Oligothiophene- and Dithienylvinylene-Dialkylfluorene Alternating Copolymers

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Introduction

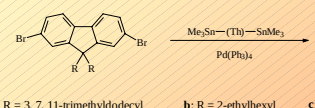
The incorporation of the 9,9-dialkylated polyfluorenes unit, a rigid biphenyl moiety, into conjugated polymers has been attracting considerable interest as they offer several advantages:
(i) no benzylic hydrogens which, are susceptible to oxidation,
(ii) side chain manipulation is relatively facile which 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]

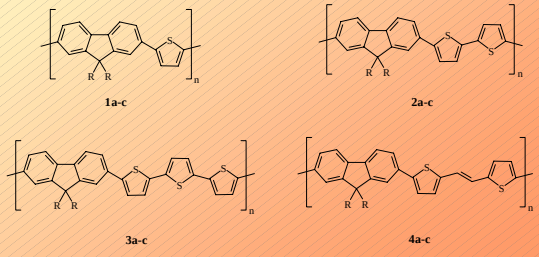
Incorporation of other arylene, especially heteroarylene (which exhibit good stability in both the neutral and doped states) moieties in fluorene-based polymers allows the preparation of tunable EL materials. [6]

Synthesis

Polycondensation of 2,7-dibromo-(9,9- dialkylfluorene) with various distannylated (oligo)thienylene component according to a Stille-type coupling reaction



a: R = 3, 7, 11-trimethyldodecyl **b**: R = 2-ethylhexyl **c**: R = octyl

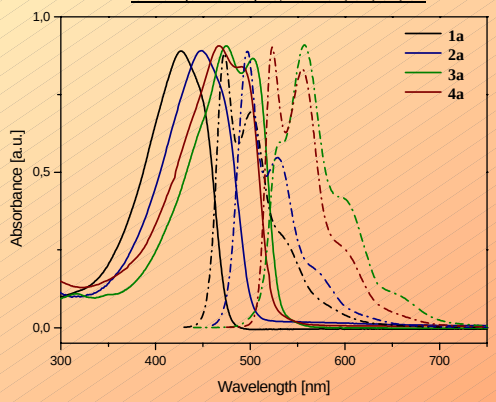


Results and Discussion

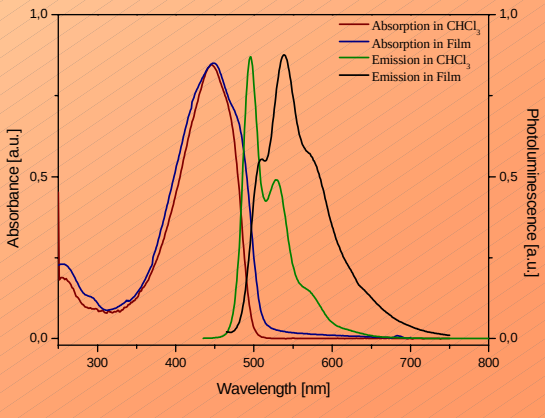
Polymer	M_w (a)	PD (M_w/M_n)	λ_{max} (solution) [nm]		λ_{max} (film) [nm]	
			Abs	PL	Abs	PL
1a	14,000	1.5	427	473, 500	427	504, 531
2a	20,800	1.8	448	497, 529	455	540, 573
2b	19,500	1.6	446	495, 528	449	510, 539
2c	19,300	1.6	447	497, 530	452	551, 581
3a	24,400	1,9	475, 503	531, 557, 595	470, 501	566, 601
3b	7,000	1.3	453	515, 547	471	567, 602
4a	31,000	1.9	467, 490	523, 555	363	595
4c	15,300	1.7	468	519, 554	383, 464(sh)	537(sh), 572

(a) GPC analysis, PS calibration

Soln. spectra of polymers **1a**, **2a**, **3a**, **4a**



Soln and film spectra of **2c**



(i) Polymers obtained in good yields (60 – 85%) and are readily soluble in common organic solvents

(ii) The M_n-values correspond to a degree of polymerization of ca. 15 - 25

(iii) As thienyl unit extended high energy abs. shoulder becomes more defined and both abs. λ_{max} and PL λ_{em} red-shifted

(iv) Alkyl chains do not significantly effect polymer backbone geometry in solution[6]

(v) PL spectra exhibit distinct vibronic structures indicating a planar excited state geometry

(vi) Bathchromic shift (~ 50 nm) of PL λ_{em} on going from solution to film attributed to the formation of ordered aggregates

References and Acknowledgements

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