Supplementary Information (SI) for Analytical Methods.

Supporting information

A Perylene-based Fluorescent Probe for Highly Efficient SDS Detection

Amrit Kaur,[a,#] Mina Bagherifard,[a,#] Alissa Brooke Anderson,[a] Neelam Tariq,[a] Zois Syrgiannis,[a] and Ioannis Spanopoulos[a,*]

[a] Department of Chemistry, University of South Florida, Tampa, Florida 33620, United States

Corresponding author:
spanopoulos@usf.edu

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S1. Materials and methods

Starting materials

All starting materials for synthesis were purchased commercially and were used without further purification. 3,4,9,10-Perylenetetracarboxylic 3,4:9,10- dianhydride (98%), and methyl iodide were purchased from Sigma-Aldrich; 1-(3-aminopropyl)imidazole (98%) was purchased from Fischer. Sodium dodecyl sulfate (SDS, 98%), glycerol, dimethylformamide, methanol (HPLC grade), metal ions and salts for UV-vis and fluorescence studies were purchased from Thermo Fischer.

^{1}H-NMR and ^{13}C-NMR

The ^{1}H and ^{13}C NMR experiments were recorded using a Bruker AVANCE III HD 600 M*Hz* in DMSO -d$_6$ as solvent. Data are reported as follows: chemical shifts in ppm, multiplicity (s= singlet, br= broad, t= triplet, multiplet = m, *J* = coupling constant represented in *Hz*.

MALDI-TOF

The mass was detected using Bruker UltraFleXtreme MALDI-TOF/TOF equipped with Smartbeam II, 2 GHz for MS and 1 GHz for MS/MS, and FlashDetector™ with 5 GS/s 10-bit digitizer for enhanced dynamic range. Ultra-pure alpha-Cyano-4-hydroxycinnamic acid matrix was used for sample investigations.

UV-Vis Spectroscopy

UV-Vis spectra were recorded on Shimadzu UV-1900i.

PL/TRPL/PLQY Measurements

PL and TRPL studies were performed using an Edinburgh Instruments FS5 spectrofluorometer equipped with a 150 W xenon lamp, a 475 nm EPL picosecond pulsed diode laser, and an integrating sphere for PLQY determination.

SEM Scanning Electron Microscopy

SEM measurements were recorded on a high-resolution thermal field emission source Hitachi SU-70. Data were acquired with an accelerating voltage of 16 kV. The samples were prepared by pressing the powder on to a substrate of carbon adhesive tape and tilting the sample to 30 degrees. The electron beam energy was set to 16 keV.

Zeta Potential

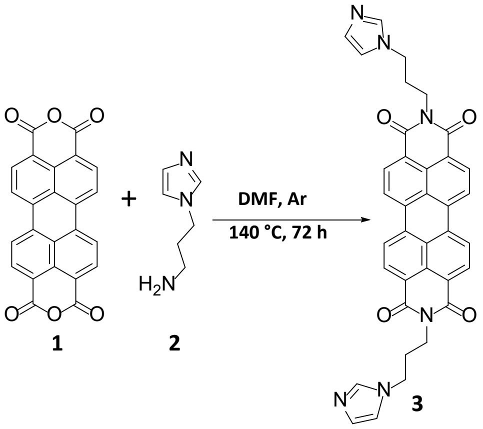
The zeta potential measurements were conducted using a Zetasizer Nano-ZS (Malvern Instruments, NanoSeries) with DTS 1070 cells.

UV-Vis and Fluorescence studies:

For the UV-Vis and fluorescence titration the 10^{-3} M stock of Compound **5** was prepared in the DMSO. A 1.0 mM stock solution of SDS was prepared by dissolving 2.8 mg SDS in 10.0 mL distilled water. A 10.0 µM concentration of compound **5** was used for each titration. The standard solution (10^{-1} M to 10^{-3} M stock) of various metal ions such as Na^+, K^+, Ca^{2+} and Mg^{2+} ions were prepared by dissolving their chloride salts. The 10^{-1} M to 10^{-3} M stock solution of inorganic anions (I^-, Br^-) were prepared by dissolving their tertabutylammonium salt, while anions such as SO_4^{2-}, NO_3^-, CH_3COO^-, were prepared by dissolving their potassium and sodium salt in 1 mL in distilled water. For the interference and competitive studies, 1.0 mM concentration of metal ions and anions was added to the titration experiment. In titration experiments, each time a 3.0 mL solution of compound **5** (30.0 µL compound **5** in 2970 µL distilled water) was filled in a quartz cuvette (path length, 1 cm) and spectra were recorded after the addition of appropriate analyte. For the detection of SDS in the household samples, household's samples (0.5 mL) were dissolved in water (15 mL); a clear solution was obtained through centrifugation for 90 minutes at 40000 rpm and stood for 48 h.[1]

S2. Synthesis

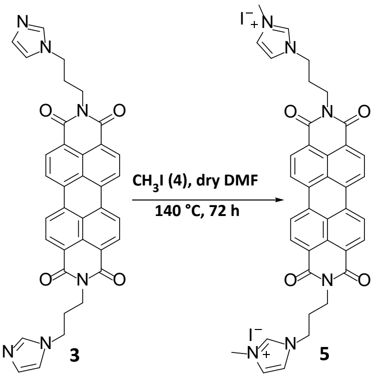
Synthesis of 2,9-bis(3-(1H-imidazol-1-yl)propyl)anthra[2,1,9-def:6,5,10-d'e'f']diisoquinoline-1,3,8,10(2H,9H)-tetraone (Compound 3):



Scheme 1 Synthesis pathway for compound **3**

To a well-stirred suspension of perylene-3,4,9,10-tetracarboxylic dianhydride **1** (1 g, 2.7 mmol) in 80 mL dry dimethylformamide, 1-(3-aminopropyl)imidazole **2** (1.5 g, 5.86 mmol) was added dropwise, followed by purging of the reaction mixture under argon (Ar) for 10 minutes. Afterward, the resulting mixture was refluxed at 140 °C for 72 h. Then, the red precipitate was filtered off and thoroughly washed with cold water and methanol to yield compound **3** (1.50 g, 93%). The melting point of compound **3** was >295 °C. As compound **3** has poor solubility in the available deuterated solvents, ^{1}H and ^{13}C NMR spectra were obtained only after methylation i.e compound **5.**

Synthesis of Compound 5 [2]:



Scheme 2 Synthesis pathway for compound **5**

To a well-stirred suspension of compound **3** (1.0 g, 1.1 mmol) in 30 mL dry DMF, methyl iodide (2.5 equiv.) was added dropwise. The resultant mixture was refluxed for 72 h at 140 ºC. The reaction mixture was cooled down, and the resultant solvent was removed under vacuum. The obtained solid was washed with water and methanol resulting in the pure compound **5** in 90% yield as reddish brown solid. ^{1}H NMR (600 M*Hz*, DMSO-*d*$_6$) δ (ppm) = 9.19 (s, 2H), 8.60 (d, *J* = 6 *Hz*, 4H), 8.35 (d, *J* = 6 *Hz*, 4H), 7.87 (s, 2H), 7.79 (s, 2H), 4.37 (t, *J* = 18 *Hz*, 4H), 4.16 (br, 4H), 3.93 (s, 6H), 2.31-2.30 (m, 4H); ^{13}C NMR (600 M*Hz*, DMSO-*d*$_6$) δ (ppm) = 163.27, 137.17, 133.93, 131.02, 128.50, 125.34, 124.44, 124.12, 122.75, 122.69, 47.43, 37.35, 36.32, 28.88. MALDI-TOF: [M-I]$^{2+}$ calculated for [$C_{38}H_{32}N_6O_4$]$^{2+}$ is 636.247; and found to be 636.247.

S3. Characterization:

NMR

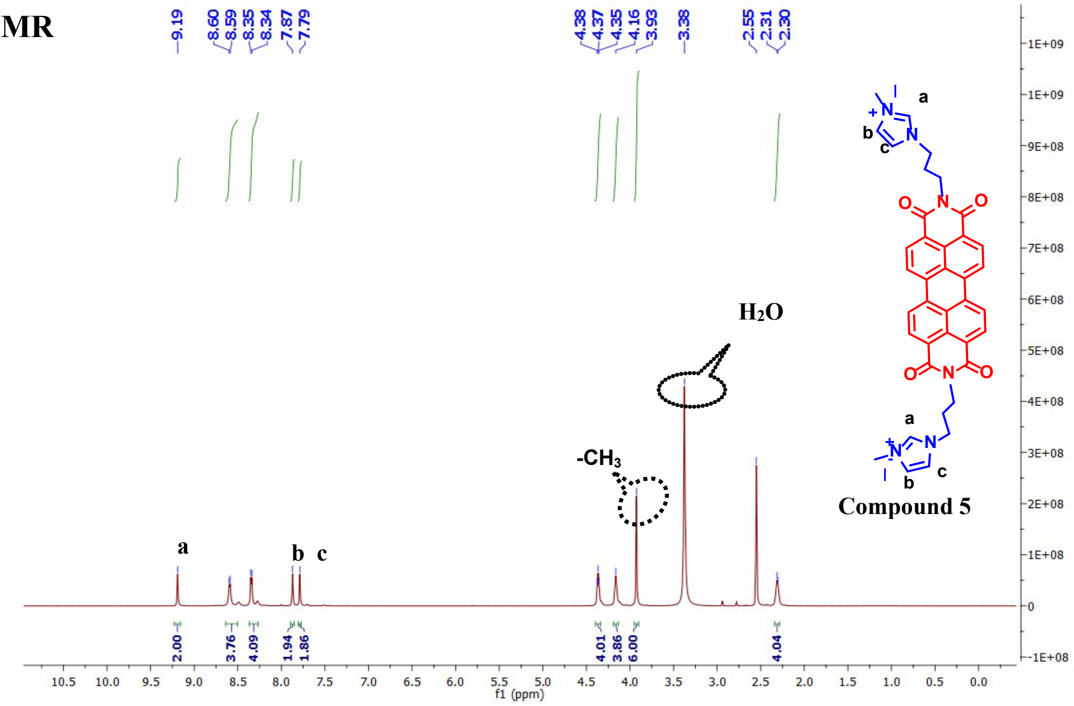


Fig. S1 The ^{1}H-NMR spectrum of compound **5** in DMSO-*d*$_6$ at 600 M*Hz*.

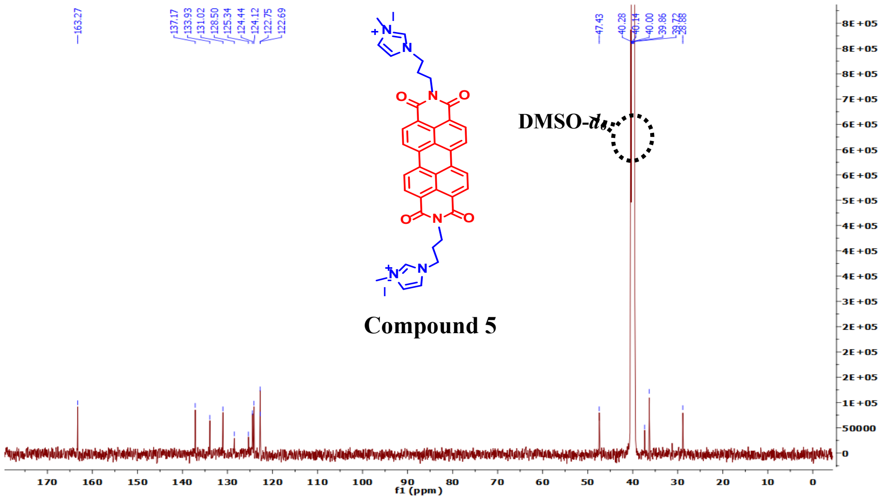


Fig. S2 The ^{13}C-NMR spectrum of compound **5** in DMSO-*d*$_6$ at 600 M*Hz*.

MALDI-TOF

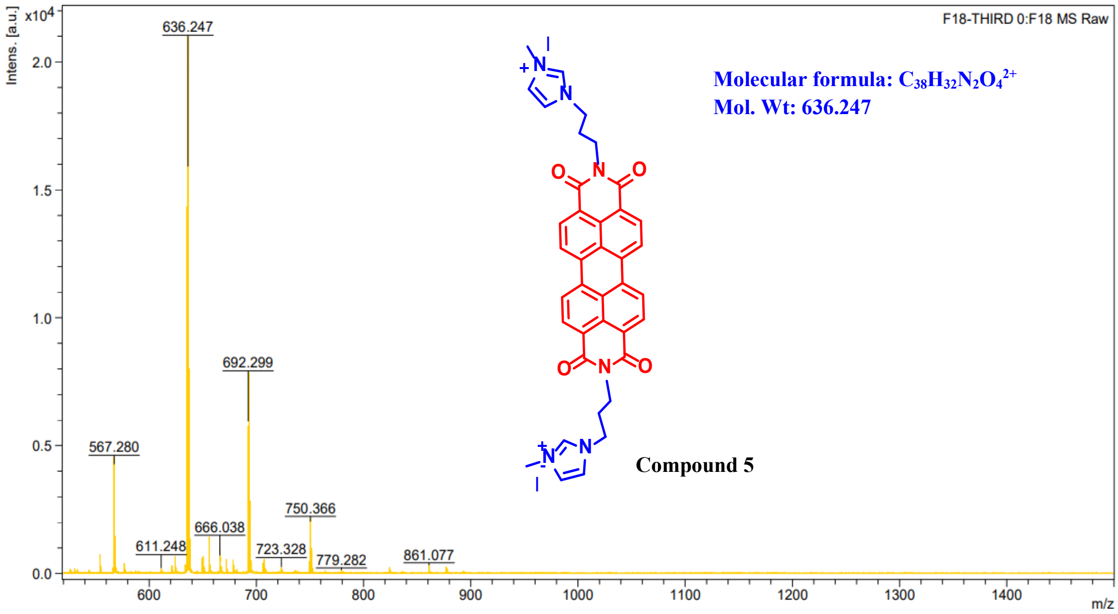


Fig. S3 The MALDI-TOF spectrum of compound **5.**

S4. Experimental data

Temperature-dependent UV-vis and fluorescence emission spectra of compound 5

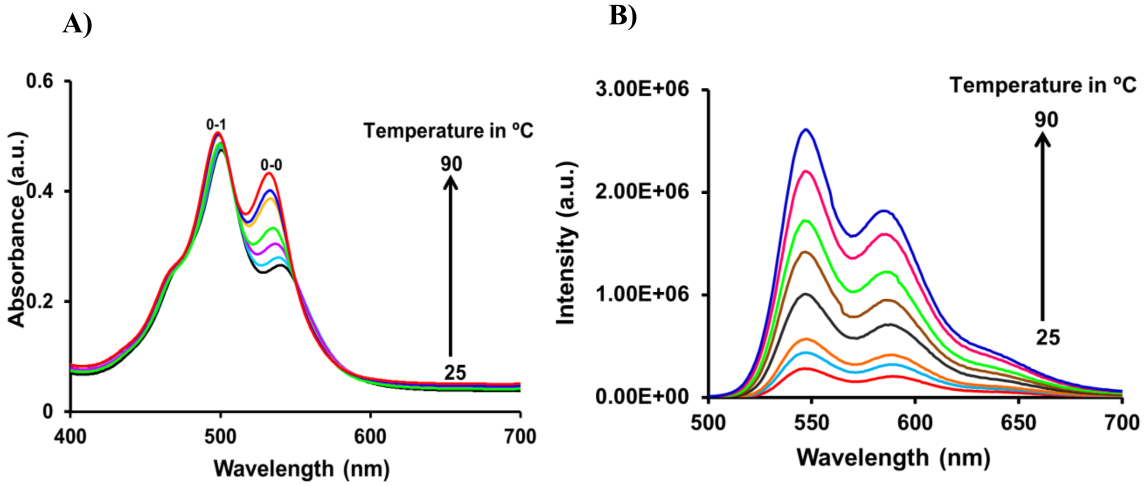


Fig. S4 A) The absorption and **B)** fluorescence spectra of compound **5** (10 µM) showing changes in absorption and emission intensity upon increasing temperature from 25 °C - 90 °C in 99% vol. fraction of H_2O in DMSO at $\lambda_{ex} = 490$ nm.

UV-vis spectra of compound 5 upon addition of SDS

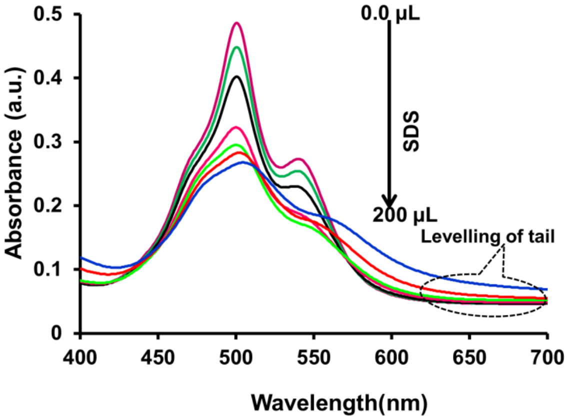


Fig. S5 The absorption spectra of compound **5** (10.0 µM) upon addition of 1.0 mM SDS solution (0.00-200.0 µL) in 99% vol. fraction of H_2O in DMSO.

Detection Limit Calculations of Compound 5 for SDS

The detection limit was calculated based on the fluorescence titration using the standard calibration method.[3] To determine the S/N ratio, the emission intensity of compound **5** without SDS was measured 10 times and the standard deviation of blank measurements was determined. The detection limit is then calculated with the following equation: DL = 3 × SD/S, where SD is the standard deviation of the blank solution measured 10 times; S is the slope of the calibration curve. From the graph, the slope was found (S) = -15,01,467.08, Thus using the formula, a Detection Limit (DL) = 8.65 X10^{-5} M (86.5 µM) is determined.

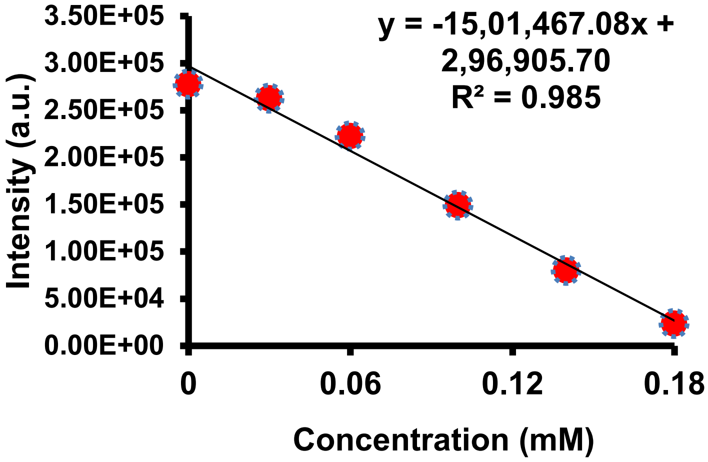


Fig. S6 The fluorescence response of compound **5** (10.0 µM) to various concentrations of SDS in 99% H_2O in DMSO at λ_{ex}= 490 nm.

Comparative and Competitive Analysis of Interfering Analytes

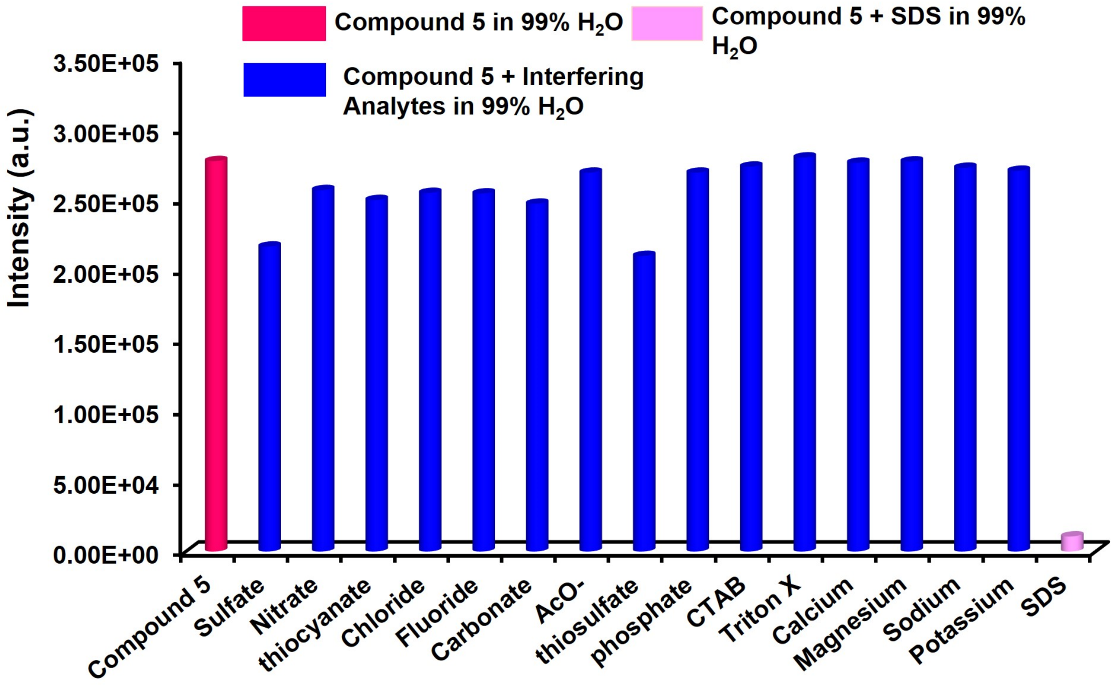


Fig. S7 The fluorescence emission response for compound **5** (10.0 µM) in 99% vol. fraction H_2O in DMSO in the presence of various interfering analytes (0-1.0 mM) at λ_{ex}= 490 nm. The red column represents the fluorescence emission of the probe alone; the blue columns represent the fluorescence emission of the probe with each interfering substance added; and the light pink column represents the fluorescence emission of the probe after SDS is added as an interfering agent.

Zeta Potential of Compound 5, SDS and Compound 5-SDS

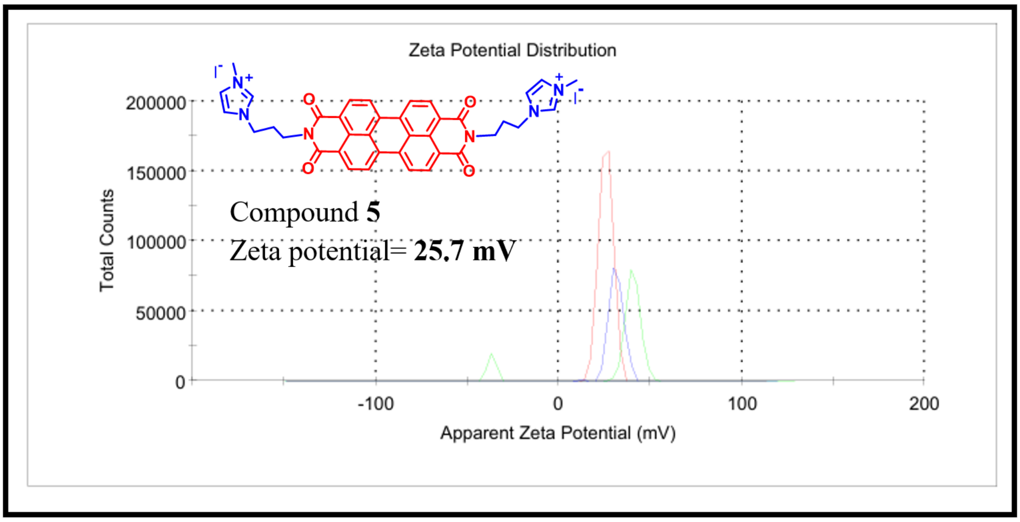


Fig. S8 The graph depicts the zeta potential of compound 5 (10.0 µM) in a 99% vol. fraction of H_2O in DMSO.

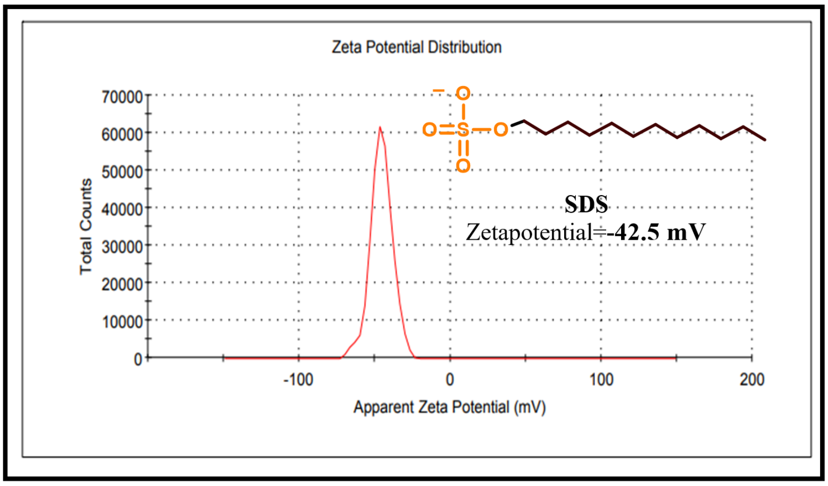


Fig. S9 The graph depicts the zeta potential of SDS (10.0 µM) in 99% vol. fraction of H_2O in DMSO.

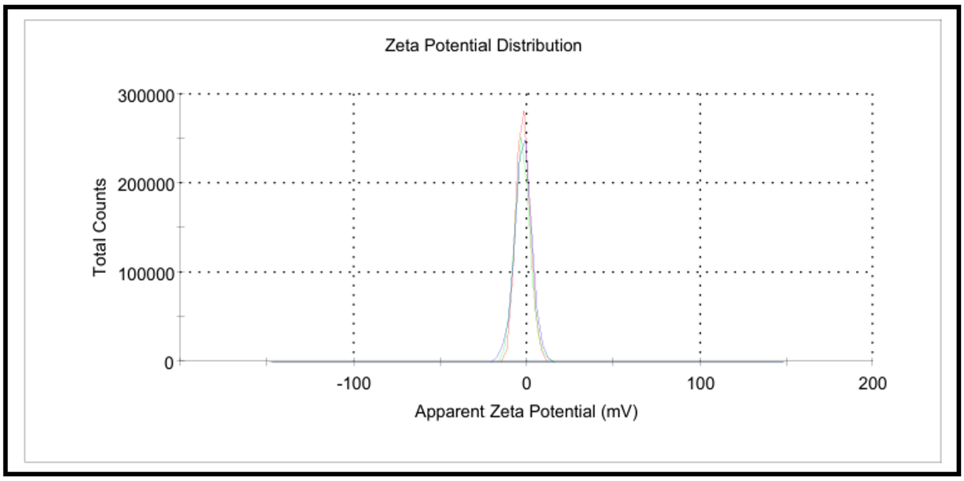


Fig. S10 The graph depicts the zeta potential of compound 5 (10.0 µM) in the presence of SDS (10.0 µM) in a 99% vol. fraction of H_2O in DMSO.

Time-resolved fluorescence studies

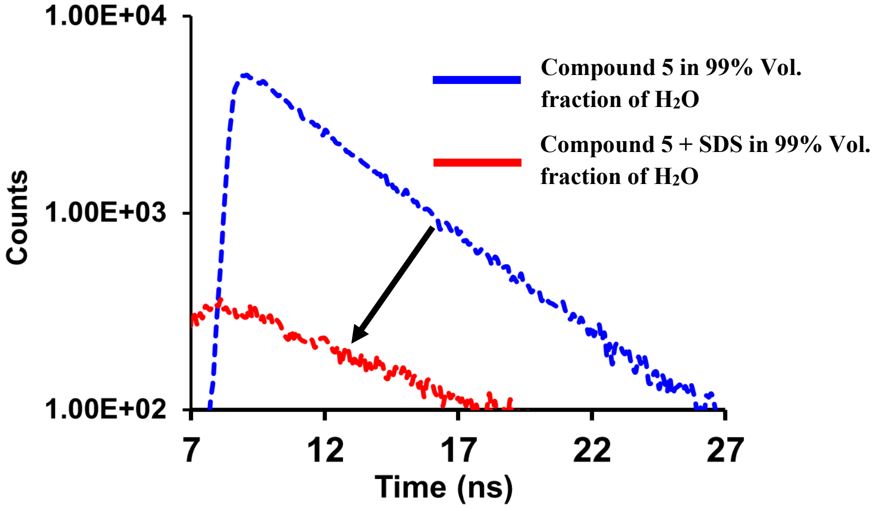


Fig. S11 The time-resolved fluorescence spectra of compound **5** (10.0 μM) upon the addition of SDS (1.0 mM) in 99% H_2O:DMSO at λ_{ex} = 475 nm.

Table S1. The table showcases various household items tested for the presence of the SDS surfactant (See also Figure 3C).

SAMPLE.NO	Sample	SDS DETECTION
1	**Handwash 1**	√
2	**Handwash 2**	√
3	**Handwash 3**	√
4	**Bodywash 1**	√
5	**Bodywash 2**	√
6	**Dishwasher1**	√
7	**Dishwasher 2**	√
8	**Dishwasher 3**	√
9	**Dishwasher 4**	√
10	**Facewash**	√
11	**Shampoo 1**	√
12	**Shampoo 2**	√
13	**Shampoo 3**	√
14	**Shampoo 4**	x
15	**Surface Cleaner 1**	x
16	**Surface Cleaner 2**	x
17	**Lens Cleaner**	x

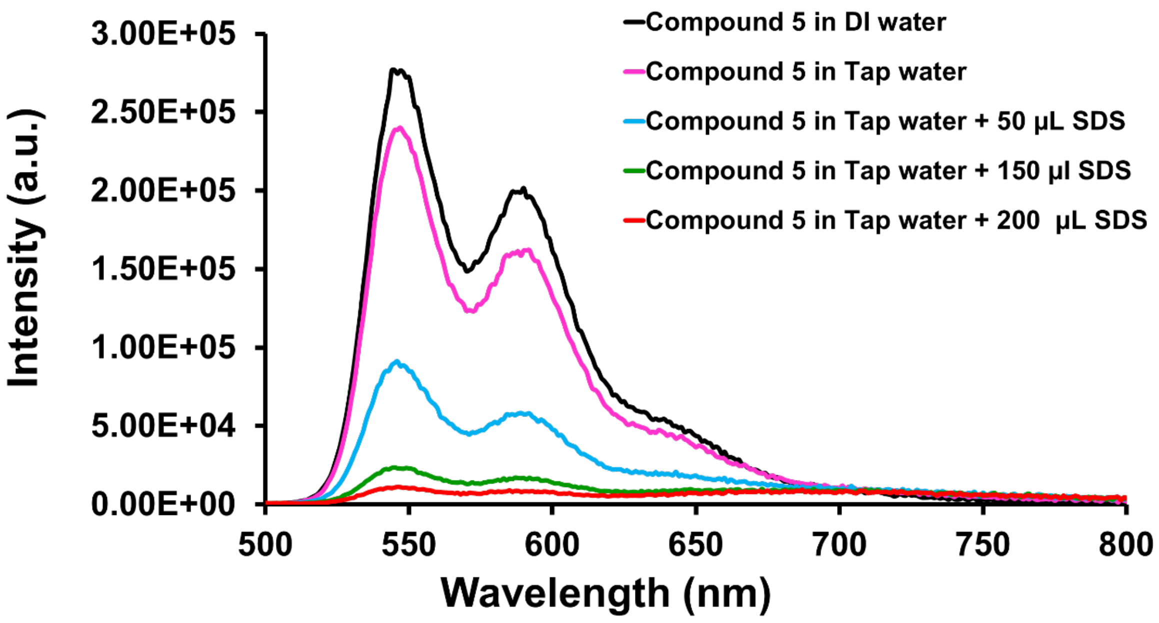


Fig. S12 The fluorescence spectra of Compound **5** (10.0 μM) upon addition of SDS (0-1.0 mM) in 150-times diluted tap water at λ_{ex}= 490 nm.

Table S2. The detection of SDS in 150-times diluted tap water

Sample Number	concentration added (mM)	concentration found (mM)	RSD (N=5)	% Recovery
1	**0.050**	**0.045**	**0.005**	**90**
2	**0.200**	**0.200**	**0.021**	**100**

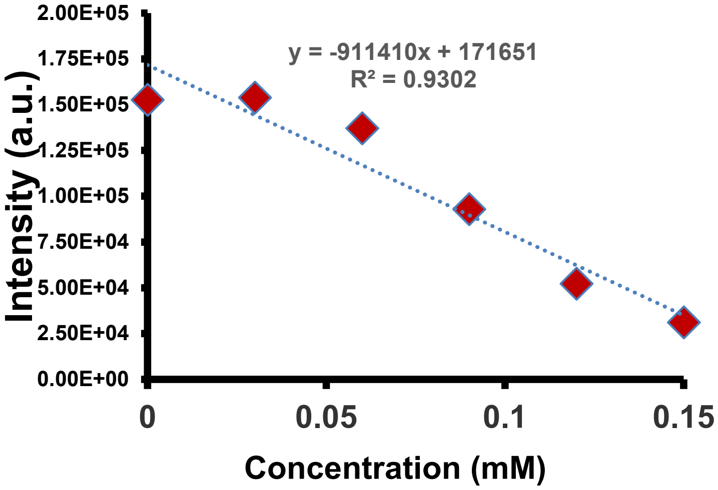


Fig. S13 The fluorescence response of Compound **5** (10.0 μM) upon addition of SDS (0-0.15 mM) in H_2O using no dilution, at λ_{ex}= 490 nm.

Table S3. Overview of literature reports on SDS detection.

#.	Material	Solvent system of detection	Response time	Application	Journal
1.	**Compound 5, PBI-Imidazolium based dye**	DMSO:H_2O (0.1:9.9, V:V)	<10s	• SDS in household items • Detection of SDS in tap water	This work
2.	**zirconium(IV)-based metal–organic framework (MOF)[4]**	Deionized water to make probe suspension	50s the preparation of sample for PL studies takes 24h	• Detection of SDS in various water samples	*Inorg. Chem.* 2023**, 62**, 8605−8614
3.	**quaternary ammonium complex of (2-(methylthio)indeno[1,2,3-gh]phenan-thridin-1-yl)(phenyl)methanon[5]**	DMSO	-	• SDS in household items	*J. Surfactants Deterg, 2024,*
4.	**UiO-66-NH_2@Au NCs)[6]**	Deionized water	4 min	• SDS in household items	*Anal. Chem.* 2024, **96**, 4987−4996.
5.	**5-hydroxytryptamine Derived carbon naoparticle[7]**	In DMSO:H_2O (3:1,v:v)	NA	• SDS in tap water and urine	*Dyes Pigm.* 2022, **208**, 110859
6.	**3-ethylbenzothiazolium iodide dyes[8]**	CH_3CN:PBS (2:8,v:v)	12 min	• Detection of SDS in various water samples	*Anal. Methods,* 2021**, 13,** 3292
7.	**Graphene oxide encapsulated Rhodamine DyeRBGO[9]**	--	20 min	• SDS in household items	*Anal. Methods,*2019,**11**,5826
8.	**Rhodamine conjugated pyrene dye[10]**	CH_3CN :H_2O (1:9,v:v)	6 hrs	• Various surfactants	*Sens. Actuators, B* 2021**, 331***,* 129408
9.	**nicotinamide-anthracene conjugates NAAN-1[11]**	H_2O/DMSO=9/1, pH = 7	30 mins	• Detection of SDS in various water samples	*Sens. Actuators, B*, 2017, **241**,8–18.
10.	**Green fluorescent protein[12]**	HEPES buffer	5 min	• SDS in tap water	*J. Sensors* 2015, **2015**, 809065
11.	**TPE-B[13]**	Pure water	30s	• SDS in tap water, river water, and drinking water	*Mater. Sci. Eng. C,* 2019, **99***,* 1092–1098

S5. References:

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