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Synthesis, characterization and luminescent properties of copper(1) halide complexes containing biphenyl bidentate phosphine ligand

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Copper(I) halide complexes having thermally activated delayed fluorescence (TADF) and phosphorescence have attracted much attention. Here, a series of four-coordinate dinuclear copper(I) halide complexes, $[CuX(bpbp)]_2$ (bpbp = 2,2'-bis(diphenylphosphino)biphenyl, X = I (1), Br (2) and Cl (3)), were synthesized, and their molecular structures and photophysical

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properties were investigated. The structural analysis reveals that two copper(I) centers are bridged by two halogen ligands to form a dinuclear structure with a four-membered Cu₂X₂ ring. These complexes exhibit yellow to blue emission in the solid state at room temperature and have peak emission wavelengths at 575-487 nm with microsecond lifetimes ($\tau = 6.2$ -19.8 µs) and low emission quantum yields (<0.01%). The emissions of **1-3** originate from MLCT, XLCT and IL (intraligand) transitions. Three complexes displayed good thermal stability.

Keywords: Neutral; Cu(I) Complexes; Photoluminescence; Synthesis; 2,2'-Bis(diphenylphosphino)biphenyl

1. Introduction

Since Tang and VanSlyke reported the first OLED, various Ir [1], Pt [2], and Os [3] based emitters have been investigated with respect to both increasing the quantum efficiency and allowing for color tuning. As an attractive alternative to expensive, less abundant, and more toxic heavy metals, electroluminescent materials containing Cu(I)-organic compounds have become popular over the past decade [4-16]. Cu(I) is the most widely investigated typical d¹⁰ metal used to construct metal-organic complexes with low-lying metal-to-ligand charger transfer (MLCT) excited states and small singlet-triplet energy gap ($\Delta E(S_1-T_1)$), thus efficiently harvesting triplet excitons for thermally activated delayed fluorescence (TADF) emission [17-19].

Cationic Cu(I) complexes based on α, α' -diimine and triphenylphosphine mixed ligands showing TADF and phosphorescence have become potential candidates for preparing highly efficient OLEDs [20, 21]. However, unexpected effects on the efficiency of OLED devices may result from the existence of counter ions in the cationic Cu(I) complexes, especially under high electrical fields [22, 23].

Photophysical studies of neutral Cu(I) complexes showing TADF have received much attention [24-28]. Recently, a highly efficient green, three-coordinate Cu(I) halide complex containing bidentate 1,2-bis(*o*-ditolylphosphino)benzene with an external quantum efficiency

(EQE) over 20% has been reported [27]. Compared to a large number of cationic Cu(I) compounds, neutral Cu(I) complexes still remain relatively rare. There are only a few reports of devices fabricated by vacuum deposition containing neutral Cu(I) complexes [11, 27, 29-32]. Neutral Cu(I) halide complexes with bidentate phosphine ligands were rarely reported.

The preparation of neutral Cu(I) complexes using different halides and phosphine ligands is still a challenge. TADF in copper complexes is still difficult to predict, as it is an excited state property. As a continuation of our previous work on a series of neutral Cu(I) halide complexes [33], we report here a series of neutral luminescent four-coordinate dinuclear Cu(I) halide complexes containing the bidentate ligand 2,2'-bis(diphenylphosphino)biphenyl, and their molecular structures and photophysical properties were investigated.

2. Experimental

2.1. General methods

All reagents and solvents are of commercial reagent grade and used without purification except where noted. Copper(I) halides and 1,2-dibromobenzene were purchased from Aladdin Company and used without purification. Tetrahydrofuran (THF) was distilled under nitrogen in the presence of sodium chips using benzophenone ketyl as an indicator. Infrared spectra were recorded on KBr pellets on a Nicolet iS10 FTIR spectrometer. ¹H NMR spectra were recorded on a Varian 600 MHz NMR spectrometer using deuterated solvents as the lock and reference. Chemical shifts were reported in ppm relative to SiMe₄ for the ¹H and 85% H₃PO₄ for the ³¹P nucleus. High-resolution mass spectra reported as *m/z* were obtained on a Bruker Autoflex MALDI-TOF mass spectrometer. C and H analyses were determined using a Vario Micro Cube elemental analyzer. The single crystal structures of **1-3** were measured at room temperature using a Bruker APEX DUO or Bruker D8 Venture diffractometer. UV–vis spectra were recorded on a Unicam Heλios α spectrometer. Photoluminescence spectra were recorded on a FLS920 steady state and time-resolved fluorescence spectrometer. Solid-state Φ_{PL} values were determined using a Hamamatsu system for absolute PL quantum yield measurements 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 Diamond TG/DTA thermal analyzer.

2.2. Syntheses

2.2.1. Synthesis of (2-bromophenyl)diphenylphosphine. This compound was synthesized from a modification of the literature protocol [34]. A solution of *n*-BuLi (1.6 M in hexanes, 6.22 mL, 9.95 mmol) was added dropwise over 45 min to a solution of 1,2-dibromobenzene (2.35 g, 9.95 mmol) in Et₂O/THF (1/1 v/v, 50 mL) at -110 °C. After 30 min of stirring at the same temperature, a white precipitate appeared and chlorodiphenylphosphine (2.20 g, 9.95 mmol) was added dropwise. The mixture was then allowed to warm to room temperature overnight and the volatile components were removed under vacuum. The residue was taken up into CH₂Cl₂/Et₂O (1/2 v/v, 15 mL) and filtered through silica which was then washed with CH₂Cl₂/Et₂O (1/2 v/v, 9 mL). The filtrate was evaporated under reduced pressure to give the pure product as a white solid (2.44 g, 72%). The characterization data were identical to those previously reported in the literature [35].

2.2.2. Synthesis of 2,2'-bis(diphenylphosphino)biphenyl (bpbp). This compound was synthesized from a modified protocol of the literature [36]. To a solution of (2-bromophenyl)diphenylphosphine (0.41 g, 1.20 mmol) in THF (5 mL) was added at -78 °C under nitrogen *n*-BuLi (1.6 M in hexane) (0.75 mL, 1.20 mmol) and the resulting solution was stirred at this temperature during one hour. A solution of Fe(acac)₃ (0.51 g, 1.44 mmol) in THF (7 mL) was then added and the stirring was maintained for one hour at -78 °C. The solution was quenched with water (2 mL) and extracted with dichloromethane (3×10 mL). The organic phases were dried over MgSO₄ and the solvent evaporated under vacuum to give a residue which was purified by chromatographic column on silica gel using petroleum ether/dichloromethane (2/1)

as eluent. The titled compound was obtained as white solid (0.15 g, 48%). ¹H NMR (600 MHz, CDCl₃): δ 7.32-7.13 (m, 24H), 7.07 (d, *J* = 6 Hz, 2H), 6.90 (d, *J* = 6 Hz, 2H).

2.2.3. Synthesis of di(μ -iodo)bis[2,2'-bis(diphenylphosphino)biphenyl copper(I)] (1). A suspension of copper(I) iodide (0.057 g, 0.30 mmol) and bpbp (0.157 g, 0.30 mmol) in 30 mL of CH₂Cl₂ was stirred for 5 h at room temperature to form a white precipitate. The precipitate was filtered off and purified by recrystallization from CH₂Cl₂/CH₃CN to give colorless crystals (Yield: 0.165 g, 77%). ¹H NMR (600 MHz, CDCl₃) δ : 8.00-7.99 (m, 8H), 7.46-7.43 (m, 8H), 7.39-7.38 (m, 12H), 7.17 (t, *J* = 6 Hz, 4H), 7.08 (t, *J* = 6 Hz, 8H), 6.91 (t, *J* = 6 Hz, 4H), 6.83 (t, *J* = 9 Hz, 8H), 6.59 (d, *J* = 6 Hz, 4H). ³¹P NMR (240 M, CDCl₃) δ : -8.73 (s). Anal. Calcd for C₇₂H₅₆I₂Cu₂P₄: C, 60.64; H, 3.96. Found: C, 60.71; H, 3.93. MS (MALDI-TOF): *m/z* calcd for [C₃₆H₂₈CuP₂]⁺, 586.0996, found: 586.0936.

2.2.4. Synthesis of di(μ -bromo)bis[2,2'-bis(diphenylphosphino)biphenyl copper(I)] (2). Complex **2** was obtained by a similar method as described for **1** using copper(I) bromide (0.043 g, 0.30 mmol) in place of copper(I) iodide. Colorless crystals of **2** were obtained (Yield: 0.158 g, 79%). ¹H NMR (600 MHz, CDCl₃) δ : 7.98-7.91 (m, 8H), 7.54-7.53 (m, 8H), 7.21-7.15 (m, 16H), 7.10 (t, J = 9 Hz, 8H), 6.91 (t, J = 6 Hz, 4H), 6.87-6.84 (m, 4H), 6.81 (t, J = 6 Hz, 4H), 6.53 (d, J = 6 Hz, 4H). ³¹P NMR (240 M, CDCl₃) δ : -11.23 (s). Anal. Calcd for C₇₂H₅₆Br₂Cu₂P₄: C, 64.92; H, 4.24. Found: C, 64.98; H, 4.20. MS (MALDI-TOF): *m/z* calcd for [C₃₆H₂₈CuP₂]⁺, 586.0996, found: 586.0949.

2.2.5. Synthesis of di(µ-chloro)bis[2,2'-bis(diphenylphosphino)biphenyl copper(I)] (3).

Complex **3** was obtained by a similar method as described for **1** using copper(I) chloride (0.030 g, 0.30 mmol) in place of copper(I) iodide. Colorless crystals of **3** were obtained (Yield: 0.150 g, 80%). ¹H NMR (600 MHz, CDCl₃) δ : 7.99 (m, 8H), 7.53 (m, 8H), 7.22-7.10 (m, 24H), 6.89-6.79 (m, 12H), 6.57-6.56 (d, *J* = 6 Hz, 4H). ³¹P NMR (240 M, CDCl₃) δ : -10.20 (s). Anal. Calcd for

C₇₂H₅₆Cl₂Cu₂P₄: C, 69.57; H, 4.54. Found: C, 69.63; H, 4.51. MS (MALDI-TOF): *m/z* calcd for [C₃₆H₂₈CuP₂]⁺, 586.0996, found: 586.0925.

2.3. X-ray crystallography

Colorless crystals of **1-3** suitable for X-ray diffraction studies were grown by slow evaporation of their respective solutions in dichloromethane and acetonitrile at room temperature. Geometric and intensity data were collected using graphite-monochromated Mo K α radiation ($\lambda =$ 0.71073 Å) on a Bruker AXS APEX II CCD area detector. The collected frames were processed with the software *SAINT* [37], and an absorption correction was applied (*SADABS*) [38] to the collected reflections. The structures were solved by direct methods (*SHELXTL*) [39] in conjunction with standard difference Fourier techniques and subsequently refined by full-matrix least-squares analyses on F^2 . All non-hydrogen atoms were assigned with anisotropic displacement parameters.

2.4. Theoretical calculations

The structural parameters for **1-3** were obtained from the crystal data which are listed in tables 1 and 2. The density functional theory (DFT) and time-dependent density functional theory (TDDFT) calculations were then performed to compute the HOMO-LUMO energy gap, the natural bond orbital (NBO) analysis as well as the properties of the excited states. All the calculations were manipulated by the Gaussian 09 suite [40] at the B3LYP/DGDZVP level.

3. Results and discussion

3.1. Description of syntheses and structures

The synthetic routes for the Cu(I) complexes are outlined in scheme 1. First, the synthesis of 2bromophenyllithium was carried out in a mixture with the mole ratio of 1:1 for 1,2dibromobenzene and *n*-butyllithium. By the addition of chlorodiphenylphosphine to 2bromophenyllithium in THF at -110 °C under nitrogen, (2-bromophenyl)diphenylphosphine was synthesized in 72% yield. Then, 2-(diphenylphosphino)phenyllithium was synthesized in a similar way in a mixture of *n*-butyllithium and (2-bromophenyl)diphenylphosphine. Under the catalysis of Fe(III) acetylacetonato, 2,2'-bis(diphenylphosphino)biphenyl (bpbp) was obtained in 46% yield by the homocoupling of (2-bromophenyl)diphenylphosphine. Complexes 1-3 were prepared in 76-80% yield by mixing a suspension of CuX (X = I for 1, Br for 2, Cl for 3) in dichloromethane with 1 equiv of bpbp. All the new Cu(I) complexes were obtained as air stable solids in high purity and found to be generally soluble in CH_2Cl_2 . They all gave satisfactory analytical data and were characterized by NMR spectroscopy, MALDI-TOF spectrometry and single crystal X-ray diffraction.



Scheme 1. Synthetic pathways to ligand bpbp and their dinuclear copper(I) complexes.

3.2. X-ray crystallographic study

Perspective views of 1-3 are shown in figure 1. There is one solvent CH_3CN molecule in the structure of 1 and one CH_2Cl_2 molecule in 2. Crystallographic data and selected bond lengths and angles are given in tables 1 and 2, respectively. The copper(I) in 1-3 exhibits distorted tetrahedral coordination, with the X–Cu–X angles ranging from 95.01 to 97.60°. Two copper(I) centers are bridged by two halogen ligands to form a dinuclear structure with a four-membered Cu_2X_2 ring.

Compared with halogen-bridged copper complexes typically having a planar Cu₂X₂ geometry [33d, 41-43], **1-3** have approximately planar Cu₂X₂ geometries. The dihedral angles between two CuX₂ triangles in Cu₂X₂ are 173.17, 176.36 and 174.83° for **1**, **2** and **3**, respectively. As listed in table 2, the Cu–X distances of **1**, **2** and **3** elongate with an increase in the van der Waals radius of X. The Cu—Cu distances are 3.625, 3.404 and 3.149 Å for **1**, **2** and **3**, respectively, indicating a weak interaction between two copper atoms, as compared with the sum of van der Waals radius of copper (2.8 Å). In **1-3**, the distances of the halogen to the closest H, H…I, H…Br and H…Cl are 2.946, 2.851 and 2.591 Å, respectively, displaying potential hydrogen bonds. In solid state, **1-3** show intermolecular C–H… π interactions between phenyl rings attached to phosphorus with the closest C-to-H distances of 2.822 Å for **1**, 2.843 Å for **2** and 2.634 Å for **3**, respectively. The smallest dihedral angles between X–Cu–X plane and phenyl ring plane of biphenyl is 33.40° for **1**, 35.50° for **2** and 42.20° for **3**, respectively.

3.3. Photophysical properties

The absorption spectra of **1-3** and bpbp in CH₂Cl₂ at room temperature are shown in figure 2. The absorption spectrum of bpbp exhibits a broad, intense band at 272 nm ($\varepsilon = 6.69 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$), which is characteristic of an arylphosphine compound. This band is assigned to a mixed transition of n- π^* and π - π^* ; the former one involves the transition of an electron from the lone pair orbital on phosphorus to an empty antibonding π^* orbital on a phenyl ring or a biphenyl ring and the latter is the internal transition from a phenyl or a biphenyl ring or the electron transition from a biphenyl ring to a phenyl ring. Complexes **1-3** have an intense absorption band with a maximum at 268-275 nm [$\varepsilon = (2.51-3.01) \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$] and a broad shoulder at 297 nm and a weaker band tail at 340-400 nm. The weaker band tail may be attributed to the electronic transition affected by the copper ions, the halide ligands, or both or ligand-to-ligand charge transfer character.

As shown in figure 3, DFT calculations carried out for **1-3** reveal that the electrons in the highest occupied molecular orbital (HOMO) are mainly distributed over the copper, halogen

atoms and phosphorus atoms, while those in the lowest unoccupied molecular orbital (LUMO) are localized on the phenyl and biphenyl rings of bpbp. We can thus conclude that the lowest excited states of **1-3** consist of metal-to-ligand charge transfer (MLCT), a halogen-to-ligand charge transfer (XLCT) state, and an intraligand transition, analogous to those in related tetrahedral complexes [11, 44, 45].

The emission spectra of **1-3** in the solid state measured at 298 and 77 K are shown in figure 4. Summarized in table 3 are the emission maxima, lifetimes and quantum yields of the complexes at 298 and 77 K, and TDDFT calculation data based on the structures obtained by X-ray structural analysis. These emission bands are broad and unstructured, suggesting that the emissive excited states have charge-transfer character. At 293 K, **1-3** show yellow, blue and green emission with λ_{max} 575, 487 and 535 nm, respectively. The emission maxima and color can be largely tuned by the halogen, quite different from previously reported neutral Cu(I) halide phosphine complexes [11, 29, 30, 33]. From the observed long emission decay times between 6.2 and 19.8 µs at 293 K, which is 1 to 3 orders of magnitude shorter than those at 77 K, an occurrence of a TADF (thermally activated delayed fluorescence) is indicated [46-51].

At 77 K, the emission maxima of 1.3 are located at 472, 528 and 512 nm, respectively. For 2 and 3, the large Stokes shifts of these lower-lying emission peaks from the dipole-allowed absorptions, plus the long emission lifetimes (1834-3163 μ s), are indicative of their triplet parentage, and they are thus assigned to the ${}^{3}(\pi\pi^{*})$ excited states (T₁ \rightarrow S₀ emission). For 1, the emission lifetime is not as long as 2 and 3 (65.6 μ s). From the peak height ratio from triplet emission to singlet emission at 77 K, which is a good parameter to evaluate the relative ISC efficiency, we can conclude that low ISC efficiency for 1 results in not very long lifetime. Low ISC efficiency can be attributed to low triplet state energy of 1 (table 3). The small dihedral angles between X–Cu–X plane and phenyl ring plane of biphenyl may be the reason which results in better conjugation in 1 that decreases the triplet energy.

Natural bond orbital (NBO) calculations and analysis indicate that the hole/electron pairs can be used to describe these transitions. The hole is approximately in the HOMO and the electron is approximately in the LUMO. The energy level of singlet and triplet states and $\Delta E(S_1-T_1)$ of **1-3** are summarized in table 3. The energy gaps between the S₁ and T₁ levels of **1-3** are small (0.1180-0.1619 eV), which provide further evidence to show that **1-3** exhibit TADF [29].

According to the calculated frontier orbitals shown in figure 3, for 1-3, the contribution from the Cu, halogen, and P to the hole distribution is 24, 31, 34; 39, 25, 17; 22, 26, 26%, respectively. The electron distribution is mainly confined to the phenyl rings of diphenyl and phenyl rings in bpbp. These indicate that the luminescence arises from the MLCT, XLCT and intraligand transitions.

3.4. Thermal properties

Since good thermal stabilities of the complexes are important for OLED applications, the onset decomposition temperatures (T_{dec}) of **1-3** were determined by thermogravimetric analysis (TGA) under a stream of nitrogen. From the onset of the TGA curves (figure 5), all complexes show good thermal stabilities with their T_{dec} values ranging from 360 to 367 °C. A sharp one-step weight loss for all the complexes of *ca*. 73-84% was observed between 482 and 548 °C, which can be ascribed to the removal of bpbp. These data render the materials suitable for the fabrication of OLEDs by using the vacuum thermal deposition method.

4. Conclusion

The first examples of neutral luminescent dinuclear copper(I) halide complexes containing biphenyl diphosphine bidentate ligand were synthesized and photophysically characterized. The halogen largely tunes the emission color from yellow to blue in the solid state at room temperature. Small S_1 – T_1 energy gaps of **1-3** in the solid state indicate that the emission occurred from a thermally activated excited singlet state at ambient temperature. The low emission quantum yields (<0.01%) are attributed to the poor, rigid environment around the copper center, which results in radiationless deactivations. More rigid bidentate diphosphines such as a 1,2diphosphinoaryl ligand and halogen ligands can be introduced to obtain high efficiency and color-tunable Cu(I) complex-based luminescent materials in the future.

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 \mathcal{C}

 \mathcal{D}







Figure 2. Absorption spectra of 1-3 and bpbp in CH_2Cl_2 at 298 K. The inset shows a magnified view of the absorption edges.



Figure 3. Molecular orbitals of 1-3 as calculated by DFT.













	$1 \bullet CH_3CN$	$2 \bullet \mathrm{CH}_2\mathrm{Cl}_2$	3	
Empirical formula	rical formula C ₇₂ H ₅₆ Cu ₂ I ₂ P ₄ •CH ₃ CN		C ₇₂ H ₅₆ Cl ₂ Cu ₂ P ₄	
Formula weight	1508.11	1416.87	1243.03	
Temperature (K)	299(2)	298(2)	293(2)	
Wavelength (Å)	0.71073	0.71073	0.71073	
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	
Space group	Pna2(1)	Pna2(1)	Pna2(1)	
<i>a</i> (Å)	18.1760(12)	17.9538(9)	17.914(4)	
<i>b</i> (Å)	17.1223(11)	17.0019(9)	15.702(3)	
<i>c</i> (Å)	20.7707(13)	20.8190(9)	22.472(5)	
$V(Å^3)$	6464.2(7)	6354.9(7)	6321.0(5)	
Ζ	4	4	4	
ho (g cm ⁻³)	1.507	1.481	1.306	
μ (mm ⁻¹)	1.755	2.155	0.900	
<i>F</i> (0 0 0)	2936	2872	2560	
θ range for data collection (°)	2.807 to 28.305	2.47 to 27.57	3.01 to 27.45	
Index ranges	$-24 \le h \le 24$	$-23 \le h \le 23$	$-23 \le h \le 23$	
	$-21 \le k \le 22$	$-22 \le k \le 22$	$-20 \le k \le 20$	
	$-27 \le l \le 23$	$-26 \le l \le 27$	$-29 \le l \le 28$	
Independent reflections	15064 [R(int) = 0.0874]	14585 [R(int) = 0.0850]	14162 [<i>R</i> (int) =	
			0.0395]	
Completeness to $\theta = 25.242^{\circ}$	99.8%	99.7 %	99.6 %	
Max. and min. transmission	0.7457 and 0.6567	0.9188 and 0.6977	0.8014 and 0.7473	
Gof	1.013	1.006	1.038	
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0531$	$R_1 = 0.0519$	$R_1 = 0.0433$	
$\bigcirc \searrow$	$wR_2 = 0.0724$	$wR_2 = 0.0737$	$wR_2 = 0.1156$	
R (all data)	$R_1 = 0.1190$	$R_1 = 0.1213$	$R_1 = 0.0538$	
(())	$wR_2 = 0.0891$	$wR_2 = 0.0883$	$wR_2 = 0.1218$	
Max/min (e Å ³)	0.919 and -1.091	0.357 and -0.447	0.988 and -0.509	

Table 1. Crystallographic data and refinement details for 1-3.

Complex	$1 \bullet CH_3CN$	2 • CH ₂ Cl ₂	3
Cu–X	2.7197(12), 2.7229(11)	2.5118(8), 2.5308(7)	2.3791(9), 2.4022(10)
	2.6846(10), 2.6658(11)	2.5176(7), 2.5310(8)	2.3757(9), 2.3770(10)
Cu–P	2.292(3), 2.289(2)	2.2689(13), 2.2706(12)	2.2600(10), 2.2598(10)
	2.278(2), 2.272(2)	2.2830(12), 2.2757(13)	2.2668(10), 2.2615(10)
Cu···Cu	3.625(1)	3.4041(7)	3.1490(7)
P-Cu-P	101.25(9), 101.26(9)	100.62(5), 101.01(5)	105.29(4), 105.15(4)
Х-Си-Х	95.58(4), 95.22(3)	95.17(2), 95.01(2)	96.82(3), 97.60(3)
Cu–X–Cu	85.30(4), 83.53(3)	85.19(2), 85.19(2)	82.95(3), 82.43(3)
P-Cu-X	109.36(6), 115.72(7)	112.43(4), 115.09(4)	112.04(4), 115.58(4)
	108.77(7), 126.11(7)	110.13(4), 123.86(4)	115.13(4), 112.30(4)
	113.44(7), 114.18(7)	111.06(4), 115.21(4)	114.22(4), 111.48(4)
	109.29(7), 123.61(7)	108.59(4), 125.94(4)	114.62(4), 114.02(4)

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Table 2. Selected bond lengths (Å) and angles (°) for 1-3.

	$\lambda_{max} \ (nm)^a$		$ au$ (µs) ^b Φ^c		Φ^{c}	S ₁ (eV) ^d	T ₁ (eV) ^d	$\Delta E(S_1 - T_1)^d (eV)$
	293 K	77 K	293 K	77 K	293 K	01(01)	11(01)	
1	436*, 472*,	472, 487*,	7.9	65.6	< 0.01%	3.2148	3.0968	0.1180
	575	577*						\land
2	487	528	6.2	3163	< 0.01%	3.2563	3.1276	0.1287
3	535	512	19.8	1834	< 0.01%	3.3613	3.1994	0.1619

Table 3. Photophysical data of 1-3 in the solid state.

^a Emission peak wavelength. Asterisks indicate emission peaks appear as shoulders or weak bands.

^b Emission lifetime. Experimental errors are \pm 5%.

^c Absolute emission quantum in the solid state. Experimental errors are \pm 5%.

^d Calculated results (S_1 and T_1 energy levels, and energy gap between S_1 and T_1) obtained using structures determined by the X-ray analysis.

Graphical abstract

