# Polymer−Dye Complexes: A Facile Method for High Doping Level and Aggregation Control of Dye Molecules

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We show that strong noncovalent interactions between a host polymer and guest dye molecules drastically suppress the dye aggregation tendency, thereby allowing high doping levels, which in turn opens possibilities for enhanced performance. We use a common azo-dye (Disperse Red 1) and three polymer matrixes: polystyrene (PS), poly(4-vinylphenol) (PVPh), and poly(styrenesulfonic acid) (PSSA). The polymer−dye systems are studied in thin films by ultraviolet−visible and infrared spectroscopy and by optical second-harmonic generation. The lack of interaction in PS-matrix limits the maximum obtainable dye loading without aggregation below 20 wt %. Due to the polar nature of PVPh matrix, ca. 40 wt % dye loading can be achieved without aggregation, whereas in PSSA an ionic complex is formed, allowing ca. 60 wt % loading. In the latter case a dye molecule is attached to approximately each polymer unit, which has typically required covalent bonding of dye molecules to the polymer. This motivates further studies of noncovalently interacting guest−host systems as a general route for functional optical materials.

## 1. Introduction

Organic dye-doped polymer materials have numerous optoelectronic applications, including frequency conversion of light, waveguiding, optical signal processing, and optical data storage[1−4] and are also established as potential laser media.[5] Compared to inorganic materials, such systems have the advantage of being highly processable; i.e., a system with desired properties can be tailored with low fabrication cost. The applications of dye-doped polymer systems are based on, e.g., nonlinear optical, fluorescent, photochromic, or photorefractive effects and exploit the high response of the active molecules to optical fields.[6−8] In many of these applications, it is essential to use high concentrations of the active molecules while preventing the aggregation of the molecules in the polymer matrix, as this leads to increased scattering losses, to changes in the spectroscopic properties, and typically also to a decrease in the overall response of the system.

The incorporation of guest molecules in a polymer matrix can be done in different ways (Figure 1). In conventional polymer systems, the active compound is incorporated into the host polymer as a dissolved guest (Figure 1a).[9] No significant intermolecular interactions occur between the active molecules and the polymer in such guest−host systems. These systems are simple and cost-effective, as they only require mixing of the constituents in order to produce the desired compound. Unfortunately, conventional guest−host systems suffer from several undesirable features that limit their usability in device applications.[9] For example, the thermal stability of such systems is poor in applications that rely on net alignment of the active molecules.[10] A more general problem is the aggregation tendency of the guest molecules in the polymer host, which limits the doping levels to moderate values,[6] typically less than 20 wt %.

To overcome the problems of the guest−host systems, the active molecules have been covalently linked to the polymer backbone (side-chain systems; Figure 1b) or chemically incorporated into the backbone itself (main-chain systems).[9] In such systems, thermal relaxation of molecular alignment is significantly reduced.[10] Moreover, an active molecule can be attached to each polymer unit (1:1 molar ratio), resulting in high doping concentrations. Covalently linked systems, however, are considerably less attractive than guest−host systems, as complicated organic synthesis is required for each combination of a polymer and an active molecule.

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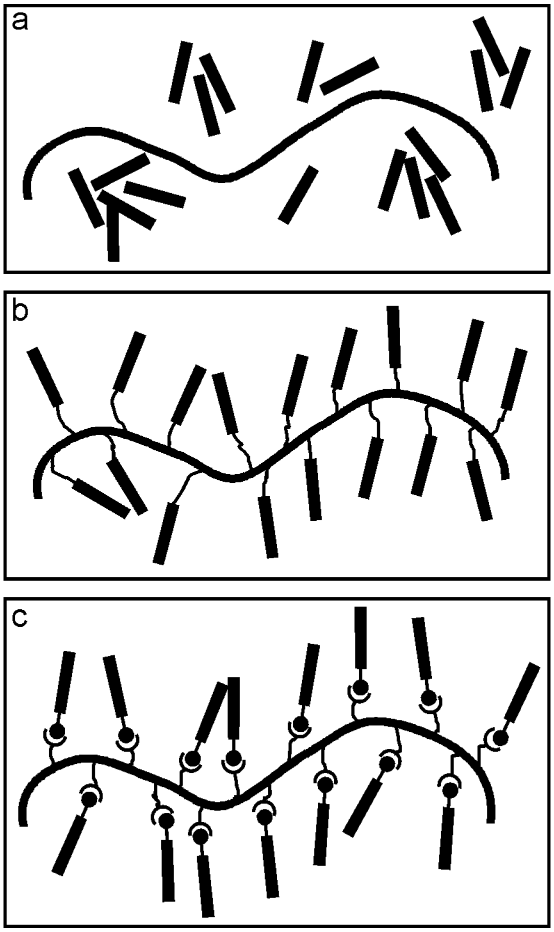

**Figure 1.** Schematic representations of dye−polymer systems: (a) conventional guest−host system with essentially no interactions between the polymer and the dye molecules easily leads to aggregation of the dyes, (b) covalently linked system, and (c) guest−host system with intermolecular interactions between the dyes and the polymer prevent their aggregation.

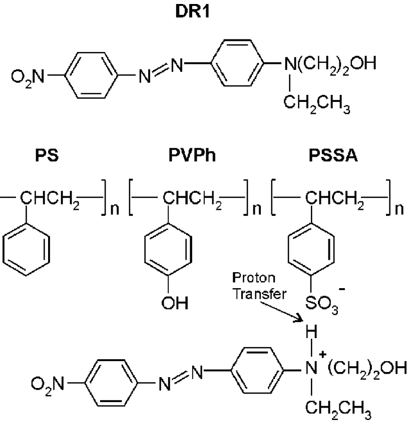

**Figure 2.** Chemical structures of Disperse Red 1 (DR1), polystyrene (PS), poly(4-vinylphenol) (PVPh), and poly(styrenesulfonic acid) (PSSA) and the proposed noncovalent interaction between DR1 and PSSA.

Noncovalent intermolecular interactions offer a new way to link the active molecules to the polymer backbone (Figure 1c). Such interactions are widely exploited in supramolecular chemistry[11] to prepare self-assembled polymer materials.[12−16] In optoelectronic applications, ionic self-assembly[16,17] and vapor deposition[18,19] have been used to produce thin films by utilizing noncovalent interactions. Although the influence of dye−dye intermolecular interactions on the performance of optoelectronic polymer systems have been thoroughly investigated,[20,21] significantly less effort has been directed toward the study of noncovalent interactions between the active molecules and host material. A significant exception is the work of Banach et al., in which the effect of the host environment on the electro-optic coefficient of doped polymer films has been investigated.[22] Furthermore, protonation of polyaniline-based polyblends with sulfonic acid containing dye molecules has been exploited to produce highly conducting coating materials.[23]

In this paper, we studied the influence of noncovalent interactions between dye molecules and polymer matrix on the aggregation tendency of the guest molecules. To do this, we incorporated a common azo-dye into host polymers that have different functional groups, potentially capable of different levels of interactions with the dye. The systems were studied by ultraviolet−visible (UV−Vis) and infrared (IR) spectroscopy as well as by optical second-harmonic generation. Our results show that intermolecular interactions between the polymer and the dye molecules can be enhanced by careful selection of the host polymer. This reduces considerably the aggregation tendency of the dye molecules and allows doping levels comparable to covalently linked polymer systems with no need for demanding organic synthesis.

## 2. Materials and Experimental Methods

The chemical structures of the materials used in this study are shown in Figure 2. As an active molecule, we used the common azo-dye Disperse Red 1 (DR1), well-known for its second-order nonlinear optical and photoactive properties.[4,24−26] DR1 contains several groups that can form noncovalent bonds. Most importantly, it contains a tertiary amine group, which has a lone electron pair and is expected to act as a base. As polymer hosts, we used polystyrene (PS), poly(4-vinylphenol) (PVPh), and poly(styrenesulfonic acid) (PSSA), which are structurally similar but contain different functional groups. The functional group of the polymer is expected to strongly influence the strength of its interaction with the DR1 molecules and, consequently, the aggregation tendency of the molecules. PS is a nonpolar polymer and therefore acts as

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an inert reference with no significant interactions with the polar DR1 molecules. PVPh contains a polar phenol group, which is expected to exhibit slightly enhanced, intermolecular interactions with DR1. In PSSA, the interaction between DR1 molecules and the polymer is expected to be stronger and more specific as proton transfer from the PSSA to the amine functionality of the dye is expected to lead to a polyelectrolyte−dye complex (see Figure 2).

All materials used were commercially available and were used without further purification. PSSA ($M_n = 70000$) was supplied by Polysciences Inc. as a 30 wt % water solution and was dried before use in 60 °C for 48 h. Five weight percent solutions of DR1 (Aldrich, 95%, $M = 314$ g/mol), PSSA, and PVPh (Maruzen Co.; $M_n = 1100-5200$) were prepared in dimethylformamide (DMF; Fluka, >99%), and 5 wt % solutions of DR1 and PS (Polymer Source Inc.; $M_n = 54000$) were prepared in tetrahydrofuran (THF; Fluka, >99%). The solutions were combined to obtain DR1/polymer solutions with nominal doping values varying from 10 to 80 wt %. The final solutions were stirred for 24 h, after which thin films were prepared on glass substrates by spin coating for 30 s at 5000 rpm. The residual solvent was removed by drying the films in a vacuum oven at 50 °C for at least 24 h. For comparison, we also prepared films of neat DR1 by spin-coating dilute (0.25−1 wt %) solutions of DR1 in THF and DMF. For second-harmonic measurements, we prepared samples with various thicknesses by changing the viscosity of the solution (2, 5, 10, and 15 wt % of constituents in the solution). The thicknesses of the samples were monitored with atomic force microscope and were observed to be nearly independent of DR1 doping level.

Molecular aggregates are known to have different spectroscopic properties than individual molecules. The spectral changes originate from the intermolecular excitonic coupling[27] and result in a shift of the linear absorption maximum toward shorter (H-type aggregation) or longer (J-type aggregation) wavelengths. The aggregation tendency of DR1 molecules in the three polymers was probed by unpolarized UV−Vis absorption measurements (Shimadzu UV-2501PC). The samples were oriented at normal incidence with respect to the incoming light beam and the reference spectrum was measured from a clean glass substrate. To investigate the influence of acid environment on the spectroscopic properties of the guest molecules, we also studied changes in the UV−Vis absorption spectrum (Perkin-Elmer Lambda 950) of DR1 in a dilute THF solution upon gradual addition of methanesulfonic acid (MSA).

Infrared spectroscopy was used to study the interactions between DR1 and the sulfonic acid functional group. MSA was used as a model compound for PSSA because it contains the same functional group and its infrared spectrum is less complex. A 1:1 complex of DR1 and MSA was dissolved as a 5 wt % solution in THF and drop-cast on a KBr pellet. Pure DR1 was mixed with KBr and pressed to a pellet, and MSA was analyzed between two polyethylene sheets (IR cards, Thermo). The spectra were taken in transmission mode with a Nicolet Magna 750 Fourier transform infrared (FTIR) spectrometer by averaging 64 scans at a resolution of 2 cm$^{-1}$.

The polymer samples were studied by second-harmonic generation (SHG), which is a sensitive probe of molecular adsorption at surfaces and interfaces.[28] The method is particularly suited for monitoring the adsorption of molecules such as DR1, which is polar and has a strong nonlinear response. The second-harmonic response of the samples was measured using a Q-switched flash-lamp pumped Nd:YAG laser (1064 nm, ~10 ns, ~5 mJ, 30 Hz) incident at 45° on the sample. The fundamental beam was linearly polarized in the plane of incidence and the transmitted second-harmonic signal was detected with a photomultiplier tube.

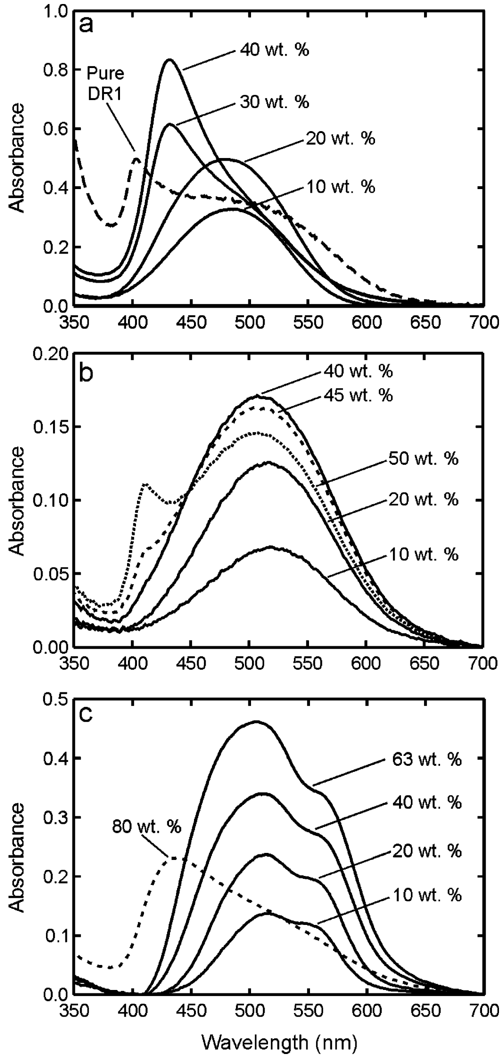

**Figure 3.** UV−Vis absorption spectra of thin films of (a) neat DR1 (normalized) and DR1 in PS, (b) DR1 in PVPh, and (c) DR1 in PSSA.

## 3. Results and Discussion

The UV−Vis spectra of the DR1/polymer films are plotted in Figure 3. As a common trend for all three polymers, the absorbance is observed to increase with increasing DR1 doping. When a certain threshold concentration is exceeded, a band due to the aggregation of DR1 appears in the lower wavelength region.[29] However, the maximum DR1 doping that can be reached without major spectral changes differs significantly for the three polymer matrixes under investigation, due to the intermolecular interactions between the dye and the polymer host. In the absence of the polymer matrix, most of the DR1 molecules form aggregates, as can be seen from the normalized spectrum of a neat DR1 film (Figure 3a).

The absorption maximum of DR1 in PS (Figure 3a) shifts from ca. 485 to 430 nm when 20 wt % doping is exceeded. This indicates that aggregation takes place already at moderate dye concentrations as expected for a conventional

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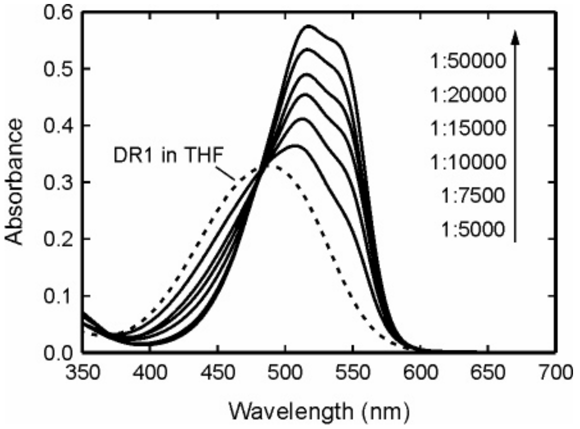

**Figure 4.** UV−Vis absorption spectrum of DR1 in THF (concentration $10^{-5}$ mol/L) with different amounts of MSA added (the labels indicate the relative number of DR1:MSA molecules).

guest−host system. In PVPh (Figure 3b), aggregation gives rise to a distinct peak at lower wavelengths (410 nm), but in this case the onset of aggregation occurs at higher (near 40 wt %) DR1 concentration. Due to the increased polarity of PVPh compared to PS, the DR1 monomer absorption band is red-shifted to ca. 515 nm. The polar functional group within the polymer chains allows the monomer concentration to be increased without aggregation, even if there is expected to be only relatively weak intermolecular interactions between the polymer and the dyes. In PSSA (Figure 3c), the absorption maximum at 515 nm is accompanied by a shoulder at ca. 550 nm even at low DR1 doping. However, no significant spectral changes are observed even at 63 wt % doping, which corresponds to the 1:1 molar ratio of DR1 in the polymer. The slight broadening of the spectrum at high dye concentrations could indicate the presence of a minor amount of dimers or higher aggregates, but could also be caused by changes in the polarity of the local environment. In any case, the observation that absorbance increases even at high dye doping levels suggests that the majority of DR1 molecules remain as monomers up to all sulfonic acid groups being occupied.

To investigate the origin of the different spectrum of DR1 in PSSA compared to the other matrixes, we measured its spectrum in a dilute ($10^{-5}$ mol/L in THF) solution environment by gradually increasing the acidity of the solution (Figure 4). We used MSA as a model compound for PSSA as they both contain the same functional group. The dilute DR1 solution has a broad absorption band with a maximum at 488 nm. Due to the low concentration, this band can be attributed to DR1 monomer absorption. The spectrum is similar as in PS and PVPh matrixes at low DR1 doping levels (see Figure 3a,b), indicating that mainly monomers are present also there. Upon addition of MSA, the spectrum gradually changes shape to reach a maximum at 518 nm and a shoulder at ca. 530 nm. This is accompanied by an increase in absorbance. In addition, an isosbestic point can be observed at ca. 480 nm, which indicates that only two spectroscopically active species are present.[30] These species correspond to protonated and unprotonated DR1 monomers, as will be demonstrated by IR spectroscopy.

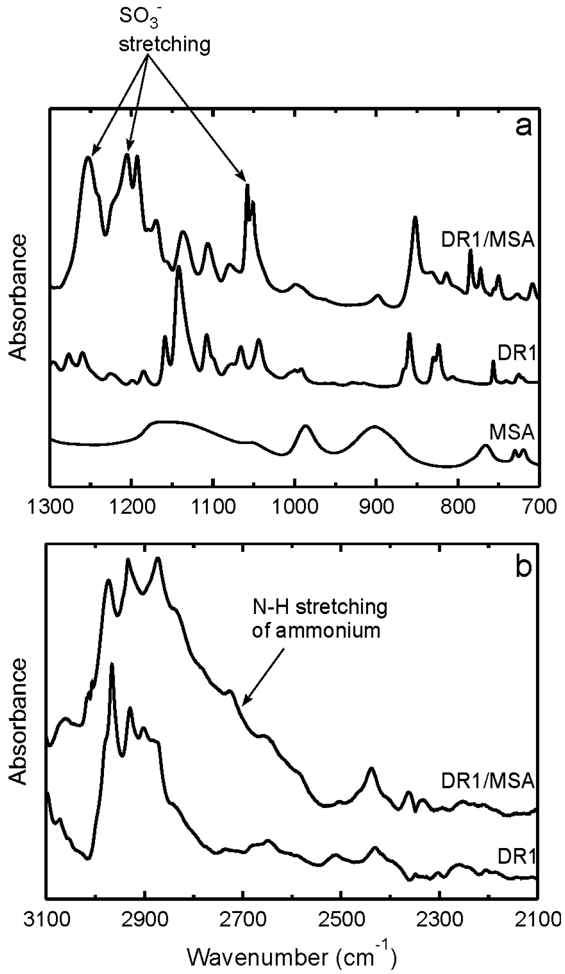

**Figure 5.** Infrared spectra of DR1, MSA, and 1:1 complex of DR1/MSA in (a) 1300−700 cm$^{-1}$ and (b) 3100−2100 cm$^{-1}$ regions.

MSA was chosen as a model compound also for studying the interaction between sulfonic acid and DR1 because the MSA spectrum is less complex than that for PSSA and thus easier to interpret. The infrared spectrum of the 1:1 DR1/MSA complex shows pronounced changes compared to the spectra of the individual constituents (Figure 5). The most obvious changes are the bands that appear at 1050, 1209, and 1250 cm$^{-1}$ (Figure 5a). The 1050 cm$^{-1}$ band is assigned to the symmetric stretching vibration of $SO_3^-$.[31] The other two bands are both assigned to the asymmetric stretching vibration of the $SO_3^-$ anions.[32] The presence of these bands indicates that the sulfonic acid group of MSA complexes with DR1 to form a sulfonate salt. Measurements in the 3100−2100 cm$^{-1}$ region (Figure 5b) reveal which functional group of DR1 is involved in the reaction. A broad band that extends from ca. 2500 to 3000 cm$^{-1}$, partially overlapping with C−H stretching vibrations, is assigned to N−H vibrations of ammonium groups.[33] This suggests protonation of the tertiary amine functionality of DR1 by sulfonic acid. Infrared spectroscopy confirms that the features in the UV−Vis spectra of DR1/MSA (Figure 4) and DR1/PSSA (Figure 3c) can be assigned to protonation of DR1.

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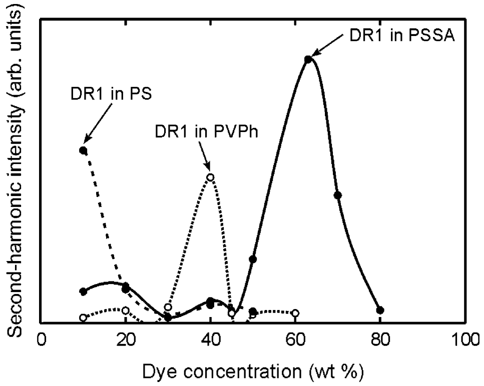

**Figure 6.** Second-harmonic signals from thin films of DR1 in PS, PVPh, and PSSA at different dye concentrations. The signal arises from DR1 molecules adsorbed at the glass substrate and can be used to probe the doping capacity of the polymer.

Complementary information on the complex formation between DR1 and the polymers was obtained by measuring the second-harmonic response of the samples. The SHG signal was observed to be independent of the film thickness (data not shown), indicating that the signal arises from the interface regions only. Possible contributions from the two interfaces (air−film and film−substrate) were addressed separately by comparing the SHG response of thick polymer films for two different sample orientations (substrate first or sample first; data not shown). The high absorbance (∼2) of the films at the second-harmonic wavelength ensured that only the signal from the back interface reached the detector. These measurements indicate that SHG signal originates from the film−substrate interface.

The second-harmonic response of the samples was measured as a function of dye concentration (Figure 6). In all three polymer matrixes, the signal was found to peak at a certain dye concentration. While the peak intensity was approximately the same in each matrix, its location varied strongly depending on the matrix used. In PS, the peak occurs below 10 wt % concentration, whereas in PVPh and PSSA, the peaks occur at ca. 40 and ca. 60 wt %, respectively. The peak intensity was rather high, but comparable to the signals from films of pure DR1 spin-coated from 0.25 wt % DMF solution. On the other hand, a film prepared by drop-casting from 5 wt % DR1 solution showed no second-harmonic signal.

The peaks in the second-harmonic response of the samples can be understood by considering the interactions of the dye molecules with the polymer matrix. At low doping levels, essentially all molecules are isotropically distributed in the polymer matrix and give rise to no second-harmonic signal. However, the polymer host can only attach a certain amount of dye molecules. Beyond the "threshold concentration", which differs for each polymer, the excess dye molecules are free to migrate to the film−substrate interface. Due to the interactions between the dyes and the substrate, the molecules at the interface show polar alignment,[34] which leads to a SHG signal. For even higher concentrations, DR1 molecules aggregate and the signal is suppressed. This interpretation correlates well with the UV−Vis absorption data. The concentration for the maximum second-harmonic signal can therefore be used as a measure of the monomer doping capacity of the polymer, indirectly verifying that the 1:1 molar ratio of DR1 can be attached to PSSA.

## 4. Conclusions

We have shown that when intermolecular interactions between a polymer host and guest dye molecules are controlled, the tendency of the molecules to aggregate can be reduced. With use of polar polymers, the monomer concentration can be increased compared to conventional guest−host systems. Furthermore, with use of ionic interaction between a basic dye and an acidic polymer, a 1:1 molar ratio of dye molecules can be attached to the polymer simply by mixing the constituents. We have also demonstrated a method based on second-harmonic generation that can be used to probe the amount of dyes that can be attached to the polymer. It yields results that correlate well with UV−Vis absorption measurements, which are more traditionally used for this purpose. Our results obtained with model compounds can be considered as a proof of concept, and we expect the method to be applicable to a variety of systems with complementary interaction groups.

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