

## Electronic Supporting Information

### **AIEE in ionic self-assembled aggregates of benzimidazolium based cyclophane and SDBS**

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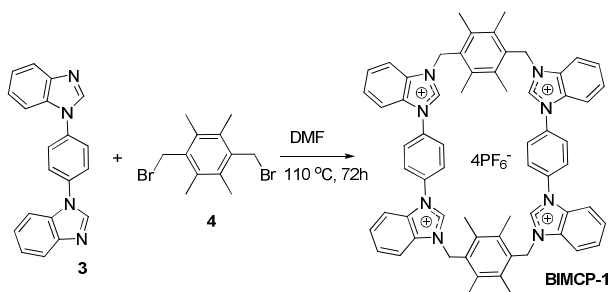
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#### **1. Experimental Details**

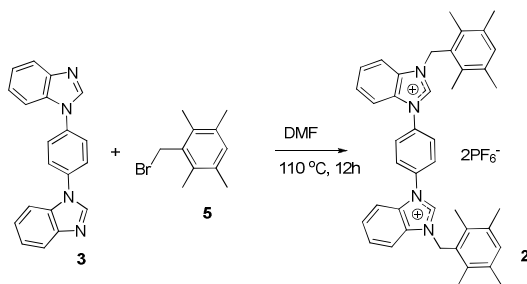
**General Remarks:** All chemicals were obtained from common suppliers (Aldrich, Across, SDFCL, Spectrochem etc.) and used without further purification. 1,4-bis(benzimidazol-1-yl)benzene<sup>3</sup> was synthesized by CuI, benzotriazole catalyzed N-arylation of benzimidazole with 1,4-diiodobenzene as reported in literature. The percentage purity of SDBS used supplied by the ACROS manufacturers was 88%. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on Bruker-400 and JEOL-300 instruments using the resonance of solvents having TMS as internal standard. Shifts are given in ppm; coupling constants in Hz. UV-Vis studies of compounds were performed on Shimadzu-2450 and fluorescence titration and life-time studies were performed on BH-CHRONOS spectrophotometers.

## 2. Synthesis of Cyclophane probe BIMCP-1.



1,4-bis(benzimidazol-1-yl)benzene **3** (1 mmol, 310 mg) and 1,4-bis(bromomethyl)-2,3,5,6-tetramethylbenzene **4** (1 mmol, 320 mg) were dissolved in DMF (70 ml) and heated at 110 °C for 72 hr. After completion of reaction, the solvent was removed under vacuum and the crude solid thus separated was dissolved in methanol (10 ml). To this methanolic solution of compound **3** was added aqueous  $\text{NH}_4\text{PF}_6$  (2 mmol, 326 mg) dropwise with continuous stirring for 12 hr. The solid separated was filtered, dried to get white colored compound **BIMCP-1** (281 mg), yield 37%. **M. pt.** 290 °C;  $^1\text{H NMR}$  ( $\text{CD}_3\text{CN}$ , 300 MHz):  $\delta$  2.36 (s, 24H,  $8 \times \text{CH}_3$ ), 5.84 (s, 8H,  $4 \times \text{CH}_2$ ), 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).  $^{13}\text{C NMR}$  ( $\text{CD}_3\text{CN}$ , 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  $\text{ES}^+$ ) calculated for  $\text{C}_{64}\text{H}_{60}\text{N}_8\text{F}_{18}\text{P}_3^+ [\text{M}^+]$ , 1375.3861; found 1375.3861. Found C, 50.55; H, 4.01; N, 7.40%;  $\text{C}_{64}\text{H}_{60}\text{N}_8\text{F}_{24}\text{P}_4$  requires C, 50.54; H, 3.98; N, 7.37%.

## Synthesis of probe 2.



1,4-Bis(benzimidazol-1-yl)benzene **3** (0.18 mmol, 54 mg) and 3-(bromomethyl)-1,2,4,5-tetramethylbenzene **5** (0.44 mmol, 100 mg) were dissolved in DMF (2 ml) and heated at 90 °C under  $\text{N}_2$  for 12 h. After completion of reaction, 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  $\text{NH}_4\text{PF}_6$  (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. pt.** 165 °C;  $^1\text{H NMR}$  ( $\text{DMSO}-d_6$ , 300 MHz):  $\delta$  2.23 (s, 12H,  $4 \times \text{CH}_3$ ), 2.25 (s, 12H,  $4 \times \text{CH}_3$ ), 5.81 (s, 4H,  $2 \times \text{CH}_2$ ), 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, Bim C2H).  $^{13}\text{C NMR}$  ( $\text{DMSO}-d_6$ , 75 MHz):  $\delta$  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  $\text{ES}^+$ ) calculated for  $\text{C}_{42}\text{H}_{44}\text{N}_4\text{F}_6\text{P}^+ [\text{M}^+]$ , 749.3202; found 749.3138. Found C, 56.42; H, 5.02; N, 6.32%;  $\text{C}_{42}\text{H}_{44}\text{N}_4\text{F}_{12}\text{P}_2$  requires C, 56.38; H, 4.96; N, 6.26%.

### 3. Spectral Analysis Data of cyclophane BIMCP-1 and 2.

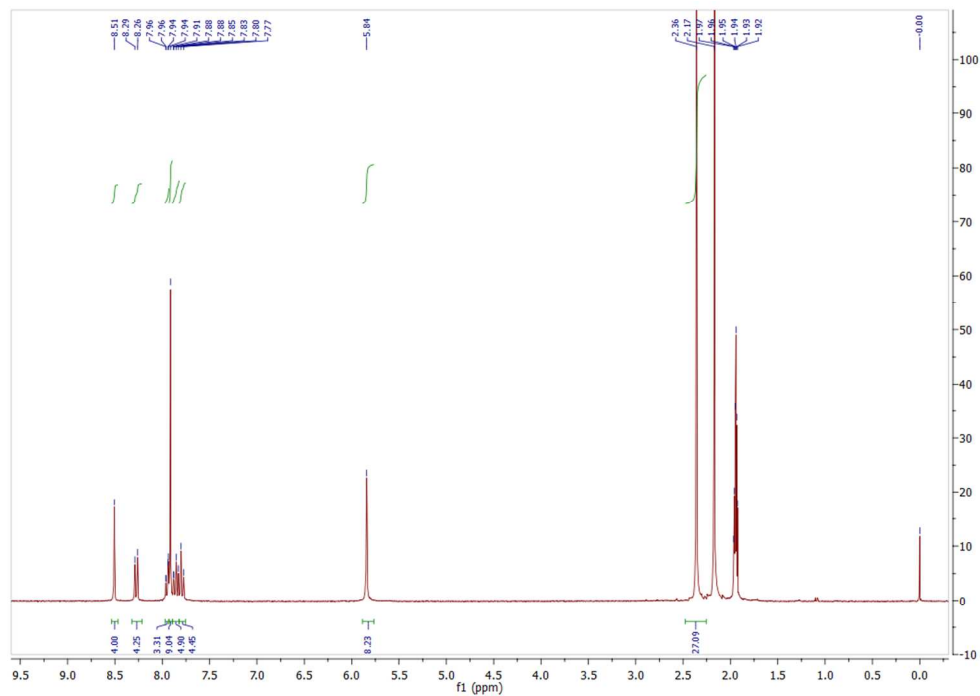


Figure SI-1.  $^1\text{H}$  NMR spectrum of BIMCP-1 in  $\text{CD}_3\text{CN}$ .

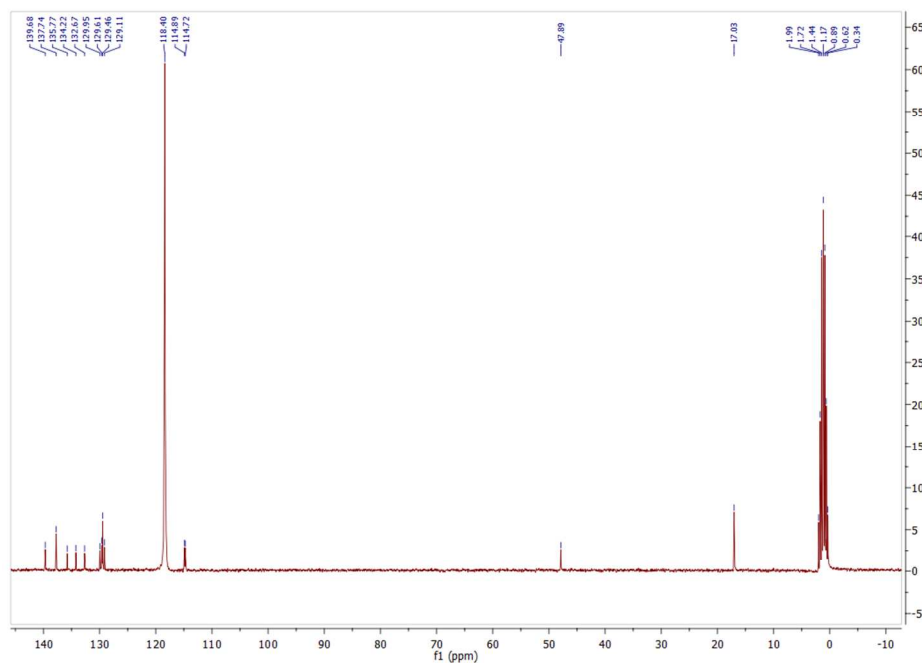


Figure SI-2.  $^{13}\text{C}$  NMR spectrum of BIMCP-1 in  $\text{CD}_3\text{CN}$ .

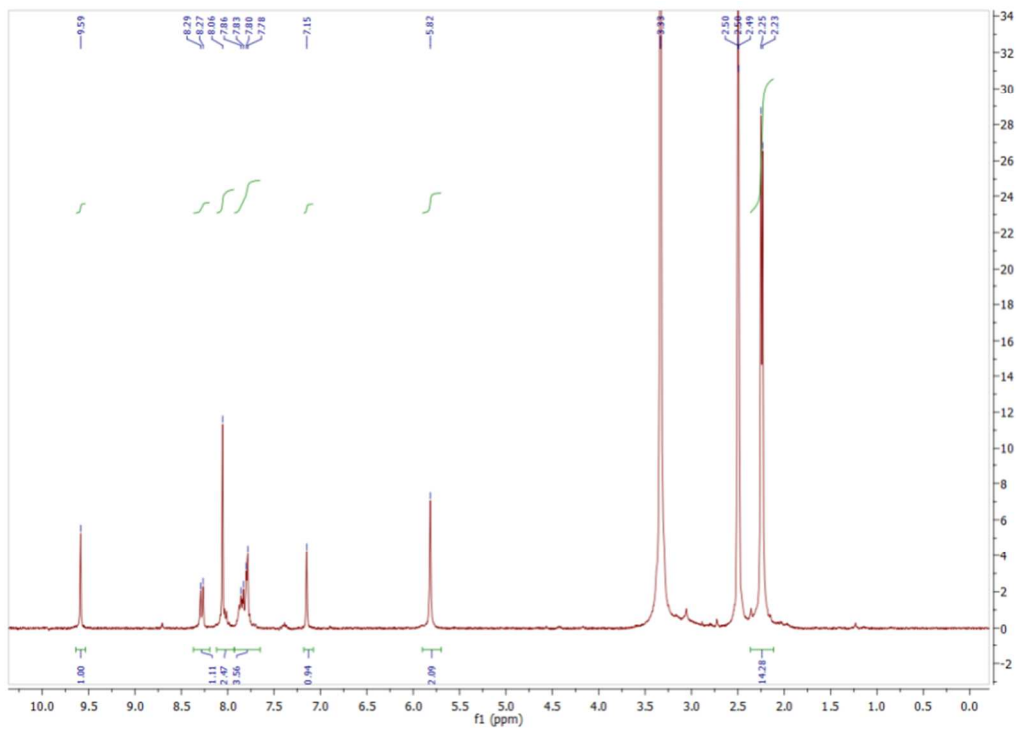


Figure SI-3.  $^1\text{H}$  NMR spectrum of **2** in  $\text{DMSO-}d_6$

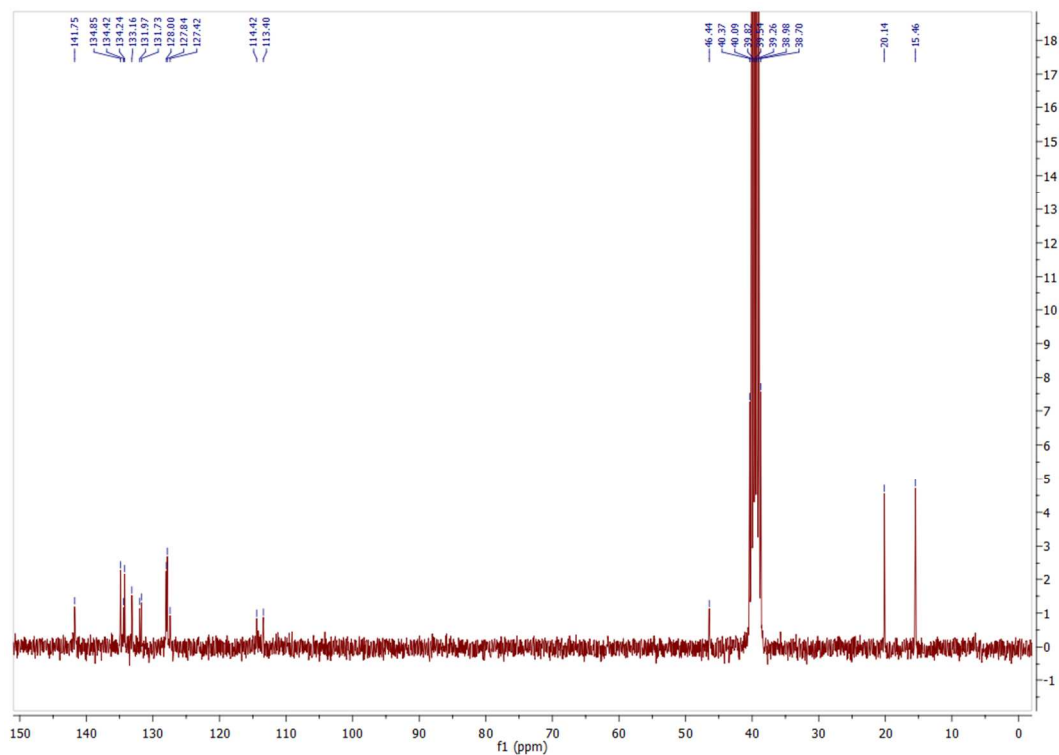


Figure SI-4.  $^{13}\text{C}$  NMR spectrum of **2** in  $\text{DMSO-}d_6$

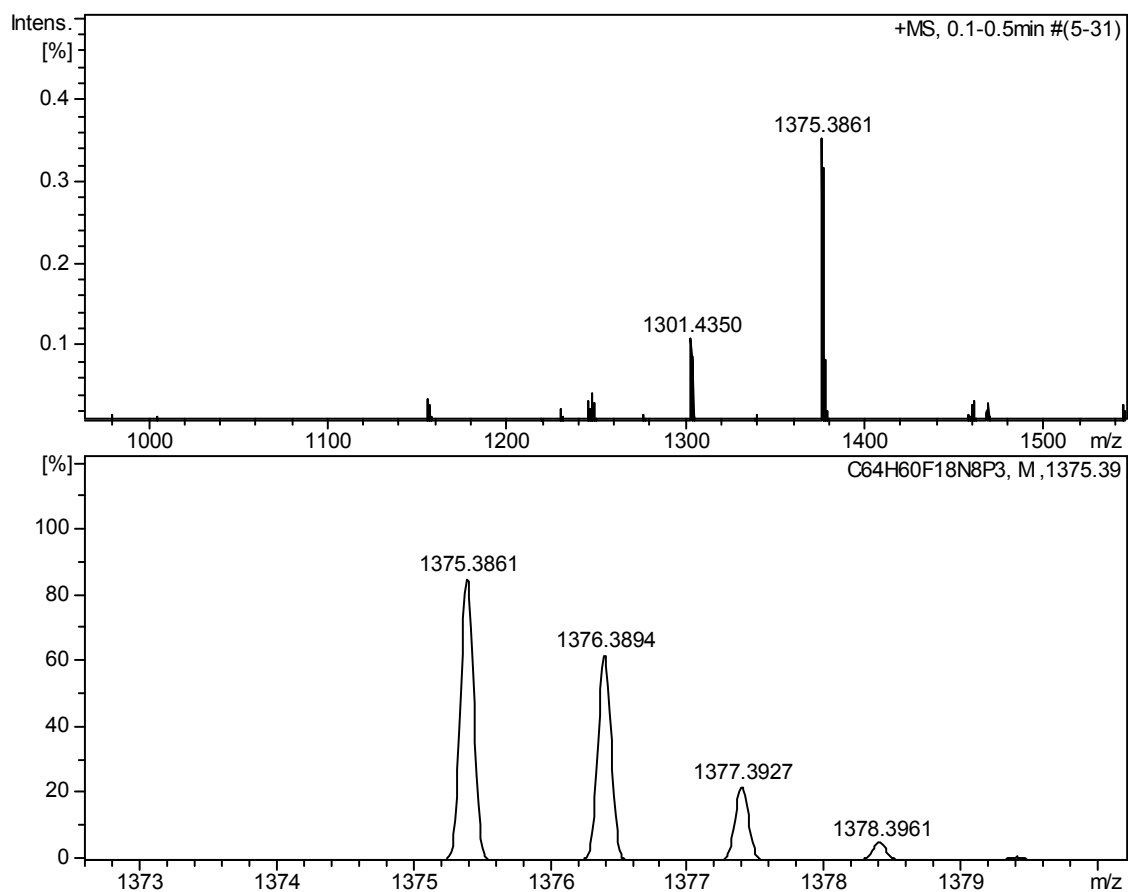


Fig SI-5 HRMS of BIMCP-1

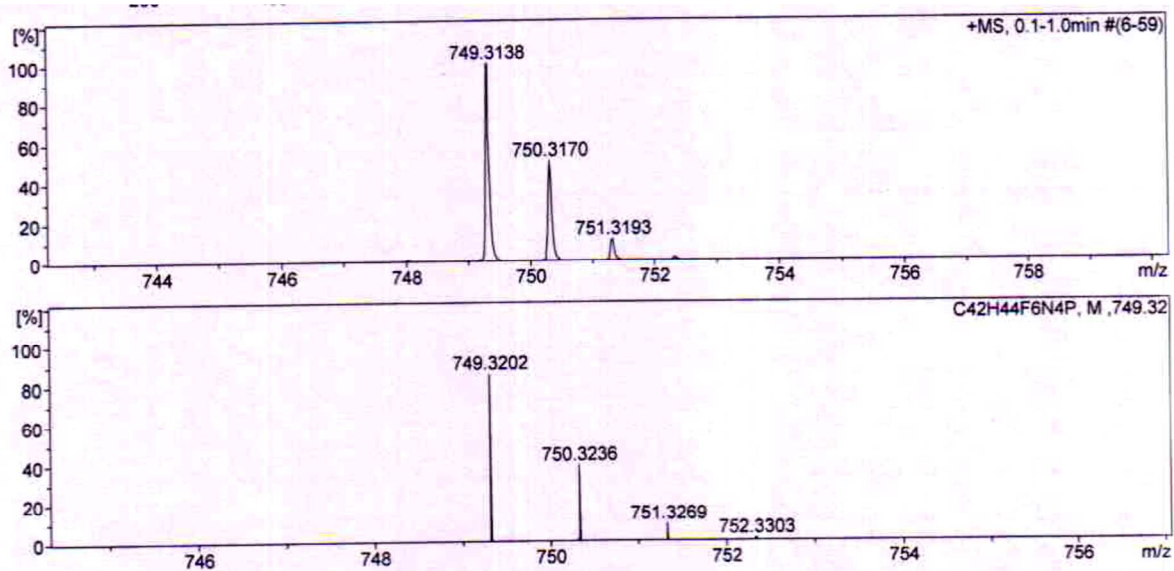


Fig SI-6 HRMS of compound 2

#### 4. Atomic Force Microscope (AFM) images of BIMCP-1 + SDBS.

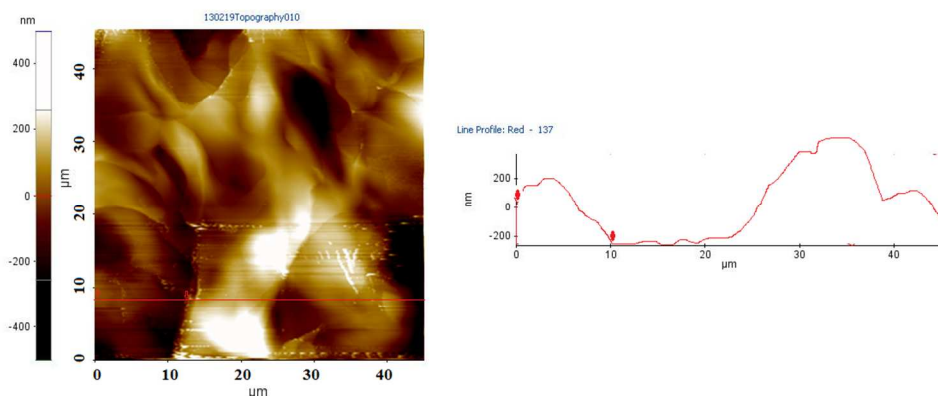


Figure SI-7. Atomic force microscope (AFM) images of BIMCP-1 + SDBS.

#### 5. Confocal images of BIMCP-1 with additions of SDBS and SDS.

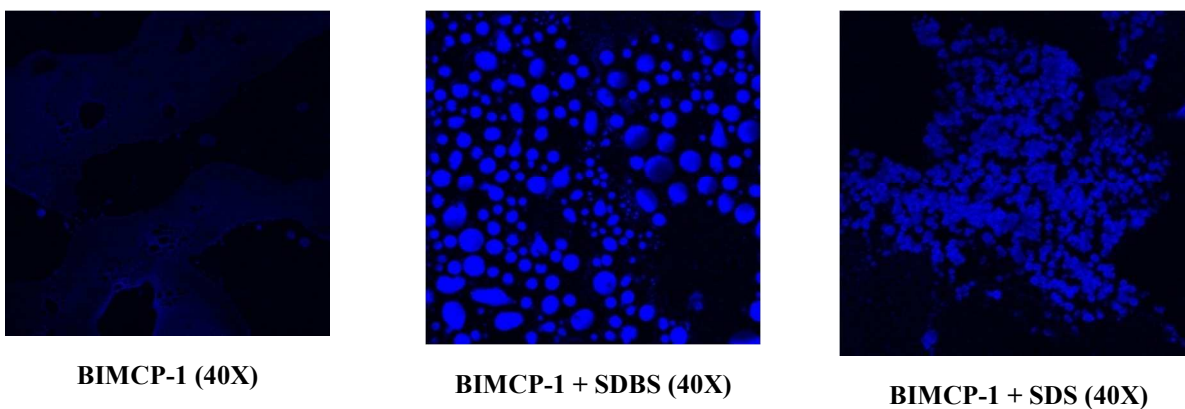


Figure SI-8. Confocal microscope images of thin films prepared by drop cast method of BIMCP-1(alone) and BIMCP-1with addition of SDBS and SDS (2 equiv.).

#### 6. Dynamic light scattering (DLS) experiment of BIMCP-1 with addition of SDBS/SDS

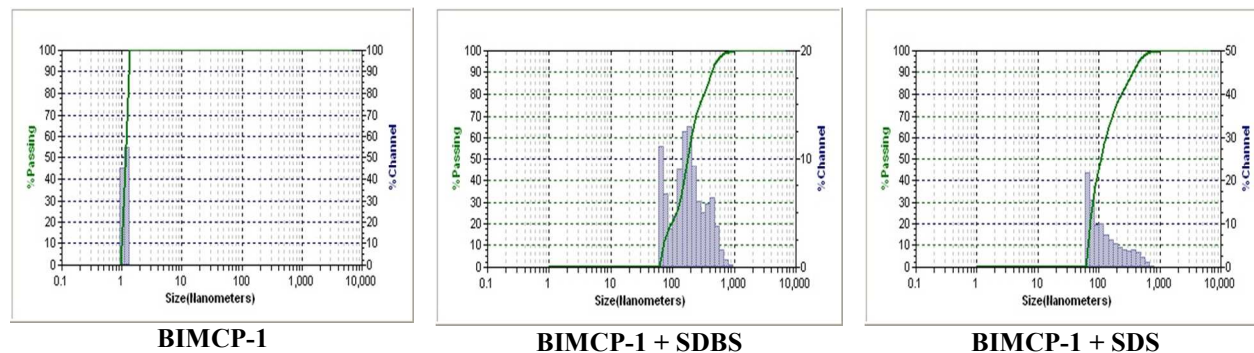


Figure SI 9. Dynamic light scattering (DLS) experiment of BIMCP-1 (5  $\mu\text{M}$ ) with addition of SDBS/SDS (2 equiv.) in 95% aqueous solution.

## 7. FI vs. [Conc.] plot of BIMCP-1 and compound 2

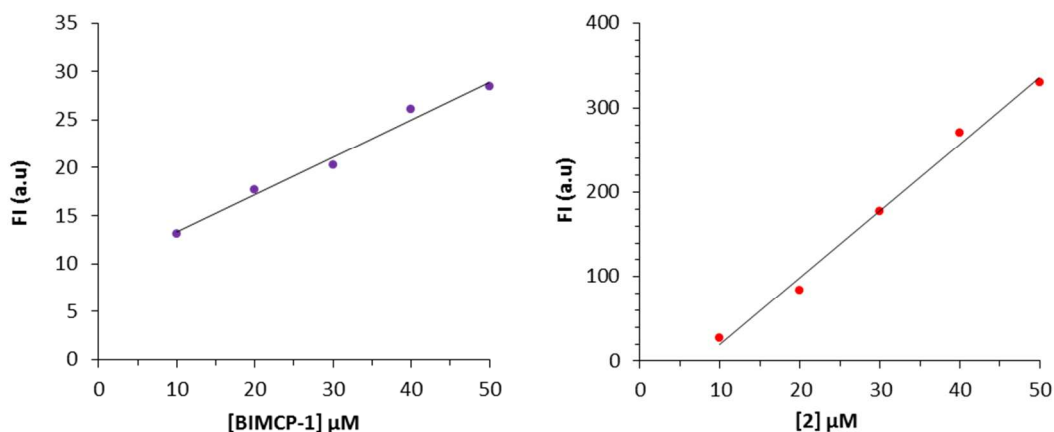


Figure SI-10. Plot of FI vs. BIMCP-1 and compound 2 in 95% aqueous solution

## 8. Anion addition studies of BIMCP-1 and 2.

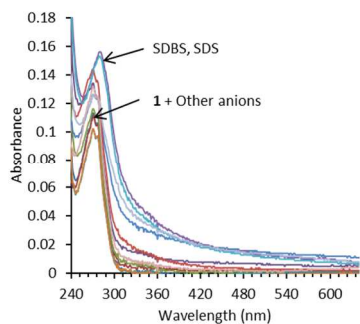


Figure SI-11a. Effect of different anions on the UV-Vis spectrum of BIMCP-1 (2  $\mu\text{M}$ ) in aqueous solution (5% DMSO).

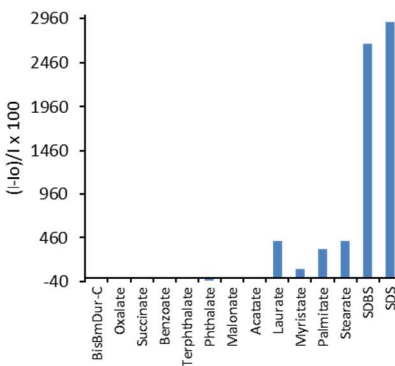


Figure SI-11b. Effect of different anions on the fluorescence spectrum of BIMCP-1 (2  $\mu\text{M}$ ) in aqueous solution (5% DMSO).

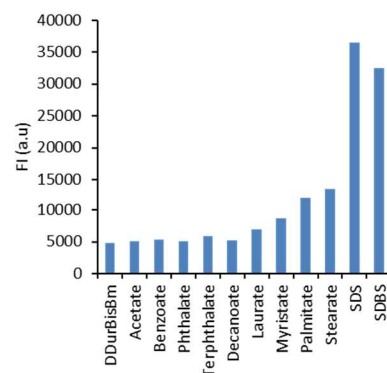


Figure SI-11c. Effect of different anions on the fluorescence spectrum of 2 (5  $\mu\text{M}$ ) in aqueous solution (5% DMSO).

Table 1. The increase in the emission intensity with addition of alkyl sulfonates/carboxylates to the 95% aqueous solution of cyclophane BIMCP-1 and 2.

BIMCP-1	Fold increase in intensity
<b>1</b>	
1 + SDS (C12)-OSO <sub>3</sub> <sup>-</sup>	32
1 + SDBS (C12)-Bz-OSO <sub>3</sub> <sup>-</sup>	27
1 + Stearate (C18)-COO <sup>-</sup>	5
1 + Palmitate (C16)-COO <sup>-</sup>	4
1 + Myristate (C14)-COO <sup>-</sup>	2
1 + Laurate (C12)-COO <sup>-</sup>	5
<b>Probe 2 (acyclic)</b>	<b>Fold increase in intensity</b>

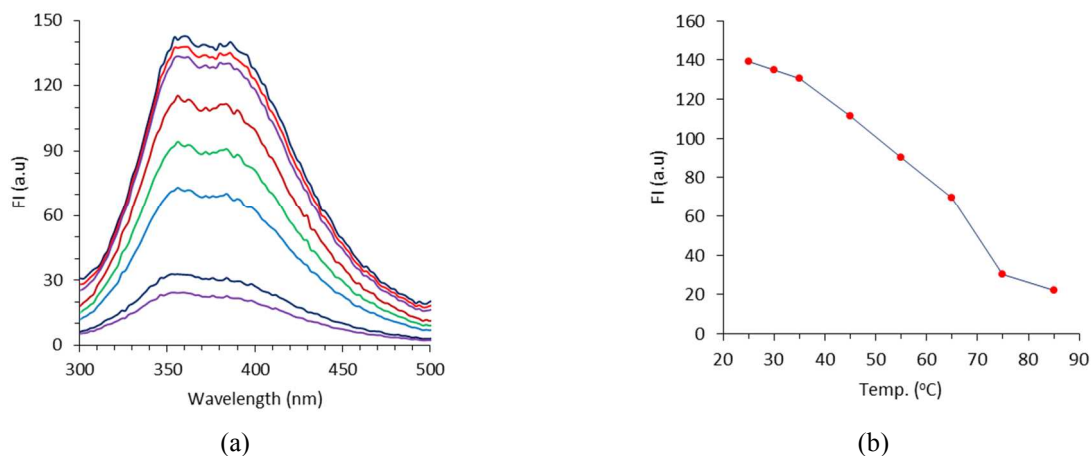
<b>2</b>	
<b>2</b> + SDS (C12)-OSO <sub>3</sub> <sup>-</sup>	7
<b>2</b> + SDBS (C12)-Bz-OSO <sub>3</sub> <sup>-</sup>	7
<b>2</b> + Stearate (C18)-COO <sup>-</sup>	3
<b>2</b> + Palmitate (C16)-COO <sup>-</sup>	2
<b>2</b> + Myristate (C14)-COO <sup>-</sup>	1.7
<b>2</b> + Laurate (C12)-COO <sup>-</sup>	1.4

**Table 2. Photophysical properties of BIMCP-1 and 2.**

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

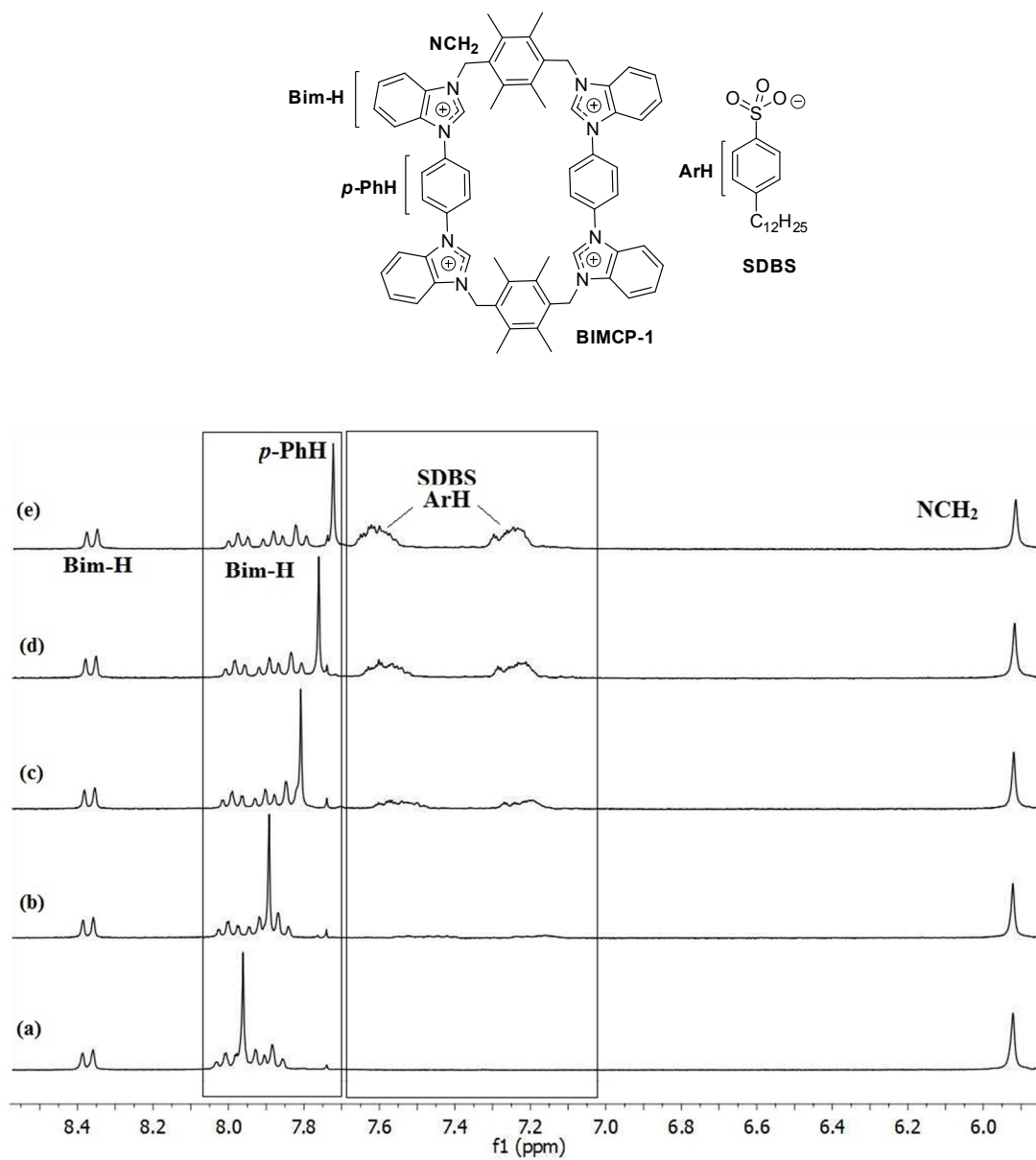
### 9. Temperature dependent variation in fluorescence intensity of BIMCP-1 + SDBS complex.

Fluorescence intensity of **BIMCP-1** + SDBS complex showed gradual decrease with increase in temperature (25 °C to 85 °C), providing evidence that de-aggregation process was favored with rise in temperature. The emission intensity of **BIMCP-1** + SDBS complex was revised again on bringing to room temperature (25 °C).

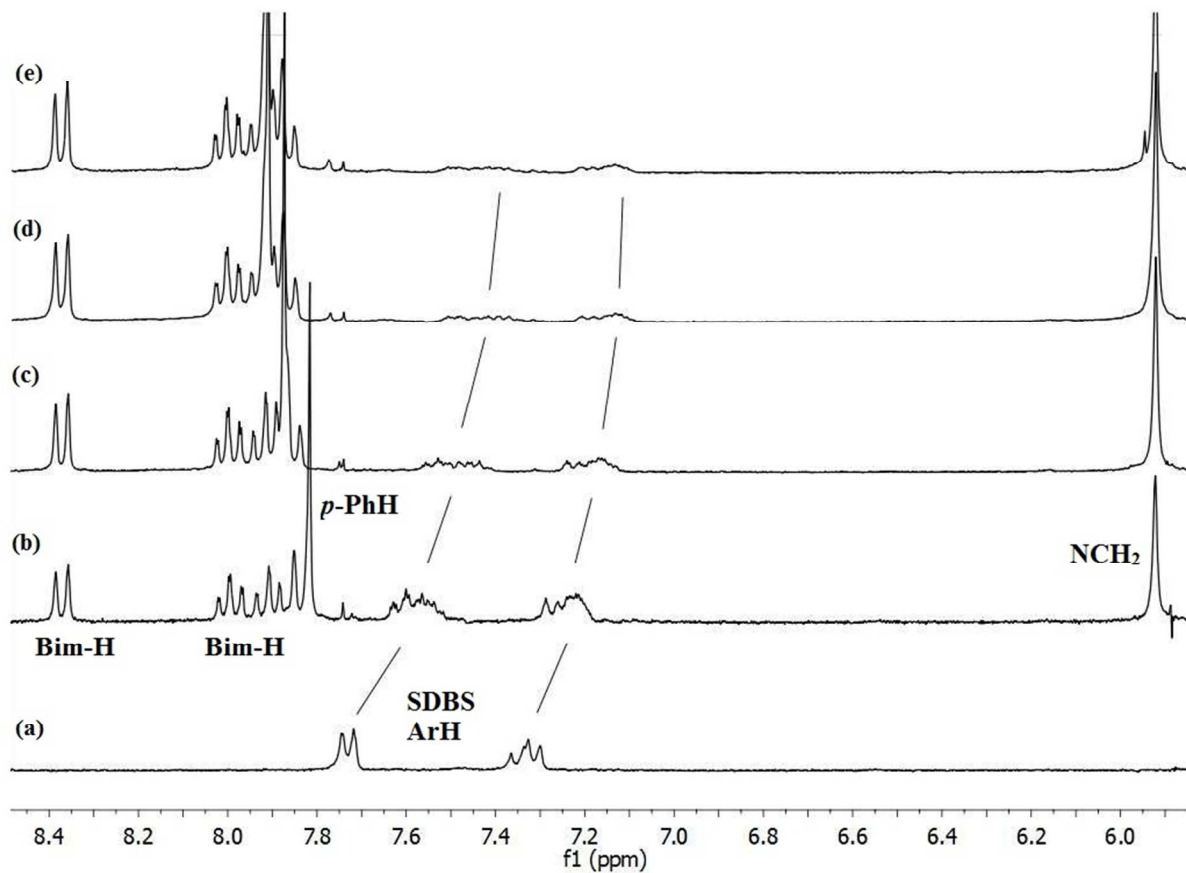


**Figure SI-12.** (a) Effect of Increasing temperature on the fluorescence intensity (FI) of the **BIMCP-1** (2  $\mu\text{M}$ ) + SDBS (50  $\mu\text{M}$ ) complex; (b) Plot of FI vs. Temp. (°C).

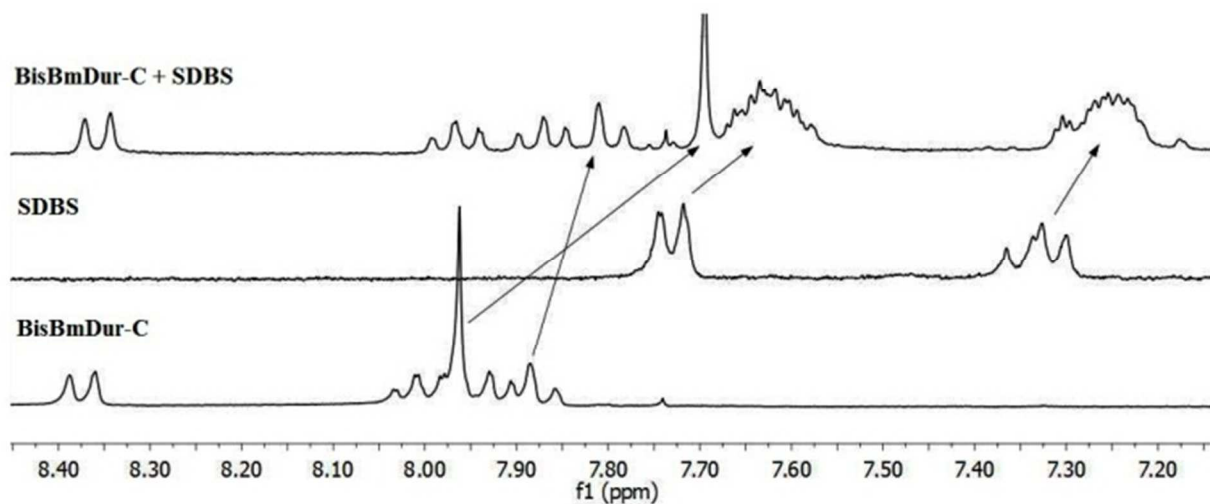
### 10. $^1\text{H}$ NMR titration profile of BIMCP-1 with SDBS



**Figure SI-13.** Partial  $^1\text{H}$  NMR spectrum of **BIMCP-1** (2.5 mM) in  $\text{CD}_3\text{CN-D}_2\text{O}$  (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) 5.0mM.



**Figure SI-14.** Partial  $^1\text{H}$  NMR spectrum of SDBS (2.5 mM) in  $\text{CD}_3\text{CN-D}_2\text{O}$  (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.



**Figure SI-15.**  $^1\text{H}$  NMR spectrum of (a) **BIMCP-1** (2.5 mM); (b) SDBS (2.5 mM); and (c) **BIMCP-1** + SDBS (3 equiv.) in  $\text{CD}_3\text{CN-D}_2\text{O}$  (1:1) mixture.

### 11. Life-time Studies of BIMCP-1 with additions of SDBS and SDS

Fluorescence Life-times were calculated on CHRONOS-BH spectrophotometer using anthranilic acid as reference standard<sup>1</sup>.

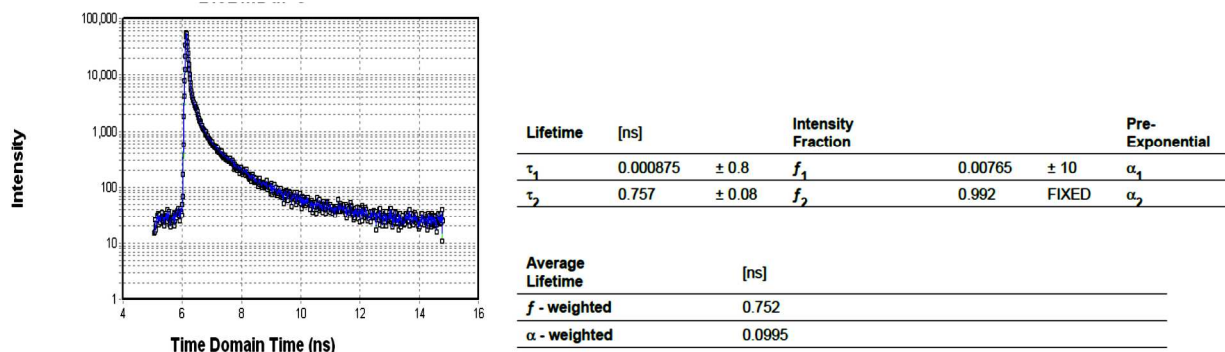


Figure SI-16. Fluorescence decay profile of BIMCP-1.

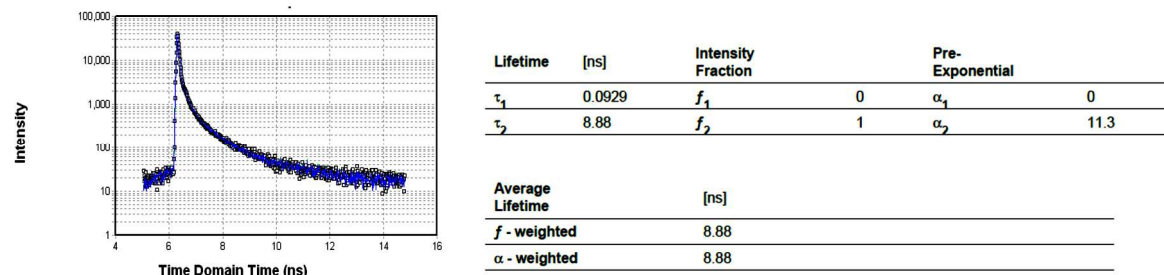


Figure SI-17. Fluorescence decay profile of BIMCP-1 + SDBS (2 equiv).

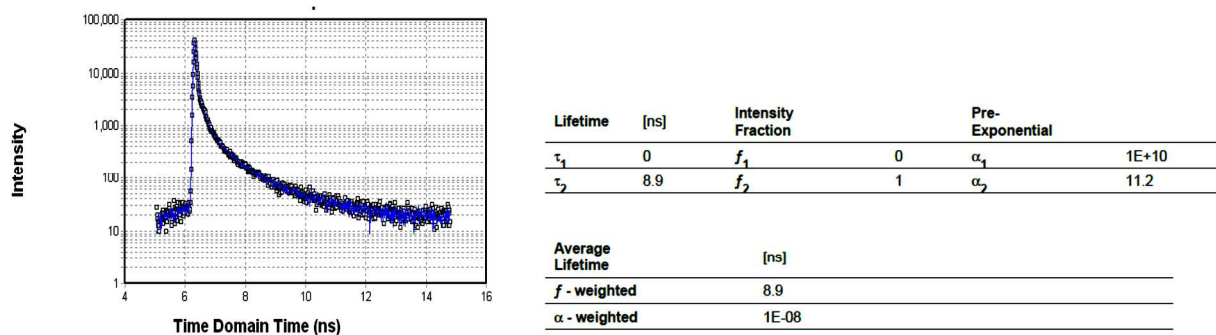
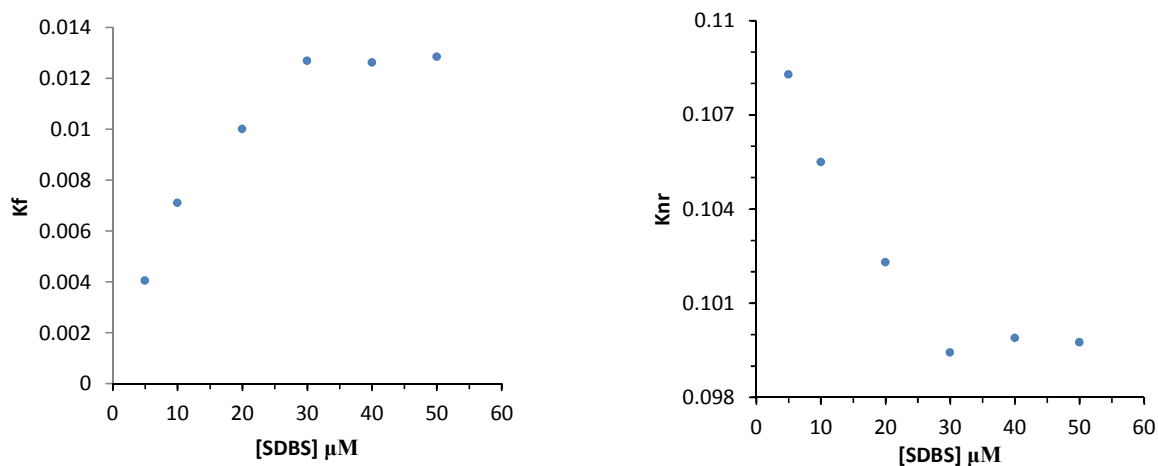


Figure SI-18. Fluorescence decay profile of BIMCP-1 + SDS (2 equiv).

1. J. R. Lakowicz, *Principles of Fluorescence Spectroscopy*, 2<sup>nd</sup> Ed., Kluwer Academic/Plenum Publishers, New York, London, Moscow, Dordrecht, 1999.

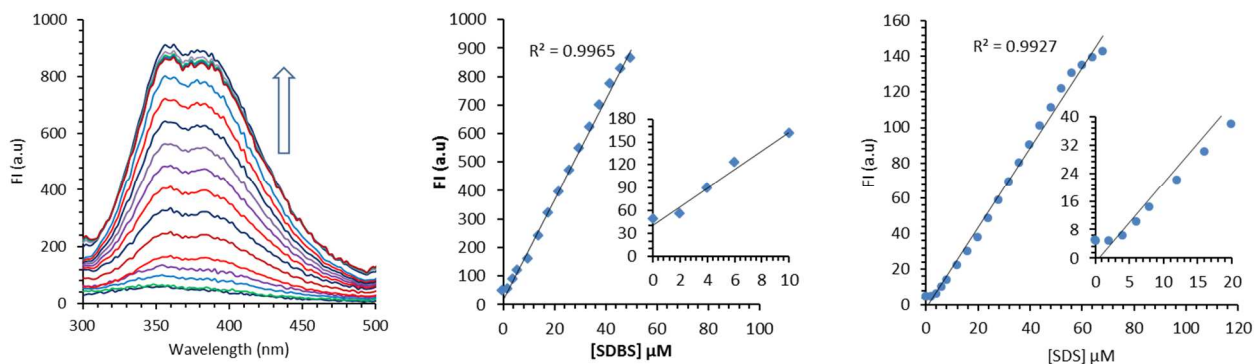
**12. Plots of  $K_f$  and  $K_{nr}$  vs concentration of BIMCP-1 + SDBS complex**



**Figure SI 19.** Plots of (a)  $K_f$  (radiative decay constant); and (b)  $K_{nr}$  (non radiative decay constant) vs. concentration of BIMCP-1 + SDBS complex.

**13. Fluorescence titration profiles of BIMCP-1 and probe 2 with SDBS and SDS**

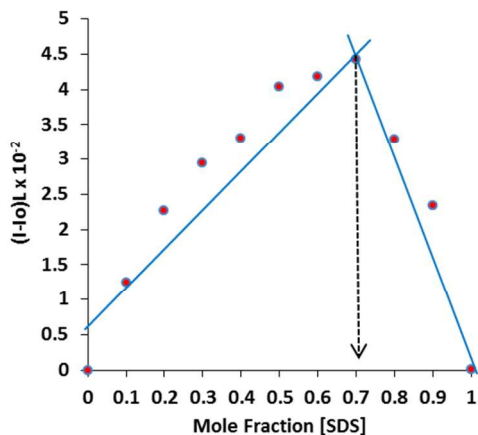
**Emission behavior of BIMCP-1 upon addition of SDS and SDBS:**



**Figure SI-20a.** Effect of gradual addition of SDS on the emission spectrum of BIMCP-1 (2  $\mu\text{M}$ ) in 95% aqueous solution.

**Figure SI-20b.** FI (380 nm) vs. [SDBS] concentration plot of BIMCP-1 on titration with SDBS in 95% aqueous solution.

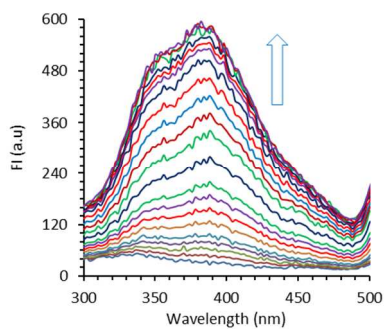
**Figure SI-20c.** FI (380 nm) vs. [SDS] concentration plot of BIMCP-1 on titration with SDS in 95% aqueous solution.



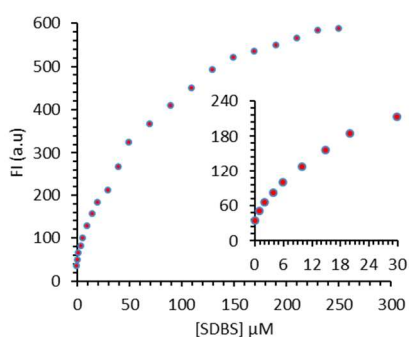
**Figure SI 21.** Job's Plot of **BIMCP-1** with SDS showing inflexion point near to 0.7 showing 1:2 (**BIMCP-1**: SDS) stoichiometry.

### Emission behavior of **2** upon addition of SDS and SDBS:

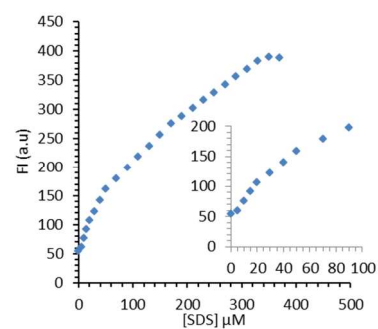
Addition of SDBS to the 95% aqueous DMSO solution of **2** resulted in increase in emission intensity between 320 to 470 nm with maxima at 385 nm. The spectral fitting of the data obtained by titration of **2** with SDBS by non-linear regression analysis programme (SPECFIT-32) shows the formation of 1:1 and 1:2 stoichiometric species (Host – guest) with association constant values of  $\log \beta_{L(SDBS)} = 4.24 \pm 0.15$ ; and  $\log \beta_{L(SDBS)_2} = 7.40 \pm 0.28$ . Similarly, the titration analysis of SDS with **2** exhibits association constant value of  $\log \beta_{L(SDS)} = 4.09 \pm 0.12$  and  $7.63 \pm 0.35$  for 1:1 and 2:1 (SDS: **2**) complexes.



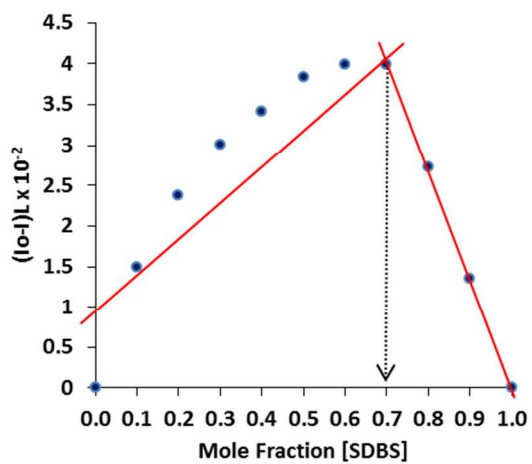
**Figure SI-22a.** Effect of gradual addition of SDSB solution to emission intensity of **2** (5 μM) in aqueous solution (5% DMSO).



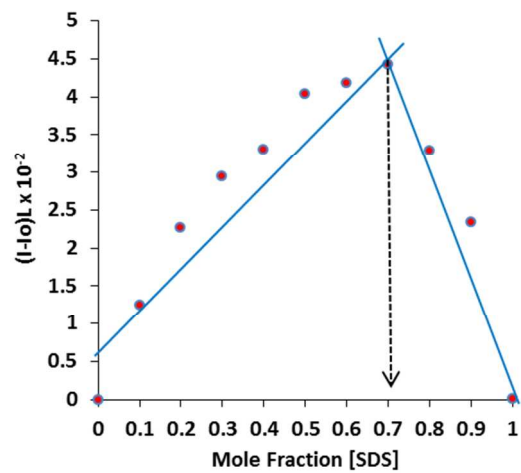
**Figure SI-22b.** Fluorescence intensity vs. [SDBS] concentration plot of **2** on titration with SDBS.



**Figure SI-22c.** Fluorescence intensity vs. [SDS] concentration plot of **2** on titration with SDS.



(a)



(b)

**Figure SI 23.** Job's Plot of **compound 2** with (a) SDBS and (b) SDS showing inflexion point near to 0.7 showing 1:2 stoichiometry.