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A two-dimensional polymer prepared by organic synthesis

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1. Two-dimensional (2D) periodic surface: various preparation methods

1.1. Recent achievements to obtain periodic 2D single-layered surface (Figure 1)

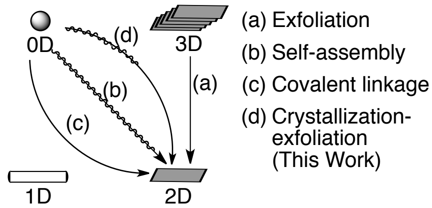


Figure 1. Four strategies to obtain 2D surface

(a) **Exfoliation of aggregated sheets**: 3D –> 2D (mica, molybdenite, graphene)

• Mechanical (exfoliation by scotch-tape) or solvent treatment (obtaining dispersion)

✓Easy method, large scale production

X Limited structure of sheets, harsh synthetic condition

(b) **Self-assembly of monomer and tuning the structure with additives**: 0D –> 2D (Figure 2)[1]

• Tuning of molecular orientation and size of oriented domains by changing an additive

✓ Easy fabrication and tuning of surface properties

X Limited substrate for fabrication

X Structural weakness (solved by cross-linking)

X Difficulty in finding the condition of controlling molecular ordering

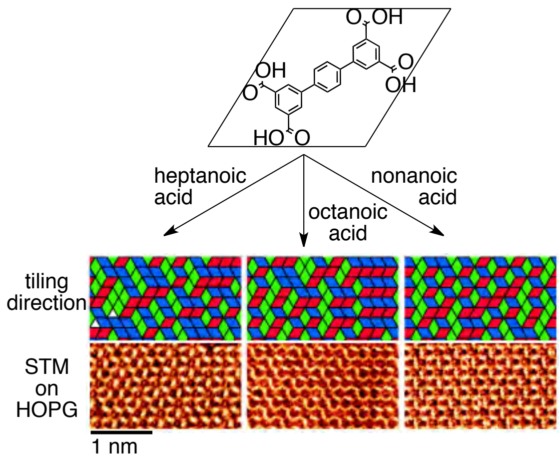


Figure 2. Formation of 2D surface on HOPG by hydrogen bonding

(c) **Covalent linkage**: 0D –>1D –>2D (Figure 3) [2]

• Anisotropic polymerization by different terminal halogen atom

✓ Ability to tune the structure, surface energy, etc.

X Defects originating from <100% reactivity

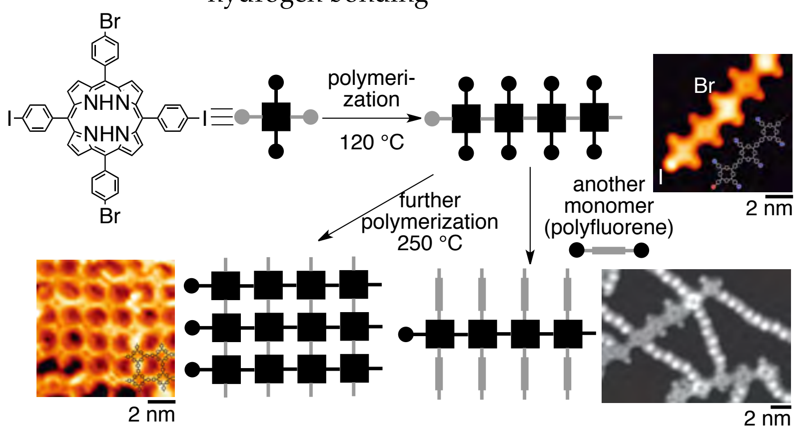


Figure 3. Formation of 2D surface by covalent bonding

• In general, polymer bearing two-dimensional **periodicity** has rarely been synthesized.

1.2. This work: polymerization of pre-organized crystal

(d) Strategy: 0D –> 3D –> 2D

✓ Polymerization using cyclization with complete site-selectivity to obtain periodic structure

✓ Preparation of polymer sheets without any supporting surface

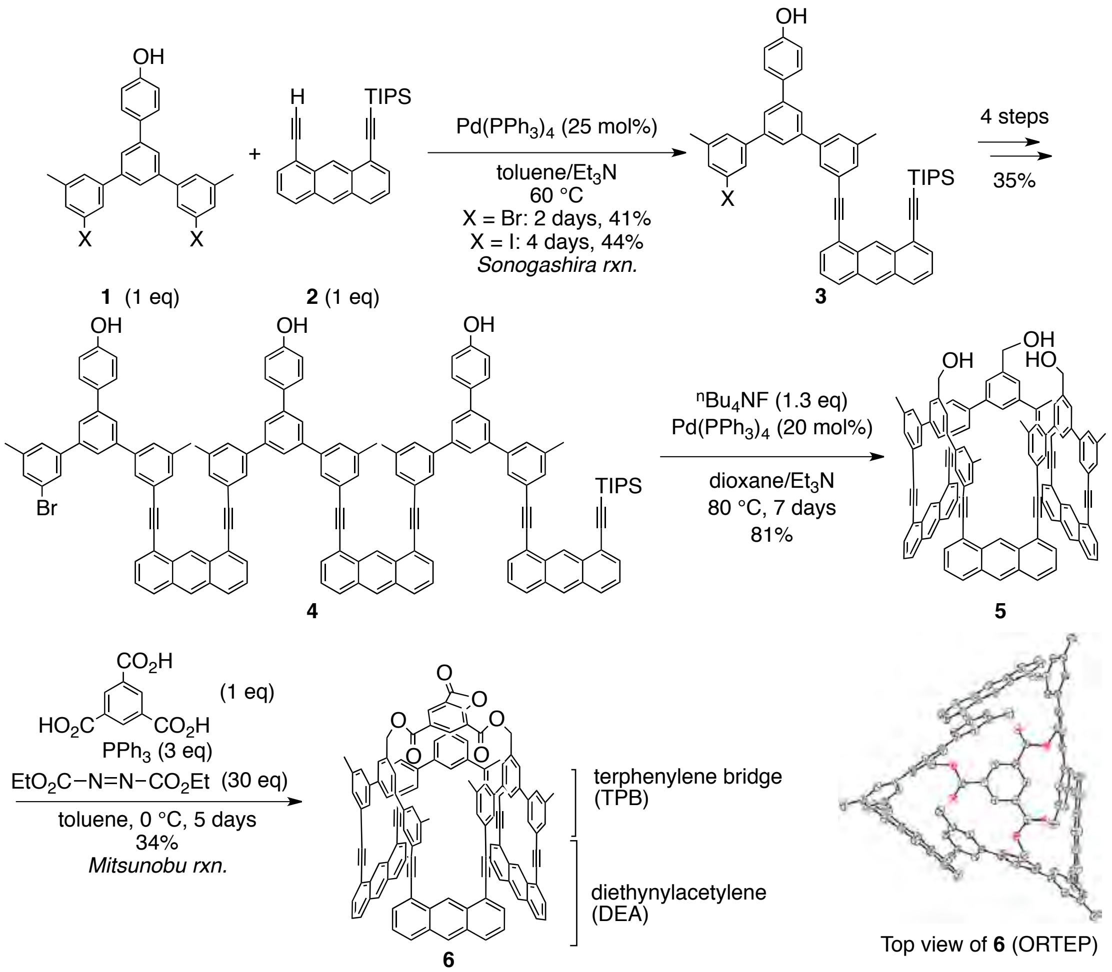
X Complicated synthetic method

2. Synthesis, crystallization of monomer, and photopolymerization

2.1. Overview of synthesis of monomer (Scheme 1)[3]

• C_3-symmetrical monomer **6** bearing terphenylene bridge (TPB) and diethynylanthracene (DEA) unit by sequential Sonogashira coupling and final capping by esterification

Scheme 1. Synthesis of monomer **6**



2.2. Crystallization, photopolymerization, and single-layer exfoliation

• C_3-symmetrical layered structure with separation of TPB and DEA

–> Prevention of interlayer polymerization by TPB "insulator"

• Plate or rod structure with hexagonal face (Figure 5)

• Exfoliation by heating in solvent (NMP)

• AFM image (Figure 6)

–> Single layered sheets with 1-2 μm lateral size

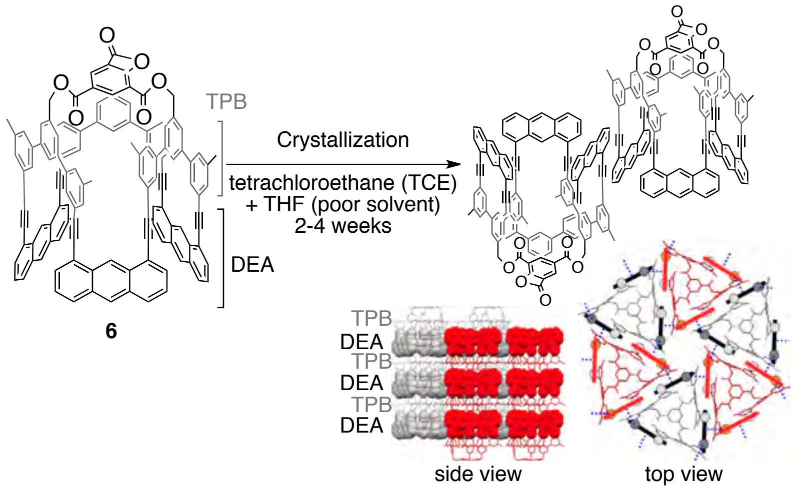


Figure 4. Crystallization of monomer **6**

• Plausible reason of exfoliation

(1) Conformational relaxation: destabilization of stacked state due to shrinkage of crystal size

(2) Shear force induced by thermal treatment and by internal strain

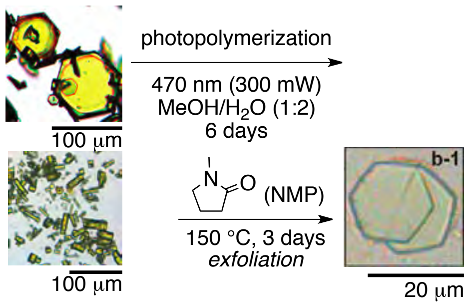


Figure 5. Optical microscopic images of the crystal before photopolymerization and after polymerization and exfoliation

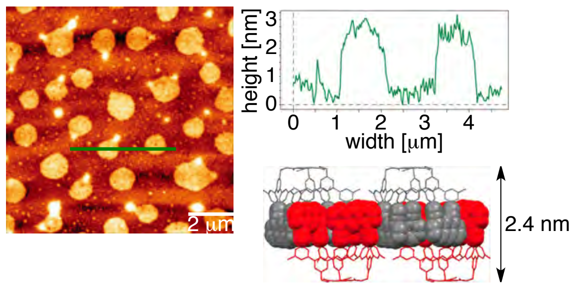


Figure 6. An AFM image of polymer sheets on mica, whose height well agreed with that of expected single layer

2.3. Insights into chemical structure (Figure 7)

• Photopolymerization reaction using a model compound –> [4 + 4] cycloaddition

• Raman spectra of polymer (Figure 8): decrease in C≡C bond signal by 50%, increase in C=C bond signal, disappearance of anthrene signals

–> [4 + 2] cycloaddition of anthracene unit

• Difference in reaction type: structural strain in the

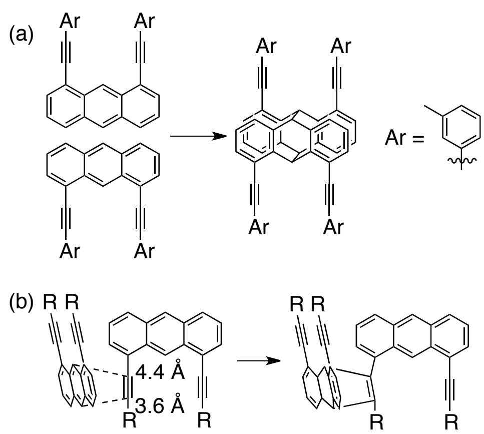


Figure 7. Plausible cyclization pathway

crystal which prohibiting [4 + 4] addition in the crystal

3. Properties of two-dimensional polymer

3.1. Internal periodicity

• TEM of eight layered sheets (single layer was unstable against electron beam, Figure 9)

–> Periodic structure with diffraction similar to that of monomer crystal

–> Retaining of structure after polymerization

3.2. Structural rigidity

• Chemical tolerance: highly stable against $CHCl_3$, TCE, etc. (Figure 10) for >4 months

• Mechanical stability: unlike graphene, no folding of polymer sheets on Cu grid

–> Polymerized structure with rigid chemical bonding (norbornene bridge)

• Mw > 10^8 Da for >1 µm^2 sheet: one of the largest polymer (cf. cellulose and polyethylene: ~10^6 Da)

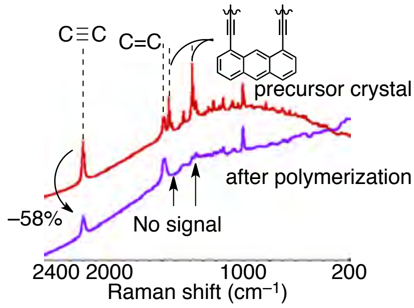


Figure 8. Raman spectra (excitation: 732 nm) of polymer precursor and 2D polymer

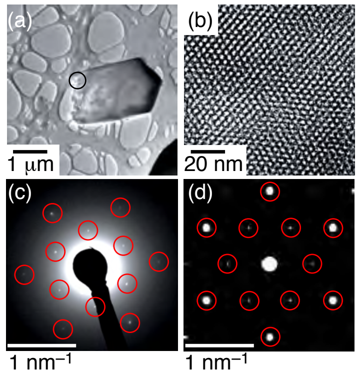


Figure 9. (a) TEM image of a stacked polymer sheet and (b) magnified image. (c) Diffraction pattern of the sheet taken at cryogenic condition and (d) of a monomer crystal

4. Conclusion and perspective

• Two-dimensional polymer bearing **internal periodicity** and **structural rigidity** was prepared by bottom-up synthesis.

• Utilization of this polymer sheets: functionalization of capped part by ester exchange for filtration of small molecules or bottom-up construction of 3D structure

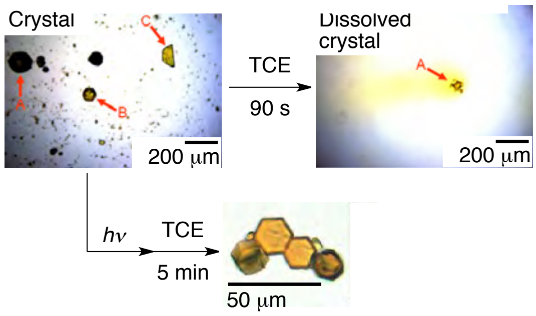


Figure 10. Optical microscopic images of crystals and polymerized crystals in 1,1,2,2-tetrachloroethane (TCE)

5. References

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2. Lafferentz, L.; Eberhardt, V.; Dri, C.; Africh, C.; Comelli, G.; Esch, F.; Hecht, S.; Grill, L. *Nat. Chem.* **2012**, *4*, 215–220.

3. (a) Kissel, P.; Schlüter, A. D.; Sakamoto, J. *Chem. Eur. J.* **2009**, *15*, 8955–5960. (b) Kissel, P.; Heijst, J.; Enning, R.; Stemmer, A.; Schlüter, D.; Sakamoto, J. *Org. Lett.* **2010**, *12*, 2778–2781.