

SUPPORTING INFORMATION

Preparation of synthetic asphaltenes:

a) 1,2-bis(4-bromophenyl)-3,4,5,6-tetraphenylbenzene

A mixture of tetraphenylcyclopentadienone (5.0 mmol), and bis(p-bromophenyl) acetylene (5.0 mmol) in diphenyl ether (20 ml) was heated to 260 °C overnight. Then the temperature was raised to 270 °C. After 69 h, the reaction mixture was cooled, and methanol (100 ml) was added. After stirring for 1 h, the product was filtered off, washed with methanol, and finally dried in vacuum overnight. Yield: Quantitative.

b) 1,2-bis(4-dodecylphenyl)-3,4,5,6-tetraphenylbenzene

1-dodecene (30.0 mmol) was slowly added to a 0.5 M solution of 9-borabicyclo[4.4.1] nonane in THF (65 ml), and the mixture was stirred at room temperature overnight. Then a solution of NaOH (45.0 mmol) in water (15 ml) was slowly added, and the mixture was stirred for 20 min. The dibromide (2.5 mmol) was added, followed by Pd(dppf)Cl₂ (80 mg). The reaction mixture was stirred at room temperature for 5 h. Then TLC analysis indicated incomplete reaction, and the temperature was increased. After boiling at reflux overnight, the reaction mixture was cooled to room temperature and concentrated in vacuo. The residue was dissolved in CH₂Cl₂, washed with water and with brine, and then dried (Na₂SO₄). The dry solution was diluted with hexane, filtered thru celite, and concentrated in vacuo. Finally the product was purified by flash chromatography (SiO₂, pentane w/ 5-10% CH₂Cl₂). Yield: 80 %.

c) 2,5-didodecylhexaperihexabenzocoronene

The didodecylhexaphenylbenzene (1.5 mmol) was dissolved in dry CH₂Cl₂ (750 ml), and argon was bubbled thru the solution for 15 min. Then anhydrous FeCl₃ (45 mmol) dissolved in nitromethane (15 ml) was added, and the mixture was stirred at room temperature while being bubbled with argon. After 75 min, the reaction mixture was poured into methanol (1 l). The reaction mixture was then concentrated in vacuo to remove most of the CH₂Cl₂, and the precipitated product was filtered off, washed thoroughly with dilute hydrochloric acid and with methanol, and then dried in vacuo. The crude product was dissolved in hot THF, precipitated once again with methanol, and finally dried in vacuum overnight. Yield: 55 %.

Confirmation of expected structure was first sought for by solid state NMR. 1H-MAS was performed to qualitatively evaluate the relative contribution of aromatic and aliphatic protons to the total resonance signal. 1H MAS solid state NMR signal shows that aromatic and aliphatic contributions are well separated. Deconvolution and integration of peaks leads to:

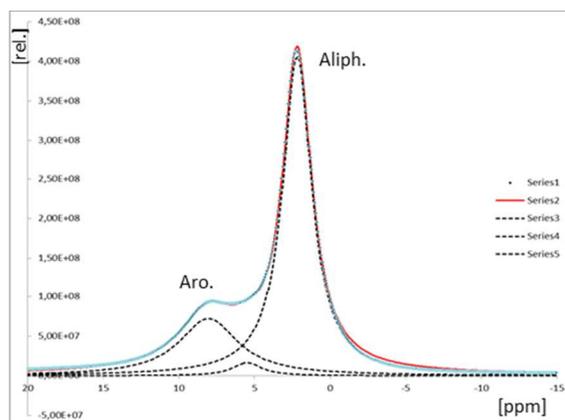
Aliphatic protons: 72 %,

Intermediate protons: 3 %

Aromatic protons: 25 %

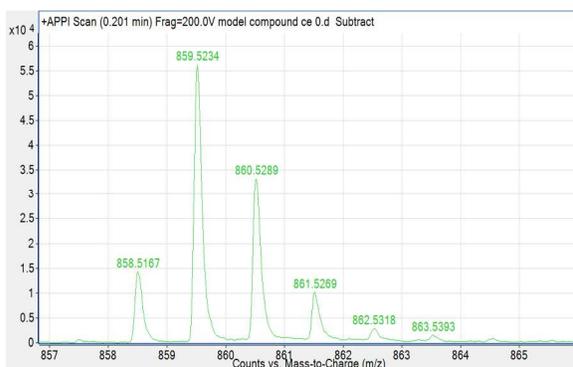
The match with the expected structure (50-16 ratio between aliphatic and aromatic protons) appears to

be fairly quantitative.

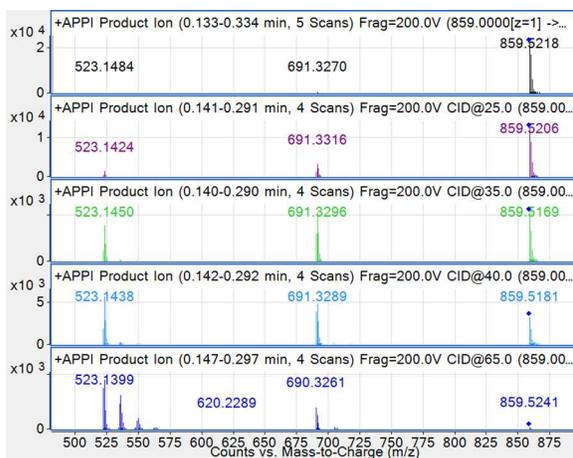


^1H -MAS solid state NMR of model asphaltenes (20kHz).

Further characterization was performed with an Agilent 6500 series Accurate-Mass Quadrupole Time of Flight Mass Spectrometer (QTOF). Atmospheric pressure Photoionization (APPI) was used as an ion source. The signal primarily consists of a set of 5 peaks starting at 858.58 Da (expected molar weight of didodecyl-hexaperihexabenzocoronene) and separated by 1 Da. They correspond quantitatively to the isotopic distribution for a mixture of 43 % radical and 57 % protonated cations. A secondary set of similar peaks starting at 893.48 Da was attributed to the substitution of one hydrogen atom by one chlorine atom on the aromatic core. The chlorinated impurities are probably due to the use of FeCl_3 for the final cyclization/oxidation step. In any case, actually observed quantities correspond to traces (0.25% of hydrogen substituted by chlorine) and should not change the overall results. MS-MS fragmentation experiments were also conducted. When collision energy is increased, peaks appear at masses corresponding to the mono-dodecyl-hexaperihexabenzocoronene (691.33 Da) and hexaperihexabenzocoronene (523.14 Da). This reveals the progressive ablation of alkyl chains and confirms the structure of both the poly-aromatic core and the side alkyl chains. The only impurities detected by QTOF MS correspond to the substitution of one or two hydrogen atoms by chlorine atoms at the periphery of the polyaromatic core (data not shown). This was confirmed by the exact mass assignment from FTICR MS.



Primary mass peaks of model asphaltenes (QTOF APPI-200V fragmentor voltage).



Collision induced fragmentation of model asphaltenes (QTOF APPI- MS/MS CID).

