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Temporary and Permanent Trapping of the Metastable Twisted Conformer of an Overcrowded Chromic Alkene via Encapsulation

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Ⓢ *Supporting Information*

ABSTRACT: An overcrowded alkene with an anti-folded conformation was converted to its twisted conformer, accompanied by a dramatic color change from yellow to deep purple, by inclusion in a self-assembled T_d-symmetric coordination cage. The shape of the caged cavity was suitable and desirable for trapping of the twisted conformer. The twisted conformation was temporarily memorized in the alkene even after guest ejection. Permanent trapping of the twisted conformation was achieved by bromination of the twisted conformer formed in situ in the cage.

Sterically overcrowded alkenes with distorted C=C bonds have received considerable attention because of their chromic behavior caused by unimolecular conformational changes.[1−3] Bis-tricyclic aromatic ene **1** (Figure 1) is one of the widely studied overcrowded alkenes with chromic properties.[3−6] Its two major conformers, anti-folded and twisted, show distinctly different colors: colorless or yellow for anti-folded conformers, but deep-colored for twisted ones.[5,6] Although a variety of derivatives of **1** have been synthesized to date,[5−7] their dynamic conformational behavior is still difficult to predict and control. Here we demonstrate that T_d-symmetric self-assembled cage **2** is a suitable host for fixing and stabilizing the twisted conformer of an overcrowded alkene (Scheme 1). The overcrowded alkene examined here, **1a**, exists as the anti-folded conformer in the solid state. We found that this anti-folded guest (hereafter, *af*-**1a**) was induced to adopt the metastable twisted conformation (hereafter, *t*-**1a**) upon inclusion in the cavity of **2**, along with a sharp color change from yellow to deep purple.[8] The stabilization of *t*-**1a** is ascribed to the perfect complement of its C_2 symmetry to the cage's T_d symmetry.[9]

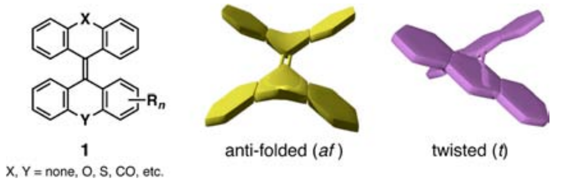
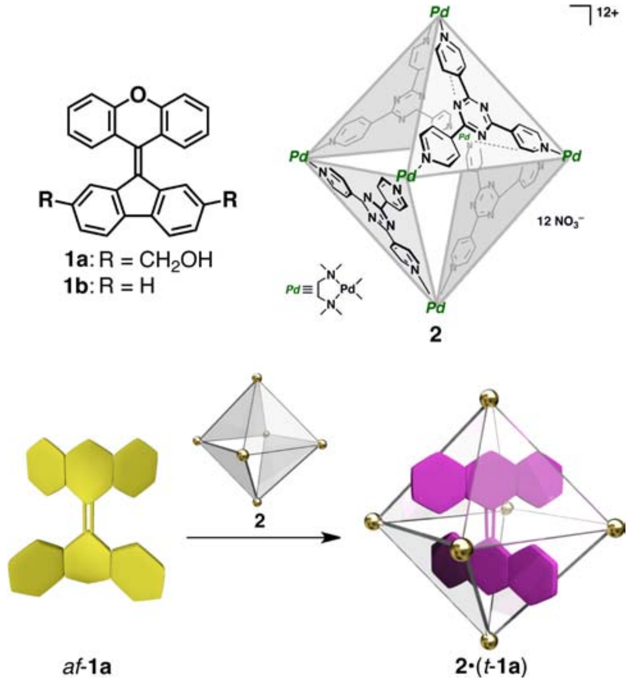


Figure 1. Cartoon representations of anti-folded and twisted conformers of overcrowded alkenes **1**.

The guest alkene *af*-**1a**, synthesized in six steps from 9-fluorenone-2,7-dicarboxylic acid and 9-xanthone (see the Supporting Information), exhibits a yellow color characteristic of the anti-folded conformation.[6] Solid *af*-**1a** (in excess) was suspended in an aqueous solution of cage **2**, and the mixture was heated under microwave conditions at 100 °C for 1 h. Water-insoluble *af*-**1a** gradually dissolved, and the solution turned deep purple. This color change suggested the inclusion of *af*-**1a** into **2** and its conformational change from the anti-folded to the twisted form. After removal of excess *af*-**1a** by filtration, ^{1}H NMR spectroscopy revealed the formation of the inclusion complex **2**·(*t*-**1a**) in ~10% yield (Figure 2). The guest signals were significantly shifted upfield as a result of shielding by the aromatic panels of cage **2**.

Scheme 1. Schematic Representation of Inclusion of Overcrowded Alkene 1a into T_d-Symmetric Cage 2



The twisted conformation of the guest in the cage was elucidated by symmetry analysis of the cage signals in the ^{1}H NMR spectrum. After guest inclusion, the T_d symmetry of cage **2** was reduced, and three sets of pyridyl protons were observed (Figure 2b). This splitting pattern is predicted when the guest

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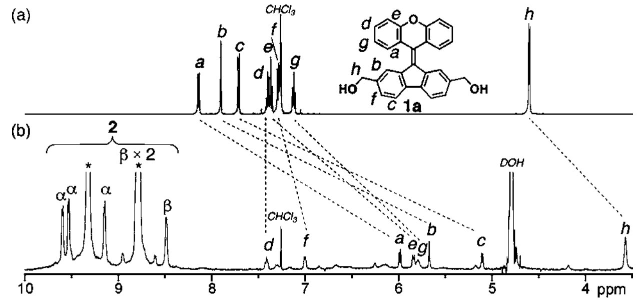

Figure 2. ^{1}H NMR spectra (500 MHz, 300 K) of (a) **1a** in $CDCl_3$ and (b) **2**·(*t*-**1a**) in D_2O (* labels denote signals of free cage **2**).

possesses D_{2d} symmetry.[10] The C_2 symmetry of *t*-**1a** can appear to be D_{2d} symmetry if racemization (via rotation around the central C═C bond) and vertical flipping of the guest in the cavity are fast on the NMR time scale. The fast racemization process in the cage is supported by the observation of the methylene protons (*h*) as a singlet. In contrast, *af*-**1a** cannot show apparent D_{2d} symmetry on any occasion.

UV−vis measurements in both solution and the solid state also revealed the selective capture of *t*-**1a** by cage **2** (Figure 3).

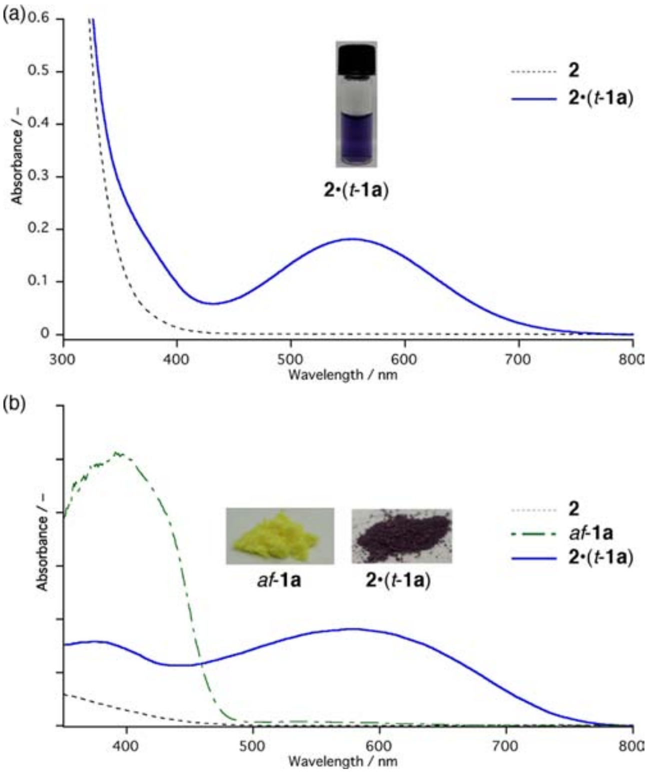

Figure 3. UV−vis spectra and photographs of (a) **2** (in H_2O, [**2**] = 1.0 mM, black dotted line) and **2**·(*t*-**1a**) (in H_2O, [**2**] = 1.0 mM, 10% inclusion of **1a**, blue solid line) and (b) **2** (black dotted line), *af*-**1a** (green dot-dashed line), and **2**·(*t*-**1a**) (blue solid line) in the solid state.

Yellow-colored *af*-**1a** showed a strong absorption at ~400 nm in the solid state, diagnostic of the anti-folded conformation. However, after inclusion in the cage in water (Figure 3a), the absorption at ~400 nm disappeared and a new strong absorption diagnostic of the twisted conformation appeared at ~550 nm.[6b] Even after evaporation of the water, the resulting powdered inclusion complex showed a similar absorption at ~570 nm (Figure 3b). Thus, the twisted conformation of **1a** was retained in the solid state.

The encapsulated *t*-**1a** was easily ejected upon the addition of 4 equiv of 1-adamantanol (**3**), an efficient guest for **2**, to the solution of **2**·(*t*-**1a**) at room temperature (Figure 4). The purple solution color turned colorless because of formation of the complex **2**·(**3**)$_4$ by guest exchange. To our surprise, the ejected **1a** precipitated as a purple solid (Figure 4b, left), indicating that the as-precipitated **1a** retained the metastable twisted conformation formed when *af*-**1a** was converted to *t*-**1a** via inclusion complex **2**·(*t*-**1a**). Interestingly, the purple color changed to yellow upon heating at 70 °C for 15 min (Figure 4b, right), indicating regeneration of the more stable *af*-**1a**. Thus, the temporarily "memorized" twisted conformation of as-precipitated *t*-**1a** could be easily "erased" upon heating.

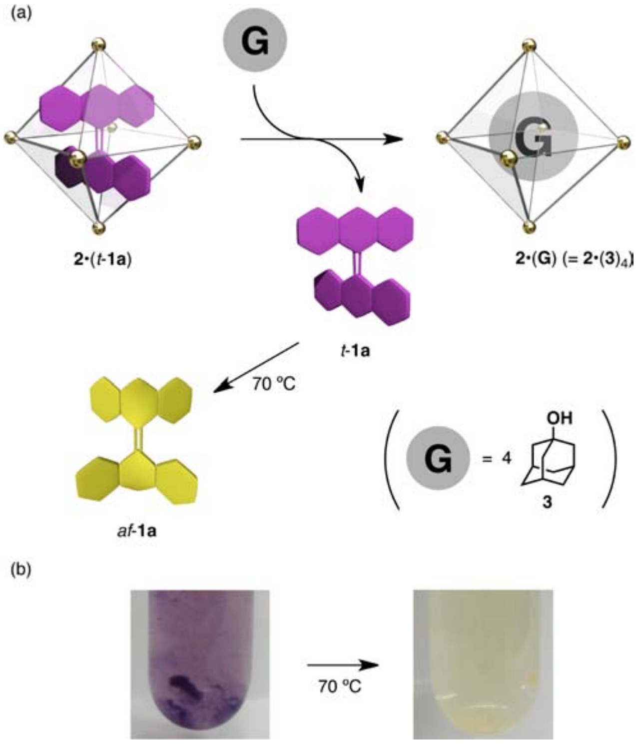

Figure 4. Ejection of *t*-**1a** from the inclusion complex **2**·(*t*-**1a**) by guest exchange. (a) Schematic representation of the ejection of *t*-**1a**. (b) Photographs of the guest exchange. Upon addition of **3** to the solution of **2**·(*t*-**1a**), the included *t*-**1a** was ejected and precipitated. The as-precipitated **1a** had a purple color (left) but turned yellow upon heating (right), indicating that the metastable twisted conformation was temporarily "memorized" in the as-precipitated **1a** and then "erased" upon heating.

We could also achieve permanent trapping of the twisted conformation of *t*-**1a** by bromination of the aromatic core (Figure 5). When an aqueous solution of the inclusion complex **2**·(*t*-**1a**) ([**2**] = 10 mM, 10% inclusion of *t*-**1a**, 50 mL) was treated with 2 equiv of *N*-bromosuccinimide (NBS), the solution color immediately changed from dark purple to green. After the mixture was stirred at room temperature for 5 min, cage **2** was decomplexed by aqueous HCl, and the product was extracted with chloroform. NMR measurements of the extracted mixture revealed the formation of tetrabrominated product *t*-**4** (29% NMR yield).[11] After isolation by column chromatography, compound *t*-**4** was obtained as a deep-blue

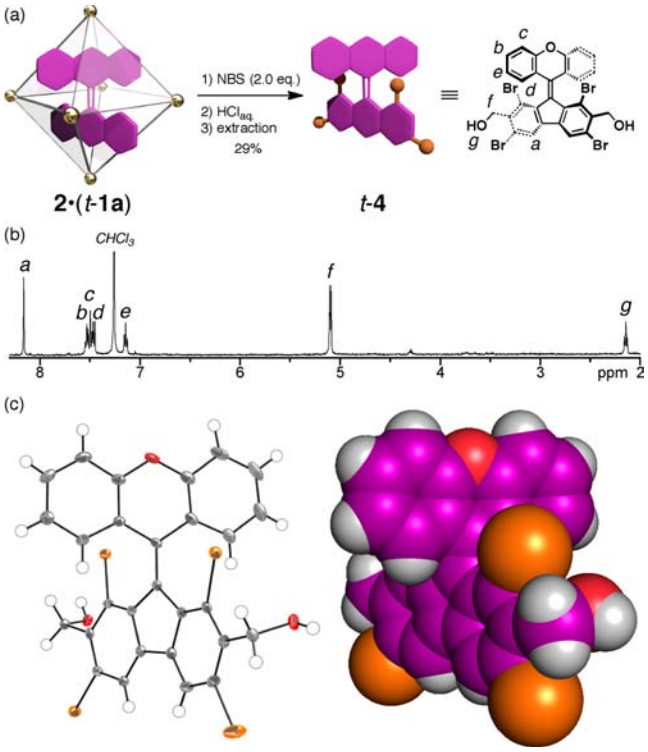

Figure 5. (a) Schematic representation of the bromination of *t*-**1a** within cage **2**. (b) ^{1}H NMR spectrum (300 K, 500 MHz, $CDCl_3$) of compound *t*-**4** obtained after purification. (c) X-ray crystal structure of *t*-**4**: (left) ORTEP drawing (ellipsoids at the 50% probability level); (right) space-filling model (C, purple; H, white; O, red; Br, orange). Solvents have been omitted for clarity.

solid. The twisted structure of *t*-**4** was clearly confirmed by X-ray crystallographic analysis (Figure 5c). Because of steric hindrance by the bromine substituents at the 1-, 3-, 6-, and 8-positions, isomerization into the anti-folded conformer is no longer possible. In fact, the deep-blue color of *t*-**4** remained unchanged even after heating at 100 °C for 2 h. These results show that *af*-**1a** was converted to highly twisted alkene *t*-**4** by bromination within cage **2**. The twist angle around the central double bond in *t*-**4** (53.3°)[12] was significantly larger than that in parent compound *t*-**1b** (42.3°).[6b] This means that the overlap of the olefin p orbitals is poorer, resulting in elongation of the double bond in *t*-**4** [1.416(5) Å for *t*-**4** compared with 1.401(6) Å for *t*-**1b**].[6b]

The chromism between the two conformers of **1a** is ascribed to a change in the HOMO−LUMO gap of the molecule, which depends on the overlap of the alkene p orbitals.[6b] Though significantly distorted, the two p orbitals of the anti-folded conformer are in the same plane. Thus, the HOMO−LUMO gap is relatively large, and absorption occurs in shorter-wavelength regions. When **1a** is twisted, the orbital overlap in the central double bond is reduced, and the HOMO−LUMO gap is narrowed, bringing the absorption into the visible region.

In summary, we have succeeded in noncovalently twisting the overcrowded alkene *af*-**1a** within self-assembled T_d-symmetric cage **2**. A dramatic color change was observed as a consequence of conformational switching by encapsulation. Furthermore, the twisted conformation of the guest can be either temporarily or permanently trapped. These observations are applicable not only to molecular sensing and information storage but also more generally to the control of physical properties of guests via cage-driven conformational twisting. Even better, the resulting conformation of the guest is easily predicted from the cavity shape.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures, physical properties, and crystallographic data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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