

# Photoinduced Interruption of Interannular Cooperativity for Delivery of Cationic Guests in Water

Radoslav Z. Pavlović,<sup>[a]</sup> Sarah E. Border,<sup>[a]</sup> Yiming Li,<sup>[b]</sup> Xiaopeng Li,<sup>[b]</sup> Jovica D. Badjić<sup>[a]\*</sup>

<sup>[a]</sup>Department of Chemistry & Biochemistry, The Ohio State University, 100 West 18th Avenue, 43210 Columbus, Ohio (USA)

<sup>[b]</sup>Department of Chemistry, University of South Florida, 4202 E. Fowler Avenue, 33620 Tampa, Florida (USA)

E-mail: [badjic.1@osu.edu](mailto:badjic.1@osu.edu)

## SUPPORTING INFORMATION

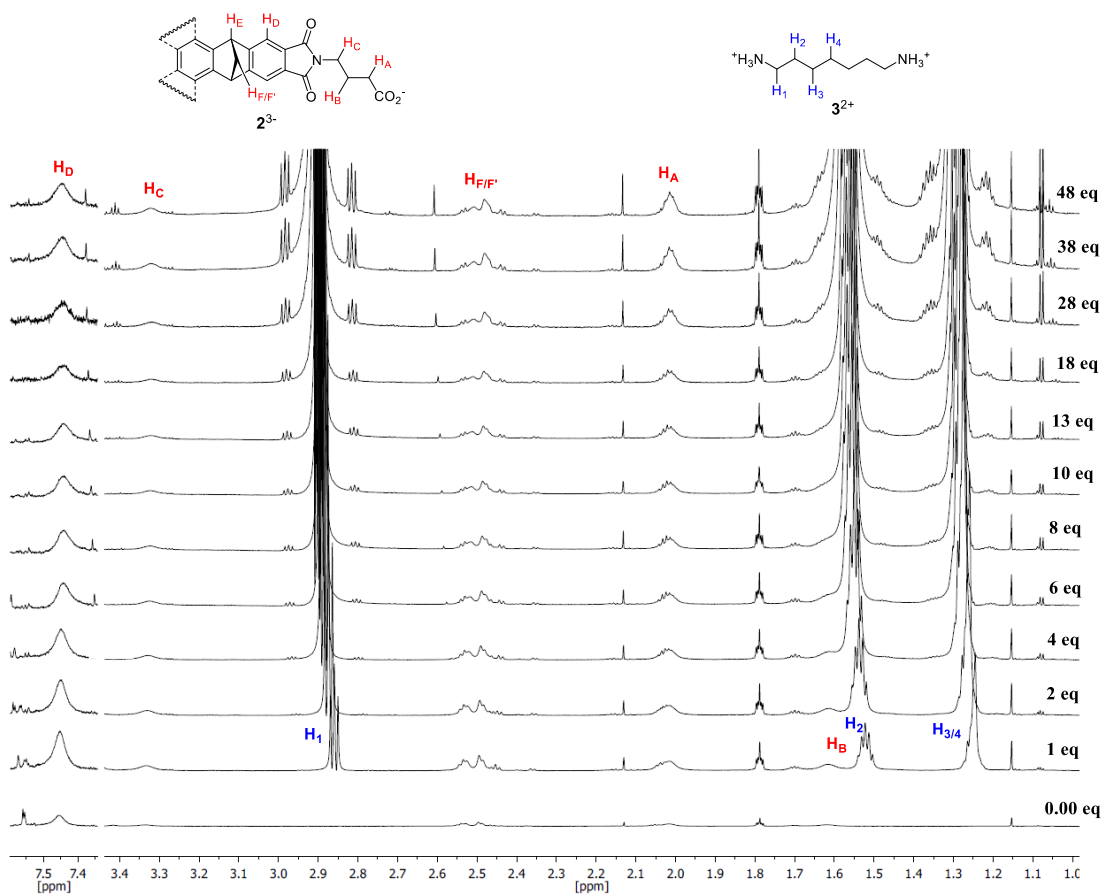
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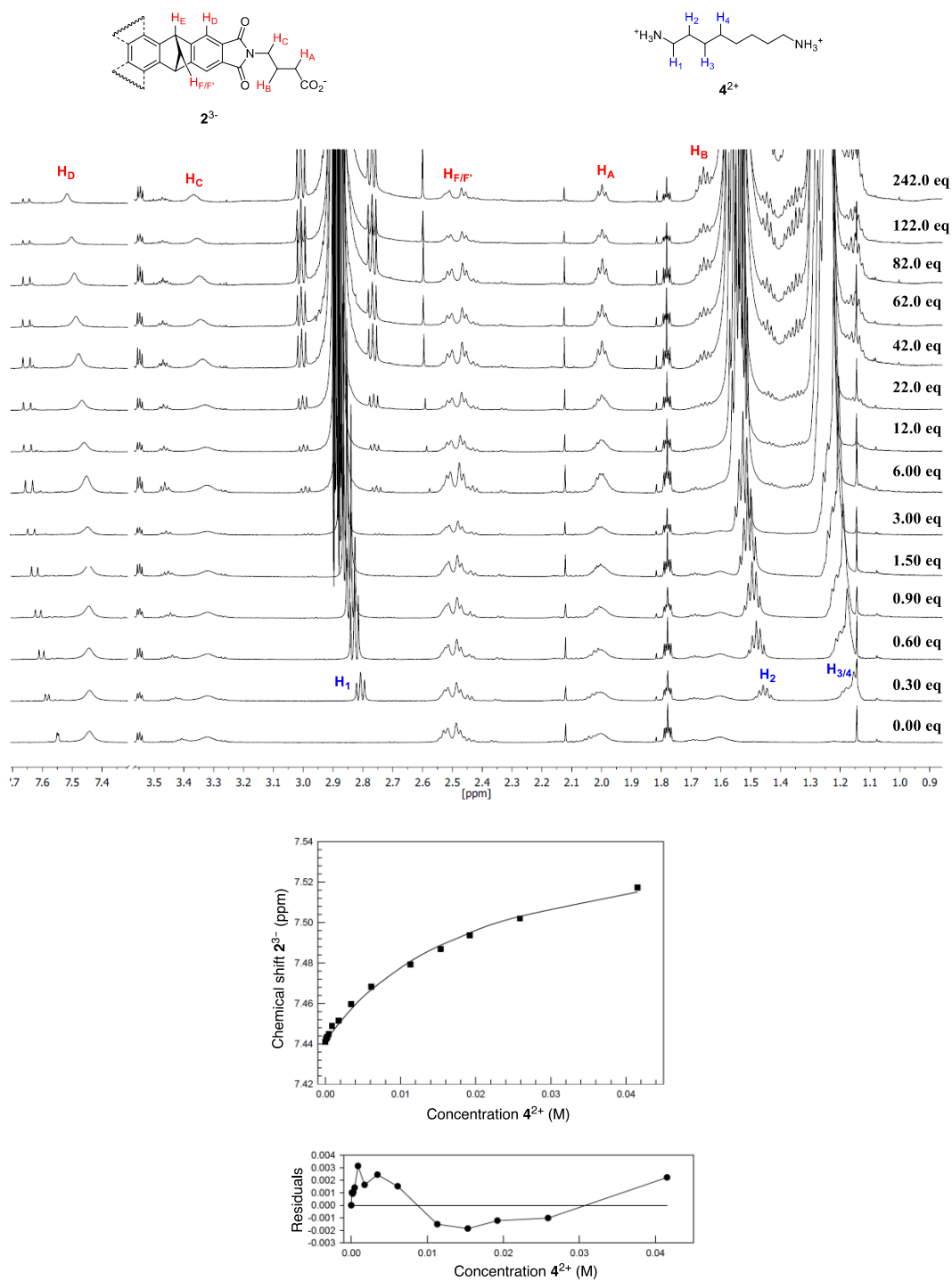
## General Information

All chemicals were purchased from commercial sources and used as received unless stated otherwise. Basket **1** was synthesized according to the procedure recently reported by our group (see: *Chem. Eur. J.* **2019**, *25*, 273-279). NMR experiments were performed with Bruker 600 (5 mm Triple-resonance Inverse (TXI) cryoprobe with Z-Gradients), 700 (5 mm Triple-resonance Observe (TXO) cryoprobe with Z-Gradients) and 850 MHz (5mm Triple-resonance Inverse (TCI) cryoprobe with Z-Gradients) spectrometers. All NMR samples were contained in class B glass NMR tubes (Wilmad Lab Glass). <sup>1</sup>H NMR data were collected using excitation sculpting perfect echo pulse sequence for water suppression. For 2D homonuclear experiments, we typically used a spectral width of 2048 × 512 complex points in F2 and F1 dimensions. NOESY spectra shown in the main text were recorded using the Bruker zero-quantum suppression sequence noesygpphzs (see *Angew. Chem. Int. Ed.*, **2003**, *42*, 3938–3941) with minor modifications to improve water suppression and reduce radiation damping at high magnetic fields equipped with cryoprobes. Zero-quantum suppression was achieved by the simultaneous application of a 20 ms adiabatic Chirp pulse with a B1\_max of 1.545 kHz and a square gradient of about 0.7 G/cm at the beginning of the NOESY mixing time. Bipolar gradients with a strength of 0.1 G/cm were applied during the indirect acquisition time to suppress radiation damping. A 50 Hz B1 field was used for additional water suppression. ESI-TOF MS was recorded on a Waters Synapt G2 mass spectrometer, using a solution of 1 mg B-Glu and 0.169 mg 1,10-diaminodecane (1:1) in 1 mL water (pH=7, adjusted with ammonium hydroxide).

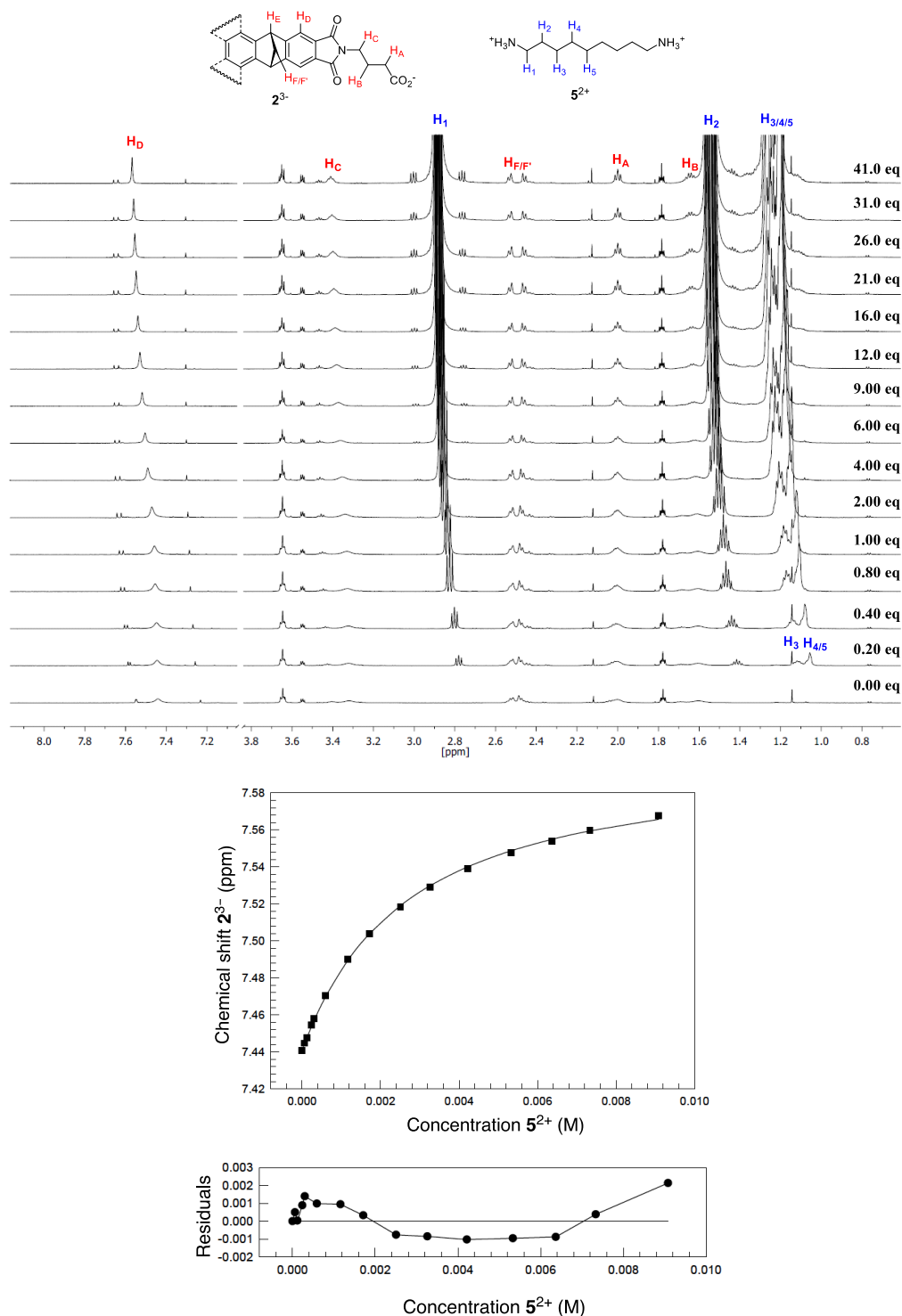
## NMR Titrations



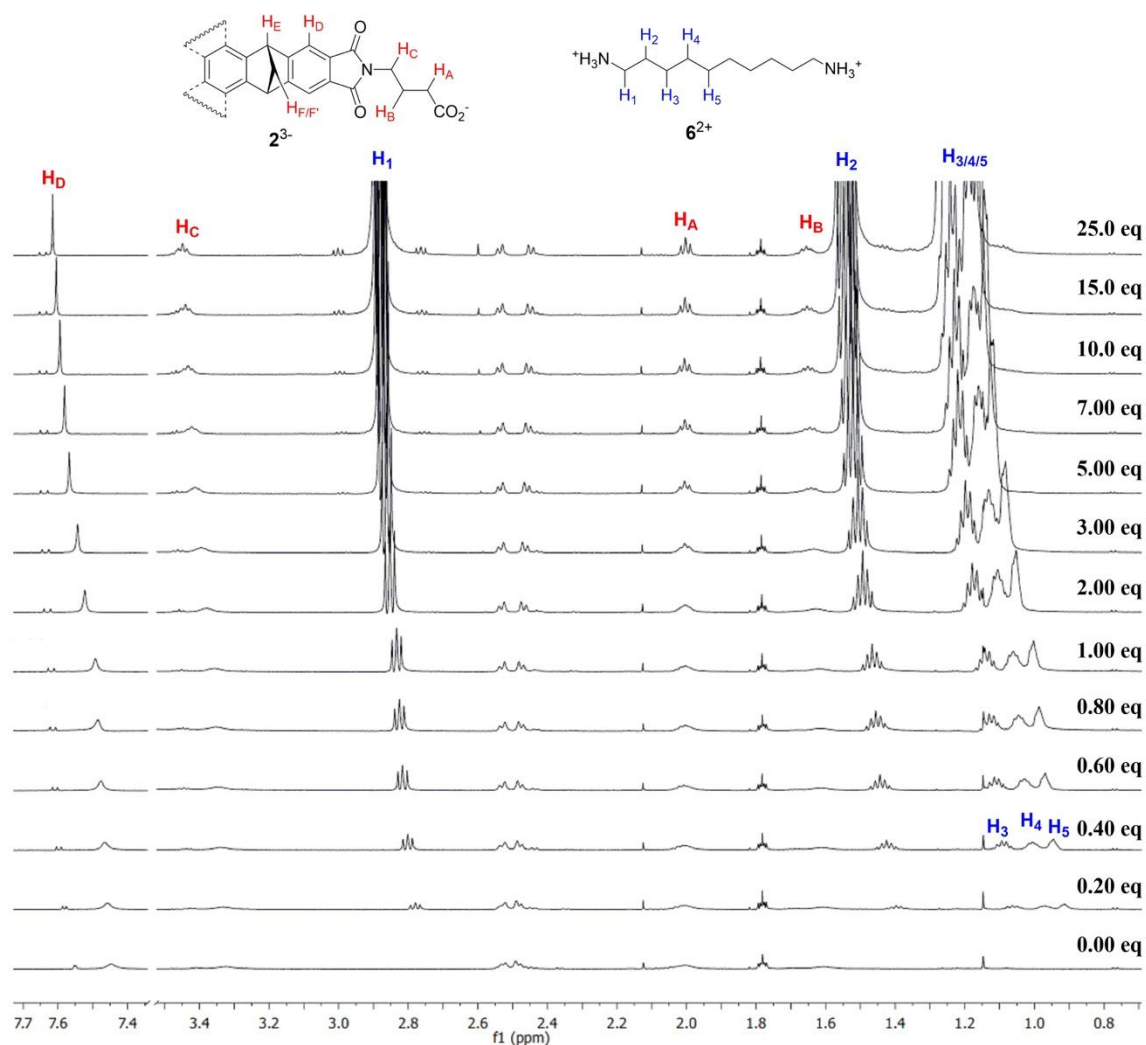
**Figure S1.** (Top) Water suppression  $^1\text{H}$  NMR spectra (850 MHz, 298 K; 30 mM phosphate buffer at  $\text{pH} = 7.0 \pm 0.1$ , 10%  $\text{D}_2\text{O}$ ) of 0.30 mM basket  $2^{3-}$  obtained upon an incremental addition of 2.0, 10.0 and 100 mM solutions of  $3^{2+}$  (30 mM phosphate buffer at  $\text{pH} = 7.0 \pm 0.1$ ). The number of molar equivalents of  $3^{2+}$  are shown on the right.



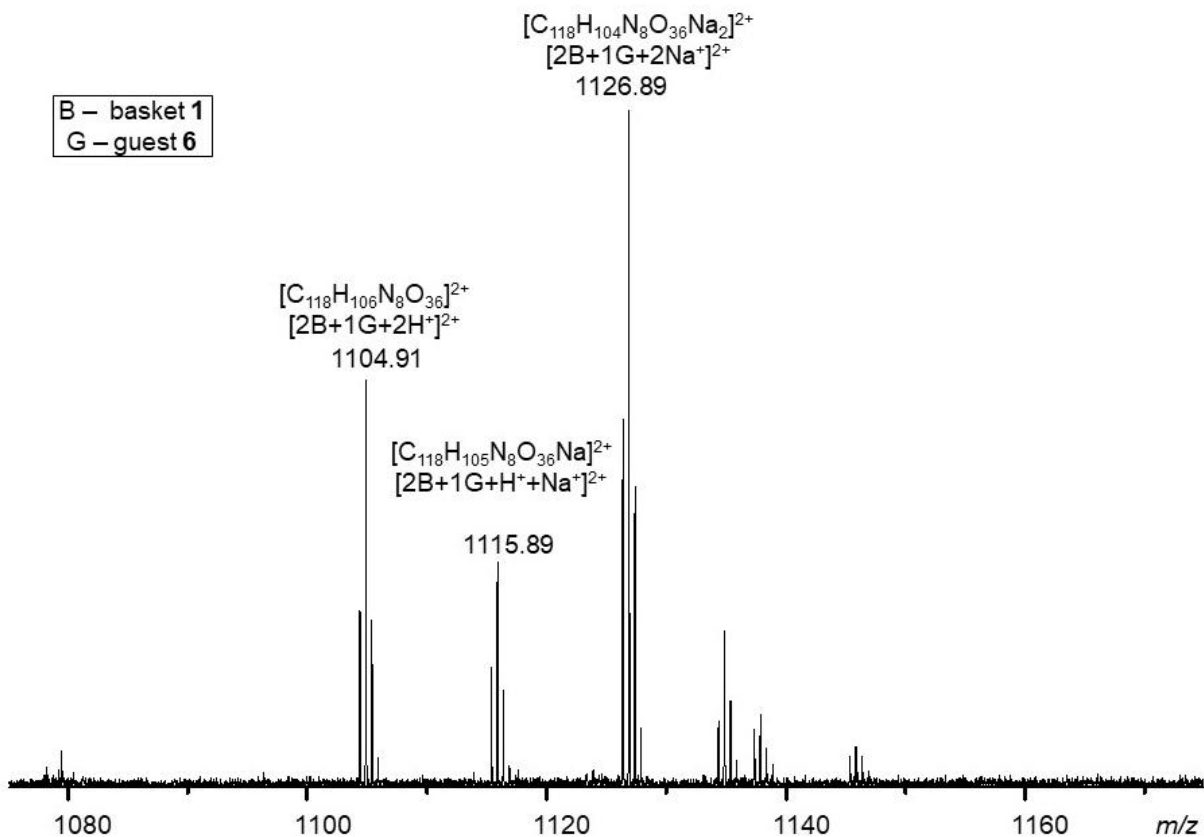
**Figure S2.** (Top) Water suppression  $^1\text{H}$  NMR spectra (600 MHz, 298 K; 30 mM phosphate buffer at pH = 7.0  $\pm$  0.1, 10%  $\text{D}_2\text{O}$ ) of 0.50 mM basket  $2^{3-}$  obtained upon an incremental addition of 2.0, 10.0 mM, 78.0 mM solutions of  $4^{2+}$  (30 mM phosphate buffer at pH = 7.0  $\pm$  0.1). The number of molar equivalents of  $4^{2+}$  are shown on the right. (Bottom) Nonlinear least-square analysis of  $^1\text{H}$  NMR binding data corresponding to the formation of  $[\mathbf{4}^{\mathbf{2+}}\mathbf{2}^{\mathbf{3-}}]^-$  complex. The data were fit to 1:1 binding model (SigmaPlot) to give  $K_1 = 52 \pm 5 \text{ M}^{-1}$ ; the residual distribution is shown below the binding isotherm.



**Figure S3.** (Top) Water suppression  $^1\text{H}$  NMR spectra (600 MHz, 298 K; 30 mM phosphate buffer at pH =  $7.0 \pm 0.1$ , 10%  $\text{D}_2\text{O}$ ) of 0.30 mM basket  $2^{3-}$  obtained upon an incremental addition of 2.0 mM and 33.0 mM solutions of  $5^{2+}$  (30 mM phosphate buffer at pH =  $7.0 \pm 0.1$ ). The number of molar equivalents of  $5^{2+}$  are shown on the right. (Right) Nonlinear least-square analysis of  $^1\text{H}$  NMR binding data corresponding to the formation of  $[\mathbf{5c2}]^-$  complex. The data were fit to 1:1 binding model (SigmaPlot) to give  $K_1 = 408 \pm 11 \text{ M}^{-1}$ ; the residual distribution is shown below the binding isotherm.

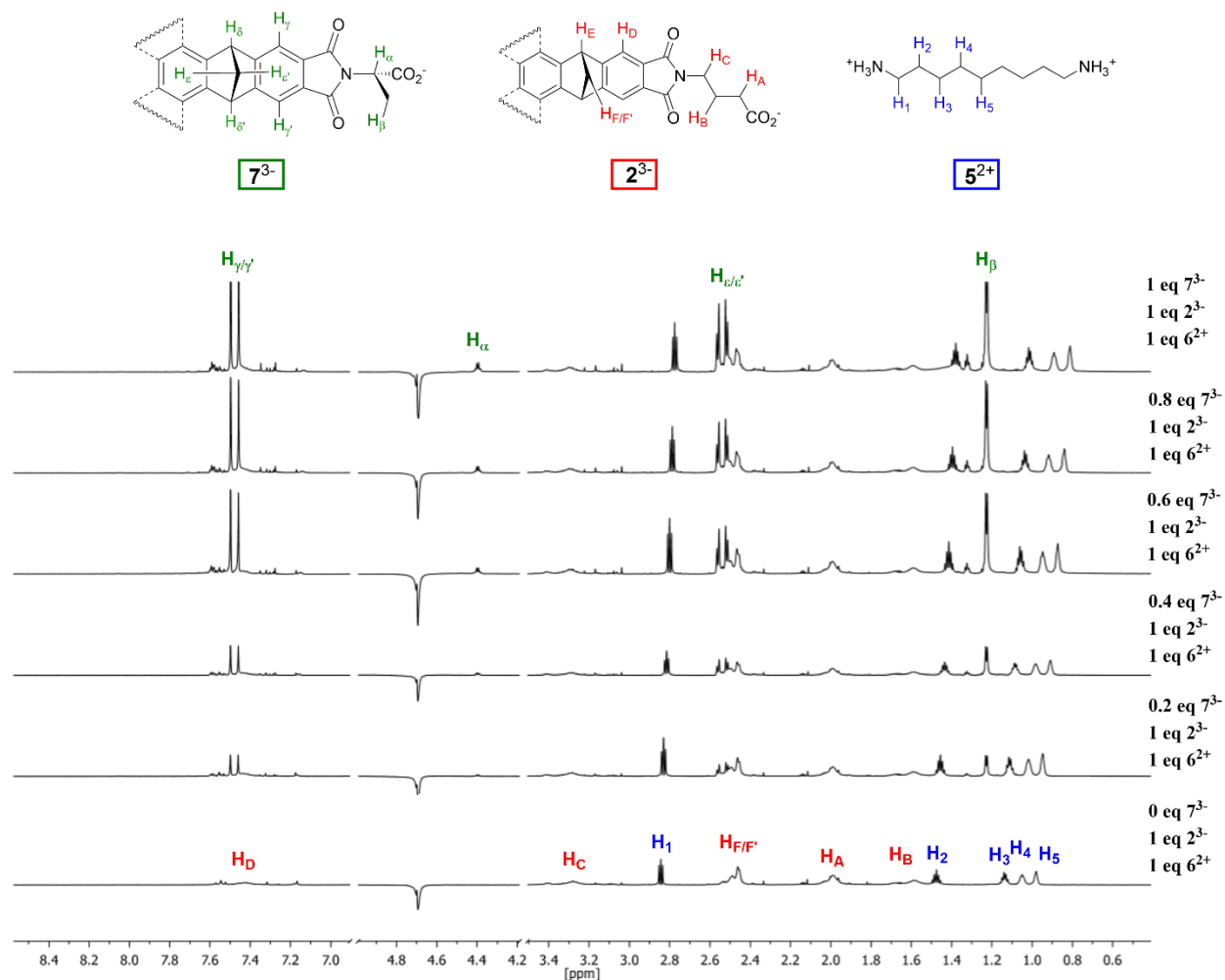


**Figure S4.** Water suppression  $^1\text{H}$  NMR spectra (600 MHz, 298 K; 30 mM phosphate buffer at pH = 7.0  $\pm$  0.1, 10%  $\text{D}_2\text{O}$ ) of 0.27 mM basket  $2^{3-}$  obtained upon an incremental addition of 2.0, 10.0 and 66.0 mM solutions of  $6^{2+}$  (30 mM phosphate buffer at pH=7.0  $\pm$  0.1) to this solution. (Right) The number of molar equivalents of  $6^{2+}$ .

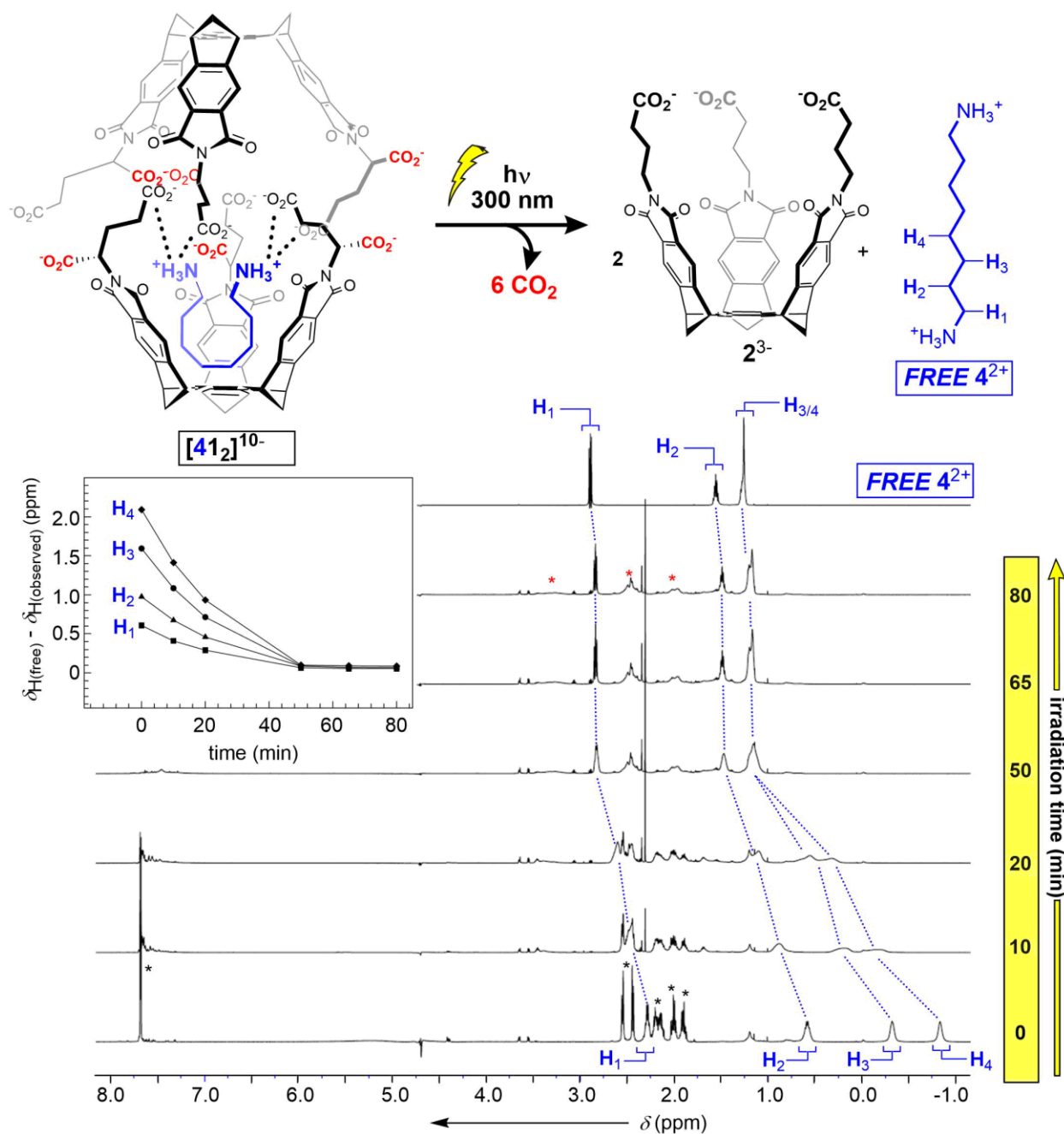


**Figure S5.** A portion of TOF-ESI mass spectrum of basket  $\mathbf{1}^{6-}$  and diammonium decane  $\mathbf{6}^{2+}$  showing signals corresponding to doubly charged ternary  $[\mathbf{6}\text{-}\mathbf{1}_2]^{2+}$  complexes. The ESI-TOF MS experiment was performed under the following conditions: ESI capillary voltage, 3 kV; sample cone voltage, 30 V; extraction cone voltage, 3.0 V; source temperature 80 °C; desolvation temperature, 80 °C; cone gas flow, 1 L per hour; desolvation gas flow, 700 L per hour ( $N_2$ ); source gas control, 0 mL per minute; trap gas control, 2 mL per minute; sample flow rate, 5  $\mu$ L per minute.





**Figure S6.** Water suppression  $^1\text{H}$  NMR spectra (850 MHz, 298 K; 30 mM phosphate buffer at  $\text{pH}=7.0 \pm 0.1$ , 10%  $\text{D}_2\text{O}$ ) of  $0.50\text{ mM}$  basket  $2^{3-}$  and  $0.5\text{ mM}$   $6^{2+}$  obtained upon an incremental addition of  $7^{3-}$  (3.1 mM solution in 30 mM phosphate buffer at  $\text{pH}=7.0 \pm 0.1$ ). (Right) The molar equivalents of the corresponding components. This experiment was conducted in order to test if one basket could primarily utilize  $\alpha$ -carboxylates ( $7^{3-}$ ) while another  $\gamma$ -carboxylates ( $2^{3-}$ ) for forming of ternary species. With the absence of a dramatic upfield shifting of the guest protons, we concluded that guest  $6^{2+}$  remained mostly free in solution with baskets  $2^{3-}$  and  $7^{3-}$  unable to form ternary complexes.



**Figure S7.** A steady irradiation (300 nm, Rayonet) of a solution of diammonium octane  $\mathbf{4}^{2+}$  (0.42 mM) and basket  $\mathbf{1}^{6-}$  (0.86 mM; 30 mM PBS at  $\text{pH} = 7.0 \pm 0.1$ ), constituting ternary  $[4\mathbf{1}_2]^{10-}$ , was monitored with  $^1\text{H}$  NMR spectroscopy (600 MHz, 298 K). The inset shows a change in the normalized chemical shift of  $\text{H}_{1-4}$  resonances from  $\mathbf{4}^{2+}$  as a function of the irradiation time.  $^1\text{H}$  NMR resonances labeled with black and red stars correspond to  $\mathbf{1}^{6-}$  and  $\mathbf{2}^{3-}$ , respectively.