

Supporting information

Encapsulation of Small Molecules by a Cavitand Porphyrin Self-assembled via Quadruple Hydrogen Bonds

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Experimental Section

Tetracarboxylcavitand•tetrapyridylporphyrin (**1•2**)

¹H-NMR (400 MHz, 1,1,2,2-tetrachloroethane-*d*₂) 16.20 (*s*, br, 4H, OH), 9.46 (*d*, 4H, 3-pyridyl), 8.66 (*s*, 8H, pyrrole α -H), 8.41-8.32 (*m*, 4H, 6-pyridyl + 5-pyridyl), 8.05 (*t*, 4H, 4-pyridyl), 7.29-6.96 (*m*, 20H, CHCH₂CH₂C₆H₅), 6.60 (*s*, 4H, Ar-H meta to OCH₂O), 4.96 (*d*, 4H, *J* = 7.8 Hz, outer OCH₂O), 4.38 (*t*, 4H, *J* = 7.8 Hz, CHCH₂CH₂C₆H₅), 3.05 (*d*, 4H, *J* = 7.8 Hz, inner OCH₂O), 2.40-2.16 (*m*, 16H, CHCH₂CH₂C₆H₅), -3.22 (*s*, 2H, NH); ESI-MS Found: *m/z* 1747.6. Calcd for C₁₀₈H₈₂N₈O₁₆: [M+H]⁺ 1748.8.

Detection of host-guest complexation by ¹H and ¹³C-NMR spectroscopy

1•2 (4 mM) was dissolved in 1,1,2,2-tetrachloroethane-*d*₂ (0.5 mL) and the guest molecule was directly bubbled or added into a gas-tight NMR tube. ¹H NMR spectra were measured on a JEOL JNM-EX400 spectrometer at various guest concentrations (5~50 mM) at 298 K. The amounts of free and encapsulated guest molecules were determined by the integration of their proton signals relative to the host signals [**1•2**; at δ = 9.46 ppm (4 protons)]. [free**1•2**] values were estimated from the amount of trapped guest molecules. The 1:1 binding constants were calculated according to the equation, $K = [\text{Host} \cdot \text{Guest}] / ([\text{Host}_{\text{free}}][\text{Guest}_{\text{free}}])$.

Measurement of exchange rates (2D-EXSY)

1 (3.8 mM) and **2** (10 mM) were dissolved in 1,1,2,2-tetrachloroethane-*d*₂ (0.7 mL). Then, ethylene gas was directly bubbled in a gas-tight NMR tube (encapsulated ethylene = 3.4 mM, free ethylene = 8.1 mM). NOESY spectra were measured on a JEOL ECA-500 spectrometer (observed range: 1 \pm 5 ppm or 7 \pm 3 ppm, data points: 512 x 256, mixing time = 0.3 or 0 s, relaxation delay = 30 s, at 298 K). Exchange rates were obtained from cross- and diagonal-peak intensities using ExsyCalc software (MestReC). *T*₁ measurement was carried out for the same solution. Followings are obtained τ values (sec): NH (**1•2**), 0.59; NH (**2**), 1.07; ethylene (encapsulated), 3.97; ethylene (free), 5.99; H_i (**1•2**), 0.55; H_o (**1•2**), 0.59; pyridine signals (**1•2**), 1.57 ~ 2.27; pyridine signals (**2**), 1.64 ~ 2.18; pyrrole- β (**1•2**), 2.34; pyrrole- β (**2**), 2.20.

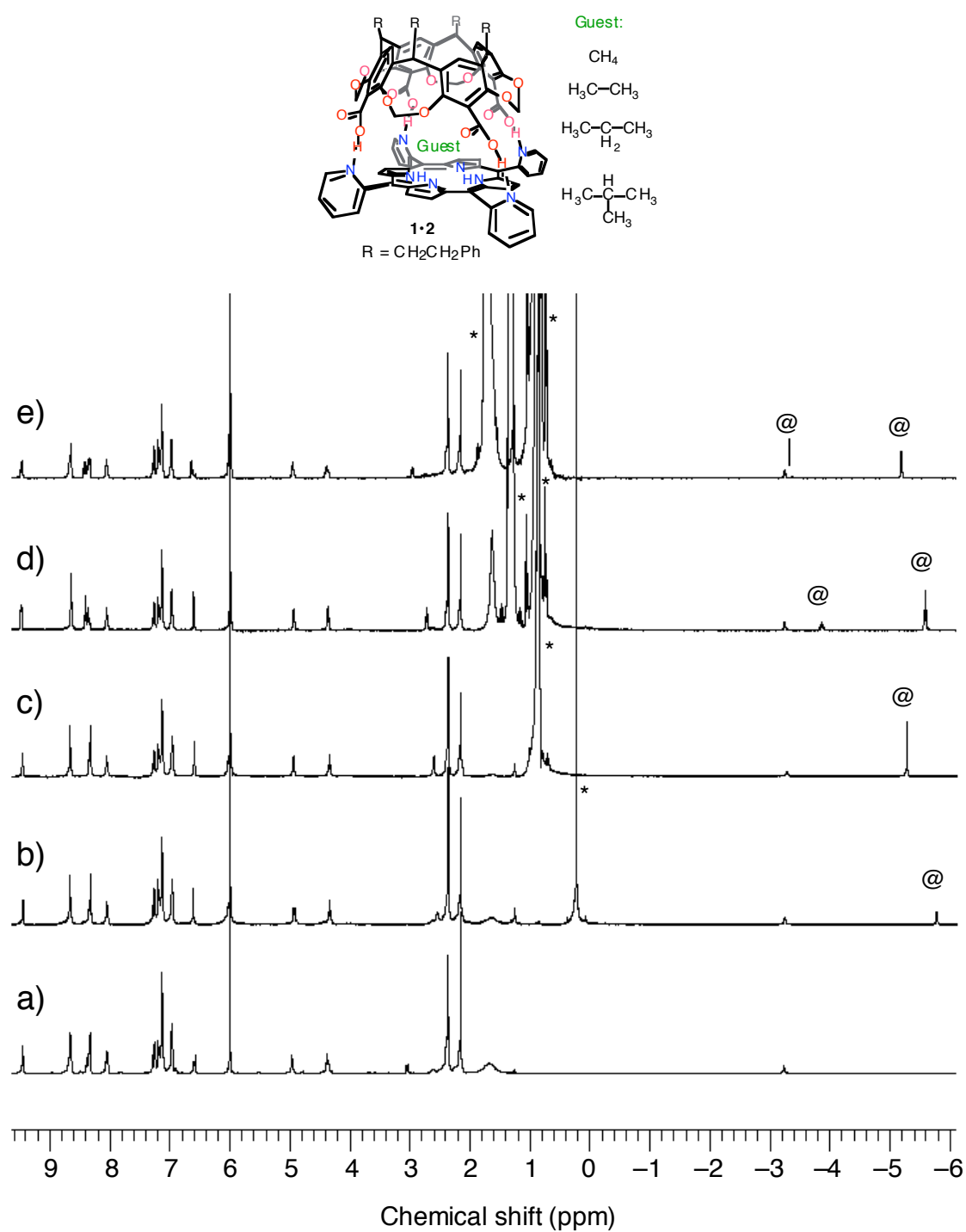


Figure S1. ^1H NMR spectra of **1•2** (2 mM) with various hydrocarbons in $1,1,2,2\text{-tetrachloroethane-}d_2$ at 298 K. a) **1•2**, b) with methane, c) with ethane, d) with propane, e) 2-methylpropane. * denotes free hydrocarbons. @ denotes encapsulated guest signals.

Table S1. ^1H NMR chemical shifts δ (ppm)^a of free and encapsulated guests in **1•2** in 1,1,2,2-tetrachloroethane- d_2 at 298 K.

| guest | δ_{free} | $\delta_{\text{encapsulated}}$ |
|--------------------|----------------------------------|--------------------------------|
| methane | 0.15 | −5.76 |
| acetylene | 1.91 | −4.51 |
| ethylene | 5.39 | −0.80 |
| ethane | 0.85 | −5.28 |
| propane | 1.31, 0.88 | −3.81, −5.57 |
| 2-methylpropane | 1.72, 0.91 | −4.34, −5.17 |
| cyclopentane | 1.52 | −4.60 |
| benzene | 7.43 | − ^b |
| cyclohexane | 1.27, 0.89 | − ^b |
| methanol | 3.49, − ^c | −3.13, − ^c |
| ethanol | 3.61, 1.14, − ^c | −2.71, −4.80, −3.07 |
| 2-propanol | 3.99, 1.19, − ^c | −1.45, −5.28, − ^c |
| 1-propanol | 3.49, 1.53, 0.93, − ^c | − ^b |
| furan | 7.50, 6.44 | 1.45, 0.19 |
| tetrahydrofuran | 3.69, 1.82 | −2.76, −4.28 |
| 1,3-oxirane | 4.88, 3.86 | −1.18, −3.19 |
| 1,3-oxirane-2-one | 4.51 | −2.95 |
| 1,3,5-trioxirane | 5.15 | −1.03 |
| dichloromethane | 5.31 | −0.47 |
| chloroform | 7.30 | 1.23 |
| dimethyl sulfide | 3.34 | −3.21 |
| dimethyl sulfoxide | 2.57 | −3.70 |
| dimethyl disulfide | 2.43 | −4.75 |
| dimethyl sulfone | 2.96 | − ^b |
| acetonitrile | 1.98 | −3.42 |
| propionitrile | 2.32, 1.23 | −3.44, −5.43 |
| fumaronitrile | 6.31 | 0.87 |
| acetone | 2.10 | −4.44 |
| 2-butanone | 2.42, 2.11, 1.01 | − ^b |
| ethyl acetate | 2.91, 2.83 | − ^b |

[a] Chemical shifts were based on TMS. [b] Not encapsulated. [c] Signals of OH protons were not detected.

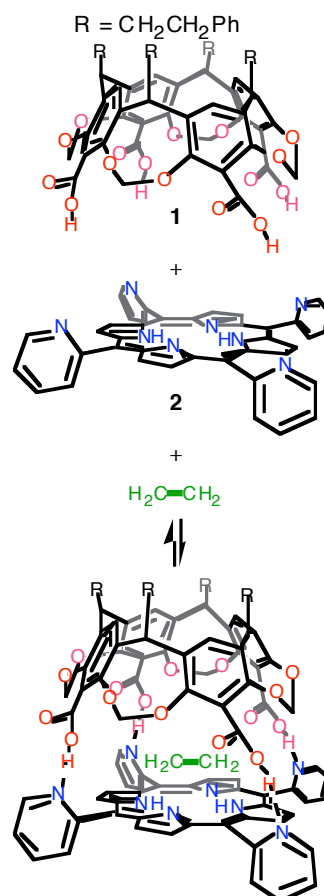
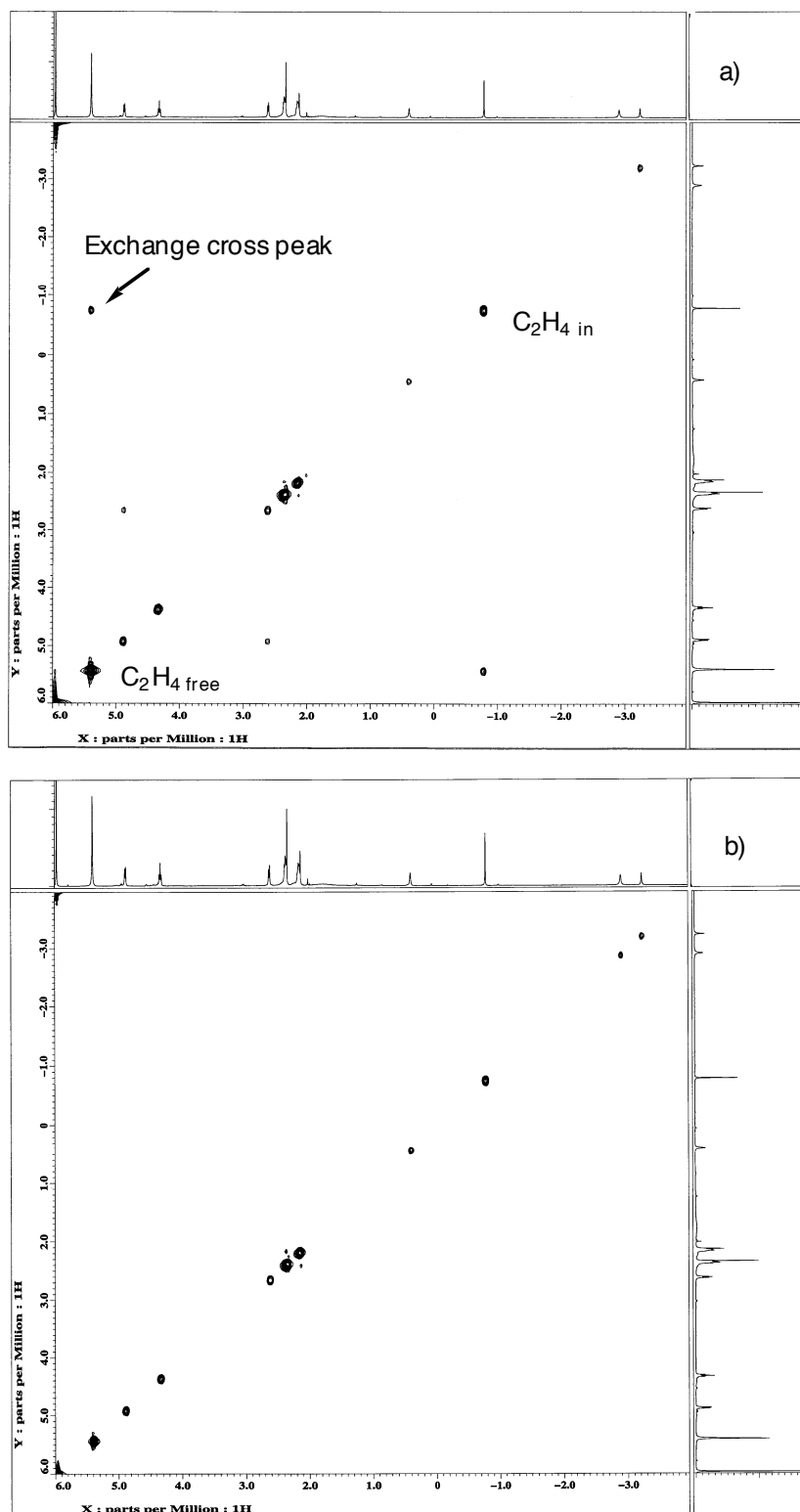


Figure S2. NOESY spectra of **1** (3.8 mM), **2** (10 mM) and ethylene (free 8.1 mM, encapsulated 3.4 mM) in tetrachloroethane- d_2 at 298 K. a) $-4 \sim 6$ ppm, mixing time = 0.3 s, b) $-4 \sim 6$ ppm mixing time = 0 s.

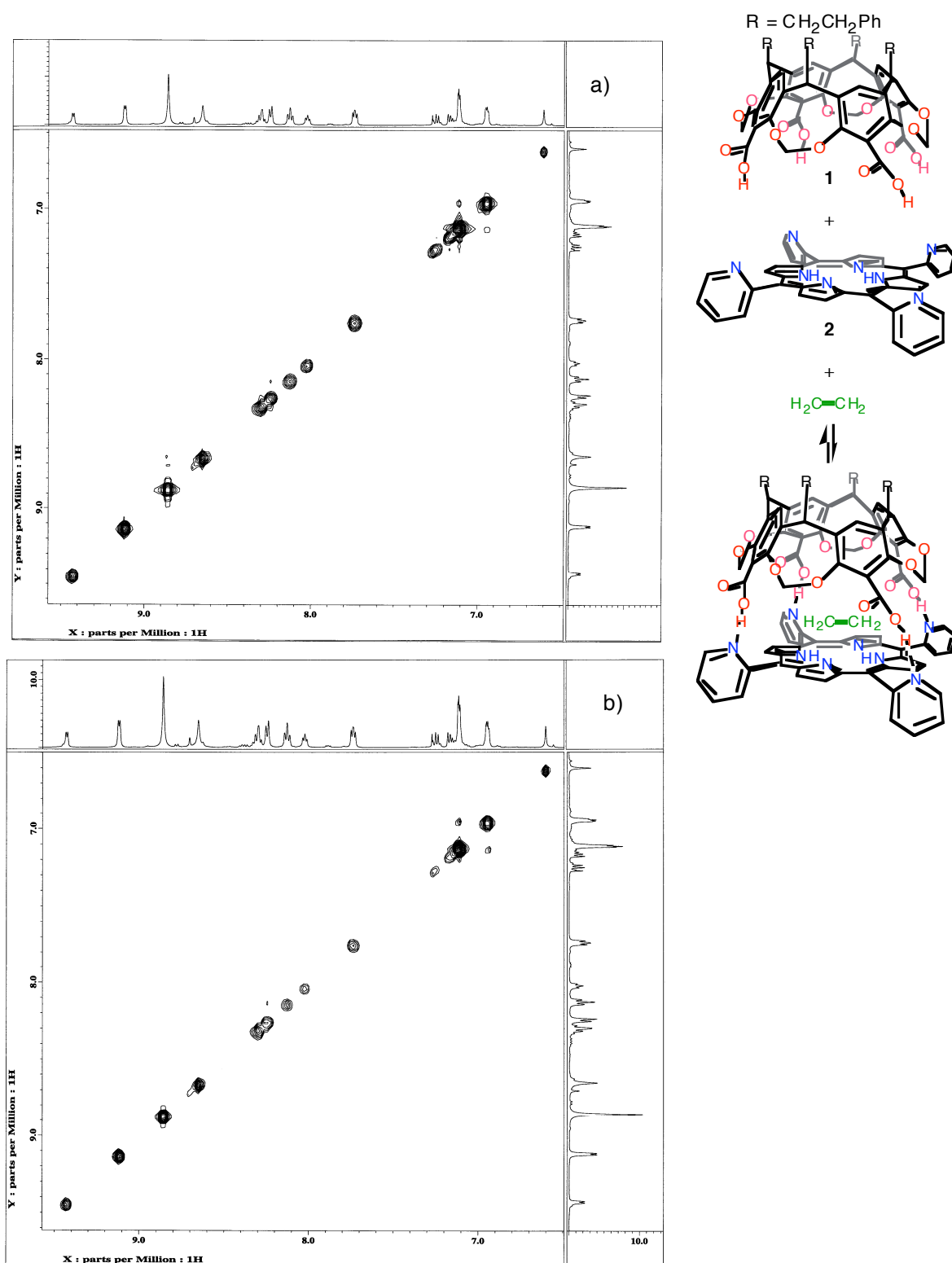


Figure S3. NOESY spectra of **1** (3.8 mM), **2** (10 mM) and ethylene (free 8.1 mM, encapsulated 3.4 mM) in tetrachloroethane- d_2 at 298 K. a) 6.5 ~ 9.5 ppm, mixing time = 0.3 s. b) 6.5 ~ 9.5 ppm, mixing time = 0 s.