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Click Chemistry Produces Hyper-Cross-linked Polymers withTetrahedral Cores

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General Remarks

NMR spectroscopy

^{1}H NMR spectra were recorded on a *Bruker* AM 400 (400 MHz) spectrometer as solutions in $CDCl_3$. Chemical shifts are expressed in parts per million (ppm, δ) downfield from tetramethylsilane (TMS, δ = 0) and are referenced to $CHCl_3$ (7.26 ppm), as internal standard. All coupling constants are absolute values and *J* values are expressed in Hertz (Hz). The description of signals include: s = singlet, bs = broad singlet, d = doublet, m = multiplet, dd = doublet of doublets. The spectra were analyzed according to first order. ^{13}C NMR spectra were recorded on a *Bruker* AM 400 (100 MHz) spectrometer as solution in $CDCl_3$. Chemical shifts are expressed in parts per million (ppm, δ) downfield from tetramethylsilane (TMS, δ = 0) and are referenced to $CDCl_3$ (77.4 ppm).

Solid-state ^{13}C NMR

Solid-state ^{13}C NMR experiments were conducted on a widebore *Bruker* Avance spectrometer operating at a ^{13}C resonance frequency of 125 MHz (^{1}H resonance frequency of 500 MHz). The ^{13}C NMR spectra were acquired under magic angle spinning (MAS) at spinning speeds between 12.5 kHz and 25 kHz, with high-power ^{1}H decoupling of 80 kHz radiofrequency field strength, using a double-tuned (HX) or triple-tuned (HXY) MAS probe for 2.5 mm or 4 mm rotors, respectively. The ^{13}C signal was enhanced using a ramped cross-polarization (CP) from ^{1}H with a contact time of 1 ms, and a radiofrequency field strength of approximately 50 kHz. The signal was acquired for 20–40 ms with a recycle delay of 4 s, processed with 20-100 Hz line broadening, and referenced to a separate sample of adamantane (downfield resonance at 38.48 ppm). Approximately 1000–5000 scans were averaged.

DSC (Differential Scanning Calorimetry)

The dynamic differential scanning calorimetry was measured on a *METTLER Toledo* dsc 30, in a sealed 40 µL alumina vessel under oxygen atmosphere. The obtained data was analyzed electronically with the software program STAR ^{e}SW 8.10 and plotted in a diagram. The enthalpy changing ΔH [mW] was plotted against the temperature (25–500 °C) of the heating rate 10 K/min.

IR (infrared spectroscopy)

IR spectra were recorded with a FT-IR *Bruker* IFS 88 spectrometer with OPUS software. IR spectra were recorded using the attenuated total reflection technique (ATR). The deposit of the absorption band was given in wave numbers ν in cm^{-1}. The forms and intensities of the bands were characterized as follows: vs = very strong 0–10% T, s = strong 11–40% T, m = medium 41–70% T, w = weak 71–90% T, vw = very weak, 91–100% T, br = broad.

Elemental Analysis (EA)

The EA measurements were performed on an Elementar vario MICRO device using a Sartorius M2P precision balance. The following abbreviations were used: calcd. = calculated data, found = measured data.

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Reagents and solvents

Solvents, reagents and chemicals were purchased from Acros, ABCR, Alfa Aesar, Fluka, IRIS, Merck, Riedel-de-Haën or Sigma-Aldrich. Ethyl acetate, cyclohexane and dichloromethane were distilled from calcium hydride prior to use. All reactions involving moisture sensitive reactants were executed under an argon atmosphere using oven dried and/or flame dried glassware. Solvent mixtures are understood as volume/volume.

Gas sorption analysis

The surface areas and pore size distributions were measured by nitrogen adsorption and desorption at 77 K using either a *Micromeritics* ASAP 2020 volumetric adsorption apparatus. The surface areas were calculated in the relative pressure (p/p_0) range from 0.01 to 0.1. Pore size distributions and pore volumes were derived from the adsorption branches of the isotherms using the nonlocal density functional theory (NL-DFT) pore model for pillared clay with cylindrical pore geometry. Samples were degassed at 200 °C for 18 h under vacuum (10-5 bar) before analysis. Carbon dioxide isotherms were measured at 195 K and 298 K and up to 10 atm using a *Micromeritics* ASAP 2050 volumetric adsorption apparatus.

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Synthetic procedures

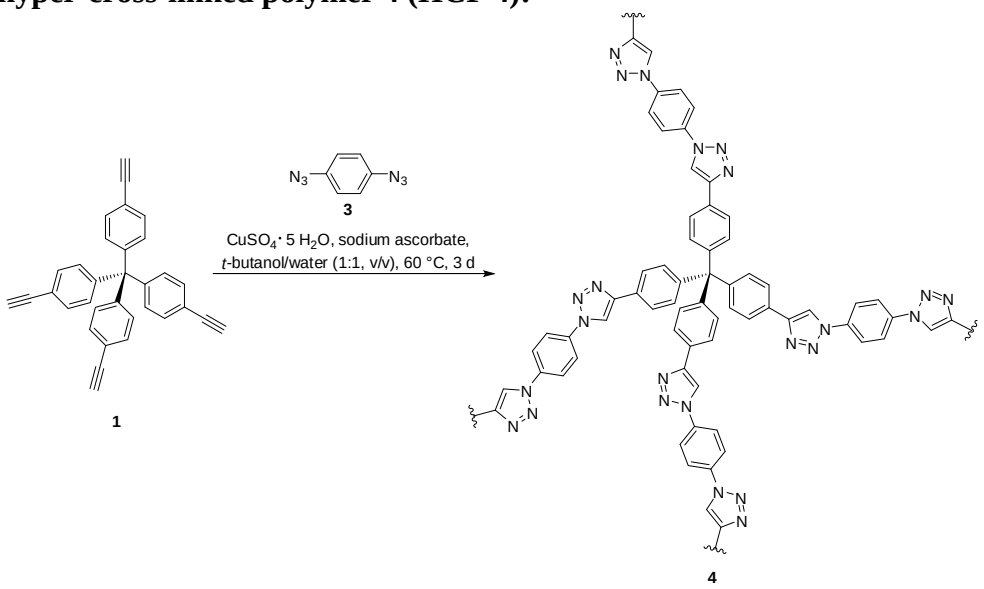
SAFETY STATEMENT: *1,4-diazidobenzene is potentially explosive. Due to high nitrogen content (ratio of carbon to nitrogen should be larger than 3:1) it should be handled with extraordinary care. All reactions and handlings should be performed behind a blast shield in a closed fume hood.*

ALL REACTIONS WERE PERFORMED BEHIND A BLAST SHIELD:

Synthesis of 1,4-diazidobenzene (3):

In a round bottomed flask 1.00 g (9.25 mmol, 1.00 equiv.) 1,4-diaminobenzene was suspended in 15 mL dry acetonitrile under argon atmosphere and cooled to 0 °C with an ice bath. To the stirred suspension, 4.9 mL (3.82 g, 37.0 mmol, 4.00 equiv.) *tert*-butylnitrite and 3.7 mL (3.20 g, 27.8 mmol, 3.00 equiv.) azidotrimethylsilane were slowly added. The reaction mixture was stirred for 2 h and allowed to warm to room temperature. Then, the volatiles were evaporated under reduced pressure. The crude product was purified by flash chromatography on silica gel using cyclohexane/ethyl acetate (20:1, v/v) as eluent. After purification, 0.720 g (4.50 mmol, 49%) 1,4-diazidobenzene (**3**) were obtained as a brown powder. The product was stored in a freezer at –20 °C. – Mp. 112 °C (decomposition). – R_f = 0.28 (cyclohexane/ethyl acetate 25:1, v/v). – ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.01 (s, 4 H, 2-*H*, 3-*H*) ppm. – ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 120.3 (+, *C*-2, *C*-3), 136.7 (C_q, *C*-1, *C*-4) ppm. – IR (ATR): $\tilde{\nu}$ = 3063 (vw), 2396 (vw), 2261 (vw), 2097 (m), 2096 (m), 1901 (w), 1497 (m), 1294 (w), 1272 (m), 1142 (w), 1125 (w), 964 (w), 779 (w), 578 (w), 526 (m), 511 (m) cm^{-1}.

Synthesis of hyper-cross-linked polymer 4 (HCP 4):



Typical procedure:

In a sealed reaction vessel, tetrakis(4-ethynylphenyl)methane (**1**, 60.0 mg, 144.1 µmol, 1.00 equiv.) was suspended in 6 mL *tert*-butanol/water (1:1, v:v). To this suspension, $CuSO_4$·5 H_2O (3.60 mg, 14.4 µmol, 0.10 equiv.), sodium ascorbate (5.70 mg, 28.8 µmol, 0.2 equiv.) and 1,4-diazidobenzene (**3**, 46.1 mg, 288.1 µmol, 2.00 equiv.) were added successively and the reaction mixture was heated for 72 h at 60 °C. After cooling to r.t., the formed precipitate was filtered off and extensively washed with chloroform and water. The obtained solid was then suspended in THF for four days – THF was removed and replaced every day. The solid was finally dried in vacuo at 100 °C for 72 h to yield 80.7 mg (76%) of HCP **4** as a brown powder.– EA ($C_{54}H_{40}N_{12}$): calcd. C 73.36, H 3.83, N 22.81; found C 67.20, H 4.03, N 20.11.

Scale-up reaction procedure:

In a 100 mL sealed tube, tetrakis(4-ethynylphenyl)methane (**1**, 690 mg, 1.66 mmol, 1.00 equiv.) was suspended in 70 mL *tert*-butanol/water (1:1, v:v). To this suspension $CuSO_4$·5 H_2O (1.65 g, 6.60 mmol, 4.00 equiv.), sodium ascorbate (2.62 g, 13.2 mmol, 8.00 equiv.) and 1,4-diazidobenzene (**3**, 0.53 g, 3.30 mmol, 2.00 equiv.) were added successively and the reaction mixture was heated for 21 d at 60 °C. Isolation and purification of the formed HCP was identical to the above mentioned procedure to yield 595 mg (49%) of HCP **4** as a brown powder.

Additional solid state ^{13}C NMR CP/MAS spectra:

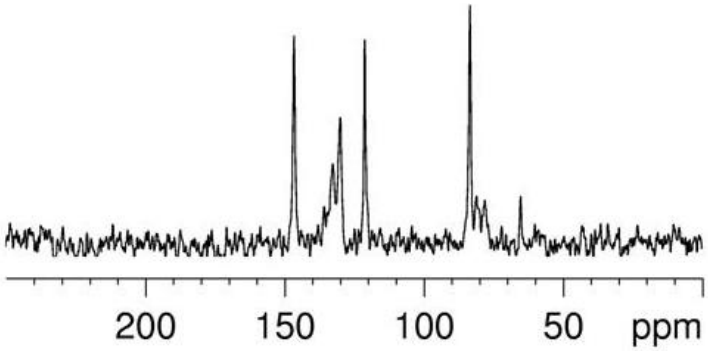


Figure S1: Solid-state ^{13}C NMR CP/MAS of compound **1**.

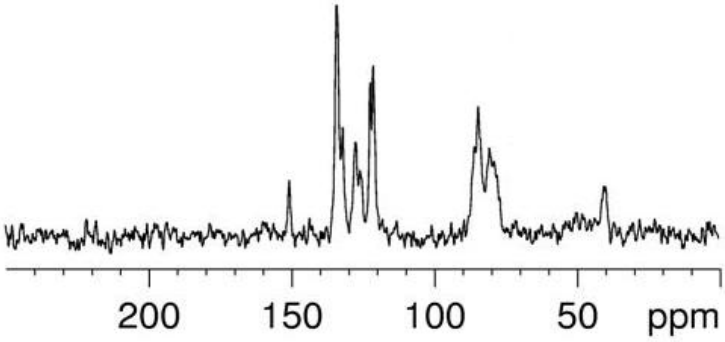


Figure S2: Solid-state ^{13}C NMR of compound **2**.

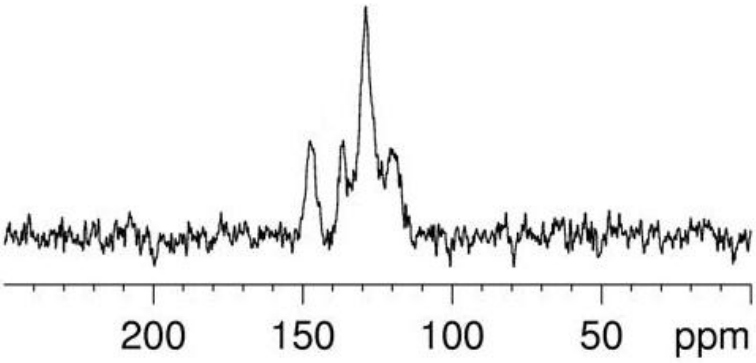


Figure S3: Solid-state ^{13}C NMR CP/MAS of compound **6**.

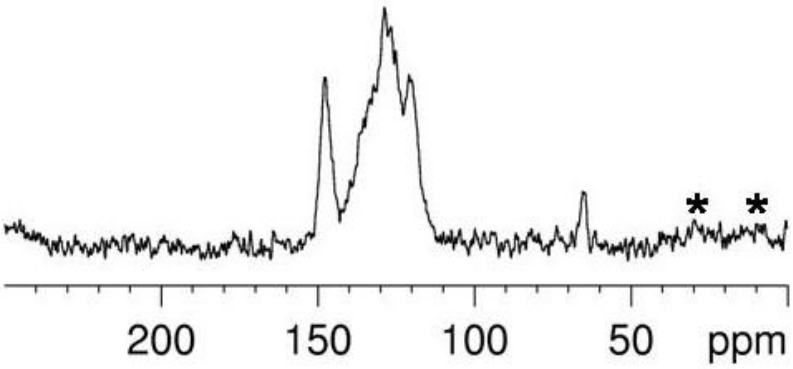


Figure S4: Solid-state ^{13}C NMR CP/MAS of Hyper Cross-linked Polymer **4**.

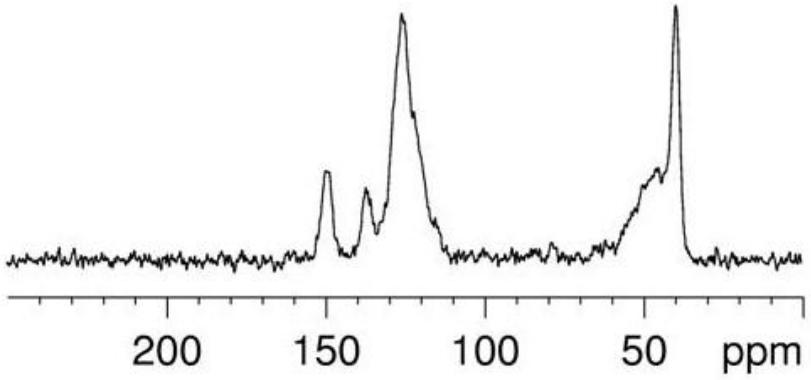


Figure S5: Solid-state ^{13}C NMR CP/MAS of Hyper Cross-linked Polymer **5**.

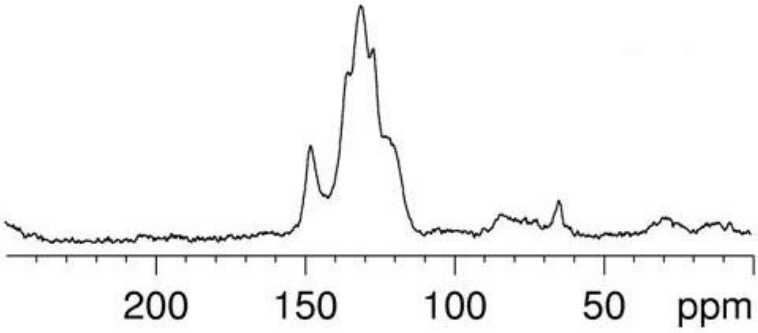


Figure S6: Solid-state ^{13}C NMR CP/MAS of inverted Hyper Cross-linked Polymer using tetrakis(4-azidophenyl)methane and 1,4-diethynylbenzene.

Table S1. Assignment of the solid-state ^{13}C NMR CP/MAS signals of HCPs **4** and **5** synthesized using click chemistry in comparison to the tetraalkyne derivatives **1** and **2**.

^{13}C chemical shift	assignment in tetraalkyne derivatives **1** and **2**	assignment in triazolyl bridged HCPs **4** and **5**
150ppm	aromatic (alpha-aliphatic)	triazol C4 aromatic (alpha-aliphatic)
135–140ppm		aromatic (alpha-N-triazol)
125–135ppm	aromatic (beta-ethynyl, beta-aliphatic)	aromatic beta-aliphatic, gamma-aliphatic, bridging phenyl)
118–122ppm	aromatic (alpha-ethynyl)	triazol C5
75–85ppm	ethynyl	
~65ppm	methane central atom	methane central atom
40–50ppm		adamantane

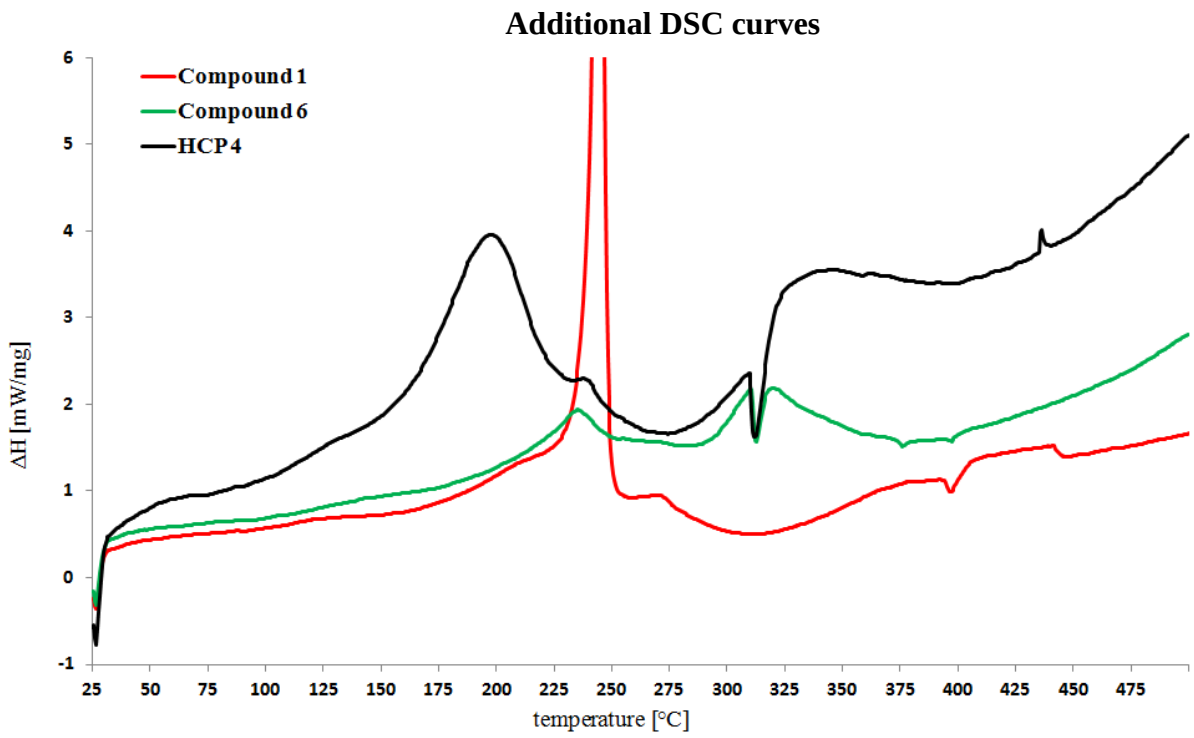


Figure S7: Overlay of measured DSC curves for the compounds **1** (red), **6** (green) and HCP **4** (black).

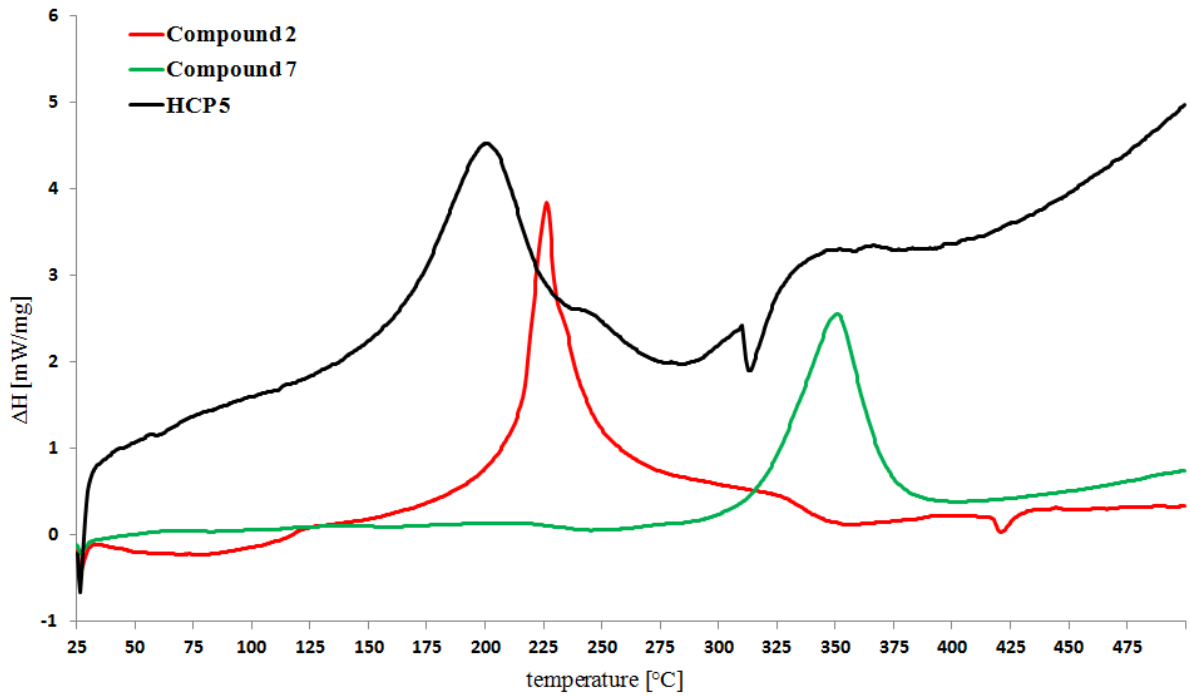


Figure S8: Overlay of measured DSC curves for the compounds **2** (red), **7** (green) and HCP **5** (black).

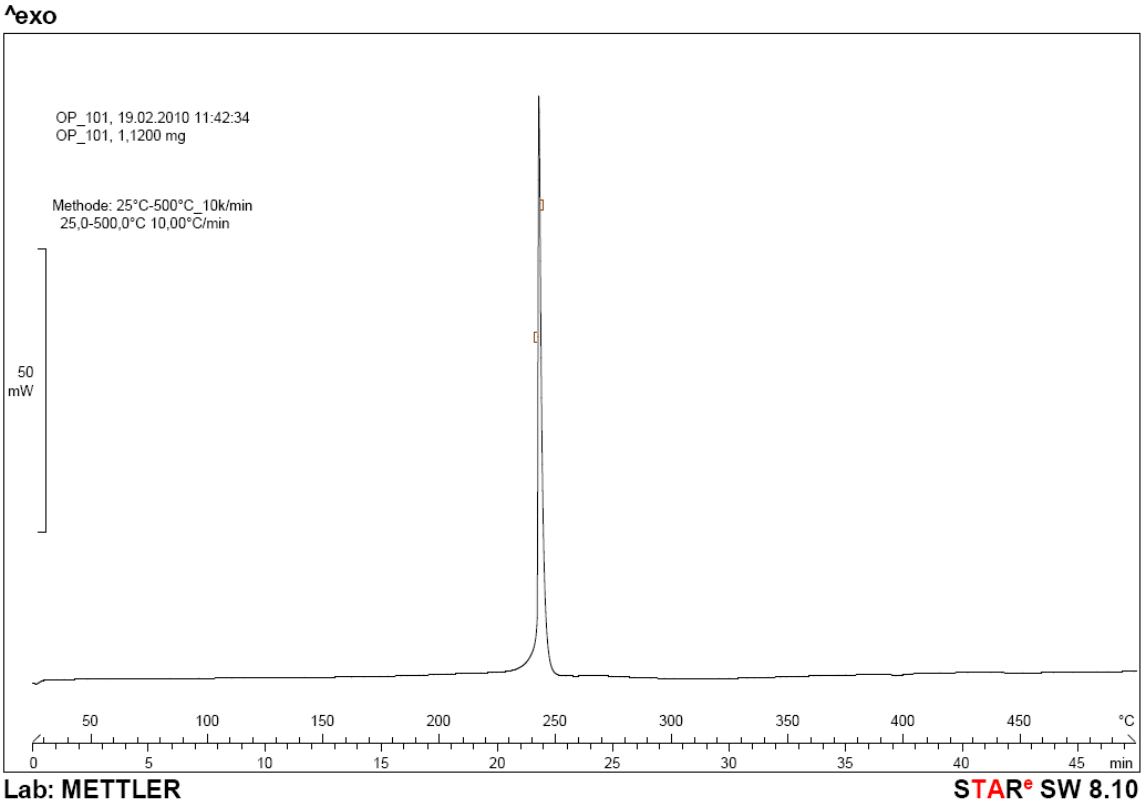


Figure S9: Single DSC curve for compound **1**.

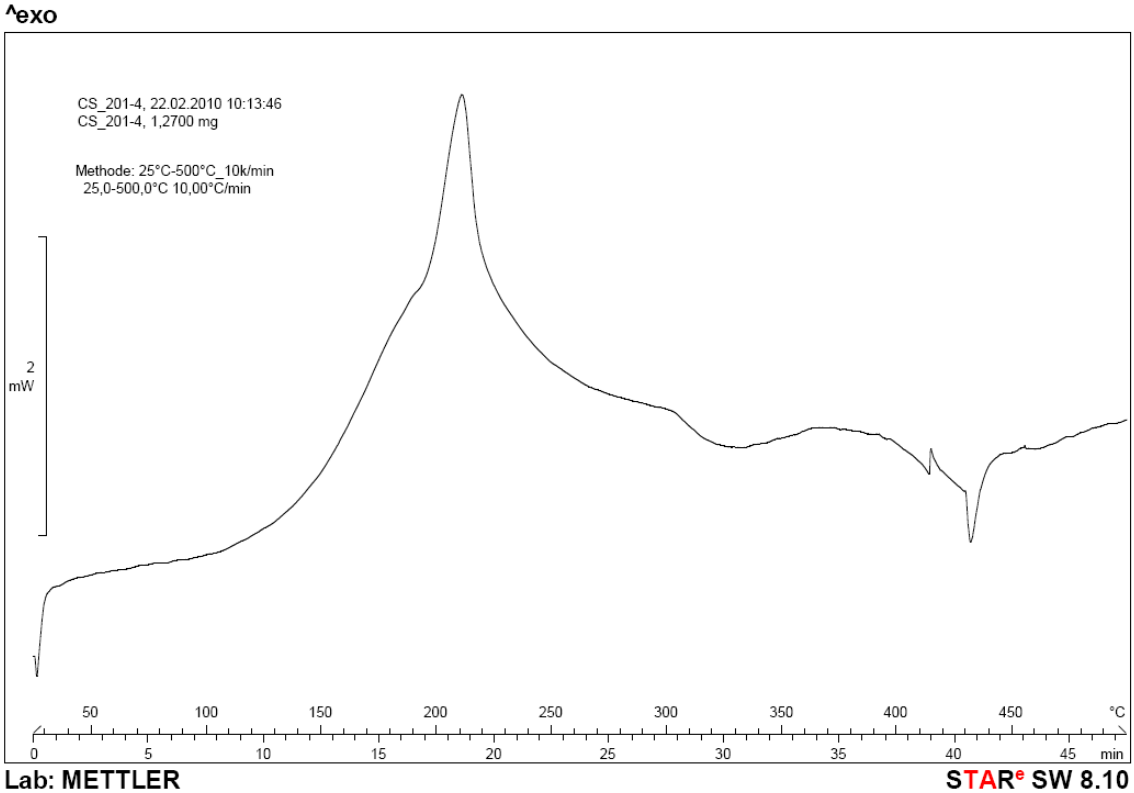


Figure S10: Single DSC curve for compound **2**.

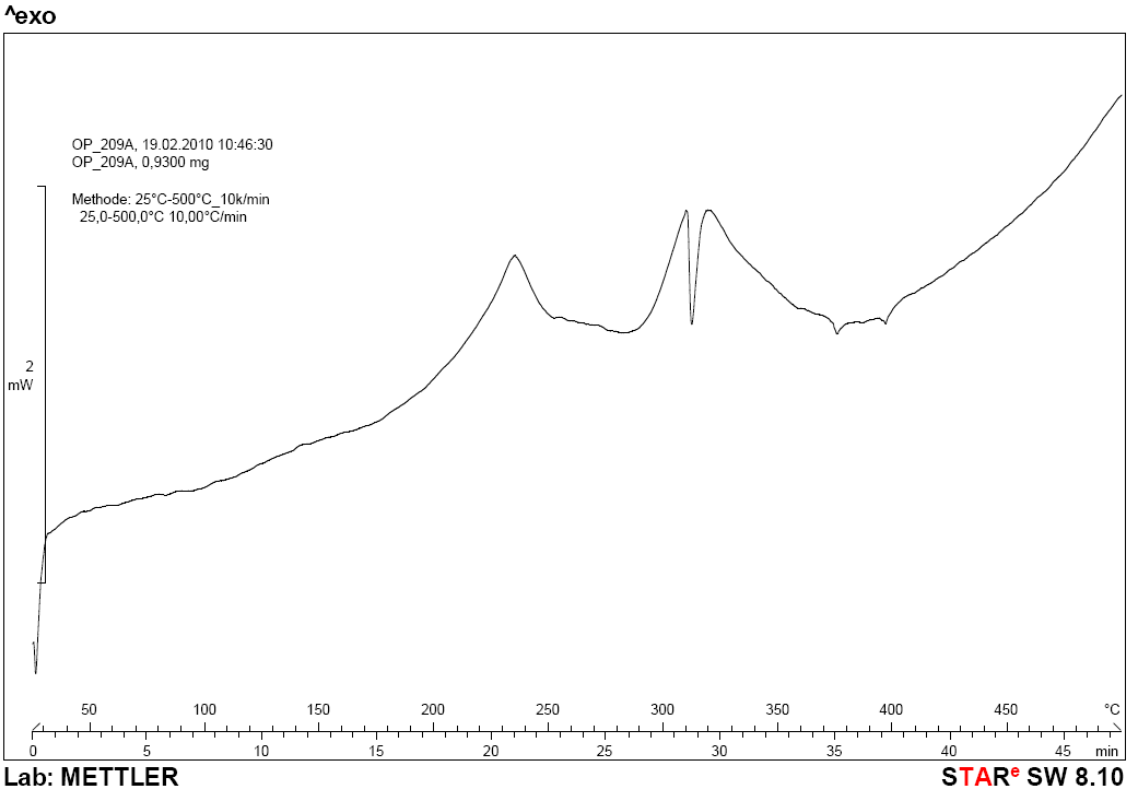


Figure S11: Single DSC curve for compound **6**.

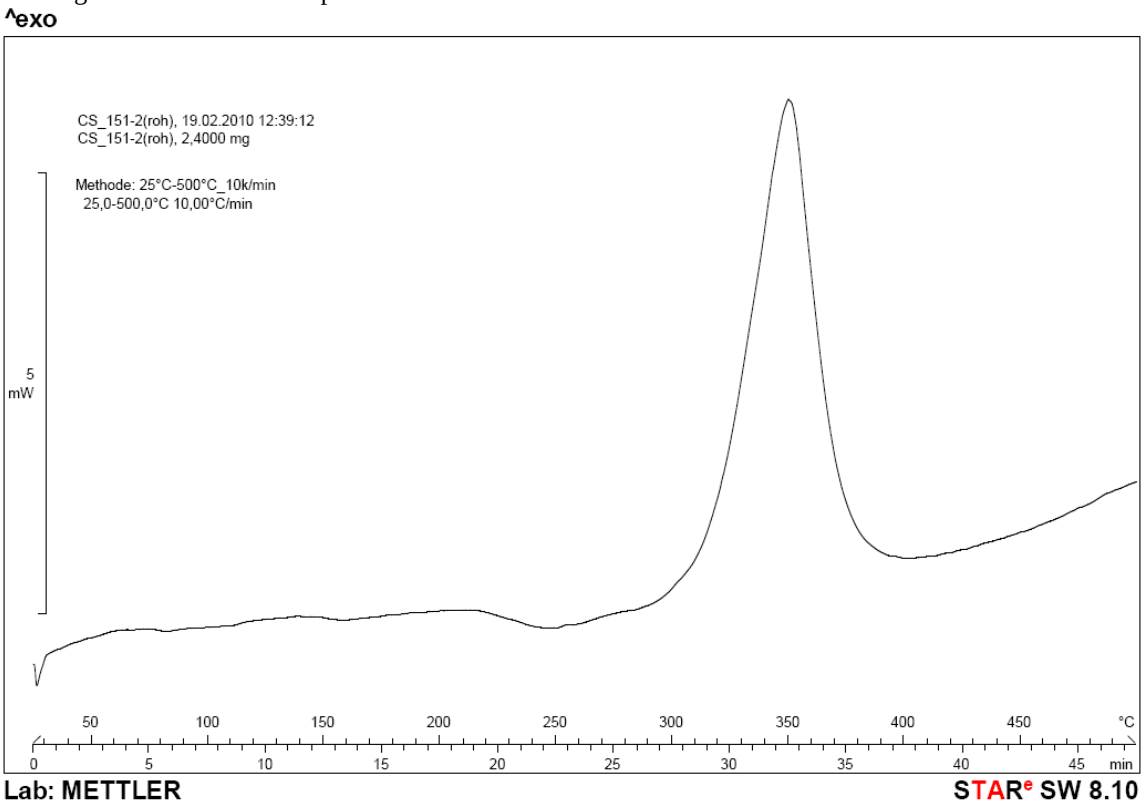


Figure S12: Single DSC curve for compound **7**.

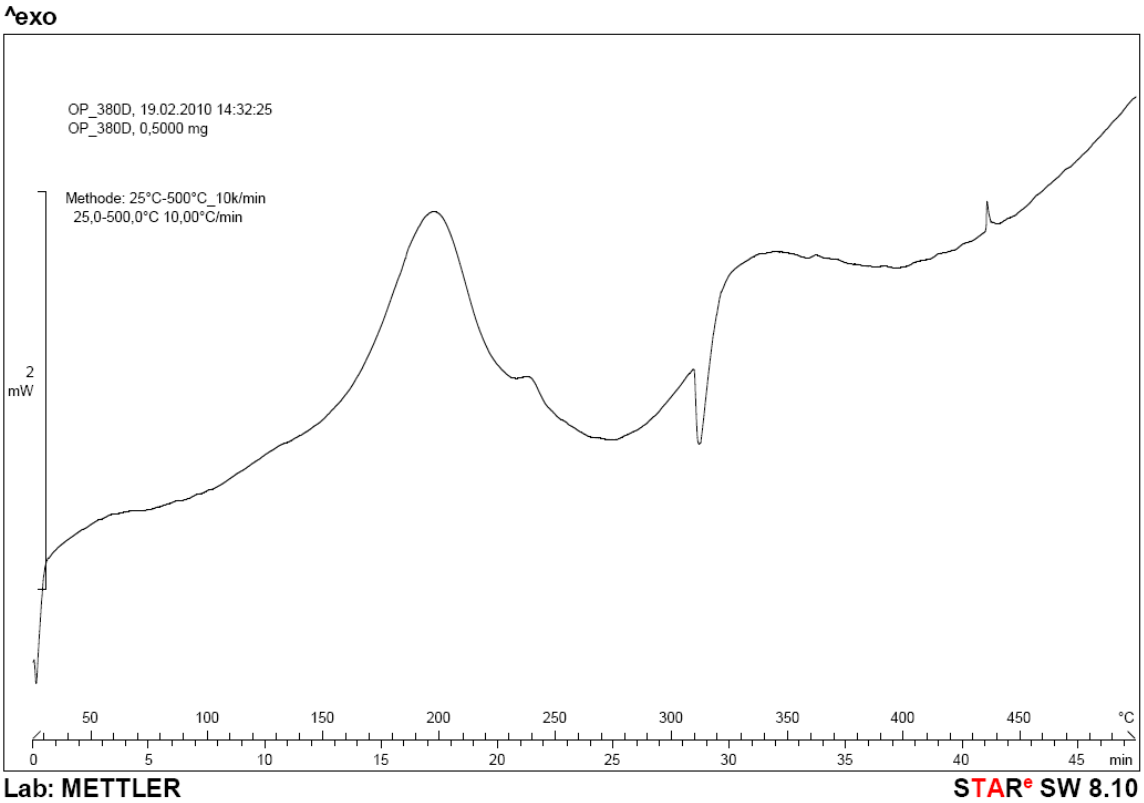


Figure S13: Single DSC curve for HCP **4**.

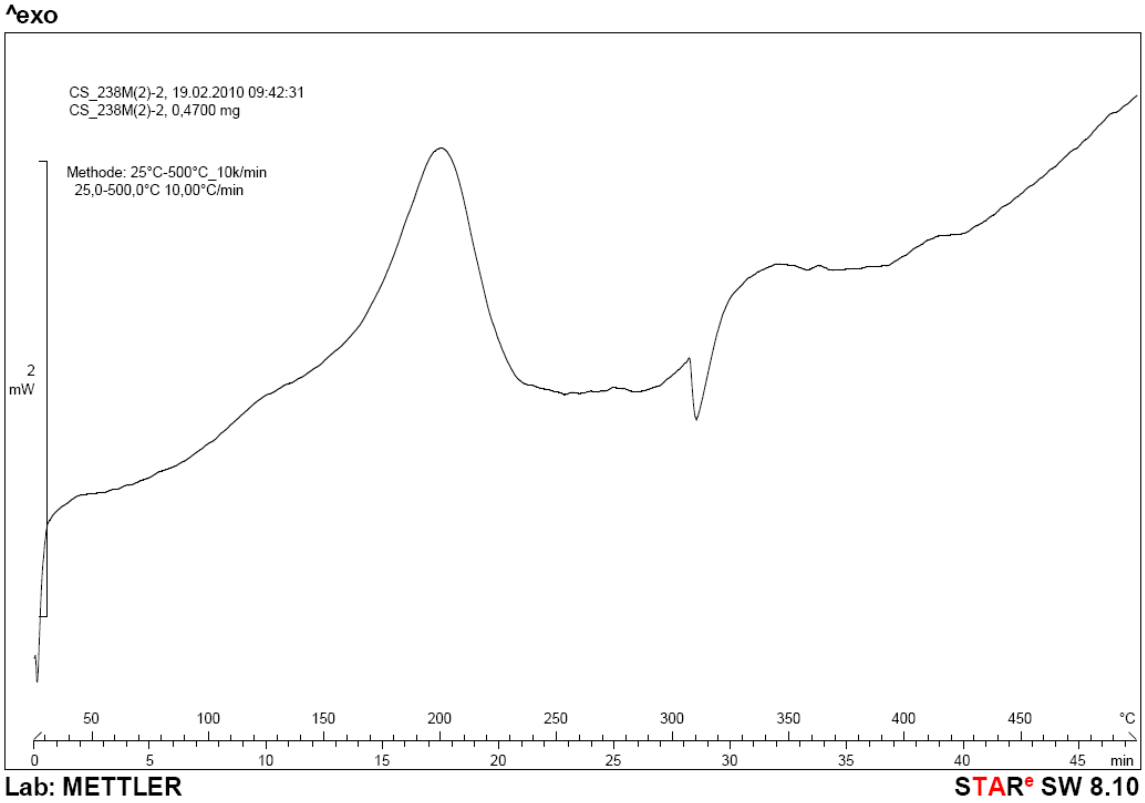


Figure S14: Single DSC curve for HCP **5**.