



New directions in supramolecular electronics

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Supramolecular organic electronics embodies one of the biggest promises made by supramolecular functional materials. Huge advancements have been made with regard to its theoretical and functional understanding over the past few decades. Among a lot of the unsolved problems that still exist, this review takes a look at a few that can be circumvented owing to some of the recent works. We have taken a critical look at supramolecular aspects of domain control, monodispersity and control of dynamics of π -conjugated molecular assemblies. We have discussed the most promising recent approaches in relevance to supramolecular electronics.

Introduction

Since its inception organic electronics has undoubtedly added a new dimension to conventional supramolecular chemistry [1]. A vast amount of research has been segregated under two major headings namely nano-sized electronics and polymer electronics [2–5]. A major theme in all these areas, apart from basic functional group modification, has been the establishment of supramolecular order at the required scale of operation in organic electronic applications. Broadly put, these methodologies come under two challenging categories. The first being the synthesis of molecules which are capable of attaining functional consistency by virtue of their design. The design keeps in mind the structural rigidity so as to decrease conformational defects and electronic continuity thus providing uninterrupted channels for the required electronic communication. The requisites in the first category might look simplistic; but any endeavor to follow this route requires designing molecules with formidable dimensions and shapes, and at the same time dealing with complex synthesis. This approach leads to synthetic mono-dispersity only in the case of small molecule synthesis. At a polymeric level it is riddled with polydispersity. The scientific literature is ripe with key contributions in this field including path breaking work on poly aromatic hydrocarbons and polymers with various strategic functional groups embedded in the main chain [6–9]. The second challenge has been using electronically active π conjugated molecules to self-assemble together

by modulating non-covalent forces. This path is synthetically simpler but deals with the challenge of overcoming the complex dynamics of non-covalent forces [10]. The task of keeping dynamics at acceptable levels so as to attain a rational supramolecular motif and hence translating it into meaningful function has been successfully carried out by many research groups [11]. Though the major strategy employed has been using the combination of hydrophobic interactions, hydrogen bonds, and π - π interaction, even after considering the appreciable returns this has been at the cost of randomness at different hierarchical levels of aggregation. This often results in high polydispersity at a supramolecular level. This polydispersity in supramolecular assemblies often results in understating the electrical properties due to various defects in packing. Hence, a mono-disperse supramolecular synthesis is very much warranted. Thus control of aggregate length or in other words mono-dispersity, translation of local supramolecular order at a nanostructure scale to global device scale, control of molecular separation so as to provide separate domains for electronic communication have been major areas of concern until now.

The pros and cons of polymer and nano-sized electronics have been extensively reviewed by some exhaustive articles [12–18]. Hence, for the purpose of this article we limit our discussion to the recent breakthroughs in the supramolecular chemistry of π -conjugated molecules in the last few years which have/can have an impact on opto-electronic functions of its assemblies. We will discuss issues which can alleviate the standing problems in supramolecular chemistry. Issues like domain control based on

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amphiphilicity and orthogonal reactions, monodispersity based on supramolecular living polymerization and finally using the dynamics itself to get a functional material will be discussed in the coming sections in detail.

Domain control

Assembling the chromophores into ordered nanostructures has become routine for supramolecular chemists [1]. However, a more challenging issue is controlling the domain separation at a supramolecular level and also controlling the randomness in orientation of nano-structures. Both of these tasks involve a common idea, that is, control of the orientation of one chromophoric stack with respect to the other chromophore. This has been addressed uniquely by Aida *et al.* using the concept of amphiphilicity [19]. It involves the induction of a major trait of amphiphiles, that is, allowing the energetically favorable domain separation which allows inherent control on the domain order. This domain control consists of building separate stacks of donor (D, *p*-type) and acceptor (A, *n*-type) molecules. Segregated stacks of donors and acceptors have a specific advantage that they do not allow fast recombination of charge carriers, increasing their lifetime and hence allowing them to be extracted for device application. They synthesized a Hexabenzocoronene (HBC, donor) based amphiphile with a Trinitrofluorene (acceptor) moiety at the hydrophilic end (**1–2**) (Fig. 1a,b). Amphiphilic assembly of **1** and **2** was brought about by diffusing methanol vapors in their THF solution. Variation of the amphiphilic concentration gave rise to segregated stacks at low concentration and mixed stacks at higher concentration with nanotube and microfiber morphology, respectively. Mixed stacks (co-facial, alternate D and A) were characterized by a charge transfer band and segregated stacks (orthogonal individual stacks of D and A) were by the absence of it. As previously postulated, a segregated assembly would have a longer recombination time and hence in terms of a device would result in higher photo-conductivities and a higher on/off ratio. The photo-conductivities of these molecules were measured by flash-photolysis

time-resolved microwave conductivity (FP-TRMC) with samples excited by a laser pulse of 355 nm. Photo-conductivity of the nanotube sample was found to be 20 times more than the micro-fibers; also the on-off ratios were greater than 10^4 hence elucidating the importance of molecular design and its impact on the property. This amphiphilic approach has been further extended to a variety of systems including usage of C_{60} moieties forming a HBC-fullerene dyad (**3**) (Fig. 1c) [20–28]. These dyads also assemble in the segregated state as nano tubes with perfectly differentiated domains (Fig. 1d). Such systems speak of the generality of the idea. However, the most important breakthrough of this approach has been the successful formation of a linear supramolecular *p–n* junction which has been axially arranged with respect to the nanostructure [29]. The formation of a supramolecular *p–n* junction has been a challenge because of the multiple issues it poses. Firstly, controlling the dynamics so as to hold nanometer domains of *p*-type and *n*-type together by a non-covalent force next to each other requires exceptional molecular design. Secondly, molecular design has to also include the fact that narcissistic self-sorting of one of the electro-active component occurs but nucleates on the counterpart, and not independently. These represent formidable challenges to overcome and Aida *et al.* take advantage of the amphiphilicity for crossing the hurdles. Their molecular design involves using an amphiphilic *p*-type HBC appended with 2,2' bipyridine moieties on the hydrophilic end (**4**) (Fig. 2a). The bipyridines have two important functions. First, as the nanotubes form, they spontaneously bundle together which can be detrimental to the final aim as it would not result in single fibers of *p–n* junctions due to ineffective 'seed' action. Thus, copper triflate is added at this point which binds to the bipyridine causing nanotubes to disperse into single nanotube due to the charge repulsion. Now, these single tubular nuclei are primed for further growth of an *n*-type molecule on them. Hence, it elucidates the second more important function of the copper bipyridine complex that is to keep the donor nucleus intact from further solution dynamics. The *n*-type molecule that needs to be chosen has to be structurally very

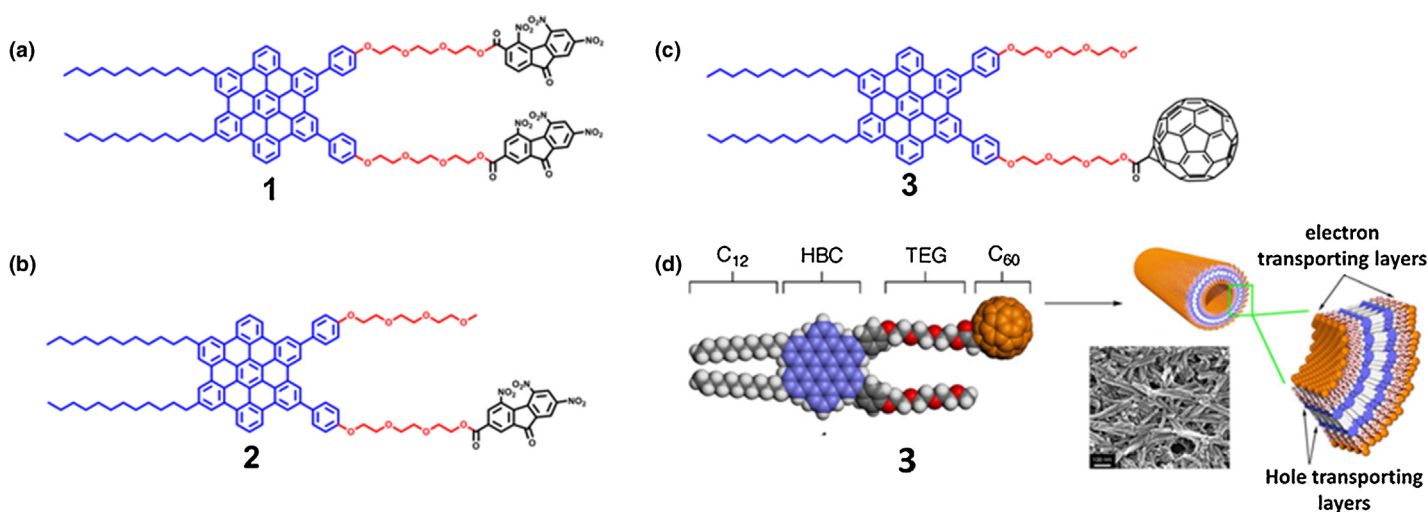


FIGURE 1

(a)–(c) Molecular structures of amphiphilic donor–acceptor molecules. (d) Schematic showing the tubular assembly of **3**, inset shows FE-SEM image of the nanotubes. Adapted from Refs. [19,28]. (d) Reproduced with permission from Ref. [28]. Copyright 2009 Proceedings of the National Academy of Sciences of the United States of America.

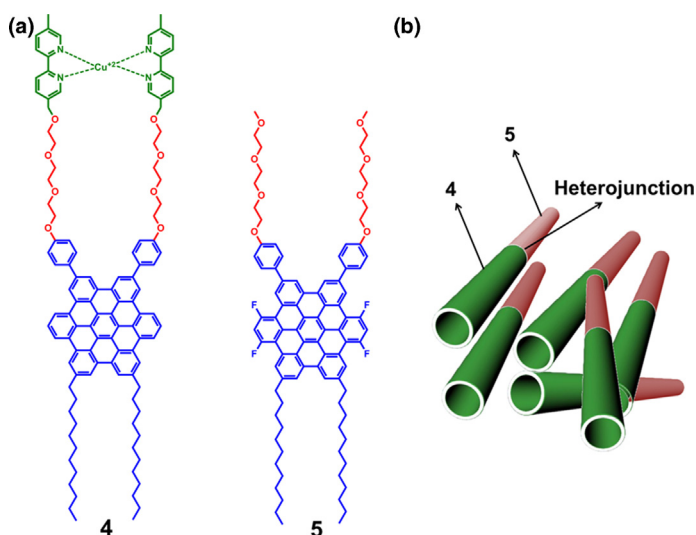


FIGURE 2

(a) Structures of the donor (4) and acceptor (5). (b) Schematic representation of the linear $p-n$ junction. Adapted from Ref. [29].

similar so as to not trigger homo-nucleation. Keeping the above in mind, the molecule chosen is the tetra fluoro derivative (5, Fig. 2a) which is in size and shape comparable but has an inverse electronic nature. Thus, as all the prerequisites are intelligently met when the p -type nuclei are mixed with monomers of n -type, they grow together to yield a linear supramolecular $p-n$ junction. Their existence can be visualized by TEM-EDX (Transmission Electron Microscopy-Energy Dispersive X-ray Analysis) mapping and FP-TRMC (Flash-Photolysis Time-Resolved Microwave conductivity) measurements further confirm their presence as elucidated by long living charge carriers ($\tau_{1/e}(\text{Block})$ is 3–6 times $\tau_{1/e}$ (individual components) where $\tau_{1/e}$ represents the lifetime of charge carriers). This work also is the only example of supramolecular block co-polymer of small molecules to date, the extreme rarity of which speaks of the inherent problems of dynamics and sorting that need to be controlled *en route*. Another example of this, albeit via a polymer self-assembly, is the supramolecular living polymerization which will be discussed in the coming sections (vide infra).

Amphiphiles have traditionally been water based aggregates. Recent reports by Nakanishi *et al.* open a new chapter in amphiphilic self-assembly to control the organization of π -conjugated molecules [30,31]. Generally, amphiphilic assembly requires aqueous environments, so as to show domain segregation based on interfacial energy differences [32]. Such a classical amphiphilic approach has been used to construct self-assembled nanostructures of p -type and mixed stack CT nanostructures with excellent mobilities [33–39]. In their work, however, they synthesize fullerene functionalized with alkyl chains and demonstrate the concept of hydrophobic amphiphiles (6, 7) (Fig. 3a). Taking advantage of the mutual immiscibility of π -block and alkyl chains, the molecules self-assemble as micelles which are reminiscent of conventional amphiphiles. Apart from micelles, structures like lamellar bilayers and hexagonally packed fibers could also be achieved. Lamellar bilayers in this respect need further elucidation. A curious experiment in the study involved assembly of these fullerene amphiphiles on addition of pristine fullerenes (Fig. 3b). The result

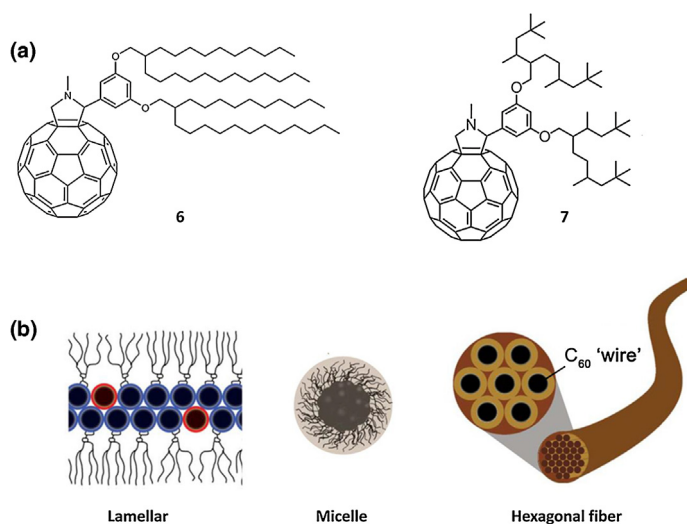


FIGURE 3

(a) Molecular structures of hydrophobic amphiphiles (6, 7). (b) Schematic representation of the three phases namely lamellar, micelle, hexagonal fiber (blue balls represent the amphiphile and red balls represent the pristine C₆₀). (a,b) Reproduced with permission from Ref. [30]. Copyright 2014 Nature publishing group.

is unique and sets a wonderful precedent for the experiments on a variety of other π conjugated chromophores. Moreover the translation of the assembly characteristic to functionality was also demonstrated by the fact that the mobility observed in these mesostructures rivaled the ones of crystalline C₆₀ which speaks of the potential of this approach. Moreover, for a practical point of view, arrangement is a prerequisite on larger scales and combining a self-assembly motif (amphiphilicity) and liquid crystallinity, as done in the above work, would be one way to achieve this. This work seems to be an optimistic start to a new era which has seemingly boundless opportunities.

Even though the amphiphilic approach is an effective solution based process, arrangement of the chromophores on the surface in domains is rudimentary for device related applications. Thus for domain control, apart from the amphiphilic approach, another interesting approach has been self-organizing surface initiated polymerization (SOSIP) of electro-active molecules on the electrode surface by Matile *et al.* [40–52]. They use a unique molecular design which uses substrate anchoring as well as an orthogonal reaction for unidirectional growth. The substrate used is indium tin oxide (ITO) and the electro-active moiety as naphthalene diimide (NDI) (8, 9) (Fig. 4a,b). These NDIs are functionalized with side chains having diphosphonates which ligate with the substrate providing the point of further growth. Another moiety in the side chain is the disulphide which are reduced by (*S,S*)-dithiothreitol once the molecule has been linked to the substrate. Once reduced the terminal thiolates are a reactive end to the incoming structurally similar chromophore, hence the growth pattern [53]. The above reaction sequence has been used to arrange multiple chromophores to yield gradient electron and hole transport. Even though the growth occurs on the surface, extraordinary complexity can be achieved via this process. Double channel photosystems are one step forward to the zipper assembly previously reported by the same group as a tool to produce double channel gradients

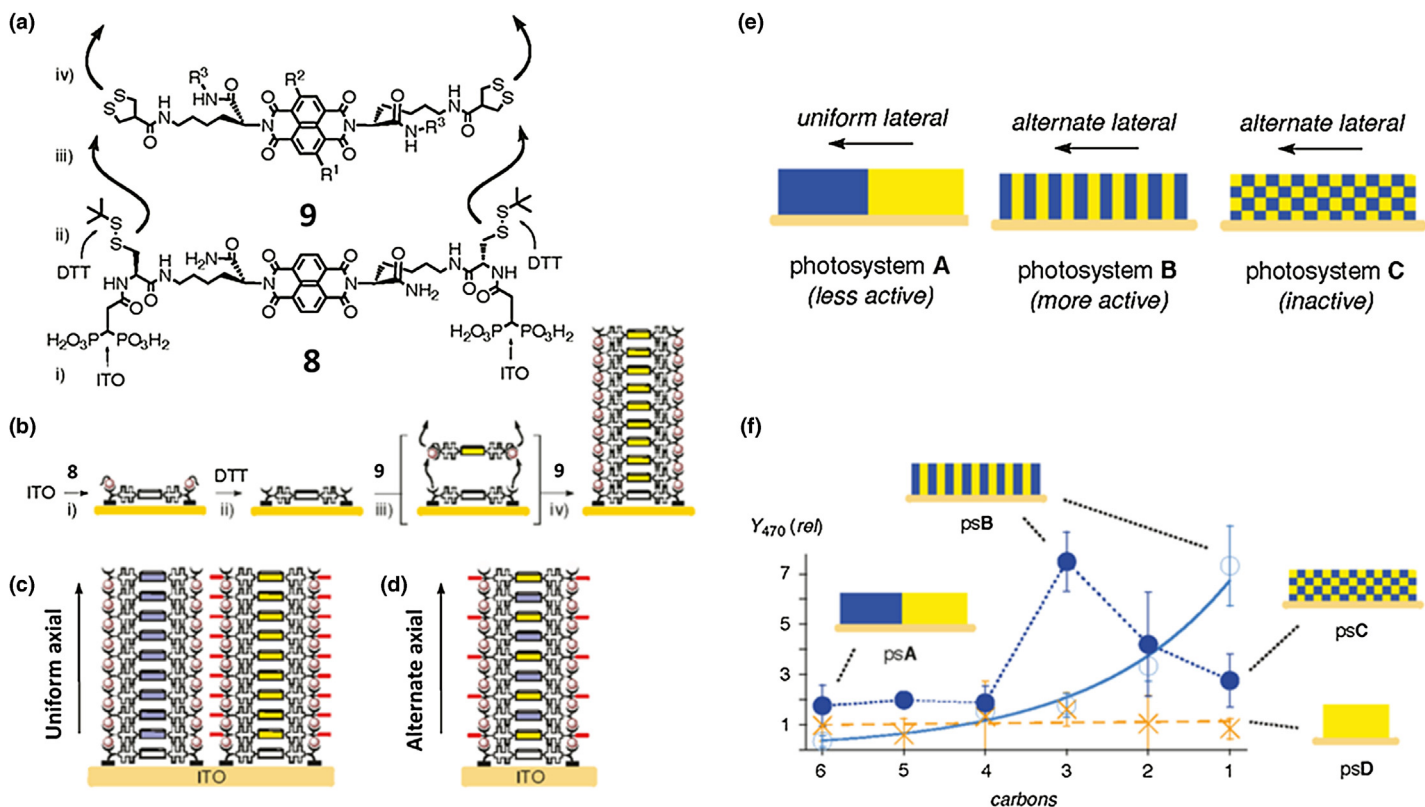


FIGURE 4

(a) and (b) Structures of the molecules involved in SOSIP with initiator (**8**) and propagator (**9**) and schematic of the deposition process. Steps (i) docking of **8** on ITO surface, (ii) activation of **8** by DTT, (iii) first propagation reaction by disulphide ring opening and (iv) continuation of propagation by subsequent ring openings. (c) and (d) Schematic showing segregated and mixed stacks of donor and acceptor molecules respectively. (e) and (f) Schematic showing various kinds of geometries and photo activity upon 470 nm excitation of various geometries as a variation of carbon in alkyl chains in NDI propagator respectively. Reproduced with permission from Refs. [53,54]. Copyright 2011 American Chemical Society.

(Fig. 4c–e) [54]. As postulated earlier, the domain control between donor and acceptor is extremely important for good device characteristics. To elucidate this fact, various geometries of D–A arrangement were tried and maximum photo current efficiency at 470 nm was found to be best in an alternate stack arrangement (Fig. 4f). Apart from the fact that by this methodology one can demonstrate the significance of alternate stacks unambiguously, the parameter that stands out is the unprecedented control over various morphologies accessible by this approach. Even though the covalent form of organization gives no room for dynamicity, that can ruin the periodicity and arrangement, controlled dynamic behavior can be introduced so as to add another dimension to the concept. Apart from the conventional SOSIP which uses sulphide exchange, they use chemically orthogonal hydrazone-oxime exchange (Fig. 5) [55]. This helps in adding complementary stacks next to pre-arranged chromophores. The molecular design has been optimized to suit the architectural prerequisites. The nucleating chromophore now contains four phosphonates to anchor with the surface and three NDI cores. The central core acts as a SOSIP initiator as well as the site for hydrazone exchange, while the flanking NDIs do not possess these functionalities. Their role is central to providing topologically similar space for the incoming chromophores for exchange. The SOSIP process starts with the propagator molecules sitting over the initiator molecules. These propagators include a non-active exchangeable moiety

attached by a hydrazone bond. Upon addition of hydroxylamine the non-active moiety leaves as an oxime, exposing the hydrazine moieties for reaction with active aldehydes. Once the SOSIP procedure is over, the global morphology resembles trenches (caused by uninitiated flanking NDIs) between NDI stacks (Fig. 5). These trenches are now primed for chromophore exchange. Various

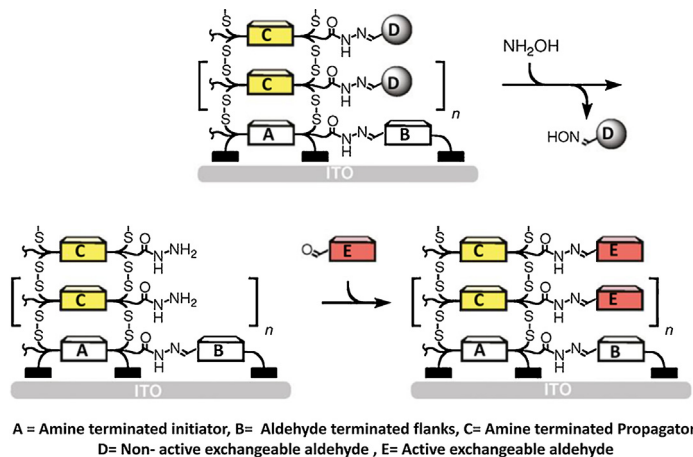


FIGURE 5

Schematic representation of stack exchange post SOSIP. Reproduced with permission from Ref. [55]. Copyright 2011 American Chemical Society.

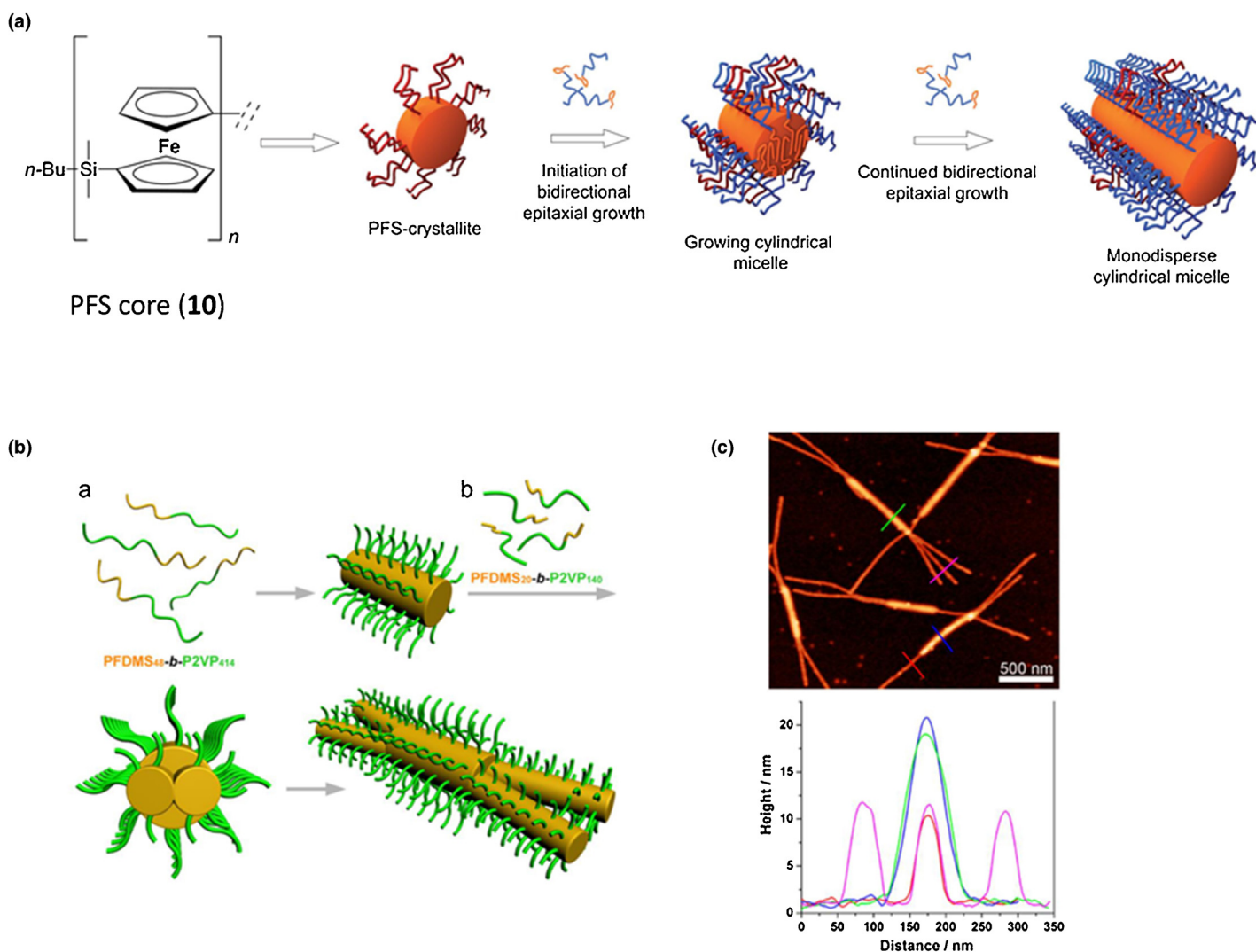


FIGURE 6

(a) Schematic representation of crystallization induced supramolecular living polymerization, (b) schematic of the process to obtain branched nano-structures and (c) AFM images of the nanostructures with height profile below. (a) Reproduced with permission from Ref. [64]. Copyright 2010 Nature publishing group. (b)–(c) Reproduced with permission from Ref. [76]. Copyright 2013 American Chemical Society.

chromophores have been used by this methodology, hence pointing out the generality of the structure. The authors could achieve multi component structures which bear a resemblance in structure as well as function to the previously reported covalent parallel channels.

Monodispersity

Apart from domain control another major requisite that can bring about a sea change in supramolecular electronics is the monodispersity of structures. Monodispersity in non-spherical objects is a requisite that supramolecular chemistry has never been famed for, until the work of Manners *et al.* involving crystallization driven self-assembly [56]. For all the promise that supramolecular chemistry holds, it was held back by its characteristic of producing aggregates with uncontrolled dimensions. This ensemble of sizes act as diluents of the functionality and precise control over these is rudimentary. Although biomolecule templated self-assembly of π -conjugated systems has been investigated to control the dimensions, hydrophobic interaction upon concentration/drying on

surfaces results in their agglomeration and thus derails the purpose [57–63]. Manners *et al.* employed a unique crystallization driven self-assembly [64–75] which was used to assemble their polymers in a way analogous to living polymerization in conventional literature. They used a diblock copolymer for their experiments. Apart from the several combinations tried, the common block remains polyferrocenylsilane (PFS) (10), which is responsible for the crystalline core. Other blocks have been selected such that there exists a selective solubility as compared to the PFS block, for example polyisoprene (PI) or poly(dimethylsiloxane) (PDMS) [64]. Selective solubility enables the PFS blocks to self-assemble as the PI or PDMS blocks wrap around making the whole structure a cylindrical micelle, with a living end capable of further propagation on monomer availability (Fig. 6a). For the experiment, seeds of pre-assembled micelles were added to the solution containing the free polymer and further growth has been investigated. The authors have pointed out that even though the ‘living’ capability exists in these polymers when seeds of a size more than 100 nm and length dispersity > 1.4, these conditions were not sufficient to

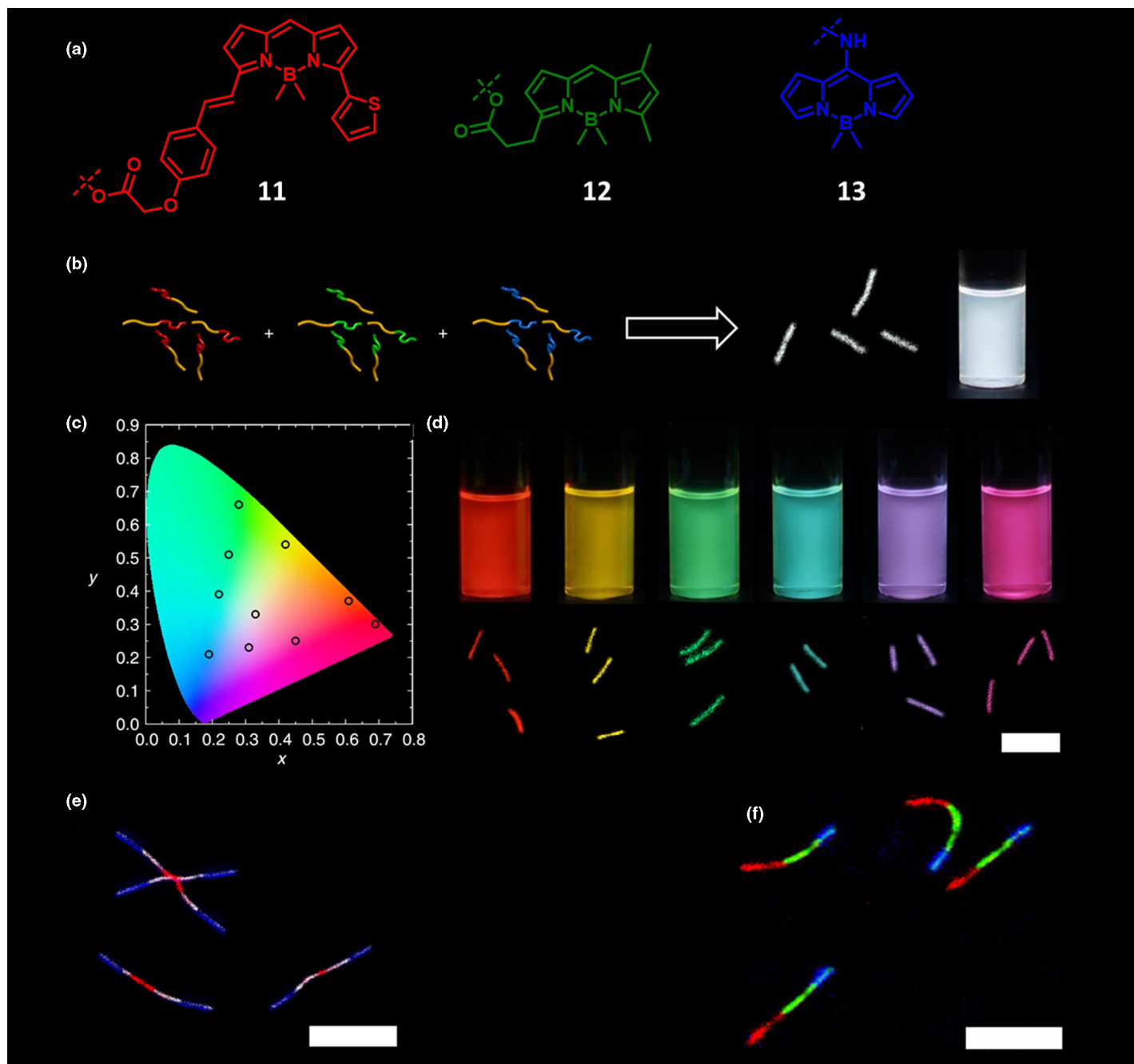


FIGURE 7

(a) Molecular structure of BODIPY dyes (**11–13**), (b) schematic representation of the process of mixing independent micelles to get structures of various colors, (c) CIE 1931 chromaticity diagram for the solutions, (d) photographs of the solutions under UV illuminations, below are their confocal images, scale $3\ \mu\text{m}$, (e) confocal images of the centro-symmetric, multi-color, multi-block, supramolecular polymer, scale $5\ \mu\text{m}$ and (f) confocal images of the non-centro-symmetric, multi-color, multi-block, supramolecular polymer, scale $5\ \mu\text{m}$. Reproduced with permission from Ref. [77]. Copyright 2014 Nature publishing group.

yield mono disperse lengths. To attain their goal they needed to decrease both the length and the dispersity which was a significant challenge by itself. They finally standardized the conditions so as to yield nuclei of a size of around $20\ \text{nm}$ and length dispersity < 1.03 . These technological leaps finally allowed them to attain mono disperse structures. This opened an avenue with enormous possibilities. One of the first issues this approach could cater to was the formation of designer aggregates, that is, aggregates which possess a variety of shapes and could be attained by simple chemical modification to the core. Demonstrating the

above in one such study, Manners *et al.* ended up creating branched micelles [76]. The block copolymer used blocks of poly(ferrocenyldimethylsilane) (PFDMS) and poly(2-vinylpyridine) (P2VP). The study uses the concept of using a seed twice the diameter as incoming polymers destined to form the supramolecular branches. This allows nucleation of more than one polymer at the seed end, hence giving the branching (Fig. 6b). Since the ferrocenyl part is the self-assembling back bone, the higher its composition, the higher the micellar diameter goes – therefore the seed contains twice as much as PFDMS as compared to the

polymers for branches. Following the addition pattern of seeds to a solution of 'to be branches' polymer, they could attain a branched micellar structure previously unattainable in such a controlled manner (Fig. 6c). This approach makes attaining supramolecular block co-polymers a mundane task, and the complexity that can be further generated has been best exemplified by the formation of multi colored fluorescent micelles in their recent report [77]. Keeping the block of ferrocenyl silane constant, the other block contained fluorescent BODIPY (boron-dipyrromethene) dyes (**11–13**). Since the block addition can be controlled, one can envisage a whole variety of colors that can be attained by mixing blocks of basic colors in various proportions. The above has been demonstrated by scaling most of the area of the CIE (International Commission on Illumination) co-ordinate space just by changing the block proportions (Fig. 7a–e). Furthermore, complex unsymmetrical optical architectures have also been achieved using unidirectionally growing nuclei (Fig. 7f). Though the method of crystallization driven self-assembly with such control has not been shown in small molecules, the above still remains the only example of such unprecedented control over the self-assembly. However, the task of obtaining large scale alignment of electronically active molecules still remains to be solved. An attempt in that direction has been taken by Giuseppone *et al.* (vide infra).

The large scale alignment of mono-disperse aggregates has also been attained in small π -conjugated molecules by Giuseppone *et al.* in a fascinating light induced living polymerization. This study features triarylamine based molecules (**14**) (Fig. 8a) [78]. They discovered that this class of molecules in chloroform solution and exposure to light readily changed color and gave rise to the triaryl ammonium radical. Evolution of the radical can be seen over time if one follows the reaction by EPR. Further analysis showed that a small quantity of these radicals formed CT pairs with neutral species upon generation and this triggers an aggregation of neutral molecules further. This represents a unique example of charge transfer driven supramolecular living polymerization in supramolecular chemistry. The whole process is triggered by light. The uniqueness of this approach was demonstrated a couple of years later by the same group. They employed the same concept of light induced aggregation, only this time across a channel with an applied voltage (Fig. 8b–d) [79]. Aggregate alignment has previously been performed by using a multitude of external physical interaction or by crosslinking the aggregates by a pincer approach [80]. As the light is shined the free radicals are created, further forming CT pairs with neutral molecules. Being charged, the pair aligns itself due to the applied voltage and hence results in further growth across the channels. This observation is groundbreaking in terms of the fact that misaligned nanostructures across an electrode channel was a major disadvantage, and the fact that they can now be grown between the gap is a unique example of soft lithography. Recently Takeuchi *et al.* have shown the existence of living supramolecular polymerization in porphyrin based dyes. This opens the path for further generalization of supramolecular living polymerization to common chromophores [81].

Dynamics

All of the above desired properties require a leash on the dynamic nature of the molecules. As the hunt for more complex systems with controlled randomness proceeds, one cannot help but think

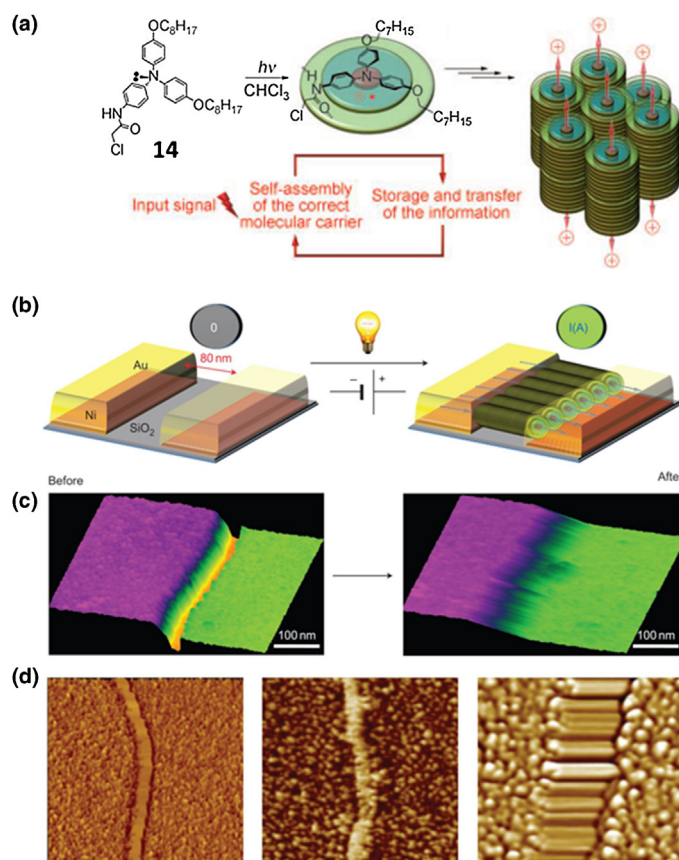


FIGURE 8

(a) Schematic representation of the light induced self-assembly of **14**, (b) schematic representation of alignment of **14** across gold electrodes upon application of light and potential, (c) AFM image of the electrode gap before (left) and after (right) of light irradiation, (d) AFM phase images of electrode gap before [1500 nm × 1500 nm] (left), after [1500 nm × 1500 nm] (middle) and after [250 nm × 250 nm] (right) irradiation. (a) Reproduced with permission from Ref. [78]. Copyright 2010 Wiley-VCH Verlag GmbH & Co. (b)–(d) Reproduced with permission from Ref. [79]. Copyright 2012 Nature publishing group.

that the direction is towards an ordered complexity in supramolecular systems. Though in most situations the dynamics are attempted to be reduced, an understanding of the combinatorial parameters can also lead to a functional material. Ulijn *et al.* interestingly reported the evolution of energy transfer (EnT) nano-structures from a gelation driven dynamic combinatorial library (Fig. 9a) [82]. An acid terminated peptide Naphthol (**15**) molecule was synthesized as an energy donor. Self-assembly was done in the presence of another amine terminated amino acid (**16**) such that on addition of thermolysin it would result in a self-assembling dipeptide (**17**). The acceptor pair was acid terminated Dansyl chloride (**18**). Naphthol (**15**) individually formed spherical aggregates and with subsequent addition of acceptor (**18**) showed partial energy transfer due to inclusion in the spherical aggregates (Fig. 9b). To this combinatorial mixture thermolysin was added, which is known to form specific amide bonds in peptides. As the amide forms it results in the formation of a conjugate that self assembles with a much higher association constant, hence tipping the equilibrium in its favor. The result is a nano fiber capable of light harvesting, formed purely by designing molecules that can champion dynamics (Fig. 9b). Recently Ulijn *et al.* extended this

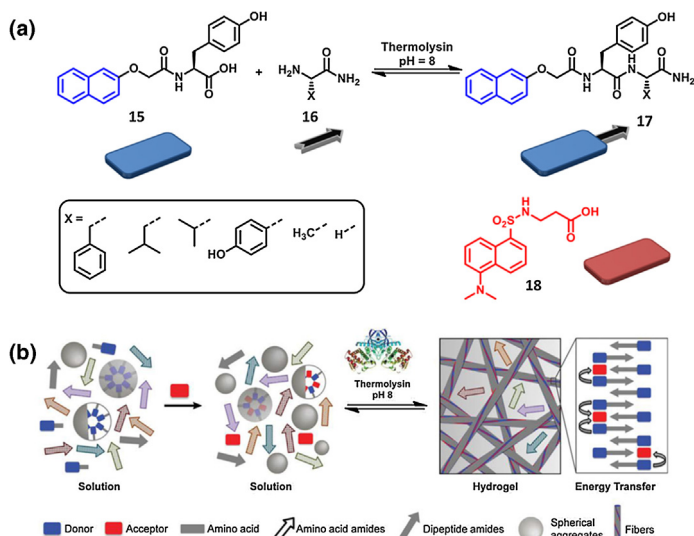


FIGURE 9

(a) Scheme showing molecules and the reactions involved in enzyme catalyzed EnT (Energy Transfer) structures, (b) schematic showing EnT in a mixture of **15**, **16** and **18** with and without thermolysin. (a) Adapted from Ref. [82]. (b) Reproduced with permission from Ref. [82]. Copyright 2013 <http://creativecommons.org/licenses/by/3.0/>.

approach towards charge transfer as well [83]. While doing so they have propagated structure optimized CT assemblies which are catalytically responsive to enzymes (Fig. 10). This extension speaks of the control that can be achieved over dynamics of the assemblies. The electronic acceptor in this case was naphthalene diimide functionalized with acid terminated peptide (**19**). Similar to the previous case, self-assembly has been performed in the presence of amine terminated amino acid (**20**) which would form

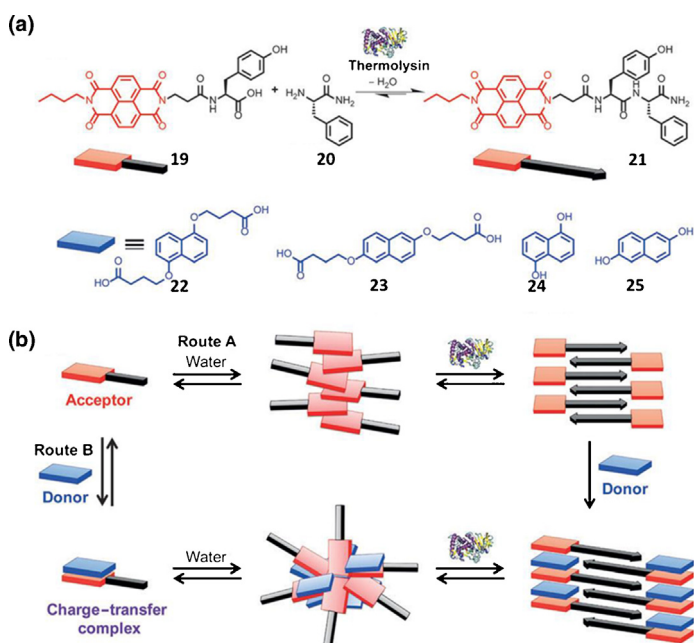


FIGURE 10

(a) Scheme showing molecules and the reactions involved in enzyme catalyzed charge transfer structures, (b) schematic representation of the whole process. Reproduced with permission from Ref. [83]. Copyright 2014 Wiley-VCH Verlag GmbH & Co.

a self-assembling dipeptide adduct (**21**) on addition of thermolysin. The electron donating counterparts are 1,5 and 2,6 dihydroxy naphthols and their alkylated versions (**22–25**). The CT structures can be attained by either pre-mixing and then adding the thermolysin or by a pre thermolysin addition followed by donor inclusion in the aggregates. In either case, since the self-assembly is caused by the dipeptides which are in turn formed due to the addition of thermolysin, a catalytic enzymatic control over self-assembly has thus been achieved. The above examples also point towards an *in situ* aggregation mechanism that can bring about functional structures owing to the fact that stabilization energy governed by self-assembly governs the ensemble equilibrium.

Outlook

As mentioned previously, supramolecular chemistry holds great promise for organic electronics. There have been great challenges in its path but due to research over the last couple of decades the tide seems to be changing. A common theme in all of these advances has been systematically eliminating the negative supramolecular cues, or in some cases even using it to one's advantage. Ultimately, some of the major criteria for a functional organic electronic device include ways to control the domains of donor and acceptor molecules, make them in a monodisperse fashion and finally have control over their dynamic behavior. As elucidated above, all of this now seems to be within reach. Domains can be controlled by either amphiphilicity or by systematic surface initiated growth. Monodispersity can be attained by either crystallization induced supramolecular polymerization, which could be a platform for various electro-active modifications, or by taking advantage of the light induced chemistry of triaryl amines. Structures can be in fact grown across an electrode in the latter case. Finally an *in situ* aggregation can be delved into, where aggregation controls the energy landscape and hence tipping the dynamicity in favor of the chemists. At this point the field of organic-inorganic hybrids also deserves a mention. The applicability of these materials in various fields of opto-electronics makes them a class of materials which can realize the potential mentioned above [84–89]. A multitude of mechanistic studies on both equilibrium and non-equilibrium aggregation processes seems to be the guiding light in these areas [90–95]. Hence, we see that new avenues have been discovered and successfully demonstrated for the construction of supramolecular electronic materials. Generalization and wider applicability is what is now needed, since these areas are still in their infancy, and perhaps a higher impetus on functional inclusion and control is warranted.

References

- [1] T. Aida, E.W. Meijer, S.I. Stupp, *Science* 335 (2012) 813–817.
- [2] A.P.H.J. Schenning, et al. *Synt. Met.* 147 (2004) 43–48.
- [3] A.P.H.J. Schenning, E.W. Meijer, *Chem. Commun.* 26 (2005) 3245–3258.
- [4] L. Brunsveld, et al. *Chem. Rev.* 101 (2001) 4071–4098.
- [5] F.J.M. Hoeben, et al. *Chem. Rev.* 105 (2005) 491–1546.
- [6] T. Qin, et al. *J. Am. Chem. Soc.* 131 (2009) 14329–14336.
- [7] A. Narita, et al. *Nat. Chem.* 6 (2014) 126–132.
- [8] K. Müllen, *ACS Nano* 8 (2014) 6531–6541.
- [9] C. Li, et al. *Chem. Rev.* 110 (2010) 6817–6855.
- [10] C. Bohna, *Chem. Soc. Rev.* 43 (2014) 4037–4050.
- [11] S. Rieth, C. Baddeleya, J.D. Badjić, *Soft Matter* 3 (2007) 137–154.
- [12] A. Ajayaghosh, S.J. George, A.P.H.J. Schenning, in: F. Würthner (Ed.), *Topics in Current Chemistry*, Springer, 2005, pp. 83–118.

- [13] D. Gonzalez-Rodriguez, A.P.H.J. Schenning, *Chem. Mater.* 23 (2011) 310–325.
- [14] D.J. Broer, et al. *Angew. Chem. Int. Ed.* 51 (2012) 7102–7109.
- [15] S.S. Babu, V.K. Praveen, A. Ajayaghosh, *Chem. Rev.* 114 (2014) 1973–2129.
- [16] F. Würthner, et al. *Angew. Chem. Int. Ed.* 50 (2011) 3376–3410.
- [17] V.K. Praveen, et al. *Chem. Soc. Rev.* 43 (2014) 4222–4242.
- [18] K. Sakakibara, et al. *J. Am. Chem. Soc.* 136 (2014) 8548–8551.
- [19] Y. Yamamoto, et al. *Science* 314 (2006) 1761–1764.
- [20] Y. Hizume, et al. *J. Am. Chem. Soc.* 132 (2010) 6628–6629.
- [21] W.-S. Li, et al. *Chem. Asian J.* 5 (2010) 1566–1572.
- [22] R. Charvet, et al. *Chem. Commun.* 47 (2011) 6825–6827.
- [23] Y. He, et al. *Adv. Mater.* 22 (2010) 829–832.
- [24] W.-S. Li, et al. *J. Am. Chem. Soc.* 130 (2008) 8886–8887.
- [25] J. Motoyanagi, et al. *J. Am. Chem. Soc.* 130 (2006) 4220–4221.
- [26] Y. Yamamoto, et al. *J. Am. Chem. Soc.* 129 (2007) 9276–9277.
- [27] T.L. Benanti, P. Saejueng, D. Venkataraman, *Chem. Commun.* (2007) 692–694.
- [28] Y. Yamamoto, et al. *Proc. Natl. Acad. Sci. U. S. A.* 106 (2009) 21051–21056.
- [29] W. Zhang, et al. *Science* 334 (2011) 340–343.
- [30] M.J. Hollamby, et al. *Nat. Chem.* 6 (2014) 690–696.
- [31] A.P.H.J. Schenning, S.J. George, *Nat. Chem.* 6 (2014) 658–659.
- [32] A. Sorrenti, et al. *Chem. Soc. Rev.* 42 (2013) 8200–8219.
- [33] K.V. Rao, et al. *Angew. Chem. Int. Ed.* 49 (2010) 4218–4222.
- [34] A.A. Sagade, et al. *Adv. Mater.* 25 (2013) 559–564.
- [35] A.A. Sagade, et al. *Chem. Commun.* 49 (2013) 5847–5849.
- [36] M. Kumar, K.V. Rao, S.J. George, *Phys. Chem. Chem. Phys.* 16 (2014) 1300–1313.
- [37] A. Jain, et al. *Chem. Eur. J.* 17 (2011) 12355–12361.
- [38] B. Narayan, et al. *Adv. Funct. Mater.* 23 (2013) 3053–3060.
- [39] X. Zhang, C. Wang, *Chem. Soc. Rev.* 40 (2011) 94–101.
- [40] R. Bhosale, et al. *Angew. Chem. Int. Ed.* 48 (2009) 6461–6464.
- [41] R. Bhosale, et al. *Chem. Soc. Rev.* 39 (2010) 138–149.
- [42] N. Sakai, et al. *J. Am. Chem. Soc.* 132 (2010) 6923–6925.
- [43] R. Bhosale, et al. *Chem. Sci.* 1 (2010) 357–368.
- [44] S. Sakurai, et al. *Energy Environ. Sci.* 4 (2011) 2409–2416.
- [45] M. Lista, et al. *Faraday Discuss.* 155 (2012) 63–77.
- [46] P. Charbonnaz, N. Sakai, S. Matile, *Chem. Sci.* 3 (2012) 1492–1496.
- [47] M. Lista, et al. *Biomol. Chem.* 11 (2013) 1754–1765.
- [48] G. Sforzini, et al. *Chem. Sci.* 4 (2013) 1847–1851.
- [49] A. Bolag, et al. *ChemistryOpen* 2 (2013) 55–57.
- [50] A. Wilson, G. Gasparini, S. Matile, *Chem. Soc. Rev.* 43 (2014) 1948–1962.
- [51] A. Bolag, et al. *Angew. Chem. Int. Ed.* 53 (2014) 4890–4895.
- [52] N. Sakai, et al. *J. Am. Chem. Soc.* 136 (2014) 5575–5578.
- [53] N. Sakai, et al. *J. Am. Chem. Soc.* 133 (2011) 15224–15227.
- [54] M. Lista, et al. *J. Am. Chem. Soc.* 133 (2011) 15228–15231.
- [55] N. Sakai, S. Matile, *J. Am. Chem. Soc.* 133 (2011) 18542–18545.
- [56] J. Schmelz, F.H. Schacher, H. Schmalz, *Soft Matter* 9 (2013) 2101–2107.
- [57] R. Iwaura, et al. *J. Am. Chem. Soc.* 128 (2006) 13298–13304.
- [58] P.G.A. Janssen, et al. *J. Am. Chem. Soc.* 129 (2007) 6078–6079.
- [59] M. Surin, *Mater. Adv.* 21 (2009) 1126–1130.
- [60] P.G.A. Janssen, et al. *Soft Matter* 6 (2010) 1494–1502.
- [61] A. Ruiz-Carretero, et al. *Angew. Chem. Int. Ed.* 49 (2010) 5335–5338.
- [62] A. Ruiz-Carretero, et al. *Chem. Commun.* 47 (2011) 4340–4347.
- [63] P.G.A. Janssen, et al. *Angew. Chem. Int. Ed.* 48 (2009) 8103–8106.
- [64] J.B. Gilroy, et al. *Nat. Chem.* 2 (2010) 566–570.
- [65] J.-C. Eloi, et al. *J. Am. Chem. Soc.* 133 (2011) 8903–8913.
- [66] S.K. Patra, et al. *J. Am. Chem. Soc.* 133 (2011) 8842–8845.
- [67] F. He, et al. *J. Am. Chem. Soc.* 133 (2011) 9095–9103.
- [68] Y. Mohd, et al. *Macromolecules* 45 (2012) 3883–3891.
- [69] A.P. Rupa, et al. *Science* 337 (2012) 559–562.
- [70] H. Qiu, et al. *Angew. Chem. Int. Ed.* 51 (2012) 11882–11885.
- [71] J. Qiu, et al. *ACS Nano* 7 (2013) 3754–3766.
- [72] H. Qiu, et al. *J. Am. Chem. Soc.* 135 (2013) 12180–12183.
- [73] J. Qian, et al. *J. Am. Chem. Soc.* 136 (2014) 4121–4124.
- [74] M.-S. Hsiao, et al. *Macromolecules* 47 (2014) 2361–2372.
- [75] G. Molev, et al. *Macromolecules* 47 (2014) 2604–2615.
- [76] H. Qiu, et al. *J. Am. Chem. Soc.* 135 (2013) 17739–17742.
- [77] Z.M. Hudson, et al. *Nat. Commun.* 5 (2014), 4372/1–4372/8.
- [78] E. Moulin, et al. *Angew. Chem. Int. Ed.* 49 (2010) 6974–6978.
- [79] V. Faramarzi, et al. *Nat. Chem.* 4 (2012) 485–490.
- [80] Y. Kubo, et al. *Angew. Chem. Int. Ed.* 45 (2006) 1548–1553.
- [81] S. Ogi, et al. *Nat. Chem.* 6 (2014) 188–195.
- [82] S.K.M. Nalluri, R.V. Ulijn, *Chem. Sci.* 4 (2013) 3699–3705.
- [83] S.K.M. Nalluri, et al. *Angew. Chem. Int. Ed.* 53 (2014) 5882–5887.
- [84] H. Zheng, et al. *Chem. Soc. Rev.* 40 (2011) 4506–4524.
- [85] H. Gan, et al. *J. Am. Chem. Soc.* 127 (2005) 12452–12453.
- [86] H. Liu, et al. *Acc. Chem. Res.* 43 (2010) 1496–1508.
- [87] Y. Li, et al. *Acc. Chem. Res.* 47 (2014) 1186–1198.
- [88] K.V. Rao, et al. *Chem. Eur. J.* 18 (2012) 2184–2194.
- [89] K.V. Rao, A. Jain, S.J. George, *J. Mater. Chem. C* 2 (2014) 3055–3064.
- [90] T.F.A. De Greef, et al. *Chem. Rev.* 109 (2009) 5687–5754.
- [91] C. Kulkarni, R. Manirathinam, S.J. George, *Chem. Eur. J.* 19 (2013) 11270–11278.
- [92] J. Boekhoven, et al. *Angew. Chem. Int. Ed.* 49 (2010) 4825–4828.
- [93] M.M.J. Smulders, et al. *Chem. Eur. J.* 16 (2010) 362–367.
- [94] C. Kulkarni, S. Balasubramanian, S.J. George, *ChemPhysChem* 14 (2013) 661–673.
- [95] F. Aparicio, F. García, L. Sánchez, *Chem. Eur. J.* 19 (2013) 3239–3248.