Supporting Information

Two-photon Absorption Enhancement of Polymer-templated Porphyrin-based J-Aggregates

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1. Linear dependence of absorption max of TSPP in water

The steady state absorption spectra of commercially available TSPP in water are shown in Figure S1. A TSPP stock solution (~ 4 x 10^{-4} M) was diluted with varying quantities of ultrapure water (~ 1 x 10^{-5} M). TSPP under neutral aqueous conditions did not show any evidence of aggregation as seen by the linear dependence of the monomeric absorption bands and the lack of appearance of any J-aggregate bands, i.e., TPPS remains as a monomeric free base due to electrostatic anionic repulsion of the sulfonate groups.

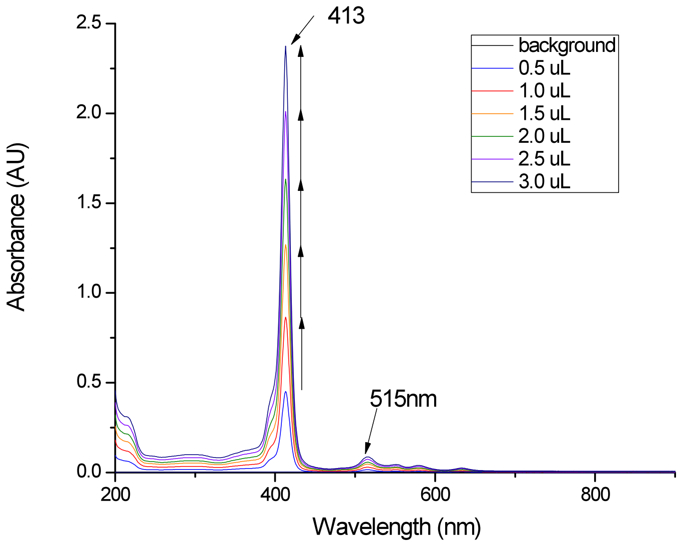

Figure S1. UV-vis absorption spectra of TSPP in water at various concentrations.

2. Molecular weight determination

Due to its lack of solubility in THF (that would have facilitated Molecular weight determination by GPC), the molecular weight of the polymer was estimated by comparison of its diffusion coefficient with the diffusion coefficients of three polyethylene glycol standards. At dilute concentrations, the molecular weight of a polymer relates to its diffusion coefficient following equation 1.

$$D=k \quad MD = kM^{-v} \qquad (1)$$

The diffusion coefficients were measured using pulsed field gradient NMR. The experiments were performed on a Varian 500 MHz NMR spectrometer using the DgcsteSL_cc (DOSY gradient compensated stimulated echo with spin lock and convection compensation) pulse sequence. The temperature was regulated at 25 °C and each sample was given a minimum of 30 min to equilibrate before data acquisition. The gradient pulses, g, were applied for 2 ms and were arrayed in ten steps of equally spaced g^2 over a range of 1.87 – 46.85 Gauss/cm (equivalent to 1000 – 25000 DAC units). The number of transients per increment was 16 for the PEG standards, and 200 for the polymer. Experiments were done in triplicate at five different diffusion times, t_{diff}, for each sample (Table 1). The calculation of D was performed by the acquisition software (VNMRJ 2.2C) using peak height. The peak at 3.61 ppm (referenced to internal $CDCl_3$) was used for the PEG samples, and peaks at 1.60 and 1.37 ppm were used for the polymer.

Table 1. Diffusion coefficients for polymer **3** and PEG standards.

	polymer peak 1		polymer peak 2		PEG 7100		PEG 12600		PEG 22000	
t_{diff} (ms)	D × 10^{12} (m^2/s)	error	D × 10^{12} (m^2/s)	error	D × 10^{12} (m^2/s)	error	D × 10^{12} (m^2/s)	error	D × 10^{12} (m^2/s)	error
100	2.462	0.025	2.371	0.046	1.122	0.009	0.641	0.004	0.343	0.002
	2.456	0.135	2.344	0.117	1.122	0.002	0.646	0.002	0.349	0.002
	2.494	0.111	2.429	0.131	1.124	0.002	0.640	0.003	0.342	0.001
200	2.260	0.184	2.098	0.189	1.111	0.002	0.632	0.002	0.339	0.001
	2.273	0.171	2.175	0.169	1.111	0.002	0.630	0.002	0.341	0.001
	2.379	0.171	2.328	0.201	1.112	0.001	0.628	0.002	0.340	0.001
300	2.354	0.215	2.178	0.208	1.107	0.002	0.626	0.002	0.334	0.001
	2.471	0.240	2.291	0.231	1.106	0.002	0.625	0.002	0.333	0.002
	2.367	0.196	2.367	0.244	1.114	0.001	0.628	0.001	0.342	0.004
400	2.479	0.209	2.379	0.244	1.105	0.002	0.623	0.002	0.329	0.002
	2.764	0.295	2.382	0.262	1.108	0.002	0.560	0.023	0.331	0.001
	2.478	0.244	2.721	0.298	1.108	0.001	0.624	0.001	0.336	0.003
500	2.561	0.260	2.517	0.262	1.106	0.003	0.686	0.028	0.318	0.002
	2.843	0.297	2.638	0.279	1.108	0.003	0.685	0.028	0.321	0.002
	2.887	0.265	2.814	0.263	1.105	0.002	0.618	0.002	0.326	0.002

A least-square regression of eq. 1 for the average values of the three PEG standards yielded $k = 13627$ and $u = 1.06$. These values and the average value of D for the two polymer peaks were used into eq. 1, yielding a molecular weight of 3411 for polymer **3** (Table 2).

Table 2. Calculated diffusion coefficients and molecular weights using three PEG standards.

M	D_{meas}	D_{calc}	M_{calc}
7100	1.111	1.127	7197
12600	0.633	0.614	12244
22000	0.335	0.34	22307
polymer	2.452		3411

3. Fluorescence Lifetimes

Fluorescence lifetimes were measured with a time-correlated single photon counting system (PicoQuant PicoHarp 300) under linear polarized femtosecond excitation at room temperature using 10 mm path length quartz cuvettes. Results for porphyrins **4** and **5** are illustrated in Figures S2 and S3, respectively.

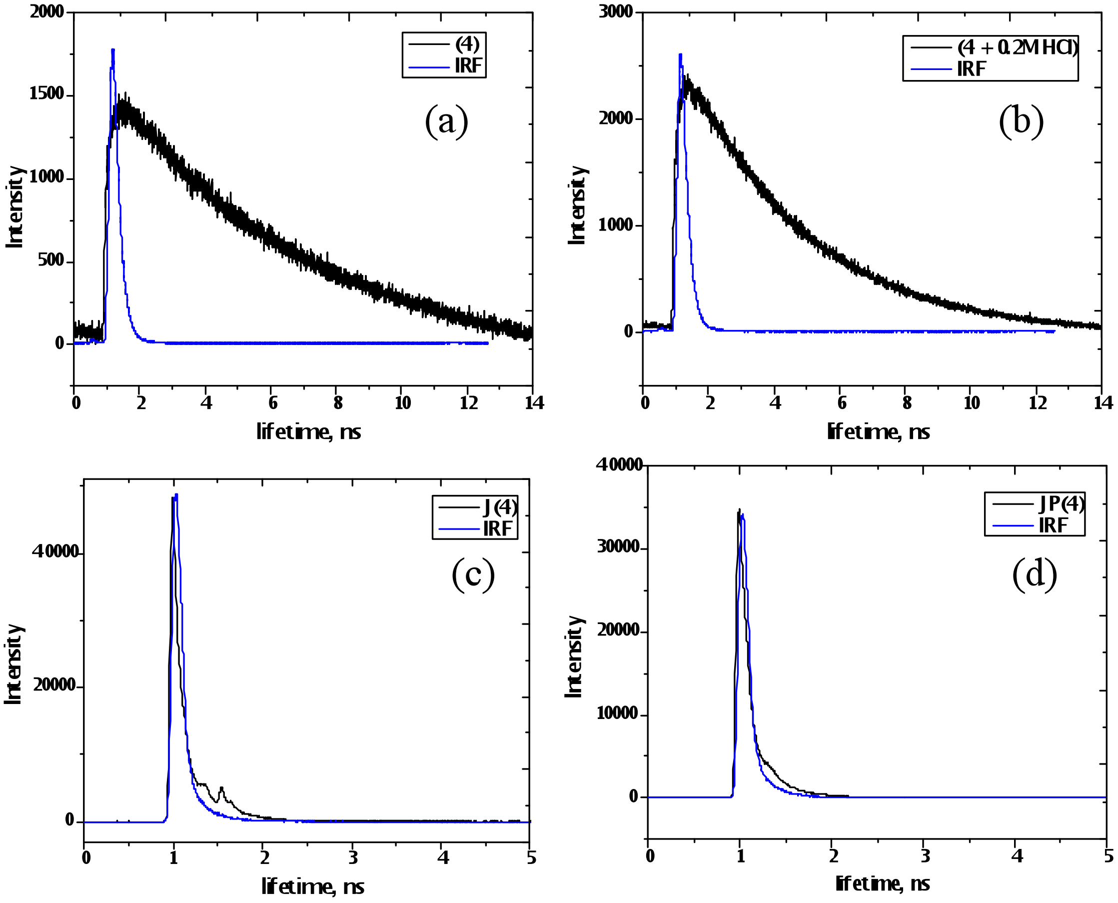

Figure S2. Fluorescence decay of TPPS monomer **4** (a) free base, (b) dianion, and J-aggregated species without (c) or with polymer **3** template (d) in water at [C] = 10^{-5} M, measured with a time correlated single photon counting method (compared with the instrument response function (IRF, blue) in each case).

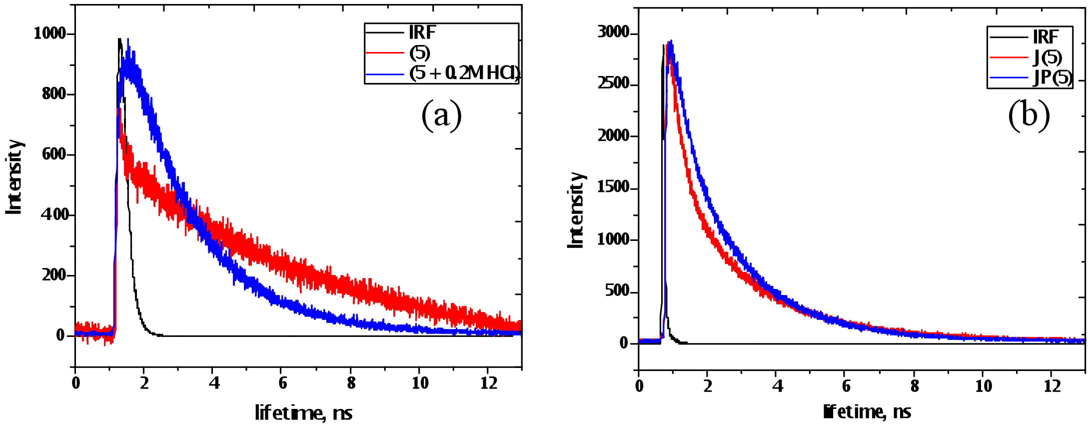

Figure S3. Fluorescence decay of (a) monomer **5** (free base (red) and dianion (blue)), and (b) J-aggregated species without (red) or with (blue) polymer **3** template in water at [C] = 10^{-5} M, measured with a time correlated single photon counting method (compared with the instrument response function (IRF, black) in each case).