Design and Synthesis of Fluorescence "Turn-on" Chemosensors Based on Photoinduced Electron Transfer in Conjugated Polymers

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ABSTRACT: A new approach to fluorescence "turn-on" chemosensors based on a photoinduced electron transfer (PET) strategy involving conjugated polymers has been developed. Two new conjugated polymers dea-PPETE and tmeda-PPETE were synthesized and characterized. These two polymers use diethylamino and *N*,*N*,*N*′-trimethylethylenediamino as receptors, respectively, on a poly[*p*-(phenyleneethylene)-*alt*-(thienyleneethynylene)] (PPETE) fluorescent conjugated polymer backbone. The polymers were found to be relatively weakly emissive at $\lambda_{max} \sim 488$ nm with quantum yields of 0.11 and 0.09, respectively, at room temperature in THF solution. Initial investigations show that the tmeda-PPETE selectively detects some metal cations by an observed increase in fluoresence. In particular, Hg^{2+} in aqueous solution causes the fluorescence of tmeda-PPETE to increase by a factor of 2.7 at less than micromolar concentrations. The photophysical results are consistent with a PET mechanism for fluorescence quenching, which is removed upon binding of the analyte.

Introduction

Fluorescent chemosensors are gaining increased attention due to their high sensitivity and ease of measurement.[1] In particular, conjugated polymer chemosensors have recently been used with great success for the detection of a range of analytes from biomolecules to explosives.[2] Fluorescent conjugated polymers have several advantages over small molecule sensors due to enhancements associated with electronic communication between receptors along the polymer backbone,[2] processability, and ease of structural modification. The vast majority of the detection methods employed involve a "turn-off" effect in the presence of analytes.[2−4] A more sensitive detection method would involve design of a "turn-on" fluorescent sensor. While the "turn-on" approach has been demonstrated for a number of small molecule sensors, we find only one literature example reporting conjugated polymers as fluorescence "turn-on"chemsensor.[5]

Photoinduced electron transfer (PET) sensors are an important family of chemosensors,[6] and small molecule fluorescence turn-on sensors have been developed and studied on the basis of the PET mechanism.[7] In such systems, the receptors usually contain a relatively high-energy nonbonding electron pair. In the absence of analytes, this electron pair quenches the fluorescence of the fluorophore by rapid intramolecular electron transfer from the receptor to the excited fluorophore, as shown in Figure 1. When this electron pair is coordinated to Lewis acid cations in solution, the HOMO of the receptor is lowered. This decreases the driving force for the PET process and can turn on the fluorescence of the chromophore. One literature example[8] of PET in polymer chemosensors involves incorporation of dyes into the polymer backbones via copolymerization with other monomers. The polymer backbones were used simply as inert scaffolds to position the fluorophores and receptors. To our knowledge, there is only one literature report[9] using the conjugated polymer backbone directly as the fluorophore for the PET process. However, this report did not extend this methodology to sensors.

By combining the transducer and receptor components on the molecular wire polymer backbone, a more versatile sensory system can be prepared. Previous conjugated polymer-based fluorescent sensors have taken advantage of the rapid mobility of the exciton along the polymer backbone to yield enhanced sensitivity. This mechanism will not provide a sensitivity enhancement in a PET-based fluorescence turn-on sensor. However, it has previously been proposed that the support of small molecule sensors on polymer substrates will yield more processable and useable systems.[8,10] Further, we have recently shown that the changes in the conjugated polymer backbone can be used to enhance the selectivity of the system.[4b] Thus, we anticipate both processing- and selectivity-based enhancements as a result of combining the PET receptors with the conjugated polymer. Further, loading variations on the conjugated polymer can also provide for a variable fluorescence through changes in conjugation.

On the basis of our previous work using poly[*p*-(phenyleneethylene)-*alt*-(thienyleneethynylene)] (PPETE) as a conjugated polymer backone and functionalizing it with different receptors,[4] we have designed a strategy to synthesize a series of fluorescence "turn-on" polymer sensors with the PPETE polymer backbone as the fluorophore and different amino groups as the receptors. With this synthetic strategy we seek to develop an addressable family of conjugated polymer PET sensors that respond to different analytes by the "turn-on" mechanism. Here we report the successful preparation and characterization of the first two polymers synthesized by this method, dea-PPETE and tmeda-PPETE. These polymers use *N*,*N*-diethylamino and *N*,*N*,*N*′-trimethylethylenediamino groups as receptors, respectively (Scheme 1). The sensing responses of each polymer toward several different cations were examined in order to evaluate the potential applications of these materials as PET sensors.

Experimental Section

Materials. All materials were purchased from Aldrich and used as received unless otherwise noted. The compounds 1,4-

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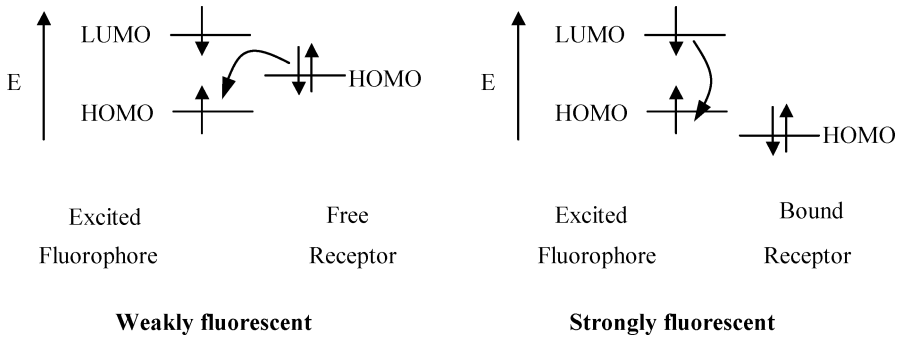
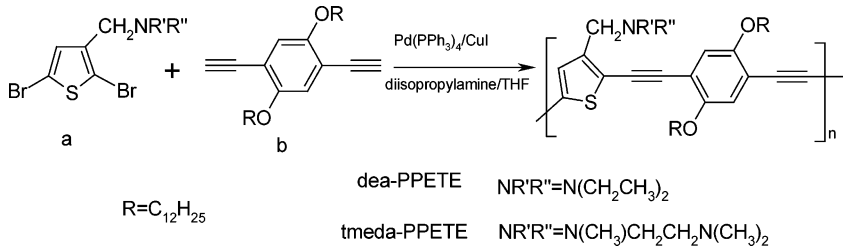


Figure 1. Orbital energy diagram for fluorescent PET sensors before and after binding cation.

Scheme 1. Synthesis of Conjugated Polymers Containing Amino Receptors



diethyl-2,5-didodecyloxybenzene[11] and 3-bromomethylthiophene[12] were synthesized according to the literature methods. Satisfactory NMR characterization of all stable intermediates was observed in each case.

General Methods. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM-360 spectrometer. Elemental analyses were performed by QTI Inc. in New Jersey. IR spectra were obtained on a FT-IR Bruker Equinox55 spectrometer at a nominal resolution of 2 cm^{-1}. The samples were prepared by adding monomers or polymers into KBr, and the mixture was ground to a fine power and pressed to form disks. The molecular weights and distribution were determined by gel permeation chromatography (GPC) using a solution of 0.1 vol % triethylamine in toluene as the mobile phase at 40 °C, relative to polystyrene standards. The GPC instrument is equipped with a Waters 510 pump, 410 differential refractive index detectors, and Waters Styragel HT6, HT4, and HT2 (7.8 mm × 300 mm) columns. UV−vis spectra were obtained on a Perkin-Elmer Lambda 2S spectrophotometer in tetrahydrofuran (THF) solution using 1 cm quartz cuvette cells. Fluorescence spectra were measured on a SLM 48000s spectrofluorometer using excitation at 410 nm with 4 nm slits. The fluorescence solutions were prepared as described previously.[4b] All the cationic solutions (Hg^{2+}, Hg^{2+}, Zn^{2+}, Ca^{2+}) were prepared by dissolving their chlorides in water. The quantum yield of fluorescence was determined relative to quinine sulfate in 0.5 M H_2SO_4 solutions with a quantum yield of 0.546, excited at 365 nm.[13] Lifetime experiments were carried out as described previously.[4b]

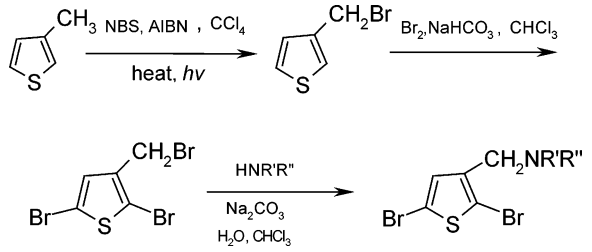
Synthesis. *2,5-Dibromo-3-bromomethylthiophene* was prepared by a modification of a previous literature report.[14] Anhydrous sodium bicarbonate (4.20 g, 0.047 mol) was added to a solution of 3-bromomethylthiophene (3.54 g, 0.020 mol) in 50 mL of chloroform, followed by the dropwise addition of bromine solution (8.16 g in 50 mL of $CHCl_3$) over a period of 1 h. The reaction mixture was stirred overnight at room temperature and then filtered. A highly lachrymatory brown oil remained following vacumm removal of solvent and residual bromine. The compound was previously reported to be unstable due to the bromomethyl group on the thiophene ring.[15] However, satisfactory NMR relative to previous literature reports was obtained, and this material was used for the next step immediately (5.29 g, 0.016 mol, yield 79%). ^{1}H NMR (360 MHz, $CDCl_3$): δ_H, 6.98 (s, 1H), 4.35 (s, 2H).

2,5-Dibromothiophen-3-ylmethyldiethylamine. A mixture of 3.35 g (0.010 mol) of 2,5-dibromo-3-bromomethylthiophene in 63 mL of ether, 3 mL (0.030 mol) of diethylamine, 38 mL of water, and 6.3 g of Na_2CO_3 was stirred for 19 h. The reaction mixture was acidified with 6 M HCl and the aqueous layer washed with ether. The aqueous layer was made basic by adding 20% Na_2CO_3 solution, and the mixture was extracted with ether (2 × 50 mL). The combined organic layer was dried over $MgSO_4$. Removal of the solvent in vacuo gave a light yellow oil (2.87 g, 8.8 mmol, yield 88%). ^{1}H NMR (360 MHz, $CDCl_3$): δ_H, 6.98 (s, 1H), 3.44 (s, 2H), 2.51 (q, 4H), 1.03 (t, 6H) ppm. ^{13}C (360 MHz, $CDCl_3$): 140.91, 131.66, 110.47, 108.92, 51.12, 46.79, 11.73 ppm. Elemental analysis: Calcd for $C_9H_{13}Br_2NS$: C, 33.04%; H, 3.98%; N, 4.28%. Found: C, 32.62%; H, 3.69%; N, 4.15%. FTIR wavenumber (cm^{-1}): 3061, 2969, 2934, 2873, 2808, 1576, 1556, 1544, 1383, 1205, 1079, 1022, 857, 806, 436.

N-(2,5-Dibromothiophen-3-ylmethyl)-N,N,N′-trimethylethane-1,2-diamine. A mixture of 3.35 g (0.010 mol) of 2,5-dibromo-3-bromomethylthiophene in 63 mL of ether, 3.88 mL (0.030 mol) of *N,N,N′*-trimethylethylenediamine, 38 mL of water, and 6.3 g of Na_2CO_3 was stirred for 19 h. The reaction mixture was acidified with 6 M HCl, and the aqueous layer was washed with ether. The aqueous layer was made basic by adding 20% Na_2CO_3 solution, and the mixture was then extracted with ether (2 × 50 mL). The combined organic layer was dried over $MgSO_4$. Removal of the solvent in vacuo gave a light yellow oil (2.53 g, 7.1 mmol, yield 71%). ^{1}H NMR (360 MHz $CDCl_3$): δ_H, 6.94 (s, 1H), 3.39 (s, 2H), 2.42−2.48 (t, 2H), 2.34−2.40 (t, 2H), 2.21 (s, 3H), 2.19 (s, 6H) ppm. ^{13}C (360 MHz, $CDCl_3$): 139.68, 131.64, 110.70, 109.87, 57.35, 55.83, 55.08, 45.78, 42.34 ppm. Calcd for $C_{10}H_{16}N_2Br_2S$: C, 33.71%; H, 4.49%; N, 7.87%. Found: C, 33.54%; H, 4.36%; N, 7.62%. FTIR: wavenumber (cm^{-1}): 3095, 2917, 2943, 2765, 1544, 1463, 1428, 1356, 1168, 1127, 1034, 1004, 914, 839, 477.

dea-PPETE. Diisopropylamine (2 mL) was added to a mixture of 2,5-dibromothiophen-3-ylmethyldiethylamine (0.327 g, 1 mmol), 1,4-diethyl-2,5-didodecyloxybenzene (0.494 g, 1 mmol), $Pd(PPh_3)_4$ (58 mg, 0.05 mmol), and CuI (20 mg, 0.10 mmol) in 10 mL of anhydrous THF under an argon atmosphere. The mixture was refluxed for 24 h, and then chloroform (20 mL) was added. The organic phase was washed twice with dilute $NaHCO_3$ solution. The solvent was removed under reduced pressure, and the residue was washed with hot water and hot methanol. The crude product was dissolved in chloroform and then precipitated in methanol twice to give a brown solid (0.579 g, yield 88%). ^{1}H NMR (360 MHz, $CDCl_3$): δ_H, 6.98−7.46 (3H), 3.95−3.99 (4H), 3.47−3.72 (2H), 2.49−2.58 (4H), 1.03−1.86 (52H). UV−vis λ_{max}: 332, 436 nm. Emission λ_{max}: 486 nm. FTIR: the formation of internal ethynyl link was confirmed by the presence of the 2193 cm^{-1} stretch.

Scheme 2. Synthesis of Monomer



tmeda-PPETE. Diisopropylamine (2 mL) was added to a mixture of *N*-(2,5-dibromothiophen-3-ylmethyl)-*N*,*N*,*N*′-trimethylethane-1,2-diamine (0.356 g, 1 mmol), 1,4-diethyl-2,5-didodecyloxybenzene (0.494 g, 1 mmol), $Pd(PPh_3)_4$ (58 mg, 0.05 mmol), and CuI (20 mg, 0.10 mmol) in 10 mL of anhydrous THF under an argon atmosphere. The mixture was refluxed for 24 h, and then chloroform (20 mL) was added. The organic phase was washed twice with dilute $NaHCO_3$ solution. The solvent was removed under reduced pressure, and the residue was washed with hot water and hot methanol. The crude product was dissolved in chloroform and then precipitated in methanol twice to give a brown solid (0.564 g, yield 82%). ^{1}H NMR (360 MHz, $CDCl_3$): δ_H, 6.9−7.2 (3H), 3.4−3.7 (2H), 2.1−2.3 (9H), 2.3−2.6 (4H), 1.8−1.9 (46H). UV−vis λ_{max}: 332, 446 nm. Emission λ_{max}: 488 nm. FTIR: the formation of internal ethynyl link was confirmed by the presence of the 2194 cm^{-1} stretch.

Results and Discussion

Synthesis. The polymers dea-PPETE and tmeda-PPETE were prepared by a step growth polymerization employing the palladium-catalyzed cross-coupling[16] of the receptor loaded monomer **a** and 1,4-diethynyl-2,5-didodecyloxybenzene (monomer **b**), as shown in Scheme 1. Monomer **b** was synthesized from 1,4-hydroquinone in four steps as described in the literature.[11] dea-PPETE and tmeda-PPETE are brown solids and very soluble in common organic solvents such as THF and chloroform. Scheme 2 shows the three-step reaction used to prepare the 2,5-dibrominated thiophene monomers with the amino receptor connected to the thiophene ring by a methylene spacer (monomer **a**). The 3-bromomethylthiophene was synthesized from commercially available 3-methylthiophene with a free radical reaction under nitrogen.[12] Bromination of this compound with Br_2 in the presence of $NaHCO_3$ gave 2,5-dibromo-3-bromomethylthiophene, which reacted with a secondary amine to give the desired monomer **a**.

The polymers were thoroughly characterized including FTIR, NMR, GPC, and photophysical characterization. The typical infrared stretching absorptions of the terminal alkyne, including a strong, sharp absorption at 3286 cm^{-1} for acetylenic C−H stretching vibration and a weak, but sharp, absorption at 2106 cm^{-1} for the C≡C stretching vibration in the monomer, were absent in both polymers. Instead, a broad, weak absorption around 2193 cm^{-1} appeared, consistent with the formation of internal ethynyl link.[17] The end groups C−H and C−Br of these two polymers were below the signal-to-noise ratio in ^{1}H NMR and ^{13}C NMR, also indicating the formation of polymer. There were also several weak peaks in the aromatic region that can be assigned to catalyst residue. For this polymerization methodology, there has been no effective way to totally remove the catalyst residue.[18] To our surprise, there were three peaks between 3.4 and 3.8 ppm where only one peak was expected for the proton in the methylene spacer between the thiophene ring and the amino receptor (Figure 2). ^{13}C DEPT (135°) and 2D heteronuclear (C, H)-correlated NMR experiments show that these peaks are related to a single secondary carbon. One explanation could be that because the substituents on both monomers are not very bulky and relatively flexible, the polymerization process can take place via head-to-tail or head-to-head−tail-to-tail. As the result of this regioisomerism, the methylene protons are in different electronic environments, which result in multiple peaks in the ^{1}H NMR.

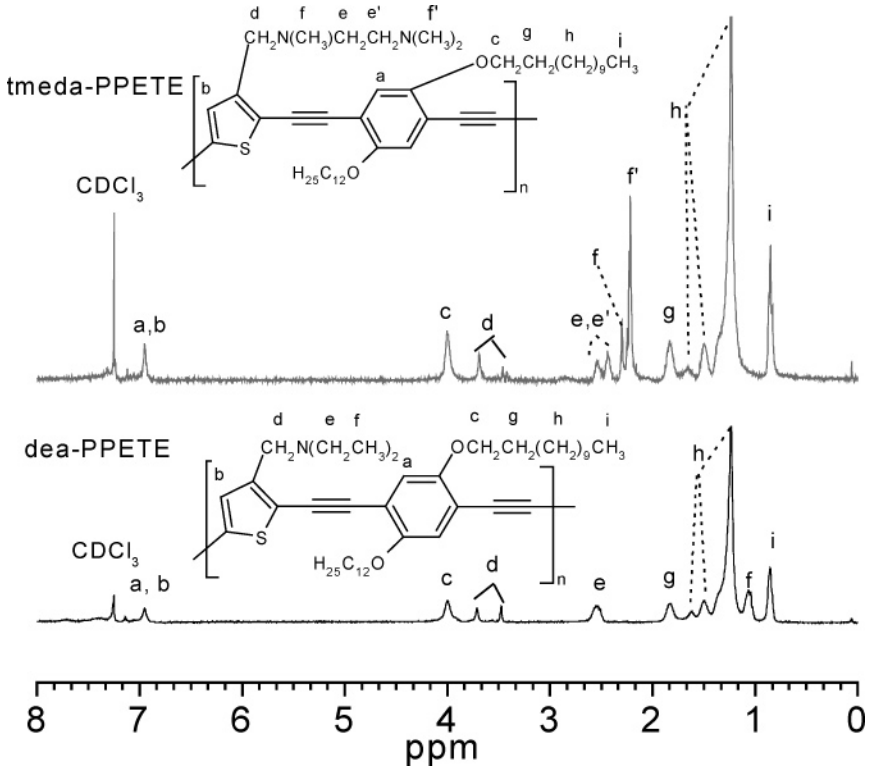


Figure 2. ^{1}H NMR spectra of tmeda-PPETE and dea-PPETE.

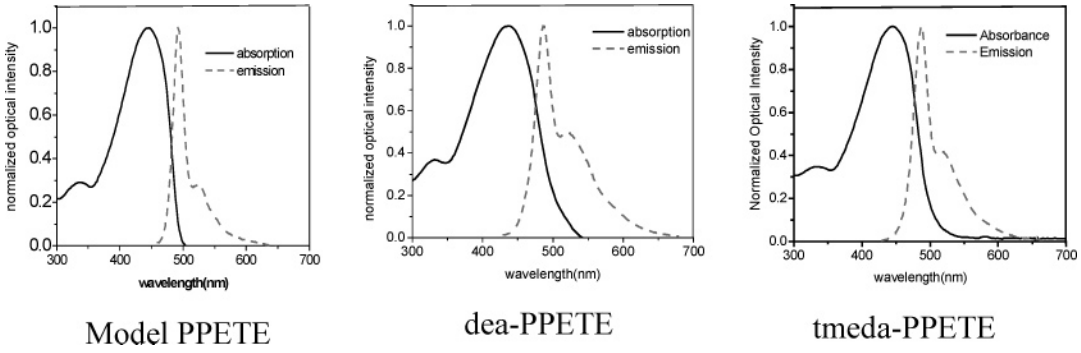


Figure 3. UV−vis and emission spectra of model PPETE, dea-PPETE, and tmeda-PPETE in THF solution at room temperature.

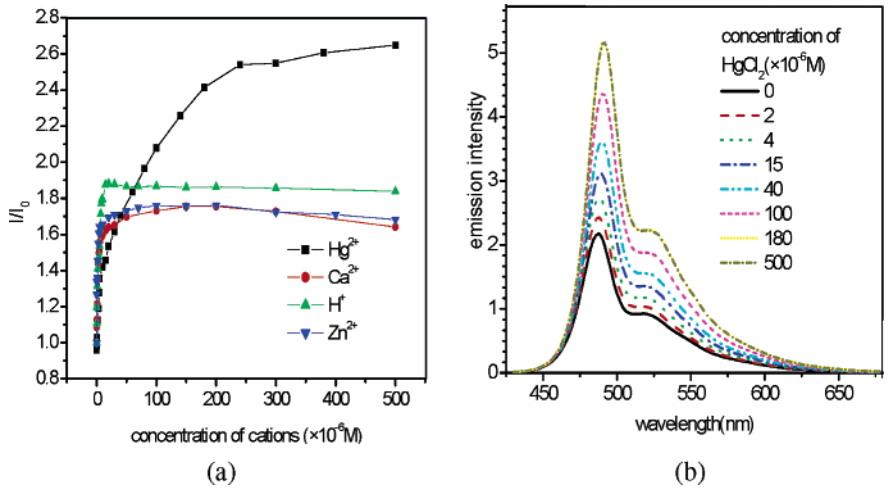


Figure 4. (a) Fluorescence enhancement of tmeda-PPETE in THF upon addition of metal cations. (b) Emission spectra of tmeda-PPETE upon addition of different concentration of Hg^{2+}. Polymer concentration was held at constant 5.0×10^{-6} M in receptor unit.

Because of the strong interaction between the amino group and the GPC column, the GPC experiments were carried out using a solution of 0.1% triethylamine (TEA) in toluene as the mobile phase. Reproducible negative peaks were observed with a refractive index detector for both polymers. The molecular weights were calculated relative to polystyrene standards, and the results are summarized in Table 1. Considering the rigidity of the PPETE backbone compared to the relatively flexible polystyrene standard, the degree of polymerization shown here might be overestimated by 2−3 times.[4a,18]

Photophysical Properties. The absorption and emission spectra of the model polymer PPETE,[4] dea-PPETE, and tmeda-PPETE are shown in Figure 3. The absorption and emission spectra of dea-PPETE and tmeda-PPETE are similar to that of the model PPETE. On the basis of previous studies,[4] the absorption peaks around 440 nm can be assigned to $\pi-\pi^*$ transitions from the conjugated polymer backbone. All the emission spectra show a maximum and a shoulder, which can be attributed to a single transition with vibronic structure.[4] From the similarity in absorption and emission spectra between model PPETE and the new polymers, we conclude that introduction of the amino receptors does not lead to significant electronic or structural distortion of the new polymers compared to the model polymer. The quantum yields of fluorescence for dea-PPETE and for tmeda-PPETE were found to be 0.11 and 0.09, respectively. For comparison, the quantum yield for model PPETE is 0.54.[4] The lower values of the quantum yields of these two polymers compared to the model polymer are consistent with a PET reduction of the excited state as expected in the absence of coordinating analytes (Figure 1). The incomplete PET quenching of these two polymers may be ascribed to a kinetic competition between the regular fluorescence process and the PET process or the presence of localized fluorescent domains that are not coupled to a receptor site. This has been suggested previously for PET in fluorescent polymers.[19]

Table 1. Molecular Weight and Polydispersity of dea-PPETE and tmeda-PPETE[a]

	M_w	M_n	PDI	deg of polymerization
dea-PPETE	1.20×10^5	6.18×10^4	1.76	206
tmeda-PPETE	1.00×10^5	3.67×10^4	2.73	106

[a] Determined by GPC at 40 °C relative to polystyrene in trimethylamine (0.1 vol %) toluene solution.

Cation Sensitivity. The influence of various metal chlorides and HCl on the fluorescence behavior of the tmeda-PPETE polymer was investigated (Figure 4a). The fluorescence was observed to increase upon titrating aqueous solution of Hg^{2+}, Zn^{2+}, Ca^{2+}, and H^+ into the polymer THF solution.[4b] We selected the carrier solvent based on its miscibility with H_2O, which was the target medium for cation detection in the environment. Addition of Hg^{2+} gave the maximum response with a 2.7-fold intensity enhancement at saturation (micromolar concentrations). Similar titrations were also carried out on the dea-PPETE, but the enhancement effects were very small, usually less than 1.2-fold. Thus, only the tmeda-PPETE polymer successfully demonstrated a

fluorescence "turn-on" response to metallic cations as designed.

The different responses of dea-PPETE and tmeda-PPETE to the same cations may be explained by the relative energy levels of the two amino receptors compared to the HOMO and LUMO of the polymer backbone. On the basis of the oxidation potentials of related small molecules,[20] we propose that the lone electron pair on diethylamino group has a lower energy level than that on the *N,N,N′*-trimethylethylenediamino group. In the absence of the cations, the driving force of the PET process is smaller for the tmeda-PPETE than for dea-PPETE (Figure 1). This is consistent with the observation that dea-PPETE has a higher quantum yield of fluorescence than tmeda-PPETE. When the electron pair on the receptor is coordinated to the cations, the driving force of the PET process for both polymers is decreased based on literature oxidation potentials vs SCE.[20] On the basis of comparisons to model compounds,[21] the monodentate dea-PPETE has a smaller binding constant to metal cations as compared to tmeda-PPETE. The higher equilibrium constant could also account for the enhanced fluorescence "turn-on" behavior for tmeda-PPETE.

As shown in Figure 4a, when tmeda-PPETE was titrated by Ca^{2+}, H^+, and Zn^{2+}, the fluorescence "turn-on" response is more rapid than by Hg^{2+}, though these cations did not yield maximum fluorescence enhancement. For Ca^{2+}, H^+, and Zn^{2+}, the fluorescence enhancement saturation was reached at a very early stage (~5 ppm), when the cation concentration was close to the concentration of the receptor unit in the solution. When the addition of these cations reached very high concentration, the fluorescence intensity actually decreased slightly. This is likely due to the dilution of the polymer solution with the aqueous cation solution, which is more easily corrected at low concentration. The polymer response toward different cations is expected, given the different association constants between cations and the amino receptor.

Upon binding these cations, there is negligible shift in both the UV−vis absorption spectra and the excitation spectra and no change in lifetime for both polymers. In some emission spectra of tmeda-PPETE, a 2−4 nm red shift of the emission maximum was observed with the increase in fluorescence intensity, but the emission profile shift is within experimental noise (Figure 4b). On the basis of these photophysical studies, we can conclude that the ion complexation does not alter the conformation of the polymers in either ground state or excited state. Given the favorable driving force for electron transfer, these results are consistent with the intensity enhancement resulting from a "switching-off" of the PET process as shown in Figure 1.

Conclusion

We present here for the first time the application of a PET strategy for the design of conjugated polymer fluorescence "turn-on" chemsensors. Two new polymers dea-PPETE and tmeda-PPETE were synthesized and characterized in this initial study. These two polymers have relatively low quantum yields in room temperature solution compared to the model PPETE, due to fluorescence quenching. The tmeda-PPETE polymer shows fluorescence enhancement upon binding Hg^{2+}, protons, and other divalent cations. The synthetic strategy provides a platform to introduce a broad series of amino receptors onto fluorescent conjugated polymers as PET sensors. A new class of sensors for a variety of cations can be envisioned with this easily modified system. On the basis of the design concept, future work is being directed to increase the sensitivity and selectivity of this class of chemosensors.

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Supporting Information Available: FTIR, ^{1}H NMR, and ^{13}C NMR spectra of the monomers and polymers; ^{13}C DEPT (135°) and 2D heteronuclear (C, H)-correlated NMR spectra of dea-PPETE. This material is free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) (a) Nolan, E. M.; Lippard, S. J. *J. Am. Chem. Soc.* **2003**, *125*, 14270. (b) Wolf, C.; Mei, X. F. *J. Am. Chem. Soc.* **2003**, *125*, 10651. (c) He, H. R.; Mortellaro, M. A.; Leiner, M. J. P.; Fraatz, R. J.; Tusa, J. K. *J. Am. Chem. Soc.* **2003**, *125*, 1468. (d) Hayashita, T.; Qing, D.; Minagawa, M.; Lee, J. C.; Ku, C. H.; Teramae, N. *Chem. Commun.* **2003**, 2160. (e) Yang, W. Q.; Yan, J.; Fang, H.; Wang, B. H. *Chem. Commun.* **2003**, 792.

(2) (a) Swager, T. M. *Acc. Chem. Res.* **1998**, *31*, 201. (b) Zhou, Q.; Swager, T. M. *J. Am. Chem. Soc.* **1995**, *117*, 12593. (c) McQuade, D. T.; Pullen, A. E.; Swager, T. M. *Chem. Rev.* **2000**, *100*, 2537.

(3) (a) Fan, C.; Plaxco, K. W.; Heeger, A. J. *J. Am. Chem. Soc.* **2002**, *124*, 5642. (b) Wang, D.; Wang, J.; Moses, D.; Bazan, G. C.; Heeger, A. J. *Langmuir* **2001**, *17*, 1262. (c) Wang, J.; Wang, D.; Miller, E. K.; Moses, D.; Bazan, G. C.; Heeger, A. J. *Macromolecules* **2000**, *33*, 5153. (d) McQuade, D. T.; Hegedus, A. H.; Swager, T. M. *J. Am. Chem. Soc.* **2000**, *122*, 12389.

(4) (a) Zhang, Y.; Murphy, C. B.; Jones, W. E., Jr. *Macromolecules* **2002**, *35*, 630. (b) Murphy, C. B.; Zhang, Y.; Troxler, T.; Ferry, V.; Martin, J. J.; Jones, W. E., Jr. *J. Phys. Chem. B* **2004**, *108*, 1537.

(5) Tong, H.; Wang, L.; Jing, X.; Wang, F. *Macromolecules* **2003**, *36*, 2584.

(6) (a) de Silva, A. P.; Gunaratne, H. O. N.; Gunnlaugsson, T.; Huxley, A. J.; McCoy, C. P.; Rademacher, J. T.; Rice, T. E. *Chem. Rev.* **1997**, *97*, 1515. (b) Valeur, B.; Leray, I. *Coord. Chem. Rev.* **2000**, *205*, 3. (c) Zang, L.; Liu, R.; Holman, M. W.; Nguyen, K. T.; Adams, D. M. *J. Am. Chem. Soc.* **2002**, *124*, 10640.

(7) (a) Huston, M. E.; Haider, K. W.; Czarnik, A. W. *J. Am. Chem. Soc.* **1988**, *110*, 4460. (b) Huston, M. E.; Akkaya, E. U.; Czarnik, A. W. *J. Am. Chem. Soc.* **1989**, *111*, 8735. (c) Van Arman, S. A.; Czarnik, A. W. *J. Am. Chem. Soc.* **1990**, *112*, 5376.

(8) Grabchev, I.; Qian, X. H.; Xiao, Y.; Zhang, R. *New J. Chem.* **2002**, *26*, 920.

(9) Sariciftci, N. S.; Smilowitz, L.; Heeger, A. J.; Wudl, F. *Science* **1992**, *258*, 1474.

(10) Daffy, L. D.; de Silva, A. P.; Nimal Gunaratne, H. Q.; Hunder, C.; Mark Lunch, P. L.; Werner, T.; Wolfbeis, O. *Chem.—Eur. J.* **1998**, *4*, 1810.

(11) Swager, T. M.; Gil, C. J.; Wrighton, M. S. *J. Phys. Chem.* **1995**, *99*, 4886.

(12) Mandal, S. S.; De Chakraborty, J. *J. Chem. Soc., Perkin Trans. 1* **1999**, 2639.

(13) Pang, Y.; Li, J.; Barton, T. J. *J. Mater. Chem.* **1998**, *8*, 1687.

(14) Lemaire, M. *J. Chim. Phys. Phys.-Chim. Biol.* **1989**, *86*, 93.

(15) Campaigne, E.; Lesuer, W. M. *J. Am. Chem. Soc.* **1948**, *70*, *1555*.

(16) Yamamoto, T.; Honda, K.; Ooba, N.; Tomaru, S. *Macromolecules* **1998**, *31*, 7.

(17) Hesse, M.; Meier, H.; Zeeh, B. *Spectroscopic Methods in Organic Chemistry*; Georg Thieme Verlag: Stuttgart, 1997.

(18) Bunz, U. H. F. *Chem. Rev.* **2000**, *100*, 1605.

(19) Guillet, J. *Polymer Photophysics and Photochemistry;* Cambridge University Press: Cambridge, UK, 1985.
(20) Meites, L.; Zuman, P. *Electrochemical Data*; John Wiley & Sons: New York, 1974.
(21) Harris, D. C. *Quntitative Chemical Analysis*, 5th ed.; W.H. Freeman and Co.: New York, 1999.

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