The influence of confinement effects on the thermophysical properties of 4-methoxyazobenzene

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Due to global warming and the high global demand for energy, the research and development of sustainable energy storage systems is of great interest. The photoswitchable phase change material 4-methoxy-azobenzene (4-MeO-Azo) allows simultaneous storage of two different forms of energy which can be released after an external trigger, shown in Fig. [1]. Herein, we report the change of the thermophysical properties of 4-MeO-Azo in confinement. Mesoporous silica like SBA-15, KIT-6 and SBA-16 were impregnated with 4-MeO-Azo to investigate the influence of different pore sizes and pore shapes on the melting point of *trans*-4-MeO-Azo by differential scanning calorimetry (DSC). The porous materials were impregnated with a load of 120 % of the theoretical pore volume measured by N_2-physisorption. The overload was used for internal signal calibration. So far, no crystallization of the *cis*-isomer has been detected, but only a glass transition, which was not investigated due to its weakness. In addition, the composites were irradiated for one hour with UV light (365 nm) to initiate *trans* to *cis* isomerization. This was followed by DSC measurement to investigate the dependence of the thermally induced *cis* to *trans* reaction on confinement. The integral of the exothermic signal enables the calculation of the conversion ratio. We were able to infer the following trends: (i) the melting point of *trans*-4-MeO-Azo decreases with decreasing pore size, (ii) the higher the mean curvature of the pores - from cylindrical (SBA-15) to curved cylindrical (KIT-6) to spherical (SBA-16) with same pore width - the lower the melting point, a trend that can be explained by the Gibbs-Thomson form factor, and (iii) the conversion ratio of the light-induced *trans* to *cis* conversion at r.t. seems to be higher in confined space compared to 4-MeO-Azo in bulk, whereas the heat-induced back reaction seems to be unaffected by the confinement.

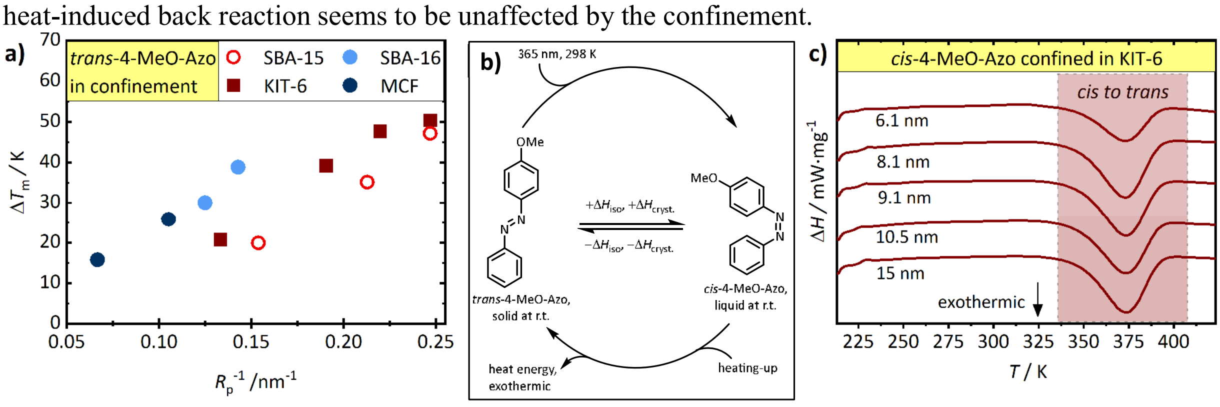

Fig. 1: a) Melting points T_{max}, b) Storage cycle of 4-MeO-Azo, c) DSC-measurement after irradiation.

References:

1. Z. Zhang, Y. He, Z. Wang, J. Xu, M. Xie, P. Tao, D. Ji, K. Moth-Poulsen, T. Li, Photochemical Phase Transitions Enable Coharvesting of Photon Energy and Ambient Heat for Energetic Molecular Solar Thermal Batteries That Upgrade Thermal Energy, J. Am. Chem. Soc., 142 (2020) 12256-12264.