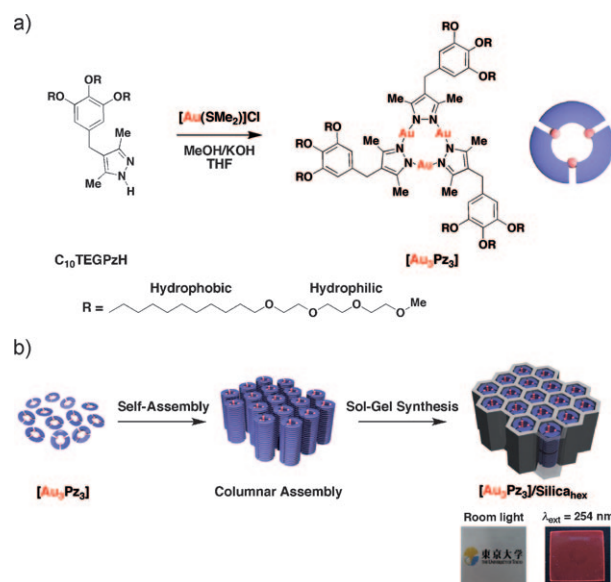


# Self-Repair of a One-Dimensional Molecular Assembly in Mesoporous Silica by a Nanoscopic Template Effect\*\*

Hendrik O. Lintang, Kazushi Kinbara,\* Kenichi Tanaka, Takashi Yamashita, and Takuzo Aida\*

Self-healing phenomena are attracting much attention for developing sustainable structural materials;<sup>[1]</sup> extensive studies have been reported on polymeric materials capable of self-repairing macroscopic fractures or recovering lost mechanical strengths.<sup>[2]</sup> On the other hand, for exploiting molecular devices that can self-repair elaborate functions, different problems may be encountered that originate from much smaller size regimes. For example, design of self-repairable optoelectronic devices, which are potentially important for sensor and display applications,<sup>[3,4]</sup> certainly requires a particular trick to realize self-reconstruction of elaborate molecular geometries for electronic communication. However, no rational strategies have yet been proposed for addressing this challenging issue.

As the first step toward this goal, we report herein that a cylindrical assembly of a trinuclear gold(I) pyrazolate complex,  $[\text{Au}_3\text{Pz}_3]$  (Figure 1a),<sup>[5]</sup> when confined in a one-dimensional silicate channel (Figure 1b), shows self-repairable luminescence properties owing to a nanoscopic template effect. The luminescence center of this assembly (Figure 1a) adopts a chair-like coordination geometry<sup>[5h,j]</sup> of polymeric  $[\text{Au}_3\text{Pz}_3]$  formed by a  $\text{Au}^{\text{I}}-\text{Au}^{\text{I}}$  metallophilic interaction. As this interaction is only as strong as a hydrogen-bonding interaction,<sup>[5c]</sup> the cylindrical assembly can easily be disrupted upon heating and lose its luminescence capability. However,



**Figure 1.** a) Synthesis and molecular structure of  $[\text{Au}_3\text{Pz}_3]$ . b) Sol-gel synthesis of  $[\text{Au}_3\text{Pz}_3]/\text{silica}_{\text{hex}}$ , a mesostructured silica with a hexagonal geometry templated by columnar assembly of  $[\text{Au}_3\text{Pz}_3]$ . Photographs were taken at room temperature under room light (lower left) and on exposure to ultraviolet light at 254 nm (lower right).

we found that the thermal resistivity of the luminescence capability is enhanced when the assembly is confined into nanoscopic channels of mesoporous silica (Figure 1b). Furthermore, the luminescence that was lost upon heating is autonomously recovered to 100 % when the material is held at 20 °C.

To incorporate the cylindrical assembly of  $[\text{Au}_3\text{Pz}_3]$  into nanoscopic silicate channels, we employed the sol-gel synthesis of mesoporous silica templated by rod micelles of surfactants.<sup>[6]</sup> In 2001, we<sup>[7]</sup> and other groups<sup>[8]</sup> demonstrated that, by using functional amphiphiles as templates, a variety of organic functionalities can be incorporated into nanoscopic channels of the resulting mesoporous silica.<sup>[9]</sup> In contrast to post-functionalization,<sup>[10]</sup> this method ensures dense filling of the silicate channels with organic functional groups.<sup>[9]</sup> Herein, we newly synthesized  $[\text{Au}_3\text{Pz}_3]$  (Figure 1a), which is an amphiphilic version of the metal pyrazolate complexes designed for phosphorescent organogels<sup>[5i]</sup> and liquid crystalline assemblies<sup>[5j]</sup> with metallophilic interactions. For the synthesis of  $[\text{Au}_3\text{Pz}_3]$ , the pyrazole ligand  $\text{C}_{10}\text{TEGPzH}$  was prepared (Supporting Information, Scheme S1)<sup>[11]</sup> and allowed to react with  $[\text{Au}(\text{Me}_2\text{S})]\text{Cl}$  in  $\text{THF}/\text{MeOH}$  in the presence of  $\text{KOH}$  at room temperature.<sup>[5g,i]</sup> After being stirred for 12 h, the reaction mixture was subjected to preparative

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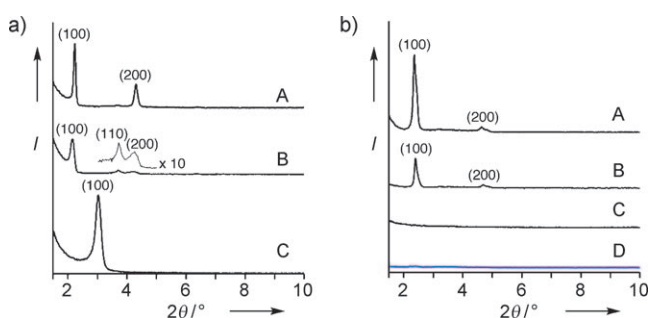
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size-exclusion chromatography to allow isolation of  $[\text{Au}_3\text{Pz}_3]$  as a pale yellow sticky solid.<sup>[11]</sup> X-ray diffraction (XRD) analysis, polarized optical microscopy (POM), and differential scanning calorimetry (DSC) indicated that bulk  $[\text{Au}_3\text{Pz}_3]$  is liquid crystalline, with a discotic lamellar mesophase at  $-3$ – $44^\circ\text{C}$ .<sup>[11]</sup> For the sol–gel synthesis of the silica composite  $[\text{Au}_3\text{Pz}_3]/\text{silica}_{\text{hex}}$  with a hexagonal geometry (Figure 1b), an acidic aqueous EtOH solution (EtOH, 29 mg, 0.6 mmol; HCl, 12 M, 0.15 mg,  $1.5 \times 10^{-3}$  mmol;  $\text{H}_2\text{O}$ , 6 mg, 0.3 mmol) of a mixture of  $[\text{Au}_3\text{Pz}_3]$  (5 mg,  $1.25 \times 10^{-3}$  mmol) and tetrabutoxysilane (TBOS, 24 mg,  $74.9 \times 10^{-3}$  mmol) was held for 12 h at room temperature ( $[\text{Au}_3\text{Pz}_3]/[\text{TBOS}]/[\text{EtOH}]/[\text{HCl}]/[\text{H}_2\text{O}] = 1:60:504:1.2:266$ ), upon which partial oligomerization of TBOS took place. The resulting viscous solution (20  $\mu\text{L}$ ) was spin-coated on a quartz plate at 3000 rpm for 15 s, affording a colorless transparent film (Figure 1b, lower left), which was then dried in air for 24 h at room temperature and additional 12 h at  $40^\circ\text{C}$ .  $[\text{Au}_3\text{Pz}_3]$  is tolerant against acidolysis under the applied sol–gel conditions and forms a columnar assembly by a  $\text{Au}^{\text{I}}\text{–Au}^{\text{I}}$  metallophilic interaction, as the acidic aqueous EtOH solution of  $[\text{Au}_3\text{Pz}_3]$ , used for the sol–gel synthesis with TBOS, was luminescent at 706 nm ( $\lambda_{\text{ext}} = 276$  nm), which is characteristic of the metallophilic interaction.<sup>[11]</sup>

A powder sample of  $[\text{Au}_3\text{Pz}_3]/\text{silica}_{\text{hex}}$ , obtained by scratching off the as-synthesized spin-coated film, has XRD peaks with  $2\theta = 2.16^\circ$ ,  $3.70^\circ$ , and  $4.30^\circ$ , which were indexed as  $d_{100}$ ,  $d_{110}$ , and  $d_{200}$ , respectively, of a hexagonal structure with an intercore distance of 4.1 nm (Figure 2a, B). On the other hand, the as-synthesized spin-coated film of  $[\text{Au}_3\text{Pz}_3]/\text{silica}_{\text{hex}}$  has XRD peaks due to  $d_{100}$  and  $d_{200}$  but not for  $d_{110}$  (Figure 2a, A), indicating that the  $c$  axis of the hexagonal unit cell is oriented parallel to the quartz surface.<sup>[8a,9a–c,f,12]</sup> Transmission electron microscopy (TEM) of a cross-section of the as-synthesized spin-coated film allowed the hexagonally aligned nanopores to be visualized (Supporting Information, Figure S4). Computer-assisted molecular modeling suggests that the core part of  $[\text{Au}_3\text{Pz}_3]$  is approximately 2 nm in diameter. Considering the coordination geometry of the luminescence center,<sup>[5b,j]</sup> along with a large volume of its side chains, the intercore distance as evaluated by XRD seems to be quite reasonable for an assumption that each silicate channel

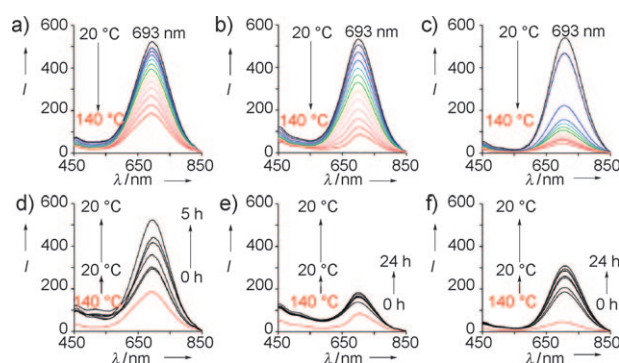


**Figure 2.** X-ray diffraction patterns of a)  $[\text{Au}_3\text{Pz}_3]/\text{silica}_{\text{hex}}$  and b)  $[\text{Au}_3\text{Pz}_3]/\text{silica}_{\text{lam}}$ . A) As-synthesized spin-coated films, B) powder samples obtained by scratching off the spin-coated films, C) spin-coated films after calcination at  $450^\circ\text{C}$  for 3 h, and D) a spin-coated film of  $[\text{Au}_3\text{Pz}_3]/\text{silica}_{\text{lam}}$  after heating at  $140^\circ\text{C}$  for 10 min (blue curve).

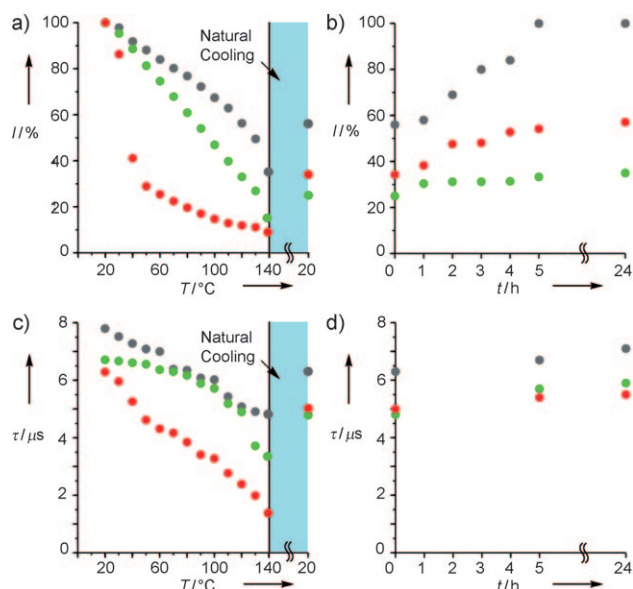
accommodates only one cylindrical assembly of  $[\text{Au}_3\text{Pz}_3]$ . The organic content in  $[\text{Au}_3\text{Pz}_3]/\text{silica}_{\text{hex}}$ , as evaluated by thermogravimetric analysis (TGA), was 41 %, which is typical of as-synthesized mesoporous silica containing organic templates.<sup>[7–9]</sup> Of note, when the molar ratio of TBOS to  $[\text{Au}_3\text{Pz}_3]$  was decreased from 60:1 to 20:1 (TBOS, 8 mg,  $25 \times 10^{-3}$  mmol), a lamellar structure ( $[\text{Au}_3\text{Pz}_3]/\text{silica}_{\text{lam}}$ ) formed with an interlayer distance of 3.7 nm (Figure 2b, A,B).

Upon exposure to 254 nm UV light with a hand-held lamp,  $[\text{Au}_3\text{Pz}_3]/\text{silica}_{\text{hex}}$  adopting a hexagonal geometry emitted red light (Figure 1b, lower right) with a luminescence center ( $\lambda_{\text{em}}$ ) at 693 nm.<sup>[11]</sup> Monitoring the emission at 693 nm provided an excitation spectrum with a peak maximum at 276 nm,<sup>[11]</sup> indicating a very large Stokes shift ( $\Delta\lambda = 417$  nm) of the luminescence. Also noteworthy is a long lifetime of this luminescence, which was evaluated as  $\tau_{20} = 7.8$   $\mu\text{s}$  at  $20^\circ\text{C}$  by means of transient emission spectroscopy upon laser excitation at 266 nm.<sup>[11]</sup> These spectral features are characteristic of phosphorescing events from metal-centered triplet excited states modified with a  $\text{Au}^{\text{I}}\text{–Au}^{\text{I}}$  metallophilic interaction.<sup>[5]</sup> Virtually identical phosphorescence properties were observed for a bulk material of assembled  $[\text{Au}_3\text{Pz}_3]$  ( $\lambda_{\text{em}} = 690$  nm,  $\tau_{20} = 6.3$   $\mu\text{s}$ )<sup>[11]</sup> and silica composite  $[\text{Au}_3\text{Pz}_3]/\text{silica}_{\text{lam}}$  adopting a lamellar geometry ( $\lambda_{\text{em}} = 690$  nm,  $\tau_{20} = 6.7$   $\mu\text{s}$ ).<sup>[11]</sup> Therefore, the photochemical properties of the cylindrical assembly of  $[\text{Au}_3\text{Pz}_3]$  are essentially maintained in both hexagonal and lamellar silicates.

The bulk material of assembled  $[\text{Au}_3\text{Pz}_3]$  became much less emissive upon heating (Figure 3c). For example, when this material was heated stepwise from  $20^\circ\text{C}$  to 40, 80, 120, and  $140^\circ\text{C}$ , the phosphorescence was progressively less intensified to 41, 20, 12, and 9 %, respectively, of its original intensity (Figure 4a, red). Likewise, the silica composite  $[\text{Au}_3\text{Pz}_3]/\text{silica}_{\text{hex}}$  with a hexagonal geometry was less emissive upon elevating the temperature (Figure 3a). However, the temperature dependency of its luminescence capability was much smaller than that of bulk  $[\text{Au}_3\text{Pz}_3]$  without silica. For example, upon heating to 80 and  $120^\circ\text{C}$ ,  $[\text{Au}_3\text{Pz}_3]/\text{silica}_{\text{hex}}$  retained even 77 and 56 % of its original luminescence intensity, respectively (Figure 4a, gray). Although the light-emitting capability of  $[\text{Au}_3\text{Pz}_3]/\text{silica}_{\text{lam}}$  with a lamellar



**Figure 3.** Luminescence spectral changes ( $\lambda_{\text{ext}} = 276$  nm) of a,d)  $[\text{Au}_3\text{Pz}_3]/\text{silica}_{\text{hex}}$ , b,e)  $[\text{Au}_3\text{Pz}_3]/\text{silica}_{\text{lam}}$ , and c,f) bulk  $[\text{Au}_3\text{Pz}_3]$  on stepwise heating from 20 to  $140^\circ\text{C}$  (red curve in (a)–(c)) and subsequent natural cooling from 140 to  $20^\circ\text{C}$ , then being held at the same temperature for 24 h (black curves in (d)–(f)).



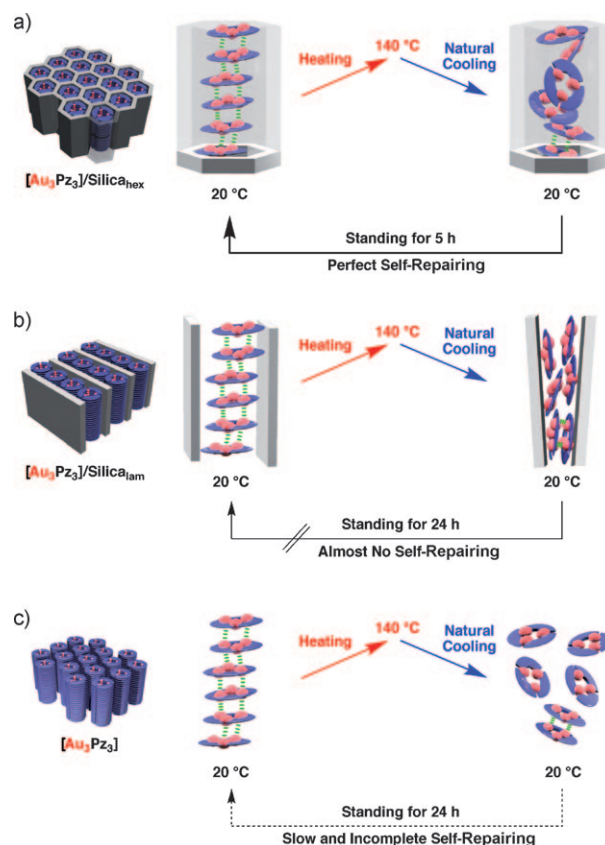
**Figure 4.** Changes in a,b) emission intensities (normalized) at 693 nm ( $\lambda_{\text{ext}} = 276$  nm) and c,d) luminescence lifetimes at 690 nm ( $\lambda_{\text{ext}} = 266$  nm) of [Au<sub>3</sub>Pz<sub>3</sub>]/silica<sub>hex</sub> (gray), [Au<sub>3</sub>Pz<sub>3</sub>]/silica<sub>lam</sub> (green), and bulk [Au<sub>3</sub>Pz<sub>3</sub>] (red) on a,c) stepwise heating from 20 to 140 °C followed by natural cooling from 140 to 20 °C and b,d) being held at 20 °C for 24 h after natural cooling from 140 °C.

geometry had a better heat resistivity (Figure 4a, green) than that of bulk [Au<sub>3</sub>Pz<sub>3</sub>] (Figure 4a, red), it was obviously inferior to that of [Au<sub>3</sub>Pz<sub>3</sub>]/silica<sub>hex</sub> adopting a hexagonal geometry (Figure 4a, gray).

In general, luminescent materials can lose the light-emitting capability upon heating owing to thermal quenching of the photoexcited state. Thermal quenching results in shortening the luminescence lifetime. In fact, we confirmed that the luminescence lifetimes of our materials all change in response to an applied sequence of temperature changes (Figure 4c,d). For example, when the temperature was varied from 20 to 140 to 20 °C and then held at 20 °C for 24 h, the luminescence lifetime changed from 6.3 → 1.4 → 5.0 → 5.5 μs for [Au<sub>3</sub>Pz<sub>3</sub>] (red), 7.8 → 4.8 → 6.3 → 7.1 μs for [Au<sub>3</sub>Pz<sub>3</sub>]/silica<sub>hex</sub> (gray), and 6.7 → 3.4 → 4.8 → 5.9 μs for [Au<sub>3</sub>Pz<sub>3</sub>]/silica<sub>lam</sub> (green). If the observed luminescence loss upon heating is induced only by thermal quenching of the photoexcited state, lowering the temperature could coincidentally result in complete restoration of the original luminescence intensity. However, all the materials, on cooling from 140 to 20 °C, displayed only a partial recovery of the luminescence intensity (Figure 4a, blue bar area): 9% → 35% for [Au<sub>3</sub>Pz<sub>3</sub>] (red), 35% → 56% for [Au<sub>3</sub>Pz<sub>3</sub>]/silica<sub>hex</sub> (gray), and 15% → 25% for [Au<sub>3</sub>Pz<sub>3</sub>]/silica<sub>lam</sub> (green). Therefore, it is likely that the luminescence loss upon heating is more or less caused by a thermally induced structural damage of the cylindrical assembly of [Au<sub>3</sub>Pz<sub>3</sub>].

In the course of the above study, we noticed that the bulk material of assembled [Au<sub>3</sub>Pz<sub>3</sub>], when allowed to stand at 20 °C after heating to 140 °C, the luminescence intensity slowly recovers (Figure 3f). Such a dynamic recovery may be one of the inherent features of soft materials. However, this

event subsided in 4 h to furnish a 35% → 54% recovery of its original luminescence intensity (Figure 4b, red). To our surprise, silica composite [Au<sub>3</sub>Pz<sub>3</sub>]/silica<sub>hex</sub> displayed perfect self-restoration of the phosphorescing capability (Figure 3d). After an identical thermal treatment to that for [Au<sub>3</sub>Pz<sub>3</sub>], the phosphorescence of [Au<sub>3</sub>Pz<sub>3</sub>]/silica<sub>hex</sub>, when held at 20 °C, gained from 56% to 80% of its original intensity in only 3 h and then intensified further to 100% after 5 h (Figure 4b, gray). This autonomous recovery indicates the occurrence of complete reconstruction of the chair-like coordination geometry<sup>[5b,j]</sup> of polymeric [Au<sub>3</sub>Pz<sub>3</sub>] for light emission in the nanoscopic silicate channels (Figure 5a). In contrast,



**Figure 5.** Schematic representations of the effects of heating on columnar assembled [Au<sub>3</sub>Pz<sub>3</sub>] confined within a) silicate nanochannels ([Au<sub>3</sub>Pz<sub>3</sub>]/silica<sub>hex</sub>), b) silicate layers ([Au<sub>3</sub>Pz<sub>3</sub>]/silica<sub>lam</sub>), and c) in the absence of silica as a reference.

[Au<sub>3</sub>Pz<sub>3</sub>]/silica<sub>lam</sub> adopting a lamellar geometry (Figure 3e), when held at 20 °C after heating, recovered from 25% up to only 35% of its original luminescence intensity after 24 h (Figure 4b, green). Namely, the lamellar silicate gives rise to a negative effect on the reconstruction of the luminescent geometry.

For the contrasting effects of the hexagonal and lamellar silicate structures on the self-repairing luminescence events, we assume if these two inorganic frameworks may possess different thermal resistivities from one another. In fact, even after calcination at 450 °C for 3 h, a film sample of [Au<sub>3</sub>Pz<sub>3</sub>]/silica<sub>hex</sub> still showed a diffraction pattern assignable to the



hexagonal geometry (Figure 2a, C). The only observation was the substantial reduction of the interpore distance between the hexagonal channels from 4.1 to 2.9 nm ( $2\theta = 2.90^\circ$  and  $5.00^\circ$  from  $2.16^\circ$  and  $4.30^\circ$ , respectively). In sharp contrast, upon calcination of  $[\text{Au}_3\text{Pz}_3]/\text{silica}_{\text{lam}}$  at  $450^\circ\text{C}$ , its lamellar structure was completely disrupted, and the characteristic XRD peaks of the sample disappeared (Figure 2b, C). Of note, such a structural crash took place even when  $[\text{Au}_3\text{Pz}_3]/\text{silica}_{\text{lam}}$  was just heated at  $140^\circ\text{C}$  for 10 min (Figure 2b, D). This observation suggests that the crashed silicate layers hamper reconstruction of the elaborate molecular geometry<sup>[5h,j]</sup> for light emission (Figure 5b).

Finally, it is worthy to discuss why  $[\text{Au}_3\text{Pz}_3]/\text{silica}_{\text{hex}}$  shows a much better self-repairing capability than bulk  $[\text{Au}_3\text{Pz}_3]$ . Previously, we have reported that a dendritic version of  $[\text{Cu}_3\text{Pz}_3]$  without triethylene glycol (TEG) segments, upon natural cooling from its hot melt to  $20^\circ\text{C}$ , forms a kinetically trapped glassy state, where the copper(I) pyrazolate core is left unstacked.<sup>[5j]</sup> On the other hand, upon annealing this glassy material at  $40\text{--}50^\circ\text{C}$ , the lost luminescence is gradually recovered, as the paraffinic side chains of the copper(I) complex melt and allow its copper(I) pyrazolate core to stack thermodynamically. Judging from the DCS profile,<sup>[11]</sup> a similar kinetic event, resulting in trapping a thermally damaged structure, is expected for bulk  $[\text{Au}_3\text{Pz}_3]$ . In fact, when bulk  $[\text{Au}_3\text{Pz}_3]$ , kept at  $20^\circ\text{C}$  after natural cooling from its hot melt, was annealed at  $40^\circ\text{C}$ , the lost luminescence was recovered almost perfectly in 25 minutes (Supporting Information, Figure S13).<sup>[11]</sup> Considering that the glassy state is formed mainly by strong association of the paraffinic parts of the side chains,  $[\text{Au}_3\text{Pz}_3]$  incorporated into the silica channel ( $[\text{Au}_3\text{Pz}_3]/\text{silica}_{\text{hex}}$ ) could possess a different kinetic profile from its bulk state. The TEG segments of the side chains of  $[\text{Au}_3\text{Pz}_3]$  are likely to be anchored to the silica wall by interpenetration.<sup>[13]</sup> We consider that this anchoring could suppress the strong association of the paraffinic domains upon cooling from its hot melt but may direct the gold(I) pyrazolate core to stack one-dimensionally (template effect). Consequently,  $[\text{Au}_3\text{Pz}_3]/\text{silica}_{\text{hex}}$  can self-repair even at  $20^\circ\text{C}$ .

In conclusion, by using the trinuclear gold(I) pyrazolate complex  $[\text{Au}_3\text{Pz}_3]$  as a self-assembling motif, we demonstrated that the nanoscopic channels of mesoporous silica not only protect included one-dimensional molecular assemblies against thermal disruption but also strongly encourage them to self-recover from a heat-induced structural damage. This phenomenon may be referred to as a nanoscopic template effect that involves both thermodynamic and entropic aspects. Considering the negative effect of lamellar silica ( $[\text{Au}_3\text{Pz}_3]/\text{silica}_{\text{lam}}$ ), the high thermal resistivity of mesoporous silica with a hexagonal geometry is of prime importance for the perfect self-repairing nature of  $[\text{Au}_3\text{Pz}_3]/\text{silica}_{\text{hex}}$ . Furthermore, we consider that the dimensional host–guest size/shape matching must be another primary factor. The present work may also shed light on a practical issue of how the high reliability of molecular devices can be ensured for long-term operation.

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