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Introduction

The luminescent copper(I) complexes have been extensively investigated for nearly forty years since the pioneering reports on their photophysical properties.¹ During the last decade particular attention was paid to systematic modulation of ligand architecture of copper-containing species due to the (i) low cost of the corresponding metal; (ii) facile coordination chemistry of the Cu(I) ion that allows for stereochemically controlled high yield preparation of a wide variety of complexes; and (iii) their capability of efficiently generating intense luminescence under ambient conditions.^{2,3–9} This attractive photophysical feature, which comprises high quantum yield in the solid state and tunable emission energy,^{7–14} has found applications in technologically important areas such as chemical sensing,¹⁵ light-emitting electrochemical cells (LEC)^{16,17} and, immensely, in organic light-emitting diodes (OLED).^{3,5–7,18,19} In the field



Gomathy Chakkaradhari,^a Andrey A. Belyaev,^b Antti J. Karttunen,^c Vasily Sivchik,^a Sergey P. Tunik^{*b} and Igor O. Koshevoy^{*a}

A rigid triphosphine PPh₂C₆H₄–PPh–C₆H₄PPh₂ (\mathbf{P}^3) reacted with Cu⁺ and a stoichiometric amount of terminal alkyne under basic conditions to give a family of copper(i) alkynyl compounds [Cu(\mathbf{P}^3)C==CR]. The number of terminal –C==CH groups in the starting ligand determines the nuclearity of the resulting complexes giving mono- ($\mathbf{1}$, R = Ph; $\mathbf{2}$, R = C₆H₄OMe; $\mathbf{3}$, R = C₆H₄NO₂; $\mathbf{4}$, R = C₆H₄CF₃; $\mathbf{5}$, R = 2-pyridyl), di- (R = -(C₆H₄)_n-, *n* = 1 ($\mathbf{6}$), *n* = 2, (7), *n* = 3 ($\mathbf{2}$)) and trinuclear complexes ($\mathbf{9}$, R = 1,3,5-(C₆H₄)₃-C₆H₃). In all the complexes the Cu(i) centers are found in a distorted tetrahedral environment that is achieved by tridentate coordination of the \mathbf{P}^3 ligand and σ -bonding to the alkynyl function. The crystal structures of $\mathbf{1}$, $\mathbf{3}$ and $\mathbf{5}$ were estimated by single crystal X-ray diffraction analysis. The ³¹P, ¹H and ¹H–¹H COSY NMR spectroscopy confirms that all the molecules remain intact in solution. The photophysical studies carried out in the solid state at 298 and 77 K revealed moderate to weak orange luminescence (ϕ_{em} up to 19%), tentatively assigned to thermally activated delayed fluorescence for the mononuclear complexes. The quantum yields of emission of **1–10** demonstrated strong dependence on the nature of the alkynyl ligand, the role of which in the electronic transitions was elucidated by TD-DFT computational studies.

of OLEDs copper(1) compounds are considered to be promising emitting materials as, in a favorable case, they are able to exhibit thermally activated delayed fluorescence (TADF) that stems from a very fast intersystem crossing between S_1 and T_1 excited states and, consequently, utilizing both singlet and triplet excitons *via* a singlet harvesting mechanism^{12,14,20,21} thus offering an improved electroluminescence efficiency.^{5,6,12,22,23}

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A rational choice of the ligands to optimize luminescence efficiency of Cu(I) species was considerably facilitated since a number of experimental approaches supported by theoretical investigations shed light on the details of structural rearrangement and electronic processes, which occur in the excited state.²⁴ One of the main shortcomings of Cu(1) complexes is structural relaxation from tetrahedral to a pseudo-planar geometry as a result of a formal oxidation to Cu(II) that takes place upon metal to ligand charge transfer (MLCT). Consequently, it increases the probability of non-radiative decay pathways leading to a dramatic drop of the emission efficiency. Thus one of the main trends in the design of Cu(I) luminophores involves the use of relatively bulky ligands to suppress solventinduced exciplex quenching,25 to increase structural rigidity3,6,26 and prevent flattening of the tetrahedral ligand arrangement around Cu(1) centres.

Different types of ligand environments have been probed to achieve intense emission and robustness of the Cu(1)

^aUniversity of Eastern Finland, Department of Chemistry, 80101, Joensuu, Finland. E-mail: igor.koshevoy@uef.fi

^bSt. Petersburg State University, Department of Chemistry, Universitetskii pr. 26, 198504, St Petersburg, Russia. E-mail: stunik@inbox.ru

^cAalto University, Department of Chemistry, FI-00076 Aalto, Finland

[†]Electronic supplementary information (ESI) available: Synthesis of the ligands; optimized Cartesian coordinates of the studied systems. CCDC 1401069–1401071 for **1**, **3** and **5**. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5dt01870f

complexes.⁴ They include thoroughly studied homo- and heteroleptic bis-diimine Cu(I) compounds $[Cu(NN)_2]^+$ (ref. 26 and 27) typically displaying weak quantum efficiency below 1%. More recently, research focus has largely shifted to the mixed phosphine-diimine complexes $[Cu(NN)(PP)]^{n+}$ (n = 0, 1) of neutral and cationic nature, for which an impressive enhancement of quantum yield was demonstrated reaching as high as 90%.^{5,12,16,18,23,25,28} The emission observed originates mainly from MLCT excited states that make possible tuning luminescence parameters through electronic and stereochemical properties of the ligands that stimulated further development of the preparative chemistry of the Cu(I) ion. Among the notable examples are the amidophosphine derivatives [Cu(PN)(PP)],¹⁰ which exhibit intense and tunable green to blue emission in solution ($\Phi_{\rm em}$ = 16–70%); highly luminescent dinuclear halide species [Cu₂(PN)₃X₂] covering the visible spectrum from blue to red ($\Phi_{\rm em}$ = up to 96%);^{7,8} families of three-coordinate complexes featuring phosphine halides [Cu(PP)X],⁶ arylamidophosphines [Cu(PP)NAr₂]¹¹ and carbene-diimines [Cu(NN)-NHC].9,13

A general common feature of the Cu(I) complexes mentioned above is a conformationally rigid chelating bidentate phosphine that brings steric bulkiness and minimizes the undesired excited state distortions. It has to be noted that triphosphine ligands have been rarely used in the synthesis of Cu(I) species with only a few reports on luminescent compounds.²⁹⁻³¹ In particular, coordination chemistry of a tridentate chelating phosphine PPh₂C₆H₄-PPh-C₆H₄PPh₂ $(\mathbf{P}^3$, see Scheme 1) with coinage metals remains poorly explored³² despite promising practical results, which were reported for these inorganic materials.^{33,34} In the current work we employ the triphosphine ligand \mathbf{P}^3 in combination with a series of mono-, di- and trialkynes for the preparation of a family of Cu(I) complexes of different nuclearity. The luminescence properties of the resulting compounds were systematically investigated in the solid state to discover the effect of the



Scheme 1 Synthesis of the complexes 1-10 (298 K, 10 h, acetone).

constituting ligand nature onto the physical characteristics of these species.

Results and discussion

Synthesis and characterization

The title compounds were obtained according to a general synthetic route shown in Scheme 1. The reactions of the $[Cu(\mathbf{P}^3)]^+$ species generated *in situ* with a stoichiometric amount of a terminal mono-, di- or trialkyne in the presence of a base allowed for the isolation of the alkynyl-triphosphine copper complexes $[Cu(\mathbf{P}^3)C_2R]$ (1–10) as air and moisture stable yellow solids. However, most of the compounds were found to be unstable in chlorinated solvents, which induce formation of a chloro derivative $[Cu(\mathbf{P}^3)(Cl)]^{34}$ through the substitution of the alkyne ligands.

The mononuclear complexes 1, 3 and 5 were characterized in the solid state by single crystal X-ray diffraction analysis (Fig. 1, crystallographic data are given in Table S1, ESI[†]). The selected structural parameters are listed in Table 1. The coordination sphere of the copper ion in 1, 3 and 5 contains chelating tridentate \mathbf{P}^3 phosphine and the σ -bound alkynyl group, which completes a pseudo-tetrahedral arrangement around the metal center. The Cu-P distances are comparable to the corresponding values reported for the related phosphine copper(1) complexes.^{31,35,36} The central P(2)-Cu bond length is slightly longer than the distances to the lateral PPh₂ groups presumably as a result of a relatively strained geometry of the \mathbf{P}^3 ligand. Additionally, the strongly donating anionic $-C \equiv CR$ fragment may enhance this effect due to a rather large C(1)-Cu(1)-P(2) angle (124 and 131°). The Cu-C (terminal alkyne) contacts are in the range of 1.921-1.927 Å and are expectedly shorter than the bond lengths in oligomeric copper alkynyl complexes, which typically demonstrate μ_2 - or μ_3 -bridging coordination mode of $-C \equiv CR$ ligands.³⁷ Due to a pronounced tendency of the alkynyl ligands to bind two or more Cu(I) centers through σ - π coordination mode a significant number of tri- and tetranuclear species have been described^{37,38} but surprisingly no monomeric alkynyl complexes were characterized to date. In this context it is worth mentioning that a congener alkynyl-phosphine compound bearing an aliphatic tripod ligand, that was initially thought to be monomeric,³⁰ which was later described as a dimer $\{Cu(\mu_2-C)=CPh\}$ -(triphos)₂ $(triphos = (PPh_2CH_2)_3CMe)$,³⁵ with only two P atoms involved in binding to the metal ion. The solution behavior of the complexes 1-10 was investigated by ¹H and ³¹P{¹H} NMR spectroscopy. All the compounds demonstrate a very similar set of resonances in the ³¹P spectra (see the Experimental section and Fig. 3 for examples) irrespective of their nuclearity that is indicative of a symmetrical arrangement of the di- (6-8) and trimetallic (9-10) species and equivalence of the constituting $\{CuP^3\}$ fragments. This A₂B system observed for the free ligand together with a downfield shift of the signals in 1-10 clearly points to the phosphorus atom coordination to the copper ions in solution. A narrow range of the chemical shifts

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Fig. 1 Molecular views of the complexes 1, 3, and 5; thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms are omitted for clarity. One of two independent molecules found in the unit cells of 1 and 3 is shown.

Table 1 Selected bond lengths and angles for complexes 1, 3, and 5 (two values for 1 and 3 correspond to the independent molecules found in the unit cell)

	1	3	5
Bond lengths, Å			
P(1)-Cu(1)	2.2798(9)	2.3049(7)	2.2864(15)
	2.2840(9)	2.3029(6)	
P(2)-Cu(1)	2.3003(9)	2.2751(6)	2.2965(14)
	2.2622(9)	2.2708(7)	. ,
P(3)-Cu(1)	2.2988(10)	2.2690(6)	2.2869(15)
	2.2899(9)	2.2961(6)	
C(1)-Cu(1)	1.925(4)	1.927(2)	1.921(5)
	1.930(3)	1.934(3)	
C(1)-C(2)	1.195(5)	1.213(3)	1.199(8)
	1.198(5)	1.199(4)	
Bond angles, °			
C(2)-C(1)-Cu(1)	171.7(3)	171.8(2)	172.1(5)
	177.2(3)	171.2(2)	
C(1)-Cu(1)-P(1)	113.21(10)	115.25(7)	120.2(2)
	118.86(10)	116.78(7)	
C(1)-Cu(1)-P(2)	131.53(11)	129.12(7)	132.3(2)
	124.17(11)	130.85(7)	
C(1)-Cu(1)-P(3)	121.94(11)	118.22(7)	114.1(2)
	116.82(11)	118.42(7)	
P(1)-Cu(1)-P(3)	114.07(3)	113.69(2)	113.7(6)
	115.20(3)	112.11(2)	
P(1)-Cu(1)-P(2)	85.18(3)	87.32(2)	85.36(5)
	88.21(3)	86.48(2)	
P(3)-Cu(1)-P(2)	84.01(3)	87.77(2)	84.73(5)
	86.62(3)	85.82(2)	

observed for 1–10 (δ_A from 1.1 to –0.5 ppm and δ_B from –1.8 to –3.1 ppm) implies a relatively small effect of the alkynyl substituents onto electronic properties of the metal centre that is also in line with the photophysical characteristics (see below).

A complete assignment of the proton spectra was done on the basis of the 1D and 2D ${}^{1}\text{H}{-}{}^{1}\text{H}$ COSY experiments (Fig. 2 and 3). Analogous to ${}^{31}\text{P}$ data, the ${}^{1}\text{H}$ signals of the \mathbf{P}^{3} phosphine protons do not demonstrate significant alterations upon variation of the alkynyl ligands to give essentially similar spectroscopic patterns with satisfactorily resolved resonances, which are clearly seen in the spectrum (see for example Fig. 2). The phenyl protons of the terminal PPh₂ groups appear as two sets of "*ortho-meta-para*" signals. The phenylene spacers of



Fig. 2 ${}^{1}H-{}^{1}H$ COSY NMR spectra of the complex 3 (acetone- d_{6} , 298 K).

the phosphine and alkynyl ligands generate four well-separated multiplets in the region 7.4–7.8 ppm, while the PPh fragment displays a non-resolved group of signals around 7.2 ppm.

Further analysis of the ¹H spectroscopic data for other compounds allows for an easy identification of the resonances of the alkyne ligands. The ¹H-¹H COSY spectrum of the trinuclear complex **10** given in Fig. 3 shows the assignment of the trialkynyl protons that confirm the C_{3v} symmetry point group of the idealized molecule. Relative intensities and multiplicities of the proton NMR signals observed for all the title compounds fit well with the composition and structures suggested in Scheme 1.

Photophysical characteristics

The complexes **1–10** do not demonstrate detectable photoluminescence in solution. Therefore, the photophysical investi-



Fig. 3 ${}^{31}P{}^{1}H{}$ (top) and ${}^{1}H{}^{-1}H{}$ COSY (bottom) NMR spectra of the complex 10 (CD₂Cl₂, 298 K).

gation was carried out in the solid state only, and the data are given in Table 2. Upon photoexcitation the mononuclear complexes 1-5 (except for 3) exhibit yellow emission of a moderate intensity ($\Phi_{\rm em}$ ranges from 6 to 19%). Fig. 4 and S2[†] show excitation and emission spectra of the solid powders at 298 and 77 K. The compounds 1, 2, 4 and 5 show broad structureless bands, the maxima of which are only slightly influenced by





1.0

0.8

Fig. 4 Normalized solid state excitation (left) and emission (right) spectra of 1 and 5 at 298 K (dashed lines) and 77 K (solid lines).

lowering the temperature to 77 K being red shifted by 6-10 nm. The room temperature excited state lifetime of the complexes under study fall in a microsecond domain and are comparable to the corresponding values of other mononuclear Cu(1) phosphine complexes.^{6,12,20,21,39,40} However, the lifetime values of 1, 2, and 4 demonstrate a very significant up to 130fold increase upon cooling down to 77 K. Together with the small red-shift of the emission energy (5-10 nm) the luminescence behavior of these complexes might be considered as thermally activated delayed fluorescence (TADF).12,20,21 Consequently, the emission at 77 K can be considered as the one from the triplet state, while at room temperature thermal equilibrium between the nearest S₁ and T₁ states leads to a population of higher lying singlets causing a blue shift of emission maximum and a considerable decrease of the τ values, which is in fact a derivative of the triplet (μ s) and singlet (ns) decay lifetimes. The double exponential treatment of the luminescence decay for the solid state emission is not surprising^{21,40,41} and may be attributed to similar electronic transitions, which differ in relaxation rates due to the local disorder in the crystal cell or to the presence of two molecules

Table 2	Photophysical properties of the complexes 1-10 in the solid stat	e

	298 K					77 K			
	$\lambda_{\rm ex}$, nm	$\lambda_{\rm em}$, nm ^{<i>a</i>}	$ au_{\mathrm{av}}$, $\mu \mathrm{s}^{\ b}$	$\Phi, \%$	$k_{\rm r}, {\rm s}^{-1 c}$	$k_{\rm nr},{\rm s}^{-1d}$	$\lambda_{\rm ex}$, nm	$\lambda_{\mathrm{em}},\mathrm{nm}$	$ au_{\mathrm{av}}, \mu \mathrm{s}^{ b}$
1	415	602	1.8	6.3	$3.4 imes 10^4$	$5.1 imes 10^5$	415	612	246
2	415	602	2.1	7.9	$3.8 imes 10^4$	$4.4 imes 10^5$	415	612	73
3	580	722	_	~ 0.1			415	717	_
4	340, 415	573	2.5	11	$4.3 imes 10^4$	$3.5 imes 10^5$	370	579	59
5	415	573	3.8	19	$5 imes 10^4$	$2.2 imes 10^5$	415	579	149
6	424	603	1.6	2.6	$1.6 imes 10^4$	6×10^5	401	540sh, 581, 635	50
7	341, 441	616	2.2	1.4	6.3×10^{3}	$4.4 imes 10^5$	426	556, 642	13
8	347, 441	629	2.2	0.6	$2.8 imes 10^3$	$4.6 imes 10^5$	426	574, 622, 683	_
9	393	638	1.0	2	$2 imes 10^4$	1×10^{6}	426	530, 575sh, 640	166
10	312, 483	560	0.3	~ 0.1	$3.5 imes 10^3$	$3.5 imes 10^6$	442	524, 570, 607, 647sh	—

 $^{a}\lambda_{exc}$ = 420 nm for **1**, **2**, **4–9**; λ_{exc} = 550 nm for **3**; λ_{exc} = 490 nm for **10**. b Average emission lifetime for the two exponential decay determined by the equation $\tau_{av} = (A_1\tau_1^2 + A_2\tau_1^2)/(A_1\tau_1 + A_2\tau_1)$. $^{c}k_r$ were estimated by Φ/τ_{av} . $^{d}k_{nr}$ were estimated by $k_r(1 - \Phi)/\tau_{av}$.



Fig. 5 Normalized solid state excitation (left) and emission (right) spectra of 8 at 298 K and 77 K.



Fig. 6 Normalized solid state excitation (left) and emission (right) spectra of **10** at 298 K and 77 K.

with slight variations in structural characteristics (see *e.g.* the structures of **1** and **3**).

It is worth noting that the complex 3, containing an alkyne functionalized with the NO₂ group, displays photophysical characteristics very different from those of other mononuclear congeners. Its emission band is considerably red shifted that is accompanied by a dramatic decrease of quantum efficiency ($\Phi_{\rm em}$ is *ca.* 0.1%). The computational results (*vide infra*) show a significant contribution of the nitro functionality to the triplet excited state that is contrasting with electronic structures of other monometallic compounds. This delocalization of the electron density might account for the observed red shift of luminescence and appearance of non-radiative decay pathways, which cause a dramatic decrease of the quantum efficiency. At room temperature the dinuclear species 6-8 demonstrate broad emission bands (Fig. 5), whereas at 77 K (Fig. S3[†]) these bands start to show the structure with a clear vibronic progression ($\nu = 1307$ and 1463 cm⁻¹) in the case of **8**, which can be assigned to intraligand transitions located at the alkynyl ligand. This observation is consistent with theoretical results that clearly point to the intraligand $T_1 \rightarrow S_0$ transition as the origin of the triplet luminescence at 77 K (Fig. 5).

A rather similar behavior is detected for trinuclear complexes **9** and **10**, which show featureless bands at 298 K. Appearance of a fine structure is observed at 77 K for **10** having the most extended alkyne ligand in this series (Fig. 6 and S4†) that testifies to the alkynyl ligand-centered nature of photoemission.

A severe drop of emission intensity for the di- and trinuclear complexes with extended alkynyl backbones (7, 8, 10) is reflected by radiative decay rate constants k_r (derived from the relationship $\Phi_{\rm em} = k_r/k_{\rm obs}$), which demonstrate a 5–10 times decrease in comparison with the mononuclear congeners (Table 2). This trend is particularly illustrated by the dinuclear compounds, for which the radiative decay rate gets slower with elongation of the phenylene spacers $\equiv -(C_6H_4)_n = 1.6 \times 10^4$ s⁻¹ (6, *n* = 1), 6.3 × 10³ s⁻¹ (7, *n* = 2), 2.8 × 10³ (8, *n* = 3). Accordingly, the nonradiative decay rate constants (defined as $k_{\rm nr} =$ $k_{\rm obs} - k_r$, $k_{\rm obs} = 1/\tau_{\rm av}$) are visibly larger for the trinuclear species **9** and **10** pointing to an ascending role of effective quenching processes for the compounds with star-like trialkynes.

Computational results

The photophysical properties of the Cu(1) complexes **1–10** were also investigated using quantum chemical methods. The geometries of the studied complexes were fully optimized at the DFT-PBE0 level of theory and the lowest energy singlet and triplet excited states were studied by means of time-dependent TD-DFT-PBE0 calculations (see the Experimental section for full computational details). The optimized geometries of the complexes **1**, **3**, and **5** are in good agreement with the available X-ray structures (the coordinates of the optimized structures are included in the ESI†). Table 3 lists the wavelengths predicted for the S₀ \rightarrow S₁ and T₁ \rightarrow S₀ electronic transitions of all studied complexes, while the corresponding electron density difference plots are shown in Fig. 7 for complexes **1**, **6**, and **9** (the other complexes are illustrated in the ESI†). For the

Table 3 Computational photophysical results for the Cu(i) complexes 1-10 in the gas phase (TD-DFT-PBE0)^a

	$\lambda \left(\mathbf{S}_{0}\rightarrow \mathbf{S}_{1}\right) \left(\mathbf{nm}\right)$		$\lambda \left(T_{1} \rightarrow S_{0} \right) \left(\right.$	nm)
	Theor.	Exp. ^a	Theor.	Exp. ^a
1	421	415	614	612
2	424	415	600	612
3	409	415	673	717
1	415	370	621	579
5	418	415	610	579
5	494	401	768	635
7	467	426	807	642
3	453	426	803	683
9	451	426	634	640
10	438	442	685	647

^{*a*} Excitation and emission wavelengths from the solid state, 77 K.

majority of the studied complexes, the predicted $S_0 \rightarrow S_1$ excitation wavelengths are in reasonable agreement with the experimental excitation energies obtained in the solid state at 77 K. For the complexes 4, 6–8, the predicted excitation wavelengths are overestimated in comparison with the experiment.



Fig. 7 Electron density difference plots for the lowest energy singlet excitation ($S_0 \rightarrow S_1$) and the lowest energy triplet emission ($T_1 \rightarrow S_0$) of the Cu(i) complexes 1, 6, and 9 (isovalue 0.002 a.u.). During the electronic transition, the electron density increases in the blue areas and decreases in the red areas. Hydrogen atoms are omitted for clarity.

In a similar fashion, the $T_1 \rightarrow S_0$ emission wavelengths are also clearly overestimated for the complexes **6–8**. For the mononuclear compounds **1–5**, the predicted emission wavelengths are rather well in line with the experimental values. In particular, the emission wavelength for the complex **3** is clearly larger in comparison with the other mononuclear complexes that are in line with experimental observations.

In the case of mononuclear complexes 1–5, the $S_0 \rightarrow S_1$ transition can be assigned to IL charge transfers involving the phosphine and alkynyl ligands, possibly mixed with MLCT/ LLCT contributions (Fig. 7). The $T_1 \rightarrow S_0$ emission turned out to be completely different from the $S_0 \rightarrow S_1$ transitions. For 1 and 4 it is practically an intraligand transition of the alkynyl ligand, while the complexes 2 and 3 also show a minor contribution from the Cu atom. In complex 5 with alkynyl-pyridine functionality the phosphine ligand together with the Cu atom participate in charge transfer processes. The reason for a lower emission energy of the complex 3 with respect to the other mononuclear congeners is not completely clear. A major difference in comparison with 1, 2, and 4 is that the nitro group in 3 contributes significantly to the $T_1 \rightarrow S_0$ emission in contrast to the X groups of the other complexes (X = OMe, H, CF_3), suggesting a more significant effect on the energy levels of the alkynyl ligand.

For the di- and trinuclear complexes **6–10**, the $S_0 \rightarrow S_1$ transition is rather similar to that of mononuclear compounds **1–5** and is mainly composed of metal-perturbed ILCT shared with some mixed MLCT/LLCT. The complex **6** is the only multinuclear compound showing significant contributions from the metal atom and the phosphine ligands in the $T_1 \rightarrow S_0$ emission. In the case of species **7–10** with extended alkynyl backbones the $T_1 \rightarrow S_0$ emission is very clearly centered on the alkynyl ligand. Analysis of electron difference density plots (Fig. 7 and S5†) implies significant ligand to ligand charge transfers for **7–10** during the $S_1 \rightarrow T_1$ transition that might result in the appearance of efficient nonradiative pathways of the excited state relaxation, which account for lower quantum yields of the di- and trinuclear compounds.

Conclusions

To sum up, chelating triphosphine PPh₂C₆H₄-PPh-C₆H₄PPh₂ (\mathbf{P}^3) was successfully used for the preparation of a series of copper(1) alkynyl compounds. Depending on the number of terminal -C=CH groups, mono- (1-5), di- (6-8) and trinuclear (9 and 10) complexes were obtained. In all the title species Cu centers adopt a distorted tetrahedral geometry, which is provided by the tridentate coordination of \mathbf{P}^3 and σ -bonding of the alkyne moiety. The complexes 1, 3 and 5 were characterized by single crystal X-ray diffraction measurements, while the composition and structures of other species were estimated by means of ³¹P, ¹H and ¹H-¹H COSY NMR spectroscopy. The title compounds exhibit moderate to weak room temperature luminescence in the solid state with quantum yields reaching 19%. Analysis of the photoemission characteristics obtained at

298 and 77 K for the mononuclear species reveals a dramatic increase of lifetime values (up to 130-fold) upon temperature decrease accompanied by a small red shift of the emission energy (5–10 nm). These observations indicate that lumine-scence of the complexes under consideration might demonstrate thermally activated delayed fluorescence (TADF), recently described for a number of copper(i) compounds. Following the hypothesis, low temperature emission is therefore governed by $T_1 \rightarrow S_0$ transition, while at 298 K a thermal equilibrium between S_1 and T_1 levels results in a significant contribution of $S_1 \rightarrow S_0$ relaxation into the radiative decay pathway. Theoretical calculations of the electronic structures of **1–10** elucidated the photophysical properties, which are strongly dependent on the nature of constituting alkynyl groups.

Experimental

General comments

(2-Bromophenyl)diphenylphosphine,⁴² 4,4'-HC₂(C₆H₄)₂C₂H (L3),⁴³ 4,4"-HC₂(C₆H₄)₃C₂H (L4),⁴⁴ and 1,3,5-(4-HC₂-C₆H₄)₃-C₆H₃ (L5)⁴⁵ were prepared according to the reported procedures. Tetrahydrofuran was distilled over Na-benzophenone-ketyl under a nitrogen atmosphere prior to use. Other reagents were used as received. The solution ¹H, ³¹P{¹H} NMR and ¹H-¹H COSY spectra were recorded on Bruker 400 MHz Avance and AMX 400 spectrometers. Microanalyses were carried out at the analytical laboratory of the University of Eastern Finland.

 $Cu(P^3)C_2C_6H_5$ (1). P^3 (100 mg, 0.159 mmol), $[Cu(NCMe)_4]$ -(BF₄) (50 mg, 0.159 mmol) and phenylacetylene (16 mg, 0.157 mmol) were suspended in acetone (10 mL) and the reaction mixture was stirred for 10 min at room temperature to give a nearly clear pale-green solution. Addition of KOH (9.2 mg, 0.164 mmol) changed its color to brown. The reaction mixture was stirred for additional 10 h, then it was filtered, evaporated and the crude solid was recrystallized by gas-phase diffusion of pentane into a THF solution of 1 at room temperature to give a pale yellow crystalline material (65 mg, 54%). ³¹P NMR (162 MHz, acetone- d_6 , 298 K, δ): AB₂ system -0.1 (2P), -2.6 (1P) J(P-P) 134 Hz. ¹H NMR (400 MHz, acetone- d_6 , 298 K, δ): PPh₂ groups 8.34 (m, 4H, ortho-H), 7.43 (m, 4H, meta-H), 7.41 (m, 2H, para-H), 7.28 (t, 2H, J(H-H) 7.5 Hz, para-H), 7.10 (dd, 4H, J(H-H) 7.5 Hz, 7.2 Hz, meta-H), 6.54 (m, 4H, J(H-H) 7.2 Hz, ortho-H); C₆H₄ groups 7.82 (m, 2H, J(H-H) 7.1 Hz, ortho-H), 7.59 (dd, 2H, J(H-H) 7.3, 7.0 Hz, meta-H), 7.50 (dd, 2H, J(H-H) ca. 7.3 Hz, 7.1 Hz, meta-H), 7.42 (m, 2H, J(H-H) 7.0 Hz, ortho-H); C₂Ph group 7.35 (m, 2H, J(H-H) 7.7 Hz, ortho-H), 7.17 (dd, 2H J(H-H) 7.7 Hz, 7.1 Hz, meta-H), 7.02 (t, 1H, J(H-H) 7.1 Hz, para-H); PPh group 7.22-7.41 (m, 5H). Anal. Calcd for C₅₀H₃₈CuP₃: C, 75.51; H, 4.81; found: C, 75.31; H, 5.02.

 $Cu(P^3)(C_2$ -4-OCH₃ $C_6H_4)$ (2). Prepared analogously to 1 starting from P^3 (50 mg, 0.079 mmol), $[Cu(NCMe)_4](BF_4)$ (25 mg, 0.080 mmol), 4-ethynylanisole (10.5 mg, 0.080 mmol) and KOH (4.8 mg, 0.085 mmol). The crude solid was dissolved in toluene (5 mL) and precipitated with excess of hexane to give a yellow solid (41 mg, 62%). ³¹P NMR (162 MHz, acetone- d_6 , 298 K, δ): AB₂ system -0.5 (2P), -3.1 (1P) J(P-P) 136 Hz. ¹H NMR (400 MHz, acetone- d_6 , 298 K, δ): PPh₂ groups 8.35 (m, 4H, ortho-H), 7.42 (m, 4H, meta-H), 7.41 (m, 2H, para-H), 7.28 (m, 2H, J(H-H) 7.4 Hz, para-H), 7.10 (dd, 4H, J(H-H) 7.4 Hz, 7.2 Hz, meta-H), 6.54 (m, 4H, J(H-H) 7.2 Hz, ortho-H); C₆H₄ groups 7.81 (m, 2H, J(H-H) 7.3 Hz, ortho-H), 7.59 (dd, 2H, J(H-H) 7.2 Hz, 7.3 Hz, meta-H), 7.49 (dd, 2H, J(H-H) 7.4 Hz, 7.2 Hz, meta-H), 7.42 (m, 2H, J(H-H) 7.4 Hz, ortho-H); 4-OCH₃C₆H₄C₂ group 7.28 (d, 2H, J(H-H) 8.1 Hz, ortho-H), 6.77 (d, 2H, J(H-H) 8.1 Hz, meta-H), 3.76 (s, 3H); PPh group 7.29–7.33 (m, 5H). Anal. Calcd for C₅₁H₄₀CuOP₃: C, 74.21; H, 4.88; found: C, 73.81; H, 5.16.

 $Cu(P^3)(C_2$ -4-NO₂C₆H₄) (3). Prepared analogously to 1 starting from P³ (30 mg, 0.047 mmol), [Cu(NCMe)₄](BF₄) (15 mg, 0.048 mmol), 4-nitrophenylacetylene (7 mg, 0.048 mmol) and KOH (2.7 mg, 0.048 mmol). Recrystallization by gas-phase diffusion of pentane into a toluene solution of 3 at room temperature gave a yellow-red crystalline material (33 mg, 83%). ³¹P NMR (162 MHz, acetone- d_6 , 298 K, δ): AB₂ system 1.1 (2P), -1.3 (1P) J(P-P) 133 Hz. ¹H NMR (400 MHz, acetone- d_6 , 298 K, δ): PPh₂ groups 8.22 (dm, 4H, J(H-H) 7.6 Hz, ortho-H), 7.44 (m, 4H, J(H-H) 7.6 Hz, meta-H), 7.43 (m, 2H, para-H), 7.31 (dm, 2H, J(H-H) 7.5 Hz, para-H), 7.12 (dd, 4H, J(H-H) 7.5 Hz, 7.3 Hz, meta-H), 6.57 (dm, 4H, J(H-H) 7.3 Hz, ortho-H); C₆H₄ groups 7.83 (dm, 2H, J(H-H) 7.4 Hz, ortho-H), 7.6 (dd, 2H, J(H-H) 7.5 Hz, 7.4 Hz, meta-H), 7.51 (dd, 2H, J(H-H) 7.7 Hz, 7.5 Hz, meta-H), 7.41 (m, 2H, J(H-H) 7.7 Hz, ortho-H); 4-NO₂C₆H₄C₂ group 8.08 (d, 2H, J(H-H) 8.9 Hz, ortho-H), 7.48 (d, 2H, J(H-H) 8.9 Hz, meta-H); PPh group 7.29-7.36 (m, 5H). Anal. Calcd for C₅₀H₃₇CuNO₂P₃: C, 71.46; H, 4.43; N, 1.66; found: C, 71.36; H, 4.71; N, 1.57.

 $Cu(P^3)(C_2-4-CF_3C_6H_4)$ (4). Prepared analogously to 1 starting from **P**³ (100 mg, 0.159 mmol), [Cu(NCMe)₄](BF₄) (50 mg, 0.158 mmol), 4-(trifluoromethyl)phenylacetylene (26 mg, 0.153 mmol) and KOH (9.2 mg, 0.164 mmol). Recrystallization by gas-phase diffusion of pentane into a toluene solution of 4 at room temperature gave a yellow solid (83 mg, 63%). ³¹P NMR (162 MHz, acetone- d_6 , 298 K, δ): AB₂ system 0.5 (2P), $-2.0 (1P) J(P-P) 133 \text{ Hz.} {}^{1}\text{H NMR} (400 \text{ MHz}, acetone-d_{6}, 298 \text{ K},$ δ): PPh₂ groups 8.28 (m, 4H, ortho-H), 7.44 (m, 6H, meta-H+ para-H), 7.32 (t, 2H, J(H-H) ca. 7.3 Hz, para-H), 7.12 (dd, 4H, J(H-H) ca. 7.3, 7.0 Hz, meta-H), 6.56 (m, 4H, J(H-H) 7.0 Hz, ortho-H); C₆H₄ groups 7.84 (m, 2H, J(H-H) 7.1 Hz, ortho-H), 7.61 (dd, 2H, J(H-H) 7.1 Hz, meta-H), 7.50 (m, 2H, J(H-H) 7.6 Hz, meta-H), 7.44 (m, 2H, J(H-H) 7.6 Hz, ortho-H); 4-CF₃C₆H₄C₂ group 7.48-7.50 (m, 4H); PPh group 7.31-7.33 (m, 5H). Anal. Calcd for C₅₁H₃₇CuF₃P₃: C, 70.95; H, 4.32; found: C, 70.68; H, 4.49.

Cu(P³)(C₂-2-C₅H₄N) (5). Prepared analogously to 1 starting from P³ (130 mg, 0.206 mmol), [Cu(NCMe)₄](BF₄) (65 mg, 0.207 mmol), 2-ethynylpyridine (21 mg, 0.203 mmol) and KOH (11 mg, 0.196 mmol). The crude solid was dissolved in toluene (10 mL) and precipitated with excess of hexane to give a yellow solid (68 mg, 42%). ³¹P NMR (162 MHz, CD₂Cl₂, 298 K, δ): AB₂ system 0.5 (2P), -1.8 (1P) *J*(P-P) 132 Hz. ¹H NMR (400 MHz, CD₂Cl₂, 298 K, δ): PPh₂ groups 8.13 (dm, 4H, *J*(H–H) 7.5 Hz ortho-H), 7.39 (m, 6H, *J*(H–H) 7.5 Hz, meta-H+ para-H), 7.25 (t, 2H, *J*(H–H) 7.6 Hz, para-H), 7.05 (dd, 4H, *J*(H–H) 7.6 Hz, 7.0 Hz, meta-H), 6.58 (dm, 4H, *J*(H–H) 7.0 Hz, ortho-H); C₆H₄ groups 7.70 (dm, 2H, *J*(H–H) 7.2 Hz, ortho-H), 7.47 (dd, 2H, *J*(H–H) 7.2 Hz, meta-H), 7.39 (m, 2H, *J*(H–H) 7.0 Hz, meta-H), 7.35 (dm, 2H, *J*(H–H) ca. 7.0 Hz, ortho-H); C₆H₄N group 8.43 (dm, 1H, *J*(H–H) 5.1 Hz, 1.8 Hz, 6-H), 7.51 (ddd, 1H, *J*(H–H) 7.8 Hz, 7.7 Hz, 1.8 Hz, 4-H), 7.35 (dm, 1H, *J*(H–H) 7.8 Hz, 3-H), 6.97 (ddd, 1H, *J*(H–H) 7.7 Hz, 5.1 Hz, 5-H); PPh group 7.20–7.36 (m, 5H). Anal. Calcd for C₄₉H₃₇CuNP₃: C, 73.90; H, 4.68; N, 1.75; found: C, 73.62; H, 5.06; N, 1.57.

 $Cu_2(P^3)_2(1,4-C_2C_6H_4C_2)$ (6). Prepared analogously to 1 using stoichiometric ratios of the reagents starting from \mathbf{P}^3 (150 mg, 0.238 mmol), [Cu(NCMe)₄](BF₄) (75 mg, 0.238 mmol), 1,4-diethynylbenzene (15 mg, 0.119 mmol) and KOH (13.8 mg, 0.246 mmol). Recrystallization by gas-phase diffusion of diethyl ether into a dichloromethane solution of 6 at room temperature gave a vellow solid (65 mg, 39%). ³¹P NMR (162 MHz, CD₂Cl₂, 298 K, δ): AB₂ system -0.4 (2P), -2.9 (1P) J(P-P) 133 Hz. ¹H NMR (400 MHz, CD₂Cl₂, 298 K, δ): PPh₂ groups 8.19 (m, 8H, ortho-H), 7.40 (m, 12H, meta-H+ para-H), 7.22 (t, 4H, J(H-H) 7.2 Hz, para-H), 7.04 (dd, 8H, J(H-H) 7.2 Hz, 6.7 Hz, meta-H), 6.57 (dm, 8H, J(H-H) ca. 6.7 Hz, ortho-H); C₆H₄ groups 7.71 (dm, 4H, J(H-H) ca. 7.2 Hz, ortho-H), 7.46 (dd, 4H, J(H-H) 7.7 Hz, 7.2 Hz, meta-H), 7.38 (m, 8H, J(H-H) 7.7 Hz, meta-H+ ortho-H); C₂C₆H₄C₂ group 7.40 (s, 4H); PPh group 7.26-7.27 (m, 10H). Anal. Calcd for C₉₄H₇₀Cu₂P₆: C, 74.64; H, 4.66; found: C, 74.91; H, 4.87.

 $Cu_2(P^3)_2(4,4'-C_2(C_6H_4)_2C_2)$ (7). Prepared analogously to 1 using stoichiometric ratios of the reagents starting from P^3 $(150 \text{ mg}, 0.238 \text{ mmol}), [Cu(NCMe)_4](BF_4) (75)$ mg, 0.238 mmol), 4,4"-di-ethynylbiphenyl (24 mg, 0.119 mmol) and KOH (13.8 mg, 0.246 mmol). The crude solid was dissolved in toluene (10 mL) and precipitated with excess of hexane to give a yellow solid (65 mg, 34%). ³¹P NMR (162 MHz, CD_2Cl_2 , 298 K, δ): AB₂ system -0.1 (2P), -2.5 (1P) J(P-P)133 Hz. ¹H NMR (400 MHz, CD_2Cl_2 , 298 K, δ): PPh₂ groups 8.21 (m, 8H, ortho-H), 7.43 (m, 12H, meta-H+ para-H), 7.24 (t, 4H, J(H-H) 7.4 Hz, para-H), 7.06 (dd, 8H, J(H-H) 7.4 Hz, 7.2 Hz, meta-H), 6.58 (m, 8H, J(H-H) 7.2 Hz, ortho-H); C₆H₄ groups 7.73 (dm, 4H, J(H-H) 7.6 Hz, ortho-H), 7.49 (dm, 8H, J(H-H) ca. 6.8 Hz, 7.6 Hz, meta-H), 7.39 (m, 4H, J(H-H) ca. 6.8 Hz, 7.5 Hz, meta-H), 7.35 (m, 4H, J(H-H) 7.5 Hz, ortho-H); $C_2(C_6H_4)_2C_2$ and PPh groups 7.26-7.50 (unresolved m, 18H). Anal. Calcd for C₁₀₀H₇₄Cu₂P₆: C, 75.60; H, 4.69; found: C, 75.31; H, 4.77.

Cu₂(P³)₂(4,4"-C₂(C₆H₄)₃C₂) (8). Prepared analogously to 1 using stoichiometric ratios of the reagents starting from P³ (30 mg, 0.047 mmol), [Cu(NCMe)₄](BF₄) (15 mg, 0.048 mmol), 4,4"-diethynyl-*p*-terphenyl (6.6 mg, 0.024 mmol) and KOH (2.7 mg, 0.048 mmol). Recrystallization by gas-phase diffusion of pentane into a THF solution of 9 at room temperature to give a yellow solid (30 mg, 75%). ³¹P NMR (162 MHz, CD₂Cl₂, 298 K, δ): AB₂ system 0.0 (2P), -2.3 (1P) *J*(P-P) 132 Hz. ¹H NMR (400 MHz, CD₂Cl₂, 298 K, δ): PPh₂ groups 8.20 (m, 8H,

ortho-H), 7.41 (m, 12H, meta-H+ para-H), 7.24 (t, 4H, J(H–H) 7.5 Hz, para-H), 7.05 (dd, 8H, J(H–H) 7.5 Hz, 7.6 Hz, meta-H), 6.59 (dm, 8H, J(H–H) 7.6 Hz, ortho-H); C₆H₄ groups 7.73 (dm, 4H, J(H–H) 7.1 Hz, ortho-H), 7.50 (dd, 4H, J(H–H) 7.5 Hz, meta-H), 7.41 (m, 4H, J(H–H) 7.1 Hz, meta-H), 7.36 (dm, 4H, J(H–H) ca. 7.5 Hz, ortho-H); C₂(C₆H₄)₃C₂ group 7.70 (s, 4H), 7.55 (d, 4H, J(H–H) 8.2 Hz), 7.51 (d, 4H, J(H–H) 8.2 Hz); PPh group 7.26–7.28 (m, 10H). Anal. Calcd for C₁₀₆H₇₈Cu₂P₆: C, 76.47; H, 4.72; found: C, 76.14; H, 4.90.

 $Cu_3(P^3)_3(1,3,5-(C_2C_6H_4)_3C_6H_3)$ (9). Prepared analogously to 1 using stoichiometric ratios of the reagents starting from P³ (150 mg, 0.238 mmol), [Cu(NCMe)₄](BF₄) (75 mg, 0.238 mmol), 1,3,5-trisubstituted benzene (27 mg, 0.071 mmol) and KOH (13 mg, 0.232 mmol). The crude solid was dissolved in THF (10 mL) and precipitated with an excess of diethyl ether to give a yellow solid (62 mg, 37%). ³¹P NMR (162 MHz, CD₂Cl₂, 298 K, δ): AB₂ system 0.0 (2P), -2.3 (1P) J(P-P) 133 Hz. ¹H NMR (400 MHz, CD₂Cl₂, 298 K, δ): PPh₂ groups 8.21 (dm, 12H, J(H-H) ca. 7.5 Hz, ortho-H), 7.42 (m, 18H, J(H-H) 7.5 Hz, meta-H+ para-H), 7.23 (t, 6H, J(H-H) 7.4 Hz, para-H), 7.05 (dd, 12H, J(H-H) 7.8 Hz, 7.4 Hz, meta-H), 6.58 (dm, 12H, J(H-H) 7.8 Hz, ortho-H); C₆H₄ groups 7.73 (dm, 6H, J(H-H) ca. 7.0 Hz, ortho-H), 7.48 (dd, 6H, J(H-H) 7.0 Hz, meta-H), 7.39 (dm, 6H, J(H-H) ca. 7.3 Hz, meta-H), 7.37 (dm, 6H, J(H-H) ca. 7.3 Hz, ortho-H); (C₆H₄)C₂ group 7.64 (d, 6H, J(H-H) 8.3 Hz), 7.54 (d, 6H, J(H-H) 8.3 Hz); C₆H₃ group 7.82 (s, 3H); PPh group 7.28-7.31 (m, 15H). Anal. Calcd for C₁₅₆H₁₁₄Cu₃P₉: C, 76.22; H, 4.67; found: C, 75.94; H, 4.65.

 $Cu_3(P^3)_3(1,3,5-(C_2C_6H_4C_2C_6H_4)_3C_6H_3)$ (10). Prepared analogously to 1 using stoichiometric ratios of the reagents starting from P³ (150 mg, 0.238 mmol), [Cu(NCMe)₄](BF₄) (75 mg, 0.238 mmol), 1,3,5-trisubstituted benzene (48 mg. 0.071 mmol) and KOH (13 mg, 0.232 mmol). The crude solid was dissolved in toluene (10 mL) and precipitated with excess of pentane to give an orange solid (46 mg, 23%). ³¹P NMR (162 MHz, CD₂Cl₂, 298 K, δ): AB₂ system 0.3 (2P), -1.9 (1P) J(P-P) 132 Hz. ¹H NMR (400 MHz, CD₂Cl₂, 298 K, δ): PPh₂ groups 8.17 (dm, 12H, J(H-H) 7.9 Hz, ortho-H), 7.43 (m, 18H, *J*(H–H) *ca.* 7.9 Hz, *meta*-H+ *para*-H), 7.25 (t, 6H, *J*(H–H) 7.0 Hz, para-H), 7.05 (dd, 12H, J(H-H) 7.5 Hz, 7.0 Hz, meta-H), 6.58 (dm, 12H, J(H-H) ca. 7.5 Hz, ortho-H); C₆H₄ groups 7.73 (dm, 6H, J(H-H) 7.5 Hz, ortho-H), 7.48 (dd, 6H, J(H-H) 7.5 Hz, *meta*-H), 7.40 (dm, 6H, J(H-H) ca. 7.6 Hz, *meta*-H), 7.34 (m, 6H, J(H-H) 7.6 Hz, ortho-H); (C₆H₄C₂)₂ group AB system 7.77 (d, 6H, J(H-H) 8.4 Hz), 7.68 (m, 6H, J(H-H) 8.4 Hz); 7.43 (m, 6H), 7.27 (m, 6H); C₆H₃ group 7.90 (s, 3H); PPh group 7.27-7.31 (m, 15H). Anal. Calcd for C180H126Cu3P9: C, 78.37; H, 4.60; found: C, 78.49; H, 4.76.

X-ray structure determination

The crystals of **1**, **3** and **5** were immersed in cryo-oil, mounted in a nylon loop, and measured at a temperature of 120 K. The diffraction data were collected with a Bruker Kappa Apex II Duo diffractometer using Mo K α radiation ($\lambda = 0.71073$ Å). The APEX2⁴⁶ program package was used for cell refinements and data reductions. The structures were solved by direct methods

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using the SHELXS-2013⁴⁷ program with the WinGX⁴⁸ graphical user interface. A semiempirical absorption correction (SADABS)⁴⁹ was applied to all data. Structural refinements were carried out using SHELXL-2013.⁴⁷

One of the phenyl rings of an alkynyl ligand in **1** was disordered between two positions and was refined with occupation factors 0.52/0.48. The aromatic rings of both components were geometrically idealized. Displacement constraints and restraints were applied to these moieties.

Some of the crystallized tetrahydrofuran (1) and water (5) molecules were partially lost and these moieties were refined with a 0.5 occupancy at each site. A series of geometry and displacement constraints and restraints were applied to the THF solvent molecules. Additionally, some of the lost solvent in 1 could not be resolved unambiguously. The missing solvent was taken into account by using a SQUEEZE routine of PLATON,⁵⁰ and its contribution wasn't included into the unit cell content.

The water hydrogen atoms were positioned according to the electron density map and constrained to ride on their parent atom O1 with $U_{\rm iso}$ = 1.5 (parent atom). All other hydrogen atoms in 1, 3 and 5 were positioned geometrically and constrained to ride on their parent atoms, with C–H = 0.95–0.99 Å, $U_{\rm iso}$ = 1.2–1.5 $U_{\rm eq}$ (parent atom). The crystallographic details are summarized in Table S1 in the ESI.†

Photophysical studies

The steady-state emission and excitation spectra of complexes **1–10** in the solid state at room temperature and at 77 K were recorded on a Fluoromax 4 Horiba spectrofluorometer. The xenon lamp (300 W) was used as a light source to obtain luminescence. A pulse laser DTL-399QT "Laser-export Co. Ltd" (maximum of emission at 351 nm, 50 mW, pulse width 6 ns, repetition rate 1 kHz), a digital oscilloscope Tektronix DPO3034 (bandwidth 300 MHz), a MUM monochromator (LOMO, interval of wavelengths 10 nm), and a photomultiplier tube Hamamatsu were used for lifetime measurements. Absolute emission quantum yield was determined using a Fluorolog 3 Horiba spectrofluorometer and a Quanta-phi integration sphere.

Computational details

The Cu(1) complexes **1–10** were studied using the hybrid PBE0 density functional method.⁵¹ The copper atoms were described by a triple-zeta-valence quality basis set with polarization functions (def2-TZVP).⁵² A split-valence basis set with polarization functions on non-hydrogen atoms was used for all the other atoms.⁵³ To facilitate comparisons with the experiments, point group symmetry was applied as follows: **1–5**: C_s ; **6–8**: C_{2v} ; **9**, **10**: C_{3v} . The geometries of all complexes were fully optimized. The excited states were investigated with the Time-Dependent DFT approach.⁵⁴ The singlet excitations were determined at the optimized ground state S₀ geometries, while the lowest energy triplet emissions were determined at the optimized T₁ geometry. All electronic structure calculations were carried out with the TURBOMOLE program package (version 6.5).⁵⁵

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