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New naphthalene polyimide with unusual molar absorption coefficient and excited state properties: Synthesis, photophysics and electrochemistry

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ABSTRACT

A high molecular weight 1,4,5,8-naphthalene polyimide (**ENPI**) by one-step polycondensation mechanism and for comparison its monomeric diimide (**ENDI**) were synthesized; the photophysical and electrochemical properties were studied in detail for **ENPI**. Monomer has shown unusual insolubility so that the characterization proven to be difficult, whereas **ENPI** has shown better solubility. The molecular weight data obtained by GPC for the polymer were $M_n=8240$ and $M_w=34,000$ g mol⁻¹ respectively with a polydispersity of 4.13. The polyimide exhibited outstandingly high molar absorption coefficients as 599,000, 1,021,000, and 972,700 M⁻¹ cm⁻¹, which is first time reported in literature for the characteristic 0–2, 0–1, and 0–0 electronic transitions, respectively. **ENPI** showed concentration dependent and red shifted excimer emission in 1,1,2,2-tetrachloroethane (TCE). The polymer has undergone multielectron reductions in CHCl₃ solution below 100 mV s⁻¹ scan rates which merged into two reversible one-electron reduction peaks at higher scan rates. In solid-state, similar scan rate dependent reduction peaks were noticed. The LUMO, HOMO and optical band gap values obtained for **ENPI** were -3.73, -6.91, and 3.18 eV respectively. **ENDI** polymer with striking features has great potential as new sensitizer for efficient dye sensitized organic cells.

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1. Introduction

As the modern technology developing rapidly, the requirements for functional materials that can be utilized in various applications are also increasing dramatically. π -functional conjugated rylene derivatives are superior in the field of supramolecular polymer systems [1,2], especially, the two simplest perylene and naphthalene core tetracarboxy bisimides were extensively studied as they exhibit exciting optical, electrochemical, photoluminescent and electroluminescent properties [3–8]. The central factors that affect the efficiency of organic photovoltaic and semiconductor devices include high optical absorption and extent of charge transport of the extended π -conjugation materials [9]. Particularly, self-assembly, π - π stacking and π -donor- π -acceptor interactions emerged as leading subjects that direct the material and its potential toward organic electronic applications [10–14]. The structurally planar naphthalene diimide (NDI) and naphthalene polyimide (NPI) derivatives usually undergo strong influence of π - π interactions leading to an enhanced π -electron

delocalization to assure a strong electron-depleted electronic structure and imparting them *n*-type characteristics based on electron affinity of imide carbonyls [15–18]. Naphthalene derivatives were therefore widely employed as *n*-type semiconductors [19–23] and the high-performance *n*-channel semiconducting ability is widely employed in the application of organic field-effect transistors (OFET) [24–29]. Recently reported solution-processable ladderized *n*-type naphthalene bisimide copolymers for OFET applications explore the importance of the NDI and NPI materials in this particular field [30]. It is well known that *N*- and bay-substitutions of naphthalene diimides and polyimides greatly affect various properties of these compounds [2,17,31–36]. The substituent-structural diversity and morphology of *N,N*-disubstituted 1,4,5,8-naphthalene-diimide and polyimides offer them to fit in optoelectronic devices as high-performing organic molecules. The nodes present in the highest occupied and lowest unoccupied molecular orbitals at the imide nitrogen atoms furnish advanced optical and electronic properties with relevant structural modifications [37]. One of the major problems associated with the processability of the *n*-type naphthalene bisimide derivatives is very low solubility which could be enhanced greatly with *N*-substitution [17,38–40]. Importantly, extended optical absorptions and emissions specifically to the near-infrared (NIR) regions of naphthalene bisimides based organic compounds are very promising for solar cell

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applications [41–47]. On the other hand, DNA intercalating and binding and anticancer characteristics [48] of naphthalene and perylene diimides [48–51] pointed out remarkable results. Specifically, the functionalization of the π -conjugated aromatic bisimide cores with soluble and electron-withdrawing substituents is essential to enhance the utility of these derivatives in modern molecular device technology.

Recently, two electrochemically active polymeric arylene bisimides with multielectron transfers have been reported [52]. From the low molecular weight of poly[(4,7,10-trioxatrideca-1,13-diyl)-(1,4,5,8-naphthalenetetracarboxylic bisimide-N,N'-diyl)], Gawrys et al. concluded that the longer chains solubility has significant influence on the formation of high molecular weight polymeric arylenes [52]. These results obtained were consistent with those reported by us [53]. We have previously reported the synthetic, optical and electrochemical properties of perylene oligomeric dye containing alternating perylene and hexa(ethylene glycol) units in the backbone with high solubility in various organic solvents [54]. It was found that the oligomer has concentration dependent color tunability, much higher thermal stability than those containing the similar flexible molecular spacers and high absorption coefficient as $150,000 \text{ L mol}^{-1} \text{ cm}^{-1}$. It must be emphasized, however, that the synthesis of some other high molecular weight perylene and naphthalene polymers with different back bones were reported by us [53,55].

On the contrary opined about the molar mass of oligoether polyimides is low, we report here the synthesis of a high molecular weight naphthalene polyimide by using the similar diamine reported by Gawrys et al. [52], poly[bis-N, N'-(3-(2-(2-(3-aminopropoxy) ethoxy) ethoxy) propyl) -1,4,5,8-naphthalene imide] (**ENPI**) with giant molar absorption coefficients, photophysical and electrochemical properties. Its monomeric diimide has been synthesized for comparison. Most especially, polymeric parameters like M_w and polydispersity greatly influence the electronic structure of the polymers. We highlight the optical and electrochemical properties of the high molecular weight polymer and the differences in its properties comparing to the recently reported low molecular weight oligomer [52].

2. Experimental

2.1. Materials

1,4,5,8-Naphthalenetetracarboxylic dianhydride (**NDA**), *m*-cresol, isoquinoline, and zinc acetate were purchased from Aldrich. 1,4,5,8-Naphthalenetetracarboxylic dianhydride was dried overnight in a Nüve vacuum oven (Model, EV 180) at 100°C prior to use. Isoquinoline and *m*-cresol were pre-dried over activated 4 Å molecular sieves and were distilled freshly prior to use. 4,7,10-trioxa-1,3-tridecanediamine (**TODA**), tetrabutylammonium hexafluorophosphate (TBAPF6) and ferrocene were obtained from Fluka and used as received. All organic solvents employed in measurements were of spectroscopic chemical grade and used as supplied.

2.2. Instruments and characterization

The data of weight-average molecular weight (M_w), number-average molecular weight (M_n) and polydispersity ($\text{PDI} = M_w/M_n$) were obtained by gel permeation chromatography (GPC) measurement. Two GPC columns, PSS-PFG (particle size: $7 \mu\text{m}$; 10^2 and 10^3 \AA , ThermoSeparationProducts), were used under the control of a high performance liquid chromatography (HPLC) system equipped with an isocratic pump, an autosampler, and a detector Shodex RI71. The GPC mobile phase was established by preparing 0.05 M potassiumtrifluoroacetate (KTFAc) buffer solution. The polymer

was dissolved in hexafluoroisopropanol (HFIP) at fixed flow rate with the buffer and calibrated with polymethylmethacrylate (12 narrow PMMA) standard at 23°C . The solution was filtered through a $1 \mu\text{m}$ filter unit and $50 \mu\text{m}$ was injected for the GPC measurement. Intrinsic viscosity $[\eta]$ of the polymer was also measured using an Ubbelohde viscometer at 27°C in *m*-cresol. It was obtained from the data of specific ($\eta_{sp} = \eta/\eta_0 - 1$) and reduced ($\eta_{red} = \eta_{sp}/c$) viscosities at respective five different concentrations; and finally by plotting η_{sp}/c vs. c , extrapolating the reduced viscosity to $c=0$.

Thin layer chromatography (TLC) was carried out on Merck silica gel 60 F₂₅₄ precoated aluminum plates to monitor the reaction progress. The plates were dried and examined under an UV lamp followed by developing the plates sprayed with acidic vanillin solution. Infrared spectra were taken on a Mattson (USA) Satellite FT-IR spectrometer using pressed circular KBr pellets. ^1H and ^{13}C NMR spectra were recorded on a Bruker DPX - 400 spectrometer. UV spectra in solution and solid-state were recorded on a Varian-Cary 100 spectrophotometer. Emission spectra were measured on a Varian-Cary Eclipse spectrophotometer equipped with a Peltier heating system. Elemental analyses were performed on a Carlo-Erba-1106 C, H, N analyzer to measure the contents of carbon, nitrogen and hydrogen presented in the compounds. Thermal properties were analyzed by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) techniques and were recorded on a Perkin-Elmer/Pyris1 at a heating rate of $10^\circ\text{C min}^{-1}$ under nitrogen and oxygen atmosphere, respectively.

Electrochemical studies were carried out both in solution and solid-state by cyclic voltammetry (CV) and squarewave voltammetry (SQWV) experiments which were performed on a REFERENCE 600 computer-controlled Potentiostat/Galvanostat/ZRA using a three-electrode cell provided with separate compartments. The glassy carbon working electrode disc was well polished using $0.05 \mu\text{m}$ BUEHLER alumina slurry prior to use in order to obtain reproducible surfaces. The reference was an Ag/AgCl electrode and Pt wire was used as a counter electrode. The solutions were $1.3 \times 10^{-4} \text{ M}$ in electroactive material and 3 M in supporting electrolyte, tetrabutylammonium hexafluorophosphate (TBAPF6).

2.3. Synthesis of bis-N, N'-(3-(2-(2-(3-aminopropoxy)ethoxy)ethoxy)propyl)-1,4,5,8-naphthalene diimide (**ENDI**)

The diimide **ENDI** was synthesized by imidization of 1,4,5,8-naphthalenetetracarboxylic dianhydride (**NDA**) (1 g, 3.7 mmol) with 4,7,10-trioxa-1,3-tridecanediamine (**TODA**) (16.4 g, 74 mmol) in solvent mixture (60 mL *m*-cresol and 10 mL isoquinoline) under argon atmosphere in a 250 mL three-necked round-bottom flask connected to a reflux condenser and equipped with a magnetic stir bar and thermometer. Reaction mixture was heated under continuous stirring at 80°C for 4 h, where the initially undissolved material turned into viscous dark mixture. Resulting reaction mixture was further stirred at 120°C for 4 h, at 160°C for 2 h and finally at 190°C for 3 h. The resulting mixture was cooled down to room temperature and poured into 300 mL of cold isopropanol. The precipitate formed was filtered off and dried at 100°C under vacuum. The crude product was then refluxed first with ethanol followed by chloroform in a Soxhlet apparatus for 24 h, producing a dark black solid product. The complete purification of naphthalene diimide **ENDI** was hampered due to its insolubility in all solvents tested. Yield: 48% (1.20 g). FTIR (KBr, thin film, cm^{-1}): 3332 (N–H), 3061 (Ar C–H), 2917 and 2864 (Al C–H), 1666 and 1634 (C=O and Ar C=C), 1348 (C–N), 1110 (C–O). Anal. calcd for $\text{C}_{34}\text{H}_{48}\text{N}_4\text{O}_{10}$, (672.78): C, 60.70; H, 7.19; N, 8.33. Found: C, 59.14; H, 7.02; N, 7.36.

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