Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

EFFECTIVE MAGNETIC MOMENT IN CYCLODEXTRIN-POLYNITROXIDES: POTENTIAL SUPRAMOLECULAR VECTORS FOR MAGNETIC RESONANCE IMAGING

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Synthesis of **CD1**

11.35 g (10 mmol) of β-CD were dissolved in 200 mL of 0.6 M NaOH(aq) at 0 °C. After 30 min, 2.3 g (12.1 mmol) of 4-Toluenesulfonyl chloride (TsCl), finely powdered with a mortar and pestle, were added to the aqueous solution. The reaction mixture was magnetically stirred for 8 h at 0°C.The unreacted TsCl was removed by filtration onto a sintered glass funnel. The aqueous phase was acidified at 0 °C with 10 mL of HCl(37%) added dropwise. The product precipitated as white solid. The mixture was kept at 4 °C overnight, filtered on paper and washed with deionized water until neutral pH. In order to reduce the content of unreacted β-CD, the solid was dispersed in 100 mL of hot water (65 °C), stirred for 10 min, and finally filtered. This procedure was qualitatively followed by TLC (eluent: 2-propanol:H_2O:EtOAc:NH_4OH=5:3:1:0.5) and repeated for 3 times until the β-CD spot on TLC (R_f:0.25) was negligible compared to the **CD1** spot (R_f:0.47). The final product was washed with acetone (100 mL × 3 times), dried in air for 24 h and under vacuum (< 5 mbar) at 25 °C for 3 h. Yield: 35% (4.50 g). The tosylation procedure gave also the formation of very small amounts of ditosylates (Rf=0.58), according to the literature [Brady2000]. Due to the small ΔR_f between the mono- and the di-tosylate no attempt of further separation was made. ESI-MS analysis performed on the final product confirmed the presence of negligible amounts of pristine CD and di-tosylate (see Fig.SI2).

[Brady2000] B. Brady, N. Lynam, T. O'Sullivan, C. Ahern, R. Darcy, 6A-O-p-toluenesulfonyl-β-cyclodextrin, Org. Synth. 2000, 77, 220.

Synthesis of **CD2**

3.48 g (3 mmol) of **CD1** were dissolved into 10 mL of DMSO. An excess of sodium azide (390 mg, 6 mmol) was added to the solution. The mixture was heated at 90 °C for 12 h. After cooling it at room temperature, the product was obtained by precipitation in acetone and filtering on filter paper. The white solid was washed with acetone (100 mL × 4 times) and dried in air. The excess of NaN_3 was removed by treating the aqueous solution containing the product (100 mL) with IRA900-Cl ionic exchange resin. Water was then removed under rotary evaporation. The white solid was finally washed with acetone (100 mL × 3 times) and dried in air. Quantitative yield.

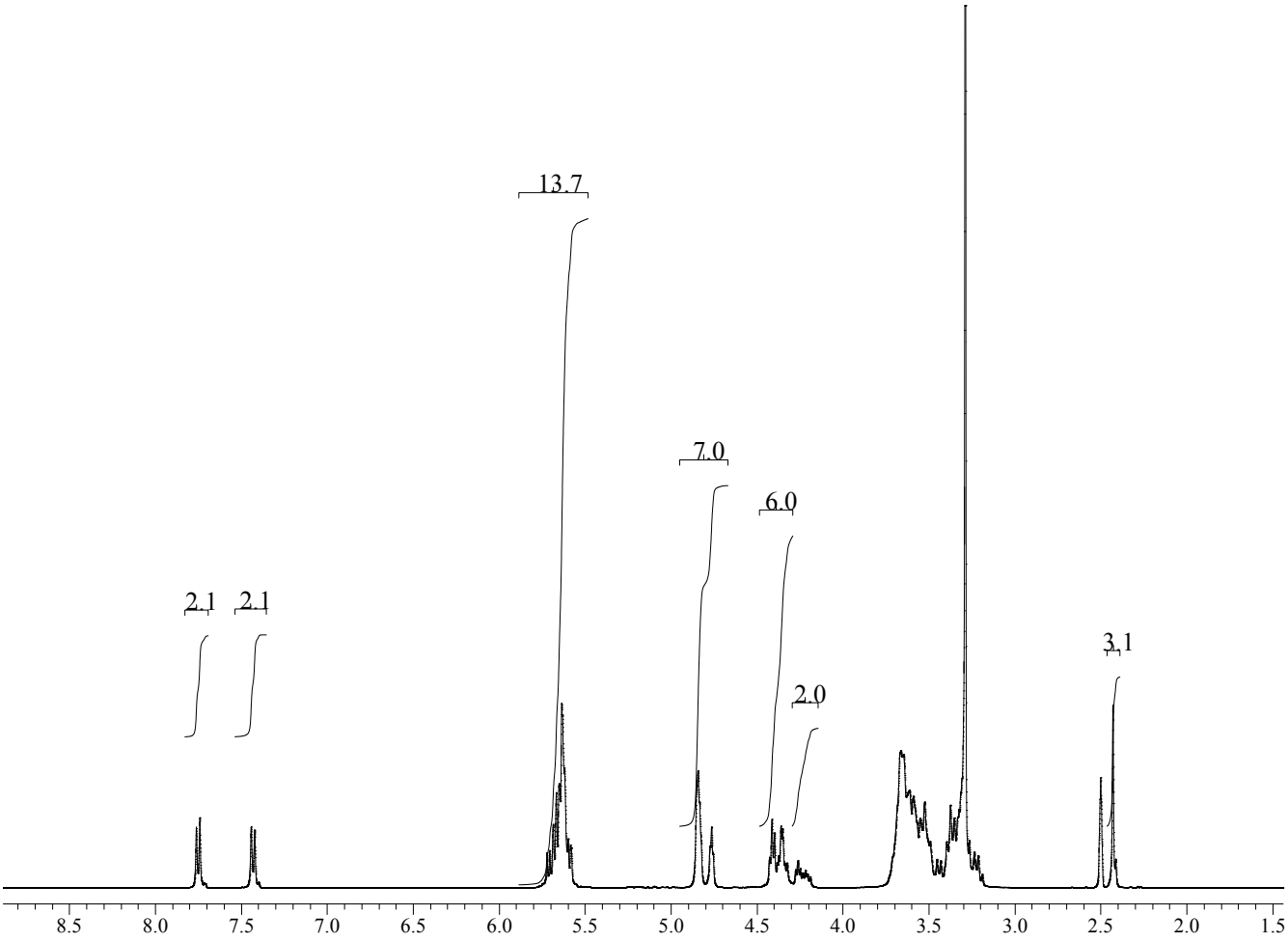

Fig.SI1. ^{1}H-NMR spectra of **CD1** in DMSO-d_6 (305 K)

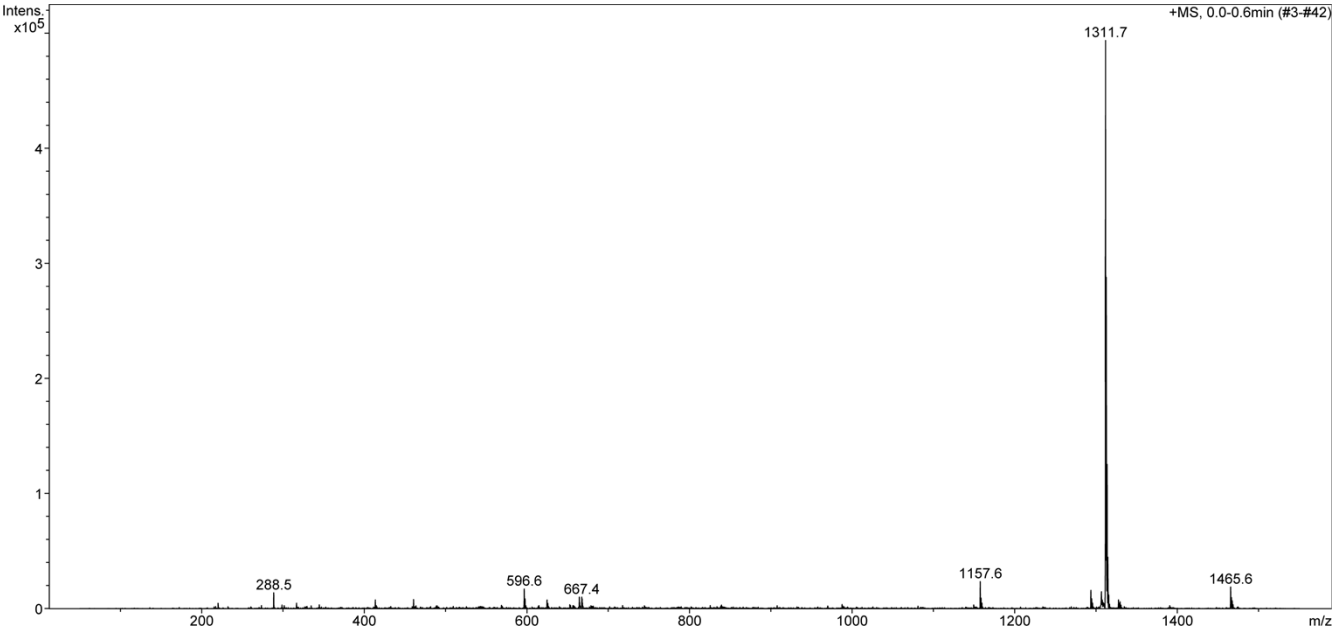

Fig.SI2. ESI-MS of **CD1**.

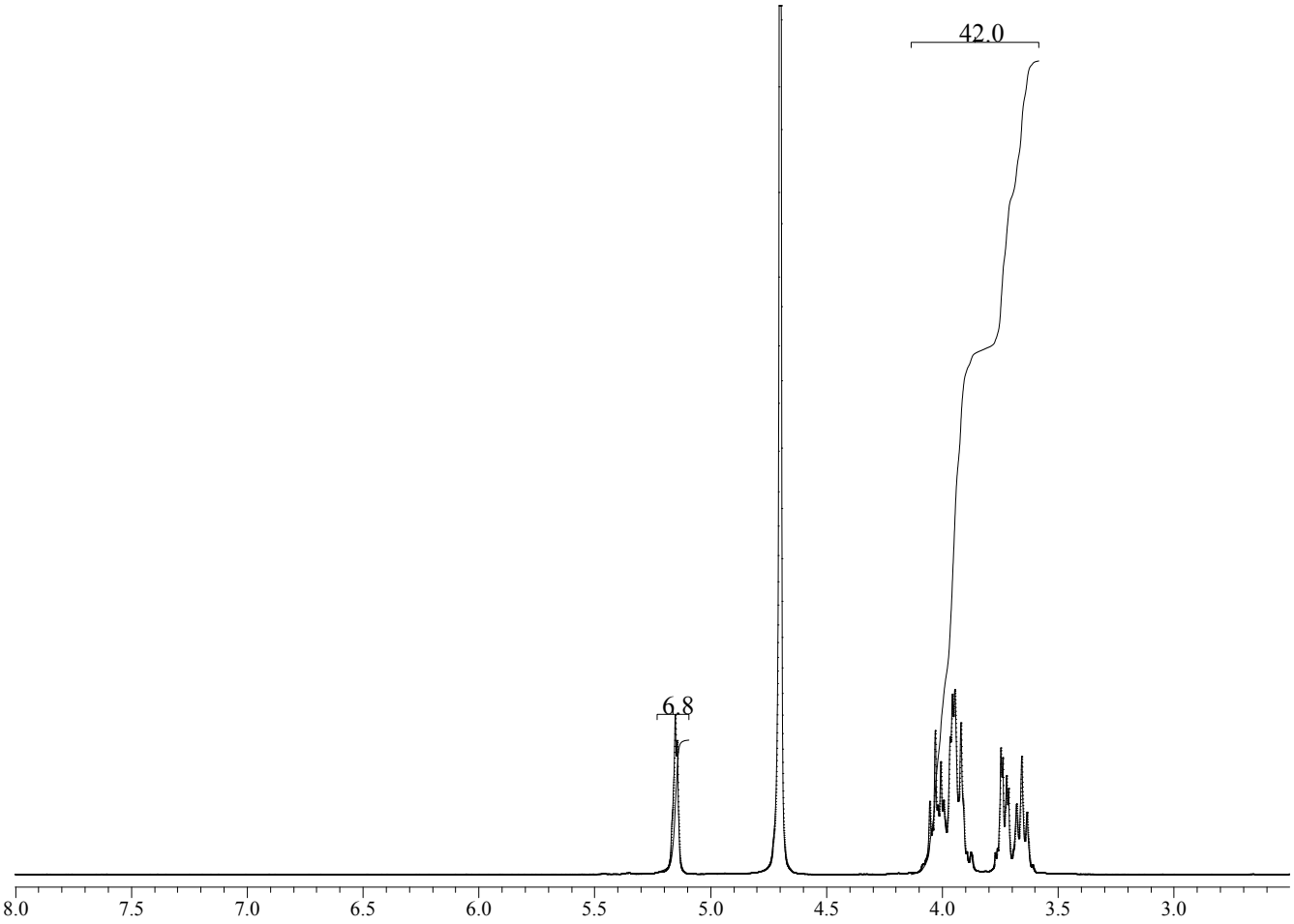

Fig.SI3. ^{1}H-NMR spectra of **CD2** in D_2O (305 K).

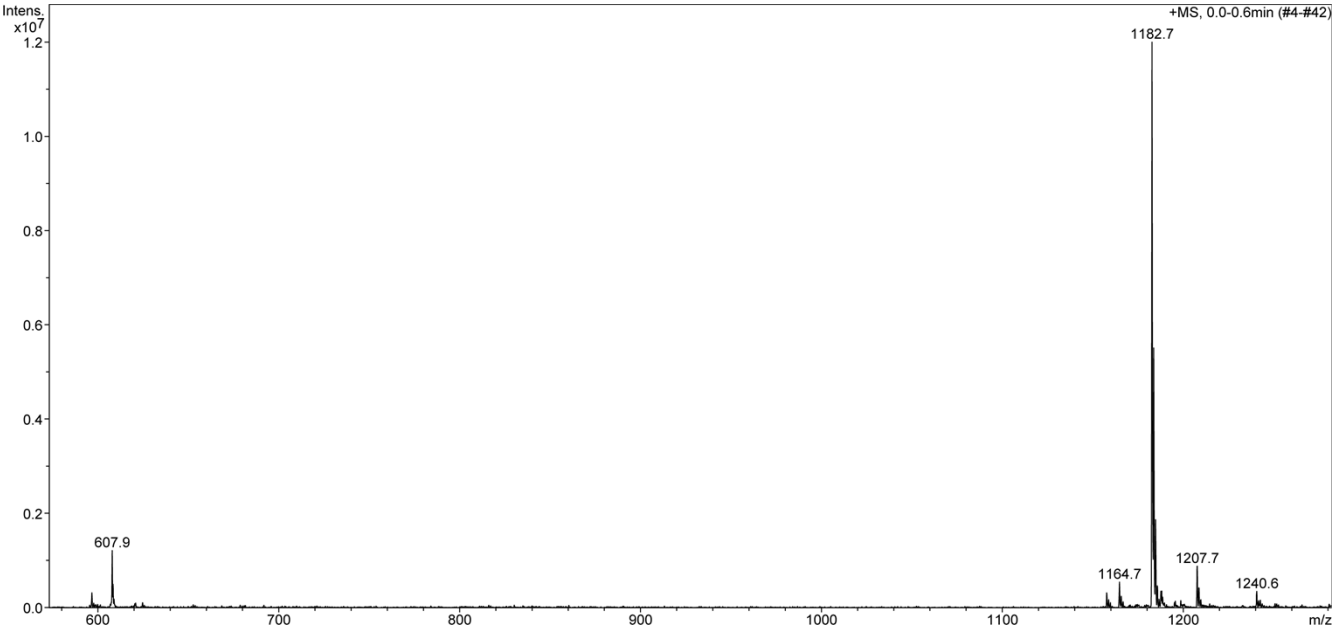

Fig.SI4. ESI-MS of **CD2**.

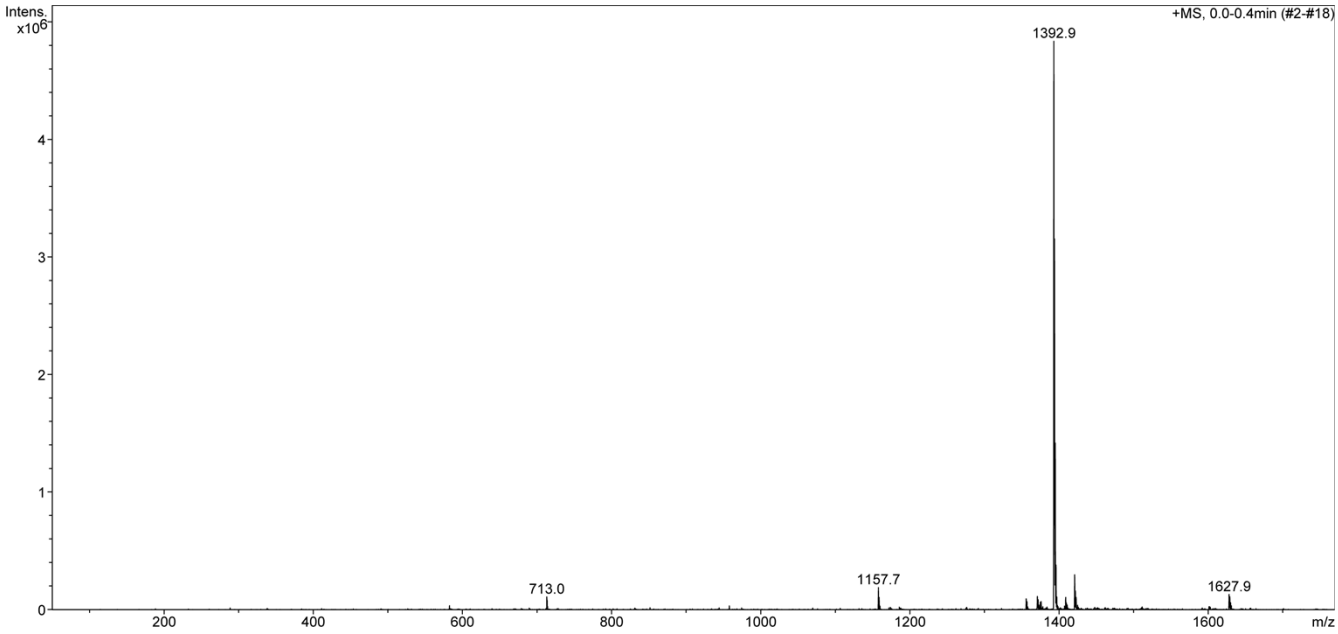

Fig.SI5. ESI-MS of **CD3**.

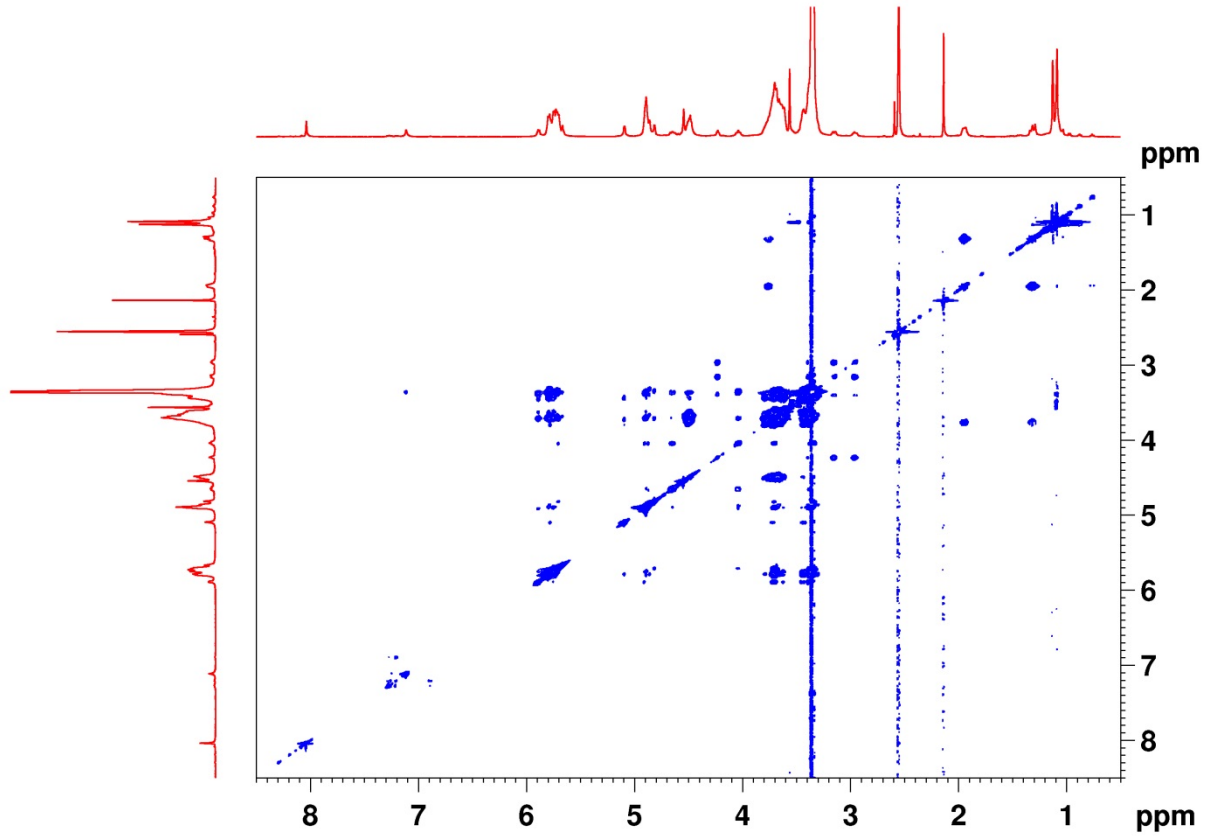

Fig.SI6. ^{1}H-^{1}H TOCSY NMR spectrum of **CD3-H** (DMSO-d_6).

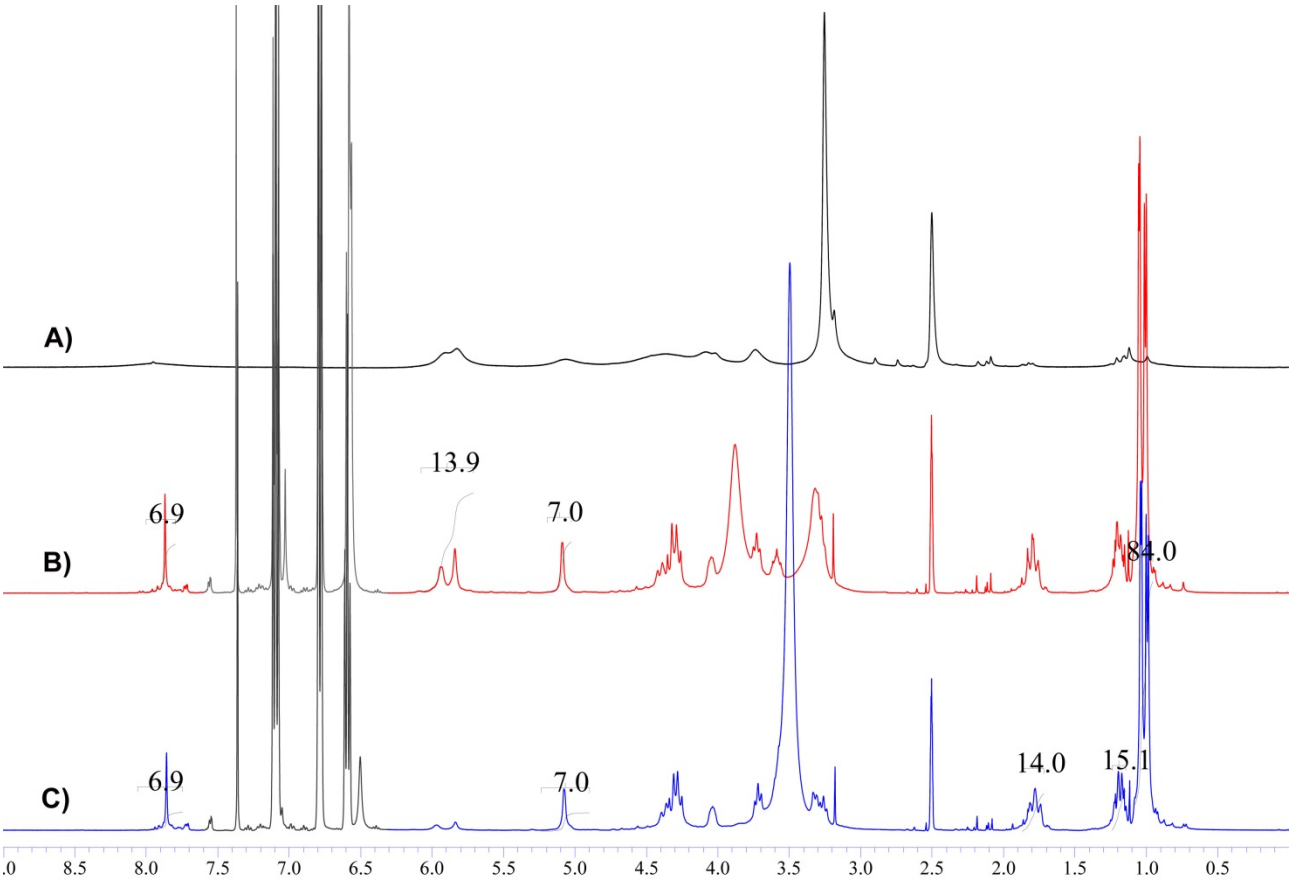

Fig.SI7. ^{1}H-NMR spectra of A) **CD6** in DMSO-d_6, B) after addition of phenylhydrazine in the nmr tube, C) after the addition of D_2O. Phenylhydrazine peaks are indicated in grey scale.

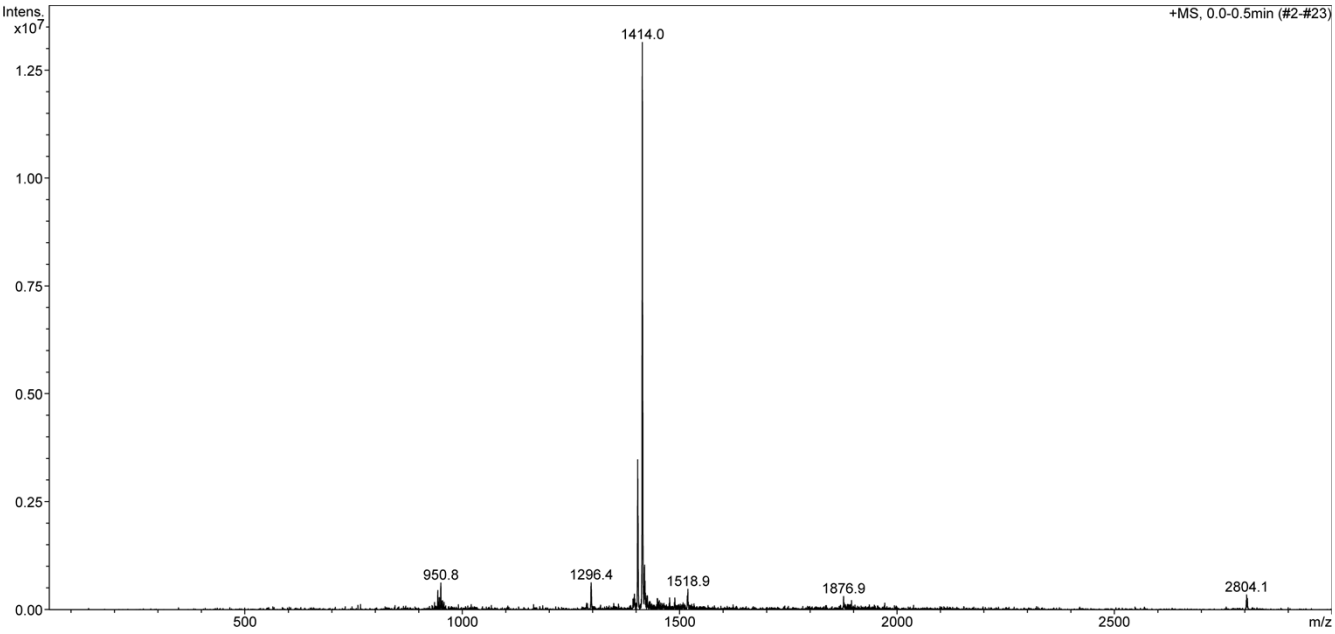

Fig.SI8. ESI-MS of **CD6**.

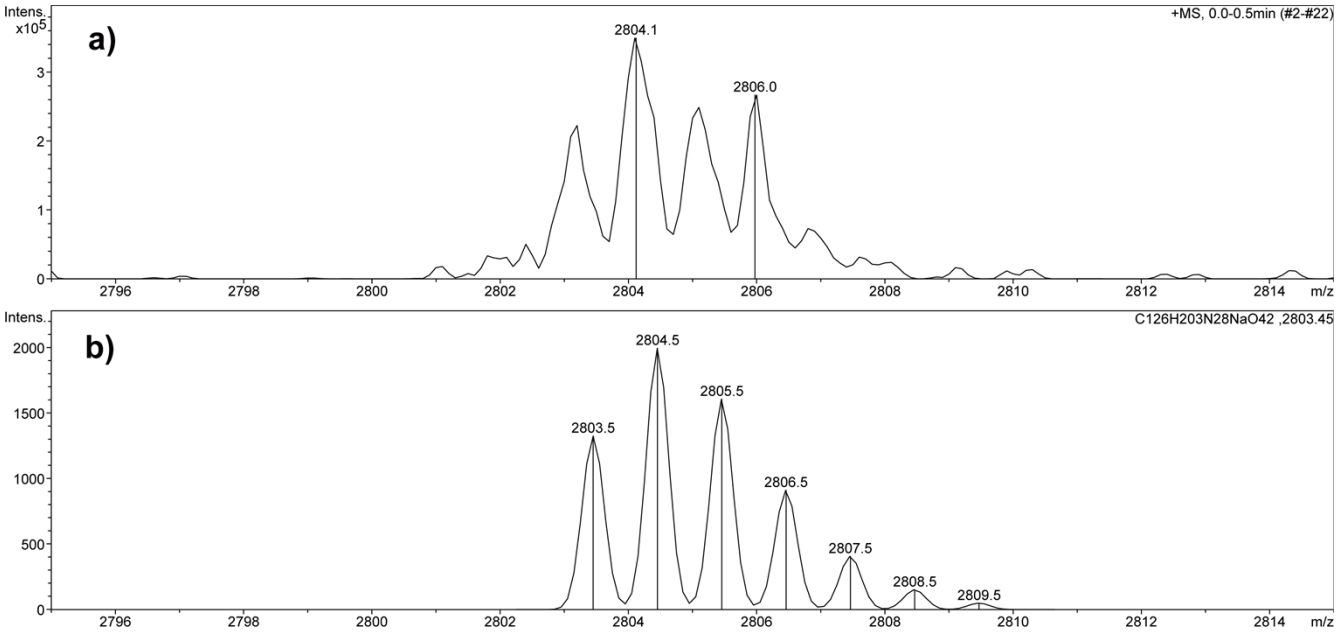

Fig.SI9. a) ESI-MS peak of the [**CD6**+Na]$^{+}$ adduct; b) simulated peak corresponding to the formula $C_{126}H_{203}N_{28}O_{42}Na$.

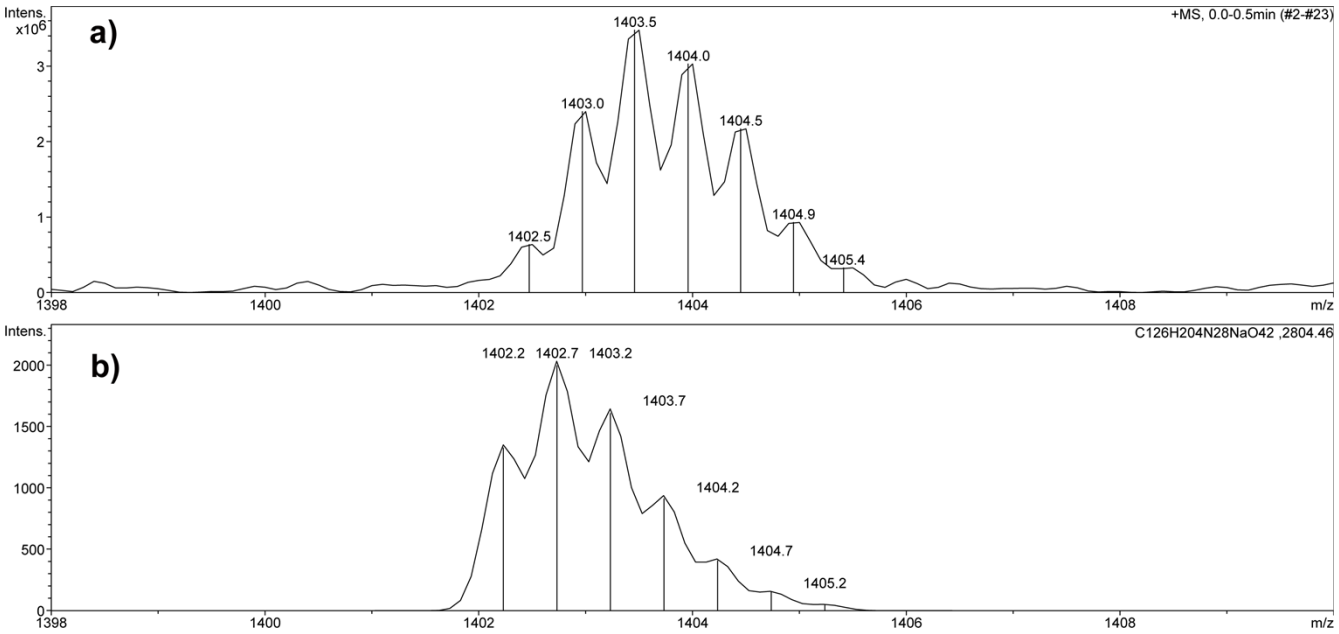

Fig.SI10. a) ESI-MS peak of the [**CD6**+Na+H]$^{2+}$ adduct; b) simulated peak corresponding to the formula $C_{126}H_{204}N_{28}O_{42}Na$.

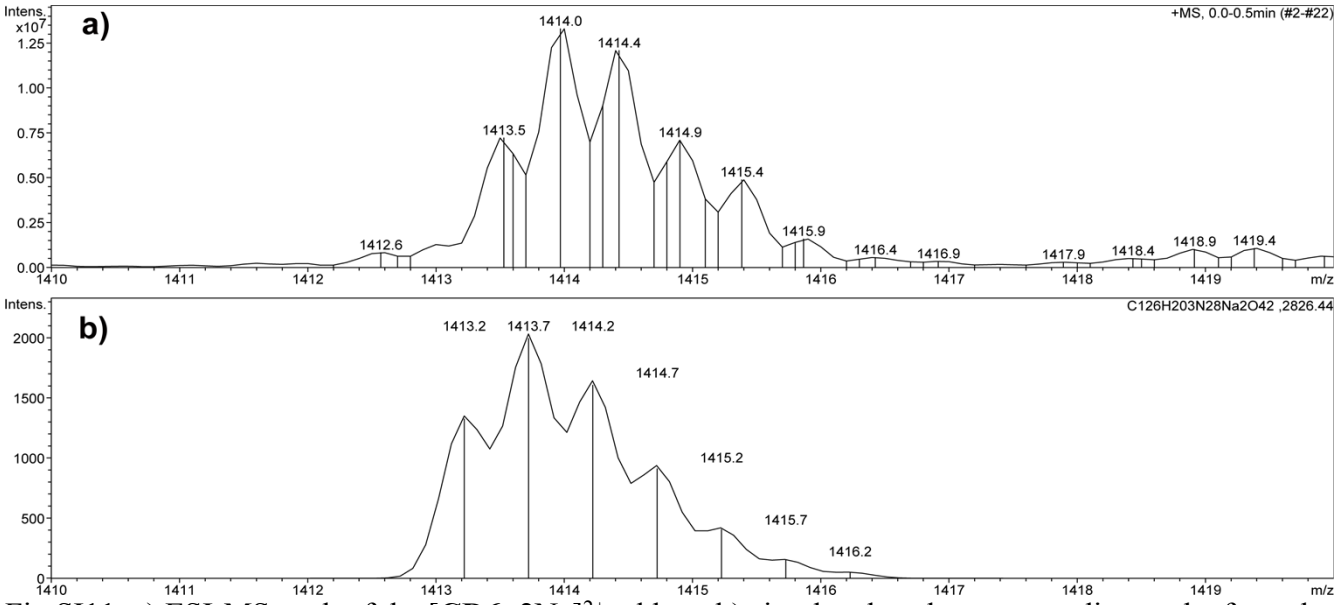

Fig.SI11. a) ESI-MS peak of the [**CD6**+2Na]$^{2+}$ adduct; b) simulated peak corresponding to the formula $C_{126}H_{203}N_{28}O_{42}Na_2$.

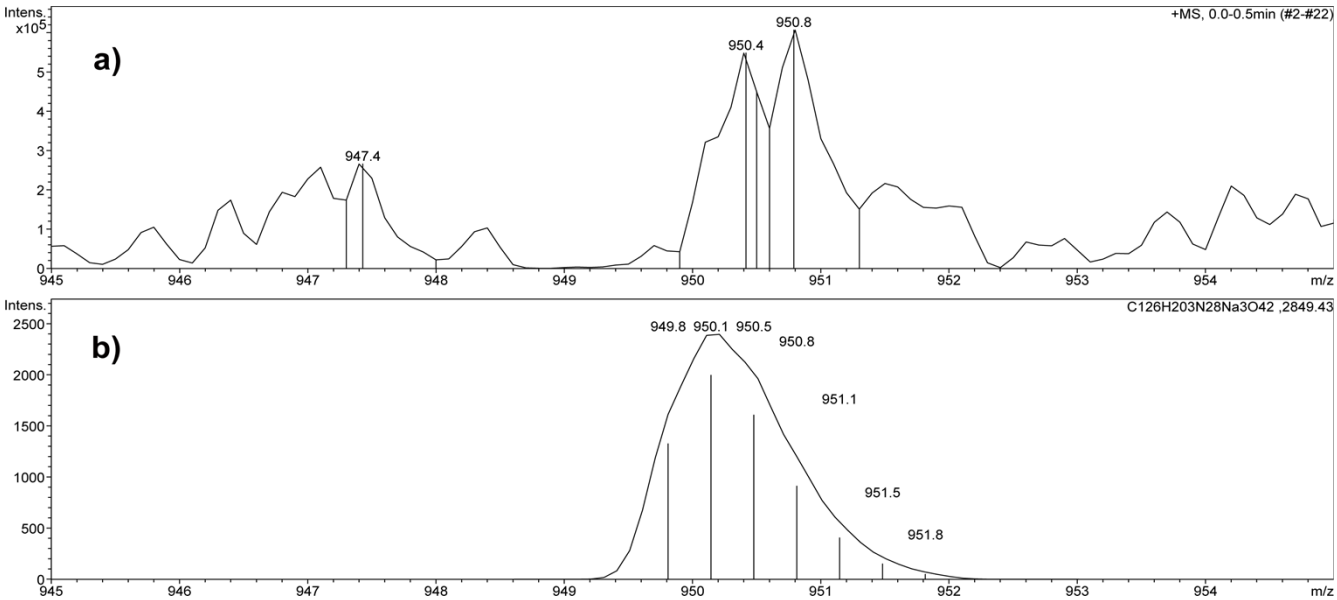

Fig.SI12. a) ESI-MS peak of the [**CD6**+3Na]$^{3+}$ adduct; b) simulated peak corresponding to the formula $C_{126}H_{203}N_{28}O_{42}Na_3$.

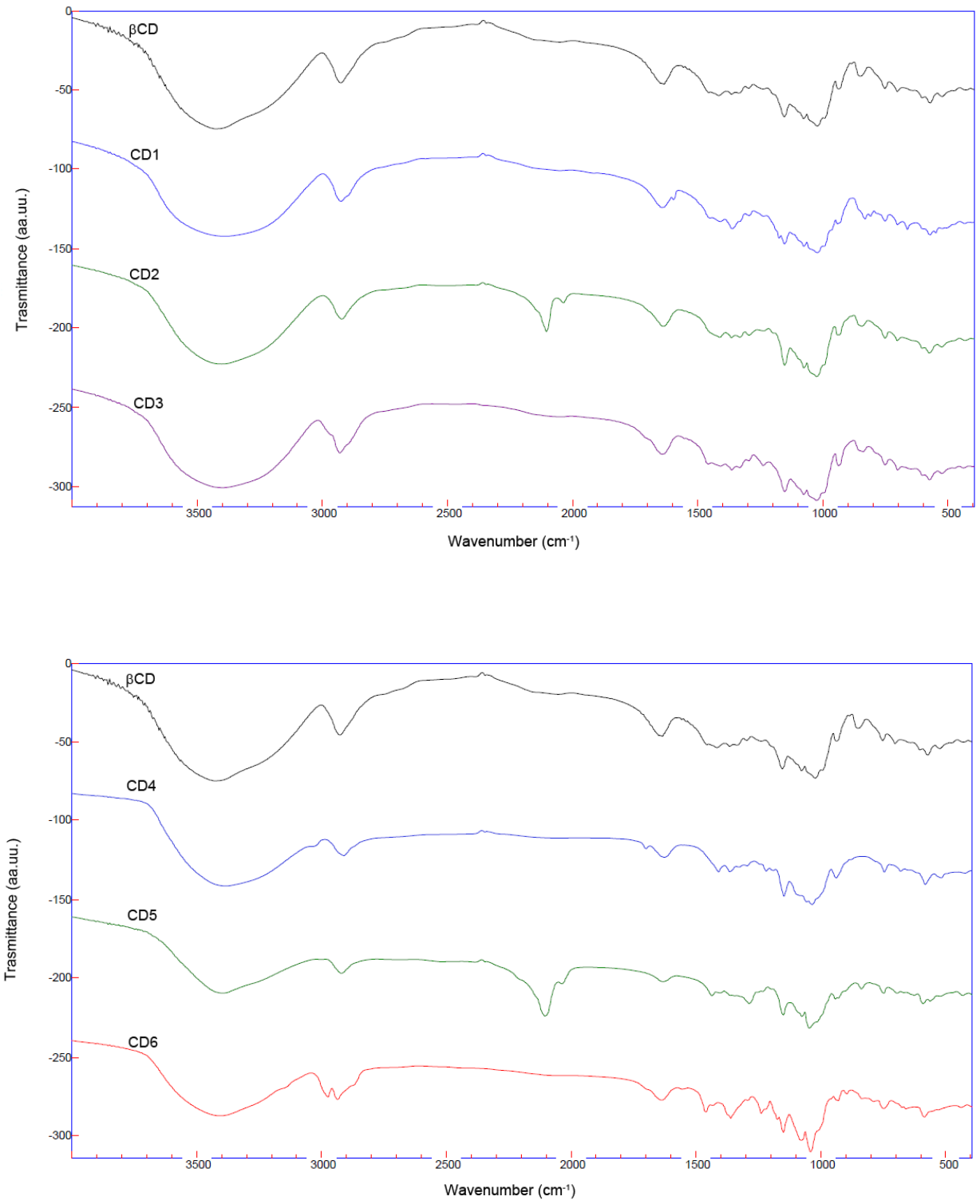

Fig.SI13. FT-IR spectra (KBr).

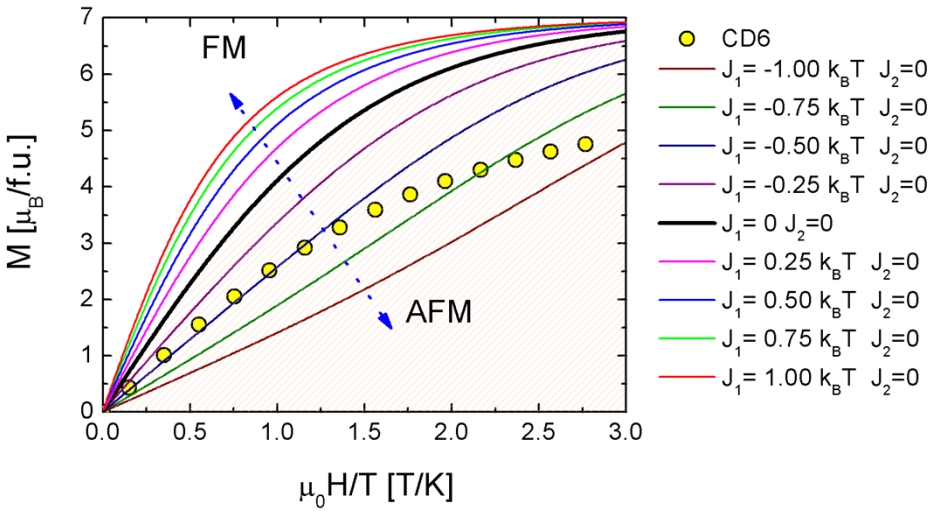

Fig. SI14: **CD6** magnetization data vs heptagonal model (see Fig. 7a in the full paper) calculations for different values of the exchange integrals: J_1 was tuned from -1 k_BT (strong AFM interactions) to 1 k_BT (strong FM interactions) setting J_2=0 for simplicity. It results that none of the theoretical curves matches the experimental data. The same simulation has been carried out scanning J_2 in a reasonable range without any significant result.