Supporting Information

Structural Implications on the Properties of Self-Assembling Supramolecular Hosts for Fluorescent Guests

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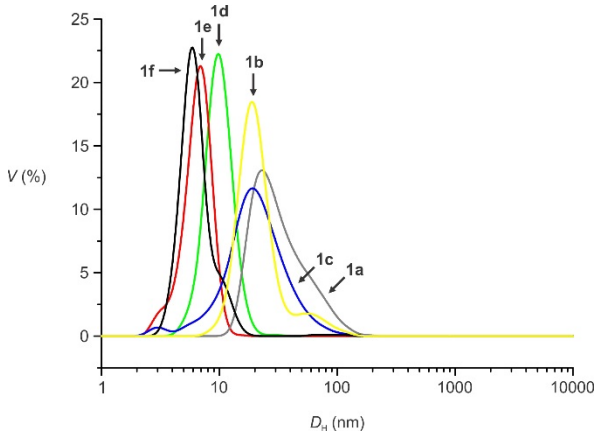

Figure S1. Statistical distributions of D_H for **1a–f** (0.5 mg mL^{-1}) determined by DLS in PBS at 22 °C.

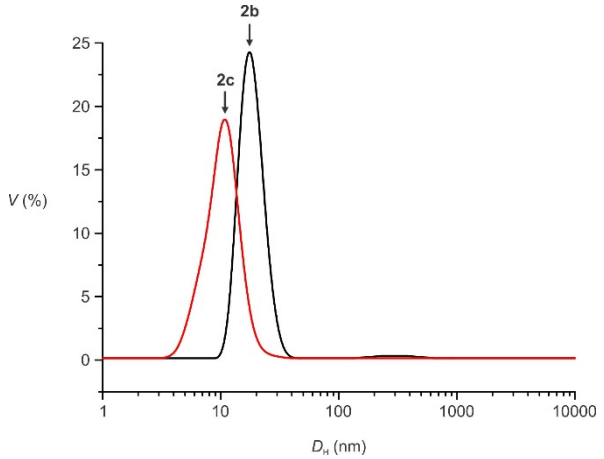

Figure S2. Statistical distributions of D_H for **2b** and **2c** (0.5 mg mL^{-1}) determined by DLS in PBS at 22 °C.

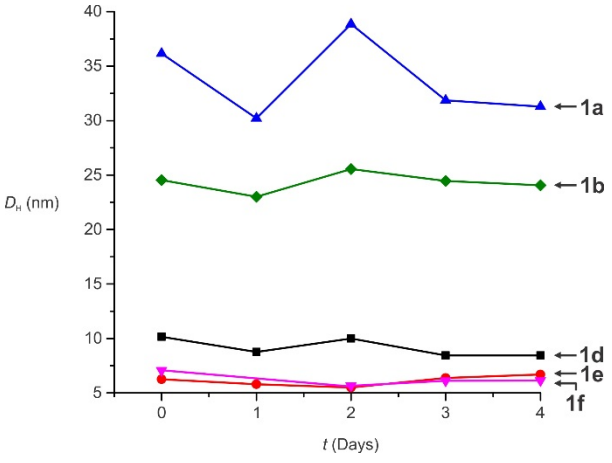

Figure S3. Temporal dependence of D_H for **1a**, **1b** and **1d–f** (0.5 mg mL^{-1}) in PBS at 22 °C.

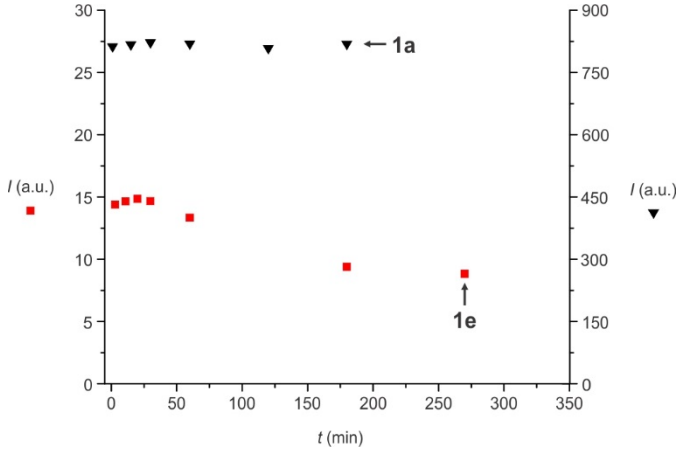

Figure S4. Emission intensity (λ_{Ex} = 500 nm, λ_{Em} = 540 nm) of nanoparticles of either **1a** or **1e**, containing **6** (6.6 μM for **1a** and 3.9 μM for **1e**), recorded in PBS at 25 °C.

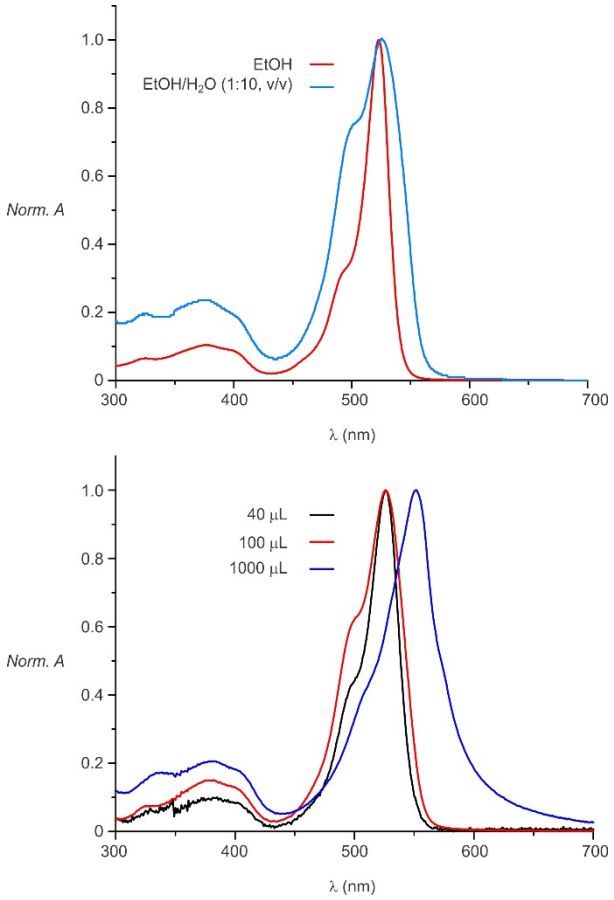

Figure S5. Normalized absorption spectra of **6** in EtOH, EtOH/H_2O (1:10, v/v) or after combining CH_2Cl_2 solutions of **6** (0.1 mM, volume indicated in the chart) and **1e** (1 mg mL^{-1}, 0.5 mL), distilling the solvent off under reduced pressure, dispersing the residue in PBS (1 mL) and passing the resulting dispersion through a nanoporous membrane.

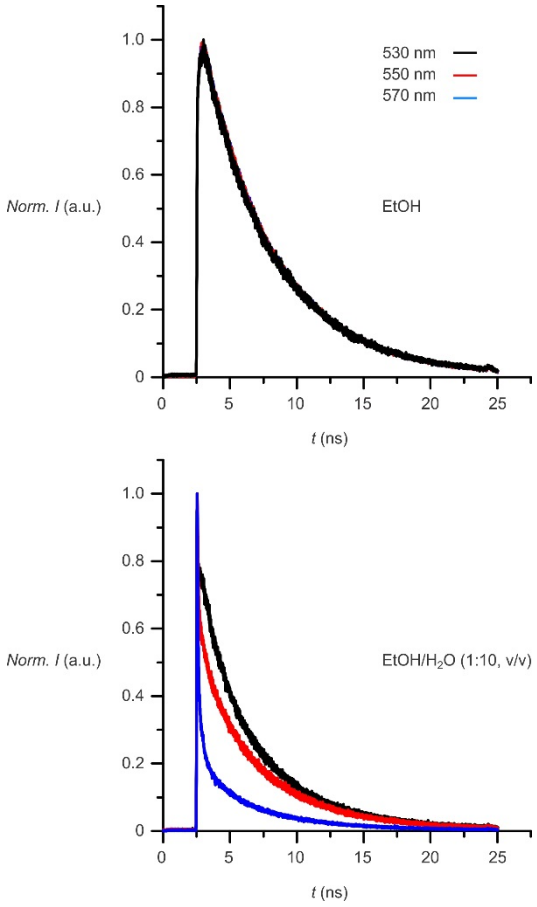

Figure S6. Fluorescence intensity decays [λ_{Ex} = 500 nm, λ_{Em} = 570 (blue), 550 (red) or 530 nm (black)] of **6** in EtOH or EtOH/H_2O (1:10, v/v). Decays were fitted with a sum of exponentials (Table S1).

Table S1. Fitting parameters [a] for the fluorescence decays of **6** [b].

	λ_{Ex} (nm)	λ_{Em} (nm)	τ_1 (ns)	%	τ_2 (ns)	%	τ_3 (ns)	%
1a (2.48 µM)	500	530	5.8	78	1.3	22%	—	—
	500	550	5.8	82	1.8	18%	—	—
	500	570	5.9	77	3.0	23%	—	—
1e (1 µM)	500	540	6.1	34	1.1	19%	0.1	47
	500	555	5.8	22	1.2	22%	0.2	56
	500	570	5.6	16	1.1	25%	0.2	59
1a (1.64 µM)	525	555	5.1	64	1.9	36%	—	—
1a (1.93 µM)	525	555	5.4	63	1.8	37%	—	—
1a (3.04 µM)	525	555	4.7	53	1.7	47%	—	—
1e (0.52 µM)	525	555	5.8	30	1.2	26%	0.08	44
1e (1 µM)	525	555	5.7	24	1.1	24%	0.2	52
1e (2.3µM)	525	555	5.8	14	0.7	17%	0.1	69
EtOH/H_2O (1:10, v/v)	500	530	5.0	14	1.5	7%	0.02	79
	500	550	5.1	19	1.3	7%	0.05	74
	500	570	4.8	6	0.7	6%	0.05	88
EtOH	500	530	5.3	100	—	—	—	—
	500	550	5.3	100	—	—	—	—
	500	570	5.2	100	—	—	—	—

[a] The fluorescence decays (Figures 7 and S6) were fitted with one, two or three exponential terms, as needed to obtain random residuals.
[b] The concentration of **6** is listed in parentheses for the experiments with **1a** and **1e**.

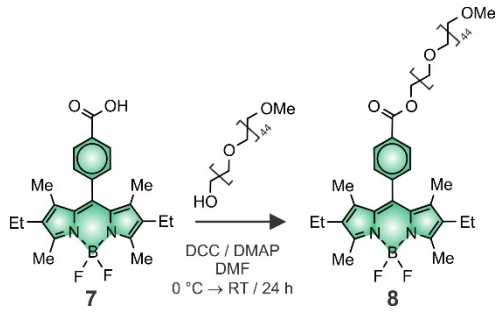

Figure S7. Synthesis of **8**.

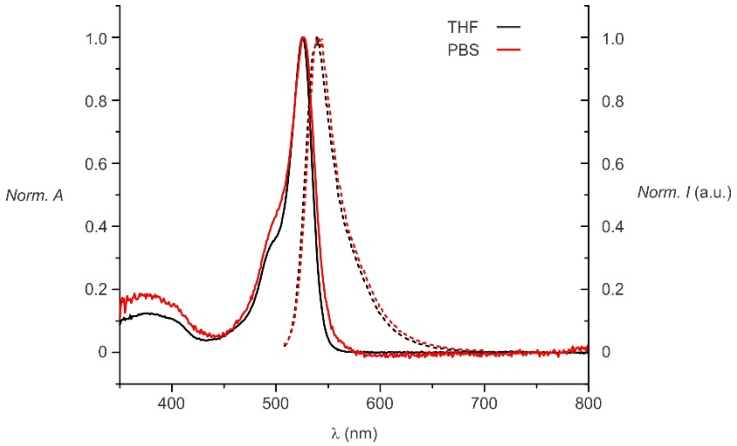

Figure S8. Normalized absorption and emission (λ_{Ex} = 500 nm) spectra of **8** in THF or PBS at 25 °C.

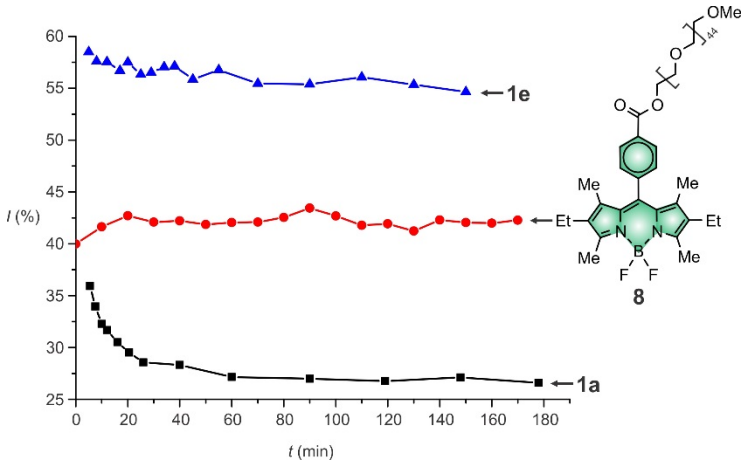

Figure S9. Temporal evolution of the emission intensity (λ_{Ex} = 500 nm, λ_{Em} = 540 nm) of nanoparticles of **1a** or **1e**, containing **6** (7.2 μM for **1a** and 2.8 μM for **1e**), recorded in PBS at 25 °C after the addition of NaI (0.1 mM) and reported relative to that measured in the absence of NaI, together with the relative emission intensity of **8** (0.1 mM) recorded after the addition of NaI (0.1 mM) under the same conditions.

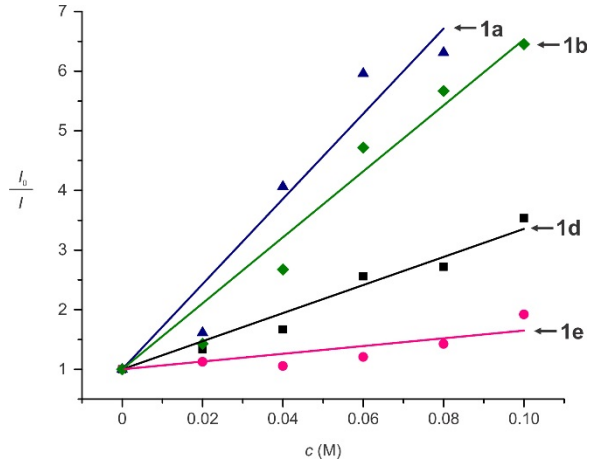

Figure S10. Plots of the relative emission intensity (λ_{Ex} = 500 nm, λ_{Em} = 540 nm) of nanoparticles of **1a**, **1b**, **1d** or **1e**, containing **6** (7.2 μM for **1a**, 7.8 μM for **1b**, 2.8 μM for **1d** and 2.8 μM for **1e**), recorded in PBS at 25 °C after the addition of increasing amounts of NaI and storage in the dark for 3 hours, against the iodide concentration.

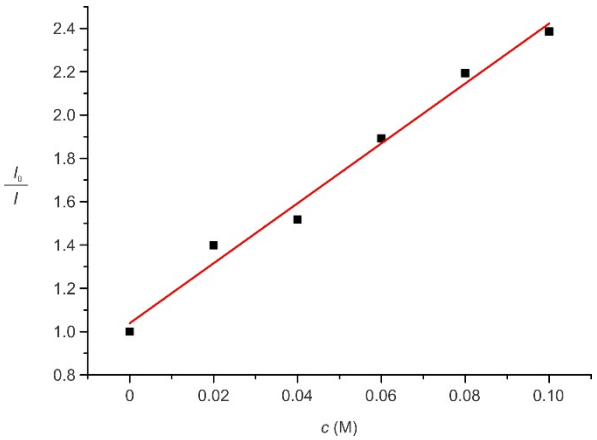

Figure S11. Plot of the relative emission intensity (λ_{Ex} = 500 nm, λ_{Em} = 540 nm) of **8** (25 μM), recorded at 25 °C in PBS and the presence of increasing amounts of NaI, against the iodide concentration.

Determination of an Upper Bound for the Solubility of 6 in PBS. First, EtOH solutions of **6** at different concentrations were prepared and the photon count rate of each solution was measured in the same FCS instrument used to acquire the autocorrelation functions reported in the manuscript. The lowest concentration with a photon count rate three times above the background was 100 pM and, therefore, it was concluded that the limit of detection of compound **6** in our instrument was 100 pM. Then, **6** was dissolved in PBS buffer and the photon count rate was measured in the same instrument. The result was indistinguishable from background, from which we conclude that the solubility of **6** in PBS is less than 100 pM.

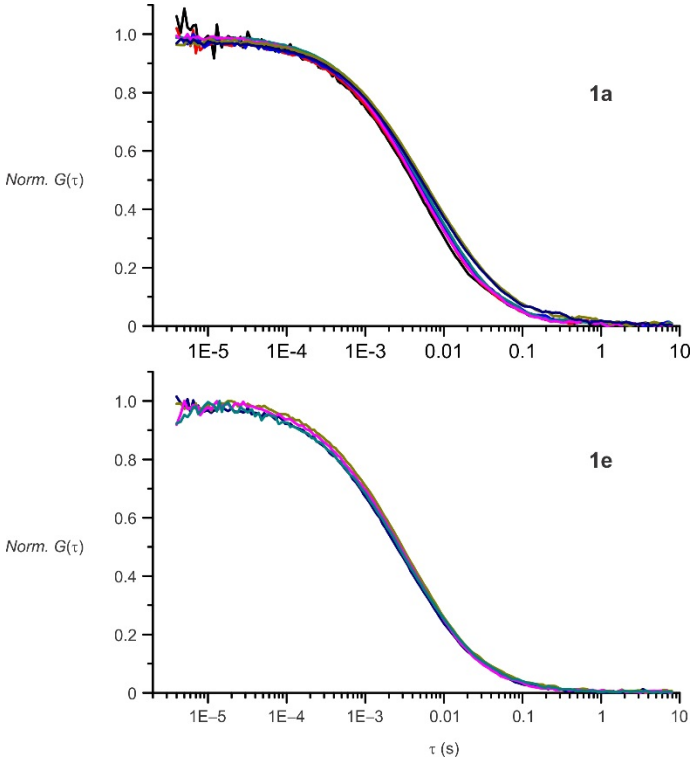

Figure S12. Autocorrelation decays of **6** incorporated into nanoparticles of either **1a** or **1e**. Samples were prepared using a concentration of 0.5 mg mL^{-1} for the polymer. The concentration of guest, after filtration, was 2.4 μM for **1a** and 1.0 μM for **1e** The solutions were sequentially diluted using PBS buffer in 6 steps, until the concentration of polymer was 6.25 μg mL^{-1} (1:80) for **1a** and 50 μg mL^{-1} (1:10) for **1e** (the supramolecular hosts are not stable at lower polymer concentrations). Results show negligible changes in the autocorrelation function.