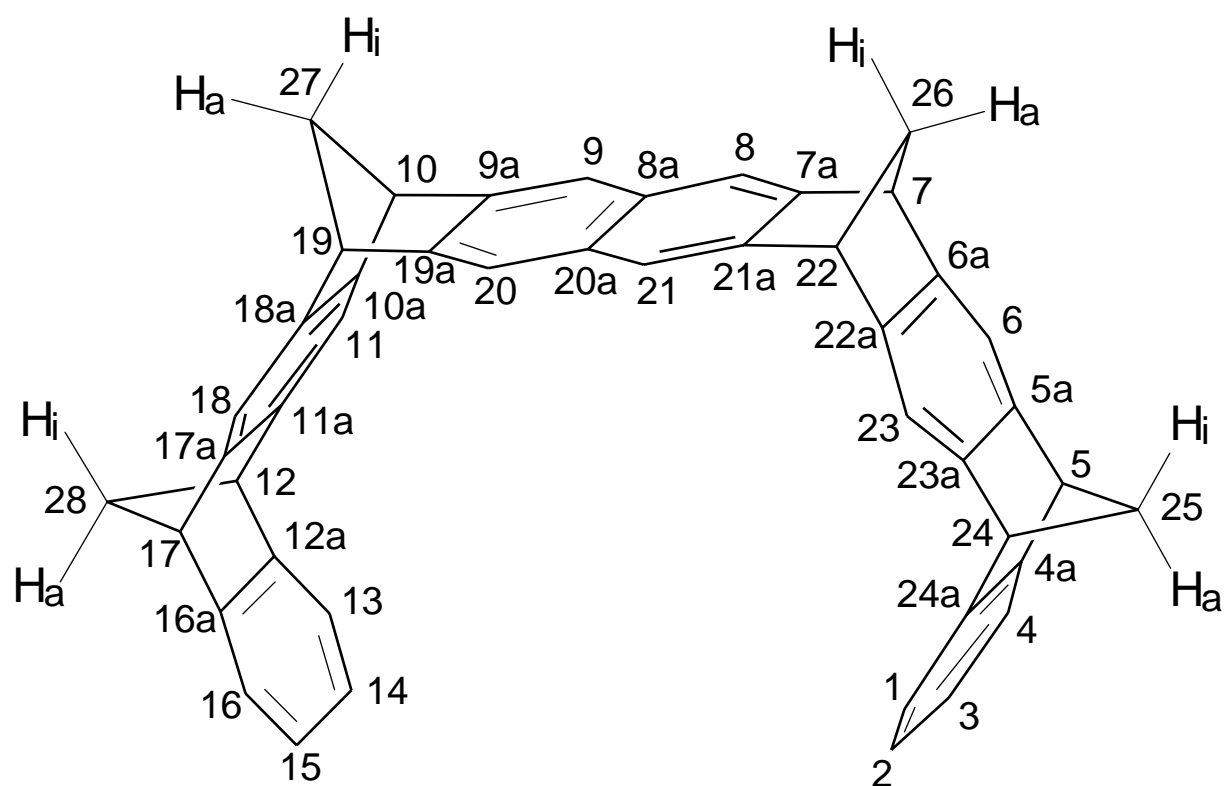
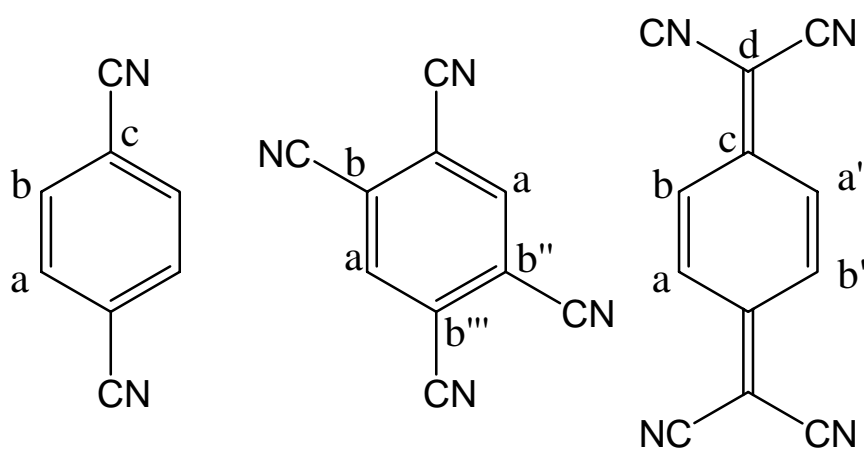


## Supporting information

### 1. Numbering of the carbon and proton positions of the tweezer



### 2. Numbering of the carbon and proton positions of the guest molecules



### 3. Solution-state NMR results

#### 3.1 Naphthalene-spaced tweezer without guest

**<sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>):**  $\delta$  = 2.45 (m, 4 H, 25-H<sup>i</sup>, 25-H<sup>a</sup>, 28-H<sup>i</sup>, 28-H<sup>a</sup>), 2.47 (dm, 2 H, <sup>2</sup>*J*(26-H<sup>a</sup>, 26-H<sup>i</sup>) = 8 Hz, 26-H<sup>a</sup>, 27-H<sup>a</sup>), 2.52 (dm, 2 H, 26-H<sup>i</sup>, 27-H<sup>i</sup>), 4.06 (s, 4 H, 5-H, 12-H, 17-H, 24-H), 4.16 (s, 4 H, 7-H, 10-H, 19-H, 22-H), 6.76 (m, 4 H, 2-H, 3-H, 14-H, 15-H), 7.05 (m, 4 H, 1-H, 4-H, 13-H, 16-H), 7.07 (s, 4 H, 6-H, 11-H, 18-H, 23-H), 7.29 (s, 4 H, 8-H, 9-H, 20-H, 21-H).

**<sup>13</sup>C-NMR (125 MHz, CDCl<sub>3</sub>):**  $\delta$  = 50.49 (d, C-7, C-10, C-19, C-22), 51.02 (d, C-5, C-12, C-17, C-24), 64.83 (t, C-26, C-27), 67.63 (t, C-25, C-28), 116.15 (d, C-6, C-11, C-18, C-23), 119.40 (d, C-8, C-9, C-20, C-21), 121.53 (d, C-1, C-4, C-13, C-16), 124.14 (d, C-2, C-3, C-14, C-15), 130.21 (s, C-8a, C-20a), 146.96 (s, C-6a, C-10a, C-18a, C-22a), 147.12 (s, C-5a, C-11a, C-17a, C-23a), 147.58 (s, C-7a, C-9a, C-19a, C-21a), 150.58 (s, C-4a, C-12a, C-16a, C-24a).

#### 3.2 Complex with 1,4- dicyanobenzene (DCNB)

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):**  $\delta$  = 2.45 (m, 4 H, 25-H<sup>i</sup>, 25-H<sup>a</sup>, 28-H<sup>i</sup>, 28-H<sup>a</sup>), 2.47 (dm, 2 H, 2*J*(26-H<sup>a</sup>, 26-H<sup>i</sup>) = 8 Hz, 26-H<sup>a</sup>, 27-H<sup>a</sup>), 2.52 (dm, 2 H, 26-H<sup>i</sup>, 27-H<sup>i</sup>), 3.45 (d, DCNB, H<sup>a</sup>, H<sup>b</sup>), 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);

**<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):**  $\delta$  = 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, DCNB, CN), 116.5 (d, C-6, C-11, C-18, C-23), 117.1 (s, DCNB, C<sub>c</sub>), 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, DCNB, C<sub>a</sub>, C<sub>b</sub>), 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).

### 3.3 Complex with 1,2,4,5-tetracyanobenzene (TCNB)

**<sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>):**  $\delta$  = 2.40 (m, 4 H, 25-H<sup>i</sup>, 25-H<sup>a</sup>, 28-H<sup>i</sup>, 28-H<sup>a</sup>), 2.45 (s, 2 H, TCNB, H<sub>a, complexed</sub>), 2.56 (dm, 2 H, <sup>2</sup>*J*(26-H<sup>a</sup>, 26-H<sup>i</sup>) = 8 Hz, 26-H<sup>a</sup>, 27-H<sup>a</sup>), 2.60 (dm, 2 H, 26-H<sup>i</sup>, 27-H<sup>i</sup>), 4.19 (s, 4 H, 5-H, 12-H, 17-H, 24-H), 4.26 (s, 4 H, 7-H, 10-H, 19-H, 22-H), 6.22 (m, 4 H, 2-H, 3-H, 14-H, 15-H), 7.00 (s, 4 H, 8-H, 9-H, 20-H, 21-H), 7.08 (m, 4 H, 1-H, 4-H, 13-H, 16-H), 7.48 (s, 4 H, 6-H, 11-H, 18-H, 23-H), ), 7.90 (s, 2 H, TCNB, H<sub>a</sub>).

**<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):**  $\delta$  = 50.3 (d, C-7, C-10, C-19, C-22), 50.9 (d, C-5, C-12, C-17, C-24), 64.6 (t, C-26, C-27), 66.2 (t, C-25, C-28), 112.3 (s, TCNB, CN), 116.3 (s, TCNB, C<sub>b</sub>, C<sub>b'</sub>), 118.5 (d, C-6, C-11, C-18, C-23), 119.2 (d, C-8, C-9, C-20, C-21), 122.1 (d, C-1, C-4, C-13, C-16), 123.6 (d, C-2, C-3, C-14, C-15), 128.8 (s, C-8a, C-20a), 142.9 (d, TCNB, C<sub>a</sub>), 147.1 (s, C-6a, C-10a, C-18a, C-22a), 148.0 (s, C-5a, C-11a, C-17a, C-23a), 148.6 (s, C-7a, C-9a, C-19a, C-21a), 151.3 (s, C-4a, C-12a, C-16a, C-24a).

### 3.4 Complex with 7,7,8,8-tetracyano-p-quinodimethane (TCNQ)

**<sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>):**  $\delta$  = 2.39 (m, 4 H, 25-H<sup>i</sup>, 25-H<sup>a</sup>, 28-H<sup>i</sup>, 28-H<sup>a</sup>), 2.51 (dm, 2 H, <sup>2</sup>*J*(26-H<sup>a</sup>, 26-H<sup>i</sup>) = 8 Hz, 26-H<sup>a</sup>, 27-H<sup>a</sup>), 2.55 (dm, 2 H, 26-H<sup>i</sup>, 27-H<sup>i</sup>), 4.16 (s, 4 H, 5-H, 12-H, 17-H, 24-H), 4.20 (s, 4 H, 7-H, 10-H, 19-H, 22-H), 6.36 (m, 4 H, 2-H, 3-H, 14-H, 15-H), 7.06 (m, 4 H, 1-H, 4-H, 13-H, 16-H), 6.97 (s, 4 H, 6-H, 11-H, 18-H, 23-H), 7.31 (s, 4 H, 8-H, 9-H, 20-H, 21-H).

**<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):**  $\delta$  = 50.3 (d, C-7, C-10, C-19, C-22), 51.0 (d, C-5, C-12, C-17, C-24), 64.3 (t, C-26, C-27), 66.7 (t, C-25, C-28), 111.8 (s, TCNQ, CN), 117.3 (d, C-6, C-11, C-18, C-23), 118.9 (d, C-8, C-9, C-20, C-21), 121.5 (d, C-1, C-4, C-13, C-16), 124.0 (d, C-2, C-3, C-14, C-15), 126.5 (d, TCNQ, C<sub>a</sub>, C<sub>a'</sub>, C<sub>b</sub>, C<sub>b'</sub>), 129.8 (s, C-8a, C-20a), 147.3 (s, C-6a, C-10a, C-18a, C-22a), 147.7 (s, C-5a, C-11a, C-17a, C-23a), 148.4 (s, C-7a, C-9a, C-19a, C-21a), 151.2 (s, TCNQ, C<sub>c</sub>), 151.3 (s, C-4a, C-12a, C-16a, C-24a).

position	<sup>1</sup> H chemical shift [ppm] from			
	Solution-state NMR	Solid-state NMR	ab initio calculations	ab initio calculations
1,4- dicyanobenzene (DCNB)			monomer	Trimer
			GIAO-HF/TZP// HF/6-31G*	GIAO-HF/TZP+ $\Delta_{Di}^{SVP} + \Delta_{Tri}^{3-21G}$ // HF/6-31G*
H <sub>8,9,20,21</sub>	7.06	7.0	7.1-7.3	6.7-7.0
H <sub>6,11,18,23</sub>	7.17	7.1	7.6-8.0	6.8-7.9
H <sub>1,4,13,16</sub>	6.98	7.0	7.2-7.5	6.8-7.2
H <sub>5,12,17,24</sub>	4.13	3.8	4.0-4.2	3.7-4.2
H <sub>7,10,19,22</sub>	4.11	3.8	3.9-4.0	3.0-3.6
H <sub>2,3,14,15</sub>	6.36	5.0	6.5	4.9
H <sub>25,26,27,28</sub>	2.47-2.52	-1.2, 2.0	2.0-2.3	-0.4-2.4
H <sub>guest,a</sub>	3.5	2.0	1.7	1.4
H <sub>guest,b</sub>	3.5	5.6	5.3	4.9
1,2,4,5-tetracyanobenzene (TCNB)			monomer	Dimer
			GIAO-HF/TZP// HF/6-31G*	GIAO-HF/TZP+ $\Delta_{Di}^{SVP}$ // HF/6- 31G*
H <sub>8,9,20,21</sub>	7.05	7.0	7.3	7.0
H <sub>6,11,18,23</sub>	7.49	7.0	8.0	7.7
H <sub>1,4,13,16</sub>	7.12	7.0	7.4	7.0
H <sub>5,12,17,24</sub>	4.32	4.0	4.2	4.0
H <sub>7,10,19,22</sub>	4.23	4.0	4.1	3.4
H <sub>2,3,14,15</sub>	6.28	4.9	6.6	4.9
H <sub>25,26,27,28</sub>	2.40; 2.47	-0.1; 1.8	2.0 – 2.3	-1.0 – 2.2
H <sub>guest,a</sub>	2.0	2.0	1.7	1.2
7,7,8,8-tetracyano-p-quinodimethane (TCNQ)			monomer	pentamer
			GIAO-HF/6- 31G*//HF/6- 31G*	GIAO-HF/6- 31G*//HF/6- 31G*

H <sub>8,9,20,21</sub>	7.31	6.8	7.2-7.4	6.0-7.2
H <sub>6,11,18,23</sub>	6.97	6.8	7.8	7.0-7.6
H <sub>1,4,13,16</sub>	7.06	6.8	7.3-7.7	6.7-7.5
H <sub>5,12,17,24</sub>	4.16	2.9	4.0-4.1	3.7-4.2
H <sub>7,10,19,22</sub>	4.20	2.9	3.9-4.1	2.8-4.0
H <sub>2,3,14,15</sub>	6.36	5.7	6.6-7.0	6.7-7.3
H <sub>25,26,27,28</sub>	2.39-2.55	0.6, 2.4	2.1-2.4	2.0-2.5
H <sub>guest,a,a',b,b'</sub>	3.87	3.5	3.4-4.1	3.0-3.4

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