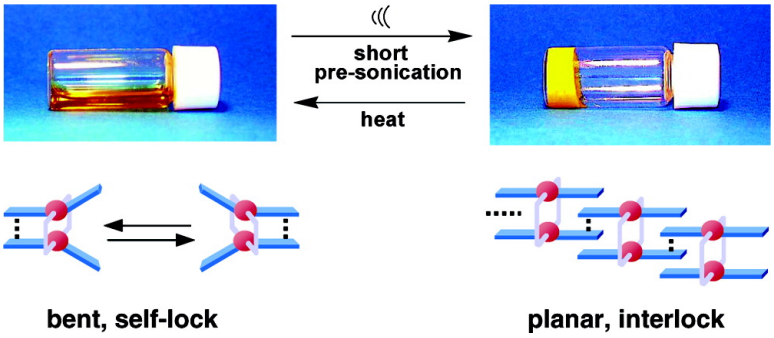
Communication

Molecules That Assemble by Sound: An Application to the Instant Gelation of Stable Organic Fluids

Takeshi Naota, and Hiroshi Koori

J. Am. Chem. Soc., **2005**, 127 (26), 9324-9325• DOI: 10.1021/ja050809h • Publication Date (Web): 11 June 2005



More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Links to the 31 articles that cite this article, as of the time of this article download
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

View the Full Text HTML

J|A|C|S
COMMUNICATIONS

Published on Web 06/11/2005

Molecules That Assemble by Sound: An Application to the Instant Gelation of Stable Organic Fluids

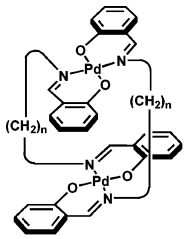
Takeshi Naota* and Hiroshi Koori

Department of Chemistry, Graduate School of Engineering Science, Osaka University, PRESTO, Japan Science and Technology Agency (JST), Machikaneyama, Toyonaka, Osaka 560-8531, Japan

Received February 8, 2005; E-mail: naota@chem.es.osaka-u.ac.jp

Stimuli-responsive aggregations of low molecular weight materials have been intensively studied in gels, micelles, vesicles, and synthetic membranes, with the aim of creating future technologies for the control of fluidity, viscoelasticity, solvent volatility, optical transmission, ion transport, etc.[1] Light[2] and electrochemical controls[3] have been explored as a means of switching molecular aggregations without the use of chemical stimuli. However, providing a method of control that is instant, positive (i.e., converting sol to aggregate), and reversible, while also being versatile and practical, remains a challenge.

Sound enhances the translational motion of molecules and was believed to be an unsuitable stimulus for molecular switching. This is because sound principally cleaves the weak noncovalent interactions between molecules, as a result of which it is widely used for the disruption of aggregations in food chemistry,[4] photographic science,[5] basic research into vesicles,[3c,6] and organometallic chemistry.[7] We report here the first molecule that assembles upon a brief irradiation with ultrasound. An association-inert dinuclear Pd complex, *anti*-**1a**, which is stabilized by intramolecular π-stacking interactions, is shown to instantly gelatinize a variety of organic solvents upon a very brief presonication. This is the first demonstration of the instant and remote control of stable sol-gel phases.



anti-**1** **a**: (n = 5)
b: (n = 6)
c: (n = 7)
d: (n = 8)

When homogeneous, clear solutions of *anti*-**1a** ($n = 5$) in various organic solvents were irradiated with ultrasound for a few seconds, the stable sol state was completely converted to the gel state immediately after sonication. Typically, sonication (0.45 W/cm^2, 40 kHz) of a 1.20×10^{-2} M solution of *anti*-**1a** in acetone for 3 s at 293 K gave an entirely opaque gel as shown in Figure 1. In the absence of sonication the same solution remains stable at ambient temperature. Solutions of *anti*-**1a** in various organic solvents, such as CCl_4 (9.00×10^{-3} M), 1,4-dioxane (1.20×10^{-2} M), and ethyl acetate (1.00×10^{-2} M), also gelled completely and instantly upon presonication for 10 s. Other related compounds, such as *syn*-**1a**, *anti*-**1b**, *syn*-**1b**, *anti*-**1c**, *syn*-**1c**, **1d** (**a**: $n = 5$; **b**: $n = 6$; **c**: $n = 7$; **d**: $n = 8$) and the mononuclear complex *trans*-bis[(2-[(pentylimino)methyl]phenolato-*N*,*O*]palladium(II) (**2**) failed to form gels in a range of organic solvents, irrespective of solution concentration and sonication time. The gels thus formed are stable but readily

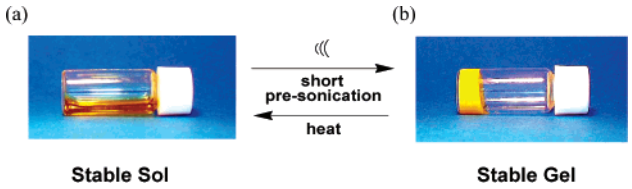


Figure 1. *anti*-**1a** in acetone at 293 K. (a) A long-lived, stable solution under nonsonication conditions. (b) A gel just after presonication (0.45 W/cm^2, 40 kHz, 3 s).

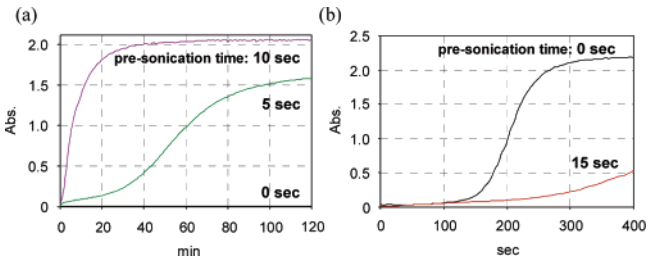


Figure 2. Contrasting gelation profiles of solutions of *anti*-**1a** (7.23×10^{-3} M (a)) and **3** (7.00×10^{-3} M (b)) in acetone at 293 K, evaluated from baseline absorption at 700 nm. Each curve indicates the results just after presonication (0.45 W/cm^2, 40 kHz, 0−15 s).

converted to the original, stable solutions upon heating at above T_{gel} and subsequent cooling to room temperature. The present sol−gel phase transition can be repeated indefinitely with no measurable degradation of the gelator, since the transition arises from a simple conformational change of the complex. This is the first quick, positive, and reversible method for the remote switching of stable sol-gel phases.[8] Conventional methods require more time to complete the stoichiometric molecular transformation of the monomer units,[2,3] and most of these methods involve negative switching from aggregates to sol states.[2a−c,3a,b] The gelation occurs exclusively upon sonication, other external stimuli such as vigorous shaking, quick heating/cooling, and microwave irradiation do not initiate aggregation.

The profile of this novel switched gelation can be visualized by the time-dependence of the UV baseline absorption at 700 nm during the formation of the opaque gel. Figure 2a shows the controlled gelation profiles of a dilute solution of *anti*-**1a** in acetone. The original stability of the solution and its response to sonication are indicated by three typical curves obtained upon presonication for 0−10 s. Similar switching profiles are observed in the gelation of a variety of organic fluids, such as ethyl acetate, 1,4-dioxane, CCl_4, and toluene. It is noteworthy that, in each case, the aggregation rate can be precisely, but drastically, controlled between "no gelation" and "instant gelation" by tuning the sonication time. The rates of conventional self-assembly depend only upon static reaction parameters such as temperature, concentration, solvents, and additives; the dynamic control of the aggregation rate shown here is a new and useful phenomenon in this field of chemistry. In

10.1021/ja050809h CCC: $30.25

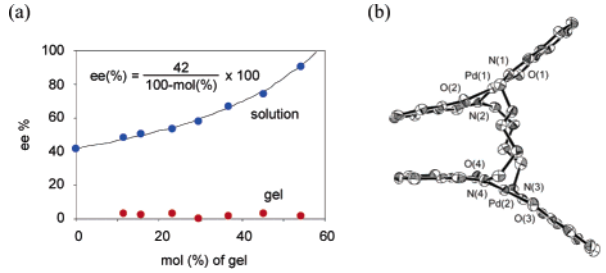


Figure 3. (a) Enantiomer excess of *anti*-**1a** in the partial gel (red dots) and the remaining solution (blue dots), obtained during the gelation of a 1.50×10^{-2} M solution of (−)-*anti*-**1a** (42% ee) in benzene after presonication (0.45 W/cm^2, 40 kHz, 10 s). (b) Molecular structure of *anti*-**1a** showing intramolecular π-stacking of the cofacial bent coordination blades. Side view of (R)-form. Selected bond distances (Å) and angles (deg): Pd(1)−O(1), 2.002(7); Pd(1)−O(2), 1.986(6); Pd(1)−N(1), 2.015(8); Pd(1)−N(2), 2.023(8); O(1)−Pd(1)−N(1), 91.3(3); O(2)−Pd(1)−N(2), 90.4(3); C(2)−N(2)−Pd(1)−O(2), 22.6(8); C(4)−N(4)−Pd(2)−O(4), 15.7(8).

marked contrast, sonication has a negative effect on conventional molecular aggregations as mentioned above.[4−7] Figure 2b shows gelation profiles of an acetone solution of *N*-lauroyl-L-glutamic acid di-*n*-butylamide (**3**), a commercially available H-bonding gelator. The results show that even a brief presonication gives rise to a considerable retardation of gelation, presumably due to the sonication breaking-up the early stage H-bonded aggregates.

Surprisingly, optically pure (−)-*anti*-**1a** (100% ee, $[\alpha]^{27}_{D}$ −375° (*c* 0.014, $CHCl_3$)) does not gelatinize any organic solvent, even after prolonged sonication. To understand the relationship between gelation and chirality, the gelation profile of a 1.50×10^{-2} M solution of 42% ee (−)-*anti*-**1a** in benzene was monitored by evaluating the optical activities of *anti*-**1a** in both the partial gel and the remaining solution. As shown in Figure 3a, the enantiomer excess of *anti*-**1a** in the gel was almost 0% ee at all stages of the gelation and that in the solution increased correspondingly, according to the theoretical curve of racemic consumption {42/[100 − (mol % of *anti*-**1a** from gel)] × 100}. These results indicate that almost complete alternate stacking of (+)- and (−)-monomer units occurs during the entire gelation process. This is a clear case of heterochiral aggregaton (RSRSRS••) occurring in both the sol and gel states and as such is quite rare, although many examples of homochiral aggregation in the sol,[9] gel,[10] and liquid crystalline states[11] have been reported.

The inertness of complexes **1** and **2** to association in solution has been confirmed by ^{1}H NMR analysis. The chemical shift of all signals was concentration independent at 293 K in $CDCl_3$ and benzene-d_6. However, a specific flipping motion due to intramolecular π-stacking interactions was observed in *anti*-**1a**, in which 1:1 splitting of the ddd signals of NCH_aH_b in toluene-d_6 occurs below the coalescence temperatures of 188 and 198 K, respectively. The activation parameters of the flipping motion, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, were determined to be 35 ± 2 kJ mol^{-1} and 0.5 ± 12 J K^{-1} mol^{-1} from the Eyring relationship of the flipping rates estimated by the line-shape method. X-ray diffraction clearly shows the specific stacking structure of *anti*-**1a** (Figure 3b). The aromatic moieties of the cofacial blades are well within the typical aromatic stacking distance 3.4−3.7 Å. This is achieved by an outward bending of the C−N−Pd−O dihedral angle to a maximum of 22.6°.[12] This is in contrast to the nonstacked, nearly planar structure of *anti*-**1c**, which bears a longer methylene spacer.[12] The ILCT (235 nm) and MLCT (390 nm) bands of *anti*-**1a** in cyclohexane are more hypochromic than those of the planar *anti*-**1c** and **2**, which indicates that the specific stacking behavior of *anti*-**1a** in solution is accompanied by a decrease in the planarity of the coordination blades.

After a brief presonication (0.31 W/cm^2, 44 kHz, 5 s), the gelation process was examined by UV−vis spectroscopic analysis of a 4.00×10^{-4} M solution of *anti*-**1a** in cyclohexane, which forms a transparent gel. Over the whole gelation process the absorbance exhibited hypo- and hyperchromic changes in the ILCT and MLCT bands, with a sharp isosbestic point at 268 nm. These results strongly suggest that gelation proceeds via the interpenetrative, consecutive stacking of planar monomer units, since the change in absorbance indicates that *anti*-**1a** is adopting a more stacked and planar conformation. This new motif in π-stacking aggregations is demonstrated by the X-ray diffraction pattern of *anti*-**1b** crystals.[12]

The sonication-induced gelation can be rationalized by assuming the following, unprecedented, aggregation polymerization. In the absence of sonication, the *anti*-**1a** complex is prevented from forming aggregates by its clothespinlike, bent conformation. A brief sonication initiates the polymerization by causing a selflock-interlock conversion, generating a small amount of the heterochiral, interpenetrative dimer, which bears rigid stacking cavities of 7 Å. This long-lived initiator species undergoes heterochiral chain association with the remaining monomer units, which are in excess. This process continues even after sonication has ceased and affords the corresponding aggregation polymer by propagation. Efforts are currently underway to investigate the full scope of the reaction, to obtain definitive mechanistic information and to apply the present reactions to other systems.

Acknowledgment. This work was supported by PRESTO, Japan Science and Technology Agency (JST).

Supporting Information Available: Movies of instant gelations (31.8 MB, mpeg), experimental details, and crystallographic data for *anti*-**1a**, *anti*-**1b**, and *anti*-**1c** (71 pages, print/PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) *Encyclopedia of Supramolecular Chemistry*; Atwood, J. L., Steed, J. W., Eds.; Marcel Dekker: New York, 2004.
(2) (a) Murata, K.; Aoki, M.; Suzuki, T.; Harada, T.; Kawabata, H.; Komori, T.; Ohseto, F.; Ueda, K.; Shinkai, S. *J. Am. Chem. Soc.* **1994**, *116*, 6664. (b) Ayabe, M.; Kishida, T.; Fujita, N.; Sada, K.; Shinkai, S. *Org. Biomol. Chem.* **2003**, *1*, 2744. (c) Ahmed, S. A.; Sallenave, X.; Fages, F.; Mieden-Gundert, G.; Müller, W. M.; Müller, U.; Vögtle, F.; Pozzo, J.-L. *Langmuir* **2002**, *18*, 7096. (d) Frkanec, L.; Jokić, M.; Makarević, J.; Wolsperger, K.; Žinić, M. *J. Am. Chem. Soc.* **2002**, *124*, 9716.
(3) (a) Saji, T.; Hoshino, K.; Ishii, Y.; Goto, M. *J. Am. Chem. Soc.* **1991**, *113*, 450. (b) Tsuchiya, K.; Orihara, Y.; Kondo, Y.; Yoshino, N.; Ohkubo, T.; Sakai, H.; Abe, M. *J. Am. Chem. Soc.* **2004**, *126*, 12282. (c) Medina, J. C.; Gay, I.; Chen, Z.; Echegoyen, L.; Gokel, G. W. *J. Am. Chem. Soc.* **1991**, *113*, 365.
(4) Seshadri, R.; Weiss, J.; Hulbert, G. J.; Mount, J. *Food Hydrocolloids* **2003**, *17*, 191.
(5) Kanegae, M.; Kou, S.; Okawa, Y.; Kobayashi, H.; Ohno, T.; Ohki, T.; Kitayama, T. *J. Photograph. Sci.* **1992**, *40*, 187.
(6) Massey, J.; Power, K. N.; Manners, I.; Winnik, M. A. *J. Am. Chem. Soc.* **1998**, *120*, 9533.
(7) Paulusse, J. M. J.; Sijbesma, R. P. *Angew. Chem., Int. Ed.* **2004**, *43*, 4460.
(8) Vigorous shaking of clay-polymer dispersions gives rise to a temporary transition to a metastable gel state, which is followed by slow relaxation to the initial sol state on standing: Pozzo, D. C.; Walker, L. M. *Colloids Surf. A* **2004**, *240*, 187 and references therein.
(9) Ishida, Y.; Aida, T. *J. Am. Chem. Soc.* **2002**, *124*, 14017.
(10) Hanabusa, K.; Yamada, M.; Kimura, M.; Shirai, H. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1949.
(11) Walba, D. M.; Stevens, F.; Clark, N. A.; Parks, D. C. *Acc. Chem. Res.* **1996**, *29*, 591.
(12) Crystallographic data for *anti*-**1**. *anti*-**1a**: monoclinic, $P2_1/c$ (#14), a = 17.5075(5) Å, b = 12.4366(4) Å, c = 36.567(1) Å, β = 100.724(1)°, V = 7822.8(4) Å^3, Z = 8, R1 = 0.123, wR2 = 0.222, GOF = 1.23. *anti*-**1b**: triclinic, $P\bar{1}$ (#2), a = 10.7005(2) Å, b = 10.8011(2) Å, c = 15.9410-(2) Å, α = 93.6235(7)°, β = 96.9252(6)°, γ = 98.9763(6)°, V = 1800.24(5) Å^3, Z = 2, R1 = 0.078, wR2 = 0.148, GOF = 1.04. *anti*-**1c**: monoclinic, $P2_1/c$ (#14), a = 9.8175(3) Å, b = 19.2070(7) Å, c = 20.1723-(6) Å, β = 98.834(1)°, V = 3758.7(2) Å^3, Z = 4, R1 = 0.078, wR2 = 0.156, GOF = 1.18.

JA050809H