

Study on the Surface Photovoltage and Fluorescence Properties of N, N'-Bis(4'-aminophenyl)-1, 4 quinonenediimine Doped with $H_4SiW_{12}O_{40}$

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Abstract: Aniline oligomer composite materials using heteropolyacid $H_4SiW_{12}O_{40}$ as dopant was synthesized, and the effect of the doping concentration on the photoluminescence and surface photovoltaic properties were investigated.

Keywords: Fluorescence property, surface photovoltage spectra, aniline oligomer, heteropoly acid.

Polyaniline, especially its acid-doping composite material, is a kind of important photoelectric material due to its potential application in many fields¹⁻³. However, it seems to be a problem that the polymers exhibit several deficiencies, including chemical and structural imperfections as a result of mislinkage, saturated sites, molecular weight distribution, the presence of the end groups and conformation defects. All of these defects affect the device efficiency and make it difficult to relate the fundamental charge transport and optical properties of the polymer to the microscopic molecular properties. Therefore, the study of defect-free conjugated oligomers is attracting more and more attentions as model compounds for their polymers^{4,5}.

N, N'-bis (4'-aminophenyl)-1, 4-quinonenediimine was synthesized according to Ref. 6, and $H_4SiW_{12}O_{40}$ was synthesized according to Ref. 7. A quantitative $H_4SiW_{12}O_{40}$ was dissolved in 25mL of distilled water, then 0.5 g (1.74 mmol) N, N'-bis (4'-amino-phenyl)-1,4- quinonenediimine was added to the solution, stirred for 48 h at room temperature, filtered, the precipitate was repeatedly washed with distilled water, the powder was dried under vacuum for 48 h. The quantity of $H_4SiW_{12}O_{40}$ was 10 g (1.74 mmol), 5 g and 2.5 g respectively. According to the data of elemental analysis the following empirical formulas were proposed as $(C_{18}N_4H_{16})(H_4SiW_{12}O_{40})_{0.64}$; $(C_{18}N_4H_{16})(H_4SiW_{12}O_{40})_{0.47}$; $(C_{18}N_4H_{16})(H_4SiW_{12}O_{40})_{0.37}$.

UV-Vis absorption spectra: intrinsic aniline oligomer, 330 and 572 nm; composite materials, 412, 572 and 771 nm.

Figure 1 gives the photoluminescence emission and excitation spectra of the intrinsic aniline oligomer and its composite materials. The intrinsic aniline oligomer has a weak emission band at about 860 nm when it was excited with $\lambda = 572$ nm (**Figure**

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1a). But when it was doped with a certain concentration range of $\text{H}_4\text{SiW}_{12}\text{O}_{40}$, the intensity of 860 nm emission bands is enhanced significantly, as shown in **Figure 1b** and **1c**. When the doping concentration increases further, the 860 nm emission band will be weakened (**Figure 1d**). These results seem to show that in a certain doping range the dopant $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ is favorable for an increase of the intensity of the emission band at 860 nm.

Figure 1 Photoluminescence emission and excitation spectra of aniline oligomer base (a), $(\text{C}_{18}\text{N}_4\text{H}_{16})(\text{H}_4\text{SiW}_{12}\text{O}_{40})_{0.37}$ (b), $(\text{C}_{18}\text{N}_4\text{H}_{16})(\text{H}_4\text{SiW}_{12}\text{O}_{40})_{0.47}$ (c), $(\text{C}_{18}\text{N}_4\text{H}_{16})(\text{H}_4\text{SiW}_{12}\text{O}_{40})_{0.64}$ (d)

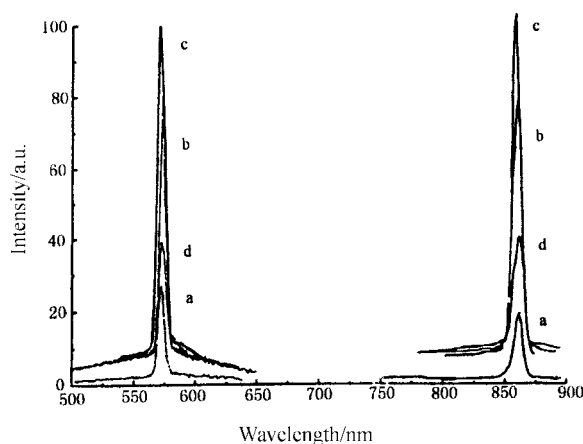
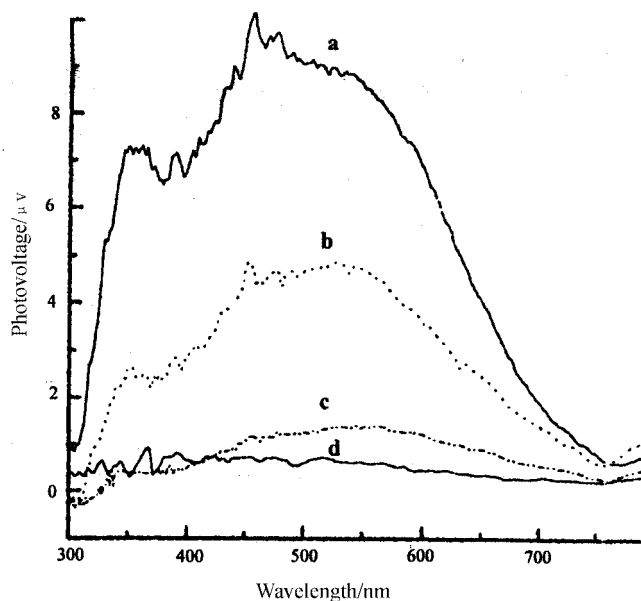


Figure 2 displays the surface photovoltage spectra of the intrinsic aniline oligomer and its composite materials. We can find that the intrinsic aniline oligomer has the strongest photovoltaic response. With the increase of the concentration of $\text{H}_4\text{SiW}_{12}\text{O}_{40}$, the photovoltaic response becomes weaker and weaker. It can be concluded that the intrinsic aniline oligomer has the highest surface potential and the surface potential decreases with the increase of the doping concentration. This shows that the photoexcited electron-hole pairs are easy to be separated under the high surface potential when aniline oligomer is undoped, therefore, the possibility of irradiation recombination is relatively small; the surface potential will be decreased when aniline oligomer is doped with $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ in a certain range, and the irradiation recombination efficiency of the photoexcited carriers is enhanced effectively, and the separation efficiency decreased; when aniline oligomer is doped at a higher concentration, the 572 nm absorption becomes too weak, along with the possible increase of the non-irradiation recombination channels due to the over doping of $\text{H}_4\text{SiW}_{12}\text{O}_{40}$.

Figure 2 Surface photovoltage spectra of aniline oligomer base (a), (C₁₈N₄H₁₆)(H₄SiW₁₂O₄₀)_{0.37} (b), (C₁₈N₄H₁₆)(H₄SiW₁₂O₄₀)_{0.47} (c), (C₁₈N₄H₁₆)(H₄SiW₁₂O₄₀)_{0.64} (d),



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References

1. J. A. Osaheni, S. A. Jenekhe, H. Vanherzeele, J. Smeth, Y. Sun, A. G. MacDairmid, *J. Phys. Chem.*, **1992**, *96*, 2380.
2. Y. Yang, E. Westerweele, C. Zhang, P. Smith, A. J. Heeger, *J. Appl. Phys.*, **1995**, *77*, 694.
3. J. Gong, R. N. Hua, Z. W. Xie, S. G. Wang, L. Y. Qu, *Polymer J.*, **2001**, *33*, 277.
4. R. E. Gill, A. Meetsma, G. Hadziioannou, *Adv. Mater.*, **1996**, *8*, 212.
5. T. Goodson, A. Gharavi, L. Yu, *Adv. Mater.*, **1997**, *9*, 639.
6. Y. Wei, C. C. Yang, T. Z. Ding, *Tetrahedron Letters*, **1996**, *37*, 731.
7. A. Teze, G. Herve, *Inorg. Synth.*, **1990**, *27*, 85.

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