Delipidated HSA (~99%) and HGG (99%) were obtained from Sigma. Aqueous HSA and HGG solutions (0.1 mg mL^{-1}) were adsorbed to the DPPC/DLPC films at 23°C by placing a sufficiently large drop of the protein solution to cover a surface of approximately 1 cm^2. After 15 min, the drop was blown off of the surface by using $N_{2(g)}$.

Au nanoparticles were prepared by the citrate reduction of $HAuCl_4$ (Aldrich).[23] A drop of the 10 nM Au-colloid solution was deposited on the protein-covered monolayer surface. After 5 min, the drop was blown off of the substrate surface. The surface was rinsed with a drop of H_2O and blown dry.

AFM images were acquired in air (relative humidity = 25–30%, T = 21–24°C) by using the tapping mode of a Nanoscope IIIa-MultiMode AFM (Digital Instruments) and etched Si cantilevers (resonance frequency = ~300 kHz, spring constant ~42 N m^{-1}). A cantilever-oscillation amplitude of 60–65 mV and an oscillation damping of 15–25% were used.

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[20] As a result of AFM tip effects and changes in the protein conformation that occur upon adsorption and air drying, other HGG orientations are possible. For these same reasons, it was impossible to estimate the depth of HSA penetration into the lipid domains.
[21] HGG can bind to Au through the asparagine subunits of its antigen-binding fragments or through the many S–S bonds that link its polypeptide chains.[17]
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Topochemical Polymerization of 7,7,8,8-Tetrakis(methoxycarbonyl)quinodimethane

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Topochemical polymerization, where the symmetry of the crystal lattice of the monomer is retained after polymerization, leads to a polymer with a highly controlled chemical structure because of the structural restraint imposed by the crystal lattice. This method is promising from the viewpoint of polymer structure control. However, monomers that can be polymerized topochemically are still limited because of the difficulties involved in controlling and predicting their crystal structures. Hasegawa reported topochemical polymerization reactions of 2,5-distyrylpyradine derivatives and related compounds and named them "four-centered photopolymerizations".[1] Topochemical polymerizations of diacetylene derivatives were first reported by Wegner[2] and afterwards a large number of diacetylene derivatives[3] and triacetylene derivatives[4] were prepared and their corresponding polymers were investigated and found to have interesting optical and electronic properties.[5] More recently, Matsumoto et al. found that polymerization reactions of derivatives of muconic acid and derivatives of sorbic acid proceed topochemically.[6] They determined several parameters for the molecular stacking of the diene moieties, and explained the relationship between the topochemical polymerization and monomer packing in crystals for diene monomers.[6] Herein we report that the conjugated monomer 7,7,8,8-tetrakis(methoxycarbonyl)quinodimethane (**1**) can be polymerized topochemically.

The monomer **1** was originally synthesized by Acker and Hertler.[7] They briefly described its properties and noted that it oligomerized on heating or on leaving it to stand at room temperature in diffuse light to give pink materials which were insoluble in common organic solvents. Later, Iwatsuki and Itoh,[8] and Hall and Bentley[9] independently reported the polymerization behavior of **1** in solution. However, the polymer products of **1** were not given much attention and not well characterized because of their insolubility. These factors gave us an indication that **1** may undergo topochemical polymerization (Scheme 1).

The monomer **1** was prepared by a new synthetic route. Knoevenagel condensation of 1,4-cyclohexanedione with methyl malonate using titanium tetrachloride and pyridine as a dehydrating system afforded 1,4-[bis(methoxycarbonyl)-

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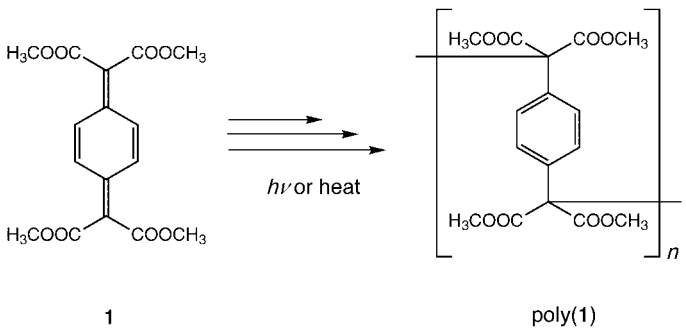

1 poly(1)

Scheme 1. Polymerization of **1**

methylene]cyclohexane (**2**) (59% yield).[10] Oxidation of **2** with activated manganese dioxide in refluxing benzene gave **1** (16% yield). Recrystallization of **1** from *n*-hexane afforded a mixture of two crystal forms, yellow prisms and yellow needles, which indicates that the organic crystals are polymorphic. After many trials to prepare each crystal form separately, we found that recrystallization from chloroform/*n*-hexane (1/3 v/v) yields yellow prisms (**1a**) exclusively and recrystallization from methanol gives yellow needles (**1b**). The two forms of **1** were each subjected to polymerization by irradiation by using a high-pressure Hg lamp at room temperature, or by heating in the dark. When the crystals of **1a** were exposed to UV light at 34°C, or heated at 60°C for 3 h in vacuo, insoluble polymers (poly(**1a**)) formed as off-white crystal-like solids in quantitative and 47% yields, respectively. In contrast, **1b** did not polymerize under either polymerization conditions and **1b** was recovered quantitatively (Table 1) after 6 hours.

Table 1. Thermal polymerization and photopolymerization of **1a** and **1b** in the solid state under vacuum, and thermal polymerization of **1** in benzene.

Entry	Compound	Amount [mg]	Light source	T [°C]	t [h]	Conv. [%]
1	**1a**	52.7	Hg lamp	34	3	100
2	**1a**	54.3	dark,	60	3	47
3	**1b**	23.5	Hg lamp	34	6	0
4	**1b**	22.2	dark	60	6	0
5	**1**[a]	418.9	dark	60	50	13.3

[a] Solution polymerization in benzene, 10 mL; AIBN, 13.5 mg.

The resulting polymers from **1a** were only characterized by IR spectroscopy, elemental analysis, and powder XRD, because of their insolubility in common organic solvents.

A characteristic absorption band at 1540 cm^{-1} assigned to the exocyclic conjugated carbon–carbon double bond of **1a** was absent in the IR spectrum of poly(**1a**), signals arising from carbon-carbon double bonds of the ring were observed at 1492 and 1411 cm^{-1} and a signal arising from out-of-plane deformation of the *para* disubstituted benzene, characteristic of a two-adjacent-hydrogen system, was observed at 811 cm^{-1}.[11] Moreover, the spectrum was identical to that obtained in the solution polymerization of **1** in benzene initiated by 2,2′-azobis[(2-methyl)propanenitrile] (AIBN, Table 1, entry 5). It is well established that polymerization reactions of substituted quinodimethane molecules occur at the disubstituted *exo* methylene carbon atoms with the formation of the corresponding stable aromatic structure.[12] Therefore, the spectrum change observed in the solid-state polymerization of **1a** strongly supports the theory that the reaction of **1a** proceeds with a conventional polymerization mode as observed for substituted quinodimethane molecules.[12] The powder XRD patterns of monomer **1a**, the reaction mixture at 36% conversion, poly(**1a**) obtained by solid state polymerization, and poly(**1**) obtained by solution polymerization are shown in Figure 1.

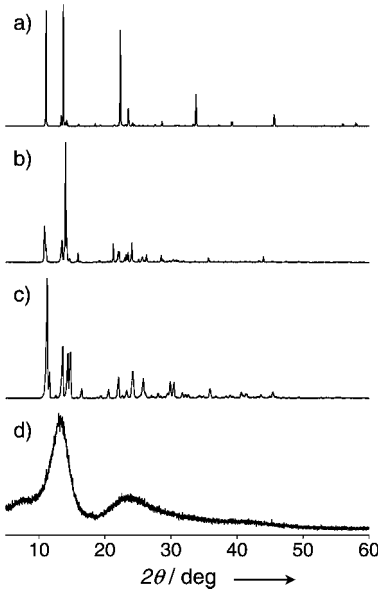

Figure 1. Powder X-ray diffraction patterns of a) monomer **1a**, b) reaction mixture at 36% conversion, c) poly(**1a**) obtained by solid-state polymerization (100% conversion), and d) poly(**1**) obtained by solution polymerization.

The very sharp diffraction patterns of the reaction mixture at 36% conversion, and of poly(**1a**) obtained from the solid-state reaction indicate that **1a** shows no loss of crystallinity during and after completion of the polymerization. Furthermore, signal positions arising from monomer **1a** are in fairly good agreement with those of poly(**1a**). The powder XRD pattern of poly(**1a**) obtained from the solid-state polymerization product is significantly different from that obtained from the solution polymerization product. These points indicate that the polymerization of **1a** proceeds topochemically. To clarify the steric requirement of the topochemical polymerization of the quinodimethane group and the drastic differences between the abilities of **1a** and **1b** to undergo polymerization, we investigated the crystal structures of both forms by X-ray crystallography (Figure 2).[13]

In the crystal structures of **1a** and **1b**, both polymorphs construct a similar one-dimensional columnar structure by the stacking of the quinodimethane rings along the crystallographic *b* axis for **1a** and *c* axis for **1b**, (Figure 3). As the stacking axes are not perpendicular to the molecular plane of the quinodimethane rings, we examined the tilt angles, defined as the angle formed between the stacking axis and longer axis of the monomer molecule (θ_1), and the shorter axis of the monomer molecule (θ_2). In the case of **1a**, θ_1 and θ_2 are

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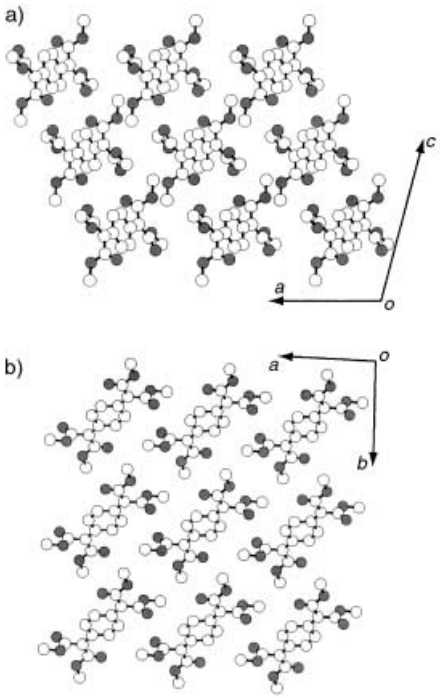

Figure 2. Crystal structures of a) **1a** viewed from the crystallographic *b* axis and b) **1b** viewed from the crystallographic *c* axis. Hydrogen atoms are omitted for clarity. Open and filled circles represent carbon and oxygen atoms, respectively.

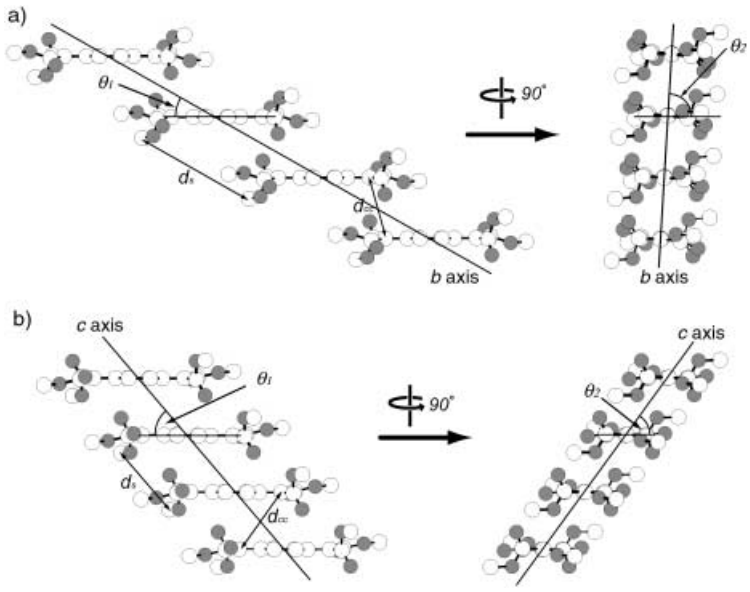

Figure 3. Geometries of **1** in the columns of a) **1a** and b) **1b** viewed from the direction parallel to the quinodimethane plane. Open and filled circles represent carbon and oxygen atoms, respectively.

30° and 89°, respectively. As a consequence of the larger θ_1 value in **1a**, the distance between equivalent atoms in the stacked monomers ($d_s = 7.6$ Å, Figure 3), and the distances between the reacting exomethylene carbon atoms ($d_{cc} = 3.9$ Å) are elongated. The latter value is similar to those found in the topochemical polymerizations of diacetylene and diene derivatives.[3] The former value can be compared to the translational distance for topochemical 1,6-polymerization of triacetylene derivatives (7.4 Å).[4] From the above points, we conclude that the polymerization reaction occurs along the columnar axis.

The **1b** form has offset stacking of the quinodimethane rings giving values of θ_1 and θ_2 as 55° and 62°, respectively. This gives a shorter stacking distance (d_s) between the quinodimethane moieties ($d_s = 5.3$ Å), and a longer intermolecular distance between the exomethylene carbon atoms ($d_{cc} = 5.0$ Å) than in **1a**. The difference in the polymerization reactivity between **1a** and **1b** indicates that the packing mode of molecules in the crystals significantly affects the polymerization reactivity in the solid state.

In conclusion, we describe the first example of the topochemical polymerization of the quinodimethane-type monomer, and compare the crystal structures of the reactive **1a** polymorph and the non-reactive **1b** polymorph. Detailed studies on the crystal structures and polymerization reactivities of other substituted quinodimethanes are now in progress.

Experimental Section

2: Titanium tetrachloride (20 mL, 183 mmol) in carbon tetrachloride (33 mL) was added dropwise under nitrogen to dry stirred THF (220 mL) cooled in an ice bath. 1,4-Cyclohexanedione (2.28 g, 20.3 mmol) and dimethyl malonate (6.69 g, 50.6 mmol) were added to the yellow mixture. Pyridine (24 mL) in THF (26 mL) was added dropwise to the resulting brown suspension over 1 h, and the reaction mixture was stirred at room temperature for 3 days. Water (150 mL) and chloroform (100 mL) were added to the reaction mixture, then the organic layer was extracted with chloroform (5 × 100 mL). The combined organic fractions were successively washed with saturated aqueous sodium chloride solution (3 × 100 mL), saturated aqueous sodium bicarbonate solution (3 × 100 mL), and dried over anhydrous magnesium sulfate, filtered, and the solvent of the filtrate was evaporated under reduced pressure. The crude product was purified by column chromatography (SiO_2, chloroform/ethyl acetate (20/1 v/v)) followed by recrystallization from a mixture of benzene and hexane to give **2** as white needles (4.11 g, 59.4 %): m.p. 133–134 °C; IR (KBr): $\tilde{\nu} = 2960$ (CH), 1695 (C=O), 1603 (C=C), 1230 (C–O) cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$, TMS): $\delta = 3.78$ (s, 12 H, CH_3), 2.75 ppm (s, 8 H, CH_2); ^{13}C NMR (67.5 MHz, $CDCl_3$, TMS): $\delta = 165.5$ (C=O), 158.4 (=C<), 122.9 (=C<), 52.2 (CH_3), 29.4 ppm (CH_2); elemental analysis calcd (%) for $C_{16}H_{20}O_8$: H 5.92, C 56.47, O 37.61; found: H 5.87, C 55.87, O 38.26.

1: Compound **2** (344 mg, 1.01 mmol) was dissolved in benzene (50 mL) and this solution was added as one portion to activated manganese dioxide (4.09 g, 47.0 mmol) in benzene (300 mL) at reflux. After stirring for 1 min at reflux, the activated manganese dioxide was removed by filtration and the solvent of the filtrate was evaporated under reduced pressure. The crude yellow product was purified by column chromatography (SiO_2, chloroform) followed by recrystallization from hexane to give **1** (52.9 mg, 16 %) as a mixture of yellow prisms (**1a**) and yellow needles (**1b**). **1a**: m.p. ≈110 °C (it was difficult to determine the melting point clearly because of facile polymerization of **1a** at 110 °C), **1b**: m.p. 141.5–143 °C; IR (KBr): $\tilde{\nu} = 2912$ (CH), 1680 (C=O), 1543 (C=C), 1197 (C–O) cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$, TMS): $\delta = 7.45$ ppm (s, 4 H, CH), 3.86 ppm (s, 12 H, CH_3); ^{13}C NMR (67.5 MHz, $CDCl_3$, TMS): $\delta = 165.1$ (C=O), 139.2 (=C<), 130.1 (CH), 125.6 (=C<), 52.7 ppm (CH_3); elemental analysis calcd (%) for $C_{16}H_{16}O_8$: H 4.80, C 57.14, O 38.06; found: H 4.78, C 56.93, O 38.29.

Polymerization: A given amount of **1a** and **1b** (see Table 1) was put in a Pyrex ampoule, which was degassed under reduced pressure and then sealed. Thermal polymerization was carried out by setting the ampoule in an oil bath at 60 °C for a given time. The polymer yield was determined by

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gravimetrical analysis after removing the residual **1a** and **1b** with chloroform. Photopolymerization was carried out at 34 °C in vacuo under UV irradiation by using a high-pressure mercury lamp (Fuji Glass Work Type BH-400, 400 W) at a distance of 12 cm. Poly(**1a**): IR (KBr): $\tilde{\nu}$ = 2914 (CH), 1706 (C=O), 1492 (C=C), 1411 (C=C), 1218 (C–O), 811 (CH) cm^{-1}; powder XRD ($Cu_{K\alpha_1}$/40 kV/150 mV, 2θ (relative intensity %): 11.24 (100), 11.62 (23), 13.60 (44), 14.38 (38), 14.78 (39), 16.46 (8), 20.56 (8), 22.06 (18), 23.30 (7), 24.18 (23), 25.80 (17), 29.90 (14), 30.44 (14), 35.94 (8), 40.66 (5), 45.42 (5); elemental analysis calcd (%) for $C_{16}H_{16}O_8$: H 4.80, C 57.14, O 38.06, found: H 4.76, C 56.99, O 38.25.

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[13] Crystal structure data for **1a** (single crystal from chloroform/hexane): formula $C_8H_8O_4$, M_r = 168.15, crystal dimensions 0.50 × 0.30 × 0.30 mm, monoclinic, space group $P2_1/n$ (no. 14), a = 8.6787(7), b = 7.5719(7), c = 12.761(1) Å, β = 105.193(2)°, V = 809.2(1) Å^3, Z = 4, ρ_{calcd} = 1.380 g cm^{-3}, $2\theta_{max}$ = 55.0°, Rigaku RAXIS-RAPID Imaging Plate diffractometer ($Mo_{K\alpha}$, λ = 0.71069 Å, graphite monochromator), ω scans, T = 303 K, 1828 measured reflections, all 1477 independent reflections used in the refinement, Lorenz and polarization factors were applied, μ = 1.12 cm^{-1}. Structure solution and refinement: direct methods (SIR92), full-matrix least-squares refinement of F^2, 109 parameters, all non-hydrogen atoms were refined anisotropically, and hydrogen atoms were located in the ideal positions without further refinement, R_1 = 0.046, R = 0.106, Rw = 0.133, GOF = 1.273, $\Delta\rho_{max}$ = 0.19 e Å^{-3}, $\Delta\rho_{min}$ = −0.25 e Å^{-3}. Crystal structure data for **1b** (single crystal from methanol): formula $C_8H_8O_4$, M = 168.15, crystal dimensions 2.00 × 0.40 × 0.10 mm, triclinic, space group $P\bar{1}$ (no. 2), a = 8.6023(4), b = 8.889(2), c = 5.2870(6) Å, α = 96.305(4), β = 105.636(5), γ = 87.323(8)°, V = 386.87(9) Å^3, Z = 2, ρ_{calcd} = 1.443 g cm^{-3}, $2\theta_{max}$ = 54.9°, Rigaku RAXIS-RAPID Imaging Plate diffractometer ($Mo_{K\alpha}$, λ = 0.71069 Å, graphite monochromator), ω scans, T = 303 K, 1711 measured reflections, all 1360 independent reflections used in the refinement, Lorenz and polarization factors were applied, μ = 1.12 cm^{-1}. Structure solution and refinement: direct methods (SIR92), full-matrix least-squares refinement of F^2, 109 parameters, all non-hydrogen atoms were refined anisotropically, and hydrogen atoms were located in the ideal positions without further refinement, R_1 = 0.062, R = 0.131, Rw = 0.183, GOF = 1.822, $\Delta\rho_{max}$ = 0.30 e Å^{-3}, $\Delta\rho_{min}$ = −0.33 e Å^{-3}. CCDC-182493 (**1a**) and CCDC-182492 (**1b**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

Spherical Homoaromaticity**

Zhongfang Chen, Haijun Jiao, Andreas Hirsch,* and Paul von Ragué Schleyer*

Since aromaticity[1] is not confined only to planar rings but also exists in three-dimensional systems,[2] the same should be true of homoaromaticity.[3–5] Although the $4N+2$ Hückel electron-counting rule is defined for planar systems it has been applied to rationalize the properties of three-dimensional homoaromatic systems.[5] Recently, the $2(N+1)^2$ counterpart of the Hückel rule[6] has been extended successfully[2e,7,8] to the aromaticity of three-dimensional delocalized systems with near spherical geometries: fullerenes, hydrogen and lithium clusters, as well as some well-known *closo*-boranes and Zintl ions. It was found that the highest degree of aromaticity can only be achieved in systems with fully filled valence shells. We now present new conceptual applications of this electron-counting rule to three-dimensional homoaromatic systems with cubane, dodecahedrane, and adamantane frameworks. Families of spherical homoaromatics with both two and eight mobile electrons (including several neutral

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