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Largely Color-Tuning Prompt and Delayed Fluorescence: Dinuclear Cu(I) Halide Complexes with *tert*-Amines and Phosphines

Ke Xu, Bu-Lin Chen, Fei Yang, Li Liu,* Xin-Xin Zhong,* Lei Wang,* Xun-Jin Zhu, Fa-Bao Li, Wai-Yeung Wong,* and Hai-Mei Qin



ABSTRACT: Luminescent copper(I) halide complexes with bi- and tridentate rigid ligands have gained wide research interests. In this paper, six tetracoordinate dinuclear copper(I) halide complexes, $Cu_2X_2(ppda)_2$ [ppda = 2-[2-(dimethylamino)phenyl(phenyl)phosphino]-*N*,*N*-dimethylanio]. Ar = I (1), Br (2), Cl (3)] and $Cu_2X_2(pfda)_2$ [pfda = 2-[2-(dimethylamino)-4-(trifluoromethyl)phenyl(phenyl)phosphino]-*N*,*N*-dimethyl-5-trifluoromethylaniline, X = I (4), Br (5), Cl (6)], were successfully prepared and systematically characterized on their structures and photophysical properties. Complexes 1–5 have a centrosymmetric form with a planar Cu_2X_2 unit, and complexe 6 has a mirror symmetry form with a butterfly-shaped Cu_2X_2 . Solid complexes 1, 4, and 5 emit delayed fluorescence at room temperature, intense blue to greenish yellow ($\lambda_{max} = 443-570$ nm) light, and their peak wavelengths are located at 443-570 nm



with microsecond lifetimes ($\tau = 0.4-19.2 \ \mu$ s, $\Phi_{\rm PL} = 0.05-0.48$). Complexes 2, 3, and 6 show prompt fluorescence, very weak yellowish green to yellow ($\lambda_{\rm max} = 534-595 \ {\rm nm}$) emission with peak wavelengths at 534-595 nm, and lifetimes in nanoseconds ($\tau = 4.4-9.3 \ {\rm ns}, \Phi_{\rm PL} < 0.0001$). (Metal + halide) to ligand and intraligand charge transitions are the main origin of the emission of the complexes. Solution-processed, complex-4-based nondoped and doped devices emit yellow green light with CIE coordinated at (0.41, 0.51), a maximum EQE up to 0.17%, and luminance reaching 75.52 cd/m².

1. INTRODUCTION

Copper(I) complexes are regarded as potential options for a realistic way to construct low-cost and high-efficiency organic light-emitting diodes (OLEDs) due to their rich structural and luminescent properties.¹⁻⁹ These complexes usually have small $\Delta E(S_1 - T_1)$ values caused by small overlapped highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), from which efficient room-temperature thermally activated delayed fluorescence (TADF) can benefit. Therefore, the emission of copper(I) complexes can combine singlet with triplet excitons by efficient reverse intersystem crossing.¹⁰⁻¹⁴

Previous studies reveal that three-coordinate planar Cu(I) complexes coordinated with rigid ligands¹⁵ or two-coordinate linear Cu(I) complexes¹⁶ can suppress the geometric distortion of the Cu(I) center by excitation. Osawa's group reported green OLEDs containing three-coordinate mononuclear Cu(I) halide complexes chelating a rigid diphosphine ligand with an external quantum efficiency (EQE) greater than 20%.¹⁵ A recent paper by Thompson et al. has reported blue-emitting two-coordinate Cu(I)-complex-based OLEDs with a EQE of 9.0%.¹⁶ Bulky or bridged ligands are used to construct a firm framework to decrease nonradiative decay, as well. Recently, a tridentate phosphine ligand was adopted by Xu's group to

synthesize a tetracoordinate mononuclear Cu(I) iodide complex in highly rigid coordination geometry, which showed a EQE up to 16.3%.¹⁷

Dinuclear Cu(I) cores possess a great advantage over mononuclear core since they have a rigid structure and thus high efficiency recorded for bulky ligand chelated complexes.¹⁸⁻²⁴ However, the reported dinuclear Cu(I) halide complexes are mainly limited to bidendate diphoshines^{20,24-31} or imine and phosphine^{18,21-23,32-36} ligands, whereas bidentate amine and phosphine ligands are rarely reported. In comparison to the great success in green emitters, it seems that blue emitters are still a challenge to meet the requirement of full color displays and white light sources.^{37,38}

With great interests to explore highly efficient blue emitters³⁹⁻⁴² and study the structure-property relationship of complexes, we combined two electron-donating NMe₂ groups into the *ortho*-position of two P-linked phenyl rings

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Scheme 1. Synthetic Pathways to Ligands ppda, pfda, and Complexes 1-6



in ligand ppda (2-[2-(dimethylamino)phenyl(phenyl)phosphino]-N,N-dimethylaniline), two electron-withdrawing CF₃ groups are introduced into the *meta*-position of NEt₂ in ligand pfda (2-[2-(dimethylamino)-4-(trifluoromethyl)phenyl-(phenyl)phosphino]-N,N-dimethyl-5-trifluoromethylaniline) to change the emissive color. Complexes **1**–**5** have a planar Cu₂X₂ core, whereas complex **6** has a butterfly-shaped Cu₂X₂ core. They showed very different emissions from previously reported ones. Here, the structures, photophysical and redox properties, and theoretical calculations of complexes **1**–**6** are reported. Also the OLED devices based on complex **4** were fabricated via a solution-processed method, and their electroluminescent behaviors were studied.

2. EXPERIMENTAL SECTION

2.1. Synthesis of pfda. At -78 °C, *n*-BuLi (2.5 M in hexane, 2.4 mL, 6 mmol) was added dropwise to a THF (10 mL) solution of 2-bromo-*N*,*N*-dimethyl-5-(trifluoromethyl)aniline (1.6 g, 6 mmol) and stirred for 30 min. Later, PhPCl₂ (0.39 mL, 3 mmol) was added in 5 min, and the subsequent reaction mixture was allowed to slowly warm to room temperature. After being stirred overnight, the reaction was quenched by the addition of water (10 mL) and then treated with aqueous NH₄Cl; CH₂Cl₂ (3 × 10 mL) was used to extract the mixture, and the combined extracts were dried by anhydrous Na₂SO₄, filtered, and concentrated to give a residue. The residue was further purified by chromatography and obtained as a white powder (0.68 g, 47% yield).

2.2. Synthesis of Complexes 1–6. All Cu(I) complexes were prepared by the following method. A mixture of copper(I) halide (1 mmol) and ppda or pfda (1 mmol) in 30 mL of CH₃CN was stirred for 2 days at room temperature to form a suspension which was then filtered off. The filtrate was concentrated to give a residue. The residue was dissolved in CH_2Cl_2/CH_3CN , and complexes were obtained as colorless crystals for 1 and yellow crystals for 2–6 after slow evaporation at room temperature.

3. RESULTS AND DISCUSSION

3.1. Syntheses and Characterizations. Scheme 1 presents the synthetic routes to ppda, pfda, and complexes 1–6. The synthesis of 2-dimethylamino-5-(trifluoromethyl)-phenyllithium was accomplished in a mixture of 2-bromo-*N*,*N*-

dimethyl-5-(trifluoromethyl)aniline and *n*-butyllithium with an equal mole in THF at -78 °C under nitrogen. After the addition of PPhCl₂ to 2-dimethylamino-5-(trifluoromethyl)-phenyllithium, pfda was prepared in 47% yield. Complexes **1**–**6** were obtained in 76–84% yields by the reaction of CuX in acetonitrile with 1 equiv of ppda and pfda. Six complexes are stable in air and dissolved in solvents of acetonitrile and chloroform. Their structures were identified (Figures 1 and S1–S22).

Figure 1 presents the perspective views of complexes 1-6, and Tables S1 and 1 give the crystallographic data and some bond lengths and angles. One solvent CH₃CN molecule is in complex 6. Two copper(I) are tetrahedrally connected to two halogen atoms and a N and a P from the ppda and pfda ligands, respectively. Complexes 1-5 have a planar Cu₂X₂ with centrosymmetry, whereas complex 6 has a mirror symmetric form with a butterfly-shaped Cu₂X₂, where Cu and Cl atoms are not located in one plane with a distinct dihedral angle Cl1-Cu2-Cu1-Cl2 of 160.82°. We found that, as the X radius increases, the bond lengths of Cu-X increase (Table 1). This trend is also found in the Cu1…Cu2 distances, which were widely reported to have important impacts on the emission of the multinuclear Cu(I) halide complexes. The Cu1…Cu2 distances are in the range of 3.014 and 3.471 Å (the sum of the van der Waals radius of copper is 2.8 Å), indicating negligible interaction between two Cu atoms in complexes 1-6. With careful contrast of previously reported $Cu_2X_2(PNMe_2)_2$ $(PNMe_2 = Ph_2P - (o - C_6H_4) - NMe_2)$ having nonplanar mirror symmetry and a butterfly-shaped Cu_2X_2 core (X = I and Br),¹⁹ the introduction of two NMe2 into the ligand ppda in complexes 2 and 3 leads to a structural change. A planar centrosymmetry motif and a larger Cu1…Cu2 distance is ascribed to the increased sterical requirement of ppda. The structures of the central Cu_2X_2 unit of complex 3 and $Cu_2Cl_2(PNMe_2)_2$ are similar, both of which are planar centrosymmetry and have similar Cu1...Cu2 distance (3.072 Å for 3 and 2.983 Å for $Cu_2Cl_2(PNMe_2)_2$). When two CF_3 groups are introduced into the ligand pfda, complexes 4 and 5 still have a centrosymmetric form with a planar Cu₂X₂, except





3

F(7)

N(3) Br(1) P(1) Cn(1 P(2) Cu(2) Br(2) 2 F(8) F(7) F(9) F(1) F(2) N(3) F(3) P(1) P(2 F(10) N(1) A N(4) F(11) F(12) F(4) F(5) F(6) F(1) F(7) F(8) F(2)





for complex 6, and the Cu1…Cu2 distances in complexes 4-6are shortened. The dihedral angles between the CuX₂ plane and bridging N,P phenyl ring plane in complexes 1-6 are shown in Table 2 and Figures S23-S28. The dihedral angles are on the order of 1 < 5 < 4 < 6 < 2 < 3. The two planes in complexes 2, 3, and 6 are close to orthogonal.

3.2. Photophysical, Redox Properties, and Theoretical Calculations. The absorption spectra of ligands ppda, pfda, and complexes 1-6 in $CH_2Cl_2(4 \times 10^{-5} \text{ M})$ at room temperature are displayed in Figure 2. The absorption spectra exhibit bands at 259 and 300 nm for ppda and 266 and 318 nm for pfda, which are ascribed to $n \to \pi^*$ and $\pi \to \pi^*$ transitions

of arylphosphine and arylamine. The absorption peak wavelength of pfda is red-shifted by about 7-18 nm compared to that of ppda. Complexes 1-3 show absorption peaks (269-271 nm), shoulders (305-314 nm), and tails (350-415 nm), and red-shifted bands are found in complexes 4-6 (274-278, 331-340, and 375-435 nm, respectively). Time-dependent density functional theory (TDDFT) calculations (Figures 3 and S44-S50 and Tables S3-S8) show that the transitions from HOMO to LUMO contribute to the lowest excited states for complexes 1 and 4-6, whereas for complexes 2 and 3, the transitions are from HOMO to LUMO+1. The shapes of the HOMO show that the electrons in the HOMO are largely pubs.acs.org/IC

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T	abl	le]	1. 9	Some	Bond	Lengths	(A)) and	Angl	les (deg)) of	Comp	lexes	1-	6
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complex	1	2	3	4	5	6·CH ₃ CN
Cu2-X1	2.5823(5)	2.4506(3)	2.3255(5)	2.6937(6)	2.5927(4)	2.3329(9)
Cu1-X1	2.7547(5)	2.4721(4)	2.3240(5)	2.5425(6)	2.3713(4)	2.3364(9)
Cu1-X2	2.5823(5)	2.4506(3)	2.3255(5)	2.6937(6)	2.5927(4)	2.3260(10)
Cu2-X2	2.7547(5)	2.4721(4)	2.3240(5),	2.5425(6)	2.3713(4)	2.3263(9)
Cu1-P1	2.2574(8)	2.2012(5)	2.1782(4)	2.2355(8)	2.2025(6)	2.1922(9)
Cu2-P2	2.2574(8)	2.2012(5)	2.1782(4)	2.2355(8)	2.2025(6)	2.1875(9)
Cu1-N1	2.292(3)	2.2899(13)	2.3692(16)	2.352(2)	2.3495(19)	2.354(3)
Cu2-N2	2.292(3)	2.2899(13)	2.3692(16)	2.352(2)	2.3495(19)	2.345(3)
Cu1…Cu2	3.471	3.133	3.072	3.053	3.050	3.014
P1-Cu1-N1	82.64(7)	84.54(3)	82.41(4)	81.06(5)	81.58(5)	82.88(7)
P2-Cu2-N2	82.64(7)	84.54(3)	82.41(4)	81.06(5)	81.58(5)	83.33(7)
X1-Cu1-X2	98.937(16)	100.956(10)	97.278(16)	108.74(2)	104.336(13)	97.50(3)
X1-Cu2-X2	98.937(16)	100.956(10)	97.278(16)	108.74(2)	104.336(13)	97.61(3)
Cu1-X1-Cu2	81.062(16)	79.043(10)	82.722(16)	71.26(2)	75.664(13)	80.39(3)
Cu1-X2-Cu2	81.062(16)	79.043(10)	82.722(16)	71.26(2)	75.664(13)	80.75(3)
X1-Cu2-Cu1-X2	0	0	0	0	0	160.82

Table 2. Dihedral Angles between the CuX_2 Plane and Bridging N,P Phenyl Ring in Complexes 1-6



Figure 2. Absorption spectra of ppda, pfda, and complexes 1-6 in CH_2Cl_2 at room temperature. The inset shows magnified absorption edges.

concentrated on the Cu, X, P, and N atoms, while the LUMO levels primarily distribute to the bridging N,P phenyl rings in ligands; similar cases are found in LUMO+1. Therefore, the lowest excited states are composed of (metal+halide) to ligand and intraligand charge transitions. Similar red shifting (5–26 nm) is observed for the absorption bands of **4–6** when compared to that with **1–3**, which is attributed to the reduced LUMO level by electron-withdrawing CF₃.

The electrochemical properties of 1-6 were determined by cyclic voltammetry (CV). Cyclic voltammograms of complexes 1-6 in 10^{-3} M CH₂Cl₂ and TBAPF₆ (0.1 M), potential data, energy levels, and gaps are shown in Figure S29 and Table S9. Cathodic peak potentials of complexes 1-6 are located at approximately -0.94 to -1.70 V, which correspond to the reduction of ligand. The first and second anodic waves were attributed to the oxidation of Cu⁺ and ligand, respectively. Compared with the lowest potential of complex 3, complex 1

has the highest first anodic wave, indicating a good stabilization of Cu^+ . We speculate that the electronic effect of groups linked to the Cu^+ center is not the main reason but steric hindrance is, which suppresses the distortion of geometry from tetrahedron to square planar, so the oxidation of Cu^+ becomes more difficult and the resulting Cu^{2+} is therefore more destabilized.

Complexes 1, 4, and 5 show intense blue to greenish yellow emissions (443-570 nm) with $\Phi_{\rm PL} = 0.05-0.48$, and complexes 2, 3, and 6 exhibit very weak greenish yellow to yellow emissions (534–595 nm) with $\Phi_{\rm PL}$ < 0.0001 at 297 K (Figure 4 and Table 3). The emission maxima of 1 is blueshifted by 31 nm compared to that of previously reported $Cu_2I_2(PNMe_2)_2$;¹⁹ as we anticipated, two electron-donating NMe₂ on the ortho-position of P-linked phenyl rings in ligand ppda can raise the LUMO level. To the best of our knowledge, this has been the first reported efficient blue light with emission maxima shorter than 440 nm from neutral dinuclear Cu(I) halide complexes. Based on the emission curve in a solid at 297 K, the CIE color coordinates of complexes 1-6 are (0.168, 0.179), (0.415, 0.456), (0.339, 0.478), (0.401, 0.514),(0.453, 0.510), and (0.500, 0.478), respectively (Figure 5). Large red-shifting of 61-105 nm for the emission bands of complexes 4 and 6 are found in comparison to those of 1 and 3, possibly ascribed to two electron-withdrawing CF_3 , which lower the LUMO level. The emission maximum of 5 is blueshifted by 4 nm compared to 2. According to the TDDFT calculation, the emission properties of complexes 2-6 were also estimated (the optimized S_1 geometry of complex 1 failed even if tried by many methods). The calculated emission wavelengths of complexes 2-5 (Table 3) are in accord with the experimental data. The contribution to the emission of complexes 2-6 mainly comes from the LUMO \rightarrow HOMO transition. The shapes of HOMOs and LUMOs and S₁ state geometries are presented in Figure 6. The HOMOs are mostly confined to Cu, X, and P and N in ligands ppda and pfda, and the LUMOs are largely concentrated on the bridging N,P phenyl ring. Therefore, the emission primarily comes from (metal + halide) to ligand and intraligand charge transitions.

The emission peak wavelengths of complexes 1-6 are located at 422–626 nm at 77 K. The emission curves of 1, 2, 4, and 5 are red-shifted compared to those at 297 K and can be explained by the dominated thermal population of a lower





excited state (T_1) at low temperature.⁴² For complexes 3 and 6, blue-shifting of the emission bands can be attributed to the changes of vibrations and rotations that suppressed the energy relaxation of the excited state.⁴² The lifetimes (Table 3 and Figures S32–S43) of 1, 4, and 5 at 297 K are 19.2, 1.1, and 0.4 μ s, respectively, which are 30–505 times shorter than that at 77 K, exhibiting the possible existence of a different emission interexchangeable and thermally activated process.¹⁹ Based on

the fluorescence and phosphorescence spectra onsets, the S_1 and T_1 energy levels are estimated (Table 3 and Figure 4), and $\Delta E(S_1 - T_1)$ values are at 0.095-0.1667 eV for complexes 1, 4, and 5, indicating they show efficient thermally activated delayed fluorescence.^{13,14,19} Complexes 2, 3, and 6 do not show efficient TADF behaviors, which are ascribed to the much larger $\Delta E(S_1 - T_1)$ values (0.3373-0.4184 eV), and that is why they display prompt fluorescence with nanosecond



Figure 4. Emission and normalized emission spectra of 1-6 in solid at 297 K [(a,b) $\lambda_{ex} = 365$ for 1, 375 for 2 and 3, 378 nm for 4-6)] and 77 K [(c) $\lambda_{ex} = 365$ for 1, 420 for 2, 360 for 3 and 5, 378 nm for 4 and 6)].

Table 3. Photophysical Data of 1-6 in a Solid



Figure 5. CIE graph of complexes 1-6.

lifetimes (4.4–9.3 ns). Additionally, the dihedral angles between the CuX₂ plane and bridging N,P phenyl ring plane in complexes **2**, **3**, and **6** (82.53–88.18°) are much larger than those in complexes **1**, **4**, and **5** (67.31–70.81°) (Table 2 and Figures S23–S28). Generally, $\Delta E(S_1 - T_1)$ relies on the exchange integral between S_1 and T_1 or approximated between the HOMO and the LUMO.⁴³ The less overlap between the frontier orbitals, the less mixing of these states, thus the less $\Delta E(S_1 - T_1)$ value, which also results in less distortion upon excitation and helps to increase the photoluminescence quantum yield.^{44–47} Therefore, substituted groups can play a very important role in sterically controlling the orientation of ligands and varying the photophysical property of complexes. The radiative rate constants k_r of complexes **1**, **4**, and **5** were calculated to be 2.5×10^4 to $1.25 \times 10^5 \text{s}^{-1}$, similar to those previously reported for Cu(I) halide complexes Cu₂X₂(PNMe₂).¹⁹

To confirm the existence of TADF, complex 4 was as a representative, and its decay times (τ_{obs}) were measured in the temperature range between 77 and 297 K (Figure 7). With thermally equilibrated S_1 and T_1 states assumed, the relationship between the decay time and temperature is shown in eq 1:

	$\lambda_{\max} (nm)^{a}$		$\tau \ (\mu s)^{b}$		Φ^c	$k_r^{d} (10^5 \text{ s}^{-1})$				
	297 K	77 K	297 K	77 K	297 K	297 K	$E(S_1)^e$ (eV)	$E(T_1)^e$ (eV)	$\Delta E (S_1 - T_1)^e (eV)$	$\lambda (nm)^{f}$
1	443	454	19.2	577	0.48	0.25	3.2461	3.1392	0.1069	
2	417*, 574	465*, 626	0.0057	2.1	< 0.0001		2.8182	2.4125	0.4047	549
3	534	422, 552*	0.0093	0.00048	< 0.0001		2.9594	2.5410	0.4184	584
4	548	551	1.1	112	0.11	1.00	2.9040	2.7373	0.1667	611
									0.1085 ^g	
5	570	576	0.4	202	0.05	1.25	2.8506	2.7556	0.095	617
6	595	582	0.0044	1.7	< 0.0001		2.9314	2.5941	0.3373	520

^{*a*}Emission peak wavelength. Asterisks indicate that emission peaks appear as shoulders or weak bands. ^{*b*}Average lifetime. ^{*c*}Absolute emission quantum. ^{*d*}Radiative decay rate constant; $k_r = \Phi/\tau_{ave}$. ^{*c*}The S_1 and T_1 energy levels were estimated based on the emission peak onsets at 297 and 77 K. ^{*f*}Calculated emission wavelengths according to the S_1 geometries optimized. ^{*g*} $E(S_1)$ and $E(T_1)$ are the vertical excitation energies, $\Delta E(S_1 - T_1) = E(S_1) - E(T_1)$.



Figure 6. S_1 geometry optimized and shapes of HOMOs and LUMOs of 2-6.

$$\tau_{\rm obs} = \frac{1 + \frac{1}{3} \exp\left(-\frac{\Delta E_{ST}}{K_{\rm B}T}\right)}{\frac{1}{\tau(T_{\rm l})} + \frac{1}{3\tau(S_{\rm l})} \exp\left(-\frac{\Delta E_{ST}}{K_{\rm B}T}\right)}$$
(1)

where $K_{\rm B}$, T, $\tau(S_1)$, $\tau(T_1)$, and ΔE_{ST} are the Boltzmann constant, the absolute temperature, the lifetimes of S_1 and T_1 , and the energy separation between S_1 and T_1 , respectively. In the temperature range, the lifetime is single-exponential. Equation 1 is fitted to the lifetime measured at various temperatures, and then lifetimes at S_1 (10.32 ns), T_1 (108.7 μ s), and ΔE_{ST} (0.103 eV) were obtained. The short lifetime of 10.32 ns substantiates its S_1 character. Therefore, the lifetime at 297 K of $\tau = 1.1 \ \mu$ s represents a delayed fluorescence. The fitted (T_1) lifetime (108.7 μ s) approximates the measured lifetime of 112 μ s of 4 at 77 K, and the $\Delta E_{\rm ST}$ (0.103 eV) is similar to the calculated one (0.1085 eV) (Figure 7 and Table 3). At temperatures below 100 K, complex 4 emits almost pure phosphorescence. As the temperature increases, the emission from the phosphorescence (T_1) decreases, and accordingly, the emission from the TADF increases.

By TDDFT calculation, the coordinative geometries of the Cu center in the optimized S_0 , S_1 , and T_1 (Table S1 and Figure S51) are tetrahedrally distorted. P-Cu-N bond angles in S_0 and S_1 geometries remain nearly unchanged. This can be attributed to the rigid ligands ppda and pfda. Larger changes in bond angles of P-Cu-X, N-Cu-X, and X-Cu-X may lead



Figure 7. Temperature versus decay lifetime of complex 4 and a fit curve.



Figure 8. TGA curves of complexes 1-6.

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to a Jahn–Teller distortion of excited states¹⁵ and thus lower emissive intensity.

3.3. Thermal Properties. For OLED applications, good thermal stabilities of emissive materials are required. Thus, thermogravimetric analysis (TGA) under nitrogen for complexes 1–6 was conducted to determine the onset decomposition temperatures (T_{dec}). It was found that 1–6 are thermally stable, with the T_{dec} values over 250 °C (Figure 8, 305–367 °C for complexes 1–3 and 268–281 °C for complexes 4–6), which meets the demand for OLED operating temperature. The introduction of two CF₃ groups in ligand pfda can make complexes 4–6 decompose more easily, ascribed to the distinct elongation of Cu–N and Cu–P bonds in complexes 4–6. Complex 1–3 lose approximately. 61–77% weight at 419–486 °C, and complexes 4–6 lose approximately 69–85% weight at 307–354 °C, which corresponds to the loss of two ligands ppda and pfpa.

3.4. Electroluminescent Properties. Complex 4 was used as the emitting material in solution-processed devices with the structure of ITO/PEDOT:PSS (40 nm)/complex 4 (20 nm)/TPBi (30 nm)/LiF (1 nm)/Al (100 nm): ITO, anode; Al, cathode; PEDOT:PSS, hole injection layer; TPBi, electron transporting layer; LiF, electron injecting layer. Figure 9a shows the energy level diagram. This device emits yellow green light (λ_{em} = 564 nm) with CIE coordinated at (0.41, 0.51). Figure 9c,d presents the EQE up to 0.17%, and the maximum luminance reaches 75.52 cd/m². Additionally, several doped devices with CBP as host materials were fabricated. However, the doped devices did not exhibit satisfactory results (Figure S52), which is possibly ascribed to the mismatching of CBP and complex 4 in energy level. Therefore, a matching host material is required to enhance device performance.

4. CONCLUSIONS

This is the first reported efficient blue light with emission maxima shorter than 440 nm from dinuclear Cu(I) halide complexes containing *tert*-amines and phosphines. The



Figure 9. (a) Energy-level drawing of the device; (b) electroluminescence spectra and corresponding CIE; (c) *J*–*V*–*L* characteristics; (d) EQE–luminance characteristics.

introduction of two electron-donating NMe2 into the orthoposition of two P-linked phenyl rings in ligand ppda and two electron-withdrawing CF₃ into the meta-position of NMe₂ in ligand pfda can sterically control the orientation of the ligands and vary the photophysical properties of the complexes. The emission color can change from blue to yellow. Complexes 1, 4, and 5 show delayed fluorescence, and complexes 2, 3, and 6 show prompt fluorescence, due to the difference in $\Delta E(S_1 - S_2)$ T_1) values (small for the former, and large for the latter). In addition, $\Delta E(S_1 - T_1)$ values depend on the dihedral angles between the CuX₂ plane and the bridging N,P phenyl ring plane, where two nearly orthogonal planes result in the large overlap between the HOMO and the LUMO and large $\Delta E(S_1)$ $-T_1$) values. It is evident that the investigation of the relationship between structure and property helps us to understand the emitting process in guarding further studies and application in OLEDs.

ASSOCIATED CONTENT

3 Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c03755.

NMR and mass data, molecular structures, cyclic voltammograms, photophysical data, computational details, and device performance of the doped device (PDF)

Accession Codes

CCDC 1897752–1897754 and 2051929–2051931 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/ data_request/cif, or by emailing data_request@ccdc.cam.ac. uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

AUTHOR INFORMATION

Corresponding Authors

- Li Liu Ministry of Education Key Laboratory for the Synthesis and Application of Organic Functional Molecules, Collaborative Innovation Center for Advanced Organic Chemical Materials Co-constructed by the Province and Ministry, Hubei University, Wuhan 430062, P.R. China;
 orcid.org/0000-0002-3684-4032; Email: liulihubei@ hubu.edu.cn
- Xin-Xin Zhong Ministry of Education Key Laboratory for the Synthesis and Application of Organic Functional Molecules, Collaborative Innovation Center for Advanced Organic Chemical Materials Co-constructed by the Province and Ministry, Hubei University, Wuhan 430062, P.R. China; Email: xxzhong@hubu.edu.cn
- Lei Wang Wuhan National Laboratory for Optoelectronics, Huazhong University of Science and Technology, Wuhan 430074, P.R. China; orcid.org/0000-0002-2141-3256; Email: wanglei@mail.hust.edu.cn
- Wai-Yeung Wong Department of Applied Biology and Chemical Technology, The Hong Kong Polytechnic University, Hong Kong, P.R. China; orcid.org/0000-0002-9949-7525; Email: wai-yeung.wong@polyu.edu.hk

Authors

Ke Xu – Ministry of Education Key Laboratory for the Synthesis and Application of Organic Functional Molecules, Collaborative Innovation Center for Advanced Organic Chemical Materials Co-constructed by the Province and Ministry, Hubei University, Wuhan 430062, P.R. China

- Bu-Lin Chen Ministry of Education Key Laboratory for the Synthesis and Application of Organic Functional Molecules, Collaborative Innovation Center for Advanced Organic Chemical Materials Co-constructed by the Province and Ministry, Hubei University, Wuhan 430062, P.R. China
- Fei Yang Wuhan National Laboratory for Optoelectronics, Huazhong University of Science and Technology, Wuhan 430074, P.R. China
- Xun-Jin Zhu Department of Chemistry, Hong Kong Baptist University, Hong Kong, P.R. China; © orcid.org/0000-0001-7929-6964
- Fa-Bao Li Ministry of Education Key Laboratory for the Synthesis and Application of Organic Functional Molecules, Collaborative Innovation Center for Advanced Organic Chemical Materials Co-constructed by the Province and Ministry, Hubei University, Wuhan 430062, P.R. China;
 orcid.org/0000-0002-1873-3128
- Hai-Mei Qin Department of Chemistry, Xiamen University, Xiamen 361005, P.R. China

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.inorgchem.0c03755

Author Contributions

K.X., B.-L.C., and F.Y. contributed equally to this work. The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

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ABBREVIATIONS

OLED, organic light-emitting diode; TADF, thermally activated delayed fluorescence; EQE, external quantum efficiency; HOMO, highest occupied molecular orbital; LUMO, lowest unoccupied molecular orbital; ITO, indium tin oxide; PEDOT, poly(3,4-ethylenedioxythiophene); PSS, poly(styrenesulfonate); TPBi, 1,3,5-tris(1-phenyl-1*H*-benzimidazol-2-yl)benzene; CBP, 1,3-bis(9-carbazolyl)benzene

REFERENCES

(1) Zhang, Q.; Komino, T.; Huang, S.; Matsunami, S.; Goushi, K.; Adachi, C. Triplet Exciton Confinement in Green Organic Light-Emitting Diodes Containing Luminescent Charge-Transfer Cu(I) Complexes. *Adv. Funct. Mater.* **2012**, *22*, 2327–2336.

(2) Tao, Y.; Yuan, K.; Chen, T.; Xu, P.; Li, H.; Chen, R.; Zheng, C.; Zhang, L.; Huang, W. Thermally Activated Delayed Fluorescence Materials Towards the Breakthrough of Organoelectronics. *Adv. Mater.* **2014**, *26*, 7931–7958.

(3) Huitorel, B.; El Moll, H.; Utrera-Melero, R.; Cordier, M.; Fargues, A.; Garcia, A.; Massuyeau, F.; Martineau-Corcos, C.; Fayon, F.; Rakhmatullin, A.; Kahlal, S.; Saillard, J.-Y.; Gacoin, T.; Perruchas, S. Evaluation of Ligands Effect on the Photophysical Properties of Copper Iodide Clusters. *Inorg. Chem.* **2018**, *57*, 4328–4339.

(4) Evariste, S.; Khalil, A. M.; Moussa, M. E.; Chan, A. K.-W.; Hong, E. Y.-H.; Wong, H.-L.; Le Guennic, B.; Calvez, G.; Costuas, K.; Yam, V. W.-W.; Lescop, C. Adaptive Coordination-driven Supramolecular Syntheses toward New Polymetallic Cu(I) Luminescent Assemblies. *J. Am. Chem. Soc.* **2018**, *140*, 12521–12526.

(5) El Sayed Moussa, M.; Khalil, A. M.; Evariste, S.; Wong, H.-L.; Delmas, V.; Le Guennic, B.; Calvez, G.; Costuas, K.; Yam, V. W.-W.; Lescop, C. Intramolecular Rearrangements Guided by Adaptive Coordination-driven Reactions toward Highly Luminescent Polynuclear Cu(I) Assemblies. *Inorg. Chem. Front.* **2020**, *7*, 1334–1344.

(6) Hupp, B.; Nitsch, J.; Schmitt, T.; Bertermann, R.; Edkins, K.; Hirsch, F.; Fischer, I.; Auth, M.; Sperlich, A.; Steffen, A. Stimulustriggered Anion-Cation-Exciplex Formation in Copper(I)-Complexes as new Mechanism for Mechanochromic Phosphorescence. *Angew. Chem., Int. Ed.* **2018**, *57*, 13671–13675.

(7) Hupp, B.; Schiller, C.; Lenczyk, C.; Stanoppi, M.; Edkins, K.; Lorbach, A.; Steffen, A. Synthesis, Structures, and Photophysical Properties of a Series of Rare Near-IR Emitting Copper(I) Complexes. *Inorg. Chem.* **2017**, *56*, 8996–9008.

(8) Chakkaradhari, G.; Eskelinen, T.; Degbe, C.; Belyaev, A.; Melnikov, A. S.; Grachova, E. V.; Tunik, S. P.; Hirva, P.; Koshevoy, I. O. Oligophosphine-thiocyanate Copper(I) and Silver(I) Complexes and Their Borane Derivatives Showing Delayed Fluorescence. *Inorg. Chem.* **2019**, *58*, 3646–3660.

(9) Chakkaradhari, G.; Chen, Y. T.; Karttunen, A. J.; Dau, M. T.; Janis, J.; Tunik, S. P.; Chou, P. T.; Ho, M. L.; Koshevoy, I. O. Luminescent Triphosphine Cyanide d^{10} Metal Complexes. *Inorg. Chem.* **2019**, *58*, 2174–2184.

(10) Czerwieniec, R.; Leitl, M. J.; Homeier, H. H. H.; Yersin, H. Cu(I) ComplexesoThermally Activated Delayed Fluorescence. Photophysical Approach and Material Design. *Coord. Chem. Rev.* 2016, 325, 2–28.

(11) Yersin, H.; Czerwieniec, R.; Shafikov, M. Z.; Suleymanova, A. F. TADF Material Design - Photophysical Background and Case Studies Focusing on Cu(I) and Ag(I) Complexes. *ChemPhysChem* **2017**, *18*, 3508–3535.

(12) Yersin, H., Ed. Highly Efficient OLEDs-Materials Based on Thermally Activated Delayed Fluorescence; Wiley-VCH: Weinheim, Germany, 2019.

(13) Li, G.; Nobuyasu, R. S.; Zhang, B.; Geng, Y.; Yao, B.; Xie, Z.; Zhu, D.; Shan, G.; Che, W.; Yan, L.; Su, Z.; Dias, F. B.; Bryce, M. R. Thermally Activated Delayed Fluorescence in CuI Complexes Originating from Restricted Molecular Vibrations. *Chem. - Eur. J.* **2017**, *23*, 11761–11766.

(14) Brown, C. M.; Li, C.; Carta, V.; Li, W.; Xu, Z.; Stroppa, P. H. F.; Samuel, I. D. W.; Zysman-Colman, E.; Wolf, M. O. Influence of Sulfur Oxidation State and Substituents on Sulfur-Bridged Luminescent Copper(I) Complexes Showing Thermally Activated Delayed Fluorescence. *Inorg. Chem.* **2019**, *58*, 7156–7168.

(15) Hashimoto, M.; Igawa, S.; Yashima, M.; Kawata, I.; Hoshino, M.; Osawa, M. Highly Efficient Green Organic Light-Emitting Diodes Containing Luminescent Three-Coordinate Copper(I) Complexes. J. Am. Chem. Soc. **2011**, 133, 10348–10351.

(16) Hamze, R.; Peltier, J. L.; Sylvinson, D.; Jung, M.; Cardenas, J.; Haiges, R.; Soleilhavoup, M.; Jazzar, R.; Djurovich, P. I.; Bertrand, G.; Thompson, M. E. Eliminating Nonradiative Decay in Cu(I) Emitters: > 99% Quantum Efficiency and Microsecond Lifetime. *Science* **2019**, 363, 601–606.

(17) Zhang, J.; Duan, C.; Han, C.; Yang, H.; Wei, Y.; Xu, H. Balanced Dual Emissions from Tridentate Phosphine-Coordinate Copper(I) Complexes toward Highly Efficient Yellow OLEDs. *Adv. Mater.* **2016**, *28*, 5975–5979.

(18) Volz, D.; Chen, Y.; Wallesch, M.; Liu, R.; Fléchon, C.; Zink, D. M.; Friedrichs, J.; Flügge, H.; Steininger, R.; Göttlicher, J.; Heske, C.; Weinhardt, L.; Bräse, S.; So, F.; Baumann, T. Bridging the Efficiency Gap: Fully Bridged Dinuclear Cu(I)-Complexes for Singlet Harvesting in High-Efficiency OLEDs. *Adv. Mater.* **2015**, *27*, 2538–2543.

(19) Leitl, M. J.; Küchle, F.; Mayer, H. A.; Wesemann, L.; Yersin, H. Brightly Blue and Green Emitting Cu(I) Dimers for Singlet Harvesting in OLEDs. J. Phys. Chem. A 2013, 117, 11823–11836.

(20) Tsuboyama, A.; Kuge, K.; Furugori, M.; Okada, S.; Hoshino, M.; Ueno, K. Photophysical Properties of Highly Luminescent Copper(I) Halide Complexes Chelated with 1,2-Bis-(diphenylphosphino)benzene. *Inorg. Chem.* 2007, 46, 1992–2001.

(21) Verma, A.; Zink, D. M.; Flechon, C.; Leganes Carballo, J.; Flugge, H.; Navarro, J. M.; Baumann, T.; Volz, D. Efficient, Inkjetprinted TADF-OLEDs with an Ultra-soluble NHetPHOS Complex. *Appl. Phys. A: Mater. Sci. Process.* **2016**, *122*, 191.

(22) Jia, J. H.; Chen, X. L.; Liao, J. Z.; Liang, D.; Yang, M. X.; Yu, R.; Lu, C. Z. Highly Luminescent Copper(I) Halide Complexes Chelated with a Tetradentate Ligand (PNNP): Synthesis, Structure, Photophysical Properties and Theoretical Studies. *Dalton Trans.* **2019**, *48*, 1418–1426.

(23) Zink, D. M.; Bächle, M.; Baumann, T.; Nieger, M.; Kühn, M.; Wang, C.; Klopper, W.; Monkowius, U.; Hofbeck, T.; Yersin, H.; Bräse, S. Synthesis, Structure, and Characterization of Dinuclear Copper(I) Halide Complexes with PN Ligands Featuring Exciting Photoluminescence Properties. *Inorg. Chem.* **2013**, *52*, 2292–2305.

(24) Kang, L.; Chen, J.; Teng, T.; Chen, X. L.; Yu, R.; Lu, C. Z. Experimental and Theoretical Studies of Highly Emissive Dinuclear Cu(I) Halide Complexes with Delayed Fluorescence. *Dalton Trans.* **2015**, *44*, 11649–11659.

(25) Li, X.; Zhang, J.; Zhao, Z.; Yu, X.; Li, P.; Yao, Y.; Liu, Z.; Jin, Q.; Bian, Z.; Lu, Z.; Huang, C. Bluish-green Cu(I) Dimers Chelated with Thiophene Ring-introduced Diphosphine Ligands for Both Singlet and Triplet Harvesting in OLEDs. ACS Appl. Mater. Interfaces **2019**, *11*, 3262–3270.

(26) Li, X.; Zhang, J.; Wei, F.; Liu, X.; Liu, Z.; Bian, Z.; Huang, C. A Series of Dinuclear Cuprous Iodide Complexes Chelated with 1,2-Bis(diphenylphosphino)benzene Derivatives: Structural, Photophysical and Thermal Properties. *CrystEngComm* **2016**, *18*, 4388–4394.

(27) Okano, Y.; Ohara, H.; Kobayashi, A.; Yoshida, M.; Kato, M. Systematic Introduction of Aromatic Rings to Diphosphine Ligands for Emission Color Tuning of Dinuclear Copper(I) Iodide Complexes. *Inorg. Chem.* **2016**, *55*, 5227–5236.

(28) Gibbons, S. K.; Hughes, R. P.; Glueck, D. S.; Royappa, A. T.; Rheingold, A. L.; Arthur, R. B.; Nicholas, A. D.; Patterson, H. H. Synthesis, Structure, and Luminescence of Copper(I) Halide Complexes of Chiral Bis(phosphines). *Inorg. Chem.* **2017**, *56*, 12809–12820.

(29) Chen, B.; Liu, L.; Zhong, X. X.; Asiri, A. M.; Alamry, K. A.; Li, G. H.; Li, F. B.; Zhu, N. Y.; Wong, W. Y.; Qin, H. M. Synthesis, Characterization and Luminescent Properties of Copper(I) Halide Complexes Containing Biphenyl Bidentate Phosphine Ligand. *J. Coord. Chem.* **2017**, *70*, 3907–3919.

(30) Wei, Q.; Chen, H.-T.; Liu, L.; Zhong, X.-X.; Wang, L.; Li, F.-B.; Cong, H.-J.; Wong, W.-Y.; Alamry, K. A.; Qin, H.-M. Syntheses and Photoluminescence of Copper(I) Halide Complexes Containing Dimethylthiophene Bidentate Phosphine Ligands. *New J. Chem.* **2019**, *43*, 13408–13417.

(31) Hong, X.; Wang, B.; Liu, L.; Zhong, X. X.; Li, F. B.; Wang, L.; Wong, W. Y.; Qin, H. M.; Lo, Y. H. Highly Efficient Blue-green Neutral Dinuclear Copper(I) Halide Complexes Containing Bidentate Phosphine Ligands. *J. Lumin.* **2016**, *180*, 64–72.

(32) Wallesch, M.; Verma, A.; Fléchon, C.; Flügge, H.; Zink, D. M.; Seifermann, S. M.; Navarro, J. M.; Vitova, T.; Göttlicher, J.; Steininger, R.; Weinhardt, L.; Zimmer, M.; Gerhards, M.; Heske, C.; Bräse, S.; Baumann, T.; Volz, D. Towards Printed Organic Light-Emitting Devices: A Solution-Stable, Highly Soluble CuI-NHetPHOS Complex for Inkjet Processing. *Chem. - Eur. J.* **2016**, *22*, 16400– 16405.

(33) Volz, D.; Zink, D. M.; Bocksrocker, T.; Friedrichs, J.; Nieger, M.; Baumann, T.; Lemmer, U.; Bräse, S. Molecular Construction Kit for Tuning Solubility, Stability and Luminescence Properties: Heteroleptic MePyrPHOS-Copper Iodide-Complexes and their Application in Organic Light-Emitting Diodes. *Chem. Mater.* 2013, 25, 3414–3426.

(34) Araki, H.; Tsuge, K.; Sasaki, Y.; Ishizaka, S.; Kitamura, N. Luminescence Ranging from Red to Blue: A Series of Copper(I)-Halide Complexes Having Rhombic $\{Cu_2(\mu - X)_2\}$ (X = Br and I) Units with N-Heteroaromatic Ligands. *Inorg. Chem.* **2005**, *44*, 9667–9675.

(35) Araki, H.; Tsuge, K.; Sasaki, Y.; Ishizaka, S.; Kitamura, N. Synthesis, Structure, and Emissive Properties of Copper(I) Complexes $[Cu^{I}_{2}(\mu-X)_{2}(\mu-1,8\text{-naphthyridine})(PPh_{3})_{2}]$ (X = I, Br) with a Butterfly-Shaped Dinuclear Core Having a Short Cu-Cu Distance. *Inorg. Chem.* **2007**, *46*, 10032–10034.

(36) Liang, P.; Kobayashi, A.; Sameera, W. M. C.; Yoshida, M.; Kato, M. Solvent-Free Thermal Synthesis of Luminescent Dinuclear Cu(I) Complexes with Triarylphosphines. *Inorg. Chem.* **2018**, *57*, 5929–5938.

(37) Kamtekar, K. T.; Monkman, A. P.; Bryce, M. R. Recent Advances in White Organic Light-Emitting Materials and Devices (WOLEDs). *Adv. Mater.* **2010**, *22*, 572–582.

(38) Zou, S. J.; Shen, Y.; Xie, F. M.; Chen, J. D.; Li, Y. Q.; Tang, J. X. Recent Advances in Organic Light-Emitting Diodes: Toward Smart Lighting and Displays. *Mater. Chem. Front.* **2020**, *4*, 788–820.

(39) Wei, Q.; Zhang, R.; Liu, L.; Zhong, X. X.; Wang, L.; Li, G. H.; Li, F. B.; Alamry, K. A.; Zhao, Y. From Deep Blue to Green Emitting and Ultralong Fluorescent Copper(I) Halide Complexes Containing Dimethylthiophene Diphosphine and PPh₃ ligands. *Dalton Trans.* **2019**, *48*, 11448–11459.

(40) Guo, B. K.; Yang, F.; Wang, Y. Q.; Wei, Q.; Liu, L.; Zhong, X. X.; Wang, L.; Gong, J. K.; Li, F. B.; Wong, W. Y.; Alamry, K. A.; Zhao, Y. Efficient TADF-OLEDs with Ultra-soluble Copper(I) Halide Complexes Containing Non-symmetrically Substituted Bidentate Phosphine and PPh₃ ligands. *J. Lumin.* **2020**, *220*, 116963.

(41) Zhang, W. J.; Zhou, Z. X.; Liu, L.; Zhong, X. X.; Asiri, A. M.; Alamry, K. A.; Li, F. B.; Zhu, N. Y.; Wong, W. Y.; Qin, H. M. Highlyefficient Blue Neutral Mononuclear Copper(I) Halide Complexes Containing Bi- and Mono-dentate phosphine ligands. *J. Lumin.* **2018**, *196*, 425–430.

(42) Osawa, M.; Hoshino, M.; Hashimoto, M.; Kawata, I.; Igawa, S.; Yashima, M. Application of Three-coordinate Copper(I) Complexes with Halide Ligands in Organic Light-emitting Diodes that Exhibit Delayed Fluorescence. *Dalton Trans.* **2015**, *44*, 8369–8378.

(43) Wallesch, M.; Volz, D.; Zink, D. M.; Schepers, U.; Nieger, M.; Baumann, T.; Bräse, S. Bright Coppertunities: Multinuclear CuI Complexes with N-P Ligands and Their Applications. *Chem. - Eur. J.* **2014**, 20, 6578–6590.

(44) Penfold, T. J.; Karlsson, S.; Capano, G.; Lima, F. A.; Rittmann, J.; Reinhard, M.; Rittmann-Frank, M. H.; Braem, O.; Baranoff, E.; Abela, R.; Tavernelli, I.; Rothlisberger, U.; Milne, C. J.; Chergui, M. Solvent-Induced Luminescence Quenching: Static and Time-Resolved X-Ray Absorption Spectroscopy of a Copper(I) Phenanthroline Complex. J. Phys. Chem. A **2013**, 117, 4591–4601.

(45) Yersin, H.; Finkenzeller, W. J.; Walter, M. J.; Djurovich, P. I.; Thompson, M. E.; Tsuboyama, A.; Okada, S.; Ueno, K.; Chi, Y.; Chou, P.-T.; Yang, X.-H.; Jaiser, F.; Neher, D.; Xiang, H. F.; Lai, S. W.; Lai, P. T.; Che, C. M.; Tanaka, I.; Tokito, S.; Dijken, A. Van; Brunner, K.; Börner, H.; Langeveld, B. M. W.; Mak, C. S. K.; Nazeeruddin, M. K.; Klein, C.; Grätzel, M.; Zuppiroli, L.; Berner, D.; Bian, Z. Q.; Huang, C. H. Highly Efficient OLEDs with Phosphorescent Materials, 1st ed.; Wiley-VCH: Weinheim, Germany, 2008.

(46) Bässler, H.; Köhler, A. Charge Transport in Organic Semiconductors. *Top. Curr. Chem.* **2011**, *312*, 1–66.

(47) Uoyama, H.; Goushi, K.; Shizu, K.; Nomura, H.; Adachi, C. Highly Efficient Organic Light-emitting Diodes from Delayed Fluorescence. *Nature* **2012**, *492*, 234–238.