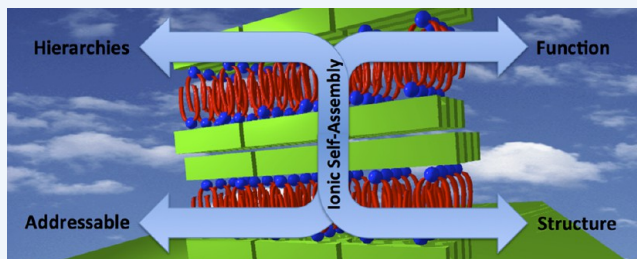


Ionic Self-Assembly for Functional Hierarchical Nanostructured Materials

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CONSPECTUS: The challenge of constructing soft functional materials over multiple length scales can be addressed by a number of different routes based on the principles of self-assembly, with the judicious use of various noncovalent interactions providing the tools to control such self-assembly processes. It is within the context of this challenge that we have extensively explored the use of an important approach for materials construction over the past decade: exploiting electrostatic interactions in our ionic self-assembly (ISA) method. In this approach, cooperative assembly of carefully chosen charged surfactants and oppositely charged building blocks (or tectons) provides a facile noncovalent route for the rational design and production of functional nanostructured materials. Generally, our research efforts have developed with an initial focus on establishing rules for the construction of novel noncovalent liquid-crystalline (LC) materials. We found that the use of double-tailed surfactant species (especially branched double-tailed surfactants) led to the facile formation of thermotropic (and, in certain cases, lyotropic) phases, as demonstrated by extensive temperature-dependent X-ray and light microscopy investigations. From this core area of activity, research expanded to cover issues beyond simple construction of anisotropic materials, turning to the challenge of inclusion and exploitation of switchable functionality. The use of photoactive azobenzene-containing ISA materials afforded opportunities to exploit both photo-orientation and surface relief grating formation. The preparation of these anisotropic LC materials was of interest, as the aim was the facile production of disposable and low-cost optical components for display applications and data storage. However, the prohibitive cost of the photo-orientation processes hampered further exploitation of these materials. We also expanded our activities to explore ISA of biologically relevant tectons, specifically deoxyguanosine monophosphate. This approach proved, in combination with block copolymer (BCP) self-assembly, very fruitful for the construction of complex and hierarchical functional materials across multiple length scales. Molecular frustration and incommensurability, which played a major role in structure formation in combination with nucleotide assembly, have now become important tools to tune supramolecular structure formation. These concepts, that is, the use of BCP assembly and incommensurability, in combination with metal-containing polymeric materials, have provided access to novel supramolecular morphologies and, more importantly, design rules to prepare such constructs. These design rules are now also being applied to the assembly of electroactive oligo(aniline)-based materials for the preparation of highly ordered functional soft materials, and present an opportunity for materials development for applications in energy storage. In this Account, we therefore discuss investigations into (i) the inclusion and preparation of supramolecular photoactive and electroactive materials; (ii) the exploitation and control over multiple noncovalent interactions to fine-tune function, internal structure, and long-range order and (iii) exploration of construction over multiple length scales by combination of ISA with well-known BCP self-assembly. Combination of ISA with tuning of volume fractions, mutual compatibility, and molecular frustration now provides a versatile tool kit to construct complex and hierarchical functional materials in a facile noncovalent way. A direct challenge for future ISA activities would certainly be the construction of functional mesoscale objects. However, within a broader scientific context, the challenge would be to exploit this powerful assembly tool for application in areas of research with societal impact, for example, energy storage and generation. The hope is that this Account will provide a platform for such future research activities and opportunities.



1. INTRODUCTION

Early work in the field of colloid science explored various aspects of polyelectrolyte–surfactant interactions, as exemplified by the reviews by Goddard et al. in 1986.¹ Simultaneously, in the related field of liquid crystals, a number of researchers also explored the production of low molecular weight liquid crystals containing ionic components.² It was however only in the mid-1990s that Antonietti and Conrad,³ followed by Thunemann,⁴ focused on the preparation of mesostructured

materials using cooperative electrostatic surfactant binding to oppositely charged polyelectrolytes. This approach, distinct from layer-by-layer (LbL) assembly based on noncooperative electrostatic interactions between oppositely charged polyelectrolytes, was first described as ionic self-assembly (ISA) by Faul and Antonietti.⁵ ISA was then expanded to encompass

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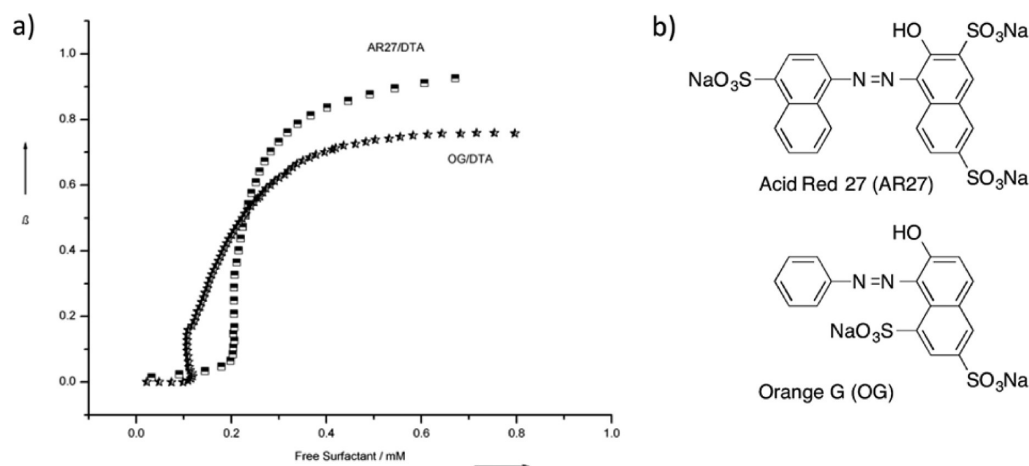


Figure 1. (a) Binding isotherm of cooperative azobenzene dye–surfactant complex formation. Reproduced with permission from ref 11. Copyright 2002 John Wiley and Sons. (b) Structures of azobenzene dyes AR27 and OG.

interactions of charged surfactants with both (high MW) polyelectrolytes and (low MW) oligomers of opposite charge. Their approach was conceptually similar to other related two-component noncovalent liquid crystal systems, as introduced by Kato and Frechet,⁶ and Lehn et al.⁷

This expansion led to ISA as a technique for the production of a wide range of materials, spanning liquid-crystalline (LC), porous, hybrid organic–inorganic,⁸ and electroactive materials. ISA has become an important part of the modern tool kit of methods and processes to construct soft and functional materials across multiple length scales, as will be shown here. The expansion of the field also impacted on related ionic LC materials, as reflected in reviews by Binnemans⁹ and Kato et al.¹⁰

In this Account, we therefore provide an overview of work from our research that contributed to establishing and advancing the use of this approach in the important area of construction of soft mesostructured organic materials, underlining some of the design rules used to tune structure and function. Our recent work, especially with electroactive materials and in combination with block copolymer (BCP) assembly, highlights opportunities to address the challenge of hierarchical self-assembly of functional materials across multiple length scales.

2. DYE–SURFACTANT FUNCTIONAL MATERIALS

As we initially aimed to explore materials other than polyelectrolyte–surfactant (PE–Surfs) systems, we focused our efforts on the formation of crystalline and LC materials based on oligoelectrolyte–surfactant systems. Initial studies utilized the readily available libraries of azobenzene dyes, after which investigations were expanded to include (mainly) perylene diimide dyes. The aim in preparing novel dye-containing LC materials was to exploit ISA as a facile and cheap alternative strategy to covalent synthesis for low-cost display applications.

Azobenzene–Surfactant Complexes

Studies into the complexation of azobenzene dyes with simple cationic surfactants of varying tail length and number confirmed a cooperative binding mechanism.¹¹ Such behavior, confirmed by determining binding isotherms (Figure 1a), showed a critical aggregation concentration (CAC) of the dye–surfactant complex several orders of magnitude below the well-known

critical micelle concentration (CMC) of the surfactants used. These binding isotherms showed that binding took place over a very narrow concentration range, tending to fully bound stoichiometric structures (at $\beta = 1$), thus ensuring repeatability and high structural fidelity. In models developed for cooperative PE–Surf interactions it was shown that binding of the first surfactant would influence the position where the next surfactant would bind (following a so-called zipper mechanism), driven by a combination of ionic and hydrophobic (van der Waals) interactions. It was therefore of interest and importance for later studies that cooperative binding was also determined for oligomeric species. The similarity in behavior to the polymer-based systems was ascribed to strong π -stacking interactions, and strong segregation between the various subphases present within the formed complex.

With cooperative behavior established, further complexes were prepared focusing on structure.^{12,13} Soft gels, liquid crystals, and platelike and needlelike single crystals¹³ (where, interestingly enough, no π -stacking was observed) were found. From a materials design perspective, double-tailed surfactants (straight-chained or branch-chained) were found to induce liquid crystallinity into ISA materials, and thus were used extensively in further studies.

Detailed studies^{14,15} then followed, exploring the induction of optical anisotropy in LC ISA materials for possible uses in low-cost optical applications (e.g., disposable security tags and polarizing filters). Complexes formed from the structurally simple ethyl orange (EO), sodium 4-(4-diethylaminophenylazo)benzenesulfonate, and double-tailed dihexyl (DiC₁₆) and didodecyl (DiC₁₂) dimethylammonium bromide surfactants, EO–DiC₁₂ and EO–DiC₁₆, exhibited thermotropic LC behavior. A temperature-dependent structural study of EO–DiC₁₂ showed columnar-to-smectic phase transitions, and changes in chromophore packing with changes in temperature and phase structure.

Processing of these thermotropic LC materials highlighted the advantages over azobenzene-functionalized polymeric materials, including low viscosity and good film-forming properties. Irradiation of thin (<100 nm) spin-coated films with linearly polarized light led to the very effective induction of optical anisotropy, a well-known and widely exploited processing method for azobenzene-containing materials.¹⁶ The degree of anisotropy, an important property when

evaluating materials for optical applications, is expressed as a dichroic ratio value (i.e., the ratio of absorbance of light polarized perpendicular to a chosen axis to absorbance of light polarized parallel to this axis). Very high maximum dichroic ratios (DRs) of 50 and 20 for the EO–DiC₁₂ and EO–DiC₁₆ complexes, respectively, were recorded (Figure 2a, b). The obtained DR values were significantly higher when compared with results from polymeric systems, where maximum DRs of 10 were routinely obtained.

Of particular interest was the sharp increase in DR at low irradiation doses during photo-orientation (Figure 2b), ascribed to a possible cooperative domain alignment process.

Complexing a range of other dyes with the DiC₁₂ surfactant also yielded stable active LC materials.¹⁵ These materials showed a range of desirable properties and functionalities, including excellent thermal stability, long-term stability of the induced anisotropy, efficient induction of optical phase grating structures (after irradiating films with two circularly polarized interfering beams (Figure 2e)), and uniform anchoring and alignment of standard liquid crystals. Noteworthy was that these photoactive materials showed no induction of surface relief gratings (SRGs) upon irradiation.

Although these promising materials addressed all of the practical difficulties when compared with polymeric materials, one critical factor has hampered any further viable commercial development:¹⁷ the extremely high energy input required (1 kJ·cm⁻²) to reach the extraordinary DRs achieved in the academic published studies.

Perylenediimide–Surfactant Complexes

Parallel to the development of azobenzene-based LCs, we prepared charged perylenediimide dyes for ISA. Perylenes are well-known n-type organic semiconductors, and have been widely investigated in the field of supramolecular chemistry.¹⁸ Obvious and important noncovalent interactions for such large π -conjugated systems are stacking interactions, which can be influenced by substitution at various positions (imide or bay) of the perylene core. Our work focused on the cationic *N,N'*-bis(2-(trimethylammonium)ethylene)-perylene-3,4,9,10-tetracarboxyldiimide bromide (PDITMA, Figure 3a), and gave us the opportunity to explore the formation of a range of different materials all related through the same cationic core.

Simple complexation with double-tailed surfactants, the straight-chained dihexadecyl phosphate and the well-known branched-chain surfactant AOT (bis(2-ethylhexyl) sulfosuccinate), produced thermotropic columnar LC materials.¹⁹ The straight-chained complex exhibited crystalline behavior at low temperature, whereas the PDITMA-AOT complex exhibited LC phase behavior (from –50 °C), indicating very wide phase boundaries. Noteworthy was that little π -stacking was observed from wide-angle X-ray scattering investigations. Shearing of these materials by hand at high temperature (200 °C) yielded modestly oriented materials with DR values between 5 and 6 (i.e., not suitable for the applications indicated above).

PDITMA-AOT exhibited amphotropic behavior in dimethyl sulfoxide (DMSO) and 1-methyl-2-pyrrolidone (NMP),²⁰ which presented opportunities for solution processing and reliable alignment of the perylene core structures, necessary prerequisites for commercial exploitation.

Neither the thermotropic nor the lyotropic phases were susceptible to alignment through the application of external alignment fields (magnetic or electrical), nor through application on prealigned surfaces. Applying shear to highly

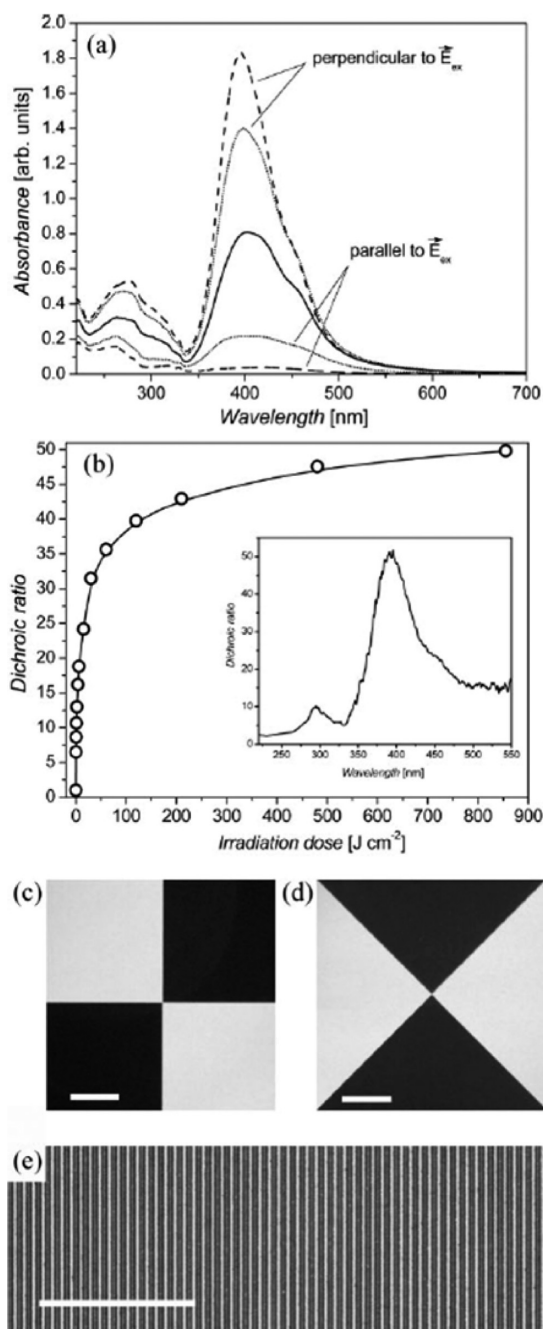


Figure 2. Induction of optical anisotropy in the EO–DiC₁₂ complex by linearly polarized Ar⁺ laser light, E_{ex} with λ_{ex} = 488 nm, P = 50 mW·cm⁻². (a) UV–vis curves showing differences in absorption depending on orientation of the sample. Dotted lines show spectra recorded after an initial dose of 0.25 J·cm⁻², and dashed lines after 850 J·cm⁻². (b) Data showing evolution of DRs of 50 after high irradiation doses. (c, d) Patterns produced after irradiation through masks and (e) manufactured diffraction gratings. Reproduced with permission from ref 15. Copyright 2006 John Wiley and Sons.

concentrated (28 wt % in DMSO) lyotropic solutions at room temperature yielded similar results.

However, drying of thin films of an isotropic solution of the complex (prepared from a mixture of DMSO and chloroform), allowed for the reformation of the lyotropic phase at the outer edges as chloroform evaporated. It was found that alignment of the PDITMA-AOT complex was induced at this phase transition front (PTF, see Figure 3b). Exploiting alignment at

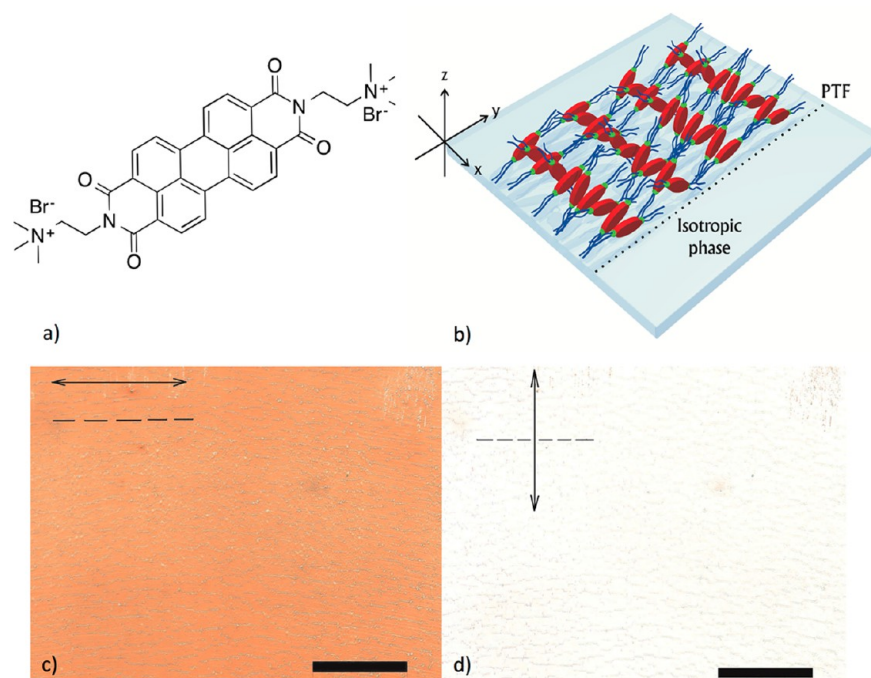


Figure 3. (a) Structure of PDITMA. (b) Scheme to show orientation of PDITMA-AOT columnar phases as prepared at a PTF. (c, d) Micrographs showing examples of aligned films with high DRs prepared at PTFs (scale bar 200 μm ; arrows represent the orientation of the polarizers, and dashed lines the orientation of the PTF). Reproduced with permission from ref 20. Copyright 2004 John Wiley and Sons.

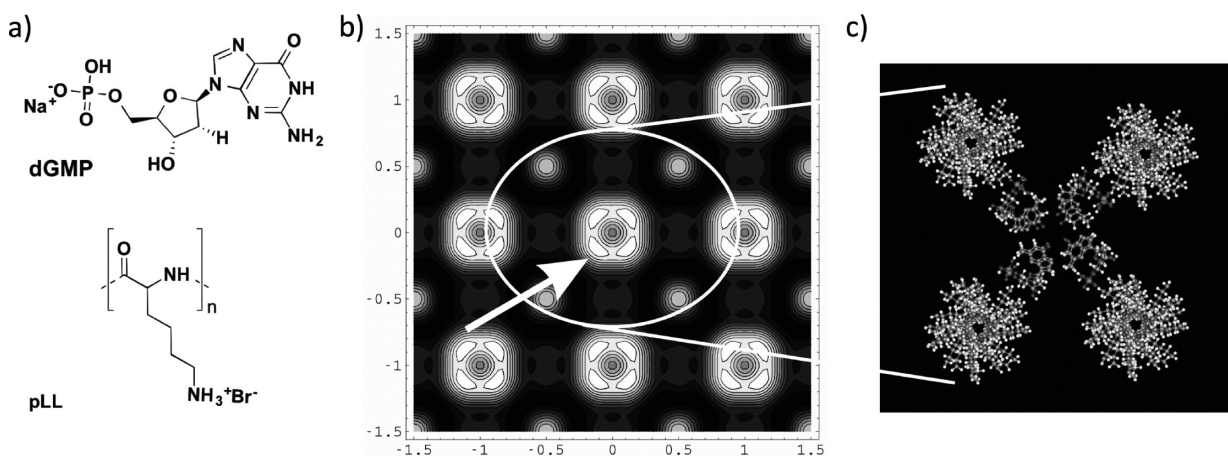


Figure 4. (a) Structures of dGMP and pLL. (b, c) Electron-density map (b) and model (c) of the highly regular quadratic columnar phases from pLL-dGMP complexes. The arrow indicates the presence of a persistent 4-fold symmetric pattern. Reproduced with permission from ref 26. Copyright 2006 The Royal Society of Chemistry.

such PTFs led to well-aligned thin films with DRs of 18 (Figure 3c and d). A combination of polarized light microscopy and null-ellipsometry measurements indicated that the columns of the complex were aligned perpendicular to the PTF, with a preferential orientation of the dipole moments of the perylene dyes within the yz (vertical) plane (Figure 3b).

The presence and high density of “hard” ionic charges, crucial for the formation of ISA materials, were identified as a major drawback for macroscopic alignment. The strong ionic interactions provided very stable materials, but reduced opportunities for relaxation and rearrangements, suppressing macroscopic alignment. These results, as well as further attempts to disperse PDITMA-BEHP aggregates in a poly-(styrene) matrix (BEHP is the phosphodiester analogue of AOT),²¹ are in marked contrast to the facile alignment and

high induced order found in hydrogen-bonded polymer–amphiphile systems,²² even those containing perylene-based amphiphiles.²³

Investigating the formation of higher order ISA structures, we focused on introducing supramolecular helicity in perylene-based structures. In the first study,²⁴ we employed cationic amino acid-based chiral surfactants in an attempt to induce helicity into an anionic perylene dye. It was found that, after complexation, the surfactants transferred supramolecular chirality to the perylene dyes, which formed left-handed helically aggregated stacks in THF. In the solid state, where significant π -stacking was observed in the formed smectic thermotropic liquid crystals, no induced helicity was observed.

In a follow-on study, complexation of PDITMA with a chiral double-tailed phosphodiester surfactant led to solvent-depend-

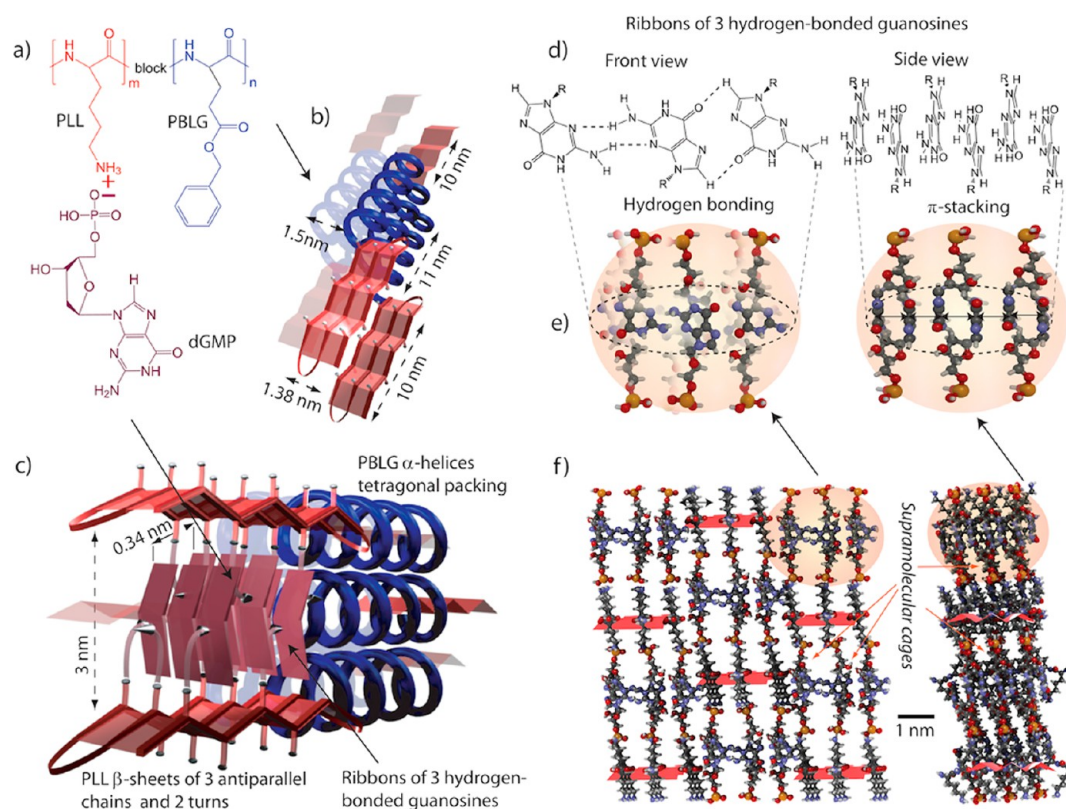


Figure 5. Multiple noncovalent interactions employed during the self-assembly of PBLG-*b*-PLL with dGMP, showing (a) ISA, (b) β -sheets and antiparallel α -helices packing in (c) to form porous structures. (d, e) Proposed ribbon structure formed by three dGMPs. (f) Formed porous supramolecular structure. Reproduced with permission from ref 29. Copyright 2011 John Wiley and Sons.

ent formation of left-handed helical superstructures of stacked perylene chromophores.²⁵ Left-handed supramolecular chirality was also found in solid-state thin films, independent of the solvent from which such films were cast. X-ray investigations showed strong π -stacking interactions for the columnar thermotropic LC materials in the bulk solid state, with casting of dilute ethanol solutions of this chiral complex producing well-defined (but achiral) fibrous structures. Here a combination of factors (solvent polarity, concentration, and preparation conditions) seemed to have favored stacking in a random fashion, thus leading to achiral fiber formation.

3. BIOMOTIF-BASED ISA MATERIALS

In an effort to utilize biological tectons (often easily available, well-defined, and functional) within ISA materials, we investigated the preparation of a supramolecular analogue of Nature's most well-known and complex structure—DNA. We chose deoxynucleotide monophosphates (dNMPs) as the surfactant analogue for ISA complexation, and combined these information-containing anionic tectons (or codons) with a well-defined polymeric cationic scaffold, poly-*L*-lysine (pLL).²⁶ As the dNMPs possess possibilities for both hydrogen bonding and ionic interactions, all complexations were carried out well above the CAC to ensure complex formation.

Complexation of dGMP (deoxyguanosine monophosphate) with pLL (Figure 4a) yielded well-organized columnar mesostructures, with small-angle X-ray (SAXS) analysis and electron-density mapping showing a regular quadratic columnar phase ($d = 3.44$ nm, Figure 4b, c). This unusually highly ordered phase was ascribed to the formation of π -stacked G-quadruplexes (i.e., G quadruplexes, through Hoogsteen hydrogen

bonding), supported by ionic interactions with polypeptide scaffolds of high structural definition and periodicity. Complexation of the other dNMPs yielded LC materials with π -stacking in evidence, with the order decreasing from pLL-dCMP, to pLL-dTMP and pLL-dAMP (both of much lower order).

The well-known Watson–Crick binding motif was then utilized, and “single-stranded” complexes of pLL-dGMP and pLL-dCMP combined and annealed for 5 days at 60 °C. Analysis of the formed product by gel electrophoresis showed that hybridization took place to yield a positively charged product with stacked base pairs (shown by ethidium bromide staining). SAXS analysis of the hybridized product confirmed π -stacking within well-ordered hexagonal columnar mesophases (d -spacing = 2.74 nm).

With this platform established, the multiple interaction motifs of dGMP presented many opportunities for the construction of well-ordered supramolecular materials. The formation of G-quadruplexes (through a combination of π -stacking, cation–dipole interactions, and Hoogsteen hydrogen bonding) was used to preform an ordered polyanionic scaffold, before complexation with various double-tailed ammonium surfactants to yield columnar mesoconstructs (as imaged by TEM and AFM).²⁷ Inclusion of Ag⁺ as stabilizing cation within the quadruplexes and consequent photoreduction produced nanoparticle-containing soft nanocomposites. The well-ordered thermotropic mesophases acted as structure-directing agent, localizing and separating nucleation sites and producing small Ag nanoparticles of narrow size distribution.

Ikkala, Houbenov, Faul, and co-workers used BCP self-assembly of well-defined and shape-persistent BCPs, in combination with nucleotide assembly, to rationally construct

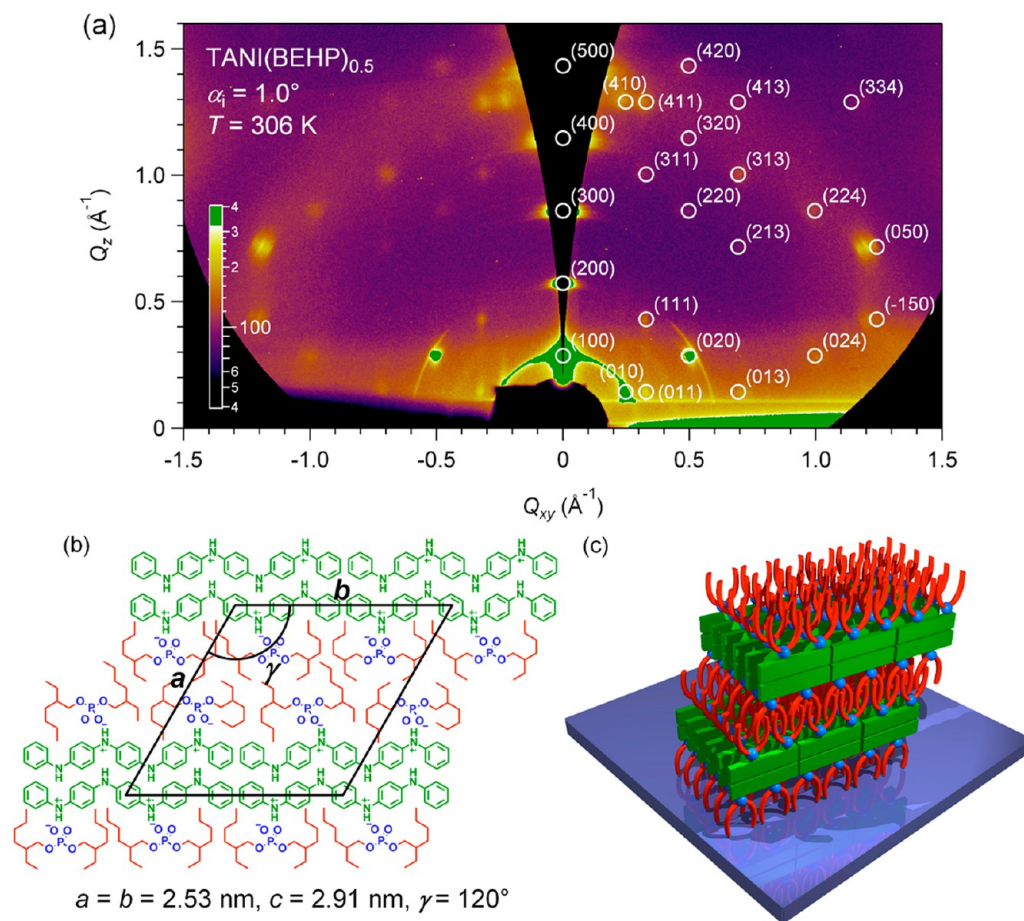


Figure 6. (a) 2D GIXS scattering pattern from TANI-BEHP, (b, c) fitted hexagonal unit cell with lattice parameters $a = b = 2.53$ nm, $c = 2.91$ nm, and $\gamma = 120^\circ$ ($\alpha = \beta = 90^\circ$). Reproduced with permission from ref 30. Copyright 2011 The Royal Society of Chemistry.

complex materials across multiple length scales.^{28,29} Following on from the original use of homopolymeric pLL,²⁶ di- and triblock copolymers of coil-like pLL and the well-known rodlike helix-forming pBLG (poly(γ -benzyl-L-glutamate)) were used for complexation with dGMP. A further design motif that became relevant during these investigations was the influence of molecular packing frustrations to contribute to hierarchical structure formation.

For the coil-rod-coil triblock copolymer pLL-pBLG-pLL,²⁸ materials exhibiting hierarchical structure formation over six length scales were prepared. This high level of organization was achieved first by Hoogsteen binding of dGMPs to form disclike quartet structures (stabilized by K^+ cation-dipole interactions), which in turn π -stacked to form extended columns of G-quadruplex structures. ISA between these preformed discs and pLL blocks produced hexagonally organized G-quartet columnar structures with $d = 2.8$ nm. However, the complexed pLL block is covalently bound to the well-defined rodlike α -helical pBLG block, which packs very efficiently with a periodicity of 1.4 nm. This incommensurability of two covalently bound mutually repulsive block structures with substantial size difference drove the formation of elongated microphase-separated fibrils. The fibrils, consisting of a tightly packed pBLG core and two outer layers consisting of hexagonal columnar phases of pLL-dGMP, extended to macroscopic length scales.

Building on the aforementioned studies, we continued investigations into rod-coil pBLG-pLL diblock-based struc-

tures (Figure 5a).²⁹ We showed that the combination of shape-persistent pLL β -sheets (formed under the correct local conditions) and pBLG α -helical rodlike structural motifs, in combination with dGMP orthogonal binding motifs (hydrogen bonding and ionic complexation), now led to incommensurability and packing frustrations, thus generating porous polymeric framework (or woodpile) structures.

The packing of the pBLG helices (at 1.5 nm) in tetragonal arrays in an antiparallel fashion (to ensure cancellation of dipoles along the helices) drives the arrangement of the attached pLL chains into folded β -sheets, now spaced at approximately 3 nm (i.e., twice the pBLG repeat unit, see Figure 5b, c). This proposal, confirmed by SAXS, TEM, and IR data, provides a regular arrangement of β -sheets in a lamellar fashion with an open porous structure available for “up” and “down” dGMP binding. Due to these physical confines and available binding opportunities, the nucleotides bind ionically to the β -sheets as short π -stacked ribbons, leaving the porous framework structure intact (Figure 5d–f). Competitive dye binding studies showed that opportunities exist to exploit the distinct chemical character of the internal surfaces. Such accessible and tunable internal surfaces, especially if the concentration of heteroatoms and pore sizes can be tuned, are of interest for CO_2 separation and capture technologies.

4. ELECTROACTIVE MATERIALS

Discussions now focus on the special case of the doping of oligo(aniline)s,^{30,31} an area closely related to the cooperative

ISA approach presented. It is well-known that poly(aniline), PANI, can be doped with acids from the half-oxidized, basic emeraldine base (EB) state to the conducting emeraldine salt (ES) state. Although doping was traditionally done with small inorganic acids (and the organic acid camphorsulfonic acid), it was also shown that acid doping could be achieved with acid surfactants (initially shown for dodecylbenzenesulfonic acid). The main motivation behind our activities in this area was to explore opportunities to produce well-defined and easily processable materials, thus enabling the exploration of anisotropic conductivity and associated optoelectronic properties for applications in (flexible) energy storage and sensing devices.

In the first publication to utilize acid surfactant doping in combination with well-defined and easily processable oligo-(aniline)s,³² we applied our ISA approach using a range of di(*n*-alkyl) phosphoric acid surfactants, notably BEHP. The choice of acid surfactant provided the opportunity to compare such structural studies with other ISA studies.

The combination of π -stacking, conjugated surfaces, and laterally (noncovalently) bound plasticizing surfactant produced well-organized 2D columnar conductive LC phases for the shortest functional oligomer, phenyl/phenyl-capped tetra-(aniline), Ph/Ph-TANI. Preparation of doped PANI and octa(aniline), OANI, systems as comparison produced hexagonal and mixed phases, respectively.

The *Col-I* phase transition of the doped Ph/Ph-TANI thermotropic LC phase caused a larger than 3-orders-of-magnitude drop in conductivity, which was fully reversible upon cooling. Optical studies confirmed that the materials did not undergo dedoping during heating, but loss of the ordered phase structure was the source of this reversible switching behavior.

In two follow-on studies,^{33,34} we investigated the *in*- and *out-of-plane* supramolecular structure of the thermoresponsive BEHP-doped Ph/Ph-TANI system. Direct comparison of Ph/Ph-TANI and Ph/Ph-OANI in the undoped and doped states, also at different doping ratios with BEHP, provided insight into the role of molecular architecture of the oligomer, as well as effectiveness of the ISA approach for the preparation of well-ordered thin films.

X-ray reflectivity (XRR) studies³³ showed that, for 400 nm thick films, plasticized BEHP-doped Ph/Ph-TANI yielded a highly ordered bilayer structure with a *d*-spacing of 2.15 nm. More impressive was the fact that these simple drop-cast films possessed a corrected coherence length of >100 nm, which corresponded to 50 layers, with an extremely low disorder parameter of 0.06. In contrast, the BEHP-doped OANI system showed a corrected coherence length of 7 nm (approximately 3 layers) for its less-ordered lamellar structure (with a similar *d*-spacing of 2.35 nm). This lower order was ascribed to the high degrees of freedom provided through multiple rotations about the phenyl–amine–phenyl bonds.

Grazing-incidence X-ray scattering (GIXS) studies were performed³⁴ to determine in-plane order and the orientation of the structures relative to the substrate. The low order (mostly short-range side-by-side and π -stacking interactions) of the noncomplexed TANI and OANI was confirmed. As expected, doping with BEHP increased the order of both oligomers dramatically. For the low-ordered OANI-BEHP system, the presence of a lamellar structure with no in-plane order, no registration between the lamellae, and very little preferential

orientation relative to the underlying substrate was confirmed in this study.

Extremely high induced order, driven mostly by dopant and oligomer architecture when confined to thin films, was found for Ph/Ph-TANI-BEHP, both out-of-plane and in-plane orientation. In short, spotlike GIXS patterns (Figure 6a) were fitted with a hexagonal unit cell (lattice parameters $a = b = 2.53$ nm, $c = 2.91$ nm and $\gamma = 120^\circ$, $\alpha = \beta = 90^\circ$, Figure 6b, c). The length scale of the determined *c*-axis here indicated eight layers in the unit cell, with the spotlike diffraction indicating a very high degree of orientation relative to the substrate. Although no data has been published yet on the influence of such high order on the desired anisotropic conductivity, these studies confirmed the opportunities afforded by the ISA approach for the preparation of highly ordered functional thin films.

In further related studies, we expanded the synthetic³⁵ approaches for Ph/Ph-TANI (and derivatives) to tune molecular architectures, optoelectronic properties, function, and processing methodologies,^{36,37} producing well-defined functional micro- and nanostructures.

5. TOWARD ELECTROACTIVE ASSEMBLIES AND COMPLEX HIERARCHICAL STRUCTURES

Our initial attempts to use PE–Surfs for other purposes than just purely structural focused on the structure-directing function of such mesostructured templates.^{38–40} Initially, a simple mesoscopic template consisting of hexagonal arrays of cylinders from [poly(diallyldimethylammonium)]-dodecyl sulfate (pDADMAC-SDS) was used to direct the formation of anisotropic polymer particles of cross-linked poly(styrene), PS. In two follow-on studies,^{39,40} a polymerizable phosphodiester surfactant, di(undecenyl) phosphate, was used as functional and structural component in an ISA complex with pDADMAC. Swelling of the hydrophobic alkyl phase with dithiols of varying length led to the efficient cross-linking of the terminal diene of the unsaturated surfactant monomer (surfmr). The use of the thiol–ene polyaddition reaction, with minimal shrinkage and volume changes, was key to the formation of well-defined lamellar polymeric structures.

Moving away from a purely functional surfactant approach, Faul and Manners launched a number of investigations into the use of metal-containing poly(ferrocenylsilane) (PFS) PE–Surf materials. Metal-containing polymers have shown great promise in a number of research and application areas,⁴¹ and provide exciting opportunities to include a range of new functionalities in ISA materials, in combination with the ability to tune polymer architectures and morphologies. In this collaborative effort, we therefore explored switchable functionality and hierarchical structure formation in mesostructured complexes using a number of different PFS-based polyelectrolytes. Materials explored included simple cationic homopolyelectrolytes,⁴² organic-PFS BCPs (with the PFS block as the cationic polyelectrolyte),⁴³ and all-PFS BCPs (with amorphous and cationic polyelectrolyte blocks).^{44,45}

In proof-of-principle studies, PFS homopolymers were prepared, in which the position (and thus availability for complexation) of the charge was changed. Generally speaking, all materials produced low-ordered lamellar thermotropic phases. Cyclic voltammetry (CV) confirmed the redox activity of the ferrocene-containing backbone was preserved, and could be reversibly switched in solution. However, chemical switching (with H₂O₂ and ascorbic acid) of thin films in the solid state severely affected film quality.

In further studies, BCP self-assembly behavior was again combined with ISA, to explore hierarchical structure formation for functional supramolecular materials.⁴³ We prepared polystyrene-*b*-poly(ferrocenylmethyl-(trimethylammoniumpropynylsilane)) of varying block ratios (the nonquaternized BCPs exhibited the as-expected classical BCP phase behavior). Variation of the block volume ratios, in combination with AOT complexation, which changed the volume fractions in a predictable way, led to the formation of hierarchical structures. However, it was found that the surfactant alkyl tails mixed efficiently into the PS phase (as in earlier studies²¹), causing distortion of the obtained phase structures. Changing the surfactant to a perfluorinated AOT analogue, which increased the difference of the Flory–Huggins χ -parameter between the two blocks, enhanced the formation of long-range well-ordered phase structures. This change led, for example, to well-defined and aligned cylinders of PS (with *d*-spacing of 35 nm) in a lamellar PFS–surfactant matrix extending over many micrometers. The etch resistance of these well-ordered PFS structures was then exploited by subjecting such samples to an etch step (exposure to an O₂ plasma) to remove the organic components. This approach yielded thin inorganic membranes with 34 nm holes (from the removal of the PS cylinders), indicating a promising approach for the formation of well-ordered inorganic templated structures.

In the foregoing studies, both redox switchability and etch resistance of the PFS components of the ISA complexes were explored. Keeping these attractive features in mind, we used our ISA approach to enable orthogonal addressability through use of ethyl orange (EO), the azobenzene dye used in earlier studies,¹⁵ as amphiphile. The complexation of EO with a PFS BCP (with a methyl–ethyl substituted amorphous PFS block and cationic polyelectrolyte block) produced hierarchically structured materials.⁴⁴

Unlike for the low MW ISA complexes, we could now inscribe SRGs using circularly polarized light. Annealing of thin films before inscription increased diffraction efficiency significantly. The modulation depth of the inscribed SRG structures could be increased dramatically through oxidation of the PFS component of the hierarchical ISA complexes, though reversibility could not be achieved (possibly due to the inability to remove counterions that diffused into the films during oxidation). Finally, we successfully removed the strongly absorbing azobenzene component from the SRG through etching (thus avoiding optical interference), and produced ceramic SRGs of high quality.

In the final collaborative study, to date, on the combination of ISA and PFS-based BCP self-assembly,⁴⁵ we expanded the range and block ratios of the methyl–ethyl substituted amorphous PFS block and cationic polyelectrolyte PFS-only BCP. Continuing to explore the AOT surfactant theme, three related surfactants (with varying tail molecular architectures) were used for complexation (see Figure 7 for the structures of the BCPs and surfactants used in this study). Variation of the BCP block ratios (including the addition of the complexed surfactant) yielded as-expected hierarchical phase morphologies (e.g., *cylinder-within-lamella* or *lamella-within-lamella*) for a number of complexes. However, two cases yielded unexpected morphologies. For the first, where a *lamellar-within-lamellar* morphology was expected with qBCP2, we argued that molecular frustration to accommodate the bulky bis(3,7-dimethyl-octyl) of the AOT-oct surfactant produced a *tetragon-within-lamellar* phase morphology. This unusual phase

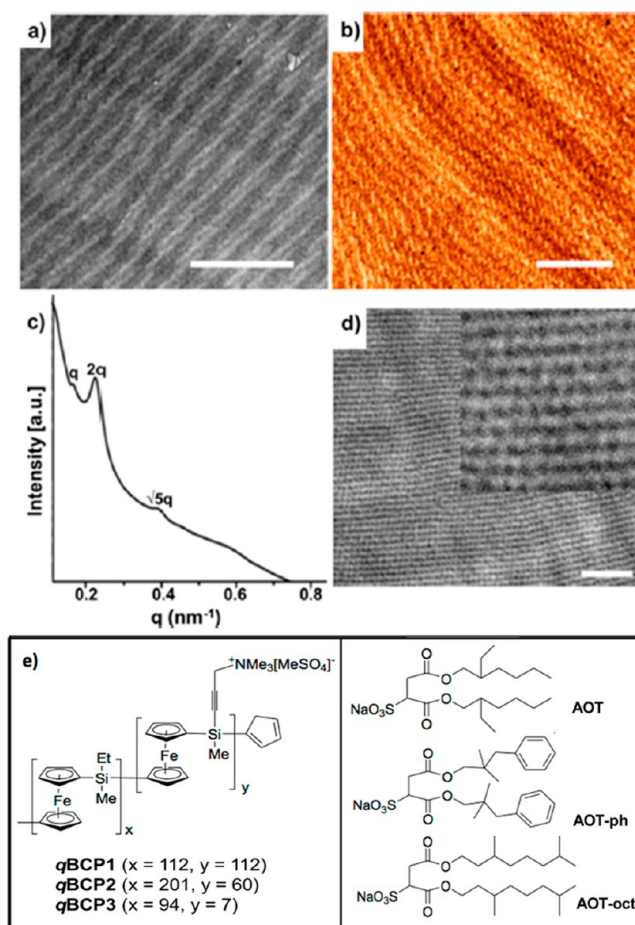


Figure 7. Morphological characterization of the supramolecular helical phase from the complexation of qBCP3 with AOT, showing (a) TEM and (b) AFM images of the helical structures. (c) SAXS and (d) TEM confirmed the tetragonal arrangement of the helices. (e) Structures of the PFS-only BCPs and surfactant used. Reproduced with permission from ref 45. Copyright 2013 American Chemical Society.

structure, which is of great interest for data storage applications and usually prepared with major synthetic efforts, was easily formed from simple ionic complexation.

However, more noteworthy was the case of the BCP with an extremely short polyelectrolyte block (7 charged monomeric units, qBCP3). Although simple calculations based on volume fractions would suggest that the charged-neutralized block would form cylinders within an amorphous PFS matrix, an unconventional helical morphology, with a pitch of 18 nm, was found. These helices packed in a tetragonal arrangement, with AFM and TEM clearly showing the helical supramolecular arrangement of the complexed block (see Figure 7a, b, and d).

The presence of this helical supramolecular phase was not affected by the nature or molecular architecture of the surfactants used here. Once again, it was suggested that incommensurability and packing frustrations of the short complexed block, in relation to the covalently attached large amorphous PFS block, were the main driving forces for the formation of these intricate structures.

6. CONCLUSIONS

This Account details the power of ISA as a facile noncovalent synthetic route to prepare a range of supramolecular constructs—from simple, nanostructured soft LC materials,

to complex hierarchical materials with multiple levels of hierarchy. The incorporation of multiple noncovalent interactions and function within the simple building blocks, whether as the oligo- or polyelectrolyte or as a functional surfactant, provides access to a range of functional materials. Careful combination of orthogonal functionalities in this ISA approach provides further scope to produce hierarchical materials with individually addressable and switchable functionality.

Furthermore, the combination of ISA with other assembly approaches, especially BCP self-assembly, provides new insight and access to intricate phases and morphologies which would otherwise be very difficult to create through conventional covalent chemistry approaches. Although more difficult to control, packing frustrations and molecular incommensurability have come to the fore as important tools to direct the formation of unexpected phase morphologies, hierarchical and porous superstructures. This approach will be a key area to explore for future control of not only structure, but also function, across multiple length scales.

We therefore believe that many opportunities still exist, especially in the combination of the ISA approach with BCP assembly; not only for the construction of functional materials^{46,47} across multiple length scales, but also moving toward mesoscopic materials synthesis. Mesoscopic synthesis, for example, was achieved by expanding on the traditional ISA approach to produce BCP-based hierarchically organized “strip” oval-shaped nanoparticles⁴⁸ through the use of Au surfactant nanoparticles (SNPs). The segregation of these SNPs at specific interfaces controlled interfacial interactions, thus driving structure formation across multiple length scales. It is expected that such approaches could open further avenues to address societal challenges (such as energy storage or conversion) if combined with functional π -conjugated BCPs and functional SNPs.

In the area of functional biobased materials, direct exploitation of cationized protein and polymeric surfactant ISA complexes as functional solvent-free liquid proteins (i.e., thermotropic protein phases) is a further exciting area of future development of biocompatible functional materials.⁴⁹ Ikkala et al. have very successfully continued to build on aspects of dGMP-based assembly to produce nacre-mimetic nanocomposites utilizing sacrificial hydrogen bonding.⁵⁰

Application of ISA materials, although actively explored in a number of instances, has not been achieved in a commercial sense yet. However, we believe that the combination of the ISA approach with the functionality of electroactive organic materials and metal-containing polymers will continue to provide exciting materials with embedded functionality, with applications in energy and data storage envisaged in the near future. Such combinations of structure, function, and finally application will continue to be a focus area for development for ISA (and related methodologies). Uptake by other researchers, as shown by the selected examples, will furthermore ensure that ISA will continue to play an important role in the preparation of complex and functional supramolecular materials, while also contributing to understanding and addressing some of the challenges presented in this Account.

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Notes

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Biography

Charl F. J. Faul received his Ph.D. in December 2000 from the University of Stellenbosch, South Africa. After working for 1 year as postdoctoral researcher with Markus Antonietti at the Max Planck Institute of Colloids and Interfaces (Potsdam, Germany), he led an independent research group exploring the principles of ionic self-assembly (ISA) until 2004 at the same institute. He moved to the School of Chemistry, University of Bristol, as Lecturer in 2005, where he currently holds the position of Reader in Materials Chemistry. He held a visiting professorship at the Helsinki University of Technology (now Aalto University) from 2006 to 2010, and in 2012, a Chinese Academy of Sciences Visiting Professorship at the National Centre for Nanoscience and Technology, Beijing. He currently holds an adjunct professorship at the Department of Chemistry, Tsinghua University, Beijing. His research efforts are broadly aimed at exploiting ISA in the development of tunable molecular architectures, functionality, and hierarchies.

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