

Fluorescence polarization measures conformation dependence of multi-chromophoric arrays — tetrakis perylene diimide (PDI) non-fullerene electron acceptors



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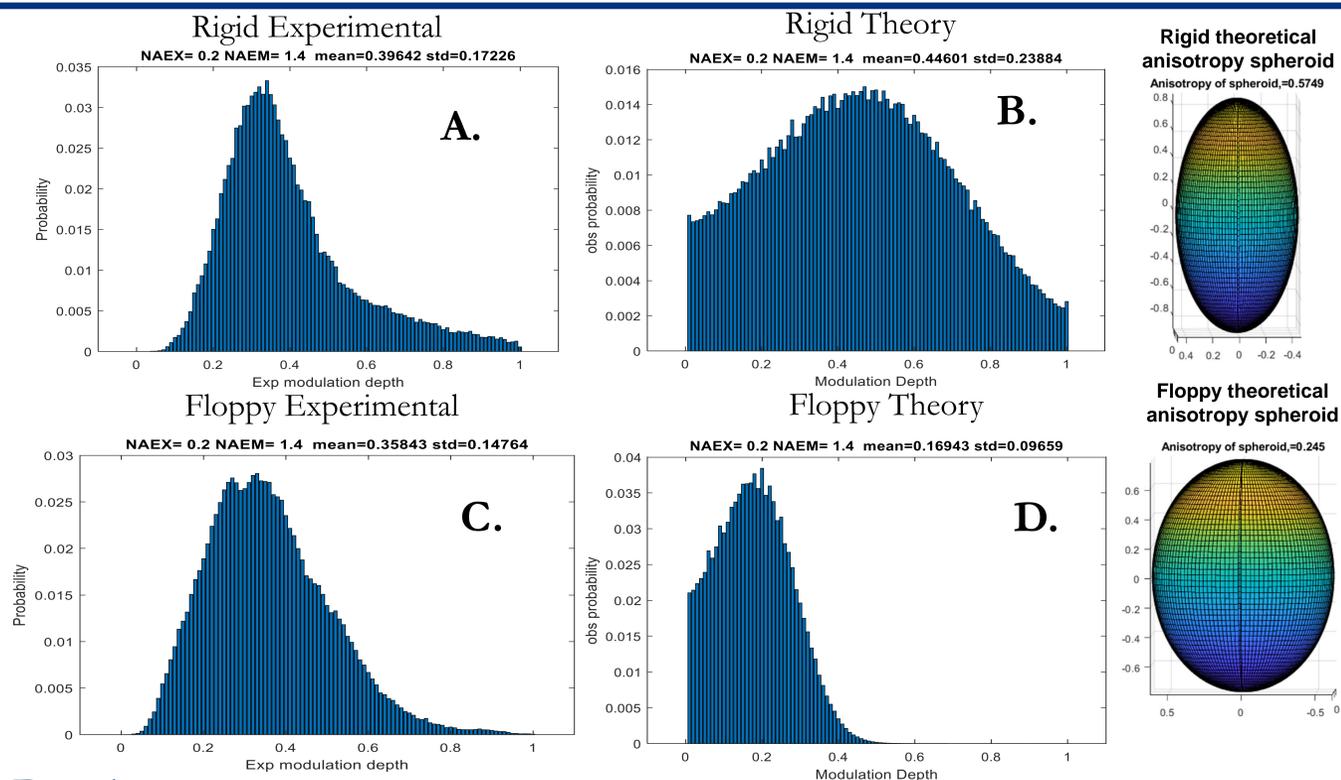
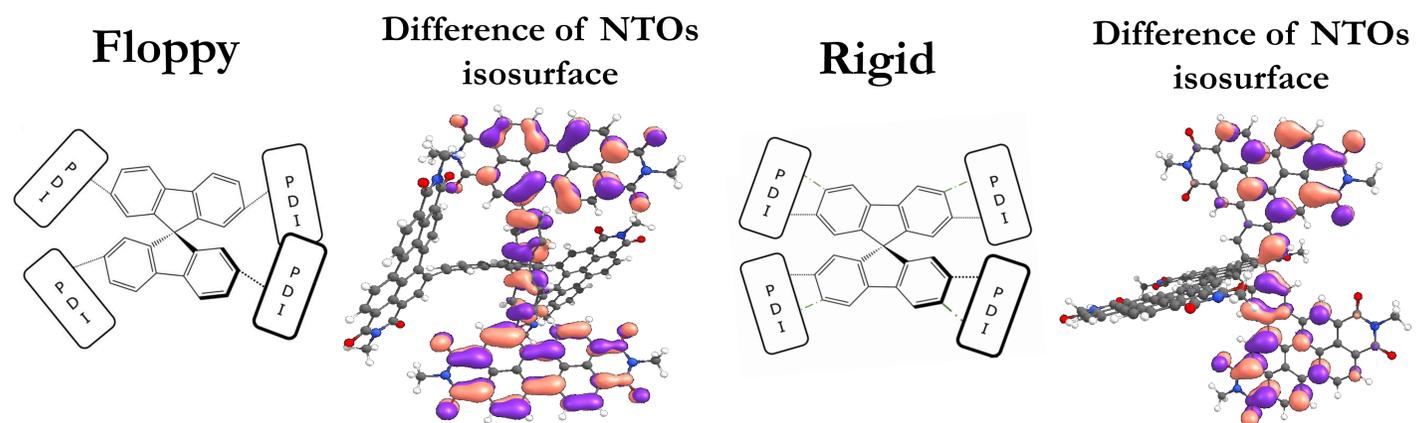
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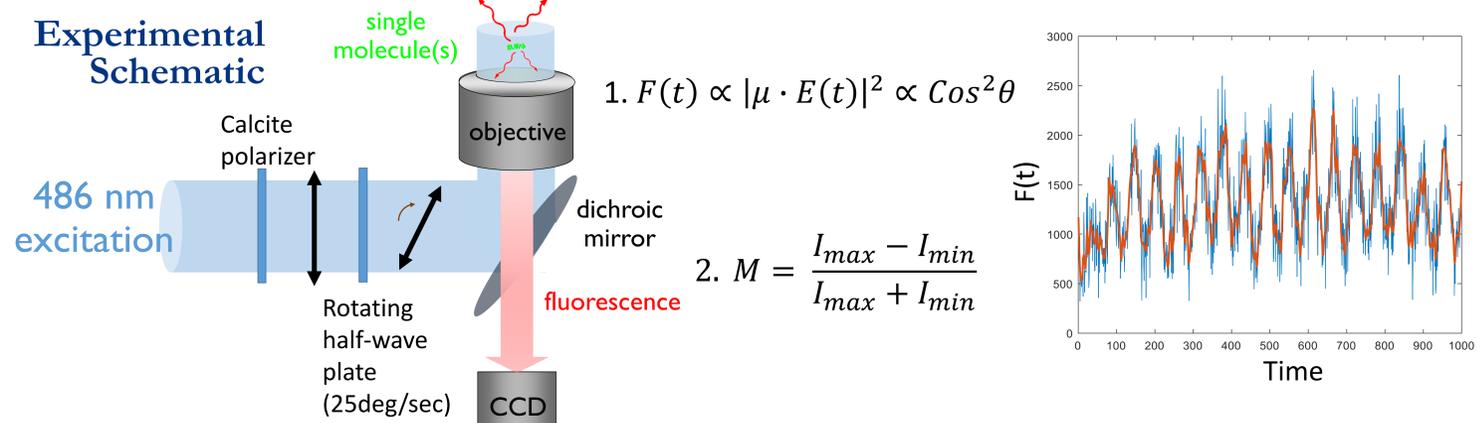
Problem: Two star-shaped perylene diimide (PDI) tetramers that have virtually the same molecular formula and only differ by the number of bay linkages of each PDI to the spiro-bifluorene core, exhibit differences in their photophysics. We refer to the molecule with one bay linkage as ‘Floppy’ and the molecule with two bay linkages as ‘Rigid’. Based on initial observations we hypothesize that conformational rigidity dictates the strength of electronic coupling.

Goal: To better understand better how conformations and packing interactions affect the electronic properties of multi-chromophoric molecules, using single molecule spectroscopy.



Results: Modulation depth is the projection of a molecule’s anisotropy value onto the laboratory frame and is dependent on the shape of the molecule as well as the orientation in relation to the laboratory frame. So molecules with different anisotropy values should have different modulation depth distributions. Shown in the panel above, is the working theory of theoretical modulation depth probability distributions of rigid (B) and floppy (D), that exhibit this behavior. But when you compare the experimental distributions of rigid (A) and floppy (C) look similar. Both distributions have various sub-ensembles, with floppy having more than rigid. It is important to note that, in single molecule spectroscopy, each molecule acts as a reporter of its nano-environment. Having sub-ensembles means that there are multiple nano-environments that each molecule feels. This could mean that even though based on rigid’s conformation it is expected to feel one nano-environment, it is acting like floppy and feeling multiple nano-environments. Some additional fluorescence polarization experiments were conducted using the same experimental set up with the addition of emission being detected through a Wollaston prism matched in orientation to the excitation light. It was found that molecules that have detectable emission in both parallel and perpendicular orientations with respect to the polarized excitation are more ambiguous in character; where $81\% \pm 6\%$ of floppy and $49\% \pm 5\%$ of rigid particles perform in this way, which could be indicative of multiple acting chromophores. Such that, rigid tends to act more like a single dipole absorber-emitter system, and floppy acts more multi-chromophorically than rigid, which agrees with floppy having more sub-ensembles than rigid. This is reinforced by the fact that rigid has a higher population of modulation depths closer to one, and by the fact that floppy has more sub-ensembles because the chromophores are acting independently such that the molecule feels more nanoenvironments. Molecules that have little detectable parallel emission but clear perpendicular emission indicate a complete reorientation of the absorbed light, and possible energy transfer; $4\% \pm 3\%$ of floppy and $26\% \pm 4\%$ of rigid do this such that rigid exhibits more absorption-emission flipping/reorientation than floppy.

Future Work: 1. Conduct fluorescence anisotropy decay experiments 2. Further testing for energy transfer (FRET) 3. Investigate the modulation depth sub-ensembles



Method: Using single molecular spectroscopy and imaging we obtained trajectories for each molecule. The graph above shows an example of how each trajectory (in blue) was fit to a sin wave (in orange). Using equation 1 we can make observations about absorption based on emission, because the equation shows how the intensity of emission signal $F(t)$ is proportional to the absorption. Where μ is the transition dipole of the molecule, $E(t)$ is the electric field and θ is the angle between the electric field and the transition dipole. Using equation 2, based on each sin wave, we then obtained the modulation depth (M) of each trajectory. Then, based on the lowest energy state of each molecule’s natural transition state (NTO) we calculated the theoretical anisotropy of each molecule. We did so by subtracting the highest occupied natural transition orbital (HONTO) isosurface from the lowest unoccupied natural transition orbital (LUNTO) isosurface (the resulting isosurfaces are above). We then calculated the major and minor axes lengths of the polarizable spheroid that would enclose the subtracted isosurface for each molecule, and using these dimensions we calculated the anisotropy for each molecule. The resulting anisotropy polarizable spheroids are to the right next to their respective distributions. Then using Monte Carlo simulations we were able to create theoretical modulation depth probability distributions based on the calculated anisotropy values to compare to our experimental modulation depth probability distributions.