

# Environmentally stable light emitting field effect transistors based on 2-(4-pentylstyryl)tetracene†

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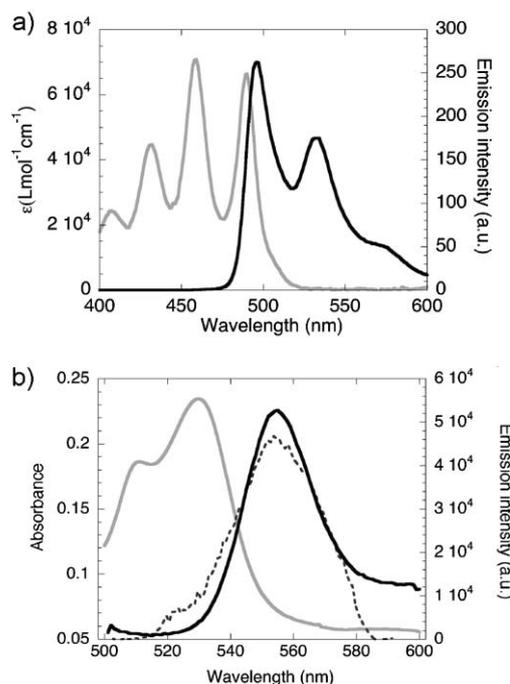
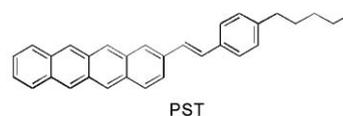
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Organic light emitting field effect transistors based on 2-(4-pentylstyryl)tetracene are able to operate in ambient air and have a shelf lifetime of several months.

Organic semiconductors (OS) exhibit a variety of physical properties, such as charge carrier transport, photoluminescence (PL) and electroluminescence (EL), that can be tuned by modification of the molecular structure.<sup>1</sup> This offers the possibility to realize multifunctional electronic devices with tunable characteristics. Field effect transistors (FETs), light emitting diodes (LEDs) and photovoltaic cells based on OS have been investigated in the last decades. The interest in OS has been recently augmented by the realization of organic light emitting field effect transistors (OLEFETs),<sup>2</sup> devices combining the current modulating function of a transistor with light emission. OLEFETs are interesting for the development of highly integrated organic optoelectronic devices such as active matrix electroluminescent displays. They are excellent test systems to investigate processes such as charge carrier injection, transport, and EL in OS. OLEFETs with unipolar or ambipolar electrical characteristics have been realized with a number of molecular and polymeric semiconductors, processed by thermal evaporation or from solution.<sup>3</sup> The possibility to move the location of the light emission region within the transistor channel as a function of the electrical bias, initially revealed with light emitting field effect transistors based on single-wall carbon nanotubes,<sup>4</sup> has been demonstrated for a few ambipolar devices.<sup>3b-c,e</sup>

The shelf lifetime and the operational stability of OLEFETs (*i.e.* the possibility to store and operate the devices in ambient conditions) are key issues for their development. In general, OS are sensitive to moisture and oxygen.<sup>5</sup> All OLEFETs reported to date have been characterized in inert atmosphere or under vacuum, except for a device based on a pentacene hole transport layer and a tris(8-hydroxyquinoline)aluminium emissive layer.<sup>6</sup>

In this work, we report on an OLEFET based on 2-(4-pentylstyryl)tetracene (PST, Fig. 1), a recently synthesized tetracene derivative.<sup>7</sup> The design of the molecule was based on hypothetical *trimming* of long acenes, to combine the inherently high charge carrier mobility of the higher acenes (provided by extended conjugation) with the greater stability of the lower acenes.<sup>1a</sup>



**Fig. 1** The PST molecule (top). Molar extinction coefficient  $\epsilon$  (grey) and PL (black) vs. wavelength of a  $5 \times 10^{-6}$  M solution of PST in 1,2-dichlorobenzene (a). Absorbance (grey), PL (black) and EL (dashed) spectra of a 50 nm-thick PST film vacuum sublimed on a glass substrate at  $0.8 \text{ \AA s}^{-1}$ . For the EL spectrum,  $V_{ds} = V_g = -60 \text{ V}$  (b).

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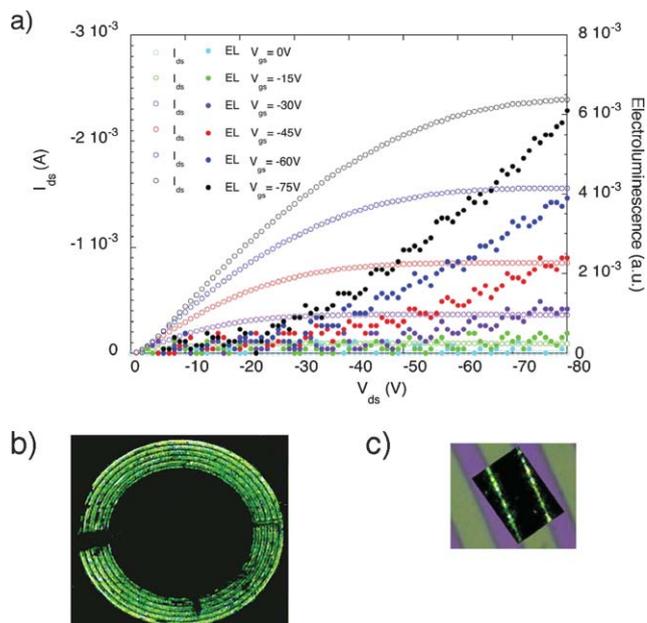
Optimized FETs based on vacuum sublimed films of PST exhibit hole mobilities as high as to  $1\text{--}2\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$ , shelf lifetime of several months and excellent environmental stability.<sup>7</sup> Interestingly, the molecular structure of PST contains the tetracene moiety, which is known to have electroluminescent properties.<sup>8</sup>

PST films were deposited by vacuum sublimation at deposition rates ranging between  $0.2$  and  $1\text{ \AA s}^{-1}$  on  $\text{SiO}_2/\text{n-Si}$  substrates pre-patterned with Au electrodes (see ESI†).<sup>9</sup> Optoelectronic measurements were carried out in ambient air, extra dry air (Praxair), and  $\text{N}_2$  (99.998%). A HP 4145 B semiconductor parameter analyzer was used as the source-measure unit. Light detection was achieved using a Hamamatsu (3137 QB) Si photodiode. A Toshiba IK 1000 charged coupled device (CCD) camera mounted on an optical microscope objective was used for EL imaging. EL spectra were acquired with a 500i Spectra Pro spectrometer (Action Research Corporation) equipped with an Andor DH501-18F-01 CCD detector. Atomic force microscopy (AFM) was performed using a DI-Enviroscope system (Veeco Instruments) operated in intermittent contact mode. The absorption and PL spectra were recorded using a Cary 300 Bio UV-Vis Spectrometer and a Cary Eclipse Fluorometer (Varian). PL quantum yields (PLQY) were estimated by comparative methods (see ESI†).

To address the applicability of PST as a LEFET material, we first studied its optical properties in solution and in thin films (Fig. 1). The absorption spectrum of PST in solution (Fig. 1a) shows the characteristic vibronic structure of acenes ( $\lambda_{\text{max}} = 407, 432, 459$  and  $490\text{ nm}$ ). The PL spectrum is also vibronically structured ( $\lambda_{\text{max}} = 495, 532\text{ nm}$  and a shoulder centered at  $573\text{ nm}$ ). The PLQY is  $0.42$ . A small Stokes' shift of  $5\text{ nm}$  is indicative of a small re-organization energy, in agreement with the high hole FET mobility observed in PST films.<sup>10</sup> In the solid state, intermolecular interactions result in a significant red-shift and broadening of both absorption and PL (Fig. 1b). These also lead to a decrease of PLQY in films to  $\sim 0.07$ . Although this value is lower than those of the best emitters used in organic LEDs (usually amorphous materials), it is higher than the solid state PLQY of tetracene ( $0.008^{11}$ ) which was used as the active material in the first OLEFETs.<sup>3a</sup>

The hole FET mobility,  $\mu_{\text{FET}}$ ,<sup>12</sup> of PST films was  $0.15 \pm 0.05\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$  (see ESI†), as evaluated from measurements in  $\text{N}_2$  atmosphere.  $I_{\text{on}}/I_{\text{off}}$  ratios are as high as  $5 \times 10^6$  (see ESI†) and threshold voltages ( $V_{\text{T}}$ ) range between  $-1$  and  $-11\text{ V}$ . For OLEFET characterization, transistor current and EL were simultaneously measured (Fig. 2a). The devices showed p-type transistor behaviour and gate modulated EL. The EL intensity increased with gate voltage ( $V_{\text{g}}$ ) and, for a fixed  $V_{\text{g}}$ , it increased with drain-source voltage ( $V_{\text{ds}}$ ). The onset of EL was  $V_{\text{g}}$ -dependent and it was located at  $V_{\text{ds}} = -16\text{ V}$ , for  $V_{\text{g}} = -60\text{ V}$ . Under a constant bias of  $V_{\text{ds}} = V_{\text{g}} = -60\text{ V}$ , the EL intensity decayed exponentially in a few seconds (see ESI†).

The initial values of EL were restored after leaving the device unbiased for a few minutes, suggesting that reversible charge carrier trapping (most likely electron trapping) rather than material or device degradation is responsible for this decay.<sup>5b</sup> The optical micrograph of the EL generated by a PST-LEFET is shown in Fig. 2b. The magnified image of the working device (Fig. 2c) shows that light emission is localized close to the electron-injecting electrode. The EL spectrum (dashed line in Fig. 1b) closely resembles the solid state PL spectrum ( $\lambda_{\text{max}}^{\text{EL}} = 554\text{ nm}$ ).

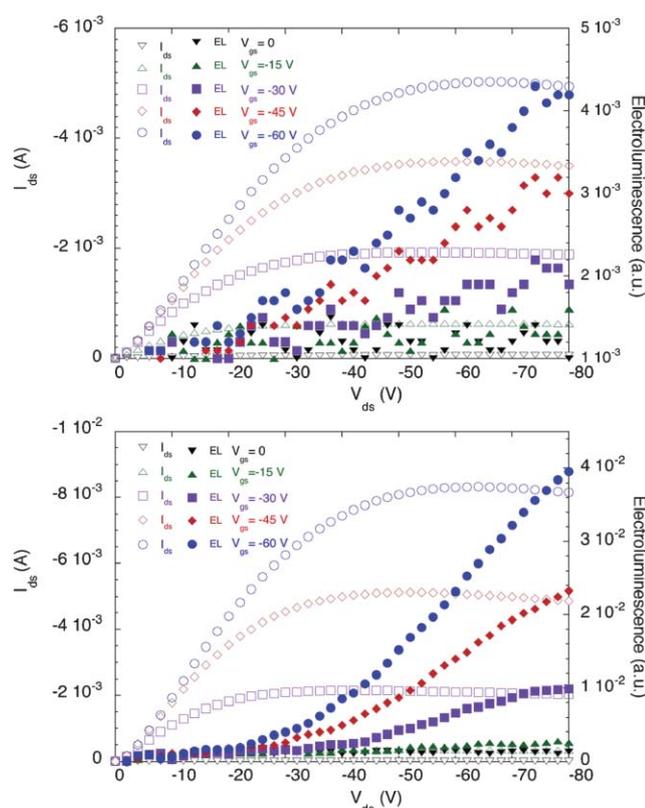


**Fig. 2** (a) Optoelectronic output curves of a LEFET based on a  $50\text{ nm}$ -thick PST film deposited at  $0.8\text{ \AA s}^{-1}$ . On the left and right  $y$  axes are reported the source-drain current ( $I_{\text{ds}}$ ) and EL. Transistor channel width,  $W$ , and length,  $L$ , are  $18800$  and  $40\text{ }\mu\text{m}$ .  $V_{\text{T}} = -1\text{ V}$  and  $\mu_{\text{FET}} = 0.1\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$ . (b) Optical image ( $1500 \times 1500\text{ }\mu\text{m}^2$ ) of the green EL generated by a PST-LEFET biased at  $V_{\text{ds}} = V_{\text{g}} = -60\text{ V}$  ( $WL = 41800/10\text{ }\mu\text{m}/\mu\text{m}$ ). (c) Magnified area ( $50 \times 42\text{ }\mu\text{m}^2$ ) from (b) (overlapped with an optical image of the device) showing the localization of EL at the drain electrode.

The localization of the EL at the electrode resembles tetracene-LEFETs and is consistent with unipolar p-type characteristics.<sup>3a,13</sup> The asymmetric positions of the HOMO and LUMO of PST (that lie at  $-5.3$  and  $-2.7\text{ eV}$ ) with respect to the work function of Au (that lies at about  $-5\text{ eV}$ ) create a high energy barrier for electron injection into PST. The resulting preferential transport of holes confines the exciton recombination zone (light emission) in the vicinity of the electron injecting electrode.

Remarkably, PST-LEFETs can operate in ambient air (Fig. 3a and ESI†). The optoelectronic characteristics in air are somewhat poorer than those obtained in  $\text{N}_2$ . However, subsequent purging of the measurement chamber with  $\text{N}_2$  gradually restores the LEFET characteristics (Fig. 3b) eventually leading to the original performance. Measurements performed in dry air led to optoelectronic characteristics similar to  $\text{N}_2$  (see ESI†). This suggests that hole-trapping states created by reversible adsorption of nucleophilic water molecules limit the performance of PST-LEFETs in ambient air.<sup>5c,d</sup> Interestingly, PST-LEFETs stored in ambient air for eight months were operated with minor changes in their transistor characteristics (see ESI†).

Several factors can explain the stability of PST-LEFETs. The HOMO of PST is lower compared to those of more investigated OS such as pentacene (whose HOMO lies at  $-5.1\text{ eV}$ ) thus retarding its doping by oxygen, one of the causes of environmental degradation. However, we also found that PST-LEFETs are significantly more stable than LEFETs based on tetracene, whose HOMO has a value similar to that of PST ( $-5.4\text{ eV}$ ).<sup>8b</sup> By itself, tetracene is a highly stable material, which can be stored in air without appreciable oxidation. Nevertheless, the low HOMOs of

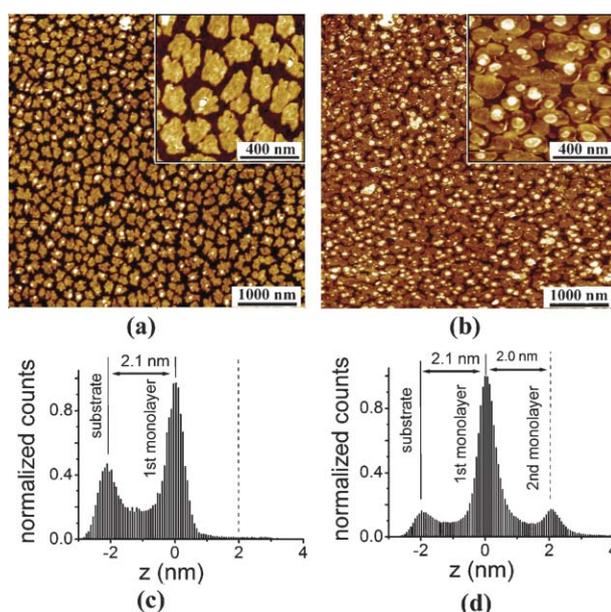


**Fig. 3** Output characteristics measured in different atmospheres of a LEFET based on a vacuum sublimed PST film with  $W/L = 42000/6 \mu\text{m}/\mu\text{m}$ . (a) Ambient air,  $V_T = 10 \text{ V}$  and  $\mu_{\text{FET}} = 0.017 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ . The onset of EL is located at  $-23 \text{ V}$  for  $V_g = -60 \text{ V}$ . (b) Same device after purging the chamber with  $\text{N}_2$  for 3 min,  $V_T = -3 \text{ V}$ ,  $\mu_{\text{FET}} = 0.05 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ .

tetracene and PST also imply a high electrophilicity of their radical cations, which are formed during the device operation as charge carriers, and can be readily trapped by nucleophiles such as water. The formation and transport of these reactive radical cation species usually occur at the semiconductor/gate dielectric interface,<sup>14</sup> deep inside the typically 30–50 nm thick films. As a consequence, we expect that the morphology of the films close to the dielectric interface significantly affects the stability of the transistor during operation in air.

To address this issue we performed an AFM study of the growth of PST films. PST films grown at  $0.2 \text{ \AA s}^{-1}$  with nominal thicknesses of 3 and 5 nm (Fig. 4a and b) have good adhesion on  $\text{SiO}_2$  since a large fraction of the substrate surface is covered at a relatively low thickness. The growth starts with the formation of flat islands (Fig. 4a, inset). When the size of the islands reaches about 200 nm, they partially coalesce and, just before the completion of the first layer, a second layer starts to form (Fig. 4b, inset).

For a thickness of 5 nm, the substrate coverage is 84% for the first layer and 15% for the second layer (Fig. 4b). The height histograms obtained from images shown in Fig. 4a and b (Fig. 4c and d) reveal that the islands in the first and in the second layer have an average height of  $2.1 \pm 0.2$  and  $2.0 \pm 0.2$  nm, which suggests that the molecules are oriented almost perpendicular to the substrate.<sup>15</sup> The continuity of PST films is expected to limit the diffusion of water and other contaminants towards the dielectric interface, thus contributing to the stability of the devices in



**Fig. 4** AFM micrographs (NSC 35 Micromasch cantilevers, resonance frequencies 150–300 kHz) of PST films (deposition rate of  $0.2 \text{ \AA s}^{-1}$ ). Nominal thickness 3 nm (a) and 5 nm (b). The insets show magnified regions. (c) and (d) Height histograms corresponding to (a) and (b).

ambient air. The flat shape and large size of the PST islands reduces the density of the grain boundaries which act as charge carrier traps, detrimental for charge transport. These factors explain the higher stability of PST vs. tetracene devices. Indeed, tetracene growth proceeds by formation of three dimensional islands so that high thicknesses and high deposition rates<sup>16</sup> are needed to achieve complete substrate coverage.

In summary, we realized PST-LEFETs that could operate in ambient air and exhibited a shelf lifetime of several months. The devices showed gate modulated green EL. The hole FET mobility, as high as  $0.2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ , approaches the level required for active matrix display applications, although device engineering is certainly needed to enable ambipolar charge transport and to improve EL properties.

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