

The Effects of Different Acids on Aggregation of A Cyanine Dye

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Abstract

The different acids were selected to investigate their effects on aggregation of a cyanine dye. It was found that, through UV-vis spectra, stronger acids would promote the cyanine dye to form J aggregates while the weaker acids did not make the dye self aggregated. Based on the prior experimental results we give a hypothesis that the stronger acids could transfer the dye from sulfonate to sulfonic acid. Moreover, the morphology of J aggregates treated with stronger acid was observed with Transmission electron microscopy (TEM), and was interlaced branches with average diameters of about 200nm.

In recent years organic molecular self-aggregation gained increasing attention due to their novel chemical, physical and optical properties. On the basis of their novel properties they have various potential applications in optical devices, solar cells and other related properties. In order to investigate their properties as well as their morphology, porphyrins and cyanine dyes are usually expected to be subject investigated¹⁻⁴. Self-aggregation of porphyrins and cyanine dyes are two kinds of aggregation, J- and H-aggregation. J aggregation of porphyrins is gained conveniently by changing the ionic strength and/or pH. Many researchers used elastic (ELS) and dynamic (DLS) light scattering to study mesoscopic structure of porphyrin J aggregation⁵⁻⁷. As for cyanine dyes many researchers focused on the influence of inorganic salts, the temperature of the solution and surfactants on the formation of J aggregation and investigated their morphologies using AFM, TEM and SEM. However, little attention was paid to the effect of H⁺ on cyanine dye. Here we studied on the effects of different acids on the spectroscopic properties through UV-Vis spectra and observed morphology of the dye using TEM.

Four different acids (CH₃COOH, HCl, H₃PO₄ and HCOOH) were selected. Their different influences on the formation of J aggregation of the dye were characterized by UV-vis spectra (figure 1). The concentration of the dye was kept unchangeable (1*10⁻⁵ mol/L) in all the solutions for measurements. In figure 1 (a), there was almost no change in UV-vis spectra, which suggested adding CH₃COOH to the aqueous dye solution didn't promote the dye aggregation. Contrarily, in figure 1 (b), a new band appeared in the longer wavelength compared with the

monomer band. That proved the dye formed J aggregation with the addition of HCl to the aqueous dye solution, although the pH adjusted by HCl was almost the same to that by CH₃COOH. And a decrease was observed in the absorbance of about 372nm accompanied by an increase in the absorbance of J aggregates with decreasing pH.

UV-vis spectra showed that in a stronger acid solution, such as HCl, the dye could form J aggregation easily, while in a weaker acid such as CH₃COOH the dye could not form J aggregation. We assumed that the reason of the formation of J aggregation is the stronger acid can transfer the dye from sulphonate to sulfonic acid in which the repulsion interaction of intramolecular is smaller and then J aggregation would be formed.

The weaker acid such as CH₃COOH, however, could not transfer the dye from the sulphonate to sulfonic acid, so it could not make the dye form J aggregation. In order to prove the hypothesis further, phosphoric acid, a stronger acid, and formic acid, a weaker acid, were selected as the H⁺ sources. Figure 1 (c,d) showed the UV-vis spectra of the dye solution in stronger and weaker acid respectively. A new band appears in the longer wavelength, which showed the formation of J aggregation in phosphoric acid solution (figure 1c). But the dye could not form J aggregation in HCOOH solution (figure 1d). It confirmed that J aggregation produced by H⁺ is because of the transformation of the dye from sulphonate to sulfonic acid.

To obtain an explicit image of J aggregation, we used TEM (JEOL JEM-200CX) to study the morphology of the dye before adding HCl (figure 2a) and after adding HCl. (fig 2b) The morphology of the aqueous dye solution without HCl was coagulation of grains. While Figure 2b showed the dye with HCl exhibited the morphology as clusters of interlaced strands aggregation with a diameter of 100-200nm. The selected-area electron diffraction (SAED) showed the structure of the dye became polycrystalline.

We also studied the different effects of stronger and weaker acids on the spectroscopic properties of the other dye, which is one of the sulphonate and similar to that of the prior dye. And the same result had been gained that the stronger acids could promote dye to form J aggregation.

In conclusion, different acids such as HCl, H₃PO₄, HCOOH and CH₃COOH selected as H⁺ source and their effects on the spectroscopic properties of the dye had been investigated via UV-vis spectra. It was found that the

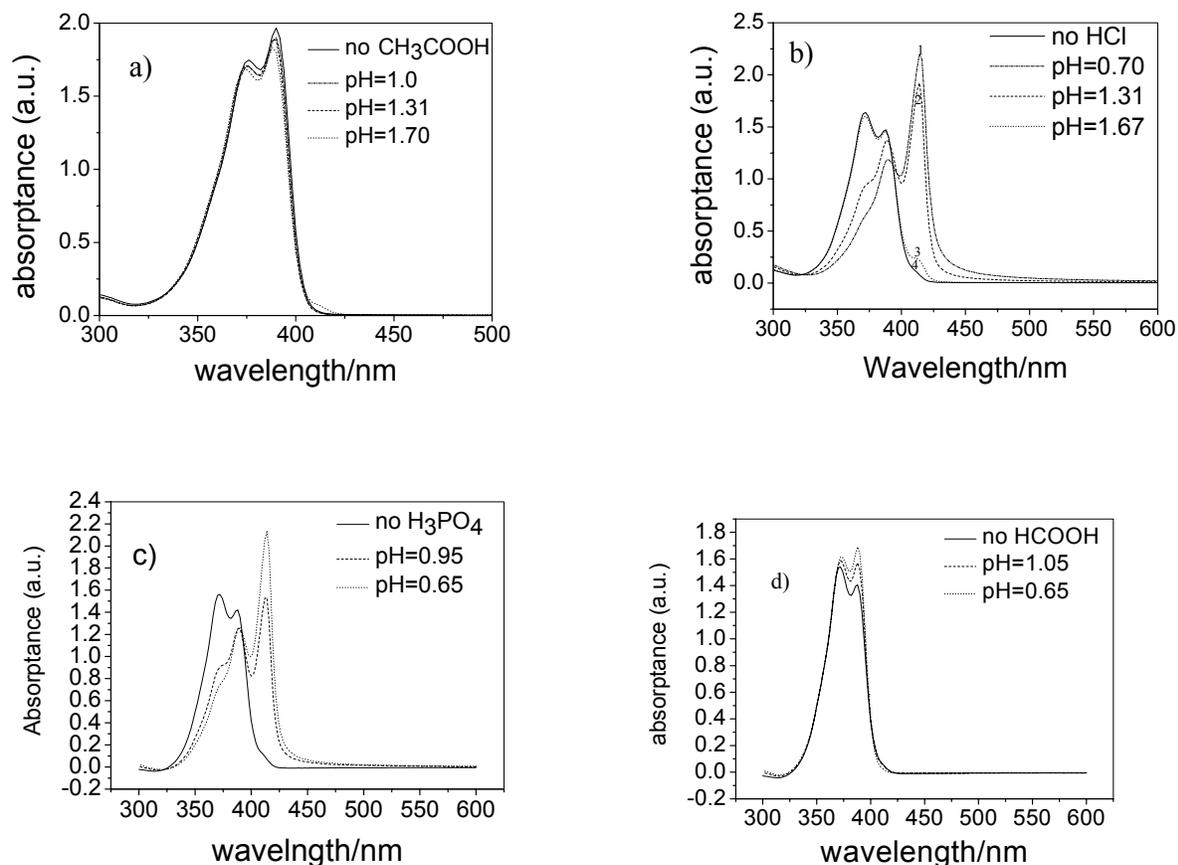


Figure 1. UV-Vis absorption spectra of the cyanine dye in different pH solutions: a) CH_3COOH , b) HCl , c) H_3PO_4 , d) HCOOH

stronger acids could promote the dye to form J aggregation whereas the weaker acids had no effect on the spectroscopic properties of the dye. We supposed the formation of J aggregation of the dye in stronger acids was possibly due to the transformation of the sulphonate to sulfonic acid. And we will have a further research about the mechanism of the

formation of J aggregation. Moreover, the distinct morphology of the dye is an evidence of the formation of J aggregation. With the addition of HCl the original coagulations turned to be one-dimensional interlaced strands with a diameter of about 200nm.

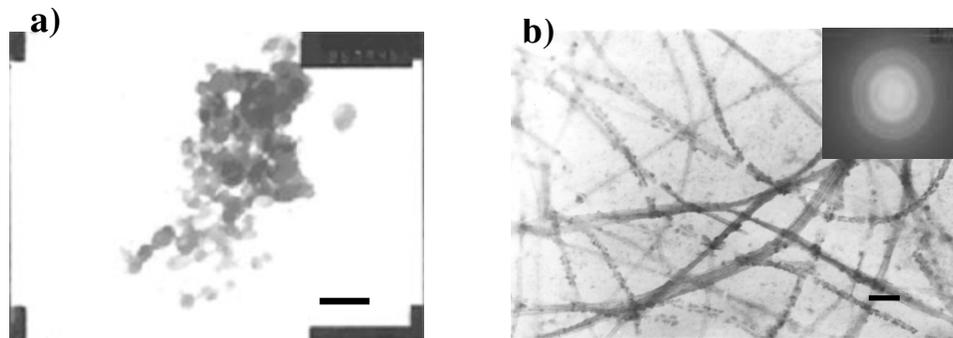


Figure 2. TEM image of the dye without HCl (a: bar=125nm) and with HCl (b: bar=500nm)

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