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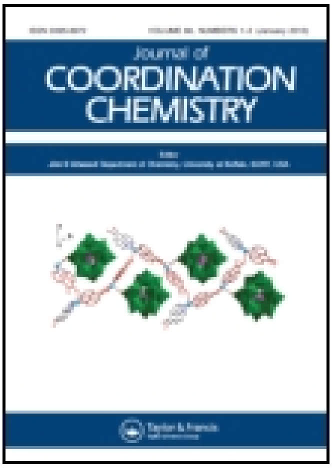

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Synthesis and characterization of emissive mononuclear Cu(I) complexes with 5-tert-butyl-3-(pyrimidine-2-yl)-1H-1,2,4-triazole

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Synthesis and characterization of emissive mononuclear Cu(I) complexes with 5-*tert*-butyl-3-(pyrimidine-2-yl)-1*H*-1,2,4-triazole

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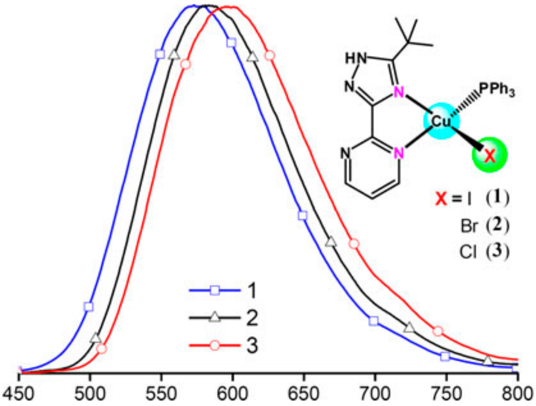

A new series of mononuclear copper(I) halide complexes possessing 5-*tert*-butyl-3-(pyrimidine-2-yl)-1*H*-1,2,4-triazole (bpmtzH) and PPh_3, $Cu(bpmtzH)(PPh_3)X$ (X = I (**1**); Br (**2**); Cl (**3**)), have been synthesized and characterized. As revealed via X-ray crystallography, **1–3** show a chiral, distorted tetrahedral N_2PX arrangement, in which bpmtzH is a neutral bidentate chelating ligand using the 4-N of the 1,2,4-triazolyl ring and one N donor from the 2-pyrimidyl ring, consistent with the computational results. A comparatively weak low-energy absorption tail is observed between 320 and 450 nm for CH_2Cl_2 solutions of **1–3** at room temperature, ascribing to charge-transfer transitions with appreciable metal-to-ligand charge transfer (MLCT) character. Complexes **1–3** in the solid state have good luminescence at ambient temperature, although they are non-emissive in solution. The solid-state emission, most likely originating from both ^{3}MLCT and ^{3}XLCT transitions, can be modulated via alteration of the halide bound to $\{Cu(bpmtzH)(PPh_3)\}$ motif.

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Keywords: Copper(I) complex; 5-*Tert*-butyl-3-(pyrimidine-2-yl)-1*H*-1,2,4-triazole, Crystal structure; Photoluminescence; Halide

1. Introduction

Emissive copper(I) complexes have been intensively studied owing to their intriguing spectroscopic properties with promising applications in materials science [1–9]. Cu(I) complexes possessing diimine and phosphine ligands are normally air-stable and emissive in solution and solids, and the electronic and structural characters of the ligands coordinated to Cu(I) have an important impact on the photoluminescence of the Cu(I) species [6–11]. The choice of the diimine ligand is critical for modulation of the emissive properties of the resulting Cu(I) complexes, since the lowest unoccupied molecular orbital (LUMO) is basically localized on the diimine ligand [7–11]. Moreover, orbitals of auxiliary ligands such as phosphines and halides are often involved in the highest occupied molecular orbital (HOMO) with a dominant metal d(Cu) character [10–21].

Cu(I) systems with 2,2′-bipyrimidine (bpym) are luminescent at ambient temperature [22, 23], whereas Cu(I) complexes containing 3-(2-pyrimidinyl)-1,2,4-triazine (pmtz) are all non-emissive in solution and as solids at room temperature [24]. In fact, pmtz has only an additional nitrogen donor relative to bpym, clearly implying that the emissive properties of Cu(I) complexes are related to the structural characteristics of the diimine ligand. To explore further the relationship between the luminescence properties of Cu(I) complexes and the structure of the *N*-heterocyclic chelating ligand, it is necessary to synthesize more Cu(I) complexes with multi-nitrogen-containing heterocyclic chelates. Herein, we describe the syntheses, crystal structures, and photophysical properties of a new series of mononuclear Cu(I) halide complexes featuring 5-*tert*-butyl-3-(pyrimidine-2-yl)-1*H*-1,2,4-triazole (bpmtzH), Cu(bpmtzH)(PPh$_3$)X (X = I (**1**); Br (**2**); Cl (**3**)), where bpmtzH serves as a neutral bidentate chelate utilizing the 4-N of the 1,2,4-triazolyl ring and one N from the 2-pyrimidyl ring, as suggested by density functional theory (DFT) calculations. It is demonstrated that **1–3** with the 1,2,4-triazolyl five-membered ring bearing a *tert*-butyl group are all emissive in the solid state at room temperature, in marked contrast to the non-emissive Cu–pmtz complexes with the 1,2,4-triazinyl six-membered ring, and that the ancillary halide bound to {Cu(bpmtzH)(PPh$_3$)} has a significant influence on the structural features and luminescent properties of the Cu(I) complexes.

2. Experimental

2.1. *General procedures and materials*

All reactions were performed under N$_2$ using anhydrous solvents. Commercially available reagents were used without purification unless otherwise stated. Dichloromethane used in the spectroscopic analyses was freshly distilled from CaH$_2$ under nitrogen. 5-*Tert*-butyl-3-(pyrimidine-2-yl)-1*H*-1,2,4-triazole (bpmtzH) was prepared according to the literature method [25].

2.2. *Physical measurements*

The ^{1}H and ^{31}P{^{1}H} NMR spectra were recorded on a Bruker Avance III (400 MHz) spectrometer with $SiMe_4$ as the internal reference (^{1}H) and 85% H_3PO_4 as the external reference (^{31}P). C, H, N elemental analyses were carried out on a Perkin-Elmer model 240C elemental analyzer. Fourier transform infrared (FT-IR) spectra were collected on an ALPHA FT-IR spectrometer (Bruker Optics, Billerica, MA, USA) using KBr pellets. Electronic absorption spectra in dichloromethane solutions were measured on a Perkin-Elmer Lambda 25 UV–vis spectrometer. Solid-state emission spectra were recorded on a Perkin-Elmer LS 55 luminescence spectrometer with a red-sensitive photomultiplier type R928.

2.3. *Synthesis of Cu(bpmtzH)(PPh$_3$)I (1)*

A mixture of CuI (18.9 mg, 0.099 mM) and PPh_3 (49.8 mg, 0.190 mM) was stirred in CH_2Cl_2 (15 mL) for 3 h at room temperature. A CH_2Cl_2 solution (3 mL) of bpmtzH (20.2 mg, 0.099 mM) was added dropwise to the resulting colorless solution. The mixture was stirred for another 4 h, and then the solvent was evaporated at reduced pressure to give a yellow residue. The residue was redissolved in CH_2Cl_2 and yellow crystals (51.1 mg, 0.078 mM, 78.7% yield) were afforded by slow diffusion of petroleum ether into the CH_2Cl_2 solution. ^{1}H NMR (DMSO-d$_6$, 400 MHz): δ 14.66 (s, 1H), 8.89–8.80 (m, 2H), 7.61–7.36 (m, 16H), 1.32 (s, 9H). ^{31}P{^{1}H} NMR (DMSO-d$_6$, 202.3 MHz): δ –6.78 (s, *P*Ph$_3$). Elem. Anal. Calcd for $C_{28}H_{28}ICuN_5P$: C, 51.27; H, 4.30; N, 10.68. Found: C, 51.03; H, 4.12; N, 10.87%. Selected IR (KBr, cm^{-1}): 3442(s), 3123(m), 3050(m), 2969(m), 1629(w), 1575(s), 1528(w), 1479(m), 1456(m), 1421(s), 1393(s), 1366(m), 1297(w), 1267(w), 1225(w), 1181(w), 1094(m), 1042(w), 822(w), 747(s), 695(s), 641(w), 523(s), 493(m).

2.4. *Synthesis of Cu(bpmtzH)(PPh$_3$)Br (2)*

Complex **2** was prepared following the procedure for **1**, using CuBr (19.6 mg, 0.137 mM), PPh_3 (71.7 mg, 0.273 mM), and bpmtzH (27.8 mg, 0.137 mM). Yellow crystals (64.6 mg, 0.106 mM, 77.6% yield) were obtained by slow diffusion of Et_2O into a 3 : 1 blend of DMF and CH_3CN. ^{1}H NMR (DMSO-d$_6$, 400 MHz): δ 14.58 (s, 1H), 8.89–8.78 (m, 2H), 7.58–7.38 (m, 16H), 1.31 (s, 9H). ^{31}P{^{1}H} NMR (DMSO-d$_6$, 202.3 MHz): δ –5.62 (s, *P*Ph$_3$). Elem. Anal. Calcd for $C_{28}H_{28}BrCuN_5P$: C, 55.22; H, 4.63; N, 11.50. Found: C, 55.38; H, 4.42; N, 11.67%. Selected IR (KBr, cm^{-1}): 3443(s), 3047(s), 2971(s), 1626(w), 1573(s), 1558(m), 1527(m), 1479(m), 1456(m), 1435(s), 1394(s), 1368(m), 1302(w), 1227(w), 1183(w), 1095(m), 1042(w), 827(w), 750(s), 696(s), 524(s), 506(m).

2.5. *Synthesis of Cu(bpmtzH)(PPh$_3$)Cl (3)*

Complex **3** was prepared following the procedure for **1**, using CuCl (16.8 mg, 0.170 mM), PPh_3 (89.3 mg, 0.340 mM), and bpmtzH (34.5 mg, 0.170 mM). Yellow crystals (64.8 mg, 0.115 mM, 67.6% yield) were obtained by slow diffusion of Et_2O into a 2 : 1 blend of CH_2Cl_2 and CH_2ClCH_2Cl. ^{1}H NMR (DMSO-d$_6$, 400 MHz): δ 14.53 (s, 1H), 8.89–8.78 (m, 2H), 7.57–7.33 (m, 16H), 1.31 (s, 9H). $^{31}P\{^1H\}$ NMR (DMSO-d_6, 202.3 MHz): δ –5.13 (s, *P*Ph$_3$). Elem. Anal. Calcd for $C_{28}H_{28}ClCuN_5P$: C, 59.57; H, 5.00; N, 12.41. Found: C, 59.43; H, 5.18; N, 12.34%. Selected IR (KBr, cm^{-1}): 3448(m), 3046(s), 2971(s), 1637(w), 1573(s), 1558(m), 1527(m), 1479(m), 1457(m), 1436(s), 1395(s), 1371(m), 1306(w), 1228(w), 1095(m), 1041(w), 997(w), 827(w), 751(s), 697(s), 639(w), 524(s), 506(m).

2.6. *X-ray crystallography*

Crystals of **1** and **2** were measured on a MAR CCD 165 nm diffractometer by the oscillation scan technique using the Beijing Synchrotron Radiation Facility with a 3W1A beam ($\lambda = 0.71073$ Å) at 194(2) K. The cell refinement and data reduction were computed using the HKL2000 software. Absorption corrections were carried out based on spherical harmonics expansion of the absorption surface using the HKL2000 software [26]. A crystal of **3** was measured on a Bruker SMART CCD area detector using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at 296(2) K. All the crystal structures were solved by the direct method using SHELXS-97 [27] and all non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogens were placed in idealized geometries and their contributions were added to the structure factor calculations. Full-matrix least-squares refinement was based on F^2 with the SHELXL-97 program [28]. The maximum theta value of **1** is low and thus its crystal data completeness is 0.914, but the other parameters are all in typical range and reasonable. Moreover, the absolute structure of **1** was confirmed by its Flack parameter of 0.083(13) [29].

2.7. *Computational methodology*

To clearly understand the binding of bpmtzH with Cu(I), theoretical calculations were implemented using Gaussian 03 program package [30]. The DFT [31] method at the

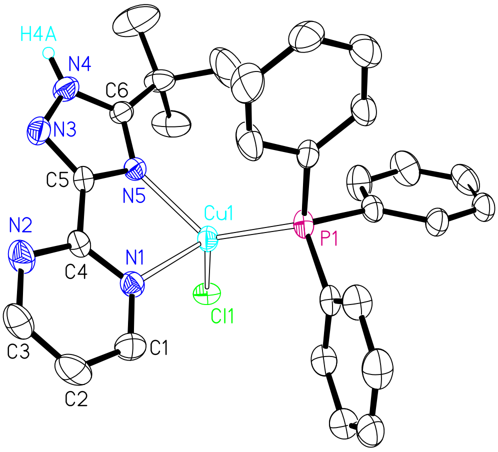


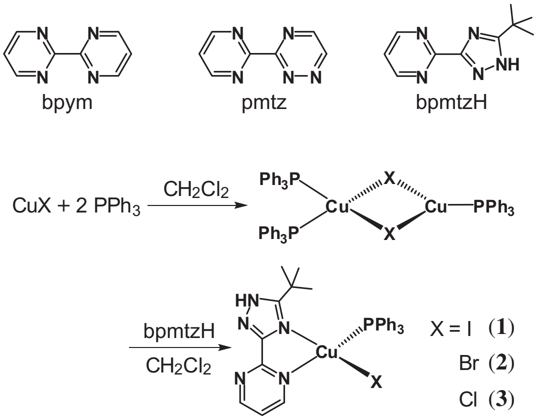
Figure 1. ORTEP drawing of **3** with 30% probability thermal ellipsoids and atom-labeling scheme. Hydrogens except H4A are omitted for clarity.

gradient-corrected correlation functional PBE1PBE level [32] was used to optimize the structures of Cu(I) complexes bearing the N1^N3 and N1^N5 chelating modes (atom labels as in figure 1) of bpmtzH in the ground state without considering any symmetry restriction. The Lanl2dz effective core potential was used to describe the inner electrons of Cu, P, and Cl [33–35], while its associated double-ζ basis set of Hay and Wadt was employed for the remaining outer electrons with *f*-[Cu ($\alpha_f = 0.24$)] and *d*-type [P ($\alpha_d = 0.34$), Cl ($\alpha_d = 0.514$)] polarization functions [36]. N, C, and H were described by the all-electron basis set of 6-31G(p,d) [37].

3. Results and discussion

3.1. *Synthesis and characterization*

This project was carried out to prepare emissive, bpmtzH-based mono-copper(I) halide complexes and explore the preferred binding mode of bpmtzH with Cu(I). Mononuclear Cu(I) halide complexes of bpmtzH, Cu(bpmtzH)(PPh_3)X (X = I (**1**); Br (**2**); Cl (**3**)), are accessible by treatment of cuprous halide with two equivalents of PPh_3 in CH_2Cl_2 solution followed by addition of one equivalent of bpmtzH (scheme 1). The unisolated intermediate has been identified as the di-copper(I) halide cluster $(PPh_3)_2Cu(\mu\text{-}X)_2Cu(PPh_3)$ via X-ray crystallography [38], and it is air-stable and soluble in CH_2Cl_2, $CHCl_3$, and CH_2ClCH_2Cl. Copper(I) halide complexes **1–3** are soluble in DMF and DMSO, and only sparingly soluble in CH_2Cl_2, $CHCl_3$, and CH_2ClCH_2Cl. Moreover, **1–3** are air-stable in the solid state and for extended periods of time (3–5 days) in solution. The infrared spectra of **1–3** show all the bands required due to the presence of bpmtzH and PPh_3. Compared with free bpmtzH (3424 cm^{-1}, figure S1 see online supplemental material at http://dx.doi.org/10.1080/00958972.2014.908465), the v(N–H) of coordinated bpmtzH in **1–3** appears as a single broad absorption at slightly higher frequency, 3440–3450 cm^{-1} (figures S2–S4). Upon P–Cu(I) coordination, the characteristic $v(P\text{–}C_{Ph})$ peak of PPh_3 in **1–3** occurs at slightly higher frequency (~1095 cm^{-1}) relative to that of free PPh_3 (1089 cm^{-1}) [39]. In the ^1H NMR spectra of **1–3** in DMSO-d_6



Scheme 1. Synthetic route to **1–3**.

(figures S5, S7, and S9), besides the aromatic proton signals (8.9–7.3 ppm) and the C–H resonance of the *tert*-butyl group as a singlet at 1.3 ppm, the characteristic N–H proton of the 1,2,4-triazolyl ring occurs at approximately 14.6 ppm as a broad singlet, implying that bpmtzH coordinates to Cu(I) as a neutral ligand without cleavage of the N–H bond, as revealed by X-ray crystallography. The $^{31}P\{^{1}H\}$ NMR spectra exhibit broad singlets at –6.78, –5.62, and –5.13 ppm for **1–3**, respectively (figures S6, S8, and S10), implying that the coordinated PPh_3 is affected by the ligand-field strength of the halide ($I^- < Br^- < Cl^-$) [15].

3.2. *Crystal structure*

X-ray crystallographic studies of **1–3** were performed to investigate the preferred binding mode of bpmtzH and the effects of the halide on coordination around Cu(I). The crystallographic data and structure refinement parameters of **1–3** are summarized in table 1 and selected bond lengths and angles of **1–3** are listed in table 2. Complexes **1–3** adopt a chiral,

Table 1. Crystallographic data and structural refinement parameters for **1–3**.

Compound	1	2	3
Empirical formula	$C_{28}H_{28}ICuN_5P$	$C_{28}H_{28}BrCuN_5P$	$C_{28}H_{28}ClCuN_5P$
Formula weight	655.96	608.97	564.51
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	$P1$	Cc	Cc
a, Å	8.7560 (18)	10.586 (2)	10.5488 (3)
b, Å	9.3260 (19)	16.742 (3)	16.7272 (5)
c, Å	18.872 (4)	15.561 (3)	15.5976 (5)
α, °	79.17 (3)		
β, °	86.49 (3)	98.23 (3)	97.030 (2)
γ, °	66.01 (3)		
V, Å^3	1382.7 (5)	2729.5(9)	2731.54 (14)
Z	2	4	4
ρ_{Calcd}, g/cm^{-3}	1.576	1.482	1.373
μ, mm^{-1}	1.990	2.349	0.982
Reflections collected/unique	7724/7724	7433/5998	11,989/5622
R(int)	0.0000	0.0212	0.0216
GOF	1.215	1.235	1.000
R_1, wR_2 ($I > 2\sigma(I)$)	0.0372, 0.0980	0.0376, 0.1033	0.0324, 0.0753
Largest diff. peak and hole (e Å^{-3})	3.045 and –1.625	2.266 and –1.181	0.536 and –0.287

Table 2. Selected bond distances [Å] and angles [°] for **1–3**.

	1[a]	2	3
Cu1–N1 (Cu2–N6)	2.135 (4), 2.183 (4)	2.193 (3)	2.229 (2)
Cu1–N5 (Cu2–N10)	2.092 (5), 2.084 (4)	2.063 (3)	2.086 (2)
Cu1–P1 (Cu2–P2)	2.2166 (15), 2.2075 (17)	2.1984 (9)	2.2044 (7)
Cu1–X1 (Cu2–X2)	2.6777 (10), 2.5757 (12)	2.4240 (9)	2.2936 (7)
N1–Cu1–N5 (N6–Cu2–N10)	80.11 (17), 79.13 (16)	79.08 (11)	77.63 (8)
N1–Cu1–P1 (N6–Cu2–P2)	118.17 (13), 103.10 (12)	110.70 (9)	110.36 (6)
N1–Cu1–X1 (N6–Cu2–X2)	97.67 (14), 106.80 (13)	109.62 (8)	108.35 (6)
N5–Cu1–P1 (N10–Cu2–P2)	128.76 (15), 125.01 (14)	122.92 (9)	122.03 (6)
N5–Cu1–X1 (N10–Cu2–X2)	113.36 (14), 114.42 (13)	111.27 (9)	111.72 (6)
P1–Cu1–X1 (P2–Cu2–X2)	110.84 (5), 116.99 (5)	116.50 (3)	118.39 (3)

[a] There are two independent molecules in the asymmetric unit of **1**. The first measurement refers to the molecule containing Cu1 and the second measurement as well as parenthetical atom labels refer to the molecule containing Cu2.

distorted tetrahedral N_2PX arrangement around Cu(I) due to the restricted bite angle of the bpmtzH chelate, and it is composed of two nitrogens from bpmtzH, one PPh_3, and one halide (figures S11, S12 and 1). The bpmtzH adopts a neutral chelating coordination mode using the 4-N of 1,2,4-triazolyl and one N of the 2-pyrimidyl. Only one enantiomer is found in the structure of **1**, as indicated by the chiral space group *P*1, while both enantiomers are present in the structures of **2** and **3**. The $Cu–N_{pyrimidyl}$ bond lengths (avg. 2.159 (4), 2.193(3), and 2.229(2) Å for **1**, **2**, and **3**, respectively) are much longer than the $Cu–N_{triazolyl}$ bond lengths (avg. 2.088(4), 2.063(3), and 2.086(2) Å for **1**, **2**, and **3**, respectively), suggesting a stronger bonding of Cu(I) to 4-N of the 1,2,4-triazolyl ring than to the 2-pyrimidyl ring, a possible result of introducing the strong electron-donating *tert*-butyl group and different from the near equivalence of the two Cu–N bond distances in literature complexes [24]. Similar Cu–N distances are also observed in other tetrahedral Cu(I) complexes with an asymmetrical N^N chelate [8, 12, 19–21, 40–42]. The $Cu–N_{pyrimidyl}$ bond lengths of **1–3** are slightly elongated with decrease of electron-donating ability of the halide ($I^- > Br^- > Cl^-$), whereas the $Cu–N_{triazolyl}$ bond distances have no apparent dependence on the ancillary halide, implying that the halide has impact only on the pyrimidyl fragment, and not the entire bpmtzH ligand. The Cu–X bond lengths in **1–3** become shorter as the van der Waals radius of X decreases. Different from $[CuI(PPh_3)(pmtz)]$ [24], a weak π–π interaction between the bpmtzH ligands of two adjacent molecules has been not observed in **1–3**, as a possible result of the 1,2,4-triazolyl ring with a bulky *tert*-butyl group in place of the 1,2,4-triazinyl ring [42].

3.3. *Photophysical properties*

The UV–vis absorption spectra of bpmtzH and its Cu-halide complexes **1–3** in CH_2Cl_2 solution at ambient temperature are presented in figure 2. The free bpmtzH displays a broad absorption centered at 255 nm attributed to $^1\pi$–π* transitions. Complexes **1–3** exhibit strong absorptions ($\varepsilon \approx 10^4\ M^{-1}\ cm^{-1}$) at 230–320 nm, probably originating from bmptzH and PPh_3, supported by a close match between bpmtzH and **1–3** in the high-energy region (≤320 nm) of the absorption spectra. In addition to the high-energy

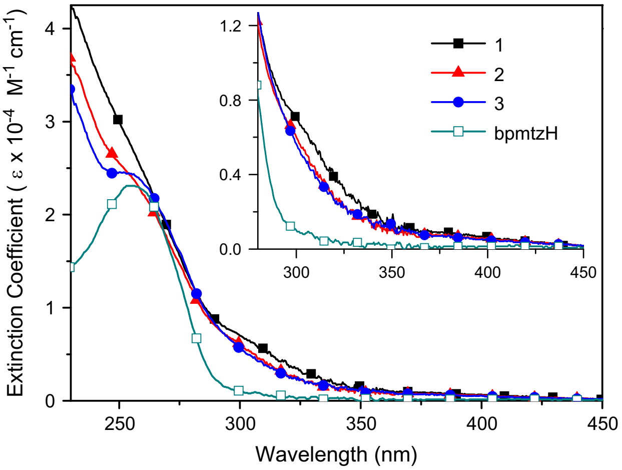


Figure 2. Absorption spectra of bpmtzH and **1–3** in CH_2Cl_2 solution (1×10^{-5} M) at ambient temperature.

absorptions, **1–3** have a relatively weaker low-energy absorption tail ($\varepsilon < 3000\,M^{-1}\,cm^{-1}$) at 320–450 nm showing no apparent dependence on the halide. This absorption may be regarded as a ^{1}MLCT transition from the d_π orbital of the $(3d^{10})Cu^+$ to the unoccupied π^* orbital of the bpmtzH, perhaps mixed with some ligand-to-ligand charge transfer (^{1}LLCT) character ($X/PPh_3 \rightarrow$ bpmtzH). Different from the apparent broad absorption band of pmtz complexes [24], only a weak low-energy absorption tail has been observed in **1–3**, similar to the reported Cu(I) halide complexes possessing 1,2,4-triazolyl [42]. This suggests that the 1,2,4-triazolyl five-membered ring with a *tert*-butyl group in place of the 1,2,4-triazinyl six-membered ring has an impact on the electronic absorption spectroscopic properties of the resulting Cu(I) complexes.

The solid-state luminescence spectra of **1–3** were measured on powder samples at room temperature (figure 3). All were strongly emissive in the solid state and exhibit a broad solid-state emission with maxima at 574, 584, and 598 nm upon excitation at 363 nm at ambient temperature for **1–3**, respectively; the Cu(I)–pmtz complexes containing a 1,2,4-triazinyl ring are all non-emissive in the solid state. This indicates that the five-membered 1,2,4-triazolyl ring in place of the six-membered 1,2,4-triazinyl ring plays a key role in the photoluminescence of the resultant Cu(I) complexes, and the substituent on the 1,2,4-triazolyl ring has an influence on the emission color of the Cu(I) species [42]. The emission wavelength maxima (λ_{max}) are in the order **1** < **2** < **3**, consistent with that of the ligand field strength of the halide ($I^- < Br^- < Cl^-$), implying that λ_{max} is related to the ligand field strength of the halide [15]. Therefore, the electronic nature of the triplet emissive state of **1–3** is affected to some degree by X → bpmtzH charge transfer transitions. With reference to previous work [1, 2, 8–23, 42, 43], the HOMOs of **1–3** are believed to be spread over the Cu(I) center and the halide, probably involving some contributions from PPh_3, while the LUMOs are thought to reside basically on the bpmtzH chelate. Hence, the emissive excited states of **1–3** are assigned as the ^{3}MLCT states with some mixing of the ^{3}LLCT transitions ($PPh_3/X \leftarrow$ bpmtzH). However, no detectable emission is observed for **1–3** in degassed CH_2Cl_2 and DMF solutions at room temperature, likely a result of fast structural relaxation occurring in the

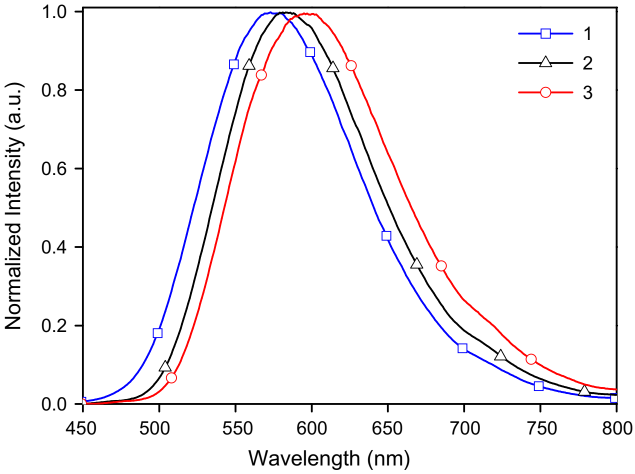
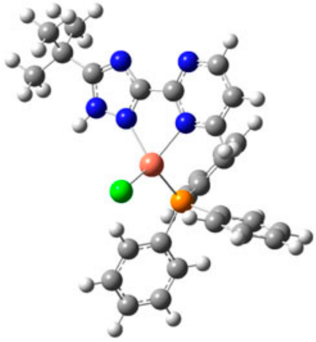
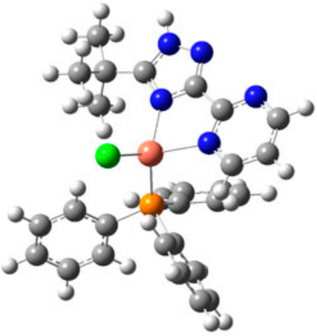


Figure 3. Solid-state emission spectra of **1–3** ($\lambda_{ex} = 363$ nm) at room temperature.

low viscosity solutions, as opposed to the bright solid-state emissions of **1–3** at ambient temperature due to the retardation of structural relaxation in the rigid medium. Therefore, this rigidochromism, which has been reported for Cu(I) systems bearing the diimine and phosphine ligands [8, 13, 42], seems to be operative for **1–3**. Additionally, it is shown that the absorption and emission spectroscopic properties of **1** are not affected by its crystalline chirality.

Table 3. Calculated energies of Cu(I) complexes with the N1^N3 and N1^N5 coordination of the bpmtzH ligand.

Chloride complex	N1^N3 coordination	N1^N5 coordination
Optimized geometry		
E (a.u.)	–1573.712377	–1573.7186944
Relative value (kJ M^{-1})	0	–16.586345324
Δ*E* (kJ M^{-1})	16.586345324	

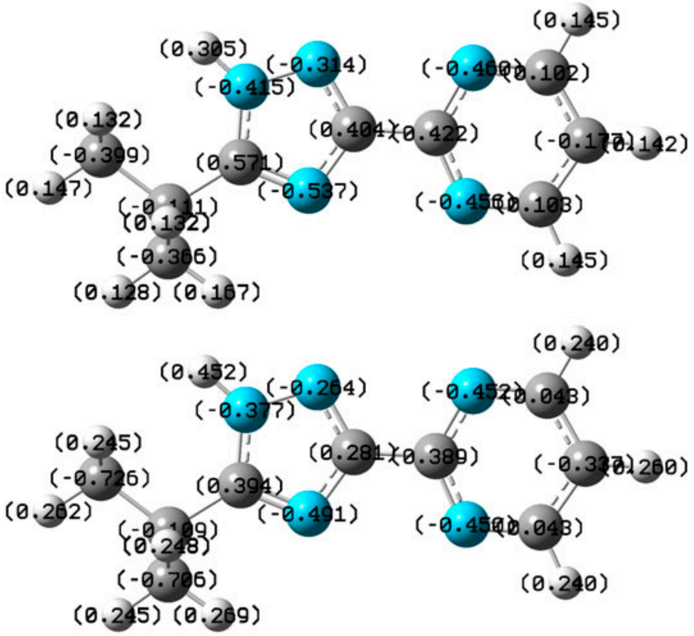


Figure 4. Electron charge distributions on the bpmtzH ligand calculated by Mulliken (top) and Natural Population Analysis (bottom).

3.4. *Theoretical investigations*

To gain insight into the binding of bpmtzH with the Cu(I) center, theoretical computations were performed according to the optimized ground-state geometries of Cu(I) complexes with the N1^N3 and N1^N5 chelating modes of bpmtzH (see labeling scheme in figure 1). As indicated in table 3, the energy of Cu(I) chloride complexes with the N1^N5 chelating is much lower than that of Cu(I) chloride complexes with the N1^N3 mode, implying that the bpmtzH ligand should preferentially coordinate with Cu(I) using the N1^N5 chelating mode. Moreover, as shown in figure 4, the N5 of bpmtzH displays a relatively higher electron density than the N3 donor of bpmtzH, further suggesting that bpmtzH easily binds to the Cu(I) utilizing N1^N5 coordination instead of N1^N3.

4. Conclusion

A new series of emissive monomeric Cu(I) complexes with 5-*tert*-butyl-3-(pyrimidine-2-yl)-1*H*-1,2,4-triazole (bpmtzH), $Cu(bpmtzH)(PPh_3)X$ (X = I (**1**); Br (**2**); Cl (**3**)), have been synthesized and characterized. BpmtzH coordinates to $\{Cu(PPh_3)X\}$ using one N of the 2-pyrimidyl and the 4-N of 1,2,4-triazolyl rings as a neutral bidentate chelating ligand, in agreement with the computational results. Complexes **1–3** with a 1,2,4-triazolyl five-membered ring are all emissive in the solid state at room temperature. Both the five-membered 1,2,4-triazolyl ring in place of the six-membered 1,2,4-triazinyl ring and the ancillary halide ligand bound to $\{Cu(bpmtzH)(PPh_3)\}$ play major roles in influencing the molecular structures and luminescence properties of Cu(I) complexes. The results presented herein provide new insight into the design and synthesis of emissive Cu(I) complexes with a functionalized bpmtzH ligand.

Supplementary material

Figures of the IR spectra of bpmtzH and **1–3**, ^{1}H and ^{31}P NMR spectra of **1–3**, and ORTEP plots of the structures of **1** and **2**. Crystallographic data for the structural analysis have been deposited at the Cambridge Crystallographic Data Center with the deposition numbers of CCDC 973017, 973016, and 914171 for **1–3**, respectively. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44 1223 336033; E-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk/deposit).

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