

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/276461935>

Stereoregular Two-Dimensional Polymers Constructed by Topochemical Polymerization

ARTICLE in MACROMOLECULES · MAY 2015

Impact Factor: 5.8 · DOI: 10.1021/acs.macromol.5b00109

CITATION

1

READS

30

9 AUTHORS, INCLUDING:



Xiaodong Hou

University of North Dakota

18 PUBLICATIONS 111 CITATIONS

SEE PROFILE



Jochem Otto F. Struppe

Bruker Corporation

36 PUBLICATIONS 778 CITATIONS

SEE PROFILE



Angel Ugrinov

North Dakota State University

59 PUBLICATIONS 922 CITATIONS

SEE PROFILE

Stereoregular Two-Dimensional Polymers Constructed by Topochemical Polymerization

Zhihan Wang,[†] Katelyn Randazzo,[†] Xiaodong Hou,[†] Jeffrey Simpson,[‡] Jochem Struppe,[§] Angel Ugrinov,^{||} Brent Kastern,[†] Erin Wysocki,[†] and Qianli R. Chu^{*,†}

[†]Department of Chemistry, University of North Dakota, Grand Forks, North Dakota 58202, United States

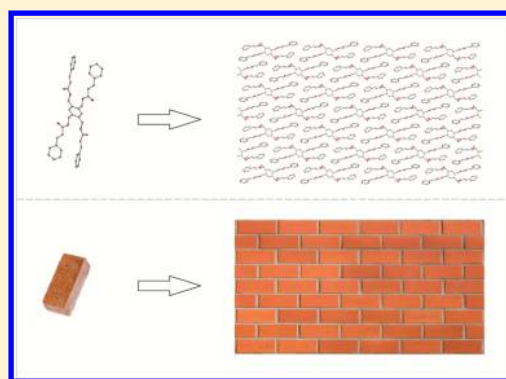
[‡]Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, United States

[§]Bruker Biospin Ltd., Billerica, Massachusetts 01821, United States

^{||}Department of Chemistry and Biochemistry, North Dakota State University, Fargo, North Dakota 58102, United States

Supporting Information

ABSTRACT: Two stereoregular 2D polyesters were synthesized by using topochemical polymerization of symmetric four-armed monomers. The monomers contain reactive carbon–carbon double bond(s) on each arm. The critical assemblies with multiple preorganized reactive centers were characterized by powder and single crystal X-ray diffraction. The solvent-free polymerization could be carried out with sunlight or UV irradiation. The locally confined photopolymerization process dimerized all of the olefins within the 2D bricklayer packing, which led to the formation of 2D polymers in the solid state. The process was monitored by FT-IR, and the products were confirmed by solid state NMR. After hydrolysis of the 2D polyester, the newly formed carbon–carbon single bonds during the [2 + 2] photocyclization were directly revealed by the single crystal structure of the hydrolysis product. Ultrathin sheets of the 2D polymer were observed under SEM and TEM after exfoliation.



■ INTRODUCTION

The synthesis of new materials is an essential element in the advancement of modern science and technology. The emerging two-dimensional (2D) polymers are valuable synthetic targets for their potential applications ranging from membranes to optics.^{1–9} 2D polymers are regarded as potential synthetic analogues of graphene. Carbon fiber represents one of the most influential and practical applications of graphene sheets. Because of the exceptional tensile strength, high stability, and light-weight of graphene sheets, carbon fiber has been used in aerospace, automobile, sporting goods, and civil engineering applications.^{10,11} However, the precise introduction of organic functional groups at the atomic level to tune the properties of graphene is difficult due to the harsh conditions in preparing graphene.¹² Distinct from graphene, a 2D polymer prepared by organic synthesis offers more flexibility in structural tailoring and opportunity for atomic level structure–property investigations.

Although there are several reports on preparing 2D polymers and discussing the possibilities of using them as porous materials and optics,^{3–9} their potentials to serve as strong and lightweight materials (SLIM) have not been fully realized. In our efforts to synthesize SLIM, we have recently achieved polymeric ladders from two-armed symmetric monomers via topochemical polymerization.¹³ Expanding this approach to the next level, we report herein the synthesis and characterization

of a stereoregular 2D polymer from four-armed symmetric monomers. To construct ladder and 2D polymers, monomers with multiple reactive centers are needed. In classic solution phase polymerization, the potential for cross-linking between the monomers poses a challenge. We have been exploring one aspect of this challenge by preorganizing the monomers with multiple reactive centers using weak intermolecular forces under mild conditions before the photopolymerization.^{13–15}

2D polymers are theorized to be stronger than traditional polymers because each monomer is connected with its neighbors by multiple covalent bonds in an organized way. Moreover, solid-state polymerization offers a unique opportunity to synthesize macromolecules with regio- and stereospecificity because topochemical reaction normally proceeds with minimum movement of atoms.^{16–20} Stereoregularity is an important property of polymers with chiral centers that directly determines the performance of the polymeric materials. Stereoregular polymers often have an array of mechanical properties that are superior to those of corresponding nonstereoregular polymers.²¹ However, it is challenging to unambiguously characterize the structure of 2D polymer, especially its stereochemistry. The novel stereoregular 2D

Received: January 18, 2015

Revised: April 14, 2015

Published: April 30, 2015

polyester in this article was achieved by the photocuring of a crystalline intermediate and fully characterized by FT-IR, solid state NMR, and the product of polymer hydrolysis.

EXPERIMENTAL SECTION

Reagents and General Methods. All the reagents were purchased from Alfa Aesar and Sigma-Aldrich and used without further purification. Thin layer chromatography (TLC) was performed on silica gel W/UV 200 μm precoated plates. The light sources used for the photopolymerization were sunlight, a Hanovia medium pressure mercury lamp (PC 451050, 450 W), or 16 RPR-3500A lamps in a Rayonet photochemical reactor. The solution phase nuclear magnetic resonance spectra (NMR) were recorded with Bruker ADVANCE (^1H : 500 MHz; ^{13}C : 125 MHz). All spectra were obtained in deuterium dimethyl sulfoxide ($\text{DMSO-}d_6$) or deuterium oxide (D_2O). For $\text{DMSO-}d_6$ or D_2O solution, the chemical shifts were reported as parts per million (ppm) with tetramethylsilane as a standard. Coupling constants were reported in hertz (Hz). Data for ^1H NMR spectra were reported as follows: chemical shift (ppm: referenced to parts per million), brs = broad singlet, s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, ddd = doublet of doublet of doublets, p = pentet, h = heptet, m = multiplet, coupling constant (Hz), and integration. Single crystal X-ray data were recorded on Bruker Kappa Apex II Duo X-ray diffractometer with Mo K α ($\lambda = 0.71073 \text{ \AA}$) or Cu K α ($\lambda = 1.54178 \text{ \AA}$). Melting points were measured on a MEL-TEMP device without correction. Infrared spectroscopy (IR) was recorded on Thermo Scientific Nicolet iS5 FT-IR spectrometer. The mass spectrometric analyses were performed using a high-resolution time-of-flight G1969A with electrospray (atmospheric pressure chemical) ionization (Agilent, Santa Clara, CA) and reported as m/z (relative intensity). Accurate masses are reported for the molecular ion $[\text{M} + \text{Na}]^+$, $[\text{M} + \text{H}]^+$, $[\text{M} + \text{NH}_4]^+$, or $[\text{M}]^+$. X-ray powder diffraction (XRD) was performed on a X'PERT-PRO X-ray diffractometer (PANalytical, Netherlands) equipped with a 3 kW copper tube X-ray generator of $\lambda = 0.1541 \text{ nm}$ under 40 mA and 45 kV. Spectra were collected at room temperature in a 2θ range of 3° – 35° at a scanning rate of $3^\circ/\text{min}$. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were recorded with Hitachi SU8010 UHR cold-emission FE-SEM. Copper grids are FCF200-Cu-50 (Formvar carbon film on 200 square mesh copper grids) and CF213-25 (C-Flat $1.2 \mu\text{m}$ hole $2 \mu\text{m}$ Space 200 mesh). Silicon wafer chips were purchased from West Chester (silicon wafer chip $5 \times 7 \text{ mm}$, PK/186).

Synthesis of Monomer I. Cinnamic acid (988 mg, 6.6 mmol), 1,2,4,5-tetrakis(bromomethyl)benzene (500 mg, 1.1 mmol), and K_2CO_3 (921 mg, 6.6 mmol) or Na_2CO_3 (700 mg, 6.6 mmol) were added to dimethyl sulfoxide (50 mL). The mixture was stirred at room temperature for 16 h. TLC showed the reaction was completed. Then the mixture was slowly poured into ice-water (300 mL). The precipitate was filtered and washed with ethanol ($50 \text{ mL} \times 2$) to give the product (2E,2'E,2''E,2'''E)-benzene-1,2,4,5-tetrayltetrakis(methylene)tetrakis(3-phenyl acrylate) (I) (670 mg, 84%) as a white solid; mp 188 – 189°C . TLC (hexanes:ethyl acetate, 3:1 v/v): $R_f = 0.54$. ^1H NMR (500 MHz, $\text{DMSO-}d_6$): δ 7.62–7.68 (m, 14H), 7.31–7.40 (m, 12H), 6.64 (d, $J = 16 \text{ Hz}$, 4H), 5.38 (s, 8H). ^{13}C NMR (125 MHz, $\text{DMSO-}d_6$): δ 166.2, 145.4, 135.5, 134.2, 131.7, 130.9, 129.2, 128.7, 117.9, 63.5. IR: 1707, 1635, 1575, 1495, 979 cm^{-1} . UV/vis: λ_{max} 275 nm. HRMS (m/z): $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{46}\text{H}_{38}\text{O}_8\text{Na}$, 741.24643; found 741.23698.

Synthesis of Monomer II. Malonic acid (10.0 g, 96.1 mmol) was added slowly to solvent pyridine (40 mL). The mixture was stirred at 45°C until a colorless solution was obtained. 12.7 g (96.1 mmol) of *trans*-cinnamaldehyde was added to the solution at 60°C and stirred for 10 min. Another 12.7 g (96.1 mmol) of *trans*-cinnamaldehyde was added slowly to the solution, and the solution was allowed to be heated at 80°C for 14 h. The reaction mixture was poured into ice and HCl solution. The precipitate was filtered to give crude product. Then the crude product was dissolved with EtOAc (500 mL) and washed with brine (300 mL). The organic layer was dried to give desired

product (2E,4E)-5-phenylpenta-2,4-dienoic acid (3) (15.1 g, 91%) as a white solid. ^1H NMR ($\text{DMSO-}d_6$, 500 MHz): δ 12.26 (s, 1H), 7.54 (d, $J = 7.5 \text{ Hz}$, 2 H), 7.30–7.40 (m, 4 H), 7.02–7.14 (m, 2H), 6.01 (d, $J = 15 \text{ Hz}$, 1H). ^{13}C NMR ($\text{DMSO-}d_6$, 125 MHz): δ 167.9, 144.6, 140.1, 136.3, 129.3, 129.2, 127.5, 126.9, 122.6.

The (2E,4E)-5-phenylpenta-2,4-dienoic acid (compound 3, 3.8 g, 21.8 mmol), 1,2,4,5-tetrakis(bromomethyl)benzene (2.0 g, 4.4 mmol), and CsF (4.0 g, 26.7 mmol) were added to DMSO (100 mL). The mixture was heated to 165°C with stirring for 5 h. A clear and light yellow solution was obtained. TLC showed the starting material 1,2,4,5-tetrakis(bromomethyl)benzene had disappeared. Then the mixture was poured into ice–water (300 mL) and filtered to give crude product as a yellow solid. The crude product was washed with EtOAc (100 mL) to give the desired product (2E,2'E,2''E,2'''E,4E,4'E,4''E,4'''E)-benzene-1,2,4,5-tetrayltetrakis(methylene)tetrakis(5-phenylpenta-2,4-dienoate) (II) (3.3 g, 90%) as a white solid; mp 204 – 205°C . ^1H NMR (500 MHz, $\text{DMSO-}d_6$): δ 7.61 (s, 2H), 7.45–7.46 (m, 12H), 7.31–7.32 (m, 12H), 7.09 (s, 8H), 6.14 (d, $J = 15 \text{ Hz}$, 4H), 5.31 (s, 8H). ^{13}C NMR (125 MHz, $\text{DMSO-}d_6$): δ 166.1, 145.7, 141.3, 136.1, 135.5, 129.5, 129.2, 129.2, 127.6, 126.6, 120.8, 63.3. IR: 1704, 1628, 1594, 1448 cm^{-1} . UV/vis: λ_{max} 307 nm. HRMS (m/z): $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{54}\text{H}_{46}\text{O}_8\text{Na}$, 845.30904; found 845.30905.

Crystallization. The crystals of I were obtained in ethyl acetate. The monomer I (20 mg) was added to solvent ethyl acetate (200 mL). The vial of the suspended mixture was put in an ultrasonic cleaner (Bransonic Models 1200) for 1 h at 57°C . The mixture was filtered into a 250 mL Erlenmeyer flask with filter paper. The flask was put on the heating plate without cover at 55°C until the solution evaporated to 20 mL. The rest of the solution was transferred into a 20 mL vial. The vial was kept at 55°C until the crystals formed.

A photostable crystal form of the monomer I was also discovered during the solvent screening. This photostable form was found in DMF by using pure compound I after column chromatography while the photoreactive form was obtained in ethyl acetate with crude monomer direct from synthesis without further purification. The crystal II was obtained from DMF at 100°C . No polymorphism has been observed for monomer II so far.

The crystallographic data for monomers I and II and the hydrolysis products α -truxillic acid (4) and α -truxillic acid 2-aminoethanaminium salt (5) are available in Cambridge Crystallographic Data Centre (CCDC# 986273, 986274 1005428, 1033828, and 1033829).

Photopolymerization. Method A, sunlight irradiation: Monomer I were irradiated in sunlight on a transparent glass slide. 10 mg of grinded crystals was evenly scattered on a glass slide, and the sample was placed outdoors for photoreaction. The process of photoreaction was monitored by FT-IR. The photoreaction of monomer I was found to be completed after 24 h, which was carried out in 2 days with 12 h solar radiation per day. The product IP of photoreaction was obtained, and it was found to be insoluble in normal organic solvents.

Method B, UV irradiation: A transparent glass slide which held 10 mg of monomer I was placed in a photochemical reactor. The photochemical reactor was equipped with a Hanovia medium pressure mercury lamp (PC 451050, 450 W) or 16 RPR-3500A lamps. The polymerization reaction was monitored by FT-IR and completed in 24 h.

Solid State NMR. The solid state ^{13}C NMR spectra were recorded on a 500 MHz Bruker Advance III spectrometer. ^{13}C cross-polarization (CP) magic angle spinning (MAS) spectra were recorded at a sample rotation rate of 12.5 kHz using total spinning sideband suppression sequence (TOSS).²² Monomer I required a recycle delay of 30 s. 243 transients were accumulated with a total experiment time of approximately 2 h and 2 min. Polymer IP required a recycle delay of 3 s. 2187 transients were accumulated with a total experiment time of approximately 3 h and 16 min. Monomer II shows high crystallinity yet relatively short relaxation rates on ^1H . The monomer II and polymer IIP do not have significantly different ^1H relaxation behavior.

Hydrolysis. The polymer IP (100 mg) was added to a solution of KOH (50%, 100 mL). The mixture was heated to 100°C for 16 h. After cooling to room temperature, the mixture was diluted with water

(100 mL) and adjusted pH to 2 with concentrated HCl. The aqueous solution was extracted with ethyl acetate (100 mL \times 3). The combined organic layers were dried over sodium sulfate and concentrated. The residue was purified by column chromatography eluted with ethyl acetate and hexane (20:1) to give pure α -truxillic acid (60 mg, yield: 74%) as a white solid. 10 mg of the isolated α -truxillic acid was recrystallized in ethanol. The single-crystal X-ray structure included in Table S1 of the Supporting Information is disordered and consistent with the reported crystal data of α -truxillic acid (4)²³ (see a short movie for the 3D structure and Scheme S2 for details of the hydrolysis in the Supporting Information); mp 276–277 °C (lit.^{24,25} 274–278 °C). ¹H NMR (500 MHz, DMSO-*d*₆): δ 12.13 (s, 2H), 7.32–7.37 (m, 8H), 7.24–7.25 (m, 2H), 4.28 (dd, *J* = 7.5 Hz, 10 Hz, 2H), 3.81 (dd, *J* = 7 Hz, 10 Hz, 2H). ¹³C NMR (125 MHz, DMSO-*d*₆): δ 173.01, 139.49, 128.20, 127.68, 126.71, 46.18, 41.06. NMR data are consistent with the reported values.^{26,27}

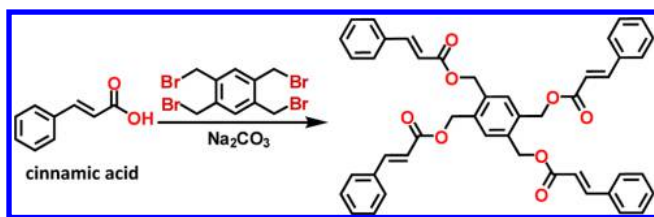
A 2-aminoethanaminium salt (5) of the above isolated α -truxillic acid was obtained, in which the α -truxillic acid anions showed no disorder. In this experiment, 10 mg of α -truxillic acid was dissolved with 3 mL of methanol. To the solution was added 0.2 mL of ethylenediamine. The mixture was kept at room temperature until the crystals (5) were formed; mp 230–231 °C. ¹H NMR (500 MHz, D₂O): δ 7.35 (m, 8H), 7.23–7.26 (m, 2H), 4.18 (dd, *J* = 7.5 Hz, 10.5 Hz, 2H), 3.70 (dd, *J* = 7.5 Hz, 10.5 Hz, 2H), 2.91 (s, 8H). ¹³C NMR (125 MHz, D₂O): δ 181.06, 141.88, 128.77, 127.90, 126.81, 49.86, 42.93, 39.96.

Exfoliation. After the photoreaction of crystals I (1 mg), the polymer IP was added into a mixture of DMF (dimethylformamide) and water (5:95, 10 mL). The suspension was heated to 100 °C for 4 days without stirring. The exfoliation process was monitored by SEM and TEM. One drop from the suspension was placed on copper grids and observed by electronic microscopy after evaporation of the solvent. The results are shown in Figures S12 and S13 of the Supporting Information.

RESULTS AND DISCUSSION

In the study, monomer I was synthesized in 84% yield by linking four cinnamic acid molecules together with 1,2,4,5-tetrakis(bromomethyl)benzene via nucleophilic substitution as shown in Scheme 1. The monomer powder I polymerized

Scheme 1. Synthesis of Monomer I from Cinnamic Acid and 1,2,4,5-Tetrakis(bromomethyl)benzene



under sunlight within 24 h in quantitative yield.²⁸ To understand the solid-state polymerization, we prepared single crystals of the four-armed symmetric monomer I suitable for X-ray diffraction analysis from ethyl acetate.²⁹ Without further processing, the powder XRD pattern of the synthesized monomer I was nearly identical to that of the ground single crystals, confirming that the powder is microcrystalline (see Figure S10 in the Supporting Information). The powder XRD results showed that the crystal structure of the monomer I was suitable to analyze and interpret the solid state polymerization of both the crystals and powder. The monomers stacked along the crystallographic *a*-axis with a repeating distance of 5.8 Å, which was too far for the C=C bonds to react with each other along this stacking direction in the solid state (Figure 1b).

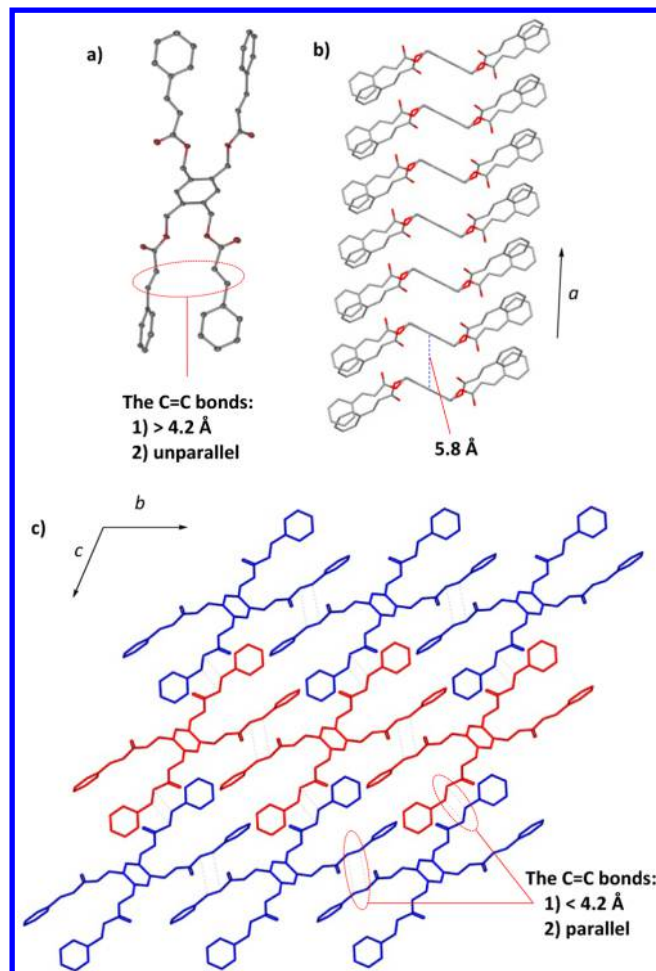


Figure 1. X-ray single crystal structure of the monomer I (hydrogen atoms are omitted for clarity): (a) Oak Ridge Thermal Ellipsoid Plot (ORTEP) representation at 50% electron density of the monomer crystal structure showing the intramolecular [2 + 2] cycloaddition is unfavorable; (b) monomers stacking along the crystallographic *a*-axis showing the C=C bonds are too far from each other to react in this direction; (c) 2D assembly of the monomers in the crystallographic *bc*-plane showing the intermolecular [2 + 2] polymerization is favorable (the dotted lines showing where the new C–C bonds form).

Meanwhile, the X-ray structure also revealed the intramolecular [2 + 2] cycloaddition to be unfavorable because the two pairs of C=C bonds are not paralleled and are separated from each other more than 4.2 Å (Figure 1a), which is the minimum viable distance for the [2 + 2] photoreaction in the solid state.^{30–34} Nevertheless, the crystal structure completed a two-dimensional assembly based on π – π interactions of the conjugated arms between the nearest monomers in the crystallographic *bc*-plane.^{35–40} The four reactive C=C bonds in each monomer were all parallel to the double bonds in the closest four adjacent monomers. The distances between the reactive *sp*²-hybridized carbons in the neighboring monomers were approximately 3.9 Å (Figure 1c). In the presence of light, the [2 + 2] cycloaddition locked the two-dimensional assembly into a covalently bonded two-dimensional polymer.^{41–43}

The sunlight polymerization process was monitored with respect to time using FT-IR. The IR spectra in Figure 2a show that the characteristic absorption peak of C=O stretching at 1708 cm^{−1} shifted to 1726 cm^{−1} in 24 h due to the deconjugation of the carbonyl group. The disappearance of

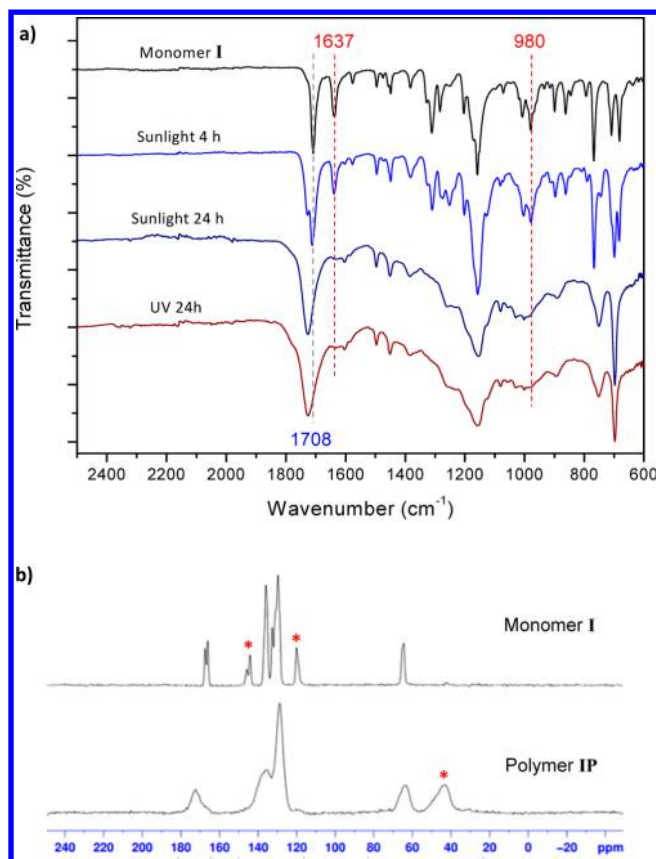


Figure 2. (a) FT-IR spectra showing the [2 + 2] photopolymerization completed by using sunlight or UV irradiation. (b) Solid state ^{13}C NMR spectra of the monomer I and polymer IP.

$\text{C}=\text{C}$ stretching (1637 cm^{-1}) and the out-of-plane twist of the carbon–hydrogen single bonds in the *trans*- $\text{CH}=\text{CH}$ (980 cm^{-1}) after the reaction was consistent with completion of the [2 + 2] photopolymerization. The polymer was also successfully obtained through UV irradiation. The UV–vis spectra, included in the Supporting Information (Figure S9), show that monomer I absorbed irradiation at values of 240–310 nm in an acetonitrile solution and at values of 240–325 nm in the solid state. When an optical filter was used to remove the irradiation below 380 nm of a mercury lamp, no reaction was observed for monomer I in 24 h. Thus, the light-induced polymerization in the solid state is highly efficient because the low concentration of UV irradiation present in sunlight was enough to complete the reaction. The IR spectra of polymers obtained from the two different light sources were nearly identical (Figure 2).

Although 2D polymers are interesting synthetic targets and have great potential for applications,^{1–9} the discovery and development of the 2D polymer has lagged behind other classic polymers, such as linear and cross-linked polymers. One persistent challenge is the characterization of 2D polymers due to poor solubility. In this study, a comparison of the solid state ^{13}C NMR spectra of the monomer I and polymer IP confirmed the formation of the 2D polymer in the crystalline solid by showing the disappearance of two olefin peaks at 118 and 146 ppm concurrent with the appearance of peaks from cyclobutane around 44 ppm (the three key peaks are marked with red stars in Figure 2b). The polymer IP spectrum looks rather

amorphous compared to the sharper resonances of the monomer.

Given the ester structure of the 2D polymer, hydrolysis offers another facile way to confirm the macromolecular structure (Figure 3a). The conversion of the hydrolysis reaction was

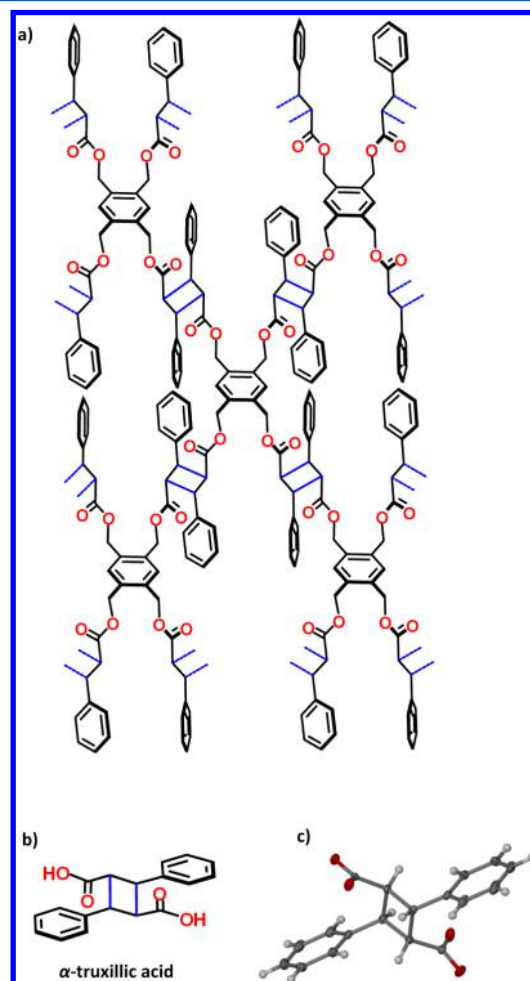


Figure 3. Newly formed C–C single bonds are shown by the α -truxillic acid from hydrolysis of the 2D polyester: (a) the chemical structure of 2D polyester IP (newly formed bonds are in blue and only five repeating units are shown for simplicity); (b) the chemical structure of α -truxillic acid; (c) ORTEP representation of the isolated α -truxillic acid salt crystal structure. Ellipsoids displayed at 50% probability and aminium cations are omitted for clarity.

nearly 100%. No undimerized cinnamic acid was observed in the hydrolysis process, which confirmed the completion of polymerization. The α -truxillic acid (head-to-tail dimer of cinnamic acid shown in Figure 3b,c and a Supporting Information video) was isolated as a polymer hydrolysis product in 72% yield⁴⁴ after column chromatography that directly revealed the newly formed C–C bonds (shown in blue).^{23,45,46} The results of hydrolysis unequivocally confirmed the polymerization and displayed excellent stereoregularity of the [2 + 2] photopolymerization because only one of the five possible stereoisomers of truxillic acid was observed (see Figure 3 and Supporting Information for X-ray single crystal structure of the isolated α -truxillic acid and chemical structures of its four possible stereoisomers). Meanwhile, the absence of β -truxinic acid (head-to-head dimer;⁴⁷ see Scheme S2 in the Supporting

Information) illustrated that intramolecular [2 + 2] cyclo-addition did not occur.

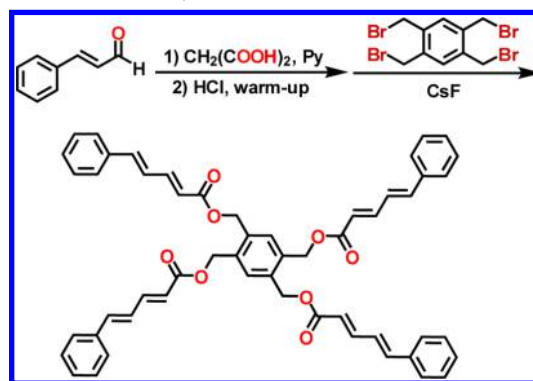
The eight carbon–carbon single bonds that each monomer formed with its four adjacent neighbors all resulted in chiral centers. All the chiral centers were generated stereospecifically since the monomer of this topochemical polymerization can only react with the neighboring monomer in a preorganized way (Figures 1 and 3).^{18–20}

Different chemical and physical properties of the 2D stereoregular polymer were studied. The polymer **IP** was insoluble in common organic solvents such as MeOH, CH₃CN, toluene, CH₂Cl, and DMSO. It tolerated bases (e.g., Et₃N and sodium hydroxide) and acids (e.g., 1 M HCl and TFA) at room temperature. However, it was degradable in aqueous potassium hydroxide at 100 °C and was oxidized by concentrated sulfuric acid. The thermogravimetric analysis (TGA, Figure S11 in the Supporting Information) of the 2D polymer showed slight weight loss around 200 °C. The differential scanning calorimetry curve (DSC, Figure 4a) of polymer **IP** showed an endothermic peak near 200 °C, but the 2D polymer did not

melt even when heated at 350 °C. This endothermic peak disappeared during the sequential heating cycles, which might indicate an annealing process. The heat released tension built within the 2D polymer structure during the photopolymerization reaction due to the restricted movement of atoms in the solid state. Since there are only weak interactions between the polymeric layers,^{35–40,48,49} the 2D polymers were exfoliated into extremely thin sheets by heating in a DMF/H₂O (5:95) solution at 100 °C. The scanning electron microscope (SEM) and transmission electron microscopy (TEM) images of a multilayered crystal before exfoliation and ultrathin sheets after exfoliation are shown in Figure 4b–e and Supporting Information Figures S12 and S13. A deepened exploration of this novel polymer may expose innovative properties and subsequent possibilities.^{1,2,50}

We also investigated a similar monomer capable of 2D polymerization. Indeed, generality is a challenge in solid-state synthesis because topochemical reactions are often sensitive to small structural changes,^{51,52} so judicious design and tests are necessary. With this in mind, the monomer **II** with two conjugated C=C bonds on each of the four arms was synthesized from cinnamic aldehyde, malonic acid, and the same tetrabromo-linker in three steps with 81% overall yield (Scheme 2). The crystal structure of the monomer **II** adopted a

Scheme 2. Synthesis of Monomer **II** from Cinnamic Aldehyde, Malonic Acid, and 1,2,4,5-Tetrakis(bromomethyl)benzene



conformation and packing very similar to those of monomer **I** (Figure 5). The monomer **II** also stacks along the crystallographic *a* axis with a repeating distance greater than 5.8 Å. Meanwhile, the π orbitals of the dienes are not pointing toward each other in the *a* axis stacking direction. Therefore, it would be difficult if not impossible for the conjugated C=C bonds to react with each other by 1,4-polymerization in the solid state.^{13,53} However, the crystals of compound **II** were photoreactive as well and polymerized readily in 24 h upon exposure to UV or sunlight. Interestingly, both the IR and solid state ¹³C NMR spectra showed that there were still a small portion of the olefins that remained untouched after the polymerization stopped although all of the C=C double bonds were preorganized in such way that each bond could be photodimerized (Figure 5c). A close examination of the crystal packing showed that there was a competing [2 + 2] dimerization for the reaction between the blue and red monomers since they were slightly offset (Figure 6, colors introduced arbitrarily for clarity in discussion). Although the olefins were aligned for formation of the three-ladderane linkage,^{54–58} the two C=C bonds closer to the ester groups

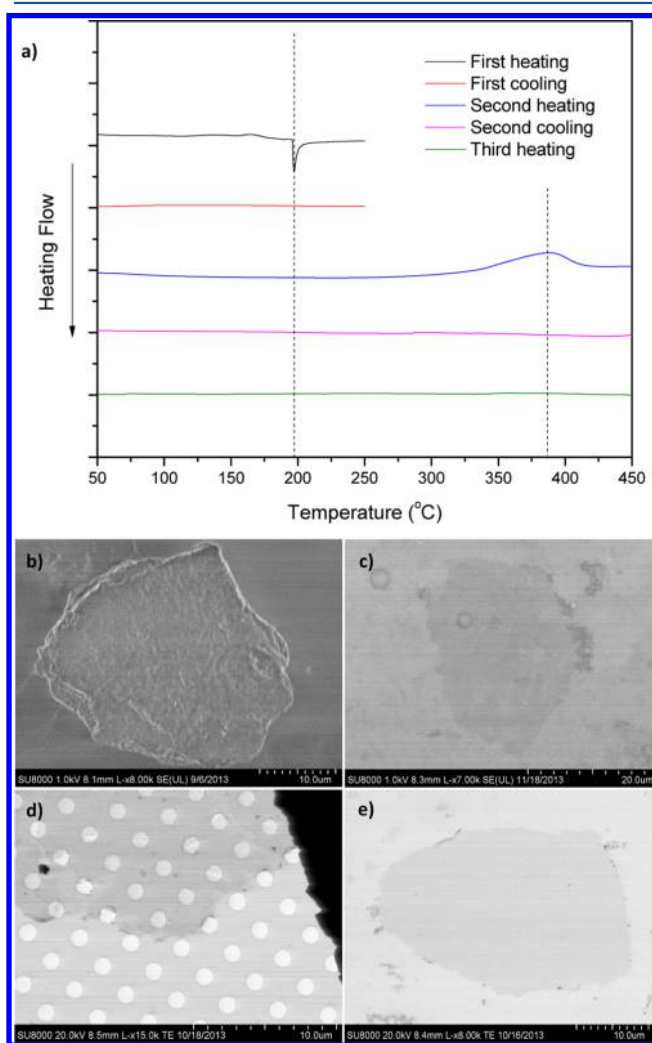


Figure 4. (a) DSC of polymer **IP** was operated under nitrogen (20 mL/min) with rate 10 °C/min. (b) SEM image of a multilayered material of **IP**. (c) SEM image of an ultrathin polymeric sheet of **IP** obtained by exfoliation. (d) TEM images of an ultrathin polymeric sheet with cracks and holes after exfoliation. (e) TEM images of an ultrathin polymeric sheet obtained by exfoliation.

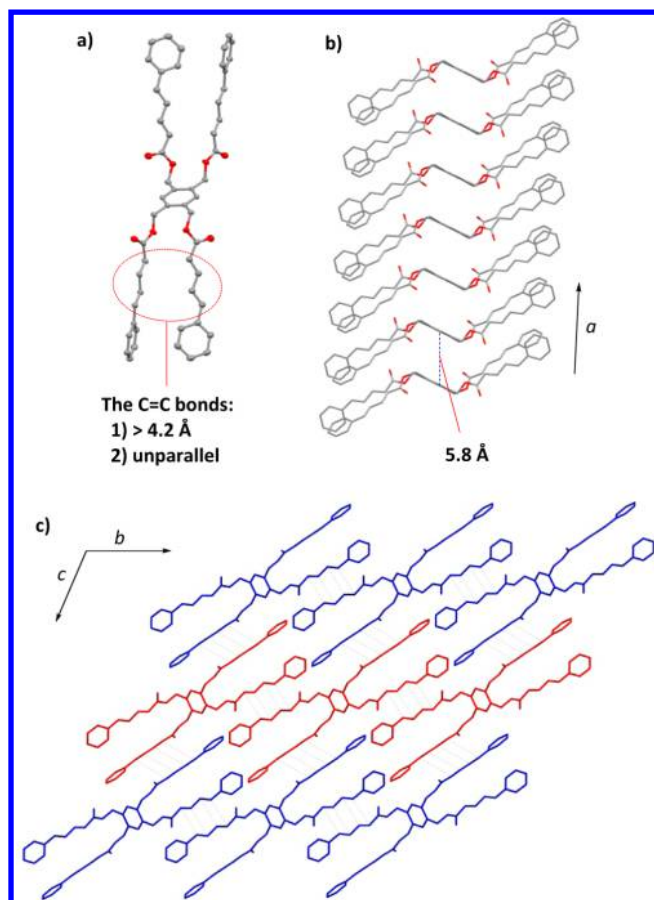


Figure 5. X-ray single crystal structure of the monomer **II** (hydrogen atoms are omitted for clarity): (a) Oak Ridge Thermal Ellipsoid Plot (ORTEP) representation at 50% electron density of the monomer crystal structure showing the intramolecular [2 + 2] cycloaddition is unfavorable; (b) monomers stacking along the crystallographic *a*-axis showing the C=C bonds are too far from each other to react in this direction; (c) 2D assembly of the monomers in the crystallographic *bc*-plane showing the intermolecular [2 + 2] polymerization is favorable (the dotted lines showing where the new C–C bonds could form).

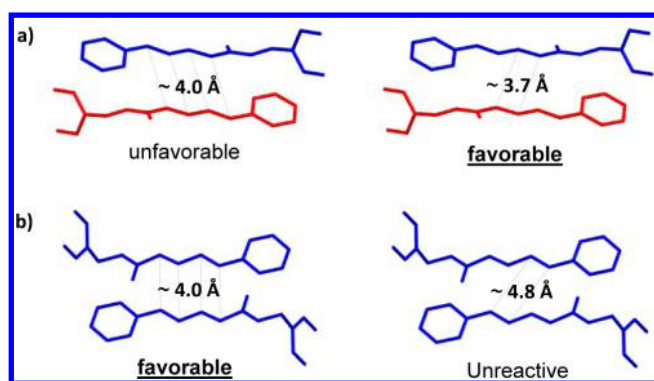


Figure 6. (a) The two competing [2 + 2] dimerization reactions in the solid state between the blue and red monomers (the dotted lines showing where the new C–C bonds could form). (b) The olefins with the same colors were aligned well to form the ladderane linkage exclusively.

could also react with each other. Since the separation between the double bonds was about 0.3 Å shorter in the latter option, it was easier to react. Therefore, two C=C bonds close to the phenyl rings were left untouched. The olefins with the same

colors were aligned well to form the ladderane linkage exclusively, and there was no competing [2 + 2] dimerization reaction between the blue monomers or the red ones. Thus, only two of the eight C=C double bonds in each monomer were left after the photopolymerization. This analysis of spatial approximation is consistent with the FT-IR and solid state NMR spectra of the polymeric product (Figures S16 and S6 in the Supporting Information). The solid state NMR spectra of monomer **II** and polymer **IIP** showed a remarkable amorphous broadening of all aliphatic resonances and some broadening of the CH and C=O resonances where the aromatic core shows few spectral differences after the photopolymerization. Nevertheless, a 2D polymeric matrix was formed after the photodimerization of each reactive arm on the monomer **II**.

CONCLUSIONS

A stereoregular 2D polyester **IP**, which could not be easily obtained by alternative synthetic routes, was prepared by topochemical polymerization. The locally confined polymerization avoids cross-linking by preorganizing the multiple reactive centers in the solid state.^{13–15,41–43} The stereoregular 2D polymer structure was unambiguously confirmed by revealing the newly formed carbon–carbon single bonds through the single crystal structure of its hydrolysis product. We have also extended the synthetic approach to another monomer with two conjugated carbon–carbon double bonds on each of the four arms. The starting materials, reagents, and necessary preparations implemented in the experiments were inexpensive and common, showing the possibility of scaling up the facile and efficient 2D polymer synthesis. The novel stereoregular 2D polyesters have potential in a variety of applications. One can envision that the application of such strong and lightweight organic materials may usher in the next generation of fuel-efficient transportation on all scales, from aircraft to automobile.

ASSOCIATED CONTENT

Supporting Information

Characterization and properties of synthesized 2D polymers, the photoreaction results, spectra, images of the crystals, crystallographic data including a video, and CIF files of the five single crystals. This material is available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Author

*E-mail chu@chem.und.edu (Q.R.C.).

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This material is based upon work supported by the Doctoral New Investigator grants of the American Chemical Society Petroleum Research Fund (PRF 52705-DNI7) and the National Science Foundation Grant (NSF EPSCoR Award IIA-1355466). The authors acknowledge Prof. J. X. Zhao (UND) for help with the high-resolution scanning electron microscope, Prof. L. Stahl (UND) for X-ray diffractometer assistance, and Prof. A. Kubátová group (UND) for aid in high-resolution mass spectrometry.

REFERENCES

- (1) Sakamoto, J.; van Heijst, J.; Lukin, O.; Schlüter, A. D. *Angew. Chem., Int. Ed.* **2009**, *48*, 1030–1069.
- (2) Colson, J. W.; Dichtel, W. R. *Nat. Chem.* **2013**, *5*, 453–465.
- (3) Kissel, P.; Murray, D. J.; Wulfstange, W. J.; Catalano, V. J.; King, B. T. *Nat. Chem.* **2014**, *6*, 774–778.
- (4) Kory, M. J.; Wörle, M.; Weber, T.; Payamyar, P.; van de PollStan, W.; Dshemuchadse, J.; Trapp, N.; Schlüter, A. D. *Nat. Chem.* **2014**, *6*, 779–784.
- (5) Baek, K.; Yun, G.; Kim, Y.; Kim, D.; Hota, R.; Hwang, I.; Xu, D.; Ko, Y. H.; Gu, G. H.; Suh, J. H.; Park, C. G.; Sung, B. J.; Kim, K. J. *Am. Chem. Soc.* **2013**, *135*, 6523–6528.
- (6) Lafferentz, L.; Eberhardt, V.; Dri, C.; Africh, C.; Comelli, G.; Esch, F.; Hecht, S.; Grill, L. *Nat. Chem.* **2012**, *4*, 215–220.
- (7) Spitler, E. L.; Dichtel, W. R. *Nat. Chem.* **2010**, *2*, 672–677.
- (8) Côté, A. P.; Benin, A. I.; Ockwig, N. W.; O’Keeffe, M.; Matzger, A. J.; Yaghi, O. M. *Science* **2005**, *310*, 1166–1170.
- (9) Stupp, S. I.; Son, S.; Lin, H. C.; Li, L. S. *Science* **1993**, *259*, 59–63.
- (10) Market Report: World Carbon Fiber Composite Market, Acmite Market Intelligence, 2010.
- (11) Hillermeier, R.; Hasson, T.; Friedrich, L.; Ball, C. Advanced Thermosetting Resin Matrix Technology for Next Generation High Volume Manufacture of Automotive Composite Structures, http://www.speautomotive.com/SPEA_CD/SPEA2012/pdf/TS/TS1.pdf (accessed April 2015).
- (12) <http://www.zoltek.com/carbonfiber/how-is-it-made/> (accessed April 2015).
- (13) Hou, X.; Wang, Z.; Lee, J.; Wysocki, E.; Oian, C.; Schlak, J.; Chu, Q. R. *Chem. Commun.* **2014**, *50*, 1218–1220.
- (14) Chu, Q.; Swenson, D. C.; MacGillivray, L. R. *Angew. Chem., Int. Ed.* **2005**, *44*, 3569–3572.
- (15) MacGillivray, L. R.; Papaefstathiou, G. S.; Friščić, T.; Hamilton, T. D.; Bučar, D.-K.; Chu, Q.; Varshney, D. B.; Georgiev, I. G. *Acc. Chem. Res.* **2008**, *41*, 280–291.
- (16) Biradha, K.; Santra, R. *Chem. Soc. Rev.* **2013**, *42*, 950–967.
- (17) Grove, R. C.; Malehorn, S. H.; Breen, M. E.; Wheeler, K. A. *Chem. Commun.* **2010**, *46*, 7322–7324.
- (18) Garcia-Garibay, M. A. *Acc. Chem. Res.* **2003**, *36*, 491–498.
- (19) Nakanishi, H.; Jones, W.; Thomas, J. M.; Hasegawa, M.; Rees, W. L. *Proc. R. Soc. London, Ser. A* **1980**, *369*, 307–325.
- (20) Wegner, G. *Makromol. Chem.* **1972**, *154*, 35–48.
- (21) Takeuchi, D. In *Stereoregular Polymers, Encyclopedia of Polymer Science and Technology*; John Wiley & Sons, Inc.: New York, 2013.
- (22) Antzutkin, O. N. *Prog. Nucl. Magn. Reson. Spectrosc.* **1999**, *35*, 203–266.
- (23) Abdelmoty, I.; Buchholz, V.; Di, L.; Guo, C.; Kowitz, K.; Enkelmann, V.; Wegner, G.; Foxman, B. M. *Cryst. Growth Des.* **2005**, *5*, 2210–2217.
- (24) Chi, Y.-M.; Nakamura, M.; Yoshizawa, T.; Zhao, X.-Y.; Yan, W.-M.; Hashimoto, F.; Kinjo, J.; Nohara, T.; Sakurada, S. *Biol. Pharm. Bull.* **2005**, *28*, 1776–1778.
- (25) Chi, Y.-M.; Nakamura, M.; Zhao, X.-Y.; Yoshizawa, T.; Yan, W.-M.; Hashimoto, F.; Kinjo, J.; Nohara, T.; Sakurada, S. *Biol. Pharm. Bull.* **2006**, *29*, 580–584.
- (26) Yang, H.; Jia, L.; Wang, Z.; Di-Cicco, A. I.; Lévy, D.; Keller, P. *Macromolecules* **2010**, *44*, 159–165.
- (27) Berger, W. T.; Ralph, B. P.; Kaczocha, M.; Sun, J.; Balias, T. E.; Rizzo, R. C.; Haj-Dahmane, S.; Ojima, I.; Deutsch, D. G. *PLoS One* **2012**, *7*, e50968.
- (28) The reaction was carried out in 2 days with 12 h of solar irradiation per day.
- (29) Singh, R.; Schober, M.; Hou, X.; Seay, A.; Chu, Q. *Tetrahedron Lett.* **2012**, *53*, 173–175.
- (30) Schmidt, G. M. J. *Pure Appl. Chem.* **1971**, *27*, 647–678.
- (31) Park, I.-H.; Chanthapally, A.; Zhang, Z.; Lee, S. S.; Zaworotko, M. J.; Vittal, J. J. *Angew. Chem., Int. Ed.* **2014**, *53*, 5232–5232.
- (32) Medishetty, R.; Husain, A.; Bai, Z.; Runčevski, T.; Dinnebier, R. E.; Naumov, P.; Vittal, J. J. *Angew. Chem., Int. Ed.* **2014**, *53*, 5907–5911.
- (33) Yang, S.-Y.; Deng, X.-L.; Jin, R.-F.; Naumov, P.; Panda, M. K.; Huang, R.-B.; Zheng, L.-S.; Teo, B. K. J. *Am. Chem. Soc.* **2013**, *136*, 558–561.
- (34) Garai, M.; Santra, R.; Biradha, K. *Angew. Chem., Int. Ed.* **2013**, *52*, 5548–5551.
- (35) Desiraju, G. R.; Vittal, J. J.; Ramanan, A. *Crystal Engineering: A Textbook*, 1st ed.; World Scientific Publishing Company: Singapore, 2011.
- (36) Steed, J. W.; Atwood, J. L. *Supramolecular Chemistry*, 2nd ed.; John Wiley & Sons, Ltd.: Chichester, 2009.
- (37) Hou, X.; Wang, Z.; Overby, M.; Ugrinov, A.; Oian, C.; Singh, R.; Chu, Q. R. *Chem. Commun.* **2014**, *50*, 5209–5211.
- (38) Wang, Z.; Lee, J.; Oian, C.; Hou, X.; Wang, Z.; Ugrinov, A.; Singh, R. K.; Wysocki, E.; Chu, Q. R. *CrystEngComm* **2014**, *16*, 7176–7179.
- (39) Hou, X.; Schober, M.; Chu, Q. *Cryst. Growth Des.* **2012**, *12*, 5159–5163.
- (40) Singh, R. K.; Hou, X.; Overby, M.; Schober, M.; Chu, Q. *CrystEngComm* **2012**, *14*, 6132–6135.
- (41) Prins, L. J.; Scrimin, P. *Angew. Chem., Int. Ed.* **2009**, *48*, 2288–2306.
- (42) Sada, K.; Takeuchi, M.; Fujita, N.; Numata, M.; Shinkai, S. *Chem. Soc. Rev.* **2007**, *36*, 415–435.
- (43) Tajima, K.; Aida, T. *Chem. Commun.* **2000**, 2399–2412.
- (44) An average yield of two experiments: 72% = (69% + 74%)/2.
- (45) Khan, M.; Brunklaus, G.; Enkelmann, V.; Spiess, H.-W. *J. Am. Chem. Soc.* **2008**, *130*, 1741–1748.
- (46) Barbour, L. J. *J. Supramol. Chem.* **2001**, *1*, 189–191.
- (47) Nishikubo, T.; Takahashi, E.; Miyaji, T.; Iizawa, T. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 3399–3400.
- (48) Chu, Q.; Wang, Z.; Huang, Q.; Yan, C.; Zhu, S. *J. Am. Chem. Soc.* **2001**, *123*, 11069–11070.
- (49) Chu, Q.; Wang, Z.; Huang, Q.; Yan, C.; Zhu, S. *New J. Chem.* **2003**, *27*, 1522–1527.
- (50) Neto, A. H. C.; Novoselov, K. *Rep. Prog. Phys.* **2011**, *74*, 082501.
- (51) Gavezzotti, A. *Acc. Chem. Res.* **1994**, *27*, 309–314.
- (52) Brock, C. P.; Dunitz, J. D. *Chem. Mater.* **1994**, *6*, 1118–1127.
- (53) Matsumoto, A.; Sada, K.; Tashiro, K.; Miyata, M.; Tsubouchi, T.; Tanaka, T.; Odani, T.; Nagahama, S.; Tanaka, T.; Inoue, K.; Saragai, S.; Nakamoto, S. *Angew. Chem., Int. Ed.* **2002**, *41*, 2502–2505.
- (54) Sinninghe Damste, J. S.; Strous, M.; Rijpsstra, W. I. C.; Hopmans, E. C.; Geenevasen, J. A. J.; van Duin, A. C. T.; van Niftrik, L. A.; Jetten, M. S. M. *Nature* **2002**, *419*, 708–712.
- (55) Hopf, H. *Angew. Chem., Int. Ed.* **2003**, *42*, 2822–2825.
- (56) Mascitti, V.; Corey, E. J. *J. Am. Chem. Soc.* **2004**, *126*, 15664–15665.
- (57) Hoffmann, N. *Chem. Rev.* **2008**, *108*, 1052–1103.
- (58) Atkinson, M. B. J.; Mariappan, S. V. S.; Bučar, D.-K.; Baltrusaitis, J.; Friščić, T.; Sinada, N. G.; MacGillivray, L. R. *Proc. Natl. Acad. Sci. U. S. A.* **2011**, *108*, 10974–10979.