

Synthesis of a New Porphyrin-fluorescein Hybrid and its Supramolecular Self-assembly with Amino-porphyrinatomanganese(III) by Hydrogen-bonding

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Abstract: A new porphyrin-fluorescein hybrid **2** (Fl-PPTPP) has been synthesized and characterized by UV-Vis, IR, ¹H-NMR, ESI-MS and elemental analysis. The supramolecular self-assembly of Fl-PPTPP with amino-porphyrinatomanganese(III) [Mn^(III) (*p*-APTTP)Cl] by hydrogen-bonding was studied using fluorescence spectroscopic titration and ESI-MS.

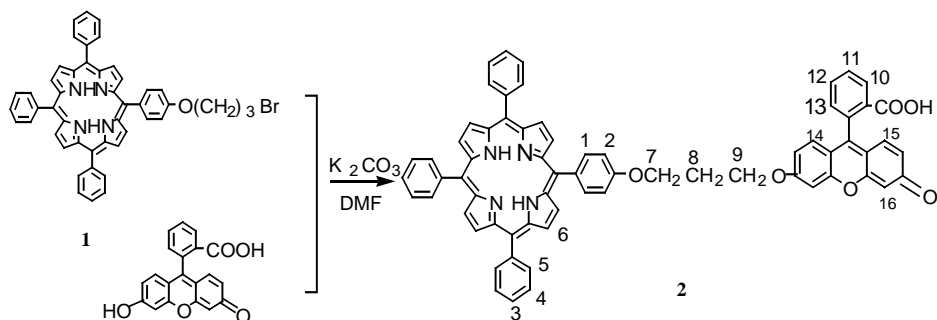
Keywords: Porphyrin, fluorescein, amino-porphyrinatomanganese(III), supramolecular, self-assembly, hydrogen-bonding.

In recent years, numerous new model have been developed for understanding electron and energy transfer processes in the photochemical reaction center of photosynthesis¹⁻⁸. There are several examples in the literature of newly created model dimeric structures that involve conjugated bridges in the context of the donor-acceptor model system of porphyrin-fluorescein with diad-chromophoric^{3,4}. Here we report the synthesis of a new porphyrin-fluorescein hybrid in which porphyrin is linked to fluorescein through an ether bond and its supramolecular self-assembly with manganese (III) chloride of 5-(*p*-amino) phenyl-10,15,20-triphenylporphyrin, Mn^(III)(*p*-APTTP)Cl by hydrogen-bonding. It will provide a new model of photochemical reaction center of photosynthesis.

The synthetic route of the new porphyrin-fluorescein hybrid was shown in **Scheme 1**. A mixture of compound **1** (0.095 g /0.125 mmol), fluorescein (0.2 g/0.65 mmol), DMF (25 mL), anhydrous potassium carbonate (0.5 g) and potassium iodide (0.05 g) was stirred for 36 h at 35°C under a nitrogen atmosphere. The mixture was diluted with 50 mL chloroform. The organic layer was washed with water (5×50 mL) and was dried with anhydrous sodium sulfate and concentrated *via* rotary evaporation. The residue was then chromatographed on a silica gel column using chloroform as eluent to give four bands. The third band was collected and stripped on a rotary evaporator. The crude products were further purified by TLC and yielded a purple solid. Yield of **2** was 47.1%. ¹H-NMR(500Hz, DMSO, δ ppm): chemical shift δ 11.23(s, 1H, COOH), 8.9-8.76(m, 8H, H-6), 8.0-8.2 (d, 6H, d, *J* = 7.8Hz, H-4), 7.88-8.0 (d, 2H, *J* = 8.0Hz, H-2), 7.80-7.86 (m, 11H, H-1, 3, 5), 7.19-7.5(d, 4H, *J* = 8.7Hz, H-10~13), 6.2-6.9(m, 6H, H-

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Scheme 1



14~16), 3.9-4.2(t, 2H, $J=6.4\text{Hz}$, H-7), 3.2(t, 2H, $J=4.6\text{Hz}$, H-8), 1.9(t, 2H, $J=6.2\text{Hz}$, H-9), -2.89 (s, 2H, pyrrole ring); IR (KBr, cm^{-1}): 3316.5(amide N-H), 1723.5 (COOH, C=O), 1639.5 (C=O); Uv-Vis (λ_{max} , CHCl_3): 417, 512, 550, 591 and 646 nm; ESI-MS (m/z): M^+ , 1003.40; Anal. calcd. (found): C 80.12 (79.93), H 4.68(4.96), N 5.58 (5.49)%.

The $^1\text{H-NMR}$, UV-Vis, IR, ESI-MS and elemental analysis were fully in agreement with the structures of **2**. It is worth noting that the characteristic proton signal at 11.23 ppm attributed to the proton of -COOH was observed and indicates that the carboxyl on fluorescein moiety is free and is not reacted with Br on **1** to form an ester bond.

The fluorescence spectroscopic titration experiment was carried out to estimate the supramolecular self-assembly of FI-PPTPP with $\text{Mn}^{(\text{III})}$ (*p*-APTPP)Cl. The fluorescence spectra ($\lambda_{\text{exc.}}=417\text{ nm}$) of FI-PPTPP in CH_2Cl_2 are shown in **Figure 1** (dot line). As it can be seen, the fluorescence intensity of FI-PPTPP at 656.4 nm decreased upon the addition of $\text{Mn}^{(\text{III})}$ (*p*-APTPP)Cl (**Figure 1**). Experiment indicated that $\text{Mn}^{(\text{III})}$ (*p*-APTPP)Cl has no fluorescent emission in any range of concentration, which is related to the paramagnetic of Mn^{3+} ion^{3, 5-7,10}. We believe that the decrease in the fluorescence intensity resulted from the interaction between FI-PPTPP and $\text{Mn}^{(\text{III})}$ (*p*-APTPP)Cl. In the control experiment, in which $\text{Mn}^{(\text{III})}$ (*p*-APTPP)Cl was replaced by $\text{Mn}^{(\text{III})}$ (TPP)Cl (TPP: 5,10,15,20-tetraphenylporphyrin), the fluorescence spectrum of FI-PPTPP did not change. On considering the structure difference between $\text{Mn}^{(\text{III})}$ (*p*-APTPP)Cl and $\text{Mn}^{(\text{III})}$ (TPP)Cl, the fluorescence quenching of the FI-PPTPP/ $\text{Mn}^{(\text{III})}$ (*p*-APTPP)Cl system is related to the amino group of $\text{Mn}^{(\text{III})}$ (*p*-APTPP)Cl, that is, a hydrogen-bonding can form through the carboxyl group in FI-PPTPP and the amino group in $\text{Mn}^{(\text{III})}$ (*p*-APTPP)Cl. It is obvious that the fluorescence quenching of FI-PPTPP by $\text{Mn}^{(\text{III})}$ (*p*-APTPP)Cl is caused by the formation of a FI-PPTPP- $\text{Mn}^{(\text{III})}$ (*p*-APTPP)Cl supramolecule self-assembled *via* hydrogen-bonding and effective photo-induced electron transfer from FI-PPTPP (electron donor) to $\text{Mn}^{(\text{III})}$ (*p*-APTPP)Cl (electron acceptor)^{3, 8-10}. Upon addition of a hydrogen-bonded solvent, such as methanol and ethanol, to the FI-PPTPP/ $\text{Mn}^{(\text{III})}$ (*p*-APTPP)Cl system, the fluorescence intensity was gradually restoration, which further supported the conclusion that hydrogen-bonding is the driving force of supramolecular self-assembly. Because the concentrations of the FI-PPTPP (fluorescent molecule) and $\text{Mn}^{(\text{III})}$ (*p*-APTPP)Cl (quencher) used in the fluorescence spectroscopic titration experiment were all in the range of $0\sim 1.2\times 10^{-7}$

mol.L⁻¹ in which the fluorescence quenching of FI-PPTPP in the FI-PPTPP/Mn^(III)(*p*-APTPP)Cl system was static quenching indicated by experiments, so the association constant K_c of FI-PPTPP-Mn^(III)(*p*-APTPP)Cl supramolecule can be calculated using the follow equation^{3,5}:

$$I_0/I_f = 1 + K_c [Q] \quad (1)$$

Where I_0 is the fluorescence intensity in the absence of quencher, I_f is the intensity in the presence of quencher at concentration $[Q]$. The association constant of FI-PPTPP-Mn^(III)(*p*-APTPP)Cl supramolecule was calculated to be $(5.87 \pm 0.21) \times 10^7$ (mol⁻¹·L) from the fluorescence titration data.

Figure 1 Fluorescence spectroscopic titration of FI-PPTPP by Mn^(III)(*p*-APTPP)Cl. [FI-PPTPP]: 3.0×10^{-8} mol/L. [Mn^(III)(*p*-APTPP)Cl]: 0~ 1.5×10^{-7} mol/L.

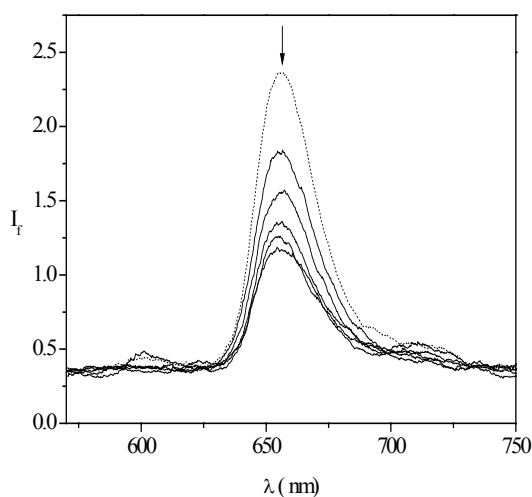
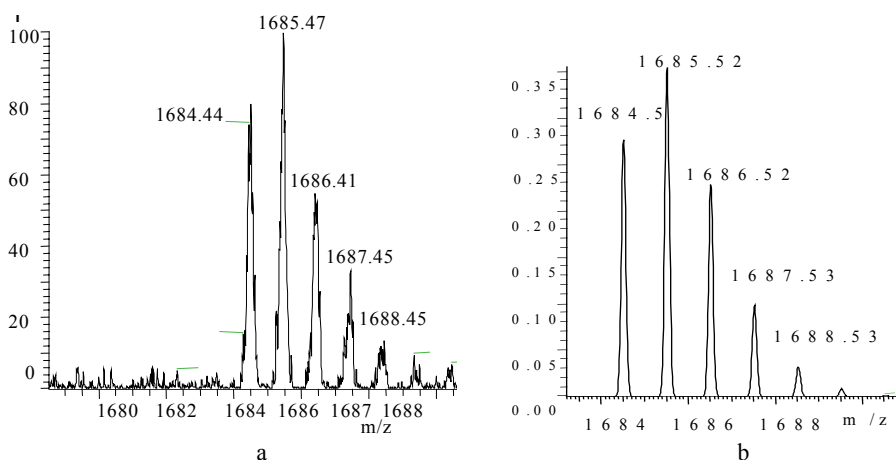


Figure 2 Selected areas of the ESI mass spectra of FI-PPTPP/ Mn^(III)(*p*-APTPP)Cl with a fixed 1:1 molar ratio in CH₂Cl₂: (a) experimental, (b) calculated (computer simulated).



The selected areas of the ESI mass spectra of a 1:1 mixture of FI-PPTPP and Mn^(III)(*p*-APTPP)Cl is shown in **Figure 2**. A pseudomono-molecular ion [FI-PPTPP-Mn^(III)(*p*-APTPP)]⁺ with the loss of Cl⁻, at *m/z* 1685.47 was observed. The result clearly shows the presence of five isotopic peaks are all in good agreement with the calculated form, indicating that the supramolecule was formed. ESI-MS supports the conclusion that FI-PPTPP-Mn- (*p*-APTPP) Cl supramolecule formed in CH₂Cl₂.

In summary, we have demonstrated a convenient route to the preparation of a new porphyrin-fluorescein hybrid and its supramolecular self-assembly with amino-porphyrinatomanganese(III) by hydrogen-bonding. Further studies including the detailed mechanisms for the photoinduced electron transfer processes in the supra-molecule are in progress.

Acknowledgments

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