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COMMUNICATION

Mechano-induced reversible colour and luminescence switching of a gold(I)-diphosphine complex

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A gold(I)-diphosphine simultaneously exhibits reversible mechanochromism and mechanochromic luminescence. The mechanical grinding can trigger a transformation from a neutral mononuclear structure exhibiting white colour and blue photoluminescence to an ionic dinuclear structure with intramolecular aurophilic interaction exhibiting yellow colour and red emission.

Luminescent stimuli responsive materials has been extensively studied in the past few years.¹ A number of mechanochromic luminescent systems based on metal complexes that exhibit drastic luminescence colour change in response to mechanical forces such as grinding, shearing, pressure, etc. have been rapidly developed.² The solid-state luminescence strongly depends on molecular structure and molecular packing modes modulated by non-covalent interactions that are susceptible to external stimuli.^{1,2} Many gold(I) compounds have been found to respond to a range of stimuli such as temperature, mechanical force, solvent vapours or anions.³ In these systems, the luminescence changes is usually associated with the alteration of non-covalent interactions, such as aurophilic interactions, hydrogen bonding, $\pi\cdots\pi$ interactions, halogen bonding or originate from molecular conformation changes.³ However, there are only few reports on systems that exhibit dual-response, namely both colour and luminescence colour change to mechanical grinding.⁴ Such dual-response is exceptionally unusual among gold(I) compounds and has only been observed for a tetrahedral $[\text{Au}(\text{dppbz})_2](\text{BF}_4)$ (dppbz = 1,2-bis(diphenylphosphino) benzene) complex.^{4a} The mechanochromism and mechanochromic luminescence of this cationic gold(I) complex has been attributed to originate from molecular conformation changes induced by mechanical stimuli.^{4a} Despite the increasing number of reported stimuli-

sensitive luminescent compounds based on transition-metal complexes, the understanding of the mechanism involved in the mechanochromic and mechanochromic luminescent properties remains limited.⁵ This is mainly because of the difficulty in structural characterization of the amorphous materials obtained upon mechanical grinding.⁶

Recently, we reported some cationic gold(I)-diphosphine $[\text{Au}_2(\text{diphos})_2]^{2+}$ complexes (diphos = diphosphine) with short intramolecular aurophilic interaction that exhibit stimuli-responsive luminescence changes upon crystalline-to-amorphous phase transition.⁷ López-de-Luzuriaga, Naumov and coworkers reported the first example of a mechanochromic and mechanochromic luminescent gold-silver heterometallic complex that suffers a reversible ionic-to-neutral phase transition and polymerization through $\text{Au}\cdots\text{Au}$ interactions induced by mechanical stimuli.^{4b} We now report a neutral gold(I)-diphosphine that exhibit dual-response to mechanical stress and undergoes mechano-induced colour and luminescence colour changes as a consequence of neutral-to-ionic phase transition. To the best of our knowledge, this is a rare example of a metal compound that suffers mechano-induced colour and luminescence colour changes as a consequence of neutral-to-ionic phase transition.

We synthesized and characterized a mononuclear $\text{Au}(\text{nixantphos})(\text{SCN})$ complex (**1W**) of the 4,6-bis(diphenylphosphino)-phenoxazine (nixantphos) ligand that shows intriguing dual-response to mechanical stress. The mechanochemical anion-exchange of a yellow $[\text{Au}_2(\text{nixantphos})_2](\text{NO}_3)_2$ complex (**1N**)⁸ with NaSCN afforded a white powder of **1W**. The electronic absorption spectrum of a colourless dichloromethane solution of **1W** shows an absorption that increases toward shorter wavelengths (Figure 1). In contrast, the electronic absorption spectrum of a yellow-coloured methanol solution of **1W** is absolutely different from that measured in dichloromethane solution and shows an intense band at 310 nm (Figure 1). Based on previous studies, this intense band is assigned to the spin-allowed $5d\sigma^* \rightarrow 6p\sigma$ transition attributed to the presence of intramolecular aurophilic $\text{Au}\cdots\text{Au}$ interaction of dinuclear $[\text{Au}_2(\text{diphos})_2]^{2+}$

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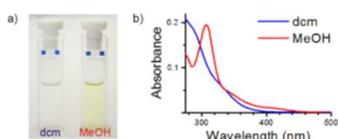


Figure 1. a) Dichloromethane and methanol solution **1W** crystals under ambient light and b) Electronic absorption spectra of **1W** crystals in methanol (red line) and dichloromethane (blue line) at room temperature.

complexes.⁹ Conductivity measurements show that ionic complexes exist in methanol solutions, whereas neutral complexes are present in dichloromethane (ESI⁺). The ³¹P NMR spectrum of **1W** crystals shows a narrower signal at 26.9 ppm and a broadened one at 30.7 ppm (Fig. S2a, ESI⁺), indicating two different phosphorous environments in CD₃OD solution. The narrower signal at 26.9 ppm is typical for mononuclear Au(diphos)(X) complexes,¹⁰ whereas the broadened resonance at 30.7 ppm is characteristic for dinuclear [Au₂(diphos)₂]²⁺ cations.^{8,10,11} This implies that the mononuclear neutral **1W** molecules are involved in associative equilibrium with their dinuclear ionic [Au₂(nixantphos)₂]²⁺ species. The ratio of mononuclear to dinuclear forms is 1:3, therefore, the dominant form is the dinuclear [Au₂(nixantphos)₂]²⁺ cation in CD₃OD solution at room temperature. In CD₂Cl₂, the intensity of the dimer resonance decreases significantly and three signals at 25.8, 21.0 and 2.1 ppm appeared in the spectrum (Fig. S2b, ESI⁺). ESI-MS spectra of **1W** demonstrated the predominance of doubly charged dimeric [Au₂(nixantphos)₂]²⁺ cations (*m/z* 748.5) in methanol, and [Au(nixantphos)]⁺ monomers (*m/z* 748.1) in dichloromethane (Fig. S3, ESI⁺). The ³¹P NMR, ESI-MS, electronic absorption spectra and conductivity measurements support the existence of dinuclear [Au₂(nixantphos)₂]²⁺ cations in yellow methanol solution. Recrystallization of the white solid of **1W** from an intense yellow methanol solution afforded colourless block crystals (Fig. S4, see ESI⁺). Single crystal X-ray diffraction of **1W** shows that the gold(I) centre is in trigonal-planar geometry, and it is coordinated to two phosphorous atom of the nixantphos and one sulphur atom of the thiocyanate ligand (Figure 2). The nixantphos ligand is chelated to the metal centre with a P1–Au1–P2 bite angle of 120.3(1)°. As shown in Figure 3, the crystal structure is composed of N–H...N hydrogen bonded (H1...N2 2.17(4) Å, N1...N2 2.98(1) Å and N1–H1...O angle 163(7)°) dimers of trigonal-planar **1W** molecules. These N–H...N hydrogen bonded dimers of **1W** molecules are loosely associated into pairs through Au...S contacts of 3.88 Å. In these pairs formed by two **1W** molecules belonging to neighbouring dimers, the Au...Au distance is 4.87 Å, the AuS...AuS unit is planar, and the Au–S...Au–S torsional angle is 0°.



Figure 2. Molecular structure of **1W**. Colour scheme: gold, yellow; phosphorous, orange; sulphur, yellowish green; carbon, grey; nitrogen, blue; oxygen, red; hydrogen, dark brown.

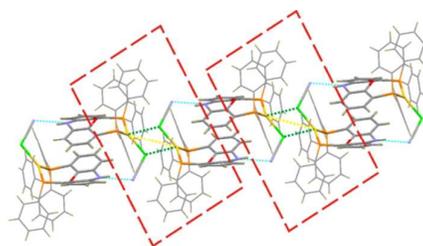


Figure 3. Crystal structure of **1W** depicting the arrangement of N–H...N hydrogen bonded (ice-blue dots) dimers and their association into pairs (represented by red dashed lines) through Au...S (green dots) and Au...Au (yellow dots) contacts. Colour scheme: gold, yellow; phosphorous, orange; sulphur, yellowish green; carbon, grey; nitrogen, blue; oxygen, red; hydrogen, dark brown.



Figure 4. Photograph of **1W** before and upon mechanical grinding and subsequent solvent treatment under: a) ambient light and b) 365 nm UV light.

Upon mechanical grinding, the sample of **1W** changed its colour from white to yellow (Figure 4a) and concomitantly alters its luminescence from blue to an intense red (Figure 4b). We used solid-state diffuse-reflectance ultraviolet visible spectroscopy (DRUVS) to study the changes in the mechanochromic behaviour of **1W**. Increase in the intensity of yellow colour of crystalline **1W** as a result of mechanical grinding for 0, 1, 2, 3, 4, 5, 7, 10, 13, 18, 25 and 30 minutes, was quantified by the Kubelka-Munk function. As shown in Figure 5a, a linear increase in the hyperchromic effect of the visible band at about 420 nm, the reflectance values reached a saturation limit with respect to the time of ball-milling. On the other hand, compound **1W** showed a significant red shift in the emission maximum during mechanical grinding (Figure 5b).

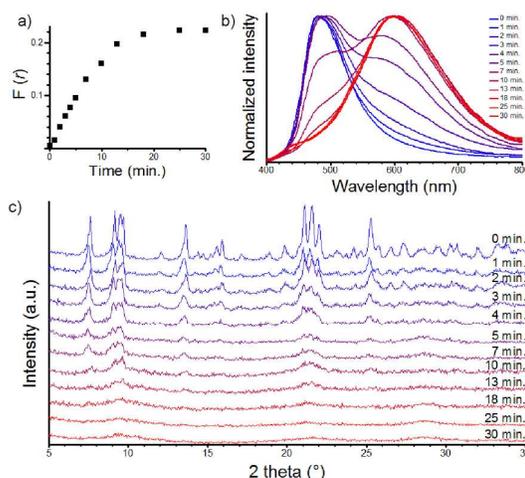


Figure 5. Grinding time-dependent a) Kubelka-Munk function $F(r)$ in diffuse-reflectance ultraviolet visible spectroscopy, b) Photoluminescence spectra and c) PXRD patterns recorded for **1W** before, and upon ball-milling.

The luminescence maximum was gradually red-shifted from 480 nm to 605 nm in response to mechanical grinding. PXRD experiments showed that as grinding time increases, the crystallinity decreases and after 13 min. of ball-milling X-ray amorphous compound was obtained (Figure 5c). Based on these findings it can be concluded that the decrease in the crystallinity is accompanied by an increase in the intensity of yellow colour and significant red shift in emission energy with respect to grinding time.

It is known that molecules can be activated by mechanical grinding treatment, and rearrangement of the molecules can occur even in the solid state.¹² The colour change from white to yellow suggests that the neutral **1W** to ionic **1Y** rearrangement can be triggered by mechanical stimuli in the solid-state. As noted already, the single crystal X-ray structural analysis revealed that hydrogen bonded dimers of **1W** are associated into pairs through Au...S and Au...Au contacts (Figure 3). It is worth mentioning that the Au...Au distance is only ca. 1.2 Å longer than the upper limit of the aurophilic bonding. This system therefore requires only minimal structural change to form aurophilic contact. Mechanical grinding by decreasing the spacing between the neutral molecules promotes the dimerization of the mononuclear neutral **1W** complexes. These significant solid-state structural changes produce shifts in the $\nu(\text{CN})$ stretching frequency of the SCN^- anion as well as changes in the solid-state UV-Vis spectra. After 18 minutes of grinding, the FTIR spectra (Figure 6a) show a significant decrease in the intensity of the absorption band at 2070 cm^{-1} , and the appearance of a new band at 2090 cm^{-1} . Based on previous studies,^{13a} this shift of the $\nu(\text{CN})$ stretching frequency to higher wavenumbers by 20 cm^{-1} indicates that the sulphur atom of the thiocyanate group is μ^2 -coordinated to two gold atoms. After further grinding (Figure 6a), the original $\nu(\text{CN})$ stretching frequency of coordinated SCN^- ligand at 2070 cm^{-1} disappeared, and a new peak corresponding to the presence of free uncoordinated SCN^- anion appears at 2050 cm^{-1} .^{13b} Dramatic changes in the N-H...N hydrogen bond system were also observed upon mechanical grinding, as the characteristic N-H stretching mode at 3255 cm^{-1} was shifted to lower frequency suggesting the strengthening of the corresponding hydrogen bond (Fig. S5, ESI[†]). The formation of the dinuclear cationic $[\text{Au}_2(\text{nixantphos})_2]^{2+}$ species in amorphous **1Y** was also ascertained by the solid state UV-Vis spectroscopy experiments. The reported dinuclear **1N** complex having short intramolecular Au...Au bond also has a yellow colour as it contains charged $[\text{Au}_2(\text{nixantphos})_2]^{2+}$ and NO_3^- species.⁸ Its solid-state UV-Vis spectrum exhibits a band at

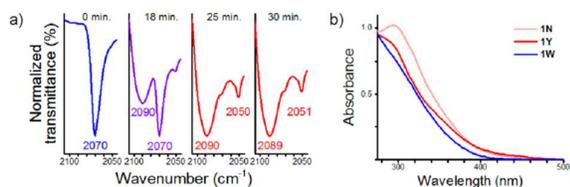


Figure 6. a) Grinding time-dependent FTIR spectra in the $2100\text{--}2050\text{ cm}^{-1}$ region and b) Solid state UV-Vis absorption spectra of **1W** (blue line), **1Y** (red line) and **1N** (light red line) complexes.

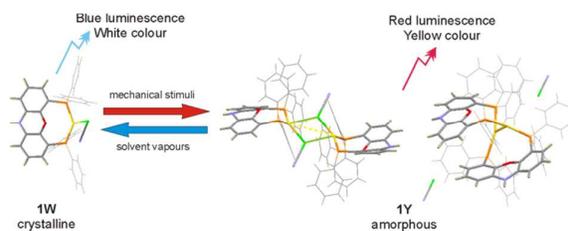


Figure 7. Schematic illustration of the structural transition of **1W** to **1Y** in the solid state.

310 nm attributed to intramolecular Au...Au interaction of dinuclear $[\text{Au}_2(\text{nixantphos})_2]^{2+}$ cation. The similarity between the solid-state UV-Vis spectrum of yellow coloured amorphous phase **1Y** with that of **1N** supports the view that dinuclear $[\text{Au}_2(\text{nixantphos})_2]^{2+}$ cations with Au...Au interaction were formed as a result of mechanical activation. Based on additional spectroscopic investigations we can conclude that the luminescence of **1Y** stems from the intramolecular aurophilic interaction, whereas the emission of **1W** originate from an intraligand type excited state (Fig. S8, for details see ESI[†]). The ^{31}P NMR of **1Y** showed that the dinuclear $[\text{Au}_2(\text{nixantphos})_2]^{2+}$ species are involved in dissociation equilibrium in CD_3OD (Fig. S6, ESI[†]). The ESI-MS spectrum of **1Y** clearly indicated the predominance of doubly charged dimeric $[\text{Au}_2(\text{nixantphos})_2]^{2+}$ cations ($m/z\ 748.5$) over $[\text{Au}(\text{nixantphos})]^+$ monomers ($m/z\ 748.1$) in methanol (Fig. S7, ESI[†]). The presence of free SCN^- ions in the FT-IR spectrum, the appearance of the 310 nm band attributed to intramolecular Au...Au interaction in the solid-state UV-VIS spectrum, as well as, the newly performed additional spectroscopic studies support the view that dinuclear $[\text{Au}_2(\text{nixantphos})_2]^{2+}$ cations were formed in the resulting yellow-coloured amorphous phase upon mechanical activation. Thus, we proposed that mechanical grinding not only promotes the activation of individual **1W** molecules by altering the mode of coordination of SCN^- ligands to form a $[\text{Au}(\text{nixantphos})(\mu^2\text{-SCN})]_2$ precursor for the subsequent solid-state dimerization, but also induces the rearrangement of activated molecules to form a new yellow-coloured amorphous solid state also comprising dimeric $[\text{Au}_2(\text{nixantphos})_2]^{2+}$ cations and SCN^- anions (Figure 7). It appears, thus, that the observed yellow colour of the amorphous **1Y** form is a consequence of ionic character of the charged $[\text{Au}_2(\text{nixantphos})_2]^{2+}(\text{SCN})_2$ dimers that result from rearrangement of neutral monomeric **1W** molecules induced by mechanical stress through neutral-to-ionic phase transition. Mechanically-induced neutral-to-ionic phase transitions accompanied by significant colour change have been observed for organic compounds.¹⁴ The tetrathiafulvalene (TTF) *p*-chloranil (CA) mixed-stack crystals undergo pressure-induced colour change from yellow to red as a consequence of neutral-to-ionic phase transition.^{14a,b} It is noteworthy that the TTF and CA molecules are alternately stacked in the neutral state, whereas, the TTF-CA molecules are dimerized in the ionic phase.^{14b}

The reverse amorphous-to-crystalline transformation accompanied by a colour change from yellow-to-white

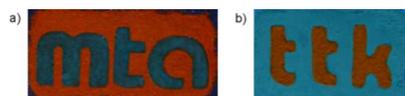


Figure 8. Luminescent patterns obtained by a) MeOH treatment on the surface of **1Y** film and b) pressing down with a spatula on the surface of **1W** film.

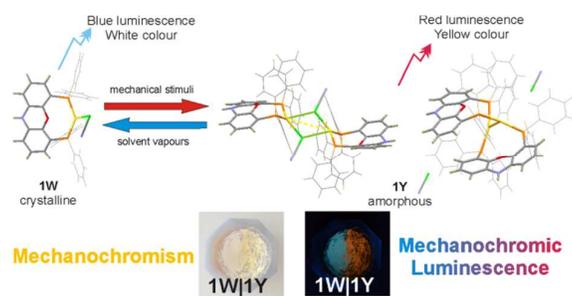
(vapochromism) and luminescence colour change from red-to-blue (vapochromic luminescence) took place upon exposure to solvent vapours. Thus, the original crystalline state of **1W** can be restored rapidly by treating the amorphous powder of **1Y** with a few drops of MeOH, as reflected by the switches in the PXRD and emission spectra (Fig. S9, ESI[†]). Exposure of **1Y** to vapours of MeOH also leads to quick colour and emission colour changes. The vapour-induced **1Y** to **1W** transition can be applied to writing of luminescent patterns with a home-made pen using MeOH as ink onto the surface of the **1Y** film by using a “mta” mask, as shown in Figure 8a. Alternatively, **1W** to **1Y** transition has been used to record the pattern of “ttk” by handwriting on a “paper” of **1W** using a spatula (Figure 8b). The mechano-induced colour and luminescence switching between neutral **1W** and ionic **1Y** forms has been repeated for multiple cycles (Table S2, ESI[†]).

In summary, we reported a neutral mononuclear gold(I)-diphosphine that simultaneously exhibits reversible mechanochromism and mechanochromic luminescence. To our knowledge, this is the first report on a stimuli-responsive gold(I) complex whose colour and emission colour switching are the result of a transformation between neutral mononuclear and ionic dinuclear structure with intramolecular aurophilic interaction. This is also the first example of a dual-responsive metal complex whose stimuli-induced optical property alterations could be attributed to a reversible neutral-to-ionic phase transition. This mechanism gives a new insight into the origin of mechanochromism and mechanochromic luminescence properties of metal complexes. The high colour contrast luminescence switching between blue and red makes such systems promising candidates for potential applications in luminescent switches, optical data recording, security papers and pressure sensors. The authors gratefully acknowledge the support by MTA (Hungarian Academy of Sciences) through the Lendület Programme (LP2012-21/2012).

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A gold(I)-diphosphine exhibits intriguing dual-response (mechanochromism and mechanochromic luminescence) to mechanical stress as a consequence of reversible neutral-to-ionic phase transition.