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### Rational Monomer Design towards 2D Polymers: Synthesis of a Macrocycle with Three 1,8-Anthrylene Units

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One monomer unit thick (or better: thin) covalent networks with a translational periodicity are referred to as 2D polymers, and these are still on the wish list of synthetic chemistry.<sup>[1]</sup> Such structures have been proposed repeatedly,<sup>[2]</sup> but have never been made and unequivocally proven. Limited numbers of 2D polymers are available from Nature. They are usually obtained by exfoliation of graphite (graphene)<sup>[3]</sup> or inorganic lamellar crystals like montmorillonite.<sup>[4]</sup> Rational synthetic avenues to 2D polymers are still awaiting to be developed. A couple of years back we started a research project aimed at providing organic chemical solutions to this burning question.

The first attempt to create sheetlike polymers was reported by Gee back in 1935.<sup>[5]</sup> This and most of the subsequent related studies are based on covalent cross-linking of monolayers by radical polymerization at interfaces<sup>[5,6]</sup> or in layered assemblies.<sup>[7]</sup> Despite the visionary character of this approach, it intrinsically gives rise to irregularly networked ultrathin structures only. The covalent stitching process unavoidably has a "random-walk" nature. In some cases of interfacial/surface polymerizations, translational order within thin films was referred to, but the aimed structures were either not realized<sup>[8]</sup> or remained unproven,<sup>[9]</sup> or were obtained only within tiny domains still having molecular dimensions.<sup>[10]</sup> Herein, we introduce some aspects of a strategy with which we hope to eventually arrive at 2D polymers. We also describe the synthesis of a potential monomer for this ultimate goal and some model reactions of relevance to this compound's usability in the concept.

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In previous studies at interfaces, most of the monomers were connected to one another through flexible linkers. This, however, prevents control over the growth directions during the polymerization, so that formation of ill-defined, irregular networks is a necessary consequence. The same is likely to hold true even if the monomers are pre-organized in a periodical array prior to the polymerization.<sup>[11]</sup> Therefore, we consider rational design of monomer structures that ensures directionality of growth a fundamental prerequisite for a successful 2D polymer synthesis.

Structural inspection of graphene can provide hints for monomer design. In a Gedanken experiment its sp<sup>2</sup>-hybridized carbon atoms can be regarded as the "repeating unit". Their three sp<sup>2</sup> orbitals lie in the same plane separated by 120° angles and ensure the regular lateral bond pattern encountered in this fascinating sheetlike polymer. These defined and fixed directions in which monomers have to grow, play a crucial role in obtaining honeycomb-like 2D networks. In other words, the structure of a 2D polymer is "programmed" in the structure of the monomer it was made from.

With this consideration in mind, a rational monomer structure for 2D polymer synthesis can be envisaged as follows (Scheme 1): three bond-forming sites are embedded in a shape-persistent cyclic skeleton so as to allow the bond formation to take place laterally within the same plane and in radial directions from the center separated by 120°. Such monomers are referred to as M3 (Scheme 1). On the basis of analogous considerations, one can also design other monomer types possessing four bond-forming sites with a 90° angular distance (M4), or even six with a 60° angular distance (M6), which can lead to formation of tetragonal and hexagonal 2D networks as a result of polymerizations, respectively.

In the present study, we selected anthracene units as the connection sites. Their dimerizations upon UV irradiation by [4+4] cycloaddition are well known<sup>[12]</sup> (Scheme 2a) and provide advantages: First, the [4+4] cycloaddition generates two parallel bonds simultaneously. This arrests the two former anthracene units in a fixed relative geometry that is





Scheme 1. Laterally periodic 2D network formation using a M3 monomer.



Scheme 2. Design of M3 monomers using anthracenes as bond-forming sites. a) Photo-induced [4+4] cycloaddition dimerization of anthracene, b) a double-stranded macrocycle, and c) a macrocycle with three anthracenes in  $D_{3h}$  and  $C_{3v}$  symmetry, respectively.

not subject to conformational changes through rotations. Second, these new bonds are oriented perpendicular to the initially opposing anthracene faces. These two aspects will help to achieve what is so highly needed in 2D polymer synthesis, namely a lateral periodic growth event. A third advantage is that anthracene absorbs UV light with a range of wavelengths not exciting its photodimer. This allows bond formation to take place under certain conditions, while under others the reverse process can be enforced, for example, by shorter wavelength irradiation. This is an important issue for aspects such as efficiency of polymerization, healing of polymer structure, and depolymerization within selected application areas such as photo lithography. Last but not least, the reaction proceeds without any use of reagents or catalysts so that it can work not only in solution but also within preorganized layers  $^{[9d,13]}$  as well as in bulk conditions where transport is hindered.  $^{[14]}$ 

Scheme 2b sketches a belt-shaped potential M3 monomer in which three anthracene units are embedded in a cyclic skeleton at the 2,3 and 6,7 positions so as to be  $D_{3h}$  symmetric. This structure looks apparently simple and potentially useful, but the synthesis will be rather laborious.<sup>[15]</sup> On the other hand, Scheme 2c depicts a  $C_{3\nu}$ -symmetric macrocycle bearing three 1,8-anthrylenes. This latter design has advantages: First, precursors of 1,8-anthrylene derivatives, a key building block for the monomer, are readily available on a multigram scale.<sup>[16]</sup> Second, related structures based on 1,8anthrylenes were investigated intensively by Toyota, et al. so that their photophysical/-chemical properties are quite well known.<sup>[17]</sup> Third, the 1,8-carbons of two anthracenes of different monomers stacked face-to-face at van der Waals distance prior to polymerization do not suffer a change of their mutual distances before and after the dimerization. This unique feature allows the 1,8-anthrylene-based monomer to be available for a topochemical polymerization in a solid



Scheme 3. A designed M3 monomer structure with three 1,8-anthrylenes built-in (1).

state as it avoids shrinkage.<sup>[1]</sup> Scheme 3 describes a concrete molecular structure for this M3 design in which the 1,8-an-thylene units were bridged by *m*-terphenylenes through ethynylene spacers (1).<sup>[18]</sup> Note that the methyl groups are introduced intentionally at the edges of the *m*-terphenylene bridges so that the monomers are expected to align preferentially in an antiparallel manner circumventing the steric hindrance imposed by them in the parallel alignment.

Compounds 2–4 were selected as building blocks for 1 (Scheme 4). Starting from the previously reported compound  $5^{[19]}$  the *m*-terphenylene bridge 2 was prepared by Suzuki–Miyaura cross-coupling (SMC), in which the reactivity difference between bromo and iodo aromatics<sup>[20]</sup> was combined with a trimethylsilyl (TMS) masking strategy (Scheme 4a).<sup>[21]</sup> Compound 5 was first subjected to SMC with  $6^{[20c]}$  to give 7, followed by electrophilic replacement of the TMS group of 7 by iodide with iodine monochloride (ICl). The obtained 8 was then subjected to SMC with  $9^{[20c]}$ 



Scheme 4. Synthesis of the building blocks 2 (a) as well as 3 and 4 (b).

to give **10**, and the TMS group was substituted by iodide using ICl to furnish **2**, which was obtained on 4 g scale.

The 1,8-anthrylene building blocks **3** and **4** were prepared starting from 1-(triisopropylsilyl)ethynyl-8-(trimethylsilyl)ethynyl-anthracene (**11**) and 1,8-di[(trimethylsilyl)ethynyl]anthracene (**12**), respectively, whose multigram scale syntheses were reported previously (Scheme 4b).<sup>[16]</sup> Compound **3** was obtained by selective deprotection of the TMS group of **11**. As for **4**, both TMS groups of **12** were first deprotected to give **13**. This was followed by silylation of **13** using one molar equivalent of BuLi and subsequent quenching with TMSCI. This reaction gave rise to a mixture of **12**, **13**, and **4**. The last one was isolated from the others by gel-permeation chromatography (GPC). Compounds **3** and **4** were thus obtained on 4 g and 1.5 g scale, respectively.

The set of building blocks 2-4 were iteratively assembled into the target compound 1 on the basis of the Sonogashira cross-coupling protocol (Scheme 5).<sup>[22]</sup> First, 2 was subjected to the cross-coupling with one molar equivalent of 4 to afford 14. This reaction proceeded selectively at the iodo terminus under the present reaction conditions at 60 °C.<sup>[20]</sup> The remaining bromide terminus of 14 was then used for the second Sonogashira cross-coupling with 3 to give 15. The TMS group of 15 was selectively deprotected with aqueous NaOH to give 16, which was followed by cross-coupling with 14 to afford 17. After TMS deprotection, 18 was subjected to the cross-coupling with 2 to obtain 19, followed by TIPS deprotection with tetra-*n*-butylammonium fluoride (TBAF) to furnish 20, which is the linear precursor of the target macrocycle 1.

Several different conditions were tested to accomplish the final cyclization to 1 as efficiently as possible. When the re-

action was carried out under the standard Sonogashira conditions, using cuprous iodide in combination with a Pd<sup>0</sup> catalyst, the yield of 1 tended to be low despite of the pseudodilution (syringe pump) conditions applied. GPC analysis of the products suggested that intermolecular coupling to produce linear oligomers was the predominant reaction. On the other hand, when the reaction was performed under cuprous-free conditions, the yield of 1 surprisingly increased to about 45%. This result is consistent with our previous observation in other macrocycle synthesis: the absence of CuI from the Sonogashira reaction can have a positive impact on the cyclization efficiency.<sup>[20b]</sup> Even though the reaction proceeded rather slowly and therefore required more Pd catalyst for its acceleration, GPC analysis of the products clearly indicated grossly reduced formation of the oligomeric side products (see the Supporting Information). Figure 1 displays



Figure 1. <sup>1</sup>H NMR spectra of the linear precursor 20 (a) and its intramolecularly cyclized product 1 (b).

the <sup>1</sup>H NMR spectra of **20** and **1**, the simplicity of the latter of which demonstrates three anthrylene units to be arranged symmetrically, as expected after cyclization.

Compound 21 was prepared as a model to provide insights into photochemical properties of monomer 1 (Scheme 6). Because of the rather complex structure of 1 as well as its limited amount so far available (ca. 50 mg), this simple model compound 21 was instead chosen to inspect the reactivity of 1 towards 2D polymer synthesis.<sup>[23]</sup> A degassed solution of 21 in benzene (28 mm) was UV irradiated at 20°C. After 5 h, about 80% of the compound was converted to its dimers 22 (anti) and 23 (syn) in a molar ratio of about 8:1. Note that virtually no side reaction was observed as long as oxygen was carefully excluded.<sup>[24]</sup> In particular, the ethynylene spacers stayed intact. The obtained anti dimer 22 was isolated by recycling GPC and then incubated in the dark as a degassed solution in deuterated 1,1,2,2-tetrachloroethylene (5 mm). Even after incubation for one week at 80°C, 22 was found to be stable; no trace of the back reaction to 21 was observed by <sup>1</sup>H NMR spectroscopy.

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Scheme 5. Iterative assembly of the building block **2–4** to the latent monomer **1**.

When the temperature was raised to 120 °C, however, 23 % back reaction was detected after two weeks at the temperature. These results indicate a considerable thermal stability of the [4+4] dimeric product.

Figure 2 exhibits UV absorption and emission spectra of model compound **21**, monomer **1**, and *anti* dimer **22** recorded from dilute dichloromethane solutions. The very similar UV absorption and emission spectra of **21** and **1** suggests that both compounds have similar photochemical properties.

polymerization of **1** including a solid-state topochemical polymerization.

#### **Experimental Section**

All experimental procedures, NMR and MS data as well as GPC elution curves on cyclization experiments are described in the Supporting Information.

8958 -

Notably, no excimer emission was observed for 1, suggesting that intramolecular [4+4] cycloaddition is unlikely.<sup>[17a,b]</sup> This is an important finding in connection with the planned polymerization for which intramolecular encounters are obviouslv detrimental. Furthermore, comparison of the UV absorption spectra of 1 and 22 confirmed that selective photo-excitation of 1 is possible by choosing the UV wavelength in a range of  $\lambda = 350-450$  nm. These results suggest that intermolecular [4+4] cycloaddition can take place irreversibly leading to the polymerization of **1**.

In conclusion, macrocycle 1 in which three 1,8-anthrylene parts are embedded in  $C_{3\nu}$  symmetry has been designed as a monomer for rational 2D polymer synthesis.<sup>[18]</sup> Feasibility of its synthesis was successfully demonstrated by iterative use of palladium-catalyzed crosscoupling protocols. A key for the success were the copperfree Sonogashira conditions applied to the final cyclization step. Accordingly, multigramscale synthesis of this macrocycle as well as a similar structure which carries free OH groups (R = H in Scheme 3) available for any subsequent functionalizations are now in progress. The results from photochemical experiments using a model compound suggest that macrocycle 1 has the potential to undergo UV-induced [4+4] cycloaddition without undesired possible side reactions, which is encouraging for our ongoing investigations on the UV-induced



Scheme 6. Model compound **21** of monomer **1** and its two photodimers **22** and **23**.



Figure 2. UV absorption and emission spectra of model compound 21 and monomer 1 together with UV spectrum of the *anti* dimer 22. Black, dark gray, and light gray lines correspond to the spectra of 1, 21, and 22, respectively. Broken and solid lines were used for the emission and absorption spectra, respectively. Concentrations: Absorption:  $30 \,\mu\text{M}$  for 21,  $10 \,\mu\text{M}$  for 1, and 15  $\mu\text{M}$  for 22. Emission:  $3 \,\mu\text{M}$  for 21 and 1  $\mu\text{M}$  for 1.

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COMMUNICATION

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includes complexation studies with guest molecules such as carborane or fullerenes. Such host-guest complexes may also be of direct interest as monomers for 2D polymer synthesis.

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- [24] The solution needed to be degassed carefully; otherwise formation of peroxidized anthracene was observed by <sup>1</sup>H NMR spectroscopy as a side reaction upon the UV irradiation.

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8960 -