A high-efficiency and low-operating-voltage green electrophosphorescent device employing a pure-hydrocarbon host material†

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A suitable triplet energy level and high morphological stability and hole mobility make indenofluorene an effective host material for green phosphorescent OLEDs.

The development of phosphorescent organic light-emitting devices (PhOLEDs) has attracted a great deal of attention because the incorporation of heavy metal-containing complexes into appropriate host materials can allow the harvesting of both singlet and triplet excitons, making it possible to render devices with close to 100% internal quantum efficiency.[1] To obtain high quantum efficiency in a PhOLED, the host materials should possess (i) triplet energies higher than those of the guest molecules (to prevent exothermic reverse energy transfer),[2] (ii) good charge balance properties (to effectively confine triplet excitons within the emitting layer), and (iii) good charge carrier transport properties (to achieve a low operating voltage). In this regard, Adachi et al.[3] demonstrated efficient green PhOLEDs exhibiting external quantum efficiencies (η_{ext}) close to 20% and power efficiencies (η_p) of 60 lm W^{-1} at low current densities (<2 μA cm^{-2}) and low brightness. The values of η_{ext} and η_p for these devices decreased significantly, however, upon increasing the current, due to triplet–triplet annihilation of the phosphors;[4] indeed, it is generally difficult to obtain high quantum efficiencies at high currents. Recently, much higher efficiencies have been obtained for modified PhOLED structures, such as those featuring hole- and exciton-blocking layers to confine holes and excitons within the emitting layer;[5] nevertheless, the voltage drop across these layers requires more power to drive the devices, leading to high operating voltages and lower power efficiencies. This problem can be solved by increasing the conductivity of the organic layers, e.g., through doping with donors and acceptors that can significantly reduce the voltage drop across these films. By introducing a p–i–n structure into an OLED, Pfeiffer et al. demonstrated highly efficient green-emitting PhOLEDs using the hole transport material TCTA as a host, obtaining high power efficiencies of 52 lm W^{-1} (η_{ext} = ca. 13.7%) with 100 cd m^{-2} at 2.75 V and 45 lm W^{-1} (η_{ext} = ca. 12.6%) with 1000 cd m^{-2} at 3.1 V.[6] Subsequently, they obtained a power efficiency of 77 lm W^{-1}

and a value of η_{ext} of 19% at 100 cd m^{-2} (2.75 V) after p-doping the hole transporting layer (HTL), n-doping the electron transporting layer (ETL) and employing a double emission layer.[7] Using a similar strategy, the Kido group recently reported ultrahigh-efficiency green PhOLEDs using Ir(ppy)$_3$ as an emitter, realizing high values of η_p and η_{ext} (133 lm W^{-1} and 29% at 100 cd m^{-2}, respectively).[8] As this approach increases the complexity of the device structure, the required fabrication processes would add considerably to the overall cost for mass production. Therefore, the challenge remains to develop new host materials to reduce the driving voltage while maintaining high quantum efficiencies at high luminance without the need for p–i–n-type OLED structures.

Several materials have been reported as hosts for highly efficient green electrophosphorescent devices, including 4,4′,4″-tris(N-carbazolyl)triphenylamine (TCTA), 4,4′-bis-(9-carbazolyl)biphenyl (CBP), 2,9-dimethyl-4,7-diphenyl-phenanthroline (BCP), 1,3-bis(N,N-tert-butylphenyl)-1,3, 4-oxadiazole (OXD7), and 3-phenyl-4-(1′-naphthyl)-5-phenyl-1,2,4-triazole (TAZ).[9] In a previous study, we employed spiro-configured bi(9,9-diarylfluorene)s (triplet energy: E_{T1} = 2.3 eV) as effective host materials in green and red PhOLEDs.[10] To better match the triplet energy of the green complexes, the conjugation length of the host must be selected carefully to achieve a wide energy gap and a high value of E_{T1}. Electron delocalization in p-phenylene linkages is extended along the elongated molecular axis, with E_{T1} decreasing with the number of phenylene rings. The Yagi group reported that p-terphenyl has a value of E_{T1} of 2.55 eV, making it suitable for use as a host for a green phosphorescent dopant.[11] In this paper, we report a unique amorphous host material, SInF3, featuring a coplanar pure-hydrocarbon p-terphenylene (indenofluorene) backbone and exhibiting a high triplet energy, excellent thermal stability, and high hole mobility, making it suitable for use in green PhOLEDs. A device incorporating SInF3 as the host, accommodating bis(2-phenylpyridinato-N,C$^{2′}$)iridium(acetylacetonate) ppy$_2$Ir(acac)[12] as the green emitter, achieved a value of η_{ext} of 15.8% (60 cd A^{-1}) and a value of η_p of 63 lm W^{-1} at a practical brightness of 50 cd m^{-2} at 3 V. Furthermore, the device provided a brightness of 10 000 cd m^{-2} at an extremely low operating voltage (5 V); the efficiencies remained at 14% (53.5 cd A^{-1}) and 33.6 lm W^{-1}—the highest values ever reported for green PhOLEDs lacking a p–i–n junction. To the best of our knowledge, this is the first report of an indenofluorene derivative being used as an efficient host material for PhOLEDs. Scheme 1 displays our synthetic route toward SInF3. Suzuki coupling of the spirobifluorene-based boronic ester 1 and 2-iodoethyl benzoate gave the ester 2 in 92% yield. Double nucleophilic addition of p-tolyllithium

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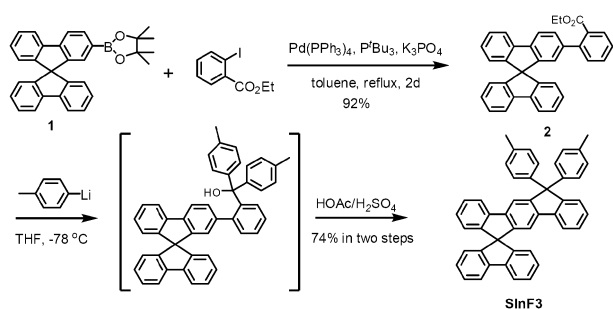
Scheme 1 Synthetic route toward **SInF3**.

onto the ester group of **2** and subsequent intramolecular Friedel–Crafts cyclization gave **SInF3** in an isolated yield of 74%.

We selected indenofluorene as the core structure of our green host because its derivatives possess rigid coplanar structures that enhance the conjugation, carrier mobility, and fluorescence quantum efficiency of the blue emission.[13] The molecular design in **SInF3** preserves the conjugated *p*-terphenyl backbone, which plays a prominent role in determining the overall electronic, electrochemical, and photophysical properties. The spiro configuration[14] and peripheral *p*-tolyl substituent groups desymmetrize the molecule, thereby improving its thermal and morphological stability. **SInF3** exhibits a high thermal tolerance [5% weight loss occurred at 354 °C, determined using thermogravimetric analysis (TGA)] and a distinct glass transition temperature (T_g) of *ca.* 171 °C [determined using differential scanning calorimetry (DSC)] (ESI,† Fig. S1). We observed completely different morphological behavior for **SInF3** relative to that of its symmetric unsubstituted[15] and *tert*-butyl-substituted[16] dispirofluorene–indenofluorene (DSF-IF) derivatives, which are highly crystalline.

The small Stokes shift (5 nm) and the mirror image of the absorption and fluorescence spectra of **SInF3** in CHCl₃ (Fig. 1) confirm its molecular coplanarity and rigidity. The value of E_{T1} of **SInF3**, which we estimated from the phosphorescence peak (492 nm) at 77 K, was 2.52 eV; this value is close to that of the parent *p*-terphenylene (E_{T1} = 2.55 eV) and higher than that of the green phosphorescent dopant ppy₂Ir(acac) (E_{T1} = 2.41 eV). We used cyclic voltammetry to investigate the electrochemical properties of **SInF3**, observing one reversible oxidation process at 1.5 eV (*vs.* Ag/AgCl) (ESI,† Fig. S2). From the redox potential referenced to the
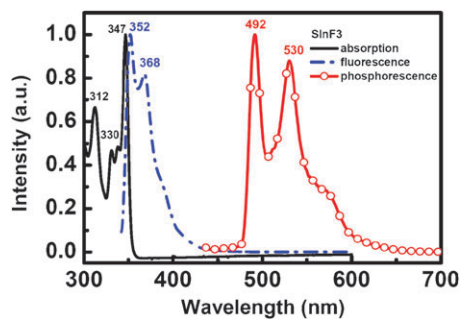

Fig. 1 Normalized UV-Vis absorption and fluorescence spectra (CHCl₃, room temperature) and phosphorescence spectrum (EtOH, 77 K) for **SInF3**.

redox couple of ferrocene, we calculated the energy level of the highest occupied molecular orbital (HOMO) to be −5.83 eV. Subtracting the optical band gap (3.49 eV, determined from the cutoff of the optical absorption spectrum) from the HOMO energy level, we estimated the energy level of the lowest unoccupied molecular orbital (LUMO) to be −2.34 eV. From the energy alignments, we anticipated efficient exothermic energy transfer from the **SInF3** triplet state to the ppy₂Ir(acac) triplet state, with excellent triplet energy confinement on the ppy₂Ir(acac) molecules.

We performed a time-of-flight (TOF) measurement to evaluate the carrier mobility of **SInF3**. The TOF transient displays non-dispersive hole-transport characteristics, implying that the carriers moved with constant velocity across the **SInF3** film (ESI,† Fig. S3). In the double-logarithmic representation (inset to Fig. S3†), the transit time (t_T) can be determined from the intersection point of the two asymptotes. The hole mobilities of **SInF3** as a function of the electric field (ESI,† Fig. S4) ranged from 3.9×10^{-3} to 5.6×10^{-3} cm² V⁻¹ s⁻¹ for fields varying from 6×10^4 to 4.8×10^5 V cm⁻¹, respectively. We attribute the high hole mobility of **SInF3** to the spiro configuration (orthogonal arrangement) of its indenofluorene and peripheral fluorene units, which bridge and enhance the intermolecular charge transport of holes.[17]

Employing **SInF3** as a host material, we fabricated a multilayer device having the configuration ITO/PEDOT–PSS (30 nm)/NPB (15 nm)/TCTA (5 nm)/10 wt% ppy₂Ir(acac)-doped **SInF3** (25 nm)/TPBI (50 nm)/LiF (0.5 nm)/Al (100 nm). In this device, PEDOT–PSS functioned as the hole injection layer; 4,4′-bis[*N*-(1-naphthyl)-*N*-phenylamino]biphenyl (NPB) was the hole transport layer. To decrease the hole-injection barrier between NPB and the emitting layer, we incorporated a layer of 4,4′,4″-tris(*N*-carbazolyl)triphenylamine (TCTA) because of its appropriately matching HOMO energy level. 1,3,5-Tris(*N*-phenylbenzimidizol-2-yl)benzene (TPBI) functioned as both the hole-blocking and ETL. Lithium fluoride (LiF) was used as the electron-injection layer; aluminium (Al) was the cathode.

Fig. 2(a) presents the current density–voltage–luminance (*I–V–L*) characteristics of this device. The *I–V* and *L–V* curves both feature steep increases after the turn-on voltage reached 2.5 V. The operating voltage for a luminance of 1000 cd m⁻² was 3.7 V; a luminance of 10 000 cd m⁻² was achieved at voltages as low as 5 V. The device exhibited an unusually high current of *ca.* 2700 mA cm⁻² at 9.5 V, giving a maximum brightness of 255 000 cd m⁻². The electroluminescence (EL) spectrum [inset to Fig. 2(a)] reveals that the emission [CIE coordinates: (0.32, 0.64)] arose purely from ppy₂Ir(acac), *i.e.*, no emission occurred from the neighboring materials. Fig. 2(b) presents the values of η_{ext} and η_p as functions of the luminance. The maximum values of η_{ext} [15.8% (60 cd A⁻¹)] and η_p (63 lm W⁻¹) were achieved at a practical brightness of 50 cd m⁻² at 3 V. It is noteworthy that even when the luminance reached 10 000 cd m⁻² (injection current density: 18.7 mA cm⁻²), the value of η_{ext} remained at 14% (54 cd A⁻¹). These results clearly indicate that appropriately designed host materials enable PhOLEDs to function with extremely low operating voltages without the need for a *p–i–n* junction. We observed only a limited roll-off in the values of η_{ext}, even when the
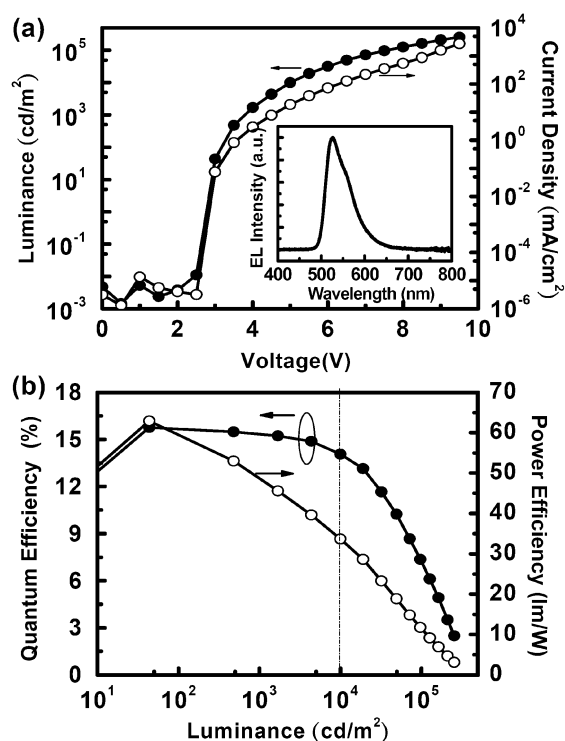
Fig. 2 (a) *L–V* and *I–V* characteristics. Inset: EL spectrum of the device. (b) Quantum efficiency–luminance and power efficiency–luminance characteristics.

luminance reached a value as high as 10 000 cd m^{-2}. We attribute the excellent performance of this device to the balanced injection of electrons and holes, and to the efficient confinement of triplet excitons generated within the emitting layer.

In conclusion, we have synthesized a pure-hydrocarbon host material, comprising a coplanar and rigid indenofluorene backbone presenting different peripheral aryl substituents, for use in green PhOLEDs. A device incorporating this tailor-made host material exhibited a brightness of 10 000 cd m^{-2} at an extremely low operating voltage (5 V), with efficiencies of 14% (53.5 cd A^{-1}) and 33.6 lm W^{-1}. Thus, PhOLEDs exhibiting high quantum efficiencies and low operating voltages at high brightness can be prepared without using complicated *p–i–n* junction techniques.

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