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Structure and Dynamics of a Molecular Tweezer Host-Guest Complex: Coupling Synthesis, Solid-State NMR, and Quantum Chemical Calculations

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Solution-state NMR of 1@2:

\(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta = 2.45\) (m, 4 H, 25-Hi, 25-Ha, 28-Hi, 28-Ha), 2.47 (dm, 2 H, 2J(26-Ha, 26-Hi) = 8 Hz, 26-Ha, 27-Ha), 2.52 (dm, 2 H, 26-Hi, 27-Hi), 3.45 (d, \(\text{H}^a, \text{H}^b\)), 4.11 (s, 4 H, 7-H, 10-H, 19-H, 22-H), 4.13 (s, 4 H, 5-H, 12-H, 17-H, 24-H), 6.36 (m, 4 H, 2-H, 3-H, 14-H, 15-H), 6.98 (m, 4 H, 1-H, 4-H, 13-H, 16-H), 7.06 (s, 4 H, 8-H, 9-H, 20-H, 21-H), 7.17 (s, 4 H, 6-H, 11-H, 18-H, 23-H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta = 50.4\) (d, C-7, C-10, C-19, C-22), 51.0 (d, C-5, C-12, C-17, C-24), 64.7 (t, C-26, C-27), 67.1 (t, C-25, C-28), 114.9 (s, CN 2), 116.5 (d, C-6, C-11, C-18, C-23), 117.1 (s, quaternary aromatic 2), 119.2 (d, C-8,
C-9, C-20, C-21), 121.5 (d, C-1, C-4, C-13, C-16), 124.1 (d, C-2, C-3, C-14, C-15), 129.8 (s, C-8a, C-20a), 131.0 (d, aromatic CH$_2$), 147.0 (s, C-6a, C-10a, C-18a, C-22a), 147.2 (s, C-5a, C-11a, C-17a, C-23a), 148.0 (s, C-7a, C-9a, C-19a, C-21a), 150.7 (s, C-4a, C-12a, C-16a, C-24a). (The notation C-xa refers to the quaternary carbon between carbons x and x+1.)

Additional Solid-State NMR Details:
Given temperatures were determined using the procedure outlined in Ref.[1]. DQ MAS experiments were performed using the Back-to-Back (BABA) recoupling sequence[2] for the excitation ($p = 0 \rightarrow p = \pm 2$, where $p$ is the coherence order) and reconversion ($p = \pm 2 \rightarrow p = 0$) of DQ coherence (DQC). The standard BABA sequence, of duration one rotor period, takes the form: $P_x - \tau - P_x - P_y - \tau - P_y$, where $P_{\phi}$ denotes a radiofrequency pulse with flip angle equal to 90° and phase $\phi$, and $\tau$ equals $\tau_R/2$ minus the pulse durations.

After the reconversion sequence, a final 90° pulse creates transverse magnetisation, with the duration of the $p = 0$ "z-filter" period set equal to one rotor period. The total phase cycle used consisted of 16 steps with four steps to select $p = \pm 2$ after the excitation sequence and four steps to select $p = 0 \rightarrow p = -1$. Sign discrimination was restored
in the $F_1$ dimension by the States-TPPI$^{[3]}$ method, which involves incrementing the phases of all excitation pulses by $45^\circ$ after recording each $t_1$ point, with $t_1$ being incremented after every second $t_1$ point; in this way, the DQ spectral width equals $1/\Delta t_1$.

The $^1H$-$^13C$ correlation spectrum was recorded using the REPT-HSQC method – this differs from the REPT-HMQC method described in Ref.$^{[4]}$ in that the $^13C$ $90^\circ$ pulse is moved from the beginning to the end of $t_1$, with the $180^\circ$ pulse at $t_1/2$ being omitted; TPPM dipolar decoupling$^{[5]}$ with a $^1H$ $B_1$ field of 125 kHz was applied during acquisition.

**Additional Quantum-Chemical Calculation Details:**

The basis sets used employ the following contraction patterns: SVP: (4s1p)/[2s1p] (for H) and (7s4p1d)/[3s2p1d] (for C); TZP: (5s1p)/[3s1p] (for H) and (10s6p1d)/[6s3p1d] (for C).


