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Synthesis and crystallographic structure of a novel photoresponsive azobenzene-containing organosilane†

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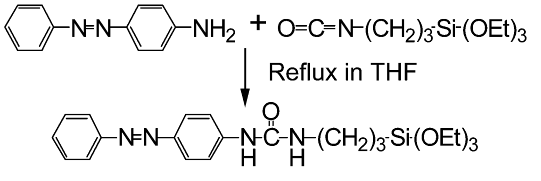
A novel photoresponsive azobenzene-containing organosilane was synthesized *via* an isocyanato-amino coupling reaction, and its crystal structure was determined by X-ray crystallography.

Materials containing photochromic azobenzene moieties have been of great interest for applications in photomemories, light-driven displays, optical data storage, optical switching, opto-mechanical actuation, and optoelectronics.[1–3] Photoirradiation may cause reversible changes in physical properties, such as surface energy and wettability, color, structure, morphology, dielectric constant, and polarity, as a result of the photo-isomerization of the azobenzene moieties.[4–9] Photoisomerization may also induce phase transitions and result in chiroptical behavior.[10,11] The synthesis of azobenzene-containing organosilanes is of interest for their potential use in functionalizing mesoporous silica materials and sol–gel materials to produce photoresponsive composites in which material properties are controlled by light. In an effort to make photoresponsive sol–gel hybrid materials, Ueda *et al*. synthesized an azobenzene-containing organosilane, 4-methoxy-4′-(*N*-(3-triethoxysilylpropyl)-carbamoylmethoxy)azobenzene (MTAB).[12] However, the yield of MTAB was low (*ca*. 27% in the report), potentially limiting its further application. Here we report the synthesis of a novel azobenzene-containing organosilane, 4-(3-triethoxysilylpropyl-ureido)azobenzene (TSUA) with high yield and high purity through an isocyanato-amino coupling reaction which has been reported previously to form urea or bisurea groups.[13–15]

As shown in Scheme 1, TSUA was synthesized from triethoxysilylpropyl isocyanate (TESPIC) and 4-phenylazoaniline (PAA) in anhydrous tetrahydrofuran (THF). After refluxing for 24 h, hexane was added to facilitate the crystalization of TSUA at a low temperature (−20 °C). Shiny needle-like orange crystals were precipitated out from the solution after 24 h. The yield was *ca*. 80%, discounting the loss of TSUA product dissolved in the solution.‡

The purity of the prepared TSUA crystals is high based on NMR spectral data and elemental analysis.§ Using thermogravimetric analysis (TGA) and differential thermal analysis (DTA), we determined the melting point and decomposition temperature of TSUA crystals in argon to be 127.5 °C and 194.3 °C, respectively. Large single crystals were grown by dissolving TSUA in acetone (0.1 g ml^{-1}) at room temperature and cooling to −5 °C. After 2 days, orange single crystals (*ca*. 2 mm × 3 mm × 14 mm) were observed.



Scheme 1 Synthesis of TSUA compound.

UV/visible spectroscopy was used to investigate the reversible photo and thermal isomerization behavior of TSUA in a dilute ethanol solution (28 μg ml^{-1}) (Fig. 1). From the absorption band at 362 nm (the π–π* transition of the *trans* isomer), we determined that $\varepsilon_{max} = 2.59 \times 10^4\ M^{-1}cm^{-1}$ using the assumption of 100% *trans* isomer in (1a), which was supported with ^1H NMR data.§ UV irradiation with a Hg arc lamp (λ_{max} = 350 nm, 30 W) decreased the intensity of the 362 nm band and slightly increased the intensity of the 450 nm band attributed to the n–π* transition of *cis* isomer; a photostationary state (spectrum 1c, *ca*. 70% *cis* isomer based on Lambert's law) was reached within *ca*. 10 min. Exposure to room light caused the reverse isomerization (*cis* → *trans*). For example, from the photostationary state (spectrum 1c), room light exposure increased the intensity of the 362 nm absorption band (spectra 1d–h) progressively. Exposure of (1c) to room light for a long time (12 h) increased the *trans* isomer to *ca*. 96%. The *Cis* <–> *trans* isomerization process was observed to be reversible over three cycles. These results demonstrate the facile photo-isomerization characteristics of the TSUA compound in solution.

The crystallographic structure of TSUA crystals was resolved using single crystal X-ray diffraction.¶ As shown in Fig. 2, there are 4 molecules in the unit cell (M1–M4, from left to right in Fig. 2). The distances between the two urea hydrogen atoms and the neighboring carbonyl oxygen atom are 2.03 and 2.08 Å, respectively, sufficiently close to form hydrogen bonds (N–H···O). The stable 6-membered ring formed by two H-bonds between two neighboring urea groups is energetically favorable, thus providing the main intermolecular interaction during the crystallization process. This is direct evidence of the H-bonding capability of urea ligands.[13–16] The azobenzene ligands are all in the *trans* conformation. Azobenzene planes in M1 and M2 are

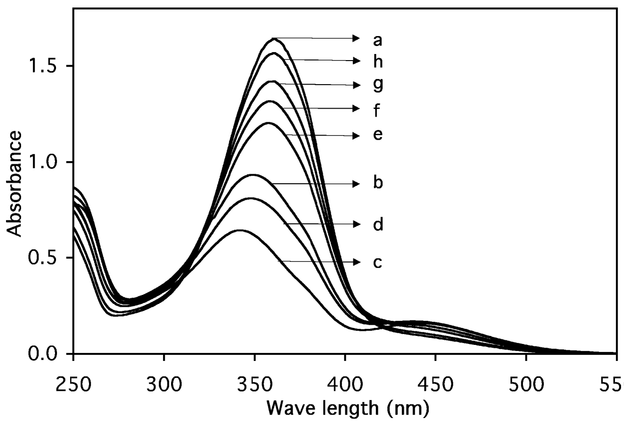


Fig. 1 UV/visible absorption spectra of: a) TSUA in EtOH (28 μg ml^{-1}); b, c) after UV irradiation of (a) for 2 and 10 min; d, e, f, g, h) after room light exposure of (c) for 3, 12, 40, 60 min, and 12 h, respectively.

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† Electronic supplementary information (ESI) available: crystallographic data of TSUA compound, including crystal data, atomic coordinates, bond length and bond angles, anisotropic displacement parameters, observed and calculated structure factors. See http://www.rsc.org/suppdata/cc/b3/b301569f/

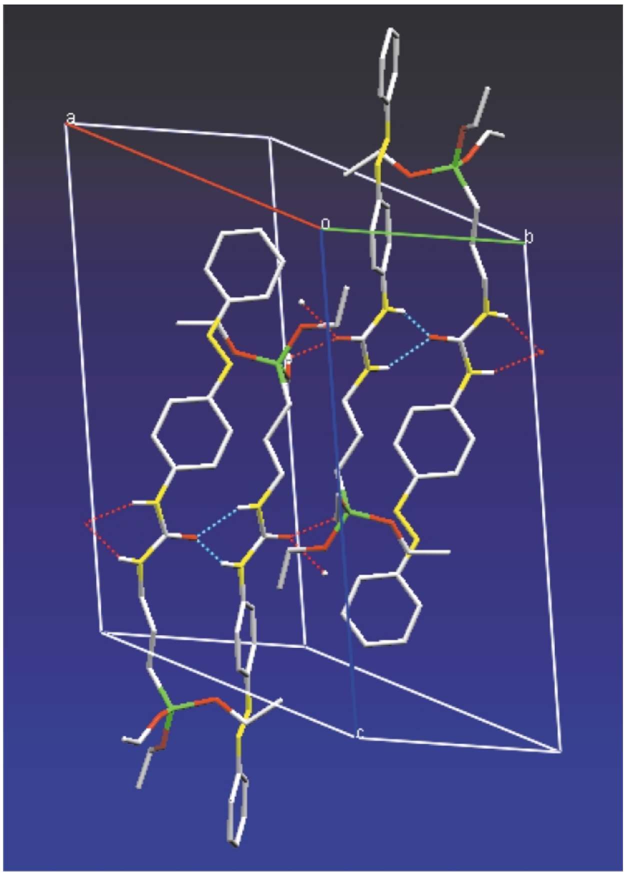

Fig. 2 Unit cell structure of TSUA. Legend: C (grey), O (red), N (yellow), Si (green), H atoms are omitted for clarity except urea H (white). Turquoise dotted bonds are H-bonds between two urea groups in the unit cell and red dotted bonds are H-bonds to the urea groups in the neighboring unit cell.

parallel to those in M4 and M3, respectively, with the angle of the two sets of planes at 81.2°. Some selected crystallographic data are listed in the footnote.‖

Work is now underway to prepare inorganic–organic hybrid mesoporous materials. Some preliminary results showed that the TSUA compound was a good precusor to make photo-responsive mesoporous materials in which the material properties can be controlled by external photo-irradiation.[17]

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Notes and references

‡ Detailed synthesis procedure: 2.05 g (8.12 mmol) triethoxysilylpropyl isocyanate (Aldrich, 98%, without further purification) was added to 1.58 g (7.85 mmol) 4-phenylazoaniline (Aldrich, 98%, without further purification) in 12 ml anhydrous THF (the molar ratio exceeds 1:1 to compensate for traces of water in the solution). After refluxing for 24 hours, 40 ml hexane was added and the solution was cooled to −20 °C for 24 hours. Shiny needle-like orange crystals that precipitated from the solution were filtered, washed with copious amounts of hexane, and vacuum dried. The overall yield was 80%.

§ NMR characterization of the product in deuterated dimethyl sulfoxide (d^6-DMSO) was performed on a Bruker DRX 400MHz instrument. ^{29}Si NMR: δ = −42 (Si). ^{13}C NMR: δ = 154.8 (C=O), 152.1, 146.1, 144.1, 130.5, 129.3, 123.9, 122.2, 117.4 (aryl C), 57.7 and 18.2 (–CH_2CH_3), 41.8 and 23.2 and 7.3 (–$SiCH_2CH_2CH_2NH$–). ^{1}H NMR: δ = 8.86 (s; urea H close to aryl, 1H), 6.32 (t, ^3J(H, H) = 5.7 Hz; the other urea H, 1H), 7.79 (d, ^3J(H, H) = 8.2 Hz; aryl H, 4H), 7.58 (d, ^3J(H, H) = 8.6 Hz; aryl H, 2H), 7.51 (t, ^3J(H, H) = 7.3 Hz; aryl H, 2H), 7.45 (t, ^3J(H, H) = 7.0 Hz; aryl H, 1H), 3.06 (multiplets, –NCH_2–, 2H), 1.47 (multiplets, –CCH_2C–, 2H), 0.53 (t, ^3J(H, H) = 8.2 Hz; –CH_2Si–, 2H), 3.70 (q, ^3J(H, H) = 6.9 Hz; –OCH_2–, 6H), 1.10 (t, ^3J(H, H) = 6.9 Hz; –CH_3, 9H). According to a previous report,[15] the urea protons will shift their positions if the azo group is in a *cis* conformation. However this is not observed, demonstrating that TSUA molecules in solution are in the *trans* conformation.

FTIR was performed using a Bruker Vector 22 spectrometer. There are three characteristic vibrational bands of the –NH–CO–NH– group: $\tilde{\nu}$ = 3287 cm^{-1} (NH stretch), 1698 cm^{-1} and 1533 cm^{-1} (amide I and II stretches).

Elemental analysis was performed on a Perkin Elmer Model 2400 CHN Elemental Analyzer. The percentage of C, H, and N is 59.58%, 7.07%, and 13.04%, respectively.

¶ An orange crystal was mounted on a thin glass fiber using fluorolube. The crystal, which was mounted from a pool of fluorolube, was then immediately placed under a liquid N_2 stream on a Bruker AXS diffractometer. The radiation used was graphite monochromatized Mo Kα radiation (λ = 0.71073 A). The lattice parameters were optimized from a least-squares calculation on ~700 centered reflections. Lattice determination and data collection were carried out using SMART Version 5.054 software. Data reduction was performed using SAINT+ 6.02 (7/13/99) software. Structure solution was performed using SHELXTL 5.1 (10/29/98) software. The structure refinement was performed using XSHELL 4.1 (11/08/2000) software. The data was corrected for absorption using the program SADABS within the SAINT+ package.

‖ *Crystal data*: $C_{22}H_{32}N_4O_4Si$, M = 444.61, monoclinic, space group $P2(1)/n$, a = 15.430(3), b = 9.2471(17), c = 18.504(3) Å, β = 114.501(4)°, V = 2402.5(8) Å^3, Z = 4, μ = 0.132 mm^{-1}, 12976 reflections measured, 2959 unique (R_{int} = 0.0832) which were used in all calculations, final R = 0.0683 (R_w = 0.1500) with reflections having intensities greater than 2σ, GOF(F^2) = 1.043. CCDC 192903. See http://www.rsc.org/suppdata/cc/b3/b301569f/ for crystallographic data in .cif or other electronic format.

1 *Photochemistry and Photophysics*, Ed. H. Rau and J. Rabek, CRC Press Inc.: Boca Raton, 1990, **Vol. II**, p Chapter 4.
2 *Photoreactive Materials for Ultrahigh-Density Optical Memory*, Ed. K. Ichimura, T. Seki, Y. Kawanishi, Y. Suzuki, M. Sakuragi, T. Tamaki and M. Irie, Elsevier, Amsterdam, 1994.
3 *Azobenzene-Containing Materials*, Ed. A. Natansohn, WILEY-VCH Verlag GmbH: Weinheim, 1999.
4 G. S. Kumar and D. C. Neckers, *Chem. Rev.*, 1989, **89**, 1915–1925.
5 T. Kuwabara, H. Nakajima, M. Nanasawa and A. Ueno, *Anal. Chem.*, 1999, **71**, 2844–2849.
6 Y. C. Sasaki, Y. Suzuki, Y. Tomioka, T. Ishibashi, M. Takahashi and I. Satoh, *Langmuir*, 1996, **12**, 4173–4175.
7 S. Kurihara, S. Nomiyama and T. Nonaka, *Chem. Mater.*, 2001, **13**, 1992–1997.
8 R. Wang, L. Jiang, T. Iyoda, D. A. Tryk, K. Hashimoto and A. Fujishima, *Langmuir*, 1996, **12**, 2052–2057.
9 H.-K. Lee, A. Kanazawa, T. Shiono, T. Ikeda, T. Fujisawa, M. Aizawa and B. Lee, *J. Appl. Phys.*, 1999, **86**, 5927–5934.
10 S. R. Lustig, G. J. Everlof and G. D. Jaycox, *Macromolecules*, 2001, **34**, 2364–2372.
11 S. Kurihara, D. Yoneyama and T. Nonaka, *Chem. Mater.*, 2001, **13**, 2807–2812.
12 M. Ueda, H. B. Kim, T. Ikeda and K. Ichimura, *J. Non-Cryst. Solids*, 1993, **163**, 125–132.
13 J. J. E. Moreau, L. Vellutini, M. Wong Chi Man and C. Bied, *J. Am. Chem. Soc.*, 2001, **123**, 1509–1510.
14 J. J. E. Moreau, L. Vellutini, M. Wong Chi Man, C. Bied, J.-L. Bantignies, P. Dieudonne' and J.-L. Sauvajol, *J. Am. Chem. Soc.*, 2001, **123**, 7957–7958.
15 N. Liu, K. Yu, B. Smarsly, D. R. Dunphy, Y.-B. Jiang and C. J. Brinker, *J. Am. Chem. Soc.*, 2002, **124**, 14540–14541.
16 T. Seki, T. Fukuchi and K. Ichimura, *Langmuir*, 2002, **18**, 5462–5467.
17 N. Liu, Z. Chen, D. R. Dunphy, Y.-B. Jiang, R. A. Assink and C. J. Brinker, *Angew. Chem., Int. Ed.*, 2003, accepted.