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# Aggregation induced FRET via Polymer-Surfactant Complexation: A New Strategy for the Detection of Spermine

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**ABSTRACT:** A new water-soluble cationic conjugated polymer [9,9-bis(6'-methyl imidazolium bromide)hexyl)fluorene-co-4,7-(2,1,3-benzothiadiazole)] (PFBT-MI) was designed and synthesized via Suzuki cross-coupling polymerization in good yields without any tedious purification steps. PFBT-MI showed excellent photophysical responses towards SDS and SDBS with a detection limit of 0.12 μM/ (34 ppb) and 0.13 μM/ (45 ppb) respectively. Furthermore, occurrence of FRET from the donor (fluorene) to acceptor (BT units), via surfactant induced aggregation results in naked-eye detection of these common anionic surfactants (SDS/SDBS) as the color changes from blue to yellowish green in aqueous solution. The polymer-surfactant nano-aggregates thus formed via electrostatic as well as hydrophobic interactions has been explored for the sensitive detection of spermine (considered as an excellent biomarker for early cancer diagnosis) with detection limit of 66 ppb (0.33 μM) which is much below the range 1-10 μM pertinent for the early diagnosis of cancer in urinary samples. This, highly sensitive technique would facilitate the direct and non-invasive detection of spermine from urine rapidly and is likely to have great significance in early cancer diagnosis.

## INTRODUCTION

Spermine, a biogenic polyamine, usually found in eukaryotic cells and body fluids, plays a vital role in the regulation of several cellular processes like cell growth and proliferation.[1-4] These polyamines are among the most abundant organic polycations found in human body and are known to be involved in numerous stages of protein synthesis, stabilization of nucleic acid conformations and cytoskeleton structures.[4] It has been observed that enhanced levels of spermine in urine and blood are liable to many types of cancer. Thus, it is regarded as an excellent biomarker for early cancer detection and an indicator for assessing the efficiency of cancer chemotherapy during the long-term continuation of patients.[5-11] Currently, spermine and its analogues are being detected using classical analytical methods *viz.* immunoassays, mass spectrometry, electrophoresis and chromatographic techniques.[5,12-15] Since, these techniques are complex, tedious, time consuming and expensive, establishment of an alternate fluorescent based method for selective and ultrasensitive detection of spermine in body fluids is highly significant in the present context.

Anionic surfactants comprising of non-polar alkyl chain (hydrophobic tail) and an anionic polar group (hydrophilic head), form a major source of environmental pollutant due to their widespread use in personal, home/car cleaning agents, industrial and agricultural processes.[16] Moreover, they are also known for their interaction with biomolecules like nucleic acids, proteins and peptides with the ability to even pierce cell membranes.[17-21] Among all anionic surfactants, sodium dodecyl benzenesulfonate (SDBS) and sodium dodecyl sulfate (SDS) are most abundant owing to their extensive industrial scale production and frequent applications in various sectors. Hence, their determination at very low levels in the waste water, food preparations, pharmaceuticals, as masking agents in drug-abuse, in biological mediums etc., is highly significant since they are considered as "emerging pollutants".[22,23] Apart from the efforts in developing methods to reduce their environmental impact, yet another key aspect is the introduction of new and improved strategy for their detection in the surroundings. Although, various sophisticated surfactant detection methods[24-27] are available, most of them are inefficient and suffer from severe drawbacks like employing large amounts of halogenated solvents, delay signal response, tedious procedures and irreproducibility. Hence, the development of more efficient and reliable method for trace detection of anionic surfactants that can overcome the limitations found in the existing methods is highly desirable.

Fluorescence technique is regarded superior among various detection methods owing to their simplicity, high sensitivity and rapid signal response time. In this context, few probes for sensing anionic surfactants have been established recently.[28-31] However, they usually depend on the change in the intensity of single emission band that might result in erratic quantitative analysis due to autofluorescence, environmental effects and instrumental fluctuation. A prospective solution to this problem is the development of suitable ratiometric probe that exhibit spectral shifts, since it provides a relative measurement of the intensities of two different emission bands and eliminate most of the possible artifacts. Interestingly, FRET assisted ratiometric detection of anionic surfactants (SDS and SDBS) using CPE has never been reported, thus, providing huge opportunities to be explored.

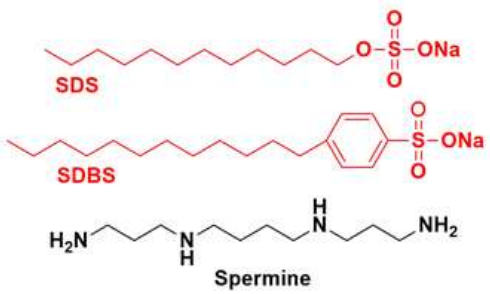
Recently, conjugated polyelectrolytes (CPEs) have emerged as excellent materials[32] in the field of sensing due to their numerous features such as remarkable sensi-

tivity, high quantum efficiency, photostability etc. These materials combine the optoelectronic properties of neutral conjugated polymers (CPs) as well as electrostatic behavior of polyelectrolytes, thus, providing an exceptional platform for the sensing of chemical and biological species.[33-44] The delocalized backbone chain of CPEs also favor rapid intra-chain and inter-chain energy transfer processes compared to small molecules.[45] However, the inter-chain Förster resonance energy transfer (FRET) is considered as more efficient than intra-chain FRET due to stronger electronic coupling and enhanced transfer range in the former[46-48] which is also highlighted by Bazan[49] and Swager's group[8] in their pioneering work on the detection of charged species. Thus, an alternate method for the detection of spermine and anionic surfactants comprising of CPE is highly significant.

Herein, we have developed a new water soluble cationic CP poly[9,9-bis(6'-methyl imidazolium bromide)hexyl) fluorene-co-4,7-(2,1,3-benzothiadiazole)] (PFBT-MI), comprising 20 mol % of benzothiadiazole (BT) via Suzuki polymerization method. The blue emitting polymer PFBT-MI displayed significant changes in its photophysical properties as well as morphology after selective interaction with anionic surfactants *viz.* SDS and SDBS followed by spermine. The formation of stable polymer-surfactant complex via Columbic as well as hydrophobic interaction induces the process of aggregation that enables the increment of local BT concentration in aqueous solution. This leads to the favorable inter-chain FRET from the donor (fluorene) to acceptor (BT units), giving rise to a blue-to-yellowish green emission that was subsequently utilized for the detection and quantification of SDS and SDBS in aqueous solution. Furthermore, the polymer-surfactant assembly was successfully used for the trace detection of biogenic amine spermine in urine specimens with high selectivity and sensitivity. To the best of our knowledge, this is the first report based on FRET assisted ratiometric detection of most common anionic surfactants (SDS and SDBS) viz-a-viz sensing of spermine using polymer-surfactant assembly.

## EXPERIMENTAL SECTION

**Materials and Instrument.** All chemicals were acquired from Aldrich, Merck, Ranbaxy (India) and were used as received. Structure of SDS, SDBS and spermine are shown in Scheme 1. UV-visible and emission spectra were recorded on a Perkin Elmer Lambda-25 and Horiba Fluoromax-4 spectrofluorometer, respectively using 10 mm path length quartz cuvettes with a slit width of 3 nm at room temperature. Milli-Q water was used in all sensing experiments. The $^1$H NMR (600 MHz and 400 MHz) and $^{13}$C NMR (150 MHz and 100 MHz) spectra were obtained on Bruker Ascend 600 spectrometer and Varian-AS400 NMR spectrometer, respectively. Gel permeable chromatography (GPC) was performed in Waters-2414 instrument (Polystyrene calibration). Zetasizer Nano ZS90, Model No. ZEN3690, Malvern was used to perform




**Scheme 1.** Structure of common anionic surfactants (SDS and SDBS) and spermine.

DLS based size and charge measurements. Morphological characterization was done using Zeiss sigma field emission scanning electron microscope (FESEM) at an accelerating voltage of 2 kV. Transmission electron microscopic (TEM) images were obtained on JEOL 2100 UHR-TEM instrument, operating at 200 KV.

**Synthesis of Monomer M1 and M2:** Monomers 2,7-dibromo-9,9-bis(6-bromohexyl)-9H-fluorene (M1) and 2,7-Bis[9,9′-bis(6″-bromohexyl)fluorenyl]-4,4,5,5-tetramethyl[1.3 .2]dioxaborolane (M2) were prepared using established procedure.[50]

**Synthesis of Poly[9,9-bis(6'-bromohexyl)fluorene-co-4,7-(2,1,3-benzothiadiazole)] (P1):** Polymer P1 was synthesized via reported procedure.[50] M1 (97.5 mg, 0.15 mmol), M2 (186.0 mg, 0.25 mmol), 4,7-dibromo-2,1,3-benzothiadiazole (29.0 mg, 0.1 mmol), [Pd(PPh$_3$)$_4$] (5 mg), and potassium carbonate (345 mg, 2.5 mmol) were kept in a 50 mL two neck round-bottom flask. A mixture of water (5 mL) and THF (15 mL) was added to the flask using syringe and degassed thrice by freeze thaw cycle to remove any oxygen. The reaction mixture was then stirred vigorously at 75°C for 24 h followed by precipitation into excess of methanol repeatedly. The precipitate was then filtered, washed and dried under vacuum for 12 h to afford the neutral dark brownish colored polymer (0.220 g, 70.0%).

$^1$H NMR (600 MHz, CDCl$_3$, δ): 8.06–7.47 (m), 7.96 (b), 7.87 (b), 7.69 (b), 7.52 (b), 7.47 (b), 3.30 (b), 2.16 (b), 1.93 (b), 1.69 (b), 1.26 (b), 0.88 (b), 0.71 (b), 0.59 (b).

$^{13}$C NMR (150 MHz, CDCl$_3$, δ): 154.57, 152.35, 139.25, 132.22, 130.52, 128.78, 126.23, 124.20, 121.77, 121.75, 121.40, 120.34, 55.73, 40.19, 34.13, 32.77, 29.85, 29.23, 27.91, 25.03, 23.63.

GPC in THF, polystyrene standard: $M_w$= 1.4103 × 10$^4$, PDI-2.1.

**Synthesis of Poly[9,9-bis(6'-methyl imidazolium bromide)hexyl)fluorene-co-4,7-(2,1,3 benzothiadiazole)] (PFBT-MI):** Brominated polymer P1 (0.05 g, 0.031 mmol, 1 eq.) dissolved in excess of 1-methyl imidazole was refluxed under stirring condition at 80°C for 24 h. The reaction mixture was then decanted into excess chloroform and stirred for 1 h to get precipitate. The yellow precipitate was then washed several times with chloroform to

remove trace quantities of methyl imidazole so as to obtain pure functionalized polymer PFBT-MI (0.043 g, 66.0%).

$^{1}$H NMR (600 MHz, $CD_3OD$, δ): 8.23–7.52 (m), 4.62 (b), 4.09 (b), 3.87 (m), 2.26 (b), 2.12 (b), 2.04 (b), 1.71 (b), 1.17 (b), 0.78 (b).

$^{13}$C NMR (150 MHz $CD_3OD$, δ): 154.45, 152.99, 151.82, 151.32, 140.34, 136.51, 136.28, 136.06, 130.57, 128.42, 126.26, 123.83, 122.65, 110.03, 55.60, 49.63, 44.83, 40.32, 39.85, 35.30, 29.77, 29.02, 25.92, 23.58.

**Preparation of Stock Solutions for Absorption and Fluorescence studies**. A stock solution of 10 mM for each analyte (surfactants, anions, metal ions, polyamines and various cancer biomarkers) was prepared in Milli-Q water and diluted to desired concentrations whenever required. A solution of PFBT-MI ($6.6 \times 10^{-6}$ M) in repeat units (RUs) in Milli-Q water was placed in a 3 mL cuvette (10 mm width) to record the fluorescence spectrum by exciting at 350 nm. Various analyte solutions were then introduced to monitor the changes in the fluorescence intensity. Similarly, the absorbance spectra of PFBT-MI ($6.6 \times 10^{-6}$ M) in Milli-Q water was recorded at room temperature in presence of SDS, SDBS and spermine to monitor the changes in absorbance.

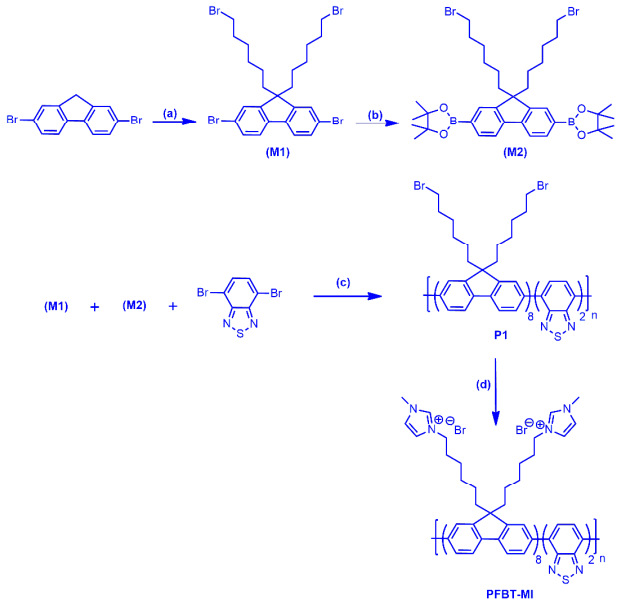
**Detection Limit Plot.** Different PFBT-MI samples (6.6 μM) each containing SDS (0, 2, 4, 6 and 8 μM) and SDBS (0, 2, 4, 6 and 8 μM) were prepared separately in Milli-Q water. The fluorescence spectrum for each sample was recorded by exciting at 350 nm at room temperature. The calibration curve for surfactants was then obtained from the plot of change in fluorescence intensity vs concentration of SDS/SDBS. The detection limit (LOD) value was determined using the equation (1);

$$LOD = 3 \times \sigma/k \quad \text{..... (1)}$$

where, k is slope of the curve and σ denotes the standard deviation for PFBT-MI solution intensity in the absence of surfactants. Similarly, various PFBT-MI/SDS (6.6 μM/18 μM) samples each containing spermine (0, 1.6, 3.3, 5.0 and 6.6 μM) were prepared and used to obtain the detection limit plot for spermine.

## RESULTS AND DISCUSSION

**Synthesis and Characterization of Polymer PFBT-MI.** The synthetic method for newly synthesized cationic polymer PFBT-MI is shown in Scheme 2. The monomers M1, M2 and 4,7-dibromo-2,1,3-benzothiadiazole were taken in the ratio of 0.3:0.5:0.2 and copolymerized by Suzuki cross-coupling polymerization to yield neutral polymer PFBT (P1). N-methyl imidazole was then strapped onto the side chain of PFBT using post functionalization method to obtain pure cationic polymer PFBT-MI in high yields without any tedious purification methods. PFBT-MI was found to be soluble in polar solvents like water, dimethyl sulfoxide, methanol etc. All the products were well characterized by $^{1}$H and $^{13}$C NMR spectroscopy (Figure S1-S8). The molecular weight ($M_w$) of the precursor polymer




**Scheme 2.** Synthesis of poly[9,9-bis(6′-methyl imidazolium bromide)hexyl)fluorene-co-4,7-(2,1,3-benzothiadiazole)] (PFBT-MI) (a) 1,6-dibromohexane, 50% aq. NaOH, TBAI, 70°C, 4 h. (b) Bis(pinacolato)diborane, [Pd(dppf)$Cl_2$], KOAc, dioxane, 85°C, 12 hr. (c) Tetrakistriphenylphosphine palladium(0), 2M $K_2CO_3$ (aq.), THF, reflux, 24 h. (d) PFBT, 1-methyl imidazole, reflux, 24 h.

PFBT was found to be 14103 g/mol with PDI-2.1 by GPC using THF as solvent and polystyrene as standard (Figure S9). The polymer PFBT-MI shows absorption maxima at 350 nm in aqueous solution that corresponds to the fluorine fragment of the polymer and a band ranging from 415-530 nm which is the characteristic of BT unit. PFBT-MI displays emission maxima at 415 nm ($\lambda_{ex}$-350 nm) with no peak in the region 500-650 nm, which indicates that polymer chains in dilute solution does not aggregate, thus preventing inter-molecular FRET to occur.

The effect of pH on the emission of PFBT-MI was monitored prior to sensing experiments by varying the pH of the solution from 1-14. The results demonstrated that PFBT-MI exhibits excellent emission in the pH range 5-8 (Figure S10), confirming its ability to work efficiently under physiological conditions. Upon successive addition of SDS and SDBS to the aqueous solution of PFBT-MI, a new peak appeared at 545 nm while the emission peak at 415 nm disappeared completely with the formation of an isoemissive point at 500 nm. This change in the emission spectra of PFBT-MI reflects the occurrence of an efficient energy transfer from fluorene fragment (donor) to BT units (acceptor) of the polymer due to an increased aggregation of polymer chains facilitated by polymer-surfactant complexation. The intensity of the emission band at 545 nm reaches its maximum value and saturated on adding total of $1.8 \times 10^{-5}$ M SDS and $2.1 \times 10^{-5}$ M SDBS, respectively (Figure 1a & 1b). The detection limits calculated for SDS and SDBS were found to be 0.12 μM (34

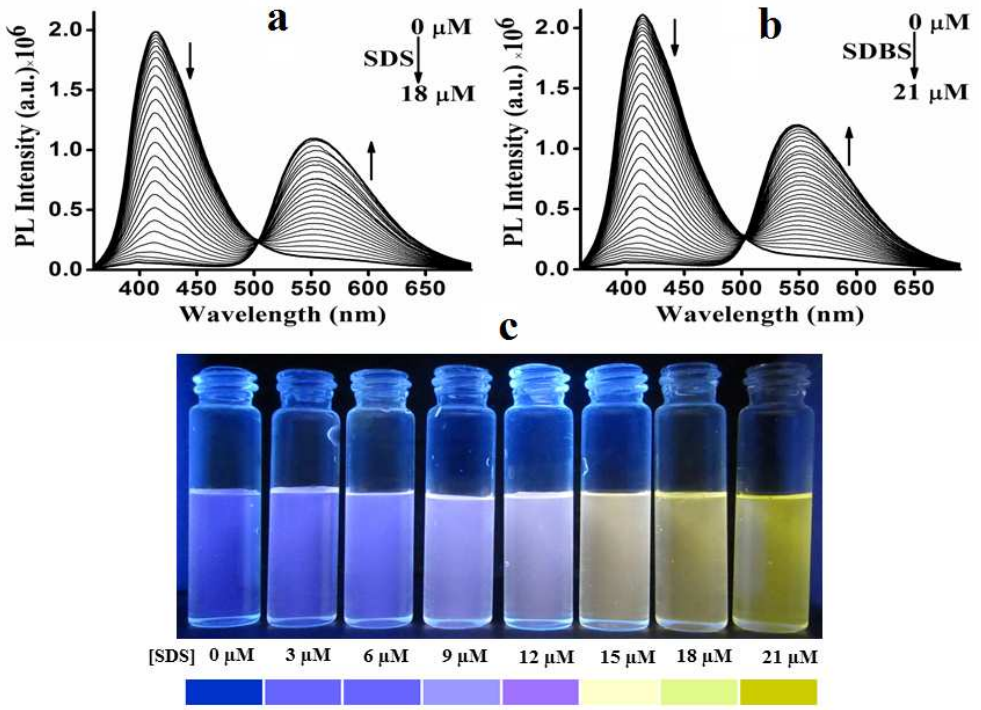



**Figure 1.** Emission spectra of PFBT-MI (6.6 μM) with increasing concentration of (a) SDS and (b) SDBS in aqueous solution. (c) Change in color of PFBT-MI (6.6 μM) solution under UV light after adding variable concentration of SDS (lamp excited at 365 nm).

ppb) and 0.13 μM (45 ppb) respectively which is lower than the standard methylene blue method[51] (Figure S11-S12). Interestingly, the solution color progressively changed from blue to yellowish green with increasing SDS/SDBS concentration that could be easily visualized by naked eye under UV-light (lamp excitation-365 nm), thus, allowing colorimetric detection of SDS/SDBS (Figure 1c).

To check the practicability of probe in real environmental conditions, selectivity studies were performed using various common analytes usually found in natural water systems. Widespread surfactants (cetyltrimethyl ammonium bromide (CTAB), triton-X-100, stearate, laurate and palmate), anions ($I^-$, $Cl^-$, $F^-$, $SO_4^-$, $SO_4^{2-}$, $PO_4^{3-}$, $PO_4^{2-}$, $PO_4^-$, $N_3^-$, $NO_3^-$, $BF_4^-$, $PF_4^-$, *p*-toluenesulfinate, benzene sulfinate, pyrophosphate and citrate) and common metal ions ($Co^{2+}$, $Cu^{2+}$, $Zn^{2+}$, $Fe^{3+}$, $Pb^{2+}$, $Cr^{3+}$, $Mn^{2+}$, $Cd^{2+}$, $Ln^{3+}$, $Eu^{3+}$ and $Yb^{3+}$) were checked and found ineffectual towards the emission of PFBT-MI (Figure 2a & 2b), since imidazolium units attached to the fluorophores typically acts[46,47,52] as a specific recognition site for SDS and SDBS.

Surfactants usually form non-covalent assemblies with amphiphilic polymers and solubilize them in aqueous solution with enhanced quantum yield. The photophysical properties of encapsulated fluorophores in such assemblies are tunable[53–55] and can be employed to detect chemical or biological species that has the capability of amending these assemblies. Thus, fluorescent

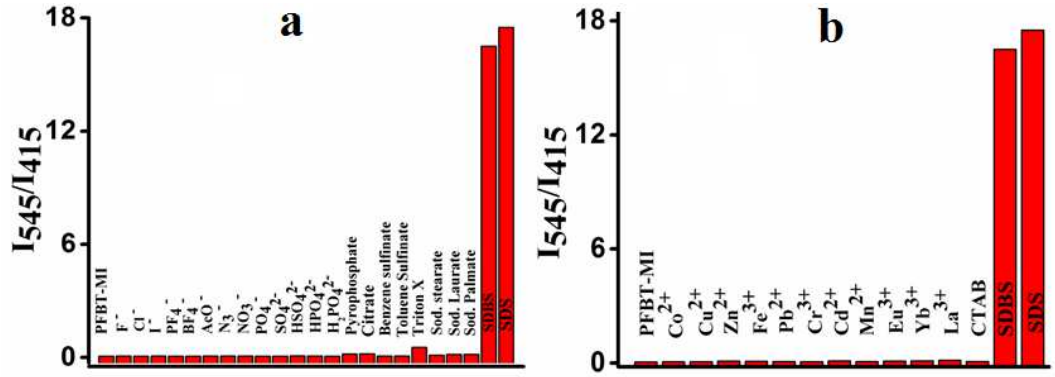



**Figure 2.** Bar diagram depicting effect of various (a) anions (20 μM) and (b) cations (20 μM) on the emission of PFBT-MI.

-surfactant assemblies have recently emerged as an excellent platform for detecting various chemical[57-59] and biological analytes.[60] Furthermore, this method reduces the dependence on molecular design viz-a-viz synthesis of new fluorophores and thus enables detection in aqueous media. Utilizing this intrinsic advantage, we prepared PFBT-MI/SDS nano-aggregates as an exceptional probe for the selective and sensitive detection of spermine in aqueous medium among various other amines like spermidine, putrescine, dodecylamine, hexylamine, L-Arginine, melamine, N,N- dimethyl ethylenediamine (DMEA), hexamethylene tetraamine (HMTA) and pyrophosphate (PPi). PFBT-MI-SDS nano-aggregates exhibits strong emission centered at 545 nm ($\lambda_{ex}$=350 nm) that was quenched on sequentially adding the aliquots of spermine (Figure 3a). This may be due to the formation of non-fluorescent complex between the positively charged analyte molecule (spermine) and the polymer-surfactant nano-aggregates. Greater the positive charge on polyamine, the stronger will be its electrostatic interaction which is in well agreement with quenching efficiency by other amines (Figure 3b) and forms the basis for the selective detection of spermine. Nearly 42% quenching was observed on adding 20 μM of spermine into the polymer-surfactant nano- aggregates that reaches to 86% at total 120 μM spermine.

To study the efficiency of quenching, Stern-Volmer (S-V) plot was obtained via $I_0/I$ vs [Q] where, $I_0$ and I represents fluorescence intensity of PFBT- MI/SDS complex in the absence and presence of spermine and Q is the respective concentration of spermine. The S-V constant ($K_{sv}$) value thus obtained for spermine was 0.35 $\times 10^5$ $M^{-1}$, confirming high sensitivity of the polymer/surfactant assembly towards spermine (Figure S13). The detection limit (0.33 μM/66 ppb) calculated for spermine (Figure S14) was found to be far below the range 1-10 μM applicable for timely diagnosis of cancer in urinary samples.[61]

Moreover, we have also monitored the effect of few other well-known cancer biomarkers[62,63] such as transferrin, prothrombin, leucine, isoleucine and valine on the emission of PFBT-MI/SDS complex. It was established (Figure S15) that these biomarkers have insignificant effect on the emission of PFBT-MI/SDS complex, indicating

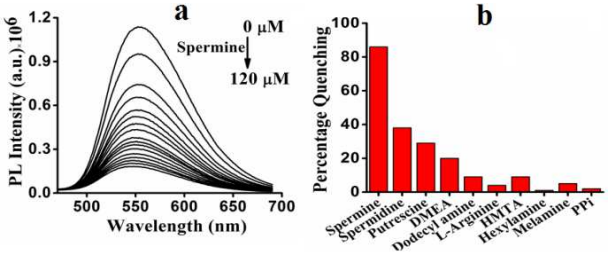



**Figure 3. (a)** Fluorescence spectral changes of PFBT-MI/SDS in aqueous solution with different concentrations of spermine. (b) Percentage fluorescence quenching (at $\lambda_{em}$= 545 nm) with spermine (120 μM) and other amines (120 μM).

the viability of this system for the detection of spermine under realistic condition.

**Complexation Studies.** To understand the complexation process, the interaction between the polymer, surfactant and spermine was monitored via UV-vis, FESEM, TEM and DLS studies. Upon successive addition of SDS and SDBS to the aqueous solution of PFBT-MI, the 350 nm absorbance peak decreases gradually with a bathochromic shift of 5 nm while the peak at 430 nm showed a significant red shift of ~20 nm (Figure 4a & 4b). These red shifts in the absorption spectra can be attributed to the complexation of PFBT-MI molecules on binding with surfactants via hydrophobic and/or hydrophilic interactions driven by Columbic attractions resulting in increased conjugation length of the PFBT-MI owing to aggregation-induced planarization of the polymer chains.[64,65] This was confirmed by FESEM and TEM studies which indicated the formation of spherical nano-aggregates having an average diameter of 230 nm in aqueous solution with the net negative charge on their surface. Hence, these polymer-surfactant nano- aggregates are presumed to have greater affinity for positively charged spermine at the interface. On introducing spermine to PFBT-MI/SDS solution, the absorption peak at 350 nm and 450 nm displayed a hypochromic shift and a hyperchromic shift was observed in the range 510-600 nm with an isosbestic point at 488 nm, demonstrating the favorable interaction between spermine and PFBT-MI/SDS nano-aggregates (Figure 4c & 4d). Since, the polymer chains are expected to remain intact at the core with surfactant molecules at the outer side, the chances for spermine molecules to interact with polymer are very less. To further confirm this presumption, a control study was performed by monitoring the change in the emission of polymer PFBT-MI after adding spermine. Interestingly,

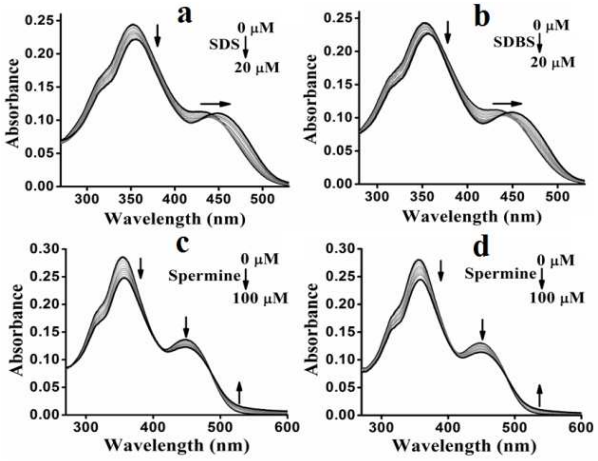



**Figure 4.** UV-vis titration spectra of PFBT-MI (6.6 μM) with increasing concentration of (a) SDS (20 μM) (b) SDBS (20 μM). Change in the absorption spectra of (c) PFBT-MI-SDS and (d) PFBT-MI-SDBS on introducing different concentrations of spermine (100 μM).

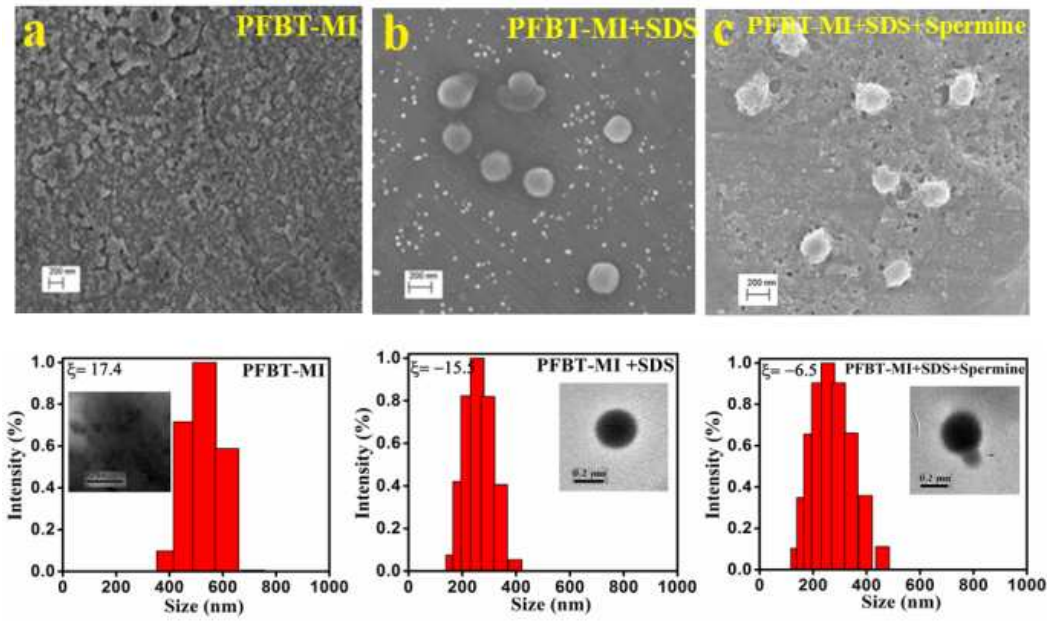



**Figure 5.** FESEM images of (a) PFBT-MI (b) PFBT-MI+SDS (c) PFBT-MI+SDS+Spermine and their corresponding light scattering measurements showing hydrodynamic diameter of 560 nm, 250 nm, and 300 nm respectively. (Inset: TEM images showing an average diameter of 230 and 280 nm respectively for PFBT-MI+SDS and PFBT+SDS+Spermine).

spermine did not cause any significant effect on the emission of PFBT-MI (Figure S16) probably due to the absence of any favorable electrostatic interaction. Thus, it can be concluded that spermine interacts with polymer-surfactant assembly at the surface and caused fluorescence quenching.

The morphological studies revealed that the average diameter of the spherical aggregate increases from 230 to 280 nm on introducing spermine while the net negative charge on surface decreases from -15.5 to -6.5. DLS experiments further confirms the formation of nano-aggregates with an average diameter of 250 and 300 nm for PFBT-SDS and PFBT-SDS-spermine respectively which is slightly greater than observed from TEM and FESEM (Figure 5). These results indicate that the polymer-surfactant complex did not disassemble in presence of spermine and remains intact on the surface via electrostatic interaction. The overall sensing mechanism for the detection of SDS/SDBS and spermine is shown in Figure 6.

**Detection of Spermine in Urine Specimens.** To validate the non-invasive nature and practical utility of PFBT-MI system, sensing studies for the detection of spermine were also performed in urine samples, since spermine is considered as one of the important biomarker for cancer detection usually found and tested in urine. Three urine samples were collected from three different individuals and used as such without further treatment. No significant change in emission of PFBT-MI was observed after introducing un-doped urine specimen, indicating the absence of spermine in the original sample (Figure S17). Each urine specimen was spiked independently with known concentrations of spermine and sensing experiment was performed in aqueous medium. The fluorescence spectra were then recorded after adding known volumes of these spiked samples to the solution of PFBT-MI/SDS (6.6 μM / 18 μM) (Figure S18) and the peaks

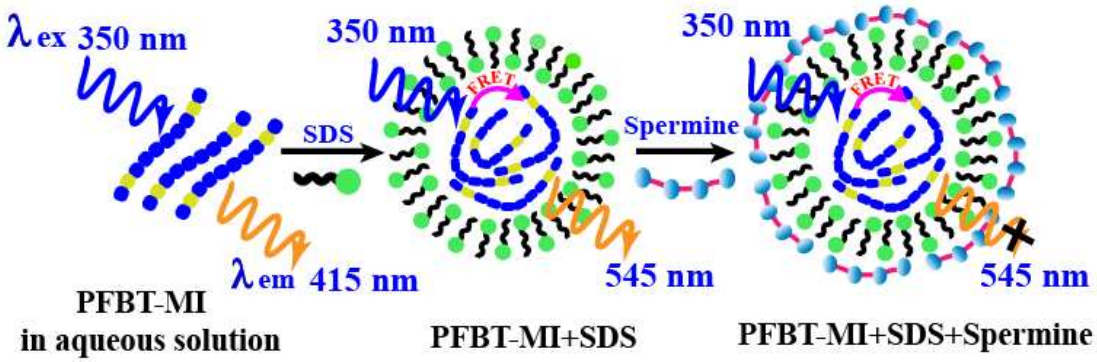



**Figure 6.** Schematic representation of proposed sensing mechanism for the detection of surfactants SDS/SDBS and spermine.

**Table 1.** Determination of spermine in urine specimen.

| Urine Samples | Spermine added ($10^{-7}$M) | Spermine found[a] ($10^{-7}$M) | Recovery (%) | RSD (%) |
|---|---|---|---|---|
| U1 | 66 | 71 | 107 | 4 |
| U2 | 100 | 105 | 105 | 5 |
| U3 | 125 | 133 | 106 | 7 |

[a]An average of three replicate measurements.

were compared with the standard calibration curve (Figure S19) after taking three replicate measurements (Table 1). These results demonstrate that PFBT-MI based system can be employed as an exceptional probe to monitor traces of spermine in the urinary specimens that can be helpful in early diagnosis of cancer.

## CONCLUSION

In conclusion, a newly developed cationic conjugated polyelectrolyte [9,9-bis(6'-methyl imidazolium bromide)hexyl)fluorene-co-4,7-(2,1,3-benzothiadiazole)] (PFBT-MI) displayed emission color change from blue to yellowish green in the presence of most common anionic surfactants SDS and SDBS in 100% aqueous solution and enables naked-eye detection and quantification of these surfactants in real time. The detection of SDS/SDBS at parts per billion levels [SDS - (0.12 μM/34 ppb) and SDBS - (0.13 μM/45 ppb)] is attributed to the inter-molecular FRET due to the aggregation of polymer chains assisted by SDS/SDBS via strong electrostatic as well as hydrophobic interactions. Furthermore, PFBT-MI/SDS ensemble serves as a unique platform for the non-invasive, rapid and sensitive detection of spermine over other relevant amines, which is much lower than the range required for early cancer diagnosis and validates the reliability of the present system for real time practical applications.

## ASSOCIATED CONTENT

### Supporting Information

It includes characterization data of monomers and polymers, pH study of PFBT-MI, detection limit plots for SDS, SDBS and spermine, $K_{sv}$ plot for spermine, plots of control studies etc. The Supporting Information is available free of charge on the ACS Publications website.

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### Notes

The authors declare no competing financial interest.

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