Synthesis, spectral properties of aluminum polymeric phthalocyanine carboxyl with low aggregation in aqueous solution

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A water soluble poly-[tetrakis-(2,3-dicarboxylate phenoxy) methyl methan] aluminum phthalocyanine (AlPPc.(COOH)x) has been synthesized from the cyclization of tetranuclear phthalonitrile and successive hydrolysis of cyano in alkaline solution. The absorption spectra showed low aggregation of this compound in pH 9.18 buffer than that of existing water soluble phthalocyanine compounds. With the addition of Triton X 100, an enhancement of fluorescence emission with quantum yield from 0.4 to 0.83 was observed; contrarily, it was thoroughly quenched by the addition of CATB in suit. A longer life time of singlet state was also detected in presence of Triton X 100. The result indicates that AlPPc.(COOH)x is desired to investigate in fluorescent probe or in fluorescence imaging diagnose.

As one of the important photosensitive compounds, phthalocyanine has been widely used in solar cells, fluorescent imagination and photodynamic therapy (PDT)[1-3]. For a photosensitizer, aqueous compatibility is crucial to its effectiveness in fluorescence diagnose and therapy in human body. For phthalocyanines, sulfonation and carboxyl-ation are two common methods to achieve water solubility. However, with better solubility, the aggregative tendency of phthalocyanine also increases. This aggregation decreases the quantum yields of singlet excited state and singlet oxygen generation, which directly inhibits the photosensitive process. Quenching of fluorescence by aggregation was reported for water soluble zinc phthalocyanines and sulfonate phthalocyanine[4,5]. The reason is deemed to be the nonradiative dissipation in triplet excited state of phthalocyanine by aggregation[6].

Durative efforts, such as dendritic phthalocyanine[7], axial substitution of phthalocyanine[8] and the addition of surfactan[9], have been made to decrease the aggregation of phthalocyanine. However, there have been few publications about polymeric phthalocyanines with good solubility and low aggregative tendency. In this study, a novel water soluble polymeric phthalocyanine was synthesized. The tetranuclear phthalonitrile was used as precursor to form an insoluble polymeric phthalocyanine with cyano as residual groups. The cyano groups were hydrolyzed to carboxyl in NaOH solution and made the polymer easily dissolve in water (Scheme 1). The fluorescence property of the synthesized polymer was investigated under different conditions.

1 Experimental

3-nitrophthalonitrile, pentaerythritol, n-pentanol, di-methyl formamide (DMF), 1,8-diaza bicycle [5,4,0]-undec-7-ene (DBU), cetyl trimethyl ammonium bromide (CTAB) and Triton X 100™ were purchased from...
commercial reagent company and were of analytical or chemical grade. The aluminum trichloride was anhydride salt agents. Sulfonate zinc phthalocyanine (ZnPcS2) was synthesized by our laboratory.

The 13C NMR was performed on a JOEL JNM-ECA300 using DMF as solvent. Electronic spectrum was recorded on an HP 5324A Uv-vis array Spectrometer; the fluorescence was recorded by a Hitachi F4500 Spectrometer with a setting of 5 nm grating slit and 700 V amplifier of photomultiplier, the fluorescence decay curves were obtained by an Edinburgh FLS920 Transient/Steady State Spectrometer. FT-IR was obtained from Avata 360A Spectrometer using solid KBr pellet. The element analysis was conducted on a Vario EL 3.

The average viscosimetric molecular weight was measured on an Ubbelohde viscometer at 298K in water solution (referring to the method in ref. [10]), and PVP-K30 (MW/n 44000-4000) was used as standard.

2.1 Fluorescence quantum yield (ΦF)
This was determined by comparative methods in pH 7.4 buffer using ZnPcS2 in DMF as a standard (ΦF=0.18). The ΦF was calculated by:

ΦF=ΦF,stad(Sstad/Astd2)/(Sstrand/An2std),

where S and Sstandard are the areas under the emission curves of the sample and standard, respectively. A and Astandard are the absorbances of the sample and standard, respectively, and n and nstandard are the refractive indexes of the solvents used for sample and standard, respectively. The error in the determination was about 10%. The absorbance of the solutions at the excitation wavelength ranged between 0.3 and 0.4. The lifetime τF was determined by the fitness of decay curves with Strichler-Berg equation.

2.2 The synthesis of poly-[tetakis-(2,3-dicarboxylate phenoxy) methyl methan] aluminum phthalocyanine
This was the same as in ref. [13]. 1 g Pn4 and 0.5 g newly prepared AlCl3 anhydrate were heated in 15 mL n-pentanol to reflux. Then 1ml DBU was added in the solution dropwise. The mixture was kept refluxing for 5 h. The precipitate was filtered and washed with 3 mol/L HCl, DMF and acetone in sequence. 0.65 g poly-[tetakis-(2,3-dicyano phenoxy) methyl methan] aluminum phthalocyanine (AlPPc) was obtained. Then the product was stirred with 50 mL 15% NaOH at 80℃ for 12 h. The AlPPc dissolved to form a green solution. The insoluble residue was isolated with centrifuge, using 6 mol/L HCl to adjust the solution to pH=1. The green solid poly-[tetakis-(2,3-dicarboxylate phenoxy) methyl methan] aluminum phthalocyanine (AlPPc(COOH)x) precipitated from the solution. Repeating the alkaline dissolution and acid-out treatments several times can improve the purity of the product. The element analysis showed C 49.3% and N 12.3%, of AlPPc, and the value of C:N ratio in AlPPc is in accordance with theoretical
results of Pn4 (C_{37}N_8O_{20}, C%:N% = 3.94). The content of carboxyl in AlPPc.(COOH)_x is 4.5% by a titration test using NaOH solution.

2 Result and discussion

In the hydrolysis to form water soluble AlPPc.(COOH)_x, the eight cyano groups of Pn are the key factors. The cyano groups can not fully react in the polymerization due to the site block. Amount of cyano groups left as residue groups in the polymeric molecular (Figure 1). It can be hydrolyzed to produce enough amount of carboxyl groups. The hydrophobic groups make the AlPPc.(COOH)_x solve in water. However, the phthalocyanine polymers synthesized from bi nuclear phthlonitrile do not have enough cyano residues as well as little carboxyl groups’ formation.

![Figure 1](image1.png)

Figure 1 Electronic spectrum of AlPPc(COOH)_x in different solution (concentration 0.5 g/L).

The FTIR spectrum showed the disappearance of characteristic CN peak at 2290 cm\(^{-1}\) and the appearance of new peaks at 1720 and 3500 cm\(^{-1}\) of COOH. The characteristic framework peaks of polymeric phthalocyanine at 1200−1600 cm\(^{-1}\) did not change obviously after hydrolysis. It verified that the cyano groups are successful converted into carboxyl groups with no breakdown of the polymeric phthalocyanine system. The \(^{13}\)C NMR of AlPPc.(COOH)_x showed new peaks of COOH groups at 170−180 ppm in DMF. The average viscosimetric molecular weight of AlPPc.(COOH)_x was about 4000−16000 in pH 9.18 buffer by viscosity method. It indicated that AlPPc.(COOH)_x can be classified as an oligomer.

Electronic spectrum of AlPPc.(COOH)_x in different solvents is shown in Figure 1. The characterized Q band of phthalocyanine is located at near 695 nm in pH 9.18 buffer solution. It shows red shift compared to in DMF solution and hexadeca carboxyl zinc phthalocyanine (680 nm, AlPc.(COOH)_16) due to the formation of carboxylic anion at high pH and the polymeric structure. The addition of CATB (0.1% weight) and Triton X 100 (0.1% weight) can not change the intensity and location of the Q band significantly. This indicates that AlPPc.(COOH)_x has low aggregation in this solution and mainly acts as monomers. Figure 2 shows the fitting of AlPPc.(COOH)_x absorbance (Q band at 700 nm) with Beer’s Law. There is only little deviation at higher than 2 g/L concentration (absorbance about 1.0). By intensifying Q bands, an aggregative degree of about 7% was calculated out in this pH 9.18 buffer. This number is very small compared with water soluble phthalocyanine, such as AlPcSx, ZnPcSx and AlPc.(COOH)_4.

On electronic emission, the strong emission is shown at 712 nm with a fluorescence quantum yield (\(\Phi_F\)) of 0.4

![Figure 2](image2.png)

Table 1 Photophysical parameters of AlPPc.(COOH)_x in different condition

<table>
<thead>
<tr>
<th></th>
<th>(Q) band (\lambda) (nm, max)</th>
<th>(Ex, \lambda) (nm, max)</th>
<th>(Em, \lambda) (nm, max)</th>
<th>(\Phi_F)</th>
<th>(\tau_F) (ns)</th>
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<tbody>
<tr>
<td>AlPPc.(COOH)_x [14]</td>
<td>680.0</td>
<td>–</td>
<td>695.0</td>
<td>0.26</td>
<td>–</td>
</tr>
<tr>
<td>(a)+CTAB</td>
<td>695.2</td>
<td>625.0</td>
<td>–</td>
<td>&lt;0.001</td>
<td>–</td>
</tr>
<tr>
<td>(a)+0.1% Triton</td>
<td>693.5</td>
<td>625.0</td>
<td>711.6</td>
<td>0.71</td>
<td>82</td>
</tr>
<tr>
<td>(a)+0.2% Triton</td>
<td>693.4</td>
<td>625.0</td>
<td>711.3</td>
<td>0.83</td>
<td>87</td>
</tr>
</tbody>
</table>


in water solution. A small Stoke shift of 15 nm indicated that the polarity of singlet excited state is similar to ground state, and the singlet state is comparatively stable AlPPc.(COOH). The addition of 0.2% Triton X 100 obviously increased it to higher than 0.83, but successive adding of CTAB completely quenched fluorescence emission in this condition. Figure 3 indicates that the increasing of fluorescence had no relation with the absorption enhancement by Triton X 100 at 695 nm. The fluorescence decay lifetime was measured in the buffer with Triton X 100. A comparatively longer lifetime of 87 ns was detected in the presence of 0.2% Triton X 100. For comparison, $\tau_F$ of (AlPPc.COOH), without Triton X 100 is 10 ns. It is believed that the longer $\tau_F$ contributes to the higher $\Phi_F$ with the existence of Triton X 100[20].

The long life time of fluorescence gives facility to detect the luminescence in application.

However, previous work by Li et al.[9] indicated that CTAB can also increase the $\Phi_F$ of non polymeric phthalocyanines in solution. Here, CTAB is a cationic surfactant while Triton X 100 is non-ionic. We believe that AlPPc.(COOH), mainly exists as carboxylic anion in pH 9.18 solution. The cationic surfactant may wrap the AlPPc.(COOH), molecules by electrostatic effect with carboxylic anion[91]. While nonionic Triton X 100 can only be effective by inserting into the places between the adjacent polymer molecules. The enveloping function of CTAB with AlPPc.(COOH), perhaps provides more routes to the nonradiative dissipation of singlet state and quenches the fluorescence. More detailed evidence is still under investigation. The control and application of the fluorescence by these two surfactants of AlPPc.(COOH), also need to be further studied.

3 Conclusion

The novel aluminum phthalocyanine polymer with carboxyl groups (AlPPc.(COOH),) has low aggregative tendency in pH 9.18 buffer solution. The result of viscosity method indicates the oligomer structure of it. AlPPc.(COOH), shows special enhancement ($\Phi_F$ 0.83) of fluorescence by adding Triton X 100 and in suit quenching by CTAB ($\Phi_F < 0.01$), which presents a novel method to control the fluorescence luminescence in the homogenous aqueous system.

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Figure 3 The fitness to Beer’s law of AlPPc.(COOH), in pH 9.18 buffer (original concentration 2 g/L).


