Brief Communication

Silylethynylated Anthracene Derivatives for use in Organic Light-Emitting Diodes

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We have prepared a series of trialkylsilylethynylated anthracenes (a–d) to investigate the effects of solid-state interactions and acene substitution on the electroluminescence spectra of OLED devices. We designed these materials to have differing amounts of π-face interactions and various film morphologies. We were particularly interested in intermolecular interactions between aromatic faces, which would manifest in the electroluminescence spectrum as a bathochromic shift and broadening of the emission peak when compared to the solution photoluminescence spectrum. The anthracene derivatives with no electronic interactions, as determined by single-crystal X-ray crystallography, produced devices that showed no bathochromic shift and better efficiencies. [DOI: 10.1143/JJAP.44.3921]

Since the first example of practical organic electroluminescence, work has progressed to design materials to replace current display technologies such as LCDs and CRTs.[1–3] Studying structure-property relationships and morphology of films that lead to efficient emitters is of particular interest. Current research suggests that, all other things being equal, an amorphous emitter should exhibit superior performance in organic light emitting diodes (OLEDs) over polycrystalline emitters by eliminating grain boundaries in films,[4] and by maximizing the distance between chromophores.[5] Excimer formation in electroluminescence is known to cause broadening and a bathochromic shift of the emission peaks as well as a lowering of the overall quantum efficiency.[6,7] Frequently, aryl groups are attached to anthracene derivatives to minimize aggregation.[8–11] However, many of these derivatives either involve multi-step syntheses or low-yielding reactions.

Our group previously added trialkylsilylethynyl groups to the 6- and 13-positions of pentacene to induce close π-face interactions in the solid-state as well as to increase solubility and oxidative stability over unsubstituted pentacene.[12,13] From an examination of a variety of pentacene derivatives, we devised an empirical rule which stated that when the trialkylsilyl group is approximately half the size of the acene core, close π-face interactions result. If the diameter of the trialkylsilyl group is significantly greater than half the length of the acene, π-face interactions are disrupted. Using this rule, we can design anthracene derivatives that should have minimal electronic interaction and should be more efficient emitters.

We prepared functionalized anthracenes from the respective anthraquinones by the same synthetic strategy reported previously for preparing ethynylated pentacenes (Fig. 1).[14]

Figure 2 displays the solution photoluminescence (PL) spectra as well as the thin film PL spectra and device electroluminescence (EL) spectra of anthracene derivatives (a)–(d). These anthracene derivatives are air stable and soluble in most organic solvents, and derivatives (a)–(c) readily formed crystals from acetone. Single-crystal X-ray diffraction of derivatives (a)–(c) shows that only tetramethoxy derivative (c) exhibits close π-face interactions (Fig. 3). Derivative (c) also showed the most interesting solution PL spectrum, with a pronounced hypsochromic shift due to steric repulsion of the oxygen lone pairs preventing the methoxy groups from participating in π-conjugation with the aromatic rings. Thin film PL spectra of derivatives (a)
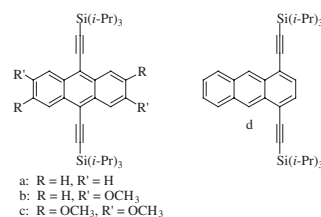

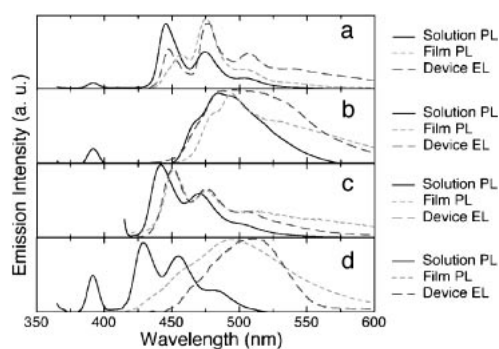Fig. 1. Chemical structures of silylethynylated anthracene derivatives.

Fig. 2. Solution PL, thin film PL, and device electroluminescence (EL) spectra of ethynylated anthracenes (a)–(d).

and (b) did not exhibit significant shifts in emission wavelength compared to their respective solution PL spectra, which suggests a lack of electronic interactions in the films.

In the absence of exciplex formation in the device configuration, the thin film PL spectra should be indicative of the expected EL spectra. The thin film PL spectrum of the tetramethoxy derivative (c) belies this compound's solid-state π-face interactions, showing the expected bathochromic shift indicative of excimer formation. The spectrum of the offset derivative (d) is also indicative of excimer formation suggesting that even though this derivative is the only one to form an amorphous thin film, it also displays significant π-interactions in the solid-state.

Derivatives (a)–(d) were incorporated into OLED devices utilizing a simplified structure of ITO/TPD (40 nm)/anthracene derivative (30 nm)/LiF (0.6 nm)/Al (60 nm). This device configuration avoided the use of accessory emitters such as Alq$_3$ or CuPc to preserve the purity of the light output from the anthracene derivatives, which function as both electron transport material and emitter. All devices
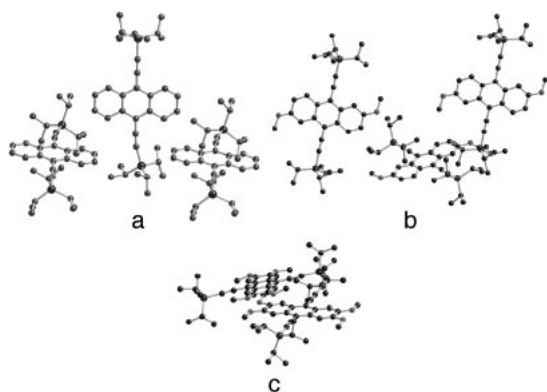
Fig. 3. Molecular packing of derivatives (a)–(c). The views show the closest aryl-aryl interaction for each derivative.

were sufficiently stable under laboratory conditions to collect EL spectra, light output and I–V data.

Devices prepared from anthracene derivative (a) had an emission wavelength of 477 nm, and the EL spectrum of this derivative was nearly identical to the solution PL spectrum (although some self-absorption was evident, Fig. 2). These devices had a turn-on voltage of 6 V and maximum output of 107 cd/m^2 at 10 V.[15] Devices prepared from compound (b) had a maximum emission wavelength of 503 nm, quite similar to both solution and thin film PL spectra (Fig. 2). This device, made from an emitter with a significantly larger separation between π-faces, had better electronic properties than (a) with a turn-on voltage of 5 V and maximum light output of 950 cd/m^2 at 10 V.[16] Devices prepared from compound (c), which exhibits small π-face interactions in the crystal, were not efficient, having a turn-on voltage of 8 V and a maximum brightness of only 3 cd/m^2 at 10 V. The EL spectrum of this device also exhibited a red-shifted emission when compared to the solution or thin film PL spectra (Fig. 2). We attribute the overall poor device performance to the extensive π-face interactions. The lack of bathochromic shift from the PL spectrum of a two-layer film of TPD and (c) suggests that there is little or no exciplex formation at the interface with the hole transport material.

Analysis of devices prepared from compound (d), the only derivative presented here to form an amorphous film, showed considerable excimer formation indicated by significant broadening and a bathochromic shift in the EL spectrum (Fig. 2). Exciplex formation between the anthracene derivative and TPD causes a further shift and broadening of the emission—this interaction was confirmed by the PL spectrum of a two-layer film of TPD and (d). The enhanced electronic interaction in compound (d), likely resulting from the larger exposed π-face of this derivative, also results in a very dim EL emission, similar in light output to devices prepared from the tetramethoxy derivative (c), with a turn-on voltage of 5 V and a maximum output of 6.5 cd/m^2 at 10 V. From the device data, we have shown that crystalline materials engineered to minimize π-face interactions have properties superior to those that possess such interactions, even if they form amorphous films.

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16) The normalized brightness of devices prepared from **2** (taking into account the spectral response based on the photopic curve) is 560 cd/m^2, which is still significantly brighter than the normalized output of 92 cd/m^2 for devices made from **1**.