# Efficient Blue-Light-Emitting Electroluminescent Devices with a Robust Fluorophore: 7,8,10-Triphenylfluoranthene**

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Silicon semiconductor technology has driven the profusion of information technology into every aspect of modern life. An obvious example of this is the emergence of portable electronic devices, such as cellular phones (mobile phones), personal digital assistants, palmtop computers, etc., that are rapidly becoming essential. These share a common Achilles heel, namely, battery life. The most obvious way to attack this problem is through replacement of the power hungry back-lit liquid-crystal displays (LCDs) that reside in all lightweight devices. It is this impetus that has brought organic light-emitting devices (OLEDs) to the forefront of modern materials science. The ability to mass produce thin, efficient, bright displays from organic polymers and small molecules that can supplant modern LCDs depends almost entirely on the ability to create new materials that can undergo efficient electroluminescence at a variety of wavelengths. This has lead to many publications and patents but to date has failed to produce an efficient, cheap, and robust blue-light emitter. It is, of course, not an easy task to find a small molecule that possesses not only a very large bandgap but also stability to the harsh electrochemical environment of OLEDs and a very large quantum yield in the solid state. One class of molecules in particular, fluorenes—especially spirofluorenes[1]—has received much attention because of the outstanding properties in this area,[2,3] but lengthy syntheses and low-yielding steps, such as boronic acid/ester formations, are less than ideal for single-layer/host materials. In an effort to redirect some of the explorations, we have investigated a close cousin of fluorenes—fluoranthenes—for applications as blue-light emitters in OLEDs (Scheme 1). In particular, we have studied 7,8,10-triphenylfluoranthene (TPF), a highly luminescent solid-state
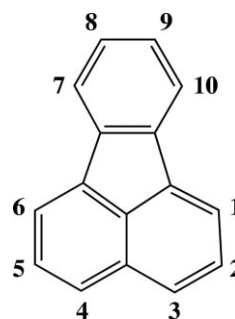
Scheme 1. The structure of fluoranthene, with relevant carbons numbered.

blue-light-emitting small molecule, which can be obtained in two steps from commercial starting materials.

After the elucidation of the structure of fluoranthene at the turn of the 20th century, the chemistry of fluoranthenes evolved rapidly.[4] Studies of the interesting photophysical properties[5,6] followed, but interest in fluoranthenes faded fast. Of particular note is the synthesis of fluoranthene derivatives by a double Knoevenagel condensation between 2-propanone and acenaphthenequinone, which allows functionalization at the carbon 7 and 10 positions.[7] A subsequent Diels–Alder addition allows further functionalization at the 8 and 9 positions.[7,8] Finally, starting from bromoacenapthenequinone,[9] the carbon 3 position is open to functionalization. With these synthetic tools in hand, we set about finding a fluoranthene derivative that would not crystallize and would remain highly blue-luminescent in the solid state. The most obvious candidate was a perphenylated derivative, which, due to steric hindrance, would keep the phenyl rings out of plane, thus presenting a ball-like surface to resist crystallization and reduce facial contacts that can lead to excimer quenching and bathochromic shifts in emission. To our surprise, only the 7,8,10-triphenyl derivative (**2**, Scheme 2) exhibited strong luminescence; the 7,8,9,10-tetraphenyl derivative is essentially non-fluorescent (in the solid state), and the 3,7,8,9-tetraphenyl derivative suffers from a large bathochromic shift in the solid state. The introduction of other functionality (e.g., esters, carboxylic acids, and halides) led to green/yellow emission and/or solubility problems. As with the other derivatives, 7,8,10-triphenylfluoranthene was synthesized via the Knoevenagel/Diels–Alder method (Scheme 2) from acenapthenequinone, diphenylacetone, and phenylacetylene, using only ethanol (EtOH) and (optionally) xylenes for solvents; all are inexpensive and readily available. Purification is uncompli-

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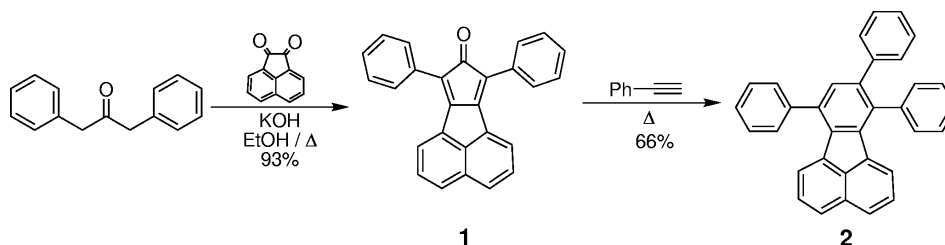
Scheme 2. The synthesis of 7,8,10-triphenylfluoranthene. (Δ: heating.)

cated and can be accomplished by precipitation from ethanol/benzene, flash chromatography, sublimation, or any combination of these.

Unsubstituted fluoranthene is known to form very stable anions that have a sufficient lifetime to dimerize.[10] Although dimerization is prevented by the three phenyl substituents in TPF, it retains a stable reversible reduction (Fig. 1). Unfortunately, the same stability is not observed in the oxidation wave by solution phase cyclic voltammetry (CV). The absence of a
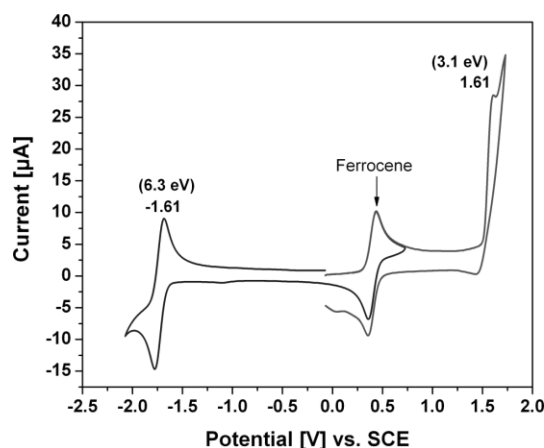

Figure 1. Cyclic voltammogram of TPF in CH_3CN per 10^{-1} M Bu_4NPF_6. The numbers above the peaks represent peak values, with the parenthetical numbers representing absolute HOMO/LUMO energies (HOMO: highest occupied molecular orbital, LUMO: lowest unoccupied molecular orbital; SCE: saturated calomel electrode).

cogent decomposition pathway for TPF (e.g., via fragmentation or gas evolution) implies the existence of a radical cation (or oxidized species) that reacts with the solvent or supporting electrolyte[11] and does not necessarily translate into reduced device performance or lifetime due to oxidative decomposition. Owing to the close proximity of the phenyl substituents, the irreversibility may also be due to an intramolecular cyclodehydrogenation of close phenyl substituents. While we were able to prepare the cyclodehydrogenated product chemically, we saw no evidence of its formation by spectroelectrochemical measurements. Despite the imposition of an irreversible oxidation wave, the introduction of three phenyl groups does not significantly change the redox potentials (or HOMO/

LUMO gap) from that of fluoranthene with: $E_p^a = 1.61$ V, $E_{1/2}^c = -1.72$ V versus saturated calomel electrode (SCE) for TPF and $E_p^a = 1.617$ V, $E_{1/2}^c = -1.81$ V versus SCE for fluoranthene (where E_p^a is the anodic peak potential, and $E_{1/2}^c$ is the cathodic half potential).

The most promising properties of TPF for device applications are its apparent resistance to solid-state quenching/excimer emission and its stability (decomposition was not observed by thermogravimetric analysis due to sublimation at ca. 300 °C, and mass loss was not observed below that temperature). As demonstrated by benzo[k]fluoranthene, which has a quantum yield of 1, the quantum yield of TPF is not the highest of the fluoranthenes. Benzo[k]fluoranthene, however, is completely quenched in the solid state, which is not true of fluoranthene or TPF. Relative quantum yield (Φ_{rel}) measurements of TPF revealed a solvent dependence, with $\Phi_{rel} = 0.38$ in CH_2Cl_2 and $\Phi_{rel} = 0.52$ in cyclohexane; this is not uncommon. More important, however, are the solid-state quantum-yield measurements of TPF films (using an integrating sphere), which reached as high as 0.86 for poly(methyl methacrylate) (PMMA) dispersions and were as low as 0.51 for pure-TPF films. The high quantum yield in PMMA dispersions is probably due to the rigid matrix, which further hinders rotation of the phenyl substituents and distortions in the fluoranthene core. The discrepancy between the pure-TPF film and the PMMA dispersion may be related to a quenching mechanism or, more likely, to the poor suitability of TPF films cast from solvents for our integrating sphere apparatus, which was much better suited for PMMA monoliths than thin films. Evaporated films were found to be simply too thin to obtain a reasonable signal-to-noise ratio. The photoluminescence (PL) spectrum at 77 K exhibits peaks at three different wavelengths (λ), at 423, 448 (λ_{max}), and 478 nm, with a small Stokes shift (Fig. 2). At room temperature, λ_{max} shifts to 458 nm in solution and shifts to 468 nm in the solid state. Although TPF emits from the triplet state, the reported phosphorescence spectrum is only attainable in a frozen glass (at 77 K) and is far less intense than any fluorescence bands; the signal was too weak for accurate lifetime measurements.

A typical blue-light emitting OLED, using TPF as a highly efficient blue-emitting material, is shown in Figure 3A, where the inset shows the device structure. A second hole-transporting layer (HTL) of 15 nm 4,4′-dicarbazolyl-1,1′-biphenyl (CBP) had to be inserted between the 4,4′-bis(1-naphthyl-N-phenylamino)-biphenyl (NPB) and TPF to increase the device
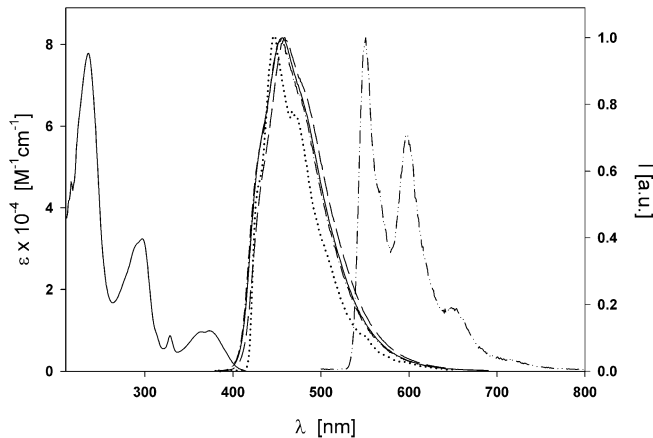
Figure 2. Absorption/normalized emission spectra of TPF; UV-vis absorption (—); fluorescence at 77 K (···); fluorescence in CH_2Cl_2 at 298 K (—·); solid-state fluorescence (— —); phosphorescence at 77 K (—··). (ε is the molar extinction coefficient.)

efficiency. The high HOMO energy of TPF (~ 6.3 eV, calculated from CV) was better matched to CBP, which has a HOMO energy of 5.7 eV and should more efficiently inject holes from the HTL into the TPF layer.[12] Figure 3A shows the current–voltage–luminescence (*I–V–L*) characteristics of the device. Under reverse bias, charge injection is difficult and the leakage current is constant at 10^{-4} mA cm^{-2}. The device current turns on at 2.3 V, which is the potential at which electron and hole injection from electrodes to the device begins. While the electrons and holes appear to reach the light-emitting layer, no light emission occurs below a voltage of 5 V. This 2.6 V difference between charge injection and light emission is accompanied by a small inflection in the *I–V* curve, but the current does not abruptly increase or saturate in the high-voltage region. This suggests that the electron and hole carriers are not well balanced, and a better-optimized device structure could further increase the efficiency. A maximum luminescence of 5910 cd m^{-2} occurs at 320 mA cm^{-2}. The fine structure of the EL spectrum, with peaks at 456 nm (λ_{max}) and 480 nm (Fig. 3B), and Commission Internationale de l'Eclairage (CIE) coordinates of $x = 0.177$, $y = 0.24$, is consistent with the PL spectra (Fig. 2); this correlation is indicative of a common charge recombination and decay mechanism for EL and PL. There is a slight broadening in the EL spectrum, as compared to the solid-state PL spectrum (of the device), and a shoulder at 500 nm is present that is not observed in either the solution or solid-state emission spectra of pure TPF at room temperature. The maximum efficiency reaches 3.02 cd A^{-1} (1.83 % external quantum yield, $\Phi_{external}$) with a power efficiency of 1.1 lm W^{-1} at 4.93 mA cm^{-2} (Fig. 3C), which is comparable to other fluorescent blue-light-emitting hydrocarbons, such as anthracene derivatives[13,14] and spirobifluorenes.[15] However, bright-blue-light emission is achieved with only a single emissive layer, which simplifies the device fabrication process. The overall efficiency may be further increased by doping with suitable phosphorescent dopants, as
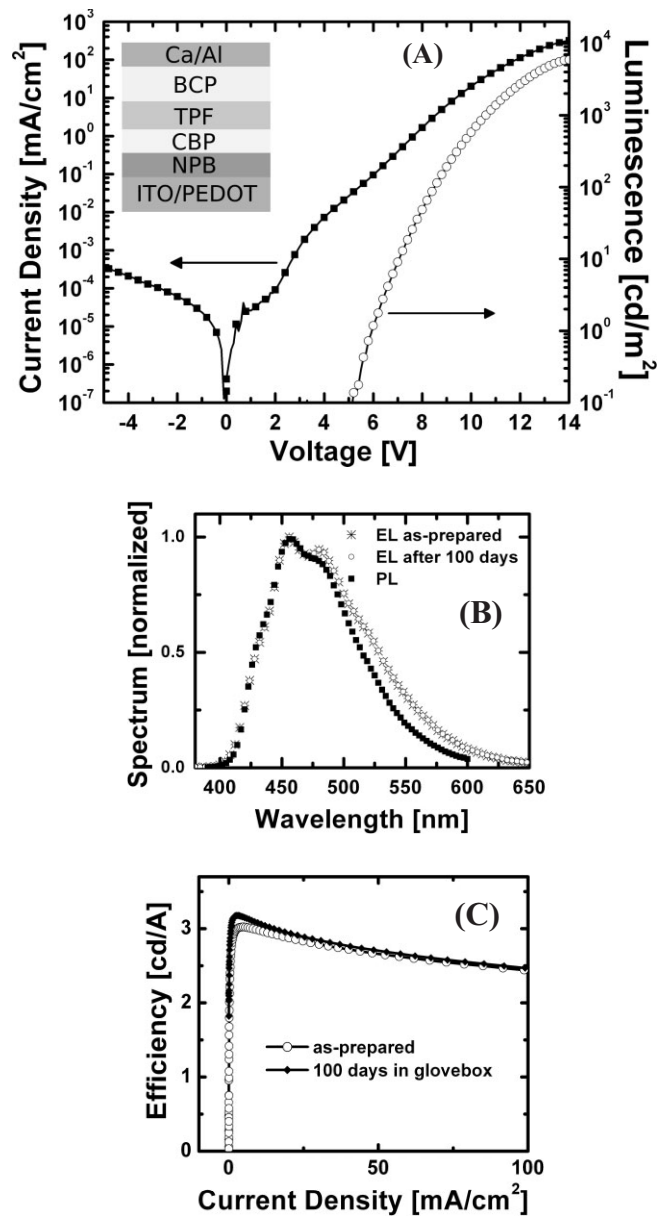

Figure 3. The electrical characteristics of a typical TPF-based OLED. A) Current–voltage–luminescence characteristics (inset shows the device structure, where ITO: indium tin oxide, PEDOT: poly(3,4-ethylenedioxy-thiophene, and BCP: bathocuproine = (2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline)), B,C) the electroluminescence (EL) spectra and electroluminescence efficiency, respectively, for a pristine device and one that has been stored under nitrogen for 100 days.

the large bandgap of TPF should allow it to readily sensitize blue–green to red dopants. The experimental detail, including synthesis and device fabrication, is available as Supporting Information.

Although fluroanthenes have been known for the better part of a century, they have, until now, been overlooked for OLED applications.[16] Starting from cheap, commercially available materials, we have synthesized a simple fluoranthene hydrocarbon that emits blue light in a single-layer de-

vice architecture with very respectable efficiencies and low turn-on voltages. Although the CIE coordinates of this initial device preclude immediate commercial applications, the ease of synthesis and derivatization makes fluoranthenes a viable new platform for future investigation as simple organic fluorophores. With further studies into device optimization, TPF may prove to be an excellent blue-light emitter or host material for future OLED display applications.

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