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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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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_2TPP.

1. Introduction

Porphyrin, 18-π 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], dye-sensitized 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 $-COOH$, $-OH$, $-NH_2$, $-CONH_2$ and $-NHCONH_2$ 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 supramolecular 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**).

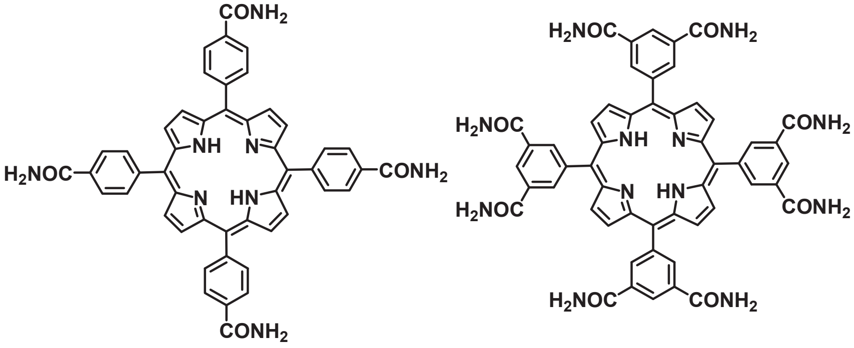
2. Experimental section

2.1. Chemicals

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

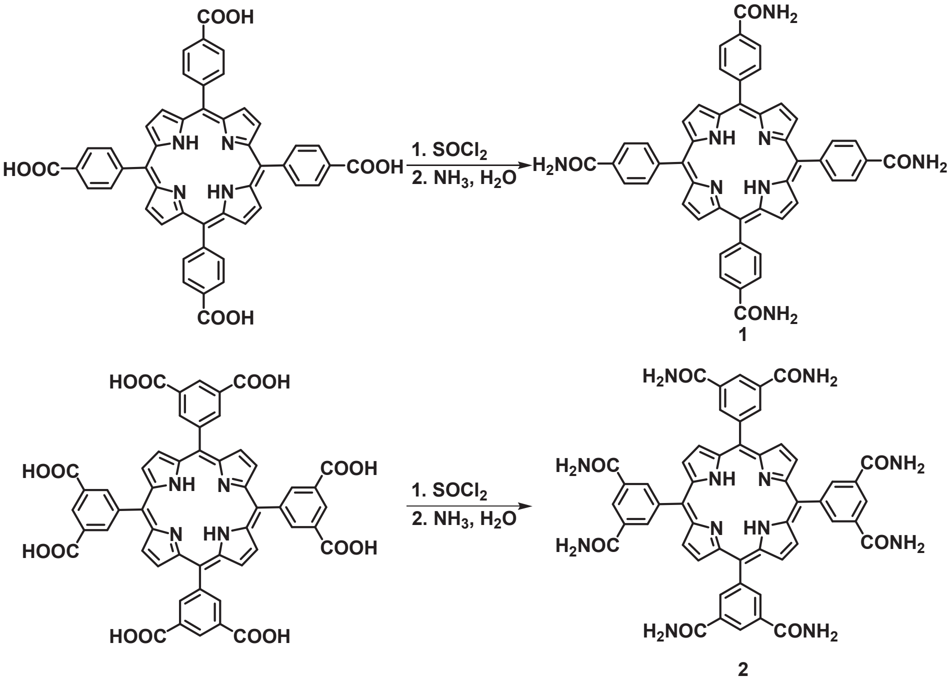
2.2. Instrumentation

UV–Visible and fluorescence spectra were recorded using Cary



1 **2**

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** (λ_{max}, nm ($\varepsilon \times 10^{-3}$, L mol^{-1} cm^{-1}) in DMSO at 298 K.

Por	$\lambda_{absorption,}$ nm ($\varepsilon \times 10^{-3}$ L mol^{-1} cm^{-1})	λ_{em} (nm)	ϕ_f	τ (ns)	k_r (10^6 s^{-1})	k_{nr}(10^7 s^{-1})
H_2TPP	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

ϕ_f = quantum yield (reference, H_2TPP in toluene 0.11); τ = fluorescence lifetime; k_r = radiative rate constant; k_{nr} = non-radiative rate constant.