Exciton Self-Trapping in [n]-Cycloparaphenylenes

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

- The electronic states of CPPs of different sizes exhibit size-dependent behaviors.
- For small CPPs, the excited states are well characterized and emit efficiently.
- For large CPPs, the excited states are more delocalized, leading to lower emission efficiency.

Proposed electronic state diagram for CPPs of different sizes:

- Predicted electronic states and transitions for CPPs of different sizes are shown.
- The S0 state is the ground state, and S1 state is the first excited state.
- The population of the excited states over time is predicted by specifying the likelihood of transition between each state.
- This model is used iteratively to fit the TA data we have collected.

Kinetics simulations can help to interpret TA data after collection:

- In order to interpret the results collected using our TA spectrometer, we are writing a program to model the signals over time.
- TA signals depend on the populations of each electronic state at each time delay.
- For this reason, a model that predicts the populations of each state at each time delay is used.
- The populations at each time can be used to predict the signals, by specifying the transition dipole intensity between each state.

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 wavelengths, which will be studied using TA.

Planned future experiments:

- Experiments will be performed to determine how to prevent the exciton from becoming trapped during relaxation.
- These 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 to the S1 state will be observed.
  - 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.

References & acknowledgements: