Living on the edge: Tuning supramolecular interactions to design two-dimensional organic crystals near the boundary of two stable structural phases

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One of the benefits of supramolecular assemblies that form at dynamic interfaces is the opportunity to develop condensed phase systems that respond to environmental stimuli. A prerequisite of this responsive behavior is that the supramolecular system be designed to sit very near the stability of two or more crystal structures. We have created such a *bi-phasic* system with aryl-triazole oligomers by investigating how phase morphology is controlled by the interplay between interactions that involve the oligomer's dipolar cores ($\Delta\mu = 3.5$ debye), van der Waals contacts of their pendant alkyl chains (C_4-C_{18}), and close-contact hydrogen bonding. Scanning tunneling microscopy experiments conducted at the solution-graphite interface allow sub-molecular resolution of the ordered monolayers to unambiguously determine the packing and structure of two principle phases, α and β . The system is balanced very near the edge of phase stability, evidenced by co-existent phases present over short time frames and by the changes in preference between the two 2D supramolecular assemblies that occur with small modifications to the molecular structure. We demonstrate that the bi-phasic behavior can be understood as a balance between electrostatic interactions and van der Waals contacts, two variables within a larger parameter space, allowing synthetic design to move this solution-surface system across the stability boundary of different condensed-phase structures. These findings are a foundation for the development of environmentally responsive 2D supramolecular arrays. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4906895>]

INTRODUCTION

Biology provides many examples of systems that activate or modify functionality in response to an environmental stimulus, often mediated by dynamic supramolecular interactions. Such bio-inspired structures are expected to lead to advances in sensing, adaptive functionality, and dynamic combinatorial libraries.^{1,2} Yet the majority of synthetic materials^{3–6} usually target robust structures, which, by nature of their stability, do not respond dynamically to their environment. In order to develop useful materials that can respond and adapt to environmental stimuli, a balance between non-covalent interactions must be achieved so that each of two states are accessible energetically—bistability. The creation of such systems^{7,8} requires a paradigm shift away from the quest for ultimate structural stability of a single polymorph to one that allows phase switching between two or more architectures. Dynamic self-assembly is one way to achieve these goals. When the constituent interactions are properly balanced, external stimuli could be used to choose between several possible structures and thus create stimuli-dependent functionality.^{9–11} Towards this end, we vary van der Waals (vdW) and electrostatic supramolecular interactions present across a synthetically tailored series of isosteric aryl-triazole oligomers to tune their condensed-phase

stabilities (Figure 1) to sit at the boundary between two 2D structures.

We approach the objective of achieving a bi-phasic system through supramolecular design by considering the lessons of prior studies on the intermolecular interactions in present 2D systems.¹² Such self-assembly processes rely on the interplay of non-covalent contacts including vdW forces,¹³ directional hydrogen bonding,^{14–17} and electrostatics (ion-ion,

FIG. 1. In this study, isosteric synthetic variation of a family of aryl-triazole oligomers is used to achieve tuning of the supramolecular crystal structure. The aryl-triazoles adopt either a head-to-tail (α phase) or head-to-head (β phase) packing, and the intermolecular interactions were tuned to successfully realize the more elusive goal of a bi-phasic system.

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ion-dipole, dipole-dipole, etc.).¹⁸ For example, alkyl chains play an important role in self-assembly at the solution-solid interface in assisting adsorption and by directing assembly.^{19–22} The role of dipolar functional groups positioned at the periphery of a molecule,^{23–28} the *anti*-parallel alignment of zwitterions on surfaces,^{29–31} and the impact of molecular dipoles^{32,33} in supramolecular self-assembly at surfaces have been studied. While these types of contacts have been extensively examined in surface-adsorbed crystals,^{34–36} the challenge now lies in balancing the weights of their relative contributions to generate bi-phasic systems. Such systems can be accessed when the stabilities of 2D structures can be tuned to find the balancing point sitting near the edge of two stable supramolecular structures.

As chemists progress towards understanding the responsiveness of individual non-covalent forces within molecular switches in homogeneous solutions, condensation into 2D assemblies provides a platform where these individual classes of interactions can grow in number and complexity. At the same time, the resulting 2D assemblies and their transformations can be scrutinized with single and sub-molecular resolution using real-space imaging afforded by scanning tunneling microscopy (STM).³⁷

Prior surface studies have examined bi-phasic behavior derived from molecular conformational changes. These structural changes are programmed to occur at the molecular level based on known solution-phase properties. They have been triggered by pH,^{38,39} light,⁴⁰ or electrochemical potential.^{41,42} In our system,⁴³ switching was stimulated by the addition of anions and found to switch by the use of electric fields from the proximal STM tip. The cores of the molecular monomers were designed to have a single rigid conformation so that the bi-phasic behavior can be derived from changes in the supramolecular interactions, both electrostatic and vdW. Polymorphism in supramolecular self-assembly often involves subtle differences in interaction energies that are difficult to predict,^{15,44} so we have taken the approach of synthetic tuning of the molecular design,^{26,45–47} to produce the desired bi-phasic behavior in the assembled structures. We demonstrate that we are able to achieve a close balance of interactions resulting in a system that sits near the edge of stability between two supramolecular structures.

We investigate the self-assembly of a homologous series of neutral aryl triazole oligomers⁴⁸ (Figure 2) using STM imaging at the interface formed between an octanoic acid solution and highly oriented pyrolytic graphite (HOPG). The oligomers were found to assemble into one of two distinct patterns that differ by the alignment of their dipolar aryl-triazole cores: head-to-tail (α) or head-to-head (β). To understand the relative contributions of the vdW and electrostatic interactions to the structures and stabilities of the resultant assemblies, we controlled the strength of intermolecular vdW coupling by varying the lengths of the terminal alkyl chains. Additionally, we investigated isosteric controls where the strength of dipolar interactions were synthetically tuned using a tetra-fluoro analogue ($Y = F$, Figure 2). Some prior studies have focused on the effect of changing the molecular structure⁴⁹ or changing the shape of the molecule's core (without varying alkyl chain length).^{46,50} However, we have tried, insofar as it is

FIG. 2. Top: Chemical structures of a series of aryl-triazole oligomers that are studied here by tuning vdW contact (R chain length) and molecular dipole ($Y = H$ or F). The homologous series is designed to keep the core the same size and shape through the systems studied. These structures incorporate intramolecular hydrogen bonds between the amide moieties present on the central phenylene and the triazoles (colored red) in order to pre-organize the central molecular core. The local dipoles from the amides (~ 3.5 debye) in combination with the triazole dipoles (~ 5 debye) give rise to a large 16 debye molecular dipole (for $Y = H$). Bottom: Schematic diagram representing the synthetic tuning of supramolecular assemblies at the octanoic acid-graphite interface reported in this work. Two phases, α and β , are observed in our study of the series of aryl triazole oligomers (blue alkyls and red aryl-triazole core). Fluoro substitution favors β phase formation, while shorter alkyl chains favor α phase.

possible to do so, to maintain a constant size and shape of the molecule's aryl-triazole core so that any close contact interactions are nearly constant. This strategy allows us to focus on the effect of the competition between intermolecular electrostatic and vdW interactions on the 2D lattice energy. Furthermore, this strategy has enabled us to tune these interactions to a point where one of the molecules exhibits bi-phasic behavior. A semi-quantitative model that decomposes the intermolecular interactions into their components is used to help investigate how the balance between electrostatics and vdW interactions allows this system to sit at the edge between α and β phases and thus give rise to bi-phasic behavior. The present study augments knowledge^{26,45–47} about how to control 2D molecular assembly through synthetic design. Overall, this work demonstrates how long- and short-range electrostatic effects, which act in concert with vdW interactions, can be preprogrammed and tuned to steer the supramolecular surface structures to the edge of stability that exists between two structural phases.

EXPERIMENTAL SECTION

Molecular design

Here, we describe the design features of the molecular adsorbates. The synthesis and characterization of all the compounds is described in detail in the supplementary material.⁵¹ Aryl-triazoles are effective^{52–54} ion-binding motifs with

straightforward^{55,56} and efficient synthesis protocols and they have been shown in solution-based supramolecular systems to act as interlocked molecules,⁵⁷ chelators,⁵⁸ and sensors.^{59–61} The particular aryl-triazole motif employed in this study (Figure 2) has been previously explored in the solution phase^{48,62} for its propensity to sequester anions from organic solvents. This property is the direct result of the electropositive pocket, which is strongly polarized by the triazoles (red in Figure 2) and amide moieties. Anion binding for these receptors has been studied in solution^{63–66} and on HOPG surfaces, where they display multi-stimuli switching.⁴³ The amides also act as a pre-organization unit to provide intramolecular NH $\cdots$ N hydrogen bonds that restrict rotation of the phenyl-triazole bond and lock the molecule into a “V” shape. This intramolecular pre-organization aligns the 3.5- and 5-debye group dipoles of the constituent amides and triazoles, respectively, to create an overall molecular dipole of 16 debye. Thus, the design of the receptor pocket also confers two properties on the molecular adsorbates, which are particularly desirable for this study: a relatively large molecular dipole moment and a rigid molecular shape. Within 2D self-assemblies, dipole-dipole interactions are ubiquitous non-covalent interactions.^{28,67–71} Here, we are utilizing molecules that have a net dipole moment located at the molecular core, a feature that complements the use of dipolar groups acting as intermolecular contact points on the molecule’s periphery. The central 16 debye dipole of the aryl-triazole oligomer is significantly larger than the outwardly directed group dipoles of esters (1.8 debye) and ketones (2.6 debye) that may make close-contact interactions. The central dipole location of the oligomers examined herein requires any dipolar coupling to act over distances further than the seam formed between molecules.

Scanning tunneling microscopy

Unless otherwise noted, all depositions and STM experiments were performed at room temperature. In some cases, lower or higher temperatures were used to change rates of structural rearrangement toward the equilibrium surface structure, as noted in the text and figure captions. Each oligomer was dissolved in octanoic acid (Aldrich) at three concentrations (1, 10, and 100 μ M). In each experiment, one droplet (5–10 μ L) of one of these solutions was applied to a freshly cleaved graphite surface. The self-assembled monolayers were investigated at the solution-solid interface by STM (pico-SPM, Agilent) operating in constant current mode. To improve the quality of imaging, electronic pulses (3–5 V) were occasionally applied to condition the tip apex. Atomic resolution of the graphite surface is achieved by lowering the surface bias to $V_{\text{sample}} = -0.002$ V (Figure S3⁵¹), which allows identification of the orientation of the molecular assemblies relative to the main symmetry axes of the graphite lattice (black lines in STM images). This method is also used for precise calibration of the STM scanner, i.e., the same area is first scanned to image the supramolecular network with high resolution, then, in the second scan, the STM bias is changed part way through the scan to get a high quality image of the graphite atomic lattice in order to precisely determine unit cell parameters of the assembly structures.

RESULTS AND DISCUSSION

First, we describe the assembly of the head-to-tail packed α phase. A different surface structure, the head-to-head β phase, is observed following synthetic modification using fluoro substituents. A bi-phasic system was then developed through further synthetic modifications of the molecule’s structure. Finally, we developed a simple computational model to describe the impact of each synthetic modification on the resultant structural observations.

Packing structure of the α -phase monolayers into anti-parallel rows

The results shown in Figures 3(a) and 3(b) represent typical STM images (overview and high-resolution) of the monolayer formed after applying a drop of a solution containing oligomer **H-C**₁₂ onto the graphite surface. Several features of the molecular design are visible in the STM image and in the ordering of the supramolecular crystalline layer. The aromatic regions of the molecule appear in the STM images (often as three bright lobes, Figure 3(b)) with significantly brighter contrast (rows B and D) compared to the alkyl chains of the molecule (rows A and C) as a result of their high tunneling efficiency.⁷² The “V” shape of the receptor pocket can be resolved in the images, revealing that the molecules pack in a head-to-tail fashion up and down each row. The rows are oriented in an *anti*-parallel manner in a structure that we refer to here as “ α phase.” The terminal alkyl chains extend outward from the molecular core at an angle of about 50° from the molecule’s quasi-C₂ axis (alkyl-to-alkyl angle of 100°). Note that while the molecules have average C₂ symmetry in solution, this is lost upon adsorption in the α phase when one considers the adsorption sites on HOPG, *vide infra*. The C₁₂ alkyl chains are seen to interdigitate with those presented by the neighboring rows. The packing density of the chains within rows A and C is about 67% of the optimum packing density; it is only every other chain-to-chain contact that is present at the ideal close-packed vdW distance described by Groszek.⁷³

A packing model reflecting the molecular ordering of **H-C**₁₂ in the α phase is shown in Figure 3(c). The unit cell consists of a two-molecule basis where the second molecule is *anti*-parallel to the first; unit cell dimensions are given in Table I. The two-molecule unit cell has an area of 7.38 nm² and does not have sufficient room to allow adsorption of the amide-linked pentyl chains at the head of the aryl triazoles. These chains are also not observed during STM imaging of the α phase and are likely back-folded into solution, an effect that has been observed for other systems.⁷⁴ This arrangement of the pentyl chains has been attributed to optimization of the overall adsorption energy by fitting more molecules onto the surface, particularly for molecules with a core moiety that is relatively more polarizable compared to the alkanes.⁷⁴ For clarity, the pentyl chains are replaced with methyl groups in the model shown in Figure 3(c).

The direction defined by the aligned rows of head-to-tail molecules present in the α phase is approximately 10° away from the main symmetry axis of HOPG. Thus, of the two alkyl chains on each molecule that are oriented 50° from this

FIG. 3. (a) STM image ($100 \times 100 \text{ nm}^2$) of **H-C₁₂** at the octanoic acid-graphite interface showing the α phase. (b) High-resolution STM image ($20 \text{ nm} \times 20 \text{ nm}$) of the α phase of **H-C₁₂** ($1.0 \times 10^{-4} \text{ M}$). (c) Tentative model of the α phase of **H-C₁₂** showing the head-to-tail *anti*-parallel packing with interdigitated alkyl chains. (d) STM image ($50 \text{ nm} \times 50 \text{ nm}$) of **H-C₄** at the octanoic acid-graphite interface showing the α phase. (e) High-resolution STM image ($10 \text{ nm} \times 10 \text{ nm}$) of the α phase of **H-C₄** ($1.1 \times 10^{-4} \text{ M}$). (f) Tentative model of the α phase of **H-C₄** showing the head-to-tail *anti*-parallel packing. Images are recorded with $I_T = ((a), (b))$ 30 pA, (d) 66 pA, (e) 116 pA and $V_{\text{sample}} = ((a), (b))$ -0.8 V, (d) -0.5 V, (e) -1.0 V. Unit cell dimensions are given in Table I.

principle row direction, only one chain can be parallel to a main symmetry axis of HOPG, while the other chain is 20° away from a main symmetry axis. The difference in the surface adsorption site between the two alkyl chains gives rise to a contrast difference observed in the STM images,⁷⁵ where the commensurate row (row A in Figure 3(b)) of alkyls appears darker than the non-commensurate row (C). Thus, the α phase structure can grow in six different directions on the surface (observed in equal populations), depending on which of the molecule's two chains (left or right) is commensurate with one of the three principle surface axes (Figures 3(a) and S3⁵¹). The angle between the molecular rows of left- and right-handed domains measures $20^\circ \pm 2^\circ$, consistent with the difference between the 120° C_3 symmetry of the HOPG lattice and the measured 100° inter-alkyl angle on a single molecule.

Chain-length dependence of the α -phase structure and its stability

In order to investigate the significance of the stabilizing intermolecular vdW interactions that are contributed by the interdigitation of alkyls in rows A and C, the length of the alkyl chains (R in Figure 2) was systematically varied. Oligomer **H-C₄** was designed with the shortest alkyl chains ($R = \text{C}_4\text{H}_9$) in the series. STM images of the C_4 -substituted oligomer **H-C₄** show retention of a head-to-tail *anti*-parallel assembly (Figures 3(d) and 3(e)) similar to **H-C₁₂**. The same α phase structure is also observed for the aryl-triazoles with longer alkyls, **H-C₁₄** and **H-C₁₆** (see Figure S8⁵¹). The primary difference between the two systems is the predictably smaller separation between *anti*-parallel molecular rows. The

TABLE I. Unit cell parameters for molecular layers determined from STM experiments. Lengths and directions of the unit cell vectors $\mathbf{a}$ and $\mathbf{b}$ are given as well as the area per molecule (half the unit cell area).

		Vector $\mathbf{a}$ length ($\text{\AA}$)	angle from HOPG ^{a,b}	Vector $\mathbf{b}$ length ($\text{\AA}$)	angle from $\mathbf{a}$ ^{a,c,d}	Area per molecule ($\text{\AA}^2$)	See Figures
H-C₁₈	α	13.6 ± 0.8	10°	64.9 ± 1.3	$\gamma = 88^\circ \pm 3^\circ$	440.6	5, 6(a)-6(b)
	β	21.6 ± 1.8	90°	50.7 ± 2.5	$\gamma = 85^\circ \pm 5^\circ$	515.2	5, 6(c)-6(d), S5 ⁵¹
H-C₁₂	α	13.8 ± 1.2	10°	53.5 ± 2.1	$\gamma = 88^\circ \pm 3^\circ$	369	3(a)-3(c)
H-C₄	α	14.2 ± 1.1	10°	37.0 ± 2.3	$\gamma = 91^\circ \pm 3^\circ$	263	3(d)-3(f)
F-C₁₈	β	20.2 ± 1.2	90°	51.5 ± 2.1	$\gamma = 87^\circ \pm 2^\circ$	515	4
F-C₁₂	β	20.2	90°	~ 45	$\gamma \sim 85$	446.8	S8 ⁵¹

^aVectors $\mathbf{a}$ and $\mathbf{b}$ are indicated in the unit cell diagrams in Figures 2 and 5 for α and β phases, respectively.

^bFor vector $\mathbf{a}$, the magnitude of the vector and its angle relative to the low-index direction of graphite is given.

^cFor vector $\mathbf{b}$, the magnitude of the vector and its angle relative to vector $\mathbf{a}$ is given.

^dCompare trends in $\mathbf{b}$ to alkyl chain lengths: 3.8 $\text{\AA}$ (C_4), 13.9 $\text{\AA}$ (C_{12}), and 21.5 $\text{\AA}$ (C_{18}).

unit cell parameter b decreases by 1.65 nm (from 5.35 nm for **H-C₁₂** to 3.70 nm for **H-C₄**), consistent with the 1 nm decrease in alkyl chain length (at an angle of $\sim 55^\circ$ to a , $1 \text{ nm}/\text{chain} \cdot 2 \text{ chains/unit cell} \cdot \sin 50^\circ = 1.53 \text{ nm}$). A model depicting the α phase of **H-C₄** is shown in Figure 3(f). The packing distance up and down each row does not change, $a(\text{H-C}_{12}) = a(\text{H-C}_4)$. Left- and right-handed domains, similar to oligomer **H-C₁₂**, are again observed in Figure 3(d). The persistence of the domain handedness observed in the oligomer **H-C₄** with its short chains indicates that close-contact interactions between the *cores* of the aryl-triazole oligomers may be responsible for producing the left- and right-handed domains. It is also interesting to note that the pentyl chains at the head of the oligomer do not appear to be adsorbed. This observation indicates that the stability of the structure for **H-C₄** is strengthened by interactions beyond simply the adsorption and packing of C_4 alkyls. The cores of the aryl-triazoles in the experimentally observed packing structure are expected to form close-contact hydrogen bonds. Those interactions may favor the 10° angle between molecule axis and row direction by bringing the amide's oxygen acceptor atom closer to the H-bond donor sites of the neighboring molecule. Dipolar interactions between the molecule cores should also contribute to the stability of this structure.

β phase monolayer packs in a head-to-head arrangement

A set of variations on the aryl-triazole's core were examined as a means to significantly lower molecular dipole moment while retaining the same shape and size as **H-C₁₂** and **H-C₄**. Symmetric substitution of hydrogen atoms for fluorines at the tail phenylenes of the aryl-triazole oligomers was chosen such that the local dipoles originating from the C-F bonds would partially offset those of the triazoles and the amides (Figure 2, $Y = \text{F}$). From *ab initio* calculations (see supplementary material⁵¹), we see that this substitution pattern significantly reduces the overall molecular dipole by 20% from 16 debye to 12.5 debye. (There is a negligible change in the dipole as a function of the tail's chain length.) At the same time, the homologous series of oligomers **F-C₁₈**, **F-C₁₂**, and **F-C₄** (Figure 2), has little impact on the molecular volume or the overall shape of the molecule when compared to the protio versions (Figure S1⁵¹).

When the molecular structure was modified in this way, we were surprised to discover a second phase, herein called the " β phase." More broadly, these fluorinated oligomers allowed us to experimentally investigate the role of electrostatic interactions, including dipolar coupling, on the relative stability of the α and β phases. STM observations (Figure 4) show that the fluorinated oligomer with the longest alkyl chains, **F-C₁₈**, assembles on the graphite surface into a stable structural phase that is very different in morphology from the α phase. In the molecular structure of **F-C₁₈**, the dipole moment has been reduced to 12.5 debye when compared to protio analogs. The presence of a lengthened alkyl chain ($R = \text{C}_{18}\text{H}_{37}$ for **F-C₁₈**) increases the relative importance of the intermolecular vdW contacts. We found this change provided a more stable β phase, compared to **F-C₁₂** and **F-C₄**, enabling precise

FIG. 4. (a) STM image ($150 \text{ nm} \times 150 \text{ nm}$) of **F-C₁₈** at the octanoic acid-graphite interface showing many different domain orientations of the β phase that are observed within 30 min of solution deposition. (b) STM image of the β phase observed after deposition of **F-C₁₈** onto the HOPG surface ($1.0 \times 10^{-4} \text{ M}$). Both STM images are recorded with $I_T = 10 \text{ pA}$ and $V_{\text{sample}} = -0.7 \text{ V}$. Unit cell dimensions are given in Table I.

structural characterization of the two-dimensional packing in the crystalline monolayer. The β phase is characterized by a high-contrast, double lamella row assigned to the aryl-triazole oligomer cores that are now arranged in a head-to-head fashion. The low contrast region separating the cores is assigned to the C_{18} -alkyl chains that extend away from the core. The chains are parallel to each other and aligned with a major axis of the graphite lattice (black lines, Figure 4(b)).

Initially, low-curvature turns and bifurcations were observed in the lamella constituted by **F-C₁₈** (Figure S5⁵¹). However, upon heating the samples to 30°C , these features converge into a single domain of the β phase (Figure S6⁵¹). This behavior confirms the thermodynamic stability of the β phase relative to α ; it is not metastable.

To investigate the impact of shortening the terminal alkyl chains across the fluorinated homologs, oligomers **F-C₁₂** and **F-C₄** were examined. STM investigations at room temperature revealed resolution of the β phase for **F-C₁₂** (Figure S7⁵¹), but it appears to be less stable than for **F-C₁₈**. The stability was judged to be lower based on the lower resolution in the images. Consequently, measurement of the unit cell dimensions was much less accurate for **F-C₁₂**, but measurements of the lamella spacing ($\sim 4.5 \text{ nm}$) are indicative of the expected β phase repeat distances for oligomer **F-C₁₂** (Figure S7b⁵¹). Use of oligomer **F-C₄** bearing shortened alkyl chains showed no stable assemblies, even at concentrations up to 1 mM (the oligomers discussed above were routinely studied at concentration of $100 \mu\text{M}$ or less). The lack of ordered assembly with **F-C₄** does not necessarily indicate that physisorption is unstable at room temperature, but rather that competitive adsorption with the solvent, octanoic acid, does not favor assembly of

F-C₄.⁷⁶ These observations of assembly behavior for **F-C₁₂** and **F-C₄** suggest that, in the absence of the strong dipolar coupling present in **H-C₄** for driving the system to the α phase packing arrangement, a sufficiently long alkyl chain is needed to provide a minimum vdW interaction for stable monolayer formation into the β phase arrangement. A corollary of this interpretation is that longer chains confer greater stability to the β phase.

Finding the edge of α - β structural phase stability

Having identified two distinct structural phases by varying the strength and type of intermolecular interactions, we next sought to demonstrate a boundary of stability between these phases. To do so, another isosteric version of the protio aryl-triazole oligomer, **H-C₁₈**, was designed. Here, greater vdW coupling is achieved with the use of C₁₈ chains, which was inferred to give greater stability to the β phase. This design feature is brought together with strong intermolecular dipole-dipole coupling (16 debye), which is believed to favor the α phase. Thus, there is a near-balance between these interactions. Upon deposition of a 100 μ M solution of **H-C₁₈** followed immediately by STM imaging (within a few minutes), two distinct structures (Figure 5(a), 6 min) are clearly observed on the surface, both the α and β phases. Subsequent images (Figures 5(b) and 5(c)) were acquired from the same location and referenced to the defect in the lower right hand corner and the horizontal edge of the α phase of the same field of view. In the next one and 2 min of scanning, the β phase has diminished at the expense of the α phase growth. After approximately 15 min have passed from the time of solution deposition, the β phase has completely dissolved and the entire surface has ripened into the α phase structure. In separate experiments, the sample was annealed at 50 °C for 60 min in the 100 μ M solution and the surface structure observed in all instances was the α phase, indicating that this is the thermodynamically favored surface assembly for oligomer **H-C₁₈**. The α phase for oligomer **H-C₁₈** (Figures 6(a) and 6(b)) has the same head-to-tail *anti*-parallel arrangement as observed for oligomers **H-C₁₂** and **H-C₄** (Figure 3) and they all share the same repeat distance up and down the rows (unit cell vector *a*) and have predictable distances between rows (unit cell vector *b*) based on alkyl chain lengths, as shown in Table I.

The presence of the short-lived β phase is consistent with Ostwald's step rule,⁷⁷ based on observations of crystallization, that unstable states are accessed first. When deposition of **H-C₁₈** is made from a lower concentration (10 μ M) solution, a higher population of the β phase structure can be imaged by STM. Interestingly, at lower temperature (19 °C), the dissolution of the β phase is slowed significantly consistent with a lowering of the kinetic factors relevant for the phase transformation.

A more detailed characterization of the metastable β phase was possible (Figure 6(c)) when using lower concentrations and temperatures. The metastable β phase of **H-C₁₈** is characterized by the expected high-contrast double lamella rows arising from the aryl-triazole oligomer cores arranged in a head-to-head fashion. Similarly, the low contrast region sepa-

FIG. 5. STM image sequence (100 nm $\times$ 100 nm) of **H-C₁₈** at the octanoic acid-graphite interface showing the surface mixture of α and β phases relative to a fixed defect point (lower right). The β phase, outlined in blue, transitions into the α phase within ~ 10 min of surface deposition. Time (*t*) from solution deposition is listed in the top right of each image (1.2×10^{-4} M). All STM images are recorded with $I_T = 15$ pA and $V_{\text{sample}} = -0.5$ V.

rating the cores is assigned to the C₁₈-alkyl chains (black lines, Figure 6(c)). The width of this alkyl region for the **H-C₁₈**, **F-C₁₈**, and **F-C₁₂** β phases can be correlated with alkyl chain length (see length of *b* in Table I). Alignment of the alkyls with the underlying surface allows resolution of the alkyl chains with some resolution of methylene pairs along the chains (Figure 6(c), inset). Smaller scan sizes reveal that the β phase of oligomer **H-C₁₈** is identical to the metastable β phase observed for oligomer **F-C₁₈** within error. These measurements revealed that the β phase has a $\sim 20\%$ lower packing density than the α phase. The extra space allows accommodation of some of the pentyl chains to the surface and may also allow some solvent adsorption. The measured length of the *a* unit cell vector is larger than needed to accommodate the alkyl chains of the molecules in the β phase at their known close-packing density.^{73,78} Therefore, the alkyls are not believed to be perfectly “close-packed.” Consistently, gaps between the alkyl chains can be observed in the STM images in addition to bending and kinks in some of the chains (blue arrow, Figure 6(c) inset).

FIG. 6. (a) STM image of the α phase of H-C_{18} at the octanoic acid-graphite interface (1.2×10^{-4} M, unit cell parameters $a = 1.36 \pm 0.08$ nm, $b = 6.49 \pm 0.13$ nm, and $\gamma = 88^\circ \pm 3^\circ$). (b) Packing model of the α phase that is stabilized by a dipole aligned head-to-tail arrangement. (c) STM image of the β phase observed after deposition of a cooled solution of H-C_{18} onto a surface at 19°C (1.2×10^{-5} M, $a = 2.16 \pm 0.18$ nm, $b = 5.07 \pm 0.25$ nm, and $\gamma = 85^\circ \pm 5^\circ$). (d) Packing model of the β phase structure with the head-to-head alignment of the aryl-triazole cores, with dipoles in a clashing arrangement, and nearly “close-packed” interdigitation of both alkyl chains along a major axis of HOPG. STM images recorded with $I_T =$ (a) 10 pA and (c) 5 pA, $V_{\text{sample}} =$ (a) -0.7 V, (c) -0.4 V, and ((c) inset) -0.2 V.

Contrary to the α phase of H-C_{18} (Figure 6(a)) and the β phase of F-C_{18} (Figure 4), the metastable β phase of H-C_{18} (Figure 6(c)) consistently lacks long-range crystalline order. The lamella can be observed to turn with respect to the underlying lattice (Figures 6(c) and S4⁵¹). The more fluid nature of the assembly is also revealed in the frequent observation of bifurcation events along lamellar rows as well as low-density regions that appear to be undergoing assembly into the β phase (Figure S4b⁵¹). Annealing to 28° for 5 min prior to re-inspection at room temperature produced only α phase, indicating that the β phase of H-C_{18} is a kinetically trapped state. The observation of defects along with the presence of mesoscale ordering of the lamella and the lack of long-range translational ordering of the individual molecules are characteristic of liquid-crystal assemblies.⁷⁹ The fact that the β phase of H-C_{18} shows some liquid crystal-like behavior while that of F-C_{18} is crystalline likely showcases a frustrated molecular arrangement. The electrostatic potential map of the aryl-triazole core provides a reasonable explanation for the turns observed in the β phase (Figure S1⁵¹). That is, a large separation in charge density can be observed between the electronegative head and the electropositive tail of the aryl-triazole core. Based on the head-to-head arrangement in the β phase, a destabilizing electrostatic interaction is expected from this large charge separation (dipole) in the core of the aryl-triazoles (*vide infra*).

FIG. 7. Phase diagram illustrating the experimentally observed structural phases for the eight oligomers studied.

Semi-quantitative analysis of packing in α and β phases

A semi-quantitative analysis was conducted to compare key energetic differences between the assemblies of the different aryl-triazole oligomers used in this study. The results show that a simple physical model reproduces the qualitative experimental observations of the preferences for the α or β phase packing of each molecule (Figure 7).

We employed a model⁸⁰ which accounts for the primary interactions that would drive ordering in the monolayer: electrostatic (ES) and vdW interactions. The contributions of the molecular dipoles to the stability of each phase are contained within the electrostatic component. Each molecule was treated as a set of partial charges located at the nuclei positions of the atoms (see supplementary material for details on the determination and list of the values⁵¹). Interaction energies between the molecules were calculated in a pairwise manner with the two components (ES and vdW) in order to calculate the energy of short- and long-range interactions of one molecule with all the other molecules in the layer. Electrostatic interactions, including screening effects from the liquid (dielectric constant ϵ_1) and the solid (ϵ_2), were calculated from the formalism of Jackson⁸¹ for electrostatic potential near the interface between two dielectric media

$$E_{ES} = \sum_{i,j} \frac{1}{4\pi\epsilon_1} \left(\frac{q_i q_j}{|r_i - r_j|} + \frac{q_i q'_j}{|r_i - r'_j|} \right), \quad (1)$$

with the double summation (i, j) over the atoms in each of the two molecules, q_i represents the charge on atom i , and q'_j is the “image charge” of j , which is positioned in the surface at a depth equal to the height of charge j above the surface and has charge q'_j that is modified by the reduced dielectric constant of the two media

$$q'_j = - \left(\frac{\epsilon_2 - \epsilon_1}{\epsilon_2 + \epsilon_1} \right) q_j. \quad (2)$$

The dielectric constant of the surface is ϵ_2 and the dielectric constant of the solution is ϵ_1 .

The other component in the calculations were the vdW interactions, modeled using a standard Lennard-Jones potential

$$E_{vdW} = 4\phi_{ij} \left[\left(\frac{\sigma_{ij}}{|r_i - r_j|} \right)^{12} - \left(\frac{\sigma_{ij}}{|r_i - r_j|} \right)^6 \right], \quad (3)$$

where ϕ_{ij} and σ_{ij} are the well depth and position of zero energy, respectively, and are calculated for interactions between different atoms as $\phi_{ij} = \sqrt{\phi_{ii}\phi_{jj}}$ and $\sigma_{ij} = \frac{\sigma_i + \sigma_j}{2}$ (note that we have used ϕ here instead of the usual ε to avoid confusion with the dielectric constant above).

The molecules were arranged in an array, either α or β phase, based on the experimentally determined unit cells of the supramolecular packing (Table I). In each phase, there are two molecules per unit cell which are *anti*-parallel (Figure 6). We assume that the molecules are rigid and flat-lying so that there are six coordinates which describe the geometry of the layer: two for each of the unit cell vectors, $\mathbf{a}$ and $\mathbf{b}$, and two for the position of the second (*anti*-parallel) molecule in the unit cell. Summation was made over all neighboring molecules within a cut-off distance that included the 10 nearest neighbor molecules (extending this cut-off distance to include more molecules had a negligible impact on the resulting energies).

Several approximations were made in this model in order to keep the calculation simple and to focus the analysis on the key differences between the α and β phases. Chief among these is the neglect of charge relaxation and induced polarization within the molecules upon their assembly. Consequently, the gas-phase single-molecule calculations of atomic charges were employed. The terms related to desorption entropy, solvation energy, and differences in adsorption of pentyl chains were neglected in order to keep the model simple. These are reasonable approximations based on the similarity between the two molecular arrangements being considered, e.g., solvation energies will be nearly identical for the molecular conformation

that packs in the α phase as for the one that packs in the β phase. The main goal of the calculation is to analyze energetic differences that could give rise to the observed structural phase behavior.

Starting from the experimentally determined unit cell values, the Nelder-Mead downhill simplex minimization method^{82,83} was used to find the minimum potential energy with respect to the six coordinates of the system. In each minimization, a set of random numbers were added to the experimentally derived starting coordinates to test for multiple local minima. In the cases of the growth phases not observed experimentally, e.g., β phase of **H-C**₁₂, starting coordinates were derived from experimental observations of the other phases and the known dimensions of the molecule. This approach was followed for each of six molecules, in each of the two structural phases and the computational simulation was conducted at least 80 times from different starting points. The lowest energy values are reported in Table II. The coordinates that correspond to these minimum energy values were found to have excellent agreement with the experimentally measured unit cell values (see comparison in Table S1⁵¹), particularly for the α phase structures (within experimental error bars).

Using these formulations for the electrostatic and vdW interactions, energies were calculated for six oligomers in their respective α and β phases (Table II). The final column of values in the table, $E_{total,A}$, provides a normalization of the total energies based on the number density of the α and β phases for each molecule; in each case, the α phase is about 20% more dense so the surface layer has a larger density of interactions per unit area. On the basis of the relative energies of the two phases, this model can be used to make predictions on the relative stabilities of the two phases for each compound examined.

TABLE II. Semi-quantitative calculation of supramolecular interaction energies. $E_{dipoles}$ is a calculation of only the molecular dipole interaction energy. E_{total} values are the minimum energy values from the calculation and the next column, $E_{total,A}$, shows those values after normalization for the unit cell size difference between α phase and β phase. The last two columns compare the computationally predicted favored growth phase with experimental observations.

		$E_{dipoles}^a$ (kJ mol ⁻¹)	E_{total}^b (kJ mol ⁻¹)	$E_{total,A}^c$ (kJ mol ⁻¹)	Predicted structure	Observed structure
H-C ₁₈	α	-9	-216	-216	α/β	α/β
	β	5	-212	-210		
H-C ₁₂	α	-9	-155	-155	α	α
	β	5	-144	-137		
H-C ₄	α	-9	-102	-102	α	α
	β	6	-64	-57		
F-C ₁₈	α	-5	-174	-174	β	β
	β	3	-200	-198		
F-C ₁₂	α	-5	-146	-146	α	β
	β	3	-134	-122		
F-C ₄	α	-5	-71	-71	α/β	— ^d
	β	-2	-79	-65		

^aDetermined from the calculated dipole moment of each molecule and the positions determined as minimum energy positions from the calculation (listed in Table S1⁵¹).

^bCalculation of the internal energy difference between the chain rotation states of each molecule are less than 1 kJ/mol.

^cBoldface letters denote the lowest energy structures.

^dAn ordered surface structure for **F-C**₄ was not observed by STM.

Remarkably, this highly simplified computational model correctly predicts the structural phase (Figure 7) of most of the molecules in this study. For the highly dipolar series **H-C₄**, **H-C₁₂**, and **H-C₁₈**, the calculated stability difference between the α and β phases decreases as the alkyl chains are lengthened. This is consistent with the experimental observation that **H-C₄** and **H-C₁₂** only form a stable α phase (despite experimental attempts to find β phase at lower temperature and lower concentration) while **H-C₁₈** shows bi-phasic behavior. For **H-C₁₈**, a liquid-crystal-like metastable β phase is seen to be prevalent at lower deposition concentrations and remains on the surface for longer times at lower temperatures before transitioning into the α phase. For the **F-C₁₈** fluorinated species, the model agrees with the observation of the β phase. However, the calculated energetic difference between phases for **F-C₁₂** does not agree with experimental observation of the β phase. We note that **F-C₄**, which was the only molecule of the six that did not form a stable monolayer, has the weakest interaction energies in the computational model.

Two other trends are readily observed from the results of the semi-quantitative model. First, the energies scale in a predictable way with alkyl chain length. This trend supports the assertion, made during the design of the molecules, that the “core” of the molecule is conformationally rigid. Consequently, modifications to the molecule are not changing the size and shape of the molecule in a significant way. Consistently, plots of energy vs. alkyl chain length are linear for each phase and for the Y = H or F substitutions they have similar slopes (see Figure S9⁵¹). In other words, electrostatic interactions (e.g., dipolar and close-contact interactions) are relatively constant for a given molecular core design.

The second trend revealed by the calculations is that the incorporation of the fluoro units into oligomers **F-C₁₈**, **F-C₁₂**, and **F-C₄** has a net destabilizing effect on the α phase. This may arise from a few possible interactions. First, close-contact interaction between fluoro units of one molecule and the amide oxygen atoms of the neighboring molecule along the molecular row. Second, the additional fluoro units reduce the molecular dipole moment and would thus decrease the stability of the dipole-aligned α phase.

The smaller molecular dipole moment of the fluoro-substituted molecules may improve relative stability of the β phase by decreasing the dipole clashing from the head-to-head packing. The contributions of the molecular dipoles to the relative stabilities of the two phases for each compound were determined. Dipoles were used from the gas-phase calculations (Figure S1⁵¹), placed on the lattice points for the simulated structures and summed in the same way as the ES + vdW calculation. The difference in dipolar coupling energies (E_{dipoles} in Table II) between the α and β phases for the protio molecules is ca. 14 kJ mol⁻¹ in favor of the α phase. This difference halves to ca. 7 kJ mol⁻¹ for the fluoro homologs.

Interactions driving structure formation

The observation of two different assemblies from the protio and fluoro aryl-triazole homologs presents an opportunity to examine which aspects of the chemical structure contribute to phase selection. The two phases (α and β) differ in the

packing of the alkyl chains as well as the arrangement of the cores (head-to-tail and head-to-head, respectively). Despite their differences, the two states must be relatively close in energy to allow simultaneous imaging of both phases in the case of **H-C₁₈** (Figure 5). Across the protio oligomer series (**H-C₁₈**, **H-C₁₆**, **H-C₁₄**, **H-C₁₂**, and **H-C₄**), STM observations revealed that only the long C₁₈-alkyl chains of oligomer **H-C₁₈** supported β phase formation albeit in a metastable state (Figure 5). The interdigitation of the long chains is expected to be a major stabilizing component of the β phase packing arrangement. However, the head-to-tail arrangement of the α phase is still thermodynamically favored for all the protio oligomers. Dipolar coupling along the rows stabilize the α phase. (The *anti*-parallel arrangement of the α phase will also provide stabilizing electrostatic interactions by dipolar cores felt across the alkyl rows, although this interaction will be significantly weaker than the interactions up and down the rows on account of the differences in intermolecular distances.)

The dipolar coupling hypothesis was tested using a fluorinated series of oligomers (**F-C₁₈**, **F-C₁₂**, and **F-C₄**). The fluoro oligomers showed only the β phase to be stable for compounds **F-C₁₈** and **F-C₁₂** (compound **F-C₄** did not form any assembly). While the effects of the molecular dipoles followed expectation, the $E_{\text{total},A}$ values suggested multiple effects are occurring with the protio-fluoro exchange. For instance, introduction of the fluoro groups destabilize both phases. These observations lead to the conclusion that the protio-fluoro substitution has a destabilizing effect on the α phase arrangement through a reduction in the dipole attractions and increased repulsions originating at the fluorines. At the same time, the β phase is also destabilized by the presence of local contacts involving the fluorine atoms of molecules arranged side-to-side in the β phase but that the change in the molecular dipoles lower the destabilizations felt from the dipolar clashes.

van der Waals Forces between the interdigitating chains act over short distances and are relatively weak (2.1–4.7 kJ mol⁻¹/methylene unit).⁸⁴ However, as the length of the chain increases, these contacts become more significant. The electrostatics originating from the core of the aryl-triazole oligomer also gives rise to strong close-contact interactions, i.e., short-range hydrogen bonds, electrostatic clashes between similar local charge on neighboring molecules and dipolar couplings.

In summary, the achievement of bi-phasic behavior through synthetic design of the aryl triazole family involves the competition of multiple interactions. Dipolar coupling, close-contact interactions, and van der Waals forces each play a role in determining the final phase behavior. We argue that the strengths of these interactions that emerge in the condensed phase are much more significant than the small internal energy differences between conformations of the alkyl chain positions of the monomolecular species, i.e., conformational changes follow rather than lead phase behavior. An *ab initio* prediction of a molecular design to achieve bi-phasic ordering would have been virtually impossible on account of the subtleties of the supramolecular interactions, but we have demonstrated that an iterative experimental approach has allowed us to “tune” the synthetic design of cohesive forces that will enable the desired bi-phasic behavior.

CONCLUSION

Bi-phasic 2D monolayers have been generated in the self-assembly of a series of rigid, aryl-triazole oligomers at the solution-graphite interface bearing two long C_{18} alkyl tails and a large 16 debye molecular dipole (**H-C₁₈**). This outcome resulted from an experimentally driven modification of the molecular structure that also helped reveal that phase selection likely arises from the balance between electrostatic dipolar coupling, vdW forces, and other close-contact interactions. The thermodynamic preference of **H-C₁₂** for the dipole-aligned α phase, selection of the β phase upon reducing the molecular dipole in oligomer **F-C₁₂**, and the lengthened alkyl chains (**H-C₁₈**, **F-C₁₈**) favoring the β phase all point to this balance. A semi-quantitative model rationalizes how these oligomers can pack into the two different relative core orientations based on electrostatic and vdW intermolecular interactions. This study provides STM experimental evidence and a simple model that describes the molecular packing and provides a foundation to start predicting phase behaviors of assemblies across a homologous series of isosteric compounds.

A key result of this study is the application of synthetic design strategies to search for a bi-phasic behavior in 2D self-assembly. We find that balance between electrostatic and vdW interactions can be achieved to create a self-assembled system that resides near the edge of stability between two phases of different morphology. This model of bi-phasic behavior provides a platform for analyzing and programming the response of such a system to environmental stimuli.⁴³ The development of condensed-phase self-assembled materials with interactions tuned to sit at the edge of stability between two phases is a design strategy that may lead to more complex organic materials with adaptive functionality and functional environmental sensitivity.

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