



BUDAPEST UNIVERSITY OF TECHNOLOGY AND ECONOMICS
FACULTY OF CHEMICAL AND BIOENGINEERING
GEORGE OLAH DOCTORAL SCHOOL

SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF METALLOSUPRAMOLECULAR SYSTEMS

Ph.D. Thesis

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1. INTRODUCTION AND LITERATURE BACKGROUND

Self-assembled gold(I) supramolecules having unusual structures and intriguing properties are in the focus of widespread research interest.¹⁻⁴ A large diversity of gold(I)-containing macrocycles, helicates, coordination polymers, clusters assembled tens or hundreds of atoms as well as heterometallic dicyanoaurate(I)-based supramolecules with intriguing structures and properties have been synthesized over the last few decades. Two-coordinate gold(I) complexes often associate through *aurophilic interactions* into more complex supramolecular structures.^{5,6} In addition to aurophilic interactions and metal–ligand dative bonds, hydrogen bonding and $\pi\cdots\pi$ stacking interactions also play an important role in specifying the unique molecular conformations and molecular packing in crystal structures.⁷ These relatively weak noncovalent interactions are often highly sensitive to external physical (thermal, optical, electrical, mechanical, etc.) or chemical (solvents, guests, anions, etc.) stimuli.^{8,9} The alteration of molecular structures and packing in response to external stimuli lead to dynamic changes in physical properties.^{8,9} This allows the synthesis of stimuli responsive functional material with specific properties.¹⁰⁻¹³

Heterometallic $\{M-NC-Au-CN\}$ supramolecular assemblies showing intriguing structural diversity often exhibit intriguing properties, such as magnetism,¹⁴⁻¹⁸ luminescence,¹⁹⁻²³ vapochromism,^{24,25} birefringence,^{22,26-29} negative thermal expansion^{30,31} and ion-exchange.³² The majority of *transition metal dicyanoaurates* are usually synthesized by simple mixing of the aqueous solutions of potassium dicyanoaurate(I) with stoichiometric amounts of transition metal salts. However, in the case of some transition metal(II) cations the aqueous solution syntheses leads to an inseparable mixture of dicyanoaurate-based heterometallic products and are often time consuming (lasting for several days).³³⁻³⁵

Mechanochemical reactions are conducted by grinding solid reactants together with no or minimal solvent in a mortar or in a ball mill.³⁶ Minimal amount of liquid present during *liquid-assisted mechanochemical reactions* can accelerate the reaction or can control the polymorph outcome of solid phase.³⁷⁻³⁹ Mechanochemical syntheses have been effectively used in the construction covalent and metal–ligand dative bonds, hydrogen-bonding and $\pi\cdots\pi$ stacking interactions.^{36-38,40} Such mechanochemical reactions have also been utilized in the construction of hydrogen-bonded host-guest molecular associations,^{41,42} cocrystals,^{43,44} crown ether complexes,⁴⁵⁻⁴⁷ mononuclear

complexes^{48–53} and coordination polymers,^{54–57} metallamacrocycles,⁵⁸ metal–organic framework with desired functional properties,^{59–62} as well as M–CN–M' cyanide-bridged *heterometallic systems*.^{63–65} Solid-state reaction methods for the synthesis of various dicyanoaurate-based heterometallic supramolecular systems have not been reported previously. On the basis of the above consideration, we aimed to develop an efficient and fast new mechanochemical method for the synthesis of *dicyanoaurate(I)-based heterometallic supramolecular systems*.

Gold(I) complexes typically show luminescent properties,^{3,4,66} which could be mainly influenced by aurophilic interactions. There are gold(I)-containing supramolecules that in response to thermal, mechanical and solvent vapour stimuli change their luminescence and show *thermochromic*,⁸ *mechanochromic*^{9,67,68} and *vapochromic luminescence*,^{69–72} respectively. To control and tune the luminescence properties of solid-state materials^{8,9,67,73–77} is essential to understand the relationship between molecular conformations, packing arrangements and photoluminescent properties. It is well-known that polymorphs (crystalline and/or amorphous) with different molecular conformations and/or packing arrangements often show different emission properties.^{8,76,77} Thus, the modification of noncovalent interactions, which govern the formation of molecular packing arrangements can be a tool to alter and fine-tune the solid-state luminescent properties. This, in turn, would allow the development of stimuli responsive luminescent materials whose emissions can be repeatedly switched between different emission colours by external stimuli.^{8,9,67,73–77} It should be mentioned that only two gold(I) complexes that exhibit *reversible mechanochromic luminescence* have been previously reported.^{78,79} However, molecular-level understanding of the mechanism of mechanically-induced reversible luminescence changes remains unclear.

The aim of our work is to study the design, synthesis and structural characterization of gold(I) complexes that exhibit reversible mechanochromic luminescence, as well as to investigate the underlying molecular mechanism, which could contribute to the in-depth understanding of the stimuli-responsive photoluminescence behaviour. These achievements could further provide new design strategies for the development of novel luminescent materials. Supramolecules that are able to *reversibly switch their luminescence in response to external stimuli* are of great interest owing to their potential use in various applications, including chemical sensors, memory, data storage, security inks.⁹

2. EXPERIMENTAL METHODS

Solid-state mechanochemical synthesis of dicyanoaurate-based heterometallic supramolecules were performed in a mortar with a pestle, while the mechanochemical anion-exchange reactions were performed by a shaker mill. All these reactions were monitored by FT-IR spectroscopy. Some of the as-synthesized new compounds were successfully crystallized and structurally characterized by single crystal X-ray diffraction. For further characterization of the new compounds, FT-IR spectroscopy, powder X-ray diffraction and elemental analysis were also applied. The solid-state luminescence of the as-synthesized compounds were studied by fluorescence spectroscopy.

3. RESULTS

The solid-state reactions of MCl_2 transition metal(II) chlorides ($M = Co, Ni, Cu$ and Zn) and $R_nSnCl_{(4-n)}$ ($R = Me, n = 2; R = Ph, n = 3$) organotin(IV) chlorides as well as $K[Au(CN)_2]$ have been studied. We have developed a new mechanochemical method that can be efficiently used to the synthesis of $KCo[Au(CN)_2]_3$ (**1**), $KNi[Au(CN)_2]_3$ (**2**), $Cu(H_2O)_2[Au(CN)_2]_2$ (**3**), $Zn[Au(CN)_2]_2$ (**4**), $Me_2Sn[Au(CN)_2]_2$ (**5**) and $Ph_3Sn[Au(CN)_2]$ (**6**) heterometallic dicyanoaurate-based complexes. By using this solid-state method, we can successfully synthesized **1**, whose solvent-based synthesis has never been reported before. The solid-state synthesis of **2** was completed only after 30 minutes, in striking contrast to its several days lasting solution-based synthesis. Moreover, the solvent-assisted solid-state synthesis of **5** was also finished only after 2 minutes of grinding. We have developed the solvent-assisted solid-state synthesis of an organotin(IV) dicyanoaurate **6**, which was structurally characterized by single crystal X-ray diffraction. We found that each $Ph_3Sn(IV)^+$ unit is linked to two others by two $[Au(CN)_2]^-$ bridges to form an infinite Au–CN–Sn cyanide-bridged chain (Figure 1). There are no $Au \cdots Au$ contacts between the chains due to the sterical hindrance of the phenyl groups.

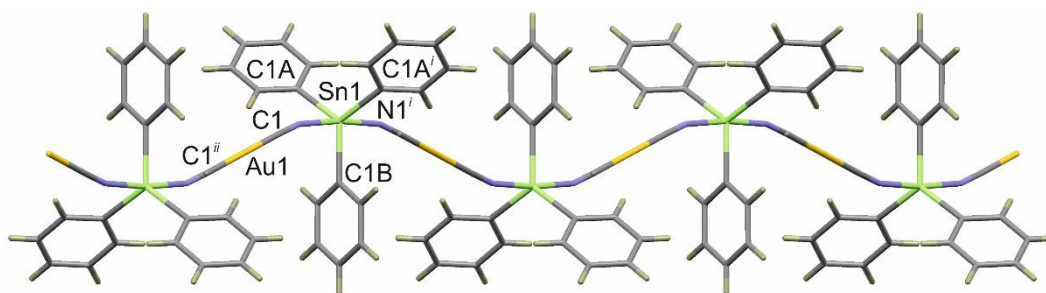


Figure 1. The crystal structure of **6**.

We investigated the metal-exchange properties of **5**, which is insoluble in water and organic solvents. We found that the $\text{Me}_2\text{Sn}^{2+}$ cations are exchanged with bivalent transition metal M^{2+} ($\text{M} = \text{Cu}, \text{Zn}, \text{Ni}$ and Co) cations, and **5** converted into corresponding **3**, **4** as well as $\text{Ni}(\text{H}_2\text{O})_2[\text{Au}(\text{CN})_2]_2$ (**8**) and $\text{Co}(\text{H}_2\text{O})_2[\text{Au}(\text{CN})_2]_2$ (**9**) complexes. These transition metal dicyanoaurates cannot be converted back into the starting compound **5**. The $\text{Me}_3\text{Sn}[\text{Au}(\text{CN})_2]$ (**7**) complex was also prepared according to a published procedure.³² We studied the gas sorption properties of all these **5–7** organotin(IV) dicyanoaurates. As it was revealed by the inspection of the N_2 , H_2 and O_2 isotherms, **6** and **7** complexes exhibited no detectable gas sorption. We found that the framework of **5** can however take up significant amounts of O_2 and CO , and only a small amount of N_2 and H_2 gases.

We also investigated the stimuli-responsive optical properties of these heterometallic dicyanoaurate-based supramolecules. The mechanochromic **9** complex exhibited a colour change from pale-pink to blue in response to mechanical grinding, during which the $\text{Co}[\text{Au}(\text{CN})_2]_2$ (**10**) complex was formed. This complex shows vapochromic responses upon exposure to the vapours of various volatile organic compounds (VOCs). As shown in Figure 2, pale-pink **10·S** ($\text{S} = \text{solvent}$) complexes were obtained upon exposure to the vapours of H_2O , MeOH , DMF , DMSO and py , whereas light-violet **10·S** complexes were formed in the presence of EtOH and THF vapours. Exposure to the vapours of NH_3 resulted in the formation of an ochre-coloured complex (Figure 2). All of these vapochromic responses are fully reversible, as these **10·S** complexes can be converted back by heating into **10**.

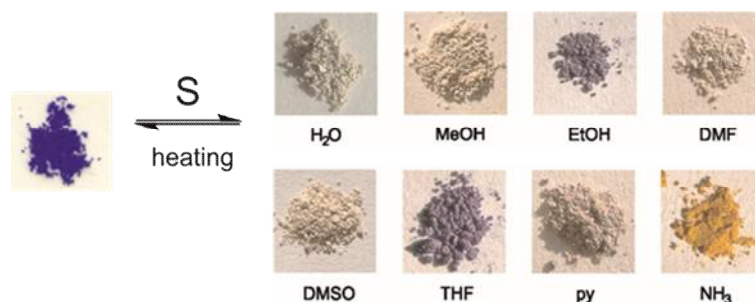


Figure 2. The reversible vapochromic colour change of **10** in response to various solvent vapours and subsequent heating.

The luminescent properties of these heterometallic dicyanoaurate-based supramolecules synthesized by mechanochemical methods have also been studied. We found that **1–3** and **8–10** transition metal(II) dicyanoaurates are not luminescent, while complex **4** shows a blue emission, consistent with the previous results.²⁵ We have shown that organotin(IV) dicyanoaurate **5** containing aurophilic interactions³² displays a blue ($\lambda_{\text{max}} = 422$ nm) emission, while **6** lacking significant Au \cdots Au contacts is not luminescent under UV irradiation. In complex **7**, the organotin(IV) dicyanoaurate chains are held together by aurophilic interactions to form a 3D supramolecular structure.³² Accordingly, its emission spectrum shows two intense ($\lambda_{\text{max}} = 442$ and 720 nm), and a weak ($\lambda_{\text{max}} = 380$ nm) emission bands. Moreover, complex **7** exhibit intriguing mechanochromic luminescence, as its orange emission turns blue ($\lambda_{\text{max}} = 444$ nm), even under a very slight mechanical stress (Figure 3).

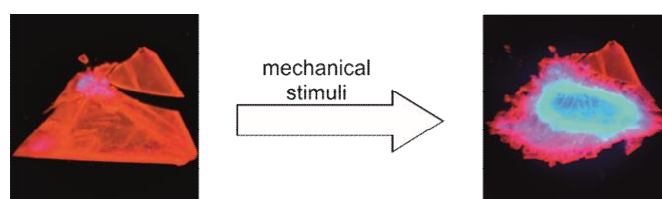


Figure 3. The mechanochromic luminescent colour change of **7** ($\lambda_{\text{ex}} = 365$ nm).

The crystal and solution structures of chiral double-stranded dinuclear $[\text{Au}_2(\text{xantphos})_2](\text{NO}_3)_2$ (**11**) helicate were previously reported by our research group.^{80,81} We performed systematic studies to synthesize various crystalline and amorphous forms of complex **11** and study their luminescence properties. By slight modification of the crystallization conditions blue *k*-**11** ($\lambda_{\text{max}} = 490$ nm), bluish-green *z*-**11** ($\lambda_{\text{max}} = 520$ nm) and yellow *s*-**11** ($\lambda_{\text{max}} = 570$ nm) emitting crystalline and red emitting *n*-**11** ($\lambda_{\text{max}} = 685$ nm) amorphous forms were obtained. The *k*-**11**, *z*-**11** and *s*-

11 crystalline phases were structurally characterized by single crystal X-ray diffraction. This provided a unique opportunity to study the effect of molecular conformations, packing arrangements and non-covalent interactions on solid-state luminescence properties. In these crystalline forms, the two Au(I) centres of $[\text{Au}_2(\text{xantphos})_2]^{2+}$ helicate are held together by aurophilic interactions of 2.838 Å (**k-11**), 2.863 Å (**z-11**) and 2.841 Å (**s-11**), respectively. The bulkiness of the xantphos ligand prevents the formation of intermolecular Au \cdots Au contacts between the $[\text{Au}_2(\text{xantphos})_2]^{2+}$ helicates, hence the molecular packing is primarily governed by $\pi\cdots\pi$ interactions. The $[\text{Au}_2(\text{xantphos})_2]^{2+}$ helicates are packed into a head-to-tail fashion to form a columnar stacks in the blue emitting **k-11** crystal (Figure 4a). In the bluish-green luminescent **z-11** crystal, the dinuclear $[\text{Au}_2(\text{xantphos})_2]^{2+}$ units are arranged into dimers showing a brick-wall packing pattern (Figure 4b), while they form helical chains in the yellow emitting **s-11** crystal (Figure 4c.). These motifs held together by $\pi\cdots\pi$ interactions build up the crystal lattice through additional $\pi\cdots\pi$ interactions.

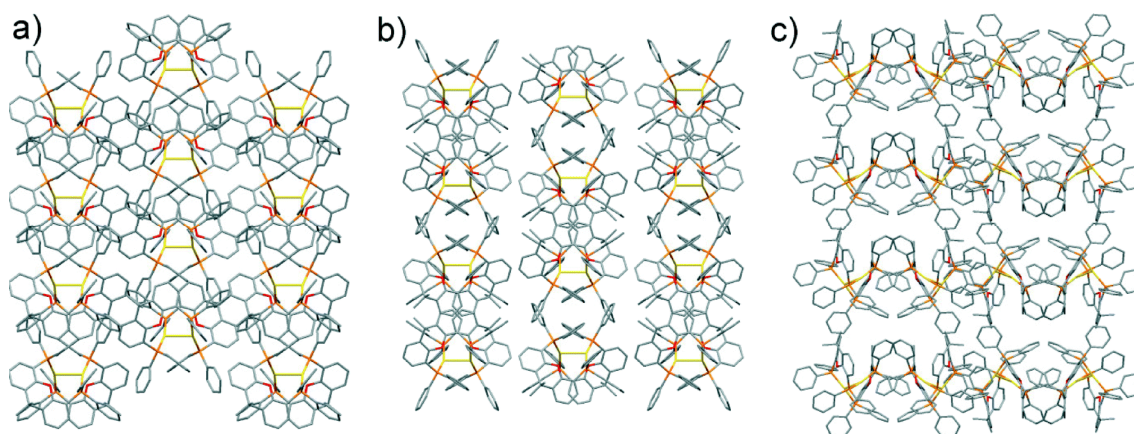


Figure 4. The arrangement of $[\text{Au}_2(\text{xantphos})_2]^{2+}$ helicates in the crystal structures of a) **k-11**, b) **z-11** and c) **s-11**, respectively. The hydrogen atoms and the non-coordinating NO_3^- anions were omitted for clarity.

We elaborated a *liquid-assisted mechanochemical method*, which was suitable for anion-exchange of the **11** and thus, for the synthesis of new $[\text{Au}_2(\text{xantphos})_2](\text{X})_2$ complexes. Using this liquid-assisted mechanochemical method, we obtained both the crystalline and amorphous phases of the $[\text{Au}_2(\text{xantphos})_2](\text{BF}_4)_2$ (**12**) complex. We have shown that the nature of the grinding liquid (dichloromethane *versus* water) governs the formation of diverse phases (crystalline *versus* amorphous). The dichloromethane assisted mechanochemical reaction afforded the crystalline **k-12**, while the water assisted method yielded the amorphous **n-12** compound. The **k-12**

crystalline phase displays blue emission ($\lambda_{\text{max}} = 457 \text{ nm}$), while the ***n*-12** amorphous phase displays orange emission ($\lambda_{\text{max}} = 685 \text{ nm}$). The amorphous phases of **11** and **12** complexes show distinctly different luminescence colours than they crystalline counterparts, thus these complexes exhibit phase-dependent luminescence properties. The stimuli-responsive luminescent properties of crystalline and amorphous dinuclear **11** and **12** complexes have also been investigated. We found that the blue luminescence of crystalline ***k*-11** phase changed in response to mechanical stimuli, and an orange-red-emitting ***n_m*-11** amorphous phase was obtained, which in response to dichloromethane vapour converted back into the original crystalline ***k*-11** form (Figure 5).

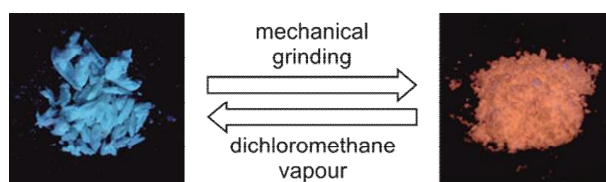


Figure 5. The reversible mechanochromic luminescence of ***k*-11** form.

The water-assisted mechanical grinding of the crystalline blue luminescent ***k*-12** phase afforded the amorphous orange-red emitting ***n_m*-12** form, which in turn converted back with dichloromethane-assisted milling to the starting ***k*-12** phase. These reversible mechanochromic luminescent systems exhibit 200 nm (**11**) and 235 nm (**12**) reversible shift in emission maxima, which are unprecedentedly large among mechanochromic luminescent compounds. We have shown that the luminescence of these ***k*-11** and ***k*-12** complexes can be reversibly switched between different emission colours by mechanical grinding or solvent vapour induced CTA|ATC phase transformations.

4. THESESES

1. We have developed a new mechanochemical method that can be effectively used in the synthesis of $\text{KCo}[\text{Au}(\text{CN})_2]_3$ (**1**), $\text{KNi}[\text{Au}(\text{CN})_2]_3$ (**2**), $\text{Cu}(\text{H}_2\text{O})_2[\text{Au}(\text{CN})_2]_2$ (**3**), $\text{Zn}[\text{Au}(\text{CN})_2]_2$ (**4**), $\text{Me}_2\text{Sn}[\text{Au}(\text{CN})_2]_2$ (**5**) and $\text{Ph}_3\text{Sn}[\text{Au}(\text{CN})_2]$ (**6**) heterometallic dicyanoaurate(I)-based supramolecular complexes. We have structurally characterized by single crystal X-ray diffraction the novel **6** complex, previously unknown in the literature.[1]

2. It has been demonstrated that the optical properties of the heterometallic dicyanoaurate(I)-based supramolecular complexes can be modified by external stimuli: the $\text{Me}_3\text{Sn}[\text{Au}(\text{CN})_2]$ (**7**) shows mechanochromic luminescent, the $\text{Co}(\text{H}_2\text{O})_2[\text{Au}(\text{CN})_2]_2$ (**9**) exhibits reversible mechanochromic, while the $\text{Co}[\text{Au}(\text{CN})_2]_2$ (**10**) displays reversible vapochromic properties.[1, 2]

3. Blue (**k-11**), bluish-green (**z-11**), and yellow (**s-11**) emitting crystalline and orange-red emitting (**n-11**) amorphous phases of the dinuclear double-stranded $[\text{Au}_2(\text{xantphos})_2](\text{NO}_3)_2$ (**11**) helicate were obtained by slight modification of the crystallization conditions. We have structurally characterized by single crystal X-ray diffraction the crystalline **k-11**, **z-11** and **s-11** forms. We have found that the $[\text{Au}_2(\text{xantphos})_2]^{2+}$ helicates are arranged into a head-to-tail fashion to form columnar stacks in the blue emitting **k-11** crystal. The $[\text{Au}_2(\text{xantphos})_2]^{2+}$ helicates form dimers showing a brick-wall packing pattern in the bluish-green luminescent **z-11** crystal, whereas helical chains are present in the yellow emitting **s-11** crystal. There are no intermolecular $\text{Au}\cdots\text{Au}$ contacts between the $[\text{Au}_2(\text{xantphos})_2]^{2+}$ helicates, hence the molecular packing is primarily governed by $\pi\cdots\pi$ interactions.[3]

4. We have developed a new liquid-assisted mechanochemical method for the anion-exchange of **11**, which afforded the $[\text{Au}_2(\text{xantphos})_2](\text{BF}_4)_2$ (**12**) helicate. We have elaborated a method, that depending on the nature of the grinding liquid (dichloromethane versus water), provided different solid phases (crystalline versus amorphous) of the resulting novel materials.[4]

5. We have shown that the **11** and **12** helicates exhibit phase-dependent luminescence behaviour. The 200 nm (**11**) and 235 nm (**12**) reversible shifts in emission maxima upon mechanical grinding, are unprecedentedly large among mechanochromic luminescent compounds. We have also shown that the luminescence of these **k-11** and **k-12** helicates can be reversibly switched between different emission colours by mechanical grinding and solvent vapour induced CTA|ATC phase transformations.[3, 4]

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6. PUBLICATIONS

6.1. Publications related to the PhD thesis

1. A Versatile Solvent-Free Mechanochemical Route to the Synthesis of Heterometallic Dicyanoaurate-Based Coordination Polymers
Cs. Jobbágy, T. Tunyogi, G. Pálinkás, A. Deák
Inorg. Chem., **2011**, *50*, 7301-7308. (IF: 4,601; FI: 13)
2. Cyanide-bridged bimetallic multidimensional structures derived from organotin(IV) and dicyanoaurate building blocks: ion exchange, luminescence, and gas sorption properties
A. Deák, T. Tunyogi, Cs. Jobbágy, Z. Károly, P. Baranyai, G. Pálinkás
Gold Bull. **2012**, *45*, 35-41. (IF: 2,434; FI: 3)
3. A stimuli-responsive double-stranded digold(I) helicate
Cs. Jobbágy, M. Molnár, P. Baranyai, A. Hamza, G. Pálinkás, A. Deák
CrystEngComm, **2014**, *16*, 3192-3202. (IF: 4,034; FI: 10)
4. Mechanochemical synthesis of crystalline and amorphous digold(I) helicates exhibiting anion- and phase-switchable luminescence properties
Cs. Jobbágy, M. Molnár, P. Baranyai, A. Deák
Dalton Trans., **2014**, *43*, 11807-11810. (IF: 4,197; FI: 6)

6.2. Other publications

5. Stimuli-Responsive Dynamic Gold Complexes
Cs. Jobbágy, A. Deák
Eur. J. Inorg. Chem., **2014**, 4434-4449. (IF: 2.942)
6. Anion-, Solvent-, Temperature-, and Mechano-Responsive Photoluminescence in Gold(I) Diphosphine-Based Dimers
A. Deák, Cs. Jobbágy, G. Marsi, M. Molnár, Z. Szakács, P. Baranyai
Chem. Eur. J., **2015**, *21*, 11495-11508. (IF: 5.771)

7. Mechano-induced reversible colour and luminescence switching of a gold(I)-diphosphine complex
P. Baranyai, G. Marsi, Cs. Jobbágy, A. Domján, L. Oláh, A. Deák
Dalton Trans., **2015**, *44*, 13455-13459. (IF: 4.177)
8. Structural characterization of dinuclear gold(I) diphosphine complexes with anion-triggered luminescence
P. Baranyai, G. Marsi, A. Hamza, Cs. Jobbágy, A. Deák
Struct. Chem., **2015**, *26*, 1377-1387. (IF: 1.854)
9. Unexpected formation of a fused double cycle trinuclear gold(I) complex supported by ortho-phenyl metallated aryl-diphosphine ligands and strong aurophilic interactions
Cs. Jobbágy, P. Baranyai, P. Szabó, T. Holczbauer, B. Rácz, L. Li, P. Naumov, A. Deák
Dalton Trans., **2016**, *45*, 12569-12575. (IF: 4.177)
10. Novel gold(I) diphosphine-based dimers with aurophilicity triggered multistimuli light-emitting properties
Cs. Jobbágy, P. Baranyai, G. Marsi, B. Rácz, L. Li, P. Naumov, A. Deák
J. Mater. Chem. C., **2016**, *4*, 10253-10264. (IF: 5.066)

6.3 Presentations:

1. Oldószermentes mechanokémiai eljárás többfemes arany(I)cianidok előállítására
Jobbágy Csaba, Tunyogi Tünde, Deák Andrea
Kálmán Erika Doktori Konferencia, 2011. május 26-27., Budapest, *Előadás*
2. Synthesis and X-ray structural characterization of 1:2 and 2:2 gold(I)-diphosphine complexes. Novel 1:2 and 2:2 gold(I)-diphosphine complexes
Deák Andrea, Tunyogi Tünde, Jobbágy Csaba and Pálincás Gábor
4th European Conference on Chemistry for Life Sciences, 2011. augusztus 31-szeptember 3., Budapest, *Poszter*

3. Külső hatásokra lumineszcens színváltozással „válaszoló” arany(I)tartalmú makrociklus
Jobbágy Csaba, Molnár Miklós, Baranyai Péter, Deák Andrea
Kutatóközponti Tudományos Napok, 2012. november 27-29., Budapest, *Előadás*

4. Solvent-Free Synthesis of Heterometallic Dicyanoaurate-Based Coordination Polymers
Jobbágy Csaba, Molnár Miklós, Deák Andrea
Coordination Chemistry Conference 2013, 2013. december 5-9., Playa del Carmen, Mexikó, *Poszter*

5. Hangolható lumineszcens tulajdonságú arany(I) helikátok
Jobbágy Csaba
Szerves Kémiai Szemináriumok, 2015. október 9., MTA TTK, Budapest, *Előadás*