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Radical Anions of Trifluoromethylated Perylene and Naphthalene Imide and Diimide Electron Acceptors

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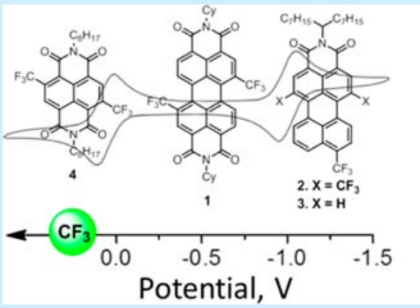
Supporting Information

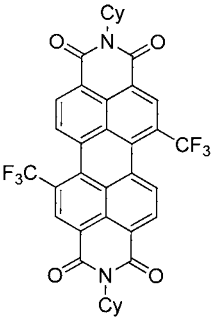
ABSTRACT: A series of electron-deficient perylene and naphthalene imides and diimides (**1**−**4**) with varying degrees of trifluoromethylation were synthesized. Single crystal X-ray analysis afforded detailed structural information, while spectroelectrochemical and EPR spectroscopy provided characterization of the radical anions of **1**−**4**. This study reveals that trifluoromethylation of the imides and diimides makes their one-electron reduction potentials substantially more positive relative to the unsubstituted counterparts, while their other properties remain largely unchanged.



Organic redox chromophores are requisite for lightweight, low-cost optoelectronic materials. Stability, chemical robustness, and ease of preparation are among a few of the necessary characteristics for organic materials used in device fabrication. Arylene imides and diimides have demonstrated significant performance as n-type semiconductors in transistors,[1,2] solar cells,[3,4] and other applications.[5] The high electron affinity of perylene and naphthalene imides and diimides makes them a logical choice when selecting an electron-accepting chromophore for optoelectronic applications. Additionally, their ability to self-assemble into complex packing motifs makes them desirable for understanding how structure determines function.[6,7]

Currently available synthetic methods allow the preparation of stable chromophores with increasingly negative reduction potentials, such as imide derivatives with electron-rich aryl and alkyl substituents at the so-called "bay"[8] and "headland"[9−11] positions. Installation of electron-deficient substituents into these chromophores to shift their reduction potentials more positive has been complicated by several problems. For instance, while halogenation yields naphthalene and perylene imides, NMI and PMI, respectively, and diimides, NDI and PDI, respectively, having increased the electron affinity, the lability of the halogen atoms makes them highly susceptible to nucleophilic aromatic substitution with even weak bases at room temperature.[12] 1,7-Dicyano-PDIs and 2,6-dicyano-NDIs, while less chemically labile, rapidly form stable radical anions due to their high electron affinities.[13] Therefore, there is a significant need for developing a synthetic route to perylene and naphthalene imides and diimides with both increased electron affinity and ambient stability.

Fluorinated alkyl substituents are stable, electron-deficient functional groups that have been employed in this field,[5,14] yet synthetic protocols remain scarce and underdeveloped. Several reported[15−18] preparations of perfluorinated alkyl substituted PDIs and NDIs have given uniformly low yields in our hands and, to the best of our knowledge, no further literature publications have followed up the subject. Recent success in the development of efficient trifluoromethylation methods[19,20] has allowed the installation of CF_3 groups onto virtually any aromatic substrate nearly independent of π electron density. A variety of conditions and CF_3 group sources are available, including CF_3TMS (Ruppert−Prakash reagent) and Cu(I) in both catalytic and stoichiometric amounts.[21−24]



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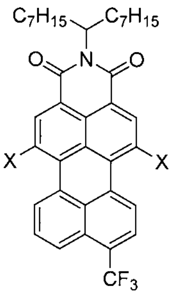
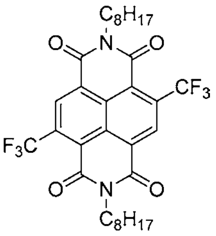


2. X = CF_3
3. X = H



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Here we report the application of these trifluoromethylation protocols to generate a series of new perylene and naphthalene imides and diimides. We prepared a series of four chromophores, **1**−**4**, in good to excellent yield and studied their structural, optical, and electronic properties. Single crystal X-ray structures were obtained to understand how functionalization impacts solid-state order. UV−vis absorption and fluorescence spectroscopy were used to characterize the neutral

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chromophores, as well as their radical anions. The EPR spectra of the radical anions were also obtained to assist in future spectroscopic investigations of electron donor−acceptor systems using these electron-deficient chromophores. Since the readily available Hartwig trifluoromethyl-copper(I)phenanthroline ($CF_3CuPhen$) reagent[22] reacts efficiently with aryl bromides, we applied this reagent to the well-known brominated perylene and naphthalene imides and diimides bearing solubilizing substituents commonly used with each of the arenes. Thus, we chose the *N,N*-bis(cyclohexyl) derivative of 1,7-dibromo-PDI because it is possible to isolate this compound in regioisomerically pure form.[25] We also employed the *N*-(1-heptyl)octyl "swallow tail" group for the PMI derivatives as an excellent solubilizing group that disrupts aggregation. Both mono- and tribromo-PMIs were prepared using previously reported methods.[26,27] NDIs were functionalized with *N*-(*n*-octyl) groups to impart the necessary solubility, yet not inhibit crystallization. Preformed $CF_3CuPhen$ in DMF proved excellent in our initial attempts to trifluomethylate brominated PDI, PMI, and NDI derivatives to give **1**−**4** in 67−80% yields. The identities of these new compounds were unequivocally established with the aid of ^1H, ^{19}F, and ^{13}C NMR spectroscopy as well as high resolution mass spectrometry. Single crystals of **1** and **4** were grown from toluene and methanol solution, and X-ray diffraction experiments were used to unambiguously determine the structures of these chromophores (Figure 1).

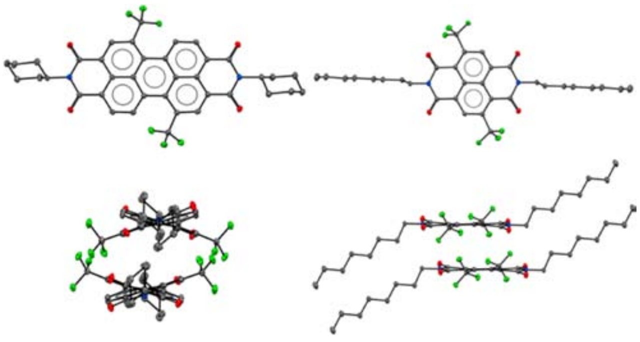

Figure 1. Single crystal X-ray structures of **1** (left) and **4** (right) shown in orthogonal directions.

The crystal structures of **1** and **4** illustrate the impact of trifluoromethylation on solid state packing. Molecular offsets were determined by first performing a coordinate rotation on the Cartesian crystal axes and then measuring the distance between their molecular centroids (see Supporting Information). The unit cell of **1** contains two molecules offset on both the long axis (5.06 Å) and the short axis (1.33 Å). The *π*−*π* stacking distance (4.02 Å) is quite large compared to van der Waals contact (3.4−3.5 Å). This is due to the substantial twist (28.8°) between the two naphthalene subunits, which results from the steric interaction between the bay CF_3 group and the hydrogen atom. Phase segregation of the CF_3 groups is also observed with all four substituents directed toward the interior of the unit cell. Adjacent molecules in the next unit cell pack with similar shifts in the short (1.27 Å), long (5.38 Å), and *π*−*π* stacking axes (3.99 Å). This results in a one-dimensional stacking arrangement very similar to the well-known 1,7-dibromo-PDI.[25] The two compounds exhibit very similar packing behavior, each demonstrating substantial core twisting and substituent segregation.

The unit cell of **4** contains only a single molecule, but is offset from the molecule in the adjacent unit cell on the long (1.43 Å), short (3.10 Å), and stacking (3.63 Å) axes. The nearly van der Waals contact between adjacent molecules suggests minimal steric interference from the CF_3, which is supported by the negligible core twist. Again, the columnar stacking motif observed is very similar to the closest reported 2,6-dibromo-NDI analog.[13] This molecule has similar offsets along the long (0.92 Å) and short axes (3.10 Å), but a slightly smaller offset along the stacking axes (3.37 Å) suggesting the CF_3 groups are slightly bulkier. Overall, the structural analysis indicates that trifluoromethylation impacts solid state packing to a similar degree as does bromination at the same positions.

The one-electron reduction potentials obtained from cyclic voltammetry (Table 1, Figure S1) are shifted strongly positive relative to those of the unfunctionalized arylene imides and diimides,[28] and thus reflect the cumulative electron withdrawing nature of the CF_3 substituents. Namely, the first reduction potential of **1** is 0.22 V more positive after bistrifluoromethylation, shifting from −0.43 V to −0.21 V (all vs SCE), while the second reduction potential undergoes approximately the same shift by 0.20 V from −0.70 V to −0.50 V. The effect of trifluoromethylation is even more dramatic in the case of **4**, where the first reduction occurs at −0.13 V, 0.35 V more positive than the reduction potential of unsubstituted NDI. The second reduction of **4** is also more positive by 0.30 V. PMI derivatives **2** and **3** display a similar trend with the first reduction potentials being shifted to −0.42 V and to −0.78 V respectively, indicating that each functionalization with one CF_3

Table 1. Electrochemical and Spectroscopic Data for 1−4 and Their Radical Anions[a]

	E_{red1}, V	E_{red2}, V	neutral: $\lambda_{max,\ nm}$	$\lambda_{max\ em,\ nm}$	Φ_{fl}	τ_F (ns)	k_R (10^8 s^{-1})	k_{NR} (10^7 s^{-1})	anion: $\lambda_{max,\ nm}$	*g*-factor
1	−0.21	−0.50	508 (60600), 474 (40200)	520	0.64	4.11 ± 0.02	1.6 ± 0.1	8.8 ± 0.1	695, 776, 842	g_{iso} = 2.00332
2	−0.42	−1.01	481 (27600), 465 (28700)	529	0.57	5.82 ± 0.02	1.0 ± 0.1	7.4 ± 0.1	590, 747, 832	g_{iso} = 2.00296
3	−0.78	−1.30	492 (37400), 464 (31400)	514	0.58	4.92 ± 0.02	1.2 ± 0.1	8.5 ± 0.1	617, 720, 811	g_{iso} = 2.00290
4	−0.13	−0.69	378 (15700), 369 (12000)	–	–	–	–	–	461, 490, 563, 620, 665, 735	g_z = 2.00260, g_y = 2.00391, g_x = 2.00421

[a] All potentials are reported as $E_{1/2} = (E_p^a + E_p^c)/2$ in V vs SCE in DMF with 0.1 M Bu_4NPF_6 supporting electrolyte. Absorption and emission data of neutral species were recorded in CH_2Cl_2 at 295 K, while the absorption spectra of the radical anions were obtained by spectroelectrochemistry in DMF with 0.1 M Bu_4NPF_6. Fluorescence quantum yields were referenced to the emission of *N,N*-bis(1-heptyloctyl)-perylene(3,4:9,10)bis(dicarboximide) (Φ = 1). Fluorescence lifetimes (τ_F) were recorded upon excitation with 415 nm, 0.1 nJ laser pulses, and monitoring the emission at 550 nm. k_R and k_{NR} are the radiative and nonradiative rate constants.

group shifts the reduction potential of PMI more positive by 0.18 V. Linear changes in reduction potentials resulting from increasing the number of electron-withdrawing substituents is indicative of a dominant inductive effect of the CF_3 group and a smaller contribution from its π-conjugation with the arylene core.

The UV−vis absorption spectra of **1**−**4** are qualitatively similar to the parent, unsubstituted arylenes;[28] however, their absorption maxima are all blue-shifted (Figure 2). The absorption maxima for the radical anions of $\mathbf{1}^{-\bullet}$ and $\mathbf{4}^{-\bullet}$ are slightly blue-shifted, while those of $\mathbf{2}^{\bullet}$ and $\mathbf{3}^{-\bullet}$ are slightly red-shifted relative to the corresponding unsubstituted radical anions (Figure S2). For comparison, the absorption spectra of $\mathbf{1}^{-2}$−$\mathbf{4}^{-2}$ are presented in Figure S3 and are similar to those of the unsubstituted dianions.[28] Along with these similarities, the trifluoromethylated PMIs remain strong fluorophores with quantum yields in the range of $\phi_F = 0.57$−0.64 relative to that of *N,N*-bis(1-heptyloctyl)-PDI ($\phi_F = 1$), while $\phi_F \cong 0$ for **4** due to rapid intersystem crossing. The lowest excited singlet states of **1**−**3** also decay with rates analogous to the unfunctionalized arylene imides and diimides (Table 1, Figure S4).

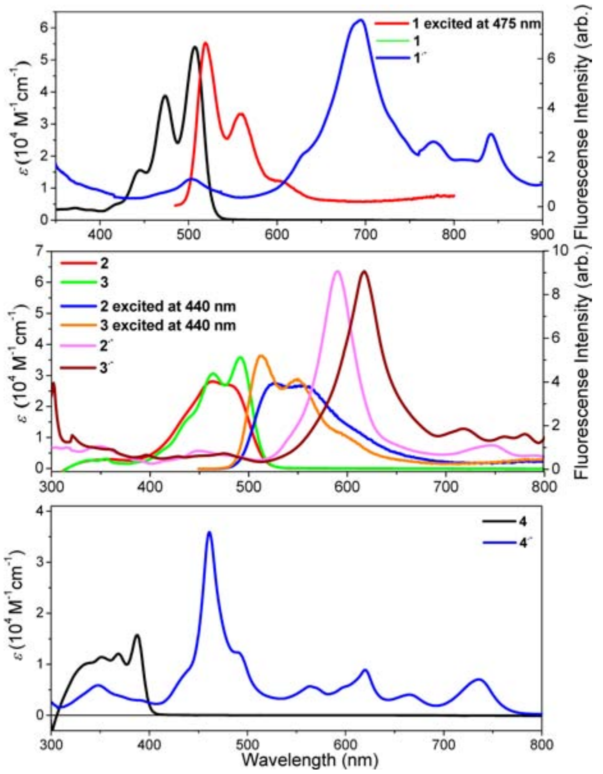

Figure 2. UV−vis absorption and fluorescence spectra of **1**−**4** and their radical anions in 0.1 M $TBAPF_6$ DMF.

EPR spectroscopy was used to obtain information on the spin density distribution within the anion radicals of **1**−**4**. Samples for EPR experiments were prepared by chemical reduction of the compounds with cobaltocene in DMF. The EPR spectra at room temperature at X-band (9.5 GHz) with 0.02 mT field modulation are shown in Figure 3. The strong interaction between the unpaired spin and the fluorine nuclei is evident in the spectra of $\mathbf{1}^{-\bullet}$ and $\mathbf{4}^{-\bullet}$ in which the spectral width is approximately double that of the respective unsubstituted PDI and NDI derivatives.[29,30] An alternating line width effect is observed for $\mathbf{4}^{-\bullet}$, which is most likely due to hindered rotation of the CF_3 resulting from steric interactions of the fluorine atoms with the imide oxygen atoms. Hyperfine coupling constants were obtained by simulating the EPR spectra (see Supporting Information) and by performing DFT calculations at the UB3LYP/EPR-II level of theory. In all cases large ^{19}F hyperfine splittings are observed, and the magnitude of the proton hyperfine couplings in $\mathbf{1}^{-\bullet}$ and $\mathbf{4}^{-\bullet}$ are reduced relative to those of their unsubstituted derivatives. To properly simulate the alternating line width observed for $\mathbf{4}^{-\bullet}$ it is necessary to consider three inequivalent pairs of fluorine atoms with hyperfine coupling constants of 0.718, 0.588, and 0.074 mT resulting from hindered rotation of the CF_3 groups. The *g*-factors of the radical anions were determined by employing an internal standard in field-swept echo-detected (FS-ED) pulsed EPR measurements at W-band (94 GHz) and are listed in Table 1. The *g*-factors for $\mathbf{1}^{-\bullet}$−$\mathbf{3}^{-\bullet}$ are highly isotropic, and the individual components could not be resolved at W-band (Figure S5).

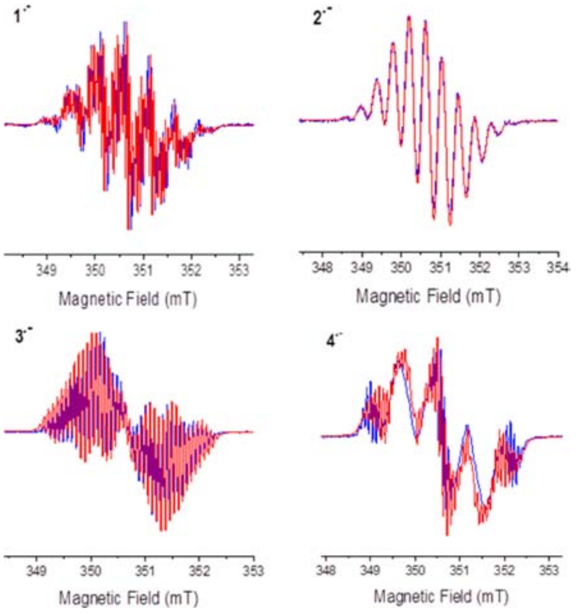

Figure 3. X-band CW-EPR spectra of the anion radicals of **1**−**4** prepared by reduction with cobaltocene in DMF. Spectra were collected at 295 K with 0.02 mT modulation amplitude. Blue trace, experimental data. Red trace, simulated data.

In conclusion, the data obtained here show that trifluoromethylated perylene and naphthalene imides and diimides provide a convenient range of electron affinities and possess chemically well-behaved radical anions that can easily be identified by their characteristic UV−vis and EPR spectra. These qualities make these electron-accepting chromophores useful in designing new electron donor−acceptor systems for organic electronics and solar energy conversion.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental and spectroscopic details for all compounds, X-ray structural CIF data for **1** and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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