Diacetylene-Based C_{2h}-Symmetric Monomers for Two-Dimensional-Polymer Synthesis

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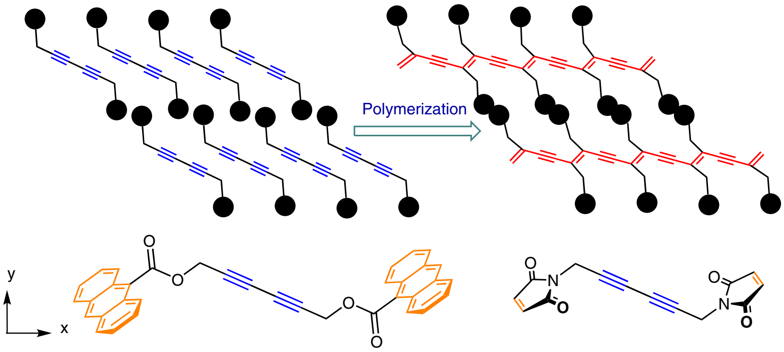

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Abstract Two linear monomers with two terminal photoreactive groups (anthracene or maleimide) embedded in a diacetylene skeleton were synthesized for two-dimensional-polymer synthesis. Both of them were crystallized and their single-crystal structures were solved. It was found that the size of terminal groups can be critical for diacetylene's arrangement. The crystal structure of dimaleimide monomer revealed that maleimide groups strongly stacking in antiparallel and the photo-induced [2+2] cycloaddition of stacked maleimides was preliminary studied.

Key words two-dimensional polymer, single crystal, topochemistry, diacetylene, maleimide

A two-dimensional (2D) polymer is a free-standing and covalently bonded polymer sheet with a few atoms thick and long-range internal order,[1] which may have potential applications in nanoseperators and electronics. Since this concept was promoted in 2009, tens of cyclic monomers were synthesized and very few of them were successfully applied in 2D-polymer synthesis in single crystals.[2] These monomers always have three photoreactive (anthracene) units embedded in a C_{3v} skeleton[3] and in this case, resulting 2D polymers bearing rigid hexgon pores (Figure 1, a).[4–6] Synthesis of such monomers are generally not simple, that is, the final cyclization reaction needs to be performed in diluted solution and always generates side products such as oligomers. In order to explore 2D polymers with different topologies from simple monomers, we designed C_{2h}-symmetric monomers with two terminal topochemically reactive groups (anthracene or maleimide) embedded in a diacetylene skeleton (Figure 1, c) and expected to utilize them to synthesize 2D polymers in single crystals (Figure 1, b). The resulting 2D polymers from them have flexible square pores. In single crystals, diacetylenes stack in an appropriate linear parallel fashion, which is feasible for topopolymerization to form polydiacetylenes along *x* axis (Figure 1, b).[7,8] The resulting polydiacetylene is stable over 300 °C.[9,10] On another hand, terminal groups face to face (*ftf*) stack, which is feasbile for the topodimerization to form polymers along *y* axis. Anthracene is topochemically reactive while it *ftf* stacks (Figure 1, d), but the resulting dimer generally decomposes over 100 °C.[11] In order to achieve high thermal stability, we further utilized maleimide as terminal groups owing to the high thermal stability of the maleimide dimer.[12,13] Schmidt demonstrated that when a couple of olefins in single crystals *ftf* pack with a distance of 3.5–4.2 Å, photoinduced [2+2] cyclization can be carried out.[14,15] Eventhough it is still no reported topodimerization between maleimides, we expected that toporeaction is possible (Figure 1, e) since [2+2] cyclization of maleimides in solution have been well documented.[16,17]

Monomer **1** was simply synthesized from propargyl alcohol and anthracene-9-carboxylic acid in two steps (Scheme 1, a). Hexa-2,4-diyne-1,6-diol (**3**) was prepared by CuCl/tetramethyl ethylenediamine (TMEDA) catalyzed air-oxidization of propargyl alcohol.[18] Double Steglich esterification[19] between **3** and anthracene-9-carboxylic acid afforded monomer **1**.[20] Single crystals were grown from ethyl acetate by slow evaporation in a glass vessel, however, irradiating (λ = 365 or 254 nm) or heating these crystals led to no reactions. X-ray crystallography analysis disclosed the reason of its nonreactivity. There are neither linear parallel stacking between diacetylenes, nor feasible *ftf* stacking between anthracenes. In a layer, neighboring anthracenes are partially off-set stacking with a distance of 3.485 Å, while diacetylenes are arranged in parallel with distance further than 10 Å (Scheme 1, b). Such far distance may be due to the large steric hindrance of anthrance, which repels diacetylene's stacking.

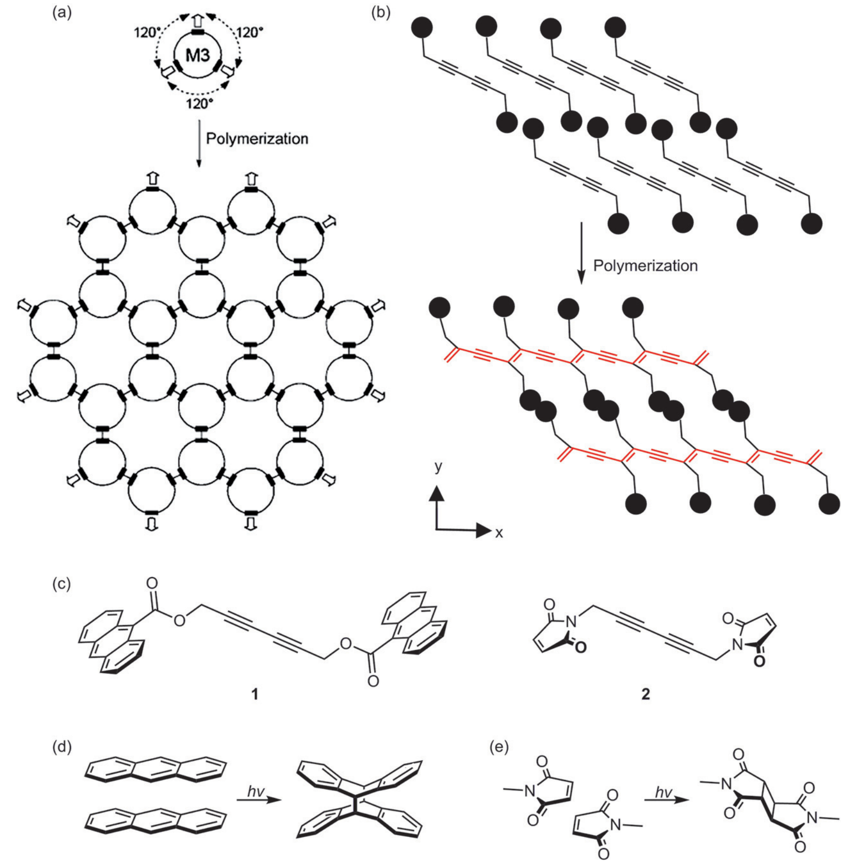
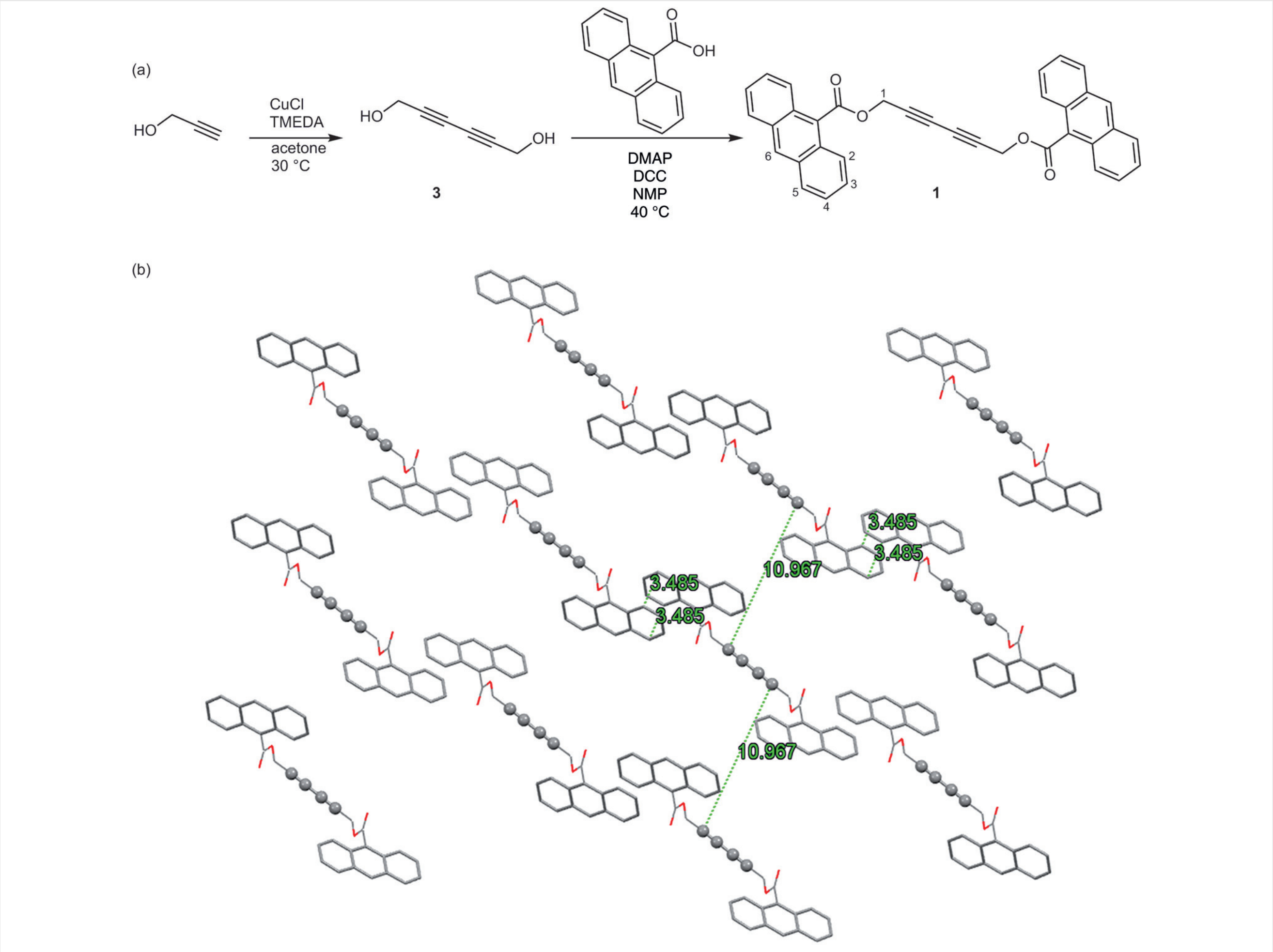


Figure 1 (a) Reported monomers having three anthracene units embedded in a C_{3v} skeleton for the synthesis of 2D polymer (bond black squares represent anthracene units; reproduced from ref. 3). (b) Synthesis of 2D polymer in single crystals from C_{2h}-symmetric monomers (black spots represent terminal photoreactive groups). (c) Molecular structure of monomer **1** and **2**. (d) Dimerization of anthracene. (e) Dimerization of maleimide via [2+2] cyclization.

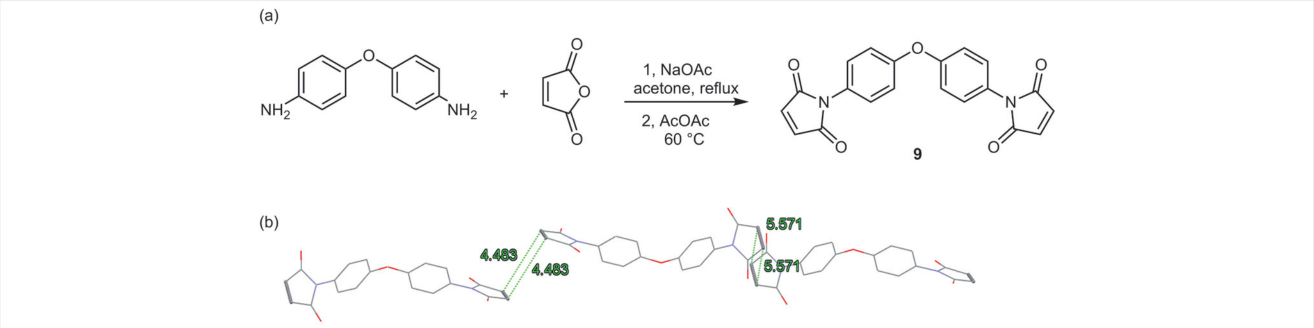
In order to confirm the packing of maleimide in single crystals, a known compound **9** embedded with two maleimide groups was firstly synthesized (Scheme 2, a). Compound **9** was synthesized from 4,4′-oxydianiline and maleic anhydride by dehydration–condensation.[21] Crystals were obtained from chloroform. X-ray crystallography analysis reveals that both terminal maleimides are off-set antiparallel arranged with their neighbors (Scheme 2, b). Even though distances are not in the range of Schmidt [2+2] cyclization (irradiation of this crystal at 365 or 254 nm led to no reaction), this crystal structure indicates that maleimide has a tendency to stack in an antiparallel fashion in single crystals.

Monomer **2** was synthesized with two synthetic procedures (Scheme 3).[22] The first procedure has five steps. A Diels–Alder reaction between maleic anhydride and furan followed by ammoniation gave the known compound **6**.[23] Nucleophilic substitution of propargyl bromide with **6** produced the compound **5**,[24] which was atmospherically oxidized with CuCl–TMEDA catalyst to yield the key intermediate **4**.[18] The monomer **2** was finally obtained by removal of furan under thermal treatment of **4**.[25] The second procedure has three steps. Propargyl maleimide **8** was synthesized by dehydration condensation between propargyl amine and maleic anhydride in two steps.[26] Compound **8** was further atmospherically oxidized yielding monomer **2**.

By slow evaporation at ambient temperature, colorless plane crystals can be obtained from the solution of monomer **2** in THF and toluene (v/v = 1:1). These crystals are quite thin with a large lateral size (ca. 1 cm; see Figure 3, a). X-ray crystallography analysis demonstrated that maleimides stacking in antiparallel. Olefinic groups between neighboring monomers are aligned with strong interactions, as indicated by a distance of 3.923 Å (Figure 2, a). This distance is in the range for topochemical [2+2] cyclization suggested by Schmidt.[14] Another pair of olefinic groups between neighboring monomers are also aligned in parallel, but the distance is too far (4.826 Å) for the [2+2] cyclization. Moreover, diacetylenes arrange in a linear fashion but the distance of potential polymerizing carbons are 4.791 Å, which is still not suitable for the topopolymerization[7,8] but much closer than that in single crystals of monomer **1**. This

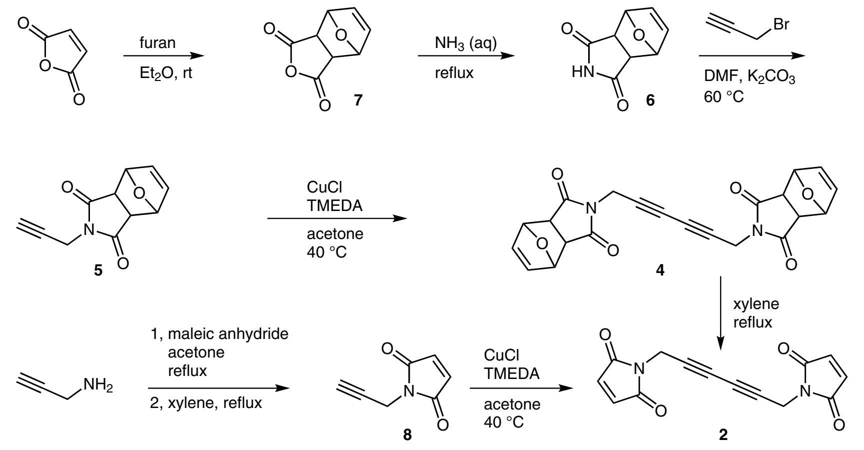


Scheme 1 (a) Synthetic procedure of monomer **1** (numbers in the chemical structure of monomer **1** are used to label its NMR data). (b) Crystal structure of monomer **1**. Hydrogens are omitted for clarity. Distance unit: Å.



Scheme 2 (a) Synthetic procedure of bismaleimide **9**. (b) Crystal structure of bismaleimide **9**. Hydrogen atoms are omitted for clarity. Distance unit: Å.

closer distance may be due to the smaller size of maleimide. It should be noted that the precursor **4** has a similar internal packing in its single crystal (Figure 2, b). Neighboring furanmaleimide groups are off-set aligned with strong interactions, as indicated by a distance of ca. 3.9 Å, while diacetylenes arrange in a linear fashion but the distance (6.627 Å) of potential polymerizing carbons is much further than that in the single crystal of monomer **2**. Such far distance



Scheme 3 Synthetic procedures of monomer **2**

may be due to the steric hindrance of furanmaleimide, as the similar effect of anthracenes in single crystals of monomer **1**.

As in the crystal of monomer **2**, olefinic groups of maleimide between neighbors are aligned in the range for topochemical [2+2] cyclization,[14] topochemical reaction was attempted by light irradiation. A glass slide was charged with crystals and then irradiated by an UV lamp (λ = 365 nm) for 15 hours. After irradiation, colorless crystals mechanically disintegrated, so as to lose X-ray quality (Figure 3, b). In order to demonstrate the chemical structure of the irradiated material, two model compounds (*N*-ethyl maleimide dimer and maleimide dimer) were synthesized (Supporting Information, compounds **10** and **11**). It was found that in IR spectra characteristic vibrations of cyclobutane ring are at ca. 748 and 647 cm^{-1} (Supporting Information, Figures S9, S10). In Raman spectra, absorptions of maleimide are at ca. 304, 1052, 1588 cm^{-1} and cyclobutane ring are at ca. 978 and 1186 cm^{-1} (Supporting Information, Figures S11, S12). Through comparing IR and Raman spectra with model compounds, a cyclobutane structure was preliminarily established in the irradiated material (Figure 6, c and d). In IR spectra, stretching vibrations of HC= (3165, 3101 cm^{-1}) and out-of-plane bending vibration of *cis*-HC=CH (696 cm^{-1}) totally disappeared while characteristic vibrations of cyclobutane ring at 732 and 614 cm^{-1} increased. In Raman spectra, absorptions of maleimide at 300, 1042, 1584 cm^{-1} was completely vanished while absorptions of cyclobutane ring at 980 and 1181 cm^{-1} appeared. It should be noted that after irradiation the diacetylene (diacetylene and polydiacetylene are Raman active but not IR active) absorption at ca. 2270 cm^{-1} retained and there are no characteristic absorptions of polydiacetylene at ca. 1470 and 2050 cm^{-1},[27] which reveals that diacetylene is nonreactive in this crystal at all. Unfortunately, this irradiated product is insoluble in any common solvents so it is impossible to measure it by liquid NMR spectroscopy or determine its molecular weight by GPC. What even more tough is that the growth of feasible single crystals is very difficult. Only a small amount of crystals was obtained at one time. We attempted a lot of times, but most of time, monomer **2** was easy to form needles, whose crystal structure cannot be solved. So it is hard to get enough materials for further characterization such as solid-state NMR spec-

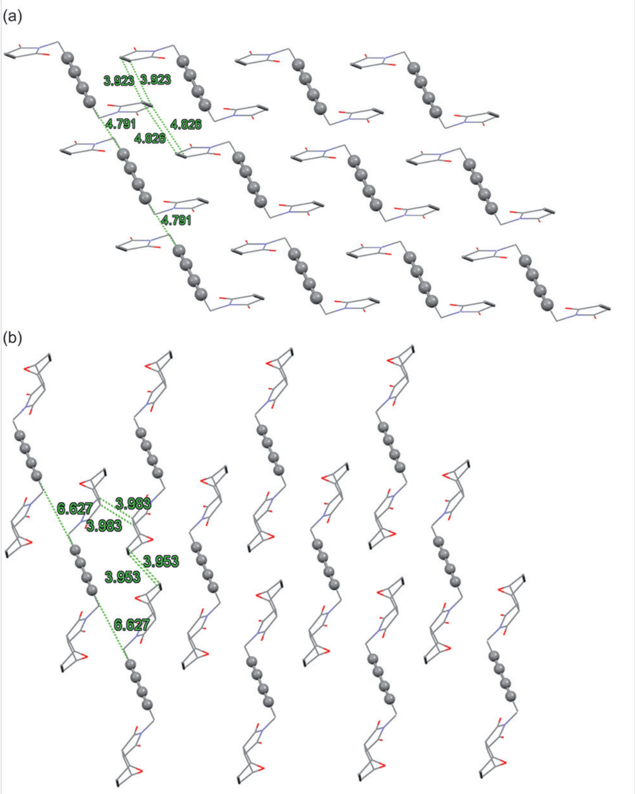


Figure 2 Crystal structure of monomer **2** (a) and compound **4** (b). Hydrogen atoms are omitted for clarity. Distance unit: Å.

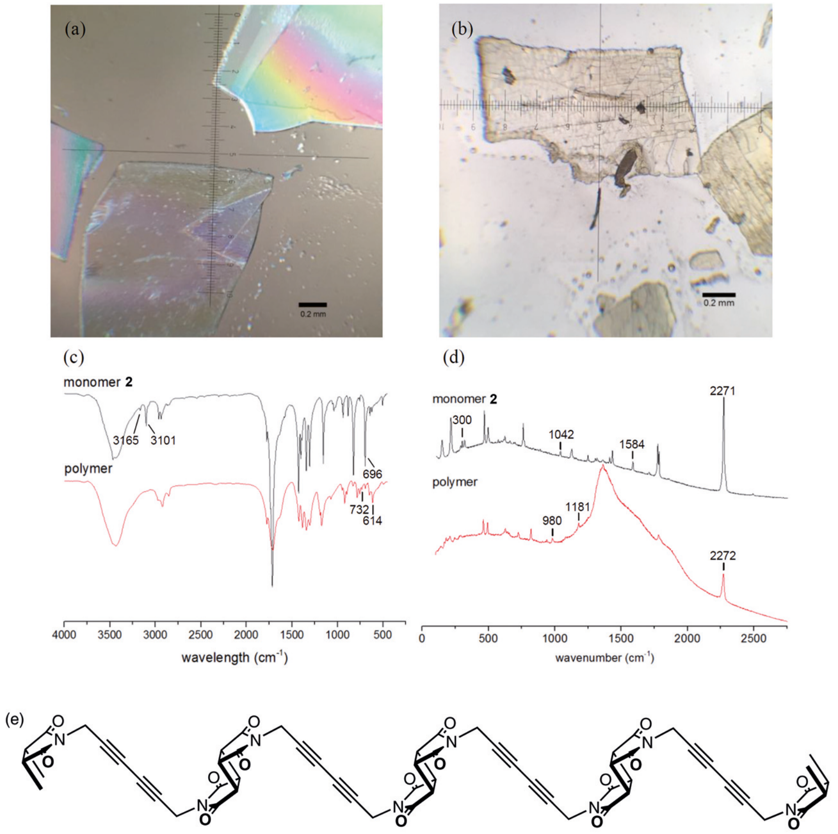


Figure 3 Optical microscope (OM) images of monomer **2** crystals (a) before and (b) after irradiation; (c) IR and (d) Raman spectra of monomer **2** before and after irradiation; (e) proposed structure of the irradiated product.

troscopy and powder X-ray diffraction. Further demonstration of its structure is possible only when enough crystal material can be obtained. Anyway, from above Raman and IR measurements, we propose a possible structure of the insoluble product as shown in Figure 3 (e).

Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) measurements were used to evaluate the thermal behavior of the irradiated product (Supporting Information, Figures S13, 14). The DSC curve shows there is no sharp endotherm peak at 147 °C (melting point of monomer **2**) but a quite broad, smooth, and weak endotherm area from 30–250 °C (21.922 kJ per mol repeating unit), which means the irradiated product is not monomer **2** anymore and it is stable and does not have a glass transition temperature (Tg) lower than 250 °C. The TGA measurement shows a similar stability pattern because the weight loss below 6% up to 250 °C. This minor weight loss may result from the removal of moisture.

In summary, two monomers (**1**, **2**) with two terminal photoreactive groups (anthracene or maleimide) embedded in a diacetylene skeleton have been successfully synthesized. Single crystals of them have been obtained and X-ray structures were solved. They all show layered structures but are still infeasible for 2D-polymer synthesis. We found that terminal groups all have some tight stacking and sizes of terminal groups can be critical for diacetylene's stacking. When terminal groups are larger, diacetylenes are arranged further to each other. Within these crystals, we found maleimides can be arranged in antiparallel with their olefin groups strongly stacking, and their Schmidt topochemical dimerization was preliminary studied. Even though these monomers are still not feasible for 2D polymerization, we believe our studies will give a clue for the further monomer design for 2D-polymer synthesis and what is more, an interesting solid-state approach for polyimide synthesis.

Acknowledgment

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Supporting Information

Supporting information for this article is available online at http://dx.doi.org/10.1055/s-0036-15886.

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(20) **Synthesis of Monomer 1**
A sealed tube was charged with compound **3** (221 mg, 2 mmol), 9-anthracene carboxylic acid (1115 mg, 5 mmol), *N,N*-dicyclohexylcarbodimide (1128 mg, 5 mmol), and 4-dimethylaminopyridine (28 mg, 0.2 mmol) in 1-methyl-2-pyrrolidone (10 mL) under argon atmosphere. The mixture was stirred at 40 °C for 5 d. The yellow mixture was washed with water and passed a silicon chromatographic column affording monomer **1** as a yellow solid (820 mg, 1.6 mmol, 79%); mp >250 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.56 (s, 2 H, H-6), 8.08 (d, *J* = 8 Hz, 4 H, H-2 or H-5), 8.03 (d, *J* = 8 Hz, 4 H, H-2 or H-5), 7.57 (m, 4 H, H-3 or H-4), 7.48 (m, 4 H, H-3 or H-4), 5.29 (s, 4 H, H-1) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 168.81, 131.03, 130.16, 128.78, 127.49, 126.24, 125.69, 124.91, 73.86, 71.17, 53.36 ppm. HRMS (LC-MS TOF, formic acid): *m/z* calcd for $C_{36}H_{22}O_4$ $[MH]^+$: 519.1591; found: 519.1587.

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(22) **Synthesis of Monomer 2**
(a) A solution of compound **4** (0.383 g, 0.95 mmol) in xylene (200 mL) was refluxed for 3 h under an argon atmosphere. After reaction, the hot solution was quickly filtered to remove insoluble byproducts and then concentrated by rotary vacuum. Monomer **2** was obtained as white solid from the cooling solution (0.168 g, 0.63 mmol, 66.3%). (b) An open beak was charged with CuCl (0.102 g, 1 mmol) and TMEDA (0.121 g, 1 mmol) in acetone (2 mL). After stirring for 3 min, compound **8** (0.654 g, 4.80 mmol) was added, and the reaction continued for 16 h at 40 °C. By extraction from the product mixture with EtOAc and concentration, monomer **2** was obtained as a pale yellow solid (0.131 g, 0.49 mmol, 20.4%); mp 147 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.75 (s, 2 H, CH), 4.33 (s, 2 H, CH_2) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 169.18, 134.72, 72.13, 67.52, 27.58 ppm. HRMS (LC-MS TOF, formic acid): *m/z* calcd for $C_{14}H_8N_2O_4$ $[MH]^+$: 269.0562; found: 269.0567.

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