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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 selfassembly 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 bonding³ are required to promote and control such aggregation of π -compounds. Recently, we have found that [3+3]cvcloalkynes. 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*)-3⁴ and 3,5diiodonitrobenzene **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 (π - π * transition) and weaker absorption in the visible region (n- π * transition).⁷





Figure 1. UV-vis spectra of (M,M,M)/(M,M,M)-1 (0.001 mM) in CHCl₃ at 25 °C.

CD (CHCl₃) 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). ¹H NMR (CDCl₃) 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 CHCl₃ 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 CHCl₃ (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 (CHCl₃) spectra of *cis*-(*M*,*M*,*M*)/(*M*,*M*,*M*)-1 are concentration-independent between 0.001 and 0.5 mM (Figure 2b,d). ¹H NMR (CDCl₃) spectra of *cis*-(*M*,*M*,*M*)/(*M*,*M*,*M*)-1 are concentration-independent below 1 mM and broaden above 1 mM.⁶ VPO in CHCl₃ 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 CHCl₃ (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 CHCl₃ 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 CHCl₃ 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)(M, M, M) - 1.



Figure 3. Degree of aggregation by VPO (CHCl₃, 35 °C) for trans-(M,M,M)/(M,M,M)-1 (O), 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), UVvis 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 CHCl₃ 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 azocompounds 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 ¹H 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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