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A Liquid Azobenzene as Solvent-Free Solar Thermal Fuel

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A liquid solar thermal fuel is developed; a low-molecular weight liquid *trans*-azobenzene derivative shows facile photoisomerization to the higher-energy *cis* isomer in neat condition so that a high volumetric energy density is achieved. Shear viscosity measurements for each isomer liquid unveiled transitions from non-Newtonian to Newtonian fluids.

The storage and conversion of solar energy into useful form of energy is one of the most important challenges in modern chemistry. Intensive studies have been devoted for the solar energy conversion, *i.e.*, artificial photosynthesis[1] and photovoltaic applications.[2] Yet another important research field is to store solar photon energy in solar thermal fuels,[3] in which light energy is converted to the chemical bond energy of metastable photoisomers. By applying external stimuli such as heat, voltage or photoirradiation, the stored energy can be discharged on demand as heat. The whole process is essentially closed cycle and when both of the photoisomerization and heat release occur reversibly, they ideally give rechargeable molecular fuels without any emission or waste. In this light, photochromic compounds such as norbornadiene (NBD),[4] ruthenium-fluvalene complex[5] and azobenzene[6] have been studied as candidates for solar thermal fuels. The valence isomerization of NBD and quadricyclane has an inherent disadvantage that NBD does not absorb sunlight itself and require additional sensitizers.[4] In addition, by-products formed in this reaction decrease overall efficiency of the process. Although the Ru-based organometallic compound has shown high cyclability without degradation,[5] the use of Ru is undesirable in the light of cost saving.

Photoisomerization of *trans*-azobenzene, meanwhile, has been extensively studied as molecular photo-switches[7] because of its superior chemical stability and the ease of synthesis. Photochemical generation of high-energy metastable *cis* isomer allows storage of photon energy in the form of molecular strain energy ($\Delta H \sim 50$ kJ mol^{-1}), which can be released as heat by subsequent *cis*-to-*trans* thermal isomerization.[3a] However, the application of *trans*-to-*cis* photoisomerization for photon energy storage has been viewed with suspicion because it is significantly suppressed in condensed states such as crystals,[8] which are desirable in terms of high energy density. Although the photoisomerization of azobenzene molecules occurs in solution, their dilution with solvents inevitably results in decrease in the total volumetric energy density. To enhance the energy storage
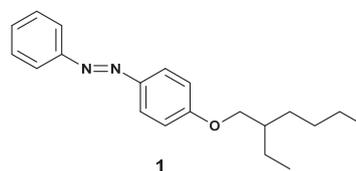

Chart 1   Chemical structure of a liquid azobenzene derivative **1**.

capacity of azobenzene chromophores, Grossman *et. al.*, recently developed azobenzene-functionalized single-walled carbon nanotubes which showed a high ΔH of 124 kJ·mol^{-1} (56 Wh·kg^{-1}).[9] However, the use of carbon nanotubes as template is undesirable, which limits the light absorbed by azobenzene chromophores and reduces gravimetric energy density of the conjugates. These hybrids are also not adequate to bulk synthesis and require dilution with organic solvents to perform photoisomerization. To solve these conflicting issues, it is of great significance to develop a reversibly photo-isomerizable, solvent-free liquid system that is one of the important requirements for solar thermal batteries.[10] Although some photo-isomerizable ionic liquids (ILs) have been reported to date,[11] their photochromism has been mostly investigated in dilute solutions or in polymer matrices. Moreover, the photoisomerization in ILs has not been performed from the perspective of molecular solar thermal fuels. Here, we describe synthesis, photo-isomerization characteristics and shear viscosity properties of a newly developed liquid azobenzene derivative **1**. The observed results unveil unknown liquid properties of each liquid isomer as well as their potential as a photon energy storage material.

To fluidify azobenzene chromophores at room temperature, a branched 2-ethylhexyl group was introduced in the 4-position of azobenzene chromophores via an ether linkage (Chart 1). This structural modification was taken from 2-ethylhexyl 4-methoxycinnamate,[12] a π-conjugated organic liquid which has been commercially used as ingredient in sunscreens. Introduction of such branched alkyl chains in racemic form drastically weaken intermolecular interactions, thereby inducing liquid phase at RT. The small molecular weight of 2-ethylhexyl group is considered to be ideal for achieving entirely condensed-phase photoisomerization while maintaining the high gravimetric and volumetric energy
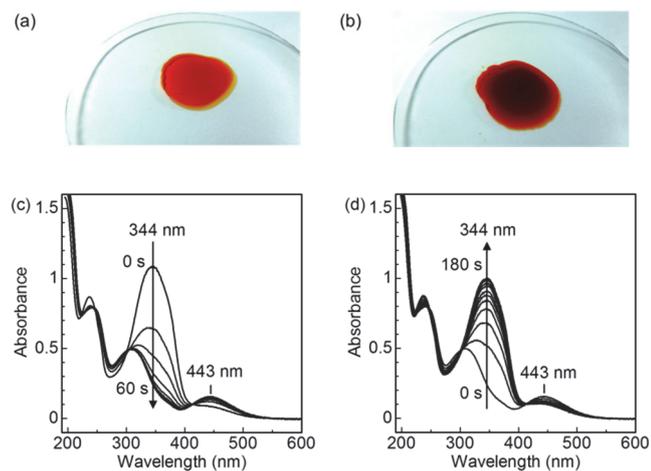
Fig. 1 Pictures of liquid **1** (a) discharged state, (b) charged state. UV-Vis absorption spectral changes of **1** upon irradiation (c) at 365 nm and (d) at 480 nm in neat conditions (no solvents). Spectra were obtained for thin liquid membranes prepared in between a quartz cell and a quartz plate.
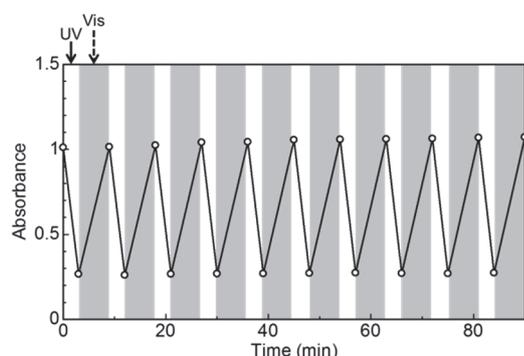

Fig. 2 Changes in the absorption intensity of liquid azobenzene **1** at 344 nm in the course of repetitive UV and Vis irradiation. The irradiation periods of UV light (365 nm) and visible light (480 nm) are 3 min and 6 min, respectively. Liquid thin film of **1** was prepared by sandwiching between a quartz cell and a quartz plate

density. The liquefaction phenomena induced by these branched alkyl chains have been recently rediscovered by the reports on liquid carbazole,[13] luminescent liquids[14] and photon upconverting liquids.[15]

The compound **1** was synthesized in one step and is compatible with quantity synthesis (*e.g.*, ~20 g at one batch in the synthesis, Scheme S1, ESI). Irradiation of UV light to the neat liquid **1** caused color change from bright orange (*trans*-**1**) to dark red (Fig.1a→1b). Figure 1c,d show UV-Vis absorption spectral changes of **1** upon UV and Vis light illumination in neat conditions. The observed π-π* absorption band for *trans*-**1** in neat condition (λ_{max} = 344 nm) is almost identical with that observed for dilute methanol solutions (λ_{max} = 345 nm, Fig. S1a and S1b), indicating the absence of appreciable intermolecular interactions in liquid azobenzene chromophores. Upon illumination of the UV light (365 nm), the π-π* absorption peak around at 344 nm showed decrease within 60 s and an n-π* absorption peak appeared around at 443 nm, which are typical of *trans*-to-*cis* photoisomerization of azobenzene chromophores. The time courses of peak absorbance changes observed for **1** upon UV and visible light irradiation are shown in Fig.S1c,d (ESI) respectively, which compares those observed for neat liquid thin films and methanol solutions (7.5 x 10⁻⁵ M). It is to note that the *trans*-to-*cis* (Fig.S1c) and *cis*-to-*trans* (Fig.S1d)
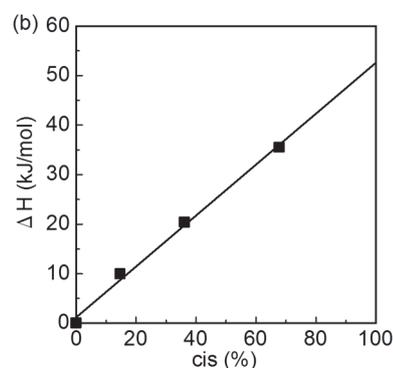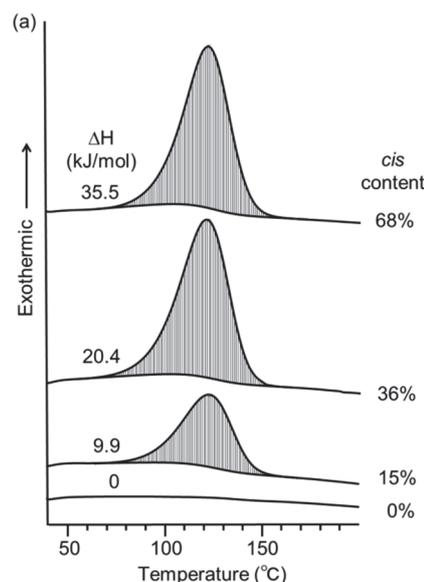

Fig. 3 (a) DSC thermograms of **1** at varied molar ratio of *cis* isomer. Heating rate, 50 K·min⁻¹. (b) Dependence of *cis*→*trans* isomerization enthalpy ΔH against the molar content of *cis* isomer.

photoisomerization of **1** in neat liquid films (filled circle) proceeded facilely as observed in methanol (open circle). It clearly shows that the photoisomerization of liquid azobenzene chromophores are not suppressed despite of the condensed state. Figure 2 shows the dependence of absorbance at 344 nm on repetitive *trans*-to-*cis* and *cis*-to-*trans* photoisomerization with UV (365 nm) and visible (480 nm) light irradiation. Clearly, the absorption intensities of the *trans*- and *cis*-azobenzene chromophores are well preserved throughout the iterative photoirradiation process, and each structural conversion process was visually monitorable by the color changes (Fig.1a, b).

To evaluate the photon-energy storage performance of **1**, thermal properties and heat storage capacity of **1** was investigated by using differential scanning calorimetry (DSC). *trans*-**1** showed a glass transition temperature at around -63 °C and no thermal decomposition peak was observed in the measured temperature range from -63 °C to 220 °C, demonstrating the stability of azobenzene liquid **1** in a wide temperature range (Fig. S2, ESI). *cis*-**1** was prepared by UV irradiation of neat liquid **1** with an ultra-high pressure mercury lamp, and the content of *cis*-**1** at the photostationary state was determined by ¹H-NMR spectroscopy. Fig. 3a shows DSC thermograms obtained for *cis*-**1** at varied photoisomerization degree. In these DSC isotherms, exothermic peaks were observed at around 120 °C which showed ΔH values varied depending on the molar ratio of *cis* isomers (Fig. 3a). At the

cis-molecular content of 68%, isomerization enthalpy (*ΔH*) and bulk energy density were calculated as 35 kJ·mol⁻¹ and 32 Wh·kg⁻¹, respectively. The heat released by thermally induced *cis*-to-*trans* isomerization showed linear dependence on the fraction of *cis*-**1**, and the *ΔH* corresponding to 100% *cis* isomer was estimated as 52 kJ·mol⁻¹ (47 Wh·kg⁻¹) by extrapolation of the plot (Fig. 3b). This value is consistent with the reported isomerization enthalpy for unsubstituted *cis*-azobenzene.[3a,16] Note that the DSC peak temperatures are amenable to change depending on the heating rate (Fig. S3, ESI), and thermograms in Fig. 3a were obtained with a high heating rate (50 K·min⁻¹). The heating conditions would be optimized in order to set up flow solar thermal conversion system, but the observation of exothermic peaks even at high heating rate is advantageous in terms of fast conversion of molecular strain energy to heat. Although the charging energy and bulk energy density reported for the state-of-the-art molecular storages such as the ruthenium-fulvalene (*ΔH* = 83 kJ·mol⁻¹, 52 Wh·kg⁻¹)[5b] and the azobenzene-functionalized single-walled carbon nanotubes[9c] are numerically higher than those observed for **1**, these previous solid materials need to be dissolved or dispersed in solvents for use. Consequently, their overall energy densities are significantly reduced by dilution. In contrast, photoisomerization of liquid azobenzene **1** facilely occurs in the neat state and decrease in the net energy density by dilution is successfully avoided. This feature renders liquid **1** a unique and potential solar thermal storage material.

As transportability is another prominent feature of the liquid molecular solar thermal system, shear viscosity measurement was conducted for *trans*-**1** and *cis*-**1** by using rheometer at ambient temperature (Fig. 4, apparatus, Anton Paar MCR 302). Viscosity of liquid arises from the friction between neighboring molecules, and consequently it depends on the size, shape of molecules and their intermolecular cohesive interactions. In Fig. 4, *trans*-**1** showed larger shear viscosity compared to that observed for *cis*-**1** in the lower shear velocity regime. This indicates the presence of larger cohesive interactions between the planar *trans*-isomers, as compared to the bent *cis*-isomers. This is potentially correlated with the larger static intermolecular interactions revealed by *trans*-azobenzene derivatives in various self-assemblies formed under thermodynamic equilibrium.[17] The shear viscosities *η* of *trans*-**1** and *cis*-**1** show decrease upon increasing the shear velocity *γ* and they reached constant values (*trans*-**1**: 0.12 Pa·s, *cis*-**1**: 0.19 Pa·s) above shear velocities of 3.0 S⁻¹ (*trans*-**1**) and 0.57 S⁻¹ (*cis*-**1**), respectively. These observed viscosities are comparable to that of olive oil (0.13 Pa·s at 10 °C),[18] an easily transportable liquid. It is noteworthy that in the smaller shear velocity regime, these *trans*- and *cis*-azobenzene liquids behave as non-Newtonian fluids and exhibiting pseudoplastic flow,[19] *i.e.*, decrease in the viscosity observed with increasing the rate of shear. The observed property as shear thinning liquids reflects decrease in the intermolecular interactions with increasing the shear velocity, which feature has not been reported for the previously reported alkylated liquid π-compounds.[13-15] Meanwhile, at the higher shear velocity, shear viscosity for these azobenzene liquids becomes independent on the shear velocity. This is a behavior typical of Newtonian fluid. The observed switching from non-Newtonian to Newtonian fluids suggests shear-induced transition from the stick to slip boundary condition, indicative of the presence of fluid clusters.[20]

Very interestingly, the shear viscosity of *cis*-**1** showed smaller dependence on shear velocity compared to *trans*-**1** and at higher shear velocity regime, the *cis*-**1** displayed higher shear viscosity (0.19 Pa·s) compared to that shown by *trans*-**1** (0.12 Pa·s). In the liquid state, molecules are densely packed and the mean molecular distance between the liquid *trans*-**1** and *cis*-**1** should not differ much from each other, since molecular volume decrease upon the *trans*-to-*cis* isomerization is reported to be small.[19] Therefore, the
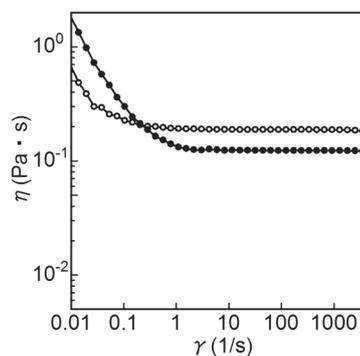

Fig. 4 Shear viscosity versus shear velocity on double-logarithmic scale for *trans*-**1** (●) and *cis*-**1** (○) at 25 ºC. The molar content of *cis* isomer was 79%.

observed difference in shear viscosity between these liquid isomers would be related to the difference in microscopic friction, which depends on the molecular structure and intermolecular interactions.[21] A rotational diffusion time *τ*_R of molecule is proportional to the shear viscosity *η* of the media, divided by *k*_B T where V is the molecular volume of the solute, *k*_B is the Boltzmann constant.[20]

$$\tau_R = (V\eta / k_B T)(fC) \qquad (1)$$

In this equation, *f* is a variable parameter ($f \geq 1$) that is dependent on molecular shape, and *C* is a parameter that accounts for variable boundary conditions.[20] For stick boundary conditions, *C* is set equal to unity and when the molecular shape parameter *f* is also set to 1, Eq.(1) reduces to the classical Stokes-Einstein-Debye (SED) equation. The SED equation is based on a hydrodynamic model that relates the rotational reorientation time to the solvent viscosity, and it has been successfully applied to systems when the size of rotating solute molecules is larger than that of solvent molecules. Although the breakdown of hydrodynamic model has been suggested when the size of solute and solvent molecules became comparable,[22] it will be allowed to assume it for qualitative consideration of the shear viscosity characteristics displayed by the *cis*-azobenzene liquid **1**. In this case, the larger shear viscosity *η* observed for *cis*-**1** at higher shear velocity regime indicates the longer rotational diffusion time *τ*_R as compared to that of *trans*-**1**. It suggests the presence of molecular friction force specific to the *cis*-isomer. The *cis*-azobenzene has a dipole moment of 3 Debye, while the nearly planar *trans*-isomer has a dipole moment near zero.[23] The dipole-dipole interaction shows potential dependence on the inverse 3rd power of the intermolecular distance *r*, and this strength (ca. 2-8 kJ mol⁻¹) often surpasses that of the van dear Waals interactions (<5 kJ mol⁻¹).[24] It is expected to play an important role in governing the rotational motion of solvent-free liquids, and we presume that the dipole-dipole interaction provide an account for the observed larger rotational friction experienced by the *cis* isomer. Yet other possible factors come up with are the shape parameter *f* and dynamical heterogeneities, which would require molecular dynamics (MD) simulations[25] to get a full picture of these photoisomerizable liquid system.

In conclusion, we have demonstrated that the liquid azobenzene **1** as a new and potential family of molecular solar thermal storages. The azobenzene liquid showed satisfactory stability over 280 K and under UV irradiation, it showed facile photoisomerization even in the neat condition. The observed photoisomerization characteristics of liquid azobenzene **1** – the efficient *trans*-to-*cis* and the backward photoisomerization with rates comparable to those observed for molecularly dissolved solutions − is a promising feature as molecular solar thermal storage materials. This neat azobenzene liquid has a remarkable advantage over the existing solid state heat

storage materials in terms of the no need for solvent-dilution, which is advantageous for attaining high energy density. Shear viscosity measurements unveiled the transition from non-Newtonian fluid to Newtonian fluid depending on the shear velocity, which provides a new perspective in the study of π-functional liquids. It is worth noting that the present liquid isomers offer an exclusive opportunity to explore intermolecular interactions of stereoisomers without the interference by solvent molecules. Thus, the present work opens a door to solvent-free liquid solar thermal fuels and understanding their structure-property relationships under conditions near or far from the thermodynamic equilibrium. Although challenges remain to resolve the intrinsic problems of azobenzene chromophores – such as limited exothermicities (< 50 kJmol[-1]), low thermal stability of *cis*-isomers (activation energy for *cis*-to-*trans* isomerization, ca. 100 kJmol[-1]) and difficulties in obtaining pure *cis*-isomers,[3a] the multifaceted property of photoisomerizable azobenzene liquid would find diverse applications in many disciplines.

Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental details, Scheme S1, Figure S1, S2 and S3. See DOI: 10.1039/c000000x/

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