

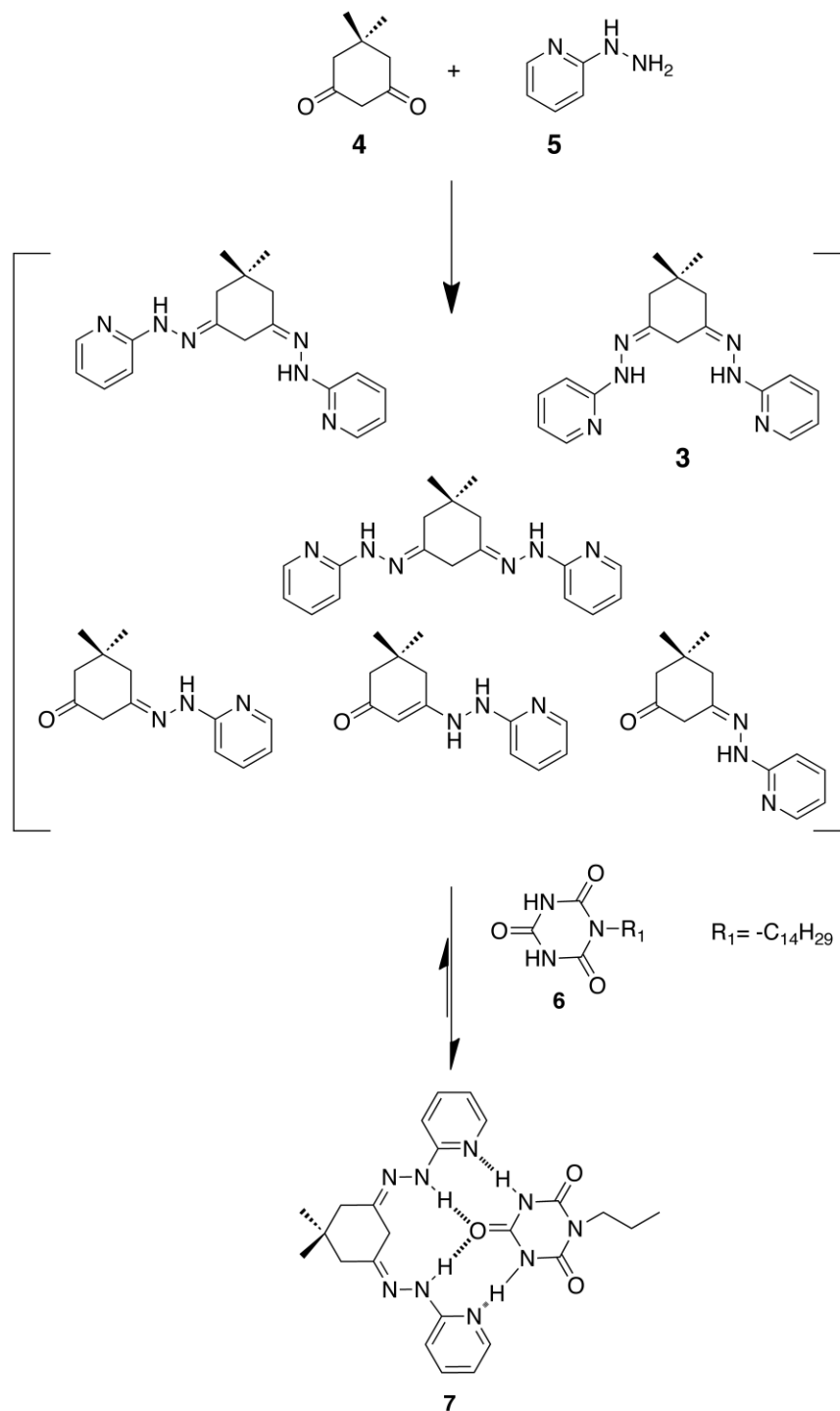
**Generation of a Main Chain Supramolecular Polymer by Oxidative Covalent  
Polymerization of a Ditopic Supramolecular Building Block**

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**SUPPORTING INFORMATION**

**Scheme S1 :**

Synthesis of the monotopic unit (**7**) with tetradecyl cyanurate (**6**):



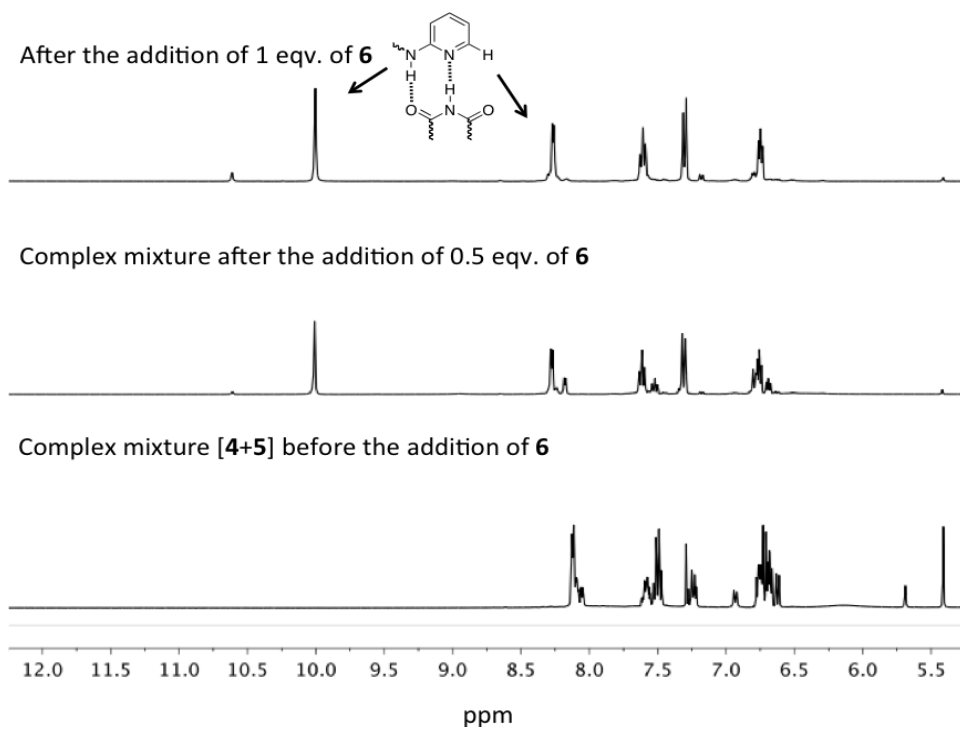
**Scheme S1.** Formation of the complex mixture [**4+5**] and of the monotopic monomer **7**.

### Formation of the complex mixture [4+5] and of the monotopic monomer 7:

To one equivalent of **4** (14.0 mg, 0.1 mmol), two equivalents of **5** (21.8 mg, 0.2 mmol) were added under N<sub>2</sub> atmosphere in CDCl<sub>3</sub> (5 mL, 10 mM) and the reaction mixture was stirred under nitrogen atmosphere for 24 hours to generate the complex mixture, containing compound **3** along with other different isomers. One equivalent of **6** (16.2 mg, 0.05 mmol) was added progressively under N<sub>2</sub> atmosphere, in course of 24 hours of stirring, leading to the formation of the monotopic entity **7**. The progress of the reaction was followed by <sup>1</sup>H NMR.

Proton NMR data for the monotopic monomer **7**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 10.00 (s, 2H), 8.26 (d,  $J$  = 8.9 Hz, 2H), 7.60 (m, 2H), 7.30 (d,  $J$  = 24.3 Hz, 2H), 6.75 (m, 2H), 3.85 (dd,  $J$  = 16.3, 9.2 Hz, 2H), 3.39 (s, 2H), 2.38 (s, 2H), 1.68 (s, 2H), 1.31 (d,  $J$  = 27.4 Hz, 22H), 1.00 (s, 3H), 0.90 (t,  $J$  = 6.5 Hz, 3H).

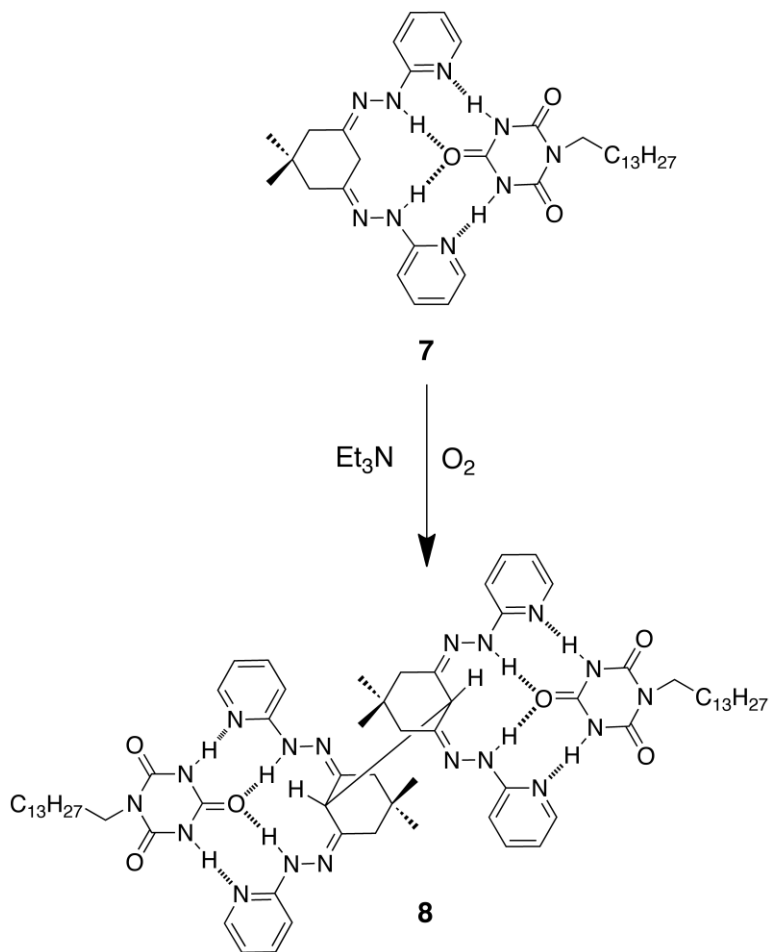
<sup>13</sup>C NMR data for the ditopic monomer **7**: <sup>13</sup>C (100.6 MHz, CDCl<sub>3</sub>)  $\delta$  = 157.07; 149.76; 146.07; 144.68; 138.96; 114.86; 107.14; 46.06; 41.66; 31.88; 29.60; 29.30; 29.20; 27.89; 26.75; 22.67; 14.10.



**Fig. S1**  $^1\text{H}$  NMR spectra of the complex mixture [**4+5**]; gradual simplification of the spectra after half equivalent and one equivalent addition of **6** to the complex mixture respectively.

**Scheme S2:**

Synthesis of the dimer unit (**8**) from the dimerization of the monotopic unit (**7**):



**Scheme S2:** Synthesis of Dimer unit (**8**).

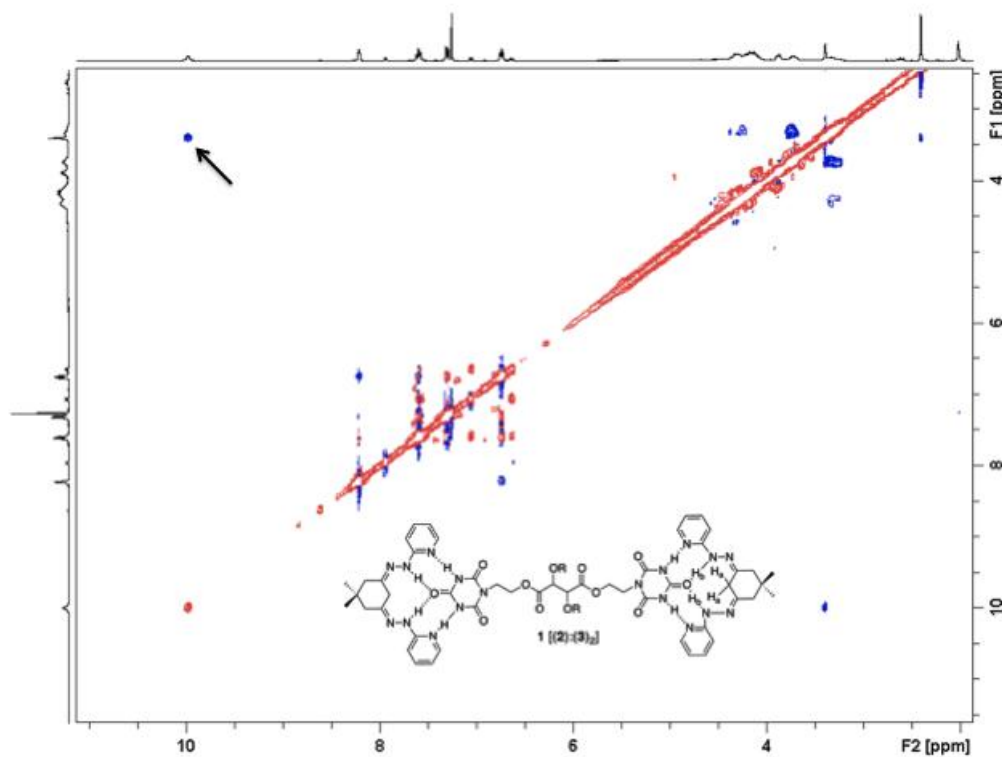
To a preformed solution of the monotopic unit **7** in CHCl<sub>3</sub>, triethyl amine (20.2 mg, 0.2 mmol, 200 mol%) was added drop wise and the reaction mixture was stirred in presence of aerial oxygen. In order to expedite the oxidation process, pure O<sub>2</sub> was purged through it at a flow rate of 100 nl/h at 1.21 bar for 15 minutes. Followed by that, the reaction mixture was kept under an O<sub>2</sub> saturated atmosphere for two days. In the course of two days after O<sub>2</sub> saturation, compound **7** underwent oxidative C-C coupling to completion to form the supramolecular dimer **8** (Scheme S2). The reaction was monitored by the <sup>1</sup>H NMR spectroscopy. The polymer formed was characterized by the <sup>1</sup>H NMR.

Proton NMR data for the monotopic monomer **8**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 13.95 (s, 4H), 10.61 (s, 4H), 8.31 (t,  $J$  = 5.2 Hz, 6H), 7.68 (t,  $J$  = 6.9 Hz, 2H), 7.60 (t,  $J$  = 7.8

Hz, 2H), 7.46 (d,  $J = 8.3$  Hz, 2H), 7.18 (d,  $J = 8.5$  Hz, 2H), 6.94 (t, 2H), 6.80 (t, 2H), 5.16 (s, 2H), 3.88 (m, 4H), 2.63 (s, 8H), 1.70 (s, 4H), 1.32 (d,  $J = 30.7$  Hz, 44H), 1.15 (s, 12H), 0.91 (t,  $J = 6.8$  Hz, 6H).

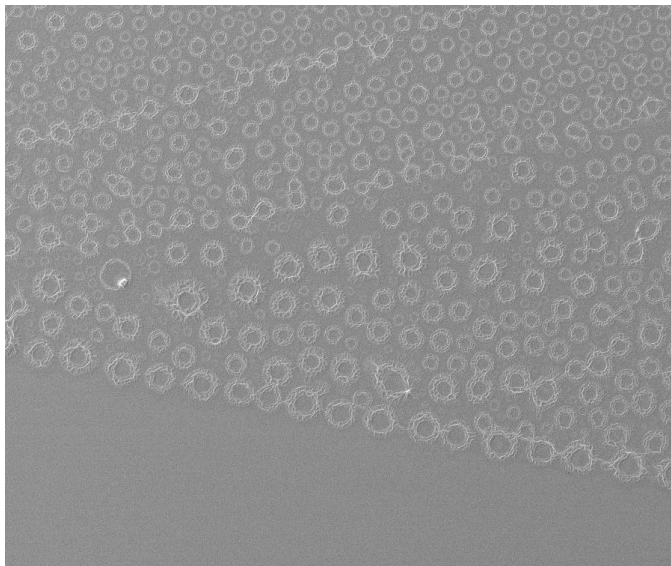
$^{13}\text{C}$  NMR data for the ditopic monomer **8**:  $^{13}\text{C}$  (100.6 MHz,  $\text{CDCl}_3$ )  $\delta = 157.44$ ; 155.64; 149.51; 148.47; 148.36; 147.20; 146.45; 145.68; 138.09; 137.98; 134.61; 118.29; 114.94; 108.56; 108.45; 107.90; 46.49; 45.65; 45.04; 41.89; 38.91; 37.69; 33.62; 31.94; 31.53; 30.98; 30.64; 29.71; 29.59; 29.38; 29.28; 28.70; 27.92; 27.76; 26.78; 24.71; 22.71; 14.14.

Figure S2 : ROESY NMR spectrum of the ditopic supramolecular monomer **1** [(**2**):(**3**)<sub>2</sub>] in  $\text{CDCl}_3$ .



**Fig. S2**  $^1\text{H}$  ROESY spectrum exhibiting the correlation of the cyclohexyl protons ( $\text{H}_a$ ) at 3.43 ppm with the H-bonded N-H protons ( $\text{H}_b$ ) (10.02 ppm) of the hydrazino pyridine motif in **1** [(**2**):(**3**)<sub>2</sub>].

Figure S3 : Ordered arrangement of the supramolecular capsules along the terminal end of the Cu-C grid on SEM.



**Fig. S3** SEM image of the ordered arrangement of supramolecular capsules along the terminal end of the grid.