[4+4] anthracene photodimerization for controlled folding of single chain polymer nanoparticles

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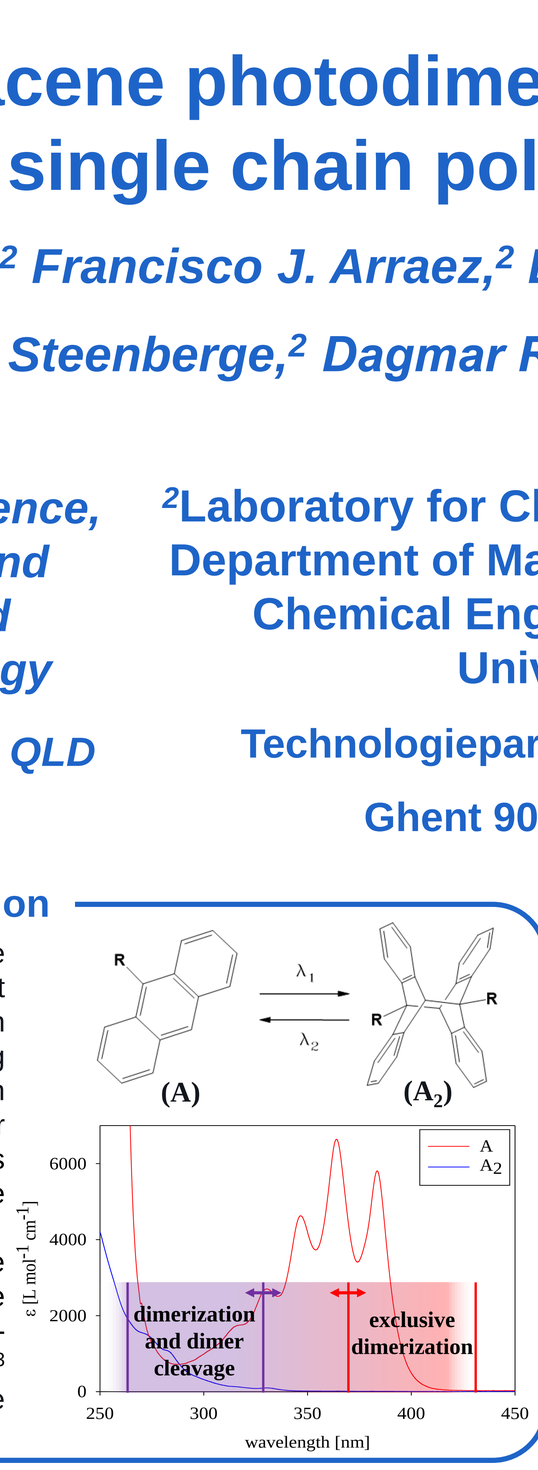
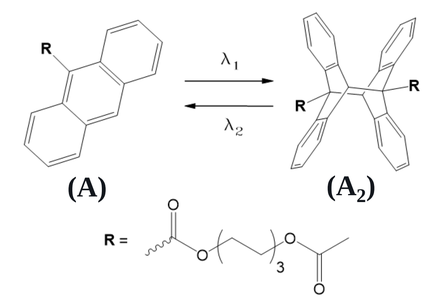
Introduction

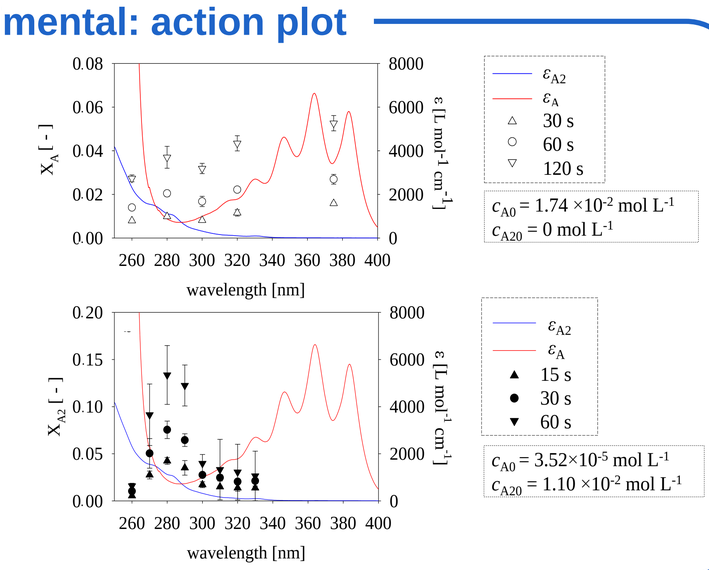
Single chain nanoparticles (SCNPs) have promising applications in a variety of fields, most notably in catalysis. Current interest lies in achieving tailored control over the resulting structure and size of the nanoparticles, which requires a high level of control over their synthesis. Reversible photochemical reactions possess the benefit of such control over the reaction in space and time.[1]

Herein, a kinetic model for small molecule photochemical reactions is developed for the reversible anthracene dimerization in solution. λ-dependent kinetic parameters are determined.[2,3] The model is currently being extended for the application in the SCNP folding.



Experimental: action plot



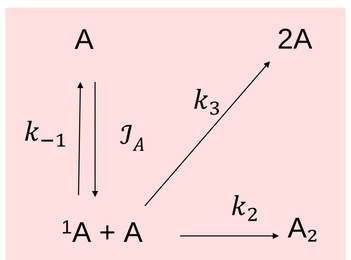


Modeling: exclusive dimerization

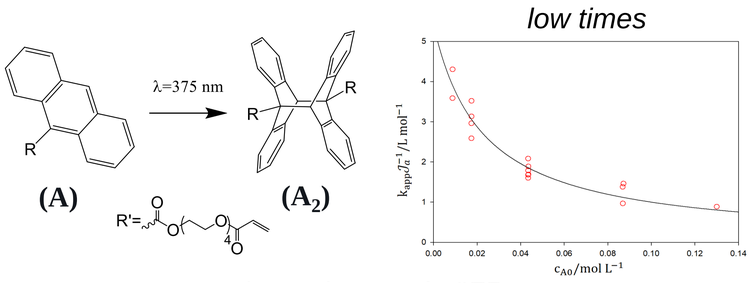
$$c_{A,t+\Delta t} = c_{At} e^{-2k_{+app}(c_{At})t}$$

$$k_{+app}(c_A) = \frac{\frac{k_2}{k_{-1}}\mathcal{J}_a(c_A)}{\left(\frac{k_2}{k_{-1}}+\frac{k_3}{k_{-1}}\right)c_A+1}$$

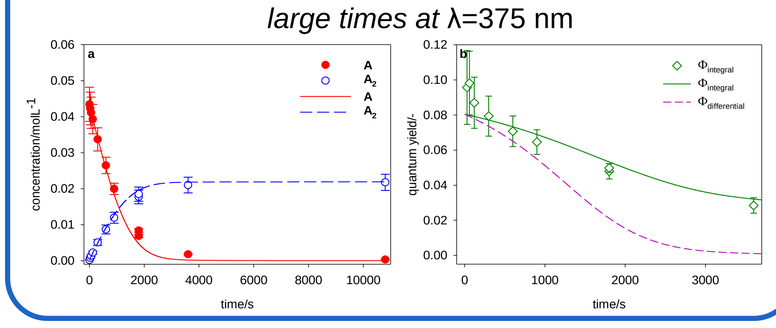
$$\mathcal{J}_A(c_A) = \frac{E_{pp}T_\lambda f}{E_\lambda N_A V}(1-10^{-\varepsilon_A c_A L})$$



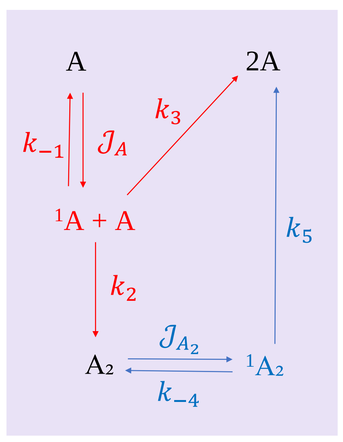
λ=375 nm
low times



large times at λ=375 nm



Modeling: wavelength dependent dimerization & cleavage



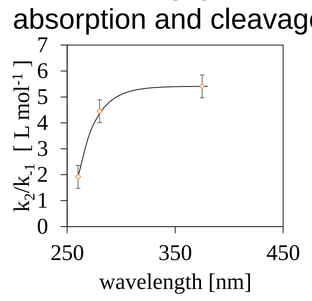
$$c_{A,t+\Delta t} = \frac{k_{-app}(c_{A,t},c_{A2,t}) - [k_{-app}(c_{A,t},c_{A2,t}) - k_{+app}(c_{A,t},c_{A2,t})c_{A,t}]\exp[-2k_{+app}(c_{A,t},c_{A2,t})\Delta t]}{k_{+app}(c_{A,t},c_{A2,t})}$$

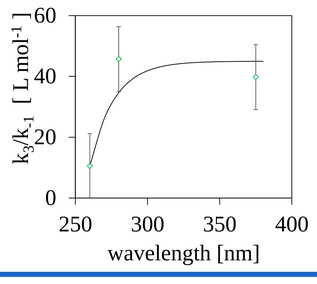
$$(for\ c_{A,0} \neq 0\ mol\ L^{-1})$$

$$k_{+app}(c_A,c_{A2}) = \frac{\frac{k_2}{k_{-1}}\mathcal{J}_a(c_A,c_{A2})}{\left(\frac{k_2}{k_{-1}}+\frac{k_3}{k_{-1}}\right)c_A+1} \qquad \mathcal{J}_A(c_A,c_{A2}) = \frac{E_{pp}T_\lambda f}{E_\lambda N_A V}\frac{\varepsilon_A c_A}{\varepsilon_A c_A+\varepsilon_{A_2} c_{A_2}}\left(1-10^{-(\varepsilon_A c_A+\varepsilon_{A_2} c_{A_2})L}\right)$$

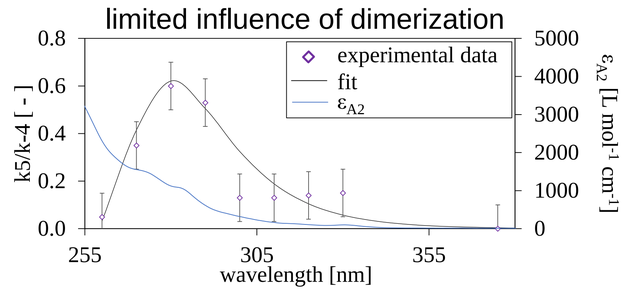
$$k_{-app}(c_A,c_{A2}) = \frac{k_5\mathcal{J}_{A_2}(c_A,c_{A2})}{k_5+k_{-4}} \qquad \mathcal{J}_{A_2}(c_A,c_{A2}) = \frac{E_{pp}T_\lambda f}{E_\lambda N_A V}\frac{\varepsilon_{A_2} c_{A_2}}{\varepsilon_A c_A+\varepsilon_{A_2} c_{A_2}}\left(1-10^{-(\varepsilon_A c_A+\varepsilon_{A_2} c_{A_2})L}\right)$$

low times; negligible dimer absorption and cleavage

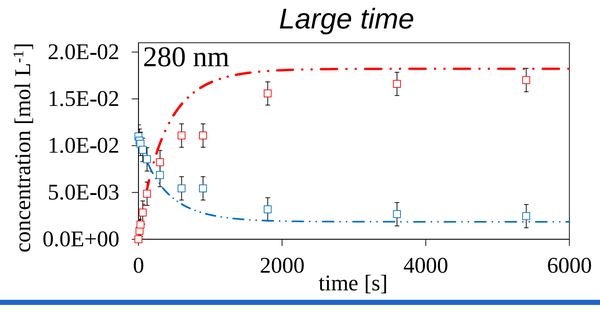


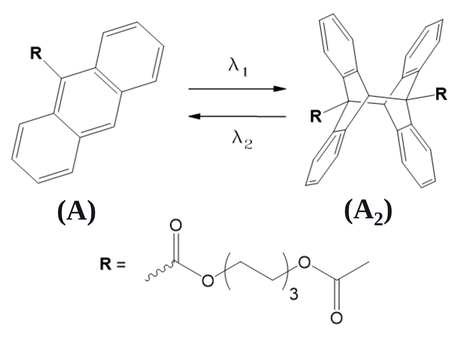


low times;
limited influence of dimerization

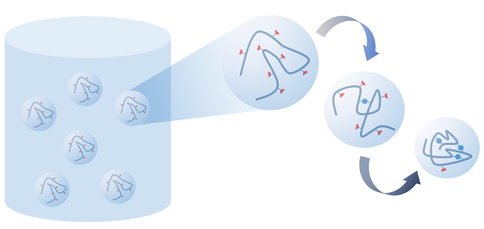


Large time





Future work: adaptation for single chain nanoparticles



375 nm
diluted

$$k_{+app}(c_{A,sol,t}, c_{A,SCNP,t}) = \frac{\frac{k_2}{k_{-1}}\mathcal{J}_{A,smn}(c_{A,sol,t})}{\left(\frac{k_2}{k_{-1}}+\frac{k_3}{k_{-1}}\right)c_{A,SCNP,t}+1} z_t$$

z_t represents restrictions imposed on the reaction due to the attachment on the polymer chain

References

1. H. Frisch, D. Kodura, F.R. Bloesser, L. Michalek, C. Barner-Kowollik, *Macromol. Rapid Commun.*, *2020*, **41**, e1900414.
2. A. Kislyak, H. Frisch, M. Gernhardt, P. H. M. Van Steenberge, D. R. D'hooge and C. Barner-Kowollik, *Chem. Eur. J.*, 2019, **26**, 478-484.
3. A. Kislyak, D. Kodura, H. Frisch, F. Feist, P. H. M. Van Steenberge, C. Barner-Kowollik and D. R. D'hooge, *Chem. Eng. J.*, 2020, **402**, 126259.

Conclusions

- a **kinetic model** for small molecule photochemical reaction is developed for reversible anthracene dimerization in solution
- determination of **wavelength dependent** kinetic parameters for anthracene dimerization and its reverse reaction performed from 260 to 330 nm
- the small-molecule model is currently being extended for the application in the **single-chain polymer nanoparticle folding** by using polymer chains synthesised with anthracene units incorporated

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