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The fluorescence property of Schiff's bases of carboxymethyl cellulose

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ABSTRACT

The Schiff's bases of cellulose derivatives, *o*-pheylene diimido carboxymethyl cellulose (PDIMCMC) and *p*-sulfophenyl imodo carboxymethyl cellulose (SPIMCMC), were synthesized by the reaction of dialdehyde carboxymethyl cellulose (DACMC) with *o*-phenylene diamine (PDM) and *p*-aminobenzen sulfonic (ASA), respectively. Their structures were characterized by FTIR. The fluorescence spectra (FS) appeared and the Schiff's bases had strong fluorescence intensities (FI). These FSs and FIs were influenced by either pH or solute concentration. For example the PDIMCMC results indicated that its FI reached maximum at pH = 6.48 and its FS shifted to a longer wavelength in acidity; its FI is the strongest in 1.2×10^{-3} g mL^{-1}.

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1. Introduction

The production of reaction aldehyde with amine, that is Schiff's base, often has the property of luminescence, especially, when it or its complexes have structure of rigidity plane and rich-electronic conjugation (Lakowicz, 2006; Sharma & Schulman, 1999; Valeur, 2002). Schiff's base compounds have occupied an important place in the photometric and fluorescent analysis. For instance, aromatic Schiff's base compounds, of the salicylidene *o*-aminophenol type, have been studied as useful fluorimetric reagents for aluminium, magnesium, and other metal ions (Argauer & White, 1964; Hassan, Mahmouda, Elmosallamyb, & Othman, 1999; Manju & Sreenivasan, 2011; Morisige, 1978; Siling et al., 2001).

Cellulose is globally very important because it is highly abundant in nature, renewable, and easily degradable. Chemical modification reactions, by which many functional groups have been introduced to cellulose, continue to play a dominant role in improving the overall utilization of cellulosic polymers. Broader and more specialized applications of advanced and trendsetting materials based on this macromolecule will increase the demand for more diverse synthesis paths and derivatives (Johnson, Thielemans, & Walsh, 2011; Li & Wu, 2009). Periodate oxidation is characterized by specific cleavage of the C—C bond of adjacent glycol, that is, the C2—C3 bond of anhydroglucose unit in the chain of cellulose (Heinze, 1998; Kim, Kuga, Wada, Okano, & Kondo, 2000; Sirviö, Liimatainen, Niinimäki, & Hormi, 2011), resulting in the formation of two aldehyde groups which can be derivatized to introduce a variety of substituent groups on the cellulose chain, such as carboxylic acid (Casu et al., 1984), hydroxyls (Casu et al., 1985), or imines (Schiff bases) formed with primary amines (Kim & Kuga, 2000, 2001; Kim, Wada, & Kuga, 2004; Maekawa & Koshijima, 1991). The last reaction, in particular, is interesting since it involves many potential uses.

In this paper, we synthesized some Schiff's bases of carboxymethyl cellulose by DACMC, that is PDIMCMC and SPIMCMC, which have excellent fluorescent properties. The structures of the products have been confirmed by FTIR.

2. Experimental

2.1. Materials

Carboxymethyl cellulose (CMC, DS = 0.89) was kindly gifted by the Laboratory of Cellulose and Lignocellulosics Chemistry, Academia sinica.

o-Phenylene diamine (PDM) was of analytical grade from Shanghai Wulian Chemical Factory in Shanghai city. *p*-Aminobenzen sulfonic (ASA) was of analytical grade from Guangzhou Reagent Factory in Guangzhou city.

2.2. Syntheses

DACMC: 0.5 g CMC was dissolved in 200 mL deionized water in the flask which was immersed in a temperature controlled water bath with a magnetic stirrer. Then, periodate solution (15 mL, 0.1 g/5 mL) at different concentrations was added to the CMC

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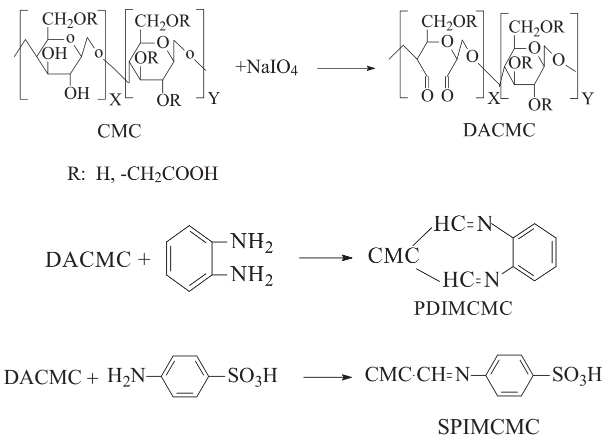

Scheme 1. The synthesis of PDIMCMC and SPIMCMC from DACMC.

solution under stirring. The reaction mixture was stirred in the dark at room temperature for 8 h. After decomposition of the periodate excess with 15.0 mL ethylene glycol and further stirring for 1 h, the oxidized product, referred to dialdehyde carboxymethyl cellulose (DACMC) was precipitated by pouring the solution into a large amount of methanol. It was then recovered and cross-washed with mixture of methanol/distilled water (2:1, V:V) until all iodic compounds were removed. The product was dried at 25 °C in vacuum for the subsequent.

PDIMCMC: A solution of PDM was slowly added to a solution of newly prepared DACMC (DACMC:PDM = 1:5 wt:wt) with stirring in darkness for 5.0 h at room temperature. The resulting mixtures were enriched to display dark brown needle crystal. After 1 h of being stationary, the filtrate with quartz funnel was stripped of solvent. The residues were purified by a few drops of 4 M HCl to pH = 5.30, following with an immediate wash with large amount of methanol and acetone in turn, and dried in vacuum.

SPIMCMC: A solution of ASA was slowly added to a solution of newly prepared DACMC (DACMC:ASA = 1:10, wt:wt) with stirring in darkness for 5.0 h at room temperature. Meanwhile, adding 20%NaOH to the mixtures to keep pH = 9.12, the resulting mixtures were enriched to display white needle crystal. After 1 h of being stationary, the filtrate with quartz funnel was stripped of solvent. The residues were purified by large amount of methanol and acetone in turn, and dried in vacuum. Their synthesis is as Scheme 1:

2.3. Measurement

Determination of aldehyde content: The degree of oxidization of CMC was evaluated by the determination of the aldehyde content (Pommerening, Rein, Bertram, & Mülier, 1992; Rahn & Heinze, 1998), which carried out by an internal Cannizzaro reaction: the 2,3-DACMC (0.0010 g) sample was heated in 4 mL of 0.5 M NaOH stirred suspensions at 70 °C for 10 min. The suspension was cooled at room temperature within 1–2 min and then quantitatively added to 0.1 M HCl (2 mL). The excess of acid was titrated with 0.1 M HaOH, using a glass electrode and a pH-meter. Here, the consumption of 0.1 M NaOH and 0.1 M HCl solution in milliliter was recorded as V_{NaOH} and V_{HCl} (2 mL), respectively. Thus, the aldehyde content (AC) in DACMC can be calculated by: $AC = (V_{NaOH} - V_{HCl}) \times 100 = 683 \pm 3$ mmol/100 g which means the millimole of aldehyde groups per 100 g DACMC.

FTIR spectra were measured with an Aralect RFX-65 FTIR spectrometer. The samples studied were dried and milled to a powder. The powder samples were mixed with KBr and were pressed, respectively, to give a pellet to be used as a FTIR analysis sample. The FTIR spectra of DACMC, PDIMCMC and SPIMCMC were illustrated in Fig. 1.

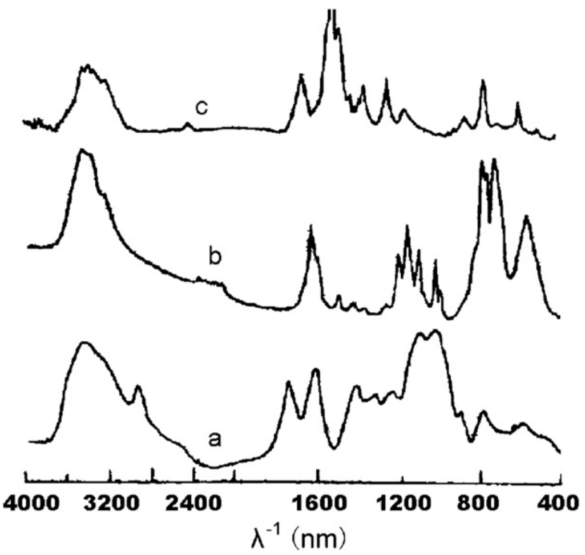

Fig. 1. The FTIR spectra of PDIMCMC and SPIMCMC: a, DACMC; b, SPIMCMC; c, PDIMCMC.

UV measurements were performed on a UV-2201 UV–vis Recording Spectrophotometer (Shimadzu, Japan) at RT. Quartz sample cells with a path length of 10 mm were used. The absorption spectra of PDIMCMC and SPIMCMC were illustrated in Fig. 2.

FS and fluorescence excitation spectra were recorded with a Shimadzu RF5001 PC spectrofluorometer with a thermostatically controlled cuvette holder (outside dimension: 10 mm × 10 mm). The fluorescence spectra were taken with excitation at 388 nm for PDIMCMC and 245 nm for SPIMCMC and a bandwidth of 3 nm on both the excitation and the emission sides. Measurements were carried out in solution of PDIMCMC and SPIMCMC, DACMC:PDM = 1:5 (wt:wt) and DACMC:ABS = 1:10 (wt:wt), at room temperature. PDIMCMC concentrations and pH used were in the range 2.4×10^{-4} g mL^{-1} to 2.4×10^{-4} g mL^{-1} and 4.58–10.42, respectively. SPIMCMC concentration and pH used were 4.4×10^{-4} g mL^{-1} and 9.12, respectively. The FS and fluorescence excitation spectra of PDIMCMC and SPIMCMC were illustrated in Figs. 3 and 4, respectively.

3. Results and discussion

3.1. FTIR

There are some differences between curve c of PDIMCMC and curve a of DACMC in Fig. 1. On curve c, the –COO$^-$ group is detected as multiple peaks at 1635 cm^{-1} and above 3000 cm^{-1}. There appear ν_{C-H} of adjacent position on benzene ring at 770–735 cm^{-1} and ν_{C-C} of skeleton of benzene ring at 1450 cm^{-1}. A typical carbonyl valence vibration at 1735 cm^{-1} disappears, instead of $\nu_{C=N}$ at 1623 cm^{-1} and $\gamma_{C=N-C}$ of imide groups at 2150 cm^{-1}. There appear no peaks of 3383 and 1729 cm^{-1} of ν_{N-H} on curve c.

To compare curve b with a, there are no typical carbonyl valence vibration of the aldehyde function and the ν_{N-H} at 3383 and 1729 cm^{-1} in curve b, instead of γ_{SO_2} at 1155 cm^{-1}. And there is a band of –COO$^-$, typical peaks of para-position on benzene ring, $\nu_{C=N}$ at 1621 cm^{-1} and typical imide group at 2100 cm^{-1}. All evidences above suggest that PDIMCMC and SPIMCMC were synthesized.

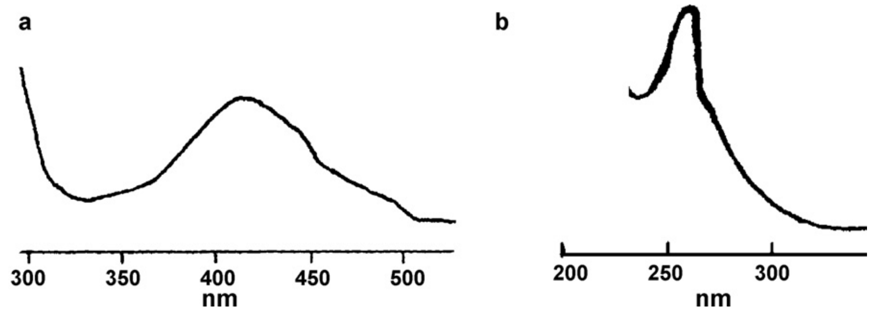

Fig. 2. Absorption spectra of (a) PDIMCMC under $C = 4.0 \times 10^{-4}$ g mL^{-1}, pH = 5.30 DACMC:PDM = 1:5 (wt:wt) and (b) SPIMCMC under $C = 4.4 \times 10^{-4}$ g mL^{-1}, pH = 9.12 DACMC:ABS = 1:10 (wt:wt) at room temperature.

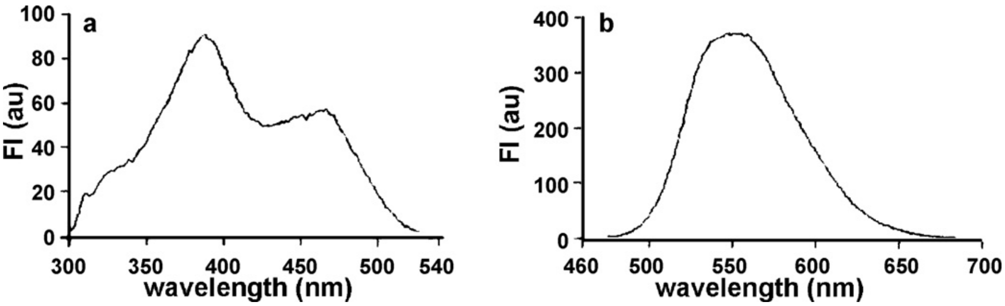

Fig. 3. Fluorescence spectra of PDIMCMC under (a) excitation spectrum with emission wavelength of 615 nm and (b) emission spectrum with excitation wavelength of 388 nm. Condition $C = 4.0 \times 10^{-4}$ g mL^{-1}, DACMC:PDM = 1:5 (wt:wt), pH = 5.30, at room temperature.

3.2. Absorption spectra

Fig. 2 is absorption spectra of PDIMCMC by the reaction of DACMC and PDM at the weight ratio of 1:5 and SPIMCMC by the reaction of DACMC and ABS at the weight ratio of 1:10; all figures involved are the same. Compared curve a with b in Fig. 2, the absorption spectrum of PDIMCMC goes to longer wavelength into the near infrared. But the absorption spectrum of SPIMCMC is still in the blue green region and just goes red shift, compared with CMC's. This owes to a larger extended π system in PDIMCMC than in SPIMCMC.

3.3. Fluorescence spectrum

From Figs. 2, 3b and 4b, it is found that the absorption and emission spectra of both PDIMCMC and SPIMCMC do not show a mirror image relationship. This is owing to the differences in the charge distributions and equilibrium geometries in the ground and excited states, the vibrational structures of these states are somewhat different.

All absorptions are considered to arise from the same vibrational level of the ground state and terminate in the various vibrational levels of the electronically excited state, i.e. the Franck–Condon

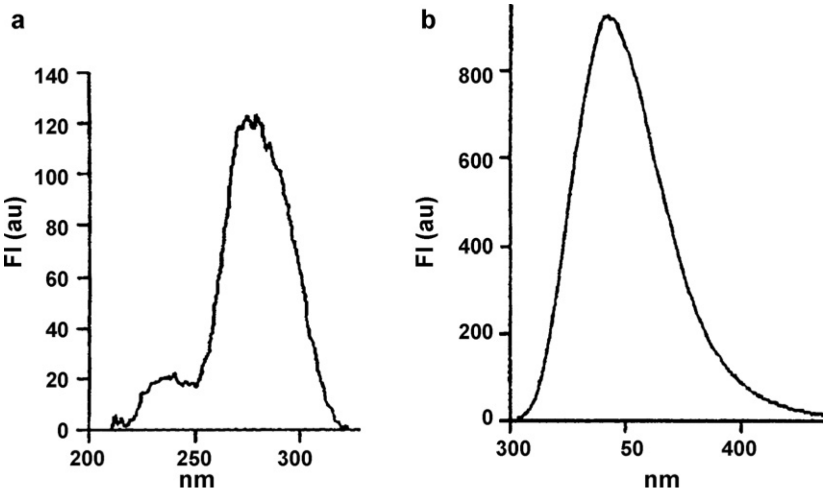

Fig. 4. Fluorescence spectra of SPIMCMC under (a) excitation spectrum with emission wavelength of 341 nm and (b) emission spectrum with excitation wavelength of 245 nm. Condition $C = 4.4 \times 10^{-4}$ g mL^{-1}, DACMC:ABS = 1:10 (wt:wt), pH = 9.12, at room temperature.

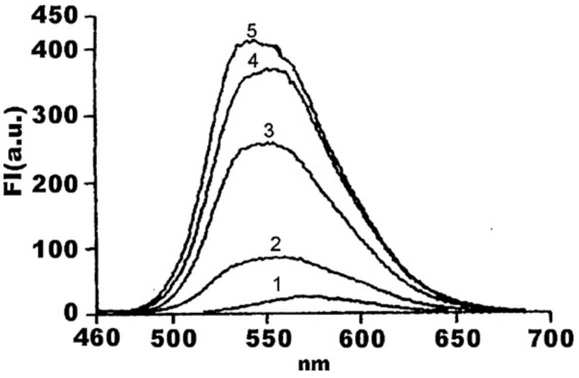

Fig. 5. Effect of pH on FI and FS of PDIMCMC with excitation wavelength of 388 nm at room temperature. Condition $C = 8.08 \times 10^{-4}$ g mL^{-1}, DACMC:PDM = 1:5 (wt:wt), pH of the curves: (1) 4.58, (2) 10.42, (3) 8.49, (4) 5.46 and (5) 6.48.

(F–C) excited state. The absorption spectra reflect the vibrational structure of the Franck–Condon excited state. Because all fluorescence arises from the same vibrational level of the lowest excited singlet state and terminates in the various vibrational levels of the ground electronic state, i.e. the F–C ground state, the fluorescence spectrum reflects the vibrational structure of the F–C ground state. There are larger aromatic structures in the macromolecular products, especially, there are some unshared electron pairs on the nitrogen and oxygen of COO$^-$. It is possible to have some isomers in various environments. So they might have the different structure on F–C ground and lowest excited singlet states. If the F–C ground and lowest excited singlet states have different vibrational structures, that is, the vibrational energy levels are differently separated in both, the fluorescence and longest wavelength absorption bands will not be mirror images of each other with the absorption spectrum lying on the short wavelength side and the fluorescence spectrum lying on the long wavelength side of the 0-0 band.

The spectra of fluorescence of PDIMCMC and SPIMCMC in aqueous solution do not reflect the photophysical properties of the benzenoid chromophore. The emissions are dominated by a broad signal centered at 550 nm and 342 nm, respectively, attributed to macromolecular Shiff's base with benzene.

Because fluorescence originates from the lowest excited singlet state and terminates in the ground state, the effects upon the position of the fluorescence band of substituents and size of the aromatic system, i.e. extension of conjugation, are qualitatively similar to those upon the position of the lowest frequency absorption band. Hence, increasing the size of the aromatic system results in longer wavelength of fluorescence of PDIMCMC than in SPIMCMC because the energy gap between the ground and excited states decreases in magnitude as the aromatic molecule increases.

3.4. Influence of pH on the fluorescence spectrum

When acidity or basicity is manifested in the excited state, competition of these chemical reactions with fluorescence of the excited species often results in multiple luminescences from solutions. Fig. 5 shows the great differences of both FS and FI in solutions with different pH. The FI of PDIMCMC is in the top in neutral condition, and the peak value of FS of PDIMCMC shifts longer wavelength in acidity.

The concentration of the fluorescence molecule, PDIMCMC, decreases with –COO$^-$ forming in alkali. On the other hand, PDIMCMC might be favorable to dissociate in acidity. These cause the FI to drop.

In the products with carboxylic groups, an electron-withdrawing group, excitation from the S_0 to the S_1 state results in the movement of electronic charge to the electron-withdrawing group. This causes the S_1 state to be stabilized to a greater degree than is the S_0 state by protonation at the electron-withdrawing group in acidity condition. This decreases the energy difference between S_0 and S_1 in the protonated molecule. The spectral result is the shifting of the fluorescence spectrum to longer wavelengths on protonation.

3.5. Influence of concentration of solution

Fig. 6 shows that in dilute solutions, the FI of the product is very weak and the peaks of these FS shift to longer wavelengths, compared with the concentrated solution indicated in Fig. 5(b), which displays, however, the FI of PDIMCMC is higher in lower concentrate of solution (1.2×10^{-3} g mL^{-1}) than that in concentrated solution (2.4×10^{-3} g mL^{-1}).

In an appropriate solute concentration, the quantities of PDIMCMC in the solution, the fluorescence material, are added with increasing concentration of solution. Meanwhile the FI of the PDIMCMC becomes higher. In dilute solutions, the intermolecular interactions were predominantly between solute and solvent. In this case, the intermolecular interactions are mainly hydrogen-bonding electrostatic between –COOH group of PDIMCMC and solvent H_2O. The relaxation processes occurring subsequent to absorption and fluorescence nearly always tend to make fluorescence move to longer wavelengths with increasing hydrogen-bonding capacity. As the solute concentration is raised,

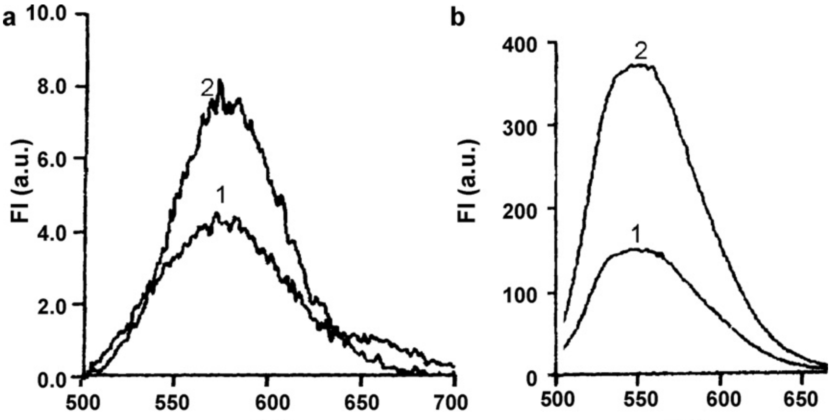

Fig. 6. The relationship between the concentration and FS and FI of PDIMCMC with excitation wavelength of 388 nm at room temperature. Condition: pH = 4.8–5.8, DACMC:PDM = 1:5 (wt), λ_{Ex} = 388 nm: (a) curve 1: 2.4×10^{-4} g mL^{-1} and curve 2: 4.8×10^{-4} g mL^{-1}; (b) curve 1: 2.4×10^{-3} g mL^{-1} and curve 2: 1.2×10^{-3} g mL^{-1}.

the frequency of encounters between solute molecules is increased. Depending on the physical dimensions of the solute molecules, PDIMCMC and PDM may be capable of forming complexes, as in the following equation. This causes the FI to decrease.

$$\mathrm{PDIMCM} - \mathrm{COOH} \underset{A}{+} o - (\mathrm{NH}_2)_2 - \mathrm{C}_6\mathrm{H}_4$$

$$\rightleftharpoons \mathrm{PDICM} - \mathrm{COOH} \underset{B}{\cdot} \mathrm{H}_3\mathrm{N} - \mathrm{C}_6\mathrm{H}_4\mathrm{NH}_2$$

4. Conclusions

The Schiff's bases PDIMCMC and SPIMCMC, by the reaction of macromolecule aldehydes based on CMC with organic amines, all have a good luminescence property which was influenced by the pH and solution concentration. We attribute the result to their chemical structure which is sensitive to the change of environment.

Acknowledgments

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