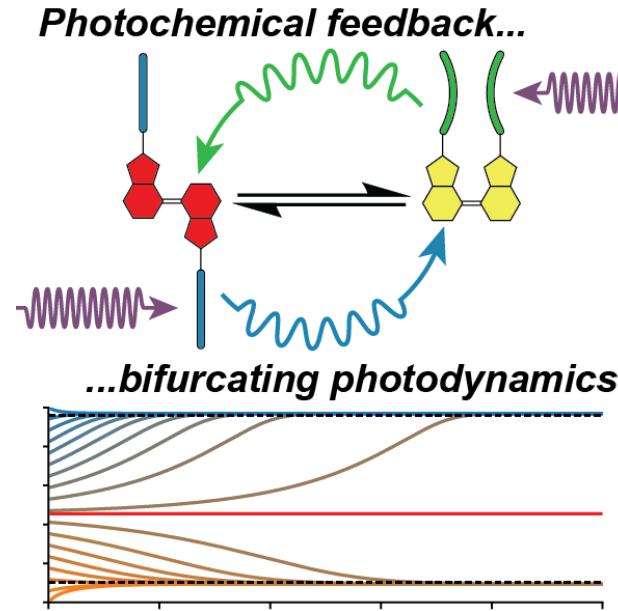


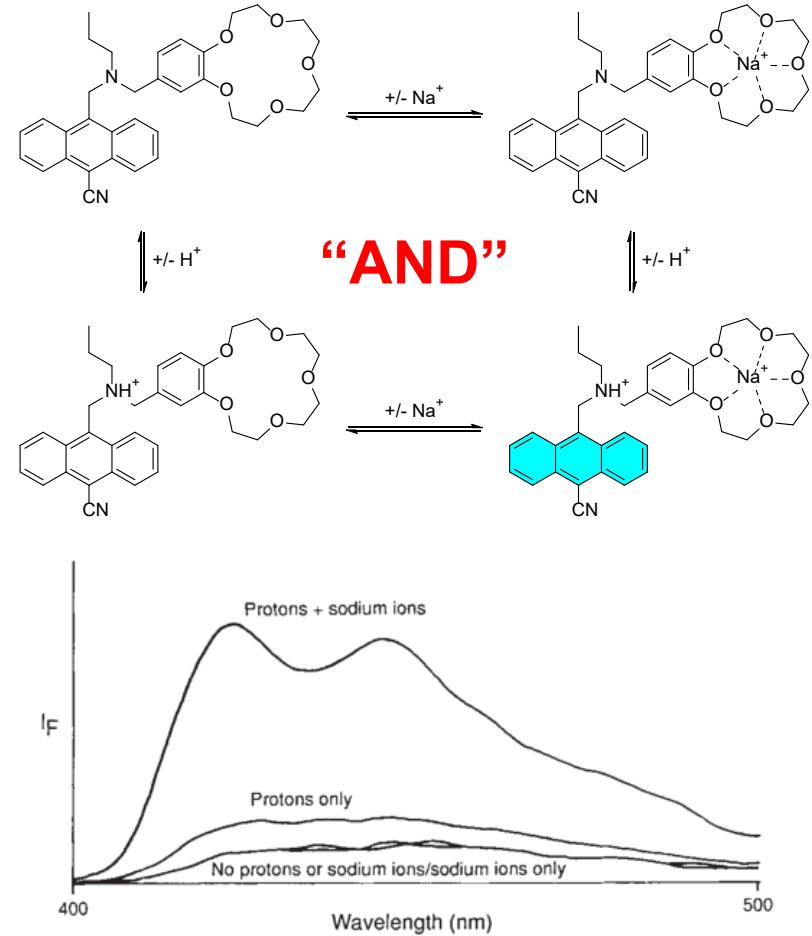
# An all-optical molecular amplifier

Thomas MacDonald, Tim Schmidt, and Jon Beves

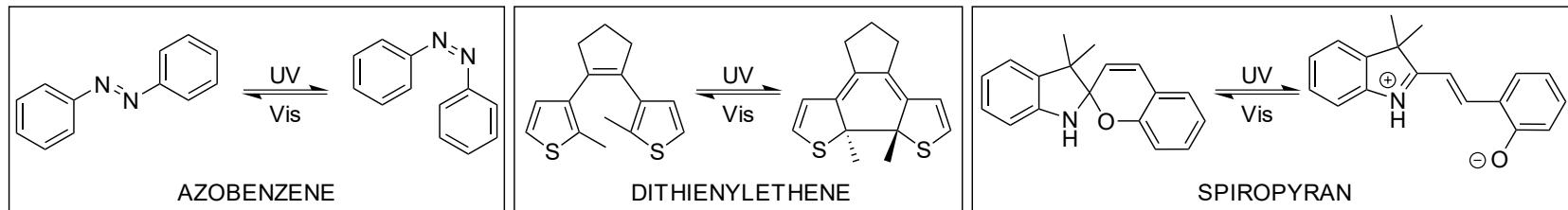


# Molecular logic

- Molecular devices that ‘do logic’ with chemical species or light
- **But**, it’s hard to cascade this logic
- Need for ***input-output homogeneity***: same outputs as inputs (like electronics!)
- For molecular logic, **light** is a good choice



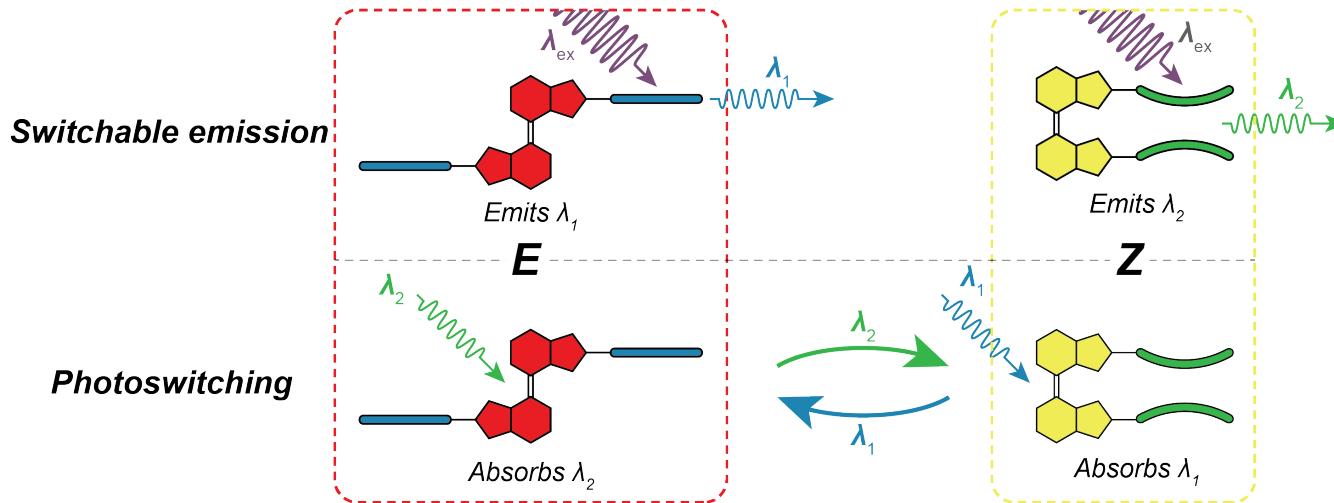
# Molecular photoswitches



- Reversible alteration of molecular structure with light
- Useful as active components in single-molecule devices

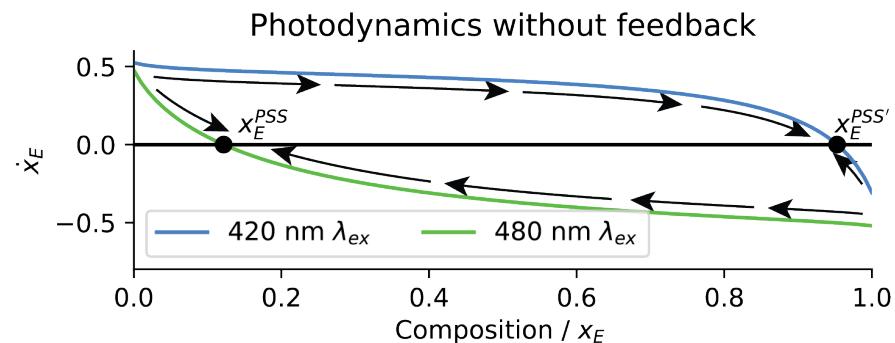
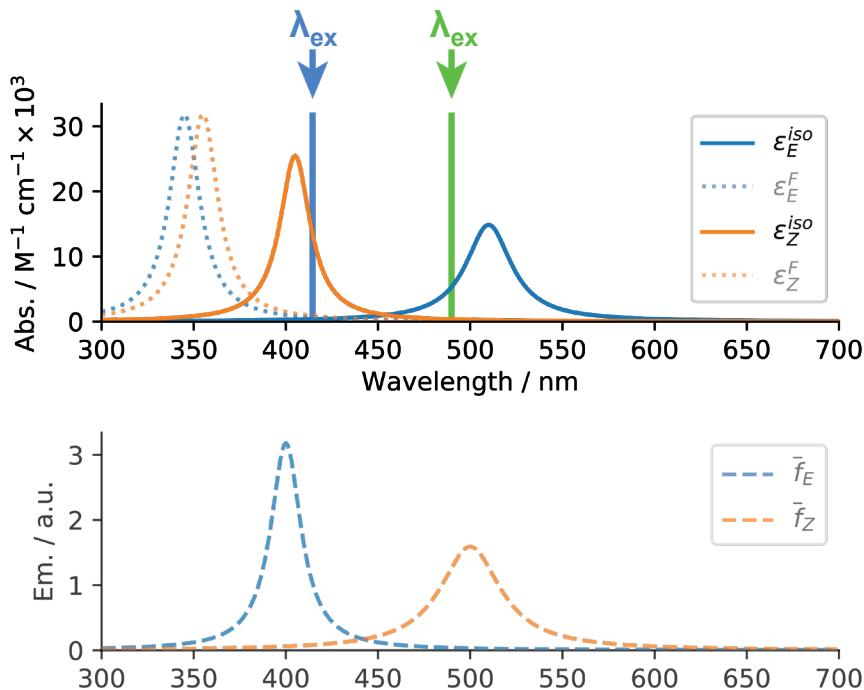
**What if we drive switching with  
internally-emitted light?**

# Proposal: all-optical feedback



- Each isomer fluorescence, with different emission bands
- Each isomer switched with light emitted by the **other** isomer
- **Positive feedback:** each isomer ‘autocatalytic’ with  $\lambda_{\text{ex}}$
- **Mathematical model constructed to study this numerically**

# Modelled photoswitching without feedback

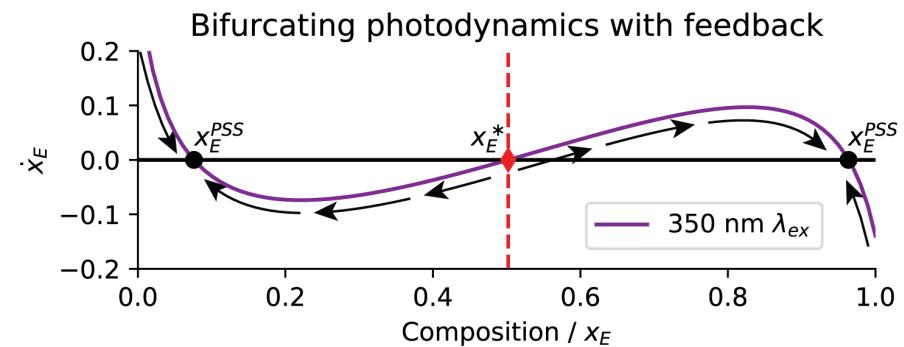
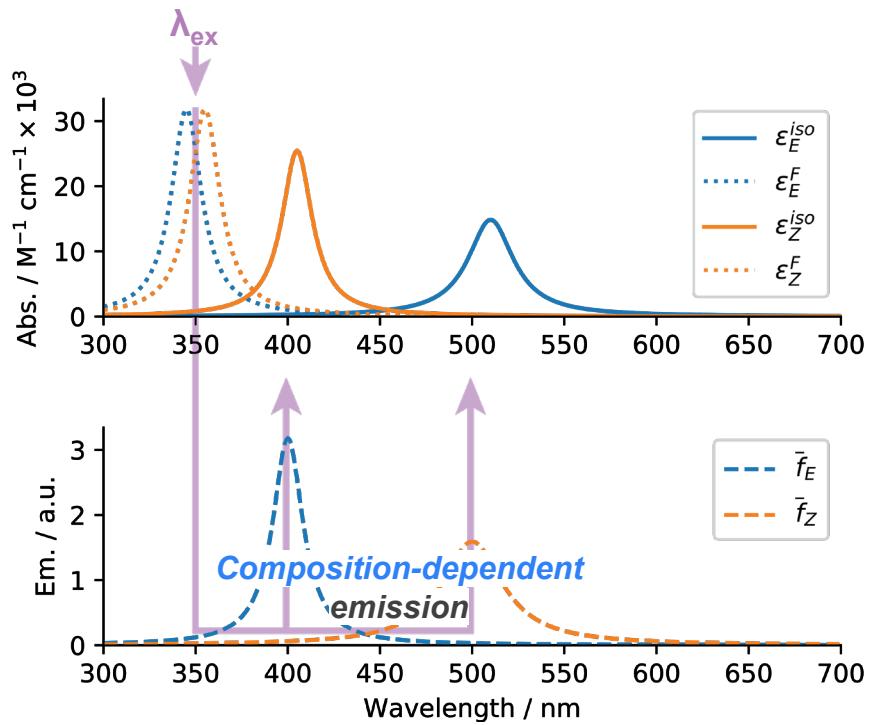


At each irradiation wavelength:

- One **unique** photostationary state (PSS) where rate of change  $\dot{x}_E = 0$

( $x_E$  = mole fraction  $E$  isomer)

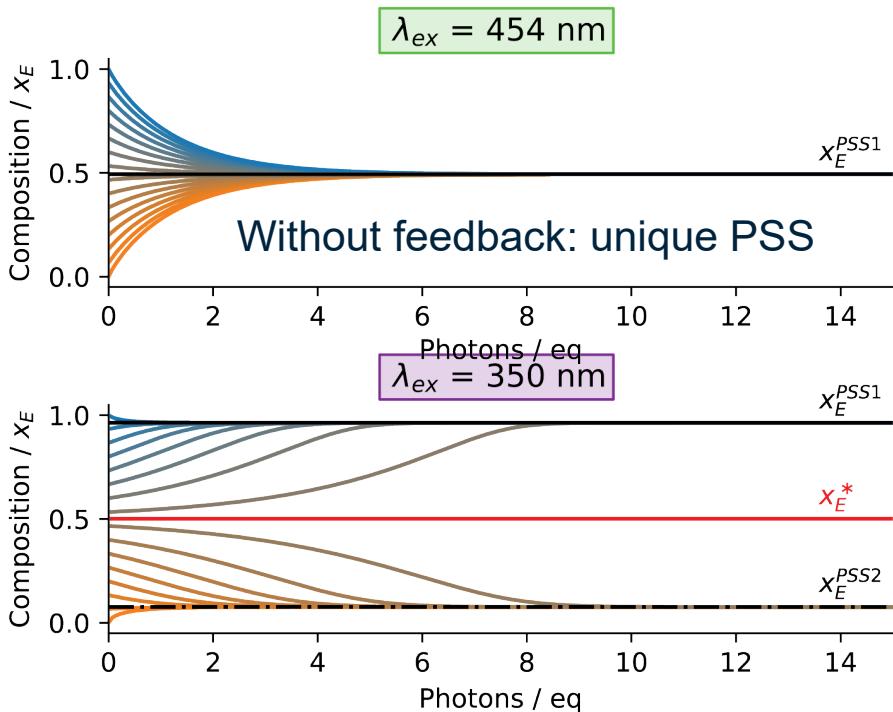
# Modelled photoswitching **with** feedback



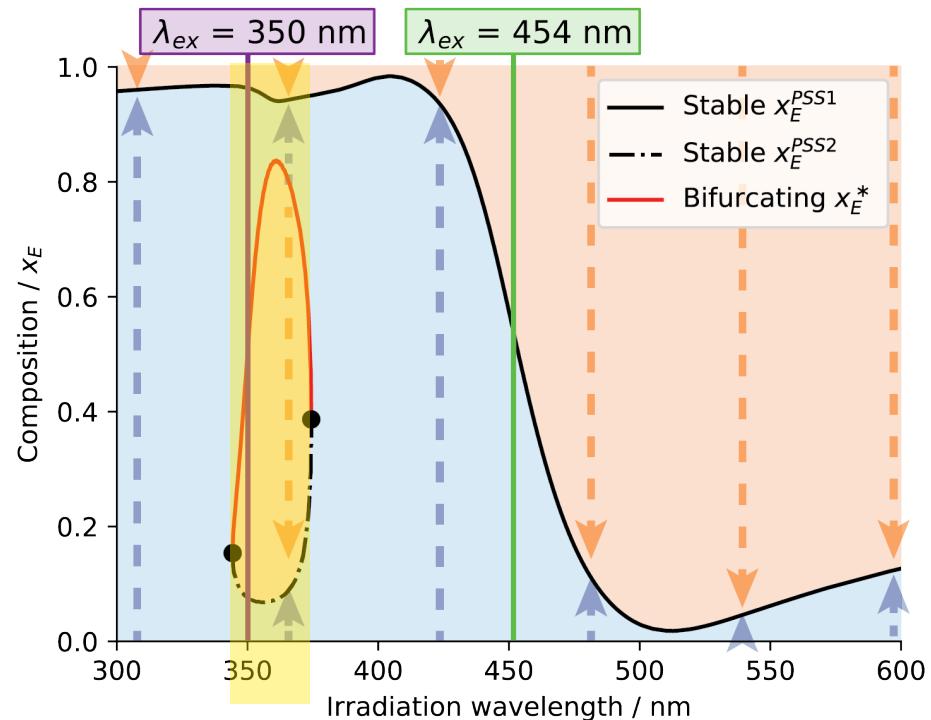
At a single irradiation wavelength:

- Three stationary points where  $\dot{x}_E = 0$
- Two dynamically stable PSSs
- One unstable bifurcation point

# Bifurcating photodynamics



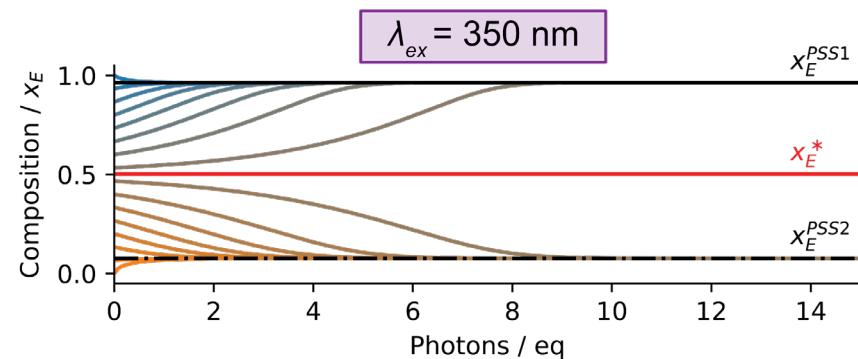
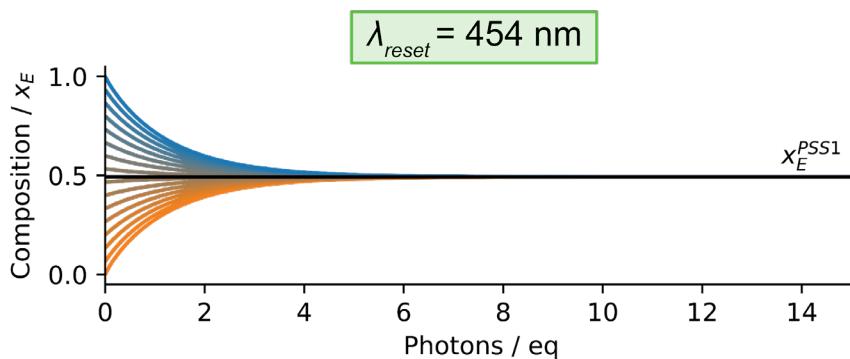
With feedback: 2 PSSs, bifurcation



Bifurcation only for limited  $\lambda_{ex}$

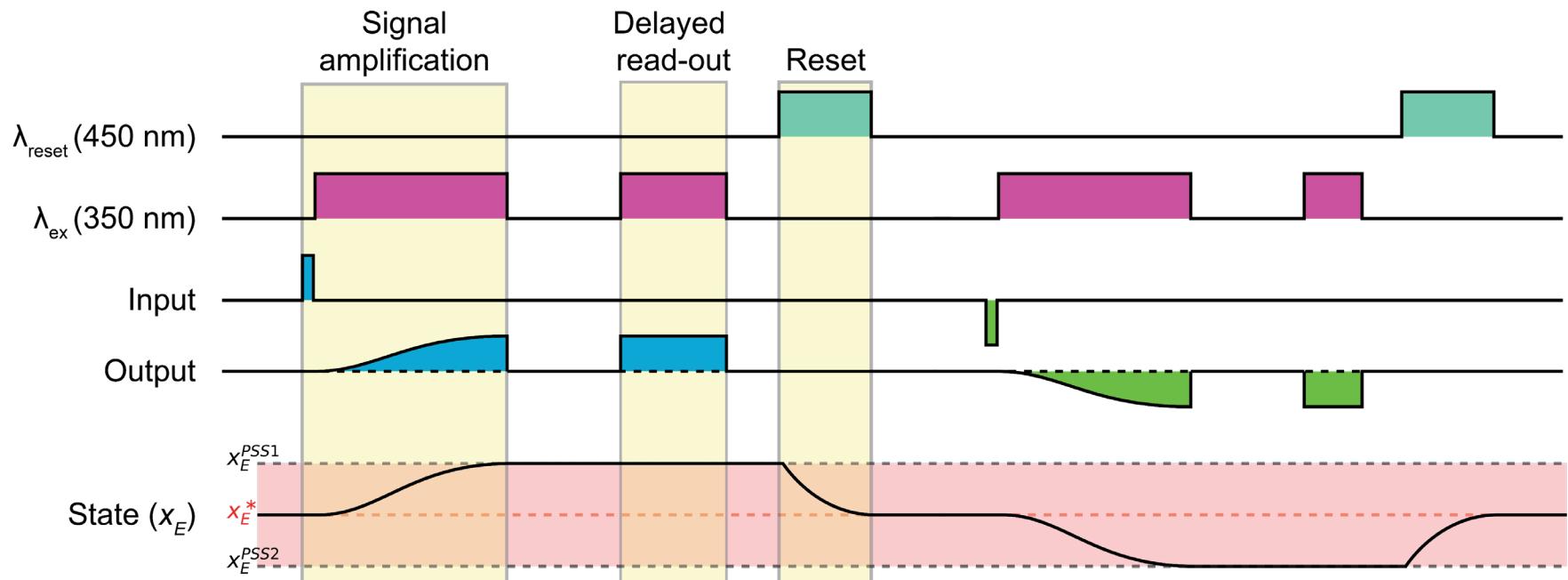
What can we do with this?

# Operation as a register (single-bit memory)



Reset to bifurcating composition  $x_E^*$

# Operation as a register (single-bit memory)



- **Input-output homogeneity**
- **Intrinsic amplification of inputs**

# Assumptions in model

1. All isomerisation is photoisomerisation
2. All intermolecular energy transfer involves emission and (re)absorption.  
No nonradiative transfer (i.e. the system is infinitely dilute)
3. All quantum yields are wavelength-independent.
4. No intramolecular energy transfer between emissive and photoswitchable electronic systems.

# Conclusions

- Conceptually new molecular device: all-optical and self-amplifying
- Behaviour supported by numerical modelling
- Potential functionality as self-amplifying memory register

**But:**

- Intramolecular energy transfer (ignored here) hard to prevent in reality.
- Switchable fluorescence and visible-light photoswitches both challenging in their own right, combination is even harder

# Acknowledgments



- A/Prof Jon Beves
- Prof. Tim Schmidt
- Beves Group UNSW
- Government for RTP

# I. Mathematical model

**Internal photon flux as function of composition:**

$$q_{int}^0(\lambda) = \sum_{j=E,Z} \phi_j^F \overline{f_j}(\lambda) \int_{\lambda} q_{ext}^0(1 - 10^{-A_{ext}}) \cdot \frac{x_j \varepsilon_j^F}{\sum_{i=E,Z} x_i \varepsilon_i^{total}} d\lambda$$

**Change in composition as function of photon flux:**

$$\dot{x}_E = - \int \left[ \frac{q_{ext}^0[1 - 10^{-A_{ext}}] + q_{int}^0[1 - 10^{-A_{int}}]}{c_0 V} \right] \left( \frac{x_E \varepsilon_E^{iso} \phi_{E \rightarrow Z}^{iso} - x_Z \varepsilon_Z^{iso} \phi_{Z \rightarrow E}^{iso}}{\sum_{i=E,Z} x_i \varepsilon_i^{total}} \right) d\lambda$$

## II. Modelled parameters

**Table 1: Lorentzian parameters used for modeled absorption and emission spectra.**

Spectrum	$\lambda_0$ / nm	$\gamma$ / nm	$\alpha$	$\varepsilon_{max}(2\alpha/\gamma\pi)$ / L mol <sup>-1</sup> cm <sup>-1</sup>
$\varepsilon_E^F$	345	20	$10^6$	$3.2 \times 10^4$
$\varepsilon_Z^F$	355	20	$10^6$	$3.2 \times 10^4$
$\varepsilon_{E \rightarrow Z}^{iso}$	510	30	$7 \times 10^5$	$1.5 \times 10^4$
$\varepsilon_{Z \rightarrow E}^{iso}$	405	20	$8 \times 10^5$	$2.6 \times 10^4$
$\overline{f}_E$	400	20	$1^a$	
$\overline{f}_Z$	500	40	$1^a$	

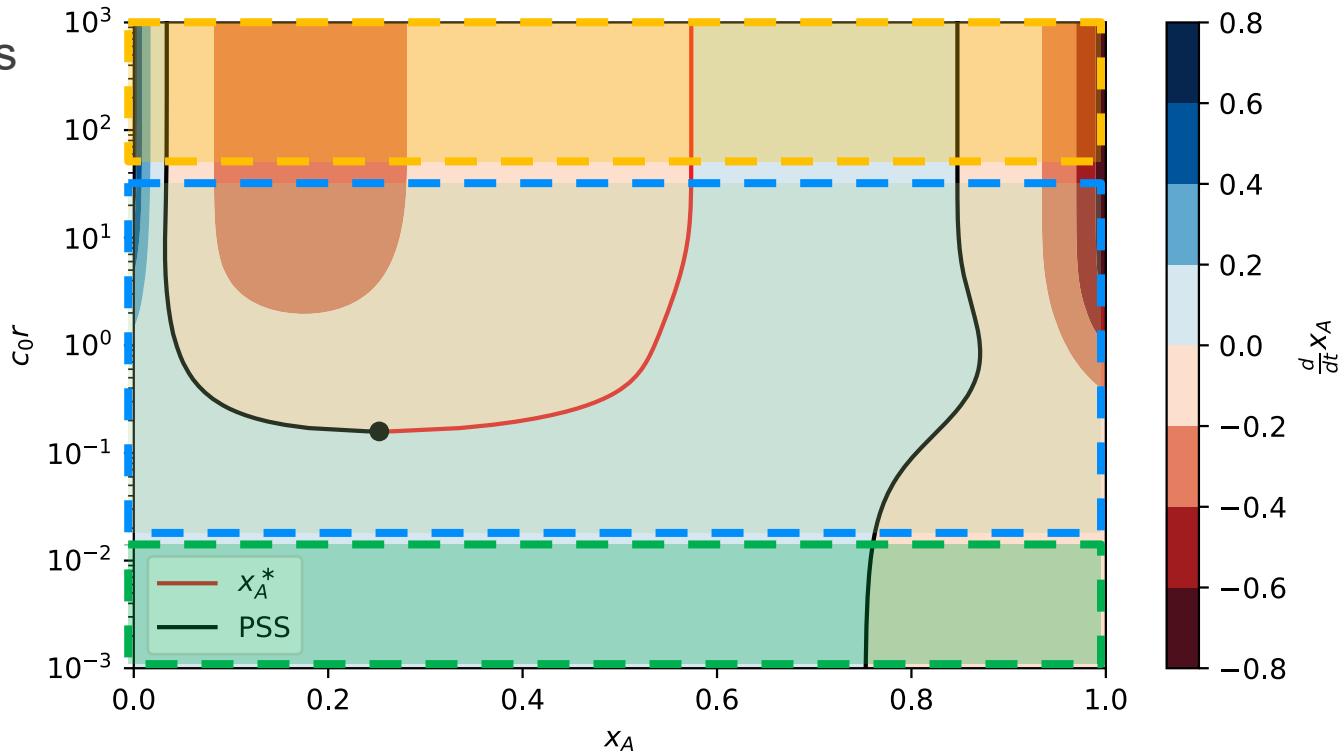
<sup>a</sup>Emission spectrum normalized to an integrated area of 1, subsequently multiplied by  $\phi^F = 0.7$ .

# III. Optical densities

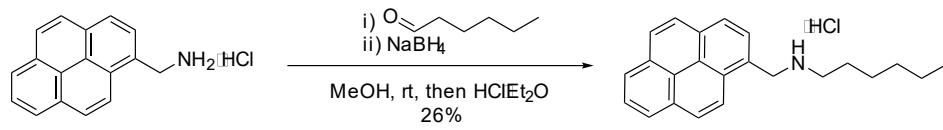
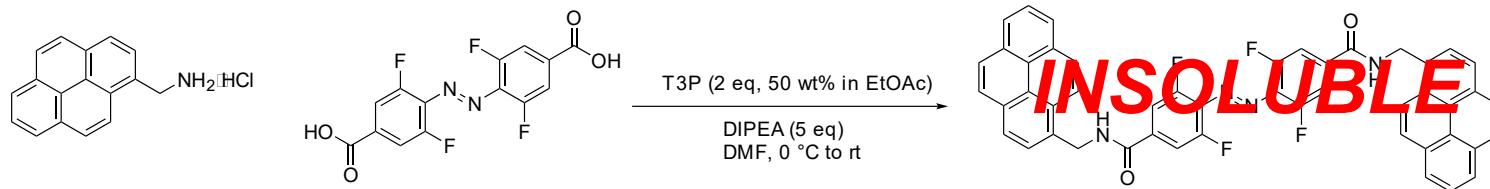
High OD: 2 stable states  
with bifurcation point

Intermediate OD:  
kind of weird?

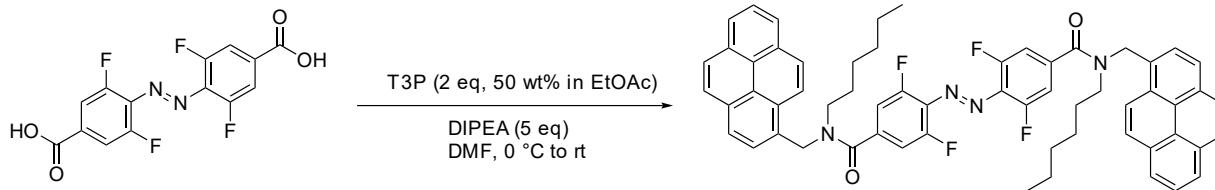
Low OD: single  
stable state



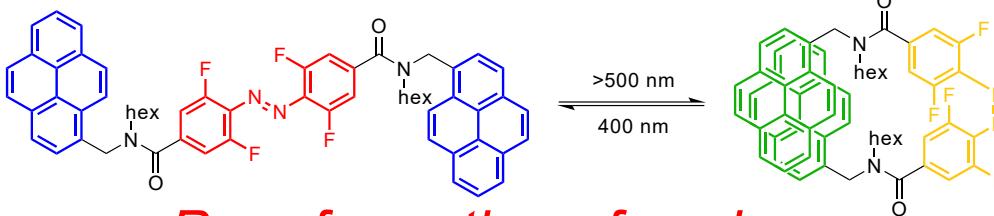
## IV. Experimental efforts



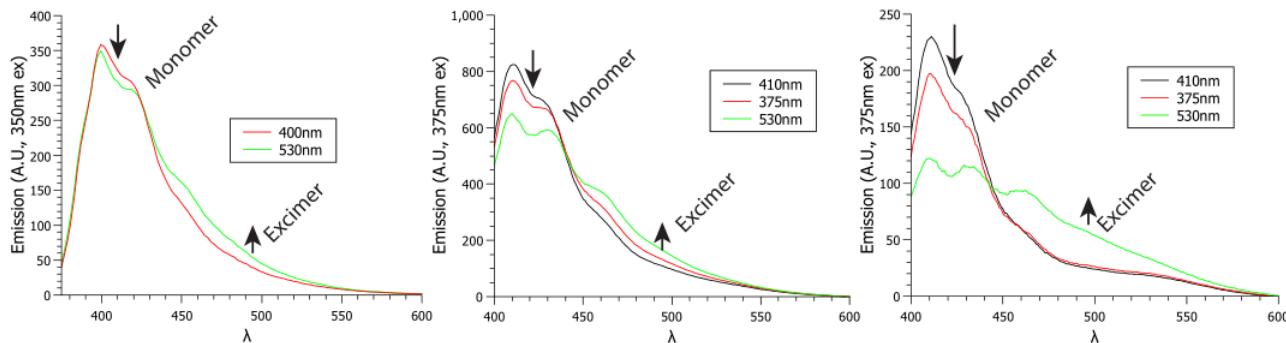
# Improved solubility



# Operation of amplifier



*Poor formation of excimer*



**Figure 5.16.** Emission spectra of **5.9** in a) cyclohexane, b)  $\text{CHCl}_3$ , c)  $\text{CHCl}_3$  at  $3 \times$  higher concentration than before. A decrease in monomer fluorescence (400–430 nm) and increase in excimer fluorescence (450–550 nm) can be seen after 530 nm irradiation and  $E \rightarrow Z$  isomerisation, but the change in emission is small. In all cases, monomer emission at approximately 400 nm is greater than excimer emission ( $>450$  nm).

# Possible explanation: amide conformers

