Dialkylfluorene/oligothiophene and Dialkylfluorene/dithienylvinylene Alternating Copolymers

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Introduction

The incorporation of the 9,9-dialkylated polyfluorenes unit, a rigid biphenyl moiety, into conjugated polymers has been attracting considerable interest as they offer several advantages:

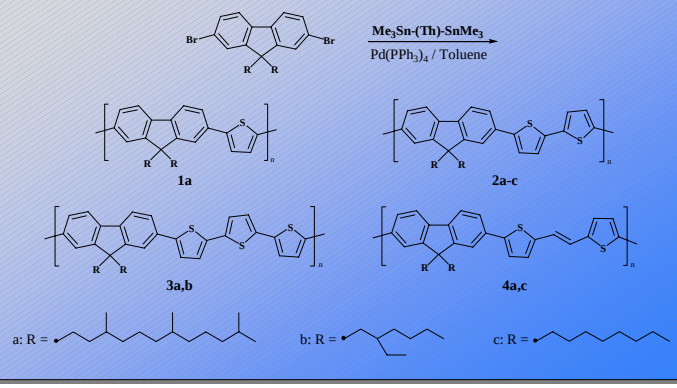
(i) no benzylic hydrogens which, are susceptible to oxidation,
(ii) side chain manipulation is relatively facile which can dramatically alter the physical and chemical properties of the polymer [1, 2]
(iii) excellent thermal stability and high stability against chemical doping [3]
(iv) high photoluminescence and high hole mobilities. [4]

However, poly(9,9-dialkylfluorene)s also exhibit high band gap energies of ca. 3.1 eV making electron injection difficult and therefore limiting their candidacy in polymer LEDs. [5]

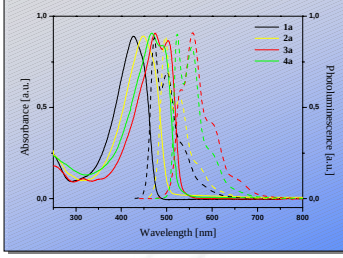
Incorporation of other arylene, especially heteroarylene (which exhibit good stability in both the neutral and doped states) moieties in fluorene-based polymers allows the preparation of tunable EL materials. [6]

Synthesis

Polycondensation of 2,7-dibromo-(9,9-dialkylfluorene) with the appropriate distannylated (oligo)thienylene component according to a Stille-type coupling reaction using $Pd(PPh_3)_4$ [7]

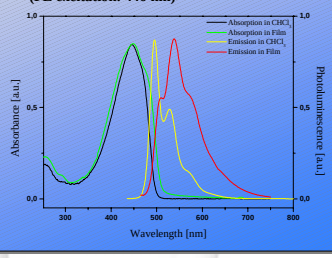


UV-Vis and photoluminescence spectra of polymers 1a, 2a, 3a, and 4a in $CHCl_3$



UV-Vis and photoluminescence spectra of polymer 2b in solution and film

(PL excitation: 446 nm)



Number-Average (M_n) Molecular Weight and UV-Vis data of Copolymers.

Polymer	M_n (a)	PD (M_w/M_n)	λ_{max} (solution) [nm]		λ_{max} (film) [nm]	
			Abs	PL	Abs	PL
1a	9,000	1.5	427	473, 500	427	504, 531
2a	11,100	1.8	448	497, 529	455	540, 573
2b	12,300	1.6	446	495, 528	449	510, 539
2c	12,000	1.6	447	497, 530	452	551, 581
3a	13,000	1,9	475, 503	531, 557, 595	470, 501	566, 601
3b	5,200	1.3	453	515, 547	471	567, 602
4a	16,000	1.9	467, 490	523, 555	363	595
4c	9,000	1.7	468, 492(s)	519, 554	383, 464(s)	537(s), 572

(a) GPC analysis, PS calibration

LC Properties

Initial examinations using DSC and polarizing microscopy reveal that the polydialkylfluorenes and some of the dialkylfluorene/oligothiophene alternating copolymers show the formation of thermotropic, nematic mesophases.

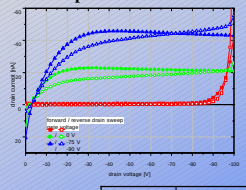
LC transistion temperatures of dialkylfluorene/-dithiophene alternating copolymers 2a-c

Polymer	LC transition temperature [°C]
2c	265 ($T_{Cr\rightarrow LC}$) [4]
2b	215 ($T_{Cr\rightarrow LC}$)
2a	120 (softening temperature, **2a** shows no crystallinity)

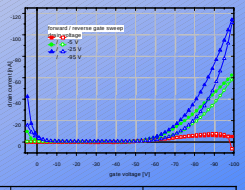
OFET Investigations based on Dialkylfluorene/oligothiophene and Dialkylfluorene/dithienylvinylene Alternating Copolymers

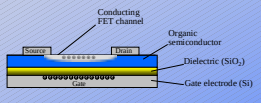
Channel width : 1.7 mm
Channel length : 65 µm
SiO_2 : 200 nm

Output of 4c device



Transfer of 4c device





Polymer	Mobility [Cm^2/Vs]	Threshold voltage [V]	On-Off ratio
2c	max. $7*10^{-4}$	-60	1300
4c	$2.5*10^{-4}$	-45	280
3a	max. $6*10^{-5}$	-60	18

Result and Discussion

(1) Polymers obtained in good yields (60 – 85%) and are readily soluble in common organic solvents.
(2) The M_n-values correspond to a degree of polymerisation of ca. 15 – 25.
(3) As thienyl unit extended high energy abs. shoulder becomes more defined and both abs. λ_{max} and PL λ_{em} red-shifted .
(4) Alkyl chains do not significantly effect polymer backbone geometry in solution.[6]
(5) PL spectra exhibit distinct vibronic structures indicating a planar excited state geometry.
(6) Bathchromic shift (~ 50 nm) of PL λ_{em} on going from solution to film attributed to the formation of ordered aggregates .
(7) The LC transition temperatures decrease with increasing length and branching of the alkyl side chains.
(8) Some of the copolymers (**2c**, **3a**, **4c**) were tested as active semiconducting layers in polymer-based organic field effect transistors (OFETs). The best performance was obtained for **4c**.
(9) The LC properties of **2a-c** may be used for the fabrication of oriented semiconducting layers in OFETs (to increase the charge carrier mobility).

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