

# Quantum dots in a metallopolymer host: studies of composites of polyferrocenes and CdSe nanocrystals

Paul W. Cyr,<sup>a,b</sup> Marian Tzolov,<sup>b,†</sup> Margaret A. Hines,<sup>a,b</sup> Ian Manners,<sup>\*a</sup> Edward H. Sargent<sup>\*b</sup> and Gregory D. Scholes<sup>\*a</sup>

<sup>a</sup>Department of Chemistry, University of Toronto, Toronto, Ontario, M5S 3H6, Canada. E-mail: imanners@chem.utoronto.ca; gscholes@chem.utoronto.ca

<sup>b</sup>Department of Electrical and Computer Engineering, University of Toronto, Toronto, Ontario, M5S 3G4, Canada. E-mail: ted.sargent@utoronto.ca

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The photoluminescence (PL) of composite materials based on ferrocene-based organometallic polymers and CdSe nanocrystals (nc-CdSe) has been investigated in solution and in thin films. The polymers studied, poly(ferrocenylmethylphenylsilane) (PFMPS), poly(ferrocenylphenylphosphine) (PFP), and poly(ferrocenylphenylphosphine sulfide) (PFP-S), all quench the PL of the nc-CdSe. In solution, the relative quenching effects are solvent dependent, and are in the order PFMPS < PFP in toluene but in the order PFP < PFP-S < PFMPS in THF. Stern–Volmer analysis is consistent with coordination of PFP to the nc-CdSe. In the thin films, the relative quenching strength of the polymers is PFMPS ~ PFP-S < PFP. Photoinduced absorption spectroscopy was employed to study the nature of the PL quenching.

## Introduction

Semiconductor nanocrystalline materials (such as ‘quantum dots’) are of great current interest.<sup>1,2</sup> In the nanometer size regime, intermediate between the molecular and bulk properties of the material, quantum confinement effects are observed which allow the tuning of the optoelectronic properties of a material of the same chemical composition simply by changing the particle size. Recent advances in the controlled synthesis of such nanocrystallites<sup>2,3</sup> have allowed extensive study of the properties of these materials. Promising potential applications of semiconductor nanocrystals are envisioned in such fields as nonlinear optics, light emitting materials, and optoelectronics. Incorporation of these materials into, for example, electroluminescent or photovoltaic devices, has been hindered by the unfavourable mechanical properties of the nanocrystals, and their lack of easy processing.

One approach toward device fabrication has been to incorporate the nanocrystals into polymer matrices in order to take advantage of the ease of processing characteristic of many polymers. The preparation and characterization of polymer/nanocrystal composite materials has thus been an area of continuing interest. A number of (mostly  $\pi$ -conjugated, organic) polymers have been studied in these materials: for example soluble PPV derivatives,<sup>4–8</sup> polypyrrole,<sup>9</sup> and polyaniline.<sup>10</sup> Strong quenching of the photoluminescence of  $\pi$ -conjugated polymers in the presence of nanocrystalline semiconductors often occurs due to rapid charge transfer,<sup>4,7</sup> and this charge separation property led to keen interest in these composites for possible device applications. The successful demonstration of electroluminescent<sup>10–13</sup> and photovoltaic<sup>4,14,15</sup> devices has thus been achieved employing such hybrid materials. A new approach for preparing such composites employed block copolymers in which phosphine functional groups were present on one of the blocks, enabling direct chemical bonding to the nanocrystal surface.<sup>11,16,17</sup> While composites of nanocrystals and organic polymers have

been and continue to be investigated, composite materials involving metal-containing polymers are unexplored. Metal-containing polymers possess properties which complement those available with conventional organic macromolecules, and the possibility of additional opportunities to control the conductive, photophysical, electrical and other properties of polymeric materials continues to drive research in the field.<sup>18,19</sup>

Polyferrocenylsilanes (PFSs) and related polyferrocene-based materials represent a well-established class of organometallic polymers with interesting properties such as redox activity which offer promise for a range of applications.<sup>18,20,21</sup> These polymers are easily synthesized and possess good processability. In addition, upon partial oxidation, PFS-type polymers become semiconducting. For example, doping of PFS with electron acceptors leads to a conductive polymer with resistivities in the semiconductor range ( $10^4$  to  $10^8 \Omega \text{ cm}$ ).<sup>22–24</sup> The doped polymer is a hole transporting material, with the conduction occurring by a proposed hole-hopping mechanism.<sup>22–24</sup> The use of polyferrocene materials as host matrices for quantum dots has appealing potential due to the intrinsic properties of the ferrocene group. For example, photoinduced electron transfer (PET) from ferrocene to electron acceptors (such as quinones and fullerenes) is well established.<sup>25–27</sup> The photoluminescence of CdS nanocrystals has been shown to be either quenched or enhanced in the presence of different ferrocenyl derivatives, the enhancement occurring when a dimethylamino-substituted ferrocene was coordinated to the nanocrystal surface *via* amine ligation.<sup>28</sup> Electrochemical modification of electronic effects of metal nanoparticles by ferrocenyl-derivative capping ligands has also been demonstrated.<sup>29</sup> In addition, it has been shown that ferrocene and ferrocenium can exert different effects on, *e.g.*, the luminescence of organic luminophores.<sup>30</sup> Thus, the possibility of changing the optoelectronic properties of a polyferrocene/nanocrystal composite material *via* choice of functional groups on the polymer and/or by the redox-switching of the ferrocene/ferrocenium couple is attractive.

We have examined the properties of composite materials of metal-containing polymers (specifically polyferrocenes) and CdSe nanocrystals (hereafter abbreviated nc-CdSe). In this

<sup>†</sup>Current address: Division of Engineering, Brown University, Providence, RI, 02912, USA.

paper we describe the results of our initial investigations into the properties of this new class (organometallic polymer-inorganic nanocrystal) of composite material.

## Experimental

### Materials

Poly(ferrocenylmethylphenylsilane) (PFMPS) was prepared by transition-metal catalyzed polymerization ( $M_w = 240\,000$ , PDI = 2.53),<sup>31</sup> poly(ferrocenylphenylphosphine) (PFP) was prepared by anionic polymerization ( $M_w = 17\,000$ , PDI = 1.02),<sup>32</sup> and poly(ferrocenylphenylphosphine sulfide) (PFP-S) was prepared *via* reaction of PFP with sulfur ( $M_w = 19\,200$ , PDI = 1.02).<sup>32</sup> Polystyrene and poly(methyl methacrylate) (PMMA) were obtained from Aldrich. The CdSe nanocrystals were prepared *via* pyrolytic reaction of  $\text{Cd}(\text{CH}_3)_2$  and Se in a mixture of trioctylphosphine (TOP) and trioctylphosphine oxide (TOPO), and were isolated *via* iterative size-selective precipitation.<sup>33</sup>

### Apparatus

Absorption and transmission spectra were collected on a Varian Cary 500 UV/Vis/NIR spectrophotometer. Photoluminescence (PL) spectra were obtained using a Photon Technologies International fluorometer. Solution samples were measured in 1 mm quartz cells with normal incidence excitation. PL of films was collected using front-face excitation at an angle of  $20^\circ$ . Quantum yields (QY) of composite films were obtained relative to a drop-coated nc-CdSe film, by integration of the peak area of the PL signal, and estimated as  $\text{QY} = C \cdot [\text{PL}/(1 - T - R)]$  where  $C = [(1 - T_{\text{ref}} - R_{\text{ref}})/\text{PL}_{\text{ref}}]$ ,  $T$  is the transmission, and  $R$  the reflectance, at the excitation wavelength (375 nm). Dynamic light scattering (DLS) measurements were performed as described previously.<sup>34</sup>

### Sample preparation

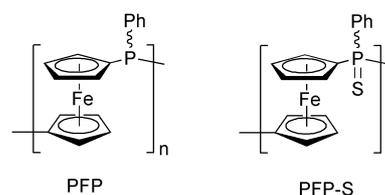
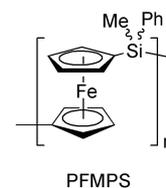
Solution samples were prepared in air. Films were prepared either by spin-coating or drop-coating (as indicated) on cleaned glass substrates.

### Sequestering experiments

In a typical experiment to determine sequestering of nc-CdSe by a polymer, 10 mg of PFMPS was dissolved in 2 mL of toluene under  $\text{N}_2$ . To this was added 36  $\mu\text{L}$  of a nc-CdSe solution in toluene (this corresponds to 2 mg of nanocrystals). The mixture was stirred for 2 h at which point the solvent was removed *in vacuo*. Washing the resulting glassy residue with hexanes (10 mL) did not remove any measureable (by UV-Vis) quantity of CdSe material. The residue was then dried *in vacuo*, redissolved in 2 mL of toluene and precipitated into 10 mL of hexanes. The resulting polymeric residue was filtered and washed with hexanes. The solvent was removed from the filtrate and the residue was dissolved in 1 mL of hexanes. The concentration of nc-CdSe in this solution was then estimated from a Beer's law plot of the nanocrystal batch used.

### Photoinduced absorption measurements

The photomodulation experiment was performed by using the 442 nm line of a He-Cd laser, mechanically chopped at 387 Hz. The probe beam from a tungsten-halogen lamp was analyzed by a single grating monochromator (TRIAx 320) coupled with a Si photodiode. The synchronous detection was performed by a lock-in amplifier (SR 830). The presented spectra show the in-phase signal after phase rotation at  $140^\circ$ , which yields a nearly zero quadrature component.



Scheme 1

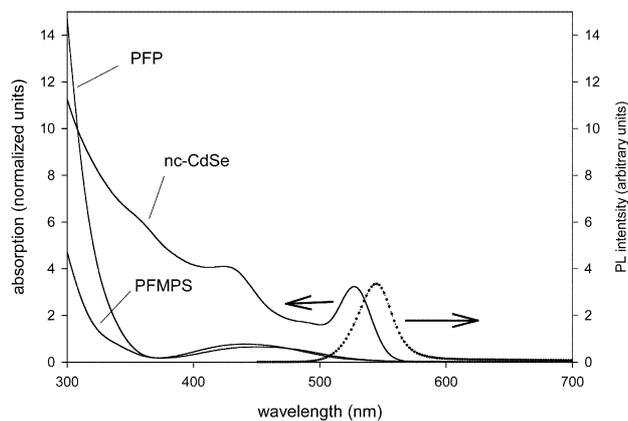
## Results and discussion

In order to examine the effects of polyferrocenes on the nc-CdSe, we chose to examine three polymers: poly(ferrocenylmethylphenylsilane) (PFMPS), poly(ferrocenylphenylphosphine) (PFP), and poly(ferrocenylphenylphosphine sulfide) (PFP-S), the structures of which are shown in Scheme 1. All three polymers are amorphous, thus the issue of crystallinity in the films is avoided. The silicon-bridged material PFMPS is a prototypical PFS derivative, while PFP and PFP-S possess phosphine and phosphine sulfide groups, respectively, which offer the potential to coordinate to the nc-CdSe surface. We wished to examine the potential of PFP and PFP-S to interact with the nanocrystal in a manner similar to that observed for organic polymers possessing phosphine-bearing pendant groups,<sup>16,17</sup> with the added potential advantage of the nc-CdSe being directly bound to the polymer backbone.

### Solution studies

In this work, composites of TOPO-capped CdSe nanocrystals (TOPO = trioctylphosphine oxide) with polyferrocene polymers containing silane and phosphine spacer groups were investigated in toluene and THF solutions. No marked differences were observed in the absorption spectra of solutions of these composites in either solvent, the resulting spectra being merely the additive combination of the separate components' spectra. However, solvent dependent differences were observed in the photoluminescence (PL) properties. Quenching of the PL of the nc-CdSe in the presence of the ferrocene polymers occurs, though the extent is strongly dependent on the polymer and the solvent. Ferrocene is a well-known quencher of PL in molecular systems. In polymeric systems, quenching of pyrene end groups in side-chain ferrocene-containing polymers has been studied.<sup>35</sup> While quenching of PL by ferrocene is common, in some cases PL may be enhanced.<sup>30</sup> The effects of different ferrocenyl derivatives on the PL of CdS nanocrystals, stabilized by inverse micelles (rather than TOPO), have also been investigated, and quenching or enhancement of the PL was observed depending on the nature of the ferrocene derivative.<sup>28</sup>

The TOPO-capped CdSe nanocrystals used in this work were prepared by the method of Murray *et al.*<sup>33</sup> The absorption feature of these nanocrystals at 530 nm in toluene solution indicates that they have a diameter of approximately 3.4 nm.<sup>33</sup> The PL maximum of these nanocrystals in toluene solution is centred at 545 nm. The absorption and PL spectra of the nc-CdSe in toluene solution are shown in Fig. 1. For comparison, the absorption spectra of PFMPS and PFP in toluene are also shown. The absorption and PL spectra are qualitatively similar in THF solution, and the PFP-S absorption spectrum is nearly the same as that of PFP. To ensure that the vast majority of light was exciting the nc-CdSe and not being absorbed by the

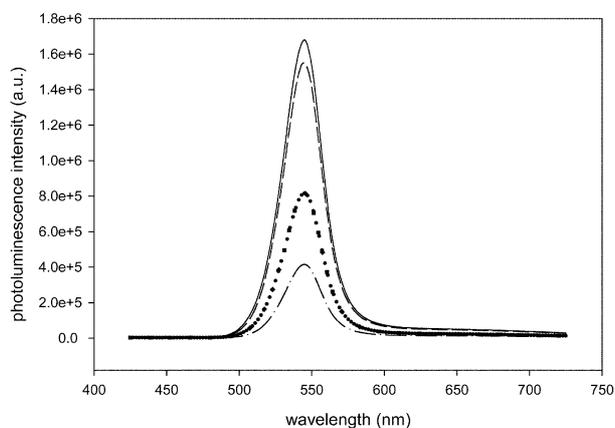


**Fig. 1** Absorption spectra of PFMPS, PFP, and nc-CdSe (solid lines) and photoluminescence spectrum of nc-CdSe (dotted line) in toluene solution (excitation at 375 nm).

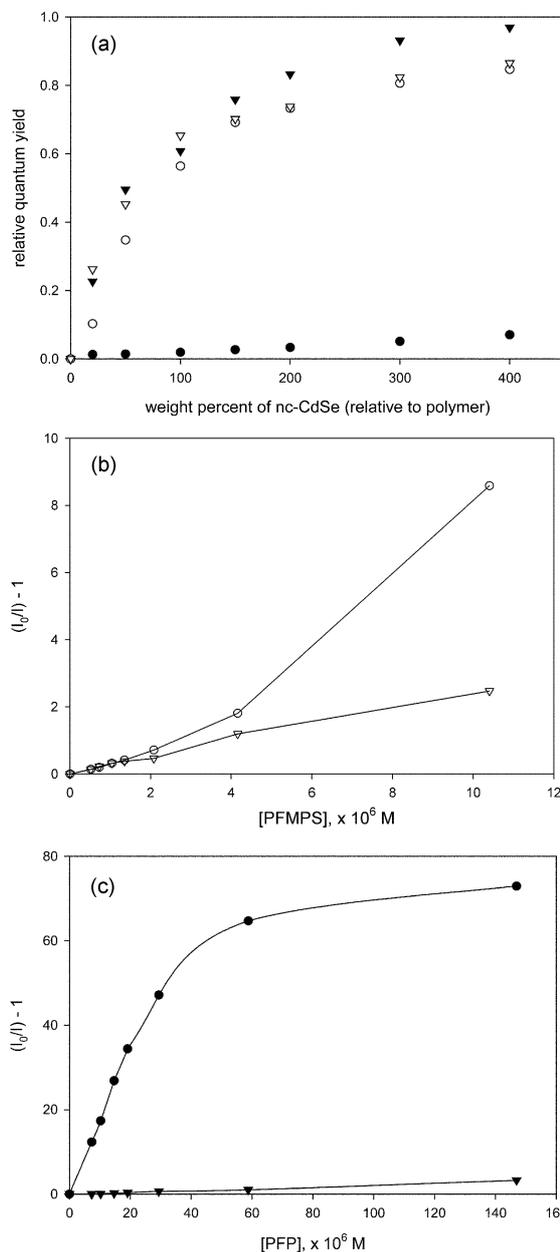
polymer, we chose the excitation wavelength 375 nm. This corresponds to a local minimum in the polymer absorption spectra, but is well within the absorption region for the nanocrystals (Fig. 1).

We initially investigated the effects of different additives on the PL intensity of nc-CdSe solutions (Fig. 2).<sup>36</sup> A slight decrease in the PL intensity of a toluene solution of nc-CdSe occurs in the presence of ferrocene, though the effect is weak (we estimate that in our experiment the ferrocene was present in a molar excess on the order of  $10^3$  relative to the nc-CdSe). However, in the presence of PFMPS, a substantial decline in PL intensity is observed. The phosphorus-bridged polymer PFP leads to an even greater quenching of the PL of the nc-CdSe. We were also interested in studying the sulfurized version of PFP, PFP-S, however this polymer has poor solubility in toluene. We therefore studied the effects of the polymers in THF solution (a better solvent for PFP-S) as well, and found a somewhat unexpected result. While PFMPS was found to quench the PL of the nc-CdSe in THF solution, in the presence of PFP the PL is only mildly quenched, and PFP-S was found to have an intermediate quenching effect. Thus, in toluene solution the relative quenching effects are PFMPS < PFP, while in THF the ordering is PFP < PFP-S < PFMPS.

To explore these phenomena further, we studied the solvent and polymer concentration dependence on the PL intensity of nc-CdSe in the presence of PFMPS and PFP. Representative results are shown in Fig. 3a. The difference in molecular



**Fig. 2** Effect of different additives on the PL of nc-CdSe in toluene solution. All solutions had the same concentration of nc-CdSe, and were 50 wt% nanocrystal relative to additive: no additive (solid line), ferrocene (dashed line), PFMPS (dotted line) and PFP (dash-dotted line).



**Fig. 3** (a) Plot of relative quantum yield of the PL of nc-CdSe in the presence of PFMPS and PFP in solution. In toluene, with PFP (filled circles) and PFMPS (open circles) and in THF, with PFP (filled triangles) and PFMPS (open triangles). (b) Stern-Volmer plot for quenching of nc-CdSe PL by PFMPS in toluene (open circles) and THF (open triangles) solution. (c) Stern-Volmer plot for quenching of nc-CdSe PL by PFP in toluene (filled circles) and THF (filled triangles) solution.

weights of PFMPS and PFP ( $M_w = 240\ 000$  and  $17\ 000$ , respectively) and the uncertainty in the molar mass of nc-CdSe must be considered. For this reason, we have compared the relative quantum yields of the polymers as a function of the weight percent of nanocrystal present relative to polymer (Fig. 3a). The quenching induced by PFMPS follows nearly the same dependence in toluene and THF (open circles and triangles, respectively, in Fig. 3a), with increased quenching observed with increased polymer concentration. However, in toluene solution PFP is strongly quenching at even very low concentrations (filled circles, Fig. 3a), while in THF the quenching effects (filled triangles, Fig. 3a) are qualitatively similar to those of PFMPS.

Stern-Volmer plots for the PFMPS and PFP systems (Figs. 3b and c, respectively) clearly show the solvent

dependence of the quenching effects. The data for PFMPs (Fig. 3b) show that in THF solution, a near linear dependence of the PL intensity on the concentration of polymer is observed, consistent with a diffusion controlled system. Similarly, for the PFP system in THF solution a linear dependence is observed (Fig. 3c). However, in toluene solution, the dependence of the PL intensity on the polymer concentration shows marked differences for PFMPs and PFP. For the PFMPs system, the Stern–Volmer plot shows an upward curvature at higher PFMPs concentrations (Fig. 3b), consistent with both dynamic (diffusion) and static quenching mechanisms being operative. In classical molecular systems, static quenching is generally due to the formation of a complex between the fluorophore and quencher in the ground state. Thus, in toluene solution, there is presumably some precipitation of PFMPs onto the nc-CdSe particles, leading to a “complex” which quenches the nc-CdSe PL in a non-diffusion controlled manner; and the extent of formation of this complex increases with the concentration of PFMPs. The Stern–Volmer plot for PFP in toluene (Fig. 3c) shows a dramatic difference from that of PFMPs. In this case, a downward curvature of the plot at higher PFP concentrations is observed. The system shows “saturation” effects, and at high concentrations of polymer, the effect of added PFP on the nc-CdSe PL intensity becomes minimal. This would be consistent with a system in which the static component (or “complex”) is at high concentration in the ground state. It is important to note the differences in the concentration scales (a result of the different molecular weights and solubilities) of the two polymers studied here. The PFP system was investigated over a much larger polymer chain concentration range than PFMPs. Thus, “saturation” of the PFMPs system was not observed in toluene solution in the concentration range available, though this may occur at sufficiently high concentrations. Thus, we propose that the quenching behaviour of PFP and PFMPs is qualitatively similar, and that this behaviour is solvent dependent. In THF solution, over the polymer concentration ranges studied, the quenching appears to be dynamic, while in toluene a combination of static and dynamic processes is occurring. The relative strengths of these effects are different for each polymer however. PFP has the potential to form a dative bond onto the nc-CdSe surface, and therefore to possibly show a stronger interaction with the nanocrystal when the static mechanism is operative.

The extent of the uptake of nc-CdSe of the polymers was investigated by performing sequestering experiments. These involved mixing the nanocrystals and polymer in solution, removing the solvent and then extraction of the residue to remove any nc-CdSe not intimately associated with the polymer. The sequestering experiments suggested that the observed solvent dependence of the PL is related to the solubility of the polymers in the solvent. In toluene, the amount of nc-CdSe sequestered (using 20 wt% nc-CdSe relative to polymer) is 80 and 100% for PFMPs and PFP, respectively. However, in THF the retention of nc-CdSe is lower, with corresponding values of 33 and 80% under similar conditions.

A possible explanation for the higher quenching and sequestering behaviour for PFP in toluene compared to THF is the greater solubility of the polymer in the latter solvent. Thus, the poorer solubility of PFP in toluene might result in precipitation of the polymer on to the colloidal nc-CdSe surfaces. However, dynamic light scattering (DLS) experiments on PFP solutions in toluene and THF showed no significant difference in the hydrodynamic radius in these solvents ( $R_h \sim 2.5$  nm), which indicated that the solvent–polymer segment interactions are similar in both solvents. A likely alternative possibility is that the PFP may coordinate to the nc-CdSe more effectively in toluene compared to in THF, a more coordinating solvent, and this is supported by the sequestering experiments and the Stern–Volmer data. Sequestering experiments have previously been used to provide evidence for the stabilization of

the nc-CdSe surface by tertiary phosphine functional groups in diblock copolymers (*via* displacement of TOPO ligands to give direct bonding of the polymer to the nanocrystal), and high retention of the nanocrystals was reported for these polymers relative to those which did not contain the phosphine groups.<sup>16</sup> Dative bonding between PFP and nc-CdSe is possible,<sup>37</sup> though the steric bulk of the bis(ferrocenyl)phenylphosphine moiety may hinder a strong interaction. Sequestration of the nc-CdSe is much greater in the PFP case compared to PFMPs regardless of solvent, and suggests that such coordination is present.

Both PFP and PFMPs show enhanced quenching relative to the corresponding concentration of molecular ferrocene. This indicates that quenching by the polymers is a cooperative phenomenon, presumably due to the multitude of weak interactions possible per macromolecule. In THF, the coordinating ability of PFP may be mitigated due to a higher solvent reorganization energy relative to the toluene system. In such a system with only a dynamic, diffusion controlled quenching, PFMPs appears to be a more effective quencher than PFP. However, in toluene solution, precipitation of the polymer on to the nc-CdSe particles may be more effective for PFP due to its coordinative ability, and in such a system with static and dynamic components, PFP demonstrates stronger quenching.

### Studies of thin films

We also examined the properties of the composite materials as thin films. Spin casting solutions of the PFMPs or PFP/nc-CdSe mixtures gave films of good optical quality. PFP-S gave poorer quality films which resulted in significant scattering effects. Photoluminescence of the nc-CdSe was observed in the composite films, though the intensities were low. Relative PL yields were obtained, and we compared the PL of nc-CdSe in polystyrene (chosen as an inert matrix), PFMPs, PFP, and PFP-S host matrices with films cast from toluene and THF solution. The results are summarized in Table 1.

The relative quantum yield measurements do not account for scattering and waveguiding effects, and thus comparisons are only qualitative. Though comparison of PL yields for films cast from different solvents are difficult, the trends within one series (*i.e.* cast from same solvent) are reasonably representative. The general trend observed is that the polyferrocene polymers strongly quench the PL of the nc-CdSe, as seen from their low relative quantum yields compared to the non-quenching<sup>36</sup> polystyrene. This suggests that there is a significant interaction between the nc-CdSe and the ferrocene containing polymers, as indicated by the solution PL measurements. The PL quenching by PFMPs is less than that of PFP in the films, regardless of the solvent used to cast the films. This indicates that in the solid state, the quenching interaction with the nc-CdSe is stronger for PFP than for PFMPs, and might be explained by the stronger coordinating ability of the former material. In the films, the static quenching is dominant, and supports the quenching effects observed in toluene solution as discussed above. Interestingly, the quenching of PFP-S in films cast from THF was weaker than for the PFP films, though in THF

**Table 1** Relative quantum yields (%) of polymer/nc-CdSe composite thin films

| Solvent for casting | Polymer matrix |       |     |                  |
|---------------------|----------------|-------|-----|------------------|
|                     | PS             | PFMPs | PFP | PFP-S            |
| toluene             | 54             | 9     | 5   | n/a <sup>a</sup> |
| THF                 | 64             | 24    | 10  | 22               |

<sup>a</sup>Value could not be obtained due to low solubility of PFP-S in toluene.

solution it was found that the PFP-S was a stronger quencher than PFP. This could be due to a weaker coordinating ability of the phosphine sulfide (PFP-S) compared to the phosphine (PFP) and lower solubility than PFP in THF. Due to the poor quality of the PFP-S films however, a more detailed comparison is difficult.

### Photoinduced absorption measurements

In order to investigate the possible charge transfer between the nc-CdSe and polymer in the composite, and to further probe the differences between PFMPS and PFP, we studied the composite films by means of photoinduced absorption (PIA) measurements. One way to demonstrate the charge transfer between the components of the composite material is to detect the existence of photoexcited states. Charge transfer between nc-CdSe and polymer matrices has been investigated using  $\pi$ -conjugated polymers such as poly(*p*-phenylene vinylene) (PPV)<sup>4-8</sup> and polyfluorene<sup>38</sup> derivatives. An essential step in these investigations was the initial removal of the surface-capping TOPO ligands (by replacement with pyridine), leading to a significant lowering of the PL of the polymer. As mentioned earlier, the potential to realize effective charge transfer between the two components of the composite material without special treatment, for example by using PFP to possibly displace the TOPO ligands on the nc-CdSe, was one motivation for this work.

In the case of the conjugated polymer/nc-CdSe composites, charge separation results in the presence of a charge on the polymer chains leading to the appearance of long-lived polaron states which can be detected by the photomodulation technique.<sup>7,37</sup> In the case of the polyferrocenes studied in this work, long lived photoexcited states were not detected for the neutral polymers. In oxidized PFS thin films, such states have been detected, and we will report on these results elsewhere.<sup>39</sup> However, the presence of separated charges can also be detected in the nanocrystals. Several authors have shown the presence of deep trap emission originating from the presence of surface states of nc-CdSe, and attributed this as being due to Se dangling bonds.<sup>40,41</sup> It is expected that after photoexcitation the occupancy of these states changes, and depending on their lifetime one can expect to detect this change in a photomodulation experiment. This was indeed the case in the samples we studied. Fig. 4 shows the induced absorption by using 442 nm pump light. A sharp feature is present near the absorption edge, similar to that reported by Ginger *et al.*,<sup>42</sup> its shape depends on the modulation frequency and its origin has complex character, including bleaching of the ground state and thermal modulation effects. We have used the intensity of this

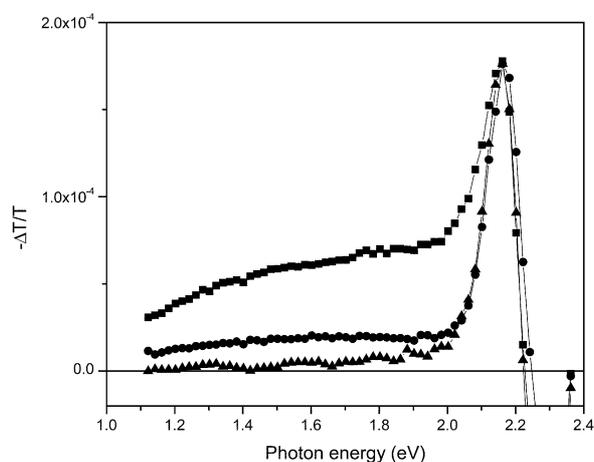


Fig. 4 Photomodulation spectra of composite films of CdSe nanoparticles with a matrix of PMMA (squares), PFMPS (circles), or PFP (triangles) (excitation at 442 nm (2.80 eV)).

feature as a reference for quantitative comparison of the signal at lower energy between the different samples. However, the tendency is the same without this normalization procedure. For nc-CdSe embedded in PMMA a broad featureless induced absorption band is present at energies below 2 eV and it decreases in intensity below 1.4 eV. We associate this band with the transition of holes trapped at Se dangling bond surface states back to the valence band states.<sup>40,41</sup> The onset of this band is below 1 eV, a reasonable value for the energy distance between the Se surface state and the valence band edge. Fig. 4 shows that the intensity of the photoinduced absorption band at  $h\nu < 2$  eV decreases in the samples having PFMPS as the matrix and is undetectable in the film having PFP as a matrix. Obviously, the lifetime of the photogenerated surface states in the sample having PFP as a matrix is very low, *i.e.* the recombination rate is very high. This result correlates with the observed decrease of the relative band edge PL observed in the samples with PFP (see Table 1).

The correlation between the decreased photoinduced absorption signal and the decreased PL in the sample having PFP as a matrix can be interpreted using two scenarios. The exchange of the TOPO capping groups by the coordinating polymer chains would lead to better coupling between the electronic systems of the polymer and the nc-CdSe, resulting in easier charge transfer/separation between the two components. This results in the decrease in the PL as well as in the occupation of the surface states. Alternatively, as the nature of the surface capping groups influences some of the electronic processes in the nanocrystals,<sup>43</sup> the lifetime of holes trapped at the surface states decreases after exchange of the TOPO capping groups with the PFP polymer. As has been shown previously,<sup>41</sup> the population of the surface states seems to be the dominant decay pathway for band edge emission on short time scales. Therefore, increasing the recombination of the trapped holes will lead to increased decay of the exciton PL as well as in low intensity of the photoinduced absorption. As PFMPS does not possess any coordinating groups which could conceivably displace the TOPO ligands from the nc-CdSe surface, yet significant quenching of the PL is observed both in solution and in films, we suggest that the observed PL quenching in these composites is mainly due to charge transfer, rather than simply surface state lifetime changes. However, in the PFP case both processes may be responsible for the observed decrease in PL.

In solution and in films, PIA was detected for the nc-CdSe, both in the presence and absence of PFMPS and PFP. However, no reproducible, discernible trend could be established regarding the intensity of these PIA bands. In solution, deposition of material on the cuvette walls is observed during the course of the experiments, indicating that the stability of the solutions under intense laser illumination is not high. We also found that the intensity dependences of the samples all give a slope of the PIA signal *vs.* intensity plot of greater than 1. This superlinear dependence can occur in the case that the trap states for the electrons and holes change upon illumination level such that one type changes to a recombination center. Thus, the lifetimes of the opposite charge carrier increase and the occupancy of the corresponding trap states will increase. A corresponding increase in the PIA signal is therefore also detected. However, confirming this hypothesis with the frequency dependence is not possible as a distribution of lifetimes is observed.

### Quenching mechanism

The quenching effects observed are due to the ferrocene centers in the polymers. We also observe that the polymers exhibit a higher quenching per monomer unit than ferrocene itself. Quenching of molecular PL systems by ferrocene is known, and can occur *via* either electron transfer, energy transfer, or a

combination of both.<sup>30</sup> For energy (Förster) transfer to occur, the absorption spectrum of the polymer must overlap with the PL spectrum of the nc-CdSe. As is clear in Fig. 1, there is little overlap in these systems. Furthermore, larger nanocrystals (with PL maximum at 570 nm, 2.17 eV) were also examined, which have even less overlap of the appropriate spectra, and similarly large quenching effects were observed. This would imply that if this mechanism was operative, then the quenching must be extremely effective given the small cross-section. Ferrocene can accept energy from excited states higher than 21 800 cm<sup>-1</sup> (or <460 nm, >2.7 eV) if the singlet excited state is the acceptor, and from excited states higher than 15 000 cm<sup>-1</sup> (<670 nm, >1.86 eV) if the triplet state is the acceptor.<sup>30</sup> This would indicate that the triplet state of the polymers must be involved if energy transfer is the mechanism of the quenching. This case requires singlet-to-triplet energy transfer from the quantum dot to the polymer, which significantly lowers the probability for the energy transfer. Thus, electron transfer is more likely to be the mechanism for quenching.

Previous work investigating the quenching of the PL of  $\pi$ -conjugated polymers in the presence of nc-CdSe found that only energy transfer could occur (with appropriate spectral overlap) when TOPO caps were present on the nanocrystals,<sup>4,7</sup> and that replacement of the TOPO groups with pyridine led to more effective electron transfer as the *ca.* 11 Å alkyl chain barrier provided by the TOPO is presumed to pose a significant hindrance to effective charge transfer.<sup>4,7</sup> However, it should be noted that injection of electrons into TOPO capped nc-CdSe, both in solution with chemical reductants and on electrodes, has been previously demonstrated, and the resultant n-type nc-CdSe were very stable.<sup>44-46</sup> Thus “tunneling” of an electron through the TOPO caps is possible. In the case that charge transfer occurs, there should be discernable signals in the PIA, arising from the trap states as discussed above, or in the NIR region (at lower energy than measurable in our study) due to the induced infrared absorption band that occurs upon reduction of the nc-CdSe by injection of electrons in to the lowest quantum-confined state of the conduction band.<sup>44,46</sup> With the present empirical evidence, although electron transfer quenching appears more likely, we cannot say definitively which mechanism is operating, or if both make a contribution.

## Summary and future work

We have studied the potential of a class of polyferrocene materials as host matrices for CdSe nanocrystals. The polymers cause quenching of the band edge photoluminescence of the quantum dots, both in solution and in films. A solvent dependence of the relative quenching effects of the polymers was found in solution studies, with PFMPS < PFP in toluene, but PFP < PFP-S < PFMPS in THF. In films, PFP, with a phosphorus spacer, has a stronger quenching effect on the nc-CdSe than the silicon-containing polymer PFMPS. Photomodulation studies show that the polymers also affect the occupancy of the surface states on the nanocrystals, and suggest a higher degree of interaction of the PFP with the electronic system of the nanocrystals. The clarification of the detailed scheme of this interaction requires further investigation. However, given that the nature of the ferrocene-containing polymer is clearly demonstrated to affect the PL of the nc-CdSe, these composite materials may prove useful in optoelectronics. The potential ability to tune the properties of the nc-CdSe *via* controlled oxidation of a PFS derivative is attractive, and could be used in electrochromics or optical switching in which the optical response of the nanocrystal is altered by the redox chemistry of the polymer.

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