Supporting Information for:

"A water-soluble hexa-*peri*-hexabenzocoronene: synthesis, self-assembly and role as template for porous silica with aligned nanochannels"

*Jishan Wu, Jixue Li, Ute Kolb and Klaus Müllen**

*1. Synthesis of compound **5**:*

1-Bromo-3,4,5-trihydroxylbenzene (**3**, 838 mg, 4.09 mmol), compound **4** (6.67g, 18.4 mmol), and powder K_2CO_3 (3.38g, 24.54 mmol) were mixed in 16 ml DMF. The mixture was heated at 80 °C under argon atmosphere for 24 hours. After cooling the mixture was poured into water and extracted by dichloromethane (DCM). The solvent in organic layer was removed under vacuum and the residue was purified by column chromatography (silica gel, eluents: petroleum ether (PE) then acetyl acetate (EtOAc) and finally with EtOAc/methanol = 1:1) and afforded 2.2 g pure product as colorless liquid (75%). FD-MS (8kV): m/z = 777.3. ^{1}H NMR (d^2-CD_2Cl_2): δ ppm 6.75 (s, phenyl ring, 2H), 4.11-3.32(m, 57H, ethylene glycol chains); ^{13}C NMR (d^2-CD_2Cl_2): δ ppm 153.82, 115.90, 111.76, 73.04, 72.79, 72.34, 71.18, 70.92, 70.71, 70.01, 69.63, 61.99, 58.94.

*2. Synthesis of compound **7**:*

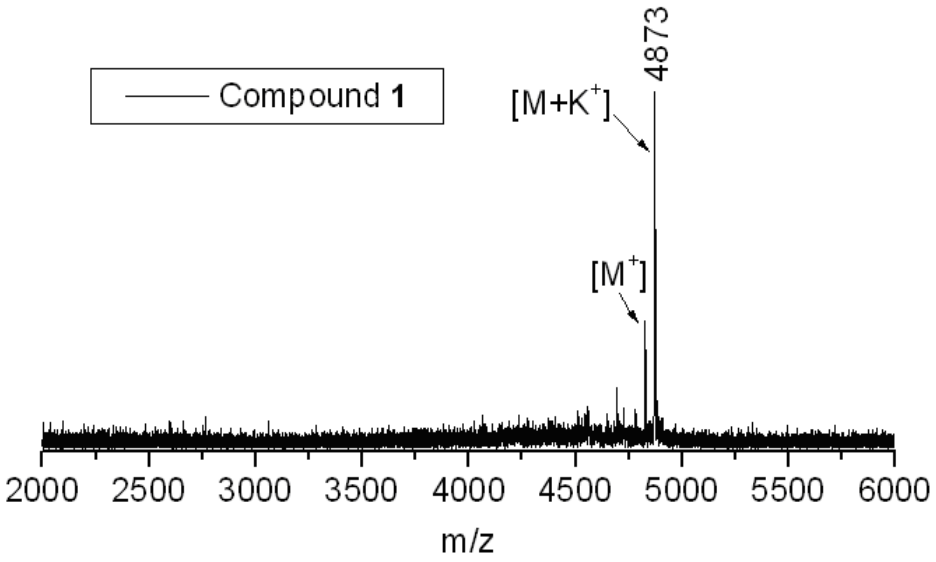
2.0 g compound **5** (2.58 mmol), 89 mg $Pd(PPh_3)_4$ (3 mol%), 29 mg CuI and 14 ml triethylamine were mixed and degassed by two "froze-pump-thaw" cycles. The mixture was heated at 80 °C under argon atmosphere for 16 hours. The solvent was removed under vacuum and the residue was purified by column chromatography (silica gel, eluents: PE/DCM = 1:1, then DCM, then DCM/methanol = 4:1 and finally EtOAc/Methanol = 4:1) and afforded 1.86 g compound **6** (91%). FD-MS: m/z = 793.5. Compound **6** was then transformed into **7** as follows: 1.7 g compound **6** (2.14 mmol) was dissolved in 15 ml methanol and then 887 mg K_2CO_3 was added. The mixture was stirred at room temperature for 45 minutes and filtrated. The solvent of filtrate was removed under vacuum and the residue was purified by column chromatography (silica gel, eluents: PE then EtOAc, and finally EtOAc/Methanol = 4:1) and afforded compound **7** in

92% yield. FD- MS: m/z = 721.3. ^{1}H NMR (d^2-CD_2Cl_2): δ ppm 6.73 (s, phenyl ring, 2H), 4.12-3.30 (m, 57H, ethylene glycol chains), 3.08 (s, C≡C-H, 1H); ^{13}C NMR (d^2-CD_2Cl_2): δ ppm 153.03, 116.67, 112.27, 83.89 (C≡C), 81.94 (C≡C), 73.00, 72.32, 71.14-70.64 (overlapped), 70.01, 61.86, 58.92.

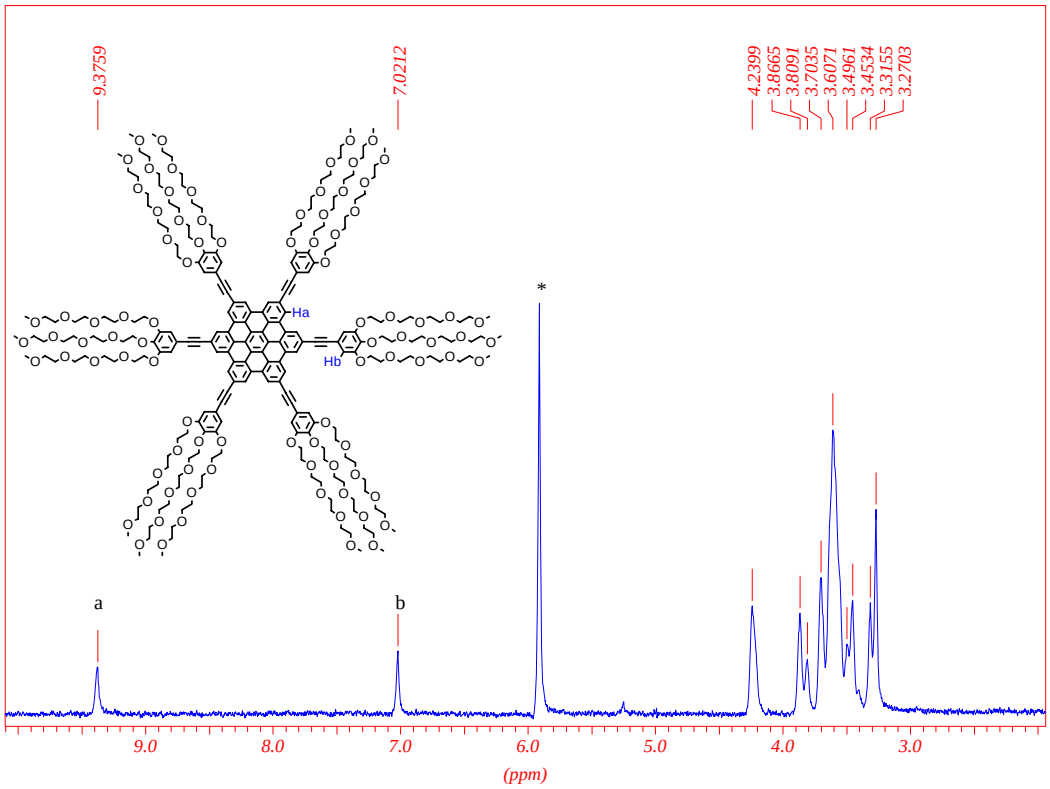
*3. Synthesis of compound **1**:*

142 mg hexaiodo-*peri*-hexabenzocoronene (**2**, 0.11 mmol), 20 mg $Pd(PPh_3)_4$ (2.5 mol% per iodine) and 6 mg CuI were mixed with 8 ml piperidine and degassed by three "freeze-pump-thaw" cycles and then 720 mg compound **7** was added. The mixture was heated at 50 °C for 48 hours. The solvent was removed under vacuum and the residue was purified by column chromatography (silica gel, eluents: EtOAc, then EtOAc/methanol = 1:2) and afforded pure compound **1** as a yellow waxy solid in 72% yield. MALDI-TOF MS (dithranol as matrix): 4835 [M^+], 4873 [$M+K^+$]. ^{1}H NMR (d^4-$CDCl_2CDCl_2$, 140 °C): δ ppm 9.38 (s, HBC core, 12H), 7.02 (s, phenyl rings, 12H), 4.24-3.27 (m, ethylene glycol chains, 342 H); ^{13}C NMR (d^2-CD_2Cl_2): δ ppm 153.13, 140.03, 130.40, 126.03, 125.21, 123.11, 121.74, 118.90, 91.62 (C≡C), 89.48 (C≡C), 73.06, 72.32, 71.19, 70.97, 70.88, 70.75, 70.12, 69.58, 58.94.

*4. MALDI-TOF MS of compound **1**:*



5. *^{1}H NMR spectrum of compound **1** in d^{4}-$CDCl_2CDCl_2$ at 140°C:*



6. Powder X-ray diffraction pattern of HBC (**1**) /SiOx composite.