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Thionated Perylene Diimides with Intense Absorbance in the Near-IR

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A synthetic strategy involving a combination of tetra-thionation and amine substitution in the bay region of a perylene diimide (PDI) leads to remarkable examples of neutral PDIs with intense absorption maxima in the near infrared. Generation of the corresponding monoanions red shifts the absorption profile to give short-wavelength infrared bands.

Perylene diimide (PDI) dyes have been studied for over a century and a range of useful properties have been demonstrated including high chemical and thermal stability, intense absorbance in the UV/visible range, high fluorescence with up to 100% quantum yields and excellent n-type semiconductivity. These properties have led to their exploitation in various applications such as organic field-effect transistors, chemical sensors, thin-film transistors, complex supramolecular systems and, increasingly, organic photovoltaics (OPVs). Recent interest in OPVs has begun to outstrip that of traditional silicon based solar cells due to their low cost, synthetic adaptability and processing ability. Currently many of the materials being investigated for these applications absorb in the UV/visible region, however, as 50% of solar energy falls in the near infrared (NIR) spectral range, the efficiency of these devices could be greatly improved by extending the absorption of these materials to 750 nm and beyond. To date, NIR absorbance of rylene dyes has been achieved by extension of the perylene core along the longer or shorter axis of the molecule, by deprotonation or via the formation of J-aggregates. Until this report the very few previous examples of neutral PDIs with absorbance in the NIR have required extensive and complex functionalization and there are no previous examples or absorption in the short-wavelength infrared (SWIR, 1400-3000 nm) for PDI-based species. Herein we report a simple approach to tuning the absorption properties of PDI-based molecules.

Traditionally the functionalization of PDIs has centred around the imide and bay regions (Scheme 1), until 2009, when the possibility of substitution at the ortho-positions was realized. However, in 2014 in an elegant study Seferos et al. discovered that the reaction of PDIs with Lawesson’s Reagent resulted in the substitution of the carbonyl oxygens with sulfur to give tetra-thionated PDIs, a strategy that was also employed with naphthalene diimides. It was found that subsequent substitutions resulted in a progressive bathochromic shift in the absorption maxima from 525 nm for the unfunctionalised N,N'-di(3-hexylundecyl)-perylenetetracarboxylic diimide A to 704 nm for the tetra-thionated analogue B. The bathochromic shift in absorbance is accompanied by a shift to more positive potentials for reduction processes. We have reported previously the synthesis of two isomers of a PDI functionalized with morpholine at the bay area (Scheme 1). These molecules display a bathochromic shift, with respect to unsubstituted PDIs, to 626 nm for the blue 1,6-isomer and 653 nm for the green 1,7-isomer.

Herein we report a strategy combining bay area functionalization and thionation of the PDI carbonyls that leads to an additive effect with an even more pronounced red shift of the main absorption band, resulting in neutral PDIs with absorption maxima in the NIR region.

Synthesis of 1 was achieved by the reaction of N,N-di(n-butyl)-1,7-dimorpholino-3,4,9,10-peryenetetracarboxylic diimide 3 with Lawesson’s reagent. The major reaction product was the tetra-thionated...
species which could be readily separated from other, much smaller quantities of lesser S-substituted products via column chromatography. The synthesis of 2 was achieved from \(N,N\)-di(n-butyl)-1,6-dimorpholino-3,4:9,10-perylenetetracarboxylic diimide 4 using the same method, see SI for details. 1 was found to be purple in both the solid state and solution yet 2 is an unexpected black colour in both cases, revealing absorbance of light across the visible spectrum (Figure 1, 3). In both instances dilute solutions of the compounds reveal dark purple and dark green colouration for 1 and 2 respectively. Importantly no decomposition of the compounds was observed when the compounds were stored below 0°C for periods of over four months.

![Figure 1. Solutions of PDI species in CH\(_2\)Cl\(_2\) solution. From left to right Br\(_2\)-PDI (mix of isomers), 4, 3, 2, 1.](image)

![Figure 2. Single crystal structures of (a) 1 and (b) 2, (c) packing observed in the crystal structure of 1 viewed along the crystallographic b-axis. Carbon - grey, nitrogen- blue, oxygen- red, sulfur- yellow. H-atoms removed for clarity.](image)

![Figure 3. UV/vis/NIR spectra of thionated species 1 (purple), 2 (black), and non-thionated, 3 (green) and 4 (blue) in CH\(_2\)Cl\(_2\) solution.](image)

Single crystals of 1 and 2 were grown by layered diffusion between a chloroform/TFA solution of the target compound and hexane. X-ray structural determinations revealed the conformational arrangements of the molecule in the solid state, further confirming the isomeric arrangement of the morpholines and the full thionation of the molecule (Figure 2). For both 1 and 2 the compounds pack in pairs which are in turn packed into extended chains as has been observed previously for disubstituted PDI species.\(^{19}\) The conformational arrangement and twisting of the perylene core is consistent with the structures of 3\(^{18}\) and 4 (see ESI).
UV/vis/NIR spectroscopic studies of 1 and 2 revealed that thionation induced a bathochromic shift in the absorption maxima into the NIR (Figure 3). The absorption maxima of 1 was found to be at 864 nm, displaying a shift of 211 nm versus 3 and a shift of 160 nm versus an unsubstitated, tetra-thionated, PDI B. The combination of thionation and morpholine substitution was found to have a dramatic increase in the wavelength of absorption versus an unsubstitated, non-thionated, PDI A of 339 nm. 2 has an absorption maxima at 838 nm, red-shifted 212 nm relative to its non-thionated counterpart 4 (almost identical to the difference between 1 and 3), and 134 nm higher than A. The black colour of 2 can be explained by the absorbance observed across the range from above 1000 nm to 230 nm showing that 2, not only has an intense absorption in the NIR, but also absorbs across the entire UV/vis region. This suggests excellent potential for incorporation into light harvesting devices. The molar extinction coefficients of the NIR bands for 1 (864 nm) and 2 (838 nm) were found to increase by around ca. 10,000 M⁻¹cm⁻¹ after thionation.

In order to probe the effect of reduction upon the optical properties of 1 and 2 their electrochemical behaviour was investigated by cyclic voltammetry, UV/vis/NIR spectreochemistry and coulometry/EPR spectroscopy. We have previously demonstrated that upon reduction of 3 and 4 the major adsorption band shifts significantly to lower energy and we anticipated that in the case of 1 and 2 this would result in a significant shift into the NIR. Unexpectedly, upon thionation the solubility of the PDIs was severely reduced. Electrochemical studies on 2 were possible in CH₂Cl₂ at 1 mM concentrations however the solubility of 1 dropped to a level that made cyclic voltammetry in this solvent problematic. It was found that 1,2-dichlorobenzene was a suitable alternative and very little change in the absorption properties of 2 were observed between the two solvents, see ESI for further details.

Cyclic voltammetric investigations of 1 and 2 revealed two closely overlapped reduction processes (Figure 4). The potentials of these reductions were determined from square wave voltammetry as -0.71 and -0.81 V for 1 and -0.69 and -0.82 V for 2, in 1,2-dichlorobenzene containing [Bu₄N][BF₄] (0.4 M) (Table 1). The potentials observed for the two isomers are very similar, and this matches the behaviour exhibited by the reductions of 3 (-1.11 and -1.29 V) and 4 (-1.11 and -1.30 V) in CH₂Cl₂ containing [Bu₄N][BF₄] (0.4 M).¹⁵ The recording of cyclic and square wave voltammetry data for 2 in CH₂Cl₂ containing [Bu₄N][BF₄] (0.4 M) gave a direct comparison with analogous measurements of 4. In CH₂Cl₂ the same two reductions noted for 2 in 1,2-dichlorobenzene were present but the potentials were shifted to -0.61 and -0.71 V for the first and second reductions, respectively. Importantly, comparison of the first reduction of the thionated and non-thionated species, 2 versus 4 in CH₂Cl₂, reveal a shift of ca. 0.50 V to less negative potentials for the thionated analogues and this is accompanied by a small drop in the separation between the first and second reduction processes which may indicate a decrease in coulombic interaction in 2⁺. These results are consistent with those reported for N,N’-di(3-hexylundecyl)-perylene-3,4,9,10-tetracarboxylic diimide (-0.68 and -0.91 V) and its tetra-thionated analogue (-0.23 and -0.33 V) recorded in CH₂Cl₂.

An oxidation process is also observed in the cyclic voltammogram of both 1 and 2, however, neither were found to be electrochemically reversible over the scan rate range 0.02 – 0.3 Vs⁻¹ (see ESI) and these oxidation processes were not subject to further investigations by spectroscopic techniques.

<table>
<thead>
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<th>Compound</th>
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<th>2nd Reduction</th>
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<tr>
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<tr>
<td>4</td>
<td>DCM</td>
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Table 1. Reduction potentials for thionated PDIs versus non-thionated morpholino-substituted PDIs. All potentials reported as E₁/₂ (Eₚ⁺ + Eₚ⁻)/2 in V vs. FeCl⁺/FeCl⁻ at 0.1 Vs⁻¹ scan rate and quoted to the nearest 0.01 V. From ref. 18. |

Coulometry confirmed the first reductions of 1 and 2 were one-electron processes and the solutions were observed to acquire a blue colour. Solutions of 1‘ and 2‘ were both found to be EPR active and gave signals consistent with the generation of radical anions with gₕ values of 2.0107 and 2.0105, respectively (see SI). Both of these gₕ values have increased with respect to 3‘ and 4‘ resulting from larger n-spin population due to an increase in spin-orbit coupling, an effect promoted by the presence of heavy (S versus O) atoms (see SI for DFT calculations illustrating S-character of the molecular orbitals). As with 3‘ and 4‘ no hyperfine splittings were observed in the EPR spectra. The second reduction process of both species was also probed using EPR spectroscopy. Direduction leads to the formation of even more intensely blue solutions, however these solutions were found to be EPR silent, with only small residual signals attributed to the presence of 1‘ and 2‘ (5% and 14% respectively).
The reduction behaviour of 1 and 2 was probed further by spectroelectrochemical methods with both the in situ one- and two-electron reductions of 1 and 2 followed by UV/vis/NIR spectroscopy (Figure 5). Upon first reduction, the main band corresponding to the neutral species reduced in intensity with new bands forming, red shifted by 98 nm to 962 nm for 1 and by 116 nm to 954 nm for 2 (see ESI), mimicking the behaviour of 3 and 4 following reduction. The extinction coefficients for these two new bands doubled in intensity compared to the neutral species. An additional considerably lower energy peak was observed at 1568 nm for 1 and 1491 nm for 2\( \text{e}^{-}\) . Absorption bands in the NIR have been observed previously for PDI radicals, for example in a tetrachloro-tetracyano-PDI monoanion,\(^{20}\) but the wavelengths observed here are at notably lower energy and in the SWIR region, to our knowledge the first reported examples of such absorption in PDIs.

![Figure 4](image_url) **Figure 4.** Cyclic voltammograms of 1 (bottom) and 2 (top) recorded in 1,2-dichlorobenzene containing [Bu\textsubscript{4}N][BF\textsubscript{4}] (0.4 M).

As the second reduction proceeded the 1\( \text{e}^{-}\) and 2\( \text{e}^{-}\) peaks diminished in intensity and new bands corresponding to the 1\( \text{e}^{2}\) and 2\( \text{e}^{2}\) species were formed, blue shifted to 684 nm and 687 nm, respectively. The blue shift from the monoanion to the dianion of PDIs is well documented, with the main dianion absorbance often lying between the main band of the anion and the neutral species,\(^{19,21,22}\) however in this case this shift is even more pronounced with the dianion absorbances appearing 180 nm and 151 nm below that of the absorbance of 1 and 2 respectively. The dianion absorbances also appear to show vibrational structure, often seen in neutral PDIs, but missing from the broad featureless absorptions of 1 and 2. Both reductions of 1 and 2 were shown to be reversible as the neutral spectra were regenerated upon reoxidation.

In conclusion we demonstrate that it is possible to shift the absorption bands of PDIs to significantly lower energy through a combination of diimide thionation and bay-region amine functionalization. Our results include examples of neutral PDIs with absorption maxima in the NIR and monoanionic PDI radicals with absorption in the SWIR, in both instances at lower energy than any previously reported examples. In one case, 2, the strong absorbance across an impressive range of the solar spectrum leading to the compound’s black colour suggests particular promise in a range of applications. We believe our strategy demonstrates great promise for further investigations into the development of NIR dyes based on PDIs and also their incorporation into OPVs.

![Figure 5](image_url) **Figure 5.** UV/vis/NIR spectra of 1/1\( \text{e}^{-}/1\) recorded in 1,2-dichlorobenzene containing [Bu\textsubscript{4}N][BF\textsubscript{4}] (0.4 M). The spectrum of the neutral species is represented by the black line, the anion the red line and the dianion the blue line.
N.R.C. gratefully acknowledges a Royal Society Wolfson Merit Award. CCDC 1434978, 1434979 and 1434980 contain the supplementary crystallographic data for this paper for 1, 2 and 4 respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Notes and references