

Probing the Hydrophobic Interactions of a Series of Pyrene End-Labeled Poly(ethylene oxide)s in Aqueous Solution Using Time-Resolved Fluorescence

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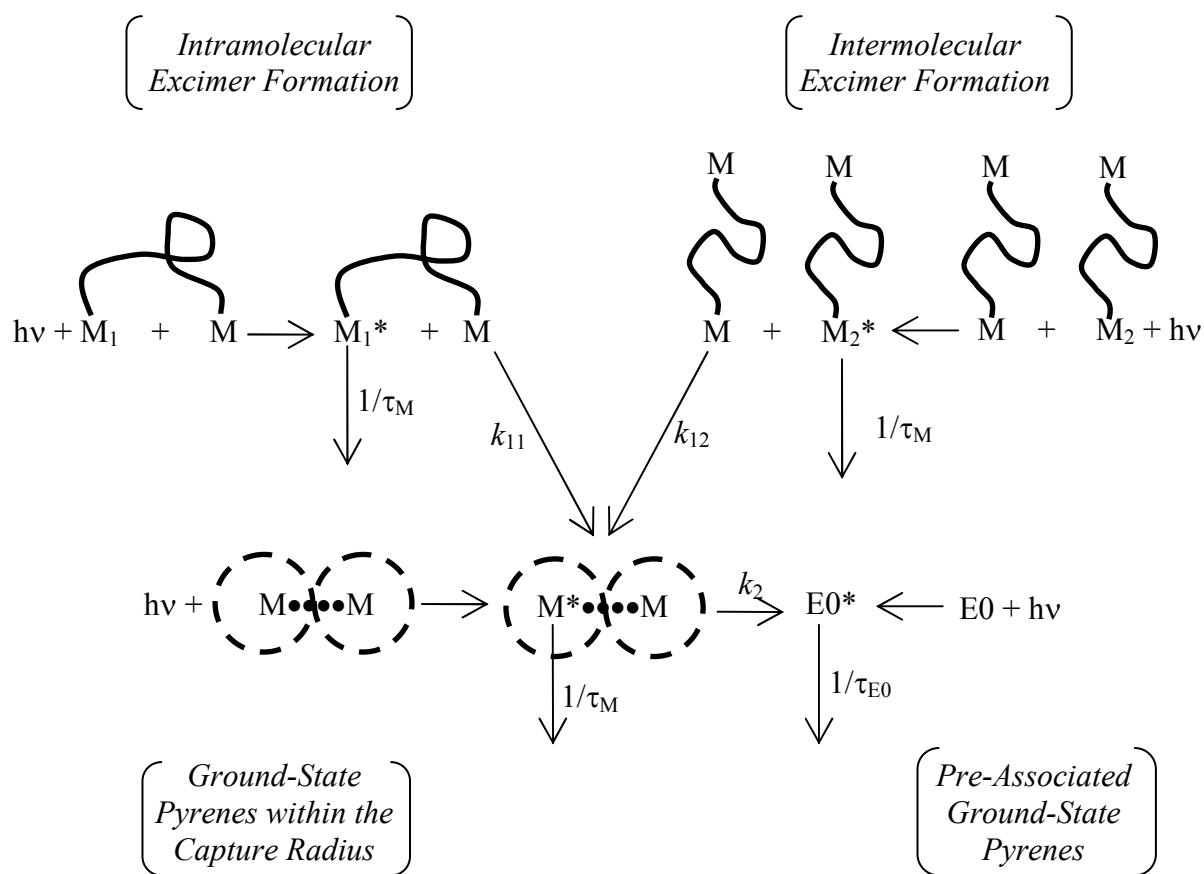
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Analysis of the Fluorescence Decays

The fluorescence decays were analysed by assuming that excimer formation proceeded in a sequential manner as shown in Scheme S1 which is a more elaborate version of Scheme 1 provided in the main text. When far apart, two pyrene monomers M in water are expected to diffuse as freely as the PEO chain to which they are tethered allows. However, if two pyrenes fall within the capture radius defined by the forces generated by their inherent hydrophobicity, they will be drawn toward each other and form excimer with a rate constant k_2 much larger than the rate constant expected from merely diffusive encounters denoted as k_{11} or k_{12} in Scheme S1 depending on whether these encounters occur intra- or intermolecularly, respectively. Within the framework of Scheme S1, k_{11} or k_{12} describe the process by which two freely diffusing pyrene monomers are brought within the capture radius. The dashed circles surrounding the species M represent the capture radius and the dotted line $M\bullet\bullet\bullet M$ separating two pyrenes indicates that these pyrenes are subject to hydrophobic forces.

The information contained in the fluorescence decays of the pyrene monomer and excimer is two folds. First, it provides a snapshot of the contributions of the different pyrene species, namely $[M_1^*]_0$, $[M_2^*]_0$, $[Agg^*]_0$, and $[E0^*]_0$, present in solution at equilibrium. This information is contained in the pre-exponential factors of Equations 5 and 6 in the main text. Second, it yields the rate constants k_{11} , k_{12} , k_2 and the lifetime τ_{E0} that describe how the different pyrene species morph from one form to another. These kinetic parameters are found not only in the decay times of the exponentials used in Equations 5 and 6, but also in the pre-exponential factors. This observation is important because contrary to what is typically done in the literature, our program for the analysis of the fluorescence decays fits the fluorescence decays not only

globally, but most importantly, as a function of the parameters $[M_1^*]_0$, $[M_2^*]_0$, $[Agg^*]_0$, $[E0^*]_0$, k_{11} , k_{12} , k_2 , and τ_{E0} . This refinement has the disadvantage of lengthening substantially the program code, but it also carries the unmatched advantage of providing a set of kinetic parameters that is drawn directly from the fit of the decays, and not questionable mathematical manipulations of the pre-exponential factors and decay times that typically take place after analysis of the fluorescence decays has been completed.



Scheme S1. Pyrene excimer formation occurring sequentially via the formation of an intermediate pyrene aggregate.

The tables provided hereafter list the parameters retrieved from the analysis of the monomer and excimer fluorescence decays based on the pathways depicted in Scheme S1.

Table SI.1: Parameters retrieved from the global SM analysis of the pyrene monomer and excimer fluorescence decays acquired with PEO(*X*)-Py₂ aqueous solution at different *C_P*. τ_M is fixed to 154 ns in the analysis.

(A) PEO(2K)-Py₂

C_P μM	k_{11} $\times 10^7 \text{ s}^{-1}$	k_2 $\times 10^7 \text{ s}^{-1}$	$f_{M1\text{diff}}$	f_{Magg}	f_{Mfree}	τ_{E0} ns	$f_{E1\text{diff}}$	f_{Eagg}	f_{EE0}	χ^2
12.5	1.35	6.7	0.05	0.87	0.08	39	0.01	0.22	0.76	1.12
5.0	1.43	6.7	0.05	0.86	0.09	39	0.01	0.22	0.77	1.14
1.3	1.30	7.0	0.05	0.88	0.08	39	0.01	0.24	0.75	1.11

(B) PEO(5K)-Py₂ ($C_P > C^F$)

C_P μM	k_{11} $\times 10^7 \text{ s}^{-1}$	k_{12} $\times 10^7 \text{ s}^{-1}$	k_2 $\times 10^7 \text{ s}^{-1}$	$f_{M1\text{diff}}$	$f_{M2\text{diff}}$	f_{Magg}	τ_{E0} ns	$f_{E1\text{diff}}$	$f_{E2\text{diff}}$	f_{EE0}	f_{Eagg}	χ^2
220	0.23	0.90	8.7	0.18	0.62	0.20	51	0.08	0.27	0.57	0.08	1.08
165	0.14	0.87	7.5	0.14	0.66	0.20	48	0.07	0.32	0.52	0.10	1.08
92	0.10	0.85	7.2	0.14	0.66	0.20	50	0.07	0.33	0.50	0.10	0.99
73	0.07	0.84	8.5	0.13	0.69	0.18	48	0.07	0.37	0.45	0.11	1.02
46	0.06	0.84	7.3	0.14	0.67	0.19	48	0.08	0.39	0.42	0.11	1.13

(C) PEO(5K)-Py₂ ($C_P < C^F$)

C_P μM	k_{11} $\times 10^7 \text{ s}^{-1}$	k_2 $\times 10^7 \text{ s}^{-1}$	$f_{M1\text{diff}}$	f_{Magg}	f_{Mfree}	τ_{E0} ns	$f_{E1\text{diff}}$	f_{Eagg}	f_{EE0}	χ^2
18	0.83	6.9	0.69	0.21	0.10	46	0.44	0.13	0.42	1.18
9.2	0.84	6.8	0.68	0.21	0.10	48	0.42	0.13	0.45	1.11
3.7	0.83	7.1	0.67	0.22	0.11	49	0.42	0.14	0.44	1.18
1.3	0.83	6.8	0.70	0.20	0.10	48	0.42	0.12	0.45	1.18

(D) PEO(10K)-Py₂

C_P μM	k_{diff} $\times 10^7 \text{ s}^{-1}$	k_2 $\times 10^7 \text{ s}^{-1}$	f_{Mdiff}	f_{Magg}	f_{Mfree}	τ_{E0} ns	f_{Ediff}	f_{Eagg}	f_{EE0}	χ^2
1338	0.90	6.5	0.72	0.28	0.00	54	0.14	0.05	0.81	1.03
621	0.54	7.3	0.88	0.10	0.01	44	0.44	0.05	0.50	1.16
382	0.35	7.2	0.88	0.11	0.01	43	0.53	0.06	0.40	1.11
191	0.26	7.8	0.87	0.07	0.05	45	0.71	0.06	0.23	1.20
96	0.19	6.6	0.86	0.05	0.09	46	0.78	0.05	0.18	1.29
67	0.17	7.6	0.85	0.04	0.11	46	0.82	0.04	0.14	1.18
48	0.15	7.8	0.90	0.04	0.06	45	0.81	0.03	0.16	1.17
24	0.15	7.8	0.80	0.03	0.16	45	0.85	0.03	0.12	1.11
9.6	0.13	6.8	0.84	0.03	0.13	46	0.85	0.03	0.11	1.07
4.8	0.13	6.7	0.82	0.03	0.14	48	0.85	0.03	0.11	1.04
1.3	0.13	7.5	0.85	0.03	0.12	47	0.85	0.03	0.11	1.08

(E) PEO(16.5K)-Py₂

C_P μM	k_{diff} $\times 10^7 \text{ s}^{-1}$	k_2 $\times 10^7 \text{ s}^{-1}$	f_{Mdiff}	f_{Magg}	f_{Mfree}	τ_{E0} ns	f_{Ediff}	f_{Eagg}	f_{EE0}	χ^2
1000	0.47	6.5	0.87	0.10	0.02	45	0.51	0.06	0.44	1.05
500	0.30	7.8	0.87	0.08	0.04	44	0.60	0.06	0.34	1.06
300	0.22	7.5	0.85	0.06	0.09	48	0.73	0.05	0.22	1.12
100	0.14	7.4	0.90	0.03	0.07	45	0.82	0.02	0.15	1.12
80	0.10	7.9	0.96	0.02	0.01	47	0.85	0.02	0.13	1.14

Table SI.2: Molar fractions obtained from the global SM analysis of the pyrene monomer and excimer fluorescence decays acquired with PEO(*X*)-Py₂ aqueous solution at different C_P . τ_M is fixed to 154 ns in the analysis.

(A) PEO(2K)-Py₂ ($f_{\text{diff}2} = 0$)

C_P μM	$f_{\text{diff}1}$	f_{agg}	f_{E0}	f_{free}	f_{diff}^{SM}	f_{agg}^{SM}	f_{free}^{SM}
12.5	0.01	0.22	0.75	0.02	0.01	0.97	0.02
5.0	0.01	0.21	0.75	0.02	0.01	0.96	0.02
1.3	0.01	0.24	0.73	0.02	0.01	0.97	0.02

(B) PEO(5K)-Py₂ ($C_P > C^F$, $f_{\text{free}} = 0$)

C_P μM	$f_{\text{diff}1}$	$f_{\text{diff}2}$	f_{agg}	f_{E0}	f_{diff}^{SM}	f_{agg}^{SM}	f_{free}^{SM}
220	0.08	0.27	0.08	0.57	0.35	0.65	0.00
165	0.07	0.32	0.10	0.52	0.39	0.62	0.00
92	0.07	0.33	0.10	0.50	0.40	0.60	0.00
73	0.07	0.37	0.11	0.45	0.44	0.56	0.00
46	0.08	0.39	0.11	0.42	0.48	0.53	0.00

(C) PEO(5K)-Py₂ ($C_P < C^F$, $f_{\text{diff}2} = 0$)

C_P μM	$f_{\text{diff}1}$	f_{agg}	f_{E0}	f_{free}	f_{diff}^{SM}	f_{agg}^{SM}	f_{free}^{SM}
18	0.41	0.13	0.40	0.06	0.41	0.53	0.06
9.2	0.39	0.12	0.42	0.06	0.39	0.54	0.06
3.7	0.40	0.13	0.41	0.06	0.40	0.54	0.06
1.3	0.40	0.12	0.43	0.06	0.40	0.54	0.06

(D) PEO(10K)-Py₂

C_P μM	f_{diff}	f_{agg}	f_{E0}	f_{free}	f_{diff}^{SM}	f_{agg}^{SM}	f_{free}^{SM}
1338	0.14	0.05	0.81	0.00	0.14	0.86	0.00
621	0.44	0.05	0.50	0.01	0.44	0.55	0.01
382	0.53	0.06	0.40	0.01	0.53	0.46	0.01
191	0.68	0.06	0.22	0.04	0.68	0.27	0.04
96	0.71	0.04	0.16	0.08	0.71	0.20	0.08
67	0.74	0.04	0.13	0.09	0.74	0.16	0.09
48	0.76	0.03	0.15	0.05	0.76	0.18	0.05
24	0.72	0.03	0.10	0.15	0.72	0.13	0.15
9.6	0.76	0.03	0.10	0.12	0.76	0.13	0.12
4.8	0.74	0.03	0.10	0.13	0.74	0.13	0.13
1.3	0.76	0.03	0.10	0.11	0.76	0.13	0.11

(E) PEO(16.5K)-Py₂

C_P μM	f_{diff}	f_{agg}	f_{E0}	f_{free}	f_{diff}^{SM}	f_{agg}^{SM}	f_{free}^{SM}
1000	0.50	0.06	0.44	0.01	0.50	0.49	0.01
500	0.59	0.06	0.33	0.02	0.59	0.39	0.02
300	0.68	0.04	0.20	0.07	0.68	0.25	0.07
100	0.77	0.02	0.14	0.06	0.77	0.16	0.06
80	0.84	0.02	0.13	0.01	0.84	0.14	0.01