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Evaluating a New Organic Solar Material: Exciton Diffusion in a Perylene Diimide Liquid Crystal

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Motivation

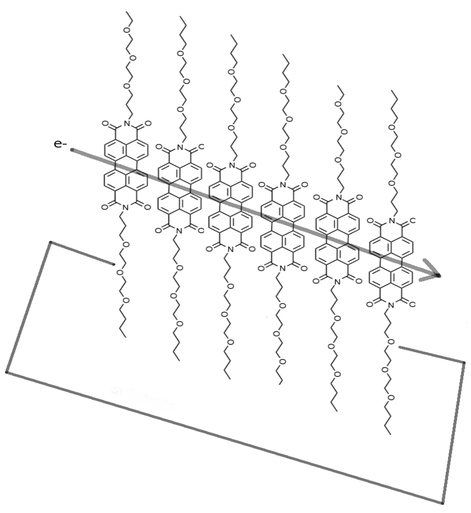
Using organic semiconductor materials for photovoltaics is attractive because of the potential for **flexible, light weight, low cost devices that easily cover large areas**. Unlike inorganic semiconductors, upon light absorption organic semiconductors form **bound electron-hole pairs called excitons**. The exciton can either recombine in the bulk semiconductor (possibly resulting in fluorescence), or the electron and hole can be separated at an interface creating an electrical current. In organic photovoltaic devices current must be derived from excitons, so the **main design constraint is the length that an exciton can travel before it recombines**.

Problem: *Short exciton diffusion length in amorphous organic materials hinders charge separation, thereby limiting the ability to extract current.*

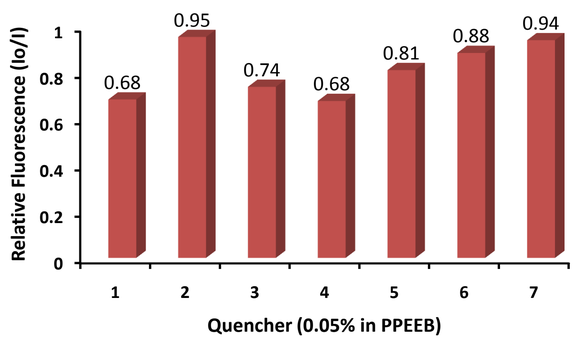
Solution: *Create an aromatic material that spontaneously forms an ordered crystal structure through which excitons can easily diffuse.*

We show long exciton diffusion in the PPEEB liquid crystal along the pi-pi-stacking axis.

Materials Selection



PPEEB can exist in two solid phases: a thermodynamically **unstable and low-order red phase**, and a **stable and highly ordered black phase**. In the black phase, the aromatic perylene cores of the molecules stack, creating a plane parallel to the substrate with stronger electronic coupling and improved exciton transport.



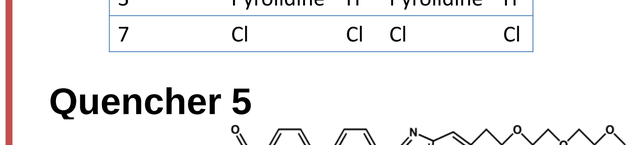
Fluorescence quenchers accept either an electron or hole from the host material, removing the possibility for recombination.

Purpose of Quenchers: Lower concentrations of a quencher within a host material correspond to longer distances over which an exciton can diffuse before it is quenched. High fluorescence means that the exciton diffusion length is shorter than the quencher separation. By fitting quenched fluorescence to the Stern-Volmer diffusion model, exciton diffusion length can be extracted from the quenching rate constant.

A good quencher must:

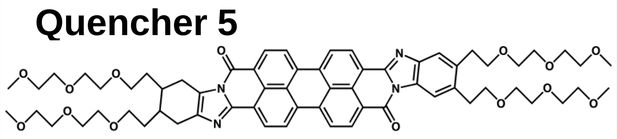
Fit into the PPEEB liquid crystal lattice

Quenchers 1-3, 7

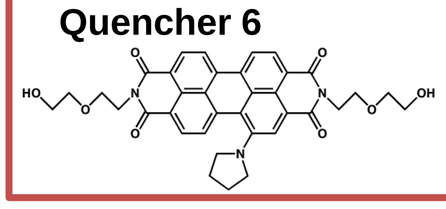


Quencher	R_1	R_2	R_3	R_4
1	Br	H	OH	H
2	Br	H	SH	H
3	Pyrolidine	H	Pyrolidine	H
7	Cl	Cl	Cl	Cl

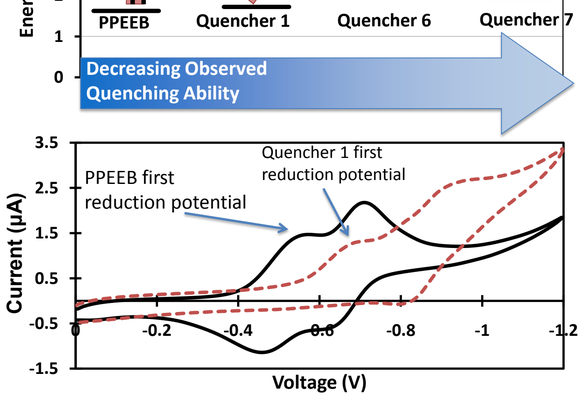
Quencher 5

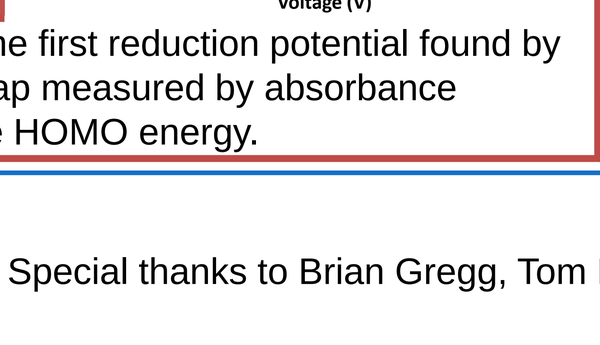


Quencher 6



Have favorably shifted highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels, allowing either hole transfer to the HOMO or electron transfer to the LUMO.





The LUMO energy was estimated as the first reduction potential found by cyclic voltammetry. The optical bandgap measured by absorbance spectroscopy was used to estimate the HOMO energy.

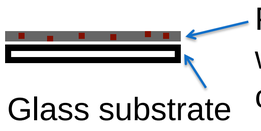
Exciton Diffusion

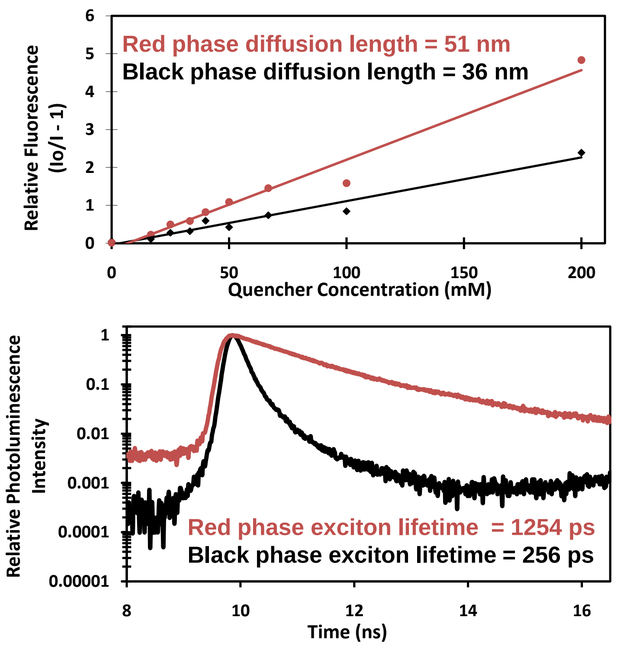
The **Stern-Volmer** diffusion model relates fluorescence intensity to quencher concentration: $\mathbf{I_0 / I = 1 + k_Q [Q]}$
where I_0 is quenched fluorescence, I is unquenched fluorescence, k_Q is the quenching rate constant, and [Q] is quencher concentration.

By assuming that excitons move through an isotropic solution via Brownian motion and that every exciton that reaches a quencher is quenched, we obtain: $\mathbf{k_Q = 4\pi r D \tau_0 = 4\pi r L^2}$
Where r is the interaction radius, D is the diffusion coeficient, τ_0 is the decay time with no quencher, and L is diffusion length.

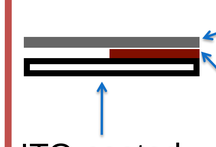
Because of these assumptions, this model estimates the **lower limit of exciton diffusion length**.

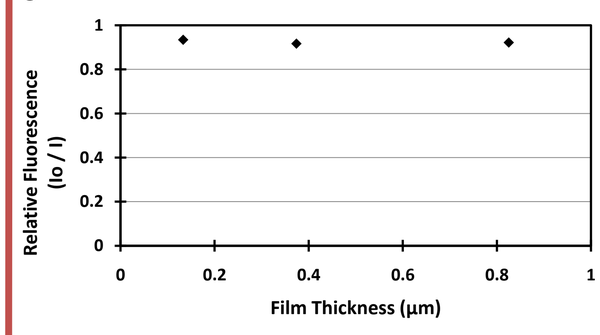
Lateral Diffusion





Perpendicular Diffusion





As expected from the lack of pi-pi-stacking in the perpendicular plane, the typical method for measuring diffusion length in organics is not applicable to PPEEB. Excitons do not diffuse perpendicularly, so little quenching was observed.

Consider:
- Red phase is less ordered and less fluorescent than black phase.

Contradicting observations:
- Red phase fluorescence measurements showed longer exciton diffusion length.
- Red phase time-resolved photoluminescence showed longer exciton lifetime.

Excitons in the red phase may be decaying by a non-radiative mechanism, and the observed fluorescence is a result of a minority decay process.

Conclusions

- Due to the similarity in structure, very little HOMO/LUMO energy level difference between PPEEB and the quenchers was observed.
- The best quenchers had a very similar structure to PPEEB, suggesting that **lattice exclusion for dissimilar quenchers** may be an issue. Lattice exclusion results in further **underestimation of exciton diffusion length.**
- Although the disordered red phase appears to have a longer exciton diffusion length and lifetime**,** low fluorescence in the red phase suggests that we are observing minority exciton decay processes.
- **Black phase exciton diffusion length is longest along the pi- stacking axis, with a lower limit of about 36 nm.** This is 5 times longer than diffusion in typical organic semiconductors, such as P3HT, suggesting a route to easily processed materials with long exciton diffusion length.
- ***Further investigation may include:***
  - Observe quencher exclusion from the PPEEB lattice by X-Ray Diffraction.
  - Determine an accurate exciton diffusion length by quantum analysis.

Selected References

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