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Fabrication of luminescent perylene bisimide nanorods

Gopal Boobalan^a, Predhanekar Mohamed Imran^b, S.G. Ramkumar^c,
Samuthira Nagarajan^{c,*}^a Department of Chemistry, Annamalai University, Annamalaiagar 608002, India^b Department of Chemistry, Islamiah College, Vaniyambadi 635752, India^c Department of Chemistry, Central University of Tamil Nadu, Thiruvarur 610004, India

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ABSTRACT

Perylene bisimides have attracted great interest as a result of their unique electrical and photophysical properties. In the present investigation a N,N'-bis(2-naphthalene-2-yl)perylene-3,4,9,10-tetracarboxylic diimide was synthesized from 2-aminonaphthalene and perylene-3,4,9,10-tetracarboxylic dianhydride. Structure and purity were confirmed by mass, NMR and other spectral techniques. Photophysical and electrochemical properties were investigated by UV-vis, fluorescence, differential scanning calorimetry and cyclic voltammetric techniques. Optical, fluorescence, scanning and transmission electron microscopies were employed in the molecular self-assembly studies. The compound self-assembled into nanorods. The competition and co-operation between the intermolecular π - π -stacking and hydrophilic/hydrophobic interactions are suggested for the observed nanostructure.

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1. Introduction

Nanostructured, one-dimensional (1D) morphologies composed of electronically active constituents have gained increasing interest in the emerging field of nanoscience in recent years, due to their immediate application in electronic and optoelectronic nanodevices, for which the device miniaturization requires small channel materials. However, most 1D nanostructures reported to date are based on inorganic compounds. Analogous research has been much less focused on organic nanomaterials, while they have already found applications in thin film based devices such as field-effect transistors, light emitting diodes, and photovoltaic cells. Recent studies suggested that self-assembly through strong π - π stacking could be an effective approach to fabricate 1D nanostructure for planar and rigid organic molecules. However, it still remains a difficult task to design and fabricate nanorods with well-defined uniform morphology.

Perylene tetracarboxylic diimides (PTCDIs) are intensively used as photoactive materials for variety of fields because of their excellent thermal stability, high luminescence efficiency and novel optoelectronic properties [1,2]. Driven by the demands of various electronic applications, the molecular modification aimed at changing the photophysical properties of PTCDIs has stimulated a lot of interest in

the recent years [3,4]. Molecules containing the perylene diimide core have been proposed for use also in artificial photosynthesis [5,6], while the related compounds like naphthalene diimides have been investigated as photoactive DNA intercalators for photodynamic cancer therapies [7]. Furthermore, liquid crystalline properties have been recently demonstrated in the nano- and mesoscopic supramolecular structures of PTCDI compounds [8,9]. PTCDIs have also been attracting considerable attention as light fast colorants [10–12], highly efficient fluorophores [13], the best *n*-type organic semiconductors [14,15] and versatile building blocks in self-assembly process [16–18].

Although a number of PTCDI compounds have been reported [19,20], most of them [21,22] are soluble in special solvents such as concentrated sulfuric acid or *m*-cresol. Even many low molecular weight PTCDIs with long *n*-alkyl chains have very low solubility in common organic solvents [23]. To get better processability, general approaches have been developed to increase π -stacking interaction and make them readily soluble. Herein, we report the synthesis of a new N,N'-bis(naphthalene-2-yl)perylene-3,4,9,10-tetracarboxylic diimide (NA-PTCDI), its characterization and self-assembly.

2. Experimental

2.1. Materials

Perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA), naphthylamine and imidazole were obtained from Aldrich Chemical Co.

* Corresponding author. Tel.: +91 94430 46272.

E-mail addresses: snagarajan@cutn.ac.in,

nagarajan.au@gmail.com (S. Nagarajan).

URL: <http://www.cutn.ac.in> (S. Nagarajan).

The solvents were obtained from commercial sources and used as received.

2.2. Equipment

The FT-IR spectrum was measured on a NICOLET AVATAR 360 FT-IR instrument. ^1H and ^{13}C NMR spectra were recorded on a 500 MHz spectrometer using TMS as standard. UV-vis absorption spectra were recorded on a Hitachi U-2001 spectrophotometer. Emission spectra were measured using an ELICO SL-174. The differential scanning calorimetry was performed using a NETZSCH DSC 204; the sample was heated at 5 K min^{-1} in nitrogen. Cyclic voltammetry was performed by using three electrode cell units, polished 2 mm glassy carbon as working electrode, Pt as counter-electrode and Ag/AgCl as reference electrode by using a CH 1604C electrochemical analyzer. Tetrabutylammonium perchlorate (Bu_4NClO_4) was used as a supporting electrolyte, and the scan rate employed was 100 mV s^{-1} and the current sensitivity was given as $0.01\text{ }\mu\text{A}$.

The optical microscopic image was recorded using a LABOMED ATC-2000 microscope. The fluorescence microscopic images were obtained with a LEICA DM-2500 microscope, which provides excitation in the range of 450–490 nm. The mass spectrum was recorded on a JEOL GCMATE 11 GC mass spectrometer. SEM measurement was performed with a Hitachi S-340W microscope. The sample was prepared by casting one drop of the nanorod suspension onto a glass coverslip, followed by drying in air and then annealing overnight in an oven at $45\text{ }^\circ\text{C}$. The dried sample was coated with gold prior to the SEM imaging. TEM was recorded using a JEOL instrument.

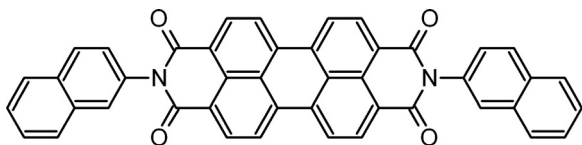


Fig. 1. Structure of NA-PTCDI.

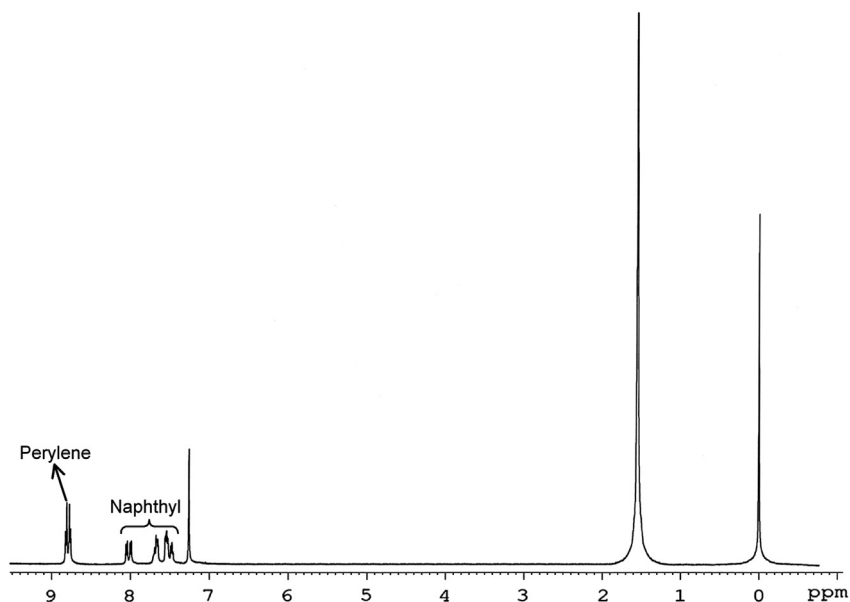


Fig. 2. ^1H NMR spectrum of NA-PTCDI.

2.3. Preparation of *N,N'*-bis(naphthalene-2-yl)perylene-3,4,9,10-tetracarboxylic diimide (NA-PTCDI)

The NA-PTCDI was synthesized following the standard condensation method [10]. Briefly, in a 250 mL round bottom flask, 39 mg (1 mmol) perylene-3,4,9,10-tetracarboxylic dianhydride, 57 mg (4 mmol), 2-aminonaphthalene and 5 g imidazole were heated at $120\text{ }^\circ\text{C}$ for 4 h. The reaction mixture was cooled to room temperature and dispersed in 3 mL ethanol, followed by addition of 50 mL of 2 N HCl. The mixture was stirred overnight, resulting in a red solid that was collected by vacuum filtration. The solid was then washed thoroughly with distilled water until the pH of washing turned to neutral. The collected solid was further purified by column chromatography on silica gel (eluent: CHCl_3).

^1H NMR (500 MHz, CDCl_3): δ 7.47 (t, 2H), 7.53–7.56 (m, 4H), 7.65–7.69 (m, 4H), 8.05 (d, 2H), 8.00 (d, 2H), 8.77 (d, 4H, perylene), 8.81 (d, 4H, perylene); ^{13}C NMR (125 MHz, CDCl_3): δ 121.7, 123.5, 125.6, 126.4, 127.2, 128.8, 129.7, 130.1, 132.1, 136.5, 143.5, 163.1; IR (KBr, cm^{-1}): ν 3420, 3095, 3063, 2922, 2852, 1704, 1667, 1593, 1509, 1352, 1396, 1252, 1181, 1022, 864, 792, 745, 666, 491; MS (CI): m/z Calcd. for $\text{C}_{44}\text{H}_{22}\text{N}_2\text{O}_4$ 642.6, found 641.7 [M-1]; UV-vis (CHCl_3): λ_{max} (nm) (ϵ) 460 (26,008), 491 (68,221), 528 (111,989);

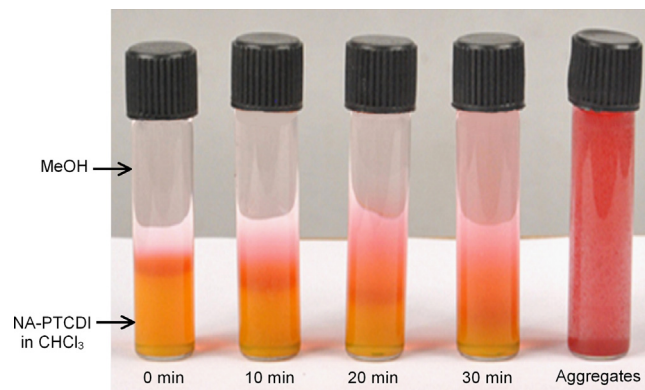


Fig. 3. Optical photographs detailing the interfacial self-assembly of NA-PTCDI.

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