

The Role of Intermolecular Interactions in Solid State Fluorescent Conjugated Polymer Chemosensors

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Received: 25 January 2011 / Accepted: 14 October 2011 / Published online: 26 October 2011
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Abstract A functionalized fluorescent conjugated polymer, tolylterpyridine poly(p-phenyleneethynylene-thienyleneethynylene (ttp-PPETE), was designed and synthesized to detect trace amounts of toxic transition metal pollutants in ground water. Photophysical studies in tetrahydrofuran (THF) successfully demonstrated this polymer as a selective and sensitive chemosensor for Ni^{2+} and Co^{2+} in aqueous solution. Solid state composites of these chemosensors have now been prepared which can be modified to provide for inexpensive and portable field based chemical detection. A solid composite of ttp-PPETE, blended with poly (methyl methacrylate) shows UV–vis absorption and fluorescence emission spectra which are red-shifted when compared to solution phase spectra, suggesting an increase in conjugation in the solid state. An additional absorption peak, not present in solution, is also observed in the solid state. The presence of this new peak provides evidence of interacting FCP chains in the solid state. Concentration dependent experiments were done on the solid composite showing red-shifted emission peaks accompanied by a significant reduction in the fluorescent quantum yield. These observations are consistent with the formation of aggregated polymer species in the solid state. Intermolecular interactions of this type can be manipulated in the design of sensitive and selective solid state fluorescent conjugated polymer sensors.

Keywords Chemosensors · Aggregation · Solid state · Intermolecular interactions

Introduction

The use of fluorescent conjugated polymers (FCPs) as effective chemical sensors (chemosensors) for toxic transition metal contaminants has significantly grown in recent years. The interest in FCPs as sensors, stem from the ease with which their fluorescence can be detected and measured [1]. They have also been reported to have extremely high sensitivity (ppb) for analytes in solution. Their enhanced sensitivity was first reported by Swager and coworkers when a cyclophane receptor-based FCP chemosensor, sensitive to paraquat (PQ^{2+}), demonstrated increased sensitivity of up to 65 fold as compared to their small molecule counterpart [2, 3]. The enhanced sensitivity of these systems has been attributed to the molecular wire effect which involves the delocalization of photo-induced excitons over long distances within the conjugated polymer backbone, to low energy trap sites [4, 5].

Numerous studies have explored a wide variety of receptor/analyte pairs having varying degrees of selectivity, sensitivity and response. Our research group has designed, synthesized and characterized a poly (p-phenyleneethynylene-thienyleneethynylene (PPETE) fluorescent conjugated polymer, loaded with a pendant tolylterpyridine (ttp) receptor which is highly sensitive to minute concentrations of Ni^{2+} and Co^{2+} cations [3, 6]. Photophysical studies of this ttp-PPETE FCP chemosensor, **2** were conducted in tetrahydrofuran (THF) solution and resulted in the development of an energy transfer based quenching model to describe the enhanced sensitivity observed [3, 7].

Application of the FCP chemosensor strategy in modern devices requires transformation from solution phase preparation to the solid state. In order to address the need for more portable field based chemical sensing devices required for environmental monitoring, solid state studies are

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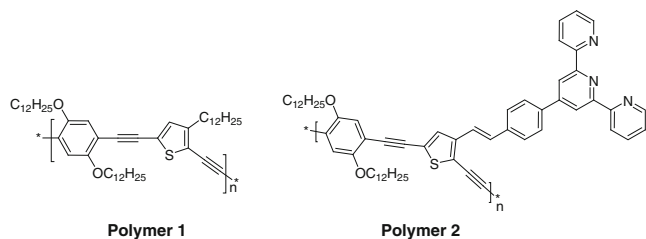


Fig. 1 Structures of Model PPETE (**Polymer 1**) and ttp-PPETE (**Polymer 2**)

particularly important [8, 9]. Several research groups have developed and studied varying types of solid state sensing devices fabricated when the FCP's is either spin-coated, dip-coated or electrospun as a solid thin film [10–12]. In most cases the resulting thin films are used as gas sensors for small molecules such as O₂, CO, TNT etc. While there are overwhelming examples in the literature of thin films and nano-structured materials being used as chemical sensors [13–16], there are very few examples fluorescent polymers and blends consisting of FCPs and other host matrices.

Herein we report the preparation of binary polymer composites of a non-functionalized FCP, model PPETE, **1** and its related functionalized FCP chemosensor **2** (Fig. 1), each blended with poly(methylmethacrylate), PMMA, an inert host polymer. The result is a free standing polymer blend of solid materials that are easily analyzed, with the potential of being incorporated into hand held devices. We also report the photophysical studies conducted on these solid composites and show that their photophysical properties are a direct consequence of intermolecular interactions among polymer chains.

Experimental

Polymer Synthesis Polymer **1** was synthesized using a palladium-catalyzed cross-coupling reaction of monomers 1,4-diethynyl-2,5-didodecyloxybenzene and 2,5-dibromo-3-dodecylthiophene (yield 88%) as shown in Scheme 1. 1,4-diethynyl-2,5-didodecyloxybenzene was synthesized as described in literature [17], while 2,5-dibromo-3-dodecylthiophene was purchased from Sigma Aldrich. Polymer **2** was synthesized under similar reaction conditions with mono-

mers 1,4-diethynyl-2,5-didodecyloxybenzene and 4'-{4-[2-(2,5-Dibromothiophen-3-yl)-vinyl]phenyl}-2,2':6',2''-terpyridine (Scheme 2) which is synthesized according to literature [7, 18].

Materials All materials were purchased from Aldrich and used as received unless otherwise noted. Tetrahydrofuran (THF), dimethylformamide (DMF), chloroform (CHCl₃) and de-ionized water were used as solvents.

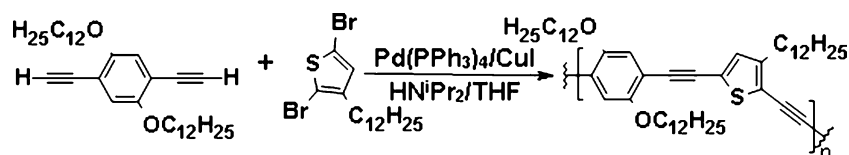
Composite Preparation Fluorescent conjugated polymer blends of **1** and **2** were prepared using the following procedure. Approximately 2.5 g PMMA (M_w 996,000 g mol⁻¹) was dissolved in 10 mL THF and then ~2 mg FCP was separately dissolved in 5 mL THF. The two solutions were subsequently combined and stirred overnight. The highly colored, viscous mixture was poured into a glass Petri dish to dry at ambient temperature for at least 24 h before use (Fig. 2). The thickness of the solid composite was approximately 0.7 mm and the concentration of the fluorescent conjugated polymer in the blend was 0.0799 wt.%.

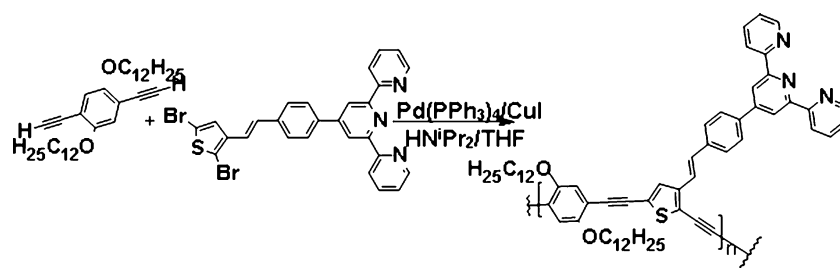
Instrumentation ¹H and ¹³C NMR for polymers **1** and **2** were recorded on a Bruker AM-360 spectrometer. UV–vis absorbance experiments were performed on a Hewlett-Packard HP 5382A diode array UV-visible spectrophotometer and accompanying software. Fluorescence emission spectra were taken on a Fluorat® -02-Panorama instrument of wavelength range 210 to 840 nm. Fluorescence decay kinetics was determined by time-correlated single photon counting (TCSPC) using a diode laser described elsewhere in literature [3]. The fluorescence decay data were analyzed by non-linear least-squares fits of individual traces with the program OriginPro 7.5. The fluorescence quantum yield for the composite blends were determined relative to 0.01 mol % 9,10-diphenylanthracene in PMMA having a fluorescence quantum yield of 83%.

Results and Discussion

The polymer chemosensors, **1** and **2**, are both soluble in THF solution. This provides a basis for the preparation of

Scheme 1 Synthesis of model polymer PPETE (1)



Scheme 2 Synthesis of chemo-sensor polymer ttp-PPETE (2)

thin polymer films by evaporation. In the experiments described here, polymer composites were prepared at room temperature by dissolving the chemsensor or model polymer in THF and mixing that with a solution of PMMA. The mixed solutions were clear and could be spin coated or dip coated onto substrates to form free standing thin films suitable for photophysical studies and evaluation of chemosensor behavior.

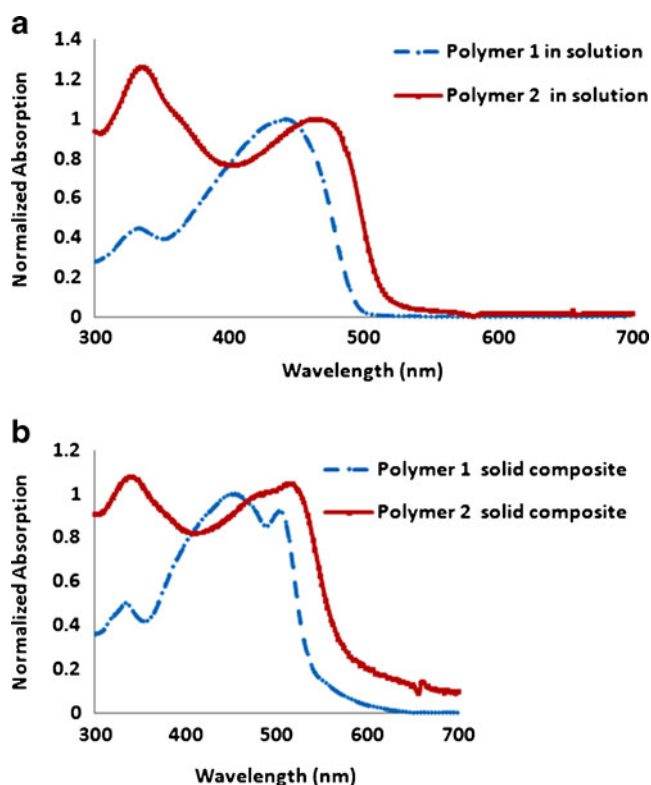
Photophysics in Solid State: Absorption and Emission The UV–vis absorption properties of polymers **1** and **2** in solution and as composites in the solid state are shown in Figs. 3 and 4 and then summarized in Table 1 below. From the absorption spectra, two primary absorption peaks were observed for **1** and **2** in the solution phase. The lower energy peaks at 442 nm and 460 nm in **1** and **2** respectively has previously been assigned to π - π^* transitions in the conjugated polymer backbone [3, 6]. The higher energy peak at \sim 330 nm can be assigned to an n - π^* transition centered on the pendant terpyridyl ligand. The low energy peak of chemosensor polymer **2** is red shifted relative to that of the model FCP polymer **1** consistent with the extended conjugation of the terpyridyl receptor.

In the solid state composites, Fig. 3b, the absorption peaks were found to be broadened. This has been observed previously in other solid state conjugated polymer systems [19, 20]. While the low energy peak of **2** in the solid matrix is red shifted to that of polymer **1**, we found that the π - π^* transition of both composites are red shifted relative to those in solution [21, 22]. A red shifted absorbance peak is consistent with extended conjugation for the FCPs in the

**Fig. 2** Solid state composite of polymer **1** (left) and polymer **2** (right) in PMMA

solid state relative to solution, and possibly a result of increased inter-polymer interactions. A new absorbance band also appeared to the red of the main π - π^* absorbance band at approximately 510 nm in both solid composites. This feature is more distinct for model polymer **1**, than the chemosensor, but is clearly present in both cases. The presence of this new band suggests possible aggregate formation may be occurring even at these low concentrations in the solid state blend [22, 23].

The fluorescence emission spectrum for each FCP was obtained in solution following excitation at their respective excitation maximum and is shown in Fig. 4. The emission band of the chemosensor polymer **2** is 22 nm red-shifted relative to that of the model FCP **1** in THF solution at room temperature. The emission profiles are similar to each other with one primary emission band in the visible region and a

**Fig. 3** Normalized absorption curve of **a** polymers **1** and **2** in THF solution, **b** polymers **1** and **2** in PMMA matrix (solid state)

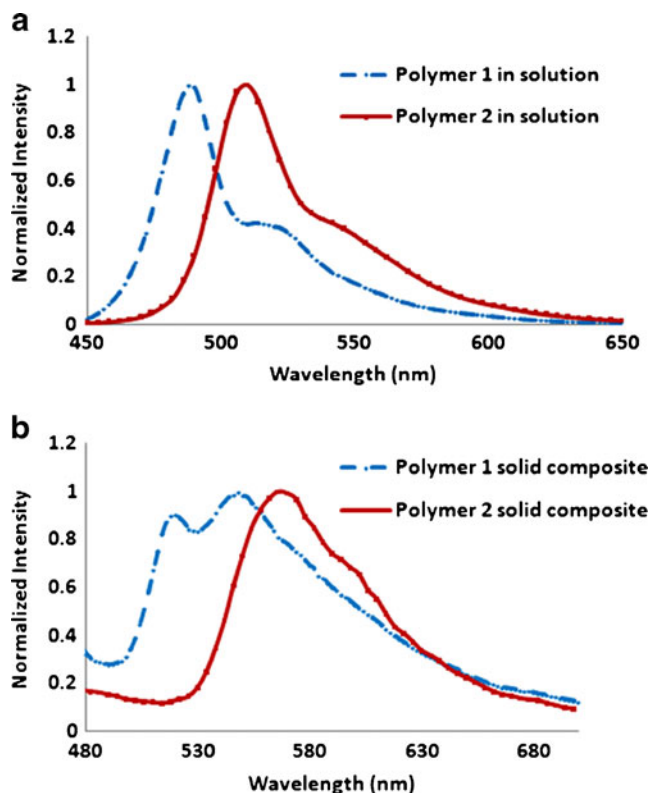


Fig. 4 Normalized emission curve of composites of **c** polymers **1** and **2** in THF solution, **d** polymers **1** and **2** in PMMA matrix (solid state)

weaker shoulder at longer wavelengths. The FCP in PMMA matrix showed a red shifted emission compared to those in solution. For solid composite **2**, the emission maximum occurred at 566 nm while composite **1** showed a different emission profile, having emission maxima at 556 nm and 522 nm as shown in Fig. 4b. The source of this higher energy peak is most likely due to vibrational fine structure resulting from the restricted environment of the polymer composite. Alternatively, it could be due to some heterogeneity in the composite as discussed further below.

Emission Lifetime Emission lifetimes were evaluated by single-photon counting following excitation at 520 nm. The lifetime data for both solid composites and solution phase systems are shown in Table 1. The fluorescence decays of the FCPs are all best fit by a single exponential, first order decay model. Single exponential decay indicates there is

only one fluorescent component present in each sample which would tend to rule out heterogeneity as the source of the additional emission bands in Fig. 3 above. It was observed that the fluorescent polymer composites have shorter decay times than those observed for the FCP's in solution. The fluorescence lifetime of the FCP chemosensor **2** is 473 ps in solution compared to 109 ps in the PMMA matrix. Similarly, the model FCP lifetime decreased from 565 ps in solution to 141 ns in the solid state. In both media the emission lifetime of the FCP sensor **2** is less than that of the model polymer **1**, an observation consistent with a smaller energy gap. These results were not consistent with previous studies of polymer photophysics in the solid state that demonstrate increased fluorescence lifetimes as a result of decreased non-radiative decay rates in restricted media. The observed decrease in emission lifetime would be consistent with self-quenching of the FCP's leading to a new non-radiative decay process. This result would be additional support for aggregation occurring in these systems even at dilute concentrations.

Intermolecular Interaction in the Solid State To determine if solvent choice affects the photophysics of our polymer in the solid state, composites were prepared as described in the “**Experimental**” section using THF and CHCl₃, solvents in which polymers **1** and **2** were also soluble. The results show that the emission intensity of composites cast from THF is higher than that of composites prepared from chloroform, of similar concentration. This observation is supported by several studies conducted by Schwartz and coworkers showing strong evidence that processing conditions such as solvent choice, polymer concentration and film thickness, can greatly affect the photophysics of the FCP incorporated in solid state films and composites [22, 24, 25]. These studies have shown that solvents such as chlorobenzene (CB) and tetrahydrofuran (THF) can affect both the configuration and degree of aggregation of the polymer strands of FCPs when cast as thin films or composites (Fig. 5).

The emission peaks for the composite prepared in THF were also blue shifted relative to those prepared from chloroform. Blue shifted emission peaks are consistent with reduced aggregation and self-quenching. Previous work by Carrie et. al. show that a co-solvent system of chloroform

Table 1 Summary of absorption, fluorescence emission and lifetime data

Polymer	Absorbance, λ_{\max} (nm)	Fluorescence, λ_{\max} (nm)	Lifetime, τ /ps (%) (R^2)
Model PPETE (1) in solution	334, 442	488 , 514(sh)	565±10 (100) (0.9968)
Model PPETE (1) in PMMA matrix	334, 450	522, 556	141±4 (100)(0.9981)
ttp-PPETE (2) in solution	334, 460	510 , 550(sh)	473±6 (100) (0.9981)
ttp-PPETE (2) in PMMA matrix	334, 518	566	109±9 (100)(0.9692)

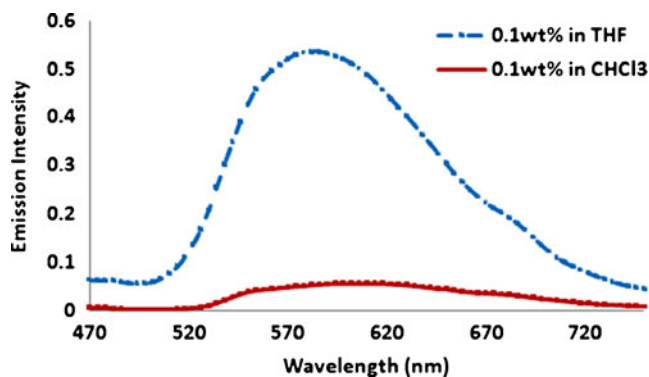


Fig. 5 Polymer 2 composite (0.1 wt.%) in THF and CHCl₃

and methanol resulted in aggregate-based self-quenching in their FCP system. This would be consistent with our observation that chloroform resulted in aggregation in our system [26]. It is generally believed that a “good solvent” such as THF tends to limit aggregation of polymer strands which would explain why the fluorescence quantum yield is greater in THF (0.011) than in CHCl₃ (0.002) [24].

Emission Excitation Experiment An excitation experiment was used to determine the excited state responsible for the emission peak observed. Polymer composites (0.1 wt.%) of 1 and 2 were excited at 560 nm, 600 nm, and 640 nm. These wavelengths were selected from three points along the tail of the emission spectrum, an area from which aggregate species are said to emit [24]. The absorption wavelength range was monitored to see which transitions were responsible for the observed emission. The excitation spectra for the polymer 1 composite, shown in Fig. 4a, have peaks at 380 nm and 426 nm with a slight shoulder at ~450 nm. Three major peaks at 426 nm, 466 nm and 528 nm were observed for the polymer 2 composite. It should be noted that three absorbance peaks were also observed for these composites which is not surprising as it is typical to observe identical excitation and absorbance spectra. By exciting the solid composites at the selected wavelengths, we were able to reproduce the new aggregated band, highlighted by the asterisk in Fig. 6a and b, which are also present in the absorption of solid composite 1 and 2 (shown in Fig. 3b). These results are consistent with the idea that aggregates originate in the ground state and can be directly excited.

Concentration Dependence of Emission Concentration dependent experiment was performed to further highlight aggregation within the solid matrices. This was done by varying the concentration of polymer 2 in the PMMA host material. The fluorescence emission data was collected at 470 nm and the normalized spectra is shown in Fig. 7. The fluorescence spectra show red shifted peaks with increased

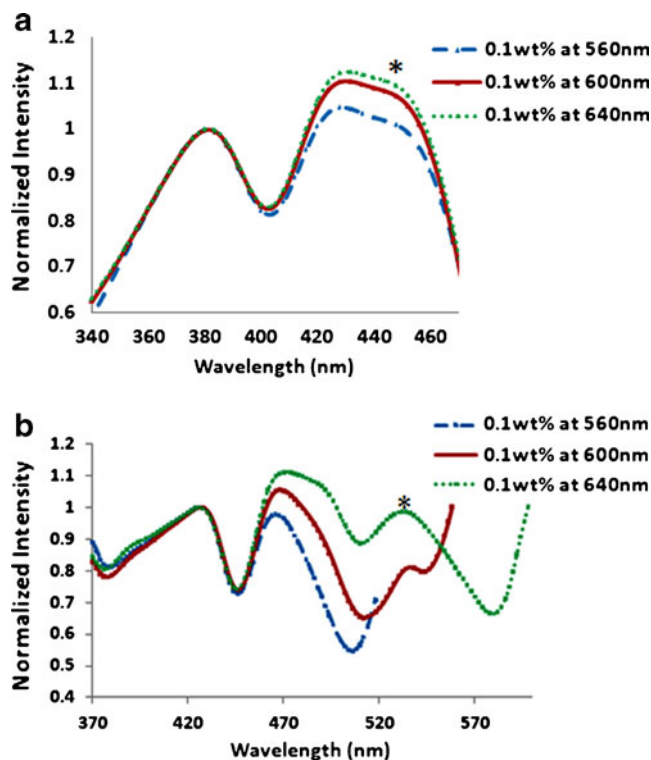


Fig. 6 Excitation spectra of 0.1 wt.% concentration of polymer 1 and polymer 2 in PMMA matrix

polymer 2 concentration, which is consistent with an increase in conjugation length of polymer 2 in the solid matrix. The red shift is also consistent with the presence of aggregated polymer strands [27]. We also took into consideration that the red shift may have been due to re-absorption of the fluorescence emission since this is commonly observed in concentrated systems. Evidence of re-absorption usually comes in the form of relatively small Stoke’s shifts, narrowing of the emission band as well as significant changes in the fluorescent lifetime of the fluorophore [28]. Further analysis of our data showed the opposite effect in all three cases. As we increased the concentration of the fluorophore

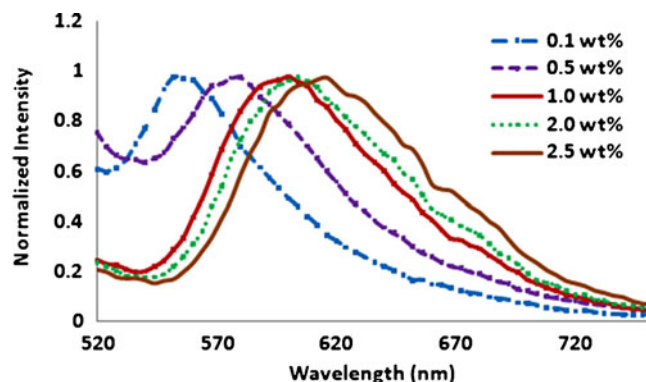


Fig. 7 Normalized fluorescence emission curves of variable concentrations of polymer 2 in PMMA matrix

in the PMMA composite we observed large Stoke's shift of up to 90 nm. The band-width of the emission bands remained relatively the same, and there was no significant change in the fluorescent lifetime.

The dependence of fluorescence quantum yield (Φ) on concentrations of **2** was similarly investigated. All the data collected in this investigation, showed a decrease in emission intensity with increased polymer **2** concentration. This indicates that concentration (self) quenching has occurred in the solid state composite. Concentration quenching which occurs in concentrated systems, as opposed to dilute ones, was supported by a decreased quantum yield with increased polymer **2** concentration within the matrix as shown in Fig. 8. We attribute the decreased fluorescence quantum yield to the formation of aggregates [29, 30] which increase the pathways the absorbed photon has to travel, within the solid matrix, before emission.

Emission Quenching in PMMA The sensitivity of our solid state sensor system to nickel was examined using polymer **2** composite. Fluorescence quenching studies show a 20% reduction in the initial fluorescence of the fluorophore upon exposure to increasing concentrations of nickel ion, as shown in Fig. 9. The solid state chemosensor is not as sensitive to the ionic quencher as it is in solution [3], an observation supported by the vast majority of recent reports on the sensitivity of solid state FCP chemosensors [5, 9]. One proposed reason for the decreased sensitivity in the solid state is the restricted mobility of analyte and/or excitation energy throughout the solid state sensor. Decreased sensitivity has also been linked to the presence of interchain species formed when polymer chains interact at the molecular level in solid state systems [31, 32].

From these results, we conclude that the 7% quenching observed is possibly due to the binding of Ni^{2+} ions by surface receptors only. Thus the quencher may not have full access to the terpyridyl receptors due to the hydrophobicity of the PMMA which makes it difficult for the Ni^{2+} ions to

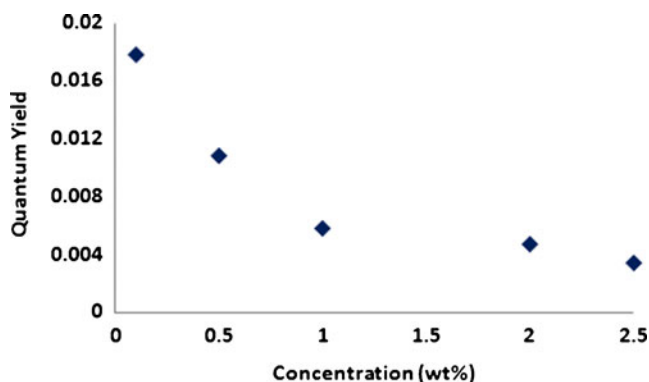


Fig. 8 Fluorescence quantum yield dependence curve of variable concentrations of polymer **2** in PMMA matrix

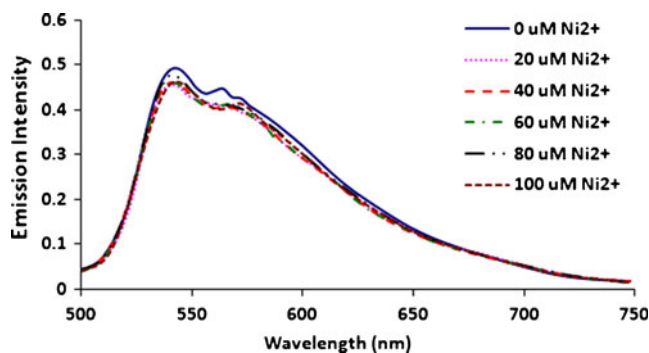


Fig. 9 Fluorescence quenching of polymer **2** in PMMA at 470 nm excitation

diffuse throughout the matrix. Therefore we designed a new quenching experiment to investigate whether receptors of the sensor are indeed embedded within the PMMA matrix. In this experiment, composites of polymer **1** in PMMA were prepared. Various concentrations of nickel ions were incorporated within each composite. The emission quenching results are shown in Fig. 10.

According to these results, up to 83% quenching is possible in solid composite material prepared in this way. The fluorescence intensity of the chemosensor was not completely quenched as indicated by the 17% residual fluorescence, a possible consequence of a portion of the sensor being inaccessible to quenchers. This result supports our hypothesis that the majority of receptor sites are embedded within the composite, with just a few found on the surface.

We also observed that the emission of the last two spectra of Fig. 10 was significantly blue shifted relative to the others. This is as a result of the three orders of magnitude increase in concentration of the Ni^{2+} ions in those two solid composites. We speculate the blue shift could be a consequence of an over-saturation of the receptors of the chemosensor by the Ni^{2+} ions, which resulted in conformational changes that decreased the conjugation length of the FCP in the solid system.

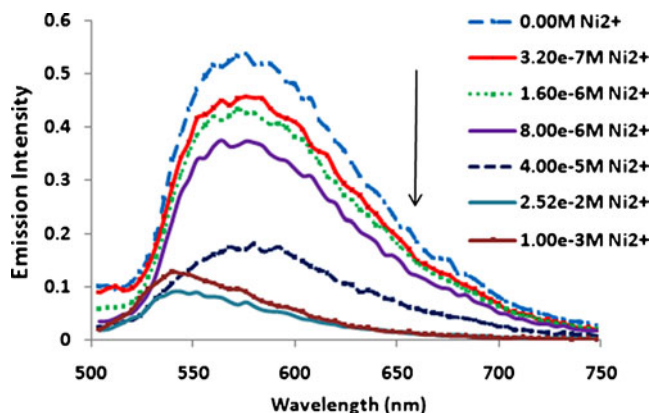


Fig. 10 Emission quenching of polymer **2** when variable $[\text{Ni}^{2+}]$ is incorporated in the PMMA composite

We also determined from this study that the solid state chemosensor is sensitive to 16 nM concentration of nickel, indicating that if the receptors were available to the analyte our solid sensor would be able to detect concentrations of nickel less than that allowable in ground water according to current EPA standards. In the future our goal is to focus on increasing the sensitivity of our solid state sensor by improving the mobility of analyte within the sensor system and decreasing inter-polymer interaction for a more efficient chemosensor.

Conclusion We have successfully fabricated a solid state sensor from our FCP and PMMA, to address the increasing need for field-based, solid state sensing devices. In transitioning from solution to the solid state we observed that the optical properties of the fluorescent conjugated PPETEs in the solid state differ from those in solution. The photophysical properties of the solid composites with PMMA depend both on the choice of solvent and the polymer concentration. Intermolecular interaction among polymer strands was clearly evident in the solid state resulting in red-shifted absorbance and fluorescence emission peaks, as well as reduced quantum yields and lifetimes. The decreased sensitivity observed has compromised the efficiency of our solid state sensor, a condition which must be remedied for improved sensor performance. Future work is therefore geared towards minimizing inter-polymer interactions providing for a more sensitive and efficient solid state chemosensor.

Acknowledgement Financial support for this work is gratefully acknowledged from National Institute of Health Grant No. IR15ES10106-01 and the Research Foundation at State University of New York.

References

1. Lakowicz JR (2006) In Principles of fluorescence spectroscopy. Springer Science+Business Media

2. Yang JS, Swager TM (1998) J Am Chem Soc 120:11864–11873
3. Murphy CB, Zhang Y, Troxler T, Ferry V, Martin JJ, Jones WE (2004) J Phys Chem B 108:1537–1543
4. Swager T (1998) Acc Chem Res 31:201–207
5. Zhao D, Swager TM (2005) Macromolecules 38:9377–9384
6. Jiang B, Zhang Y, Sahay S, Chatterjee S, Jones WE Jr (1999) Proc SPIE-Int Soc Opt Eng 212
7. Fan LJ, Zhang Y, Murphy C, Angell S, Parker M, Flynn B, Jones WE Jr (2009) Coord Chem Rev 253:410–422
8. Yang JS, Swager TM (1998) J Am Chem Soc 120:5321–5322
9. Wilson DM (2001) IEEE Sensor J 1:256–274
10. Gao L (1998) Chem Mater 10:2481–2489
11. Wang X, Kim Y, Drew C, Ku C, Kumar J, Samuelson LA (2004) Nano Letters 4:331–334
12. Rose A, Zu Z, Madigan CF, Swager TM, Bulov V (2005) Nature (London) 434:876–879
13. Janata J, Josowicz M (2003) Nat Mater 2:19–24
14. Liu H, Kameoka J, Czaplewski DA, Craighead HG (2004) Nano Letters 4:671–675
15. Kolmakov A, Moskovit M (2004) Annu Rev Mater Res 34:151–180
16. Wan QH, Li QH, Chen YJ, Wang TH, He XL, Li JP, Lin CL (2004) Appl Phys Lett 84:3654–3656
17. Swager TM, Gil CJ, Wrighton MS (1995) J Phys Chem 99:4886–4893
18. Zhang YY (2002) Macromolecules 35:630–636
19. Zheng M (2001) Mater Res Bull 36:853–859
20. O'Connell MJ, Bachilo SM, Huffman CB, Moore VC (2002) Science (New York, NY) 297:593–596
21. Amrutha SR, Jayakannan M (2008) J Phys Chem B 112:1119–1129
22. Schwartz BJ (2003) Annu Rev Phys Chem 54:141–172
23. Grell MM (1998) Acta Polymerica 49:439–444
24. Nguyen TQ, Martini IB, Liu J, Schwartz BJ (2000) J Phys Chem B 104:237–255
25. Nguyen TQ, Doan V, Schwartz BJ (1999) J Chem Phys 110:4068
26. Halkyard CE, Rampey ME, Kloppenburg L, Studer-Martinez SL, Bunz UHF (1998) Macromolecules 31:8655–8659
27. Ding L, Egbe DAM, Karasz FE (2004) Macromolecules 37:6124–6131
28. Christmann DDR (1981) Anal Chem (Wash) 53:276–280
29. Collison CJ, Tremanekarn V, Oldham WJ, Hsu WJ, Rothberg LJ (2001) Synth Met 119:515
30. Collison CJ, Rothberg LJ, Tremanekarn V, Li Y (2001) Macromolecules 34:2346–2352
31. Cornil J, Heeger AJ, Bredas JL (1997) Chem Phys Lett 272:463–470
32. Moon JH, Swager TM (2002) Macromolecules 35:6086–6089