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Dynamic Covalent Switches and Communicating Networks for Tunable Multicolor Luminescent Systems and Vapor-Responsive Materials

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尤磊 研究员

2003年本科毕业于复旦大学化学系国家理科基础科学人才培养基地班；

2008年在美国圣路易斯华盛顿大学获得有机化学博士学位；

2013年到中国科学院福建物质结构研究所工作，任结构化学国家重点实验室研究员，课题组长。

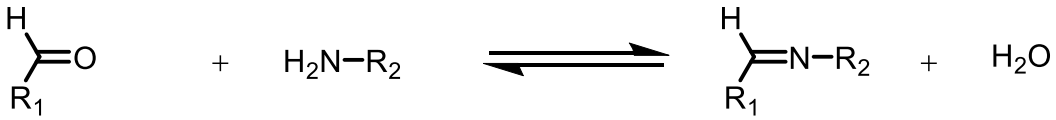
主要从事超分子化学、有机化学和化学生物学等领域的交叉研究，重点研究新型动态作用和组装及其在传感、标记和催化等方面的应用。

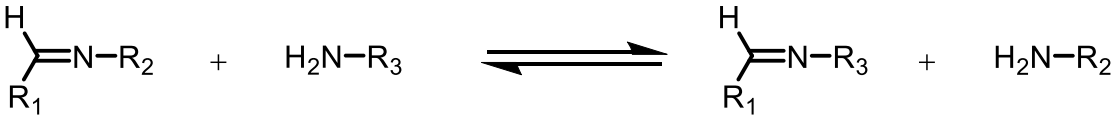
Dynamic Covalent Chemistry（DCC）

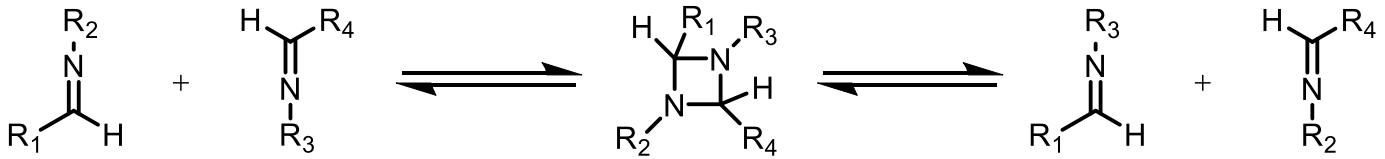
动态共价化学（DCC）涉及的是一系列基于热力学平衡的可逆平衡的共价化学反应，其核心概念是可逆共价化学键，如亚胺键、酰腙键、双硫键、酯键等。

可逆共价键特点：非共价键的可逆性和不可逆共价键的稳定性

可逆亚胺键：

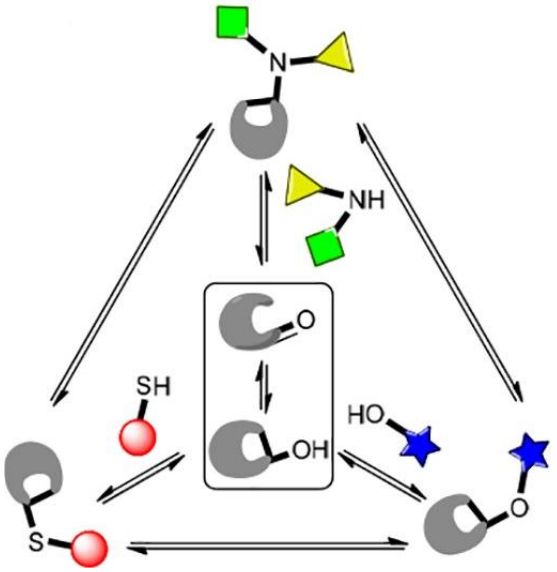
(a) 

(b) 

(c) 

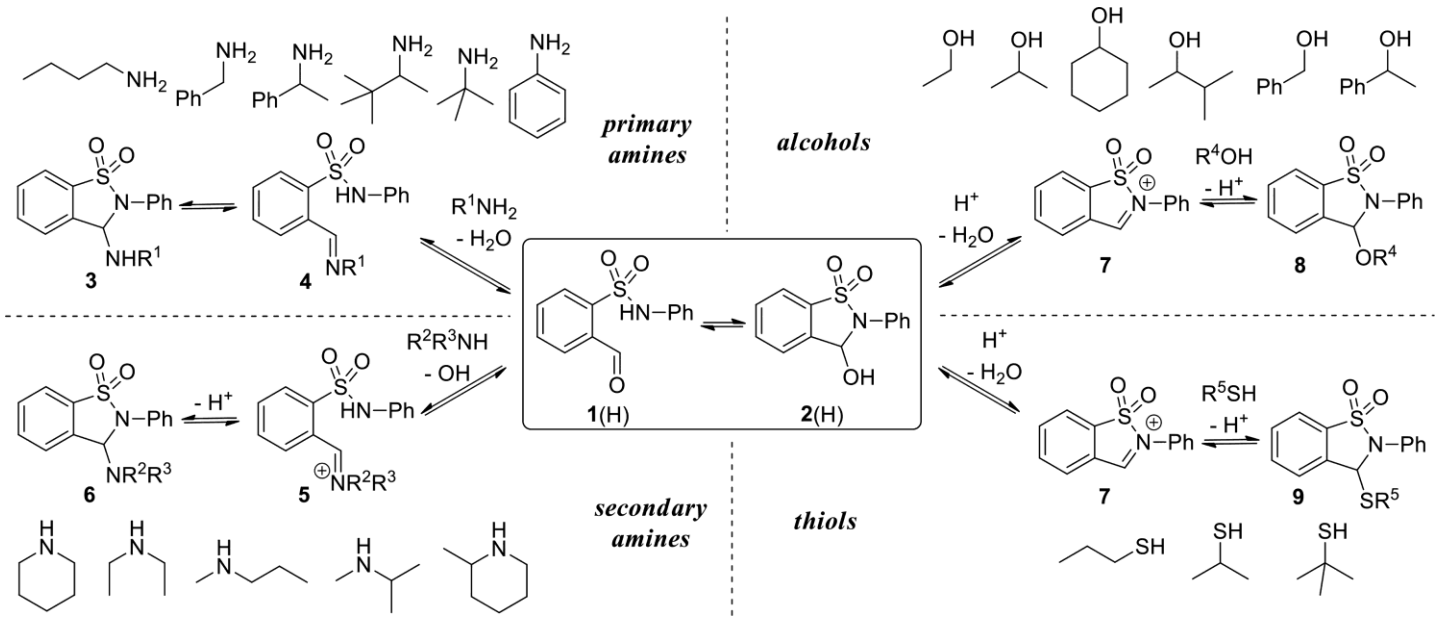
Chem. Soc. Rev., 2013,**42**, 6634-6654

Dynamic Covalent Chemistry（DCC）



This work

- √ *General strategy with interconverting tautomers*
- √ *Efficient DCRs from amines, alcohols, and thiols*
- √ *Orthogonality based on control of dual reactivity*
- √ *Stimuli-responsive switch between DCRs*
- √ *Creation of complex communicating networks*



J. Org. Chem., 2018, **83**, 9858−9869

Design and Synthesis

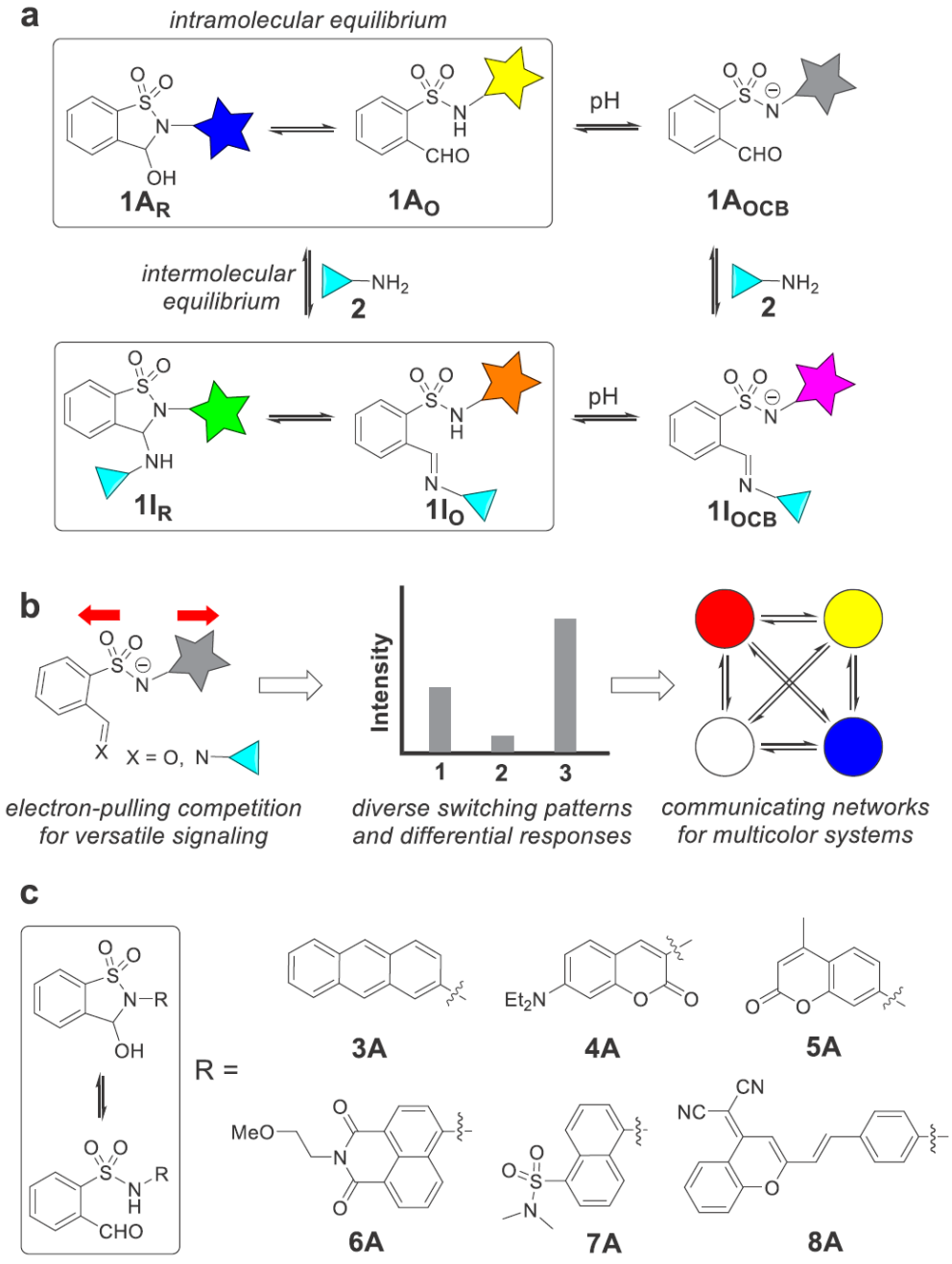
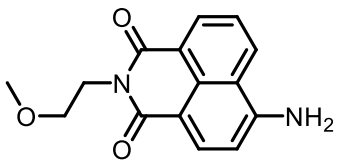


Figure . (a) Multiple states within dynamic covalent switching systems, with the star representing the fluorophore. (b) The electron-withdrawing competition for the regulation of fluorophores (using conjugate base as an example) and the creation of communicating networks. (c) Structures of 3A−8A.

Design and Synthesis

Probe	Ring (%) [a]	Open (%)	λ_{ex} (nm)	λ_{em} (nm)[b]	ϕ
3A	>95	<5	358	427	0.353
4A	88	12	380	463	0.412
5A	94[c]	6	324	386	0.036
6A	88	12	344	450	0.178
7A	>95	<5	298	411	0.074
8A	78	22	526	704	0.035



λ_{ex}=420nm, λ_{em}=517nm

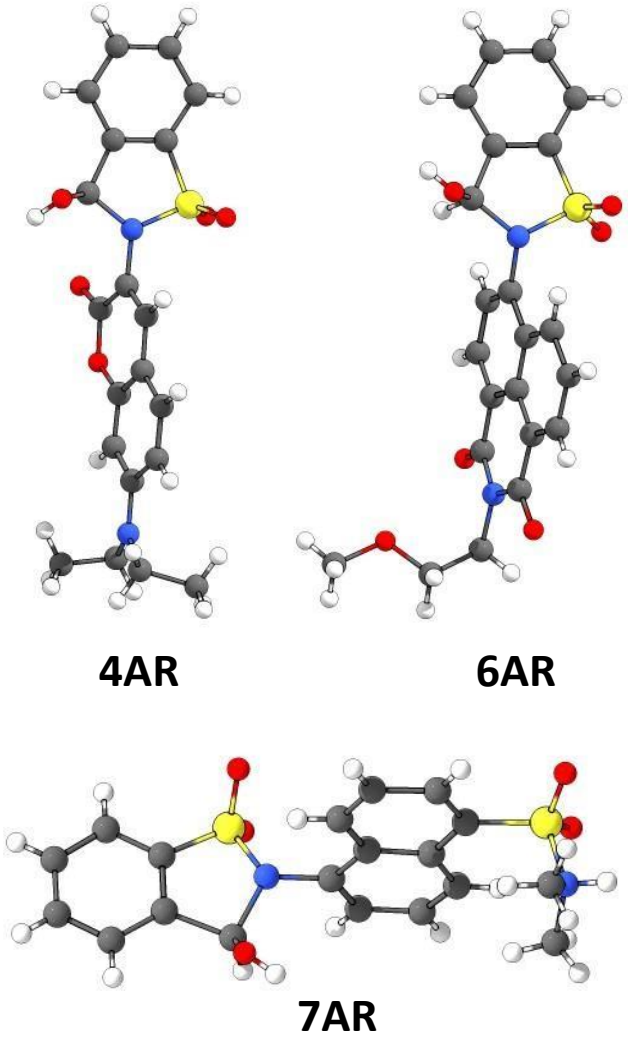
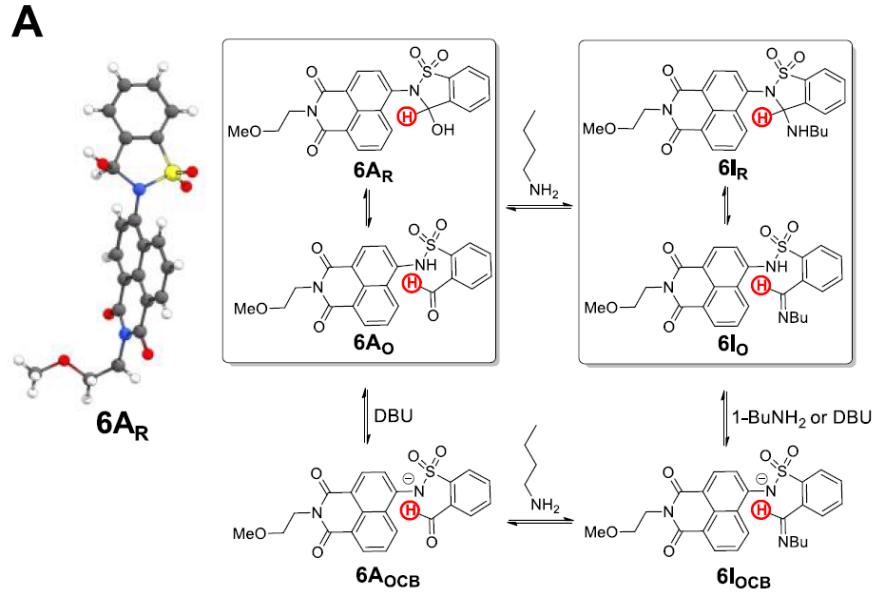
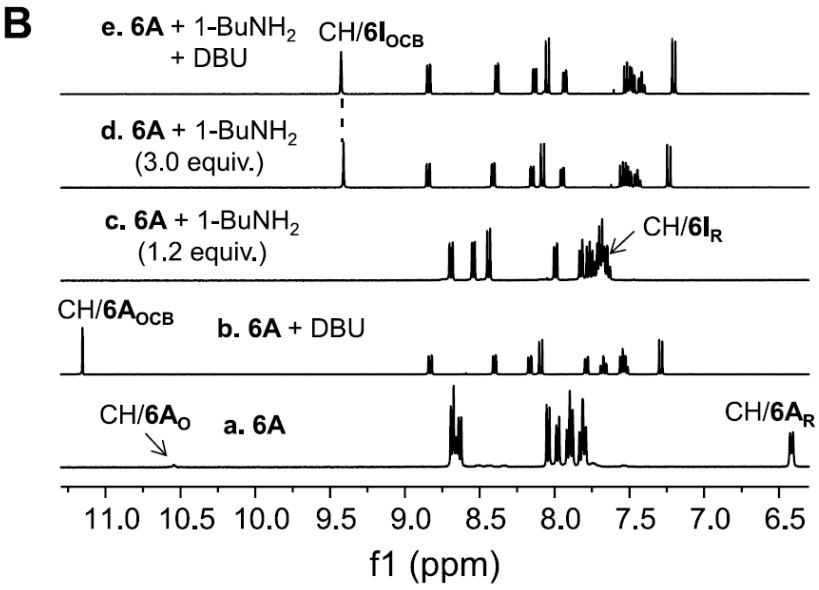
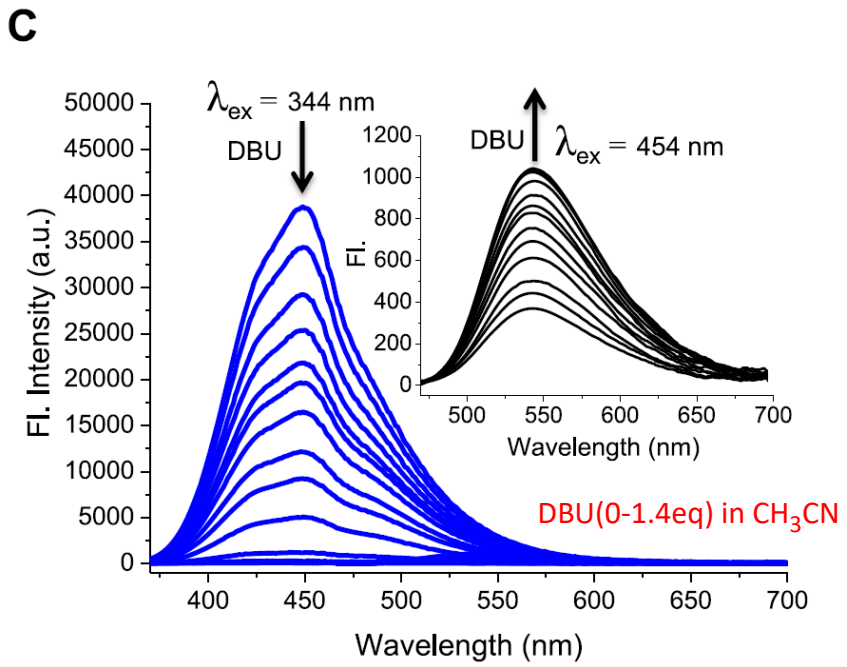


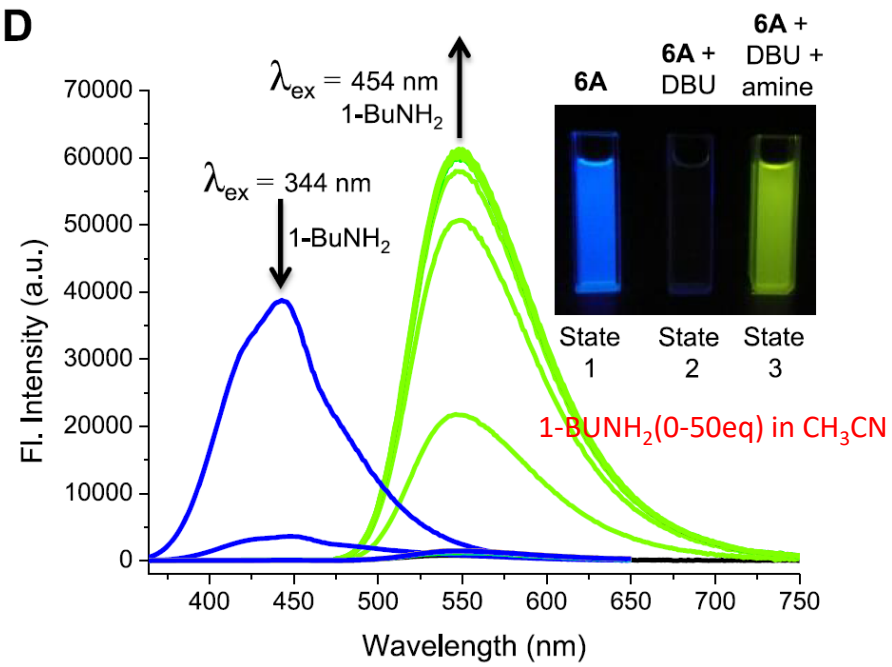
Figure . Crystal structures of 4AR, 6AR, and 7AR.

Fluorescence Studies-6A









pH and Amine Controlled Switching

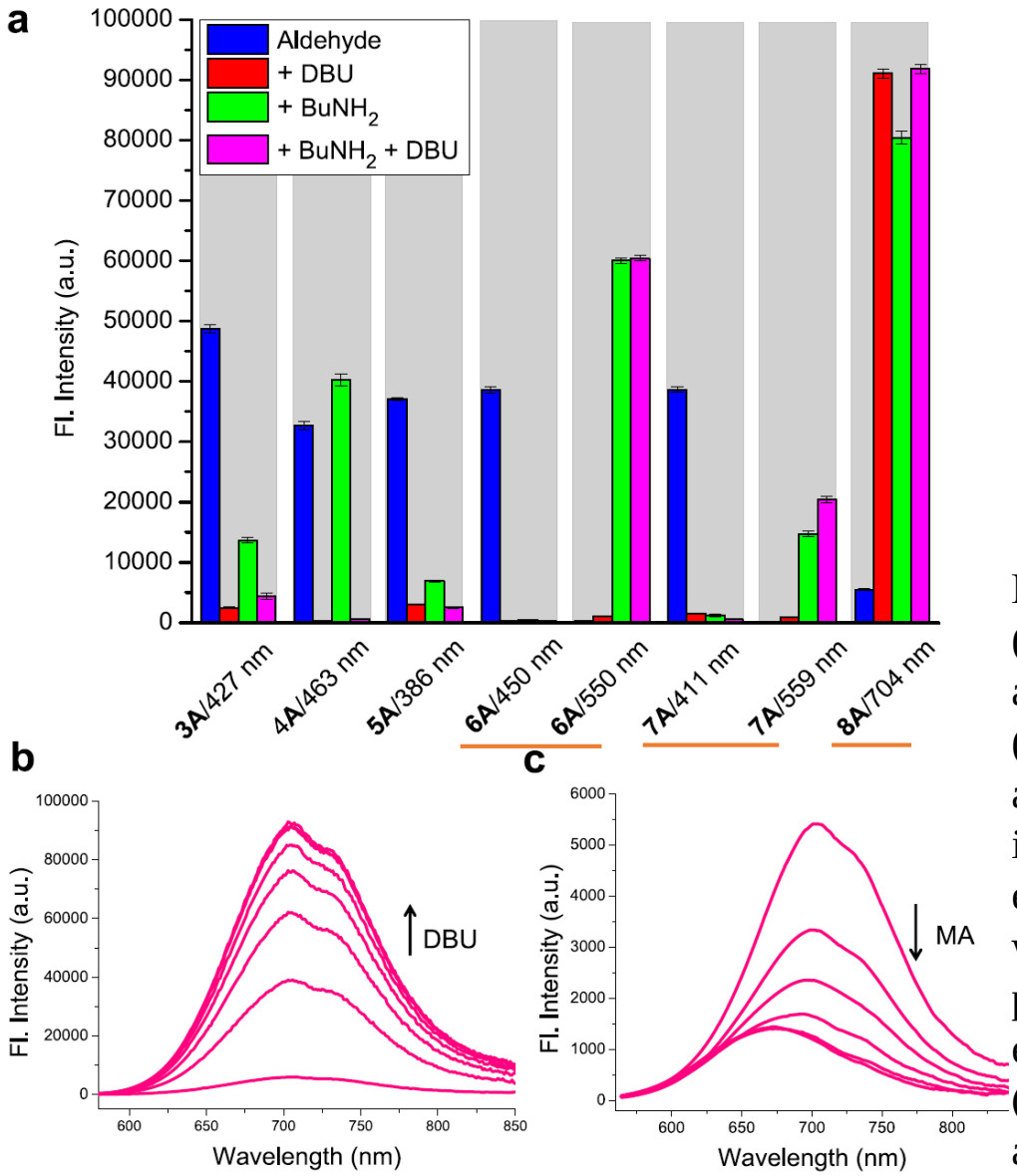
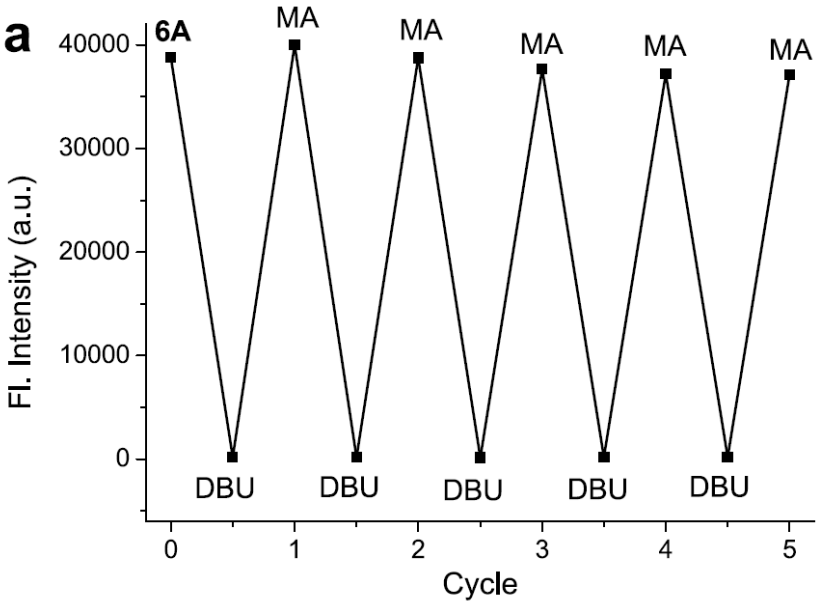
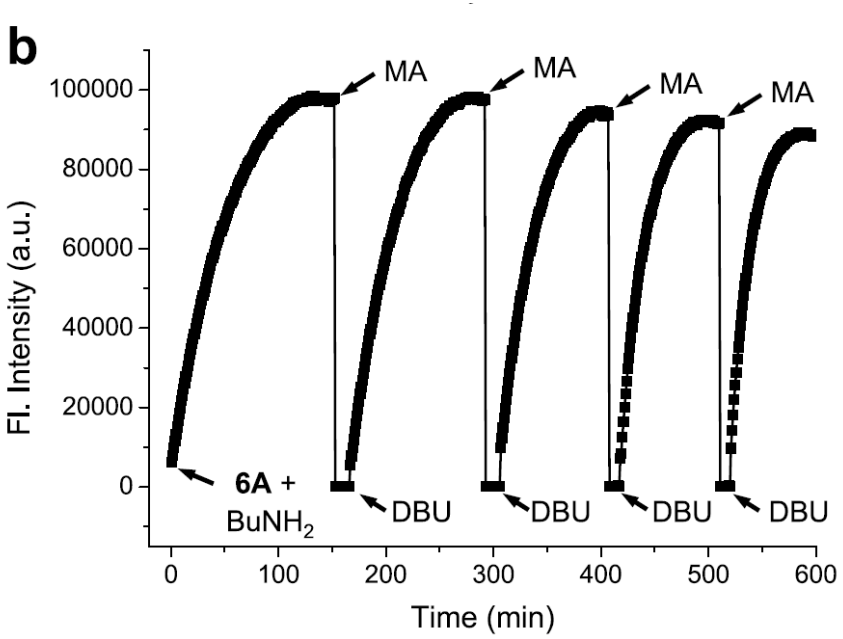


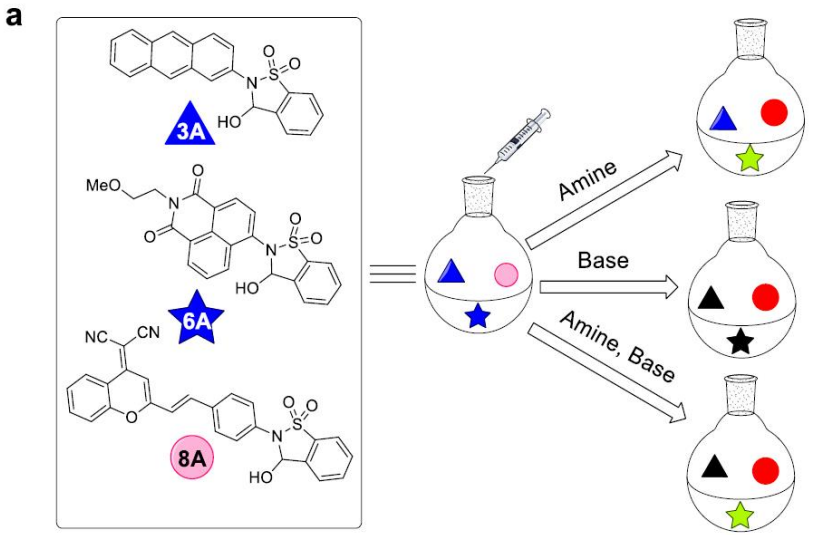
Figure . (a) Fluorescence intensity of3A−8A (50 μM, blue) and the response to the addition of DBU (1.2 equiv, red), 1-BuNH2 (50 equiv, green), and both DBU (1.2 equiv) and 1-BuNH2 (50 equiv, pink). Each intensity is shown at maximum emission, after being excited at corresponding maximum excitation wavelength. The original and red-shifted ICT peaks of 6A and 7A are shown. Changes in emission spectra upon the titration with DBU (0−1.2 equiv, b) and MA (0−1.2 equiv, c) into a solution of 8A (50 μM) in CH3CN (λex = 526 nm).

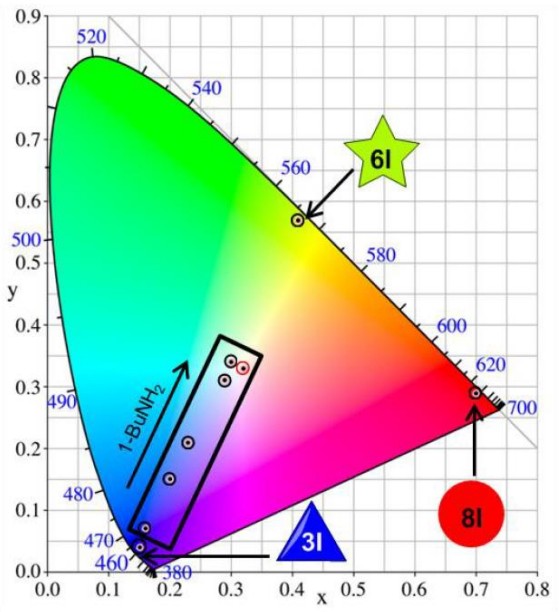
Reversibility

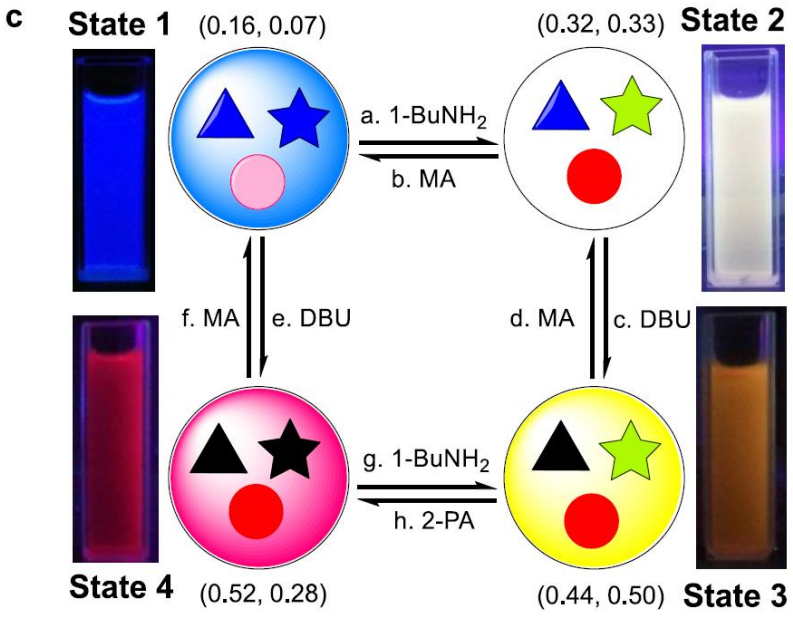


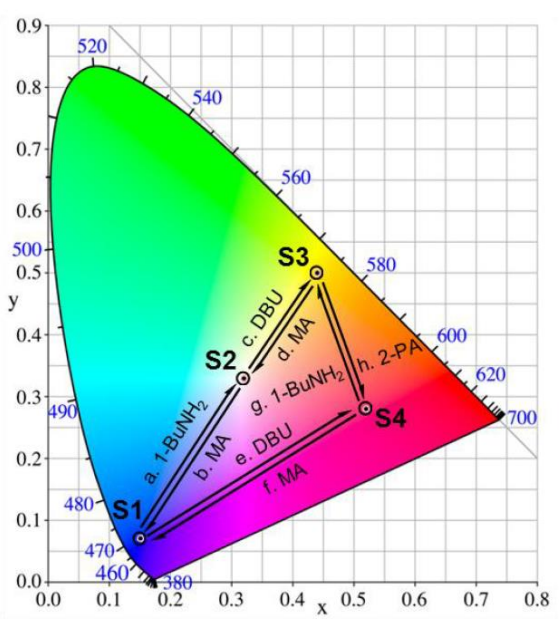


Communicating Networks

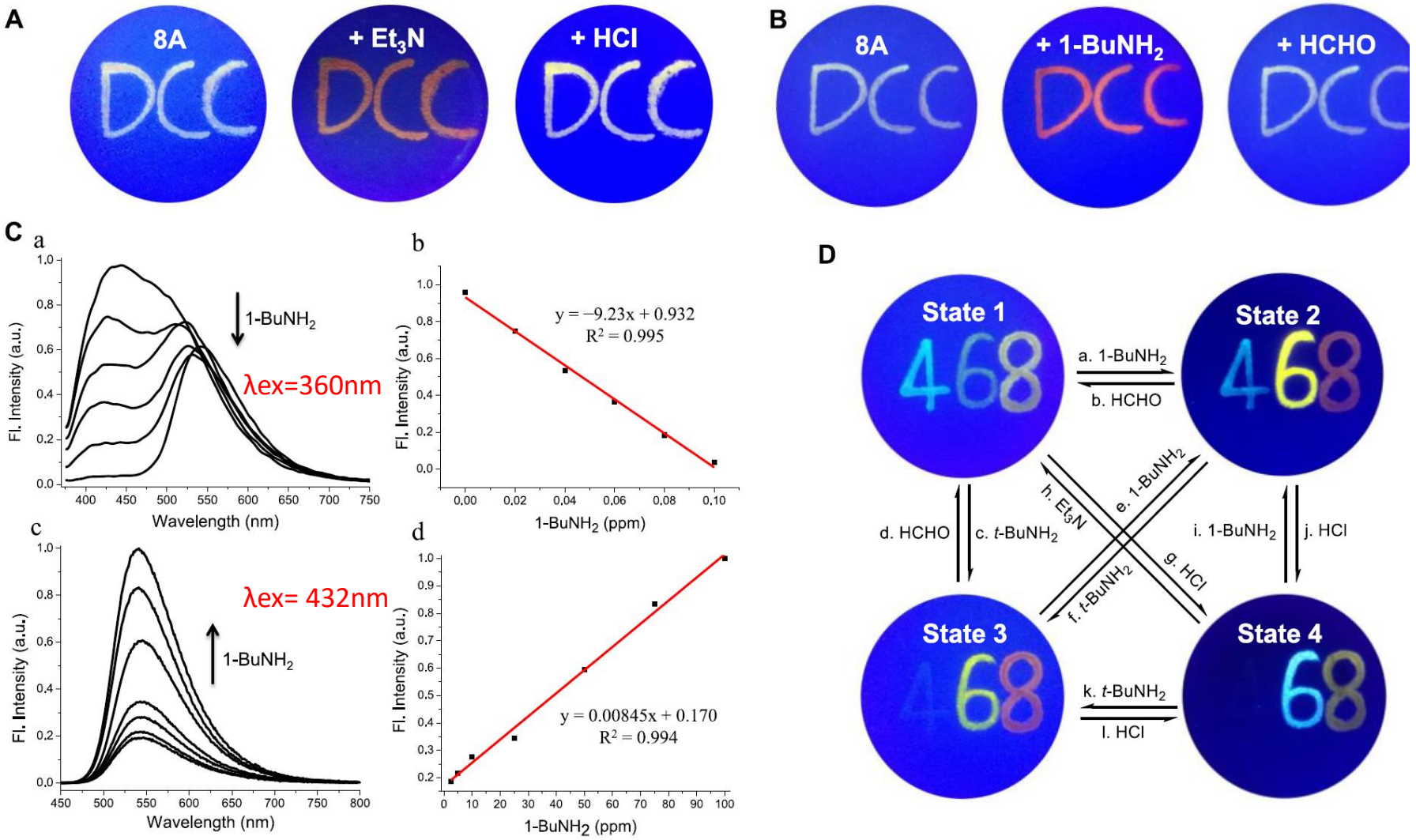




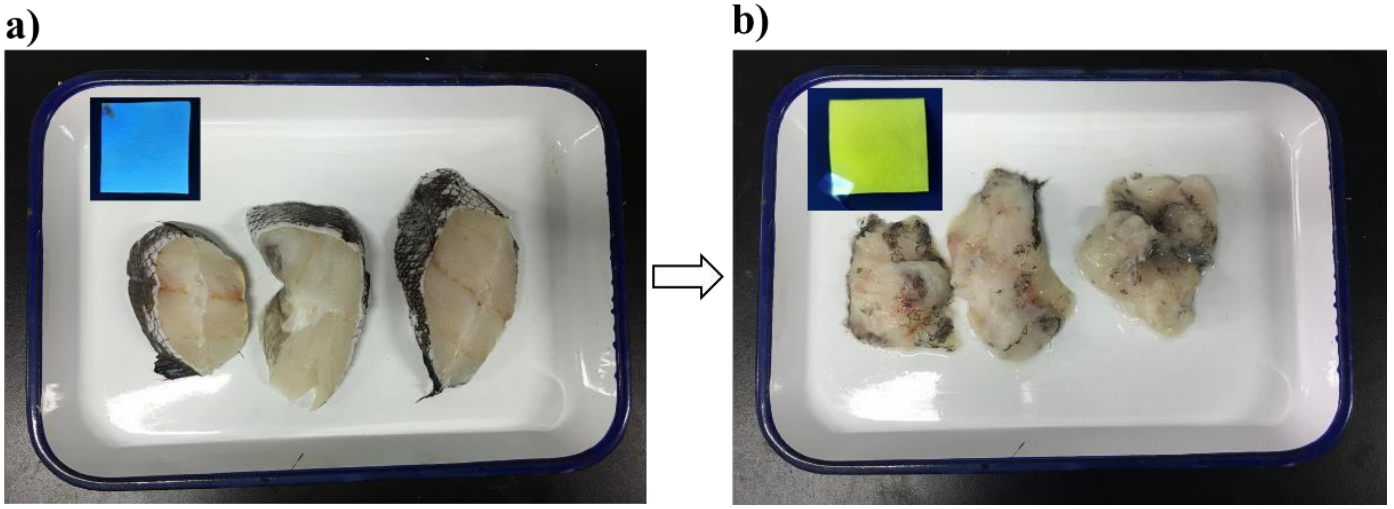




Vapor-Responsive Luminescent Materials

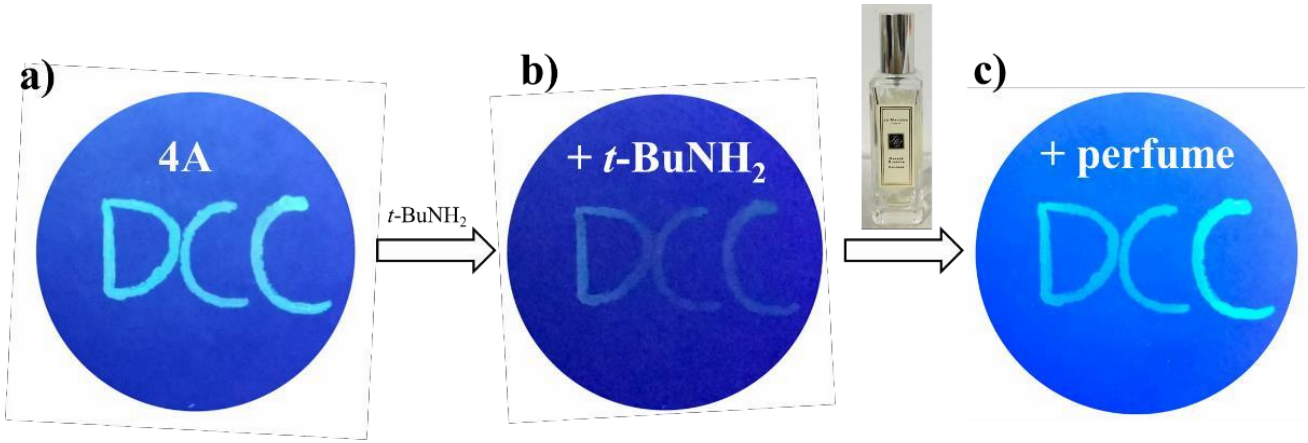


Vapor-Responsive Luminescent Materials

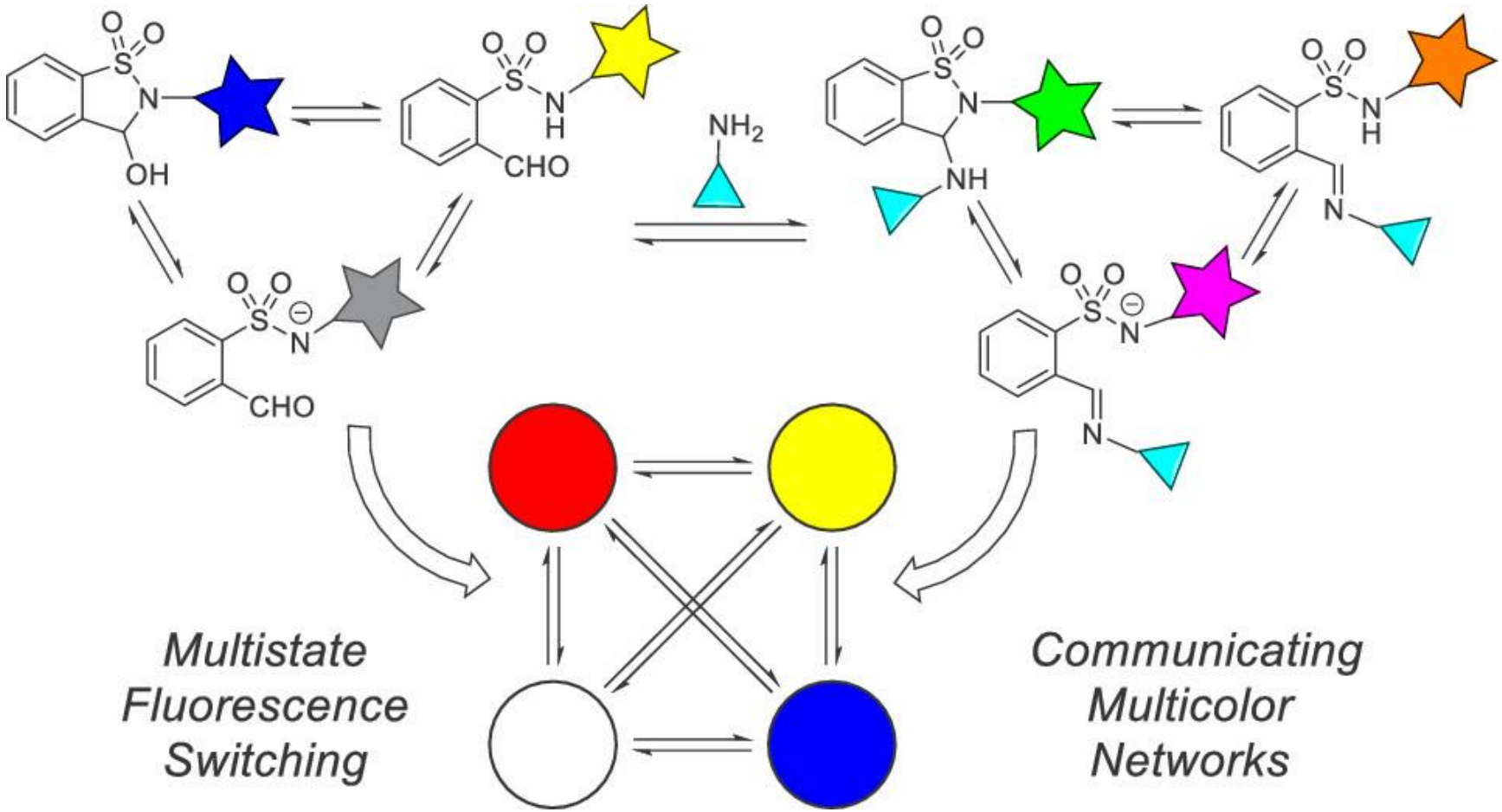


6A with fresh codfish

6A exposure to codfish after two days



Summary


NH2
Multistate
Fluorescence
Switching
Communicating
Multicolor
Networks