

Access to luminescent mesophases of chiral gold(I) complexes by thermal or mechanic stimuli. The role of the tertiary carbon

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

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DOI: 10.1039/x0xx00000x

Chiral gold(I) isocyanide complexes $[\text{Au}(p\text{-C}_6\text{F}_4\text{OR}^1)(p\text{-CNC}_6\text{H}_4(\text{O}_2\text{CC}_6\text{H}_4(\text{OR}^2))]$ with R^1 , R^2 or both being (*R*)-2-octyl, display an interesting and unprecedented response to mechanical or thermal stress. For all the complexes, heating leads to formation of Sm mesophases identified by POM, DSC, and X-ray diffraction studies. On the other hand, grinding produces soft materials which are eventually identified also as Sm metastable mesophases formed at temperatures much below the melting point. Intriguingly, only some of these mesophases (those with the tertiary carbon in the isocyanide ligand) display a strong green luminescence. The X-ray analysis supports that the melting of the crystals, either by mechanical or by thermal stress, produces a transition from regular Sm-like molecular arrangement in the solids to interdigitated-Sm arrangement in the mesophases. The molecular slippage producing this interdigitation is conditioned by the position of the bulky tertiary carbon in the molecule, which allows or impedes formation of the Au...Au interactions that give rise to luminescence.

Introduction

Mesomorphic $[\text{AuX}(\text{CNR})]$ complexes, are a well-defined molecular type of metallomesogens.^{1–10} Their properties can be easily tuned by selective functionalization on the isocyanide group or on the ancillary X ligand. Their potential applications go beyond those of other liquid crystals and include photonic devices with luminescent materials,^{11–14} and organometallic dyes.¹⁰ Many non-mesomorphic gold complexes of this type display luminescent mechano-responses,^{15–23} including luminescence mechanochromism,²⁴ multiple-colour mechanochromism^{25,26} and IR-emissive mechanochromism.¹⁶ These studies have always focused on the mechanical control of the solid molecular structures and crystal phase changes.

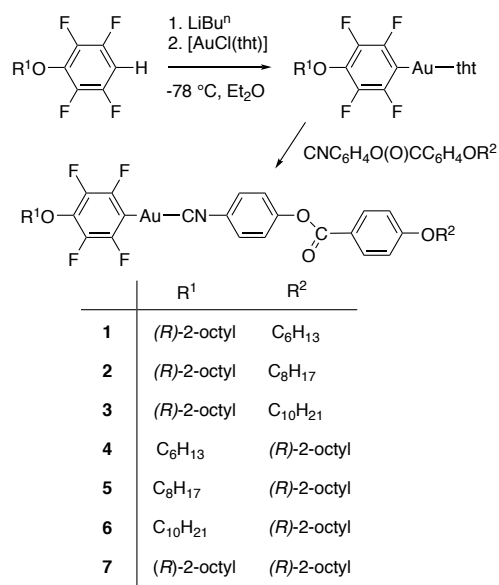
Here we focus our attention to the extraordinary and puzzling behaviour of some structurally simple mesomorphic arylgold(I) isocyanide complexes with a tertiary carbon in the alkoxy chains. Some of them display reversible mechano- and thermo-responsive luminescence, while others do not. This study concludes that both methods to provoke luminescence involve the same mesophase, and uncovers the intriguing role of the tertiary carbon atom. To the best of our knowledge, there is only one interesting precedent of such a behaviour, namely one luminescent organic molecule where a metastable solid phase

is transformed into a liquid crystal phase through mechanical stimulation, and then to a crystalline phase. This occurs with change in colour of the luminescence.²⁷

Results and discussion

The gold(I) complexes, containing one or two (*R*)-2-octyloxy groups, were prepared according to Scheme 1, as reported for similar tetrafluorophenyl-gold(I) isocyanide derivatives.²⁸ All the complexes were obtained as white solids in high yield. Details of their synthesis and characterization can be found in the ESI.

Scheme 1. Synthesis of the chiral gold isocyanide complexes.



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Electronic Supplementary Information (ESI) available: Materials and methods. Full details of synthetic methods, spectroscopic data and analytical data for the new compounds. POM textures and DSC scans. Additional X-ray diagrams. See DOI: 10.1039/x0xx00000x

The mesomorphic properties were studied by polarized optical microscopy (POM), differential scanning calorimetry (DSC), and X-ray scattering. The thermal and thermodynamic, and optical data are gathered in Table 1. Whereas the free 4-isocyanophenyl 4-alkoxybenzoates with the alkoxy groups $O-C_nH_{2n+1}$ ($n = 6, 8, 10$) form nematic (N) and/or smectic A (SmA) phases in the range 61–84 °C,²⁹ the chiral isocyanate ligand with the alkoxy group *O-(R)-2-octyl* is not liquid crystal and melts directly to an isotropic liquid at 22.1 °C. In contrast, all the gold compounds (**1-7**) are mesomorphic. Their mesophases were assigned from their POM textures,³⁰ and were confirmed by X-ray diffraction studies. The chiral smectic C phases showed the characteristic broken focal-conic texture on cooling from the SmA phase with a focal-conic fan texture, or a fingerprint texture on cooling homeotropic regions of the SmA phase (see representative pictures in ESI, Figures S35 and S36). A similar mesomorphic behavior has been reported for the corresponding derivatives with 1-octyloxy instead of 2-octyloxy,²⁸ but our 2-octyloxy derivatives **1-7** display lower transition temperatures reflecting the greater steric demand of the tertiary carbon at the 2-octyloxy substituent. It is worth noting that when the chiral substituent is located in the isocyanide ligand (complexes **4-6**), the transition temperatures are significantly lower than for the corresponding complexes containing the 2-octyloxy chain in the tetrafluoroaryl group (complexes **1-3**), suggesting a larger weakening of intermolecular interactions in **4-6**. Consistently, the transition to the isotropic phase occurs at significantly lower temperature for compound **7**, with two 2-octyloxy chains containing a tertiary carbon atom.

Table 1. Thermal, thermodynamic, and luminescence data for complexes **1-7**, in dichloromethane solution at 298 K.

Cpd.	Transition ^a	T ^b (°C)	ΔH ^b	λ _{max,ex} ^c	λ _{max,em} ^c
1	Cr → SmA	103	22.4	304	378
	SmA → I	163	2.4		
2	Cr ¹ → Cr ²	-17	6.6	305	379
	Cr ² → SmC*	98	18.8		
	SmC* → SmA	123	0.2		
	SmA → I	168	3.5		
3	Cr ¹ → Cr ²	12	8.2	306	379
	Cr ² → SmC*	92	17.6		
	SmC* → SmA	129	0.2		
	SmA → I	167	3.5		
4	Cr → SmA	77	16.5	305	375
	SmA → I	139	2.8		
5	Cr ¹ → Cr ²	40	3.6	305	377
	Cr ² → SmC*	78	17.2		
	SmC* → SmA	93	0.1		
	SmA → I	135	3.0		
6	Cr ¹ → Cr ² → SmC*	65	19.3	306	378
	SmC* → SmA	96	0.1		
	SmA → I	133	3.2		
7	Cr ¹ → Cr ²	45	-7.7	307	384
	Cr ² → SmA	62	24.5		
	SmA → I	73	1.1		

^aCr: crystal phase; Sm: smectic mesophase; I: isotropic liquid. ^bData collected from the second heating DSC cycle (kJmol⁻¹). Transition temperatures given as peak onsets. ^cnm.

The complete data of the electronic spectra (UV-Visible and luminescence) of the free isocyanides and their corresponding tetrafluorophenylgold(I) isocyanide complexes are summarized in Table S1 and in Figures S46–S67). The UV-Visible spectra show one strong UV absorptions assigned to phenyl-localized $\pi-\pi^*$ transitions. This absorption undergoes a slight bathochromic shift, relative to the free ligands, upon coordination of the isocyanide to gold, as reported for analogous systems.¹¹ The free ligands and the gold(I) complexes show very similar luminescent behaviour in dichloromethane solution. They all show, under UV irradiation at 294–307 nm, one strong UV emission in the range 373–384 nm, with lifetimes in the range of nanoseconds, as reported for analogous systems.³¹ Consequently this fluorescent emission is assigned to intraligand $\pi-\pi^*$ transitions with little Au orbital contribution.^{32,11} In the solid state this luminescence is lost due to the formation of excimer or excimer-like adducts (Figures in ESI S68–S71).^{4,33}

A very intriguing behavior was found when the crystalline complexes **1-7** were submitted to mechanical (grinding) or to thermal (heating) stress. Complexes **4-6** (with the tertiary carbon at the isonitrile ligand) and also complex **7** (with a tertiary carbon in the two alkoxy chains), produced upon heating Sm phases with simultaneous emergence of an intense green luminescence, persistent in the mesophase conditions. When submitted to mechanical stress (grinding), a waxy material was produced and a visually identical green luminescence emerged, reversible and fading off after some seconds. As an example of the behavior of **4-7**, Figure 1 shows the effect of grinding a crystalline sample of **7** in a mortar: a the waxy material formed produces an intense green emission under UV irradiation at 365 nm. This green emission vanishes spontaneously after a few seconds as the material returns to the original crystalline phase (see ESI video).

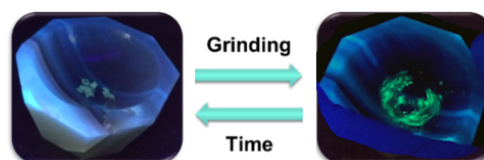


Figure 1. Photographs showing complex **7** on an agate pestle under UV irradiation (365 nm), before (left) and after (right) grinding structures. b

In contrast, complexes **1-3**, with the tertiary carbon at the tetrafluorophenyl group, melted to Sm mesophases upon heating but these did not show any luminescent response. When submitted to mechanical stress they formed also waxy materials, as **4-7** did, but no sign of luminescence. Consequently, the two series coincide in producing viscous materials rather than powders upon grinding, and Sm mesophases upon heating. But they differ in that only complexes **4-7** give rise to luminescence, whether upon mechanical or upon thermal stress.

The nature of the luminescence observed in the materials formed upon submitting the crystals of **4-7** to mechanical or

thermal stress can be fully characterized in the thermal mesophases (Table S2 and technical procedures in ESI). The emission maxima appear at about 530 nm, with lifetimes in the range of microseconds. The lifetime values, together with the Stokes shift between the absorption and emission bands, support phosphorescence for the green emission (see ESI video, Table S2 and Figures S68-S77). Only for compound **7**, with higher emission intensity, we have been able to record also the emission spectrum of the ground phase. The spectrum is almost coincident with that of the thermal mesophase (Figure 2), considering that small structural changes are expected for the same mesophase submitted at different temperatures.

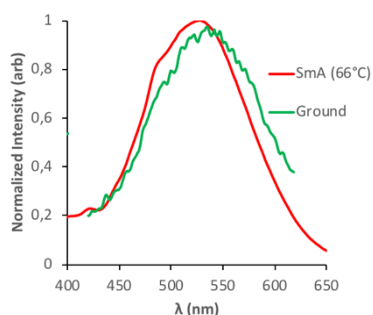


Figure 2. Emission spectra ($\lambda_{\text{exc}} = 330$ nm) of **7** in the thermal SmA mesophase at 66 °C and in the ground phase at 25 °C.

All the soft materials formed by grinding **1-7** show similar POM features, and always the waxy material reverts quickly to a crystalline phase. Consequently, the presence or absence of luminescence must have some more specific origin. The POM features are well represented by the pictures of Figure 3. They correspond to complex **7** submitted to grinding (under a cover glass) and shearing (without a cover glass) at 25 °C. The images are typical of liquid crystal mesophases and are compatible with a SmA phase. For compound **2** a fluid “grayish texture” compatible with a SmC phase is observed (Figure S37c).

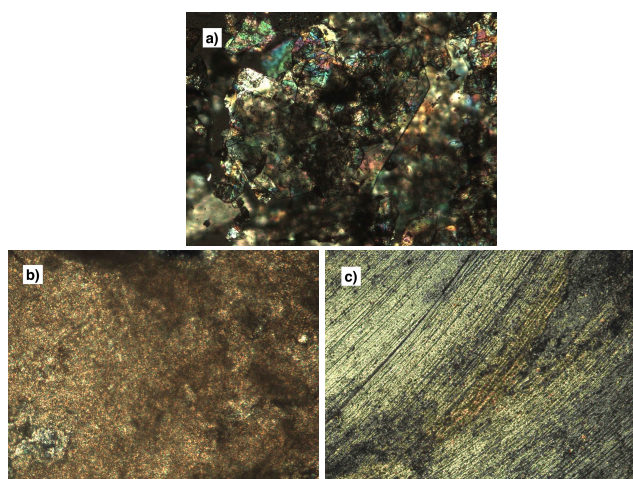


Figure 3. POM textures (x100, crossed polarizers) observed for **7** at 25 °C. a) virgin crystalline sample; b) sandy-like texture obtained by grinding the sample under a cover glass; c) oily-streak lines obtained by shearing the sample without a cover glass.

Since the thermal study (Table 1) shows that all the gold complexes have in common that they present Cr \rightarrow Sm transitions with a reasonably low enthalpic cost of about 5 kcal.mol⁻¹ it is not unreasonable to imagine that the energy available at grinding can be sufficient to overcome this low barrier also, producing slippage of the rod-like molecules and giving rise to the same Sm mesophases obtained on melting. This suggestion is supported by the ephemeral existence of the soft material, which is well understood considering that for all the complexes the Sm mesophase is metastable at 25 °C and, in a fluid material, should revert fast to a smectic-like crystal phase.

In order to obtain more structural information on the crystal and LC phases obtained upon heating, a detailed variable temperature X-ray diffraction study was performed for compounds **2**, **5** and **7** as representative examples. The temperature-dependent X-ray diffraction experiments were carried out cooling from the isotropic liquid down to room temperature. The X-ray diffraction patterns of compound **5** (Figure 4) are representative of all the others.

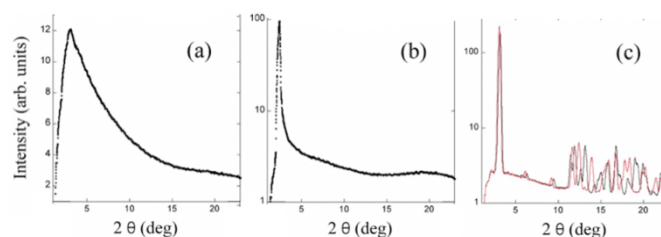


Figure 4. X-ray diffraction patterns of compound **5**. (a) in the isotropic phase. (b) at 100 °C in the interdigitated smectic A phase, where the layer spacing is 37.2 Å. (c) in the low temperature crystalline phases Cr² (red line) and Cr¹ (black line).

For the three compounds, the X-ray diffraction patterns of the isotropic liquids show two broad diffuse reflections: one at 4.5 Å ($2\theta \sim 20^\circ$) corresponds to the molten chains in liquid disorder; the other appears at smaller angles $2\theta = 2.77^\circ$ (32 Å) for **2**, $2\theta = 3.05^\circ$ (29 Å) for **5**, and $2\theta = 2.95^\circ$ (30 Å) for **7** (see Figure S78a, Figure 4a and Figure S82a in the ESI). On cooling, the three compounds show an interdigitated SmA phase (Figure 5), with a smectic layer spacing clearly larger than the molecular length (38 Å for compound **2**, 37 Å for compound **5**, and 35 Å for compound **7** (see Figure 4b for compound **5**, and Figure S82b in the ESI for compound **7**). In the cases of **2** and **5** the layer spacing further decreases on cooling, and a transition takes place to a different interdigitated SmC* phase where the molecules are tilted.

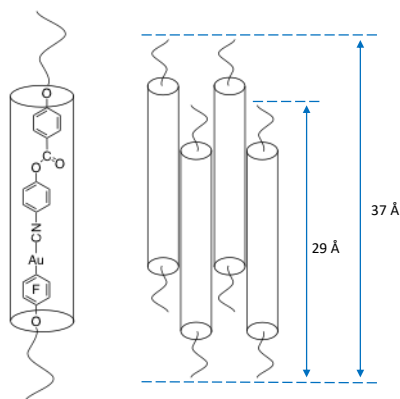


Figure 5 Molecular arrangement in interdigitated SmA mesophases. The distances correspond to the case of complex **5** and its interdigitated phase. Tilting occurs for SmC*.

The smectic spacing variation with temperature shown in Figures S79 and S81, reflects clearly the transition between the two interdigitated smectic phases. Further cooling causes crystallization. In compounds **2** and **5** we found Cr² and Cr¹ solid phases displaying smectic-like character, with spacing slightly smaller than the molecular length in the crystal phases (29 Å and 28 Å in Cr² and Cr¹ respectively, for complex **5**; see Figure 4c). Compound **7** also shows two crystal phases. Cr² is metastable at room temperature and relaxes into Cr¹ after a few hours. Cr¹ is again smectic-like with spacing slightly smaller than the molecular length (see Figure S81c in the ESI).

In summary, the X-ray studies reveal that all the molecules adopt ordinary (non-interdigitated) smectic-like arrangements in the crystal phases, presumably stabilized by interactions of antiparallel molecules, as is the usual case for asymmetric molecules. Similar arrangements have been reported for cyanobiphenyls³⁴ and related gold(I) complexes.¹⁰ Upon heating, molecular slippage leads to formation of interdigitated SmC* and/or SmA phases with a relatively small enthalpic cost of about 20–25 kJmol⁻¹ (Figure 5). The dimensions of smectic arrangements in the crystals, and also those in the mesophases are very similar for the two families of products, those displaying luminescence above the melting transition and those not showing luminescent response.

Discussion

The results commented in the studies above raised a number of questions about the behavior of our systems, probably summarized in the following points: *i*) are the soft materials obtained for **1–7** via grinding stress the same obtained via melting stress? *ii*) is the formation of Au...Au interactions the origin of the strong green luminescence? *iii*) why **1–3** and **4–7** behave differently relative to luminescence.

The first question was already answered above. Considering the identical color of the luminescent materials obtained thermally or by heating, grinding at 25 °C is able provide the energy needed to induce a molecular slippage from the structural arrangement in the smectic-like solid-state phases to an intermolecular arrangement very similar or identical to the one

achieved in the mesophase formed at the melting temperatures. However, the grinding-induced mesophases are formed out of the equilibrium conditions that rule the thermal transitions. For this reason, the resulting mesophases are metastable at 25 °C and, being non-rigid materials, revert quickly to the solid state. To the best of our knowledge, these gold complexes are unprecedented examples of direct crystal-to-mesophase transitions induced by grinding at temperatures way below the required melting points.

For the second question we take into account well known examples of related non-mesogenic gold(I) isocyanide complexes (without alkoxylic chains), where the emergence upon grinding of mechano-luminescence at similar $\lambda_{\max,em}$ values is associated to formation of intermolecular Au...Au interactions in the ground powder.^{25,35} For the formation of these Au...Au interactions, at least part of the intermolecular π - π stacking interactions holding together the crystalline structure have to be broken by the grinding in order to allow for adoption of a new solid state phase with the gold atoms close enough to establish aurophilic interactions. By similarity with the behavior of solid-to-solid phase transitions upon grinding, in the case of solid-to-mesophase phase transitions upon heating or cooling, the features of the luminescence observed support unambiguously the existence of Au...Au interactions in the mesophases of compounds **4–7**, and their absence in the case of compounds **1–3**, as well as in the solid crystal phases or in the isotropic phases of all the compounds. Obviously, the formation of Au...Au interactions non-existing in the solid requires molecular slippage and consequently formation of interdigitated mesophases. There are reports for platinum^{36–38} and gold^{12,13,39} mesogenic complexes supporting that metallophilic interactions existing in the crystals can survive in the mesophases. This is not surprising, since these are of the order of hydrogen bonds. But only in one Pt case has been reported the formation of Pt...Pt interactions in the mesophase that did not exist in the parent crystal,³⁶ as it is the case of our Au complexes.

Assuming that it is reasonable to consider that the luminescence observed in some of our compounds (in **4–7**), fugacious in the metastable soft material after grinding and permanent in the mesophase, emerges when formation of Au...Au interactions inexistent in the smectic-like crystal phases occurs in the mesophase, the question is now why the groups of compounds **1–3** or **4–7**, both leading to interdigitated smectic phases, behave different towards luminescence. Or, in other words, why these groups differ in the result of their slippage upon melting (or grinding). Our proposal is that this is due to the presence of a bulkier tertiary carbon in one or the two chains of the molecules, as illustrated in Figure 6. The **1–3** compounds have this group in the tetrafluoro aryl, whereas the **4–6** group have it in the isocyanide group. In both series, in the ordinary smectic-like order existing in the solid this tertiary carbon is more comfortably located in the zone of the alkoxylic chains (Figure 6). From this starting point, the intermolecular slippage with the lowest barrier should be the one where the movement of the bulk tertiary carbon disturbs less the existing intermolecular aromatic interactions (the cylinders highlight

this zone of the molecule). This means that the low cost allowed slippage should keep the tertiary carbon in the zone of the alkoxy chains. With these premises, Figure 6 shows clearly that the molecules should slip following in the direction of the blue arrows in each case. Interestingly the slippage for **4-6** reduces the Au...Au distances in the interdigitated structure, favoring aurophilic interactions and emergence of luminescence. On the contrary, for **1-3** the Au...Au distance (already too long for aurophilic interactions in the smectic-like arrangement of the solid) increases.

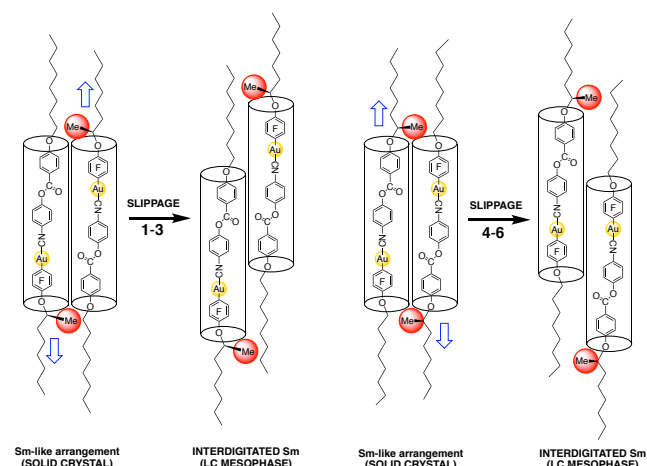


Figure 6. The two effects of slippage (indicated by the blue arrows) on the resulting interdigitated Sm mesophase, depending on the position of the tertiary C* in the molecule.

From a thermodynamic point of view for **4-6** the slippage at the mesophase should compensate the reduction of aromatic interactions existing in the solid with the stabilizing Au...Au interactions plus the favorable increase in entropy at the mesophase temperature, which in practice leads to Au...Au distances short enough to give rise to luminescence. For the **1-3**, where Au...Au interactions are out of reach, sufficient aromatic interactions should be retained to stabilize, in conjunction with the entropic contribution, the interdigitated smectic phase. The X-ray studies show that the parameters turn out to be quite similar for both series. Their Sm mesophase ranges are 60-75 °C with clearing temperatures around 165 °C for **1-3**, and 58-68 °C with clearing temperatures around 136 °C for **4-6** (Table 1).

A marked difference exists with the thermal data for complex **7**, which has a short mesophase range of 11.6 °C and much lower melting (61.7 °C) and clearing (73.3 °C) temperatures. This difference illustrates the important effect of the presence of tertiary carbons on the intermolecular interactions. The presence of two tertiary carbons in **7** diminishes seriously the efficiency of these interactions and leads to a marked reduction of all the transition temperatures. Obviously, the prediction of the preferred slippage in Figure 6 is not easy in this case, but the experimental result (luminescence observed) suggests that the presence of the bulky carbon on a single aryl zone is more disturbing than on the diaryl ester zone, already requiring more space.

Conclusions

In the complexes studied here both processes, heating or mechanical grinding, are able to induce melting to the same Sm mesophase, in the grinding case way below the equilibrium melting point of the material. The mechanism is the intermolecular slippage from smectic-like arrangement in the solid to interdigitated SmA or SmC* mesophases. The possible slippage is conditioned by the lowest barrier, which excludes the bulky tertiary carbon from invading the aromatic zone. This eventually determines that **4-7** give rise to interdigitated Sm mesophases with Au...Au interactions, hence luminescent, whereas **1-3** produce non-luminescent Sm mesophases lacking aurophilic interactions (Figure 7).

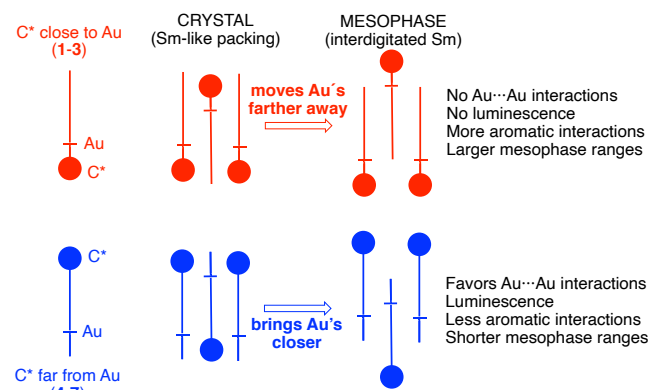


Figure 7. The two effects of mechanically- or thermally-induced slippage (indicated by the blue arrows) depending on the position of the tertiary carb in the molecule, and derived properties.

The formation of a metastable luminescent mesophase upon grinding **4-7**, by "melting at temperature below the melting point", is an infrequent but thermodynamically possible case where the small activation energy required for the slippage, and the fast detection facilitated by the appearance of luminescence, made an instantaneous observation possible, but the same transition is also taking place in the shadow for **1-3**, where the phenomenon would have gone unnoticed.

For **4-7**, on/off switching of the Au...Au interactions is possible manipulating the sample either thermally or by mechanical treatment, with the same result. The case studied here is reminiscent of the strain-induced mesophase reported in amphiphilic oligo(*p*-phenylenevinylene) luminophores²⁷ and polylactide materials.^{40,41} These observations are interesting for future tailoring of metallomesogens combining chirality, luminescence, thermal response and mechanical response.

Author Contributions

The authors have contributed equally to the paper.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was sponsored by the Ministerio de Ciencia e Innovación (Projects CTQ2017-89217-P and PID2020-118547GB-I00), the Junta de Castilla y León (Project VA224P20), and the UPV/EHU (Project GIU18/146). We thank Prof. J. M. López-de-Luzuriaga (University of La Rioja) for life-time measurements. M. B. thanks the Junta de Castilla y León for a PhD grant.

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