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Solvatochromism, anion binding and electrochemistry in 5,15-porphodimethenes

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ABSTRACT

Synthesis and characterization of substituted 5,15-bis-(4′-hydroxy-3′,5′-di-*tert*-butyl-phenyl)-porphodimethenes (**3a-b**), are described. Spectroscopic studies of redox-active 3,5-di-*tert*-butyl-4-hydroxyphenyl substituted porphodimethene **3a, 3b** reveal a change in conformation via acid/base-switched tautomerism by simultaneously switching between porphodimethene and porphyrinogen accompanied by visible chromogenic changes. The novel prototype exhibits a positive solvatochromism and chromogenically senses fluoride (specifically in polar solvents) and hydroxide ion (in all solvents). The unique structural changes along with distinct color changes were monitored by UV–Vis, fluorescence, cyclic voltammetry NMR spectroscopic techniques and DFT computations.

1. Introduction

Tetrapyrrole macrocycles are promising candidates for incorporation into electronic, photovoltaic or sensing devices because of their synthetic flexibility [1,2]. Calix[4]phyrin or 5,15-porphodimethene, an intermediate between calix[4]pyrrole and porphyrin, is an assembly comprised of two dipyrrin fragments linked through sp^3-hybridized *meso*-carbon atoms which interrupts the ring current in the macrocycle thus, adopting nonplanar conformation [3,4]. This partially flexible framework as well as the rigid π-conjugated network provides them a vital role in coordination chemistry [5], as catalysts [6,7], and as sensors for anions, cations, or neutral substrate recognition in supramolecular chemistry [8,9].

Porphyrinoids bearing phenolic groups are known to undergo structural changes, with similarities to the reversible hydroquinone/quinone redox system depending on their state of protonation and oxidation [10,11]. As reported earlier, 5,10,15,20-tetrakis-(3,5-di-*tert*-butyl-4- hydroxyphenyl)porphyrin underwent fluoride triggered aerial oxidation, while 5,15-bis-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-10,20-diphenylporphyrin did not oxidize at all [12]. However, till date there has been no report on anion/solvent triggered reversible structural changes of 5,15-porphodimethenes. With this in mind, introduction of 3,5-di-*tert*-butyl-4-hydroxyphenyl at 5,15 position in porphodimethene provides an ideal archetypal molecule with dynamic interconversion between phenolic and oxo form, which can be used to study the detailed process involving investigations of the N–H tautomerism. Also, the sp^3-hybridized *meso*-carbon atom in 5,15-porphodimethenes interrupting the ring current in macrocycle makes the core nitrogen and N–H units more accessible for coordination as compared to porphyrin [13–15].

In this work, hydroxy porphodimethene molecules as potent host have been synthesized which have the ability to change color when complexed to appropriate guest or solvent molecules with drastic variations of both electronic and conformational structures, as demonstrated by UV–vis absorption spectroscopy, fluorescence spectroscopy, and ^{1}H NMR studies. This solution-based switching presents a novel concept for information processing and solution-state technologies and could be used further in developing molecular memory. Further anion binding studies of various anions for these molecules were performed and harnessed using various spectroscopic techniques.

2. Experimental

2.1. Materials

Pyrrole was distilled prior to use. All other reagents Trifluoroacetic acid, N-bromosuccinimide, 2,6-di-*tert*-butyl-4-

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methylphenol, Acetone, Cyclohexanone were purchased from Spectrochem and used without any further purification. The quaternary ammonium salts (n-Bu_4NF, n-Bu_4NCl, n-Bu_4NBr, n-Bu_4NI), tetrabutylammonium acetate (n-Bu_4NOAc) and tetrabutylammonium hydroxide in methanol (n-Bu_4NOH) were purchased from Sigma Aldrich. Solvents used for purification and UV–Vis spectroscopy were of analytical grade and used without further purification. Solvents for the electrochemical measurements were distilled from calcium hydride under argon. The compounds were purified by column chromatography using silica gel (60–120 mesh) and neutral alumina.

2.2. Instruments

The IR spectra were recorded on a Perkin Elmer 1710 FTIR spectrometer and the ν_{max} are expressed in cm^{-1}. The electronic spectra were recorded on a Perkin Elmer Lambda-35 UV/Vis spectrophotometer and the λ_{max} are expressed in nanometers. The ^1H NMR spectra were recorded on Bruker Avance-400 spectrometer using TMS as internal standard (chemical shifts in ppm). Fluorescence spectra were recorded on Varian Cary fluorescence spectrometer. MALDI Spectra were recorded on MS - ABI Sciex 5800 TOF/TOF System with LC-MALDI in cinnamic acid matrix. ESI-MS spectra were recorded on Agilent Technologies 6530 Accurate-Mass Q-TOF LC/MS. Cyclic voltammograms of the samples were obtained using CHI 600D electrochemical analyzer. Molecular modelling study of our molecules were done using Gaussian 09W software. Structures were drawn in GaussView and they were optimized to find its energy minimized structures and geometries. EPR measurements were carried out using JES - FA200 ESR Spectrometer with X and Q band having EStandard Frequency (X band) - 8.75–9.65 GHz; Sensitivity-7x109spins/0.1mT; Resolution - 2.35(micro)T. All the molecules were optimized using DFT calculations with B3LYP functional in Gaussian 09W program [16]. In order to study the anions and their interactions 6-31 + G (d,p) basis set were employed in all calculations. For investigating the effect of solvent on the conformational preference and the anion binding energies of the molecules SCIPCM model was used in two solvent media dichloromethane ($\varepsilon = 8.93$) and dimethylsulfoxide ($\varepsilon = 46.7$).

2.3. Synthesis of porphodimethenes

To the stirred solution of 4-hydroxy-3,5-di-*tert*-butyl substituted dipyrromethane (2.87 mmol) and ketone (2.90 mmol) in dichloromethane, trifluoroacetic acid (0.06 ml) was added at room temperature under argon atmosphere. The mixture was stirred at room temperature for 2 h. After completion of reaction, the reaction mixture was oxidized by DDQ, solvent was removed under reduced pressure and crude mixture was purified by column chromatography from dichloromethane/hexane.

2.3.1. 5,15-Bis-(3,5-di-tert-butyl-4-hydroxyphenyl)-10,10′,20,20′-tetramethyl porphodimethene, **3a**

Physical state: red solid; Yield: 222.90 mg (20%); mp: >300 °C; MS (ESI) *m*/*z*: Calculated ($C_{52}H_{64}N_4O_2$), 776.5029; experimental $(M + H)^+$ 777.5110; δ_H (400 MHz, $CDCl_3$): 1.39 (s, 36H, $-C(CH_3)_3$), 1.93 (s, 12H, $-CH_3$), 5.32 (s, 2H, −OH), 6.21 (d, 4H, $J = 3.68$ Hz, β-pyrrolic), 6.13 (d, 4H, $J = 3.68$ Hz, β-pyrrolic), 7.21 (s, 4H, Ar–H), 14.30 (br s, 2H, −NH); ^{13}C (100 MHz, $CDCl_3$): 29.6, 30.3, 31.9, 113.7, 128.2, 128.4, 134.6, 140.4, 154.6, 164.6.

2.3.2. 5,15-Bis-(3,5-di-tert-butyl-4-hydroxyphenyl)-10,10′,20,20′-dispirocyclohexyl porphodimethene, **3b**

Physical state: red solid; Yield: 319.65 mg (26%); MS (ESI) *m*/*z*: Calculated ($C_{58}H_{72}N_4O_2$), 856.5655; experimental $(M + H)^+$ 857.5738; δ_H (400 MHz, $CDCl_3$): 1.37 (s, 36H, $-C(CH_3)_3$), 1.47 (s, 4H, $-CH_2$), 1.62 (s, 4H, $-CH_2$), 1.69 (s, 4H, $-CH_2$), 2.1 (s, 4H, $-CH_2$), 2.8 (s, 4H, $-CH_2$), 5.27 (s, 2H, −OH), 6.1 (d, 4H, $J = 3.84$ Hz, β-pyrrolic), 6.2 (d, 4H, $J = 3.84$ Hz, β-pyrrolic), 7.16 (s, 2H, Ar–H), 7.25 (s, 2H, Ar–H), 14.50 (br s, 2H, −NH); ^{13}C (100 MHz, $CDCl_3$): 29.6, 30.2, 30.3, 31.9, 34.2, 100.9, 127.5, 127.8, 130.0, 132.4, 146.2, 147.8, 162.7.

3. Results and discussion

3.1. Synthesis and characterization

Synthesis of porphodimethene **3a** involves the use of 3,5-di-*tert*-butyl-4-hydroxybenzaldehyde to form a substituted dipyrromethane followed by its condensation with acetone in presence of catalytic amount of trifluoroacetic acid under nitrogen atmosphere in dichloromethane as solvent for 3 h. The completion of the reaction was monitored by thin layer chromatography followed by DDQ oxidation [17]. The desired porphodimethene **3a** was purified by silica gel chromatography in 20% yield using dichloromethane/hexane (4:6). To avoid the formation of open chain byproducts, acetone was added in excess. The appearance of band at 429 nm with additional bands at 339 and 502 nm in UV–vis spectrum shows the formation of porphodimethene moiety. A characteristic signal of two deshielded NH protons in ^1H NMR spectrum was obtained at 14.3 ppm due to hampered aromatic current of the ring, along with peak at 7.2 ppm for the phenyl ring protons with the β-pyrrolic protons resonating as a double doublet at 6.2 ppm and 6.3 ppm and a singlet at 1.9 ppm was assigned to methyl protons. A sharp M^+ signal at *m*/*z* 777.5110 in MALDI confirms the synthesis of hydroxy porphodimethene **3a**. The other porphodimethene **3b** was also synthesized via similar schematic route (Scheme 1).

3.2. Solvatochromism behaviour

Hydroxy porphodimethenes are influenced by the surrounding medium and solvents as depicted by UV–vis absorption spectrum. Fig. 1, S5 shows the UV–vis spectral changes of **3a** and **3b** in eight organic solvents of varying polarities, respectively. A bathochromic shift is observed for both the synthesized porphodimethene sequentially in the order of increasing polarity: benzene, dichloromethane, THF, acetone, acetonitrile, methanol, DMF and DMSO, accompanied by a rapid color change from orangish-yellow to reddish-pink (Fig. S10). With increasing polarity the intensity of the bands at 420–430 nm diminishes and new bands arose at 518 nm for acetone, 533 nm for acetonitrile, 537 nm for methanol, 559 nm for DMF and 567 nm for DMSO. Both the porphodimethenes undergo quantitative tautomeric conversion from the phenolic to oxo state upon the addition of polar solvents stabilizing the molecule in the first excited state relative to the ground state which leads to positive solvatochromism (red shift) resulting in the formation of oxoporphyrinogen (Scheme 2) [18,19].

Further varying the chain length in different alcohols from less polar dodecanol to more polar methanol, as the solvent polarity increases the oxo form predominates, thus exhibiting positive solvatochromism (Fig. 1b). This was further confirmed by UV–vis spectral changes, when small aliquots of water were added to a solution of porphodimethene **3a** in THF, $\lambda_{max} = 412$ nm was attenuated and a broad shoulder arising at $\lambda = 520$ nm indicates the formation of a well-defined new species, due to tautomerization (Fig. S8). The effect of solvents on the spectral positions has been summarised in Table 1.

To obtain the further insights about the nature of transformation ^1H NMR spectral changes in C_6D_6, CD_2Cl_2, CD_3CN and DMSO-d_6 were recorded (Fig. 2). In benzene and dichloromethane, phenolic