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Molecular Motions in AIEgen Crystals: Turning on Photoluminescence by Force-Induced Filament Sliding

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ABSTRACT: Life process is amazing and it proceeds against the eternal law of entropy increase through molecular motion and takes energy from the environment to build high-order complexity from chaos to achieve evolution with more sophisticated architectures. Inspired from the elegance of life process and also to effectively exploit the undeveloped solid-state molecular motion, two unique chiral Au(I) complexes were elaborately developed in this study, in which their powders could realize a dramatic transformation from non-emissive isolated crystallites to emissive well-defined microcrystals under the stimulation of mechanical force. Such an unusual crystallization was presumed to be caused by molecular motions driven by the formation of strong aurophilic interactions as well as multiple C–H…F and π - π interactions. Such a prominent macroscopic off/on luminescent switching could also be achieved through extremely subtle molecular motions in the crystal state and presented a filament sliding occurred in a layer-by-layer molecular stacking fashion with no involvement of any crystal phase transition. Additionally, it had been demonstrated that the manipulation of the solid-state molecular motions could result in the generation of circularly polarized luminescence.

INTRODUCTION

The fundamental law of nature is that the total entropy of an isolated system is continually increasing if no work is done by external force.¹ As a consequence, any system has the tendency to be chaotic and disordered. However, life process proceeds against this eternal law and it itself is one of negative entropy and takes energy from the environment to build high-order complexity from chaos.² In another aspect, mobility as one of the inherent properties and a convincing indicator of living things, is also negative entropy, whereby life achieves evolution towards highly-organized and more sophisticated architecture.³ For instance, the precisely directed differentiation of pluripotent embryonic stem cells in tissue engineering and regenerative medicine is a typical example of a gradual evolutionary process towards a highly ordered and more refined direction.⁴ Similar examples are ubiquitous in life process.

Inspired by such extraordinary achievements of highly-ordered structures and intriguing molecular motion of nature, scientists have devoted enormous efforts to enter the molecular world and decipher the inherent mechanism. In recent years, great progress has been achieved on this aspect. Among these endeavors, the biggest breakthrough is brought by the exploration of artificial molecular machines that mostly

refer to the molecular motion in the solution phase.⁵ It has been recognized that the delicate regulatory control of molecular motion in the solution state is quite difficult due to the high mobility of molecules and the perturbation from the surrounding environmental factors such as the interactions from solvent molecules. Consequently, the successfully designed molecular machines are usually constituted by multiple complicated molecular components with precisely defined translational and rotary motion.⁵ This brings unlimited opportunities but also an incredibly big challenge for synthetic chemists. In another aspect, solid-state molecular motion is relatively less investigated because it is generally accepted that the mobility of molecules in the solid state is quite low due to strong intermolecular interactions.6 However, there is no doubt that the manipulation of molecular motion in the solid state is a viable approach to the eventual realization of molecular machines in our real-life applications.7 Given these critical points, we conjectured that could we in turn effectively exploit this solid-state motion and elaborately manipulate it to construct desired and ordered structures like nature?

As a matter of fact, scientists and engineers already attempt to realize this point by utilizing external stimuli including light, heating, electric and magnetic fields or force.⁸ Amongst, mechanical force is very simple and is preferentially employed by researchers to induce solid-state molecular motion due to

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its easy accessibility. In this aspect, researchers working on aurophilic systems have presented many elegant and impressing Au-containing complexes or nanoclusters.9 In these systems, the involved unique aurophilic interactions could be effectively manipulated by mechanical force through solid-state molecular motions due to their sensitive response to external force. And the mechanism is usually associated with molecular packing transition from crystal-to-amorphous or crystal-to-crystal.^{6b,9f,10} For example, Ito et al. have reported several intriguing Au(I) isocyanide complexes that exhibited typical crystal-to-crystal transformation under the stimulation of mechanical force because of the change of aurophilic interactions resulted from molecular motions.¹⁰ From most of the previous works, we realized that it is much easier to change the packing of solid-state molecules from order to disorder in the presence of external force.^{6b,10} And realizing the transformation between two different ordered crystal states usually requires the manipulation of some strong intermolecular interactions, such as aurophilic interactions, as demonstrated by Ito et al. Accordingly, it is especially difficult to achieve an inverse molecular packing transition from a disordered state to a well-ordered state through molecular motions triggered by external mechanical force and this is rarely attempted by far.

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With this in mind, we come up with an idea: can we manipulate the solid-state molecular motions of a system by utilizing unique aurophilic interactions to achieve highly-ordered molecular architecture from their original chaotic states? If yes, it would simultaneously lead to a remarkable change of photophysical properties that can in turn signal the molecular motions. Herein, the systems with aggregation-induced emission (AIE) characteristics are considered to be promising candidates to accomplish the above proposal based on our previous related research.6a,6b Additionally, they are anticipated to signal molecular motion in the form of luminescence. Accordingly, we designed two chiral AIE-active isomers, namely (1R,2R)-DPIEAuF ((R,R)-1)and (1S,2S)-DPIEAuF ((S,S)-1) (Figure 1A) via an elaborate structural tailoring. In these two systems, a flexible diphenyl-ethane moiety was selected to achieve unique AIE property and the pentafluorophenyl (C₆F₅)-Au termini were introduced to form strong aurophilic interactions (more design details vide infra). As envisioned above, in the presence of in-situ stimulus of mechanical force, the initally randomly-oriented nano-sized crystallites of the powders can rearrange orderly and further assemble into well-defined micron-scale microcrystals, which is a hitherto rare phenomenon. In addition, this process could be visualized through the turn-on photoluminescence (PL) signal. More strikingly, in their crystals, such a prominent macroscopic off/on luminescent switching could also be achieved through extremely subtle molecular motions occurred in a layer-by-layer molecular stacking without causing any change in the crystal phase. Such a phenomenon has not been observed before. It is anticipated that the present results will provide new insights into the exploration of molecular motions in the solid state.



Figure 1. (A) Molecular structures of the chiral complexes (\mathbf{R}, \mathbf{R}) -1 and (S, S)-1. (B) Photoluminescence (PL) spectra of (\mathbf{R}, \mathbf{R}) -1 (2.0 × 10⁻⁵ M) in THF/water mixtures with different water fraction (f_{w}) . $\lambda_{ex} = 365$ nm. (C) Plot of relative emission peak intensity (α_{AIE}) at 504 nm versus f_w of the THF/water mixtures of (\mathbf{R}, \mathbf{R}) -1 and (S, S)-1, where $\alpha_{AIE} = I/I_0$, I = emission intensity and I_0 = emission intensity in THF solution. Inset: photos taken under 365 nm UV irradiation. (D) Powder X-ray diffraction patterns of (\mathbf{R}, \mathbf{R}) -1 and (S, S)-1 powders obtained by evaporation of their THF/water mixtures (1:99, v/v).

RESULTS AND DISCUSSION

Molecular Design and Aggregation-Induced Emission

First, the two target Au(I) complexes (R,R)-1 and (S,S)-1 were designed and synthesized as shown in Figure 1A. Two dominant and seemingly contradictory factors, *i.e.*, flexibility and stability, were considered in the designing of such unique systems. Hence, introducing different kinds of intermolecular interaction, especially the unique aurophilic (Au-Au) interactions,^{11,12} were indispensable for the present system. Specifically, (1) the flexible diphenyl-ethane moiety was selected to primarily maintain the flexibility of the systems and it is also a vital factor to achieve unique AIE property. (2) The pentafluorophenyl (C₆F₅)-Au termini are introduced to form strong aurophilic interactions and further stabilize the basic building units used for the construction of layer-by-layer molecular stacking as inspired from the previous works of Ito and ours.^{10g-10j,13} (3) Finally, the desired multiple weak intermolecular interactions including C-H-F interaction and π - π interaction may exist between the -C₆F₅ termini and the phenyl units and they therefore play a vital role in coordinating the stability and the flexibility, which are considered to be readily perturbed by the external stimuli.10g-10j,13

Then, the target complexes were prepared by the synthetic route as depicted in Scheme S1. All intermediates and target products were well characterized by NMR and high-resolution

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mass spectroscopy with satisfactory results (Figures S1-S12). Both (R,R)-1 and (S,S)-1 exhibited high stability under ambient conditions. In addition, they exhibited typical AIE properties as anticipated. As presented in Figure 1B and 1C and Figure S13, their diluted THF solutions were completely non-emissive. However, upon the addition of a poor solvent such as water into their respective THF solutions with a content 99 vol%, green PL with a maximum at 504 nm was observed. According to the images of scanning electron microscope (SEM) imaging and patterns of powder X-ray diffraction (PXRD) (Figures S14 and 1D), the aggregates formed in 99% aqueous solution were obviously crystalline, implying their easy crystallization properties.

Mechanical Force Induced Emission, Crystallization and Related Mechanism

As a matter of fact, the pristine powders of (R,R)-1 and (S,S)-1obtained by rapid precipitation of their dichloromethane (DCM)/hexane mixtures were first investigated and they were all found to be non-emissive. Generally, AIE compounds often show strong PL in the aggregated state or solid state.¹⁴ Thus, the present phenomenon seems to be strange and unusual. However, surprisingly, when the pristine powder of (R,R)-1 was gently scratched using a spatula, bright green PL could be immediately observed under 365 nm UV with an absolute quantum yield (QY) of 15%. The maximum wavelength was detected to be at ~500 nm (Figure 2A) and the associated lifetime was 12 ms, indicative of phosphorescence nature of the light emission (Figure S15). Such impressive phenomenon compelled us to make a detailed analysis on its powder in different states. According to the PXRD patterns in Figure 2B, the pristine powder of (R,R)-1 exhibited weak diffraction peaks to demonstrate a partially crystalline state. Amazingly, after scratching, all the peaks were dramatically intensified without any shift and were well consistent with those simulated from the single crystal X-ray data (details vide infra). These results clearly indicated that the mechanical force unexpectedly facilitated the crystallization of (R,R)-1 powder. At this point, the results looked even more abnormal and enigmatic.



Figure 2. (A) PL spectra of (R,R)-1 powder in different states. Scr'ed = scratched. Inset: photos of (R,R)-1 powder in different states taken under 365 nm irradiation. (B) PXRD patterns of (R,R)-1 in different states and simulated from crystal structure.

Accordingly, the morphology of (R,R)-1 powder were further carefully investigated in different states by SEM. More striking discovery was found as illustrated in Figure 3. The pristine powder of (R,R)-1 was composed of numerous disordered nano-sized crystallites and a lot of amorphous species (Figure 3A-3C). After being scratched, plenty of beautiful and well-defined rod-like crystals were formed with regular arrangements (Figure 3D-3F). Amplification of the image showed that the length of the most notable microcrystals in the field of view could reach above 1.5 µm (Figure 3F). To further confirm that the scratched powder of (**R**,**R**)-1 was indeed highly crystalline, *in-situ* scratching of its powder under fluorescence microscope was performed and numerous microcrystals appeared in places where the needle had passed (Figure S16A and S16C). Such ordered microcrystal structures were also verified by transmission electron microscopy (TEM) and the corresponding electron diffraction of the selected area (Figure S16B and S16D). This intriguing phenomenon is by no means an accident. The scratched powder of another isomer was also identified. As depicted in Figures 3G-3I and S17, (S,S)-1 showed completely similar turn-on phosphorescence behavior with a QY of 16% and consistent microcrystal formation after scratching.

Given their above unique properties, the following writing and erasing application by taking (R,R)-1 as a representative was tentatively performed. Figure 4A demonstrated that the luminescence of the scratched (R,R)-1 powder became weaker after heating to 90 °C for 30 min. When the temperature was raised to 100 °C that was far below the melting point of (R,R)-1, the emission of the molecule was completely quenched. The luminescence was only partially recovered when the temperature was naturally lowered to room temperature (RT). After being scratched, the molecule emitted intensely again. Such a switching could be repeated many times without fatigue. The PL spectral change of the scratched (R,R)-1 powder with temperature at nitrogen atmosphere provide more detailed and further convincing information for the above observations (Figure S18). When the above process was carefully analyzed, we were confused that why the luminescence could not be restored after cooling to RT? Considering its easy crystallization in both the aggregated state and the solid state, we initially surmised the reason should be that heating not only activated the molecular motions and promoted non-radiative attenuation, but also destroyed the crystalline structure and caused an amorphous transition. To validate the above presumption, the PXRD patterns of (R,R)-1 powder at different states were collected and presented in Figure 4B. Surprisingly, except the peak intensity, all the patterns obtained were almost identical and suggested their crystalline nature. However, we are even more confused and then a question arises: the state obtained by cooling from 100 °C to RT was highly crystalline, rather than amorphous as we originally envisaged, why it was still non-emissive?



Figure 3. (A-F) SEM images of (R,R)-1 in the pristine state (A-C) and the scratched (Scr'ed) state (D-F). (G-I) SEM images of (S,S)-1 in the pristine state (G) and the scratched state (H and I).



Figure 4. (A) Photos of (R,R)-1 powder in different states taken under 365 nm irradiation to indicate its mechanochromic and temperature-dependent properties. (B) PXRD patterns of (R,R)-1 powder in different states.

Fortunately, the pristine crystals (Xtals) of these two complexes are easily obtained by slow diffusion of poor solvent hexane into their respective DCM solution (Tables S1 and S2). It is especially worth noting that their Xtals recrystallized from DCM/hexane mixtures are non-emissive (Figure 5A and 5B), which is similar to the sample obtained by cooling the scratched powder from 100 $^{\circ}$ C to RT in terms of both the non-luminescent and the crystalline features. For

clarity, (R,R)-1 was chosen as a representative for further investigation. If the above non-emissive Xtals of (R,R)-1 were gently scratched by a needle, bright green PL could be observed immediately (Figure 5E-5H and video in the Supporting Information). As illustrated in Figure 5I, the PXRD pattern of the scratched (R,R)-1 crystal was similar to that of its pristine Xtals, and both patterns were also identical to those of the corresponding powder in the pristine and

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scratched states. Further combining the questions raised in the scratching and heating experiments, it was tentatively presumed that appropriate motions of (R,R)-1 molecules might occur in the microcrystal-producing process through scratching, heating its powder or in the process of scratching its crystals. These subtle changes could not result in an obvious transformation of crystal phase but could cause a macroscopically remarkable and visible off/on switching of luminescence. Here it is also worth noting that PXRD can provide some structural information but fails to give the important one and fine structure due to the random accumulation of millions of crystallites in the powder.¹⁵ Another yellow-emissive crystal of (R,R)-1 was also obtained from DCM/EtOH mixture (Figure 5C and 5D, Figure S19). And its PXRD pattern was strikingly similar to that of the non-emissive form (Figure 5I) and all its crystal parameters are amazingly very close to those of the non-emissive crystal (details vide infra), which further reinforced the idea that (R,R)-1 could realize an off/on emission switching without changing the crystal phase via subtle molecular motions.

Considering that if the non-luminescent nature of the pristine powders and crystals of (R,R)-1 and (S,S)-1 are resulted from the molecular motions, they should emit once

such motions are restricted. Accordingly, the PL spectra of their crystals and the scratched powders were measured at low temperature (77 K). Excitedly, obvious yellow PL was observed in their originally non-emissive crystals (Figure 5J). Regarding their scratched powders, dramatically enhanced and red-shifted luminescence was observed at low temperature (Figure 5K), which is probably due to the formation of stronger aurophilic interactions.^{10g,16} Additionally, when high pressure was applied on the prisitne powders of (R,R)-1 and (S.S)-1, their PL was gradually enhanced (Figures 6A, 6B and S20). Accompanying the above change was obvious red shifts of the wavenumbers corresponding to the typical v(N=C)vibration in the Raman spectra (Figures 6C, S20 and S21), which implied much stronger intermolecualr interactions under high pressure. These observations further rationalize that molecular motions can result in a turn-on luminescent transition. When the pressure was released, the PL profiles could not return to their initial states.¹⁷ Thus, it was surmised that the formed intermolecular interactions in the present Au(I) systems under pressure might be very stable and difficult to break even after removal of the applied pressure (Figures 6D and S22).



Figure 5. (A-D) Photos of (R,R)-1 crystal (Xtal) obtained by crystallization from DCM/hexane (non-emissive, A and B) and DCM/EtOH (emissive, C and D), taken under day light (A and C) and 365 nm UV light (B and D) at room temperature (RT). (E-H) Photos of (R,R)-1 crystal (non-emissive, crystallization from DCM/hexane) showing luminescence during the scratching process taken under 365 nm UV light at RT. (I) PXRD patterns of (R,R)-1 powder and different crystals in different states measured by synchrotron X-ray (non-emissive crystal: crystallization from DCM/hexane, emissive crystal: crystallization from DCM/EtOH). (J and K) PL spectra of (R,R)-1 and (S,S)-1



Figure 6. (A) Photos of (*S*,*S*)-1 powder taken under different pressure. (B) PL and (C) Raman spectra in the spectral region of $v(N \equiv C)$ mode of (*S*,*S*)-1 powder at different pressure of up to 2.41 GPa via diamond anvil cell. (D) PL spectral comparison of (*S*,*S*)-1 powder in different states. $\lambda_{ex} = 365$ nm (PL and photos), $\lambda_{ex} = 633$ nm (Raman spectra).

To ultimately unveil how the related molecular motions occur, we attempted to search for hints from the fundamental crystal structures. Considering that lowing the temperature could light up the emission of non-emissive (R,R)-1 crystal, the structural data of (R,R)-1 crystal at different temperatures was collected and compared (Figure 7, Tables 1 and S1). According to the crystal data at RT, we found that the molecules of (R,R)-1 exist as dimers (Figure 7A). As anticipated, in each dimer unit, there were double strong aurophilic interactions with Au-Au distance of 3.197 Å and 3.291 Å, respectively (Figure 7A).^{10g-10j} Meanwhile, there existed multiple intermolecular C-H…F interactions formed between the $-C_6F_5$ termini and the phenyl units (Figure 7B). According to the calculation results based on crystal structure, the complexation energy of the present dimer is up to ~44 kcal/mol (Figure S23), indicative of a particularly solid structure. Here, according to the calculated results, we can see that the strong aurophilic interactions play a pivotal role to stabilize the dimer and the multiple C-H…F interactions provide synergistic contributions (Figure S23). Furthermore, the adjacent dimers connect through multiple C-H…F interactions to form a hand-in-hand layer (Figure 7B-7D). Regarding the (S,S)-1 crystal, completely similar situations could be found (Figures S24 and S25). In view of this, combined with the impressive phenomena we observed above, it could be reasonably proposed that such attractive aurophilic interactions together with multiple C-H…F interactions would undoubtedly form a powerful force driving the molecules to reorganize and arrange along distinct directions to form ordered architectures. This may help explain why the original randomly-oriented crystallites of (R,R)-1 and (S,S)-1 powders

could readily rearrange and assemble into micron-sized microcrystals under the stimulation of external force. In another aspect, once such solid layers formed, they are considered not easy to be perturbed by additional external factors such as force or even heating. This might be the reason why we did not observe any crystal phase transitions from the XRD patterns after scratching or heating their powder or crystals. In sharp contrast, there are only very weak π - π interactions between the neighboring layers thus resulting in their loose layer-by-layer stacking (Figures S26 and S27). This might endow (*R*,*R*)-1 and (*S*,*S*)-1 with sensitive responses to external perturbation.

To gain further insight into the related mechanism, the data of the non-emissive crystal of (R,R)-1 at RT were compared with those of at 213 K and 100 K and that of emissive crystal at RT. As illustrated in Figure 7E-7I and Table 1, a series of parameters for the present system were tentatively defined to represent and compare the degree of variation within layers and between layers. According to the pertinent data depicted in Table 1, all the parameters of the non-emissive crystal at RT are very close to those of the yellow-emissive crystal at the same temperature. In addition, four prominent changes of the non-emissive crystal with temperature decline were summarized: 1) the crystal system and the space group remained unchanged, while the unit cell (V) underwent obvious shrinkage and the two Au···Au distances $(d_{Au \cdot \cdot Au})$ became shorter suggesting more stronger aurophilic interactions, 2) each molecular layer was compressed and its thickness $(T_{\rm L})$ became smaller, and 3) comparatively, the space between the two adjacent layers ($d_{\rm L}$ and $d_{\rm p,n}$) underwent more noticeable reduction than the layer thickness. In addition,

obvious sliding occurred between the neighboring layers (Θ and ΔL). It should be mentioned that the tendencies for the parameter change of (*S*,*S*)-1 crystal with temperature are also

similar to those we summarized above (Figure S28B and Table S3).



Figure 7. (A) Intermolecular Au···Au, C–H···F interactions in the dimer and (B) intermolecular C–H···F interactions between dimers of (R,R)-1 crystal (non-emissive, crystallization from DCM/hexane) at 294 K. (C and D) Intermolecular packings of (R,R)-1 crystal (non-emissive, crystallization from DCM/hexane) in different views (C: side view, D: front view) at 294 K. (E-I) Illustration of different crystal parameters of (R,R)-1 crystals defined in Table 1 to show subtle differences among different crystals obtained from different conditions and at different temperatures. Specific definition of these parameters has been shown in the footnotes in Table 1 and comparative data have been presented in Table 1.

	Parameter	Non-emissive cystal (Xtal,n; DCM/Hexane)			Emissive crystal (Xtal,e; DCM/EtOH)
		294 K	213 K	100 K	294 K
	Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
	Space group	$P2_1$	$P2_1$	$P2_1$	$P2_1$
	Final R indices	0.0329	0.0385	0.0364	0.0394
	a [Å]	12.5557(2)	12.520(3)	12.430(3)	12.5655(3)
	<i>b</i> [Å]	7.79490(14)	7.6887(18)	7.6204 (19)	7.79233(17)
	<i>c</i> [Å]	28.3004(5)	28.217(4)	28.2096(6)	28.3028(7)
	$V[Å^3]$	2743.34(8)	2692.4(9)	2651.83(11)	2744.80(12)
	$d_{\rm Au \cdots Au}$ [Å]	3.197, 3.291	3.177, 3.250	3.157, 3.220	3.196, 3.289
	$T_{\rm L}{}^{b}$ [Å]	5.610	5.567 (0.77%) ^c	5.580 (0.54%) ^c	5.600
	$d_{\mathrm{L}^{d}}[\mathrm{\AA}]$	6.614	$6.542 (1.09\%)^{e}$	$6.488 (1.91\%)^{e}$	6.613
		$3.394 (d_{p,1})$	$3.379(d_{\rm p,1})$	$3.355(d_{\rm p,1})$	$3.385 (d_{p,1})$
	7 (5%)	$3.406 (d_{p,2})$	$3.342 (d_{p,2})$	$3.280 (d_{p,2})$	$3.366 (d_{p,2})$
	$a_{\mathrm{p,n'}}$ [A]	$3.413 (d_{p,3})$	$3.373 (d_{p,3})$	$3.385 (d_{p,3})$	$3.447 (d_{p,3})$
		$3.344 (d_{p,4})$	$3.315(d_{p,4})$	$3.245 (d_{p,4})$	$3.343 (d_{p,4})$
	$\Theta^{g}[^{\circ}]$	47.67	$48.27 (1.26\%)^{h}$	$48.73 (2.22\%)^{h}$	47.68
	ΔL^{i} [Å]	4.11	4.02 (-2.19%) ^y	3.98 (-3.16%) ^y	4.11

Table 1. Comparison of crystal parameters of (R,R)-1 crystals obtained from different conditions and at different temperatures.^{*a*}

^a All parameters were illustrated in Figure 7. Non-emissive cystal = Xtal,n; Emissive crystal = Xtal,e. ^b Thickness of layer. ^c

 $\Delta T_{\rm L}/T_{\rm L,294} = (T_{\rm L,t} - T_{\rm L,294})/T_{\rm L,294}. \ ^d \text{ Distance between the central horizontal planes of the two adjacent layers. } ^e \Delta d_{\rm L}/d_{\rm L,294} = (d_{\rm L,t} - d_{\rm L,294})/d_{\rm L,294}. \ ^f \text{ Distance between the two closer atoms in } \pi - \pi \text{ interactions. } ^g \text{ Angle of peak to trough in dimers (Figure S28A). } ^h \Delta \Theta / \Theta_{294} = (\Theta_{\rm t} - \Theta_{294})/\Theta_{294}. \ [i] \Delta L = [b^2 - a^2 b^2/(a^2 + b^2)]^{1/2}. \ ^j \Delta (\Delta L)/\Delta L_{294} = (\Delta t_{\rm t} - \Delta L_{294})/\Delta L_{294}.$

Herein, taking all the data together enabled us to rationalize the mechanisms of all the mysterious phenomena observed above. As illustrated in Figure 8, the molecules of (R,R)-1 and (S,S)-1 showed (I) a natural tendency to form solid dimers driven by the strong aurophilic interactions and multiple C-H...F interactions. These dimers further connected with each other to form stable molecular layers through multiple C-H...F interactions. (II) Loose stackings via weak π - π interactions exist between layers and they are more sensitive to external perturbation than the interactions formed within the layers. (III) Thus, once triggered by external force, the neighboring layers will slide in a manner similar to the filament sliding accompanied with a certain extent of compression within layers. Here, we used a familiar filament sliding model of muscle motion as an analogy to better illustrate this subtle change.¹⁸ Accordingly, such subtle molecular motions similar to filament sliding are not enough to induce crystal phase transition but could result in the dramatic conversion between the non-radiative state and the radiative state thus causing an off-to-on luminescent switching. It should be mentioned that we also found that the scratching is much more effective than the high pressure to induce the

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turn-on luminescence. These results in turn reinforce the sliding mechanism we proposed above given that anisotropic shearing force is much easier to trigger the sliding between the layers. In another aspect, the unique aurophilic interactions together with multiple C-H…F interactions also endow the molecules of (R,R)-1 and (S,S)-1 with a natural tendency to reorganize and form ordered structures. This should be the reason why the disordered crystallites of (R,R)-1 and (S,S)-1 powders can transform to well-defined microcystals under the stimulation of mechanical force.

Given that (R,R)-1 and (S,S)-1 are chiral and they all exhibits unique mechano-induced PL behaviors, their chiroptical properties were tentatively investigated by conducting circular polarized luminescence (CPL) measurements. As demonstrated in Figure S29, we observed completely mirror circurlar dichroism signals of their ground powders with appropriate intensity. Delightfully, their ground powders also presented clear mirror-image CPL signals with luminescence dissymmetry factors (Ig_{lum}I) of 4×10^{-3} . These results demonstrate that we can realize the output of CPL by tuning the solid-state molecular motions.



Figure 8. Schematic illustration of the proposed force-induced solid-state molecular motion and luminescence mechanism.

CONCLUSIONS

In conclusion, two new chiral AIE-active Au(I) complexes were designed and synthesized, and it has been well demonstrated that the morphology of their powders could realize a dramatic transformation from disordered crystallites to well-defined microcrystals by *in-situ* scratching. Such a phononmenon could be visulized by the turn-on phosphorescence signal and was proposed to be caused by molecular motions driven by the formation of dominant strong aurophilic interactions as well as multiple C-H…F and π - π interactions. The non-emissive crystals of these two

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complexes also showed a similar off/on luminescent switching triggered by mechanical force. Such macroscopically remarkable changes were mainly originated from very subtle molecular motions showing a layer-by-layer filament sliding occurred in molecular stackings accompanied with a certain extent of compression within molecular layers. Thus, these processes do not involve any crystal phase transitions. The ground powders of these chiral complexes were also found to show CPL signals with Ig_{lum}I values of 4×10^{-3} . Therefore, the present systems well demonstrated that extraordinary construction of ordered structures approaching the elegance of 10 life process could be realized by simple manipulation of 11 solid-state molecular motions. The subtle changes of 12 molecular motion could also bring about dramatic 13 macroscopic alterations of morphology and photophysical 14 properties. It is anticipate that this work provides new insights 15 into the exploration of molecular motions in the solid state and 16 offers more inspirations to researchers to effectively exploit 17 solid-state molecular motions to do meaningful work. 18

ASSOCIATED CONTENT

Supporting Information

Materials and methods, computational details, synthetic procedures, crystallographic data and characterizations are available in the supporting information.

This material is available free of charge on the ACS Publications website.

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Notes

The authors declare no competing financial interest.

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