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Novel Properties of Supramolecular Complexes Formed by Pairing Cationic Porphyrin and Anionic Metal-Oxo Cluster

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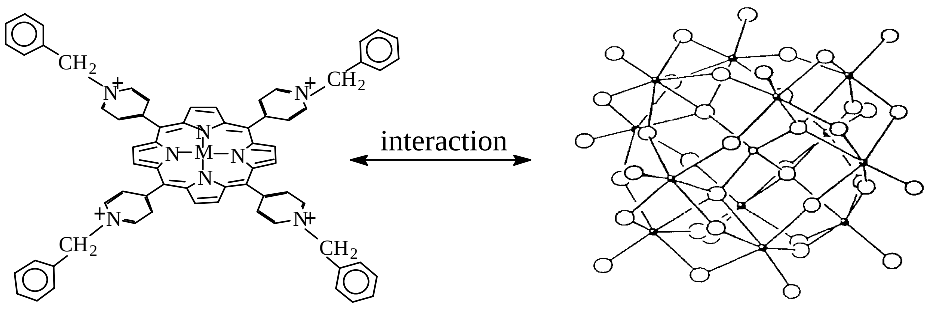
Abstract: MTBPyP (meso-tetrakis(4-N-benzylpyridyl)porphyrin, M=H_2, Zn) bearing positive charge has been shown to associate with $SiW_{12}O_{40}^{4-}$ in water solution. The spectral evolution and Job's plots analyses reveal that the relatively stable aggregates contain equal numbers of $MTBPyP^{4+}$ and $SiW_{12}O_{40}^{4-}$.

Keywords: Cationic porphyrin, anionic metal-oxo cluster, ion pair supramolecular complex.

There are numerous examples of supramolecular assemblies bound by ion pair attraction in solution [1~8]. In most cases, the properties of such complexes differ notably from those of the parent individual compounds. It is well known that charged porphyrins bind oppositely charged molecules with the aid of electrostatic interactions [8~10]. We now report some novel properties of supramolecular complexes formed by spontaneous association of cationic porphyrins ($MTBPyP^{4+}$, M=H_2, Zn) and anionic metal-oxo cluster ($SiW_{12}O_{40}^{4-}$) (**Scheme 1**).

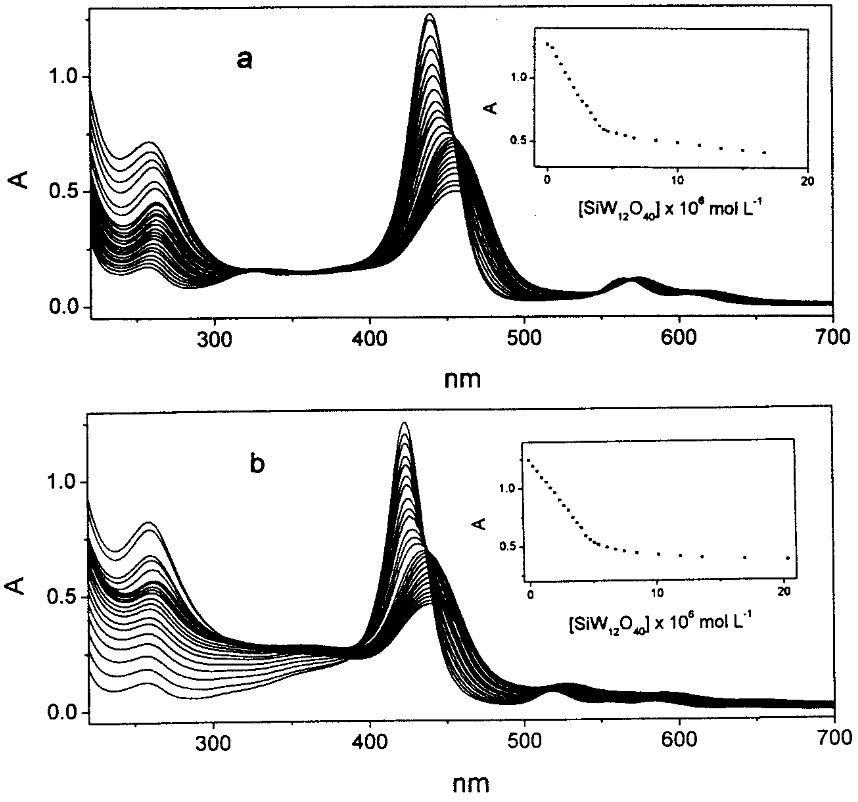
Scheme 1



$MTBPyP^{4+}$, M=H_2, Zn

$SiW_{12}O_{40}^{4-}$

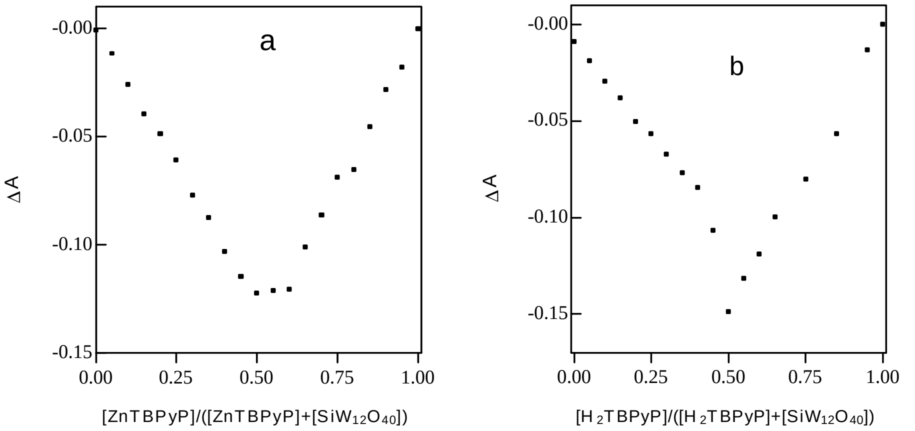
Figure 1 Spectral evolution of (a) a solution of 4.8x10^{-6}mol L^{-1} ZnTBPyP in H_2O upon addition of small aliquots of 10^{-3}mol L^{-1} $SiW_{12}O_{40}^{4-}$ (insert chart is A_{440nm} *vs* increasing concentration of $SiW_{12}O_{40}^{4-}$). (b) A solution of 6.1x10^{-6}mol L^{-1} H_2TBPyP in H_2O upon addition of small aliquots of 10^{-3}mol L^{-1} $SiW_{12}O_{40}^{4-}$ (insert chart is A_{423nm} *vs* increasing concentration of $SiW_{12}O_{40}^{4-}$).



Heteroaggregation of oppositely charged porphyrins and phthalocyanines can be conveniently studied by spectroscopic methods [8]. In this paper, we studied the interaction between $MTBPyP^{4+}$ (M= H_2, Zn) and $SiW_{12}O_{40}^{4-}$ in water solution using UV-Vis absorption spectroscopic method. **Figure 1a** gives the spectral evolution of a solution of ZnTBPyP in H_2O, upon titration with a solution of $SiW_{12}O_{40}^{4-}$. Similarly, the spectral evolution of a solution of H_2TBPyP in H_2O upon addition of $SiW_{12}O_{40}^{4-}$ is shown in **Figure 1b**. In above-mentioned both cases, the reaction proceeds with an isosbestic point (at 454, 436 nm, respectively) and linear hypochromophores effect in the Soret band of porphyrins (insert chart), which is completed when the 1:1 stoichiometry is nearly reached. At the 1:1 stoichiometryic point, the resulting spectrum differs remarkably from the sum of those of the reactants, revealing the formation of at least one new species, in which the porphyrin chromophores interact strongly with the metal-oxo clusters. Over the 1:1 stoichiometry, the isosbestic point disappears and the absorbance at the Soret of porphyrins decreases slightly but no new break point occurs which probably suggests the formation of unstable higher aggregates with the stoichiometry other than 1:1.

The data from the spectroscopic titration experiments were treated with Job's methods[11], which is constructed to ascertain the stoichiometries of the aggregates. **Figure 2** displays the Job's plots examined at Soret band of porphyrins, and it suggests the formation of the stable 1:1 complexes, [ZnTBPyP] [$SiW_{12}O_{40}$] and [H_2TBPyP] [$SiW_{12}O_{40}$], respectively. The similarity in the observations of [ZnTBPyP] [$SiW_{12}O_{40}$] and [H_2TBPyP] [$SiW_{12}O_{40}$] systems suggests that the interaction is primarily electrostatic and the central ions of porphyrins do not play an important role in determining the nature of the interaction.

Figure 2 Job's plots for (a) [ZnTBPyP][$SiW_{12}O_{40}$] (λ=440nm) and (b) [H_2TBPyP][$SiW_{12}O_{40}$] (λ=423nm) system in H_2O.



Acknowledgments

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