Exciton Self-Trapping in [n]-Cycloparaphenylenes

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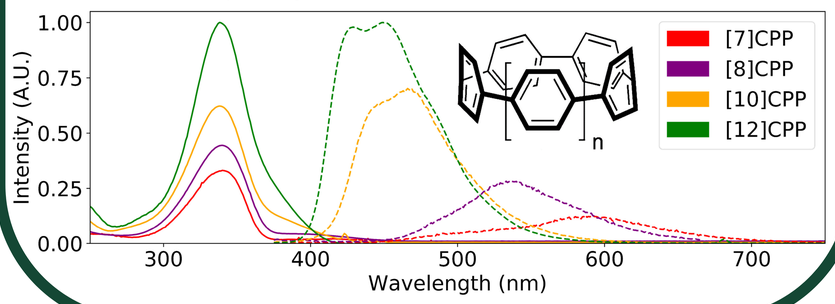
The strange size-dependence of the electronic properties of CPPs:

- [n]-Cycloparaphenylenes (CPPs) (below) are promising for applications in light absorbing and emitting technologies.
- Large CPPs are good emitters, but the emissive state is not well characterized.
- Strangely, all observed CPPs exhibit an absorption peak near 340 nm, regardless of size, but their fluorescence peaks redshift, broaden, and weaken as the CPP becomes smaller.[1,2]
  - This is counter to the trend observed in linear paraphenylenes, for which increasing length produces a redshift.[2]
- There is computational evidence that this behavior is due to random structural fluctuations which allow the exciton to become localized, or "trapped" in part of the ring.[3]
- I will observe whether this trapping occurs for various CPP samples using transient absorption (TA) spectroscopy. TA spectroscopy will be used to determine whether CPPs will access a deformed geometry ($S_{1'}$) during relaxation after photoexcitation.

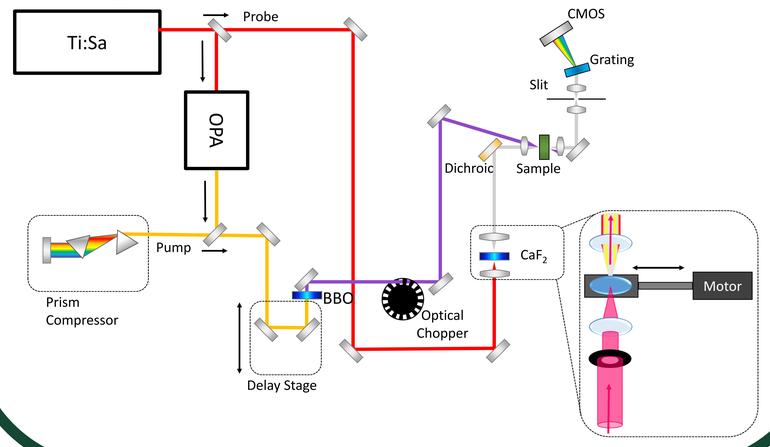
Absorbance (solid) and fluorescence (dashed) data were provided by our collaborators in the Jasti lab at the University of Oregon.



Transient absorption spectroscopy can probe short-lived electronic states:

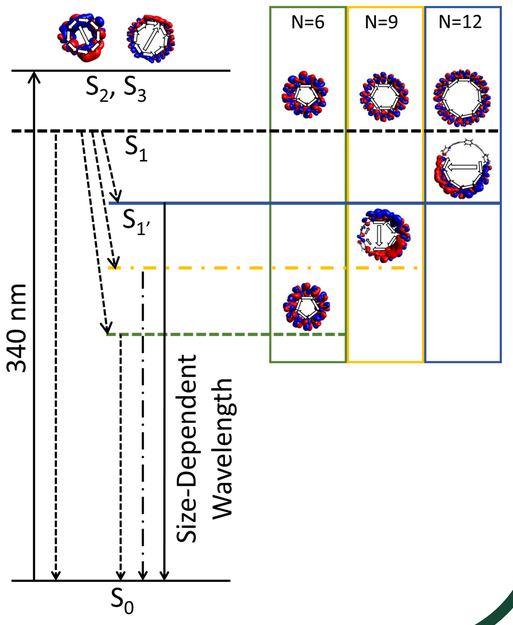
Transient absorption experiments measure the absorption of a sample at very short times after excitation. In order to collect a spectrum at each time delay, we have built the pictured spectrometer apparatus. A 700 nm pump beam (shown in orange) is compressed and then frequency-doubled to 350 nm (shown in purple), which excites the sample from the ground state to the $S_{2,3}$ states. The probe beam is a white-light probe (shown in gray) generated using CaF_2 pumped with 800 nm light (shown in red).

The white light is collected after shining through the sample, and is focused through a slit. After the slit, its wavelengths are separated using a diffraction grating. Each wavelength is then collected simultaneously using a CMOS camera. The difference in absorption between before and after excitation gives information on the excited states that are populated at that time delay.



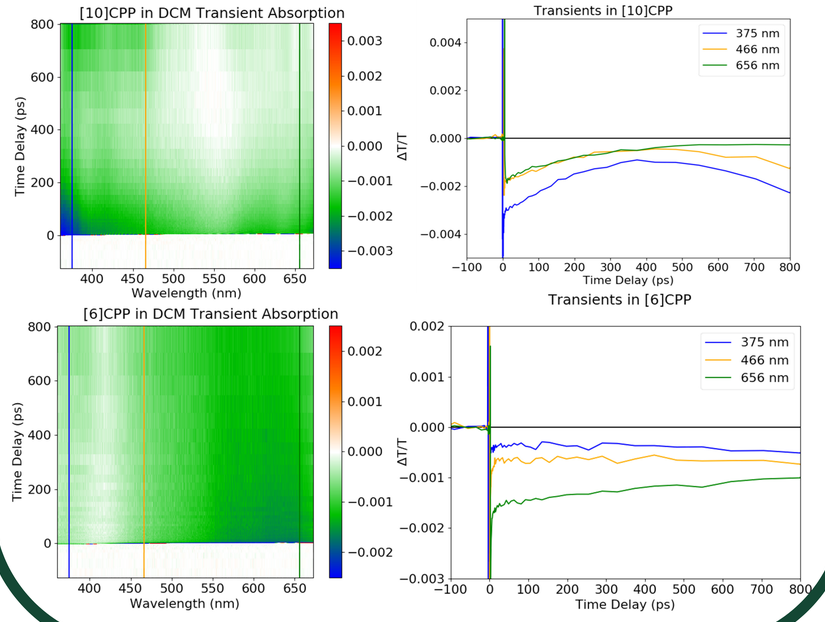
Proposed electronic state diagram for CPPs of different sizes:

Predicted electronic states and transitions for [6], [9], and [12]CPP are shown to the right. CPPs are excited to the S_2 and S_3 states, and nonradiatively relax to a dark S_1 state. In large CPPs, ring deformation in the S_1 state is predicted to lead to exciton self-trapping, here called the $S_{1'}$ state. More deformation in a structure leads to higher energy than in a less-deformed ring. Note the transition dipole moment for each state to the ground state: in small CPPs, there is no net transition dipole to the ground state and so the $S_{1'}$ state is dark. In larger CPPs, there is some transition dipole and the exciton emits from the $S_{1'}$ state. Source for electron density images: ref 3.



Preliminary data have been collected for [10]CPP and [6]CPP solutions:

Preliminary data for [10]CPP and [6]CPP solutions in dichloromethane (DCM) solvent have been collected. These sizes were chosen because [10]CPP is predicted to undergo exciton self-trapping, whereas [6]CPP is not. Our spectrometer was showing fringe-like artifacts at short time delays (shorter than 500 fs) which obscures the fastest dynamics. Upgrades to our instrument have been undertaken to prevent this, offering more information at short time delays when exciton self-trapping is expected to occur.

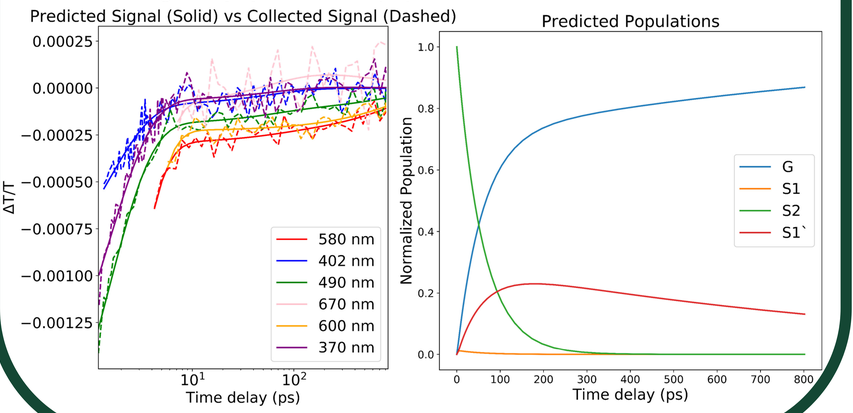


Kinetics simulations can help to interpret TA data after collection:

In order to interpret the results collected using our TA spectrometer, I am writing a program to model the signals over time. TA signals depend on the populations of each electronic state over time. For this reason, a model that predicts the populations of each state over time and the signal produced by each state predict the physical processes indicated by the TA data.

The population of the excited states over time are predicted by specifying the likelihood of transition between each state. Then the populations at each time can be used to predict the signals, by specifying the transition dipole intensity between each state.

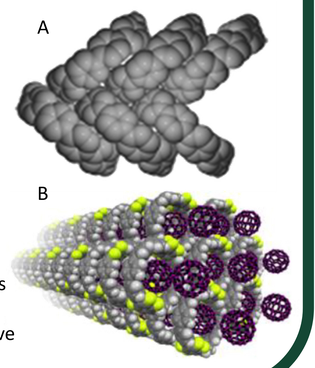
This model is used iteratively to fit the TA signals we have collected. A preliminary attempt to fit six wavelengths of [10]CPP data is displayed below:



Planned future experiments:

Experiments will be performed to determine how to prevent the exciton from becoming trapped during relaxation. These will include:

- **Viscosity Studies:** Solutions of CPPs of varying viscosities will be studied using TA. Random structural fluctuations of CPP rings can be slowed by increasing the viscosity in solution. If the random structural fluctuations occur at a slower rate, and exciton trapping occurs because of random structural fluctuations, then trapping of excitons should also happen at a slower rate.
- **Packing Structure Effects:** Solid aggregates of CPPs will be studied using TA spectroscopy. CPPs can form a "herringbone" structure (A), which may hinder structural fluctuations that lead to exciton trapping.[2] Our collaborators in the Jasti lab have also synthesized derivatives of CPPs which form noncovalent nanotubes (B), which may also serve to prevent exciton trapping.[4]



References & acknowledgements:

(1) Jasti, R.; Bhattacharjee, J.; Neaton, J. B.; Bertozzi, C. R. Synthesis, Characterization, and Theory of [9]-, [12]-, and [18]Cycloparaphenylene: Carbon Nanohoop Structures. *J. Am. Chem. Soc.* **2008**, *130* (52), 17646–17647.

(2) Darzi, E. R.; Jasti, R. The dynamic, size-dependent properties of [5]–[12]cycloparaphenylenes. *Chem. Soc. Rev.* **2015**, *44*, 6401.

(3) Adamska, L.; Nayyar, I.; Chen, H.; Swan, A. K.; Oldani, N.; Fernandez-Alberti, S.; Golder, M. R.; Jasti, R.; Doorn, S. K.; Tretiak, S. Self-Trapping of Excitons, Violation of Condon Approximation, and Efficient Fluorescence in Conjugated Cycloparaphenylenes. *Nano Lett.* **2014**, *14* (11), 6539–6546.

(4) Raden, J. M. Van; Leonhardt, E. J.; Zakharov, L. N.; Lonergan, M. C.; Jasti, R. Fluorination as a Strategy to Assemble Nanohoops Into Non- Covalent Nanotubes. Submitted.

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