ChemComm

A Non-Luminescent Polymorph of [(Cyclohexyl Isocyanide)2Au]PF6 that Becomes Luminescent Upon Grinding or Exposure to Dichloromethane Vapor

Journal:	*ChemComm*
Manuscript ID	CC-COM-09-2020-006161.R2
Article Type:	Communication

Journal Name

COMMUNICATION

A Non-Luminescent Polymorph of [(Cyclohexyl Isocyanide)$_2$Au]PF$_6$ that Becomes Luminescent Upon Grinding or Exposure to Dichloromethane Vapor

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

rsc.li/chemcomm

Lucy M. C. Luong, Marilyn M. Olmstead, Alan L. Balch *

The discovery of a third, non-luminescent crystalline polymorph of [(C$_6$H$_{11}$NC)$_2$Au]PF$_6$ is reported. Remarkably, crystals of this polymorph are sensitive to mechanical pressure or to exposure to dichloromethane vapor. In both cases, the conversion produces the yellow, green luminescent polymorph of [(C$_6$H$_{11}$NC)$_2$Au]PF$_6$ and not the colorless, blue luminescent polymorph.

Polymorphic crystals contain the same moieties in different crystallographic organizations.[1] Variations in molecular arrangements can alter the physical properties of the crystalline solid. The behaviors of polymorphs are important in the pharmaceutical industry, where the differences in crystals can influence critical issues of solubility, stability and bioactivity.[2,3] The formation of polymorphs is also important in determining the physical properties of energetic materials[4] and in electronic materials.[5,6,7] Transformations between polymorphs can also lead to the development of novel optical materials and materials suitable for sensing.[8,9]

Gold(I) complexes frequently aggregate in the solid state through weak aurophilic interactions that are readily modified when polymorphs form.[10] Luminescent gold(I) complexes exhibit transformations between polymorphs that are initiated by changes in the surrounding vapor, pressure or temperature as shown in the following examples.[11] Crystals of α-Au$_2$(μ-Ph$_2$PCH$_2$CH$_2$PPh$_2$)$_2$I$_2$·2OCMe$_2$ (1) with orange luminescence and a Au···Au separation of 3.6720(2) Å and β-Au$_2$(μ-Ph$_2$PCH$_2$CH$_2$PPh$_2$)$_2$I$_2$·2OCMe$_2$ (2) with a green luminescence and Au···Au separation of 3.3955(2) Å are interconverted through contact with acetone vapor, although both have the same composition and acetone content.[12] Crystallization of phenyl(phenyl isocyanide)gold(I) produces a blue luminescent form with its shortest Au···Au contact of 5.733 Å and a yellow luminescent form with a closer contact of 3.177 Å. Upon application of pressure, the blue luminescent form is transformed into the yellow luminescent form.[13] The colorless salt, [μ$_3$-S(AuCNC$_7$H$_{13}$)$_3$](SbF$_6$), which displays red luminescence (emission maximum 667 nm) and crystallizes with three close Au···Au contacts between pairs of cations, undergoes a phase change upon cooling that alters the luminescence (emission maxima at 490 and 680 nm) and results in expansion of the Au···Au contacts in one pair of dimers and a contraction of the Au···Au contacts in the other dimer.[14]

Previous work has shown that the two-coordinate gold(I) complex [(C$_6$H$_{11}$NC)$_2$Au](PF$_6$) can crystalize as two luminescent polymorphs: green luminescent [(C$_6$H$_{11}$NC)$_2$Au]PF$_6$ (**1**), which appears as yellow crystals in ambient light, and blue luminescent [(C$_6$H$_{11}$NC)$_2$Au]PF$_6$ (**2**), which occurs as colorless crystals under room light.[15] In green luminescent [(C$_6$H$_{11}$NC)$_2$Au]PF$_6$ (**1**), the cations form kinked chains with four cation in the asymmetric unit and short Au•••Au contacts of 2.9803(6), 2.9790(6), 2.9651(6), and 2.9643(6) Å. In blue luminescent [(C$_6$H$_{11}$NC)$_2$Au]PF$_6$ (**2**), the cations again self-associate into linear columns with two half cations in the asymmetric unit with an Au•••Au separation of 3.1822(3) Å. The close approach of the cations is responsible for the luminescence since solutions of either polymorph are colorless and non-luminescent.

Crystals of blue luminescent [(C$_6$H$_{11}$NC)$_2$Au]PF$_6$ (**2**) can be obtained by crystallization of either polymorph from hot 1-propanol. Both polymorphs crystallize concomitantly from a mixture of dichloromethane as solvent and diethyl ether as anti-solvent.[16,17] When a gradient of these two solvents is used, blue luminescent [(C$_6$H$_{11}$NC)$_2$Au]PF$_6$ (**2**) forms in the dichloromethane-rich region, while green luminescent [(C$_6$H$_{11}$NC)$_2$Au]PF$_6$ (**1**) crystallizes in the diethyl ether-rich region. Below we document our recent discovery of a third polymorph of [(C$_6$H$_{11}$NC)$_2$Au]PF$_6$, which is not luminescent. This polymorph can be selectively transformed into green luminescent [(C$_6$H$_{11}$NC)$_2$Au]PF$_6$ (**1**) by either mechanical pressure or dichloromethane vapour and is the first example of such a crystal that is simultaneously responsive to these two different stimuli to form a common product.

Colorless crystals of the non-luminescent [(C$_6$H$_{11}$NC)$_2$Au]PF$_6$ (**3**) were obtained by layering diethyl ether over a benzene solution of [(C$_6$H$_{11}$NC)$_2$Au]PF$_6$ and storing the mixture at 5-10 °C for three weeks. This polymorph crystallizes in the monoclinic space group, *C*2/*c*. The asymmetric unit consists of one half of a cation and

[a] *Department of Chemistry, University of California, Davis, California, USA.*

E-mail: albalch@ucdavis.edu; Fax: +1 530 752 2820; Tel: +1 530 752 0941

Electronic Supplementary Information (ESI) available: Crystal data, CCDC 2031599. See DOI: 10.1039/x0xx00000x one half of an anion. The gold ion resides on a two-fold axis while the phosphorus is situated on a center of symmetry. As expected, the two-coordinate cation has nearly linear coordination with a C1-Au1-C1' angle of 177.90(11)° as seen at the top of Figure 1. As the drawing shows, the isocyanide groups are in an axial position with respect to the cyclohexane ring. Fig. 1 also shows the packing of the anions within the unit cell. Unlike the situation in the two luminescent polymorphs of $[(C_6H_{11}NC)_2Au]PF_6$, the cations in non-luminescent $[(C_6H_{11}NC)_2Au]PF_6$ (**3** are widely dispersed. The shortest distance between two gold ions is 7.985 Å. Thus, there are no aurophilic interactions in this polymorph and it is non-luminescent. Note that $[(CH_3NC)_2Au](PF_6)$, which also lacks close contacts between the gold ions, is also non-luminescent.[15]

Upon grinding with a glass rod, crystals of non-luminescent $[(C_6H_{11}NC)_2Au]PF_6$ (**3**) become luminescent as shown in Fig. 2. The excitation and emission spectra of a ground sample of non-luminescent $[(C_6H_{11}NC)_2Au]PF_6$ (**3**) taken at room temperature and at 90 K are shown in Fig. 3. These emission spectra match the emission spectra of the green luminescent $[(C_6H_{11}NC)_2Au]PF_6$ (**1**), which shows emission maxima at 481 at room temperature and at 509 and 554 nm at 90 K as seen in parts (c) and (d) of Fig. 3. In contrast, blue luminescent $[(C_6H_{11}NC)_2Au]PF_6$ (**2**) shows an emission maximum at 425 nm at room temperature and at 442 nm at 90 K (*vide infra*). Thus, we conclude that the mechanochromic process leads exclusively to the transformation of non-luminescent $[(C_6H_{11}NC)_2Au]PF_6$ (**3**) to green luminescent $[(C_6H_{11}NC)_2Au]PF_6$ (**1**).

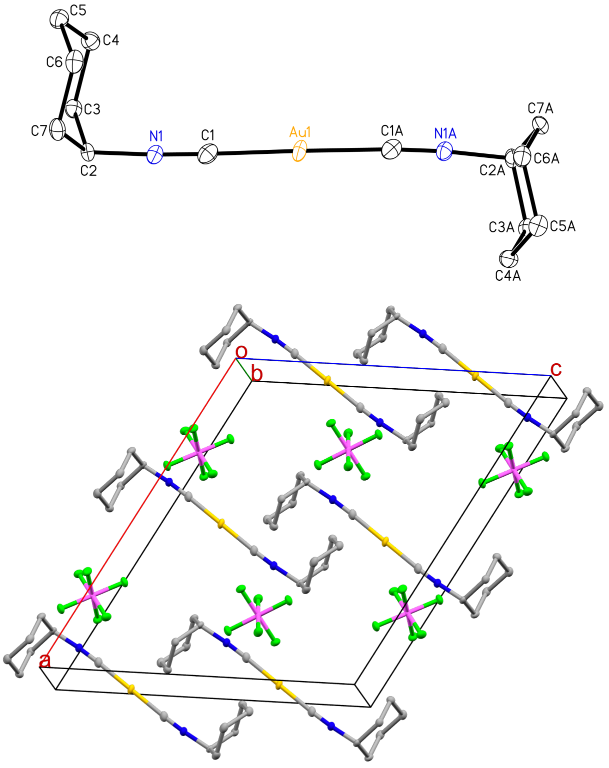


Fig. 1 Top, the structure of the cation in non-luminescent $[(C_6H_{11}NC)_2Au]PF_6$ (**3**). Bottom, crystal packing structure of the non-luminescent $[(C_6H_{11}NC)_2Au]PF_6$ (**3**) showing the lack of aurophilic interactions. The closest Au(I)-Au(I) contact is 7.985 Å. Atom colors: gold, yellow; carbon, grey; nitrogen, blue; phosphorus, violet; fluorine, green.

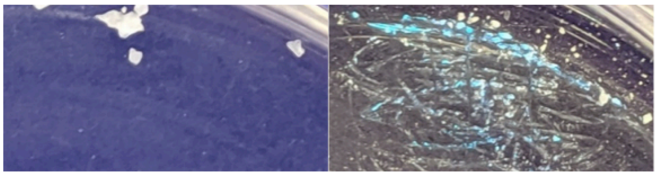


Fig. 2 Left, a photograph, taken under ambient light, showing colorless crystals of the non-luminescent $[(C_6H_{11}NC)_2Au]PF_6$ (**3**). Right, a photograph, taken under UV light, showing the luminescence of the crystals of (**3**) after they were ground using a glass stir rod.

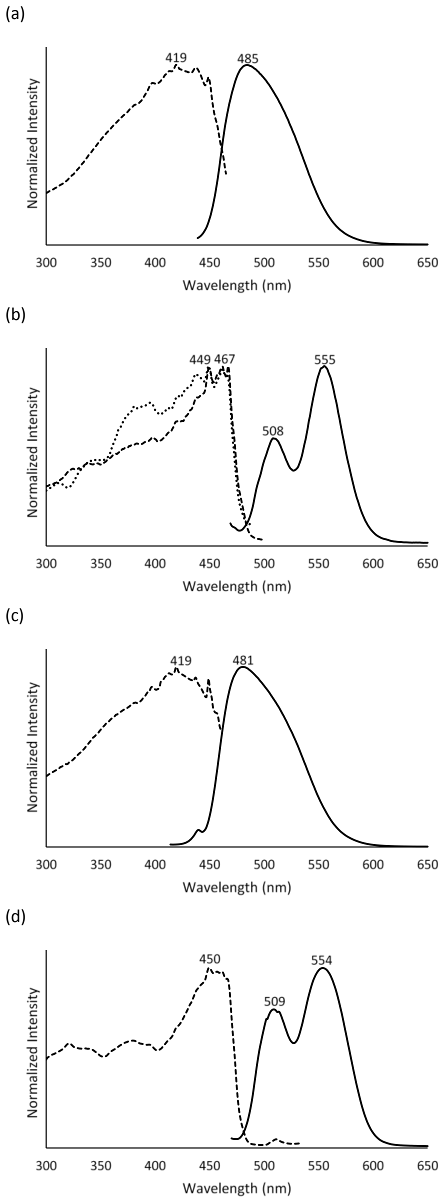


Fig. 3 The luminescence spectra of non-luminescent $[(C_6H_{11}NC)_2Au]PF_6$ (**3**) after grinding (final color and luminescence: yellow and green, respectively). (a) Excitation (dashed) and emission (solid) spectra at 298 K. (b) Excitation (dotted) and emission (solid) spectra at 77 K. These spectra are consistent with the formation of green luminescent $[(C_6H_{11}NC)_2Au]PF_6$ (**1**) upon grinding. The excitation (dashed) and emission (solid) spectra of green luminescent $[(C_6H_{11}NC)_2Au]PF_6$ (**1**) are shown in (c) at 298 K and (d) at 77 K.

Additionally, crystals of non-luminescent $[(C_6H_{11}NC)_2Au]PF_6$ (**3**) become yellow and display green luminescence when exposed to dichloromethane vapor. Fig. 4 shows the emission and excitation spectra of a sample of non-luminescent $[(C_6H_{11}NC)_2Au]PF_6$ (**3**) that was exposed to dichoromethane vapour over a five minute period. The spectra closely resemble those obtained by grinding (**3**), which are shown in Fig. 3 and the spectra obtained from green luminescent $[(C_6H_{11}NC)_2Au]PF_6$ (**1**) also shown in Fig. 3.

When the sample used to obtain the data in Fig. 4 was re-exposed to a higher concentration of dichloromethane vapour over a ten minute period, a second transformation occurred, which resulted in the formation of blue luminescent crystals that produced the emission and excitation spectra shown in Fig. 5. Traces (a) and (b) show the excitation and emission spectra at room temperature and 90 K respectively. Traces (c) and (d) show the excitation and emission spectra at room temperature and 90 K respectively for an authentic sample of blue luminescent $[(C_6H_{11}NC)_2Au]PF_6$ (**2**). These data indicate that blue luminescent $[(C_6H_{11}NC)_2Au]PF_6$ (**2**) is produced upon prolonged exposure of a sample of non-luminescent $[(C_6H_{11}NC)_2Au]PF_6$ (**3**) to dichloromethane vapor.

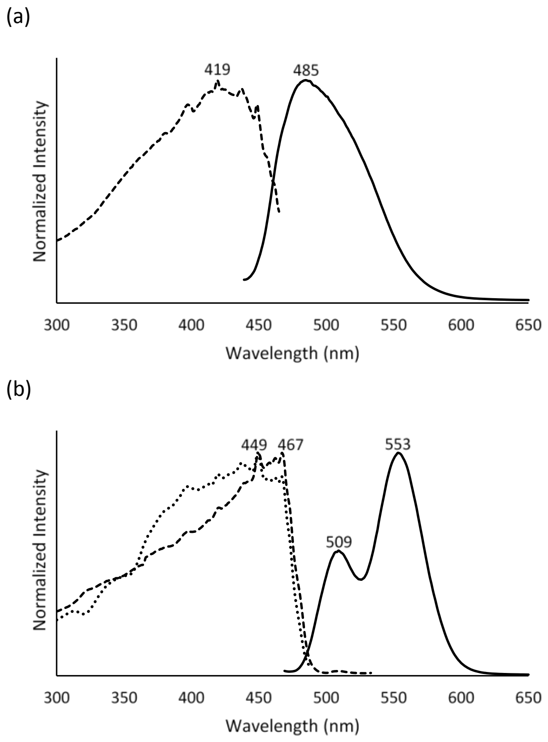


Fig. 4 The luminescence spectra of non-luminescent $[(C_6H_{11}NC)_2Au]PF_6$ (**3**) after exposure to dichloromethane vapor (final color and luminescence yellow and green, respectively). The excitation (dashed) at 485 nm and emission (solid) at 419 nm at 298 K and shown in (a). The excitation (dotted) at 509 nm, excitation (dashed) at 553 nm, and emission (solid) at 449 nm at 77 K are shown in (b). These spectra are consistent with the formation of green luminescent $[(C_6H_{11}NC)_2Au]PF_6$ (**1**) upon exposure to dichloromethane vapor.

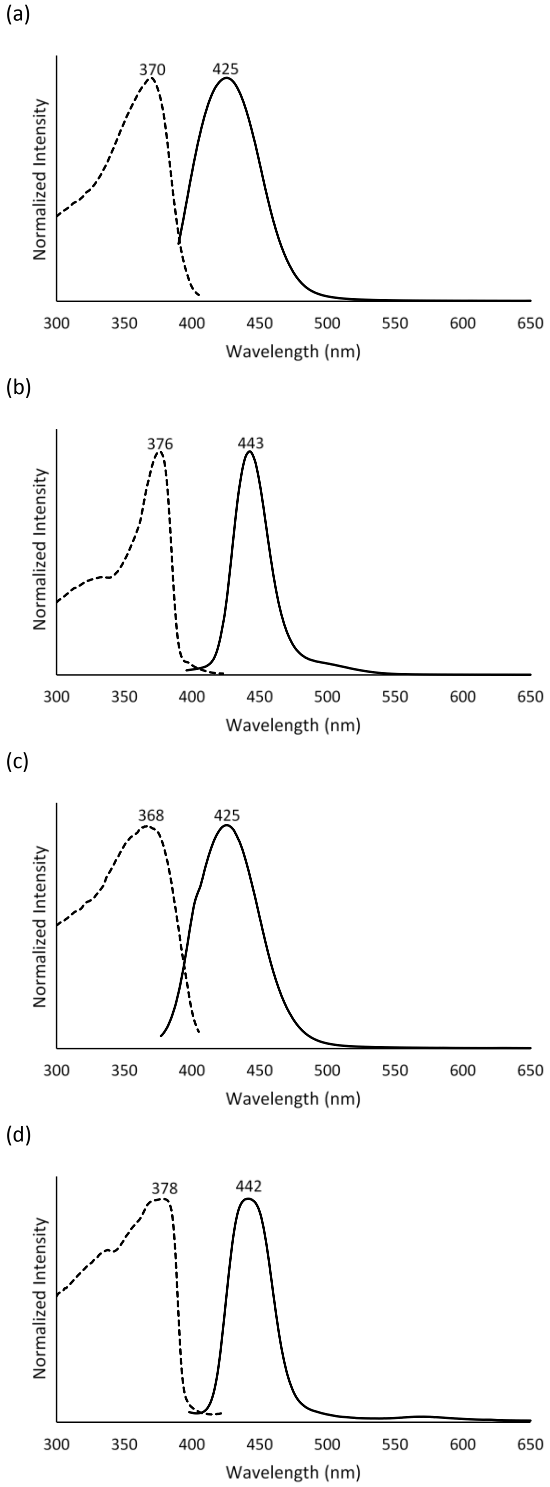
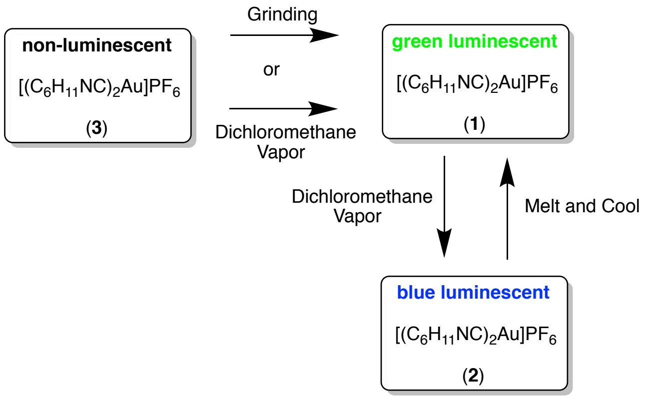


Fig. 5 The luminescence spectra of the non-luminescent $[(C_6H_{11}NC)_2Au]PF_6$ (**3**) after a second, longer exposure to dichloromethane vapor (final color and luminescence, colorless and blue, respectively). The excitation (dashed) at 425 nm and emission (solid) at 370 nm at 298 K are shown in (a). The excitation (dashed) at 433 nm, and emission (solid) at 376 nm at 77 K are shown in (b). These spectra are consistent with the formation of blue luminescent $[(C_6H_{11}NC)_2Au]PF_6$ (**2**) upon prolonged exposure to dichloromethane vapor.

Scheme 1 summarizes the interrelationships among the three polymorphs of $[(C_6H_{11}NC)_2Au]PF_6$. Here, we have discovered a new polymorph, non-luminescent $[(C_6H_{11}NC)_2Au]PF_6$ (**3**). Moreover, this polymorph is sensitive to both grinding and to dichloromethane vapour. Either treatment results in its conversion selectively into green luminescent $[(C_6H_{11}NC)_2Au]PF_6$ (**1**) rather than blue luminescent $[(C_6H_{11}NC)_2Au]PF_6$ (**2**). In order for this solid state transformation to occur, the cations must aggregate to allow creation of the aurophillic interactions that are key to formation of the luminophore in green luminescent $[(C_6H_{11}NC)_2Au]PF_6$ (**1**). Additionally, half of the cyclohexyl groups must change from axial positions in (**3**) to equatorial positions found in (**1**) since the positions of the cyclohexyl groups alternate between axial and equatorial along the columns of cations in green luminescent $[(C_6H_{11}NC)_2Au]PF_6$ (**1**).[15] Previous work had shown that green luminescent $[(C_6H_{11}NC)_2Au]PF_6$ (**1**) was transformed into blue luminescent $[(C_6H_{11}NC)_2Au]PF_6$ (**2**) through exposure to vapors of several organic solvents including dichloromethane without the uptake of these vapors. That work also showed that melting a sample of $[(C_6H_{11}NC)_2Au]PF_6$ (**2**) and subsequent cooling led to the formation of green luminescent $[(C_6H_{11}NC)_2Au]PF_6$ (**1**) as shown on the right side of Scheme 1.



Scheme 1. The interrelationships between the three polymorphs of $[(C_6H_{11}NC)_2Au]PF_6$.

The behaviour of non-luminescent $[(C_6H_{11}NC)_2Au]PF_6$ (**3**) toward two different stimuli is unusual and unique in that the two different stimuli produce the same product. There are cyclometallated platinum(II) complexes that are simultaneously sensitive to vapour and mechanical pressure but produce different products.[18,19] There are also solvated crystals that undergo a reversible cycle of solvate loss upon grinding and the solvate uptake upon exposure to the appropriate vapour.[20,21] Non-luminescent $[(C_6H_{11}NC)_2Au]PF_6$ (**3**) is also unusual in that it is transformed into a luminescent form upon exposure to dichloromethane vapour but there is no incorporation of the vapour into the solid.

Our work also presents a new demonstration of the profound effect of non-coordinating anions on the behaviour of gold(I) complexes.[22,23] Under conditions similar to those used to form non-luminescent $[(C_6H_{11}NC)_2Au]PF_6$ (**3**), crystallization of $[(C_6H_{11}NC)_2Au]AsF_6$ or $[(C_6H_{11}NC)_2Au]SbF_6$ produces the benzene solvates, $[(C_6H_{11}NC)_2Au]AsF_6 \bullet (C_6H_6)$ or $[(C_6H_{11}NC)_2Au]SbF_6 \bullet (C_6H_6)$,[24] which also are non-luminescent because the positions of the benzene molecules in the crystals interrupt any aurophilic interactions. However, $[(C_6H_{11}NC)_2Au]PF_6$ does not form a benzene solvate and luminescent $[(C_6H_{11}NC)_2Au]AsF_6$ or $[(C_6H_{11}NC)_2Au]SbF_6$ have not been found to crystallize as a non luminescent form analogous to non-luminescent $[(C_6H_{11}NC)_2Au]PF_6$ (**3**).[20]

We thank the ARCS Foundation for two awards to LMCL and the National Science Foundation (Grant CHE-1807637) for partial support of this project.

Conflicts of Interest

There are no conflicts to declare.

Notes and References

1 J. Bernstein, Polymorphism in Molecular Crystals, Oxford University Press, New York, 2008.

2 D.-K. Bučar, R. W. Lancaster and Joel Bernstein. *Angew. Chem. Int. Ed.* 2015, **54**, 6972 –6993.

3 R. Hilfiker, Ed. Polymorphism in the Pharmaceutical Industry. Wiley-VCH, Weinheim, 2006.

4 R. Bu, H. Li and C. Zhang, *Cryst. Growth Des*. 2020, **20**, 3561−3576.

5 D. Gentili, M. Gazzano, M. Melucci, D. Jones and M.Cavallini, *Chem. Soc. Rev*. 2019, **48**, 2502−2517.

6 D. Liu, C. Li, S. Niu, Y. Li, M. Hu, Q. Li, W. Zhu, X. Zhang, H. Dong and W. Hu, *J. Mater. Chem. C*, 2019, **7**, 5925−5930.

7 C. Cappuccino, L. Catalano, F. Marin, G. Dushaq, G. Raj, M. Rasras, R. Rezgui, M. Zambianchi, M. Melucci, P. Naumov and L. Maini, *Cryst. Growth Des*. 2020, **20**, 884−891.

8 O. S. Wenger, *Chem. Rev*. 2013, **113**, 3686−3733.

9 X. Zhang, B. Li, Z.-H. Chen and Z.-N. Chen, *J. Mater. Chem*. 2012, **22**, 11427–11441.

10 H. Schmidbaur, A. Schier, *Chem. Soc. Rev*. 2012, **41**, 370-412.

11 N. Mirzadeh, S. H. Privér, A. J. Blake, H. Schmidbaur and S. K. Bhargava, *Chem. Rev*. 2020, **120**, 7551−7591.

12 S. H. Lim, M. M. Olmstead and A. L. Balch. *Chem. Sci*., 2013, **4**, 311-318.

13 H. Ito, M. Muromoto, S. Kurenuma, S. Ishizaka, N. Kitamura, H. Sato and T. Seki, *Nat. Commun*. 2013, **4**, 2009.

14 E. M. Gussenhoven, J. C. Fettinger, D. M. Pham, M. A. Malwitz and A. L. Balch, *J. Am. Chem. Soc*. 2005, **127**, 10838.

15 R. L. White-Morris, M. M. Olmstead and A. L. Balch, *J. Am. Chem. Soc*. 2003, **125**, 1033-1040.

16 M. A. Malwitz, S. H. Lim, R. L. White-Morris, D. M. Pham, M. M. Olmstead and A. L. Balch, *J. Am. Chem. Soc*. 2012, **134**, 10885-10893.

17 L. M. C. Luong, M. A. Malwitz, V. Moshayedi, M. M. Olmstead and A. L. Balch, *J. Am. Chem. Soc.*, 2020, **142**, 5689−5701.

18 C.-Y. Lien, Y.-F. Hsu, Y.-H. Liu, S.-M. Peng, T. Shinmyozu and J.-S. Yang, *Inorg. Chem*. 2020, **59**, 11584−11594.

19 C.-J. Lin, Y.-H. Liu, S.-M. Peng, T. Shinmyozu and J.-S. Yang, *Inorg. Chem*. **2017**, *56*, 4978−4989.

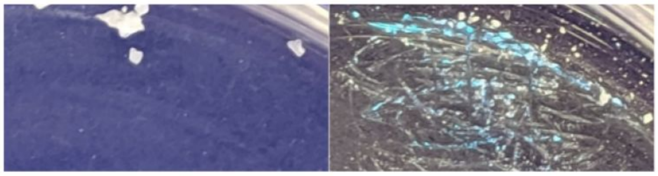
20 A. Chu, F. K.-W. Hau, L.-Y. Yao and V. W.-W. Yam, *ACS Materials Lett*. 2019, **1**, 277−284.

21 M. Osawa, I. Kawata, S. Igawa, M. Hoshino, T. Fukunaga, and D. Hashizume, *Chem. Eur. J*. 2010, **16**, 12114 – 12126

22 J. Schießl, J. Schulmeister, A. Doppiu, Eileen Wörner, M. Rudolph, R. Karch and A. S. K. Hashmi, *Adv. Synth. Catal*. 2018, **360**, 2493 – 2502.

23 J. Schießl, J. Schulmeister, A. Doppiu, Eileen Wörner, M. Rudolph, R. Karch and A. S. K. Hashmi, *Adv. Synth. Catal*. 2018, **360**, 3949 – 3959.

24 L. M. C. Luong, C. D. Lowe, A. V. Adams, V. Moshayedi, M.M. Olmstead and A. L. Balch, *Chem. Sci*. 2020, **11**, 11705-11713.



Colorless crystals of the new non-luminescent polymorph of $[(C_6H_{11}NC)_2Au]PF_6$ (**3**) become luminescent upon grinding or exposure to dichloromethane vapour.