

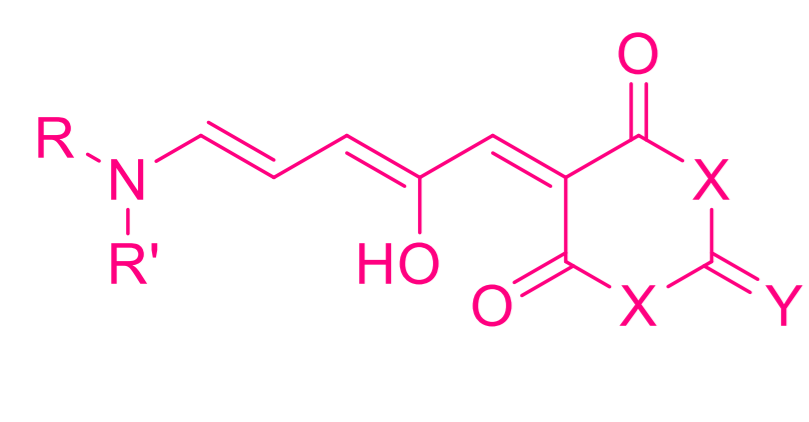
Donor-Acceptor Stenhouse Adduct (DASA)-polydimethylsiloxane (PDMS) conjugates for enhanced photoswitching in solid matrices

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Introduction



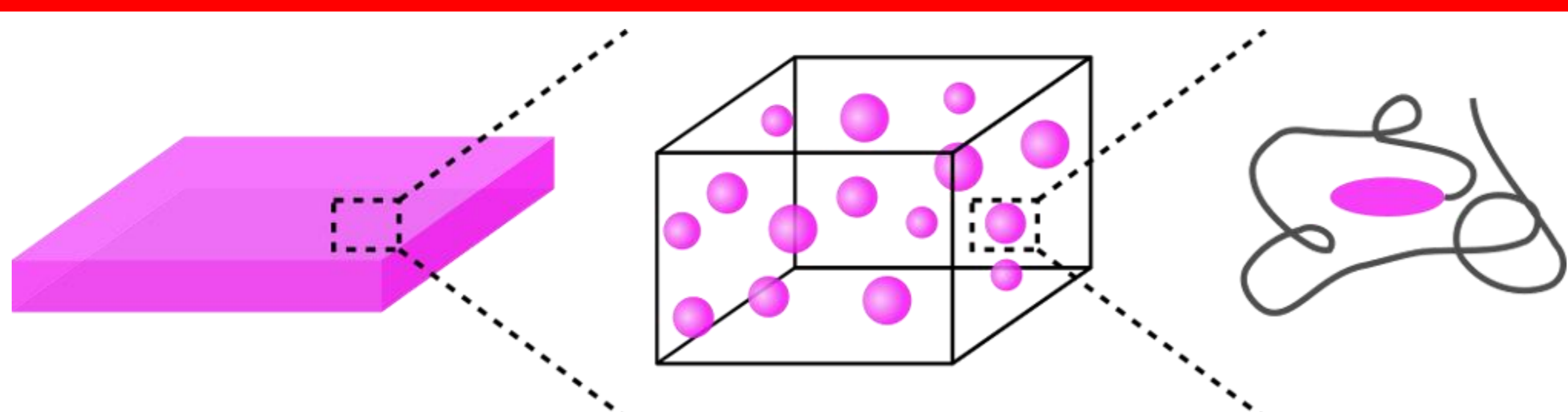
Colour
Polarity
Volume

DASAs are a class of photoswitches with

- visible light-responsiveness,
- thermal reversibility and
- negative photochromism.

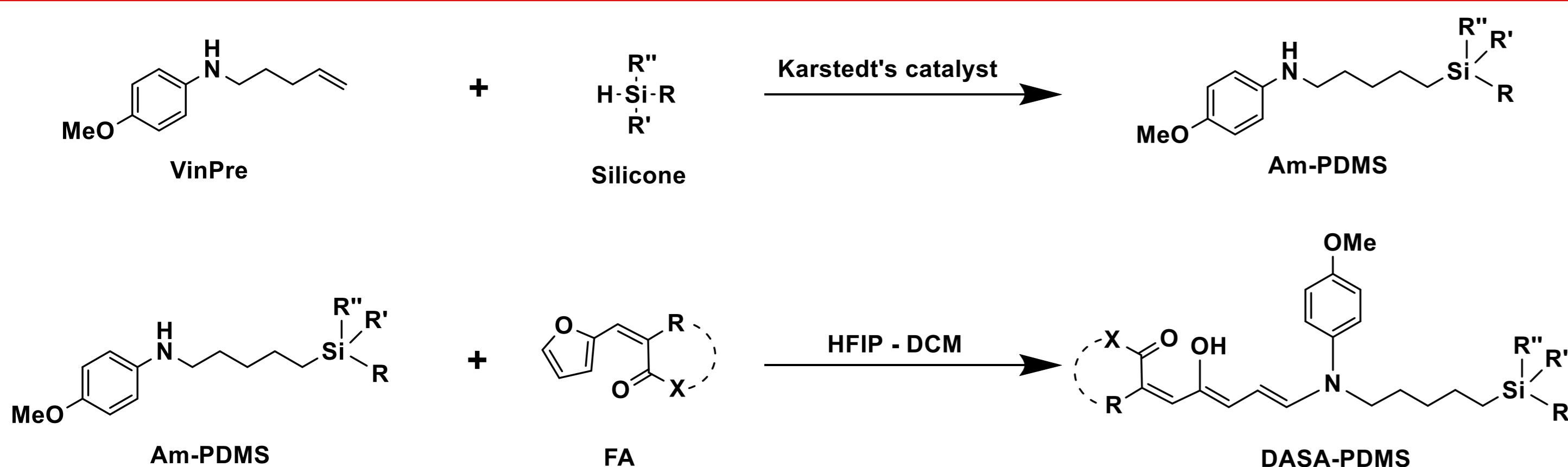
Their photoswitching heavily depends on the environment. Three generations of DASAs were synthesized so far, none of them can switch in aprotic solvents^{1,2}.

Objectives

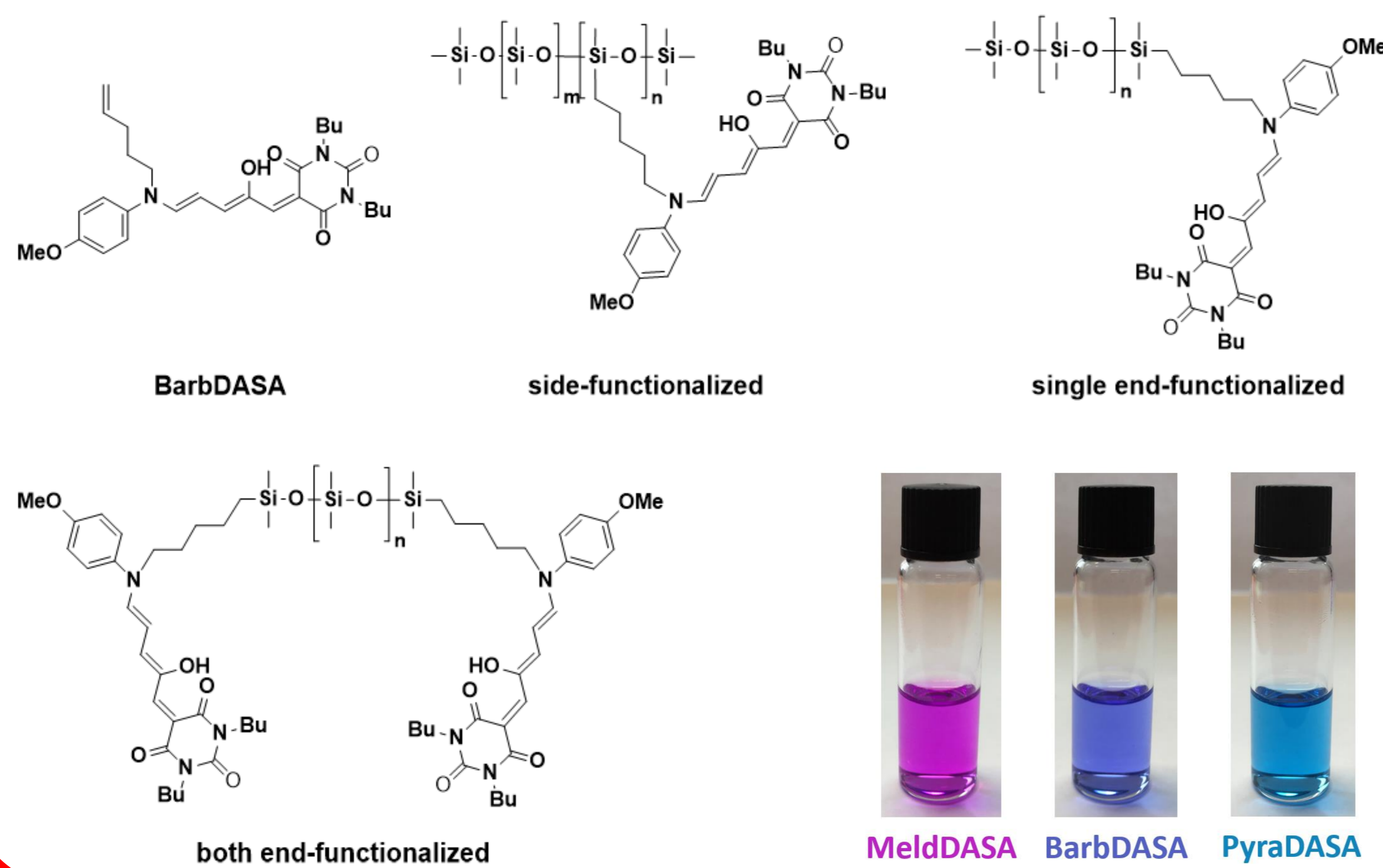


In addition to aprotic solvents, DASA photoswitching is limited in rigid polymer matrices because of their high structural change upon photoisomerization. Evans et al. developed a concept where soft oligomers are attached to photoswitches to enable faster switching in rigid polymer matrices³. We applied this concept on DASAs to create DASA-based visible light responsive rigid polymer matrices. To do so, we synthesized DASA-PDMS conjugates and investigated their behavior in solution and in polymer matrices.

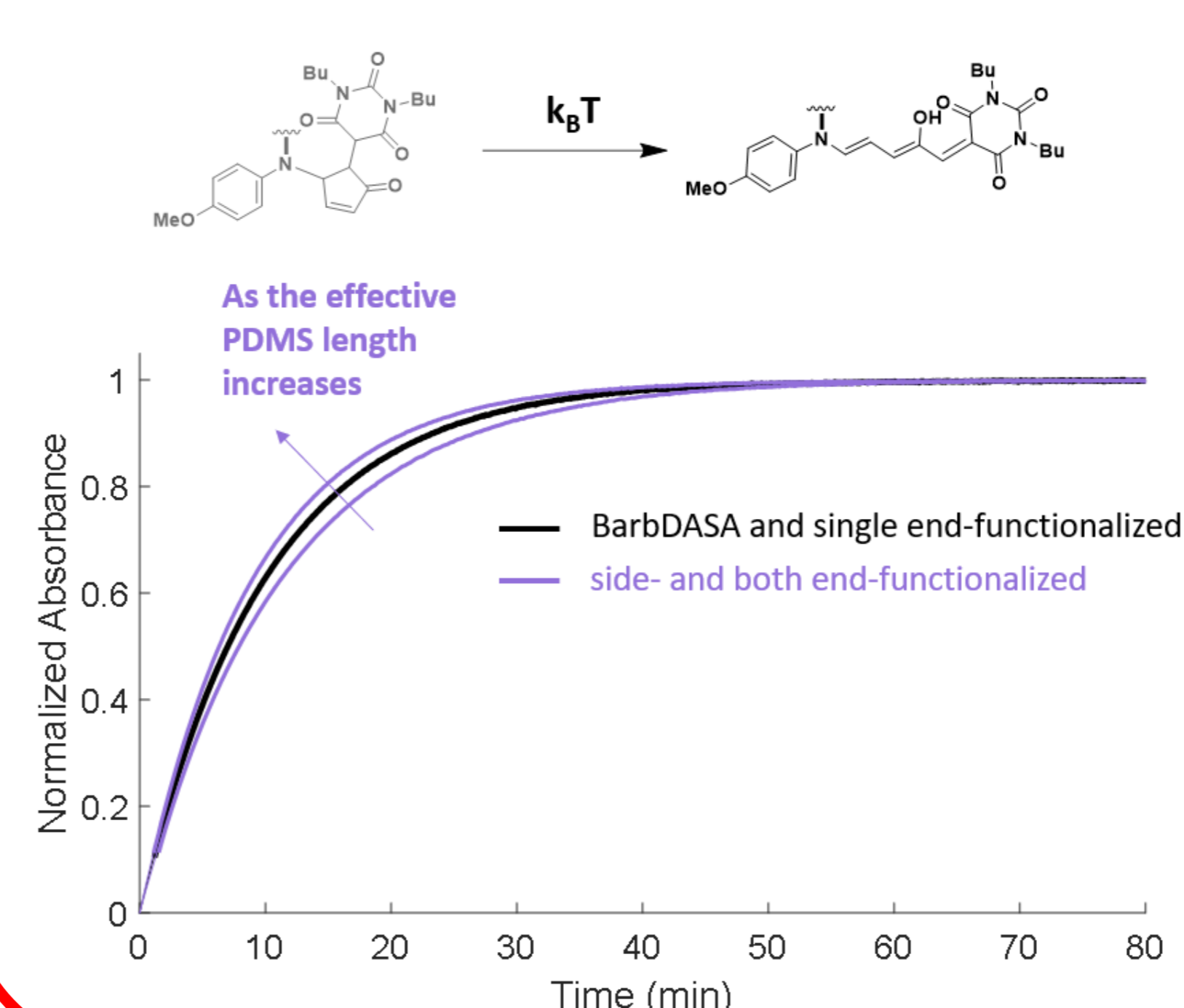
DASA-PDMS Synthesis



The synthesis of the DASA-PDMS conjugates comprises of two main steps: (1) the attachment of a vinyl terminated aromatic amine precursor (VinPre) to a PDMS chain by hydrosilylation and (2) DASA synthesis on polymer by reaction of the amine functionalized PDMS (Am-PDMS) with an excess of furan adduct (FA). Synthesized DASA-PDMS conjugates differ from each other regarding their PDMS chain length, conjugate architecture (side-functionalized, single end-functionalized or both end-functionalized) and DASA type (Meldrum's acid based (**MeldDASA**), Barbituric acid based (**BarbDASA**) and pyrazolone based (**PyraDASA**)).



DASA-PDMS in Solution

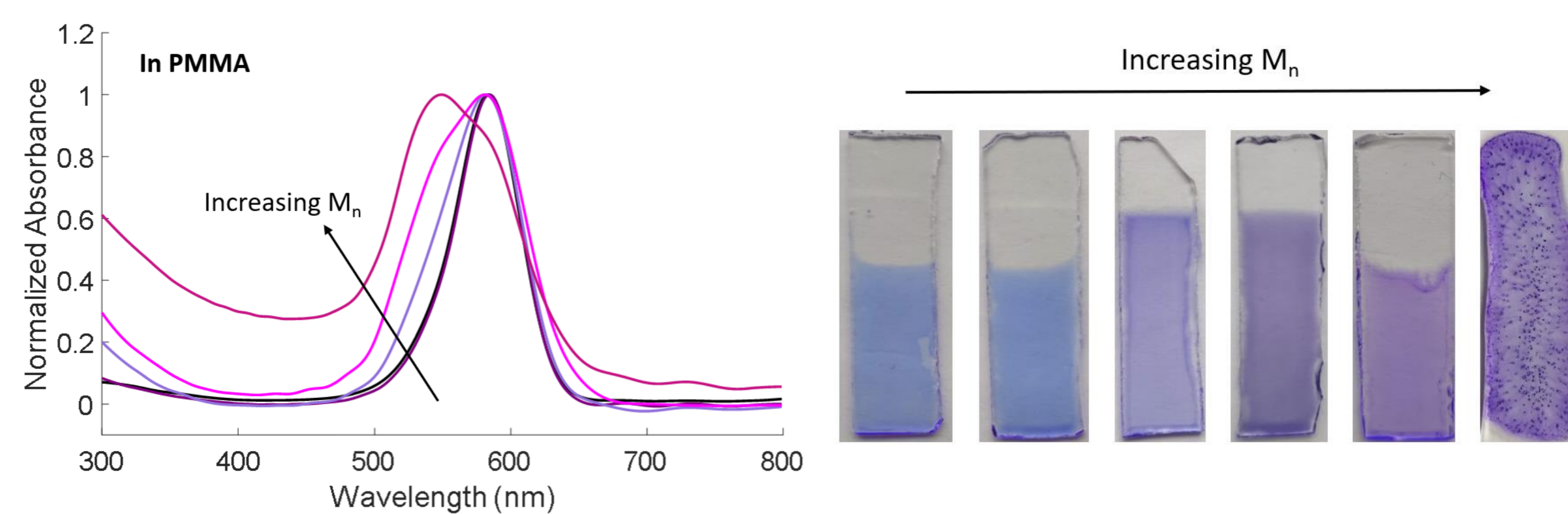


DASAs and their conjugates were characterized by UV-Vis spectroscopy. No change in absorbance profile was observed with the attachment of PDMS chains. However, kinetic measurements on BarbDASA and its conjugates dissolved in THF demonstrated the influence of the conjugate architecture and the effective PDMS length (PDMS molecular weight per DASA).

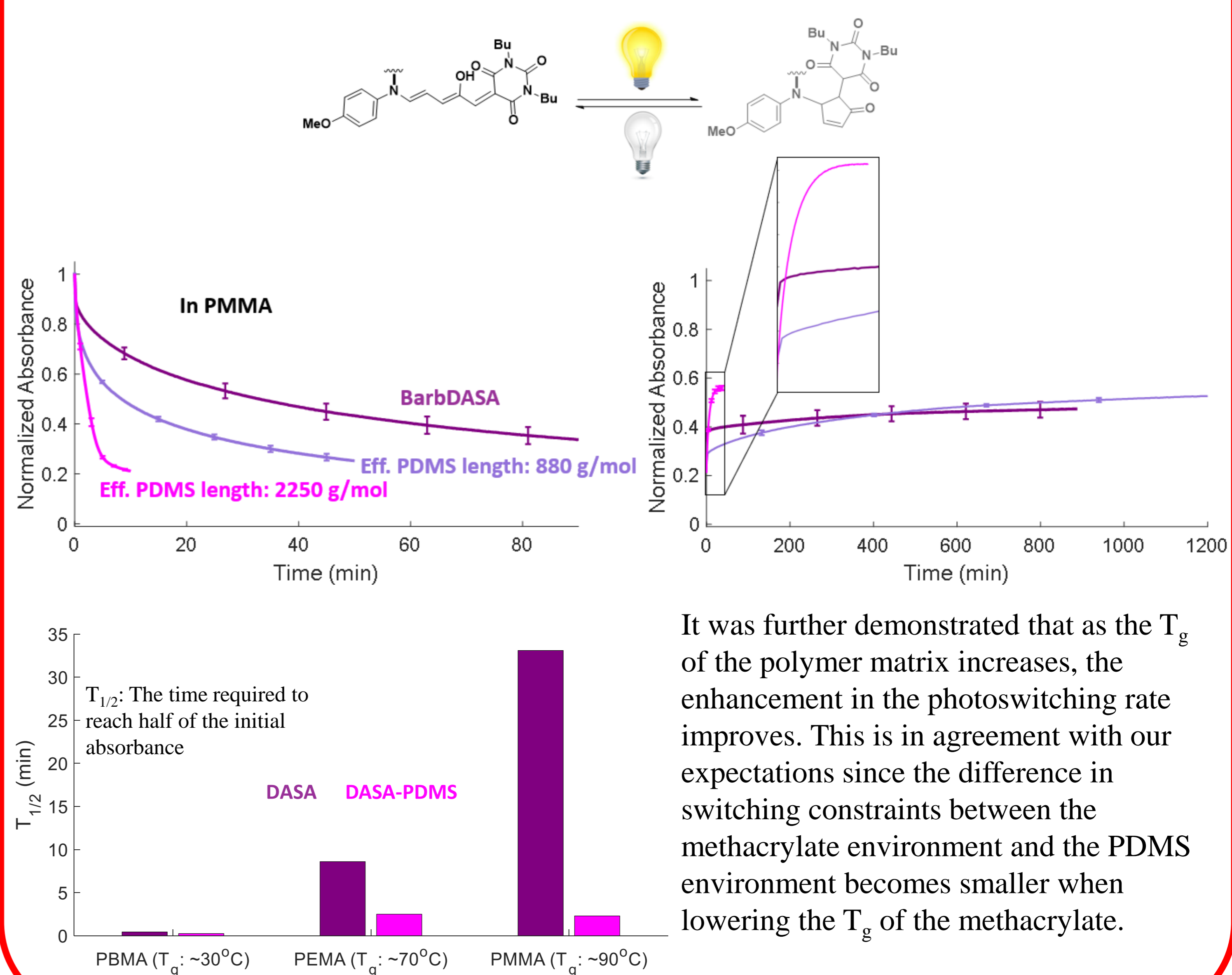
DASA-PDMS in Thin Films

The matrices are required to be amorphous (for transparency) and aprotic to allow for reversible switching of the DASA. In addition, the matrix has to have a glass transition temperature (T_g) higher than room temperature to be rigid which is usually a requirement in optical applications. Considering these requirements, we selected polymethacrylates (PMMA, PEMA and PBMA) as the polymer matrix for our thin films.

One challenge we faced during this study was the low miscibility of PDMS in polymethacrylates which compromises the transparency of the films. Therefore, we were limited to PDMSs with relatively low molecular weight (<5000 g/mol) in this study.



Kinetic measurements by UV-Vis spectroscopy demonstrated the effectiveness of the PDMS attachment to DASAs in the polymer matrices tested. Moreover, the positive influence of the effective PDMS length in the photoswitching and recovery rate of the conjugates was shown with PMMA thin films.



It was further demonstrated that as the T_g of the polymer matrix increases, the enhancement in the photoswitching rate improves. This is in agreement with our expectations since the difference in switching constraints between the methacrylate environment and the PDMS environment becomes smaller when lowering the T_g of the methacrylate.

Conclusions

- Depending on the balance between the DASA-DASA and the DASA-PDMS interactions, the back recovery of DASA-PDMS can be slightly faster or slower than the DASA itself in THF.
- The attachment of PDMS improved both photoswitching and recovery kinetics of DASAs in the three polymer matrices tested.
- The enhancement in photoswitching was more pronounced as the T_g of the matrix increases.

References

- (1) M. M. Lerch, W. Szymański, and B. L. Feringa, "The (photo)chemistry of Stenhouse photoswitches: Guiding principles and system design," *Chemical Society Reviews*, vol. 47, no. 6, pp. 1910–1937, 2018.
- (2) J. R. Hemmer et al., "Controlling Dark Equilibria and Enhancing Donor-Acceptor Stenhouse Adduct Photoswitching Properties through Carbon Acid Design," *J. Am. Chem. Soc.*, vol. 140, no. 33, pp. 10425–10429, 2018.
- (3) R. A. Evans et al., "The generic enhancement of photochromic dye switching speeds in a rigid polymer matrix," *Nat. Mater.*, vol. 4, no. 3, pp. 249–253, 2005.