Supplementary Material (ESI) for Organic and Biomolecular Chemistry

Supporting Information for

Construction and Transmembrane Dissociation Behavior of Supramolecular Assembly of Quinolylcyclodextrin with Porphyrin

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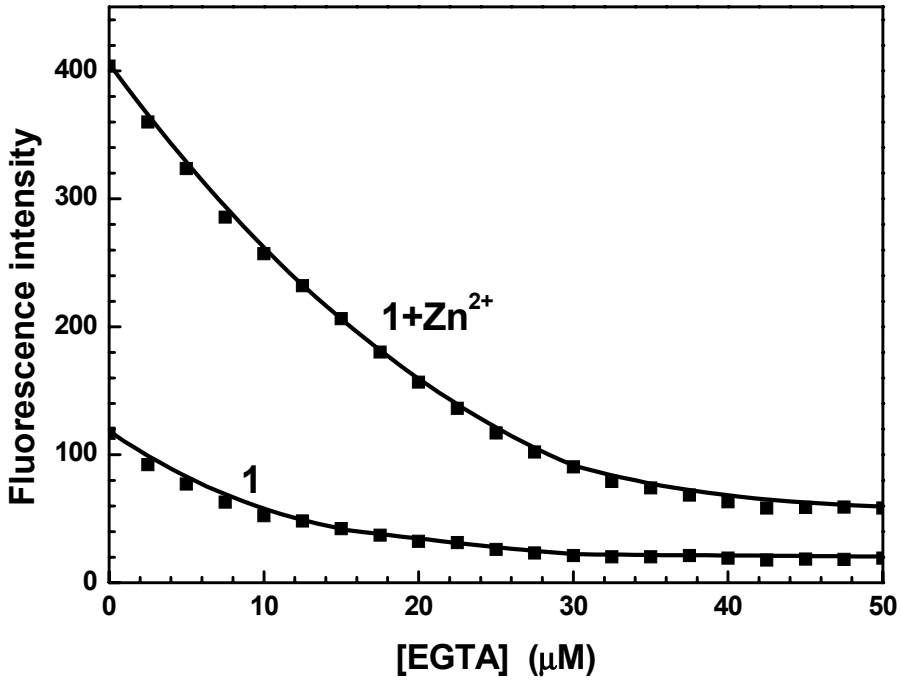

Figure S1: Fluorescence intensity changes of **1** (20 μmol L^{-1}) and **1**+Zn^{2+} system ([**1**] = 20 μmol L^{-1}, [Zn^{2+}] = 5 μmol L^{-1}) upon the titration of EGTA (ethylene glycol tetraacetic acid) with various amounts in aqueous buffer solution (pH 7.2, I = 0.1 mol L^{-1} $NaNO_3$, 25 °C, λ_{ex}=362 nm, λ_{em} = 502 nm).

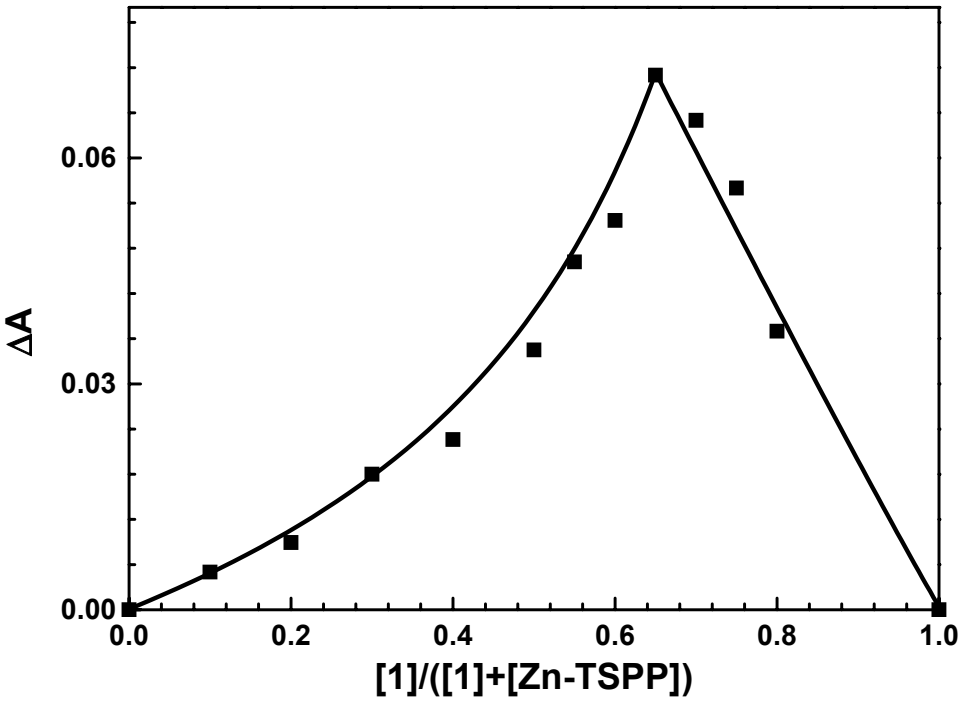

Figure S2. Job's plot of **1**/ZnTSPP system produced with data taken from UV-vis spectra at 556 nm in buffer solution (pH 7.20, I = 0.1 mol L^{-1} $NaNO_3$, 25 °C, [ZnTSPP] + [**1**] = 50 μmol L^{-1}).

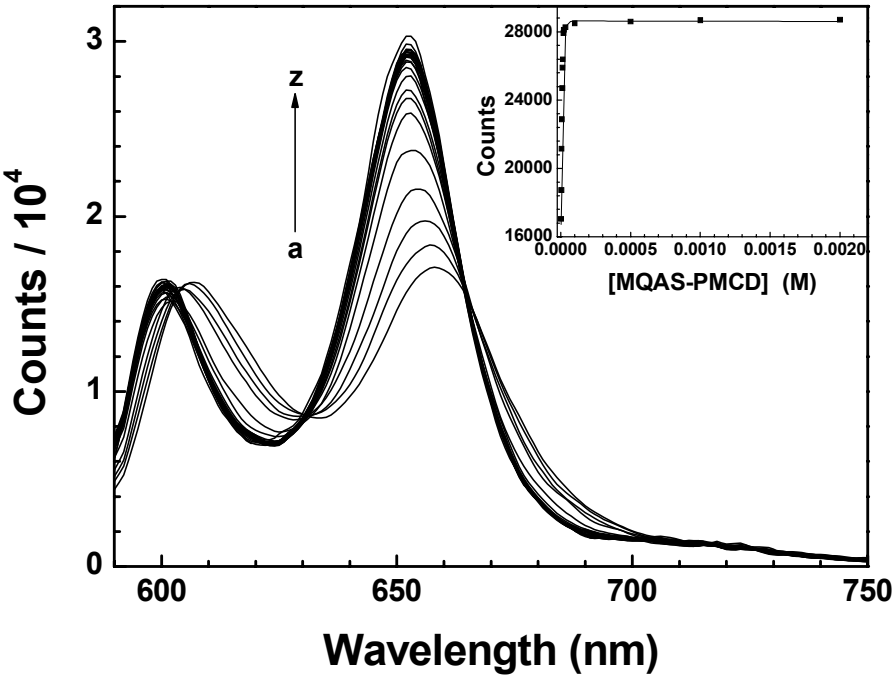

Figure S3. a) Fluorescence spectra of ZnTSPP (1.0×10^{-5} mol L^{-1}) upon addition of **1** (a to u, 0–4×10^{-5} mol L^{-1}; and v to z, 0.1, 0.3, 0.5, 1, 2 mmol L^{-1}) in buffer solution (pH 7.20, I = 0.1 mol L^{-1} $NaNO_3$, 25 °C, λ_{ex} = 556 nm). b) The nonlinear least-squares analysis of the differential intensity (ΔF) at 650 nm to calculate the complex formation constant (K).

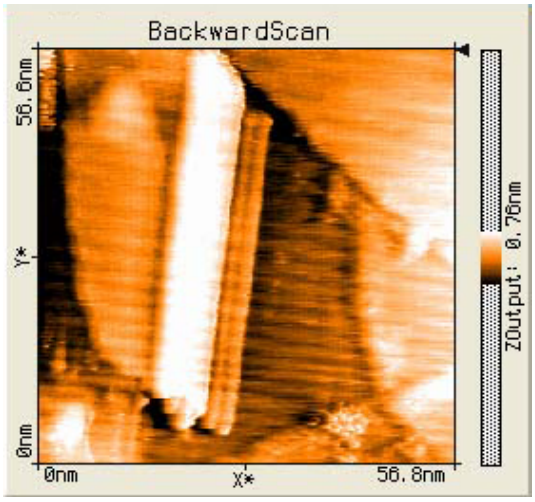

Figure S4. STM image of **2** on the HOPG surface.

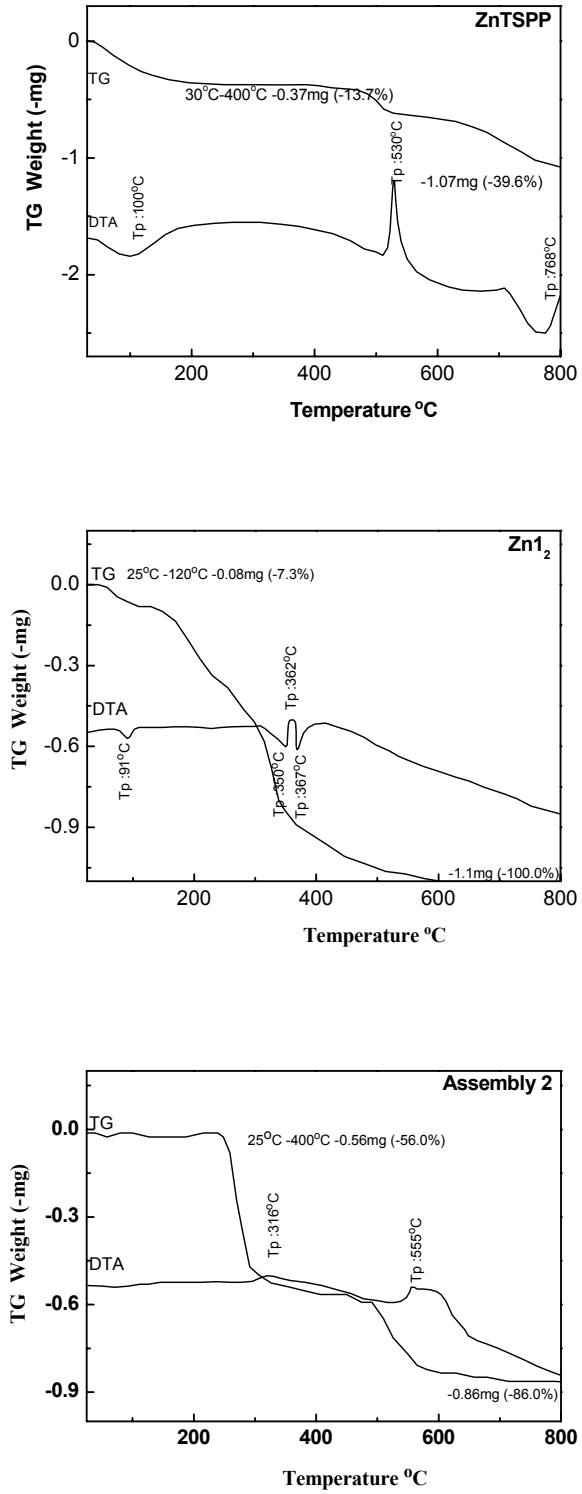

Figure S5. TG-DTA curves of a) ZnTSPP; b) Zn·**1**$_2$; c) assembly **2**.

TG-DTA analysis. The molecular weight of assembly **2** could be deduced from the TG curves (Figure S5).[1] Considering the very strong association constants between Zn^{2+} and **1**, we could deduce that the assembly chain should be terminated in the ZnTSPP or Zn·$\mathbf{1}_2$. On the other hand, considering the different thermal stability of ZnTSPP (ZnTSPP lost 39.6% of its weight below 800 °C) and Zn·$\mathbf{1}_2$ (Zn·$\mathbf{1}_2$ was decomposed completely below 800 °C) in the control experiment. We deduced that the remaining weight below 800 °C (14.0%) in the TG curve of 2 should be assigned to the residue of ZnTSPP. By defining the number of complex Zn·$\mathbf{1}_2$ as n, we can set up the following equation for the case of terminal group as ZnTSPP.

$$14.0\% \times [nM + (n + 1) \times 1088] = 60.4\% \times (n + 1) \times 1088$$

M (ca. 3681) is the molecular weight of Zn·$\mathbf{1}_2$. From this equation, we could deduce that the assembly chain composed of ca. 48 units of Zn·$\mathbf{1}_2$ and ZnTSPP was the major species contained in the assembly, and the molecular weight of assembly **2** could be calculated from $[nM + (n + 1) \times 1088]$ as ca. 2.3×10^5 g mol^{-1}. However, it should be noted that the TG-DTA analysis method to deduce the molecular weight of the inclusion polymer would suffer from a serious lack of sensitivity when the number of units increased.

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1 Liu, Y.; Chen, G.-S.; Chen, Y.; Zhang, N.; Chen, J.; Zhao, Y.-L. *Nano Lett.*, **2006**, *6*, 2196.

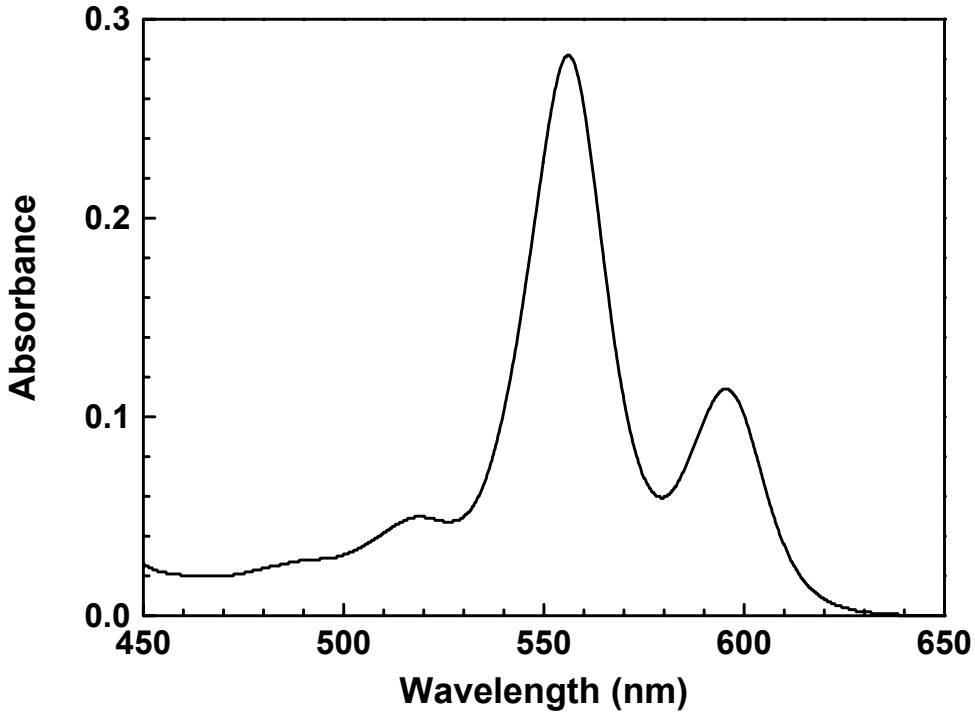

Figure S6. UV/vis absorbance of ZnTSPP (30 μmol L^{-1}) in aqueous buffer solution (pH 7.20, I = 0.1 mol L^{-1} $NaNO_3$, 25 °C).

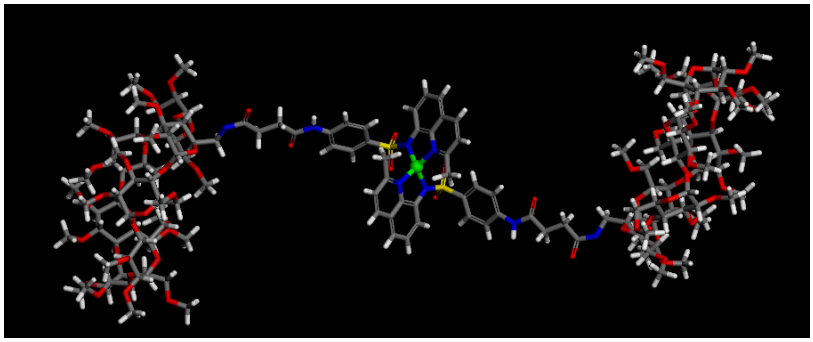

Figure S7. Optimized molecular modeling of Zn·$\mathbf{1}_2$. The geometries were optimized by the molecular dynamic method with the Dreiding force field.