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## Near-infrared reflective properties of perylene derivatives

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## ABSTRACT

Dyes and pigments with high reflectance in the near-infrared (NIR) region can extensively control the heat buildup. Perylene-based pigments exhibit considerable reflectance in the NIR region. The reflectance of a material depends upon a number of factors, such as particle size, concentration of the reflective material, the distribution of particles within the material and the material's refractive index. The refractive index, in turn, depends on the electronic structure of the material. Therefore,differently substituted perylene compounds are expected to exhibit different reflectance in the NIR region. To elaborate this point, different perylene bisimide derivatives have been synthesized, and their ability to reflect in the NIR region has been determined and compared to the results for commercially available pigments. Significant variation in the relative reflectance of different perylene tetracarboxy diimide derivatives (PCIs) was also compared to the reflectance of 3,4:9,10-perylenetetracarboxylic dianhydride (PTCA), the precursor from which the PCIs are commonly synthesized. PTCA exhibits significantly higher relative reflectance in the given region than any of the diimide derivatives synthesized from it in this study.

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## 1. Introduction

Approximately 5% of solar energy reaches Earth in the form of ultraviolet radiation (200-400 nm), 43% in the form of visible radiation (400-700 nm), and 52% is constituted by the nearinfrared (NIR) region [1]. The human eye is sensitive only to the visible range of the solar spectrum. The absorption of solar radiation in this wavelength range by objects gives them a visual appearance of color that depends on the wavelengths they absorb or reflect. For example, an object appears white if it reflects rather than absorbs all of the wavelengths in the visible region, whereas black objects absorb all of wavelengths in the visible region but reflect none of these wavelengths. The NIR region makes no contribution to the visual appearance of color. The absorption of radiation in this wavelength region results only in heat gain. Therefore, by rejecting solar radiation in the NIR region, a significant amount of heat "buildup" can be reduced while maintaining an object's colorful aesthetic appearance. Colorants (a term that includes both dyes and pigments) with the ability to interact selectively in the visible and NIR regions of the solar spectrum are called NIR-reflective colorants. The optical properties of coatings in different wavelength regions are primarily influenced by colorants

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[2]. Therefore, the incorporation of NIR-reflective colorants both reduces heat buildup and maintains the aesthetic look of an object.

NIR-reflective colorants are also known as "cool colorants" because they keep the surface as well as the interior of coated surfaces relatively cool. They absorb a significant amount of solar radiation in the visible region (400–700 nm) to create an optical illusion of darkness, whereas they reflect a considerable amount of energy in the NIR (700–2500 nm) region. These colorants have been well explored in cool-roof technology [3,4], and high solar reflectance is the primary requirement to keep the coated surface of roofs as well as a building's interior cool. As the NIR region constitutes nearly half of the solar energy received by Earth, an increase in the NIR reflectance of a material by one unit results in an increase of the total solar reflectance by 0.5 units. A recent study has demonstrated that the replacement of a traditional pigment by a cool pigment can result in a change in solar reflectance of 22 units, with a corresponding temperature difference of 10.2 °C for summer conditions [5].

To date, numerous cool pigments of inorganic origin have been reported, including Pigment Black 30, C.I. Pigment Green-17, metal-coated pigment particles and composites consisting of a coloring agent, a white pigment such  $TiO_2$ , and another non-absorbing pigment [6–8]. More recently, specialized complex inorganic color pigments manufactured by Ferro and Shepherd have also been introduced. These metal-based pigments, however, are associated with a toxicity issue.





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Fig. 1. (a) Perylene (PR) and (b) 3, 4:9,10-Perylenetetracarboxylic acid dianhydride (PTCA).



Fig. 2. 3,4:9,10-Perylenetetracarboxylic acid diimide (PCI).

Cool pigments of organic origin, in contrast, are relatively rare. Examples of these pigments include black pigment containing copper phthalocyanine, azo pigments and a few perylene-based pigments, Lumogen (LG) and Paliogen (PG), developed by BASF [9]. Perylene derivatives have also been used in camouflage paints because of their strong reflectance in the NIR region. Along with their ability to reflect in the NIR region, perylene-based dyes exhibit all the characteristics of high-performance colorants, such as high thermal stability, high tinctorial strength, weather stability, and photo stability [10]. Perylene compounds have a wide range of applications besides pigments, such as electro-photographic photoreceptors, light-emitting diodes, field-effect transistors, solar cells and other optoelectronic photonic devices [11–15].

Perylene dyes are usually *N*, *N'*-disubstituted perylene-3,4:9,10-bis(dicarboximide)s (PCIs) synthesized from their anhydride precursor (Fig. 1b). To date, a large number of reports regarding perylene-based (Fig. 1a) compounds have appeared, including accounts of the synthesis of different diimide derivatives and detailed studies of their optical properties in the UV–visible region. However, interactions of these compounds in the NIR region have not been addressed.

The reflectance of a material comprises two components: specular reflectance and diffuse reflectance. Diffuse reflectance is a major component of reflectance in matte surfaces, such as coatings and polymeric materials. The diffuse reflectance of a material depends on a variety of factors, such as particle size, particles distribution, particle shape, chemical composition and refractive index of the material. Refractive index is associated with a material's electronic structure. For example, TiO<sub>2</sub> existing in different phases have shown different refractive indices [16]. This means that PCIs with different N-substituents could differ in their ability to reflect in the NIR region. To elucidate the relationship between the identity of the substituents and reflectance, different PCIs (Fig. 2) have been synthesized, and their NIR reflectance has been measured after the derivatives were dispersed in a polymer at a fixed concentration.

#### Table 1

The identities of different R group for different PCIs.

Name of pigment	Nature of R group	Color
P <sub>1</sub>	-(CH <sub>2</sub> ) <sub>6</sub> -OH	Black
P <sub>2</sub>	(CH <sub>2</sub> ) <sub>2</sub> NO	Dull red
P <sub>3</sub>	(CH <sub>2</sub> ) <sub>3</sub> N_O	Maroon
P <sub>4</sub>	——————————————————————————————————————	Dark red

#### 2. Experimental

#### 2.1. Materials

PTCA was obtained from TCI Europe, Lumogen FK 4281 (LG) was obtained from BASF, and ethylene glycol was obtained from Chem-Supply, whereas all other chemicals were supplied by Sigma-–Aldrich and were used without further purification. The polypropylene (PP) was Adflex X 500F supplied by Lyondell Basell.

#### 2.2. Equipment

All pigments were dispersed in PP using a 9000 Rheocord HAAKE mixer. The reflectance of all pigments was measured using a Varian Cary 500 UV–VIS–NIR spectrophotometer in reflectance mode. A FEI Quanta 200 environmental electron scanning microscope (ESEM) in low-vacuum mode was used to study the morphology of pigments in powder form, as well as those dispersed in PP. Thermo gravimetric analysis (TGA) was used for thermal stability studies. All NMR spectra were run in deuterated sulfuric acid (d<sub>2</sub>-D<sub>2</sub>SO<sub>4</sub>) purchased from Sigma–Aldrich, the signal of which was referenced at 11.27 ppm with respect to sodium trimethylsilyl propionate (TSP).

# 2.3. General procedure for the synthesis of perylene bisimide derivatives

Different PCIs were synthesized from PTCA and the corresponding amine reacted in molar ratios of 1:3. The mixtures were heated in ethylene glycol at 140 °C for 16 h under N<sub>2</sub> (Fig. 3). The reaction mixture was allowed to cool to approximately 80 °C, then diluted with methanol and filtered. The residue was further washed with an excess of water and dried. The dried solid was stirred with 200 mL of 10% potassium carbonate solution at 50 °C for 1 h to separate perylene bisimide from perylene dianhydride.

Four PCIs, P<sub>1</sub>, P<sub>2</sub>, P<sub>3</sub> and P<sub>4</sub>, were prepared that differ by the R group attached to the N atom of PCI. Table 1 shows the R groups for these derivatives as well as their visual appearance.



Fig. 3. General scheme for the synthesis of different PCIs.



Fig. 4. Relative reflectance of different bisimide derivatives and polypropylene.

The PCIs were characterized by proton nuclear magnetic resonance (<sup>1</sup>H-NMR) and infrared (IR) spectroscopy. The yield, <sup>1</sup>H-NMR and IR data for these derivatives is given below.

## 2.3.1. Compound P<sub>1</sub>

Yield 76%; <sup>1</sup>H-NMR (D<sub>2</sub>SO<sub>4</sub>),  $\delta$  (ppm) = 9.02 (*d*, 4H, Ar.), 8.96 (*d*, 4H, Ar.), 4.36 (*t*, 8H), 1.83 (*m*, 4H), 1.76 (*m*, 4H), 1.45(*b*, 8H; IR (KBr) Presence of two strong absorption signals at 1692 cm<sup>-1</sup> and 1655 cm<sup>-1</sup> due to imide carbonyl group and absence of signals due to anhydride carbonyl in the range of 1720–1760 cm<sup>-1</sup>.

#### 2.3.2. Compound P<sub>2</sub>

Yield 69%; <sup>1</sup>H-NMR (D<sub>2</sub>SO<sub>4</sub>),  $\delta$  (ppm) = 8.99 (*d*, 4H, Ar.), 8.91 (*d*, 4H, Ar.), 4.75 (*b*, 4H), 4.34 (*d*, 4H), 4.04 (*t*, 4H), 3.37 (*t*, 4H); IR Presence of two strong absorption signals at 1690 cm<sup>-1</sup> and 1653 cm<sup>-1</sup> due to imide carbonyl group and absence of signals due to anhydride carbonyl in the range of 1720–1760 cm<sup>-1</sup>.

#### 2.3.3. Compound P<sub>3</sub>

Yield 68%; <sup>1</sup>H-NMR (D<sub>2</sub>SO<sub>4</sub>),  $\delta$  (ppm) = 9.04 (*d*, 4H, Ar.), 8.96 (*d*, 4H, Ar.), 4.26 (*d*, 4H), 3.57 (*d*, 8H), 3.37 (*d*, 8H), 2.35 (*s*, 4H); IR Presence of two strong absorption signals at 1694 cm<sup>-1</sup> and 1658 cm<sup>-1</sup> due to imide carbonyl group and absence of signals due to anhydride carbonyl in the range of 1720–1760 cm<sup>-1</sup>.

## 2.3.4. Compound P<sub>4</sub>

Yield 62%; <sup>1</sup>H-NMR (D<sub>2</sub>SO<sub>4</sub>):  $\delta$  (ppm) = 8.94 (*m*, 8H, Ar.), 7.89 (*d*, 4H, Ar.), 7.59 (*d*, 4H, Ar); IR Presence of two strong absorption signals at 1692 cm<sup>-1</sup> and 1654 cm<sup>-1</sup> due to imide carbonyl group and absence of signals due to anhydride carbonyl in the range of 1720–1760 cm<sup>-1</sup>.

## 2.4. Dispersion of pigments into polymer

A uniform distribution of the pigments in the medium under investigation is crucial for reliable reflectance results because the



Fig. 5. Comparison of relative reflectance of different pigments at 980 nm and 1300 nm.



Fig. 6. Comparison of reflectance of bisimide derivative with commercial pigments.

dispersion of pigments significantly influences reflectance in the NIR region. All pigments were dispersed in PP using a melt mixing process at a temperature above the melting temperature of the polymer. The melt mixing process can be used for these pigments because all of the pigments are thermally stable up to 330 °C (section 3.3), The pigments were dispersed in PP at 2% concentration (900 mg of pigments in 45 g of PP) using a 9000 Rheocord HAAKE mixer at 180 °C at 80 rpm for 10 min to maintain a consistent particle size and distribution.

## 2.5. NIR reflectance measurements

## 2.5.1. Sample preparation and reflectance measurements

The PP samples containing dispersed pigments were molded 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 same size, shape and thickness which eliminated errors resulting from these variables. There are two purposes for dispersing pigments into a polymer:

- 1) To develop standardization across all samples to avoid errors in the results from sampling errors, such as compactness, amount of pigment and smoothness of the sample; such errors are common when samples are prepared in powder form.
- 2) To check the ability of these coloring agents to color polymeric materials.

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 diffuse reflectance of different materials was measured in the wavelength region 700–2500 nm



Fig. 7. Comparison of relative reflectance of PTCA with perylene (PR) and  $P_1$  in NIR region.



Fig. 8. Diagrammatic definition of D<sub>NN</sub>, D<sub>OO</sub> and d<sub>oo</sub>.

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-µm particle size obtained from Sigma–Aldrich was used as the reference, as described elsewhere [17].

## 3. Results and discussion

### 3.1. NIR reflectance

Results for the NIR reflectance measurements of different PCIs are shown in Fig. 4. The strong absorption signals observed at 1730 nm, 1285 nm and 1080 nm are characteristics of PP and originate from the combination and overtone of fundamental vibrations that are already documented in the literature [18]. Clearly, the reflectance of PP increases when the four PCIs ( $P_1$ ,  $P_2$ ,  $P_3$  and  $P_4$ ) are incorporated into the PP.

To allow for the easy comparison of the NIR reflectance results for different synthesized perylene pigments and the commercial pigments, two wavelengths—980 nm and 1300 nm—were chosen rather than the entire NIR wavelength region. These two wavelengths were selected because the 700–1300 nm wavelength region constitutes 80% of the total energy of the NIR region. Different PCIs synthesized in this study have shown significant variation in the relative reflectance in the NIR region. The relative reflectance of different pigments synthesized in this study varies from 38 to 65 at 980 nm, and from 37 to 54 at 1300 nm (Fig. 5).

The reflectance of the diimide derivatives (P<sub>1</sub>, P<sub>2</sub>, P<sub>3</sub> and P<sub>4</sub>) in the NIR region was also compared with that of commercially available pigments, including carbon black (CB), Lumogen (LG) and titanium

Table 2

Particle size of different pigments (perylene derivatives).

Name of pigment	Average particle size (µm)
P <sub>1</sub>	6.54
P <sub>2</sub>	3.02
P <sub>3</sub>	5.07
P <sub>4</sub>	3.49
Lumogen (LG)	3.66
Carbon black (CB)	2.50

dioxide (TiO<sub>2</sub>); the results are shown in Fig. 6. These pigments were selected because CB is a well-known absorber of solar radiation, LG is known as a cool black pigment, and TiO<sub>2</sub> is known as one of the best NIR-reflective pigments. The relative reflectance of CB is 2–4 over the entire NIR region, which means it significantly absorbs solar radiation. All of the PCIs ( $P_1$ ,  $P_2$ ,  $P_3$  and  $P_4$ ) synthesized in this study exhibited higher reflectance values than CB in the NIR region. Although the CB,  $P_1$  and LG appear black, their relative NIR reflectance varies substantially. The relative reflectance of  $P_1$  is 65, compared to 22 for LG at 980 nm. The reflectance values are comparable, however, at 1300 nm (54 for  $P_1$  vs. 52 for LG). High reflectance in the 700–1000 nm region is essential to maintain a high total solar reflectance because this region constitutes approximately 50% of the energy of the NIR region and 25% of the total solar energy.

Because PCIs are commonly synthesized from PTCA (Fig. 2b), we compared the NIR reflectance of PTCA with different synthesized PCIs. The reflectance of PTCA is compared with that of perylene (PR) and P<sub>1</sub> (Fig. 7). Only P<sub>1</sub> was included in this comparison because it exhibits the highest relative reflectance among the synthesized PCIs. Interestingly, PTCA exhibits a reflectance significantly higher than any of the PCIs synthesized from it in this study, and its relative reflectance is closer to that of TiO<sub>2</sub> (90 vs. 102 at 1300 nm, and 108 vs. 130 at 980 nm). On the other hand PR falls on the lower end of reflecting ability over the entire NIR region in comparison to both PTCA and P<sub>1</sub>, which indicates the importance of the anhydride entity in achieving high reflectance in the specified region.

These results suggest that the electronic environments of a material's constituent molecules significantly affect its ability to



Fig. 9. ESEM images of different perylene derivatives and some commercial pigments in powder form.

interact in the NIR region. For example incorporation of an anhydride entity to perylene (Fig. 7) dramatically increased its reflectance in the NIR region, although these two molecules are rigid and contain planes of symmetry. Some variation can be expected because of differences in particle size and their distribution between samples, but the electronic distribution also appears to play a role. With the introduction of the anhydride entity, the conjugated system is not located in the center of the molecule, but rather spreads outward toward the peripheral region. This rearrangement of the conjugation system might be responsible for the large difference in the ability of PTCA to reflect in the NIR region.

Differences in the relative reflectance of different diimide derivatives (P<sub>1</sub>, P<sub>2</sub>, P<sub>3</sub> and P<sub>4</sub>) may be attributable to the electronic effects of different substituents attached to the N atom, as investigated by Pichierri [19] in a computational study where different N-substituents were observed to significantly influence  $D_{NN}$ ,  $D_{OO}$ and  $d_{00}$  (see Fig. 8 for definitions of  $D_{NN}$ ,  $D_{OO}$  and  $d_{00}$ ). Another possibility for the observed differences in the relative percentage reflectance values is the different twist angle between the two naphthalene rings induced by different N-substituents, as studied by Liang et al. [20]. When this twist angle is taken into account, derivative P<sub>4</sub> is expected to maintain a rigid planar symmetry because of the aromatic nature of its substituent; the other three derivatives contain aliphatic groups attached to the N atom. On this basis, P<sub>4</sub> should exhibit a higher relative reflectance, whereas the results show that P<sub>1</sub> exhibits a higher reflectance in the NIR region.

The higher relative reflectance of  $P_1$  compared to that of  $P_2$  and  $P_3$  can be explained, however, in terms of dipole moments. The alkyl chain of  $P_1$  is expected to be perpendicular to the plane of the perylene ring and on the opposite side of the ring than the chains in  $P_2$  and  $P_3$ . In this high-symmetry conformation,  $P_1$  possesses a net dipole moment of zero. Additionally, the morpholine ring in  $P_2$  and  $P_3$  is expected to lower the molecules' symmetry. As a consequence, systems  $P_2$  and  $P_3$  possess net dipole moments. Because the morpholine group is more remote to the perylene ring in  $P_3$  than in  $P_2$ , the influence of the morpholine group is more pronounced in  $P_2$ . Consequently, the distortion of the  $P_2$  symmetry system is more pronounced, and this distortion influences its NIR reflectance.

## 3.2. Particle size and particle morphology after dispersion in polymer

Particle size represents an important consideration because it can influence the reflectance of the sample to a considerable extent. Two theories have emerged to explain the relationship between a material's particle size and reflectance. The Mie theory describes this relationship well for spherical particles that are isolated and homogenous, whereas the Kubelka–Munk (KM) theory is well accepted for describing the relationship between the NIR reflectance and particle size in coatings where the particles are nonspherical and inhomogeneous, as is the case here.

According to KM theory:

$$(1 - R\infty)^2 / 2R\infty \equiv F(R) = K/S \tag{1}$$

where *K* is the absorption coefficient, *S* is the scattering coefficient and  $R \propto$  is the reflectance of the sample at infinite thickness. *F*(*R*) represents the KM function, also known as the remission function. The reflectance of the sample depends upon the ratio of *K* and *S*, but not upon the absolute values of *K* and *S*. As the particle size decreases, the scattering coefficient increases; therefore, the reflectance of the sample also increases, i.e., an inverse relationship exists between a material's particle size and reflectance. A recent study on the influence of particle size on NIR reflectance has revealed that NIR reflectance can increase up to 15% when the particle size is decreased from micron-sized to nano-sized for chemically identical materials [17]. Therefore, a 1000-fold variation in the particle size could result in a significant difference in the observed NIR reflectance.

The particle size of the different pigments under study was measured manually using the software package ImageJ (version 1.41) on the ESEM images of powder pigments, as shown in Fig. 9. The average particle size for all of the investigated pigments (which represents area of particles) ranges from 3 to 7  $\mu$ m (Table 2), and the variation in the particle sizes is not sufficient to significantly contribute to the observed relative reflectance.

Because the parameters of dispersion time, mixer speed and pigment concentration (as described in section 2.4) were kept constant for purposes of comparison, the possibility of variation between the dispersions was minimal. Moreover, the pigments



Fig. 10. Electron Scanning Micrographs of different derivatives after their dispersion in polypropylene (PP).

should disperse well in the non-polar PP based on the compatibility factor (non-polar–non-polar). The uniformity of the dispersions is further evidenced from the SEM micrographs of the pigments after dispersion in PP (Fig. 10).

## 3.3. Thermal stability

All synthesized PCIs exhibited thermal stability up to 330 °C, which is in agreement with earlier studies. Decomposition of the pigments occurs in two stages. First, degradation in mass occurs in the range of 330–400 °C, which represents the decomposition of the N-substituent. The second stage occurs after 700 °C and represents the oxidation of the central perylene core in air. Derivative P<sub>1</sub> exhibits thermal stability up to 400 °C, whereas P<sub>2</sub> was the least thermally stable derivative and decomposed at 330 °C.

### 4. Conclusions

PTCA, which is commonly used as a starting material in the synthesis of various PCIs, exhibited significantly higher reflectance in the NIR region than any of the PCIs synthesized from it in this study. Significant variation in the NIR reflectance of the PCIs synthesized in this study was observed, despite the samples exhibiting similar ranges of particle size  $(3-7 \ \mu m)$ . All of the synthesized PCIs were thermally stability up to 330 °C. No direct correlation between the nature of the N-substituent and reflectance in the NIR region could be established on the basis of this limited study. However, this study is significant due to the establishment of a potential relationship between the nature of the substituent and the expected reflectance in the NIR region, pending further computational studies on these derivatives.

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