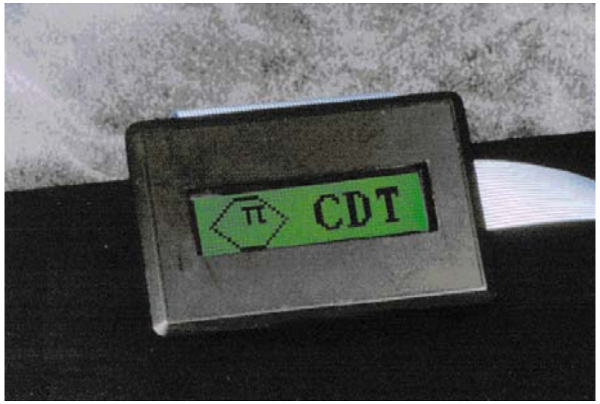
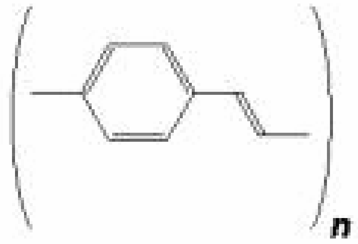
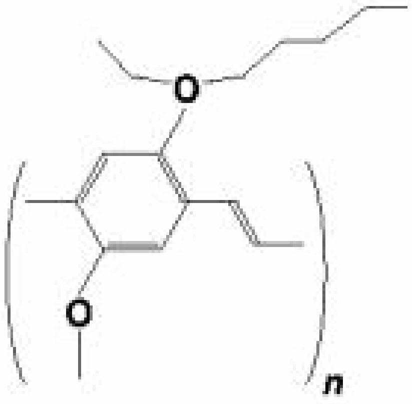
Emitting Materials I

- Poly(*p*-phenylene vinylene) (PPV)





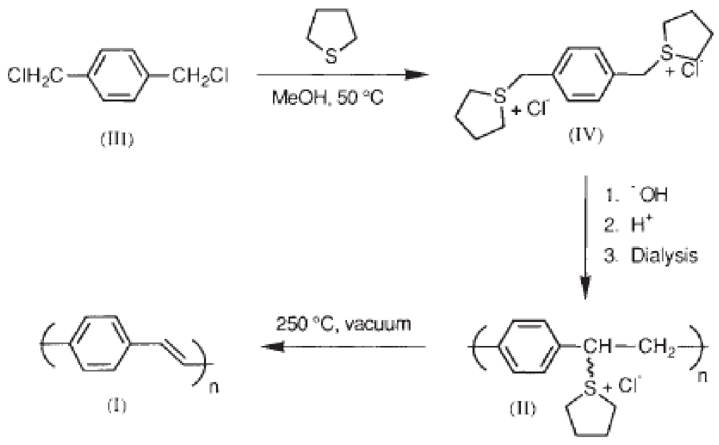
PPV

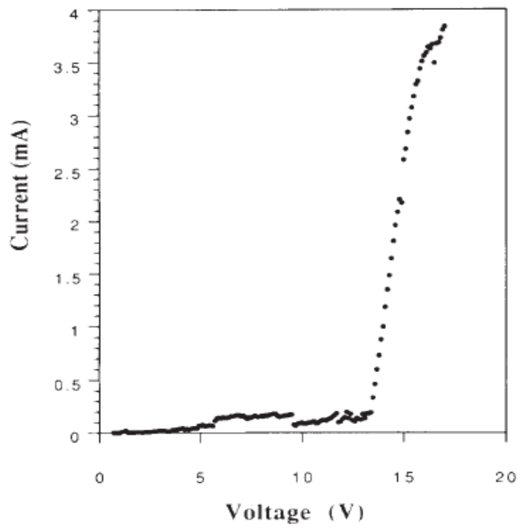


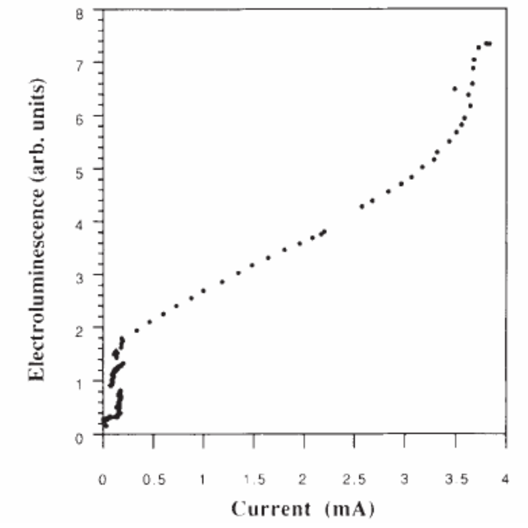
MEH-PPV

Polymer Light-Emitting Device

The first PLED was reported by Cambridge group using poly(*p*-phenylene vinylene)



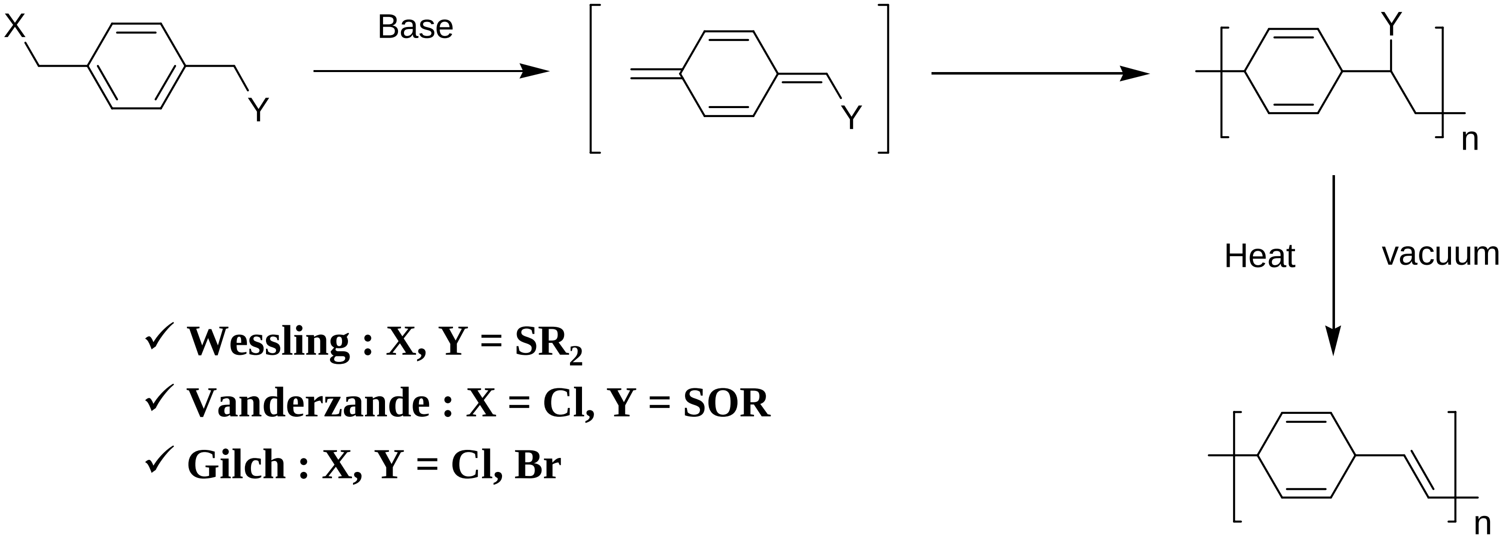




Nature, 347, 539, 1990

Electroluminescence in conjugated polymers was first discovered during investigations into the electrical properties of poly(1,4-phenylene vinylene) (PPV), the simplest and cheapest poly(arylene vinylene).

The precursor polymer route to PPV via a quinodimethane



PPV

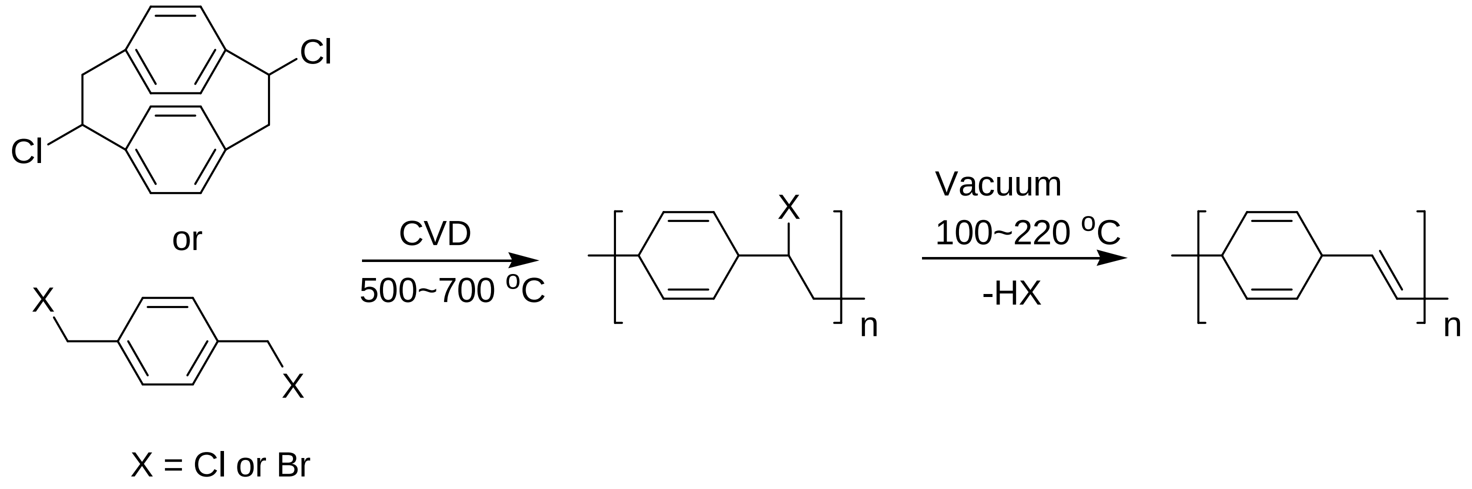
- ✓ **Wessling : X, Y = SR_2**
- ✓ **Vanderzande : X = Cl, Y = SOR**
- ✓ **Gilch : X, Y = Cl, Br**

The origin of the field of EL polymers is connected with the 1990 article by Friend and co-works that describes an EL device based on conjugated Poly(*p*-phenylen vinylene)

PPV is a highly stable conjugated polymer and its yellow color is due to an absorption band centered at 400~420 nm with band gap of 2.5 eV

PPV is a bright yellow, fluorescent polymer. Its emission maxima at 551 nm (2.25 eV) and 520 nm (2.4 eV) are in the yellow-green region of the visible spectrum.

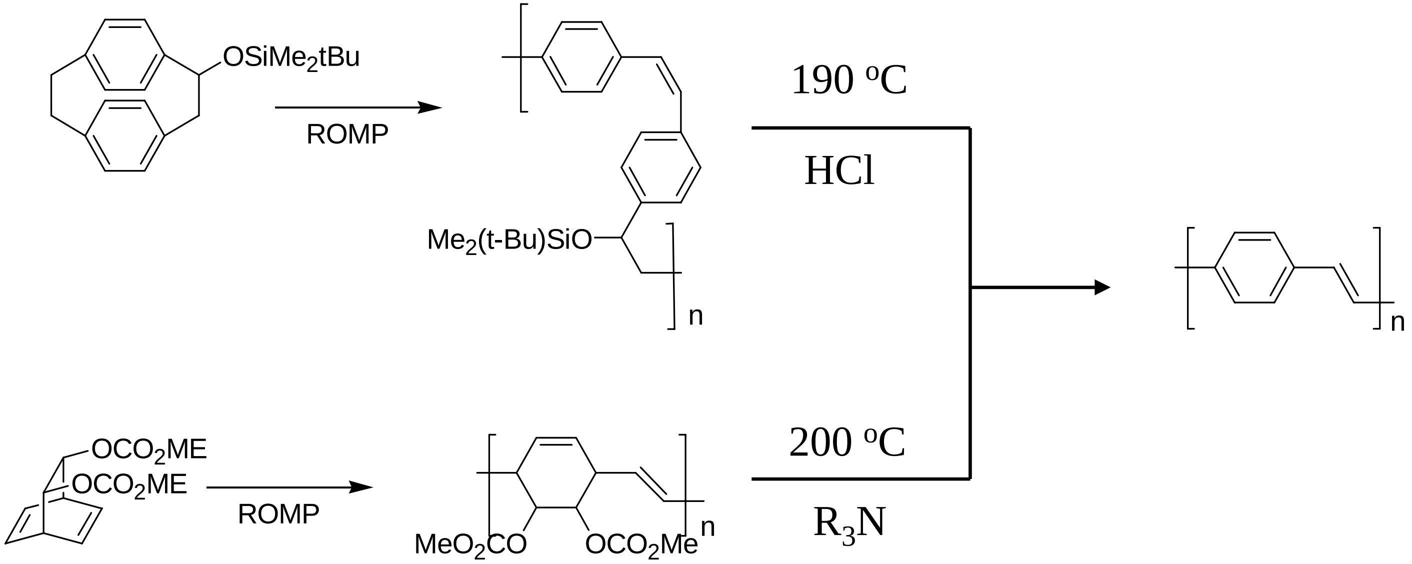
Chemical vapor deposition route to PPV



- ➢ **CVD method can afford uniform and patterned thin film,**
- ➢ **Requires heating at 500~700 °C, which may give rise to by-product impurities**

  → Such harsh conditions and difficulties of complete removal of the halogen result in ill-defined material, which affords very low-performance PLEDs

Ring-opening metathesis polymerization (ROMP)



➢ **The drawback of the CVD method is eliminated in ROMP, which is based on a catalytic reaction, occurring in rather mild conditions.**

➢ **A living ROMP reaction results in soluble precursors with rather low PDI.**

➢ **However, the film-forming properties of ROMP precursors are usually rather poor, resulting in poor uniformity of the PPV films.**

Direct route to PPV - Soluble Poly(phenylene vinylene)

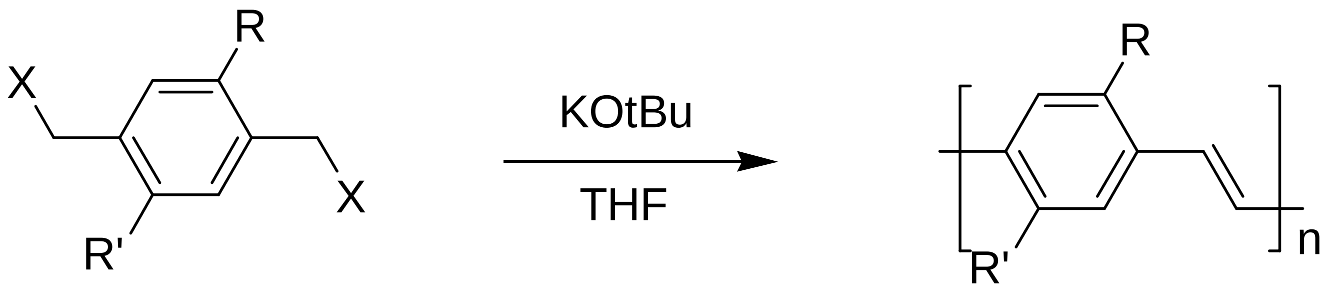
❖ The precursor method polymer is insoluble, intractable, and infusible.

❖ Any synthesis of PPV directly from a monomer produces an insoluble material, which cannot be easily processed such as solution processing by spincoating.

Solution-Processible Poly(phenylene vinylene)

✓ Gilch polymerization
✓ Nonionic route
✓ Knoevenagel polycondensation
✓ Heck-coupling polymerization
✓ Wittig-Horner condensation

General synthetic route – Gilch route to PPV



- A general and most widely used method for the synthesis of PPV derivatives.

- Avoid high temperature conditions.

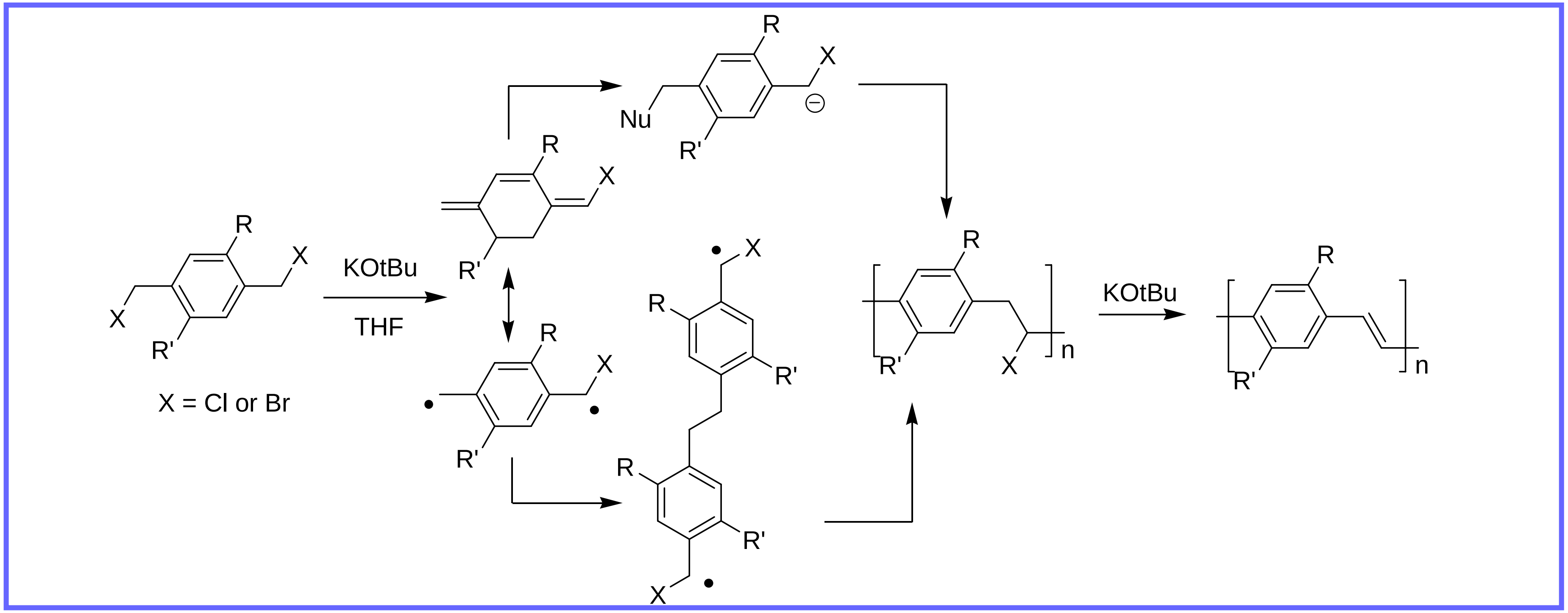
- For device applications, as-synthesis PPV materials need to be soluble in organic solvents

- The mechanism of Gilch polymerization is still a subject of some controversy.

➡ It is well accepted to proceed through a reactive quinodimethane intermediate, followed by either a radical or a living chain anionic polymerization.

- A MW decrease upon the addition of chain transfer radical agent – radical mechanism same effect imposed by nucleophilic initiator – nucleophilic chain growth mechanism

General synthetic route – Gilch route to PPV

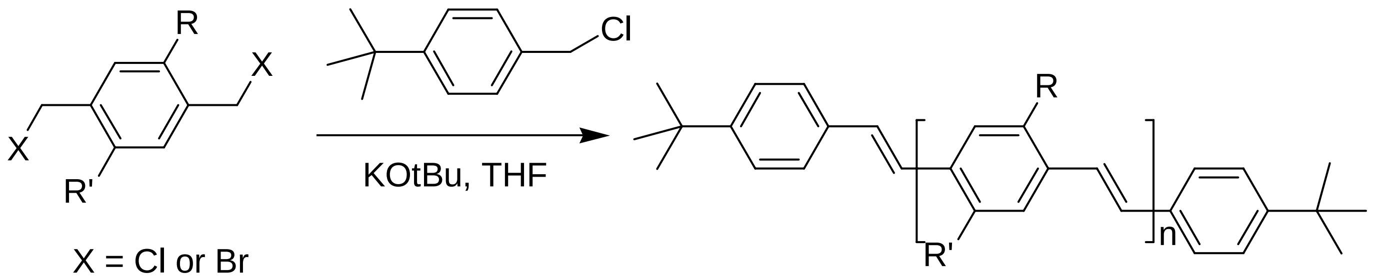


- **In both mechanism, the regularity of the polymer conjugation chain is challenged by the possibility of side reaction – 'head-to-head' (HH) or 'tail-to-tail (TT)**

- **The MW can be controlled (50,000 ~1,000,000) by changing the reaction temperature and time, the solvent, the conc. of monomer, and the amount of base.**

- **High MW polymers and a high content of *trans* double bonds are the reasons for the wide usage of Gilch polymerization in the synthesis of PPV homo- and copolymers**

End-capping modification of the Gilch polymerization



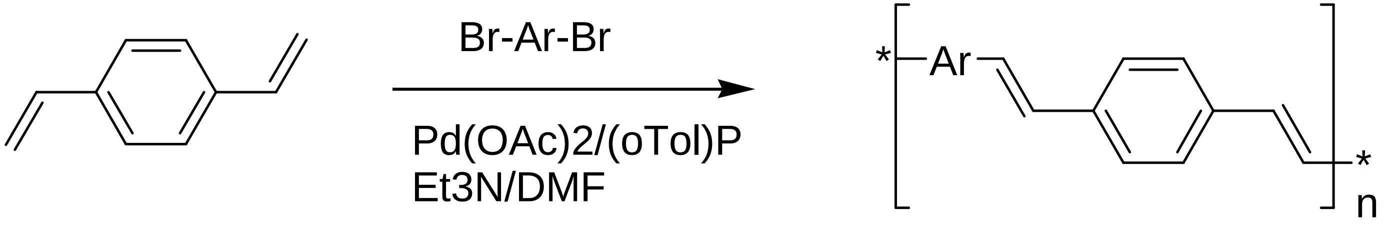
Macromolecules, 30, 8094, 1997

- 4-tert-butylbenzyl chloride as an initiator and end-capping reagent to control the MW of the Gilch synthesis of MEH-PPV

- Adding different amounts (0.6~60 mol%) of end capper results progressively in a decrease in the MW of polymer (M_n = 66,500 for 6 %), suppressing the undesirable gel formation effect.

- However, the polymerization yield under these conditions was found to be rather low (35 % for 6 % and 20 % for higher amount of initiator), which can be logically expected, considering possible side reactions of the initiator in strongly basic media.

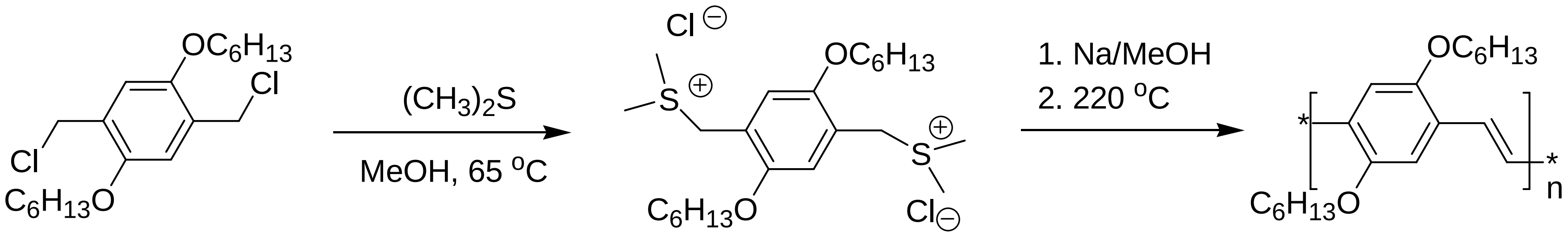
Heck-coupling route to PPV copolymers



Macromolecules, 28, 4525, 1995

- The PPV-polymer chain can also be constructed by Heck coupling of aromatic dihalides with a divinylbenzene.
- In contrast to above-described methods, the Heck coupling is a Pd catalyzed reaction with very mild conditions.
- The polymerization normally leads to all-*trans* geometry with very few side reactions.
- This method is of great utility in the preparation of alternating copolymers.

Alkoxy-substituted poly(*p*-phenylene vinylene)s



Synth. Met., 29, E129, 1989

DH-PPV

✓ **Poly[(2,5-dialkoxy-1,4-phenylene)vinylene]s with at least one long, solubilizing alkoxy side chain dissolve in various organic solvents such as chloroform or THF.**

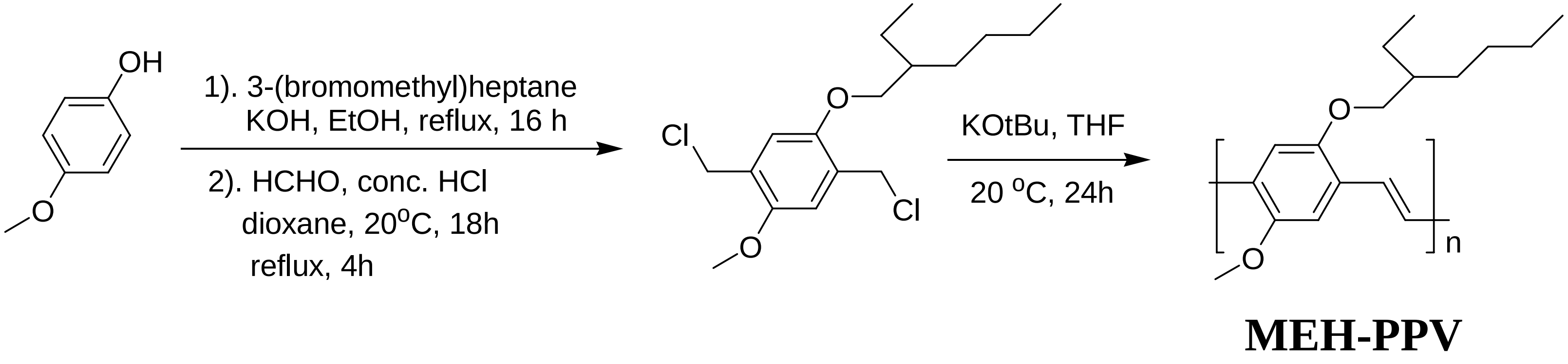
✓ **In addition, their emission maximum is red-shifted [to ca. 590 nm (2.1 eV)] compared with that of PPV.**

✓ **The long side chains, which keep the conjugated polymer backbones apart from each other, apparently have a beneficial effect on the polymers' fluorescence and electroluminescence quantum yields.**

✓ **However, the solubility of this materials at rt. was still not high enough due to the "side-chain crystallization effect"**

➡ **To solve the problem, highly asymmetric substituents pattern polymers (well-known as MEH-PPV)**

Asymmetric alkoxy-substituted PPV

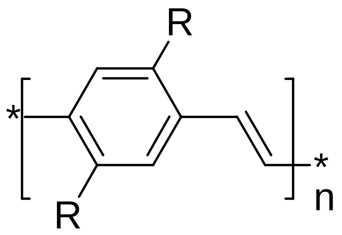


- ➢ The side-chain disorder results in a high solubility in spite of extremely high MW ($>10^6$ Da), Careful control of concentration is needed to avoid gelation.

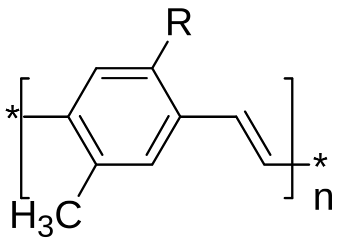
- ➢ MEH-PPV : bright-orange material (λ_{max}–490 nm), red-orange emission (λ_{PL}–590 nm)

- ➢ The ethylhexyl substituent MEH-PPV showed similar electronic behavior to the 3,7-dimethyloctyl substituent, but an additional branching further improved its solubility and the film-forming properties.

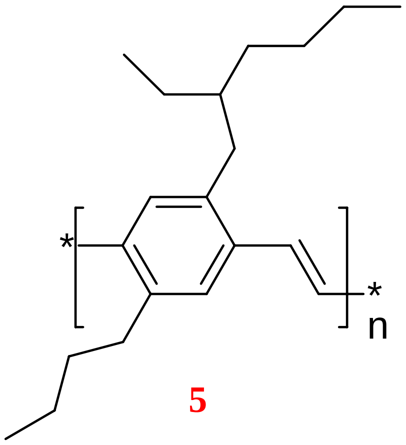
Alkyl-substituted poly(*p*-phenylene vinylene)s



1. R = CH_3
2. R = C_7H_{15}



3. R = 3,7-dimethyloctyl
4. R = n-$C_{12}H_{25}$



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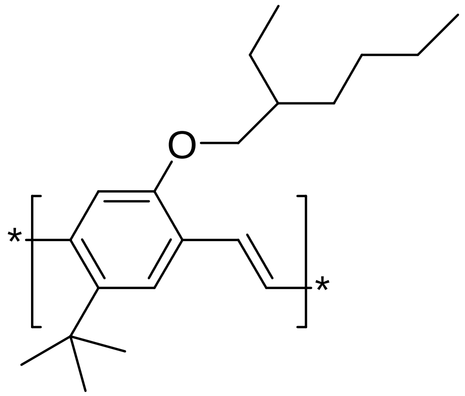


6

- **A number of alkylated-PPV polymers have been reported.**

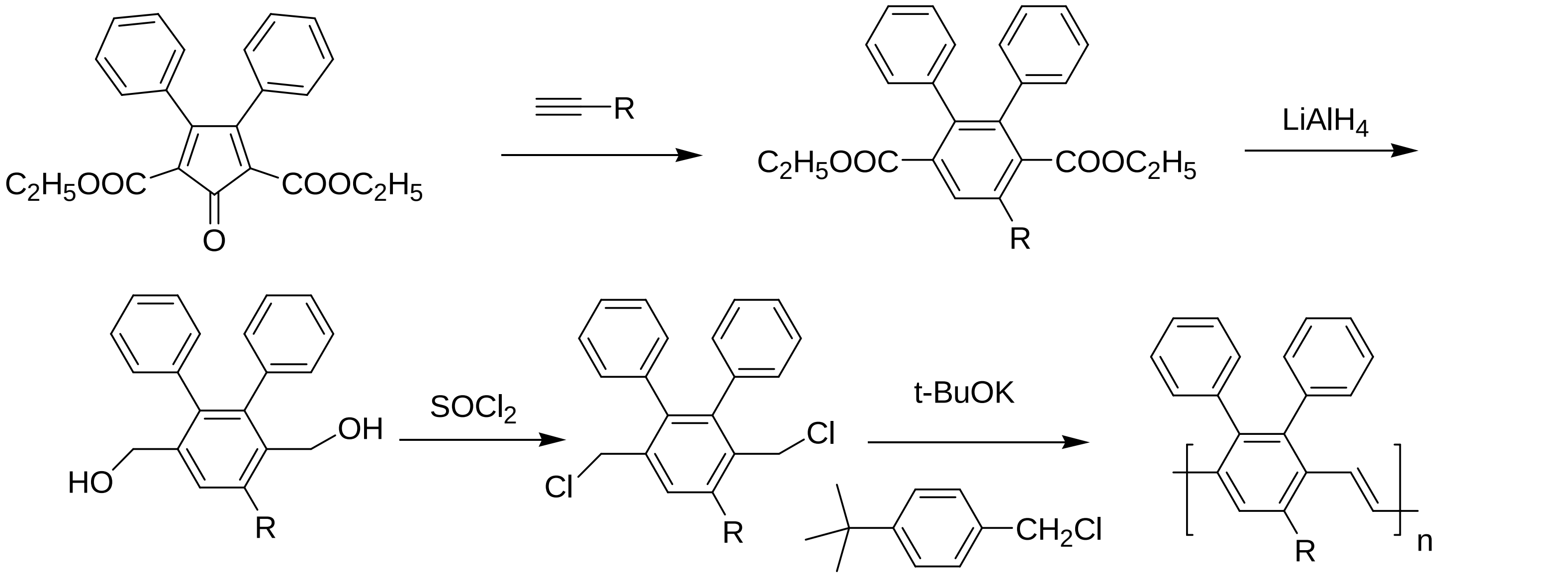
- **The absorption of dialkylated PPVs is very close to that of unsubstituted PPV (2:λ_{max} = 404 nm -sol'n, 5: λ_{max} = 422 nm -film) and hypsochromically shifted with respect to dialkoxy-PPVs**

- **The dialkylated PPV 5 can be used as a new type of solid-state laser material.**

- **The polymer 3 emitted with λ_{max} = 530~560 nm, but the reported Φ_{EL} = 0.2 % was lower compared with alkoxy-PPV**

- **Very high QE PLEDs were fabricated with 6, emitted green light with Φ_{EL} = 2.7 %**

Aryl-substituted poly(*p*-phenylene vinylene)s



1. R = C_nH_{2n-1} (n=6, 8, 10)
2. R = Ph
3. R = biphenyl

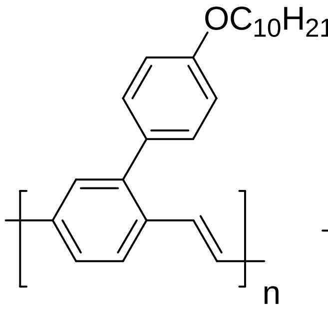
- ✓ **Soluble diphenyl-PPV derivatives via an ingenious route based on a Diels-Alder reaction**

- ✓ **Diels-Alder approach eliminates the problem of isomer formation**

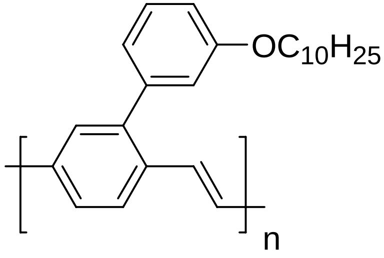
- ✓ **Due to significant steric factors of the substitution pattern, the emission of polymer 3 is blue-shifted to a λ_{max} of 490 nm, which is very low for fully conjugated PPV**

- ✓ **The solid-state PL efficiency also reached a very high value of 65 % due to the preventing the intermolecular packing of highly distorted polymer chains.**

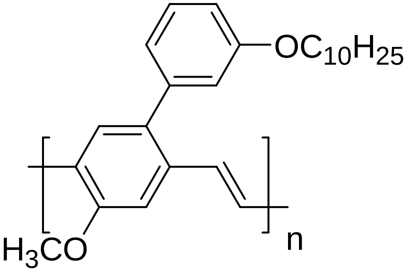
Aryl-substituted poly(*p*-phenylene vinylene)s



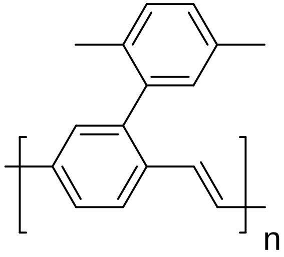
1



2



3



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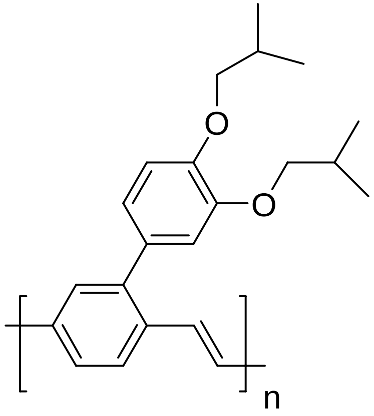


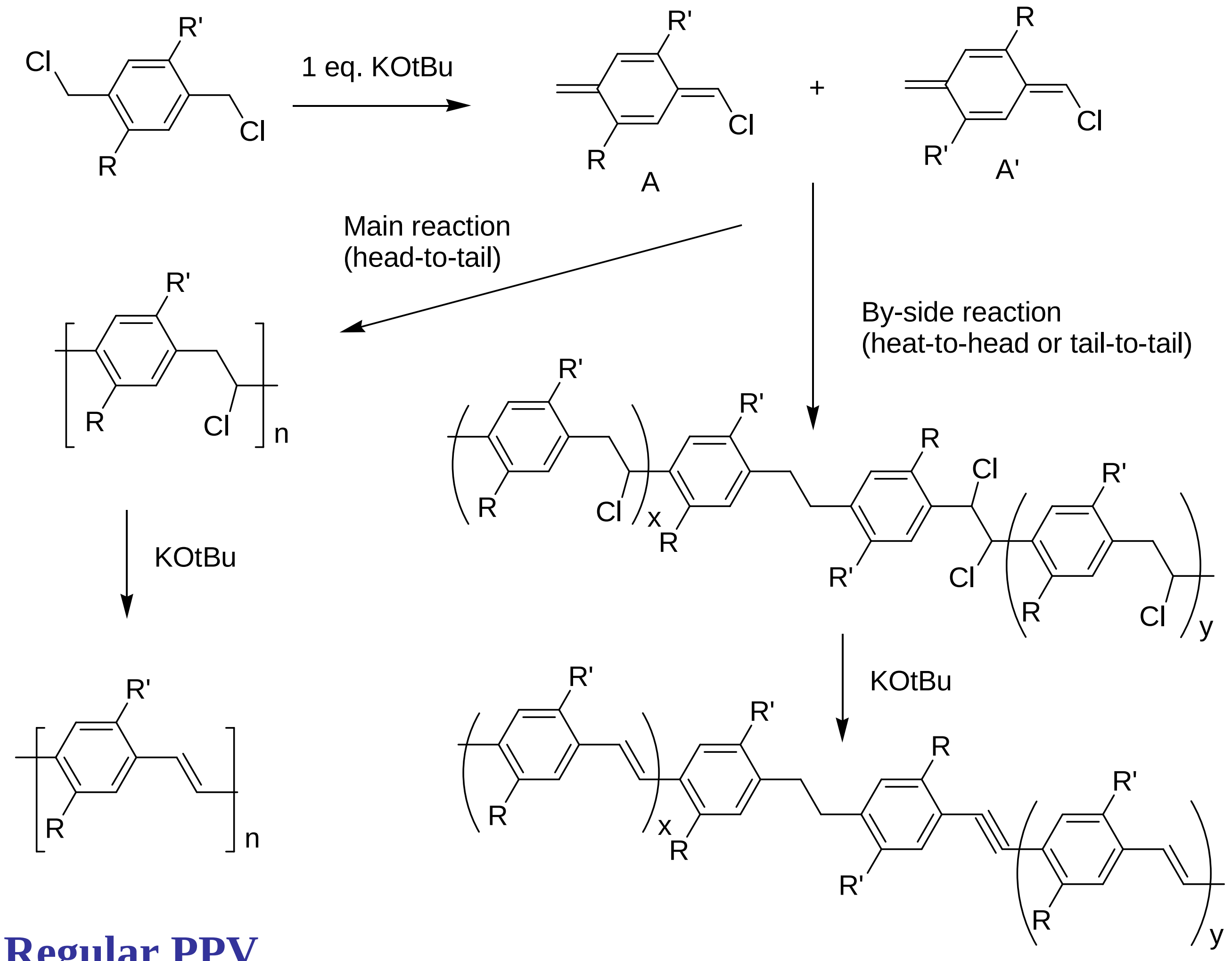
5

- **The solubility of the phenyl-PPVs can be greatly improved by the introduction of alkoxy substituents into the pendant phenyl groups.**

- **These polymers exhibited high PLQY and improved EL performance owing to their good film-forming properties. – green-emitting PLED of 2 : Φ_{EL} = 3.1 % (7.9 cd/A)**

- **However, phenyl-substituted PPV have a significant level of defect tolane-bisbenzyl (TBB) moieties, this defects have moderate influence on the photophysical properties, but strongly affect the PLED device lifetime.**

The mechanism of formation of TBB in Gilch polymerization



1 eq. KOtBu

Main reaction
(head-to-tail)

By-side reaction
(heat-to-head or tail-to-tail)

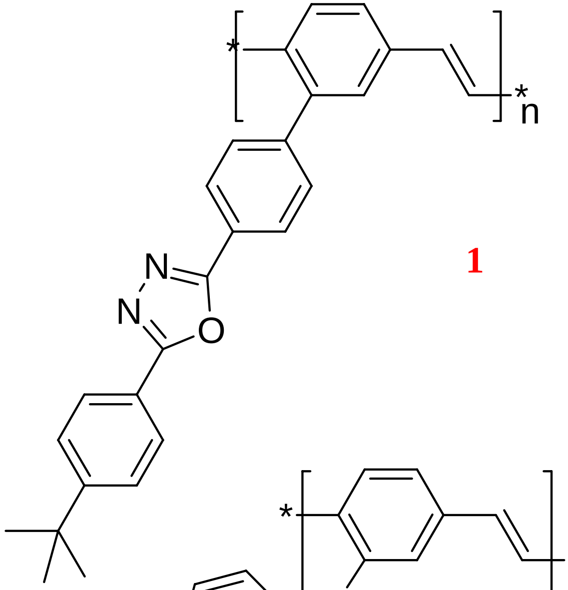
KOtBu

KOtBu

Regular PPV

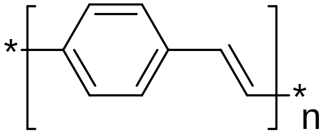
Tolane-bisbenzyl defect

PPV homopolymers with electron-withdrawing and donating substituents



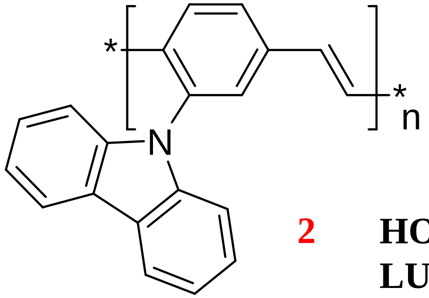
1

HOMO : -6.42 eV
LUMO : -3.93 eV



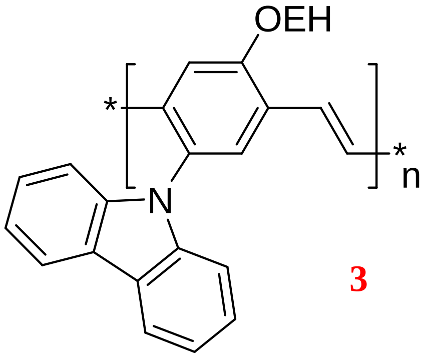
PPV

HOMO : -6.12 eV
LUMO : -3.75 eV



2

HOMO : -6.12 eV
LUMO : -3.64 eV

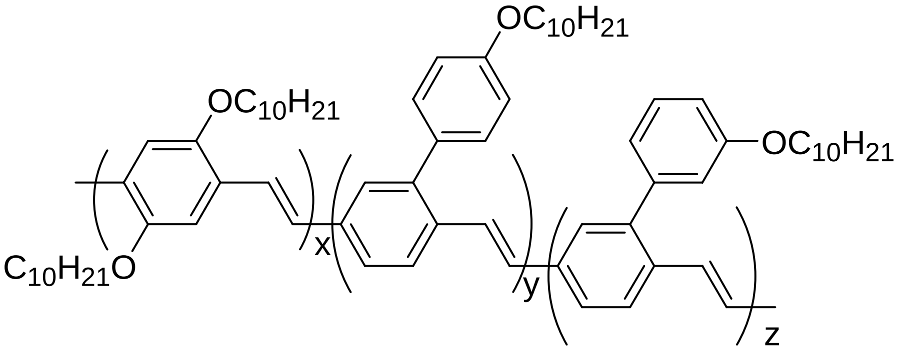


3

HOMO : -5.50 eV
LUMO : -3.20 eV

✓ Electronic properties of PPV polymers can tuned by substitution of an electron acceptor and an electron donor

PPV copolymers with electron-donor and aryl substituents



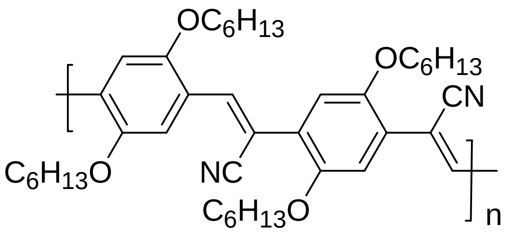
a : x:y:z = 0:50:50	EL : 515 nm	11.5 cd/A
b : x:y:z = 1:49.5:49.5	EL : 530 nm	12.9 cd/A
c : x:y:z = 2:49:49	EL : 540 nm	14.8 cd/A
d : x:y:z = 4:48:48	EL : 547 nm	10.5 cd/A
e : x:y:z = 10:45:45	EL : 567 nm	9.6 cd/A
f : x:y:z = 100:0:0	EL : 583 nm	2.0 cd/A

- ✓Synthesis of phenyl- or alkoxy-substituted PPV copolymers was first reported by Spreitzer, who studied in detail the dependence of the EL on the comonomer ratio.

- ✓All copolymers showed high EL efficiency, low-driving voltage, and high emission brightness (10,000 cd/m^2) was easily achieved by reasonable voltage of 6 to 8 V.

- ✓The emission color of **a** is green, whereas increasing the ratio of dialkoxy phenylene vinylene unit results in a **gradual red shift** of the emission, through yellow(**e**) to orange color (**f**).

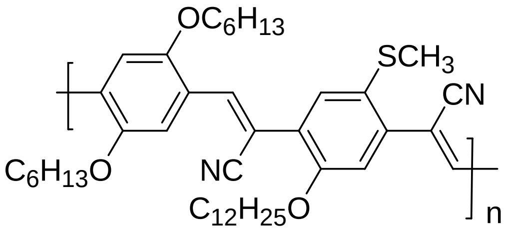
PPV copolymers with electron-withdrawing substituents



1

PL = 710 nm, Eg = 2.1 eV

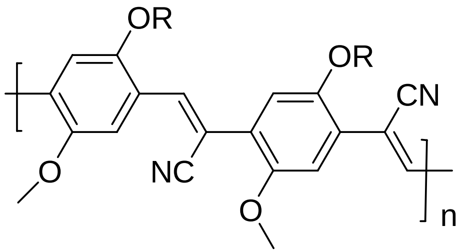
Red



2

PL = 610 nm, Eg = 2.2 eV

Yellow



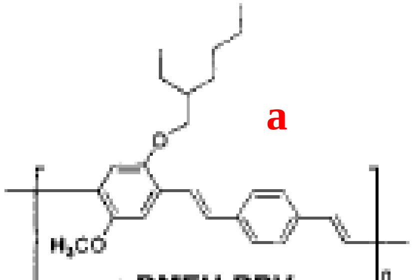
3

PL = 610 nm, Eg = 2.0 eV

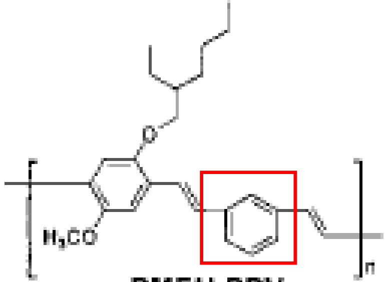
Yellow

- ✓ **Electron acceptor cyano substituents lower the HOMO and LUMO levels of the polymer – CN-PPV**
- ✓ **In 1993, the Cambridge group reported the first soluble CN-PPV copolymers 1, 2**
- ✓ **The presence of two electron donor alkoxy (1, 2) significantly reduced the electron-accepting effect of the CN groups, but compared to the most widely used dialkoxy-PPVs, the electron injection in 1, 2 is facilitated, allowing the use of less-reactive Al electrode.**
- ✓ **CN groups reduce the hole-transporting properties of the diode**

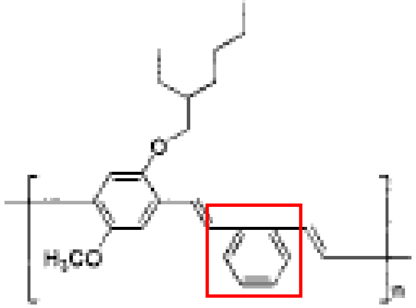
Formally conjugated systems with twists, meta-links, and sp-hybridized atoms in the backbones



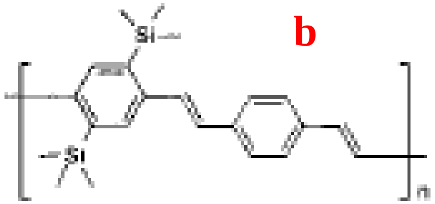
p-PMEH-PPV



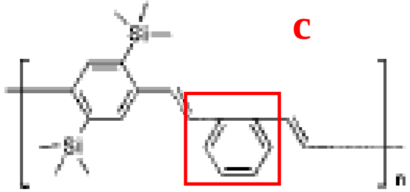
m-PMEH-PPV



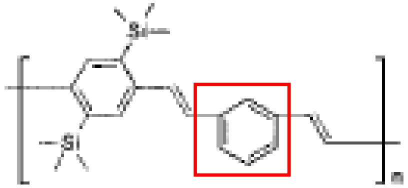
o-PMEH-PPV



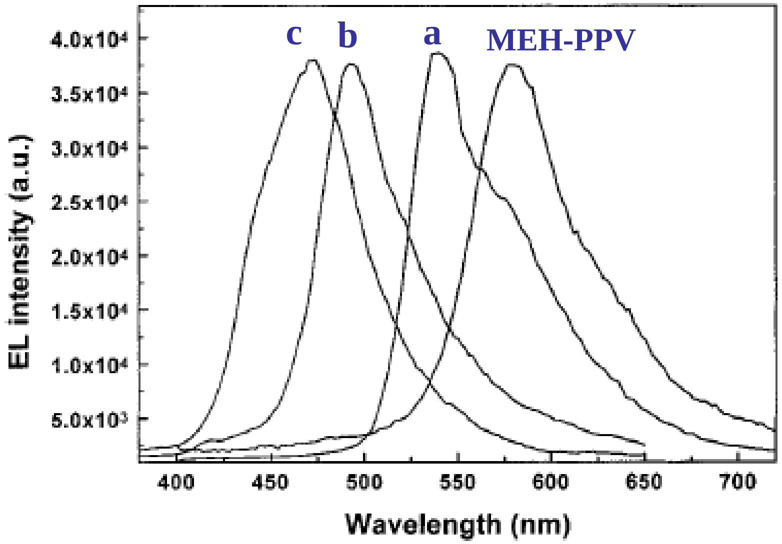
p-PBTMS-PPV



o-PBTMS-PPV



m-PBTMS-PPV



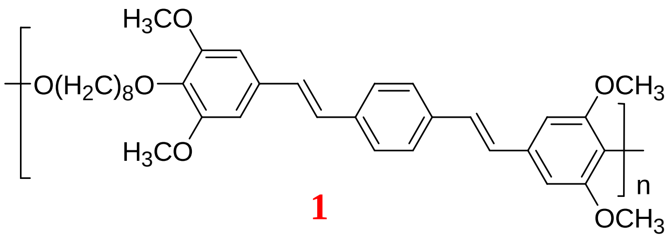
Macromolecules, 32, 3279, 1999

In fact, blue-emitting PPV are subject of significant research interest, but generally unavailable conjugated PPV due to relatively low band gap.

How to decrease the effective conjugation length??

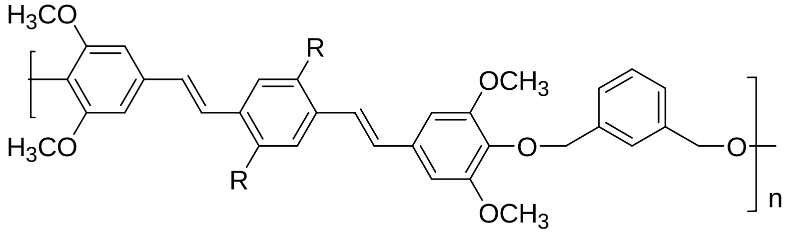
- ✓ Introducing either nonconjugated block or sp3 defect into the PPV chain
  - → *m*-phenylene unit do not allow direct conjugation → hypsochromic shift
  - → *o*-linking is formally conjugated but due to steric hindrance → decrease conjugation length

Conjugated and nonconjugated PPV block copolymers



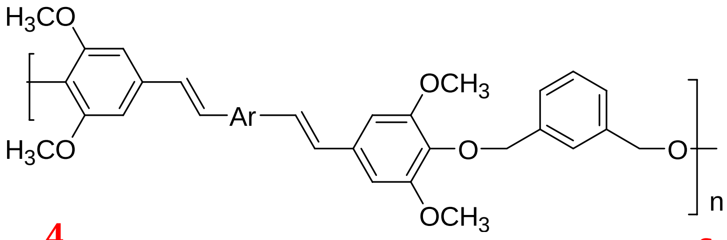
1

PL : 465 nm



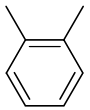
2-R = H **PL:439 nm** **E_g:2.95 eV**

3-R = $OC_{16}H_{33}$ **PL:453 nm**



4

Ar =

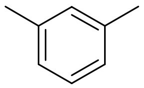


PL:435 nm

E_g:3.25 eV

5

Ar =

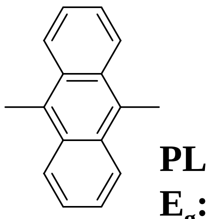


PL:409 nm

E_g:3.35 eV

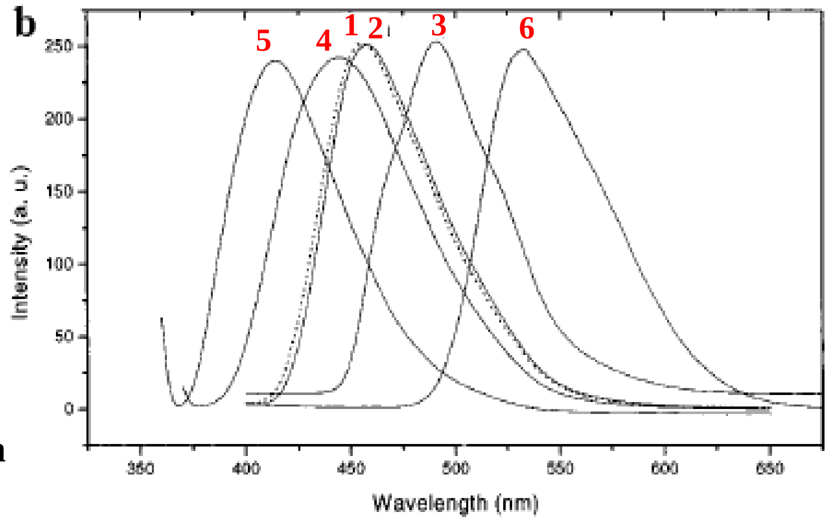
6

Ar =



PL:490 nm

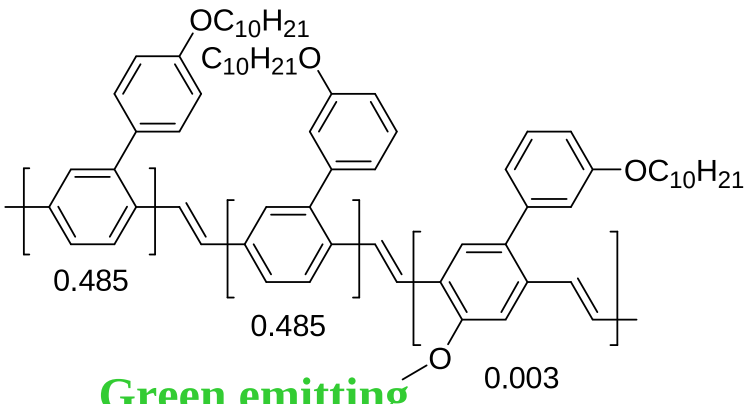
E_g:2.65 eV



Macromolecules, 33, 7426, 2000

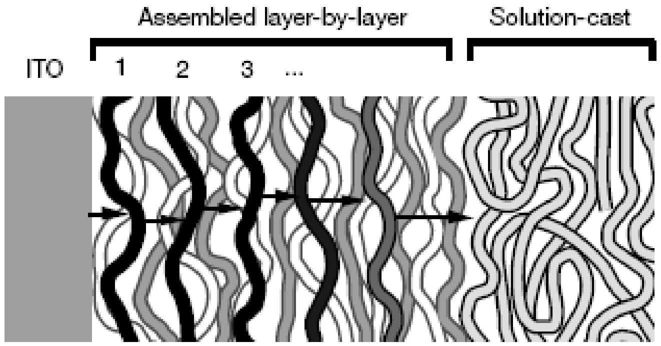
By changing the substituents in the central ring of the phenylene vinylene block or altering the conjugation by changing the aromatic unit, the emission band can be tuned b/w 413~533 nm

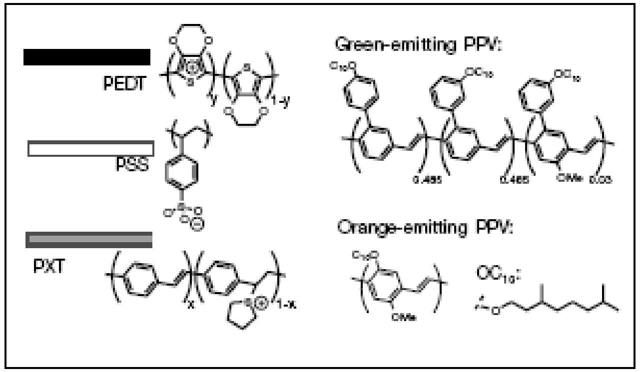
The best performing PPV light-emitting polymer I

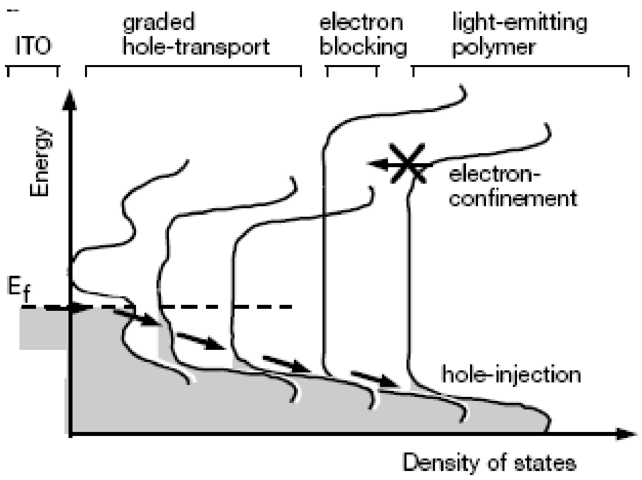


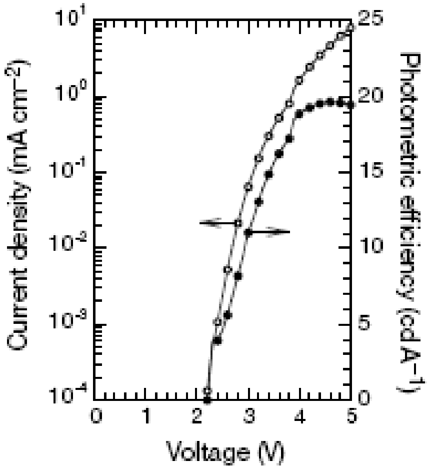
Green emitting

PLED: ITO/PEDOT/polymer/Ca
Turn on voltage : 2.2 V
Brightness : 1600 cd/m^2 (at 5 V)
Max EL effi. : 22 cd/A





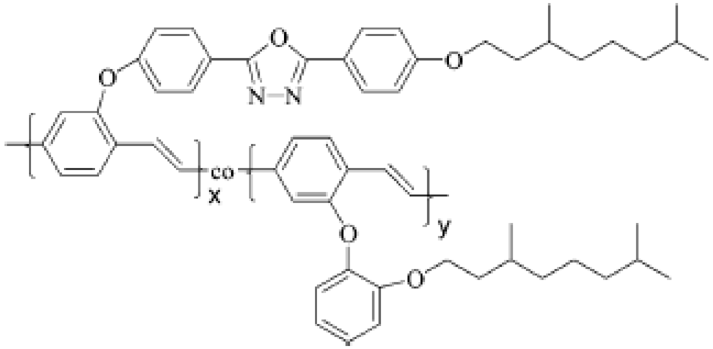




Nature, 404, 481, 2000

Graded hole-transport layer using assembled layer by layer

The best performing PPV light-emitting polymer II

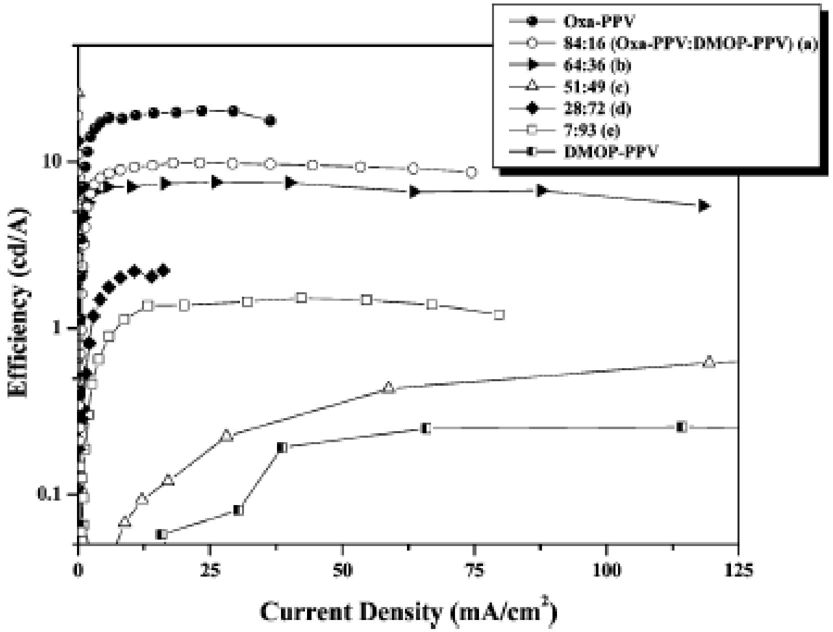


x=100, y=0 (Oxa-PPV)
x=84, y=16 (a)
x=64, y=36 (b)
x=51, y=49 (c)
x=28, y=72 (d)
x=7, y=93 (e)
x=0, y=100 (DMOP-PPV)

PLED: ITO/PEDOT/polymer/Al
λ_{EL} = 591 nm
Turn on voltage : 5.0 V
Brightness : 19,395 cd/m^2 (at 14 V)
Max EL effi. : 21.1 cd/A

Yellow-orange emitting

J. Am. Chem. Joc., 126, 2474, 2004

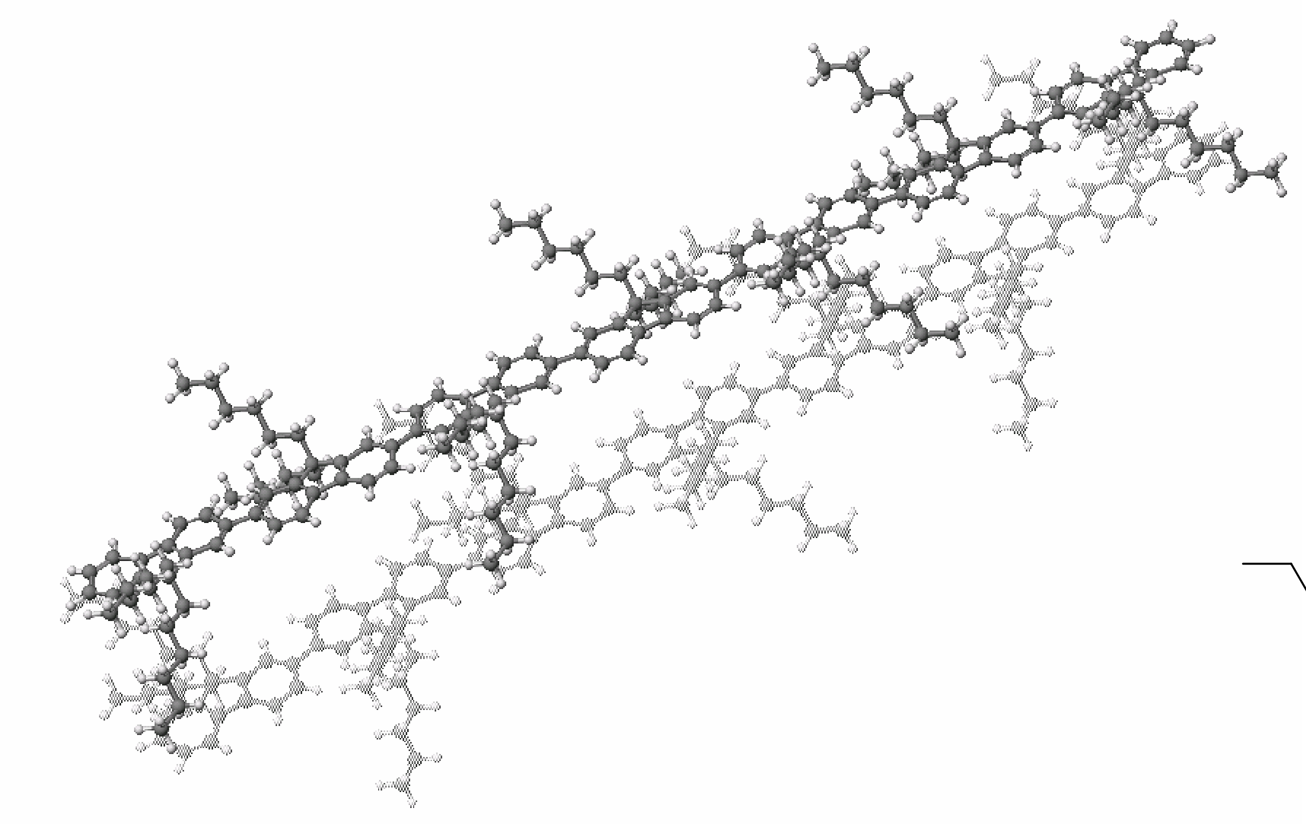


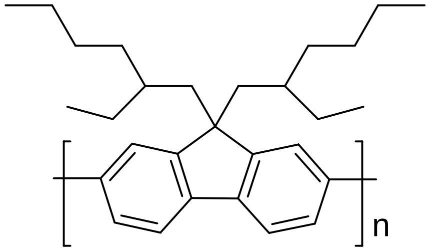
The emission colors could be tuned from green to yellowish-orange via intramolecular energy transfer.

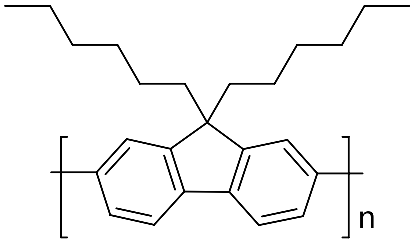
The improved device performance of Oxa-PPV over DMOP-PPV and Oxa-PPV-co-DMOP-PPV may be due to better electron injection and charge balance between holes and electrons and also efficient intramolecular energy transfer from 1,3,4-oxadiazole units to PPV backbones.

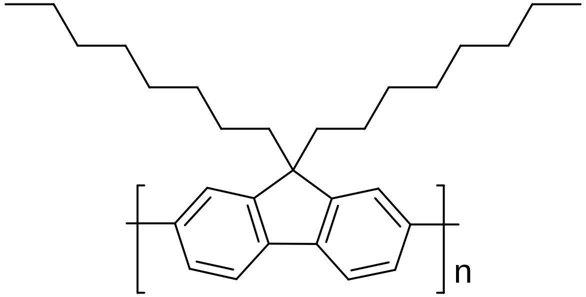
Emitting Materials II

- Poly(fluorene) (PF) I

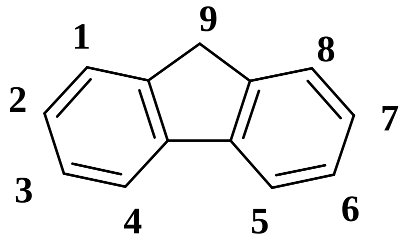




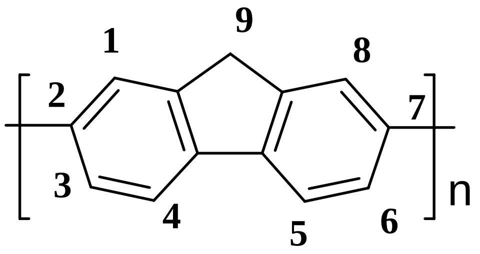




poly(fluorene) derivatives



Fluorene



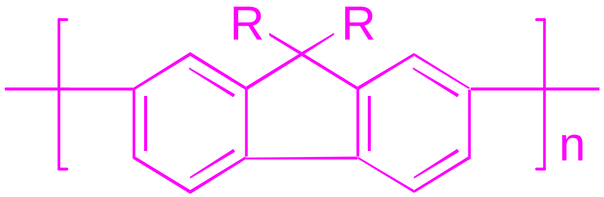
Poly(fluorene)

Fluorene is a polycyclic aromatic compound, which received its name due to strong violet fluorescence arising from its highly conjugated planar π-electron system.

Positions 2 and 7 in fluorene are the most reactive sites toward electrophilic attack, which allows construction of a fully conjugated rigid-rod polymer chain by substitution reactions.

The varieties, excellent optical and electronic properties, and high thermal and chemical stability of PFs make them an attractive class of materials for PLEDs

Why poly(fluorene) derivatives !!!



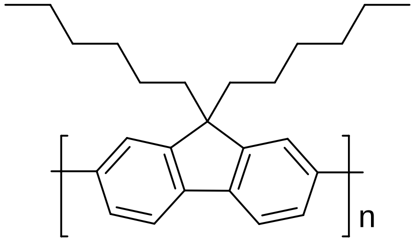
Advantages

- Thermally and chemically stable
- Facile substitution at 9-position allows to control properties such as solubility, morphology, etc.
- Solution fluorescence quantum yields are high (0.6-0.8), rivaling those of some laser dyes and quantum yields in solid can approach those in solution
- Large band-gap for blue emitting material

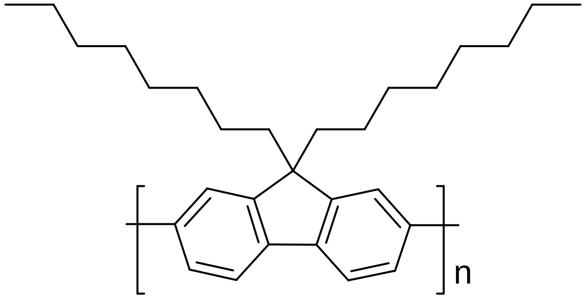
Disadvantages

- excimers are formed upon annealing at elevated temperature or passage of current

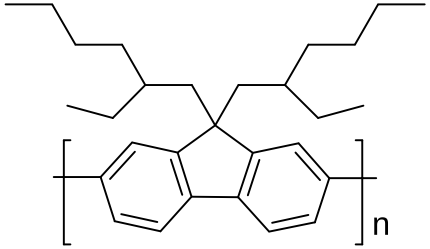
Stability and phase behavior of PFs



PDHF



PFO



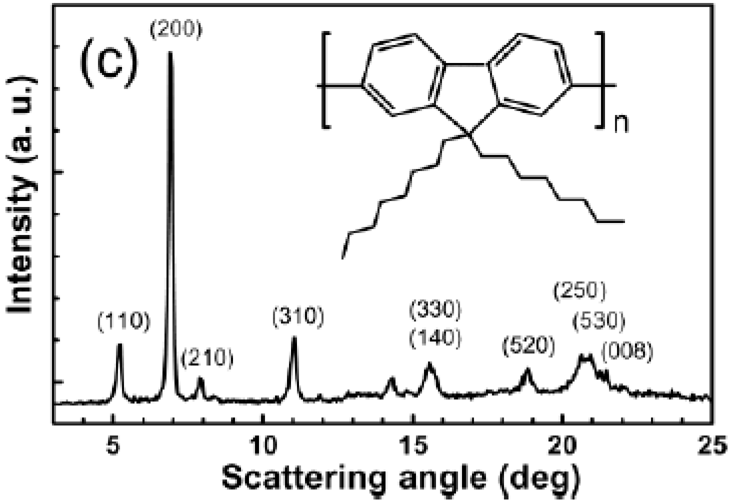
PEHF

The PF homopolymers and copolymers obtained by different synthetic procedures, the M_n ranges from 10,000 to 200,000 with PDI=1.5~3.

Generally, homo- and copolymers show excellent thermal stability : T_d exceed 400 ℃

Whereas PDHF is generally considered as amorphous, PF with long octyl side chain, PFO, is crystalline material. Many PFs exhibit LC behavior, opening a possibility to fabricate polarized LEDs.

Crystalline Poly(9,9-di-n-octyl-2,7-fluorene)



XRD powder pattern of highly crystalline thick-film PFO

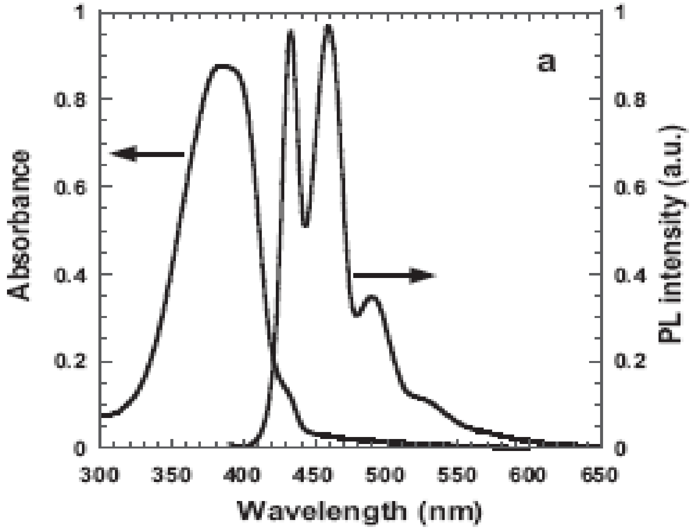
Macromolecules, 37, 6833, 2004

PFO is clearly crystalline with a Tm around 150 ℃, above which a nematic mesophase exists up to ca. 300 ℃. Nanoscale crystallinity of PFO was demonstrated by XRD.

For the crystalline phase, a periodicity in the plane of the surface of 4.15 Å corresponded to half the fluorene ring report distance along the backbone.

Octyl chains of two neighboring polymer backbones are believed to intercalate, allowing a more efficient space filling. This side-chain packing may be responsible for an unusual ability of PFO and related PF to undergo thermotropic alignment into monodomain structure. PFO is the most studied PF for its crystallinity and LC.

Optical and Electronic properties



Typical absorption and PL spectra of pristine thin films of PFO

Adv. Funct. Mater., 13, 325, 2003

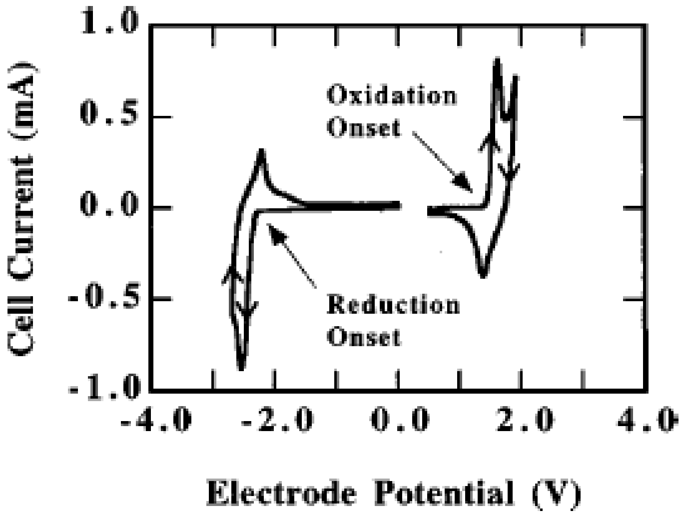
The electronic absorption spectra of dilute solutions of poly(9,9-dialkylfluorene) show a sharp peak with λ_{max} ~ 385-390 nm (3.2 eV) of π-π^* electronic transition.

Thin solid films reveal similar absorption with a slightly red-shift (~10 nm) and relatively broader peak due to intermolecular interaction.

PL of PFs show well-resolved structural features with max. at 420, 445, and 475 nm assigned to the 0-0, 0-1, and 0-2 intrachain singlet transition, respectively.

Due to the tail emission of PFs, the thin films emit bright sky-blue light. The QE of the PFs is very high, typically in range of 40 to 80 %.

Optical and Electronic properties



Typical cyclic voltammograms (CV) recorded at a scan rate of 20 mV/s for a PFO thin film

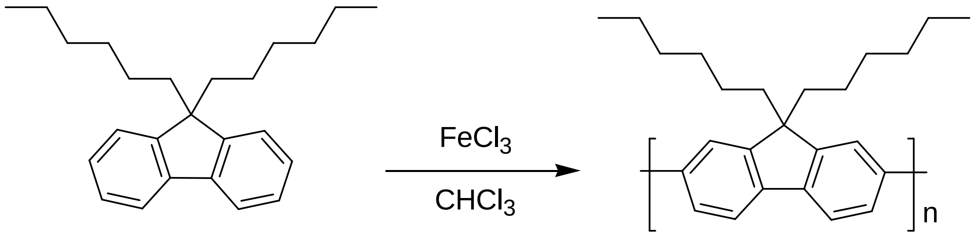
APL, 73, 2453, 1998

The band gap determined as the onset of the absorption band in thin films is 2.9 eV, which also determined redox waves in CV experiments to estimate the IP and EA.

The gap b/w the obtained energy levels (5.8 eV for IP & 2.12 eV for EA) 3.8 eV is substantially higher than the optical band gap.

Although optical absorption and electrochemistry test two physically different process (vertical electron excitation and adiabatic ionization) and are not expected to be the same, very good agreement b/w methods for conjugated polymer systems.

General methods in synthesis of PF homopolymers



Oxidative polymerization

Jpn. J. Appl. Phys., Pt. 2-Letters, 28, L1433, 1989

The first poly(9,9-dialkylfluorene) with long-chain solubilizing hexyl groups was synthesized via an oxidative coupling reaction using ferric chloride in $CHCl_3$

This resulted in polymers with relatively low MW (Mn up to 5,000).

The regioregularity of the polymerization process in these conditions was rather poor due to nonregiospecific oxidation reactions resulting in some degree of branching and nonconjugative linkages through the position other than 2 and 7.

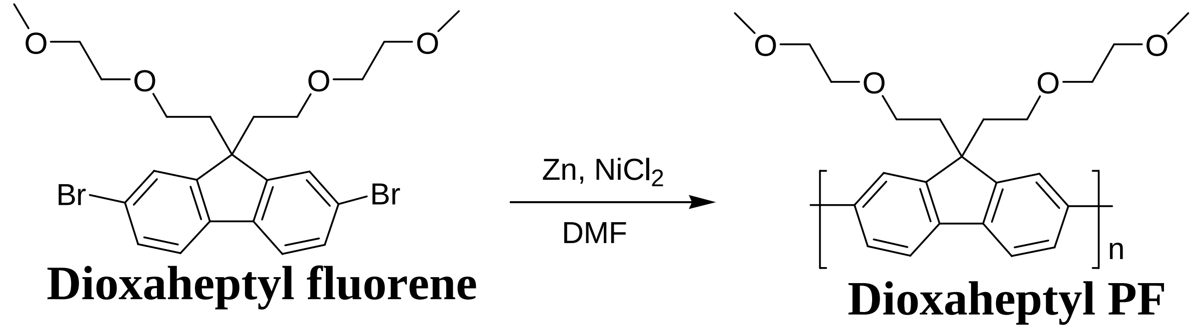
The PLED fabricated using this material gave relatively low QE, and in spite of a well-resolved vibronic structure of the PL band, the EL emission showed a very broad band.

A serious drawback of this synthetic method was also a significant amount of residual metal impurities, which dramatically affected the PLED performance.

General methods in synthesis of PF homopolymers

Yamamoto polymerization

J. Am. Chem. Soc., 118, 7416, 1996



The next step toward soluble PF as materials for PLEDs, was an application of Yamamoto synthesis to polymerize various 2,9-dihalo-9,9-R^1,R^2-fluorene.

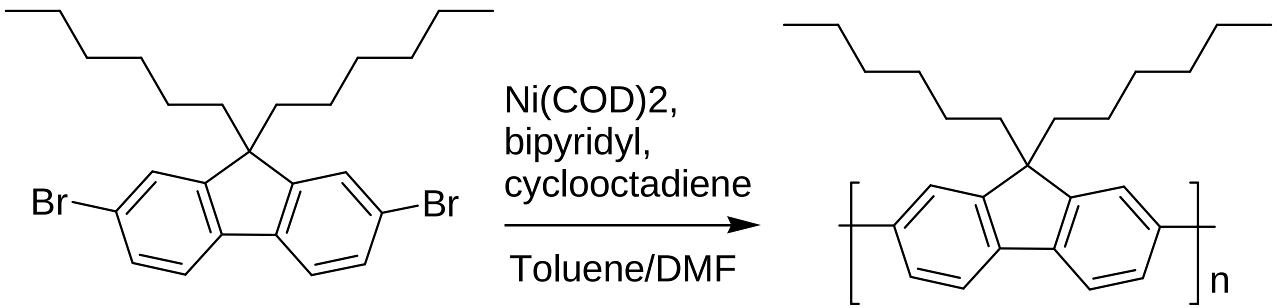
UNIAX Corporation first reported a reductive polymerization of dioxaheptyl fluorene in DMF using zinc as a reductant and reactive Ni(0) as a catalyst, resulting in high MW PF (M_n = 94,000)

Although Ni-catalyzed reaction allowed improvement of the regiospecificity and minimization of cross-linking and mislinking reactions compared to $FeCl_3$ oxidation method, it employs a large amount of metals (Ni, Zn) during the synthesis.

In addition, because of the nonpolar hydrophobic nature of poly(dialkylfluorene)s, the polymer chain growth in polar solvents (DMF or DMA) is terminated by polymer precipitation from the reaction mixture. Thus, whereas relatively high MW (Mn=94,000) can be achieved containing hydrophilic side-chain.

General methods in synthesis of PF homopolymers

Yamamoto type-polycondensation



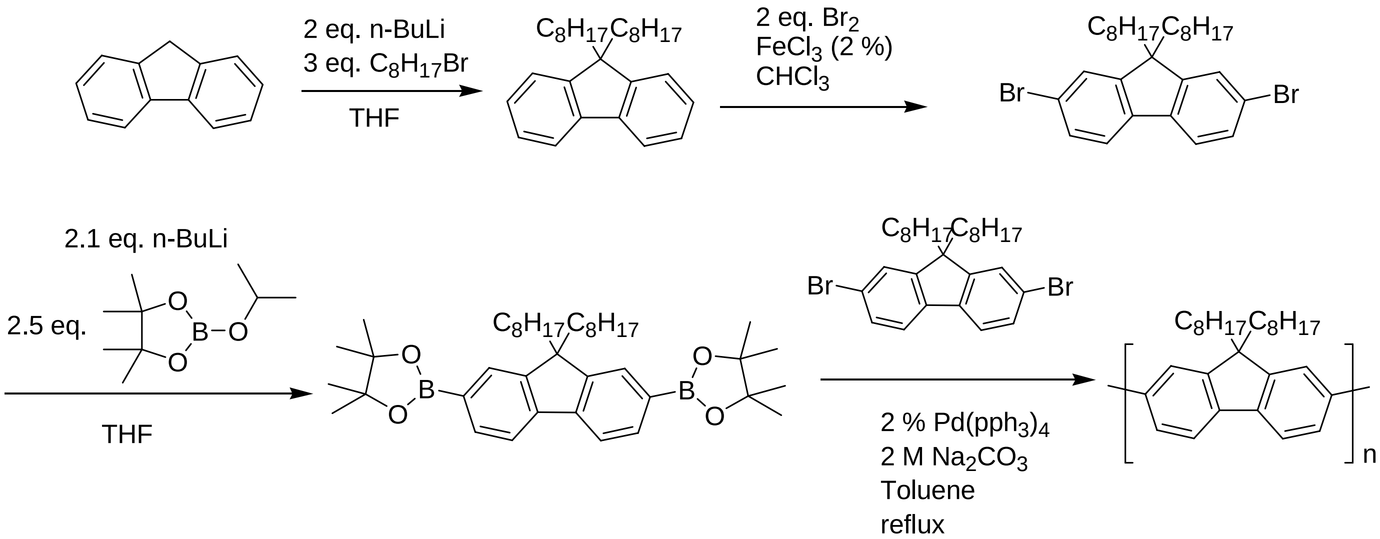
Macromolecules, 31, 1099, 1998

Another Yamamoto-type polycondensation was performed coupling using Ni(COD)$_2$ /cyclooctadiene/2,2'-bipyridyl in a toluene-DMF solvent mixture.

This method allows preparation of PFs with very high MW M_n up to 250,000 and the usage of Ni(COD)2 as reductive transition metal-based coupling agent is very convenient.

General methods in synthesis of PF homopolymers

Suzuki coupling reaction



Chem. Commun., 1597, 1997

Suzuki-coupling synthesis of PF could minimize the problem of metal impurities by employing catalytic amount of $Pd(pph_3)_4$, and the use of a phase transfer catalyst gives higher MW (Mn = 50,000).

Although the MW of PF achieved by Yamamoto coupling are higher than Suzuki coupling, reaching such high MW is controlled not only by the method of the coupling but mainly by careful purification of the monomers and by optimization of the reaction condition, as well as by the solubility of the polymer in the reaction mixture.

Problem of pure blue emission in PFs : Excimer and Aggregate formation or fluorenone defect?

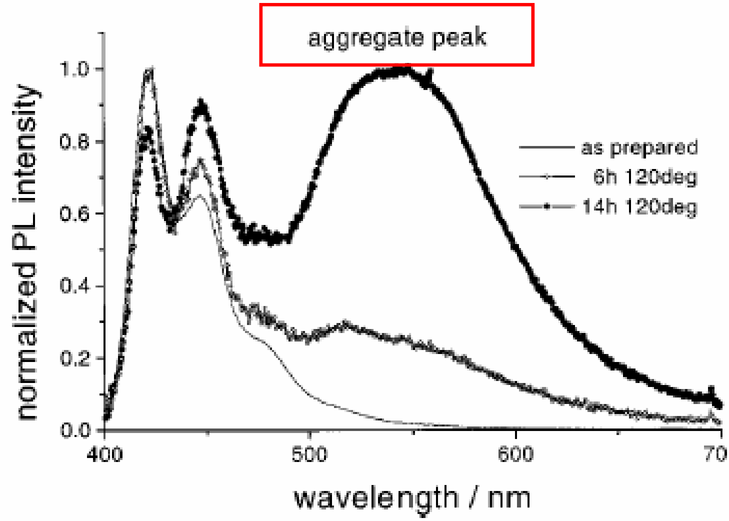


FIG. 2. Change in PL spectra on thermal annealing at elevated temperatures. The same PDOFO material as in Fig. 1 was used.

Weinfurtner et al. *Appl. Phys. Lett.***2000**

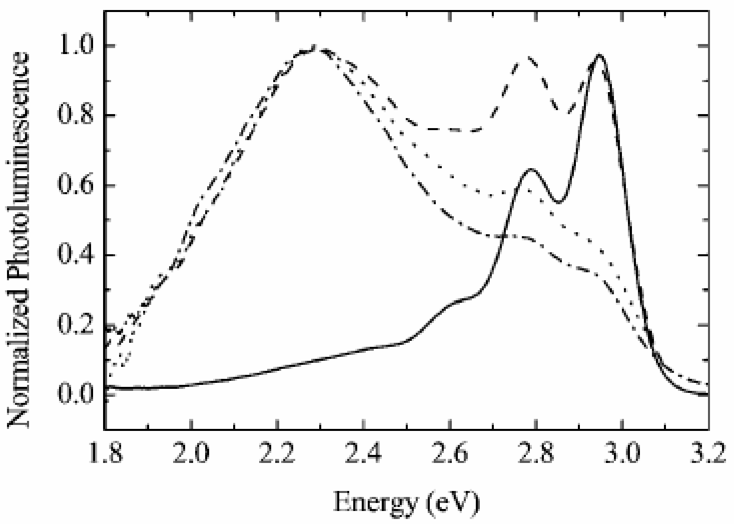
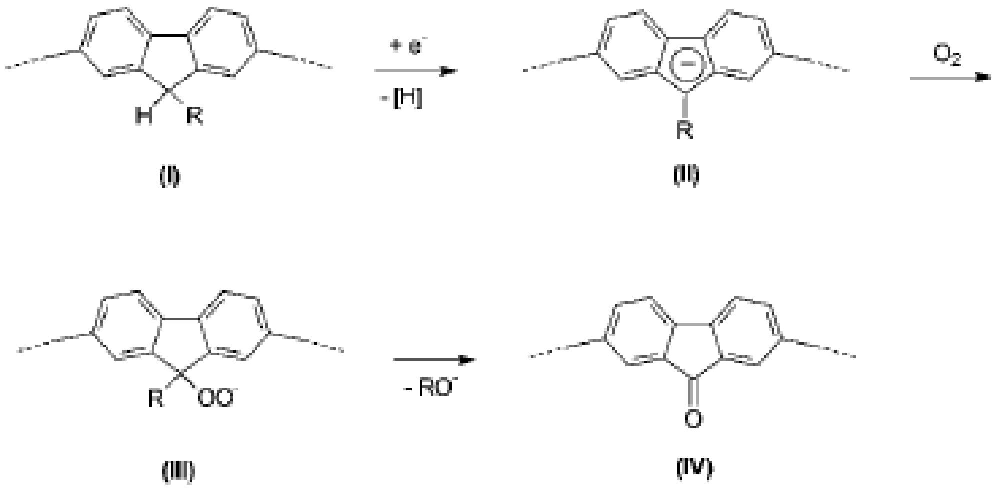


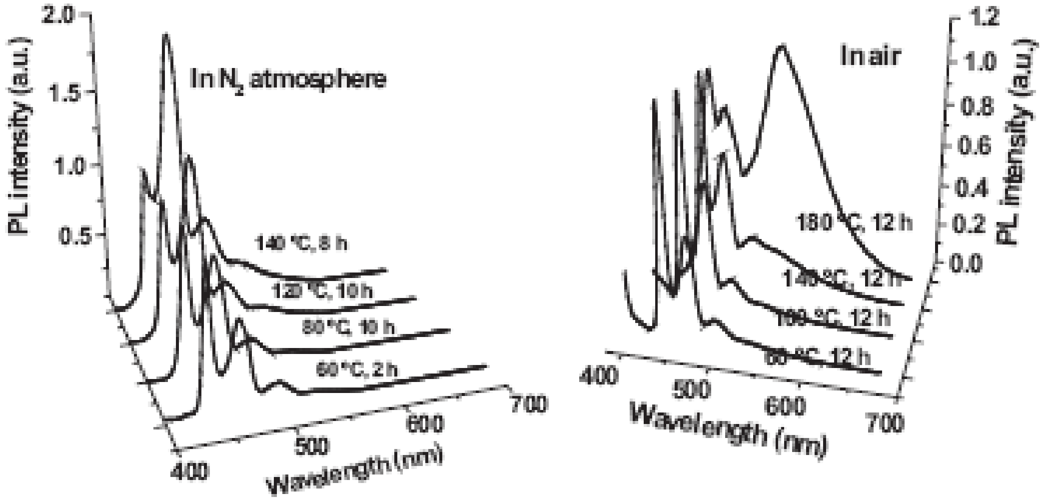
Fig. 4. PL emission spectrum of a pristine PF-b film (solid line), and after photooxidation with a 1000 W xenon lamp under air for 2 min (dashed line), 4 min (dotted line), and 6 min illumination (dash-dotted line).

Sherf et al. *Adv.Mater*.**2002**

- Long wavelength emission after heat treatment, UV irradiation or device operation due to aggregate formation and/or oxidation

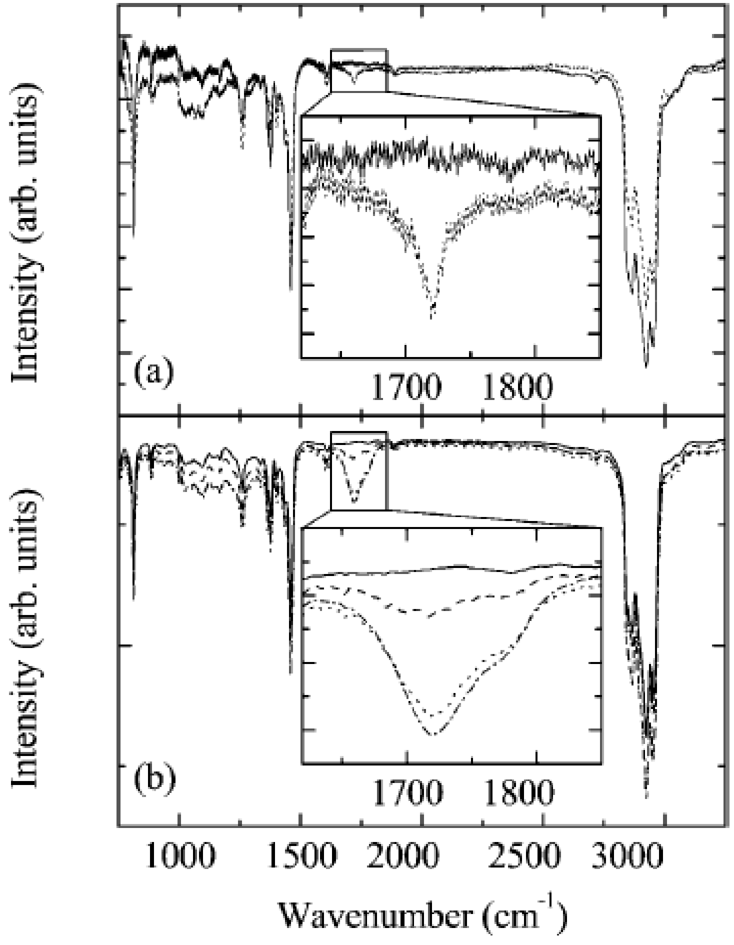
Problem of pure blue emission in PFs :
Excimer and Aggregate formation or fluorenone defect?





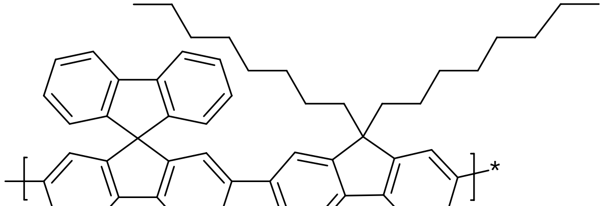
Adv. Funct. Mater., 13, 325, 2003

IR transmission spectra

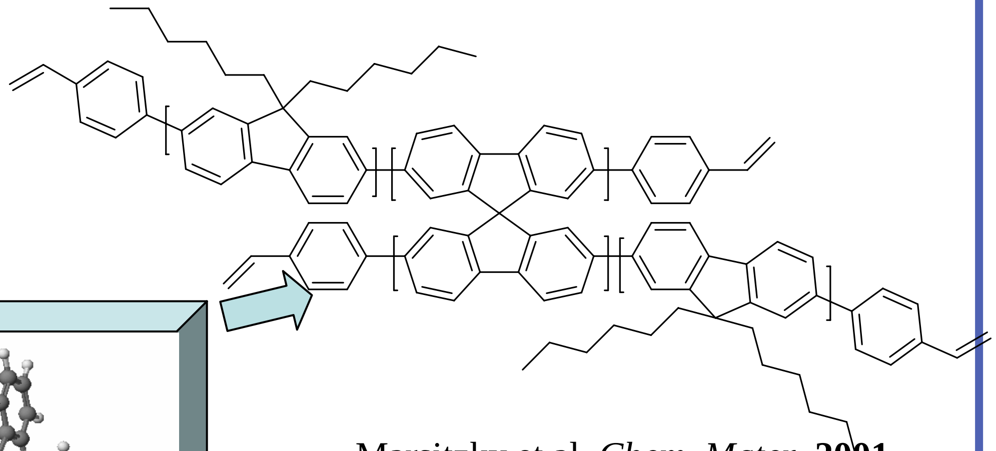


Adv. Mater., 14, 374, 2002

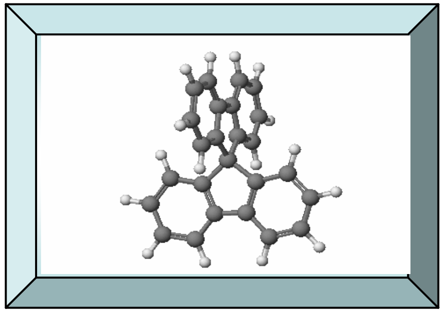
Solution - Spirobifluorene:
- Protect the 9-position and reduce the packing

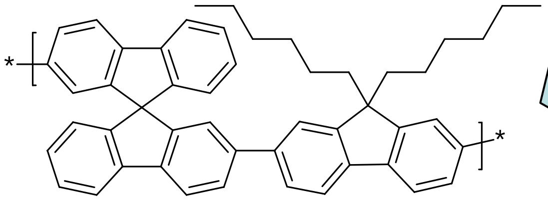


Yu et al. *Adv. Mater.* **2000**

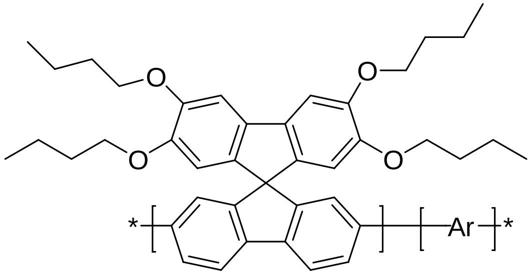


Marsitzky et al. *Chem. Mater.* **2001**





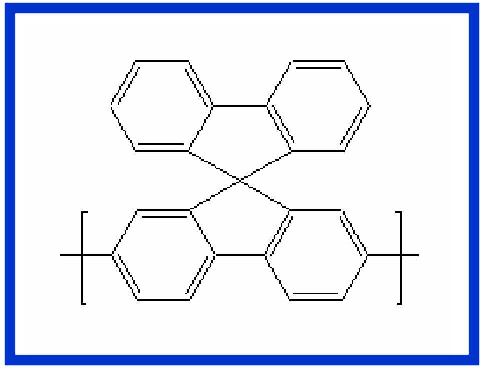
Wu et al. *J. Mater. Chem.* **2002**

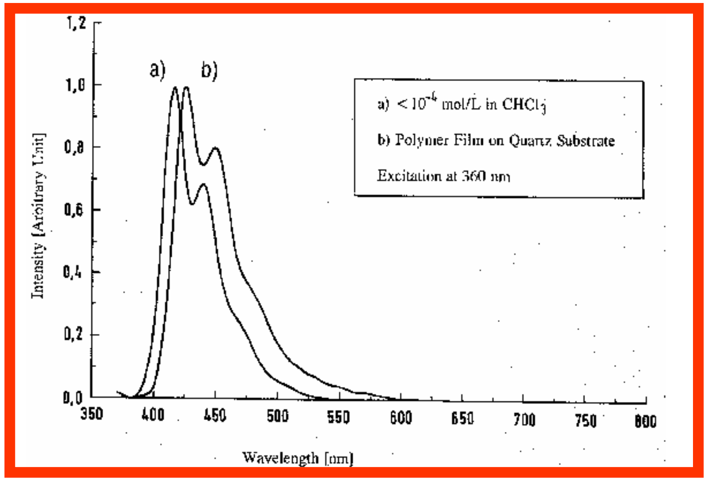


Müller et al. *Nature* **2003**

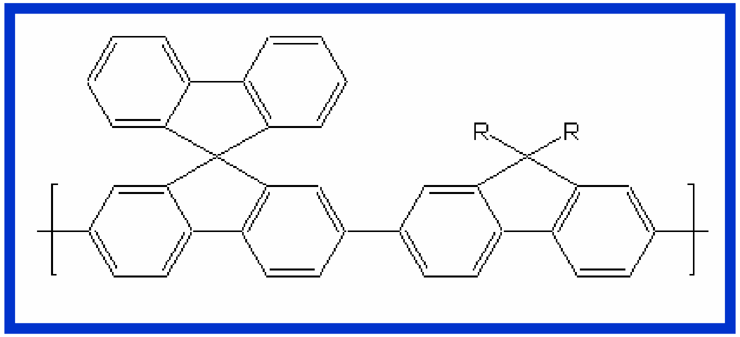
The 3-dimensional spirobifluorene structure can reduce close packing of polymer backbone and can stabilize amorphous state of polymers

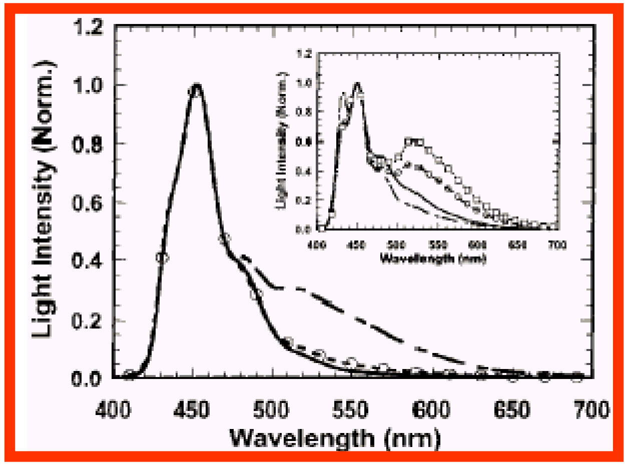
Poly(spirobifluorene)





W. Kreuder, D. Lupo, J. Salbeck, H. Schenk, T. Stchlin, US patent 5,621,131

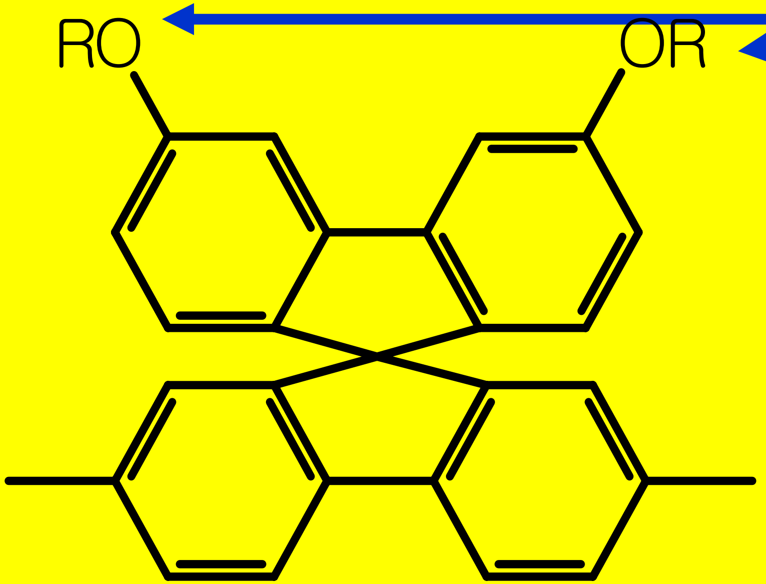




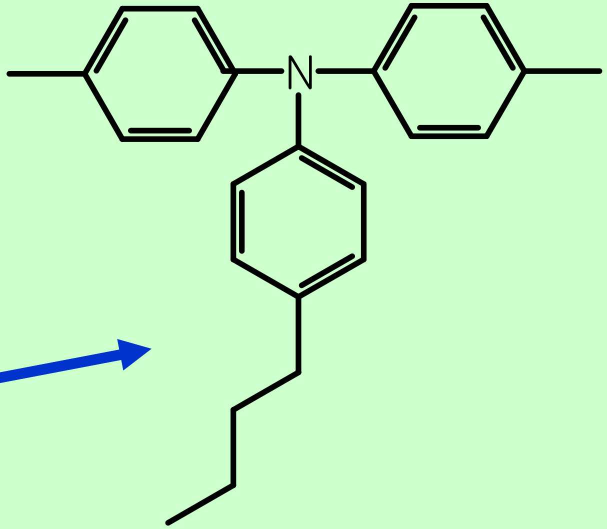
W.-L Yu, J. Pei, W. Huang, A. J. Heeger, Adv. Mater. 2000, 12(11), 828-831

But poor solubility!!!

Soluble Poly(spirobifluorene)

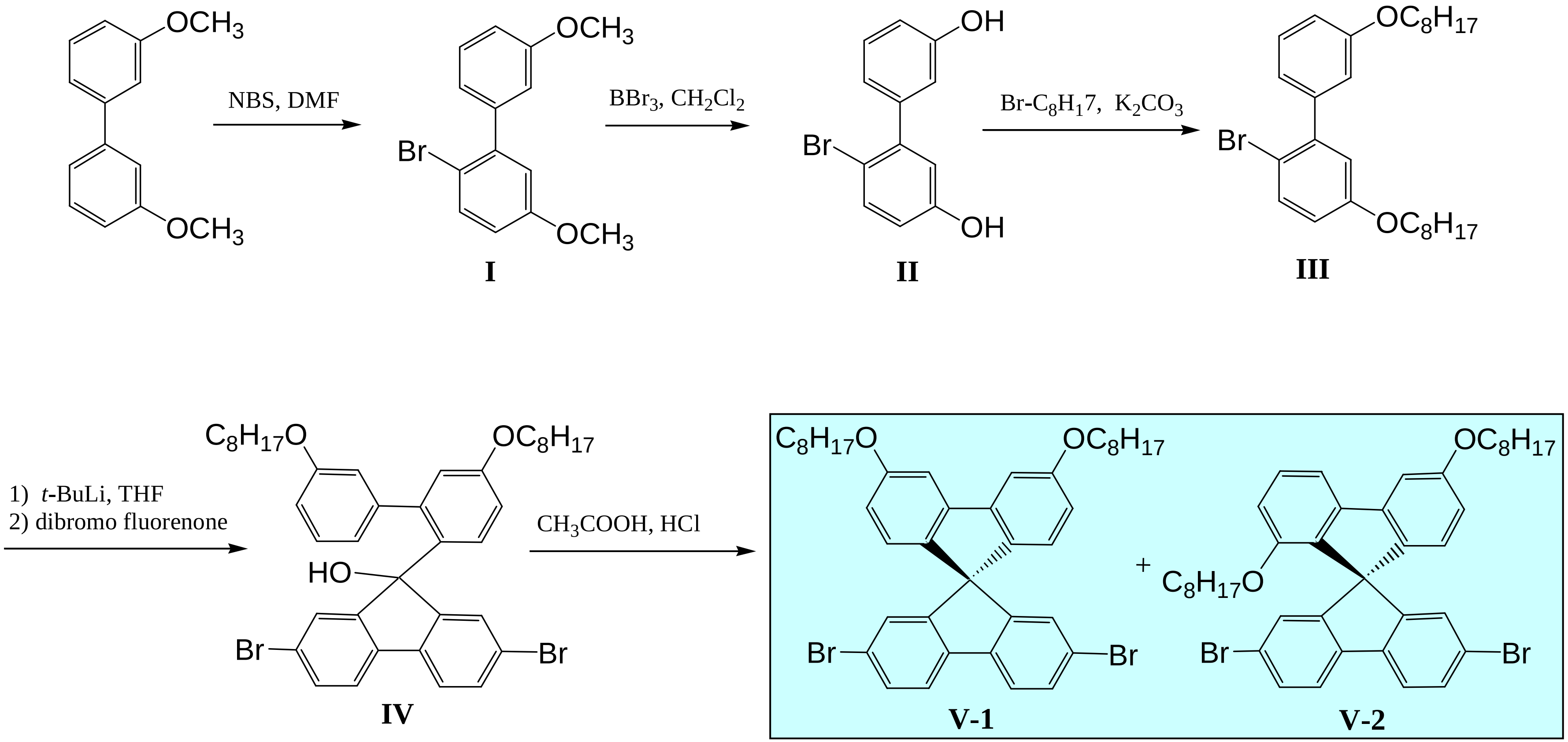


Solubility enhancement



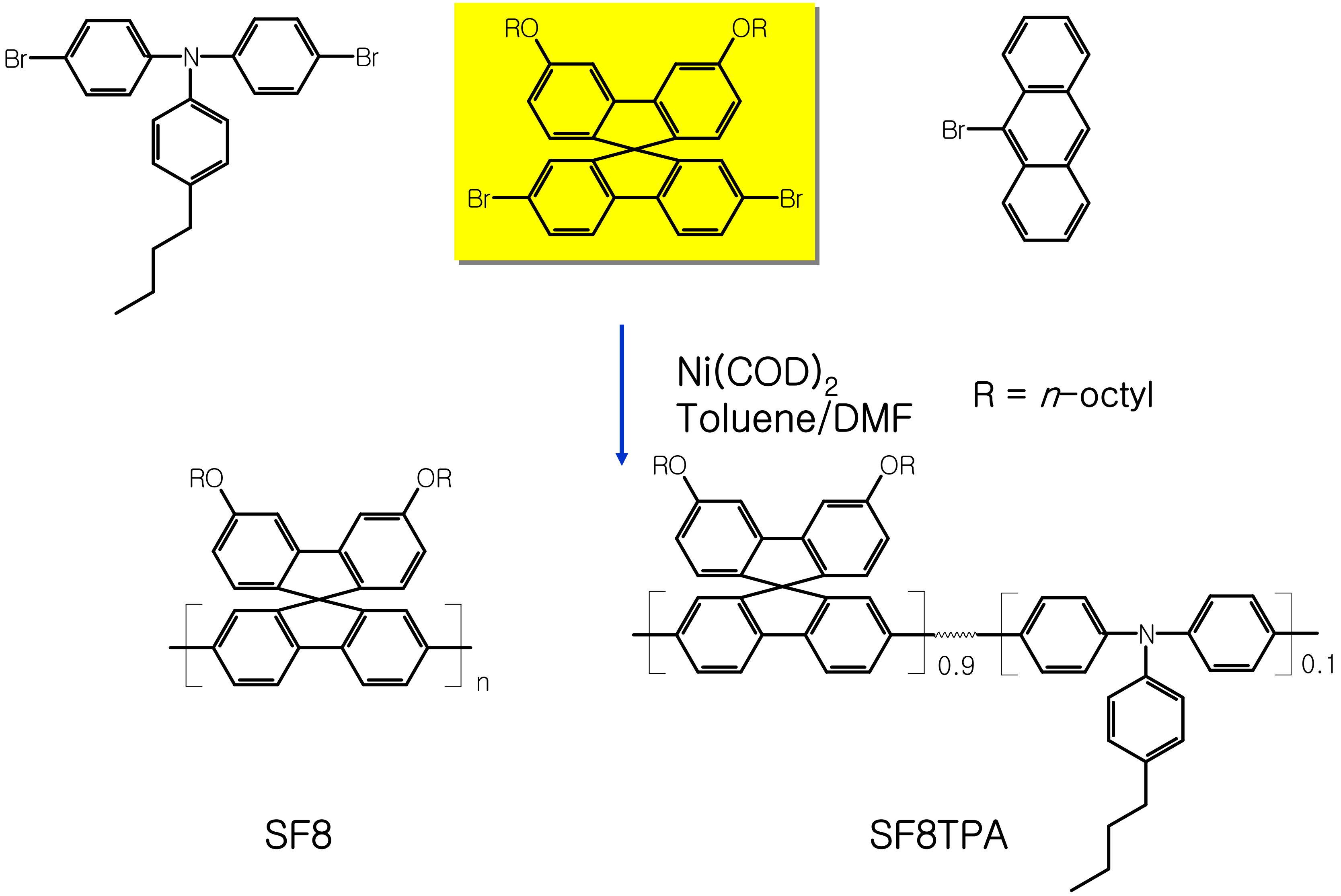
Comonomer for efficiency enhancement

Monomer synthesis



H. Lee et al., *Tetrahedron*, 2003, vol. 59, p 2773

Polymer synthesis



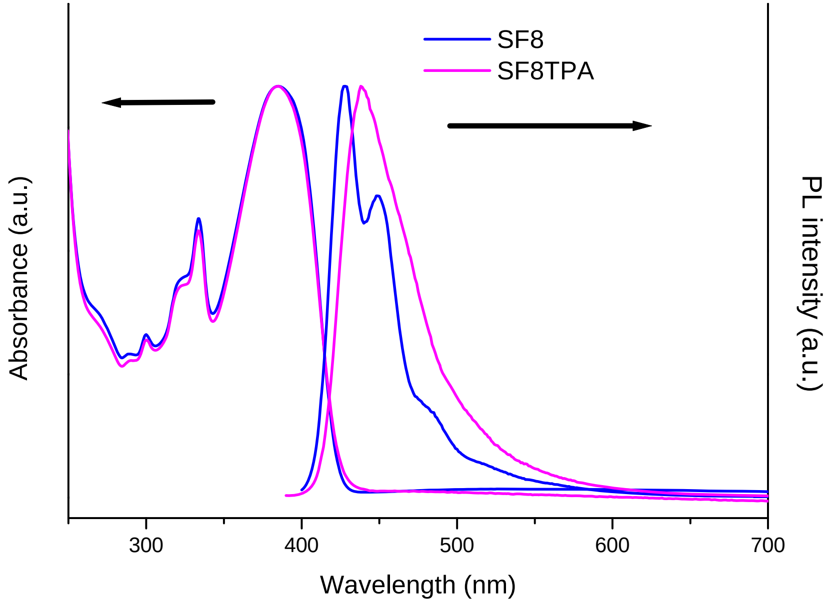
$Ni(COD)_2$
Toluene/DMF

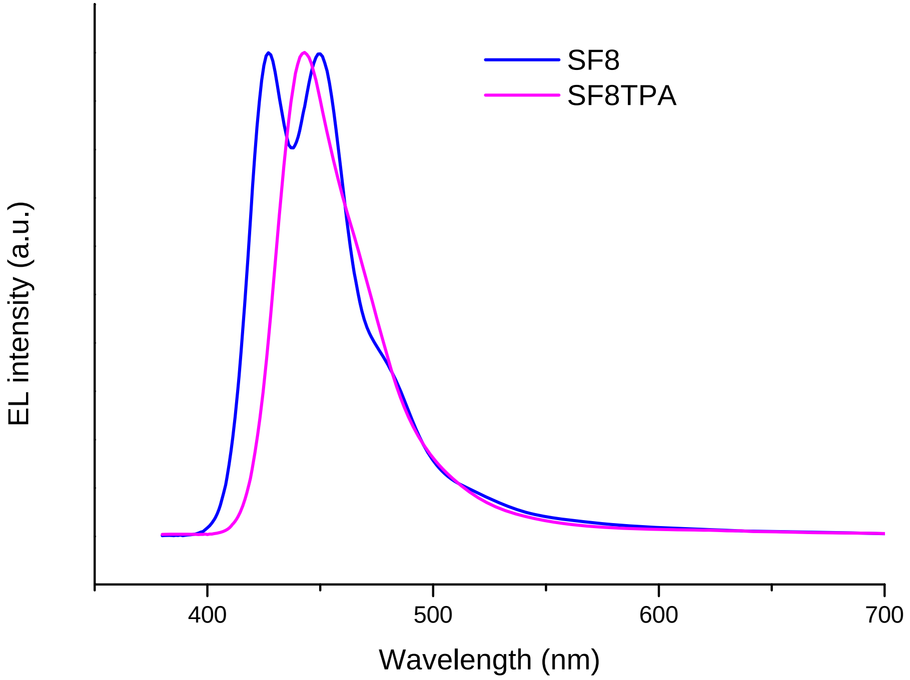
R = *n*-octyl

SF8

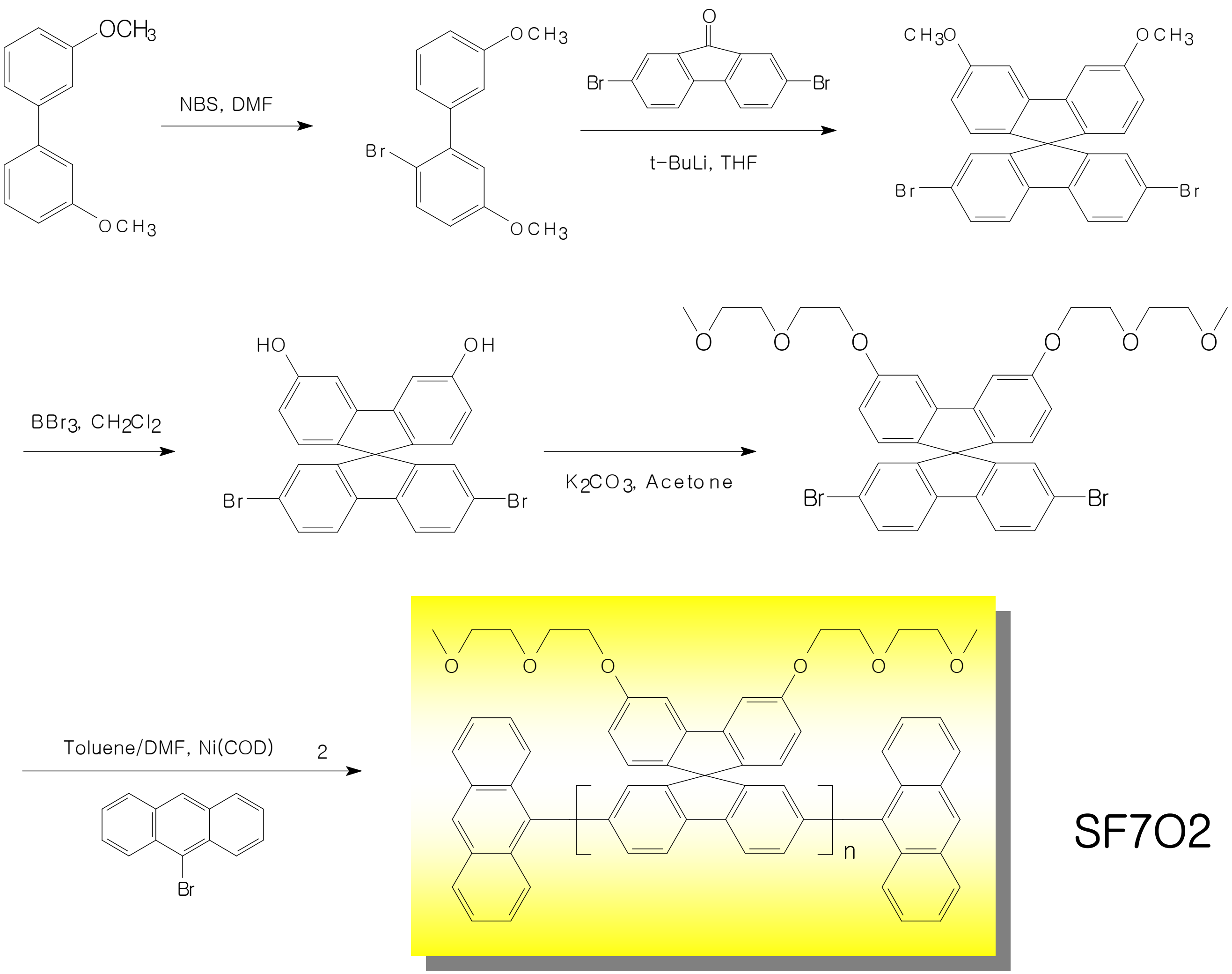
SF8TPA

UV, PL, and EL properties



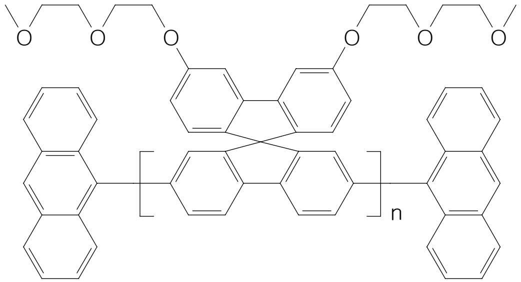


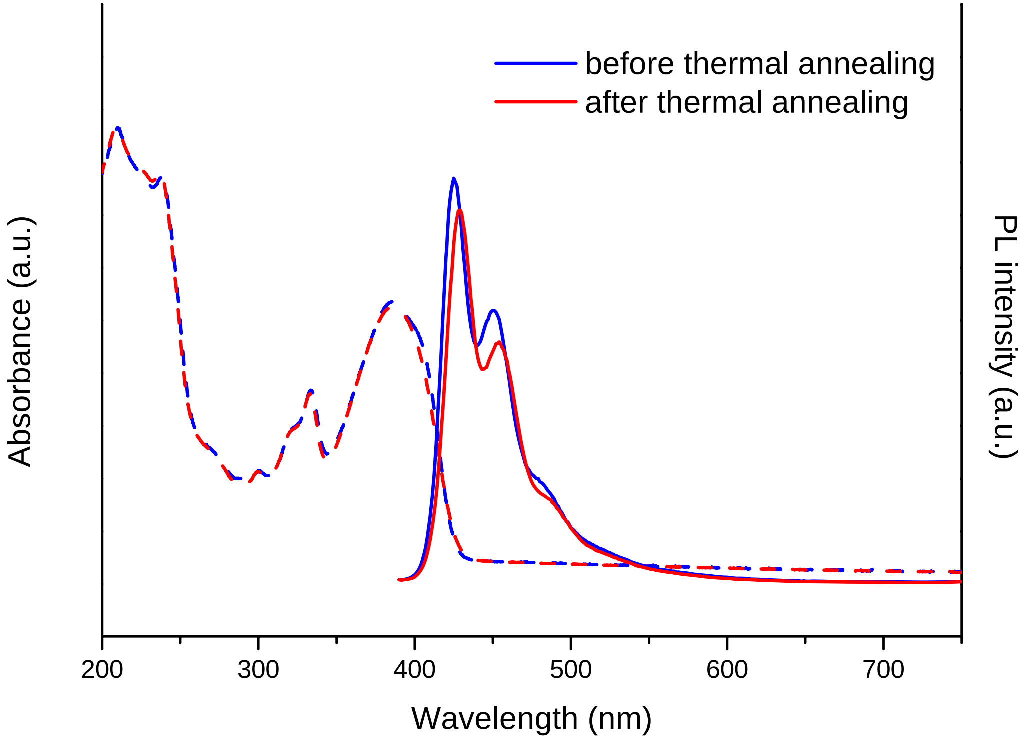
Soluble Poly(spirobifluorene)



SF7O2

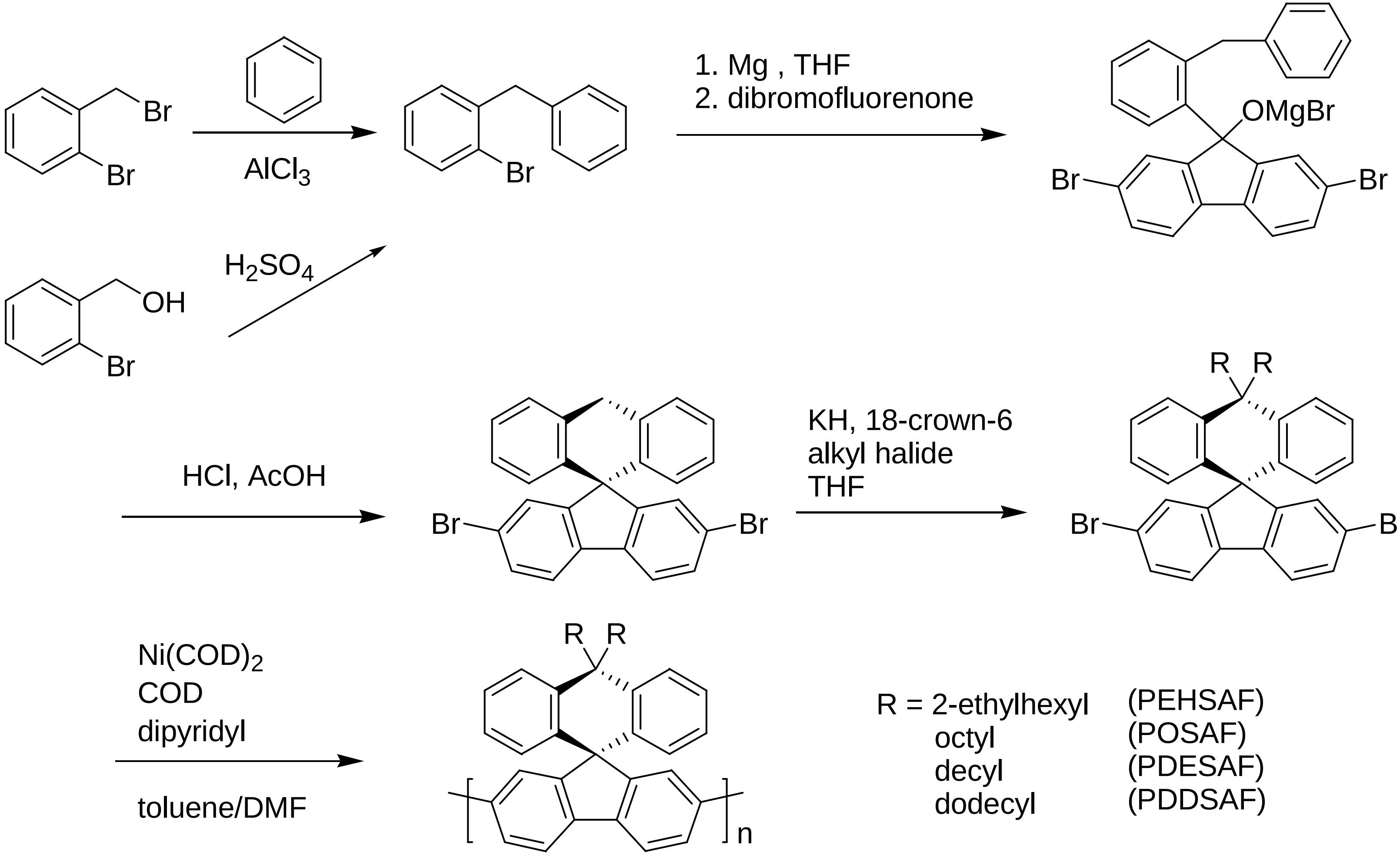
PL spectra with thermal annealing





* Annealing was carried out at 200 ^{o}C under a nitrogen atmosphere for 4 hours

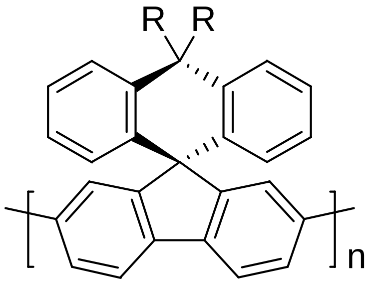
Synthesis of soluble spiro-anthracene PFs



R = 2-ethylhexyl (PEHSAF)
octyl (POSAF)
decyl (PDESAF)
dodecyl (PDDSAF)

J. Mater. Chem., 14, 1342, 2004

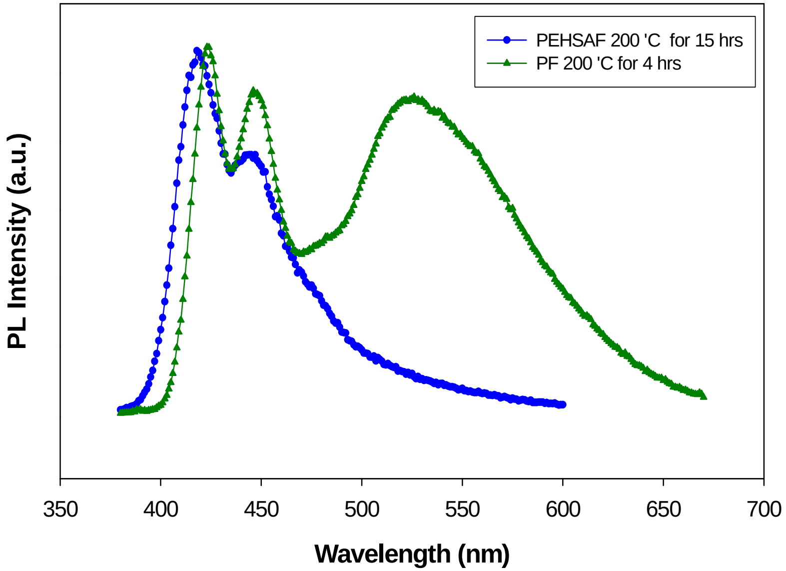
Soluble spiro-anthracene PFs



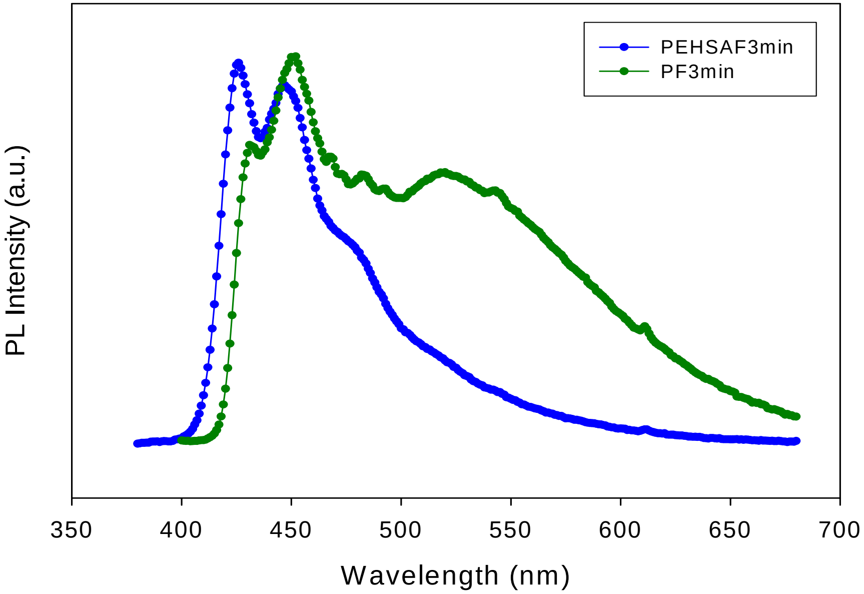
R = 2-ethylhexyl (PEHSAF)
octyl (POSAF)
decyl (PDESAF)
dodecyl (PDDSAF)

Deep-blue

PL Spectra After Heat Treatment



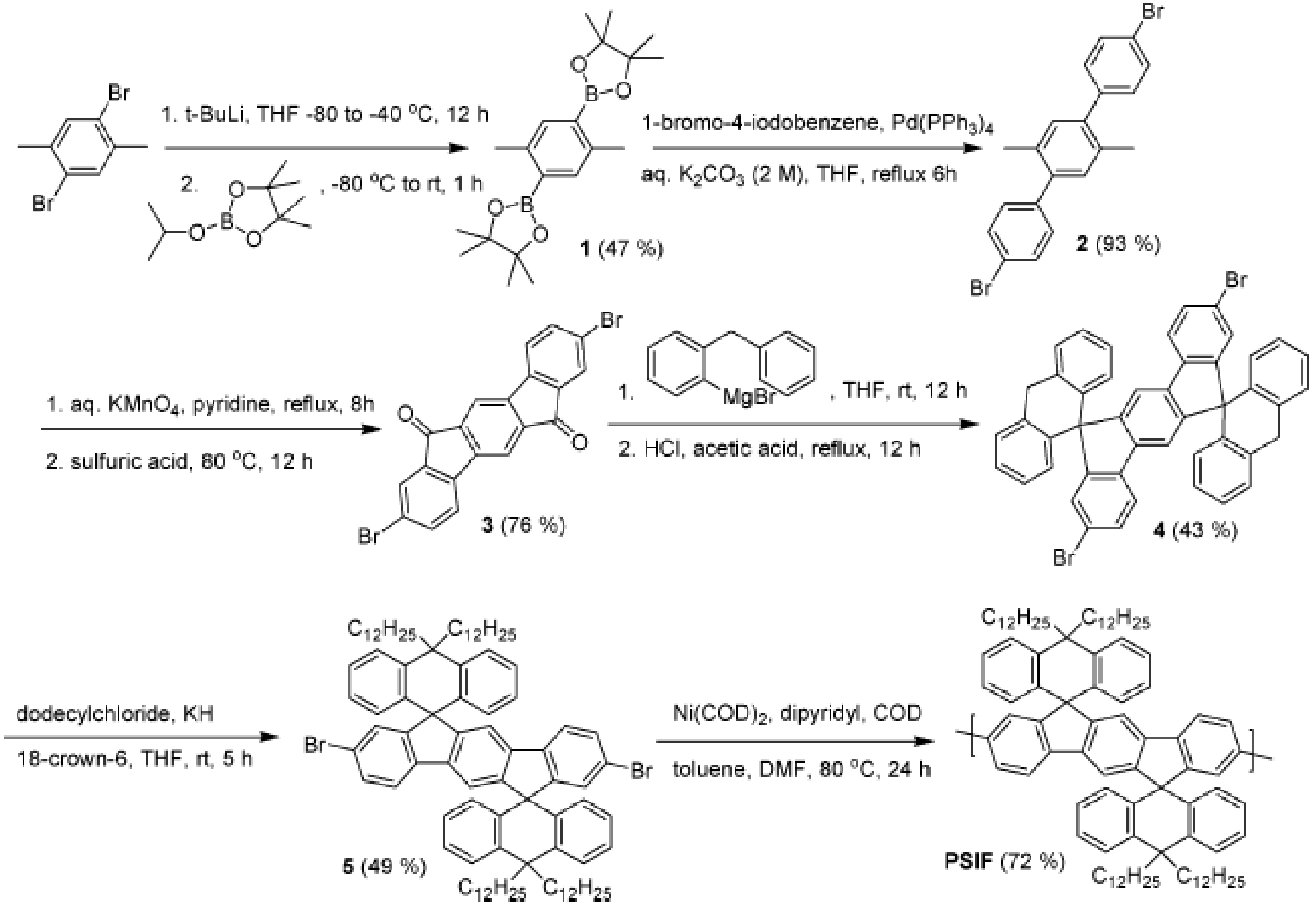
PL Spectra After UV Irradiation



PEHSAF : 10-position of the anthracene allows a facile substitution with alkyl groups for improving the solubility.

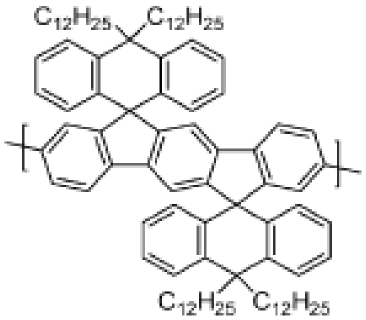
The polymer showed high spectral stability toward heat treatment, UV irradiation.

Spiro-Polyindenofluorene with a Stable Blue Emission



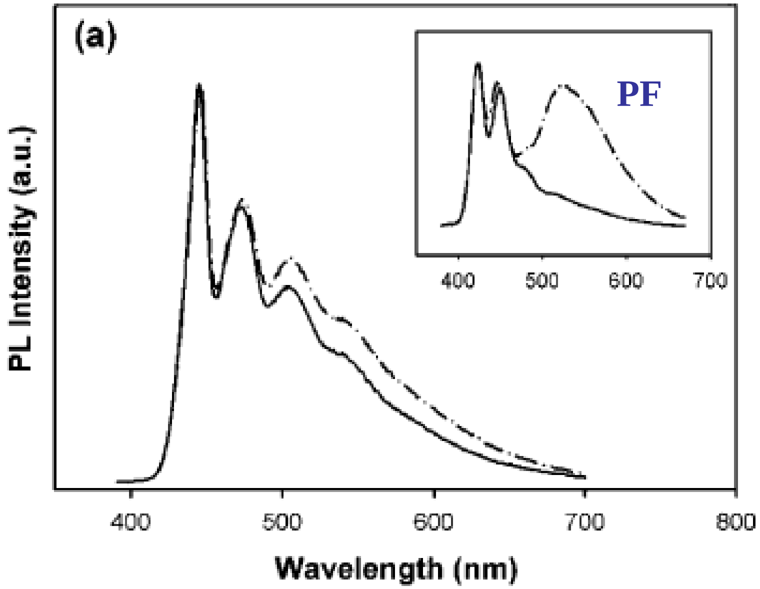
Org. Lett., 7, 4229, 2005

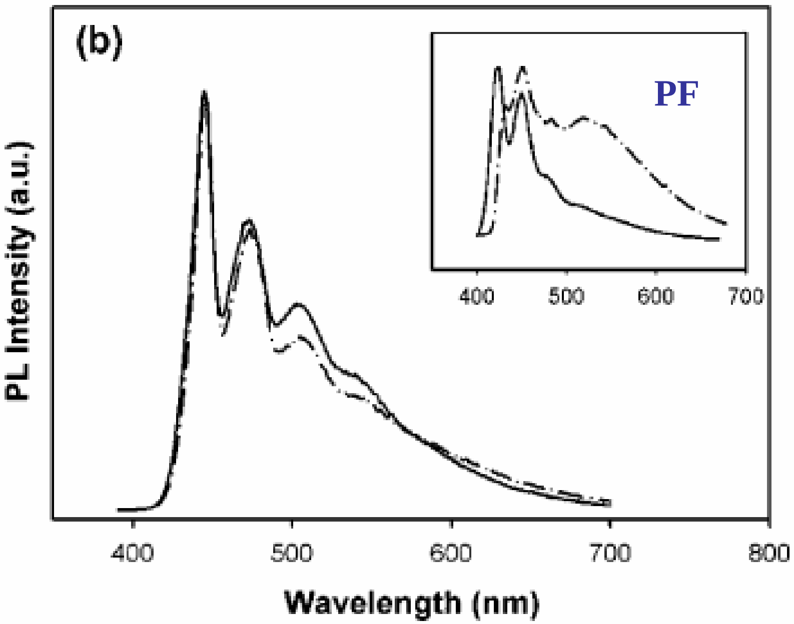
Spiro-Polyindenofluorene with a Stable Blue Emission



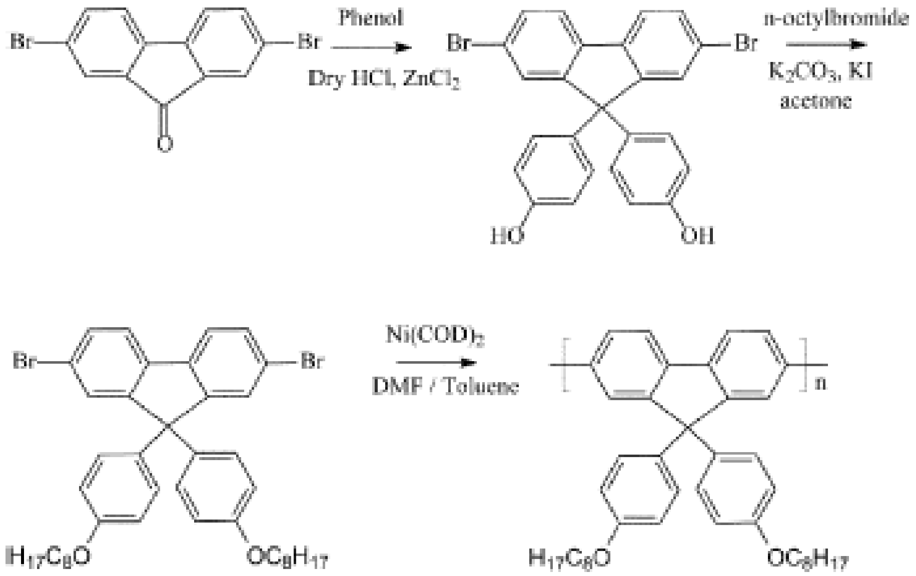
PL Spectra After Heat Treatment

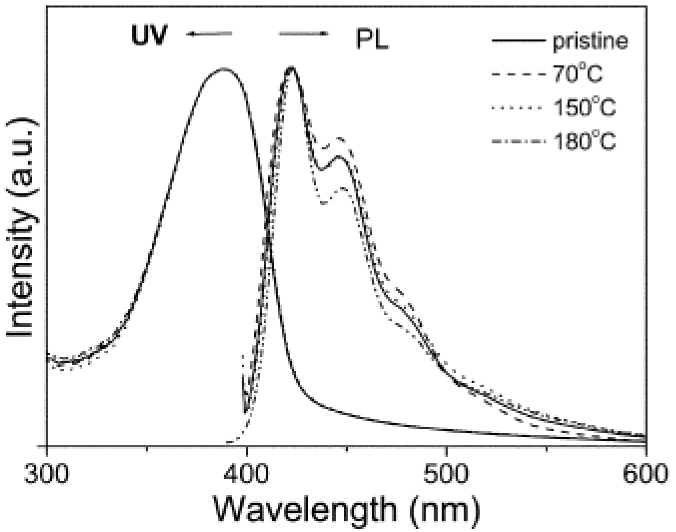
PL Spectra After UV Irradiation





Side-chain modification in PFs



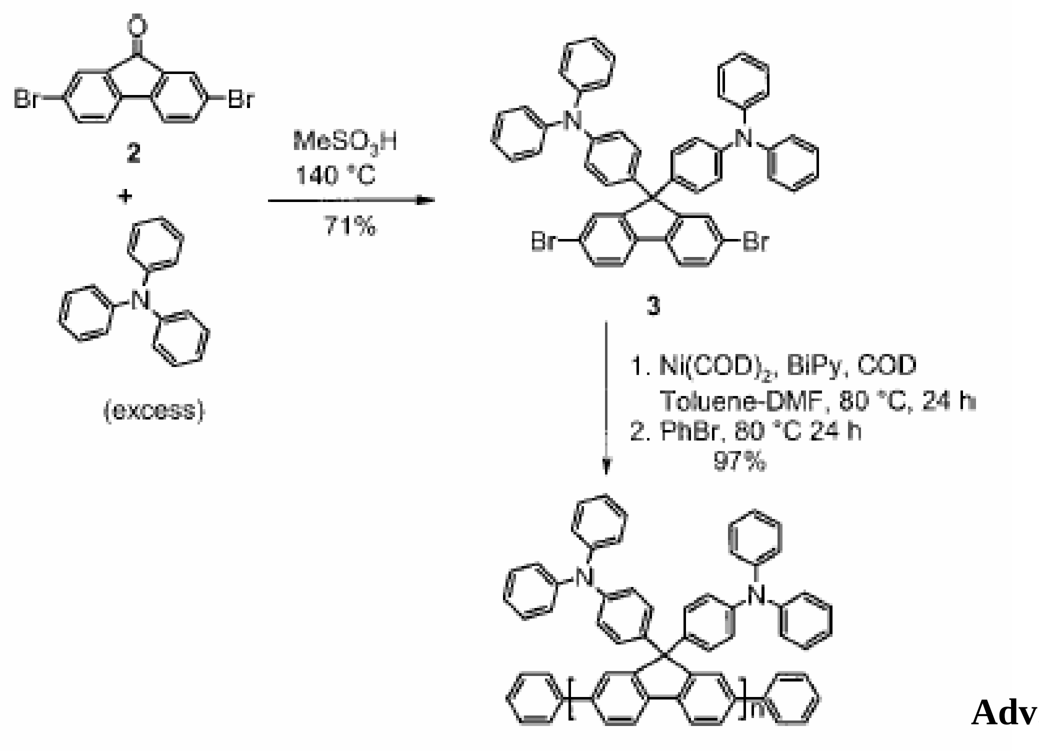


Blue

Chem. Commun., 28, 2836, 2003

This polymer showed bright-blue emission with PL max. in a film at 430 nm. Its emission was found to be very stable toward thermal annealing.

Side-chain modification in PFs



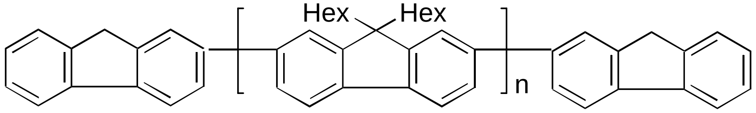
Adv. Mater., 14, 809, 2002

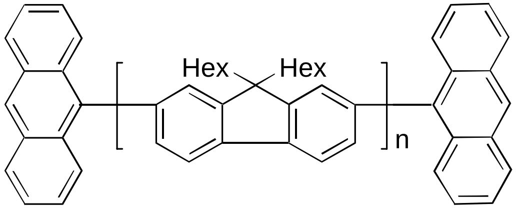
Introduce the triphenylamine groups as side chain at the PF backbone.

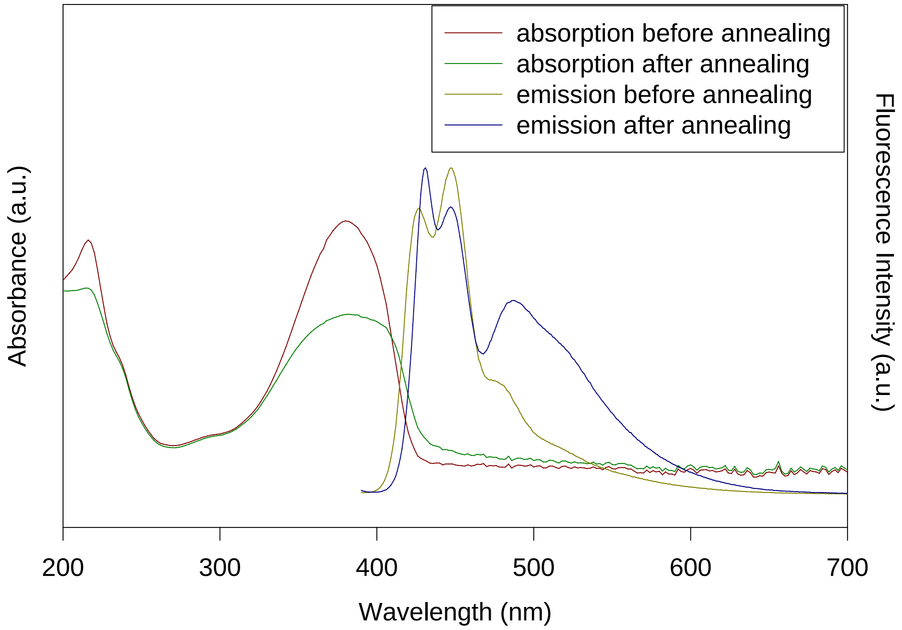
The TPA substituents improve the hole-transport properties of PF, prevent aggregate formation due to steric shielding effect, and bring high solubility to the material.

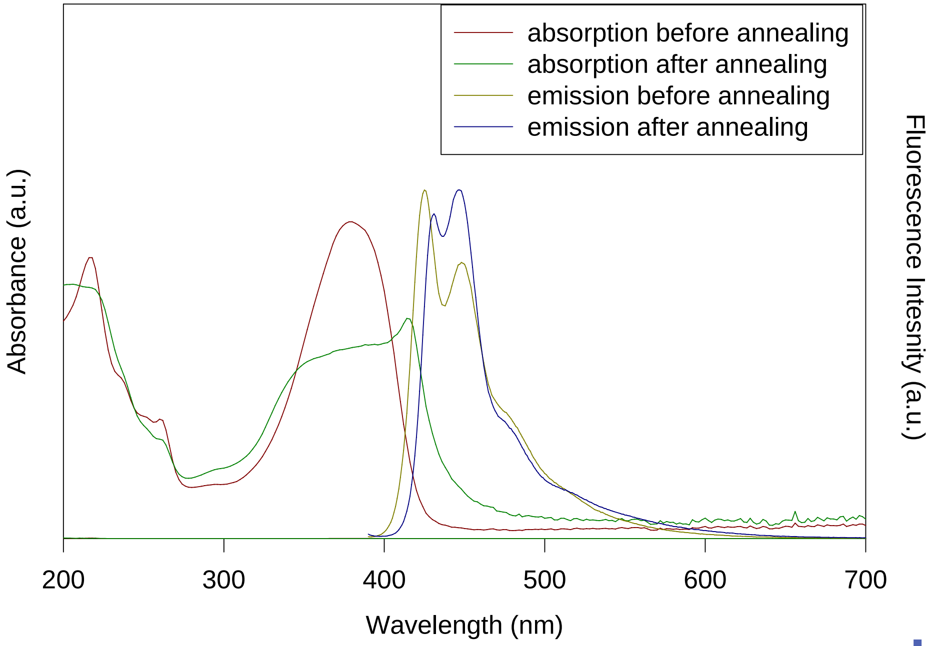
The TPA groups in polymer improve the HT properties and reduce the diode turn-on voltage.

Reduce the aggregation



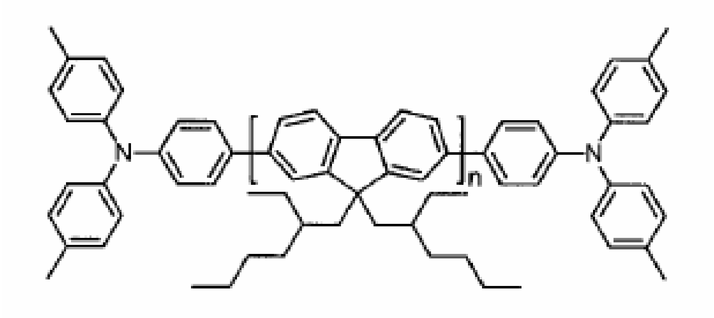




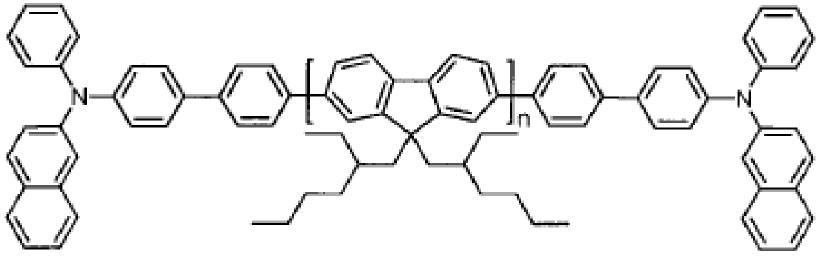


ETRI Journal, Jeong-Ik Lee, V. Y. Lee, Robert D. Miller, 2002, 24, 409.

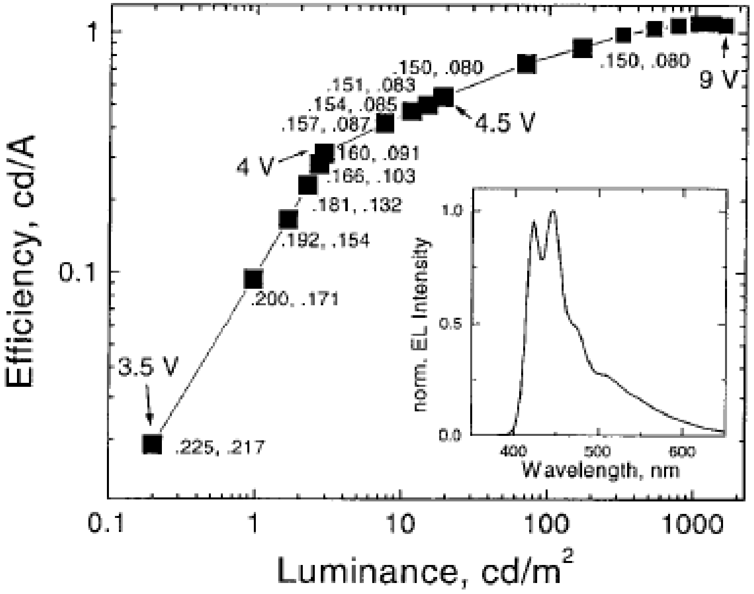
End-capped PFs



1



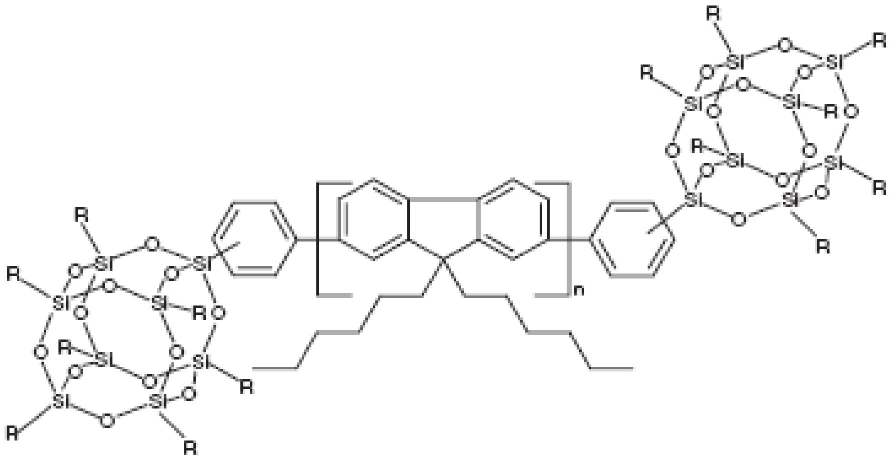
2

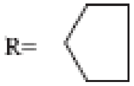


A high-efficiency PLED with excellent color stability has been fabricated with PFs end capped with hole transporting triarylamine moieties.

The parasitic green emission in 1 and 2 was completely suppressed, giving pure blue color (CIE : x = 0.15, y = 0.08) at above 4 V.
This effect can be attributed to less effective e-h recombination on the green-emitting species defect due to competing charge trapping on the hole-transporting units.

Stabilization of Semiconducting Polymers with POSS





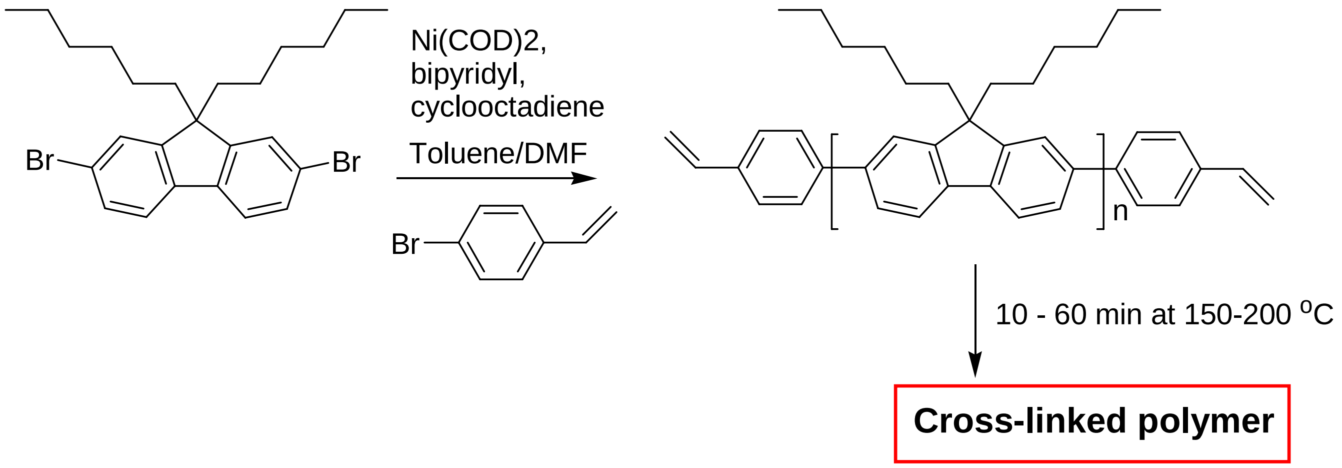
Adv. Funct. Mater., 13, 25, 2003

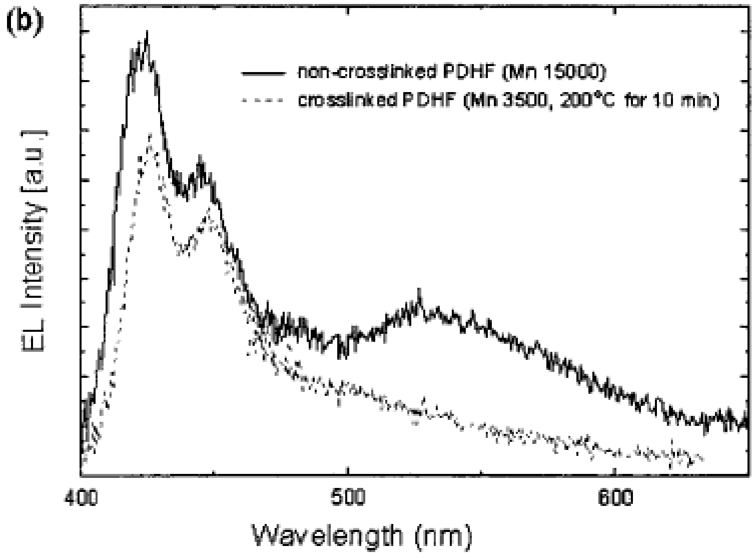
PF capping with a bulky polyhedral oligomeric silsesquioxane (POSS) group.

The hybrid organic-inorganic polymers have several advantages such as increased thermal stability and improved adhesion b/w the substrate and polymer layer.

There is no essential difference in UV and PL b/w POSS-PF and PF, but the PLED device showed increased QE and somewhat improve blue color purity (which still suffered from residual green emission)

Cross-linkable Polymers Based on Dialkylfluorenes





Chem. Mater., 11, 1800, 1999

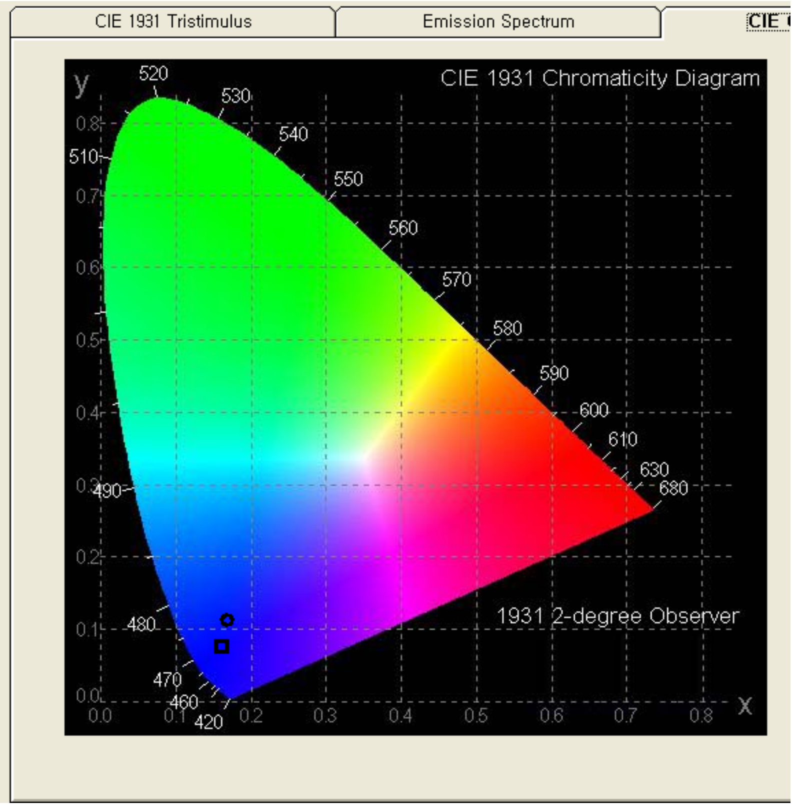
The cross-linking during thermal annealing of the file render an insoluble material, which can be used as a substrate for spin casting the next layer in multilayer LEDs.

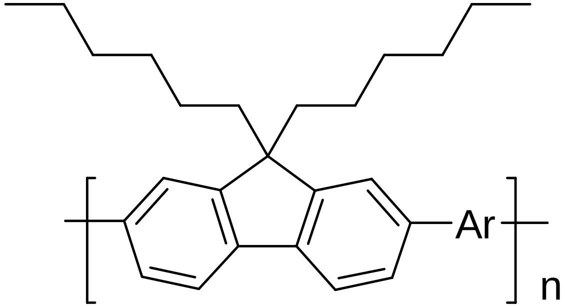
In addition, X-linking drastically increases the T_g, thus suppressing the formation of aggregates and giving pure blue emission.

Emitting Materials III

- Poly(fluorene) (PF) II-copolymers

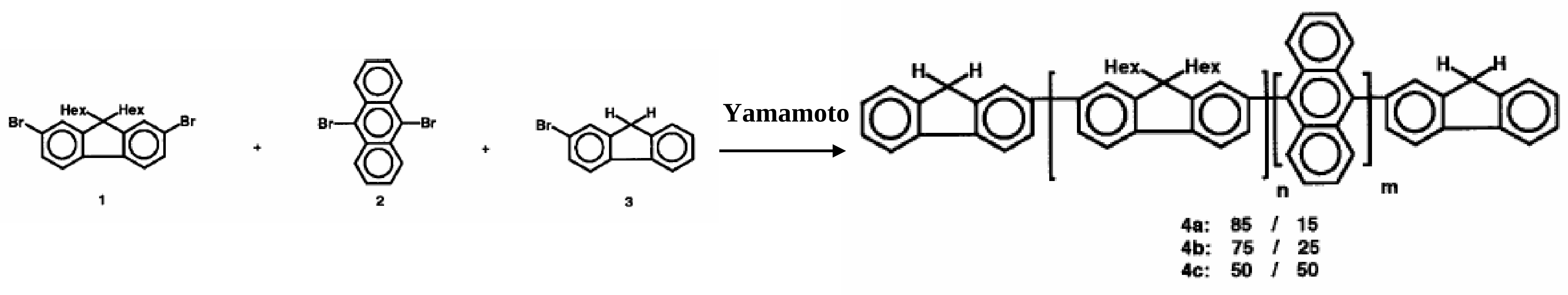
& color tuning in PF copolymers





Red (0.68, 0.32) Green (0.28, 0.60) Blue (0.15, 0.07)

Fluorene-anthracene copolymers



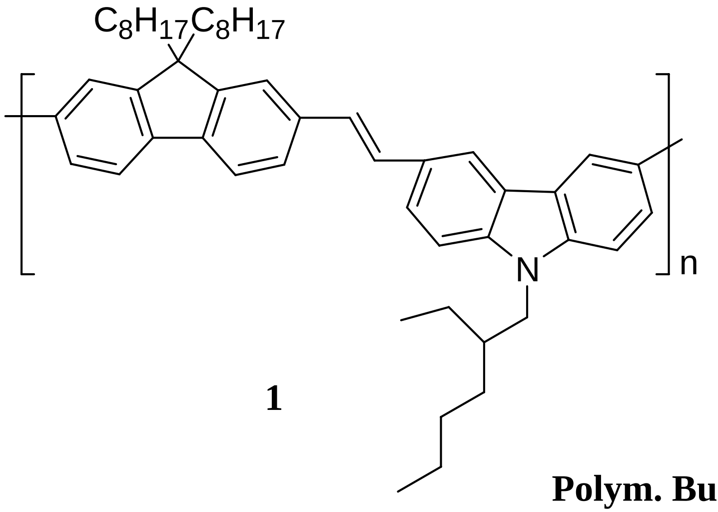
Adv. Mater., 10, 993, 1998

Copolymerization of fluorene with other highly luminescent materials offers a possibility of fine-tuning the emitting and charge-transport properties of PF.

Random fluorene-anthracene copolymers, which showed high MW (M_n = 73,000 – 89,000), good thermal stability (T_d>400 ℃), high T_g(=135~139 ℃), and a high QE of PL (53~76 % in films).

An increased stability of blue emission (for 4a even after annealing at 200 ℃ for 3 days) was explained in terms of preventing excimer formation due to incorporation of anthracene units that are orthogonal to the plane of the fluorenes in the backbone, although this can also be an effect of diminishing exciton migration toward fluorene defects.

Fluorene-carbazole copolymers



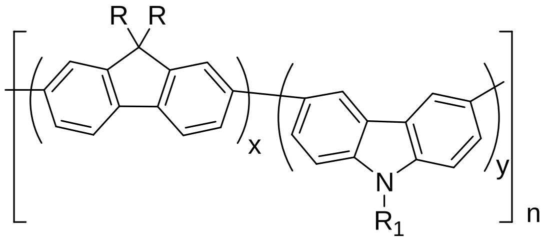
1

Polym. Bull., 38, 169, 1997

Carbazole has higher HOMO than fluorene, and many of its oligomers and polymers are good hole-transporting materials, so such copolymers could improve the HT properties.

Copolymer 1 was reported one of the first alternating fluorene-carbazole polymers, synthesized by Wittig reaction of 3,6-dialdehyde carbazole with the corresponding 2,7-bis(trithenylmethylenephosphonium)fluorene salt.

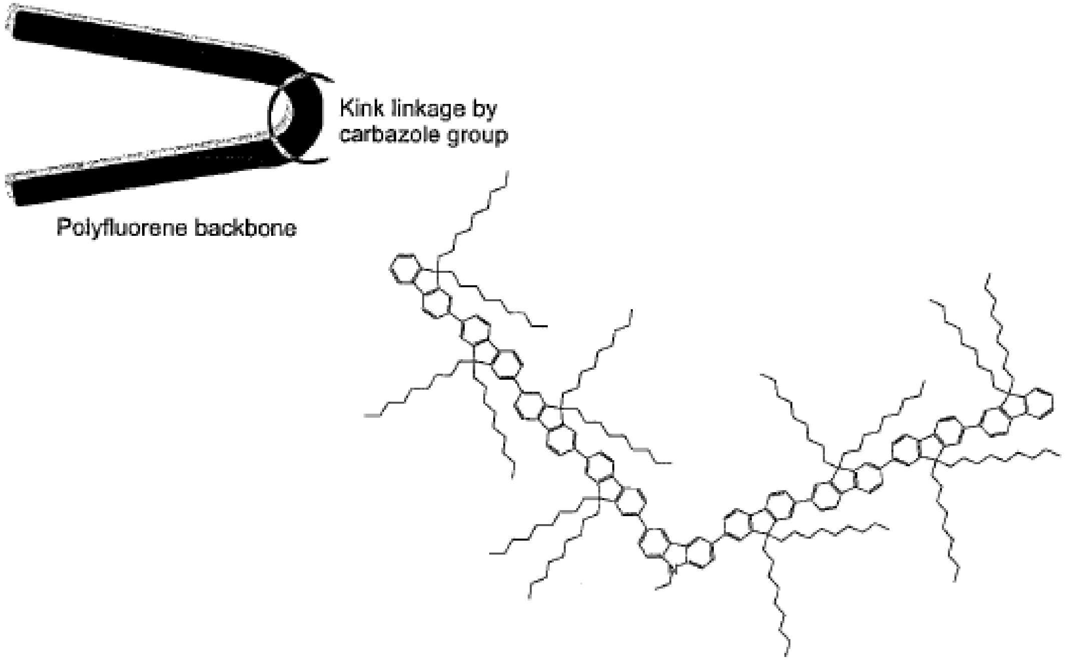
Fluorene-carbazole copolymers



1 - R=C_6H_{13}, R_1=C_6H_{13}, x:y=4:1
2 - R=C_6H_{13}, R_1=C_6H_{13}, x:y=1:4
Synth. Met., 106, 115, 1999

3 - R=C_8H_{17}, R_1=C_2H_5, x:y=9:1
4 - R=C_8H_{17}, R_1=C_2H_5, x:y=7:3

Macromolecules, 34, 5854, 2001

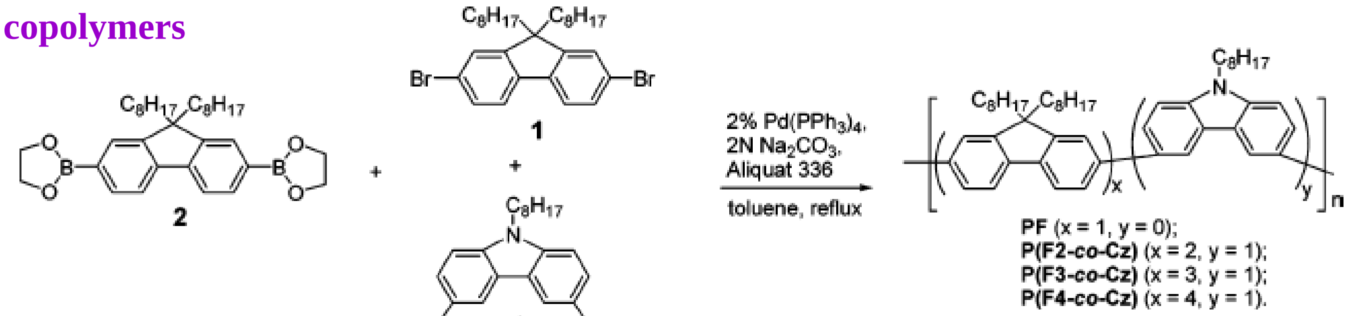


The PL spectrum of polymer 1 is identical to that of the corresponding fluorene homo-polymer and increasing the amount of carbazole (from 1:4 to 4:1 - 2) only results in decreasing emission intensity.

Copolymers 3, 4 synthesized by Yamamoto coupling have much higher MW. Carbazole units in the backbone of the copolymers do not change emission in both solution and solid state, which corresponds well to that of PFO homopolymer, but increase the solid-state QE of PL and improve the PL color stability toward thermal annealing. This was attributed to a disorder in the polymer chain, brought about by carbazole units-3,6-linking.

Effect of regularity in fluorene-carbazole copolymers

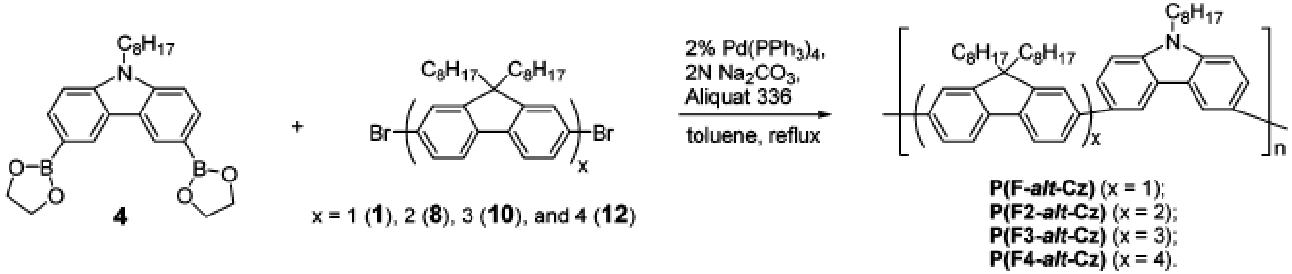
Random copolymers



1

Alternating copolymers

Chem. Mater, 16, 2165, 2004



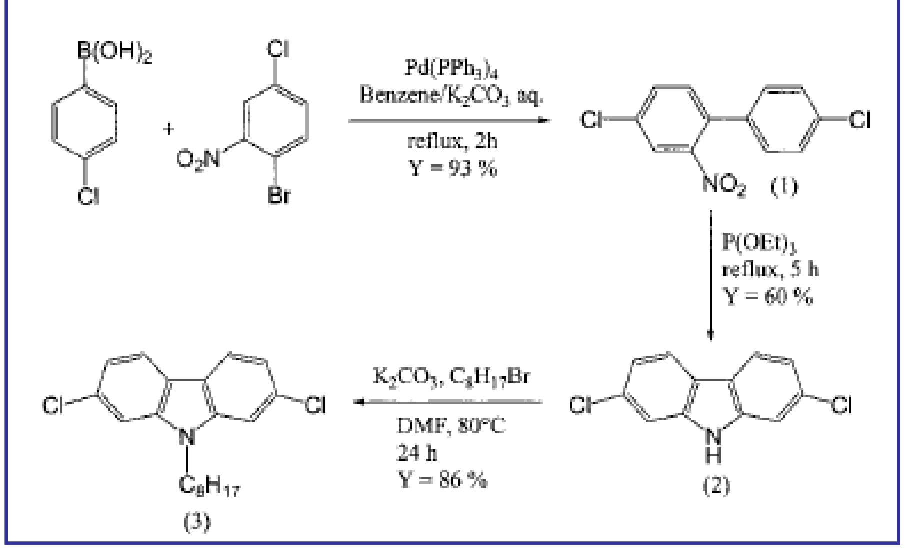
2

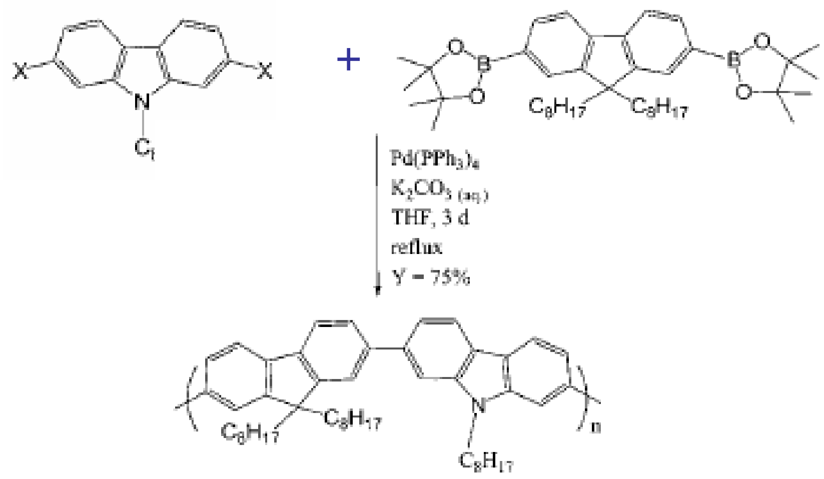
Both random and alternating copolymers showed progressive blue shifts in absorption with increasing carbazole content. A similar blue shift was observed in PL for copolymers 2 but all random copolymers 1 showed almost identical PL spectra, similar to that for PFO.

This difference b/w the 1 and 2 copolymers was attributed to the longer fluorene sequences (> 5 fluorene units) in random copolymers and migration of the excitons to these segments where the emission occurs.

Fully conjugated system in fluorene-carbazole copolymers

Synthesis of 2,7-carbazole





1

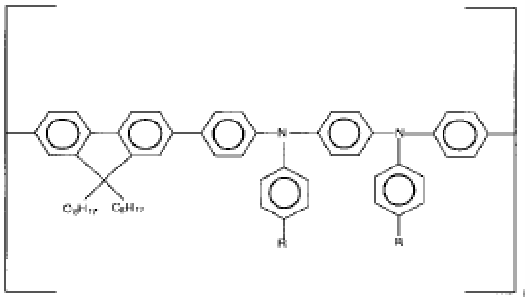
Macromolecules, 34, 4680, 2001

Mario Leclerc's group in Canada first synthesized PF copolymer based on 2,7-carbazole units that is a fully conjugated system.

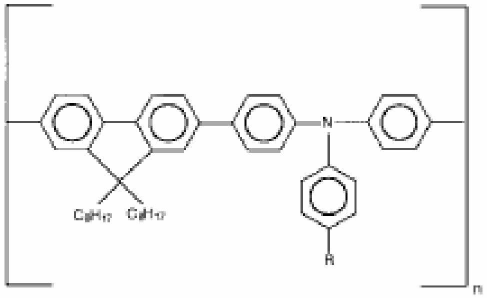
Just as in 3,6-carbazole based copolymers, 2,7-carbazole based copolymers 1 showed absorption and PL spectra similar to those of PFO, with almost the same PL QE.

However, there was no sign of the green emission band in 1 after thermal annealing.

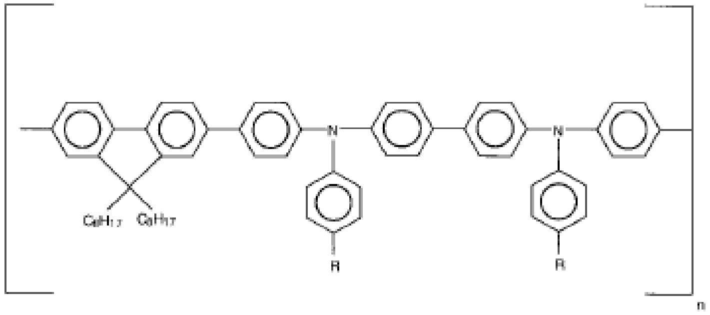
Fluorene-triarylamine copolymers



PFB: R = C_4H_9 ,
PFM: R = CH_3
PFMO: R = OCH_3



TFB: R = C_4H_9



BFB: R = C_4H_9

Adv. Mater, 11, 241, 1999

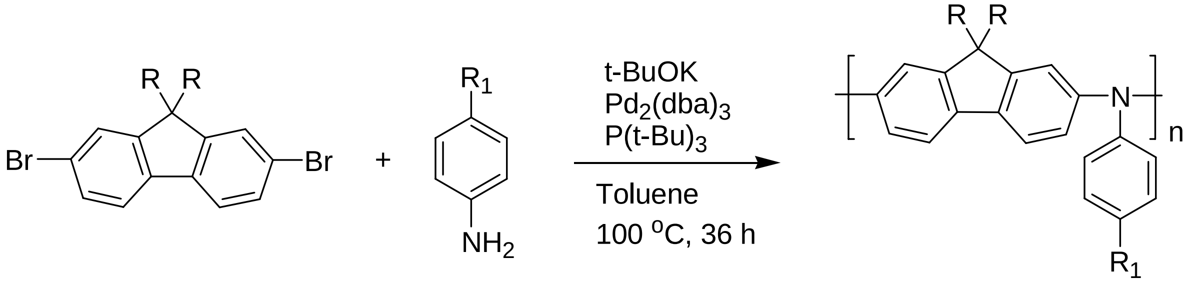
Copolymerization of fluorene with triarylamine compounds was shown to increase the hole-transport properties of the polymers.

Several copolymers of triarylamine and fluorene synthesized by Suzuki coupling were reported by Bradley et al.

The hole's mobility of the copolymers was in the range of 3 x 10^{-4} cm^2/Vs to 3 x 10^{-3} cm^2/Vs, and the IP was as low as 5.0-5.3 eV (cf. 5.8 eV for PFO), which is well-matched with the work function of the ITO/PEDOT electrode.

Unfortunately, no PL or EL properties have been reported in the paper.

Fluorene-triarylamine copolymers



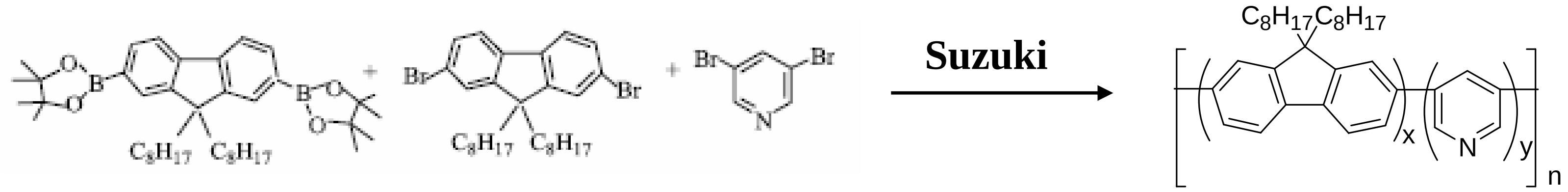
Macromolecules, 35, 2282, 2002

Molecular triarylamine-based hole-transporting materials are usually synthesized by Ulmann-coupling or Pd-catalyzed amination, although polymerization using these reactions is difficult.

Shim and coworkers reported successful Pd-catalyzed copolymerization of dibromo fluorene derivatives with anilines and obtained thermally stable, reasonably high MW (Mn=12,300-14,000) copolymers.

The HOMO levels of these copolymers (ca. -5.1 eV) matched well with ITO anode. The LEDs consisting of these polymers as buffer layer demonstrated a lower turn-on voltage, enhanced efficiency, and higher maximum luminance due to improved hole injection.

Fluorene-pyridine copolymers



Polymer, 45, 865, 2004

1 - x:y=95:5, Abs : 380 nm, PL : 422 nm, EL : 446 nm
2 - x:y=90:10, Abs : 383 nm, PL : 422 nm, EL : 442 nm
3 - x:y=80:20, Abs : 380 nm, PL : 422 nm, EL : 442 nm
4 - x:y=70:30, Abs : 370 nm, PL : 420 nm, EL : 438 nm
5 - x:y=60:40, Abs : 380 nm, PL : 419 nm, EL : 440 nm
6 - x:y=50:50, Abs : 350 nm, PL : 413 nm, EL : 424 nm

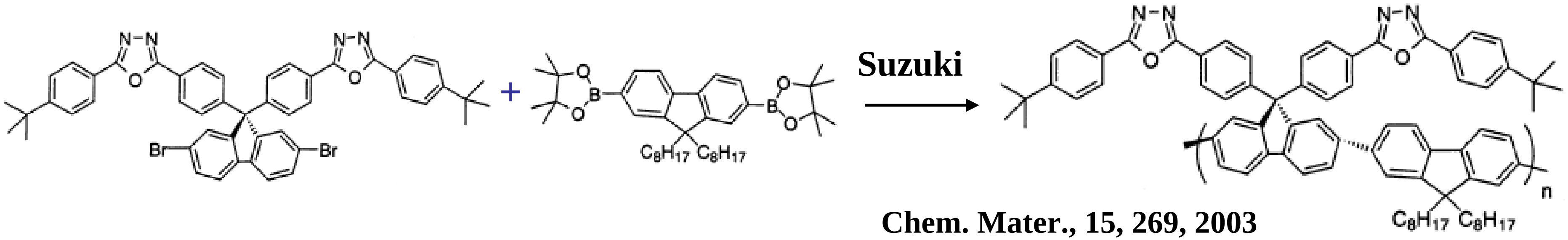
A series of random fluorene-pyridine copolymers have been prepared by Suzuki coupling of fluorene with 3,5-dibromopyridine.

The *meta*-linkage of the pyridine units is expected to interrupt conjugation but no regular spectral dependence was observed for different pyridine loadings.

PL spectra for all copolymers are very close, expect for 6, for which the PL and EL spectra are shifted by ~10-20 nm, compared to other copolymers.

All materials (expect 6) showed narrow, pure blue EL emission and turn-on voltage of 5-6 V.

Fluorene-oxadiazole copolymers



Chem. Mater., 15, 269, 2003

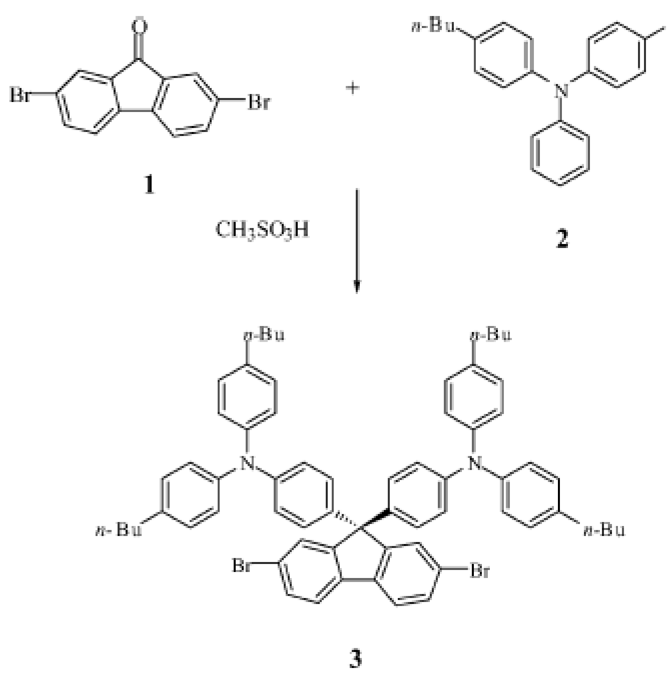
The introduction of oxadiazole units into the PF can potentially improve the electron transport properties of the polymers, while their bulkiness can help to suppress aggregation effects.

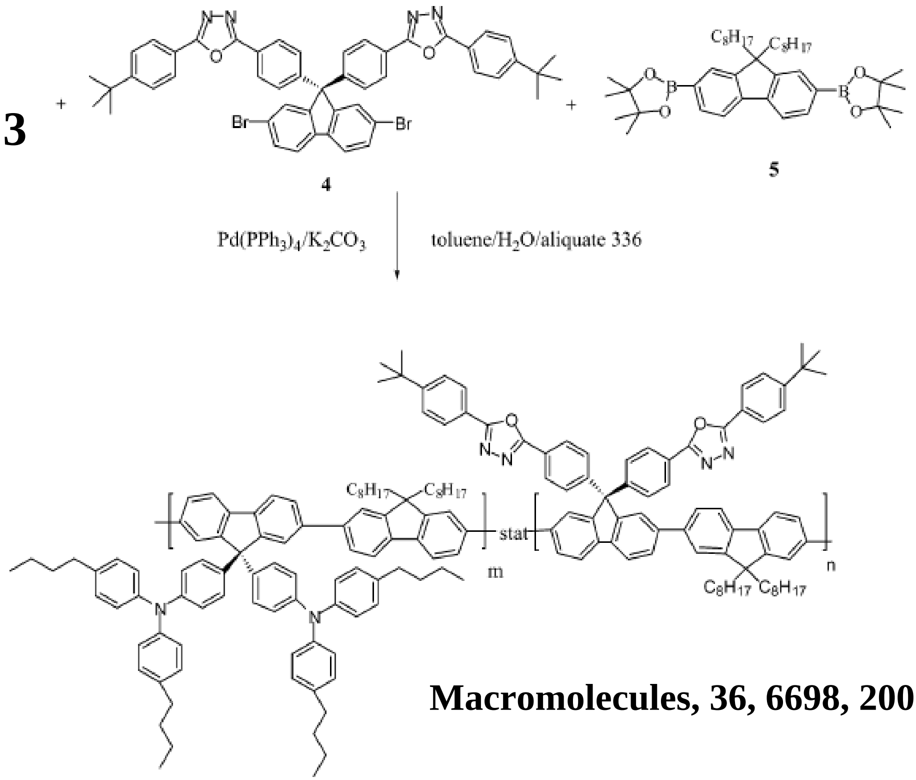
The polymer possessed excellent thermal stability and electrochemically determined HOMO-LUMO levels were -5.76 and -2.47 eV, which are similar to those of PFO(-5.8 and -2.6 eV), with only slightly improved electron affinity.

The absorption spectrum in THF solution showed two major peaks at 297 and 390 nm, the former peak is attributed to the aromatic oxadiazole group and the latter to the π-π* transition of the polymer backbone.

There is essentially no influence of the attached oxadiazole on the conjugated backbone: the PL spectrum displays a blue emission with two sharp peaks at 419 and 444 nm, and a small shoulder at 469 nm, very similar to PFO

Fluorene-oxadiazole-triarylamine copolymers



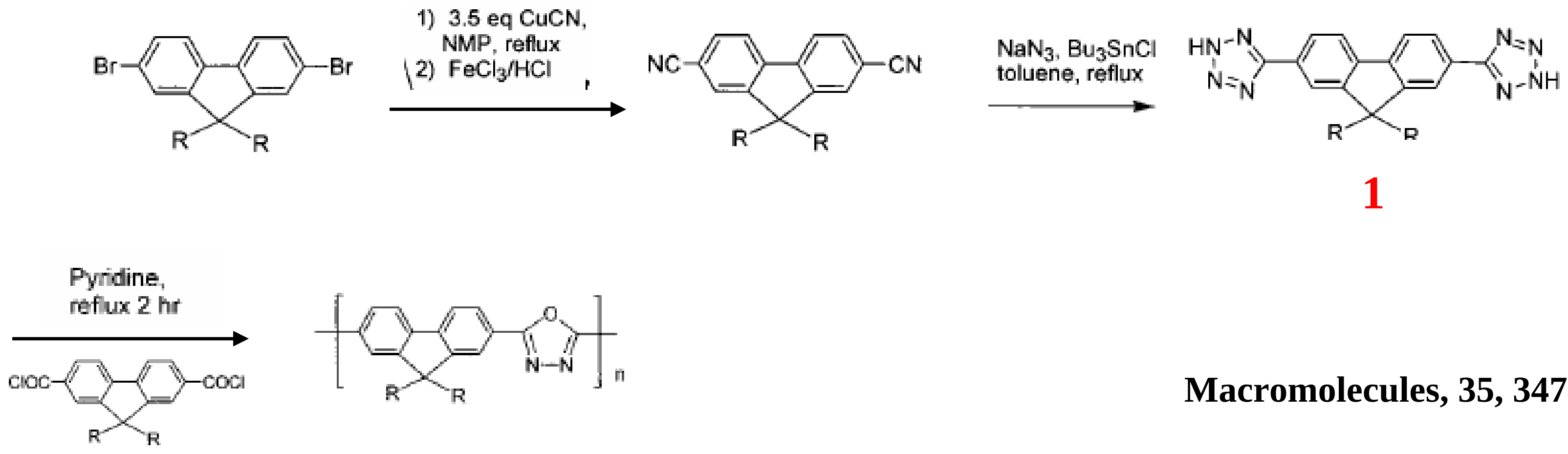


Macromolecules, 36, 6698, 2003

A highly efficient blue color emission PF copolymers incorporating both triphenylamine & oxadiazole pendant groups. This statistical copolymer was designed to bring together good hole transporting and electron transporting properties.

The electron-rich and electron-deficient substituents endow rather high HOMO (-5.30) and relatively low LUMO (-2.54 eV)-energy levels that are expected to facilitate charge injection and transport.

Fluorene-oxadiazole copolymers



1

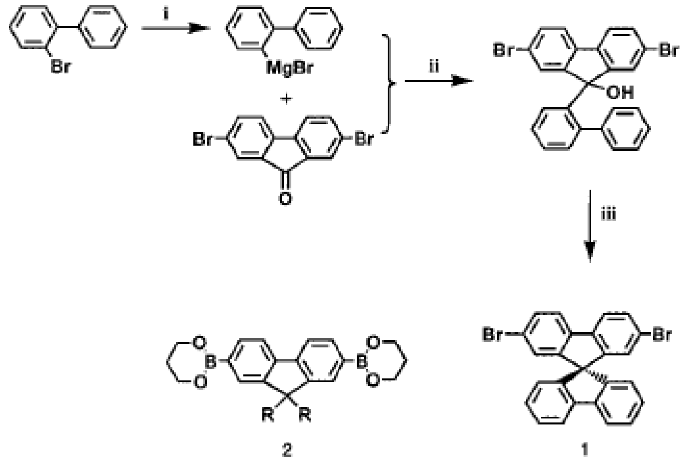
Macromolecules, 35, 3474, 2002

Oxadiazole units were also introduced into the backbone of fluorene-alternating copolymers. The key monomer was 2,7-bis(tetrazolyl)fluorene derivatives 1.

This tetrazole route has several advantages over other oxadiazole ring formation reactions : fast and clean reaction, mild reaction conditions, high yields, and hign polymer MWs.

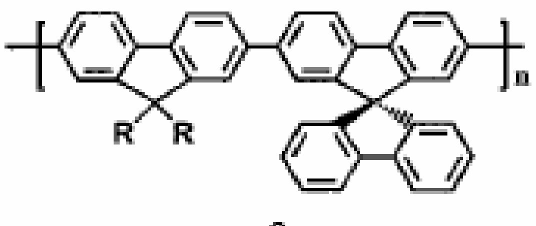
The UV and PL spectra of the copolymer was very similar to those of fluorene homopolymers with only slight red shifts in absorption (10-12 nm) and emission (5-7 nm) spectra. The copolymers also demonstrated high Φ_{PL} – 70 % in DCM solution.

Spiro-fluorene copolymers



$R = C_6H_{13}$ a

C_8H_{17} b



3

Adv. Mater., 12, 828, 2000

A spiro-bifluorene moiety was used to construct alternating copolymers with dialkylfluorene units. The aim of this modification was to increase the T_g of the material, so that moderate heating during the device operation would not result in aggregate formation.

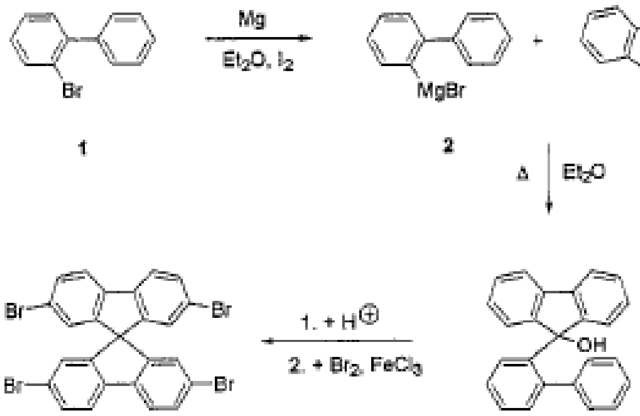
A 90° geometry of spiro-annulated bifluorene units prevents interchain aggregation, whereas the long-alkyl substituents in the second comonomer improve the solubility.

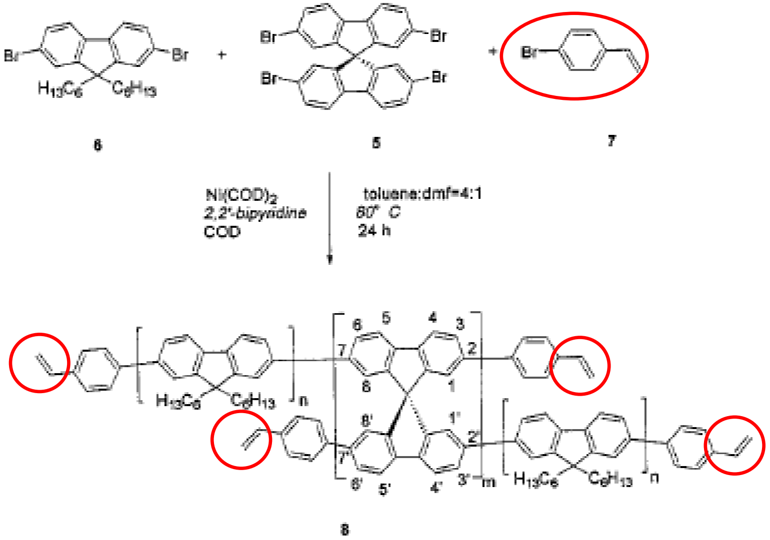
The copolymers are only partially soluble in THF and chloroform, but can be completely dissolved in chlorobenzene.

The T_g of copolymers is higher than that of PDHF. Consequently, no long wavelength emission was found for films annealed at 100 ℃, although further annealing above Tg at 150 ℃ does result in appearance of a strong emission band at 525 nm.

Another feature of these copolymers is their narrow emission spectra compared to dialkylfluorene, attributed to less dense molecular packing.

Spiro-fluorene copolymers





Chem. Mater., 13, 4285, 2001

Ni(0)-mediated random copolymerization of 9,9-dihexyl-2,7-dibromofluorene with this spiro-bifluorene monomer resulted in 3D-branched copolymers.

Due to the expected insolubility of such materials at high degree of polymerization owing to the network formation, the MW was controlled at Mn=3,800~12,800, by adding end-capper. The latter also serves as a X-linkable unit that allowed to obtain an insoluble polymer film by heating of soluble spin-coated polymer.

The resulting amorphous polymers demonstrated excellent thermal stability.

Color tuning in PF copolymers

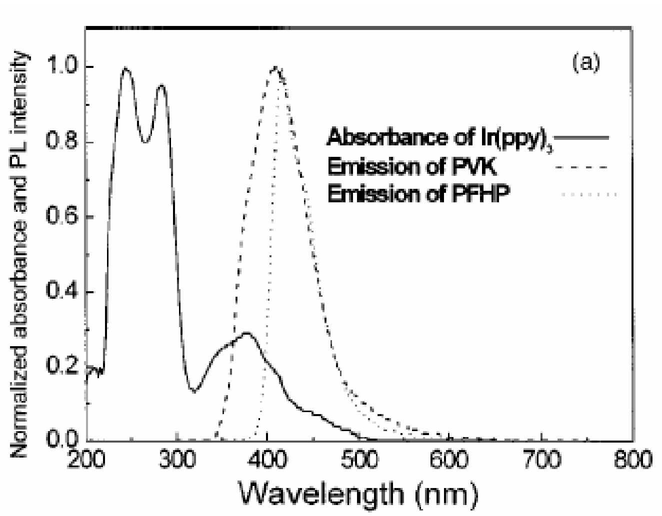
The above strategies were focused on creating highly stable PFs with pure blue emission.

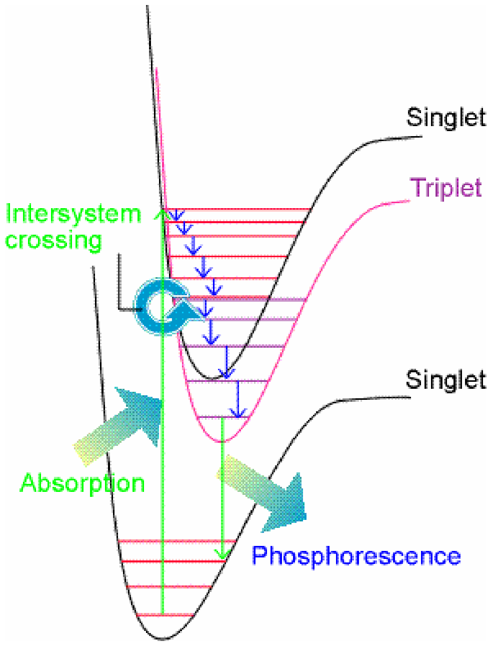
However, other emission colors can also be achieved through doping with fluorescent dyes or through a copolymerization strategy in either alternating or random PF copolymers.

Through careful selection of suitable comonomers, considering their effect on HOMO-LUMO levels of the polymer, one can achieve a whole range of emission colors from PF-based materials.

Doping with low molar-mass dyes

✓ **Spectrum overlap**

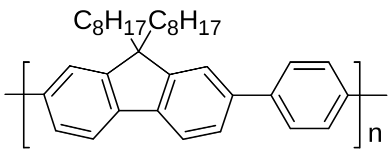




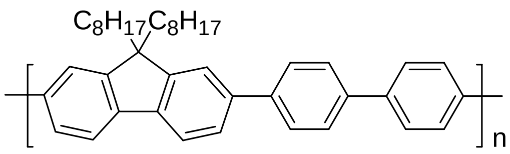
The high-energy blue emission of PF polymers can be changed into virtually any color by adding a small amount of low energy-emitting materials. This approach, based on energy transfer, is of prime importance for phosphorescent PLEDs, although non phosphorescent dyes were used to tune the PF emission color. Thus, efficient Förster energy transfer from blue to red was demonstrated for porphyrin dye-doped PFO based LED as a result of good overlap b/w PF emission and absorption of porphyrin dye.

We are going to study such energy-transfer next class – Host-Guest molecules.

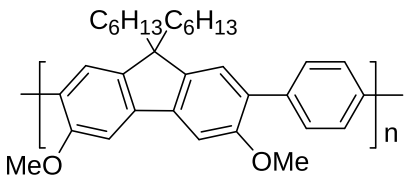
Alternating copolymers



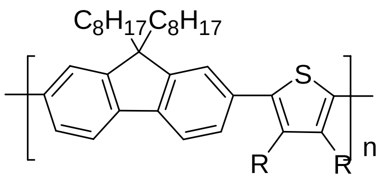
Abs : 365 nm, PL : 420, 442 nm
EL : 419 nm, Blue violet



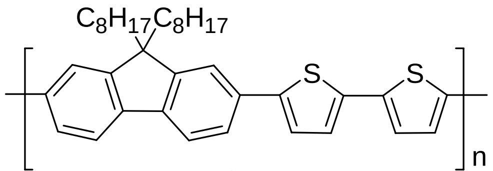
Abs : 365 nm, PL : 418, 440 nm
EL : 416 nm, Blue violet



Abs : 366 nm, PL : 424 nm
Blue violet

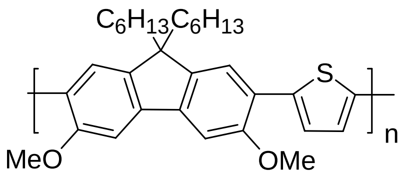


R=H ; Abs : 438 nm, PL : 485, 512 nm
EL : 480 nm, Greenish blue
R=CH3 ; Abs : 384 nm, PL : 460 nm
EL : 468 nm, Pale blue

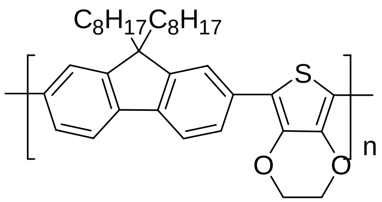


F8T2

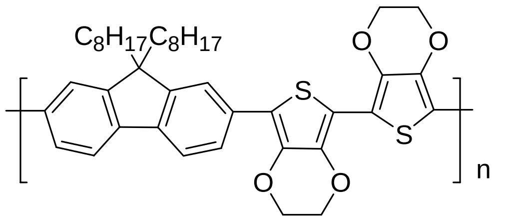
Abs : 427 nm, PL : 548 nm
EL : 545 nm, Green



Abs : 446 nm, PL : 510 nm
Greenish blue



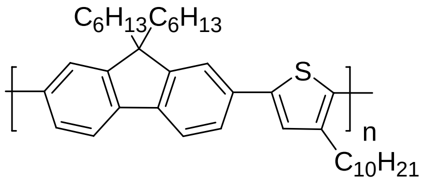
Abs : 444 nm, PL : 494, 526 nm
EL : 588 nm, Pale yellow



Abs : 517 nm, PL : 532, 574 nm
EL : 536 nm, Green

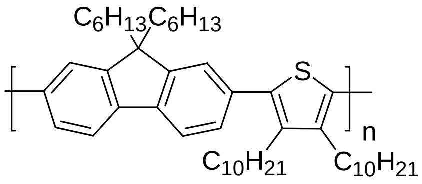
Efficiently tuned the emission from blue to green and yellow by introducing various phenylene and thiophene units, although no simple correlation b/w the polymer structure and the EL color was found.

Fluorene-thiophene copolymers



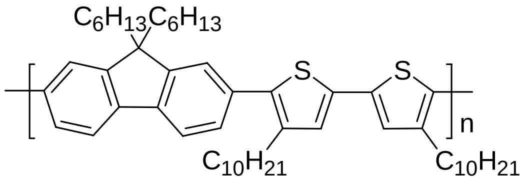
1- Abs : 412 nm, PL : 492, 477 nm

Bluish green



2- Abs : 378 nm, PL : 458, 475 nm

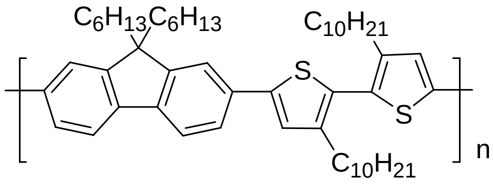
Blue



3- Abs : 403 nm, PL : 490, 520 nm

Green

E_g= 2.49 eV



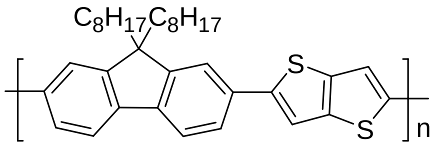
4- Abs : 401 nm, PL : 493, 520 nm

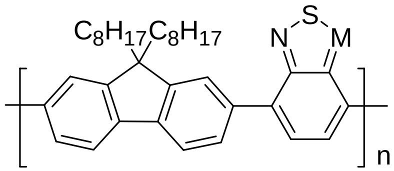
Green

E_g = 2.58 eV

In contrast to polythiophene homopolymers, the regioregularity of the bithiophene fragments in their copolymers show little influence on the optical band gap or the emission maxima, but the HH copolymer 4 was significantly more thermally stable.

Fluorene-thiophene copolymers





1- Abs : 448, 471 nm, PL : 495, 511, 548 nm
EL : 515 nm, Green, CIE (0.29, 0.63)

2- Abs : 390 nm, PL : 540 nm
EL : 545 nm, Green, CIE (0.394, 0.570)

A very efficient green-emitting fluorene copolymer 1 was synthesized by Shim's group via Suzuki coupling.

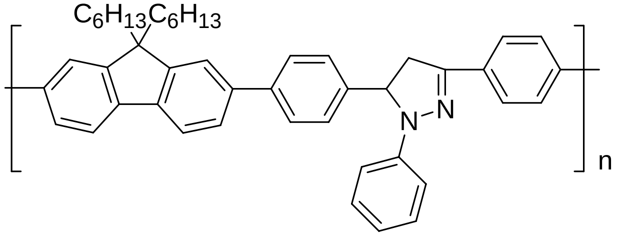
Both the absorption and emission spectra of 1 are red-shifted compared with PFO but slightly blue-shifted compared to F8T2.

A green-emitting fluorene-benzothiadiazole (F8BT) 2 was synthesized by Dow Chemicals by Suzuki coupling. A high-performance green emission PLED was demonstrated with this copolymer.

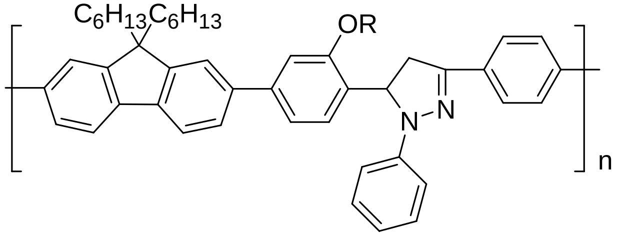
In contrast to other PFs, which demonstrate high-mobility nondispersive hole transport, F8T2 (2)shows a weak and highly dispersive electron transport.

Since 2 has an electron-deficient moiety in the polymer backbone, a stable anode electrode such as Al can be used.

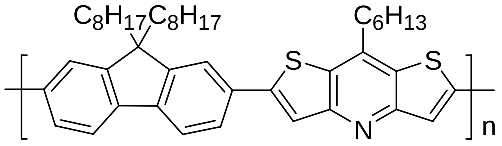
Fluorene-pyrazoline or pyridine copolymers



1- Abs : 339, 395 nm, PL : 508 nm
Green



2- R=C_6H_{13}; Abs : 337, 399 nm, PL : 508 nm, Green
3- R=$C_{12}H_{25}$; Abs : 336, 398 nm, PL : 508 nm, Green

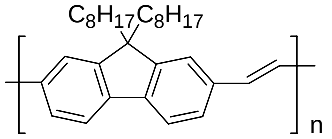


4- Abs : 415 nm, PL : 481, 536 nm
EL : 480, 536 nm, Blue-green

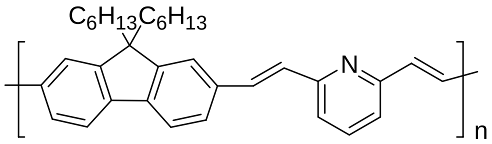
Green-emitting fluorene copolymers were also obtained by introducing pyrazoline moieties into the backbone that completely interrupt the conjugation due to sp^3 carbons in the ring. These polymers emit green light with a PL efficiency of 49-59 % in films.

Introduction of electron-accepting bithieno[3,2-b:2’,3’-e]pyridine units resulted in copolymer 4 with ca. 0.5 V lower reduction potential compared to the parent PFO. Upon excitation at 420 nm, 4 exhibited blue-green emission with two peaks at 481 and 536 nm.

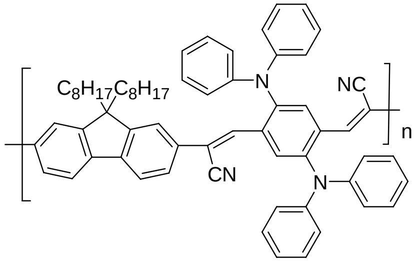
Fluorene-phenylene vinylene copolymers



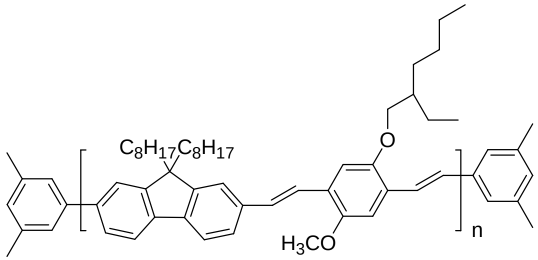
1- Abs : 418 nm, PL(EL) : 465, 500, 530 nm
Greenish-blue CIE(0.23, 0.38)
HOMO: -5.73 eV, LUMO: -3.13 eV



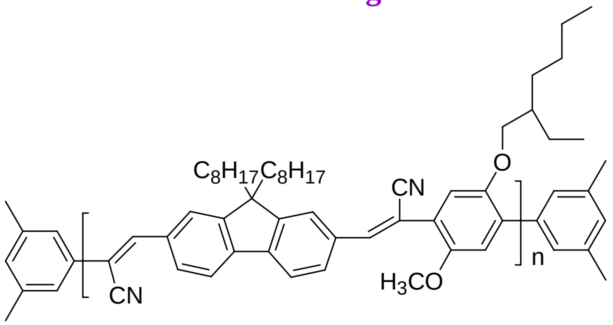
2- Abs : 375 nm, PL: 440, 465, 540 nm
EL: 540 nm, Yellowish-green
HOMO: -5.67 eV, LUMO: -2.82 eV



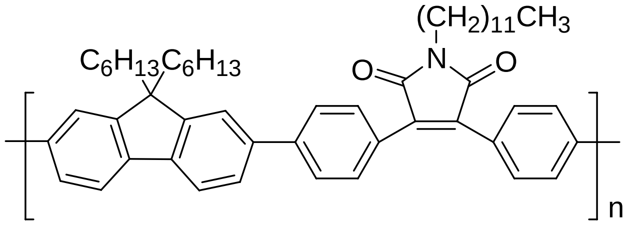
3- Abs : 404 nm, PL: 664 nm EL: 668 nm,
Saturated red, CIE(0.68, 0.32) ,
Eg:2.05 eV



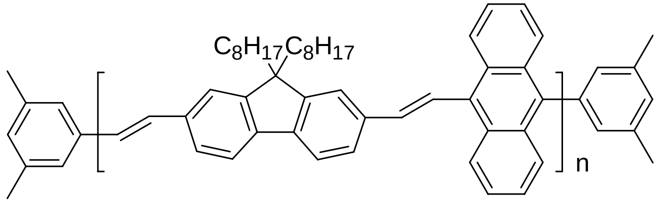
4- PL : 539 nm
Green



5- PL : 495 nm (THF)
Green



7- Abs : 412 nm, PL: 592 nm, EL: 562 nm,
Yellow, HOMO: -6.20 eV, LUMO: -3.79 eV



6- PL : 576 nm
Orange-red

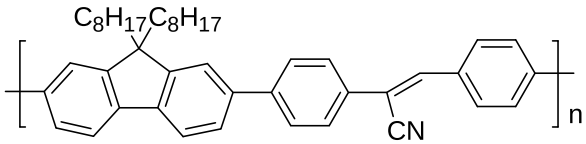
Fluorene-phenylene vinylene copolymers

Various fluorene-phenylenevinylene alternating copolymers with different emission colors have been synthesized, e.g., 1~7 in the front page.

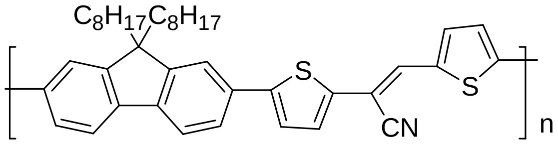
Introducing electron-rich (as in polymers 4 and 6), electron-deficient (as in compounds 2 and 7), or both of these units (as in compounds 3 and 5) in the PF chain allow for precise tuning of the emission wavelength, the HOMO-LUMO levels, and the charge injection and transport properties.

However, no high-performance PLEDs based on the above copolymers have yet been reported.

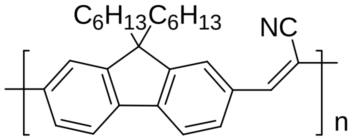
Fluorene-phenylene vinylene copolymers



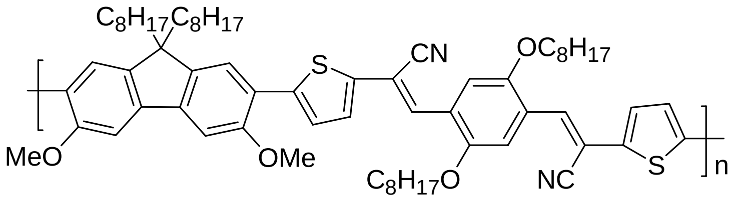
Abs : 403 nm, PL : 476 nm
EL : 466 nm, Blue



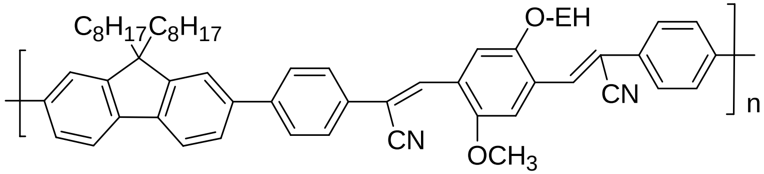
Abs : 500 nm, PL : 610 nm
EL : 610 nm, Red-orange



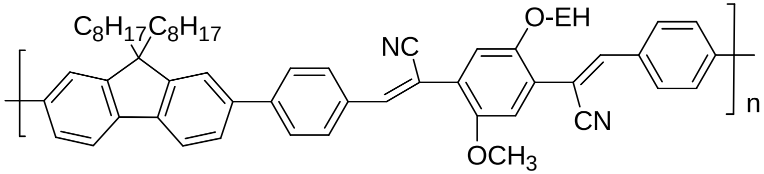
Abs : 440 nm, PL : 535 nm
EL : 535 nm, Green



Abs : 563, 601 nm, PL : 656, 702 nm
Red

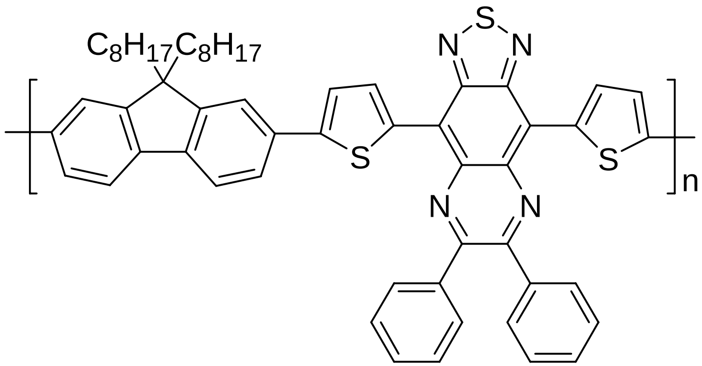


Abs : 468 nm, PL : 555 nm
EL : 554 nm, Yellow-orange, CIE(0.48, 0.51)



Abs : 372 nm, PL : 525 nm
EL : 547 nm, Yellowish-green, CIE(0.40, 0.53)

Very low band-gap fluorene copolymers



Abs : 400, 780 nm, PL : 1035 nm
EL : 970 nm, NIR, Eg : 1.27 eV

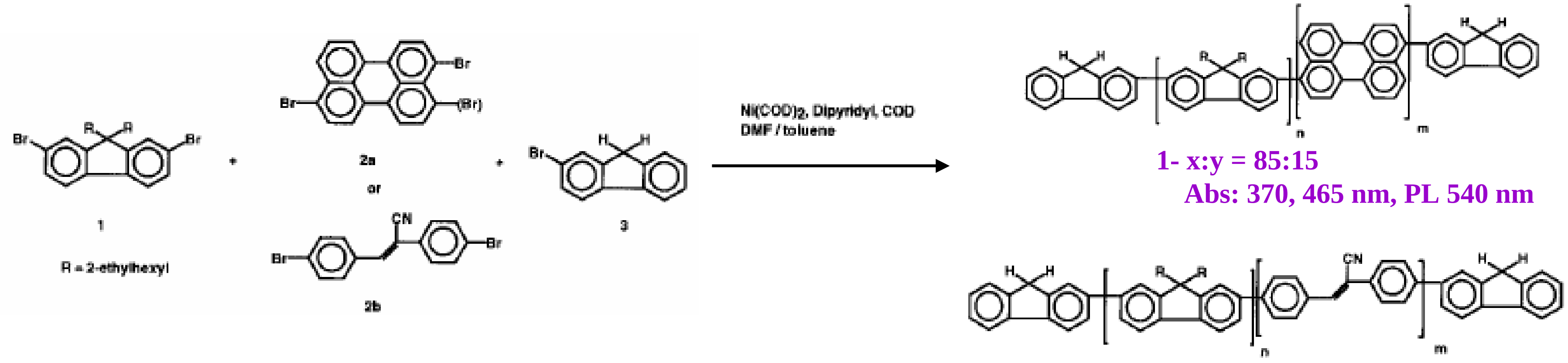
PL and EL emissions from a very low band-gap copolymer was demonstrated.

The material has two absorption peaks at 400 and 780 nm and emits light in the NIR region.

The PL spectrum of thin films has one peak at 1035 nm, which is blue-shifted by ca. 60 nm on annealing at 200 °C for 10 min.

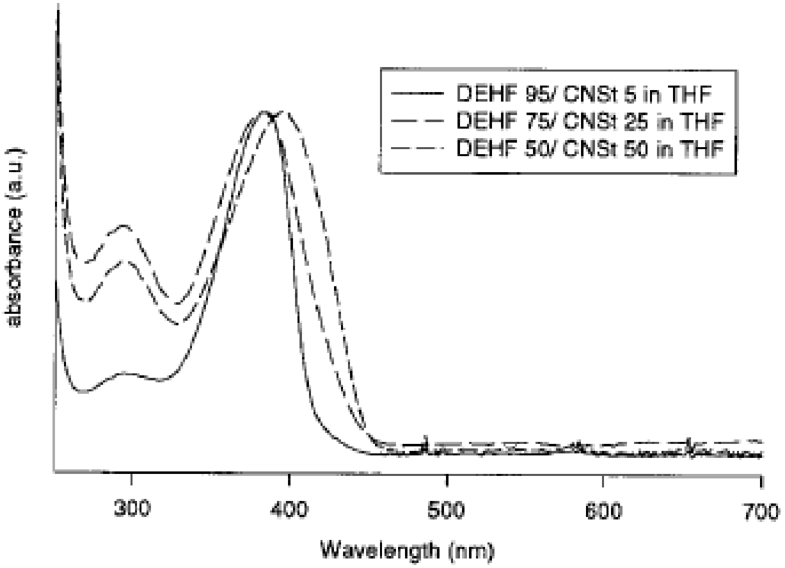
EL from PLED in the NIR can be important for communication and sensor technologies.

Random copolymers



1- x:y = 85:15
Abs: 370, 465 nm, PL 540 nm

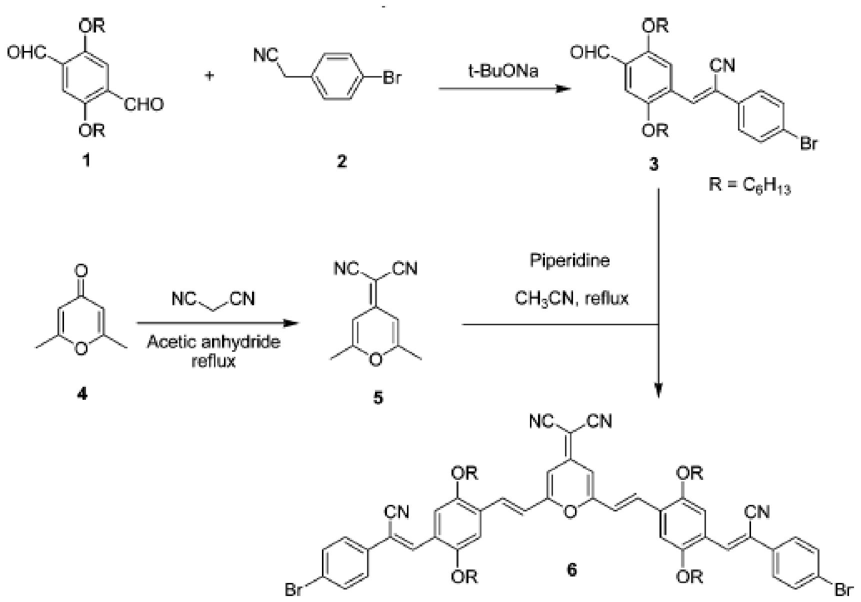
2- x:y = 95:5, Abs: 376 nm, PL 466 nm
3- x:y = 75:25, Abs: 374 nm, PL 481 nm
4- x:y = 50:50, Abs: 390 nm, PL 510 nm



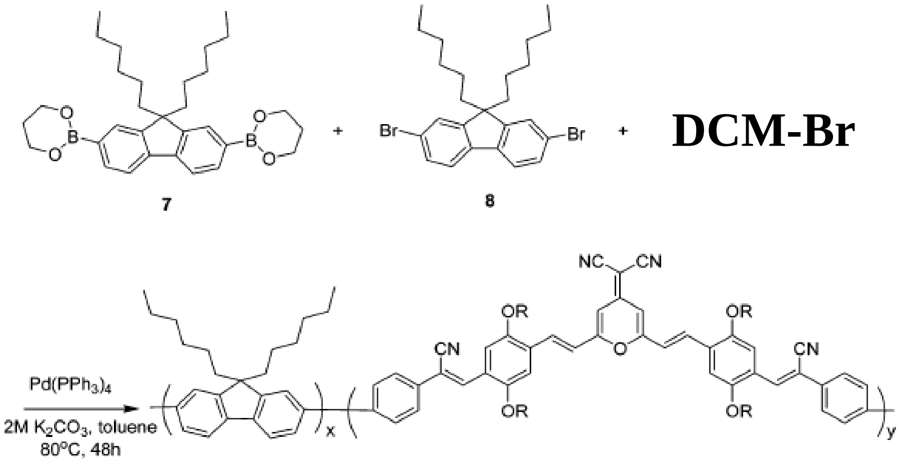
Copolymers 1~4 are soluble in organic solvents. They are thermally stable and show no color change upon thermal annealing.

The emission color is strongly dependent on the feed ratio of the comonomers. For example, in the case of copolymer 2~4, the emission color can be turned from blue (2, 466 nm) through blue-green (3, 481 nm) to pure green (4, 510 nm).

Copolyfluorenes containing DCM derivatives



DCM-Br



	in feed
PFD0.5	x = 0.995, y = 0.005
PFD1	x = 0.99 , y = 0.01
PFD5	x = 0.95 , y = 0.05
PFD10	x = 0.90 , y = 0.10
PFD25	x = 0.75 , y = 0.25
PFD50	x = 0.50 , y = 0.50

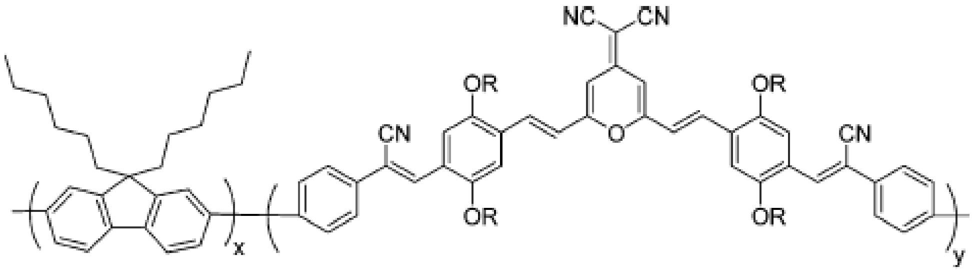
Macromolecules, ma071271y, 2007

The copolymer films showed absorption peaks at 383-397 and 481-496 nm, and PL peaks at 421-424 and 560-596 nm originated from fluorene and DCM segments, respectively.

The longer wavelength PL peak red-shifted gradually from 560 to 596 nm with increasing DCM contents (0.83% → 49.8%).

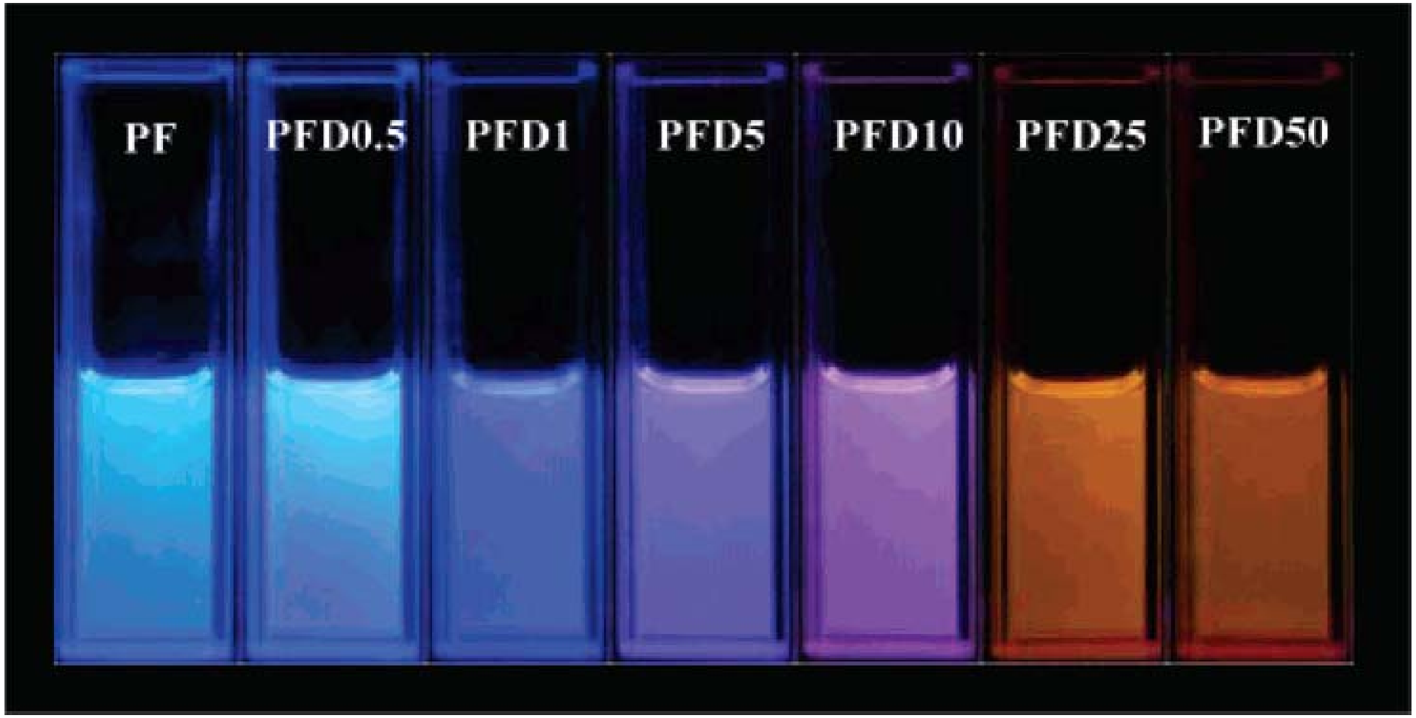
The LUMO energy levels lowered as the content of DCM units increased (-2.75 eV → -3.70 eV), whereas the HOMO levels remained almost unchanged (-5.68 eV → -5.64 eV).

Copolyfluorenes containing DCM derivatives

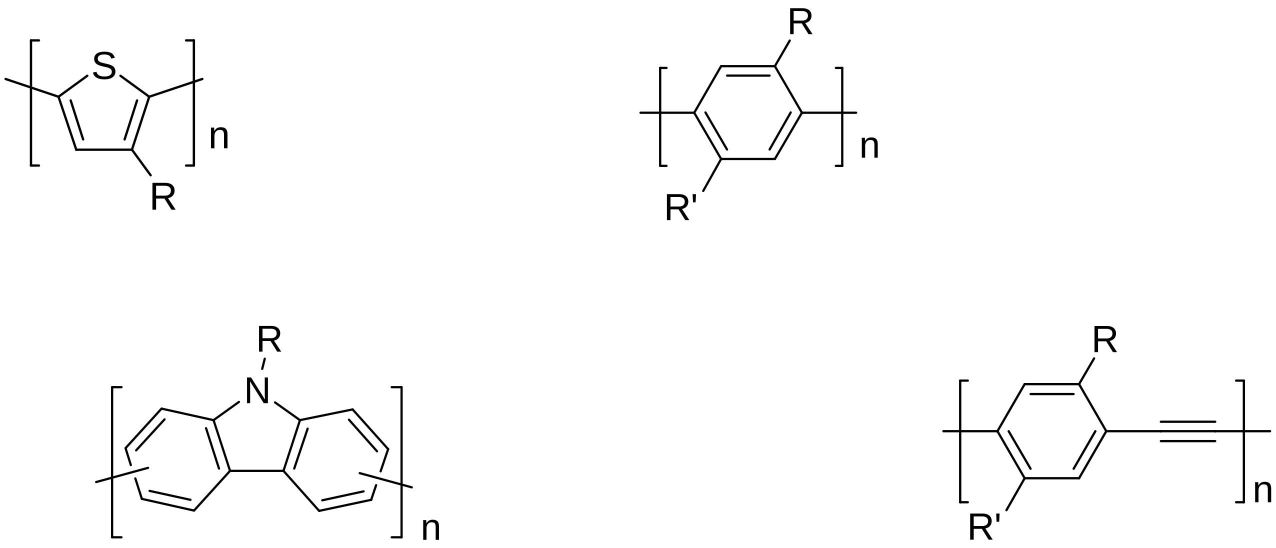


	in feed
PFD0.5	x = 0.995, y = 0.005
PFD1	x = 0.99 , y = 0.01
PFD5	x = 0.95 , y = 0.05
PFD10	x = 0.90 , y = 0.10
PFD25	x = 0.75 , y = 0.25
PFD50	x = 0.50 , y = 0.50

Macromolecules, ma071271y, 2007



Another emitting polymers



Polythiophene, poly(p-phenylene), polycarbazole, and poly(phenylene ethynylene) derivatives have light-emitting properties, which were studied by many research groups.

These materials are also used other application such as OTFT and OSC, so we will study up on these materials next chapter.