Stellate Macroscopic Crystals from Cationic and Anionic Porphyrins

Hiroyasu Yamaguchi and Akira Harada*
Department of Macromolecular Science, Graduate School of Science, Osaka University, Toyonaka, Osaka 560-0043

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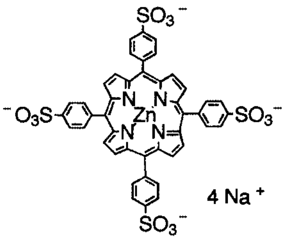
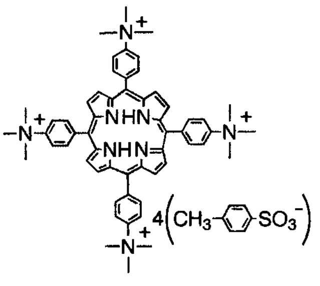
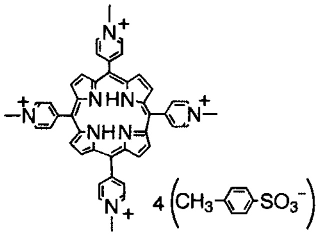
Mixing tetrasodium [*meso*-tetrakis(4-sulfonatophenyl)porphinato]zinc (Zn-TSPP) and *meso*-tetrakis(4-(trimethylammonio)phenyl)porphine tetratosylate (TTMAPP) in dimethylsulfoxide leads to formation of a star-like (stellate) microcrystal.

Molecular self-assembly is an active area of research with many accomplishments, but the sizes are limited to those of nanometers and micrometers. In recent years, much attention has been directed toward construction of mesoscale structures by assembly using nonmolecular objects.[1] Now, it is the biggest challenge to construct mesoscale architectures by using molecular assembly. One of the attractive targets in the molecular assembly system to make functional materials is supramolecular structures of porphyrins because of the similarities to a reaction center in natural photosynthetic systems.[2] Porphyrins associate themselves at high concentration by π-stacking to give rather complicated structures because of the non-specific face-to-face porphyrin interactions. In order to construct the porphyrin arrays artificially, many attempts have been made to prepare porphyrin dimers via covalent[3] or noncovalent[4–7] bond. In noncovalently assembled porphyrin system, various interactions were utilized to construct the supramolecular (dimeric and oligomeric) structures: hydrogen bonding,[4] metal coordination,[5,6] and electrostatic interactions.[7] The most convenient method to make special stacked-porphyrin dimers (homo- and hetero-) is the use of the electrostatic interactions in polar solvents. The formation of binary heteroassemblies of oppositely charged porphyrins has been widely studied and now it becomes possible to build "chiral heteroassemblies" of cationic and anionic porphyrins on anionic chiral matrixes.[8] However, there are no reports describing the structures of oppositely charged porphyrin aggregates in the solid state. We report here supramolecular crystal formation of cationic *meso*-tetrakis(4-(trimethylammonio)phenyl)porphine (TTMAPP) with anionic [*meso*-tetrakis(4-sulfonatophenyl)porphinato]zinc (Zn-TSPP) in dimethylsulfoxide (DMSO).

A combination of metalloporphyrin and free-base porphyrin was taken to differentiate each porphyrin clearly by spectroscopic measurements. The counter ions of Zn-TSPP and TTMAPP are sodium and tosylate (TsO$^-$), respectively. At lower concentrations ($< 1.2 \times 10^{-4}$ M), the UV–vis spectra of the mixtures of porphyrins with the equimolar ratio were not the sum of the component porphyrin spectra. The Soret band was broadened, extending to both higher and lower energies than that of the component porphyrins in DMSO, indicating the electrostatic interactions between cationic and anionic porphyrins. The relationship between absorbance of cationic–anionic porphyrin complexes and concentration of porphyrins obeys Lambert–Beer's law. Therefore, the broadening factor in UV–vis spectra is considered to be a simple interaction between cationic and anionic porphyrins not to give complicated aggregates. However, mixing DMSO solution of Zn-TSPP and TTMAPP produces precipitates at the total concentrations of porphyrins above 1.2×10^{-4} M.


Zn-TSPP


TTMAPP


TMPyP

These two porphyrins were mixed at various ratios to evaluate the stoichiometry for the association of cationic and anionic porphyrins. The ^{1}H NMR spectra were measured for TTMAPP and Zn-TSPP mixtures fixed the total concentration of porphyrins at 1.8 mM in DMSO-d_6. Only the protons for one of the porphyrins and TsO$^-$ were detected in DMSO solution. The protons assigned to porphyrin rings of TTMAPP and Zn-TSPP disappeared and only tosylate protons were observed in a solution of a 1:1 mixture. These results show that the complete phase separation of the 1:1 porphyrin aggregate and counter ion exchanges occur in the association of cationic and anionic porphyrins. Similar results were observed in D$_2$O solution. The proton NMR spectra reveal that the association of these porphyrins can simply be described by the equations below:

$$\text{Zn-TSPP}^{4-}(4\text{Na}^+) + \text{TTMAPP}^{4+}(4\text{TsO}^-) \rightarrow \text{Zn-TSPP-TTMAPP} + 4\text{NaTsO}$$

The topological structures of the precipitates formed in DMSO were observed by optical microscopy. Figure 1 shows the optical microscopic images of the aggregates obtained from the DMSO solution (a, b) or aqueous solution (c). We found that the precipitation from DMSO solution gives microcrystals with a stellar shape. One of the petals can be seen separately with ca. 30 μm length in diameter. The resulting macrostructure has 50 μm length in diameter and tetrapetals with rotating at 90° and crossing at the center (Figure 1(b)). In aqueous solution of Zn-TSPP and TTMAPP, a linear structure was observed

(Figure 1(c)). From the results of elemental analysis, the precipitate was found to include two DMSO molecules in porphyrin dimer unit. It is indicated that solvent molecules play an important role to control the π-stacking interaction between porphyrin faces and the electrostatic interaction of the heteroassemblies in the formation of higher-order structures.

Another molecular assembly system was examined using *meso*-tetrakis(*N*-methylpyridinium-4-yl)porphine *p*-toluenesulfonate (TMPyP). In the case of the mixture of Zn-TSPP and TMPyP, we obtained only structurally undefined powder, although the aggregate of these porphyrins is considered to be 1:1 composition by ^{1}H NMR measurement in DMSO-d_6. Considering that the mixture of *meso*-tetraanionic and β-tetracationic porphyrins instead of *meso*-tetracationic one gives not only heterodimers but also heterotrimers,[9] the positions of charges (inside or outside aromatic ring) and substituent groups on the porphyrin ring also influence the structural regulation of mesoscale architectures.

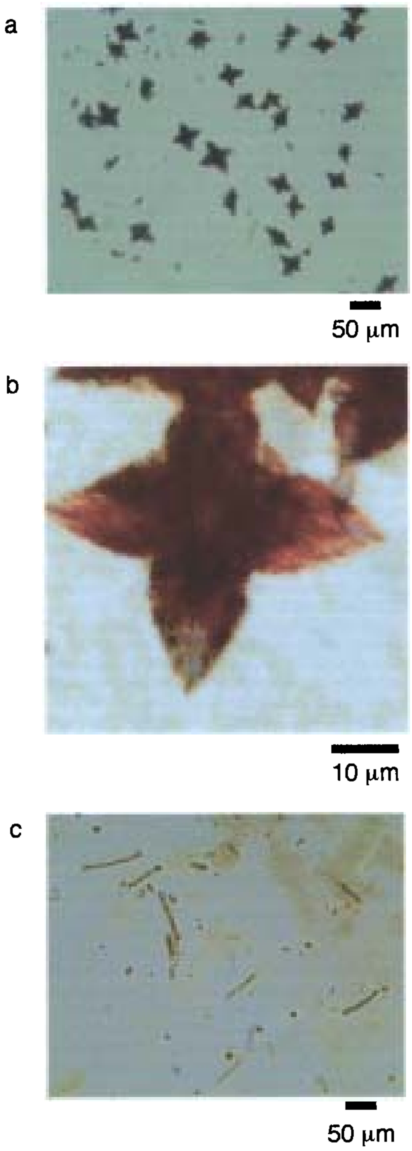


Figure 1. Optical microscopic images of Zn-TSPP-TTMAPP complexes formed from DMSO solution (a, b) and from aqueous solution (c).

Our observations suggest that a suitable selection of ionic porphyrin pairs and solvents can make it possible to construct mesoscale architectures by controlling the electrostatic interaction of opposite charges and π–π interaction between the porphyrin rings in molecular assembly system. Detailed structural analysis and their functional properties are now being investigated.

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