

Stereoregular hybrid azobenzene-cyclosiloxanes with photoinduced reversible solid to liquid transition properties

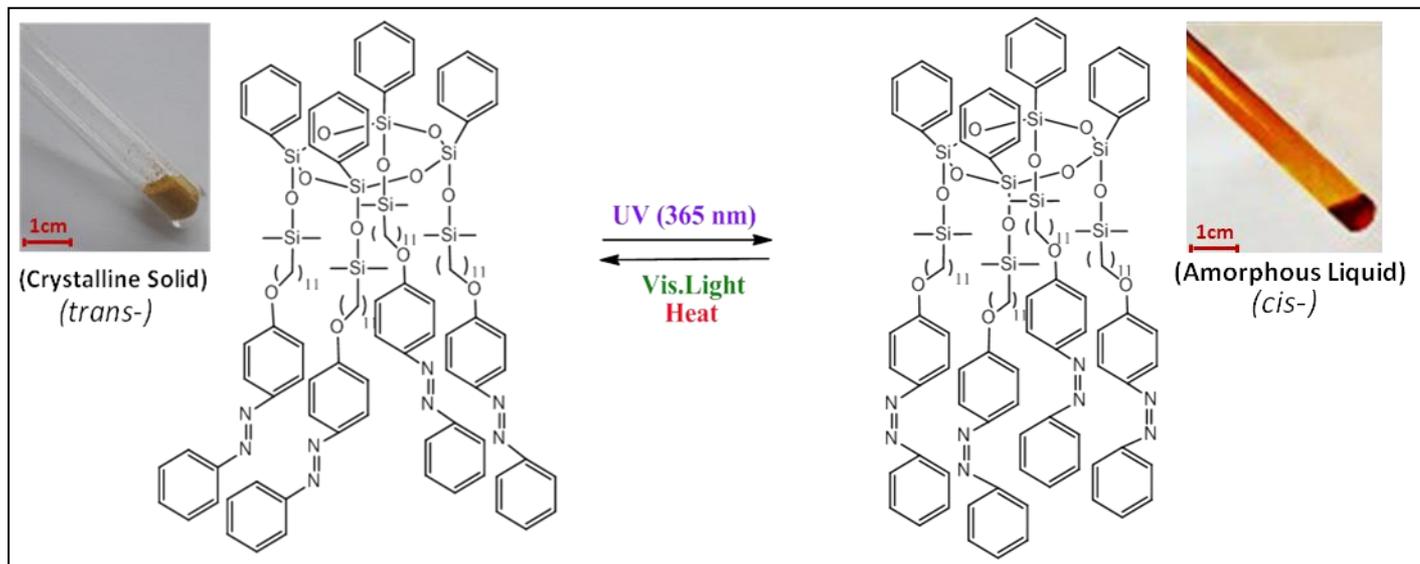
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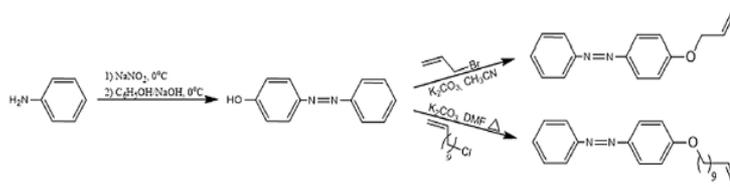
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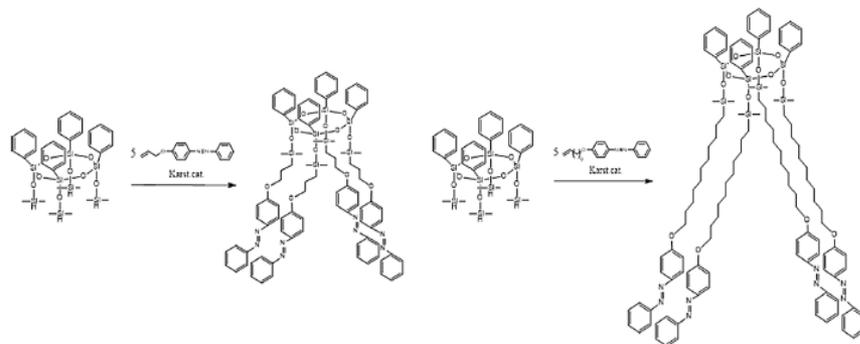
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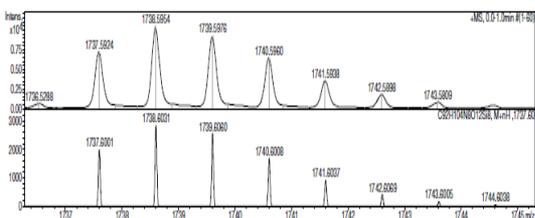
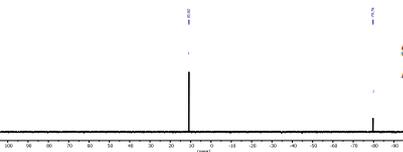
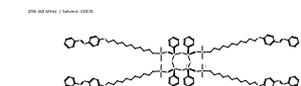
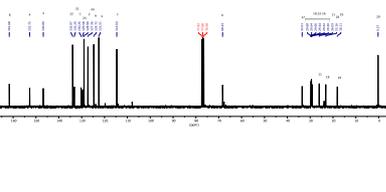
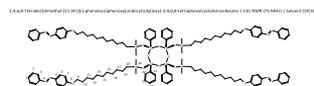
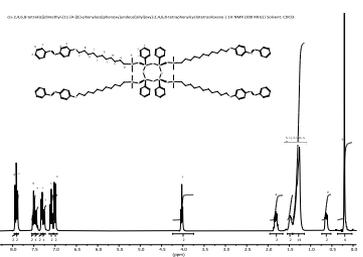
Synthesis and characterization



Scheme 1. Synthetic scheme of preparation of substituted azobenzenes.



Scheme 2. Synthetic scheme of preparation of unidirectionally oriented azobenzene-cyclosiloxane conjugates: $[\text{PhSiOSi}]_4-(\text{C}_5\text{-Azo})_4$ (left) and $[\text{PhSiOSi}]_4-(\text{C}_{11}\text{-Azo})_4$ (right).



HRMS (ESI-MS) of 6: m/z calculated for $[\text{M}(\text{C}_{92}\text{H}_{104}\text{N}_8\text{O}_{12}\text{Si}_8) + \text{H}]^+$, 1738.6031; found 1738.5954

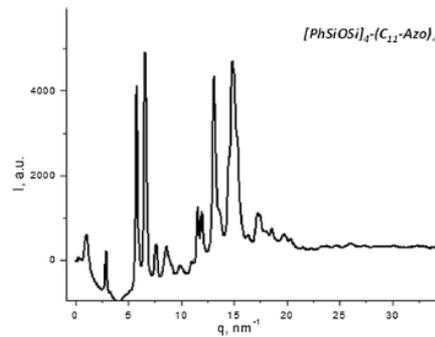
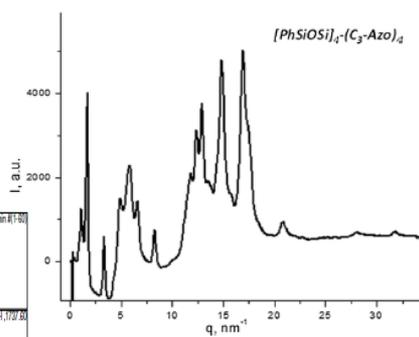
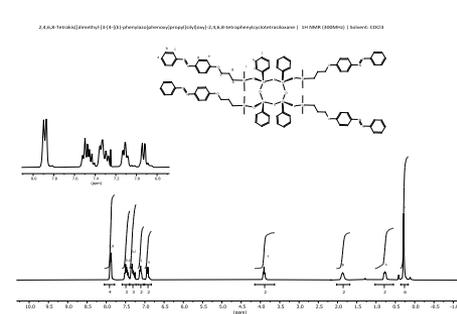
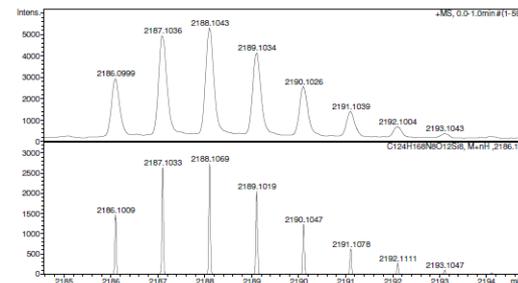
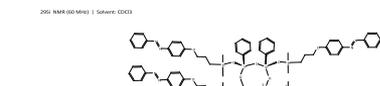
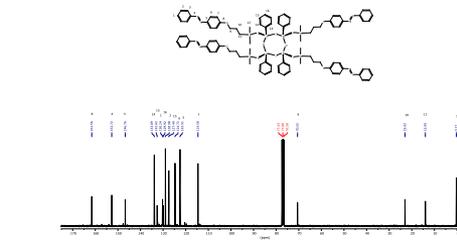


Fig. 1. XRD patterns of $[\text{PhSiOSi}]_4-(\text{C}_5\text{-Azo})_4$ and $[\text{PhSiOSi}]_4-(\text{C}_{11}\text{-Azo})_4$ at room temperature.



1H NMR (500 MHz) Spectrum of 6



HRMS (ESI-MS) of 7: m/z calculated for $[\text{M}(\text{C}_{124}\text{H}_{168}\text{N}_8\text{O}_{12}\text{Si}_8) + \text{H}]^+$, calc. 2187.1033; found 2187.1036

Kinetics of photoinduced trans-cis-trans isomerization

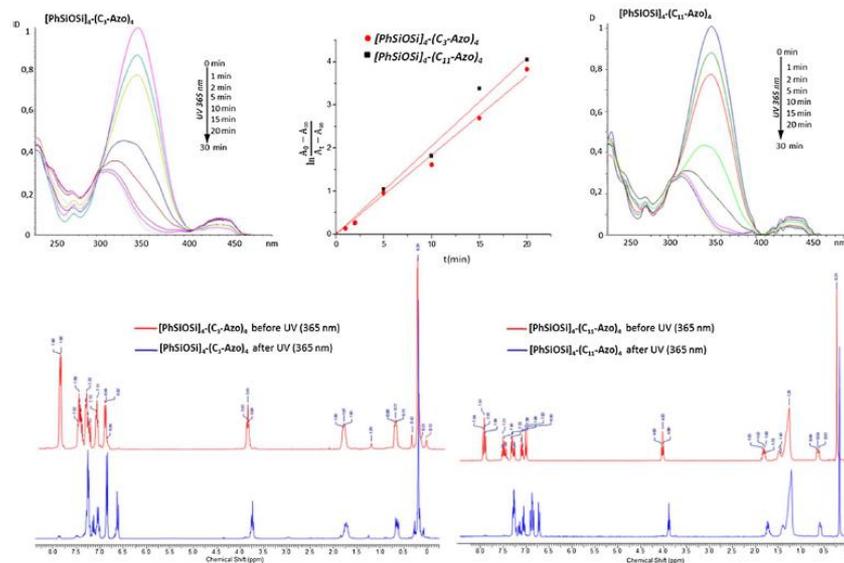


Fig. 4. UV-vis absorbance changes and kinetic plots at $\lambda = 347$ and 349 nm of $[\text{PhSiOSi}]_4-(\text{C}_3\text{-Azo})_4$ and $[\text{PhSiOSi}]_4-(\text{C}_{11}\text{-Azo})_4 - \text{CH}_2\text{Cl}_2$ solutions respectively under UV-irradiation (max. emission at 365 nm, total intensity 2.3 mW/cm^2) (top). $^1\text{H-NMR}$ spectra of $[\text{PhSiOSi}]_4-(\text{C}_3\text{-Azo})_4$ and $[\text{PhSiOSi}]_4-(\text{C}_{11}\text{-Azo})_4$ before and after UV irradiation (bottom).

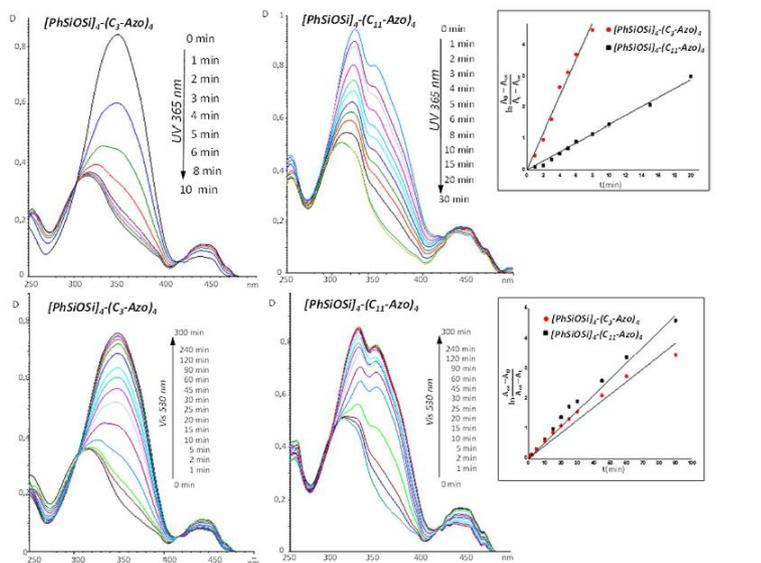


Fig. 6. UV-vis absorbance changes of spin-coated films of $[\text{PhSiOSi}]_4-(\text{C}_3\text{-Azo})_4$ and $[\text{PhSiOSi}]_4-(\text{C}_{11}\text{-Azo})_4$ under UV-irradiation (max. emission at 365 nm, total intensity 9.2 mW/cm^2) and Vis-irradiation (max. emission at 530 nm, total intensity 11.9 mW/cm^2) (left); and kinetic plots at $\lambda = 348$ and 329 nm for $[\text{PhSiOSi}]_4-(\text{C}_3\text{-Azo})_4$ and $[\text{PhSiOSi}]_4-(\text{C}_{11}\text{-Azo})_4$ films respectively.

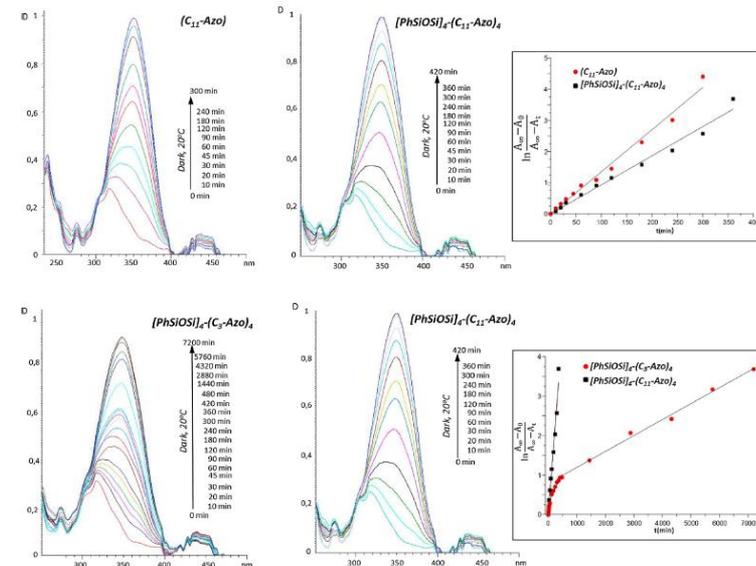


Fig. 5. UV-vis absorbance changes of $[\text{PhSiOSi}]_4-(\text{C}_3\text{-Azo})_4$ and $[\text{PhSiOSi}]_4-(\text{C}_{11}\text{-Azo})_4 - \text{CH}_2\text{Cl}_2$ solutions in the dark and their kinetic plots at $\lambda = 347$ and 349 nm for $[\text{PhSiOSi}]_4-(\text{C}_3\text{-Azo})_4$ and $[\text{PhSiOSi}]_4-(\text{C}_{11}\text{-Azo})_4 - \text{CH}_2\text{Cl}_2$ solutions respectively.

Thermodynamics of photoinduced phase transition processes

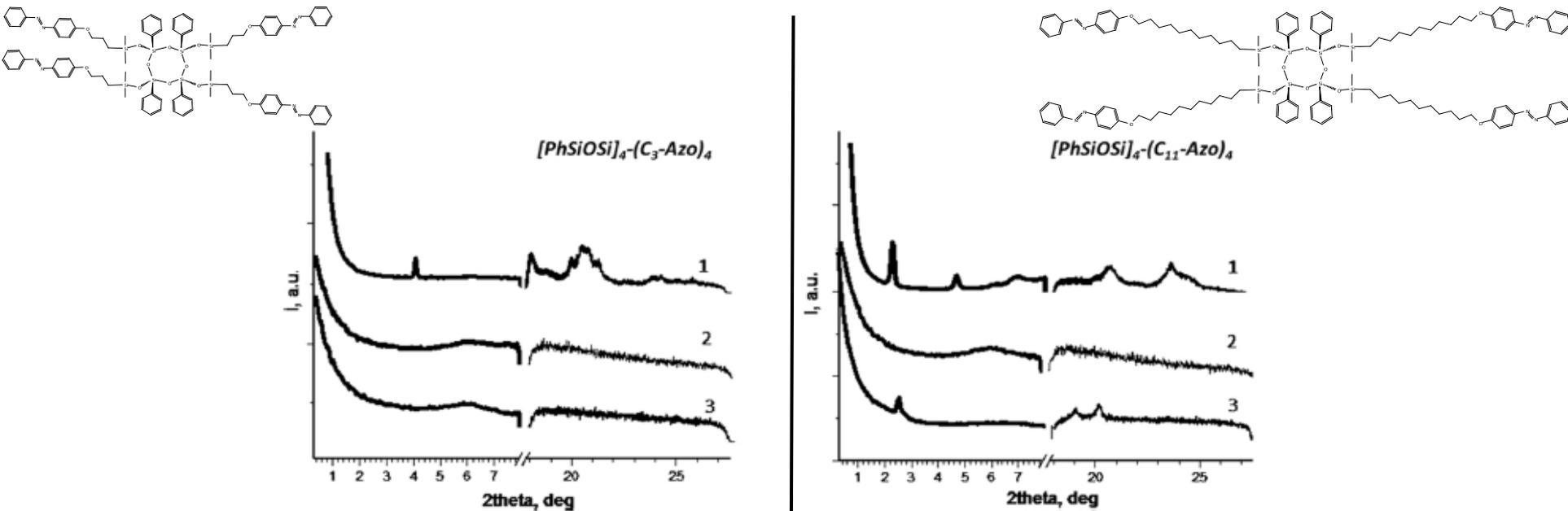


Fig. 7. XRD patterns of $[\text{PhSiOSi}]_4\text{-(C}_3\text{-Azo)}_4$ and $[\text{PhSiOSi}]_4\text{-(C}_{11}\text{-Azo)}_4$ at room temperature (curves shifted vertically for clarity); 1 - trans-state (initial – before UV-irradiation); 2 - cis-state (after UV-irradiation); 3 - trans-state (relaxed after heating).

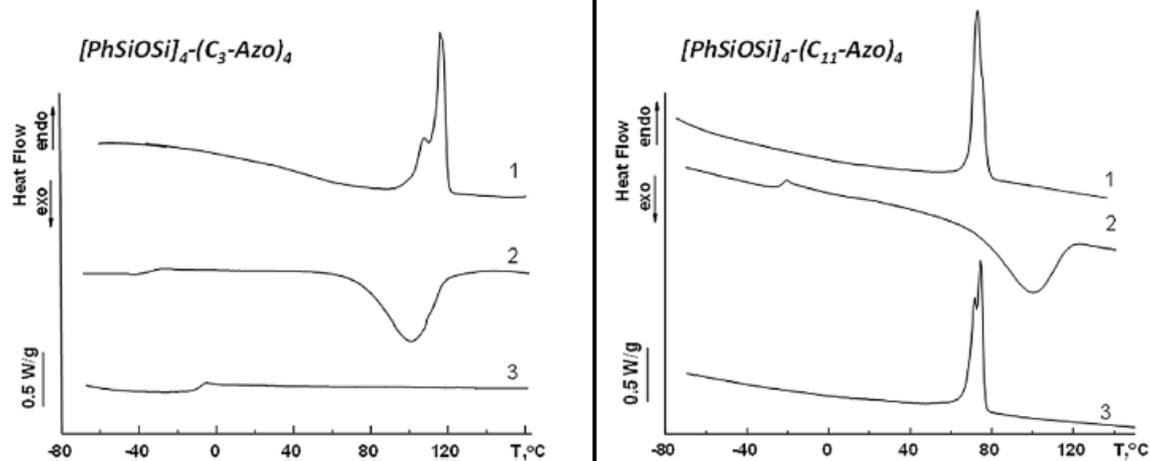


Fig. 8. DSC curves of $[\text{PhSiOSi}]_4\text{-(C}_3\text{-Azo)}_4$ (left) and $[\text{PhSiOSi}]_4\text{-(C}_{11}\text{-Azo)}_4$ (right); 1 - trans-state (initial – before UV-irradiation); 2 - cis-state (after UV-irradiation); 3 - trans-state (relaxed after heating).

Conclusions:

- A new type of hybrid azobenzene-cyclosiloxane molecules with unidirectionally oriented photoactive azobenzene groups showed the capability for crystal solid-to-liquid transitions in response to UV light, and backward solidification induced by heat or visible light.
- It was estimated that the length of alkyl spacers between the cyclosiloxane frame and azobenzene moieties has a significant influence on the intra and intermolecular interactions and affects the molecular packing arrangement, kinetics and thermodynamics of photo- and thermoinduced cis-trans isomerization processes of hybrid azo-cyclosiloxanes. Investigation of solution photoisomerization kinetics provided evidence for the intramolecular interactions between adjacent azobenzene moieties connected to one cyclosiloxane frame through short propyl spacers as in the case of $[\text{PhSiOSi}]_4\text{-(C}_3\text{-Azo)}_4$.
- Comparison of the trans-cis photoisomerization processes in bulk showed that transformations occur much faster in less organized films of $[\text{PhSiOSi}]_4\text{-(C}_3\text{-Azo)}_4$ with non-aggregated azo-chromophores, while the backward cis-trans relaxation on the contrary proceeds faster in $[\text{PhSiOSi}]_4\text{-(C}_{11}\text{-Azo)}_4$ films due to the existing H-aggregation effect between adjacent azobenzene groups.
- Both $[\text{PhSiOSi}]_4\text{-(C}_3\text{-Azo)}_4$ and $[\text{PhSiOSi}]_4\text{-(C}_{11}\text{-Azo)}_4$ compounds were able to undergo transformation from crystalline solids (trans-state) in to liquids (cis-state) upon UV-irradiation.
- Backward crystallization generated by heat or visible light was significantly affected by the length of the alkyl spacer and proceeded much faster in $[\text{PhSiOSi}]_4\text{-(C}_3\text{-Azo)}_4$ with less sterically hindered azobenzene groups.

Thank you for your attention!