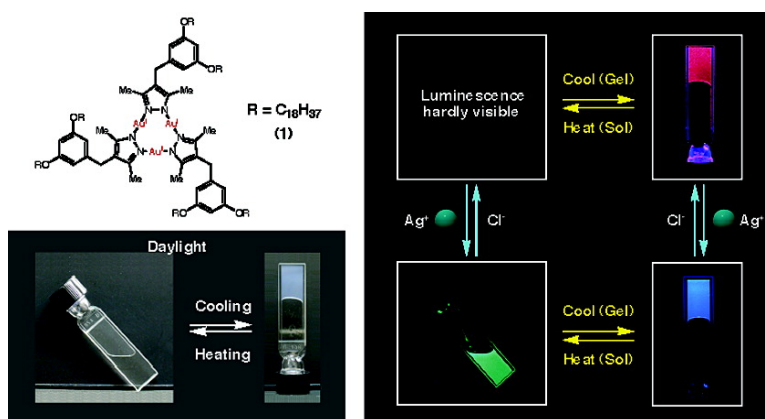


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Akihiro Kishimura, Takashi Yamashita, and Takuzo Aida

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## Phosphorescent Organogels via “Metallophilic” Interactions for Reversible RGB–Color Switching

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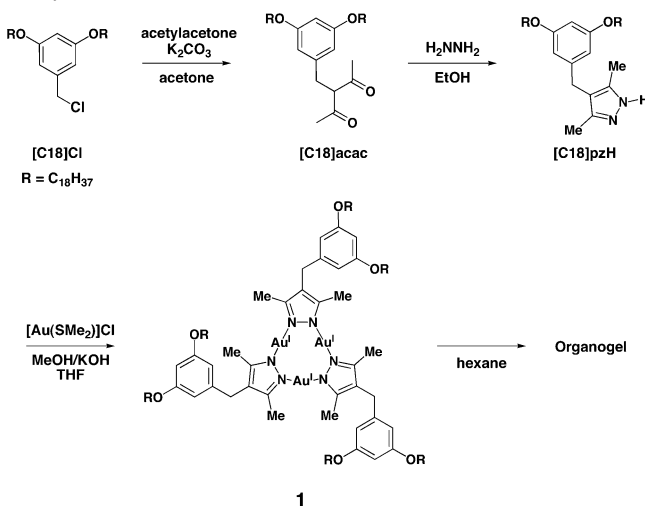
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**Abstract:** A trinuclear Au(I) pyrazolate complex bearing long alkyl chains (**1**) in hexane self-assembles via a Au(I)–Au(I) metallophilic interaction, to form a red-luminescent organogel ( $\lambda_{em} = 640$  nm,  $\lambda_{ext} = 284$  nm). Scanning electron microscopy (SEM) and X-ray diffraction (XRD) analysis of an air-dried gel with **1** show the presence of heavily entangled fibers, each consisting of a rectangularly packed columnar assembly of **1**. Doping of the organogel with a small amount of Ag<sup>+</sup> results in a blue luminescence ( $\lambda_{em} = 458$  nm,  $\lambda_{ext} = 370$  nm) without disruption of the gel, while removal of doped Ag<sup>+</sup> with cetyltrimethylammonium chloride results in complete recovery of the original red-luminescent gel. Upon heating, these organogels undergo gel-to-sol transition due to the destabilization of the metallophilic interactions, where the red luminescence of the nondoped system becomes hardly visible, while the blue luminescence of the Ag<sup>+</sup>-doped system turns green ( $\lambda_{em} = 501$  nm,  $\lambda_{ext} = 370$  nm). On cooling, these solutions undergo gelation and synchronously recover the original luminescences. The observed RGB (red–green–blue) luminescences are all long-lived (3–6  $\mu$ s) and assigned to electronic transitions from triplet-excited states.

### Introduction

In general, phosphorescence is characterized by its longer lifetime and higher luminescence quantum yield than fluorescence. Therefore, phosphorescent materials that are capable of reversibly changing their luminescence colors are interesting in application for sensors<sup>1</sup> and displays.<sup>2</sup> Although there have been reported a variety color-tunable fluorescent materials in response to physical and chemical stimuli, only a few examples of phosphorescent materials with such color-tuning capabilities have been reported,<sup>3</sup> since compounds that can phosphoresce at ambient temperatures are limited.<sup>4</sup> Here we report a novel phosphorescent organogel formed with trinuclear Au(I) pyrazolate complex **1** (Scheme 1) via a Au(I)–Au(I) metallophilic interaction, where the luminescence color can be changed

### Scheme 1. Schematic Representation of Synthesis of Au(I) Complex 1



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<sup>§</sup> Japan Science and Technology Agency.

- (1) Demas, J. N.; DeGraff, B. A. *Coord. Chem. Rev.* **2001**, *211*, 317–351.
- (2) Baldo, M. A.; O'Brien, D. F.; You, Y.; Shoustikov, A.; Sibley, S.; Thompson, M. E.; Forrest, S. R. *Nature* **1998**, *395*, 151–154.
- (3) Recent examples: (a) Dias, H. V. R.; Diyabalanage, H. V. K.; Rawashdeh-Omary, M. A.; Franzman, M. A.; Omary, M. A. *J. Am. Chem. Soc.* **2003**, *125*, 12072–12073. (b) White-Morris, R. L.; Olmstead, M. M.; Balch, A. L. *J. Am. Chem. Soc.* **2003**, *125*, 1033–1040.
- (4) (a) Tsuzuki, T.; Shirakawa, N.; Suzuki, T.; Tokito, S. *Adv. Mater.* **2003**, *15*, 1455–1458. (b) Tsuboyama, A.; Iwawaki, H.; Furugori, M.; Mukaiide, T.; Kamatani, J.; Igawa, S.; Moriyama, T.; Miura, S.; Takiguchi, T.; Okada, S.; Hoshino, M.; Ueno, K. *J. Am. Chem. Soc.* **2003**, *125*, 12971–12979. (c) Coppo, P.; Plummer, A. P.; De Cola, L. *Chem. Commun.* **2004**, 1774–1775. (d) Wang, Q.-M.; Lee, Y.-A.; Crespo, O.; Deaton, J.; Tang, C.; Gysling, H. J.; Gimeno, M. C.; Larraz, C.; Villacampa, M. D.; Laguna, A.; Eisenberg, R. *J. Am. Chem. Soc.* **2004**, *126*, 9488–9489.

synchronously to thermoreversible sol–gel transition and doping/dedoping of Ag<sup>+</sup>. Metallophilic interactions are known to operate among closed-shell group 11 metal ions such as Au(I), Ag(I), and Cu(I), where the  $\Delta G$  values with Au(I), for example, are as large as those of hydrogen-bonding interactions.<sup>5</sup> Another important aspect of metallophilic interactions is that they can provide phosphorescent solids or crystalline metal complexes,<sup>3,6</sup>

(5) Pyykkö, P. *Chem. Rev.* **1997**, *97*, 597–636.

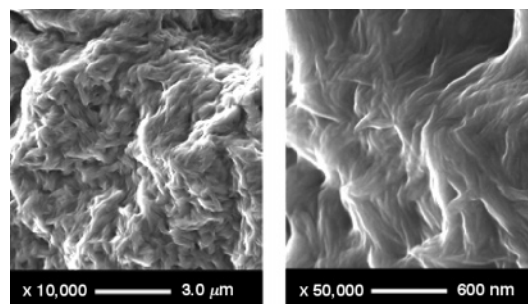
some of which serve as potential EL materials.<sup>7</sup> We have reported that trinuclear dendritic pyrazolate complexes of group 11 metal ions self-assemble in paraffinic solvents via metallophilic interactions to give luminescent superhelical fibers.<sup>8</sup> More recently, Omary and co-workers have reported that a Cu(I) bis-(trifluoromethyl)pyrazolate complex in frozen solvents at 77 K self-assembles via a metallophilic interaction and becomes phosphorescent,<sup>3a</sup> where the phosphorescence color can be tuned by changing the solvent and concentration. Balch and co-workers have reported similar phenomena for a Au(I) isocyanide complex in several frozen solvents at 77 K.<sup>3b</sup> In the present work, we synthesized a novel Au(I) pyrazolate complex carrying long octadecyloxy chains (**1**), with an expectation that a strong self-assembling nature of the paraffinic side chains could promote the metallophilic interaction even at room temperature in appropriate solvents. The present paper reports detailed accounts of a study along this conception, with an emphasis on the luminescence color switching in response to external physical and chemical stimuli.

## Results and Discussion

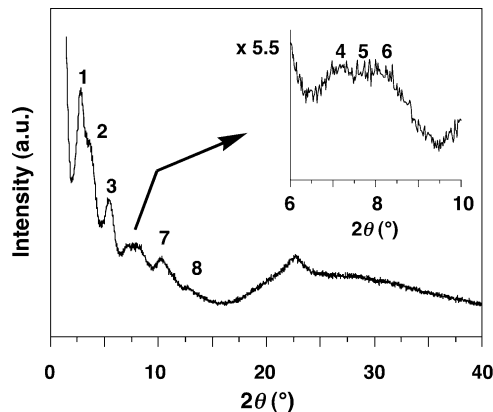
**Gelation with a Trinuclear Au(I) Pyrazolate Complex (1).** 4-(3,5-Dioctadecyloxybenzyl)-3,5-dimethylpyrazole ([C18]pzH) was synthesized by the reaction of 4-(3,5-dioctadecyloxybenzyl)-2,4-pentanedione ([C18]acac) and hydrazine according to Scheme 1<sup>8</sup> and unambiguously characterized by <sup>1</sup>H NMR, MALDI-TOF-MS spectrometry, and elemental analysis. [C18]-pzH was allowed to react with [Au(Me<sub>2</sub>S)]Cl in THF/MeOH containing KOH, and the resulting trinuclear Au(I) pyrazolate complex (**1**) was isolated by preparative size-exclusion chromatography and characterized by <sup>1</sup>H NMR, MALDI-TOF-MS spectrometry, and elemental analysis.

When a hexane (0.3 mL) suspension of Au(I) complex **1** (10.4 mg,  $3.8 \times 10^{-3}$  mmol) was once heated to 40–50 °C and allowed to cool to room temperature, the resultant solution turned to an opaque gel (critical gel concentration; 5 wt %). This sol–gel transition took place thermoreversibly at around 35–40 °C. Scanning electron microscopy (FE-SEM) of an air-dried gel (xerogel) with **1** showed the presence of heavily entangled fibrous assemblies (Figure 1). X-ray diffraction (XRD) analysis of the material indicated a rectangular columnar packing with a symmetry group *C2mm* (Figure 2, Table 1). The lattice parameters *a* and *b* were evaluated as 64.0 and 26.4 Å, respectively, which are similar to those reported for crystalline Au(I) pyrazolate complexes.<sup>9</sup>

**Switching of Luminescence Colors.** Upon excitation at 254 nm with a hand-held UV lamp, the organogel with Au(I) complex **1** emitted a red luminescence (Figure 3b). On heating, the gel turned to a clear solution and lost the red luminescence (Figure 3a). On the other hand, when the solution was cooled



**Figure 1.** Field-emission scanning electron microscopy (FE-SEM) of an air-dried gel (xerogel) with **1**, spattered with Pt under an electric current of 15 mA at 10 Pa for 10 s.



**Figure 2.** X-ray diffraction (XRD) patterns of an air-dried gel (xerogel) with **1**.

**Table 1.** Indexation of an Air-dried Gel with **1**<sup>a</sup>

| peak no. | <i>hk<sup>b</sup></i> | $\theta_{\text{obsd}}^c$ | $\theta_{\text{calcd}}^c$ | $d_{\text{obsd}}^c$ | $d_{\text{calcd}}^c$ |
|----------|-----------------------|--------------------------|---------------------------|---------------------|----------------------|
| 1        | 20                    | 1.38                     | 1.38                      | 32.0                | 32.0                 |
| 2        | 11                    | 1.81                     | 1.81                      | 24.4                | 24.4                 |
| 3        | 40                    | 2.75                     | 2.76                      | 16.1                | 16.0                 |
| 4        | 22                    | 3.60                     | 3.62                      | 12.3                | 12.2                 |
| 5        | 51                    | 3.80                     | 3.84                      | 11.6                | 11.5                 |
| 6        | 60                    | 4.13                     | 4.13                      | 10.7                | 10.7                 |
| 7        | 71                    | 5.11                     | 5.12                      | 8.65                | 8.64                 |
| 8        | 91                    | 6.39                     | 6.44                      | 6.92                | 6.87                 |

<sup>a</sup> Rectangular *C2mm* symmetry, lattice parameters *a* = 64.0 Å, *b* = 26.4 Å. <sup>b</sup> Indexation of two-dimensional lattice. <sup>c</sup> Observed and calculated values for diffraction angle (deg) and corresponding spacing (Å).

to room temperature, it again became a gel and recovered the red luminescence (Figure 3b). Thus, the red luminescence can be switched “on” (sol-to-gel) and “off” (gel-to-sol) synchronously to the phase transition. This synchronous luminescence color switching could be repeated many times without any decay.

A trinuclear Au(I) complex with benzylimidazolite ligands, when crystallized in the presence of Ag<sup>+</sup>, has been reported to give a green-luminescent solid material, where Ag<sup>+</sup> is intercalated into a columnar assembly of the Au(I) complex.<sup>10</sup> In relation to this observation, upon addition of AgOTf to a hot hexane solution of **1**, a green-luminescent, clear yellow solution resulted, which however did not gel even on cooling, when the ratio [AgOTf]/[**1**] was as high as unity. In contrast, on addition of 0.01 equiv of AgOTf with respect to **1** (Figure 3c; [AgOTf]/[**1**] = 0.01/1), the hot solution gelled when allowed to cool to room temperature. While the gel thus formed emitted an intense

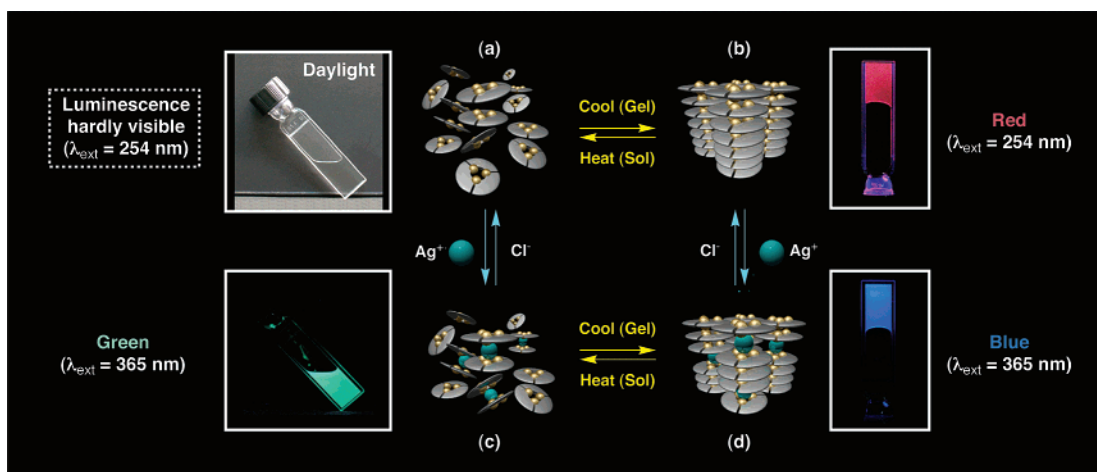
(6) (a) Yam, V. W.-W.; Lo, K. K.-W. In *Multimetallic and Macromolecular Inorganic Photochemistry*; Ramamurthy, V., Schanze, K. S., Eds.; Molecular and Supramolecular Photochemistry; Marcel Dekker: New York, 1999; pp 31–112. Vol. 4. (b) Forward, J. M.; Fackler, J. P., Jr.; Assefa, Z. Photophysical and Photochemical Properties of Au(I) Complexes. In *Optoelectronic Properties of Inorganic Compounds*; Roundhill, D. M., Fackler, J. P., Jr., Eds.; Plenum Press: New York, 1999; pp 195–229.

(7) Ma, Y.; Che, C.-M.; Chao, H.-Y.; Zhou, X.; Chan, W.-H.; Shen, J. *Adv. Mater.* **1999**, *11*, 852–857.

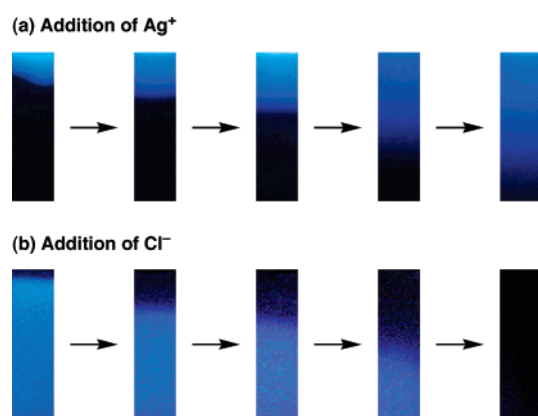
(8) Enomoto, M.; Kishimura, A.; Aida, T. *J. Am. Chem. Soc.* **2001**, *123*, 5608–5609.

(9) (a) Kim, S. J.; Kang, S. H.; Park, K.-M.; Kim, H.; Zin, W.-C.; Choi, M.-G.; Kim, K. *Chem. Mater.* **1998**, *10*, 1889–1893. (b) Barberá, J.; Elduque, A.; Giménez, R.; Lahoz, F. J.; López, J. A.; Oro, L. A.; Serrano, J. L. *Inorg. Chem.* **1998**, *37*, 2960–2967.

(10) Burini, A.; Bravi, R.; Fackler, J. P., Jr.; Galassi, R.; Grant, T. A.; Omary, M. A.; Pietroni, B. R.; Staples, R. J. *Inorg. Chem.* **2000**, *39*, 3158–3165.



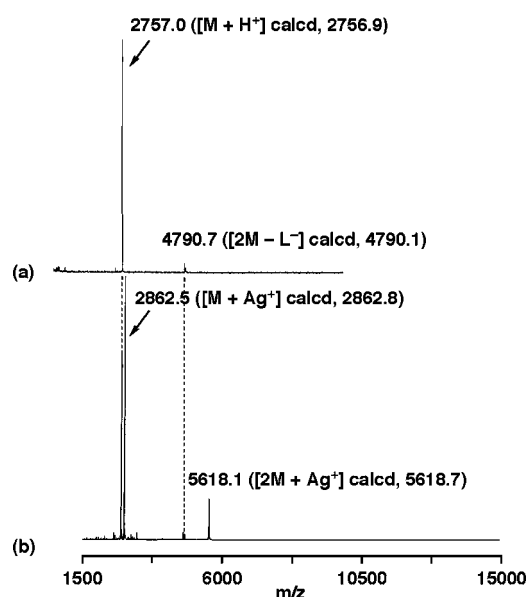
**Figure 3.** Luminescence profiles of Au(I) pyrazolate complex **1** in hexane. Pictures and schematic self-assembling structures; (a) sol, (b) gel, (c) sol containing AgOTf (0.01 equiv), and (d) gel containing AgOTf (0.01 equiv).



**Figure 4.** Selected pictures (illuminated at 365 nm), taken over a period of 24 h after the addition of (a) one drop of a THF solution of AgOTf (10 mM) onto a hexane gel prepared with **1** ( $[\text{AgOTf}]/[\mathbf{1}] = 0.01/1$ ) and (b) one drop of a  $\text{CHCl}_3$  solution of CTAC (10 mM) onto the resulting  $\text{Ag}^+$ -doped organogel ( $[\text{AgOTf}]/[\text{CTAC}] = 1/1$ ).

blue luminescence when excited at 365 nm (Figure 3d), a bluish-red luminescence resulted when excited at 254 nm, due to the presence of the original red-luminescent species in the gel. Such a luminescence color change accompanying the sol–gel transition was thermoreversible. We also found that removal of  $\text{Ag}^+$  from the green-luminescent hot solution using cetyltrimethylammonium chloride (CTAC) (Figure 3a), followed by cooling, resulted in the recovery of the red-luminescent gel (Figure 3b).<sup>11</sup>

Interestingly, when one drop of a THF solution of AgOTf (10 mM;  $[\text{AgOTf}]/[\mathbf{1}] = 0.01/1$ ) was put on the hexane gel prepared with **1**, the luminescence color of the upper part of the gel changed to blue when excited at 365 nm (Figure 4a), while the lower part remained nonluminescent (red-luminescent when  $\lambda_{\text{ext}}$  [excitation wavelength] = 254 nm).<sup>12</sup> The blue-luminescent part then spread downward without disruption of the gel, as the result of permeation and intercalation of  $\text{Ag}^+$ , and finally the whole gel turned blue-luminescent after 1 day. On the other hand, when one drop of a  $\text{CHCl}_3$  solution of CTAC (10 mM;  $[\text{CTAC}]/[\text{AgOTf}] = 1/1$ ) was put on the resulting blue-luminescent gel, CTAC permeated the gel without its disruption and converted the intercalating  $\text{Ag}^+$  ions into AgCl. Conse-



**Figure 5.** MALDI-TOF-MS spectra (dithranol as a matrix) of (a) **1** alone and (b) an equimolar mixture of **1** and AgOTf.

quently, the gel became nonluminescent when excited at 365 nm (Figure 4b), while it recovered the original red luminescence upon excitation at 254 nm.<sup>12</sup>

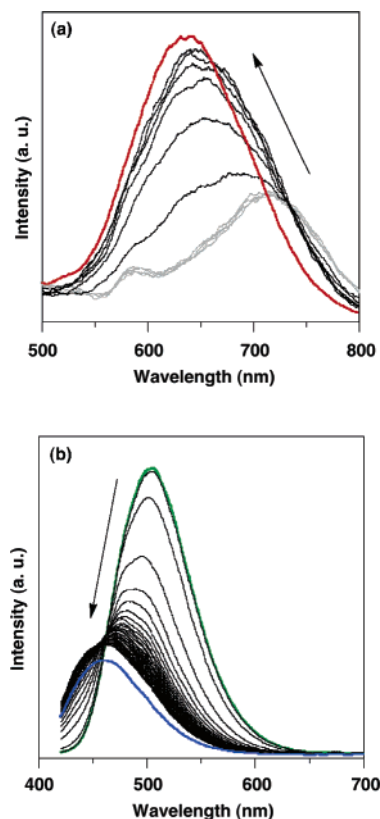
When a hexane gel prepared at  $[\text{AgOTf}]/[\mathbf{1}] = 0.01/1$  (Figure 3d) was air-dried, a blue-luminescent xerogel resulted, which adopted, as observed by XRD, a rectangular packing geometry, identical to that formed without AgOTf (Figure 2). We also found that **1** does not undergo metal ion scrambling with  $\text{Ag}^+$  even in the presence of a large amount of AgOTf (e.g.,  $[\text{AgOTf}]/[\mathbf{1}] = 1/1$ ), where only intact **1** and its  $\text{Ag}^+$  adducts ( $\mathbf{1}/\text{Ag}^+$  and  $\mathbf{1}_2/\text{Ag}^+$ ) were detected by MALDI-TOF-MS spectrometry (Figure 5). Furthermore, **1** was recovered almost quantitatively when the mixture was treated with an equimolar amount of CTAC with respect to AgOTf.<sup>13</sup> Owing to such a chemical robustness of the trinuclear Au(I) pyrazolate complex (**1**), the blue and green luminescence colors could be switched reversibly in response to repeated sol–gel transitions in the presence of  $\text{Ag}^+$ .

(11) See Supporting Information.

(12) Addition of one drop of THF or  $\text{CHCl}_3$  alone did not result in any change of the luminescence color.

(13) Preparative TLC on a silica gel plate allowed quantitative recovery of **1**, which was identified by MALDI-TOF-MS and  $^1\text{H}$  NMR analyses.

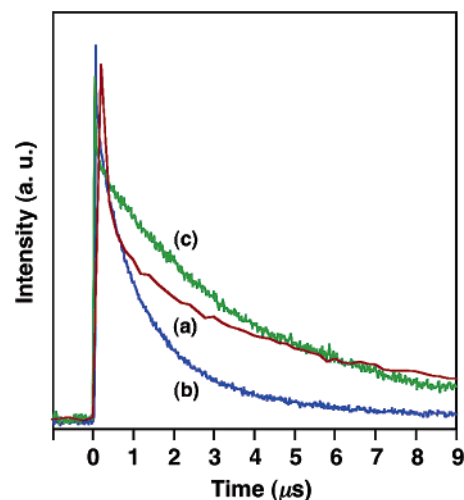




**Figure 6.** (a) Emission spectra ( $\lambda_{\text{ext}} = 284$  nm) of a hexane gel with **1** (red) and its solution (gray) and time-dependent spectral change at 25 °C over a period of 30 min immediately after the sol-to-gel transition. (b) Emission spectra ( $\lambda_{\text{ext}} = 370$  nm) of a hexane gel with **1** containing  $\text{Ag}^+$  ( $[\text{AgOTf}]/[\mathbf{1}] = 0.01/1$ ) (blue) and its solution (green) and time-dependent spectral change at 25 °C over a period of 120 min immediately after the sol-to-gel transition. The spectra were taken every 3 min.

**Spectroscopy and Lifetime Analysis.** The red light-emitting gel formed with **1**, upon excitation at 284 nm, showed a luminescence centered at 640 nm (red curve, Figure 6a).<sup>14</sup> On heating to induce the gel-to-sol transition, the emission was red-shifted to 704 nm and became weak (gray curve, Figure 6a), so that it was hardly visible for human eyes (Figure 3a). On the other hand, when the hot solution was cooled to 25 °C and held at the same temperature, the gelation progressed gradually and a blue shift of the luminescence center continuously from 704 to 640 nm followed (black curves, Figure 6a). The gel finally formed displayed an excitation band centered at 286 nm,<sup>11</sup> which is far apart from the luminescence band at 640 nm (Stokes shift  $\Delta\lambda = 354$  nm). Analogous large Stokes shifts have been reported for solid materials involving a Au(I)–Au(I) metallophilic interaction, such as  $[\text{Au}(\text{dmpz})_3]$  (dmpz = 3,5-dimethylpyrazolate) (299/680 nm,  $\Delta\lambda = 381$  nm) and  $[\text{Au}(4\text{-Me-pz})_3]$  (4-Me-pz = 4-methylpyrazolate) (230/631 nm,  $\Delta\lambda = 401$  nm).<sup>15</sup> Analysis of the emission decay profile of the gel (Figure 7a) gave a lifetime of 6  $\mu\text{s}$ , indicating that this emission is phosphorescence assignable to a triplet metal-centered excited-state modified with a Au(I)–Au(I) metallophilic interaction.<sup>6</sup>

We also investigated the luminescence properties of the  $\text{Ag}^+$ -containing system ( $[\text{AgOTf}]/[\mathbf{1}] = 0.01/1$ ) before and after the gel-to-sol transition and found that the blue-luminescent gel emitted at 458 nm (blue curve, Figure 6b;  $\lambda_{\text{ext}} = 370$  nm),<sup>14</sup>



**Figure 7.** Luminescence decay profiles at 25 °C of (a) a hexane gel with **1** ( $\lambda_{\text{ext}} = 266$  nm), (b) a hexane gel with **1** containing  $\text{Ag}^+$  ( $[\text{AgOTf}]/[\mathbf{1}] = 0.01/1$ ), and (c) its solution ( $\lambda_{\text{ext}} = 355$  nm) measured immediately after the gel-to-sol transition.

while the green-luminescent solution emitted at 501 nm (green curve, Figure 6b).<sup>16</sup> When the hot solution was cooled and thermostated at 25 °C, a continuous blue shift of the luminescence center took place from 501 to 458 nm (black curves, Figure 6b) as the gelation proceeded. When monitored at 458 nm, the gel displayed an excitation spectrum with a major peak at 369 nm and a broad shoulder centered at 300 nm,<sup>11</sup> again indicating a large Stokes shift. Upon heating to induce the gel-to-sol transition, the major peak in the excitation spectrum was red-shifted to 396 nm.<sup>11</sup> As shown by the decay curves in Figure 7b and c, the blue and green luminescences are both long-lived with decay lifetimes of 3 and 5  $\mu\text{s}$ , respectively, again indicating that these emissions are phosphorescence.

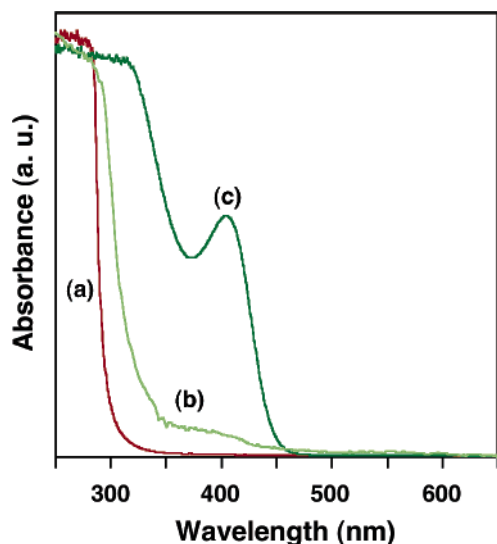
Due to the opacity, the physical gels prepared with **1** alone and **1**/AgOTf (1/0.01) gave absorption spectra that were contaminated with scattered lights. On the other hand, we successfully obtained a qualified absorption spectrum of the hexane solution of **1** by a quick measurement before the gelation started. As shown in Figure 8a, the spectrum showed only an intense absorption band at  $\lambda < 300$  nm, which is mostly due to the aromatic parts of **1**. Likewise, we could measure the absorption spectrum of the green-luminescent solution of a mixture of **1** and AgOTf (1/0.01) before the gelation (Figure 8b), which showed a weak absorption band at around 400 nm in addition to the intense absorption band due to **1**. Such a weak absorption band, assignable to a Au(I)–Ag(I) heterometallic species, was pronounced when an equimolar amount of AgOTf with respect to **1** was added (Figure 8c). While the system at this stage lost the ability of forming a gel (vide ante), the absorption spectrum was essentially identical to the excitation spectrum, indicating that the heterometallic Au(I)–Ag(I) species is the origin of the 500-nm green phosphorescence.

**Secondary Effects of Self-Assembly on Luminescences.** As described in the above section, the gelation processes with **1** alone and **1**/ $\text{Ag}^+$  (1/0.01) are both accompanied by a continuous blue shift in their luminescence spectra. This trend appears to be incompatible with a general consideration that growth of the

(14) The emission spectrum did not change when the gel was air-dried.

(15) Yang, G.; Raptis, R. G. *Inorg. Chem.* **2003**, *42*, 261–263.

(16) Without  $\text{Ag}^+$  doping, the hexane gel with **1** alone did not emit at 458 nm, irrespective of whether it was excited at 254 or 365 nm.



**Figure 8.** Electronic absorption spectra at 25 °C of hexane solutions of (a) **1** (5 wt %) and mixtures of **1** with AgOTf at [AgOTf]/[**1**] = (b) 0.01/1 and (c) 1/1. Samples a and b were measured immediately after the gel-to-sol transition. The spectra were not normalized.

self-assembly via metallophilic interactions should result in lowering the HOMO–LUMO gap.<sup>17</sup> In fact, the luminescence of a nongelling Cu(I) pyrazolate complex has been reported to be red-shifted when the solution is concentrated to allow propagation of the metallophilic interaction.<sup>3a</sup> We also observed that a reference complex without long alkyl chains such as [Au(MeO-pz)<sub>3</sub>] (MeO-pz = 4-(3,5-dimethoxybenzyl)-3,5-dimethylpyrazolate), in the presence of an equimolar amount of AgOTf, shows a red shift of the luminescence from 485.5 to 500.5 nm when it is solidified from a solution.<sup>11</sup> Thus, the blue shift of the luminescence upon growth of the self-assembled structure is unique to our sol–gel systems. We consider that, as the fibers grow and form a bundle with one another, the luminescent species would be forced to adopt a distorted

geometry<sup>15</sup> possibly due to a secondary interaction among the long alkyl chains. Consequently, the gelation is likely accompanied by an increase in the HOMO–LUMO gap.

## Conclusions

We have reported the first phosphorescent organogels via metallophilic interactions, using a trinuclear Au(I) pyrazolate complex (**1**) carrying long C18 alkyl chains, where the sol–gel transition, coupled with Ag<sup>+</sup> doping/dedoping, allows reversible switching of the RGB luminescence color. While related systems so far reported are operative under frozen or solid-state conditions to stabilize metal–metal bonds, our strategy makes use of the strong self-assembling nature of the ligand, which enables metallophilic interactions even at ambient temperatures. Although several fluorescent materials that can switch their luminescence colors in response to phase transitions have been reported,<sup>18–20</sup> they are mostly utilizing changes in orientation or association of organic dye molecules for luminescence color switching. Thus, our system is essentially different from these fluorescent systems in terms of the switching mechanism of the luminescence color. Considering also the easy processability of soft materials, application of our phosphorescent system to imaging media is one of the interesting subjects worthy of further investigation.

**Acknowledgment.** A.K. thanks the JSPS Young Scientist Fellowship.

**Supporting Information Available:** Full experimental details, an emission spectrum of an organogel with **1**/Ag<sup>+</sup> (1/0.01) after treatment with CTAC, excitation spectra of organogels and a solution of **1**/Ag<sup>+</sup> (1/0.01), emission spectra of [Au(MeO-pz)<sub>3</sub>] in CHCl<sub>3</sub>/THF and its solid. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(17) (a) Mansour, M. A.; Connick, W. B.; Lachicotte, R. J.; Gysling, H. J.; Eisenberg, R. *J. Am. Chem. Soc.* **1998**, *120*, 1329–1330. (b) Rawashdeh-Omary, M. A.; Omary, M. A.; Patterson, H. H. *J. Am. Chem. Soc.* **2000**, *122*, 10371–10380. (c) Zyl, W. E.; López-de-Luzuriaga, J. M.; Fackler, J. P., Jr. *J. Mol. Struct.* **2000**, *99*–106. (d) Rawashdeh-Omary, M. A.; Omary, M. A.; Patterson, H. H. *J. Am. Chem. Soc.* **2001**, *123*, 11237–11247. (e) White-Morris R. L.; Olmstead M. M.; Jiang, F.; Balch, A. L. *Inorg. Chem.* **2002**, *41*, 2313–2315. (f) White-Morris, R. L.; Olmstead, M. M.; Jiang, F.; Tinti, D. S.; Balch, A. L. *J. Am. Chem. Soc.* **2002**, *124*, 2327–2336. (g) Lee, Y.-A.; McGrath, J. E.; Lachicotte, R. J.; Eisenberg, R. *J. Am. Chem. Soc.* **2002**, *124*, 10662–10663.

(18) Recent examples of color-tunable fluorescent materials: (a) Davis, R.; Rath, N. P.; Das, S. *Chem. Commun.* **2004**, 74–75. (b) Giménez, R.; Piñol, M.; Serrano, J. S. *Chem. Mater.* **2004**, *16*, 1377–1383. (19) Recent examples of fluorescent organogels: (a) Ajayaghosh, A.; George, S. J.; Praveen, V. K. *Angew. Chem., Int. Ed.* **2003**, *42*, 332–335. (b) Sugiyasu, K.; Fujita, N.; Takeuchi, M.; Yamada, S.; Shinkai, S. *Org. Biomol. Chem.* **2003**, *1*, 895–899. (c) Ryu, S. Y.; Kim, S.; Seo, J.; Kim, Y.-W.; Kwon, O.-H.; Jang, D.-J.; Park, S. Y. *Chem. Commun.* **2004**, 70–71. (d) An, B.-K.; Lee, D.-S.; Lee, J.-S.; Park, Y.-S.; Song, H.-S.; Park, S. Y. *J. Am. Chem. Soc.* **2004**, *126*, 10232–10233. (20) A representative review article on fluorescent organogels: Terech, P.; Weiss, R. G. In *Surface Characterization Methods*; Milling, A. J., Ed.; Surfactant Science Series; Marcel Dekker: New York, 1999; pp 285–344, Vol. 87.