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Photoinduced Crystal-to-Liquid Phase Transitions of Azobenzene Derivatives and Their Application in Photolithography Processes through a Solid–Liquid Patterning

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S *Supporting Information*

ABSTRACT: The direct and reversible transformation of matter between the solid and liquid phases by light at constant temperature is of great interest because of its potential applications in various manufacturing settings. We report a simple molecular design strategy for the phase transitions: azobenzenes having *para*-dialkoxy groups with a methyl group at the meta-position. The photolithography processes were demonstrated using the azobenzene as a photoresist in a single process combining development and etching of a copper substrate.

Phase transitions of matter are generally induced by heat. In contrast, some materials, such as azobenzene,[1] undergo photochromic reactions that result in photoinduced phase transitions involving liquid crystal phases,[1f,i,j] sol–gel transitions,[1g,i] and fluidity changes in thin film surfaces.[1d,h] In particular, the photoinduced transition between the solid and liquid phases for azobenzene induced by light at rt[2,3] has attracted significant interest from the application viewpoint. The direct phase conversions of bulk materials and the reversibility of such compounds suggest simple and resource-saving applications in reusable smart materials. An intriguing application has been proposed for use as photocontrollable adhesives[3] that can perform photoattaching and detaching. Another possible application of such phase-transition materials is as photoresists that enable solid/liquid patterning. Currently, conventional photoresists[4] are not reusable because they use irreversible photopolymerization, degradation, or cross-linking reactions. In addition, significant amounts of acids and/or bases are used to remove the photoresists in the development/washing processes.[4] By using phase transition materials, the isothermal solid/liquid patterning provides simple development processes such as wiping, blowing, or washing by solvents, and thus it is expected to reduce the chemical waste and to simplify the photolithography process. However, until now, there has been no report of even a simple demonstration of photolithographic processes using such phase-transition materials.

Although solid-state (crystalline) organic photochemistry has been extensively studied in various compounds,[5] little is known about azobenzene-based systems; thus, molecular design criteria need to be established. Earlier, the *trans*-to-*cis* photoisomerization of azobenzene had been long believed not to take place in the crystal bulk phase.[6] Later, it was found to take place on the surface of the crystals because of the crystal packing and steric hindrance.[7,8] More recently, we and others found that several azobenzene-based compounds undergo crystal-to-liquid phase transitions,[2,9] but their complex molecular structures obfuscate the molecular design criteria. Thus, we set our target to find simpler molecules that show the photoinduced phase transition and can be used as a photoresist.

Here, we report a simple molecular design strategy that is very effective for the crystal-to-liquid phase transition. Introduction of a methyl group at the 3-position on rod-shaped azobenzene derivatives drastically alters the photoinduced phase transition behavior (Figure 1). Despite their simple molecular structures, these are new compounds. These materials could also be used as photoresists to pattern copper substrates, such as those used in printed circuit boards. The liquefied region of a pattern can be readily removed by wiping, blowing, or washing, and the substrate can then undergo etching. Notably, the proposed process provides a new concept in application of phase transition materials because this process does not require the acids and/or bases currently necessary to remove conventional photoresists.

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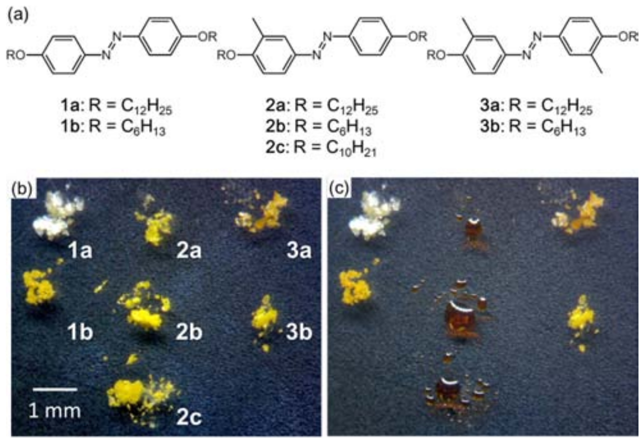

Figure 1. (a) Chemical structures and (b) photographs of the crystalline powders of the azobenzene derivatives **1a–b**, **2a–c**, and **3a–b**. (c) The same powders after irradiation with 365 nm light. The irradiation period was 30 min at an intensity of 100 mW cm^{-2}.

We selected rod-shaped molecules because of their facile synthesis and simple structure–property relationships. Methyl groups were introduced at the 3-position (**2a–c**) or the 3- and 3′-positions (**3a–b**), anticipating reduced intermolecular $\pi-\pi$ interactions that could potentially retard photoisomerization in the solid phase. The parent azobenzenes (**1a–b**)[10] were also investigated as controls. The syntheses of these compounds were achieved via two conventional reactions in fair yields. In the case of **2a**, for example, the first step is a synthesis of 4,4′-dihydroxy-3-methyl-azobenzene by diazo coupling between 4-aminophenol and *o*-cresol with a 53% yield. The second step involves alkylation of the hydroxyl groups by dodecyl bromide with a 96% yield. Compounds with three different alkoxy chain lengths (C12, C6, and, for **2** only, C10) were synthesized (see Supporting Information (SI) for further details). The thermal phase transition temperatures of the final products were determined by differential scanning calorimetry (DSC). All compounds were crystalline at rt (Table 1 and SI).

Table 1. Thermal Phase Transition Temperatures[a] of the Azobenzene Derivatives

	phase transition temperature (°C)[b]	
molecule	heating	cooling
1a	Cr_{II} 97 Cr_I 107 I	I 105 N 99 Cr_I 88 Cr_{II}
1b	Cr 102 N 114 I	I 113 N 99 Cr
2a	Cr 66 N 72 I	I 72 N 53 Cr
2b	Cr 87 I	I 78 Cr
2c	Cr_{II} 59 Cr_I 60 N 75 I	I 74 N 51 Cr_{II}
3a	Cr_{II} 54 Cr_I 83 I	I 62 Cr_I 51 Cr_{II}
3b	Cr_{II} 94 Cr_I 105 I	I 92 Cr_{II}

[a] Determined by DSC at scan rate of 2 K min^{-1}. [b] Cr: crystal. N: nematic liquid crystal phase. I: isotropic liquid phase. Subscripts (I and II) indicate polymorphism.

In the solid state at rt, photoinduced phase transitions were only observed for **2a–c** (Figures 1b, 1c, 2, and SI video), whereas the photoisomerization of all the compounds was confirmed in chloroform (Figure S4–S6). The irradiation time required for complete liquefaction strongly depended on the sample thickness: although it required 30 min (at 100 mW cm^{-2}) to complete the liquefaction of a pile of crystal powder (Figure 1b,c), it took less than 1 min for a thin film (Figure 2b). Crystalline films show slight scattering, but it does not significantly affect the optical measurements (Figures 1b, S4–S6). A crystalline film of **2b** showed absorption bands around 390 nm; these diminished upon irradiation using 365 nm light, accompanied by the appearance of an absorption band around 450 nm (Figure 2b). Polarization optical microscopy (POM) showed a loss in birefringence of the crystal on irradiation at 365 nm, indicating that a phase transition occurred due to photoisomerization (Figure S7). At the photostationary state, the content of the *cis* isomer in this film is 90% estimated by dissolving the film into a solvent and measuring ^1H NMR and absorption spectra.

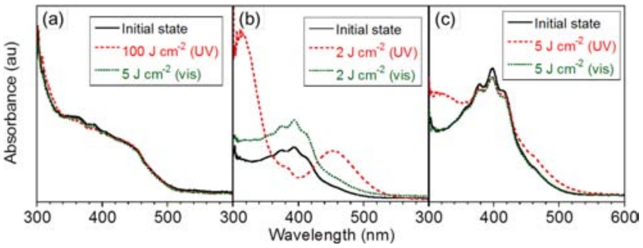

Figure 2. UV–vis absorption spectra of (a) **1b**, (b) **2b**, and (c) **3b** in the crystalline phase upon photoirradiation.

The viscosity of photoirradiated **2b** was 460 mPa·s, clearly revealing its liquid state.[11] The liquefied samples remained in their liquid phase for ~1 h at rt after ceasing the irradiation (Figure S8). Reverse photoisomerization (*cis*-to-*trans*), and the consequent crystallization, was observed on irradiation with visible (436 nm) light (Figure S7). An exceptional case was observed in **3b**; although its crystals exhibited a slight change in the absorption spectrum on irradiation (Figure 2c), no phase transition was observed (Figure 1b and 1c) at rt. Although **3a** has a lower melting point (mp, 83 °C) than that of **2b** (87 °C), **3a** does not show the phase transition. The temperature increase of the crystal powder surface, measured using an infrared radiation thermometer, was about 3 K during irradiation at 200 mW cm^{-2}. To confirm that the heating effects are not the main reason for the liquefaction, an irradiation experiment at lower intensity of light (4.6 mW cm^{-2}) was carried out, and we observed the phase transition (Figure S9). Since the deactivation process of photoexcited molecules involves dissipation of energy as heat, a temperature increase cannot be avoided. However, the above-mentioned results show that the heating effects are not the main reason for the phase transition.

To understand the crystal-to-liquid phase transition, let us consider the isomerization and melting steps separately. First, it is presumed that the photoisomerization takes place at the surface of the crystals.[7,8] The intensity of the incoming light is highest here, and thus, photons are primarily absorbed at the outer surface. The molecular packing and dynamic nature of the crystal might affect its photoisomerization ability. To study this, single crystal X-ray analyses were performed to determine the crystal structures of **1b**, **2a–c**, and **3b** (Figure 3; see SI for details). Comparing the crystal structures of **2b** and **3b**, their single molecular conformations are very close to each other and similar molecular assembly structures are formed in the *ab* planes. However, within a single layer, molecules of **2b** form a zigzag molecular assembly, whereas **3b** molecules are linearly assembled with interdigitated alkyl chains.

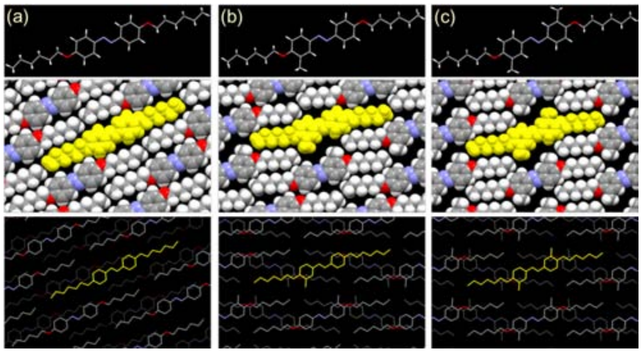

Figure 3. Crystal structures of **1b**, **2b**, and **3b**. Top: single molecule structures. Middle: crystal faces parallel to the molecular plane of (a) the (10$\bar{1}$) face of **1b**, (b) the (001) face of **2b**, and (c) the (001) face of **3b**, displayed as space-filling models. Bottom: the same crystal faces as in the middle images showing two molecular layers, where the front and rear layers are shown as stick and wireframe models, respectively. A single molecule in each image is highlighted for clarity.

Second, the *cis* isomers generated by light irradiation at the crystal surface should affect the macroscopic phase of the sample. When the *cis* isomer has an mp sufficiently higher than rt, the crystal does not melt. The solid *cis* isomer prevents further isomerization because of steric hindrance.[12] When the mp is lower than rt, the liquid *cis* isomer appears and results in further isomerization at the crystal−liquid interface. To estimate the mp of the corresponding *cis* isomers, the thermal behavior of the photoirradiated samples was investigated using POM. It was revealed that the mp of the *cis* isomer of **2b** is around −6 °C (Figure S15), whereas that of **3b** is around 90 °C (Figures S16 and S17). These results show that the mp of the *cis* isomer changes drastically because of the rather small molecular modification upon the introduction of a methyl group.

Since the phase transition occurs at the crystal surface, the irradiation time strongly depends on the sample thickness for the complete liquefaction. Therefore, it requires less photons when the sample is thinner (Figure S9). In addition, the melted state (liquid) covers the crystal and absorbs the incoming photons resulting in slowing down the transition. Melting occurs when the conversion at the crystal surface reaches the ratio at which the mp of the isomer mixture is below rt.

For photolithography, a photoresponsive material should possess film-forming ability, sensitivity to light exposure, spatial resolution, compatibility with development chemicals, robustness against etching reagents, low cost, low toxicity, and so on. We fabricated spin-coated films (thickness: $\sim 1\ \mu$m) on a cover glass and observed that **2c** was able to form a good film (Figure S18). The X-ray diffraction profile of the **2c** thin film was similar to that of the crystalline powder, indicating that it is also crystalline (Figure S19).

When exposed to 365 nm light through a mask, the spin-coated **2c** exhibited a photoinduced phase transition to liquid selectively in the irradiated regions (Figure S18). It should be noted that the liquefaction of the thin film occurred within 60 s of irradiation, much faster than the transition in the crystal powder (Figure 1) at the same light intensity. We found no significant dependence of the phase transition property on the sample preparation method (crystalline films prepared by cooling from the melt or by spin coating). Blowing, wiping, or blotting can remove the liquid material (viscosity 425 mPa·s), although each method must be optimized for complete removal. We could also selectively remove the liquid material by immersing the film in aqueous propanol (H_2O/2-propanol = 2:3 v/v) for 10 min at rt (Figure S20).

The chemical etching of copper is widely used in art and industry. It is an important photolithographic process in the production of printed circuit boards, the substrates on which electronic parts are placed.[13,14] Generally, a photoresist film is formed on a copper substrate and exposed to light through a mask. Then, the exposed/modified resist film is developed to produce a pattern. An etching process removes the copper that is not protected by the remaining resist. In the final step, the remaining resist is stripped, leaving the patterned features of the substrate.[4,13]

Etching of a copper substrate was successfully achieved using **2c** as a photoresist (the sequence (1) → (2) → (3) → (4) → (6) in Figure 4a). A spin-coated film of **2c** on a copper substrate (commercially available copper-clad) was irradiated at 365 nm through a mask, and the substrate was immersed in a propanol solution (Figure 4b and 4d). Then the substrate was placed in an etching solution (23% $FeCl_3$ in H_2O). The substrate was rinsed with water, and then with acetone, to remove the unexposed **2c** on top of the unetched copper layer (Figure S22b). Thus, the spin-coated layer of **2c** resists the etching solution.

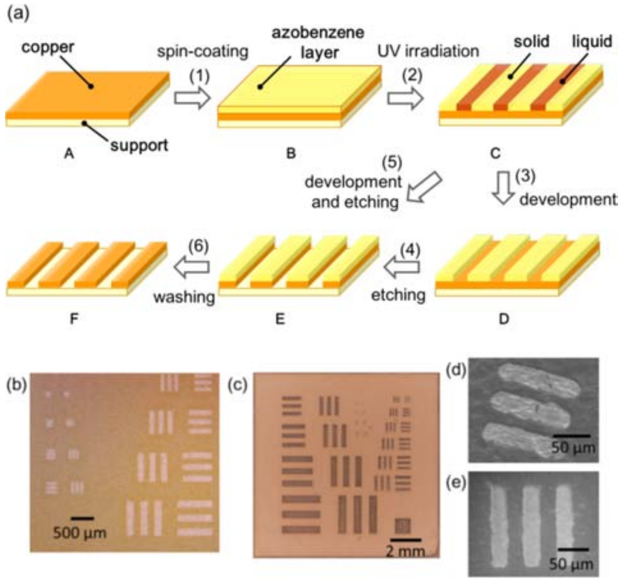

Figure 4. (a) Photolithographic process for the selective etching of copper substrates. (b) Optical photomicrograph of a patterned azobenzene **2c** on a copper substrate (state D in (a)). (c) Photograph of a patterned copper substrate being subjected to the processes (1) → (2) → (5) → (6) (obtaining state F). (d) SEM image of the substrate shown in (b). (e) SEM image of the copper substrate shown in (c).

In addition, the developing and etching steps were combined and carried out simultaneously by simply adding 2-propanol (2.5% v/v) to the etching solution (the sequence (1) → (2) → (5) → (6) in Figure 4a). A photograph and an SEM image of the final product are shown in Figure 4c and 4e, respectively.

In summary, we have shown that simple rod-shaped azobenzenes having a methyl group at the 3-position and *para*-alkoxy chains exhibited crystal-to-liquid photoinduced phase transitions at rt as revealed by optical observations, spectroscopic analysis, and viscosity measurements. The molecular packing and melting points of the corresponding *cis* isomers provide information on the phase transition. Further studies including observing the dynamic behavior of molecules in the crystal phase, obtaining a complete phase diagram of the phase transition, and improving their photosensitivity are currently ongoing. One of the compounds, possessing an excellent film-forming ability, can be used as a photoresist, and the selective etching of copper was successfully achieved using a simple photolithographic method. The azobenzene is easily removed using common organic solvents such as acetone and 2-propanol. No acids or bases are required to develop or to remove the resist. These new materials also can be used to fabricate patterns on solid surfaces sensitive to acids/bases. In principle, the azobenzene can be recovered and reused. Our molecular design strategy is simple but very effective for the development of phase-transitionable materials. The results described here provide significant knowledge of azobenzene-based materials and a novel concept of their application that will contribute to energy and resource saving technologies.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures; synthesis and characterization data of 4,4′-dihydroxy-3-methylazobenzene, **2a–c**, and **3b**; Figures S1–S24; crystallographic information files (CIF) for **1b**, **2a–c**, and **3b**, video of phase transition. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Reviews of azobenzenes: (a) Bandara, H. M. D.; Burdette, S. C. *Chem. Soc. Rev.* **2012**, *41*, 1809–1825. (b) Mahimwalla, Z.; Yager, K. G.; Mamiya, J.; Shishido, A.; Priimagi, A.; Barrett, C. J. *Polym. Bull.* **2012**, *69*, 967–1006. (c) Merino, E.; Ribagorda, M. *Beilstein J. Org. Chem.* **2012**, *8*, 1071–1090. (d) Lee, S.; Kang, H. S.; Park, J.-K. *Adv. Mater.* **2012**, *24*, 2069–2103. (e) Beharry, A. A.; Woolley, G. A. *Chem. Soc. Rev.* **2011**, *40*, 4422–4437. (f) Yu, H.; Ikeda, T. *Adv. Mater.* **2011**, *23*, 2149–2180. (g) Yagai, S.; Kitamura, A. *Chem. Soc. Rev.* **2008**, *37*, 1520–1529. (h) Seki, T. *Bull. Chem. Soc. Jpn.* **2007**, *80*, 2084–2109. (i) Kato, T.; Hirai, Y.; Nakaso, S.; Moriyama, M. *Chem. Soc. Rev.* **2007**, *36*, 1857–1867. (j) Ikeda, T.; Mamiya, J.; Yu, Y. *Angew. Chem., Int. Ed.* **2007**, *46*, 506–528.

(2) (a) Norikane, Y.; Hirai, Y.; Yoshida, M. *Chem. Commun.* **2011**, *47*, 1770–1772. (b) Uchida, E.; Sakaki, K.; Nakamura, Y.; Azumi, R.; Hirai, Y.; Akiyama, H.; Yoshida, M.; Norikane, Y. *Chem.—Eur. J.* **2013**, *19*, 17391–17397. (c) Hoshino, M.; Uchida, E.; Norikane, Y.; Azumi, R.; Nozawa, S.; Tomita, A.; Sato, T.; Adachi, S.; Koshihara, S. *J. Am. Chem. Soc.* **2014**, *136*, 9158–9164.

(3) (a) Akiyama, H.; Yoshida, M. *Adv. Mater.* **2012**, *24*, 2353–2356. (b) Akiyama, H.; Kanazawa, S.; Okuyama, Y.; Yoshida, M.; Kihara, H.; Nagai, H.; Norikane, Y.; Azumi, R. *ACS Appl. Mater. Interfaces* **2014**, *6*, 7933–7941.

(4) (a) Okoroanyanwu, U. *Chemistry and Lithography*; SPIE PressJohn Wiley & Sons: Bellingham, WA, Hoboken, NJ, 2010. (b) Madou, M. J. *Fundamentals of Microfabrication*; CRC Press: Boca Raton, FL, 2002.

(5) (a) Keating, A. E.; Garcia-Garibay, M. A. In *Organic and Inorganic Photochemistry*, Vol. 2; Ramamurthy, V., Schanze, K., Eds.; Marcel Dekker: New York, 1998; pp 195–248. (b) Garcia-Garibay, M. A. *Acc. Chem. Res.* **2003**, *36*, 491–498. (c) de Loera, D.; Stopin, A.; Garcia-Garibay, M. A. *J. Am. Chem. Soc.* **2013**, *135*, 6626–6632.

(6) Tsuda, M.; Kuratani, K. *Bull. Chem. Soc. Jpn.* **1964**, *37*, 1284–1288.

(7) (a) Nakayama, K.; Jiang, L.; Iyoda, T.; Hashimoto, K.; Fujishima, A. *Jpn. J. Appl. Phys.* **1997**, *36*, 3898–3902. (b) Ichimura, K. *Chem. Commun.* **2009**, 1496–1498.

(8) (a) Koshima, H.; Ojima, N.; Uchimoto, H. *J. Am. Chem. Soc.* **2009**, *131*, 6890–6891. (b) Nakano, H. *J. Mater. Chem.* **2010**, *20*, 2071–2074. (c) Bushuyev, O. S.; Singleton, T. A.; Barrett, C. J. *Adv. Mater.* **2013**, *25*, 1796–1800. (d) Bushuyev, O. S.; Tomberg, A.; Friščić, T.; Barrett, C. J. *J. Am. Chem. Soc.* **2013**, *135*, 12556–12559. (e) Nath, N. K.; Pejov, L.; Nichols, S. M.; Hu, C.; Saleh, N.; Kahr, B.; Naumov, P. *J. Am. Chem. Soc.* **2014**, *136*, 2757–2766.

(9) Okui, Y.; Han, M. *Chem. Commun.* **2012**, *48*, 11763–11765.

(10) (a) Kidowaki, M.; Moriyama, M.; Wada, M.; Tamaoki, N. *J. Phys. Chem. B* **2003**, *107*, 12054–12061. (b) Ruslim, C.; Ichimura, K. *J. Mater. Chem.* **1999**, *9*, 673–681.

(11) Viscosity of *trans* isomer of **2b** observed at 100 °C was 12 mPa·s.

(12) Sworakowski, J.; Janus, K.; Nešpůrek, S. *Adv. Colloid Interface Sci.* **2005**, 97–110.

(13) Khandpur, R. S. *Printed Circuit Boards: Design, Fabrication, Assembly and Testing*; Tata McGraw-Hill: New Delhi, 2005; pp 365–383.

(14) The etching process of the copper substrate has been adopted as educational experiment programs. For example, see: Outreach resources, The National HE STEM Programme, Royal Society of Chemistry. http://www.rsc.org/Education/HESTEM/Outreach/photolithography.asp (accessed July 27th, 2014).