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Synthesis of highly fluorescent and water soluble perylene bisimide

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Abstract

Designed and synthesized a new highly water soluble N,N'-bis(2-(((5-((dimethylamino)methyl)furan-2-yl)methylthio)ethyl)perylene-3,4,9,10-tetracarboxylic diimide from 2-((5-((dimethylamino)methyl)furan-2-yl)methylthio)ethanamine and perylene-3,4,9,10-tetracarboxylic dianhydride. The compound was characterized by ¹H, ¹³C, 2D NMR, mass and IR techniques. The compound is highly fluorescent with good solubility in water and other polar solvents.

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Perylene tetracarboxylic diimide's (PTCDI) are highly versatile molecules, which attract a great interest owing to their applications in diverse fields of organic electronics, such as dye lasers [1] light harvesting arrays [2] and other electronic devices [3–5]. These compounds have also been widely studied for biochemical and pharmacological purposes because perylene bisimides are considered as potential antitumor drugs acting as telomerase inhibitors [6,7]. Various types of PTCDI have been extensively studied for applications due to their high molar absorptivity, high quantum yield of fluorescence with excellent photochemical and thermal stability [8]. Depending on the substituents, perylene derivatives can exist in a wide range of hues; they provide yellow, orange, red, bordeaux, brown and even black shades [9]. All these properties of this family of molecules largely depend on the nature and position of substituents attached to the main perylene board and on the matrix in which they are embedded [10–12]. Various types of new PTCDI molecules are synthesized for numerous applications in modern electronics. In this article, we designed and synthesized a new highly fluorescent and water soluble PTCDI molecule namely, N,N'-bis(2-((5-((dimethylamino)methyl))furan-2-yl)methylthio)ethyl)perylene-3,4,9,10-tetracarboxylic diimide for potential application in organic electronics. The compound was characterized using various spectral techniques.

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1. Experimental

1.1. Preparation of compounds

2-((5-((Dimethylamino)methyl)furan-2-yl)methylthio)ethanamine **1**: In a 250 mL round bottom flask, a mixture of furfuryl alcohol (0.98 g, 10 mmol), formaldehyde (0.30 g, 10 mmol) and dimethylamine hydrochloride (0.45 g, 10 mmol) was dissolved in 50 mL absolute methanol. The reaction mixture was heated at 70–80 °C for 12 h. After 12 h 2-aminoethanthiol hydrochloride (1.13 g, 10 mmol) was added, stirred and heated at 120–130 °C for additional 7 h. The reaction mixture was cooled and poured into water. The suspension was extracted with chloroform and the solvent was removed. The product formed as yellow oil (yield 85%). ¹H NMR (500 MHz, CDCl₃): δ 2.16 (s, 2H, NH₂), 2.23 (s, 6H, CH₃), 2.59 (t, 2H, *J* = 6.5 Hz, CH₂), 2.80 (t, 2H, *J* = 6.5 Hz, CH₂), 3.41 (s, 2H, CH₂), 3.68 (s, 2H, CH₂), 6.11 (s, 2H, CH); ¹³C NMR (125 MHz, CDCl₃): δ 27.4 (C1'), 35.1 (C3'), 40.1 (C4'), 44.2 (C3''), 55.1 (C1''), 107.3 (C3), 108.7 (C4), 150.5 (C2), 151.1 (C5); MS (CI, *m/z*): [M⁺] calcd. for C₁₀H₁₈N₂OS, 215.3; found, 215.8.

N,*N*[']-Bis(2-((5-((dimethylamino)methyl)furan-2-yl)methylthio)ethyl)perylene-3,4,9,10-tetracarboxylic diimide **3**: The compound **3** was synthesized following the standard condensation method developed by Langhals [13]. Briefly, in a 250 mL round bottom flask, **2** (3.7 g, 9.4 mmol), **1** (3.29 g, 23 mmol) and 15 g imidazole were stirred 5 h at 180 °C. The mixture was cooled to room temperature, taken up in 100 mL ethanol, treated with 400 mL 2 mol/L HCl and stirred overnight. The dark red precipitate was filtered washed with triethylamine and little dichloromethane. The filtered product was dried at 130 °C. ¹H NMR (500 MHz, DMSO-*d*₆): δ 2.72 (s, 16H, CH₂ and CH₃ (merged)), 3.92 (s, 4H, CH₂), 4.00 (s, 4H, CH₂), 4.37 (s, 4H, CH₂), 6.48 (s, 2H, CH), 6.74 (s, 2H, CH), 7.66–7.38 (m, perylene H); ¹³C NMR (125 MHz, DMSO-*d*₆): δ 27.0 (C1'), 28.2 (C3'), 39.5 (C4'), 41.2 (C3''), 51.4 (C1''), 109.1 (C3), 115.2 (C4), 119.1, 120.7, 126.5, 129.4, 132.1, 134.1 (Ar–C), 144.0 (C2), 153.3 (C5), 161.6 (CO); IR (KBr): ν = 3421 (m), 2922 (m), 2853 (m), 1690 (s), 1653 (vs), 1591 (s), 1339 (s), 1160 (m), 1018 (m), 808 (m), 744 (m) cm⁻¹; MS (CI, *m/z*): [M⁺] calcd. for C₄₄H₄₀N₄O₆S₂, 784.9; found, 784.5.UV–vis (MeOH): λ_{max} (ϵ) 459 (18,511), 486 (37,809), 522 nm (50,993); fluorescence (MeOH): $\lambda_{max} = 534$, 572 nm ($\lambda_{exc} = 460$); yield: 84%.

1.2. Computational details

The molecule was first constructed using Chemcraft programme [Chemcraft, tool for treatment of the chemical data, version 1.5 (build 286), Zhurko and Zhurko, www.chemcraftprog.com]. This was subjected to Molecular Mechanics corrections using Discovery Studio Visualizer [www.accelrys.com]. This was done for molecules using both symmetry point groups, *i.e.* C_2 and C_i . These structures were separately optimized using MOPAC, a semi-empirical programme. The theoretical NMR calculation was done for the DFT optimized geometry using Gaussian 03 and NMR tensors were viewed with Gaussview.

The fluorescence microscopy image was recorded with a LEICA BM-2500 microscope, which provides excitation in the range of 450–490 nm; emission >515 nm.

2. Results and discussion

The water soluble PTCDI molecule was designed by incorporating polar tails in the aromatic perylene board. The starting material 2-((5-((dimethylamino)methyl)furan-2-yl)methylthio)ethanamine **1** was prepared from furfuryl alcohol, dimethylamine hydrochloride, formaldehyde and 2-aminoethanethiol hydrochloride by refluxing in methanol at 120–130 °C. The condensation of perylene-3,4,9,10-tetracarboxylic dianhydride **2** and **1** using imidazole as a solvent resulted in the formation of *N*,*N'*-bis(2-((5-((dimethylamino)methyl)furan-2-yl)methylthio)ethyl)perylene-3,4,9,10-tetracarboxylic diimide **3** (Scheme 1). The compounds **1** and **3** were characterized by mass, IR, ¹H, ¹³C and 2D NMR (¹H–¹H COSY and ¹H–¹³C COSY) techniques. The ¹H NMR spectrum of the compound **3** was recorded in D₂O and DMSO-*d*₆. In D₂O the aliphatic proton signals were well resolved and the aromatic perylene protons signals were observed as a singlet at 7.40 ppm. The absence of coupling in the aromatic protons may be due to the π – π stacking. In DMSO, the NMR spectrum shows the characteristic aromatic proton peaks. The IR spectrum of **3** in KBr shows the bands at 2922–2853 (C–H stretching), 1339 (C–N stretching), 1591 (C=C stretching) and 1690, 1653 cm⁻¹ (C=O stretching). The spectral data are consistent with the proposed structure of the molecule. Table 1 shows the 2D NMR data of **3**.



Scheme 1. Synthesis of compound 3.

Table 1 1 H, 13 C and 2D NMR (1 H– 1 H COSY, 1 H– 13 C COSY) for compound **3.**

Atom position	$\delta_{ m H}$	$\delta_{ m C}$	¹ H– ¹ H COSY	¹ H– ¹³ C COSY
a	_	161.6	_	-
b	_	134.1	_	-
c	7.66-7.38 (m, 8H perylene)	129.4	_	C–c
d		119.1	_	Cd
e	_	132.1	_	-
f	_	120.7	_	-
g	_	126.5	_	-
1'	3.92 (s, 4H)	27.0	_	C-1′
3'	2.72 (s, 16H)	28.2	H-4'	C-3'
3″		41.2	_	C-3"
4′	4.00 (s, 4H)	39.5	H-3'	C-4′
2	_	144.0	_	-
3	6.48 (s, 2H)	109.1	H–4	C-3
4	6.74 (s, 2H)	115.2	H–3	C-4
5	_	153.3	_	_
1″	4.37 (s, 4H)	51.4	-	C-1″

The compound **3** is soluble in water (1.2 mg/mL), MeOH (0.8 mg/mL), DMF (0.6 mg/mL) and DMSO (1.0 mg/mL). The absorption spectrum of **3** shows typical monomeric π - π transition band with three pronounced peaks at 522, 486 and 459 nm, which correspond to the 0–0, 0–1 and 0–2 electronic transitions, respectively (Fig. 1a) [14,15]. There is no shift in λ_{max} position with increasing the concentration of the compound. Fig. 1b shows the fluorescence spectra



Fig. 1. (a) UV-vis absorption; (b) fluorescence spectra of 3 MeOH; (c) UV-vis absorption spectra of 3 in polar solvents.

Table 2 UV–visible absorption maxima of **3** in various solvents.

Solvent	λ_1 (nm)	λ_2 (nm)	$\lambda_3 (nm)$
МеОН	522	486	459
DMF	527	490	461
DMSO	530	492	462
Water	563	533	478

of **3** in methanol at various concentrations, with $\lambda_{exc} = 460$ nm. The fluorescence emission peaks appeared at 534 and 572 nm. The fluorescence spectrum depicts the mirror image of the absorption; due to two nitrogen's position at the node in π orbitals. The solubility of **3** in polar solvents allowed us to compare its UV–visible spectra in a range of polar solvents (CH₃OH, DMSO, DMF and H₂O). The spectra are shown in Fig. 1c and the λ_{max} values are given in Table 2. The spectral shape is similar in solvents and the spectral shift is not straightly dependent on the solvent polarity. This may be due to some specific solvent molecule interactions at various solvents. However, solvatochromism was observed in water as shown by decreased extinction coefficient and a bathochromic shift of absorption peaks. The observed decrease in molar extinction coefficient of the compound in water with respect to organic solvents may be due to the self-aggregation despite its water solubility. Similar trends were also reported for the perylene diimide hydrochlorides and coronene derivatives [16]. Furthermore, the relative intensities of the absorption peaks changed, with the $0 \rightarrow 1$ transition (at 533 nm) becoming λ_{max} . Similar behaviour has been reported for tehered oligomers of perylene diimides as well as concentrated solutions of perylene diimides [17]. The compound **3** is more soluble in water than organic solvents due to the polar side chain. The greater conformational flexibility of the 2-((5-((dimethylamino)methyl)furan-2-yl)methylthio)ethyl side chain (compared to alkyl chains) affords sufficient



Fig. 2. Fluorescent microscopic image of 3 coated on glass plate.



Fig. 3. NMR shielding regions of 3 generated by GIAO method.

solubility for the PTCDI molecule in water, while the increased density of the side chain allow for tight packing of the perylene backbones to maximize the $\pi - \pi$ interaction.

Fig. 2 shows the fluorescent microscopic image of the compound **3** coated on the glass plate using spin coater. The compound exhibits strong green fluorescence. To measure the property of the shielding due to the central π -system a theoretical NMR study was done at the 3-21G* level using Gauge-Including Atomic Orbital (GIAO) method. The shielding tensor was generated with respect to the terminal nitrogen atom. The image shows a large shielding region at the centre (Fig. 3). It can be implied that due to π -stacking interactions, chemical shifts of the perylene protons are highly shielded in the NMR.

3. Conclusions

We designed and synthesized a novel water soluble perylene diimide. The compound was characterized by various spectral techniques. The new compound was studied for its photophysical properties. Organization and π – π stacking of the perylene diimide chromophores in solution was evident from upfield shifts in the NMR. The *N*-alkyl substituents and heterocylic rings import solubility through the polar groups. Conclusively, the electron transporting characteristics and packing will also be modified by the polar tail.

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