

Kinetics of Charge Trap Formation in *n*-Channel Semiconductors Studied by Time- and Wavelength-Resolved Electric Force Microscopy

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Stable electron-conducting organic materials are critical for the development of all-organic electronic devices,¹ yet few examples are widely used, in large part due to stability issues. Where *p*-channel materials often suffer degradation simply by being exposed to ambient conditions, organic *n*-channel semiconductors are generally stable while neutral.² Instead, the main challenge for *n*-channel materials is stabilizing the radical anion during device operation. Many *n*-channel organic devices develop large positive threshold voltage shifts and decreased mobility during operation, indicating the presence of trapped charge.³ In this work, we study the trap formation kinetics and spectral dependence of trap clearing in perylene diimide (PDI) derivatives using electric force microscopy.

Thermodynamic arguments suggest that lower LUMO energies should impart greater stability to an organic radical anion against attack by water and oxygen;⁴ this design rule has yielded a handful of relatively air-stable *n*-channel materials.^{2,5} However, we have recently shown that for the *p*-channel molecule pentacene, the active trap precursor is not the thermodynamically predicted species.⁶ It is from this perspective that we approach PDI derivatives.

Perylene diimides substituted with strong electron-withdrawing groups have been shown to be air-stable in transistor devices (Fig. 1a);⁵ however, we are interested in other members of this class of molecules for their application to organic photovoltaics. It has been shown that PDI derivatives that are left unsubstituted in the imide position can hydrogen bond to diketopyrrolopyrrole (DPP) derivatives, forming a self-assembled donor-acceptor system (Fig. 1c).⁷ Since the PDI derivatives used in these donor-acceptor systems are not substituted with strong electron-withdrawing groups, they have higher LUMO levels and are thermodynamically predicted to be less stable as anion radicals.

In this work, we studied PDI transistors to better understand the stability of these low-LUMO PDI derivatives. We thermally deposited 1,7-diethyloctyl perylene diimide (dEO PDI, Fig. 1b) synthesized by Dr. David Ley of the Braunschweig group onto bottom-contact transistor substrates where the SiO₂ dielectric was treated with hexamethyldisilazane (HMDS) or left bare. We considered several possible mechanisms for charge trapping in these devices: grain boundaries,⁸ dielectric disorder,⁹ chemical impurities,⁶ reaction with SiOH,¹⁰ and a complex between the radical anion, PDI⁻, and oxygen.⁴

Using our custom-built electric force microscope, we mapped trapped charge in our devices. We found uniform charge trapping in both types of samples, ruling out grain boundaries and dielectric disorder as the dominant trap mechanism. We measured the first-ever trap-clearing spectra⁶ in *n*-channel materials, which both tracked the PDI absorption spectrum. This finding does not rule out a chemical impurity trap, but simply means that excitation of the neutral PDI dominates light-enhanced trap-clearing.

We next used a pulsed-gate experiment to measure how fast trapped charge was generated in each sample.¹¹ Contrary to our prediction, we found that more traps built up at a faster rate on HMDS-treated than bare SiO₂, ruling out a PDI/O₂ complex (in which case the substrate should not affect rate of trap formation). Surprisingly, the trap-formation rate saturated versus free charge on bare SiO₂ but did not saturate on HMDS-treated SiO₂ (Figure 2). This observation rules out reaction with SiOH as the dominant mechanism of trap formation. We believe this finding may mean that SiOH deactivates an unknown trap precursor species in dEO PDI.

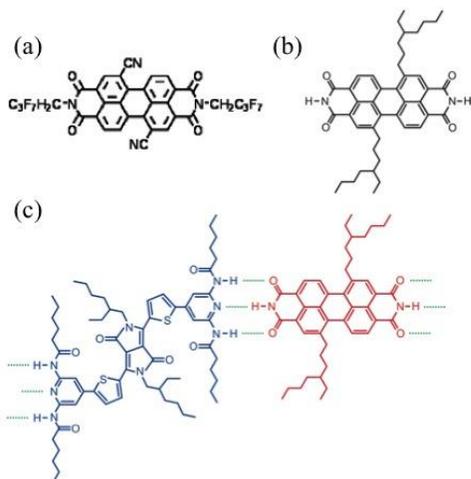


Figure 1: (a) Commercially available, relatively air-stable PDI-FCN₂, (b) dEO PDI, (c) dDPP-dEO PDI donor-acceptor complex.

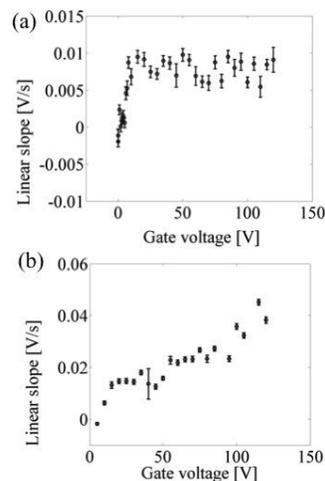


Figure 2: Trap formation rate versus gate voltage for (a) dEO PDI on bare SiO₂ transistor channel and (b) dEO PDI on HMDS-treated SiO₂ transistor channel.

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