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Toward a Highly Sensitive Fluorescence Sensing System of an Amphiphilic Molecular Rod: Facile Synthesis and Significant Solvent-Assisted Photophysical Tunability

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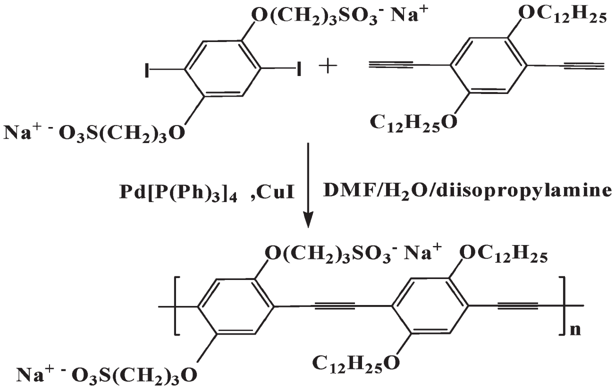
ABSTRACT: A conjugated polyelectrolyte with symmetrically assembled hydrophilic and hydrophobic side groups along the backbone has been successfully synthesized and demonstrated significant photophysical tunability with 65 nm of wavelength shift and 10-fold of intensity enhancement for the emission maximum, through solvent composition adjustment. The highest fluorescence quenching effect ($I/I_0 = 148$) toward 10 μM of Fe^{3+} was achieved in the solution having a THF/H_2O ratio of 30/70, which could be attributed to a delicate balance among the influencing factors for the fluorescence quenching systems, the initial fluorescence, the rate of energy migration, and the accessibility of the receptors. The amplified symmetrical aggregation−nonaggregation inversion and the asymmetrical cation sensitivity across the whole range of H_2O/THF composition were consistent with the molecular design.

Introduction

Conjugated polyelectrolytes (CPEs), usually composed of rigid-rod polymer backbones and ionic side groups, have been devoted considerable research interest due to their unique properties.[1−12] The combination of the ionic characteristic and the "molecular wire" nature[13] offers CPEs new opportunities in the biosensor, electronics, and optoelectronics.[14−21] Basically, CPEs, such as poly[2,5-bis(3-sulfonatopropoxy)-1,4-phenylethynylene-*alt*-1,4-poly(phenyleneethynylene)]) (PPESO$_3$),[5−7] exhibit aggregated states in the aqueous environment with the side chains extending out and the polymer backbones stacking up inside. However, the aggregated CPEs can rarely be redissolved after drying up since the strong $\pi-\pi^*$ stacking is hard to break up. In addition, the aggregation induces the self-quenching of the polymer fluorescence. While strategies such as the addition of the surfactants into the systems[22−24] and direct introduction of branched long hydrophilic chains as the pendant groups through the synthetic effort[14,25] have been developed to circumvent these limitations, very few reports have discussed using component solvents to tune the emission and solubility.[4,6,26−28] Here we report the preparation of a new conjugated polymer, a poly(*p*-phenyleneethynylene) (PPE) with alternating monomeric building blocks through Sonogashira coupling (A_2B_2 protocol).[29] We have designed one monomeric building block with two *para*-charged hydrophilic linear side groups (A_2) on the phenyl ring and the other with two *para*-hydrophobic linear side groups (B_2). Several advantages are anticipated for this strategy. First, "structurally similar" side groups with opposite solubility in common solvents are introduced onto rigid-rod backbones to form surfactant-like macromolecules, which is expected to amplify the solvent controllability in creating supramolecular assembly; second, both types of side groups are linear, instead of branched, which facilitates the assembly of these macromolecules into highly ordered structures; finally, the A_2B_2 protocol is adapted to intentionally weaken the $\pi-\pi^*$ interaction in the aggregated state since the polymer backbones have to take a side-by-side conformation, or face to face with at least one type of the side groups lying between the backbones.[30] These advantages will not be simultaneously achieved in the case of having oligoethylene glycol side groups, which is soluble in both water and polar organic solvents,[14,25,30] or assembling hydrophilic and hydrophobic groups on the *para*-position of the same phenyl ring.[12,30] Compared to other literature reports about the solvent tunability, such as in phenyleneethynylene or fluorenephenylene systems having only hydrophilic side groups,[6,26,27] this molecular design should offer enhanced solvent tunability due to the existence of the hydrophobic side groups.

Scheme 1. Synthetic Strategy for PPESO$_3$OR



A new conjugated polyelectrolyte (PPESO$_3$OR) was synthesized according to the A_2B_2 protocol (Scheme 1). The sulfonate group would provide the hydrophilicity and the interaction with the cations or biomolecules.[5−9,14] The alkoxyl group would provide the hydrophobicity. This polymer would be expected to inherit the advantages from the well-studied PPESO$_3$ but overcome its shortcomings, such as the inconvenience in the storage and transportation since PPESO$_3$ had to be kept in methanol.[5−7]

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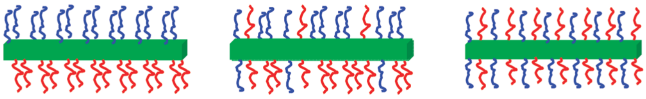

Figure 1. Schematic diagram of side group arrangements within certain microenvironments for PPESO$_3$OR in different solvents, where hydrophilic and hydrophobic groups were separately located (left), one type of group preferably located at one side (middle), or randomly located (right) at the two sides of the polymer backbone. Blue lines denote the hydrophilic groups, and red lines denote the hydrophobic groups.

In addition, conformation and spatial arrangement of the PPESO$_3$OR polymer chains, especially the side groups, would be tuned by adjusting the solvent composition which made it readily obtain the best condition for sensing application. We could envision the following possible arrangements of the side chains no matter in supramolecular structures or in isolated chains: the sulfonate groups and the alkoxyl groups would be arranged on the opposite sides of the backbone, or one type of the groups preferably located at one side, or the side groups arranged randomly at both sides of the polymer backbone (Figure 1). The difference in these arrangements would affect the stacking model of the polymer chains and therefore the photophysics. The experimental results demonstrated the enhanced facile phophysical tunability of this polymer system, with 60 nm of wavelength shift and 10-fold of intensity enhancement for the emission maximum. In addition, cation titration also verified the possibility of using it as a highly sensitive fluorescence chemosensor.

Experimental Section

Materials. Tetrakis(triphenylphosphine)palladium ((PPh$_3$)$_4$Pd) and cuprous iodide (CuI) were purchased from Alfa Aesar Chemical Co.; *N,N*-dimethylformamide (DMF), tetrahydrofuran (THF), and cation chlorides were from Sinopharm Chemical Reagent Co., Ltd. All materials were of analytical grade and used as received unless otherwise noted. Diisopropylamine was distilled from potassium hydroxide (KOH). 1,4-Diethylnyl-2,5-didodecyloxybenzene[31] and 1,4-diiodo-2,5-di(propyloxysulfonate)benzene[7] were synthesized according to procedures published.

General Methods. ^{1}H NMR spectra were recorded on an Inova 400 MHz NMR spectrometer. The FTIR spectrum of the polymer was obtained on Nicolet 6700 FTIR spectrophotometer (thermo). 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 weight was determined by static light scattering, which was carried out on a modified commercial light scattering spectrometer (ALV/SP-125) equipped with an ALV-5000 multitau digital time correlator and a He−Ne laser (output power) 35 mW at λ_0 (632.8 nm). The polymer was dissolved in methanol with concentrations of 0.2, 0.4, 0.6, and 0.8 mg/mL, and the M_w was calculated according to the literature.[32,33] The detailed UV−vis spectra were obtained on a Hitachi U-3900/3900H spectrophotometer, and fluorescence spectra were measured on a Horiba FluoroMax-4 spectrofluorometer using excitation at 420 nm with 1 nm slits. The PPESO$_3$OR stock solution was prepared by dissolving certain amount of polymer in H$_2$O to achieve a repeat unit concentration held at 1 mM. All the cationic solutions were freshly prepared by dissolving their chlorides in water. Before the titration of cations, 10 μL of the polymer stock solution was added into 10 mL of the mixed solvent with different ratio between THF and water to obtain polymer solutions with a concentration of 1 μM with respect to the repeat unit. The cation titration was carried out through continuous adding aliquots of cationic stock solution. All the titrations were repeated at least three times, and the data were reproducible within the experimental noise. The quantum yields of the fluorescence in different solvents were determined relative to quinine sulfate in 0.5 M H$_2$SO$_4$ solutions with a quantum yield of 0.546, excited at 365 nm.

Synthesis. Typical process for the synthesis of PPESO$_3$OR and work-up is as follows: 0.1316 g (0.202 mmol) of 1,4-diiodo-2,5-di(propyloxysulfonate)benzene and 0.1000 g (0.202 mmol) of 1,4-diethylnyl-2,5-didodecyloxybenzene, 11.6 mg (10.1 μmol) of Pd(PPh$_3$)$_4$, and 1.9 mg (10.1 μmol) of CuI were placed in a flask connected with an isobarically funnel and deoxygenated by several cycles of vacuum−argon cycling. 10 mL of mixed solvent DMF/H$_2$O/diisopropylamine (3/2/1, ratio in volume, the same below), which was pre-deoxygenated by a gentle flow of argon for 30 min, was quickly placed into the funnel under an argon atmosphere and dropped into the flask slowly. The final mixture was then stirred at 80 °C for 24 h. The reaction mixture was slowly added to 100 mL of a methanol/acetone/ether mixture (10:40:50) after being cooled to room temperature. The precipitate was centrifugated and redissolved in 20 mL of water/methanol (7/3), followed by being treated with 0.01 g of sodium sulfide (Na$_2$S). The mixture was filtered. The filtrate was added into a large volume of methanol/acetone/ether (10/40/50). The upper liquid was carefully removed, and the resulting mixture was centrifuged to collect PPESO$_3$OR as a light yellow powder and very soluble in water (131 mg, yield 65%). ^{1}H NMR (DMSO-d_6; δ_{ppm} from TMS, 30 °C): 6.80−8.00 (4H), 4.00−4.10 (4H), 3.90−4.00 (4H), 2.58−2.70 (4H), 1.80−2.15 (4H), 1.60−1.80 (4H), 0.90−1.40 (32H), 0.65−0.92 (6H). FTIR ($\nu_{\mathrm{max.}}$ cm^{-1}, KBr): 2924, 2853, 1629, 1510, 1469, 1424, 1396, 1224, 1048, 935, 827, 766, 723, 605, 530. M_w = 8.800 × 10^6 g/mol (in methanol).

Alternative method for the work-up: The reaction mixture was slowly added to 100 mL of a methanol/acetone/ether mixture (10:40:50) after being cooled to room temperature. The preciptate was centrifugated and redissolved in 20 mL of DMF/H$_2$O/diisopropylamine, the same component as the reaction solvent, followed by being treated with 0.01 g of sodium sulfide (Na$_2$S). The mixture was filtered. The water and diissopropylamine in the filtrate were removed by rotary evaporation. The concentrated filtrate was added into a large volume of methanol/acetone/ether (10/40/50). The resulting mixture was centrifuged to collect PPESO$_3$OR as a light yellow powder and slightly soluble in water, not soluble in THF but very soluble in the mixture of water and THF with whatever combination of water and THF.

Results and Discussion

Synthesis. The polymer was prepared through the Sonogashira coupling. Interestingly, the solubility of the resulting polymer was found to be dependent on the detailed steps during the work-up. In a typical process, the crude product was redissolved in water/methanol mixture and reprecipitated out in methanol/acetone/ether again. The final product after drying in vacuum could be easily redissolved in water with a concentration of more than 6 mg/mL and was also soluble in H$_2$O/THF mixture, but not in pure THF. However, if the crude product was redissolved in DMF, the dried product displayed limited solubility in pure water or THF, but very good solubility in H$_2$O/THF. This phenomenon could be explained by considering the solubility amphiphilicity of the molecular rod. Generally, a PPE with only sulfonate side groups would dissolve in water or methanol and precipitate out of THF or ether, whereas the PPE with only alkoxyl side groups would dissolve in THF or chloroform but precipitate out of water or methanol. In PPESO$_3$OR, the coexistence of both side groups resulted in the observed intriguing solubility behavior. The redissolving of crude product in water/methanol might lead to a tight aggregation of the polymer chains with the sulfonate groups extending out of the aggregates, favorable for dissolving in water after drying.

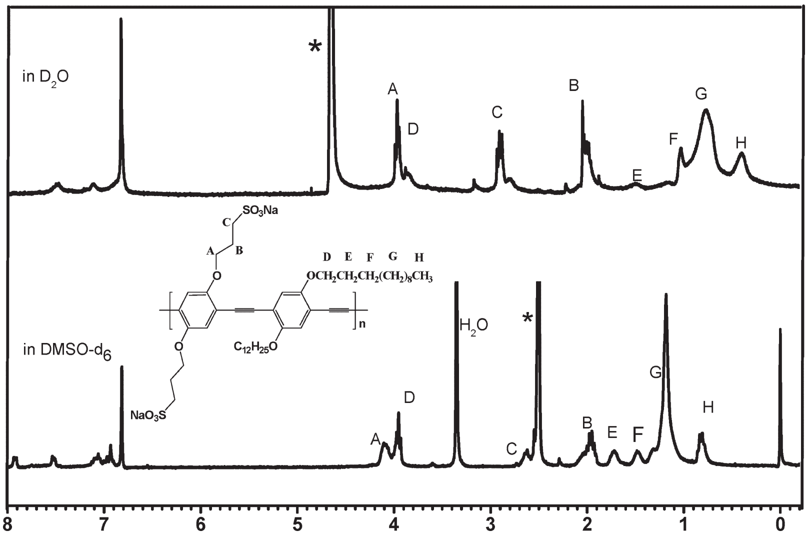

Figure 2. ^{1}H NMR of $PPESO_3OR$ in DMSO (up) and D_2O (bottom). Asterisk denotes the solvent peak.

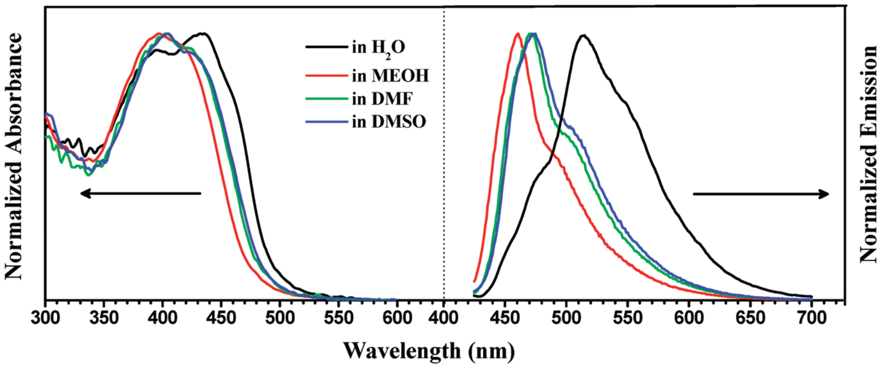

Figure 3. Normalized spectra for absorbance and emission of $PPESO_3OR$ in different solvents.

However, if the crude product was redissolved in DMF, a good solvent for both side groups, and the polymer precipitated out quickly, both hydrophilic and hydrophobic groups might be on the surface of aggregated structure. In this case, the complete dissolution of the molecular rod required the H_2O/THF combination. The polymer prepared in a typical process (crude product redissolved in water/methanol) was used in the following study.

^{1}H NMR spectra of $PPESO_3OR$ in D_2O and in DMSO-d_6 are shown in Figure 2. The peaks for protons on the alkoxyl group in D_2O were relatively broad and appeared at lower chemical shift, compared to those in DMSO-d_6. This phenomenon could be attributed to the restricted movement of these alkoxyl groups buried inside the aggregates and the more shielding of the alkoxy protons when the polymer was dissolved in the water.[34] These NMR spectra were obtained at room temperature (30 °C). It was more convenient than the NMR measurement for the $PPESO_3$, which had to be carried out in DMSO at elevated temperature, such as 100 °C, as reported in the literature.[5] The mass average molecular weight was found to be 8.800×10^6 g/mol in methanol, using static light scattering method.[32,33] Considering the possible aggregation to some degree when the polymer was dissolved in the methanol under the static light scattering required concentration, the M_w might be overestimated. However, the attempt to running GPC in aqueous solution or in DMF turned out unsuccessful, probably due to the interaction between the GPC column and the ionic group.[35] Literature reports of similar CPEs, such as, PPE-SO_3, did not give the exact value of molecular weight.[5−7,9]

Table 1. Photophysical Data for $PPESO_3OR$ in Different Solvents

			emission (nm)	
solvent	quantum yield	absorption peak (nm)	peak	shoulder
water	0.112	436	515	475
methanol	0.708	400	460	490
DMF	0.758	405	470	505
DMSO	0.678	405	475	510

Photophysics. Generally, amphiphilic structure has a strong tendency to form clusters, even in good solvent and relatively dilute solution.[36,37] In the case of that the polymer backbones were closely packed, tightly aggregated state might form due to the π interaction among the polymer backbones. The aggregation would result in a red shift of the emission wavelength and a broadening of the spectra compared to the nonaggregated one. However, in the case of that the chains was loosely packed, the nonaggregated state would be found in the spectra with a blue-shifted and relatively sharp emission, similar to the situation at which the polymer existed as isolated chains in the diluted solution. The absorbance and emission of $PPESO_3OR$ in various solvents were studied (Figure 3 and Table 1). The polymer was aggregated in dilute aqueous solution, with a broad emission peak around 515 nm and low quantum yield of emission. The emission in water was about 35 nm blue-shifted to that of $PPESO_3$ in Schanze's system.[5] This blue

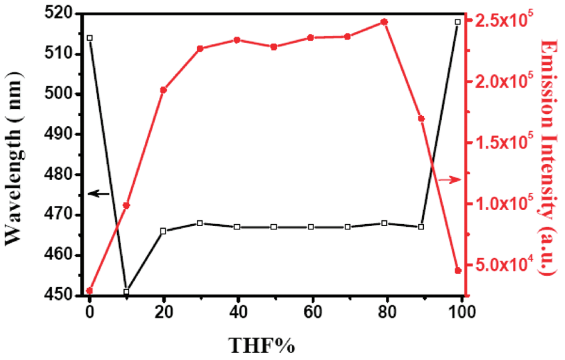

Figure 4. Emission wavelengths and the intensities at the emission maxima of the $PPESO_3OR$ in the H_2O/THF mixed solvent with different percentage of THF. The polymer concentrations were fixed at 1 μM with respect to the repeat unit. The excitation was at 420 nm.

shift could be attributed to the weakening of the polymer backbones interaction by introducing the alkoxyl groups. Relatively sharp emission peaked around 470 nm was found for the polymer in methanol, DMF, or DMSO with high quantum yields, suggesting that the polymer was in nonaggregated states in these solvents. The results from the photophysical study were consistent with the NMR spectra (Figure 2).

Solvent-Assisted Aggregation–Nonaggregation–Aggregation Transformation. Different supramolecular assemblies formed by $PPESO_3OR$ could be switched by varying the composition of a mixed solvent, as indicated from the fluorescence emission of the polymer (Supporting Information). The intensities and wavelengths for the emission maxima in H_2O/THF mixed solvent with THF content from 0 to 99.9% (in volume, the same below) are shown in the Figure 4. The emission maximum blue-shifted from 515 nm in pure water to 450 nm in the mixed solvent with 10% of THF and then slightly red-shifted to 465 nm with 20–90% of THF. Higher emission intensity was achieved in the solvent having 30%–80% of THF. Further increase of THF percentage led to the red shift of emission and decrease in the intensity again. This photophysical "symmetry" (in the nonstrict sense), exhibited by the polymer across the whole range of THF/water combination, was consistent with the molecular design. Polymer chains in water were strongly aggregated. In the solvent with an appropriate H_2O/THF ratio, both side chains and the conjugated polymer backbone could be well solvated. Therefore, the polymer chains became nonaggregated. When the THF became the dominating component in the solvent, another aggregated state formed with the alkoxyl group solvated outside and the sulfonate groups buried inside. Solvent tunability was also reported in the literature while most systems were of one-directional aggregation–nonaggregation inversion.[5,6,27] Very few were about the reversible aggregation–nonaggregation–aggregation transition.[26,28,38] In addition, much greater solvent tunability, 65 nm wavelength shift and 10-fold intensity enhancement for emission maximum, were achieved in this $PPESO_3OR$ system, compared to 10 nm wavelength shift and 2-fold intensity enhancement for the polyfluorene system in H_2O/THF reported by Bazan et al.[26] Recently, Burrow et al. reported another polyfluorene system with sulfonate side groups which also exhibited the aggregation–nonaggregation–aggregation transition in H_2O/dioxane with about 15 nm wavelength shift.[28] The enhanced tunability in the $PPESO_3OR$ system could be simply attributed to the additional introduction of the hydrophobic side group.

To get a close observation on the transformation of $PPESO_3OR$ from the aggregated state to the nonaggregated state, tiny aliquots of THF were gradually titrated into the $PPESO_3OR$ aqueous system and the development of emission spectra was tracked (Figure 5a). The change was similar to the one by varying the THF/H_2O ratio. The broad low emission appeared with the peak around 515 nm at the beginning, followed by the gradual increase of the intensity and the emergence of peak around 475 nm and then 450 nm. Finally, the spectrum developed into a profile similar to the one in methanol or DMF, with the emission maximum around 465 nm and a shoulder around 505 nm. The slight red shift of the emission maximum from 450 to 465 nm could be attributed to the existence of the more extended polymer chains in the medium range of THF/H_2O ratio at which both side groups could be well dissolved.[12] A similar change was observed during the process of titrating water into the polymer solution in 99.9% of THF (Figure 5b). However, less amount of water was needed to complete the whole transformation, which was consistent with the results obtained from polymer emission spectra in the THF/H_2O mixed solvent as shown in Figure 4. This difference between the titration of water into polymer THF solution and the titration of THF into polymer aqueous solution implied that the polymer aggregation in THF was less compact than that in water, possibly due to the repulsion among the negative sulfonate groups lying inside and the existence of a small quantity of water. Therefore, the symmetrical arrangement of hydrophilicity and hydrophobicity of the side groups on the polymer backbone was demonstrated to be very useful in controlling the transformation between the aggregated and the nonaggregated structures, with monitoring the emission of $PPESO_3OR$ in various mixed solvents.

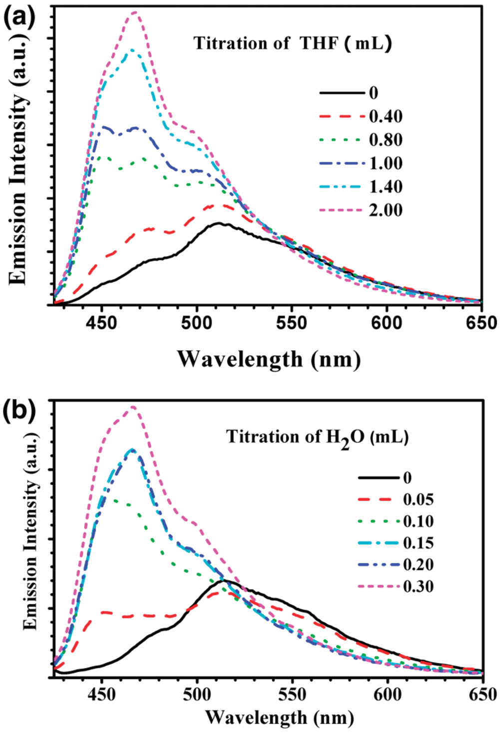

Figure 5. (a) Emission spectra of titrating THF into 10 mL of $PPESO_3OR$ aqueous solution (top). (b) Emission spectra of titrating THF into 10 mL of $PPESO_3OR$ in 99.9% THF solution (bottom). The polymer concentration was 1 μM with respect to the repeat unit at the beginning. The excitation was at 420 nm.

One interesting issue worthy of noting is that there appeared one emission maximum around 450 nm and two shoulders around 470 and 510 nm, for the polymer dissolved directly in H_2O/THF with 10% of THF (Figure 4 and Figure 2S in the Supporting Information), while there were two

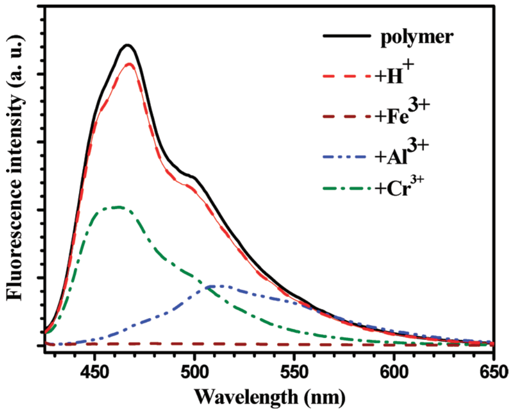

Figure 6. Influence of adding 20 μM of different cations on the emission spectra of PPESO$_3$OR (1 μM with respect to the repeat unit in H$_2$O/THF = 1/1). The excitation was at 420 nm.

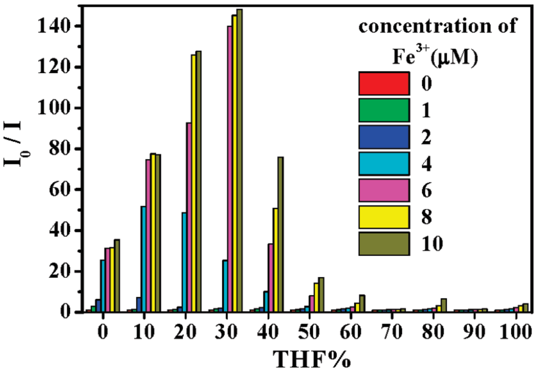

Figure 7. Fluorescence quenching (I_0/I) of PPESO$_3$OR in H$_2$O/THF mixed solvent with various percentage of THF, toward the titration of Fe^{3+} into room temperature solution. The 99.9% of THF in the mixed solvents appears as 100% in the X-axis. I_0/I is the ratio between the initial and final intensities of the emission maxima.

emission peaks, around 450 and 470 nm when titrating 1 mL of THF into 10 mL of polymer aqueous solution (9% of THF in the system). It could be inferred that even only increasing 1% of THF in the system, more polymer in aggregated state responsible for 470 nm changed into non-aggregated state responsible for 450 nm emission.

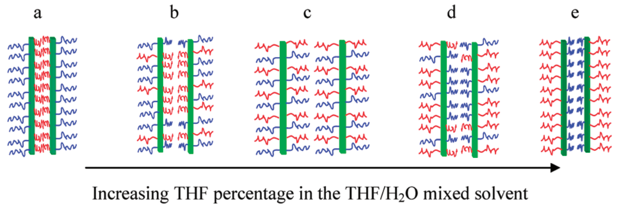

Figure 8. Schematic diagram for side group arrangement and relative distance between the polymer backbones in the mixed solvent with increasing the THF percentage. This diagram does not represent the exact packing pattern of the polymer chains. Blue lines denote the hydrophilic sulfonate groups, and the red lines denote the hydrophobic groups. (a) Aggregated, low I_0, fast EM; (b) compacted but nonaggregated, high I_0, fast EM; (c) loose assembly, high I_0, slow EM; (d) compacted but nonaggregated, high I_0, fast EM; (e) aggregated, low I_0, fast EM.

Optimization for Sensing Application. To further optimize such polymer systems for sensor application, freshly prepared dilute Fe^{3+}, Cr^{3+}, Al^{3+}, and H$^+$ aqueous solutions were added into H$_2$O/THF (1/1 in volume, Figure 6). Results from the photophysical study showed that the fluorescence was almost totally quenched by Fe^{3+}, which was consistent with the literature.[9] In addition, Cr^{3+} caused partial fluorescence quenching, while Al^{3+} led to red shift of the emission maximum accompany with the quenching. The red shift could be attributed to the metal-induced aggregation of the polymer chains.[9] The possibility of quenching by the protons released from the hydrolysis of cations in water could be ruled out since direct addition of H$^+$ showed a negligible effect on the emission.[39] Considering a possibility of ligand–metal charge transfer (LMCT) which would lead to metal complex absorption at the excitation wavelength in the case of the chloride as the counterion of Fe^{3+}, the same titration of Fe^{3+} into the polymer solution in THF/H$_2$O was carried out and UV–vis spectra were recorded. There was very slight change in the absorbance at the excitation wavelength (see Supporting Information for the UV–vis spectra). A conclusion could be made that the slight increase (9%) in the absorbance will not be the main reason for such great decrease in the emission. The decrease in the emission intensity could be attributed to the cation quenching instead of the increased self-absorption. Thus, the following cation titration was carried out using Fe^{3+} as the representative analyte since it was demonstrated to be effectively detected, aiming to obtain an optimized PPESO$_3$OR sensing system in mixed solvent.

The Fe^{3+} titration was carried out toward PPESO$_3$OR in solution with different H$_2$O/THF ratios (see Supporting Information for all the emission spectra). Generally, a slight blue shift in the emission maximum accompanied by the intensity quenching was found in all systems, which precluded the metal-induced aggregation as mentioned in some systems.[6] The blue shift could be attributed to that the quenching first began with the low-energy emission species.[40–46] Interestingly, much higher quenching efficiency was realized in the water-rich systems than the THF-rich system, with as least 30% fluorescence quenching by addition of 1 μM of Fe^{3+}. The highest quenching effect for PPESO$_3$OR, with an I_0/I of 148 toward 10 μM of Fe^{3+}, was achieved in the mixed solvent with 30% of THF (Figure 7). This quenching value was quite high compared to other conjugated polymer sensing systems[6,8,9] In addition, relatively fast response toward cations at low concentration (≤ 2 μM) in the system having 0–10% of THF.

In general, the ready access to the receptors, the high initial fluorescence (I_0), and the fast energy migration (EM) would be favorable for achieving high sensitivity in a fluorescence quenching sensory system. However, these influence factors would not reach the best situation simultaneously for the sensing application simply by increasing or decreasing THF percentage in the mixed solvent. Figure 8 illustrates the probable side-chain arrangement and relative distance between the polymer backbones in the mixed solvent with increasing THF percentage. Obviously, the sulfonate groups were more accessible in the water-rich systems (Figure 8a,b) but more buried inside in the THF-rich systems (Figure 8d,e). However, the high initial fluorescence could only be obtained in the nonaggregated systems (Figure 8b–d), while the rate of energy migration usually would be faster in the closely packed polymer assemblies (Figure 8a,b,d,e) since the intermolecular migration existed other than the intramolecular migration.[3,6] Taking all the factors into account, the highest sensitivity would be achieved in the solvents having 20–30% of THF (Figure 8b). In those systems, the polymer chains were compacted to a certain degree at which the intermolecular energy migration could exist while self-quenching was avoided since no strong aggregation was found at the photophysical level.[40,42,43] Meanwhile, there were sufficient sulfonate groups extending out of the polymer assembly to interact with cations. Lower sensitivity in other systems with high initial fluorescence, such as the systems having 50−80% of THF in the solvent, could be mainly attributed to the less exposure of receptors to the analytes. Additionally, the even greater intermolecular energy migration resulted from strong aggregation (Figure 8a) could explain the relatively fast response toward cations at low concentration ($\leq 2\ \mu$M) in the system having 0−10% of THF. The asymmetry from the sensing results across the whole range of THF percentage was also consistent with the amphiphibilic character of the conjugated polymer. Several models for the similar aggregation−nonaggregation−aggregation observation were advanced in the literature.[26,28] Especially, Burrow et al.[28] presented their detailed study by molecular dynamics simulation correlated with the fluorescence and other techniques, giving a nice model for their system. However, the PPESO$_3$OR system was different from other systems due to the coexistence of the hydrophilic side and hydrophobic side groups. Investigation into the exact structure of the polymer assembly and the mode-of-action are currently underway in our lab.

Conclusion

In conclusion, a conjugated polymer with hydrophilic sulfonate and hydrophobic alkoxyl side groups was successfully synthesized. The polymer was found to have a tightly aggregated state, from the photophysical study, in aqueous solution or 99.9% of THF, and changed into nonaggregated states in the H$_2$O/THF mixed solvents. The reversible transition between the aggregated and nonaggregated states was further confirmed by titration of THF into polymer aqueous solution or titration of water into polymer in 99.9% of THF. The Fe^{3+} titration into the polymer solutions showed that the highest sensitivity was achieved in the system with 30% of THF in the mixed solvent, and the water-rich systems were more sensitive than the THF-rich systems. This result was explained by considering the combination of several factors, i.e., the initial emission intensity, the rate of energy migration, and the accessibility of the sulfonate receptors. The symmetrical aggregation−nonaggregation inversion and the asymmetrical cation sensitivity were observed across the whole range of H$_2$O/THF compositions. The symmetry in the structure resulted in the symmetry in the photophysics and the asymmetry in the functionality resulted in the asymmetry in the sensitivity, which was consistent with the molecular design. Future work would be directed to find out the exact assembly structure in these systems and modification of the polymer side groups for sensing other analytes based on the enhanced photophysical tunability owned by the A$_2$B$_2$ type of conjugated polymers.

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Supporting Information Available: FTIR spectra as well as some absorption and emission spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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