Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Complexation of β-cyclodextrin with dual molecular probes bearing fluorescent and paramagnetic moieties linked by short polyether chains

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Table S1. Fluorescence quantum yields (Φ) of $Py(EG)_nT$ dual probes; S_{probe}/S_{PyCOO-} is the ratio of the integrated emission intensities of the probe and $PyCOO^-$, indicating the extent of intramolecular quenching by the paramagnetic moiety

Probe	**Φ**	S_{probe}/S_{PyCOO-}
$Py(EG)_1T$	0.096	0.093
$Py(EG)_2T$	0.051	0.064
$Py(EG)_3T$	0.159	0.310
$Py(EG)_4T$	0.127	0.173
$Py(EG)_5T$	0.151	0.205
$Py(EG)_6T$	0.234	0.246
$Py(EG)_1$	0.556	0.874
$Py(EG)_6$	0.574	0.913

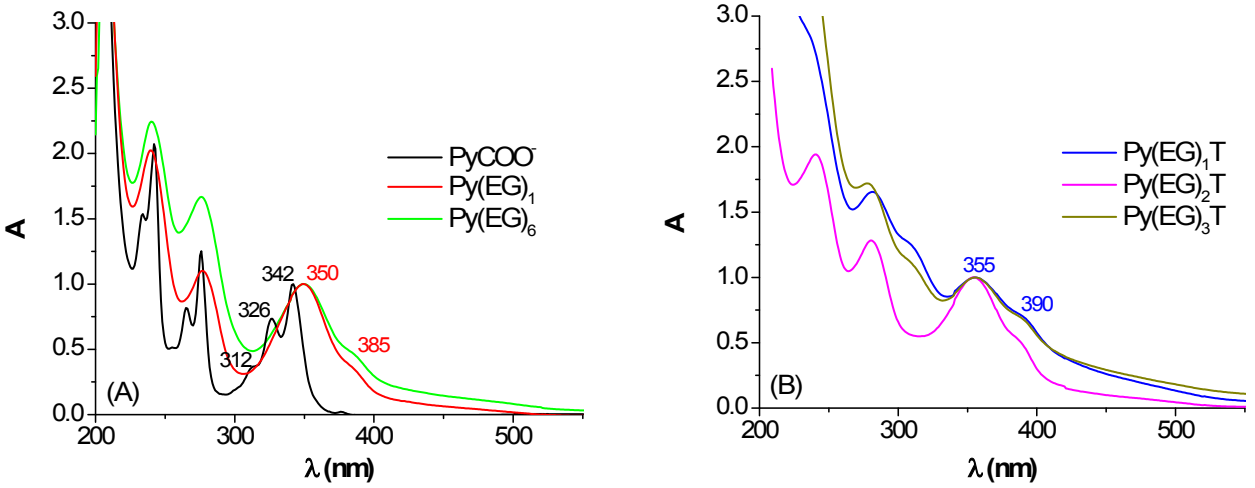

Fig. S1. Normalized absorption spectra of (A) $PyCOO^-$ and relevant $Py(EG)_n$ parent compounds, and (B) selected $Py(EG)_nT$ dual probes, in pH 7.4 phosphate buffer at 20°C.

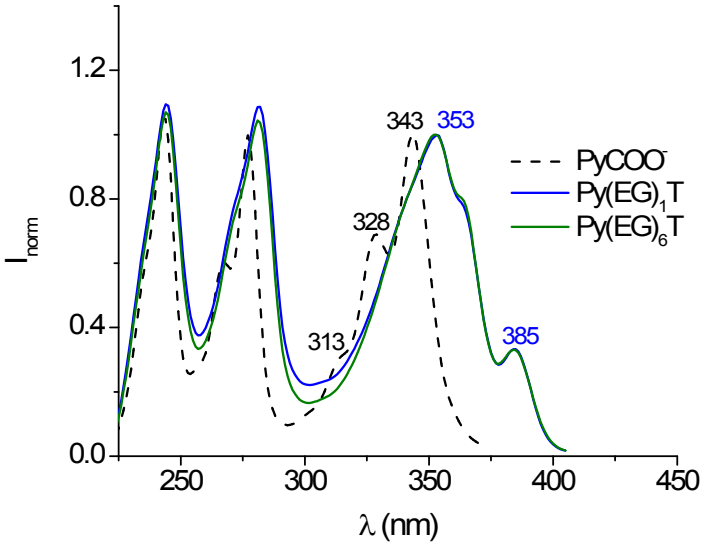

Fig. S2. Excitation spectra of $PyCOO^-$ and selected $Py(EG)_nT$ probes in pH 7.4 phosphate buffer at 20°C; λ_{em} = 380 nm for $PyCOO^-$ and 415 nm for $Py(EG)_nT$.

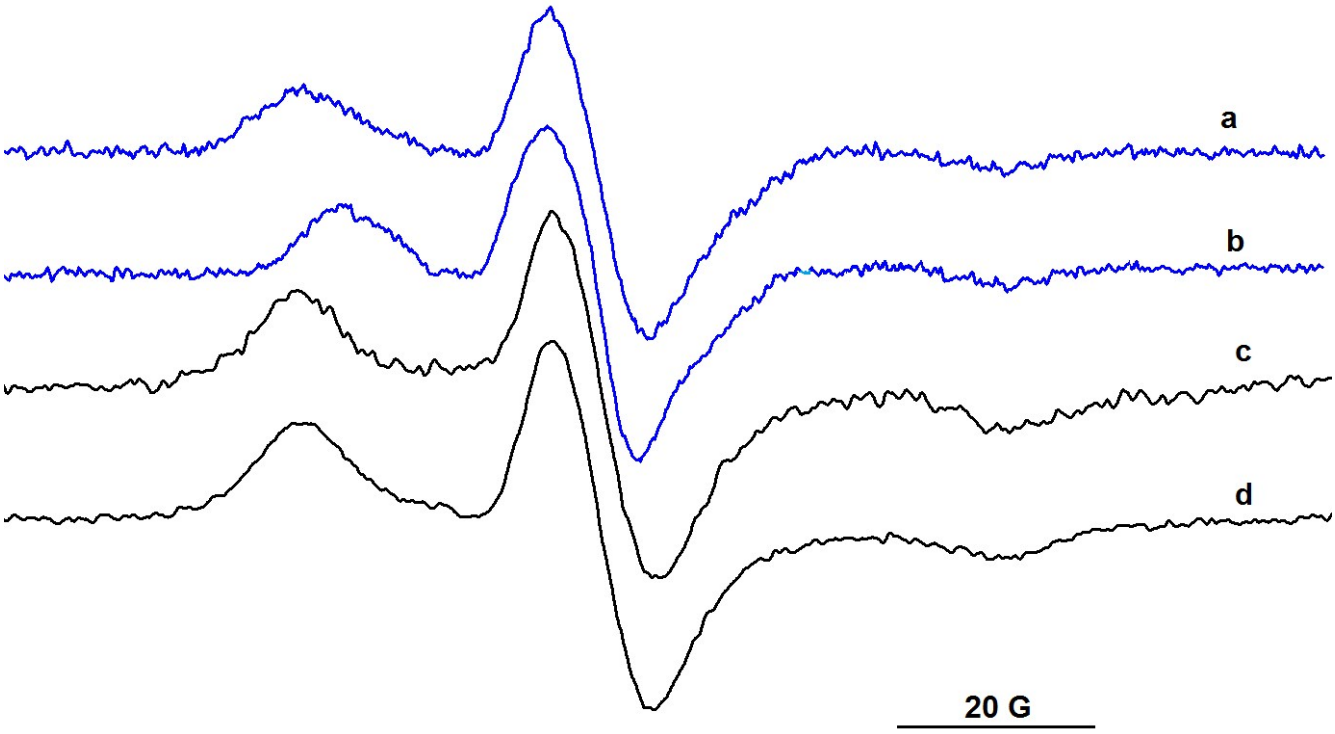

Fig. S3. The EPR spectra of $Py(EG)_1T$ in the absence (a) and in the presence of β-CD (b) and $Py(EG)_6T$ in the absence (c) and in the presence of β-CD (d)in water/glycerol (9:1). Concentration of β-CD is 10^{-2} M.

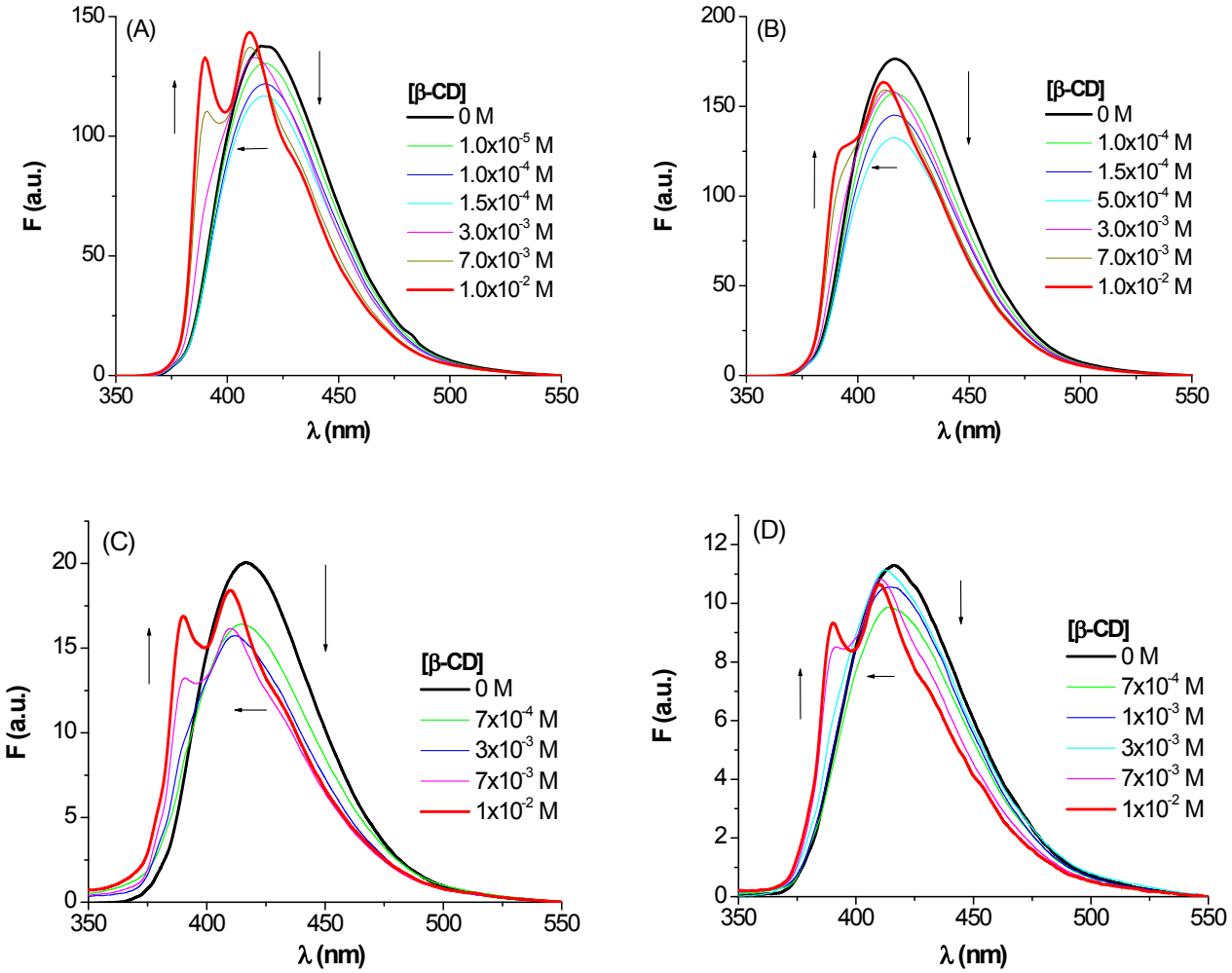

Fig. S4. Steady-state fluorescence spectra of (A) $Py(EG)_1$ and (B) $Py(EG)_6$ parent compounds, (C) $Py(EG)_1T$ and (D) $Py(EG)_6T$ dual probes in the presence of increasing concentrations of β-CD.

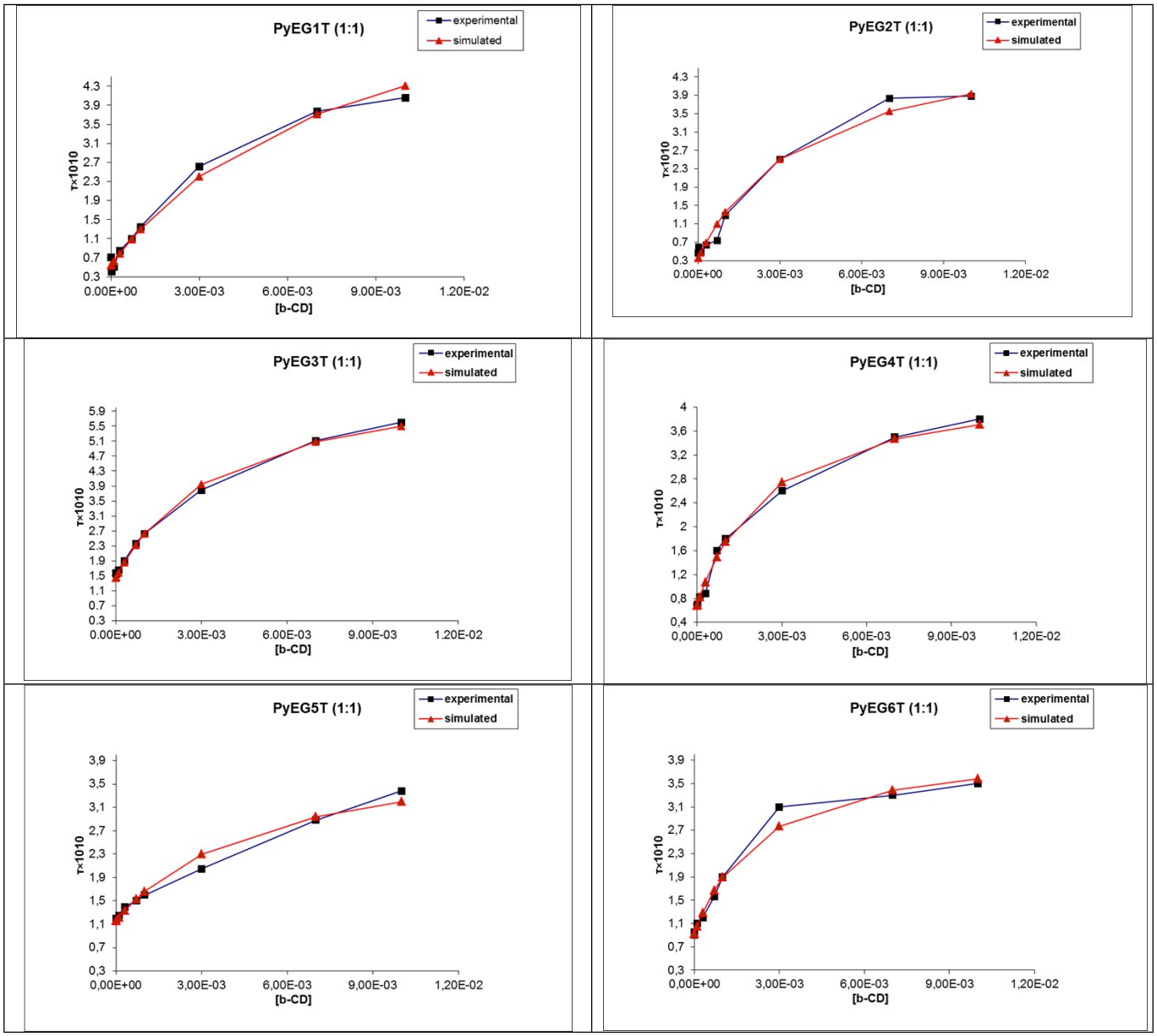

Fig. S5. Dependence of τ_c on the β-CD concentration: experimental (blue) and best fit for 1:1 stoichiometry (red).

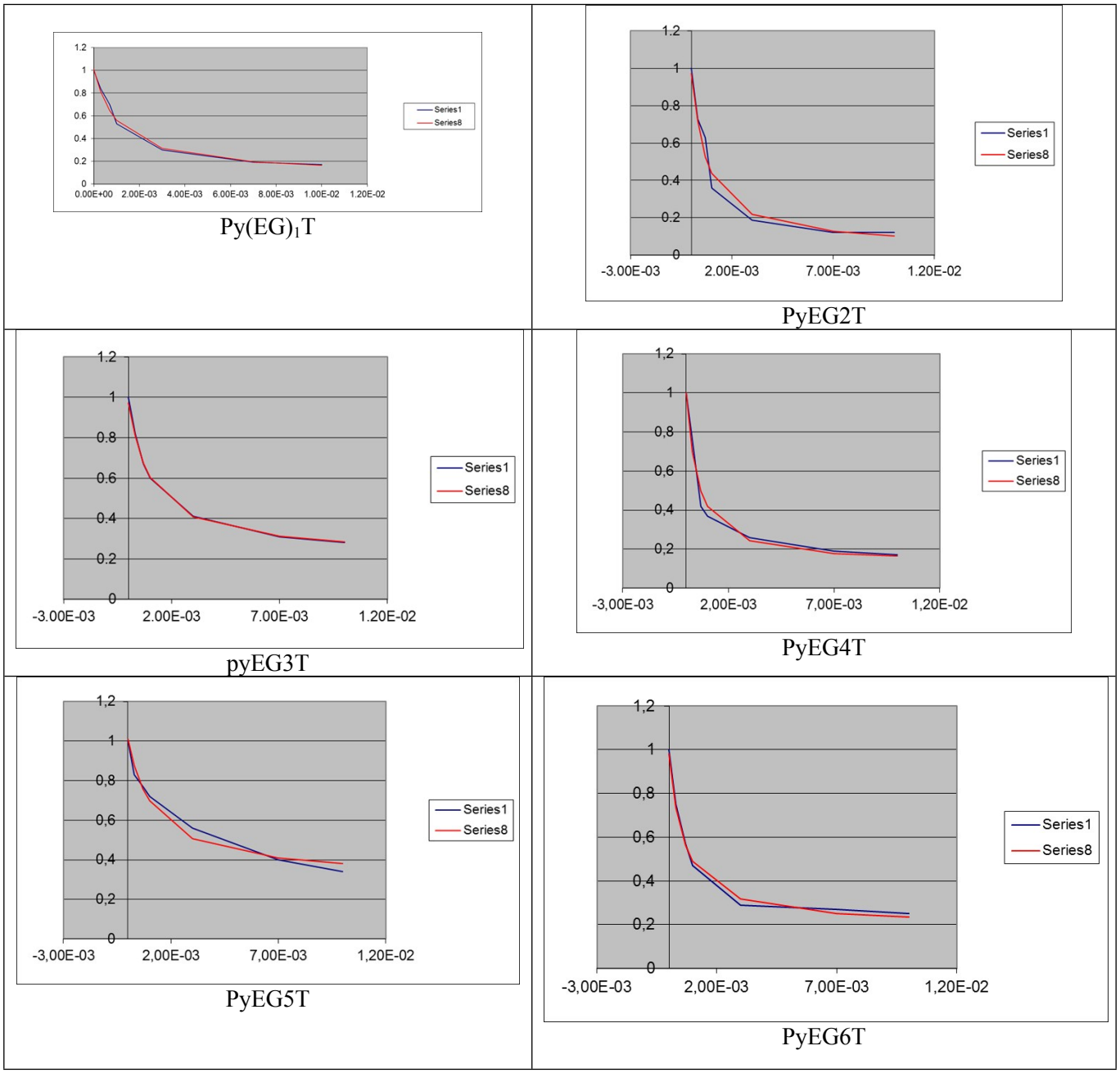

Fig. S6. Dependence of τ_c on the β-CD concentration: experimental (blue) and best fit for 1:2 stoichiometry (red).

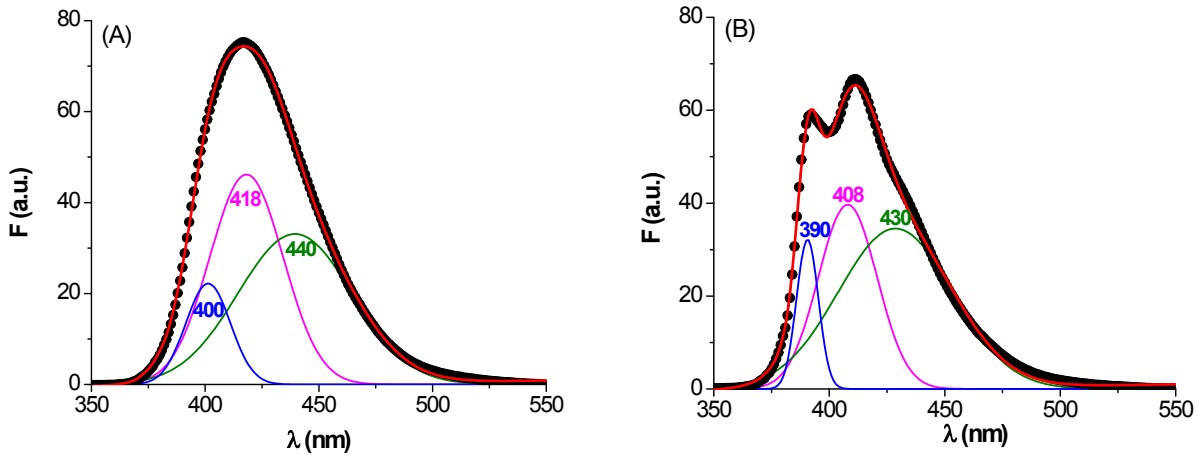

Fig. S7. Deconvoluted steady-state fluorescence spectra of $Py(EG)_4T$ in the absence (A) and in the presence (B) of 10^{-2} M β-CD.

The association constants, K, characterizing the equilibria in solution have been determined according to eq. (S1) assuming a 1:1 stoichiometry of the interaction. In order to minimize band superposition effects, the K values have been computed employing the area (S in Table S2) of the band at ~440 nm, obtained by deconvolution. In the case of the probes that present little band superposition at ~450 nm, we checked that similar K values can be obtained when employing the decrease in fluorescence intensity at 445 nm.

$$S = \frac{S_0 + K\ S_c[CD]}{1 + K\ [CD]} \quad \text{(S1)}$$

In eq. (S1), S_0 and S_c are band areas of the guest in the absence of CD and of the 1:1 complex, respectively.

Table S2. Positions (λ, in nm) and relative areas (S, %) of the peaks in the deconvoluted emission spectra of $Py(EG)_nT$ dual probes in the absence and in the presence of β-CD

Probe	[β-CD] (M)	λ_1	S_1	λ_2	S_2	λ_3	S_3
$Py(EG)_1T$	0	402.4	14.5	419.8	42.3	441.6	42.2
	10^{-2}	389.1	9.4	407.0	25.5	425.1	63.9
$Py(EG)_2T$	0	405.4	26.9	425.9	43.6	448.6	27.0
	10^{-2}	391.1	13.7	409.3	25.1	427.1	60.0
$Py(EG)_3T$	0	405.3	23.8	425.3	44.4	448.6	28.6
	10^{-2}	390.0	12.4	408.6	25.8	427.2	60.4
$Py(EG)_4T$	0	401.3	12.1	418.2	41.3	439.5	46.0
	10^{-2}	390.6	10.0	408.0	33.3	428.6	56.3
$Py(EG)_6T$	0	401.5	10.4	418.4	45.5	441.6	40.6
	10^{-2}	389.2	8.9	407.4	28.4	428.6	60.9

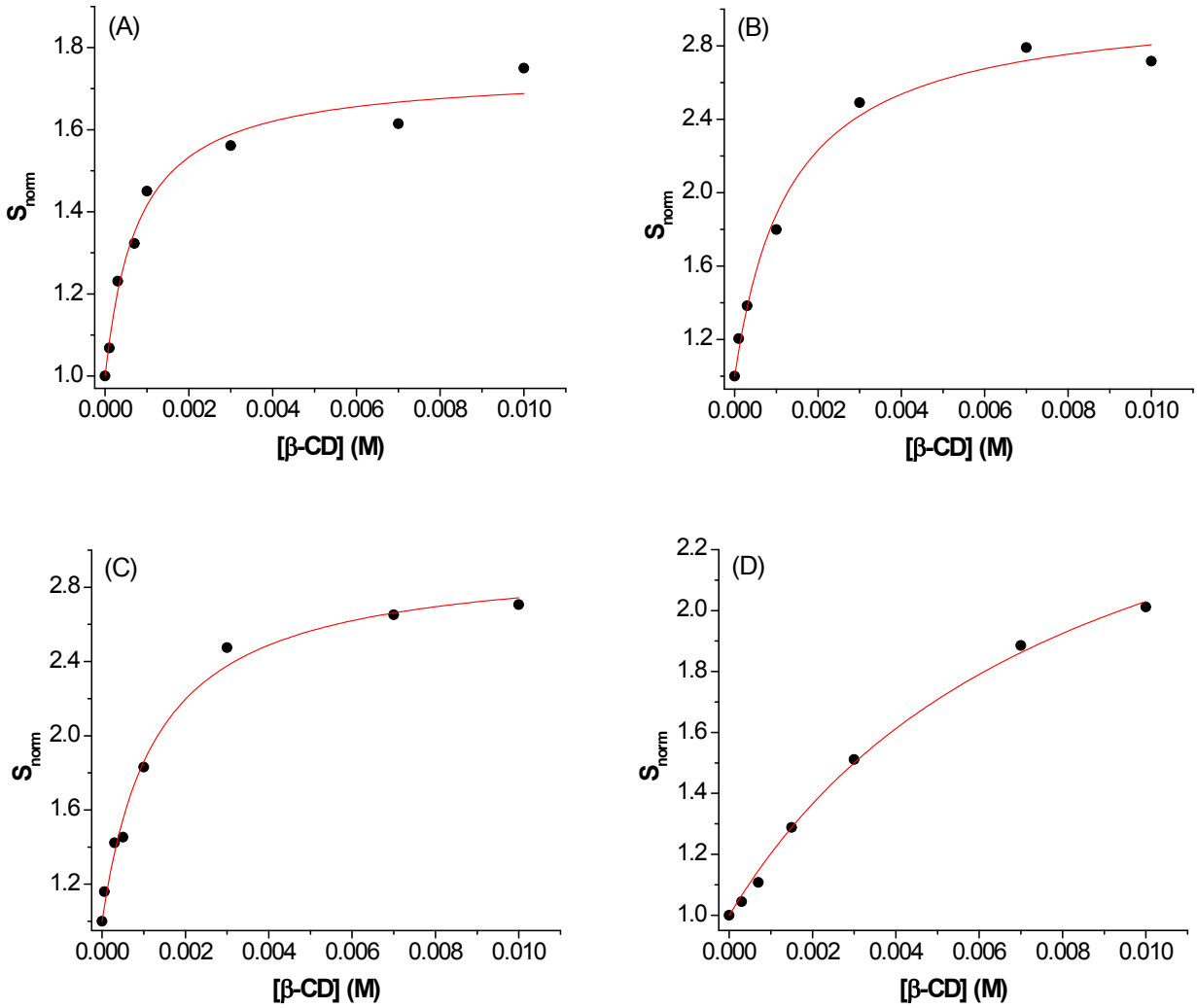

Fig. S8. Dependence of the normalized fluorescence emission on the β-CD concentration for selected $Py(EG)_nT$ probes: (A) $Py(EG)_1T$, (B) $Py(EG)_2T$, (C) $Py(EG)_3T$ and (D) $Py(EG)_6T$. The solid lines represent the best fits according to eq. (S1) for 1:1 stoichiometry.

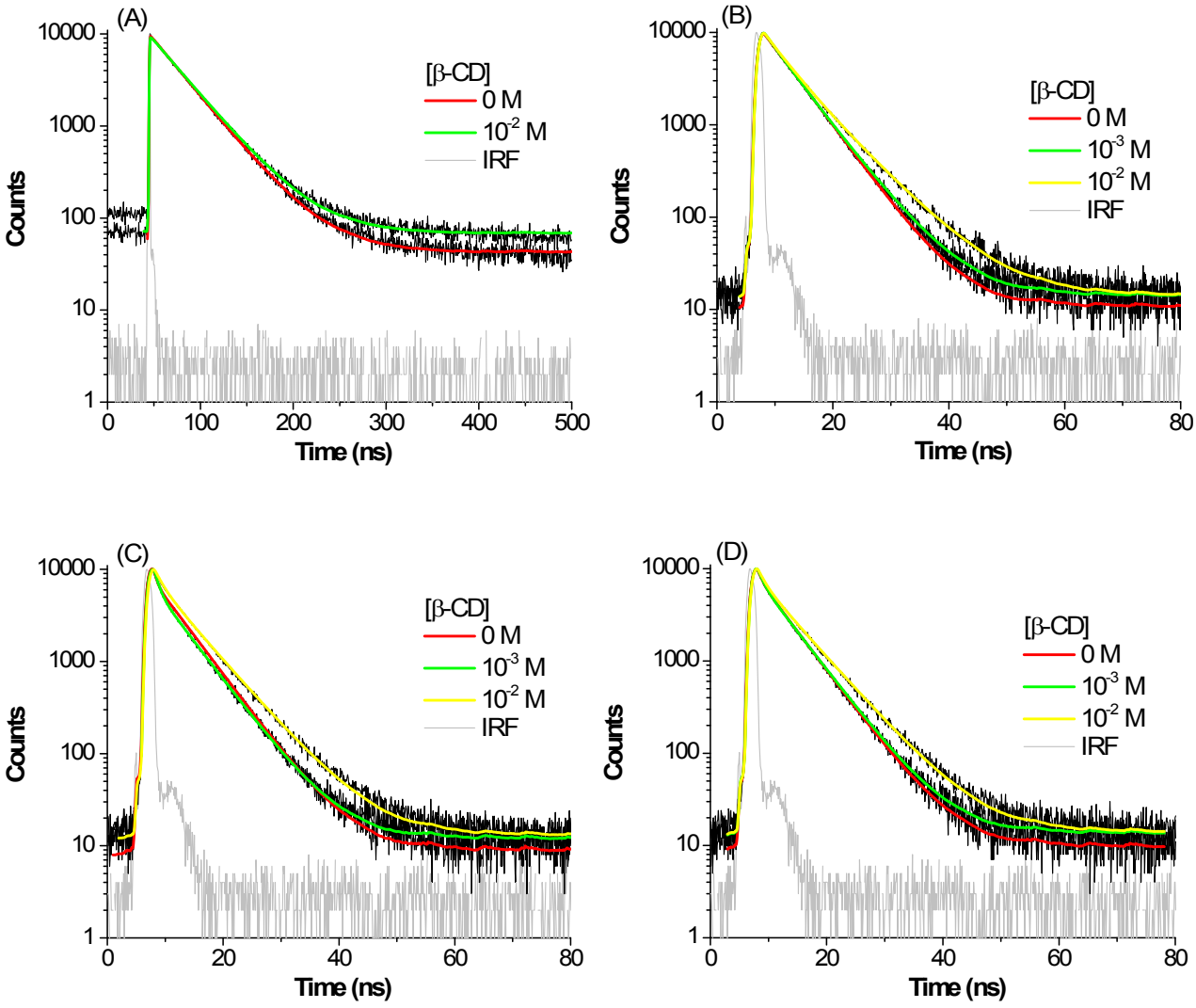

Fig. S9. Fitted fluorescence intensity decays of (A) $PyCOO^-$, (B) $Py(EG)_6$, (C) $Py(EG)_2T$ and (D) $Py(EG)_3T$ in the absence and in the presence of β-CD; λ_{em} = 380 nm for $PyCOO^-$ and 415 nm for $Py(EG)_nT$; IRF = instrument response function.

Table S3. Fluorescence decay fitting parameters of $Py(EG)_nT$, $Py(EG)_n$ and $PyCOO^-$ in the absence and in the presence of β-CD; λ_{em} = 415 nm for $Py(EG)_nT$ and $Py(EG)_n$, and 380 nm for $PyCOO^-$

Probe	[β-CD] (M)	τ_1 (ns)	B_1	f_1	a_1	τ_2 (ns)	B_2	f_2	a_2	$\langle\tau\rangle$ (ns)	χ^2
$Py(EG)_1T$	0	5.17	0.087	–	–	–	–	–	–	–	1.05
	10^{-3}	5.35	0.071	0.90	0.72	1.45	0.028	0.10	0.28	4.98	1.03
	10^{-2}	6.35	0.053	0.78	0.62	2.79	0.033	0.21	0.38	5.58	1.07
$Py(EG)_2T$	0	5.18	0.064	0.86	0.47	0.76	0.071	0.14	0.53	4.56	1.03
	10^{-3}	5.26	0.052	0.79	0.39	0.91	0.080	0.21	0.61	4.34	1.10
	10^{-2}	6.05	0.063	0.85	0.62	1.75	0.038	0.15	0.38	5.41	1.07
$Py(EG)_3T$	0	5.17	0.068	0.89	0.61	1.01	0.043	0.11	0.39	4.71	1.12
	10^{-3}	5.28	0.065	0.87	0.57	1.02	0.050	0.13	0.43	4.73	1.08
	10^{-2}	6.12	0.064	0.88	0.62	1.42	0.039	0.12	0.38	5.54	1.16
$Py(EG)_6T$	0	5.15	0.090	–	–	–	–	–	–	–	1.19
	10^{-3}	5.70	0.067	0.84	0.76	3.48	0.021	0.16	0.24	4.92	1.22
	10^{-2}	7.96	0.048	0.70	0.55	4.05	0.040	0.30	0.45	5.21	1.17
$Py(EG)_1$	0	5.22	0.088	1	–	–	–	–	–	–	1.06
	10^{-3}	5.49	0.082	0.96	0.91	2.38	0.008	0.04	0.09	5.36	1.10
	10^{-2}	8.22	0.045	0.66	0.52	4.55	0.041	0.34	0.48	6.99	1.11
$Py(EG)_6$	0	5.12	0.089	1	–	–	–	–	–	–	1.23
	10^{-3}	5.48	0.073	0.88	0.80	2.92	0.018	0.12	0.20	5.18	1.01
	10^{-2}	6.91	0.051	0.72	0.57	3.58	0.039	0.28	0.43	5.96	1.20
$PyCOO^-$	0	35.20	0.332	1	1	–	–	–	–	–	1.01
	10^{-2}	36.47	0.501	1	1	–	–	–	–	–	1.15

Note: The maximum error in τ is ±0.02 ns.

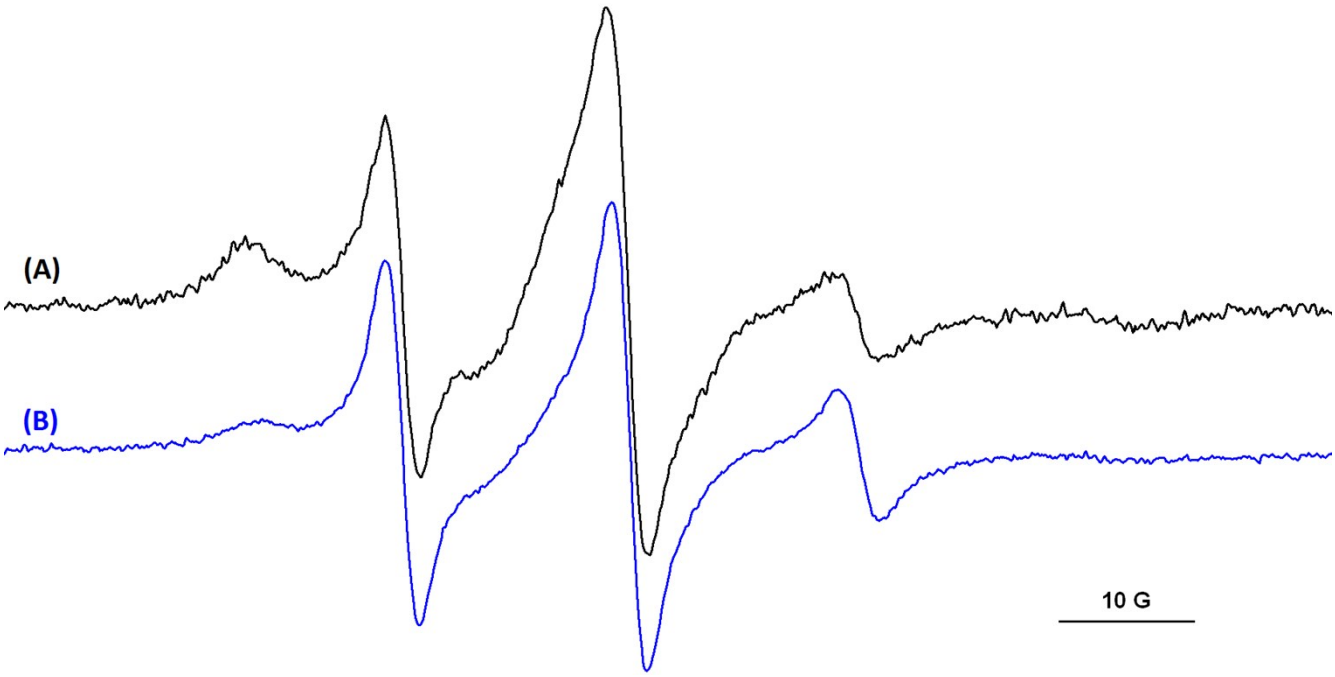

Fig. S10. EPR spectra of $Py(EG)_6T$ loaded in PEG900/β-CD (A) without adamantol and (B) with adamantol.

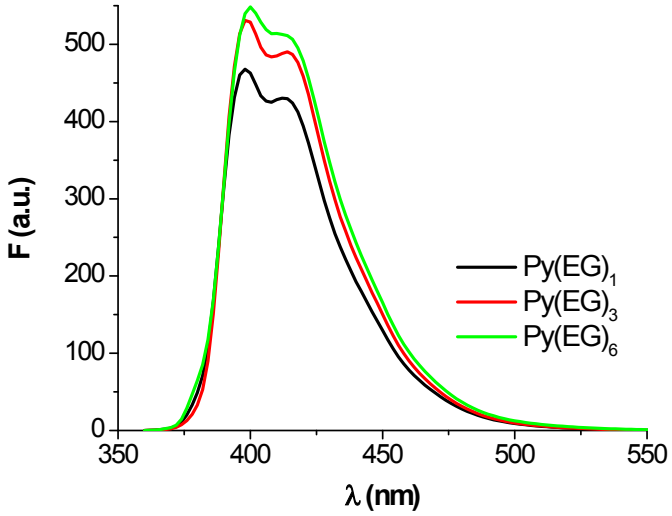

Fig. S11. Steady-state fluorescence spectra of $Py(EG)_n$ probes after diffusion in PEG900/β-CD gel.