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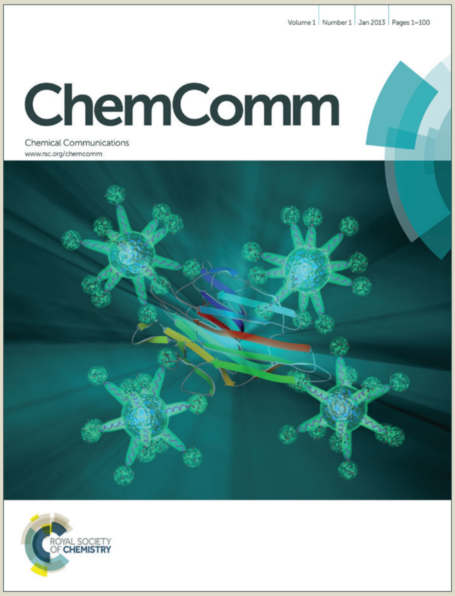

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ARTICLE TYPE

Photoresponsive supramolecular self-assembly of monofunctionalized pillar[5]arene based on stiff stilbene

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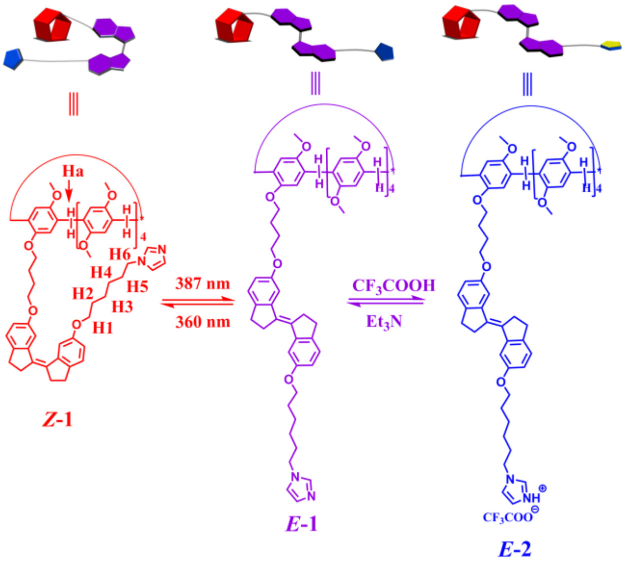
We report a photoresponsive monofunctionalized pillar[5]arene based on stiff stilbene. The *Z* isomer, *Z*-1, tends to form self-complexing [1]pseudorotaxanes and [c2] daisy chains, whereas the *E* analog, *E*-1, forms supramolecular polymers.

Pillar[n]arenes (n = 5-10), composed of hydroquinone units linked by methylene bridges at para positions, are rigid and easily soluble in organic solvents as well as conveniently functionalizable with various substituents at the hydroquinone unit.[1] Both cations and neutral molecules can be incorporated into their cavities.[2] These attributes make pillararenes attractive macrocyclic hosts in supramolecular chemistry.[3] Monofunctionalized pillararenes have been shown to have very interesting self-assembly behaviour, including the formation of [1]rotaxanes (or [1]pseudorotaxanes),[4] [c2] daisy chains[5] and supramolecular polymers.[6] The control of the self-assembly behaviour of monofunctionalized pillararenes by external stimuli is promising for use in smart functional materials, but it remains rarely explored.[7] Among diverse external stimuli (chemical, electrostatic and electromagnetic), light is unique in allowing a remote control of assembly behaviour with potentially excellent temporaspatial resolution and without adding any chemical agents to the system.

Here, we report a photoresponsive monofunctionalized pillar[5]arene based on stiff stilbene (1,1-biindane, Scheme 1). The configuration of *Z*-**1** is favourable for forming self-complexing [1]pseudorotaxanes or [c2] daisy chains, while *E*-**1** forms supramolecular polymers. Furthermore, the degree of polymerization of *E*-**1** can be controlled by pH, by protonation of the imidazole guest.

Stiff stilbene as a novel chromophore in photoresponsive supramolecular systems possesses advantages over other chromophores such as azobenzene. High stability of its *Z* isomer (with a half-life of ~10^9 years at 300 K) and relatively high quantum yields of photoisomerization of *Z* and *E* isomers as well as easy peripheral substitution make it a good candidate as a component of photoresponsive supramolecular systems.[8] Here, we monofunctionalized pillar[5]arene with stiff stilbene to control the self-assembly behaviour by light.

The ^{1}H NMR spectra of *Z*-**1** at 5 mM in $CDCl_3$ (Fig. S7, ESI) contained two sets of resonances for alkyl protons H2-H6 (Scheme 1). We assigned the major set of the resonances that were substantially shifted upfield to the alkyl "tail" of *Z*-**1** threaded through the cavity of pillar[5]arene.[9] The strong correlations between these resonances and the bridging methylene protons Ha of pillar[5]arene (Scheme 1) in a 2-D ROE spectrum (Fig. 1) further confirmed that the alkyl part was included into the cavity of pillar[5]arene.



Scheme 1 Chemical structures of *Z*-**1**, *E*-**1**, *E*-**2**.

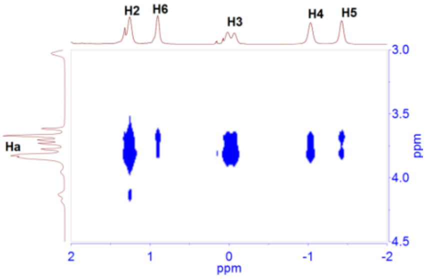
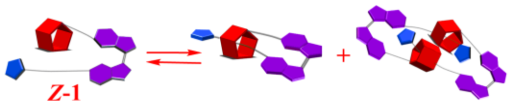


Fig. 1 Partical ROE spectra of *Z*-**1** at 150 mM in a $CDCl_3$ solution.

We studied the aggregate size of *Z*-**1** at 5-150 mM in $CDCl_3$ by two-dimensional diffusion-ordered ^{1}H NMR spectroscopy (DOSY).[10] At 5 mM one set of DOSY signals was observed (Fig. S9, ESI), which in conjunction with the presence of two sets of signals in ^{1}H NMR spectra (above) suggests that at 5 mM *Z*-**1** forms self-complexing [1]pseudorotaxane. Two sets of signals were found at 20-100 mM, with one set having the diffusion constant close to that at 5 mM. This data suggests an equilibrium between [1]pseudorotaxane (higher diffusion coefficient) and [c2] daisy chains (lower diffusion coefficient, Scheme 2). Finally, at 150 mM, the high-diffusion-coefficient signals disappear, suggesting that the equilibrium is dominated by [c2] daisy chains. We suggest that the bent conformation of *Z*-**1**, sterically suppresses polymerization. This conclusion was confirmed by viscometry, which is a classic method to estimate weight distributions of self-assembled systems. We measured the specific viscosities of *Z*-**1** solutions in CHCl$_3$ at 291 K (Fig. 2a). We observed a slope of 1.02 in the double logarithmic plots of specific viscosity versus concentration at 5-200 mM, consistent negligible polymerization of *Z*-**1** at these concentrations.



Scheme 2 The illustrations of the supramolecular assemblies of *Z*-**1**.

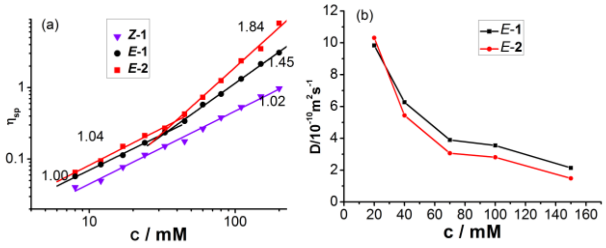
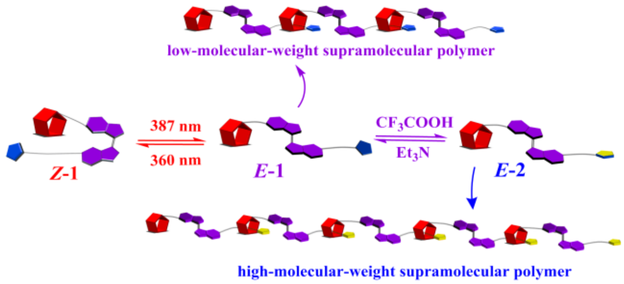


Fig. 2 (a) Specific viscosity of *Z*-**1**, *E*-**1** and *E*-**2** in CHCl$_3$ solutions versus the concentration (291K). Values on the curves indicate the slope. (b) Concentration dependence of diffusion coefficient D (from ^{1}H NMR spectroscopy 600 MHz, CDCl$_3$, 298K) of *E*-**1**, *E*-**2**.

Irradiating of *Z*-**1** at 387 nm resulted in the formation of *E*-**1** with 97% yield which was determined by ^{1}H NMR spectroscopy (Fig. S5, ESI). Viscosity of chloroform solutions of *E*-**1** increased linearly with concentration up to ~33 mM, consistent with the presence of only low-molecular weight species. Above 33 mM viscosity increased with concentration to the power of 1.45, suggesting the formation of supramolecular polymers.[6a,10,11] The DOSY experiments were consistent with the results of the viscosity studies (Fig. 2b): when the concentrations of *E*-**1** increased from 20 to 150 mM, the measured weight-average diffusion coefficients decreased from 9.83 $\times 10^{-10}$ to 2.14 $\times 10^{-10}$ m^{2}s^{-1}. These results indicate that the *E*-**1** has the tendency to form linear supramolecular polymers at concentrations above ~33 mM, which can be ascribed to the linear and stiff structure of *E*-**1**.

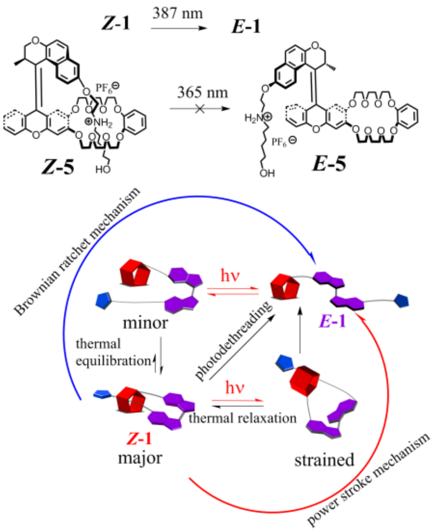
Owing to the relatively low binding constant of imidazole to pillar[5]arene in the absence of preorganization (~230 M^{-1}), the degree of polymerization of *E*-**1** was low, as suggested by the relatively low viscosity of *E*-**1** solutions (Fig. 2a). Because protonation of imidazole to imidazolium increases the association constant by ~50-fold (to ~10^4 M^{-1}) we studied polymerization of *E*-**2** (Scheme 3).



Scheme 3 The illustrations of the supramolecular assemblies of *E*-**1**, *E*-**2**.

Adding trifluoroacetic acid to a solution of *E*-**1** at <38 mM had negligible effect on solution viscosity. At concentrations >38 mM, protonation of imidazole was associated both with an increase in the solution viscosity and the dependence of the viscosity on concentration (i.e., increase in the slope of the doubly-logarithmic plot from 1.45 to 1.84, Fig. 2). The totality of the data suggests that protonation of *E*-**1** increases its degree of polymerization by increasing the affinity of imidazole for pillar[5]arene.

We also obtained *E*-**2** nearly quantitatively by irradiating of protonated *Z*-**1** which was determined by ^{1}H NMR spectroscopy (Fig. S6, ESI). In contrast to our observation of photoisomerization of *Z*-**1** / protonated *Z*-**1** pseudorotaxane to *E*-**1** / *E*-**2**, a related pseudorotaxane based on the *Z* isomer of a crowded aromatic chromophore and protonated amine/crown-ether host–guest complex (**5**, Scheme 4) was reported to be stable towards photoinduced dethreading upon irradiation at the wavelength where the free *Z* isomer photoisomerizes efficiently to the *E* analog.[12] In other words, the R$_2$NH$_2$$^+$/crown ether host–guest complex acted as a "lock" on photoisomerization of the *Z* chromophore. Understanding the difference in the response of *Z*-**1** and *Z*-**5** to irradiation may yield insights into which of the two chromophores is the more efficient photoactuating moiety, i.e., one that can operate against larger loads.[13]



Scheme 4 The structure of *Z*-**5** reported in reference and the illustrations of the photoisomerization processes of *Z*-**1**.

Because photoisomerization of C=C bonds is much faster (4 ps)[8f] than host−gust decomplexation (typically ms or longer)[9b], the two processes needed for photoinduced dethreading of a pseudorotaxane (photoisomerization of the C=C bond and host−guest decomplexation, Scheme 4) must occur sequentially. Two limiting mechanisms are plausible. In a small-molecule analogy of the power-stroke mechanism,[8d,14] absorption of a photon by the *Z* chromophore of the pseudorotaxane quickly generates a highly strained transoid form of the C=C bond. It then slowly (ms) relaxes, by thermally activated decomplexation (yielding the *E* isomer) or thermal isomerization of the highly strained C=C bond (yielding the reactant). Compressive loads on *E*-olefins are known to increase the quantum yield of *E*→*Z* photoisomerization and the rate of thermal *E*→*Z* isomerization.[8b] If the power-stroke mechanism dominates photodethreading of *Z*-**1** and *Z*-**5**, the difference in photochemical behaviour of *Z*-**1** and *Z*-**5** suggests that either the quantum yield of *E*→*Z* photoisomerization of stiff stilbene is less sensitive to load than that of the olefin in *Z*-**5**, or the larger barrier of *E*→*Z* isomerization of stiff stilbene prevents it from unproductive relaxation back to *Z*-**1** before undergoing thermal relaxation.

In the alternative (Brownian ratchet),[15] photoisomerization occurs only in the non-psuedorotaxane fraction of *Z*-**1** or *Z*-**5** (i.e., the fraction in which imidazole and pillar[5]arene of *Z*-**1** or $R_2NH_2^+$/crown ether of *Z*-**5** are uncomplexed). This thermally populated minor fraction is trapped by photoisomerization. The dominance of this mechanism would be suggested if the self-associated constants of *Z*-**1** were considerably lower than *Z*-**5**. We are currently conducting experimental and computational studies to probe these possibilities.

In conclusion, we reported a photoresponsive monofunctionalized pillar[5]arene based on stiff stilbene. The two isomers of the molecule, *Z*-**1**/*E*-**1,** exhibited different self-assembly behaviour. *Z*-**1** forms self-complexing [1]pseudorotaxane and [c2] daisy chains, depending on concentration. *E*-**1** tends to form linear polymers, whose degree of polymerization is sensitive to solution pH. The complexation of pillar[5]arene / imidazole does not prevent photoisomerization of *Z* stiff stilbene in *Z*-**1**. Our studies reveal subtle correlation between monomer structure and aggregation behaviour which may yield insights into the behaviour of existing and help design new photoresponsive supramolecular self-assemblies.

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† Electronic Supplementary Information (ESI) available: Experimental details, synthesis of compounds, ^{1}H NMR, COSY, DOSY, and other materials. See DOI: 10.1039/b000000x/

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