

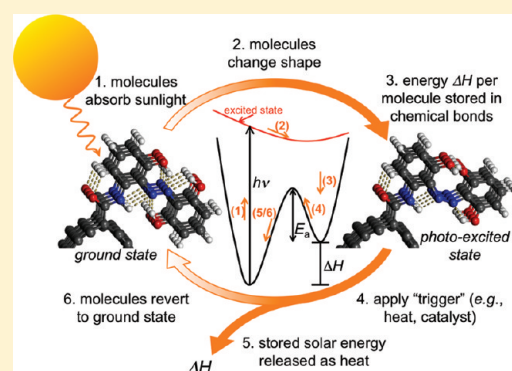
Azobenzene-Functionalized Carbon Nanotubes As High-Energy Density Solar Thermal Fuels

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ABSTRACT: Solar thermal fuels, which reversibly store solar energy in molecular bonds, are a tantalizing prospect for clean, renewable, and transportable energy conversion/storage. However, large-scale adoption requires enhanced energy storage capacity and thermal stability. Here we present a novel solar thermal fuel, composed of azobenzene-functionalized carbon nanotubes, with the volumetric energy density of Li-ion batteries. Our work also demonstrates that the inclusion of nanoscale templates is an effective strategy for design of highly cyclable, thermally stable, and energy-dense solar thermal fuels.

KEYWORDS: Solar thermal fuel, renewable energy, photoswitch, carbon nanotubes, density functional theory



The development of new energy technologies that are simultaneously economically viable, clean, sustainable, and easily transportable has become one of the most important research goals of the 21st century. Full utilization of the largest and most obvious source of renewable energy, the sun, requires advanced technologies for converting light into other useful forms of energy, as well as novel means for storing energy for convenient transport and on-demand use. One promising concept that has recently become the focus of renewed attention^{1,2} is that of solar thermal fuels, which store energy from the sun in the chemical bonds of photoactive molecules. This process is illustrated schematically in Figure 1. Upon absorption of light with energy $h\nu$, a photoactive “fuel” molecule undergoes a conformational change to a higher energy metastable state, thus storing energy ΔH . To obtain the stored energy, an external trigger (e.g., heat, light, voltage, or a chemical reaction) is applied, providing energy to overcome the thermal barrier, E_a , and releasing a net energy of ΔH per molecule. The fuel can subsequently be “recharged” via exposure to light; in principle, the entire operation can be repeated ad infinitum.

There are clearly important advantages to this solar energy storage concept; it is potentially 100% renewable, produces no emissions, and is easily transportable in the form of a liquid or powder. It is thus not surprising that the concept of storing solar energy in the chemical bonds of molecules is not a new one. A number of photoisomerization reactions, in particular norbornadiene \leftrightarrow quadricyclane³ and anthracene \leftrightarrow dianthracene, were investigated extensively for this purpose in the 1970s and 1980s. While storage and retrieval of solar energy in these molecules was demonstrated experimentally, the concept of solar thermal fuels was generally dismissed as being practically unfeasible,³ primarily due to the degradation of the fuel such that it could not be reused after only a few cycles of energy conversion and release.

Recently, however, the synthesis of a new solar fuel candidate, tetracarbonyl-diruthenium fulvalene, that can cycle through this process numerous times³ without degradation has renewed interest in the possibility of practical solar thermal fuels. However, despite showing resistance to degradation, the Ru-fulvalene is not a practical candidate for large-scale use due to the requirement of Ru, a rare and expensive element, and to date efforts to replace the Ru with cheaper and more abundant transition metals (e.g., Fe) have faced the challenges of poor thermal stability and/or low-energy density.⁴ In addition, while the gravimetric energy density of the Ru-fulvalene fuel is comparable to that of current Li-ion batteries,⁴ its volumetric energy density in solution is several orders of magnitude smaller, making portability unfeasible as well as increasing storage costs. Our efforts to increase the energy storage capacity via substitution of functional groups in several photoisomers have led only to small (~ 10 – 20%) increases in ΔH , and furthermore often result in an undesired decrease of E_a . All of these issues suggest that new materials may have an important role in transforming solar thermal fuels into a commercially viable energy technology.

Here we suggest a new approach to the design of high-energy density solar thermal fuels, based on combining well-studied photoswitch molecules⁴ with demonstrated high-degradation resistance with carbon nanotubes to increase the energy storage capacity and thermal stability of the photoswitch molecules. We demonstrate the effectiveness of this approach by investigating a set of hybrid nanostructures composed of azobenzene derivatives (collectively referred to as “azo” in the following) covalently bound to CNT substrates.

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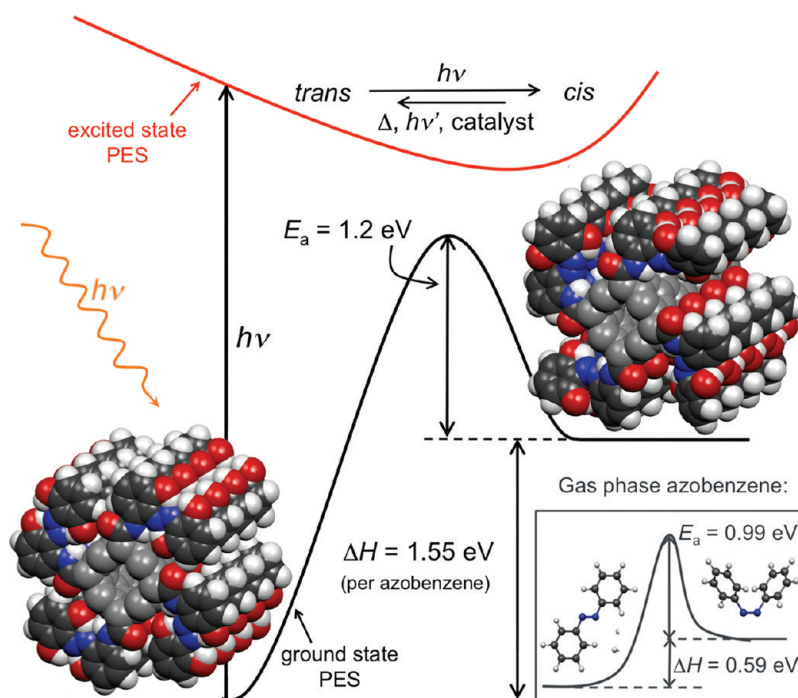


Figure 1. Solar thermal energy storage. 2,2',5'-trihydroxy diazobenzene molecules covalently attached to a CNT undergo a photoinduced trans-to-cis isomerization, storing $\Delta H = 1.55$ eV per azobenzene. A thermal barrier, E_a , prevents the back reaction from occurring under storage conditions; an external trigger controls the release of the stored energy. The inset shows the corresponding parameters for untethered azobenzene molecules. White, gray, blue, and red spheres represent H, C, N, and O atoms, respectively; nanotube carbons are a lighter gray for clarity.

The potential advantages of azo/CNT hybrid nanostructures as solar thermal fuels stem from the close-packed, highly ordered array of adsorbed photomolecules imposed by the CNT substrate⁶ (see Figure 2). The existence of this crystalline-like state, which, importantly, persists when the nanostructures are in solution, has two key effects. First, the number of photoactive molecules per volume (i.e., photoisomer concentration) is significantly increased with respect to a solution of free photomolecules, leading to an increased volumetric energy density of 5–7 orders of magnitude (depending on the solubility of a given substituted azobenzene species⁷). Second, and even more important, both the proximity and the ordered arrangement of the adsorbed molecules enable systematic manipulation of the inter- and intramolecular interactions, providing a highly effective set of tuning parameters for maximizing both the energy storage capacity and the storage lifetime of the solar thermal fuel. Additional tuning parameters include the molecular packing density, the chemistry of the linker group (see Figure 2), the diameter of the CNT, and the orientation of the adsorbed molecules and any functional groups on the adsorbed molecules with respect to the CNT.

The azo/CNT system is also an ideal platform from a practical perspective. While azobenzenes have previously been studied for energy storage,^{8,9} to our knowledge azo/CNT nanostructures have not. However, they can be experimentally synthesized,⁶ and the resulting hybrid nanostructures are observed to have close-packed arrays of covalently attached azobenzene molecules aligned parallel to the long axis of the nanotube.^{6,10} Furthermore, reversible photoinduced switching between the metastable cis and trans isomers of the adsorbed azobenzene molecules has been experimentally demonstrated.^{6,10} Finally, the photoinduced behavior of numerous azobenzene derivatives both in solution and on substrates has been well studied (c.f. refs 5, 11, and 12),

demonstrating high cyclability and providing a wealth of information to guide the design of an optimal hybrid system.

Below, we use density functional theory to investigate several new solar thermal fuel candidates based on the azo/CNT system. We demonstrate the dramatic effects on energy density and thermal stability enabled by the presence of the substrate and the crystalline-like azobenzene state, and we discuss the chemical and geometric interactions that lead to this behavior. Finally, we show that it is possible to obtain azo/CNT solar thermal fuels with volumetric energy densities comparable to or even larger than that of state-of-the-art Li-ion batteries.

Computations are performed using density functional theory and ultrasoft pseudopotentials¹³ within the Quantum Espresso¹⁴ code. We employ the Perdew-Burke-Ernzerhof¹⁵ generalized gradient approximation (PBE-GGA) to exchange and correlation. Simulation supercells include 15 Å of vacuum separating periodic copies in the *y*- and *z*-directions. The nanotube long axis is oriented along the *x*-direction with a periodicity of 4.24 Å or multiples thereof (to determine the behavior with respect to adsorbate separation distance). Convergence of total energies and electronic properties is achieved for an $8 \times 1 \times 1$ Monkhorst-Pack *k*-point sampling for the smallest simulation cell. To determine the minimum energy structures, several initial positions/orientations of the adsorbed molecules are considered. All atoms in the nanotube and the adsorbate are fully relaxed until the force on each is less than 0.01 eV/Å. Nudged elastic band¹⁶ calculations are performed to determine transition pathways and thermal barriers.

Figure 3 shows the computed values of ΔH for a number of representative azo/CNT systems. As the figure indicates, we observe a significant increase in ΔH compared to an isolated azobenzene molecule (dashed line) in all cases. The increased

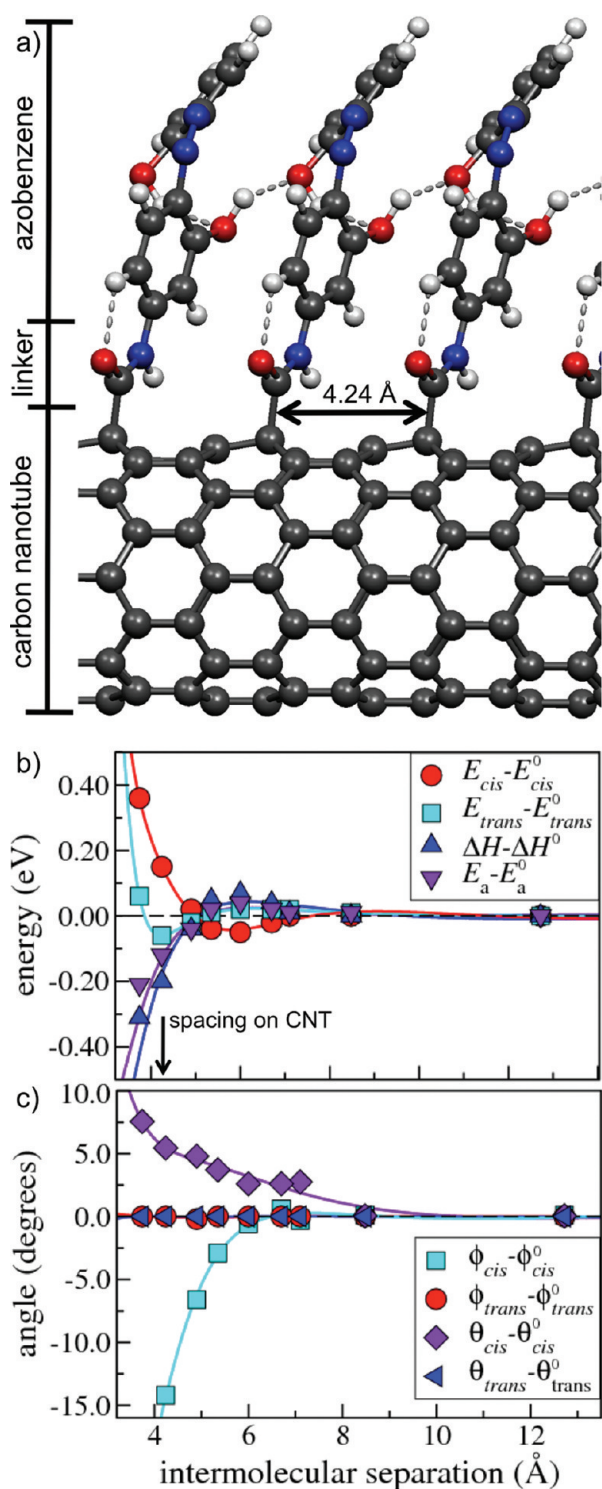


Figure 2. Adsorbate packing interactions. (a) Side view of a row of cis-2,2'-dihydroxy-diazobenzene molecules covalently bound to an (8,0) CNT via amide linkers at the para position, showing the optimal ground state adsorbate packing density parallel to the nanotube axis (one adsorbate per 4 CNT carbon atoms). For clarity, the system has only a single adsorbate in the direction perpendicular to the nanotube long axis. Dashed gold lines indicate H-bonds. (b) ΔH , E_a , and total energies of the cis (red circles) and trans (cyan squares) isomers of unsubstituted azobenzene as a function of intermolecular spacing. (c) Phenyl (ϕ) and C–N=N (θ) angles vs intermolecular spacing. All values in (b,c) are given with respect to the computed values for an isolated azobenzene molecule.

energy difference between the *cis* and *trans* configurations arises from a combination of effects, as emphasized by the shaded regions for the examples shown in Figure 3. In the following, we discuss the mechanisms and implications of these effects.

The primary role of the CNT is to facilitate a crystalline, close-packed, ordered arrangement of the adsorbed photoactive molecules. The effect of the molecular packing is demonstrated in Figure 2b, which plots the energy of *cis* and *trans* azobenzene molecules as a function of their separation distance. As the figure shows, the energy of the metastable *cis* isomer (red circles) initially decreases with decreasing intermolecular distance due to attractive π – π interactions between neighboring molecules, which lead to a shallow minimum for a separation of ~ 6 Å. Below 6 Å, the energy increases steeply as repulsive interactions begin to dominate the behavior. As demonstrated by the large deviations in both the C–N=N angle and the angle between intramolecular phenyl groups in this regime (Figure 2c), neighboring adsorbates prevent each other from attaining their minimum energy geometry, decreasing the overlap of the N–N π states and thus weakening the diazo bond and shifting the highest occupied molecular orbital (HOMO) significantly upward in energy.

In contrast, the energy of the *trans* state (cyan squares) exhibits a minimum for an intermolecular separation of ≈ 4.24 Å, the distance between every fourth carbon atom along the CNT axis. In this case, steric effects do not play an important role, as the molecules are essentially planar in the *trans* state. Instead, the optimal intermolecular distance is determined primarily by the interactions between π -electrons in neighboring phenyl rings. The net result of the packing interactions is thus a large increase in the magnitude of ΔH with decreasing intermolecular distance. As Figure 2b shows, the packing interactions due to unsubstituted azobenzene alone lead to a net increase of 0.2 eV per molecule in the magnitude of ΔH for a spacing of 4.24 Å. In other words, the formation of an ordered close-packed array increases the energy storage capacity per molecule by $\sim 30\%$ compared to gas-phase azobenzene.

It is clear that van der Waals interactions, which can be poorly described within DFT, depending on the choice of functional, can play an important role in these ordered structures. We therefore perform a set of test calculations with several functionals that provide a more accurate description of weak interactions. Employing the semiempirical Grimme functional,¹⁷ as implemented in Quantum Espresso and the wB97XD¹⁸ and M06¹⁹ hybrid functionals in Gaussian09,²⁰ we observe a 12–17% reduction in ΔH for all of the systems in Figure 3. However, a similar reduction is also observed in the computed ΔH values of the corresponding nontemplated azobenzenes; for example, the value of ΔH for unsubstituted azobenzene in the gas phase is found to be -0.49 eV, which is smaller than both the PBE-GGA and the experimental values (~ -0.59 eV). Consequently, the fractional increase in ΔH due to the packing interactions on the CNT template is relatively insensitive to the inclusion of weak interactions.

In addition to providing a template for ordered interactions, the CNT substrate also produces a significant effect on ΔH by breaking the symmetry of the adsorbed azobenzene molecules. When the molecules are bound to the CNT, several orientations are possible depending on the position of the linker group with respect to the nitrogen double bond in the azobenzene. The large geometry changes and the subsequent changes in ΔH are illustrated for three different azo derivatives bound to CNT substrates

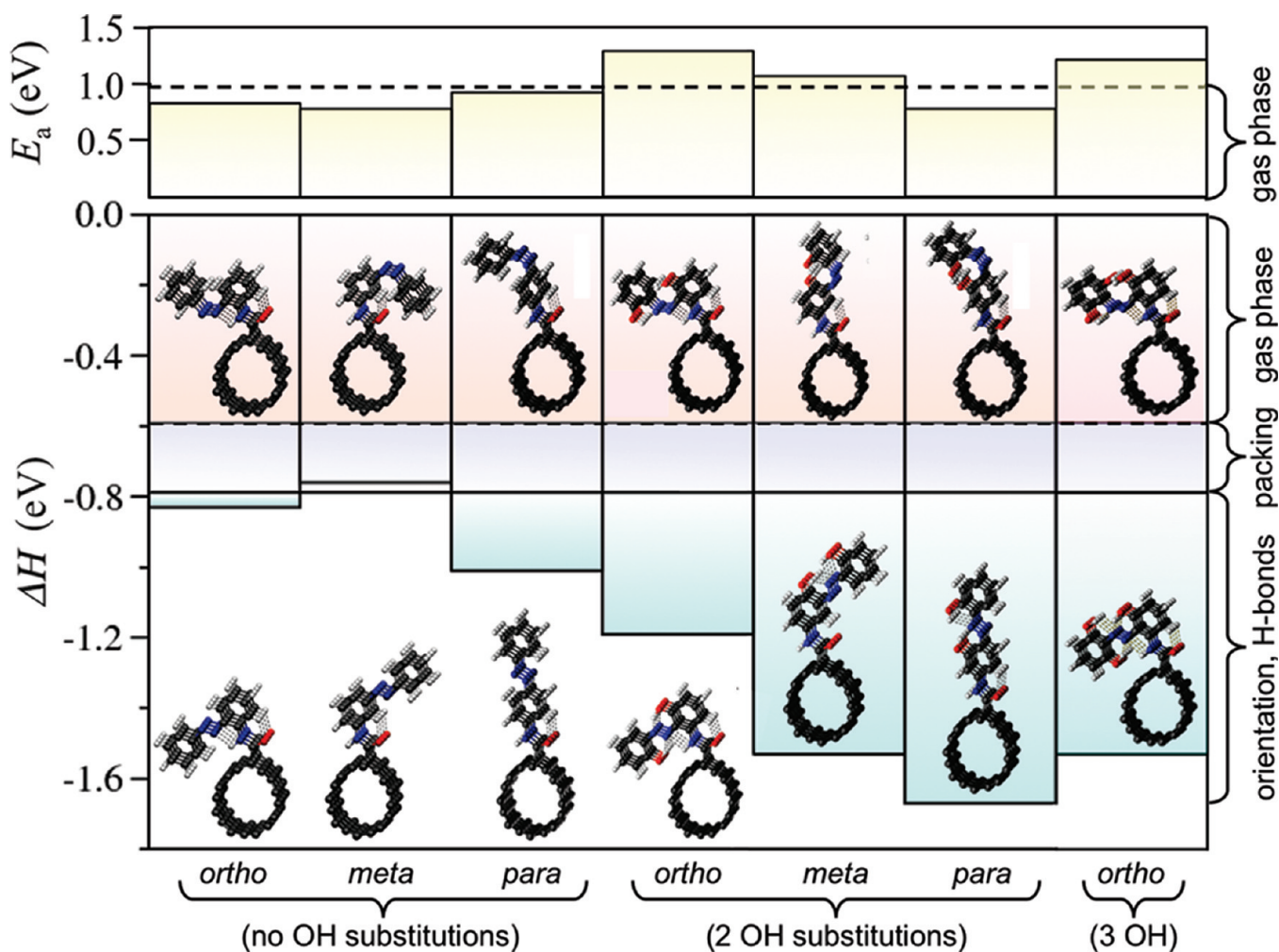


Figure 3. DFT-computed values of ΔH and E_a for a representative sample of the azo/CNT systems studied. The increase of ΔH with respect to isolated azobenzene arises from the presence of the CNT substrate which (i) imposes a close-packed crystalline-like state, (ii) breaks molecular symmetry, and (iii) enables design of specific ordered, fixed interactions between functional groups on neighboring molecules.

with ortho, meta, and para attachments. In most of the azo/CNT systems investigated, the ortho attachment is energetically preferred over the other possible attachments in both the cis and trans states. This stability, which arises from strong proximity-induced interactions between the linker and the azobenzene and between the azobenzene and the CNT, results in a relatively minor increase in ΔH for the nonsubstituted azobenzene, as indicated in Figure 3. In contrast, systems with the linker in the para position tend to have the least stable cis configuration, resulting in larger values of ΔH .

In addition to packing and orientation effects, the CNT substrate enables specific, fixed interactions between neighboring molecules, which can have significant effects on the energetics of the system. For example, in the hybrid nanostructure, substitutional groups will interact with neighboring molecules with a much higher frequency than in solution. Furthermore, they interact in an ordered manner, potentially providing a systematic route toward designing the properties of the hybrid nanostructure.

We have primarily investigated the substitution of hydroxyl groups for one or more hydrogens on the phenyl rings with the aim of modifying the relative stability of the two isomers via the addition of H-bonds. In general, structures with more H-bonds and/or stronger (shorter) H-bonds are more stable; thus, maximizing the number of H-bonds in the trans state while

minimizing the H-bonds in the cis state will provide a larger ΔH . In addition, H-bonds composed of OH...N are typically found to be stronger than those with OH...O. Because of the symmetry breaking imposed by the CNT, it is therefore possible to optimize ΔH by choosing the position of hydroxyl groups (or other functional groups). For example, Figure 4, which shows several possible patterns for two OH groups on an azobenzene with a linker in the meta position, illustrates the dependence of ΔH on the relative positions of two hydroxyl groups; these positions determine the number and strength of the H-bonds in the cis and trans configurations. As Figure 3 shows, these interactions provide a very effective means of tuning the properties of the solar thermal fuel; just considering two hydroxyl substituents yields an increase in the energy stored per molecule of up to a factor of 3 compared to gas phase azobenzene; additional hydroxyl groups and/or other functional groups may increase ΔH even further.

The utility of a solar thermal fuel is contingent not only upon its energy storage capacity but also on its thermal stability in the photoexcited state. In most azobenzene derivatives, the half-life of the photoexcited state is on the order of minutes to hours due to a relatively low thermal barrier for the cis \rightarrow trans back reaction.^{21,22} As mentioned above, simultaneously increasing

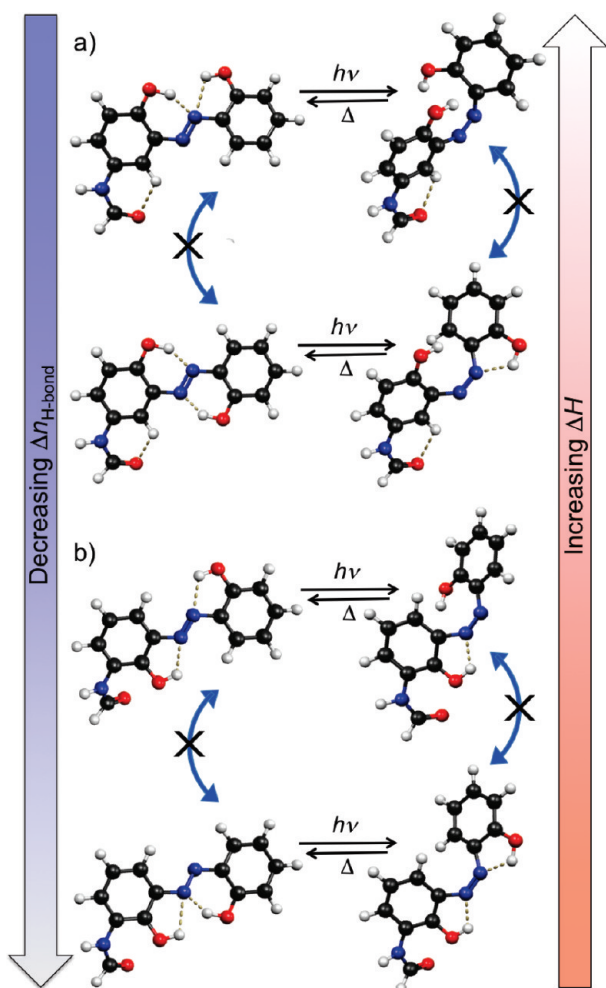


Figure 4. Hydrogen bonding effects. The cis and trans isomers of several possible dihydroxy azobenzene molecules bound to a CNT substrate via an attachment at the meta position. The CNT substrate breaks the symmetry of the azobenzene adsorbates, increasing the potential phase space for H-bond formation: the close-packed arrangement prevents isomerization via rotation of phenyl rings, increasing the number of distinguishable states. This behavior also preserves H-bond interactions at high temperatures. Examples of isomerization pathways that are available in azobenzene but inhibited in the azo/CNT nanostructures are indicated by the crossed out blue arrows.

both ΔH and E_a is challenging, as methods to increase the former often rely on decreasing the latter. This is observed, for example, for the unsubstituted meta- and ortho azo/CNT structures illustrated in Figure 3; the increase in ΔH relative to gas phase azobenzene is almost all due to the destabilizing effect of the packing interactions on the cis isomer, which leads to a concomitant decrease in E_a .

One can, however, increase both E_a and ΔH by designing interactions that will stabilize the cis configuration by some amount E and the trans configuration by some larger amount $E + \delta E$. As a result of the symmetry-breaking, the short intermolecular separation, and the fixed orientation of azobenzene molecules chemisorbed on a CNT substrate, the positions of functional groups provide an ideal means by which to achieve this goal. For example, in the simplest picture, increasing the stability of the cis configuration by enabling the formation of n H-bonds, each with an average energy of $\langle E_{\text{H-bond}} \rangle$, while also stabilizing the trans state with $n + 1$ H-bonds will increase both E_a and ΔH by $\langle E_{\text{H-bond}} \rangle$.

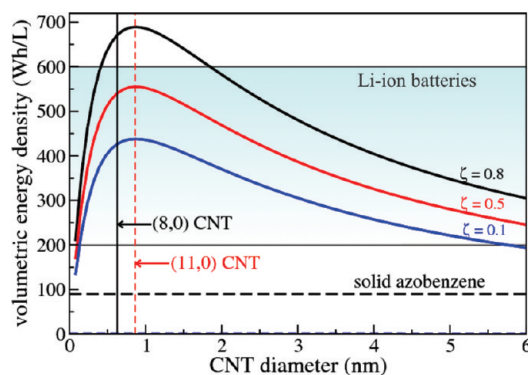


Figure 5. The volumetric energy density as a function of CNT diameter for several nanotube packing densities (ζ). For comparison, the shaded region indicates the range for Li-ion batteries, and the horizontal dashed line shows the value for solid azobenzene. The volumetric energy densities of azobenzene and Ru-fulvalene solutions (<0.1 Wh/l) are not seen on this scale. Note that the gravimetric energy density of the azo/CNT fuel, which is independent of the CNT diameter for constant adsorbate coverage, is similar to that of both Li-ion batteries and Ru-fulvalene, all of which are around 100–200 Wh/kg.

Figure 1 illustrates a successful example of an azo/CNT nanostructure with both enhanced energy storage and thermal stability. In this case, six H-bonds per molecule (four intramolecular H-bonds and two intermolecular H-bonds formed between neighbors around the CNT circumference) significantly stabilize the trans configuration, while four H-bonds per molecule increase the stability of the cis configuration. The net result is a 260% increase in ΔH and a 20% increase in E_a relative to gas phase azobenzene. Using the experimental rate for the thermal cis \rightarrow trans reaction²³ and the computed values of E_a , we predict that the photoexcited state of the azo/CNT nanostructure shown in Figure 1 will exhibit a half-life of greater than one year, an enormous improvement in stability compared to gas phase azobenzene.

Depending on the adsorbate orientation, we find that an (8,0) carbon nanotube can support 4–8 azobenzene molecules around the circumference for each 4.24 Å distance along the CNT long axis. Approximating each azo/CNT nanostructure as a cylinder with outer bounds determined by the van der Waals radii, and assuming the maximum packing efficiency for cylinders (79.2%), we predict that the azo/CNT systems discussed above can have volumetric energy densities up to 690 Wh/L (see Figure 5), comparable to the theoretical volumetric energy densities in state-of-the-art Li-ion batteries (200–600 Wh/L)²⁴ and 4 orders of magnitude greater than that of the Ru-fulvalene solar thermal fuel. (The volumetric energy density of tetracarbonyl-diruthenium fulvalene is determined to be ~ 0.02 Wh/L based on the concentration reported in ref 3). Furthermore, the azo/CNT nanostructures exhibit a 7-fold increase in volumetric energy density compared to solid azobenzene (~ 90 Wh/L); an even larger improvement is observed relative to various substituted azobenzenes in solution, which have volumetric energy densities on the order of 10^{-2} – 10^{-7} Wh/L, depending on the substituent and the solvent.⁷ These values clearly illustrate the utility of including nanoscale components as a means to increase the energy storage capacity of common photoswitch molecules; in addition, they suggest that the same approach can be applied to other photoswitch/nanoscale–substrate hybrids.

The volumetric energy density estimated above is determined under the assumption that the azo/CNT nanostructures are

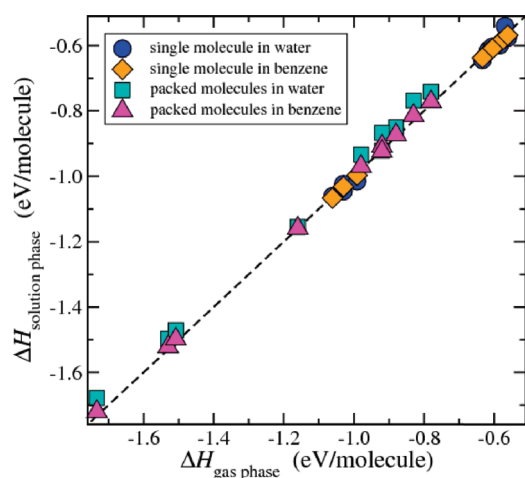


Figure 6. Computed values of ΔH for templated azobenzene derivatives in both water (squares) and benzene (triangles) solvents, compared to the computed gas-phase ΔH values, demonstrating the small effect of solute–solvent interactions. Similar changes in the magnitude of ΔH occur for the corresponding free azobenzenes (circles and diamonds for water and benzene solutions, respectively); thus, the relative increase in ΔH due to the CNT template is essentially independent of the solvent.

sufficiently soluble in some medium to achieve a very high packing density (corresponding to a molar concentration of $\sim 4.6 \times 10^{-3}$). Because of exposed OH functional groups on the outer “surface” of the hybrid nanostructures (e.g., see Figure 1), we predict that most of the nanostructures will be water-soluble. Tests show that additional substitution with polar functional groups at positions that are exposed to the solvent in both the cis and trans states (and thus do not interact significantly with neighboring azobenzenes or the CNT substrate) can also be performed without a net change in ΔH or E_a , thereby enabling one to tune solubility as well. Furthermore, as a result of the close-packed array of adsorbates on the CNT substrate, there is little room to admit solvent molecules in between azobenzene molecules, so one could, for example, also include hydrophobic interactions between adsorbates without impacting the water solubility of the system.

In addition to high solubility, we hypothesize that the functionalized nanotubes may achieve a very high concentration given that the photoactive azobenzene molecules on each nanotube are already in a crystalline state. For example, an azo/CNT nanostructure in a dilute water solution will have a shell of solvent water molecules interacting via hydrogen bonds with the exposed OH groups. Similarly, an azo/CNT nanostructure in a closed-packed array of azo/CNT nanostructures will also interact primarily via H-bonds, in this case between OH groups on neighboring azo/CNT nanostructures as well as with OH groups on surrounding water molecules. Therefore, one can reasonably consider formation of a highly concentrated solution.

The concentration-independent close-packed crystalline structure of the azobenzene adsorbates also suggests that the presence of a polar solvent will not disrupt the H-bond interactions that play such an important role in determining ΔH and E_a , as most interactions with the solvent will be mediated through surface polar groups and thus not affect the intra- and intermolecular interactions between adsorbates. As a first-order test of this prediction, we performed DFT calculations including solvent effects for 11 different templated azobenzene derivatives

(including all those in Figure 3) via the polarizable continuum model²⁵ implemented in Gaussian09.²⁰ As illustrated in Figure 6, our results confirm the minor role of solvent interactions, showing only a small change in ΔH (3 and 2% decreases for water and benzene solvents, respectively) over all 11 derivatives.

An important consequence of this behavior is that, unlike H-bonds between free molecules in solution, the H-bond interactions in the azo/CNT system will not provide a significant entropic contribution to the free energy of the system by breaking and reforming with high frequency. Breaking an inter- or intramolecular H-bond in the ordered state requires rotation of the phenyl rings, a mode that is sterically inhibited by the short intermolecular separation of adsorbates and the rigidity of the structure. Test computations of the barrier to phenyl rotation for close-packed azobenzene molecules confirms this picture, indicating that events requiring such rotations will not occur at any reasonable temperature.

While simultaneously increasing the volumetric energy density and the thermal stability is arguably the most important goal in designing a practical high-energy density solar thermal fuel, several other properties require consideration. In particular, the temperature of the heat released by the back reaction is important in many applications. Assuming that the heat capacity, C_p , is similar to that of azobenzene, the temperature of the heat released upon cis \rightarrow trans isomerization in the azo/CNT system is $T_{\text{released}} \approx \Delta H/C_p = 620$ K. In contrast, $T_{\text{release}} \approx 220$ K for azobenzene without the CNT substrate. Investigation into mechanisms for lowering the heat capacity could enable the hybrid system to produce even higher temperatures; further increases in ΔH will also lead to increases in T_{release} .

Finally, knowledge of the overall efficiency of the solar-to-heat conversion in the azo/CNT nanostructures is useful for comparison between different types of energy conversion systems. The overall conversion efficiency of the azo/CNT solar thermal fuel is given by $\eta = f_{\text{absorbed}} f_{\text{converted}}$, where f_{absorbed} is the fraction of the AM1.5 solar irradiance absorbed by azobenzene and $f_{\text{converted}}$ is the fraction of each absorbed photon that is stored and eventually converted to heat. Assuming that every absorbed photon induces an isomerization event, the latter is given by $f_{\text{converted}} = \Delta H / \int_0^{\text{gap}} h\nu d\nu$, where $h\nu_{\text{gap}} = E_{\text{gap}}$ is the band gap (or HOMO–LUMO (lowest unoccupied molecular orbital) difference) of azobenzene (~ 3.4 eV). For $\Delta H = 1.7$ eV, we find a total efficiency, representing both conversion and storage, of $\eta = 7.2\%$.

In conclusion, we have proposed a new approach to the design of solar thermal fuels and predicted the properties of several promising new candidates. Using DFT computations, we have shown that by combining the photoactive behavior of well-known photoisomers with the structural stability and nanoscale properties of CNTs, one obtains a set of highly tunable hybrid nanostructures that exhibit large increases in both the energy storage capacity per molecule and the number of photoactive molecules per volume. Together, these properties result in volumetric energy densities $\sim 10^4$ greater than that of the Ru-fulvalene solar thermal fuel and equivalent to or higher than those reported for state-of-the-art Li-ion batteries. In addition, we have shown that the intermolecular interactions available in the hybrid nanostructures provide means by which to simultaneously increase the energy storage capacity and the lifetime of the photoexcited state. Our work illustrates a clean, renewable, and potentially economically feasible pathway toward long-term storage and convenient use of solar energy on a large scale. In addition, our results suggest that one can generalize the concept of hybrid photoisomer–substrate nanostructures to other photoactive

molecules, different substrates, and different linker chemistries, potentially leading to a wide range of novel degradation resistant high-stability, high-energy density solar thermal fuels.

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