Electronic supplementary information (ESI)

Oxidative transformation of thiol groups to disulfide bonds in mesoporous silicas: A diagnostic reaction for probing distribution of organic functional groups

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Density Functional Calculations.[1] The B3LYP density functional, Becke's three-parameter exchange functional,[2] and Lee–Yang–Parr gradient-corrected correlation functional[3] with moderate-sized 6-31G(d,p) basis set[4] were utilized to calculate the optimized structure of the T^3-$(Q^4)_n$-T^3 motifs (n = 0-3) in which each peripheral Si atom was capped and saturated with hydrogen atoms.

References

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(2) A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648.

(3) C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785.

(4) G. A. Petersson and M. A. Al-Laham, *J. Chem. Phys.*, 1991, **94**, 6081.

Table S1. Textural properties of the adsorbents studied.

	Surface area (cm^2/g)	Pore volume (cm^3/g)	Pore size (nm)
S1-0.06	800	0.44	3.0
S1-0.2	710[a]	0.32[a]	2.5
S15-0.14	560	0.66	4.6
M-0.14	240	0.26	3.6

[a]This sample contains a surface area of 350 cm^2/g and a pore volume of 0.19 cm^3/g due to micropores.

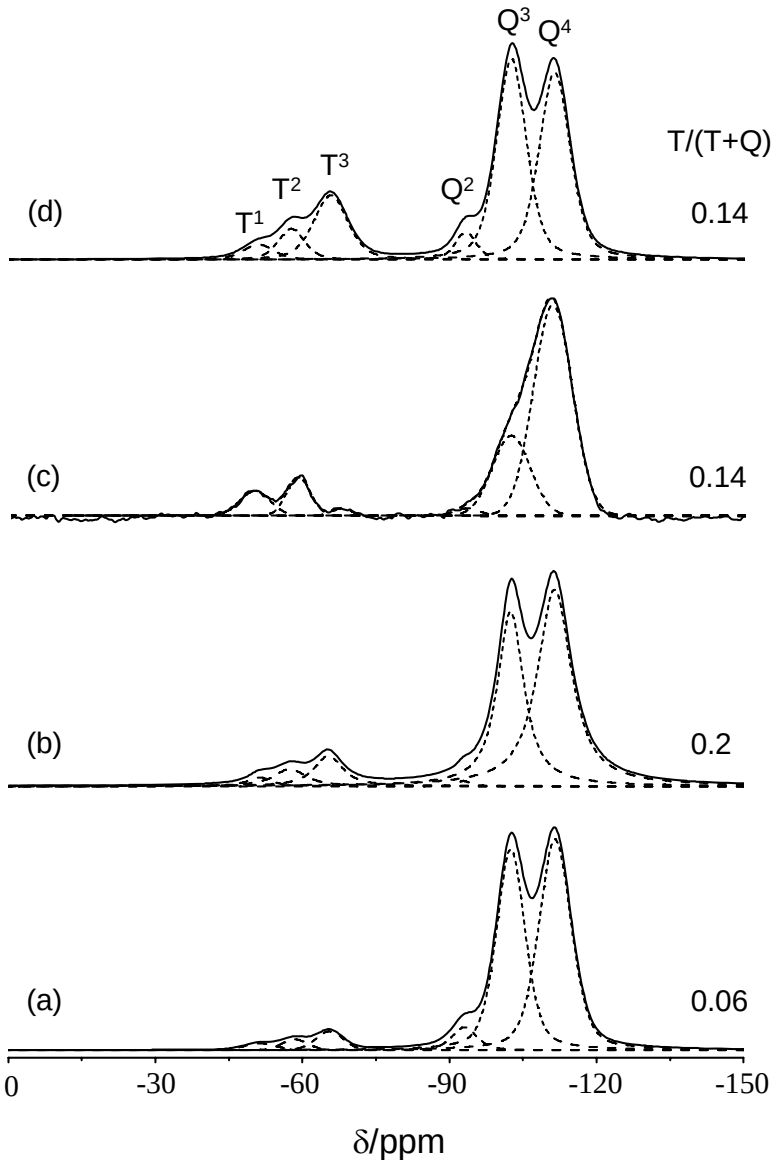

Fig. S1. ^{29}Si MAS NMR spectra of (a) S1-0.06, (b) S1-0.2, (c) M-0.14, and (d) S15-0.14. The dashed lines represent the components used for spectral deconvolution and the T/(T + Q) ratios are indicated in the figure.

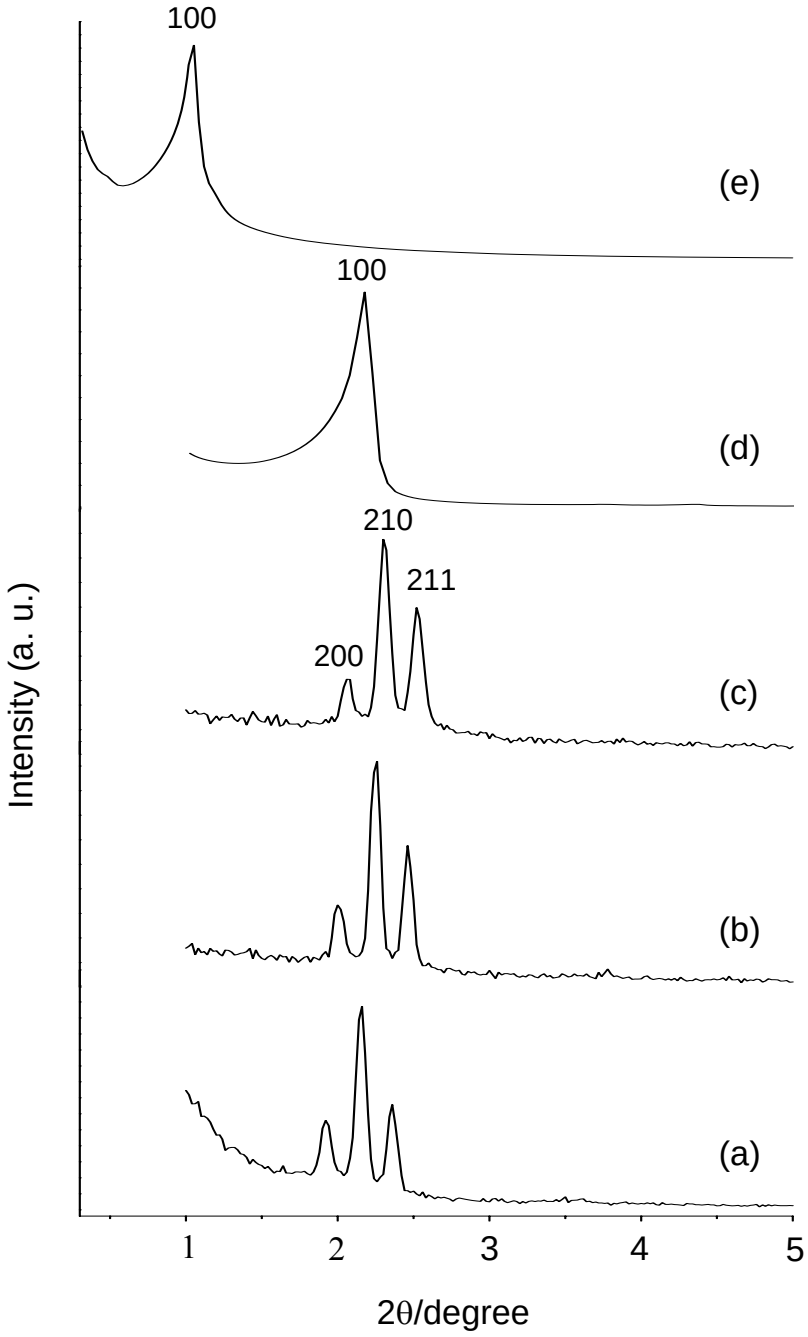

Fig. S2 Powder XRD patterns of (a) S1-0.06, (b) S1-0.1, (c) S1-0.2, (d) M-0.14, and (e) S15-0.14.

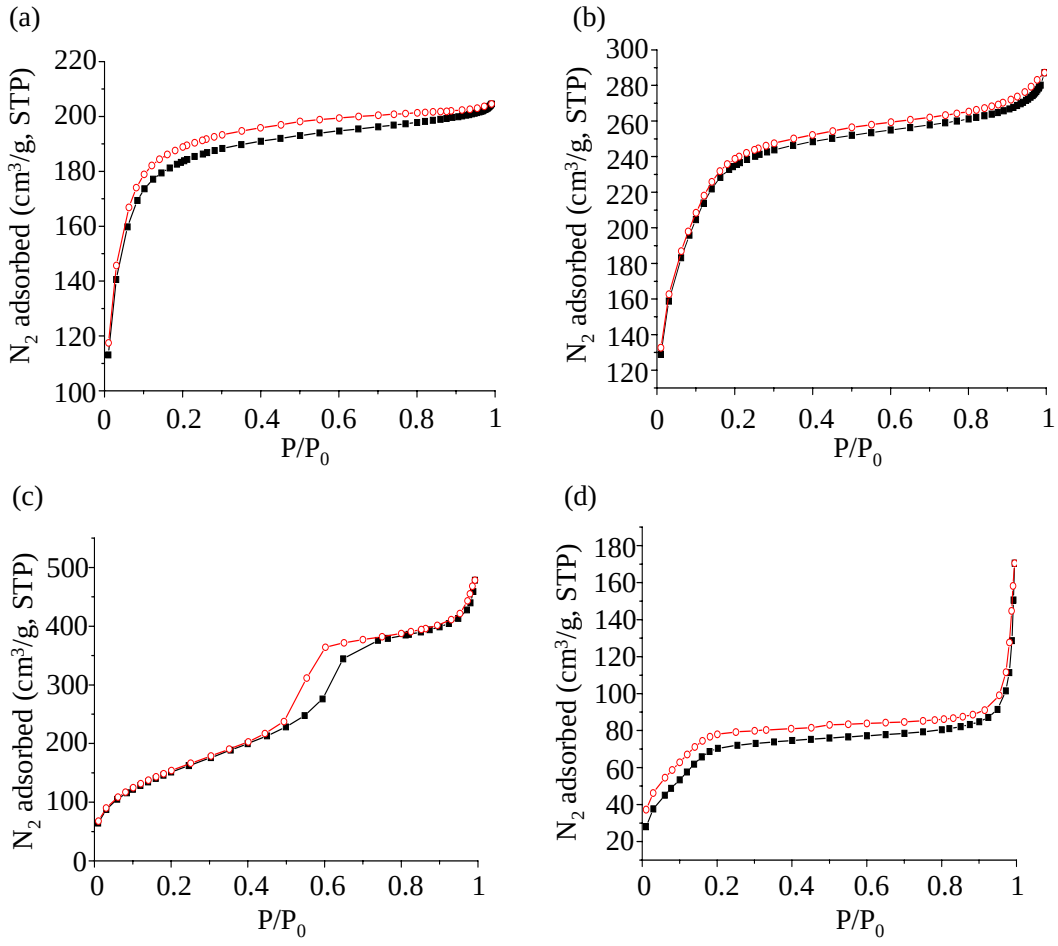

Fig. S3 N_2 adsorption-desorption isotherms of (a) S1-0.2, (b) S1-0.06, (c) S15-0.14, and (d) M-0.14. The black and red parts represent the adsorption and desorption isotherms, respectively.

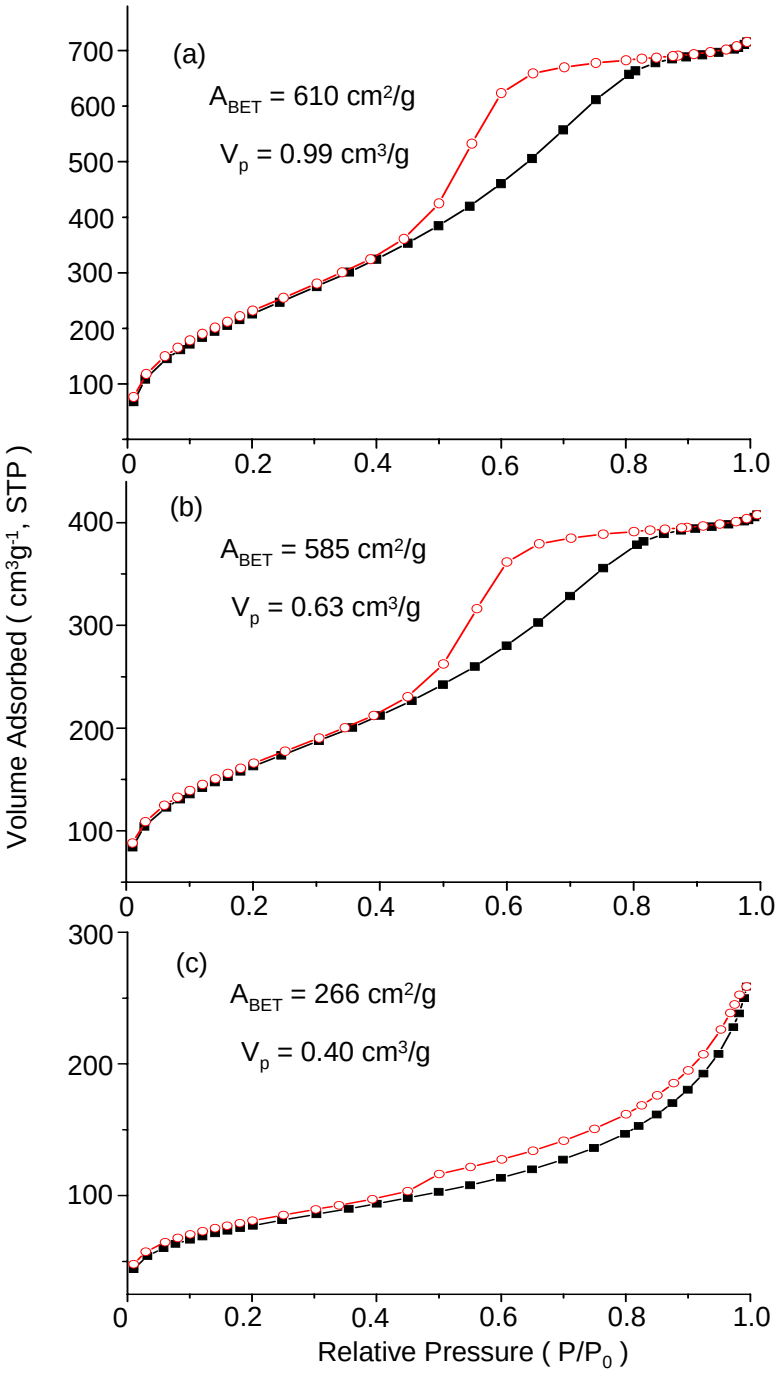

Fig. S4 N_2 adsorption-desorption isotherms of the SiO_2 samples, prepared with identical experimental conditions of SBA-15 under template-free conditions (i.e., without P123 templating), functionalized with (a) 0, (b) 10, and (c) 20% of thiol groups. The black and red parts represent the adsorption and desorption isotherms, respectively.

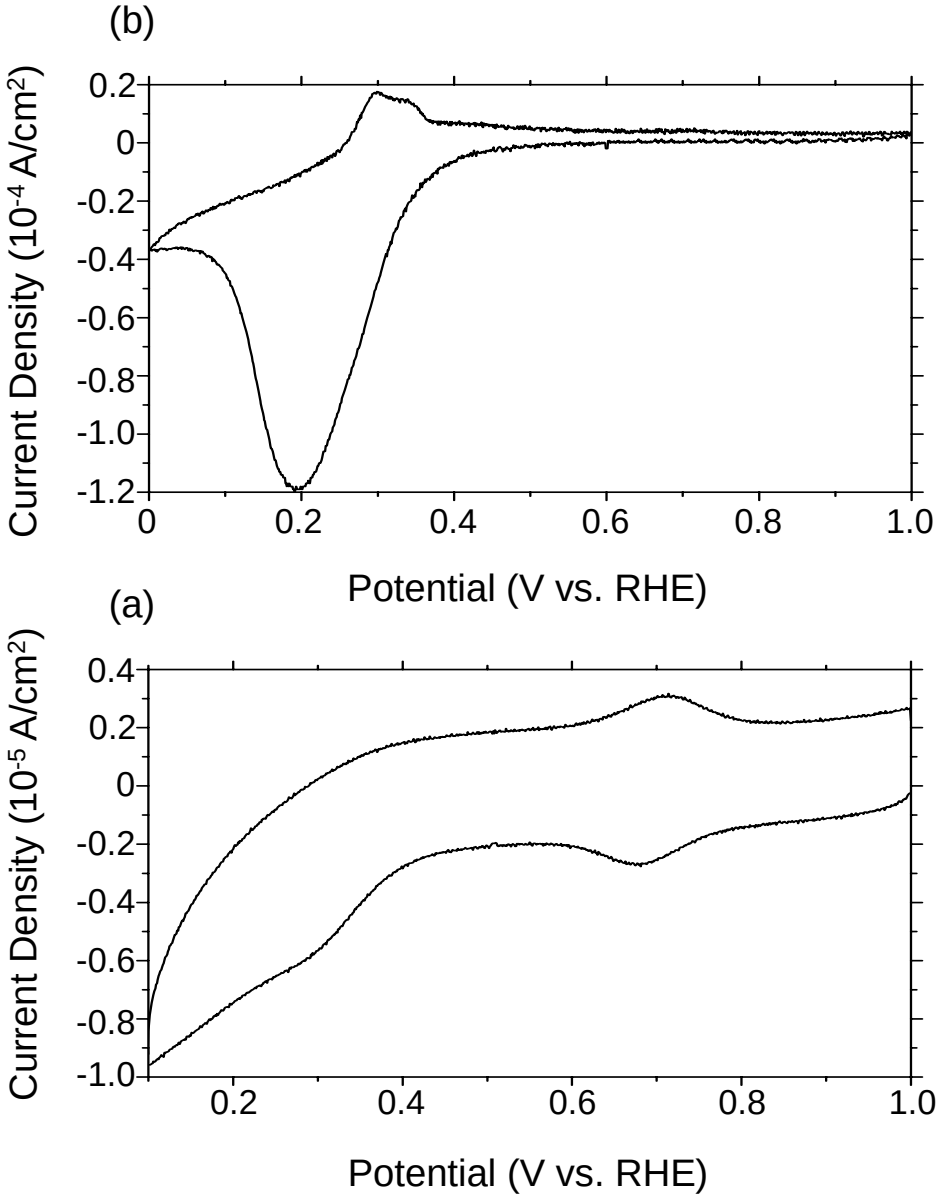

Fig. S5 Cyclic voltammograms of the S1-0.2 sample after Cu^{2+} adsorption of solutions containing (a) 140 and (b) 1000 ppm of Cu^{2+} ions.

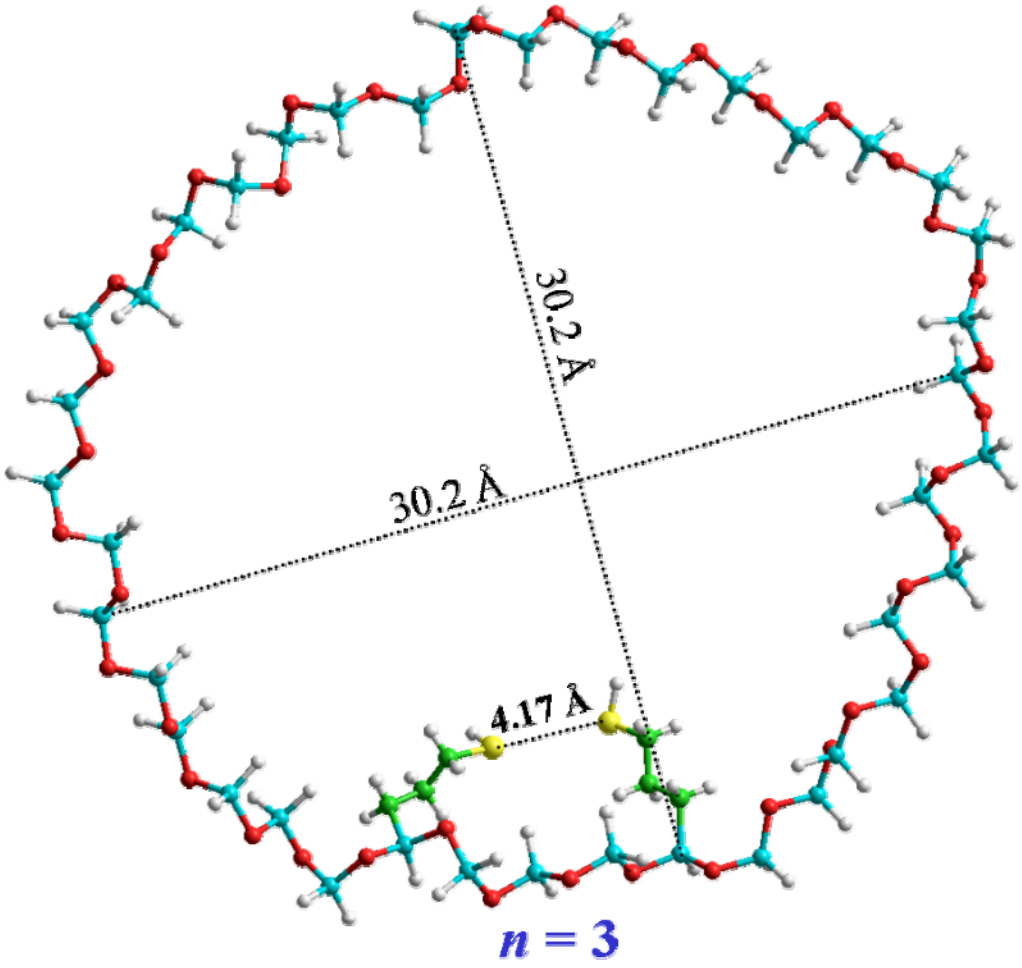

Fig. S6 The optimized structure of T'-$(Q')_3$-T'-$(Q)_{35}$ (n = 3) obtained from the MM+ molecular mechanics force field in the suite of HyperChem program. Si: Cyan; C: Green; S: Yellow; O: Red; H: White. The S--S distance is 4.17 Å in this model.

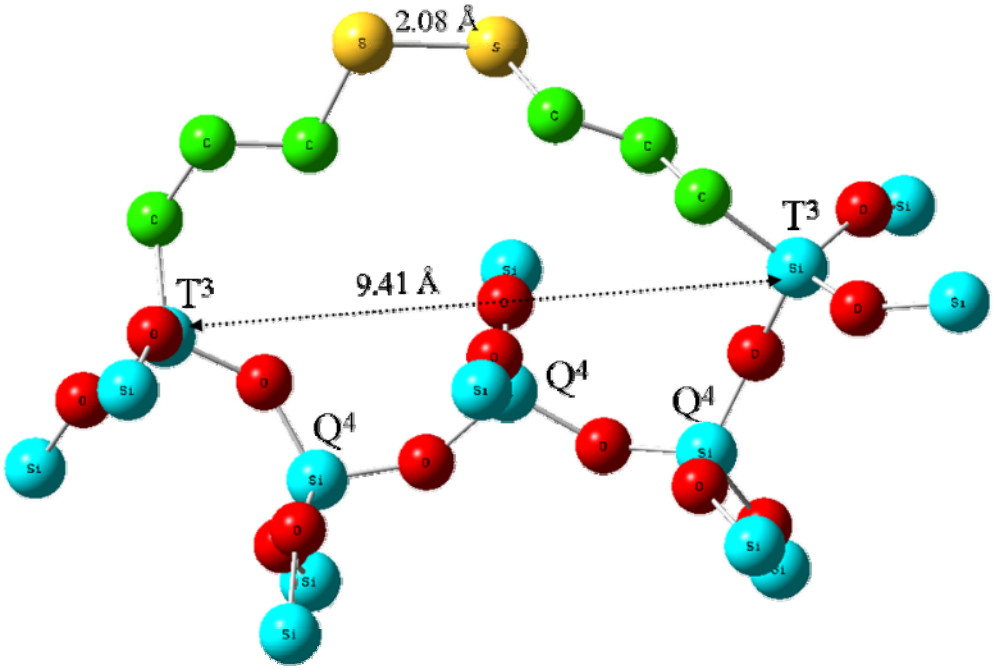

Fig. S7 The optimized structure of the T^3-$(Q^4)_3$-T^3 motif obtained from DFT calculations. Si: Cyan; C: Green; O: Red and S: Yellow. The S--S distance is 2.08 Å. The hydrogen atoms are not shown in the figure for clarity.

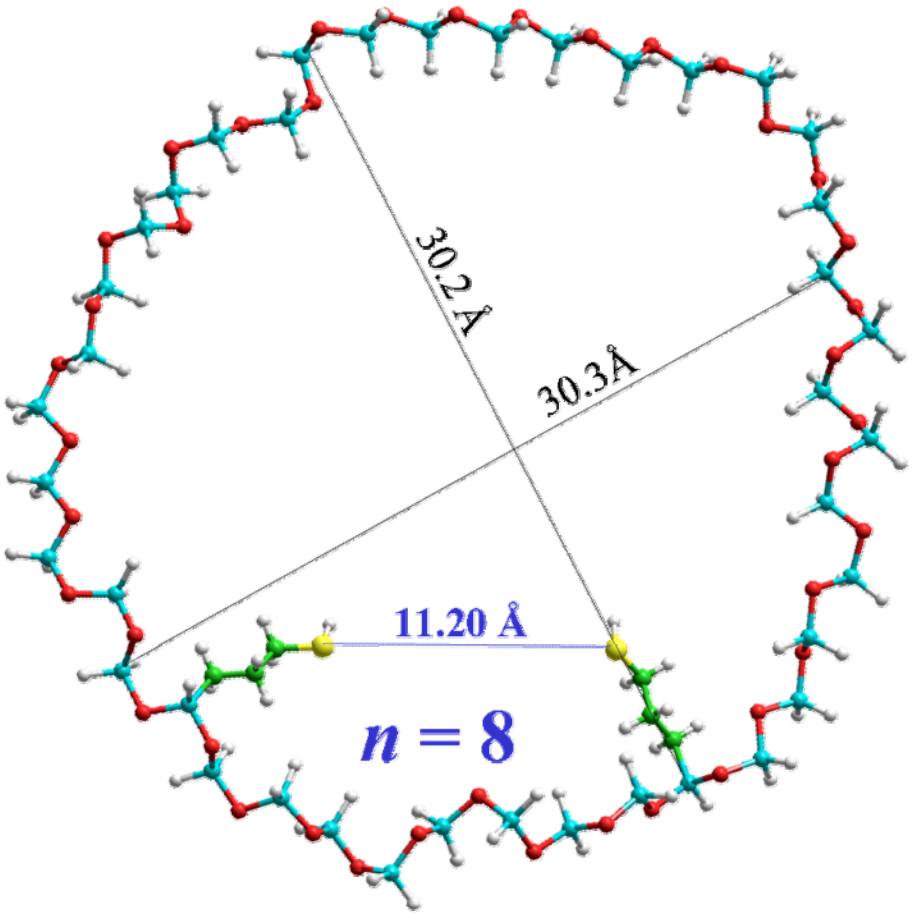

Fig. S8 The optimized structure of T'-(Q')$_8$-T'-(Q)$_{30}$ (n = 8) obtained from the MM+ molecular mechanics force field in the suite of HyperChem program. Si: Cyan; C: Green; S: Yellow; O: Red; H: White. The S--S distance is 11.20 Å in this model.