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Dynamic Covalent Bond Based on Reversible Photo [4 + 4] Cycloaddition of Anthracene for Construction of Double-Dynamic Polymers

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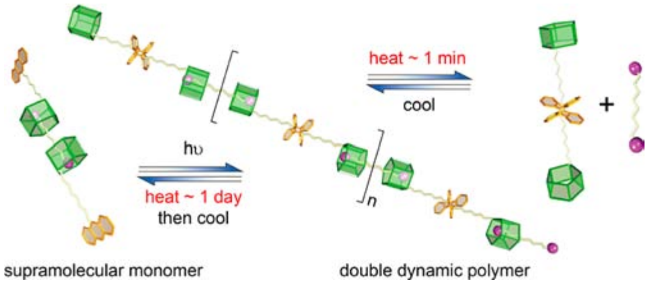
ABSTRACT



Dynamic covalent bonds supplied by reversible anthracene dimerization were combined with pillar[5]arene/imidazole host–guest interactions to construct double-dynamic polymers. Heating such polymers (in solution or as a gel) led to depolymerization by dissociation of either the host–guest complexes alone or the complexes and the anthracene dimers, depending on the extent of heating. The polymers reformed readily upon cooling or irradiation.

Dynamic covalent bonds break and reform reversibly under suitable conditions with minimal side reactions.[1] Dynamic covalent bonds have increasingly been exploited for constructing diverse functional polymers. Examples include thermo-, chemo-, mechano-, and photoresponsive dynamic polymers formed by polycondensation of components through dynamic imine, disulfide, and other bonds.[2] Although impressive progress has been achieved with these dynamic covalent bonds, catalysts (acid, base, or redox agents) are usually needed to access the reversibility of these bonds, and the systems are hard to trap at a nonequilibrium state. It is highly desirable to identify and develop dynamic covalent bonds whose formation/cleavage kinetics and thermodynamics can be easily controlled.

The potential use of reversible photo [4 + 4] cycloaddition of anthracene and dissociation of its dimers (Scheme 1) as a basis of a new type of dynamic covalent bond was mentioned briefly several years ago,[1c] but this idea has never been realized. In the past, anthracene dimerization/dimer dissociation was prototyped for photo-cross-linking of functional materials, for data and energy storage, and as a molecular switch.[3] Anthracene

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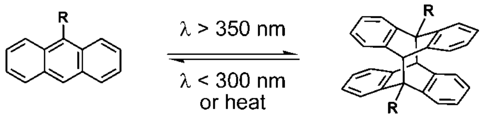
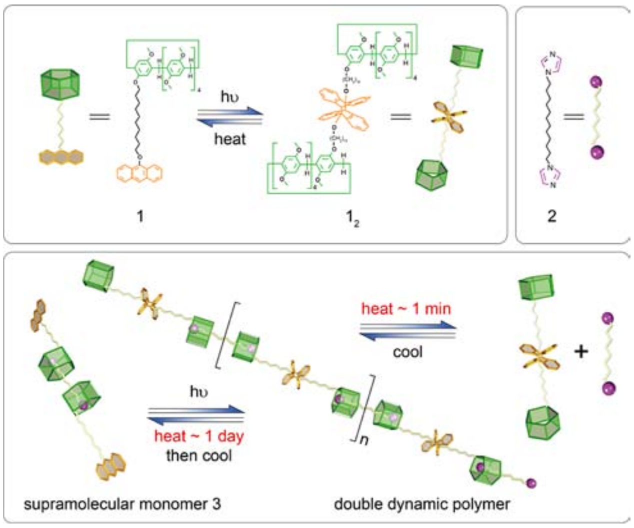
dimerization based dynamic covalent bonds offer considerable advantages over the widely used imines and disulfide bonds. Anthracene and its derivatives dimerize when irradiated at wavelengths above ~350 nm, and the dimers dissociate upon exposure to light of less than 300 nm or heating (E_a 111−160 kJ/mol).[4] The activation energy of thermal dissociation can be varied over ~50 kJ/mol by peripheral substitution. The cycle of photodimerization/dissociation can be repeated hundreds of times without accumulation of side products,[3f] and the reaction can be trapped at a nonequilibrium state. Hence, the compositions and degrees of polymerization of dynamic polymers constructed with such dynamic covalent bonds can be easily controlled by adjusting the temperature or photon flux.

Scheme 1. Conversions between Anthracene and Its Dimer[5]



Here we introduce dynamic covalent bonds based on anthracene dimerization into supramolecular polymers built on host−guest interactions between pillar[5]arene and imidazole. We exploit thermal control of host−guest interactions and dissociation of anthracene dimers, together with photochemical control of anthracene dimerization to construct double-dynamic polymers (Scheme 2).[6] Such polymers are doubly dynamic because they are held together by reversible interactions on both the molecular and supramolecular levels, and respond to more stimuli than conventional dynamic polymers, where reversible interactions are limited to either the covalent or supramolecular levels. Our double-dynamic polymers were formed by irradiation of anthracene-terminated supramolecular monomers **3**, which formed spontaneously upon mixing solutions of **1** and **2**.

Scheme 2. Cartoon Representation of the Formation and Response of the Double-Dynamic Polymers



Pillar[n]arenes (n = 5−10) are a new type of macrocyclic host made up of hydroquinone units linked by methylene bridges at the para positions to form pillar-like architectures.[7] Pillararenes are rigid and can be conveniently functionalized with different substituents at the hydroquinone unit. These attributes make pillararenes attractive building blocks for supramolecular polymers.[8] In our approach, we exploited the recently reported high affinity of imidazole for pillar[5]arene.[9] We synthesized anthracene-derivatized pillararene **1** in two steps with 48% overall yield and bisimidazole alkane **2** in one step with 90% yield (Supporting Information (SI), Schemes S1, S2).

^{1}H NMR spectra of mixtures of **2** (10 mM) and varying concentrations of **1** in $CDCl_3$ confirmed host−guest complexation, as evidenced by an upfield shift of resonances of the alkylic protons of **2**. The presence of signals for both complexed and uncomplexed guest **2** suggests slow exchange on the NMR time scale (Figure S4). High resolution ESI mass spectrometry of a mixture of **1** and **2** (2:1 molar ratio) revealed the molecular peak at m/z = 1220.6731 corresponds to $[\text{Guest+2Host+2H}]^{2+}$, which

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(5) Photodimerization of 9-substituted anthracene derivatives may lead to head-to-head (hh) and head-to-tail (ht) dimers. The formation of the ht dimer is favored because the hh dimer is thermally unstable; see ref 4.

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suggests the formation of 2:1 host–guest complex **3** (Figure S5). Finally, irradiation of **1** at $\lambda > 360$ nm yielded quantitatively anthracene dimer $\mathbf{1_2}$.

As illustrated in SI, supramolecular polymerization of photodimerized compound $\mathbf{1_2}$ and monomer **2** was confirmed by ^{1}H NMR spectroscopy (Figure S6a), diffusion-ordered ^{1}H NMR spectroscopy (DOSY) (Figure S6b), and viscometry (Figure S6c).

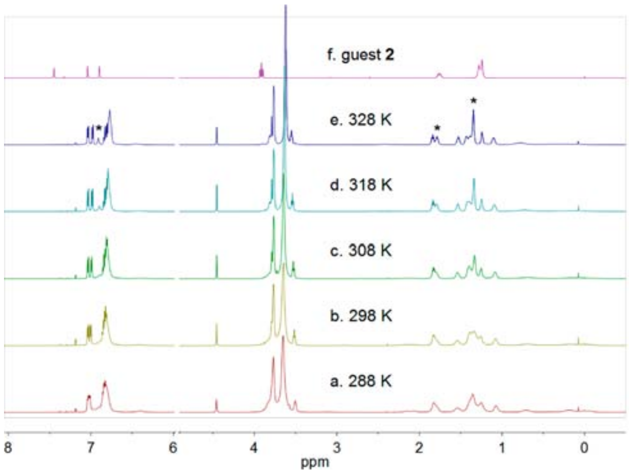

Figure 1. Partial ^{1}H NMR spectra of equimolar $\mathbf{1_2}$ and **2** (150 mM, 400 MHz, $CDCl_3$) at various temperatures (a–e) and guest **2** (f). Asterisks represent the signals for free guest **2**.

Our polymers show dynamic behavior simultaneously on the molecular and supramolecular levels. It is well-known that the host–guest interactions can be controlled by temperature since heating typically reduces binding constants. Thermally reversible polymerization/depolymerization of our supramolecular polymers was demonstrated by variable temperature ^{1}H NMR spectroscopy of an equimolar mixture of $\mathbf{1_2}$ and **2** (150 mM) in $CDCl_3$ (Figure 1). At a relatively low temperature (288 K), the ^{1}H NMR spectra are nearly devoid of the signals for monomers, being replaced by a broad resonance, suggesting strong intermolecular complexation. As the temperature rose, the original broad peaks became well-resolved and the new signals appeared were tentatively assigned to the free guest **2**. These results show that the host–guest complexation is temperature-controllable.

In contrast to the host–guest interactions, which change strongly with temperature, anthracene dimers remain kinetically stable under modest heating/cooling cycling. However, heating at temperatures above 333 K for over 20 h caused the dissociation of anthracene dimers and irreversible thermal depolymerization. Irradiating the resulting solution at $\lambda > 360$ nm reformed anthracene dimers and yielded the original polymers. The cycles of reversible photoinduced polymerization and thermal depolymerization were confirmed by NMR spectroscopy. The DOSY spectra of a solution of guest **2** (150 mM) and host **1** (300 mM) in $CDCl_3$ revealed one set of signals with a diffusion coefficient of 15.74×10^{-11} m^2 s^{-1}, suggesting the almost complete formation of the 2:1 host–guest complex **3** (Figure 2a). Irradiation of the above solution under UV light ($\lambda > 360$ nm) for 5 h yielded a viscous solution, for which the ^{1}H NMR spectra were obtained and showed the proton signals of anthracene were replaced with those of the anthracene dimer, confirming the formation of $\mathbf{1_2}$. Dimerization of anthracenes is expected to result in polymerization, which was confirmed by a DOSY experiment. DOSY spectra manifested a broad distribution and the much smaller weight average diffusion coefficient ($D = 3.602 \times 10^{-11}$ m^2 s^{-1}) corresponding to the high molecular weight supramolecular polymers (Figure 2b). The weight average diffusion coefficient recovered to its original level upon heating the resulted supramolecular polymer solution at 333 K for 30 h. The repeated cycles of UV irradiation and heating of the monomer solution induced the reversible transitions between low molecular weight host–guest complexes and supramolecular polymers (Figure 2c).

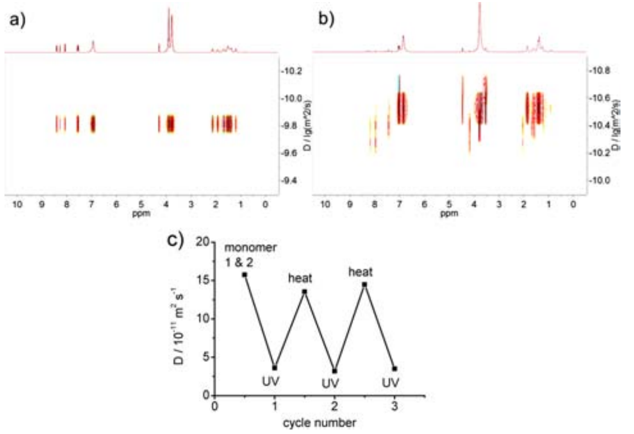

Figure 2. DOSY spectra (600 MHz, $CDCl_3$, 298 K) of (a) 300 mM **1** and 150 mM **2**, (b) irradiation of (a) for 5 h ($\lambda > 360$ nm), (c) cyclic changes in the measured weight average diffusion coefficients (600 MHz, $CDCl_3$, 298 K) of (a) upon > 360 nm irradiation and 333 K heating.

Our double dynamic polymers form a dual-mode thermoresponsive gel. Supramolecular gels, as a type of adaptive soft materials, can respond to external stimuli and have attracted increasing attention because of their

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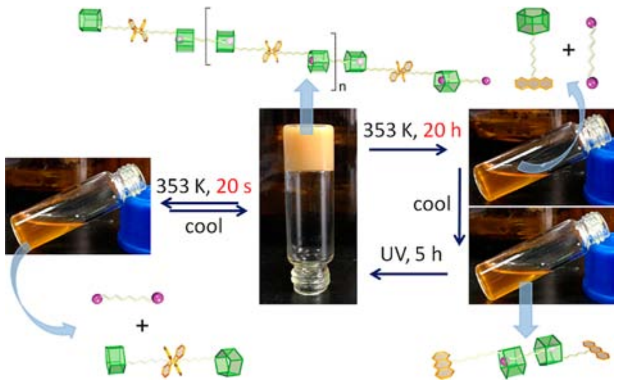

Figure 3. Supramolecular gel formed by equimolar amounts of $\mathbf{1_2}$ and **2** (0.1 M) in 1,2-$C_2H_4Cl_2$/cyclohexane (1/6, v/v) and its dual-mode response to heat.

potential applications as drug carries, chemical sensors, and functional membranes.[10] We prepared the gel by heating an equimolar solution of $\mathbf{1_2}$ and **2** in a mixture of 1,2-dichloroethane and cyclohexane (1:6 by volume) until a transparent solution formed, followed by cooling to rt. The critical gel concentration was determined to be about 60 mM. The morphology of the xerogels was examined by SEM, revealing an interconnected porous gel network (Figure S8).

As expected, the thermal gel/sol transition is readily visible. Heating the gel at 333−353 K for less than 1 min resulted in a reversible transition, which we ascribed to the disruption and restoration of pillar[5]arene/imidazole complexes (i.e., deploymerization on the supramolecular level). In contrast, when the gel was heated at 353 K for 20 h, the resulting liquid did not revert to gel upon cooling to rt. ^{1}H NMR spectra of the liquid revealed a near-quantitative dissociation of anthracene dimers (Figure S7), which led to depolymerization at the molecular level with the formation of supramolecular monomer **3** upon cooling the solution. The gel reformed upon irradiation of the liquid at $\lambda > 360$ nm, which resulted in photodimerization of anthracene moieties and formation of the polymers as evidenced by the absence of the signals for anthracene monomers in the ^{1}H NMR spectra of the reformed gel (Figure S7).

Figure 3 shows a reversible photocontrolled and thermally controlled gel/sol transition. At 333−353 K, whether the transition is reversible or not is determined by the extent of heating. And although gel is probably the thermodynamically favorable state of the system at ambient temperature, the room-temperature sol state is easily achievable by heating the gel at 353 K sufficiently long to induce complete thermal dissociation of anthracene dimers. Among the reported thermoresponsive gels such a property is unique to our double dynamic polymers. The solution of anthracene-terminated supramolecular monomer **3** reformed to gel upon irradiation with light. The dual-mode thermoresponsive gel shows advantages such as good controllability and a response to multiple stimuli over traditional thermoresponsive gels, resulting from the controllability and reversibility of the formation/cleavage of the dynamic covalent bond based on the reversible dimerization of anthracene.

In summary, we introduced a novel kind of dynamic covalent bond based on the reversible photo [4 + 4] cycloaddition of anthracene combined with reversible noncovalent host−guest interactions between pillar[5]arene and imidazole to construct double-dynamic polymers. Our double-dynamic polymers resulted from photodimerization of anthracene-terminated supramolecular monomers, which form spontaneously upon mixing solutions of **1** and **2** (Scheme 2). Such dynamic polymerization/depolymerization is controllable by variation of the temperature and/or photoirradiation. Heating polymers (in solution or as a gel) lead to its depolymerization by dissociation of either the host−guest complexes alone or the complexes and the anthracene dimers, depending on the extent of heating. The polymers reform readily upon cooling or irradiation. We suggest that the dynamic covalent bond based on dimerization of anthracene would be useful for the construction of diverse smart materials with fine-tuned responses to external stimuli.

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Supporting Information Available. Experimental details, synthesis of compounds, NMR spectra, host−guest complexation of **1** and **2**, characterization of the supramolecular polymers, SEM image of the gel, and other materials. This material is available free of charge via the Internet at http://pubs.acs.org.

The authors declare no competing financial interest.