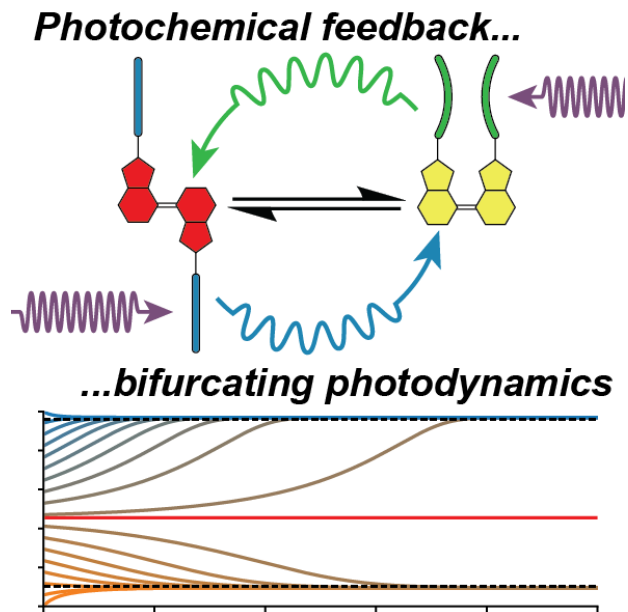


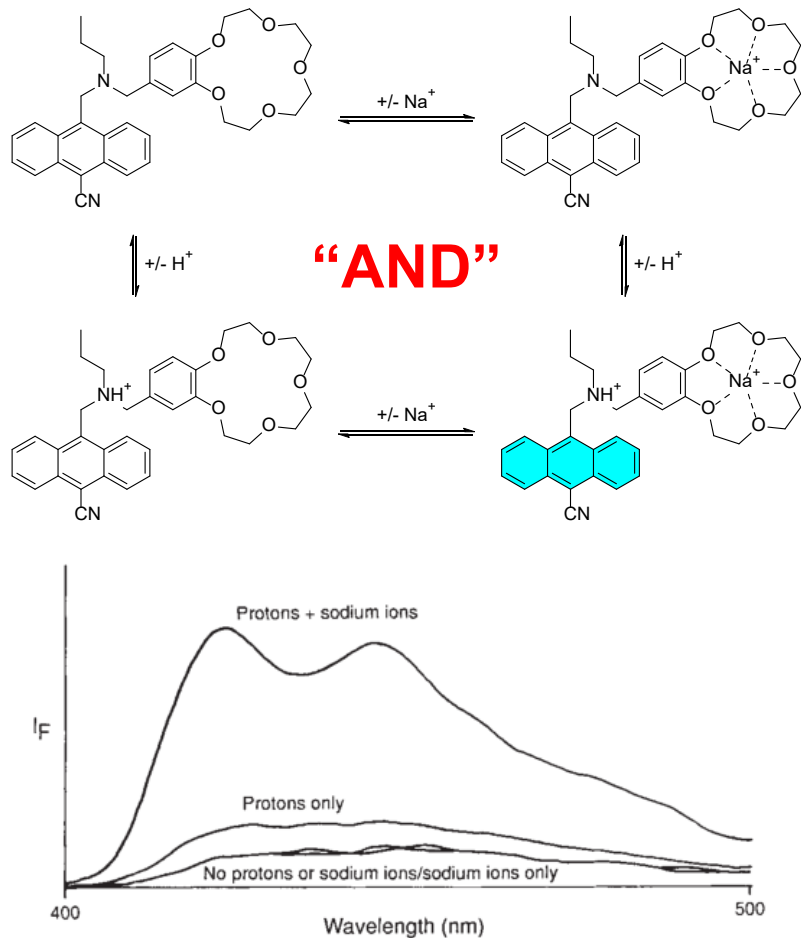
An all-optical molecular amplifier

Thomas MacDonald, Tim Schmidt, and Jon Beves

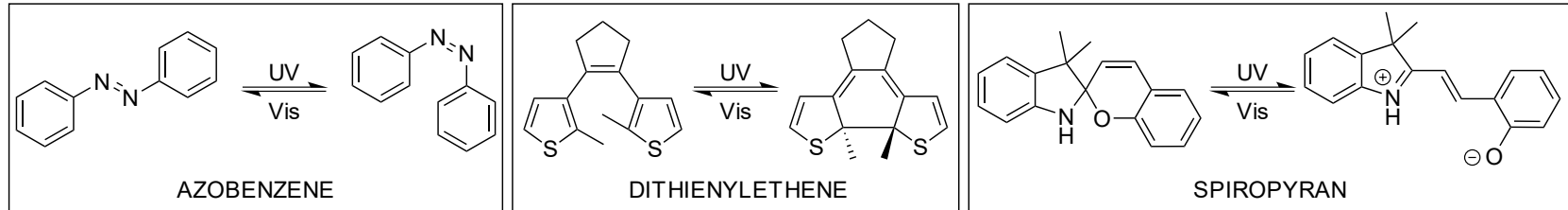


Molecular logic

- 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



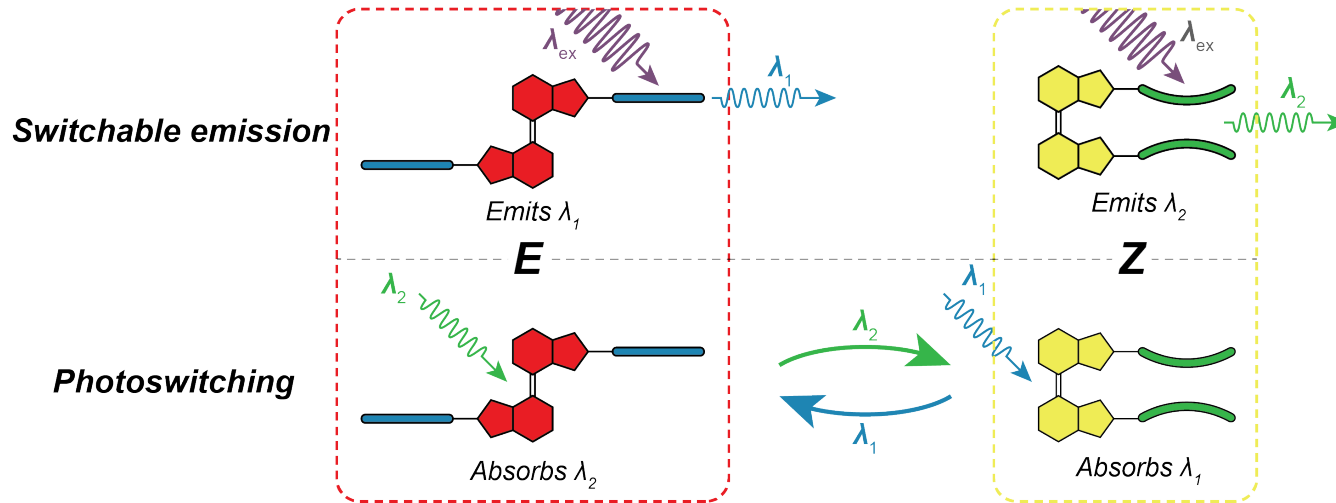
Molecular photoswitches



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

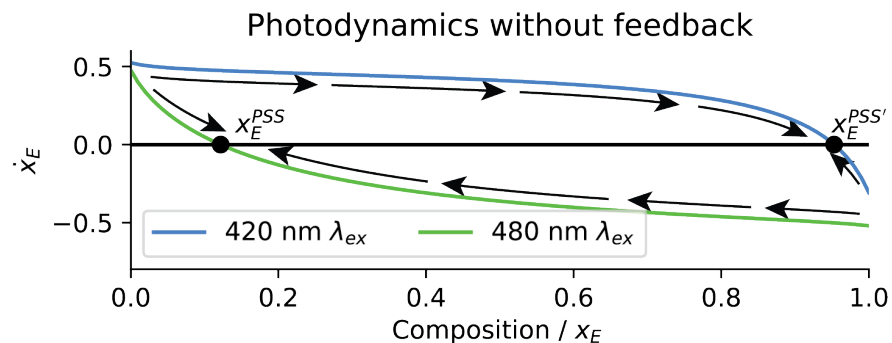
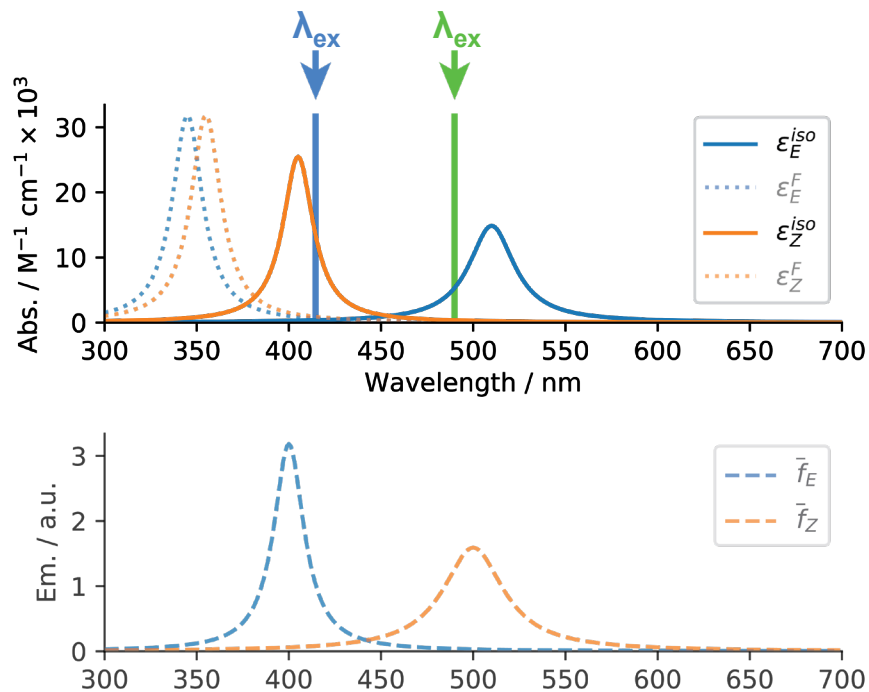
What if we drive *switching* with *internally-emitted* light?

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 λ_{ex}
- **Mathematical model constructed to study this numerically**

Modelled photoswitching without feedback

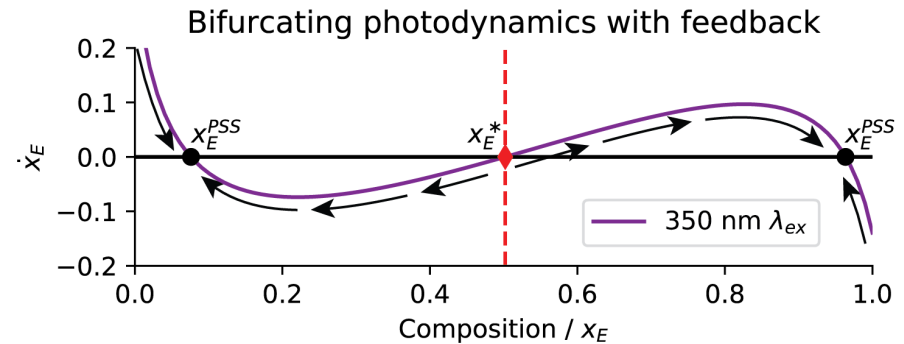
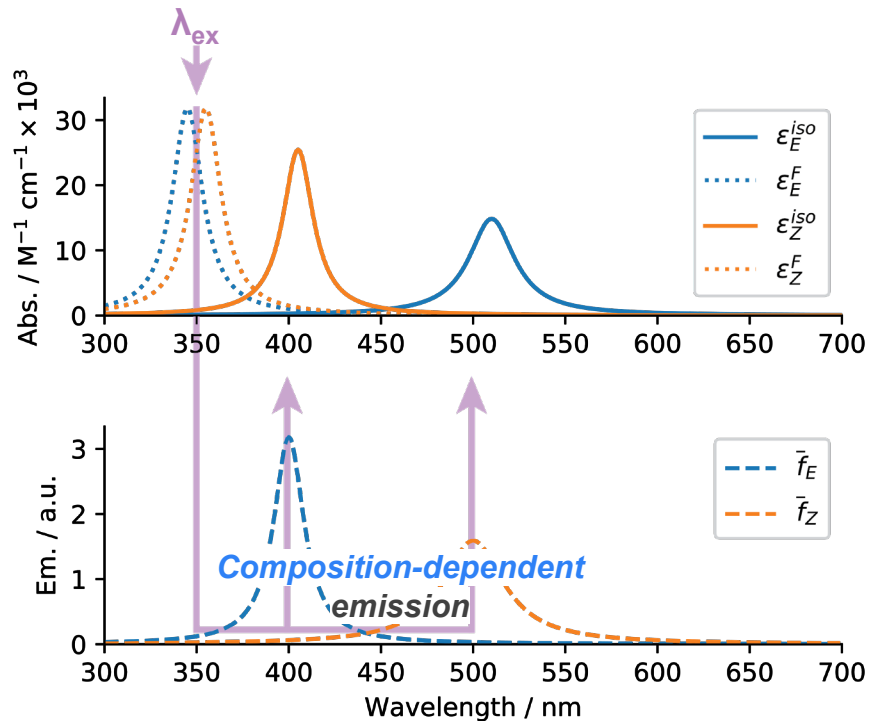


At each irradiation wavelength:

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

(x_E = mole fraction E isomer)

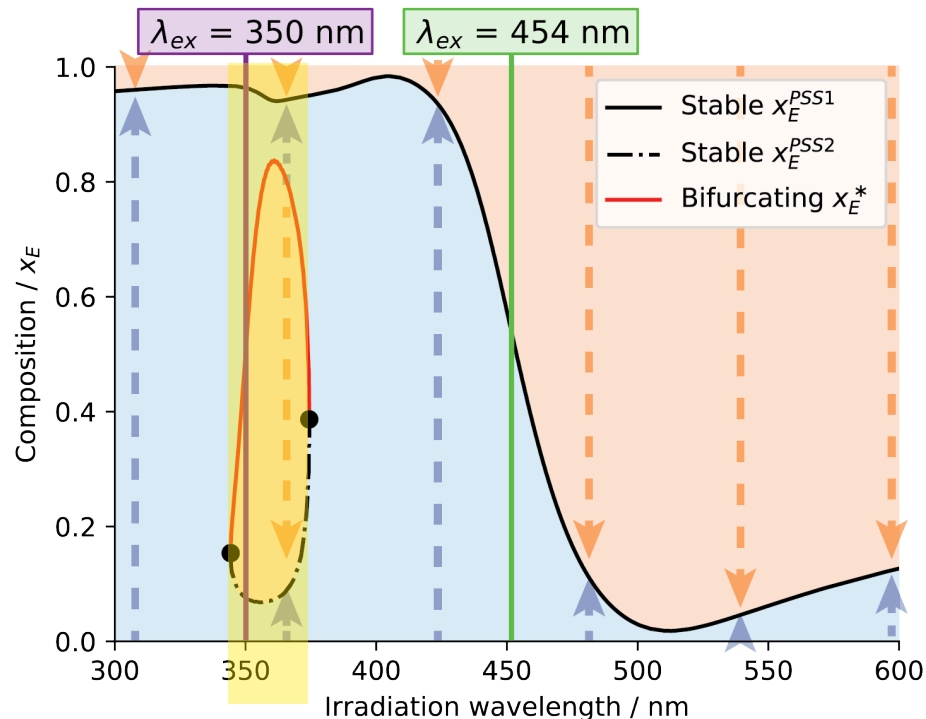
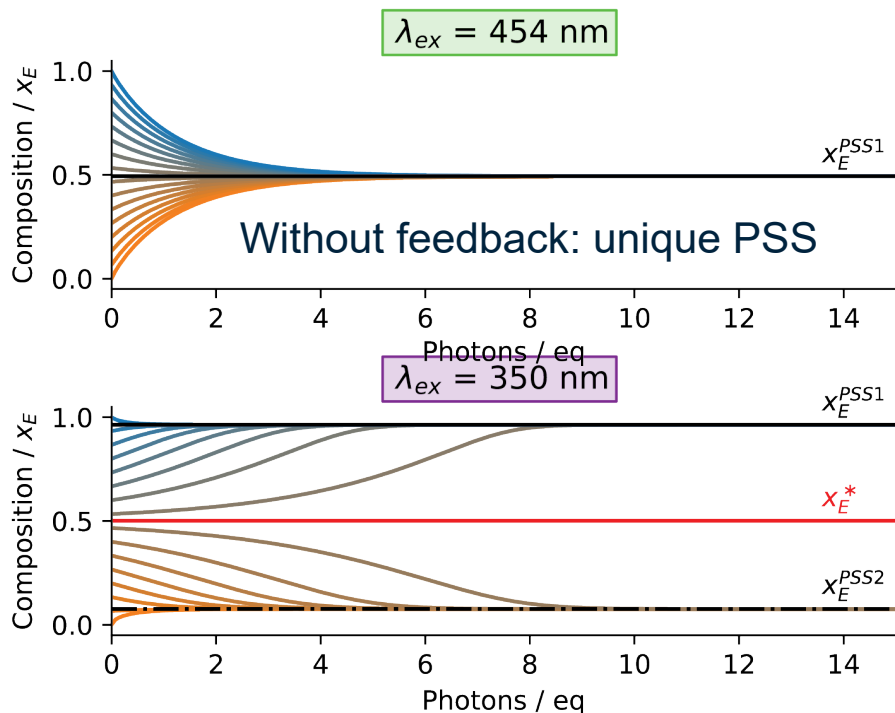
Modelled photoswitching *with* feedback



At a single irradiation wavelength:

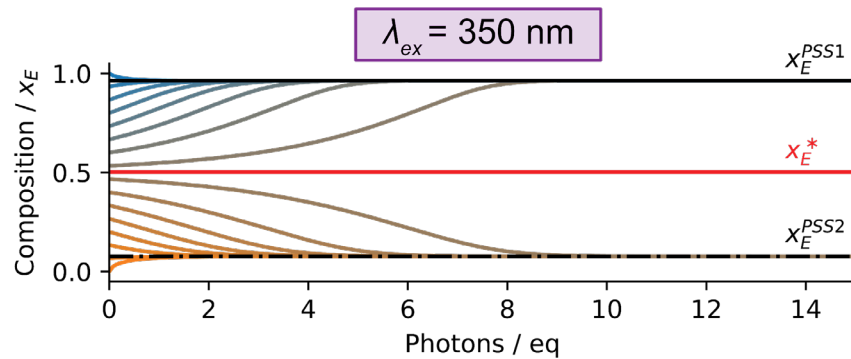
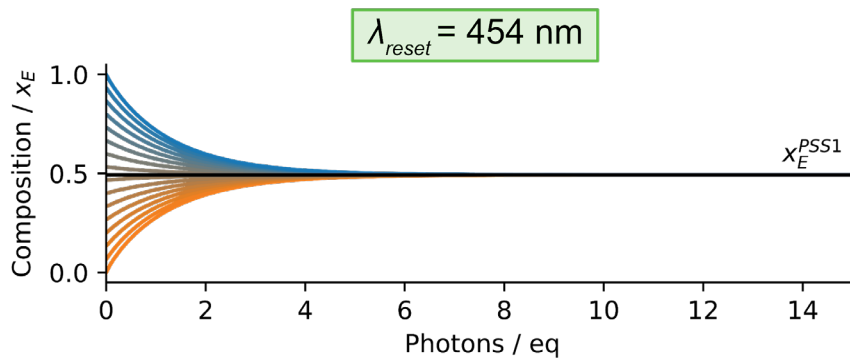
- Three stationary points where $\dot{x}_E = 0$
- Two dynamically stable **PSSs**
- One unstable **bifurcation point**

Bifurcating photodynamics



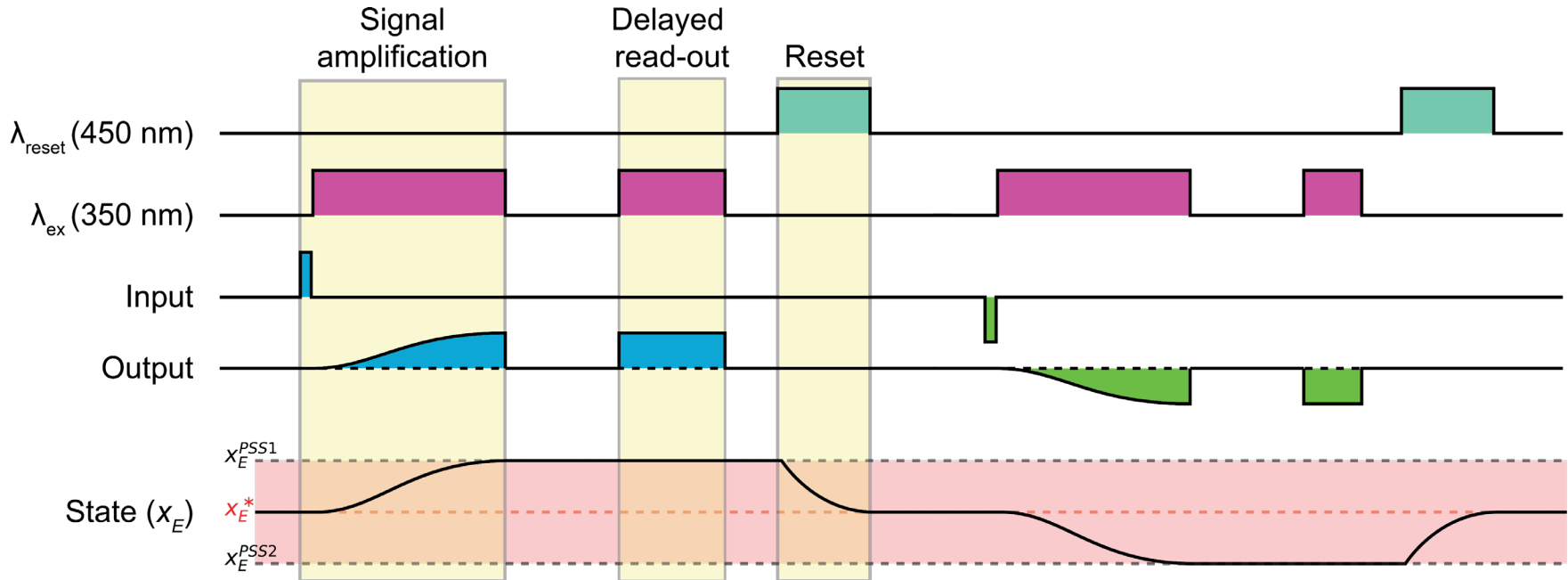
What can we do with this?

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**:

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

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	λ_0 / nm	γ / nm	α	$\varepsilon_{max}(2\alpha/\gamma\pi) / \text{L mol}^{-1} \text{cm}^{-1}$
ε_E^F	345	20	10^6	3.2×10^4
ε_Z^F	355	20	10^6	3.2×10^4
$\varepsilon_{E \rightarrow Z}^{iso}$	510	30	7×10^5	1.5×10^4
$\varepsilon_{Z \rightarrow E}^{iso}$	405	20	8×10^5	2.6×10^4
f_E	400	20	1^a	
f_Z	500	40	1^a	

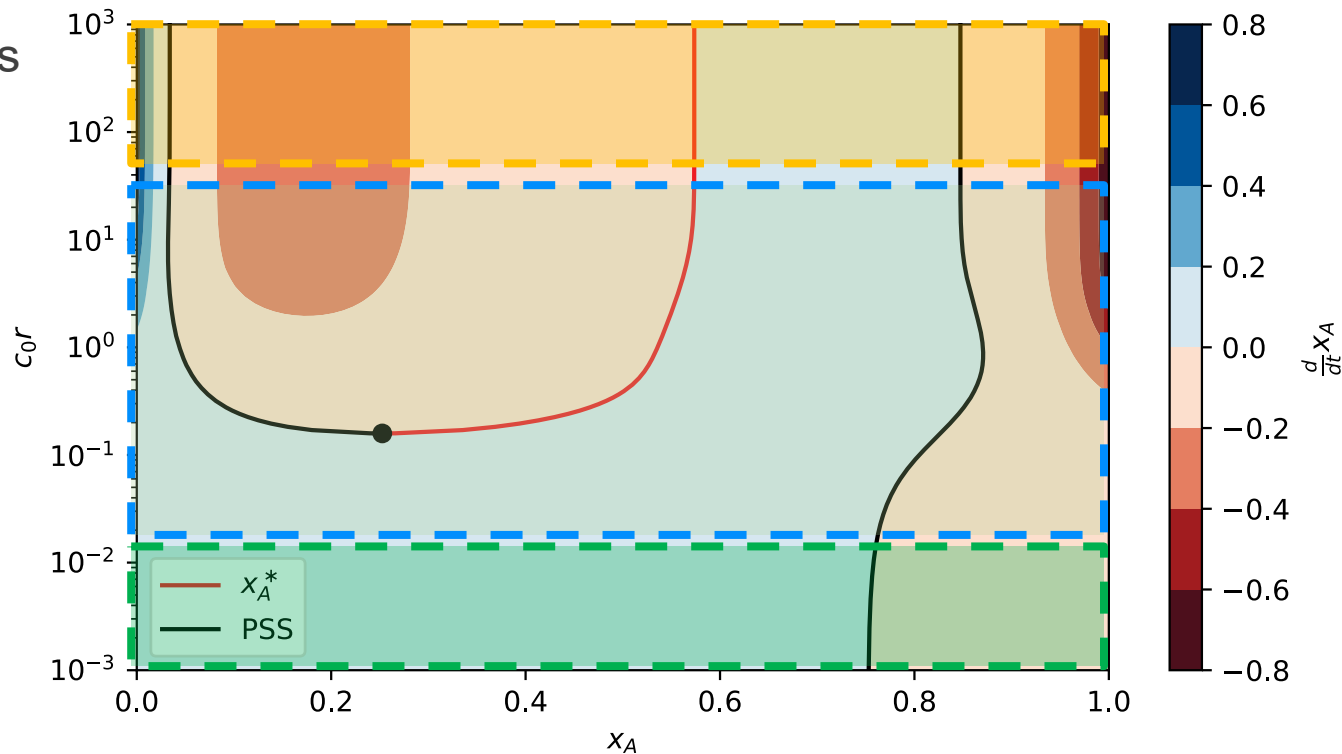
^aEmission spectrum normalized to an integrated area of 1, subsequently multiplied by $\phi^F = 0.7$.

III. Optical densities

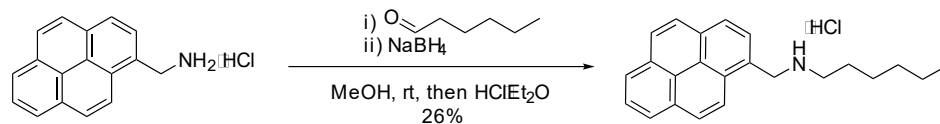
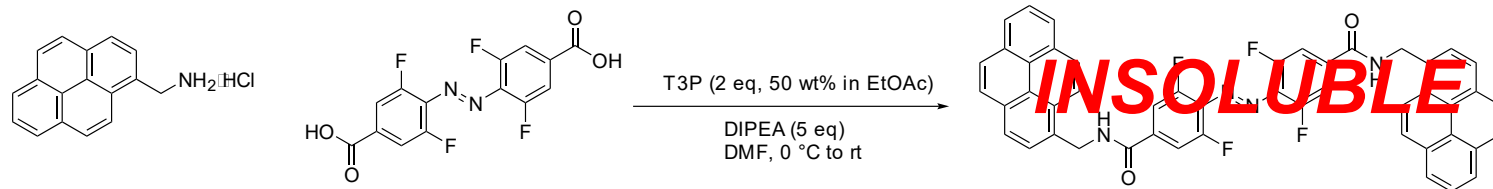
High OD: 2 stable states with bifurcation point

Intermediate OD: kind of weird?

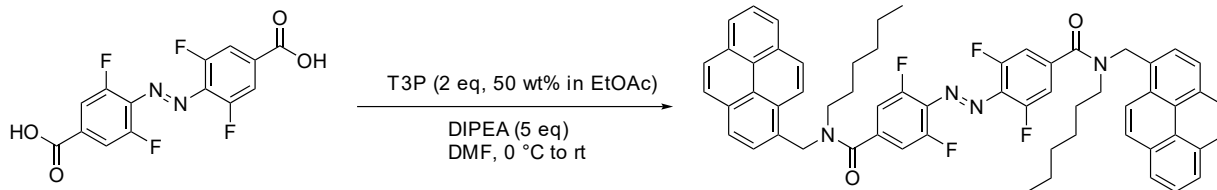
Low OD: single stable state



IV. Experimental efforts



Improved solubility



Operation of amplifier

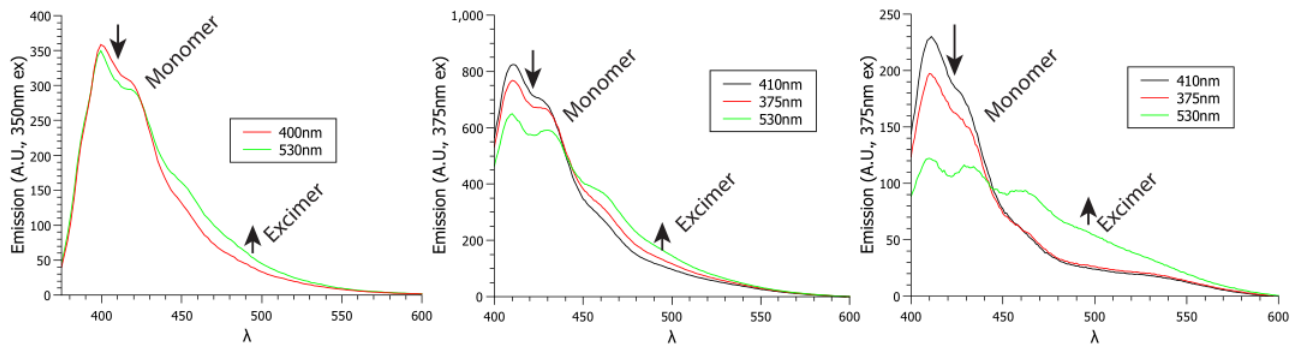
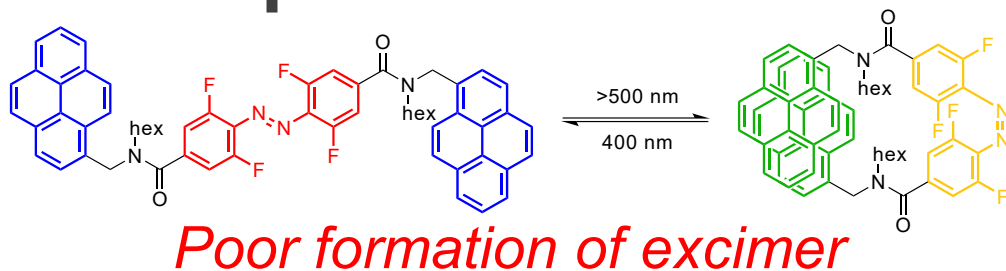


Figure 5.16. Emission spectra of **5.9** in a) cyclohexane, b) CHCl_3 , c) CHCl_3 at $3 \times$ higher concentration than before. A decrease in monomer fluorescence (400–430 nm) and increase in excimer fluorescence (450–550 nm) can be seen after 530 nm irradiation and $E \rightarrow Z$ isomerisation, 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

1 : ~2.5

