

REVERSIBLE PHOTOISOMERIZATION AND PHOTOINDUCED BIREFRINGENCE IN MAIN-CHAIN AZOBENZENE POLY(ARYLENE ETHER) FILMS

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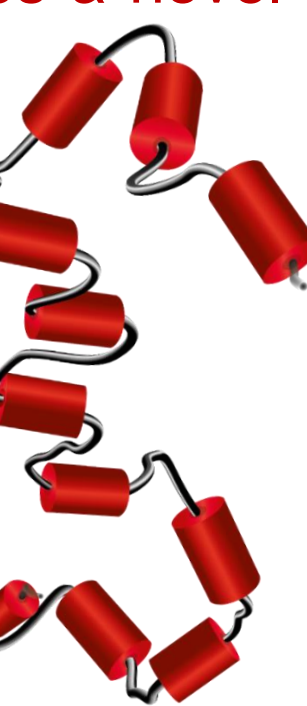
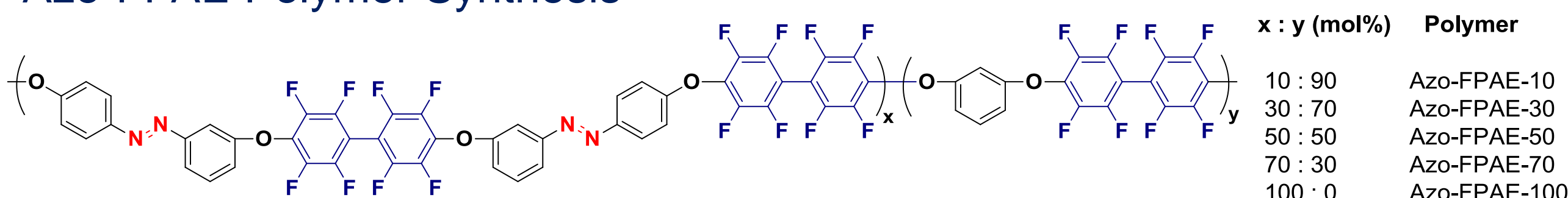
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Azobenzene-based polyethers provide a versatile platform for developing thermo- and mechanically-stable materials with macroscopic properties that can be manipulated by light, making them highly functional. These light-powered functional polymeric systems, capable of undergoing efficient and reversible photochemical reactions of azo groups to switch between trans (or E)- and cis (or Z)-isomers with markedly different properties, continue to impact the materials world. In the case of polarized light, this repeated isomerization induces reorientation of the azobenzene molecules aligning them perpendicular to the polarization direction of the incident light. **The current study introduces a novel approach to designing an azo-containing polymer with azobenzene and octafluorobiphenylene fragments in the main chain - Azo-FPAE.**

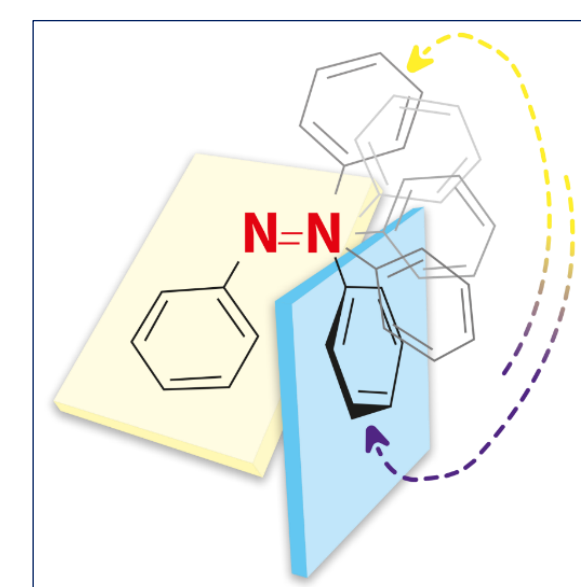
Azo-FPAE Polymer Synthesis



- The target Azo-FPAE polymers were synthesized by polymerization of combinations of *bis*-azo-based monomer, decafluorobiphenyl and resorcinol.
- The success of the synthesis of the Azo-FPAE polymers is confirmed with ¹H NMR, ¹⁹F NMR, FTIR and Raman spectroscopy techniques.

Optical images of self-supporting Azo-FPAE films

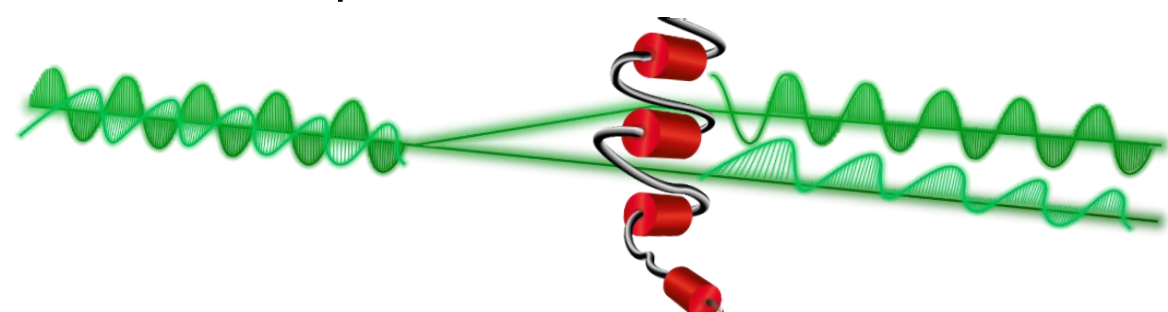
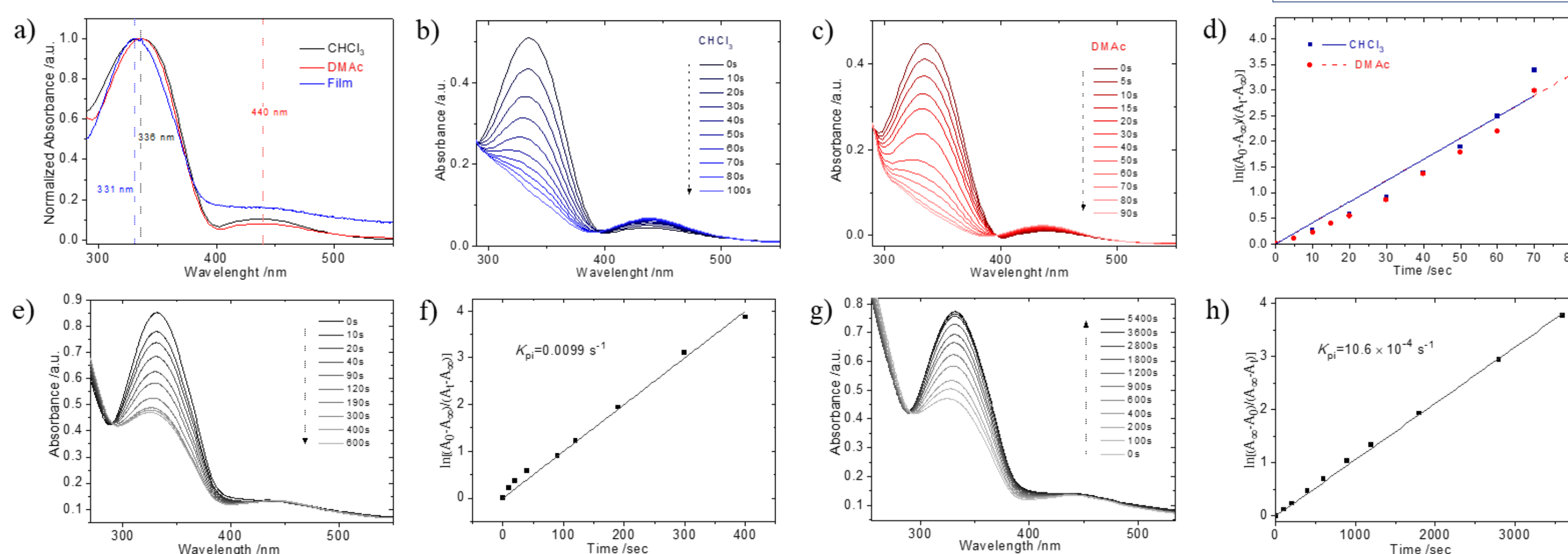
Solution casting technique (solvent – chloroform; substrate - glass)



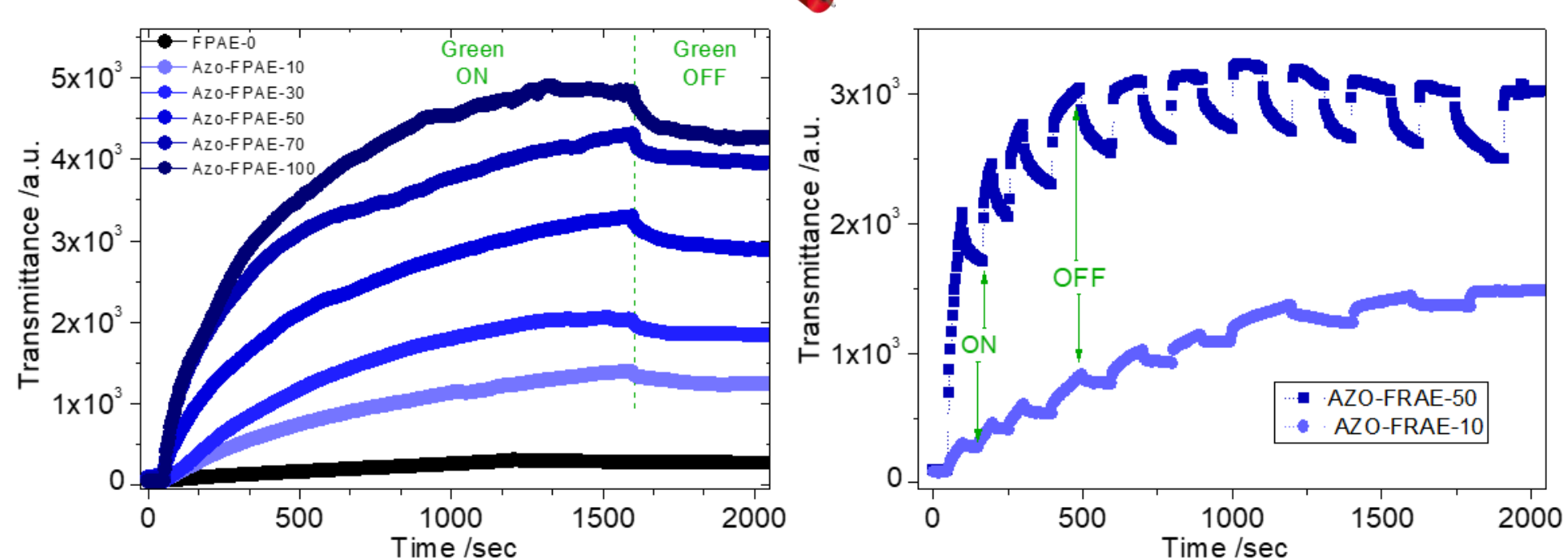
Photoisomerization of Azo-FPAE Polymers in Solution and Thin Film

Photo-optical behavior of Azo-FPAE-100 is presented as an example

- Normalized UV-vis absorbance spectra of polymer in CHCl₃, DMAc and solid film
- Trans-cis* photoisomerization in CHCl₃
- Trans-cis* photoisomerization in DMAc
- kinetic of the *trans-cis* photoisomerization in CHCl₃ and DMAc
- trans-cis* isomerization in film ($\lambda = 365$ nm, 3-4 mW);
- kinetic of the *trans-cis* photoisomerization
- cis-trans* photoisomerization (deuterium lamp, $\lambda = 275 \pm 25$ nm, 8-12 mW)
- kinetic of the *cis-trans* photoisomerization.



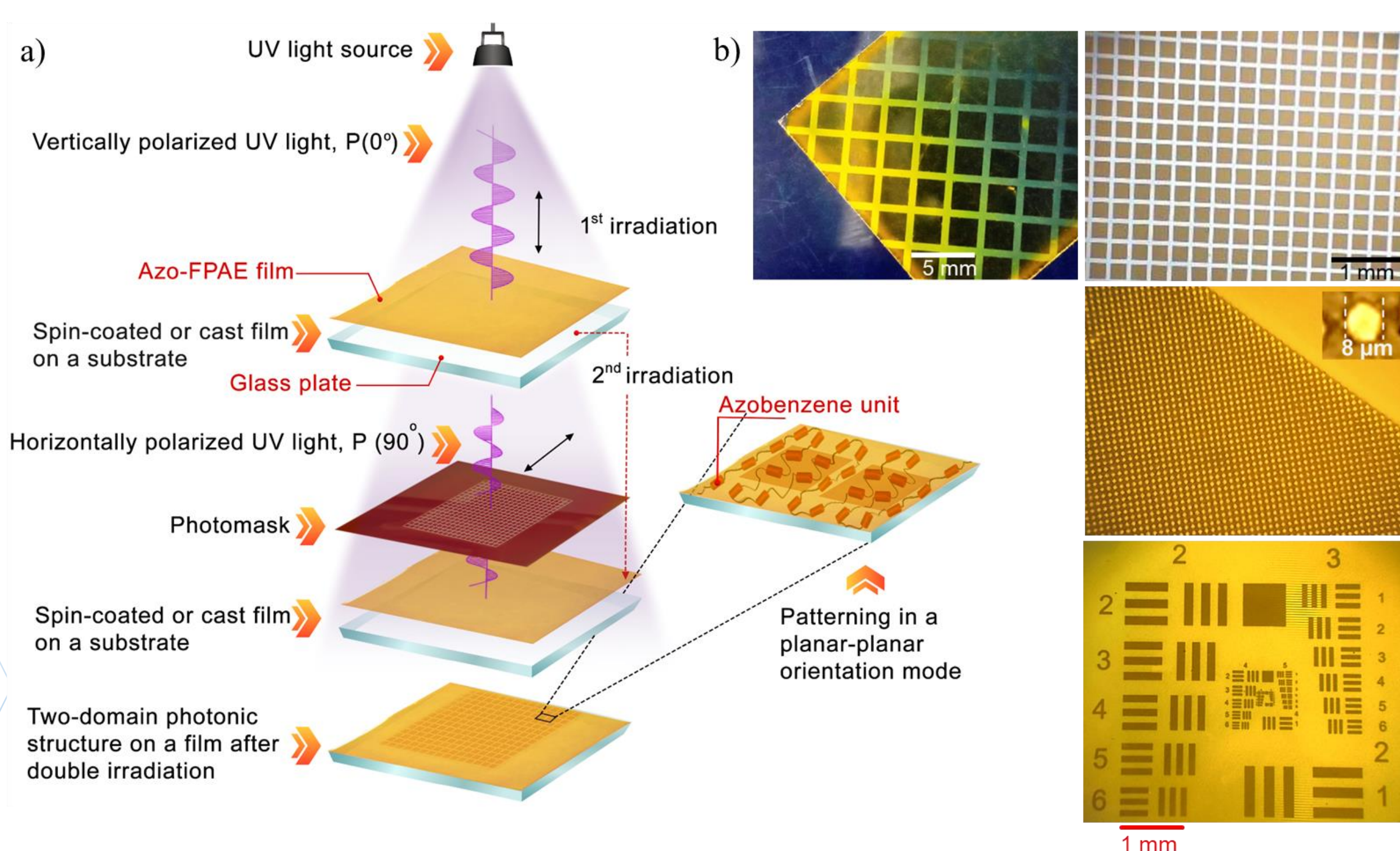
Birefringence Measurements



Kinetics curves for the buildup and relaxation of birefringence in Azo-FPAE film ($\lambda=532$ nm, $P \sim 10$ mW).

Multiple optical switching of the photochromic Azo-FPAE-10 and Azo-FPAE-50 systems ($\lambda=532$ nm, $P \sim 10$ mW).

- Scheme showing the procedures for the in-plane photopatterning of the Azo-FPAE polymer films by a linearly polarized UV light.
- The optical images of Azo-FPAE-50 film fragments under crossed polarizers capturing diverse results from different photomask applications for photopatterning.



Conclusions

This study explores a straightforward and effective method for synthesizing novel fluorinated polyethers with azobenzene groups in the main chains. The polymers demonstrate excellent solubility and film-forming abilities. UV irradiation induces E-to-Z photoisomerization, while white light induces the reverse Z-to-E isomerization of azo units in both chloroform solution and the solid state, indicating great potential for reversible photo-switching. The photoorientation ability of azobenzenes in the films, when irradiated by $\lambda=532$ & 365 nm, results in anisotropic properties, showcasing potential for fabricating diffraction gratings and photoalignment of liquid crystals.

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