

Tri-, Tetra- and Pentamers of 9,9'-Spirobifluorenes through Full *ortho*-Linkage: High Triplet-Energy Pure Hydrocarbon Host for Blue Phosphorescent Emitter

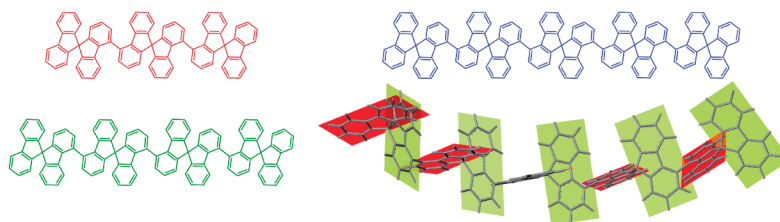
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Received October 7, 2010

ABSTRACT



4,4'-Dibromo-9,9'-spirobifluorene was first synthesized, and from this intermediate, three fully *ortho*-linked tri-, tetra-, and pentamers of 9,9'-spirobifluorenes were constructed. The full *ortho*-linkage impedes the π conjugation of fluorene units, and guarantees their high triplet energies ($E_T = 2.80$ eV). A device with the trimer as the first pure hydrocarbon host material for blue phosphor FIrpic shows a maximum current efficiency of 25 cd/A.

Spiro compounds have been widely applied in organic optoelectronics due to their rigid structures, good solubility and amorphous nature.¹ Among them, 9,9'-spirobifluorene and its derivatives have evoked considerable interest for application in organic light-emitting diodes (OLEDs), photovoltaic cells and field-effect transistors.² Apart from the general properties of

spiro compounds, 9,9'-spirobifluorene and its derivatives exhibit high quantum efficiency and nondispersive ambipolar carrier transporting properties,³ making them desirable host materials in OLEDs. Up to the present, most of the 9,9'-spirobifluorene-based small molecules and polymers are constructed by para-linkage,⁴ which are usually derived from 2-bromo-9,9'-spirobifluorene or 2,7-dibromo-9,9'-spirobifluorene. However, we note that the modifications on the para-linked oligo(9,9'-spirobifluorene)s usually bring about the π conjugation between chromophores, leading to the depreciation of the triplet energy.⁵ Therefore, their usage as host materials for phosphorescent emitters is limited, especially for blue phosphorescent emitters.

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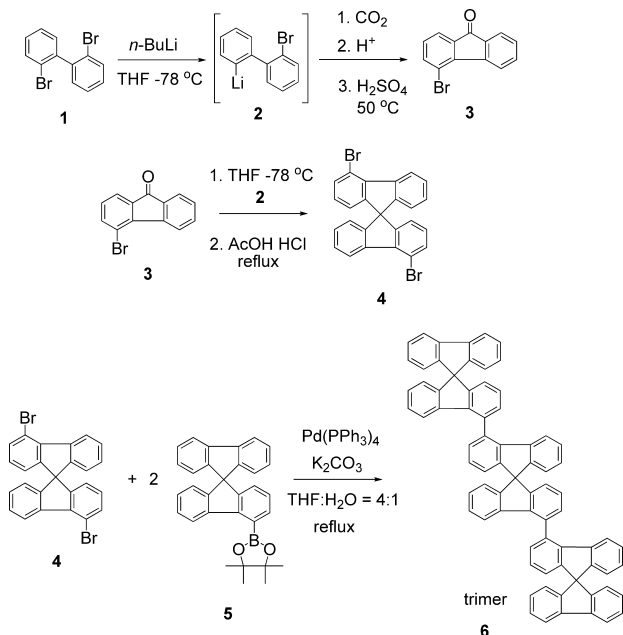
We have previously reported that the oligo(9,9'-spirobifluorene) 24TSF by partial ortho-linkage exhibits a higher triplet energy ($E_T = 2.55$ eV) than its para-linked isomer ($E_T = 2.28$ eV), and 24TSF can be utilized as full-hydrocarbon host material for green and red electrophosphorescence.⁶ In this letter, we report the elegant synthesis of new tri-, tetra- and pentamers of 9,9'-spirobifluorenes by full ortho-linkage. The molecular design impedes the π conjugation of fluorene units, and guarantees their high triplet energies ($E_T = 2.80$ eV). We also report their unique photophysical properties as well as their application as host materials for blue phosphorescent OLEDs.

To obtain the fully ortho-linked oligo(9,9'-spirobifluorene)s, 4,4'-dibromo-9,9'-spirobifluorene (**4**) is a key intermediate, which cannot be synthesized from the direct

with 1 equiv of *n*-BuLi by a lithium-halogen exchange reaction, then reacted with carbon dioxide followed an dehydration in concentrated sulfuric acid to afford 4-bromo-9-*H*-fluoren-9-one (**3**).^{7,8} Afterward, **3** was treated with 1 equiv of (2'-bromobiphenyl-2-yl) lithium (**2**), followed by an intramolecular ring-closure reaction to afford the desired **4** in a good isolated yield of 87%. The fully ortho-linked trimer (**6**) was synthesized by Suzuki coupling reaction of **4** with 2 equiv of 9,9'-spirobifluorene-4-yl pinacol boronic ester (**5**)^{6a} with an isolated yield of 56% (Scheme 1).

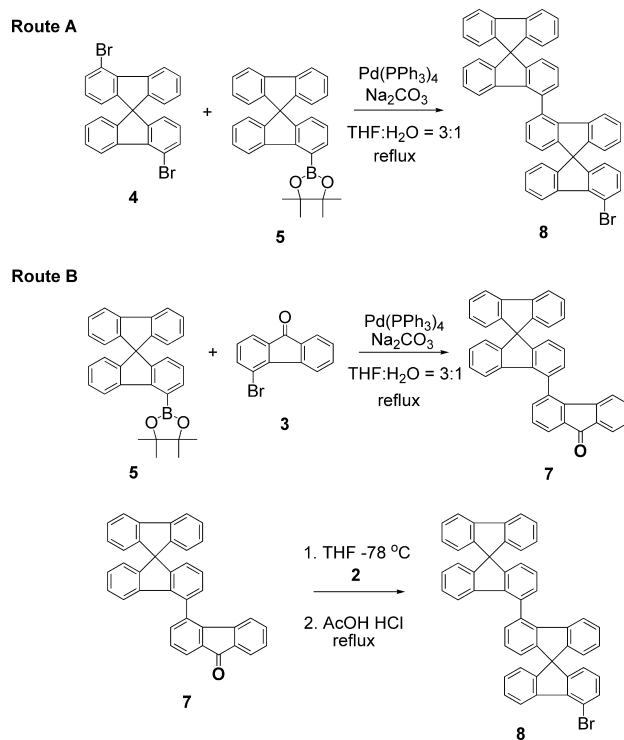
To build up the fully ortho-linked tetramer (**10**), a single ortho-brominated dimer, 4-(4'-bromo-9,9'-spirobifluorene-4-yl)-9,9'-spirobifluorene (**8**) is needed. As shown in Scheme 2, there

Scheme 1. Synthesis of the Key Intermediate 4,4'-Dibromo-9,9'-spirobifluorene **4** and the Fully ortho-Linked Trimer **6**



bromination of 9,9'-spirobifluorene due to the regioselectivity. An alternative synthetic route is adopted as shown in Scheme 1. 2,2'-Dibromobiphenyl (**1**) was initially treated

Scheme 2. Synthesis of the Single ortho-Brominated Dimer **8**



are two synthetic routes for **8**. Though only one step reaction in route A, the yield was low (ca. 20%) due to the formation of the trimer **6**. In route B, 4-(9,9'-spirobifluorene-4-yl)-9-*H*-fluoren-9-one (**7**) was first obtained by combination of **3** and **5** through Suzuki coupling reaction, and then the dimer **8** can be achieved from **7** according to the same strategy mentioned above, with an excellent yield of 91%. Subsequently, **8** was conveniently converted to its pinacol boronic ester **9**. Accordingly, the tetramer **10** can be synthesized by the combination

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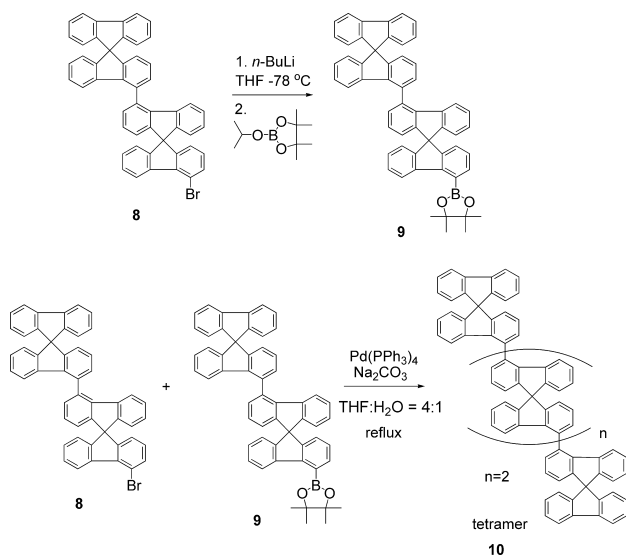
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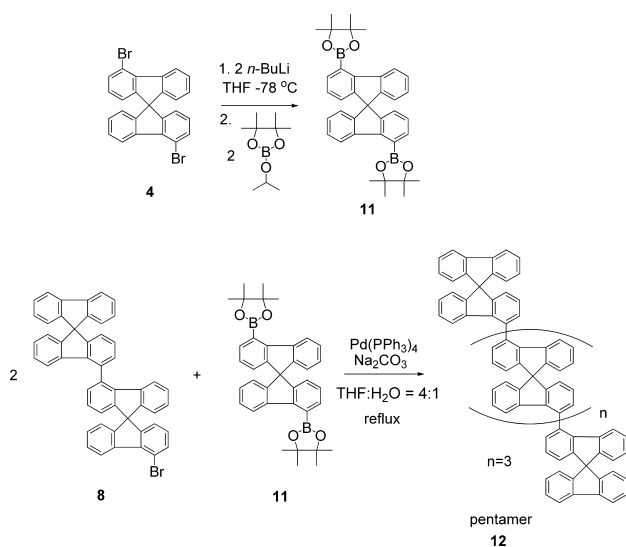
of the dimer **8** and its pinacol boronic ester **9** through Suzuki coupling reaction with an isolated yield of 50% (Scheme 3).

Scheme 3. Synthesis of the Fully ortho-Linked Tetramer **10**



Based on the obtained intermediates, the fully ortho-linked pentamer (**12**) can be facilely constructed (Scheme 4). After converting **4** to 4,4'-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9'-spirobifluorene (**11**), the pentamer **12** was afforded by treating 2 equiv of the dimer **8** and 1 equiv of **11** through Suzuki coupling reaction with a good yield of 80%. All the compounds have been fully characterized by ^1H NMR, ^{13}C NMR, mass spectrometry, and elemental analysis (see Supporting Information).

Scheme 4. Synthesis of the Fully ortho-Linked Pentamer **12**



The glass transition temperatures (T_g) of the three oligomers increase with the enlargement of the molecular system

from 244 °C (trimer), 280 °C (tetramer), to 326 °C (pentamer). The very high T_g of the oligomers enable them to be highly amorphous solids. The three oligomers show irreversible oxidation process in the cyclic voltammetry like the case of the single 9,9'-spirobifluorene unit, possibly due to the unblocked electrochemical active sites of the molecules.⁹ Their HOMO levels evaluated from the onsets of the oxidation potentials are equal (−6.08 eV, relative to vacuum level).

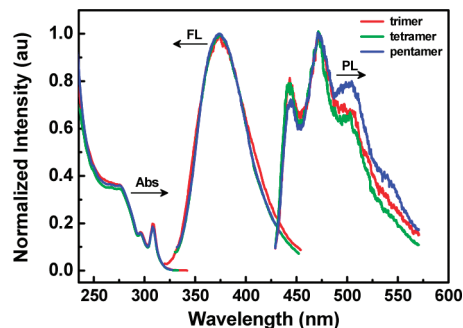


Figure 1. Absorption and emission spectra of the three oligomers in CH_2Cl_2 solution at room temperature and their phosphorescence spectra in film at 77 K.

Figure 1 shows the absorption and fluorescence spectra of the three oligomers in CH_2Cl_2 solution at room temperature and their phosphorescence spectra in film at 77 K. The oligomers show almost identical electronic spectra with the maximum absorption at 308 nm, which is attributed to the $\pi-\pi^*$ transition of the fluorene unit.¹⁰ This contrasts to the fully para-linked oligo(9,9'-spirobifluorene)s,¹¹ which show consistent red shift in the peak wavelength from 334 nm (dimer), 350 nm (trimer) to 360 nm (tetramer) with the backbone length. The optical band gaps (E_g) determined from the onsets of the absorption spectra are 3.93 eV. Similarly, the three oligomers exhibit the same fluorescence spectra with the maximum emissions at 374 nm. Their triplet energies (E_T) are determined to be the same level of 2.80 eV by the highest-energy vibronic sub-band of the phosphorescence spectra. Compared with the para-linked oligo(9,9'-spirobifluorene), namely SSS ($E_T = 2.28$ eV),^{5a} or the partially ortho-linked oligo(9,9'-spirobifluorene), namely 24TSF, ($E_T = 2.55$ eV),^{6a} the fully ortho-linked trimer shows the significantly higher triplet energy. Moreover, the triplet energies remain invariant with the extension of the spirobifluorene units. This indicates that full ortho-linkage of 9,9'-spirobifluorene completely impedes the π conjugation of fluorene units. The optical data are collected in Table 1.

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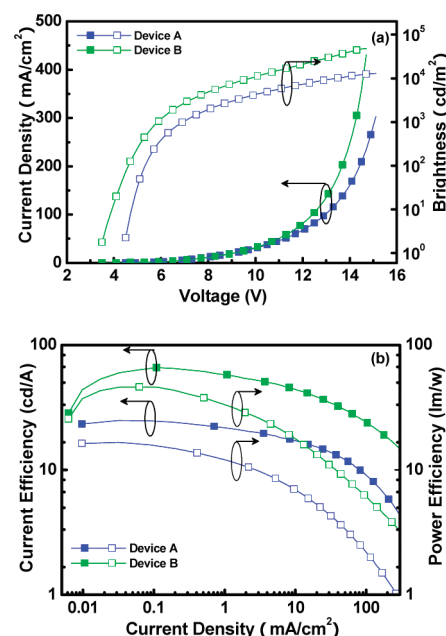
Table 1. Optical Properties of the Three Oligomers

	$\lambda_{\text{abs, max}}$ (nm) ^a	$\lambda_{\text{PL, max}}$ (nm) ^a	Φ_{sol} (%) ^b	HOMO (eV) ^c	LUMO (eV) ^d	E_{T} (eV) ^e
trimer	308	374	63	6.08	2.15	2.80
tetramer	308	374	58	6.08	2.15	2.80
pentamer	308	374	60	6.08	2.15	2.80

^a Measured in CH₂Cl₂ solution. ^b Quantum yields in CH₂Cl₂ solution (9,10-diphenylanthracene in cyclohexane as reference, $\Phi_{\text{F}} = 0.90$). ^c Determined from the onsets of oxidation potentials in CV. ^d Deduced from HOMO and E_{g} . ^e Determined from the phosphorescence spectra in film.

The triplet energies of the three oligomers are high enough for blue phosphorescent emitters, hence we fabricated the devices by using the trimer as host for blue and green phosphorescent emitters. The device configurations are as follows: blue device A: ITO/MoO₃ (10 nm)/NPB (80 nm)/TCTA (5 nm)/ trimer:FIrpic (20 nm)/TPBi (30 nm)/LiF (1 nm)/Al (120 nm); green device B: ITO/MoO₃ (10 nm)/NPB (80 nm)/TCTA (5 nm)/ trimer:Ir(ppy)₃ (20 nm)/TPBi (40 nm)/LiF (1 nm)/Al (120 nm). In these devices, 1,4-bis(1-naphthylphenylamino)-biphenyl (NPB) is used as the hole-transporting material; 4,4',4''-tri(*N*-carbazolyl)triphenylamine (TCTA) is used as exciton blocking material; 1,3,5-tris(*N*-phenylbenzimidazol-2-yl)benzene (TPBi) is utilized as electron transporting as well as hole blocking material; iridium(III) [bis(4,6-difluorophenyl)pyridinato-*N*,C2']picolinate [FIrpic] or iridium(III) *fac*-tris(2-phenylpyridine) [Ir(ppy)₃] is used as the triplet emitter, with optimized doping levels of FIrpic and Ir(ppy)₃ at 8% and 11%, respectively; MoO₃ and LiF serve as hole- and electron-injecting materials, respectively. Current density–voltage–luminance (J–V–L) characteristics and current efficiency, power efficiency versus current density of the devices are shown in Figure 2. Device A displays a typical emission from the blue phosphor FIrpic with CIE coordinates (0.16, 0.33), and achieves a maximum current efficiency of 25 cd/A, a maximum power efficiency of 17 lm/W, and a maximum luminance of 13 073 cd/m² at 15 V. Device B reveals a maximum current efficiency of 66 cd/A, a maximum power efficiency of 46 lm/W, and a maximum luminance of 47 885 cd/m² at 15 V, which are comparable with the results we recently reported.¹² Noticeably, the efficiencies (η_{c}) of the devices decay gently with the increasing current density. At the brightness of 100 cd/m² and 1000 cd/m², the current efficiencies are still as high as 23 cd/A and 19 cd/A for blue device A, 65 cd/A and 54 cd/A for green device B, respectively. This could be attributed to the effective separation of the guest molecules by the unique three-dimensional conformation of the host.

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**Figure 2.** (a) J–V–L characteristics. (b) Current efficiency and power efficiency versus current density of the devices.

In summary, we have successfully synthesized three novel fully ortho-linked oligo(9,9'-spirobifluorene)s from the intermediate 4,4'-dibromo-9,9'-spirobifluorene. We note that the glass transition temperatures of the three oligomers significantly increase with the enlargement of the molecular system; however their absorption and emission peaks show no red shift and their high triplet energies remain invariant. This indicates that full ortho-linkage of 9,9'-spirobifluorene completely impedes the π conjugation of fluorene units. The devices with trimer as host material and FIrpic or Ir(ppy)₃ as guest emitter show maximum external quantum efficiencies of 11.6 and 17.3% for blue and green electrophosphorescence, respectively. This represents the first example of using a pure hydrocarbon small molecule as an efficient host for blue phosphorescent emitter.

Acknowledgment. We thank the National Natural Science Foundation of China (Project Nos. 90922020, 50773057), and the National Basic Research Program of China (973 Program 2009CB623602, 2009CB930603) for financial support.

Supporting Information Available: General experimental information; synthesis and characterization of all intermediates and the three oligomers; DSC and CV curves of the three oligomers; EL spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

OL1024184