Electronic Supplementary Information for Highly efficient blue-green delayed fluorescence from copper(I) thiolate complexes: luminescence color alteration by orientation change of the aryl ring

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Experimental Detail

1. Materials: Sodium hydride and benzenethiol were obtained from Wako Chemicals. $L_{Me}CuBr$ and $L_{iPr}CuBr$ were prepared according to the literature.^{1,4}

2. General Remarks. All synthetic reactions were carried out under an atmosphere of Ar unless otherwise indicated. ¹H and ³¹P NMR spectra were recorded on a Bruker AVANCE-400 spectrometer. ¹H chemical shifts were referenced to the residual solvent peaks. ³¹P chemical shifts were referenced to external 85% phosphoric acid ($\delta = 0$ ppm). Elemental analyses (C and H) were carried out with an elemental analyzer Vario EL CHNOS from Elementar Analytical. For emission studies, dissolved oxygen was removed by repeated freeze-pump-thaw cycles. Steady-state absorption and emission spectra were recorded at room temperature and 77 K using a Hitachi U-3010 spectrophotometer and a Hitachi F-7000 spectrofluorometer, respectively. The light intensity distribution of a Xenon lamp incorporated in the spectrofluorometer was corrected using Rhodamine B in ethylene glycol. The output of the photomultiplier was calibrated in the wavelength range of 300-850 nm using a secondary standard lamp. Laser photolysis studies were carried out using a Nd:YAG laser (Sure Light 400, Hoya Continuum Ltd.) equipped with second, third, and fourth harmonic generators. The excitation light used for emission lifetime measurements was the third harmonic (355 nm). The duration and energy of the laser pulse were 5 ns and 30 mJ/pulse, respectively. The system used to monitor the decay of emission has been reported elsewhere.² A cryostat, OptistatDN-V₂, from Oxford instrument was used for measurements of decay times in the temperature range 300 - 77 K. Emission quantum yields in solution at room temperature and 77 K were determined with an absolute PL quantum yield measurement system (C-9920-02G, Hamamatsu). Crystallographic data and results of structure refinements are summarized in Table S1. In the reduction of data, Lorentz, polarization and empirical absorption corrections were made. Structures were solved by direct methods (SIR2004).³ All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were fixed at calculated positions. Computational details were reported elsewhere.^{1,4}

References

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3. Synthetic Procedures for 1 and 2

 $Cu(L_{Me})$ (SPh) 1



A THF solution (25 ml) of sodium bezenethiolate was prepared from sodium hydride (8.4 mg, 0.34 mmol) and benzenthiole (37.6 mg, 0.34 mmol). $L_{Me}CuBr$ (0.2 g, 0.31 mmol) was added to the THF solution of sodium bezenethiolate. The mixture was stirred for 1 h at room temperature. The reaction mixture was filtrated, and the solvent was removed in vacuo to give a pale yellow powder. The residue was purified by recrystallization from THF / diethyl ether to give yellow crystals. Yield 142 mg, 68%.

¹H NMR (400 MHz, CD₂Cl₂, 210 K) δ 2.26 (s, 6H, methyl), 2.42 (s, 6H, methyl), 6.50 (m, 2H, *o*-tolyl), 6.55 (t, 2H, phenyl), 6.63 (t, 1H, phenyl), 6.75 (m, 2H, *o*-tolyl), 6.80 (t, 2H, *o*-tolyl), 6.98 (d, 2H, J = 7.26 Hz, phenyl), 7.07 (t, 2H, *o*-tolyl), 7.14 (m, 4H, *o*-tolyl), 7.26 (m, 4H, *o*-phenylene), 7.39 (t, 2H, *o*-tolyl), 7.51 (m, 2H, *o*-tolyl); ³¹P NMR (162 MHz, CD₂Cl₂, 210 K) δ -24.4. Calcd for C₄₀H₃₇CuP₂S: C, 71.14; H, 5.52. Found C, 71.06; H, 5.47.



This compound was prepared similarly to **1**, except that the $L_{Me}CuBr$ (0.24 g, 0.31 mmol) was used instead of $L_{Me}CuBr$. Analytically pure material was obtained by recrystallization from THF

/ diethyl ether to give yellow crystals. Yield 89 mg, 45%.

¹H NMR (400 MHz, CD₂Cl₂, 210 K) δ 0.69 (d, 6H, J = 6.53 Hz, mrthyl), 0.72 (d, 6H, J = 6.60 Hz, mrthyl), 0.85 (d, 6H, J = 6.60 Hz, methyl), 1.32 (d, 6H, J = 6.53 Hz, methyl), 3.35 (m, 2H, methine), 3.63 (m, 2H, methine), 6.47 (m, 2H, 2-iPrphenyl), 6.53 (t, 2H, phenyl), 6.60 (t, 1H, phenyl), 6.71 (t, 2H, phenyl), 6.81 (m, 2H, *o*-tolyl), 7.13 (m, 8H, phenyl and 2-iPrphenyl), 7.31 (m, 2H, 2-iPrphenyl), 7.44 (m, 4H, *o*-phenylene), 7.50 (m, 2H, 2-iPrphenyl); ³¹P NMR (162 MHz, CD₂Cl₂, 210 K) δ -26.2. Calcd for C₄₈H₅₃CuP₂S: C, 73.21; H, 6.78. Found C, 73.12; H, 6.61.

[Note]

Complexes 1 and 2 were also obtained from the reaction of copper(I) thiophenolate (CuSPh) with diphosphine ligands (L_{Me} and L_{iPr}). However, yields are low (55% for 1 and 28% for 2).

4. Crystal Structure Determination

	1	2
formula	$C_{40}H_{37}CuP_2S$	$C_{40}H_{53}CuP_2S$
formula weight	675.24	787.44
cryst syst	Triclinic	triclinic
space group	PĪ	$P2_1/n$
<i>a</i> / Å	10.8776 (1)	13.8491 (1)
<i>b</i> / Å	13.0996 (2)	21.0479 (2)
<i>c</i> / Å	13.2500 (2)	14.1578 (1)
α / deg	82.1651 (7)	-
eta / deg	76.9886 (9)	91.5815 (6)
γ/\deg	66.0524 (8)	-
V / Å ³	1679.05 (4)	4125.35 (6)
Ζ	2	4
$d_{\rm calcd}$ / g cm ⁻³	1.336	1.268
T/K	90(2)	90(2)
radiation	Μο Κα	Μο Κα
	$(\lambda = 0.71073 \text{ Å})$	$(\lambda = 0.71073 \text{ Å})$
μ/ cm^{-1}	0.836	0.690
diffractometer	Rigaku AFC-8	Rigaku AFC-8
max 2θ / deg	60	60
reflns collcd	27037	108726
indep reflns	9883	12169
	(Rint = 0.0315)	(Rint = 0.0412)
no. of param refined	426	502
$R1,^{[a]} wR2 (I > 2\sigma I)^{[b]}$	0.0324, 0.0773	0.0306, 0.0783
S	1.042	1.043

Table S1. Cryatallographic data for 1 - 2.

[a] $RI = \Sigma ||Fo| - |Fc|| / \Sigma |Fo|$. [b] $wR2 = [\Sigma w(|Fo| - |Fc|)^2 / \Sigma w |Fo|^2]^{1/2}$

_	2
Cu-P1	2.2589(3)
Cu-P2	2.2633(3)
Cu-S	2.1713(4)
P1-Cu1-P2	88.06(1)
P1-Cu1-S1	138.46(1)
P2-Cu1-S1	133.07(1)

Table S2. Comparison of bond lengths (Å) and angles (°) for 2.

Fig. S1. Molecular structures of **2**. Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted for clarity.



5. Photophysical properties of 2 in 2-MeTHF



Fig. S2 Absorption spectra of **2** in 2-MeTHF and emission spectra of **2** in 2-MeTHF at 293 K (orange line) and at 77 K (blue line).

	293 K		77 K		
	$k_{ m r}$	$k_{ m nr}$	$k_{ m r}$	$k_{ m nr}$	
1	1.7×10^{5}	5.4×10^5	7.3×10^{2}	39	
2	1.0×10^{5}	9.0×10^{5}	4.1×10^{2}	3	
Cu(LMe)Br	$9.5 imes 10^4$	1.4×10^{5}	4.9×10^2	0	
Cu(LiPr)Br	$5.8 imes 10^4$	7.6×10^{4}	9.0×10^{2}	100	

Table S3 k_r and k_{nr} values of **1**, **2**, Cu(L_{Me})Br, and Cu(L_{iPr})Br in 2-MeTHF

5. Theoretical Studies



Fig. S2 NTO pairs for the lowest singlet excited (S_1) state of 1 in X-ray crystal structure.



Fig. S3 NTO pairs for the lowest triplet excited (T_1) state of 1 in X-ray crystal structure.

	percentage composition (%) ^a			
	hole electron differences			
Cu	3.45	1.44	2.03	
S	58.5	0.23	58.3	
Р	0.18	7.23	-7.07	
Р	0.20	3.89	-3.70	
others	37.7	87.2	-49.5	

Table S4 Compositions of hole and electron in S₁ of 1. (X-ray crystal structure)

^{*a*} In the molecular orbitals, the atomic component is evaluated by the sum of the square of the LCAO coefficients which belong to the corresponding atom.

	percentage composition (%) ^a				
	hole	hole electron differences			
Cu	3.57	1.58 1.99			
S	56.9	0.34	56.6		
Р	0.18	6.68	-6.50		
Р	0.19	3.89	-3.70		
others	39.2	87.5	-51.6		

Table S5 Compositions of hole and electron in T₁ of 1. (X-ray crystal structure)

^{*a*} In the molecular orbitals, the atomic component is evaluated by the sum of the square of the LCAO coefficients which belong to the corresponding atom.



Fig. S4 NTO pairs for S_1 state of 2 in X-ray crystal structure.



Fig. S5 NTO pairs for T_1 state of 2 in X-ray crystal structure.

	percentage composition (%) ^a				
	hole electron differences				
Cu	3.44	0.55	2.90		
S	60.5	0.10	60.4		
Р	0.23	4.20	-4.00		
Р	0.23	1.93	-1.71		
others	35.6	93.2	-57.6		

Table S6 Compositions of hole and electron in S_1 of 2. (X-ray crystal structure)

^{*a*} In the molecular orbitals, the atomic component is evaluated by the sum of the square of the LCAO coefficients which belong to the corresponding atom.

Table S7 (Compositions	of hole and	electron in	T_1 of 2 .	(X-ray crystal structur	re)
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	perce	percentage composition (%) ^a			
	hole	hole electron differences			
Cu	3.60	1.13	2.46		
S	59.1	0.27	58.8		
Р	0.28	4.09	-3.82		
Р	0.26	5.39	-5.13		
others	36.8	89.1	-47.7		

^{*a*} In the molecular orbitals, the atomic component is evaluated by the sum of the square of the LCAO coeffiients which belong to the corresponding atom.



Fig. S6 Optimized S_1 geometry of 2; dihedral angle and S_1 and T_1 energies.

6. Temperature dependence of decay time

[Fitting procedure]

 $\tau_{\rm T}$ (decay time from of the T₁ state), $\tau_{\rm S}$ (decay time of the prompt fluorescence), and $\Delta E(S_1-T_1)$ (activation energy) were determined from a fit of Eq. 1 to measured $\tau_{\rm av}$ (25 points) by least-square method.

Complex 1 $\tau_{\rm T} = 1.14 \text{ ms}$ $\tau_{\rm S} = 90.4 \text{ ns}$ $\Delta E(S_1-T_1) = 686 \text{ cm}^{-1}$

Complex 2 $\tau_{\rm T} = 2.06 \text{ ms}$ $\tau_{\rm S} = 79.8 \text{ ns}$ $\Delta E({\rm S}_1 - {\rm T}_1) = 627 \text{ cm}^{-1}$



Figure S7 Temperature dependence of decay time for **1** (powder). The parameters $\tau_{\rm T}$, $\tau_{\rm S}$ and $\Delta E(S_1-T_1)$ were obtained as 1.1 ms, 90 ns and 690 cm⁻¹, respectively.



Figure S8 Temperature dependence of decay time for **2** (powder). The parameters $\tau_{\rm T}$, $\tau_{\rm S}$ and $\Delta E(S_1-T_1)$ were obtained as 2.1 ms, 80 ns and 630 cm⁻¹, respectively.

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