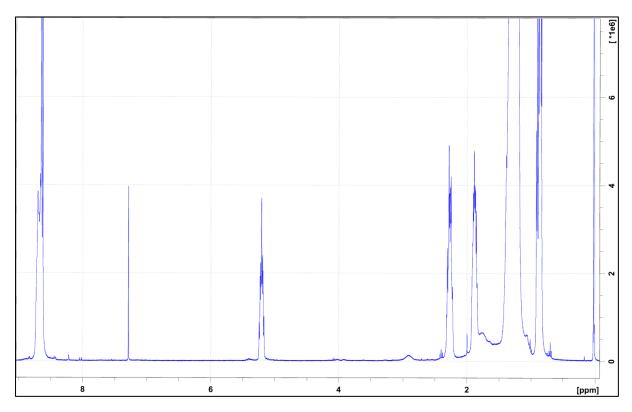
## **Supporting Information**

## Microcalorimetry Study of the Adsorption of Asphaltenes and Asphaltene Model Compounds at the Liquid-Solid Surface.

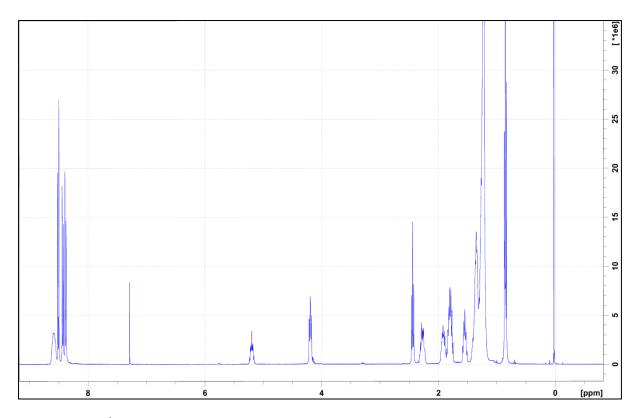
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## <sup>1</sup>H NMR spectra of BisAC11and C5PeC11.

Figures S1 and S2 show the <sup>1</sup>H NMR spectra of the model compounds BisAC11 and C5PeC11 respectively measured on a 400 MHz apparatus and whose structure is shown in Table 3 of the main article. For both spectra, the interpretation of the peaks is in the figure caption. It is important to note that the peak located at  $\delta$  (ppm) 7.25 ppm corresponds to the solvent used for the measurement, in this case, CDCl<sub>3</sub>. The letters *m* and *t* denote multiplets and triplets respectively. Further details of the synthesis of these compounds can be found in Nordgård et al<sup>1</sup> and Wei et al<sup>2</sup>.



**Figure S1.** <sup>1</sup>H NMR spectrum of the compound BisAC11. The peaks are: δ 8.65 (8H, *m*, perylene), δ 5.2 (2H, *m*, 2 CHN), δ 2.25 (4H, *m*, CH<sub>2</sub>CHN), δ 1.85 (4H, *m*, CH<sub>2</sub>CHN), δ 1.2-1.4 (72H, *m*, 36 CH<sub>2</sub>), δ 0.85 (12H, *t*, CH<sub>3</sub>), δ 2.9 (small impurity).



**Figure S2.** <sup>1</sup>H NMR spectrum of the compound C5PeC11. The peaks are: δ 8.65 (8H, *m*, perylene), δ 5.2 (1H, *m*, CH<sub>2</sub>CHN), δ 4.2 (2H, *t*, NCH<sub>2</sub> on the acidic side), δ 2.4 (2H, *t*, HOOCCH<sub>2</sub>), δ 2.25 (2H, *m*, CH<sub>2</sub>CHN), δ 2.0 – 1.0 (44H, *m*, 22 CH<sub>2</sub>), δ 0.85 (6H, *t*, CH<sub>3</sub>).

## FTIR spectra of esterified and non-esterified asphaltenes.

Figure S3 shows the FTIR spectra of esterified and non-esterified asphaltenes. Interpretation of the characteristic peaks is as follows<sup>3-6</sup>. The stretching and bending vibrations of aliphatic  $-CH_2$  and  $-CH_3$  groups are located at 2920, 2850, 1450 and 1375 cm<sup>-1</sup> respectively; the stretching vibrations typical of aromatic rings are located at 1600 cm<sup>-1</sup>; Their in- and out-of-plane bending vibrations are seen at 869, 810 and 745 cm<sup>-1</sup>. All these peaks are the same in figure S3, the only difference between the spectra is a peak located between 1720-1730 cm<sup>-1</sup> which corresponds to the stretching vibrations of C=O ester bonds (or the Carboxyl-Carbonyl area as defined by Juyal et al.<sup>7</sup>) indicating the complete replacement of the –COOH groups from the non-esterified asphaltenes. The peaks located between 2300-2400 cm<sup>-1</sup> correspond to the presence of CO<sub>2</sub> in air.

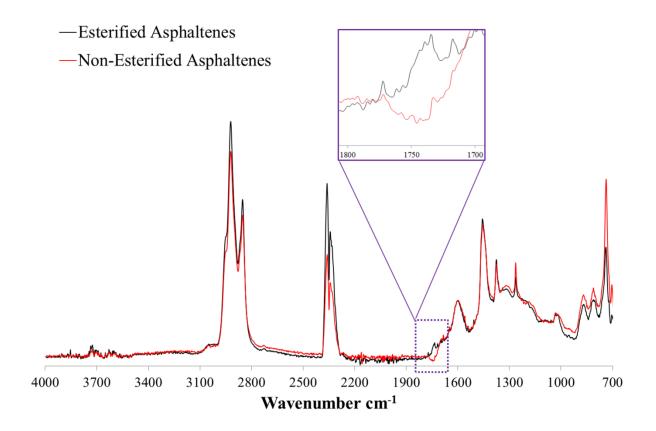


Figure S3. FTIR spectra of esterified and non-esterified asphaltenes. The inlet shows a magnification of the peak between 1720-1730 cm<sup>-1</sup> which represents the stretching vibrations of C=O ester bonds.

 Table S1. Weight percentage (%wt) of mass desorbed after 3 consecutive washouts with

 toluene determined through QCM-D measurements. The asphaltene concentration before the

 desorption step was 1.5 g/L.

Surface	Esterified Asphaltenes (wt%)	Non-esterified Asphaltenes (wt%)
Silica	22 ± 3	16 <u>+</u> 2
Stainless Steel	15 <u>+</u> 1	19 <u>+</u> 1

1. Nordgård EL, Sjoblom J. Model compounds for asphaltenes and C80 isoprenoid tetraacids. Part I: Synthesis and interfacial activities. Journal of Dispersion Science and

Technology 2008;29:1114-22.

2. Wei D, Orlandi E, Barriet M, Simon S, Sjöblom J. Aggregation of tetrameric acid in xylene and its interaction with asphaltenes by isothermal titration calorimetry. Journal of Thermal Analysis and Calorimetry 2015;122:463-71.

3. Sjöblom J, Aske N, Auflem IH, et al. Our current understanding of water-in-crude oil emulsions. Recent characterization techniques and high pressure performance. Advances in Colloid and Interface Science 2003;100-102:399-473.

4. Ese M-H, Galet L, Clausse D, Sjöblom J. Properties of Langmuir Surface and Interfacial Films Built up by Asphaltenes and Resins: Influence of Chemical Demulsifiers. Journal of Colloid and Interface Science 1999;220:293-301.

5. Fossen M, Kallevik H, Knudsen KD, Sjöblom J. Asphaltenes Precipitated by a Two-Step Precipitation Procedure. 2. Physical and Chemical Characteristics. Energy & Fuels 2011;25:3552-67.

6. Simon S, Sjöblom J, Wei D. Interfacial and Emulsion Stabilizing Properties of Indigenous Acidic and Esterified Asphaltenes. Journal of Dispersion Science and Technology 2016:DOI: 10.1080/01932691.2015.1135808.

7. Juyal P, Merino-Garcia D, Andersen SI. Effect on Molecular Interactions of Chemical Alteration of Petroleum Asphaltenes. I<sup>+</sup>. Energy & Fuels 2005;19:1272-81.