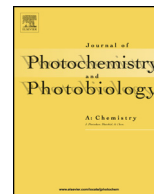




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Synthesis, characterization, optical and electrochemical properties of a new chiral multichromophoric system based on perylene and naphthalene diimides



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ABSTRACT

A new chiral and multichromophoric macromolecular system based on a perylene diimide chromophore consisting of two 1,4-bis(3-aminopropyl) piperazine linkers and two terminal chiral naphthalene bisimide chromophores has been synthesized. All of the chromophoric units are not π -conjugated with each other and could behave independently due to the presence of the nonconjugated linker. A new symmetrical dehydroabietyl substituted naphthalene diimide was also synthesized for comparison purposes. The bulky and chiral substituent is included at the peripheral positions of macromolecular system to increase the solubility and introduce directionality to the intermolecular interactions. The multichromophoric macromolecule showed new and distinctive photophysical properties that are different from the properties in the monomeric states of the components and in blends. It exhibited strong absorption in a wide range (320–600 nm) with enhanced light absorption due to higher molar absorption coefficients. It is observed that the absorption, emission and electrochemical characteristics are delicate interplay among intermolecular interactions in the macromolecule both in solutions and solid-state. Photoinduced electronic excitation energy transfer was noticed in various solvents from energy-harvested peripheral chromophores to the centered perylene core.

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1. Introduction

Perylene and naphthalene chromophoric dyes are excellent materials of aromatic π -conjugated heterocyclic family [1]. The rigid structure of perylene and naphthalene chromophores causes strong intermolecular π - π interactions giving rise to versatile optical and electronic characteristics [2–6]. With the advantages of tailoring the imide and bay positions of perylene and naphthalene structures, exclusive benefits were achieved such as n -type semiconducting character, extended absorption coefficients, high photoluminescence quantum yields, self-assembly behaviors, thermal and photostabilities [7–14]. A vast variety of exotic optoelectronic applications were reported based on their structural architectures, especially in organic light emitting diodes, field effect transistors and photovoltaics [15–19]. Thereby, perylene and naphthalene chromophoric dyes are demonstrated as building blocks for the construction of functional multichromophoric and supramolecular systems with unique applications [1,15,20–22].

Multichromophoric systems are under investigation for application as artificial supramolecular assemblies that mimic natural light harvesting photosynthetic functional moieties [23–28]. ‘Dendritic framework’ composed of assembling multiple peripheral chromophores around a single core unit is one of the most investigated multichromophoric synthetic systems that can efficiently imitate natural species [23,24,29–31]. The basic idea of dendrimer framework is to form a light harvesting antenna, which can facilitate funneling via efficient energy transfer from energy-harvested peripheral chromophores to the centered core [24,32–34]. Based on this strategy, multichromophoric dendrimers encapsulating various multiple individual fluorophores such as perylene dyes were established to enhance the optical properties (mainly fluorescence intensity) for biological labels [23,29,30,33–38]. However, the design and synthesis of such dendrimers are rather complex and the expected applications could be inhibited by several issues: (i) intramolecular aggregation due to long chains that are covalently attached to peripheral chromophores, (ii) inefficient energy transfer and charge transport due to long distances between the cores, (iii) self-quenching of individual dyes, and (iv) improper spatial arrangements of the peripheral chromophores [23,24,29,30,36]. Therefore, there has been increasing interest in

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preparing representative multichromophoric systems by concentrating more and more materials in a confined volume with maximum synergism that better reflect the natural systems [39,40].

We report herein a new chiral and multichromophoric macromolecular system based on a perylene diimide chromophore (NPM) consisting of two 1,4-bis(3-aminopropyl) piperazine linkers and two terminal chiral naphthalene bisimide chromophore. The non conjugated linker is used in order to prevent π -conjugation of the two different chromophoric units. All of the chromophoric units could behave independently from each other and aggregation of the molecules could produce many interesting novel properties, which are applicable in photonic and optoelectronic devices.

The bulky and chiral substituent is included at the peripheral positions of macromolecular system to increase the solubility and introduce directionality to the intermolecular interactions. Notably, all of the chromophores in the multichromophoric macromolecular system are hydrophobic. The macromolecule was synthesized via three different steps. The first step involved the condensation reaction of perylene-3,4,9,10-tetracarboxylic dianhydride with 1,4-bis(3-aminopropyl) piperazine to produce the symmetrical diimide (PDI). This step was followed by the synthesis of *N*-(dehydroabietyl)-1,4,5,8-naphthalenetetracarboxylic-1,8-anhydride-4,5-imide (NMI). Finally, chiral naphthalene monoimides were linked to the system through the non-conjugated linker 1,4-bis(3-aminopropyl) piperazine. *N,N'*-bis-(dehydroabietyl)-1,4,5,8-naphthalenetetracarboxylic diimide (NDI) was also synthesized for comparison. We kept our focus on aggregation properties, optical and redox properties of individual chromophores, their variations in a multichromophoric array, optoelectronic properties of multichromophoric macromolecule toward applications of photovoltaics, and finally the intramolecular energy transfer characteristics between naphthalene and perylene cores similar to dendritic systems.

2. Experimental section

2.1. Materials

Perylene-3,4,9,10-tetracarboxylic dianhydride and 1,4,5,8-naphthalenetetracarboxylic dianhydride were purchased from Aldrich and dried under vacuum at 100 °C overnight. Similarly, isoquinoline and *m*-cresol were freshly distilled and dried over activated molecular sieves and all other reagents (from Aldrich) were used as received. All reactions were carried out under an inert atmosphere.

2.2. Methods

FTIR spectra of all synthesized compounds as circular KBr discs were recorded on a JASCO FT/IR-6200 spectrometer. Elemental analyses were measured on a Carlo Erba-1106 (C, H, and N) elemental analyzer. The ¹H and ¹³C nuclear magnetic resonance (NMR) spectra were studied on a Bruker DPX-400 NMR. The chemical shifts are reported in the units of ppm (parts per million) and were referenced to internal standard, TMS (tetramethylsilane). The spectroscopic UV–vis absorption and emission measurements in solutions were recorded on a Varian–Cary 100 spectrophotometer and Varian–Cary Eclipse fluorescence spectrophotometer, respectively. Solid-state absorption spectra were recorded on a PerkinElmer UV–vis/NIR Lambda 19 spectrometer. Mass spectra were determined by using MS/MS System 3200 QTRAP instruments at Fragmentor 50 eV ionization energy. The differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) thermograms were obtained from PerkinElmer/DSC/Jade DSC under nitrogen atmosphere and PerkinElmer/TGA/Pyris 1 under oxygen, respectively, with a heating rate of 10 °C min⁻¹.

Electrochemical properties of all the synthesized compounds in solution and solid-state were investigated using Gamry instruments workstation equipped with a PC computer monitoring Reference 600 Potentiostat/Galvanostat/ZRA system. Redox data from cyclic (CV) and square-wave voltammetry (SWV) measurements were recorded using three-electrode system throughout the work, which are working-glassy carbon, counter-platinum wire, and reference-Ag/AgCl electrodes. Prior to use, the surface of the working electrode was polished carefully with 0.05 μ m alumina slurry for better precision. The supporting electrolyte (0.1 M NaBF₄ in dimethyl sulfoxide (DMSO)) solution was measured first to produce a blank surface and added the PDI, NMI and NPM analytes (1.76 $\times 10^{-5}$ M) to measure their redox potentials with an internal reference ferrocene. Solid-state redox potentials of the analytes were recorded in 1 M HCl solution by immobilized microparticles voltammetry technique. This technique is a very useful tool for organic materials that are insoluble in water and the methodology can be found elsewhere [4,12,13]. Multiple cycles of redox processes were carried out throughout the electrochemistry investigation and confirmed the reproducibility of resulting oxidation/reduction peak potentials.

2.3. Synthesis

2.3.1. Synthesis of *N,N'*-bis-[4-(3-amino-propyl)-piperazin-1-yl]-propyl]-3,4,9,10-perylenebis(dicarboximide), PDI

Perylene-3,4,9,10-tetracarboxylic dianhydride (1.00 g, 2.55 mmol), 1,4-bis(3-aminopropyl) piperazine (2.10 g, 10.20 mmol) and Zn(OAc)₂·2H₂O (0.55 g, 2.50 mmol) were heated in a carefully dried solvent mixture (60 mL *m*-cresol and 8 mL isoquinoline) under argon atmosphere at 140 °C for 15 h and at 200 °C for 2 h. The solution was allowed to cool and then poured into 300 mL acetone. The precipitate was filtered off and dried at 100 °C under vacuum. The product was treated with methanol (MeOH) in a Soxhlet apparatus for 1 day in order to get rid of unreacted starting materials and high boiling solvents. Further purification was performed by sublimation of PDI at 400–500 °C under reduced pressure of 10⁻² mbar. Sublimation process was repeated several times in order to ensure maximum purity. Pure product PDI was obtained as a dark brown powder (1.68 g, 88% yield). FTIR (KBr, cm⁻¹): ν = 3432, 3182, 2933, 2812, 1693, 1651, 1594, 1343, 813. UV–vis (CHCl₃): λ_{\max} , nm (ϵ_{\max} , cm⁻¹ M⁻¹) = 461 (37,000), 490 (49,000), 527 (63,000). Fluorescence (CHCl₃) λ_{\max} , nm: 535, 576, 627. Fluorescence quantum yield (CHCl₃, reference, dodecyl diimide (CHCl₃) with Φ_f = 100%): 40%. Anal. calcd. for C₄₄H₅₂N₈O₄ (*M_w*, 756.95); C, 69.82; H, 6.92; N, 14.80. Found: C, 69.47; H, 6.54; N, 14.41.

2.3.2. Synthesis of *N*-(dehydroabietyl)-1,4,5,8-naphthalenetetracarboxylic-1,8-anhydride-4,5-imide, NMI

1,4,5,8-Naphthalenetetracarboxylic dianhydride (1.00 g, 3.73 mmol) was added in a mixture of water (175 mL) and aqueous KOH (1.0 M, 33 mL) at room temperature and stirred for 2 h. Then dehydroabietylamine (1.1 g, 3.68 mmol) was added and heated for 20 h at 80 °C. The reaction mixture was cooled to room temperature and filtered. The filtrate was acidified with 10% acetic acid and the resulting precipitate was collected by vacuum filtration, washed with water and dried in vacuum at 100 °C. The crude product was purified by silica gel column chromatography with CHCl₃ as eluent to give a yellow solid NMI (0.927 g, 47% yield). FTIR (KBr, cm⁻¹): ν = 3084, 2942, 2854, 1789, 1752, 1708, 1673, 1584, 1329, 765. ¹H NMR, δ_H (ppm) (400 MHz, CDCl₃): 7.24 (d, *J* = 2.00 Hz), 7.19 (s, 4Ar-H, C(1), C(2), C(5), C(6)), 6.59 (d, *J* = 1.76 Hz, 3Ar-H, C(24), C(25), C(27)), 3.78 (s, 2CH, C(30), C(19)); 1CH₂, C(13)), 1.97 (s, 1CH₂, C(21)), 1.52–1.17 (4CH₃, C(28), C(29), C(31), C(32)); 3CH₂, C(16), C(17), C(20)), 0.83–0.76 (m, 1CH₂, C(15)). ¹³C NMR, δ_C (ppm)

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