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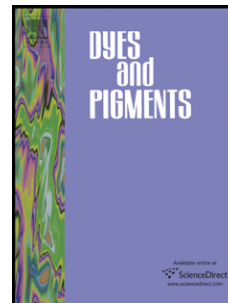
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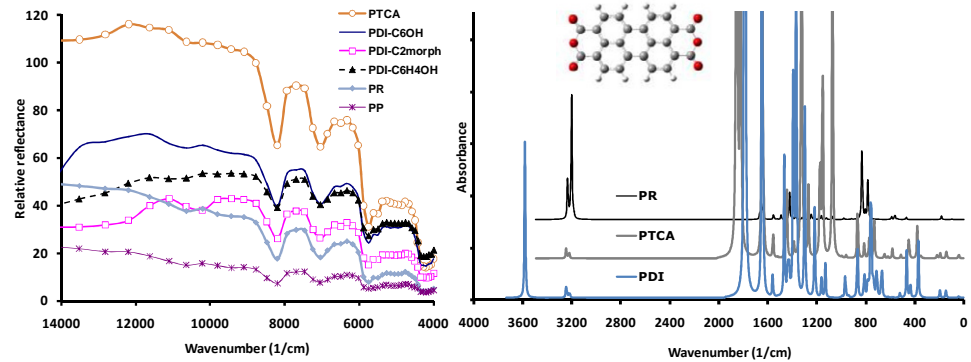
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Interpreting the near-infrared reflectance of a series of perylene pigments

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Abstract

Near-infrared (NIR) reflecting pigments offer the potential to incorporate thermal insulating qualities into paint coatings. Experimental reflectance measurements are presented of a series of perylene based pigments, revealing significant variations in the NIR region as a function of derivatisation and substitution. Theoretical methods are applied to account for the observed trends. Derivatisation of perylene leads to an extension of the π -aromatic system, resulting in a bathochromic shift of UV/Vis absorption maxima towards the NIR region. However, this is insufficient to account for the observed variations in NIR reflectance. In comparison, overtones and combination modes of fundamental IR vibrations appear to be more important in explaining the observed variations in NIR reflectance/absorbance. Aromatic groups lead to a small number of intense NIR bands, while alkyl groups generally lead to a greater number of less intense NIR bands. However, neighbouring group effects and/or a molecular dipole moment can substantially alter the intensity of these bands.

Keywords:

Pigments, Solar absorption, Near-infrared reflectance, anharmonicity, overtone, combination mode

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1. Introduction

Only 38 % of solar energy reaching the Earth's surface is in the form of visible light. The remaining 62 % is composed mainly of lower energy near infrared radiation (53 %) and a small proportion of higher energy ultraviolet radiation (~9 %). Considerable effort has been directed to the development of pigments or additives that reflect UV light or protect coatings against UV damage [1], [2]. Near-infrared light makes no contribution to the visible appearance (colour) of a material, however, absorption of NIR radiation does result in heat gain. For many buildings the amount of heat gained from NIR light, over the course of a day, can be substantial and generally the only means to combat this is through costly conventional insulation. However, the development of pigments that have a low NIR absorbance (i.e. a high NIR reflectance) and can be applied to the exterior of buildings, might provide a low cost alternative for prevention of heat "build-up."

The electronic properties of perylene based compounds (Fig. 1a) have made them suitable for a wide variety of applications including, electro-photographic photoreceptors, light-emitting diodes, field-effect transistors, solar cells and other optoelectronic photonic devices [3]. The key to the optoelectronic characteristics of perylene is the conjugated π -system of the polycyclic aromatic structure (Fig. 1a). A considerable amount of research into perylene compounds has focussed on either tuning the absorption of the molecules to specific bands, increasing the range of frequencies absorbed or in controlling the electron transport for organic based electronics. However, perylene dyes also have a number of properties that make them suitable for incorporation into coatings including, high thermal stability, high tinctorial strength, good weather stability and good photo-stability.

Derivatization of perylene can be used to influence both structural and electronic properties of the ring system and can therefore be used to change the optoelectronic and reflectance properties. One of the principal derivatives of perylene is perylene-3,4:9,10-tetracarboxylic dianhydride (PTCA) [4-6] (Fig. 1b) which can be further modified by introduction of substituents into the bay region at positions 1, 6, 7 and 12. Alternatively, PTCA

can be converted into perylene-3,4:9,10-tetracarboxylic diimide (PDI) (Fig. 1c) by reaction with primary amines which enables introduction of substituents at the N-atom of the resulting diimides [7].

A wide range of experimental and theoretical studies have explored the synthesis and applications of perylene compounds. For example Würthner et al. [8] carried out a detailed study of bromination of PTCA and subsequent imidization, identifying issues relating to the regioselectivity of these reactions. Through a careful purification process they were able to isolate pure 1,7-dibromoperylene bisimide and then to proceed to synthesise 1,7-di-functionalised PDIs with a range of interesting properties. Pichierri [9] used density functional theory to investigate the effects of electron-donating and electron-withdrawing substituents on the electronic properties of PDI, for potential application as organic semiconductors. Schmidt et al. [10] subsequently reported the synthesis of a range of PDI derivatives with halide substituents in the bay region (positions 1, 6, 7 and 12) and fluorinated imide substituents. The influence of the substituents on the electronic properties of the compounds was characterised by cyclic voltammetry and several compounds were identified as suitable to act as n-channel transistors. Complementary to this work, Chai et al. [11] carried out a DFT study of electron-withdrawing substituent effects on the properties of perylene bisimide derivatives and found important trends for tuning the geometry of these molecules, to achieve high performance as semiconductors.

Liang et al. [12] used density functional theory to further explore the structures and spectra of 1,7-functionalised PDI derivatives and found good consistency between theory and experiment for UV/Vis and IR spectra. They noted that the twisting of the perylene core, induced by side groups, depends mainly on the linking atoms and can have a significant effect on the electronic absorption spectra. A subsequent experimental study [13] of PDI with cyclic amino side groups revealed, that even small differences in molecular structure can have significant effects of the absorption characteristics and electrochemical properties. Interestingly, Dinçalp et al. [14] found that unsymmetrical substitution with electron donating

groups led to a broad absorption band in the NIR region offering the potential for incorporation in dye sensitised solar cells. In comparison, our recent experimental study [15], of a series of perylene derivatives dispersed in polypropylene revealed interesting properties in the NIR region including significant variation in the levels of NIR-reflectance. The purpose of this study is to combine experimental NIR measurements with detailed theoretical characterisation, to account for the observed trends in reflectance for this series of molecules.

2. Experimental and Computational Procedures.

2.1 Experimental NIR Reflectance Measurements

All PDI derivatives in this study were prepared as reported previously [15]. All pigments were dispersed in polypropylene (PP) using a 9000 Rheocord HAAKE mixer. NIR reflectance measurements of all the pigments dispersed in PP were performed on a Varian CARY 500 scan UV/VIS-NIR spectrophotometer, equipped with a “Praying Mantis” diffuse reflectance accessory (DRA). The PP samples containing dispersed pigments were moulded into rectangular sheets of uniform size and thickness and then cut into circular shapes with diameters equal to that of the standard sample holder. All of the samples had the same size, shape and thickness which eliminated errors resulting from these variables. The diffuse reflectance of different films was measured in the wavelength region 700 - 2500 nm using the standard sampling cup. The reflectance was measured as relative reflectance, which is defined as the ratio of flux reflected by a specimen to the flux reflected by a reference surface. PTFE (Teflon) powder of 1-mm particle size obtained from Sigma-Aldrich was used as the reference, as described elsewhere [17].

2.2 Computational Procedures

Standard density functional theory calculations were performed using the GAUSSIAN03 [16] and GAUSSIAN09 [17] computer program. The B3LYP functional has been successfully applied in previous studies investigating the structures, electronic properties and spectral characteristics of dye compounds [9], [12], [18], [19]. Therefore, optimized geometries were obtained for all species at the B3LYP/3-21G(d) and B3LYP/6-31G(d) levels of theory.

Vibrational frequencies were used to characterize each stationary point as a local minimum (no imaginary frequencies).

Three key intramolecular distances have previously been defined to characterise the structures of perylene derivatives (Fig. 2) [9], [20]. The D_{XX} value is defined as the distance between the central atoms of the 3,4-functional group and the 9,10-functional group, the D_{OO} is defined as the distance between the oxygen atoms of the carbonyl groups at the 3- and 10-positions and the d_{OO} value is defined as the distance between the oxygen atoms of the carbonyl groups at the 3- and 4-positions. These three structural values are related to the degree of aromatisation in the system and are sensitive to changes in the level of π -conjugation, as a result of different substituents [20].

Harmonic vibrational frequency analysis was performed at the B3LYP/6-31G(d) level on the corresponding geometries to provide simulated IR spectra. Anharmonic vibrational frequency analysis was performed at the B3LYP/3-21G(d) level, on the corresponding geometries to determine the degree of anharmonicity for fundamental vibrations and the corresponding vibrational overtone and combination modes. Due to the computational expense of these calculations, anharmonic analysis of the N-substituted PDI molecules was performed on 50% fragments of the total molecules i.e. the fragments consisted of the substituent, a diimide group and a naphthalene subunit of the perylene core. Vibrational modes associated with the C-H bonds introduced in place of the bridging C-C bonds are excluded from the analysis and discussion.

Charge population calculations were performed with full natural bond order (NBO) population analysis [21] Electronic absorption calculations were carried out using time-dependant density functional theory (TD-DFT) at the B3LYP/6-31G(d) level to obtain excited states and vertical excitation energies. The simulated spectra were determined from the excitation energies and corresponding oscillator strengths using Gaussian broadening with a peak half-width at half height of $\sim 2500 \text{ cm}^{-1}$.

Extended tables of structural parameters and atomic charges can be found in Tables S1 and S2 of the Supplementary Data, respectively.

3. Results and Discussion

Derivatives of perylene-3,4:9,10-tetracarboxylic diimide (PDI) with N-hexanol (PDI-C₆OH), N-ethylmorpholine (PDI-C₂morph), and N-para-phenol (PDI-C₆H₄OH) substituents have been found to exhibit interesting near-infrared characteristics [15]. Plots of the relative NIR reflectance of these PDI derivatives in polypropylene films are depicted in Figure 3. Also included are analogous reflectance measurements of perylene (PR) and the closely related perylene-3,4:9,10-tetracarboxylic dianhydride (PTCA) as well as the background reflectance measurement of a pure polypropylene (PP) film. The polypropylene film has strong absorptions at 5780 cm⁻¹, 7780 cm⁻¹ and 9250 cm⁻¹ which are evident in all systems. Nevertheless, it is clear from these plots that addition of the perylene derivatives to the PP matrix leads to a significant increase in relative reflectance of the films i.e. a significant decrease on the overall level of absorption. However, within this group of pigmented films there are significant variations. For example, the relative reflectance values range from 38 to 108 at 10240 cm⁻¹ (980 nm) and 20 to 65 at 6000 cm⁻¹ (1665 nm). As noted previously,[15] the PDI-C₆OH pigment is black in appearance but exhibits significantly greater reflectance than carbon black at 10,000 cm⁻¹. N,N'-Bis(2,6-diisopropylphenyl)-1,6,7,12-tetraphenoxyperylene-3,4:9,10-tetracarboxdiimide (LG) is a well-known NIR pigment, that is also based on a PDI core. However, it differs from the PDI based molecules of our current study in that it contains phenoxy substituents at the 1, 6, 7 and 12 positions, in the bay region of the perylene. For comparison, we have measured the NIR-reflectance of LG (Fig. 3) and found that it exhibits similar performance to PDI-C₆OH and PDI-C₆H₄OH in the 6000 – 8500 cm⁻¹ range. At frequencies below this range, the reflectance of LG is slightly lower than PDI-C₆OH and PDI-C₆H₄OH. In comparison at frequencies above 9000 cm⁻¹, the relative reflectance drops off significantly compared to all of the PDI-based molecules. Surprisingly PTCA exhibits greater reflectance than LG or any of the substituted PDI pigments at all but the lowest frequencies. In

comparison, the base perylene molecule (PR) exhibits quite low reflectance at low frequencies but there is a gradual increase in reflectance with frequency. At 6000 cm^{-1} the order of reflectance (and measured reflectance values) of the perylene based pigments is as follows:

PTCA (65) > PDI-C₆OH (43), PDI-C₆H₄OH (42), LG (39) > PDI-C₂morph (28) > PR (20)

Clearly, the different substituents have a significant effect on the reflectance/absorbance properties of the polypropylene films. By studying this series of molecules it should be possible to identify some general features that can be used to understand the NIR reflectance/absorbance of this class of materials.

The specular reflectance of a material is dependent on the refractive index and consequently on the electronic structure of the material. Therefore, variations in NIR-reflectance of these perylene based pigments could be the result of substituent effects, leading to a shift of electronic absorption maxima to/from the near-infrared region. Generally the compounds considered in this study give similar UV/Vis spectra comprised of three main peaks (Fig. 4). However, within this group of compounds there are subtle differences that can be related to the structural and electronic properties of the individual molecules.

The position of the first peak in the electronic spectrum of pristine perylene (PR) is calculated to occur at 429 nm in excellent agreement with the experimental value (430 nm), obtained in an N₂ matrix at 20 K [22]. This peak arises from a singlet transition from the HOMO to the LUMO. The HOMO of perylene is in fact a set of doubly degenerate π bonding orbitals located on the central bonds of the naphthalene subunits of the molecule (Fig. 5a). Likewise, the LUMO of perylene is composed of a set of doubly degenerate π^* antibonding orbitals located on the same bonds. The energy gap (E_{H-L}) between the frontier orbitals of perylene is 3.06 eV, providing a first approximation of the excitation energy, which plays an important role in determining the optical and electronic properties of the molecule. The second and third peaks, located at 253 nm and 189 nm, correspond to a complex set of excitations

involving transitions from a set of fourfold degenerate sub-HOMO π orbitals to a set of degenerate post-LUMO π^* orbitals, all of which are located in the bay region.

Derivatisation of perylene to PTCA leads to a decrease in E_{H-L} and a corresponding shift of all three peaks to longer wavelengths (Fig, 4a, Table 1). Similarly, conversion of PTCA to PDI leads to a further shift of the first and third peaks to longer wavelength but a slight shift of the second peak to shorter wavelength. The first peak of PDI is calculated to occur at 506 nm which is in satisfactory agreement with the experimental value (524 nm) in DMSO. However, we note that solvent effects can be significant for this class of compounds [23]. The peaks for PTCA and PDI arise from a similar set of electronic transitions, as noted for perylene [24]. However, the π -aromatic system of these molecules has been substantially extended to include the carbonyl groups of the anhydride and diimide groups, respectively, as can be seen from the HOMO and LUMO projections (Fig 5b). Nevertheless, these absorptions remain outside the NIR-region.

Several studies have looked at correlations between structural parameters, such as the length of the π -aromatic system (D_{XX}) and absorption characteristics of organic pigment molecules. Pschirer et al. [20] were able to correlate the maximum absorption in the UV/Vis region with the inverse squared length of the π -aromatic system and achieved a large bathochromic shift of the absorption maximum, by increasing the degree of annulation i.e. adding rylene units. Pristine perylene has a planar highly symmetric structure with bond lengths characteristic of aromatic rings. Likewise, the two key derivatives of perylene, PTCA and PDI, also have planar structures [12] and the introduction of the anhydride or diimide functionality leads to only modest changes in the bonding of the perylene core [25]. However, as noted above, the anhydride and diimide functionalities significantly increase the length of the π -aromatic system which leads to the observed bathochromic shift in the UV/Vis absorption spectra. The D_{XX} values (11.373 Å and 11.333 Å, respectively) for these two molecules are very similar which corresponds with the similarity in the position of the first peak in the UV/Vis spectrum. Likewise, the E_{H-L} values of PTCA and PDI are very similar but

substantially smaller than E_{H-L} for perylene, which is again consistent with the position of the first peaks in the UV/Vis spectra. These results also demonstrate that a significant lowering of the HOMO-LUMO gap could lead to increased NIR-absorption [3], [26].

The PDI molecule can be further derivatized via the introduction of substituents to the nitrogen atoms of the imides. The N-hexanol substituent (PDI-C₆OH) leads to a slight decrease in E_{H-L} , which corresponds with a shift of the first peak to slightly longer wavelength (Fig. 4b). The second peak is also shifted to longer wavelength, while the third peak is observed to move to shorter wavelength upon substitution. Table 1 also includes data for the N-butanol (PDI-C₄OH) and N-ethanol (PDI-C₂OH) derivatives of PDI, to highlight any effects that might arise from decreasing the substituent alkyl chain length. It is clear from the E_{H-L} and UV/Vis data that the position of the absorption maxima for this series of molecules is largely independent of the length of the substituent alkyl chain, within this range (C2 – C6). For completeness we also provide data for the N-butyl (PDI-C₄) derivative. Comparison between PDI-C₄ and PDI-C₄OH reveals that there is essentially no difference in the UV/Vis absorption characteristics of these two molecules, indicating that this is independent of the terminal OH substituent.

The position of the first peak of the PDI-C₂morph molecule also appears to be independent of the N-alkyl substituent. However, the E_{H-L} for PDI-C₂morph is significantly smaller than for the other PDI derivatives and the second and third peaks are significantly shifted, suggesting involvement of the terminal morpholine group in the absorption characteristics. Introduction of N-aryl groups leads to either a slight increase or no change in E_{H-L} and corresponding shifts in the absorption maxima. Comparison between the N-phenyl derivative (PDI-C₆H₅) and the N-para-phenol derivative (PDI-C₆H₄OH), reveals only a marginal difference in E_{H-L} . However, there is a slight shift of the first and second peaks to longer wavelength, with a more significant shift of the third peak. The E_{H-L} for LG is 2.526 eV which is only marginally lower than E_{H-L} for PDI-C₆H₅, indicating that the addition of phenoxy groups to the bay region of the perylene core has a minimal effect on the electronic spectrum of this system.

As noted above, changes in the absorption maxima can often be correlated with structural variations induced by substituents. The introduction of R groups to the nitrogen atoms of the diimides (P1 – P4) i.e. end-substitution, is found to have a slight effect on the local bond lengths (N-C_f) but relatively little effect on the more remote bonds. However, in all of the substituted diimide compounds there is an overall lengthening of D_{XX} and d_{OO} and a shortening of D_{OO} . This is due largely to changes in the O-C_f-N and C_f-N-C_f angles of the diimides, in agreement with the observation of Pichierri, [9] that an increase in D_{XX} generally correlates with a decrease in D_{OO} . However, given the small magnitude of the variations, it is difficult to detect a direct relationship between these structural parameters (D_{XX} , D_{OO} and d_{OO}) and the observed shifts in UV/Vis absorption maxima or NIR reflectance.

Han and co-workers [27-30] have shown that intermolecular interactions can have a significant effect on the photophysical and photochemical properties of chromophores. H-bonding to a range of chromophores is found to be significantly strengthened upon photoexcitation and has a significant effect on absorption and fluorescence spectra. Consequently, we have investigated the effect of H-bonding on the UV/Vis absorption spectra of selected perylene pigments. In particular, we have calculated the absorption spectra of PDI with a water molecule coordinated to the diimide group and found no change in the position of the first peak but a slight shift to longer wavelength (~ 4 nm) for the second peak and a shift to shorter wavelength for the third peak (~ 9 nm). Similarly, we investigated the effects of water coordination to both the carbonyl oxygen and the bridging oxygen of the anhydride groups and found that there is only a very slight shift of the first peak to longer wavelength (~ 4 nm) and no change at all for the second and third peaks. Therefore, unlike coumarin and fluoenone, [30] which are carbonyl chromophores, PDI and PTCA are relatively unaffected by intermolecular H-bonding.

In a similar context, we have investigated the effects of solvation through the application of a self-consistent reaction field (SCRF) with a dielectric constant of $\epsilon = 78.3553$,

which is appropriate for modelling water. In the case of PDI, the first peak in the electronic spectrum exhibits a shift to longer wavelength (~ 18 nm) but as for the explicit H-bonding interactions discussed above, this is insufficient to impact on absorbance in the NIR. We note that the second peak exhibits a similar shift to longer wavelength but that the third peak is unaffected. The PTCA pigment exhibits very similar behaviour in the presence of the water SCRF.

The energies of the frontier orbitals of PTCA and PDI based molecules show significant variation with substituent. However, as noted above there are only slight variations in E_{H-L} with N-substitution, which corresponds with the experimental observations of Klebe et al. [34] that N-substituted PDI monomers generally show closely related absorption maxima, regardless of the substituents. Pichierri [9] also observed that E_{H-L} remains almost constant for N-alkyl and N-aryl derivatives of PDI, due to a strong linear correlation ($R^2 = 0.9994$) between E_{LUMO} and E_{HOMO} . As Huang et al. [31] have noted, the nitrogen atoms of PDI are at a nodal plane for both the HOMO and LUMO. Therefore, the introduction of substituents at N is likely to have only an inductive effect on both frontier orbitals, leading to little change in E_{H-L} and the optical properties. The terminal OH groups of PDI-C₆OH, PDI-C₄OH and PDI-C₂OH are too remote to have any significant inductive effect on E_{H-L} . However, as noted above, the PDI-C₂morph derivative has a significantly lower E_{H-L} value than the other PDI derivatives. Figure 5c reveals that the HOMO of PDI-C₂morph is located on the substituent rather than the perylene core and is significantly raised in energy, which should lead to a decrease in excitation energy. However, the first peak remains in essentially the same position because this still corresponds to excitation from the π bonding orbital to the π^* anti-bonding orbital of the PDI. In comparison, peaks 2 and 3 are moved to longer wavelengths compared to the other alkyl substituted PDIs, due to the influence of the morpholine group. In particular, the peak at 343 nm is largely due to a singlet excitation from the HOMO, located on morpholine, to a post-LUMO orbital located on the PDI. However, there are also contributions from excitations of lower energy occupied orbitals delocalised across the PDI and ethyl groups to the LUMO. Likewise, the peak at 255 nm involves singlet excitations from occupied orbitals on

morpholine to unoccupied orbitals centred on the PDI. Pichierri [9] noted that PDIs with N-methyl-pyridyl cation and N-p-phenylazophenyl substituents also have HOMOs located on the substituents and exhibit small E_{H-L} values and we suggest that these compounds might therefore exhibit similar features in their UV/Vis spectra.

The para-OH group of PDI-C₆H₄OH appears to have a slight inductive effect, with the first and second peaks moving to slightly longer wavelengths compared to PDI-C₆H₅. The third peak shows the largest move to longer wavelength because it largely arises from excitations of either occupied orbitals delocalised across the phenol groups to unoccupied orbitals of the PDI or, alternatively, from occupied PDI orbitals to unoccupied orbitals delocalised across the phenol groups. However, once again these variations in UV/Vis peak positions are insufficient to account for the observed trends in reflectance.

NIR absorption can also arise from overtones and combinations of fundamental IR vibrations. Simulated IR spectra for selected molecules are shown in Figure 6. The IR spectrum of perylene contains a range of intense peaks in the low frequency region including, out-of-plane distortions at 782 cm⁻¹ and 830 cm⁻¹, an in-plane rocking mode at 1423 cm⁻¹ and aromatic C-C stretches at ~ 1650 cm⁻¹. However, two of the most intense peaks in this spectrum occur in the high frequency region (~3200 cm⁻¹) and are due to asymmetric and symmetric C-H stretches. The PTCA molecule has a range of very intense peaks in the low frequency region of the spectrum due to, C-O vibrations of the anhydride (1070, 1151 cm⁻¹), C=O stretching (1853 cm⁻¹) and C-C aromatic stretches (1645 cm⁻¹). However, introduction of the dianhydride groups removes several C-H bonds and the remaining vibrations associated with C-H stretching (~ 3250 cm⁻¹) are extremely weak.

The most intense absorptions in the IR spectra of the PDI based molecules (Fig. 6b) are due to the C=O bonds of the carboximides (1780 – 1860 cm⁻¹) and the aromatic C-C bonds of the perylene core (1260 – 1650 cm⁻¹). For the unsubstituted PDI molecule the only significant absorption in the high-frequency region is the N-H stretch of the carboximide, located at 3523

cm^{-1} . Substitution at the nitrogen of the carboximide naturally removes the N-H stretch from the IR spectrum, however, this generally introduces a range of new absorption peaks in the high frequency region ($3000 - 3240 \text{ cm}^{-1}$), corresponding to C-H vibrations of the alkyl chains. For PDI-C₆OH, PDI-C₄OH and PDI-C₂OH, an additional low intensity absorption at $\sim 3750 \text{ cm}^{-1}$ corresponds to the O-H stretch of the terminal alcohols. PDI-C₂morph also has a collection of alkyl C-H absorptions but not the O-H stretch. In PDI-C₆H₄OH the most intense new peak in the high frequency region is due to the phenolic OH stretch (3752 cm^{-1}). However, there are also a collection of low-intensity aromatic C-H stretches ($3175 - 3240 \text{ cm}^{-1}$). In the case of LG, there are vibrations arising from both the alkyl and aromatic C-H bonds and these lead to a significant cluster of peaks in the high frequency region, that are more intense than those observed for PDI-C₆H₄OH or PDI-C₆OH.

Overtone of the high-frequency fundamental vibrations (C-H, O-H and N-H) make the most significant contribution to absorption in the NIR region [32]. Likewise, combinations of these high-frequency fundamental vibrations also extend into the NIR region. Therefore, we focus primarily on these high frequency modes to gain a better understanding of the NIR-reflectance/absorbance characteristics of these selected pigments. Vibrational overtone and combination bands occur as a result of anharmonicity, which arises from the fact that the potential energy of bonds in real molecules is better described by Morse functions, than the idealised quadratic functions of the harmonic oscillator [32]. Anharmonicity also arises from the fact that there is a non-linear relationship between the dipole moment of a bond and the displacement of the bonded atoms during a vibration [32]. Generally anharmonicity leads to a lowering of the frequency of the fundamental vibrations, overtones and combination modes. Table 2 presents a list of the high-frequency IR active fundamental vibrations, determined harmonically and anharmonically, with the corresponding first overtones ($2\nu_1$) and binary combinations ($\nu_1 + \nu_2$), for PR, PDI and PTCA.

PR has three high frequency fundamental vibrations of strong, medium and weak intensity, respectively. Both the harmonic and anharmonic overtones extend into the NIR

region. However, overtones from the strong intensity asymmetric and medium intensity symmetric stretches of the C-H bonds at the 3, 4, 9 and 10 positions, lead to the greatest absorption in the NIR region. Similarly, combination bands of the three high frequency fundamental vibrations of PR extend into the NIR region and lead to significant absorbance. The high symmetry of this molecule also facilitates coupling of C-H vibrations with aromatic C-C vibrations leading to additional complex combination modes in the NIR (not shown).

Derivatisation of PR to PTCA removes the C-H stretches arising from positions 3, 4, 9, and 10 of the perylene ring. Consequently there are no corresponding overtone or combination modes, leading to significantly reduced absorbance in the NIR. However, the electron withdrawing dianhydride groups also result in the remaining high-frequency fundamental vibrations of PTCA moving to slightly higher frequency than the corresponding vibrations of PR. Consequently, the remaining overtones and combination modes extend further into the NIR than for PR. However, as noted earlier, these vibrations are extremely weak, leading to minimal absorption in the NIR, which explains the large variation in NIR absorbance/reflectance observed between PR and PTCA. PDI has only one strong intensity absorption in the high frequency region, due to the N-H stretch, and several weak intensity C-H modes, and therefore, should have greater NIR reflectance than PR but lower reflectance than PTCA.

The PDI derivatives share features in common with PTCA in that they have a reduced number of perylene C-H stretches. However, as noted above, the N-hexanol, N-ethylmorpholine, and N-phenol substituents introduce additional C-H and O-H vibrations (Table 3) that have overtones and combinations in the NIR. In the first instance, this accounts for the lower NIR reflectance of these molecules relative to PTCA. However, additional factors need to be considered to account for the relative absorbance of the PDI molecules. Importantly, combination bands can only arise from vibrations involving the same functional group and having the same symmetry [32]. Therefore the perylene C-H bonds remain isolated from the

high-frequency vibrations of the N-substituents and only make a minimal contribution to the observed NIR absorbance.

PDI-C₆OH and PDI-C₆H₄OH exhibit similar NIR reflectance levels at 6000 cm⁻¹, despite having quite different profiles in the high-frequency IR region. For example, PDI-C₆OH has quite a large number of high-frequency C-H fundamental vibrations which leads to a large number of overtones in the NIR (Table 3). In comparison, PDI-C₆H₄OH has relatively few high frequency vibrations and therefore has a correspondingly small number of overtones. However, one of the factors affecting the intensity of overtone and combination bands is the degree of anharmonicity associated with the vibrations. In this regard the average anharmonicity of the aromatic C-H vibrations is higher than the average anharmonicity of the alkyl C-H vibrations. Therefore, the overtones of the aromatic groups are of higher intensity than the corresponding hexyl overtones. Likewise, both molecules have high frequency O-H stretches but this mode is quite weak in the PDI-C₆OH molecule. In comparison the O-H stretch of PDI-C₆H₄OH is quite strong, which contributes to higher absorption in the NIR, partly offsetting the advantage of having fewer high-frequency C-H vibrations. The LG pigment has a similar reflectance profile to PDI-C₆OH and PDI-C₆H₄OH at the low frequency region of the NIR-region. However, LG contains multiple alkyl and aromatic groups, with a large number of high-frequency C-H fundamental vibrations. Consequently, this leads to a large number of overtones and combinations in the high-frequency end of the NIR-region, and significantly diminished reflectance.

Equation 1 demonstrates the relationship between the energy of an oscillating bond (E), the force constant of the bond (k) and the effective mass of the subunit (m_{eff}).

$$E = \frac{h}{2\pi} \sqrt{\frac{k}{m_{\text{eff}}}} \quad (1)$$

Consequently, the atomic masses and bond strengths of the functional groups in a molecule have a significant impact on the positions and intensities of NIR bands. Table 3 includes data on force constants and effective masses associated with the high frequency vibrations of the selected PDI derivatives.

Comparison of PDI-C₆OH with PDI-C₆H₄OH reveals that the force constants for the high frequency aromatic C-H vibrations are higher than the force constants for alkyl C-H stretches, which leads to a significant difference in the intensities of the absorption bands of the corresponding overtones and combinations. Additionally, the C-H force constants for the phenol group of PDI-C₆H₄OH are fairly consistent, contributing to a consistent level of absorption by this group of vibrations. In comparison, the C-H force constants of the hexyl group of PDI-C₆OH span a larger range than observed for the phenyl group, which leads to variability in absorption intensities. In comparison, there is relatively little difference in the effective masses of the CH and CH₂ vibrational modes.

PDI-C₂morph like PDI-C₆OH contains a largely alkyl based substituent but exhibits a significantly poorer level of NIR reflectance. The ethylmorpholine substituent of PDI-C₂morph contributes a large number of high-frequency alkyl C-H vibrations to the IR spectrum of the molecule. However, unlike PDI-C₆OH, all of the CH₂ groups are adjacent to electronegative substituents. Consequently, neighbouring group effects are particularly strong in PDI-C₂morph, leading to larger force constants compared to the hexyl group of PDI-C₆OH and stronger absorption. A significant number of the ethylmorpholine vibrations are also asymmetric vibrations. These asymmetric vibrations are generally more anharmonic than corresponding symmetric stretching vibrations and consequently overtones of the asymmetric stretches are generally more intense. This makes a significant contribution to the lower NIR reflectance of PDI-C₂morph.

Band intensity (I) is also directly proportional to the square of the change of the dipole moment (μ) according to:

$$I = \left(\frac{d\mu}{dQ} \right)_0^2 \quad (2)$$

where Q represents the normal coordinate of the vibration. The bond dipole moments are naturally very dependent on the structure, symmetry and charge distributions within the molecule. Molecular dipole moments are also particularly important, as coupling of molecular vibrations with changes in the dipole moment cause absorption in the near infrared region [33].

The charge distribution for perylene is quite simple with the bridging carbon atoms almost neutral while the peripheral carbons carry negative charges that are balanced by the positive charges of the hydrogen atoms. Upon conversion to PTCA or PDI there is only a very minor redistribution of the charges of the perylene core, while the peripheral carbon atoms show decreases in charge due to the introduction of the anhydride or diimide groups, respectively. Naturally the carbon atom of the carbonyl groups carry a substantial positive charge (+0.684) and the adjacent oxygen and/or nitrogen atoms carry substantial negative charges (-0.580 and -0.657, respectively). The polarity of these bonds contributes to the strong intensity of their corresponding IR vibrational modes. Nevertheless, these planar molecules have no overall molecular dipole moment.

Introduction of both N-alkyl and N-aryl substituents to PDI has only a minor effect on the charges of the diimide groups, while the perylene core remains largely unchanged. Therefore, the conformations and charge distributions of the terminal substituents are most important in determining the dipole moments of these molecules.

The lowest energy structures of PDI-C₆OH (P1), PDI-C₄, PDI-C₄OH and PDI-C₂morph have the alkyl chains in an extended conformation (Fig. 7), in agreement with crystal structures for N-alkyl substituted PDIs [34]. Additionally, PDI-C₆OH, PDI-C₄, PDI-C₄OH all have C₂ symmetry with terminal substituents aligned along the axis on opposite sides of the molecule

so that there is no net dipole moment. For PDI-C₂morph both high symmetry (C₂) and low symmetry structures were identified as local minima. However, the C₁ structure (Fig. 7) has one of the morpholine rings twisted relative to the C₂ axis of the molecule and this structure is 2.80 kJ mol⁻¹ lower in energy than the C₂ structure. Naturally, the C₂ structure of PDI-C₂morph has no net dipole moment. However, in the C₁ structure the twisting of the morpholine ring results in the molecule having an overall dipole moment of 0.486 D, directed at an angle of 30-45° to the plane of the perylene ring. The presence of this conformation within pigment particles will have a substantial effect on NIR absorbance, and accounts for the lower reflectance observed by the PDI-C₂morph system. The lowest energy conformation of pigment PDI-C₆H₅ and PDI-C₆H₄OH have the phenol substituents perpendicular to the plane of the perylene ring, which is in accord with previously reported [9] aryl substituted PDI structures. However, the symmetrical nature of these substitutions means that there is no net dipole moment.

One of the limitations of these compounds is their poor solubility in a range of solvents, due to strong intermolecular packing of the pigment molecules. One way to address this is through the addition of bulky substituents, to both the bay region of the perylene and the nitrogen of the diimide of PDI. As shown by LG, these may have little effect on the molecular electronic spectrum of the compound but can have a significant effect on the vibrational spectrum, particularly in the high frequency region.

4. Conclusions

Experimental measurements reveal that the order of reflectance (and measured relative reflectance values) at 6000 cm⁻¹ for selected perylene based pigments is as follows:



Theoretical calculations combined with these experimental measurements have enabled interpretation of the absorption spectra of these pigments and provided a basis for understanding the variations in near-infrared (NIR) reflectance.

Derivatisation of perylene to perylene-3,4:9,10-tetracarboxylic dianhydride (PTCA) and perylene-3,4:9,10-tetracarboxylic diimide (PDI) leads to an extension of the π -aromatic system resulting in a decrease in the energy gap (E_{H-L}) between frontier orbitals. Consequently, there is a bathochromic shift of UV/Vis absorption maxima towards the NIR region. Substitution at the nitrogen of PDI generally has only an inductive effect on the π -aromatic system, leading to minor shifts in the UV/Vis spectra. However, these trends are insufficient to account for the observed variations in NIR reflectance.

Infrared spectra reveal the presence of a number of high-frequency fundamental vibrations that have overtones and combination modes in the NIR region. However, the number and strength of these high-order modes is functional group dependant. Aromatic groups lead to a small number of intense NIR bands, while alkyl groups generally lead to a greater number of less intense NIR bands. The intensity of the bands can be related to the anharmonicity of the fundamental vibrations, the force constants and change in dipole moment of the vibrating bonds. However, neighbouring group effects and/or a molecular dipole moment can substantially alter the intensity of these bands. These results lead us to the conclusion that to achieve high reflectance/low absorbance in the NIR region, it is necessary to use pigments that have a minimal number of functional groups with high-frequency fundamental vibrations, and sufficient symmetry so as to ensure that the molecules have no net dipole moment, as is found in PTCA.

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Figure Captions:

Figure 1 (a) Perylene (PR), (b) perylene-3,4:9,10-tetracarboxylic dianhydride (PTCA), (c) perylene-3,4:9,10-tetracarboxylic diimides (PDI).

Figure 2. Designation of key atoms and distances in perylene derivatives.

Figure 3. NIR reflectance of selected perylene based pigments and polypropylene.

Figure 4. Simulated UV/Vis spectra for (a) PDI based molecules, (b) for PTCA based molecule and (c) for perylene molecules.

Figure 5. Frontier Molecular Orbitals of selected perylene based pigments

Figure 6. IR spectra for (a) perylene and derivatives and (b) PDI-based derivatives.

Figure 7. Optimised Geometries of selected PDI-based pigments.

Table 1. Selected molecular properties for perylene and perylene derivatives.

System		D_{XX} (Å)	D_{OO} (Å)	d_{OO} (Å)	E_{H-L} (eV)	UV/Vis (nm)		
						First peak	Second Peak	Third Peak
PR					3.060	429	253	189
PDI	R = H	11.333	11.448	4.551	2.541	506	317	264
PDI-C₆OH	R=C ₆ H ₁₂ OH	11.416	11.396	4.571	2.535	511	330	238
PDI-C₄OH	R=C ₄ H ₈ OH	11.414	11.397	4.571	2.535	509	330	236
PDI-C₄	R=C ₄ H ₉	11.415	11.396	4.574	2.534	508	330	236
PDI-C₂OH	R=C ₂ H ₄ OH	11.415	11.396	4.571	2.533	509	330	233
PDI-C₂morph	R=C ₂ H ₄ NC ₄ H ₈	11.414	11.398	4.571	2.131	510	343	255
PDI-C₆H₅	R=C ₆ H ₅	11.416	11.395	4.581	2.541	509	322	236
PDI-C₆H₄OH	R=C ₆ H ₄ OH	11.421	11.392	4.582	2.543	515	326	251
PTCA	R', R'' = H	11.373	11.462	4.449	2.558	500	340	236

Table 2. High frequency IR active Vibrations, Overtones and Combinations (cm^{-1}).

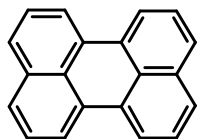
System	Fundamentals		Overtones ($2\nu_1$)		Combinations ($\nu_1 + \nu_2$)		
	Harmonic ^a	Anharmonic	Harmonic	Anharmonic	Harmonic	Anharmonic	
PR	3240.8	3079	6482	6125	6430	6123	
	(m)						
	3208.5 (s)	3053	6417	6103	6449	6122	
	3189.7 (w)	3027	6379	6072	6398	6070	
PDI	R = H	3523.2 (s)	3354	7046	6674	6773	6463
		3249.5 (w)	3106	6499	6197	6759	6435
		3236.0 (w)	3075	6472	6136	6745	6428
		3221.6 (w)	3067	6443	6136	6485	6149
						6471	6157
				6458	6124		
PTCA	R', R" = H	3253 (w)	3113	6506	6209	6491	6155
		3239 (w)	3078	6478	6141	6479	6186
		3227 (w)	3077	6453	6121	6466	6141

^a labels indicate intensity of peak: s = strong, m = medium, w = weak.

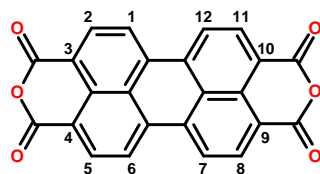
Table 3. Vibrational data for N-substituents of PDI-C₆OH, PDI-C₂morph and PDI-C₆H₄OH (cm⁻¹).

System	Group	Fundamentals				Overtones (2ν ₁)	
		Harmonic ^a	Anharmonic	<i>k</i>	<i>m</i> _{eff}	Harmonic	Anharmonic
PDI-C₆OH	O-H	3470 (w)	3283	7.566	1.066	6940	6399
	C-H	3230 (w)	3075	6.723	1.093	6461	6136
	C-H	3114 (m)	2947	6.316	1.106	6228	5875
	C-H	3074 (w)	2994	6.152	1.104	6150	5801
	C-H	3064 (m)	2882	5.846	1.057	6128	5709
	C-H	3060 (w)	2871	5.826	1.056	6120	5699
	C-H	3052 (w)	2892	6.042	1.100	6106	5746
	C-H	3034 (m)	2867	5.739	1.056	6073	5707
	C-H	3028 (w)	2863	5.698	1.055	6056	5679
	C-H	3000(m)	2841	5.871	1.107	6002	5602
	C-H	2977 (m)	2849	5.491	1.052	5954	5652
PDI-C₂morph	C-H	3231 (w)	3075	6.725	1.093	6462	6108
	C-H	3195 (w)	3061	6.542	1.087	6390	5958
	C-H	3128 (w)	2946	6.107	1.059	6257	5888
	C-H	3121 (w)	2965	6.238	1.087	6243	5831
	C-H	3121 (m)	2964	6.300	1.098	6242	5893
	C-H	3118 (m)	2959	6.277	1.096	6236	5830
	C-H	3103 (m)	2936	6.178	1.089	6207	5754
	C-H	3092 (m)	2927	6.140	1.090	6185	5735
	C-H	3024 (s)	2846	5.743	1.066	6048	5612
	C-H	3018 (w)	2851	5.720	1.065	6037	5671
	C-H	2972 (s)	2816	5.568	1.070	5945	5528
	C-H	2960 (m)	2798	5.524	1.070	5920	5521
	C-H	2955 (m)	2794	5.504	1.069	5910	5481
	PDI-C₆H₄OH	O-H	3524 (m)	3327	7.799	1.066	7049
C-H		3241 (w)	3083	6.765	1.094	6480	6074
C-H		3231 (w)	3076	6.723	1.093	6461	6136
C-H		3223 (w)	3068	6.692	1.093	6448	6026
C-H		3219 (w)	3047	6.646	1.088	6439	6011
C-H		3187 (m)	3022	6.510	1.088	6373	5935

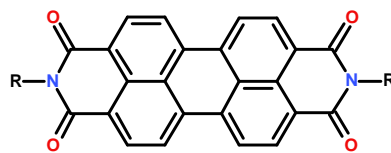
^a labels indicate relative intensity of peak: s = strong, m = medium, w = weak.



1a

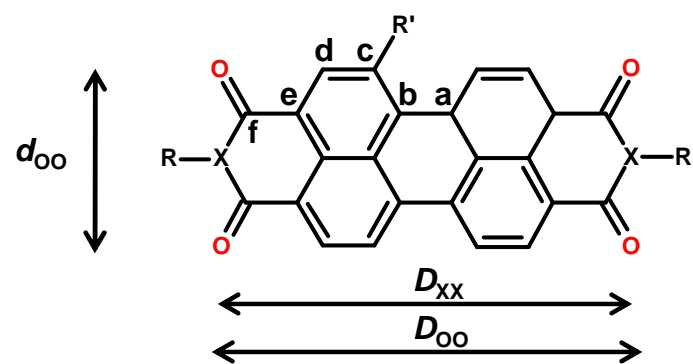


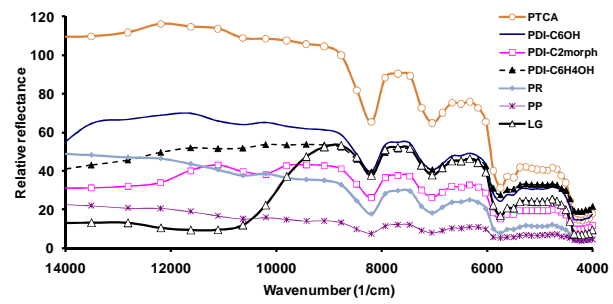
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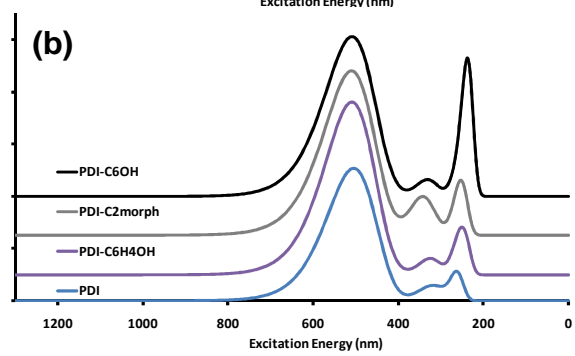
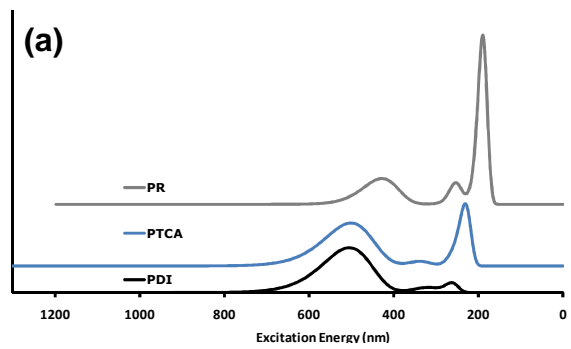


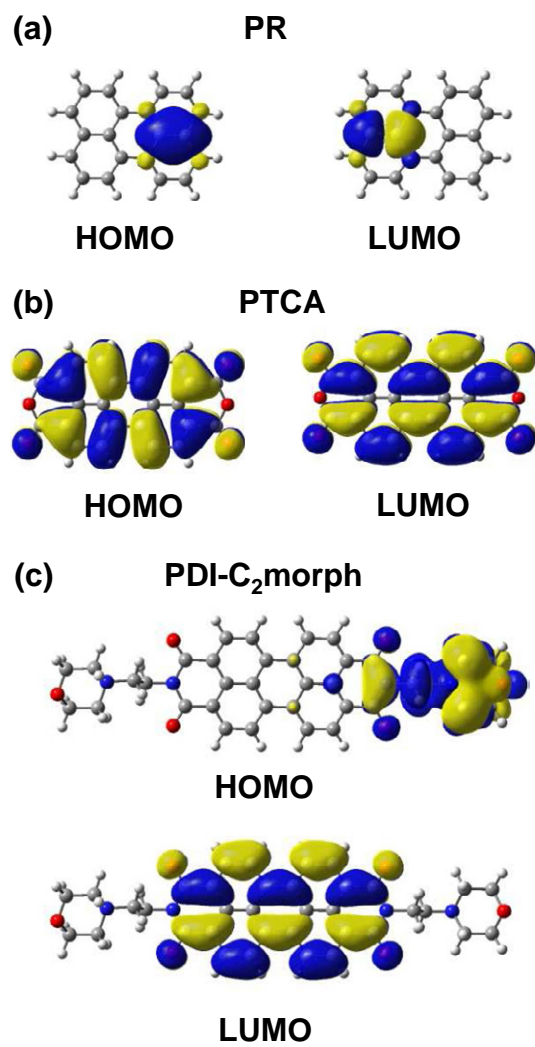
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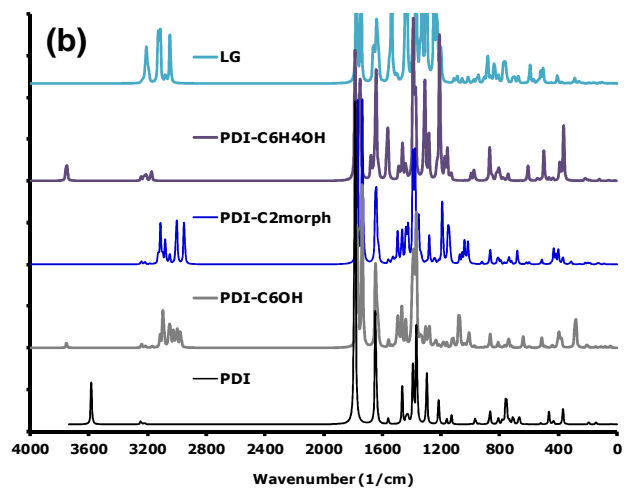
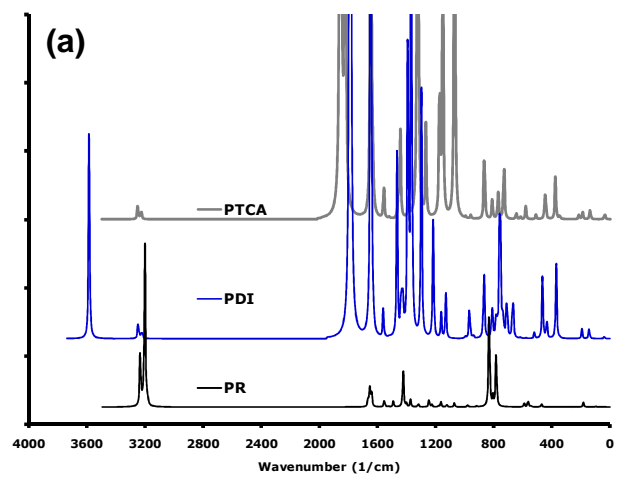
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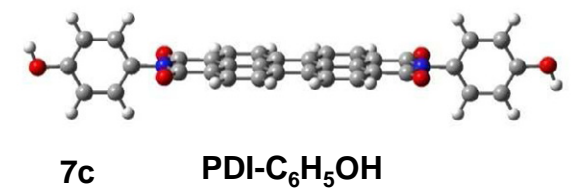
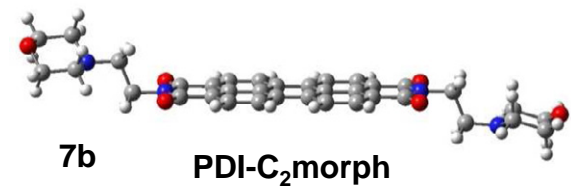
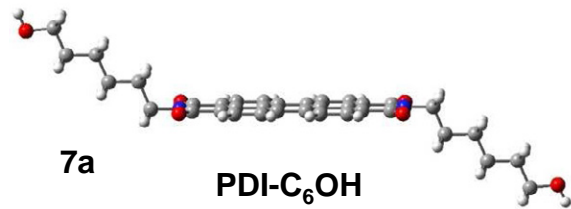


Table S1. Selected bond lengths (Å) and twist values (°) for perylene and perylene derivatives at B3LYP/6-31G(d)

System		D_{XX}	D_{OO}	d_{OO}	$r(R-X)$	$r(X-C_f)$	$r(C_f-O)$	$r(C_f-C_e)$	$r(C_e-C_d)$	$r(C_d-C_c)$	$r(C_c-C_b)$	$r(C_b-C_a)$	Twist
PR									1.375	1.406	1.392	1.477	0.0
PDI	R = H	11.333	11.448	4.551	1.015	1.394	1.221	1.483	1.383	1.398	1.396	1.471	0.0
PDI-C₆OH	R=C ₆ H ₁₂ OH	11.416	11.396	4.571	1.476	1.402	1.225	1.483	1.384	1.399	1.396	1.471	0.0
PDI-C₄OH	R=C ₄ H ₉ OH	11.414	11.397	4.571	1.475	1.402	1.224	1.483	1.384	1.400	1.396	1.471	0.0
PDI-C₂morph	R=C ₂ H ₄ NC ₄ H ₈	11.414	11.398	4.571	1.473	1.402	1.224	1.483	1.384	1.399	1.396	1.471	0.0
PDI-C₆H₄OH	R=C ₆ H ₄ OH	11.421	11.392	4.582	1.446	1.410	1.220	1.484	1.384	1.399	1.396	1.471	0.0
PTCA	R', R'' = H	11.373	11.462	4.449		1.387	1.205	1.477	1.384	1.399	1.397	1.471	0.0

Table S2 Atomic Charges and dipole moments for different perylene derivatives at B3LYP/6-31G(d)

System	R ^a	X	O	C _f	C _e	C _d	C _c	C _b	C _a	Dipole moment (D)
PR					-0.205	-0.229	-0.206	-0.029	-0.029	0.000
PDI	+0.445	-0.657	-0.580	+0.684	-0.130	-0.158	-0.199	-0.009	-0.009	0.000
PDI-C₆OH	-0.261	-0.477	-0.590	+0.689	-0.121	-0.159	-0.200	-0.010	-0.010	0.000
PDI-C₄OH	-0.260	-0.477	-0.590	+0.689	-0.122	-0.159	-0.200	-0.010	-0.010	0.001
PDI-C₂morph	-0.267	-0.480	-0.591	+0.688	-0.122	-0.158	-0.199	-0.009	-0.009	0.000
PDI-C₆H₄OH	+0.114	-0.495	-0.573	+0.694	-0.124	-0.159	-0.200	-0.010	-0.010	0.000
PTCA		-0.538	-0.535	+0.812	-0.155	-0.153	-0.198	-0.006	-0.006	0.0

^aCharge on atom linking R to X.

- Near infrared reflectivity was measured for a series of perylene pigments
- Significant variations were observed in the NIR reflectivity across the series
- Absorption characteristics were related to electronic and vibrational properties
- Anharmonicity, force constants and dipole moment are important factors

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