Bis-Sulfone- and Bis-Sulfoxide-Spirobifluorennes: Polar Acceptor Hosts with Tunable Solubilities for Blue-Phosphorescent Light-Emitting Devices


Abstract: Bis-sulfone- and bis-sulfoxide-spirobifluorenes are a promising class of high-triplet-energy electron-acceptor hosts for blue phosphorescent light-emitting devices. The molecular design and synthetic route are simple and facilitate tailoring of the solubilities of the host materials without lowering the high-energy triplet state. The syntheses and characterization (including single crystal structures) of four electron-accepting hosts are reported; the trend in their reduction potentials is consistent with the electron-withdrawing nature of the sulfone or sulfoxide substituents. Emission maxima of 421–432 nm overlap with the MLCT absorption of the sky-blue emitter bis(4,6-difluorophenylpyridinato)(picolinate)iridium(III) (FIrpic), allowing effective energy transfer from the acceptor hosts to FIrpic. Theoretical calculations show that the introduction of sulfone groups leads to better electron acceptors compared to analogous phosphine oxide functionalized hosts and, at the same time, preserves the energy of the lowest-lying triplet above that of the FIrpic emitter. The new hosts have been tested in phosphorescent light-emitting electrochemical cells (LECs). Large effects of the various solubilizing moieties on the device performance are observed and discussed.

Introduction

Organic light-emitting diodes (OLEDs) promise to have a great potential for high efficiency using high triplet energy, good electron-transport properties, and good color purity.[1] Moreover, the polar PO group can be used in modifiers to lower the work function of metal electrodes.[3] We have recently reported the advantage of a PO-acceptor host in phosphorescent light-emitting electrochemical cell (LEC) devices.[4]

Kippelen and coworkers have shown that bis-sulfonyl-biphenyl is a good acceptor host for blue OLEDs.[7] The sulfone group lowers the LUMO energy more than the PO group.[7] Sasabe et al.[8] have recently used a terphenyl-sulfone derivative to obtain highly efficient blue multi-layer OLEDs. However, the low solubility of these hosts coupled with the multi-layer device architecture requires the use of expensive vapor-deposition techniques.

The introduction of sulfone and sulfoxide groups in host structures[9] is attractive for several reasons: i) the acceptor groups exert a strong inductive electron-withdrawing effect, which lowers both the HOMO and LUMO energies of the triplet synthon and improves electron injection; ii) the heteroatom interrupts conjugation to neighboring \( \pi \)-systems and preserves the high-energy triplet of the host; iii) molecules with strongly polarized SO bonds can be expected to function as electrode modifiers analogously to those bearing PO groups; iv) the simplicity and broad scope of the sulfone/sulfoxide chemistry is highly appealing.[7, 10]

Here we report the design, synthesis, and photophysical and electrochemical properties of four electron-acceptor hosts:

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Supporting information for this article is available on the WWW under http://www.chemeurj.org/ or from the author.
SPSO1, SPSO2, SPSO3, and SPSX (Scheme 1). The experimental study is complemented by theoretical calculations. The sulfoxide functionalization (not previously reported in host materials in LECs) should give rise to higher-energy triplet materials. The new hosts were tested in LECs, and the influence of the various solubilizing moieties on the photophysical properties and the LEC performance was investigated. The spirobifluorene moiety is generally preferred over smaller biphenyl structures as it leads to more stable amorphous thin-film structures. However, the structural rigidity of spirobifluorenene tends to hamper solution processing.

**Scheme 1.** Chemical structures of the electron-acceptor host compounds.

**Results and Discussion**

**Synthesis and NMR spectroscopic characterization:** All hosts were synthesized from the commercially available 2,7-dibromo-9,9′-spirobifluorene. Reaction with the appropriate thiol yielded the bis-thioether derivatives 1–3 (Scheme 2) which were subsequently oxidized to the final acceptor hosts. The top reaction in Scheme 2 was achieved through either aromatic nucleophilic (S_NAr) substitution (method a) or Pd-cross-coupling (method b, see the Supporting Information) to give 1 in good yield. Alternatively, 1 was synthesized starting from 2,7-bis(phenylthio)-9H-fluoren-9-one (4, see the Supporting Information). We note that 4 can also be used to design mixed n- and p-type high-energy triplet cores. Compound 4 was treated with diphenyl-2-yl magnesium bromide to give 1 in 44% over 3 steps (method c, see the Supporting Information). Due to its simplicity, the S_NAr reaction (method a in Scheme 2) was preferred over the transition-metal catalyzed reaction to give the bis-thioethers. Thus, compounds 2 and 3 were obtained by applying the S_NAr method (Scheme 2). However, the Pd-catalyzed cross-coupling methodology offers a viable alternative if the thiol precursor is not readily accessible. A long reaction time was required to obtain 2, probably due to the steric hindrance of the mesitylene-CH_3 groups in ortho-position.

![Scheme 2. Synthetic routes to obtain the thioethers.](image)

![Scheme 3. Selective oxidation of the various thioethers. Reaction conditions are listed in Table 1.](image)

To afford the final acceptor hosts, different oxidation conditions were tested (Table 1). Selective and stepwise oxidation of the symmetric bis-thioethers 1–3 gave the bis-sulfoxide SPSX and the bis-sulfoxides SPSO1, SPSO2, and SPSO3 (Scheme 3). All hosts were obtained by metal-catalyst-free oxidation reactions using H_2O_2 or mCPBA as oxidant.

Selective oxidation of 1 with an equimolar amount of H_2O_2 at room temperature gave the bis-sulfoxide SPSX. The presence of two stereogenic sulfur centers leads to the formation of the enantiomeric R,R- and S,S-pair and the R,S-meso-form. The ^1H and ^13C NMR spectroscopic data show that SPSX exists as a 1 : 1 mixture of diastereoisomers (R,R/S,S and meso), consistent with there being no inversion at sulfur on the NMR spectroscopic
timescale at 295 K. Oxidation of bis-thioether 1 with mCPBA\(^{[16]}\) was not as selective giving the asymmetric sulfone side-product 5 (see the Supporting Information). Treatment of 1 with an excess of H\(_2\)O\(_2\) gave exclusively the bis-sulfone SPSO1 in high yield. High temperatures decreased the reaction time and led to higher yields of 1.

<table>
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<tr>
<th>Table 1. Conditions for the oxidation of the bis-thioethers.(^{[16]})</th>
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<td>Substrate</td>
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<tr>
<td>1</td>
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<td>1</td>
</tr>
<tr>
<td>1</td>
</tr>
<tr>
<td>1</td>
</tr>
<tr>
<td>2</td>
</tr>
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</table>

[a] Entries 1, 4–6 in the table are described in the main paper; entries 2 and 3 are given in the Supporting Information. [b] Solvent systems: A = AcOH (CHCl\(_3\)), B = CH\(_3\)Cl, C = AcOH\(\cdot\)EtOAc.

Oxidation of 2 afforded the bis-mesitylsulfone SPSO2 in good yield. Similarly, oxidation of 3 gave SPSO3 in satisfactory yield. While conversions of 1 and 3 required the use of chlorinated solvents during the oxidation, oxidation of 2 to SPSO2 proceeded smoothly in ethyl acetate. This points to the improved solubilizing effect of the mesityl group. All new compounds were fully characterized by \(^1\)H and \(^13\)C NMR and IR spectroscopies, mass spectrometry and elemental analysis.

Crystal structures of SPSO1-\(2\)CH\(_2\)Cl\(_2\), SPSO2, and SPSO3: Single crystals of SPSO1-\(2\)CH\(_2\)Cl\(_2\) were grown from CHCl\(_3\) overlaid with MeOH. X-ray quality crystals of SPSO2 were obtained from a recrystallization of the bulk material from cyclohexane and toluene, and those of SPSO3 were grown from a CHCl\(_3\) solution of the compound overlaid with n-hexane. The structures of the three compounds were determined by single crystal X-ray diffraction. SPSO1-\(2\)CH\(_2\)Cl\(_2\) crystallizes in the space group \(P2_1/c\) with one molecule and two disordered CH\(_2\)Cl\(_2\) molecules in the asymmetric unit. Each solvent molecule has been modeled over two positions with fractional occupancies of 0.70/0.30 and 0.84/0.16 respectively. Figure 1a shows the structure of the SPSO1 molecule with selected bond parameters given in the figure caption. SPSO2 and SPSO3 both crystallize in the \(C2/c\) space group with half the molecule in the asymmetric unit; the second half is generated by a 2-fold axis (Figure 1b and 1c).

Figure 1. X-ray structures of (a) SPSO1 in SPSO1-\(2\)CH\(_2\)Cl\(_2\), (b) SPSO2, and (c) SPSO3. Solvent molecules are omitted for clarity. Ellipsoids plotted at the 40% probability level. Selected bond parameters: SPSO1: S1–O1 = 1.4419(13), S1–O2 = 1.4429(12), S2–O3 = 1.4347(17), S2–O4 = 1.4471(18), C16–S1 = 1.7626(15), C26–S1 = 1.7632(16), C23–S2 = 1.7679(17), C32–S2 = 1.7563(17) Å; C26–S1–C16 = 105.72(7), C26–S1–O1 = 108.05(8), C16–S1–O1 = 107.73(7), C26–S1–O2 = 107.78(7), C16–S1–O2 = 107.25(7), O1–S1–O2 = 119.52(8), C26–S2–C32 = 105.08(8), C23–S2–O3 = 107.33(10), C32–S2–O3 = 108.37(9), C23–S2–O4 = 107.73(9), C32–S2–O4 = 107.37(10), O3–S2–O4 = 120.02(12)\(^{[2]}\). SPSO2: S1–O1 = 1.4389(10), S1–O2 = 1.4373(10), C12–S1 = 1.7753(12), C14–S1 = 1.7859(13) Å; C14–S1–C12 = 106.93(9), C14–S1–O1 = 107.60(6), C12–S1–O1 = 107.70(6), C14–S1–O2 = 109.28(6), C12–S1–O2 = 107.09(6), O1–S1–O2 = 117.75(6)\(^{[2]}\) (symmetry code i = 1–x, y, 1/2–z). SPSO3: S1–O1 = 1.4406(11), S1–O2 = 1.4427(12), C10–S1 = 1.7680(15), C14–S1 = 1.7705(17) Å; C14–S1–C10 = 103.68(7), C14–S1–O1 = 109.70(7), C10–S1–O1 = 108.16(7), C14–S1–O2 = 107.74(7), C10–S1–O2 = 108.13(7), O1–S1–O2 = 118.43(7)\(^{[2]}\) (symmetry code i = 1–x, y, 1/2–z).
The X-ray diffraction data confirm that the compounds possess the expected structures, with bond parameters that are similar to one another and which are consistent with other organic sulfones.[16] Dominant packing interactions in SPSO1·2CH₂Cl₂ involve short S–O···HC and Cl···HC contacts. In addition to exhibiting short SO···HC contacts of 2.51 Å, molecules of SPSO2 pack so that centrosymmetric pairs of fluorene domains interact through weak face-to-face π-interactions (Figure 2). Although the interplane separation is 3.1 Å, the intercentroid distance between arene rings is too large (4.9 Å) for this to be more than a very weak contact. Short S–O···HC contacts are also a dominant feature of the molecular packing in SPSO3. The n-pentyl chain is in a partially folded conformation and is accommodated in a cleft between two fluorene domains of adjacent molecules (Figure 3). Short CH···π contacts operate between the two methylene units and the arene ring (Figure 3).

Electrochemical and photophysical studies: Reversible reduction processes were observed for compounds SPSO1–3 at similar potentials (E_{1/2}^{red}, Table 2 and Figure 4). This is in agreement with the Hammett constants reported for SO₂-aryl (σ = 0.68) and SO₂-alkyl-substituents (σ = 0.72–0.77) indicating a similar electron-withdrawing strength for both groups.[17] In contrast, E_{1/2}^{red} for SPSX is shifted to more negative potential (Figure 4 and Table 2).

Table 2. Photophysical and electrochemical data.

<table>
<thead>
<tr>
<th>Host</th>
<th>E_{1/2}^{red} (V)</th>
<th>λ_{abs}^{bi} (nm)</th>
<th>λ_{em}^{bi} (nm, eV)</th>
</tr>
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<tbody>
<tr>
<td>SPSO1</td>
<td>−2.00</td>
<td>284, 330</td>
<td>432, 2.87</td>
</tr>
<tr>
<td>SPSO2</td>
<td>−2.07</td>
<td>285, 327</td>
<td>421, 2.95</td>
</tr>
<tr>
<td>SPSO3</td>
<td>−2.12</td>
<td>279, 322</td>
<td>422, 2.94</td>
</tr>
<tr>
<td>SPSX</td>
<td>−2.24</td>
<td>273, 326</td>
<td>380, 3.26</td>
</tr>
</tbody>
</table>

[a] First reduction wave, measured in CH₃CN with [TBA][PF₆] against Fc/Fc⁺ as internal reference. [b] Measured in CH₃CN at 298 K (1 × 10⁻⁵ M).

The absorption and the photoluminescence (PL) spectra of the sulfoxide and sulfone hosts are shown in Figure 5. The structured absorption observed above 270 nm for all four compounds is attributed to π→π* transitions centered on the spirobifluorene core. The bis-sulfonly-functionalized hosts exhibit very similar PL spectra with a maximum emission, λ_{em}, in the range of 421–432 nm. This emission overlaps well with the This emission overlaps well with the metal-to-ligand charge transfer (MLCT) absorption of the sky-blue emitter bis(4,6-difluorophenylpyridinato)(picolinato)iridium(III) (FIrpic),[18] enabling efficient energy transfer from the bis-sulfone acceptor hosts to FIrpic.[7] The PL emission maxima of the bis-sulfoxide SPSX is shifted by 50 nm into the deep-blue/near-UV compared to the bis-sulfones.[11]
Theoretical calculations: To gain further insight into the electrochemical and photophysical properties, the molecular and electronic structures of the sulfoxide and sulfone hosts were investigated by performing density functional theory (DFT) calculations at the B3LYP/6-31G** level in the presence of the solvent (acetonitrile). The non-substituted 9,9’-spirobifluorene molecule (SP) and the 2,7-bis(diphenylphosphoryl)-9,9’-spirobifluorene phosphine oxide (SPPO13) were also calculated at the same theoretical level as reference systems for comparison purposes.

The molecular geometries of the substituted systems were fully relaxed with the two substituent groups pointing to different sides of the fluorene plane to which they are attached and converged to C2-symmetry conformations (see Figure S1 in the Supporting Information). Calculations correctly reproduce the structural features obtained from X-ray single-crystal analysis for SPSO1–3. The fluorene moieties are almost orthogonal forming dihedral angles of about 88.5º and the sulfone groups exhibit near-tetrahedral structures. For instance, SPSO1 is computed to have average C–S–C, C–S–O, and O–S–O bond angles of 105.85, 107.58, and 119.87º, respectively, in very good accord with the experimental X-ray average values (105.40, 107.70, and 119.77º, respectively). Calculations predict a linearly extended conformation for the n-pentyl chains attached to the sulfur atoms in the SPSO3 molecule. The folded conformation observed experimentally (Figure 1c) is stabilized by the interaction between adjacent molecules.

Figure 6 compares the electron density contours calculated for the highest-occupied (HOMO) and lowest-unoccupied molecular orbital (LUMO) of SPSO1, as a representative example, with those computed for non-substituted spirobifluorene. The topology of the frontier MOs of all the other hosts is similar to that depicted for SPSO1 (see Figure S2 in the Supporting Information). Table 3 collects the energies calculated for the HOMO, the LUMO, and the HOMO–LUMO gap for all the hosts and SP. It also includes the electron affinities computed as the energy difference between the neutral host and its radical anion at their respective minimum-energy optimized geometries.

The SP molecule presents a D1h symmetry with two equivalent fluorene moieties over which molecular orbitals are equally distributed. Functionalization lowers the molecular symmetry and breaks the equivalence of the fluorene moieties. As observed in Figure 6 for SPSO1, the LUMO in the host is fully localized on the fluorene to which the sulfone groups are attached, whereas the HOMO mainly resides on the non-functionalized fluorene. This suggests that, upon reduction, electron injection takes place on the functionalized fluorene fragment. This is illustrated in Figure 7 for SPSO1, for which the unpaired electron in the anion is fully localized on the substituted fragment.
Functionalization with electron-withdrawing sulfone groups determines a drastic stabilization of the LUMO that lowers in energy from −0.97 eV in SP to −2.09 eV in SPSO1. The stabilization of the HOMO is significantly smaller (0.22 eV) because the sulfone groups do not participate in this orbital (Figure 6). The HOMO−LUMO gap therefore decreases by almost 1 eV in passing from SP (4.85 eV) to SPSO1 (3.94 eV). Compared to SPP013 bearing phosphine PO groups, the sulfone SO2 groups in SPSO1 lower the energy of the LUMO in a higher degree (−2.09 vs. −1.73 eV) and leads to a higher electron affinity (2.39 vs. 2.02 eV). This supports the results previously found for biphenyl-based hosts,[7] and confirms the higher electron-withdrawing character of the sulfone group compared with the phosphine group.

The LUMO of SPSO2 (−1.95 eV) and SPSO3 (−1.97 eV) are calculated to be slightly higher in energy than the LUMO of SPSO1 (−2.09 eV). The destabilization is due to the fact that this orbital is delocalized over the terminal phenyl groups for SPSO1 (Figure 6), whereas it remains more confined over the fluorene moiety for SPSO2 and especially for SPSO3 (Figure S2). This suggests that SPSO1 presents a more effective electronic conjugation through the sulfone groups than SPSO2 and SPSO3. The sulfoxide groups in SPSX exert a weaker electron-withdrawing effect than the sulfone groups and, as a consequence, induce a smaller stabilization of the LUMO that is calculated at −1.62 eV. The computed electron affinity decreases along the series SPSO1 (2.39 eV) > SPSO2 (2.29 eV) > SPSO3 (2.28 eV) > SPSX (2.09 eV) in good agreement with the more negative reduction potentials measured along this series (−2.02, −2.07, −2.12, and −2.24 V, respectively, Table 2). The values obtained for the electron affinities suggest that the sulfone and sulfoxide hosts are better electron acceptors than the phosphine oxide SPP013 host for which an EA of 2.02 eV is computed. Owing to the almost constant energy of the HOMO (Table 3), the HOMO−LUMO gap increases along the series SPSO1 (3.95 eV) < SPSO2 (4.07 eV) < SPSO3 (4.07 eV) < SPSX (4.33 eV) pointing to a blue shift of the absorption and emission wavelengths along the series.

Time dependent DFT (TD-DFT) calculations were performed on the geometry of the electronic ground state (S0) to obtain information about the nature of the singlet excited states (S1) involved in the absorption spectra. Calculations assign the low-intensity band above 300 nm (Figure 5) to the S0 → S1 electronic transition calculated around 3.4−3.7 eV for SPSO1−3 and SPSX (Table S1 in the Supporting Information). This transition has a charge transfer (CT) nature since it implies an electron promotion from the HOMO, located on the non-functionalized fluorene, to the LUMO, spreading over the functionalized fluorene (Figure 6). The CT character of the transition explains the low intensity of the absorption band. The more intense band observed between 250 and 300 nm involves excitations to several excited singlets calculated in the 4.0−4.5 eV range with high oscillator strengths (f > 0.1, Table S1). These transitions mainly imply π→π* excitations within the spirofluorene core.

To obtain an estimation of the emission energies, the geometry of the first singlet excited state was fully relaxed using the TD-DFT method. According to the calculations, emission takes place from the charge transfer S1 state resulting from the HOMO→LUMO excitation for all the hosts. The emission energies follow the trend expected from the HOMO−LUMO gaps, with the value calculated for SPSO1 (2.77 eV, 448 nm) slightly red shifted compared with SPSO2 (2.84 eV, 437 nm) and SPSO3 (2.83 eV, 438 nm) in excellent agreement with the emission maxima measured experimentally (432, 421, and 422 nm, respectively, Table 2). For SPSX (2.96 eV, 419 nm), calculations reproduce the shift to bluer wavelengths observed experimentally (Figure 5), although the predicted shift with respect to SPSO1 (29 nm) underestimates the experimental value (52 nm).

<table>
<thead>
<tr>
<th>Host</th>
<th>E(S0→T1)</th>
<th>ΔE(T1,S0)</th>
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<tr>
<td>SP</td>
<td>3.05</td>
<td>2.98</td>
</tr>
<tr>
<td>SPSO1</td>
<td>2.86</td>
<td>2.77</td>
</tr>
<tr>
<td>SPSO2</td>
<td>2.88</td>
<td>2.78</td>
</tr>
<tr>
<td>SPSO3</td>
<td>2.92</td>
<td>2.83</td>
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<tr>
<td>SPSX</td>
<td>2.90</td>
<td>2.81</td>
</tr>
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<td>SPP013</td>
<td>2.90</td>
<td>2.81</td>
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<td>FFripic</td>
<td>2.83</td>
<td>2.73</td>
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The nature of the lowest-energy triplet excited state (T1) was first investigated by performing a TD-DFT study at the optimized geometry of S0. For all the hosts, TD-DFT calculations predict that T1 mainly results from the HOMO−1→LUMO excitation, which mostly concerns the functionalized fluorene moiety (see Figure 6 for SPSO1), and that the triplet state associated to the charge transfer HOMO→LUMO promotion appears higher in energy (Table S2 in the Supporting Information). The vertical excitation energies calculated at the TD-DFT level from S0 to T1 (E(S0→T1)) are similar for all the hosts and are given in Table 4. In a second step, the geometry of the lowest-energy triplet was fully optimized using the spin-unrestricted UB3LYP approach.
After full-geometry relaxation, the unpaired-electron spin density computed for T1 shows the same distribution for all the hosts, including the phosphine oxide compound SPPO13, and is mainly confined on the functionalized fluorene moiety as depicted in Figure 8 for SPSO1. This confirms the electronic nature predicted for T1 by TD-DFT calculations. The adiabatic energy of T1 (computed as the difference in the DFT energies of S0 and T1 at their respective optimized geometries, \( \Delta E(T_1-S_0) \)) is nearly identical for all the hosts, being between 2.77 eV for SPSO1 and 2.83 eV for SPSO3. The energy calculated for T1 in SPPO13 (2.81 eV) is intermediate between these two values and is in very good accord with the experimental value of 2.73 eV obtained from low-temperature photoluminescence measurements.\(^{[4a]}\) Calculations therefore show that although the introduction of sulfone groups significantly reduces the energy of the LUMO and leads to better electron acceptors compared to SPPO13, as discussed above, it mainly preserves the energy of the T1 triplet. The adiabatic T1 energies estimated for all the hosts are indeed higher than the value of 2.73 eV calculated for FIrpic (experimental value of 2.65 eV). This suggests that the sulfone SPSO1-3 and sulfoxide SPSX systems can be used as effective hosts with the FIrpic phosphor as blue dopant.

**Electroluminescent devices:** The main advantages of LECs over OLEDs are their simple structure (consisting of a single active layer processed from solution) and their insensitivity to the work function of the electrodes employed.\(^{[19]}\) However, attempts to fabricate blue phosphorescent LECs (electroluminescence emission below 480 nm) based on ionic transition-metal complexes remain extremely challenging due to self-quenching of the active material and unbalanced carrier transport in the emissive layer. Due to these factors, a maximum luminance of 94 cd m\(^{-2}\) (maximum efficacy of 4.3 cd A\(^{-1}\)) was reported for blue iridium phosphors.\(^{[8]}\) Furthermore, light-emitting devices that use 100% rare-earth-based materials are not economically viable. The host-guest approach is an alternative that promises an improved balance of the hole and electron charge carriers in LECs.\(^{[23]}\)

We have tested the solution-processable SPSO1-3 hosts as electron transporters in blue host-guest LEC devices using FIrpic as the blue dopant and a previously synthesized ionic hole-transporting material NMS25 (see Scheme S1 in the Supporting Information for the molecular structure).\(^{[8]}\) Solubility tests for the sulfone-host series are given in Table S3 in the Supporting Information. The performances of the blue host-guest LECs are illustrated in Figure 9 and are summarized in Table 5.

In Figure 9, we observe a drop in the driving voltage of 1.0 V in LEC 1 (3.6 V) when using the host SPSO1 compared to LEC 3 (4.6 V) with the host SPSO3 (Table 5). The lowered operating voltage may be attributed to the strong polarization effect of the aryl-sulfone group in SPSO1 forming a dipole layer at the Al-cathode,\(^{[6a]}\) lowering the electron injection barrier. It can be speculated that the highly flexible alkyl-chains in SPSO3 effectively hinders the interaction of the sulfone-group with the Al-cathode. A low operating voltage of 3.8 V was observed with the host SPSO2 (LEC 2), bearing rigid mesityl groups. From the X-ray structures (Figure 1), it is obvious that the steric vicinity of the sulfone groups in SPSO2 is very similar to that in SPSO1. The lifetimes of LECs 1 and 2 with host SPSO1 and SPSO2, respectively, are significantly longer than that of LEC 3 (Table 5).

However, the performance of the LECs with the bis-n-alkyl-sulfone host, SPSO3, was considerably improved when the ratio SPSO3:NMS25 was increased in LEC 4 (Figure 10 and Table 5). This results in a doubling of the brightness and efficacy (123 cd m\(^{-2}\) and 0.55 cd A\(^{-1}\), respectively), and can be attributed to an improved balance of the hole and electron charge carriers within the emissive layer.\(^{[14, 6, 21]}\) Moreover, the lifetime of the SPSO3 LEC was increased 14 times in LEC 5 when using the
lipophilic ionic liquid (IL) [THA][BF₄]⁻ ([THA]⁺ = tetra-n-hexyl ammonium) and the non-ionic hole transporting material TCTA (see Figure 10 and Scheme 1 in the Supporting Information for the chemical structure of TCTA). This improvement in lifetime can be attributed to the better compatibility of the IL and the acceptor host SPSO3 resulting in increased stability of the emissive thin film. At the same time, the turn-on time in LEC 5 is increased. This trend of increase in turn-on time leading to an increase in lifetime is often observed in LECs and is due to the role of ionic motion in these devices. In LEC 5 using lipophilic ions, the mobility is reduced explaining the observed results in lifetime and turn-on time.

However, it is demonstrated that all members of the sulfone host series give working LEC devices. The introduction of sulfone groups significantly reduces the energy of the LUMO and leads to better electron acceptors compared to analogous phosphine oxide functionalized hosts, it does not affect the energy of the lowest lying triplet (~2.80 eV) which is maintained above the triplet of FIrpic. The acceptor hosts have been tested in LEC devices, LECs containing the sulfone hosts SPSO1 and SPSO2 (aryl sulfones) perform better than those with SPSO3 (long chain alkyl sulfone substituents); no working LEC was obtained with the sulfoxide-functionalized host material.

The study has revealed a promising class of acceptor hosts for use in LECs. The synthetic route used to prepare SPSO1, SPSO2 and SPSO3 can be readily adapted using the pool of commercially available aryl- and alkyl-thiols, functionalized with ethers, alcohols, esters, and carboxylic acids to obtain a wide range of polar acceptor-hosts with tailor-made solubility properties required for solution-based materials deposition.

Conclusions

Four electron-acceptor hosts SPSO1, SPSO2, SPSO3, and SPSX containing sulfone- or sulfoxide-functionalized spirobifluorones have been prepared and characterized. The single crystal structures of SPSO1, SPSO2 and SPSO3 have been determined. Trends in the electrochemical behaviour of the compounds are consistent with the electron-withdrawing properties of the sulfone or sulfoxide groups. The emission maxima of all four hosts lie in the range 421–432 nm, which overlaps with the MLCT absorption of the sky-blue emitter FIrpic, and thus leads to energy transfer from the acceptor hosts to FIrpic. Theoretical calculations show that although the introduction of sulfone groups significantly reduces the energy of the LUMO and leads to better electron acceptors compared to analogous phosphine oxide functionalized hosts, it does not affect the energy of the lowest lying triplet (~2.80 eV) which is maintained above the triplet of FIrpic.

No working LEC device was obtained with the host SPSX which may be related to a decomposition reaction at the Al-cathode. However, it is demonstrated that all members of the sulfone-acceptor host series give working blue-phosphorescent LECs.

Experimental Section

General: All of the starting materials were commercially available, of reagent grade, and used without further purification. The solvents were reagent grade or distilled, except for the p-xylene which was dried by refluxing over NaH. Column chromatography was performed using Fluka silica gel 60 (40–63 µm), Silicycle SilicaFlash P60 (40–63 µm). ¹H and ¹³C NMR spectra were recorded on a Bruker DRX400 (400 MHz) or on a Bruker DRX500 (500 MHz) spectrometer at 295 K. The chemical shifts were referenced with respect to residual solvent peaks with δ (TMS) = 0. IR spectra were recorded on a Shimadzu FTIR-8400S spectrophotometer using neat samples and a Golden Gate attachment for solid state samples. EI mass spectra were recorded on a Finnigan MAT 95Q spectrometer. MALDI-TOF mass spectrometry was done using a Voyager-DE PRO spectrometer. Measurement of UV-Vis spectra was carried out on an Agilent Technologies UV-Visible 8453 spectrophotometer and a Shimadzu RF-6301PC spectrophorometer was used to measure the photoluminescence spectra. Cyclic voltammetry was recorded on a CH Instruments 900B potentiostat with glassy carbon working and platinum auxiliary electrodes; a silver wire was used as a pseudo-reference electrode and ferrocene as internal reference.

Table 5. Performance of LEC devices.

<table>
<thead>
<tr>
<th></th>
<th>L</th>
<th>Host mixture</th>
<th>$t_{on}$ (min)</th>
<th>Lum $^{21}_{max}$ (cd m$^{-2}$)</th>
<th>$t_{off}$ (min)</th>
<th>Efficacy $^{21}$ (cd A$^{-1}$)</th>
<th>$t^{1/2}$ (min)</th>
<th>$U^{21}$ (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>SPSO1:NMS25 (1:1)</td>
<td>0.83</td>
<td>21</td>
<td>19.3</td>
<td>0.10</td>
<td>3.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>SPSO2:NMS25 (1:1)</td>
<td>&lt; 0.1</td>
<td>49</td>
<td>46$^{31}$</td>
<td>0.23</td>
<td>3.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>SPSO3:NMS25 (1:1)</td>
<td>0.18</td>
<td>56</td>
<td>1.2</td>
<td>0.25</td>
<td>4.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>SPSO3:NMS25 (2:1)</td>
<td>0.29</td>
<td>123</td>
<td>1.6</td>
<td>0.55</td>
<td>5.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>SPSO3:TCTA</td>
<td>3.4</td>
<td>92</td>
<td>23.0</td>
<td>0.43</td>
<td>4.0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

[a] FIrpic was 10% in all LEC devices. [b] The turn-on time ($t_{on}$) is the time to reach the maximum luminance. [c] Maximum luminance. [d] The lifetime ($t_{off}$) is the time to reach half of maximum luminance. [e] Maximum efficacy. [f] Operating average voltage. [g] Lower lifetime mainly due to higher luminance, not an indication of lower stability.

The syntheses of compounds 4 and 5, and alternative syntheses of SPSO1 and SPSX are given in the Supporting Information. See Supporting Information for the atom labelling for NMR assignments.

2,7-Bis(phenylthio)-9,9’-spirobifluorene (1): Method a: A dried flask was charged with 2,7-dibromo-9,9’-spirobifluorene (371 mg, 0.782 mmol,
2.7-Bis(phenylsulfonyl)-9,9'-spirobifluorene (SPSOI): Oxidation at elevated temperature: 15 mL of a 0.89 M H₂O₂ (13.4 mmol, 7.13 eq.) solution in AcOH (100 %) were added to a solution of 2,7-bis(phenylthio)-9,9'-spirobifluorene (1, 1.00 g, 7.86 mmol, 1.00 eq.) in CHCl₃ (15 mL) at 0°C. The solution was stirred for 1 h at room temperature, heated to reflux for 2 h, then stirred at room temperature overnight, heated to reflux again for 1.5 h, and cooled to room temperature. The solution was poured onto H₂O and extracted with CHCl₃. The combined organic layers were washed with H₂O until no peroxide was present any more, dried over Na₂SO₄, and the solvent was removed under reduced pressure. The residue was purified by column chromatography (SiO₂; cyclohexane:EtOAc = 1:1) recrystallized from 1,4-dioxane, and dried under vacuum to yield the SPSOI as colourless crystals. Yield: 1.0 g, 1.77 mmol, 89 %. H NMR (500 MHz, CDCl₃); δ ppm = 7.95 – 7.88 (m, 6 H; H3,4,5,6,4',5'), 7.78 – 7.76 (m, 4 H; SO₂Ph-H2), 7.51 (t, J(H,H) = 7.5 Hz, J(H,H) = 1.2 Hz, 2H; SO₂Ph-H4), 7.45 – 7.40 (m, 8 H; H1,8,3',6', Ph-SO₂Ph-H3), 7.08 (pseudo-tt, J(H,H) = 7.5 Hz, J(H,H) = 1.1 Hz, 2H; H2',7'), 6.54 (pseudo-tt, J(H,H) = 7.6 Hz, J(H,H) = 0.9 Hz, 6H; H1',8'), 1.11 (C1'H) NMR (126 MHz, CDCl₃); δ ppm = 151.50 (C2',7'), 128.36 (C6',3',7, C6',3',2'), 128.34 (C6',3',2'), 127.68 (SO₂Ph-CO), 123.87 (C1',8'), 123.77 (C1',8'), 121.84 (C4',5'), 120.85 (C4',5'), 66.18 (C9), IR (solid); δ v/cm⁻¹ = 3069 (w), 1446 (m), 1402 (w), 1314 (m), 1177 (w), 1145 (s), 1089 (s), 1063 (w), 1004 (m), 935 (w), 821 (m), 769 (s), 750 (s), 721 (s), 691 (s), 682 (s). UV/Vis (MeCN, 1.0 × 10⁻³ mol dm⁻³); δmax (ε, λₑm) = 227 (sh, 6040), 250 (sh, 33400), 286 (42600), 299 (41300), 323 nm (15400 cm⁻¹ mol⁻¹). Fluorescence (MeCN, 1.0 × 10⁻³ mol dm⁻³; δmax (ε) = 116 (cm⁻¹ mol⁻¹); δmax (ε) = 52.3 % (M) [100 % (calcld. 53.2)]. See the Supporting Information for Methods b and c.
The solvents were evaporated under reduced pressure and the crude bis-spirofluorene (2, 158 mg, 0.256 mmol, 11% yield) was dissolved in EtOAc (20 mL) and AcOH (100 %, 5 mL). H2O (30 %, 0.250 mL, 352 mmol, 3.10 mmol, 12.1 eq.) was added and the solution was heated to reflux for 18 h. The solution was poured onto H2O and extracted with EtOAc. The combined organic layers were washed with H2O until no peroxide was present any more, dried over Na2SO4, and the solvent was removed under reduced pressure. The residue was recrystallised from a mixture of cyclohexane and toluene and dried under vacuum. Purification by column chromatography (SiO2; cyclohexane/EtOAc 3:1) yielded SPSO2 as a colourless powder. Yield: 110 mg, 0.26 mmol, 63 % (H NMR (500 MHz, CDCl3); δ/ppm = 7.88 (d, J(H,H) = 7.6 Hz, 7H), 7.63 (d, J(H,H) = 8.1 Hz, 2H), H4',5'), 7.59 (dd, J(H,H) = 8.1 Hz, J(H,H) = 1.1 Hz, 2H, H3,6), 7.43 – 7.40 (m, 4H, H1,3,8,9), 7.10 (pseudo-t, J(H,H) = 7.6 Hz, 2H, H1',2'), 6.86 (s, 4H, SO{2}Mes-3H), 6.58 (s, 2H), 6.43 (s, H9), 5.79 (s, 2H, SO{2}Mes-2H), 2.40 (s, 12H, SO{2}Mes-C2), 2.26 (s, 6H, SO{2}Mes-C4), 1.33(H) NMR (126 MHz, CDCl3); δ/ppm = 150.57 (C2, 27.7), 145.47 (C4a,4b,9a,9b), 143.92 (C4a,4b,9a,9b), 134.55 (SO{2}Mes-C4), 142.22 (C4a,4b), 139.92 (SO{2}Mes-C2), 134.05 (SO{2}Mes-C1), 132.33 (SO{2}Mes-C3), 128.79 (C3,6'), 128.21 (C7,7'), 127.63 (C8,8'), 126.30 (C1,1'), 123.01 (C1,1'), 121.52 (C5,5'), 120.90 (C4,5',6'), 66.18 (C9), 22.71 (SO{2}Mes-C2,CH3), 21.13 (SO{2}Mes-C4,CH3). IR (solid): δ/cm-1 = 2932 (w), 1605 (w), 1558 (w), 1443 (m), 1396 (w), 1381 (s), 1304 (s), 1210 (s), 1126 (m), 1034 (m), 1003 (w), 996 (3), 879 (m), 849 (w), 818 (w), 764 (s), 733 (m), 694 (s), 663 (s), 640 (s), 617 (s), 617 (m). UV/Vis (MeCN, 1.0 × 10-5 mol dm-3); λmax (ε) = 230 (sh, 6600), 285 (44000), 307 (49000), 327 (14000 dm3 mol-1 cm-1). Fluorescence (MeCN, 1.0 × 10-5 mol dm-3); λmax (ε) = 422 nm. MS (EI, 70 eV); m/z = 662.0 (M+) [100], (calcld. 662.0). Partial recrystallisation from a mixture of cyclohexane and toluene and dried under vacuum. Purification by column chromatography (SiO2; cyclohexane/EtOAc 3:1) yielded SPSO2 as a colourless powder. Yield: 110 mg, 0.26 mmol, 63 % (H NMR (500 MHz, CDCl3); δ/ppm = 7.88 (d, J(H,H) = 7.6 Hz, 7H), 7.63 (d, J(H,H) = 8.1 Hz, 2H), H4',5'), 7.59 (dd, J(H,H) = 8.1 Hz, J(H,H) = 1.1 Hz, 2H, H3,6), 7.43 – 7.40 (m, 4H, H1,3,8,9), 7.10 (pseudo-t, J(H,H) = 7.6 Hz, 2H, H1',2'), 6.86 (s, 4H, SO{2}Mes-3H), 6.58 (s, 2H), 6.43 (s, H9), 5.79 (s, 2H, SO{2}Mes-2H), 2.40 (s, 12H, SO{2}Mes-C2), 2.26 (s, 6H, SO{2}Mes-C4), 1.33(H) NMR (126 MHz, CDCl3); δ/ppm = 150.57 (C2, 27.7), 145.47 (C4a,4b,9a,9b), 143.92 (C4a,4b,9a,9b), 134.55 (SO{2}Mes-C4), 142.22 (C4a,4b), 139.92 (SO{2}Mes-C2), 134.05 (SO{2}Mes-C1), 132.33 (SO{2}Mes-C3), 128.79 (C3,6'), 128.21 (C7,7'), 127.63 (C8,8'), 126.30 (C1,1'), 123.01 (C1,1'), 121.52 (C5,5'), 120.90 (C4,5',6'), 66.18 (C9), 22.71 (SO{2}Mes-C2,CH3), 21.13 (SO{2}Mes-C4,CH3). IR (solid): δ/cm-1 = 2932 (w), 1605 (w), 1558 (w), 1443 (m), 1396 (w), 1381 (s), 1304 (s), 1210 (s), 1126 (m), 1034 (m), 1003 (w), 996 (3), 879 (m), 849 (w), 818 (w), 764 (s), 733 (m), 694 (s), 663 (s), 640 (s), 617 (s), 617 (m). UV/Vis (MeCN, 1.0 × 10-5 mol dm-3); λmax (ε) = 230 (sh, 6600), 285 (44000), 307 (49000), 327 (14000 dm3 mol-1 cm-1). Fluorescence (MeCN, 1.0 × 10-5 mol dm-3); λmax (ε) = 422 nm. MS (EI, 70 eV); m/z = 662.0 (M+) [100], (calcld. 662.0).
substrates were cleaned by sonication in water-soap, water, and isopropanol baths. After drying, the substrates were placed in a UV-ozone cleaner (Jelight 42–220) for 20 min. The blue phosphorescent devices were made as follows. First, a 70-80 nm layer of PEDOT/PSS (CLEVIOS P VP Al 4083, Heraeus) was spin-coated on the ITO substrates to improve the reproducibility. The synthesized acceptor-hosts were dissolved in anisole, followed by dissolving the hole-transporting hosts NMS25 (see Supporting Information for structure) or TCTA (Lumtec, see Supporting Information for structure) and 10% Flrpic (Lumtec) as the dopant. The total concentration of dissolved hosts and dopants was 20 mg/mL. In the LEC 5, a molar ratio of the host-FIrPic blend and the ionic liquid [THA][BF4] (Sigma Aldrich) was 8:1.

The device life-time was measured by applying pulsed current (average: 100 A m−2) with a duty cycle of 50% and monitoring the average voltage and luminance by a True Colour Sensor MAZeT (MTCSICT Sensor) with a Botest OLTL Lifetime-Test System.

Acknowledgements

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Bis-sulfone- and bis-sulfoxide-spirobifluorenes are a promising class of high-triplet-energy electron-acceptor-hosts for blue phosphorescent light-emitting devices. The molecular design and synthetic route is simple and allows tailoring the solubility of hosts without lowering the high-energy triplet state. A series of polar acceptor hosts has been synthesized and tested in LECs. Large effects of the various solubilizing moieties on the LEC performance were observed and are discussed.

**Topic:** Host materials in LECs

Cathrin D. Ertl, Henk Bolink, Catherine E. Housecroft,* Edwin C. Constable, Enrique Ortí, José M. Junquera-Hernández, Markus Neuburger, Nail M. Shavaleev, Mohammad Khaja Nazeeruddin, David Vonlanthen*

**Bis-Sulfone- and Bis-Sulfoxide-Spirobifluorenes: Polar Acceptor-Hosts with tunable Solubilities for Blue-Phosphorescent Light-Emitting Device**