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Fluorene-Based Conjugated Oligomers for Organic Photonics and Electronics

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Abstract Recent advances in fluorene-based conjugated oligomers are surveyed, including molecular design, material synthesis and characterization, and potential application to organic photonics and electronics, such as light-emitting diodes, solid-state lasers, field effect transistors, and solar cells.

Keywords Fluorene-based conjugated oligomers · Material synthesis and characterization · Molecular design · Organic photonics and electronics

Abbreviations

AcOH	Acetic acid
ASE	Amplified spontaneous emission
cd	Candela
CIE	Commission Internationale de l'Eclairage
CuI	Copper Iodide
CV	Cyclic voltammetry
DMSO	Dimethylsulfoxide
E_a	Electron affinity
EL	Electroluminescence
Et_2O	Diethylether
EQE	External quantum efficiency
ϕ	Photoluminescent quantum efficiency
G	Glassy state
g_e	Dissymmetry factor
H_2SO_4	Sulfuric acid
HCl	Hydrochloric acid
HOMO	Highest occupied molecular orbital
HWE	Horner–Wadsworth–Emmons reaction
ICl	Iodine monochloride
ITO	Indium tin oxide
I	Isotropic state
I_p	Ionization potential
IR	Infrared
KOH	Potassium hydroxide
KO-*t*-Bu	Potassium *tert*-butoxide
LCD	Liquid crystal display
LiF	Lithium fluoride
LUMO	Lowest unoccupied molecular orbital
MALDI-TOF	Matrix-assisted laser desorption/ionization time of flight
Mg:Ag	Magnesium:silver alloy (20 : 1)
n-BuLi	*n*-Butyllithium
Nem	Nematic state
NaOH	Sodium hydroxide
Ni(COD)	Bis(1,5-cyclooctadiene)nickel(0)
NMR	Nuclear magnetic resonance
NTSC	National Television System Committee
OFET	Organic field effect transistor
OLED	Organic light emitting diode
$PdCl_2(dppf)$	[1,1′-Bis(diphenylphospino)ferrocene] dichloropalladium(II)
$PdCl_2(PPh_3)_2$	Bis(triphenylphosphino) dichloropalladium(II)
$Pd(OAc)_2$	Palladium(II) acetate
$Pd(PPh_3)_4$	Tetrakis(triphenylphosphino)palladium(0)
PEDOT/PSS	Poly(3,4-ethylenedioxythiophene)/poly(styrenesulfonate)
S	Orientational order parameter

$SiMe_3$	Trimethylsilyl
T_c	Clearing (or isotropization) temperature
T_g	Glass transition temperature
TGA	Thermal gravimetric analysis
THF	Tetrahydrofuran
TPBI	1,3,5-Tri(phenyl-2-benzimidazole)-benzene
UPS	Ultraviolet photoemission spectroscopy
UV	Ultraviolet
UV-Vis	Ultraviolet-Visible
wt. %	Weight percent

1
Introduction

Fluorene is a common polycyclic aromatic hydrocarbon found even in engine exhaust (see Fig. 1 for its structure). Fluorene has long been known for the intense violet fluorescence, after which it was named [1]. Fluorene-based conjugated oligomers can emit deep blue light at an efficiency of up to 99% in solution and 90% in neat solid films [2], which is rare in this spectral region.

The decoupling provided by bonding groups to fluorene's 9-position is also noteworthy, as these groups are placed at 90° angles to the π-conjugated system comprising fluorene molecules (also see Fig. 1). This allows a fluorene compound's solubility and aggregation behavior to be modulated independently of its electronic properties [3].

These properties have been exploited extensively in polyfluorenes that have grown to be a major player in organic electronics and photonics [4–8], exhibiting efficient polarized light emission [9–13], long-lasting blue electroluminescence [14], impressive lasing gain [15–18], and promising performance in organic solar cells [19, 20].

The field of organic electronics has also seen a growing focus on oligomeric materials, with sizes and properties intermediate between small

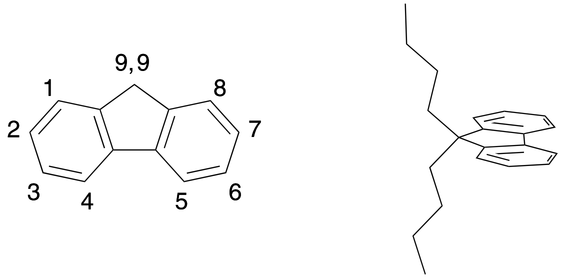


Fig. 1 Fluorene structure showing numbering of sites available for substitution, as well as an illustration of the decoupling provided by bonding groups to its 9-position

molecules and polymers [21]. Using correlations from oligomers to gain insight into their analogous polymers has been a long tradition in polymer chemistry, as numerous properties, such as glass transition and electronic band gap, vary monotonically with molecular weight before reaching their asymptotic values [22–29]. Such correlations, however, are known to be imperfect [30–33]. In addition to offering structure–property relationships, monodisperse oligomers are attractive as active materials in their own right, with properties such as higher field-effect mobilities [34], stronger chiroptical activities [35], greater optical amplification of quenching [36], and better lasing efficiency [37] than their polymeric analogues.

These unique properties of oligomers make them an ideal complement to conjugated polymers in organic electronics and photonics. While the synthesis of long oligomers becomes rather laborious in comparison to that of polymers, the more rigorous purification techniques available to oligomers are advantageous for practical applications [38]. Oligomers are generally devoid of chain folds and kinks [39] and chain defects [37] that tend to compromise polymers' performance. Moreover, polydispersity can render polymer properties difficult to reproduce [40, 41]. Because of their lower melt viscosities, oligomers are easier to process than polymer analogues, and many oligomers can also be readily vacuum-deposited.

This review focuses on the synthesis, characterization, and performance of monodisperse fluorene-based conjugated oligomers with potential applications to organic electronics and photonics. Included herein are oligomers and co-oligomers that contain at least two fluorene units in their backbone structures, while excluding those with a lone spirofluorene unit without other fluorene units in the backbone, as these have been covered elsewhere [42, 43].

2
Material Synthesis

2.1
Synthetic Approaches to Oligofluorenes

The synthesis of fluorene oligomers is intensive in terms of number of steps, but the unique properties and the new insight into structure–property relationships are well worth the effort. A number of approaches have been developed from the initial brute force fractionation of polydisperse systems to the more elegant deterministic synthesis of monodisperse systems.

Synthesis obviously begins with the monomers themselves. Figure 2 shows four of the most common types of substituents on fluorene, illustrated with typical pendants, accompanied by synthetic pathways. Alkyl pendants are readily attached with sodium hydroxide in DMSO [44], e.g., converting compound **1** into **2**, while the aryl pendants, such as in compound **5**, require

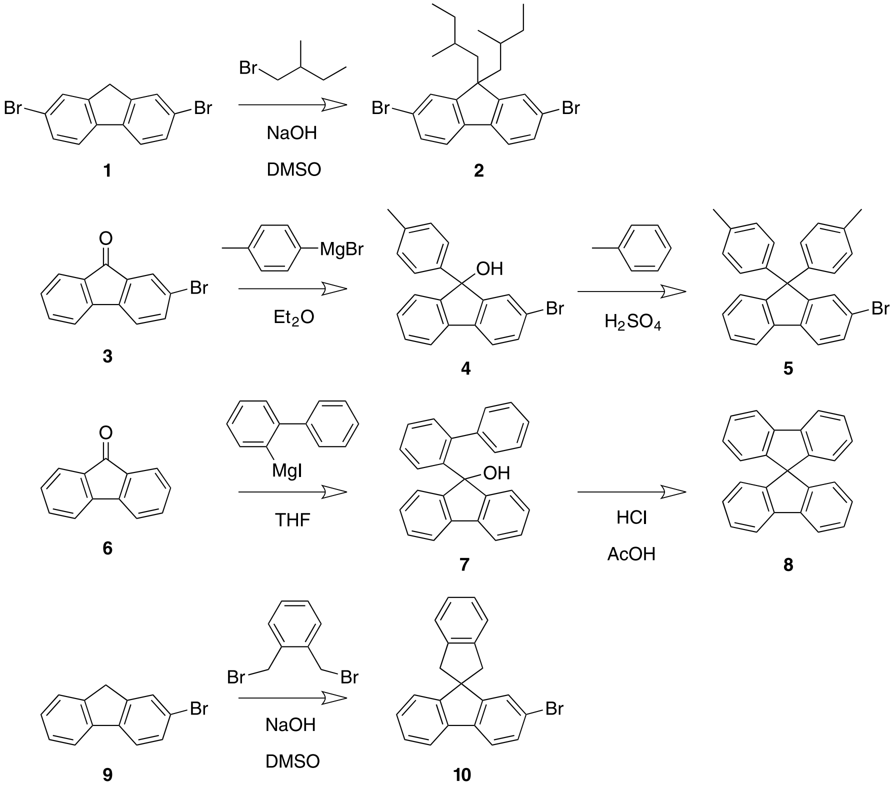
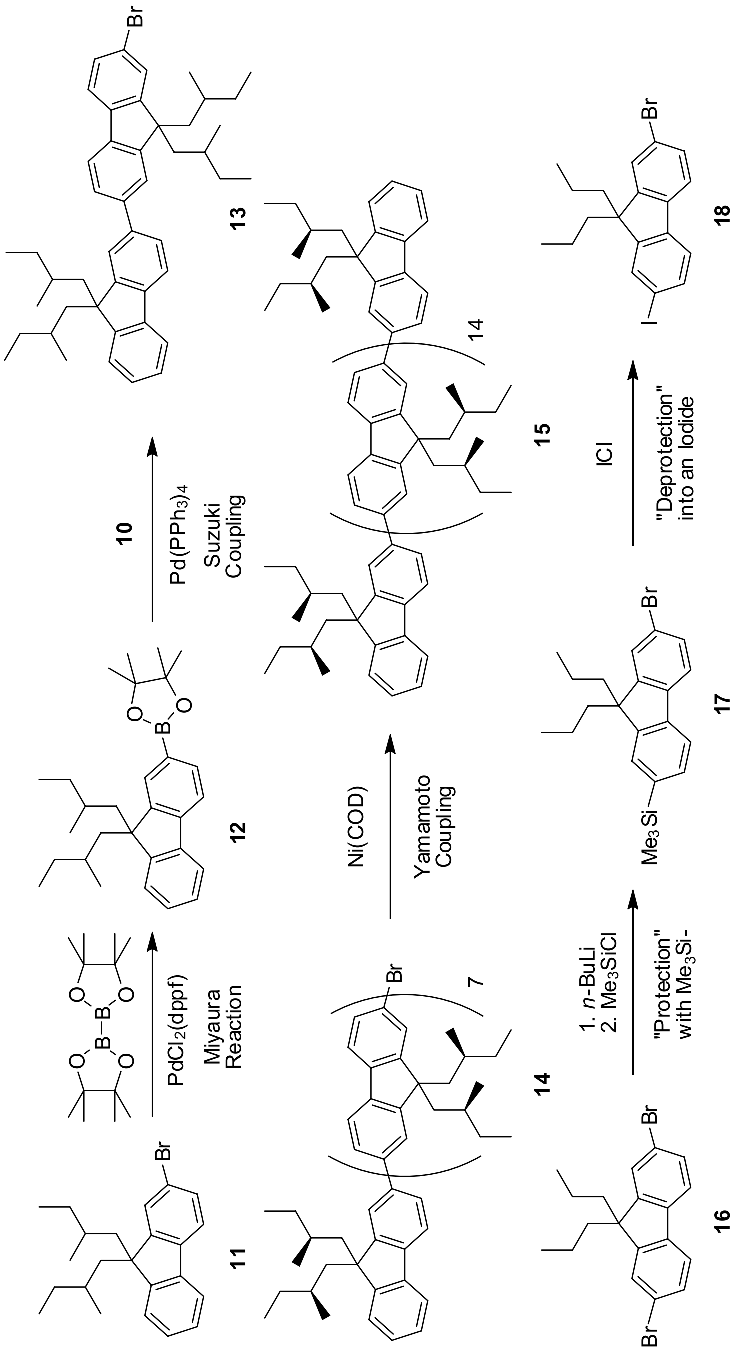


Fig. 2 Various substitution schemes of fluorene monomers shown for representative structures

two steps, a Grignard reaction to form compound **4** and an acid-catalyzed condensation reaction [2]. Spiro-linked fluorene derivatives (compound **8**) have been known for some time [45] and are readily synthesized starting with a fluorenone, such as compound **6** [46]. Other types of spiro-configured fluorene monomers have also been synthesized, as illustrated with compound **10** [47]. Starting with bromine-substituted fluorene or bromination that results in mono- or di-functionalized fluorene (e.g., compounds **9** and **1**, respectively), oligofluorenes are constructed in subsequent reactions. A wide variety of functionalizations of spirofluorene have been summarized in a recent review article [42].

Various carbon–carbon cross-coupling reactions are employed to arrive at oligomers from fluorene monomers, including nickel-cataylzed Yamamoto coupling between aryl halides [48], palladium(0)-catalyzed Suzuki coupling between boronic acids/esters and halides [49], and ferric-chloride-catalyzed Scholl reaction, also called Friedel–Crafts arylation, of bare fluorenes [50, 51].


Br
11
O
B
B
O
PdCl2(dppf)
Miyaura
Reaction
12
10
Pd(PPh3)4
Suzuki
Coupling
Br
13
14
7
Ni(COD)
Yamamoto
Coupling
15
14
Br
16
1. n-BuLi
2. Me3SiCl
"Protection"
with Me3Si-
Me3Si
17
ICl
"Deprotection"
into an Iodide
I
18

◀ **Fig. 3** Common reactions and cross-couplings in oligofluorene synthesis shown for example structures, where $PdCl_2$(dppf) is [1,1′-bis(diphenylphospino)ferrocene] dichloropalladium(II), $Pd(PPh_3)_4$ is tetrakis(triphenylphosphino)palladium(0), and Ni(COD) is bis(1,5-cyclooctadiene)nickel(0)

Yamamoto and Suzuki coupling, and other common reactions in fluorene oligomer synthesis are illustrated in Fig. 3.

Yamamoto coupling was used for one of the first isolations of a series of oligofluorenes, but even with end-capping it required extensive and time-consuming fractionation [52]. This approach has been recently used to synthesize polydisperse oligofluorenes for ease of synthesis [53] to demonstrate interesting properties. More relevant to deterministic synthesis, Yamamoto coupling has been used for symmetric coupling of monofunctional oligomeric intermediates. For example, Yamamoto coupling was used to join two monobromo-octafluorene units (compound **14**) into a symmetric hexadecamer (compound **15**) [35].

However, the most prominent reaction used to synthesize fluorene oligomers is Suzuki, or more fully Suzuki–Miyaura, coupling. This high-yield reaction between two different functionalities, one a boronic acid or ester (such as compound **12**) and the other a halide or similar leaving group (such as compound **2**), has allowed considerable control in building up oligomers in a stepwise manner. An obvious method is simply to use a monomer with a single boronic acid group for reaction with an excess of a dibromofluorene monomer, as illustrated in the synthesis of compound **13** [54]. This product can then be converted into a boronic acid for subsequent coupling and lengthening of the oligomer. Excess boronic acid or ester can also be used, but often leads to a side reaction where the desired remaining boronic acid/ester group is converted to a hydrogen atom [55], resulting in a low yield.

More advanced approaches utilize either a difference in reactivity in Suzuki coupling or a protecting group during the Suzuki coupling steps. The high selectivity of Suzuki coupling for aryl iodides [56] or aryl diazonium salts [57] over aryl bromides has been effectively used in oligofluorene synthesis, with difunctional intermediates. In addition, nitro groups are excellent masking groups for amino groups during Suzuki couplings [58], which can be converted into diazonium salts or used for other chemistry. A more generic protecting group is the trimethylsilyl moiety, which acts as a dormant iodide or bromide [35]. It can be introduced selectively to one side of a dibromofluorene unit (as with **16** into **17**), remains intact under Suzuki conditions, and can be easily converted to an iodide by iododesilylation using iodine monochloride (of **17** into **18**), or to a bromide by similar reaction with molecular bromine.

While adding one unit at a time to reach the final products results in a repetitive divergent approach [59], purification can become an issue as the separation between longer oligomers becomes increasingly challenging.

Thus, the iterative divergent–convergent strategy has been applied to the synthesis of oligofluorenes for ease of purification, by adding larger pieces at a time, at the cost of a greater number of intermediates. This approach has allowed access to oligomers of all lengths from dimer to dodecamer, with hexadecamer also synthesized in concert [35]. This can even be accomplished with mixed, or nonuniform, pendants placed in a controlled manner to realize other desirable properties [60]. The versatility of this approach to test a wide variety of structures relatively rapidly is of great advantage in establishing structure–property relationships, but is not the most efficient way to reach a single large target or simply to synthesize a series of uniform oligomers.

2.2
Synthetic Incorporation of Comonomer Units

The incorporation of other co-monomers into fluorene backbones can require a number of additional chemical reactions. Suzuki coupling is still immensely useful in this regard, but is not always easy or possible to use with various sensitive groups. The Miyaura [61] reaction (see reaction of **11** into **12**) to introduce boronic esters via palladium catalysis instead of harsh butyl lithium treatment is quite useful to access an array of co-monomers for Suzuki coupling [57], but still does not encompass many desirable targets. Palladium(II)-catalyzed Kumada coupling between aryl Grignard reagents and halides provides another option [62], as illustrated for the synthesis of **20** from **19**. Relatively early work to incorporate ethynylene groups utilized the Pd/Cu-catalyzed Sonogashira reaction and 3-methyl-1-butyn-3-ol masked reagents [63]. Shortly after that, vinylene and various phenylene vinylene groups were incorporated [64] with one of two prominent reactions: Heck coupling (to synthesize **22**) of vinyl groups to aryl halides, or Horner–Wadsworth–Emmons reaction (shown in making **23**) of aldehydes with phosphonic acid esters. Stille coupling [65] is valuable with thiophene units due to the ease of introducing the requisite trialkyltin groups to couple with halofluorenes [64]. These coupling reactions are illustrated in Fig. 4.

Two approaches using co-monomers have allowed for additional flexibility in synthesis of fluorene oligomers. The first takes advantage of the fact that Kumada, Heck, and Stille couplings are done under anhydrous conditions to allow coupling reactions to proceed while leaving boronic esters intact for subsequent steps [66]. In the second, an alternating series of reactions, drastically changing the polarity of the intermediates back and forth, substantially facilitates the purification, opening the door to a direct divergent method which is

Fig. 4 Additional reactions and cross-couplings that are commonly used to synthesize fluorene co-oligomers, where $Pd(OAc)_2$ is palladium(II) acetate and $PdCl_2(PPh_3)$ is bis(triphenylphosphino) dichloropalladium(II) ▶

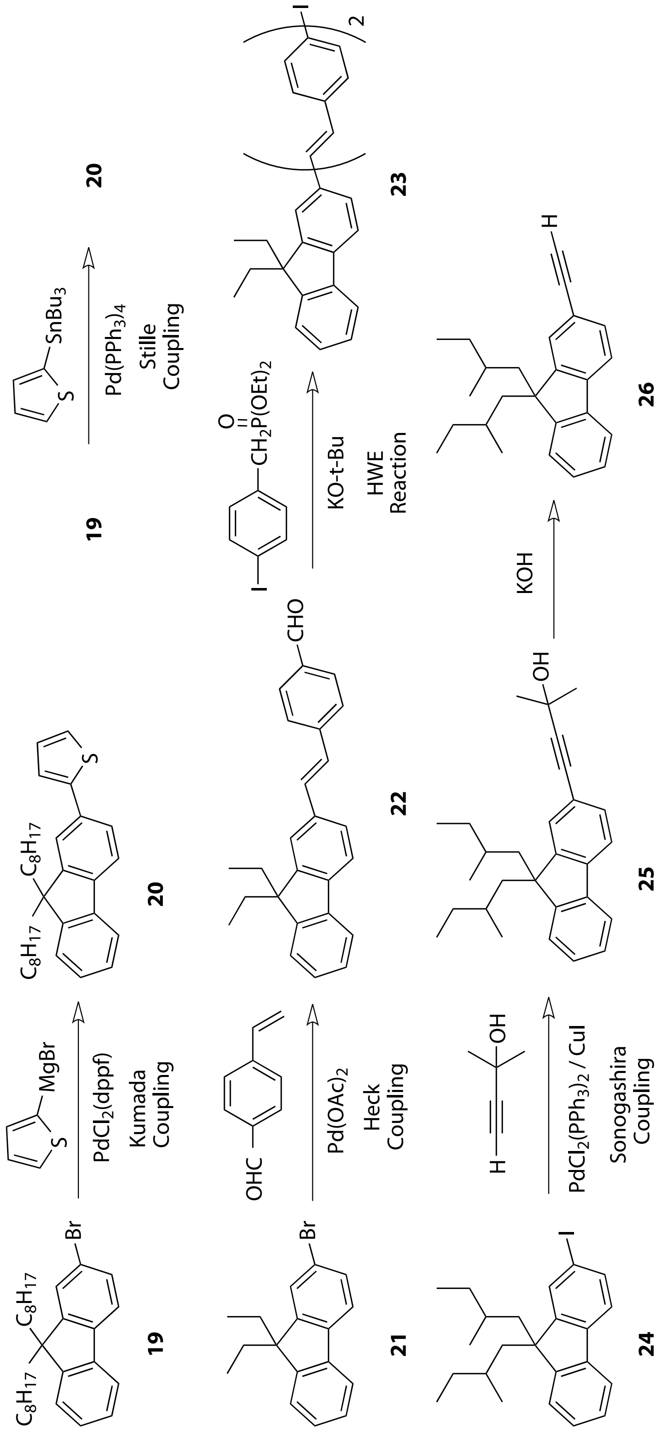

C_8H_{17}
C_8H_{17}
Br
19
MgBr
S
$PdCl_2(dppf)$
Kumada
Coupling
C_8H_{17}
C_8H_{17}
S
20
19
S
$SnBu_3$
$Pd(PPh_3)_4$
Stille
Coupling
20
Br
21
OHC
$Pd(OAc)_2$
Heck
Coupling
CHO
22
I
O
$CH_2P(OEt)_2$
KO-t-Bu
HWE
Reaction
I
2
23
I
24
H
OH
$PdCl_2(PPh_3)_2$ / CuI
Sonogashira
Coupling
OH
25
KOH
H
26

Fig. 5 Example structures of fluorene co-oligomers and functionalized oligofluorenes ▶

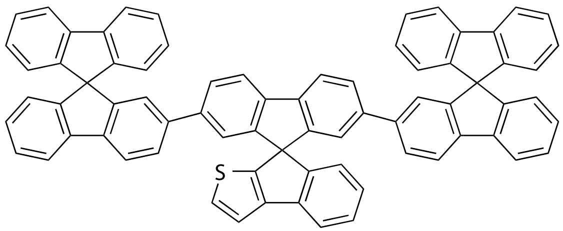
much more efficient, and requires fewer extraneous intermediates [67]. This method is used to synthesize oligomers up to undecafluorene.

In addition to the aforementioned ethynylene, vinylene, and phenylene vinylene groups, a wide variety of groups have been introduced as co-monomer units. Thiophenes, bithiophenes [68], dibenzothiophene [69], and longer oligothiophene segments have all been incorporated [70]. Some additional examples are shown in Fig. 5. An exotic unit incorporating a thiophene as part of a spirofluorene has been synthesized (compound **27**) [71]. Anthracene (e.g., compound **28**) [72, 73] and perylene [74] are useful for sky-blue emission from fluorene oligomers. Fluorenone has been incorporated with fluorene units to study the resultant co-oligomers as possible defect sites in polyfluorenes [75–79]. Benzothiadiazole is a useful green emitter and electron-deficient moiety [64], and can also give rise to red emission when connected to fluorene via phenylene-vinylene segments, as in compound **29**. Thiophene-*S*,*S*-dioxide and dibenzothiophene-*S*,*S*-dioxide are other electron-deficient co-monomers [69, 80, 81] used with fluorene.

2.3
Synthesis of Fluorene-Based Oligomers with Other Functionalities

A number of functionalities have been included with oligofluorenes that are not strictly co-monomers. One creative approach uses boronic acid end groups to form immobilized networks of oligofluorenes [82], in contrast to the conventional functionalizations of oligofluorenes with convenient polymerizable groups to form insoluble networks [55]. Hydrophilic, or even ionic, side chains to the 9-position of fluorene have been used to realize self-condensed nanoparticles of fluorene (with compound **30**) [83] and to realize sensing of oligonucleotides [84]. Hydrogen-bonding oligofluorenes have also been synthesized through the attachment of ureidopyrimidinone end groups (compounds **31**–**33** in Fig. 5) [58].

There are also a number of compounds with central cores to which oligofluorene arms are directly attached. These have shown differences in thermal [85] and optical [86] properties compared to linear oligomers, including much stronger nonlinear absorption [87] when put on a single benzene core or into a dendritic structure. On a truxene core, electrochromism and improved fluorescence have also been observed [88]. Compounds with oligofluorene pendants to functional cores have also been synthesized. With oligofluorenes bonded to an emissive core, energy transfer from the pendants to the core is permitted while preventing molecular aggregation [89, 90]. Attachment of oligofluorenes to a charge-transporting core enables the energy levels of the hybrid molecule to be modulated [91].



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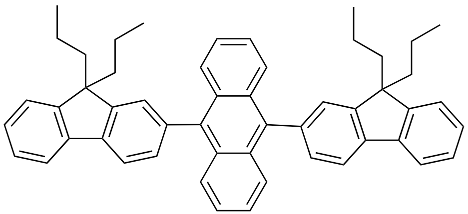

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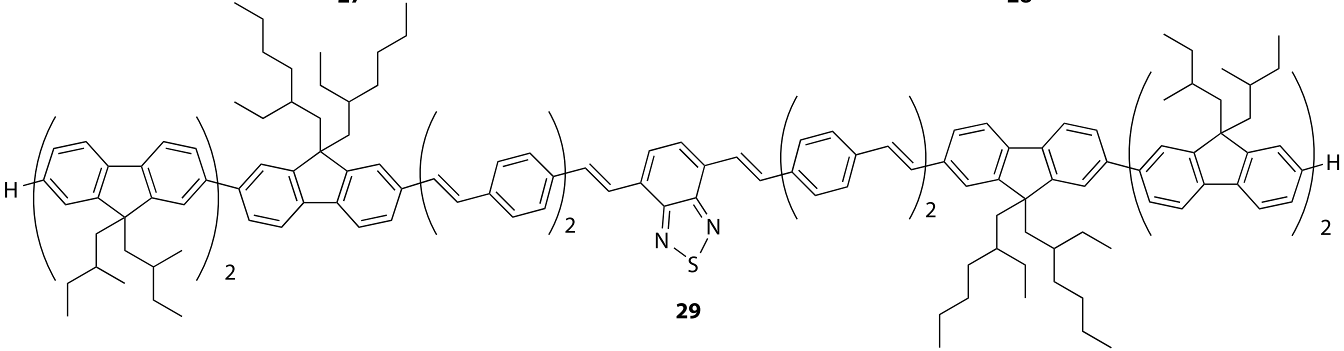

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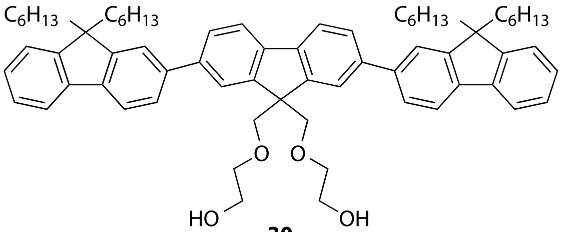

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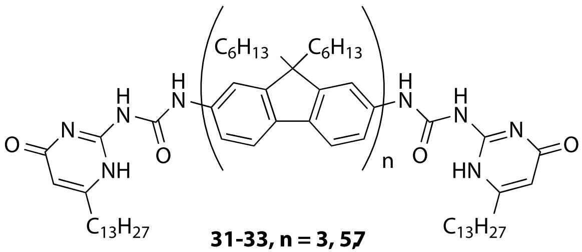


31-33, n = 3, 5, 7

The most prevalent trend in modifying fluorene oligomers is to introduce hole and sometimes electron-transporting moieties to enhance their performance in organic light-emitting diodes. The most common method is end-capping with triarylamine groups through either Suzuki coupling or palladium-catalyzed amination [92] of halogen-decorated oligomers, as seen in a number of papers [93–100]. One paper puts one of each type of charge transport moiety on the oligofluorene [101]. Some also introduce these charge-transporting moieties as a central core with arms attached in direct conjugation [91, 102] or as a central unit in the oligomer [103]. Direct conjugation with these moieties does influence their electronic and optical properties, which can be avoided by employing spiro-linked transport moieties [104], 9-position attachment of these arylamines [105], or alkyl spacers between the moieties [106, 107].

For oligomers, as opposed to polymers [9], the inclusion of functional moieties tends to disrupt the mesomorphic and self-organizing properties of the resulting multifunctional materials with one notable exception. Attachment of oligofluorenes through a flexible alkyl spacer on the 2 -position of the oligomer to a charge transport core allows the pendant oligomers to align into nematic films through deformation of the spacer [106]. Synthetically, this is accomplished by Suzuki coupling of the boronic acid of the oligofluorene to allyl bromide, followed by activation of the allyl group with hydroboration for Suzuki coupling to a halogen-bearing functional core. The advantages of this approach will be discussed more fully in the appropriate sections below.

2.4
Polymers Containing Flourene Oligomers in Repeat Units

While polyfluorenes and their copolymers are usually easier to synthesize than oligomers, a number of papers have focused on incorporating oligofluorenes as structural units in polymers and copolymers. Such systems take advantage of the desirable properties of these oligomers while retaining the advantages of full-fledged polymers. Most of these studies target terfluorene [108–115] as an optimum element in terms of the ease of synthesis and excellent blue light emission characteristics. Two of these reports also discuss testing the performance of a pentafluorene [114, 115], and one paper looks at a series of oligomeric segments containing two to seven fluorene units in the polymer backbone [113]. Two groups use fluorene co-oligomers [116, 117], while yet another uses only a hexafluorene [118]. Most studies utilize oligofluorene as a unit in the main chain [110–114] or in the side chain [115–117], and also as a macroinitiator for atom transfer radical polymerization to form rod-coil block copolymers [108, 109, 118]. In addition, the variety of polymer types is impressive: polyesters [110, 111], polyether [112], polycarbonate [113], poly(aryl ether)s [114, 115], polynorbornene [116], and polystyrene (as the backbone [117] or the other block [108, 109, 118]).

3

Morphological Properties

With the ease and variety of substitutions at their C-9 positions, fluorene units offer considerable control over a conjugated oligomer's solubility and molecular packing behavior. As a result, a wide range of morphological properties can be realized through molecular design.

3.1

Thermal Stability and Solubility

Fluorene-based conjugated oligomers are capable of a high degree of thermal stability. Thermal gravimetric analysis (TGA) has shown that fluorene oligomers decompose at temperatures higher than 400 °C, specifically reaching 5% mass loss in the range of 400–450 °C at a heating rate of 20 °C min^{-1} under nitrogen [2]. Another group of researchers measured decomposition temperatures of end-dendronized oligofluorenes within a few degrees of 600 °C, without specifying the mass loss in their TGA experiments [97]. In addition, many fluorene oligomers can be purified by sublimation and can be vacuum deposited as thin films. In fact, a tetrafluorene derivative can be vacuum deposited without experiencing decomposition [119]. However, oligomers comprising more than four fluorene units cannot be sublimed and must be solution processed.

Fluorene oligomers, especially those functionalized at the C-9 position, are readily soluble in common organic solvents. The most striking example is in a study of a series of oligofluorenes' static and dynamic solution properties, where they remain soluble at concentrations greater than 500 g L^{-1} in toluene, or > 50 wt. %, and even up to 800 g L^{-1} in the case of a terfluorene [120]. Routinely, fluorene oligomers are purified in solvent mixtures consisting mostly of nonpolar hexanes, and then solution-cast into thin films.

3.2

Crystallization Versus Glass Transition

While many polymers form glasses, oligomers are more likely to crystallize [21, 23]. Polyfluorene itself is often semi-crystalline, but, depending on the details of its substitution, it can range from mostly glassy to highly crystalline [4]. Fluorene oligomers fall on one side or the other of this semi-crystalline middle ground, being either intrinsically glass-forming or highly crystalline.

Fluorene oligomers can form morphologically stable organic glasses. Annealing samples of certain nematic oligofluorenes above their glass transition temperatures, T_g do not form any crystallites detectable by electron diffraction even after 96 h [60]. In addition, a fully spiro-configured terfluorene has

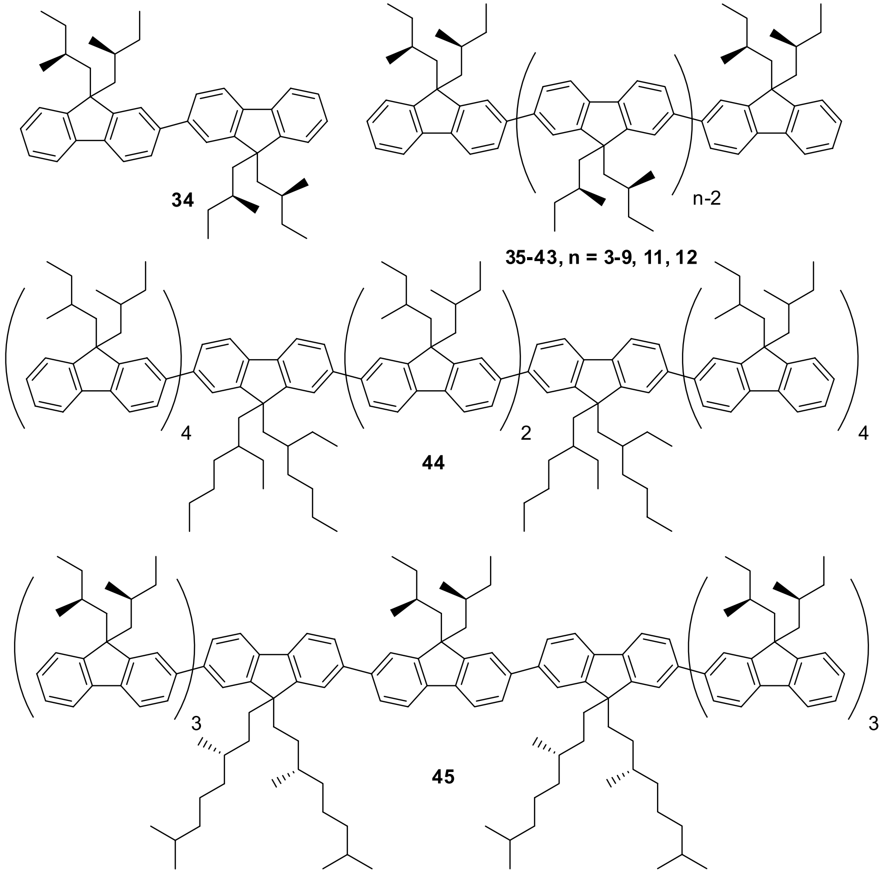


Fig. 6 Structures of uniform chiral oligofluorenes and representative nematic and chiral oligofluorenes with mixed pendants

shown a T_g of 296 °C, the highest reported for organic molecular systems at the time [47]. Later that year, a more extended spiro-configured pentafluorene set the new record with a T_g of 330 °C, showing no crystallization or melting transition up to 550 °C [121].

An illustrative example is a series of chiral oligofluorenes, uniformly substituted with 2*S*-methylbutyl pendants [35], shown in Fig. 6 as compounds **34–43.** Glass transitions without any crystallization are seen from two units up to five units; unstable glasses that crystallize on heating but not cooling are seen from six to eight units; and no glass transitions but strong crystallization is seen from nine units up to the polymer (equivalent to 70 units on average). As expected, the relevant phase transition temperatures increase with oligomer length. An important strategy to prevent crystallization is the use of mixed pendants, and especially the inclusion of branched alkyl pendants, providing stable glassy morphologies in oligofluorenes up to 12 units in length, as with compound **44** [60, 122].

A few other approaches have been taken to ensure that a given fluorene oligomer will form a stable glass. Kelly et al. have done considerable work with photopolymerizable groups on fluorene-containing chromophores, some of which classify as oligomers of fluorene, to form crosslinked networks [123, 124]. Strohriegl et al. have also developed such systems from their broad experience in crosslinkable liquid crystals [55]. Another approach to a crosslinked fluorene oligomer network is to dehydrate terminal boronic acids, with the added advantage of being reversibly recovered [82]. In addition to crosslinking, attaching fluorene oligomers in a rigid manner to a tetrahedral core has also been shown to result in formation of stable glassy phases [85].

The details of morphology in the glassy state of fluorene oligomers have also been examined. Wegner et al. modeled the conformations of oligofluorenes, showing that inversion of their helical motifs can occur and that excimer formation is discouraged by steric hindrance [125]. The same group has also investigated motions in glassy and melt states with dielectric spectroscopy [30] as well as orientational dynamics during their glass formation with dynamic light scatting and dynamic NMR spectroscopy [126]. Wu et al. used spectroscopic ellipsometry to show that the anisotropy present in their vacuum-deposited oligofluorene films disappears upon thermal annealing [127, 128]. Aggregation has been investigated using solvent interactions in water-soluble, self-condensed oligofluorene nanoparticles, where the choice of solvent can influence their packing [83]. Such aggregation is seen in red-shifted emission spectra, which is evident to a large degree in a six-armed star structure [129].

In contrast to these glass-forming oligomers, highly crystalline fluorene oligomers are also desirable for certain applications, in particular as active layers in organic field effect transistors. Some fluorene oligomers will form highly structured polycrystalline films upon vacuum deposition onto substrates heated to 140 °C [130]. These crystalline domains can grow as large as ten microns [130], and the details of the crystal structures of these fluorene oligomers are very sensitive to their substitution [131]. In one carefully examined case, the crystal structure was found to depend on the thickness of the deposited layer [132].

3.3
Liquid Crystallinity

One very attractive feature of extended fluorene compounds is their mesomorphism, or liquid crystalline self-organization [8]. Their chemical structure classifies them as hairy-rod liquid crystals with a rigid conjugated backbone decorated with flexible alkyl side chains. In order of descend-

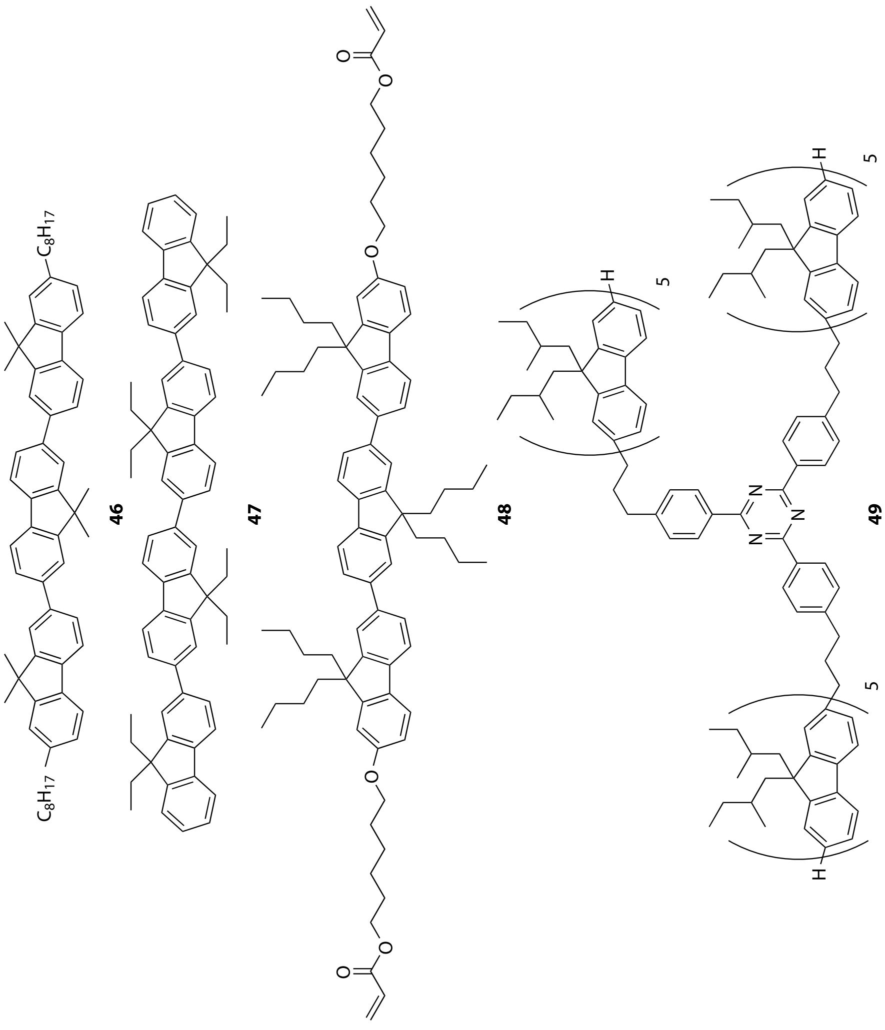


Fig. 7 Additional example structures of liquid crystalline oligofluorenes

ing molecular ordering, fluorene oligomers primarily exhibit three different mesophases: smectic, cholesteric (also known as chiral-nematic), and nematic [133]. The glass transitions of many oligofluorenes allow these unique and useful liquid crystalline morphologies to be frozen into the solid state without crystallization in order to be exploited for a range of optical and electronic applications. To take advantage of these ordered morphologies, alignment layers are used, including the most commonly employed rubbed polymer films [134], but also photoalignment layers which are effective with some oligofluorenes [135, 136].

Oligofluorenes exhibiting smectic mesomorphism organize into layers, resulting in one-dimensional positional order as well as orientational order. The shortest oligofluorene to exhibit any mesomorphism is a smectic trimer (compound **46**, Fig. 7) with only methyl groups as side chains and *n*-octyl as end chains, which is unfortunately highly crystalline [137]. Wegner et al. synthesized a series of oligofluorenes, from four to seven units in length, substituted with ethylhexyl side chains, and they observed excellent quality X-ray and electron diffraction patterns of their layered structures [138]. The broadest mesophase range of these oligomers is the heptamer with a T_g of 17 °C and a clearing temperature (T_c, or transition to isotropic liquid) of 221 °C.

Cholesteric oligofluorenes have a low enough viscosity to form highly oriented films, exhibiting very high degrees of chiroptical activity. Uniformly substituted with 2*S*-methylbutyl side chains, cholesteric mesomorphism begins with five units and persists up to the polymer [35], but crystallization is often encountered. With mixed chiral pendants (as in compound **45**, Fig. 6), glassy-cholesteric morphology is exclusively realized, and selective reflection bands are readily preserved into the solid state. The strong chiroptical activity observed was found to be dominated by their helical stacking in thin films, as opposed to molecular level helical conformations [122]. The cholesteric mesophase range of the mixed-pendant nonamers (such as compound **45**) was broad with T_g around 86 °C and T_c around 283 °C.

Glassy nematic oligofluorenes form large monodomain anisotropic thin films. Depending on their molecular aspect ratio, an order parameter, *S*, of 0.84 can be achieved. A very broad nematic range is exhibited by the dodecamer (compound **44**) from its T_g of 123 °C to beyond 375 °C [60]. Fluorene co-oligomers with large groups in their centers, can still exhibit broad nematic mesophase ranges of over 250 °C [64]. The shortest nematic pure oligofluorene consists of four units, as in compound **47** shown in Fig. 7, but its short ethyl pendants render it crystalline at room temperature [119]. A number of crosslinkable nematic oligofluorenes exhibit a moderate to high degree of order [55, 123, 124], such as compound **48** shown in Fig. 7.

Lastly, an interesting case is that of hybrid oligofluorene compounds [106, 139], one of which is shown as the last example in Fig. 7 (compound **49**). Here, pentafluorenes are attached to an electron-transporting core via flexible alkyl spacers. Unlike all the other fluorene oligomers modified with charge transport moieties, this type of compound manages to retain mesomorphism in the presence of the alkyl spacers which allow the oligomeric pendants to orient themselves. In fact, their order parameters in thin films assume the same values as that of the stand-alone oligofluorene. These hybrid compounds demonstrate the versatility of the core-pendant concept in affording multifunctional glassy liquid crystals [140], where oligofluorene pendants and a large non-mesogenic functional core are incorporated in a single molecular entity.

4
Photophysical Properties

4.1
Efficient Blue Emission

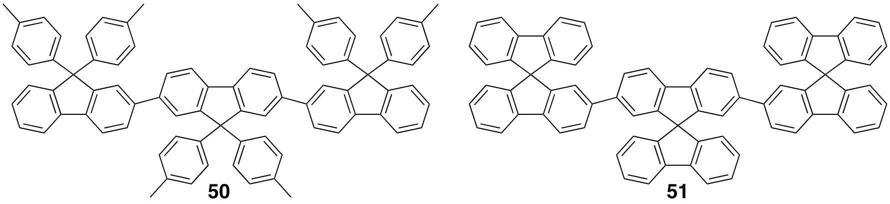
One of the reasons fluorene is appealing is its efficient emission of ultraviolet or deep blue light. Terfluorenes have several emission maxima at around 393, 412, and 441 nm [2]. The photoluminescent quantum yields, ϕ, of two ter(9,9-diaryl)fluorenes (compounds **50** and **51**, Fig. 8) are both 99% in solution and 90% in solid films [2]. However, most oligofluorenes have a photoluminescence quantum yield in the range from 40 to 70% [35, 54, 60, 141].

In addition, among oligofluorenes there is virtually no "long wavelength" or green emission, even after extended thermal annealing [47, 54, 60]. In contrast, polyfluorenes are known to suffer from undesirable green emission [142–144]. This may well be due to the higher purity accessible with oligomers, as very carefully purified monomers can also result in polyfluorenes showing stable blue emission [145].

4.2
Full Color Light Emission

The fluorene backbone also enables efficient emission of light across the visible spectrum with an incorporation of other chromophores. The photoluminescent quantum yield in solution can be as high as 75 to 82% from the sky blue to the orange with a slightly lower efficiency in the red at 47% [64]. A number of fluorene co-oligomers have emission at wavelengths across the visible spectrum, from sky-blue [72–74, 95, 146–149] to green [67, 98, 124, 150, 151], yellow [72] and red [69, 90, 152]. Attached as ligands to iridium, oligofluorenylpyridines are capable of red phosphorescence with emission efficiencies up to 24% [153].

Energy transfer, either within the oligomer or to neighboring groups, governs the efficiency of the full-color emission. Fluorene-ethynylene-pyrene teroligomers were synthesized and characterized to demonstrate that pyrene's



50 **51**

Fig. 8 Two terfluorenes with very high photoluminescent quantum yields in the solid state position is critical to the efficiency with which it accepts intramolecular energy transfer, the center position being the most favorable [146]. A variety of energy acceptors were also tested through close proximity, either physically or, more preferably, through hydrogen bonding [58]. The solvent effects on such transfer processes have also been examined [80]. In addition, Förster resonance energy transfer from oligofluorenes to co-oligomers has been quantified and subsequently exploited to generate white light emission [74]. Finally, fluorene oligomers have been used as conjugated molecular wires to mediate energy transfer between different moieties [89].

4.3
Studies of Excited Electronic States

The chain length dependence of the photophysical properties of oligofluorenes has been studied in detail. As the length increases, the energies of their fluorescence, phosphorescence, triplet–triplet absorption, and their fluorescent lifetime all decrease, while the magnitude of the transition dipole moment increases [154, 155]. Furthermore, the triplet state was found to be only slightly more confined than the singlet state [155].

A number of studies have examined various other aspects of the photophysical processes involved in fluorene oligomers' light emission. A theoretical model has reproduced the observed vibrational structures in their absorption and emission spectra [156]. The contributions of two conformations to light emission [157] and their conformational dynamics [158] have also been reported. Moreover, model systems have been used to look at the effects of their packing in the solid state on their emission spectra [159]. In addition, the efficiency of intersystem crossing from singlet to triplet excitons has been measured to be approximately 6% [160], but it is sensitive to heavy atoms such as sulfur [161]. Measurements of electric-field-assisted dissociation have indicated the singlet fraction for charge recombination may be as high as 35% [162, 163], instead of the statistical 25%. On a very different note, the nonlinear optical properties, and in particular two-photon absorption, of oligofluorenes have been characterized [56, 87]. A number of other theoretical studies have been conducted on fluorene oligomers [100, 164–168].

4.4
Polarized Photoluminescence

Liquid crystalline fluorene oligomers can emit polarized light with proper alignment of their molecular axes and, hence, of their transition dipole moments. For example, linearly polarized emission results from uniaxial alignment of fluorene oligomers. One common way to characterize linearly polarized emission is to measure its emission dichroism, viz. the emission

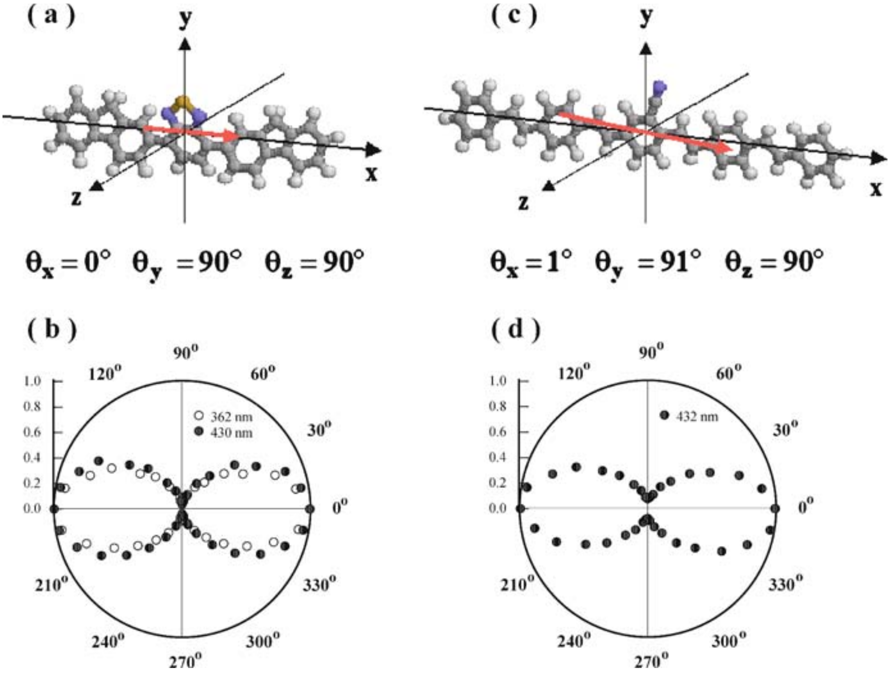


Fig. 9 Quantum mechanical calculations performed using the Gaussian 98 package to locate electron transition dipoles of the central segments: **a** 4,7-bis(2,2′-fluorene)-2,1,3-benzothiadiazole and **c** 1,4-bis[2-(4-[2-(4-phenyl)ethenyl]phenyl)ethenyl]-2-cyano-benzene, of two co-oligomers; and the UV-Vis absorption dichroism at absorption maxima of glassy-nematic films of co-oligomers containing these two segments, (**b**) and (**d**), respectively, indicating that the central segments responsible for absorption are aligned with the nematic director placed along 0 and 180° in the polar coordinates. Used with permission [64]

intensity parallel over that perpendicular to the director. A dodecafluorene (compound **44**) has exhibited a very high emission dichroism of 17 : 1, but even a heptamer with short enough pendants can reach a ratio of 14 : 1 [60]. Crosslinkable liquid crystalline fluorene oligomers have also yielded a high emission dichroism [55, 124]. For colors other than blue, it is important that the transition dipole moment of the chromophore inserted into an oligofluorene is along the molecular axis of the entire oligomer. Molecular modeling has shown its feasibility for a variety of inserted chromophores (for two examples, see Fig. 9), and the resultant emission dichroic ratios are from 9 : 1 to 14 : 1 across the visible spectrum [64]. Other nematic liquid crystalline oligomers have been synthesized, but generally have a lower degree of order and, thus, smaller emission dichroism, of 4 : 1 to 7 : 1 [169].

Circularly polarized light can be emitted by chiral oligofluorenes. The chiral side chains cause the oligofluorene backbones to preferentially twist into one helical conformation over the other. This chiral preference has been revealed by molecular simulations as well as exciton coupling signatures in circular dichroism [35, 122], resulting in a low degree of circularly polarized light absorption and emission. However, when annealed into a well-aligned helical stack characteristic of cholesteric mesomorphism, the degree of circular polarization, quantified by the dissymmetry factor, g_e, increases by nearly an order of magnitude to 0.7 [122]. Note that a g_e value of ± 2 represents perfect circularly polarized light emission. For circularly polarized light emitted by a thin film g_e value of 0.7 is a very high value which, coupled with a circular dichroism of up to 12 degrees, testifies to the supramolecular chirality achievable with cholesteric mesomorphism manifested by chiral oligofluorenes.

5

Electronic Properties

5.1

Electrochemistry: Energy Levels and Properties of Ionic States

The electronic properties of a material are highly relevant to a variety of organic electronic applications. These include the energy levels of the material, the properties of their ionic states, and their charge transport properties. The energy levels of a compound refer to its highest-occupied molecular orbital (HOMO) and lowest-unoccupied molecular orbital (LUMO). These roughly correspond to its ionization potential (I_p) and its electron affinity (E_a), respectively.

Oligofluorenes' LUMO and HOMO energy levels are slightly farther apart than polyfluorenes' because of the shorter conjugation lengths and larger band gaps. A study by Wegner et al. illustrates the oligomer length dependence as its properties approach that of the analogous polymer [170]. In appropriate solvents, oligofluorenes exhibit electrochemical stability as demonstrated by the reversibility of the cyclic voltammetry (CV) scans for both oxidation and reduction (see Fig. 10 for a representative example). In addition, the electrochemically inactive substituents at fluorene's C-9 position have an insignificant effect on the energy levels associated with the backbone [171], as shown by ultraviolet photoemission spectroscopy (UPS), which is expected of electronic decoupling. The exception to this rule is a spirofluorene linkage, which does influence the energy levels to some degree through spiroconjugation [171].

For fluorene co-oligomers, the band gap often changes with concomitant changes to the energy levels of the compound [69]. Inclusion of electron-rich co-monomer units, predominantly raises the HOMO level [147, 172], while electron-deficient moieties mostly lower the LUMO level [69, 80, 173]. Attachment through direct conjugation with electronically neutral cores has more

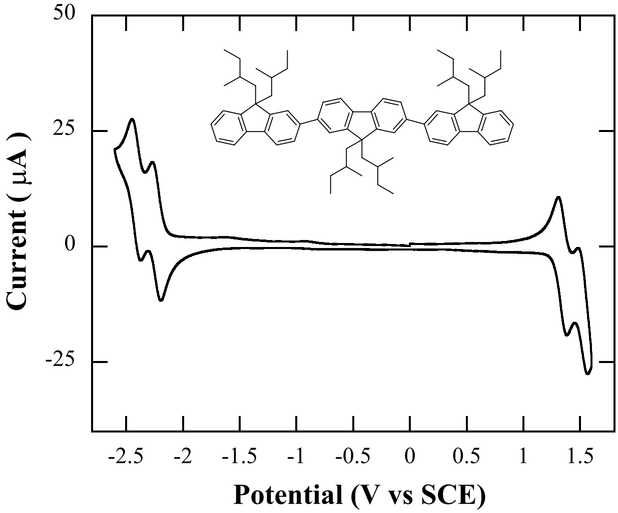


Fig. 10 Cyclic voltammetric (CV) reduction and oxidation scans of a terfluorene at 2.5×10^{-4} M in acetonitrile and toluene (1 : 1 v/v) with 0.1 M tetrabutylammonium tetrafluoroborate as the supporting electrolyte using a glassy carbon electrode

subtle effects through complex conjugation behavior between the various segments [174, 175].

In addition, through end-capping [93–100], substitution at the C-9 position [105], direct connection to such a core [91, 102], or non-conjugated attachment through a flexible spacer [106, 176], functionalization with electron-rich moieties contributes additional oxidation peaks in the CV scans. Similar non-conjugated attachment of electron-deficient moieties results in additional peaks in the reduction scans [106, 176]. Functionalization has also been performed with both moieties on a single oligomer, one electron-rich and the other electron-deficient, showing additional peaks in both oxidation and reduction scans [101].

The properties of ionized, or charged, oligofluorenes have been characterized and modeled [177–179]. One of these studies has found that charge carriers on oligo- or poly-fluorene backbones delocalize to a greater extent than a neutral exciton [177]. In addition, the fluorene backbone is more planar in the charged state than in the neutral state [178, 179].

5.2
Bipolar Charge-Carrier Transport

Oligofluorenes are exceptional in their charge transport properties, exhibiting relatively high bipolar charge-carrier mobilities in comparison to other non-crystalline organic materials. An interesting study of the dependence

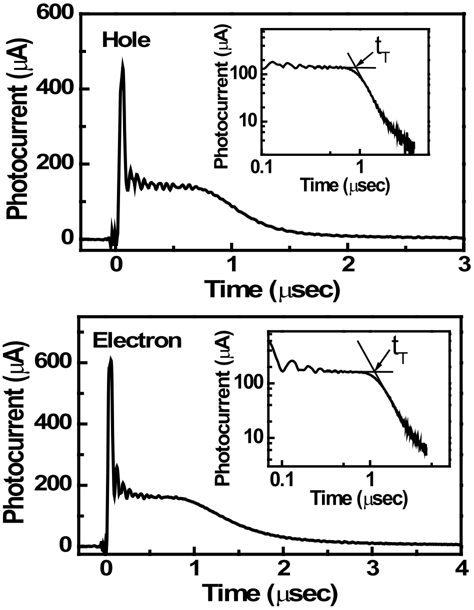


Fig. 11 Representative time-of-flight transients for 2,2″-bi-9,9′-spirobifluorene (2.1 μm thick): **a** hole, $E = 4.83 \times 10^4$ V/cm, **b** electron, $E = 9.53 \times 10^4$ V/cm. *Insets* of **a** and **b** are double logarithmic plots of **a** and **b**, respectively. Used with permission [180]

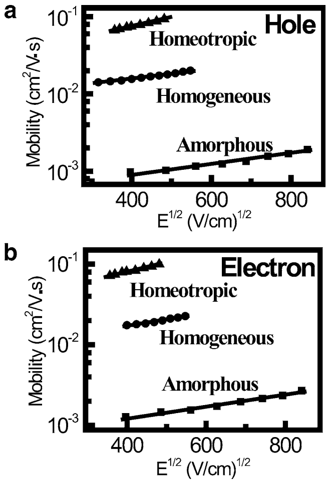


Fig. 12 **a** Hole mobilities and **b** electron mobilities vs. $E^{1/2}$ for a tetrafluorene (compound 47) in the amorphous state, the homogeneously aligned glassy-nematic state (charge moving perpendicular to the average long molecular axis), and in the homeotropically aligned glassy-nematic state (charge moving along the average long molecular axis). Used with permission [182]

of the carrier mobilities on oligomer length was undertaken by Wu et al., showing the bipolar nature of these compounds [180]. Figure 11 shows the non-dispersive electron and hole transients for a spirobifluorene dimer. Similar bipolar properties are also present in alkyl-substituted oligofluorenes, as seen in a terfluorene measured by photocurrent time-of-flight, and used as a charge generation layer to aid in the measurement of a number of other compounds for both hole and electron mobility [181].

The liquid crystalline order of oligofluorenes also sets them apart from many other materials. The advantage of order in charge transport is apparent in a liquid crystalline tetrafluorene (compound **47**), which exhibits over an order of magnitude increase in both its electron and hole mobilities upon homogeneous alignment into a glassy liquid-crystal film [119]. By aligning it in a homeotropic fashion, further work with this compound enhances the bipolar transport by another order of magnitude, yielding the hole and electron mobilities both nearly $0.1\,\mathrm{cm}^2\,\mathrm{V}^{-1}\,\mathrm{s}^{-1}$ [182]. The results also indicate the charge transport to be highly anisotropic, being preferentially along the oligofluorene backbone by roughly a factor of five, see Fig. 12.

6
Photonic and Electronic Applications

6.1
Organic Light-Emitting Diodes

The efficient photoluminescence, relatively high bipolar charge transport, morphological stability, and ease of processing all render fluorene oligomers potentially useful to organic light-emitting diodes, or OLEDs. Oligofluorenes emit light of a deep blue color with CIE (Commision Internationale de l'Eclairage) coordinates roughly in the range of (0.16, 0.04) to (0.17, 0.12), very close to the NTSC (National Television System Committee) standard blue color characterized at (0.14, 0.08) used in televisions and monitors [183]. This deep blue color is useful for achieving a wide color gamut in displays and for improving the quality of white OLEDs [184]. Many of these oligomers can be readily vacuum deposited into complex device structures, but others employ low-cost solution processing, most often by spin-coating. In addition, the mesomorphism of some of these oligomers provides opportunities for intrinsically polarized light emission from an OLED.

The highest efficiency OLED utilizing a spiro-terfluorene (compound **51**) in a "double confinement" device structure [185], reaches an external quantum efficiency (EQE) of 5.3%, or $1.53\,\mathrm{cd\,A}^{-1}$, with CIE coordinates of (0.158, 0.041). Others using similar "double confinement" structures have achieved

EQEs of 1.8 to 4.1% [186–189]. Incorporating electron-deficient moieties allows for a simpler device structure with an EQE of 1.6% [104], which can be an advantage or a disadvantage over non-functionalized oligofluorenes [103, 104], depending on the details of the device structure [190]. To attain higher efficiencies with simpler, solution-processed devices, hole-transport moieties are often incorporated into these oligomers with EQEs ranging from 1.4 to 3.7% [91, 102, 107, 173, 191, 192]. Note that EQE is much more fair for the comparison of efficiency, as cd A^{-1} varies sharply with CIE color coordinate in the blue region of the spectrum [193].

Device lifetime, especially for blue-emitting devices, is a key concern. One oligofluorene derivative, a ditolylamine end-capped terfluorene, has been demonstrated in a device with a time to half luminescence of 500 h at 1100 cd m^{-2}, which is extrapolated to over 10 000 h at a typical display brightness of 200 cd m^{-2} [189]. A study on a series of anthracene-containing fluorene oligomers suggested that the difference in hole mobility through the emitter layer was responsible for the observed difference in OLED device lifetime [148].

In addition to blue-emitting devices, fluorene oligomers have been used to emit colors across the visible spectrum. Shifting the color slightly into the sky-blue has been accomplished with phenylene-vinylene [149], perylene [74], and anthracene [73, 148] units, reaching efficiencies up to 3.2 cd A^{-1} with a CIE of (0.17, 0.19) [73]. Green-emitting fluorene oligomers have reached an impressive efficiency of 11 cd A^{-1} [124] as a neat fluorescent layer, by incorporating fluorene-vinylene [67], oligothiophenes [124, 150], and thiophene-*S*,*S*-dioxide [151], among others. Red-emitting derivatives (such as compound **29**) have employed thiophenes and benzathiadiazole units [64, 69]. However, the most impressive red-emitting oligofluorene is a terfluorene-pyridine ligand to iridium, which results in red electrophosphorescence with an EQE of 2.8% [153]. Three papers span most of the visible spectra with their wide variety of incorporated units [64, 69, 74]. In addition, an efficient white OLED has been fabricated using a terfluorene and rubrene to reach an efficiency of 6.15 cd A^{-1} and a CIE of (0.32, 0.37) [187]. Lastly, a bifluorene has been used to realize electroluminescence in the ultraviolet region with a notable efficiency of 3.6% EQE [194].

Liquid crystalline fluorene oligomers have shown excellent performance in polarized OLEDs. Linearly polarized OLEDs could be used as backlights for LCD displays, saving energy by allowing more of the light to be utilized without losing it to the initial polarizer [195]. In addition, stereoscopic displays and projection displays are other opportunities for linearly polarized OLEDs. For a dodecafluorene (compound **44**), efficiencies of up to 1.07 cd A^{-1}, with CIE coordinates of (0.159, 0.062), have been realized with linear polarization ratios (integrated over its emission spectrum) up to 24.6 (or 31.2 at 448 nm) [196], as can be seen in its electroluminescence spectra in Fig. 13, along with the device structure as the inset. A simplified structure resulted

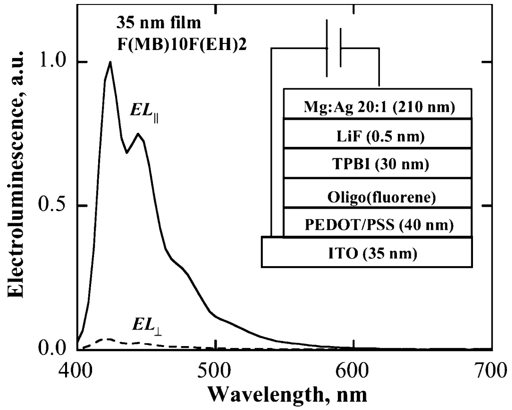


Fig. 13 Polarized electroluminescence (EL) spectra and device structure of an OLED containing a 35 nm thick dodecafluorene (compound **44**) film at a current density of 20 mA cm^{-2}. Used with permission [196]

in a loss in efficiency, down to 0.18 cd A^{-1}, but a sizeable gain in polarization ratio of 50.1 at 448 nm [197]. For green, red, and white OLEDs, polarization ratios of 17.7 (at 504 nm), 17.9 (at 620 nm), and 16.6 (integrated), and efficiencies of 6.4, 1.5, and 4.5 cd A^{-1}, respectively, have been achieved with fluorene co-oligomers [64, 74].

The performance achieved by these devices was record-setting, with each of their characteristics independently superior to reported values from any other polarized OLEDs, including those using polyfluorenes [9–13]. Recently, an integrated polarization ratio of 31 has been reported but with an efficiency of 0.3 cd A^{-1} for a deep blue OLED comprising poly(9,9-dioctylfluorene) [198]. Two other papers have reported polarization ratios at their emission maxima of 25.7 [199] and 29 [200], which are still slightly lower than 31.2 reported for the blue dodecafluorene device [196].

The fluorene oligomers in these record-setting devices have also been used to investigate polarized OLEDs in more detail. The first parameter of interest was the chain length. As expected, the longer the oligomer length, the higher the order and resultant polarization ratio, from 11.8 for a pentamer to the 31.2 of the dodecamer [196]. The dependence of the emitter layer thickness was also investigated for the dodecamer (compound **44**), showing an increasing polarization ratio at a decreasing film thickness [196]. The effect of thermal annealing was also explored, and it was found that pristine, isotropic devices had the same performance as the annealed, polarized devices [197], in sharp contrast to many polarized OLEDs containing polyfluorenes [11–13].

In addition, chiral oligofluorenes have exhibited circularly polarized electroluminescence with the highest polarization to date, as characterized by the dissymmetry factor, without addition of optical elements external to the OLED device. This device had an efficiency of 0.94 cd A^{-1} in the deep blue, with a dissymmetry factor of 0.35, which remained over 0.3 across the majority of its emission spectrum [122]. Circularly polarized OLEDs allow the use of circular polarizers on OLED displays to block glare from ambient light, thus increasing the display's contrast without losing output intensity [201]. For colors other than blue, doping could readily result in circularly polarized emission across the visible spectrum, including white light as was done with linearly polarized OLEDs [64, 74].

6.2
Solid-State Organic Lasers

Organic materials have been used as lasing media, both as laser dyes in solution or, more recently, in the solid-state. The use of oligofluorenes as dye

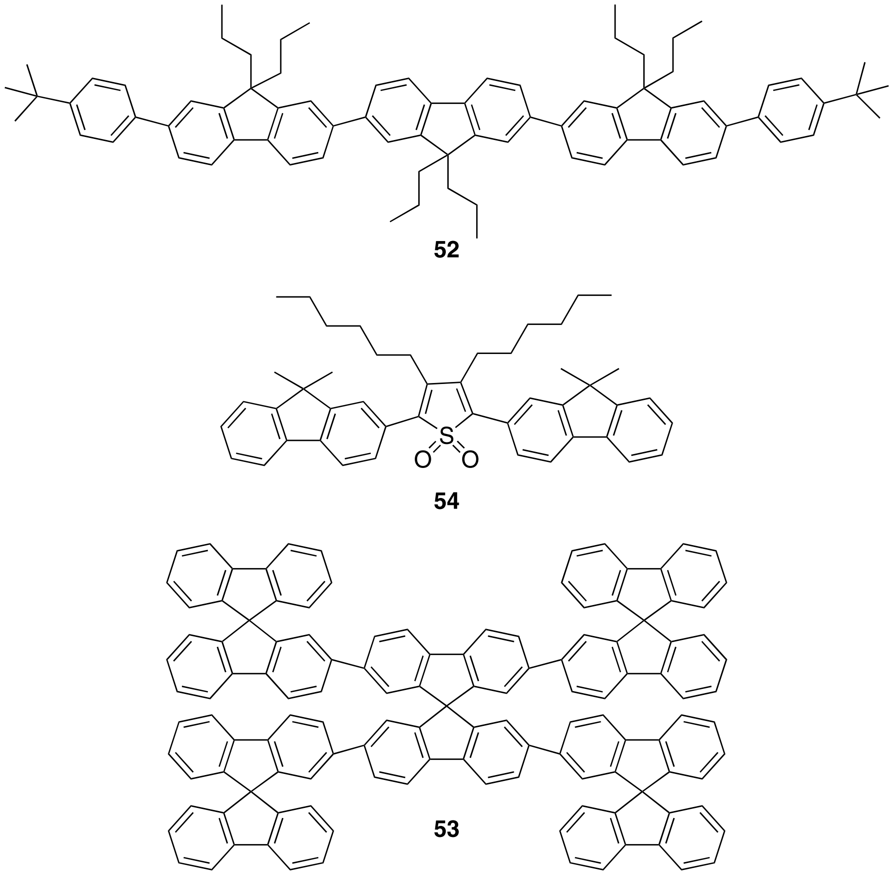


Fig. 14 Representative fluorene oligomers used in lasing and amplified spontaneous emission (ASE)

lasers was among the first indications of their excellent performance in lasers. When excited by excimer lasers or appropriate flashlamps, bifluorenes [202] up to tetrafluorenes [203] showed excellent lasing performance in the UV to deep blue. Outstanding among them is a laser dye now known as Exalite 428 (compound **52**), marketed by Exciton Inc., shown in Fig. 14 [203]. It exhibits relatively high conversion efficiency and a long lifetime (in terms of energy input to a single batch of laser dye solution).

As for organic solid-state lasers, polyfluorenes took an early lead, demonstrating their favorable characteristics [15] and culminating in relatively efficient photo-pumped lasing across the visible spectrum [16–18]. Work with fluorene oligomers has focused on their suitability as lasing media, as characterized through amplified spontaneous emission, ASE, which indicates their potential as excellent solid-state lasers when implemented in optical resonators. Salbeck et al. were the first to report the use of oligofluorenes as neat materials for solid-state ASE [121]. These structures are highly spiro-functionalized and have very high glass transition temperatures. Compound **53**, shown in Fig. 14, exhibits an ASE threshold of 3.2 μJ cm^{-2} [121], which is lower than that of the corresponding spiro-oligophenylene [204].

Using a fluorene-*S*,*S*-dioxide-thiophene co-oligomer (compound **54**, Fig. 14), Lattante et al. have realized a gain of 8 cm^{-1} at 550 nm [81]. The threshold was higher, but comparable to other small molecules used as organic active media. An aryl-substituted terfluorene (compound **50**), which exhibits anisotropic optical properties upon vacuum deposition [127], has shown excellent stimulated emission characteristics. When in the anisotropic state, the gain reaches an impressive 78 cm^{-1} [205], an improvement of nearly an order of magnitude over that in its isotropic state. In addition, controlled annealing of compound **50** allows for one-time tuning of the ASE wavelength subsequent to device fabrication, from 426 to 413 nm, shown in Fig. 15 [128].

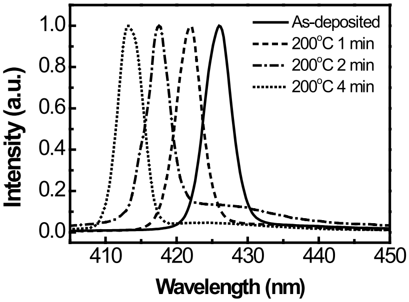
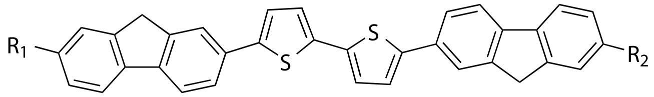


Fig. 15 Tunable amplified spontaneous emission (ASE) spectra of a 47-nm-thick terfluorene (compound **50**) film measured as deposited and after annealing at 200 °C for 1, 2, and 4 min. Used with permission [128]

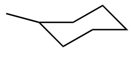
6.3
Organic Field Effect Transistors

Many high-performance organic field effect transistors, abbreviated as OFETs, are composed of small molecular weight compounds, oligomers being prominent among them [34]. In particular, oligothiophenes are attractive, but their stability against oxidation and, therefore, ambient exposure is poor. Instead of oligothiophenes, fluorene-thiophene co-oligomers have emerged as more oxidatively stable materials in p-type OFETs. This is evidenced by oligomer FTTF (compound **55**), depicted in Fig. 16, which shows no decrease in hole mobility or on/off ratio after two months of ambient exposure [206]. As demonstrated by Noh et al., if present, fluorenone defects are detrimental to device performance despite the improved oxidative stability [207, 208]. However, without intense UV irradiation, these fluorenone defects are not observed [206].

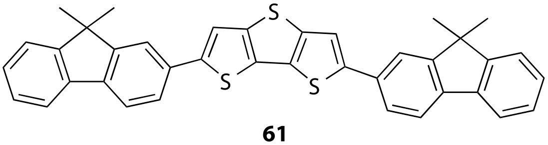
In addition to their relative stability under ambient conditions, these fluorene-thiophene oligomers are attractive because of their good mobility and the potential for further improvement through understanding their structure–property relationships. Various derivatives have all shown mobilities slightly above 0.1 cm^2 V^{-1} s^{-1}, which is on the order of amorphous silicon, such as DHFTTF [209], DDFTTF [131], CHFTTF [130], C8FTTF [210], and C12FTTF [210], all shown in Fig. 16 as compounds **56–60**. Other fluorene co-oligomers incorporating a dithienothiophene unit (such as compound **61**)



55, FTTF: $R_1 = R_2 = H$
56, DHFTTF: $R_1 = R_2 = C_6H_{13}$
57, DDFTTF: $R_1 = R_2 = C_{12}H_{25}$

58, CHFTTF: $R_1 = R_2 =$ 

59, C8FTTF: $R_1 = H; R_2 = C_8H_{17}$
60, C12FTTF: $R_1 = H; R_2 = C_{12}H_{25}$



61

Fig. 16 Structures of crystalline fluorene co-oligomers used in organic field effect transistors (OFETs) exhibit slightly lower mobilities [211, 212], while oligofluorenes can reach a field effect mobility of $1.2 \times 10^{-2}\ \mathrm{cm}^2\ \mathrm{V}^{-1}\ \mathrm{s}^{-1}$ [213].

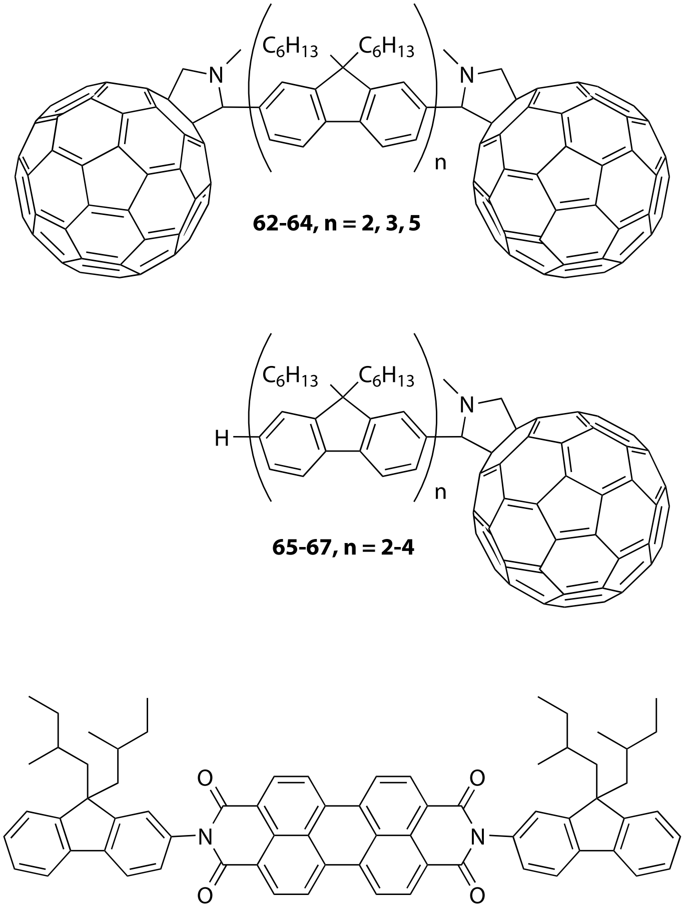
From these studies a number of structure-property relationships have emerged. First, bithiophene is the optimal length for the central thiophene group [209]. The presence of alkyl end groups is very important for good crystal packing which is essential to reaching high mobilities [131]. Cyclohexyl groups in particular can form large crystal domains up to $10\ \mu\mathrm{m}$ in size [130]. It is interesting to note that an alkyl end group is only needed on one end to reach relatively high mobilities, as in compounds **59** and **60** [210]. Returning to the crystal structures, the film thickness was found to affect molecular packing, and thus the mobility, of one of these compounds [132]. Noh et al. indicated that biphenyl groups are more stable than fluorene groups against oxidation by air in the presence of UV light, as the C-9 position of fluorene appears to be the most vulnerable site [214].

Thanks to their mesomorphism, oligofluorenes are of interest for OFETs which exhibit anisotropic field effect mobility. Indeed, interest in liquid crystalline materials in OFETs is on the rise [215]. Such anisotropy can help to diminish cross-talk as carriers move more slowly in the direction perpendicular to the channel than parallel to it. Glassy liquid crystalline films of oligofluorenes have shown their promise in this regard, reaching a degree of anisotropy in their field effect mobilities of 6.3 to 1. With a long enough oligomer, their performance surpassed that of the analogous polymer system [213], reaching a mobility of $1.2 \times 10^{-2}\ \mathrm{cm}^2\ \mathrm{V}^{-1}\ \mathrm{s}^{-1}$ for a dodecamer (compound **44**). The highest mobility for these nematic oligofluorenes is seen along the long axis of these molecules in a monodomain film where the shortest number of rate-limiting hops would occur, followed in decreasing order by a polydomain film, a monodomain film measured perpendicular to the nematic director, and a disordered amorphous film. This anisotropic field effect mobility would become potentially useful in practice should the mobility of similar oligomers be raised by one to two orders of magnitude.

6.4
Organic Solar Cells

Fluorene oligomers have seen only limited use in organic solar cells to date. If they incorporate any fluorene units at all, most efforts have focused on polyfluorene derivatives [19, 20]. For example, Bryce et al. synthesized a series of oligofluorene-fullerene derivatives to study their fundamental photophysical and charge transfer properties [216] (compounds **62–67** in Fig. 17), but have not pursued such structures for organic solar cells yet.

Kelly et al. remain the primary group involved in using fluorene oligomers for solar cell applications. Their initial effort utilized a fluorene oligomer, which incorporated a perylene diimide central unit (compound **68**) [217],



62-64, n = 2, 3, 5

65-67, n = 2-4

68

Fig. 17 Fluorene co-oligomers potentially useful for fabrication of organic solar cells

to achieve a vertically segregated interface with low molecular weight cross-linkable compounds. Subsequent work using a co-oligomer of fluorene and thiophene as the p-type component, along with a fluorene-perylene diimide oligomer as its n-type counterpart, results in a slightly higher conversion efficiency of 0.8% in a distributed bilayer structure [218]. Both of these studies involved the utilization of liquid crystalline mesomorphism to control the morphology, showing promise for future improvement.

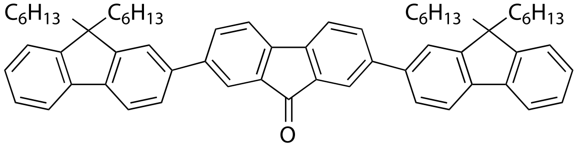
7
Fluorene-Based Oligomers to Probe Polyfluorenes

In addition to many of the unique properties and advantages of fluorene oligomers surveyed in this article, they also serve as model systems for understanding the behavior of polyfluorenes, which have been widely explored for organic electronics. Many research groups have synthesized a series of oligomers to learn about the analogous polymeric systems. One of the early synthetic efforts with oligofluorenes was undertaken to determine the effective conjugation length of polyfluorene based on the position of the absorption maximum [52]. More recent studies have also looked at the energy levels of oligofluorenes in comparison to polyfluorene [170], delocalization lengths of charge carriers [177], and detailed photophysical studies [155], among other less direct but still useful surveys of oligomer series. Departures from such correlations, however, are well known [21, 30–33].

7.1
Fluorene-Fluorenone Co-oligomers

One particular area that has garnered considerable attention is the green emission that often plagues polyfluorene light-emitting materials [142, 143]. While there is still debate over the prevalence of two different mechanisms, it is settled that fluorenone defects do play a role in this green emission band in the absence of aggregation, as clearly illustrated in a paper by Becker et al. [144]. This has spawned a number of studies on fluorene oligomers containing fluorenone units. Their synthesis is straightforward with simple Suzuki couplings to the halo- or dihalo-fluorenone units [75], although treatment of these ketones with butyllithium should obviously be avoided in subsequent steps.

The first use of fractionated oligofluorenes to explore the origin of green emission from polyfluorenes reported green emission from both material classes in solution and neat film [219], in contrast to the more recent experimentation with monodisperse oligofluorenes [47, 54, 60]. Time-resolved spectroscopy was used in an attempt to exclude the influence of excimers, which became a repeated theme in future articles. Another group synthesized the first fluorene-fluorenone co-oligomer (compound **69** in Fig. 18) to examine the origin of green emission and the electroluminescence of these compounds, finding the fluorenone unit to be a decent green emitter in an OLED [77]. Wegner et al. added to this understanding by doping co-oligomers consisting of one, two, and three fluorene units at both the 2- and 7-positions of a central fluorenone into a highly defect-free polyfluorene [78], with another group confirming that an equivalent pentamer is an accurate reproduction of the photophysics of the emitting species in degraded green-emitting polyfluorene samples [79]. Synthetically, a number of placements of



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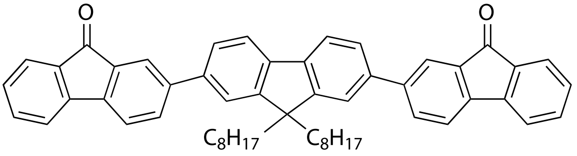

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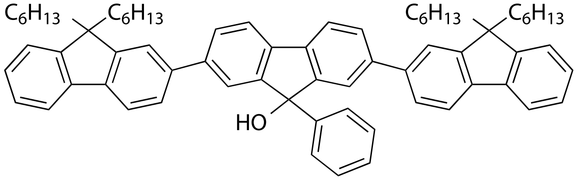


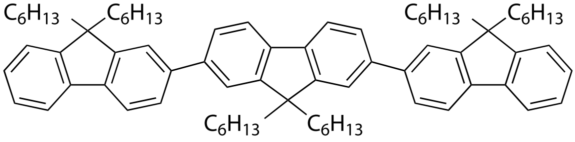
71

Fig. 18 Two fluorene-fluorenone co-oligomers and an additional model compound at an intermediate stage of oxidation

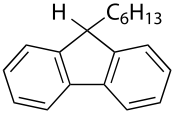
fluorenone in such co-oligomers (e.g., compound **70**) are predictable in terms of the intensity of green emission based on the number of ketone groups present [75]. Another interesting oligomer was synthesized with a hydroxyl group at the C-9 position of fluorene on the central unit (compound **71**), also shown in Fig. 18. This compound showed only a slight red shift of the blue emission without any green emission [76]. While aggregation may still play a role in the undesired green emission from polyfluorenes, fluorene-based oligomers have helped to elucidate that fluorenone is a primary cause.

7.2
Insight into Degradation Processes

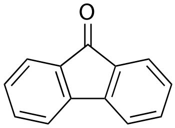
Not departing too far from fluorenones, Liu et al. have done an elegant study on the photodegradation of fluorene oligomers [220]. The structures they use vary from that of compound **51** to compound **72**, shown in Fig. 19, by varying the amount of alkyl versus spiro-substitution. These compounds are carefully characterized and found to contain no detectable fluorenone as synthesized. Also shown are a number of defect sites they propose and subsequently detect after photoirradiating the samples. Figure 20 shows the matrix-assisted laser



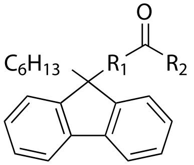
72, T1



73,
9-H Defect Site



74, D1



75, D2

Fig. 19 A representative terfluorene used to study photodegradation, with a number of monomers showing the types of defect sites found experimentally after intense photo-irradiation

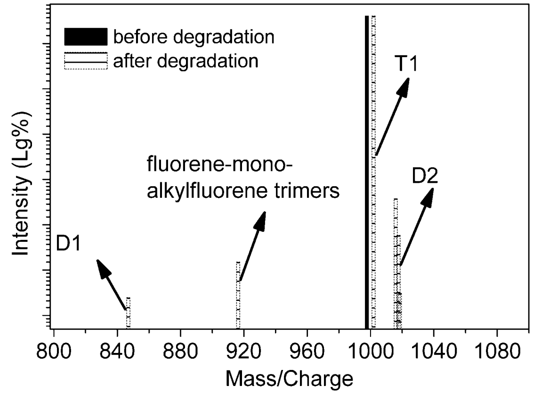


Fig. 20 MALDI-TOF mass spectra of **T1** (compound **72**) and the soluble part after 30 min of UV irradiation by a 125 W high-pressure mercury-arc light source. The *arrows* point towards the possible products with different masses (with **73–75** as defect sites). Used with permission [220]

desorption/ionization time of flight (MALDI-TOF) spectra of compound **72** and the detected degradation products, containing the defect sites shown in Fig. 19 by their mass (and confirmed by IR spectroscopy). They propose that photodegradation occurs via a radical chain reaction process that is propagated by the alkyl side chains, which also explains the stability of aryl-substituted fluorenes as they exhibit almost no degradation (only seen in a slight increase in the tail of its photoluminescence).

Kondakov et al. have reported the analysis by high performance liquid chromatography of degradation products of a phosphorescent OLED based on evaporable materials [221]. This work has inspired confidence in using fluorene-based oligomers, evaporable or solution-processable, as model compounds for continuing effort to address the OLED device instability issue through the isolation and identification of degradation products. Similarly, the ability to isolate and identify the products of electrochemical degradation involving the more tractable oligofluorenes than polyfluorenes [222] would be a fruitful line of investigation.

8
Summary

Fluorene-based conjugated oligomers represent an emerging class of materials that complement the properties of their polymer analogues, bringing a number of unique strengths to the arsenal of organic optoelectronics. A wide diversity of structures is readily accessible with versatile synthetic strategies supported by various cross-coupling reactions. Through molecular design, fluorene-based conjugated oligomers can be tailored from highly crystalline to morphologically stable amorphous materials. Oligofluorenes are quite attractive for the fabrication of blue-emitting devices because of their high photoluminescence quantum yields of up to 90% in the solid state. Emission of green, red, and white light is also feasible via insertion of proper chromophores in oligofluorenes aided by Förster energy transfer. Furthermore, their fast bipolar charge transport is a unique asset to organic semiconductors. With sufficiently high molecular aspect ratios, fluorene oligomers have been shown to exhibit nematic, cholesteric, and smectic liquid crystalline mesomorphism with elevated glass transition and clearing temperatures. Thanks to their low viscosities in the absence of chain entanglement and their ability to form self-organized solid films across a large area, liquid crystalline conjugated oligomers have found potential applications where a high degree of optical or electronic anisotropy is advantageous or essential. Through supramolecular chirality, oligofluorenes with enantiomeric aliphatic pendants are capable of extremely high chiroptical activities in thin film. In a nutshell, fluorene-based conjugated oligomers are expected to play a prominent role in organic electronics and photonics, from polarized and unpolarized light-emitting diodes, through tunable organic lasers, environmentally stable charge transport in organic transistors, and emerging application in organic solar cells. Additionally, fluorene-based conjugated oligomers have been instrumental to furnishing fundamental insight into the chemistry and instability issues confronting polyfluorenes as the prime candidate for blue light emission.

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