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Novel Oligo-9,9′-spirobifluorenes through *ortho*-Linkage as Full Hydrocarbon Host for Highly Efficient Phosphorescent OLEDs

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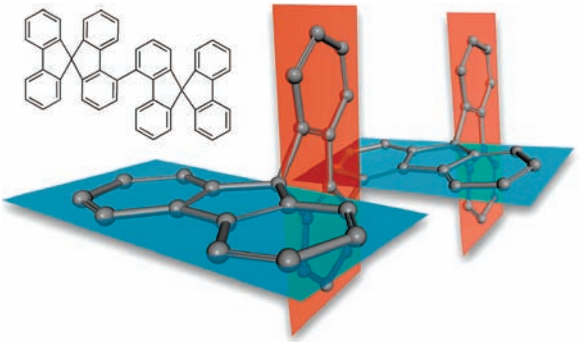
ABSTRACT



4-Bromo-9,9′-spirobifluorene is facilely synthesized, and from this precursor, two *ortho*-linked oligo-9,9′-spirobifluorenes, 44BSF and 24TSF, are constructed. Devices with 24TSF as the full-hydrocarbon host material and Ir(ppy)$_3$ or (ppq)$_2$Ir(acac) as the triplet emitter show maximum external quantum efficiencies of 12.6 and 10.5% for green and red electrophosphorescence, respectively.

Spirobifluorene-based compounds have attracted considerable attention in recent years in organic optoelectronic devices, such as light-emitting diodes, photovoltaic cells, field-effect transistors, and plastic lasers,[1] owing to their high thermal and morphological stabilities, high fluorescent quantum efficiencies, and ambipolar carrier transporting properties.[2] Most of the spirobifluorene-based oligomers and polymers are constructed by *para*-linkage, usually derived from 2-bromo-9,9′-spirobifluorene or 2,7-dibromo-9,9′-spirobifluorene.[3] Up to date, there have been few reports on *ortho*-linked spirobifluorene,[4] possibly due to the lack of a convenient synthetic method. In fact, *ortho*-linked spirobifluorene may have unique photophysical properties and high triplet energy because of the π-conjugation interruption between spirobifluorene units, as well as twisted conformation in molecular architecture.[5] In this regard, the *ortho*-linked spiro-structure is of great significance for further expansion of the scope of spirobifluorene-based optoelectronic materials. For this purpose, 4-bromo-9,9′-spirobifluorene is a good starting point to construct the *ortho*-linked spirobifluorene by a coupling reaction. However, there has

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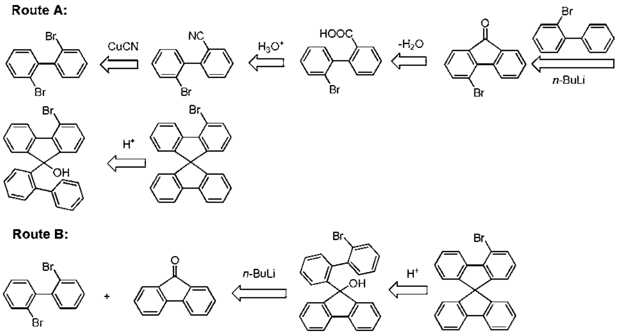
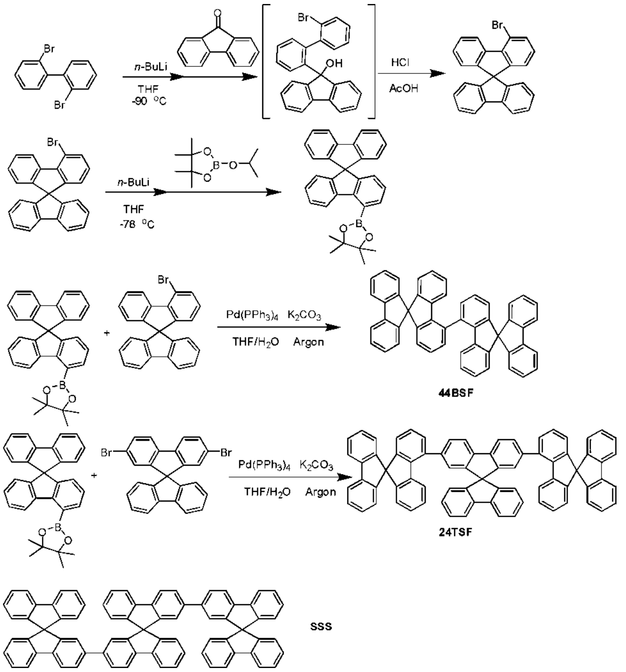
been only one example of an analogue of 4-bromo-9,9′-spirobifluorene, that is, 4-bromo-1,3′-dimethoxy-9,9′-spirobifluorene, which was produced as a byproduct in a complicated multistep synthesis.[6] In this letter, we describe a facile synthesis for 4-bromo-9,9′-spirobifluorene, and from this precursor, two novel oligo-9,9′-spirobifluorenes through *ortho*-linkage are constructed. We also report their photophysical properties and application as host material in phosphorescent organic light-emitting diodes.

As we know, 2-bromo-9,9′-spirobifluorene can be readily synthesized from 2-bromo-9-fluorenone by reacting with a Grignard reagent of 2-bromobiphenyl.[7] However, this method is unsuitable for the synthesis of 4-bromo-9,9′-spirobifluorene because the preparation of the key intermediate 4-bromo-9-fluorenone appears to be time-costly from the retrosynthetic analysis (route A, Scheme 1). To avoid the problem, we designed a new straightforward route B, in which the bromine substituent is introduced on the nucleophile, not the fluorenone. In the new route, 2,2′-dibromobiphenyl is treated with 1 equiv of *n*-BuLi by a lithium-halogen exchange reaction, then reacted with fluorenenone followed an intramolecular ring-closure through Friedel−Crafts reaction to afford the desired 4-bromo-9,9′-spirobifluorene in a good isolated yield of 83%. 4-Bromo-9,9′-spirobifluorene is conveniently converted to its pinacol boronate. Finally, two *ortho*-linked oligo-9,9′-spirobifluorene, namely, 44BSF and 24TSF, are synthesized by Suzuki coupling reaction with yields of 72 and 81%, respectively (Scheme 2). These compounds were fully characterized by ^{1}H NMR, ^{13}C NMR, mass spectrometry, and elemental analysis (see Supporting Information).

Scheme 1. Retrosynthetic Analysis for 4-Bromo-9,9′-Spirobifluorene



Scheme 2. Synthesis of 44BSF and 24TSF



Colorless crystals of 44BSF suitable for X-ray crystallographic analysis were grown by carefully layering a dichloromethane solution of 44BSF with ethanol. Its molecular structure by ORTEP drawing is depicted in Figure 1. It can be seen that the *ortho*-linked fluorene planes form an approximate right angle with a dihedral angle of 88.3°, which means less π-conjugation between the two spirobifluorene moieties. Considering the cross-shaped molecular

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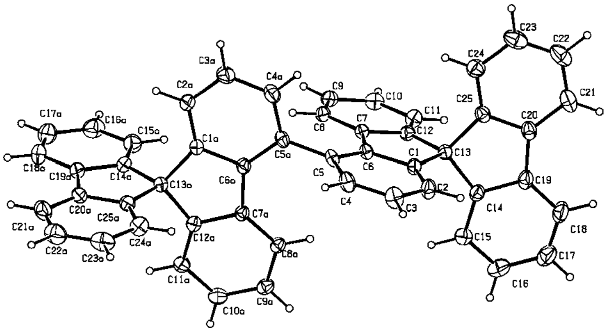

Figure 1. ORTEP diagram of 44BSF.

structure of spirobifluorene, it is quite interesting that the four fluorene units are almost perpendicular to each other. This unique arrangement of the π-systems implies the electronic independence of the two 9,9′-spirobifluorene moieties.

The excellent thermal stability of oligo-9,9′-spirobifluorene is indicated by the high decomposition temperatures (T_d, corresponding to 5% weight loss) of 360 °C for 44BSF and 535 °C for 24TSF in the thermogravimetric analysis. Their glass transition temperatures (T_g) are observed at 170 °C for 44BSF and 232 °C for 24TSF, through differential scanning calorimetry (DSC) (see Supporting Information). Their high thermal and morphological stabilities could be ascribed to the rigid spiro conformation. As a consequence, the novel compounds can form morphologically stable and uniform amorphous films, an essential property for OLEDs upon thermal evaporation.[8]

Figure 2 shows the absorption and emission spectra of 44BSF and 24TSF in CH_2Cl_2 solution at room temperature, and phosphorescence spectra in frozen toluene at 77 K. 44BSF exhibits a sharp peak at 309 nm, while 24TSF shows a low-energy absorption band around 325 nm besides the peak of 309 nm. 24TSF exhibits an emission around 390 nm, which is red-shifted by 17 nm as compared to that of 44BSF. The additional absorption of 24TSF, as well as the bathochromic emission could be attributed to its greater delocalization of π-electrons.

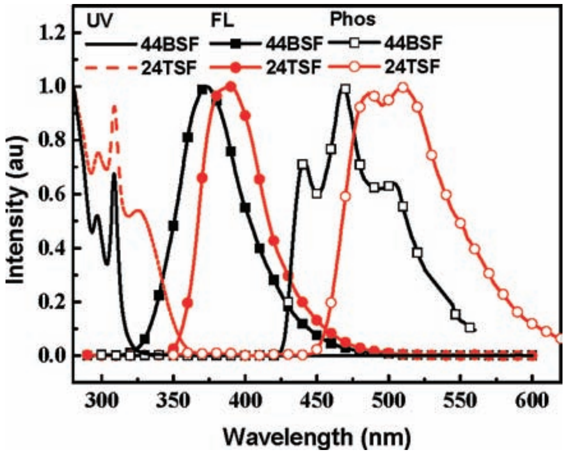

Figure 2. Absorption and emission spectra of 44BSF and 24TSF in CH_2Cl_2 solution at room temperature, and phosphorescence spectra in toluene at 77 K.

The first example of using a full hydrocarbon small molecule as host material for electrophosphorescent devices was reported by Wong et al., and this host is a *para*-linked oligo-9,9′-spirobifluorene (namely SSS, see Scheme 2).[9] As we know, the primary requirement for efficient host material is that the triplet energy (E_T) of host should be higher than that of guest to prevent reverse energy transfer from the guest back to host and confine triplet excitons on guest molecules.[10] The triplet energy of SSS is as low as 2.28 eV, which can only host red electrophosphorescence. The triplet energy of *ortho*-linked 24TSF is determined to be 2.55 eV by the highest-energy vibronic sub-band of the phosphorescence spectrum at 77 K. This value is significantly higher than that of SSS, due to its decreased conjugation and twisted conformation as a result of the *ortho*-linkage. We envisaged that 24TSF may act as appropriate host material for green and red phosphorescent emitters, such as the common green-emitter iridium(III) *fac*-tris(2-phenylpyridine) [$Ir(ppy)_3$, $E_T = 2.42$ eV] and the red-emitter bis(2,4-diphenylquinolyl-N,C^2) iridium (acetylacetonate) [$(ppq)_2Ir(acac)$, $E_T = 2.01$ eV].

To evaluate the performance of 24TSF as a host material, the electrophosphorescent devices were fabricated with a typical structure consisting of multiple organic layers sandwiched between the bottom indium tin oxide (ITO) and the top metal cathode (Al). The device configuration is ITO/MoO_3 (10 nm)/1,4-bis[(1-naphthylphenyl)amino]biphenyl (NPB, 40 nm)/24TSF: $Ir(ppy)_3$ (Device A) or $(ppq)_2Ir(acac)$ (Device B) (30 nm)/2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP, 10 nm)/tris(8-hydroxyquinoline)aluminum (Alq_3, 30 nm)/LiF (1 nm)/Al (100 nm). NPB and Alq_3 are used as the hole- and electron-transporting materials, respectively; $Ir(ppy)_3$ or $(ppq)_2Ir(acac)$ doped in host 24TSF is used as the emitting layer, with optimized doping levels of $Ir(ppy)_3$ at 8% and $(ppq)_2Ir(acac)$ at 6 wt %; BCP is used as the hole and exciton blocking layer; MoO_3 and LiF serve as the hole- and electron-injecting layers, respectively. Current−voltage−luminance (J−V−L) characteristics and current efficiency and power efficiency versus current density of the devices are shown in Figure 3. Device A with $Ir(ppy)_3$ as dopant exhibits a maximum current efficiency of 48.2 cd/A, a maximum power efficiency of 26.8 lm/W, equivalent

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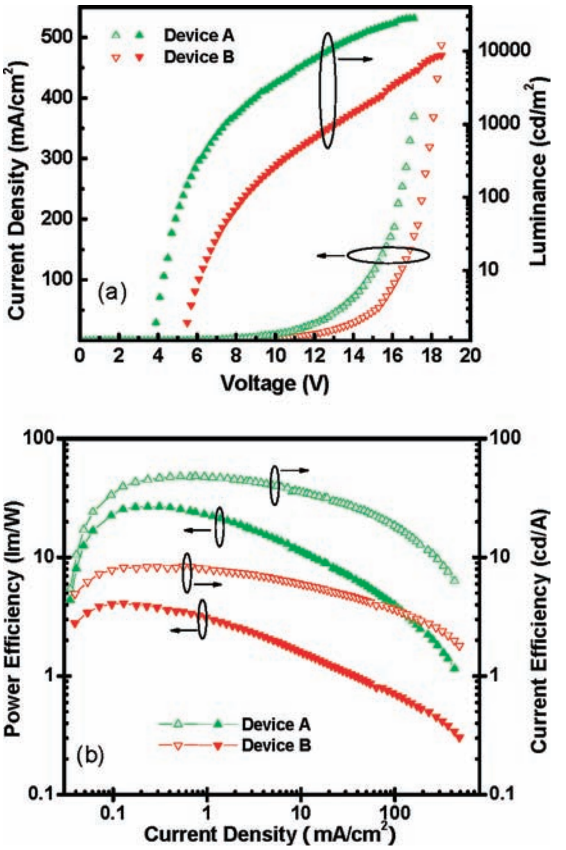

Figure 3. (a) J−V−L characteristics. (b) Current efficiency and power efficiency versus current density of the devices.

to an external quantum efficiency of 12.6%. Device B with $(ppq)_2Ir(acac)$ as dopant shows a maximum current efficiency of 8.4 cd/A, a maximum power efficiency of 4.1 lm/W, and a maximum external quantum efficiency of 10.5%. The device efficiencies (η_c) decay gently with the increasing of current density. At the high brightness of 1000 cd/m^2, the current efficiency is still as high as 45 cd/A for Device A; at the normally practical brightness of 100 cd/m^2, the current efficiency remains 7.8 cd/A for Device B. This could be attributed to effective separation of the triplet guest molecules by the unique three-dimensional conformation of 24TSF.[10] We note that the performances are among the highest for the full hydrocarbon-based host materials and even better than the common carbazole-based 4,4′-bis(9-carbazolyl)-2,2′-biphenyl (CBP) hosted devices.[12]

In summary, we have successfully developed a convenient and efficient synthesis for 4-bromo-9,9′-spirobifluorene, from which we exquisitely synthesized two *ortho*-linked oligo-9,9′-spirobifluorenes, 44BSF and 24TSF. The new compounds exhibit excellent thermal and morphological stabilities owing to the rigid spiro skeleton. We note that the *ortho*-linked oligo-9,9′-spirobifluorene 24TSF has a higher triplet energy than its *para*-linked isomer SSS. Devices with the 24TSF as host material and $Ir(ppy)_3$ or $(ppq)_2Ir(acac)$ as guest show maximum external quantum efficiencies of 12.6 and 10.5% for green and red electrophosphorescence, respectively. This work reveals that the *ortho*-linked spirobifluorene derivatives can be a type of very promising optoelectronic material.

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Supporting Information Available: General experimental information; synthesis and characterization of all intermediates, 44BSF and 24TSF; X-ray structural analysis of 44BSF. This material is available free of charge via the Internet at http://pubs.acs.org.

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