



# Solar-Thermal Energy Conversion and Storage Using Photoresponsive Azobenzene-Containing Polymers

Si Wu\* and Hans-Jürgen Butt

Photoswitchable compounds are promising materials for solar-thermal energy conversion and storage. In particular, photoresponsive azobenzene-containing compounds are proposed as materials for solar-thermal fuels. In this feature article, solar-thermal fuels based on azobenzene-containing polymers (azopolymers) are reviewed. The mechanism of azopolymer-based solar-thermal fuels is introduced, and computer simulations and experimental results on azopolymer-based solar-thermal fuels are highlighted. Different types of azopolymers such as linear azopolymers, 2D azopolymers, and conjugated azopolymers are addressed. The advantages and limitations of these azopolymers for solar-thermal energy conversion and storage, along with the remaining challenges of azopolymer-based solar-thermal fuels, are discussed.

## 1. Introduction

Solar energy is one of the most important renewable energies. Many techniques have been developed for solar energy conversion and storage. The development of solar-thermal fuels using photoresponsive compounds represents a unique strategy for solar-thermal energy conversion and storage.<sup>[1–6]</sup> Azobenzene is an important compound that is proposed for solar-thermal fuels.<sup>[3–9]</sup> Azobenzene is a photoswitchable compound (Figure 1a).<sup>[10–12]</sup> Usually, *trans* azobenzene is thermal stable. UV irradiation induces a *trans*-to-*cis* isomerization. Because the energy level of *cis* azobenzene is  $\approx 50 \text{ kJ mol}^{-1}$  ( $275 \text{ kJ kg}^{-1}$ ) higher than that of the *trans* isomer (Figure 1b),<sup>[11]</sup> solar energy is stored in the metastable *cis* isomer. The stored solar energy in *cis* azobenzene can be released as heat spontaneously, by heating or catalysis (Figure 1c). Upon energy release, *cis*

azobenzene is switched back to the *trans* isomer that is ready for the next charging cycle (Figure 1c).

There were early studies using photoisomerization of azobenzene compounds for solar energy conversion and storage more than 30 years ago. In 1983, Olmsted et al. studied photochemical storage potential of azobenzene compounds.<sup>[13]</sup> They concluded that azobenzene compounds were not favorable for photochemical solar energy storage because of limited solubility and rapid thermal reversion rates in polar solvents. In 1987, Taoda et al. reported their study on photochemical conversion and storage of solar energy by azobenzene.<sup>[14]</sup>

They suggested keeping the storage tank of azobenzene solutions in a dark, cool room because *cis* azobenzene is apt to convert into *trans* form at high temperatures. The required cool storage hinders the use of azobenzene for solar-thermal energy conversion and storage.

In general, materials for solar-thermal energy conversion and storage should exhibit high energy conversion efficiency, high energy storage capacity, good stability in charging–discharging cycles, and be able to utilize light in the broad solar spectrum. The abovementioned issues make the use of azobenzene for solar-thermal energy conversion and storage undeveloped for a long time. Based on the new developments of organic chemistry, materials chemistry, polymer chemistry, photochemistry, and computer simulations of azobenzenes, it is now possible to address some of the problems. A few groups including our group restarted developing solar-thermal fuels using azobenzene-containing materials. Some newly developed azobenzene derivatives<sup>[7,15]</sup> can address the problems of the azo compounds that were used in 1980s.

With the development of solar-thermal fuels based on photoresponsive materials, comprehensive reviews have been done. For example, Boulatov and coworkers have reviewed chemical solutions for the molecular design of solar thermal fuels;<sup>[4]</sup> Feng and coworkers reviewed azobenzene-based solar thermal fuels.<sup>[3]</sup> Solar-thermal fuels based on small azobenzene molecules<sup>[16,17]</sup> are out of the focus of this Feature Article. Instead of writing a comprehensive review, we focus on azobenzene-containing polymers (azopolymers) for solar-thermal energy conversion and storage in this Feature Article. Azopolymers have improved processability and are suited to construct solid-state devices. We will introduce how to design solar-thermal fuels from polymer point of view. Linear polymers, conjugated polymers, and 2D polymers (e.g., graphenes), azobenzene-functionalized carbon nanotubes (CNTs) that are

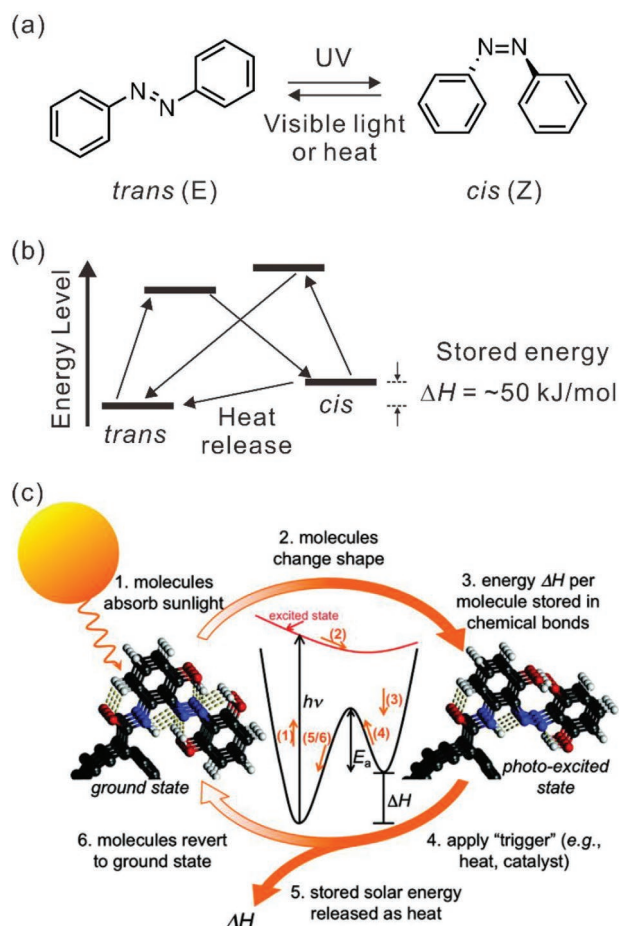
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DOI: 10.1002/marc.201900413



**Figure 1.** a) Photoisomerization of azobenzene. UV light induces *trans*-to-*cis* isomerization. The *cis*-to-*trans* isomerization takes place thermally or can be induced by visible light. b) Schematic illustration of solar energy storage and heat release using simplified energy levels of azobenzene. The energy level of the *cis* isomer is  $\approx 50 \text{ kJ mol}^{-1}$  ( $275 \text{ kJ kg}^{-1}$ ) higher than that of the *trans* isomer. For comparison: the energy of 300 nm photons is  $400 \text{ kJ mol}^{-1}$ . Upon excitation by light with a wavelength in the *trans* absorption band, *trans*-azobenzene isomerizes into the *cis* form. Excitation of the *cis* form using light with a wavelength in the *cis* absorption band can induce *cis*-to-*trans* back isomerization. These photoisomerizations usually have picosecond timescales. Alternately, *cis*-to-*trans* back isomerization can be induced thermally, which has a timescale ranging from milliseconds to days depending on the substituents and local environments. c) The concept of using azobenzene compounds for solar-thermal energy conversion and storage. Panel (c) reproduced with permission.<sup>[18]</sup> Copyright 2011, American Chemical Society.

functionalized with azobenzene groups for solar-thermal fuels will be introduced. We will show how to design azopolymers to overcome some obstacles for solar-thermal conversion and storage.

## 2. Solar-Thermal Fuels Using Nanocarbon-Based Azopolymers

In this section, we introduce fabrication of solar-thermal fuels using 2D polymers such as graphenes and 1D polymers such as CNTs that are functionalized with azobenzene groups.



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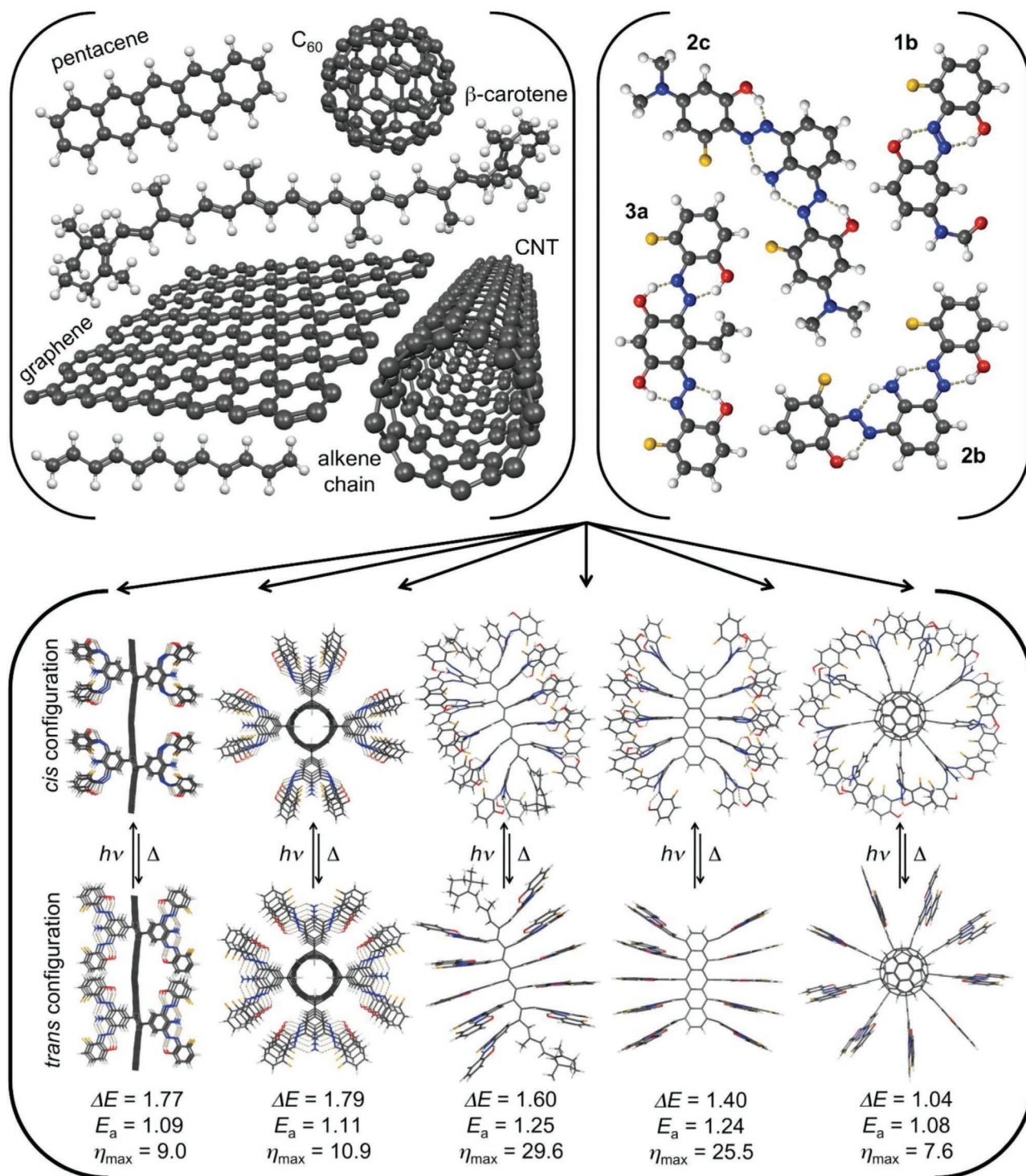
**Hans-Jürgen Butt** is a director at the Max Planck Institute for Polymer Research (MPIP), Mainz, Germany. He studied physics in Hamburg and Göttingen. He defended his Ph.D. thesis in 1989 at the Max Planck Institute for Biophysics (MPIBP). After a one-year postdoc at the University of California, he moved back to MPIBP and

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A problem for azobenzene-based solar-thermal fuels is that their energy storage capacities are low because the energy level between *trans* and *cis* azobenzenes is only  $50 \text{ kJ mol}^{-1}$  ( $275 \text{ kJ kg}^{-1}$ ). To tackle this problem, Kolpak and Grossman used density functional theory (DFT) computer simulations on azobenzene-functionalized CNTs (Figure 1c).<sup>[18]</sup> In their design, CNTs are templates to regulate the packing of azobenzene groups. Their results suggested that the combination of azobenzene with CNTs large increased the energy storage capacity per molecule. The computer simulation results showed that the volumetric energy densities of azobenzene-functionalized CNTs are equivalent to or higher than those reported for state-of-the-art Li-ion batteries.<sup>[18]</sup> The increase of the performance using azobenzene-functionalized CNTs is because the intermolecular interactions simultaneously increase the energy storage capacity and the lifetime of the photoexcited state. The use of CNTs as templates for azobenzene groups provides a new strategy for design of highly cyclable, thermally stable, and energy-dense solar-thermal fuels.

After they proposed the concept of using CNTs as templates, the same group also used DFT computations to study azobenzene-functionalized graphene,  $\beta$ -carotene, pentacene, and  $C_{60}$  (Figure 2).<sup>[19]</sup> The computer simulation results showed

azobenzene-functionalized carbon materials can reversibly store solar energy at densities comparable to Li-ion batteries.<sup>[19]</sup> Additionally, variation of the template material in combination with azobenzene groups can be used to optimize performance of

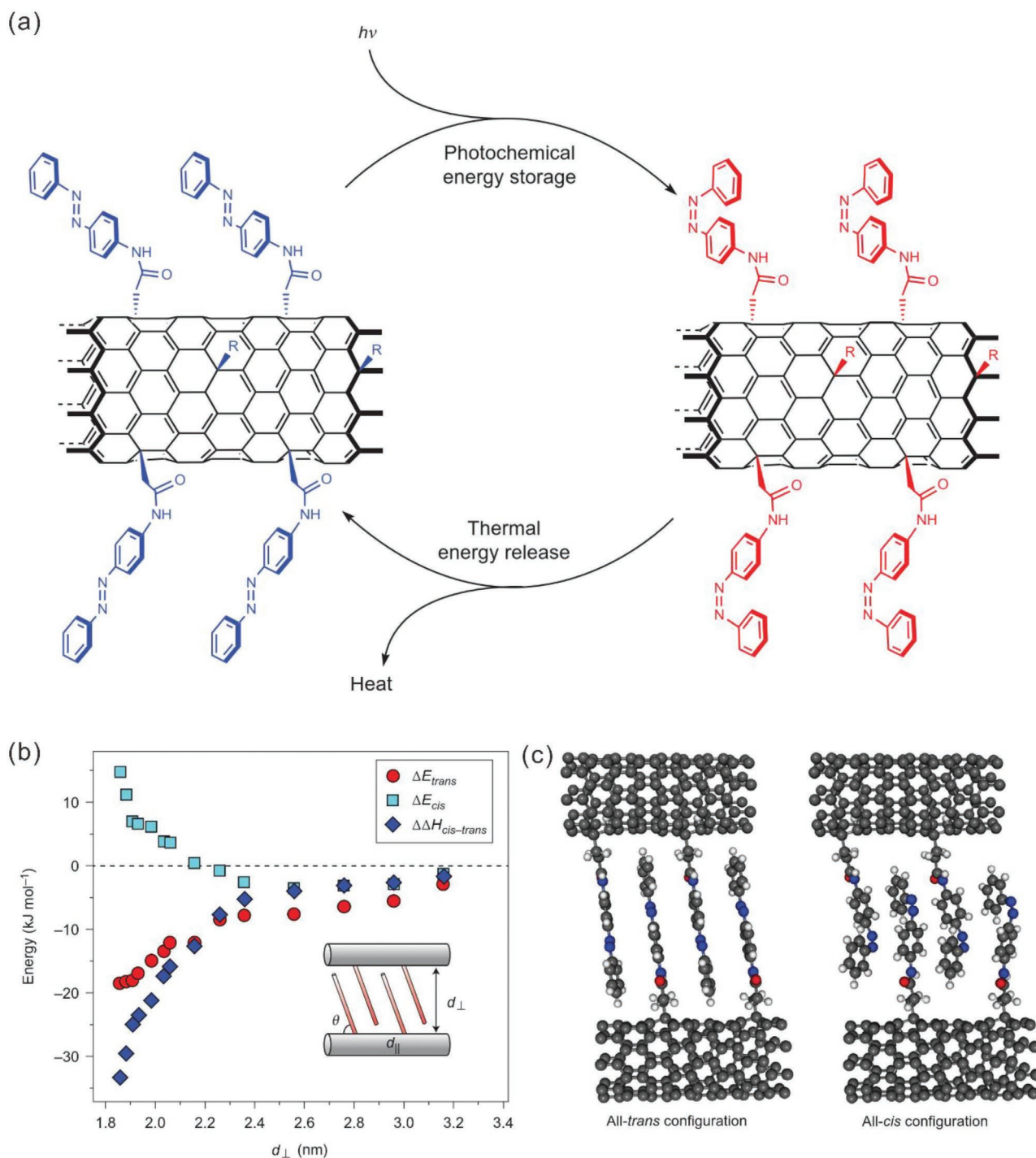


**Figure 2.** (Top) The template materials (graphene, CNT,  $\beta$ -carotene, pentacene, and  $C_{60}$ ) and several azobenzene derivatives (3a, 1b, 2b, and 2c). (Bottom) Computed atomic structure and properties of 2b/graphene, 2b/CNT, 2b/ $\beta$ -carotene, 2b/pentacene, and 2b/ $C_{60}$  (from left to right). White, dark gray, blue, red, and orange balls/sticks represent H, C, N, O, and F atoms, respectively. Reproduced with permission.<sup>[19]</sup> Copyright 2013, AIP Publishing.



solar-thermal fuels such as the energy density, the storage lifetime, the temperature of the output heat, and the efficiency of the solar-to-heat conversion. Furthermore, the theoretical maximum

efficiency is as high as 50% for this class of solar-thermal fuels.<sup>[19]</sup> The computer simulation results suggest that solar-thermal fuels may become a competitive renewable energy technology.



**Figure 3.** a) Photochemical charging and thermal activation of energy release in azobenzene-functionalized CNTs. b,c) Energy storage as a function of template-packing parameters. b) Enthalpy difference  $\Delta H_{cis-trans}$  for intercalated azobenzene-functionalized CNTs (blue diamonds), as well as total energy per azobenzene of the *cis* (cyan squares) and *trans* (red circles) conformations, as a function of CNT separation. Energies are relative to the respective values for an isolated azobenzene-functionalized CNT with 1/16 packing density. The inset schematic defines the geometric parameters. c) Computed atomic structures at the minimum-energy *trans* separation distance. Reproduced with permission.<sup>[20]</sup> Copyright 2014, Springer Nature.

After they demonstrated that azobenzene-functionalized CNTs are potential solar-thermal fuels using DFT calculations, Grossman, Nocera, Kucharski, and coworkers synthesized azobenzene-functionalized CNTs and studied these materials experimentally (Figure 3).<sup>[20]</sup> This design increased the amount of energy stored per azobenzene from 58 to 120 kJ mol<sup>-1</sup>. Azobenzene-functionalized CNTs also showed good stability and cyclability. The good performance of the solar-thermal fuels based on azobenzene-functionalized CNTs is because of templating azobenzene groups on rigid CNTs. Interactions between azobenzene groups on neighboring CNTs can potentially be even more important than those on an individual CNT. The enforcement of conformational restriction and photochemically generated steric strain in azobenzene-functionalized CNTs increased both the amount of energy stored per azobenzene groups by more than 200% and the storage lifetimes by orders of magnitude,<sup>[20]</sup> along with resisting material degradation under repeated cycling. It was demonstrated that azobenzene-functionalized CNTs in acetonitrile can be optically cycled for more than 500 time by alternative UV and visible light irradiation.<sup>[20]</sup> This work establishes the feasibility of increasing bulk gravimetric energy densities of azobenzene compounds despite the obvious potential decrease associated with the addition of a non-energy-storing templating material. These experimental results are quite close to the computer simulations.<sup>[18,19]</sup> Thus, the use of CNTs as templates for azobenzene groups opens up an avenue for designing solar-thermal fuels.

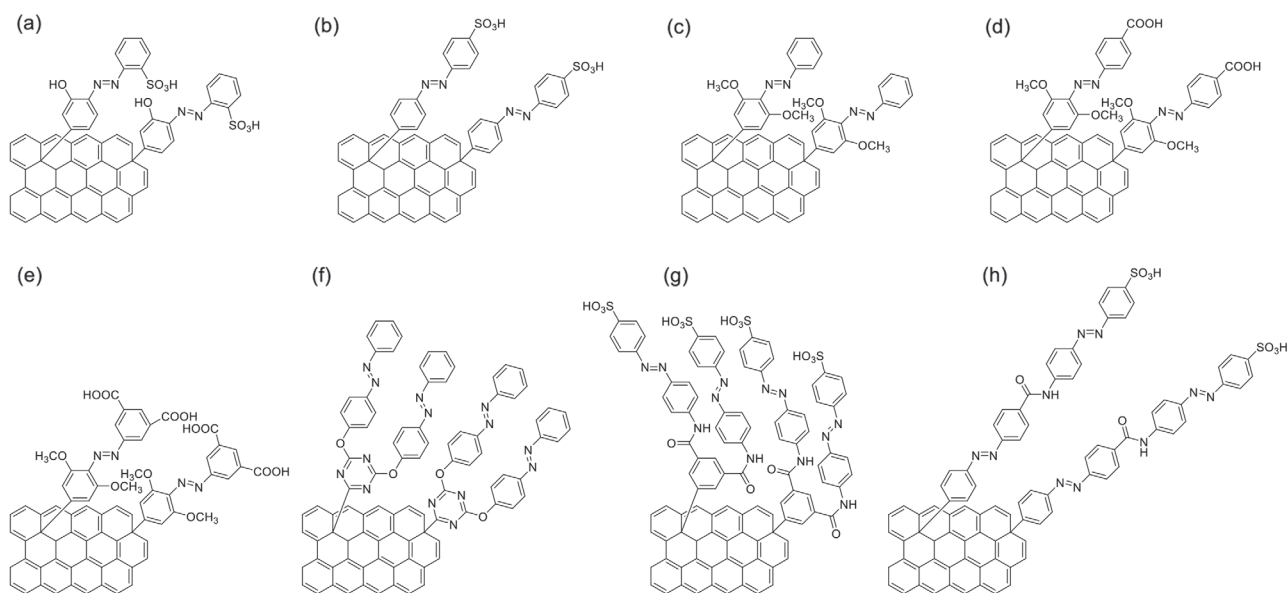
The computer simulations showed that not only azobenzene-functionalized CNTs but also azobenzene-functionalized graphenes are promising candidates for solar-thermal fuels (Figure 2).<sup>[19]</sup> Feng and coworkers experimentally studied azobenzene-functionalized graphenes.<sup>[21–23]</sup> They synthesized AZO-RGO hybrids by covalently grafting azobenzene groups on reduced graphene oxide (Figure 4). Similar to CNTs, graphenes in AZO-RGO serve as templates for azobenzene groups.

In addition, Feng and coworkers systematically studied how substituents on AZO-RGO hybrids influence photoswitching, energy density, and reversible charging–discharging cycles. The important parameters for increasing the performance of solar-thermal fuels based on AZO-RGO hybrids are H-bonding, distance between two adjacent azobenzene groups, and electronic interactions (Figure 5). They showed that the energy density of AZO-RGO hybrids was increased by increasing the number of molecular interactions, improving the grafting density, optimizing the steric configuration, and attaching suitable substituents to different positions of azobenzene groups.

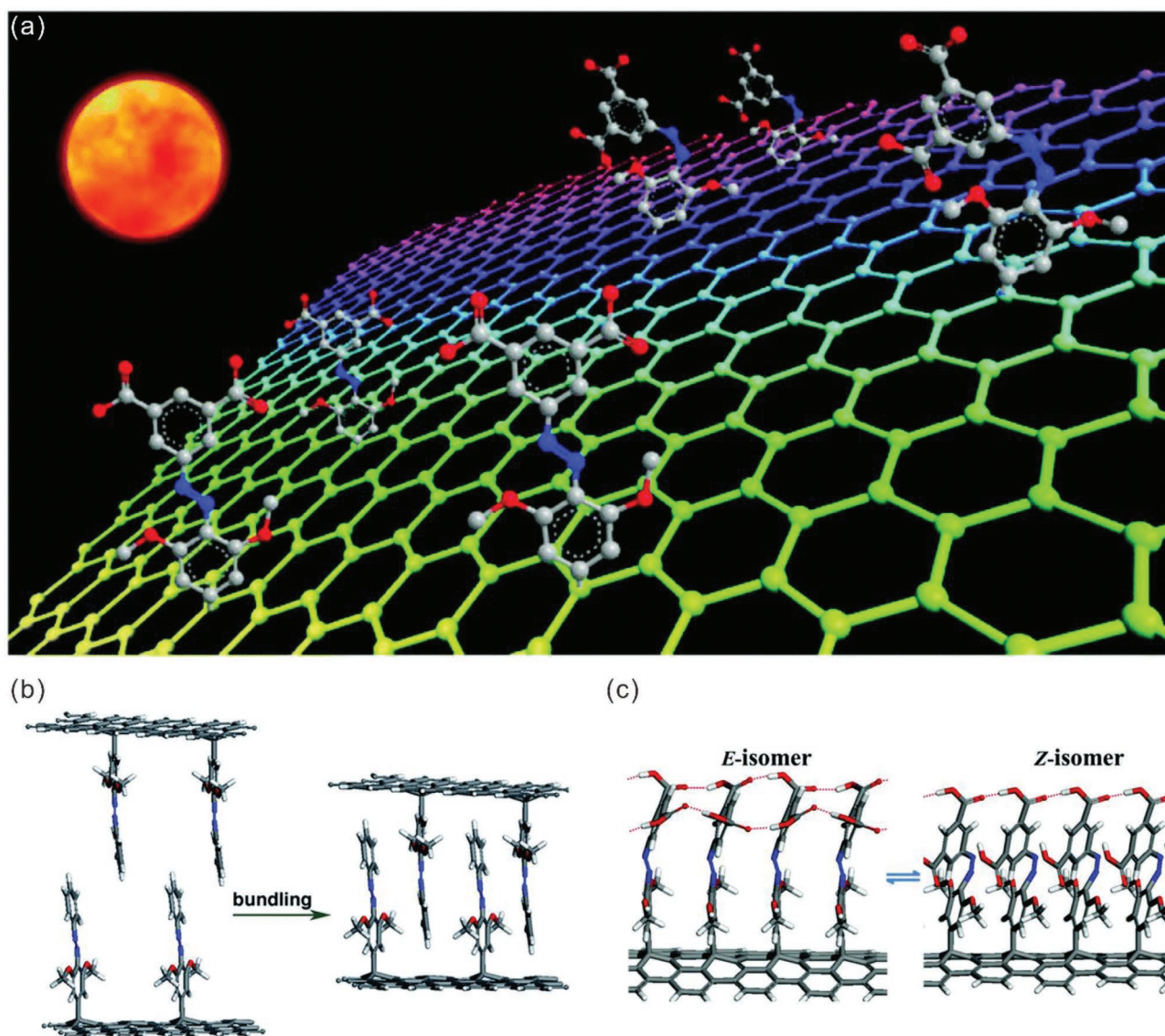
Recently, Feng and coworkers also demonstrated the use of assembled films of azo compounds and RGO as a source of solar-thermal energy for application in thermochromic displays.<sup>[24]</sup> This idea is based on outputting solid-state heat via a closed cycle of light harvesting, energy storage, and heat release. The heat released from a solar-thermal storage film was improved by increasing the degree of *trans*–*cis* isomerization of the azo compounds on RGO. The heat output was applied to a thermochromic display to induce color changes. This work demonstrates a new application of solar-thermal fuels.

### 3. Solar-Thermal Fuels Using Conjugated Azopolymers

Besides CNTs and graphenes, other  $\pi$ -conjugated systems were also used as templates for azobenzene groups to construct solar-thermal fuels. Polydiacetylenes are conjugated polymers that are prepared by topochemical polymerization of diacetylene monomers in ordered structures.<sup>[25–27]</sup> One of us and coworkers have systematically investigated azobenzene-functionalized polydiacetylenes.<sup>[28–30]</sup> Based on the development of azobenzene-functionalized polydiacetylenes, Han et al. recently used azobenzene-functionalized polydiacetylenes for



**Figure 4.** Chemical structures of AZO-RGO hybrids.<sup>[21–23]</sup>



**Figure 5.** a) Schematic illustration of the AZO–RGO hybrid as a solar-thermal storage material based on photoisomerization. b) Mechanism of inter-planar bundling for AZO–RGO hybrids. There is no packing in solution (left) because of a large interlayer spacing; in contrast, there are packing interactions in the solid state because of the bundling with a low interlayer space (right). c) Stable models of E- and Z-isomers of AZO–RGO hybrids by DFT calculations. Reproduced with permission.<sup>[21,22]</sup> Copyright 2015, Royal Society of Chemistry.

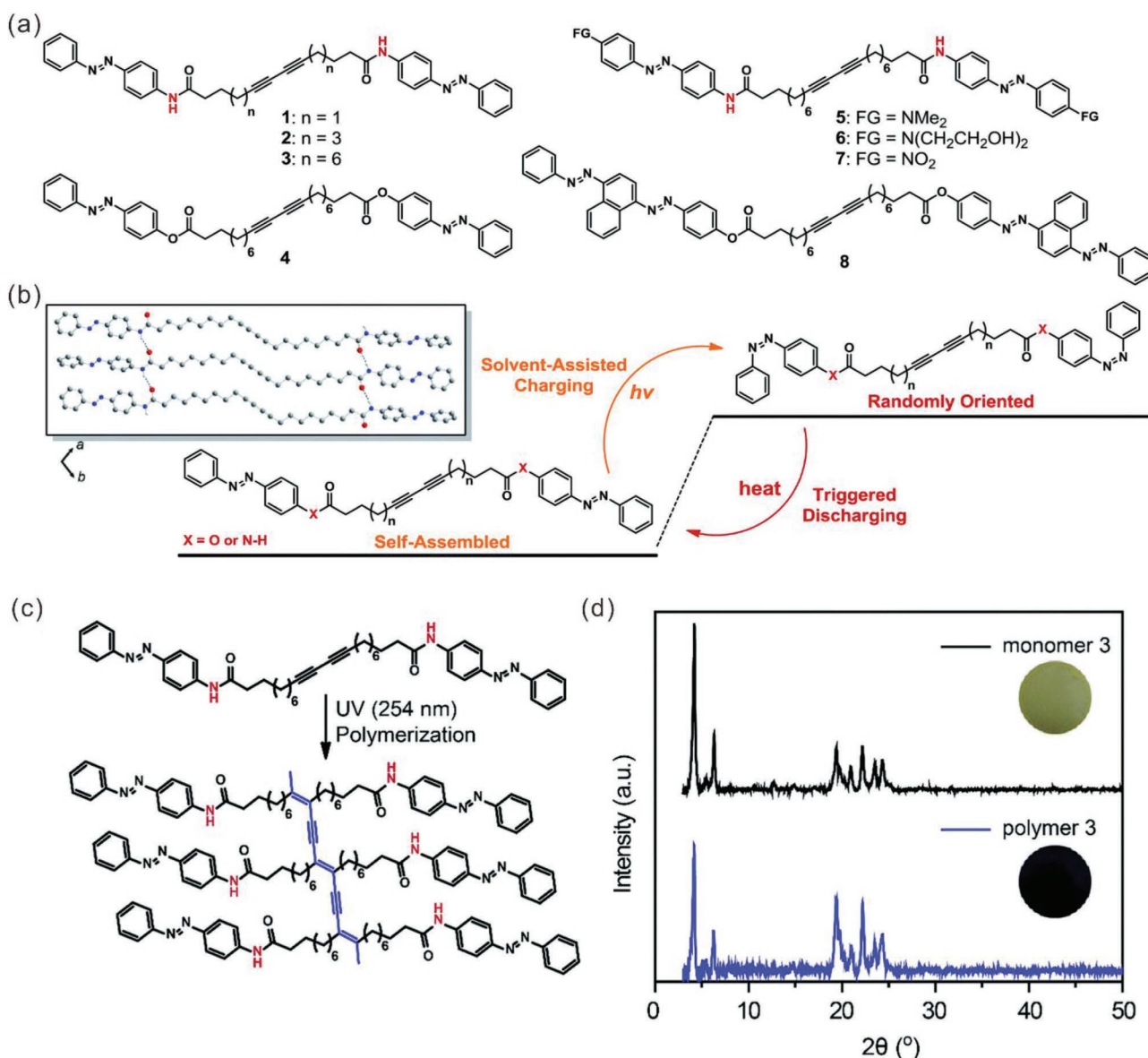
solar-thermal fuels (Figure 6).<sup>[31]</sup> Azobenzene groups in these compounds can undergo photoisomerization (Figure 6b). UV irradiation resulted in polymerization of close-packed diacetylenes and formation of conjugated polydiacetylenes (Figure 6c). Both the monomers and polymers form crystalline structures (Figure 6d). Azobenzene-functionalized diacetylenes and polydiacetylenes can store up to  $243.7 \text{ kJ kg}^{-1}$  ( $276.9 \text{ kJ kg}^{-1}$ , if completely charged). The extra energy storage is because of the combination of the isomerization enthalpy of azobenzene groups and the different phases of the materials in ground state (crystalline solid) and in metastable state (amorphous solid/liquid). These results showed that azobenzene-functionalized polydiacetylenes resemble the structure of rigid templates decorated with closely packed azobenzene

groups, which are similar to azobenzene-functionalized CNTs and graphenes.

#### 4. Solar Thermal Fuels Using Linear Azopolymers

Although solar-thermal fuels based on azobenzene-functionalized CNTs, graphenes, and conjugated polymers have increased energy density and good recyclability, Zhitomirsky et al. realized the limitations of those materials:<sup>[32]</sup> carbon scaffolds increased synthesis complexity, cannot be deposited into uniform films, contribute to the optical density without resulting in photocharging, introduce uncontrollable morphological effects that may limit charging, and hinder photoisomerization in the

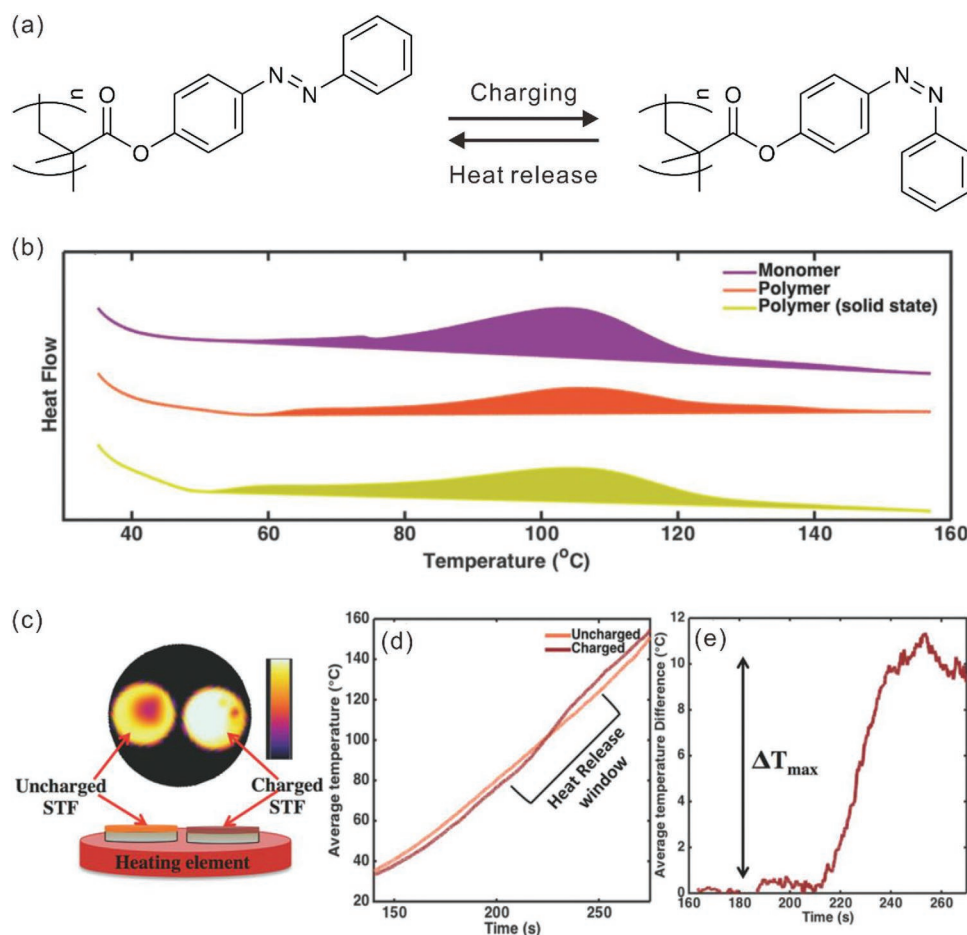




**Figure 6.** a) Azobenzene-functionalized diacetylenes with varying alkyl chain lengths, H-bonding units (marked in red), terminal functional groups, and an extended  $\pi$ -system. b) A schematic image describing photoisomerization and triggered reverse isomerization of compounds 1–4. The inset shows a crystal structure of compound 3. The dotted lines indicate intermolecular H-bonding. Red, gray, blue, and white spheres represent O, C, N, and H atoms, respectively. H atoms without hydrogen bonding are omitted for clarity. c) A schematic photopolymerization of monomer 3 and the structure of polymer 3 with a conjugated backbone. d) Powder X-ray diffraction patterns and photographs of monomer 3 and polymer 3 in the solid state. Reproduced with permission.<sup>[31]</sup> Copyright 2016, Royal Society of Chemistry.

solid state. To overcome these problems, Zhitomirsky et al. synthesized a linear azopolymer as solid-state solar-thermal fuels (Figure 7a). This design enables preparing uniform films capable of appreciable heat storage of up to 108 kJ kg<sup>-1</sup> and that can withstand temperature of up to 180 °C (Figure 7b). Importantly, a macroscopic energy release is demonstrated using spatial infrared heat maps with up to a 10 °C temperature change (Figure 7c–e). These findings pave the way for developing highly efficient and high energy density solar-thermal fuels for applications in solid state.

Another advantage of using linear azopolymers is that the chemistry of such azopolymers has been well developed in the past years, their properties have been intensively studied, and it is possible to synthesize a large scale of linear azopolymers.<sup>[33–36]</sup> Thus, not only the linear azopolymer in Figure 7a is suitable for solid-state solar-thermal fuels, but also many azopolymers developed in the past can be used for this purpose. The rich chemistry available on azobenzene-containing monomers and polymers enables the application of azopolymers for solar-thermal fuels.



**Figure 7.** a) Chemical structure of the linear azopolymer and schematic of charging and heat release based on *trans-cis* isomerization. b) Differential scanning calorimetry traces for monomer and polymer charged under various conditions. The +y direction represents heat release and the Gaussian regions colored overlap a flat baseline represent the integrated energy release. c) Top-view IR heat map of uncharged and charged solar-thermal energy capacitors placed on a heating element, with side-view illustration below. Heat map depicted for maximal temperature difference between samples with color bar indicating relative heat magnitude. d) Average temperature recorded on the surface of each sample plotted as a function of experiment time. e) Average temperature differences between the two samples after normalization at the stabilization temperature  $\approx 160$  s into the experiment, at least a 10 °C total change ( $\Delta T_{\max}$ ) in temperature was observed between the samples due to heat release by the charged azopolymer. Reproduced with permission.<sup>[32]</sup> Copyright 2016, Wiley-VCH.

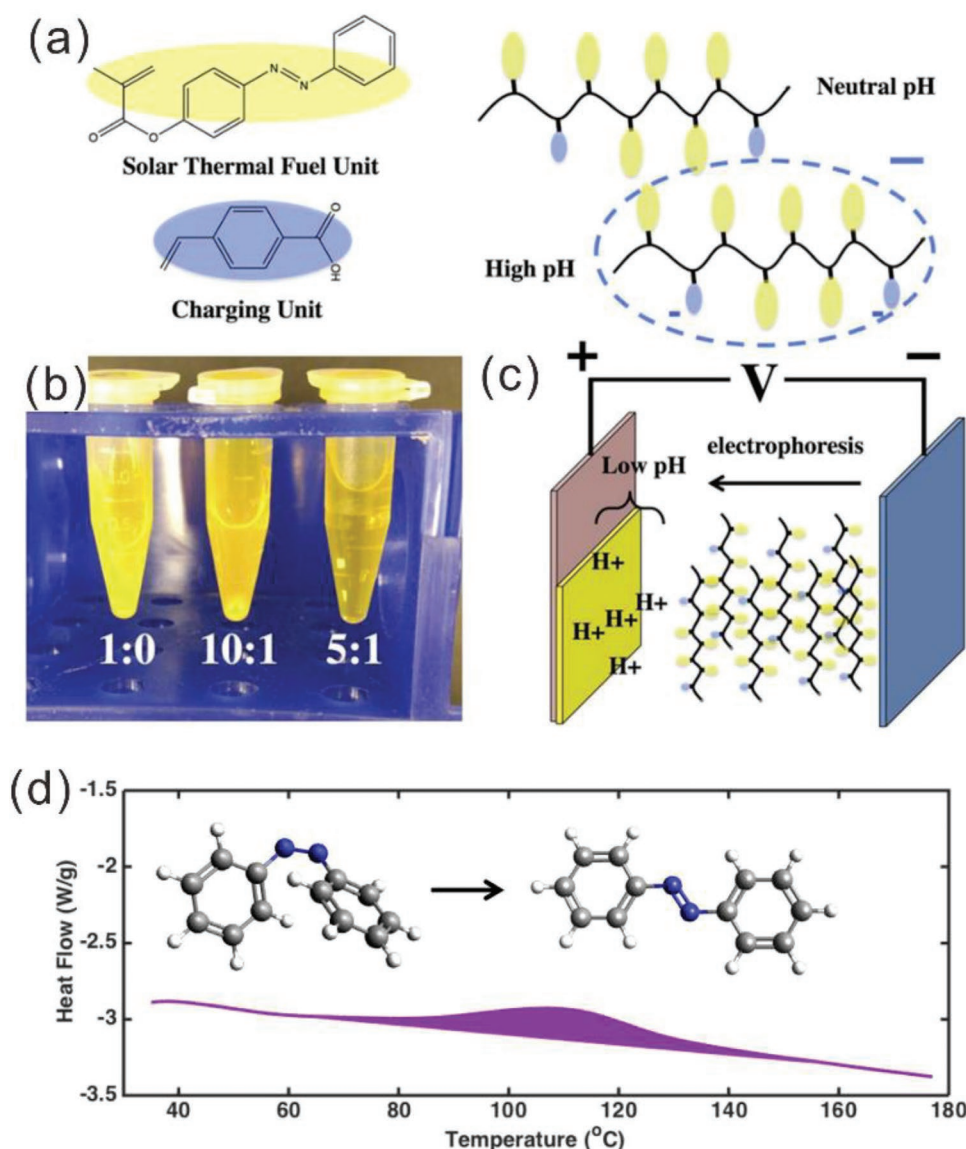
To prepare solid devices for solar-thermal fuels, Zhito-mirsky and Grossman develop a methodology employing an electrodepositable azobenzene-containing copolymers (Figure 8a,b).<sup>[37]</sup> The copolymers have azobenzene moieties as solar thermal fuel units and 4-vinyl-benzoic acid moieties as charging units that facilitates electrodeposition. This design enables deposition from low concentration solutions in methanol, resulting in uniform and large-area thin films (Figure 8c). This approach also enables conformal deposition on a variety of conducting substrates that can be either flat or structured depending on the application. Solar-thermal fuel properties studied using DSC showed that the copolymer had an energy density of  $\approx 90$  J g<sup>-1</sup> (Figure 8d). The copolymer can be charged in the solid state.

Our group synthesized a series of azopolymers for other purposes (photoinduced reversible solid-to-liquid transitions) (Figure 9a).<sup>[38–41]</sup> Our azopolymers showed photoisomerization in solid state. Thus, they are potential candidates as solid-state

solar-thermal fuels. In addition, our *cis* azopolymers showed triggered heat release (Figure 9b). The advantages of these azopolymers are good processability and solid-state charging and discharging. Some azobenzene-containing small molecules showed additional heat release based on liquid-to-solid transition.<sup>[17]</sup> Although the azopolymers also showed reversible solid-to-liquid transitions, no additional heat release via liquid-to-solid transition was observed.

A major problem for azobenzene-based solar-thermal fuels is that they are charged using UV light. However, sunlight only has a small fraction of UV light (4.5%). Even if an azobenzene-based solar-thermal fuel has high energy density, most solar irradiance could not be stored using such conventional azobenzene-based solar-thermal fuels. In addition, visible light in the solar spectrum hinders the storage of UV light because visible light discharges the fuels via visible-light-induced *cis*-to-*trans* back isomerization. Thus, almost all reported azobenzene-based solar-thermal fuels only store UV light as a proof of concept.

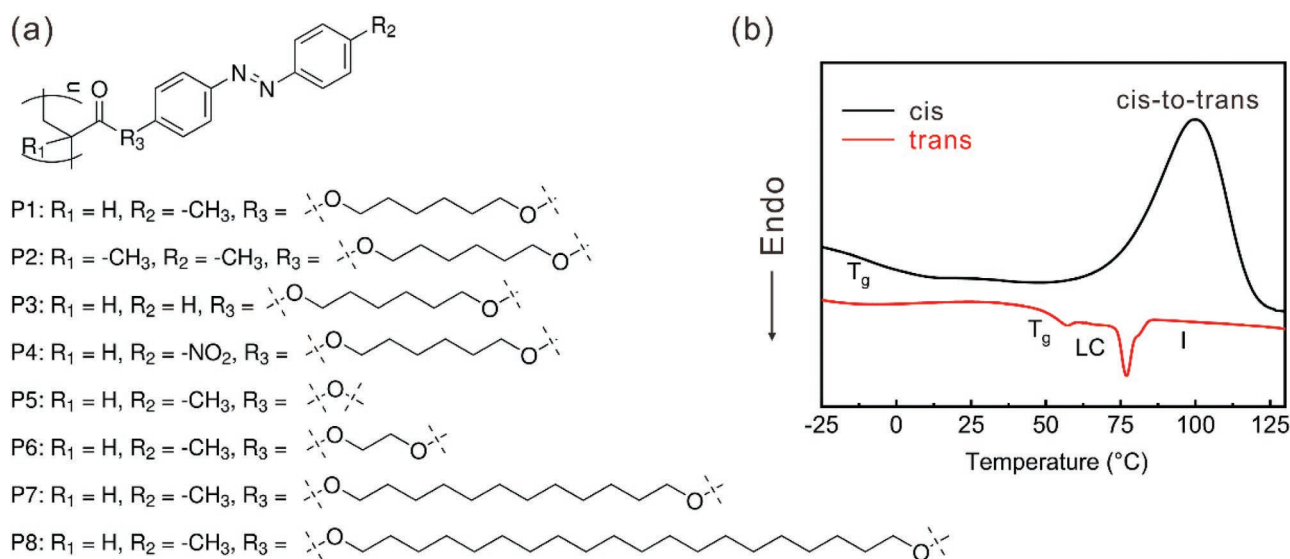




**Figure 8.** Solar-thermal fuel copolymer for electrodeposition. a) Structures representing the solar-thermal fuel and charging units. Incorporation of these units into a copolymer enables to change the charge and thus solubility based on the pH, thus enabling to generate solid-state coatings under neutral or low pH conditions. b) Photograph depicting the solubility of various synthesized polymers based on solar thermal fuel: charging unit ratio. At low charging unit concentrations, even at high pH, the polymer cannot dissolve evidently by the turbid solution, whereas at 5:1, the solution becomes clear, indicating solubility. c) Concept of the electrodeposition scheme, where the charged polymer in basic solution migrates in response to an electric field and deposits on the positive electrode where protons are generated, thus enabling a pH drop. d) Scanning differential calorimetry carried out on the charged copolymer, whereby the *cis* isomer is converted to the *trans* variant (depicted). A heat release corresponding to a gravimetric energy density of 90 kJ kg<sup>-1</sup> was observed. Reproduced with permission.<sup>[37]</sup> Copyright 2016, American Chemical Society.

To overcome this problem, our group recently demonstrated an integrated azopolymer-based device that could efficiently store both UV and visible light under sunlight irradiation (Figure 10).<sup>[42]</sup> From top to bottom, our device consisted of Coumarin 314, visible-light-responsive azopolymer poly(6-(4-((2,6-dimethoxyphenyl)diazanyl)-3,5-dimethoxyphenoxy)hexyl methacrylate) (PmAzo),<sup>[43]</sup> a UV-pass filter, and UV-light-responsive azopolymer poly(6-(4-(p-tolyldiazanyl)phenoxy)hexyl methacrylate) (PAzo)<sup>[38]</sup> (Figure 10d). The four-layer device featured two active cells to store solar energy and two filtering layers to modify the effective incident spectrum. The two active layers

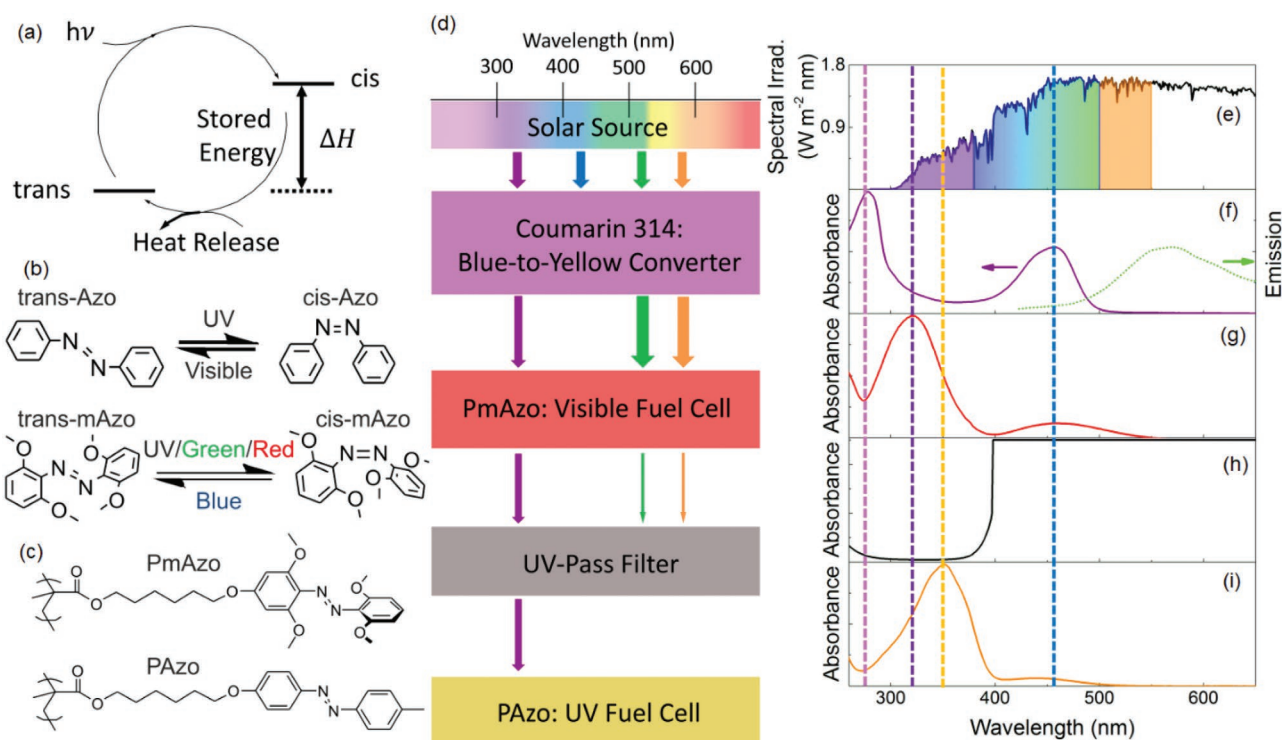
were different azopolymers, PAzo, and PmAzo that store energy by isomerization of the azobenzene groups in the polymers from the low energy *trans* isomers to the higher energy *cis* isomers. Recently, some azobenzene compounds that show visible-light-induced isomerization have been developed.<sup>[44–51]</sup> PmAzo is different from conventional azopolymers that show *trans*-to-*cis* isomerization under UV irradiation. We found green or red light can induce *trans*-to-*cis* isomerization of PmAzo.<sup>[43]</sup> Thus, PmAzo provides the opportunity to store visible light. However, blue light still induces *cis*-to-*trans* back isomerization, making the storage of sunlight problematic (Figure 10b). Therefore,



**Figure 9.** a) Chemical structures of some azopolymers synthesized by the authors' group. b) DSC heating curves for *cis* and *trans* P3. *Cis* P3 has an exothermal peak when *cis*-to-*trans* isomerization was induced thermally, which shows heat release of the polymer. Panel (b) Reproduced with permission.<sup>[38]</sup> Copyright 2016, Springer Nature.

we designed a dye layer (Coumarin 314) to convert blue light into green light. By selectively blocking wavelengths that induce *cis*-to-*trans* back isomerization, *cis* conversion competitive with

monochromatic irradiation (60–70%) was achieved. Rational device design along with improved spectral overlap permitted a remarkable enhancement of the solar efficiency to 0.4%; the

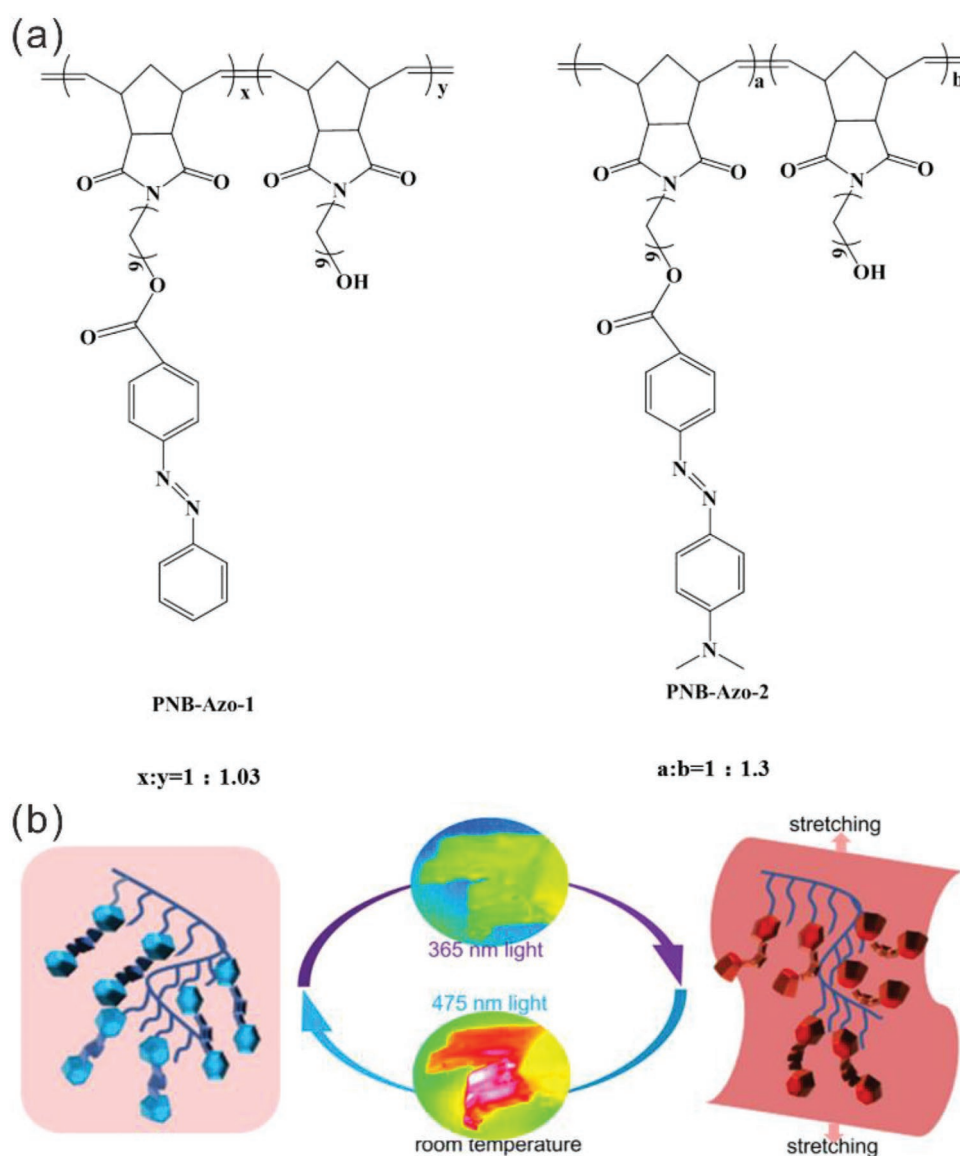


**Figure 10.** a) Solar-thermal energy conversion and storage based on isomerization of azobenzene compounds. b) Photoisomerization of Azo and mAzo chromophores. c) Chemical structures of the azopolymers PAzo and PmAzo. d) Schematic of four-layer UV-vis solar-thermal cell depicting transmission or absorbance of representative wavelengths. e) Solar spectrum (AM 1.5), f) UV-vis and fluorescence ( $\lambda_{\text{ex}} = 470$  nm) spectra of Coumarin 314, g) UV-vis spectrum of PmAzo in tetrahydrofuran (THF) ( $2 \times 10^{-4}$  M), h) UV-vis spectrum of UV-pass (UG-11) filter, and i) UV-vis spectrum of PAzo in THF ( $6 \times 10^{-5}$  M). Reproduced with permission.<sup>[42]</sup> Copyright 2016, Wiley-VCH.

solar efficiency was calculated by the method of Scharf et al.<sup>[52]</sup> PAzo also demonstrated that chemical structure of the chromophore can serve as a handle for increasing the gravimetric energy density ( $147 \text{ kJ kg}^{-1}$ ). Estimations of solid-state switching up to 72.7% represent progress toward the ideal of solid-state solar-thermal fuels.

Not only poly(meth)acrylates with azobenzene groups for solar-thermal fuels have been investigated, but also polynorbornenes with azobenzene groups on the side chains have been studied. Feng's group prepared films using polynorbornenes PNB-Azo-1 and PNB-Azo-2 to investigate the stretching-enhanced solar thermal utilization (**Figure 11**).<sup>[53]</sup> PNB-Azo-1 showed a relatively high-degree *trans*-to-*cis* isomerization (72%) and stable energy storage because of the intermolecular interactions and steric hindrance. In contrast, PNB-Azo-2 showed a

low-degree of *trans*-to-*cis* isomerization (19.2%) and rapid *cis*-to-*trans* thermal relaxation because of the pull-push substituents on the azobenzene groups. Feng and coworkers<sup>[53]</sup> showed that stretching increased the degree and rate of isomerization because it increased the free volume. The stretched azopolymer film with a strain of 20% combined high-degree photocharging (85%) and high energy density ( $176.4 \text{ kJ kg}^{-1}$ ). Heat release was induced by blue-light (475 nm) irradiation at room temperature. They also demonstrated that dynamic stretching results in a rapid temperature increase. Reversible electric-driven dynamic stretching enabled the PNB-Azo-1 fingers to release heat at a high rate, resulting in a temperature increase of  $1.5^\circ\text{C}$  (**Figure 11b**). The flexible stretchable PNB-Azo films may be developed for a high-power dynamic solar heat source by controlling the deformation.



**Figure 11.** a) Chemical structure of PNB-Azo-1 (left) and PNB-Azo-2 (right). b) Schematic illustration of light energy storage via UV light-induced *trans*-to-*cis* isomerization, effects of stretching, and thermal energy release induced by blue light irradiation. Reproduced with permission.<sup>[53]</sup> Copyright 2019, American Chemical Society.



## 5. Summary and Perspective

We summarized the development of solar-thermal fuels based on azopolymers such as azobenzene-functionalized 2D polymers, conjugated polymers, and linear polymers. Solar-thermal energy storage and release are based on reversible *trans-cis* isomerization of azobenzene groups. The polymers serve as templates/matrices for azobenzene groups. CNTs and graphenes largely enhanced the energy storage density because they template the packing of azobenzene groups. Linear azopolymers are processable and ideal matrices for solid-state photoisomerization. Azopolymers are good model systems to study fundamentals of solar thermal fuels. Although this field progressed significantly, some challenges remain.

First, most reported solar-thermal fuels based on azopolymers can only store UV light and we reported a solar-thermal fuel that can store both UV and visible light. However, near-infrared (NIR) light, which is about half of the solar irradiance, cannot be stored. The development of solar-thermal fuels that can store NIR light poses a challenge. Some NIR photoswitchable compounds<sup>[54]</sup> have been developed recently but their performance as solar-thermal fuels has not been tested yet.

Second, although the use of CNTs and graphenes as templates can increase energy density, the packing of azobenzene groups in these templates hinders photoisomerization in solid state. Alternative ways to enhance energy density and facilitate photoisomerization in solid state are yet to be explored.

Third, heat releasing (discharging) is usually based on thermal relaxation or heat-induced *cis-to-trans* isomerization of azobenzene groups. There is an example that catalysts can speed up heat release.<sup>[14]</sup> It is highly desirable to have solar-thermal fuels that have user-defined heat release profiles. Controlled heat release is also yet to be explored.

## Acknowledgements

S.W. acknowledges the Thousand Talents Plan, Anhui Provincial Natural Science Foundation (No. 1908085MB38), and the Deutsche Forschungsgemeinschaft (DFG, WU 787/2-1, and WU 787/8-1) for financial support.

## Conflict of Interest

The authors declare no conflict of interest.

## Keywords

azobenzene, energy, photoresponsiveness, polymers, solar thermal fuels

Received: August 12, 2019

Revised: September 28, 2019

Published online: November 18, 2019

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