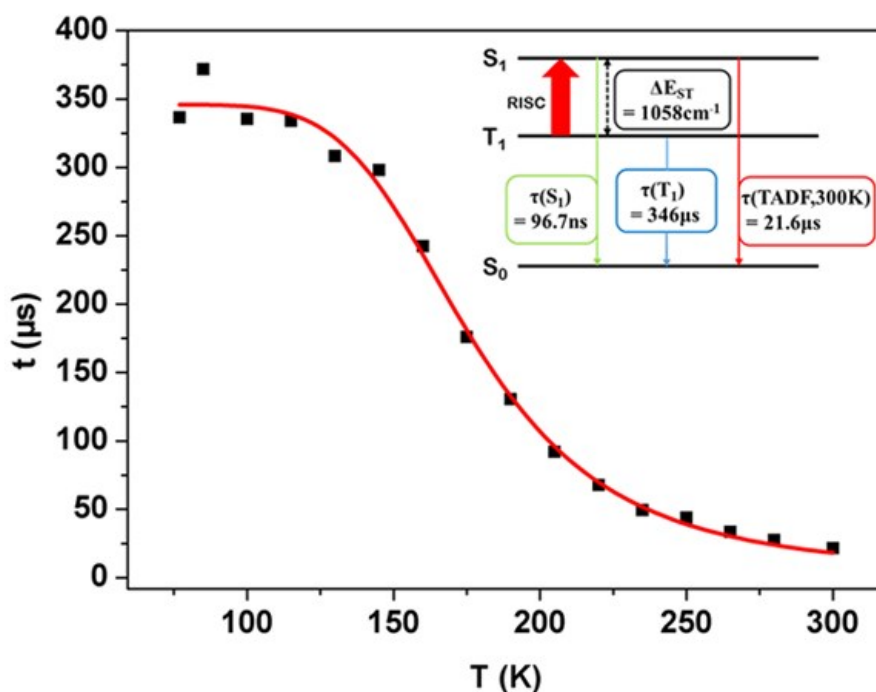


Fig. S16. Temperature-dependent emission lifetimes of **1Y**.

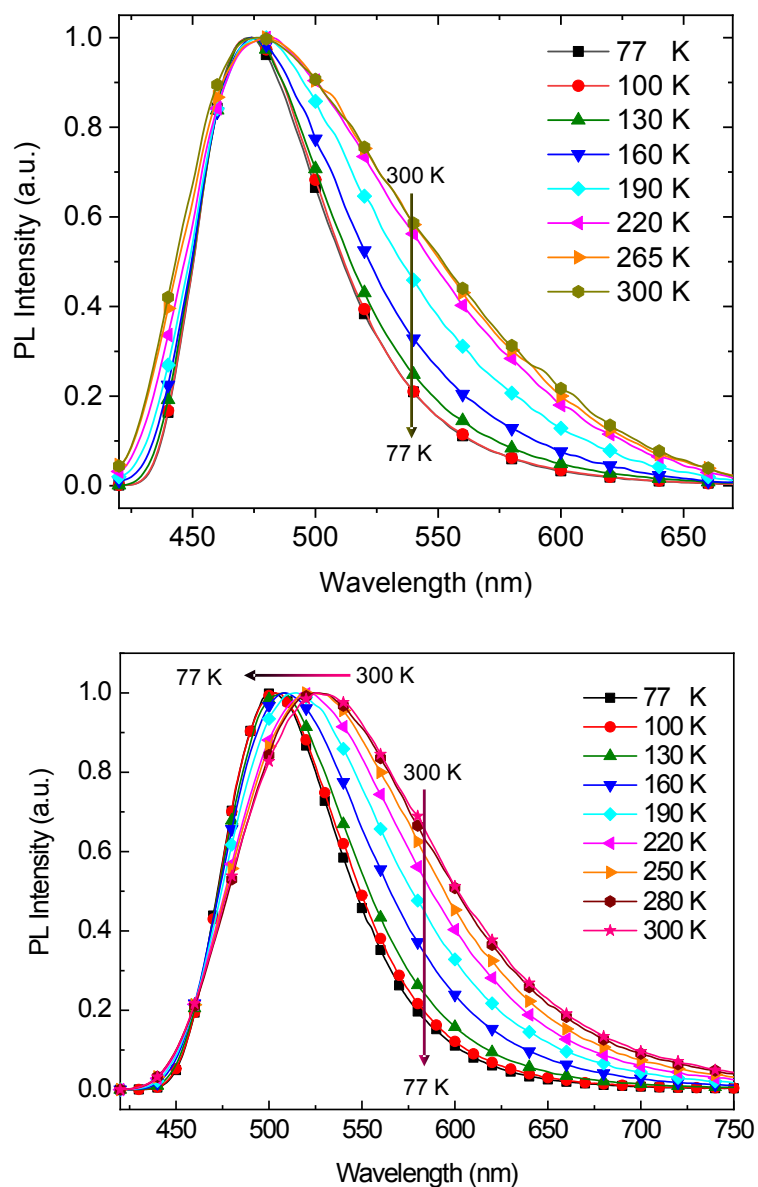


Fig. S17. Temperature dependent photoluminescence spectra of **1B** (top) and **1Y** (bottom). The excitation wavelength of **1B** is 400 nm. The excitation wavelength of **1Y** is 340 nm.

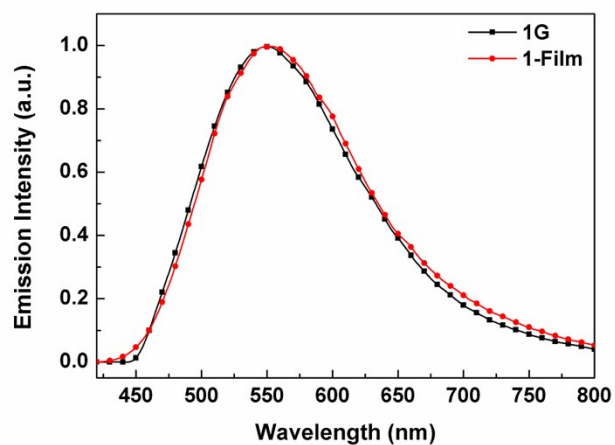


Fig. S18. Photoluminescence spectra comparison of **1G** and **1-Film**.

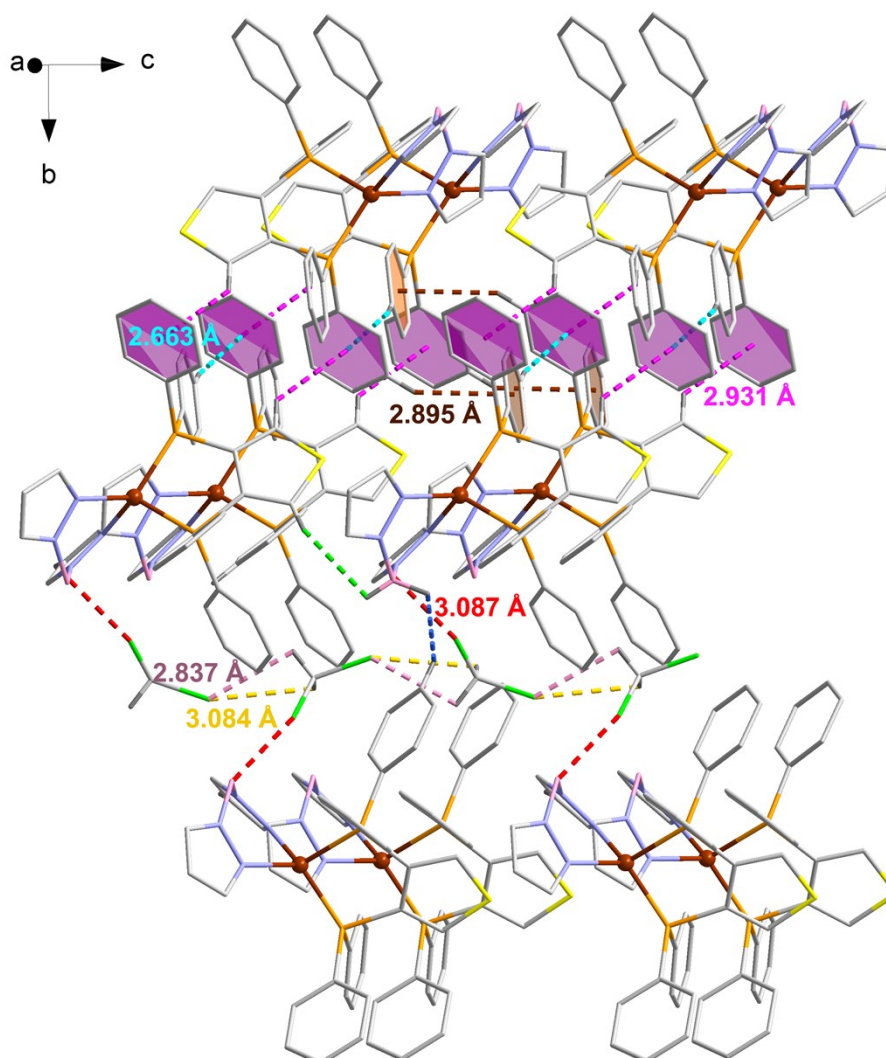


Fig. S19. Illustration of rich intermolecular forces in **1B**, including C-H \cdots π bonds (2.931, 2.663, and 2.895 Å), and C-H \cdots Cl bonds (2.837, 3.084, and 3.087 Å).

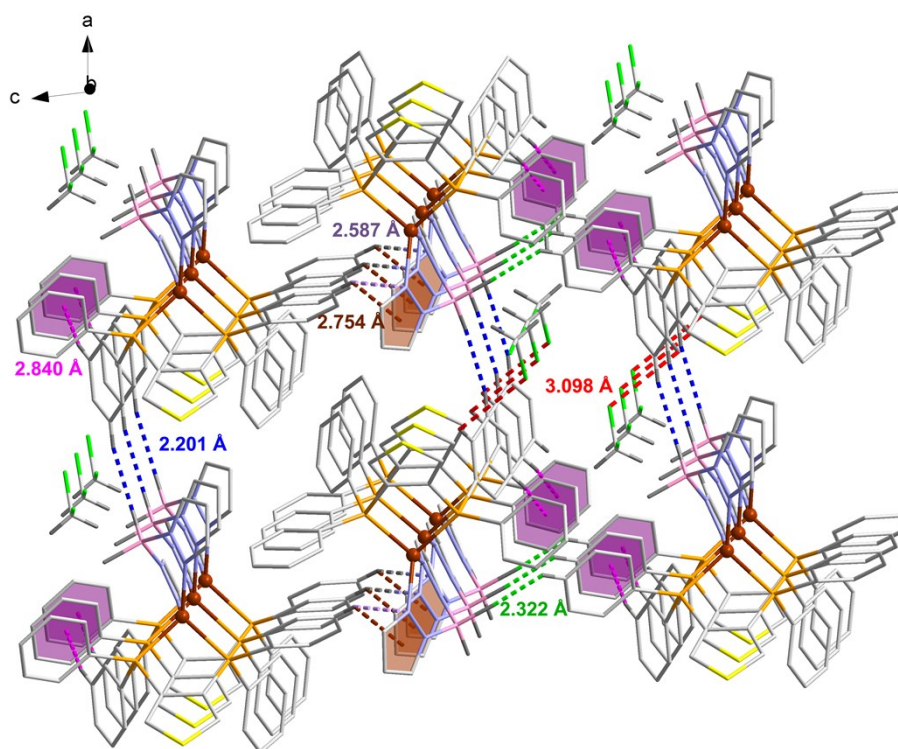


Fig. S20. Illustration of rich intermolecular forces in **1Y**, including C-H \cdots π bonds (2.754 and 2.840 Å), B-H \cdots H-C dihydrogen bonds (2.201 Å, 167.90° and 2.322 Å, 176.13°), C-H \cdots Cl bond (3.098 Å), and C-H \cdots N bond (2.587 Å).

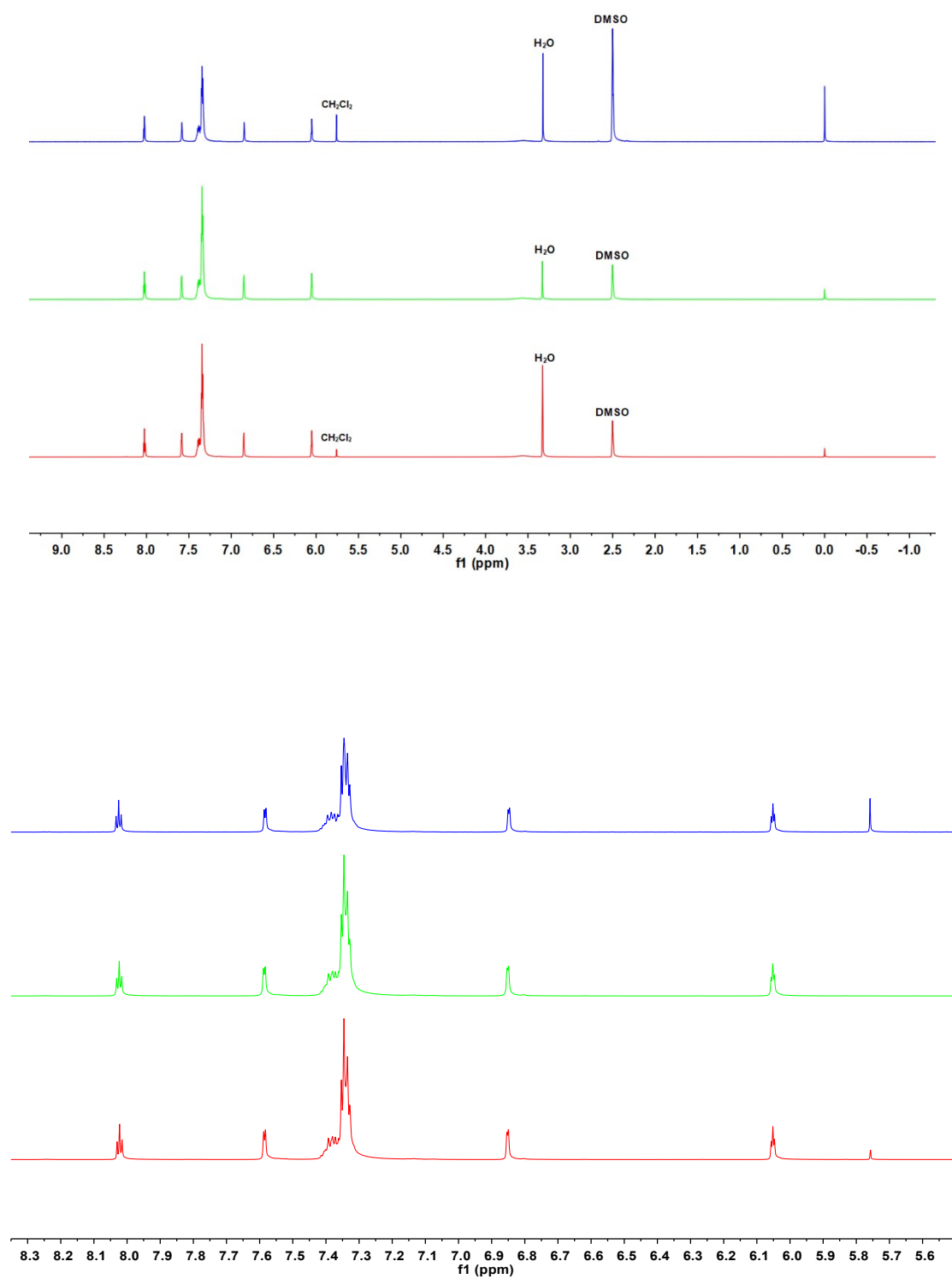


Fig. S21. ¹H NMR of **1B** (red), **1G** (green) and **1G-F1** (blue). The bottom picture is magnification of the 8.3 ppm-5.5 ppm area of the top picture.

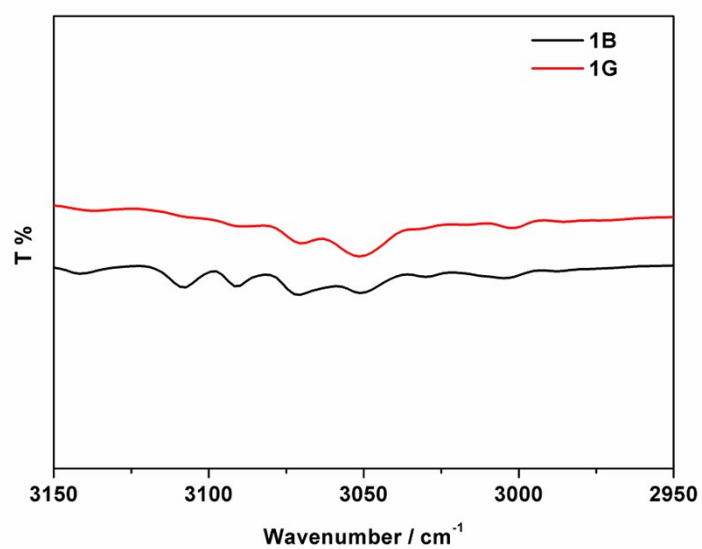
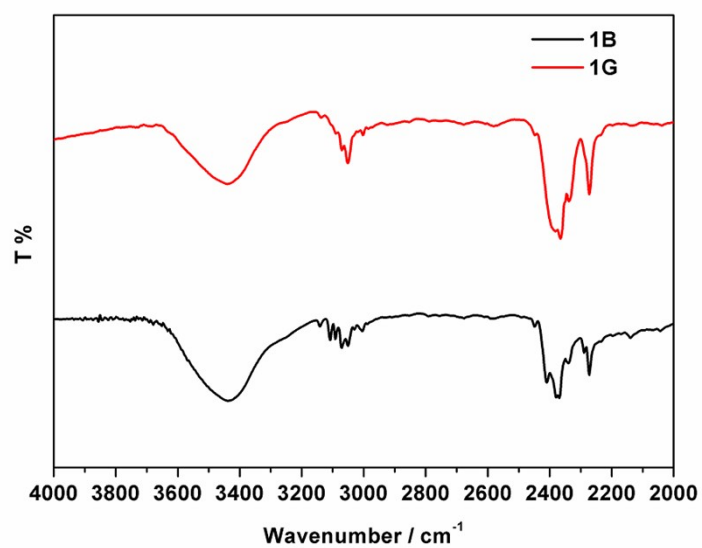


Fig. S22. Infrared spectra of **1B** and **1G**. The bottom picture is magnification of the 3150 cm^{-1} – 2950 cm^{-1} area of the top picture. In this area, the peak positions are not change, but some peaks almost disappeared after grinding.

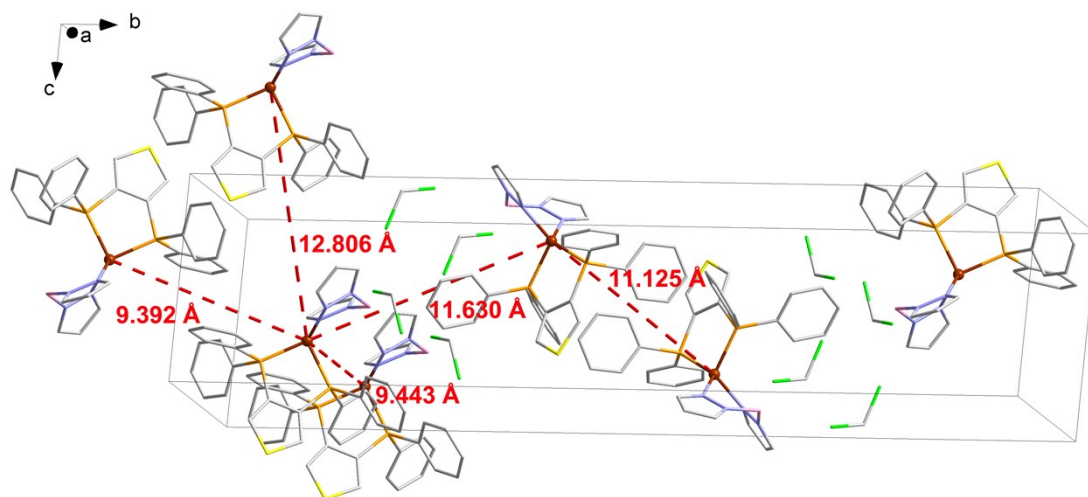


Fig. S23. The Cu-Cu distances in **1B**.

Theoretical details

Coordinates of the optimized ground state S_0 of complex **1**.

Cu	0.11960809	1.12878846	0.11645937
P	-1.81138764	-0.22008312	-0.12691391
P	1.46189362	-0.77953044	-0.34879199
S	-0.90627858	-3.84381836	-2.35740469
N	0.62093980	1.92628103	1.96921930
N	1.50374493	2.94510774	1.96020915
N	0.36812615	2.88856318	-0.92852157
N	1.27920338	3.75329086	-0.43921174
C	0.52501479	-3.07324577	-1.79917019
H	1.49184487	-3.46219550	-2.08158699
C	0.25737017	-1.96502663	-1.05517070
C	-3.25429352	0.17519592	-1.19575299
C	-4.57800060	0.03383262	-0.79040225
H	-4.80697027	-0.34025792	0.20007597
C	-2.57644757	-0.79141170	1.43707145
C	-1.89522200	-2.66803781	-1.59185940
H	-2.96892436	-2.71091315	-1.69913500
C	-2.98318966	0.19504825	2.33808784
H	-2.82649606	1.24173910	2.09839168
C	2.14705307	-1.62597884	1.12406911
C	2.83603661	-0.80455396	-1.55823881
C	-2.75225059	-2.13003385	1.77638671
H	-2.42874138	-2.90836836	1.09595559
C	-1.15990347	-1.72629241	-0.93749646
C	1.16897857	4.93091803	-1.06729231
H	1.82335263	5.74762879	-0.80746910
C	1.97564059	-2.97940124	1.40482477
H	1.39788493	-3.60415226	0.73388417

C	-2.98806367	0.66582304	-2.47591019
H	-1.96023433	0.78361258	-2.80405015
C	-3.74950094	-1.49023282	3.87141170
H	-4.20279874	-1.76276670	4.81794969
C	1.63986846	3.43710211	3.19929964
H	2.31219229	4.25939094	3.38595370
C	-3.33201234	-2.47609600	2.99017954
H	-3.45611869	-3.52244961	3.24640348
C	0.20445974	1.78356166	3.22494596
H	-0.51112725	1.01372984	3.47176206
C	-3.57575505	-0.15201637	3.54215785
H	-3.89024763	0.62457557	4.23033443
C	-5.61578010	0.37410073	-1.65071964
H	-6.64274444	0.26170890	-1.32095616
C	-5.34233199	0.85222805	-2.92207301
H	-6.15343577	1.11714347	-3.59104729
C	2.88074650	0.22979730	-2.49156462
H	2.14435794	1.02502832	-2.44379849
C	-0.31924838	3.53910343	-1.86555269
H	-1.12678824	3.04580401	-2.38525480
C	-4.02292447	0.99478166	-3.33502311
H	-3.80030251	1.37000894	-4.32771245
C	3.82184775	-1.79022150	-1.58288050
H	3.82285876	-2.57614292	-0.83548937
C	0.15266244	4.84435869	-2.00153153
H	-0.19493140	5.61205728	-2.67393010
C	0.82295079	2.72013451	4.05446145
H	0.69561021	2.85675964	5.11635946
C	2.53184311	-3.53475036	2.54993974
H	2.38906249	-4.58924817	2.76002324

C	4.82088593	-1.75500750	-2.54466288
H	5.58725750	-2.52238978	-2.55415065
C	4.84629519	-0.73403815	-3.48565698
H	5.63117397	-0.70541985	-4.23349874
C	3.87834470	0.25944080	-3.45563170
H	3.90779105	1.07116505	-4.17378352
C	2.87262310	-0.83279326	2.01560957
H	2.98584097	0.22868972	1.82441552
C	3.26525809	-2.74408468	3.42190697
H	3.69847720	-3.17856874	4.31618425
C	3.43414503	-1.39230144	3.15241372
H	3.99396310	-0.76506648	3.83685955
B	2.28690783	3.33536528	0.67031118
H	2.91656649	2.37526564	0.28771288
H	2.98461944	4.28512253	0.92586074

Reference

- [1] Zhang, Q.; Wilson, P.; Li, Z.; McHale, R.; Godfrey, J.; Anastasaki, A.; Waldron, C.; Haddleton, D. M. Aqueous Copper-Mediated Living Polymerization: Exploiting Rapid Disproportionation of CuBr with Me₆TREN. *J. Am. Chem. Soc.* **2013**, *135*, 7355-7363.
- [2] Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. OLEX2: A Complete Structure Solution, Refinement and Analysis Program. *J. Appl. Cryst.* **2009**, *42*, 339-341.
- [3] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09, Revision D.01*; Gaussian, Inc.: Wallingford CT, **2013**.
- [4] Yanai, T.; Tew, D.; Handy, N. A New Hybrid Exchange–Correlation Functional Using the Coulomb-Attenuating Method (CAM-B3LYP). *Chem. Phys. Lett.* **2004**, *393*, 51-57.
- [5] Trofimenko, S. Boron-pyrazole chemistry. II. Poly(1-pyrazolyl)-borates. *J. Am. Chem. Soc.* **1967**, *89*, 3170-3177.
- [6] Clifton, J.; Habraken, E. R. M.; Pringle, P. G.; Manners, I. Subtle Effects of Ligand Backbone on the Efficiency of Iron-Diphos Catalysed Negishi Cross-Coupling Reactions. *Catal. Sci. Technol.* **2015**, *5*, 4350-4353.
- [7] Igawa, S.; Hashimoto, M.; Kawata, I.; Yashima, M.; Hoshino, M.; Osawa, M. Highly Efficient Green Organic Light-Emitting Diodes Containing Luminescent Tetrahedral Copper(I) Complexes. *J. Mater. Chem. C* **2013**, *1*, 542-551.
- [8] (a) Czerwieniec, R.; Yu, J.; Yersin, H. Blue-Light Emission of Cu(I) Complexes and Singlet Harvesting. *Inorg. Chem.* **2011**, *50*, 8293-8301; (b) Czerwieniec, R.; Yu, J.; Yersin, H. Correction to Blue-Light Emission of Cu(I) Complexes and Singlet Harvesting. *Inorg. Chem.* **2012**, *51*, 1975-1975.