Shape-persistent arylenevinylene macrocycles (AVMs) prepared *via* acyclic diene metathesis macrocyclization (ADMAC)†

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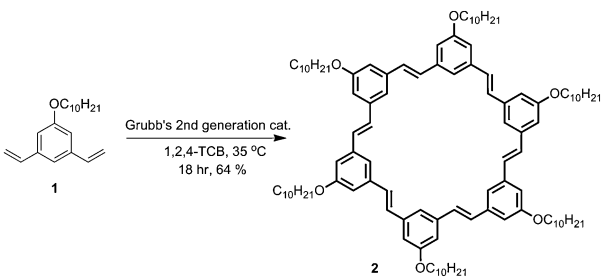
Shape-persistent arylenevinylene macrocycles (AVMs) were successfully prepared in one step from readily available aromatic diene monomers through olefin metathesis in good yields. ^{1}H NMR, UV-Vis absorption and fluorescence studies revealed the aggregation behavior of the obtained macrocycles. SEM characterization showed AVM nanofibril formation.

Shape-persistent macrocycles have attracted great attention in the past two decades, due to their unique structures, novel properties, and potential applications.[1] These macrocycles usually have rigid, planar hydrocarbon backbones, which can form ordered structures under certain conditions. There has been significant progress in the preparation of aryleneethynylene macrocycles (AEMs) through dynamic covalent chemistry (DCC),[2] namely alkyne-metathesis-mediated cyclooligomerization in which the thermodynamically most favored target macrocycles can be obtained in one step and high yield from simple diyne monomers.[3] In contrast to the intensive research efforts devoted to AEMs, the studies on their hydrogenated analogues, arylenevinylene macrocycles (AVMs), have lagged far behind.[4] AVMs presumably have more conformational freedom compared to AEMs, and would diminish the rigidity of the backbone since the vinylene group could undergo conformational isomerization. Although olefin metathesis[5] has been intensively used in synthesis of flexible large cyclic compounds, to our best knowledge, there has been no report on its application in shape-persistent macrocycle synthesis through one-step cyclooligomerization. In this work, we report the first successful synthesis of AVMs through Acyclic Diene Metathesis Macrocyclization (ADMAC). Such a dynamic covalent approach shows a general scope. The observed self-aggregation behavior of the obtained AVMs and their fabrication into nanofibrils will also be discussed.

In contrast to conformationally flexible cycles, shape-persistent macrocycles generally have a regular repeating unit with few degrees of conformational freedom. Under a certain monomer concentration, macrocyclic strain and entropy considerations determine the preferred ring size, with macrocycles having the smallest number of monomer units being entropically favored. The bond angles and conformational rigidity of the monomer determine if a particular macrocycle is strained or strain-free. The energy gap between the most stable product and the second most stable product determines whether a unique product will be formed under reversible conditions.[1a] Given the above considerations, the potential challenges in AVM synthesis can be envisioned as follows: (1) the uncontrolled double bond configuration (*E*/*Z*) in olefin metathesis could lead to a variety of macrocyclic products with different angles and geometry; (2) the higher reactivity of the alkene metathesis catalyst on end groups than on internal double bonds[6] may also hamper selective generation of a complex, thermodynamically most stable structure: formation of some intermediate compounds may not be truly reversible due to the relative inertness of the internal double bonds. Nonetheless, it is highly desired to explore the feasiblity of utilizing olefin metathesis in AVM preparation, and the success of the ADMAC approach would open new possibilities for generating novel AVMs and studying their unique properties.

Initially, we conducted the ADMAC reaction of divinyl-substituted monomer **1** catalyzed by Grubbs' 2nd generation catalyst. The reaction that was conducted in 1,2,4-trichlorobenzene under nitrogen at 35 °C turned out to be very successful, affording AVM **2** in 64% isolated yield (eqn (1)).‡[7] The reaction progress was monitored by gel permeation chromatography (GPC, Fig. 1). The GPC traces after 1, 4, 8 and 18 h showed the initial formation of high molecular weight polymers and/or large cyclic intermediates, which gradually transformed into cyclohexamer **2** along the reaction pathway, thus indicating the reversibility of such a cyclooligomerization process and the thermodynamic stability of the target macrocycle.



(1)

The cyclic structure of AVM **2** precludes the *cis* conformation of the –C═C– bond, which would induce significant angle strain. The ^{1}H NMR spectrum of AVM **2** showed only three aromatic signals, including vinyl protons, which suggests that the conformational isomerism arising from the –C═C– rotation around phenylene–vinylene–phenylene linkages, if any, is occurring rapidly on the NMR time scale.

It has been well demonstrated that shape-persistent phenylene–acetylene macrocycles (PAMs) tend to form aggregates *via* self-association induced by aromatic π–π interactions.[8]

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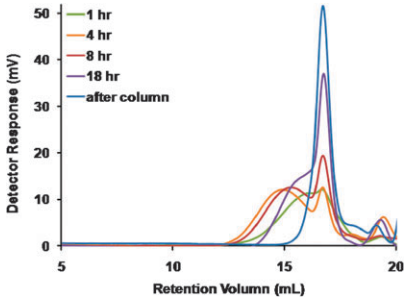


Fig. 1 ADMAC reaction progress of diene monomer **1** as monitored by GPC (THF, 30 °C).

The electronic character and orientation of the substituents on the PAMs strongly influence their self-associating tendency. PAMs substituted with electron donating alkoxy or alkanoate groups don't favor aggregation, while PAMs with electron withdrawing ester groups showed strong aggregation behavior.[8d]

Interestingly, in great contrast to the non-aggregation character of alkoxy substituted PAMs, AVM **2**, which is substituted with six decyloxy groups,[9] showed strong self-aggregation in organic solvents. A ^{1}H NMR study showed the strong dependence of the aromatic chemical shifts of this macrocycle on its concentration. At ambient temperature, the chemical shifts in $CDCl_3$ of the two anisochronous aromatic protons and vinyl protons shifted from δ 7.38 ppm to 7.24 ppm, from δ 7.15 ppm to 7.00 ppm, and from 6.98 ppm to 6.85 ppm respectively as the concentration changed from 0.1 to 10 mM (Fig. 2). The chemical shifts of the aliphatic protons, unlike those of the aromatic and vinylic protons, remained relatively unchanged over the same concentration range. These observations suggest that AVM **2** self-associates in the $CHCl_3$ solution, and the –C≡C– bond does not significantly interfere with the backbone π–π stacking interactions.

The UV-Vis spectra of AVM **2** in four different solvents are shown in Fig. 3. The absorption shifts from 302 nm in cyclohexane to 318 nm in methanol, and an isosbestic point at 323 nm is observed, indicating a conversion from a free single macrocycle to aggregated species. In acetonitrile and methanol, the absorption band was broader along with a long tail absorption extending up to 500 nm, which also indicates the aggregation of AVM **2** in these solvents.

Investigation of the fluorescence emission of AVM **2** in various solvents at a concentration of 5 μM gave more insight.

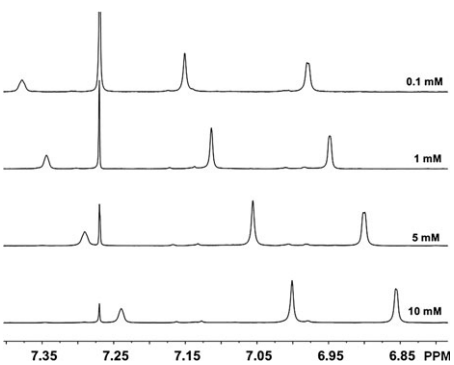


Fig. 2 Concentration-variable NMR spectra of AVM **2** in $CDCl_3$ at 20 °C.

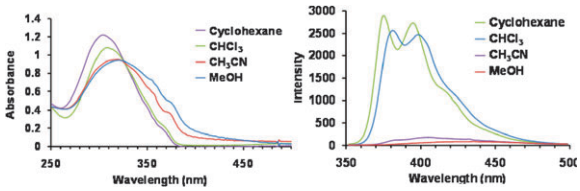
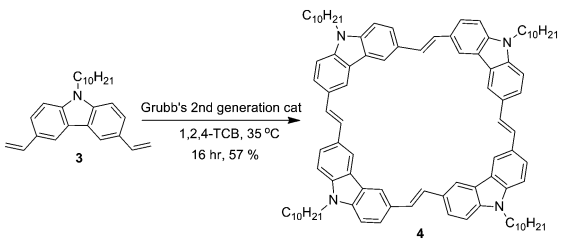


Fig. 3 UV-Vis absorption spectra (left) and fluorescence emission spectra (right, λ_{ex} = 324 nm) of AVM **2** in various solvents (5 μM).

In cyclohexane, strong fluorescence signals (Fig. 3) were observed at 375 nm and 394 nm with a shoulder band at 414 nm. The spectrum obtained in chloroform showed similar emission intensity, but the emission shifted to 380 nm and 398 nm respectively, and the shoulder band is less significant. In contrast to the strong emissions observed in cyclohexane and chloroform, AVM **2** in acetonitrile and methanol only showed very weak fluorescence emissions, presumably due to the fluorescence quenching,[10] which resulted from the macrocycle aggregation induced by the poor solvent. The signal observed in methanol is almost featureless.

To demonstrate the general scope of the ADMAC approach in preparation of AVMs, we also successfully synthesized a carbazole-based AVM **4** starting from the diene monomer **3**. The reaction was also conducted in 1,2,4-trichlorobenzene at 35 °C, and the cyclotetramer **4** was obtained in 57% yield (eqn (2)), thus showing a general scope of such a cyclo-oligomerization approach to AVMs.



(2)

More interestingly, rapid dispersion of the concentrated solution of AVM **2** or **4** in $CHCl_3$ into CH_3CN induced self-assembly of these two macrocycles into 1D nanofibrils, which were characterized by scanning electron microscopy (SEM, Fig. 4). Most of the fibers are around tens of μm in length, and their diameters are around a few hundred nm. Presumably, the nanofibril formation is induced by the strong self-aggregation of these macrocycles. The π–π interactions between aromatic backbones and the side chain entanglement are the two key factors contributing to the observed morphology of the aggregates.[11]

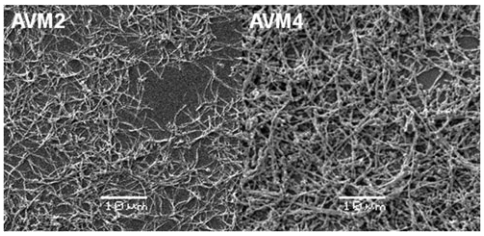


Fig. 4 SEM images of AVM **2** (left) and AVM **4** (right) fabricated by rapid solution dispersion.

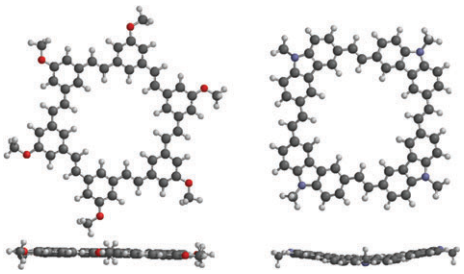


Fig. 5 The most favored conformer of AVM **2′**: top view (top left), side view (bottom left), and AVM **4′**: top view (top right), side view (bottom right). Methyl group was used in calculation instead of decyl for simplification. Energy minimization was performed with Spartan 04 at semi-empirical PM3 level.

The most favored conformer of methyl substituted analogue AVM **2′** has a planar carbon backbone, and the molecule is highly symmetrical, which is fully consistent with the NMR characterization data (Fig. 5). The favored conformer of AVM **4′** is not perfectly planar, and has a saddle-like conformation with alternating carbazole moieties tilted up and down. However, the distorted non-planar conformation seems not to impede the self-aggregation of AVM **4**, as evidenced by successful nanofibril fabrication, which is probably due to the conformational flexibility provided by the vinylene linkage.

In summary, we successfully developed a one-step synthetic approach to shape-persistent AVMs from simple aromatic dienes. The highly efficient ADMAC method is generally applicable, and AVMs with different shape and geometry can be prepared. The AVMs showed a strong self-aggregation behavior, and can be fabricated into nanofibrils. Considering the great importance and growing interest in 1D self-assembly of planar aromatic molecules into well-defined nanowires or nanotubes,[12] the AVMs reported herein open many new possibilities for novel tubular nanomaterial fabrication. The substrate scope of such an ADMAC approach, the AVM self-association behaviors, as well as the structure–function relationship of the aggregation-induced nanofibrils are being investigated in our lab and will be reported in due course.

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Notes and references

‡ **Procedure for the synthesis of AVM 2:** To a Schlenk tube were added 1,3-divinyl-5-decyloxy-benzene (**1**, 217 mg, 0.76 mmol) and a solution of Grubbs' 2nd generation catalyst (48 mg, 0.076 mmol) in 1,2,4-trichlorobenzene (14 mL). The reaction apparatus was evacuated and refilled with nitrogen, and this process was repeated three times. The red solution was heated at 35 °C under nitrogen for 18 h. All the solvent was removed and diethyl ether (100 mL) was added. The ethereal solution was washed with water (3 × 50 mL), dried over Na_2SO_4, and concentrated to give the crude product. Purification by flash column chromatography using CH_2Cl_2 and hexane (1 : 1, v/v) as the eluent afforded AVM **2** as a white solid (109 mg, 64%).

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7 Presumably the presence of *cis* double bonds results in high angle strain in the macrocycles, so the unfavored cyclic products were converted into the most stable cyclohexamer **1** under the reversible, thermodynamically-controlled condition.

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