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Supporting Information

Sulfur-based hyper cross-linked polymers

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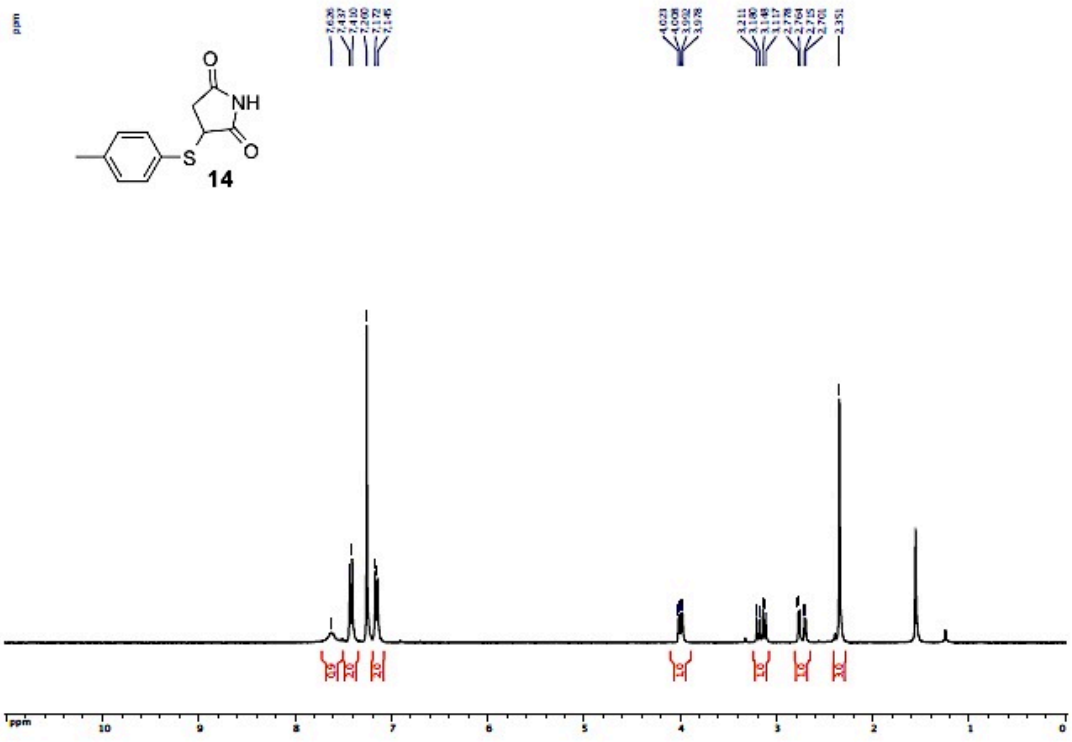
General Remarks

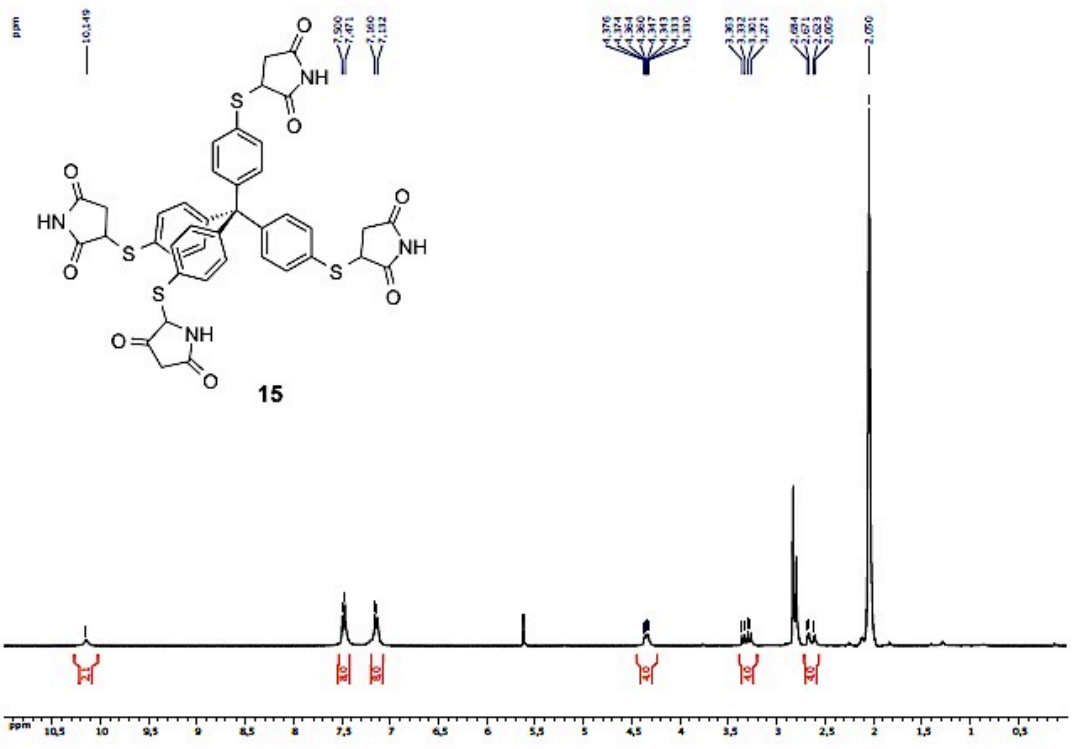
NMR spectra were recorded on a *Bruker* AM 300 (300 MHz) as solutions in $CDCl_3$. Chemical shifts are expressed in parts per million (ppm, δ) downfield from tetramethylsilane (TMS) and are referenced to $CHCl_3$ (7.26 ppm), as internal standard. The spectra were analysed according to first order. The solid-state NMR spectra were measured on a *Bruker Avance* 400 spectrometer operating at 100.6 MHz for ^{13}C NMR. The ^{13}C CP/MAS (Cross-Polarization with Magic Angle Spinning) experiments were carried out at MAS rates of 14 kHz using densely packed powders of the compounds in 4 mm ZrO_2 rotors. The ^{1}H $\Pi/_2$ pulse was 4 *m*s and decoupling was used during the acquisition. The Hartmann-Hahn condition was optimized with adamantane at a rotational speed of 5 kHz. All spectra were measured using a contact time of 1.5 ms and a relaxation delay of 10.0 s, and 6000 FIDs were accumulated. The dynamic differential scanning calorimetry (DSC) was measured on a *METTLER Toledo dsc 30*, in a sealed aluminium 40 μL pan under argon atmosphere. The obtained data were analysed 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 (−50°C to 250 °C) with a heating rate of 10°C/min. IR spectra were recorded with a *FT-IR Bruker IFS 88* spectrometer with OPUS software using the attenuated total reflection technique (ATR). The deposit of the absorption band was given in wave numbers *v* 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. MS (EI) (electron impact mass spectrometry) was performed by using a *Finnigan MAT 90* (*70 eV*). The EA measurements were performed on an *Elementar vario MICRO* device using a Sartorius M2P precision balance. The following abbreviations were used: calc. = calculated data, found = measured data. Gas adsorption isotherms were measured volumetrically using a surface analyser ThermoScientific Surfer Gas adsorption Porosimeter. A liquid nitrogen bath (77K) was used and the N_2 gas used was UHP grade. For measurement of the specific surface areas (S_{BET}, $m^2.g^{-1}$) the BET method was applied. For all isotherms plots, closed circles are used for adsorption data points and open circles are used to indicate desorption data points. The pore size distribution was obtained with the Horvath-Kawazoe model[1] for the microporous HCPs or the Cranston and Inkley model[2] for the mesoporous HCPs. Solvents, reagents and chemicals were purchased from Sigma-Aldrich, ABCR and Acros Organics. All solvents, reagents and chemicals were used as purchased unless stated otherwise. Tetrakis(4-thyilphenyl)methane **1**,[3] 1,4-benzenedithiol **3**,[4] 1,4-benzidinedithiol **5**,[4] 1,3,5-benzenetrithiol **7**[4] and N-arylbismaleimide linkers[5] were obtained according to literature procedures. All reagents and solvents were used as received.

^{1}H NMR Analysis

1) ^{1}H NMR of 3-(*p*-tolylthio)pyrrolidine-2,5-dione **14** in $CDCl_3$

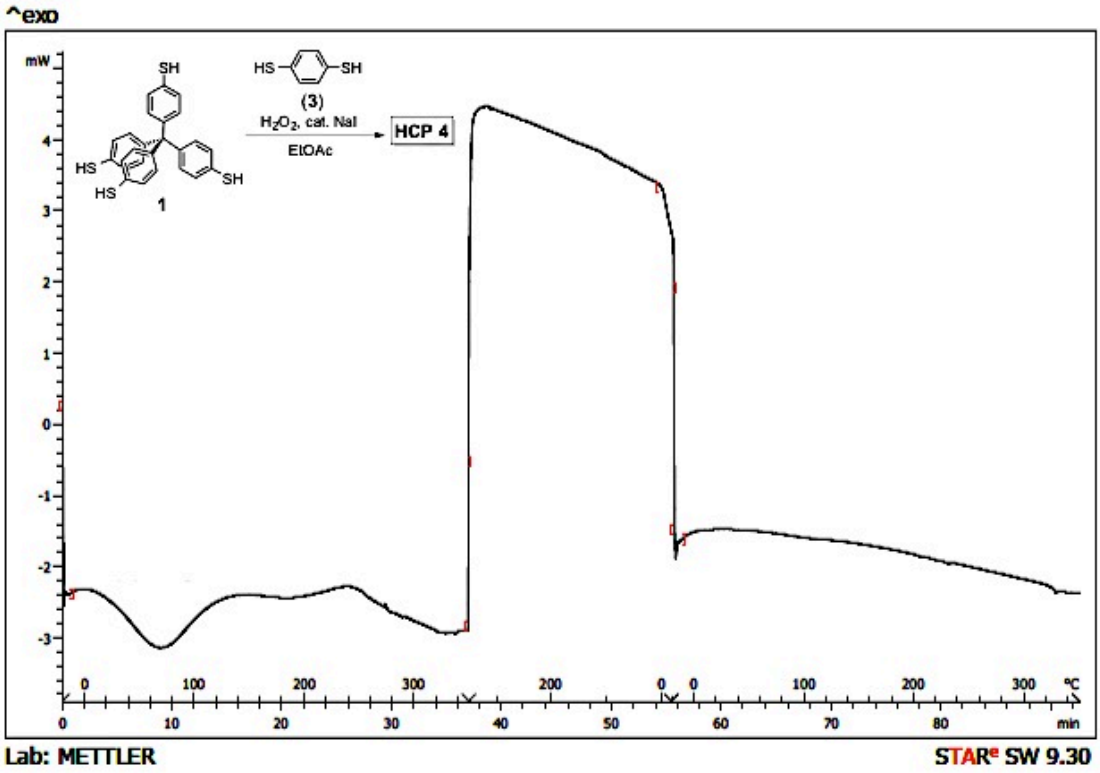


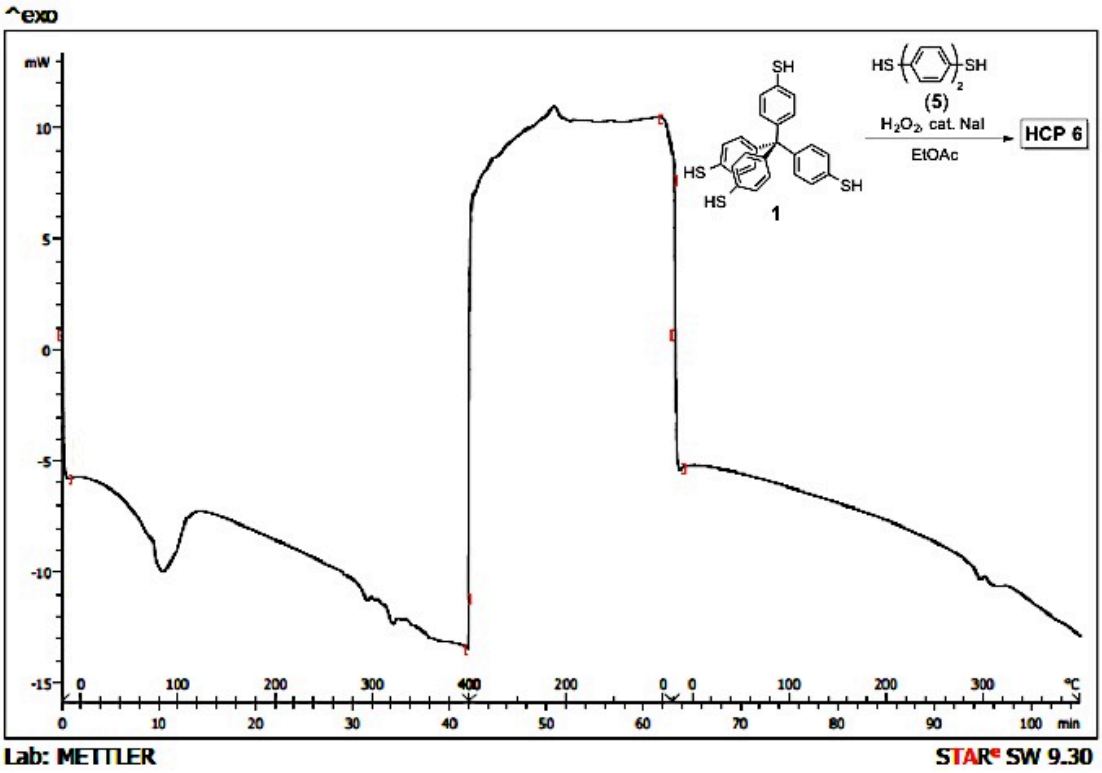
2) ^{1}H NMR of 3,3',3",3"'-[(methanetetrayltetrakis(benzene-4,1-diyl))tetrakis(sulfanediyl)]tetrakis(pyrrolidine-2,5-dione) **15** in acetone-d_6

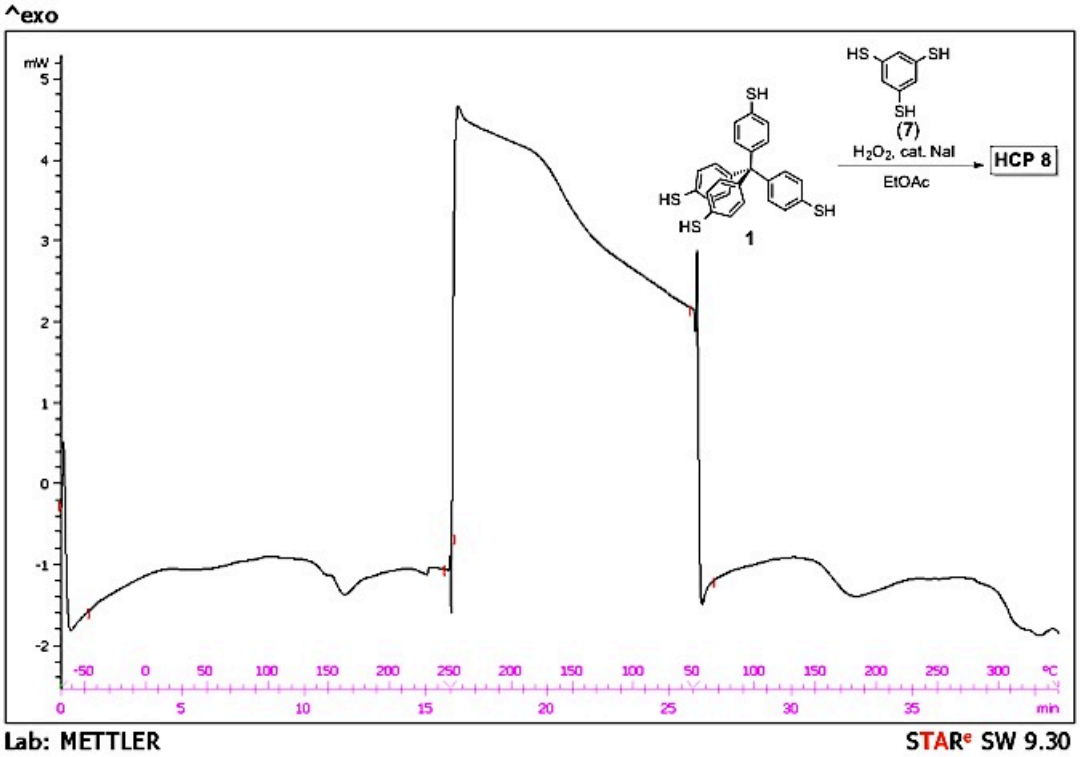

15

DSC Analysis

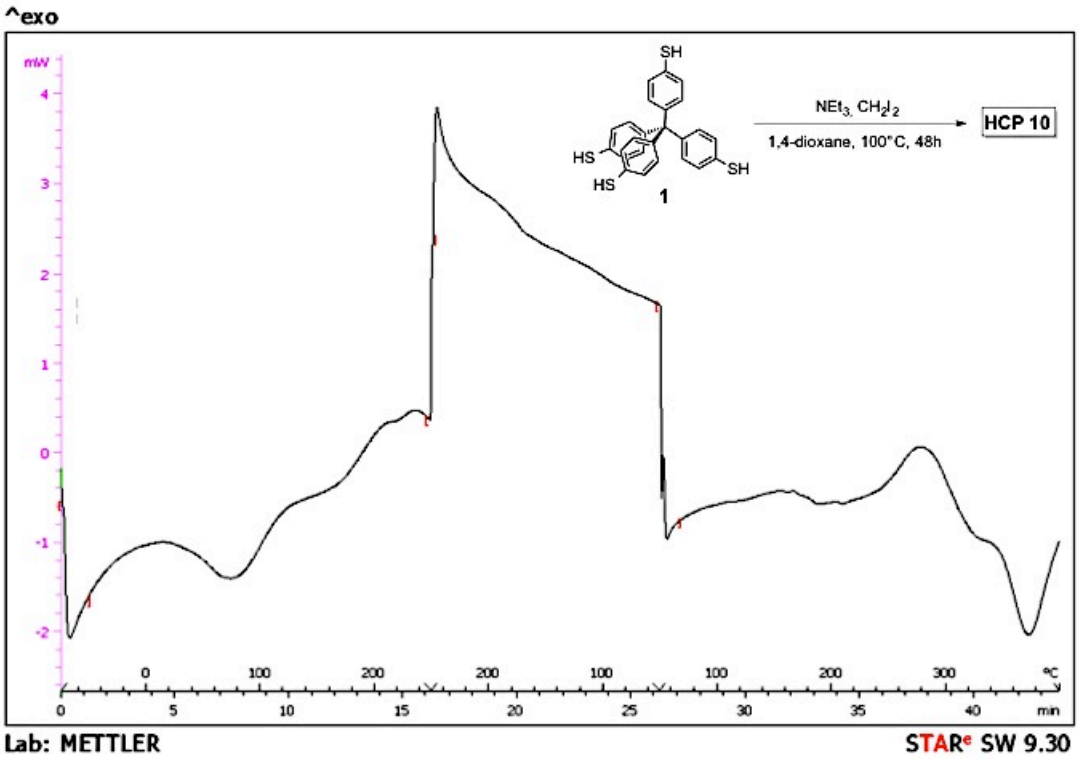
1) Disulfide based networks 4, 6 and 8

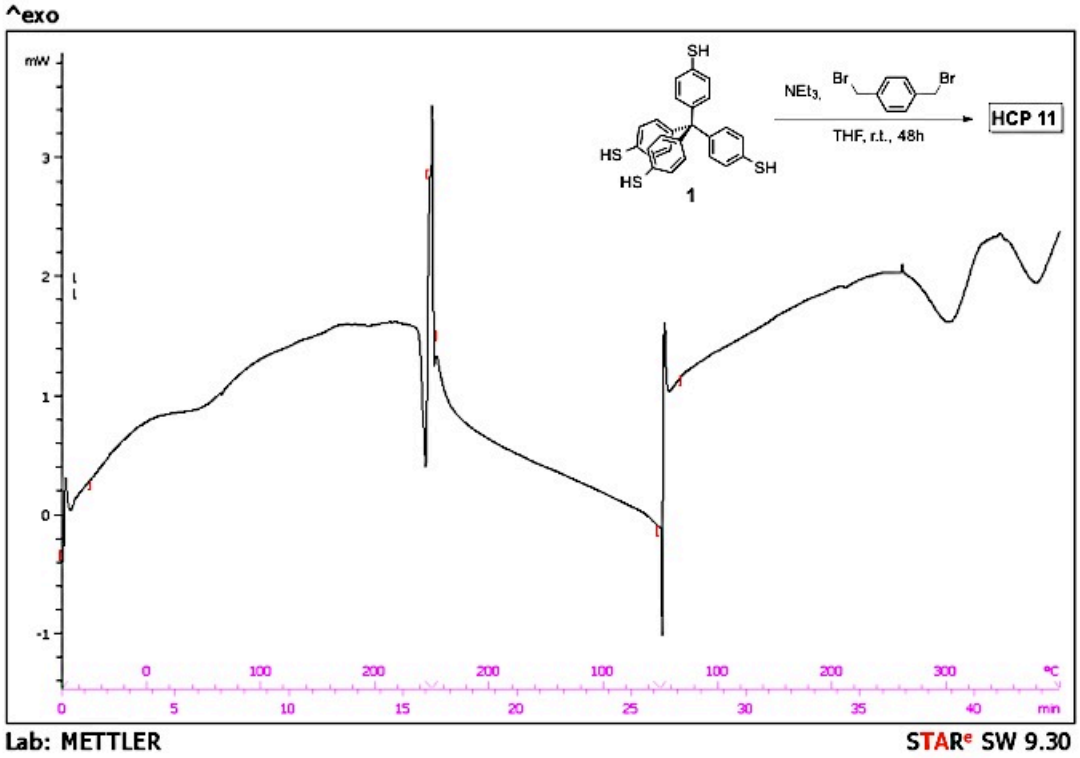




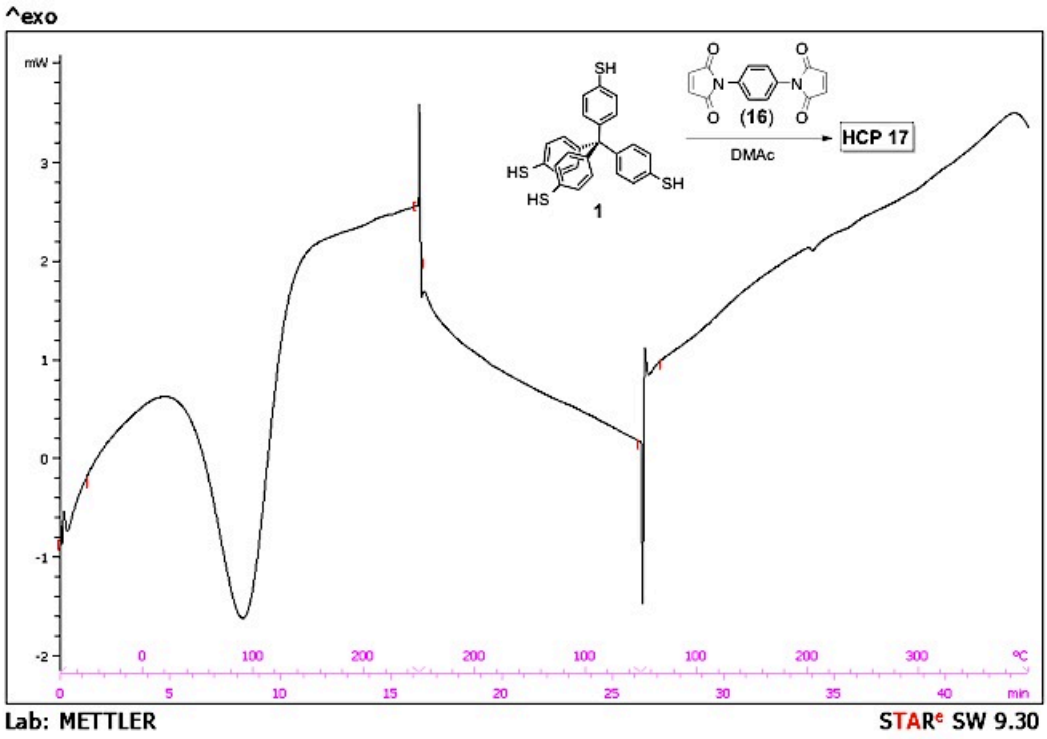


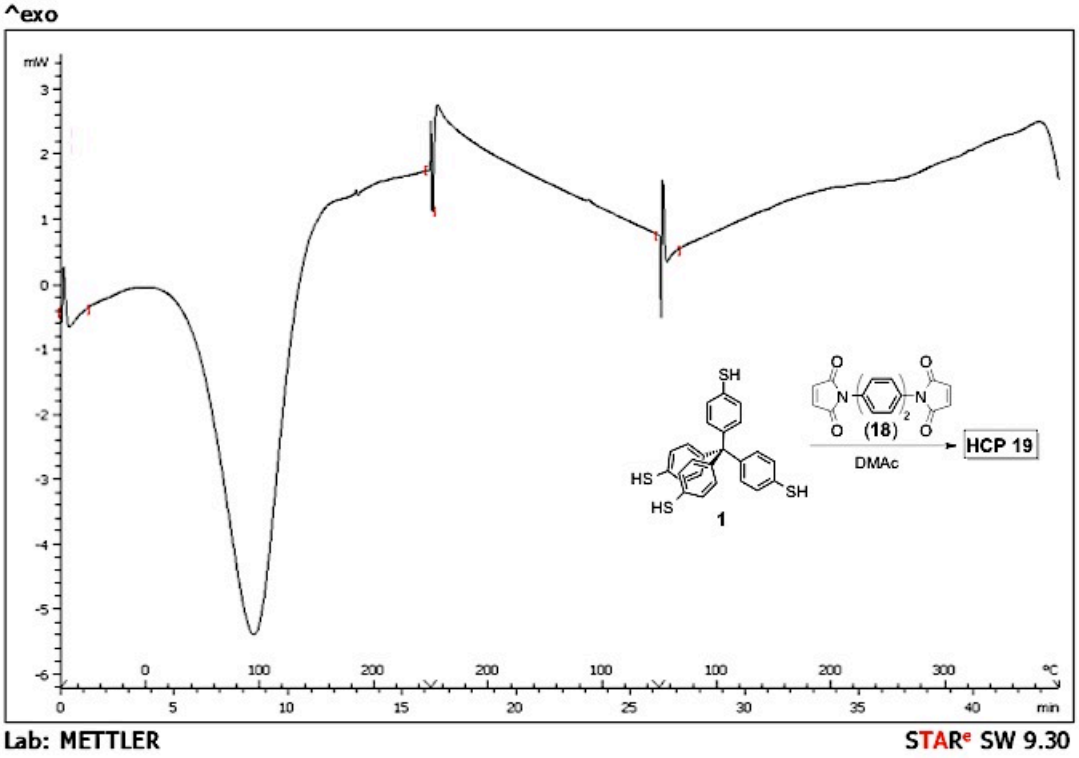
2) HCPs 10 and 11 generated by nucleophilic substitution





3) Networks 17, 19 and 21 generated by Thia-Michael addition

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100
200
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100
100
200
300
°C
0
5
10
15
20
25
30
35
40
min
SH
HS
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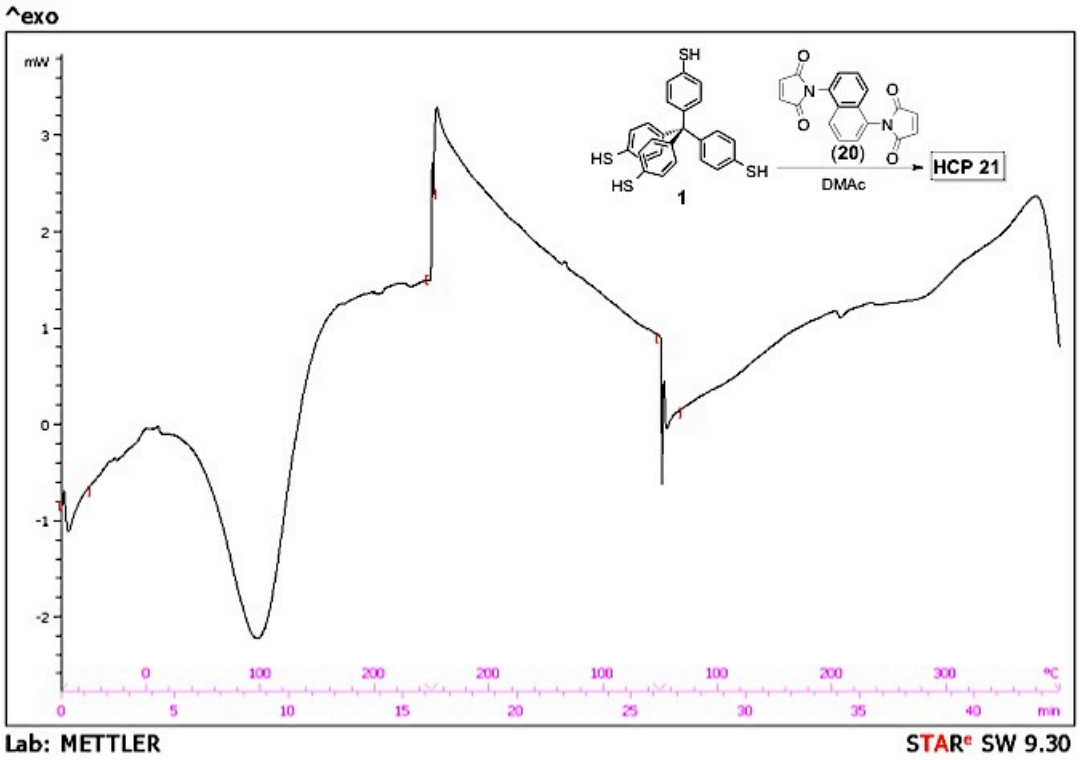
HCP 19
Lab: METTLER
STARe SW 9.30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300
°C
0
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20
25
30
35
40
min
SH
HS
HS
SH
1
(20)
DMAc
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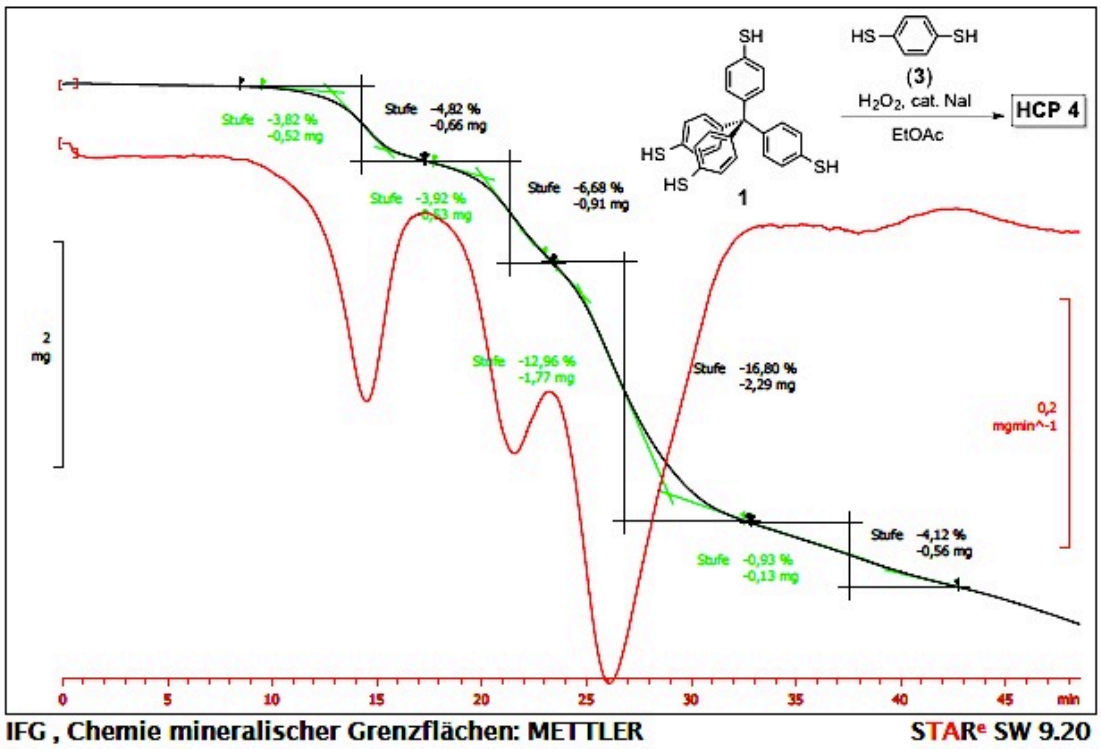
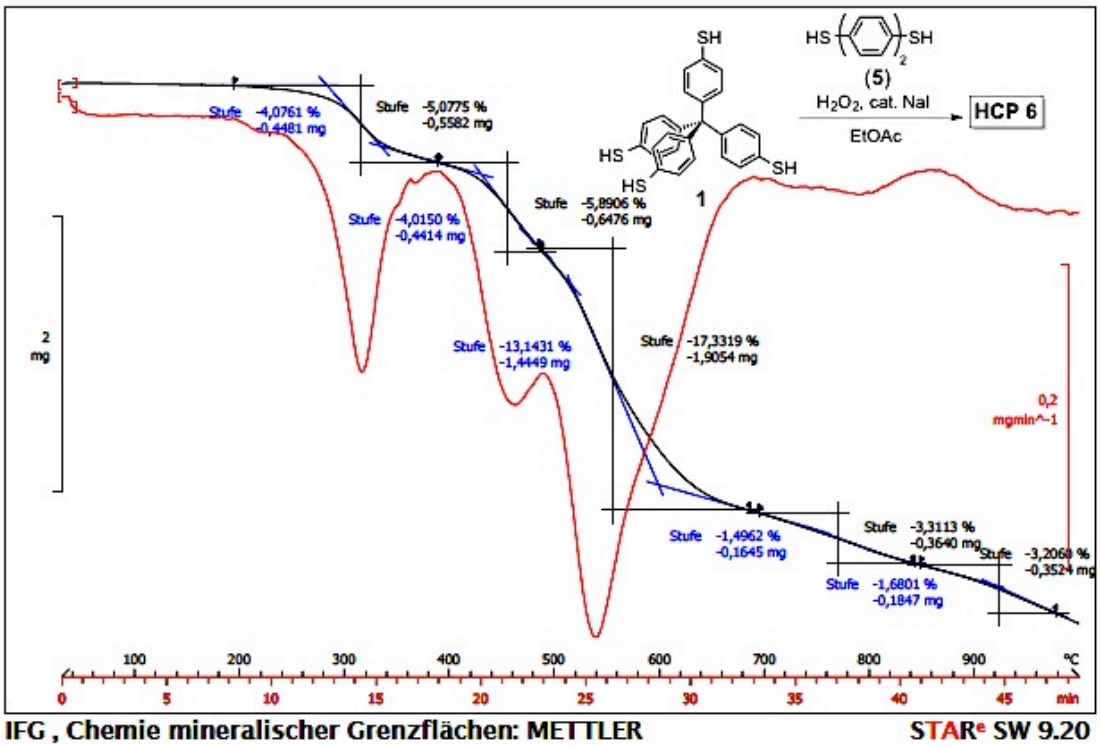
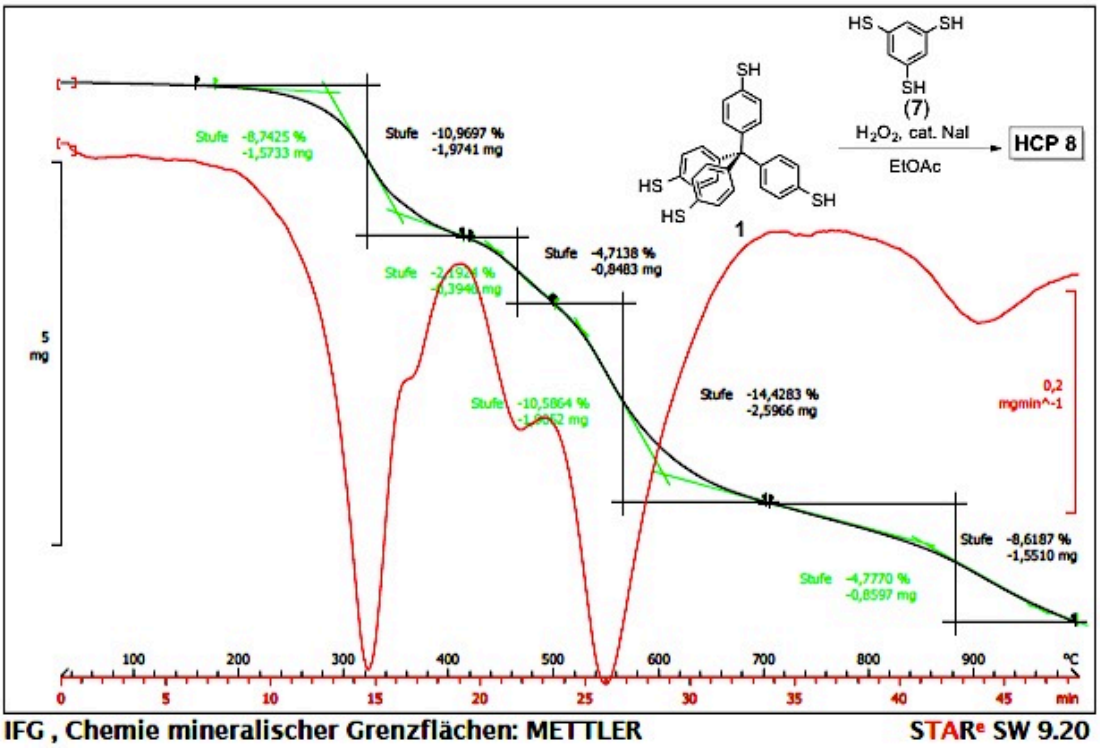
STARe SW 9.30

TGA Analysis

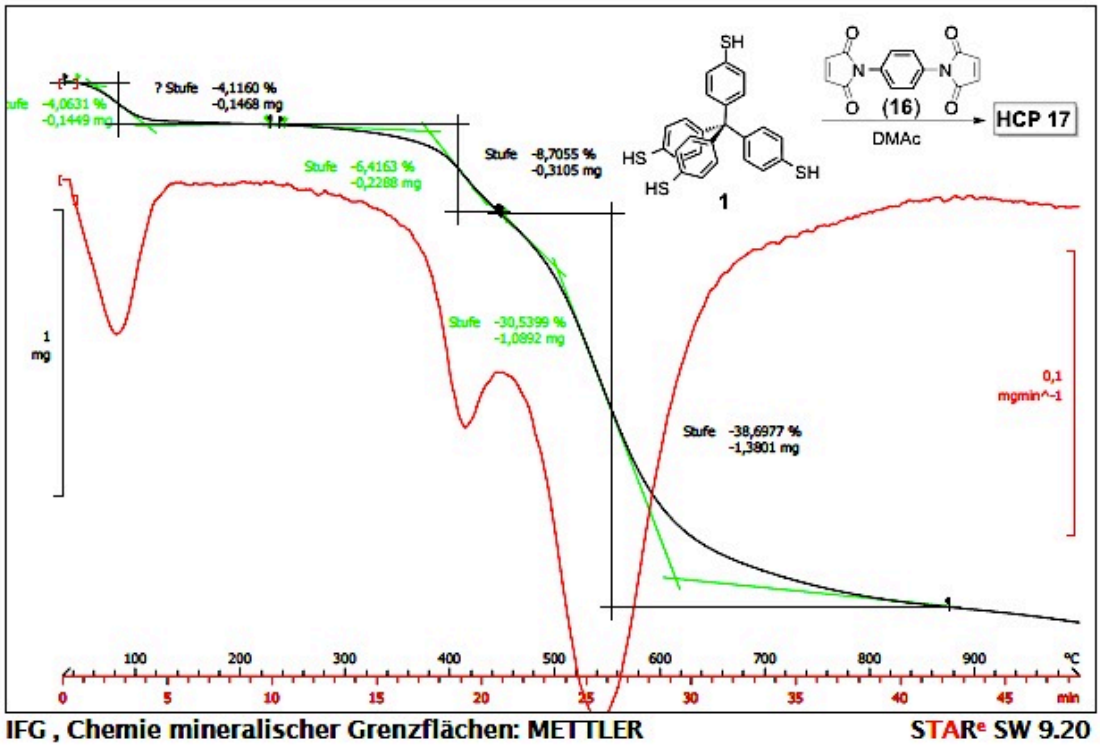
1) Disulfide based networks

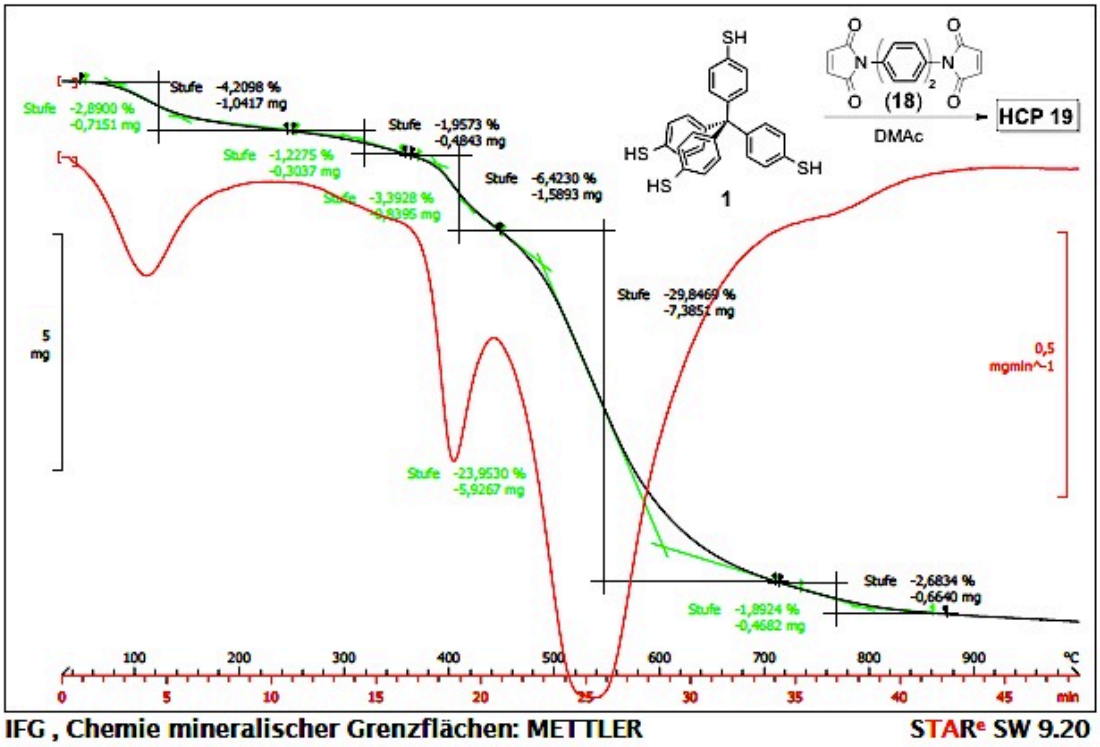




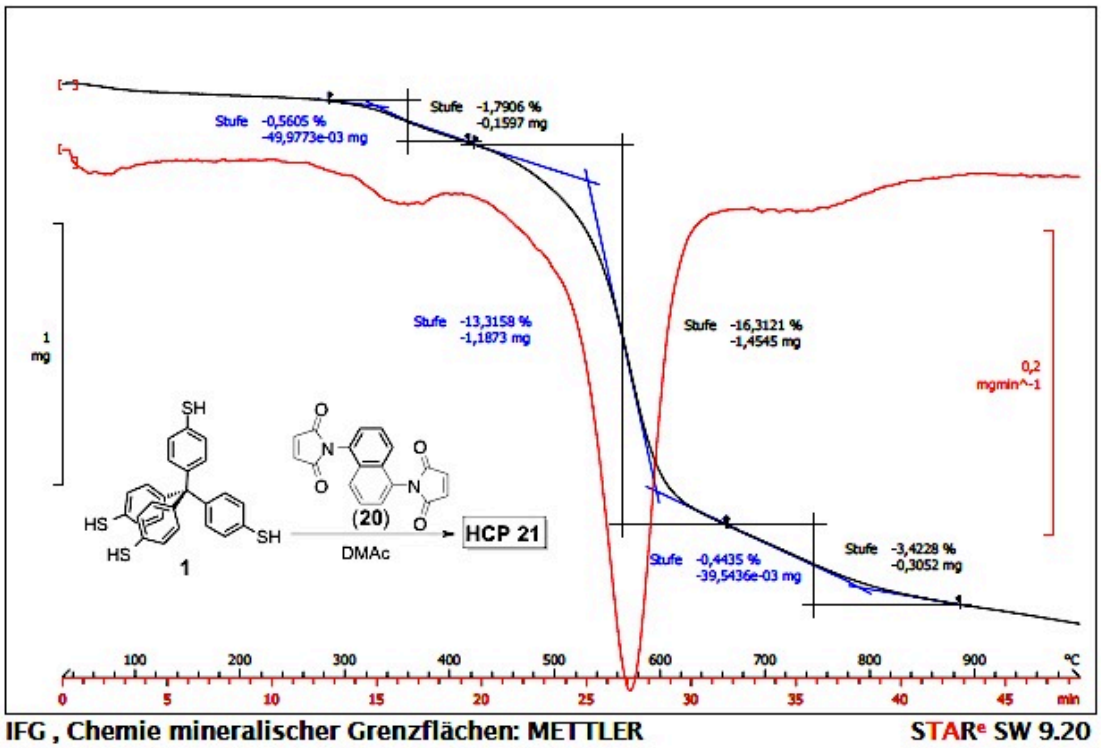


2) Networks 17, 19 and 21





IFG , Chemie mineralischer Grenzflächen: METTLER STARe SW 9.20



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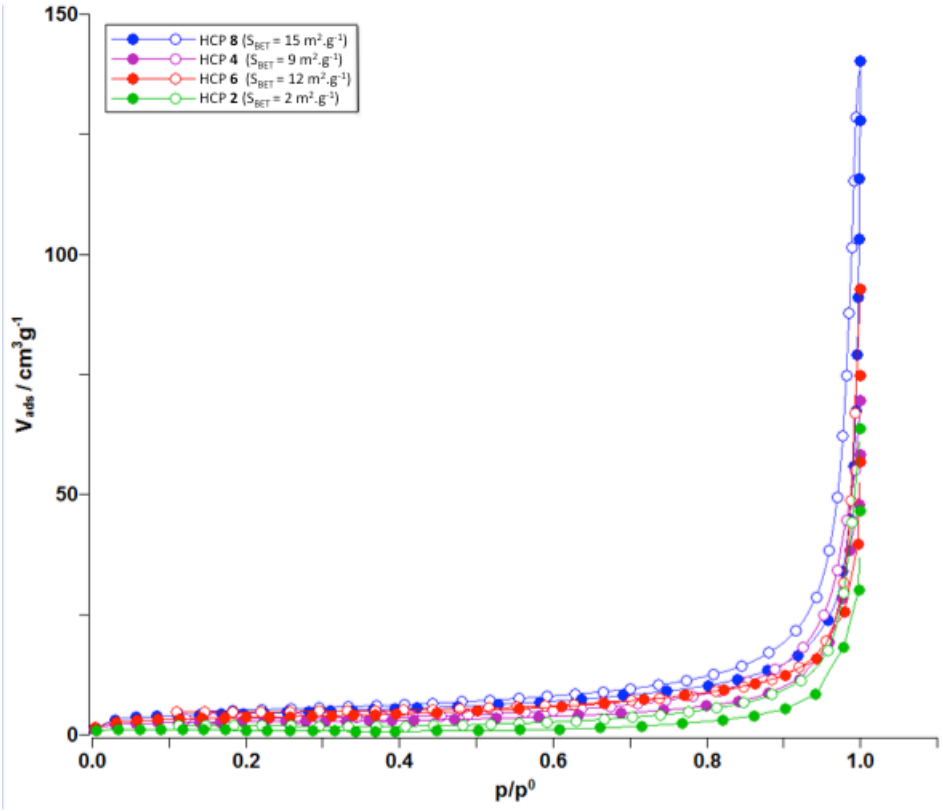
N_2 adsorption measurements of HCPs 2, 4, 6 and 8

Closed circles are used for adsorption data points and open circles are used to indicate desorption data points.



- Adsorption data of HCPs **2**, **4**, **6** and **8**.

Entry	HCP	Specific Surface Area[a]		Total Pore volume[b]
		BET	Langmuir	
1	**2**	2	3	0.0018
2	**4**	8	13	0.0041
3	**6**	12	18	0.0053
4	**8**	15	22	0.0065

[a] Surface area calculated over the relative pressure range P/P_0 = 0.05-0.3. Specific surface area is expressed in m^2g^{-1}. [b] Total pore volume for P/P_0 = 0.99 and is expressed in $cm^3.g^{-1}$.

References

[1] G. Horváth and K. J. Kawazoe, *Chem. Eng. Jpn.*, 1983, **16**, 470-475.

[2] R. W. Cranston and F. A. Inkley, *Adv. Catal.*, 1957, **9**, 143-154.

[3] L. Monnereau, M. Nieger, T. Muller, S. Bräse, *Adv. Funct. Mater.* **2014**, *24*, 1054-1058.

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[5] a) D. C. Liao, K. H. Hsieh and S. C. Kao, *J. Polym. Sci., Part A: Polym. Chem.* **1995**, *33*, 481-491; b) J. V. Crivello, *J. Polym. Sci.: Polym. Chem. Ed.* **1976**, *14*, 159-182.