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# 缺電性共軛寡聚合物與高分子合成與物理性質之研究(3/3)

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# Research Report

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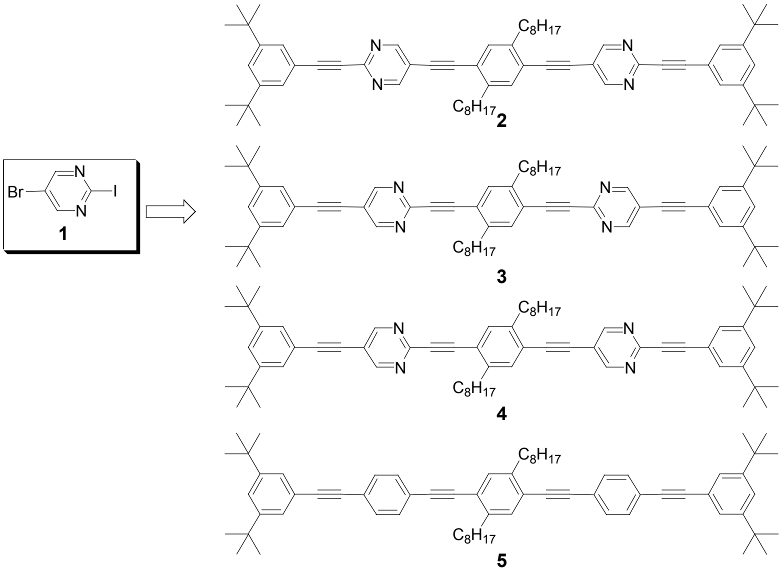
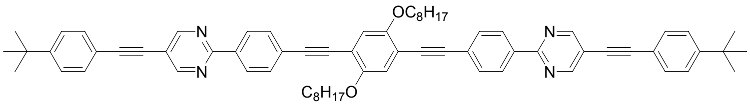
## A. Pyrimidine-Containing π-Conjugated Systems

Linear organic molecules with extended π-conjugation have received a lot of attention due to their potential use as molecular wires. Many practical synthetic approaches and testing methods have been developed for constructing and evaluating molecular wires of different length. More interestingly, there are significant progresses on modifying the primary structure of the conjugated system for developing *functional* molecular wires. In my laboratory, we first aimed at the synthesis of a new linear π-conjugated system by manipulating the orientation of dipolar component in the backbone. This approach ultimately changes the dipolar character of a π-conjugated system that may lead to the development of an interesting method to probe the structure-property relationship.

We utilized a highly electronegative pyrimidine ring as the dipolar moiety to incorporate into the conjugated backbone. Starting from 5-bromo-2-iodopyrimidine (**1**), successful control on the arrangement of dipolar orientation of pyrimidine was achieved by applying Sonogashira coupling reaction with different synthetic sequences. We have synthesized ethyne-linked linear molecules **2-4** with different arrangement of dipolar orientation of pyrimidine moieties[1].



Along this synthetic strategy, a pyrimidine-containing linear molecule **6** with longer conjugation length has also been synthesized[2].



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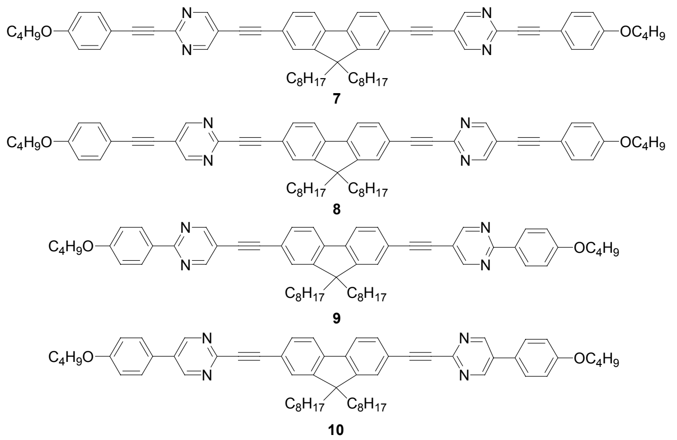
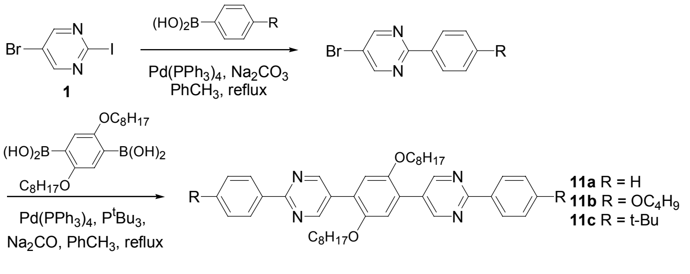
For probing the structure-property relationship, we observed that there was no remarkable dependence of the photophysical properties on the arrangement of dipolar orientation of pyrimidine in the conjugated backbone. By comparing with the corresponding model compound **5**, the π−π* band gap in these new pyrimidine-containing conjugated systems (**2-4**) is significantly reduced. Apparently, the alternating arrangement of π-donating (alkyl substituted phenylene) and π-accepting (pyrimidine) character along the π-conjugation contributes to lowering the HOMO-LUMO energy gap. The cyclic voltammetry experiments conducting on these linear molecules have revealed that there are very interesting dependence of the redox behavior on the different arrangement of dipolar orientation of pyrimidine[3]. Theoretical calculation also indicates that the localization of polaron along the conjugation intriguingly depends on the different arrangement of pyrimidine rings along the molecular axis[4]. According to these results, the electrical property of a well-defined conjugated system now can be fine-tuned by controlling the arrangement of dipolar subunits in the backbone. These linear molecules are intensively blue-fluorescent with modest quantum yields range from 0.61 to 0.75. The quantum yield of the photoluminescence can be further improved to close to unity by introducing 9,9-dioctylfluorene as a central linkage with similar synthetic manner (Scheme 1) [3]. Due to their high quantum yields, we have successfully applied these materials as an active emissive dopant in PVK for light-emitting devices. However, the introduction of C-C triple bond as a linker for constructing these linear molecules makes the further purification by thermal evaporation more difficult. The unstability of C-C triple bond upon heating also limits these materials to produce amorphous thin film by thermal sublimation. The reversible reduction behavior of pyrimidine-containing linear molecules trigger our interest to develop new conjugated systems that are suitable for electron-transporting materials for OLED. According to this idea, a Suzuki coupling approach for the synthesis of new pyrimidine-phenylene alternating oligomers was successfully achieved[5] (Scheme 2).

**Scheme 1**

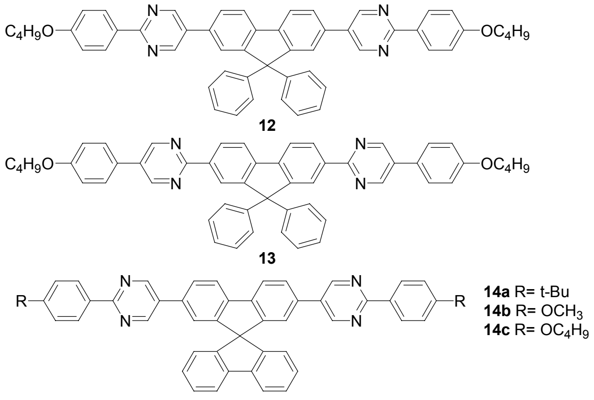


**Scheme 2**



These oligomers (**11a-c**) exhibit weak intermolecular π−π and dipole-dipole interactions, which are characterized by the X-ray structure analyses. Two absorption bands are observed, as the long wavelength band shows a bathochromic shift in the thin film. Interestingly, oligomers **11a-c** exhibit strong blue fluorescence in dilute solution with emission maximum centered at 419 nm irrespective to the nature of the terminal substituents. It is worth noting that, in the solid film, **11a**-**c** exhibit PL spectra without distinct red shift when compared to those in solution. The identity of emission behavior suggests that the excited state of **11a**-**c** could have a similar conjugation length in dilute solution and in the solid film. Two quasi-reversible cathodic reduction couples were observed by cyclic voltammetry experiment, the reduction potentials are dependent on the nature of the terminal substituents. These two reductions were believed to occur at the pyrimidine rings successively. The redox behavior of **11a-c** indicates that the pyrimidine moiety could serve as an electron-accepting center once it was incorporated into a π-conjugated system. The photoluminescence properties and quasi-reversible redox behavior of these oligomers make them applicable as an active material for light-emitting device. Blue light-emitting electroluminescent devices with the external quantum efficiency up to 1.8% and brightness over 2000 cd/m$^2$ have been fabricated. These results are rather encouraging since these devices are non-doped; optimization of device structures and material properties will further enhance the blue-emitting device performance. Indeed, further modification on the central linkage by introducing a rigid skeleton for creating pyrimidine-containing glassy materials was successfully achieved in my laboratory. 9,9-Diphenylfluorene and 9,9-spirobifluorene were introduced by Suzuki coupling reaction as the central linkage of the pyrimidine-based conjugated molecules. The resulting materials (Scheme 3) exhibit distinct glass transition temperature (*T*g) with very high quantum yield of photoluminescence.

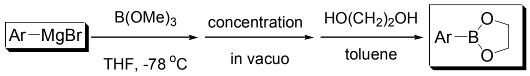
**Scheme 3**



We first selected **14a** as a model compound for optimizing a standard device configuration due to its high *T*g (195 °C) and its high thermal stability. The thermal analysis of **14a** reveals the decomposition temperature of **14a**, corresponding to 5% weight loss upon heating is around 420 °C. The steric hindrance inherent with the molecular structure renders the material a record-high neat-film photoluminescence (PL) quantum yield of 80% as a pure blue emitter (PL peak at 430 nm) of low molecular weight. Blue OLEDs[6] employing this compound as the emitting host exhibit unusual endurance for high currents (device configuration: [ITO/PEDT/NCB/**14a** (1% perylene) /Alq3/LiF/Al]). Injection current over 5000 mA/cm$^2$ and maximal brightness of ~80000 cd/m$^2$ had been achieved, representing the highest values reported for blue OLEDs under dc driving. The EL efficiencies of devices at 100 cd/m$^2$ are about 2.3% photon/electron (1.6 cd/A) and 4% (5.2 cd/A) for non-doped and doped devices, respectively. Full utilization of high $\Phi_{film}$ for device efficiency may rely on further improving the hole injection/hole transport by using multiple hole-transport layers or by tuning energy levels of the blue-emitting compound.

During the preparation of diboronic ester as building blocks for pyrimidine-containing oligomers, we have successfully established an efficient and convenient non-aqueous procedure for the large-scale preparation of arylboronic esters (Scheme 4) [7.] In one-pot, arylhalides that are possible to be transformed into their corresponding Grignard reagents could be used for the preparation of aryl boronic ester easily. The lowest molecular weight diol, ethylene glycol, not only serves as a replacement of water for the work-up step, but also acts as the reagent for the synthesis of the corresponding boronic esters in good to excellent yields. The boronic residue was dissolved in ethylene glycol, leading to no boron-contaminated aqueous waste. Instead of using ethylene glycol, other diols such as 1,3-propanediol, pinacol and diethyl L-tartrate are also effective for this new procedure.

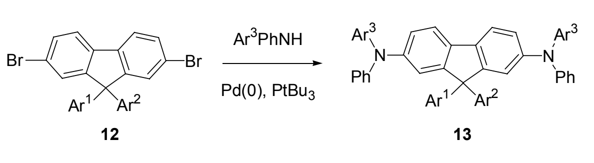
**Scheme 4**



## B. Novel Triaryldiamines: Conformational Control on the HOMO Energy Level

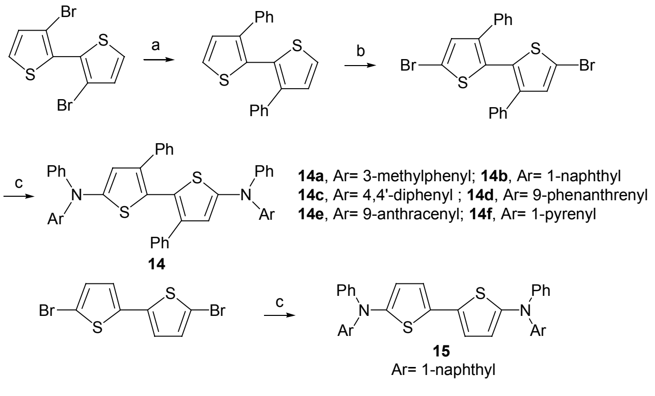
For hole transporting, triarylamines are the most used materials in OLEDs for this purpose. Among these triarylaimnes, α-NPB is the most popular one. However, the *ortho-ortho* steric interaction forces the biphenyl linkage to have a twisted ground state, which will lower the HOMO energy level and subsequently increase the difficulty of the hole injection from the anode. The rotation about this single bond in the excited state may also reduce the photoluminescence quantum yield. We were very interested to see the influences on the physical properties if we could lock the conformation of the central biphenyl linkage of α-NPB. Based on the success of the synthesis of fluorene-based pyrimidine-containing oligomers, we have developed an efficient synthetic protocol to synthesize 9,9-diaryl-2,7-dibromofluorene (**12**), which can serve as a conformation locked core for novel triaryldiamines. The diaryl amino groups outside the core were introduced by Buchwald-Hartwig amination using a Pd-catalyst in the presence of a catalytic amount of bulky $P^tBu_3$ (Scheme 5) [8].

**Scheme 5**



The rigidity of the 9,9-diarylfluorene central linkage, and the higher molecular weight both are beneficial to the high morphological stability. The *T*gs of these new materials are increased by ca. 30 °C when compared to that of α-NPB. Due to the coplanar conformation of the central linkage, the absorption maxima of fluorene-based triaryldiamines are red-shifted, but the emission maxima and quantum yield are almost the same as α-NPB, while triaryldiamines contain the same diaryl amino group as α-NPB. The emission behavior is predominated by the substituents outside the core structure. We can fine-tune the emission maximun by changing the nature of diaryl amino group outside the central linkage. The electrochemical properties of these new materials were investigated by cyclic voltammetry. These materials exhibit two reversible oxidation couples, the fluorene-based traryldiamines display lower in the first oxidation potential when compared to that of α-NPB, however, the second oxidation potentials are very similar to that of α-NPB. We believed that, when the first radical cation formed in α-NPB, the cation intends to delocalize in the whole molecule along the π-conjugation, which makes the biphenyl linkage rotates to reach a coplanar conformation, resulting a similar second oxidation potential as the fluorene-based ones. Locking the conformation of the ground state can efficiently raise the HOMO energy level, which can subsequently improve the hole injection efficiency in OLEDs. In other words, the HOMO energy level can be reduced in certain extent by strongly twisting the ground state conformation of the central linkage. We started from the 3,3’,5,5’-tetrabromo-2,2’-bithiophene, by selectively removing 5,5’-bromo groups with Zn, then introduced the phenyl group at 3,3’-positions by a typical Suzuki coupling reaction, then re-borminated the 5,5'-positions. Finally, we played with the same tricks to introduce the diarylamino groups by Pd-catalyst, affording a new class of triaryldiamines based on 2,2’-bithiophene as a central linkage (Scheme 6)[9.] A model compound **15** without phenyl groups at the 3 and 3' positions were also synthesized for comparison.

**Scheme 6**



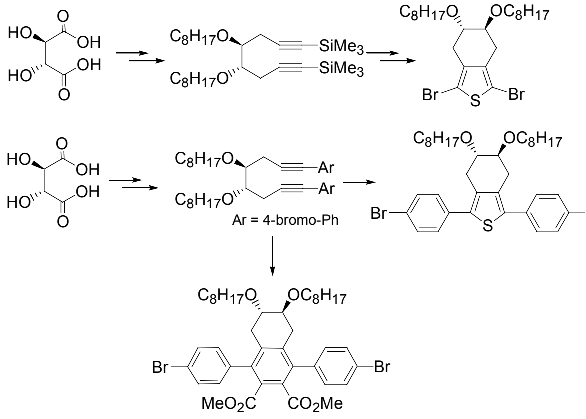
Reagents and conditions: a, $PhB(OH)_2$, $Pd(PPh_3)_4$, $Na_2CO_3$, DME, reflux 2d , 86%; b, $Br_2$, AcOH/$CHCl_3$ (1/2), 0 °C to r. t. 98%; c, diarylamine, $Pd(OAc)_2$, $PBut_3$, NaOBut, toluene, reflux overnight.

These novel triaryldiamines exhibit an amorphous nature evidenced by the presence of the glass transition temperature. The asymmetric diarylamino substituent and the diphenyl substituted central bithiophene linkage significantly contribute to the high $T_g$s. The $T_g$s are very dependent on the diaryl amino substituents. These compounds exhibited quasi-reversible anodic oxidation. The onset of oxidation and $E_{pa}$ (V vs. Ag/AgCl) varied with the nature of the terminal diarylamino groups. Differing from the conventional bis(triarylamines), only one redox couple ($E_{pa}$ 550 mV, $E_{pc}$ 430 mV vs. Ag/AgCl) was detected for **14a**. Coulometry in a thin layer cell confirmed the redox process of **14a** to be a two-electron oxidation. The lack of co-planarity of the central 3,3'-diphenyl-2,2'-bithiophene linkage prevents the extension of π-conjugation along the molecular axis. The rate of second oxidation in **14a** may be faster than the conformational change to reach a more coplanar conformation. Therefore, the first radical cation can not efficiently delocalize in the whole molecule; the two triarylamine systems behave independently but are oxidized simultaneously without any communication. The electrochemical properties are also dependent on the nature of the diaryl amino substituents. Bithiophene-based triaryldiamine (**14e**) with diaryl amino group containing anthracene showed two partially resolved oxidation couples. The model compound **15** exhibited two well-resolved redox couples ($E_{pa}$ 460 mV, $E_{pc}$ 385 mV and $E_{pa}$ 695 mV, $E_{pc}$ 610 mV vs. Ag/AgCl). The lower oxidation onset and larger potential difference (230 mV) of **15** reveal that the central bithiophene linkage adopts a coplanar conformation in the ground state. The introduction of the phenyl groups can efficiently block the electron delocalization by twisting the ground state conformation of bithiophene core, resulting in the two triarylamine systems behave independently. For fine tunning the physical proterties, we were able to introduce different aryl group at the 3 and 3' positions of the bithiophene central linkage.

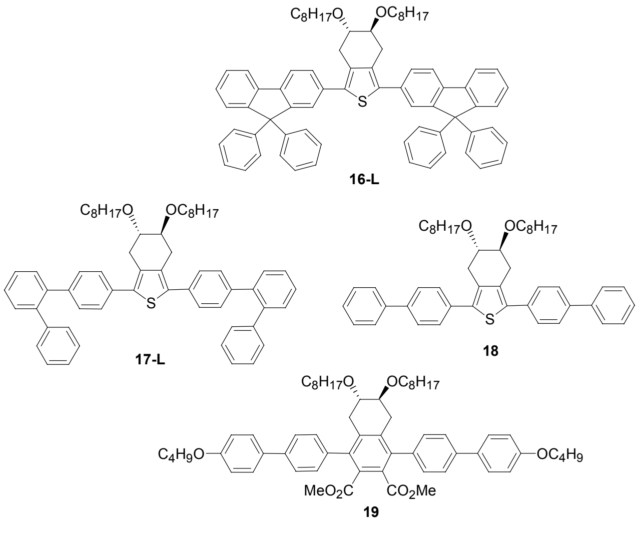
## C. Synthesis and Properties of Novel Chiral π-Conjugated Oligomers

Intensive investigations on π-conjugated system have resulted in a great research success on the new development of synthetic methodologies. Among these efficient strategies for constructing π-conjugated oligomers with precise conjugation length, zirconocene diyne-coupling pathway has been used to synthesize conjugated system with novel architecture. Zirconocene-promoted intramolecular cyclization of diynes generates synthetic intermediates containing zirconacyclopentadiene unit(s), which can be subsequently transformed into a variety of structures, for example thiophene, thiophene-1-oxide, thiophene-1,1-dioxide, phosphole, germole and highly functionalized phenylene[6]. These subsequent chemical transformations can be used to tailor the structure of conjugated backbones, giving a new possibility for efficiently tuning the electronic and optical properties. Along this line, we take advantage of the Zr-promoted cyclization of diyne as a versatile tool to introduce side chains with $C_2$-chirality, which is originated from tartaric acid, giving a series of interesting precursors for new conjugated system. Intramolecular zirconocene coupling of diynes for the synthesis of new chiral dibromide building blocks is outlined in Scheme 7.[10] The validity for the synthesis of conjugated molecules based on these chiral dibromide cores was also investigated. The extension of the conjugation length of the chiral core by Suzuki coupling reactions of dibromide with arylboronic ester or a various arylboronic was achieved (Scheme 8). The appearance of a mirror image CD spectra of **16-L** vs. **16-D** and **17-L** vs. **17-D** indicates that the optical behavior of the conjugated backbone is strongly relying on the chirality of the side chain. The chiral information originated from the tartaric acid is effectively transferred to the conjugated chromophore, which consequently induce the conjugated chromophore with interesting optical activity.

**Scheme 7**

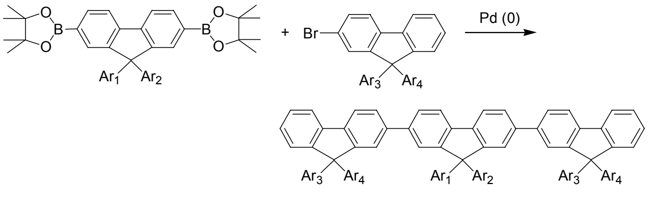


**Scheme 8**



## D. 9,9-Diarylfluorene-Based Conjugated Oligomers

Oligo- and polyfluorenes are generally regarded as promising candidates for blue light-emitting electroluminescent device. However, the intramolecular π−π interactions normally have a detrimental effect on the quantum yield of emission. In addition to that the long wavelength excimer emission results in poor color purity has obscured their prospective utilization in OLEDs and PLEDs. Many synthetic works have concentrated on suppressing the intermolecular aggregation by introducing steric bulky groups at the C9 position of fluorene.[11] However, the photo- and/or electro-oxidized cleavage of alkyl pendant group(s) attached to C9 position of fluorene in a ployfluorene has recently reported as another possible pathway for generating long wavelength emission tail.[12] Reported terfluorenes,[13] fully spiro-configured terfluorene[14] and oligomeric fluorenes[15]have been shown to exhibit interesting photophysical properties. In order to increase the morphology stability, the relevant molecular weight of oligomeric fluorene has to be increased substantially, resulting in the high difficulty of further purification by vacuum sublimation. For example, the oligomers based on 2,2’,7,7’-tetra-substituted-9,9’-spirobifluorene as a core structure exhibited extremely high thermal stability and interesting photophysical properties.[16] The steric bulky nature of these oligomers can effectively prevent the intermolecular interactions. However, the high molecular weight of these tetra-substituted spirofluorene-based oligomers makes the further purification by thermal evaporation very difficult. Our previous results have revealed that 2,7-disubstituted-9,9’-spirobifluorene-based compounds can exhibit high quantum yields in their thin films and give enough high $T$g for OLEDs applications. With this point in our mind, we recently have synthesized a series of ter(9,9-diarylfluorene)s (**20**) (Scheme 9)[17]. The terfluorenes **20** basically is a hexaphenylene conjugated system with locked coplanar conformation between the adjacent two phenylene rings. The moderately high molecular weight makes the further purifying process by high vacuum sublimation possible. The C9 aryl substituents here play irrelevant role on the photophysical properties (all terfluorenes exhibited PL $\lambda_{max}$ centered at ~394 nm). However, the introduction of aryl substituents is significantly beneficial for the high morphology stability and the resistance to thermal decomposition. DSC analyses of these terfluorenes revealed the existence of distinct glass transition temperature ($T_g$) ranging from 189 °C to 235 °C. It is worthy to note that the C9 carbon of **20f** is a chirality center, whereby diastereomeric mixtures were formed, resulting in a discrete $T_g$ up to 231 °C, which is relatively high for an amorphous solid with relatively low molecular weight. More importantly, no further phase transition was observed upon heating over its $T_g$ to 350 °C. *This result represents a new approach for molecular design of amorphous materials by introducing tetraaryl chiral centers in close proximity to the conjugated chromophore*. These terfluorenes are thermally very stable, the temperature corresponding to a 5% weight-loss upon heating (10 °C/min.) under nitrogen by TGA analyses are ranging from 400 °C to 450 °C.



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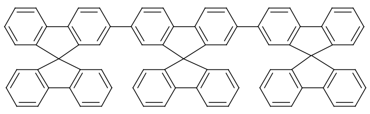
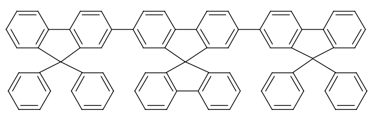
**Scheme 9**



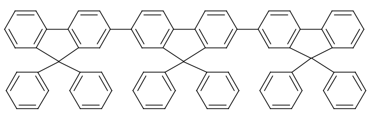
$Q_{\mathrm{film}}$ 90%, $T_{\mathrm{g}}$ 235 $^{\circ}$C

**20a**



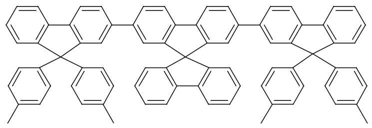
$Q_{\mathrm{film}}$ 82%, $T_{\mathrm{g}}$ 201 $^{\circ}$C

**20b**



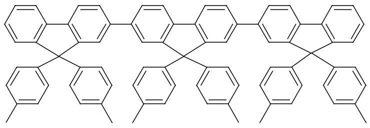
$Q_{\mathrm{film}}$ 78%, $T_{\mathrm{g}}$ 189 $^{\circ}$C

**20c**



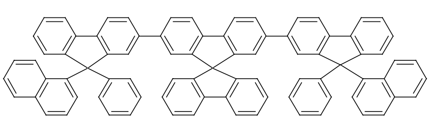
$Q_{\mathrm{film}}$ 87%, $T_{\mathrm{g}}$ 210 $^{\circ}$C

**20d**



$Q_{\mathrm{film}}$ 90%, $T_{\mathrm{g}}$ 204 $^{\circ}$C

**20e**

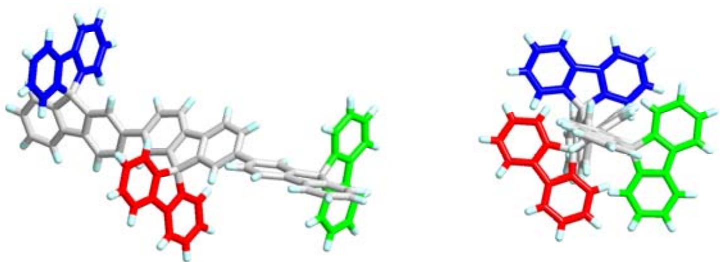


$Q_{\mathrm{film}}$ 66%, $T_{\mathrm{g}}$ 231 $^{\circ}$C

**20f**

The aryl substituents out of the conjugation plane are expected to play important roles on blocking the intramolecular π–π interactions. This is confirmed by the inspection of the X-ray molecular structure of **20a** which indicates that the two outside fluorene moieties of the conjugated chromophore backbone are highly twisted relative to the central one by 134.6$^{\circ}$ and –128.3$^{\circ}$ respectively (Scheme 10a). Which leads the conjugated chromophore to adopt a helical conformation as viewed along the molecular axis (Scheme 10b). This conformation can effectively release the steric interaction between the fluorene moieties and prevent inter-chromophore interactions, resulting in the high quantum yields of photoluminescence of their solid films.

**Scheme 10**



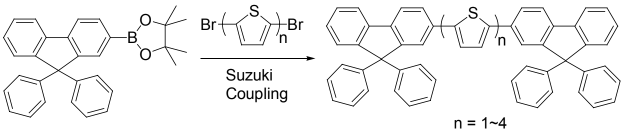
(a) (b)

More importantly, the cyclic voltammetry experiments conducting on these terfluorenes indicated that these terfluorenes have bipolar characteristics, two reversible oxidations and reductions were observed. These significant properties, together with the high quantum yields of their solid thin films, rendering these terfluorenes very promising materials for OLEDs. A highly efficient blue OLED device has been fabricated with excellent properties[17].

## E. 9,9-Diarylfluorene as Functional End-capping Groups

Oligothiophenes with well-defined structures are of great interest due to their unique electronic properties. Oligothiophenes have been used in many applications as active materials, including, for example, field-effect transistors[18] and light emitting diodes[19]. The primary properties of crystalline oligothiophenes can be modified or improved upon by introducing pendant groups into the conjugated backbone[20]. The strategy of introducing different terminal groups to cap oligothiophenes has been used to diversify the structure of a conjugated backbone, giving a new possibility to efficiently tune the electronic and optical properties. For example, oligothiophenes terminated with phenyl or biphenyl groups exhibit interesting electroluminescent behavior[21]. Oligothiophenes with terminal groups bearing diarylamino functional groups recently have been used as efficient emitters and have been reported to be potential hole transporting materials[22]. The introduction of planar fluorene moieties as the end groups of bithiophene facilitates the π–π stacking of the crystals, resulting in the formation of new materials that exhibit extremely high field-effect mobility[23]. Other oligothiophene end-capping groups including diarylboryl, pyridyl, diphenylphosphine, and groups capable of charge transfer have also been documented[24]. We have established an efficient synthesis of a series of novel 9,9-diarylfluorene-capped oligothiophenes (Scheme 11)[25].

**Scheme 11**

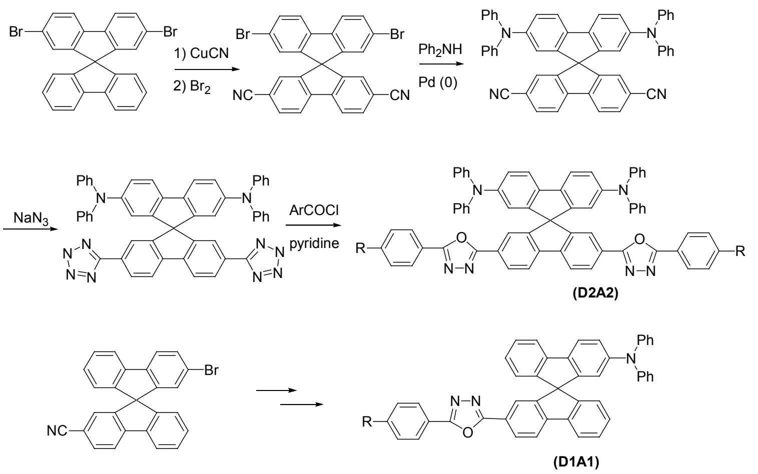


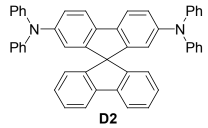
The X-ray crystal structure showed an unusual cis-configuration of bithiophene-cored molecule (n=2), the bulky fluorene end groups play an important role on preventing the intermolecular interactions. The color of the emission can be adjusted by varying the conjugation length of the oligothiophene core. The quantum yields of the homologies are ranging from 0.26 to 0.56. The bulky and rigid terminal groups of the resulting oligomers are also significantly beneficial for their high morphological and thermal stability. More interestingly, These new oligothiophenes exhibit intriguing bipolar properties, which exhibited both reversible oxidation and reduction redox behavior. The introduction the 9,9-diphenylfluorene as the end capping groups ultimately alters the physical properties of the original oligothiophenes. The higher quantum yields of the homologues can be attributed to the rigid skeleton of the fluorene moieties.

## F. Synthesis and Physical Properties of 9,9’-Spirobifluorene-bridged Bipolar Systems

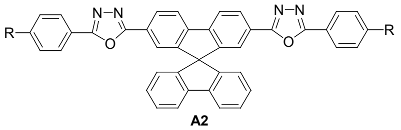
Organic materials based on charge-transfer (CT) interactions play an important role in the design of molecular devices. The acceptor and donor used to compose such materials or devices have been limited to normally planar π-conjugated systems. In such design, increasing the donor or acceptor strength shifts the λmax to a longer wavelength. Three-dimensional designs in molecular devices based on spiro-bridged bipolar systems have been shown to exhibit charge-transfer absorption through "spiroconjuagtion".[26] The phenomenon of spiroconjugtion arising from the effective overlap of the relevant frontier orbital of the orthogonal arranged π-networks with correct antisymmetry. Such orbital interactions result in the formation of new spiroconjugated molecular orbital spanning the entire molecule, leading to an allowed higher energy CT transition. As a result of the weak dependence of the CT band position on the strength of donor and acceptor used to compose the spiro compound, the physical properties can be easily manipulated by the adjustment of the electronic structure within the donor and acceptor almost independently. Thus, the strength of the intramolecular interactions could be controlled by the adjustment of the LUMO energy of the acceptor and the HOMO energy of the donor. In addition, a sipro-bridged conjugated π-network without spiroconjugation exhibits complete intramolecular energy transfer over the spiro center.[27] With the success in manipulating the synthesis of spirobifluorene derivatives, we propose to construct two bipolar π-networks fixed in perpendicular orientations through spirobifluorene. The synthetic pathways towards these two molecules **D2A2,** (**D**: donor; **A**: acceptor**)**, **D1A1** and model compounds **D2** and **A2** has been achieved and illustrated in Scheme 19. The preliminary studies on the photophysics of dipolar system **D2A2** has revealed interesting characteristics with strong charge transfer reactions[28]. Studies on the photophysical behavior of these bipolar systems should provide enough information for understanding the intramolecular charge-transfer or energy-transfer phenomenon. These studies may present a new pattern of excited-state interaction distinguishable from that of exciplex formation in intermolecular quenching and electron transfer through rigid σ-bond system. The structural features of these bipolar systems make these studies of interest. Exciplex emission from the interfacial region of a multilayer OLEDs device is common if the energy levels are ill matched.[29] For our new spiro-bridged bipolar systems, the 1,3,4-oxadiazole-containing conjugated molecule usually used as a good electron-transport material[30] in OLEDs is selected as the acceptor part, in which the triarylamine moiety capable of hole-transporting acts as the donor part. This molecular design with three dimensionalities may conceptually lead to develop new materials that are suitable for OLEDs as an interfacial layer or a bifunctional layer with intramolecular exciplex electroluminescence. Theoretically, it is feasible to adjust the D/A strength as well as the number of spirobifluorene conjugation so that the flow of electrons can be precisely regulated. Such a conceptual design may be advantageously exploited in e.g. photovoltaic devices.

**Scheme 12**





**D2**



**A2**

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