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Fluorescence Spectra of Model Compounds for Light-emitting Alternating Copolymers in Heterogeneous Environments

Jun Lin YANG, Hong Zhen LIN, Min ZHENG, Feng Lian BAI*

Organic Solids Laboratory, Center for Molecular Sciences, Institute of Chemistry,
Chinese Academy of Sciences, Beijing 100080

Abstract: In this paper, the fluorescence spectra of model compounds of light-emitting alternating copolymers, M (TPA-PPV) and M (TPA-PAV) (**Scheme 1**) were studied and the effect of KNO_3 on the interaction between model compounds and ionic micelle-water interface was also investigated. It is found that (I) The fluorescence changes of M (TPA-PPV) are related to the state of CTAB and SDS solution. (II) Aggregated state can be formed in M (TPA-PAV) solution at low concentration of CTAB. (III) Higher concentration of KNO_3 may affect the interaction between model compounds and ionic micelle-water interface.

Keywords: Alternating copolymer, charge transfer, ionic micelle–water interface, salt effect, cetyltrimethylammonium bromide, sodium dodecylsulfate.

Cao[1] *et al.* reported that certain surfactant-like additives dissolved or dispersed in the EL polymer significantly improved electron injection from relatively high work function metals such as Al. The open question is what effect of surfactant on the photophysical properties is. Up to now, no report concerning this aspect has been documented. In our previous work[2], a type of novel high-efficiency light-emitting nitrogen-containing poly (phenylene vinylene) (PPV)-related copolymers was synthesized. Correspondingly, their model compounds, M (TPA-PPV) and M (TPA-PAV) are also prepared. In the present paper, M (TPA-PPV) and M (TPA-PAV) are used to investigate the effect of sodium dodecyl sulfate (SDS) and cetyltrimethylammonium bromide (CTAB) on their fluorescence spectra. The effect of inorganic salt is also mentioned.

Materials and Methods

M (TPA-PPV) and M (TPA-PAV) were synthesized as described elsewhere[2]. Cetyltrimethylammonium bromide (CTAB) was an AR grade of Shanghai the First Chemical, and was used after recrystallization from absolute ethanol. Sodium dodecylsulfate (SDS) was product of Merck. KNO_3 was of AR grade, purchased from Beijing Chemical Factory. Re-distilled double deionized water was used for all experiments.

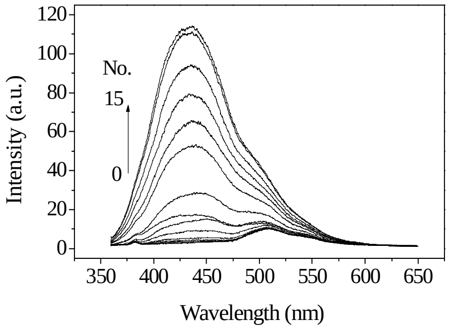
Fluorescence spectra were recorded on an Hitachi F-4500 fluorescence spectro-photometer. A low scan rate was chosen in spectra recording. All measurements were made at 40°C.

Results and discussion

Figure 1 displays fluorescence spectra of M (TPA-PPV) in CTAB solution. Concerning the peak position and profile of the spectra, they are similar to those found in benzene. Dual fluorescence that may be characteristic of the presence of the excited state intramolecular charge transfer (CT) process of M (TPA-PPV)[3,4] can be observed. The emission in the long wavelength region is assigned to the CT state, usually called a band emission, while the shorter wavelength emission called b band, is due to the locally excited (LE) state. From **Figure 1**, it obviously appeared that the dual fluorescence of M (TPA-PPV) in the surfactant solution is sensitive to surfactant concentration. With the concentration of surfactant increasing, the intensities of both the LE and the CT bands are enhanced. The 'S'-shaped curves can be obtained (shown in **Figure 2**) for M (TPA-PPV) in CTAB by plotting the intensity ratio of the LE band to the CT band, I_b/I_a , against the concentration of surfactant, which indicates the onset of the micelles[5].

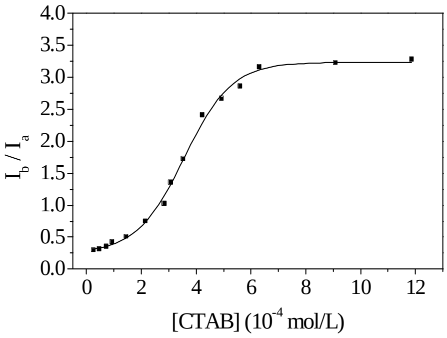
This fact is in agreement with the assumed two-state model for micelle formation. From the two 'S'- shaped curves, the critical micelle concentrations (CMCs) are read out to be 5.6×10^{-4} mol/L for CTAB and 11.8×10^{-3} mol/L for SDS, respectively. Both values are well consistent with the reported data[6,7]. In addition, it is noted that the I_b/I_a ratios in both CTAB and SDS solutions are displayed leveling off after micelle formation, in spite of the continuous increasing of the surfactant concentrations. These findings demonstrate that the fluorescence spectrum changes of M (TPA-PPV) are related to the state of surfactants in solution. It can be reasonably speculated that M (TPA-PPV) probably locates in the water-micelle interface. Accordingly, M (TPA-PAV) was investigated in CTAB and SDS. It is interestingly shown that with the concentration

Figure 1 The fluorescence spectra of M (TPA-PPV) in CTAB



Excitation wavelength: 340 nm.
CTAB (10^{-4} mol/L): 1, 0.27; 2, 0.47; 3, 0.73; 4, 0.93; 5, 1.46; 6, 2.15; 7, 2.84; 8, 3.07; 9, 3.54; 10, 4.23; 11, 4.92; 12, 5.62; 13, 6.31; 14, 9.08; 15, 11.85.

Figure 2 Fluorescence intensity ratio of LE band to the CT band I_b/I_a of M (TPA-PPV) versus CTAB concentration in aqueous solution



increasing of CTAB, the fluorescence of M (TPA-PAV) is gradually quenched and a new band with an isoemission point appears in the long wavelength region. This fact indicates that an aggregated state, *e.g.* an exciplex is formed in the presence of CTAB of low concentrations comparing to M (TPA-PPV) in CTAB solution. In this case, the concentration of CTAB is much lower than CMC of CTAB. Therefor, M (TPA-PAV) still stays in water phase. Taking into account the optimized configuration of M (TPA-PAV), the exciplex should not come from the whole molecule but from the anthracyl group. However, not any change of the fluorescence spectra of M (TPA-PAV) is observed upon adding SDS. Therefore, it is straightforward to conclude that unlike M (TPA-PPV), M (TPA-PAV) shows quite different photo-physical properties in anionic or cationic surfactants. Mini-structural differences between M (TPA-PPV) and M (TPA-PAV) should be considered as the causes for the difference in these two micelles. Meanwhile, the effects of these structural differences in micelles are subject to the position of fluorophores in the micelles.

As in cyclodextrin system[8] (Equation (1) and (2)), the magnitude of M (TPA-PPV)-micelle binding constant, K, would be calculated, providing more direct support for the occurrence of these two interactions. For these calculation, micelle is taken as a host similar to cyclodextrin and K’s are determined according to Equation (3), where I_0, I, and I_c are fluorescence intensities of the fluorophore (F) in the absence of micelle, in the presence of a given amount of micelle, and when the fluorophore is completely bound to the micelle (M), and [M] is the concentration of micelle which is related to surfactant concentration, C, and average aggregation number, N, given by Equation (4).

$$F + M \Leftrightarrow F\text{-}M \qquad (1) \qquad\qquad K = [F\text{-}M]/[F][M] \qquad (2)$$

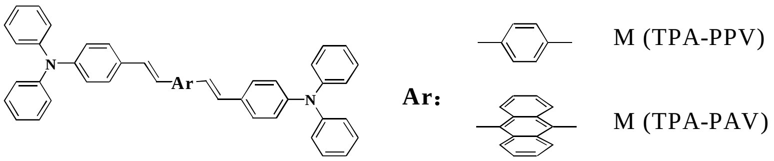
$$(I - I_0)/[M] = KI_c - KI \qquad (3) \qquad\qquad [M] = (C - CMC)/N \qquad (4)$$

According to Equation (3), the K values of M (TPA-PPV)/CTAB-micelle and M (TPA-PPV)/SDS-micelle are calculated to be 2.1×10^5 and 1.7×10^5 L/mol, respectively. These higher K values suggest the presence of electrostatic interaction besides hydrophobic interaction between M (TPA-PPV) and these two micelles. The electrostatic interaction probably resulted from the CT state of M (TPA-PPV) and the ionic micelle-water interface.

To prove the proposition above that ionic micelle-water interface played an important role on the interaction between M (TPA-PPV), M (TPA-PAV) and ionic micelle-water interface. The investigation of KNO_3 effect on the photophysical properties was also done. At certain concentration higher than CMC of CTAB or SDS and with the concentration of KNO_3 increasing, the fluorescence intensity of both M (TPA-PPV) and M (TPA-PAV) in two surfactant solutions gradually increases till the concentration of KNO_3 reaches a specific point. After this point, the fluorescence intensity exhibits decreasing with the concentration of KNO_3 further increasing. This fact, to some extent supports our proposition. Detail investigations are in progress.

Summarizing, the results show the fluorescence changes of M (TPA-PPV) and M (TPA-PAV) are related to the state of CTAB and SDS in solution.

Scheme 1 The structures of M (TPA-PPV) and M (TPA-PAV)



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