

Electronic Supplementary Information:

Properties and Evolution of Emission in Molecular Aggregates of a Perylene Ammonium Derivative in Polymer Matrices

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1. Dimer formation in aqueous solution.

The equilibrium between the monomer and the dimer is represented by the following equation as indicated in the main text.

$$K = \frac{\frac{1}{2}x}{(M_0 - x)(M_0 - x)} \quad (1).$$

Solving Eq.1 for x ,

$$x = \frac{\left(2M_0K + \frac{1}{2}\right) \pm \sqrt{\left(2M_0K + \frac{1}{2}\right)^2 - 4M_0^2K^2}}{2K} \quad (2).$$

Fig. S1 shows the K value dependence of the dimer concentration as a function of concentration.

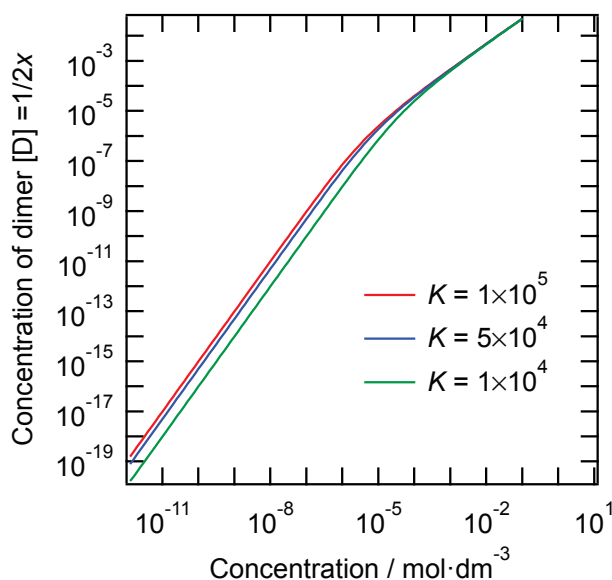


Fig. S1 The dimer concentration as a function of concentration estimated by the monomer-dimer equilibrium of Eq.1 with $K = 1 \times 10^4$, 5×10^4 and $1 \times 10^5 \text{ M}^{-1}$.

2. Fluorescence excitation spectrum of PeryAm in aqueous solution.

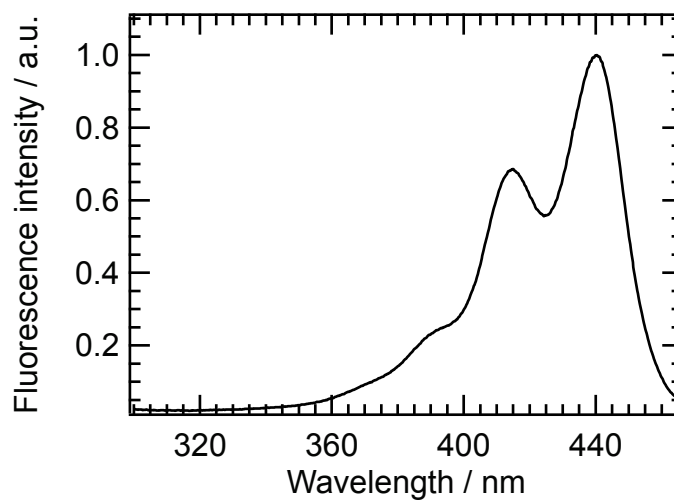


Fig. S2 Fluorescence excitation spectrum of $1 \times 10^{-6} \text{ mol} \cdot \text{dm}^{-3}$ PeryAm in aqueous solution. Fluorescence at 470 nm was monitored.

3. Fluorescence anisotropy spectra of PeryAm in PVA films.

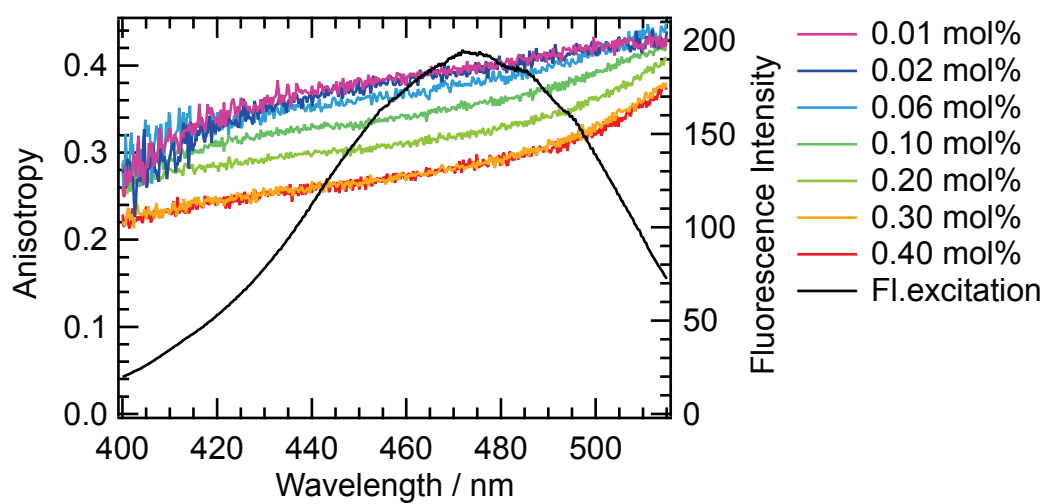


Fig. S3 Fluorescence excitation anisotropy spectra of PeryAm in PVA films. Fluorescence at 530 nm was monitored.

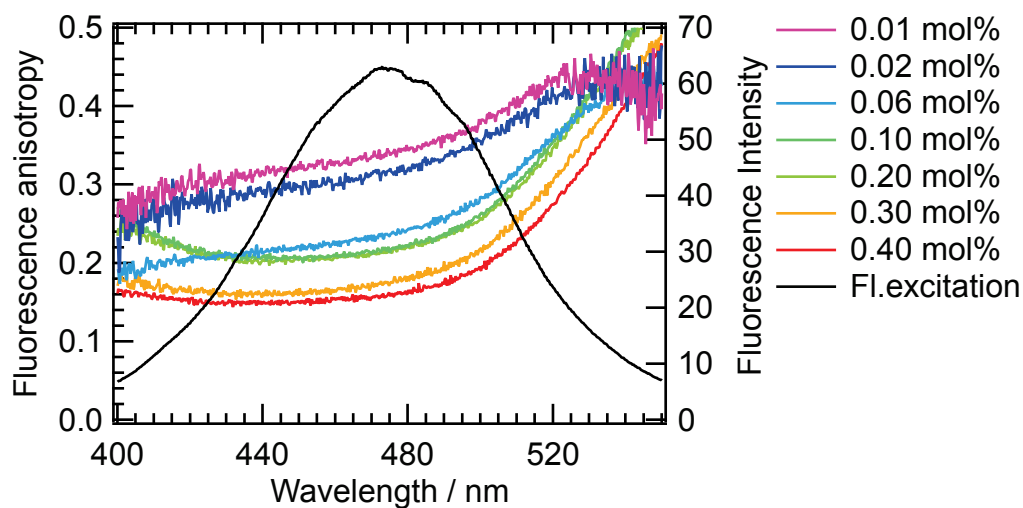


Fig. S4 Fluorescence excitation anisotropy spectra of PeryAm in PVA films.
Fluorescence at 650 nm was monitored.

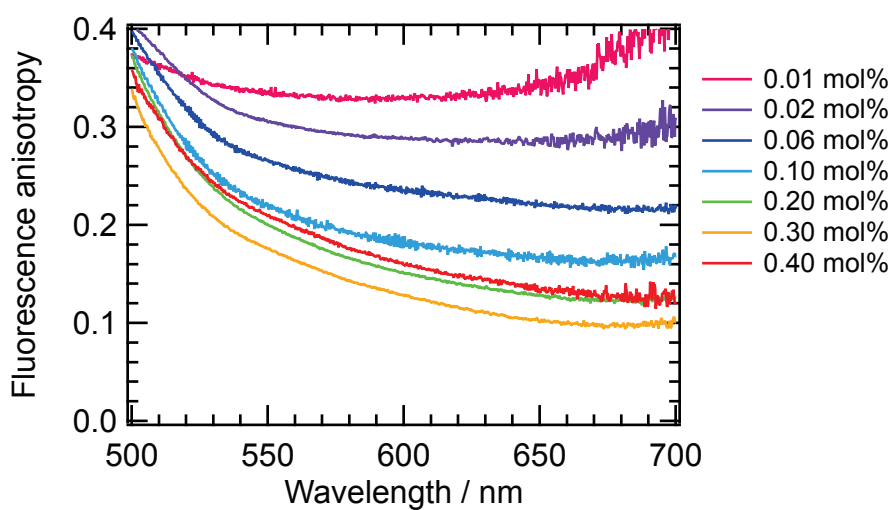


Fig. S5 Fluorescence anisotropy spectra of PeryAm in PVA films excited at 450 nm.

4. Fluorescence time profiles of PeryAm in PVA films.

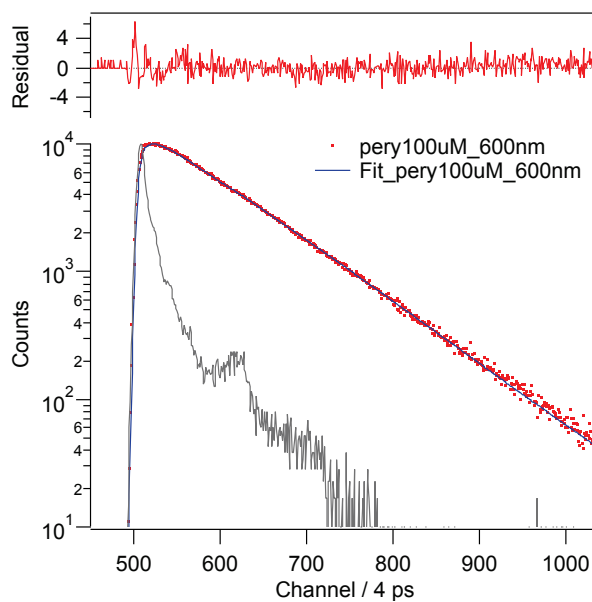


Fig. S6 Fluorescence time profile of $1 \times 10^{-4} \text{ mol} \cdot \text{dm}^{-3}$ PeryAm in aqueous solution monitored at 600 nm.

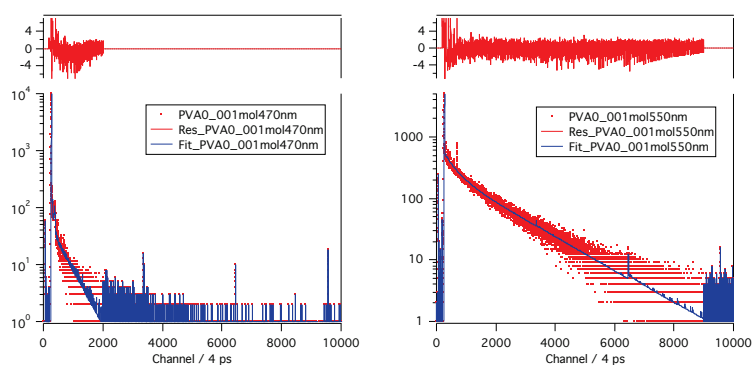


Fig. S7 Fluorescence time profile of 0.001 mol% PeryAm in PVA film.

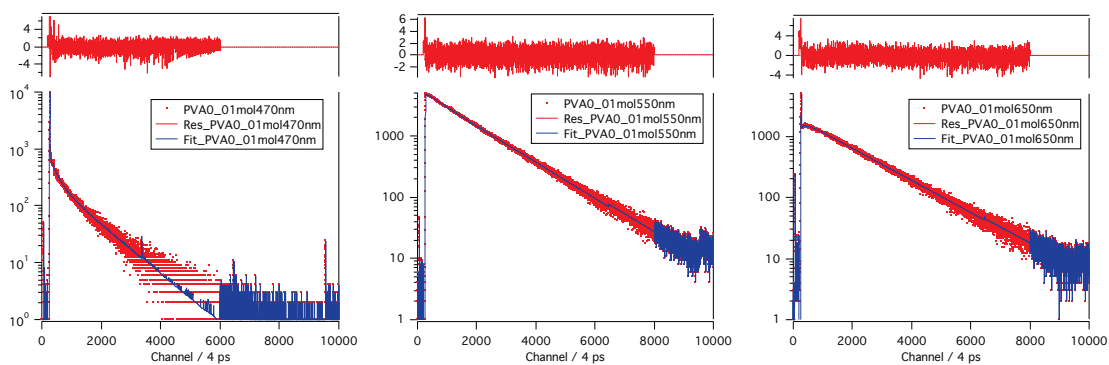


Fig. S8 Fluorescence time profiles of 0.01 mol% PeryAm in PVA film.

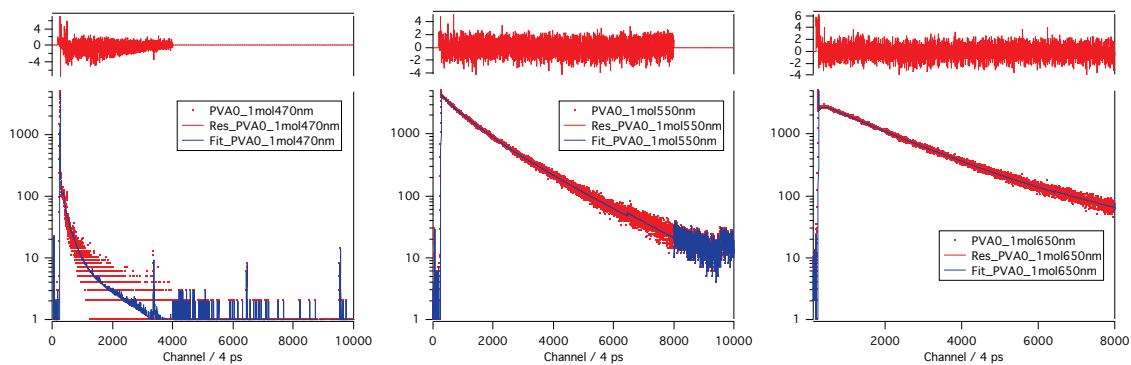


Fig. S9 Fluorescence time profiles of 0.1 mol% PeryAm in PVA film.

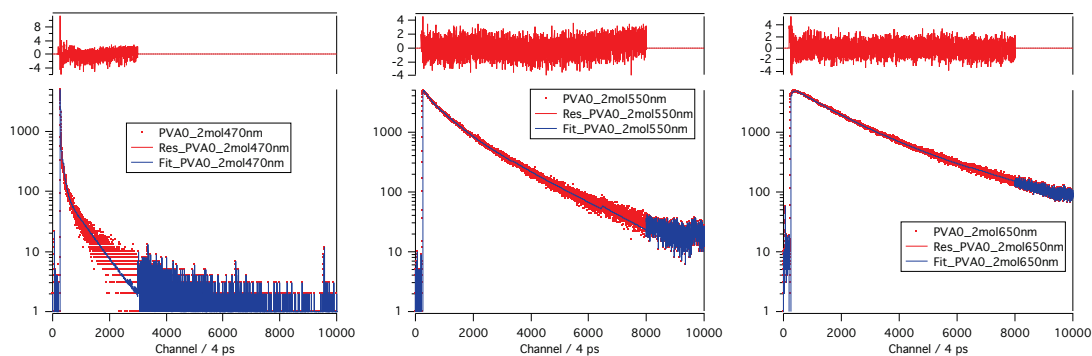


Fig. S10 Fluorescence time profiles of 0.2 mol% PeryAm in PVA film.

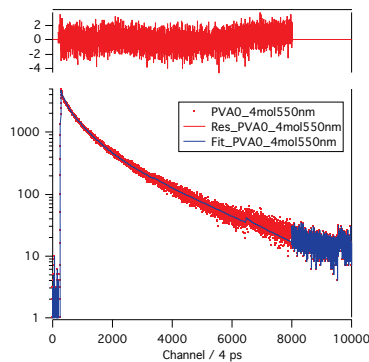


Fig. S11 Fluorescence time profile observed at 550 nm of 0.4 mol% PeryAm in PVA film.

Table S1 Fluorescence lifetime of PeryAm in PVA flims observed at 470 nm.

C / mol%	$\tau_1/\text{ns}(A_1)$	$\tau_2/\text{ns}(A_2)$	$\tau_3/\text{ns}(A_3)$	$\tau_{\text{ave}}/\text{ns}$
0.001	0.009 (0.991)	1.80 (0.001)		0.010
0.01	0.012 (0.980)	0.95 (0.011)	3.86 (0.008)	0.053
0.10	0.016 (0.992)	0.84 (0.007)	5.15 (0.001)	0.025
0.20	0.016 (0.950)	0.34 (0.040)	2.63 (0.006)	0.045
0.40	0.009 (0.991)	0.45 (0.007)	3.49 (0.001)	0.021

Table S2 Fluorescence lifetime of PeryAm in PVA flims observed at 550 nm.

C / mol%	$\tau_1/\text{ns}(A_1)$	$\tau_2/\text{ns}(A_2)$	$\tau_3/\text{ns}(A_3)$	$\tau_4/\text{ns}(A_4)$	$\tau_{\text{ave}}/\text{ns}$
0.001	0.013 (0.97)	1.50 (0.017)	6.17 (0.016)		0.14
0.01	0.014 (0.39)	5.81 (0.570)	2.45 (0.045)		3.41
0.10	0.015 (0.47)	0.61 (0.078)	3.44 (0.277)	6.91 (0.178)	2.21
0.20	0.477 (0.19)	2.70 (0.513)	7.01 (0.300)		3.57
0.40	0.088 (0.18)	2.58 (0.452)	0.61 (0.290)	8.33 (0.114)	2.23

Table S3 Fluorescence lifetime of PeryAm in PVA flims observed at 650 nm.

C / mol%	$\tau_1/\text{ns}(A_1)$	$\tau_2/\text{ns}(A_2)$	$\tau_3/\text{ns}(A_3)$	$\tau_4/\text{ns}(A_4)$	$\tau_{\text{ave}}/\text{ns}$
0.001			N.D.		
0.01	0.75 (-0.02)	0.01 (0.880)	6.51 (0.09)		0.61
0.10	0.38 (-0.04)	0.01 (0.750)	6.11 (0.19)	19.04 (0.01)	7.00
0.20	0.30 (-0.15)	5.30 (0.680)	13.90 (0.19)		7.15
0.40	0.01 (-0.002)	3.90 (0.600)	13.43 (0.40)		7.71

The τ_{ave} is estimated only used τ -values with positive pre-exponential factor.

5. Fluorescence microscope image of PeryAm in PVA films before and after UV irradiation.

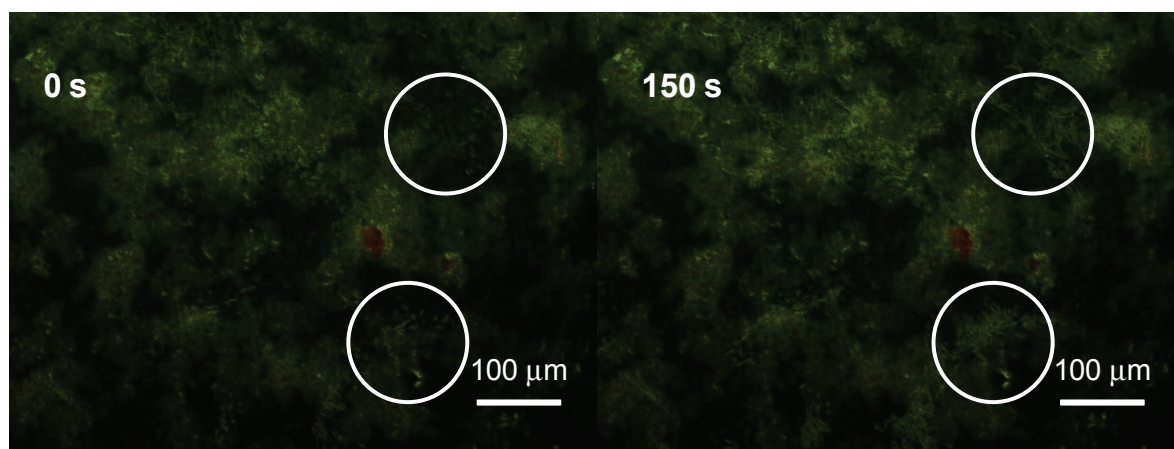


Fig. S12 Fluorescence microscope image observed WIB filter (excitation: 460-490 nm, monitor: over 560 nm) of 0.4 mol% PeryAm in PVA film before and after the irradiation by the WU filter (excitation: 330-385 nm, monitor: over 420 nm).