Supporting Information

Mechanistic Insights of Seeded Diamond Growth from Molecular Precursors

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1. Experimental section

1.1 Chemicals

Besides 2-azaadamantane, the reagents and solvents were commercially available and used without further purification. 1-adamantylamine (Sigma, 97%), adamantane (Sigma, ≥ 99%), tetracosane (TCI, > 99%), anisole (Merck, ≥99%), TLC aluminum sheets, silica gel 60 F254 (Merck), isopropyl alcohol (Fisher Chemical, 99.98%), dichloromethane (Sigma, 99%), CDCl3 (Sigma, 99.8 atom% D), silica 60 M 0.04–0.063 mm (Macherey), chloroform (fisher, ≥ 99.8%), ammonia (VWR chemicals, 28%), ethanol (Honeywell, ≥ 99.8%), methanol (VWR chemicals, HPLC grade), 2-azaadamantane-2-ol (TCI, > 98%).

1.1.1 Synthesis of 2-azaadamantane

Synthesis of 2-azaadamantane was performed according to the protocol of Betley et al.‡ 2-azaadamantane-2-ol (200 mg, 1.31 mmol, 1.00 equiv.) was dissolved in ethanol and degassed
with argon. Subsequently, an aqueous suspension of activated Raney-Nickel (2.80 mL) was added. The reaction mixture was flooded with H₂ (5 min) and stirred for 5 h at room temperature (1 atm). The resulting mixture was filtered over Celite and the residue was washed with ethanol. Remaining Raney-Nickel was quenched with diluted HCl solution. Removing the ethanol under reduced pressure yielded 165 mg (92%) 2-azaadamantane (colorless solid).

$^1$H NMR (300 MHz, CDCl₃): δ/ppm = 1.64-2.16 (m, 12 H), 3.16 (s, 2H).

MS (APCI) of C₉H₁₆N⁺ [M⁺H]⁺ = calc. 138.1

exp. 138.2

1.2 Sample preparation for the diamond anvil cell (DAC) experiments

151 mg of adamantylamine and 1.02 g of tetracosane were dissolved in dichloromethane under stirring. After the mixture was stirred for 30 min, the solvent was completely evaporated in the rotary evaporator. In this way, a mixture of adamantylamine and tetracosane with the molar ratio of 1:3 was obtained and used as the precursors for the HPHT experiments. The samples were loaded into the DAC gasket using a Tungsten-Carbide (WC) needle (TED PELLA, INC: 13562-10). After the sample was placed into the gasket hole, the DAC was closed to force the sample to completely fill the chamber.

1.3 HPHT experimental procedures

The pressure inside the DAC (Almax-easyLabs HeliosDAC) was generated using a gas membrane pressure inducer controlled using the Almax-easyLabs iGM software. The temperature inside the DAC was controlled with a resistive heating wire made of Nichrome surrounding one of the diamond anvils and the heating current was regulated by a control system connected to a
thermocouple in contact with the diamond anvil. The Inconel gaskets were drilled with 150 µm diameters using an electrode drilling machine (EDM) (Almax-easyLab) with a depth typically of 100 µm, the needles for drilling were made of WC. After drilling, the gaskets were ultra-sonicated for 5 min to remove any residue from the EDM needle or the gasket. The diamond anvils (Almax-easyLabs) were Type 1a (100)-oriented 16-sided with 500 µm cullet diameter. The pressure inside the sample chamber was monitored in situ using the fluorescence from ruby chips placed inside the sample chamber. The pressure was increased stepwise to around 14.0 GPa at room temperature. Then the temperature was increased to 450 °C and held for 2.5 h. After letting the DAC cooled to room temperature, the pressure was released and the product was extracted directly on a carbon film grid (Plano GmbH).

1.4 General procedure for pyrolysis experiments:

The samples (adamantane, 1-adamantylamine, 2-azaadamantane, tetracosane, or a mixture of adamantane/1-adamantylamine/2-azaadamantane and tetracosane) were loaded in flame-dried borosilicate glass ampoule. The ampoules were evacuated in high vacuum (10⁻³ mbar), sealed and heated to 380, 400, 420, 450 or 470 °C in 1 h and kept at this temperature for 2.5 h or 5 h. After cooling to room temperature, the ampoules were opened. Before analysis, amine containing samples were separated using TLC. Samples without amine function were filtered over silica (0.5 × 3 cm, CHCl₃).

2. Characterization methods

2.1 Nuclear magnetic resonance (NMR) spectroscopy

NMR spectra were recorded on a BRUKER AVANCE 300 spectrometer using the remaining CHCl₃ signal (7.26 ppm) in CDCl₃ solvent as reference at 298 K. The data was analyzed with MestReNova.
2.2 Gas chromatography-mass spectrometry (GC-MS)

Gas chromatography-mass spectrometry (GC-MS) was performed on a Shimadzu GC-2010 plus gas chromatograph and QP2010 ultra mass spectrometer with fused silica column (7HG-G010-11, ZB-SMS, Phenomenex) using the following two programs: 1) Helium carrier gas, injection temperature 310 °C, detector temperature 310 °C, flow rate: 0.88 mL/min, start temperature 50 °C, heating rate 50 K/min, end temperature 310 °C for 10 min. 2) Helium carrier gas, injection temperature 310 °C, detector temperature 310 °C, flow rate: 0.88 mL/min, start temperature 50 °C (hold for 2 min), heating rate 6 K/min, end temperature 310 °C for 3 min. The data was analyzed with OpenChrom®.

2.3 Transmission electron microscopy (TEM)

The high resolution TEM images and electron diffraction were obtained with Field-emission transmission electron microscopy (FE-TEM, Tecnai G2 F20 U-TWIN). The grid was treated at 200 °C in air for 2 h before TEM measurement.

2.4 In situ Raman characterization

The in situ Raman imaging is conducted using a home-built confocal microscope with 532 nm excitation laser (LaserQuantum Tau532) typically operating at 100mW output power focused onto the sample using a 10x Mitutoyo air objective with long working distance. The laser power into the sample was typically 5 mW (measured using PM100D ThorLabs Digital Optical and Energy Power Meter and ThorLabs S121C Standard Photodiode Power Sensor) and we note here that 5 mW power is not strong enough to cause photothermal damage to the TC or to the synthesized nanodiamonds. Raman signal from the sample was analyzed using a grating spectrometer
2.5 Thin-layer chromatography-mass spectrometry (TLC-MS)

Selected spots of the TLC plate were directly analyzed by APCI-MS (atmospheric pressure chemical ionization-mass spectrometry) using the TLC plate reader “Plate Express” and the “expression L” mass spectrometer from Advion.

3. Experimental results

3.1 Pyrolysis experiment of 1-adamantylamine

The glass ampoule was loaded with 1-adamantylamine (1.90 mg, 12.56 µmol) and treated according to the general procedure (section 1.4, 2.5 h). The pyrolysate was obtained as a colorless solid. The product was subjected to NMR analysis with tetracosane (2.30 mg, 6.78 µmol) as an internal standard (Figure S1). The terminal C–H of 1-adamantylamine were integrated with the internal standard. NMR analysis showed, that 93% of the 1-adamantylamine stayed intact.
Figure S1: $^1$H-NMR spectrum of 1-adamantylamine after thermal treatment. The product was subjected to NMR analysis with tetracosane (2.30 mg, 6.78 μmol) as an internal standard at 298 K. The stability was calculated referring to the integrals of the signals of CH$_3$ (TC, 0.89 ppm) and bridgehead CH (AdNH$_2$, 2.07 ppm).

3.2 Pyrolysis experiment of adamantane

The glass ampoule was loaded with adamantane (12.1 mg) and treated according to the general procedure (section 1.4, 2.5 h). The pyrolysate was obtained as a colorless solid and subjected to NMR analysis with an internal anisole standard (9.6 mg, 88.86 μmol). Integration of the terminal C–H of adamantane showed a stability of 100% during pyrolysis (Figure S2).
Figure S2: $^1$H-NMR spectrum of adamantane after thermal treatment. The product (12.1 mg, 88.82 µmol) was subjected to NMR analysis with anisole (9.6 mg, 88.82 µmol) as an internal standard at 298 K. The stability was calculated referring to the integrals of the signals of CH$_3$ (anisole, 3.84 ppm) and bridgehead CH (Ad, 1.90 ppm).

3.3 Pyrolysis experiment of 2-azaadamantane

The glass ampoule was loaded with 2-azaadamantane (4.30 mg, 31.1 µmol) and treated according to the general procedure (section 1.4, 2.5 h). The pyrolysate was subjected to NMR analysis with an internal anisole standard (5.76 mg, 53.3 µmol). Integration of the N–C–H of 2-azaadamantane showed a stability of 62% during pyrolysis (Figure S3).
Figure S3: $^1$H-NMR spectrum of 2-azaadamantane after thermal treatment. The product (4.30 mg, 31.3 µmol) was subjected to NMR analysis with anisole (5.76 mg, 53.3 µmol) as an internal standard at 298 K. The stability was calculated referring to the integrals of the signals of CH$_3$ (anisole, 3.84 ppm) and bridgehead N-CH (Ad, 3.16 ppm).

3.4 Pyrolysis experiment of tetracosane

The glass ampoule was loaded with tetracosane (36.5 mg, 108 µmol) and treated according to the general procedure (section 1.4, 2.5, or 5 h). The pyrolysate was obtained as a brown volatile liquid and subjected to GC-MS analysis. The main fraction in the chromatogram is still unmodified tetracosane (Figure S4-6). Nevertheless, smaller and more volatile hydrocarbon species were also observed.
Figure S4: GC-MS analysis of TC after pyrolysis for 2.5 h at 380 °C (a), 400 °C (b) and 420 °C (c). GC-MS was conducted using program B.

Figure S5: Detailed GC-MS analysis of TC after pyrolysis for 2.5 h at 420 °C (program b). The results show the different alkane / olefin fragments.
3.5 Pyrolysis experiment of 1-adamantylamine/tetracosane mixture

The glass ampoule was loaded with 1-adamantylamine (2.9 mg, 19.1 μmol) and tetracosane (19.5 mg, 57.3 μmol) in a molar ratio of 1:3 and treated according to the general procedure (section 1.4, 2.5 h). The product mixture was separated on a silica TLC plate (4 × 9 cm) using CHCl₃/MeOH/NH₃(28%) (9/1.4/0.14) as an eluent, stained with iodine, and analyzed with TLC-MS. The main spot on the TLC plate is unmodified 1-adamantylamine (R_f = 0.48). Nevertheless, a mixture of methyl-1-adamantylamine, dimethyl-1-adamantylamine, and/or ethyl-1-adamantylamine were detected (R_f = 0.54) with APCI-MS (Figure S7). Each individual compound shows a characteristic mass spectrum with two mass peaks [M+H⁺] and [M+H⁺-NH₃].
Figure S7: APCI-MS spectra of AdNH\textsubscript{2}/TC mixture after pyrolysis treatment for 2.5 h at 450 °C. Separation of the mixture via TLC resulted in two spots. Spot a refers to the AdNH\textsubscript{2} seed with the characteristic mass peaks m/z = 152 ([151+H]\textsuperscript{+}) and m/z = 135 ([152-NH\textsubscript{3}]\textsuperscript{+}). Spot b refers to the alkylated species of AdNH\textsubscript{2} with the characteristic mass peaks of methyl-1-adamantylamine m/z = 166 ([M+H]\textsuperscript{+}) and m/z = 149 ([M-NH\textsubscript{3}]\textsuperscript{+}), ethyl-1-adamantylamine and/or dimethyl-1-adamantylamine m/z = 180 ([M+H]\textsuperscript{+}) and m/z = 163 ([M-NH\textsubscript{3}]\textsuperscript{+}).

### 3.6 Pyrolysis experiment of 2-azaadamantane/tetracosane mixture

The glass ampoule was loaded with 2-azaadamantane (4.5 mg, 32.8 μmol) and tetracosane (25.5 mg, 75.4 μmol) in a molar ratio of 1:2.3 and treated according to the general procedure (section 1.4, 2.5 h). The product mixture was separated on a silica TLC plate (4 × 9 cm) using CHCl\textsubscript{3}/MeOH/NH\textsubscript{3}(28%) (9/1.4/0.14) as an eluent, stained with iodine and analyzed with TLC-APCI-MS. The main spot on the TLC plate is unmodified 2-azaadamantane (R\textsubscript{f} = 0.40). Nevertheless, a mixture of several alkylated species (C2 – C11) were detected (Rf = 0.49) with APCI-MS (Figure S8).
3.7 Pyrolysis experiment of adamantane/tetracosane

The glass ampoule was loaded with Ad (7.0 mg, 51.4 μmol) and TC (19.1 mg, 56.5 μmol) in a molar ratio of 1:1.1 and treated according to the general procedure (section 1.4, 5 h). The product mixture was filtered over a silica column (0.5 × 3 cm, CHCl₃). A mixture of several alkylated (C₁ – C₉) Ad species was detected with GC-MS measurement in SIM mode ([M⁺]₁ = 135, [M⁺]₂ = 136) (Figure S9). The formation of the higher diamondoid diamantane (DA) could be discovered at a retention time (rt) of 21.12 min (Figure S10). The [M⁺] mass peak of DA was determined at 188 m/z (Figure S11).
Figure S9: SIM mode ([M']_1 = 135, [M']_2 = 136) GC-MS spectrum after filtration. Several alkylated species (C_1 – C_9) could be detected. Peak 2 corresponds to 1-ethyladamantane and peak 2' corresponds to 2-ethyladamantane.

Figure S10: GC-MS spectrum after filtration. Product mixture of alkylated adamantane species. The main compound is unmodified adamantane rt = 11.31 min. The peak at rt = 21.12 min might correspond to the higher diamondoid diamantane (DA).
Figure S11: Mass spectra acquired at rt = 21.12. The peak at m/z = 188 could be assigned to the molecule ion peak \([M^+]\) of diamantane (DA).

Figure S12: Pyrolysis of Ad/TC with different molar ratios (1:1.1, 1:2.2, 1:4.4).
3.8 *In Situ* HPHT experiments with DAC

![Graph showing Raman spectra before and after heating](image)

*Figure S13: Raman spectra before (a) and after (b) the heating cycle under high pressure.*

4. References

1. C. Kleinlein, A. J. Bendelsmith, S. Zheng and T. A. Betley, *Angew. Chemie Int. Ed.*, 2017, **56**, 12197–12201.