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Electron Hopping in π-Stacked Covalent and Self-Assembled Perylene Diimides Observed by ENDOR Spectroscopy

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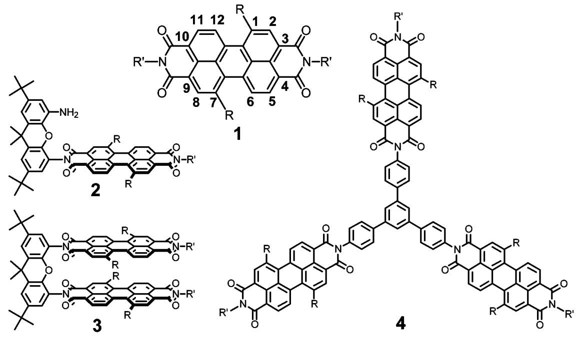
The delocalization or rapid hopping of charge among neighboring molecules is a requirement for organic electronics including photovoltaics.[1,2] Pioneering studies of charge delocalization in both photosynthetic proteins and aromatic molecules in solution have used electron paramagnetic resonance (EPR) and electron−nuclear double resonance (ENDOR) spectroscopy to reveal charge sharing in dimers, indicated by a halving of the electron−nuclear hyperfine coupling constants (hfcc).[3−9] Dimers formed from $\pi-\pi$ interactions between radical cations and neutral aromatic molecules in solution are well-known;[6,10−12] however, the corresponding dimers of radical anions with neutral aromatics have been reported only once in solution,[13] even though examples in cyclophanes are known.[14] Recently, we and others have shown that photoinduced charge separation occurs readily in both covalent and self-assembled systems based on robust perylene-3,4:9,10-bis(dicarboximide) (PDI) molecules.[15−17] To address the question of whether unpaired electrons are delocalized or hopping among the PDI derivatives in self-assembled materials, we have carried out room-temperature, solution-phase EPR and ENDOR studies of the radical anions of a PDI monomer (**1**), a covalent, cofacial PDI dimer (**3**), and a covalent trefoil-PDI$_3$ molecule (**4**) that self-assembles into π-stacked dimers (**4**)$_2$.



1 **2** **3** **4**

R = 3,5-di-tert-butylphenoxy; R' = 2-ethylhexyl

The synthesis and characterization of **1** and **4** are reported in the Supporting Information, while that of **2** and **3** were reported earlier.[18] Monomers **1** and **2** absorb strongly across the visible spectrum with peaks at or near 548 nm (Figure 1), whereas the peak maxima of **3** and **4** are significantly blue-shifted to ~513 nm. These absorption changes are characteristic of exciton coupling in an H-aggregate geometry and reveal that **4** forms π-stacked aggregates in CH$_2$Cl$_2$.[17,18] Gel permeation chromatography (GPC) on **4** in CH$_2$Cl$_2$ (Figure S1) and NMR in CD$_2$Cl$_2$ (Figure S4) indicate the formation of dimers at the 10^{-3} to 10^{-4} M concentrations of the ENDOR experiments, which is consistent with the previous observation of dimers formed by a closely related trefoil-PDI.[19] Furthermore, small-angle X-ray scattering (SAXS) data strongly support a dimeric, cofacial structure for (**4**)$_2$ and exclude formation of larger aggregates even in toluene, a solvent that more strongly favors aggregation than CH$_2$Cl$_2$ (Figures S5−S9).

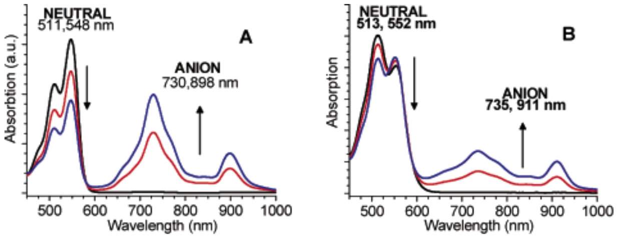


Figure 1. UV−Vis spectra in CH$_2$Cl$_2$−3% TEA. (A) **1** and $\mathbf{1}^{\bullet-}$. These spectra correspond closely to those of **2** and $\mathbf{2}^{\bullet-}$, with peak shifts ≤ 2 nm. (B) **4** and $\mathbf{4}^{\bullet-}$. These spectra correspond closely to those of **3** and $\mathbf{3}^{\bullet-}$, except maxima of **3** are red-shifted 3−4 nm relative to those of **4**.

A polar solvent, CH$_2$Cl$_2$, was selected for our ENDOR studies to diminish the effects of counterions that are known to influence charge sharing among aromatic systems in less polar solvents such as ethers.[7] Solutions of **1**−**4** in dry CH$_2$Cl$_2$ with 3% triethylamine (TEA) (w/w) were prepared, loaded into quartz tubes, and sealed in an N$_2$-filled glovebox. Radical anions were generated by photoexcitation of PDI with an Ar$^+$ laser at 457−488 nm (7−40 mW). Electron transfer from TEA to ^{1*}PDI, followed by proton loss from TEA$^{\bullet+}$, leads to formation of a stable cation TEA−H$^+$.[20] Upon photoreduction of **1** or **2**, near-infrared (NIR) bands due to PDI$^{\bullet-}$ appear at ~730 and ~898 nm (Figure 1).[21] Similarly, as a solution of **3** or (**4**)$_2$ is reduced, anion bands at ~735 and ~910 nm appear, and the exciton-enhanced band diminishes. The reductions of **3** and (**4**)$_2$ were halted before 50 and 15% completion, respectively, to ensure maximal production of the singly reduced species $\mathbf{3}^{\bullet-}$ and $(\mathbf{4})_2^{\bullet-}$.

EPR and ENDOR spectra were acquired with a Bruker E-580 spectrometer, fitted with an EN801 resonator, and RF power amplifier (ENI A-500). Temperatures were maintained at or near 290 K. The EPR spectra of $\mathbf{1}^{\bullet-}$ to $(\mathbf{4})_2^{\bullet-}$ are either line-broadened or featureless spectra with $g = 2.0028-20029$ (Figure S10). The proton ENDOR spectrum[22] of $\mathbf{1}^{\bullet-}$ in CH$_2$Cl$_2$ exhibits four line pairs, with isotropic hyperfine splittings of 4.81, 2.20, 1.61, and 0.36 MHz (Figure 2a). DFT calculations are used to assign the three largest hfcc's to the perylene protons at the (6,12), (5,11), and (2,8) positions, respectively. The smallest hfcc is assigned to the protons of 2-ethylhexyl that are closest to the imide nitrogens. Simulation of the EPR spectrum indicates that the nitrogen hfcc of $\mathbf{1}^{\bullet-}$ is 1.74 MHz, in agreement with the DFT calculation.[23] The hfcc's obtained here for $\mathbf{1}^{\bullet-}$ are consistent with more highly resolved EPR/ENDOR spectra acquired in our lab and elsewhere on PDI with an unsubstituted perylene core.[24−26] The ENDOR spectrum of $\mathbf{2}^{\bullet-}$ in CH$_2$Cl$_2$ shows that each of the perylene proton lines splits into two

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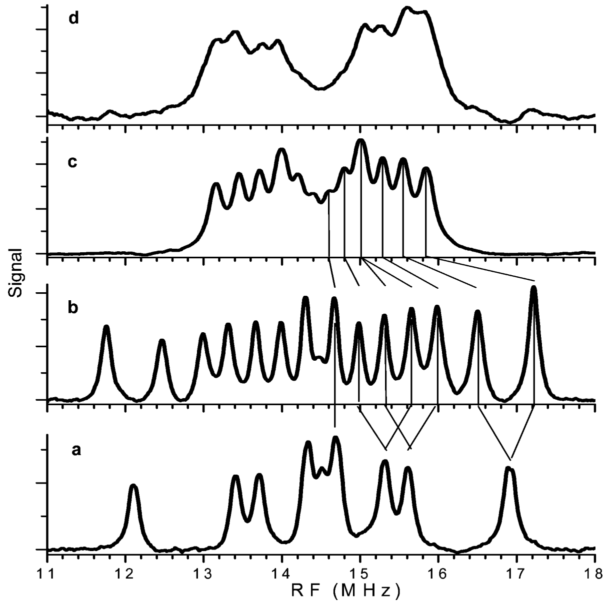

Figure 2. Proton ENDOR spectra in CH_2Cl_2−3% TEA solution of: (a) **1**$^{\bullet-}$, (b) **2**$^{\bullet-}$, (c) **3**$^{\bullet-}$ at 290 K, and (d) self-assembled (**4**)$_2^{\bullet-}$ at 297 K. Microwave powers were 4−20 mW, RF power 300−800 W, with frequency modulation depth 50 or 100 kHz.

resonances 1.3−1.4 MHz apart, whereas the single methylene imide line pair remains unsplit (Figure 2b). These additional splittings are much smaller in the more polar solvent *N*,*N*-dimethylformamide (DMF, not shown); thus, we conclude that they originate from ion pairing of TEA−H$^+$ with the asymmetrically substituted PDI$^{\bullet-}$. Unfortunately, the insolubility of **1** and **4** in DMF precludes the general use of this solvent here.

The ENDOR spectrum of **3**$^{\bullet-}$ reveals hfcc's that are almost exactly half of those of the monomer **2**$^{\bullet-}$ (Figure 2c). The peaks of **3**$^{\bullet-}$ show a 1−1 correspondence with those of **2**$^{\bullet-}$, with the exception of two peaks that are likely merged. The halving of the hfcc's of **3**$^{\bullet-}$ indicates that the sharing of charge is complete in the cofacial dimer. Remarkably, the ENDOR spectrum of (**4**)$_2^{\bullet-}$ exhibits a spectral width that is within 10% of the width of the cofacial dimer. The unpaired electron is evidently shared completely between two PDIs in the self-assembled dimer. For comparison, the EPR spectrum of a nonaggregating version of **4** (see Supporting Information, molecule **5**[27]) reveals overall breadth and features that are similar to the monomeric PDI anion, which eliminates fast intramolecular electron hopping among the PDIs of a single trefoil-PDI$_3$ molecule as the interpretation for the ENDOR spectrum of (**4**)$_2^{\bullet-}$.

The combination of electronic absorption and ENDOR spectroscopy described above establishes limits on the time scale for electron transfer between π-stacked chromophores.[7] The 50% reduction of hfcc's for the dimeric systems relative to the monomer models reveals that the rate of electron hopping between the PDIs in both **3**$^{\bullet-}$ and (**4**)$_2^{\bullet-}$ must be many times faster than the ENDOR time scale ($>10^7$ Hz). However, on the time scale of electronic absorption ($>10^{14}$ Hz) the UV−vis spectra of **3**$^{\bullet-}$ and (**4**)$_2^{\bullet-}$ indicate that the best qualitative description of charge residence in these cofacial systems in polar solution is in terms of one neutral and one reduced PDI, with only minor perturbations due to electronic interactions between the chromophores.

The ENDOR data clearly show that rapid electron hopping occurs in both covalent and self-assembled π-stacked PDI molecules. The observation of a $>10^7$ Hz electron hopping rate between chromophoric pairs in the self-assembled dimer provides a useful comparison to electron transport within more extended organic molecular materials, including other systems that self-assemble in solution.[28] Our results contrast with the full delocalization (bandlike charge transport) found recently in highly crystalline molecular materials.[1,29] The alternative localized hopping mechanisms that describe charge transport within some PDI-based materials are likely more closely related to the results found here.[1,30]

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Supporting Information Available: Synthesis and characterization of **1**, **4**, and **5**. Spectroscopic, SAXS, and GPC data as well as DFT calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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