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Mixed star-shaped POSS-based molecule with hydroxy group-containing units and azobenzene fragments as two types of arms

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Experimental

Materials. Octakis(dimethylsilyloxy)silsesquioxane **1**, platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex solution (Karsted's catalyst) in xylene (Pt ~ 2%) and 2-allyloxyethanol (**3**) were purchased from Sigma-Aldrich. Dye phenyl[4-(prop-2-en-1-yloxy)phenyl]diazene (**2**) was synthesized as reported [I. M. Tkachenko, Ya. L Kobzar, O. G. Purikova, A. L. Tolstov, O. V. Shekera and V. V. Shevchenko, *Tetrahedron Lett*., 2016, **57**, 5505]. Toluene was distilled over calcium hydride. Other reagents and solvents were purified routinely.

Measurements. The NMR spectra were recorded on Bruker DMX 400 spectrometer at room temperature in $CDCl_3$. Chemical shifts are reported relative to chloroform (δ = 7.25 ppm for ^{1}H NMR and δ = 77.00 ppm for ^{13}C NMR). FTIR spectrum (4000−400 cm^{-1}) of compound **4** was recorded on a TENSOR 37 spectrometer using KBr pellet. The UV-Vis spectra were recorded on Shimadzu UV-2450 spectrophotometer. In order to achieve photoisomerization, the solution of **4** in chloroform (0.005 mg ml^{-1}) was prepared. Photoisomerization experiment was performed by irradiating the sample **4** (chloroform solution – 0.005 mg ml^{-1}) at 10 cm distance with 365 nm UV light from DeLux EBT-01 mercury lamp (26 W) followed by recording the absorbance spectra. The first-order rate constant of photoisomerization were determined from the slope of the plot of $\ln[(A_0 - A_\infty)/(A_t - A_\infty)]$ vs time, where A_0, A_∞, and A_t are the absorbances before irradiation, after reaching a photostationary state, and at a given time, respectively [P. A. Ledin, I. M. Tkachenko, W. Xu, I. Choi, V. V. Shevchenko and V. V. Tsukruk, *Langmuir*, 2014, **30**, 8856]. Mass spectrum was obtained using MALDI-TOF instruments (ABISciex 5800 MALDI-TOF-TOF) with dithranol as a matrix in positive reflector mode.

*Synthesis of conjugate **4**.* Compound POSS **1** (0.150 g, 0.147 mmol), azo dye **2** (0.211 g, 0.884 mmol) and compound **3** (0.030 g, 0.295 mmol) were dissolved in toluene (3 ml), and the Karsted's catalyst (30 μl) was added to the reaction solution. The mixture was stirred at 40 ^{o}C under nitrogen for 72 h and then cooled to room temperature. The solvent was removed by evaporation *in vacuo*, and the residue was dissolved in CH_2Cl_2 and passed through a silica gel. The solvent was concentrated, and the obtained solid was purified by double precipitation from chloroform solution into hexane. The final product was dried in a vacuum oven overnight at 40 °C. Yield: 0.300 g.

^{1}H NMR ($CDCl_3$, 400 MHz, δ, ppm): 0.15-0.20 (m, -Si$(CH_3)_2$-), 0.58 (m, -SiC**H$_2$**CH_2CH_2O-ethanol), 0.72 (m, -SiC**H$_2$**CH_2CH_2O-dye), 1.86 (m, -$SiCH_2C$**H$_2$**CH_2O-), 3.40 (m, -$SiCH_2CH_2C$**H$_2$**O-ethanol), 3.48 (m, -OC**H$_2$**CH_2OH), 3.67 (m, -OCH_2C**H$_2$**OH), 3.82 (br.s, -OH), 3.88-3.98 (m, -$SiCH_2CH_2C$**H$_2$**O-dye), 6.93 (m, Ph), 7.46 (m, Ph), 7.84 (m, Ph). ^{13}C NMR ($CDCl_3$, 100.62 MHz, δ, ppm): -0.33 (Si$(CH_3)_2$-dye), 1.01 (Si$(CH_3)_2$-alcohol), 13.71 and 22.90 (-Si**C**H_2**C**H_2CH_2O-), 61.78 (-CH_2OH), 70.50 (-$SiCH_2CH_2$**C**H_2O-dye), 71.82 (-**C**H_2CH_2OH), 73.76 (-$SiCH_2CH_2$**C**H_2O-ethanol), 114.58, 122.52, 124.75, 128.97 and 130.26 (Ar-C), 146.80 and 152.71 (Ar-C-N), 161.51 (Ar-C-O). FTIR (KBr, cm^{-1}): 3600-3200 (-OH), 3100-2800 (C-H), 1603, 1516 (C=C, arom.), 1258 (C-O-C), 1099 (Si-O-Si). UV-vis, $CHCl_3$: λ_{max} = 348 nm.

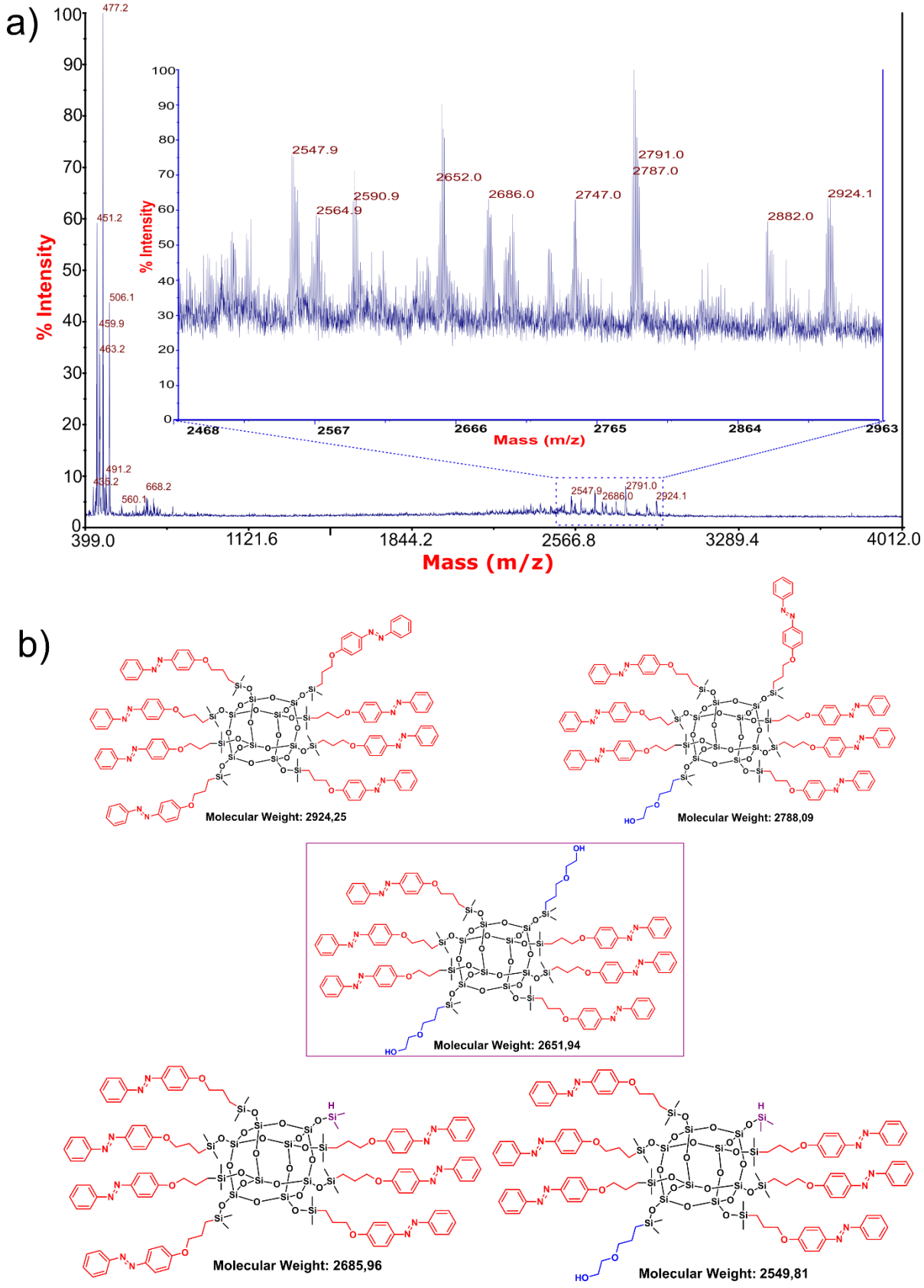

Figure S1. (a) MALDI-TOF MS spectrum of substance **4** (a mixture of different structures); (b) the ideal structure of **4** (in pink square) and other chemical structures that can be formed during the synthesis of **4**.

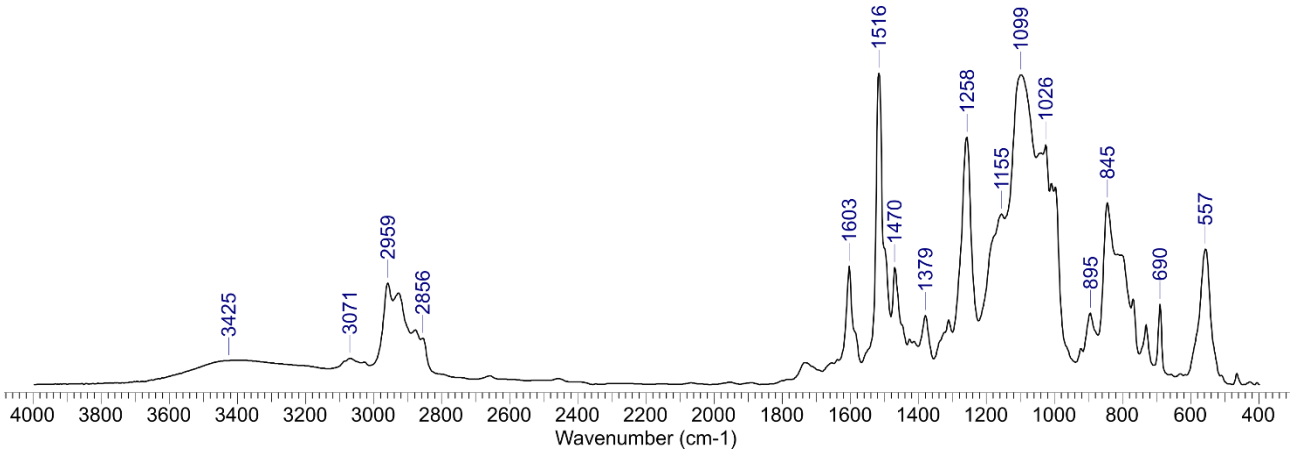

Figure S2. FTIR spectrum of substance **4**.

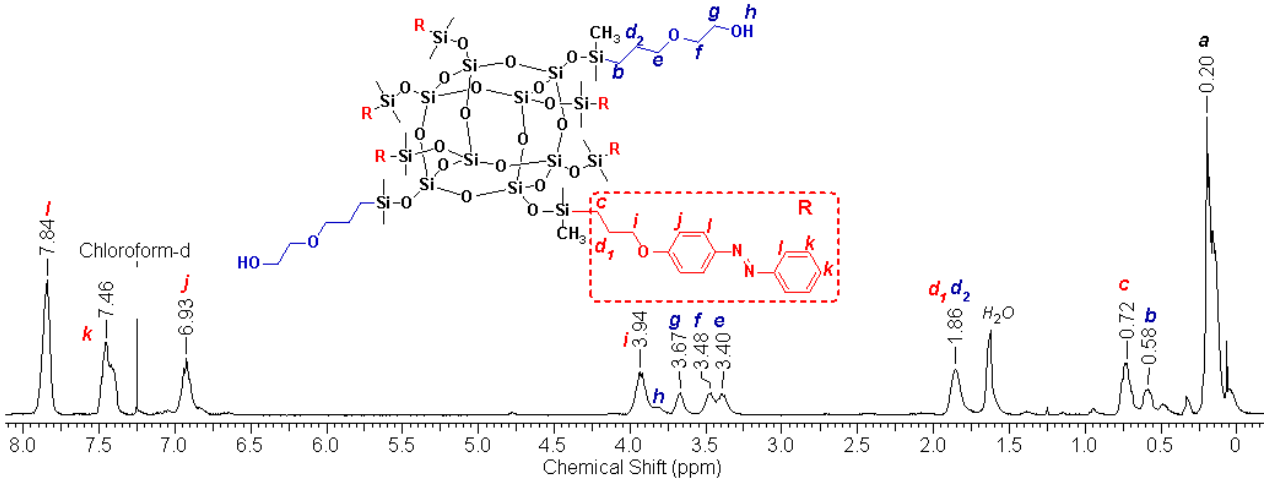

Figure S3. ^{1}H NMR spectrum of substance **4.**

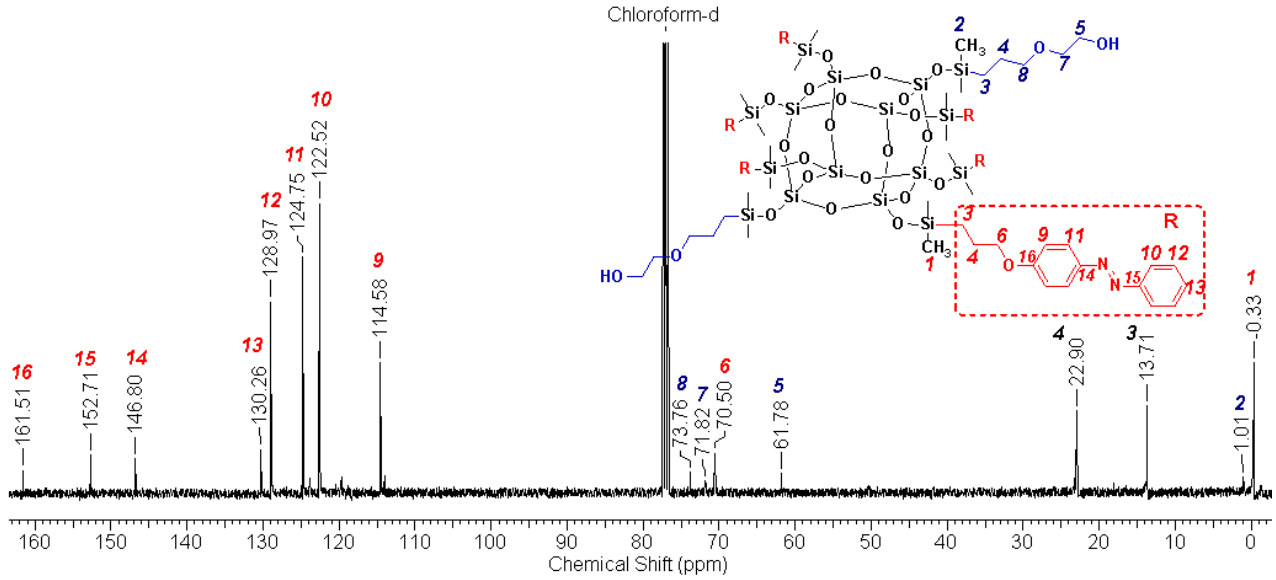

Figure S4. ^{13}C NMR spectrum of substance **4.**