Supporting Information

Dual Self-sorting by Cucurbit[8]uril to Transform a Mixed Micelle to Vesicle

Julfikar Hassan Mondal, Titli Ghosh, Sahnawaz Ahmed, and Debapratim Das

Department of Chemistry

Indian Institute of Technology Guwahati

Assam 781039, India

Email: ddas@iitg.ernet.in

Contents:

Synthesis

Cucurbit[8]uril (CB[8]): CB[8] was synthesized following a previously published protocol.[25] ^{1}H NMR (600 MHz, $D_2O/CF_3CO_2D/D_2SO_4$ (1:1:0.15)): δ 4.25 (d, 16H), 5.55 (s, 16H), 5.86 (d, 16H); MS (ESI): m/z 1461.41 $(CB[8] + Cs)^+$.

HDEV: 1g (6.4 mmol) of 4,4'-dipyridyl was mixed with 5 mL (67 mmol) ethyl bromide in dichloromethane and refluxed for three days and excess (0.5 ml) ethylbromide was added after every 6h. A yellow precipitate formed. The volatiles were removed on a rotory evaporator before washing the residue several times with toluene and finally with diethyl ether to get a yellow solid as mono-ethylviologen (yield: 1.6 g, 95%). The purity of the product was confirmed by ^{1}H NMR spectroscopy. The obtained solid was then further alkylated on the other pyridyl group by taking it in 7:3 acetonitrile/methanol and refluxing the mixture in presence of 2.75 g (9.05 mmol, 1.5 equiv.) of 1-bromohexadecane for 24 h. The precipitate obtained was filtered and washed several times with toluene followed by diethyl ether. The surfactant was further purified by recrystalizing it three times from methanol/diethyl ether (Yield: 70%).^{1}H NMR (600 MHz, D_2O) $\delta =$ 9.39 (d, 2H), 9.24 (d, 2H), 8.73 (d, 2H), 8.68 (d, 2H), 4.94 (t, 2H), 4.84 (q, 2H), 2.26 (t, 3H), 1.75 (m, 2H) 1.45 (br, 26H), 0.95 (t, 3H); ^{13}C NMR (D_2O, 100 MHz): δ 149.89, 149.56, 145.67, 145.34, 127.30, 127.21, 62.01, 57.73, 32.10, 31.28, 30.19, 30.01, 29.86, 26.38, 22.77, 15.85, 14.01; E.A : calculated for $C_{28}H_{46}Br_2N_2$: C, 58.95; H, 8.13; N, 4.91. Found : C, 58.88; H, 8.17; N, 4.94; MS (ESI): m/z calcd for $[M-Br]^+$ $C_{28}H_{46}N_2Br$: 489.28, found: 489.35.

DEV: Excess (7.5 ml, 99.8 mmol) Ethylbromide was mixed with 4,4'-dipyridyl (1.56 g, 9.98 mmol) in a glass tube and the mouth of the tube was sealed. The tube was heated to 80 °C for 24 h. After cooling down to room temperature the seal was broken and the material was concentrated on a rotory evaporator and the residue was crystallized three times from methanol-diethyl ether to get a yellow solid (Yield: 35%). ^{1}H NMR (600 MHz, D_2O) δ 9.15 (d, 4H), 8.56 (d, 4H), 4.77(m, 4H), 1.73 (t,

6H); ^{13}C NMR (100 MHz, D_2O): δ 148.46, 145.65, 126.61, 56.43, 16.39; E.A : calculated for $C_{14}H_{18}Br_2N_2$: C, 44.95; H, 4.85; N, 7.49. Found : C, 44.92; H, 4.87; N, 7.52; MS (ESI): m/z calcd for $[M-Br]^+$ $C_{14}H_{18}N_2Br$: 293.06, found: 293.15.

Table S1. CMC values of surfactants and their mixtures determined using surface tension and conductometry at 298 K.

System	CMC (mM) Surface Tension	CMC (mM) Conductometry	CMC_{av} (mM)
CTAB	**0.99**	**1.10**	**1.05**
HDEV	**2.77**	**2.85**	**2.81**
CTAB-HDEV (1:1)	**1.17**	**1.23**	**1.20**
CTAB-HDEV-CB[8] (1:1:1)	**1.26**	**1.34**	**1.30**

Table S2. Binding constants (K_a) and related thermodynamic parameters for the complexation of CTAB and HDEV with CB[8] at 298 K in 100 mM phosphate buffer pH 7.

Guest	K_a [M^{-1}]	$H°$ [kj mol^{-1}]	$T\Delta S°$ [kj mol^{-1}]
CTAB	$(2.0 \pm 0.1) \times 10^5$	-27.1± 0.1	2.97± 0.1
HDEV	$(3.8 \pm 0.1) \times 10^5$	-25.3± 0.1	6.5 ± 0.1

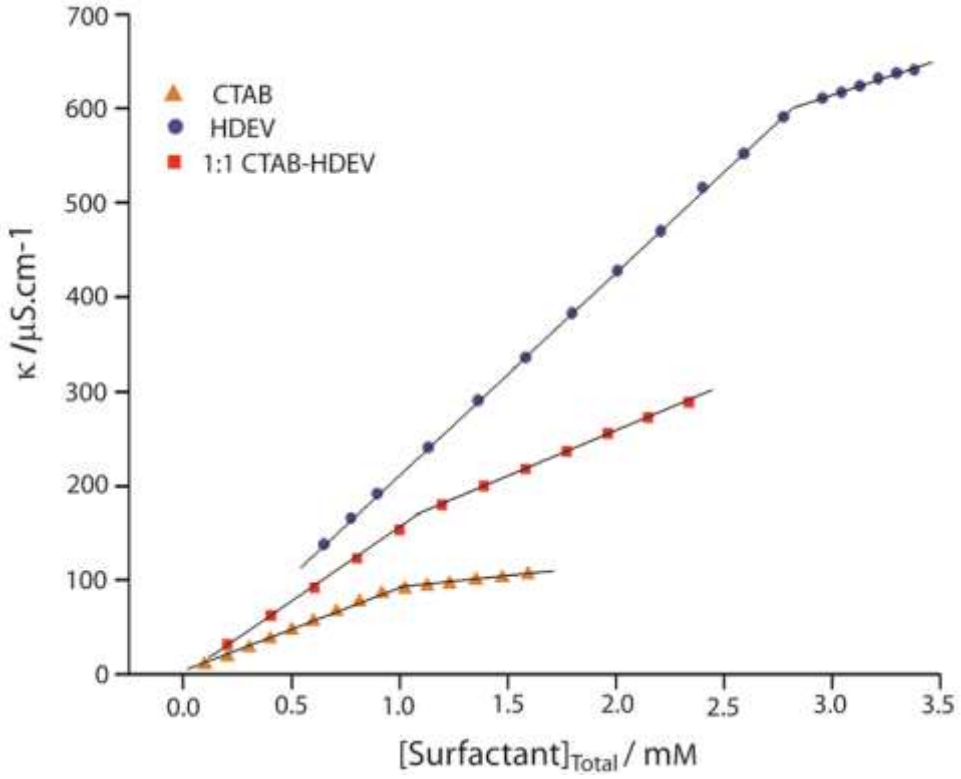

Figure S1. Conductomentric determination of the CMCs of CTAB, HDEV and 1:1 CTAB-HDEV at 298 K.

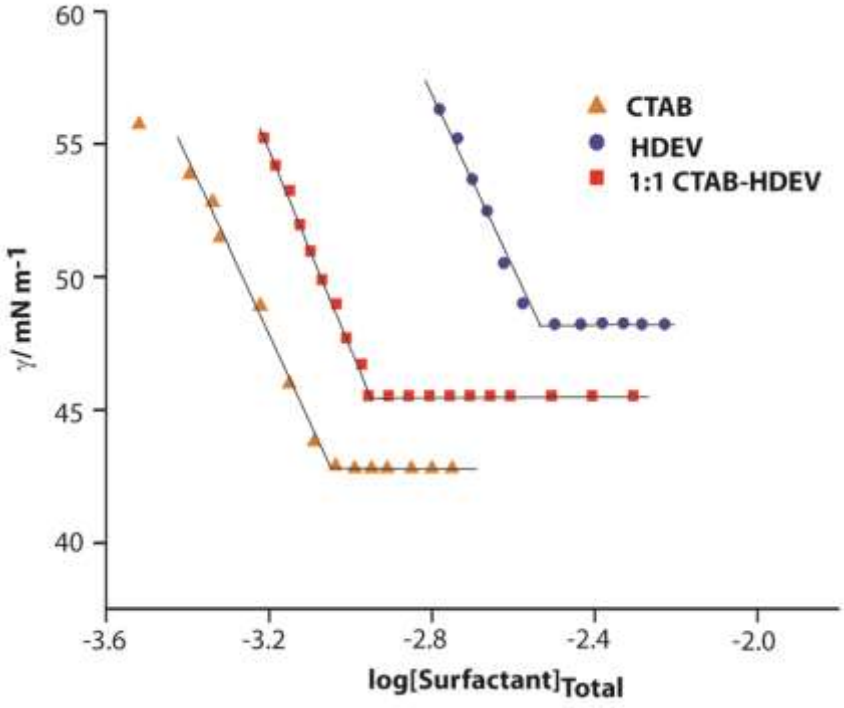

Figure S2. Tensiometric determination of the CMCs of CTAB, HDEV and 1:1 CTAB-HDEV at 298 K.

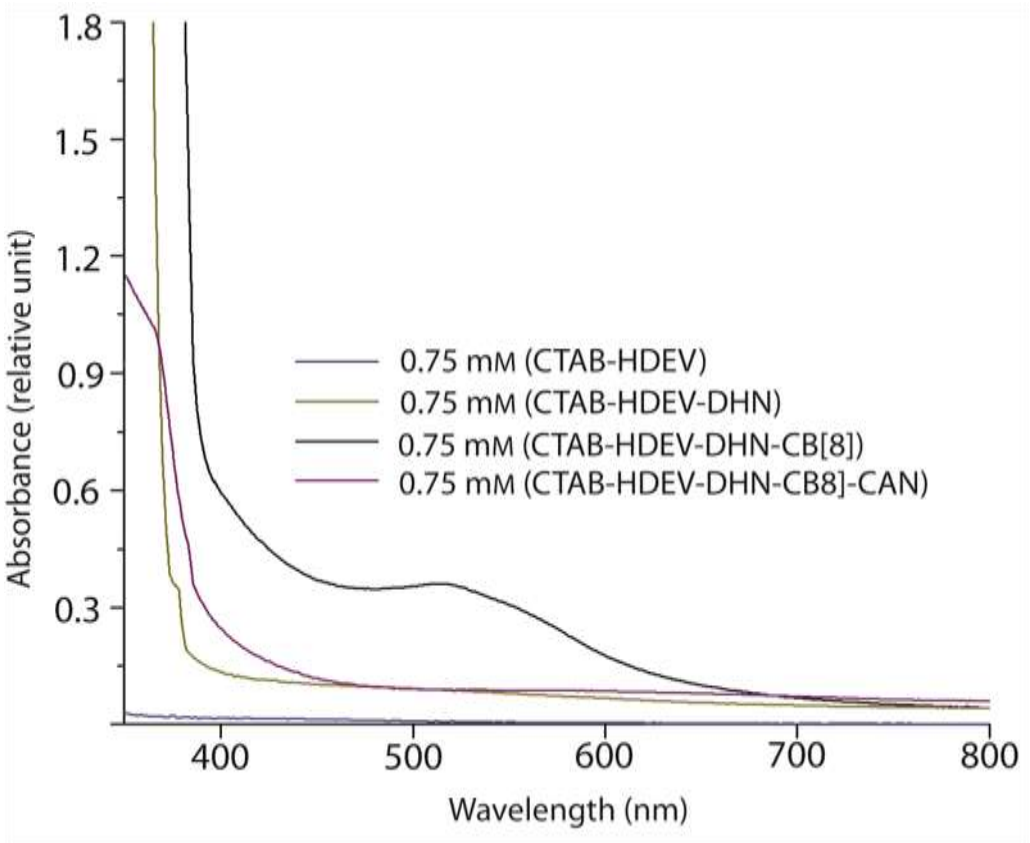

Fig. S3. UV-Visible spectra of aqueous solutions prepared by the mixture of CTAB, HDEV, DHN, and CB[8] at different combinations at 298 K showing the appearance of the charge transfer band upon formation of HDEV-DHN@CB[8] ternary complex and the disappearance of the same upon treatment with CAN.

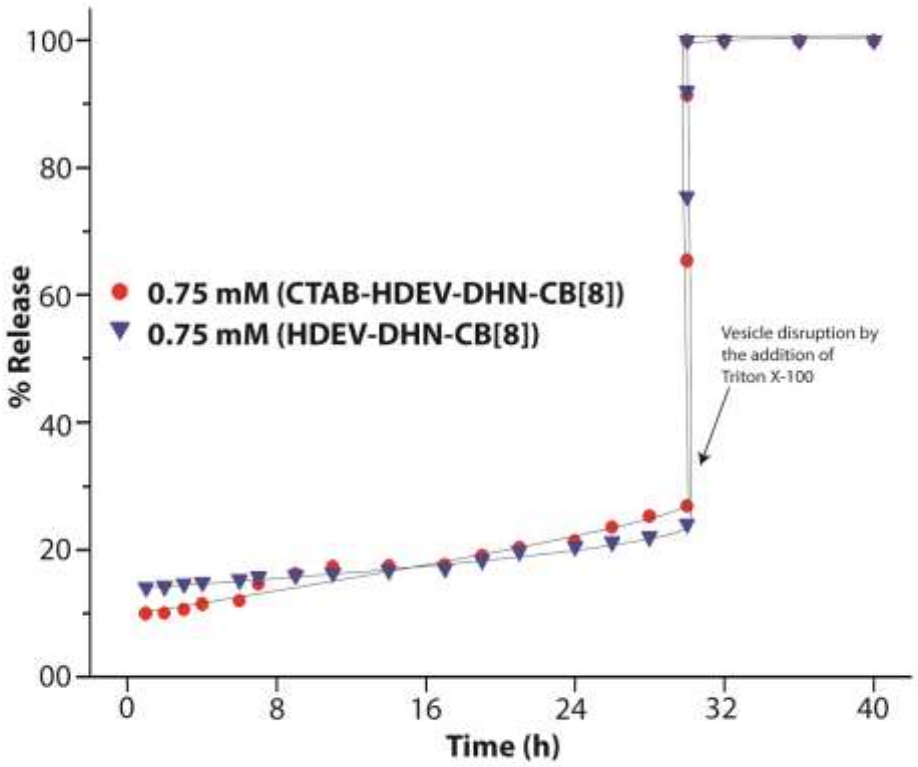

Fig. S4. Release profile of 5(6)-carboxyfluorescein trapped inside the vesicles formed by different combinations of CTAB, HDEV, DHN and CB[8] in water at 298 K.

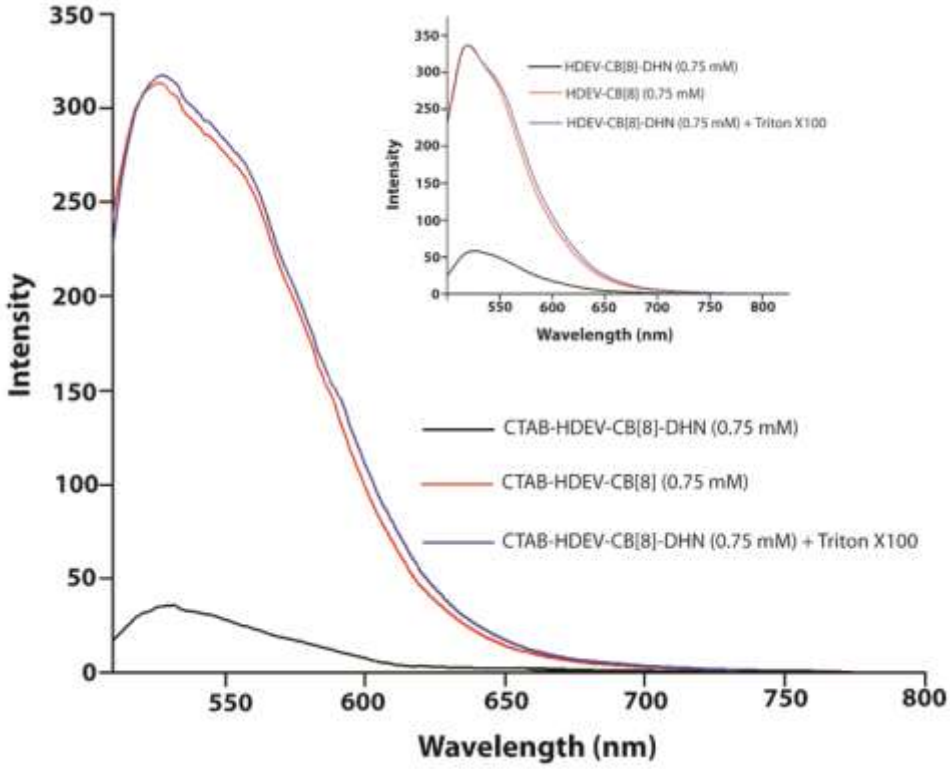

Fig. S5. Flurescence spectra of CF in the micelles and vesicles formed by CTAB-HDEV-CB[8] and CTAB-HDEV-DHN-CB[8] and after the addition of Triton-X100 into the vesicle. Inset: the same with HDEV alone (in absence of CTAB).

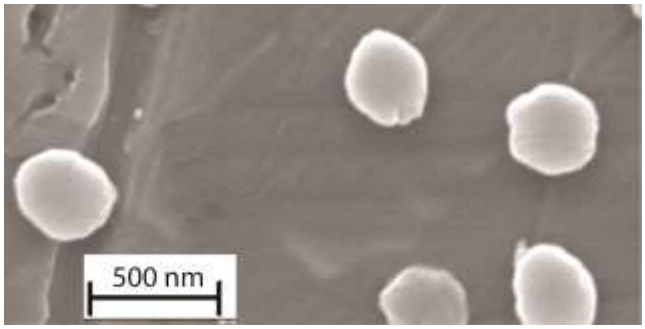

Fig. S6. SEM image of the vesicles formed by 0.75 mM (HDEV-DHN-CB[8]).

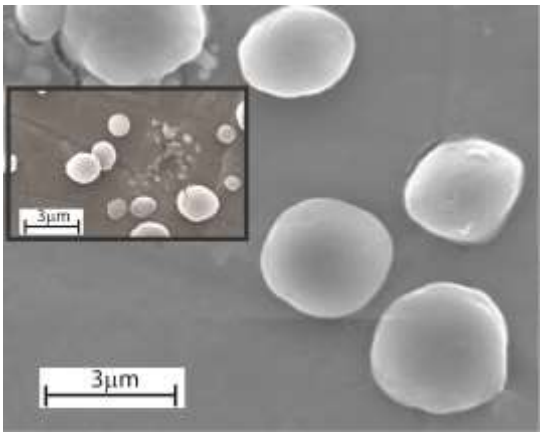

Fig. S7. SEM image of the vesicles formed by 0.75 mM (CTAB-HDEV-DHN-CB[8]).

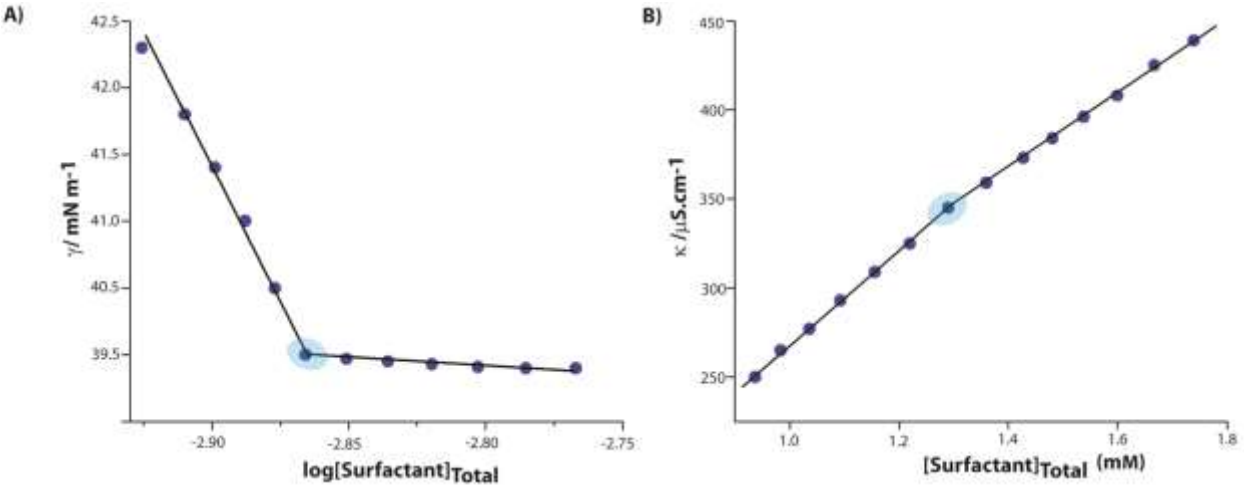

Fig. S8. Tensiometric (A) and conductometric (B) determination of the CMC of 1:1:1 CTAB-HDEV-CB[8] mixture at 298 K.

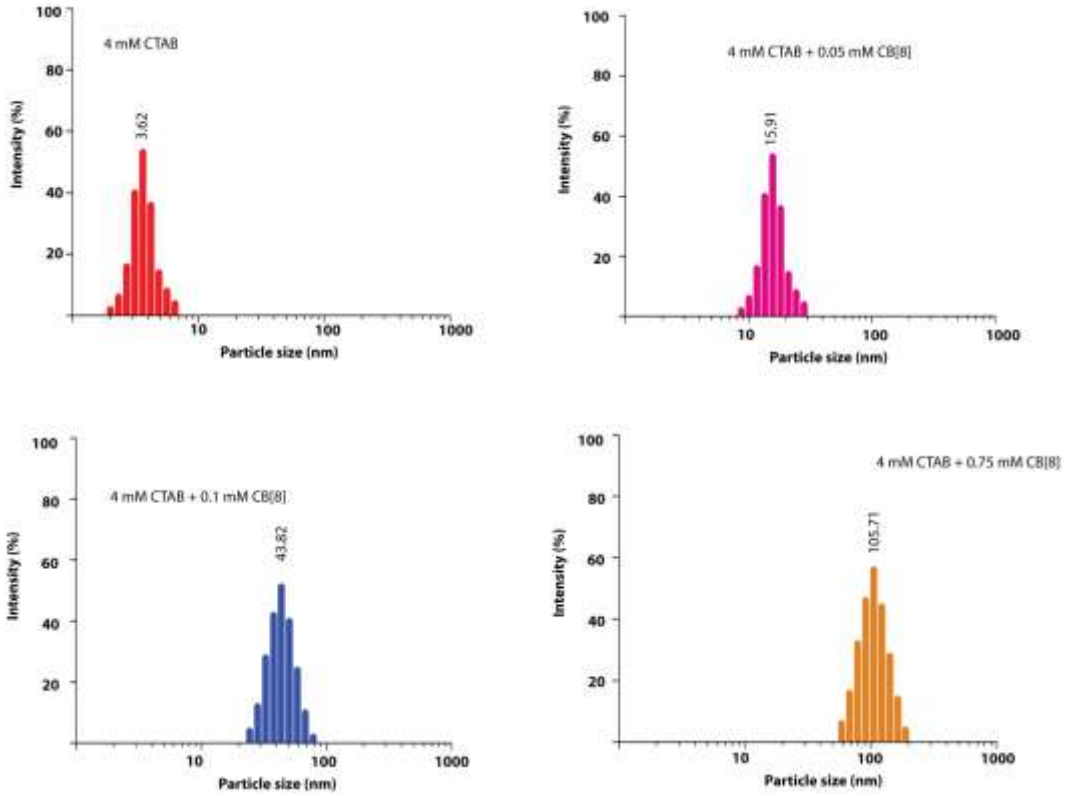

Fig. S9. Intensity-weighted distributions obtained from DLS measurements of CTAB and CTAB-CB[8] systems.

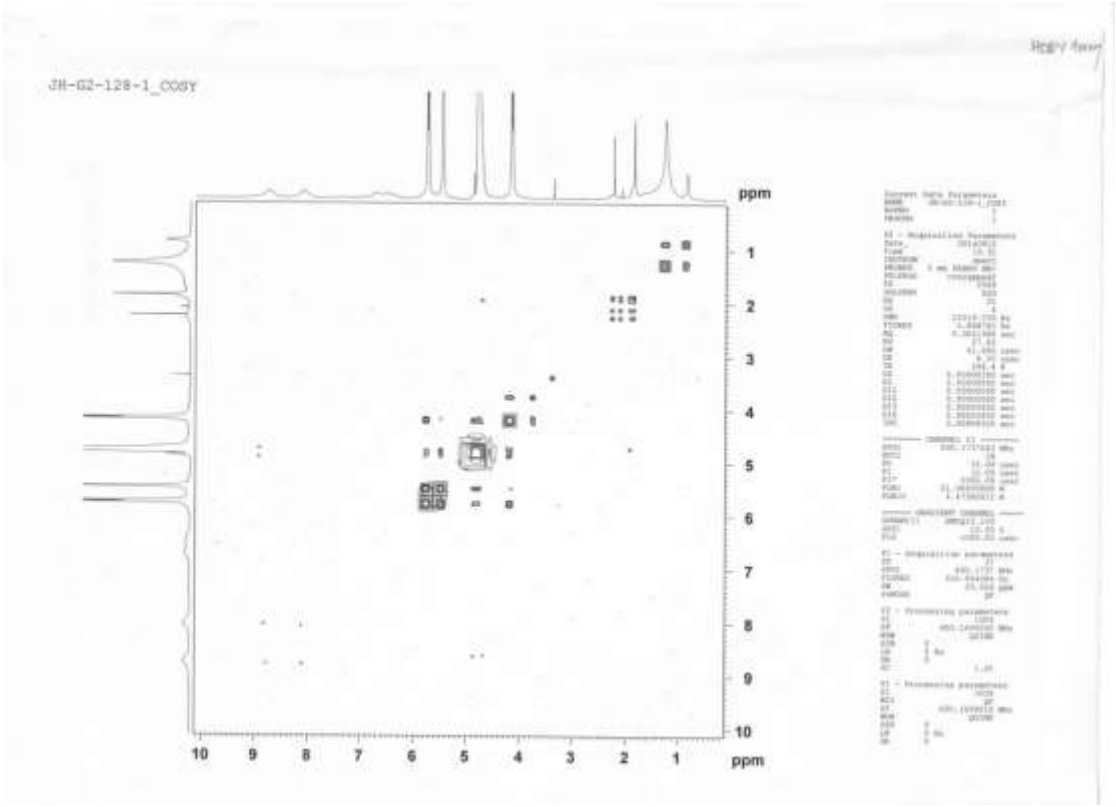

Fig. S10. ^{1}H-^{1}H COSY Spectrum of 0.75 mM (HDEV-DHN-CB[8]) in D_2O.

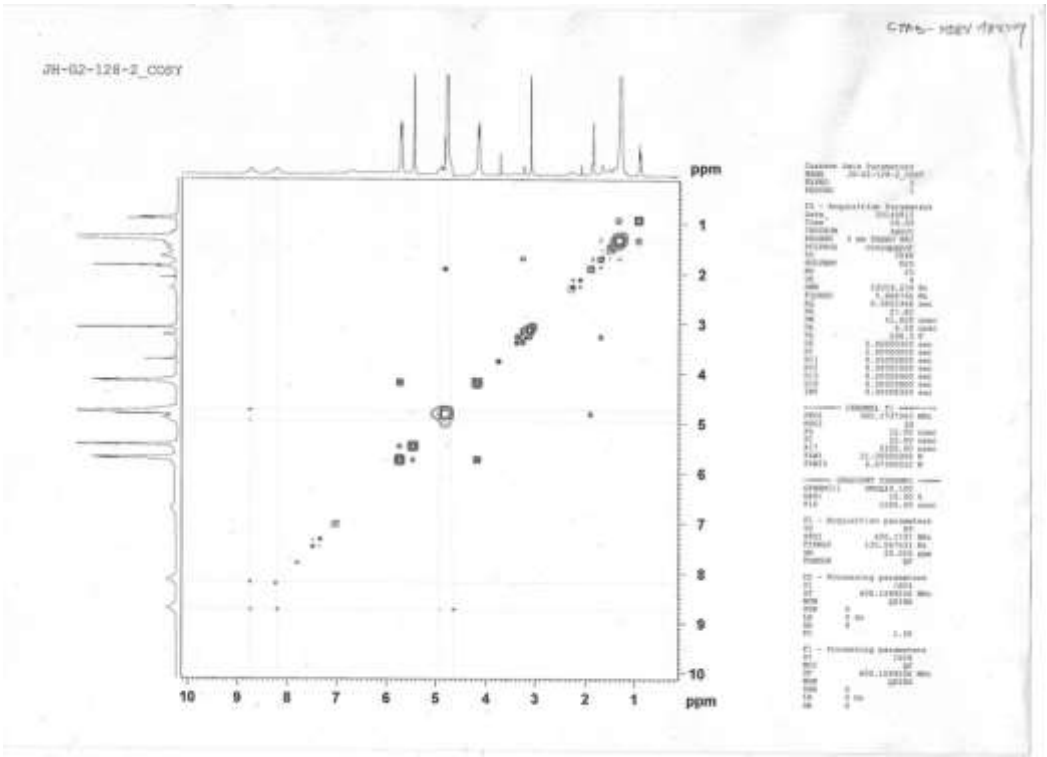

Fig. S11. ^{1}H-^{1}H COSY Spectrum of 0.75 mM (CTAB-HDEV-DHN-CB[8]) in D_2O.

Experimental detail for the proof of Micelle to Vesicle Transformation

In order to understand whether this is a case of micelle to vesicle transformation, we have premixed the surfactants in water to get an overall surfactant concentration of 1.5 mM. To this mixed micellar system, CB[8] was added and sonicated for six hours to achieve the inclusion complex as well as reach a 1:1:1 molar ratio of CTAB, HDEV, and CB[8]. CF was mixed in this solution followed by dividing the solution in two parts (Solutions A and B). In solution A, was added one equivalent of DHN and both the solutions (A and B) were sonicated for one hour and allowed to stand for two days. Simultaneously, another solution (C) was prepared where all the ingredients were mixed together in water to get exactly the same concentration ranges as in case of solution A and sonicated for one hour followed by standing for two days. The emission spectra recorded for all three solutions showed that the intensity of the emission peaks (λ_{em}= 512 nm) were significantly lower in case of A and C than that of the solution (B) (Supporting Information). The intensity enhanced significantly in case of solution A and C upon addition of Triton X-100 and showed similar value as in case of solution B. These results indicate the entrapment of the dye and hence the formation of vesicles in case of solution A and C but not in case of B where it remain in micellar form. When the dye release profiles of solution A and C were recorded, both showed similar results. The entrapment of the dye in case of solution A and C suggests formation of vesicle and the process is independent of the order of addition of DHN. This is a clear indication of the micelle to vesicle transition aided by the ternary complexation by CB[8], viologen unit and DHN. Similar experiments with HDEV alone also provided alike results.

Explanation of the ^{1}H-^{1}H COSY Spectra

The protons from individual components were identified in these ternary mixtures using the correlation spectra. The supramolecular binding with CB[8] though impart changes in the chemical shifts of individual protons bound inside the CB[8] cavity, does not show any correlation with protons two atoms apart. The aromatic protons from viologen and the naphthalene units could easily been identified through the correlation between two protons in the viologen ring whereas there is no such correlation observed between the naphthalene protons and the viologen protons. The N^{+}-C*H*$_2$ protons from HDEV are buried inside the big peak from *H*OD and their locations could only be found through the analysis of the ^{1}H-^{1}H COSY spectra. In the mixture of CTAB-HDEV-DHN-CB[8], the presence of two aliphatic chains makes it extremely complicated to identify the protons from the aliphatic chains even with thorough examination of the correlation spectrum. Whereas in case of HDEV-DHN@CB[8], the individual protons could be identified through the correlation between the N^{+}-C*H*$_2$ and N^{+}-CH$_2$-C*H*$_2$ protons.