Supporting Information

for the Manuscript:

Associations Between a Pyrene-Labeled Hydrophobically Modified Alkali Swellable Emulsion Copolymer and Sodium Dodecyl Sulfate Probed by Fluorescence, Surface Tension, and Rheology

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Fitting the Excimer Fluorescence Decays with a Sum of Exponentials:

The excimer fluorescence decays were fitted with Equation SI.1.

$$I_E(t) = \sum_{i=1}^{3} A_{Ei} \exp(-t/\tau_{Ei}) \qquad \text{(SI.1)}$$

The pre-exponential factors A_{Ei} and decay times τ_{Ei} obtained from the fit of the excimer fluorescence decays with Equation SI.1 are listed in Table SI.2.

Fitting the Fluorescence Decays with the Fluorescence Blob Model (FBM):

Work from this laboratory has established that at least four pyrene species need to be considered when studying a pyrene-labeled polymer in solution.[1-9] These species are the pyrene monomers which are isolated on the chain and are too far from another ground-state pyrene to form an excimer (Py_{free}), the pyrene monomers which form excimer via diffusion (Py_{diff}), the pyrene excimer which are formed by either diffusion or direct excitation of ground-state pyrene aggregates (*E0**), and the long-lived pyrene dimers (*D*). The parameters describing the photophysical properties of all four pyrene species are listed in Table SI.1.

Table SI.1: Symbols representing the extinction coefficients, the lifetimes, and the radiative rate constants of the four pyrene species.

Species	Extinction Coefficient	lifetime	Radiative Rate Constant
Py_{diff}	ε_M	τ_M	k_{rad}^{M}
Py_{free}	ε_M	τ_M	k_{rad}^{M}
$E0*$	ε_{E0}	τ_{E0}	If formed by diffusion: $k_{rad}^{E0(diff)}$ If formed via direct excitation: $k_{rad}^{E0(agg)}$
$D*$	ε_D	τ_D	k_{rad}^{D}

The monomer and excimer fluorescence decays were fitted with Equations SI.2 and SI.3, respectively, as done in references #1,2.

$$I_M(t) = \alpha_M(\lambda_{ex}, \lambda_{em}) \left\{ \varepsilon_M \; k_{rad}^{M} \; [Py_{diff}^{*}]_{(t=0)} \; G_M(t) + \varepsilon_M \; k_{rad}^{M} \; [Py_{free}^{*}]_{(t=0)} \exp(-t/\tau_M) \right\} \quad \text{(SI.2)}$$

$$I_E(t) = \alpha_E(\lambda_{ex}, \lambda_{em}) \left\{ -\varepsilon_M k_{rad}^{E0(diff)} [Py_{diff}^{*}]_{(t=0)} \; G_E(t) \right.$$

$$\left. + \left(\varepsilon_{E0} k_{rad}^{E0(agg)} [E0*]_{(t=0)} + \varepsilon_M k_{rad}^{E0(diff)} [Py_{diff}^{*}]_{(t=0)} \; G_E(t=0) \right) e^{-t/\tau_{E0}} + \varepsilon_D k_{rad}^{D} [D*]_{(t=0)} \; e^{-t/\tau_D} \right\}$$

(SI.3)

In Equations SI.2 and SI.3, the parameters $\alpha_M(\lambda_{ex}, \lambda_{em})$ and $\alpha_E(\lambda_{ex}, \lambda_{em})$ depend on the geometry and the excitation and emission wavelengths of the time-resolved fluorometer. All other parameters used in Equations SI.2 and SI.3 have been defined in Table SI.1. The expressions of the functions $G_M(t)$ and $G_E(t)$ are given in Equations SI.4 and SI.5, respectively.

$$G_M(t) = \exp(-(A_2 + \frac{1}{\tau_M})t - A_3(1 - \exp(-A_4 t))) \quad \text{(SI.4)}$$

$$G_E(t) = e^{-A_3} \sum_{i=0}^{\infty} \frac{A_3{}^i}{i!} \frac{A_2 + i A_4}{\frac{1}{\tau_M} - \frac{1}{\tau_{E0}} + A_2 + i A_4} \exp\left(-\left(\frac{1}{\tau_M} + A_2 + i A_4 \right) t \right) \quad \text{(SI.5)}$$

The expressions of the parameters A_1, A_2, and A_3 are given in Equation SI.6.

$$A_2 = \langle n \rangle \frac{k_{blob} k_e [blob]}{k_{blob} + k_e [blob]} \quad A_3 = \langle n \rangle \frac{k_{blob}^2}{(k_{blob} + k_e [blob])^2} \quad A_4 = k_{blob} + k_e [blob] \quad \text{(SI.6)}$$

In Equation SI.6, the parameters k_{blob}, $k_e[blob]$, and $\langle n \rangle$ help quantify the diffusional encounters taking place between the pyrene pendants of a pyrene-labeled polymer using the *blob* model. A *blob* is defined as the volume being probed by an excited pyrene during its lifetime and the *blob* model uses this volume unit to divide the polymer coil into *blobs*.[10] These parameters are the rate constant for diffusional encounters between one excited pyrene and one ground-state pyrene located inside the same *blob* (k_{blob}), the rate constant of exchange for pyrenes moving in-and-out of a *blob*

(k_e), the *blob* concentration inside the polymer coil ([*blob*]), and the average number of pyrenes per *blob* (<*n*>).

The pre-factors $\varepsilon_M\, k_{rad}^{M}\,[Py_{diff}^{*}]_{(t=0)}$, $\varepsilon_M\, k_{rad}^{M}\,[Py_{free}^{*}]_{(t=0)}$, $\varepsilon_M\, k_{rad}^{E0(diff)}\,[Py_{diff}^{*}]_{(t=0)}$, $\varepsilon_{E0}\, k_{rad}^{E0(agg)}\,[E0^*]_{(t=0)}$, $\varepsilon_M\, k_{rad}^{E0(diff)}\,[Py_{diff}^{*}]_{(t=0)}$, and $\varepsilon_D\, k_{rad}^{D}\,[D^*]_{(t=0)}$ retrieved from fitting the monomer and excimer fluorescence decays with Equations SI.2 and SI.3 yield the fractions f_{diff}, f_{free}, f_{E0}, and f_D whose expressions are listed in Equations SI.7-10.[1,2]

$$f_{diff} = \frac{[Py_{diff}^{*}]_{(t=0)}}{[Py_{diff}^{*}]_{(t=0)} + [Py_{free}^{*}]_{(t=0)} + \dfrac{\varepsilon_{Eo}\, k_{rad}^{E0(agg)}}{\varepsilon_M\, k_{rad}^{E0(diff)}}[E0^*]_{(t=0)} + \dfrac{\varepsilon_D\, k_{rad}^{D}}{\varepsilon_M\, k_{rad}^{E0(diff)}}[D^*]_{(t=0)}} \tag{SI.7}$$

$$f_{free} = \frac{[Py_{free}^{*}]_{(t=0)}}{[Py_{diff}^{*}]_{(t=0)} + [Py_{free}^{*}]_{(t=0)} + \dfrac{\varepsilon_{Eo}\, k_{rad}^{E0(agg)}}{\varepsilon_M\, k_{rad}^{E0(diff)}}[E0^*]_{(t=0)} + \dfrac{\varepsilon_D\, k_{rad}^{D}}{\varepsilon_M\, k_{rad}^{E0(diff)}}[D^*]_{(t=0)}} \tag{SI.8}$$

$$f_{E0} = \frac{\dfrac{\varepsilon_{Eo}\, k_{rad}^{E0(agg)}}{\varepsilon_M\, k_{rad}^{E0(diff)}}[E0^*]_{(t=0)}}{[Py_{diff}^{*}]_{(t=0)} + [Py_{free}^{*}]_{(t=0)} + \dfrac{\varepsilon_{Eo}\, k_{rad}^{E0(agg)}}{\varepsilon_M\, k_{rad}^{E0(diff)}}[E0^*]_{(t=0)} + \dfrac{\varepsilon_D\, k_{rad}^{D}}{\varepsilon_M\, k_{rad}^{E0(diff)}}[D^*]_{(t=0)}} \tag{SI.9}$$

$$f_{D} = \frac{\dfrac{\varepsilon_D\, k_{rad}^{D}}{\varepsilon_M\, k_{rad}^{E0(diff)}}[D^*]_{(t=0)}}{[Py_{diff}^{*}]_{(t=0)} + [Py_{free}^{*}]_{(t=0)} + \dfrac{\varepsilon_{Eo}\, k_{rad}^{E0(agg)}}{\varepsilon_M\, k_{rad}^{E0(diff)}}[E0^*]_{(t=0)} + \dfrac{\varepsilon_D\, k_{rad}^{D}}{\varepsilon_M\, k_{rad}^{E0(diff)}}[D^*]_{(t=0)}} \tag{SI.10}$$

The fractions f_{diff}, f_{free}, f_{E0}, and f_D represent an estimate of the fractions of the pyrene species which are present in solution as Py^*_{diff}, Py^*_{free}, $E0^*$, and D^*.

The parameters k_{blob}, $k_e[blob]$, $<n>$, $\varepsilon_M\, k_{rad}^M\, [Py^*_{diff}]_{(t=0)}$, $\varepsilon_M\, k_{rad}^M\, [Py^*_{free}]_{(t=0)}$, $\varepsilon_M\, k_{rad}^{E0(diff)}\, [Py^*_{diff}]_{(t=0)}$, $\varepsilon_{E0}\, k_{rad}^{E0(agg)}\, [E0^*]_{(t=0)}$, $\varepsilon_M\, k_{rad}^{E0(diff)}\, [Py^*_{diff}]_{(t=0)}$, and $\varepsilon_D\, k_{rad}^D\, [D^*]_{(t=0)}$ were retrieved by optimizing their value and comparing the result of the convolution of the functions $I_M(t)$ and $I_E(t)$ given, respectively, in Equations SI.2 and SI.3 with the instrument response function and the experimental fluorescence decays of the pyrene monomer and excimer. The values of these parameters are listed in Tables SI.3. The fits were performed with the Marquardt-Levenberg algorithm.[11] In these analyses, the monomer and excimer fluorescence decays were fitted globally to improve the accuracy on the recovered parameters.[12]

In Table SI.3, the fractions f_{Mdiff}, f_{Mfree}, f_{Ediff}, f_{EE0}, and f_{ED} are reported. They represent the ratios listed in Equations SI.11-15. They are being used to determine the fractions f_{diff}, f_{free}, f_{E0}, and f_D in Equations SI.7-10.

$$f_{Mdiff} = \frac{[Py^*_{diff}]_{(t=0)}}{[Py^*_{diff}]_{(t=0)} + [Py^*_{free}]_{(t=0)}} \tag{SI.11}$$

$$f_{Mfree} = \frac{[Py^*_{free}]_{(t=0)}}{[Py^*_{diff}]_{(t=0)} + [Py^*_{free}]_{(t=0)}} \tag{SI.12}$$

$$f_{Ediff} = \frac{[Py^{*}_{diff}]_{(t=0)}}{[Py^{*}_{diff}]_{(t=0)} + \frac{\varepsilon_{Eo}\, k_{rad}^{E0(agg)}}{\varepsilon_{M}\, k_{rad}^{E0(diff)}}[E0^{*}]_{(t=0)} + \frac{\varepsilon_{D}\, k_{rad}^{D}}{\varepsilon_{M}\, k_{rad}^{E0(diff)}}[D^{*}]_{(t=0)}} \quad \text{(SI.13)}$$

$$f_{EE0} = \frac{\frac{\varepsilon_{Eo}\, k_{rad}^{E0(agg)}}{\varepsilon_{M}\, k_{rad}^{E0(diff)}}[E0^{*}]_{(t=0)}}{[Py^{*}_{diff}]_{(t=0)} + \frac{\varepsilon_{Eo}\, k_{rad}^{E0(agg)}}{\varepsilon_{M}\, k_{rad}^{E0(diff)}}[E0^{*}]_{(t=0)} + \frac{\varepsilon_{D}\, k_{rad}^{D}}{\varepsilon_{M}\, k_{rad}^{E0(diff)}}[D^{*}]_{(t=0)}} \quad \text{(SI.14)}$$

$$f_{ED} = \frac{\frac{\varepsilon_{D}\, k_{rad}^{D}}{\varepsilon_{M}\, k_{rad}^{E0(diff)}}[D^{*}]_{(t=0)}}{[Py^{*}_{diff}]_{(t=0)} + \frac{\varepsilon_{Eo}\, k_{rad}^{E0(agg)}}{\varepsilon_{M}\, k_{rad}^{E0(diff)}}[E0^{*}]_{(t=0)} + \frac{\varepsilon_{D}\, k_{rad}^{D}}{\varepsilon_{M}\, k_{rad}^{E0(diff)}}[D^{*}]_{(t=0)}} \quad \text{(SI.15)}$$

Table SI.2a: Parameters retrieved from fitting a triexponential function to the excimer fluorescence decay of 0.1 g/L Py–HASE in 0.01 M Na_2CO_3 solution at pH 9.

[SDS] mmol/L	τ_{E1} ns	A_{E1}	τ_{E2} ns	A_{E2}	τ_{E3} ns	A_{E3}	χ^2
0	28.5	-0.10	49.1	0.92	121.0	0.18	1.00
0.14	11.6	-0.07	51.1	0.89	121.0	0.18	1.05
0.21	30.3	-0.19	47.2	0.99	117.7	0.20	1.00
0.50	16.0	-0.10	48.9	0.91	120.0	0.19	0.96
1.00	9.9	-0.16	51.9	1.01	137.1	0.15	0.98
1.26	11.6	-0.22	49.7	1.09	129.4	0.13	1.07
1.56	10.4	-0.29	49.9	1.16	128.9	0.13	1.14
1.77	11.7	-0.47	48.9	1.32	120.8	0.15	1.19
2.00	11.1	-0.67	51.0	1.57	136.1	0.10	1.09
2.50	17.3	-1.89	53.4	2.83	147.2	0.06	1.05
3.00	25.0	-4.16	57.6	4.58	87.1	0.58	0.99
3.25	25.0	-4.51	58.2	3.09	64.0	2.42	1.09
3.50	27.7	-4.97	62.7	5.31	79.2	0.66	1.14
3.74	29.3	-4.66	69.9	5.66	N/A	N/A	1.24
4.10	31.1	-6.01	52.8	3.83	76.8	3.18	1.06
4.50	30.4	-5.80	42.5	1.53	71.2	5.27	1.16
5.00	30.1	-5.40	57.7	2.68	77.3	3.72	1.12
6.00	34.4	-6.89	49.0	3.85	78.5	4.04	1.16
7.00	29.2	-4.80	70.8	5.80	N/A	N/A	1.25
8.00	28.6	-4.93	72.0	5.93	N/A	N/A	1.16
10.00	35.4	-9.34	44.4	6.19	77.6	4.15	1.13
20.00	31.7	-5.06	61.2	2.22	78.4	3.84	1.16
50.00	34.8	-6.71	49.6	3.68	81.9	4.03	1.04
60.01	32.5	-4.45	77.1	5.45	N/A	N/A	1.04
69.98	32.6	-4.00	80.9	5.00	N/A	N/A	1.04
80.00	37.1	-6.13	47.5	3.10	84.5	4.03	1.08
89.97	33.1	-4.94	74.8	5.65	137.9	0.29	0.99

Table SI.2b: Parameters retrieved from fitting a triexponential function to the excimer fluorescence decay of 1 g/L Py–HASE in 0.01 M Na_2CO_3 solution at pH 9.

[SDS] mmol/L	τ_{E1} ns	A_{E1}	τ_{E2} ns	A_{E2}	τ_{E3} ns	A_{E3}	χ^2
0	37.2	-0.29	46.6	1.12	116.2	0.17	1.03
0.13	30.8	-0.09	49.7	0.95	126.7	0.13	1.14
0.21	14.1	-0.05	49.7	0.88	117.9	0.17	1.18
0.51	19.4	-0.05	51.0	0.91	131.6	0.13	0.96
1.04	13.6	-0.05	51.5	0.92	131.1	0.13	1.05
1.25	15.0	-0.07	50.7	0.95	135.4	0.12	0.95
1.50	11.1	-0.14	49.1	1.01	122.0	0.13	1.06
1.81	12.3	-0.58	50.5	1.51	146.9	0.07	1.10
2.05	13.0	-0.89	51.8	1.80	129.9	0.09	1.07
2.51	14.7	-1.46	50.1	2.38	121.2	0.08	1.14
3.00	18.5	-2.68	53.7	3.66	157.9	0.02	1.15
3.85	24.7	-4.40	58.5	5.40	N/A	N/A	1.12
4.01	28.4	-5.62	44.6	2.83	66.2	3.79	0.87
4.25	27.5	-4.78	63.8	5.78	N/A	N/A	1.16
4.50	31.7	-6.15	49.1	4.06	73.9	3.10	1.13
5.00	32.5	-5.94	55.1	4.17	81.4	2.77	1.13
6.02	31.9	-5.82	50.4	3.03	76.0	3.78	1.13
7.00	30.1	-4.68	74.1	5.68	N/A	N/A	1.20
8.00	32.5	-5.27	59.4	2.67	85.5	3.60	1.07
10.04	31.4	-5.21	77.3	6.21	N/A	N/A	1.11
20.03	33.9	-6.72	54.9	3.41	82.2	4.31	1.17
49.98	33.4	-5.57	62.1	2.19	85.5	4.38	1.10

Table SI.2c: Parameters retrieved from fitting a triexponential function to the excimer fluorescence decay of 10 g/L Py–HASE in 0.01 M Na_2CO_3 solution at pH 9.

[SDS] mmol/L	τ_{E1} ns	A_{E1}	τ_{E2} ns	A_{E2}	τ_{E3} ns	A_{E3}	χ^2
0	31.3	-0.28	46.4	1.10	122.2	0.18	0.99
0.10	29.1	-0.14	47.0	0.98	118.8	0.16	1.09
0.24	29.7	-0.21	46.8	1.05	121.8	0.16	1.12
0.51	23.6	-0.12	48.1	0.99	127.3	0.13	1.00
1.00	13.3	-0.26	49.4	1.11	126.2	0.15	0.90
1.25	13.3	-0.33	49.1	1.20	130.3	0.13	0.94
1.50	12.2	-0.43	49.8	1.31	130.3	0.12	1.04
1.75	11.7	-0.61	49.3	1.50	130.5	0.11	1.09
2.00	16.2	-0.55	46.9	1.44	108.7	0.11	1.07
3.00	14.7	-1.56	50.9	2.51	143.9	0.05	1.14
4.03	20.1	-2.92	48.3	3.02	73.3	0.90	1.25
5.00	20.1	-3.31	48.5	3.47	68.2	0.84	1.26
6.00	23.3	-4.03	55.9	4.14	73.1	0.89	1.18
7.08	24.3	-4.39	58.6	4.43	70.5	0.96	1.13
8.14	26.1	-4.84	58.9	4.24	70.4	1.60	1.14
9.00	27.1	-5.04	59.8	4.98	77.2	1.06	1.11
10.00	29.0	-5.37	60.8	4.95	79.4	1.43	1.08
12.42	31.2	-5.93	48.0	2.20	74.4	4.73	1.22
15.00	37.4	-9.09	48.6	6.49	84.5	3.60	1.16
17.52	34.7	-5.85	56.2	3.09	84.5	3.76	1.07
20.00	33.9	-5.40	57.5	3.43	82.7	2.97	1.18
40.00	36.6	-4.82	62.5	3.18	89.8	2.64	1.12

Table SI.3a: Parameters retrieved from the global analysis of the monomer and excimer fluorescence decays of 0.1 g/L Py–HASE in 0.01 M Na_2CO_3 solution at pH 9 using the blob model.

[SDS] mmol/L	k_{exch} ×10^7 s^{-1}	f_{Mdiff}	k_{blob} ×10^7 s^{-1}	$\langle n \rangle$	τ_M ns	f_{Mfree}	χ^2
0	1.11	0.30	3.01	0.6	165	0.70	1.08
0.14	0.63	0.32	1.46	0.7	165	0.68	1.11
0.21	0.25	0.40	1.48	0.6	165	0.60	1.10
0.50	0.61	0.36	2.11	0.6	165	0.64	1.14
1.00	0.71	0.31	3.48	0.6	165	0.69	1.01
1.26	0.75	0.32	4.21	0.7	165	0.68	1.07
1.56	0.60	0.35	3.77	0.7	165	0.65	1.21
1.77	0.55	0.37	3.50	0.7	165	0.63	1.15
2.00	0.57	0.29	3.11	1.2	165	0.71	1.17
2.50	0.22	0.47	2.39	1.5	165	0.53	1.04
3.00	0.29	0.60	1.15	2.5	165	0.40	1.13
3.25	0.53	0.68	0.96	2.4	165	0.32	1.13
3.50	0.66	0.76	0.91	2.1	165	0.25	1.28
3.74	0.70	0.74	0.84	2.0	165	0.26	1.27
4.10	0.89	0.77	0.98	1.6	165	0.24	1.13
4.50	0.90	0.72	0.95	1.7	165	0.28	1.25
5.00	0.74	0.72	0.94	1.8	165	0.28	1.09
6.00	0.47	0.77	0.70	2.0	165	0.23	1.25
7.00	0.92	0.68	0.80	1.8	165	0.32	1.17
8.00	0.84	0.67	0.86	1.8	165	0.33	1.09
10.00	0.83	0.67	0.92	1.7	165	0.33	1.13
20.00	0.40	0.67	0.73	1.8	165	0.33	1.14
50.00	0.69	0.60	0.46	2.2	165	0.40	1.30
60.01	0.66	0.57	0.61	1.9	165	0.43	1.25
69.98	0.59	0.58	0.65	1.8	165	0.42	1.11
80.00	0.62	0.52	0.69	1.7	165	0.48	1.09
89.97	0.68	0.58	0.60	1.6	165	0.42	1.26

Table SI.3b: Parameters retrieved from the global analysis of the monomer and excimer fluorescence decays of 0.1 g/L Py–HASE in 0.01 M Na_2CO_3 solution at pH 9 using the blob model.

[SDS] mmol/L	f_{Ediff}	τ_{E0} ns	f_{EE0}	τ_D ns	f_{ED}	χ^2
0	0.13	51.1	0.80	104.6	0.07	1.08
0.14	0.22	48.3	0.68	127.1	0.10	1.11
0.21	0.25	47.0	0.63	121.8	0.12	1.10
0.50	0.26	46.4	0.62	112.7	0.12	1.14
1.00	0.28	48.7	0.64	136.4	0.08	1.01
1.26	0.35	46.5	0.60	133.3	0.05	1.07
1.56	0.41	45.2	0.55	126.0	0.04	1.21
1.77	0.51	44.3	0.47	126.0	0.02	1.15
2.00	0.51	42.3	0.45	126.0	0.04	1.17
2.50	0.53	47.6	0.30	0	0	1.04
3.00	0.81	54.4	0.19	0	0	1.13
3.25	0.84	47.6	0.16	0	0	1.13
3.50	0.87	47.8	0.13	0	0	1.28
3.74	0.87	51.3	0.14	0	0	1.27
4.10	0.89	46.8	0.11	0	0	1.13
4.50	0.88	48.8	0.12	0	0	1.25
5.00	0.88	51.4	0.12	0	0	1.09
6.00	0.88	50.9	0.12	0	0	1.25
7.00	0.89	46.9	0.11	0	0	1.17
8.00	0.88	49.5	0.12	0	0	1.09
10.00	0.88	52.3	0.12	0	0	1.13
20.00	0.88	51.7	0.12	0	0	1.14
50.00	0.90	44.4	0.10	0	0	1.30
60.01	0.88	50.4	0.12	0	0	1.25
69.98	0.87	54.8	0.13	0	0	1.11
80.00	0.86	56.1	0.14	0	0	1.09
89.97	0.90	47.9	0.10	0	0	1.26

Table SI.3c: Parameters retrieved from the global analysis of the monomer and excimer fluorescence decays of 1 g/L Py–HASE in 0.01 M Na_2CO_3 solution at pH 9 using the blob model.

[SDS] mmol/L	k_{exch} $\times 10^7$ s^{-1}	f_{Mdiff}	k_{blob} $\times 10^7$ s^{-1}	$<n>$	τ_M ns	f_{Mfree}	χ^2
0	0.41	0.43	1.63	0.6	165	0.57	1.13
0.13	0.61	0.40	2.32	0.6	165	0.60	1.06
0.21	1.13	0.30	4.00	0.6	165	0.70	1.11
0.51	1.43	0.27	5.78	0.7	165	0.73	1.14
1.04	0.75	0.35	4.80	0.7	165	0.65	1.17
1.25	0.80	0.36	5.80	0.7	165	0.64	0.97
1.50	0.75	0.37	4.19	0.6	165	0.63	1.19
1.81	0.56	0.34	3.84	1.0	165	0.66	1.11
2.05	0.38	0.39	3.60	1.1	165	0.61	1.11
2.51	0.41	0.43	2.89	1.6	165	0.57	1.16
3.00	0.42	0.50	1.49	2.6	165	0.50	1.11
3.85	0.80	0.68	1.10	2.4	165	0.32	1.16
4.01	1.02	0.71	1.02	2.2	165	0.29	1.11
4.25	1.25	0.74	1.14	1.7	165	0.26	1.18
4.50	0.88	0.75	0.88	2.0	165	0.25	1.06
5.00	0.58	0.75	0.80	2.0	165	0.25	1.14
6.02	1.17	0.69	0.96	1.6	165	0.31	1.07
7.00	0.58	0.71	0.79	1.9	165	0.29	1.12
8.00	0.52	0.70	0.81	1.8	165	0.30	1.11
10.04	0.49	0.68	0.76	1.9	165	0.32	1.08
20.03	0.66	0.67	0.84	1.6	165	0.33	1.09
49.98	0.59	0.57	0.73	1.8	165	0.43	1.04

Table SI.3d: Parameters retrieved from the global analysis of the monomer and excimer fluorescence decays of 1 g/L Py–HASE in 0.01 M Na_2CO_3 solution at pH 9 using the blob model.

[SDS] mmol/L	f_{Ediff}	τ_{E0} ns	f_{EE0}	τ_D ns	f_{ED}	χ^2
0	0.21	45.4	0.65	108.1	0.14	1.13
0.13	0.17	47.0	0.70	11.7	0.13	1.06
0.21	0.07	50.7	0.82	133.1	0.11	1.11
0.51	0.10	49.9	0.79	130.8	0.11	1.14
1.04	0.11	50.5	0.78	128.9	0.11	1.17
1.25	0.14	49.6	0.76	130.0	0.10	0.97
1.50	0.38	46.5	0.59	140.0	0.03	1.19
1.81	0.52	44.0	0.47	126.0	0.01	1.11
2.05	0.59	46.0	0.40	126.0	0.01	1.11
2.51	0.66	44.7	0.33	126.0	0.01	1.16
3.00	0.74	46.2	0.25	126.0	0.01	1.11
3.85	0.83	48.0	0.18	0	0	1.16
4.01	0.84	47.3	0.15	126.0	0.01	1.11
4.25	0.870	46.3	0.13	0	0	1.18
4.50	0.86	48.7	0.14	0	0	1.06
5.00	0.87	52.5	0.12	126.0	<0.01	1.14
6.02	0.88	47.6	0.12	0	0	1.07
7.00	0.87	52.6	0.13	0	0	1.12
8.00	0.87	58.2	0.13	0	0	1.11
10.04	0.88	56.5	0.12	126.0	<0.01	1.08
20.03	0.90	52.7	0.10	0	0	1.09
49.98	0.89	56.9	0.11	0	0	1.04

Table SI.3e: Parameters retrieved from the global analysis of the monomer and excimer fluorescence decays of 2.5 g/L Py–HASE in 0.01 M Na_2CO_3 solution at pH 9 using the blob model.

[SDS] mmol/L	k_{exch} $\times 10^7$ s^{-1}	f_{Mdiff}	k_{blob} $\times 10^7$ s^{-1}	<n>	τ_M ns	f_{Mfree}	χ^2
5.07	0.30	0.71	0.7	2.8	165	0.29	1.08

Table SI.3f: Parameters retrieved from the global analysis of the monomer and excimer fluorescence decays of 2.5 g/L Py–HASE in 0.01 M Na_2CO_3 solution at pH 9 using the blob model.

[SDS] mmol/L	f_{Ediff}	τ_{E0} ns	f_{EE0}	τ_D ns	f_{ED}	χ^2
5.07	0.80	48.4	0.20	126.0	0.01	1.08

Table SI.3g: Parameters retrieved from the global analysis of the monomer and excimer fluorescence decays of 6 g/L Py–HASE in 0.01 M Na_2CO_3 solution at pH 9 using the blob model.

[SDS] mmol/L	k_{exch} $\times 10^7$ s^{-1}	f_{Mdiff}	k_{blob} $\times 10^7$ s^{-1}	$\langle n \rangle$	τ_M ns	f_{Mfree}	χ^2
5.04	0.64	0.66	1.0	2.7	165	0.34	1.28
7.01	0.35	0.82	0.8	2.5	165	0.18	1.22
9.04	0.77	0.79	0.8	2.1	165	0.21	1.17
10.00	0.88	0.78	0.8	2.0	165	0.22	1.22
20.00	0.97	0.65	0.7	1.8	165	0.35	1.09
50.07	0.49	0.52	0.7	1.7	165	0.48	1.16

Table SI.3h: Parameters retrieved from the global analysis of the monomer and excimer fluorescence decays of 6 g/L Py–HASE in 0.01 M Na_2CO_3 solution at pH 9 using the blob model.

[SDS] mmol/L	f_{Ediff}	τ_{E0} ns	f_{EE0}	τ_D ns	f_{ED}	χ^2
5.04	0.81	44.2	0.19	0	0	1.28
7.01	0.81	47.9	0.19	0	0	1.22
9.04	0.87	47.7	0.13	0	0	1.17
10.00	0.87	48.3	0.13	0	0	1.22
20.00	0.87	53.4	0.13	0	0	1.09
50.07	0.85	59.3	0.15	0	0	1.16

Table SI.3i: Parameters retrieved from the global analysis of the monomer and excimer fluorescence decays of 10 g/L Py–HASE in 0.01 M Na_2CO_3 solution at pH 9 using the blob model.

[SDS] mmol/L	k_{exch} $\times 10^7$ s^{-1}	f_{Mdiff}	k_{blob} $\times 10^7$ s^{-1}	$\langle n \rangle$	τ_M ns	f_{Mfree}	χ^2
0	0.44	0.45	1.70	0.7	165	0.55	1.12
0.10	0.39	0.44	1.30	0.8	165	0.56	1.07
0.24	0.59	0.46	2.45	0.6	165	0.54	1.00
0.51	0.48	0.49	1.80	0.7	165	0.51	1.13
1.00	0.70	0.31	2.75	0.9	165	0.69	1.01
1.25	0.51	0.39	2.90	0.7	165	0.61	1.14
1.50	0.51	0.38	3.80	0.9	165	0.62	1.02
1.75	0.39	0.43	4.30	0.9	165	0.57	1.14
2.00	0.53	0.39	3.00	1.3	165	0.62	1.12
3.00	0.29	0.48	2.70	1.7	165	0.53	1.12
4.03	0.29	0.56	1.50	2.6	165	0.44	1.09
5.00	0.27	0.61	1.40	2.5	165	0.39	1.16
6.00	0.46	0.66	1.10	2.7	165	0.34	1.27
7.08	0.59	0.72	1.00	2.5	165	0.28	1.17
8.14	0.55	0.76	0.90	2.6	165	0.24	1.16
9.00	0.53	0.78	0.90	2.4	165	0.22	1.06
10.00	0.29	0.83	0.80	2.5	165	0.17	1.14
12.42	0.57	0.80	0.80	2.1	165	0.20	1.17
15.00	0.52	0.76	0.80	1.8	165	0.24	1.16
17.52	0.53	0.73	0.70	1.8	165	0.27	1.05
20.00	0.74	0.70	0.70	1.7	165	0.30	1.24
40.00	0.87	0.60	0.90	1.3	165	0.40	1.29

Table SI.3j: Parameters retrieved from the global analysis of the monomer and excimer fluorescence decays of 10 g/L Py–HASE in 0.01 M Na_2CO_3 solution at pH 9 using the blob model.

[SDS] mmol/L	f_{Ediff}	τ_{E0} ns	f_{EE0}	τ_D ns	f_{ED}	χ^2
0	0.23	47.3	0.66	126.0	0.11	1.12
0.10	0.17	47.6	0.73	126.0	0.10	1.07
0.24	0.19	47.9	0.71	126.0	0.10	1.00
0.51	0.27	45.6	0.65	126.0	0.07	1.13
1.00	0.38	43.3	0.56	126.0	0.06	1.01
1.25	0.45	43.7	0.51	126.0	0.04	1.14
1.50	0.45	44.7	0.51	126.0	0.04	1.02
1.75	0.51	45.3	0.47	126.0	0.02	1.14
2.00	0.42	44.4	0.55	126.0	0.03	1.12
3.00	0.66	45.4	0.33	126.0	0.01	1.12
4.03	0.74	48.7	0.25	126.0	0.01	1.09
5.00	0.77	46.0	0.23	0	0	1.16
6.00	0.80	51.6	0.20	0	0	1.27
7.08	0.83	50.2	0.18	0	0	1.17
8.14	0.84	50.0	0.16	0	0	1.16
9.00	0.85	49.6	0.15	0	0	1.06
10.00	0.85	52.6	0.15	0	0	1.14
12.42	0.87	52.2	0.13	0	0	1.17
15.00	0.88	55.4	0.12	0	0	1.16
17.52	0.88	55.2	0.12	0	0	1.05
20.00	0.89	48.7	0.11	0	0	1.24
40.00	0.89	53.3	0.11	0	0	1.29

Table SI.4a: Fractions of all pyrene species determined by the global analysis of the Py–HASE decays as a function of SDS concentration. Three Py–HASE solutions were prepared in 0.01 M Na_2CO_3 at pH 9 with polymer concentrations of 0.1, 1, and 10 g/L.

0.1 g/L				1 g/L				10 g/L			
[SDS] mmol/L	f_{diff}	f_{agg}	f_{free}	[SDS] mmol/L	f_{diff}	f_{agg}	f_{free}	[SDS] mmol/L	f_{diff}	f_{agg}	f_{free}
0	0.10	0.68	0.23	0	0.16	0.61	0.22	0	0.18	0.61	0.22
0.1	0.15	0.54	0.31	0.1	0.14	0.66	0.20	0.1	0.14	0.68	0.18
0.2	0.18	0.54	0.27	0.2	0.06	0.79	0.15	0.2	0.16	0.66	0.19
0.5	0.18	0.50	0.32	0.5	0.08	0.70	0.22	0.5	0.21	0.56	0.22
1.0	0.17	0.44	0.39	1.0	0.09	0.73	0.17	1.0	0.20	0.34	0.46
1.3	0.20	0.37	0.43	1.2	0.11	0.68	0.20	1.2	0.26	0.33	0.41
1.6	0.23	0.34	0.43	1.5	0.23	0.38	0.39	1.5	0.26	0.32	0.42
1.8	0.27	0.26	0.46	1.8	0.26	0.24	0.50	1.7	0.31	0.29	0.40
2.0	0.23	0.22	0.55	2.1	0.30	0.21	0.48	2.0	0.25	0.34	0.40
2.5	0.37	0.21	0.42	2.5	0.35	0.18	0.47	3.0	0.38	0.19	0.42
3.0	0.52	0.13	0.35	3.0	0.43	0.15	0.42	4.0	0.47	0.17	0.37
3.2	0.60	0.11	0.28	3.9	0.59	0.13	0.28	5.0	0.52	0.16	0.33
3.5	0.68	0.10	0.22	4.0	0.63	0.12	0.25	6.0	0.57	0.14	0.29
3.7	0.66	0.10	0.23	4.3	0.67	0.10	0.23	7.1	0.62	0.13	0.24
4.1	0.70	0.09	0.21	4.5	0.66	0.11	0.23	8.1	0.66	0.13	0.21
4.5	0.66	0.09	0.25	5.0	0.67	0.10	0.23	9.0	0.69	0.12	0.19
5.0	0.66	0.09	0.26	6.0	0.64	0.08	0.28	10.0	0.73	0.13	0.15
6.0	0.70	0.09	0.21	7.0	0.64	0.09	0.27	12.4	0.71	0.11	0.18
7.0	0.62	0.08	0.30	8.0	0.63	0.10	0.27	15.0	0.69	0.10	0.22
8.0	0.61	0.08	0.31	10.0	0.62	0.08	0.30	17.5	0.67	0.09	0.24
10.0	0.62	0.09	0.30	20.0	0.62	0.07	0.31	20.0	0.65	0.08	0.27
20.0	0.61	0.08	0.30	50.0	0.53	0.07	0.40	40.0	0.56	0.07	0.37
50.0	0.56	0.06	0.38								
60.0	0.53	0.07	0.40								
70.0	0.53	0.08	0.39								
80.0	0.48	0.08	0.44								
90.0	0.54	0.06	0.40								

Table SI.4b: Fractions of all pyrene species determined by the global analysis of the Py–HASE decays as a function of SDS concentration. Two Py–HASE solutions were prepared in 0.01 M Na_2CO_3 at pH 9 with polymer concentrations of 2.5 and 6 g/L.

2.5 g/L				6 g/L			
[SDS] mmol/L	f_{diff}	f_{agg}	f_{free}	[SDS] mmol/L	f_{diff}	f_{agg}	f_{free}
5.0	0.60	0.16	0.24	5.0	0.57	0.14	0.29
				7.0	0.69	0.16	0.15
				9.0	0.70	0.11	0.19
				10.0	0.70	0.10	0.20
				20.0	0.60	0.09	0.32
				50.0	0.48	0.09	0.44

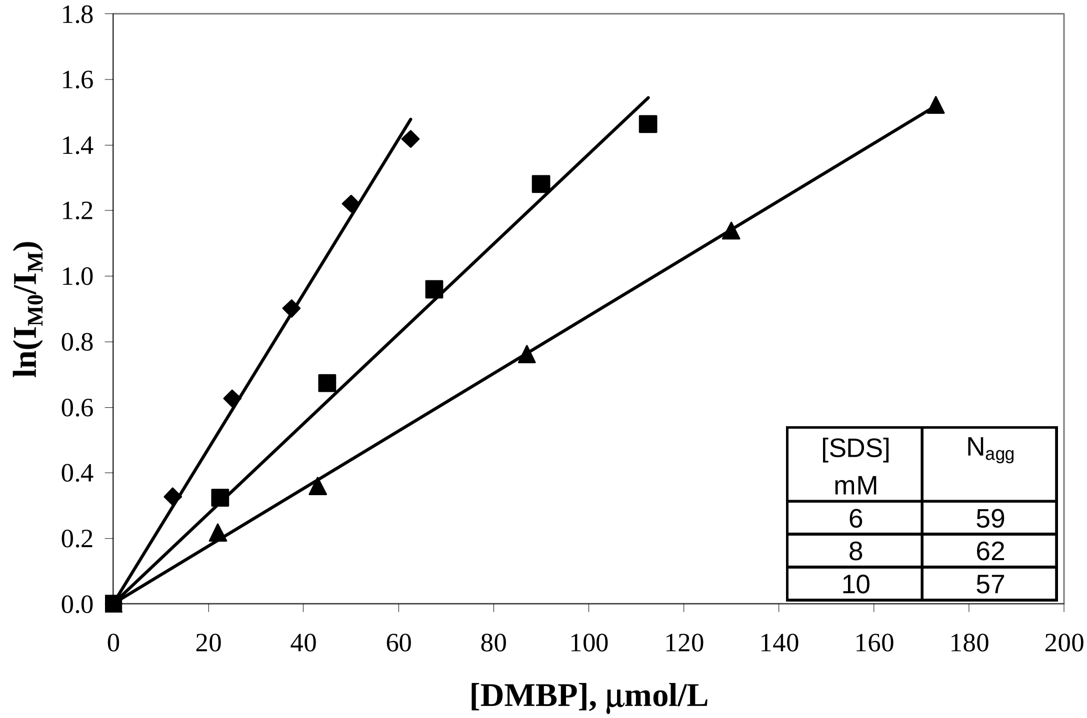

Figure SI.1: Micellar quenching of pyrene by 3,4-dimethylbenzophenone in 6 (◆), 8 (■), and 10 (▲)mM SDS, 0.01 M Na_2CO_3, pH 9 solutions. The pyrene concentration equals 2.5×10^{-6} M. Inset: N_{agg} values determined from slopes.

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