Supplementary Material (ESI) for Chemical Communications

Supporting Information

Discrete, multi-component complexes with cucurbit[8]uril in the gas-phase

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All starting materials were purchased from Alfa Aesar and Sigma Aldrich and used as received unless stated otherwise. **CB[8]** and **NpPEG** (2000 g/moL) were prepared according to previously published procedures.[1,2]

^{1}H and ^{13}C NMR spectra were recorded on Bruker Avance 500 BB-ATM and Bruker Avance 500 TCI (both 500 MHz) spectrometers.

Nano-electrospray mass spectra were recorded on a LCT MS (Micromass, UK) equipped with nanoflow Z-spray source. Data were analyzed using Masslynx 4.0 software (Micromass, UK). The spectra were obtained with the following parameters: needle voltage = 1.5 kV, skimmer cone voltage = 10-30 V and skimmer offset = 5 V. It should be noted that absolute intensity of peaks in electrospray spectra is dependent on the ionization efficiency of the species. It is valid, however, to make relative comparisons between the intensity of the four host-guest complexes.

Synthesis of (**MVdimer** $\cdot$ 4Br$^-$): A 500 mL RB flask was charged with **mBIPY** (3.6 g, 12 mmol), 1,2-bis(2-bromoethoxy)ethane (0.8 g, 3 mmol) and acetonitrile (200 mL). The reaction mixture was heated to reflux for 48 h under a nitrogen atmosphere. A red precipitate was collected and dissolved in the minimum volume of H_20 and a concentrated aqueous solution of NH_4PF_6 was added until no further precipitation was observed. The precipitate was filtered off, washed with water and recrystallized from water to give pure **MVdimer** $\cdot$ 4PF$_6^-$. The counterions were exchanged to Br$^-$ using tetraoctylammonium bromide to yield **MVdimer** $\cdot$ 4Br$^-$ as a yellow solid (0.55 g, 24%). ^{1}H NMR (D_2O): δ = 9.06 (d, 4H), 9.00 (d, 4H), 8.51 (d, 4H), 8.47 (d, 4H), 4.86 (t, 4H), 4.46 (s, 6H), 4.04 (t, 4H), 3.64 (s, 4H) ppm.

1-Methyl-4,4'-bipyridinium iodide (**mBIPY**): A 500 mL RB flask was charged with 4,4'-bipyridine (10.0 g, 64 mmol) in 150 mL dichloromethane. Methyl iodide (5.0 mL, 81 mmol) in dichloromethane (50 mL) was added drop-wise to the stirred flask. The mixture was refluxed for 1 hour and left to cool with stirring. The yellow product was filtered off, purified by recrystallization from methanol and finally washed with ether (15.44 g, 81%). ^{1}H NMR (d_3-MeCN): δ = 8.84 (d, 2H), 8.79 (d, 2H), 8.32 (d, 2H), 7.80 (d, 2H), 4.35 (s, 3H) ppm.

Synthesis of tri(ethylene glycol) 2-naphthyl ether (**NpTEG**): 2-Naphthol (14.4 g, 0.1 mol), potassium hydroxide (5.6 g, 0.1 mol) and 2-(2-(2-Chloroethoxy)ethoxy)ethanol (16.8 g, 0.1 mol) were dissolved in 100 mL butanol and refluxed for 16 h. The mixture was then filtered and the solvent removed under vacuum. The product was then isolated by column chromatography (16.1 g, 58%). ^{1}H NMR (d_6-DMSO): δ = 7.82 (m, 3H), 7.46 (t, 1H), 7.35 (t, 1H), 7.33 (s, 1H), 7.18 (d, 1H), 4.57 (t, 1H), 4.22 (t, 2H), 3.82 (t, 2H), 3.63 (m, 2H), 3.57 (m, 2H), 3.50 (m, 2H), 3.45 (t, 2H) ppm.

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References

[1] J. Kim, I. S. Jung, S. Y. Kim, E. Lee, J. K. Kang, S. Sakamoto, K. Yamaguchi, K. Kim, *J. Am. Chem. Soc.* **2000**, *122*(3), 540–541.

[2] U. Rauwald, O. A. Scherman, *Angew. Chem. Int. Ed.* **2008**, *47*(21), 3950–3953.

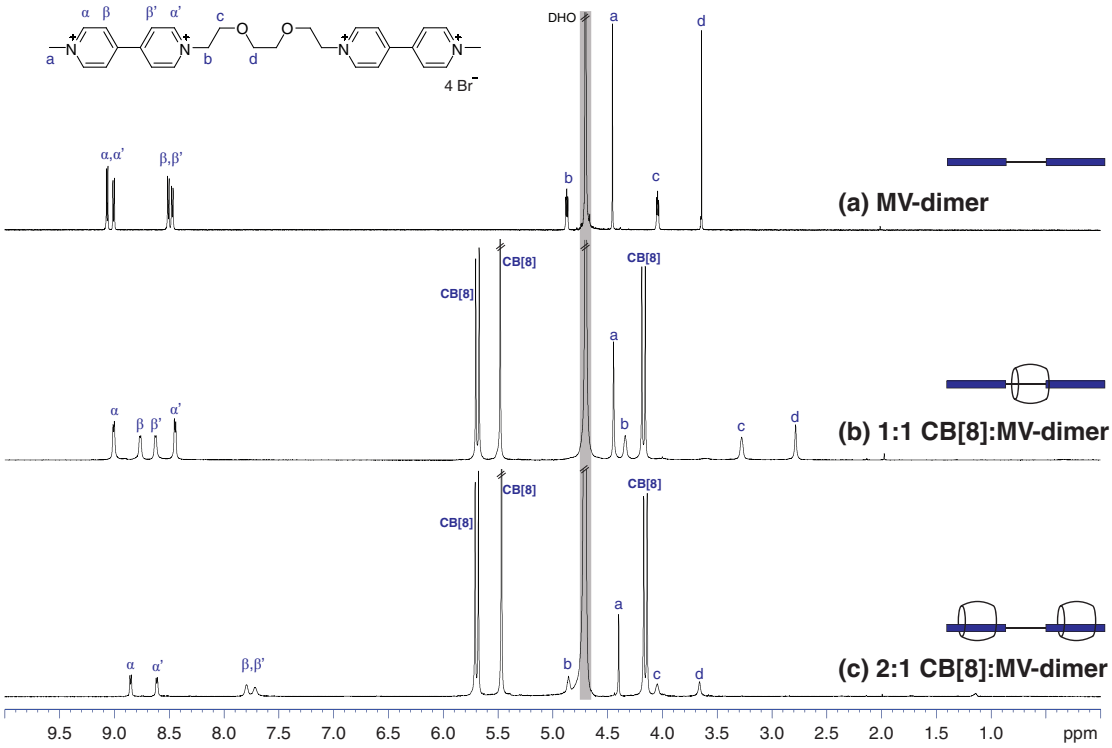

Figure S 1: ^{1}H NMR spectra (500 MHz) of **MVdimer** in D_2O (a) before and (b) after addition of 1 equiv. of **CB[8]** or (c) after addition of 2 equiv. of **CB[8]**.

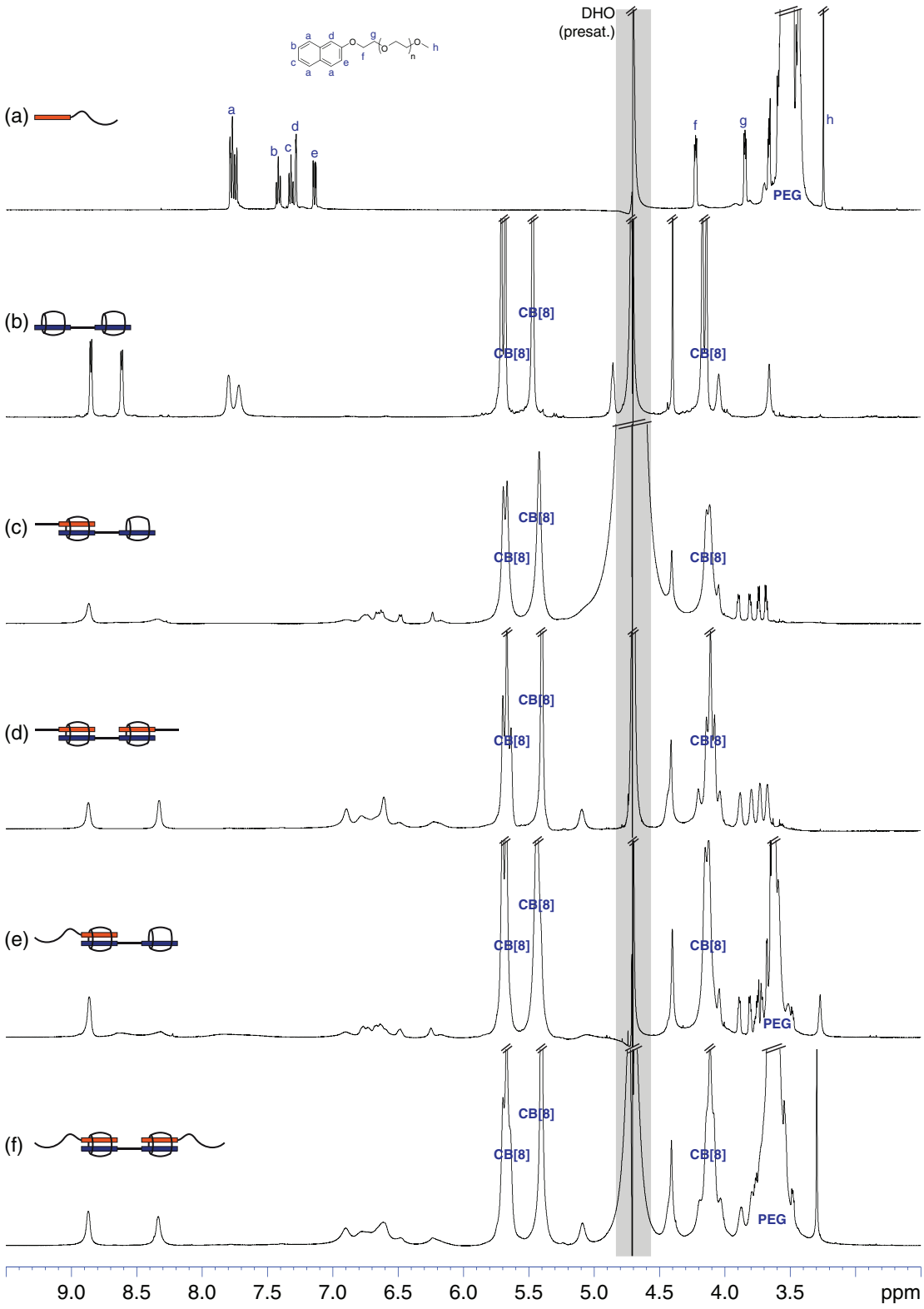

Figure S 2: ^{1}H NMR spectra (500 MHz) in D_2O of **NpPEG** (a) and of the complexes **CB[8]**:**MVdimer** 2:1 (b), **CB[8]**:**MVdimer**:**NpTEG** 2:1:1 (c), **CB[8]**:**MVdimer**:**NpTEG** 2:1:2 (d), **CB[8]**:**MVdimer**:**NpPEG** 2:1:1 (e) as well as **CB[8]**:**MVdimer**:**NpPEG** 2:1:2 (f).

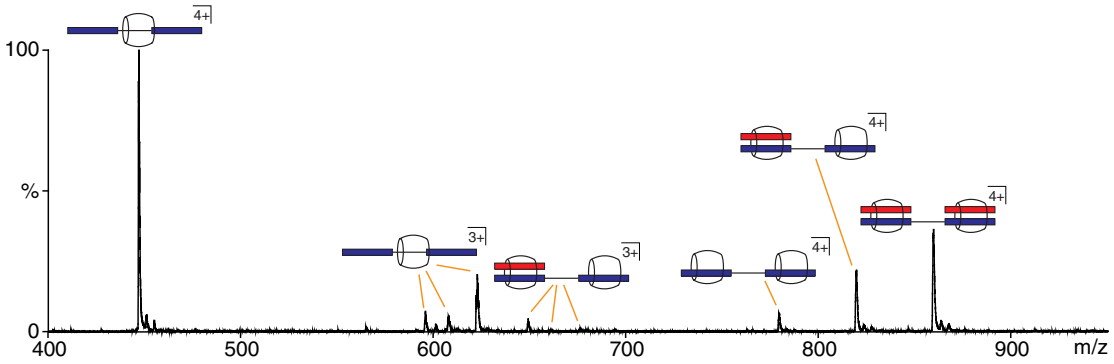

Figure S 3: ESI MS spectrum of a 1:1:1 **CB[8]**:**MVdimer**:**DNp** aqueous solution.

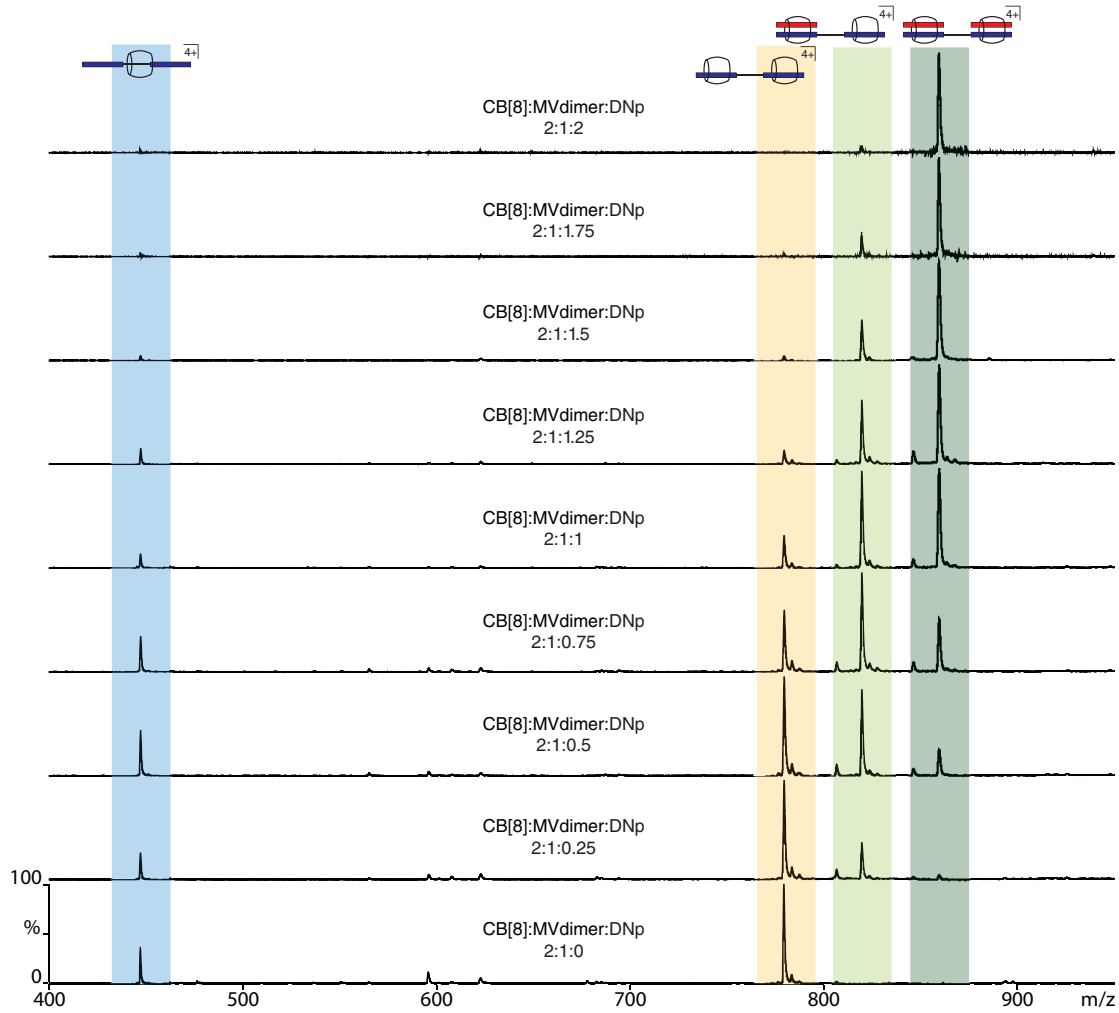

Figure S 4: ESI mass spectra for the titration of a 2:1 **CB[8]**: **MVdimer** solution with **DNp**, from 0 to 2 equivalents.