Clustering behaviour of polyaromatic compounds mimicking natural asphaltenes

Dorin Simionesie,¹ Greg O'Callaghan,² Joao L. L. F. S. Costa,³ Leonardo Giusti,⁴

William J. Kerr,⁴ Jan Sefcik,⁵ Paul A. Mulheran,⁵ and Zhenyu J. Zhang^{1,*}

¹School of Chemical Engineering, ²School of Chemistry, University of Birmingham, Edgbaston, Birmingham, B15 2TT, UK

³Curso de Engenharia Química, Universidade Federal de Alagoas, Camous A.C. Simões, Maceió, AL 57072, Brazil

⁴Department of Pure and Applied Chemistry, WestCHEM, University of Strathclyde, 295 Cathedral Street, Glasgow G1 1XL, UK

⁵Department of Chemical and Process Engineering, University of Strathclyde, 75 Montrose Street, Glasgow G1 1XJ, UK

*Corresponding E-mail: Z.J.Zhang@bham.ac.uk

This is the peer reviewed, accepted author manuscript of the following research article:
Simionesie, D., O'Callaghan, G., Costa, J. L. L. F. S., Giusti, L., Kerr, W., Sefcik, J., ... Zhang, Z. J. (2020). Clustering behaviour of polyaromatic compounds mimicking natural asphaltenes. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 603, [125221].
<https://doi.org/10.1016/j.colsurfa.2020.125221>

ABSTRACT

Clustering behaviour of hexa-*tert*-butylhexa-*peri*-hexabenzocoronene (HTBHBC) and its derivatives has been used as a model system to mimic that of natural asphaltenes. We used light scattering and ^1H -NMR spectroscopy, complemented by molecular dynamics simulation, to examine HTBHBC and its derivatives in toluene and toluene/heptane mixture, over a range of concentrations. The dispersibility of HTBHBC in toluene was found to be strongly dependent on its concentration. At concentrations below 5 mg/mL, HTBHBC appears to be fully dispersed and clustering equilibrium was reached within minutes as shown by scattering intensity measurements. At greater concentrations, the scattering intensity was approximately similar for all concentrations initially, but then decreased very slowly towards an apparent clustering equilibrium within two weeks. The mean hydrodynamic diameter of clusters, measured by dynamic light scattering, was initially around 1 micron for all concentrations greater than 5 mg/mL and then gradually reduced to around 0.4 micron at clustering equilibrium. At concentrations of 10 mg/mL and above, solid deposits were observed in toluene solutions when equilibrium was reached. ^1H -NMR spectroscopy showed that the precipitate was high purity HTBHBC possessing a planar structure, while the liquid phase contained a mixture of planar HTBHBC and its non-planar derivatives, forming colloidal clusters. The results show that the clustering process of asphaltene mimics in toluene can be extremely slow and great care should be taken when preparing equilibrated solutions. We also showed that observations of the solid-liquid equilibrium and clustering behaviour can be strongly dependent on the molecular structure of the polyaromatic compounds found in natural asphaltenes, and the structural and compositional evolution of colloidal clusters following an initial dispersion of asphaltene mimics in solvents.

INTRODUCTION

Asphaltenes, consisting of multiple aromatic rings and various proportions of aliphatic chains, comprise the heaviest fraction of crude oil and,¹ along with their high polarity, play a vital role in the characteristics of the crude oil.² In terms of solubility, they are broadly defined as soluble in aromatic solvents, such as toluene and xylene, but insoluble in *n*-alkanes, e.g. *n*-heptane and pentane.³ It is generally accepted that asphaltene molecules predominantly possess a single aromatic core composed of multiple rings substituted with peripheral *n*-alkanes, and their typical molecular weight is around 750 Da.^{4,8} Their strong tendency to aggregate and precipitate, triggered by various environmental factors, such as temperature, pressure, solvent quality or mechanical shear, has significant implications on both upstream and downstream operations.^{9,10} For example, deposition of asphaltenes on reservoir rock or refining equipment would significantly reduce permeability of the wellbore area, alter surface wettability, and decrease energy efficiency, respectively.¹¹⁻¹⁴

Asphaltenes follow a complex aggregation mechanism, driven by polar, π -stacking, and van der Waals interactions.¹⁵ Various techniques have been employed to investigate the relationships between molecular structure, nanoscopic configuration, colloidal stability, and aggregation mechanisms over multiple length scales.^{4,16-19} However, establishing the relationship between their chemical structures and clustering behavior remains a challenging task, which attracts extensive research interest. This is because the chemical structure and composition of asphaltenes are largely dependent upon the geological origin of the crude oil, the oil recovery method, and the history of extraction.¹⁸

To elucidate the specific influence of functional groups and chemical structures on the aggregation process of asphaltene, one approach is to develop model polyaromatic compounds with well-controlled structure, mimicking that of natural asphaltene.²⁰⁻²³ A model system that can be studied by both experimental and computational methods offers significant advantage in establishing how molecular structures determine clustering behaviour.²⁰ A recent study investigated the structural and compositional aspects of asphaltenes by comparing the aggregation behaviour of continental, archipelago, and anionic continental model asphaltenes using molecular simulations.²⁴ It was concluded that the polyaromatic rings of both archipelago and island model asphaltenes form nano-aggregates in toluene by stacking, suggesting that the formation of nano-aggregates is dependent more on chemical structure and concentration than solvent quality.²⁴⁻²⁶

A study concerning the self-association of model compounds based on pyrene and alkyl bridge dipyrrene suggested that polar groups play a major role in the self-association of aggregates larger than a dimer.²⁷ However, an hexabenzocoronene model (hexa-*tert*-butylhexa-*peri*-hexabenzocoronene (HTBHBC)) that possesses an increased number of aromatic rings show greater tendency for aggregation due to enhanced π -stacking interactions.²⁸⁻³¹ The significant influence of heteroatoms and acid groups on aggregation was recognised in both organic solvents and at the oil-water interface.³²⁻³⁴ It has also been suggested that side group and its chain length could influence the size and number of aggregates formed. However, the self-association behaviour of each model system is still influenced by the solvent species,³⁵ as aromatic solvent competitively hinders π -stacking in comparison to the aliphatic solvents which favours such interactions.³⁶ Another set of studies focused on attaching different terminal groups to branched alkyl chains of model asphaltenes with a consistent polyaromatic core called perylene.³⁷⁻³⁹ The studies suggest that only a small number of natural asphaltenes, that possess functional groups, are the cause of major industrial challenges.

In an experimental sense, the aggregation process of natural asphaltene has been studied by light scattering techniques.^{32,40} However, due to the significant variation in the chemical

nature of asphaltenes used in the literature, inconsistent results have been reported. Furthermore, when natural asphaltenes are dispersed in organic solvents, e.g. toluene, the dispersion becomes opaque, or less opaque at low concentrations, which results in low scattering intensity, making the measurements unreliable. In order to overcome the challenges aforementioned, backscattering and corner scattering set-ups were used to measure particle size distributions over a concentration range of 1-10 mg/mL.^{32, 41} It was suggested that concentrations below and above the critical cluster concentrations could lead to different aggregation mechanisms upon addition of *n*-heptane to the asphaltenes dispersed in toluene, which is in agreement with the Yen-Mullins model.¹ Other studies focused on the initial formation of nano-aggregates, suggesting that they occur near 0.01 mg/mL, i.e. lower than the frequently reported critical concentrations in the Yen-Mullins model (0.1 mg/mL).^{7, 42} These results suggested that part of the asphaltene molecules are more soluble than others, hence there is a consistent difference between the asphaltenes at the core of the cluster and those on the corona when clusters are formed.⁴²

Studies combining DLS and MD show how variations in the structure of side chains and polarity of functional groups lead to significant variations in molecular association, which have a profound effect on the diffusion coefficient of the aggregates formed, as the strength of intermolecular interactions is directly affected. Such effects can be found to play role in a broad range of applications based on supramolecular assembly of nanoparticles.^{43, 44} Another study shows how natural asphaltene nano-aggregates cluster (100 nm hydrodynamic radius) in a toluene dispersion at 0.3 mg/mL with the addition of *n*-heptane.⁴⁵ They aggregate and form flocs that ultimately precipitate. The study compares the aggregation behaviour of natural asphaltenes to a model compound, which is known to self-assemble due to its large aromatic area, which facilitates π -stacking interactions.^{46, 47} It was found that HTBHBC dispersed in toluene at 5 mg/mL show a similar aggregation pathway to that of natural asphaltenes, with a continuously increased hydrodynamic radii over a period of 5 hours upon the addition of *n*-heptane. However, stability of HTBHBC in toluene, which plays a significant role to the aggregation process, remains unclear.

To further understand the structural and solvent dependence of the asphaltene aggregation mechanism, a planar model compound, HTBHBC and its non-planar derivatives have been used in the present work. We attempt to study HTBHBC as a complex mixture, thereby replicating natural asphaltene behaviour more closely.

Work by Rathore and Burns demonstrated that HTBHBC can be synthesised, along with side products, in a one pot reaction.⁴⁸ In previous studies, HTBHBC was found to aggregate under the addition of *n*-heptane, however the stability of the HTBHBC-toluene dispersion, at different concentrations, prior to *n*-heptane addition, has not been investigated. It is possible that aggregation driven by concentration and *n*-heptane addition could be structurally, compositionally and kinetically dependent. This work aims to examine how the planarity of a model asphaltene influences the aggregation in toluene without the presence of heteroatoms, polar functional groups, and long chain *n*-alkanes. The effect of *n*-heptane was also investigated, by adding *n*-heptane after the clusters dispersed in toluene equilibrated. Molecular dynamic simulations were used to help to understand the affinity of the chemical structures towards themselves and towards the solvents.

EXPERIMENTAL

Materials

Hexaphenylbenzene (HPB), iron(III) chloride, 2-chloro-2-methylpropane (*t*-BuCl), anhydrous iron(III) chloride, dichloromethane (DCM), methanol (MeOH), nitromethane (MeNO₂), petrol ether, ethyl acetate, and deuterated (d₈) toluene were purchased from

Sigma-Aldrich (Dorset, UK) and used as received. Toluene (99.85%, Extra Dry), *n*-heptane (99.85%, Extra Dry), and PTFE syringe filters (pore size 100 nm) were purchased from Fisher Scientific (Loughborough, UK).

Preparation of HTBHBC samples

The synthesis (details included in the Supporting Information) yielded a powder product of dark amber, with the possible molecular structures presented in Figure 1. Samples for DLS and ^1H -NMR were prepared by adding the HTBHBC powder to toluene followed by vigorous shaking. At low concentrations (below 10 mg/ml), this resulted in clear solutions, while some visible solids remained and sedimented rapidly at higher concentrations. The dispersion becomes clear after 168 hours at which time the supernatant was extracted or additional *n*-heptane was introduced to achieve target toluene volume percentage of 80, 60, 40, 20% (in terms of volume parts of toluene out the combined volume of toluene and *n*-heptane used).

Figure 1. Molecular structure of (a) HTBHBC, $\text{C}_{66}\text{H}_{66}$; $M_w = 858.6$ g/mol and (b) Hypothesized derivative structure (DevHTBHBC) as suggested from ^1H -NMR and MALDI-TOF spectroscopy.

Dynamic light scattering (DLS)

DLS measurements were performed using a compact goniometer system (ALV/CGS-3, ALV-Laser, Germany) in conjunction with a multiple tau digital correlator (ALV/LSE-5004) at laser wavelength $\lambda = 632.8$ nm and scattering angle $\theta = 45^\circ$. The optical cell, washed with toluene and dried with nitrogen, was placed in a toluene bath to reduce spurious scattering and to improve temperature control. All experiments were performed at room temperature ($22 \pm 0.5^\circ\text{C}$) and ambient pressure. Toluene was filtered three times using PTFE filters (pore size 100 nm) before the HTBHBC powder was added at concentrations 1, 2, 3, 4, 5, 10, 15, 20, 30, 40, and 50 mg/mL. All samples were kept at room temperature without any further agitation prior to measurements. Time averaged scattering intensities and intensity autocorrelation functions were acquired for each sample at four different time intervals (0, 24, 168, and 336 hours).

At each time interval, 100 light scattering measurements were performed over a 30 minutes period. Scattering intensity data was normalized with respect to the incident beam intensity and to subtract the background scattering by toluene. The mean diffusivity, D , of clusters dispersed in the solution was calculated based on the initial decay rate of the normalised intensity autocorrelation function acquired, $g_2(\tau)$, based on:

$$g_2(\tau) = e^{-2Dq\tau} \quad (1)$$

where τ is the delay time and q is the scattering wave vector magnitude that can be calculated by the following equation:

$$q = \frac{4\pi n}{\lambda} \sin\left(\frac{\theta}{2}\right) \quad (2)$$

where n is the refractive index of the solvent, λ is the wavelength of the laser, and θ is the scattering angle. Stokes-Einstein equation was then used to calculate the mean hydrodynamic radius of dispersed clusters, r_H

$$r_H = \frac{kT}{6\pi\eta D} \quad (3)$$

where k is Boltzmann's constant, T is the absolute temperature, and η is the viscosity of the solvent.⁴⁹⁻⁵¹

¹H-NMR Spectroscopy

¹H-NMR spectroscopy (Bruker AVANCE III equipped with a 5 mm PABBO probe head) was used to quantify the relative purity of the HTBHBC powder dissolved in d₈-toluene. The sweeping frequency was 300 MHz, and chemical shifts were reported relative to CDCl₃. The peak (Figure 2) corresponding to the aromatic protons of HTBHBC at 9.76 ppm was used as reference, so that the molar ratio of the HTBHBC and derivative HTBHTC can be examined. The area under the reference peak was integrated and set to 1 and the variations in areas under the other peaks (10.86 ppm and 10.46 ppm - aromatic derivatives) were compared to it. Solvent peaks at 2.36 ppm were also integrated for each measurement to account for the concentration change as a result of solvent evaporation. Of the 12 HTBHBC samples (20 mg/mL in d₈-toluene), 3 were randomly examined by ¹H-NMR spectroscopy at each time interval (1, 24, 168, 336 hours), the supernatant extracted and the precipitate re-dissolved in d₈-toluene.

Molecular Dynamics Simulations

Molecular dynamics (MD) simulations were performed using GROMACS v4.6.5 simulation package.⁵² Optimized potential for liquid simulations/all atoms (OPLS/AA) force field was employed.^{53,54} A protocol previously used by this group⁵⁵ was used to build an HTBHBC model and its derivative (DevHTBHBC). One dimer formed of two HTBHBC molecules was constructed and placed by turn in a toluene and *n*-heptane solvated simulation box. Simulations were subsequently performed to generate the potential of mean force (PMF) between HTBHBC molecules, by separating the centres of mass (COMs) of the tightly-packed dimer in a direction normal to the aromatic plane of the dimer. A secondary set of simulations using seven model molecules (either HTBHBC or DevHTBHBC) were solvated in simulation boxes by toluene, a mixture of 50/50 toluene/*n*-heptane, or *n*-heptane, to examine the intermolecular interactions between the model polyaromatic compounds, and the solvent effect on each chemical structure. All simulations were performed for 100 ns. Radial distribution function (RDF) was used to analyse the averaged distance between the 7 model molecules in each simulation box, which reveals the magnitude of intermolecular interactions.

RESULTS AND DISCUSSION

Chemical analysis of liquid and solid phases

¹H-NMR spectroscopy and MALDI-ToF measurements were carried out to confirm the purity of the compound after being dispersed for 24 hours in toluene, with the resulting ¹H-NMR spectra as shown in Figure 2 and that of the MALDI-ToF in the SI. In Figure

2a, the peak at 9.76 ppm corresponds to the aromatic C-H of HTBHBC; solvent peaks for toluene are observed at 7.2 ppm, and 2.1 ppm. The hydrogens of the *t*-Bu groups within HTBHBC are observed at 1.9 ppm. The minor peaks observed between 8 and 10 ppm are derivatives of HTBHBC, formed in the one-pot synthesis, which shows a fraction of the derivatives with extra *tert*-butyl functional groups. The mixture represents a scenario where both symmetric and asymmetric polyaromatic compounds are present in the dispersion and separate over time into a solid deposit (HTBHBC) and a supernatant (liquid phase with clusters containing a mixture of HTBHBC and its derivatives). Chemical structure for one of the major derivatives is also shown in Figure 1.

Figure 2b shows the ^1H -NMR spectrum of the dissolved solid precipitate after the initial solution has reached apparent equilibrium (24 hours), with the major peaks corresponding to the solvent and the symmetrical HTBHBC molecule. Comparing to the spectrum of the initial dispersion (Figure 2a), multiple smaller peaks are no longer present in Figure 2b, which suggests the absence of non-symmetrical chemical structures, hence a HTBHBC compound with increased purity.

Figure 2. ^1H -NMR spectra of (a) synthesised HTBHBC in d_8 -toluene and (b) spectrum of the dissolved solid deposit and re-dispersed in d_8 -toluene. There are multiple peaks present, suggesting the existence of derivative compounds.

Clustering of HTBHBC in toluene

To examine the clustering behaviour of the polyaromatic mixture, light scattering measurements were performed in toluene as a function of concentration. Both time-averaged scattering intensity (static light scattering) and autocorrelation function (dynamic light scattering) were recorded. The initial decay of the collected autocorrelation functions at low concentration was too noisy to be fitted reliably, and hence, in such cases, mean hydrodynamic radii could not be estimated. Instead, time averaged scattering intensities,

providing reliable quantitative information about HTBHBC dispersions, were used. The scattering intensity depends on the following factors: concentration of clusters, size of clusters, and their refractive index contrast with respect to solvent. The scattering intensity will vary proportionally to the concentration of clusters of a given size and structure.⁵⁶⁻⁵⁸

Figure 3 presents the scattering intensity as a function of time for HTBHBC powder in toluene at low concentrations (1–5 mg/mL). It was found that the acquired intensity remains nearly constant at the lowest concentration (1 mg/mL). This suggests that there is no clustering whilst HTBHBC and its derivatives were readily solvated in toluene. The result is consistent with literature on natural asphaltenes where cluster sizes are stable at low concentrations.^{59, 60} It is worth noting that sizes and concentrations of natural asphaltene aggregates reported in the literature are sample dependent and inconsistent.^{59, 61-63} A previous study, that compared natural asphaltenes to the HTBHBC compound, performed measurements at 0.3 mg/mL (natural asphaltenes) and 5 mg/mL (HTBHBC), respectively. The very low natural asphaltene concentration is due to the opacity of the mixture that prevents the acquisition of scattered light through solution.⁴⁵

The initial scattering intensity was found to increase over two orders of magnitude with increasing concentration of HTBHBC in toluene from 1 to 5 mg/mL, indicating that large clusters were present upon introduction of the polyaromatic compounds to toluene. Subsequently, an increasingly long period is required for the intensity to stabilize with samples of increased concentration. For example, it takes 5 minutes for the 2 mg/mL sample to equilibrate, but it is longer than 24 hours for the 5 mg/mL sample. As no visible solid deposits were observed, the decrease in scattering intensity during the stabilisation process is likely due to the reconfiguration of those initially formed clusters, gradual dispersion of loosely aggregated assemblies into smaller colloidal scale entities, or possibly sedimentation of a few larger clusters.

Previous studies suggest two possible molecular arrangements that asphaltenes might adopt. Asphaltenes could form nanoaggregates at lower concentrations (~ 0.1 mg/mL), but cluster at higher concentrations (1–10 mg/mL) that are above the critical cluster concentration (CCC).^{7, 64} In the present work, the initial scattering intensity was found to increase with the increased concentration of HTBHBC (from 1 to 5 mg/mL). It is probable that both HTBHBC and its derivatives self-associated and formed clusters as concentration increases. A similar concentration range (0.1–10 mg/mL) was reported, where aggregation of natural asphaltenes collected from different origins were reported as a function of concentration.³³

Figure 3. Normalised scattering intensity of HTBHBC in toluene as a function of time for low concentrations (1–5 mg/mL).

To further investigate the effect of concentration on the clustering behaviour of the polyaromatic compounds prepared, concentrations between 10 and 50 mg/mL were examined. After introducing HTBHBC into toluene, undissolved solids appeared and sedimented readily. Figure 4a presents the measured scattering intensity over an extended period of time (up to 336 hours). The time averaged scattering intensity acquired within the first hour for all samples examined is similar to that obtained for the 5 mg/mL sample. However, within the first 24 hours, there is a significant reduction in scattering intensity. This again can be attributed to the same factors identified for the low concentrations. The scattering intensity continues to decrease beyond 24 hours, albeit at a reduced rate, until it remains relatively constant after about 2 weeks, suggesting that the clustering reached an equilibrium configurational arrangement.⁴²

Figure 4. (a) Normalised scattering intensity and (b) mean hydrodynamic radius of HTBHBC in toluene as a function of time acquired from HTBHBC in toluene at high concentrations (10 – 50 mg/mL).

Based on the autocorrelation functions collected, hydrodynamic radii of the HTBHBC clusters were calculated and presented for different initial concentrations, as shown in Figure 4b. The initial mean hydrodynamic radius of the HTBHBC clusters was found to be around 1 micron for all HTBHBC concentrations. The radii of the HTBHBC clusters remained largely constant for the first 24 hours, whilst the scattering intensity reduced significantly during the same period (see Figure 4a). This supports the rationale (*vide supra*) that there is a reconfiguration process of the initially formed clusters where their internal structure changes and so does their refractive index. Furthermore, it rules out the possibility of gradual dispersion of loosely aggregated assemblies, or sedimentation of large clusters, because either of these would result in reduced hydrodynamic radius within the

first 24 hours. After 168 hours, the radii of clusters were reduced to nearly half of those measured at 24 hours. We note that no reliable autocorrelation function data could be acquired for samples at 10, 15, and 20 mg/mL after 24 hours, even though the intensity was similar to what acquired in other samples.

Because the ratio between HTBHBC (symmetric structure with planar configuration) and the derivatives (asymmetric structure with non-planar configuration) remains the same for all samples examined, and those with planar configuration are expected to be more likely to aggregate due to π -stacking, it is probable that the aggregation and dissociation observed is related to the variations in the HTBHBC's derivative chemical structures.⁶⁵⁻⁶⁷ The potential of HTBHBC to cluster and precipitate suggests that planar HTBHBC molecules are more prone to phase separation at high concentrations, whilst its non-planar derivatives stay in solution more readily. The derivatives could possibly form mixed clusters together with the planar HTBHBC, re-configuring themselves into smaller, more stable clusters as suggested by the decreased scattering intensities and hydrodynamic radii indicated in Figure 4.

In order to better understand the clustering behaviour of the polyaromatic mixture after reaching equilibrium (no change in scattering intensity), in Figure 5 the scattering intensity values at 168 hours are presented as a function of the initial concentration. These values correspond to steady state, implying equilibrium configuration, where the number of clusters after 168 hours is stable after clusters had undergone rearrangement to energetically more favourable states. It can be seen that the scattering intensity increases with concentration for the range examined (1–50 mg/mL). The relationship between the scattering intensity and concentration is linear at low concentrations (up to about 10 mg/mL) but it becomes sublinear at higher concentrations. As the scattering intensity deviates from linearity with increasing concentration, and supported by the ¹H-NMR data shown in Figure 2, is it most likely that the planar HTBHBC molecules precipitate as they reach a critical concentration, while the non-planar derivatives remain dispersed, so that the proportion of HTBHBC decreases in relation to its derivatives in the dispersed clusters. This is consistent with the visual observation of HTBHBC solutions (Figure S2 in the Supporting Information) where no sediment was observed at low concentration (up to 5 mg/mL), while a noticeable amount of sedimented solids can be seen at high HTBHBC concentration (30 mg/mL).

Figure 5. Mean normalised scattering intensity acquired at 168 hours as a function of initial concentration. The relationship is linear in the low concentration regime but becomes sub-linear as concentration increases. Dashed lines are used for visual aid only.

Effect of molecular structure on aggregation pathway

Our previous molecular simulation work suggests that modifications to the structure of HTBHBC could result in different aggregation pathways.⁵⁵ ¹H-NMR spectra were acquired at time intervals 1, 24, 168, and 336 hours for the 20 mg/mL suspension to identify the chemical nature of the compounds that were present in the liquid phase and in the solid deposit (re-dispersed in toluene), respectively. The peak at 9.76 ppm (see Figure 2) that corresponds to the aromatic protons of HTBHBC was chosen as the reference peak. Consequently, the area under this specific peak was integrated, against which the areas under the other two peaks at 10.86 ppm and 10.46 ppm, that are attributed to alternative aromatic derivatives, were normalized. This approach enables us to distinguish the non-planar derivatives from the planar HTBHBC in each phase at the point of collection. As the planar molecules precipitate at higher concentrations, the liquid phase remains increasingly dominated by non-planar derivative compounds as the concentration increases.

By analysing the supernatant and re-dispersed sediment, this separation can be observed. Figure 6 shows changes in areas under peaks as the solids were collected from the liquid supernatant and re-dispersed in toluene. Sample Set 1, consisting of three dispersion samples, was kept intact without disruption. The consistent relative integral acquired at different collection time confirms that the chemical nature and fraction of the molecules in toluene remain constant over the time. Meanwhile solid precipitate was collected from the bottom of samples in sets 2, 3, and 4, at 24, 168 (1 week), and 336 (2 weeks) hours, respectively. These were re-dispersed in toluene, examined by ¹H-NMR spectroscopy, and as presented in Figure 6 as Precipitate. The sum of integrated areas under the peaks corresponding to DevHTBHBC (10.86 ppm and 10.46 ppm) is normalised against that of the reference peak. It is shown clearly that the relative integral, the ratio between derivatives and pure HTBHBC, is reduced substantially for all three precipitate samples, which suggests that there is very little DevHTBHBC in the precipitate. This also confirms that HTBHBC is predominately present in the solid precipitate, whilst the derivative (DevHTBHBC) remains dispersed in toluene. As a control measure, one of the three dispersion samples from sets 2, 3, 4, was kept intact and measured at each collection point. They show very similar behaviour to set 1, eliminating the possibility of errors caused between sample sets. The significantly reduced values in relative integral for precipitates collected at different points suggest that since HTBHBC can readily aggregate due to its large, planar surface area, which facilitates π -stacking to form large clusters, this is far more likely to be the species that is precipitating.

Figure 6. Change in the relative integral of the DevHTBHBC peak compared to the HTBHBC peak over time. Filled symbols represent re-dispersed precipitate, and empty symbols represent the corresponding filtrate. Samples from Set 2, 3 and 4 were re-dispersed in toluene and measured at 24, 168 and 336 hours, respectively. Sample from Set 1 was left uninterrupted throughout the duration of the experiment. All samples were kept at room temperature for the entire time interval.

At the beginning of the experiment, it was found that HTBHBC was the dominant peak, although other aromatic species were present as shown in Figure 2, suggesting a mixture of the pure compound and its derivatives. A significant decrease in the relative integral of the DevHTBHBC peak (quantified in Figure 6) suggests an increase in HTBHBC purity in the precipitate. This analysis implies that the HTBHBC in toluene separates according to molecular structure, with the pure compound aggregating and precipitating out of solution, while the derivatives remain dispersed.

*Effect of *n*-heptane*

Once the equilibrium was reached after 168 hours, there are stable clusters which are likely to be composed of the mixture of HTBHBC and its derivatives (see Figure 4). A controlled volume of *n*-heptane was introduced to the stable dispersion to investigate its effect on the clustering. The normalised scattering intensity is plotted as a function of the initial concentration in Figure 7. Different *n*-heptane to toluene volume ratios were examined, from 100 to 20 V% toluene. It was found that the scattering intensity for each initial concentration decreased proportionally to the dilution factor upon addition of *n*-heptane, which implies that the addition of *n*-heptane does not have notable impact on clusters already stabilised in toluene. This is surprising as it is contrary to the behaviour previously reported for natural asphaltenes and other model compounds as discussed above. Although precipitation of HTBHBC did occur in toluene at higher concentrations before the addition of *n*-heptane, no further changes were observed upon addition of *n*-heptane to equilibrated clusters beyond a simple dilution effect.

Figure 7. Mean normalised scattering intensity of HTBHBC in toluene after 168 hours, with the addition of four volumes of *n*-heptane (80, 60, 40, 20% of toluene volume) as a function of initial concentrations.

This lack of further aggregation in response to the addition of *n*-heptane could be attributed to the composition and configuration of the clusters that are present after 168 hours in toluene. In contrast to natural asphaltene, that have been reported to precipitate upon the addition of *n*-heptane, the equilibrated clusters composed of mixtures of HTBHBC and its non-planar derivatives dispersed in toluene solutions investigated here appear to be unresponsive to the *n*-toluene addition. However, natural asphaltene molecules exhibit a far larger variety of aromatic core sizes and functional groups, which further complicate the aggregation mechanism and may increase their responsiveness to *n*-heptane, in which they tend to precipitate. This suggests that specific features of the asphaltene molecular structure are crucial in determining its sensitivity towards solvents and hence raises the question of how the different chemical structures (HTBHBC and DevHTBHBC) interact with each other as well as with various solvents.

Molecular Dynamics simulations

We performed Molecular Dynamics simulations, following a previous protocol,⁵⁵ to investigate the aggregation of HTBHBC and DevHTBHBC, and the impact of the solvent on the process. We started by studying the free energy of dimerisation on HTBHBC in toluene and then in *n*-heptane. A pre-assembled HTBHBC dimer was created by the parallel stacking of two molecules with small separation between the centre-of-mass (COM) of each molecule. The dimer was solvated, in turn, by toluene and *n*-heptane. Pulling simulations were performed to generate the potential of mean force (PMF) between the two HTBHBC molecules, by separating the COMs in a direction normal to the aromatic plane. Figure 7 presents the energy profiles for the two solvents that show similar characteristics: an increasing energy barrier can be seen between 0.25 and 0.75 nm, indicating the distance at which the molecules most influence each others' motion. From these simulations it is clear that more energy is required to separate a HTBHBC dimer in *n*-heptane than in toluene, indicating less solubility and a higher aggregation potential in the alkane than in the aromatic solvent. This is in agreement with previous literature where the aggregation of HTBHBC was recorded with the addition of *n*-heptane.^{35, 45}

Figure 7. PMF profiles for HTBHBC dimers in toluene and *n*-heptane

Figure 7 shows that the optimum distance between HTBHBC COMs is around 0.25-0.45 nm, in the vicinity of the closest-approach parallel stacking (0.35 nm). This suggests that a slightly offset stacking might be the preferred configuration, due to the impact of the small side-chains. For distances beyond 0.75 nm, the PMF profile has a plateau, suggesting the molecules are free to diffuse at these separations. These results support the aggregation potential of HTBHBC in contrast to its non-parallel derivatives [46] and further shows how the solute-solvent relation is affected by the molecular structure. We note that it was not possible to form a similar stable dimer for DevHTBHBC, demonstrating the importance of the planar structure of HTBHBC for closely-stacked aggregation.

It is tempting to assume that the aggregation of HTBHBC will be rapid, since there is no obvious barrier to aggregation apparent (Figure 7). However, our previous MD simulations have shown that this is not the case.⁵⁵ Freely diffusing monomers of HTBHBC do not readily form closely-stacked dimers on the timescale of 100 ns, since the process is kinetically limited; the monomers must approach along a very particular pathway for a successful dimer formation, and this is a rare process. This perhaps explains the long timescales required experimentally for the dispersed HTBHBC to sediment out of solution, even at high concentrations.

To better understand the difference in molecular behaviour between the HTBHBC, and the derivative DevHTBHBC, a series of un-biased MD simulations were performed. Seven HTBHBC molecules were placed in turn in simulation boxes solvated by toluene, *n*-heptane, and a 50/50 toluene/*n*-heptane mixture. Similarly, the dynamics of seven DevHTBHBC molecules were simulated in the same solvent mixtures, leading to a total of 6 simulations, each of 100 ns duration. From these trajectories, the molecules' COM-COM radial distribution functions (RDF) were collected and compared.

Figure 8. Normalised COM radial distribution functions of the HTBHBC, and of the DevHTBHBC, model compounds in (a) toluene, (b) 50/50 toluene/*n*-heptane mixture, and (c) *n*-heptane averaged over 100 ns trajectories. Note the changing scale on the vertical axes required for the different solvents.

The RDFs displayed in Figure 8 show the propensity of the different molecules to aggregate in the different solvents. In Figure 8a, we see that the HTBHBC tends to remain dispersed in toluene, despite the possibility of dimer formation, as shown in Figure 7. The reason for this is that the aromatic solvent wets the HTBHBC core, so that pathway to dimer formation is severely restricted. In Figure 8b and 8c, we see that the presence of *n*-

heptane promotes aggregation as expected.⁴⁵ However, we note that the RDF peaks at 0.7-0.8 nm. Referring to Figure 7, this is at the start of the free energy plateau for dimer formation. This means that the HTBHBC molecules are loosely aggregating, but not able to form tight dimers on the timescale of these trajectories (100 ns).

In contrast, the RDFs for the DevHTBHBC consistently show that the molecules do not tend to aggregate in any of the solvents. In Figure 8a for the pure toluene solvent, the DevHTBHBC has small peaks at 0.9-1.0 nm, showing that the molecules cannot approach one another as closely as the HTBHBC. This is due to the steric hindrance of the out-of-plane defect structure illustrated in Figure 1b. The 50:50 mixture of toluene and *n*-heptane, and, indeed, the pure *n*-heptane solvents (Figure 8b and 8c) do not substantially affect the aggregation propensity of the DevHTBHBC molecules.

There is a clear contrast between the behaviour of the HTBHBC and DevHTBHBC molecules revealed in these MD simulations:

1. HTBHBC can form closely stacked dimers in toluene and *n*-heptane, but the process is very slow, particularly in toluene when the molecules tend to stay apart, making dimerisation an extremely rare kinetically-limited event. The addition of *n*-heptane will however cause loosely-bound aggregation, which might therefore promote more rapid dimerisation, although this is not seen on the 100 ns trajectory timescale.
2. DevHTBHBC does not form stacked structures and, furthermore, does not show much propensity to form even loose aggregates in either toluene nor *n*-heptane.

These behaviours resonate with the results of our experiments:

1. In a mixture of HTBHBC and DevHTBHBC molecules in toluene, there is a slow precipitation of the HTBHBC with the DevHTBHBC remaining in solution.
2. The dilution of the solvent with *n*-heptane does not dramatically impact the process; the HTBHBC still precipitates, and the DevHTBHBC remains in solution.

We therefore conclude that the simulations reinforce our conclusions regarding the importance of steric interactions in the aggregation and solvation of the compounds, and the need to allow long timescales for the equilibration processes to occur.

Summary

In the present work, several experimental methods were employed to investigate the molecular interactions and corresponding clustering of the HTBHBC and its derivatives, dispersed in toluene, as a function of concentration and time. It was observed that, at low concentrations, the intensity stabilizes with no visible precipitation, suggesting both the HTBHBC and its derivatives are well dispersed in stable clusters in such concentrations. The decreasing scattering intensity over time and onset of precipitation at concentrations above 10 mg/mL suggests that the clusters are changing their structural and/or compositional arrangement, and striving towards a more stable configuration over times up to 2 weeks long. The scattering intensity after 168 hours shows a direct relation to the concentration. Further analysis using MALDI-TOF and ¹H-NMR spectroscopies shows that precipitation deposits formed at higher concentrations are nearly pure HTBHBC, implying that equilibrated clusters are mixtures of HTBHBC and its derivatives with decreasing portion of HTBHBC as the overall concentration increases. Surprisingly, these equilibrated clusters were then found stable upon addition of *n*-heptane to their dispersion in toluene.

A selective aggregation mechanism is identified, as the planar, pure HTBHBC molecules, preferentially aggregate and precipitate, while the non-planar derivatives remain

dispersed in solution. At concentrations above 5 mg/mL, the HTBHBC molecules overcome the steric repulsion barrier set by the solvent, as suggested by the simulations, leading to their precipitation. The non-planar derivatives remain in dispersion as their non-planar structure hinders stacking interactions, regardless of concentration or solvent, although they readily form disordered colloidal clusters together with HTBHBC remaining in the liquid phase. The selective aggregation mechanisms proposed in this work depicts the impact of the chemical structure on concentration induced clustering and precipitation of model asphaltene compounds.

References

1. Mullins, O. C.; Sheu, E. Y.; Hammami, A.; Marshall, A. G., *Asphaltenes, heavy oils, and petroleomics*. Springer Science & Business Media: 223 Spring Street, New York, NY 10013, USA, 2007.
2. Hammami, A.; Ratulowski, J., Precipitation and deposition of asphaltenes in production systems: a flow assurance overview. In *Asphaltenes, heavy oils, and petroleomics*, Springer: New York, NY, 2007; pp 617-660.
3. Subirana, M.; Sheu, E. Y., *Asphaltenes: fundamentals and applications*. Springer Science & Business Media: 223 Spring Street, New York, NY 10013, USA, 2013.
4. Sabbah, H.; Morrow, A. L.; Pomerantz, A. E.; Zare, R. N. Evidence for island structures as the dominant architecture of asphaltenes. *Energy Fuels*, **2011**, *25*, 1597-1604.
5. Andrews, A. B.; Guerra, R. E.; Mullins, O. C.; Sen, P. N. Diffusivity of asphaltene molecules by fluorescence correlation spectroscopy. *J. Phys. Chem. A*, **2006**, *110*, 8093-8097.
6. Lisitza, N. V.; Freed, D. E.; Sen, P. N.; Song, Y.-Q. Study of asphaltene nanoaggregation by nuclear magnetic resonance (NMR). *Energy Fuels*, **2009**, *23*, 1189-1193.
7. Mullins, O. C.; Sabbah, H.; Eyssautier, J.; Pomerantz, A. E.; Barré, L.; Andrews, A. B.; Ruiz-Morales, Y.; Mostowfi, F.; McFarlane, R.; Goual, L. Advances in asphaltene science and the Yen–Mullins model. *Energy Fuels*, **2012**, *26*, 3986-4003.
8. Schuler, B.; Meyer, G.; Peña, D.; Mullins, O. C.; Gross, L. Unraveling the molecular structures of asphaltenes by atomic force microscopy. *J. Am. Chem. Soc.*, **2015**, *137*, 9870-9876.
9. Chaisoontornyotin, W.; Haji-Akbari, N.; Fogler, H. S.; Hoepfner, M. P. Combined asphaltene aggregation and deposition investigation. *Energy Fuels*, **2016**, *30*, 1979-1986.
10. Wang, X.; Zhang, R.; Liu, L.; Qiao, P.; Simon, S. C.; Sjoblom, J.; Xu, Z.; Jiang, B. Interactions of Polyaromatic Compounds. Part 2: Flocculation Probed by Dynamic Light Scattering and Molecular Dynamics Simulation. *Energy Fuels*, **2017**, *31*, 9201–9212.
11. Ali, M. A.; Islam, M. R. The effect of asphaltene precipitation on carbonate-rock permeability: an experimental and numerical approach. *SPE Production & Facilities*, **1998**, *13*, 178-183.
12. Newberry, M. E.; Barker, K. M. In *Formation damage prevention through the control of paraffin and asphaltene deposition*, SPE Production Operations Symposium, 1985; Society of Petroleum Engineers: 1985.
13. Leontaritis, K. J.; Amaefule, J. O.; Charles, R. E. A systematic approach for the prevention and treatment of formation damage caused by asphaltene deposition. *SPE Production & Facilities*, **1994**, *9*, 157-164.
14. Thomas, D. C.; Becker, H. L.; Del Real Soria, R. A. Controlling asphaltene deposition in oil wells. *SPE Production & Facilities*, **1995**, *10*, 119-123.
15. Rashid, Z.; Wilfred, C. D.; Gnanasundaram, N.; Arunagiri, A.; Murugesan, T. A comprehensive review on the recent advances on the petroleum asphaltene aggregation. *J. Pet. Sci. Eng.*, **2019**, *176*, 249.

16. Zajac, G. W.; Gallas, J. M.; Alvarado - Swaisgood, A. E. Tunneling microscopy verification of an x - ray scattering - derived molecular model of tyrosine - based melanin. *J. Vac. Sci. Technol., B*, **1994**, *12*, 1512-1516.
17. Pomerantz, A. E.; Hammond, M. R.; Morrow, A. L.; Mullins, O. C.; Zare, R. N. Two-step laser mass spectrometry of asphaltenes. *J. Am. Chem. Soc.*, **2008**, *130*, 7216-7217.
18. Groenzin, H.; Mullins, O. C., *Asphaltene molecular size and weight by time-resolved fluorescence depolarization*. 2007; p 17-62.
19. Sharma, A.; Groenzin, H.; Tomita, A.; Mullins, O. C. Probing order in asphaltenes and aromatic ring systems by HRTEM. *Energy Fuels*, **2002**, *16*, 490-496.
20. Sjöblom, J.; Simon, S.; Xu, Z. Model molecules mimicking asphaltenes. *Adv. Colloid Interface Sci.*, **2015**, *218*, 1-16.
21. Subramanian, S.; Sørland, G. H.; Simon, S.; Xu, Z.; Sjöblom, J. Asphaltene fractionation based on adsorption onto calcium carbonate: Part 2. Self-association and aggregation properties. *Colloids Surf., A*, **2017**, *514*, 79-90.
22. Liu, L.; Sjöblom, J.; Xu, Z. Nanoaggregation of polyaromatic compounds probed by electrospray ionization mass spectrometry. *Energy Fuels*, **2016**, *30*, 3742-3751.
23. Law, J. C.; Headen, T. F.; Jiménez-Serratos, G.; Boek, E. S.; Murgich, J.; Müller, E. A. Catalogue of plausible molecular models for the molecular dynamics of asphaltenes and resins obtained from quantitative molecular representation. *Energy Fuels*, **2019**, *33*, 9779.
24. Kuznicki, T.; Masliyah, J. H.; Bhattacharjee, S. Aggregation and partitioning of model asphaltenes at toluene– water interfaces: Molecular dynamics simulations. *Energy Fuels*, **2009**, *23*, 5027-5035.
25. Kuznicki, T.; Masliyah, J. H.; Bhattacharjee, S. Molecular dynamics study of model molecules resembling asphaltene-like structures in aqueous organic solvent systems. *Energy Fuels*, **2008**, *22*, 2379-2389.
26. Jian, C.; Tang, T.; Bhattacharjee, S. Probing the effect of side-chain length on the aggregation of a model asphaltene using molecular dynamics simulations. *Energy Fuels*, **2013**, *27*, 2057-2067.
27. Akbarzadeh, K.; Bressler, D. C.; Wang, J.; Gawrys, K. L.; Gray, M. R.; Kilpatrick, P. K.; Yarranton, H. W. Association behavior of pyrene compounds as models for asphaltenes. *Energy Fuels*, **2005**, *19*, 1268-1271.
28. Rakotonradany, F.; Fenniri, H.; Rahimi, P.; Gawrys, K. L.; Kilpatrick, P. K.; Gray, M. R. Hexabenzocoronene model compounds for asphaltene fractions: synthesis & characterization. *Energy Fuels*, **2006**, *20*, 2439-2447.
29. Wagner, C.; Kasemann, D.; Golnik, C.; Forker, R.; Esslinger, M.; Müllen, K.; Fritz, T. Repulsion between molecules on a metal: Monolayers and submonolayers of hexa-*peri*-hexabenzocoronene on Au(111). *Phys. Rev. B*, **2010**, *81*, 035423.
30. Gross, L.; Moresco, F.; Ruffieux, P.; Gourdon, A.; Joachim, C.; Rieder, K.-H. Tailoring molecular self-organization by chemical synthesis: Hexaphenylbenzene, hexa-*peri*-hexabenzocoronene, and derivatives on Cu (111). *Phys. Rev. B*, **2005**, *71*, 165428.
31. Yang, Y.; Chang, Z.; Yang, X.; Qi, M.; Wang, J. Selectivity of hexaphenylbenzene-based hydrocarbon stationary phase with propeller-like conformation for aromatic and aliphatic isomers. *Anal. Chim. Acta*, **2018**, *1016*, 69.
32. Anisimov, M. A.; Yudin, I. K.; Nikitin, V.; Nikolaenko, G.; Chernoutsan, A.; Toulhoat, H.; Frot, D.; Briolant, Y. Asphaltene aggregation in hydrocarbon solutions studied by photon correlation spectroscopy. *J. Phys. Chem.*, **1995**, *99*, 9576-9580.
33. Yudin, I. K.; Nikolaenko, G. L.; Gorodetskii, E. E.; Kosov, V. I.; Melikyan, V. R.; Markhashov, E. L.; Frot, D.; Briolant, Y. Mechanisms of asphaltene aggregation in toluene– heptane mixtures. *J. Pet. Sci. Eng.*, **1998**, *20*, 297-301.

34. Cai, L.; Wang, L.; Kang, S.; Geng, Y.; Deng, K.; Zheng, Q.; Zeng, Q. Supramolecular self-assembly of hexaphenylbenzene derivatives with different symmetry and number of carboxylic acid at liquid/solid interfaces. *J. Phys. Chem. C*, **2016**, *120*, 27259.
35. Oh, K.; Ring, T. A.; Deo, M. D. Asphaltene aggregation in organic solvents. *J. Colloid Interface Sci.*, **2004**, *271*, 212-219.
36. Teklebrhan, R. B.; Ge, L.; Bhattacharjee, S.; Xu, Z.; Sjöblom, J. Probing structure–nanoaggregation relations of polyaromatic surfactants: a molecular dynamics simulation and dynamic light scattering study. *J. Phys. Chem. B.*, **2012**, *116*, 5907-5918.
37. Nordgård, E. L.; Landsem, E.; Sjöblom, J. Langmuir films of asphaltene model compounds and their fluorescent properties. *Langmuir*, **2008**, *24*, 8742-8751.
38. Nordgård, E. L.; Sjöblom, J. Model compounds for asphaltenes and C80 isoprenoid tetraacids. Part I: Synthesis and Interfacial Activities. *J. Dispersion Sci. Technol.*, **2008**, *29*, 1114-1122.
39. Nordgård, E. L.; Sørland, G.; Sjöblom, J. Behavior of asphaltene model compounds at W/O interfaces. *Langmuir*, **2009**, *26*, 2352-2360.
40. Burya, Y. G.; Yudin, I. K.; Dechabo, V. A.; Kosov, V. I.; Anisimov, M. A. Light-scattering study of petroleum asphaltene aggregation. *Appl. Opt.*, **2001**, *40*, 4028-4035.
41. Yudin, I. K.; Nikolaenko, G. L.; Gorodetskii, E. E.; Markhashov, E. L.; Agayan, V. A.; Anisimov, M. A.; Sengers, J. V. Crossover kinetics of asphaltene aggregation in hydrocarbon solutions. *Phys. A* **1998**, *251*, 235-244.
42. Evdokimov, I. N.; Eliseev, N. Y.; Akhmetov, B. R. Asphaltene dispersions in dilute oil solutions. *Fuel*, **2006**, *85*, 1465-1472.
43. Li, H.; Zhao, J.; Wang, A.; Li, Q.; Cui, W. Supramolecular assembly of protein-based nanoparticles based on tumor necrosis factor-related apoptosis-inducing ligand (TRAIL) for cancer therapy. *Colloids Surf., A*, **2020**, *590*, 124486.
44. Li, H.; Zhao, Y.; Jia, Y.; Qu, C.; Li, J. Covalently assembled dopamine nanoparticle as an intrinsic photosensitizer and pH-responsive nanocarrier for potential application in anticancer therapy. *Chem. Commun.*, **2019**, *55*, 15057.
45. Breure, B.; Subramanian, D.; Leys, J.; Peters, C. J.; Anisimov, M. A. Modeling asphaltene aggregation with a single compound. *Energy Fuels*, **2012**, *27*, 172-176.
46. Hill, J. P.; Jin, W.; Kosaka, A.; Fukushima, T.; Ichihara, H.; Shimomura, T.; Ito, K.; Hashizume, T.; Ishii, N.; Aida, T. Self-assembled hexa-peri-hexabenzocoronene graphitic nanotube. *Science*, **2004**, *304*, 1481-1483.
47. Wu, J.; Fechtenkötter, A.; Gauss, J.; Watson, M. D.; Kastler, M.; Fechtenkötter, C.; Wagner, M.; Müllen, K. Controlled self-assembly of hexa-peri-hexabenzocoronenes in solution. *J. Am. Chem. Soc.*, **2004**, *126*, 11311-11321.
48. Rathore, R.; Burns, C. A Practical One-Pot Synthesis of Soluble Hexa-peri-hexabenzocoronene and Isolation of Its Cation-Radical Salt. *J. Org. Chem.*, **2003**, *68*, 4071.
49. Pecora, R., *Dynamic light scattering: applications of photon correlation spectroscopy*. Springer Science & Business Media: 223 Spring Street, New York, NY 10013, USA, 2013.
50. Vaccaro, A.; Šefčík, J.; Morbidelli, M. Characterization of colloidal polymer particles through stability ratio measurements. *Polymer*, **2005**, *46*, 1157-1167.
51. Pusey, P. N.; Van Megen, W. Dynamic light scattering by non-ergodic media. *Phys. A* **1989**, *157*, 705-741.
52. van der Spoel, D.; Lindhal, E.; Hess, B.; Team, T. G. D. Gromacs User Manual Version 4.6.5. **2013**.
53. Boek, E. S.; Yakovlev, D. S.; Headen, T. F. Quantitative molecular representation of asphaltenes and molecular dynamics simulation of their aggregation. *Energy Fuels*, **2009**, *23*, 1209-1219.

54. Headen, T. F.; Boek, E. S.; Skipper, N. T. Evidence for asphaltene nanoaggregation in toluene and heptane from molecular dynamics simulations. *Energy Fuels*, **2009**, *23*, 1220-1229.
55. Costa, J. L. L. F. S.; Simionesie, D.; Zhang, Z. J.; Mulheran, P. A. Aggregation of model asphaltenes: a molecular dynamics study. *J. Phys.: Condens. Matter*, **2016**, *28*, 394002.
56. Finsy, R. Particle sizing by quasi-elastic light scattering. *Adv. Colloid Interface Sci.*, **1994**, *52*, 79-143.
57. Pusey, P. N., *Introduction to scattering experiments*. 2002; Vol. 46, p 3-22.
58. Lindner, P.; Zemb, T., *Neutron, X-ray and light scattering: introduction to an investigative tool for colloidal and polymeric systems*. North-Holland Delta Series; 1991; 385 p; North-Holland; Amsterdam (Netherlands), 1991.
59. Eyssautier, J.; Levitz, P.; Espinat, D.; Jestin, J.; Gummel, J.; Grillo, I.; Barré, L. Insight into asphaltene nanoaggregate structure inferred by small angle neutron and X-ray scattering. *J. Phys. Chem. B.*, **2011**, *115*, 6827-6837.
60. Eyssautier, J.; Frot, D.; Barré, L. Structure and dynamic properties of colloidal asphaltene aggregates. *Langmuir*, **2012**, *28*, 11997-12004.
61. Sheu, E. Y.; Storm, D. A., Colloidal properties of asphaltenes in organic solvents. In *Asphaltenes*, EY Sheu, O. M., Ed. Springer: New York: Plenum, 1995; pp 1-52.
62. Barré, L.; Simon, S.; Palermo, T. Solution properties of asphaltenes. *Langmuir*, **2008**, *24*, 3709-3717.
63. Barré, L.; Jestin, J.; Morisset, A.; Palermo, T.; Simon, S. Relation between nanoscale structure of asphaltene aggregates and their macroscopic solution properties. *Oil Gas Sci. Technol.*, **2009**, *64*, 617-628.
64. Dechaine, G. P.; Gray, M. R. Membrane diffusion measurements do not detect exchange between asphaltene aggregates and solution phase. *Energy Fuels*, **2010**, *25*, 509-523.
65. Alameddine, B.; Aebischer, O. F.; Amrein, W.; Donnio, B.; Deschenaux, R.; Guillon, D.; Savary, C.; Scanu, D.; Scheidegger, O.; Jenny, T. A. Mesomorphic hexabenzocoronenes bearing perfluorinated chains. *Chem. Mater.*, **2005**, *17*, 4798-4807.
66. Kastler, M.; Pisula, W.; Wasserfallen, D.; Pakula, T.; Müllen, K. Influence of alkyl substituents on the solution and surface-organization of hexa-peri-hexabenzocoronenes. *J. Am. Chem. Soc.*, **2005**, *127*, 4286-4296.
67. Feng, X.; Marcon, V.; Pisula, W.; Hansen, M. R.; Kirkpatrick, J.; Grozema, F.; Andrienko, D.; Kremer, K.; Müllen, K. Towards high charge-carrier mobilities by rational design of the shape and periphery of discotics. *Nat. Mater.*, **2009**, *8*, 421-426.

This is the Supporting Information for the author accepted version of:

“Clustering behaviour of polyaromatic compounds mimicking natural asphaltenes”

D. Simionesie, G. O’Callaghan, J. L. L. F. S. Costa, L. Giusti, W. J. Kerr, J. Sefcik, P. A. Mulheran, and Z. J. Zhang, *Colloids Surf., A*, **2020**, DOI: 10.1016/j.colsurfa.2020.125221

Supporting Information

Preparation of HTBHBC

The synthesis of HTBHBC was carried out based on a previous procedure¹ where hexaphenylbenzene (HPB) was subjected to Friedel-Craft alkylation with 2-chloro-2-methylpropane (16 equivalents added compared to the 8 equivalents used by the reference to increase the reactivity of the synthesis). Anhydrous iron(III) chloride was used both as a Lewis acid and stoichiometric oxidant. A one-pot synthesis was performed in a 3-necked 250 mL round bottom flask, flame dried under vacuum, and set to cool under a blanket of argon. It was then filled with HPB (0.2 g, 0.374 mmol), *t*-BuCl (0.36 mL, 3.28 mmol) and dry DCM (12 mL), followed by FeCl₃ (1.213 g, 7.48 mmol) dissolved in 7.5 mL MeNO₂. The solution was heated to and kept at 40 °C for 2 h while a gentle stream of argon was bubbling through. The mixture was allowed to cool to room temperature in remaining solution (up to 9.6 g) of FeCl₃ was added to the flask. The mixture was stirred further for 3 hours, followed by introduction of 40 mL of cold (5°C) MeOH. The yellow precipitate obtained was filtered and washed with cold MeOH (20 mL x 2). The crude material obtained was further purified via flash chromatography (Petrol Ether/ Ethyl acetate 9:1) yielding 185 mg of a dark orange powder.

Chemical analysis of HTBHBC

A time-of-flight (TOF) micromass liquid chromatography (Waters - MALDI micron MX) with electrospray ionisation and a CH₃OH mobile phase was used to examine the chemical composition of the dried solid deposit and supernatant at 168 hours. Ion detection was done by a dual micro channel plate detector assembly and data was acquired using a 4.0 GHz time-to-digital converter; all data was processed by the MassLynx software system and presented in Figure S1.

Figure S1. MALDI TOF spectra of the HTBHBC (858.6m/z) and derivatives; (a) shows the spectra of dissolved solid deposit with the major peak belonging to the pure HTBHBC compound; (b) the liquid supernatant shows a variety of peaks that indicate the existence of multiple derivatives.

Images of the HTBHBC suspensions

Pictures of HTBHBC dispersed in toluene after one week are presented in Figure S2. Although the darkness of the solution increases with an increasing concentration, from 2 to 5 mg/mL in Figure S2a, no precipitate nor aggregate was observed. However, high HTBHBC concentration (30 mg/mL) resulted in noticeable precipitate at the bottom of the vial.

Figure S2. Pictures of HTBHBC dispersed in toluene after one week. (a) Concentration of HTBHBC is 2, 3, 4, and 5 mg/mL from left to the right. No precipitate nor aggregate was observed. (b) Concentration of HTBHBC is 30 mg/mL. There is a noticeable amount of precipitate at the bottom of the vial.

Equilibrium condition of the HTBHBC dispersion

Variation of the intensity acquired from the light scattering instrument, determined by changes in either size or concentration, was used as the criteria to judge whether a dispersion reaches a local pseudo-equilibrium – only solutions that show stable intensity over 30 minutes, during which 100 data points were collected, were recognised as having reached pseudo-equilibrium conditions. To demonstrate the criteria, raw light scattering intensity data for HTBHBC dispersion of 30 mg/mL is presented in the figure below, showing that the intensity signal remained stable over 30 mins, over which the averaged data is presented in Figure 4 of the manuscript. The same protocol is used throughout the present work.

Figure S3. Normalised scattering intensity data for HTBHBC dispersions of 30 mg/mL is presented over a 30 minutes measurement period, when the equilibrium was reached.

References

1. Rathore, R.; Burns, C. A Practical One-Pot Synthesis of Soluble Hexa-peri-hexabenzocoronene and Isolation of Its Cation-Radical Salt. *J. Org. Chem.*, **2003**, *68*, 4071.