

## Supporting Information for

# Probing the Closed Association of Oligoquinoline Foldamers by Time-Resolved Fluorescence Anisotropy

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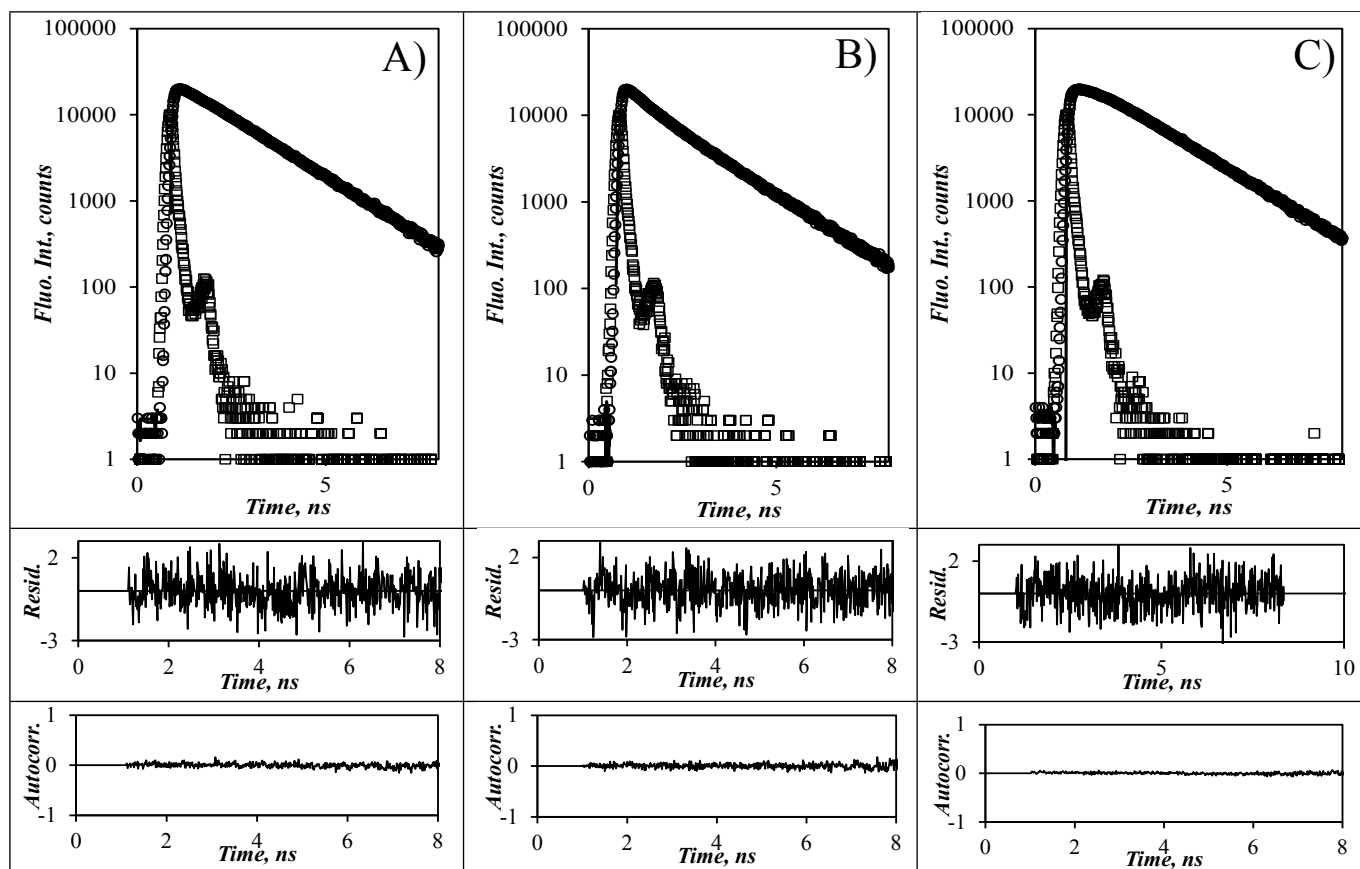
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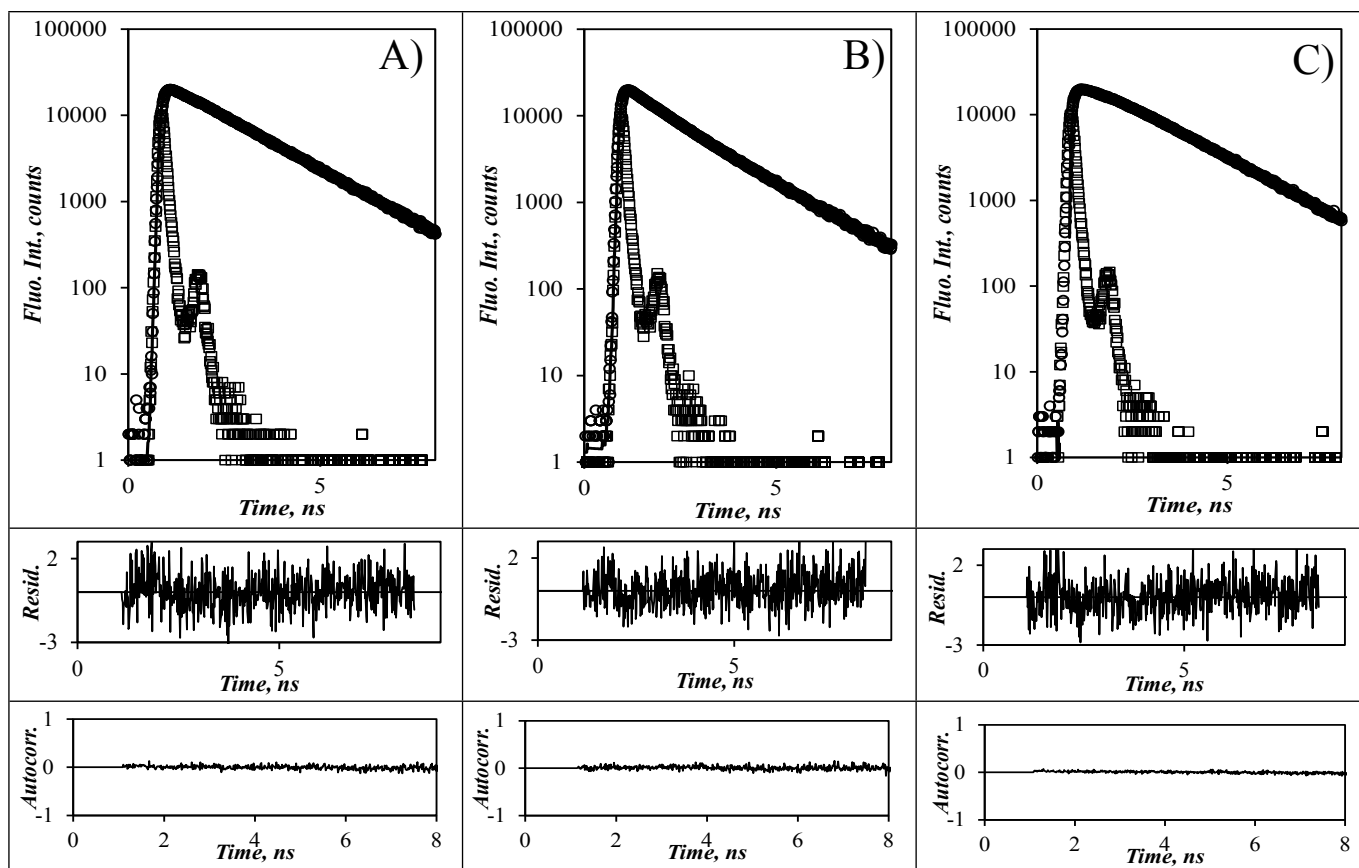
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## A) Fluorescence decays used in the TRFA experiments

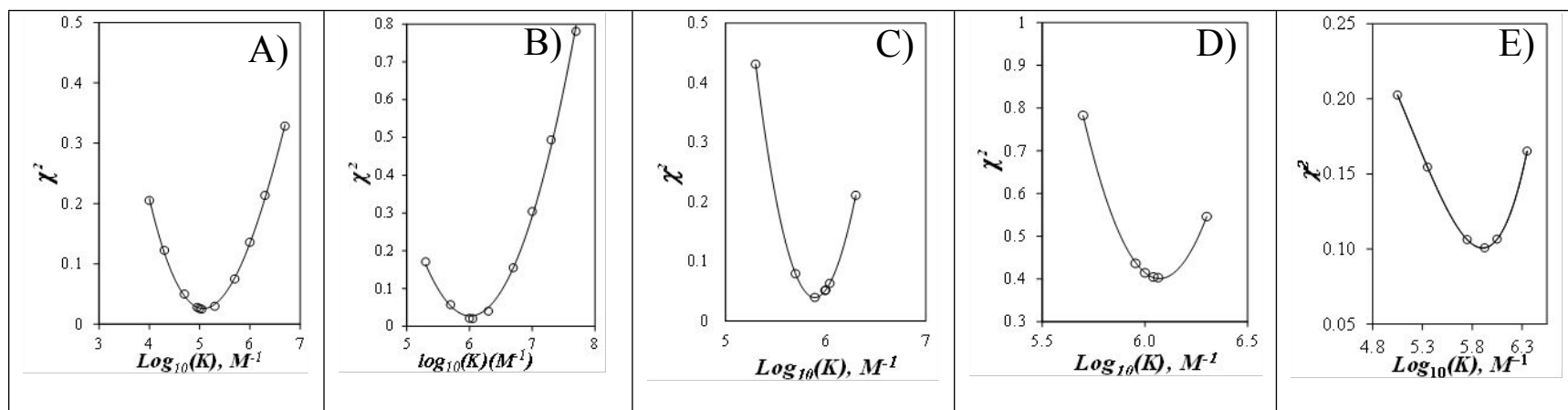


**Figure S1.** Fluorescence decays for OPV-labeled octamer in chloroform (with residuals and autocorrelation of the residuals) acquired with vertically polarized light at 479 nm and with the emission at 510 nm obtained with the emission polarizer placed A) at the magic angle ( $I_{VM}(t)$ ), B) vertically ( $I_{VV}(t)$ ), and C) horizontally ( $I_{VH}(t)$ ).



**Figure S2.** Fluorescence decays for OPV-labeled octamer in chloroform after the addition of 0.1 mL of 16 M NaOH aqueous solution (with residuals and autocorrelation of the residuals) acquired with vertically polarized light at 479 nm and with the emission at 510 nm obtained with the emission polarizer placed A) at the magic angle ( $I_{VM}(t)$ ), B) vertically ( $I_{VV}(t)$ ), and C) horizontally ( $I_{VH}(t)$ ).

## B) Determination of the equilibrium constants for the complexation of the oligoquinoline foldamers



**Figure S3.** Plots of  $\chi^2$  as a function of  $\log_{10}(K)$  for the dimerization of A) OPV-Q<sub>4</sub>A, B) OPV-Q<sub>8</sub>A, C) OPV-Q<sub>17</sub>A, and D) OPV-Q<sub>33</sub>A, and E) the complexation of OPV-Q<sub>8</sub>A with Q<sub>33</sub>A. The  $\chi^2$ -vs.- $\log_{10}(K)$  plots were fitted with third order polynomials yielding  $K_n$  values of  $1.1 (\pm 0.1) \times 10^5 M^{-1}$ ,  $1.1 (\pm 0.2) \times 10^6 M^{-1}$ ,  $7.8 (\pm 0.4) \times 10^5 M^{-1}$ , and  $1.10 (\pm 0.03) \times 10^6 M^{-1}$  and a  $K_c (=K_p)$  value of  $7.5 (\pm 0.1) \times 10^5 M^{-1}$  at their minimum, respectively.

**C] Parameters retrieved from the fluorescence decay analysis**

**Table S1.** Parameters obtained from the global analysis of  $I_{VV}(t)$  and  $I_{VH}(t)$  for the protonated OPV-Q<sub>4</sub>A samples in chloroform.

Concentration ( $\mu\text{M}$ )	mexpscatbg		aniso01d-extension				G-factor	extension
	$\tau_o$ (ns)	$\chi^2$	$\tau_o$ (ns)	$r_o$	$\phi$ (ns)	$\chi^2$		
0.10	1.71	1.05	1.71	0.378	0.59	0.99	0.46	7k
0.76	1.71	1.03	1.71	0.391	0.59	1.00	0.46	7k
2.51	1.71	1.05	1.71	0.388	0.59	1.02	0.46	4k
5.60	1.70	1.04	1.70	0.387	0.58	1.06	0.46	4k
40.6	1.71	1.01	1.71	0.386	0.58	1.13	0.46	4k
681	1.83	1.04	1.85	0.310	0.60	1.15	0.54	4k

**Table S2.** Parameters obtained from the global analysis of  $I_{VV}(t)$  and  $I_{VH}(t)$  for the OPV-Q<sub>4</sub>A samples in chloroform after addition of 0.1 mL of 16 M NaOH aqueous solution.

Concentration ( $\mu\text{M}$ )	mexpscatbg		aniso01d-extension				G-factor	extension
	$\tau_o$ (ns)	$\chi^2$	$\tau_o$ (ns)	$r_o$	$\phi$ (ns)	$\chi^2$		
0.3	1.71	1.08	1.72	0.377	0.57	1.01	0.47	4k
0.7	1.72	1.11	1.72	0.397	0.58	1.01	0.47	4k
1.3	1.72	1.09	1.72	0.392	0.58	0.99	0.47	4k
2.8	1.72	1.03	1.72	0.384	0.60	1.00	0.47	4k
6.3	1.70	1.13	1.70	0.294	0.73	1.15	0.51	7k
33	1.72	1.02	1.72	0.248	0.86	1.05	0.55	7k
170	1.77	1.09	1.78	0.187	0.94	0.99	0.63	4k
313	1.81	1.09	1.83	0.166	0.99	1.10	0.66	4k
532	1.83	0.99	1.85	0.171	0.97	1.10	0.65	4k
681	1.84	1.06	1.85	0.179	0.98	1.01	0.64	4k

**Table S3.** Parameters obtained from the global analysis of  $I_{VV}(t)$  and  $I_{VH}(t)$  for the protonated OPV-Q<sub>8</sub>A samples in chloroform.

	mexpscatbg		aniso01d-extension					
Concentration (μM)	$\tau_o$ (ns)	$\chi^2$	$\tau_o$ (ns)	$r_o$	$\phi$ (ns)	$\chi^2$	G-factor	extension
0.041	1.60	1.04	1.60	0.398	0.82	1.16	0.44	7k
0.184	1.57	1.07	1.57	0.335	0.76	1.03	0.51	7k
1.12	1.57	1.16	1.57	0.325	0.77	1.07	0.50	7k
4.99	1.59	1.02	1.59	0.374	0.78	1.08	0.45	7k
52.7	1.60	1.04	1.60	0.391	0.77	0.99	0.45	7k
296	1.66	1.11	1.66	0.307	0.80	1.04	0.51	4k

**Table S4.** Parameters obtained from the global analysis of  $I_{VV}(t)$  and  $I_{VH}(t)$  for the OPV-Q<sub>8</sub>A samples in chloroform after addition of 0.1 mL of 16 M NaOH aqueous solution.

	mexpscatbg		aniso01d-extension					
Concentration (μM)	$\tau_o$ (ns)	$\chi^2$	$\tau_o$ (ns)	$r_o$	$\phi$ (ns)	$\chi^2$	G-factor	extension
0.013	1.61	1.14	1.61	0.376	0.77	1.16	0.42	7k
0.046	1.60	1.07	1.60	0.328	0.77	1.12	0.49	7k
0.077	1.60	1.06	1.60	0.315	0.83	1.20	0.49	7k
0.2378	1.59	1.05	1.59	0.384	0.90	1.07	0.42	7k
0.458	1.59	1.19	1.59	0.327	1.01	1.21	0.43	7k
0.558	1.60	1.06	1.60	0.363	1.02	1.03	0.43	7k
1.12	1.59	1.15	1.59	0.292	1.08	1.26	0.50	7k
4.74	1.58	1.08	1.58	0.355	1.16	1.08	0.42	7k
62.3	1.61	1.04	1.61	0.350	1.30	1.09	0.42	4k
101	1.63	1.12	1.63	0.300	1.37	1.18	0.47	7k

**Table S5.** Parameters obtained from the global analysis of  $I_{VV}(t)$  and  $I_{VH}(t)$  for the protonated OPV-Q<sub>17</sub>A samples in chloroform.

Concentration ( $\mu\text{M}$ )	mexpscatbg		aniso01d-extension				G-factor	extension
	$\tau_o$ (ns)	$\chi^2$	$\tau_o$ (ns)	$r_o$	$\phi$ (ns)	$\chi^2$		
0.035	1.57	1.07	1.58	0.367	1.30	0.99	0.41	7k
0.186	1.57	1.06	1.57	0.369	1.28	1.08	0.41	7k
1.54	1.57	0.98	1.57	0.366	1.28	1.06	0.41	4k
6.80	1.58	0.99	1.57	0.361	1.28	1.07	0.41	4k
70.3	1.60	1.09	1.63	0.277	1.30	1.08	0.50	4k
379	1.70	1.02	1.71	0.281	1.30	1.12	0.49	4k

**Table S6.** Parameters obtained from the global analysis of  $I_{VV}(t)$  and  $I_{VH}(t)$  for the OPV-Q<sub>17</sub>A samples in chloroform after addition of 0.1 mL of 16 M NaOH aqueous solution.

Concentration ( $\mu\text{M}$ )	mexpscatbg		aniso01d-extension				G-factor	extension
	$\tau_o$ (ns)	$\chi^2$	$\tau_o$ (ns)	$r_o$	$\phi$ (ns)	$\chi^2$		
0.035	1.59	1.08	1.59	0.373	1.26	1.02	0.41	4k
0.057	1.60	1.05	1.59	0.365	1.28	0.99	0.42	4k
0.088	1.58	1.07	1.58	0.368	1.31	1.05	0.43	7k
0.185	1.58	1.02	1.58	0.359	1.38	1.05	0.38	7k
0.373	1.58	1.06	1.58	0.339	1.51	1.06	0.41	7k
1.65	1.58	1.05	1.58	0.322	1.77	1.05	0.44	7k
3.19	1.57	1.10	1.57	0.321	1.95	1.10	0.44	7k
8.70	1.58	0.96	1.58	0.323	2.09	1.10	0.42	7k
17.5	1.59	1.15	1.59	0.326	2.20	1.08	0.42	7k
36.9	1.60	0.99	1.60	0.318	2.30	1.07	0.41	7k
69.2	1.59	1.06	1.63	0.241	2.41	1.03	0.52	4k
97.4	1.60	1.10	1.65	0.244	2.51	1.07	0.53	4k
137	1.63	1.07	1.67	0.245	2.51	1.16	0.51	4k
314	1.66	1.00	1.69	0.252	2.45	1.08	0.51	4k



**Table S7.** Parameters obtained from the global analysis of  $I_{VV}(t)$  and  $I_{VH}(t)$  for the OPV-Q<sub>33</sub>A samples in chloroform.

	mexpscatbg		aniso01d-extension					
Concentration ( $\mu$ M)	$\tau_o$ (ns)	$\chi^2$	$\tau_o$ (ns)	$r_o$	$\phi$ (ns)	$\chi^2$	G-factor	extension
0.053	1.59	0.98	1.59	0.323	2.33	1.03	0.43	7k
0.810	1.59	1.05	1.59	0.325	2.08	1.09	0.43	7k
11.3	1.58	1.05	1.58	0.332	2.27	1.09	0.43	7k
190	1.61	1.05	1.64	0.245	2.10	1.10	0.52	7k

**Table S8.** Parameters obtained from the global analysis of  $I_{VV}(t)$  and  $I_{VH}(t)$  without  $r_\infty$  for the OPV-Q<sub>33</sub>A samples in chloroform after addition of 0.1 mL of 16 M NaOH aqueous solution.

	mexpscatbg		aniso0X-ext								
Conc. ( $\mu$ M)	$\tau_o$ (ns)	$\chi^2$	$\tau_o$ (ns)	$r_{o1}$	$\phi_1$ (ns)	$r_{o2}$	$\phi_2$ (ns)	$\langle\phi\rangle$ (ns)	G-factor	$\chi^2$	X-ext.
0.025	1.59	0.96	1.59	0.316	2.26	0.000	0.00	2.26	0.42	0.99	1d-7k
0.053	1.61	1.00	1.61	0.318	2.31	0.000	0.00	2.31	0.43	1.02	1d-7k
0.446	1.61	1.09	1.61	0.287	3.18	0.070	0.79	2.71	0.42	1.06	2d-3k
2.07	1.61	0.99	1.61	0.265	3.77	0.065	0.50	3.12	0.42	1.03	2d-3k
5.49	1.59	1.00	1.59	0.283	4.31	0.087	0.81	3.49	0.38	1.12	2d-3k
11.0	1.59	1.12	1.59	0.270	5.51	0.112	0.74	4.12	0.34	1.10	2d-3k
33.0	1.61	0.97	1.61	0.216	5.15	0.069	0.65	4.06	0.46	1.01	2d-3k

**Table S9.** Parameters obtained from the global analysis of  $I_{VV}(t)$  and  $I_{VH}(t)$  with  $r_\infty$  for the OPV-Q<sub>33</sub>A samples in chloroform after addition of 0.1 mL of 16 M NaOH aqueous solution.

Concentration ( $\mu\text{M}$ )	bexpscatbg					aniso02d-4k									
	$\tau_{o1}$ (ns)	$a_1$	$\tau_{o2}$ (ns)	$a_2$	$\chi^2$	$\tau_o$ (ns)	$\phi_1$ (ns)	$r_1$	$\phi_2$ (ns)	$r_2$	$r_\infty$	$\phi_{total}$ (ns)	$r_o$	$G$ <i>factor</i>	$\chi^2$
61.1	1.47	0.58	1.76	0.42	1.04	1.60	5.77	0.192	0.72	0.071	0.005	4.40	0.27	0.49	1.08
79.6	1.16	0.15	1.65	0.85	0.941	1.61	5.80	0.207	0.61	0.070	0.074	4.49	0.35	0.39	1.05
262	1.63	0.77	1.80	0.23	1.01	1.67	5.06	0.197	0.87	0.033	0.170	4.46	0.40	0.33	1.13

**Table S10.** Parameters obtained from  $I_{VM}(t)$  with in1xpscatbg and the global analysis of  $I_{VV}(t)$  and  $I_{VH}(t)$  with iniso01d7k for OPV-Q<sub>8</sub>A and Q<sub>16</sub>A sample mixtures in chloroform.

Concentrations ( $\mu\text{M}$ )			mexpscatbg		aniso01d-extension					
[acid] ( $\mu\text{M}$ )	[OQ <sub>8</sub> A] ( $\mu\text{M}$ )	[Q <sub>16</sub> A] ( $\mu\text{M}$ )	$\tau_o$ (ns)	$\chi^2$	$\tau_o$ (ns)	$r_o$	$\phi$ (ns)	$\chi^2$	G-factor	ext.
0.087	0.012	0.075	1.59	1.16	1.59	0.339	0.77	1.19	0.50	7k
1.32	0.196	1.12	1.59	1.00	1.59	0.382	0.78	1.04	0.44	7k
12.6	1.90	10.7	1.59	0.93	1.59	0.373	0.80	0.98	0.43	7k
516	434	82.2	1.61	1.13	1.63	0.311	0.82	1.05	0.49	4k

**Table S11.** Parameters obtained from the global analysis of  $I_{VV}(t)$  and  $I_{VH}(t)$  for the OPV-Q<sub>8</sub>A and Q<sub>16</sub>A samples in chloroform after addition of 0.1 mL of 16 M NaOH aqueous solution.

Concentrations ( $\mu\text{M}$ )			mexpscatbg		aniso01d-extension					
[acid] ( $\mu\text{M}$ )	[OQ <sub>8</sub> A] ( $\mu\text{M}$ )	[Q <sub>16</sub> A] ( $\mu\text{M}$ )	$\tau_o$ (ns)	$\chi^2$	$\tau_o$ (ns)	$r_o$	$\phi$ (ns)	$\chi^2$	G-factor	ext.
0.040	0.0046	0.0311	1.62	1.13	1.62	0.398	0.83	1.11	0.42	7k
0.100	0.0127	0.0855	1.62	1.06	1.62	0.369	0.84	1.13	0.44	7k
0.140	0.0182	0.122	1.61	1.09	1.61	0.384	0.81	1.08	0.44	7k
0.230	0.0330	0.195	1.60	1.07	1.60	0.367	0.85	1.21	0.43	4k
0.650	0.0975	0.554	1.60	1.03	1.60	0.348	1.02	1.02	0.44	7k
1.32	0.196	1.12	1.61	1.17	1.61	0.341	1.09	1.19	0.44	7k
4.24	0.636	3.60	1.60	1.15	1.60	0.338	1.18	1.18	0.43	7k
46.9	7.70	39.2	1.60	1.09	1.62	0.270	1.33	1.07	0.47	4k
82.5	13.7	68.8	1.59	1.22	1.62	0.278	1.46	0.97	0.49	4k
160	27.2	133	1.58	1.10	1.62	0.275	1.67	1.05	0.43	4k
558	96.9	461	1.62	1.04	1.64	0.286	1.63	1.10	0.48	4k
937	156	781	1.67	1.10	1.69	0.284	1.66	1.04	0.50	4k

**D] Derivation for the expression for the average rotational time  $\langle\phi\rangle$  in Equation 11:**

Equations S1 and S2 describe the contribution from the OPV-Q<sub>n</sub>A unimers (OQ<sub>n</sub>) and dimers ((OQ<sub>n</sub>)<sub>2</sub>) to the  $I_{VV}(t)$  fluorescence decays. The first sum of exponentials with the  $b_j$  pre-exponential factors and  $\tau_j$  decay times represents the fluorescence decay of the OPV dye which is the same for the unimers and dimers and was defined in Equation 3. The indices  $M$  and  $E$  in Equations S1 and S2 indicate whether a parameter is attributed to a unimer or a dimer, respectively. The other parameters  $r_o$ ,  $a_i$ , and  $f_i$  were defined in Equation 6.

$$[OQ_n]_{(t)}^{VV} = [OQ_n]_o \sum_{j=1}^p b_j \exp(-t / \tau_j) \times \left[ 1 + 2r_{o,M} \sum_{i=1}^{nM} a_{i,M} \exp(-t / \phi_{i,M}) \right] \quad (S1)$$

$$[(OQ_n)_2]_{(t)}^{VV} = [(OQ_n)_2]_o \sum_{j=1}^p b_j \exp(-t / \tau_j) \times \left[ 1 + 2r_{o,D} \sum_{i=1}^{nD} a_{i,D} \exp(-t / \phi_{i,D}) \right] \quad (S2)$$

Considering that an OQ<sub>n</sub> unimer and an (OQ<sub>n</sub>)<sub>2</sub> dimer contribute, respectively, one and two OPV dyes to the total dye concentration, the  $I_{VV}(t)$  decay would be represented by Equation S3.

$$I_{VV}(t) = [OQ_n]_{(t)}^{VV} + 2 \times [(OQ_n)_2]_{(t)}^{VV} \quad (S3)$$

Equation S3 can be expanded into Equation S4, where  $w_M$  and  $w_D$  are the weight fractions of the OQ<sub>n</sub> unimer and (OQ<sub>n</sub>)<sub>2</sub> dimers, respectively,  $r_o$  is the average initial anisotropy equal to  $w_M r_{o,M} + w_D r_{o,D}$ , and all the other parameters were defined earlier.

$$I_{VV}(t) = [OQ_n]_o \sum_{j=1}^p b_j \exp(-t / \tau_j) \times \left[ 1 + 2r_o \left( \frac{r_{o,M} w_M}{r_o} \sum_{i=1}^{nM} a_{i,M} \exp(-t / \phi_{i,M}) + \frac{r_{o,D} w_D}{r_o} \sum_{i=1}^{nD} a_{i,D} \exp(-t / \phi_{i,D}) \right) \right] \quad (S4)$$

A similar procedure can be applied to yield Equation S5 to represent the  $I_{VH}(t)$  fluorescence decay.

$$I_{VH}(t) = [OQ_n]_o \sum_{j=1}^p b_j \exp(-t / \tau_j) \times \left[ 1 - r_o \left( \frac{r_{o,M} w_M}{r_o} \sum_{i=1}^{nM} a_{i,M} \exp(-t / \phi_{i,M}) + \frac{r_{o,D} w_D}{r_o} \sum_{i=1}^{nD} a_{i,D} \exp(-t / \phi_{i,D}) \right) \right] \quad (S5)$$

Equation S6 provides the anisotropy of the OQ<sub>n</sub> and (OQ<sub>n</sub>)<sub>2</sub> mixture, which is a sum of exponentials that can be represented by Equation 6.

$$r(t) = r_o \left( \frac{r_{o,M} w_M}{r_o} \sum_{i=1}^{nM} a_{i,M} \exp(-t / \phi_{i,M}) + \frac{r_{o,D} w_D}{r_o} \sum_{i=1}^{nD} a_{i,D} \exp(-t / \phi_{i,D}) \right) = r_o \sum_{i=1}^n a_i \exp(-t / \phi_i) \quad (S6)$$

The average rotational time ( $\langle \phi \rangle$ ) is obtained by integrating Equation S6 from 0 to infinity as shown in Equation S7, where  $\phi_1$  and  $\phi_2$  are the number average rotational times of the unimers and dimers, respectively.

$$\langle \phi \rangle = \int_0^{\infty} r(t) dt = \frac{r_{o,M} W_M}{r_o} \sum_{i=1}^{nM} a_{i,M} \phi_{i,M} + \frac{r_{o,D} W_D}{r_o} \sum_{i=1}^{nD} a_{i,D} \phi_{i,D} = \frac{r_{o,M} [OQ_n] \phi_1 + 2 \times r_{o,D} [(OQ_n)_2] \phi_2}{r_o ([OQ_n] + 2[(OQ_n)_2])} \quad (S7)$$

Assuming that the unimers and dimers share a similar initial anisotropy ( $r_o = r_{o,M} = r_{o,D}$ ), Equation S7 simplifies to yield Equation S8, which is the same as Equation 11 in the main text. In Equation S8,  $[OQ_n]_o$  is the total concentration of free or complexed  $OQ_n$  molecules in the solution.

$$\langle \phi \rangle = \frac{[OQ_n] \phi_1 + 2 \times [(OQ_n)_2] \phi_2}{[OQ_n]_o} \quad (S8)$$