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Luminescence thermochromism of gold(I) phosphane-iodide complexes: a rule or an exception?

Nina Glebko,^[a] Thuy Minh Dau,^[a] Alexei S. Melnikov,^[b] Elena V. Grachova,^[c] Igor V. Solovyev,^[c] Andrey Belyaev,^[a,c] Antti J. Karttunen*^[d] and Igor O. Koshevoy*^[a]

Abstract: The series of gold(I) iodide complexes 1-11 have been prepared using di-, tri- and tetraphosphane ligands. Crystallographic studies reveal that the di- (1-7) and tetrametallic (11) compounds feature linearly coordinated Au(I) ions with short aurophilic contacts. Their luminescence behavior is determined by the joint influence of the phosphane properties, metal-metal and the intermolecular lattice-defined interactions. The proposed variable contribution of ³(X+M)-centered and ³XLCT electronic transitions into the lowest lying excited state influenced by the supramolecular packing, is presumably responsible for the alteration of room temperature emission color from green (545 nm, 11) to near-IR (698 nm, 2). Dinuclear compounds 6 and 7 exhibit distinct luminescence thermochromism with up to 5750 cm⁻¹ blue shift upon cooling. Such dramatic change of emission energy is assigned to the presence of two coupled triplet excited states of ${}^{3}\pi\pi^{*}$ and ${}^{3}(X+M)C/{}^{3}XLCT$ nature, the presence of which depends on both molecular structure and the crystal lattice arrangement.

Introduction

Photoemissive compounds and materials, which demonstrate a detectable response of physical parameters (wavelength, intensity, lifetime) to the temperature changes (i.e. luminescent thermometers), play an essential role in optical monitoring of thermal variations, performed for the different temperature ranges, surrounding media, scales of the measured objects and local environment.^[1] Thermally induced switching of the luminescence color due to (*i*) the large shift of emission maximum, or, particularly, (*ii*) the presence of two distinct and variable emission bands, remains a more rare optical behavior than rather common relationships between the lifetime or intensity and the temperature.^[2]

Thermally regulated dual emission has been successfully achieved for a number of transition metal complexes containing two or more interacting metal ions. These compounds potentially can have several accessible excited states of intraligand (IL),

[a]	N. Glebko, T. M. Dau, A. Belyaev, Prof. I.O. Koshevoy						
	Department of Chemistry, University of Eastern Finland,						
	Yliopistokatu 7, Joensuu, Finland						
	E-mail: igor.koshevoy@uef.fi						
[b]	Dr A. S. Melnikov						
	Peter the Great StPetersburg Polytechnic University						
	Polytechnicheskaya, 29, StPetersburg, Russia						
[c]	I. V. Solovyev, Prof. E. V. Grachova						
	Institute of Chemistry, StPetersburg State University						
	26 Universitetskiy pr., Petergof, StPetersburg, Russia						
[c]	Prof. A. J. Karttunen						
	Department of Chemistry and Materials Science,						
	Aalto University, FI-00076 Aalto, Finland						

E-mail: antti.j.karttunen@aalto.fi

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charge transfer (metal to ligand, ligand to metal, ligand to ligand) and metal/cluster-centered (CC) origin. The population of such energetically different excited states is governed by intramolecular reorganization (e.g. by means of non-covalent contacts)^[3] or weak intermolecular interactions (mostly defined by crystal lattice in the solid state),^[4] thermally dependent modulation of which is responsible for the emergence of controllable panchromatic luminescence.

In this respect, cluster complexes of copper subgroup metals, are capable of displaying thermochromic emission for the cases of properly selected ligand environment that normally contains halide ions. Noteworthy, these compounds often feature short metal-metal contacts, which are typically considered as metallophilic bonding based on the results of structural analysis. The tetranuclear cubane species $[Cu_4I_4L_4]$ (L = phosphane, pyridine) represent the most well studied family of temperatureresponsive d¹⁰ dual luminophores.^[5] These iodide compounds exhibit intense low energy emission (green-yellow) under the ambient conditions, assigned to the triplet cluster-centered excited state (CC), while at 77 K the domination of high energy band (deep-blue emission) is attributed to charge transfer character (metal to ligand and halogen to ligand, MLCT/XLCT) of the excited state, which is unable to undergo transition to the ³CC one because of the lack of vibration energy.^[5c] A similar behavior has been recently reported for [Cu₄I₄(PN)₂] compound (PN = phospholan-pyridine) with square planar metal arrangement.^[6] Alternatively, the 2D metal-organic framework, built of Cu₆I₆ clusters and tridentate N-donor ligands, shows a substantial hypsochromic shift of phosphorescence (4554 cm⁻¹, from 611 nm at 298 K to 478 nm at 77 K) presumably without changing the origin of the emission (MLCT/XLCT), but due to crystal packing-induced destabilization of the LUMO.^[7] Furthermore, the decoration of $\{Cu_2I_2\}$ core with two Cu_6L_3 motifs (L = pyrazolyl pyridine derivative) produced dually emissive complex with variable relative intensities of low and high energy bands in a wide range of temperatures.^[8]

Conversely, silver polynuclear compounds with thermally variable dual luminescence are very scarce. The reported examples encompass Ag_{31}/Ag_{33} thiolate clusters with up to 2856 cm⁻¹ bathochromic shift of emission upon cooling from 298 to 77 K,^[9] and cubane iodide complex [Ag₄I₄(phosphane)₄], which demonstrates contrary temperature dependent behaviour for crystalline and powdered samples.^[10]

Gold(I) ions have higher oxidation potential compared to copper and silver metals and therefore are less prone to participate in MLCT transitions. Thus, the rare cases of Au(I) thermally responsive emitters primarily imply $\pi\pi^*$ intraligand (IL), metalcentered and LM(M)CT excited states, which might result in the appearance of two or more emission bands.^[11] A remarkable luminescence thermochromism has been reported for [Au₃(pyrazolate)₃] complex, whose emission of ³CC type (both at 77 K and 298 K) was proposed to be strongly affected by

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Scheme 1. The phosphane ligands and their gold(I) complexes 1–11, described in this work.

intermolecular spacing.^[12] Similarly, single crystal phase change that occurs upon cooling, was observed for the cationic sulfide trinuclear cluster [S(AuCNR)₃]⁺. This process generates two different types of intermolecular aggregates at 77 K via modulation of aurophilic contacts, and consequently causes two phosphorescence signals maximized at 490 and 680 nm.^[4a] A very large emission thermochromism of 10164 cm⁻¹, ascribed to internal conversion between T_2 and T_1 excited states, has been lately described for a trinuclear imidazolate Au(I) cluster.^[13] Essentially, this appealing photophysical behaviour could not be correlated with changes of intra- or intermolecular metal-metal distances or phase changes. The intramolecular switching of luminescence origin upon changing the temperature has been described only for few di- and triphosphane halide^[14] and cationic^[15] gold(I) species, for which blue shifted IL phosphorescence prevails at low temperature, while metaldominated LE emission with poor quantum yields (ϕ_{em} of ca. 1– 2%)^[14a] was observed at 298 K.

A limited understanding of the factors, which guide thermochromic properties of Au(I)-based materials, prevents rational design of these complexes on the molecular and macroscopic levels. Nevertheless, it is important that the ligand (phosphane) orbitals can significantly contribute into the emissive states of gold luminophores. This fact points to a potentially high tunability of their photophysical performance that could make simple and easy to prepare phosphano-halide Au(I) complexes a diverse alternative to copper thermally switchable phosphors. To extend a so far limited class of temperature responsive gold(I) species, herein we report on the preparation, systematic structural and photophysical investigations of a series of iodide complexes using a selection of di-, tri- and tetraphosphane ligands.

Results and Discussion

Synthesis and structural characterization. The digold(I) iodide phosphane complexes and the related species of higher nuclearity generally can be obtained in a straightforward way by reacting the stoichiometric amounts of Aul and the corresponding ligand.^[16] This simple approach was used to prepare the bimetallic compounds [(Aul)₂(diphosphane)] 1-3 and 7 (diphosphane = dppb, biphep, dpbp, tpdpO, respectively), isolated as nearly colourless solids after conventional recrystallization, see Scheme 1 and experimental section (ESI). For the synthesis of the complexes with diphosphane-diphenyl ether ligands (DPEphos, 4; N-XantPhos, 5 and XantPhos, 6) we used a solvothermal method (acetonitrile, 200 °C, N₂ 40 atm), which afforded crystalline materials suitable for XRD analysis, though in visibly lower yields particularly for 5 and 6 (39 and 41%). Compounds 2,^[17] 4^[18] and 6^[18] were obtained previously utilizing different protocols; 4 and 6 were reported in different crystalline modifications. Also, the optical properties of 2, 4, 6 were not investigated and therefore these species were included in the current study.

In the case of N-XantPhos and XantPhos ligands the mononuclear complexes [Aul(diphosphane)] (8 and 9) are obtained in substantially better yields than their dinuclear congeners (Scheme 1). The easier formation of the monometallic species could be a reason for the relatively

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Figure 1. Molecular views of complexes 1–3 (thermal ellipsoids are shown at 50% probability). Symmetry transformations used to generate equivalent atoms (') in 1: 1–x, y, 0.5–z.

ineffective synthesis of the digold compounds **5** and **6** even if correct stoichiometry is obeyed. This preference of chelating *vs* bridging coordination mode probably arises from the rigidity of the ligands' xanthene backbone and the appearance of the unfavourable strain while binding to the Au₂ motif.

To extend the series, the triphosphane tpdp was employed to produce a four-coordinate complex [Aul(tpdp)] (8). Unfortunately, the attempts to prepare a trinuclear iodide analogue of $[(AuCl)_3(tpdp)]^{[19]}$ were unsuccessful and gave **10** along with unidentified dark side product. The reaction of the tetradentate ligand tppb with 4 equivalents of Aul leads to an insoluble precipitate. To prove its composition, the crystalline form of $[(Aul)_4(tppb)]$ (**11**) was obtained following a solvothermal protocol, applied for the synthesis of **4–8** (ESI).

The solid state structures of all the title compounds were determined by single crystal XRD analysis (Figures 1-3 and S1; crystal data is given in Table S1, Supporting Information). The digold complexes 1-7 and the tetranuclear relative 11 demonstrate the Au-Au contacts, which fall in the range from 2.9767 to 3.3156 Å (Table S2). These values are below the sum of two van der Waals radii for gold (3.32 Å) and are typical for gold-gold separations, associated with aurophilic bonding.^[20] However, it should be pointed out that short distances do not unambiguously prove the presence of a bond between the metal centers because they can be caused by the ligand environment and packing effects. As a result of possible metal-metal attraction, the P-Au-I angles in these species visibly deviate from linearity and approach the value of 162.25 ° (6), while in the absence of Au-Au contacts (4 C₆H₆) these angles are 178.17° and 178.67°. However, bending of the P-Au-I motif can arise from other than aurophilic non-covalent interactions, which are induced by the crystal packing. This can be illustrated e.g. by the complex [(Aul)2(BINAP)][21] with the corresponding angle of 172.20° attained without short Au-Au separations. Except 1, the gold ions in 2-7 and 11 are structurally inequivalent and adopt slightly different coordination geometries. The general feature of 1-7 and 11 is the twisting of the {PAul}2 motifs (I-Au-Au-I torsion angles are 56.7-92.8 °) that apparently reflects the trend to decrease dipole-dipole interactions (i.e. the repulsion between the iodine *p*-orbitals), which are minimized in the perpendicular systems formed in the absence of steric strain.[18, 22] The distortions of the phosphane scaffold are dictated by their stereochemistry and flexibility, which tends to reduce the stain

appearing upon bridging the digold moieties. Thus, the smallest torsion angle P–C_{ipso1}– C_{ipso2}–P (< 4.6 °, Table S2) is observed for complexes **1** and **11** as a result of the suitable bite angle and the ligand rigidity, while the diphosphanes with bendable spacers attain the optimal geometries through the formation of highly twisted configurations. The structural peculiarities of the chloroform solvate of **4** and of the bromide analogue of **6** have been discussed in detail by Gray.^[18]

Molecular arrangements of **1** and **2** are essentially similar to those of the chloride congener $[(AuCl)_2(dppb)]^{[23]}$ and of closely related complexes with biphep-like ligands ($[(Aul)_2(2,2^-Et_2PC_6H_4C_6H_4PEt_2)]^{[17]}$ and $[(Aul)_2(Me-biphep)]^{[24]}$), respectively. Compound **3** has the longest gold–gold distance that might be a result of a weak Au–O interaction. One such contact in **3** equals 3.148 Å (Table S2) and represents the shortest Au–O separation found among the dinuclear complexes **3–7** with oxygen-containing phosphanes, indicating a possible donation of some electron density to the metal center that possibly affects the Au–Au separation.

Complex 4 crystallizes in several forms depending on the solvent used; the resulting materials show different optical behavior (see the photophysical studies below). The crystallographic parameters of the dichloromethane solvate 4 CH₂Cl₂ (spacegroup, unit cell dimensions, see Table S1) are virtually identical to those of 4 CHCl₃.^[18] Expectedly, the corresponding structural characteristics of 4 CH₂Cl₂ and 4 CHCl₃ have nearly the same values. On the contrary, the modification of 4 C₆H₆ obtained from benzene shows no aurophilic interaction (Figure S1), the absence of which is presumably compensated in energy by rather extensive inter- and intramolecular π - π interactions compared with 4 CH2 Cl2. Using a solvothermal method, a solvent-free modification 4 was isolated from its acetonitrile solution. The molecular conformation of 4 closely resembles that of $4 \cdot CH_2CI_2$ though has a noticeably longer Au-Au distance (3.0682 Å) than the dichloromethane solvate (2.9459 Å). Noteworthy, according to the calculated density of the crystals, 4 adopts the most compact packing with respect to its solvated forms. This may be attributed to the combination of intermolecular π -stacking and I \cdots H hydrogen bonding that results in a more rigid lattice of 4 (Figure S1) and determines its distinct photophysical performance (vide infra).



Figure 2. Molecular views of complexes 5, 7 and 11 (thermal ellipsoids are shown at 50% probability).

The molecular structures of **5** and **6** (Figures 2 and S2) are very much alike; not surprisingly the latter is also akin to complexes $[(AuHal)_2(XantPhos)]$ (Hal = Cl, Br).^[18, 25] The main difference can be seen in the distortion of the diphosphane's backbone, which is less pronounced in the case of **5** (PCCP torsion angle is 17.5 ° *vs* 37.6 ° in **6**) seemingly due to a somewhat larger separation between phosphorus atoms in **5** (4.732 Å) compared to **6** (4.657 Å).

The given structural analysis indicates that Au–Au dispersive interactions are not likely to play the main role in producing the molecular arrangements with metal–metal contacts. These separations show a substantial deviation in length (2.9767 to 3.3156 Å) and are largely determined by the appropriate bite angle of the bridging ligand along with favourable packing of the discrete molecules in the crystal cell.

The mononuclear compounds **8–10** are not exceptional and match the structures of their (pseudo)halide relatives.^[26] Thus, in the diphosphane complexes **8** and **9** the metal ions adopt trigonal coordination geometry, while in the case of **8** the triphosphane tpdp and the iodide ligands form a tetrahedral-like environment around gold atom (Figure S3), where the Au–P distances for the lateral P(1) and P(3) donors (2.3689 and 2.3361 Å) are visibly shorter than that involving the central phosphorus atom (2.4621 Å, Table S3). The Au–O spacing in **8** and **9** exceed 3.14 Å that implies very weak interactions. Overall, the Au–P and Au–I contacts in **8–10** are systematically longer than the corresponding values in **1–7** and **11**, where the Au(I) ions are two-coordinate.

Crystalline compounds **5**, **6**, **8** and **11** are virtually insoluble in common organic solvents that prevented their characterization in solution. The ³¹P NMR spectra of **1–4** and **9** show a singlet resonance each that corresponds to the equivalence of the phosphorus atoms; their coordination to the gold ions is confirmed by the typical low field shifts of the signals with respect to the parent ligands. In the case of **2–4** it indicates that the molecules adopt higher symmetry than that found in the solid state due to the fast intramolecular motion, which might involve dissociation of the Au–Au bonds. The dinuclear complex **7**, however, demonstrates a substantially higher rigidity than **2–4** under the ambient conditions. Its ³¹P NMR pattern consists of

three signals of 1:1:1 relative intensity (Figure S4). This is compatible with stereochemically different P nuclei of tpdpO ligand meaning that the crystal structure of **7** is retained in fluid medium at 298 K. Raising the temperature to 353 K increases the rate of the dynamic processes and makes the terminal PPh₂ groups equivalent in the NMR time scale. Complex **10** displays an AB₂ spin system in its ³¹P NMR spectrum that is in accordance with the data for other tpdp-containing compounds.^[26c, 27]

Solid state photophysical properties. Soft iodide ligand has been chosen for this series due to its reported ability to facilitate the aurophilic bonding,^[28] which often has a strong impact on the photophysical behaviour of gold complexes. Additionally, it has been noticed that the effect of temperature on the emission energy is more prominent for the I-containing compounds.[14a] None of the soluble complexes under study (1-4, 9 and 10) shows appreciable luminescence in fluid medium, therefore the investigation of the photophysical properties was carried out for crystalline materials only, the corresponding data is listed in Table 1. Among the dinuclear species 1-7 and their tetragold congener 11, which demonstrate metal-metal contacts, compounds 3 and 5 are barely emissive at room temperature (Figure S5) with quantum yields being less than 10⁻³. Complex 3 features the broad band centered at ca. 650 nm. accompanied by a shoulder at ca. 500 nm. The low energy band could be tentatively associated with (M+X)-centered (X = iodide) excited state of the triplet nature that is in line with earlier reports on the gold phosphane-halide systems,^[11a, 14a, 22b] though a precise assignment of the nature of the electronic states in such systems is still pending The high energy shoulder, considerably enhanced at 77 K, presumably originates from the metalperturbed intraligand (phosphane) transitions. Similarly, weak luminescence of **5** under ambient conditions ($\lambda_{em} = 472 \text{ nm}, \tau_{av} =$ 54 μ s) can be attributed mainly to the ³IL excited state that is evidenced by a distinguishable vibrational structure of the emission band (v = ca. 1330 cm⁻¹). This behaviour of 5, containing N-XantPhos ligand, contrasts with that of [Au2(N-XantPhos)2]²⁺ series, for which the observed yellow-orange phosphorescence (λ_{em} = 583–623 nm, τ_{av} = 0.3–2 µs) was

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Table 1. Solid state photophysical properties of 1–7, 9–11 and (Aul) ₂ (BINAP) (AB).											
			298	77 K							
	λ_{exc} , nm	λ_{em} , a nm	<i>τ</i> , μS	$oldsymbol{\Phi}_{em}$	<i>k</i> r, s ^{-1 c}	<i>k</i> nr, S ^{-1 <i>d</i>}	λ_{exc} , nm	λ _{em} ,ª nm	<i>τ</i> , μS		
1	327	551	3.7	0.26	7.0×10 ⁴	2.0×10 ⁵	327	583	4.6		
2	332	698	5.0	0.12	2.4×10 ⁴	1.8×10 ⁵	306	654	15 ^b		
3	311	~650, ~500 ^{sh}	27 ^b	<10 ⁻³	<37	3.7×10 ⁴	311	~670, ~490	35		
AB	335	527	226 ^b	0.02	88.5	4.3×10 ³	330	527	~4000 ^b		
4	336	637	4.3	0.19	4.4×10 ⁴	1.9×10 ⁵	326	654	7.2		
5	370	472	54 ^b	<10 ⁻³	<19	1.9×10 ⁴	332, 363 ^{sh} , 387 ^{sh}	519	2400 ^b		
6	328	562	3.4	0.28	8.2×10 ⁴	2.1×10 ⁵	320	450	1200 ^b		
7	320	663	5.8	0.54	9.3×10 ⁴	7.9×10 ⁴	320	480	368.0		
9	341, 363	486	9.1 ^{<i>b</i>}	0.28	3.1×10 ⁴	7.9×10 ⁴	327, 361 ^{sh}	500	16 ^b		
10	418	640	1.8	0.35	1.9×10 ⁵	3.6×10 ⁵	418	660	30.1		
11	332, 380	545	2.8	0.17	6.1×10 ⁴	3.0×10 ⁵	335, 385	545	5.6		

^a λ_{axc} = 351 nm; ^b average emission lifetime for the two-exponential decay determined by the equation $\tau_{av} = (A_1r_1^2 + A_2r_2^2)/(A_1r_1 + A_2r_2)$, A_i = weight of the *i* exponent; ^c k_r values were estimated by Φ/τ_{av} . ^d k_{rr} values were estimated by k_r (1- Φ)/ τ_{av} .



Figure 3. Normalized solid state excitation (dotted lines) and emission (solid lines) spectra of complexes 1, 2, 4 and 11 at 298 K.

assigned to Au_2 -based transitions,^[29] indicative that the relaxation to the lower-lying metal-centered excited state in complex **5** is blocked at room temperature.

For the sake of comparison, optical behaviour of the $[(Aul)_2(BINAP)]^{[21]}$ complex without metallophilic interactions has been evaluated. The structured emission profile (v = ca. 1250 cm⁻¹) and the lifetime of 226 µs at 298 K point to the ${}^3\pi\pi^*$ excited state, most probably located on the binaphtyl motif. Such long lived excited state is compatible with the data obtained for other gold(I) compounds, bearing phosphane ligands with extended π -chromophore backbones.^[30] The emission lifetimes for **3** and **5** observed at 298 K (27 and 54 µs, respectively),

visibly differ from those deduced for other complexes studied here, and suggest extremely slow radiative rate constants k_r at 298 K (Table 1) with respect to non-radiative decays that accounts for low intensity long-lived luminescence.

The influence of the temperature on the emission energies of **5** and (AuI)₂(BINAP) is relatively minor (Figure S5); cooling the samples to 77 K leads to the dramatic increase of the decay times up to 2.4 and 4 ms that has been noticed previously for some other gold species.^[31] This effect can be tentatively explained in terms of very inefficient spin-orbit coupling (SOC) due to the same parentage ($\pi\pi^*$) of the lowest lying S₁ and T₁ excited states.

Another group of complexes comprises moderately intense luminophores **1**, **2**, **4** and **11**, which exhibit room temperature phosphorescence with quantum yields 0.12–0.26 and the lifetimes in the range 2.8–5.0 µs that gives radiative lifetimes ($r_r = r_{obs}/\Phi_{em}$) of 14.2–41.7 µs indicative of strong SOC. These compounds display broad and featureless spectroscopic patterns (Figure 3) suggesting a significant charge transfer character of the excited states. Taking into account high oxidation potential of the Au(I) ion, it is reasonable to hypothesize a negligible contribution of MLCT (Au→phosphane) transitions into the emissive T₁ states of these molecules. Thus, the nature of the lowest triplet excited state can be presumably described as a substantial charge re-distribution occurring within the {Au₂I₂} motifs, i.e. (X+M)-centered transitions, mixed with XL (iodide→phosphane) charge transfer.

This conclusion correlates with earlier assignments made for gold phosphane-iodide compounds.^[14a] Unfortunately computational investigation of the triplet excited states was not possible as the DFT-PBE0 method severely underestimated the

triplet emission energies, resulting in a very poor agreement with the experimental values. Because of this failure (i.e. inadequate triplet state geometries and the electron distribution), theoretical studies are not included in the discussion.

The luminescence colours for 1, 2, 4, 11 and 6, 7 (vide infra) under ambient conditions span from green (545 nm, 11) to near-IR (698 nm, 2) and do not reveal any systematic dependence on the ground state Au⁻¹Au distances.This variation of the emission energies might arise from different contributions of ³(X+M)-centered and ³XLCT character into the lowest energy excited state that is responsible for a hypsochromic shift of the emission, observed for 1, 6 and 11.

It is worth noting, that the photophysical properties of the title complexes should be correlated with molecular structure only with a certain care. As mentioned above, 4 has been characterized in three different modifications, out of which only the solvent-free form exhibits distinct emission. If in the case of its benzene solvate, 4 C₆H₆, the lack of luminescence can be attributed to the absence of Au. Au interaction, for 4 CH₂Cl₂ with gold-gold separation of 2.9459 Å (cf. 3.0682 Å in 4) it is difficult to find a plausible simple explanation relying on the structural analysis of an isolated molecule in the ground state. It is known that the aurophilic contacts cannot be quantitatively correlated with emission wavelengths.^[11a, 32] The examples of 4·CH₂Cl₂ and 5 indicate that the presence of short Au. Au distances is not the only condition for the emergence of metal-centered luminescence, which is evidently influenced by the array of intraand intermolecular non-covalent interactions; the latter involve H^{\cdot}Hal hydrogen bonding and π -stacking. The importance of the crystal lattice on the photoinduced distortions in d¹⁰ metal clusters has been clearly shown by the combined experimental and computational studies.[33]

Upon cooling to 77 K complexes **1** and **4** demonstrate moderate bathochromic shift of emission bands (996 and 408 cm⁻¹, respectively), while **11** shows no alteration at all (Figure S6). The lifetimes for these complexes also undergo insignificant increase at low temperature and together with nearly invariable excitation spectra indicate that the nature of the emissive excited states remains unchanged in 77–298 K window (Table 1). Despite the emission of compound **2** at 77 K displays moderate gain in energy (964 cm⁻¹ blue shift), it probably arises from the stabilization of the ground state but not the change of the excited state, as indicated by 2559 cm⁻¹ hypsochromic shift of the excitation maximum and only a modest growth of the lifetime (from 5 to 15 μ s) that is typical for pure phosphorescence.^[34]

The last set of complexes with short metal-metal distances includes the bimetallic species **6** and **7**, which clearly exhibit temperature-switchable emission. At 298 K these compounds demonstrate yellow ($\lambda_{em} = 562 \text{ nm}$, **6**) or red phosphorescence ($\lambda_{em} = 663 \text{ nm}$, **7**) with characteristic lifetimes of few µs; the quantum efficiency reaches the magnitude of 0.54 for **7**. The latter shows the highest radiative rate constant ($k_r = 9.3 \times 10^4 \text{ s}^{-1}$) among the di-/tetranuclear complexes studied here that testifies to strong SOC operating in **7**.





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1.0 -Normalized intensity [a.u.] 0.8 -0.6 -400 500 600 700 800 0.4 0.2 00 600 700 800 900 300 400 500 Wavelength [nm]

Figure 4. Normalized solid state excitation (dotted lines) and emission (solid lines) spectra of complex 7 at 298 and 77 K; the inset shows VT emission spectra in the range of 180–116 K.

Crystalline 6 and 7, when immersed in liquid nitrogen, reveal a dramatic blue shift of emission, which amounts to 5750 cm⁻¹ for 7. Warming the samples to room temperature completely recovers the initial low energy (LE) luminescence (Figures 4 and S7). The variable temperature emission spectra of 6 and 7 demonstrate a gradual decrease of LE bands accompanied by the growth of high energy (HE) band at 450-480 nm upon cooling. The lifetimes of the HE emissions at 77 K (T = 1200 and 368 µs for 6 and 7, respectively) are orders of magnitude longer than those obtained at 298 K that manifests different excited states operating at low temperature and at ambient conditions. Somewhat distinguishable fine structure of the HE bands and the lifetimes comparable to those of 5, (Aul)₂BINAP and the related Xantphos-containing dinuclear congeners^[15] suggest the triplet intraligand (phosphane) origin of luminescence at 77 K. For both complexes 6 and 7 the isosbestic points are found in their VT emission spectra that is typical for the presence of two thermally equilibrated excited states.^[5c] This conclusion is also supported by the nearly identical excitation spectra, recorded at 77 K and 298 K for HE and LE bands (Figures 4 and S7).

Thus, it is reasonable to propose that the initial excitation $S_0 \rightarrow S_n$ of the title complexes is followed by the relaxation to the S_1 state, presumably of IL (phosphane) nature, which then undergoes fast intersystem crossing to the metal-perturbed ${}^3\pi\pi^*$ IL (T_2) state of the triplet manifold, possibly mixed with some XLCT character (Figure 5). At low temperature, the lack of thermal energy kTdoes not allow passing the barrier E_a that prevents populating the lowest energy T_1 state. The long lifetimes, associated with this intermediate T_2 excited state, indicate relatively weak SOC that correlates well with its ${}^3\pi\pi^*$ nature. The given assignment is additionally corroborated by ${}^3\pi\pi^*$ -luminophores **5** and [(Aul)₂BINAP]. Increasing the temperature depopulates the high energy T_2 level due to the transition of the system to the lowest lying T_1 state of (X+M)C origin (likely mixed with some XLCT).

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Figure 5. Proposed energy levels diagram of complex 7

The large Stokes shifts between the maxima of the excitation and emission bands (12694 and 16167 cm⁻¹ for **6** and **7**) require substantial structural distortions, which might occur in the excited states. For the di- and polynuclear d¹⁰ complexes such changes are often related to the shortening of the metal–metal contacts,^[33, 35] that seems to be a reasonable scenario for **6** and **7** too.

It is essential that significant involvement of the ligands orbital into the T_2 state and possible mixing with T_1 state in **6** and **7** potentially offers an appealing possibility of tuning the dual emission with respect to the wavelengths and energy barrier between the triplet excited states.

The presence of two thermally equilibrated triplet excited states with predominant ³IL and ³MMLCT origin producing the dual HE and LE emission has been reported for the dynamic diplatinum complexes,^[36] where the energy barrier was related to the structural changes dramatically altering metal–metal distances. In the case of **6** and **7** the exact nature of the barrier between the T_2 and T_1 , however, remains an open question. The examples of pronounced luminescence thermochromism, which can be treated in terms of two distinct excited states, has been described for a very limited number of gold(I) complexes,^{[11a, 11b, ^{11d, 14a]} including few dinuclear compounds with XantPhos ligand.^[14b, 15] For the latter case the large hypsochromic shift of the emission has been tentatively explained by the short Au^{...}Au contacts, which cannot contract further upon cooling.^[15]}

To check this hypothesis, we have carried out the VT XRD analysis of compounds **1**, **2**, **6** and **7**, the results of which are summarized in Table S2. The structural data, in particular the magnitude and the VT behaviour of Au^{...}Au distances in the ground state do not show any systematic influence on the photophysical properties of these materials. Thus, the gold–gold separation in thermochromic **6** at 298 K (2.984 Å) is shorter than that in **1** (3.019 Å), the emission of which does not switch at low temperature. In both cases, decreasing the temperature to 90 K (95 K for **6**) results in a very minor Au^{...}Au contraction (ca. 0.005 Å for **1** and 0.007 Å for **6**). For **7**, however, the Au^{...}Au shortening (0.04 Å) is more significant when the temperature is lowered from 270 K to 90 K. Moreover, the intermetallic contact

steadily decreases within the given temperature range (270 K: 3.035 Å; 170 K: 3.013 Å; 120 K: 3.001 Å; 90 K: 2.995 Å, Figure S8) even after the luminescence has already switched (i.e. below 120 K for **7**).

Apparently, this temperature-dependent optical functionality should be considered as a synergistic effect of the molecular structure and the crystal lattice, where the latter determines the non-covalent intramolecular interactions and the molecular conformations. Indeed, grinding the crystalline samples completely removes thermochromic properties of compounds **6** and **7** and makes them virtually non-emissive at room temperature; similar crystal-only behaviour has been described for imidazolate Au₃ phosphor.^[13] In addition, complex **7** does not show detectable LE luminescence in dmso solution both in liquid and frozen forms that confirms its crucial dependence on the presence of weak intra- (aurophilic) and intermolecular bonding, which get disrupted in fluid medium and in the ground amorphous state.

Complex 8 shows weak light blue luminescence at room temperature, but its substantial decomposition under irradiation prevented proper investigation. Photoemission characteristics of the mononuclear species 9 and 10 are reminiscent of those acquired earlier close for their analogues. [(AuSCN)(XantPhos)]^[15] and [(AuCN)(tpdp)],^[27] respectively (Figure S9). The large difference in emission energies between 9 (λ_{em} = 486 nm) and 10 (λ_{em} = 640 nm) evidently arises from unequal coordination numbers of gold(I) centers in these compounds that is in compliance to the literature data on trigonal and pseudo-tetrahedral Au species.[37] The excited states of 9 and 10 are tentatively associated with a mixture of XLCT (iodide \rightarrow phosphane) and intra-phosphane $\pi \rightarrow \pi^*$ charge transfer. In the case of 9 this assignment allows to rationalize blue shifted emission compared to [(AuSCN)(XantPhos)] (λ_{em} = 511 nm) due to the effect of X ligand. However, both 10 and [(AuCN)(tpdp)] emit at the same wavelength with very similar lifetimes (1.8 and 1.4 µs) that might result from a small contribution of XLCT (or L'LCT) transition into the emissive triplet states for these tetracoordinate complexes. Nevertheless, the X ligand has a non-innocent influence on luminescence efficiency as the iodide induces 3-fold increase of the radiative rate constant ($k_r = 1.5 \times 10^5 \text{ s}^{-1}$ for **10** vs $5.8 \times 10^4 \text{ s}^{-1}$ for [(AuCN)(tpdp)]) and consequently enhances by a factor of 4 the quantum yield of $10~(\Phi_{\text{em}}$ = 0.35) with respect to its cyanide congener ($\Phi_{em} = 0.08$).^[27] The radiative lifetime at 298 K for **10** $(r_r = 5.1 \ \mu s)$ is compatible with thermally activated delayed fluorescence behaviour, [38] which has been suggested earlier for [Au(dppb)(PS)] (PS 2complex а = diphenylphosphinobenzenethiolate)[37c] and thus cannot be excluded for 10, but still remains an extremely rare phenomenon for the gold(I)-containing compounds.[35d]

Conclusions

The range of multidentate phosphane ligands was employed to synthesize di- (1-7), mono- (8-10) and tetranuclear (11) gold iodide complexes, the majority of which exhibit close aurophilic

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Keywords: gold complexes • luminescence • thermochromism • aurophilicity • phosphane ligands

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contacts in the solid state, as confirmed by the results of crystallographic analysis. Their luminescence properties evidently reflect a cooperative influence of intramolecular features (metal-metal bonding, stereochemistry and electronic characteristics of the phosphanes) along with subtle but noninnocent intermolecular non-covalent interactions, predominantly governed by the crystal packing. Consequently, the emission energies for these compounds at room temperature cover a broad range of the visible spectrum from green (545 nm, 11) to near-IR (698 nm, 2). We hypothesize that this variation is determined by the different contributions of ³(X+M)-centered and ³XLCT transitions into the emissive excited states, which are eventually perturbed by the lattice-dependent intermolecular interactions. The presence of short Au-Au distances does not appear to be a necessary requirement to achieve efficient low energy phosphorescence as the pseudo-tetracoordinate mononuclear complex 10 exhibits emission maximum at 640 nm with guantum yield of 0.35. In line with previous findings,^[11a, 32] ground state metal-metal separations do not offer an unequivocally interpretable correlation with photophysical parameters obtained for the title complexes. Therefore, for an adequate description of the solid-state optical behavior of compounds featuring metallophilic interactions, it is necessary to consider their excited state properties preferably in a view of supramolecular arrangement in the crystal.^[13, 33] The crucial importance of the ordered solid matrix is demonstrated by the bimetallic luminophores 6 and 7, which reveal the presence of two coupled triplet excited states T_2 and T_1 of IL ${}^3\pi\pi^*$ and ³(X+M)C (mixed with ³XLCT) origin, respectively. Due to the energy barrier between the T_2 and T_1 , crystalline 6 and 7 exhibit high and low energy emissions with thermally variable intensities ratio. These excited states T_2 and T_1 are equilibrated at the temperatures above 170 K and lead to LE phosphorescence under the ambient conditions, while at 77 K a dramatic hypsochromic shift of the emission (up to 5750 cm⁻¹, 7) is detected. Such thermally induced switching highlights the significance of both individual molecular structure and the supramolecular lattice effects on the unconventional optical functionality of the given class of phosphors. Despite it is still difficult to rationalize and predict the exact relationships between molecular stereochemistry, crystal packing and the photophysical performance of this type of compounds, the results point to a promising potential of simple gold(I) phosphane-iodide complexes to serve as efficient and tunable temperature-responsive materials.

Experimental Section

Syntheses, details of X-ray structural determination and photophysical measurements are given in the supporting information.

CCDC 1586836-1586852 contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre. See the Supporting Information for experimental details.

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A delicate interplay of intramolecular features and subtle intermolecular interactions is capable to produce gold(I) complexes with distinct thermochromic luminescence, resulting from reversible switching between two coupled excited states.



Nina Glebko, Thuy Minh Dau, Alexei S. Melnikov, Elena V. Grachova, Igor V. Solovyev, Andrey Belyaev, Antti J. Karttunen*, Igor O. Koshevoy*

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Luminescence thermochromism of gold(I) phosphane-iodide complexes: a rule or an exception?