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SUPPLEMENTARY INFORMATION (SI)

Novel Branched Nanostuctures Based on Polyhedral Oligomeric Silsesquioxanes and Azobenzene-Based Dyes Containing Different Alkyl Chains and Isolation Groups

Ihor M. Tkachenko,[a] *Yaroslav L. Kobzar,*[a] *Volodymyr F. Korolovych,*[b] *Alexandr V. Stryutsky,*[a] *Liubov K. Matkovska,*[a] *Valery V. Shevchenko,**[a] *Vladimir V. Tsukruk**[b]

[a] Institute of Macromolecular Chemistry, National Academy of Sciences of Ukraine, Kharkivske shosse 48, Kyiv, 02160, Ukraine

[b] School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia, 30332, United States

*Corresponding authors' e-mail: valpshevchenko@gmail.com (Valery V. Shevchenko) and vladimir@mse.gatech.edu (*Vladimir V. Tsukruk*)

General Experimental

Materials

Initial azo dyes **1-5** and **4-TMS** were synthesized as described previously.[1] All chemicals were purchased from Sigma-Aldrich. Octakis(dimethylsilyloxy)silsesquioxane (**POSS-H**), octavinyloctasilasesquioxane (**POSS-vinyl**), platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex solution (Karsted's Catalyst) in xylene (Pt ~ 2%) were used as received. Toluene was distilled over calcium hydride. All other reagents and solvents were used as received from standard vendors.

Measurements

^1H NMR spectra were recorded on a Varian VXR-300 instrument or on a Bruker Avance DRX 500 instrument, ^{19}F and ^{13}C NMR spectra – on a Bruker Avance 400 instrument at room temperature in $CDCl_3$. Chemical shifts are reported relative to chloroform (δ = 7.25 ppm for ^1H NMR and δ = 77.00 ppm for ^{13}C NMR). For ^{19}F NMR fluorotrichloromethane was used as the internal standard. Fourier transform infrared (FTIR) spectra (4000−600 cm^{-1}) of synthesized compounds were recorded on a TENSOR 37 spectrometer using KBr pellets.

The UV-Vis spectra were recorded on Shimadzu UV-2450 spectrophotometer. In order to achieve photoisomerization of the azobenzene derivatives in solution, the respective solutions in chloroform (0.005 mg/mL) were prepared. Photoisomerization experiments were performed by irradiating the samples 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. The photoisomerization experiments were performed in triplicate for each sample.

The DSC analyses were run using a TA Q200 instrument. Heating rate was 10°C/min from -50 to 150 °C performing three successive runs (heating–cooling–heating), with ca. 4 mg samples. The glass transition temperature was taken as the midpoint of the heat capacity transition between the upper and lower points of the deviation from the extrapolated glass and liquid lines.

The structures of Azo-POSS-1 and Azo-POSS-3 were investigated using wide angle X-ray diffraction (XRD) instrument Dron 2.0 (Bourevestnik, Inc., St. Petersburg, Russia) using an X-ray tube with a copper anode and a nickel filter at 30 kV and 20 mA. The XRD patterns were collected in the range of angles 2θ from 5 to 40° that corresponds to a wave vector (q) values 3.6–27.9 nm^{-1}, where $q = 4\pi\sin\theta / \lambda$ (θ – a half of the diffraction angle, λ – 0.154 nm).

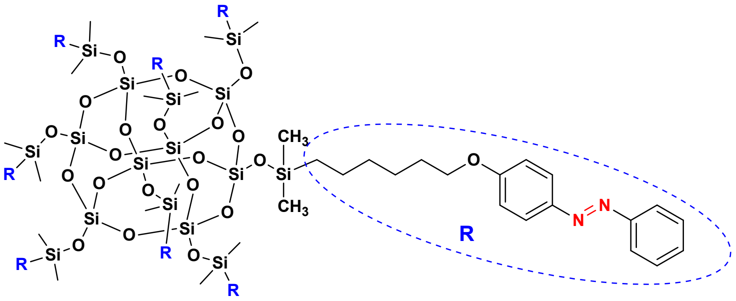
Quartz substrates with dimensions of 1 cm x 2 cm and the [100] orientation (Semiconductor Processing) were cleaned with piranha solution (3:1 concentrated sulfuric acid and hydrogen peroxide mixture.[2] Caution strong oxidizer!) in accordance with the usual procedure. Subsequently, they were abundantly rinsed with Nanopure water and dried with a dry nitrogen stream. Spin-assisted deposition method was performed by dropping the star molecules solution in toluene (20 mg/mL) onto the quartz substrate, rotating for 30s at 3000 rpm on a spin-coater (Laurell), and the solution was filtered by filter with mesh size of 200 nm before spin coating and the films were dried in ambient conditions before measurements.

Spectroscopic ellipsometry measurements were performed in air with M-2000U ellipsometer (Woollam). The spectral range was 245-1000 nm (D2 and QTH lamps). Ellipsometry data from all samples were acquired at 65°, 70°, and 75° angles of incidence over the spectral range. The POSS-Dye-Layers were fitted with a three layer model which consists of silicon substrate, silicon oxide layer (2 nm layer thickness), and a Cauchy layer (MSE<4) in the range from 550 to 1000 nm. The complex refractive index was then determined by point-by-point fitting over the entire spectral range. This reference function was used in the general oscillator layer to obtain dispersion curves by fitting five-six Gaussian functions.

AFM images were obtained using an ICON Dimension microscope (Bruker) with AFM tip Hi'Res-C15/Cr-Au (MikroMash) in air at 90° scan angle and 0.2-0.45 Hz scan rate according to the well-established procedure.[3] All silicon wafers were pre-cleaned by "piranha solution" (*caution: strong oxidizer!)* according to the typical procedure.[3,4] Image processing was performed using NanoScope 1.40 and Gwyddion 2.36 software.

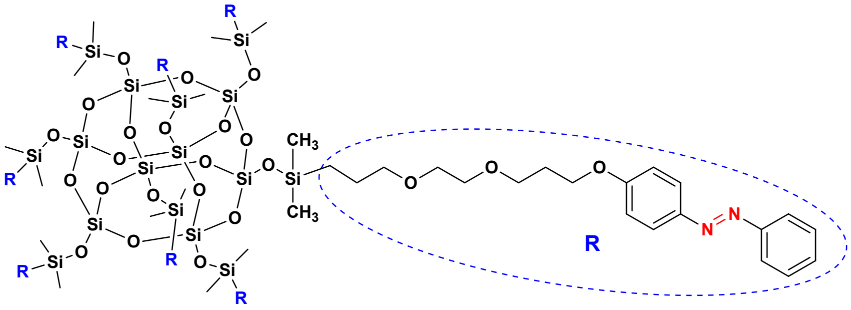
Synthetic Procedures

*Synthesis of **Azo-POSS-1** derivative.*



A total of 0.300 g (1.070 mmol) of azo dye **1** and 0.136 g (0.134 mmol) of **POSS-H** was dissolved in 3 mL of toluene, and 30 μL of Karsted's Catalyst was added to the reaction solution. The reaction mixture was stirred at 40^{o}C for 72 h and then cooled to room temperature. After removing all the solvents at reduced pressure, 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^{o}C. Yield: 60%. ^{1}H NMR ($CDCl_3$, 400 MHz, δ, ppm): 0.13 (s, -Si(CH_3)$_2$), 0.60 (br.s, -SiC**H$_2$**CH$_2$-), 1.37 (br.s, -CH$_2$CH$_2$-), 1.45 (br.s, -SiCH$_2$C**H$_2$**-), 1.77 (br.s, -C**H$_2$**CH$_2$O-), 3.96 (br.s, -CH$_2$C**H$_2$**O-), 6.95 (d, *J*=7.8 Hz, Ph), 7.39-7.49 (m, Ph), 7.84-7.88 (m, Ph). ^{13}C NMR ($CDCl_3$, 125.73 MHz, δ, ppm): -0.26 (Si(CH_3)$_2$), 17.64 (-SiCH$_2$-), 22.90, 25.74, 29.17 and 33.12 (-(CH_2)$_4$-), 68.27 (-OCH$_2$-), 114.62, 122.51, 124.71, 128.98 and 130.25 (Ar-C), 146.81 (Ar-C-N), 152.75 (Ar-C-N), 161.66 (Ar-C-O). FTIR (KBr, cm^{-1}): 3100-2800 (C-H), 1601, 1502 (C=C, arom.), 1254 (C-O-C), 1096 (Si-O-Si). UV-vis, $CHCl_3$: λ_{max} = 347 nm.

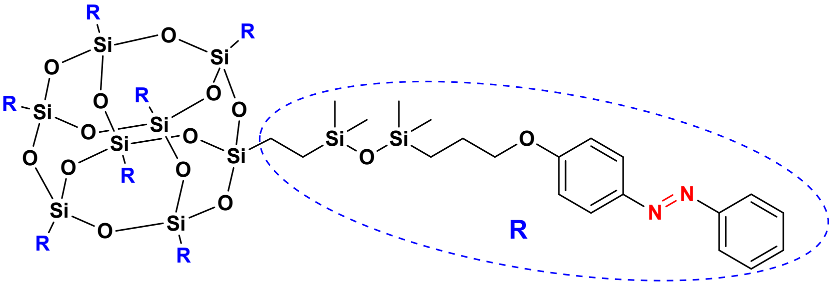
*Synthesis of **Azo-POSS-2** derivative.*



The **Azo-POSS-2** was prepared in the same manner as **Azo-POSS-1**, with azo dye **2** used instead of compound **1**. Yield: 50%. ^{1}H NMR ($CDCl_3$, 500 MHz, δ, ppm): 0.12 (s, -Si(CH_3)$_2$), 0.57 (br.s, -SiC**H$_2$**CH$_2$CH$_2$O-), 1.61 (br.s, -SiCH$_2$C**H$_2$**CH$_2$O-), 2.07 (br.s, -OCH$_2$C**H$_2$**CH$_2$O-), 3.40 (br.s, -OC**H$_2$**CH$_2$CH$_2$OAr), 3.57 (br.s, -OCH$_2$CH$_2$O-), 3.64 (br.s, -SiCH$_2$CH$_2$C**H$_2$**O-), 4.11 (br.s, -OCH$_2$CH$_2$C**H$_2$**OAr), 6.99 (d, *J*=7.7 Hz, Ph), 7.41 (t, *J*=6.6 Hz, Ph), 7.48 (t, *J*=6.6 Hz, Ph), 7.85-7.89 (m, Ph). ^{13}C NMR ($CDCl_3$, 125.73 MHz, δ, ppm): -0.36 (Si(CH_3)$_2$), 13.61

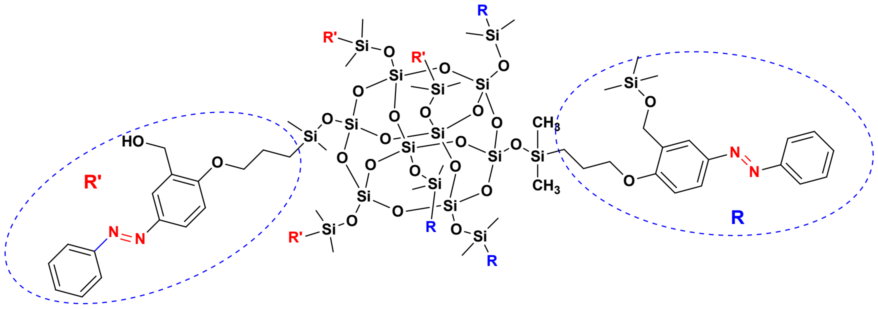
(-Si$CH_2CH_2CH_2$-), 23.08 (-Si$CH_2CH_2CH_2$-), 29.54, 65.20, 67.67 (-$OCH_2CH_2CH_2O$-), 69.96 and 70.32 (-OCH_2CH_2O-), 74.04 (-Si$CH_2CH_2CH_2$-), 114.68, 122.51, 124.71, 128.99 and 130.29 (Ar-C), 146.88 (Ar-C-N), 152.74 (Ar-C-N), 161.52 (Ar-C-O). FTIR (KBr, cm^{-1}): 3100-2800 (C-H), 1607, 1504 (C=C, arom.), 1259 (C-O-C), 1103 (Si-O-Si). UV-vis, $CHCl_3$: λ_{max} = 347 nm.

*Synthesis of **Azo-POSS-3** derivative.*



A total of 0.500 g (1.342 mmol) of azo dye **3** and 0.106 g (0.168 mmol) of **POSS-vinyl** was dissolved in 4 mL of toluene, and 40 µL of Karsted's Catalyst was added to the reaction solution. The reaction mixture was stirred at 40°C for 48 h and then cooled to room temperature. After removing all the solvents at reduced pressure, 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: 65%. ^1H NMR ($CDCl_3$, 400 MHz, δ, ppm): 0.07 (s, -Si$(CH_3)_2$-), 0.10 (s, -Si$(CH_3)_2$-), 0.59 (s, -Si$(CH_3)_2C\mathbf{H_2}$-), 0.64 (br. s, -Si$C\mathbf{H_2}$-),1.82 (br.s, -$C\mathbf{H_2}CH_2O$-), 3.96 (br.s, -$CH_2C\mathbf{H_2}O$-), 6.98 (d, J=8.7 Hz, Ph), 7.42-7.48 (m, Ph), 7.86-7.91 (m, Ph). ^{13}C NMR ($CDCl_3$, 125.73 MHz, δ, ppm): -0.29 and -0.28 (-Si$(CH_3)_2$-), 3.87 and 9.54 (-Si$(CH_3)_2\mathbf{C}H_2\mathbf{C}H_2$Si-), 14.26, 23.18 and 70.73(-Si$CH_2CH_2CH_2O$-), 114.65, 122.52, 124.74, 128.99 and 130.25 (Ar-C), 146.84 and 152.77 (Ar-C-N), 161.63 (Ar-C-O). FTIR (KBr, cm^{-1}): 3100-2800 (C-H), 1601, 1502 (C=C, arom.), 1254 (C-O-C), 1142 (Si-O-Si from POSS cage), 1053 (Si-O-Si from linker). UV-vis, $CHCl_3$: λ_{max} = 344 nm.

*Synthesis of **Azo-POSS-4-TMS** derivative.*

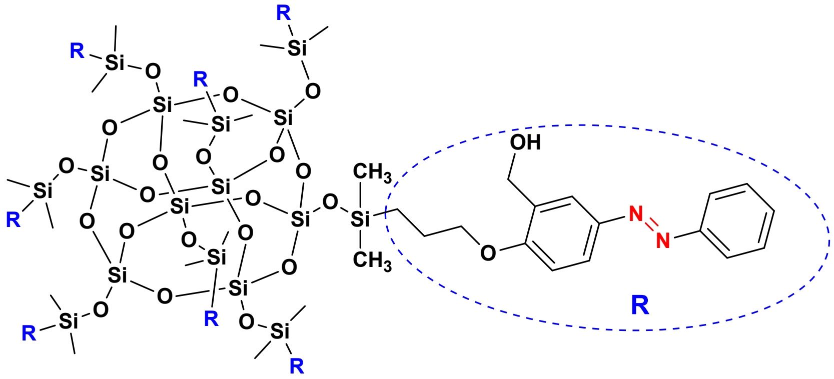


The **Azo-POSS-4-TMS** was prepared in the same manner as Azo-POSS-1, with azo dye 4-TMS used instead of compound 1.

*Trimethylsilyl-protected **Azo-POSS-4-TMS** is easily hydrolyzed by moisture, even in air. Therefore, according to FTIR, ^{1}H and ^{13}C NMR spectrometry, a partial hydrolysis of TMS groups occurs during purification and storage.*

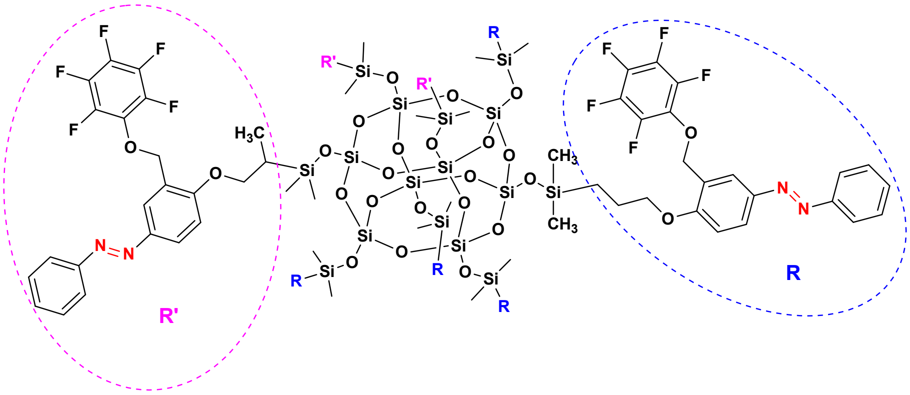
Yield: 59% (taking into account the 8-substituted **Azo-POSS-4-TMS** derivative and excluding the desilylation reaction). ^{1}H NMR ($CDCl_3$, 300 MHz, δ, ppm): 0.15-0.20 (m, -$SiCH_3$), 0.71 (br.s, -$SiC\mathbf{H_2}CH_2CH_2O$-), 1.84 (br.s, -$SiCH_2C\mathbf{H_2}CH_2O$-), 2.07 (br.s, -OH), 3.94 (br.s, -$SiCH_2CH_2C\mathbf{H_2}O$-), 4.70 (br.s, -$C\mathbf{H_2}OTMS$ and -$C\mathbf{H_2}OH$), 6.83 (br.s, Ph), 7.43 (br.s, Ph), 7.83 (br.s, Ph). ^{13}C NMR ($CDCl_3$, 100.62 MHz, δ, ppm): -0.37 (-$Si(CH_3)_2$), 13.67 and 22.89 (-$Si\mathbf{C}H_2\mathbf{C}H_2CH_2O$-), 59.50 (-$\mathbf{C}H_2OTMS$), 61.26 (-$CH_2OH$), 70.59 (-$SiCH_2CH_2\mathbf{C}H_2O$-), 110.86, 121.71, 122.57, 125.33 and 128.98 (Ar-C), 130.02 (Ar-$\mathbf{C}$-CH_2-), 130.35 (Ar-C), 146.60 and 152,67 (Ar-C-N-), 158.84 (Ar-C-O-). FTIR (KBr, cm^{-1}): 3600-3200 (-OH), 3100-2800 (C-H), 1601, 1493 (C=C, arom.), 1254 (C-O-C), 1097(Si-O-Si), 872 ($Si(CH_3)_3$).

*Synthesis of **Azo-POSS-4** derivative.*



A solution of compound **Azo-POSS-4-TMS** (0.120 g) and acetic acid (0.2 ml) in methanol (5 mL) was stirred at room temperature for 2 h. The solvent was evaporated *in vacuo* to give compound **Azo-POSS-4** as orange solid. The obtained solid was purified by precipitation from diethyl ether solution into hexane. Yield 0.106 g. ^{1}H NMR ($CDCl_3$, 300 MHz, δ, ppm): 0.16-0.20 (s, -$Si(CH_3)_2$-), 0.71 (br.s, -$SiC\mathbf{H_2}CH_2CH_2O$-), 1.86 (br.s, -$SiCH_2C\mathbf{H_2}CH_2O$-), 2.28 (br.s, -OH), 3.94 (br.s, -$SiCH_2CH_2C\mathbf{H_2}O$-), 4.70 (br.s, -$C\mathbf{H_2}OH$), 6.85 (br.s, Ph), 7.43 (br.s, Ph), 7.83 (br.s, Ph). ^{13}C NMR ($CDCl_3$, 100.62 MHz, δ, ppm): -0,36 (-$Si(CH_3)_2$-), 13.64 and 22.87 (-$Si\mathbf{C}H_2\mathbf{C}H_2CH_2O$-), 61.18 (-$CH_2OH$), 70.57 (-$SiCH_2CH_2\mathbf{C}H_2O$-), 110.82, 121.63, 122.56, 125.36 and 128.97 (Ar-C), 129.98 (Ar-$\mathbf{C}$-CH_2-), 130.34 (Ar-C), 146.54 and 152.61 (Ar-C-N-), 158.82 (Ar-C-O-). FTIR (KBr, cm^{-1}): 3600-3200 (-OH), 3100-2800 (C-H), 1601, 1495 (C=C, arom.), 1254 (C-O-C), 1094 (Si-O-Si). UV-vis, $CHCl_3$: λ_{max} = 348 nm.

*Synthesis of **Azo-POSS-5** derivative.*



The **Azo-POSS-5** was prepared in the same manner as **Azo-POSS-1**, with azo dye **5** used instead of compound **1**. Yield: 65%. ^{1}H NMR (CDCl$_3$, 400 MHz, δ, ppm): 0.03 (br.s, -Si(CH$_3$)$_{2\text{-}\beta\text{-}isomer}$), 0.16 (br.s, -Si(CH$_3$)$_{2\text{-}\gamma\text{-}isomer}$), 0.69 (br.s, -SiC$\mathbf{H_2}CH_2CH_2$O-), 0.87 (br.s, -SiCH**(**C$\mathbf{H_3}$)CH$_2$O-), 1.80 (br.s, -SiCH$_2$C$\mathbf{H_2}$CH$_2$O-), 2.01 (br.s, -SiC**H(**CH$_3$)CH$_2$O-), 3.92 (br.s, -SiCH$_2$CH$_2$C$\mathbf{H_2}$O- + -SiCH**(**CH$_3$)C$\mathbf{H_2}$O-), 5.21 (br.s, -C$\mathbf{H_2}$OAr$_F$), 6.89 (br.s, Ph), 7.44 (br.s, Ph), 7.83 (br.s, Ph), 7.96 (br.s, Ph). ^{13}C NMR (CDCl$_3$, 100.62 MHz, δ, ppm): -0,59 (-Si(CH$_3$)$_2$-), 13.49 (-SiCH(**C**H$_3$)CH$_2$O-), 22.71 (-Si**C**H$_2$CH$_2$CH$_2$O-), 29.39 (-Si**C**H(CH$_3$)CH$_2$O-), 29.67 (-SiCH$_2$**C**H$_2$CH$_2$O-), 70.80 (-SiCH(CH$_3$)**C**H$_2$O-), 72.01 (-**C**H$_2$OAr$_F$), 111.24, 122.58 and 124.46 (Ar-C), 128.16 (Ar-**C**-CH$_2$-), 129.01 and 130.56 (Ar-C), 133.36 (Ar$_F$-C-O-), 136.62, 139.19, 140,74 and 143.27 (Ar$_F$-C), 146.31 and 152.57 (Ar-C-N-), 159.29 (Ar-C-O-). ^{19}F NMR (CDCl$_3$, 376.47 MHz, δ, ppm): -163.53 (br.s, Ar-F), -163.14, (br.s, Ar-F), -155.71 (br.s, Ar-F). FTIR (KBr, cm^{-1}): 3100-2800 (C-H), 1603, 1516 (C=C, arom.), 1258 (C-O-C), 1099 (Si-O-Si), 1009, 997 (C-F). UV-vis, CHCl$_3$: λ_{max} = 344 nm.

NMR, FTIR and UV SPECTRA

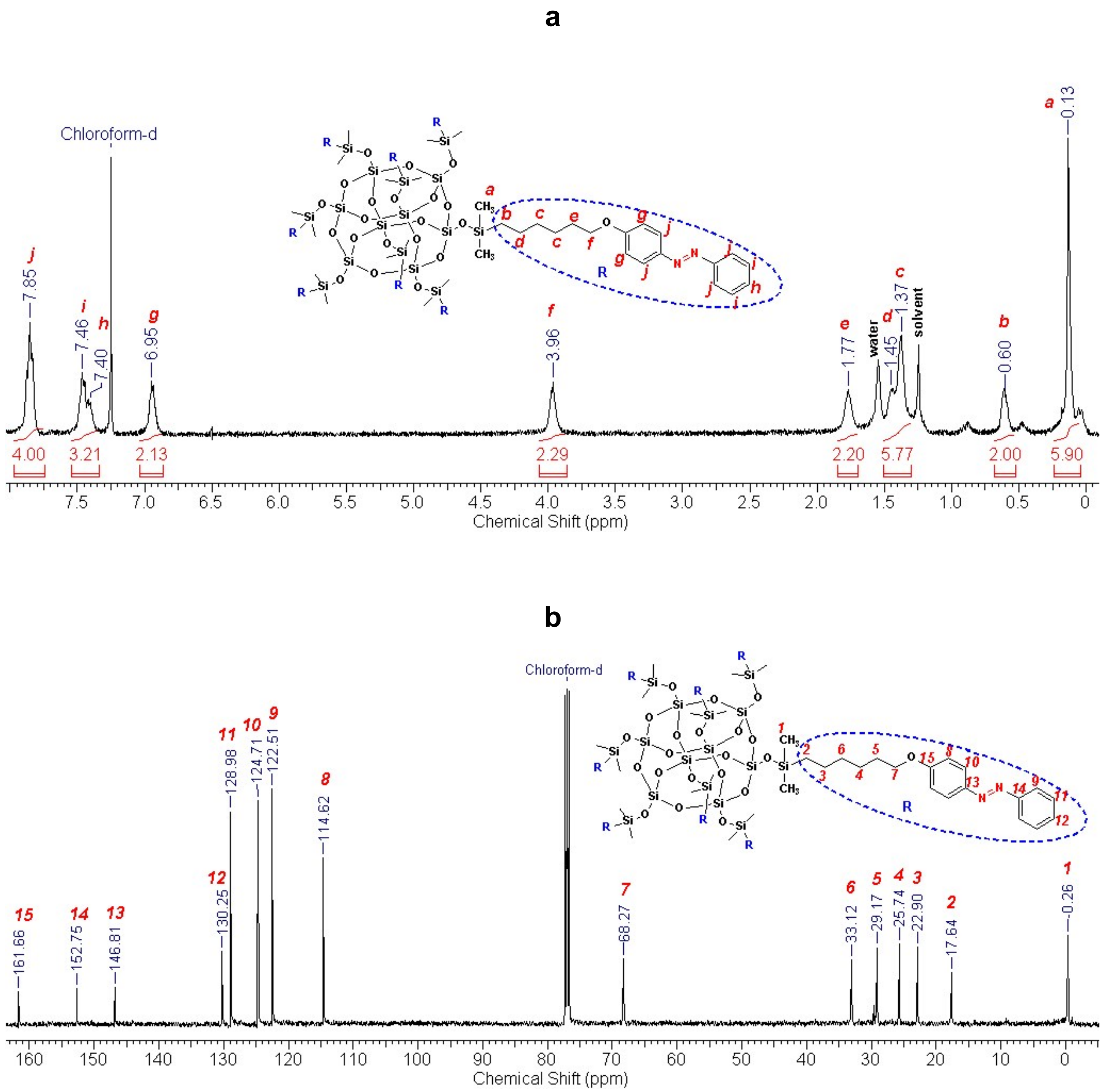


Figure SI1. ^{1}H (a) and ^{13}C NMR (b) spectra of **Azo-POSS-1**

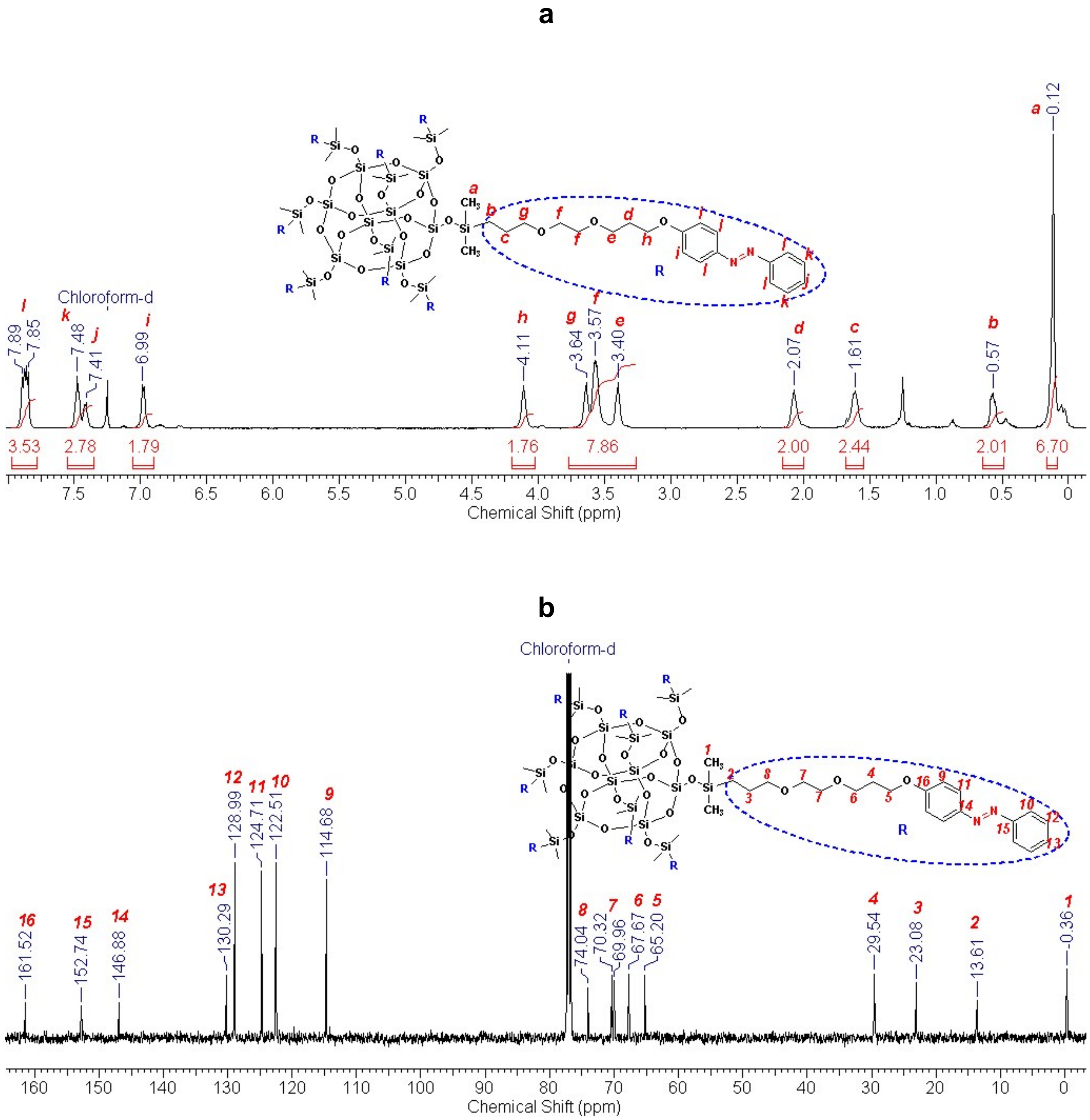


Figure SI2. ^{1}H (a) and ^{13}C NMR (b) spectra of **Azo-POSS-2**

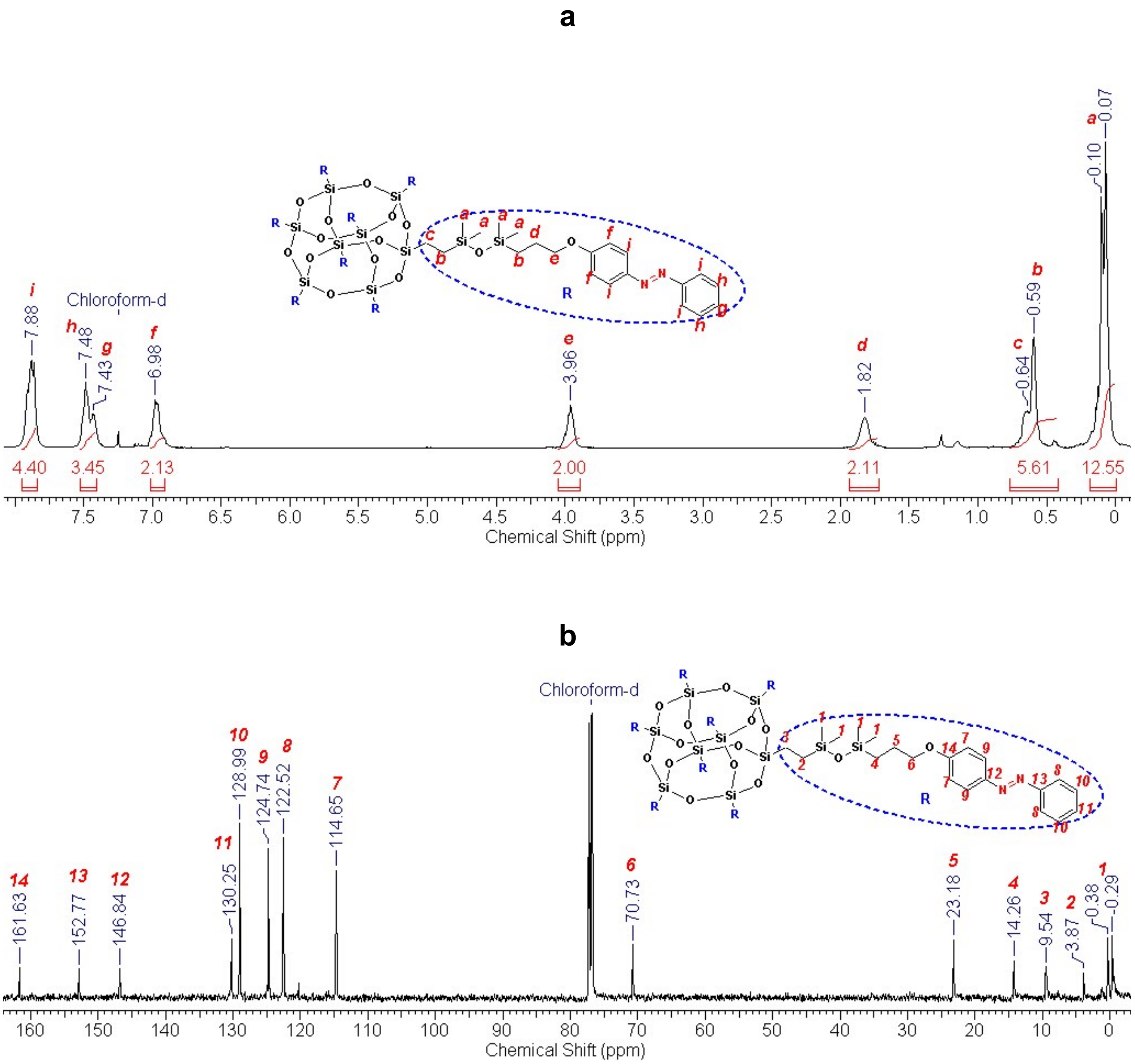


Figure SI3. ^{1}H (a) and ^{13}C NMR (b) spectra of **Azo-POSS-1**

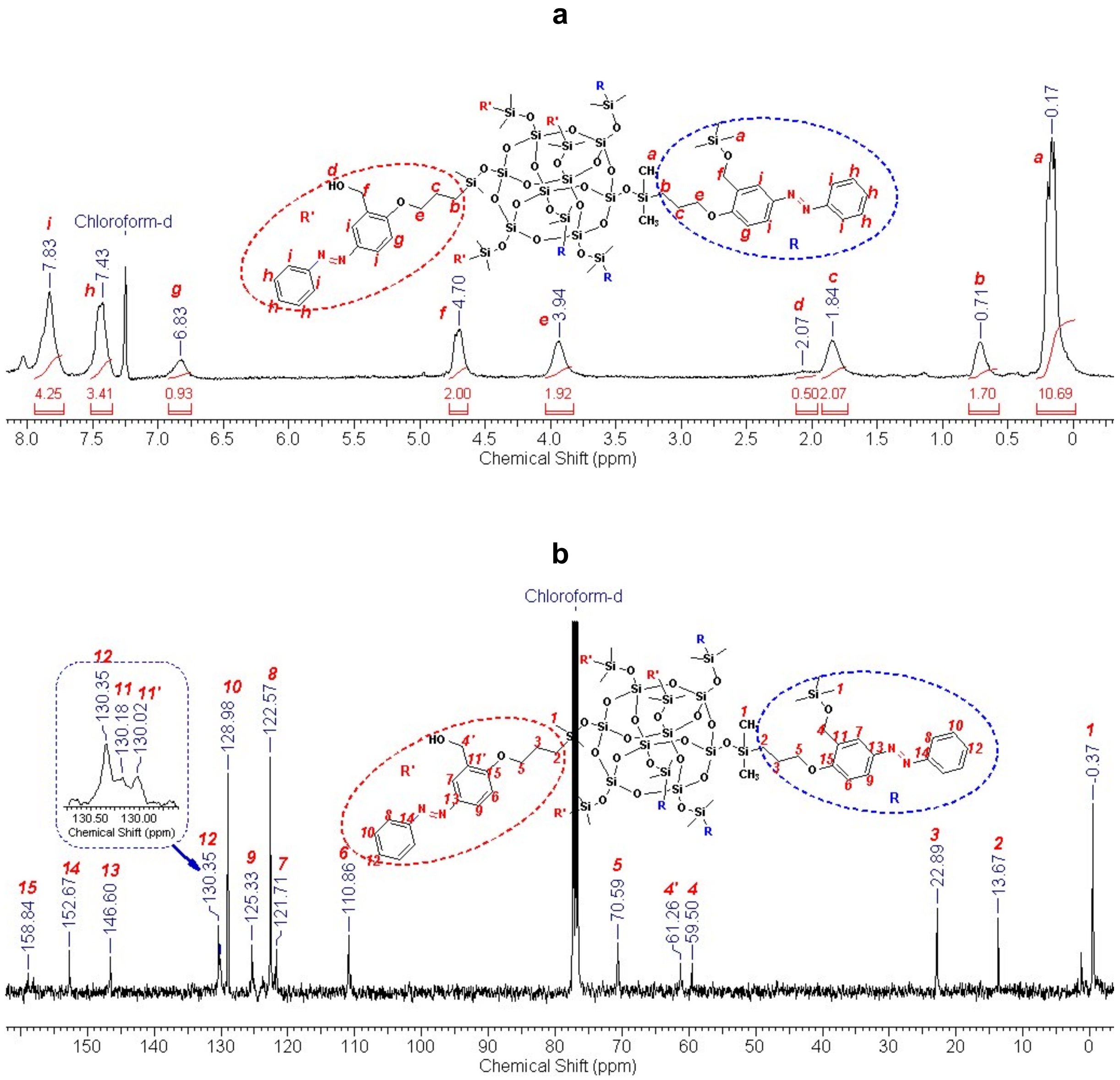


Figure SI4. ^{1}H (a) and ^{13}C NMR (b) spectra of **Azo-POSS-4-TMS** *(partially hydrolyzed – explanations in main text)*

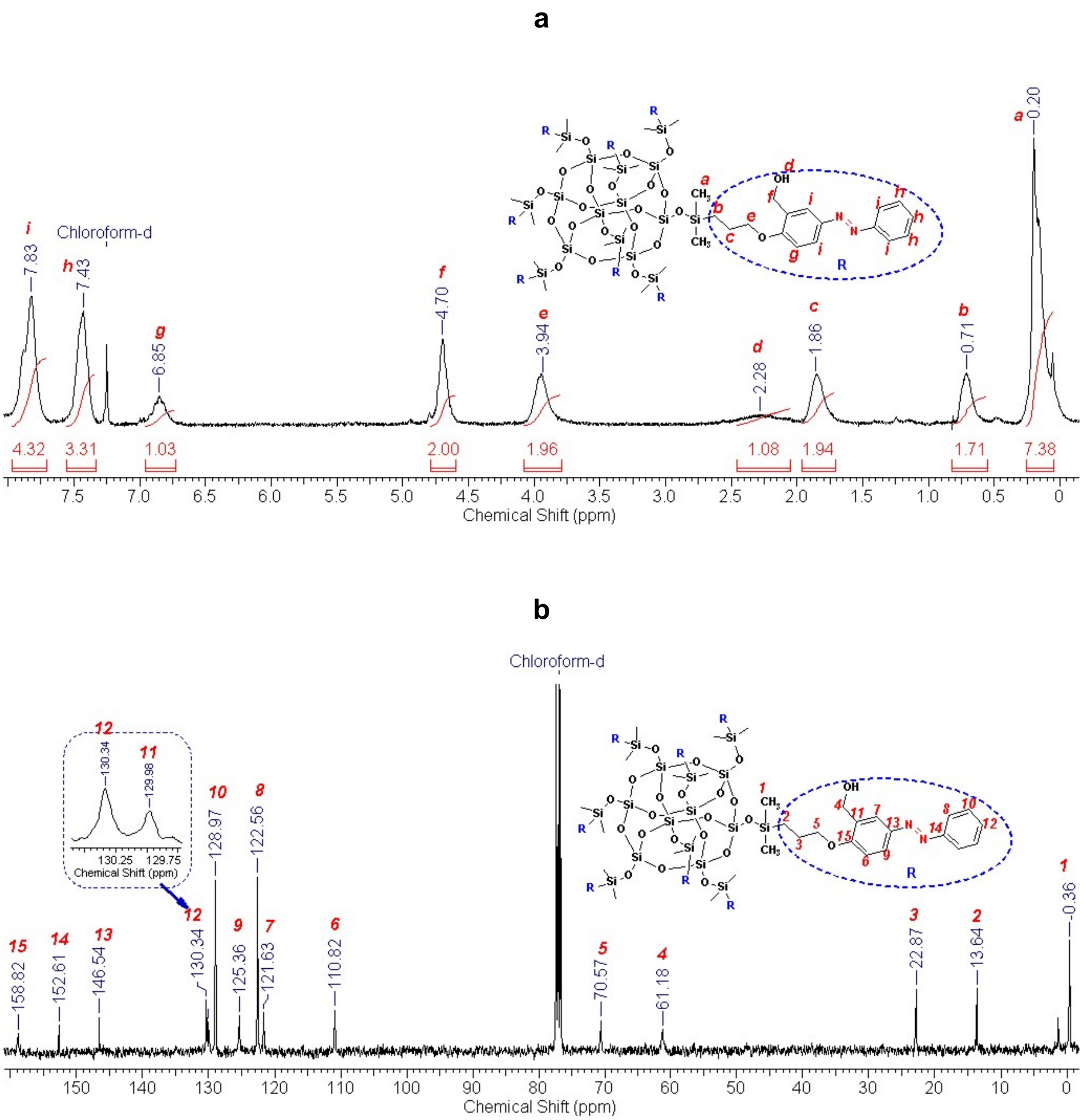


Figure SI5. ^{1}H (a) and ^{13}C NMR (b) spectra of **Azo-POSS-4**

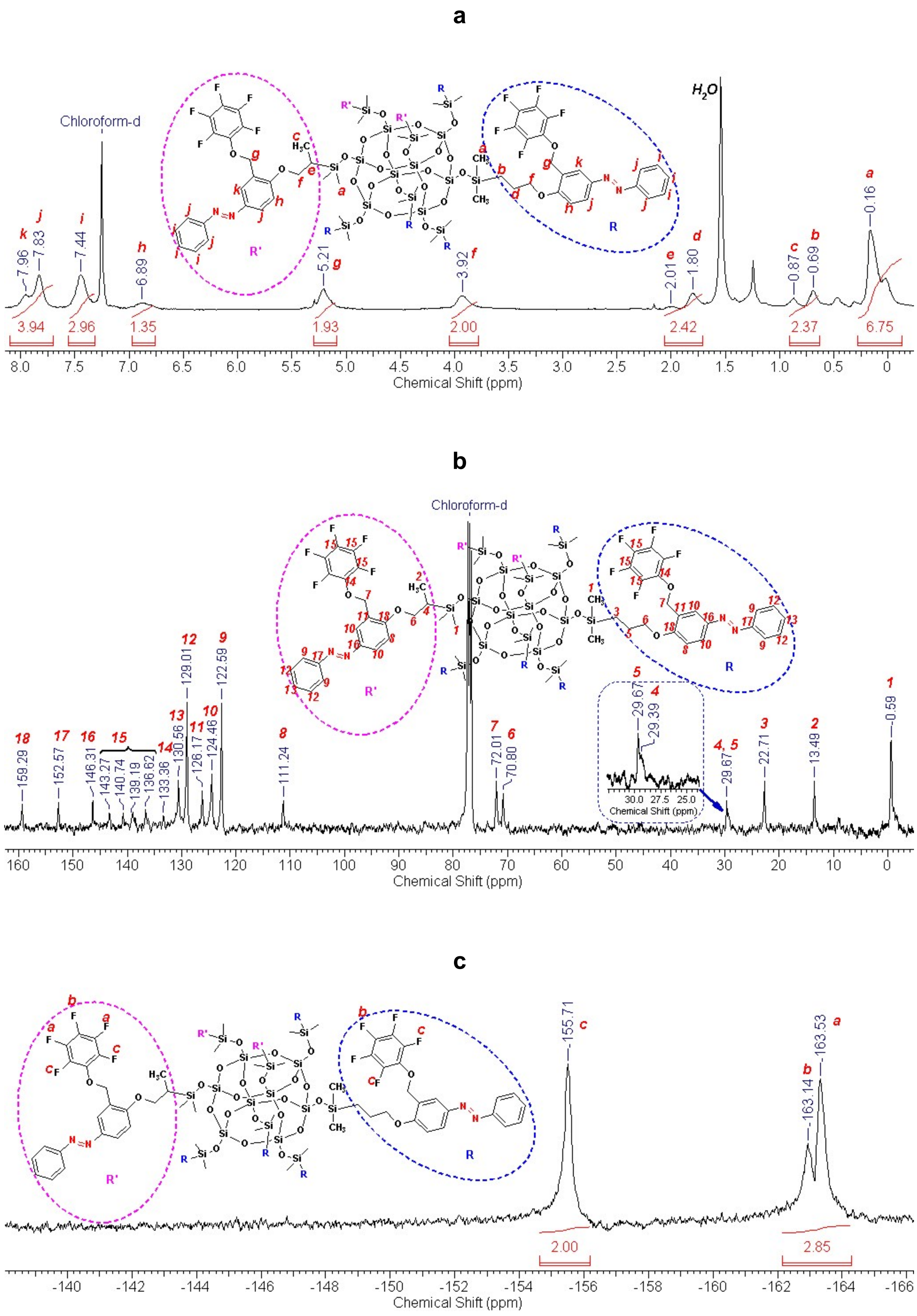
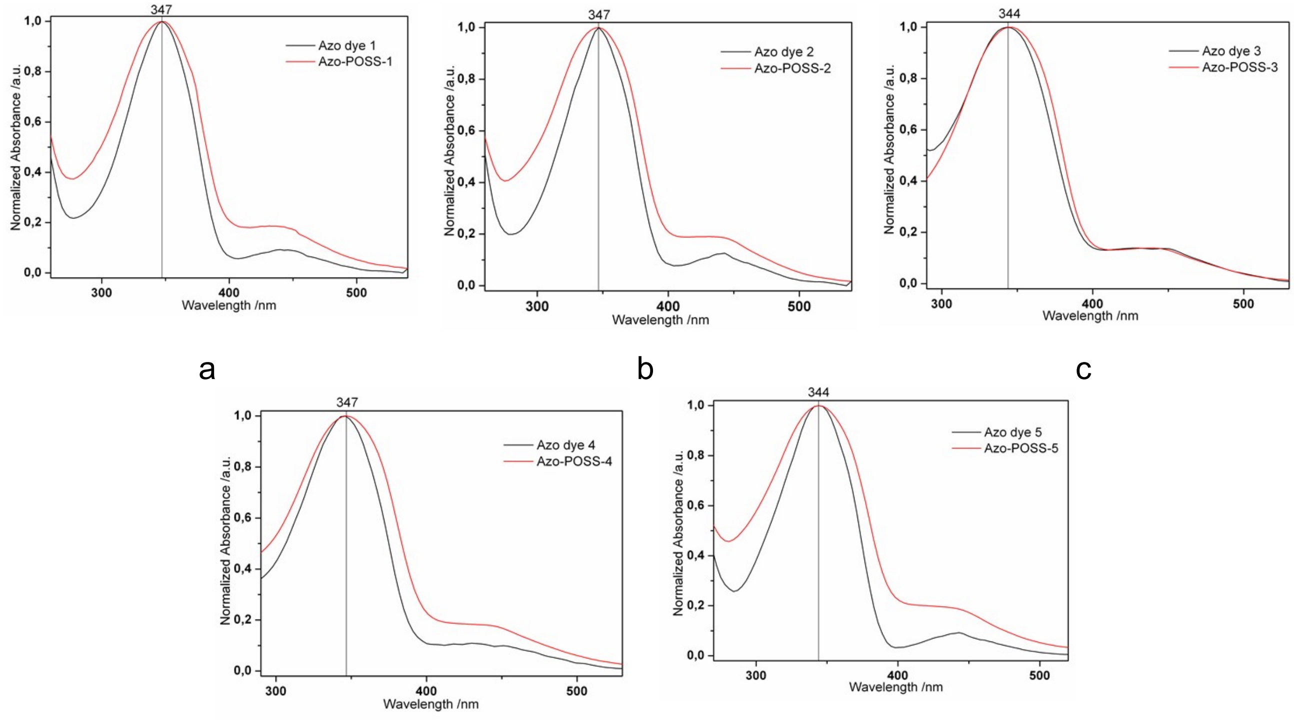


Figure SI6. ^{1}H (a), ^{13}C (b) and ^{19}F NMR (c) spectra of **Azo-POSS-5**



a b c

d e

Figure SI7. (a-e) UV-vis absorbance spectra of dyes **1-5** and respective conjugates **Azo-POSS-1−Azo-POSS-5** in $CHCl_3$ (0.005 mg/mL).

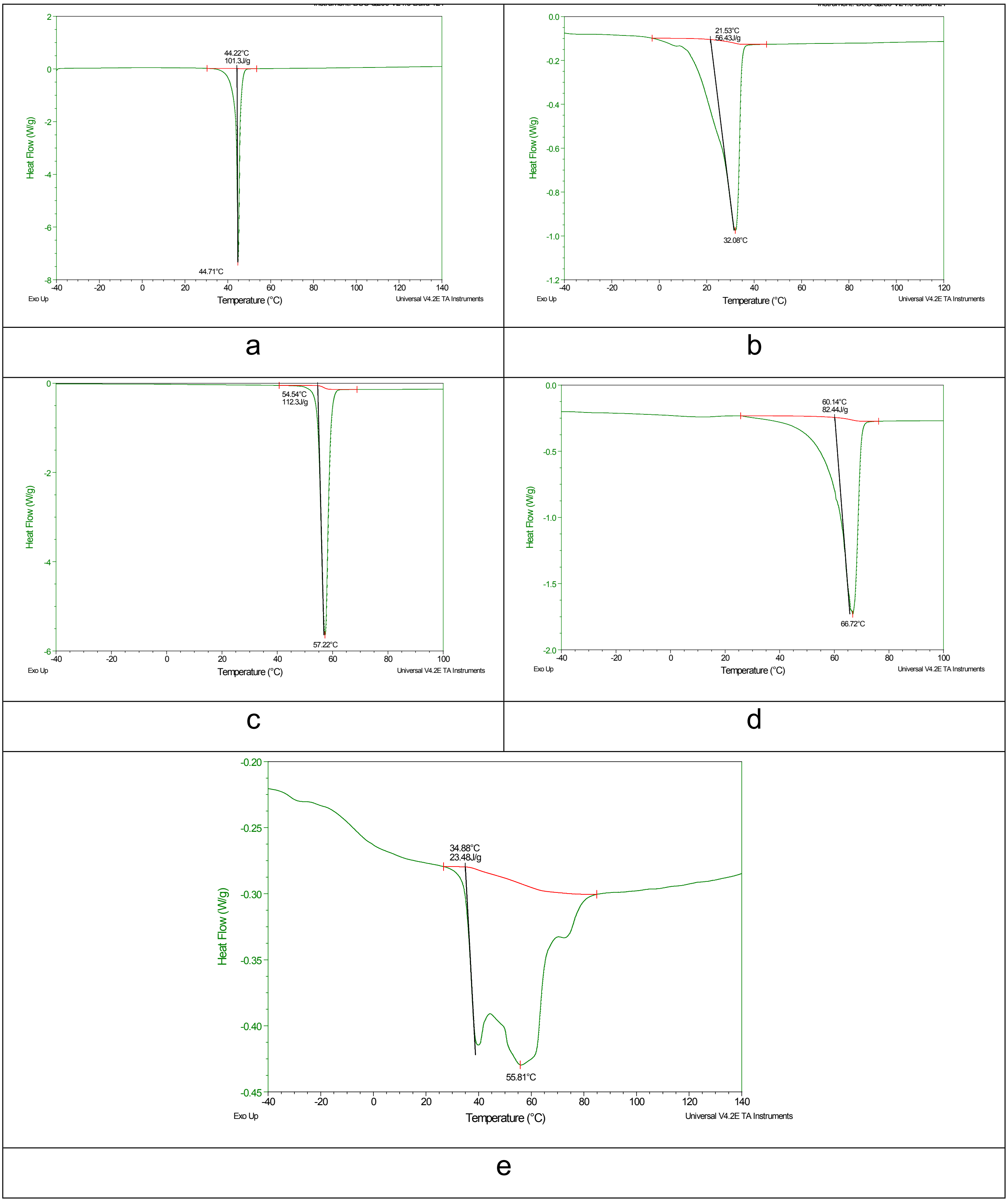


Figure SI8. DSC thermograms for the dyes **1** (a), **3** (b), **4** (c), **5** (d) and system **Azo-POSS-1** (e) showing the melting transition peak temperatures (T_m) and the melting enthalpy ($_{\Delta}H_m$).

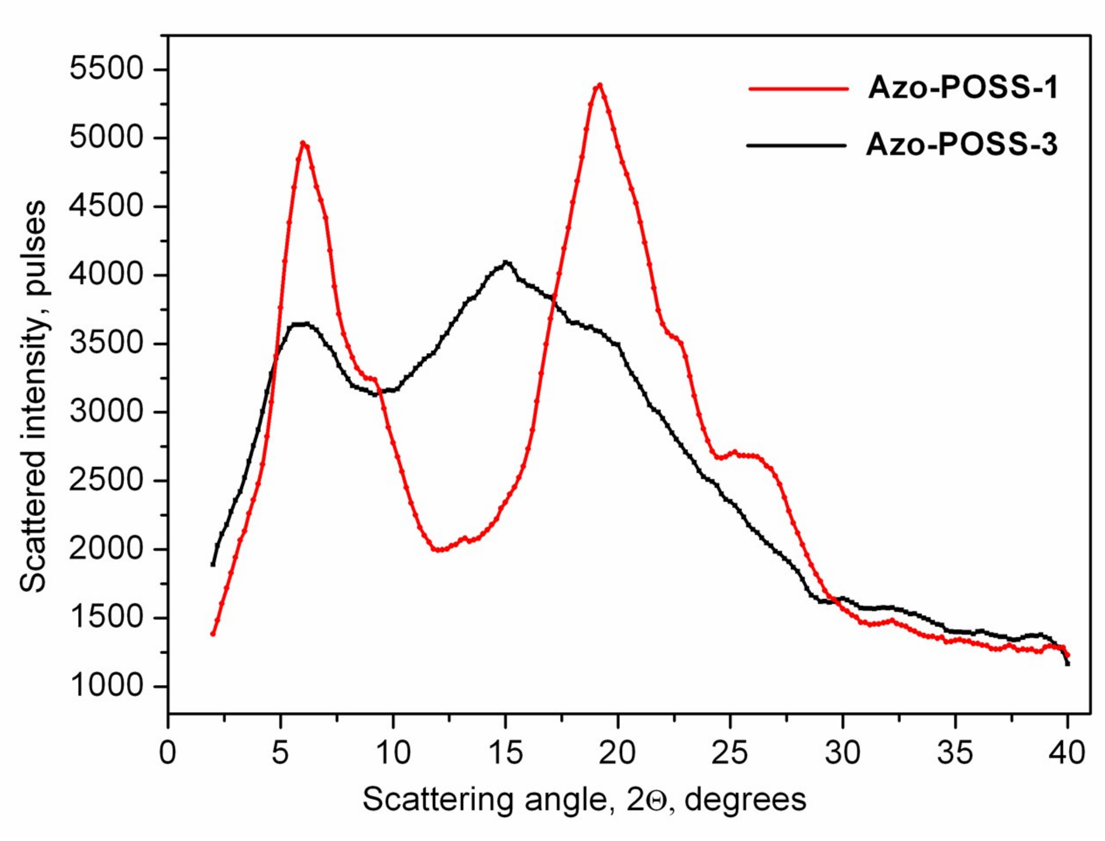


Figure SI9. XRD patterns of **Azo-POSS-1** and **Azo-POSS-3**.

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