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Ravi Mosurkal[a]; Lynne A. Samuelson[a]; Jayant Kumar[b]; David Waller[c]; Russell Gaudiana[c]
[a] U.S. Army Natick Soldier Research Development and Engineering Center, Kansas St, Natick, MA [b] Center for Advanced Materials, University of Massachusetts, Lowell, MA [c] Konarka Technologies Inc., Lowell, MA

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Synthesis of a Soluble Pentacene Derivative: 6,13-bis(*m*-trifluoromethyl phenyl ethenyl) Pentacene†

RAVI MOSURKAL[1], LYNNE A. SAMUELSON[1], JAYANT KUMAR[2] DAVID WALLER[3]
and RUSSELL GAUDIANA[3]

[1] *U.S. Army Natick Soldier Research Development and Engineering Center, Kansas St, Natick, MA 01760*
[2] *Center for Advanced Materials, University of Massachusetts, 265 Riverside Street, Lowell, MA 01854*
[3] *Konarka Technologies Inc., 100 Foot of John Street, Lowell, MA 01854*

We report the synthesis and characterization of a new pentacene derivative, 6,13- bis(*m*-trifluoromethyl phenylethynyl)pentacene. This pentacene derivative is soluble in common organic solvents and found to have the HOMO energy level at −5.45 eV in solution.

Keywords: Soluble pentacene, redox potential, HOMO-LUMO.

1. Introduction

There has been tremendous interest in organic electronics due to a variety of potential applications including organic light emitting diodes (OLEDs), field effect transistors (FETs) and photovoltaic cells (1). Polycyclic aromatic compounds have been extensively investigated for their interesting molecular geometries and high field effect mobilities (2). Recently, high performance transistors and circuits fabricated using a fluorinated acene derivative as a component were reported by Gundlach et al. (3). Much attention has been devoted to pentacene, as it is one of the best performing organic semi-conductors showing the highest mobilities in thin film transistors for p-type semi-conductors. Due to their extremely poor solubility and instability in solution, pentacenes were modified by substituting alkyllsilylethynyl groups at the 6 and 13 positions. For example, 6,13-bis(trimethlsilylethynyl) pentacene (TMS, Figure 1) and related compounds were first reported along with their crystal structures by Anthony et al. (4). The triisopropyl derivative, TIPS, demonstrated a reduced band gap and FET devices with a hole mobility of 0.4 cm^2/Vs (4). Recently, Li et al. reported the synthesis and characterization of long chain alkyl, alkoxy and *para*-CF_3 substituted (**2**, Figure 1) pentacenes and they found mobility in an OTFT device fabricated using a solution processed alkyl derivative to be 0.52 $cm^2V^{-1}s^{-1}$ (5). However, relatively very few examples of pentacenes substituted with conjugated aromatic groups at the 6,13 position, such as the molecules shown in Figure 1 (**1**-**3**), were studied (6). In this paper, we present synthesis, characterization, photophysical and redox properties of a soluble pentacene derivative, 6,13-bis(*m*-trifluoro methyl phenylethenyl)pentacene, **3** or MCF3 (Figure 1).

2. Experimental

2.1. *Materials and methods*

6,13-Pentacenequinone, 3-ethynyl-trifluorotoluene, butyllithium, Tin (II) chloride and all the solvents were purchased from Sigma-Aldrich. ^{1}H-NMR spectra were recorded on a Bruker 250 MHz ARX spectrometer. UV-Visible spectra were recorded using a Perkin-Elmer Lambda 9 spectrophotometer. Fluorescence spectra were measured on a Perkin-Elmer LS-55 spectrophotometer. Redox potentials were measured by cyclic voltammetry using a VoltaLab-40 potentiostat in a standard three-cell electrode arrangement. Voltammograms were recorded using a glassy carbon electrode in a 2mM solution of MCF3 containing 0.1M tetrabutylammonium hexafluorophosphate as a supporting electrolyte.

All the pentacene derivatives including TMS were synthesized following the procedure [4d] exemplified for MCF3 below (Scheme 1). To a three-neck round bottom flask was added 3-ethynyl-trifluorotoluene (1.14 g, 6.7 mmol)

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†Dedicated to the memory of Professor Sukant K.Tripathy

Address correspondence to: Ravi Mosurkal, U.S. Army Natick Soldier Research Development and Engineering Center, Kansas St, Natick, MA 01760. E-mail: Ravi_Mosurkal@uml.edu or Jayant Kumar, Center for Advanced Materials, University of Massachusetts, 265 Riverside Street, Lowell, MA 01854. E-mail: Jayant_Kumar@uml.edu

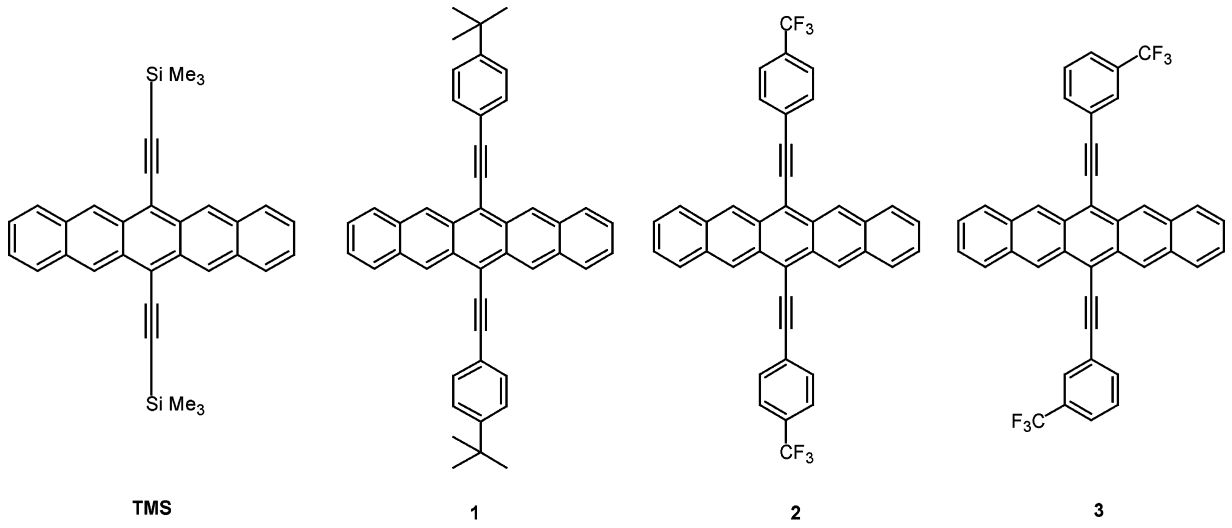


Fig. 1. Structures of functionalized pentacenes.

and equimolar amount of butyllithium (1.6 M in hexane, 3.78 ml) under nitrogen atmosphere. The reaction mixture was stirred for 0.5 h and was added 6,13-pentacenequinone (0.45 g, 1.5 mmol) and stirred the mixture at 60°C for 12 h. After cooling to room temperature, the reaction was quenched by adding 1 ml of water. To this solution tin(II)chloride (0.9 g) dissolved in 2 ml of 10% HCl was added and continued stirring at 60°C for another 2 h. A blue product began to precipitate in the flask. To this solution was added 20 ml of tetrahydrofuran and the product precipitated completely. A blue powder was filtered and washed with water several times to obtain 1.3 g of MCF3. The product was further purified by column chromatography using chloroform as an eluent.

The product was characterized by ^{1}H-NMR, elemental analysis and FAB mass. Yield = 60%, ^{1}H-NMR (CDCl$_3$, 250 MHz) δ 9.24 (s, 4H), δ 8.16 (m, 4H), δ 8.08 (m, 2H), δ 7.8 (d, 2H), δ 7.6 (s, 4H), 7.48 (m, 4H); MS(FAB) m/z 614(100%, M$^+$); Anal. Calcd. %C: 78.17, %H: 3.28, %F: 18.55. Found %C: 77.38, %H: 3.10, %F: 18.51.

3. Results and discussion

In this work, pentacenes with various substituted aromatic groups were investigated in an attempt to find a promising hole conductor with a low HOMO energy level and strong absorption in the visible region for photovoltaic applications. It was also speculated that substituting conjugated aromatic groups, instead of labile silyl groups, would improve the stability of the pentacenes. The reported pentacenes with alkylsilyl groups are easily hydrolyzed in basic environments and the instability of the resulting acetylinic intermediates could lead to undesired compounds. In fact, the silyl groups are used as protecting groups in preparing polyethynyl aromatics using the Sonogashira coupling method (8). It is desirable to have a material with an oxidation potential such that it is not easily susceptible to oxidative degradation but at the same time taking care so that the interfacial properties with some commonly used electrodes is still favorable. To address this, the structures shown in Figure 1 were synthesized with trifluoromethyl groups to shift the HOMO level further lower. Unfortunately, the solubility of **1** and **2** (also ref. 5) is very poor and limited any further study. However, surprisingly, **3** showed very good solubility in chloroform and other organic solvents and led to the investigation of its redox and photophysical properties.

The absorption spectra of all the compounds measured in chloroform solution were compared with TMS in Figure 2.

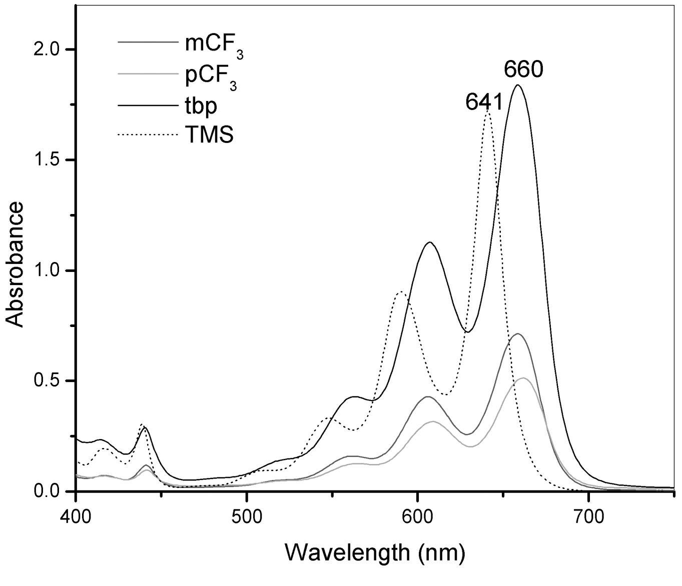
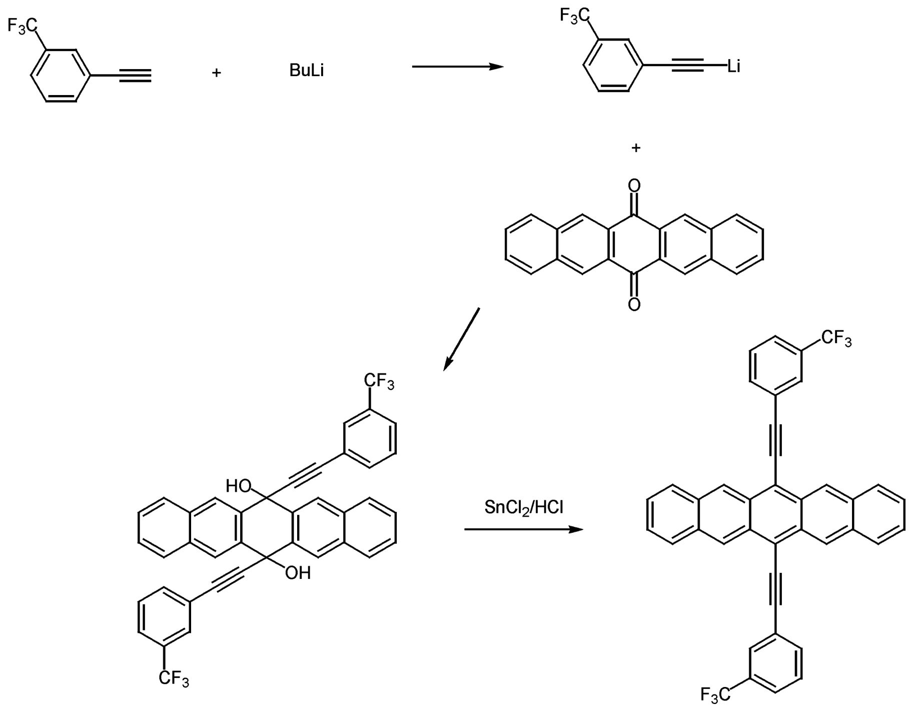


Fig. 2. Absorption spectra of MCF3 and other pentacenes in chloroform solution.



Sch. 1. Synthesis of MCF3.

As can be seen from the figure, there is a 19 nm red shift in absorption in our pentacenes compared to TMS. The solution fluorescence of MCF3 at different concentrations were recorded and are shown in Figure 3. With an increase in concentration, the peak intensities at 672 nm first increase and then decrease. The peak position also shifts to 698 nm. The shoulder peak at approximately 730 nm becomes more obvious at higher concentration. Both features imply that the MCF3 tends to form aggregates in solution at higher concentrations.

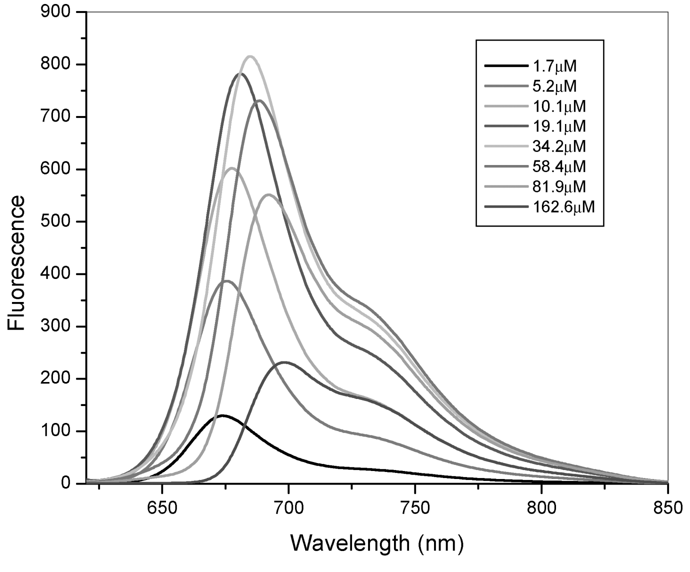


Fig. 3. Fluorescence spectra of MCF3 in $CHCl_3$ with different concentrations as indicated in the legend. $\lambda_{ex} = 610$ nm, scan rate: 240 nm/min.

The cyclic voltammogram of MCF3 (Figure 4) scanned from 0-1200 mV, showed a reversible redox potential, $E_{ox} = +0.703$ mV vs NHE (TMS, $E_{ox} = 691$ mV vs NHE) and the HOMO level of the MCF3 is found to be -5.45 eV. The HOMO-LUMO gap was determined by the crossing point of the absorption and emission spectra followed by the estimation of the LUMO level of the MCF3. All the values are provided in Table 1. Thermal gravimetric analysis on MCF3 showed that it is stable up to 293°C. The differential scanning calorimetry (DSC) studies on this material did not show any significant transitions. This indicates that the irreversible Diels-Alder type decomposition which is common in substituted pentances is not taking place in MCF3 and it is stable.

4. Conclusions

The meta substitution of trifluoromethyl group on aromatic ring in the phenylethynyl pentacenes led to a soluble and thermally stable pentacene derivative, MCF3 with desired HOMO energy level. The oxidation potential of MCF3 is found to be comparable to other alkylsilyl pentacene derivatives. This new pentacene derivative could not only be a potential p-type semiconductor for various optoelectronics applications including polymeric photovoltaics but also its synthesis may open up a new class of soluble pentacene derivatives.

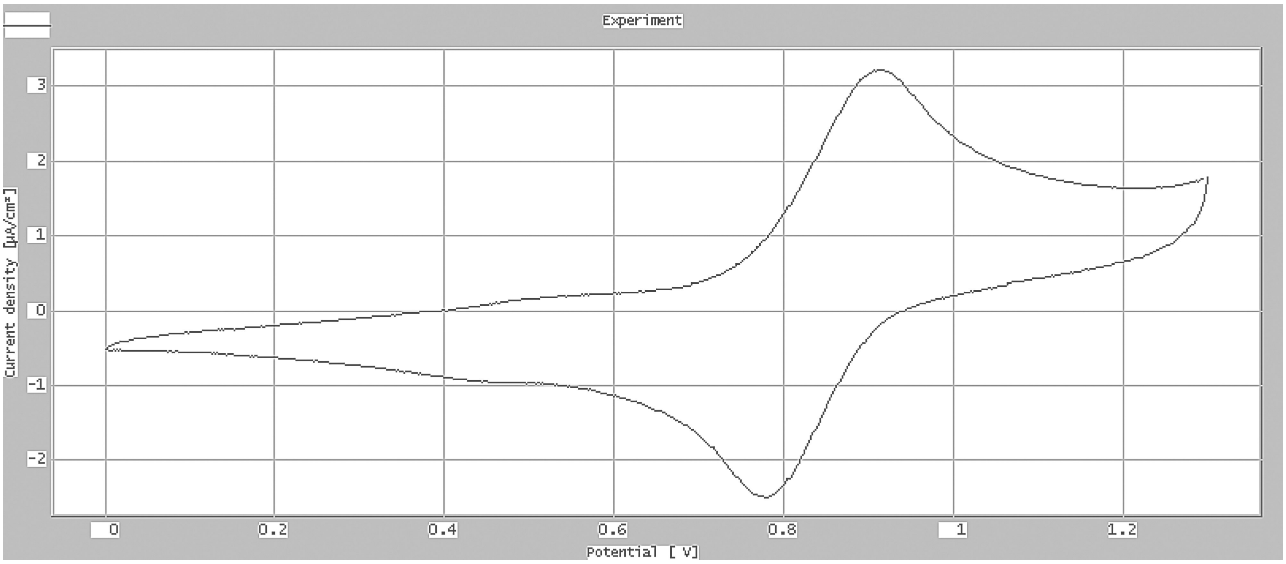


Fig. 4. Cyclic voltammogram of MCF3 in 0.1 M TBA PF6 in dichloromethane using Ag/AgCl (3M NaCl) as reference, and glassy carbon as working and a platinum wire as auxillary electrodes at scan rate, 150 mV/sec. Ferrocene was used as an external reference.

Table 1. UV-Visible Absorption and fluorescence maxima, HOMO, LUMO energies and HOMO-LUMO gap of MCF3

optical		energy		
absorption λ_{max} (nm) ε ($M^{-1}cm^{-1}$)	flurescence λ_{max} (nm)	HOMO (eV)	LUMO (eV)	HOMO-LUMO gap (eV)
659 (48,400)	672 730	−5.45	−3.50	1.95

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