

Host Materials in LECs

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

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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-di-

fluorophenyl-pyridinato)(picolinato)iridium(III) (Flrpic), allowing effective energy transfer from the acceptor hosts to Flrpic. 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 Flrpic 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 thin flat-panel displays and general lighting in the forthcoming future.^[1] In phosphorescent OLEDs, host materials transfer energy from singlet and triplet states to the phosphor resulting theoretically in 100 % internal quantum efficiency.^[2]

Good electron-acceptor host materials for blue and white electroluminescent devices possess high triplet energy, good electron-transport properties, and improve the electron injection.^[1a] However, the limited availability of electron-transporting host materials, in particular those that are suitable for solution processing, is one of the bottlenecks to providing cheap, economically competitive, white electroluminescent devices.

Phosphine oxide (PO) functionalization of biphenyl-type structures has proved to be a good strategy for obtaining high-triplet-energy electron-acceptor host materials with low-lying LUMOs.^[3] Highly efficient blue and white multi-stack OLEDs using various PO-acceptor hosts have been reported.^[4] Moreover, the polar PO group can be used in modifiers to lower the work function of metal electrodes.^[5] We recently reported on the advantages of a PO-acceptor host in phosphorescent light-emitting electrochemical cell (LEC) devices.^[6]

Kippelen and co-workers 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] 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 π -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;^[5] *iv*) the simplicity and broad scope of the sulfone/sulfoxide chemistry is highly appealing.^[7,10]

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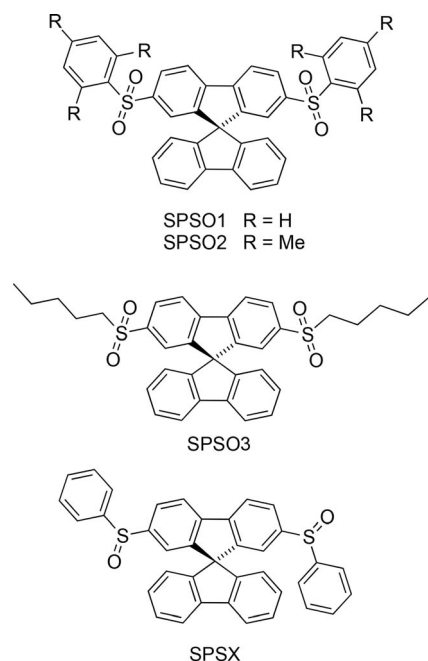
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Here we report the design, synthesis, and photophysical/electrochemical properties of four electron-acceptor hosts: SPSO1, SPSO2, SPSO3, and SPSX (Scheme 1). The experimental study is complemented by theoretical calculations. We hypothesized that sulfoxide functionalization (not previously reported in host materials in LECs) should give rise to higher-energy triplet materials.^[11] The new hosts were tested in LECs, and the influence of various solubilizing moieties on the photophysical properties and LEC performance was investigated. The spirobifluorene moiety is generally preferred over smaller biphenyl structures as it leads to more stable amorphous thin-film structures.^[12] However, the structural rigidity of spirobifluorenes tends to hamper solution processing.

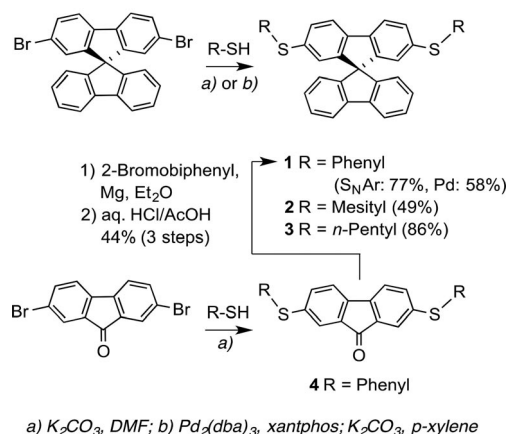


Scheme 1. Chemical structures of the electron-acceptor host compounds.

Results and Discussion

Synthesis and NMR Spectroscopic Characterization

All hosts were synthesized from commercially available 2,7-dibromo-9,9'-spirobifluorene. Reactions with the appropriate thiols yielded bis-thioether derivatives **1–3** (Scheme 2) which were subsequently oxidized to the final acceptor hosts. Thiolations^[13] in Scheme 2 were achieved through either aromatic nucleophilic (S_NAr) substitution (Method *a*) or Pd-cross-coupling (Method *b*, Supporting Information) to give **1** in good yield. Alternatively, **1** was synthesized starting from 2,7-bis(phenylthio)-9H-fluoren-9-one (**4**, Supporting Information). We note that **4** can also be used to design mixed *n*- and *p*-type high-energy triplet cores.^[10] Compound **4** was treated with biphenyl-2-ylmagnesium bromide to give **1** in 44 % yield over 3 steps (Method *c*, Supporting Information).



Scheme 2. Synthetic routes to thioethers of interest.

Due to its simplicity, the S_NAr reaction (Scheme 2, Method *a*) was preferred over the transition-metal-catalyzed reaction to give bis-thioethers. Thus, compounds **2** and **3** were obtained using 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-CH₃ groups in the *ortho*-positions of the thio-phenol-based nucleophile.

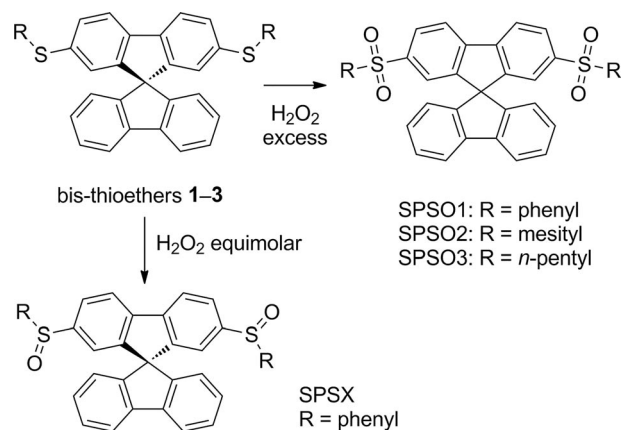
To afford the final acceptor hosts, different oxidation conditions were tested (Table 1). Selective and stepwise oxidation of symmetric bis-thioethers **1–3** gave bis-sulfoxide SPSX and bis-sulfones SPSO1, SPSO2, and SPSO3 (Scheme 3). All hosts were obtained by metal-catalyst-free oxidation reactions using H₂O₂ or mCPBA.

Table 1. Conditions for oxidation of the bis-thioethers.^[a]

Substrate	Oxidant (equiv.)	Solvent/conditions ^[b]	Host (yield [%])
1	H ₂ O ₂ (2.0)	A, r.t. (30 h)	SPSX (70)
1	mCPBA (2.0)	B, 0 °C, then r.t. (overnight)	SPSX (47)
1	H ₂ O ₂ (exc.)	A, r.t. (21 h)	SPSO1 (77)
1	H ₂ O ₂ (exc.)	A, reflux (3.5 h)	SPSO1 (89)
2	H ₂ O ₂ (exc.)	C, reflux (18 h)	SPSO2 (63)
3	H ₂ O ₂ (exc.)	A, r.t. (24 h), then 40 °C (0.5 h)	SPSO3 (55)

[a] Entries 1, 4–6 are described in the main paper; entries 2 and 3 are described in the Supporting Information. [b] Solvent systems: A = AcOH/CHCl₃, B = CH₂Cl₂, C = AcOH/EtOAc.

Selective oxidation^[14] of **1** with an equimolar amount of H₂O₂ at room temperature gave 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^[15] was not as selective giving the asymmetric sulfone side-product **5** (see Supporting Information). Treatment of **1** with excess H₂O₂ gave exclusively bis-sulfone SPSO1 in high



Scheme 3. Selective oxidation of the various thioethers. Reaction conditions are listed in Table 1.

yield. Notably, high temperatures allowed for a decrease in reaction time and led to higher yields of **1**.

Oxidation of **2** afforded bis-mesitylsulfone SPSO2 in good yield. Similarly, oxidation of **3** gave SPSO3 in satisfactory yield. Whereas 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 observation points to the improved substrate solubility attributable to the mesityl group. All new compounds were fully characterized by ^1H and ^{13}C NMR and IR spectroscopy, mass spectrometry and elemental analyses.

Crystal Structures of SPSO1·2CH₂Cl₂, SPSO2, and SPSO3

Single-crystals of SPSO1·2CH₂Cl₂ were grown from CH₂Cl₂ overlaid with MeOH. X-ray quality crystals of SPSO2 were obtained from recrystallization of the bulk material from cyclohexane and toluene, and those of SPSO3 were grown from a CHCl₃ solution of the compound overlaid with *n*-hexane. The structures of the three compounds were determined by single-crystal X-ray diffraction. SPSO1·2CH₂Cl₂ crystallizes in the space group $P2_1/c$ with one molecule and two disordered CH₂Cl₂ 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 1 (a) shows the structure of the SPSO1 molecule with selected bond parameters given in the Figure caption. Compounds SPSO2 and SPSO3 both crystallized in the $C2/c$ space group with half of each molecule in the asymmetric unit; the second half, in each case, was generated by a twofold axis (Figure 1, b and c).

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

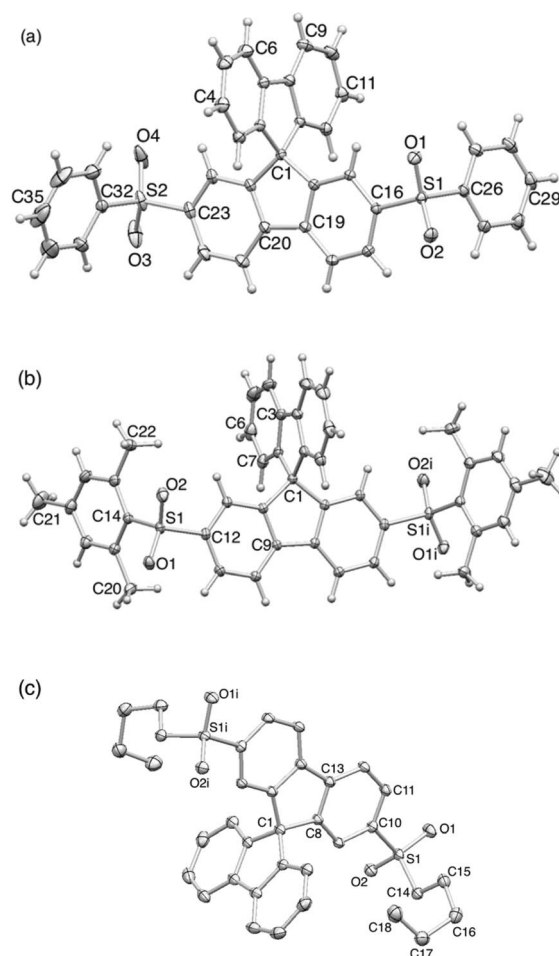


Figure 1. X-ray structures of (a) SPSO1 in SPSO1·2CH₂Cl₂, (b) SPSO2, and (c) SPSO3. Solvent molecules are omitted for clarity. Ellipsoids plotted at the 40 % probability level. Selected bond parameters: SPSO1: S1–O1 1.4419(13), S1–O2 1.4429(12), S2–O3 1.4347(17), S2–O4 1.4417(18), C16–S1 1.7626(15), 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), C23–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)°; 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(6), 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)° (symmetry code i: $-x, y, 1/2 - z$). SPSO3: S1–O1 1.4406(11), S1–O2 1.4427(12), C10–S1 1.7808(15), C14–S1 1.7705(17) Å; C14–S1–C10 103.69(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)° (symmetry code i: $1 - x, y, 1/2 - z$).

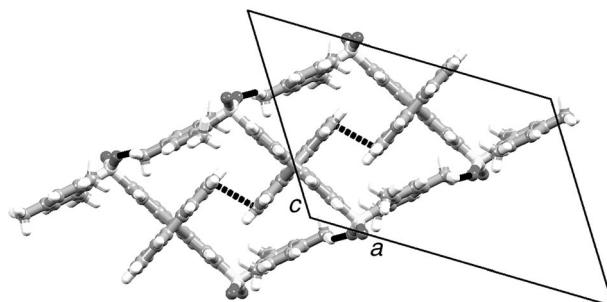


Figure 2. Packing of molecules of SPSO2 showing short S–O···HC and π -contacts (see text) in black hashed lines.

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 appear to operate between the two methylene units and the arene ring (Figure 3).

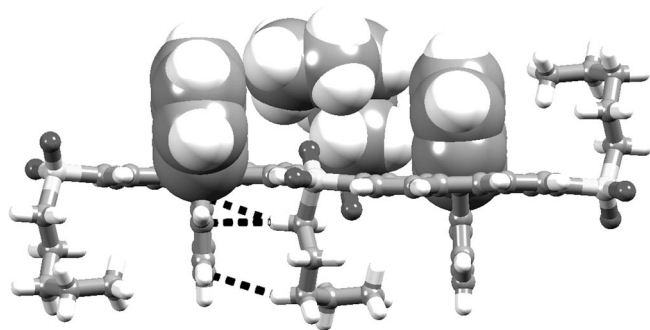


Figure 3. Packing of molecules of SPSO3 showing sandwiching of the folded *n*-pentyl chains between pairs of fluorene domains of adjacent molecules. Short CH... π -contacts are shown by black hashed lines.

Electrochemical and Photophysical Studies

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

Table 2. Photophysical and electrochemical data.

Host	$E_{1/2}^{\text{red}}$ [V] ^[a]	λ_{abs} [nm] ^[b]	λ_{em} [nm, eV] ^[b]
SPSO1	–2.00	284, 330	432, 2.87
SPSO2	–2.07	285, 327	421, 2.95
SPSO3	–2.12	279, 322	422, 2.94
SPSX	–2.24	273, 326	380, 3.26

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

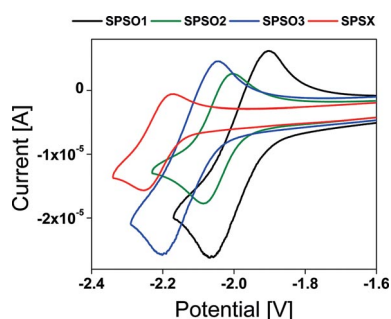


Figure 4. Cyclic voltammograms of SPSO1–3 and SPSX in CH₃CN with [TBA]⁺[PF₆][–] against Fc/Fc⁺ (as an internal reference).

The absorption and the photoluminescence (PL) spectra of the sulfoxide and sulfone hosts are shown in Figure 5. The struc-

tured absorption observed above 270 nm for all four compounds is attributed to $\pi \rightarrow \pi^*$ transitions centered on the spirobifluorene core. The bis-sulfonyl-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 metal-to-ligand charge transfer (MLCT) absorption of the sky-blue emitter bis(4,6-difluorophenylpyridinato)(picolinate)iridium(III) (Flrpic),^[18] enabling efficient energy transfer from the bis-sulfone acceptor hosts to Flrpic.^[7] The PL emission maxima of the bis-sulfoxide SPSX is shifted by 50 nm into the deep-blue/near-UV region relative to the bis-sulfones.^[11]

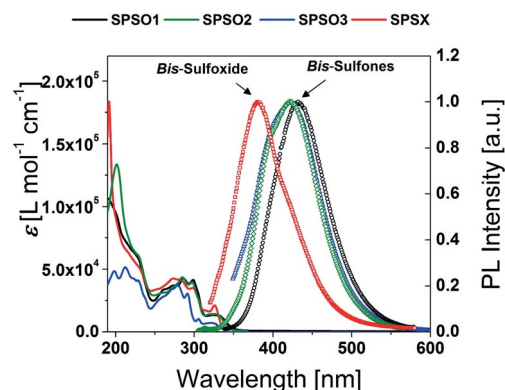


Figure 5. UV and PL spectra of SPSO1–3 and SPSX in CH₃CN. Solution concentrations: 1.0×10^{-5} mol dm^{–3}.

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 solvent (CH₃CN). Non-substituted 9,9'-spirobifluorene (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 88.5° 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 119.87°, respectively, in very good accord with the experimental X-ray average values (105.40, 107.70, and 119.77°, 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 1, c) is stabilized by interactions 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, Supporting Information). Table 3 depicts the energies calculated for the HOMO, the LUMO, and the HOMO–LUMO gap for all the hosts and SP. Table 3 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.

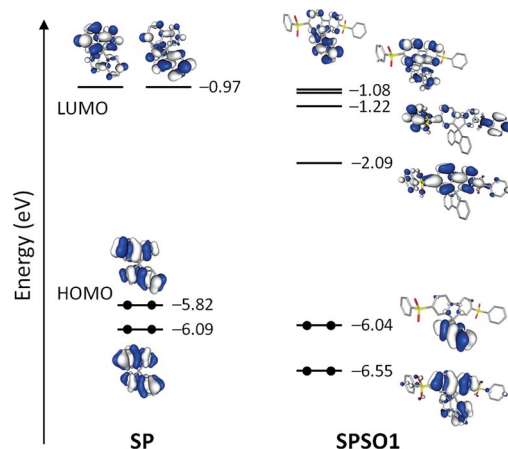


Figure 6. Schematic representation showing the isovalue contours (± 0.03 a.u.) and energies calculated for the frontier molecular orbitals of SP and SPSO1. Hydrogen atoms are omitted.

Table 3. B3LYP/6-31G** values computed for the energy of the HOMO (E_{HOMO}) and the LUMO (E_{LUMO}), the HOMO–LUMO energy gap ($\Delta E_{\text{HOMO-LUMO}}$), and the electron affinity (EA). All values are given in eV units.

Host	E_{HOMO}	E_{LUMO}	$\Delta E_{\text{HOMO-LUMO}}$	EA
SP	-5.82	-0.97	4.85	1.20
SPSO1	-6.04	-2.09	3.95	2.39
SPSO2	-6.02	-1.95	4.07	2.29
SPSO3	-6.04	-1.97	4.07	2.28
SPSX	-5.95	-1.62	4.33	2.09
SPPO13	-5.98	-1.73	4.25	2.02

The SP molecule presents a D_{2d} 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 enables 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

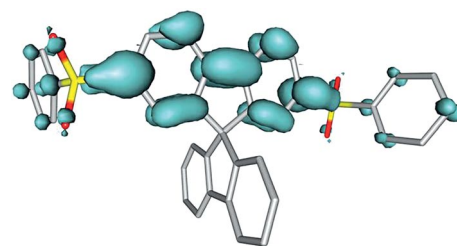


Figure 7. Unpaired-electron spin density contours (0.002 a.u.) calculated for the anion of SPSO1.

HOMO–LUMO gap therefore decreases by almost 1 eV in going from SP (4.85 eV) to SPSO1 (3.94 eV). Compared to SPPO13 (bearing phosphine PO groups), the sulfone SO_2 groups in SPSO1 lower the energy of the LUMO to a higher degree (-2.09 vs. -1.73 eV) and leads to a higher electron affinity (2.39 vs. 2.02 eV). This is in accordance with 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). This 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, Supporting Information). This observation suggests that SPSO1 presents a more effective electronic conjugation through the sulfone groups than do 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 to be -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 (-2.00, -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 SPPO13 host for which an electron affinity 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 blueshift 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 (S_0) to obtain information about the nature of the singlet excited states (S_n) involved in the absorption spectra. Calculations assign the low-intensity band above 300 nm (Figure 5) to the $S_0 \rightarrow S_1$ electronic transition calculated around 3.4–3.7 eV for SPSO1–3 and SPSX (Table S1, 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 $\pi \rightarrow \pi^*$ 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 S_1 state resulting from the HOMO \rightarrow 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 redshifted relative to 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).

The nature of the lowest-energy triplet excited state (T_1) was first investigated by a TD-DFT study at the optimized geometry of S_0 . For all the hosts, TD-DFT calculations predict that T_1 mainly results from the HOMO–1 \rightarrow LUMO excitation, which mostly involves the functionalized fluorene moiety (see Figure 6 for SPSO1), and that the triplet state associated to the charge transfer HOMO \rightarrow LUMO promotion appears higher in energy (Table S2, Supporting Information). The vertical excitation energies calculated at the TD-DFT level from S_0 to T_1 [$E(S_0 \rightarrow T_1)$] 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 T_1 shows the same distribution for all the hosts, including phosphine oxide compound SPPO13, and is mainly confined to the functionalized fluorene moiety as depicted in Figure 8 for SPSO1. This confirms the electronic nature predicted for T_1 by TD-DFT calculations. The adiabatic energy of T_1 [computed as the difference in the DFT energies of S_0 and T_1 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 T_1 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 intro-

duction 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 T_1 triplet. The adiabatic T_1 energies estimated for all hosts are indeed higher than the value of 2.73 eV calculated for Flrpic (experimental value of 2.65 eV). This suggests that sulfone SPSO1–3 and sulfoxide SPSX systems can be used as effective hosts with the Flrpic phosphor as blue dopant.

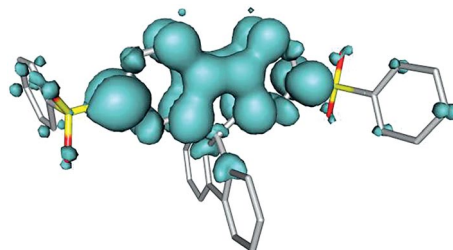


Figure 8. Unpaired-electron spin density contours (0.002 a.u.) calculated for the fully-relaxed T_1 triplet state of SPSO1.

Electroluminescent Devices

The main advantages of LECs over OLEDs are their simple structures (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.^[20] Furthermore, light-emitting devices that use 100 % rare-earth-based materials are not economically viable. The host–guest approach is an alternative that promises cheaper, more stable, and brighter LEC devices.^[6,21]

We have tested the solution-processible SPSO1–3 hosts as electron transporters in blue host–guest LEC devices using Flrpic as the blue dopant and a previously synthesized ionic hole-transporting material NMS25 (see Scheme S1, Supporting Information, for the molecular structure).^[6] Solubility tests for the sulfone-host series are given in Table S3 in the Supporting Information. The performance data of the blue host–guest LECs are illustrated in Figure 9 and 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 host SPSO1 compared to LEC 3 (4.6 V) with host SPSO3 (Table 5). The lowered operating voltage may be attributed to the strong polarization effect^[5a] of the aryl-sulfone group in SPSO1 forming a dipole layer at the Al cathode,^[5b] lowering the electron injection barrier. It can be speculated that the highly flexible alkyl-chains in SPSO3 effectively hinder the interaction of the sulfone-group with the Al-cathode. A low operating voltage of 3.8 V was observed with 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 found in

Table 4. B3LYP/6-31G** values computed for the vertical TD-DFT excitation energy from the ground state to the lowest triplet excited state [$E(S_0 \rightarrow T_1)$] and for the adiabatic energy difference between S_0 and T_1 [$\Delta E(T_1-S_0)$]. All values are in eV.

Host	$E(S_0 \rightarrow T_1)$	$\Delta E(T_1-S_0)$
SP	3.05	2.98
SPSO1	2.86	2.77
SPSO2	2.88	2.78
SPSO3	2.92	2.83
SPSX	2.90	2.80
SPPO13	2.90	2.81
Flrpic	2.83	2.73

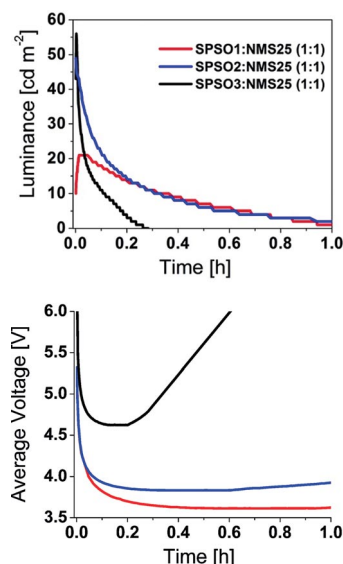


Figure 9. (top and bottom) Luminance and average voltage vs. time of LEC devices with the acceptor hosts.

Table 5. Performance data for LEC devices.^[a]

LEC	Host mixture	$t_{on}^{[b]}$ [min]	$Lum_{max}^{[c]}$ [cd m ⁻²]	$t_{1/2}^{[d]}$ [min]	Efficacy ^[e] [cd A ⁻¹]	$V^{[f]}$ [V]
1	SPSO1:NMS25 (1:1)	0.83	21	19.3	0.10	3.6
2	SPSO2:NMS25 (1:1)	< 0.1	49	4.6 ^[g]	0.23	3.8
3	SPSO3:NMS25 (1:1)	0.18	56	1.2	0.25	4.6
4	SPSO3:NMS25 (2:1)	0.29	123	1.6	0.55	5.2
5	SPSO3:TCTA (2:1) + IL	3.4	92	23.0	0.43	4.0

[a] Flrpic 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 ($t_{1/2}$) 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.

SPSO1. The lifetimes of LECs 1 and 2 with hosts SPSO1 and SPSO2, respectively, are significantly longer than that of LEC 3 (Table 5).

However, the performance of the LECs with di-*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.^[1a,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*-hexylammonium) and the non-ionic hole transporting material TCTA (see Figure 10, and Scheme S1 in 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. Notably, no working LEC de-

vice was obtained with SPSX as the host and this may be related to a decomposition reaction at the Al-cathode. However, it is clear that all members of the sulfone-acceptor host series give working blue-phosphorescent LECs.

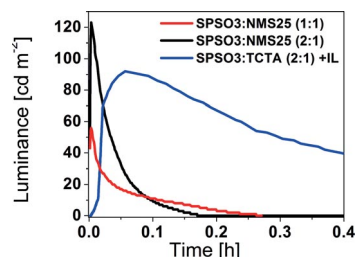


Figure 10. Luminance vs. time of LEC devices with SPSO3.

Conclusions

Four electron-acceptor hosts SPSO1, SPSO2, SPSO3, and SPSX containing sulfone- or sulfoxide-functionalized spirobifluorenes have been prepared and characterized. The single-crystal structures of SPSO1, SPSO2 and SPSO3 have been determined. Trends in the electrochemical behaviour of these 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 Flrpic, and thus leads to energy transfer from the acceptor hosts to Flrpic. 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 (ca. 2.80 eV) which is maintained above the triplet of Flrpic. 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.

This study has revealed a promising class of acceptor hosts for use in LECs. The synthetic routes 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 produce a wide range of polar acceptor-hosts with tailored solubility properties required for solution-based deposition processes.

Experimental Section

General: All 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{¹H} NMR spectra were recorded with a Bruker DRX400 (400 MHz) or a Bruker DRX500 (500 MHz) spectrometer at 295 K. The chemical shifts were referenced with respect to residual solvent peaks with $\delta(TMS) = 0$. IR spectra were recorded with a Shimadzu FTIR-8400S spectrophotometer using neat samples

and a Golden Gate attachment for solid state samples. EI mass spectra were recorded using 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 with an Agilent Technologies UV/Visible 8453 spectrophotometer and a Shimadzu RF-5301PC spectrofluorometer was used to measure the photoluminescence spectra. Cyclic voltammetry was recorded using 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.

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, 1.00 equiv.), K_2CO_3 (554 mg, 4.01 mmol, 5.12 equiv.), and thiophenol (0.82 mL, 884 mg, 8.02 mmol, 10.3 equiv.) under an argon atmosphere. Dry DMF (4 mL) was added and the suspension was stirred for 22 h at 140 °C. CH_2Cl_2 was added to the mixture and the precipitate was filtered off. The filtrate was washed with H_2O , the aqueous layer was extracted with CH_2Cl_2 and the combined organic layers were washed three times with H_2O and dried with Na_2SO_4 . The solvent was removed under reduced pressure. Cyclohexane was added to the residue and the suspension was heated until everything had dissolved. The precipitate was filtered, washed with cyclohexane, dissolved with $CHCl_3$, and the solvent was removed under reduced pressure. The residue was recrystallized from cyclohexane and dried under vacuum, the filtrate was concentrated under reduced pressure and the residue was again recrystallized from cyclohexane and dried under vacuum. From both recrystallizations, the product **1** was obtained as colourless crystals, yield 320 mg, 0.60 mmol, 77 %. 1H NMR (500 MHz, CD_2Cl_2): δ = 7.84 [pseudo-dt, 3J (H,H) = 7.8, 4,5J (H,H) = 0.9 Hz, 2 H, H4',5'], 7.77 [dd, 3J (H,H) = 8.1, 5J (H,H) = 0.6 Hz, 2 H, H4,5], 7.39 [pseudo-td, 3J (H,H) = 7.6, 4J (H,H) = 1.1 Hz, 2 H, H3',6'], 7.29 [dd, 3J (H,H) = 8.1, 4J (H,H) = 1.7 Hz, 2 H, H3,6], 7.23–7.14 (m, 12 H, H2',7', SPh-H2,4), 6.77–6.75 (m, 4 H, H1,8,1',8') ppm. $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2): δ = 150.54 (C2,7), 148.25 (C8'a,9'a), 142.33 (C4'a,4'b), 140.94 (C4a,4b), 136.53 (SPh-C1), 135.56 (C8a,9a), 131.54 (C3,6), 130.70 (SPh-C2/C3), 129.62 (SPh-C2/C3), 128.59 (C3',6'), 128.44 (C2',7'), 127.42 (C1,8/SPh-C4), 127.36 (C1,8/SPh-C4), 124.27 (C1',8'), 121.46 (C4,5), 120.79 (C4',5'), 66.21 (C9) ppm. IR (solid): $\tilde{\nu}$ = 3062 (w), 1573 (w), 1472 (m), 1446 (m), 1439 (s), 1399 (m), 1252 (w), 1179 (m), 1154 (w), 1070 (m), 1024 (m), 1000 (w), 959 (w), 920 (w), 860 (m), 809 (s), 763 (s), 751 (s), 744 (s), 733 (s), 723 (s), 704 (s), 692 (s), 684 (s), 679 (m), 673 (s) cm^{-1} . UV/Vis (MeCN, 1.0×10^{-5} mol dm^{-3}): λ_{max} (ϵ) = 220 (sh, 82000), 270 (sh, 37000), 334 nm (29000 dm^3 cm^{-1} mol^{-1}). Fluorescence (MeCN, 1.0×10^{-5} mol dm^{-3} , λ_{ex} = 320 nm): λ_{em} = 374 nm. MS (EI, 70 eV): m/z (%) = 532.1 [M]⁺ (100, calcd. 532.1).

See the Supporting Information for Methods **b** and **c**.

2,7-Bis(phenylsulfinyl)-9,9'-spirobifluorene (SPSX): Oxidation with H_2O_2 : 0.89 M H_2O_2 (0.508 mmol, 2.0 equiv.) solution (0.57 mL) in AcOH (100 %) were added to a solution of 2,7-bis(phenylthio)-9,9'-spirobifluorene (**1**, 135 mg, 0.254 mmol, 1.00 equiv.) in a 1:1 mixture of $CHCl_3$ and AcOH (3 mL) at 0 °C. The solution was stirred for 30 h at room temperature, poured onto H_2O and extracted with CH_2Cl_2 . The combined organic layers were washed with H_2O until no peroxide was present any more, dried with Na_2SO_4 , and the solvent was removed under reduced pressure. The residue was purified by column chromatography (SiO_2 ; cyclohexane/EtOAc, 9:1 → 1:1) and dried under vacuum to yield SPSX as a colourless

powder, yield 0.10 g, 0.18 mmol, 70 %. 1H and ^{13}C NMR signals of the two diastereomers are marked with and without an asterisk: 1H NMR (500 MHz, $CDCl_3$): δ = 7.88–7.85 (m, 4 H, H4,5,4',5',4',5'*, 7.54–7.51 (m, 2 H, H3,6,3',6*), 7.48–7.44 [m, 4 H, S(O)Ph-H2,2', 7.44–7.34 [m, 8 H, H3',6',3'',6'',S(O)Ph-H3,4,3',4'*, 7.15–7.14 (m, 2 H, H1,8,1',8*), 7.12–7.05 (m, 2 H, H2',7',2'',7''), 6.61–6.57 (m, 2 H, H1',8',1'',8'*) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ = 150.88 (C2,7/C2',7'), 150.87 (C2,7/C2',7'), 146.45 (C8'a,9'a,8'a*,9'a*), 146.19 (C8a,9a,8a*,9a*), 145.52 [S(O)Ph-C1/C1*], 145.51 [S(O)Ph-C1/C1*], 143.31 (C4a,4b/C4a*,4b*), 143.30 (C4a,4b/C4a*,4b*), 142.14 (C4'a,4' b/ C4'a*,4'b*), 142.13 (C4'a,4'b/C4'a*,4'b*), 131.192 [S(O)Ph-C4/C4*], 131.186 [S(O)Ph-C4/C4*], 129.41 [S(O)Ph-C3], 128.61 (C3',6'/C3',6'*, 128.59 (C3',6'/C3',6'*, 128.56 (C3',6'/C3',6'*, 128.21 (C2',7'/C2',7'*, 128.18 (C2',7'/C2',7'*, 128.15 (C2',7'/C2',7'*, 124.98 [S(O)Ph-C2/C2*], 124.97 [S(O)Ph-C2/C2*], 124.87 (C3,6,3',6*), 123.94 (C1',8'/C1',8'*, 123.91 (C1',8'/C1',8'*, 123.86 (C1',8'/C1',8'*, 121.56 (C4,5/C4*,5*), 121.54 (C4,5/C4*,5*), 121.27 (C1,8/C1',8*), 121.23 (C1,8/C1',8*), 120.64 (C4',5',4',5'*, 66.13 (C9,9*) ppm. IR (solid): $\tilde{\nu}$ = 3056 (w), 2925 (w), 1474 (m), 1442 (m), 1398 (m), 1082 (s), 1070 (m), 1040 (s), 1020 (m), 1002 (m), 997 (m), 818 (m), 761 (s), 744 (s), 734 (s), 726 (s), 686 (s), 636 (s) cm^{-1} . UV/Vis (MeCN, 1.0×10^{-5} mol dm^{-3}): λ_{max} (ϵ) = 230 (sh, 77000), 273 (42000), 326 nm (21000 dm^3 cm^{-1} mol^{-1}). Fluorescence (MeCN, 1.0×10^{-5} mol dm^{-3} , λ_{ex} = 300 nm): λ_{em} = 380 nm. MS (EI, 70 eV): m/z (%) = 564.1 [M]⁺ (100, calcd. 564.1). $C_{37}H_{24}O_2S_2$ (564.72): calcd. C 78.70, H 4.28; found C 78.52, H 4.58.

2,7-Bis(phenylsulfonyl)-9,9'-spirobifluorene (SPSO1): Oxidation at elevated temperature: 0.89 M H_2O_2 (13.4 mmol, 7.13 equiv.) solution (15 mL) in AcOH (100 %) were added to a solution of 2,7-bis(phenylthio)-9,9'-spirobifluorene (**1**, 1.00 g, 1.88 mmol, 1.00 equiv.) in $CHCl_3$ (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 H_2O and extracted with CH_2Cl_2 . The combined organic layers were washed with H_2O until no peroxide was present any more, dried with Na_2SO_4 , and the solvent was removed under reduced pressure. The residue was purified by column chromatography (SiO_2 ; cyclohexane/EtOAc, 1:1), recrystallized from 1,4-dioxane, and dried under vacuum to yield the SPSO1 as colourless crystals, yield 1.0 g, 1.7 mmol, 89 %. 1H NMR (500 MHz, $CDCl_3$): δ = 7.95–7.88 (m, 6 H, H3,4,5,6,4',5'), 7.78–7.76 (m, 4 H, SO_2 Ph-H2), 7.51 [tt, 3J (H,H) = 7.5, 4J (H,H) = 1.2 Hz, 2 H, SO_2 Ph-H4], 7.45–7.40 (m, 8 H, H1,8,3',6', SO_2 Ph-H3), 7.08 [pseudo-td, 3J (H,H) = 7.5, 4J (H,H) = 1.1 Hz, 2 H, H2',7'], 6.54 [pseudo-dt, 3J (H,H) = 7.6, 4J (H,H) = 0.9, 5J (H,H) = 0.6 Hz, 2 H, H1',8'] ppm. $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ = 151.40 (C2,7), 145.44 (C8'a,9'a), 144.40 (C4a,4b), 142.30 (C8a,9a/C4'a,4'b), 142.19 (C8a,9a/C4'a,4'b), 141.40 (SO_2 Ph-C1), 133.36 (SO_2 Ph-C4), 129.39 (SO_2 Ph-C3), 128.88 (C3',6'), 128.36 (C3,6/C2',7'), 128.34 (C3,6/C2',7'), 127.68 (SO_2 Ph-C2), 123.87 (C1',8'), 123.77 (C1,8), 121.84 (C4,5), 120.85 (C4',5'), 66.18 (C9) ppm. IR (solid): $\tilde{\nu}$ = 3069 (w), 1446 (m), 1402 (w), 1314 (m), 1306 (s), 1177 (w), 1145 (s), 1089 (s), 1063 (w), 1004 (m), 935 (w), 821 (m), 769 (s), 750 (s), 721 (s), 691 (s), 682 (s) cm^{-1} . UV/Vis (MeCN, 1.0×10^{-5} mol dm^{-3}): λ_{max} (ϵ) = 227 (sh, 60400), 260 (sh, 33400), 286 (42600), 299 (41300), 323 nm (13400 dm^3 cm^{-1} mol^{-1}). Fluorescence (MeCN, 1.0×10^{-5} mol dm^{-3} , λ_{ex} = 297 nm): λ_{em} = 432 nm. MS (EI, 70 eV): m/z (%) = 596.1 [M]⁺ (100, calcd. 596.1). $C_{37}H_{24}O_4S_2$ (596.71): calcd. C 74.48, H 4.05; found C 74.13, H 4.05.

2,7-Bis(mesitylthio)-9,9'-spirobifluorene (2): A dried flask was charged with 2,7-dibromo-9,9'-spirobifluorene (**1**), (400 mg, 0.844 mmol, 1.00 equiv.), K_2CO_3 (587 mg, 4.25 mmol, 5.03 equiv.), and 2,4,6-trimethylthiophenol (0.38 mL, 2.52 mmol, 2.99 equiv.) un-

der an argon atmosphere. Dry DMF (4 mL) was added and the suspension was stirred for 18 h at 140 °C. More 2,4,6-trimethylthiophenol (0.25 mL, 1.66 mmol, 1.97 equiv.), more K₂CO₃ (485 mg, 3.51 mmol, 4.16 equiv.), and more dry DMF (2 mL) were added and the mixture was stirred for 4 d at 140 °C. The mixture was poured into H₂O (100 mL) and extracted with CH₂Cl₂ (4 × 50 mL). The combined organic layers were washed with H₂O (3 × 50 mL) and dried with Na₂SO₄. The solvent was removed under reduced pressure and the residue was diluted with CH₂Cl₂ (100 mL) and washed twice with H₂O. The organic layers were again dried with Na₂SO₄ and the solvent was removed under reduced pressure. The residue was again diluted, washed, and dried and the residue was then purified by column chromatography (SiO₂; cyclohexane/CH₂Cl₂, 1:0 → 9:1) and dried under vacuum, yield 255 mg, 0.414 mmol, 49 %. ¹H NMR (500 MHz, CDCl₃): δ = 7.82 [pseudo-dt, ³J (H,H) = 7.5, ^{4,5}J (H,H) = 0.9 Hz, 2 H, H4',5'], 7.43 [dd, ³J (H,H) = 7.7, ⁵J (H,H) = 1.1 Hz, 2 H, H4,5], 7.38 [pseudo-td, ³J (H,H) = 7.5, ⁴J (H,H) = 1.1 Hz, 2 H, H3',6'], 7.14 [pseudo-td, ³J (H,H) = 7.5, ⁴J (H,H) = 1.1 Hz, 2 H, H2',7'], 6.93 (s, 4 H, SMes-H3,5), 6.75 [pseudo-dt, ³J (H,H) = 7.6, ^{4,5}J (H,H) = 0.8 Hz, 2 H, H1',8'], 6.57–6.54 (m, 4 H, H1,3,6,8), 2.28 (s, 6 H, SMes-C4-CH₃), 2.26 (s, 12 H, SMes-C2,6-CH₃) ppm. ¹³C{¹H} NMR (126 MHz, CDCl₃): δ = 149.37 (C2,7), 148.59 (C8'a,9'a), 143.51 (SMes-C2,6), 141.81 (C4'a,4'b), 139.21 (SMes-C4), 138.49 (C4a,4b), 137.66 (C8a,9a), 129.38 (SMes-C3,5), 127.91 (C2',7'/C3',6'), 127.87 (C2',7'/C3',6'), 127.35 (SMes-C1), 124.47 (C3,6), 124.25 (C1',8'), 122.27 (C1,8), 120.12 (C4,5/C4',5'), 120.08 (C4,5/C4',5'), 65.70 (C9), 21.83 (SMes-C2,6-CH₃), 21.23 (SMes-C4-CH₃) ppm. IR (solid): ν̄ = 2916 (m), 2847 (w), 1597 (m), 1566 (w), 1443 (s), 1404 (m), 1373 (w), 1281 (w), 1250 (w), 1173 (w), 1157 (w), 1057 (m), 1034 (w), 957 (w), 849 (m), 810 (s), 764 (m), 733 (s), 687 (m), 640 (m) cm⁻¹. UV/Vis (MeCN, 1.0 × 10⁻⁵ mol dm⁻³): λ_{max} (ε) = 225 (sh, 71000), 317 (37000), 340 nm (34000 dm³ cm⁻¹ mol⁻¹). Fluorescence (MeCN, 1.1 × 10⁻⁵ mol dm⁻³, λ_{ex} = 320 nm): λ_{em} = 359 nm. MS (EI, 70 eV): m/z = 616.2 [M]⁺ (100, calcd. 616.2), 308.1 [M]²⁺ (8.6).

2,7-Bis(mesitylsulfonyl)-9,9'-spirobifluorene (SPSO2): 2,7-Bis(mesitylthio)-9,9'-spirobifluorene (**2**, 158 mg, 0.256 mmol, 1.00 equiv.) was dissolved in EtOAc (20 mL) and AcOH (100 %, 5 mL). H₂O₂ (30 %, 0.250 mL, 352 mg, 3.10 mmol, 12.1 equiv.) 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 with 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 %. ¹H NMR (500 MHz, CDCl₃): δ = 7.88 [d, ³J (H,H) = 7.6 Hz, 2 H, H4',5'], 7.85 [d, ³J (H,H) = 8.1 Hz, 2 H, H4,5], 7.59 [dd, ³J (H,H) = 8.1, ⁴J (H,H) = 1.7 Hz, 2 H, H3,6], 7.43–7.40 (m, 4 H, H1,8,3',6'), 7.10 [pseudo-td, ³J (H,H) = 7.6, ⁴J (H,H) = 1.1 Hz, 2 H, H2',7'], 6.86 (s, 4 H, SO₂Mes-H3), 6.58 [d, ³J (H,H) = 7.6 Hz, 2 H, H1',8'], 2.40 (s, 12 H, SO₂Mes-C2-CH₃), 2.26 (s, 6 H, SO₂Mes-C4-CH₃) ppm. ¹³C{¹H} NMR (126 MHz, CDCl₃): δ = 150.57 (C2,7), 145.47 (C8'a,9'a), 143.92 (C4a,4b,8a,9a), 143.55 (SO₂Mes-C4), 142.22 (C4'a,4'b), 139.92 (SO₂Mes-C2), 134.05 (SO₂Mes-C1), 132.33 (SO₂Mes-C3), 128.79 (C3',6'), 128.21 (C2',7'), 126.93 (C3,6), 123.60 (C1',8'), 123.01 (C1,8), 121.52 (C4,5), 120.90 (C4',5'), 66.18 (C9), 22.71 (SO₂Mes-C2-CH₃), 21.13 (SO₂Mes-C4-CH₃) ppm. IR (solid): ν̄ = 2932 (w), 1605 (w), 1558 (w), 1443 (m), 1396 (w), 1381 (w), 1304 (s), 1180 (w), 1165 (w), 1142 (s), 1126 (m), 1072 (m), 1034 (w), 1003 (w), 964 (w), 933 (w), 879 (w), 864 (w), 849 (w), 818 (w), 764 (s), 733 (m), 717 (m), 694 (s), 663 (s), 640 (s), 617 (w) cm⁻¹. UV/Vis (MeCN, 1.0 × 10⁻⁵ mol dm⁻³): λ_{max} (ε) = 230 (sh, 66000), 285 (44000), 297 (40000), 327 nm (14000 dm³ cm⁻¹ mol⁻¹).

Fluorescence (MeCN, 1.0 × 10⁻⁵ mol dm⁻³, λ_{ex} = 285 nm): λ_{em} = 421 nm. MS (EI, 70 eV): m/z = 680.2 [M]⁺ (100, calcd. 680.2).

2,7-Bis(pentylsulfonyl)-9,9'-spirobifluorene (SPSO3): 2,7-Dibromo-9,9'-spirobi-[fluorene] (4.34 g, 9.14 mmol), K₂CO₃ (7.58 g, 54.9 mmol, 6.0 equiv.) and 1-pentanethiol (3.9 mL, 31.1 mmol, 3.4 equiv.) was added to dry DMF (4 mL) and the suspension was stirred for 16 h at 140 °C. More 1-pentanethiol (9.14 mmol, 1.0 equiv.) was added and the mixture was stirred for another 6 h at 140 °C. The mixture was poured into H₂O and extracted with CH₂Cl₂. The combined organic layers were washed several times with H₂O and dried with Na₂SO₄. The solvent was removed under reduced pressure and the crude bis-thioether **3** (4.11 g, 86 %) was used without further purification for the next step. Bis-thioether **3** (2.5 g, assuming 4.8 mmol) was dissolved in a mixture of AcOH (25 mL), ethyl acetate (40 mL) and H₂O₂ (30 %, 4.8 mL, 10.0 equiv.). After stirring at room temperature for 2 d, CHCl₃ (20 mL) was added. The clear solution was stirred again at room temperature for 1 d and then at 40 °C for 30 min. The solvents were evaporated under reduced pressure and the residue was purified by column chromatography (SiO₂; ethyl acetate/cyclohexane, 2:5 → 4:5). The white product was further purified by recrystallization from dry EtOH. The fine white needles were filtered off and washed with pentane/diethyl ether (4:1), yield 1.54 g, 55 %. ¹H NMR (500 MHz, CDCl₃): δ = 8.09 (d, J = 8.0 Hz, 2 H, H4',5'), 7.98 (dd, J = 8.1, 1.7 Hz, 2 H, H3',6'), 7.88 (pseudo-td, J = 7.6, 0.9 Hz, 2 H, H4',5'), 7.42 (pseudo-td, J = 7.6, 1.1 Hz, 2 H, H2',7'), 7.30 (d, J = 1.6 Hz, 2 H, H1',8'), 7.11 (pseudo-td, J = 7.5, 1.1 Hz, 2 H, H3',6'), 6.62 (pseudo-dt, J = 7.7, 0.9 Hz, 2 H, H1',8'), 2.99–2.87 (m, 4 H, H^{SO2CH2}), 1.61–1.50 (m, 4 H, H^{SO2CH2CH2}), 1.28–1.11 (m, 8 H, H^{CH2}), 0.78 (t, J = 7.1 Hz, 6 H, H^{CH3}) ppm. ¹³C{¹H} NMR (126 MHz, CDCl₃): δ = 151.4 (C2',7'), 145.5 (C4'a,4'b), 144.8 (C4a,4b), 142.2 (C8'a,9'a), 140.1 (C8a,9a), 129.0 (C2',7'), 128.5 (C3',6'), 128.4 (C3',6'), 124.4 (C1',8'), 123.7 (C1',8'), 121.8 (C4',5'), 120.9 (C4',5'), 66.1 (C9), 56.4 (C^{SO2CH2}), 30.3 (C^{CH2}), 22.3 (C^{SO2CH2CH2}), 22.1 (C^{CH2}), 13.7 (C^{CH3}) ppm. UV/Vis (MeCN, 1.0 × 10⁻⁵ mol dm⁻³): λ_{max} (ε) = 197 (47650), 211 (51000), 223 (sh, 42400), 259 (sh, 27500), 277 (36700), 290 (29800), 304 (9660), 318 nm (6900 dm³ cm⁻¹ mol⁻¹). MS (MALDI-TOF, without matrix): m/z (%) = 585.5 [M]⁺ (calcd. 584.2). C₃₅H₃₆O₄S₂ (584.79): calcd. C 71.88, H 6.20; found C 71.65, H 6.37. Fluorescence (MeCN, 1.0 × 10⁻⁵ mol dm⁻³): λ_{em} = 422 nm.

Crystallography: Data were collected on a Bruker-Nonius KappaAPEX diffractometer with data reduction, solution, and refinement by using the programs APEX2.^[22] Mercury v. 3.1^[23] was used to analyze and display the X-ray structures.

SPSO1-2CH₂Cl₂: C₃₉H₂₈Cl₄O₄S₂, M = 766.59, colorless block, monoclinic, space group P2₁/c, a = 11.9690(6), b = 12.9602(6), c = 23.1478(11) Å, β = 93.801(3)°, U = 3582.8(3) Å³, Z = 4, D_c = 1.421 Mg m⁻³, μ(Mo-K_α) = 0.488 mm⁻¹, T = 123 K. Total 89315 reflections, 13057 unique, R_{int} = 0.036. Refinement of 9162 reflections (498 parameters) with I > 2σ(I) converged at final R1 = 0.0572 (R1 all data = 0.0744), wR2 = 0.0597 (wR2 all data = 0.0968), gof = 1.0852. CCDC 974892.

SPSO2: C₄₃H₃₆O₄S₂, M = 680.89, colorless block, monoclinic, space group C2/c, a = 19.2422(4), b = 15.6495(4), c = 13.1743(3) Å, β = 123.096(2)°, U = 3323.54(15) Å³, Z = 4, D_c = 1.361 Mg m⁻³, μ(Mo-K_α) = 0.206 mm⁻¹, T = 173 K. Total 21904 reflections, 6040 unique, R_{int} = 0.036. Refinement of 4110 reflections (222 parameters) with I > 2σ(I) converged at final R1 = 0.0458 (R1 all data = 0.0610), wR2 = 0.0484 (wR2 all data = 0.0775), gof = 1.0852. CCDC 974893.

SPSO3: C₃₅H₃₆O₄S₂, M = 584.80, colorless plate, monoclinic, space group C2/c, a = 19.5503(8), b = 10.7566(4), c = 15.8860(7) Å, β = 118.486(2)°, U = 2936.3(2) Å³, Z = 4, D_c = 1.323 Mg m⁻³, μ(Cu-K_α) =

0.488 mm⁻¹, $T = 123$ K. Total 11690 reflections, 2698 unique, $R_{\text{int}} = 0.033$. Refinement of 2380 reflections (186 parameters) with $I > 2\sigma$ (I) converged at final $R1 = 0.0376$ ($R1$ all data = 0.0404), $wR2 = 0.0400$ ($wR2$ all data = 0.0487), $\text{gof} = 1.0884$. CCDC 993287.

Theoretical Calculations: Density functional calculations (DFT) were carried out with the D.01 revision of the Gaussian 09 program package^[24] by using Becke's three-parameter B3LYP exchange-correlation functional^[25] together with the 6-31G** basis set for H, C, S, O, and P^[26] and the "double-z" quality LANL2DZ basis set for the Ir element.^[27] The geometries of the singlet ground state (S_0) and the lowest-energy singlet (S_1) and triplet (T_1) states were fully optimized without imposing any symmetry restriction. All the calculations were performed in the presence of the solvent (acetonitrile). Solvent effects were considered within the self-consistent reaction field (SCRF) theory by using the polarized continuum model (PCM) approach.^[28] Time-dependent DFT (TD-DFT) calculations of the lowest-lying 20 singlets and triplets were performed in the presence of the solvent at the minimum-energy geometry optimized for S_0 . The geometry of the S_1 singlet state was optimized at the TD-DFT level and that of the T_1 triplet state at the spin-unrestricted UB3LYP level.

LEC Device Preparation and Characterization: The solvents were supplied by Aldrich. The thickness of films was determined with an Ambios XP-1 profilometer. Indium tin oxide ITO glass plates were patterned by conventional photolithography. The substrates were cleaned by sonication in water-soap, water, and 2-propanol 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 % Irpic (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 OLT OLED Lifetime-Test System.

CCDC 974892 (for SPSO1·2CH₂Cl₂), 974893 (for SPSO2) and 993287 (for SPSO3) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

Acknowledgments

The authors thank the Swiss National Science Foundation, the University of Basel, the Spanish Ministry of Economy and Competitiveness (MINECO) (MAT2014-55200, CTQ2012-31914, CTQ2015-71154, and Unidad de Excelencia María de Maeztu MDM-2015-0552), the Generalitat Valenciana (Prometeo/2012/053), the European Research Council (Advanced grant number 267816 LiLo), and European FEDER funds (CTQ2012-31914) for financial support. PD Dr. Daniel Häussinger is thanked for assistance with the NMR spectroscopy.

Keywords: Donor–acceptor systems · Photophysics · Phosphorescence · OLEDs · LECs · Sulfones

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Received: March 3, 2016

Published Online: March 29, 2016