Scalable Synthesis of Two-dimensional Polymer Crystals and Exfoliation into Nanometer-thin Sheets

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Abstract: Two-dimensional materials have moved into the spotlight of researchers. The isolation of single graphene sheets has shown that restricted dimensionality can lead to interesting properties. Bottom-up synthesis of organic, covalently-bonded structures is, however, still challenging. In this publication we give a synopsis of a recently published monomer that is easily accessible and reversibly provides chiral two-dimensional polymer single crystals, which can be exfoliated into nanometer-thin sheets and show promise for applications in, for example, nonlinear optics and ultrathin membranes.

Keywords: Photochemistry · Polymers · Solid-state chemistry · Two-dimensional materials · X-ray crystallography

In 2004 Novoslov and Geim discovered that graphite can be exfoliated by the simple use of scotch tape down to mono-layered graphene sheets.[1] The phenomenal properties of graphene sparked the interest of many researchers to look at this novel material.[1,2] Today, research efforts have been widened to include other two-dimensional materials such as MoS_2, h-BN, *etc*.[3] These materials show great promise for applications in next-generation electronics.[4] They are mainly obtained by exfoliation of their layered bulk precursors or through chemical vapor deposition of the corresponding precursors at elevated temperatures.[5,6] The mild organic synthesis of periodic, monolayered sheets – two-dimensional polymers (2DP) – from cheap chemicals, however, is still challenging. Such a synthesis would enable a tunability of the 2DP-sheet structure and thus of the sheet properties.[7] In 2012 and 2013, the first organic syntheses of 2DPs were achieved.[8,9] They employed anthracene-based monomers that were preorganized in layered single-crystals and subsequently polymerized by a photoreaction to the corresponding 2DPs.

In both of these cases, however, the structural changes upon irradiation caused the single crystals to lose their integrity, rendering structural analysis by single-crystal X-ray crystallography impossible. Moreover, the reported syntheses for the monomer systems were rather laborious and did not allow for larger amounts, as required for application-oriented explorations of the corresponding 2DPs.

In back-to-back publications with the King group, we recently reported two new monomer systems that led to the synthesis of the first crystallographically proven synthetic 2DPs according the above definition.[10,11] The monomers employ the well-studied [4+4] photodimerization reaction of anthracene (see Fig 1b) for polymerization.

In the following we recall important steps of our findings.

Monomer **1** (see Fig. 1a) is a rotor-shaped double-decker compound. It is based on two triazine cores to which three anthracene blades are symmetrically connected. Synthesis of **1** is highly scalable and can be achieved from cheap, commercially available starting materials without any column chromatographic purification, only by simple precipitation.[12] The low solubility of the monomer was intended to enhance crystallizability. And indeed, dissolution in high-boiling solvents such as nitrobenzene or benzonitrile gave needle-shaped crystals by cooling of the hot solutions. Single-crystal X-ray analysis revealed a desired layered structure. Within the individual layers the anthracene-units of the monomers, however, stack in an edge-to-face fashion, thus a monomer packing not suitable for two-dimensional polymer synthesis (Fig. 2).

Other organic solvents were therefore tested. 2-cyanopyridine (*cpy*) proved particularly useful. Monomer crystallization from *cpy* now revealed a different crystal
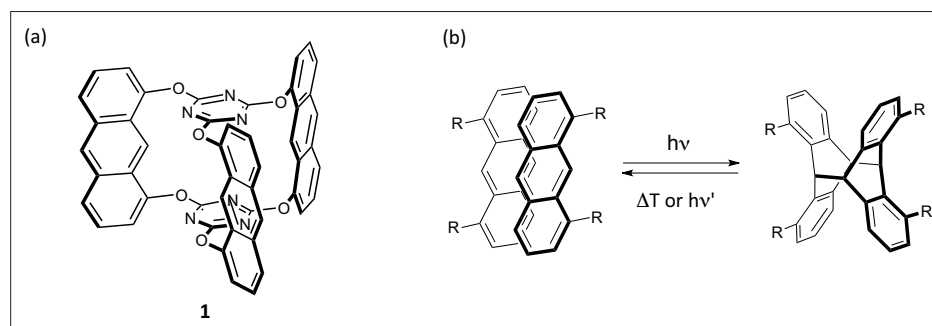

Fig. 1. (a) Molecular structure of the rotor-shaped double-decker monomer employed for the synthesis of the two-dimensional polymer single crystals. (b) Well-studied [4+4] photodimerization of anthracene and its thermally or photo-triggered back-reaction.

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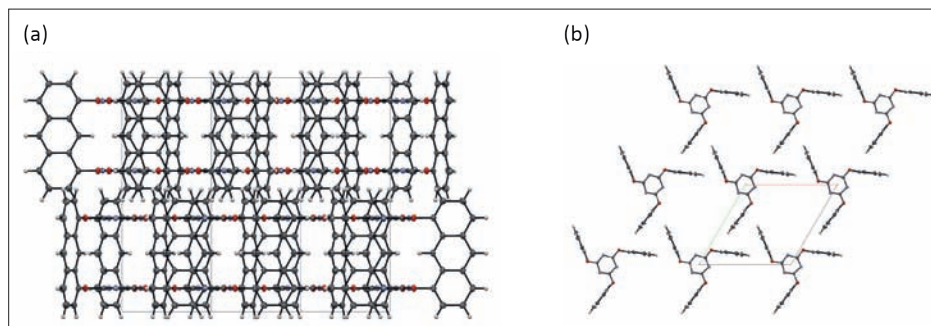E-mail: dieter.schlueter@mat.ethz.ch

Fig. 2. (a) Layered crystal structure of monomer compound **1** obtained through crystallization from benzonitrile. (b) Edge-to-face packing of the anthracene blades of the monomer units. This arrangement is not suitable for two-dimensional polymerization.

habit. In addition to needle-shaped crystals also platelet-shaped and hexagonal crystals were observed. These crystals exhibited a packing, where the anthracene blades of adjacent monomer units stack face-to-face to form an infinite hexagonal arrangement (Fig. 3a). In this arrangement the cavities are filled with a template that consists of monomer compound **1** (shown in red) and *cpy* solvent molecules (shown in black): three solvent molecules around compound **1** of the template and additional *cpys* sandwiched between the layers. Crystallization from *cpy* was optimized such that now controlled crystallizations of the monomer

can give single crystals with desired shapes and sizes of up to a millimeter.

To transform the hexagonal face-to-face arrangement of the monomer units into the corresponding covalently bonded two-dimensional network, platelets or hexagonally-shaped single crystals were irradiated with UV-light. (λ = 465 nm, 48 h). The crystals fully retained their birefringence. Single-crystal X-ray analysis revealed their polymerization. Anthracene-blades of adjacent monomer units that were previously stacking face-to-face, undertook dimerization by the desired [4+4] photoreaction. At the same time compound

1 of the template was moved upwards and became slightly tilted (see Fig. 3c,d).

To test the feasibility of polymerizations on larger scales, crystal irradiations were carried out on a gram-scale. To this purpose crystals of diameter 20–30 μm were suspended in argon-purged methanol. After 90 minutes no further conversion was visible, as determined by IR-spectroscopy and powder X-ray analysis.

As a next step, exfoliation of the polymerized crystals to the individual 2DP sheets was addressed. The exfoliation of two-dimensional materials in liquids bears several advantages; it is potentially scalable, and allows for the formation of thin films and composites.[13] For the 2DP crystals described, it was found that polymerized crystals strongly swell up in perfluoro carboxylic acids. Fig. 4 shows an SEM picture of crystal swollen in perfluoro heptanoic acid. Gentle stirring was shown to delaminate the crystals in nanometer-thin sheets (Fig. 5). In many cases the crystals retained their original dimensions.

Reversibility of the Employed Polymerization

The polymerization based on the [4+4] photodimerization of anthracene offers the opportunity to thermally induce a back reaction. This was tested by heating polymerized single crystals to a temperature of 180 °C. Single-crystal X-ray analysis of crystals heated for 4 days showed that two-thirds of the polymer had reacted to monomer, crystals heated for 21 days revealed the monomer crystal structure. In another experiment monomer single crystals were polymerized, heated to induce full back reaction, and then repolymerized. The process could be monitored by IR-spectroscopy proving the reversibility of the photopolymerization reaction.

Conclusion

Utilizing the novel triazine-based double-decker monomer **1**, monomer single crystals can be grown in a controlled fashion and subsequently polymerized to the corresponding 2DP crystals, of which the structure could be solved by single-crystal X-ray crystallography. This establishes the first unequivocal proof of a 2DP. When exposed to perfluoro carboxylic acids, the polymerized crystals swell up; mild stirring of the crystal suspensions in acid leads to the crystals' exfoliation into nanometer-thin sheets. Heating the polymerized crystals causes back reaction to the corresponding monomer crystals in a single-crystal-to-single-crystal fashion. This process could be shown to be reversible,
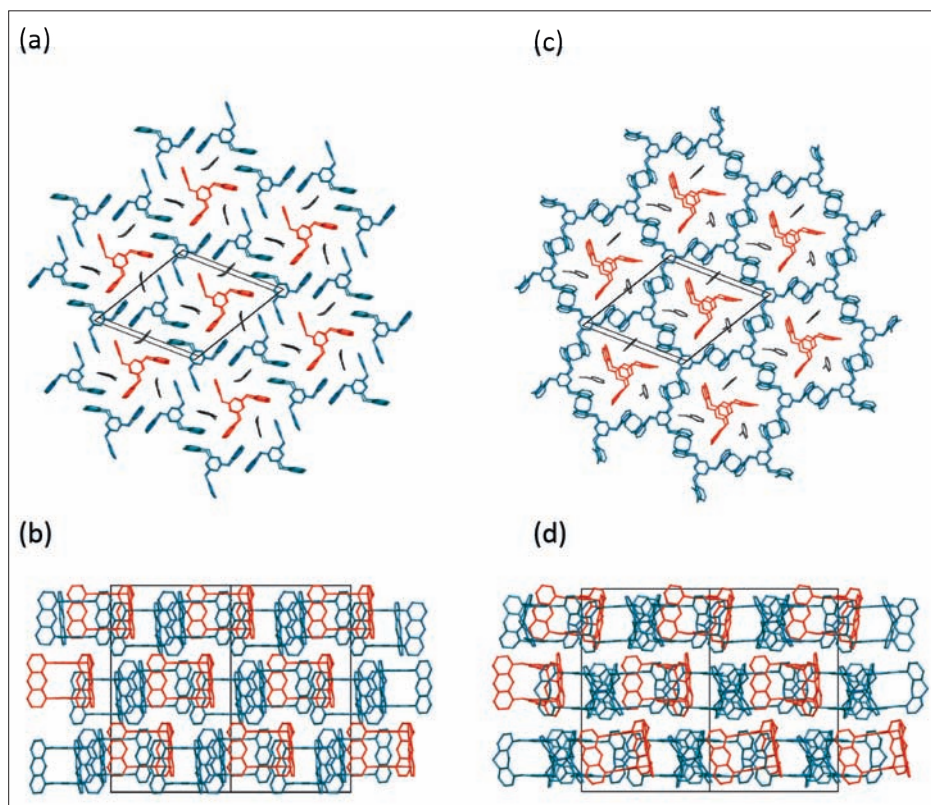

Fig. 3. (a) Top view of the monomer crystal structure. Monomer compound **1** serves two functions: 1) as reactive species for two-dimensional polymerization (blue) as part of the template (red). Compound **1** of the template is surrounded by three 2-cyanopyridine molecules. (b) Side view of the monomer crystal structure. (c) Top view of the polymer crystal structure. The monomer units have reacted to form a two-dimensional polymer. (d) Top view of the polymer crystal structure. Compound **1** of the template is moved upwards and becomes slightly tilted.
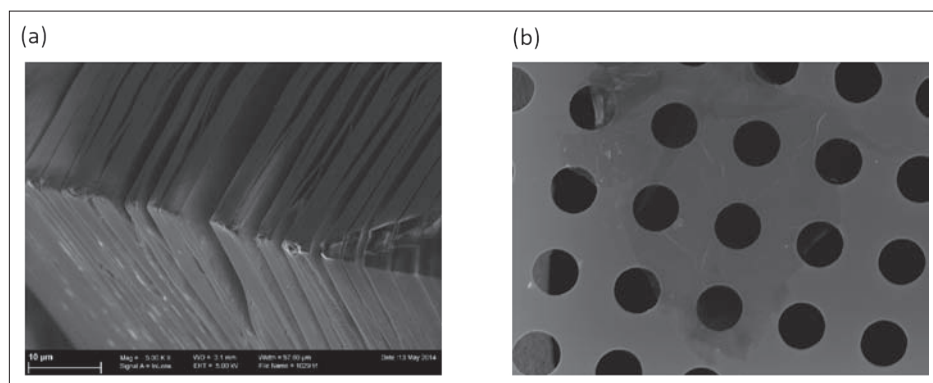
Fig. 4. (a) SEM picture (2kV) of a swollen two-dimensional polymer crystal after exposure to per-fluoro heptanoic acid for 5 days. (b) SEM picture (2kV) of a very thin sheet package on a quantifoil grid. The hole size is 2.5 μm.
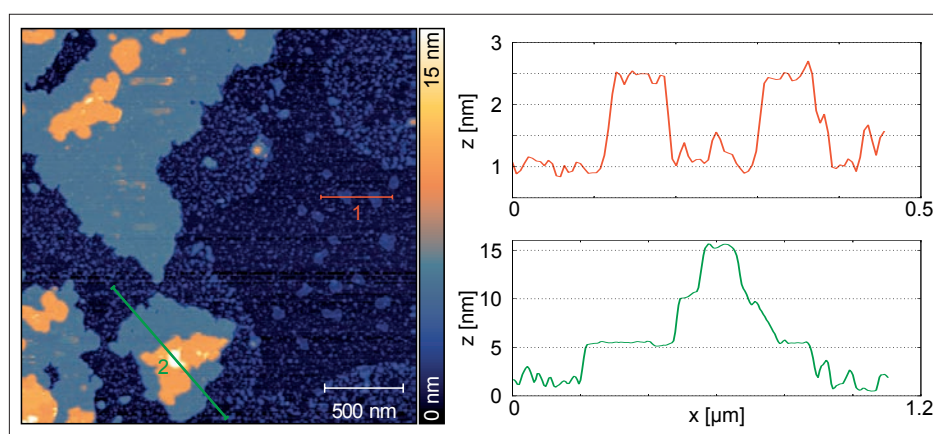

Fig. 5. AFM picture of nanometer-thin two-dimensional polymer sheets and their height profile.

which is truly remarkable considering the large structural changes occurring during polymerization and depolymerization. The accessibility of the 2DP sheets combined with their manifold properties provide a promising starting point for application-oriented explorations.

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