

# Synthesis and Characterization of Heteroatom-Bridged Bisspirobifluorenes for the Application of Organic Light-Emitting Diodes

Cheng-Lung Wu,<sup>†,‡</sup> Chao-Tsen Chen,\*,<sup>†</sup> and Chin-Ti Chen\*,<sup>‡</sup>

<sup>†</sup>Department of Chemistry, National Taiwan University, Taipei 10617, Taiwan <sup>‡</sup>Institute of Chemistry, Academia Sinica, Taipei 11529, Taiwan

**Supporting Information** 

**ABSTRACT:** Pure 2-iodo-9,9'-spirobifluorene was synthesized by an efficient method without troublesome iodination of 9,9-spirobifluorene (SP) or the Sandmeyer reaction of 2-amino-9,9'-spirobifluorene. A series of main group element-bridged bis-9,9'-spirobifluorene derivatives were synthesized via coupling reactions of 2-iodo-9,9'-spirobifluorene and main group element-containing precursors. These heteroatom-bridged bis-spirobifluorenes show large triplet state energy gaps, high glass transition



temperatures, and varied charge-transporting properties advantageous to the host materials for blue phosphorescence organic light-emitting diodes.

rganic materials with a spiromolecular structure have been widely used in organic optoelectronics due to their structural rigidity and high thermal or morphological stabilities.<sup>1</sup> In application of blue fluorescent emitter, the specific rigid structure provided a promising design to achieve intramolecular excimer emission.<sup>2</sup> Specifically, 9,9'-spirobifluorene compounds comprise a famous family known for high fluorescence quantum efficiency, high glass transition temperature, and ambipolar charge-transporting properties.<sup>3</sup> In this work, we focused our attention on the design, synthesis, and characterization of a new series of host materials based on bis-9,9'-spirobifluorene derivatives (SP2X) for blue phosphorescence organic light-emitting diodes (OLED). Main-group elements are designed as the linking elements between two 9,9'-spirobifluorene moieties, such as SP2N (6a), SP2Si (6b),  $SP_2PO$  (6c),  $SP_2O$  (6d), and  $SP_2SO_2$  (6e) (Scheme 1) because of their potential charge (electron or hole)-transporting properties.

Phosphorescent OLEDs have attracted much attention because near 100% internal quantum efficiency can be achieved via utilization of both singlet and triplet excitons. Because of their relatively long emission lifetime, a phosphorescence emitter is doped into a suitable host material in order to alleviate triplet-triplet annihilation. Therefore, an ideal host material needs to have a high triplet energy gap ( $E_T$ ), greater than ~2.60 eV for blue phophorescent dopant FIrpic, for instance.<sup>4</sup> Moreover, an ideal host material should be chargebalanced in order to enhance efficiency of the charge recombination on phosphorescence dopant. Finally, a high glass transition temperature ( $T_g$ ) of the host material is most needed if the morphological stability of the amorphous film is necessary. 9,9'-Spirobifluorene compounds are one of the few materials having both high  $E_T$  (over 2.8 eV) and morphology Scheme 1<sup>a</sup>



<sup>a</sup>Reagents and conditions: (i) NH<sub>3(l)</sub>, 50% Cu<sub>2</sub>O, 0.5% Pd(OAC)<sub>2</sub>, NMP, 800 psi, 130 °C, 24 h; (ii) **1**, Cs<sub>2</sub>CO<sub>3</sub>, Pd(OAC)<sub>2</sub>, P(*t*-Bu)<sub>3</sub>, toluene, reflux, 36 h; (iii) iodobenzene, Cu, K<sub>2</sub>CO<sub>3</sub>, 18-crown-6, o-dichlorobenzene, reflux, 18 h; (iv) (a) *n*-BuLi, THF, -78 °C, 1 h, (b) Cl<sub>2</sub>Ph<sub>2</sub>Si, 12 h; (v) (a) *n*-BuLi, THF, -78 °C, 1 h, (b) Cl<sub>2</sub>Ph<sub>2</sub>Si, 12 h; (v) (a) *n*-BuLi, THF, -78 °C, 1 h, (b) Cl<sub>2</sub>PhP, 18 h, (c) H<sub>2</sub>O<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>, rt, 24 h; (vi) **5**, 10% Cu<sub>2</sub>O, Cs<sub>2</sub>CO<sub>3</sub>, Salox, sulfolane, 140 °C, 72 h; (vii) (a) H<sub>2</sub>O<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>, HOAc, rt, 24 h.

stability  $(T_g > 150 \text{ °C})$ ,<sup>3</sup> which are advantageous to electroluminescence (EL) efficiency and stability of OLEDs.

In terms of synthetic strategy, we were able to prepare  $SP_2X$  series from 2-bromo-, 2-hydroxyl-, or 2-iodo-9,9'-spirobifluorene (i.e., 1, 4, or 5 in Scheme 1). Whereas 1 and 4 can be readily prepared according to the reported procedures,<sup>5</sup> we have encountered difficulty in the preparation of 5. In fact, 5 is

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a previously unknown compound, and no synthesis report can be found in the literature.

In general, there are three synthetic strategies used to prepare monosubstituted 9,9'-spirobifluorene (SP). The first one we tried is similar to the preparation of 1, i.e., synthesis from 2iodo-9-fluorenone by reacting with a Grinard reagent of 2bromobiphenyl.<sup>5</sup> However, such reaction conditions were too harsh to obtain intact 5. The other plausible procedure is a direct iodination on 9,9'-spirobifluorene. The reaction we tried yielded complicate products including mono- and multiple dior triiodo species, which are virtually inseparable from each other, or pure 2 was only obtained in very low yields. Alternatively, 5 can be prepared by the replacement of the amino group of 2-amino-9,9'-spirobifluorene (2) by potassium iodide following a conventional Sandmeyer procedure.<sup>6</sup> However, in addition to biphenyl-, azobenzene-, and phenoltype side products, Sandmeyer reactions are often plagued with position isomers of halide substituents. In this case, 5 was obtained together with 3-iodo-9,9'-spirobifluorene and 9,9'spirobifluorene as well. The separation of 5 from these side products has been proven difficult and hampers further materials application.

Accordingly, a renovated and reliable synthesis has been successfully developed for the preparation of 5 in the present study (Scheme 2).



After modification from our previous synthesis of 2,2′dibromo-9,9′-spirobifluorene,<sup>7</sup> compound **5** was readily prepared from 4-(trimethylsilyl)-2′-bromobiphenyl (7) with a twostep reaction. Compound **5** prepared by our new method was pure with high isolation yields of 83%. The better reactivity of the  $C_{sp2}$ –I bond facilitates the iodine replacement with oxygen or sulfur in the following synthesis of **SP**<sub>2</sub>**O** and **SP**<sub>2</sub>**SO**<sub>2</sub>, where the bromo congener **1** fails to convert.

For the preparation of  $SP_2N$ , one key precursor 2-amino-9,9'-spirobifluorene (2) was synthesized cleanly with high isolation yields. Our synthesis of 2 is different from that of conventional reduction of 2-nitro-9,9'-spirobifluorene or 2,2'dinitro-9,9'-spirobifluorene.<sup>8</sup> The synthesis of 2 was achieved smoothly via copper-mediated amination of 1 under a high pressure of ammonia. For the copper-mediated amination reacion herein, an addition of 0.5 mol % of palladium(II) acetate was found very effective in promoting reaction yields.  $SP_2Si$  and  $SP_2PO$  were facilely synthesized from treating lithium–halogen exchanged 1 with dichlorodiphenylsilane and dichlorophenylphosphine, respectively.

The UV-vis absorption and photoluminescence (PL) spectra of SP<sub>2</sub>X series were studied in dichloromethane (Figure S24, Supporting Information), and data are shown in Table 1. Except for SP<sub>2</sub>N and SP<sub>2</sub>O, the absorption spectra of SP<sub>2</sub>X series exhibit little red-shifting compared with that of SP. The results can lead us to conclude that silicon, phosphine oxide, and sulfur dioxide bridging moieties can break up the extension of  $\pi$ -conjugation between two 9,9'-spirobifluorene moieties. However, due to the  $\pi$ -conjugation nature of the lone-pair

Table 1. Physical Properties of the SP<sub>2</sub>X Series

	SP	$SP_2N$	$SP_2Si$	SP <sub>2</sub> PO	$SP_2O$	SP <sub>2</sub> SO <sub>2</sub>
$\lambda_{\max}^{aba}$ (nm)	297, 309	308, 369	295, 308	307, 319	296, 309	298, 309
$\lambda_{\max}^{\text{fl}a}$ (nm)	328	420	339	348	344	390
$E_{g}^{b}$ (eV)	3.91	3.10	3.82	3.72	3.37	3.57
HOMO <sup>c</sup> (eV)	-5.64	-5.49	-5.87	-5.88	-5.55	-5.71
LUMO <sup>d</sup> (eV)	-1.73	-2.39	-2.05	-2.16	-2.18	-2.14
$T_{g}^{e}$ (°C)	82	153	132	156	149	145
$T_{\rm c}^{\ e}$ (°C)	145	242	223	280	g	219
$T_{\rm m}^{\ e}$ (°C)	206	346	283	324	255	289
$T_{\rm d}^{f}(^{\circ}{ m C})$	257	442	459	429	414	426
$E_{\rm T}^{h}$ (eV)	2.97	2.55	2.86	2.81	2.82	2.83

<sup>*a*</sup>Measured in dichloromethane. <sup>*b*</sup>Optical gap energy estimated from the onset of the absorption spectrum in thin film state. <sup>*c*</sup>Measured in the solid state by a low-energy photoelectron spectrometer (Riken-Keiki AC-2). <sup>*d*</sup>LUMO =  $E_{g_r}$  + HOMO. <sup>*e*</sup>Obtained by differential scanning calroimetry (DSC). <sup>*f*</sup>Obtained by thermogravimetric analysis (TGA). <sup>*g*</sup>Not observed. <sup>*h*</sup>Measured in 2-methyltetrahydrofuran at 77K.

electron on amine nitrogen donor, SP2N display significant redshifting in absorption wavelength. Similarly, the lone-pair electron on aryloxy oxygen donor of SP2O causes absorption wavelength red-shifting but to a smaller extent compared with that of SP<sub>2</sub>N, although SP<sub>2</sub>O exhibits some weak absorption bands extended beyond 350 nm. On the other hand, solution (in dichloromethane) PL spectra of SP<sub>2</sub>X series are all redshifted when compared with that of SP. Although the most redshifting compound is SP2N similar to that observed in absorption spectra, the second most red-shifting compound is SP<sub>2</sub>SO<sub>2</sub> instead of SP<sub>2</sub>O. Different red-shifting trends found for absorption and PL spectra is not uncommon. The absorption energy is basically determined by Frank-Condon excited states, which are transformed to other energy-stabilized states before light emission based on Kasha's rule. Such energystabilized states (or light-emitting states) are dependent on the nature of surrounding matrix of the compound. Therefore, the second most red-shifting PL spectra of SP<sub>2</sub>SO<sub>2</sub> may be attributed to the relatively large molecular dipole moment among the series. The light-emitting state of a compound with larger dipole moment is more susceptible to the surrounding matrix which is dichloromethane solvent in this case. A different red-shifting trend has been observed for the thin film samples, with PL (fluorescence) wavelengths of 335, 432, 390, 380, 387, and 393 nm for SP, SP2N, SP2Si, SP2PO, SP2O, and SP2SO2, respectively. For gauging the difference of  $E_{\rm T}$  in solution and thin film, the time-delayed neat film PL (phosphorescence) spectrum was also recorded for SP2N. When compared with the wavelength (~486 nm) of the solution PL spectrum, the highest energy emission band appears as a shoulder sideband (~498 nm) in the PL spectrum of  $SP_2N$  neat film (Figure 1). Such results illustrate that the rigid and bulge chemical structure of SP greatly hinders the molecular aggregation in condense phase and inhibits  $E_{\rm T}$  from largely decreasing. Except for  $SP_2N$ ,  $E_T$ 's of  $SP_2X$  series are all greater than 2.80 eV, which is sufficiently high for the host material of blue phosphorescent dopant FIrpic. Somewhat different from those red-shifting trends observed for absorption and fluorescence, the second most red-shifting phosphorescence is not from SP<sub>2</sub>SO<sub>2</sub> or SP<sub>2</sub>O but from SP<sub>2</sub>PO. Similar to the dipolar sulfone group of  $SP_2SO_{2i}$  phosphine oxide of  $SP_2PO$  has dipolar characteristics.



Figure 1. Absorption and fluorescence (in  $CH_2Cl_2$ ) and phosphorescence (in 2-Me-THF, 77K) spectra of  $SP_2N$ . Time-delayed neat film PL spectrum at 15 K is also included.

The electrochemical properties of the SP<sub>2</sub>X series should be highly informative about the energy level of frontier molecular orbitals. However, cyclic voltammetry (CV) measurement only acquired the oxidation potentials of SP2N and SP2O and featureless reduction voltammograms were obtained for all SP<sub>2</sub>X series (see Figure S25, Supporting Information). Hence, we estimated the highest occupied molecular orbital (HOMO) energy level of SP2X series in solid state by a low energy photoelectron spectrometer (Riken-Keiki AC-2). The lowest unoccupied molecular orbital (LUMO) energy level was calculated from the HOMO energy level and the optical gap (absorption onset energy) of the materials measured in thin film state. Based on our measurement, HOMO energy levels varied from -5.49 to -5.88 eV, of which SP<sub>2</sub>N and SP<sub>2</sub>O have the higher levels than the other three consistent with the electron-donating nature of the bridging heteroatom. Excluding SP2N and SP2O, SP2PO and SP2SO2 are two materials with deeper LUMO energy levels, which are in accordant with the non- $\pi$ -conjugated electron withdrawing nature of phenylphosphine oxide and sulfone, respectively. Differently, SP2N and  $SP_2O$  have any arylamine and any loxy as a  $\pi$ -conjugated bridging donor, respectively. Such bridging donors potentially induce intramolecular charge transfer (ICT) which decreases LUMO energy level as well.

All five compounds of the SP<sub>2</sub>X series are thermally stable with  $T_d$  414–459 °C, which ensure the materials safely manageable in vacuum-thermal-deposition process. Moreover, all six compounds of the SP<sub>2</sub>X series essentially inherited the high  $T_g$  nature of 9,9'-spirobifluorene because high  $T_g$  in a range of 130–150 °C was observed (see Figure S26, Supporting Information). Figure 2 exhibits the photo image of thin film samples of SP<sub>2</sub>X series on a glass substrate, which were prepared by vacuum-thermal deposition. Whereas thin films of SP<sub>2</sub>N, SP<sub>2</sub>PO, SP<sub>2</sub>O, and SP<sub>2</sub>SO<sub>2</sub> are transparent, both thin films of SP and SP<sub>2</sub>Si are totally opaque and semiopaque, respectively. Nontransparent feature of the samples can be attributed to the relatively low  $T_g$  of SP (82 °C) and SP<sub>2</sub>Si (132



Figure 2. Photo images of thin film samples on glass substrate: SP, SP<sub>2</sub>N, and SP<sub>2</sub>Si (top row from left to right); SP<sub>2</sub>PO, SP<sub>2</sub>O, and SP<sub>2</sub>SO<sub>2</sub> (bottom row from left to right).

°C), which are prone to submicrometer-size aggregation scattering visible light.

Four SP<sub>2</sub>X-hosted FIrpic dopant OLED devices were fabricated by sequential thermal vacuum deposition of thin film layer of organic material and LiF–Al as the final cathode electrode on ITO (indium–tin-oxide)-coated glass substrate, ITO/NPB (40 nm)/TCTA (10 nm)/SP<sub>2</sub>X:10% FIrpic (20 nm)/TPBI (30 nm)/LiF (1 nm)/Al (100 nm). As clearly shown in the data (Figure 3 and Table 2), OLEDs having



Figure 3. Electroluminescence characteristics of OLEDs.

Table 2. Characteristics of OLEDs

	$\max_{\rm (cd/m^2)}^{\rm max \ L}$	L, EQE, voltage $(cd/m^2, \%, V)^a$	max efficiency (%, cd/A, lm/W)	CIE $(x, y)^b$			
SP <sub>2</sub> Si	5845	208, 5.0, 6.6 2043, 4.0, 9.4	5.6, 12.6, 8.1	(0.17, 0.38)			
SP <sub>2</sub> O	7579	191, 4.5, 6.2 1598, 3.8, 8.6	4.5, 9.6, 6.1	(0.17, 0.39)			
SP <sub>2</sub> PO	6405	258, 5.9, 4.9 2204, 5.0, 7.5	6.0, 13.1, 8.9	(0.17, 0.41)			
SP <sub>2</sub> SO <sub>2</sub>	6200	272, 6.1, 5.1 2164, 5.0, 7.6	6.1, 13.4, 8.7	(0.19, 0.42)			
'At 2 and 20 mA/cm <sup>2</sup> , respectively. <sup><i>b</i></sup> At ~7 V.							

SP<sub>2</sub>PO or SP<sub>2</sub>SO<sub>2</sub> as the host material exhibit much better performance than SP<sub>2</sub>Si and SP<sub>2</sub>O, in terms of external quantum efficiency (%), luminous efficiency (cd/A), or power efficiency (lm/W). We may attribute such results to the bipolar properties of host materials, SP<sub>2</sub>PO and SP<sub>2</sub>SO<sub>2</sub>. Both phenylphosphine oxide and sulfur dioxide bridging moieties are electron deficient functional groups that enhance the electron transporting ability of SP<sub>2</sub>X host materials, of which hole transporting is the main characteristic. Considering the charge balance of OLEDs, SP<sub>2</sub>PO and SP<sub>2</sub>SO<sub>2</sub> can be expected to be better host materials than SP<sub>2</sub>Si or SP<sub>2</sub>O.

In order to understand the hole and electron transporting nature of  $SP_2X$  series, we also fabricated two kinds of singlecharge carrier-dominated devices for exploring the nature of material charge carrier in terms of the current density of such devices. The hole-dominated device has a configuration of ITO/NPB(40 nm)/TCTA(10 nm)/SP<sub>2</sub>X(15 nm)/NPB(20 nm)/Al(100 nm). The electron-dominated device has a configuration of ITO/BCP(10 nm)/SP<sub>2</sub>X(15 nm)/TPBI(20 nm)/LiF(1 nm)/Al(100 nm). As shown in the inset of Figure 4, we used high-lying LUMO NPB to limit the electron carrier in a hole-dominated device and low-lying HOMO BCP and TPBI to limit the hole carrier in electron-dominated device.



Figure 4. Current density characteristic of the hole-dominated (top) and electron-dominated (bottom) devices.

Considering the current density of hole-dominated devices studied herein (Figure 4 top), the results indicate that the hole mobility of SP<sub>2</sub>X series is descending in order of  $SP_2N \gg SP_2O > SP_2Si > SP_2PO$  and  $SP_2SO_2$ . The situation of the current density of electron-dominated device is quite similar but in a reverse order (Figure 4 bottom). The magnitude of current density clearly is decreasing in the order of  $SP_2PO > SP_2SO_2 > SP_2Si > SP_2O > SP_2N$ , which is accordant with the anticipated order of material electron mobility based on the structure feature of electron deficient bridging moiety.

In summary, we have successfully synthesized and characterized a series of heteroatom-bridged bis-spirobifluorene derivatives SP<sub>2</sub>X. Regarding material synthesis, we were able to synthesize previously unknown 2-iodo-9,9'-spirobifluorene. We have reported an improved method of high-yield synthesis of 2-amino-9,9'-spirobifluorene. Except for SP<sub>2</sub>N, these bisspirobifluorene new compounds have sufficiently high E<sub>T</sub> as host material for FIrpic blue phosphorescent dopant in OLED. Most of them are morphologically stable with  $T_g > 140$  °C. We have demonstrated that the performance of such OLEDs is highly dependent on charge carrier nature. Based on our device data, bipolar SP<sub>2</sub>PO and SP<sub>2</sub>SO<sub>2</sub> outperform SP<sub>2</sub>Si and SP<sub>2</sub>O because of their electron-transporting characteristics.

# ASSOCIATED CONTENT

## **S** Supporting Information

Synthetic details, structural characterizations, physical characterizations, and OLED fabrication and measurement. This material is available free of charge via the Internet at http:// pubs.acs.org.

## AUTHOR INFORMATION

### **Corresponding Authors**

\*E-mail: chintchen@gate.sinica.edu.tw.

\*E-mail: chenct@ntu.edu.tw.

# Notes

The authors declare no competing financial interest.

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