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# Facile synthesis, photophysical and electrochemical redox properties of octa- and tetracarboxamidophenylporphyrins and the first example of amido-imidol tautomerism in porphyrins

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#### ABSTRACT

5,10,15,20-tetrakis(4'-carboxamidophenyl)porphyrin (**1**) and 5,10,15,20-tetrakis(3',5'-dicarboxamidophenyl) porphyrin (**2**) have been synthesized in excellent yields and characterized by various spectroscopic techniques and cyclic voltammetric studies. Notably, **1** and **2** exhibited amido-imidol tautomerism in DMSO- $d_6$ . The imido tautomer (-C(OH)=NH) was stabilised in DMSO- $d_6$  at 293 K while the same was converted into amido form ( $-CONH_2$ ) at high temperature (418 K). This is a first example of amido-imidol tautomerism in porphyrins. The moderate electron withdrawing nature of imidol groups at *meso*-phenyl rings lead to 80 –95 mV anodic shift in their first ring reduction potential whereas 50–110 mV anodic shift in first ring oxidation potential as compared to that of H<sub>2</sub>TPP.

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## 1. Introduction

Porphyrin,  $18-\pi$  aromatic macrocycle is a most significant pigment found in nature, having four pyrrole units joined through methine carbons. The four pyrrole nitrogens are positioned at the four corners of the square and are ideal for coordination to metal ions. Porphyrin has been successfully utilized across a wide range of research disciplines due to their numerous profitable properties such as attractive absorption and emission properties, strong aromaticity and rich metal coordination chemistry [1–5]. Porphyrins and their metal complexes were used in catalysis [6-10], dyesensitized solar cells (DSSC) [11–14], photodynamic therapy (PDT) [15,16], molecular sensors [17,18], nonlinear optics (NLO) [19–21], and the construction of multiporphyrinic arrays [22-24] due to their prominent absorption in the UV-vis region and interesting physicochemical properties. The construction of supramolecular architectures from small organic or metal-organic compounds via non-covalent interactions, such as hydrogen bonding and metal coordination is highly useful in shape-selective catalysis, enantiomeric separation and molecular storage. In recent years, the development of new types of intermolecular interactions has been grown tremendously. In particular, hydrogen bonding is one of the

most interesting non-covalent interactions as it showed real promises in different fields such as catalysis, medicinal chemistry, and molecular recognition [8,25,26]. Hydrogen bonding is a specific, directional, reversible and strong noncovalent bonding interactions and a useful approach in supramolecular assembly.

Usually, functional groups having hydrogen atom(s) such as -COOH, -OH, -NH<sub>2</sub>, -CONH<sub>2</sub> and -NHCONH<sub>2</sub> located at the periphery of organic molecules, are commonly used in the construction of supramolecular assemblies. This allows their effective interaction with an electron-rich atom such as N, O and F that acts as a Lewis base. In recent years, chemists have paid much interest towards crystal engineering of supramolecular self-assemblies of tetraarylporphyrins by hydrogen bonding and coordination, or tessellated by external metal ion or organic ligand bridging auxiliaries [27-32]. In recent years, meso-carboxyphenylporphyrins and meso-pyridylporphyrins were turned out as a useful basic unit for the construction of multiporphyrin arrays, metal organic framework (MOF) and supramolecular capsules. The pyridyl porphyrins exhibit a high tendency to react through their peripheral N-sites with a variety of transition metal ion connectors and yielded hybrid organic-inorganic coordination networks with varying topology and porosity. The peripheral -COOH and pyridyl group exhibit a high tendency to construct self-assemblies, yielding multiporphyrin networks and frameworks in crystalline solids of varying topology and dimensionality. Metal insertion into the porphyrin core allows another dimension to the binding ability of this ligand







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along the equatorial and axial directions [32]. Notably, benzanilide exhibited temperature and solvent dependent amido-imidol tautomerism [33,34]. To the best of our knowledge, such type of tautomerism is not known in porphyrin chemistry. Keeping this in mind, we aim to synthesize carboxamido substituted porphyrins (1 and 2, Chart 1) which have shown the interesting amido-imidol tautomerism and also one can construct porphyrin-based supra-molecular assemblies. Herein, we demonstrate the facile synthesis, photophysical and electrochemical redox properties and temperature dependent amido-imidol tautomerism of tetra- and octaamide substituted porphyrins (1–2).

## 2. Experimental section

## 2.1. Chemicals

All required chemicals were purchased from Alfa Aesar. Tetra/ octa-carboxyphenylporphyrins were synthesized by modified literature methods [35,36].

## 2.2. Instrumentation

UV-Visible and fluorescence spectra were recorded using Cary



Chart 1. Molecular structures of synthesized porphyrins (1-2).



Scheme 1. Synthesis of tetra/octa-carboxamidophenylporphyrins (1-2) from their corresponding carboxyphenylporphyrins.

**Table 1** Electronic spectral and photophysical data of **1** and **2** ( $\lambda_{max}$ , nm ( $\varepsilon \times 10^{-3}$ , L mol<sup>-1</sup> cm<sup>-1</sup>) in DMSO at 298 K.

Por	$\lambda_{absorption,} nm \left( \varepsilon \times 10^{-3} \text{ L} \text{ mol}^{-1} \text{ cm}^{-1}  ight)$	$\lambda_{em}$ (nm)	φ <sub>f</sub>	τ (ns)	$k_r (10^6 \; s^{-1})$	$k_{nr}(10^7 \ s^{-1})$
H <sub>2</sub> TPP	417(513), 515(23.9), 549(5.01), 590(1.66), 647(1.58)	654, 718	0.110	11.4 (91%)	9.65	7.81
1	419(123), 515(5.0), 550(2.0), 590(1.11), 645(0.80)	654, 718	0.089	11.7 (96%)	7.61	7.79
2	421(303), 516(11.0), 550(2.3), 590(1.50), 645(0.52)	653, 718	0.069	11.4 (93%)	6.05	8.17

 $\phi_f$  = quantum yield (reference, H<sub>2</sub>TPP in toluene 0.11);  $\tau$  = fluorescence lifetime;  $k_r$  = radiative rate constant;  $k_{nr}$  = non-radiative rate constant.



Fig. 1. Optical absorption spectra of 1 and 2 in DMSO at 298 K.

100 spectrophotometer and Hitachi F-4600 spectrofluorometer, respectively. All <sup>1</sup>H NMR measurements were performed using JEOL-400 MHz spectrometer in DMSO-*d*<sub>6</sub>. Electrochemical measurements were carried out using CHI-620E electrochemical workstation. A three electrode system made up of Pt-button working electrode, Ag/AgCl reference electrode and a Pt-wire counter electrode was used. The porphyrin concentration was maintained approximately 1 mM throughout the experiment. All measurements were performed in DMF which was purged with Ar gas, using 0.1 M TBAPF<sub>6</sub> as the supporting electrolyte.

## 2.3. Synthesis of tetra- and octaacid substituted porphyrins

Tetramethylester (0.593 g, 0.70 mmol) or octaethylester porphyrin (0.834 g, 0.70 mmol) was dissolved in 100 mL THF in a two neck round bottom flask. To this, 10 mL of aq. solution of KOH (300 equivalents) was added and refluxed for 16 h at 75 °C. After completion of the reaction, THF was removed using rotary evaporator and the resulting residue was treated with 2N HCl (150 mL) which resulted green precipitate, filtered and washed with water





Fig. 2. Variable temperature <sup>1</sup>H NMR spectra of 1 in DMSO-*d*<sub>6</sub> from 293 K to 418 K.

(50 mL  $\times$  5). The protonated porphyrin was neutralized with pyridine (15 mL). Then, the pyridine was removed by rotary evaporation and the resulting residue was washed with water (50 mL  $\times$  3) and dried under vacuum. The crude porphyrin was recrystallized from CHCl<sub>3</sub> and acetone mixture (3:7, v/v). The yield was found to be 0.54 g (98%) for the corresponding tetraacid and 0.680 g (100%) for octaacid.

#### 2.4. Synthesis of tetra- and octaamide porphyrins (1 and 2)

293 K

9.0

Tetraacid (0.35 g, 0.443 mmol) or octaacid (0.428 g, 0.443 mmol) was taken in a 50 mL RB flask. To this, distilled SOCl<sub>2</sub> (2 mL, 0.0274 mol) was added dropwise and refluxed for 1 h. Then excess amount of SOCl<sub>2</sub> was removed by vacuum distillation. To this, cold NH<sub>4</sub>OH (6 mL) was added slowly till the precipitate was formed. The precipitate was filtered and washed with water (50 mL  $\times$  3). The crude porphyrins were recrystallized from CH<sub>3</sub>OH and acetone mixture (2:8, v/v). Yield was found to be 98% (0.34 g, 0.432 mmol) for **1** and 97% (0.411 g, 0.428 mmol) for **2**.

**1:** UV/Vis (DMSO):  $\lambda_{max}$  (nm) ( $\varepsilon \times 10^{-3}$  L mol<sup>-1</sup> cm<sup>-1</sup>) 417(513), 515(23.9), 549(5.01), 590(1.66), 647(1.58). <sup>1</sup>H NMR in DMSO-*d*<sub>6</sub>:  $\delta$  (ppm) 8.82 (s, 8H, β-pyrrole-H), 8.33 (s, 4H, O–H of imidol), 8.28 (s, 16H, *meso*-phenyl-H), 7.63 (s, 4H, N–H of imidol), -2.98 (s, 2H, N–H). ESI-MS (*m*/*z*): found 787.837 [M+H]<sup>+</sup>, calcd. 787.843. Anal. calcd. for C<sub>48</sub>H<sub>34</sub>N<sub>8</sub>O<sub>4</sub>: C, 73.27; H, 4.36; N, 14.24%. Found: C, 73.40; H, 4.58; N, 14.17%.

**2:** UV/Vis (DMSO):  $\lambda_{max}$  (nm) ( $\varepsilon \times 10^{-3}$  L mol<sup>-1</sup> cm<sup>-1</sup>) 421(303), 516(11.0), 550(2.3), 590(1.50), 645(0.52). <sup>1</sup>H NMR in DMSO-*d*<sub>6</sub>:  $\delta$  (ppm) 8.91–8.86 (m, 20H, *meso*-phenyl-H and β-pyrrole-H), 8.32 (s, 8H, O–H of imidol), 7.66 (s, 8H, N–H of imidol), –2.89 (s, 2H, NH). ESI-MS (*m*/*z*): found 959.818 [M+H]<sup>+</sup>, calcd. 959.943. Anal. calcd. for C<sub>52</sub>H<sub>39</sub>N<sub>12</sub>O<sub>8.5</sub>: C, 64.52; H, 4.06; N, 17.36%. Found: C, 64.59; H, 4.17; N, 17.45%.

## 3. Results and discussion

Tetra- and octa-carboxyphenylporphyrins were synthesized in quantitative yields and characterized by various spectroscopic



f1 (ppm)
 Fig. 3. Variable temperature <sup>1</sup>H NMR spectra of 2 in DMSO-d<sub>6</sub> from 293 K to 418 K.

8.0

7.5

7.0

8.5

techniques [35,36]. The carboxy substituted porphyrins were treated with SOCl<sub>2</sub> in order to get the corresponding acid chlorides which reacted with aqueous ammonia to yield amide porphyrins (1–2) as shown in Scheme 1. The newly synthesized porphyrins were characterized by UV–vis, fluorescence and <sup>1</sup>H NMR spectroscopic techniques, mass spectrometry and electrochemical studies.

The optical absorption spectra of 1 and 2 were recorded in DMSO at 298 K. Table 1 lists the absorption spectral data of these porphyrins in DMSO. 1 and 2 exhibited a marginal red-shift in Soret band (B band) at 419 and 421 nm, respectively as compared to H<sub>2</sub>TPP (417 nm) whereas Q-bands weren't much influenced (Fig. 1). The marginal shift in optical absorption spectra of 1-2 with respect to H<sub>2</sub>TPP is possibly due to the large distance of amide groups from the porphyrin aromatic core. There is no shift in the emission spectra of **1** and **2** as compared to  $H_2$ TPP as shown in Fig. S1 in the supporting information (SI). The emission intensity of **1** and **2** is considerably decreased with respect to H<sub>2</sub>TPP (Fig. S1 in the SI) while maintaining the same concentration for all leading to lower quantum yields (Table 1) and follows the order:  $H_2TPP > 1 > 2$ . The emission spectral data, quantum yields, radiative rate constants (k<sub>r</sub>) and non-radiative rate constants  $(k_{nr})$  of **1** and **2** are listed in Table 1. The fluorescence quantum yields and radiative rate constants of 1 and **2** were decreased as compared to H<sub>2</sub>TPP whereas the increase in non-radiative rate constants suggest a weak intramolecular charge transfer interaction between the porphyrin core and mesophenyl groups containing imidol moieties.

## 3.1. Variable temperature (VT) NMR studies

The synthesised porphyrin derivatives (1-2) were characterised by <sup>1</sup>H NMR spectroscopy in DMSO- $d_6$  at 298 K. The <sup>1</sup>H NMR spectra of **1** and **2** were presented in Figs. S2 and S3 in the SI.

**1** exhibited a singlet of  $\beta$ -pyrrole protons at 8.82 ppm and another singlet corresponds to meso-phenyl protons were observed at 8.28 ppm in DMSO- $d_6$  at room temperature as shown in Fig. S2 in the SI. Two broad singlets of imidol -OH and -NH protons observed with four protons intensity each at 8.33 and 7.63 ppm, respectively. This observation confirms that 1 exists in imidol form in DMSO at 298 K. In case of 2, a multiplet was observed in the range of 8.91-8.86 ppm which corresponds to o,p-protons of mesophenyl rings and  $\beta$ -protons as shown in Fig. S3 in the SI. Further, the observed two broad singlets at 8.32 and 7.66 ppm correspond to imidol –OH and –NH protons (Fig. S3 in SI), respectively. This also further confirms that 2 also exists in imidol form at room temperature. The variable temperature (VT) <sup>1</sup>H NMR spectra of **1** and **2** in DMSO- $d_6$  are shown in Figs. 2 and 3, respectively. While increasing the temperature from 293 K to 418 K, -OH protons (signal b as indicated in Fig. 2) disappears and -NH (signal a) starts to shift. The observed coalescence temperature was at 353 K. While increasing from 353 K, a new signal starts appearing at 7.54 ppm while no signal was observed for -OH and -NH. Notably at 418 K, a broad singlet at 7.42 ppm with eight protons intensity corresponds to amide  $(CONH_2)$  functionality indicating that **1** exists in amido form at high temperature. On the other hand, there is no shift in the position of  $\beta$ -pyrrole protons (8.85 ppm) whereas the signal sharpens at high temperatures. Interestingly, the singlet (AB type) at 8.32 ppm (at 293 K) which corresponds to o,m-protons of mesophenyl ring was converted to AB quartet at 418 K without changing its position. These results clearly indicate that 1 exists in imidol form at room temperature and exists in amido form at higher temperatures in polar solvents such as DMSO- $d_6$ . Fig. 3 represents the VT NMR spectra of 2 in DMSO- $d_6$ . As observed for 1, two broad singlets at 7.66 and 8.32 correspond to -NH and -OH of imidol moiety at 293 K. While increasing from 293K to 353 K, the singlets observed for -NH and -OH of imidol moiety were completely disappeared which represents the coalescence temperature. Finally at 418 K, a broad singlet at 7.45 ppm with 16 protons intensity was appeared which corresponds to amido  $(-CONH_2)$  functionality. On the other hand, a multiplet (8.91–8.86 ppm range) at 293 K which corresponds to *o*,*p*-protons of *meso*-phenyl rings and  $\beta$ -protons was boarded at 418 K without shifting its peak position.

Over all, <sup>1</sup>H NMR studies clearly suggest that **1** and **2** exhibit imidol form at room temperature and amido form at high temperature. To the best of our knowledge, this is a first example which shows temperature dependent amido-imidol tautomerism in porphyrins.

## 3.2. Electrochemistry

To probe the influence of imidol moieties on porphyrin  $\pi$ -system, we have carried out the cyclic voltammetric studies of these porphyrins in DMF at 298 K. The cyclic voltammograms of H<sub>2</sub>TPP, **1** and **2** were shown in Fig. 4. Table 2 lists the comparative electrochemical redox potentials (*vs.* Ag/AgCl) of imidol porphyrins in DMF. These porphyrins exhibited one irreversible oxidation and two reversible reductions. The moderate electron withdrawing nature of imidol groups is reflected in cyclic voltammetric studies. For example, the first ring oxidation of **2** is 60 mV anodically shifted



Fig. 4. Cyclic voltammograms of 1 and 2 in DMF containing 0.1 M TBAPF<sub>6</sub> using Ag/ AgCl as reference electrode with a scan rate of 0.1 V/s at 298 K.

Table 2

Electrochemical redox data (vs Ag/AgCl) of amide porphyrin derivatives in DMF containing 0.1 M TBAPF<sub>6</sub> at 298 K.

Por	Oxidation (V) <sup>a</sup> I	Reduction (V)		$\Delta E_{1/2} (V)$	
		Ι	II		
H <sub>2</sub> TPP	1.17	-1.00	-1.47	2.18	
1	1.22	-0.93	-1.33	2.15	
2	1.28	-0.91	-1.34	2.19	

<sup>a</sup> Data obtained from DPV.



Fig. 5. DFT calculations of 1 and 2 using B3LYP functional, 6-31G basis set and IEFPCM polarized method in DMSO.

as compared to **1** which intern further 50 mV anodically shifted with respect to  $H_2TPP$  (Table 2) and follows the order: **2** > **1** >  $H_2TPP$ .

Imidol substitution at *meso*-phenyl rings lead to 80-95 mV anodic shift in their first ring redox potentials as compared to H<sub>2</sub>TPP. The positive shift in first ring redox potentials of these porphyrins, is interpreted in terms of electron withdrawing nature of imidol groups on *meso*-phenyl ring. As observed from 1st ring reduction potentials, imidol substitution at *para*-position of phenyl ring leads to more anodic shift as compared to di-*meta*-substitution due to resonance (-R) and inductive (-I) effects of *para*-substituent whereas *meta*-substituent can show only inductive effect (-I). Further, the electron withdrawing nature of imidol substituents is also reflected in the 1st ring oxidation process of **1** and **2**.

## 3.3. DFT studies

To examine the influence of imidol substituents on porphyrin macrocycle, the DFT calculations have been carried out using B3LYP functional and 6-31G basis set in DMSO with default IEFPCM polarized method. **2** exhibited a quasi-planar geometry with mean plane deviation of 24 core atoms,  $\Delta 24 = \pm 0.189$  Å and mean plane deviation of  $\beta$ -pyrrole carbons  $\Delta C_{\beta} = \pm 0.283$  Å while **1** exhibited planar conformation with very small deviation ( $\Delta 24 = \pm 0.041$  Å,  $\Delta C_{\beta} = \pm 0.079$  Å) from 24 atom core of porhyrin ring as shown in Fig. 5. DFT studies suggest that the imidol substitution at *meso*-phenyl rings has little influence on porphyrin macrocycle conformation.

## 4. Conclusions

In conclusion, we have developed a facile synthetic route for 5,10,15,20-tetrakis(4'-carboxamidophenyl)porphyrin (1) and 5,10,15,20-tetrakis(3',5'-dicarboxamidophenyl)porphyrin (2) in excellent yields from the corresponding ester porphyrins. 1 and 2 have shown planar conformation of the porphyrin macrocycle and exhibited a marginal red-shift in electronic spectral features as compared to H<sub>2</sub>TPP. Herein, we successfully demonstrated the temperature dependent amido-imidol tautomerism of 1 and 2 in DMSO- $d_6$ . Interestingly, these porphyrins exist in imidol form at room temperature (293 K) whereas the same was converted to amido form at higher temperature (418 K). To the best our knowledge, this is a first report on amido-imidol tautomerism in

porphyrin chemistry. Further, these porphyrins exhibited anodic shift in their 1<sup>st</sup> oxidation ( $\Delta E_{\frac{1}{2}} = 50-110$  mV) and reduction ( $\Delta E_{\frac{1}{2}} = 80-95$  mV) potentials as compared to H<sub>2</sub>TPP due to moderate electron withdrawing nature of imidol moieties. These porphyrins can be utilized for the construction of supramolecular assemblies in their imidol form and the attempts are in progress.

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## Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.dyepig.2016.10.053.

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