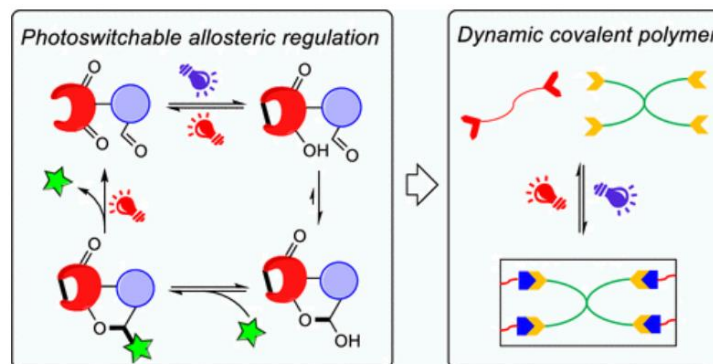


Photoswitchable Cascades for Allosteric and Bidirectional Control over Covalent Bonds and Assemblies

Published on April, 2024

J. Am. Chem. Soc. **2024**, *146*, 11392–11399



Who are the corresponding authors and what are their research areas?



Pr. Lei You

Research Professor (2013-present)

**Fujian Institute of Research on the Structure of Matter
Chinese Academy of Sciences**

Research interests: dynamic interactions, molecular assemblies, and their applications in sensing, labeling, and catalysis.

- **Ph.D at the University of Washington in St. Louis in 2008**

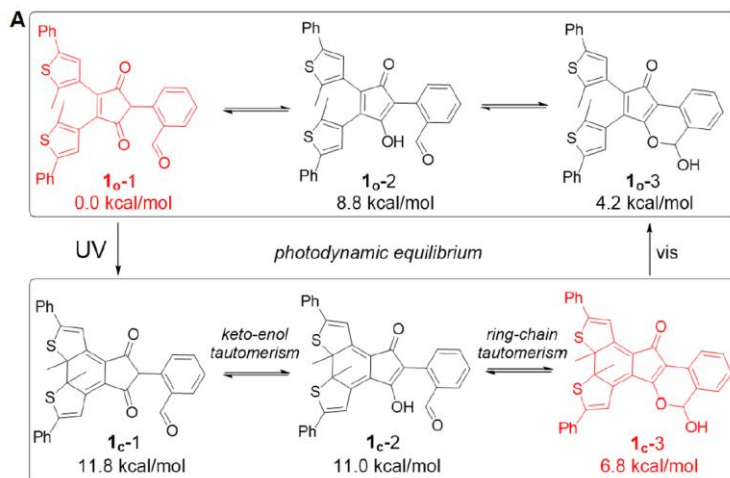
With Pr. **George W. Gokel** mostly focused on peptide mediate anion transport through phospholipid membranes employing weak supramolecular interactions.

- **Postdoc at The University of Texas at Austin**

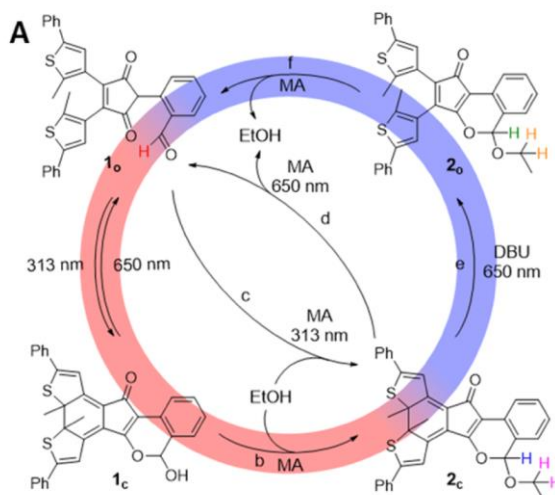
with Pr. **Eric V Anslyn** mostly focused on dynamic covalent chemistry for chirality sensing and binding.

What is the main claim of the article?

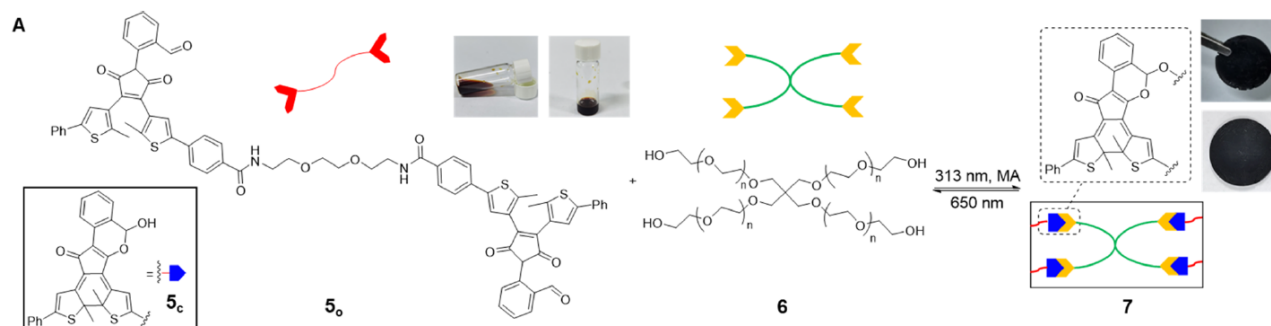
In this work the authors (1) develop a rare example of “**a bidirectional photoinduced dynamic multistep chemical Cascade**” by employing dynamic covalent interactions that can be activated by light irradiation of a photoswitch.



(2) They then employed this strategy to demonstrate dynamic capture/release of alcohols or thiols.



(3) The chemistry was further used to control the formation, structure and properties of dynamic polymers.



How is it demonstrated?

The light-triggered cyclization and the sequential enol/keto tautomerization and chain-chain equilibrium were followed by NMR spectroscopy and structures confirmed by X-ray and Mass spectrometry.

The reaction of the closed form with ethanol/thiols was confirmed by 2D NMR and mass spectrometry. DFT calculations also demonstrated the thermodynamic drive for this reaction where the product has lower free energy.

Rheology was used to study the properties of the polymers formed.

What are the typical experimental conditions?

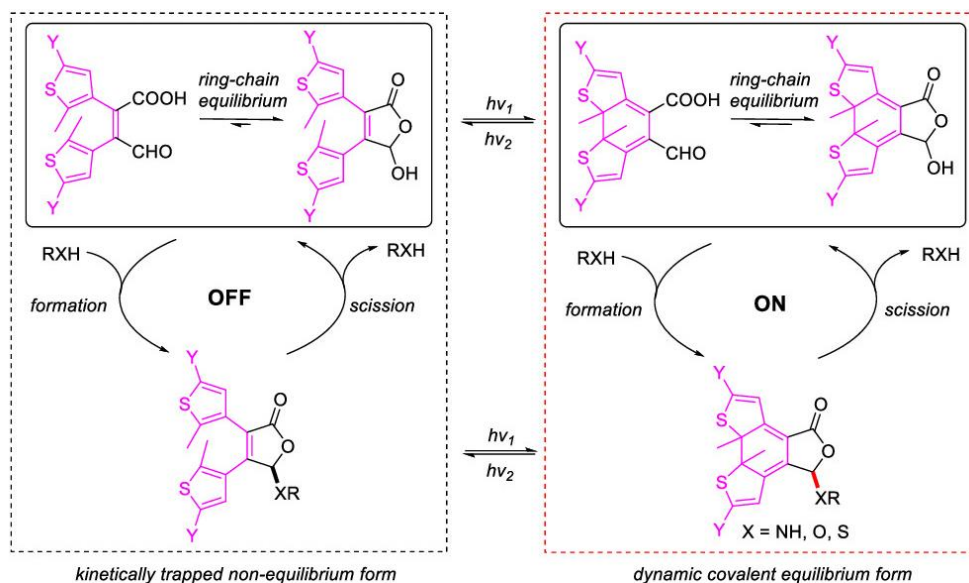
NMR in CDCl_3 at 10 mM

DTE ring closing: irradiation at $\lambda^{\text{UV}} = 313$ nm

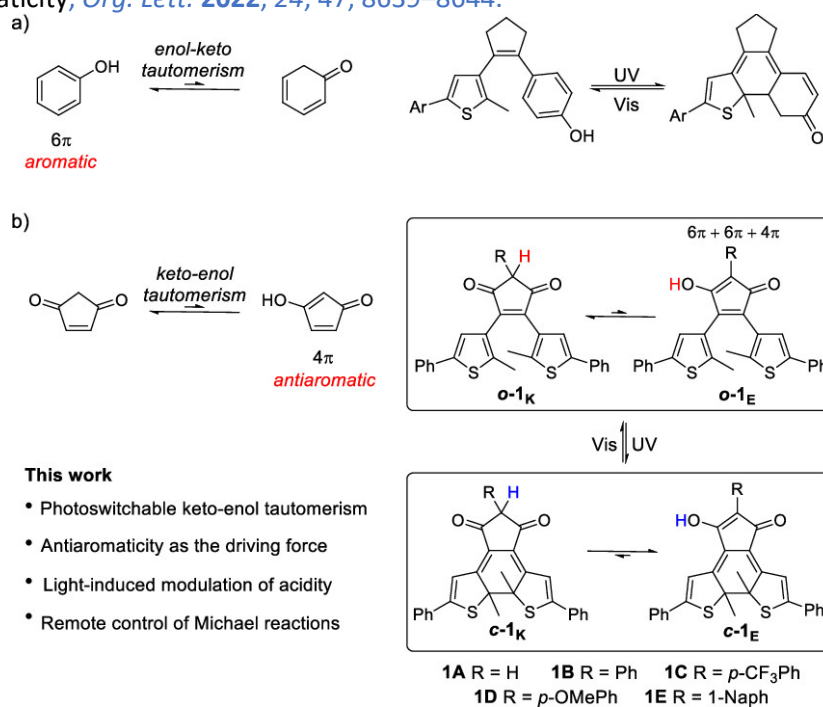
DTE ring opening, irradiation at $\lambda^{\text{vis}} = 650$ nm

Which are the key related papers?

Y. Hai, H. Ye, Z. Li, H. Zou, H. Lu, L. You, Light-Induced Formation/Scission of C–N, C–O, and C–S Bonds Enables Switchable Stability/Degradability in Covalent Systems, *J. Am. Chem. Soc.* **2021**, *143*, 48, 20368–20376.



H. Lu, H. Ye, M. Zhang, L. Wang, L. You, Photoswitchable Keto–Enol Tautomerism Driven by Light-Induced Change in Antiaromaticity, *Org. Lett.* **2022**, *24*, 47, 8639–8644.



Examples on Cascade reactions based on Dynamic covalent chemistry:

V. E. Campbell, X. de Hatten, N. Delsuc, B. Kauffmann, I. Huc, J. R. Nitschke, Cascading transformations within a dynamic self-assembled system, *Nat. Chem.* **2010**, *2*, 684–687.

Y. Ren, L. You, Dynamic Signaling Cascades: Reversible Covalent Reaction-Coupled Molecular Switches, *J. Am. Chem. Soc.* **2015**, *137*, 44, 14220–14228.