Supporting Information

White phosphorescent coordination polymers with Cu_2I_2 alternating units linked by benzo-18-crown-6

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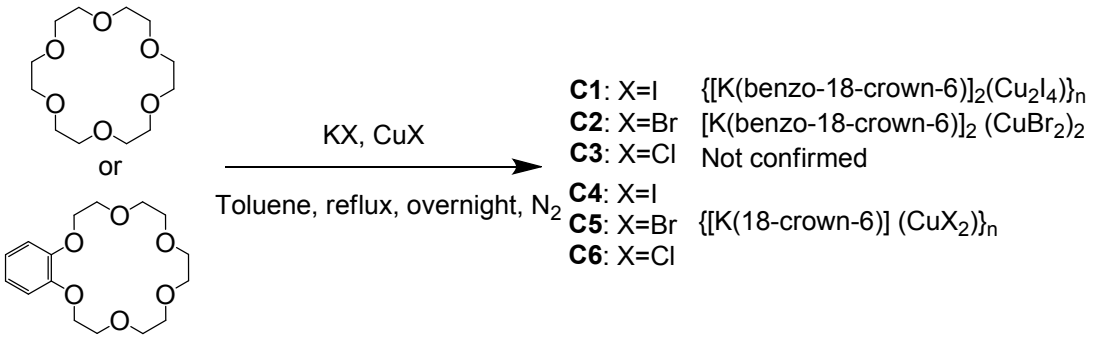
1. Experimental section

1.1. Synthesis

All experiments were carried out without special treatments. The copper(I) complex $[Cu(CH_3CN)_4]BF_4$ was purchased from Aldrich Chemical Co. Solvents were freshly distilled over appropriate drying regents under an N_2 atmosphere. The synthetic routes of Cu(I) complexes are shown in Scheme S1.



Scheme1. The synthetic routes for the Cu(I) complexes.

*General Procedure for the Preparation of **C1–C6***

To a dry and degassed toluene (10 mL) solution of crown ether (1 mmol) was added CuX (4 mmol) and KX (4 mmol). The mixture was heated under nitrogen at reflux for 24 h. The solution was cooled to room temperature and filtered through Celite. Solvent was removed under vacuum to give an oily residue which was redissolved in degassed dichloromethane. A white solid was collected after slow addition of dry hexane and then washing with dry diethyl ether.

C1. ^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm 3.74 (m 8H, CH_2), 3.84 (t, 4H, *J*(HH) = 2.4 Hz, CH_2), 4.05 (t, 4H, *J*(HH) = 2.0 Hz, CH_2), 4.21 (t, 4H, *J*(HH) = 2.4 Hz, CH_2), 6.85 (m, 2H, Ph) and 6.94 (m, 2H, Ph). IR data (KBr, cm^{-1}): 2925s, 1594w, 1505s, 1453s, 1350m, 1257vs, 1210s, 1101vs, 1067s, 952vs, 833w, 784w, 754s, 603vw, 510vw.

C2. ^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm 3.75 (m 8H, CH_2), 3.82 (t, 4H, *J*(HH) = 2.4 Hz, CH_2), 3.99 (t, 4H, *J*(HH) = 2.0 Hz, CH_2) , 4.23 (t, 4H, *J*(HH) = 2.4 Hz, CH_2), 6.88 (m, 2H, Ph) and 6.95 (m, 2H, Ph). IR data (KBr, cm^{-1}): 2898s, 1592m, 1503s, 1451s, 1349m, 1254vs, 1215vs, 1105vs, 1072vs, 954vs, 835m, 783m, 755vs, 601w, 512w.

C3. ^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm 3.74 (m 8H, CH_2), 3.82 (t, 4H, *J*(HH) = 2.4 Hz, CH_2), 3.98 (t, 4H, *J*(HH) = 2.0 Hz, CH_2) , 4.22 (t, 4H, *J*(HH) = 2.4 Hz, CH_2), 6.88 (m, 2H, Ph) and 6.95 (m, 2H, Ph). IR data (KBr, cm^{-1}): 2892s, 1592m, 1501vs, 1461s, 1351s, 1253vs, 1203vs, 1109vs, 1050s, 954vs, 835m, 750vs, 509w.

C4. ^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm 3.68 (s, 24H, CH_2). IR data (KBr, cm^{-1}): 2898s, 1467m, 1348m, 1281m, 1246m, 1103vs, 961s, 835m.

C5. ^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm 3.69 (s, 24H, CH_2). IR data (KBr, cm^{-1}): 2901s, 1470m, 1348m, 1281m, 1247m, 1104vs, 963s, 838m.

C6. ^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm 3.68 (s, 24H, CH_2). IR data (KBr, cm^{-1}): 2902s, 1471m, 1349s, 1281m, 1247m, 1104vs, 963s, 840m.

1.2. Crystal Structures

Single crystals suitable for crystal structure analysis were obtained by slow evaporation of a dichloromethane–hexane solution of the complex at room temperature. X-Ray diffraction data were collected on an Enraf-Nonius Kappa CCD area-detector diffractometer. The programs DENZO and COLLECT were used in data collection and cell refinement. The structures were solved using program SIR97 and refined with program SHELX-97. The SQUEEZE option of PLATON was used in order to remove the disorder of 1/8 of an ethanol molecule from the calculations. Molecular plots were obtained with program ORTEP-3. The crystallographic and refinement data are collected in **Table S1**.

1.3. Instrumentation and Spectroscopic Methods

NMR spectra were recorded on a Bruker Ultrashield 400 Plus NMR spectrometer. The ^{1}H NMR chemical shifts were referenced to tetramethylsilane, TMS (δ = 0.00). Luminescence spectra of the complexes were recorded using an Edinburgh Instrument FLS920 Combined Fluorescence Lifetime and Steady state spectrophotometer. Photoluminescence (PL) quantum yields were determined using a Hamamatsu system for absolute PL quantum yield measurements (type C9920-02) equipped with an integrating sphere with Spectralon inner surface coating. The samples were carefully degassed by at least five freeze-pump-thaw cycles. Thermogravimetric analysis (TGA) was performed on a Perkin-Elmer thermal analyzer.

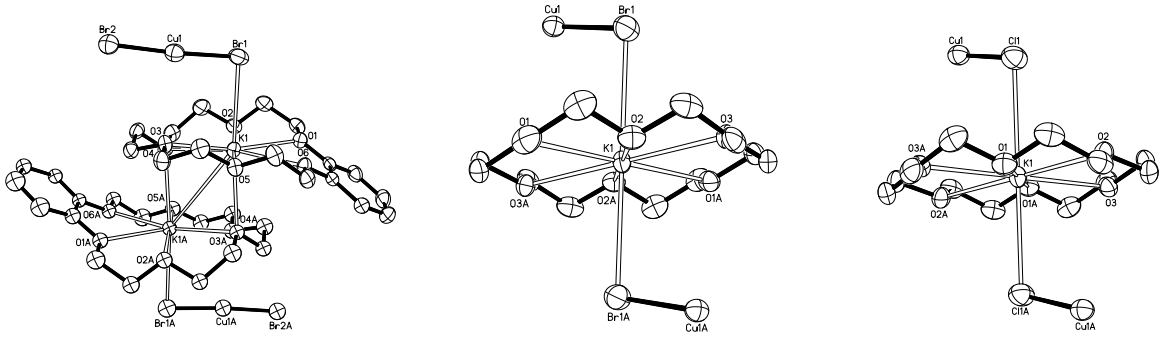


Fig. S1. Single crystal structures of complexes **C2**, **C5** and **C6** (hydrogen atoms are omitted for clarity).

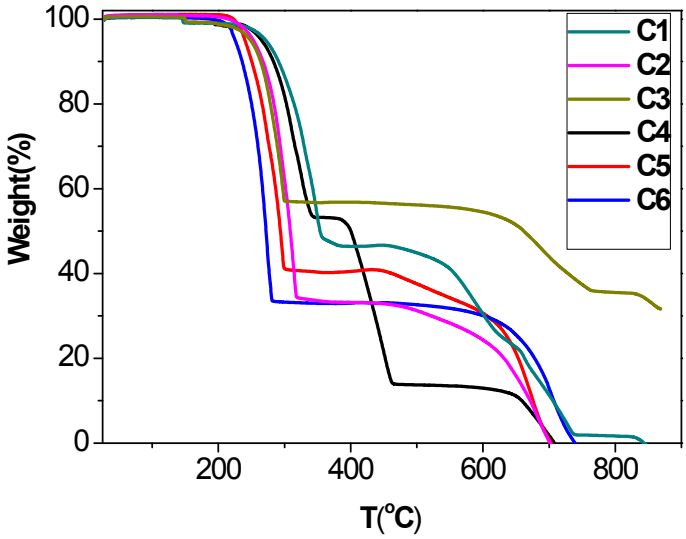


Figure S2. TGA traces of the compounds **C1-C6.**

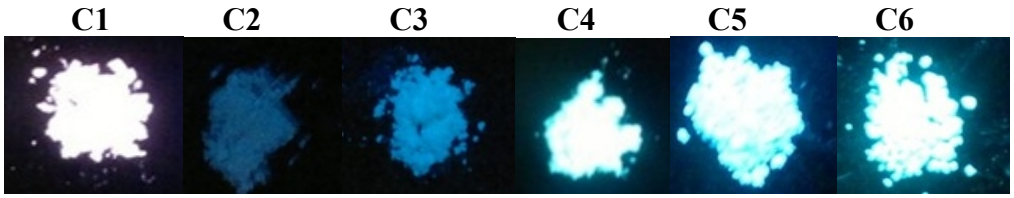


Fig. S3. Photographs of the solid powders of **C1**–**C6** under UV irradiation at 254 nm (UV lamp) at room temperature.

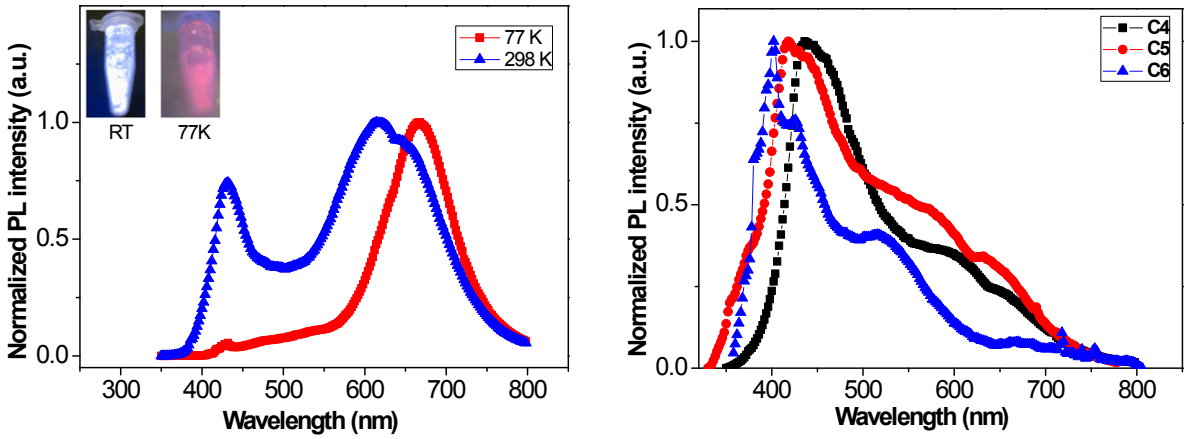


Fig. S4. Solid-state luminescence spectra of **C1** recorded from 298 K to 77 K (λ_{ex} = 337 nm). Inset shows the photographs of **C1** under UV irradiation at 254 nm (UV lamp) at room temperature (left) and in liquid nitrogen (right); Solid-state luminescence spectra of **C4**-**C6** at 77 K (λ_{ex} = 337 nm).

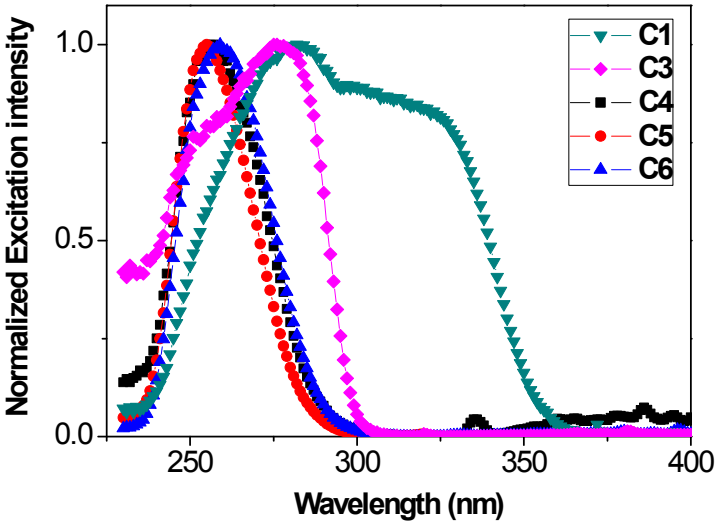


Fig. S5. Excitation spectra of the Cu (I) complexes in solid state at room temperature.

Table S1. Summary of Crystallographic Data

Parameter	C1	C2	C5	C6
Formula	$C_{16}H_{24}CuI_2KO_6$	$C_{32}H_{48}Br_4Cu_2K_2O_{12}$	$C_{12}H_{24}Br_2CuKO_6$	$C_{12}H_{24}Cl_2CuKO_6$
Fw	668.79	1149.62	526.77	437.85
T (K)	223(1)	296(2)	296(2)	296(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Cryst syst	triclinic	Monoclinic	monoclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/n$	$P2_1/n$	$P2_1/n$
a(Å)	9.382(5)	9.9380(12)	8.7518(11)	8.7001(8)
b (Å)	9.764(4)	17.818(2)	8.3464(10)	8.1573(7)
c (Å)	12.821(5)	12.4460(14)	13.8610(18)	13.8280(12)
α(deg)	92.459(5)	90.00	90.00	90.00
β (deg)	93.353(6)	100.936(2)	102.934(2)	102.880(2)
γ (deg)	109.055(5)	90.00	90.00	90.00
V(Å^3)	1105.8(9)	2163.9(4)	986.8(2)	956.67(15)
Z	2	2	2	2
ρ_{calcd} (g cm^{-3})	2.009	1.764	1.773	1.520
Absorption coefficient (mm^{-1})	3.994	4.921	5.387	1.659
F(000)	644	1144	524	452
Crystal size (mm^3)	0.30 x 0.22 x 0.21	0.41 x 0.35 x 0.35	0.35 x 0.32 x 0.31	0.31 x 0.21 x 0.10
θ_{min}, θ_{max} (deg)	2.91, 27.48	2.02, 25.05	2.87, 25.05	2.54, 25.05
limiting indices	$-11 < h < 11$, $-11 < k < 11$, $-15 < l < 15$	$-6 < h < 11$, $-19 < k < 21$, $-14 < l < 13$	$-10 < h < 7$, $-7 < k < 9$, $-16 < l < 16$	$-10 < h < 9$, $-9 < k < 9$, $-16 < l < 16$
No. reflns collected	11814	11955	3658	5167
No. unique reflns	3895	3830	1742	1695
R_{int}	0.0255	0.0344	0.0215	0.0216
Data/restr/params	3895 / 0 / 332	3830/ 0/ 236	1742/ 0/ 103	1695 / 0 / 104
GOOF on F^2	1.064	0.982	1.087	0.990
Final R_1, wR_2 $[I > 2\acute{o}(I)]$ [a]	0.0302, 0.0626	0.0318, 0.0661	0.0444, 0.1284	0.0241, 0.0491
R_1, wR_2 (all data)	0.0382, 0.0667	0.0624, 0.0765	0.0595, 0.1371	0.0397, 0.0557
Largest diff peak and hole (e•Å^{-3})	1.188 and -1.249	0.443 and -0.380	0.598 and -0.730	0.202 and -0.155

[a]. $R1 = \Sigma \left| |F_o| - |F_c| \right| / \Sigma |F_o|$. $wR2 = [\Sigma w(|F_o^2| - |F_c^2|)^2 / \Sigma w|F_o^2|^2]^{1/2}$

Table S2. Selected Bond Lengths (Angstrom) and Angles (Degree)

C1		C2		C5		C6	
K1-I1	3.6823(16)	K1-Br1	3.2964(9)	K1-Br1	3.3722(8)	K(1)-Cl1	3.2699(7)
K1-O4	2.871(3)	K1-O3	2.934(3)	Cu1-Br1	2.2012(7)	Cu1-Cl1	2.0948(7)
K1-O4	3.088(3)	K1-O3	2.886(2)	O3-K1-O3	180.00(16)	O3-K1-O3	179.999(1)
Cu3-I1	2.5095(11)	Cu1-Br1	2.2234(7)	O3-K1-O1	60.05(12)	O3-K1-O1	60.50(5)
Cu3-I2	2.5093(11)	Cu1-Br2	2.2187(7)	O3-K1-Br1	103.21(8)	O3-K1-Cl1	98.22(3)
Cu3-I2	2.5818(10)	K1-K1	4.1365(15)	O3-K1-Br1	76.79(8)	O3-K1-Cl1	81.78(3)
Cu3-Cu3	2.7972(16)	O3-K1-O3	89.42(7)	O1-K1-Br1	97.29(8)	O1-K1-Cl1	98.65(3)
K1-O4-K1	99.43(8)	O3-K1-Br1	101.10(5)	Br1-K1-Br1	180.0	Cl1-K1-Cl1	180.00(3)
I1-Cu3-I2	124.54(3)	O3-K1-Br1	166.88(5)	Cu1-Br1-K1	94.63(2)	Cu1-Cl1-K1	96.52(2)
I1-Cu3-Cu3	178.16(4)	Br2-Cu1-Br1	176.34(3)	Br1-Cu1-Br1	180.00(4)	Cl1-Cu1-Cl1	179.999(1)
K1-I1-Cu3	101.59(3)	Cu1-Br1-K1	94.34(2)				
Cu3-I2-Cu3	65.74(4)						
I2-Cu3-Cu3	57.30(3)						
I2-Cu3-Cu3	56.96(3)						