Supplementary Information

Design of peptide-based bolaamphiphile exhibiting heat-set hydrogelation *via* retro-Diels-Alder reaction

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Contents:

1. Analytical HPLC of 1•2-*endo*

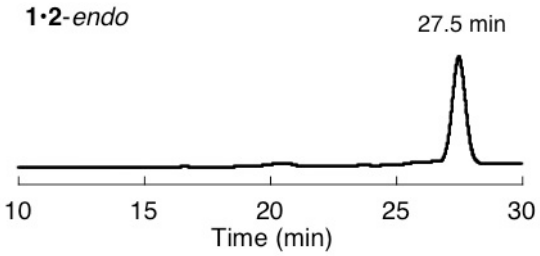

Fig. S1. HPLC chart of **1•2**-*endo* (RP-HPLC (column: YMC-Triart C18 column (250 mm × 4.6 mm I.D.), eluent: acetonitrile/water (containing 0.1 % TFA) = 25:75 to 80:20 over 40 min (linear gradient), flow rate = 1.0 mL/min, detection wavelength = 220 nm)).

2. Photograph and TEM image of FurTpa-BPh-F (1) hydrogel

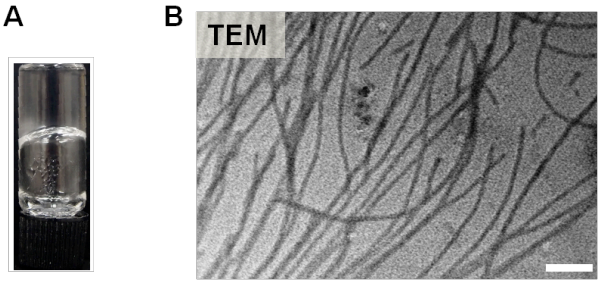

Fig. S2. (**A**) Photograph and (**B**) typical TEM image of FurTpa-BPh-F (**1**) hydrogel. Conditions: [FurTpa-BPh-F (**1**)] = 0.06 wt% (1.0 mM), 200 mM HEPES (pH 7.2). Scale bar is 200 nm.

3. Photographs of aqueous solutions of 1•2-*endo* incubated at room temperature

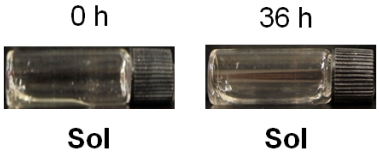

Fig. S3. Photographs of aqueous solutions of **1•2**-*endo* (18 mM, 200 mM HEPES (pH 7.2), 100 μL) before and after incubation at room temperature.

4. HPLC analysis of dissociation of 1•2-*endo* at 60 ºC and RT

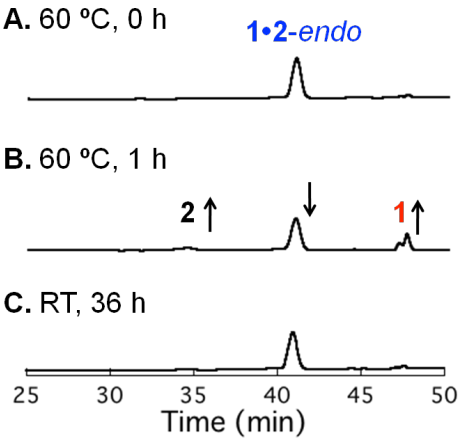

Fig. S4. HPLC traces of aqueous solutions of **1•2**-*endo* (18 mM, 200 mM HEPES (pH 7.2)) (**A**) before and (**B**) after heating at 60 ºC, and (**C**) after incubation at room temperature for 36 h. HPLC conditions: acetonitrile/water (containing 0.1 % TFA) = 0:100 to 80:20 over 50 min (linear gradient), flow rate = 1.0 mL/min, detection wavelength = 220 nm).

5. Aggregation property of 1•2-*endo* in aqueous media

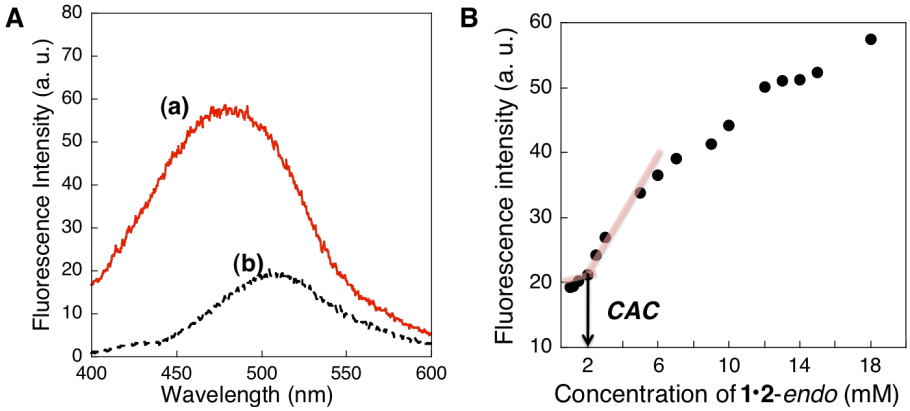

Fig. S5. (**A**) Fluorescence spectra (λ_{ex} = 375 nm) of 1-anilino-8-naphthalene sulfonate (ANS, 20 μM) in (**a**) the presence or (**b**) the absence of **1•2**-*endo* (18 mM). (**B**) Fluorescence intensity of ANS at 475 nm depending on the **1•2**-*endo* concentrations, which yielded ca. 2 mM as critical association concentration (*CAC*) at 25 ºC. Conditions: [**1•2**-*endo*] = 0–18 mM, 200 mM HEPES (pH 7.2).