An unprecedented ambipolar charge transport material exhibiting balanced electron and hole mobilities†

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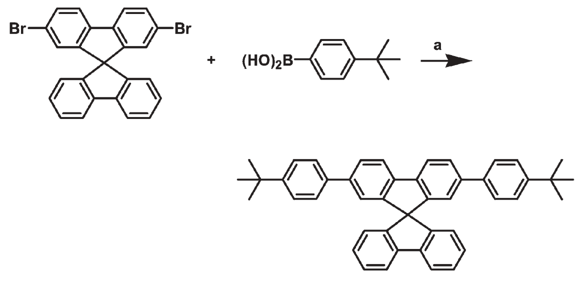
2,7-Bis(4-*tert*-butylphenyl)-9,9′-spirobifluorene exhibits balanced electron and hole mobilities of up to 10^{-3} cm^2 V^{-1} s^{-1}, as measured using time-of-flight techniques.

The performance of organic optoelectronic device used in xerography, light-emitting diode (OLED), thin-film transistor and solar cell applications is strongly affected by the charge transport characteristics of π-conjugated materials. Although many high-mobility hole-transporting materials have been prepared using various structural elements,[1] amorphous materials that display respectable electron- and/or ambipolar carrier-transporting capabilities are relatively rare.[2] For practical applications, it would be most cost-effective for devices to incorporate a single layer of an organic material that exhibits balanced electron and hole mobilities.[3] The quest for suitable ambipolar transport materials—in particular, efficient bipolar transport materials possessing only a single chromophore—remains a great challenge. Recent reports describing the excellent nondispersive ambipolar carrier-transport properties of oligofluorenes suggest a possible approach toward the preparation of novel ambipolar materials; unfortunately, even though the hole and electron mobilities of most oligofluorenes are comparable, but they are far from well-balanced.[4] Among the oligofluorenes, bifluorenes exhibit the best characteristics for charge transport. It is generally accepted that the charge mobility is mainly governed by factors such as backbone length, side chain type/length, and rigidity of molecules. Thus, we believed that we would be able to improve the charge transport balance through modification of the molecular configuration of the four consecutively linked phenylene rings similar to bifluorene, while enhancing its intermolecular interactions and retaining its ability to form stable amorphous states—a critical issue for solid state devices. Here, we report an amorphous material, 2,7-bis(4-*tert*-butylphenyl)-9,9′-spirobifluorene (**27BPSF**),‡ that exhibits nearly identical electron and hole mobilities of up to 10^{-3} cm^2 V^{-1} s^{-1} at room temperature, as measured using time-of-flight (TOF) techniques. This balanced ambipolar transport behaviour of **27BPSF** is unsurpassed at present.



27BPSF

Scheme 1 Synthesis of **27BPSF**. *Reagents and conditions*: (a) Pd(PPh$_3$)$_4$, *t*-Bu$_3$P, K$_2$CO$_3$, toluene.

Scheme 1 illustrates our synthetic approach toward **27BPSF**, which possesses 4-*tert*-butylphenyl groups at the 2- and 7-positions of a 9,9′-spirobifluorene core. A Pd-catalysed Suzuki coupling of 2,7-dibromo-9,9′-spirobifluorene and 4-*tert*-butylphenylboronic acid provided **27BPSF** in 83% yield.

27BPSF exhibits high thermal tolerance—its 5% weight loss occurred at a temperature of 350 °C, as analysed using thermogravimetric analysis (TGA)—and a distinct glass transition temperature (T_g) of *ca.* 150 °C, as analysed using differential scanning calorimetry (DSC) (Fig. S1, ESI†), reflecting the benefits of utilizing spirobifluorene as the core framework.[5] As a consequence, **27BPSF** can form homogeneous and stable amorphous films upon thermal evaporation. The bipolar electrochemical character of **27BPSF** was verified with cyclic voltammetry (CV); we observed one reversible oxidation potential (at +1.41 V) and one reduction potential (at −2.30 V; *vs.* Ag/AgCl) (Fig. 1). These features clearly indicate that the radical cation and radical anion of **27BPSF** are sufficiently stable entities.

We used the TOF transient photocurrent technique[6] to perform charge-carrier mobility measurements of **27BPSF** in thin films. The Pd-free sample after purification by sublimation (Fig. S2, ESI†) was thermally deposited (at 10^{-6} Torr) into a device having the configuration of glass|Ag (30 nm)|**27BPSF** (3 μm)|Ag (150 nm), which was then placed inside a cryostat under vacuum. A nitrogen pulse laser (λ = 337 nm) was used as the excitation light source; it was passed through the semitransparent electrode (Ag) to induce a thin sheet of excess carriers. Under an applied dc bias, the transient photocurrent was recorded using a digital storage oscilloscope as the carriers swept across the bulk of the organic film to reach the counter electrode (Ag). The charge transit times (t_T) were measured and the mobilities were calculated according to $\mu = D/(t_T E) = D^2/(t_T V)$, where V is the applied bias and D is the thickness of the organic layer. The mobilities of different carriers (holes or electrons) were determined by switching the polarity of the applied dc bias.

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† Electronic supplementary information (ESI) available: DSC analysis, SEM and EDx analysis, GDM analyses based on field- and temperature-dependence of mobility measurements, absorption and emission spectra. See DOI: 10.1039/b617821a

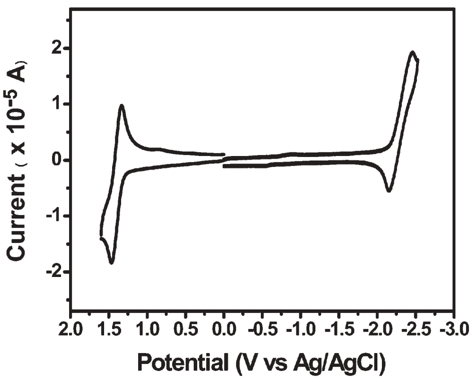

Fig. 1 Cyclic voltammogram of **27BPSF**. Scan rate: 100 mV s^{-1}; working electrode: glassy carbon; reference electrode: Ag/AgCl. Oxidation CV was performed in CH_2Cl_2 containing 0.1 M n-Bu_4NPF_6 as the supporting electrolyte. Reduction CV was performed in anhydrous THF containing 0.1 M n-Bu_4ClO_4 as the supporting electrolyte.

Fig. 2(a) and (b) display the TOF transients of electrons and holes, respectively, for **27BPSF**, as measured at room temperature under an applied field of 3.7×10^5 V cm^{-1}. The appearance of constant photocurrent plateaus for both electrons and holes indicates that nondispersive ambipolar charge transport occurred. The transit time (t_T) can be evaluated unambiguously from the intersection point of the asymptotes of the plateau and tail sections in the double-logarithmic representation (inset of Fig. 2). The extracted transit times for electrons and holes were nearly identical; thus, the mobility of each was 8.5×10^{-4} cm^2 V^{-1} s^{-1} at $E = 3.7 \times 10^5$ V cm^{-1}.

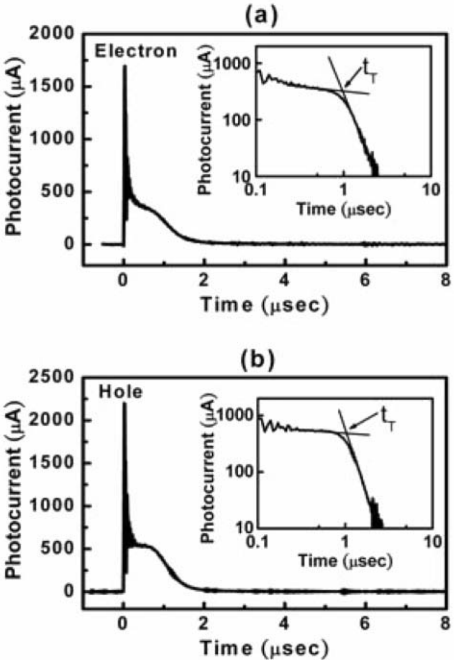

Fig. 2 Representative TOF transients for **27BPSF** (thickness: 3 μm; $E = 3.7 \times 10^5$ V cm^{-1}): (a) electrons, (b) holes. The insets display the corresponding double-logarithmic plots.

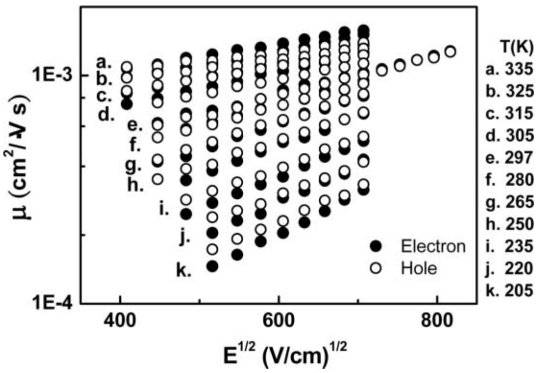

Fig. 3 Electron and hole mobilities for **27BPhSF** at various temperatures, plotted semi-logarithmically as a function of the square root of the electric field.

To shed light on the carrier transport mechanism of **27BPSF**, we determined the temperature- and field-dependences of the electron and hole mobilities. Fig. 3 displays the field-dependence of both the electron and hole mobilities for **27BPSF** at various temperatures. We observed almost identical values for the electron and hole mobilities over a wide range of applied voltages and temperatures. In addition, at temperatures above ambient conditions, both the electron and hole mobilities reached as high as 10^{-3} cm^2 V^{-1} s^{-1} under a high field. The field-dependences of the electron and hole mobilities are in excellent agreement with the Poole–Frenkel (PF) relationship, $\mu \propto \exp(\beta E^{1/2})$, where β is a PF constant that decreases upon increasing the temperature.[7] Such a relationship is often observed in disordered organic systems, where it agrees with the predictions of the Gaussian disorder model (GDM) proposed by Bässler and coworkers.[8] The GDM assumes that charge transport within amorphous organic solids occurs through a hopping mechanism associated with Gaussian-distributed energetic disorder of localized hopping sites and intermolecular positional disorder. Table 1 summarizes the values of the disorder-free mobility (μ_0), the degree of energetic disorder (σ) and the parameter of positional disorder (Σ), which we extracted (see ESI† for details) from Fig. 3 using the Bässler formalism (eqn (1)),

$$\mu(E,T) = \mu_0 \exp\left(-\left[\frac{2\sigma}{3k_B T}\right]^2\right)\exp\left(C\left[\left(\frac{\sigma}{k_B T}\right)^2 - \Sigma^2\right]\sqrt{E}\right) \quad (1)$$

where k_B is the Boltzmann constant and C is an empirical constant. The extracted values of μ_0, σ and Σ for electrons and holes of **27BPSF** fall within the bounds of values determined for similar systems. Such consistency suggests that amorphous **27BPSF** films possess inherently identical charge transport properties for electrons and holes.

Although the detailed alignment of molecules in amorphous solids is difficult to determine, their crystalline structures (if available) can serve as extreme examples of the intermolecular relationships in amorphous molecular solids. Single crystals of

Table 1 Hole and electron transport parameters of **27BPSF**, calculated using GDM

	μ_0/cm^2 V^{-1} s^{-1}	σ/eV	Σ	C ($\times 10^{-4}$)
Hole	6.5×10^{-3}	6.5×10^{-2}	1.6	4
Electron	7.4×10^{-3}	6.9×10^{-2}	1.4	3.6

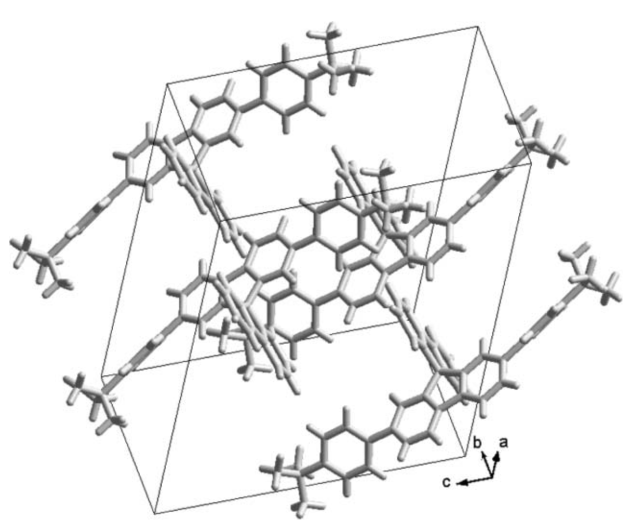

Fig. 4 Partial molecular packing of **27BPSF** in the unit cell; the solvent molecules have been omitted for clarity.

27BPSF suitable for X-ray crystallographic analysis§ were obtained through two-layer diffusion of CH_2Cl_2 and CH_3OH. **27BPSF** was crystallized with crystallography imposed twofold symmetry, and one CH_2Cl_2 and two CH_3OH disordered molecules were co-crystallized, Fig. 4 depicts a partial molecular packing diagram within the unit cell. The phenylene rings are twisted from the coplanar fluorene ring with an averaged dihedral angle of 47.3°. It is clear that the introduction of bulky terminal units to the rigid bifluorene core efficiently suppresses its intermolecular interactions, resulting in the vacuum-deposited thin films of **27BPSF** having stable amorphous states. Although there is no distinct evidence that can indicate significant intermolecular interactions occurred in the amorphous sample of **27BPSF** (Fig. S4, ESI†). The unsymmetrical substitution on the different branches of the spirobifluorene core guides the alignment of neighbouring molecules along the long molecular axis in an antiparallel manner. We believe that the anisotropic molecular alignment observed in the crystals of **27BPSF** may be crucial for efficient charge transport to occur through hopping pathways in its amorphous thin films.

In summary, we have synthesized and characterized a novel spirobifluorene-based material, **27BPSF**, the thin films of which exhibit an unprecedented balance of electron and hole mobilities, as observed using TOF transient photocurrent techniques. The ambipolar charge carrier mobilities reached as high as 10^{-3} cm^2 V^{-1} s^{-1} at temperatures above ambient conditions and under high electric fields. The similar parameters extracted, on the basis of the GDM, from measurements of the field- and temperature-dependent mobilities confirm that **27BPSF** exhibits a near-identical bipolar charge-transport capacity.

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Notes and references

‡ *Spectroscopic* characterisation of **27BPSF**: mp 265–266 °C; IR (KBr) 3057w, 2949s, 2890m, 2858m, 1636s, 1461s cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.89 (d, J = 7.9 Hz, 2H), 7.84 (d, J = 7.6 Hz, 2H), 7.61 (d, J = 7.9 Hz, 2H), 7.38–7.32 (m, 10H), 7.10 (t, J = 7.5 Hz, 2H), 6.91 (s, 2H), 6.81 (d, J = 7.6 Hz, 2H), 1.28 (s, 18H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 150.1, 149.7, 148.7, 141.7, 140.6, 140.4, 138.0, 127.8, 126.6, 125.4, 124.2, 122.6, 120.1, 119.9, 66.0, 34.4, 31.2; Anal. Calc.: C, 93.06; H, 6.94. Found: C, 93.16; H, 7.25%.

§ *Selected crystallographic data* for **27BPSF**: $C_{46.5}H_{45}ClO$, M = 655.28, monoclinic, space group $C2/c$, a = 21.5203(6), b = 10.2141(3), c = 16.7850(4) Å, U = 3653.22 (17) Å^3, D_c = 1.172 Mg m^{-3}, T = 295(2) K, Z = 4, μ = 0.070 mm^{-1}, F(000) = 1384, crystal size 0.50 × 0.10 × 0.02 mm, θ_{max} = 27.47°. 2317 Reflections were observed with $I \geqslant 2\sigma(I)$ among the 4140 unique reflections, and 11051 reflections were used in the refinement. The final indices were $R1$ = 0.0678, $wR2$ = 0.1965. CCDC 630057. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b617821a

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