

Feature Article

Progress in Fluorene-based Wide-bandgap Steric Semiconductors^{*}

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Abstract Molecular bulks are favorable for the thermal and morphological stability in organic wide-bandgap semiconducting polymers with potential applications in both information and energy electronics. In this review, we present our progress in the design of fluorene-based bulky semiconductors with a fractal four-element pattern. Firstly, we established one-pot methods to spirofluorenes, especially spiro[fluorene-9,9'-xanthene] (SFX) serving as the next-generation spiro-based semiconductors. Secondly, we observed the supramolecular forces at the bulky groups and discovered the supramolecular steric hindrance (SSH) effect on polymorphisms, nanocrystals as well as device performance. Thus, a synergistically molecular attractor-repulsor theory (SMART) was proposed for the control of nanocrystal morphology, thin film phase and morphology. Thirdly, the third possible type of defects has been identified to generate green band (g-band) emission in wide-bandgap semiconductors by the introduction of molecular strain design of cyclofluorene. Finally, the first bulky polydiarylfuorene with highly crystalline and β conformation was achieved by an attractor-repulsor design of tadpole-shape monomer, which offered an effective platform to fabricate stable wide-bandgap semiconducting devices. All the discoveries offer the solid basis to break through bottlenecks of organic/polymer wide-bandgap semiconductors by the improvements of overall performances.

Keywords Organics; Steric effect; Attractor-repulsor; Molecular defects; Wide-bandgap

INTRODUCTION

Organic/polymer semiconductors have attracted considerable attention because of their obvious advantages, including molecular diversity and polymer soft matter, low-cost fabrication, large-area and flexible devices, as well as portable and light convenience equipments^[1–3]. Milestones in the history of plastic electronics include

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that Shirakawa *et al.*^[4] and Heeger^[5] discovered the conductivity of polyacetylene (PA) by doping of halogen and Burroughes *et al.* fabricated the first polymer light-emitting diodes (PLEDs) of poly(*p*-phenylenevinylene) (PPV)^[1], together with the polythiophene transistor in 1987^[6]. Up to date, all aspects of polymer semiconductors have been systematically explored by scientists and engineers from bottom to top level, including molecular design, morphological control, ink formulas, film procedures, structure-parameter relationship, devices architectures as well as device operation and evaluation. Organic/polymer semiconductors have been extensively applied to the light-emitting devices for displaying and lighting sources^[7, 8], lasers^[9, 10], solar cells^[11], photodetectors^[12], as well as transistor memories^[13] for integration circuits. Furthermore, flexible devices, stretchable devices, and e-textile were also fabricated by several groups^[14–16], and exhibited huge potential applications in our daily life. Many efforts have been made to improve device performance, stability and repeatability, while plastic electronics still face severe challenges in comparison to the inorganic counterparts^[17–20], especially in the background of the break through on wet processing engineering and flexible technology recently.

One typical example is the organic wide-bandgap semiconductor polymers (OWBSPs) that are one of the key components for the white lighting source and RGB display, lasing, radar, and radio frequency devices that have been achieved by inorganic GaN. If organic wide-bandgap polymers really reach the GaN-like performance in plastic electronics, they would be applied not only in diodes, but also in power electronics. Wide-bandgap leads to intrinsically low mobility, poor stability as well as large binding energy that all become thorny issues in organic and plastic electronics. Although OWBSPs have been reported since early 1990s, all the device parameters, such as efficiency and stability as well as procedure yield, were improved limitedly^[21]. There is a huge gap between scientific research and commercialization. Many issues still exist and suspend that require the step-by-step breakthrough gradually. One of the issues is the stability of OWBSP. Many works have been done to clarify the mechanism and to develop stabilization strategies in the last two decades. In the past, bulky conjugated polymers showed one impressive feature of thermal stability without changing wavelength of luminescence (Chart 1). Bulky groups are the sp^3 carbon-containing groups which possess the steric hindrance effect that can reduce the rate of reaction in organic chemistry. The typical bulks contain sp^3 carbon owing to 3-dimensional feature in organics, such as *t*-butyl groups, trityl group (triphenylmethyl), phenylfluorenyl groups and diarylmethelene, spirofluorene groups. Compared to other groups, they show the repulsive nature in the aggregates or crystalline growth. Bulky semiconductors have the obvious advantages over the counterpart with alkyl side chains, such as stability. Functionalized bulky groups were introduced into optoelectronic materials or semiconductors which acted as the suppression of intermolecular force, resulting in the morphological stability and the glass transition temperature (T_g) improvement^[22]. Bulky groups can be regarded as organizers to change the arrangement of active π -segments, especially resulting in the increase of π - π stacking distance. The separation of π -segments affords organic semiconductor with higher luminescence quantum efficiency. However, the detailed role of bulky groups remains unclear in the whole landscape of chemistry principle of organic/polymer semiconductors. In fact, among non-active segments in organic/polymer semiconductors, alkyl side chains with van der Waals' (VDM) force not only afford solubility, but also assist the backbone to assemble into the specific arrangement for effectively manipulating electron or exciton behaviors^[23–27].

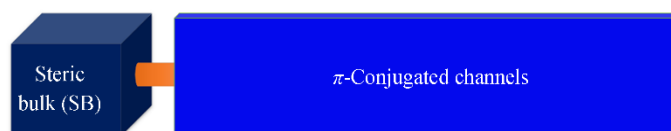


Chart 1 Cartoon of organic polymer steric/bulky semiconductors

Fluorene is a basic building block to design the wide-bandgap polymers which is advantageous over benzene in terms of flexible functionalization at 9-position, including soluble groups, transport groups,

supramolecular groups, and sterically bulky groups. Bulky fluorenes are ideal models for identifying the complex roles of bulks and getting deep insight into the effects on exciton, mobility and stability as well as processing procedures. Here, we devote our efforts to introduce the progress in steric and strain design of bulky fluorenes from CMSOD@IAM in the last decade. First, a green and eco-friendly pot, atom and step economic (PASE) route is a prerequisite to obtain bulky groups for wide-bandgap semiconductors. Second, we proposed a rational synergistically molecular attractor-repulsor theory (SMART) to control over the aggregates of semiconductors. Third, we got a deep understanding of the mechanism of g-band defects by cyclofluorene-based molecular model compounds. Finally, a new kind of high crystallinity polyfluorene materials with integration of bulky groups was highlighted for the next-generation wide-bandgap polymers.

One Pot, Atom and Step Economic (PASE) Route to Bulky Fluorenes

Before the introduction of bulky groups into molecular backbone of OWBSPs, we firstly explored the bulky structures and their methodology that are the prerequisite to identify the roles of molecular segments, to get insight into mechanisms and to overcome the defect, as well as to set up the crucial rules for the rational guideline of high-performance semiconductor design. Our initial motivation under the trend of green electronics is to explore the low-cost and eco-friendly synthesis of typical bulky group units, such as spirofluorenes^[28] and diarylfluorenes^[29]. Among the various spiro-based semiconductors, representative spirobifluorene (SBF) derivatives have extensive applications in organic optoelectronic field, such as organic light-emitting diodes (OLEDs)^[30–32], solar cells^[33], organic field-effect transistors (OFETs)^[34–36], and lasers^[37] as well as photodetectors^[38] (Fig. 1). Spirobifluorenes were first synthesized by Clarkson and Gomberg in 1930^[39], and Salbeck *et al.* applied them in organic electronics in 2007^[30]. However, they also have the drawbacks of expensive stuffs and laborious synthetic routes with three steps^[39]. Until 2006, Xie *et al.* discovered the concise synthesis of spiro[fluorene-9,9-xanthene] (SFX) with a yield of ~80% by accidental one-pot reaction in our laboratory^[40]. SFX shows the similar steric hindrance effect of bulky groups with the unique asymmetric geometry owing to the introduction of oxygen atom. One-pot protocol to SFXs was highlighted by Lin *et al.*^[41], and has absolute advantages in terms of the cost that 4BrSFX was estimated 30 times lower than the counterpart 4BrSBF^[42, 43]. After establishing the unexpected one-pot protocol to SFXs, we made an attempt to expand the substrates^[44], including diazafluorenes, nathenenes^[45] and other substituted phenol derivatives^[46]. Moreover, nitrogen function of spirofluorenes, named spiroacridine, was also designed by one-pot protocols to give spiro[fluorene-9,7'-dibenzo[c,h]acridine]-5'-one (SFDBAO) *via* visible-light-induced photooxidation^[47]. This case inspired us to explore the eco-friendly organic semiconductors that have four basic features, including biomass as stuffs, PASE route to synthesis, water-based inks, as well as bio-friendly recyclable devices^[18]. On the way to devices, some issues still remain for the one-pot to synthesize spirobifluorenes, such as how to synthesize the fluorenes starting from biomass and to overcome the toxicity of fluorene-based semiconductors as well as how to make cycles after the device performance improvement to the standard of commercialization. Green organic semiconductors (GOS) would be attractive in the future electronics *via* green synthesis method, low-cost and environmentally friendly process, and biodegradable products^[48]. To this end, PASE becomes an eco-friendly protocol for bulky organic semiconductors.

An alternative set of bulky building blocks are diarylfluorenes, which possess some difference from spirofluorenes. In order to easily synthesize the building blocks and functionalize active groups, we explored the Friedel-Crafts (F-C) reaction^[49], C—H bond activation^[50], and made the unique substrates^[51] *via* the Baeyer-Villiger oxidation rearrangements to obtain the complex diarylfluorenes (CDAFs) with diverse shapes. In addition, intramolecular stack with molecular strains was realized by *ortho*-substituent effects in overcrowded molecules^[52]. Supramolecular functionalized diarylfluorenes were also synthesized with various weak forces, such as hydrogen bond, C—H...N, van der Waals (VDW) force, as well as π - π stacking force that offer a series of supramolecular bulks for the new molecular design principle by integrating a pair of molecular opposites between steric repulsion and noncovalent attraction *via* covalent linkage.



Fig. 1 A SFX building block as an alternative to SBF for bulky semiconductors

After the modification of fluorene-base bulk units, various models of complex bulks, such as dumbbellshaped^[53, 54], hindrance-capped tadpole shapes^[51], attractor-repulsor molecules^[52], multibulks^[54–56], multiarm bulks^[57], polybulks^[58], bulky tetramers and bulky grids^[59] have been designed with CDAFs, together with spirofluorenes, and synthesized *via* Suzuki or Frediel-Crafts reactions that derivate the bulky arene chemistry. CDAFs as a collective set offer the platform to uncover the single role, multirole, synergetic role and hierarchical role of molecular segments into the right zone of function contribution. CDAFs offer a series of state-of-the-art models to get insight into steric hindrance, conformation, and strain effects on exciton, charge transport and FRET as well as electronic transfer^[60]. CDAFs-based bulky organics have the advantage of a diverse and hierarchical platform ranging from small molecules, oligomers and nanomolecules^[61], as well as polymers and macromolecules^[62]. The established bulky platform would be starting points for the exploration of the rational design principle to guide OWBSP materials. Finally, the diverse and infinite virtual molecular library guarantee systemic demonstration of the possibility of organic wide-bandgap semiconductor polymers from science to commercialization.

Synergistically Molecular Attractor-Repulsor Theory (SMART) to Tune the Molecular Aggregates

All the device parameters such as efficiency, mobility, stability, reliability, repeatability as well as reproducibility are dominated by two key aspects in films, that is, electronic landscape and phase morphology. One prerequisite to rationally design the semiconductors with controllable bandgaps and aggregates is to control over the molecular packing and special state of polymorphism from solution to thin films. Aggregates are key intermediates between molecules and films to make the device complex that requires the effective guideline principle. Until now, bulky groups are one kind of substituents that have three possible roles for structure-based design of organic semiconductors. Firstly, intramolecular steric effect is to change the inner conformations and strains, followed by the change of conjugation length and finally change the exciton or electrons as well as their collective set or current behaviors. The other role of molecular bulky groups is preventing the interaction of active π -backbones owing to the existence of steric hindrance effect, which facilitates the emission by suppressing the quenching from the molecular packing. The third role of bulky groups is to increase the molecular weight to improve the viscosity of solution with the better uniform amorphous film formation and to possess higher glass transition temperature.

During the exploration of bulky groups to suppress low-energy green band (g-band) emission by decreasing π - π stacking interactions among backbone and improving the chemical stability of 9-position *via* the arylation, we observed that the bulky groups could not always suppress g-band defects effectively in polyfluorenes^[27], which is generally owing to either the aggregates or the ketone. However, arylation makes 9-position robust that leads to the seldom chance to form ketone. Therefore, the most possibility is that bulky groups could not suppress the molecular packing completely which lead to generation of g-band emission. Our question is what the real role of bulky groups is and whether the synergetic role exists. Answer to this question would offer one crucial basis to guide molecular design of bulky groups. In this background, we observed a series of small molecular bulks with single-crystalline X-ray diffraction to cover the detailed intermolecular interaction and to

demonstrate the detailed roles. In fact, it is of great importance to not only identify the well-defined molecular entity of function in polymer semiconductors, but also to clarify the roles of non-active segments. Initially, there is no obvious intermolecular interaction of bulky SFX observed. Bulky structure here is represented as a cube (Fig. 2). However, bulky group with weak interaction was observed after the supramolecular analysis of single crystalline spiro-bridged oligothiophene-S,S-dioxides (BSiSDTFO) that changed the mind on the ideal repulsion roles of bulky groups^[63]. To be specific, there are a C—H...O weak interaction and a π - π stacking interaction with a distance of about 0.26 and 0.35 nm, respectively. Furthermore, we observed the bulky groups with some weak nonbonding contacts from diffraction analysis. In fact, bulky groups could contact with other molecular building blocks or itself *via* the supramolecular bonding or force. Intermolecular forces include the repulsion and attraction, that is steric hindrance and noncovalent force. After the systematic investigation, we re-described the bulky groups with weak contact that were reflected from single crystals. In order to accurately describe the observation of noncovalent contact at bulky groups, we described this kind of bulky groups with the cartoon of cube tethered with two-arm sheets for the representation of weak noncovalent touch again (Fig. 2). We also regarded the steric bulks as repulsor and supramolecular synthons as attractors that could be designed rationally *via* molecular engineering. The attractor is a well-defined molecular segment with noncovalent intermolecular force and the repulsor is a concrete molecular building block with steric force. For example, the typical attractors are carbazole or pyrene groups with attractive π - π stacking forces and the typical repulsors are bulky groups, such as spiro-configuration or arylfluorene moieties. A direct joining can be realized between bulky groups of 9-phenylfluorene and the pyrene by the strong π - π stacking interactions for a model of the attractor-repulsor molecular design^[64]. As a result, a synergistically molecular attractor-repulsor theory (SMART) was proposed by us that tells that the combination of attractor and repulsor could generate the synergetic effect, offering an unprecedented tool to self-assemble or control molecular function^[64].

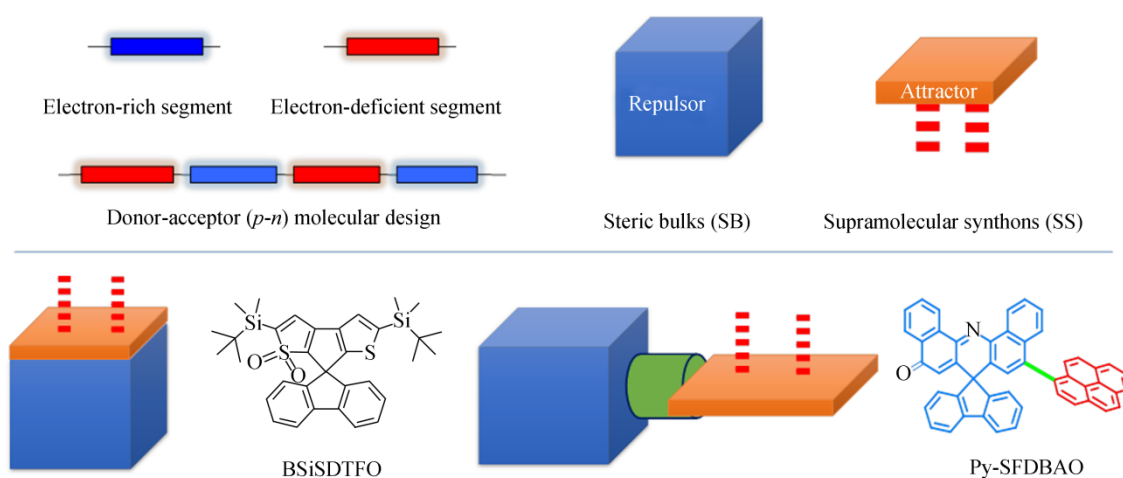


Fig. 2 A complementary molecular design based on attractors/repulsors after donor/acceptor design (Reproduced with permission from Ref. [64]; Copyright (2016) John Wiley & Sons, Inc.)

It is significant for the rational molecular design to explore the cooperative effect between different segments. A pair of intramolecular opposite forces are the impetus of intermolecular aggregates and morphology. Before proof-of-concept design, supramolecular steric hindrance (SSH) effect was defined as the synergetic effects between bulky groups with repulsive force and supramolecular groups with attractive force^[65]. One central mission is to seek the SSH effect with the cooperation between repulsion of bulky groups and attraction of noncovalent groups. Therefore, we designed a series of oligofluorenes with the bulky groups or the repulsors, such as 9,9-diphenylfluorenes, SBF, SFX, SFDBAO and supramolecular moieties (attractors), such as pyrene, —OH, hydrogen bonding scaffold. To this end, the central task is to seek the SSH effects *via* the design

of the state-of-the-art model to strictly identify supramolecular contribution at the bulky moieties to device performance.

Nanocrystals form an unambiguous bridge to link the molecules and microscopic materials. We get insight into the nanocrystal platform to uncover the detailed intermolecular force with diversity. Fortunately, we find the growth of spirofluorenes into polyhedral shape that could be regarded as one kind of SSH effect. Impressively, according to SMART, we designed a series of attractor-repulsor molecules with one bulky group and one supramolecular synthon. Pyrene-functionalized SFDBAO (Py-SFDBAO) as one model molecule could assemble into the two-dimensional nanocrystal that resembles the lipid bilayer-like architectures (Fig. 3). We observed that SFDBAO is regarded as bulky group and Py as a strong π - π stacking synthon in Py-SFDBAO. As a consequence, it became the first proof-of-concept model to unambiguously prove the existence of synergetic SSH effect^[66].

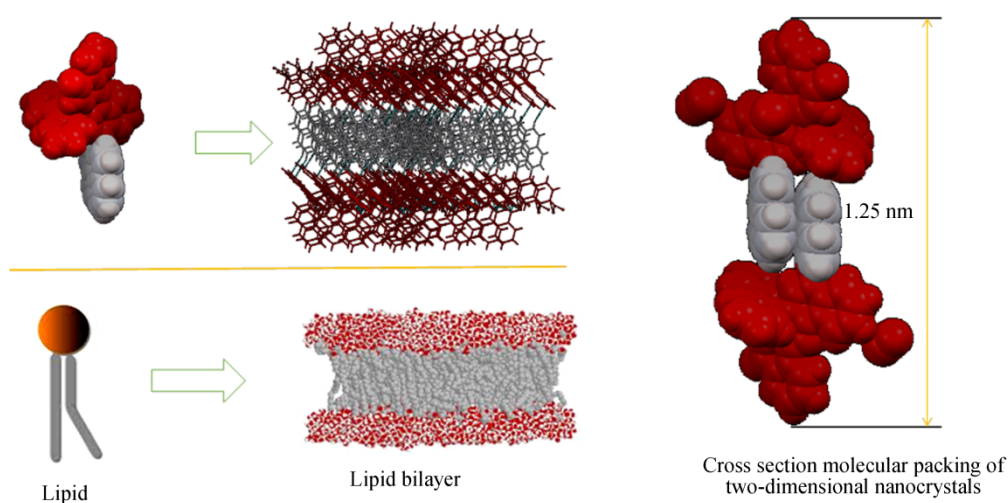


Fig. 3 A universal principle of organic two-dimensional nanosheets or nanomosaics with a lipid bilayer mode (Reproduced with permission from Ref. [64]; Copyright (2016) John Wiley & Sons, Inc.)

SSHs are easily integrated into supramolecular conjugated polymers (SCPs) that are promising for advanced multifunctional materials with the merits of both semiconductors and supramolecules. In this aspect, the second SSH effect can be found in poly{9-[4-(octyloxy)phenyl]fluoren-9-ol-2,7-diyl} (PPFOH) by the comparison of the effect of supramolecular forces on the photophysical behaviors. We found that PPFOH-based PLEDs exhibit the full color emission from blue, green, yellow, and white merely by means of changing the solvent and molecular weight^[67], which demonstrated the existence of SSH effect. In order to afford organic semiconductors both stability and charge delocalization ability, we seek the third SSH effect by attractor-repulsor molecular design to balance between repulsion of bulky groups and attraction of noncovalent groups. Until now, we realized the rational design of β -phase by means of the synergistic and/or cooperative effects of bulky groups with repulsive force and supramolecular groups with attractive force. Bulky polyfluorene with β -phase will be introduced in the last section^[51]. The established SMART becomes an effective chemical strategy to design supramolecular bulk for organic advanced materials and biomedicine. SMART is prerequisite to tune the molecular packing, supramolecular motifs, film phase, aggregates and morphology in the concrete external conditions. SMART is different from the concept of donor-acceptor (D-A) design which directly tunes the electronic structures, charge transport and excited states^[68, 69]. Beyond D-A molecular design strategy, molecular attractor and repulsor are a key pair of opposites (Fig. 2) that exhibits the possibility to guide two-dimensional nanocrystals formation and conformational transition.

Strain Design of G-band Defect in Wide-bandgap Polyfluorenes

After the identification of bulk roles and the exploration of SMART principle, defect analysis and design were conducted in order to fully understand the interplay between bulks and defects. In order to make the right decision, defect analysis requires the advanced characterization techniques such as various spectroscopies, time-resolved techniques, *in situ* characterization tools, synchrotron radiation tools, and various X-ray techniques, such as grazing incidence wide-angle X-ray diffraction (GIXD), small-angle X-ray scattering (SAXS), X-ray photoelectron spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (UPS), nuclear magnetic resonance (NMR) and others. Defect with photo-luminescence would facilitate to observe sensitively with various spectroscopy tools. The g-band emission defect could be easily tracked by photoluminescence spectra. The g-band emission is typical defect in polymer semiconductors that hinders the progress of organic polymer wide-bandgap semiconductors^[21, 70, 71].

Owing to high fluorescence quantum yield, polyfluorenes have emerged as a promising class of light-emitting materials for realizing polymer light-emitting diodes^[72–76]. By now, even all-solution processed polymer light-emitting diodes have been achieved with PFs as the blue light-emitting materials by Zheng *et al.*^[77]. Thereinto, extensive research efforts have been made to improve the efficiency and stability of polyfluorene-based PLEDs during the past decades, such as the optimization of hole transport layer^[78], control of charge recombination^[79], improvement of energy transfer^[80], self-doped by controlling the conformation transition^[81] and utilization of complex/composite materials^[82, 83]. Even after these discoveries, the strict standard of commercialization, which requires high stability, is still unreachable for blue PLEDs. The main restriction comes from the g-band of PFs, which acts as the defect to quench emission, especially for the electroluminescence devices. Early in 1995, Lemmer *et al.* firstly observed the low-energy emission band in the photoluminescence spectrum of solid films of the conjugated polymer ladder-type poly(*para*-phenylene) (LPPP), and they ascribed the low-energy luminescence to aggregates between subunits of the polymer chains^[84]. For polyfluorene, Pei and Yang firstly saw a broad and intense peak in the green region which attributed to interchain excimer emission^[85]. After that, many observations of g-band phenomena were reported in polyfluorene solutions, thin films or devices under the operation voltages. Initially, many findings supported the excimer or aggregate formation as the primary source for the g-band^[86, 87]. Despite intense scientific efforts, the origin of this low-energy emission band was discussed in many literatures and is still controversial. Mainly, aggregates or excimers^[88–91] on the one hand, or direct emission from chemical defects (“keto defects”) on the other hand are thought to be responsible for the observed optical effect^[92–94].

Molecular defect design is another way to examine defect species by transferring defect mechanism into well-defined molecular entities that can be characterized systematically. Dramatically different from inorganic semiconductors, molecular defect design would be effective to identify the defect species of OWBSPs. By this way, aside from aggregates or excimers, the more possible origins of g-bands can be explored by conducting a rational molecular design principle that would be beneficial to answer the question completely. It is a crucial step to design and synthesize the prototype models with the nature of defects. Aiming at solving the g-band defects completely, fluorene-based g-band molecules are highlighted as follows.

The ketone hypothesis was first proposed by List *et al.* indeed, there is g-band occurrence in ketone-containing polyfluorenes and oligofluorenes^[92]. The ketone mechanism is easily proved by ketone-containing oligofluorenes and polyfluorenes. Indeed, g-band at ~550 nm occurs in ketone-containing polymers. We introduced the carbonyl groups (as keto defect sites) into the 9-position of diazafluorene (DAF) directly and synthesized a number of oligofluorenes and polyfluorenes^[95]. The low energy g-band emission at 500 nm to 575 nm appeared as the solvents polarity increased from *n*-hexane to *N,N*-dimethylformamide (DMF). The phenomena supported the hypothesis that the formation of keto defects during polymer synthesis was one reasonable pathway to green emission. However, ketone is only the sufficient condition to g-band. More evidence is required to prove the only reason to cause the spectral instability in electroluminescence devices.

The design of g-band molecules is more difficult according to the aggregate-induced g-bands than ketone

mechanism. We have collected several examples of oligofluorenes that were not deeply investigated from the view of aggregates or excimer^[96–98]. In order to design g-band molecules with aggregates, the central cause-effect relation requires the introduction of chemical force to facilitate interaction among backbones. The rational design guided us to explore one new kind of supramolecular conjugated polymers (SCPs) by introducing the supramolecular synthons into fluorene backbones that would give rise to double optoelectronic and assembling nature by the strong coupling between electronic structure and morphology. Under this idea, various weak noncovalent forces and supramolecular bondings, such as C—H...N^[95], hydrogen bonds^[67], π - π stacking, were introduced into polyfluorenes and oligofluorenes to enforce the interaction among polymer chains. We made an attempt to introduce the hydrogen bonding of hydroxyl to synthesize SCPsPPFOH with the abundant emission colors under the different states, such as solution, nanoparticles, films and devices^[67, 99]. In PPFOH thin film, the cooperation between hydrogen bonding and π - π stacking interactions should be the main reason to result in the shoulder peaks at 550–560 nm that attributed to the emission from excimer or aggregate. Besides, oligofluorenols also acted as alternative models to examine the aggregate mechanism. Terfluorenols with one octyl side chain (TFOH-1) exhibit a g-band at $\sim$ 520 nm^[100], which exhibited the concentration dependent photoluminescence (PL) spectra in toluene solution (0.01–12 mg/mL). We performed titration experiments to examine reversible features of PL spectra of TFOH in toluene solution (8 mg/mL) by adding different amounts of methanol (0%–10%), suggested the aggregate-induced colour change. To clarify structure-property relationships of oligofluorenols, alkyl chain effect was investigated on g-band emission. Alkyl side chain could assist the aggregates to emit green band. Terfluorenol without alkyl side chain could not emit the g-band in solution and the intensity of g-band was weak in films. Oligofluorenols indeed supported the opinion on the aggregate-induced g-band that suggested g-band with special aggregates can be regarded as g-phase. Furthermore, white LEDs have been realized by single component PPFOH with g-phase. However, the unknown packing mode to generate green band is one key wavering issue.

The strain-induced g-band was proposed by us under the inspiration from the changeable colors of cycloparaphenylenes (CPPs). A new entanglement hypothesis was inspired by the observation of polyfluorene chains from high-resolution scanning tunneling microscopy (STM) at molecular scale^[101]. The observation of the poly(9,9-dioctylfluorene) (PFO) bending chains along with out-of-plane and in-plane directions on highly oriented pyrolytic graphite (HOPG) (tunneling condition: -650 mV, 321 pA) indicated that the bending chains could be a reasonable hypothesis in consideration of chain entanglements of conventional polymers. [4]Cyclofluorene ([4]CF) is a fragment from [8,8]CNT which can be acted as a model of chain bending, together with the corresponding chemical structure of linear oligofluorene of [4]LF for comparison^[102]. A schematic route of [4]CF with a yield of 5% and linear quarter fluorenes as a byproduct with a yield of 25% *via* palladium-catalyzed synthesis. [4]CF exhibited obvious green emission in dilute THF solution (10^{-5} mol/L) and kept in 1,2-dichloroethane (DCE) from 10^{-3} mol/L down to 10^{-9} mol/L, suggested the intrinsic low-energy emission nature of single molecules rather than aggregation. G-band also can be observed in spin-coated film in chloroform, drop coated films and crystal under the ultraviolet lamp (365 nm) that offer the indirect evidence on the strain-induced green emission. CFs also became a new kind of strained semiconductors with different electronic structures. Molecular strains will be another way to tune organic semiconductors.

To this end, there are three possible manners to cause g-band that have been supported by corresponding model compounds, including ketone, molecular aggregates and steric strains. In the future, it is emerging to further identify the differences among three kinds of g-bands by comparison. The unique feature of three different defect species would be the key standard or criteria on the *in situ* g-band emission in electroluminescent devices. The unique features can be found by characterizing the energy transfer photophysics behaviors among three species with blue polyfluorenes. It is emergent to answer the precise relation between stabilization strategies and three different types of defects. Chain bending offers a new explanation of various stabilization strategies. For example, crystalline β -phase could avoid chain bending and entanglement that is possible cause of β -phase benefiting for device stability. What is the bulks role on three types of defect design? SSH effect could

explain the aggregates of bulky polymers with g-bands^[58]. A whole chemical picture with three defect species offers a fundamental principle to guide molecular design of stable organic WBG polymers (Fig. 4). Well-defined defect molecules with the g-band will be a component to construct white electroluminescence (EL) devices by blending.

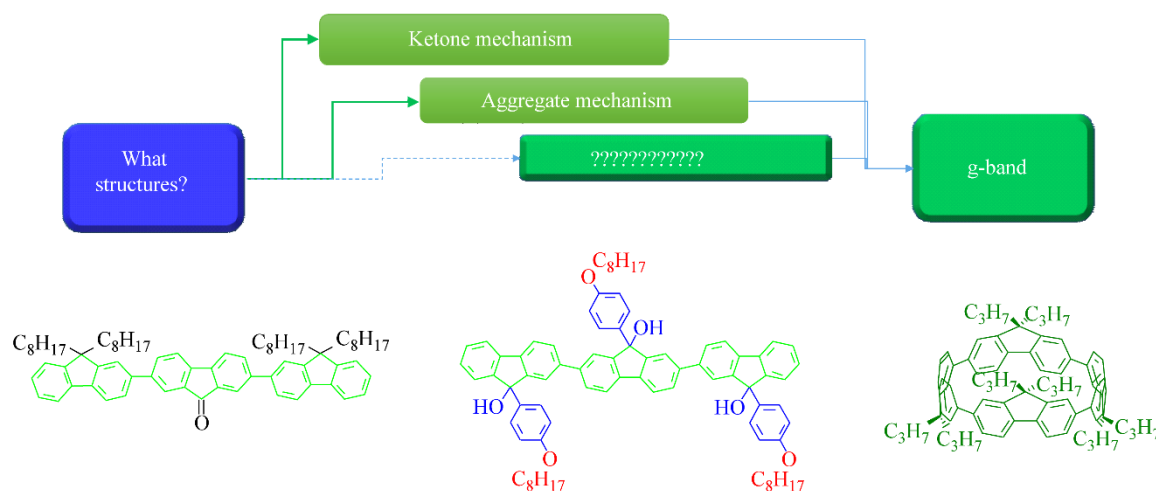


Fig. 4 The pathway analysis of g-band defects in polyfluorenes, together with the modelling oligofluorenes

Bulkys PODPF with Crystalline β -Phase

OWBS polymers lag far behind GaN and diamond in terms of not only luminescence efficiency, but also carrier mobility as well as stability, although they have been extensively investigated in the last two decades. After the molecular platform of bulks, the morphology principle exploration and the defect mechanism analysis, the rational molecular analysis and design of stable and high performance polymers are conducted for the final targets of material chemists. Chain pathway analysis tells us that polyfluorenes suffer from more than seven single state, including oxygenized ketone, g-phase with aggregates, chain bending or entanglements, α -phase that refer to polyfluorene with a dihedral angle of $\sim 135^\circ$, β -phase with a dihedral angle of $\sim 165^\circ$, γ -phase with a dihedral angle of $\sim 150^\circ$, together with gel state. The achievement of stability and high performance strongly depends on the selection of pathway or creation of the effective pathway toward high-performance wide-bandgap semiconductors by molecular design, external condition control, as well as the accurate and precise characterization, together with the theoretical prediction. In fact, to carefully identify the contribution of various molecular segments with the special linkage manners on the various g-bands and phases under the accurate and precise characterization is the prerequisite for rational design. Besides bulky groups, various stabilization strategies were developed, such as copolymer generation, attachment of dendritic substituents, endcapping, spiro-linking, crosslinking, incorporation of linked structures or oxygen scavengers as promising alternatives for realizing stable blue emitting materials^[62, 103–107]. Until now, three pathways suffer from chemical or physical defect species that lead to g-band that should be avoided by combining molecular design and external condition control. There are three other pathways, that is, the amorphous state, β -phase, and gemma phase, together with the liquid crystal phase. In all the pathways, β -phase is another effective stabilization strategy to suppress the g-bands. Stability and high performance are two interplay barriers for the commercialization of wide-bandgap polymers. This strategy improves not only the spectral stability, but also the luminescent efficiency owing to effective charge injection. One effective way to endorse stable polyfluorenes with the improvement of charge transporting is to lead bulky polyfluorene against the 9-position oxygenation of fluorenes by β -phase, which is typical of multi-target-directed rational design.

We explored the bulky OWBSPs with the β -phase behaviours by controlling external condition and

molecular design. Initially, in order to obtain β -phase bulky polyarylfuorenes, we first examined the external condition. In fact, PFO could generate high content of β -phase in the suitable external conditions, especially in gelation state. Under the clue, we recognized that β -phase conformation chain could survive in the networks of gel. A series of bulky copolyfluorenes were synthesized by introducing different steric hindrance groups into the molecular backbones^[108]. The uncomplete suppression of g-band was confirmed by those bulky polyfluorenes. Among them, SFX-functionalized PFX showed better thermal, morphology, and EL spectral stability. In order to obtain β -phase of bulky conjugated polymers, we test the gelation in various solvents of bulky polyfluorene. 1,2-Dichloroethane (DCE) solvent indeed enabled to induce gelation network of poly(diarylfuorene) with β -phase that has a unique feature peak at ~ 436 nm in UV absorption spectra^[101]. However, β -phase can only survive in gel, rather than solution and film. Furthermore, β -phase disappeared when the temperature was increased in bulky PFX, resulting in transition from gel to solution, which was different from the typical PFO^[108]. Nevertheless, this observation encouraged us to explore β -phase of bulky polyfluorenes.

β -Phase is metastable compared to amorphous states. Energy harvest process is required to overcome the steric strains between fluorenyl repeat units by suffering from the transformation from intermolecular force into intramolecular forces. Up to date, many efforts have been made to investigate the formation of β -phase in polyfluorene^[109–114]. There exists a competition between g-phase aggregate morphology pathway and β -conformation. In this design, the key challenge is how to avoid the pathway of g-band and reach the β -phase for polyfluorene chains. SSH effect will offer a possible tool to balance the chain conformation to choose the pathway of β -phase rather than g-phase. SMART tells us that balance between steric bulks and VDW noncovalent force could result in a phase change. In order to adopt bulky β -phase rather than g-phase, the attractor could not be too strong, otherwise it would lead to the g-phase. Finally, a tadpole-shaped monomer as an attractor-repulsor was designed with the unique feature of the two sides where bulky diaryl groups at one side of backbone and alkyl side chains at the other side of backbone (Fig. 5)^[51]. Moreover, we successfully synthesized a model polyfluorene, poly[4-(octyloxy)-9,9-diphenylfluorene-2,7-diyl]-co-[5-(octyloxy)-9,9-diphenylfluorene-2,7-diyl] (PODPF). As a result, although PODPF was a random polymer without region-regularity that was demonstrated by NMR data, it still exhibited the β -phase according to the characterization of UV and PL spectra in dilute solution and film of toluene, rather than chloroform (amorphous state). Besides, we constructed a stable β -phase with highly crystalline structure from PODPF films by simple thermal treatment. Crystallization and abundant aggregation domains after annealing treatment suggested that the occurrence of regular chain arrangement of the polymer chains and the compact packing mode afforded a driving force to overcome the steric repulsion and planarized the polymer backbone. GIXD characterization of PODPF suggested highly crystalline morphology with a film texture of edge-on orientation. Aggregation and crystallization offer energy and force to trigger conformational change into β -phase that can be regarded as a result of SSH effect. We also investigated alkyl chain length effect on β -phase formation of PODPF. An optimal chain length for the formation of β -phase is revealed as octyl and heptyl side chains, which are easier to form the interdigitation packing than any other lengths. Thermal-induced β -phase in polydiarylfuorene facilitated the introduction of β -phase into films and devices towards efficient and stable blue electroluminescence^[115]. β -Phase of PODPF existed in not only gel states, but also solutions and films as well as devices. PODPF thin film exhibited excellent spectral stability without green band emission under thermal annealing in air at 200 °C for 3 h (Fig. 5)^[51]. We also compared device performance of PODPF with and without β -phase. β -Phase PLED exhibits the stable electroluminescence with highest current efficiency (CE) of 1.8 cd/A (6.0 V) higher than α -phase ones with CE of 1.1 cd/A (5.6 V). PODPF with different contents of β -phase can serve as the lasing gain media with amplified spontaneous emission (ASE) with 0-1 transition of α -phase (461 nm) in low content of β -phase, and ASE with 0-1 transition of β -phase (483 nm) at high content, and dual-wavelength ASE (463 and 483 nm) at medium content owing to limited energy transfer.

PODPF with octyl side chain exhibited crystalline β -phase which can become a beginning for the

improvement of overall performance. The disadvantage of bulky groups is the small transfer integral that leads to low chance to hopping electrons, resulting in the low charge mobility that is unfavourable for the design of high mobility design. However, under the SMART, one perspective is to design both high mobility and wide-bandgap polymer by balancing the steric effect and supramolecular attraction. Another perspective is to explore OWBSP with both high-efficiency thermally activated delayed fluorescence (TADF) and high mobility.

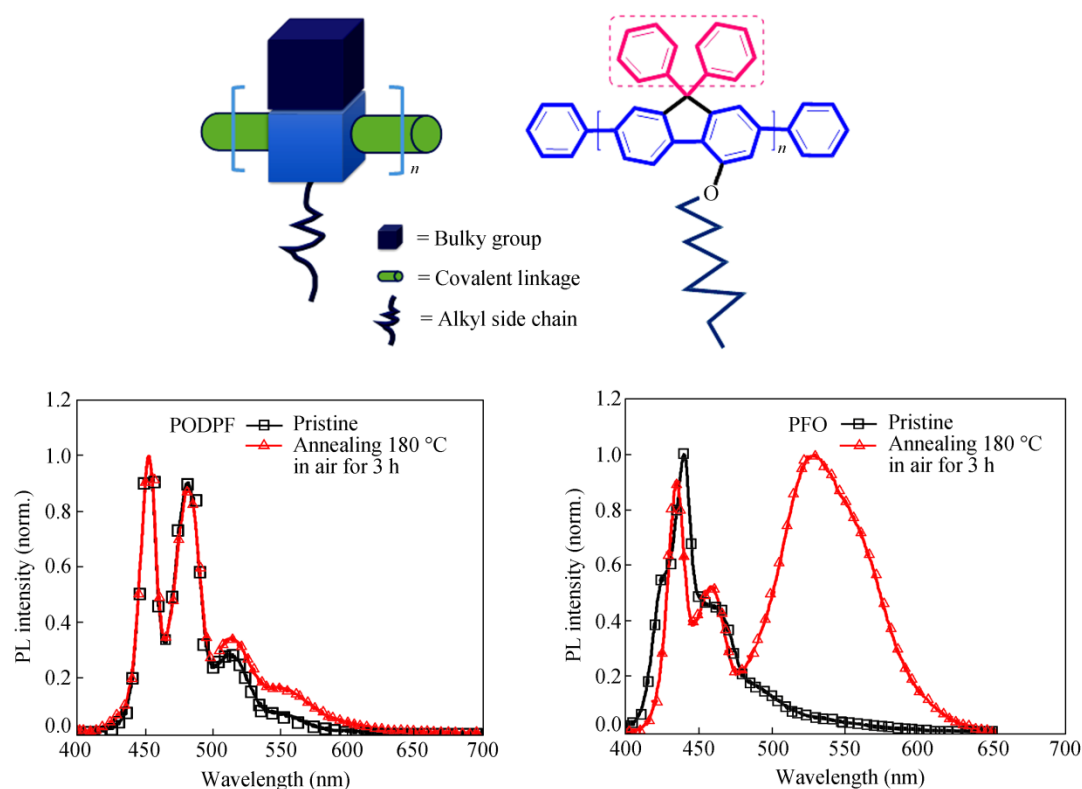


Fig. 5 A model of tadpole monomer with SSH effect and the chemical structure of PODPF, the photoluminescence spectra of PFO and PODPF at the pristine and annealing films (Reprinted with permission from Ref. [115]; Copyright (2016) American Chemical Society.)

CONCLUSIONS AND OUTLOOK

A four-element uninstalling paradigm has been demonstrated in order to challenge one of the basic issues of stability in bulky OWBSP. We start from a diverse molecular platform of bulky building blocks based on SFX and CDAFs *via* green and eco-friendly PASE routes. One-pot protocols (Xie-Huang's method) to spirofluorenes were established. The roles of bulky groups were recognized with supramolecular weak noncovalent force that resulting in the discovery of synergetic molecular attractor-repulsor theory (SMART). This observation inspired us to explore the cooperative effect between bulky groups with repulsion and supramolecular groups with attraction by molecular design. We found a series of supramolecular steric hindrance (SSH) effects on OLEDs, two-dimensional nanocrystals, and β -phase transition in polyfluorenes. SMART becomes an effective tool to tune the molecular aggregates from solution to films and SSH effect helps to explain the complex of OWBSP. Oligofluoreneol supported aggregate-induced g-band that can be called as g-phase in terms of morphology. After ketone and aggregates, cyclofluorenes offer the evidence of the third kind of defects with strain-induced g-band that suggests the existence of bending chain or entanglement in polyfluorenes or conjugated polymers. Bulky PODPFs show the highly crystalline feature of β -phase that become the robust next-generation organic wide-

bandgap polymers after PFO.

After the conclusion of bulky OWBSP, we expand the paradigm from OWBSP to the whole organic conjugated polymer or polymer semiconductors for the summarization of the chemical principles, besides the physical work principle. A schematic diagram of the conjugated polymers with the π -backbones, and functional alkyl side chain, bulky groups and supramolecular synthon was described to really make rational design of organic polymer semiconductors under the basic frameworks of donor-acceptor theory and SMART (Fig. 6).

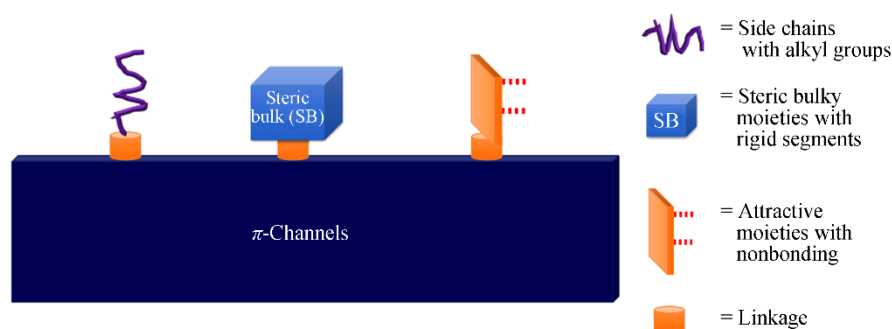


Fig. 6 A cartoon model of the attractor-repulsor conjugated polymer semiconductors

The chemical diagram described the key factors of organic/polymer semiconductors beyond the control of electronic structures. SMART will unravel the SSH effect which is cooperative effect of bulky groups and supramolecular synthons on assembly, phase change and luminescence switch. The four-element diagram, including electronic structures, steric effects, conformational topology, and supramolecular attraction, which becomes the basis to clarify the roles of segments, multirole, synergetic roles, as well as hierarchical roles. The adoption of real roles and functional zones would facilitate the exploration of the complex organic polymer semiconductors for the exploration of structure diversity, polymorphism, and electronic state change. The coarse diagram will bridge the robust relation between organic semiconductors and devices that were decoded at least into three levels, including devices with the electrode, thin films and molecular scale. Under this objective, a chemically hierarchical architecture diagram of organic devices also described the multiscale uninstalling paradigm from the devices, to films, mesoscale, nanoscale, supramolecular level and molecular level to atom in the periodic table of elements to guide organic semiconductors for chemists. To this end, chemical principle of organic semiconductors was established with two key diagrams in the last few decades. After this, the cycle of molecular systems and organic devices (CMSOD) offers a hierarchically chemical platform to explore the philosophy of systems chemistry and organic polymer systematic semiconductors. Organics would become a versatile platform for artificial intelligence technology with a label of robot toward an era of consciousness (EOC) that is the future in the 21 century.

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