Supporting Information

A Sensitive and Visible Fluorescence-Turn-on Probe for the Determination of Critical Micelle Concentrations

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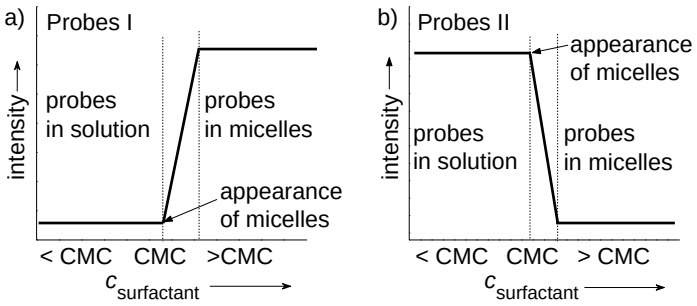
Determination mechanisms of critical micelle concentration (CMC) via probes based on changes in fluorescence intensities

Probes based on the sharp changes in fluorescence intensities can be classified into probes I and II according to their relative fluorescence intensities in solutions and in micelles. Probes I/II are fluorophores that show weaker/stronger fluorescence intensities in solutions than those in micelles. Scheme S1 a/b schematically shows the typical changes in fluorescence intensities of probes I/II with surfactant concentrations. As shown in Scheme S1a/b, probes I/II exhibit in solution showing the weakest/strongest fluorescent intensity below CMC and gradually transfer into micelles with the sharp changes in fluorescent intensity from the weakest/strongest (the lower/upper inflexion) to the strongest/weakest (the upper/lower inflexion) as surfactant concentration increases from CMC to the concentration at which almost all probes can be included in micelles. Ideal probes I/II are those showing no emission in solutions/micelles but strong emission in micelles/solutions. That is, ideal probes I and II are fluorescence-turn-off and -on probes, respectively, and hence probes II is expected to have higher sensitivity than probes I. It is generally accepted that micelles enhance the fluorescence of probes owing to sequestration, isolation from quenchers and increased microviscosity of the environment.[1] To the best of our knowledge, all probes for CMC based on changes in fluorescence intensity are probes I except for 1,2-diphenyl-1,2-di(*p*-tolyl)ethene (TPE). TPE shows strong aggregation-induced emission (AIE)[2] in solution but very weak emission in micelles.[3] However, the lower

inflexion with the weakest fluorescence (Scheme S1b) was used to indicate CMC,[3] which means that TPE is still a fluorescence-turn-off probe for CMC. Hence, the development of fluorescence-turn-on probes II is very important because their high sensitivity and different mechanism.



Scheme S1 Changes in the fluorescent intensities of a) probes I and b) II with the concentrations of surfactants

Materials and instruments

All chemicals used in this paper were obtained from commercial suppliers and used without further purification. Excitation and emission spectra were recorded on a Shimadzu RF5301PC spectrofluorophotometer (slit widths: 3 and 5 nm or 5 and 5 nm; emitted at 483 nm; excited at the lowest energy excitation peaks). All measurements were done at room temperature (25±1°C). Photos were taken by Canon 60D under UV 365 nm.

Preparation of samples for fluorescence measurement via reported method 1

a) Preparation of the ethanol stock solution of THP-1 (1.00 mM)

4.56 mg of THP-1 (Mr = 456) and about 5 mL of ethanol were added into a 10 mL volumetric flask successively, followed with ultrasonic treatment for dissolving THP-1, then filling the flask to the mark with ethanol.

b) Preparation of concentrated SDS solution (10.0 mM)

288 mg of SDS (Mr = 288) was added into a 100 mL volumetric flask and dissolved by about 50 mL of doubly distilled water, then filling the flask to the mark with doubly distilled water.

c) Preparation of different concentrations of SDS solutions containing THP-1 (10.0 μM)

As described in Table S1, at room temperature (25±1ºC), different volumes of concentrated SDS solutions were added in different 10 mL volumetric flasks, respectively. Then, 100 μL of THP-1 ethanol stock solution (1.00 mM) was added into these flasks, respectively, filling the flask to the mark with doubly distilled water. These prepared solutions were kept at room temperature or in ultrasonic bath for different times.

Table S1 Preparation of different concentrations of SDS solutions

entry	1	2	3	4	5	6	7	8	9	10	11	12
SDS/mM	0	3	4	5	6	6.2	6.4	6.6	6.8	7	8	10
SDS[a]/mL	0	3	4	5	6	6.2	6.4	6.6	6.8	7	8	10
THP-1[b]/μL	100	100	100	100	100	100	100	100	100	100	100	100

[a] SDS concentrated solution (10 mM); [b] THP ethanol stock solution (1 mM).

Preparation of samples for fluorescence measurement via reported method 2

a) Preparation of the ethanol stock solution of THP-1 (1.00 mM)

4.56 mg of THP-1 (Mr = 456) and about 5 mL of ethanol were added into a 10 mL volumetric flask successively, followed with ultrasonic treatment for dissolving THP-1, then filling the flask to the mark with ethanol.

b) Preparation of concentrated SDS solution (10.0 mM) containing THP-1 (10 μM)

288 mg of SDS (Mr = 288) was added into a 100 mL volumetric flask and dissolved by about 50 mL of doubly distilled water, then, 1 mL of THP-1 stock solution was added, filling the flask to the mark with doubly distilled water.

c) Preparation of different concentrations of SDS solutions containing THP-1 (10.0 μM)

As described in Table S2, at room temperature (25±1ºC), different volumes of concentrated SDS solutions and THP-1 stock solutions were added in different 10 mL volumetric flasks successively, respectively, filling the flask to the mark with doubly distilled water. These prepared solutions were kept at room temperature for different times.

Table S2 Preparation of different concentrations of SDS solutions

entry	1	2	3	4	5	6	7	8	9	10	11	12
SDS/mM	0	3	4	5	6	6.4	6.8	7	7.5	7.8	8	10
SDS[a]/mL	0	3	4	5	6	6.4	6.8	7	7.5	7.8	8	10
THP-1[b]/μL	100	70	60	50	40	36	32	30	25	22	20	0

[a] SDS concentrated solution (10 mM) containing THP-1 (10 μM); [b] THP ethanol stock solution (1 mM).

Preparation of samples for fluorescence measurement via new method (method 3)

a) Preparation of the ethanol stock solution of THP-1 (1.00 mM)

4.56 mg of THP-1 (Mr = 456) and about 5 mL of ethanol were added into a 10 mL volumetric flask successively, followed with ultrasonic treatment for dissolving THP-1, then filling the flask to the mark with ethanol.

b) Preparation of concentrated SDS solution (10.0 mM) containing THP-1 (6, 10 or 15 μM)

288 mg of SDS (Mr = 288) was added into a 100 mL volumetric flask and dissolved by about 50 mL of doubly distilled water, then, 0.6, 1 or 1.5 mL of THP-1 stock solution (1.00 mM) was added, filling the flask to the mark with doubly distilled water.

c) Preparation of different concentrations of SDS solutions containing different concentrations of THP-1

As described in Table S3, at room temperature (25±1ºC), different volumes of concentrated SDS solutions were added in different 10 mL volumetric flasks, respectively, filling the flask to the mark with doubly distilled water. These prepared solutions were kept at room temperature for different times.

Table S3 Preparation of different concentrations of SDS solutions

entry	1	2	3	4	5	6	7	8	9	10	11	12
SDS/mM	0	3	4	5	6	6.4	6.8	7	7.5	7.8	8	10
SDS[a]/mL	0	3	4	5	6	6.4	6.8	7	7.5	7.8	8	10

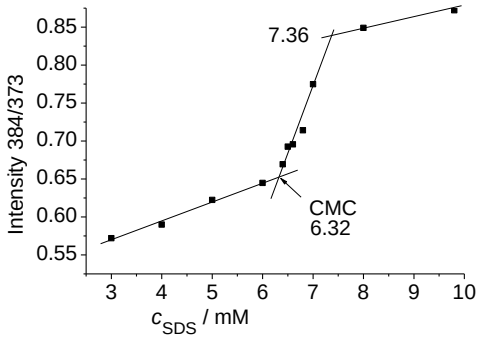
[a] SDS concentrated solution (10 mM) containing THP-1 (6, 10 or 15 μM)

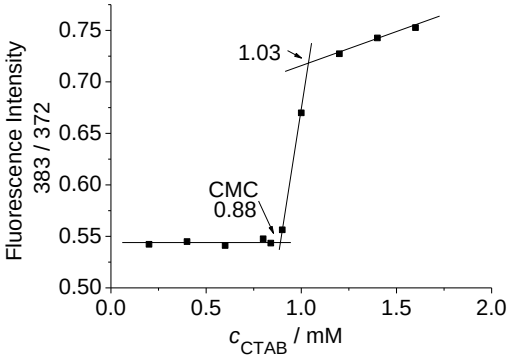
Note: the procedures of preparing different concentrations of CTAB and CHAPS for fluorescence measurement are the same as described above for SDS.

CMC determination of SDS, CTAB and CHAPS by pyrene[4]

Experimental procedures are as described as reference 1 with minor changes in preparing pyrene stock solution. 2 mL of pyrene saturated water solution was added into 10 mL volumetric flasks containing 8, 7, 6.8, 6.6, 6.5, 6.4, 6, 5, 4, 3 mL of 10 mM SDS solution (or containing 7, 4.5, 4.2, 4, 3.5, 3, 2.5, 2, 1 mL of 2 mM CTAB solution), respectively, filling the flask to the mark with doubly distilled water, mixed and kept at room temperature for 30 min for fluorescence measurement (excitation wavelength: 334 nm, emission spectrum: 360 to 450 nm; slit width: 3 and 3 nm). The fluorescence intensities of the peaks at ~372 nm (I_1) and ~383 (I_3) were extracted from the spectra, and the I_3/I_1 value vs. surfactant concentration was used for CMC determination. Two inflection points were observed for SDS and CTAB. 0.5 mL of pyrene saturated water solution was added into 5 mL volumetric flasks containing 10, 9, 8, 7.5, 7, 6, 5.5, 5, 4.5, 4, 3.5, 3mL of 15 mM CHAPS, respectively, other procedures are the same as for SDS and CTAB. Only one

inflexion was observed. Experiments were conducted at room temperature (25±1ºC).





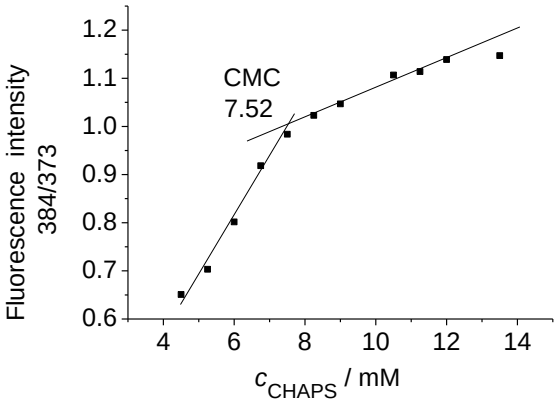


Fig. S1-S6

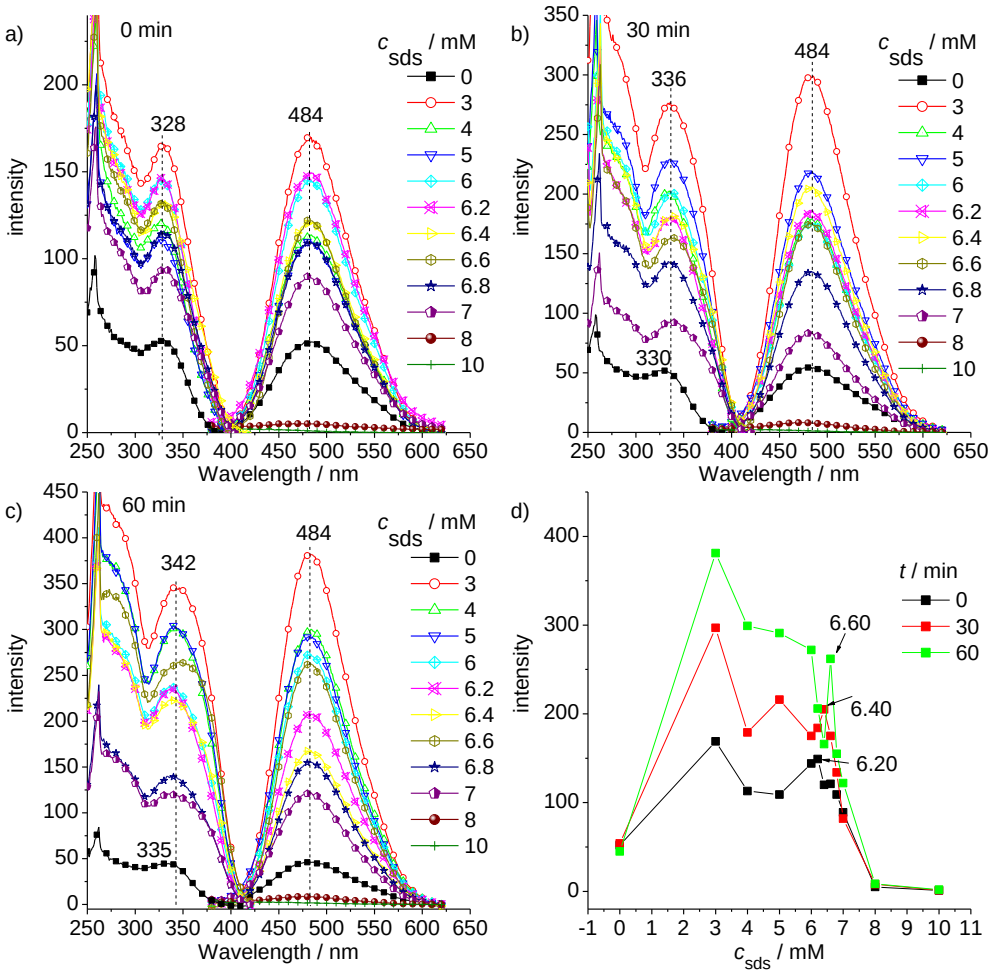


Fig. S1 CMC determination of SDS using THP-1 as a fluorescence probe (samples prepared by reported method 1 and kept at room temperature for different times). Excitation and Emission spectra of different concentrations (from 0 to 10 mM) of SDS solutions containing 10 uM of THP-1 kept for a) 0, b) 30 and c) 60 min. d) Relationship between the intensity at 484 nm and the concentrations of SDS. Slid widths: 3 and 5 nm.

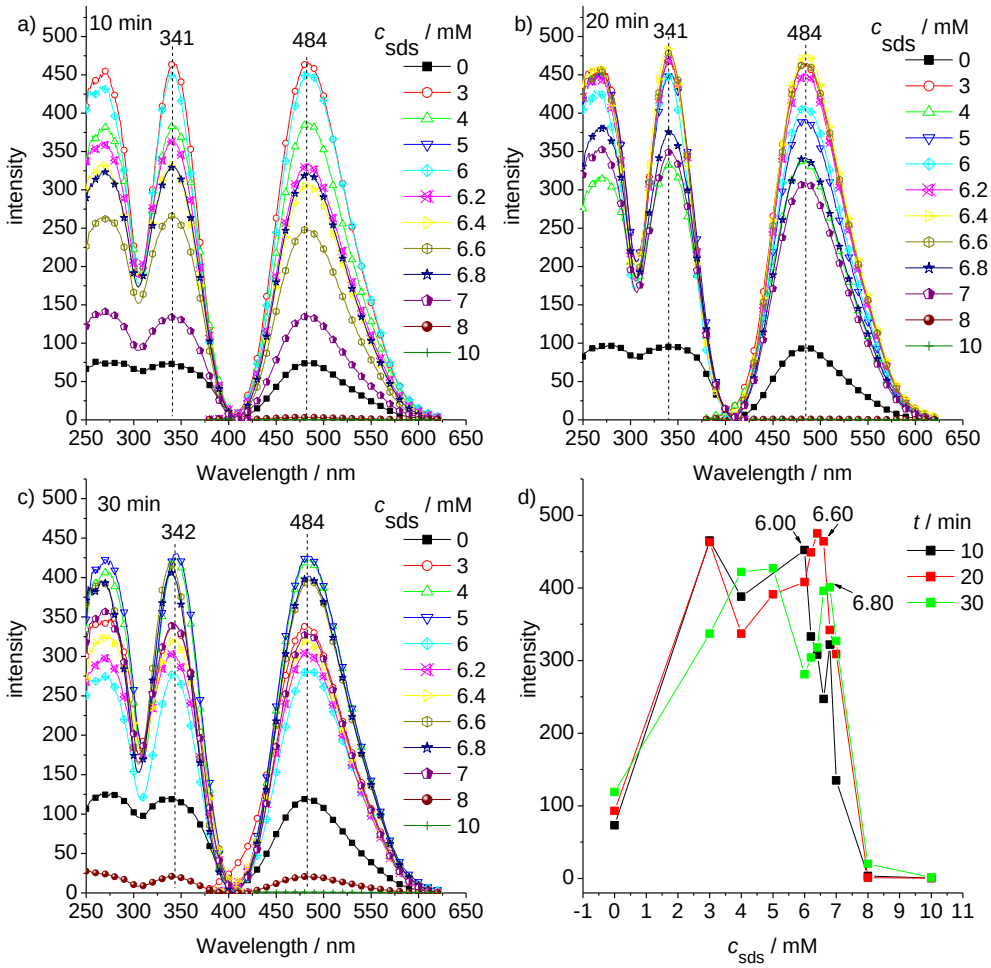


Fig. 2S CMC determination of SDS using THP-1 as a fluorescence probe (samples were prepared by reported method 1 and followed with ultrasonic treatment in a water bath for different times). Excitation and Emission spectra of different concentrations (from 0 to 10 mM) of SDS solutions containing 10 uM of THP-1 at a) 10, b) 20 and c) 30 min. d) Relationship between the intensity at 484 nm and the concentrations of SDS. Slid widths: 3 and 5 nm

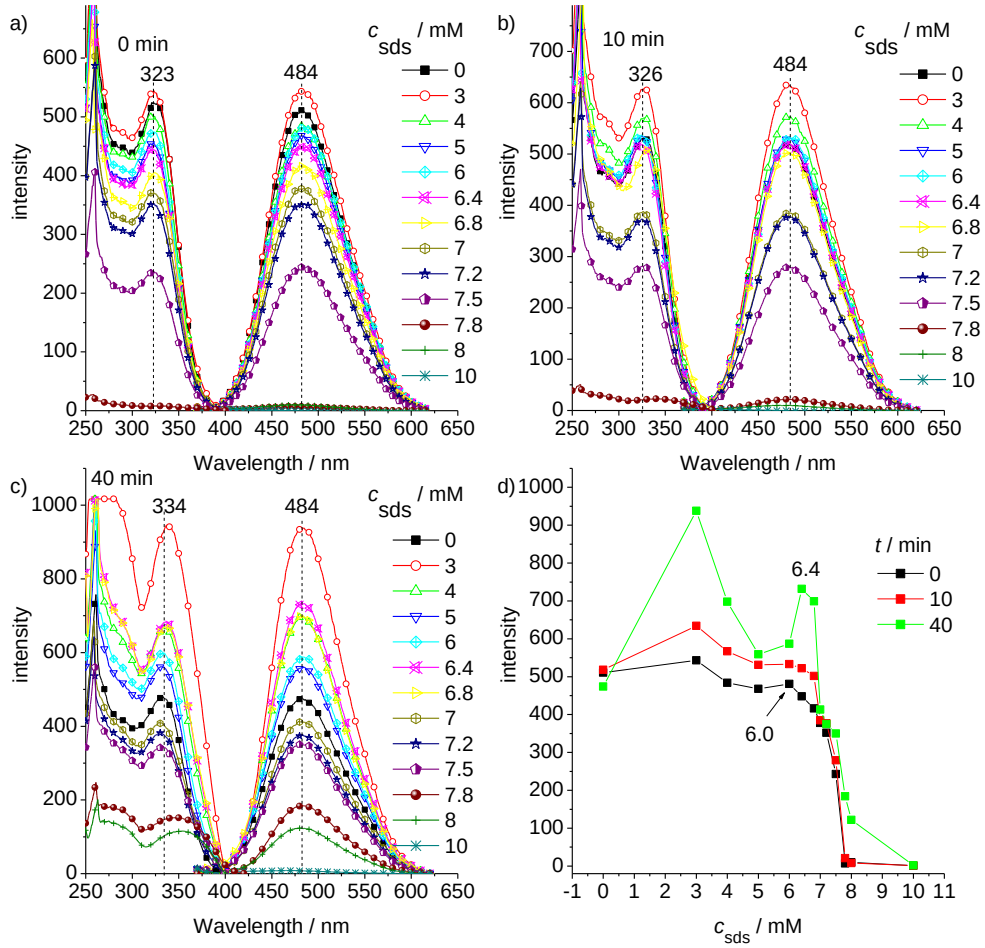


Fig. S3 CMC determination of SDS using THP-1 as a fluorescence probe (samples prepared by reported method 2 and kept at room temperature for different times). Excitation and Emission spectra of different concentrations (from 1 to 10 mM) of SDS solutions (10 mM of concentrated SDS containing 10 uM THP-1) kept for a) 0, b) 10 and c) 40 min. d) Relationship between the intensity at 484 nm and the concentrations of SDS. Slid widths: 5 and 5 nm

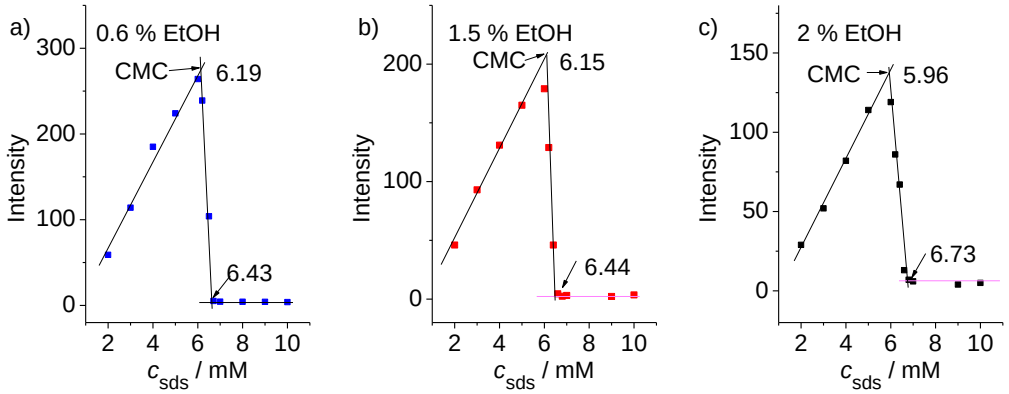


Fig. S4 Relationship between the concentrations of SDS and the fluorescence intensities at 484 nm of THP-1. Samples for fluorescence measurement were prepared by method 3 and kept at room temperature for 10 min. The concentration of THP-1 in the most concentrated SDS solution is 6 μM, the concentration of ethanol (EtOH) is a) 0.6, b) 1.5 or c) 2% v/v. Slid widths: 5 and 5 nm

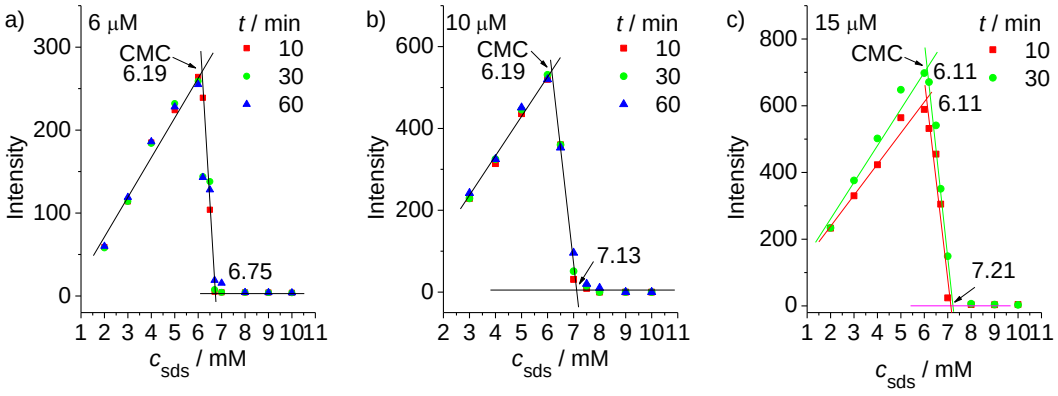


Fig. S5 Relationship between the concentrations of SDS and the fluorescence intensities at 484 nm of THP-1. Samples for fluorescence measurement were prepared by method 3 and kept at room temperature for different times. The concentration of THP-1 in the most concentrated SDS solution is a) 6, b) 10 or c) 15 μM. Slid widths: 5 and 5 nm

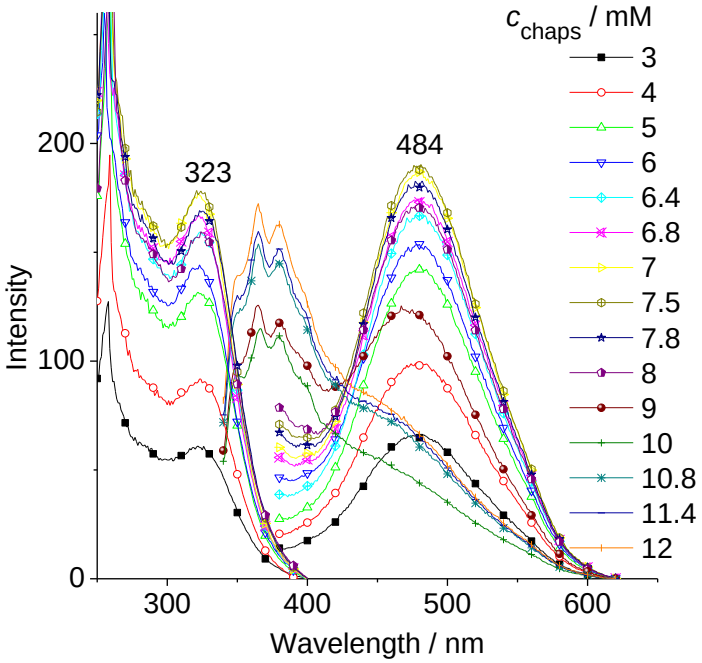


Fig. S6 Excitation and Emission spectra of different concentrations (from 3 to 12 mM) of CHAPS solutions (samples were prepared by method 3, 12 mM of concentrated CHAPS solution containing 12 uM THP-1) kept at room temperature for 10 min. Slid widths: 5 and 5 nm

Reference

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