Exploring the Photophysics of N-Type Polymer N2200

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N2200: A Promising n-Type Polymer

Use in OTFTs and OPVs

- High mobility (μ_e ~ 0.45-0.85 $cm^2 V^{-1} s^{-1}$)[1]
- Low band gap (1.55 eV) due to internal donor-acceptor character[2]
- All-polymer solar cells of up to 11.76% PCE[3]

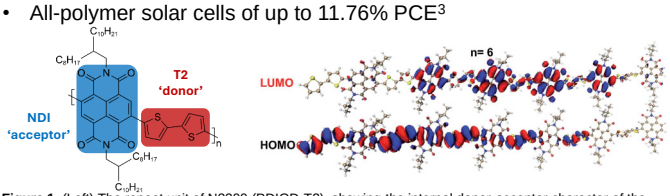


Figure 1. (Left) The repeat unit of N2200 (PDIOD-T2), showing the internal donor-acceptor character of the polymer. (Right) Calculated frontier molecular orbitals for an N2200 oligomer showing[2] poor orbital overlap, potentially leading to less-than-ideal photophysics.

Incorporation into Photoelectrochemical Cells (PECs)

- Utilize light energy to drive HER
  - What are the fundamental photophysics of the polymers used?
  - How does the **interphase** (polymer/solvent/electrolyte mixture):
    - Influence the dielectric environment ε_r?
    - Swell and experience morphological changes?
    - Support the chemistry of interest?

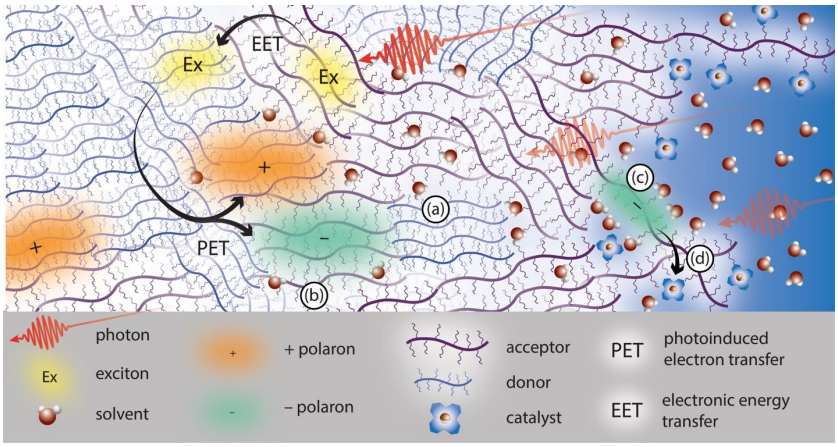
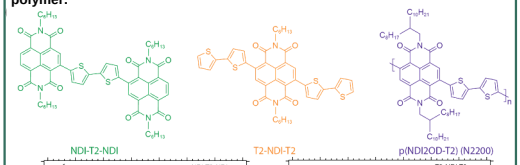


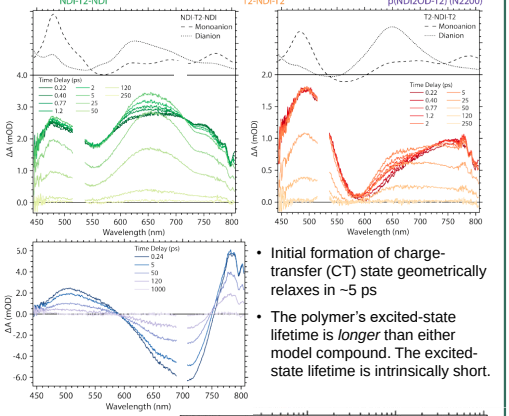
Figure 2. Illustration of the polymer interphase showing (a) the ingress of solvent into the donor-acceptor polymer blend, (b) a photoinduced electron transfer event leading to dissociation of an exciton into an electron and hole, (c) a potential solvent-polaron stabilization interaction, and (d) electron transfer to a catalyst to perform the desired chemistry.[4]

Intrinsic Carrier Lifetime in N2200[5]

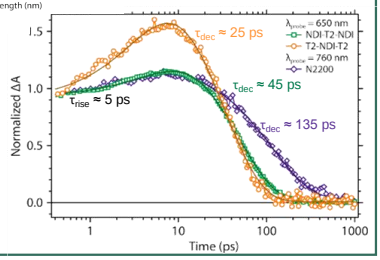
Is the short lifetime of N2200 intrinsic or a byproduct of aggregation?

Model 1.5-mers to reveal the intrinsic dynamics of the unaggregated polymer:





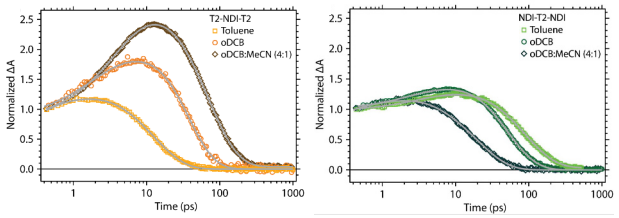
- Initial formation of charge-transfer (CT) state geometrically relaxes in ~5 ps
- The polymer's excited-state lifetime is *longer* than either model compound. The excited-state lifetime is intrinsically short.
- Inhibition of torsional motions and/or formation of interchain CT states could be responsible for slowing the polymer's return to the ground state vs. the model compounds



Solvent Variation Induces Photophysical Changes

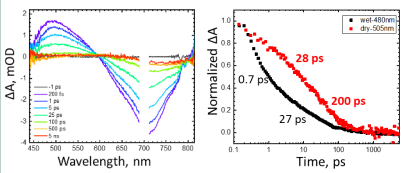
The model compounds' excited-state dynamics showed kinetic changes with solvent.

- Increasing ε_r from toluene to o-dichlorobenzene to 4:1 dichlorobenzene:MeCN stabilizes the CT state $T2^{+}$-NDI^{-}-T2, increasing CT state signal intensity and lengthening lifetime.
- Opposite rate trends were observed for T2-NDI-T2 and NDI-T2-NDI. Differences in torsional motions and concomitant changes to the reorganization energies of the two molecules are suspected to contribute to shifting the two molecules around the Marcus rate parabola differently.

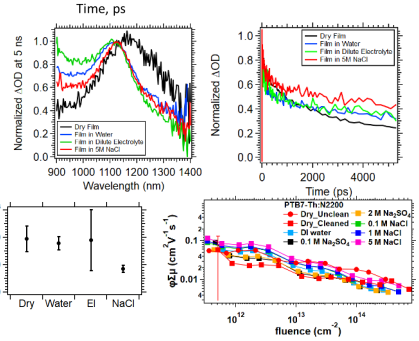


Does This Hold for Films in Electrolyte?

N2200 was investigated on its own and blended with donor polymer PTB7-Th in aqueous environments like those used in a PEC.



- The excited state of neat N2200 decays more rapidly to the ground state when the film is exposed to water. It is unknown whether this is due to morphological or energetic changes.
- PTB7-Th:N2200 blends are slightly stabilized by increasing ionic strength of the electrolyte, as shown by TA spectral shifts, lengthening of polaron lifetimes, reduction in polaron peak energetic relaxation over time, and a minor increase in the yield-mobility product in time-resolved microwave conductivity (TRMC).



Future Direction

Changes to hydrophobic film in aqueous electrolyte are small; a more extreme model system would help elucidate the fundamental processes to a greater degree. These may include:

- Exploring actively-swelled films, in which an electrochemical bias is used to force electrolyte into the polymer.
- Passive swelling of the polymer film with a less-polar solvent and electrolyte combination (e.g., MeCN and NBu_4PF_6).
- Combining electrochemical generation of polarons with photochemical generation and examining the resulting changes in dynamics.
- Using a more hydrophilic polymer, e.g., P90 (N2200 with oligo-ethylene glycol chains on 90% of the imide nitrogens), to exaggerate uptake of the aqueous electrolyte.

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