

High-efficiency and low-operating-voltage green electrophosphorescent device employing a pure-hydrocarbon host material

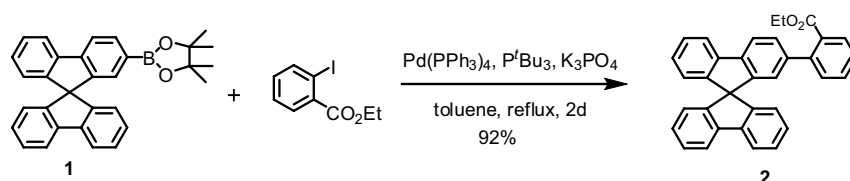
Liang-Chen Chi^a, Wen-Yi Hung^{b*}, Hao-Chih Chiu^b, Ken-Tsung Wong^{a*}

^a Department of Chemistry, National Taiwan University, Taipei 106, Taiwan. Fax 886 2 33661667; Tel: 886 2 33661665; E-mail: kenwong@ntu.edu.tw

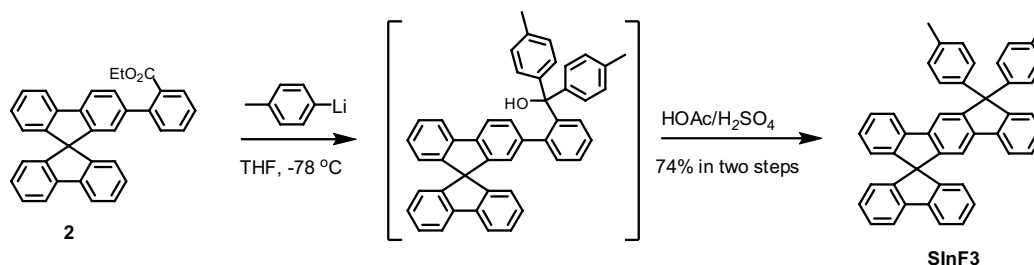
^b Institute of Optoelectronic Sciences, National Taiwan Ocean University, Keelung 202, Fax: 886 2 24634360; Tel: 886 2 24622192 ext. 6718; E-mail: wenhung@mail.ntou.edu.tw

Electronic Supplementary Information

Synthesis



A mixture of 2-(9,9'-spirobifluorenyl) dipinacol boronate(**1**)¹ (5.57 g, 12.6 mmol) and ethyl 2-iodobenzoate (4.60 g, 16.38 mmol), Pd(PPh₃)₄ (727 mg, 0.63 mmol), K₃PO₄ (19 mL, 2 M), tri-*tert*-butylphosphine (13 mL, 0.05 M in toluene, 1.2 mmol) in toluene (80 mL) was refluxed for 2 days. After cooling to room temp., the mixture was extracted twice with CH₂Cl₂. The combined organic solution was washed with brine and dried over MgSO₄, the product was isolated as white crystals by recrystallization from CH₂Cl₂/hexanes (5.26 g, 92 %). mp 180~181 °C ; IR (KBr) ν 3054, 2987, 1720, 1422, 1265, 896, 735, 705 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 7.87 (dd, *J* = 1.2, 8.0 Hz, 2H), 7.83 (d, *J* = 7.2 Hz, 2H), 7.65 (dd, *J* = 1.4, 7.4 Hz, 1H), 7.41-7.25 (m, 8H), 7.14-7.09 (m, 3H), 6.80-6.74 (m, 3H), 6.67 (s, 1H), 3.79 (q, *J* = 7.2 Hz, 2H), 0.91 (t, *J* = 8.0 Hz, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ 168.6, 148.8, 148.6, 148.4, 141.6, 141.3, 140.8, 140.7, 131.4, 130.6, 130.3, 129.2, 127.9, 127.7, 127.6, 126.9, 123.9, 120.0, 119.5, 65.9, 60.8, 13.9; MS (*m/z*, FAB⁺) 464 (100); HRMS (*m/z*, FAB⁺) Calcd for C₃₂H₂₄O₂ 464.1776, found 464.1784.



4-Bromotoluene (14.7 g, 86.2 mmol) in THF (120 mL) were treated with *n*-BuLi (54 mL, 1.6 M in hexane, 86.2 mmol) at -78 °C and quenched with a solution of ester **2** (5.0 g, 10.77 mmol) dissolved in THF (80 mL). The reaction mixture was kept at -78 °C for 1 hour and slowly warmed to room temp.

¹ K.-T. Wong, Y.-Y. Chien, R.-T. Chen, C.-F. Wang, Y.-T. Lin, H.-H. Chiang, P.-Y. Hsieh, C.-C. Wu, C. H. Chou, Y. O. Su, G.-H. Lee, S.-M. Peng, *J. Am. Chem. Soc.* 2002, **124**, 11576.

for stirring another 12 hours. The solution was quenched with water (150 mL). The organic solvent was removed by rotary evaporation. The resulting white solids were collected by filtration and washed with hexanes, and then extracted into CH_2Cl_2 . The combined organic solution was dried (MgSO_4) and concentrated by rotary evaporation. The crude product was dissolved into boiling acetic acid (150 mL) and added with concentrated $\text{HCl}_{(\text{aq})}$ (20 mL) dropwisely. The reaction was allowed to reflux for 3 hours then quenched with water (100 mL). The precipitate was collected and washed twice with water, affording product **SInF** as a white solid (4.65 g, 74 %). mp 427.3 °C (DSC) ; IR (KBr) ν 3054, 2987, 1422, 1265, 896, 739 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ 7.89 (d, J = 7.6 Hz, 2H), 7.83 (s, 1H), 7.72 (d, J = 7.2 Hz, 1H), 7.42-7.38 (m, 3H), 7.33-7.28 (m, 2H), 7.18-7.04 (m, 14H), 6.81 (d, J = 7.6 Hz, 2H), 6.70 (d, J = 7.2 Hz, 1H), 2.34 (s, 6H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 151.1, 151.0, 148.6, 148.4, 147.8, 142.7, 141.3, 141.2, 139.9, 139.3, 135.7, 128.5, 127.8, 127.5, 127.3, 127.2, 127.0, 126.8, 125.5, 123.9, 123.6, 119.8, 119.6, 119.5, 117.3, 115.5, 65.8, 64.6, 21.4; MS (m/z , FAB^+) 584 (100); HRMS (m/z , FAB^+) Calcd for $\text{C}_{46}\text{H}_{32}$ 584.2504, found 584.2522; Anal. Calcd. C, 94.48; H, 5.52. found C, 94.42; H, 5.49.

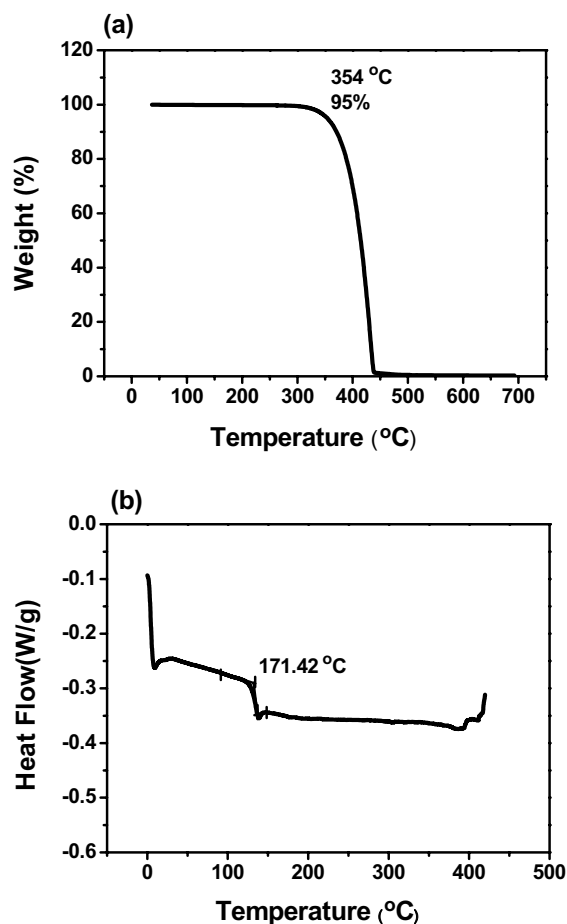


Fig. S1 TGA (a) and DSC (b) analysis of **SInF3**. Thermogravimetric Analyzer (TGA) analyses were performed on a TA Instruments Q500 TGA, the sample was heated from room temperature (10 °C/min) to decompose under nitrogen. Differential scanning calorimetry (DSC) analyses were performed on a

TA Instrument DSC-2920 Low-Temperature Difference Scanning Calorimeter, the sample was firstly heated (20 °C/min) to melt, then quenched with liquid nitrogen, T_g s were recorded by heating (10 °C/min) the quenched sample.

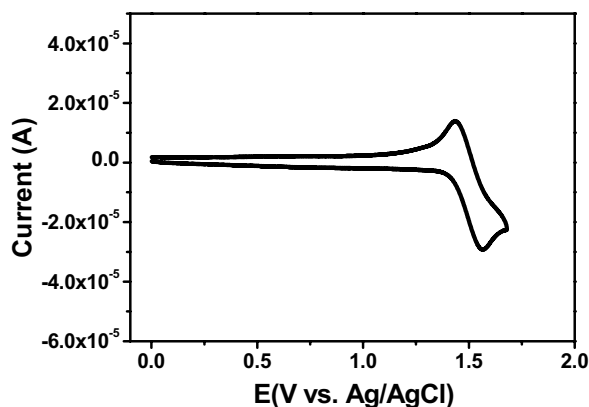


Fig. S2 Cyclic voltammograms (CV) of **SInF3**. For this work, CVs were performed at a scan rate of 100 mV/s using a glassy carbon electrode as the working electrode and Ag^+/AgCl as a reference electrode. Oxidation CV was performed in CH_2Cl_2 with 0.1 M of $n\text{Bu}_4\text{NPF}_6$ as a supporting electrolyte.

Time-of-Flight Mobility Measurements.

The samples for the TOF measurement² were prepared by vacuum deposition using the structure: glass/Ag(30 nm)/ organic (1.6 μm)/ Al(150 nm), and then placed inside a cryostat and kept under vacuum. All organic materials were purified by train sublimation before used. The thickness of organic films were monitored in situ with a quartz crystal sensor and calibrated by a profilometer (Tencor Alpha-step 500). A pulsed nitrogen tunable dye laser was used as the excitation light source (to match the absorption of organic films) through the semitransparent electrode (Ag) induced photogeneration of a thin sheet of excess carriers. Under an applied dc bias, the transient photocurrent was swept across the bulk of the organic film toward the collection electrode (Al), and then recorded with a digital storage oscilloscope. Depending on the polarity of the applied bias, selected carriers (holes or electrons) are swept across the sample with a transit time of t_T . With the applied bias V and the sample thickness D , the applied electric field E is V/D , and the carrier mobility is then given by $\mu = D/(t_T E) = D^2 / (V t_T)$, in which the carrier transit time, t_T , can be extracted from the intersection point of two asymptotes to the plateau and the tail sections in double-logarithmic plots. The observed constant-current plateaus in typical photocurrent transients of the hole mobility measurements are illustrated below (Fig. S3). This observation indicates that the charge carriers (i.e., holes) attained a constant drift velocity and, hence, non-dispersive transport occurred.

² (a) J. Mort, D. M. Pai., *Photoconductivity and Related Phenomena*; Elsevier: New York, 1976; (b) P. M. Borsenberger, D. S. Weiss, *Organic Photoreceptors for Imaging Systems*; Marcel Dekker: New York, 1993.

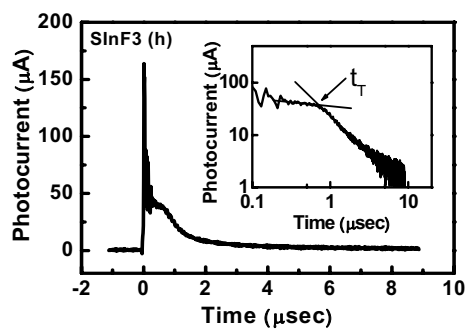


Fig. S3 Representative TOF transients for SInF3 (1.6 μm thickness; $E = 6 \times 10^4$ V/cm). Inset: Double-logarithmic plot.

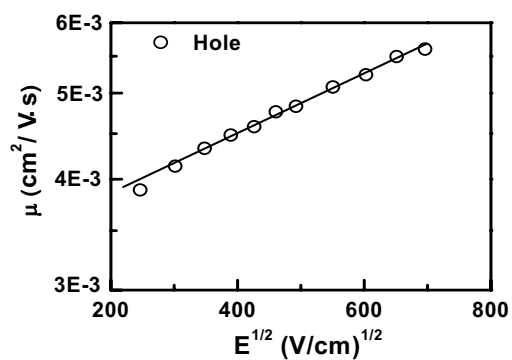


Fig. S4 Hole mobility of SInF3 plotted with respect to $E^{1/2}$.