

Synthesis, structural characterization and luminescent properties of a series of Cu(I) complexes based on polyphosphine ligands†

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A series of Cu(I) complexes with a [Cu(NN)(PP)]⁺ moiety, [Cu(phen)(pba)](BF₄) (1a), [Cu₂(phen)₂(pbaa)](BF₄)₂ (2a), [Cu₂(phen)₂(pnaa)](BF₄)₂ (3a), [Cu₂(phen)₂(pbbaa)](BF₄)₂ (4a), [Cu(dmp)(pba)](BF₄) (1b), [Cu₂(dmp)₂(pbaa)](BF₄)₂ (2b), [Cu₂(dmp)₂(pnaa)](BF₄)₂ (3b) and [Cu₂(dmp)₂(pbbaa)](BF₄)₂ (4b) (phen = 1,10-phenanthroline, dmp = 2,9-dimethyl-1,10-phenanthroline, pba = *N,N*-bis((diphenylphosphino)methyl)benzenamine, pbaa = *N,N,N',N'*-tetrakis((diphenylphosphino)methyl)benzene-1,4-diamine, pnaa = *N,N,N',N'*-tetrakis((diphenylphosphino)methyl)naphthalene-1,5-diamine and pbbaa = *N,N,N',N'*-tetrakis((diphenylphosphino)methyl)biphenyl-4,4'-diamine), were rationally designed and synthesized. These complexes were characterized by ¹H and ³¹P NMR, electrospray mass spectrometry, elemental analysis and X-ray crystal structure analysis. Introduction of different central arene spacers (phenyl, naphthyl, biphenyl) into ligands, resulting in the size variation of these complexes, aims to tune the photophysical properties of the complexes. Each Cu(I) ion in these complexes adopts a distorted tetrahedral geometry constructed by the chelating diimine and phosphine groups. Intermolecular C–H⋯π and/or π⋯π interactions are involved in the solid states. The dmp-containing complex exhibits better emission relative to the corresponding phen complex due to the steric encumbrance of bulky alkyl groups. Furthermore, for complexes with identical diimine but different phosphine ligands, the tendency of increased emission lifetime as well as blue-shifted emission in the solid state follows with the decrease in size of complexes. Intermolecular C–H⋯π interactions have an influence on the final solid state photophysical properties through vibrationally relaxed non-radiative energy transfer in the excited state. Smaller-sized complexes show better photophysical properties due to less vibrationally relaxed behavior related to flexible C–H⋯π bonds. Nevertheless, the tendency for increased quantum yield and emission lifetime, as well as blue-shifted emission in dilute solution goes with the increase in size of complexes. The central arene ring (phenyl, naphthyl or biphenyl) has an influence on the final photophysical properties. The larger the π-conjugated extension of central arene ring is, the better the photophysical properties of complex are. The rigid and large-sized complex 3b, with a high quantum yield and long lifetime, is the best luminophore among these complexes.

Introduction

The photoluminescent properties of transition metal complexes have garnered much attention due to their potential applications in dye-sensitized solar cells, light-emitting or electrochemical devices and photochemical catalysts.^{1,2} Searching for highly efficient

luminescent complexes, ligand strategy, which is dedicated to tuning steric, electronic and conformational effects, is popularly used to mediate the photophysical and photochemical properties of metal complexes.³ The destabilization between ligand and central metal is imposed on slight structure changes, electronic spectra and excited state energies.

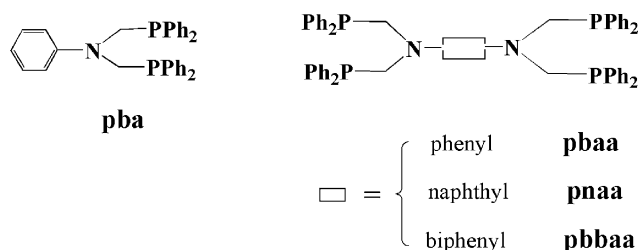
Cu(I) complexes, as potentially inexpensive photofunctional molecules, have been recently widely reported.⁴ The typical example is the [Cu(NN)₂]⁺ system (NN = diimine).⁵ However, the emission signal from the charge transfer (CT) excited state of the copper(I) complex is typically weak and short-lived because the lowest-energy CT state involves excitation from a metal–ligand dσ* orbital. Furthermore, the excited state of Cu(I) typically prefers a tetragonally flattened geometry,

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deviating from the tetrahedral-like coordination geometry in the ground state. An important consequence of the steric encumbrance of the bulky substituents on the diimine ligands is that they can restrict the pseudotetrahedral Cu(I) to be flattened in the excited state and extend the lifetime for the photoprocess, while intermolecular interactions mediated by the bulky substituents could also make the ground-state geometry distorted and favor photo-oxidation of the metal with little structural change. Recently, the [Cu(POP)(NN)]⁺ family (POP = bis[2-(diphenylphosphino)phenyl]ether) with highly effective luminescence suggested that we should extensively investigate these heteroleptic complexes.⁶ The introduction of bulky phosphine groups effectively avoids the geometric relaxation of the excited state, as well as solvent attack, exhibiting an unprecedentedly high quantum yield and a long lifetime at room temperature. Therefore, new functional organophosphine ligands, such as angular bis[2-(diphenylphosphino)phenyl]ether (POP),^{6a} rigid 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene⁷ and 1,2-bis(diphenylphosphino)benzene,⁸ hetero-donor 8-diphenylphosphanylquinoline⁹ and bis(2-(diisobutylphosphino)phenyl)amide¹⁰ were designed to explore highly efficient photofunctional Cu(I) complexes and the photoluminescent molecular mechanical system.¹¹ The previous demonstration and calculation show that the low-lying metal-to-ligand charge transfer (MLCT) transition in the [Cu(NN)(PP)]⁺ system is dominated by the d orbital of the copper(I) ion, mixed with a contribution from the phosphorous and a small contribution from the diimine ligand.¹² The electron donating properties and the bite angle of the phosphine moiety could be effective to destabilize the electronic character of the copper–phosphine fragment. Furthermore, luminescence enhancement is also triggered by molecular interactions in the solid state.¹³

For pursuing a highly efficient photoprocess, our efforts are devoted to designing a series of new functional ligands to mediate the photophysical properties of the [Cu(NN)(PP)]⁺ system. Here, four polyphosphine ligands, *N,N*-bis((diphenylphosphino)methyl)benzenamine (pba), *N,N,N',N'*-tetrakis((diphenylphosphino)methyl)benzene-1,4-diamine (pbaa), *N,N,N',N'*-tetrakis((diphenylphosphino)methyl)naphthalene-1,5-diamine (pnaa) and *N,N,N',N'*-tetrakis((diphenylphosphino)methyl)biphenyl-4,4'-diamine (pbbaa) were developed first from arene amines (Scheme 1). These ligands are expected to coordinate in a bidentate P,P fashion and the bite angle of the phosphine moiety attached to the Cu center could be confined by the conformation of the tertiary amine. In addition, the tertiary N atoms of the arene amine can donate their electron lone pairs to conjugate with the central arene ring, resulting in the arene ring being an electron-rich π system that can act as an acceptor for the C–H $\cdots\pi$ weak interactions.¹⁴



Scheme 1

The change of the central arene spacer in a ligand will be anticipated to tailor intermolecular C–H $\cdots\pi$ interactions and the photophysical properties of the complex. Actually, the central arene spacer can perform as an organic chromophore to influence the final photophysical properties of complexes. Compounds with multichromophores (organic and complex chromophores) are popular candidates for harnessing light energy.¹⁵ Here, eight complexes [Cu(phen)(pba)](BF₄) (1a), [Cu₂(phen)₂(pbaa)](BF₄)₂ (2a), [Cu₂(phen)₂(pnaa)](BF₄)₂ (3a), [Cu₂(phen)₂(pbbaa)](BF₄)₂ (4a) [Cu(dmp)(pba)](BF₄) (1b), [Cu₂(dmp)₂(pbaa)](BF₄)₂ (2b), [Cu₂(dmp)₂(pnaa)](BF₄)₂ (3b) and [Cu₂(dmp)₂(pbbaa)](BF₄)₂ (4b) (phen = 1,10-phenanthroline, dmp = 2,9-dimethyl-1,10-phenanthroline) are reported. They are characterized by X-ray diffraction, NMR, elemental analysis, UV-Vis and emissive spectra. Complexes 1a and 1b are mononuclear, and the other six complexes are dinuclear. All eight complexes contain a similar structure moiety of [Cu(NN)(PP)]⁺ in which the polyphosphine ligand acts in a chelating coordination mode to coordinate to the Cu(I) ion.

Result and Discussion

X-ray single-crystal diffraction analyses show that both 1a and 1b contain a [Cu(NN)(PP)]⁺ moiety constructed by bidentate pba, but each of the other six complexes (2a–4b) contains two [Cu(NN)(PP)]⁺ moieties that are linked by the corresponding bridging tetradentate phosphine pbaa, pnaa or pbbaa (Fig. 1–8). The copper ion in the [Cu(NN)(PP)]⁺ moiety adopts a distorted tetrahedral geometry. Selected structural data are summarized in Table S1.† The Cu–P and Cu–N bond lengths, as well as the N–Cu–N bond angles in these eight complexes are in the range 2.01–2.10 and 2.20–2.30 Å, and 80–82°, respectively, which are not significantly different to previously studied [Cu(NN)(PP)]⁺ systems.^{16,17} The P–Cu–P bond angles in the reported complexes (in the range of 100–107°) are smaller, which may be modulated by the geometric configuration of the tertiary amine. The dihedral angles between the NCuN and PCuP planes in [Cu(NN)(PP)]⁺ moieties are in the range of 89–98°, exhibiting a flattened distorted or rocked distorted tetrahedral geometry.^{5c}

Except for complex 4a, all other three phen complexes exhibit intermolecular π – π stacking interactions between phen ligands in the solid states (Fig. 1, Fig. S1 and S2†), but dmp complexes are not involved in intermolecular π – π stacking interactions between dmp moieties, possibly due to steric encumbrance. In the crystal structures of 2a, 2b and 3a, the central arene rings are involved in intermolecular C–H $\cdots\pi$ interactions with phenyl H atoms (Fig. 3, 4 and 5), and adjacent molecules are held together by these C–H $\cdots\pi$ interactions in one-dimensional chains. These chains in 2a and 3a are further extended into 2-D supramolecular structures through π – π stacking interactions between parallel phen planes (Fig. S1 and S2†). However, the central arene rings in 3b and 4a are involved in intermolecular C–H $\cdots\pi$ interactions with H atoms of phen or dmp to build 2-D supramolecular structures in which adjacent molecules are in a T-shaped orientation relative to each other (Fig. 6, 7, Fig. S3 and S4†). Such a T-shaped packing mode results in complex cations loosely arranged in the lattice. Nevertheless, in the crystal structure of 4b, the central arene ring is involved in intermolecular C–H $\cdots\pi$ interactions with methylene H atoms. No apparent C–H $\cdots\pi$ interaction is involved for the

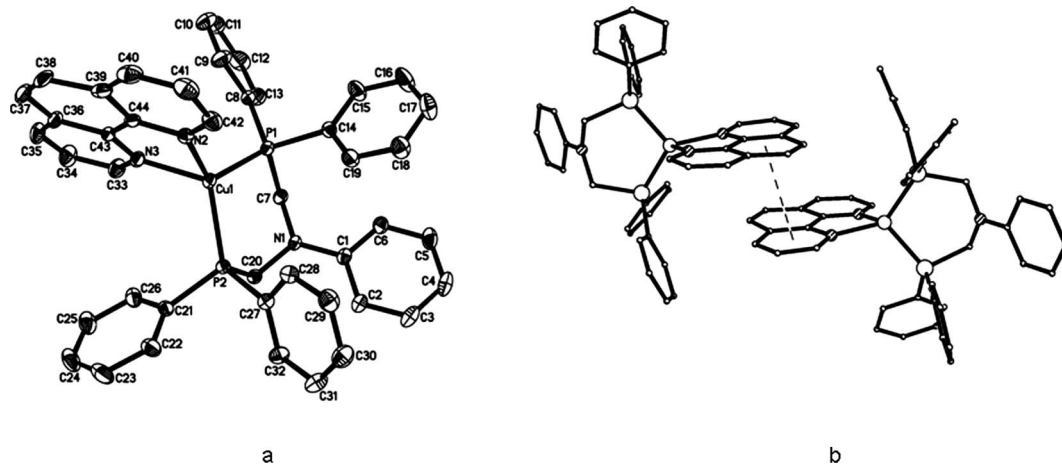


Fig. 1 (a) An ORTEP view of **1a** with 30% thermal ellipsoids, showing the local coordination environment of Cu^+ . The dihedral angle between the NCuN and PCuP planes is 90.5° . (b) The $\pi \cdots \pi$ interaction of a pair of symmetry-related complexes with a ring central–central distance of 3.572 \AA .

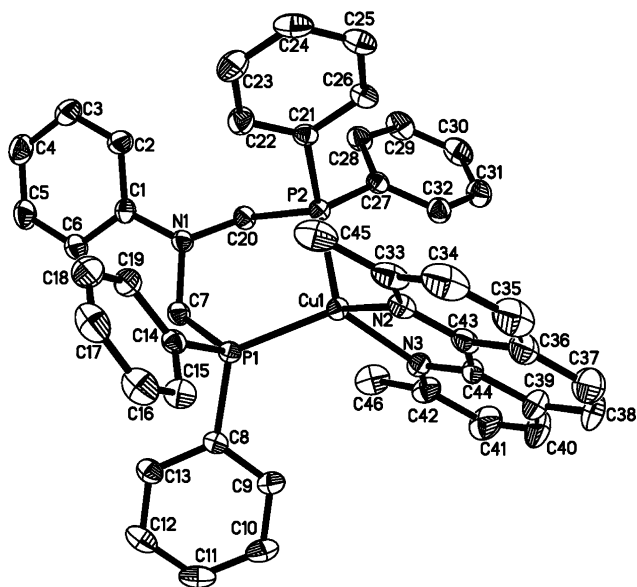


Fig. 2 An ORTEP view of **1b** with 30% thermal ellipsoids, showing the local coordination environment of Cu^+ . The dihedral angle between the NCuN and PCuP planes is 90° .

phenyl amine moiety in **1a** and **1b**, maybe due to the relatively less conjugated electrons of the phenyl amine moiety in pba. Of course, the $\text{C-H} \cdots \text{F}$ contacts between complex cations and anions surely

exist in the crystal lattices, but they are not discussed here. The biphenyl moieties in **4a** and **4b** exhibit twisted conformations with twist angles between phenyl rings of 34.3 and 26.3° , respectively. But complexes with pbaa or pbbaa ligands exhibit relatively rigid features.

Spectroscopic properties

The optical properties of the eight complexes are summarized in Table 1. These complexes have intense absorption bands at ~ 240 and 280 nm , which are assigned to the $\pi\text{-}\pi^*$ transition of intraligands. The less intense broad absorption bands at $350\text{--}490 \text{ nm}$ ($\epsilon = 2500\text{--}6300 \text{ M}^{-1} \text{ cm}^{-1}$) are attributed to the $d\pi\text{-}\pi^*$ MLCT absorption, whose magnitude of the extinction coefficient is of the order expected for a $d\pi\text{-}\pi^*$ transition. Compared with the previously investigated analogous $[\text{Cu}(\text{NN})(\text{PP})]^+$ series,¹⁶ the MLCT absorption maxima of the reported complexes occur at slightly longer wavelengths. Accounting for this, selected DFT calculations of **2a**, **2b** and **3b** were undertaken. Calculation results, similar to those previously reported,¹⁷ show that the HOMOs in these complexes are dominated by the copper d-orbital with admixed phosphine ligand character (Fig. 9, Fig. S5 and S6[†]), while the LUMOs predominantly consist of the π -electron system of phen or dmp. This fact confirms that the electron structures and orbital couplings in this system should be modified by the phosphine moiety, and the lowest energy CT excitation inevitably stems from a metal–ligand $d\sigma^*$ orbital. According to angular

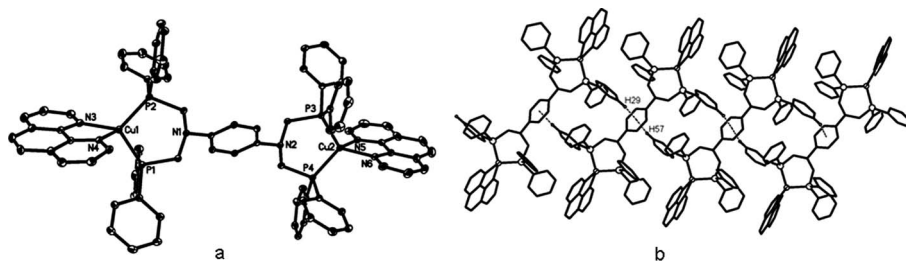


Fig. 3 (a) An ORTEP view of **2a** with 30% thermal ellipsoids, showing the local coordination environment of Cu^+ . The dihedral angles between the NCuN and PCuP planes around Cu1 and Cu2 are 97.4° and 97.4° , respectively. (b) The 1D chain structure constructed by intermolecular $\text{C-H} \cdots \pi$ interactions between arene amine rings and phenyl H atoms ($\text{H29} \cdots \pi_{\text{centroid}} = 2.908 \text{ \AA}$, $\text{H57} \cdots \pi_{\text{centroid}} = 2.984 \text{ \AA}$).

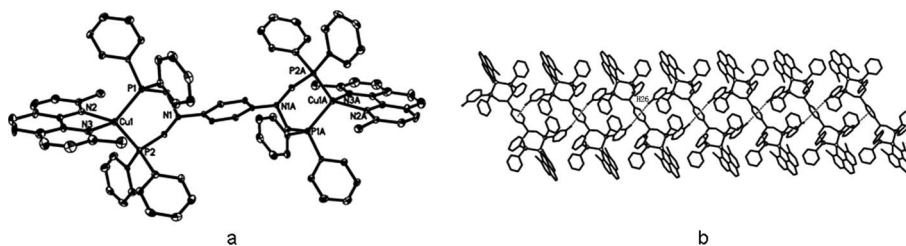


Fig. 4 (a) An ORTEP view of **2b** with 30% thermal ellipsoids, showing the local coordination environment of Cu^+ . The dihedral angle between the NCuN and PCuP planes is 91.9° . (b) The 1D chain structure constructed by intermolecular $\text{C-H}\cdots\pi$ interactions between arene amine rings and phenyl H atoms ($\text{H26}\cdots\pi_{\text{centroid}} = 2.868 \text{ \AA}$).

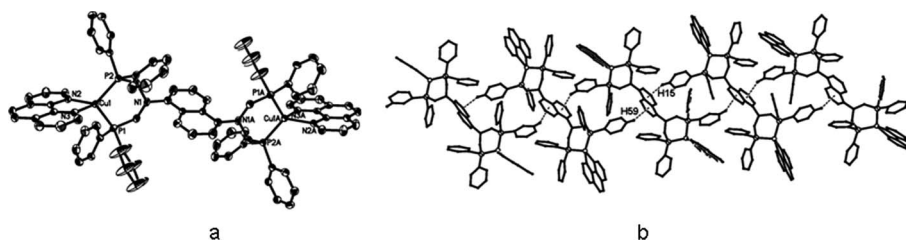


Fig. 5 (a) An ORTEP view of **3a** with 30% thermal ellipsoids, showing the local coordination environment of Cu^+ . The dihedral angle between NCuN and PCuP planes is 91.6° . (b) Showing 1D chain structure constructed by intermolecular $\text{C-H}\cdots\pi$ interactions between arene amine rings and phenyl H atoms ($\text{H59}\cdots\pi_{\text{centroid}} = 2.631 \text{ \AA}$, $\text{H15}\cdots\pi_{\text{centroid}} = 2.566 \text{ \AA}$).

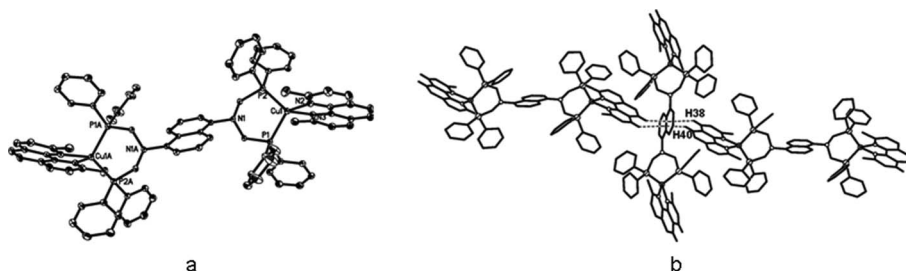


Fig. 6 (a) An ORTEP view of **3b** with 30% thermal ellipsoids, showing the local coordination environment of Cu^+ . The dihedral angle between the NCuN and PCuP planes is 96.8° . (b) The intermolecular T-shaped structure induced by intermolecular $\text{C-H}\cdots\pi$ interactions between arene amine rings and phenyl H atoms ($\text{H38}\cdots\pi_{\text{centroid}} = 2.615 \text{ \AA}$, $\text{H40}\cdots\pi_{\text{centroid}} = 2.697 \text{ \AA}$).

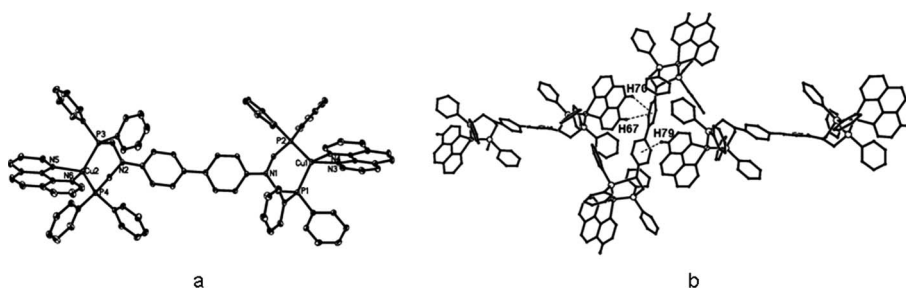


Fig. 7 (a) An ORTEP view of **4a** with 30% thermal ellipsoids, showing the local coordination environment of Cu^+ . The dihedral angles between the NCuN and PCuP planes around Cu1 and Cu2 are 91.4° and 91.3° respectively. (b) The intermolecular T-shaped structure induced by intermolecular $\text{C-H}\cdots\pi$ interactions between arene amine rings and phenyl H atoms ($\text{H67}\cdots\pi_{\text{centroid}} = 2.819 \text{ \AA}$, $\text{H70}\cdots\pi_{\text{centroid}} = 2.948 \text{ \AA}$, $\text{H79}\cdots\pi_{\text{centroid}} = 2.797 \text{ \AA}$).

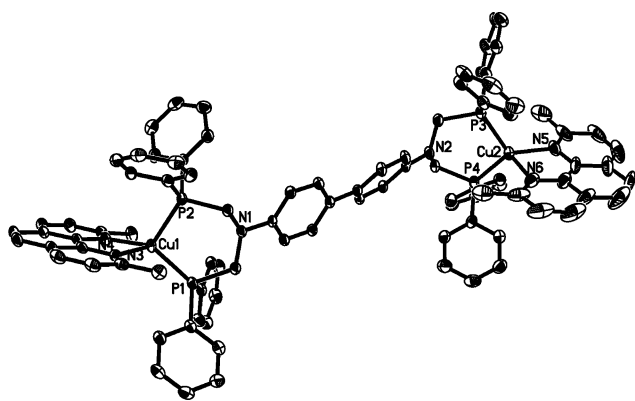
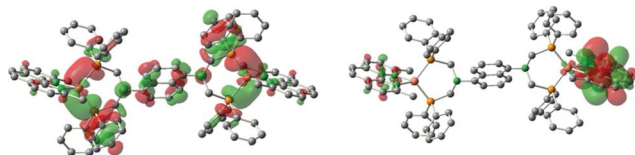
orbital model considerations, the destabilization of the copper d-orbital can be minimized by increasing the angle θ between the Cu-center and the two σ -donor ligands situated at the corners of the tetrahedron. That is to say, a smaller bite angle of the phosphine in the $[\text{Cu}(\text{NN})(\text{PP})]^+$ moiety can induce a larger orbital overlap integral between the P-localized lone-pairs and one of the occupied $d\pi$ -orbitals of the copper center, resulting in lower MLCT transitions. Therefore, the longer-wavelength

absorption maxima in the reported complexes are attributed to the destabilization effect of smaller P–Cu–P bite angles.

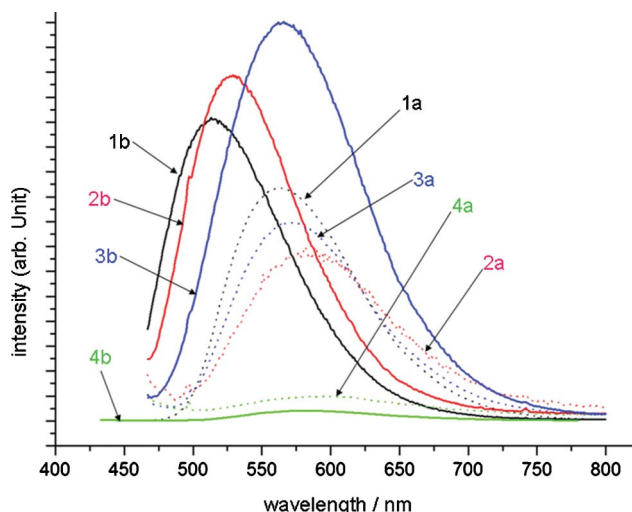
Upon excitation at 425 nm, the solid state emission spectra of **1a–4b** from the MLCT excited states occur in the visible region 513–595 nm at room temperature (Fig. 10). Comparing complexes with different NN ligands, incorporating bulky alkyl groups in the 2 and 9 positions of phenanthroline ligand leads to increased excited state lifetime as well as a blue-shifted emission

Table 1 The photophysical properties of eight complexes at room temperature

Complex	λ_{\max} (e) (nm)	Emission						Solid state	
		Solution (in CH ₂ Cl ₂)						λ_{\max} (nm)	τ (μ s)
		λ_{\max} (nm)	Φ_{em}	τ (μ s)	K_r (s ⁻¹)	k_{nr} (s ⁻¹)			
1a	412 (2400)	620	0.00093	4.14	2.25×10^2	2.41×10^5	563	19.95	
2a	422 (5000)	618	0.00215	6.77	3.18×10^2	1.47×10^5	582	15.82	
3a	425 (5200)	610	0.00162	5.56	1.54×10^2	9.48×10^4	572	15.83	
4a	418 (4900)	612	0.00991	8.15	1.21×10^3	9.67×10^4	595	14.57	
1b	397 (2900)	637	0.00305	7.55	4.04×10^2	1.32×10^5	513	50.94	
2b	400 (6200)	615	0.03520	14.90	2.36×10^3	6.48×10^4	529	34.28	
3b	389 (5200)	596	0.31300	18.95	1.65×10^4	3.62×10^4	566	28.57	
4b	395 (3400)	583	0.07150	15.21	4.50×10^3	6.10×10^4	589	14.82	

**Fig. 8** An ORTEP view of **4b** with 30% thermal ellipsoids, showing the local coordination environment of Cu⁺. The dihedral angles between the NCuN and PCuP planes around Cu1 and Cu2 are 96.6° and 89.8° respectively.**Fig. 9** Contour plots of the HOMO (left) and LUMO (right) of complex **3b**.

band. The reason for these is that bulky substituents can sterically prevent structural relaxation in the MLCT states, and decrease non-radiative decay. Furthermore, for complexes with identical diimine but different phosphine ligands, the tendency toward an increased lifetime, as well as for a blue-shifted emission, goes with the decrease in size of the phosphine ligands. Intermolecular C–H \cdots π interactions can trigger vibrationally relaxed energy transfer in the excited state, and subsequently result in non-radiative decay. A larger-sized central arene ring is favorable for forming intermolecular C–H \cdots π interactions (see the above-discussed crystal structure). Therefore smaller-sized complexes exhibit longer lifetimes and blue-shifted emissions in the solid state due to less vibrationally relaxed behavior related to flexible C–H \cdots π bonds. Complexes **4a** and **4b** exhibit the lowest intensity luminescence and the shortest lifetime, maybe due to the biphenyl moiety in dppaa, which can be rotated, enhancing the vibrationally relaxed CT excited state.

**Fig. 10** The emission spectra of complexes in the solid state at room temperature, upon excitation at 425 nm.

At room temperature, the luminescence spectra of complexes in dilute CH₂Cl₂ solution were also recorded upon excitation at 425 nm (Fig. 11). Similar to the solid state luminescence, the dmp-containing complex exhibits an increased quantum yield and excited-state lifetime, as well as blue-shifted emission relative to the corresponding phen complex, due to the steric encumbrance of the bulky alkyl group, which will moderate the structural relaxation/reorganization that attends formation of the CT excited state in solution. In fact, the structural relaxation/reorganization will narrow the gap between the ground and excited state, enhance the coupling between the two states, and shorten the excited state lifetimes. Generally, phen complexes exhibit similar luminescence in solution. Concerning complexes with identical dmp ligands but different phosphine ligands, the tendency toward increased quantum yield and lifetime, as well as the blue-shifted emission, goes with the size increase of complexes. It seems that the central arene rings (phenyl, naphthyl or biphenyl) have an influence on the final photophysical properties of complexes. The larger the π -conjugated extension of the central arene ring is, the better the photophysical properties of the complex are. So it can be deduced that the central arene ring performs as an organic chromophore, and the cooperative effect of the complex chromophore is related to the central metal and the central organic chromophore results in the final photophysical properties of the complex. **3b** with a

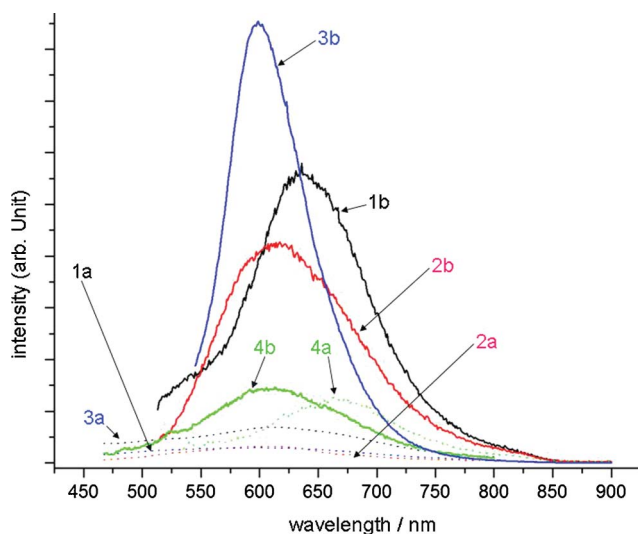


Fig. 11 The emission spectra of complexes in CH_2Cl_2 solution (5×10^{-4} M) at room temperature, upon excitation at 425 nm.

rigid naphthalene ring exhibits the best emission with the largest quantum yield (0.313) and the longest emission lifetime (18.95 μs). The influence of intermolecular interactions on luminescent properties is much weaker in dilute solution. It should be noted that complexes **4a** and **4b** have relatively better emissions in solution, maybe due to the increasing coplanarity of two phenyl rings in the biphenyl moiety in solution leading to extended intraligand electron delocalization and minimized excited state distortion of the corresponding complex.¹⁸ Nevertheless, the fact that the emission of **4b** is similar to **2b**, but not as good as that of rigid complex **3b**, shows that the rotating/vibrating behavior of the biphenyl moiety is still not ignored in solution. The emission yields of our phen-complexes are similar to that of $\text{Cu}(\text{phen})(\text{POP})^+$, but their lifetimes are longer than that of the latter. However, the lifetimes of dmp complexes in our system are comparable with those of $[\text{Cu}(\text{dmp})(\text{POP})]^+$ or $[\text{Cu}(\text{dbp})(\text{POP})]^+$,^{6a} but the yields are a little lower than those of the latter complexes. Complex **3b** is exceptional, its emission yield is higher than $[\text{Cu}(\text{dmp})(\text{POP})]^+$, even comparable with that of $[\text{Cu}(\text{POP})(\text{DMPP})]^+$ (DMPP = 2,9-dimethyl-4,7-phenylphenanthroline), which was reported as a good luminophore with the highest quantum yield in the $[\text{Cu}(\text{NN})(\text{PP})]^+$ system.¹⁹

The experimentally measured τ and Φ values were used to calculate the radiative, k_r , and the nonradiative, k_{nr} , rate constants. The k_r values of dmp complexes exhibit a marked increase with size increase, but the k_{nr} values of phen complexes slightly decrease with size increase, showing that the bulkiness of ligand preventing complexes from distorting in the excited states plays a dominant role in solution. The k_{nr} values of **2b** and **4b** are similar, though their sizes are very different. The highest k_r value, as well as the low nonradiative decay of **3b** results from the cooperative effects of structural rigidity and steric encumbrance.

In conclusion, the crystal structures and photophysical properties of these eight complexes are discussed in detail. Results show that the steric encumbrance of bulky substitutes in the 2 and 9 positions of phenanthroline plays a dominant role in the luminescent properties of the $[\text{Cu}(\text{NN})(\text{PP})]^+$ system. Furthermore, intermolecular $\text{C-H} \cdots \pi$ interactions have an influence on the final

solid state photophysical properties. For complexes with identical diimine but different phosphine ligands, smaller-sized complexes show better photophysical properties due to less vibrationally relaxed behavior related to flexible $\text{C-H} \cdots \pi$ bonds. Nevertheless, in dilute solution, the backbone (phenyl, naphthyl or biphenyl) has an influence on the final photophysical properties. The larger the π -conjugated extension of the central arene ring is, the better the photophysical properties of the complex are. The rigid and large complex **3b** exhibits extraordinary emission. Intermolecular $\text{C-H} \cdots \pi$ interactions are very weak in dilute solution.

Experimental Section

General

All chemicals were of reagent grade and were used as received without further purification. Elemental analyses were performed with a Carlo ERBA 1106 analyzer; ^1H and $^{31}\text{P}\{^1\text{H}\}$ spectra were recorded on a Bruker 500 spectrometer at 500.13 and 202.46 MHz, respectively. Electrospray mass spectra were recorded on a Bruker HCT ESI spectrometer. Absorption spectra were measured with a Varian CARY-100UV spectrophotometer. The luminescence spectra and emission lifetimes were measured at room temperature on a FL3-P-TCSPC spectrophotometer with a xenon lamp as the light source. The absorption and luminescence spectra of complexes were measured in CH_2Cl_2 . Emission quantum yield, Φ , was measured with the use of $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$ in MeCN as a standard ($\Phi = 0.09$). Ligands pba, pbaa, pnaa and pbbaa are reported first here and synthesized according to references.²⁰

X-ray crystallography

Reflection intensity data for **1a**, **1b**, **2b** and **4a** were collected (**1a** and **1b** at a temperature of 296 K, **2b** and **4a** at 173 K) on a Bruker APEX CCD diffractometer with graphite monochromated Mo- $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) using the ω technique, and data for **2a**, **3a**, **3b** and **4b** were collected at 150 K on a Oxford 'Xcalibur, Sapphire3, Gemini ultra' diffractometer with Enhance Ultra (Cu) X-ray Source ($\lambda = 1.5418 \text{ \AA}$) using the ω technique. All the structures were solved by direct methods and refined with the full-matrix least-squares on F^2 using SHELXTL. The structure of **2a** contains solvent accessible voids of 205 \AA^3 , indicating that there may be solvents occupied in the voids. However, they cannot be found in the crystal structure. Maybe they are likely too diffuse/disordered to be resolved. During the structure refinement of **4b**, an unidentified and badly disordered solvent molecule (probably DMF) was removed with the squeeze option in PLATON.²¹ No hydrogen atoms were assigned on water molecules O1 and O2. Crystal and structure refinement data are summarized in Table S2.†

Computational details

The Gaussian03 program²² was used in the molecular orbital calculations on the basis of corresponding coordinates of the X-ray crystal structures. All calculations were performed with the B3LYP method and the 6-311++G(d,p) basis sets.²³

$[\text{Cu}(\text{phen})(\text{pba})(\text{BF}_4)]$ (**1a**)

A typical procedure is as follows. A mixture of $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{BF}_4$ (0.016 g, 0.05 mmol) and phosphine ligand (0.0245 g, 0.05 mmol)

in 4 ml CH₃CN was stirred at room temperature for 0.5 h and then phen (0.009 g, 0.05 mmol) was added. This reaction mixture was stirred for an additional 1 h and filtered. The vapor diffusion of diethyl ether into the resulting clear yellow filtrate afforded yellow crystals of the complex. The complex was obtained by filtration, washed by diethyl ether and dried *in vacuo*. Yield: 0.034 g (83%). Anal. calcd for C₄₄H₃₇N₃BF₄P₂Cu: C, 64.39; H, 4.51; N, 5.12. Found: C, 64.21; H, 4.70; N, 5.52. ¹H NMR (CD₃SOCD₃, 25 °C, TMS): δ = 5.0 (4H, -CH₂-), 6.4–6.8 (5H, C₆H₅-N), 7.2–7.4 (20H, C₆H₅-P), 7.8–8.8 ppm (8H, H-phen). ³¹P{¹H}-NMR (CDCl₃): -14.95. ESI-MS (+): *m/z* 733 [Cu(pda)(phen)]⁺.

The procedures for the synthesis of **1b–4b** were essentially identical to that described in **1a**, only different ligands are used.

[Cu(dmp)(pba)](BF₄) (1b)

Yield: 0.032 g (76%). Anal. calcd for C₄₆H₄₁N₃BF₄P₂Cu: C, 65.09; H, 4.83; N, 4.95. Found: C, 64.82; H, 4.91; N, 5.12. ¹H NMR (CD₃SOCD₃, 25 °C, TMS): δ = 2.7 (6H, CH₃-), 5.3 (4H, -CH₂-), 7.4–7.6 (5H, C₆H₅-N), 7.7–7.9 (20H, C₆H₅-P), 8.2–9.1 ppm (6H, H-phen). ³¹P{¹H}-NMR (CDCl₃): -19.83. ESI-MS (+): *m/z* 761 [Cu(pda)(dmp)]⁺.

[Cu₂(phen)₂(pbaa)](BF₄)₂ (2a)

Yield: 0.045 g (58%). Anal. calcd for C₈₂H₆₈N₆B₂F₈P₄Cu₂, C, 63.00; H, 4.35; N, 5.38. Found: C, 63.45; H, 4.68; N, 5.41. ¹H NMR (CD₃SOCD₃, 25 °C, TMS): δ = 4.7 (8H, -CH₂-), 6.2 (4H, N-C₆H₄-N), 7.2–7.4 (40H, C₆H₅-P), 7.0–8.8 ppm (16H, H-phen). ³¹P{¹H}-NMR (CDCl₃): -16.08. ESI-MS (+): *m/z* 694 [Cu₂(pbaa)(phen)₂]²⁺.

[Cu₂(dmp)₂(pbaa)](BF₄)₂ (2b)

Yield: 0.035 g (43%). Anal. Calcd for C₈₆H₇₆N₆B₂F₈P₄Cu₂, C, 63.78; H, 4.70; N, 5.19. Found: C, 63.50; H, 4.89; N, 5.44. ¹H NMR (CD₃SOCD₃, 25 °C, TMS): δ = 2.4–2.7 (12H, CH₃-), 4.8–5.2 (8H, -CH₂-), 7.2–9.1 ppm (56H, 4H (N-C₆H₄-N) + 40H (C₆H₅-P) + 16H (H-phen)). ³¹P{¹H}-NMR (CDCl₃): -20.16. ESI-MS (+): *m/z* 722 [Cu₂(pbaa)(dmp)₂]²⁺.

[Cu₂(phen)₂(pnaa)](BF₄)₂ (3a)

Yield: 0.022 g (27%). Anal. calcd for C₈₆H₇₀N₆B₂F₈P₄Cu₂, C, 64.02; H, 4.34; N, 5.21. Found: C, 63.88; H, 4.63; N, 5.01. ¹H NMR (CD₃SOCD₃, 25 °C, TMS): δ = 4.6 (8H, -CH₂-), 6.9–8.9 ppm (62H, (6H, N-C₁₀H₆-N) + (40H, C₆H₅-P) + (16H, H-phen)). ³¹P{¹H}-NMR (CDCl₃): -16.25. ESI-MS (+): *m/z* 719 [Cu₂(phen)₂(pbaa)]²⁺. Single crystals were collected by vapor diffusion of diethyl ether into a solution of complex in mixtures of MeCN-toluene.

[Cu₂(dmp)₂(pnaa)](BF₄)₂ (3b)

Yield: 0.018 g (21%). Anal. calcd for C₉₀H₇₈N₆B₂F₈P₄Cu₂, C, 64.75; H, 4.68; N, 5.04. Found: C, 64.43; H, 4.94; N, 4.86. ¹H NMR (CD₃SOCD₃, 25 °C, TMS): δ = 2.5–2.8 (12H, CH₃-), 4.6 (8H, -CH₂-), 7.2–9.3 (58H, (6H, N-C₁₀H₆-N) + (40H, C₆H₅-P) + (12H, phen)). ³¹P{¹H}-NMR (CDCl₃): -18.81. ESI-MS (+): *m/z* 747 [Cu₂(dmp)₂(pbaa)]²⁺. Single crystals were collected by vapor

diffusion of diethyl ether into solution of complex in mixture of MeCN-toluene.

[Cu₂(phen)₂(pbaa)](BF₄)₂ (4a)

Yield: 0.031 g (38%). Anal. calcd for C₈₈H₇₂N₆B₂F₈P₄Cu₂, C, 64.47; H, 4.40; N, 5.13. Found: C, 64.83; H, 4.21; N, 5.58. ¹H NMR (CD₃SOCD₃, 25 °C, TMS): δ = 5.1 (8H, -CH₂-), 6.5–6.9 (8H, N-C₆H₄-C₆H₄-N), 7.3–7.5 (40H, C₆H₅-P), 7.7–8.8 ppm (16H, phen). ³¹P{¹H}-NMR (CDCl₃): -14.85. ESI-MS (+): *m/z* 732 [Cu₂(phen)₂(pnaa)]²⁺.

[Cu₂(dmp)₂(pbaa)](BF₄)₂ (4b)

Yield: 0.035 g (41%). Anal. calcd for C₉₂H₈₀N₆B₂F₈P₄Cu₂, C, 65.17; H, 4.72; N, 4.96. Found: C, 65.52; H, 4.97; N, 5.05. ¹H NMR (CD₃SOCD₃, 25 °C, TMS): δ = 2.4–2.5 (12H, CH₃-), 5.1–5.3 (8H, -CH₂-), 7.5–7.8 (8H, N-C₆H₄-C₆H₄-N), 7.8–8.0 (40H, C₆H₅-P), 8.2–9.1 ppm (12H, H-phen). ³¹P{¹H}-NMR (CDCl₃): -20.77. ESI-MS (+): *m/z* 760 [Cu₂(dmp)₂(pnaa)]²⁺. Single crystals were collected by vapor diffusion of diethyl ether into DMF solution of complex.

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