

Anion Sensors in Polyurethane Matrices: Synergy Between Matrix and Sensor Materials Improves Selectivity of the Sensing Process

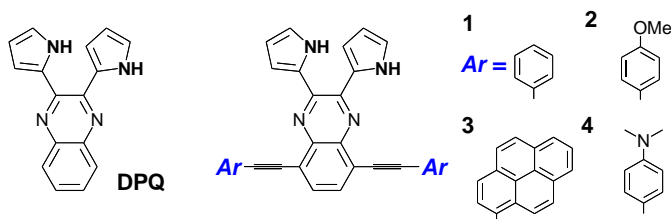
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INTRODUCTION

The significant role anions play in both biological systems and industrial processes¹ demands the development of highly sensitive and selective anion sensors capable of operating in various media, particularly in water. Numerous anion receptors and sensors utilizing hydrogen bonding have been synthesized.^{1,2} Hydrogen bonds, unlike electrostatic interactions, are directional and may be used to induce selectivity in an anion-sensor interaction. Unfortunately, hydrogen bonds are also relatively weak, which makes reliable sensing in strongly competitive media such as water difficult and less reliable in real-life applications. The downside of using anion receptors and sensors utilizing stronger but non-directional electrostatic interactions is, however, lower selectivity because all anions present in the medium are indiscriminately attracted to such receptors.

Here we present materials utilizing synergy between a polymer matrix and simple sensor moieties. These materials consist of blends of hydrogen-bond-based colorimetric anion sensors (2,3-di(pyrrole-2-yl)quinoxaline, DPQ)^{3,4} with extended conjugated chromophores embedded in hydrophilic polyurethane matrices. Anion sensors embedded in the hydrophilic polyurethane matrix have the advantage of water being stripped off hydrated anions thus removing the competing hydrogen bonding from water. The resulting semi-wet sensors may use both the change in color and in fluorescence as a signal output. We present multi-well micro-assays for small anions based on the polyurethane-embedded fluorescent sensors **1**, **2**, **3** and **4**. These assays use 0.2 μL of aqueous analytes in each well and respond with a response time of <30s.



DISCUSSION

Because fluorescence-based sensing is generally very sensitive, the performance of DPQ sensors may be improved by increasing the luminescence quantum yield (Φ_F) of the sensors. Also potential interference with other absorbing/emissive impurities may be avoided if one can tune the optical properties of the sensors. This is achieved by attaching extended conjugated moieties to the quinoxaline chromophore via an acetylenic spacer.

Studies in organic solution such as MeCN or DMSO confirm that fluorescence amplification is achieved through effective excited state delocalization along the conjugated arylene-ethynylene backbone. This is confirmed by the significant shift of the emission wavelength, as well as a two-fold increase in the fluorescence quantum yield and lifetime (Table 1).

Table 1. Optical Properties of Sensors 1-4 in Solution. ^a1 μM Solutions in Dichloromethane. ^b $\text{Mol}^{-1}\cdot\text{cm}^{-1}$; ^cDetermined Using Quinine Sulfate as a Standard

Sensor	A_{max} (ϵ) ^b	λ_F [nm]	Φ_F ^c	τ_F [ns]
DPQ	410 (1.2×10^4)	495	0.18	1.8
1	419 (2.1×10^4)	529	0.33	4.0
2	436 (2.6×10^4)	531	0.31	4.2
3	463 (2.3×10^4)	549	0.35	3.7
4	458 (3.3×10^4)	612	0.27	5.3

Anion binding studies in solution were performed by monitoring the changes in UV-Vis and steady-state emission spectra of sensors **1-4** upon addition of hydrated TBA salts of anions. The values of the sensor-anion affinity constants are listed in Table 2.

Table 2. Affinity Constants ($\text{dm}^3\cdot\text{mol}^{-1}$) for 1-4 (2.0 μM in MeCN) Derived from Fluorescence Titrations with Hydrated Anions. ^a1 μM Solutions in Dichloromethane. Pyrene-Based Sensor **1c** Showed Tendency to Aggregate in Acetonitrile

Sensor	Anion				
	F^-	Cl^-	CN^-	H_2PO_4^-	$\text{HP}_2\text{O}_7^{3-}$
DPQ	25 000	100	500	200	3 000
1	95 000	200	75 000	400	4 500
2	23 000	100	3 000	100	5 000
3 ^a	19 600	< 100	5 000	200	9,500
4	16 000	<50	2 000	400	5 000

Further application of the DPQ sensors is difficult because of their low compatibility with water, a natural solvent for most anions. DPQ sensors would require structural modifications that would render them water-compatible. Such transformations could decrease the anion affinity and could also be quite costly. For this reason, we decided to increase the water compatibility by embedding the DPQ sensors in hydrophilic polyurethane (PU) matrices.⁵⁻⁷ Hydrophilic polyurethanes were synthesized to take up a certain amount of water in equilibrium, bringing the soluble salts including an anion into a close contact with DPQ sensors embedded within the matrix.

In a way, the matrix extracts the anions from the bulk environment, together with a limited amount of water. The exact amount of water depends critically on the hydrophilicity of the matrix.

In order to study the anion-sensing properties of DPQ-PU materials we have fabricated a micro-well sensor chip, where we cast the solution of the DPQs embedded in the PUs. Due to the high emission of the sensors, the DPQ-PU materials are also highly emissive. Upon UV excitation (370 nm), the visible light emitted from the sensor material may be observed by a naked eye or recorded using a CCD camera-based detection system. The rapid response of the material, which is not "limited" by diffusion, is attributed to its small size and a thin sensor film.

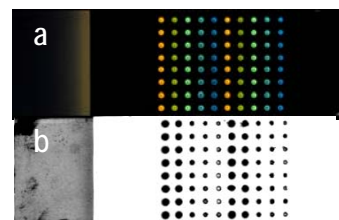


Figure 1. The sub-micro-assays shown below were read with two different detection systems: **a)** CCD camera image ($\lambda_{\text{exc}} \sim 365\text{nm}$). **b)** monochromatic image generated from a GE Typhoon Scanner ($\lambda_{\text{exc}} = 532\text{nm}$).

While the presence of pure water did not induce any change in the emission of the sensor, the addition of various anionic analytes

resulted in anion-specific quenching of fluorescence of the sensor materials.

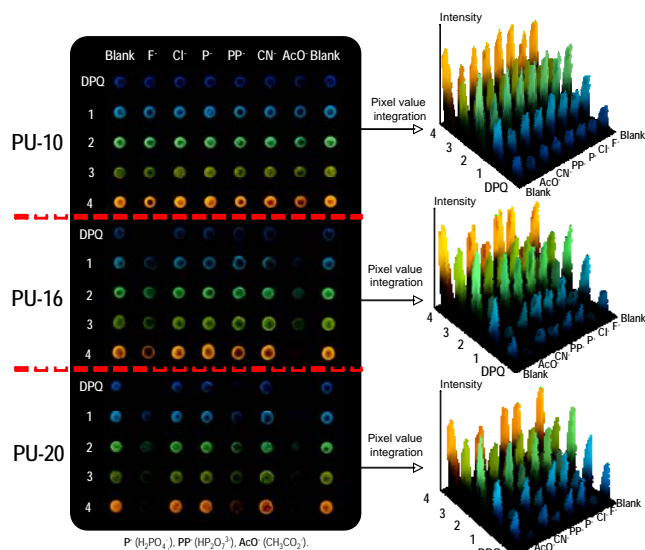


Figure 2. Anion-induced changes in fluorescence intensity upon addition of aqueous anion [$(^t\text{Bu})_4\text{N}$ salts] (200 nL, 10 ppm) to sensors 1-4 in PU-10, PU-16 and PU-20 (0.6 % weight).

It is also remarkable that the PU polymer matrix induces selectivity different than the one observed in solution (Table 2). For example, pyrophosphate can be detected in the PU-20 matrix but not in PU-16, nor PU-10.

The increasing concentration of the quenching anions results in an augmented quenching process. These experiments suggest the potential of assays for quantitative sensing of anions.

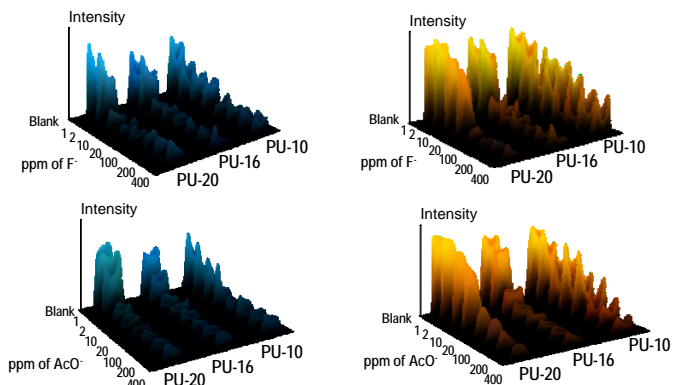


Figure 3. Response of sensors 1 and 4 in PU-10, PU-16 and PU-20, upon addition of 200 nL of anion solution at different concentrations (1-400 ppm).

Fluorimetric titrations of the sensor films with anions show the effect of the matrix on the sensing process. In the case of fluoride the change in the PU matrix does not show a significant difference in the quenching of the sensor-film. On the other hand, acetate shows clear preference for a less hydrophilic PU-16 sensor material. In the case of PU-20 even after the addition of an excess of acetate (100:1) further quenching of the film was not observed.

The fact that the response of the sensor material may be modulated by the degree of polymer hydrophilicity may be further used to tune the anion selectivity of the final sensor material. This aspect is of particular importance for anion sensing in complex analytes where competing anions may be present.

In summary, the use of synergy between hydrophilic matrices and anion sensors for sensing of aqueous analytes allows for using simpler and less expensive receptors and opens up new possibilities for the development of high performance anion sensors with good selectivity and response profiles at a fraction of cost of most anion sensors.

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