CHAPTER - 4

Aggregation Induced Emission Enhancement in Ionic Self-Assembled Aggregates of Benzimidazolium Based Cyclophane and Sodium Dodecylbenzenesulfonate: Highly Selective Detection of SDBS and SDS

4.1 Abstract

Benzimidazolium-durene based cyclophane BIMCP-1 exhibits detection of surfactants in 95% aqueous solution. Fluorescence, NMR studies, SEM and confocal microscope studies demonstrate that cyclophane on interaction with SDBS/SDS leads to spherical aggregates which results in aggregation induced fluorescence enhancement. This allows highly selective detection of SDBS and SDS even in the presence of number of other anions.

4.2 General introduction

In light of the inspirations which natural processes\(^1\) have provided us, substantial advances in design and fabrication of appealing supramolecular assemblies have been achieved by chemists through bottom-up approach by elegantly utilizing non-covalent interactions such as electrostatic, hydrophobic, van der Waals and hydrogen bonding etc.\(^2,3\) Among many techniques of self-assembly, the class of ionic self-assembly has attracted considerable attention for various applications such as optical materials and advanced nano-devices. It involves coupling of structurally different building blocks (ionic pairs) by electrostatic interactions.\(^3\) Various combinations between peptides, polyelectrolytes, surfactants and extended rigid organic scaffolds could be employed for creating new material via ionic self-assembly.\(^4\) Another promising feature of these supramolecular assemblies in concern is their emissive behavior in solution and solid state. The assemblies thus formed can exhibit either aggregation induced emission enhancement (AIE or AIEE) or aggregation caused quenching (ACQ).\(^5,6\)

Molecules with AIEE properties shows enhanced fluorescence emission efficiency in an aggregated state as compared to in a solution state. In this context, AIEE phenomena became a key point in developing materials for optoelectronic
devices, fluorescent sensors and cell imaging. Up to now, the AIEE mechanism has been observed in silole derivative,\textsuperscript{7} 1,1,2,2-tetraphenylethene (TPE),\textsuperscript{8} 1-cyano-trans-1,2-bis-(4-methylphenyl) ethylene (CN-MBE),\textsuperscript{9} which could be used as a stimuli responsive material capable of detecting volatile organic vapor, explosives, biological polymer, pH changes, metal etc. However AIEE phenomena in benzimidazolium based organic molecules has been scarcely studied.

Surfactants due to amphiphilic nature readily produce various supramolecular aggregates like micelles and vesicles in aqueous solution.\textsuperscript{10} So, to achieve ordered supramolecular assemblies, surfactant could be used as a coupling unit because it would induce the structural changes by ionic self-assembly with polycationic moiety and would help in separating the hydrophilic and hydrophobic domains being stabilized by non-covalent forces. Although ionic interactions between surfactants and ionic dyes/imidazolium/porphyrin with AIEE phenomena for various applications are reported in the literature,\textsuperscript{11} however, no reference reported the induced fluorescence emission enhancement of benzimidazolium based cyclophane with surfactants. These observations and our interest on benzimidazolium based derivatives stimulated our research group to think about surfactants as potential candidates for designing, creating and modulating the aggregation as well as fluorescence behavior of benzimidazolium based cyclophane in water.

Herein, we report the synthesis, photophysical and morphological characteristics of cyclophane which consists of four hydrophilic benzimidazolium moieties present at the corners of the cyclophane interconnected with each other by phenyl and 2,3,5,6-tetramethylbenzene in sequence at the both sides. Bim-Cyclophane 1 which lacks any characteristic fluorescent moiety on addition of SDBS and SDS, much below their CMC values, undergoes aggregation induced emission enhancement (AIEE) to enable fluorescent determination of SDBS and SDS. The SEM, confocal images, temperature dependent titration and \textsuperscript{1}H NMR spectroscopy confirms the polymeric nature of these aggregates.

\textbf{4.3 Synthesis of probes BIMCP-1 and 2}

1,4-Bis(benzimidazol-1-yl)benzene 3 was synthesized by bis-heteroarylation of 1,4-diiodobenzene with benzimidazole in DMSO by using CuI, benzotriazole, and
KOBU as catalyst, ligand and base respectively. The cyclo-alkylation of 1,4-bis(benzimidazol-1-yl)benzene 3 with 1,4-bis(bromomethyl)-2,3,5,6-tetramethylbenzene 4 in DMF at 100 °C, with subsequent conversion to its hexafluorophosphate derivative gave BIMCP-1, yield 37%; m.p. 290 °C; HRMS m/z (TOF MS ES+ ) 1375.7388. 1H NMR spectrum of BIMCP-1, exhibited four singlets at δ 2.36 (8 × CH3), 5.84 (4 × CH2) due to aliphatic protons and at δ 7.91 (ArH) and δ 8.50 (bimC2H), along with other aromatic signals in it 1H NMR spectrum, and its 13C NMR spectrum displayed 13 magnetically nonequivalent signals. These spectral data corroborate the structure BIMCP-1 for this compound.


Similarly, alkylation of 1,4-bis(benzimidazol-1-yl)benzene 3 with 3-(bromomethyl)-1,2,4,5-tetramethylbenzene 5 in DMF at 100 °C, with subsequent conversion to its hexafluorophosphate gave probe 2, yield 88%; m.p. 165 °C; HRMS m/z (TOF MS ES+) 749.3218. 1H NMR spectrum of probe 2 exhibited six singlets at δ 2.23 (4 × CH3) and 2.25 (4 × CH2), and at δ 5.81 (4 × CH2) due to aliphatic protons, and at δ 7.14, 8.05, and 9.58 (bimC2H), along with other aromatic protons and its 13C NMR spectrum displayed 15 magnetically nonequivalent signals. These data corroborate the structure 2 for this compound.

4.4 Photophysical studies of BIMCP-1 and 2

BIMCP-1 is a tetracationic molecule and thus shows considerable water solubility and is expected to show fewer tendencies to aggregate due to repulsive interactions between the benzimidazolium groups. The UV-Vis spectrum of BIMCP-1 and 2 exhibited the absorption maxima at 265 nm (±5 nm). On excitation
at 270 nm, BIMCP-1 and 2 showed the two emission maxima at 360 nm and 385 nm. In order to scrutinize the variations in fluorescence intensity for BIMCP-1 and 2 upon addition of various anions, the additions of methyl sulfonate (MeSO$_3^-$), butyl sulfonate (BuSO$_3^-$), octyl sulfonate (OctSO$_3^-$), decyl sulfonate (DecSO$_3^-$), octyl sulfate (OctOSO$_4^{2-}$), decyl sulfate (DecOSO$_4^{2-}$) etc. or inorganic anions viz. halides, H$_2$PO$_4^-$, CN$^-$, SCN$^-$, HSO$_4^-$, SO$_4^{2-}$ (100 μM each) etc. to the solutions of BIMCP-1 (2 μM) and 2 (5 μM) in H$_2$O (5% DMSO) were performed and corresponding emission behavior is shown in figure 1. The addition of sodium dodecylbenzenesulfonate (SDBS) and sodium dodecyl sulfate (SDS) (50 μM) lead to respective 32 and 27 fold increase in emission intensity at 360 and 380 nm. The acyclic analog 2 exhibited only ~3 fold emission intensity enhancement on addition of 50 μM SDS and SDBS and ~7 fold emission intensity enhancement at > 400 μM concentration of SDBS and SDS. Remarkably, the sodium salts of long chain carboxylates like laurate, myristate, palmitate and stearate (100 μM each) caused < 1 fold increase in the emission intensity of BIMCP-1 and 2, whereas other anions caused insignificant change in both the absorption and emission spectrum of BIMCP-1 and 2. Thus, BIMCP-1 shows remarkably high sensitivity towards SDBS and SDS (Figure 1a).

![Figure 1](image_url)

**Figure 1.** Effect of different anions on the fluorescence spectrum of (a) BIMCP-1 (2 μM); (b) probe 2 (5 μM) in H$_2$O-DMSO (19:1).

The solutions of both BIMCP-1 and 2 displayed linear increase in the fluorescence intensity between 1-50 μM concentration and point to the absence of
aggregation or any intramolecular interaction in various components of BIMCP-1 (Figure 2).

![Figure 2. Plot of FI vs. [BIMCP-1] (a); and [probe 2] (b); in water-DMSO (9:1).](image)

**Table 1.** Photophysical properties of BIMCP-1 and 2 in water-DMSO (19:1).

<table>
<thead>
<tr>
<th>Compounds</th>
<th>$\lambda_{max}$ (ε)</th>
<th>$\lambda_{em}$</th>
<th>Quantum Yield ($\phi$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BIMCP-1</td>
<td>270 nm (59,750)</td>
<td>354 nm</td>
<td>0.018</td>
</tr>
<tr>
<td>BIMCP-1 + SDBS</td>
<td>285 nm (75,340)</td>
<td>354 nm, 380 nm</td>
<td>0.107</td>
</tr>
<tr>
<td>BIMCP-1 + SDS</td>
<td>283 nm (77,320)</td>
<td>354 nm, 382 nm</td>
<td>0.112</td>
</tr>
<tr>
<td>2</td>
<td>265 nm (37,940)</td>
<td>358 nm, 390 nm</td>
<td>0.026</td>
</tr>
<tr>
<td>2 + SDBS</td>
<td>270 nm (49,143)</td>
<td>358 nm, 384 nm</td>
<td>0.055</td>
</tr>
<tr>
<td>2 + SDS</td>
<td>270 nm (48,980)</td>
<td>358 nm, 384 nm</td>
<td>0.052</td>
</tr>
<tr>
<td>3</td>
<td>260 nm (54,120),</td>
<td>330 nm</td>
<td>0.15</td>
</tr>
<tr>
<td></td>
<td>280 nm (32,100)</td>
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</tr>
</tbody>
</table>

Weakly fluorescent BIMCP-1 (2 μM, H$_2$O-DMSO; 19:1) showed gradual increase in fluorescence intensity on gradual addition of SDBS or SDS up to 50 μM (25 equiv.) and then achieved plateau. The regression analysis of the titration data shows the formation of 1:2 (BIMCP-1:SDBS or BIMCP-1:SDS) stoichiometric complexes with stability constant (log $\beta$) values of 9.11 ± 0.04 and 8.61 ± 0.02, respectively. The concentration of the surfactants required for bringing the fluorescence change is significantly far lower than the critical micelle concentration (CMC) of SDBS (1500 μM) and SDS (7000 μM) alone. So, the observed emission enhancement changes cannot be assigned to the aggregation of SDBS, SDS or BIMCP-1 alone. It could be attributed that the surfactant SDBS binds strongly with BIMCP-1 through electrostatic interactions between oppositely charged BIMCP-1.
and sulfonate moiety of surfactant along with some extent of $\pi$-$\pi$ interactions between the phenyl ring of the SDBS and phenylene core of BIMCP-1 to produce ionic self-assembled aggregates. The life time measurement of the excited state of BIMCP-1 in the presence of two equiv. or more of SDBS or SDS showed increase in life time from 0.76 ns to 8.9 ns. Both the increase in fluorescence of BIMCP-1-SDBS complex and decrease in the deactivation of the excited state through non-radiative processes due to restricted rotation of the aryl rings in these aggregates contribute to the overall emission enhancement.

**Figure 3.** (a) Effect of gradual addition of SDBS on the emission spectrum of BIMCP-1 (2 μM) in water (5% DMSO); (b) Job’s plot analysis of fluorescence titration of BIMCP-1 with SDBS shows 1:2 (BIMCP-1: SDBS) stoichiometries; (c) FI (380 nm) vs. [SDBS] concentration plot of BIMCP-1 on titration with SDBS.

**Figure 4.** (a) Effect of gradual addition of SDS on the emission spectrum of BIMCP-1 (2 μM) in water (5% DMSO); (b) Job’s Plot analysis of fluorescence titration of BIMCP-1 with SDS shows 1:2 (BIMCP-1: SDS) stoichiometries; (c) FI (380 nm) vs. [SDS] concentration plot of BIMCP-1 on titration with SDS.

The gradual addition of aliquots of SDBS to the solution of BIMCP-1 (2 μM) in 95% aqueous solution showed gradual increase in fluorescence and achieved plateau
after addition of 50 μM (25 equiv.) of SDBS (Figure 3). Similarly, the addition of SDS to the solution of BIMCP-1 resulted in increase in emission intensity and achieved plateau at 50 μM of SDS (Figure 4). The lowest detection limit for both SDBS and SDS is 4.0 μM (1.4 ppm). The Job’s plot of cyclophane BIMCP-1 with both SDBS and SDS shows inflexion point near to 0.7 and further confirms the formation of 1:2 (1:SDBS/SDS) stoichiometric complex.

On the other hand, acyclic analog 2 (5 μM, water (5% DMSO) on addition of SDBS or SDS exhibited relatively small increase in the emission intensity at 352 nm and 385 nm and achieved plateau after addition of 400 μM of SDBS/SDS (Figures 5 and 6). The spectral fitting of these titration data by non-linear regression analysis (SPECFIT-32) shows the formation of mixture of 1:1 and 1:2 stoichiometric species

![Figure 5](image1.png)

**Figure 5.** (a) Effect of gradual addition of SDBS on the emission spectrum of probe 2 (5 μM) in water (5% DMSO); (b) Job’s Plot analysis of fluorescence titration of probe 2 with SDBS shows 1:2 (2: SDBS) stoichiometries; (c) FI (380 nm) vs. [SDBS] concentration plot of probe 2 on titration with SDBS.

![Figure 6](image2.png)

**Figure 6.** (a) Effect of gradual addition of SDS on the emission spectrum of probe 2 (5 μM) in water (5% DMSO); (b) Job’s Plot analysis of fluorescence titration of probe 2 with SDS shows 1:2 (2: SDS) stoichiometries; (c) FI (380 nm) vs. [SDS] concentration plot of probe 2 on titration with SDS.
(2:SDBS/SDS) with relatively lower binding constant values \([\log \beta_{L(SDBS)} = 4.24 \pm 0.15; \log \beta_{L(SDBS)2} = 7.40 \pm 0.28\) and \(\log \beta_{L(SDS)} = 4.09 \pm 0.12; \log \beta_{L(SDS)2} = 7.63 \pm 0.35\) than those observed with BIMCP-1.

Figure 7. Plot of fluorescence intensity \((I/I_o)\) vs. concentration of SDBS and SDS for BIMCP-1 and probe 2 in water (5% DMSO).

The variation in temperature of the solution of BIMCP-1 - SDBS (2 \(\mu\)M : 50 \(\mu\)M) reveals that the formation of aggregates between BIMCP-1 and SDBS, which are responsible for AIEE phenomena, is fully reversible. On increasing the temperature of the solution of BIMCP-1 and SDBS/SDS from 25 °C to 85 °C, the fluorescence emission intensity of the solution decreased ~ 7 fold due to the de-aggregation process (Figure 8) and again on cooling it increased.

Figure 8. (a) Effect of Increasing temperature on the FI of the BIMCP-1 (2 \(\mu\)M) + SDBS (50 \(\mu\)M) complex; (b) Plot of FI vs. variable temperature (°C).
**4.5 $^1H$ NMR studies**

Furthermore, $^1H$ NMR spectroscopy of **BIMCP-1** as solutions in CD$_3$CN-D$_2$O (1:1) mixture revealed pronounced chemical shifts. On addition of 2 equiv. of SDBS to the solution of **BIMCP-1** (2.5 mM), the $p$-phenylene protons of 1, underwent upfield shift by 0.27 ppm (from $\delta$ 7.96 to 7.69), whereas the signals due to the benzimidazolium moiety did not undergo any significant change in the chemical shift (Figures 9). Reverse $^1H$ NMR titration was also performed with addition of aliquots of solution of **BIMCP-1** to the solution of SDBS (2.5 mM) in CD$_3$CN-D$_2$O (1:1) mixture, which showed upfield shift in the aromatic signals of SDBS, along with downfield shift of the $p$-phenylene protons (Figure 10).

![Diagram](image.png)

**Figure 9.** Partial $^1H$ NMR spectrum of **BIMCP-1** (2.5 mM) in CD$_3$CN-D$_2$O (1:1) mixture with gradual additions of SDBS (a) 0 mM (b) 1.25 mM; (c) 2.5 mM; (d) 3.75 mM and (e) 5.0 mM.
Figure 10. Partial $^1$H NMR spectrum of SDBS (2.5 mM) in CD$_3$CN-D$_2$O (1:1) mixture with gradual additions of BIMCP-1 solution (a) 0 mM (b) 1.25 mM; (c) 2.5 mM; (d) 5 mM and (e) 7.5 mM.

4.6 Morphological (SEM, Confocal microscope, AFM, and DLS) studies of BIMCP-1 with SDBS/SDS additions

Further, to evaluate the aggregation behavior of BIMCP-1, the thin films of BIMCP-1 (10 µM) and its 1:2 solution with SDBS/SDS (2 equiv.) were prepared in >98% aqueous solution on the glass surface using drop cast method. The respective films were studied both under confocal microscope and scanning electron microscope (SEM) and it has been observed that the respective films of BIMCP-1 alone do not show any morphology under both confocal microscope and scanning electron microscope (SEM). The films of BIMCP-1 and SDBS exhibit spherical structures with diameter in the range of 0.4-1.2 µm which shows uniformly distributed spherical morphology (Figure 11). The formation of these aggregates is in consonance with sharply increased fluorescence of BIMCP-1 on interaction with SDBS. These spheres on enlargement under SEM show them to be formed by the aggregation of fiber like structures. The film of BIMCP-1:SDBS (1:2) under confocal microscope shows circular aggregates with size between 0.5-1.5 µm and drastically increased blue fluorescence which is again in consonance with drastic 32-
fold increase in fluorescence on addition of SDBS to the solution of BIMCP-1. These spheres on enlargement under SEM show spheres being formed by the aggregation of fiber like structures. In case of SDS, the hemispheres formed by aggregation of BIMCP-1 with SDS were also evenly distributed throughout the film (Figure 11b, and 11d) and exhibited increased luminescence under confocal microscope.

Figure 11. SEM (a-b) and confocal (c-d) images respectively, of BIMCP-1 with different surfactants; (a,c) BIMCP-1 + SDBS; (b,d) BIMCP-1 + SDS.

Figure 12. Atomic force microscope (AFM) images of BIMCP-1 + SDBS.
AFM images of these films are also in consonance with the formation of spherical morphology (Figure 12). Dynamic light scattering experiments of BIMCP-1-SDS and BIMCP-1-SDBS (1:2) complexes at 5 μM show the formation of aggregates with 100 nm to 1000 nm size and are in agreement with aggregation of BIMCP-1 with SDS and SDBS under fluorescence experimental conditions (figure 13).

We propose that the mechanism for the observation of these fine spherical morphologies for BIMCP-1:SDBS complex is related with micelle type
aggregation. In polar solvent (H$_2$O), the polar benzimidazolium moieties of cyclophane BIMCP-1 complexed with sulfonate groups, are present on outside surface of the aggregates to form the hydrophilic exterior, whereas the dodecyl chains (hydrophobic tails) tend to gather in the core to stabilize the aggregates and result in aggregation induced fluorescence enhancement. The encapsulation of the anionic surfactant molecules in the cyclophane cavity largely neutralizes the positive charge of BIMCP-1; reduces the repulsive electrostatic interactions among the molecules of BIMCP-1 and in turn facilitates the aggregation process.

In conclusion, the cyclophane BIMCP-1 in the presence of 1-50 μM SDBS / SDS undergoes aggregation induced emission enhancement well below their CMC values and allows fluorescence based determination of SDS/SDBS. Confocal imaging and SEM studies confirm the formation of aggregates.

### 4.7 Experimental

#### 4.7.1 General note:
All reagents were purchased from commercial suppliers and used without further purification. Solvents used were purified and dried by standard methods prior to use. TLC analyses were performed on silica gel plates and column chromatography was conducted over silica gel (mesh 100-200). $^1$H NMR spectra and titrations were carried out using JEOL A1 spectrometer operating at 300 MHz at Guru Nanak Dev University, Amritsar or using Brucker 400 MHz machine at RSIC, Chandigarh. $^{13}$C NMR spectra were recorded at 75 MHz. All chemical shifts are reported in ppm relative to the TMS as an internal reference. UV-Vis studies were carried out on a Shimadzu UV-1601 PC or Shimadzu UV-2400 machines using slit width of 1.0 nm and matched quartz cells. HRMS spectra were recorded on Brucker MicroToff/QII. The fluorescence experiments including life time measurements were performed on Shimadzu 1501 and CHRONOS-BH fluorescence spectrophotometer. The particle sizes of the BIMCP-1 + SDBS/SDS aggregates in solution were determined using Metrohm Microtrac Ultra Nanotrac Particle Size Analyzer. The images of thin films were recorded using Nicon-A1R confocal microscope, high resolution scanning electron microscope machine Carl Zeiss Supra-55 and atomic field microscope machine Park Systems XE-100. Elemental
analysis was performed on Flash EA-1112 series CHNS-O analyzer instrument operative at GNDU.

4.7.2 Synthesis of BIMCP-1

1,4-Bis(benzimidazol-1-yl)benzene 4 (1 mmol, 310 mg) and 1,4-bis(bromomethyl)-2,3,5,6-tetramethylbenzene 5 (1 mmol, 320 mg) were dissolved in DMF (70 ml) and heated at 110 °C for 72 h. The solvent was removed under vacuum and crude solid thus separated was dissolved in methanol (10 ml). To this methanolic solution of compound was added aqueous NH$_4$PF$_6$ (2 mmol, 326 mg) dropwise with continuous stirring for 12 hr. The solid separated was filtered, dried to get white colored compound 1 (281 mg). Yield 37 %; m.p. 290 °C; $^1$H NMR (CD$_3$CN, 300 MHz): $\delta$ 2.36 (s, 24H, 8 × CH$_3$), 5.84 (s, 8H, 4 × CH$_2$), 7.80 (t, $J$ = 8.1 Hz, 4H, ArH), 7.86 (d, $J$ = 8.1 Hz, 4H, ArH), 7.91 (s, 8H, ArH), 7.95 (dd, $J_1$ = 6.9 Hz, $J_2$ = 1.2 Hz, 4H, ArH), 8.27 (d, $J$ = 8.4 Hz, 4H, ArH), 8.50 (s, 4H, bimC2H). $^{13}$C NMR (CD$_3$CN, 75 MHz): $\delta$ 17.0, 47.8, 114.6, 114.7, 128.9, 129.3, 129.4, 129.8, 132.5, 134.0, 135.6, 137.5, 139.5. HRMS $m/z$ (TOF MS ES$^+$) calculated for C$_{64}$H$_{60}$N$_8$F$_{18}$P$_3$ $^+$ [M$^+$], 1375.3877; found 1375.7388. (Found C, 50.58; H, 4.01; N, 7.39%; C$_{66}$H$_{57}$N$_6$P$_3$F$_{18}$ requires C, 50.54; H, 3.98; N, 7.37 %).

4.7.3 Synthesis of probe 2

1,4-Bis(benzimidazol-1-yl)benzene 4 (0.18 mmol, 54 mg) and 3-(bromomethyl)-1,2,4,5-tetramethylbenzene 6 (0.44 mmol, 100 mg) were dissolved in DMF (2 ml) and heated at 90 °C under N$_2$ for 12 h. Then, the solvent was removed under vacuum. The crude solid was dissolved in methanol (5 ml) and was filtered to remove any insoluble impurities. The aqueous NH$_4$PF$_6$ (0.5 mmol, 81 mg) was added drop wise with continuous stirring and stirring was continued for 24 h. Solid separated was filtered and dried under vacuum to get 2 as off-white solid. Yield 88 %; m.p. 165 °C; $^1$H NMR (DMSO-$d_6$, 300 MHz): $\delta$ 2.23 (s, 12H, 4 × CH$_3$), 2.25 (s, 12H, 4 × CH$_3$), 5.81 (s,
4H, 2 × CH₂), 7.14 (s, 2H, ArH), 7.78 - 7.86 (m, 6H, ArH), 8.05 (s, 4H, ArH), 8.27 (d, 2H, J = 8.7 Hz, ArH), 9.58 (s, 2H, bimC2H). ¹³C NMR (DMSO-d₆, 75 MHz): δ 15.5, 20.1, 46.4, 113.3, 114.3, 127.2, 127.7, 127.8, 131.5, 131.8, 133.0, 134.1, 134.2, 134.7, 141.6. HRMS m/z (TOF MS ES⁺) calculated for C₄₂H₄₄N₄F₆P⁺ [M⁺], 749.3213; found 749.3218. (Found C, 56.40; H, 4.51; N, 6.23%; C₄₂H₄₄N₄P₂F₁₂ requires C, 56.38; H, 4.96; N, 6.26%).

4.7.4 Synthesis of 1,4-bis(benzimidazolyl)benzene (3)

1,4-Diiodobenzene (5.0 g, 15.2 mmol), CuI (144 mg, 0.75 mmol) and benzotriazole (179 mg, 1.5 mmol) were dissolved in DMSO (10 ml). To this stirred solution was added benzimidazole (4.3 g, 36.5 mmol) and K-OBu' (4.9 g, 43.8 mmol) under N₂ and resulting reaction mixture was heated at 110 ºC till the completion of reaction as monitored by TLC. The reaction mixture was cooled to room temperature and water (20 ml) was added, followed by the addition of saturated solution of sodium sulfide (10 ml). The solid was filtered and crystallized from methanol to yield 3 as white crystalline solid. Yield 85%; ¹H NMR (DMSO-d₆ + CDCl₃): δ 7.48-7.09 (m, 4H, ArH), δ 7.73 (dd, 4H, J₁ = 8.7 Hz, J₂ = 3.0 Hz, ArH), δ 7.92 (s, 4H, ArH), δ 8.58 (s, 2H, bimC2H); ¹³C NMR (CDCl₃): δ 115.0, 118.2, 122.8, 124.3, 127.8, 134.4, 140.6, 143.9. (Found C, 77.48; H, 4.59; N, 18.05%; C₂₀H₁₄N₄ requires C, 77.40; H, 4.55; N, 18.05 %).

4.7.5 Procedure for photophysical studies of BIMCP-1

Stock solution of chemosensor BIMCP-1 and probe 2 were prepared at 10⁻³ M in DMSO and was then diluted to 5 μm by DMSO-H₂O mixture (5 : 95). The resulting solution was shaken well before recording the absorption or fluorescence spectra. The solutions of all the anions including surfactants were prepared in de-ionized water. Titration experiments were performed by placing 3 ml of a solution of chemosensor in a quartz cuvette of 1 cm optical path length, and then adding the surfactant or long chain carboxylate stock solution incrementally by means of a micro-pipette. Spectra were recorded 3 min after the addition.
All absorption scans and fluorescence spectra were saved as ACS II files and further processed in Excel™ to produce all graphs shown. Stability constants were determined by fitting the absorption and emission spectra recorded during the titrations of the chemosensor with surfactants and long chain carboxylates. The data was fitted with the global analysis program SPECFIT-32. For determining the stoichiometry of the various complexes, Job’s plot method was used. For this the ratio of intensities \( I_0/I \) (initial intensity / intensity at specific conc. of SDS/SDBS) vs. mole fraction of SDS/SDBS were plotted. The inflexion point in the Job’s plot analysis gives the stoichiometry of the complex.

To determine the particle sizes, the pre-incubated (40 °C) solution of BIMCP-1 (5 µM) and BIMCP-1 : SDBS/SDS (2 equiv.) were analysed under Metrohm Microtrac Ultra Nanotrac Particle Size Analyzer and respective histograms were obtained. The thin films of BIMCP-1 (10 µM) and its 1:2 solution with SDBS/SDS (2 equiv.) were prepared in > 98% aqueous solution on the glass surface using drop cast method. The images of these thin films were recorded using Nicon-A1R confocal microscope. The high resolution electron microscopic images of thin films were recorded under Scanning Electron Microscope machine Carl Zeiss Supra-55 and atomic field microscopic image of thin film of BIMCP-1 + SDBS (1:2) was recorded using Park Systems XE-100 machine.
References


