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Photophysical Studies of Anion-Induced Colorimetric Response and Amplified Fluorescence Quenching in Dipyrrolylquinoxaline-Containing Conjugated Polymers

Cheng-Yang Wu,[a] Min-Shen Chen,[a, b] Chih-An Lin,[a] Su-Ching Lin,[a] and Shih-Sheng Sun*[a]

Abstract: The dipyrrolylquinoxaline (DPQ)-containing monomer and polymers were synthesized and employed as chromogenic and fluorescent chemosensors for inorganic anions. We have found that in the presence of fluoride or pyrophosphate, the receptors do not form hydrogen bonds between the pyrrole protons and anions. The colorimetric responses and fluorescence quenching in these chemosensors are indeed the result of deprotonation of the N-H proton. The anion selectivity is primarily determined by the relative basicity of anions. The sensitivity of DPQ-based chemosensor was found to display a 34-fold enhancement by incorporation into the conjugated polymer. The anion-induced deprotonation generates low-energy, non-fluorescent trapping sites and is responsible for the signal amplification where the quenching of the excited state occurs from the deprotonated DPQ site in the network by rapid exciton migration along the polymeric backbone.

Keywords: absorption • anions • fluorescence • polymers • receptors

Introduction

The development of anion-sensing systems is of considerable current interest because of the biological, environmental, and pharmaceutical concerns.[1] Design and synthesis of receptors, which are sensitive to interactions between the host and guest molecules and able to exhibit either a chromogenic and/or fluorogenic response upon receptor–anion interaction, has particularly gained considerable recent attention.[2] The appeal of sensors containing luminescence chromophores stems from the high sensitivity of luminescence detection compared to other spectroscopic methods. The binding of anionic species to the recognition sites leads to changes in certain properties of the receptors (such as fluorescence intensity, wavelength, lifetime) that then serve as an indicator of guest association.

The integration of receptor moieties into fluorescent conjugated polymer is particularly attractive in terms of a signal amplification effect.[3] Because of the delocalization of the π–π electrons in the conjugated backbones of polymers, their fluorescence can be efficiently quenched through an exciton migration process. Thus, fluorescence sensing is amplified upon analyte–receptor interaction because of this "molecular wire effect", which requires much lower analyte concentration than its monomer unit. Although numerous fluorescent conjugated polymers have been documented in the literature for amplified analyte sensing,[3] most cases are based on non-specific electrostatic interactions, which provide strong static polymer–quencher binding in order to compensate the inefficient dynamic quenching for fluorescent materials with short excited state lifetimes. Moreover, only a few examples have been reported for sensing anions.[4]

The strategy we employed to improve the specific analyte–polymer interaction is to incorporate the receptors ca-

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pable of interacting with targeted anions. The anion-recognition motif we chose to introduce into fluorescent poly(phenylene ethynylene) is dipyrrolylquinoxaline (DPQ). Since DPQ was first introduced by Sessler and co-workers for efficient fluoride sensor in 1999,[5] its judicious designed derivatives have been proved to be highly selective and sensitive sensors to various anions.[4c,6] In most cases, both color and fluorescence intensity of DPQ or its derivatives changed dramatically upon addition of fluoride into their solution. The bathochromic shift of absorption spectra as well as fluorescence quenching was ascribed to the formation of hydrogen bonding between anion and pyrrole protons. Nevertheless, there was no further experimental evidence to support this argument. In fact, the hydrogen-bonding interaction can be regarded as an "incipient" and "frozen" proton-transfer process.[7] It seems to be unlikely to bring about such large electronic perturbation (typical bathochromic shift of $\approx 5000\,\text{cm}^{-1}$ upon addition of fluoride anions) by simple hydrogen-bonding interactions. In this paper, we present our studies on the mechanism of spectral shift and fluorescence quenching in DPQ-based anion-sensing systems. We also demonstrated that the sensitivity of DPQ-based sensors can be greatly enhanced by incorporation into the conjugated poly(phenylene ethynylene) polymer by efficient exciton migration along the polymer backbone.

Results and Discussion

Synthesis and characterization: Palladium-catalyzed Sonogashira cross-coupling procedures were employed in the synthesis of all of the DPQ-based monomer and polymers.[8] Schemes 1 and 2 summarize the synthetic procedures.

Photophysical properties: The photophysical parameters of all compounds studied here are summarized in Table 1. Figure 1 shows the absorption and emission spectra of monomer **1** and polymer **3**. The absorption spectra of these compounds exhibit two bands in the UV and near UV region that represent typical absorptions from π–π* transitions. For monomer **1**, the electron density of HOMO is mainly localized on the pyrrole ring whereas in the LUMO the electron density is accumulated on the quinoxaline nitrogen according to the ZINDO calculation. All compounds exhibit very bright luminescence with excited state lifetimes in the range of a few nanoseconds that are typical of singlet emission.[9] The fluorescence intensity of compounds **1**–**3** is sensitive to the presence of proton donors in solution. The addition of water or acetic acid efficiently quenches the fluorescence of all three compounds presumably due to the proton transfer to the lowest π–π* excited state where the LUMO is localized on the quinoxaline nitrogen.[10] The absorption and emission spectra are not very sensitive to the degrees of polymerization but do show some red shift with a higher degree of polymerization. This phenomenon is consistent with the fact that the band gap of a conductive polymer is determined by low degrees of polymerization.[11]

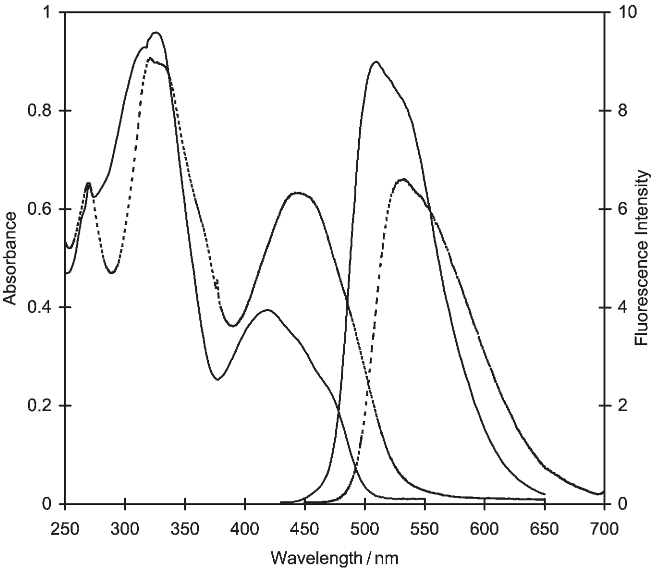
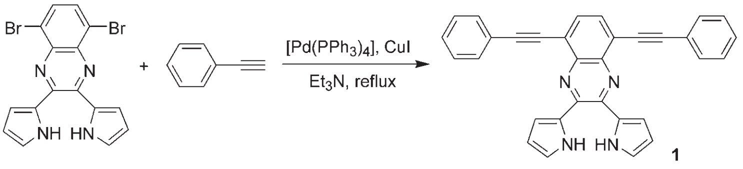
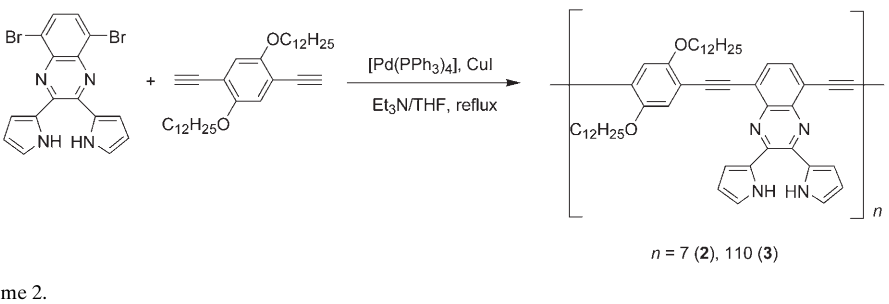


Figure 1. Absorption and fluorescence spectra of monomer **1** (——) and polymer **3** (•••••) in CH_2Cl_2 solution.



Scheme 1.



Scheme 2.

Anion-induced colorimetric response and fluorescence quenching: Figure 2 shows the absorption spectra of monomer **1** upon addition of fluoride. Upon addition of fluoride or pyrophosphate anions in CH_2Cl_2 solution, the absorption bands of monomer **1** at 413 nm gradually decreases and a new band centered at 540 nm starts to develop, indicating strong ground state interactions between monomer **1** and these anions. The clear isosbestic points indicate a clean conversion throughout the titration process. Concomitantly, the fluorescence intensity of monomer **1** at 523 nm decreases as the concentration of fluoride or pyrophosphate anions increases (see inset of Figure 2 for the case of fluoride). Monomer **1** also experienced a colorimetric response and fluorescence quenching toward acetate or cyanide anions, albeit the effect was much minor than fluoride and pyrophosphate anions. Conversely, nearly no detectable color changes or fluorescence quenching are observed upon addition of large excess of chloride, bromide, iodide, hydrogen phosphate, and nitrate. The ground-state association constants obtained from the absorption spectral titration are listed in Table 2.

Table 2. Ground-state association constants[a] and excited state quenching constants[b] in CH_2Cl_2 solution at 293 K.

Sensor	Anion	Association constants/M^{-1}	Quenching constants K_{SV}/M^{-1}
1	Cl^-, Br^-, I^-, $H_2PO_4^-$, NO_3^-	<10	<10
	OAc^-	50	40
	CN^-	310	150
	F^-	2.52×10^3	1.68×10^4
	$HP_2O_7^{3-}$	1.44×10^3	1.12×10^4
2	F^-		7.02×10^4
	$HP_2O_7^{3-}$		4.93×10^4
3	F^-		5.20×10^5
	$HP_2O_7^{3-}$		3.80×10^5

[a] Derived from absorption spectral titrations. [b] Derived from fluorescence spectral titrations.

Table 1. Absorption and emission spectral data in CH_2Cl_2 at 293 K.

Compounds	Absorption λ_{max}/nm ($\varepsilon\times10^{-3}$/$M^{-1}cm^{-1}$)	Emission[a] λ_{em}/nm	Φ_{em}	τ/ns
1	322 (43.3), 413 (18.9)	523	0.53	3.6
2	321, 446	542	0.37	2.6
3	324, 450	548	0.26	2.4

[a] $\lambda_{ex}=360$ nm.

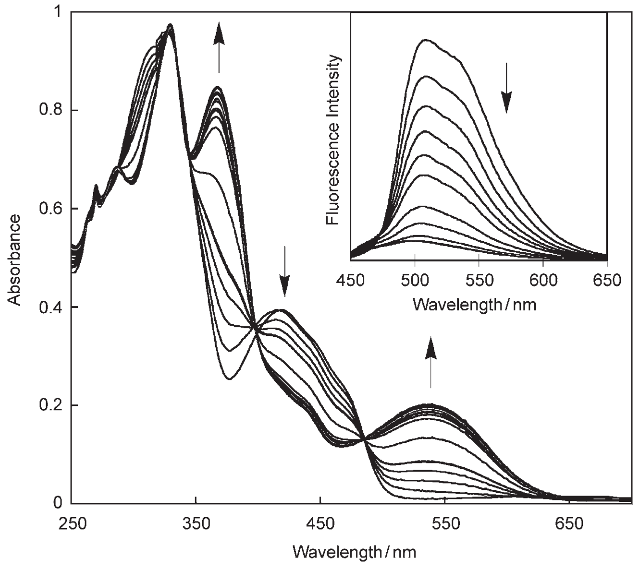
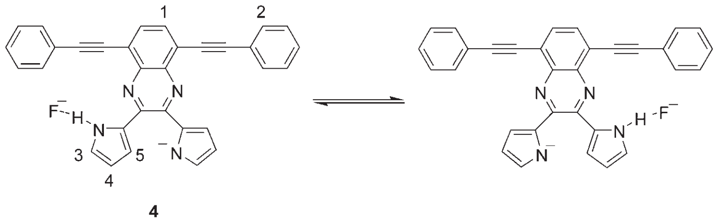


Figure 2. Absorption spectra changes of monomer **1** titrated with Bu_4NF in CH_2Cl_2 solution. Inset shows the respective fluorescence spectral changes.

It was postulated that the anion-induced colorimetric response of DPQ and its derivatives was a result of the formation of hydrogen bond between anion and pyrrole protons and the perturbation in the orbital overlap between the pyrrole and quinoxaline moiety while the observed fluorescence quenching was left unexplained.[5] It seems to be unlikely that pure hydrogen-bonding interactions could result in such large electronic perturbation (bathochromic shift of $\approx$5000 cm^{-1} upon addition of fluoride anion). In fact, the hydrogen-bonding interaction can be regarded as an "incipient" and "frozen" proton-transfer process.[7] The pyrrole protons may undergo deprotonation with appropriate anions in solution. Very recently, a number of fluorogenic and/or chromogenic anion sensors comprising recognition moieties with acidic protons such as urea, thiourea, or amide have been reported to undergo an anion-induced deprotonation.[12] The observed colorimetric responses in these reports were primarily due to the transformation from the native sensing molecules to their deprotonated species in solution.

To further elucidate the nature of the intermolecular interactions between the monomer **1** and fluoride anion, the ^1H NMR titration experiments were conducted in [D$_6$]DMSO solution. Figure 3 shows the ^1H NMR spectra of monomer **1** and its complex with different fluoride anion concentrations. Upon addition of fluoride, the pyrrole N-H signal at 11.2 ppm gradually broaden and completely disappeared after the addition of 2 equiv of F^-. Meanwhile, new peaks at δ 20.6 and 16.1 ppm started to appear. The triplet resonance at 16.1 ppm is the characteristic resonance of bifluoride (HF_2^-) while the singlet peak at 20.6 ppm is assigned to the formation of hydrogen-bonded complex between deprotonated **1** and F^- (**1**$-H^+ + F^-$, compound **4**, see below).[13] Notably, the resonance of all protons except the β protons of pyrrole (H_5) upfield shift indicating the through-bond effect exerted by N-H deprotonation. On the other hand, the H_5 proton, which is the closest atom to the negatively charged nitrogen, experiences a strong through-space electrostatic interaction and the resonance undergoes a downfield shift of 1.01 ppm.[14] A similar pattern was also observed on titration with pyrophosphate anion.



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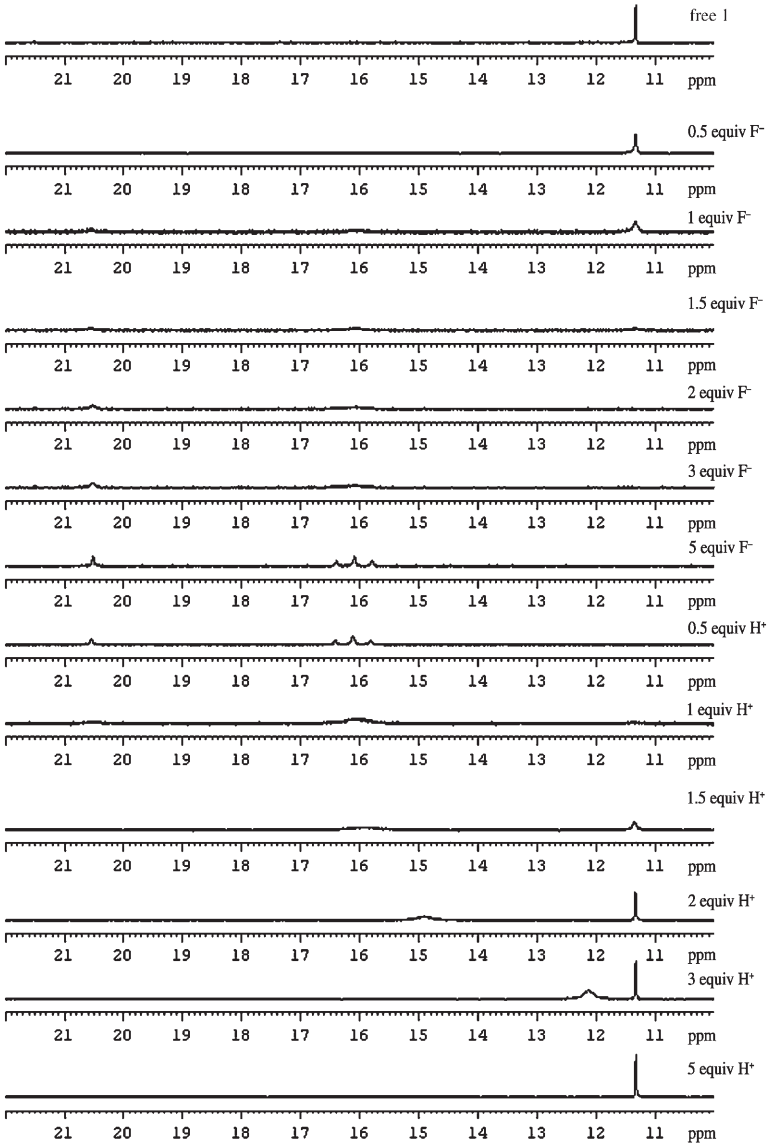

Figure 3. Plots of ^{1}H NMR spectra of monomer **1** in [D$_6$]DMSO after addition of various quantities of Bu_4NF to demonstrate the reversible nature of the interaction between the receptor and fluoride.

The formation of deprotonation product is further confirmed by the ESI-MS spectra with the molecular peaks of $[\mathbf{1}-H^{+}+2Bu_4N^{+}]^{+}$ at 944.56 (calculated m/z 944.45) and $[\mathbf{1}-H^{+}+F^{-}+3Bu_4N^{+}]^{+}$ at 1206.46 (calculated m/z 1205.91) in the mixture of **1** and Bu_4NF.[14] Semiempirical ZINDO calculations also support the arguments that the colorimetric response is due to the formation of deprotonated **1**. Figure 4 compares the absorption spectra of **1**, $\mathbf{1}\cdot F^{-}$, and $\mathbf{1}-H^{+}$ on the basis of the ZINDO calculations. The enhanced π-delocalization upon deprotonation is believed to be responsible for the substantial bathochromic shift (413 to 540 nm) of the lowest energy π–π* transition. Moreover, the proton dissociation–association process is fully reversible. The ^{1}H NMR indicated that the intact monomer **1** could be fully recovered by adding equal equivalent of trifluoroacetic acid to the F^{-} containing solution (see Figure 3). Meanwhile, the absorption spectra and fluorescence spectra also converted back to original profiles upon addition of acid. The equilibrium constants derived from the absorption spectral titration are in the order of $F^{-} > HP_2O_7^{-3} > CN^{-} > OAc^{-} > H_2PO_4^{-} \approx Cl^{-} \approx Br^{-} \approx I^{-} \approx NO_3^{-}$ and qualitatively correlated with the basicity of these anions.

The mechanism of fluorescence quenching in the presence of fluoride or pyrophosphate anions is somewhat ambiguous. Stern–Volmer quenching constants of the measured fluorescence intensities versus anion concentration are collected in Table 2. Again, the quenching constants are in line with the equilibrium constants derived from absorption spectral titrations. In addition, measurements of the lifetimes as a function of anion concentration show no changes within experimental error. Thus, it is apparent that the deprotonated species $[\mathbf{1}-H^{+}]^{-}$ is either nonfluorescent in solution or its fluorescence lifetime is too short to be detected by our instrument (< 20 ps). In either way this implies the deprotonated species $[\mathbf{1}-H^{+}]^{-}$ exhibits rapid radiationless decay from the excited state. It is reasonable to suggest that the charged nature of $[\mathbf{1}-H^{+}]^{-}$ is likely to result in a greater degree of distortion between its excited and the ground state potential surfaces compared with its neutral form of **1**. The smaller energy gap between the ground and excited states as well as the greater distortion of the excited state potential surface is expected to increase the probability of radiationless transitions as predicted by energy gap law.[9,15] In addition, the significant overlap between the fluorescence spectrum of **1** and absorption spectrum of $[\mathbf{1}-H^{+}]^{-}$ also facilitates the inner filter effect and further enhances the fluorescence quenching.[16]

Amplified fluorescence quenching in conjugated polymers: Pioneered by Swager and co-workers, the strategy of employing fluorescent conjugated polymer with judicious design of pendant recognition moieties has been successfully demonstrated; they were able to amplify the signal transduction events effectively as a result of rapid exciton migration along the polymeric backbone.[3,4,11,17] We reasoned that

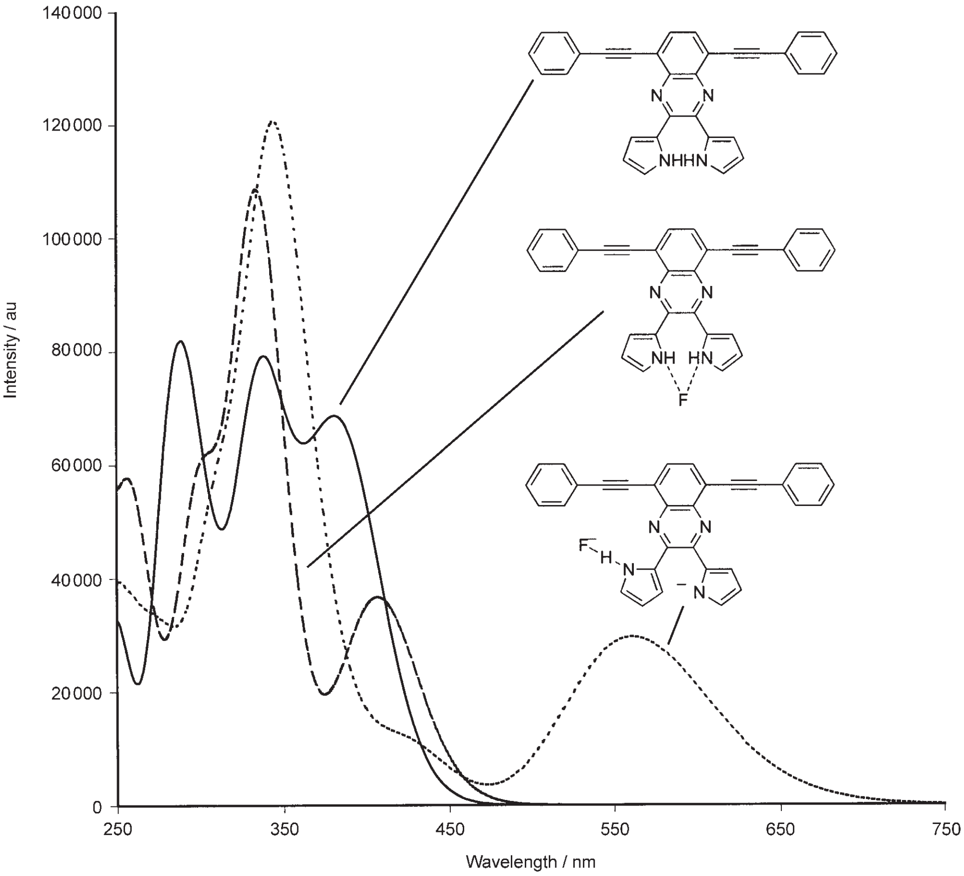

Figure 4. Simulated absorption spectra of **1** (——), **1**+F$^-$ (-----), and deprotonated **1**+F$^-$ (•••••).

DPQ would be a perfect candidate to use this strategy. Upon addition of fluoride or pyrophosphate anions, the resulting deprotonated DPQ unit will form a low-energy, nonfluorescent energy-trapping site in an array of DPQs interconnected by polyconjugated macromolecules. The DPQ sites are bound within the conjugated framework of the polymer structure so that quenching of the excited state occurs from the deprotonated DPQ site in the network by rapid exciton migration.[18] The result is an amplified fluorescence quenching response even at very low quencher concentrations, since binding of only one of the many possible receptor sites results in complete quenching of the polymer-based fluorescence.

Similar colorimetric responses were observed upon addition of fluoride or pyrophosphate anions to polymers **2** or **3** where the instantaneous color changes from yellow to red in polymers **2** or **3** were also ascribed to the anion-induced deprotonation (see Figure 5 for the case of polymer **3**). As expected, the sensitivity of anion-induced fluorescence quenching is significantly enhanced in the cases of polymers **2** and **3** compared with monomer **1**. Anzenbacher and coworkers reported that the p-doped electropolymerized DPQ-based polymers exhibited enhanced affinity toward anions which was ascribed to stronger hydrogen bonding between DPQ unit and anions upon doping positive charge into polymer.[4c,6h] In fact, we believe that the observed affinity enhancement is simply due to the higher proton acidity of DPQ unit upon p-doping which allows easier deprotonation by the anions.

The Stern–Volmer plots of polymers **2** and **3** with addition of fluoride or pyrophosphate all display linear relationships. Figure 6 shows the Stern–Volmer plots of polymer **3** with addition of F$^-$. Again, the fluorescence lifetimes of the polymer solution do not vary with the concentrations of the anion, indicating that a statically quenched polymer–anion complexes dominates the fluorescence quenching mechanism in these systems. The quenching constants derived from the Stern–Volmer equation are also included in Table 2. These results clearly demonstrated that the conjugated polymer with about ten-repeating recognition sites is able to induce substantial quenching effect with the sensitivity enhancement up to 34-fold over corresponding monomeric sensor. Our findings also provide the implication that many reported small molecule fluorescence anion-sensing systems based on simple anion-induced proton dissociation process are all potential

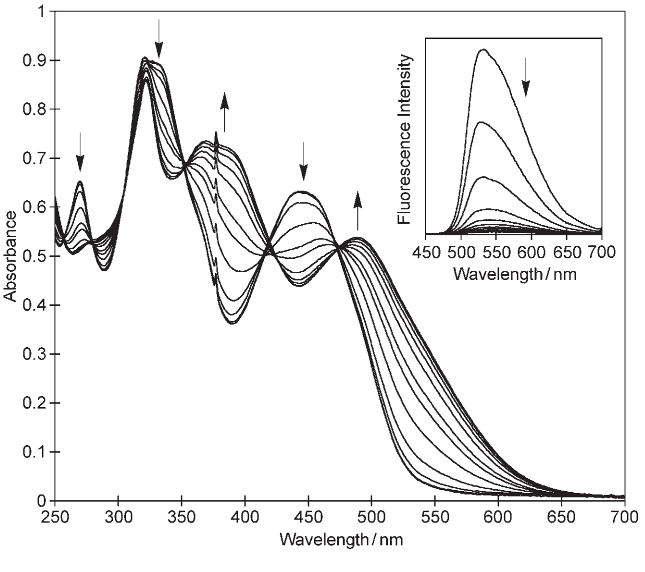

Figure 5. Absorption spectra changes of polymer **3** titrated with Bu_4NF in CH_2Cl_2 solution. Inset shows the respective fluorescence spectral changes.

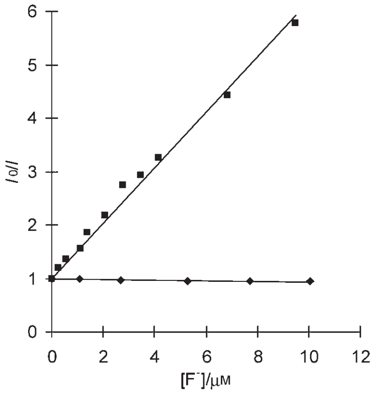

Figure 6. Stern–Volmer plots of polymer **3** with addition of F^-, ■: I_0/I, ◆: τ_0/τ.

candidates for signal amplification by incorporation into polymeric backbones.

Conclusions

In summary, the origin of anion-induced colorimetric response and fluorescence quenching in DPQ-based chemosensor has been demonstrated to be the anion-induced deprotonation by a variety experimental evidences and semiempirical calculations. The anion selectivity is primarily determined by the relative basicity of anions. The sensing system is fully reversible upon addition of equal equivalent of acid. The sensitivity of DPQ-based chemosensor can be easily enhanced by incorporation into conjugated polymer. The anion-induced deprotonation generates low-energy, non-fluorescent trapping sites where the quenching of the excited state occurs from the deprotonated DPQ site in the network via rapid exciton migration along the polymeric backbone.

Experimental Section

Materials and general procedures: The starting materials, 5,8-dibromo-2,3-di(1*H*-2-pyrrolyl)quinoxaline[6f] and 1,4-bis(dodecyloxy)-2,5-diethynylbenzene,[19] were prepared according to published methods. Dichloromethane was distilled over calcium hydride. Tetrahydrofuran (THF) and diethyl ether were distilled over sodium/benzophenone. All solvents were distilled under nitrogen and saturated with nitrogen prior to use. All other chemical reagents were commercially available and used without further purification unless otherwise noted. Flash column chromatography was carried out with 230–400 mesh silica gel from Merck by using the wet-packing method. NMR spectra were recorded on either a Bruker AMX400 (400.168 MHz for ^{1}H and 100.622 MHz for ^{13}C) or a Bruker AV500 spectrometer (499.773 MHz for ^{1}H, 125.669 MHz for ^{13}C). ^{1}H and ^{13}C chemical shifts are reported in ppm downfield from tetramethylsilane (TMS, δ scale) with the solvent resonances as internal standards. Electrospray mass spectra were obtained by using a Thermo Finnigan LCQ mass spectrometer equipped with an electrospray interface.

Emission spectra were recorded in air-equilibrated CH_2Cl_2 solution at 293 K with a Fluorolog II photoluminescence spectrometer. The emission spectra were collected on samples with OD $\approx$0.1 at the excitation wavelength. UV-visible spectra were checked before and after irradiation to monitor possible sample degradation. Luminescence quantum yields were calculated relative to 9,10-diphenylanthracene in cyclohexane solution ($\Phi_{em}=0.95$).[20] Corrected emission spectra were used for the quantum yield measurements. Luminescence quantum yields were taken as the average of three separate determinations and were reproducible to within 10%.

Fluorescence lifetimes were measured on an Edinburgh Instruments Mini-τ single photon counting lifetime spectrometer. The samples were excited at 370 nm with a diode laser. Nonlinear least squares fitting of the decay curves were performed with the Levenburg–Marquardt algorithm and implemented by the Edinburgh Instruments T900 software. The errors for fitted lifetimes were estimated to be within 10%.

The molecular weights of the emitting polymers were estimated by gel permeation chromatography (GPC). A JASCO PU-1580 HPLC pump delivered the deoxygenated THF mobile phase at a flow rate of 1.00 mL min^{-1}. All samples were prepared in THF. Data points were collected every 0.25 seconds, and molecular weights were calculated relative to polystyrene standards.

Fluorescence quenching studies were performed using a 2.5 mL emitting sample solution in CH_2Cl_2 titrated with a sample of the quenchers prepared with the same emitting sample solution. Emission intensity was monitored by integration of the spectrum.

Semiempirical ZINDO calculation was performed to estimate the HOMO–LUMO gap and the corresponding absorption wavelength. The structure was first optimized by semiempirical AM1 calculations. Subsequently, the difference between electron affinity and ionization potential was calculated employing ZINDO using the program package CAChe.[21]

Binding constants for a 1:1 complexation determined by UV/Vis titrations were obtained according to Equation (1):[22]

$$A = K_0 + \{(A_{\lim} - A_0)/2[R_0]\}([R_0] + [c_A] + 1/K + \{([R_0] + [c_A] + 1/K)^2 - 4[R_0][c_A]\}^{1/2}) \tag{1}$$

where A_0 and A are the absorbance of the receptor at a selected wavelength in the absence and presence of the anion, respectively, $[R_0]$ is the total concentration of the receptor, $[c_A]$ is the concentration of the anion, $A_{\lim}$ is the limiting value of absorbance in the presence of excess anion, and K is the binding constant.

Fluorescence quenching constants determined by fluorescence intensity or excited state lifetime were obtained by Stern–Volmer equation:[16]

$$I_0/I \text{ or } \tau_0/\tau = 1 + K_{SV}[Q] \tag{2}$$

where I_0 and τ_0 are the fluorescence intensity and excited state lifetime without added quencher (anion), respectively, I and τ are the fluorescence intensity and excited state lifetime with added quencher (anion), respectively, and K_{SV} is the Stern–Volmer constant.

Synthesis

5,8-Diphenylethynyl-2,3-bis(1*H*-pyrrol-2-yl)quinoxaline (1): Under an atmosphere of nitrogen, a 50 mL Schlenk flask equipped with a magnetic stir bar and a refluxed condenser was charged with phenylacetylene (0.23 g, 2.2 mmol), 5,8-dibromo-2,3-di(1*H*-2-pyrrolyl)quinoxaline (0.42 g, 1.0 mmol), $[Pd(PPh_3)_4]$ (120 mg, 0.1 mmol), CuI (20 mg, 0.1 mmol), and NEt_3 (10 mL) and heated under reflux for 24 h. After the reaction, the volatile solvent was removed under reduced pressure. Subsequently, water (100 mL) was added and the brown suspension was extracted with CH_2Cl_2 (100 mL × 3). The organic layer was collected, dried over $MgSO_4$, filtered through a short neutral alumina column, and then evaporated to dryness. The resulting brown residue was dissolved in CH_2Cl_2 and loaded on silica gel (5 cm × 20 cm) and subjected to column chromatography with CH_2Cl_2/hexanes 1:1. The desired product eluted as a yellow band which was collected. The solvent was evaporated on a rotary evaporator to yield a yellow solid (0.22 g, 47%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.85 (s, 2H), 7.73 (s, 2H), 7.64 (dd, 4H, $^3J=7.8$ Hz, $^4J=2.2$ Hz), 7.43–7.38 (m, 6H), 7.21 (m, 2H), 7.03 (m, 2H), 6.28 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.2, 139.5, 131.9, 131.7, 129.1, 128.6, 128.5, 123.4, 122.1, 122.0, 113.7, 110.2, 96.9, 86.8; HR-EI-MS: m/z: calcd for: 460.1688;

found: 460.1685 [M^+]; elemental analysis calcd (%) for $C_{32}H_{20}N_4$: C 83.46, H 4.38, N 12.17; found: C 83.26, H 4.14, N 12.44.

Polymer 2 (M_n=4280, PDI=1.75): Under an atmosphere of nitrogen, a 50 mL Schlenk flask equipped with a magnetic stir bar and a refluxed condenser was charged with 1,4-bis(dodecyloxy)-2,5-diethynylbenzene (0.25 g, 0.5 mmol), 5,8-dibromo-2,3-di(1*H*-2-pyrrolyl)quinoxaline (0.21 g, 0.5 mmol), [$Pd(PPh_3)_4$] (60 mg, 0.05 mmol), CuI (10 mg, 0.05 mmol), and NEt_3 (10 mL) and heated at 70 °C for 72 h. After the reaction, the volatile solvent was removed under reduced pressure. Subsequently, water (100 mL) was added and the brown suspension was extracted with CH_2Cl_2 (100 mL × 3). The organic layer was collected, dried over $MgSO_4$, filtered through a short neutral alumina column, and then evaporated to dryness. The residue was washed with MeOH until the solution was colorless to afford yellow solid (0.12 g, 47 %). ^1H NMR (400 MHz, $CDCl_3$): δ = 10.2 (s), 7.65 (brs), 7.51 (brs), 7.37 (m), 7.24 (m), 6.96 (m), 6.29 (s), 4.16 (m), 1.95–1.79 (m), 1.41–1.18 (m), 0.83 (brs); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.7, 133.0, 132.1, 132.0, 131.9, 131.6, 131.2, 128.5, 128.4, 122.6, 122.3, 114.3, 110.3, 94.1, 93.4, 92.0, 71.8, 69.6, 47.7, 31.9, 30.3, 29.6, 29.3, 29.2, 25.9, 22.7, 19.3, 14.1.

Polymer 3 (M_n=7720, PDI=3.26): Essentially the same procedure as above was employed to synthesize this compound. The polymer was isolated as a yellow solid (57 %). ^1H NMR (400 MHz, $CDCl_3$): δ = 9.86 (s), 7.65 (brs), 7.53 (brs), 7.45 (m), 7.23 (m), 7.06 (m), 6.27 (s), 4.09 (m), 1.85–1.78 (m), 1.49–1.14 (m), 0.85 (brs); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.7, 133.0, 132.1, 132.0, 131.9, 131.6, 131.2, 128.5, 128.4, 122.6, 122.3, 114.3, 110.3, 94.1, 93.4, 92.0, 71.8, 69.6, 47.7, 31.9, 30.3, 29.6, 29.3, 29.2, 25.9, 22.7, 19.3, 14.1.

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