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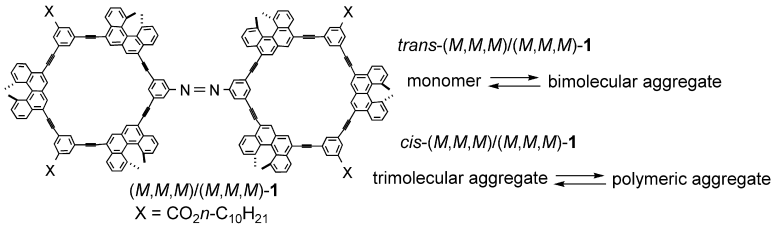

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[3+3]Cycloalkyne Dimers Linked by an Azo Group: A Stable *cis*-Azo Compound Forms Polymeric Aggregates by Nonplanar $\pi-\pi$ Interactions

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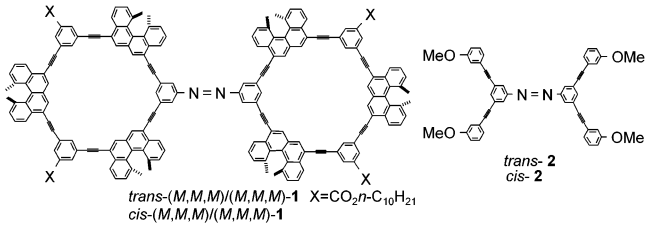
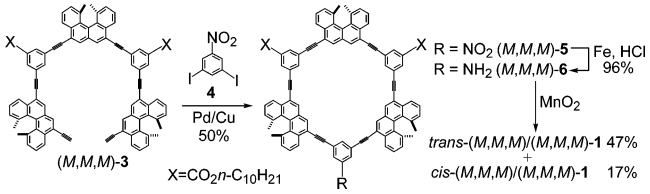
The $\pi-\pi$ interactions are noncovalent bondings between π-electron systems with a face-to-face orientation. Construction of a self-assembly system based on the $\pi-\pi$ interactions, however, is not facile, because the interactions are weak and result in a higher degree of aggregation under forced conditions. Usually, external factors such as templates,[1] solvophobic effects,[2] or hydrogen bonding[3] are required to promote and control such aggregation of π-compounds. Recently, we have found that [3+3]cycloalkynes, which are chiral macrocyclic alkynes containing three helicenes, form a strong and selective bimolecular aggregate in organic solvents.[4] It was also observed that the aggregation of [3+3]cycloalkyne oligomers could be controlled by changing the structure of the linker moieties:[5] Oligomers with flexible linkers form intramolecular aggregates, and those with rigid linkers form bimolecular aggregates without forming a higher degree of aggregation. We were then interested in the formation of polymeric aggregates using this system, and we describe here our finding that a [3+3]cycloalkyne dimer *cis*-(*M*,*M*,*M*)/(*M*,*M*,*M*)-**1** possessing a *cis*-azo linker does polymerize, while *trans*-(*M*,*M*,*M*)/(*M*,*M*,*M*)-**1** forms a bimolecular aggregate without forming a higher degree of aggregation. This is a self-assembly system employing only the nonplanar $\pi-\pi$ interactions of helicenes, which appear to be much stronger than the planar $\pi-\pi$ interactions. It was also observed that the *trans*- and *cis*-(*M*,*M*,*M*)/(*M*,*M*,*M*)-**1** do not isomerize when subjected to heating or irradiation.



Isomeric *trans*- and *cis*-(*M*,*M*,*M*)/(*M*,*M*,*M*)-**1** were synthesized as shown in Scheme 1. Cyclization of (*M*,*M*,*M*)-**3**[4] and 3,5-diiodonitrobenzene **4** produced a nitro derivative (*M*,*M*,*M*)-**5** in 50% yield, which was reduced by iron to form an amine (*M*,*M*,*M*)-**6** in 96% yield. Oxidative coupling with manganese(IV) oxide in toluene generated *trans*- and *cis*-(*M*,*M*,*M*)/(*M*,*M*,*M*)-**1** in 47% and 17% yields, respectively, which were readily separable by GPC.[6] The *cis*/*trans*-stereochemistry was determined by UV−vis spectroscopy (Figure 1): The *trans*-(*M*,*M*,*M*)/(*M*,*M*,*M*)-**1** with a larger retention volume by GPC exhibits stronger absorption at 300−400 nm ($\pi-\pi^*$ transition) and weaker absorption in the visible region ($n-\pi^*$ transition).[7]

Scheme 1



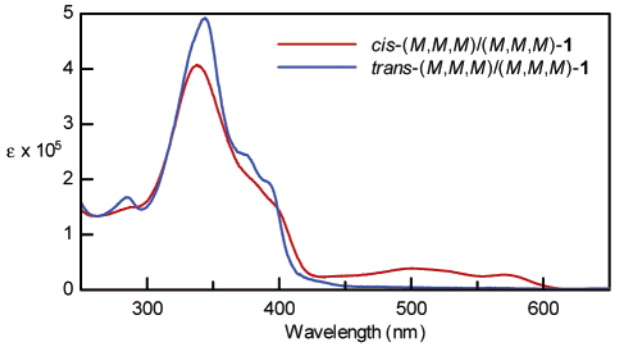


Figure 1. UV−vis spectra of (*M*,*M*,*M*)/(*M*,*M*,*M*)-**1** (0.001 mM) in $CHCl_3$ at 25 °C.

CD ($CHCl_3$) spectra of *trans*-(*M*,*M*,*M*)/(*M*,*M*,*M*)-**1** are concentration-independent below 0.01 mM and concentration-dependent above 0.01 mM, providing isosbestic points at 280, 320, 345, and 395 nm (Figure 2a,c). ^{1}H NMR ($CDCl_3$) signals of *trans*-(*M*,*M*,*M*)/(*M*,*M*,*M*)-**1** shift upfield and broaden as the concentration increases from 0.1 to 10 mM.[6] Vapor pressure osmometry (VPO) in $CHCl_3$ revealed bimolecular aggregate formation of the compound above 2 mM (Figure 3). The retention volume of GPC provided an apparent molecular weight of 6400 in $CHCl_3$ (2 mM); the MW of *trans*-(*M*,*M*,*M*)/(*M*,*M*,*M*)-**1** was 3033.[6] These analyses indicate that *trans*-(*M*,*M*,*M*)/(*M*,*M*,*M*)-**1** is monomeric below 0.01 mM, and a bimolecular aggregate is selectively formed above 2 mM without forming a higher degree of aggregation.

CD ($CHCl_3$) spectra of *cis*-(*M*,*M*,*M*)/(*M*,*M*,*M*)-**1** are concentration-independent between 0.001 and 0.5 mM (Figure 2b,d). ^{1}H NMR ($CDCl_3$) spectra of *cis*-(*M*,*M*,*M*)/(*M*,*M*,*M*)-**1** are concentration-independent below 1 mM and broaden above 1 mM.[6] VPO in $CHCl_3$ revealed trimolecular aggregate formation below 1 mM and polymeric aggregate formation above 1 mM (Figure 3). The GPC analysis gave a molecular weight of 8400 in $CHCl_3$ (1 mM).[6] It has become clear that *cis*-(*M*,*M*,*M*)/(*M*,*M*,*M*)-**1** polymerizes in solution employing the nonplanar $\pi-\pi$ interactions as the only driving force.

It is also noticed that *trans*- and *cis*-(*M*,*M*,*M*)/(*M*,*M*,*M*)-**1** are inert toward heat and light. *trans*-(*M*,*M*,*M*)/(*M*,*M*,*M*)-**1** in $CHCl_3$ at 5 and 0.1 mM does not isomerize when subjected to irradiation at

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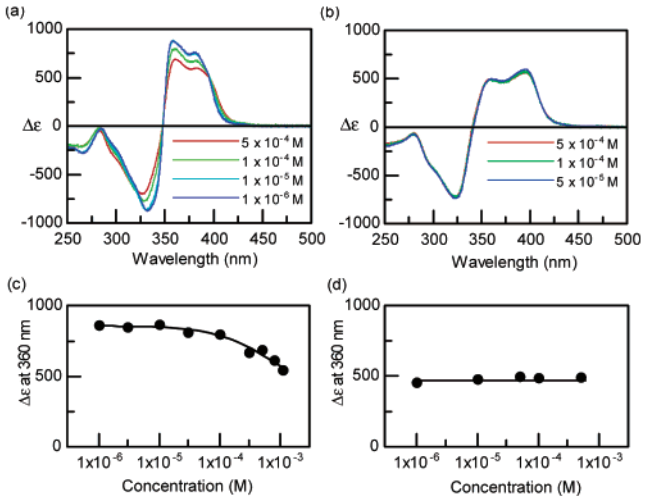

Figure 2. CD spectra of (a) *trans*-(*M*,*M*,*M*)/(*M*,*M*,*M*)-**1**, and (b) *cis*-(*M*,*M*,*M*)/(*M*,*M*,*M*)-**1** in $CHCl_3$ at 25 °C. Plots of $\Delta\epsilon$ at 360 nm versus concentration for (c) *trans*-(*M*,*M*,*M*)/(*M*,*M*,*M*)-**1**, and for (d) *cis*-(*M*,*M*,*M*)/(*M*,*M*,*M*)-**1**.

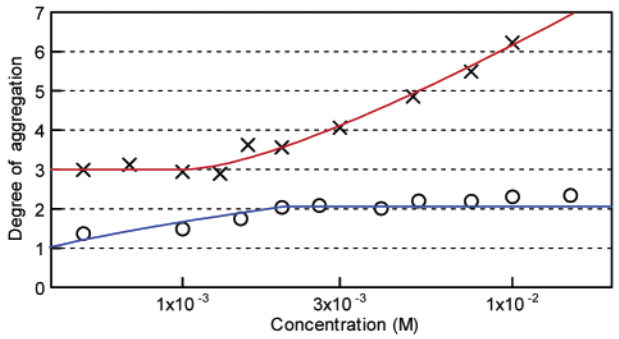

Figure 3. Degree of aggregation by VPO ($CHCl_3$, 35 °C) for *trans*-(*M*,*M*,*M*)/(*M*,*M*,*M*)-**1** (○), and *cis*-(*M*,*M*,*M*)/(*M*,*M*,*M*)-**1** (×). The red and blue lines are drawn to guide the eye.

365 nm for 30 min.[6] At a lower concentration (0.001 mM), UV−vis absorption of *trans*-(*M*,*M*,*M*)/(*M*,*M*,*M*)-**1** decreases following irradiation at 365 nm because of the decomposition.[6] *cis*-(*M*,*M*,*M*)/(*M*,*M*,*M*)-**1** in $CHCl_3$ at 0.1, 0.01, 0.001, and 0.0005 mM also does not isomerize when subjected to irradiation of visible light at above 450 nm for 30 min or to heating in refluxing toluene (0.1 mM) for 3 h.[6] In contrast, the model compound **2**, lacking the cyclic helicene moiety, readily isomerizes under these conditions.[6] Several methods of stabilizing diaryl *cis*-azo compounds were reported, which utilize inclusion complex formation,[8] hydrogen bonding,[9] and hydrophobic interactions.[10] It may therefore be interesting to note that azo-compounds can be stabilized by another driving force, possibly by self-aggregation.

A polymeric aggregate is currently obtained using *cis*-(*M*,*M*,*M*)/(*M*,*M*,*M*)-**1** in a series of [3+3]cycloalkyne oligomers.[5] This is probably because *cis*-(*M*,*M*,*M*)/(*M*,*M*,*M*)-**1** cannot form either an intramolecular aggregate or a bimolecular aggregate (Figure 4). The rigid *cis*-azo structure possessing a 120° direction does not allow the formation of the intramolecular aggregated structure. Because two [3+3]cycloalkyne moieties of *cis*-(*M*,*M*,*M*)/(*M*,*M*,*M*)-**1** cannot

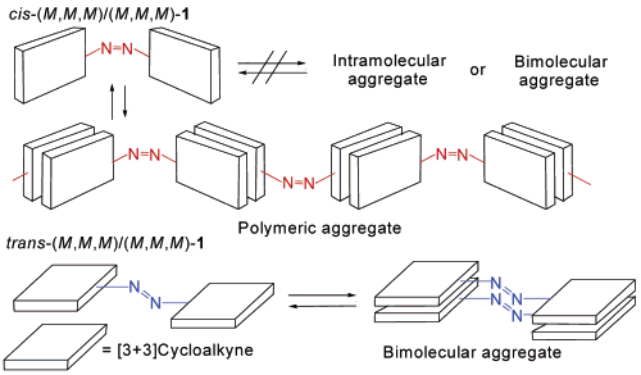

Figure 4. Aggregation behaviors of (*M*,*M*,*M*)/(*M*,*M*,*M*)-**1**.

exist in the same plane,[11] they do not aggregate in a bimolecular fashion. As a result, *cis*-(*M*,*M*,*M*)/(*M*,*M*,*M*)-**1** gives trimolecular or higher aggregates. It is in contrast to the bimolecular aggregate formation of *trans*-(*M*,*M*,*M*)/(*M*,*M*,*M*)-**1**, the [3+3]cycloalkyne moieties of which can exist in the same plane.[5,12] The present finding would provide a novel methodology for constructing a controlled self-assembly system involving selective bimolecular $\pi-\pi$ interactions of helicene.

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Supporting Information Available: Experimental procedures for the synthesis of **1**, **2**, **5**, and **6**, GPC chromatogram and ^{1}H NMR spectra of *trans*-(*M*,*M*,*M*)/(*M*,*M*,*M*)-**1** and *cis*-(*M*,*M*,*M*)/(*M*,*M*,*M*)-**1**, isomerization experiment procedures for **1** and **2** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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