Electronic Supplementary Material (ESI) for Analyst.

Aggregation Enhanced Excimer Emission (AEEE) of Benzo[ghi]perylene and Coronene: Multimode Probes for Facile Monitoring and Direct Visualization of Micelle Transition

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Fluorescence Lifetime Measurement

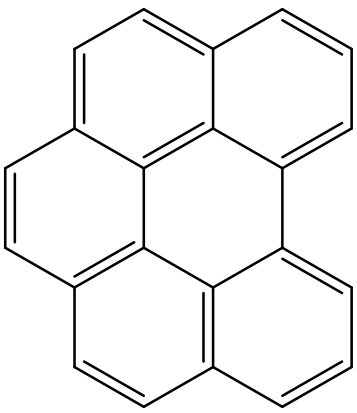
Lifetime of BzP in the samples of various concentration of SDS was measured. The fluorescence decay of probe in the surfactant solutions was measured at a wavelength of 430 nm upon its excitation at 370 nm. The fluorescence decay curves can be fitted exactly at triple exponential decay functions: [s1]

$$I(t) = I_o + A_1 \exp\left(-t/\tau_1\right) + A_2 \exp\left(-t/\tau_2\right) + A_3 \exp\left(-t/\tau_3\right)$$

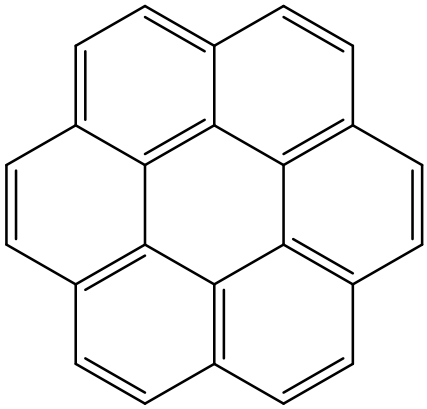
I and I_o are fluorescence intensities at time t_1 and t_0. A_1, A_2 and A_3 are exponential constants. τ_1, τ_2 and τ_3 are fluorescence decay times, and t is the time. The average lifetime of emission decay was calculated by the equation: [s1]

$$\tau_{ave} = A_1\tau_1^{\,2} + A_2\tau_2^{\,2} + A_3\tau_3^{\,2}/A_1\tau_1 + A_2\tau_2 + A_3\tau_3$$

Thus the average lifetime increasing from 69 to 122 ns was obtained moving from lower to higher concentration of SDS.



Benzo[*ghi*]perylene



Coronene

Fig. S1: The chemical structures of benzo[*ghi*]perylene and coronene.

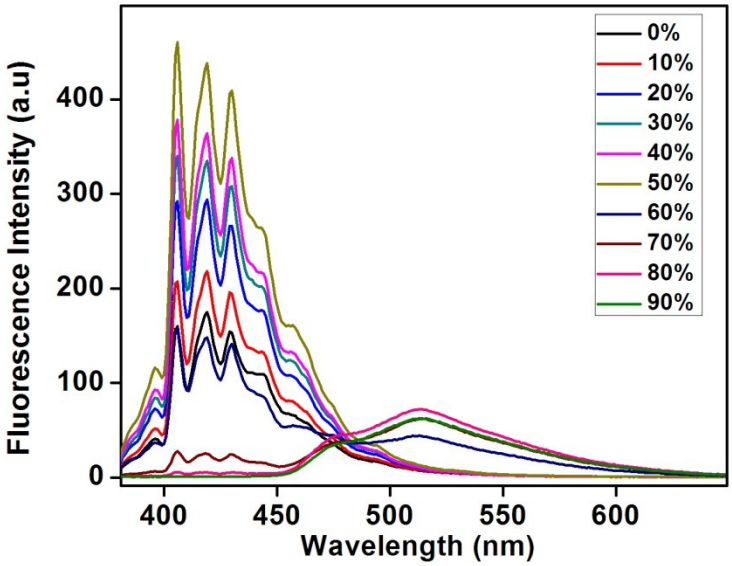


Fig. S2: Fluorescence emission spectral changes of BzP with increasing percentage of water in the ethanol-water mixture.

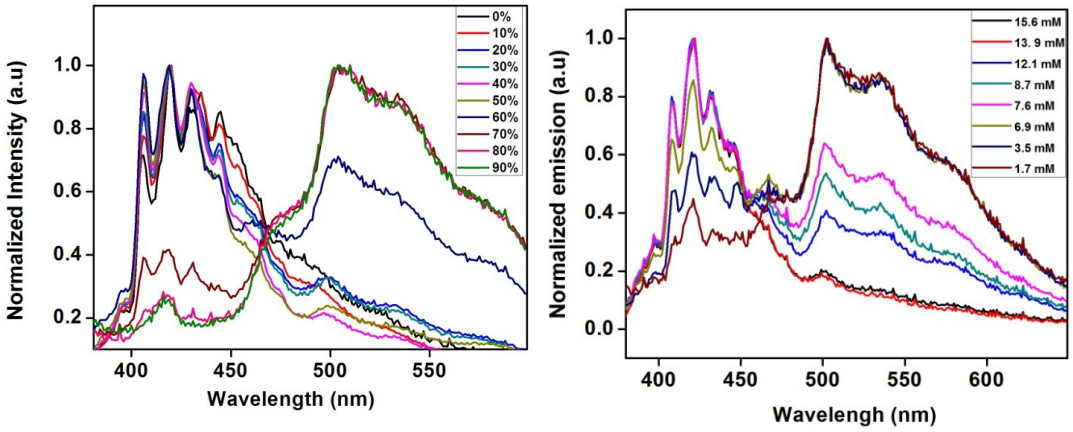
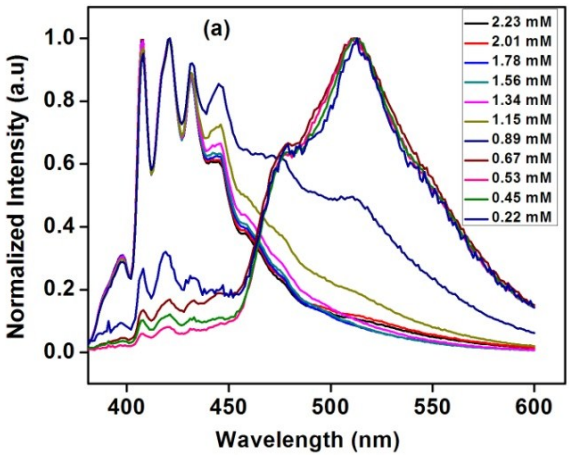
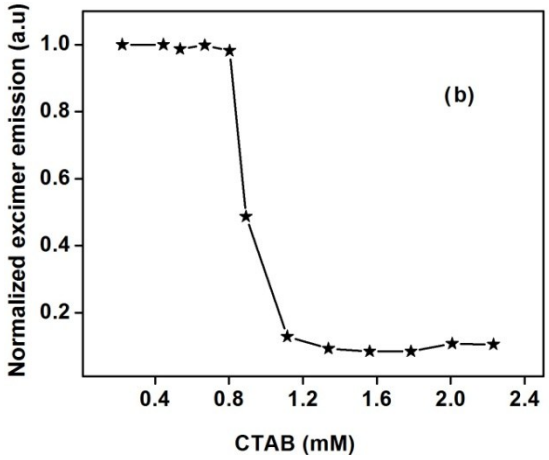
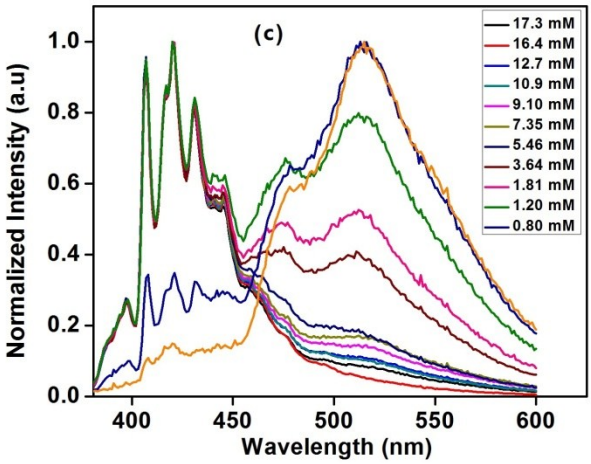
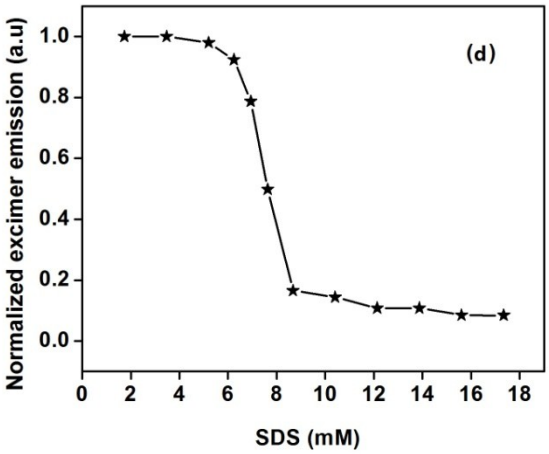


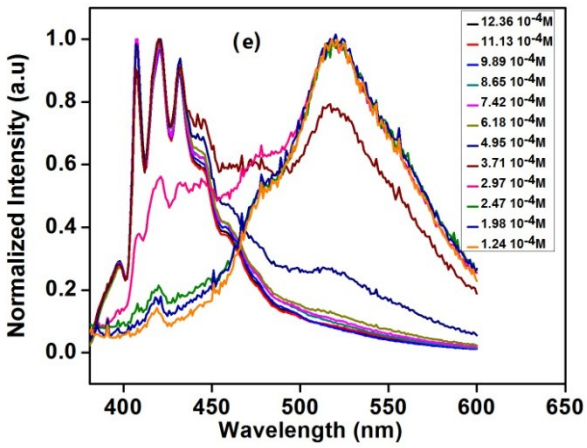
Fig. S3: Fluorescence spectra of coronene with increasing water percentage in ethanol-water mixture (Left), and at various concentration of SDS aqueous solution (Right). Cron: 6 μM; λ_{ext}: 365 nm; slit: 2 nm.


(a)
2.23 mM
2.01 mM
1.78 mM
1.56 mM
1.34 mM
1.15 mM
0.89 mM
0.67 mM
0.53 mM
0.45 mM
0.22 mM
Normalized Intensity (a.u)
Wavelength (nm)


(b)
Normalized excimer emission (a.u)
CTAB (mM)


(c)
17.3 mM
16.4 mM
12.7 mM
10.9 mM
9.10 mM
7.35 mM
5.46 mM
3.64 mM
1.81 mM
1.20 mM
0.80 mM
Normalized Intensity (a.u)
Wavelength (nm)


(d)
Normalized excimer emission (a.u)
SDS (mM)


(e)
12.36 10-4M
11.13 10-4M
9.89 10-4M
8.65 10-4M
7.42 10-4M
6.18 10-4M
4.95 10-4M
3.71 10-4M
2.97 10-4M
2.47 10-4M
1.98 10-4M
1.24 10-4M
Normalized Intensity (a.u)
Wavelength (nm)

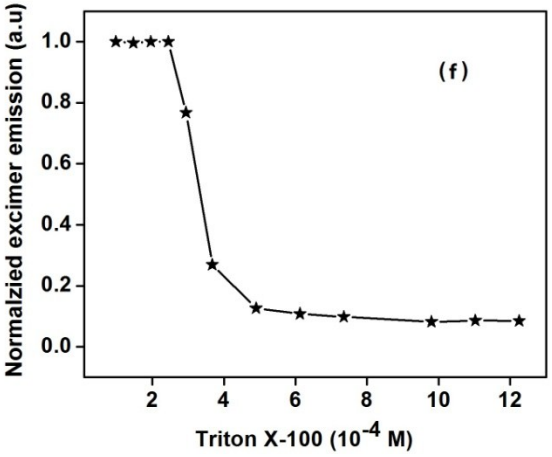

(f)
Normalzied excimer emission (a.u)
Triton X-100 (10-4 M)

Fig. S4: Changes in the fluorescence emission spectra and the excimer emission of 6 μM BzP at 520 nm with the concentration of CTAB (a, b), SDS (c, d), and Triton X-100 (e, f). λ_{ex}: 365 nm; slit: 2 nm.

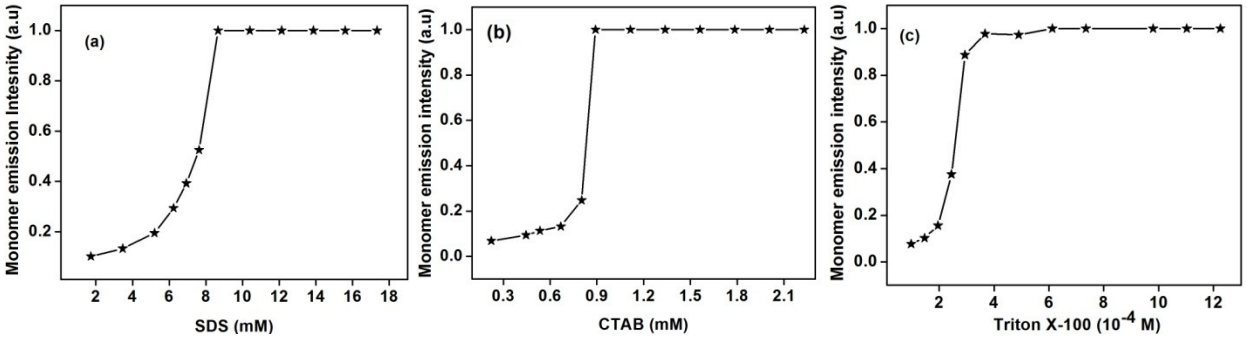


Fig. S5: Changes in monomer emission of BzP at 430 nm with the concentration of SDS (a), CTAB (b), and Triton X-100 (c).

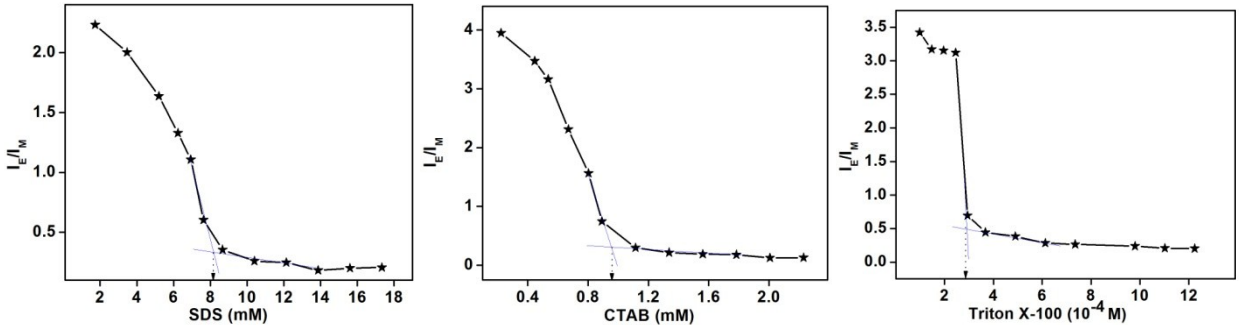


Fig. S6: The plots of excimer and monomer emission intensity ratio (I_E/I_M) of Cron as a function of the concentration of SDS, CTAB, and Triton X-100.

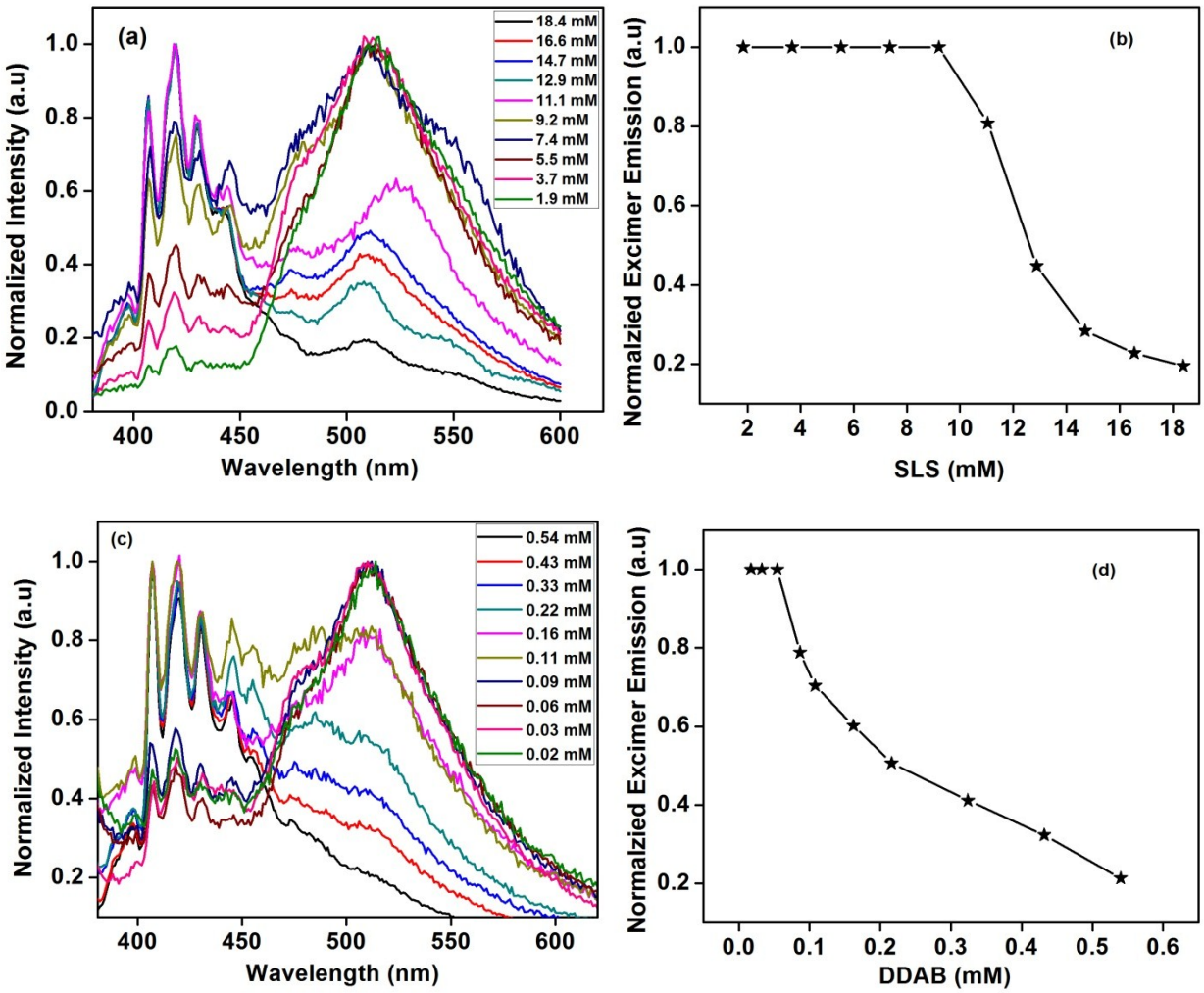


Fig. S7: Changes in the fluorescence emission spectra and the excimer emission of 6 μM BzP at 520 nm as a function of the concentration of SLS (a, b), and DDAB (c, d). λ_{ex}: 365 nm; slit: 2 nm.

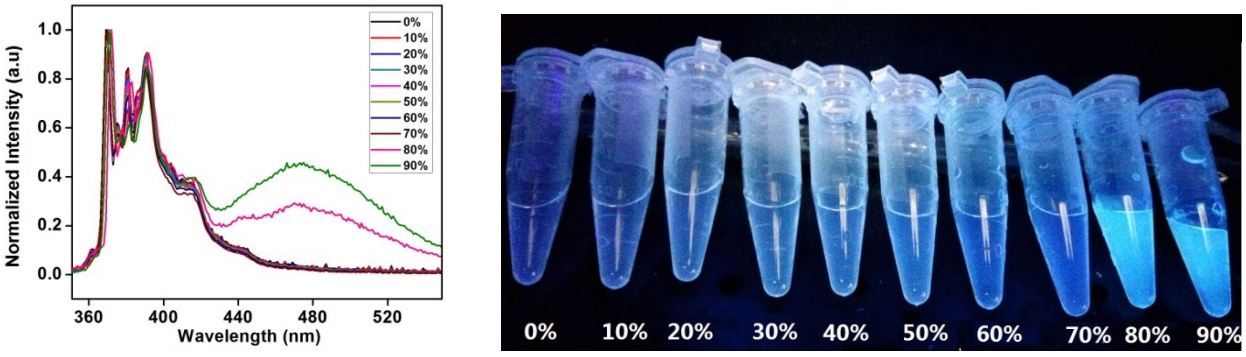


Fig. S8: a) Normalized fluorescence spectra of pyrene showing changes with increasing percentage of water in ethanol solution (Pyrene, 80 μM; λ_{ext}, 310 nm; slit, 2 nm). b) Pyrene solutions in varying ethanol-water compositions under UV lamp.

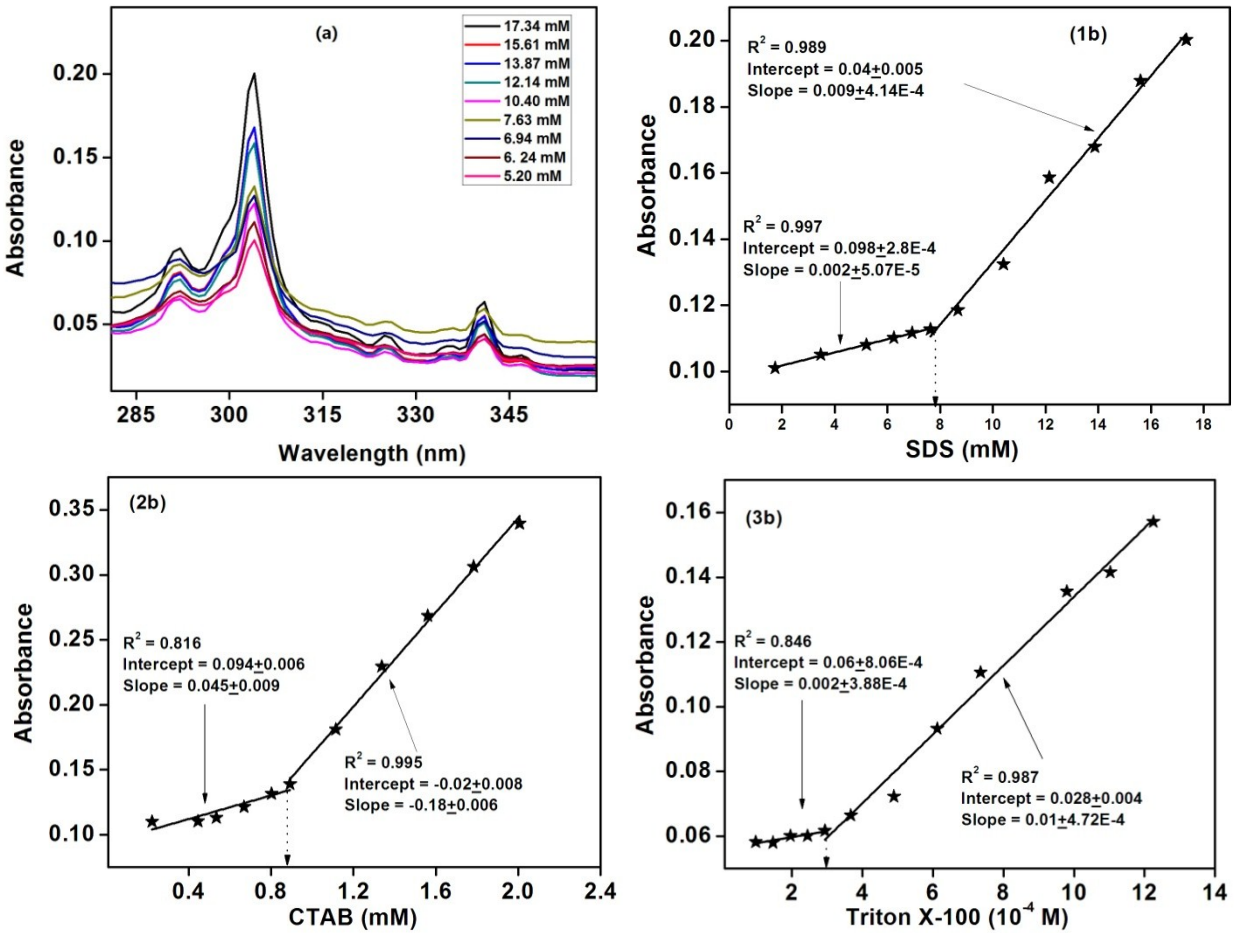


Fig. S9: a) UV-vis absorption spectra of Cron at various concentration of SDS. b) Absorption changes of Cron at 305 nm as a function of the concentration of SDS (1b), CTAB (2b), and Triton X-100 (3b). Cron: 6 μM.

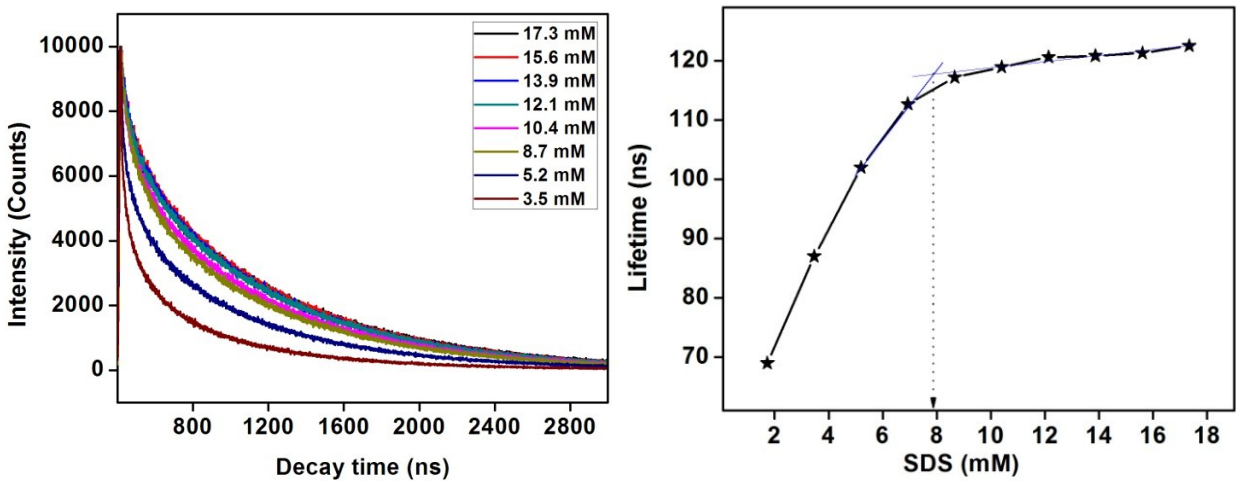


Fig. S10: Changes in lifetime of benzo[ghi]perylene fluorescence emission with SDS concentration. BzP: 6µM λ_{ex}: 375 nm; λ_{em}: 430 nm.

Table S1: The values of critical micelle concentration (CMC) determined by multiple approaches.

Probe	Method	SLS (mM)	DDAB (mM)
Benzo[ghi]perylene	Excimer	12.1-12.6	0.06-0.08
	Monomer	12.3-12.6	0.06-0.07
	I_E/I_M	12.1±0.06	0.07±0.008
	Visual Inspection	12.1-12.8	0.07-0.08
	UV-vis	12.4± 0.3	0.08±0.01
Coronene	Excimer	12.1-12.6	0.05-0.07
	Monomer	12.1-12.4	0.06-0.08
	I_E/I_M	12.1±0.06	0.07±0.01
	UV-vis	12.4±0.2	0.08±0.01
Literature	Ref [7-10]	12.1	0.05-0.08

Standard deviations (SD) were estimated from three measurements

Table S2: Comparison between the methods of CMC determination with representative CMC values of CTAB.

Probe	Method	Parameter	CMC (mM)
Pyrene	Fluorescence	Vibronic band ratio	0.80[8a]
5-, 16-doxyl stearic acid	ESR	Microviscosity	0.83 [5]
Coumarine 153	Fluorescence	Spectral shift of I_{max}	0.86 [8d]
-	Conductivity	Conductance	0.98 [7b]
-	Surface tension	Surface tension	0.96 [7c]
Nile Red	Fluorescence	Intensity	1.2 [8d]

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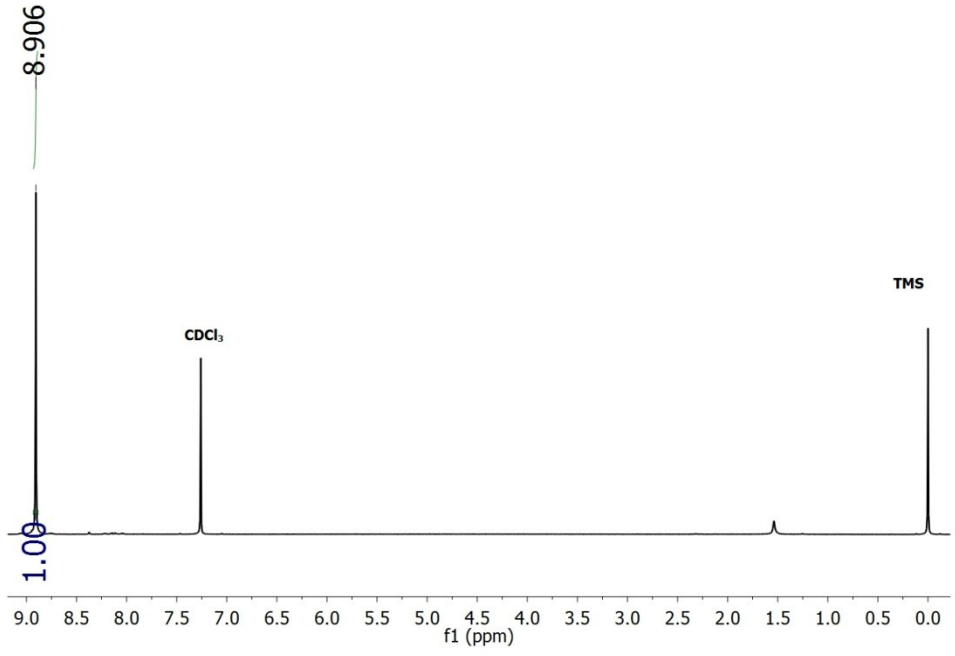

Fig. S11: NMR spectra of coronene recorded at 500 MHz in $CDCl_3$.

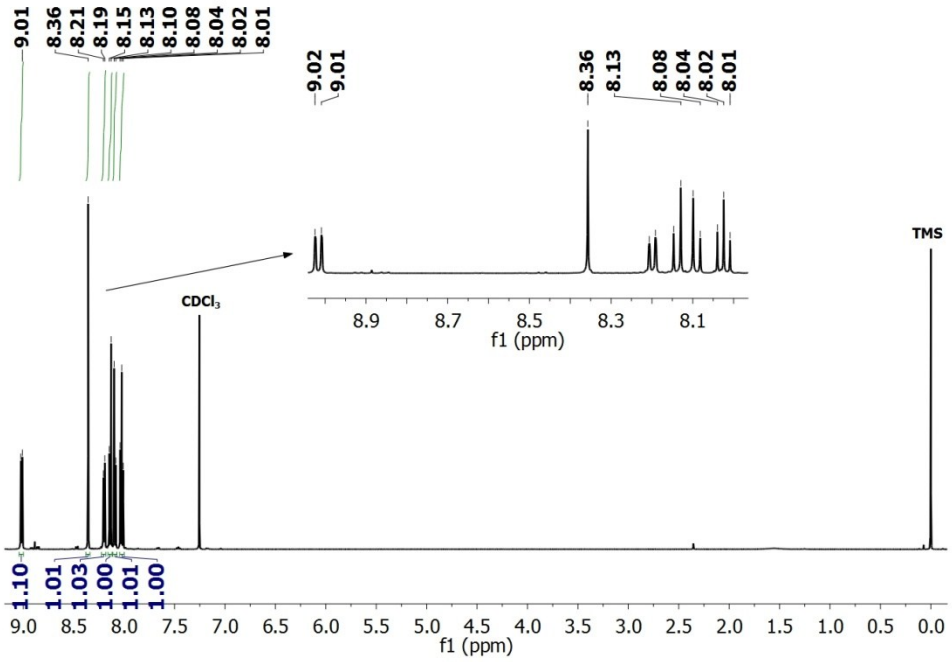

Fig. S12: NMR spectra of benzo[ghi]perylene recorded at 500 MHz in $CDCl_3$.

Reference

s1. M. I. Halawa, W. Gao, M. Saqib, S. A. Kitte, F. Wu, G. Xu, *Biosens. Bioelectron*., 2017, **95**, 8-14.