Reversible protonation of amine-functionalized luminescent Au–Cu clusters: characterization, photophysical and theoretical studies[†]

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Reaction of the polymeric alkynyl complexes $(AuC_2C_6H_4R)_n$ (R = 4-NH₂ and 3-NH₂) with the diphosphine $PPh_2C_6H_4PPh_2$ in the presence of Cu⁺ ions gave two novel heterometallic aggregates [{ $Au_3Cu_2(C_2C_6H_4R)_6$ } $Au_3(PPh_2C_6H_4PPh_2)_3$](PF₆)₂ (R = 4-NH₂ (**2**), 3-NH₂ (**3**)). The compounds obtained were characterized by NMR spectroscopy and ESI-MS measurements. The solid-state structure of their 4-NMe₂ congener 1 is reported. The complexes 1-3 reversibly react with strong (HSO₃Me and HSO₃CF₃) acids to give the adducts $[{Au_3Cu_2(C_2C_6H_4-R)_6*(R'SO_3H)_6}Au_3(PPh_2C_6H_4PPh_2)_3](PF_6)_2 (R = 4-NMe_2 (4), 4-NH_2 (5), 3-NH_2 (5), 3-NH_2 (6), 3-NH_2 (6)$ (6)) with six acid molecules bound to the amine groups of the alkynyl ligands. Composition and structure of the adducts were established using ESI-MS and multinuclear (³¹P, ¹H and ¹H-¹H COSY) NMR spectroscopy. It was found that formation of these adducts results in crucial changes of luminescence characteristics of the complexes 1-3 to give substantial (ca. 100 nm) blue shift of the emission maxima and a sharp increase (about an order of magnitude) in luminescence quantum yield for 4-NR₂ substituted derivatives. In the case of 3-substituted complex 3 the effect of adduct formation is much less pronounced and leads to blue-shift of emission maximum for 30 nm accompanied with a small drop in emission quantum yield. Computational studies have been performed to provide additional insight into the structural, electronic and photophysical properties of the starting complexes and their acid adducts. Interpretation of the photophysical effects induced by the adduct formation was suggested.

Introduction

Synthesis, structural characterization and investigation of d¹⁰ coinage metal complexes remain in the focus of many research groups because of their unique photophysical characteristics and growing potential of their application in various fields of modern technology such as dopant emitters, NLO devices and OLED displays.¹ Another point of academic interest in this class of compounds consists of the ability of the d¹⁰ coordination centers to give secondary homo- and heterometallophilic bonds that results in formation of supramolecular architectures with unusual chemical and physical properties.² In our recent papers³⁻⁵ we present a series of Au–Cu and Au–Ag alkynyl-phosphine complexes, which display extremely effective phosphorescence with nearly negligible oxygen quenching. The unique photophysical

the specific features of their molecular and electronic structure. It is also interesting from the viewpoint of practical applications that the luminescent properties of these complexes may be easily fine-tuned through variations of the metal core composition and electron donor ability of the alkynyl ligand substituents. For example, Au-Ag heterometallic complexes structurally analogous to the Au-Cu compounds display hypsochromic shift of the luminescence maxima of about 100 nm,3,6 whereas an increase in basicity of the alkynyl substituents in the gold-copper compounds $[Au_6Cu_2(C_2C_6H_4-R)_6(PPh_2C_6H_4PPh_2)_3]^{2+}$, R varies from 4-NO₂ to 4-NMe₂,⁴ gives a bathochromic shift of nearly the same magnitude. It is also well known that protonation of the aromatic and aliphatic amine groups in coordinated ligands may result in substantial variations of luminescent properties (λ_{em} , τ_{obs} , luminescent quantum yield) of the corresponding complexes. Depending on the nature of the orbitals responsible for emission and their relation to the amine functionality the protonation of the coordinated ligands may decrease⁷ or even completely quench⁸ luminescence whereas for the other complexes emission quantum yield can be substantially increased9 upon addition of a proton to an amine group. The complexes, which display various types of pH sensitive luminescence, can be used for the design of specific pH sensors as well as for the construction of pH switchable "onoff" molecular devices. In this respect we became interested in the experimental and theoretical investigations of protonation effects on the photoluminescent properties of the previously reported

characteristics of this group of compounds are determined by

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[†] Electronic supplementary information (ESI) available: X-ray crystallographic data in CIF for 1; ESI-MS spectra of 2, 3 and the protonated forms of 1–3; selected NMR spectra of 2, 3; optimized Cartesian coordinates of 1–6. CCDC reference numbers 753058. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b922803a

cluster $[Au_6Cu_2(C_2C_6H_4-4-NMe_2)_6(PPh_2C_6H_4PPh_2)_3]^{2+4}$ bearing 4-NMe₂ groups and of its novel relatives containing 4-NH₂ and 3-NH₂ substituents in the phenylene spacers of the alkynyl ligands.

Experimental

1,4-Bis(diphenylphosphino)benzene¹⁰ and $[{Au_3Cu_2(C_2C_6H_4-NMe_2)_6}Au_3(PPh_2C_6H_4PPh_2)_3][PF_6]_2$ (1)⁴ were synthesized according to published procedures. Complexes ${Au(1-C_2-C_6H_4-R)}_n$ ($R = 4-NH_2$, 3-NH₂) were prepared analogously to $(AuC_2Ph)_n^{11}$ using commercially available alkynes $1-HC_2-C_6H_4-R$. Anhydrous dichloromethane (Aldrich) was used for the photophysical measurements. Other reagents and solvents were used as received. The solution 1D ¹H, ³¹P NMR and ¹H COSY spectra were recorded on Bruker Avance 400 and Bruker DPX 300 spectrometers. Mass spectra were measured on a Bruker APEX-Qe ESI FT-ICR instrument, in the positive ion mode. Microanalyses were carried out in the analytical laboratories of the University of Joensuu and St. Petersburg State University.

General procedure for the preparation of heterometallic Au–Cu complexes

 ${Au(1-C_2-C_6H_4-R)}_n$ (0.5 mmol) was suspended in CH_2Cl_2 (15 cm³) and a slight excess of a crystalline diphosphine (0.28 mmol) was added. The reaction mixture was stirred for 30 min in the absence of light and then a solution of $Cu(NCMe)_4PF_6$ (0.17 mmol) in CH_2Cl_2 (5 cm³) was added dropwise to afford a nearly transparent red solution (2) or orange suspension (3). The solids were filtered off, the solvent was removed on a rotovap to give the residues which were repetitiously recrystallized by gas-phase diffusion of diethyl ether into their dichloromethane solutions at +5 °C (1 was recrystallized by slow evaporation of its acetone–methanol solution at +5 °C).

[{Au₃Cu₂(C₂C₆H₄-4-NH₂)₆}Au₃(PPh₂C₆H₄PPh₂)₃][PF₆]₂ (2). Dark red. Yield 63%. ES MS (m/z): [Au₆Cu₂(C₂C₆H₄NH₂)₆-(PPh₂C₆H₄PPh₂)₃]²⁺ 1671 (calcd 1671). ³¹P{¹H} NMR (acetoned₆; δ): 43.0 (s, 3P), -144.8 (sept, 1P, PF₆). ¹H NMR (acetone-d₆; δ): {Au(C₂C₆H₄-4-NH₂)₂}: 6.53 (d, H-*ortho*, 12H, J(H–H) 8.5 Hz), 6.20 (d, H-*meta*, 12H, J(H–H) 8.5 Hz) diphosphine: 7.94 (dm(AXX'), H-*ortho*, 24H, J(H–H) 7.6, J(P–H) 13 Hz), 7.69 (m(A₂X₂), {P–C₆H₄–P} 12H, <J(P–H)> 3.3 Hz), 7.63 (t, H-*para*, 12H, J(H–H) 7.5 Hz), 7.46 (dd, H-*meta*, 24H, J(H–H) 7.6, 7.5 Hz). Anal. Calc. for C₁₃₈H₁₀₈Au₆Cu₂F₁₂N₆P₈: C, 45.60; H, 2.99; N, 2.31. Found: C, 45.99; H, 3.36; N, 2.30%.

[{Au₃Cu₂(C₂C₆H₄-3-NH₂)₆}Au₃(PPh₂C₆H₄PPh₂)₃][PF₆]₂ (3). Orange. Yield 62%. ES MS (m/z): [Au₆Cu₂(C₂C₆H₄NH₂)₆·(PPh₂C₆H₄PPh₂)₃]²⁺ 1671 (calcd 1671). ³¹P{¹H} NMR (acetone-d₆; δ): 43.6 (s, 3P), -144.8 (sept, 1P, PF₆). ¹H NMR (acetone-d₆; δ): {Au(C₂C₆H₄-3-NH₂)₂}: 6.67 (dd, 5-H, 6H, J(H–H) 8.0 Hz), 6.50 (dm, 4-H, 6H, J(H–H) 8.0 Hz), *ca* 6.16 (m, 2-H and 6-H, 12H) **diphosphine:** 7.97 (dm(AXX'), H-*ortho*, 24H, J(H–H) 8, J(P–H) 14 Hz), 7.70 (m(A₂X₂), {P-C₆H₄–P} 12H, <J(P–H)> 3.4 Hz), 7.65 (t, H-*para*, 12H, J(H–H) 7.5 Hz), 7.48 (dd, H-*meta*, 24H, J(H–H) 8, 7.5 Hz). Anal. Calc. for C₁₃₈H₁₀₈Au₆Cu₂F₁₂N₆P₈: C, 45.60; H, 2.99; N, 2.31. Found: C, 46.01; H, 3.30; N, 2.26%.

Protonation of 1-3 in solution (CD₃COCD₃ for NMR experiments and CH₂Cl₂ for photophysical measurements) was

performed by micropipette addition of a fresh aliquot of $MeSO_3H$ to a sample solution of the corresponding complex. Exhaustive protonation was usually accomplished with *ca*. 100-fold excess of acid.

NMR characteristics of protonated forms of the complexes

Photophysical measurements

An LED (emission maximum at 385 nm) was used to pump luminescence. The LED was used in continuous and pulse mode (pulse width 1–20 µs, pulse rise time ~90 ns, repetition rate 100 Hz– 10kHz). A digital oscilloscope Tektronix TDS3014B (Tektronix, bandwidth 100 MHz), monochromator MUM (LOMO, spectral resolution 10 nm) and photomultiplier tube (Hamamatsu) were used for life-time measurements. Emission spectra were recorded using a HR2000 spectrometer (Ocean Optics). Halogen lamp LS-1-CAL (Ocean Optics) and deuterium lamp DH2000 (Ocean Optics) were used to calibrate the absolute spectral response of the spectral system in the 200–1100 nm range. All solutions were carefully degassed before life-time measurements. The absolute emission quantum yield was determined by Vavilov's method¹² using LED (385 nm, continuous mode) pumping and rhodamine 6G in ethanol ($\Phi_{em} = 0.95 \pm 0.03$) as standard.

Computational details

The structures of the studied complexes were optimized using the BP86 density functional method.¹³ Standard GGA density functionals such as BP86 cannot accurately describe the energetics

of weak dispersive metal-metal interactions between closed-shell metal atoms. However, the structural chemistry of the supramolecular complexes studied here is dominated by the electrostatic interactions between the Cu(I) ions, the [PhC2AuC2Ph] rods, and the gold-diphosphine "belt".^{4,6} The copper and gold atoms were described with a triple-valence-zeta quality basis set with polarization functions (def2-TZVP),14 employing a 60-electron relativistic effective core potential for gold.¹⁵ A split-valence basis set with polarization functions on non-hydrogen atoms was used for all the other atoms (def2-SV(P)).¹⁶ The multipoleaccelerated resolution-of-the-identity technique was used to speed up the calculations.¹⁷ Solvent effects were taken into account by using the COSMO solvation model¹⁸ (solvent: CH₂Cl₂, dielectric constant $\varepsilon = 9.1$ at 20 °C). Due to the symmetric nature of the studied systems, the reported computational results were obtained using the following point group symmetries to facilitate comparisons with the experiments: D_{3h} for 1 and 2; C_{3h} for **3–6**. However, unconstrained optimizations were also performed to check that the symmetry constraints did not introduce any inconsistencies. All electronic structure calculations were carried out with TURBOMOLE program package (version 5.10).¹⁹

Results and discussion

Synthesis and characterization

In our recent publications we reported a synthetic strategy to prepare a family of the heterometallic $Au^{I}-Cu^{I}$ clusters of the general formula $[Au_{6}Cu_{2}(C_{2}C_{6}H_{4}-R)_{6}(PPh_{2}C_{6}H_{4}PPh_{2})_{3}][PF_{6}]_{2}$ $(R = NO_{2}, H, OMe, NMe_{2}.^{4}$ Using this approach two novel substituted derivatives $(R = 4-NH_{2} \text{ and } 3-NH_{2})$ were obtained in a moderately good yield as shown in Scheme 1.



Scheme 1

Clusters 2 and 3 didn't give single crystals suitable for X-ray diffraction analysis and their composition and structure were established on the basis of analytical data, ESI-MS, NMR spectroscopic study and comparison with the corresponding parameters of the congeners mentioned above. Both compounds appeared as doubly charged $[Au_6Cu_2(C_2C_6H_4-NH_2)_6(PP)_3]^{2+}$ (*PP* = PPh₂C₆H₄PPh₂) molecular ions in the ESI-MS spectra, see Fig. S1 (ESI⁺), with the isotopic patterns of these signals matching completely the calculated ones. This observation is indicative of preparation of the "rods-in-belt" supramolecular aggregate closely analogous to the complexes synthesized earlier⁴ using other substituted alkynyl ligands (Fig. 1).

The NMR spectroscopic data give further evidence in favor of this structural hypothesis. The ${}^{31}P$ NMR spectra of 2 and



Fig. 1 Schematic structure of the dications $[Au_6Cu_2(C_2C_6H_4-R)_6(PP)_3]^{2+}$ (1–3), (R = 4-NMe₂, 4-NH₂, 3-NH₂).

3 display singlet signals (43.0 ppm and 43.6 ppm) in accord with the D_{3h} symmetry of both molecules with the coordinated phosphorus atoms positioned in the corners of the $[Au_3(PP)_3]$ triangular "belt". The 1D and COSY 1H NMR spectra of both compounds (see Experimental and Fig. S2-S3[†]) show a typical set of resonances in the low-field part of the spectra corresponding to the protons of the diphosphine ligands. It is worth noting that the position of these resonances and observed coupling patterns are nearly identical to those found earlier^{4,6} for the other "rodsin-belt" structures based on the PPh₂C₆H₄PPh₂ ligand, which is a consequence of a very weak effect⁴ of the alkynyl substituents on the phosphine proton shielding. The high field part of the proton spectra of 2 and 3 displays the signals of protons of the alkynyl phenylene spacers, which appear as AB system in $2(4-NH_2)$ substituent) and as a more complicated set of resonances for a less symmetric phenylene moiety containing the NH₂ substituent in the 3-position. According to the relative intensities of the signals observed in the ¹H NMR spectra of 2 and 3 three diphosphine ligands of the "belt" and all six alkynyl ligands of the central $\{Cu_2(Au(C_2C_6H_4-R)_2)_3\}$ core are equivalent, which is a clear indication of the D_{3h} symmetry of the molecules under study as shown in Scheme 1.

It has been found that the clusters 1–3 containing amine nitrogen in the peripheral part of the molecule can be protonated using an excess of the strong non-coordinating sulfonic acids (MeSO₃H and CF₃SO₃H). Exhaustive protonation of all six amine groups is completed under *ca*. 100-fold excess of the acids, the methylsulfonic acid affords more stable protonated products. Investigation of the acetone solution of 1 in the presence of an excess of CH₃SO₃H using ESI-MS, Fig. 2, revealed a weak signal of the non-protonated starting cluster M²⁺, observed at *m*/*z* 1755, together with the following signals of protonated forms: [M + MeSO₃H + H]³⁺ (*m*/*z* 1202), [M + MeSO₃H + 2H]⁴⁺ (*m*/*z* 902), [M + 2MeSO₃H + 2H]⁴⁺ (*m*/*z* 926).

These observations indicate that the starting supramolecular "rods-in-belt" aggregate is not destroyed in the



Fig. 2 ESI-MS spectrum of **1** in the presence of MeSO₃H. Inset–spectrum of **1** under acid-free conditions.

protonation reaction, which is evidently related to the amine groups of the alkynyl ligands. Emergence of the signals containing nondissociative acid molecules evidently stems from the unfavorable electrostatic effect of proton addition to the amine groups, which would eventually bring six more positive charges to the relatively small fragments of the molecule in the case of exhaustive protonation. Compensation of the proton positive charges by the acid counterion helps to relieve the electrostatic repulsion and stabilizes the final product. It is also worth noting that instability of the purely protonated adducts formed upon reaction with stronger CF₃SO₃H acid (Fig. S4[†]) can be also considered as an additional argument in favor of the acid counterion stabilizing effect. ESI-MS experiments did not show the signals corresponding to addition of five and six protons (acid molecules) to the amine substituents very probably due to instability of these aggregates under the conditions of the ESI-MS measurements, in particular, due to extremely high dilution of the mixture that shifts the equilibrium towards acid dissociation products. Nevertheless, partial protonation of 1 (addition of less than six acid molecules) in the presence of acid excess is not compatible with the NMR spectroscopic data, vide infra, which clearly point to retention of the D_{3h} symmetry for the protonated product. Thus, the $[Au_6Cu_2(C_2-C_6H_4-NMe_2*HO_3SMe)_6(PP)_3]^{2+}$ composition can be most probably ascribed to the final adduct formed upon exhaustive protonation of 1.

$$[Au_{6}Cu_{2}(C_{2}C_{6}H_{4}NMe_{2})_{6}(PP)_{3}]^{2+} + MeSO_{3}H \rightleftharpoons [Au_{6}Cu_{2}(C_{2}C_{6}H_{4}NMe_{2}*HSO_{3}Me)_{6}(PP)_{3}]^{2+}$$
(1)

The ESI-MS pattern obtained for the reaction mixture containing the protonated form of 2 displays an analogous set of signals (Fig. S5[†]) that is indicative of essentially similar adduct composition formed in this case. The ESI-MS spectrum of 3 in the presence of MeSO₃H excess (Fig. S6[†]) displays a weak signal of nonprotonated M²⁺ ion together with two signals of mono- and doubly protonated ions, $(M + H)^{3+}$ and $(M + H)^{3+}$ 2H)⁴⁺, respectively. No signals corresponding to coordinated acid molecules or multiple protonated adducts were found in the spectra. This observation can be explained by the *meta* amine group location on the phenylene spacer in 3. Such stereochemistry evidently results in orientation of the NH₂ substituents outside the cluster core and probably makes the addition of the acid molecules sterically hindered because of the van der Waals contacts with the diphosphine belt. However, the NMR spectroscopic data obtained for the protonated adduct of 3 still require symmetrical and exhaustive protonation of this complex that is compatible with

both $[Au_6Cu_2(C_2-C_6H_4-3-NH_2)_6^*(H^+)_6(PP)_3]^{8+}$ and $[Au_6Cu_2(C_2-C_6H_4-3-NH_2)_6^*(MeSO_3H)_6(PP)_3]^{2+}$ stoichiometries for **6**.

The ¹H NMR experiments on the protonation of 1–3 were carried out in deuterated acetone because of considerably higher solubility of the protonated clusters in this solvent compared to CD₂Cl₂. This allows precipitation of the products to be avoided and keeps the solutions under study homogeneous. Stepwise addition of the acid to the starting solution of 1 (Fig. 3) showed very minor changes in the low field signals corresponding to the diphosphine belt. In contrast, the signals of the NMe2 moiety and those of the alkynyl-phenylene spacers immediately start to broaden, which points to a dynamic exchange between partially protonated forms of the cluster. As expected all these signals experience low field drift, the phenylene spacer resonance corresponding to the protons adjacent to amine group has been eventually shifted for ca. 1.2 ppm. The resulting spectrum of 4 (Fig. 3, complex to acid ratio 1:90) displays a spectroscopic pattern, which looks very similar to that of the starting cluster. It contains the singlet of methyl groups (protonated NMe2 fragment), the AB system of the protons of phenylene spacers and nearly unchanged resonances of the tri(gold-diphosphine) belt in the low field part of the spectrum. The acidic protons associated with the amine groups do not appear in the spectrum due to fast exchange with free acid molecules. Relative intensities of the signals and their multiplicity fit completely the D_{3h} symmetry group of the molecule formed upon protonation as shown in Scheme 1. It is hardly possible to exclude the acid counterion dissociation but this or any other dissociative process is obviously very fast in the NMR time scale, which keeps observed spectroscopic patterns compatible with the D_{3h} symmetry of the adduct.



Fig. 3 ¹H NMR spectra of 1 in the aromatic region upon stepwise addition of MeSO₃H, concentration of 1 is *ca.* 5×10^{-3} M, 298 K, acetone-d₆.

Essentially similar spectroscopic changes were observed upon addition of $MeSO_3H$ to the acetone-d₆ solutions of **2** and **3** (Fig. S7[†] and Experimental). The amine moieties in both **2** and **3** are easily protonated to give the adducts **5** and **6**, respectively,

which retain the structure of the starting clusters with six acid molecules symmetrically added to the NH_2 substituents. In the proton spectra of **5** and **6** one can observe a typical set of resonances corresponding to the tri(gold-diphosphine) belt, which remains nearly unchanged upon protonation together with the signals of the phenylene spacers being shifted downfield compared to the starting clusters. The acidic proton bound to the amine group [$-NH_2*HSO_3Me$] appears in the spectrum as a broadened singlet at *ca* 10.6 ppm upon addition of a large excess of the acid. Thus, the most probable structure of **5** and **6** resembles that shown in Scheme 1 and Fig. 1 with the acid molecules (protons) bound to the nitrogen atoms of the corresponding amine groups.

It has been found earlier that cluster 1 demonstrates decent luminescence in dichloromethane solution²⁰ which was ascribed to the phosphorescence from the triplet excited state associated with electron transitions between the orbitals located mainly within the heterometallic cluster core. It was also shown that among their close relatives containing various *para*-substituents (NO₂, H, OMe) in the phenylene spacers of the alkynyl ligands the amine derivative shows the lowest quantum yield and longest emission wavelength, the latter being ascribed⁴ to the strong donor properties of the amine moiety, which increase the HOMO energy to a higher extent compared to the shift of the LUMO. These orbitals give the main contribution to the LSOMO-HSOMO pair of the triplet emitting state for the complexes under study that decreases the MO gap responsible for the emission observed. This is indicative of fairly strong electronic communication between the heterometallic cluster core and *para*-substituents of the aromatic ring through the phenylene spacer.

Compounds 2 and 3 display closely analogous UV-vis spectroscopic characteristics summarized in Table 1. Similar to 1 these complexes show strong absorption bands at *ca* 260 nm, featureless-shoulder absorption between 290 and 315 nm and clear-cut long wavelength bands at 395, 397 and 401 nm for 1, 2, and 3, respectively. According to the electronic structure analysis, see computational section and ref. 4, the high energy absorption can be assigned to the intraligand $\pi \rightarrow \pi^*$ (C=CAr) transitions in the alkynyl moiety, featureless absorption at about 300 nm to the transitions from $\sigma(Au-P)$ orbitals to antibonding orbitals of alkynyl or phosphine ligands, whereas low energy absorption bands with a tail extended to 550 nm have primarily MLCT character, from the orbitals of central cluster fragment to the orbitals of the phosphine ligands and alkynyl π^* orbitals, see below.

In general luminescence of the complexes studied shows a substantial Stokes shift (210–320 nm) and an emission lifetime in the microsecond domain that is characteristic of its origination from the triplet state manifold. However, in contrast to similarity in absorption properties the phosphorescence characteristics of 1 and 2 differ substantially to those revealed for 3. Emission wavelengths of 1 and 2 in dichloromethane solution are close each other (715 and 708 nm) whereas that of 3 (608 nm) is blue-shifted for about one hundred nm. Analogously, lifetimes of emitting excited states for 1 and 2 (0.81 and 0.32 μ s) are considerably shorter compared to 3.30 μ s in the case of 3. And finally, the emission Q. Y. for 3 is an order of magnitude higher compared to those found for 1 and 2.

These observations illustrate clearly a well known strong *resonance conjugation* between the *para*-substituents of the aromatic ring and a much weaker *inductive* influence of the *meta*-substituents that determines a lower donor effect of the 3-NH₂ group compared to those of NMe₂ and NH₂ in *para*-position. Because of this the electron density transfer onto MOs responsible for the triplet state emission is substantially higher in 1 and 2, which results in a bathochromic shift of the emission maxima (see above) and in a dramatic decrease in the phosphorescence Q. Y. The effects observed are completely in line with the experimental data⁴ obtained for a series of closely analogous "rods-in-belt' complexes containing *para*-substituents (NO₂, H and OMe) of various electron donor strengths in the alkynyl ligands, the higher donicity causing a red shift of emission maximum and decrease in emission Q. Y.

The most interesting feature of the complexes under study is a variation of their photophysical properties upon protonation of the amine groups. Luminescence and absorption responses of 1 in the CH_2Cl_2 solution during titration with $MeSO_3H$ are shown in Fig. 4 and Fig. S8†, respectively. The absorption spectrum variation is rather small, whereas the luminescence characteristics experience dramatic changes both in emission wavelength and intensity.

The acid addition first results in nearly complete emission quenching in the area corresponding to incomplete protonation of the starting cluster and then appears at substantially shorter wavelength demonstrating a sharp growth in Q. Y. The completely protonated complex 4 displays a slightly lower lifetime but the radiative decay rate constant and Q. Y. are approximately an order of magnitude higher compared to the initial values. A closely analogous behavior was observed upon protonation of 2 with

Table 1The photophysical properties of complexes 1–6 in CH_2Cl_2 , 298 K

R	Complex	$\lambda_{abs}/nm (10^{-3} \epsilon/cm^{-1} M^{-1})$	$\lambda_{\rm em}/{\rm nm}^b$	Quantum yield (Q. Y.) ^e	$ au_{ m obs}/\mu{ m s}$	$10^{-5} k_{\rm r} / {\rm s}^{-1}$	$10^{-6} k_{\rm nr}/{\rm s}^{-1}$
4-NMe ₂	1	262 (165), 291 (137), 315sh (129), 395 (78)	715	0.06 ± 0.01	0.81 ± 0.08	0.74 ± 0.05	1.2 ± 0.1
-	4 (protonated) ^{a}	262 (168), 325sh (60), 408 (51)	575	0.48 ± 0.05	0.54 ± 0.05	8.9 ± 0.9	1.0 ± 0.2
4-NH ₂	2	262 (79.6), 290 sh (117), 312sh (93) 397 (63)	708	0.018 ± 0.003	0.32 ± 0.03	0.56 ± 0.05	3.1 ± 0.3
-	5 (protonated)	262 (175), 332sh (50.0), 408 (48.0)	580	0.6 ± 0.1	0.52 ± 0.05	12.1 ± 1.0	0.71 ± 0.15
3-NH ₂	3	263sh (159), 313sh (59), 401 (52)	608	0.41 ± 0.05	3.3 ± 0.3	1.24 ± 0.1	0.18 ± 0.03
	6 (protonated)	264 (164), 332sh (76), 407 (54),	575	0.26 ± 0.04	$1.0 \pm 0.2 \ (1.0)^d$	2.6 ± 0.3^{e}	0.7 ± 0.2
	u				$3.3 \pm 0.5 (0.2)^d$		

^{*a*} Protonation performed with 100-fold excess of MeSO₃H. ^{*b*} $\lambda_{ex} = 385$ nm. ^{*c*} Rhodamine 6G was used as a standard for the quantum yield measurements. ^{*d*} Relative contribution of the corresponding exponent into double-exponential decay. ^{*e*} Relative to main component of the decay.



Fig. 4 Changes of emission spectra of 1, $C = 2.3-2.7 \times 10^{-4}$ M, in degassed CH₂Cl₂ upon addition of MeSO₃H, room temperature, $\lambda_{ex} = 385$ nm.

extremely high growth in emission efficiency to give rise to a Q. Y. value of 0.6 and $k_r = 12.1 \times 10^5 \text{ s}^{-1}$ for the protonated adduct **5** (*cf.* 0.018 and 0.56 × 10⁵ s⁻¹ for **2**). It is worth noting that the protonation reaction is reversible and its equilibrium can be easily shifted backwards upon addition of NEt₃ to restore initial emission properties that can be considered as a "turn-on-turn-off" tool.

Very different variations in luminescence characteristics were found in the case of meta-substituted complex 3, Table 1. Upon exhaustive protonation this compound displays a moderate (33 nm) blue shift in emission maximum and, in contrast to complexes 1 and 2, relatively small reduction in Q. Y. The effects observed are evidently related to the alteration of the amine group donor properties accounted for by addition of a proton to the nitrogen atom (formation of the adduct with the acid molecule). In the case of the para-substituted alkynyl ligands the effect of donicity reduction is easily transferred to the orbitals of the heterometallic core to increase the energy gap between MOs responsible for triplet state emission as described earlier⁴ and to give 140 and 128 nm blue shifts in emission wavelengths. Protonation of the meta-substituents in 3 quite expectedly causes much lower changes in electron density on the cluster core orbitals that provokes a relatively small hypsochromic shift of emission maximum.

Computational results

The structural and electronic properties of the Au¹–Cu¹ clusters were further elucidated by means of density functional calculations (for computational details, see the Experimental section). The availability of an X-ray crystal structure of **1** (Figure S9†) allows for the comparison between the experimental and theoretical geometries, which are in good agreement. The properties of the structurally optimized clusters **1–6** are summarized in Table 2 and Figure S10.†

In the case of the protonated clusters **4–6**, complete protonation is sterically feasible without any significant changes to the general structural motif of the clusters. This process is energetically feasible, as well. For example, in the case of cluster **1**, the reaction energies for the protonation, calculated as $\Delta E_{\text{prot}} = E[\mathbf{1}^*(\text{MeSO}_3\text{H})_n] - [E(\mathbf{1}) + n E(\text{MeSO}_3\text{H})]$, are -98, -142, -201, -256, -287, and -338 kJ mol⁻¹ for n = 1-6.

The different donor properties of the *para-* and *meta*substituents give rise to some evident structural trends. In clusters 4 and 5, where the protonation strongly reduces the ability of the NMe₂ and NH₂ groups to contribute electron density to the central

Table 2Selected interatomic distances and electronic properties of the
heterometallic Au^{I} - Cu^{I} clusters 1-6 obtained at the BP86 level of theory

	1 (X-ray)	1	2	3	4	5	6
Interatomic distances/Å							
Au(central)-Au(belt)	2.82-2.84	2.90	2.91	2.93	2.96	2.97	2.93
Au(central)–Au(central)	3.20-3.51	3.46	3.44	3.43	3.39	3.35	3.42
C(Ph)–N	1.37-1.42	1.38	1.38	1.39	1.48	1.46	1.47
N-H ⁺					1.14	1.19	1.09
$O(MeSO_3^-) \cdots H^+$					1.44	1.36	1.63
HOMO-LUMO gap (eV)		1.27	1.35	1.64	2.01	1.99	1.79

fragment, the metal–metal distances within the heterometallic core decrease in comparison to the non-protonated clusters 1 and 2. This effect, illustrated by the changes in the Au–Au distances, is absent in the case of the clusters 3 and 6, where the electron donor effect of the *meta*-NH₂ group is lower. The N–H⁺ distances are shortest in the *meta*-substituted cluster 6. In clusters 4 and 5 the acid molecules are clearly connected to the amine groups only through one O···H⁺ contact, while in cluster 6 the acid molecules also show a second fairly short O···H⁺ distance of 1.81 Å (Figure S10⁺).

We investigated the frontier orbital characteristics of both S_0 and T_1 states of the clusters **1–6** to shed light on their photophysical behavior. The relaxed geometry of the lowest energy triplet state T_1 was generally found to be very close to the ground state structure for all clusters, the general structural motif of the clusters remaining unperturbed. Accordingly, for the studied T_1 states, the highest singly occupied orbital (HSOMO), occupied by the excited electron, is closely related to the LUMO of the S_0 state, and the lowest singly occupied orbital (LSOMO) is closely related to the HOMO of the S_0 state. Hence, it can also be expected that the theoretical HOMO-LUMO gaps reproduce the observed qualitative trends for the emission characteristics. The calculated HOMO-LUMO gaps of the non-protonated clusters decrease in the order 3 > 2 > 1 (Table 2), which is also the experimentally observed ordering of the emission wavelengths for these clusters. Furthermore, in agreement with the experimentally observed blue shift of the emission maxima for the protonated clusters, the energy gaps of the clusters 4-6 are larger than the energy gaps of the nonprotonated clusters, particularly for the para-substituted ones.

As can be expected from the structural characteristics of the para-substituted clusters 1 and 2, their HOMOs are very similar to each other (Figures S10 and S11⁺). The HOMOs are delocalized within the heterometallic central fragment and the contribution of the NMe₂ and NH₂ groups is significant. The LUMOs of 1 and 2 are mainly centered on the "belt" fragment, with some small contributions from the alkynyl groups of the Au-Cu central cluster. In the case of the meta-substituted cluster 3, the HOMOs are also delocalized within the heterometallic core (Figure S12[†]), but due to the lower electron-donating effect of the *meta*-NH₂ group the HOMOs lie lower in energy in comparison to 1 and 2, resulting in a larger HOMO-LUMO gap. This effect influences the LUMOs of 3, as well the alkynyl groups of the central fragment contributing more to the LUMO in comparison to 1 and 2. Investigation of the frontier orbital characteristics of the lowest energy triplet state does not change the general picture, but the HSOMOs of the clusters 1 and 2 do possess some additional

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contributions from the central fragment in addition to the orbitals of the "belt" fragment.

Protonation has significant effects on the frontier orbital characteristics of the clusters, as the protonated NMe₂ and NH₂ groups contribute much less electron density to the central fragment. Because of the significantly reduced substituent effects, the orbitals of the central fragment centered on the heterometallic core and the alkynyl groups are shifted down in energy and the composition of the HOMOs is fairly similar for clusters **4–6**. Analogously, for clusters **4–6**, the LUMO is centered primarily on the alkynyl groups of the central fragment, and the LUMO+1 is centered on the "belt" fragment. The lowest energy triplet states consistently possess the same central fragment based characteristics, with LSOMO related to HOMO and HSOMO related to LUMO.

One of the interesting photophysical aspects of the studied clusters is the greatly improved quantum yield of clusters 1 and 2 upon complete protonation. In the protonated clusters 4 and 5, the frontier orbital characteristics suggest the triplet emission occurs within the core of the central fragment, in which case spin–orbit coupling due to metal orbitals would enable efficient radiative decay of the excited triplet state. On the contrary, in the case of the non-protonated complexes 1 and 2, the excited triplet state strongly involves the π^* orbitals of the "belt" fragment, hindering efficient spin–orbit coupling with the metal orbitals of the central fragment thus promoting radiationless decay.

Another intriguing photophysical feature of the present Au-Cu clusters 1 and 2 is the nearly complete disappearance of emission resulting from the partial protonatation of the amine groups. We elucidated the photophysical effects of the partial protonation by inspecting the frontier orbitals of the cluster 1 with the number of MeSO₃H molecules varying from zero to six. Partial protonation has distinct effects on the frontier orbital characteristics, as illustrated for a four-fold protonated cluster 1*(MeSO₃H)₄ in Figure S13.[†] As the protonation of the amine groups reduces their electron-donating effects, the orbitals of the protonated $C_2C_6H_4$ -4-NMe₂ ligands are shifted down in energy and the HOMOs become localized on the non-protonated C₂C₆H₄-4-NMe₂ ligands. In contrast, the dominant contributions to the LUMO come from the protonated ligands, the non-protonated ligands having a smaller contribution. The strongly reduced delocalization of the central fragment based frontier orbitals makes the excited triplet state much less susceptible to spin-orbit coupling effects of the metal orbitals, thus annihilating pathways for effective radiative decay.

Conclusion

We have reported the structurally similar luminescent $Au^{I}-Cu^{I}$ alkynyl-diphosphine clusters **1–3** bearing NMe₂ and NH₂ groups and their reactions with strong sulfonic acids (HSO₃Me and HSO₃CF₃), which result in protonation of the amine functionalities and formation of the adducts [Au₆Cu₂(C₂C₆H₄-4-R)₆*(R'SO₃H)₆(PPh₂C₆H₄PPh₂)₃](PF₆)₂ (R = 4-NMe₂ (**4**), 4-NH₂ (**5**), 3-NH₂ (**6**)). The photophysical measurements revealed a considerable hypsochromic shift of the emission maxima for the protonated species (*ca.* 100 nm for **4** and **5**) and large increase in phoshorescence quantum yield (8-fold for **4**, 33-fold for **5** related to the parent species **1** and **2**, respectively). The adduct formation was found to be reversible as addition of a base (NEt₃) restores initial emission properties that can be considered as a "turn-on-turn-off" tool. Protonation of the $3-NH_2$ substituted complex 3 demonstrated much smaller blue-shift of emission wavelength (*ca.* 30 nm) and *ca.* 40% drop in quantum yield. The computational studies performed proved the energetic feasibility of the complete protonation of the clusters 1-3 and revealed the structural trends accompanying this process. Analysis of the frontier orbital characteristics of the complexes 1-6 suggested a tentative explanation of the photophysical changes observed.

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