Intermolecular interactions in asphaltene aggregation: terahertz spectroscopic study of model asphaltene compounds

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Asphaltenes are heavy polar components of petroleum that form nanoaggregates and precipitate in light hydrocarbons such as pentane and heptane, but have significant solubility in polar liquids such as toluene or chloroform. [1-3] Interest in the properties of asphaltene nanoaggregates is two-fold, as understanding of their properties may 1) inform approaches to mitigating asphaltene deposits in petroleum production lines, and 2) suggest possible applications of asphaltene compounds in electronic and other devices. Here, we study the

Figure 1. *VO-79 molecule.*

optical and electronic properties of a model asphaltene compound, violanthrone-79 (VO-79). It consists of a large aromatic core and aliphatic side chains (Fig. 1), and captures the main features of the continental-type asphaltenes.
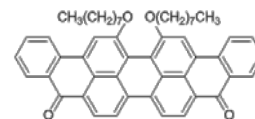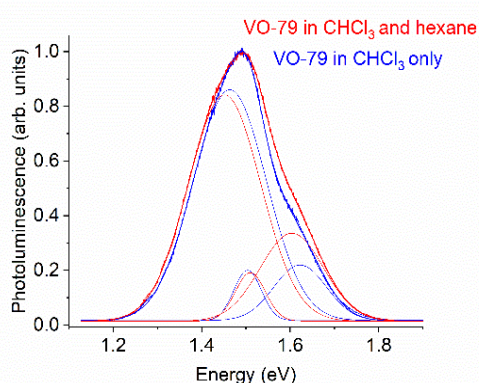

Figure 2. *Luminescence spectra of VO-79 films excited by 400 nm. Thin lines: Gaussian peaks used to fit the spectra*

Aggregation of violanthrone derivatives has been previously studied by molecular dynamics simulations, UV-VIS and two-dimensional infrared (2D IR) spectroscopy, which have shown that it is driven by π-π stacking of molecules with anti-parallel alignment of dipole moments.[4-6] We have studied aggregation of VO-79 in chloroform, toluene and methanol solutions and the properties of VO-79 thin film, prepared from VO-79/chloroform solution at a concentration above the aggregation threshold. In Year 1, we have used UV-VIS spectra to establish that the critical concentration of VO-79 in chloroform for significant aggregation from UV-VIS spectra is 0.5-0.6 mM, consistent with the previously reported 0.1 – 1.0 mM range.[5] In Year 2, we have focused on properties of VO-79 aggregated in thin films. ***Using optical pump – THz probe spectroscopy (OPTPS), we have demonstrated that delocalization of π electrons in the film results in band-like carriers that remain free within individual aggregates for tens of picose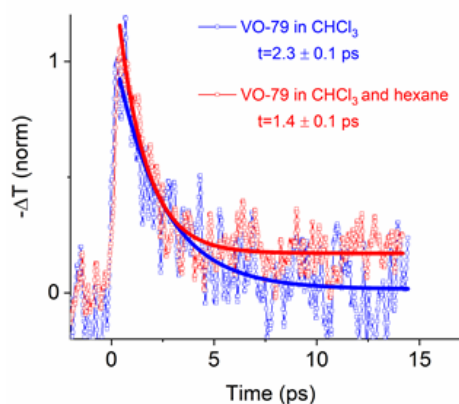conds after photoexcitation.*** This observation confirms formation of extended aggregates, and suggests applications of VO-79 and similar compounds in organic optoelectronic devices. We have also studied the impact of introducing a small amount of a poor solvent such as hexane on the properties of the resulting VO-79 thin films. Using fluorescence spectroscopy and OPTPS, ***we find that the addition of hexane enhances aggregation, resulting in a less continuous film consisting of individual aggregates that are likely of higher crystallinity than in the film prepared from pure chloroform solution.*** AFM studies aimed at confirming this hypothesis and correlating the structure and sizes of aggregates to optical and electronic properties of the films are currently underway.

Fig. 2 shows fluorescence spectra of VO-79 films, excited by 400 nm laser beam. Films were prepared by dropcasting of 10 mg/mL solutions of VO-79 either in pure chloroform ($CHCl_3$) or in a $CHCl_3$/hexane mixture (4:1 v/v) onto quartz. Precise thickness and morphology will be determined using AFM measurements and profilometry. Both films exhibit bright, spectrally broad photoluminescence in the red/near-IR that consists of three emission bands. The two most pronounced emission bands at ~1.45 eV and ~ 1.6 eV are red-shifted in the film from the $CHCl_3$/hexane mixture, and the higher energy shoulder peak is also more prominent, implying that intermolecular π-π interactions in the solid film are enhanced by a non-polar solvent and lead to a higher degree of aggregation.[4]

Optical pump – THz probe spectroscopy monitors frequency-resolved complex photoconductivity with sub-picosecond time resolution[7] and

Figure 3. *Normalized differential transmission of the THz probe pulse peak as a function of pump-probe delay time under 100 fs, 400 nm excitation. Lines: tits with a single exponential function with decay times indicated in the legend.*

provides a unique window into the properties of VO-79 aggregates. Fig. 4 shows the negative differential transmission of the THz probe pulse as a function of delay time after excitation with 100 fs, 600 μJ/cm^2, 400 nm pulse and reflects the dynamics of the transient photoconductivity. We find that the transient photoconductivity in both films is characterized by fast (<400 fs) charge carrier photogeneration, followed by decay due to trapping and recombination of carriers. The initial decay is slightly faster in the film from a CHCl$_3$/hexane mixture, likely due to better defined, smaller aggregates induced by the addition of a poor solvent, which results in more trap states at aggregate edges. However, after the initial decay, carriers that exhibit band-like transport within the aggregates remain free for longer times in the film from a CHCl$_3$/hexane mixture. In fact, free carriers persist for 20 ps and beyond, underscoring high crystallinity of the aggregates and low concentration of defects.
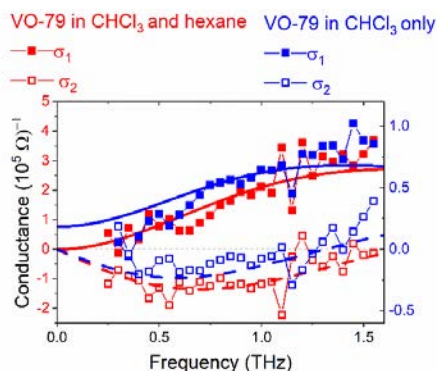

Figure 4. *The photoconductance 5 ps after excitation with 100 fs, 400 nm pulse. Lines are global fits of real (σ_1) and imaginary (σ_1) conductance the Drude-Smith model.*

Frequency-resolved complex conductivity at a fixed time (5 ps) after photoexcitation (Fig. 4), confirms this hypothesis and yields additional insight. In the figure, solid symbols represent real (σ_1) and open symbols – imaginary (σ_2) film photo-conductance. For both films, data is well-described by the Drude-Smith conductivity model[8-9], a phenomenological model that provides a good description of free, band-like carriers localized by the grain boundaries in terms of the carrier density, effective carrier scattering time, and a parameter c, a measure of carrier localization within individual grains. We find that scattering time is large, ~ 100 fs, in both films, indicative of carrier mobility that is higher than typically observed in organic semiconductors and suggesting application of VO-79 and related compounds in optoelectronic devices. The difference in the behavior of carriers in the two films is captured by the difference in the c parameter: at c=-1.00 ±0.02, carriers are fully localized within aggregates formed in the presence of a poor solvent, hexane. On the other hand, carrier localization within individual grains is not complete in the film prepared from pure chloroform solution, as c=-0.86 ±0.04, and non-zero long-range transport of carriers through the film is possible. Additional THz and optical experiments, as well as morphological studies are now underway. These results represent the first study of photoexcited carrier dynamics in the model asphaltene compound aggregates, and provide important insights into aggregate properties and possible applications of asphaltene compounds.

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