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# Composition of Hyperbranched Conjugated Polymers with Nanosized Cadmium Sulfide Particles

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Received January 23, 2001. In Final Form: June 4, 2001

On the basis of a series of hyperbranched conjugated polymers (HPV) synthesized in our laboratory, the composition of HPV with nanosized cadmium sulfide (CdS) particles is investigated by means of static and dynamic fluorescence spectroscopies and atomic force microscopy (AFM). The apparent association constant between HPV and CdS can be obtained from the plot of the relative fluorescence quantum yields versus the reciprocal concentrations of CdS. The electron injection rate from excited HPV to the conduction band of CdS can also be calculated. Both the constant and the electron injection rate are related to the chain length of the alkoxy group on the connecting modules, leading to the conclusion that the modification of HPV at certain substitution sites can control the interaction between HPV and nanosized CdS particles. The CdS particles with different surface charge may result in significant changes of the apparent association constants, which shows that the electrostatic force probably plays a key role in the combination of HPV with CdS. AFM images indicate that films with good qualities can be formed on a mica substrate using the composite of HPV with nanosized CdS particles. The presence of HPV can decrease the self-aggregation of cadmium sulfide particles.

## Introduction

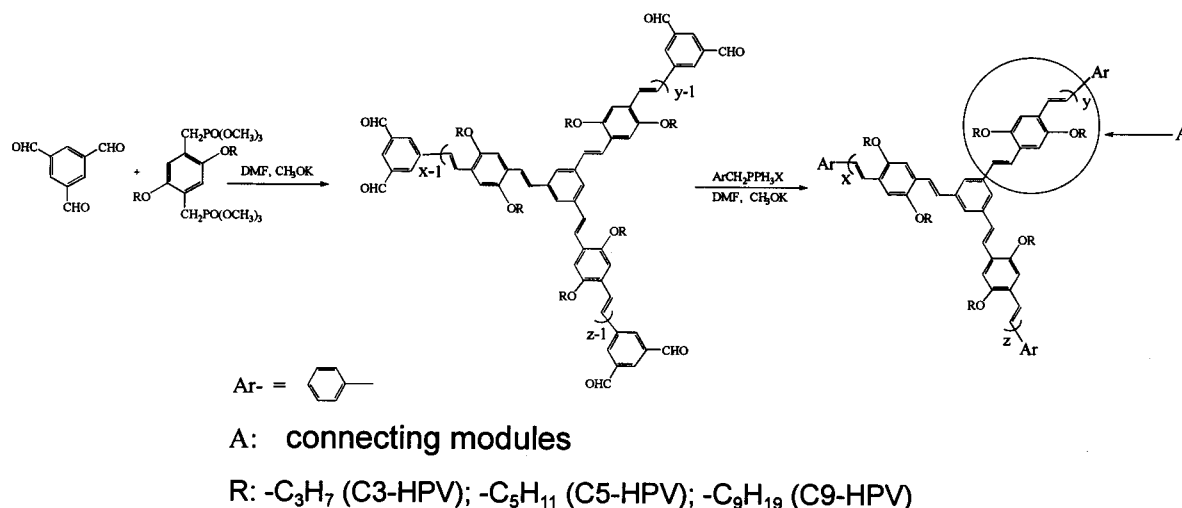
A considerable amount of work has been recently carried out on the properties of low-dimensional semiconductor materials that differ drastically from those of the bulk semiconductors due to the quantum size effect.<sup>1–4</sup> The mechanism of electron transfer in the nanoscaled system is the subject of numerous studies.<sup>5,6</sup> Interest in the detailed mechanism of illuminated semiconductor reactions results from the intensive use of aqueous semiconductors in photocatalytic organic reactions and also their unusual physical and chemical properties.<sup>7–9</sup> Several papers have also appeared in the past illustrating the various aspects of photoelectrochemical sensitization process at single crystal and polycrystalline semiconductor electrodes.<sup>10,11</sup> In those papers, interfacial charge transfer and the dynamics of photoexcited-state relaxation in nanosized semiconductors were under extensive investigation.<sup>12–16</sup> Moreover, there is an increasing interest to

combine organic dyes with nanoscopic wide band gap inorganic semiconductors. The most promising example for future applications has been a ruthenium dye-sensitized nanocrystalline TiO<sub>2</sub> solar cell with a conversion efficiency of about 10% developed by Grätzel.<sup>17</sup> In recent years, combinations of polymer semiconductors (e.g., polythiophenes and poly(*p*-phenylene vinylene)s) with colloidal nanocrystals of (wide band gap) inorganic semiconductors (e.g., TiO<sub>2</sub> and CdS) have been investigated as well, and blending of these materials is certainly an emerging area of research.<sup>18,19</sup> In principle, the dye–electrolyte combination can be replaced by a single conjugated polymer combining together the functions of light absorption and charge transport.<sup>20</sup> For the blending systems, one may ask, what is the interaction point between conjugated polymers and nanosized inorganic semiconductor particles? The answer to the question would benefit the controlling interaction between sensitizers and inorganic semiconductors, which will probably result in a further increasing of the conversion efficiencies through modification of conjugated polymers. To our rough knowledge, no work concerning this aspect has been documented. Various attempts have been made to characterize the kinetics of photoexcited charge transfer by several methods in a wide range of time scales, down to femtoseconds. Techniques such as laser flash photolysis,<sup>21</sup> resonance Raman spectroscopy,<sup>22</sup> diffuse reflectance,<sup>23</sup> and microwave absorption<sup>24</sup> have been demonstrated to be useful in investigating the mechanism of charge injection from

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- (1) Brus, L. *J. Phys. Chem.* **1986**, *90*, 2555.
- (2) Spanhel, L.; Weller, H.; Henglein, A. *J. Am. Chem. Soc.* **1987**, *109*, 6632.
- (3) Bavykin, D. V.; Savinov, E. N.; Parmon, V. N. *Langmuir* **1999**, *15*, 4722.
- (4) Serpone, N.; Lawless, D.; Khairutdinov, R. *J. Phys. Chem.* **1995**, *99*, 16646.
- (5) Zhang, J. Z.; O'Neil, R. H.; Roberti, T. W. *J. Phys. Chem.* **1994**, *98*, 3859.
- (6) Kamalov, V. F.; Little, R.; Logunov, S. L.; El-Sayed, M. A. *J. Phys. Chem.* **1996**, *100*, 6381.
- (7) Fujihira, M.; Satoh, Y.; Osa, T. *Nature* **1981**, *293*, 206.
- (8) Hoffmann, M. R.; Martin, S. T.; Choi, W.; Bahnemann, D. W. *Chem. Rev.* **1995**, *95*, 69.
- (9) Stark, J.; Rabani, J. *J. Phys. Chem. B* **1999**, *103*, 8524.
- (10) Meier, H. *Photochem. Photobiol.* **1972**, *16*, 219.
- (11) Itoh, K.; Chiyokawa, Y.; Nakao, M.; Honda, K. *J. Am. Chem. Soc.* **1984**, *106*, 1620.
- (12) Grätzel, M. *Acc. Chem. Res.* **1981**, *14*, 376.
- (13) Kiwi, J. *Chem. Phys. Lett.* **1981**, *80*, 594.
- (14) Kamat, P. V.; Chauvet, J.-P.; Fessenden, R. W. *J. Phys. Chem.* **1986**, *90*, 1389.
- (15) Kamat, P. V. *J. Phys. Chem.* **1992**, *96*, 1423.

- (16) Kamat, P. V.; Ford, W. E. *Chem. Phys. Lett.* **1987**, *137*, 421.
- (17) O'Regan, B.; Grätzel, M. *Nature* **1991**, *335*, 737.
- (18) Hide, F.; Schwartz, B. J.; Diaz-Garcia, M.; Heeger, A. J. *Chem. Phys. Lett.* **1996**, *256*, 424.
- (19) Christiaans, M. P. T.; Wienk, M. M.; van Hal, P. A.; Kroon, J. M.; Janssen, R. A. J. *Synth. Met.* **1999**, *101*, 265.
- (20) Savenije, T. J.; Warman, J. M.; Goossens, A. *Chem. Phys. Lett.* **1998**, *287*, 148.
- (21) Kamat, P. V. *J. Phys. Chem.* **1989**, *93*, 859.
- (22) Rossetti, R.; Brus, L. E. *J. Am. Chem. Soc.* **1984**, *106*, 4336.
- (23) Kamat, P. V.; Gopidas, K. R.; Weir, D. *Chem. Phys. Lett.* **1988**, *149*, 491.



**Figure 1.** The synthesis route of HPVs.

the excited state of the sensitizer to the conduction band of the inorganic semiconductor. In addition, the peculiarities of luminescence quenching may actually reflect some sophisticated details of the interaction process between photoexcited conjugated polymers and semiconductor particles.<sup>25</sup>

The aim of this paper is to investigate the interaction between conjugated polymers and nanosized CdS. To do that, a type of novel conjugated polymers called hyperbranched conjugated polymers is designed and synthesized. It is shown that the interaction can be controllable through the modification of hyperbranched conjugated polymers.

### Experimental Section

**Materials.** Tetrahydrofuran, cadmium chloride (CdCl<sub>2</sub>·2.5H<sub>2</sub>O), sodium sulfide (Na<sub>2</sub>S·9H<sub>2</sub>O), sodium hexametaphosphate (NaPO<sub>3</sub>)<sub>6</sub>, and acetonitrile were AR grade reagents purchased from the Beijing Chemical Plant without further purification prior to use. Redistilled double deionized water was used. Interference fluorescence was not observed under the experimental conditions.

**Preparation of CdS Particles.** Fifty milliliters of solution with  $6 \times 10^{-3}$  M CdCl<sub>2</sub>·2.5H<sub>2</sub>O and  $6 \times 10^{-3}$  M (NaPO<sub>3</sub>)<sub>6</sub> was very slowly mixed with a certain volume of  $6 \times 10^{-3}$  M Na<sub>2</sub>S·9H<sub>2</sub>O and  $6 \times 10^{-3}$  M (NaPO<sub>3</sub>)<sub>6</sub> in a 250 mL vessel standing in an ice-water bath at nitrogen atmosphere under vigorous stirring. Note that the preparation condition was well controlled; otherwise, it would lead to a different case. The color of the produced transparent solution was yellow. The particle diameter ( $2R$ ) was measured from transmission electron micrographs (TEM) after well-defined images of the small CdS particles were obtained. The typical size lay within the range of  $4 \pm 2$  nm. (NaPO<sub>3</sub>)<sub>6</sub> was used in this case to stabilize CdS particles. Control experiments showed that the protective agent had practically no effect on characteristics of the fluorescence spectra of hyperbranched conjugated polymers.

**Hyperbranched Conjugated Polymers.** Hyperbranched conjugated polymers were synthesized in our laboratory, as schematically represented in Figure 1. A detailed description is given in our previous work.<sup>26,27</sup> These polymers are characterized by element analysis, IR, NMR, and so forth. The molecular weights were obtained by gel permeation chromatography (GPC) (polystyrene as the standard), which are listed in Table 1. In the following text, hyperbranched conjugated polymers will be

**Table 1. Molecular Weights and Relative Fluorescence Quantum Efficiencies ( $\phi$ ) of Hyperbranched Conjugated Polymers**

| HPV    | Mn <sup>a</sup> | Mw   | PDI  | $\phi$ |
|--------|-----------------|------|------|--------|
| C3-HPV | 1113            | 1424 | 1.28 | 0.22   |
| C5-HPV | 2012            | 2668 | 1.33 | 0.46   |
| C9-HPV | 3106            | 4338 | 1.40 | 0.32   |

<sup>a</sup> Mn, Mw, and PDI were obtained by gel permeation chromatography using polystyrene as the standard.

abbreviated as C3-HPV, C5-HPV, and C9-HPV, according to the length of the alkoxy group on the connecting modules (see Figure 1).

**Apparatus.** UV-visible absorption spectra were taken on a Hitachi U-3010 spectrophotometer. The fluorescence spectra were recorded on a Hitachi F-4500 spectrophotometer. The relative fluorescence quantum efficiencies in dichloromethane solutions were determined from the corrected spectra against anthracene as a standard ( $\phi = 0.36$ ) excited at 323 nm, also demonstrated in Table 1. Fluorescence lifetime measurements were performed on a Horiba NEAS-1100 ns spectrometer by the time-correlated single-photon-counting technique. Lifetimes were calculated by reiterative least-squares fitting with variable zero time shift between the instrument response function and measured decay curve. The time resolution of the present system is ca. 200 ps. Oxidation potentials ( $E(D^{\cdot+}/D)$ ) of HPVs were measured by cyclic voltammetry on a Princeton Applied Research potentiostat (model 283) in a conventional three-electrode cell equipped with Pt wire as working and counter electrodes and an Ag<sup>+</sup>/Ag electrode (+0.8 V versus NHE) as a reference electrode at a low scan rate. In each case, the solution contains  $1.0\text{--}5.0 \times 10^{-3}$  M HPV with 0.1 M tetrabutylammonium borate, and acetonitrile was the solvent. Thin films formed from the composite of HPV with CdS or the solely CdS colloidal solution were spin coated on mica substrates. The topography of the film was examined with an atomic force microscope (AFM) (NanoScope III; Digital Instruments, Santa Barbara, CA).

### Results

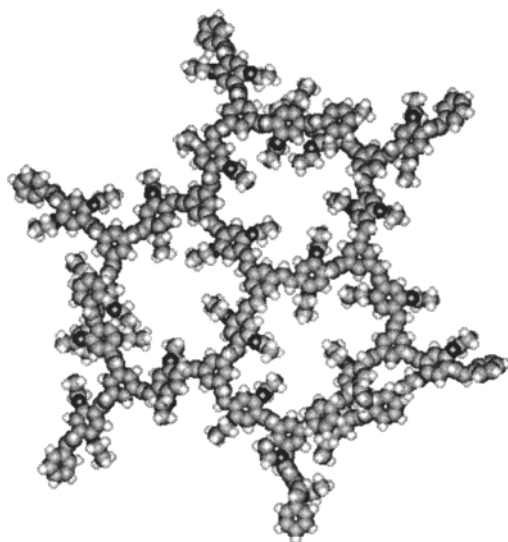
**Ground-State Geometry of HPV.** The ground-state geometry of HPV was optimized using the semiempirical PM3 method employing Alchem2000 software taking the ethoxy group (C2-) on the connecting modules as an example. C2-HPV contains several single bonds, and hence optimized geometries of various conformers were obtained. The structure with the lowest energy is given in Figure 2, from which it can be known that the HPV molecule contains many cavities. The main components constructing the cavity walls are the alkoxy groups. The

(24) Fessenden, R. W.; Kamat, P. V. *Chem. Phys. Lett.* **1986**, *123*, 233.

(25) Xiang, J.; Chen, C.; Zhou, B.; Xu, G. *Chem. Phys. Lett.* **1999**, *315*, 371.

(26) Lin, T.; He, Q.; Bai, F.; Dai, L. *Thin Solid Films* **2000**, *363*, 122.

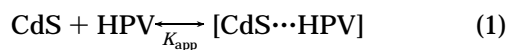
(27) He, Q.; Lin, T.; Bai, F. *Chin. Sci. Bull.* **2000**, *45*, 2367.



**Figure 2.** The optimized ball-stick model of RO-HPV ( $R = -C_2H_5$ ) with the third generation calculated by the semi-empirical PM3 method.

optimization also indicates that the so-called cavity size of HPVs with the above-mentioned ideal structure is  $\sim 3$  nm.

**Static-State Fluorescence.** Figure 3a shows that the fluorescence yield decreases upon successive addition of CdS colloidal particles to a solution of C3-HPV. The pronounced decrease in the fluorescence yield was due to the quenching of the excited singlet state of C3-HPV by CdS colloidal particles, which could be attributed to the energy and/or electron transfer to the semiconductor CdS colloidal particles. Moreover, a new band with an iso-emission point appeared in the long wavelength region with the increasing concentrations of CdS colloidal particles. The analysis of the fluorescence quenching process can be carried out here using the method reported by Kamat et al.<sup>15</sup> If we assume that the quenching of the excited singlet of HPV is due to the relatively strong adsorption of HPV branches on CdS colloidal particles, an association between CdS colloidal particles and HPV can be expressed by considering the equilibrium between adsorbed and unadsorbed molecules of HPV with an apparent association constant  $K_{app}$ :



The observed fluorescence quantum yield ( $\phi_f(obsd)$ ) of HPV in the presence of CdS colloidal particles can be related to the fluorescence yields of the unadsorbed ( $\phi_f^0$ ) and the adsorbed ( $\phi_f'$ ) molecules of HPV by the following equation:

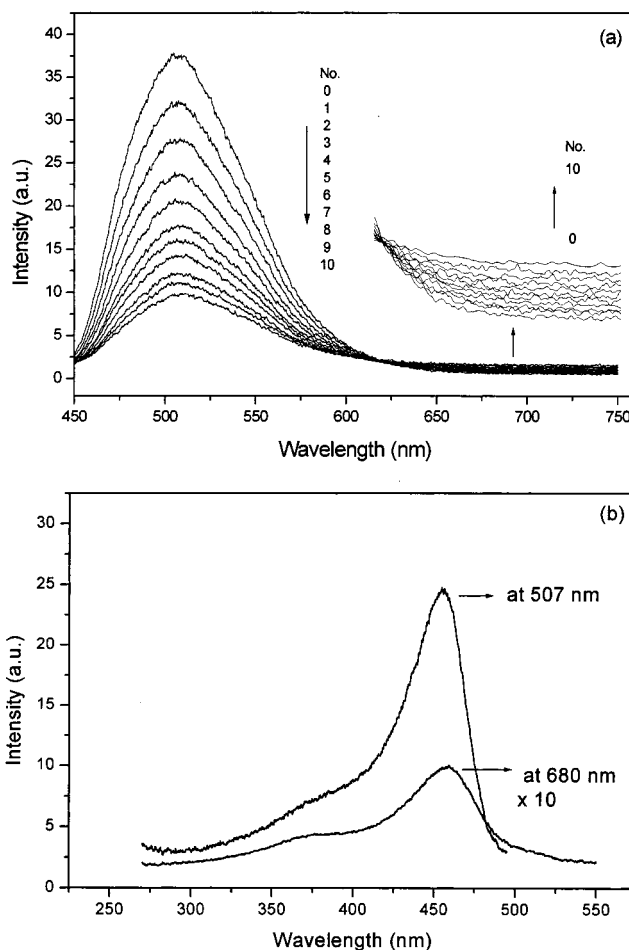
$$\phi_f(obsd) = (1 - \alpha)\phi_f^0 + \alpha\phi_f' \quad (2)$$

where  $\alpha$  is the degree of association between CdS colloidal particles and HPV. Equation 2 can be rewritten to the form

$$\phi_f^0 - \phi_f(obsd) = \alpha(\phi_f^0 - \phi_f') \quad (3)$$

In our case, the concentrations of CdS are relatively high, that is,  $[CdS] \gg [HPV]$ , and one can write

$$\alpha = \frac{K_{app}[CdS]}{1 + K_{app}[CdS]} \quad (4)$$



**Figure 3.** (a) Fluorescence of C3-HPV quenched by nanosized CdS particles. Solvent: tetrahydrofuran/water = 1:6 (v/v). Concentration of C3-HPV:  $2.5 \times 10^{-5}$  M. Concentration of CdS colloidal particles ( $\times 10^{-4}$  M): 0, 0; 1, 1.50; 2, 3.00; 3, 4.50; 4, 6.00; 5, 7.50; 6, 9.00; 7, 10.50; 8, 12.00; 9, 13.50; 10, 15.00. (b) Fluorescence excitation spectra collected at 680 and 507 nm. Concentration of C3-HPV: see (a). Concentration of CdS colloidal particles:  $1.5 \times 10^{-4}$  M.

Upon substituting the value of  $\alpha$  in eq 3, we obtain

$$\frac{1}{\phi_f^0 - \phi_f(obsd)} = \frac{1}{\phi_f^0 - \phi_f'} + \frac{1}{K_{app}(\phi_f^0 - \phi_f')[CdS]} \quad (5)$$

If the observed quenching of HPV entirely originates from the association of HPV with CdS colloidal particles, one may expect a linear dependence of  $1/(\phi_f^0 - \phi_f(obsd))$  on the reciprocal concentration of CdS colloidal particles with a slope equal to  $1/\{K_{app}(\phi_f^0 - \phi_f')\}$  and an intercept equal to  $1/(\phi_f^0 - \phi_f')$ . Indeed, the linear plot obtained in our present experiment confirms the existence of the dependence. Figure 4 shows a typical plot for C3-HPV, from which the apparent constant  $K_{app}$  and the association degree can be calculated. All these constants for C3-HPV, C5-HPV, and C9-HPV are given in Table 2.

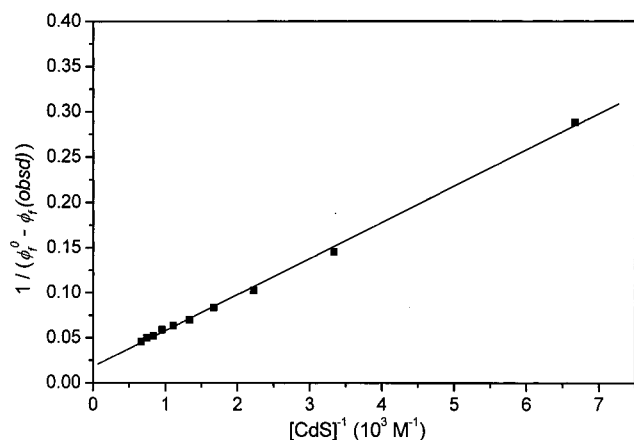
**Fluorescence Lifetime.** Table 2 also demonstrates the lifetimes of HPVs with and without CdS colloidal particles. In homogeneous solution, HPV generally had a single-exponential decay with a relatively longer excited singlet lifetime. However, in the presence of CdS colloidal particles, the fluorescence emission of HPV displayed not a single-exponential decay but a two-exponential decay profile. The fitting of the fluorescence decay to a two-exponential decay indicates that two components coexist



**Table 2.** Summary of the Apparent Association Constant ( $K_{\text{app}}$ ), Association Degree ( $\alpha$ ), Oxidation Potential ( $E(\text{HPV}^+/\text{HPV})$ ), Lifetime ( $\tau$ ), and Electron Injection Rate ( $k_{\text{et}}$ )

| HPV    | $K_{\text{app}}$<br>( $10^2 \text{ M}^{-1}$ ) | $\alpha$ | $E(\text{HPV}^+/\text{HPV})^a$<br>(V) | lifetime ( $\tau$ , ns) <sup>b</sup> |                      |               |                 |               |                 | $k_{\text{et}}$<br>( $10^8 \text{ s}^{-1}$ ) |
|--------|---|----------|---------------------------------------|--------------------------------------|----------------------|---------------|-----------------|---------------|-----------------|--|
|        |   |          |                                       | without CdS                          |                      | with CdS      |                 |               |                 |  |
|        |   |          |                                       | $\tau$                               | $a (\times 10^{-1})$ | $\tau_1$      | $a_1 (10^{-1})$ | $\tau_2$      | $a_2 (10^{-2})$ |  |
| C3-HPV | $4.6 \pm 0.3$                                 | 0.53     | 0.38                                  | $4.7 \pm 0.3$                        | 2.23                 | $1.1 \pm 0.2$ | 3.34            | $6.8 \pm 0.8$ | 4.05            | 7.6  |
| C5-HPV | $3.3 \pm 0.4$                                 | 0.45     | 0.90                                  | $4.9 \pm 0.2$                        | 2.01                 | $2.6 \pm 0.3$ | 2.02            | $7.9 \pm 1.0$ | 6.36            | 2.6  |
| C9-HPV | $2.0 \pm 0.2$                                 | 0.33     | 0.88                                  | $5.8 \pm 0.3$                        | 1.90                 | $2.4 \pm 0.7$ | 2.06            | $8.9 \pm 2.5$ | 1.36            | 3.0  |

<sup>a</sup> Versus  $\text{Ag}^+/\text{Ag}$ . <sup>b</sup> The decay curves were fitted with an exponential function as  $I(t) = \sum a_i \exp(-t/\tau_i)$ .

**Figure 4.** Dependence of  $1/(\phi_t^0 - \phi_t(\text{obsd}))$  on the reciprocal concentration of CdS colloidal particles.

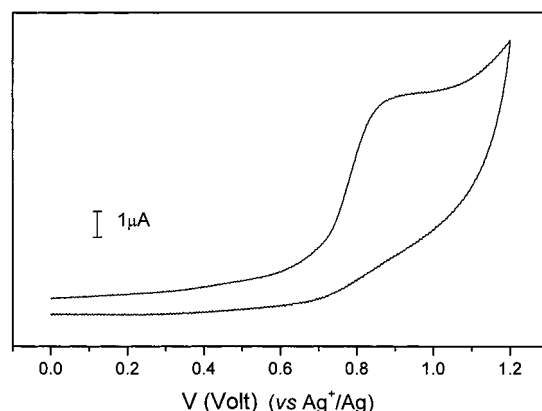
in the excited state of HPV. The fluorescence lifetimes of the two species are attributed to HPV adsorbed on CdS colloidal particles and unadsorbed HPV. It was generally accepted that the sensitizer, that is, HPV molecules adsorbed on the CdS colloidal surface, had a shorter excited singlet lifetime than in homogeneous solution. This implies that the longer lifetime is probably assigned to the unadsorbed HPV in the excited state. If we assume that the observed decrease in fluorescence lifetime solely results from the electron injection from excited HPV ( $\text{HPV}^*$ ) to the conduction band of CdS colloidal particles and the other photophysical processes of HPV associated with CdS take place at the same rate as in homogeneous solution, one can calculate the specific rate ( $k_{\text{et}}$ ) of the charge injection process through the correlation of the observed lifetimes as follows:<sup>28</sup>

$$k_{\text{et}} = \frac{1}{\tau_{\text{ads}}} - \frac{1}{\tau} \quad (6)$$

where  $\tau$  and  $\tau_{\text{ads}}$  are the lifetimes of HPV in solution and adsorbed on the CdS surface, respectively.

**Voltammetry.** The electrochemical oxidation of HPVs gave one peak in cyclic voltammetry. Figure 5 presents an example of C5-HPV, which clearly shows that the reaction is irreversible. This is undoubtedly attributed to the overoxidation of HPV.<sup>29</sup> Those oxidation potentials ( $E(\text{HPV}^+/\text{HPV})$ ) for all HPVs studied here are also collected in Table 2.

**AFM Measurement.** The surface topography of film obtained from the composite of HPV and CdS colloidal particles on a mica substrate was observed by an AFM. As an example, the image of a film for C5-HPV with CdS is shown in Figure 6a. For comparison, the image of a film formed by only CdS colloidal solution is also presented in Figure 6b.

**Figure 5.** Cyclic voltammogram of C5-HPV in 0.1 M  $(\text{Bu})_4\text{NBO}_3/\text{CH}_3\text{CN}$  solution.

## Discussion

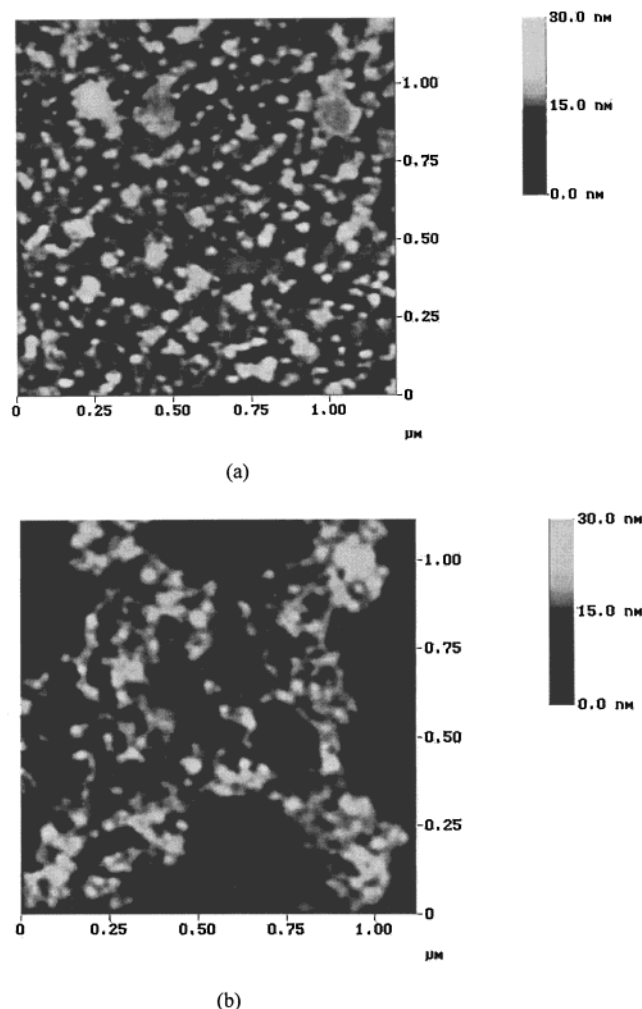
In this study, we investigated the interaction between HPV and CdS colloidal particles. The starting point was the systematic variation of CdS particle concentrations on the fluorescence quantum yields. Due to the profile similarity of the fluorescence excitation spectra collected at ca. 680 nm and the peak position located in the shorter wavelength region (see Figure 3b), the weak long fluorescence in Figure 3a may possibly arise from the sensitized CdS emission. The new emission band appearing in the long wavelength region also probably results from the excited complex (exciplex) formation between HPV and CdS. Exciplex is usually encountered in organic photochemistry, while examples of inorganic and organometallic complexes that display exciplex emission are also reported by Yam.<sup>30,31</sup> However, the formation of exciplex between organic molecules and inorganic semiconductors is rare. The exciplex formation of  $\text{HPV}^*$  with CdS particles at least shows that the interaction force between HPV and CdS is not weak. From Table 2, it can be known that both the apparent association constants ( $K_{\text{app}}$ ) and degrees ( $\alpha$ ) of HPVs with CdS follow the order C3-HPV > C5-HPV > C9-HPV. Taking into consideration the molecular structures, the main difference among the HPVs is the length of the alkoxy group on the connecting modules, and thus the order demonstrates that the interaction between HPV and CdS colloidal particles is somewhat related to the alkoxy group. As mentioned above, the alkoxy groups are the main elements forming the cavity walls of HPV. Thus, the evidence indicates that the modification of HPV at the substitution sites on the connecting modules may reach the aim to control the composition of HPV with CdS colloidal particles. It is evident that the sizes of CdS particles and the cavity of HPV are not well-matched. This suggests that the

(28) Kamat, P. V.; Fox, M. A. *Chem. Phys. Lett.* **1983**, 102, 379.

(29) Cervini, R.; Li, X.-C.; Spencer, G. W.; Holmes, A. B.; Moratti, S. C.; Friend, R. H. *Synth. Met.* **1997**, 84, 359.

(30) Yam, V. W. W.; Lee, V. W. M. *J. Chem. Soc., Dalton Trans.* **1997**, 3005.

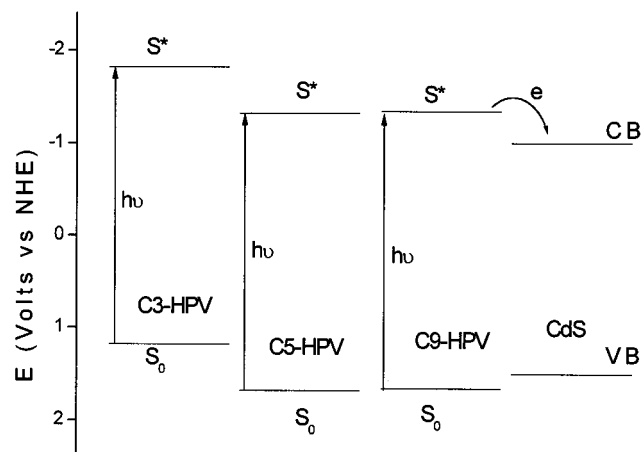
(31) Yam, V. W. W.; Li, C. K.; Chan, C. L. *Angew. Chem., Int. Ed. Engl.* **1998**, 37, 2857.



**Figure 6.** (a) AFM image of the film formed by the composite of C5-HPV and CdS. (b) AFM image of the film formed by the solution of CdS without HPV.

branches of HPV practically do not extend exactly in a plane. Hence, the practical so-called cavity size may be larger than that in ideal optimized molecular structure.

Figure 4 provides evidence that no sign for "negative curvature" in  $F_0/F$  is presented. Moreover, the fact that their value of  $k_{et}$  is a lower bound proves that the fluorescence quenching is a mixture of static and dynamic quenching and in this case the apparent value of  $k_{et}$  may reflect the joint process of energy transfer to the quenching site on the CdS surface. The possibilities for creating photovoltaic cells based on conjugated polymers and inorganic semiconductor colloidal particles depend on the photoinduced electron-transfer reaction.<sup>19</sup> To examine the possibility in our case, we calculated the oxidation potential of excited HPV (HPV<sup>\*+/HPV\*</sup>), combining the oxidation potential of HPV in the ground state with the exciting energy ( $h\nu_{exc}$ ). The involved energy levels for the composition between HPV and CdS are schematically depicted in Figure 7. It is noted that  $\lambda_{max}$  values of the absorption spectrum for the three HPVs are almost identical, which is reflected in Figure 7; that is, the band gaps for the three HPVs are nearly the same. Indeed, the same excitation wavelengths were chosen when the fluorescence quenching investigation was performed. It is clearly shown that electron injection from the excited HPV to the conduction band of CdS colloidal particles can be carried out from the thermodynamic point of view. The largest driving force of the electron injection process is



**Figure 7.** Schematic diagram describing the conduction and valence bands for CdS and the electron-donating energy levels for HPV.

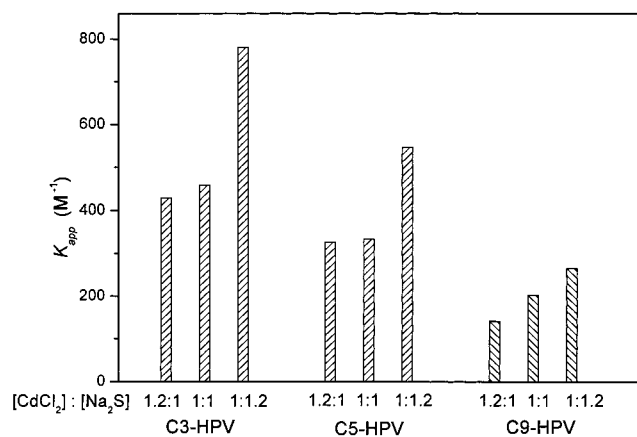
attributed to the composition system containing C3-HPV, which leads to the largest electron injection rate from excited C3-HPV to the conduction band of CdS colloidal particles. The longer the length of the alkoxy group, the lower the apparent association constant and the electron injection rate, that is,  $k_{et}$ . On the basis of this fact, it is suggested that the approach of the CdS particle to the oxygen atom in the alkoxy group is the important process in the composition. The longer length of the alkyl chain would interfere with the access. In addition, longer alkyl chains will make the so-called cavity more hydrophobic, which does not facilitate CdS particles to stay in such a microregion.

Small differences exist in the oxidation potential and unquenched fluorescence lifetime ( $\tau_0$ ) as a function of the alkoxy group. A corresponding shift in  $\lambda_{max}$  of the fluorescence spectrum was displayed (not shown) although the shift was definitely not large. Here, we presume these differences could be rationalized on the basis of conformational differences or the degree of polymerization and hence the range of conjugation lengths in the HPVs.

To make clear the real nature of the interaction force between HPV and CdS colloidal particles, we changed the concentration ratio of CdCl<sub>2</sub> to Na<sub>2</sub>S to prepare three kinds of CdS colloidal particles with different surface charges.<sup>32</sup> By use of the same method, the apparent association constant between one HPV and any of the three kinds of CdS particle was obtained, as displayed in Figure 8. This figure shows that CdS colloids with a Cd<sup>2+</sup> ion excess will lower the apparent association constants. In contrast, CdS colloids with an excess of S<sup>2-</sup> ions will enhance the constants. It is straightforward to draw a conclusion that the electrostatic force has a significant effect on the composition of HPV with CdS colloidal particles.

It is well-known that the morphology of a film is generally an important factor to determine the performance of optoelectronic devices. Thus, the surface topography of films formed from the composition solution of HPV with CdS colloidal particles and the solution of solely CdS particles is compared by AFM. Figure 6a shows that CdS particles can disperse well into HPV molecules in the presence of HPV, while large aggregates of CdS would be formed without HPV (See Figure 6b). Dots are not shown in good quality from Figure 6a, while the case was changed in higher resolution; especially on a mica substrate covalently linked by HPV, dots can be clearly seen (this

(32) Bavykin, D. V.; Savinov, E. N.; Parmon, V. N. *J. Photochem. Photobiol., A* **2000**, *130*, 57.



**Figure 8.** Relationship between the association constants and the concentration ratio of CdCl<sub>2</sub> to Na<sub>2</sub>S used to make CdS nanosized particles.

result will appear elsewhere). In our present case, we would just like to demonstrate with the images that the presence of HPV could decrease the self-aggregation of CdS particles. There has been considerable interest in the general properties of dendrimers, especially in their use as stabilizers in the synthesis of metal nanoclusters.<sup>33</sup> HPV is a kind of dendrimer-like polymer, which motivates

us to make inorganic semiconductor particles with different sizes taking HPV as a template. In this way, HPV has two roles. One is stabilizer. The other is sensitizer. Detailed investigation of such composites of HPV with inorganic semiconductor particles will probably result in new systems with specific optoelectronic effects. The investigation of optoelectronic properties of the composition system of HPV with CdS colloidal particles is in progress. Anyway, the different optoelectronic effects of the composition systems containing either linear conjugated polymers or HPVs will be expected.

Summarizing, this study demonstrates that the chain length of alkoxy groups on the connecting modules can control the interaction between HPV and nanosized CdS particles. The electrostatic force plays a key role in the combination of HPV with CdS. AFM images indicate that films with good qualities can be formed on a mica substrate using the composite of HPV with nanosized CdS particles. The presence of HPV can decrease the self-aggregation of cadmium sulfide particles.

**Acknowledgment.** This project is financially supported by the Natural Science Foundation of China (Nos. 29992530 and 29873060), the "973" Foundation (G1999064504), and CAS. Dr. T. Lin is acknowledged for his valuable help in molecular simulation. These authors also thank the anonymous reviewers for their excellent suggestions to improve our manuscript.

(33) Hanus, L. H.; Sooklal, K.; Murphy, C. J.; Ploehn, H. J. *Langmuir* **2000**, *16*, 2621.