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Synthesis, characterization and near infra-red properties of perylenebisimide derivatives

Majid Mazhar[a], Majid Abdouss[a,*], Kamaladin Gharanjig[b,c], Reza Teimuri-Mofrad[d]

[a] Department of chemistry, Amirkabir University of Technology, Tehran, Iran
[b] Department of Organic Colorants, Institute for Color Science and Technology, Tehran, Iran
[c] Centre of Excellence for Colour Science and Technology, Institute for Colour Science and Technology, Tehran, Iran
[d] Department of Organic and Biochemistry, Faculty of Chemistry, University of Tabriz, Tabriz, Iran

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ABSTRACT

In this study, several perylene bisimide derivatives are synthesized and their ability to act as cool pigments is investigated. Synthesized pigments are characterized using FTIR, HNMR and XRD techniques. Reflectance of the pigments in the ultraviolet, visible and near-infrared (NIR) regions is investigated on two optically different substrates namely high absorptive substrate and high reflective substrate. The results show that this method is an efficient method to investigate the NIR properties of the pigments. Synthesized pigments exhibit different reflectance extents in the NIR region despite their structural similarities illustrating that the NIR properties are dependent on the N-substituent nature and electronic environment of the pigments. Direct correlation between crystallinity percentage and NIR transparency is observed in this study. However, results of this study are not completely in agreement with previous studies suggesting that the main factor affecting NIR properties of the perylene pigments is missing in the literature.

1. Introduction

Nowadays, the world around us is experiencing extreme population growth and urban sprawl with long commuting distances. Urban areas are growing and residential buildings have replaced open spaces covered with natural vegetation. Solar energy which was reflected by forests and vegetation is now absorbed by building roofs, walls and pavements, causing the surface temperature of urban structures to become several degrees higher than ambient air temperature. Hot surfaces of buildings and pavements convect the heat to ambient air resulting in overall ambient temperature increment. This unfavorable phenomenon is called the “urban heat island” [1–4]. Additionally, absorbed heat can convect to the interior of buildings causing temperature increment and human inconvenience. One of the accepted ideas to overcome to these unfavorable phenomena is the application of cool roofs that are constructed by cool materials. The term cool material refers to the material that highly reflects incident solar radiations (high solar reflectance) and highly releases away absorbed energy (high thermal emissivity) [5]. Routine construction materials except metals are known to be highly emissive but they are characterized by high solar absorption, which subsequently they experience extreme temperature rise under solar radiation [5].There are currently a number of cool materials commercially available for buildings and other surfaces in the urban environment. These include cool surface coatings, cool single ply membranes, reflective tiles, metal roofs, light-colored marble and mosaic, as well as concrete and conventional asphalt with white aggregate. All of these materials are white or light-colored [1]. However, homeowners with pitched roofs visible from the ground level often prefer non-white roofing products such as cool darker paints for aesthetic considerations [6,7].

Approximately 43% of solar energy reaches earth in the form of visible radiation and 57% of incident solar radiation is in invisible form [8]. To be more precise, only 43% of solar energy makes a contribution to the visual appearance of objects by the amount of reflection and absorption of different visible wavelengths and the reflection or absorption of the remaining portion makes no contribution to the color of the objects. Absorption of this invisible portion will result in heat gain but the reflection of it will

* Corresponding author at: Department of Chemistry, Amirkabir University of Technology (Polytechnic), P. O. Box: 159163-4311, Tehran, Iran.
E-mail address: phdabdouss44@aut.ac.ir (M. Abdouss).

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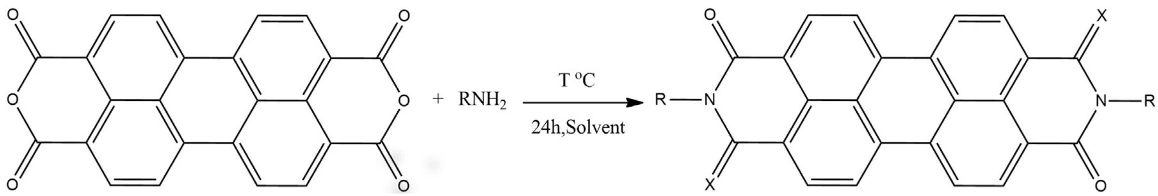


Fig. 1. General procedure for synthesis of perylene derivatives (X in all pigments is O except P2 which is N).

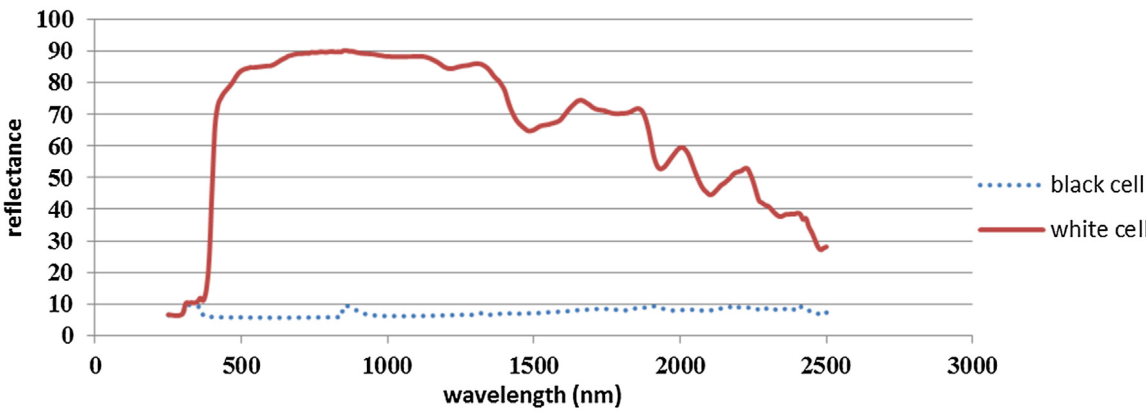
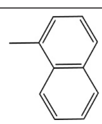
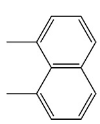
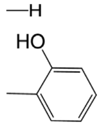
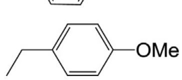
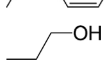
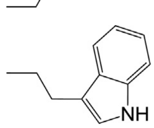


Fig. 2. UV–vis-NIR reflectance of the checkerboard chart used as substrate.

Table 1
Naming of the synthesized pigments, their color and synthesis conditions.

Pigment name	Nature of R group	Color	CIE Lab			synthesis Solvent	synthesistemperature(°C)	catalyst
			L*	a*	b*			
P1		Light red	40	61	49	–	160	Zinc acetate
P2		black	17	2	2	Molten imidazole	170	Zinc acetate
P3	—H	violet	14	22	4	Water	75	-
P4		Dark violet	5	20	3	Molten imidazole	170	Zinc acetate
P5		Black	16	1	4	Ethylene glycol	150	Zinc acetate
P6		Dark brown	11	17	10	–	150	-
P7		red	27	46	32	Molten imidazole	150	-

reduce energy accumulation on the surface of the object resulting in temperature reduction. Although dark cool pigments significantly absorb the main part of visible wavelengths, they strongly reflect the near infrared region (NIR) of the solar spectrum and subsequently reduce heat gain of the object surface. These pigments have been explored in cool roof technology [9]. Some researchers have estimated a potential saving of the peak-cooling load of 11–27% for air-conditioned buildings depending on the climatic conditions [10].

Cool pigments are categorized into two organic and inorganic groups of which some of the inorganic ones are subjected to toxicity issues [11] and the organics especially perylenes are less toxic or non-toxic [12]. Copper phthalocyanine [13], azo pigments [14] and perylene base pigments are the main subgroups of organic cool pigments [15,16]. Perylene pigments are known as high performance colorants as they have high thermal stability, high tinctorial strength, high weather and light fastness. In addition, they exhibit high chemical inertness, solvent stability, good to very good migra-