Supporting Information to:

A shape-persistent exo-functionalized [4+6] imine cage compound with a very high specific surface area

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Contents

1. General remarks

Melting points (not corrected) were measured with a Büchi Melting Point B-545. IR-Spectra were recorded as KBr-pellets on a Perkin Elmer Spectrum 2000 FT-IR spectrometer. NMR spectra were recorded on a Bruker DRX 400 at 278 K at 400 MHz (^{1}H) and 100 MHz (^{13}C). ^{13}C MAS NMR spectra were measured on a Bruker DS400WB calibrated on adamantane as external standard (38.48 ppm) with the pulse program CP4C.98 (parameters are as follows: rotational frequence: 10 KHz and 12KHz, 7000 scans, D1: 3s, Aq: 50ms, contact puls: 4ms, broadband decoupling: TPPM, BF1: 100.564993 MHz, O1p 100ppm, SW 267.3 ppm, BF2 399.94, O2p: 8ppm, p3: 3us).[S1] MALDI-TOF MS experiments were carried out on a Bruker Daltonik Reflex III with dithranol (98.5%, Aldrich) as matrix and HR-MALDI MS were measured on a Fourier Transform Ion Cyclotron Resonance (FT-ICR) mass spectrometer solariX (Bruker Daltonik GmbH, Bremen, Germany) equipped with a 7.0 T superconducting magnet and interfaced to an Apollo II Dual ESI/MALDI source. Elemental analyses were determined with an Elementar Vario *EL*. Ethanol was dried over molecular sieves prior to use. Dimethyl formamide (Prolabo), 4,6-Dihydroxy-5-methyl-1,3-diformyl benzene (Frontier Scientific, 96%), glacial acetic acid (Prolabo), 3,4-Dimethylaniline (Alfa Aesar, 98%) are commercial available and were used without further purification. 2,7,14-Triaminotriptycene[S2] was synthesized by a procedure published before. The surface areas and porosities of cage compound **5** were characterized by nitrogen adsorption and desorption analysis at 77.35 K with an autosorb computer controlled surface analyzer (AUTOSORB-1, Quantachrome). Each sample was degassed at 280 ºC for 10 h before analysed. The Brunauer-Emmett-Teller (BET) surface area was calculated assuming a value of 0.162 nm^2 for the cross-sectional area of the nitrogen molecules in the pressure range P/P_0 = 0.01-0.1.

2. Synthesis and Characterisation

Synthesis of 4,6-bis((3,4-dimethylphenylimino)methyl)-2-methylbenzene-1,3-diol (6): 4,6-Dihydroxy-5-methyl-1,3-diformyl benzene (80.6 mg, 0.45 mmol) was dissolved under argon in dry ethanol (5 mL) and glacial acetic acid (0.02 mL) and stirred at 50 °C. 3,4-Dimethylaniline (120.9 mg, 1.00 mmol) dissolved in dry ethanol (4 mL) was added over a period of 5 min. After addition, the yellow solution was refluxed for 6 h. The solution was cooled to room temperature and the precipitate was collected by suction filtration and washed twice with 4 mL ethanol. After drying in vacuum, 150 mg (86%) of **6** were obtained as orange solid. M.p. 170-171 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ = 14.96 (s, 2H), 8.88 (s, 2H), 7.69 (s, 1H), 7.41 - 7.01 (m, 6H), 2.26 (s, 6H), 2.24 (s, 6H), 2.07 (s, 3H) ppm. ^{13}C NMR (101 MHz, DMSO-d_6) δ = 164.3 (s), 161.1 (d), 144.3 (s), 137.5 (s), 136.4 (d), 135.1 (s), 130.4 (d), 122.2 (d), 118.2 (d), 112.1 (s), 110.9 (s), 19.5 (q), 19.0 (q), 7.4 (q) ppm. IR (KBr): $\tilde{\nu}$ = 3437 (m), 2965 (w), 2918 (m), 2855 (w), 2730 (w), 1626 (s), 1587 (s), 1501 (m), 1455 (w), 1400 (m), 1368 (s), 1282 (w), 1175 (s), 1153 (m), 1114 (w), 1017 (w), 968 (w), 875 (w), 865 (w), 818 (w), 764 (w), 669 (w), 464 (w), 439 (w) cm^{-1}. MS (CI-MS): *m/z* (%) = 415 (8) $[M+C_2H_6]^+$, 388 (17), 387 (100) $[M+H]^+$, 386 (20) $[M]^+$, 385 (8). Elemental analysis calcd. (%) for $C_{25}H_{26}N_2O_2$: C 77.69, H 6.78, N 7.25; found: C 77.93, H 6.66, N 7.18.

Synthesis of cage compound 5: 2,7,14-Triaminotriptycene (109.8 mg, 0.37 mmol) and 4,6-Dihydroxy-5-methyl-1,3-diformyl benzene (98.8 mg, 0.55 mmol) were dissolved in dimethylformamide (52 mL) under argon and TFA (4.4 µL, 2 mol%) was added. The solution was refluxed for 4 d at 110 ºC. After cooling the reaction mixture to room temperature, the solid was collected by filtration, washed with DMF (3 x 5 mL) and immersed in THF (10 mL, three times for 8 h). After removing of the solvent and drying under vacuum, 120 mg (63%) of cage compound **5** were obtained as orange solid. M.p. > 410 °C; ^{13}C MAS NMR: δ = 164.7, 158.2, 145.4, 135.9, 130.0, 124.3, 113.1, 97.5, 54.1, 7.4 ppm. IR (KBr): $\tilde{\nu}$ = 3435 (m), 2955 (w), 2968 (w), 1624 (s), 1583 (s), 1470 (s), 1423 (w), 1369 (m), 1288 (w), 1169 (s), 1132 (m), 1088 (w), 1062 (w), 954 (m), 856 (m), 766 (w), 670 (w), 597 (w), 500 (w), 471 (w) cm^{-1}; HRMS (MALDI, dithranol): *m/z* = 2061.70370 (calc. for $C_{134}H_{92}N_{12}O_{12}$: 2061.70304). Elemental analysis calcd. (%) for $C_{134}H_{92}N_{12}O_{12}\cdot 3H_2O$: C 76.05, H 4.67, N 7.94; found: C 76.00, H 4.67, N 7.89.

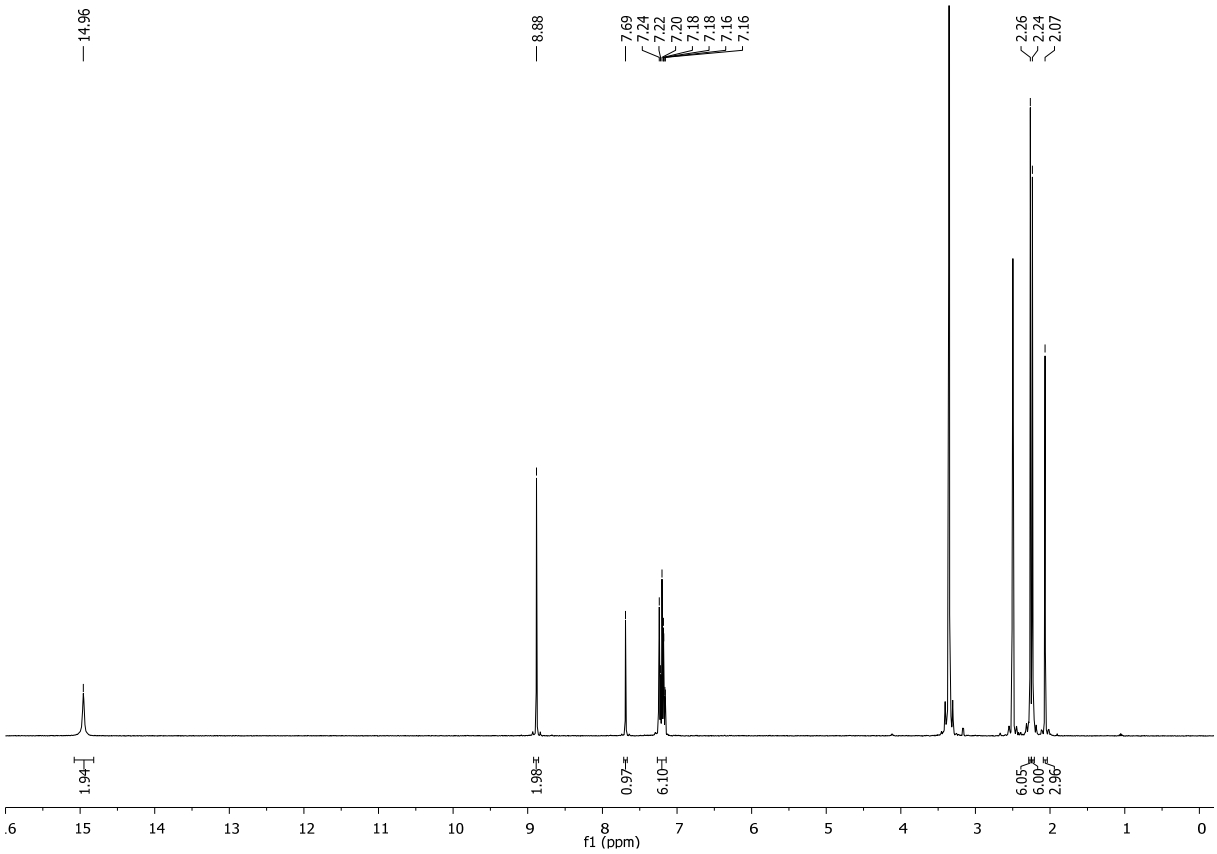

Figure S1: ^{1}H NMR spectrum (400 MHz, DMSO-d_6) of compound **6**.

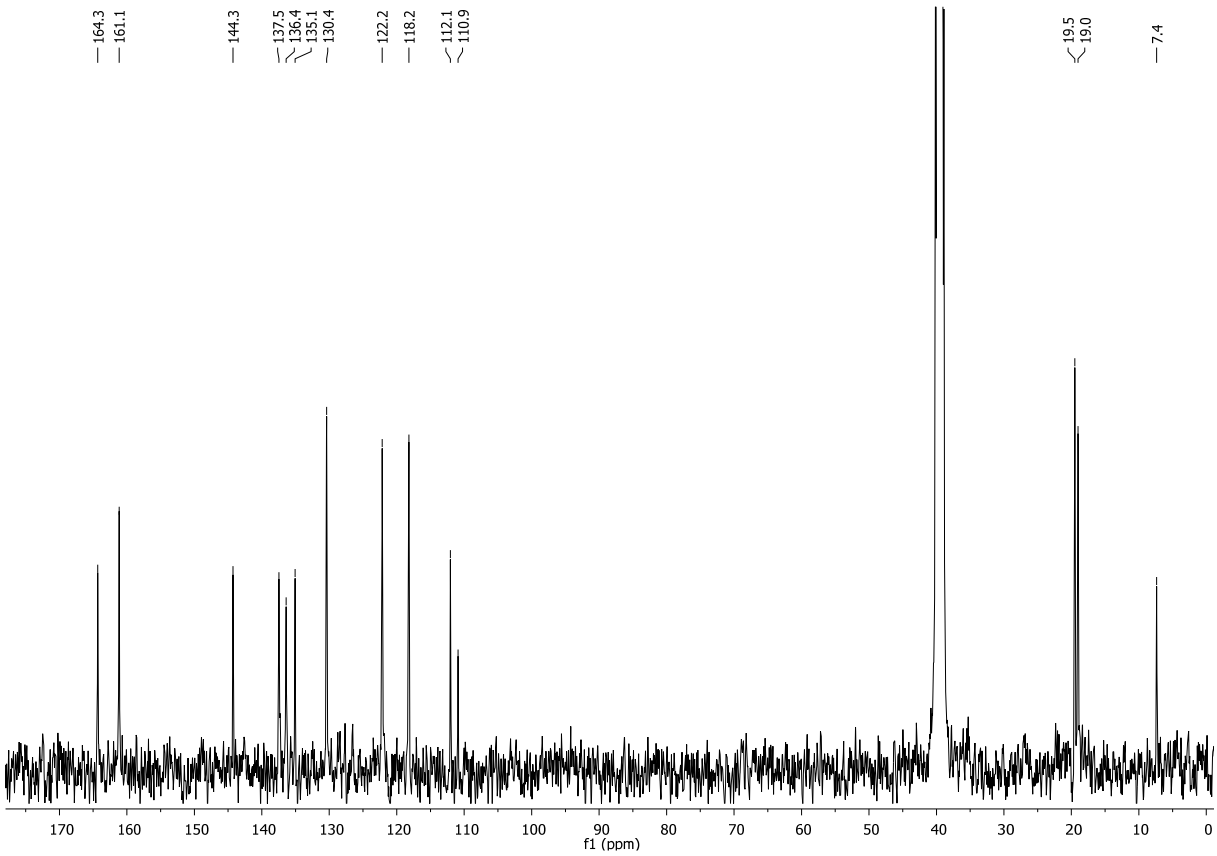

Figure S2: ^{13}C NMR spectrum (100 MHz, DMSO-d_6) of compound **6**.

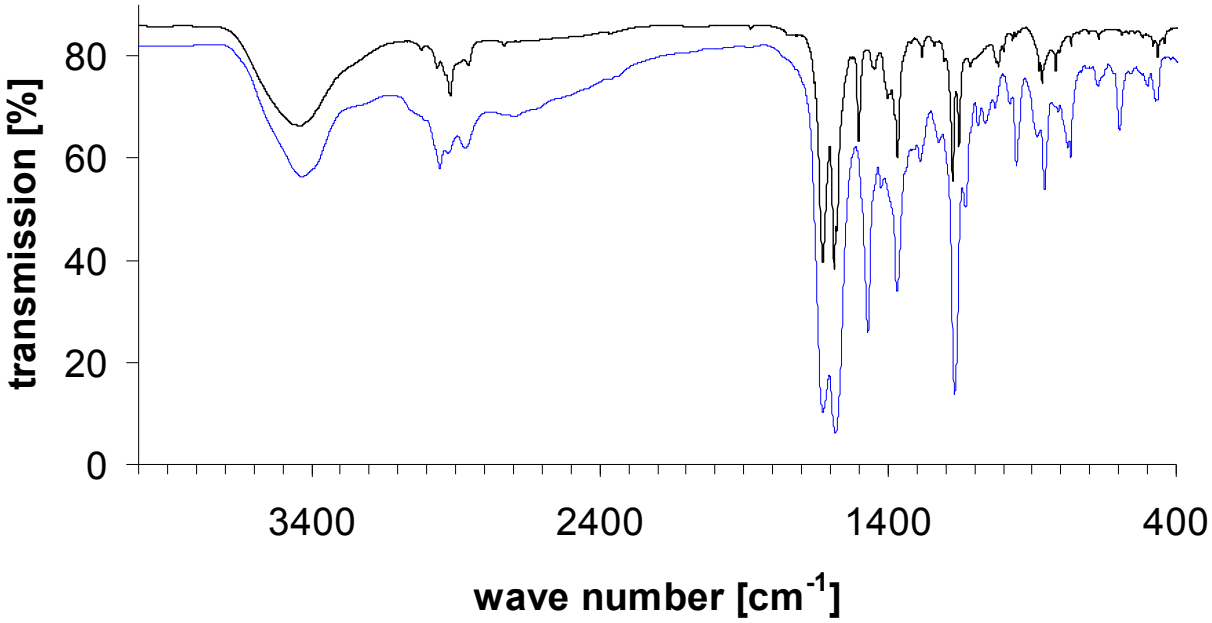

Figure S3: FT-IR spectrum of model compound **6** (black) and cage compound **5** (blue).

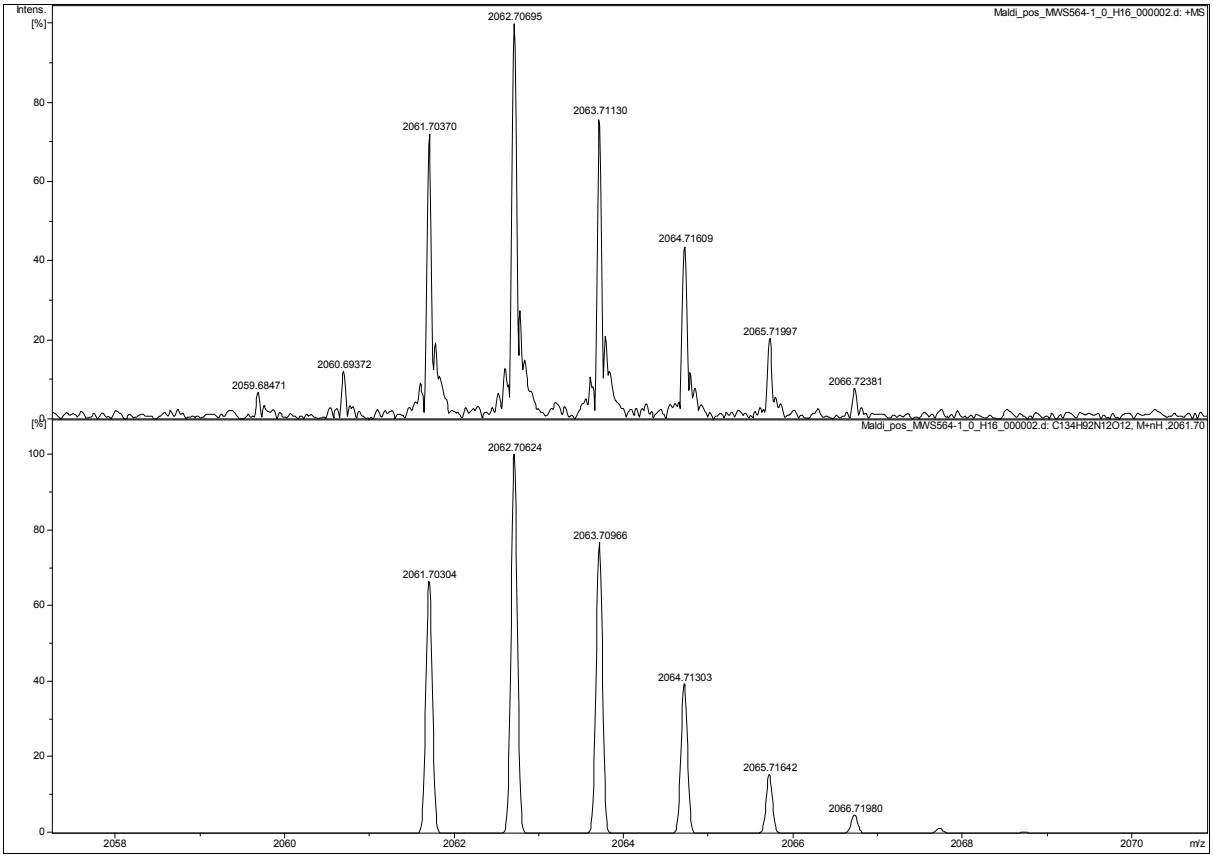

Figure S4: HR-MALDI mass spectrum of cage compound **5**. Top: zoom in section of the basis; bottom: calculated pattern.

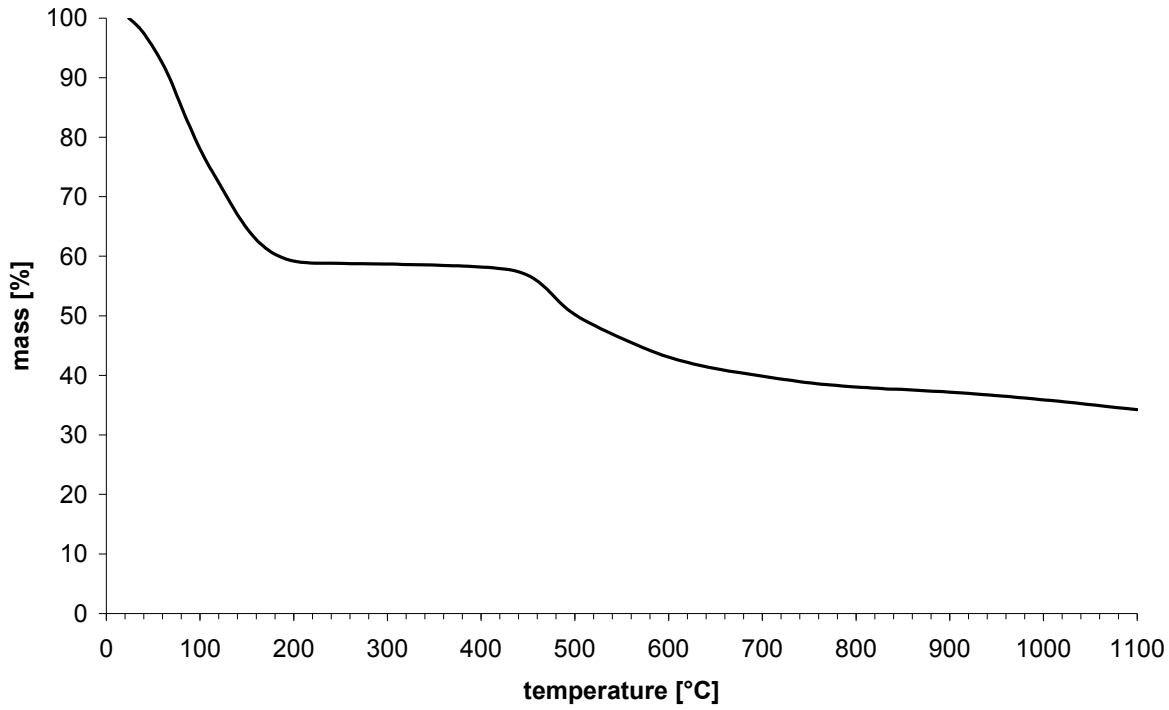

Figure S5: Thermogravimetric analysis of cage compound **5**.

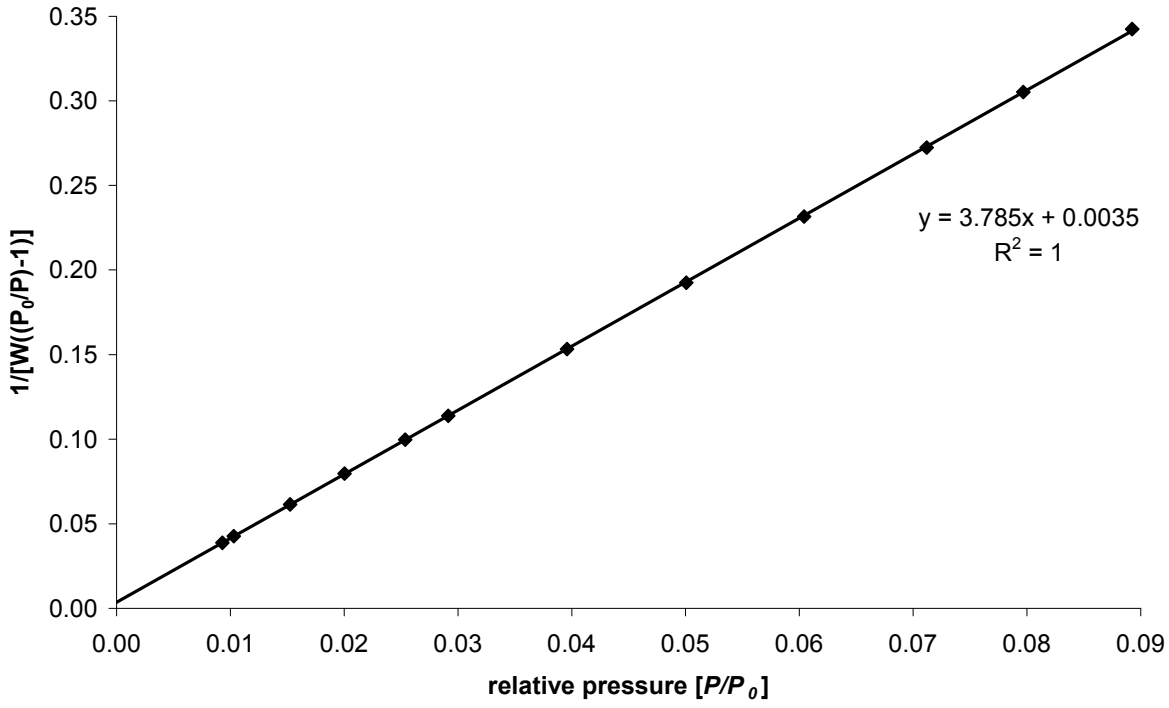

Figure S6: BET-plot for [4+6] cage compound **5**.

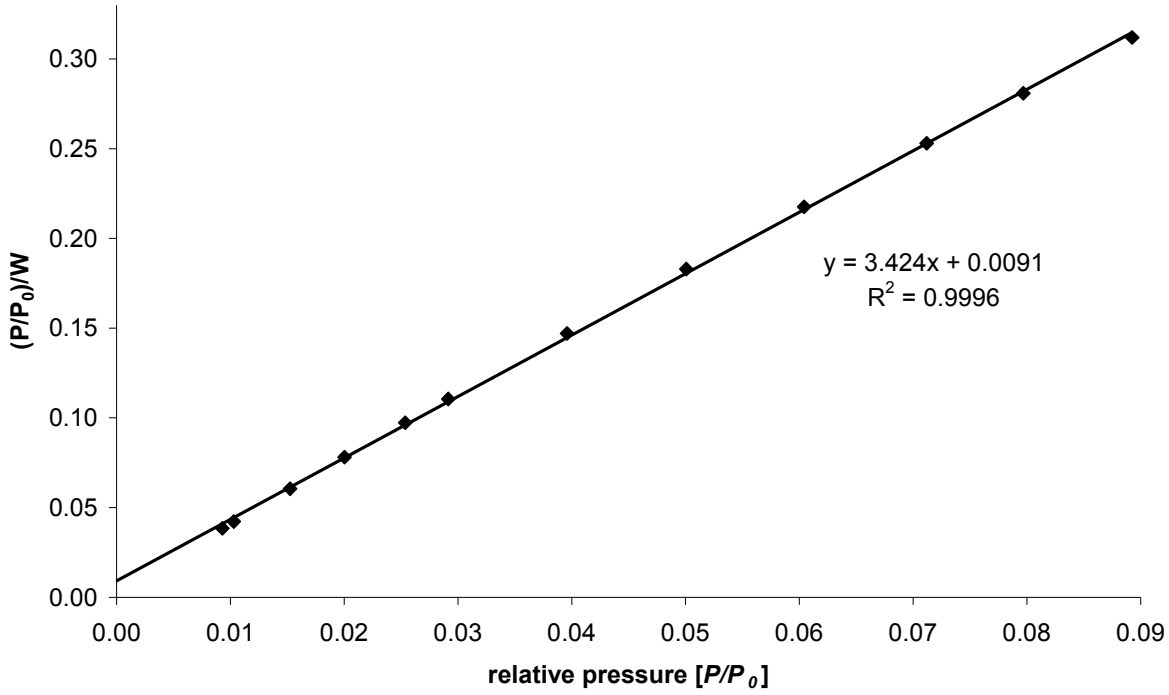

Figure S7: Langmuir-plot for [4+6] cage compound **5**.

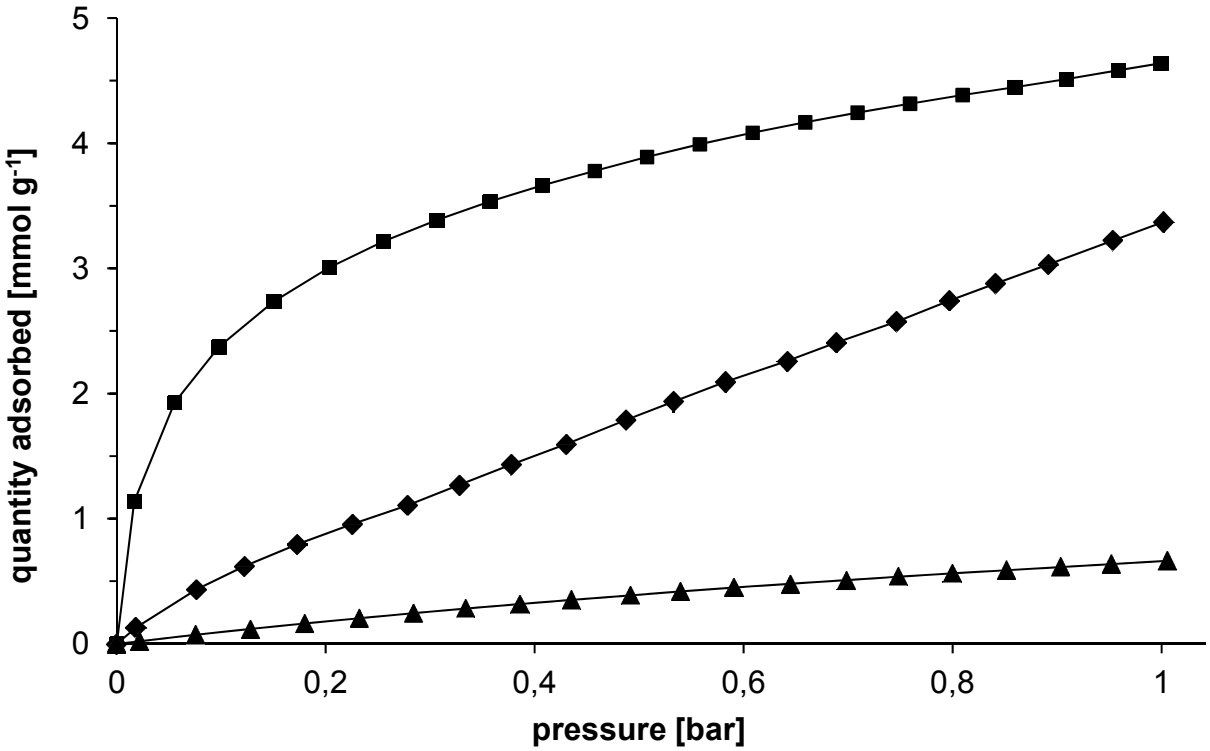

Figure S8: Gas adsorption isotherms for H_2 (squares, 77 K), CO_2 (diamonds, 273 K) and CH_4 (triangles, 273 K) for cage compound **5**.

3. Several reasons against the formation of polymeric by-products

i) If the reaction did not run to completion, e.g. at lower reaction temperature, we observed the formation of condensation products, which can be assigned to smaller intermediates of the final cage compound [4+6]-12 H_2O (cage compound **5**) with [n(T)+m(D)]-x(H_2O) (with T = triptycene triamine and D = dialdehyde). These intermediates are already insoluble as is the title compound **5** and cannot be removed from the product mixture by further purification methods.

ii) We never observed [n(T)+m(D)]-x(H_2O) products with n > 4 and m > 7 under any conditions. Also, in the MALDI-TOF MS of the title product no signals could be observed even in the range of *m/z* with values up to 5000. For us it seems unlikely that we are able to detect only cage compound **5** by MALDI-TOF MS and smaller intermediates, but not higher condensation products. Therefore, we can exclude the formation of oligomers with 8 > n > 4 and 12 > m > 6.

iii) It seems to us even more unlikely, that polymeric condensation products with n > 8 and m >12 **and only** cage compound **5** (n = 4; m = 6), but no oligomers or polymers of intermediate sizes have been formed. We are not aware of any such phenomenon for the formation of similar nano sized molecules/objects (e.g. macrocycles or cages) by dynamic covalent chemistry described till date.

iv) Cage compounds **3a** and **3b** that have been previously described are synthesized basically in the same manner: they are formed as a precipitate from solution. The MALDI-TOF MS of **3a** and **3b** show, as same as for **5**, only one peak. Here, we could proof by ^{1}H NMR and X-ray crystallography that these cages (**3a** and **3b**) are pure and did not have to be separated from oligomers or polymers. By the similarity of the reaction of **4** and **1** to **5** to the reactions of **2a** or **2b** and **1** to **3**, we assume similar distribution of the members of the virtual dynamic library.

v) If we would expect other oligomers or polymers than the cage compound **5**, there must be unreacted amine and/or aldehyde functions left, for which we would expect certain bands in the IR spectrum. This is not the case, since the IR spectra of **5** and model compound **6** are in very good agreement. We do not see any bands according to a stretching of any aldehydic C=O bond.

4. References

[S1] E. O. Stejskal, J. D. Memory, High-Resolution NMR in the solid state, Fundamentals of CP MAS NMR. Oxford University Press, **1994**.

[S2] C. Zhang, C.-F. Chen, *J. Org. Chem.* **2006**, *71*, 6626-6629.