Switch to Bend: The Advantage of SEC in Quantifying Photoisomerism of Uniform Oligomers

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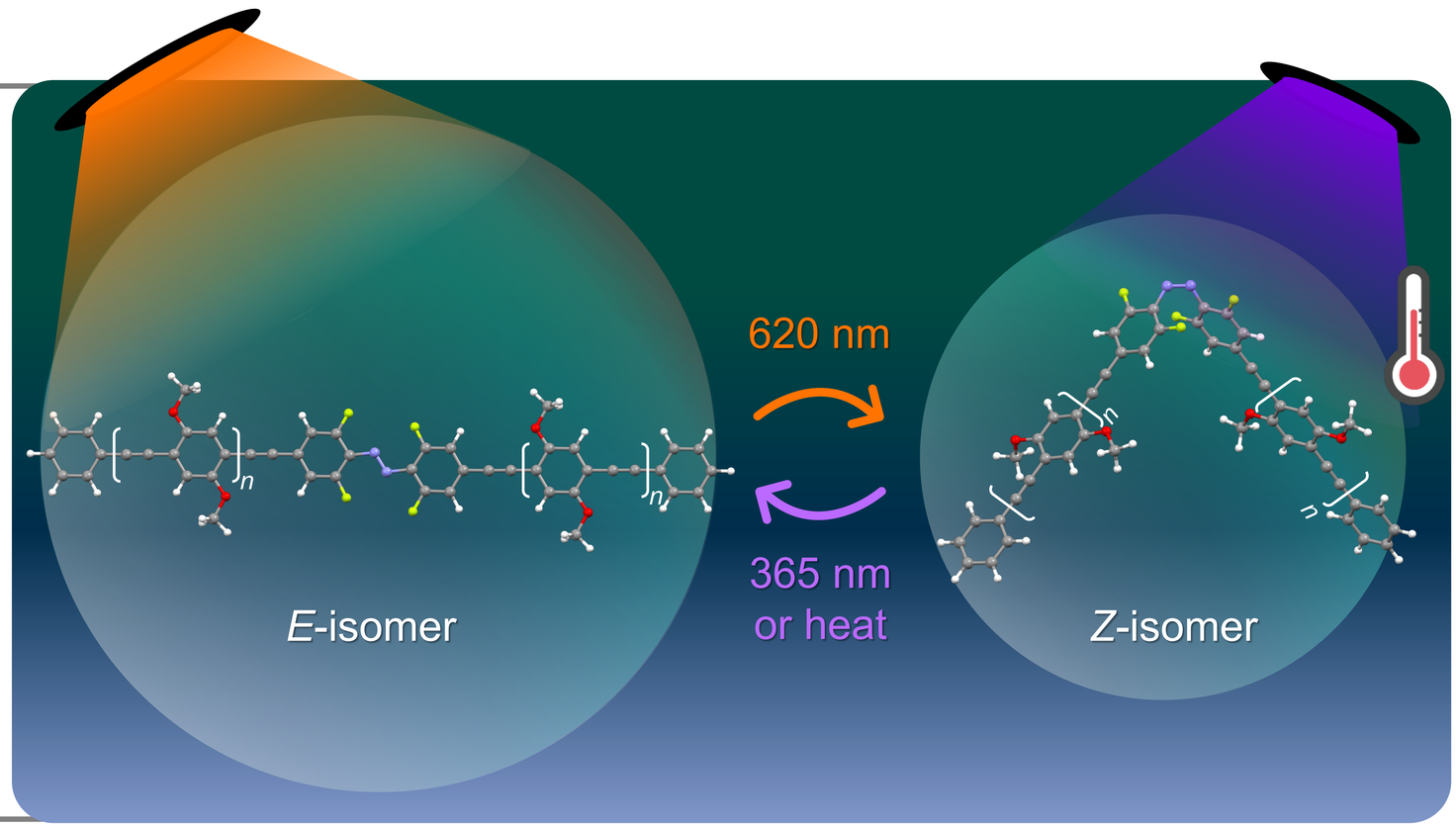
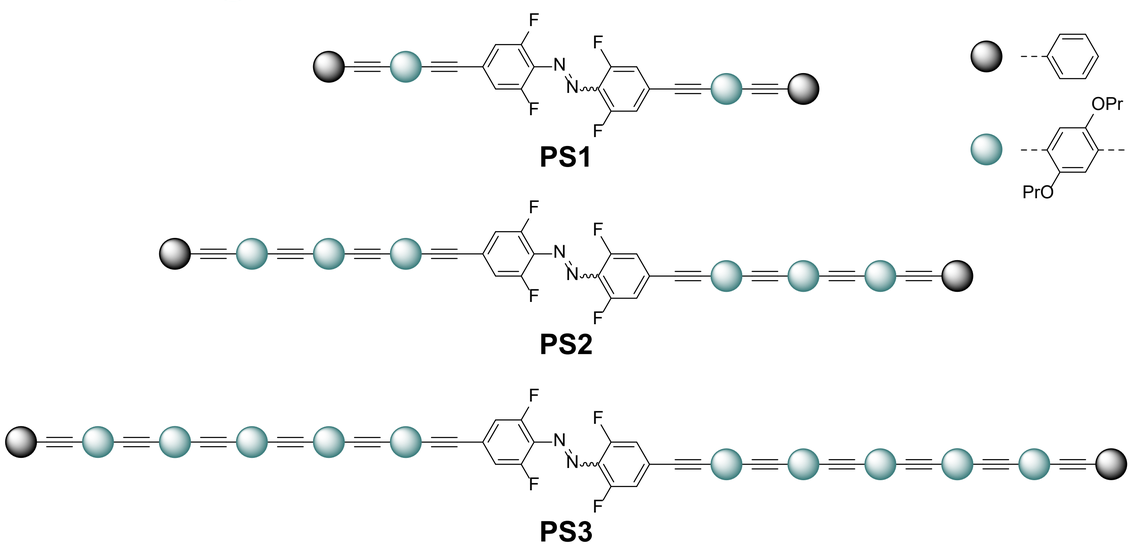
Motivation

Sequence-defined conjugated oligomers with rigid π-backbones offer precise structural control and enable detailed structure–property studies. Incorporating azobenzene switches allows reversible *E*/*Z* isomerization, but quantification by NMR spectroscopy is challenging in oligomeric systems due to signal overlap. SEC separates *E*/*Z* isomers based on hydrodynamic volume, with rigid full-conjugated backbones amplifying size differences for improved resolution.

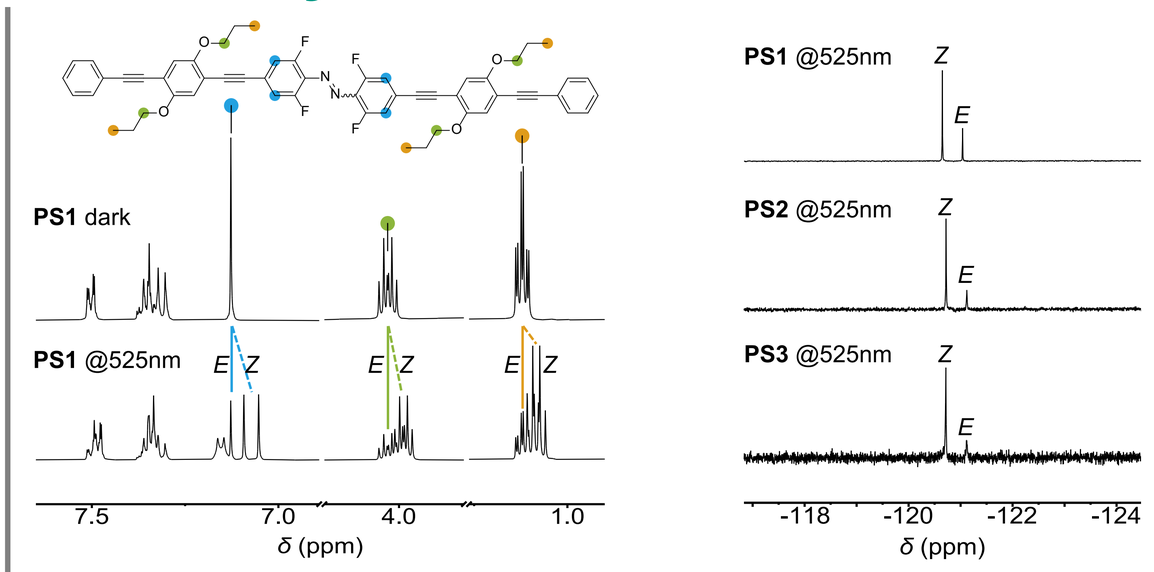


OPE Oligomers



- iterative synthesis → sequence-defined structures
- *o*-tetrafluoroazobenzene → improved thermal stability
- rigid OPE → enhanced hydrodynamic sensitivity

NMR Analysis



^{1}H NMR (THF-*d*8)

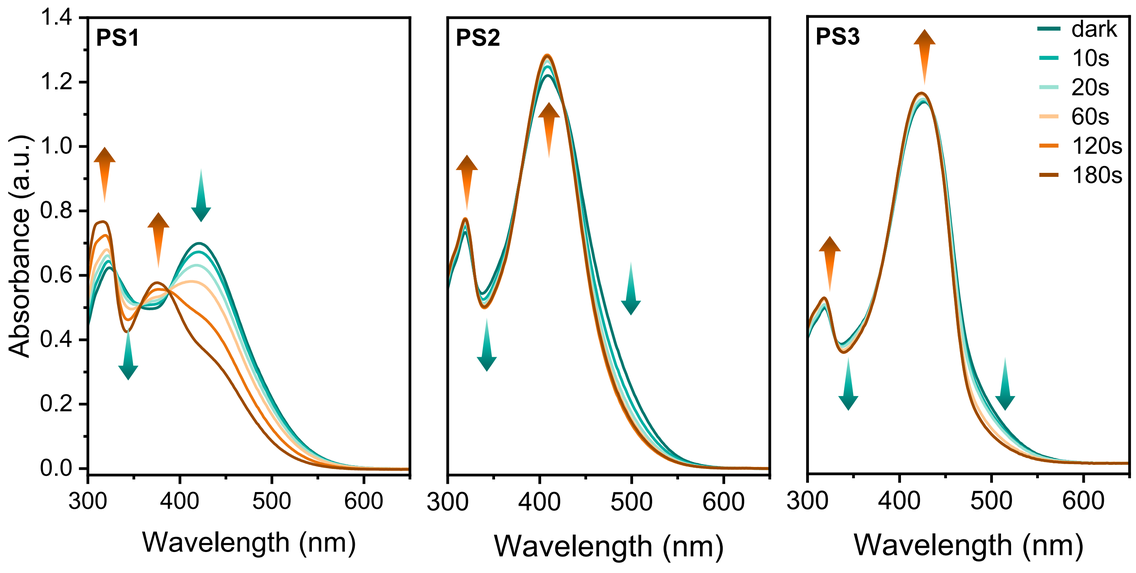
✓ **PS1** analyzable despite signal overlap

✗ **PS2**&**PS3** not analyzable

^{19}F NMR (THF-*d*8)

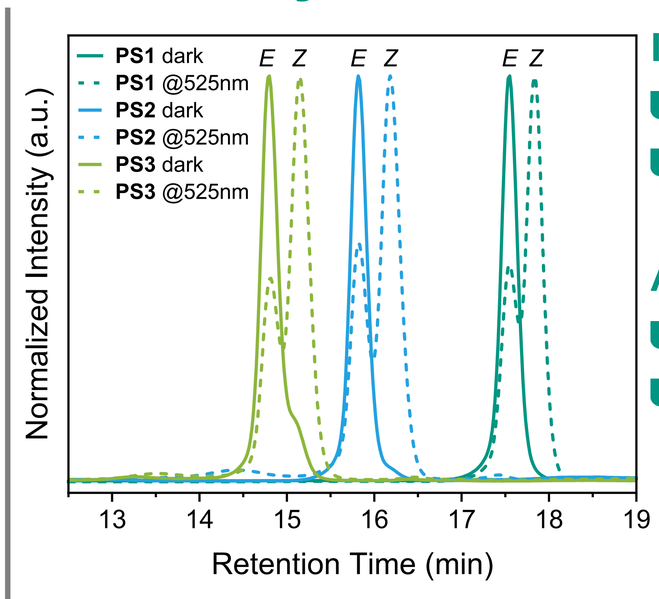
👍 a straightforward method but requires F

UV-Vis Spectroscopy



20 μM in THF, at 20°C, irradiated @525nm.

SEC Analysis



Initial state

- **PS1**&**PS2** >99% *E*/*Z*
- **PS3**: visible Z-isomer

After irradiation

- distinguishable *E*/*Z*-peaks
- quantification after calibration based on ^{19}F NMR method

Table. Comparison of *Z*-isomer content (*Z*%) determined by different methods.

Entry	*Z*%		
	^{1}H NMR	^{19}F NMR	SEC
PS1	71	73	73
PS2	*	78	79
PS3	*	81	83

* Not possible due to peak overlap.

Conclusions & Outlook

- first use of SEC for E/Z ratio quantification
- new means for analyzing macromolecular photoresponsive systems
- investigation in thermal stability of the photostates
- calculation of hydrodynamic volumes via molecular dynamic simulation