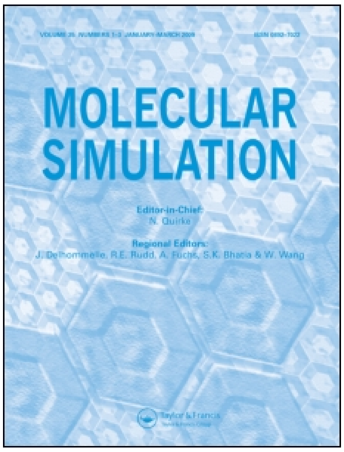

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Industrial Uses of Computational Models in the Development of Novel Nanosystems

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Industrial Uses of Computational Models in the Development of Novel Nanosystems

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Nanosystems represent new opportunities, new research and development efforts and new possibilities for advanced materials. Many industrial scientists are focusing on nanotechnology and many chemical industries are indeed funding ambitious but valuable efforts. These efforts are based on the belief and realization that nanosystems are basic and important blocks for building new businesses. Industrial computational experts find themselves at the right intersect: an intersect where their technology is uniquely capable to access understanding, to stimulate thoughts and possibilities, to run "what-if" scenarios, and to "truly" discover new nanosystems capable of providing the advanced material capability that future businesses foresee. This paper will focus on describing computational methodologies that we are currently using. The paper will also extend to cover the application of these methods to aromatics, in particular, pentacenes and benzene derivatives.

Keywords: Nanosystems; Computational models; Pentacenes; Clathrates; Self-assembly

Industrial scientists face the challenge of developing advanced materials by manipulating the relation between the chemical structure and the desired performance. Structure–property predictions have become a significant focus of computer modeling activities in the industrial world. In our laboratory, 3M Corporate Research Materials Laboratory, we contribute to the innovation process via the utilization of mathematical and computational models that simulate material behavior. Predicting the final performance property requires an integrated approach among the various length and time scales of material behavior.

Nanosystems represent new opportunities, new research and development efforts and new possibilities for advanced materials. Many industrial scientists are focusing on nanotechnology and many chemical industries are indeed funding ambitious and valuable efforts. These efforts are based on the belief and realization that nanosystems are basic and important blocks for building new businesses. Industrial computational experts find themselves at the right intersect: an intersect where their technology is uniquely capable to access understanding, to stimulate thoughts and possibilities, to run "what-if" scenarios, and to "truly" discover new nanosystems capable of providing the advanced material capability that future businesses foresee. This paper will follow an outline that starts with a general description of our methodologies and follows with the three different illustrations of self-organizing materials better known as self-assembling materials.

METHODOLOGY

Industrial materials modeling demands an integrated approach among the various length scales and time scales of material behavior (Fig. 1). At very small scales, on the order of angstroms, and time scales, less than picoseconds, electronic structure interactions are driving the material behavior. Therefore, electronic characterization and computational methods (quantum mechanics) are employed. Moving up in the scales, to picoseconds/nanoseconds and nanometers, we are located in the atomistic scale or nanoscale. Here, atomic and molecular analytical techniques and atomistic computational methods (molecular dynamics, Monte Carlo) are used. At the opposite side of the scales, millimeters/meters, and milliseconds/seconds, we find ourselves in the macroscopic world where continuum methods in structural

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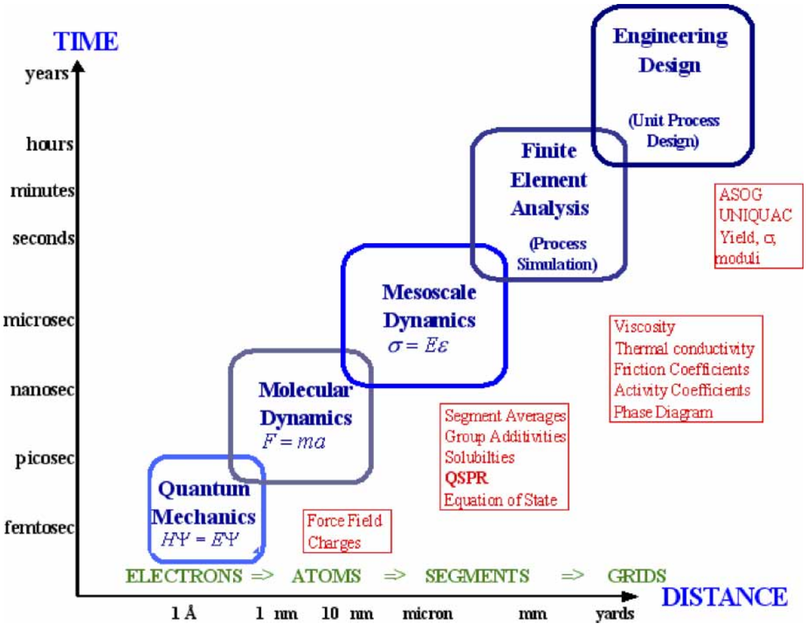


FIGURE 1 Modeling hierarchy. (Colour version available online.)

mechanics, fluid dynamics and mass transport provide good solutions for describing the material behavior.

There is something in between—the mesoscale—which is relevant and challenging for us as industrial scientists. In this paper, we define the mesoscale as the length scale ranging from 1 nm to 1 μm. Here, "coarser" descriptions (relative to atomistic) are needed. It is the intent of this paper to highlight the importance of nano and mesoscales in an industrial setting that is focusing on advancing nanotechnology solutions.

Design of industrial products require the use of computational simulations together with real experiments to identify key variables. The computational model is created and validated against a set of known experimental results. Once the model is validated, we then use it to produce understanding or significant information that guides the development or design of new experiments and aids in interpreting the results. We strive to strengthen the connection between computational experiments and "real" experiments. This connection is vital to produce structure–property relations or predictions to relate mesoscopic details of the system to the desired performance properties of the material. Key methodologies that are used include molecular mechanics, molecular dynamics and coarse graining of molecular structures and force fields [1–4].

PENTACENE AND ITS DERIVATIVES

As part of an effort to design thin coatings based on molecular information, we are investigating pentacene and substituted pentacenes for application in high performance integrated circuits. In this regard, we would like to be able to predict the electron and hole transport properties in organic solids. Having an understanding of the molecular structure, the crystal packing (Fig. 2) [5], the electronic structures including band structure, ionization potential and valence and conduction bandwidths, is critical. The total mobility in a device depends on the intrinsic mobility of the semiconductor, the nature of the semiconductor interfaces, the impurities, the morphology of the semiconducting materials, the size of crystal/grain boundaries, the orientation and the device environment. Single crystal pentacene, by itself, has high

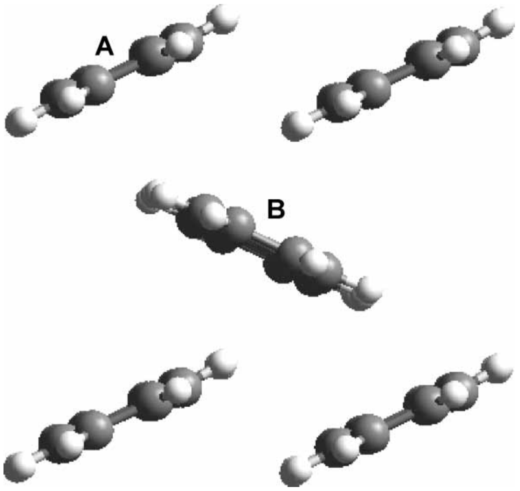


FIGURE 2 One of the experimental crystal structures of pentacene. Molecules labeled A and B are the two inequivalent molecules comprising the unit cell.

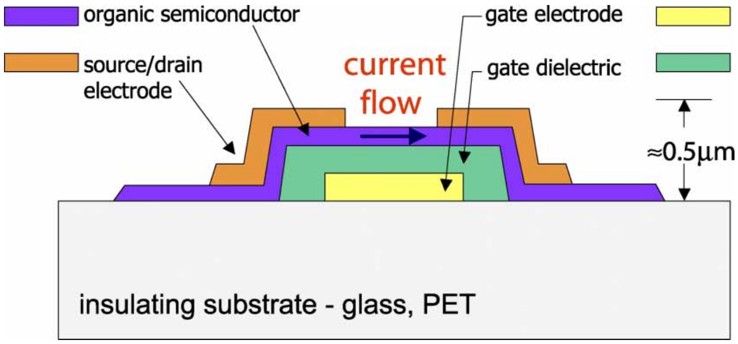


FIGURE 3 Schematic of a transistor based on a thin film organic semiconductor. (Colour version available online.)

mobility and good stability, but practical applications would require the use of inexpensive organic films deposited on a wide variety of substrates.

The semiconductor interface is also an area which greatly affects the electronic properties of the organic semiconductor [6]. Investigation of many different coatings between the gate dielectric and the organic semiconductor (Fig. 3), it was found that hydrocarbon self-assembled monolayers (SAMs) (Fig. 4) enhanced the performance of the organic semiconductor, in this case pentacene. The interface modification appears to impact crystal nucleation and growth and the number of nucleation sites (Fig. 5).

Another objective was to prepare pentacene derivatives with improved processability and better environmental stability. Currently, we are investigating the effects of substituting alkyl chains on the terminal rings (Fig. 6). The most promising candidate is 2,9-dimethylpentacene (Fig. 6a). As of yet a single crystal X-ray diffraction pattern of 2,9-dimethylpentacene has not been measured due to the extremely small size of the crystal. Molecular modeling techniques were used to predict the unit cell of 2,9-dimethylpentacene (Fig. 7). The structure prediction was not obtained from the more robust crystal structure packages [7]. Rather, the pentacene crystal structure was used as a template, then NPT molecular dynamics were run at 500 K then every 2000 steps the system was quenched and minimized. By comparing the resulting simulated X-ray powder pattern, we were able to identify a reasonable unit cell for the 2,9-dimethylpentacene. Our calculations show a calculated length of the molecule of 17.4 Å. This simulated pattern is in good agreement with the experimentally determined X-ray pattern of a 2,9-dimethylpentacene thin film (Fig. 7). Identifying the crystal packing and providing a model of the structure of the thin film phase is extremely valuable.

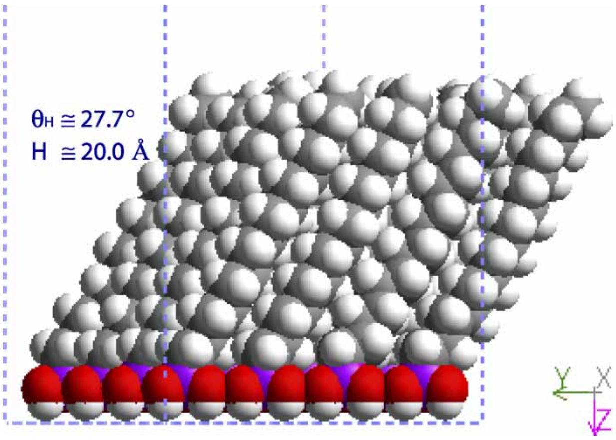


FIGURE 4 Model of an alkyl phosphonic acid SAM. For the $C_{16}H_{32}PO(OH)_2$, the estimated tilt angle is 28° and the height is 20 Å. (Colour version available online.)

Computational results were obtained using software programs from Accelrys Inc. Dynamics calculations were performed with the Open Force Field module using the Dreiding force field [8]. Graphical displays were generated with the Cerius2 molecular modeling system. Atomistic charges were obtained from Quantum Mechanical calculations using DFT with B3LYP and 6311g** basis set using the Jaguar [9] software.

SELF-ASSEMBLY IN CLATHRATES

The self-assembly of colloidal nanoparticles has become a viable "bottom-up" route for generating mesoscopic architectures. Hi-tech industrial applications engineer materials at the nanoscale to control properties (electronic and optical) of materials [10].

An example of such nanoscale engineering is presented in the modeling of clathrates [11]. Clathrates provide a rich scenario to study self-assembly via Monte Carlo simulations. These simulations quantify the interaction energies of the equilibrium structures of Guanidinium 4,4′-biphenyldisulfonate ($(G)_2$(BPDS)) host–*para*-xylene guest complex ($(G)_2$(BPDS)·*p*-xylene) and the *meta*-xylene guest complex ($(G)_2$(BPDS)·*m*-xylene). It is found that electrostatic interactions contribute significantly to the interaction energy as well as the molecular order of the clathrate system under investigation. This study also

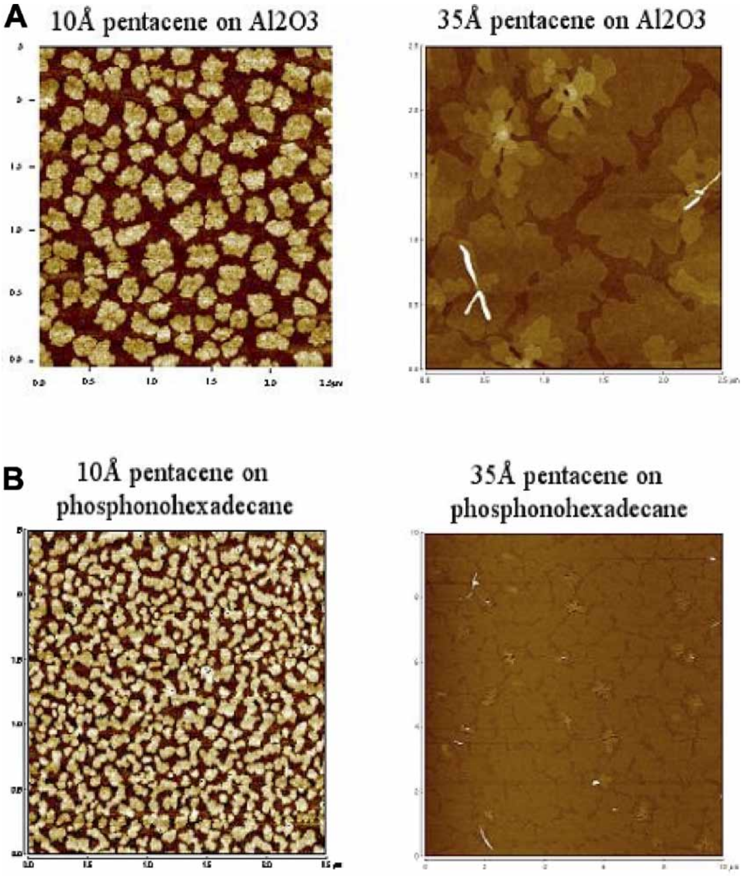


FIGURE 5 Pentacene vapor deposited on (A) Al_2O_3, and (B) hexadecane phosphonic acid SAMS on Al_2O_3. The pentacene seems to have less nucleation sites on the native oxide and the pentacene consequently grows in crystallites perpendicular to the substrate. On the modified surface, there are much more nucleation sites and the pentacene layer is more evenly distributed, especially on the initial layers. (Colour version available online.)

identifies the significant difference in structure of the guest–host complex owing to small changes in guest structure.

Clathrates are a broad class of compounds generally defined by their ability to include guest molecules within the pore cavities of the porous solid state structure. The basic building blocks of clathrates are organic molecules with specific size, shapes and chemical properties that enable the formation of open/flexible framework structures through metal coordination [12,13] and/or hydrogen bonds [14–16]. This framework can be modified at the molecular level to change with respect to shape and structure of the cavities based on the change in shape, size and chemistry of the guest molecules [17]. Recent studies have shown that organic-based clathrates can be engineered to encapsulate cavities of various shapes and connectivity [18–20]. Encapsulation of specific guest molecules is of high interest to industry research and development.

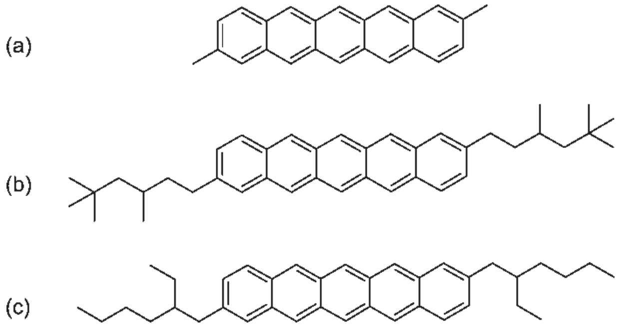


FIGURE 6 Various alkyl substituted pentacenes to improve solubility.

The aim of this study is to first identify the molecular interactions that contribute significantly to the structure and stability of the self-assembled clathrate complexes, in particular the $(G)_2(BPDS)$ host–xylene isomer guest complex. During the simulation and by switching the electrostatic interactions off and on, their importance to the configuration of the complexes is highlighted. We know little of the energy involved in clathrate complexes. The host structure is influenced considerably by the structure of the guest. Thus, the clathrate host framework cannot be assumed rigid, an approximation that would have made simulating this system considerably easier. Other than van der Waals interactions, electrostatic interactions will also have to be considered. van der Waals interactions are

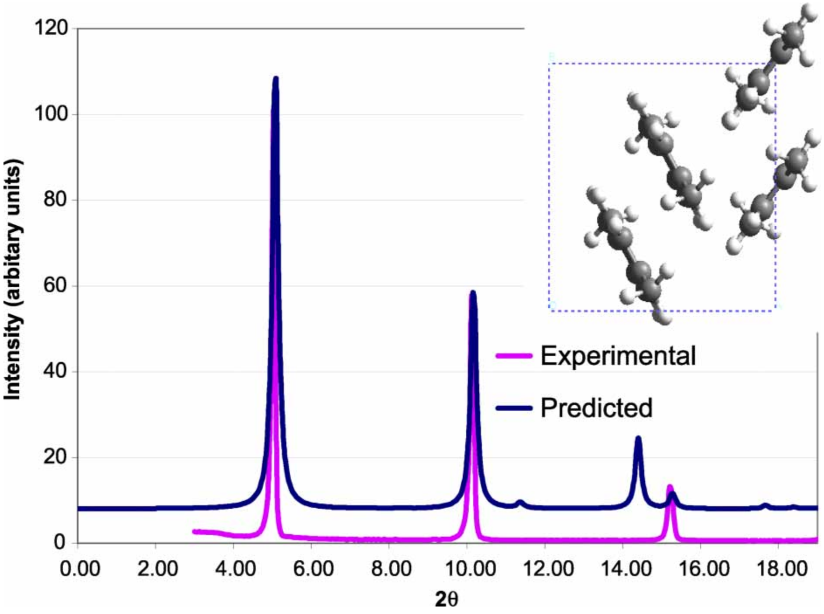
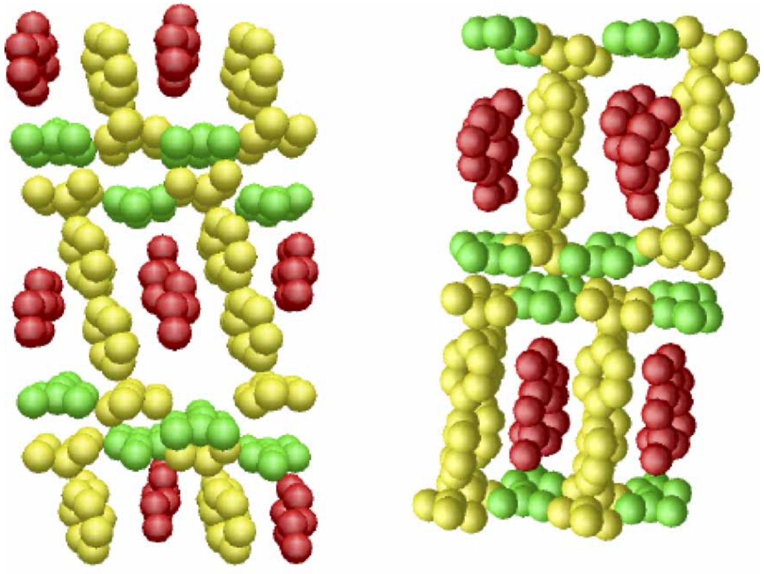


FIGURE 7 X-ray patterns of 2,9-dimethylpentacene. (—) is the Experimental powder pattern and (—) is the simulated powder pattern based on the predicted crystal structure. The simplified unit cell has $a = b = 8.7$ Å and $c = 17.4$ Å. (Colour version available online.)

assumed to be pair wise additive. The interaction U_{ij}, between two atoms (i and j) is approximated by the Lennard–Jones 6–12 model:

$$U_{ij} = \varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - 2\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right]$$

where ε_{ij} is the energy parameter, σ_{ij} the size parameter and r_{ij} is the distance between the centers of the two atoms. Universal Force Field parameters are used in the simulation. Maximum loading of this complex implies one guest molecule per set of host molecules ($((G)_2(BPDS)$ complex) as shown in Fig. 8. All simulations will be at this loading. Bond lengths were not allowed to oscillate owing to internal vibrations, nor were atoms allowed to rotate around their connecting bonds, but solid body rotation and translation were allowed. For all these calculations periodic boundary conditions were used at 300 K with a simulation cell consisting of $4 \times 4 \times 4$ sets of host–guest units; four along each side of a cuboid. The long-range electrostatic interactions are incorporated using the Ewald sum technique.



(a) p-xylene encapsulated

(b) m-xylene encapsulated

FIGURE 8 Snapshot of the p- and m-xylene encapsulated clathrate structures during the simulations. (Colour version available online.)

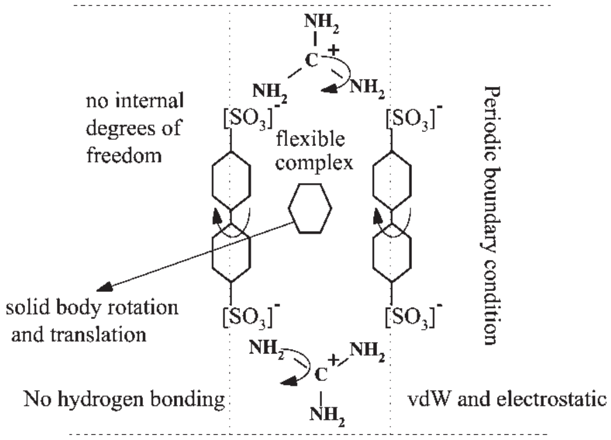


FIGURE 9 Schematic of Monte Carlo simulation to ascertain equilibrium positions.

We used a constant N, P, T Monte Carlo technique to perturb the system that is known to be at equilibrium experimentally (Fig. 9) and allow it to relax under various combinations of electrostatic switched on and off along with van der Waals interactions. The initial state of the simulation system is the crystal configuration suggested by the experimental studies of Swift *et al.* [12] for *p*-xylene and *m*-xylene encapsulated in $(G)_2(BPDS)$. This is an anisotropic system. The supercell is allowed to equilibrate at a given pressure by independent fluctuations along the three lattice directions with the electrostatic interactions turned on and off in separate cases. The simulation allowed the system to equilibrate over 500,000 iterations and provided a snapshot of the molecular arrangement of the molecules in the complexes.

Electrostatic interactions contribute significantly to the energy of the complex as seen in Table I. The $\pi-\pi$ interactions are important in defining the structure of the complex. The final structure from simulations predicts positions of the atoms to be within 6% of the experimentally estimated positions [12].

SELF-ASSEMBLY OF AROMATIC BASED AMPHIPHILES

Another class of lyotropic materials has presented its significance to the scientific and industrial community in the last quarter of a century—that of aromatic based lyotropic materials. These materials have included a wide range of drugs and dyes. Unlike usual amphiphiles, these molecules do not manifest significant surfactant properties. The molecules themselves are disc- or plate-like rather than rod-like and consist of an aromatic core with hydrophilic ionic or hydrogen-bonding solubilizing groups arranged at the periphery. While there has been significant insight gained on these systems in the last decade [13], the mechanisms that hold these aggregates together are still not understood well. In the absence of such understanding, it is difficult to engineer such materials for specific functions and needs.

We have studied the aggregation of some of the systems mentioned in Lydon's work [21] and have concluded that the aggregation is a result of competition between solubilizing forces, aromatic π-ring interactions between the interactions and hydrophobic effects. The π-ring interactions provide an orientational order to the molecules in these aggregates that is largely missing from usual amphiphiles. These interactions are also responsible for various kinds of aggregation and the corresponding phases that are observed in these systems. Figure 10 presents the differences between usual amphiphilic micelles and aromatic based lyotropic materials. Figures 11 and 12 present examples of self-aggregation of copper-tetracarboxyphthalocyanine and disodium cromoglycate, respectively, in solution with water. In each of these aggregates, the molecules have fixed orientations and high order. It is this order that can be engineered for application of these aggregates as molecular enzymes or molecular carriers of specific molecules. Another difference with micellar aggregates is that such aromatic stacks may include water molecules between the aromatic molecules. Such water molecules seem to be tightly bound within the stack and may play a key role in screening repulsive interactions between functional groups in the molecule. These aspects of the self-aggregation process were understood through molecular modeling and will help us control the structure and properties of these aggregates more effectively.

CONCLUSIONS

Simulations are becoming a necessary activity for the development of nanomaterials, in particular, to quickly examine the relationship between

TABLE I Contribution of electrostatic interactions to the guest–host interactions

Energies in RT	*$(G)_2(BPDS)\cdot p$-xylene* *$(Q + vdw)$*	*$(G)_2(BPDS)\cdot m$-xylene* *$(Q + vdw)$*	*$(G)_2(BPDS)\cdot p$-xylene* *(vdw)*	*$(G)_2(BPDS)\cdot m$-xylene* *(vdw)*
Total energy	−7.62	−5.98	−4.58	−3.24
Guest–guest interaction	−0.06	−0.31	−0.03	−0.26
Host–guest interaction	−2.66	−1.55	−1.94	−1.35
Host–host interaction	−4.90	−4.12	−2.61	−1.63

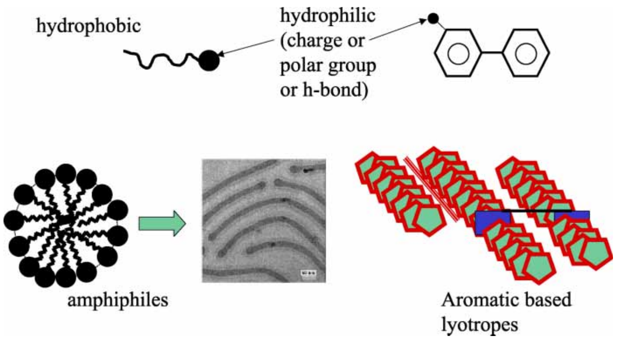


FIGURE 10 Comparing amphiphiles with aromatic based lyotropic materials. (Colour version available online.)

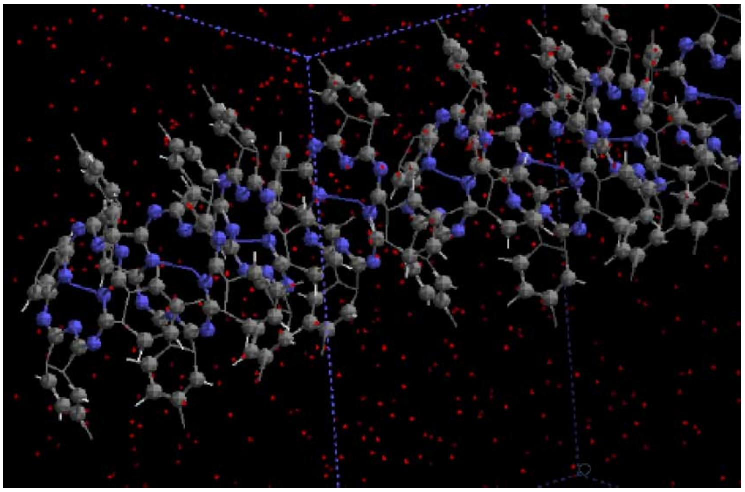


FIGURE 11 Lyotropic self-assembly of tetracarboxyphthalocyanine in water. (Colour version available online.)

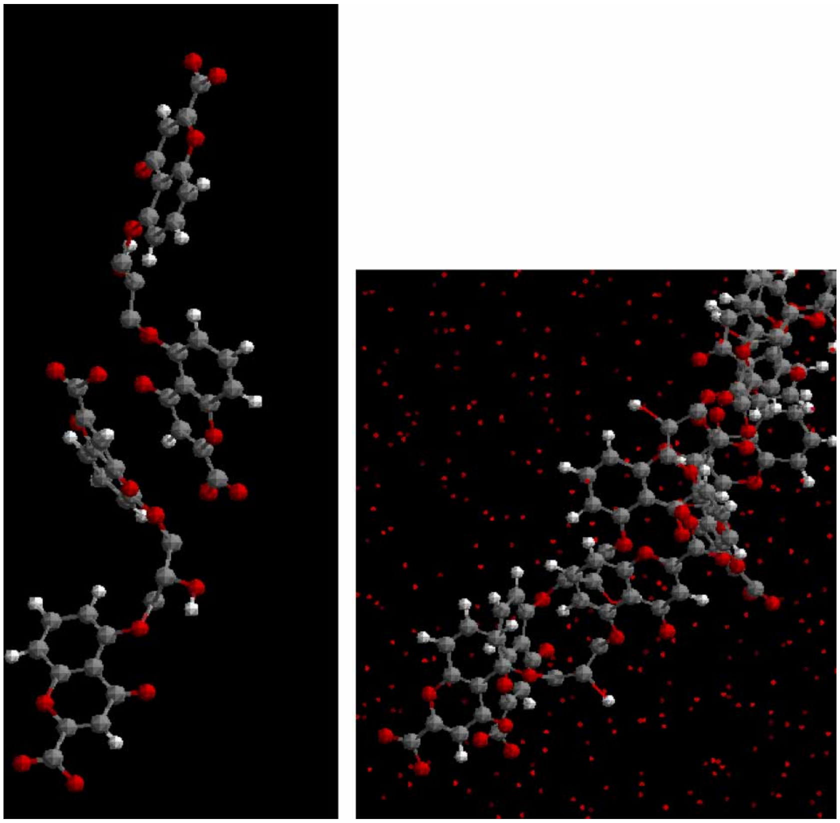


FIGURE 12 Self-assembly of disodium cromoglycate in water. (Colour version available online.)

the molecular architecture and the chemical functionality. In our group, the prediction of interfacial properties is a key enabler to the development of novel thin coatings and surface treatment. We utilize atomistic and coarse grained simulation for probing the structure–property relations on these compounds.

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