Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

Fluorescence of *N*-acylated dansylamide with long hydrophobic tail: selective sensing of premicellar aggregates of sodium deoxycholate

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Experimental section for synthesis. All reactions were carried out in dried glassware. Triethylamine and DCM were distilled by calcium hydride. Tetrahydrofuran (THF) was dried before use. All commercially available chemicals were used without further purification reactions were monitored by thin layer chromatography (TLC). ^{1}H (500 MHz) and ^{13}C (125 MHz) NMR spectra were recorded on and Bruker Avance 500 spectrometer. High resolution mass spectrometry (HRMS) measurements were carried out using Micromass Q-ToF ESI instrument using direct inlet mode. Melting points were recorded using Sigma melting point apparatus in capillary tubes. IR spectra were recorded on JASCO FT-IR-4100 spectrometer.

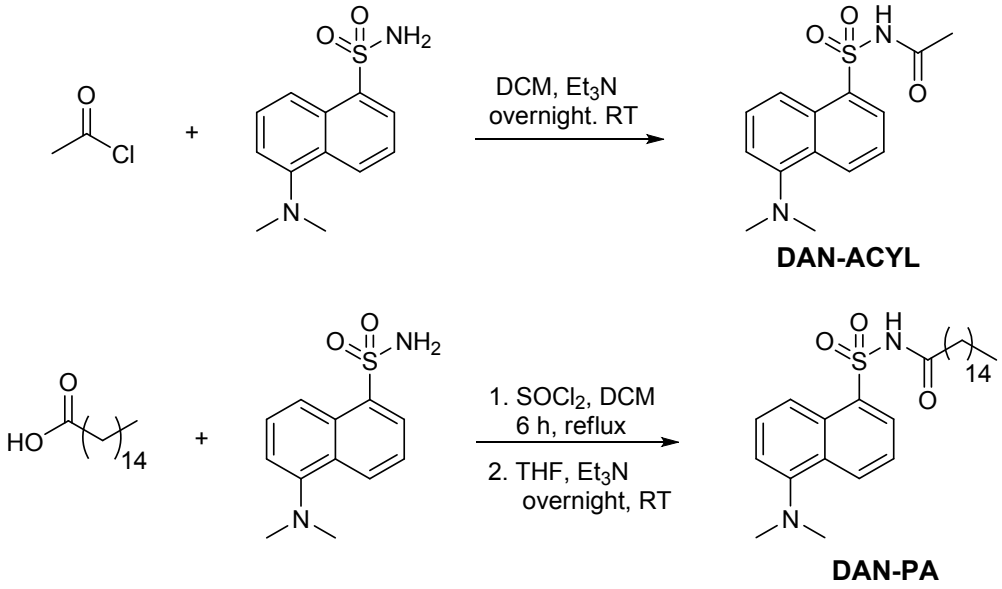
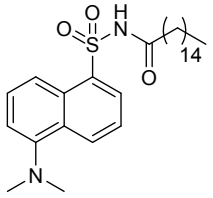


Fig. S1: Synthetic routes of both the dansyl conjugates.

Synthesis of N-(5-(dimethylamino)naphthalen-1-ylsulfonyl)palmitamide (DAN-PA).

Synthesis of N-(5-(dimethylamino)naphthalen-1-ylsulfonyl)palmitamide (DAN-PA) was carried using literature reported procedure.[1-3] To a solution of palmitic acid (3.9 mmol) in 20 mL of dry DCM, were added 0.4 mL of thionyl chloride (5.8 mmol). The mixture was refluxed for 6 h, and then solvent was removed under reduced pressure, maintaining nitrogen atmosphere. Again after addition of 10 mL of dry THF, a solution of dansylamide (5.07 mmol) and triethylamine (11.7 mmol) in 20 mL of THF was added in the reaction mixture. The mixture was stirred at room temperature for overnight. Solvent was removed under reduced pressure and the crude solid was extracted with ethyl acetate. The combined organic phases were dried (MgSO4) and concentrated under reduced pressure. The resulted crude solid was purified by column chromatography (hexane/ ethyl acetate 60:40). Yellow solid. Yield = 42%.



DAN-PA

R_f**:** 0.5 (1:1, Ethyl acetate: Hexane).

m.p. 202 ºC.

IR (neat) (cm^{-1}): 624, 788, 881, 1099, 1202, 1322, 1426, 1561, 1619, 1730, 2351, 2776, 2847, 2929, 3250.

^{1}H NMR (500 MHz, DMSO(d6), δ (ppm): 0.81-0.84 (t, 3H); 1.21 (s, 24H); 1.44–1.47 (t, 2H); 2.15-2.17 (m, 2H); 3.30 (s,3H); 7.65-7.69 (m,2H); 7.93-7.94 (d,2H); 8.08-8.10(m, 1H); 8.40-8.42(d, 2H); 8.98-8.99(d,1H).

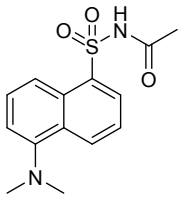
^{13}C NMR (125 MHz, DMSO(d6), δ (ppm): 14.12 ($-CH_3$), 22.24 ($-CH_2$), 24.64 ($-CH_2$), 28.67 ($-CH_2$), 28.84 ($-CH_2$), 28.86 ($-CH_2$), 29.03 ($-CH_2$), 29.10 ($-CH_2$), 29.15 ($-CH_2$), 31.43 ($-CH_2$), 33.83 ($-CH_2$), 38.99 ($-CH_2$), 39.16 ($-CH_2$), 39.33 ($-CH_2$), 39.49 ($-CH_2$), 39.66 ($-CH_2$), 39.83 ($-CH_2$), 46.63 ($-CH_3$), 118.29 (-CH), 122.75 (-C), 125.46 (-CH), 125.56 (-CH), 125.59 (-CH), 122.98 (-CH), 126.51 (-CH), 129.17 (-CH), 130.15 (-C), 139.73 (-C), 144.91 (-C), 174.76 (-C=O).

^{13}C DEPT-135 (125 MHz, DMSO (d6), δ (ppm):14.37 (-CH_3), 22.53 (-CH_2), 24.95 (-CH_2), 28.98 (-CH_2), 29.14 (-CH_2), 29.16 (-CH_2), 29.33 (-CH_2), 29.41 (-CH_2), 29.44 (-CH_2), 29.46 (-CH_2), 31.73 (-CH_2), 34.13 (-CH2), 46.92 (-CH_3), 118.55 (-CH), 123.06 (-CH), 125.75 (-CH), 125.85 (-CH), 126.76 (-CH), 129.42 (-CH).

HRMS (ESI, M+H^+): m/z calcd. for $C_{28}H_{45}N_2O_3S$ is 489.73, found 489.3141.

Synthesis of N-(5-(dimethylamino)naphthalen-1-ylsulfonyl)acetamide (DAN-ACYL).

Synthesis of N-(5-(dimethylamino)naphthalen-1-ylsulfonyl)acetamide (DAN-ACYL) was done by direct condensation of dansylamide (1.52 mmol) with acetylchoride (1.27 mmol) in presence of triethylamine (3.8 mmol) in dry DCM at room temperature. The reaction mixture was stirred for 8 h. The reaction mixture was diluted with 10 mL of water and the aqueous layer was extracted with DCM. The organic layer was dried over anhydrous sodium sulphate. DCM was removed under reduced pressure and the crude product was recrystallized with EtOH to get the pure product. Yellow solid. Yield = 52%.



DAN-ACYL

R_f**:** 0.3 (1:1, Ethyl acetate: Hexane)

m.p. 195 ºC

IR (neat) (cm^{-1}): 624, 799, 1003, 1260, 1317, 14005, 1449, 1634, 2358, 2856, 2922, 3456.

^{1}H NMR (500 MHz, DMSO (d6), δ (ppm): 1.87 (s, 3H); 2.81 (s, 6H); 7.25–7.26 (d, 1H); 7.26-7.68 (m, 2H); 8.16-8.18 (d, 1H); 8.25-8.27 (m, 1H); 8.50-8.51(d, 1H).

^{13}C NMR (125 MHz, DMSO (d6), δ (ppm): 28.37 (-CH_3), 50.27 (-CH_3), 120.46 (-CH), 122.98 (-CH), 123.14 (-CH), 128.77 (-CH), 133.76 (-CH), 134.05 (-C), 136.09 (-CH), 136.22 (-C), 139.37 (-C), 156.90 (-C), 173.94 (-C=O).

^{13}C DEPT-135 (125 MHz, DMSO (d6), δ (ppm): 28.37 (-CH_3), 50.27 (-CH_3), 120.55 (-CH), 122.96 (-CH), 123.17 (-CH), 128.73 (-CH), 133.79 (-CH), 136.01(-CH).

HRMS (ESI, M+H^+): m/z cacd. for $C_{14}H_{17}N_2O_3S$ is 293.10, found 293.0960.

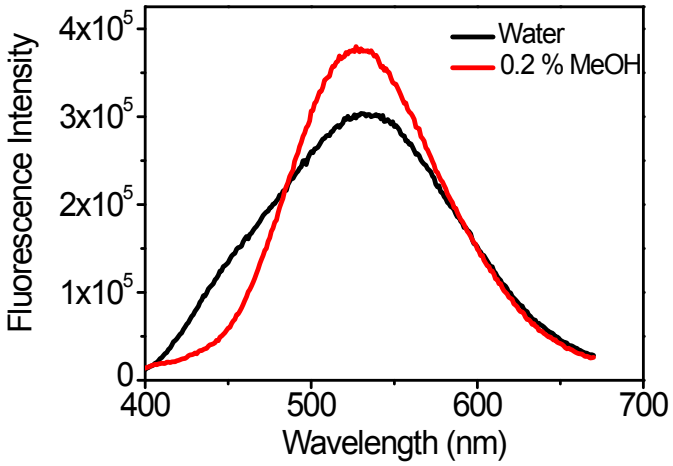


Fig. S2: Emission spectra of DAN-PA in water and 0.2 % of MeOH in water (5 µM, λ_{ex} 340 nm).

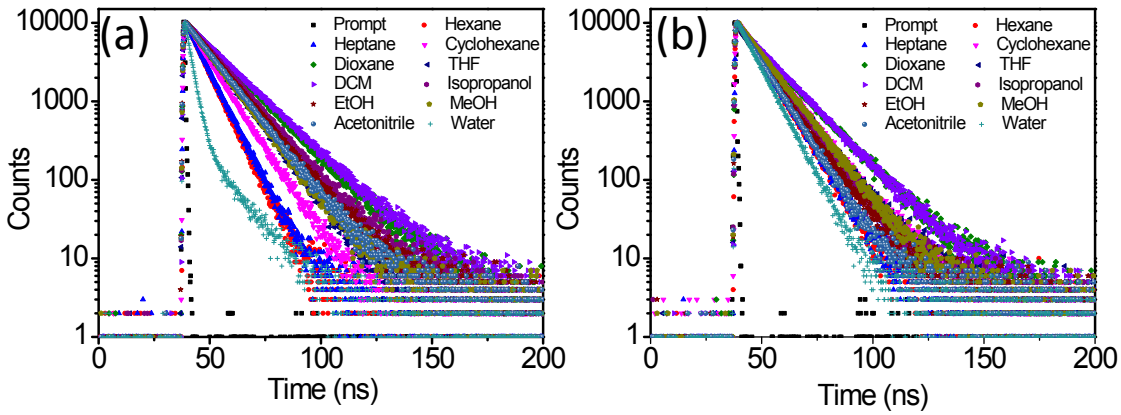


Fig. S3: Decay profile of (a) DAN-PA and (b) DAN-ACYL (5 µM, λ_{ex} 340 nm and λ_{em} 550 nm) in different solvents.

Table S1: Time resolved fluorescence decay parameters (lifetime, τ_1 and τ_2; relative excited state population, β_1 and β_2 and relative amplitude, α_1 and α_2) of DAN-PA in water and 0.2% MeOH in water mixture. (λ_{ex} = 340 nm, λ_{em} = 470 and 550 nm).

% of MeOH	λ_{em} 470nm			λ_{em} 550nm		
	τ_1 (ns) (β_1) (α_1)	τ_2 (ns) (β_2) (α_2)	χ^2	τ_1 (ns) (β_1) (α_1)	τ_2 (ns) (β_1) (α_2)	χ^2
0	2.73 (65.0) (28.1)	12.93 (35.0) (71.8)	1.19	2.44 (95.8) (80.7)	13.35 (4.1) (19.2)	1.30
0.2	2.46 (98.0) (79.8)	11.68 (5.0) (20.1)	0.94	2.32 (75.0) (69.1)	3.15 (30.8) (25.0)	1.26

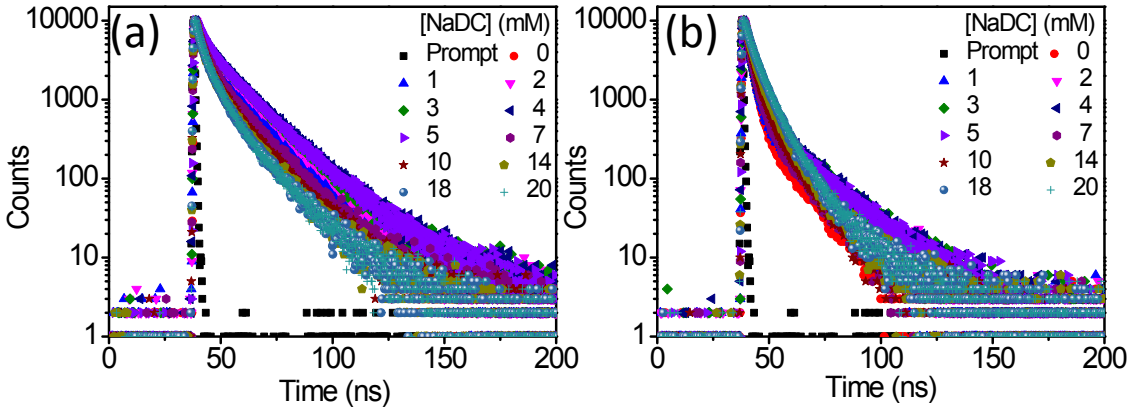


Fig. S4: Decay profile of DAN-PA (5 µM, λ_{ex} 340 nm) with increasing concentration of NaDC at different emission wavelengths (a) λ_{em} 470 nm and (b) λ_{em} 550nm.

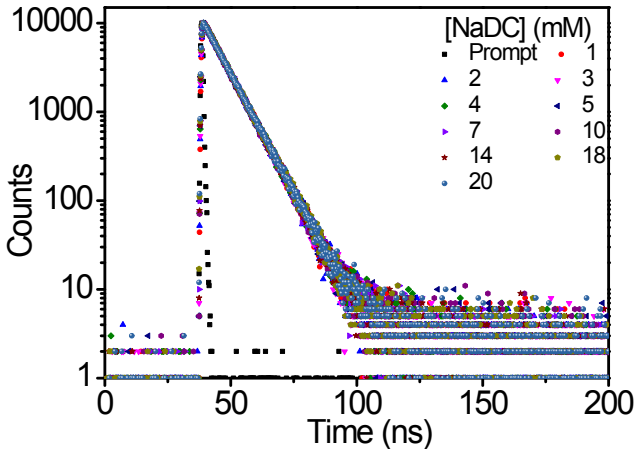


Fig. S5: Decay profile of DAN-ACYL (5 µM, λ_{ex} 340 nm) with increasing concentration of NaDC at λ_{em} 550nm.

Table S2: Time resolved fluorescence decay parameters (lifetime, τ_1 and τ_2; amplitude, β_1 and β_2) of DAN-ACYL in various concentration of NaDC (λ_{ex} = 340 nm, λ_{em} = 550 nm).

NaDC (mM)	DAN-ACYL		
	τ_1 (ns) (β_1)	τ_2 (ns) (β_2)	χ^2
1	7.98	-	1.21
2	8.03	-	1.23
3	7.99	-	1.38
4	7.98	-	1.37
5	6.42(3.0)	8.08(97.0)	1.15
7	4.02(3.0)	8.16(97.0)	1.33
10	4.06(4.0)	8.09(96.0)	1.27
14	4.02(4.0)	8.19(96.0)	1.33
18	4.01(4.0)	8.11(96.0)	1.04
20	8.81(4.0)	8.80(96.0)	1.21

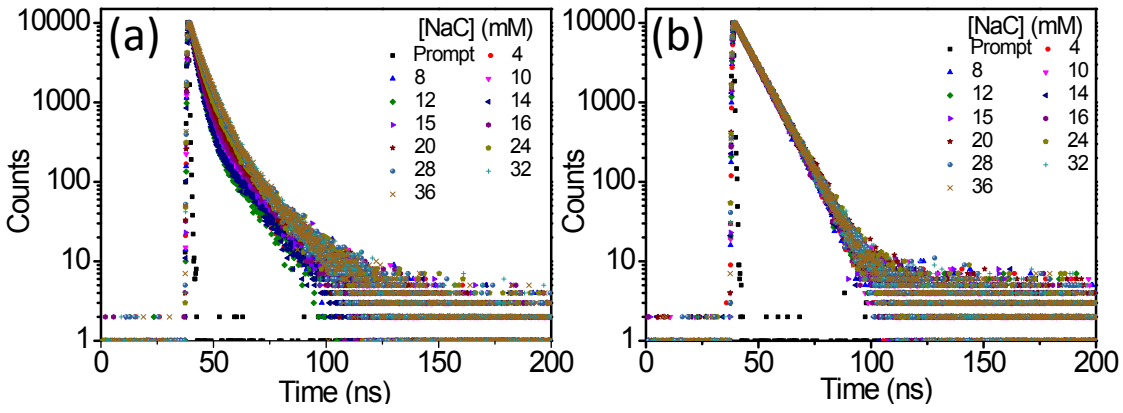


Fig. S6: Decay profile of (a) DAN-PA and (b) DAN-ACYL (5 μM, λ_{ex} 340 nm and λ_{em} 550 nm) with increasing concentration of NaC.

Table S3: Time resolved fluorescence decay parameters (lifetime, τ_1 and τ_2; amplitude, β_1 and β_2) of DAN-PA and DAN-ACYL in various concentration of NaC (λ_{ex} = 340 nm, λ_{em} = 550 nm).

NaC (mM)	DAN-PA			DAN-ACYL		
	τ_1 (ns) (β_1)	τ_2 (ns) (β_2)	χ^2	τ_1 (ns) (β_1)	τ_2 (ns)(β_2)	χ^2
4	2.69(97.0)	12.68(3.0)	1.01	8.04	-	1.32
8	2.85(96.0)	13.64(4.0)	1.10	8.07	--	1.29
10	2.89(95.0)	13.02(5.0)	1.06	8.10	-	0.98
12	2.65(95.0)	12.15(5.0)	1.03	8.16	-	1.33
14	2.56(94.0)	12.50(5.0)	1.13	8.13	-	1.25
15	2.84(92.0)	12.10(8.0)	1.21	8.12	-	1.39
16	3.00(92.0)	12.42(8.0)	0.96	8.13	-	1.14
20	3.20(90.0)	11.28(10.0	0.95	6.16(1.0)	8.14(99.0)	1.03
24	3.48(85.0)	10.30(15.0)	1.14	4.20(1.0)	8.35(99.0)	1.07
28	4.15(84.0)	10.08(16.0)	1.04	4.12(3.0)	8.25(97.0)	1.21
32	4.83(84.0)	10.60(16.0)	1.24	4.05(5.0)	8.18(95.0)	1.16
36	4.50(83.0)	9.98(17.0)	1.20	7.49(23.0)	8.43(77.0)	0.99

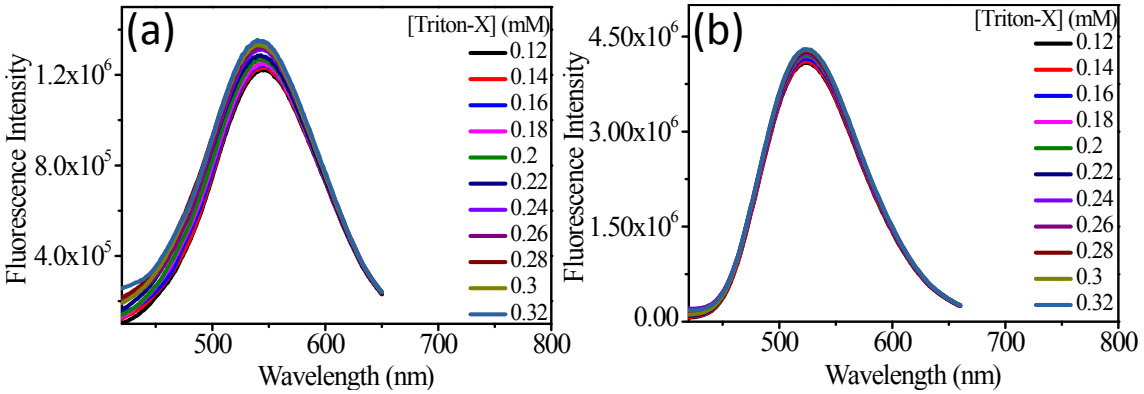


Fig. S7: (a) and (b) fluorescence spectra of DAN-PA and DAN-ACYL (5 µM), respectively with increasing concentration of TritonX-100.

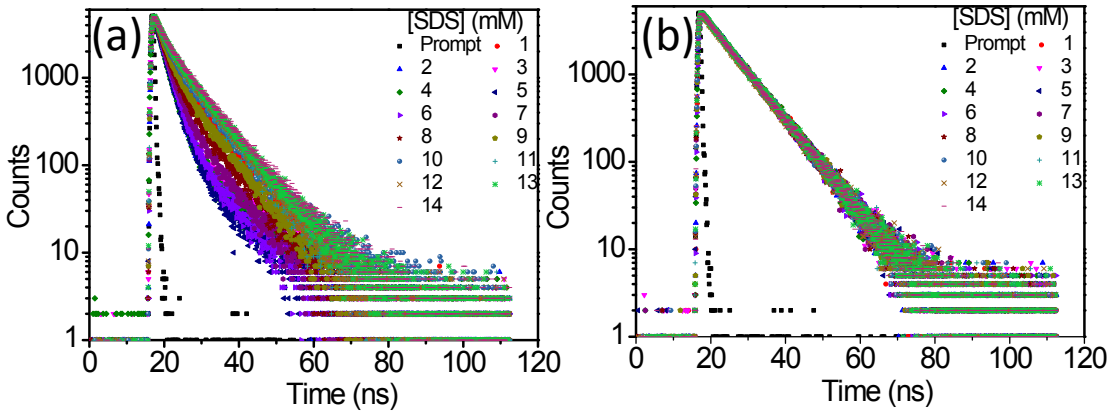


Fig. S8: Decay profile of (a) DAN-PA and (b) DAN-ACYL (5 µM, λ_{ex} 340 nm and λ_{em} 550 nm) with increasing concentration of SDS.

Table S4: Time resolved fluorescence decay parameters (lifetime, τ_1 and τ_2; amplitude, β_1 and β_2) of DAN-PA and DAN-ACYL in various concentrations of SDS (λ_{ex} = 340 nm, λ_{em} = 550 nm).

SDS (mM)	DAN-PA			DAN-ACYL		
	τ_1 (ns) (β_1)	τ_2 (ns) (β_2)	χ^2	τ_1 (ns) (β_1)	τ_2 (ns) (β_2)	χ^2
1	2.65(96.0)	8.23(4.0)	1.01	7.98	-	1.11
2	2.55(96.0)	11.86(4.0)	1.12	7.95	-	1.07
3	2.53(96.0)	11.624.0)	1.23	7.99	-	1.04
4	2.54(96.0)	11.78(4.0)	1.24	7.94	-	1.12
5	2.53(96.0)	8.08(4.0)	1.16	8.00	-	1.18
6	2.58(93.0)	8.02(7.0)	1.02	8.03	-	1.07
7	2.62(89.0)	8.55(11.0)	1.12	8.00	-	1.12
8	2.70(82.0)	8.75(18.0)	1.01	3.86(3.0)	8.03(97.0)	1.03
9	2.58(70.0)	7.93(30.0)	1.13	3.82(5.0)	8.09(95.0)	1.08
10	2.52(56.0)	8.26(44.0)	0.98	3.77(9.0)	8.20(91.0)	1.02
11	2.41(53.0)	7.95(47.0)	1.32	3.74(9.0)	8.12(91.0)	1.07
12	2.58(48.0)	8.13(52.0)	0.91	3.71(11.0)	8.29(89.0)	1.20
13	2.65(46.0)	8.30(54.0)	1.00	5.99(23.0)	8.08(78.0)	0.95
14	2.82(44.0)	8.49(56.0)	1.17	6.81(33.0)	8.50(66.0)	1.02

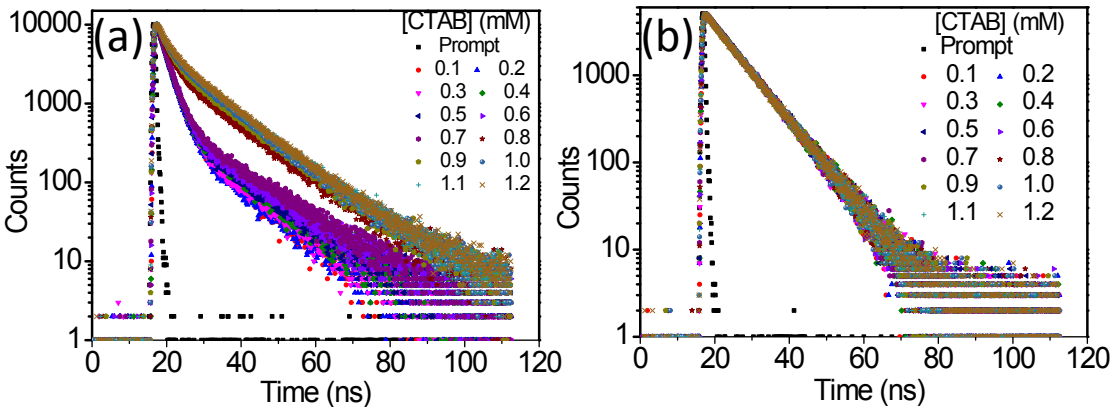


Fig. S9: Decay profile of (a) DAN-PA and (b) DAN-ACYL (5 μM, λ_{ex} 340 nm and λ_{em} 550 nm) with increasing concentration of CTAB.

Table S5: Time resolved fluorescence decay parameters (lifetime, τ_1 and τ_2; amplitude, β_1 and β_2) of DAN-PA and DAN-ACYL in various concentrations of CTAB (λ_{ex} = 340 nm, λ_{em} = 550 nm).

CTAB (mM)	DAN-PA			DAN-ACYL		
	τ_1 (ns) (β_1)	τ_2 (ns) (β_2)	χ^2	τ_1 (ns) (β_1)	τ_2 (ns) (β_2)	χ^2
0.1	2.52(97.0)	12.39(3.0)	1.12	8.03	-	1.03
0.2	2.57(97.0)	12.81(3.0)	1.26	8.02	-	1.06
0.3	2.50(96.0)	12.49(4.0)	1.04	8.01	-	1.08
0.4	2.50(96.0)	13.07(4.0)	1.02	8.01	-	1.17
0.5	2.52(96.0)	13.31(4.0)	1.08	8.04	-	1.04
0.6	2.52(96.0)	13.76(4.0)	1.14	8.03	-	1.17
0.7	2.61(93.0)	14.66(7.0)	1.23	8.05	-	1.06
0.8	2.61(78.0)	12.32(22.0)	1.14	8.17	-	0.99
0.9	2.76(69.0)	12.21(31.0)	1.14	3.84(3.0)	8.21(97.0)	1.11
1.0	2.61(62.0)	11.89(38.0)	1.08	3.90(5.0)	7.98(95.0)	1.16
1.1	2.82(56.0)	11.94(44.0)	1.27	3.91(5.0)	8.10(95.0)	1.10
1.2	2.83(55.0)	11.84(45.0)	1.27	4.40(8.0)	8.20(92.0)	1.26

Table S6: Some literature reported dansyl derivatives used as a fluorophore in bile salts and surfactants medium.

Name of probe	study	references
Dansyl derivatives of cholic acid	Build speciation diagrams for bile salts aggregation	Mendoza *et al*. *J. Phys. Chem. B*, 2012, **116**, 14776–14780.
Dansyl cadaverine	Formation of primary and secoundary aggregates	Ranajit *et al*. *Chem. phys. Lip.* **25**, 345-356.
4-Aminobutyroyl-spaced oligocholates	Aggregation of oligocholates in SDS Micelles (CMC of SDS = 8mM)	Zhao *et al*. *J. Org. Chem.* 2009, 74, 7470–7480
Dansylglycine	Aggregation property of aqueous solutions of Cationic detergents (CMC= 0.6 to 0.9 mM)	Clark *et al*.1970, **579**, 5089–5090.
Sodium 12-(*N*-dansyl)aminododecanate (12-DAN-ADA)	Shape transitions in self-assembled systems (CMC of SDS = 8.2 mM and CMC of Triton X-100 = 0.3mM)	*Gao et al. J. Colloid Interface Sci*. **323** (2008) 420–425.

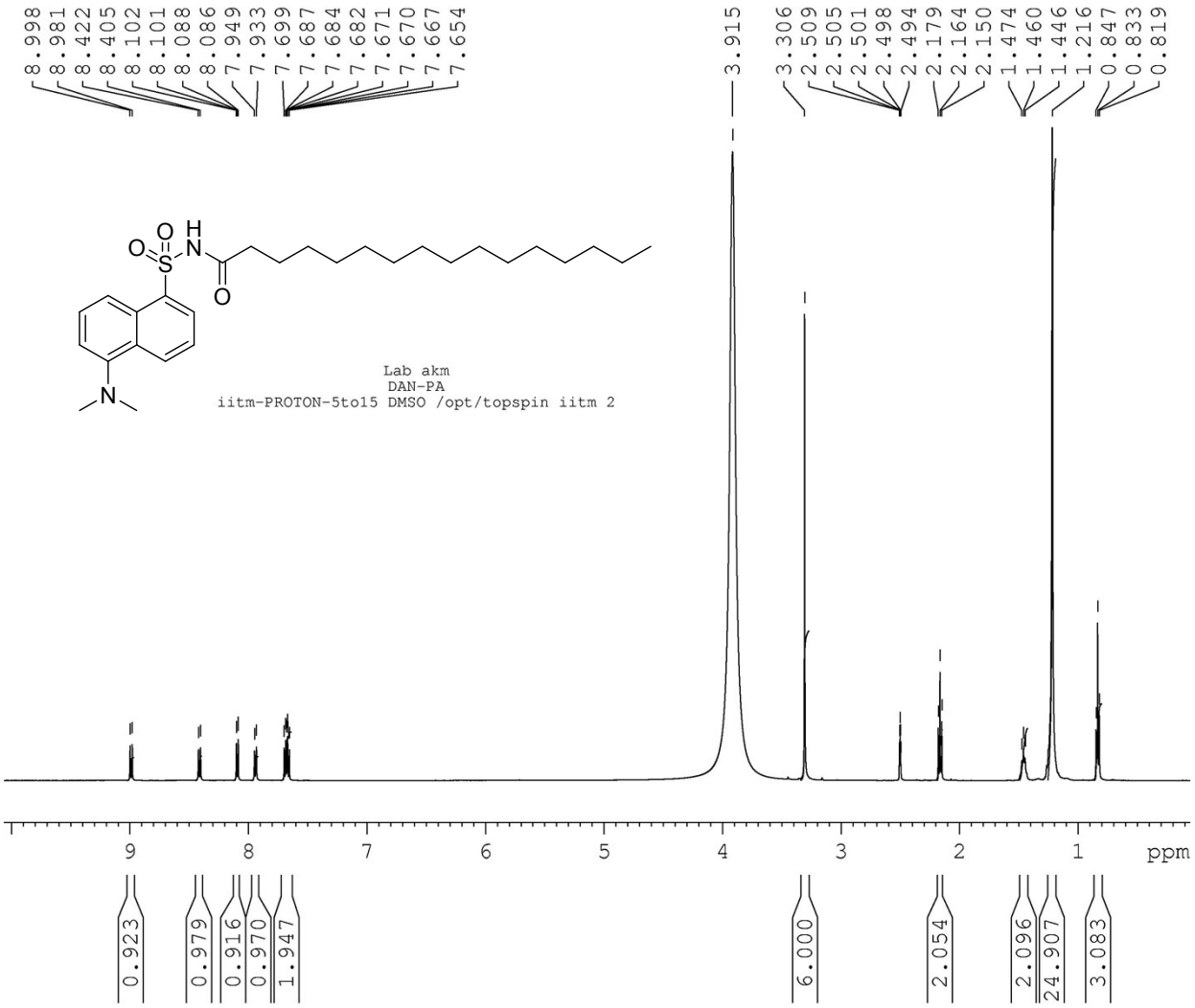


Fig. S10: ^{1}H NMR (500 MHz) spectrum of DAN-PA in DMSO (d6).

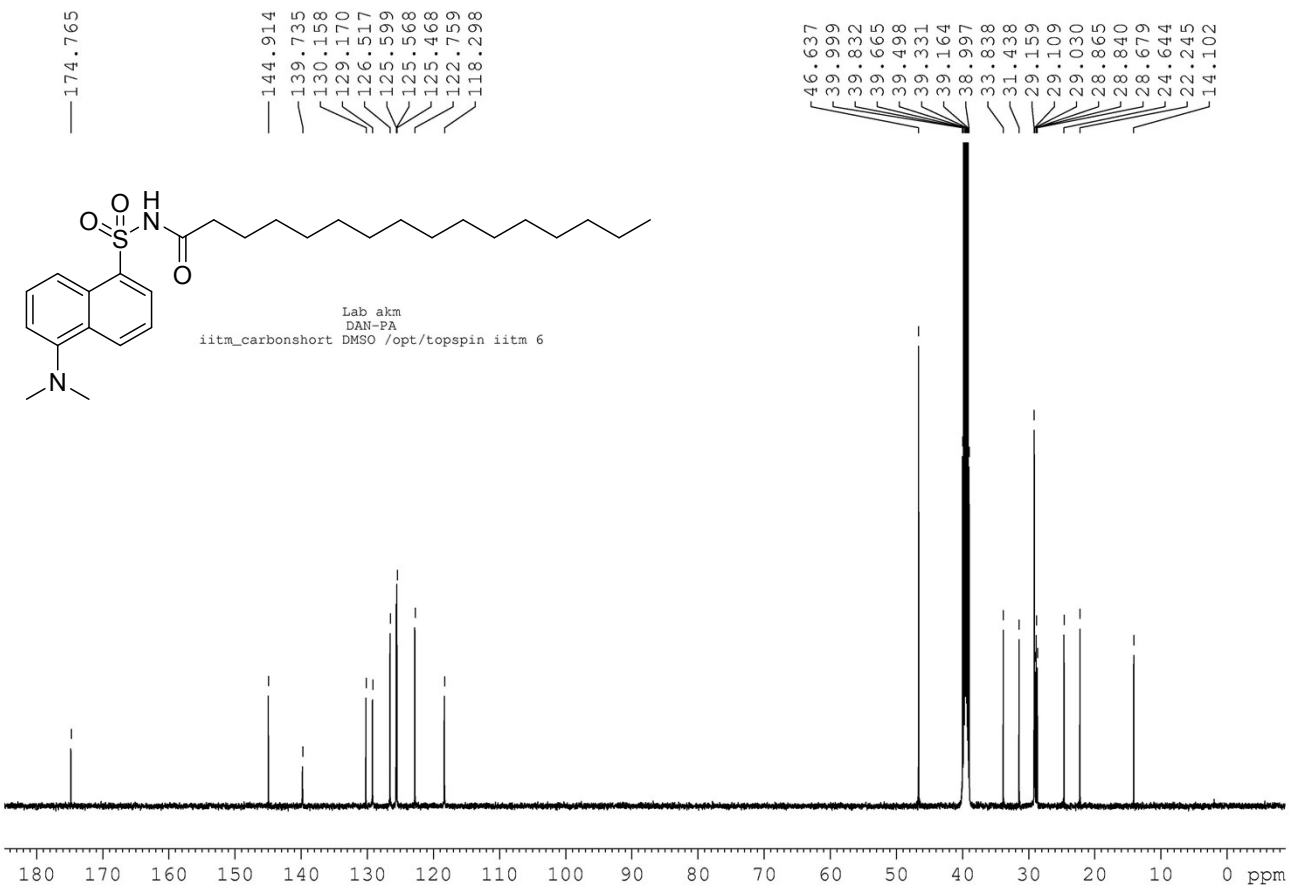


Fig. S11: ^{13}C NMR (125 MHz) spectrum of DAN-PA in DMSO (d6).

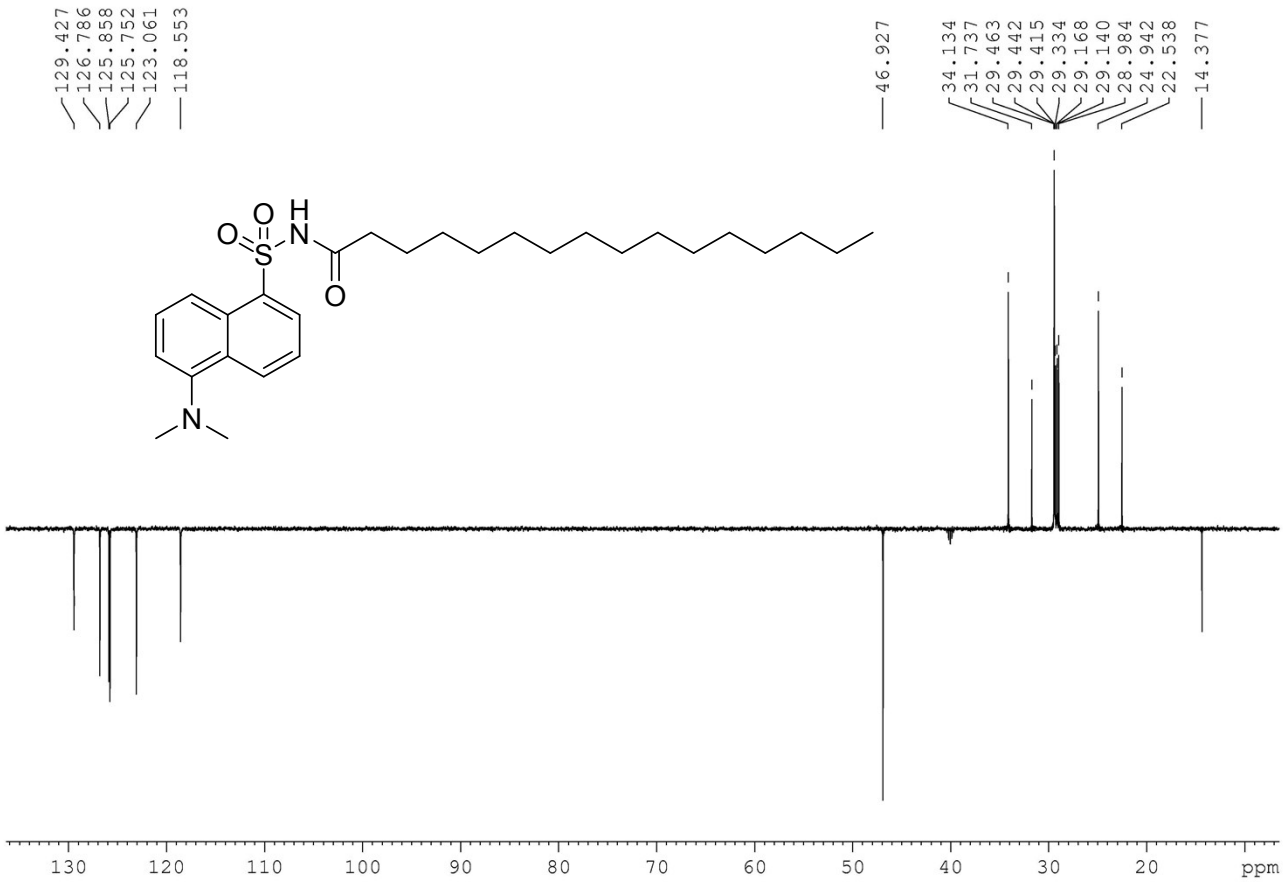


Fig. S12: ^{13}C DEPT-135 (125 MHz) of DAN-PA in DMSO (d6).

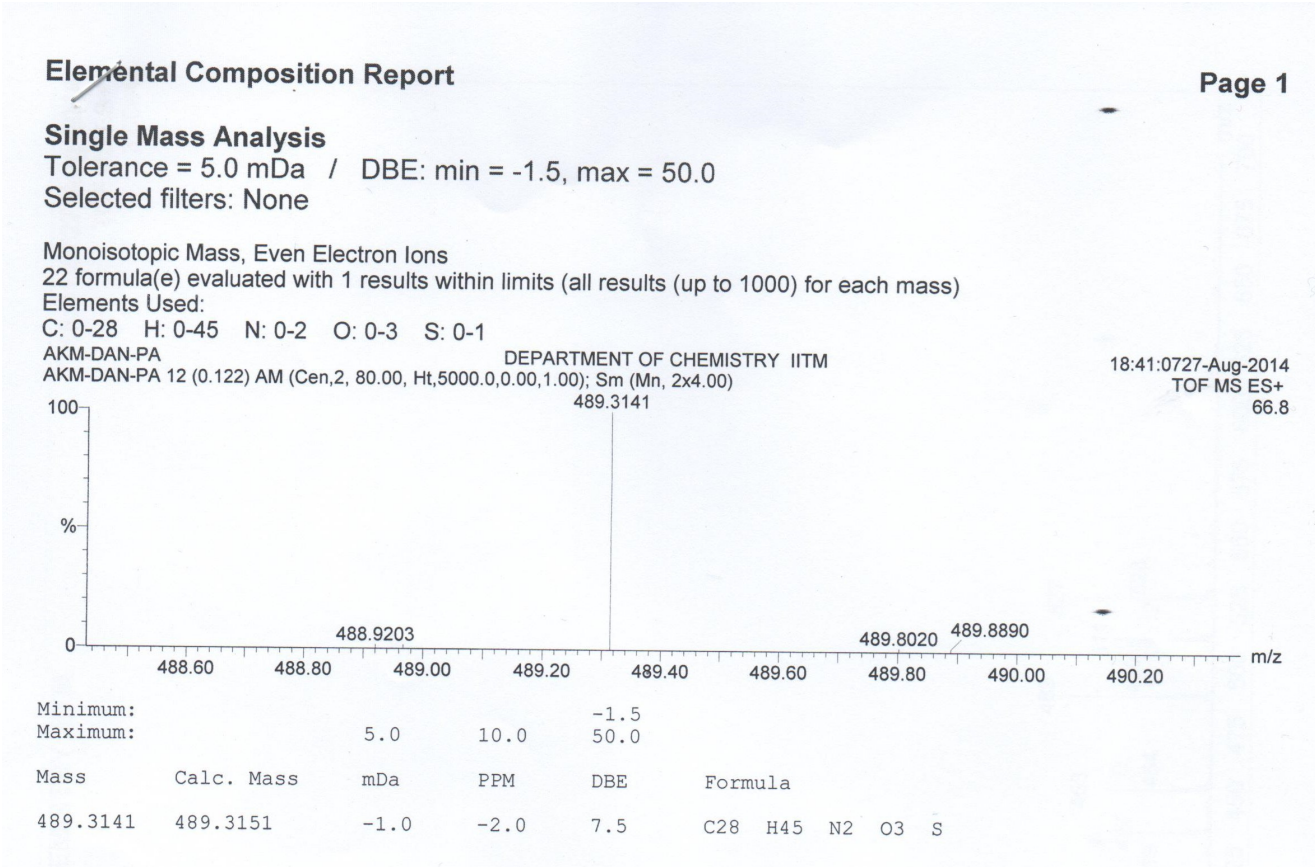


Fig. S13: HRMS Spectrum of DAN-PA

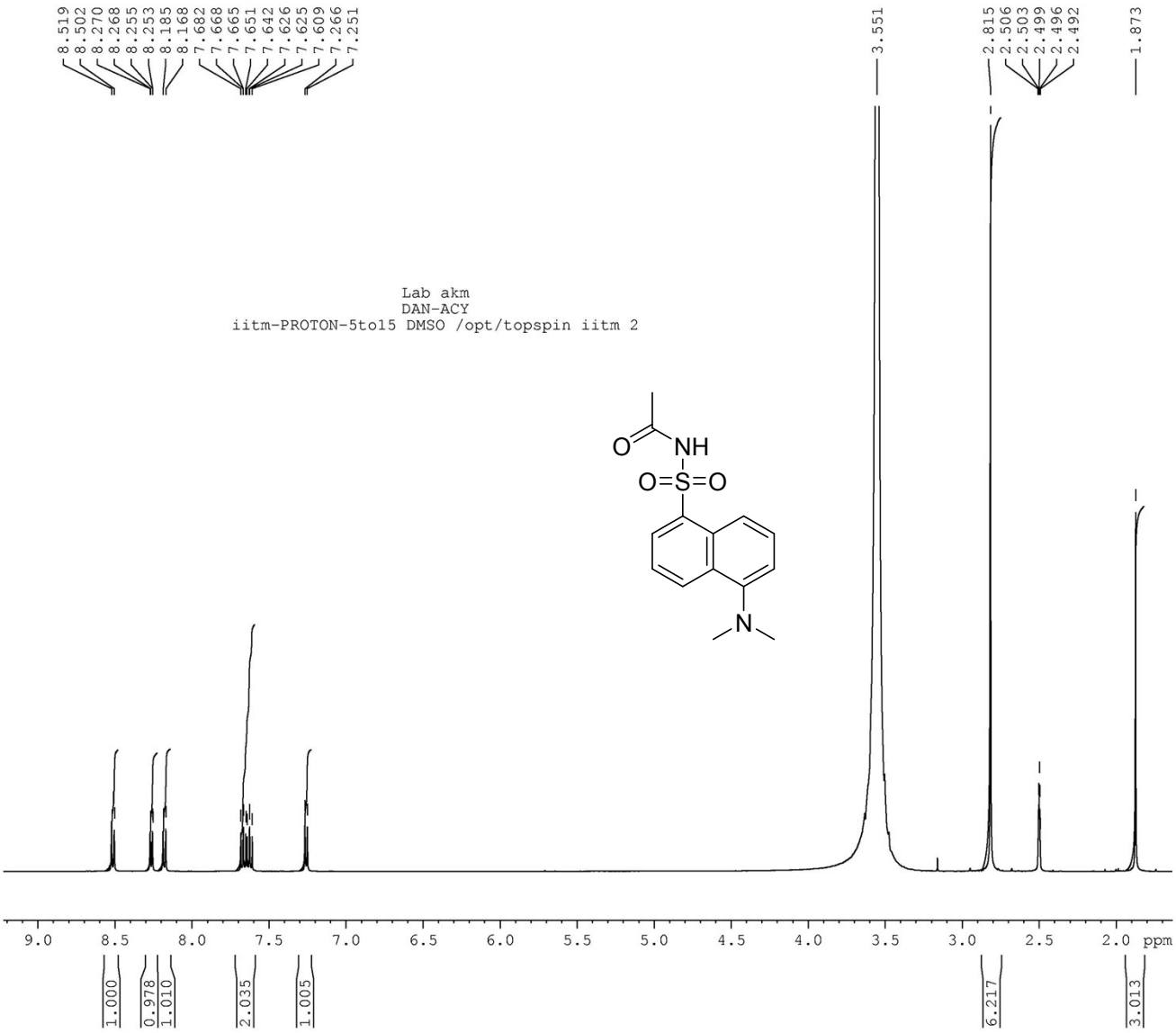


Fig. S14: ^{1}H NMR (500 MHz) spectrum of DAN-ACYL in DMSO (d6).

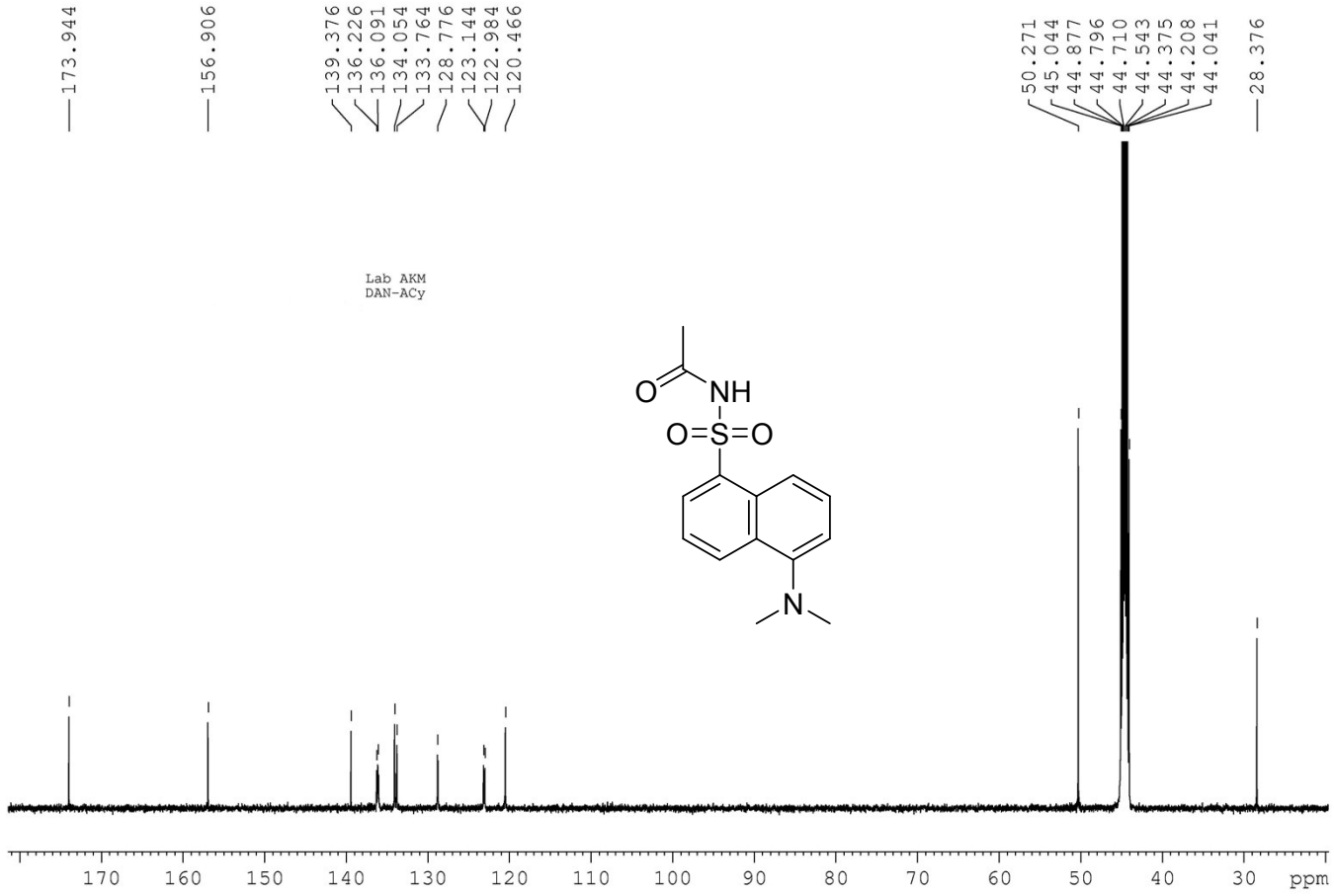


Fig. S15: ^{13}C NMR (125 MHz) spectrum of DAN-ACYL in DMSO (d6).

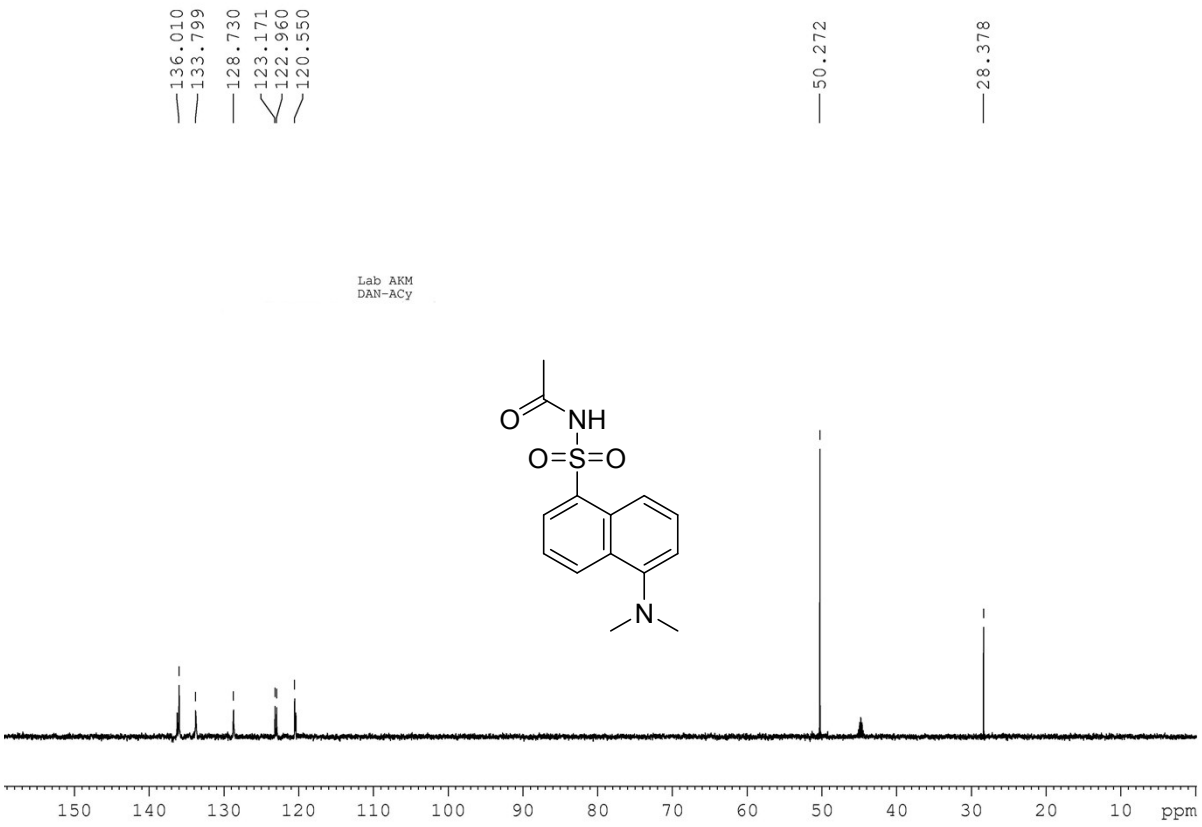


Fig. S16: ^{13}C DEPT-135 (125 MHz) of DAN-ACYL in DMSO (d6).

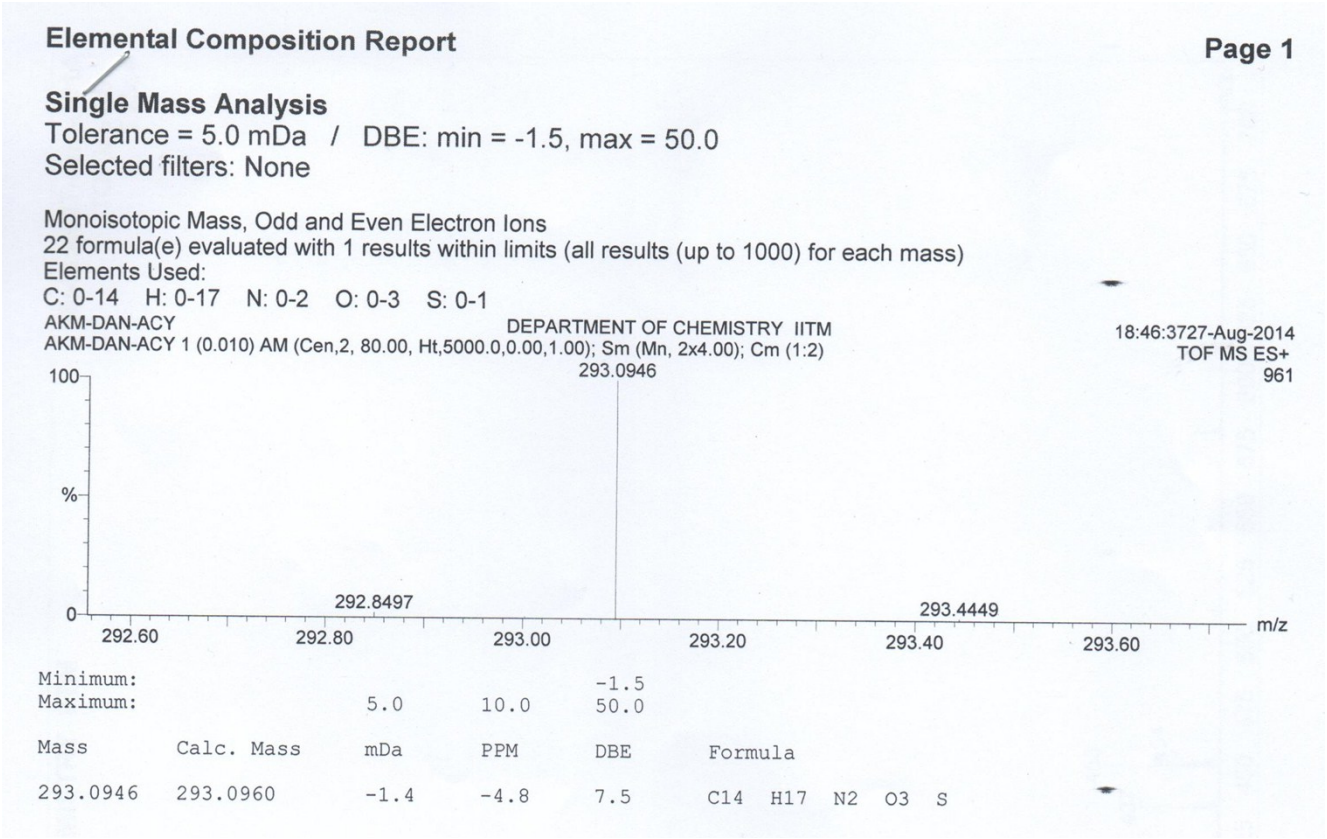


Fig. S17: HRMS Spectrum of DAN-ACYL.

Dynamic Light Scattering Plot

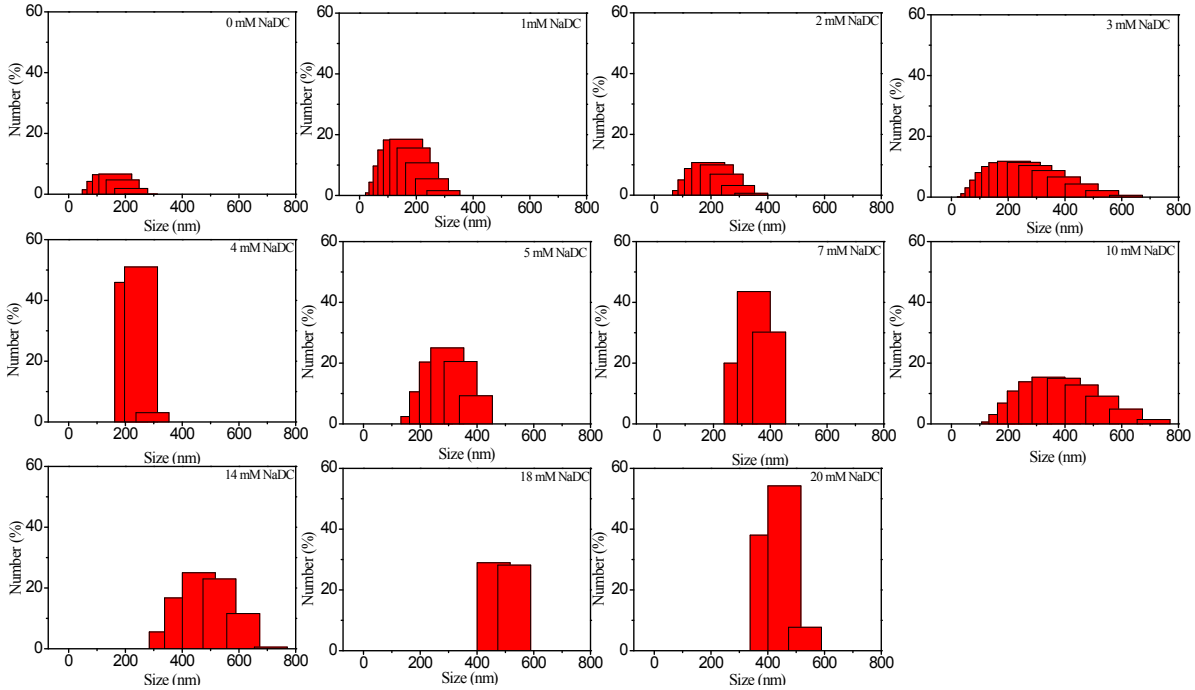


Fig. S18: Size distribution histograms of premicellar and micellar state of NaDC.

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3. H. Zhang, P. Wang, Y. Yang, and H. Sun*, Chem. Commun*., 2012, **48**, 10672–10674.