

Light-Emitting Polythiophenes**

By Igor F. Perepichka,* Dmitrii F. Perepichka,* Hong Meng,* and Fred Wudl*

Polythiophenes are one of the most important classes of conjugated polymers, with a wide range of applications, such as conducting films, electrochromics, and field-effect transistors, which have been the subject of a number of older and more recent reviews. Much less attention has been paid to the light-emitting properties of this class of materials, although their unique properties present a number of opportunities unavailable from more popular polymeric light emitters such as polyfluorene or poly(p-phenylene vinylene). This article reviews achievements to date in applications of thiophene-based polymers and oligomers as electroluminescent materials. We demonstrate the basic principles of controlling the optical properties of polythiophenes through structural modifications and review the most important light-emitting materials created from thiophene derivatives. Special attention is paid to consequences of structural variations on the performance of light-emitting diodes fabricated with these materials.

1. Introduction

In 1990 Friend and co-workers described a green electroluminescent device based on a layer of pure conjugated poly(p-phenylene vinylene) (PPV) placed between indium tin oxide (ITO) and Al electrodes.^[1] The device efficiency and relative-

ly low turn-on voltage promised commercial applications in the near future. It was clear that such progress would require not only improved device-engineering techniques, but also sophisticated control of the materials' luminescence color, efficiency, and charge-transport properties, challenging the polymer chemistry community to create new types of light-emitting polymeric materials with tailored properties. In fact, for more than ten years the prospect of polymer light-emitting diodes (PLEDs) has remained one of the major applications maintaining researchers' interest in conjugated polymers. Large numbers of different classes of light-emitting conjugated polymers have been developed, e.g., poly(carbazole)s, poly(fluorene)s (PFs), PPVs, poly(phenylene ethynyls), and poly(thiophene)s (PTs). While PPV and its derivatives are still the leading materials for green-light-emitting PLEDs, the larger-bandgap PFs are the top polymeric blue-light emitters. Both of these classes of light-emitting materials have been extensively reviewed in recent years. Relatively less attention was given to PTs as light-emitting materials, even though they can easily produce a red color that is difficult to achieve with other conjugated polymers. Furthermore, very-high-efficiency PLEDs have been demonstrated with some thiophene-derived copolymers.

Generally, PTs are one of the most studied and important classes of linear conjugated polymers.^[2] Versatile synthetic approaches to PTs, both chemical^[3] and electrochemical,^[4] easy functionalization, and unique electronic properties that can be widely tuned result in a tremendous amount of interest being focused on this class of polymers as materials for electronic and optoelectronic applications. Due to the electron-rich character

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[**] DFP acknowledges support from the National Science and Engineering Research Council of Canada. FW is indebted to the Office of Naval Research and the Air Force Office for Scientific Research for support.



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of the thiophene ring, PTs can be easily and reversibly oxidized by chemical or electrochemical means to form p-doped, usually highly conducting materials. The first electronic transition of undoped PT (which strongly depends on the structure) lies between 300 and 500 nm (molar extinction coefficient, $\epsilon \sim 10\,000\text{ M}^{-1}\text{ cm}^{-1}$).^[5] Upon doping, it undergoes a dramatic bathochromic shift transforming into the so-called “conducting” band, which tails from the visible to the deep-IR region. In contrast to undoped PTs, which exhibit reasonably strong luminescence in the visible region of the spectrum, the doped PTs are not luminescent, although partially doped PTs have been used in light-emitting electrochemical cells (LECs), and doped poly(3,4-ethylenedioxythiophene) (PEDOT) is routinely used as an electrode for PLEDs (mostly as a second layer on ITO-covered glass).

Usually, PTs emit orange–red light, consistent with their bandgap of ca. 2 eV. Often the luminescence efficiency of PTs in the solid state is relatively low,^[6,7] much lower than that of PPV and PF. A possible explanation is a tendency of strong interchain interactions (especially for low-molecular-weight oligomers). This feature is an advantage of PTs in some electronic applications, such as field-effect transistors.^[8] However, it becomes one of the most critical drawbacks for applications as emissive materials in LEDs. Whereas in solution the photoluminescence efficiency (Φ_{PL}) of poly(3-alkylthiophenes) (PATs) is $\sim 30\text{--}40\%$, it drastically drops to 1–4% and lower in the solid state due to the increased contribution of non-radiative decay via interchain interactions and intersystem crossing caused by the heavy-atom effect of sulfur.^[9] For the same reason, thiophene-based polymers have stronger spin-orbital coupling than benzene-based polymers, and hence triplet-state processes play a greater role in their photophysics.^[10]

Another feature of PTs is the phenomenon of thermochromism,^[11,12] which has been shown for PATs in many publications. It is believed that the thermochromism observed in PAT films originates from the thermal movement of the side chains, shifting a predominantly planar structure of chains at low temperatures to a random-coil conformation when the temperature is increased, thus forcing the polymer backbone out of planarity. This leads to a decreased orbital overlap and shorter effective conjugation length,^[13] resulting in a bandgap increase and blue-shifted polymer absorbances (from red to purple or purple–blue).^[11,12] The process is completely reversible, and on cooling the initial color is restored. Although thermochromism is of theoretical interest for understanding the effect of structural and electronic features of PTs, it is undesirable for LED applications, as it could lead to changes of the emission wavelength and the quantum efficiency (QE) of the device during operation.

In what follows, we will briefly introduce general synthetic approaches to PT (Sect. 2), followed by an in-depth description of different subclasses of light-emitting thiophene-based polymers. Starting with PT homopolymers (Sect. 3), we will introduce the two most basic concepts in tuning the emissive properties in PT materials: reducing the luminescence

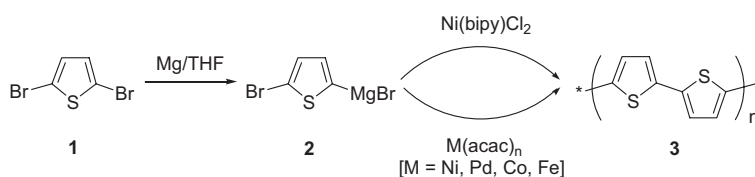
quenching in the solid state by suppressing the aggregation effect, and tuning the emission color by changing the effective conjugation length. This discussion is continued in Section 4 with a focus on block copolymers. Sections 5,6 present PT copolymers with a variety of conjugated units. We will discuss the effect of electronic structure of the comonomers (donor/acceptor properties and conjugation pattern) on the luminescent and charge-transport properties of the copolymers and demonstrate how the copolymerization approach can result in highly efficient thiophene-containing light-emitting materials.

2. General Synthetic Routes to PTs

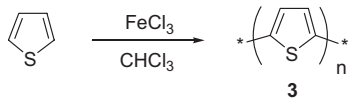
Polymerization of thiophenes can be carried out in many different ways, and the most used methods can be generalized into three categories: i) electropolymerization, ii) metal-catalyzed coupling reactions, and iii) chemical oxidative polymerization. Electropolymerization is a widely used method to prepare insoluble films of PTs and represents a simple and efficient way to study optical and electronic properties of PTs,^[4] although it is rarely used in preparation of electroluminescent materials. In 1980 Yamamoto et al. reported the Ni-catalyzed polycondensation of 2,5-dibromothiophene **1**. The latter was allowed to react with Mg in tetrahydrofuran (THF) affording 2-magnesiobromo-5-bromothiophene **2**, that in the presence of Ni(bipy)Cl₂ (bipy: 2,2'-bipyridyl) produced PT **3** (Scheme 1).^[14] The same year, Lin and Dudek described another example of the metal-catalyzed route to unsubstituted PT **3**, exploiting acetylacetonates of Ni, Pd, Co, or Fe as catalysts.^[15]

PT synthesized by these methods is low-molecular-weight material due to the fact that even at low molecular weights, the material is insoluble and precipitates from THF; moreover, the elemental analysis indicates the presence of 1–3% of Mg.^[3] Later, a Ni(dppp)Cl₂ (dppp: 1,3-bis(diphenylphosphino)propane) catalyst was exploited for polycondensation polymerization of bromo- (or iodo-) Grignard reagents of type **2**.^[16] Another polycondensation approach to PT, also reported by Yamamoto,^[17] included heating of **1** with Ni(cod)₂ (cod: 1,5-cyclooctadiene) and triphenylphosphine in *N,N*-dimethylformamide (DMF) at 60–80 °C. Due to the very high yield (near quantitative), this reaction has been applied in syntheses of a wide range of conjugated polymers.

The FeCl₃-mediated polymerization of thiophene in chloroform was described twenty years ago^[18] and currently is the most widely exploited oxidative route to 3- or 3,4-substituted PTs (Scheme 2). It produces rather high-molecular-weight



Scheme 1. Synthesis of PT via metal-catalyzed couplings.

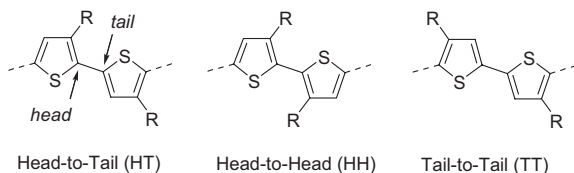


Scheme 2. Synthesis of PT via chemical oxidation polymerization.

polymers (with weight-average molecular weights (M_w) often ranging from 20 000 to 400 000 g mol^{-1}) with polydispersities ranging from 1.3 to 5.^[19] Other oxidative agents (e.g., ammonium persulfate) are of limited use, although oxidative coupling with CuCl_2 is widely used as a dimerization reaction of lithiothiophenes in syntheses of oligothiophenes.

As already mentioned, unsubstituted PT is an insoluble and infusible material. Once the polymer is prepared it is difficult (if not impossible) to further process it as a material for electronic applications. The solubility can be greatly enhanced by introduction of side chains at position 3 (or at both positions 3 and 4). The most widely studied side chains are *n*-alkyl substituents that can be easily introduced into the thiophene core by reaction of 3-bromothiophene with alkyl Grignard reagents from alkyl halides.^[20]

While 3-substitution efficiently improves the solubility and the processability of the PTs, polymerization of 3-substituted thiophenes can result in three different types of coupling of the thiophene rings along the polymer main chain, i.e., head-to-tail (HT), head-to-head (HH), and tail-to-tail (TT).



Generally, both oxidative polymerization and metal-catalyzed polycondensation afford all three possible types of isomers, i.e., HH, HT, and TT, although this process is not completely random and electronic and steric factors have an influence, so that HT coupling is somewhat preferred, sometimes reaching more than 80–94%.^[21,22] Amou et al. showed that the regioregularity of FeCl_3 -synthesized poly(3-*n*-hexylthiophene) (P3HT, **9f**) depends on the temperature of the reaction and the concentration, and in diluted solutions at -45°C the regioregularity of P3HT approaches 90%.^[21] A 100% regioregular HHTT PT consisting of alternating HH and TT coupling sites can be prepared by oxidative polymerization of substituted HH-coupled bithiophenes.^[23]

Several approaches leading to selective formation of the least sterically hindered HT-regioregular PTs have been developed in the last decade. The McCullough method was the first synthesis of regioregular HT-PATs (**HT-6**), yielding almost

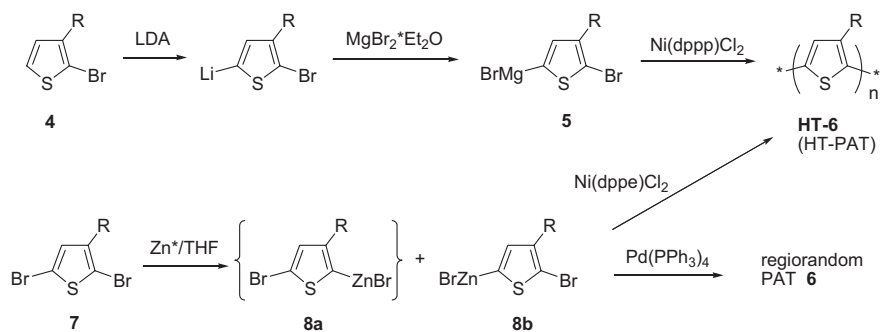
100% HT coupling (Scheme 3).^[24] It is based on regiospecific metallation of 2-bromo-3-R-thiophene **4** with lithium diisopropylamide (LDA) at position 5 and its further transformation into Grignard derivative **5**. The latter is polymerized with catalytic amounts of $\text{Ni}(\text{dppp})\text{Cl}_2$ using the Kumada cross-coupling method. The important modification of this synthetic route replaces the lithiation reaction by treatment of the dibromothiophene derivative with methylmagnesium or vinylmagnesium bromide, affording the Grignard intermediate in one step.^[25] Other methods for preparing regioregular PTs exploiting Stille^[26] or Suzuki^[27] coupling instead of Grignard reagents have also been developed. Rieke has used highly reactive “Rieke zinc” (Zn^*) that reacts with 2,5-dibromo-3-R-thiophenes (**7**) at low temperatures, predominantly affording the 5-metallated compound (**8a,b**), which can be polymerized with the Kumada catalyst $\text{Ni}(\text{dppp})\text{Cl}_2$ to produce HT-regioregular PATs (**HT-6**). (In contrast, the monodentate $\text{Pd}(\text{PPh}_3)_4$ -ligated catalyst yields regiorandom PATs **6** under the same conditions.^[28]) McCullough^[3] recently reviewed the detailed aspects of regioregular PT synthesis and characterization.

The presence of HH coupling in irregular PTs causes an increased twist of the thiophene units (due to steric repulsion) with concomitant loss of conjugation. This results in an increased bandgap (blue-shift in absorption and luminescence), decreased conductivity, and other undesirable changes to the electronic properties. As will be shown below, regioregularity also plays an important role in luminescence properties of PTs and is used as a tool to tune the properties of PT-based LEDs.

3. Light-Emitting Thiophene Homopolymers

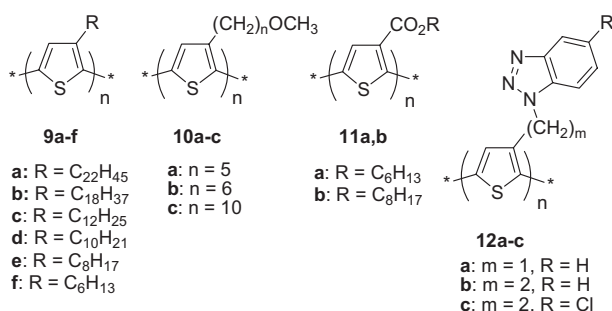
3.1. PTs as Red-Light Emitters

PT LEDs were first reported by Ohmori et al. in 1991,^[29] who described PATs **9a–c** (prepared by oxidation of 3-alkylthiophenes with FeCl_3 in chloroform^[18]) as red–orange-light-emitting materials (peak emission at 640 nm for **9a**) in single-layer ITO/PT/Mg:In devices. Shortly afterwards, Heeger’s group reported electroluminescence (EL) in poly(3-oc-



Scheme 3. McCullough and Rieke methods of synthesis of regioregular HT-PATs HT-6.

thiophene) (P3OT) **9e** that showed red–orange luminescence with an external electroluminescence ($\Phi_{\text{EL}}^{\text{ex}}$) QE of 0.025 % in an ITO/**9e**/Ca configuration.^[30] It was shown that the luminescence efficiency depends on the length of the alkyl chain, showing about a four-fold increased EL efficiency for PT **9a** with R = C₂₂H₄₅ compared to **9c** with R = C₁₂H₂₅ (although no quantum-yield values were given in these reports).^[31] Greenham et al. also mentioned a significantly higher emission efficiency of 0.2 % for dodecyl-substituted **9c** as compared with hexyl-substituted **9f** (0.05 % with the same Ca electrode).^[32] This effect can be explained by improved confinement of excitons on the main chain due to increased interchain separation for polymers with longer side substituents.



Bolognesi et al. prepared poly(3-(ω -methoxy)alkylthiophene)s **10a–c** by Ni-initiated polymerization of 2,5-diiodothiophenes.^[33–35] A small red-shift in EL of polymer **10c** compared to polymer **9e** (from 1.8 eV to 1.95 eV) was presented as an indication of a lower bandgap in the former.^[30,33]

although it could be the result of asymmetry of the wide emission band (comparison with poly(3-decylthiophene) (P3DT) **9d** reveals a smaller blue-shift of 0.05 eV^[36]). Polymers **10a,b** showed high (for PTs) photoluminescence (PL) quantum yields in solution (38–45 % in THF); however, these quantum yields decreased in the films.^[35] A general explanation of this decrease as a result of the interchain interactions is supported by temperature-dependent PL experiments. On gradually heating the sample to 140 °C, the PL intensity increased by ≈ 2 and ≈ 6 times for **10a** and **10b**, respectively. The $\Phi_{\text{EL}}^{\text{ex}}$ for **10a** and **10b** in ITO/polymer/Al diodes were relatively low (10^{-5} – 10^{-4} % and 5×10^{-3} %, respectively, at the same voltages).

An expectedly larger blue-shift in fluorescence was observed for alkoxy-carbonyl-substituted PTs **11a,b** prepared from 2,5-dibromosubstituted monomers by either an Ullmann reaction with Cu powder or Ni⁰-mediated polymerization.^[37] Both polymers had similar molecular weights (number-average molecular weights (M_n) of 3000 g mol⁻¹), although the Cu-prepared polymers showed less defects and lower polydispersity indexes. PL emission maxima for the Cu-prepared polymers **11a,b** were red-shifted compared to the Ni-prepared polymers (by 13–15 nm (≈ 0.05 – 0.06 eV) in solution and 25–30 nm (≈ 0.08 – 0.10 eV) in films, see Table 1). This demonstrates that the properties of the polymer depend on the preparation method and, consequently, conclusions based on small shifts of 0.05–0.1 eV in PL/EL energies of the materials prepared by different methods may not always be valid.

A series of PT derivatives **12a–c** with electron-transporting benzotriazole moieties in the side chains was prepared.^[38] The polymer **12a** was insoluble in common organic solvents (THF, CHCl₃, and DMF). In contrast, polymers **12b,c**, endowed

Table 1. Properties of PATs, prepared by the Ullmann, Yamamoto, or FeCl₃ polymerizations (sh: shoulder).

Polymer (method)	$\lambda_{\text{max}}^{\text{abs}}$ [nm]		$\lambda_{\text{max}}^{\text{PL}}$ [a] [nm]		$\lambda_{\text{max}}^{\text{EL}}$ [nm]	$\Phi_{\text{EL}}^{\text{ex}}$ [%]	Ref.
	Solution (solvent)	Film	Solution (solvent)	Film			
9e (FeCl ₃)		500		655	650 [b]	0.012 [b]	[38]
9f (50% HT)	413 (CHCl ₃)	420	567, 600 [9%]	608 [0.8%]			[39]
9f (60% HT)	420 (CHCl ₃)	432	572, 600 [12%]	608, 643 [0.3%]			[39]
9f (70%-HT)		456		650	630 [c]	1.3×10^{-5} [c]	[7]
9f (80% HT)	440 (CHCl ₃)	518	580, 614 [14%]	670, 714 [0.2%]			[39]
HT-9f (98%-HT)		510		717	662 [c]	3.85×10^{-4} [c]	[7]
10a (Ni)	451 (toluene)	550		660sh, 730	670, 720 [b]	10^{-5} – 10^{-4} [b]	[34,35]
10b (Ni)	450 (toluene)	535		670sh, 730 [d]	650 [b]	5×10^{-3} [b]	[34,35]
10c (Ni)	448 (toluene)	530					[34]
10c (Ni)		470		660	635 [b]		[33]
11a (Cu)	423 (THF)	447	570 (THF)	620			[37]
11b (Cu)	430 (THF)	450	568 (THF)	630			[37]
11a (Ni)	408 (THF)	429	555 (THF)	595			[37]
11b (Ni)	408 (THF)	430	555 (THF)	600			[37]
11a	410 (THF)	434		600	600 [b]	0.016 [b]	[43]
11b	439 (THF)	460		610	615 [b]	0.018 [b]	[43]
HHTT-11a	387 (THF)	377		590	590 [b]	0.0085 [b]	[43]
HHTT-11b	389 (THF)	381		600	600 [b]	0.0047 [b]	[43]
12b (FeCl ₃)		444		580	580 [b]	0.09 [b]	[38]
12c (FeCl ₃)		446		588	600 [b]	0.04 [b]	[38]

[a] Values in square brackets correspond to Φ_{PL} . [b] ITO/polymer/Al. [c] ITO/polymer/Mg/Al. [d] Phase transition with a blue-shift in PL is observed on heating ($\lambda_{\text{max}}^{\text{PL}} = 630, 680$ nm at 142 °C).

with longer tethers, possessed improved solubilities as well as high molecular weights and thermal stabilities (decomposition temperature $T_{dec} > 300^\circ\text{C}$). They showed pronounced blue-shifts of 50–70 nm in absorption, and PL and EL maxima comparable to P3OT (**9e**, Table 1), which was somewhat speculatively attributed to steric hindrance.^[38] The EL efficiency was not enhanced as dramatically as the authors expected, although they showed 3–7 times higher Φ_{EL}^{ex} values. This was rationalized by considering the energy diagram in Figure 1. The highest occupied molecular orbital (HOMO) levels found from photoelectron spectroscopy were –5.45, –5.62, and –4.57 eV for **12b,c** and P3OT (**9e**), respectively, and the lowest unoccupied molecular orbital (LUMO) energy levels (estimated as the energy of the HOMO, E_{HOMO} , plus the optical

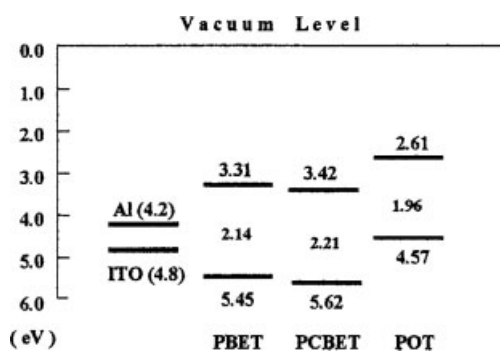


Figure 1. Energy diagram of substituted PTs **12b** (PBET), **12c** (PCBET), and **9e** (POT). Reprinted with permission from [38]. Copyright 2001 American Chemical Society.

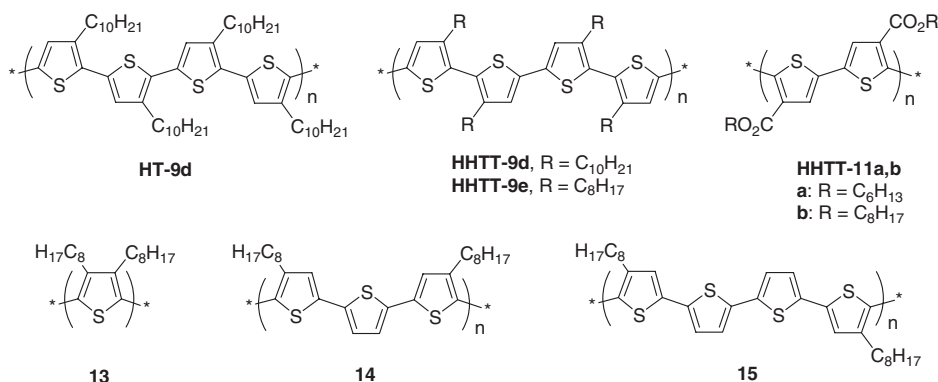
bandgap from UV-vis spectra) were correspondingly at –3.31, –3.42, and –2.61 eV. Thus, both the HOMO and LUMO levels of **12b** and **12c** were lowered compared with those of P3OT **9e** through introduction of the electron-withdrawing benzotriazole moieties. However, this strong effect is certainly due to the replacement of the alkoxy substituents with alkyl groups and not due to the triazole moieties. The authors note that the total barrier to charge injection was not reduced, although Φ_{EL}^{ex} enhancement was observed. The observed enhancement should not be surprising in our opinion, because

the hole- and electron-injection balance (which was improved significantly), rather than total barrier, should determine the EL efficiency.

3.2. The Effect of Regioregularity of PTs on EL

The above-mentioned aspect of regioregularity in PTs plays an important role in their bandgap control. The random polymerization of 3-alkylthiophenes leads to a large degree of HH-coupling that decreases the effective conjugation in the chain due to a large twist distortion. Xu and Holdcroft studied the effect of regioregularity on the luminescent properties of P3HT **9f**.^[39] They found that increasing the percentage of HT coupling in P3HT from 50 % HT to 80 % HT results in red-shifts of both absorption and emission maxima as well as in increased fluorescence efficiency in solution, from 9 % to 14 % (Table 1). On the other hand, an increased planarization of regioregular HT PT facilitates aggregation, which results in a decrease of the Φ_{PL} emission efficiency in the solid state (from 0.8 % for 50 % HT to 0.2 % for 80 % HT). Later McCullough performed comparative studies on EL performance of HT-regioregular and regiorandom P3HT **9f**.^[7] Compared to non-regioregular material, the HT-regioregular polymer showed a narrower EL spectrum and an approximately doubled Φ_{EL}^{ex} ($1.5 \times 10^{-4} \%$ versus $7 \times 10^{-5} \%$ at 6 mA current, Table 1); however, a very low QE and preferential degradation of LEDs with irregular P3HT might be responsible for the difference.

Regioregular HT-coupled poly(3-decylthiophene) (**HT-9d**) is an electroluminescent polymer exhibiting a well-defined vibronic structure in its absorption spectrum (Fig. 2a; 0–0 transition at 2.0 eV) and red-light emission with good color purity that showed a rather low QE in the solid state ($\Phi_{PL}^{film} = 1 \pm 0.1 \%$).^[40] Its regioregular HH/TT-coupled isomer polymer **HHTT-9d**^[41] showed large blue-shifts (Fig. 2b) in its absorption, fluorescence, and electroluminescence spectra; in addition, it emits green light with one order-of-magnitude higher PL ($\Phi_{PL}^{film} = 11 \pm 0.1 \%$) and two orders-of-magnitude higher EL ($\Phi_{EL}^{int} = 0.001$ and 0.25–0.30 %, respectively), but requires a higher turn-on voltage.^[40] The blue-shifts and the increased emission efficiency of HHTT-regioregular polymers



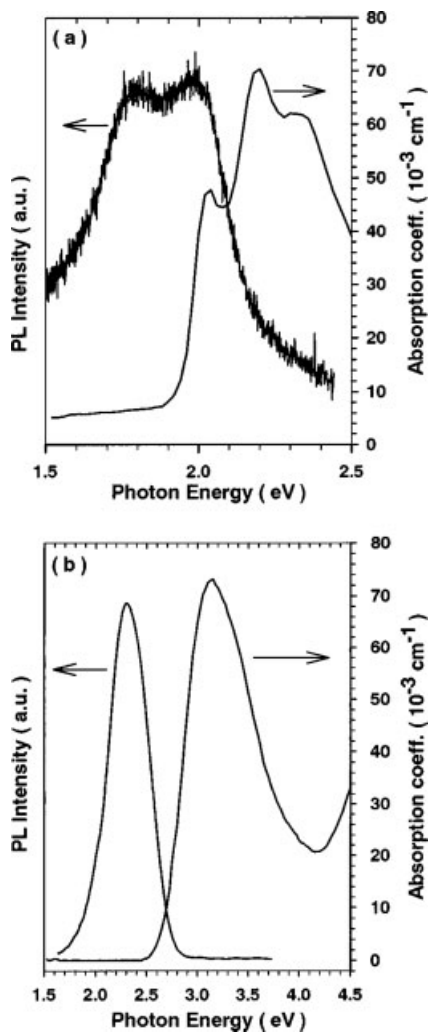


Figure 2. PL and absorption spectra of thin films of a) regioregular PTs **HT-9d** and b) **HHTT-9d**, spin-coated on a fused silica substrate. Reprinted with permission from [40]. Copyright 1998 American Institute of Physics.

were explained by pronounced interannular conformational distortion in its HH fragment ($\sim 70^\circ$ in HH and $\sim 0^\circ$ in HT fragments, as suggested by AM1 semiempirical calculations^[42]).

Pomerantz et al. prepared regioregular polymers **HHTT-11a,b** and compared them with previously synthesized^[37] irregular polymers **11a,b**. Regioregular polymers showed blue-shifts in absorption for solution and films (23–30 nm and 57–79 nm, respectively; Table 1), interpreted in terms of shorter conjugation lengths. Blue-shifts in PL and EL were much less pronounced (10–15 nm), and the PLED showed 2–4 times lower $\Phi_{\text{EL}}^{\text{ex}}$ (Table 1).^[43]

Hadziioannou and co-workers synthesized a number of regioregular alkylated polymers **HHTT-9e** and **13–15**, and demonstrated PL and EL color tuning through a variation of the length of the coplanar blocks between the HH links.^[44] They also found blue-shifts of more than 100 nm in absorption,

photoluminescence, and electroluminescence spectra, with decreasing I_{max} in the sequence **15** > **14** > **HHTT-9e** > **13**, i.e., an increasing HOMO–LUMO gap with increasing steric hindrance. The energies of absorption and emission maxima were linear functions of the inverse number of thiophene units ($1/n$) between the two consecutive HH links, in agreement with theoretical predictions that the bandgap scales linearly with the inverse of the chain length.^[45] These results clearly demonstrate that the effective conjugation length is limited by the HH links.

3.3. Emission Color Tuning in PTs

Although the first publications on EL of PATs described materials with red–orange emission (610–640 nm), later a large number of PTs with emissions covering the full visible region, i.e., from blue to red and into the near-IR (NIR), have been reported. These EL color changes were achieved by structural variations in PT side chains, as well as by controlling the regioregularity. Such wide variations of the emission color in a *homopolymer* is remarkable, and cannot be achieved in other conjugated polymers (except via copolymerization approaches). To understand the wide range of colors available from PTs, it is necessary to look at the underlying phenomena. The PT emission color directly depends on the effective conjugation length determined by the twist angle between the thiophene units. Theory predicts a large change in the bandgap of PT depending on the torsion angle between thiophene units: the difference in the bandgap of fully planar and 90° -twisted PTs is calculated to be 1.7 eV.^[46]

These observations inspired Inganäs and co-workers to exploit the principle of steric hindrance to design PTs with emission colors spanning the full visible spectrum.^[47–49] A wide range of 3-substituted and 3,4-disubstituted thiophenes were synthesized and successfully polymerized by FeCl_3 in chloroform, affording polymers **16–29**.^[22,48,50] Although the emission of substituted PTs is not very predictable due to the interplay of several factors (steric effects, regioregularity, electronic effects, side-chain crystallization, etc.), the full visible range of PL and EL emissions, from red to blue, can be covered by variations of the PT structure via substituents in the 3,4-positions (Fig. 3). A shift in bandgap can also be seen through the change of electrochemical oxidation potentials. Additional evidence for the modification of the effective conjugation in these PTs was also found from Raman spectroscopy studies (shift of the symmetrical C=C stretching, from 1442 to 1506 cm^{-1}).^[48] However, calculation of the chromatic coordinates for these polymers showed that they cover only part of the chromatic space (Fig. 4): no deep-green colors are available in this family of PTs, mostly due to the broadness of the emission spectra. Some absorption and emission data of these polymers are collected in Table 2. The large steric hindrance in **24** allowed shifting the EL down to 460 nm, with a concomitant drop in QE.

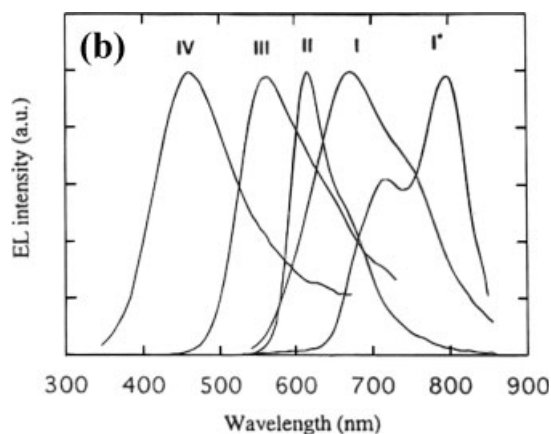
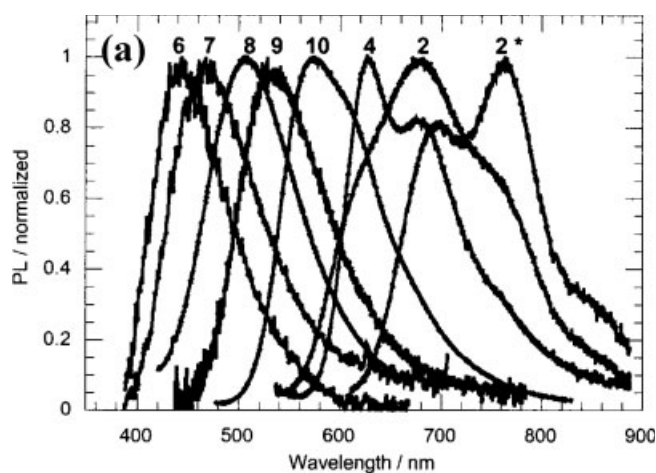
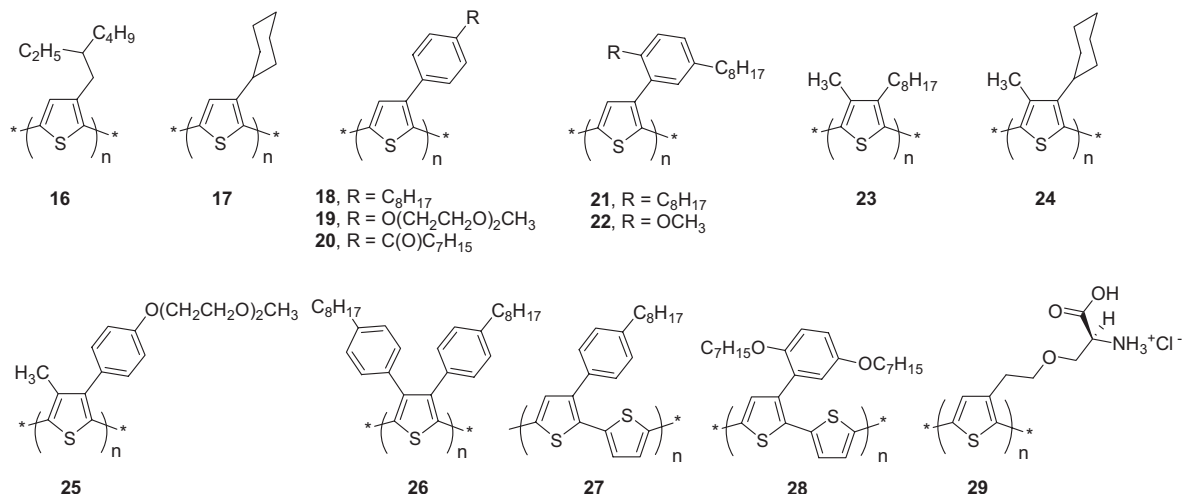


Figure 3. a) PL spectra from spin-coated films of PTs: (2) = **18**, (4) = **27**, (6) = **24**, (7) = **23**, (8) = **26**, (9) = **25**, (10) = **17**; (2*) = **18** treated with chloroform vapor at room temperature. Reprinted with permission from ref. [49]. Copyright 1999 The Royal Society of Chemistry. b) EL spectra of ITO/polymer/Ca/Al devices: (I) = **18**, (II) = **27**, (III) = **17**, (IV) = **23**; (I*) = **18** upon thermal treatment or by exposure to chloroform vapor. Reprinted with permission from [48]. Copyright 1995 American Chemical Society.

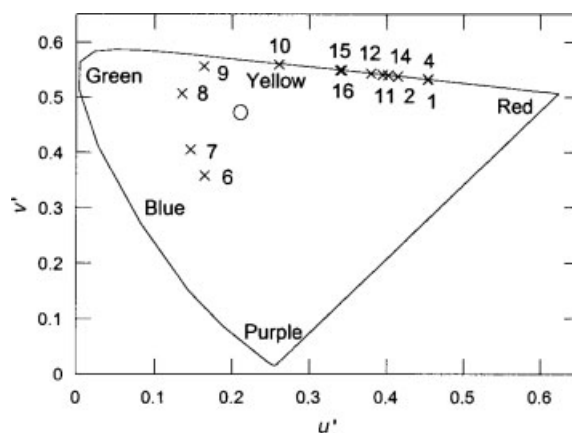


Figure 4. Chromatic coordinates for PTs: (1) = **9e**, (2) = **18**, (4) = **27**, (6) = **24**, (7) = **23**, (8) = **26**, (9) = **25**, (10) = **17**, (11) = **19**, (12) = **20**, (14) = **21**, (15) = **16**, (16) = **22**, and the white point (O). (The u' - v' coordinates are 1976 modification of Commission Internationale de l'Éclairage (CIE) xy coordinates; the white point $x=y=0.33$ corresponds to $u'=0.211$, $v'=0.474$.) Reprinted with permission from [49]. Copyright 1999 The Royal Society of Chemistry.

However, there is a limit beyond which any further distortion of the planarity of the PT chain would suppress the luminescence efficiency, even in solution. Although introducing two substituents in PT in the 3,4-positions does allow the emission to be shifted through the whole visible range and prevents interchain interactions (resulting in a smaller decrease of the quantum yield in the solid state compared to solution), highly crowded disubstituted PTs **23–26** already show very low luminescence efficiencies in solution (Table 2) because of the large distortion of the thiophene units.^[48,49]

In this context, polymer **21** represents a well-balanced material showing high PL efficiency in both solution and the solid state. The steric factor of the dialkylphenyl substituent is similar to those in **18–20**, as follows from the similarity of their absorption and emission energies. Molecular-structure

Table 2. Tuning the properties of electroluminescent PTs via conjugation control.

Polymer	Regioregularity [% H-T linkages]	M_n [g/mol]	PDI	λ_{abs} , film [nm]	λ_{PL} , film [nm]	Φ_{PL} , (CHCl ₃) [%]	Φ_{PL} , (film) [%]	λ_{EL} [b] [nm]	$\Phi_{\text{EL}}^{\text{ex}}$ (at voltage [V]) [b] [%]	Turn-on voltage [V]	Ref.
P3OT, 9e	70	35 000	3.14	506		27	4				[49]
16	~70			464	593	26	9				[49]
17	77	6000	9.3	405 [413 ^[48]]	574	27	9	555	0.01 (7)	2.4	[49,48]
18	94	8000	6.25	482 555 [a]	677 764 [a]	18	9 3 [a]				[49]
		23 000	2.26	485	670			670	0.3 (6)	1.4	[48]
19	88	7800	3.2	476 552 [a]	616 783 [a]	20	8				[49]
20	85	9400	2.9	454 555 [a]	638 795 [a]	14	10				[49]
21	90	36 000	1.94	494, 532, 577	606, 659, 720	37	24		0.1 [b] 0.7 [c]		[49,51]
22	90	46 000	3.48	470	590	29	11				[49]
23		42 000	2.17	326	468	4.6	2.2				[49]
24		26 000	2.77	303 [305 ^[48]]	442	1.3	0.8	460 [c]	0.6 (25) [c] <0.0001 (4)	7 [c]	[49,48]
25		16 000	3.0	380	532	3.8	2.8				[49]
26		21 000	3.0	346	504	1.1	1.0				[49]
27		9000	9.1	513 [518 ^[48]]	627	27	5	610	0.1 (8)	1.6	[49,48]
28		24 500	4.3	510	598	31	4				[49]
34a		2300	2.0	332	428						[74]
34b		3400	3.4	342	429, 470, 520			415, 474, 508			[74]
34c		5000	5.0	384	524						[74]
34d		6800	6.8	389	470,525						[74]
35a		4300	4.3	443	605			607			[74]
35b		5600	5.6	451	620			612			[74]

[a] Annealed film. [b] ITO/polymer/Ca/Al. [c] ITO/polymer/PBD/Ca/Al.

simulation shows that two octyloxy groups in the phenyl ring force it to rotate $\sim 90^\circ$ out of the thiophene plane.^[49] In such a configuration, the bulky side chains prevent interchain interactions between the backbones of the polymer molecules, yet allows conjugation within the backbone. Spin-coated films of **21** show clear vibronic features in both absorption ($\lambda_{\text{max}} = 532$ nm, $\Delta E = 0.18$ eV) and photoluminescence ($\lambda_{\text{max}} = 659$ nm, $\Delta E = 0.16$ eV) spectra, which, together with a very small Stokes shift of only 0.10 eV, suggest a highly ordered film (Table 2). Several PLEDs prepared with this polymer with structures ITO/**21**/Ca/Al and ITO/**21**/PBD/Ca/Al configurations (PBD: 2-(4-biphenyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole) showed $\Phi_{\text{EL}}^{\text{ex}} = 0.1$ % and 0.7 %, respectively.^[51]

The highly regioregular polymer **18** obtained by oxidative polymerization with FeCl₃ (94 \pm 2 % HT) requires some special attention because it exists in two different forms, an amorphous form and a semicrystalline form with an interchain stacking distance of 5 Å. In its pristine amorphous form, the absorption maximum of spin-cast films is 493 nm (2.68 eV).^[22,52] On treating the films with chloroform vapor,

the maximum was shifted to 602 nm (2.06 eV), and the spectrum showed a fine vibronic structure with $\Delta E = 0.19$ eV, typical of a more-planar ordered conformation (Fig. 5a). This conversion could also be achieved by heating the film and, in contrast to the widely observed thermochromism in PTs, is irreversible, indicating the formation of a thermodynamically stable semicrystalline form. The PLEDs prepared with spin-coated **18** show red-light EL centered at 670 nm (1.85 eV). When the diodes are heated, the emission is shifted continuously well into the NIR as a function of heating time and increasing temperature. On prolonged heating, **18** is converted into an ordered film with an EL emission maximum at 800 nm (1.55 eV) (Fig. 5b).^[53] Even more rapid and pronounced ordering of the polymer occurs on simple exposure to chloroform vapor.

As an alternative strategy, the high luminescence efficiency observed in solution can be preserved by incorporating the polymer into an inert solid matrix. Thus, polymer **29**, when blended with a poly(acrylic acid) (PAA) matrix, shows no phase separation due to attractive ionic/hydrogen bonding in-

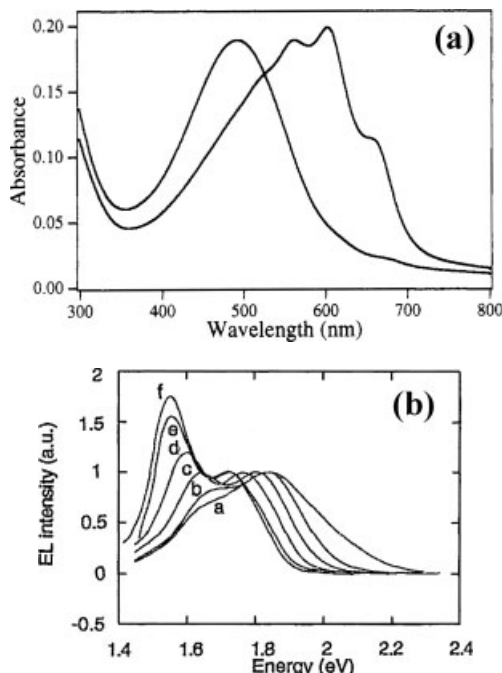
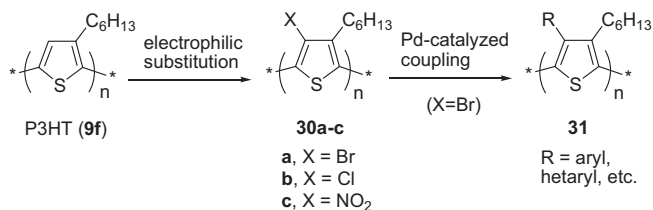


Figure 5. a) UV-vis absorption spectra of a spin-coated film of **18** on glass ($\lambda_{\text{max}}=493$ nm) and the same film treated with chloroform vapor ($\lambda_{\text{max}}=602$ nm, $\Delta E=0.19, 0.15, 0.19$ eV). Reprinted with permission from ref. [22]. Copyright 1994 American Chemical Society. b) EL of ITO/**18**/Ca/Al device at different heating temperatures: (a) unheated device; (b) $T=100^\circ\text{C}$, 6 s; (c) 100°C , +6 s; (d) 200°C , +10 s; (e) 200°C , +20 s; (f) treated with chloroform before evaporating the contact. Reprinted with permission from [53]. Copyright 2001 American Institute of Physics.

interactions between the PT and the matrix.^[51,54] As a result, the PL QE of **29**/PAA (1:100) was 16 % (as compared to 26 % in solution), much higher than in **29** films (4 %). Unfortunately, no PLED with this material was reported, and one can suggest that the performance of such a device would be low due to the very low concentration of the emitting (and conducting) component.

Another approach to tuning the optical properties and improving the emission of PT derivatives in the solid state was proposed by Holdcroft and co-workers.^[55] They used post-functionalization of P3HT **9f** by electrophilic substitution reaction (to afford polymers **30**) followed by Pd-catalyzed coupling (Suzuki, Stille, or Heck methodologies) to afford polymers **31**.^[56] In this case, functionalization with bulky aryl substituents (**31**) hindered the interchain interactions and allowed a substantial increase of Φ_{PL} in the films from 1.6 % to 13–22 %.



3.4. Blends of PTs

It was demonstrated that blends of 3- and 3,4-substituted PT derivatives of different bandgaps gave rise to a voltage-controlled variable-color light source.^[57] Because of different turn-on voltages of high- and low-bandgap polymers, the emission color can be potentially tuned by applying different biases: when a relatively low voltage was applied to the polymer blend PLED, the low-bandgap polymer started to emit first, followed by higher bandgap emitters as the voltage increased. An effective phase separation, however, is required to minimize Förster energy transfer to the low-bandgap species. A blend of PTs **24/27** (50:50) at 22 V showed EL at ca. 630 nm originating from the lower bandgap polymer **27**. When the voltage was increased, an additional emission at ca. 440 nm (corresponding to the EL of the higher-bandgap polymer **24**) appeared, reaching a comparable intensity at 27 V.^[57,58]

Another combination of PTs in a blend, **23/17/27**/poly(methyl methacrylate) (PMMA) (10:4:1:1), produced EL emission in the ITO/polymer blend/PBD/Ca/Al device at 20 V, very close to the equienergy white point as defined by the CIE, while providing a relatively high $\Phi_{\text{EL}}^{\text{x}}=0.4\text{--}0.6\%$ (at 20 V) (Fig. 6).^[59] PMMA was used in this case to diminish the energy transfer from the high-bandgap to the low-bandgap polymer. Several other inert polymer matrixes (e.g., polystyrene, polycarbonate, poly(vinyl chloride), poly(2,6-dimethyl-1,4-phenyleneoxide)) showed similar effects.^[60]

Destri et al. reported the electrochemical synthesis of polymer **32** that produced a mixture of oligomers up to the dodecamer. Whereas the ITO/**32**/Ca/Al device emits red light (580–650 nm) comparable to that for regioregular PATs, blending **32** with poly(*N*-vinylcarbazole) (PVK) and PBD re-

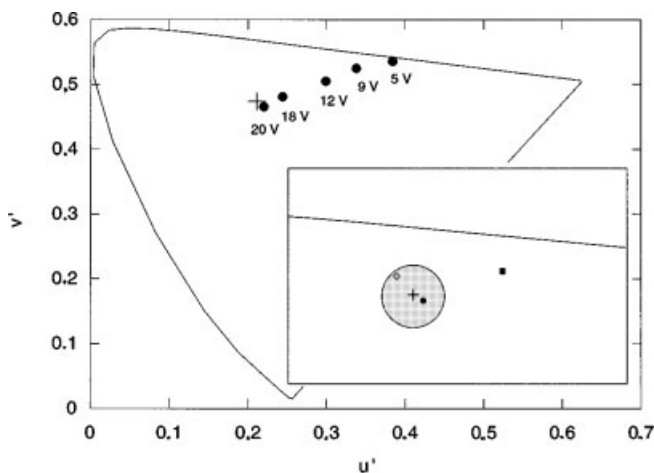
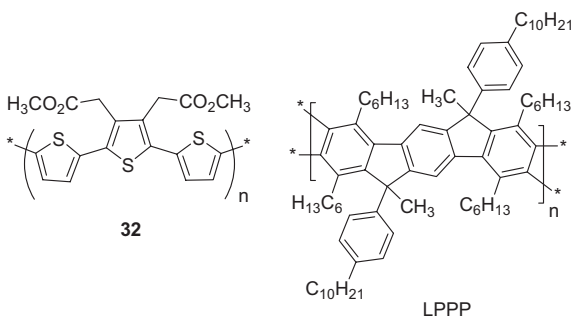


Figure 6. Chromaticity diagram showing the color of the LED with **23/17/27**/PMMA (10:4:1:1) polymer blend at different voltages. Inset: magnified part of the chromaticity diagram; the shaded circle represents the area which is defined as white (radius 0.028 and centered at equienergy white point); the u' - v' coordinates are from the 1976 modification of CIE xy coordinates; the white point $x=y=0.33$ corresponds to $u'=0.211$, $v'=0.474$). Reprinted with permission from [59]. Copyright 1996 American Institute of Physics.

sulted in a white-light-emitting diode with 0.03 % EL efficiency.^[61] Blending with PBD also effectively increased the $\Phi_{\text{EL}}^{\text{ex}}$ of highly sterically hindered disubstituted PT **24**, from <0.0001 % to 0.6 %, with no change in EL maximum.^[48]

The emission spectrum of some PT/PBD polymer bilayer devices cannot be explained by a linear combination of emissions of the components. Thus, efficient white-light emission of the PLED ITO/**27**/PBD/Al ($\Phi_{\text{EL}}^{\text{ex}}$ = 0.3 % at 7 V) consisted of blue (410 nm), green (530 nm), and red–orange (620 nm) bands. Whereas the first and the last EL peaks are due to EL from the PBD and the PT layers, respectively, the green-light emission probably originates from a transition between electronic states in the PBD layer and hole states in the polymer layer.^[62] Similar results (additional green–blue EL at ~495 nm) were demonstrated by the PLED ITO/**27**/PBD/Ca/Al.^[63]

Blending low-bandgap PTs with other electroluminescent polymers was employed to increase the EL efficiency of a PLED, and it was demonstrated that even small additions of PTs can improve the device performance. $\Phi_{\text{EL}}^{\text{ex}}$ of red-light-emitting ITO/P3HT (**9f**)/MEH-PPV/Ca diodes (P3HT: poly(3-hexylthiophene); MEH-PPV: poly(2-methoxy-5-(2-ethylhexyloxy)-*p*-phenylene vinylene)) initially increased with P3HT content and went through a maximum at 1 wt.-% P3HT with $\Phi_{\text{EL}} = 1.7$ %,^[64] which is 2–3 times higher than in the neat ITO/MEH-PPV/Ca diode and three orders-of-magnitude higher than in the ITO/P3HT (**9f**)/Ca diode. Later, List et al. reported a similar observation of efficient yellow-light emission from the blend of blue-light-emitting ladder poly(*p*-phenylene) (LPPP) with small additions (0.5–2 %) of orange-light-emitting **9d**.^[65,66] When the concentration of P3DT **9d** was as small as 1 %, the external EL efficiency of the Al/polymer blend/ITO device was also significantly higher ($\Phi_{\text{EL}}^{\text{ex}}$ = 4.2 %) than in pure LPPP (2 %).



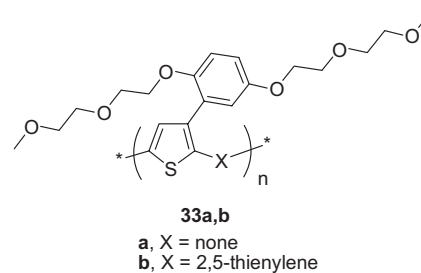
3.5. PTs for Advanced LED Applications

Apart from tunable color emission covering the full visible range, white-light emission from precisely prepared blends of PTs with different bandgaps, and internal color conversion of other LEPs by adding small amounts of PTs, there are several other aspects fueling the interest in PTs for PLEDs. PTs are a classic example of conjugated polymers with intrinsically one-dimensional polymer chains which, when aligned, could show anisotropy in macroscopic properties, such as electrical trans-

port or optical properties. Polarized EL with $\Phi_{\text{EL}}^{\text{ex}} = 0.05$ % was observed in the multilayer Langmuir–Blodgett (LB) film PLED ITO/**10c**/Al, with an EL ratio between the parallel and perpendicular orientations of 1.3.^[67] An even higher ratio of 2.4 was achieved with an ITO/**27**/Ca/Al diode made from a stretch-oriented polymer film.^[68] However, this anisotropy is quite low, considering that a ratio of >60:1 was achieved for emission of MEH-PPV (in photoluminescence spectra).^[69]

Among other specific applications of PTs as light-emitting materials, it is necessary to mention microcavity LEDs prepared with PTs **27** and **21**^[70], and nanometer-scale LEDs demonstrated for a device with a patterned contact structure and PT **27** blended in a PMMA matrix, which emits from 50–200 nm phase-separated domains.^[71]

Two polymers with hydrophilic oligo(ethylene oxide) side chains, **33a,b**, have been studied in light-emitting electrochemical cells (LECs).^[72] Under applied bias, *p*-doping of the EL polymer took place at the anode, whereas at the opposite electrode the cathode material was reduced, although the reported $\Phi_{\text{EL}}^{\text{ex}}$ was relatively low (~10⁻² %).

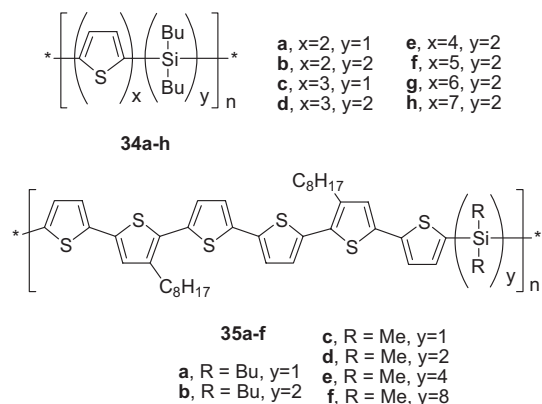


Inganäs and co-workers demonstrated that PTs can be used as host materials in electrophosphorescent PLEDs.^[73] The large bandgap of dialkyl-PT **23** (3.2 eV) allows efficient energy transfer to the red phosphorescent dye PtOX (platinum(II) 2,8,12,17-tetraethyl-3,7,13,18-tetramethyl porphyrin), as demonstrated by complete replacement of the blue-light PT emission (480 nm) with the red-light-emission (650 nm) of the complex. The triplet excitons transferred to PtOX can decay radiatively, which results in a 12 times increase in the current efficiency of the corresponding PLED upon introducing the dye (0.7 cd A⁻¹).

4. Electroluminescent Thiophene Block Copolymers and Glass-Forming Oligomers

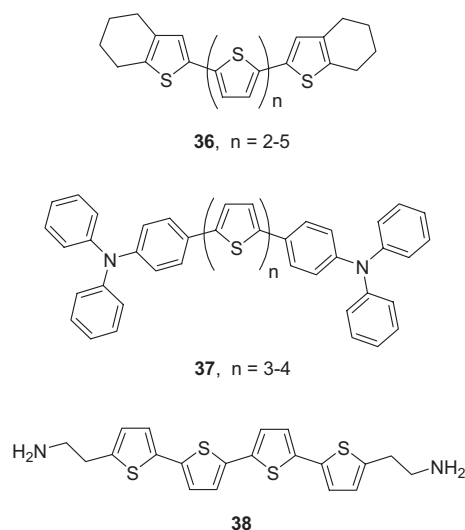
The above approaches used the idea of conjugation-length control in PTs by distorting the polymer backbone with bulky substituent side groups. Hadziioannou and co-workers demonstrated PL and EL tuning via exciton confinement with block copolymers **34a–d** and **35a–f** containing oligothiophene and alkylsilanyl units.^[74] Precise control of the conjugation length of the oligothiophene blocks, interrupted by silanyl units, allowed tuning the emission from blue to orange–red (Table 2). Later, Yoshino et al. reported similar extended

block-copolymers **34d–h** that showed changes in EL color from green to red with increasing oligothiophene block length.^[75]

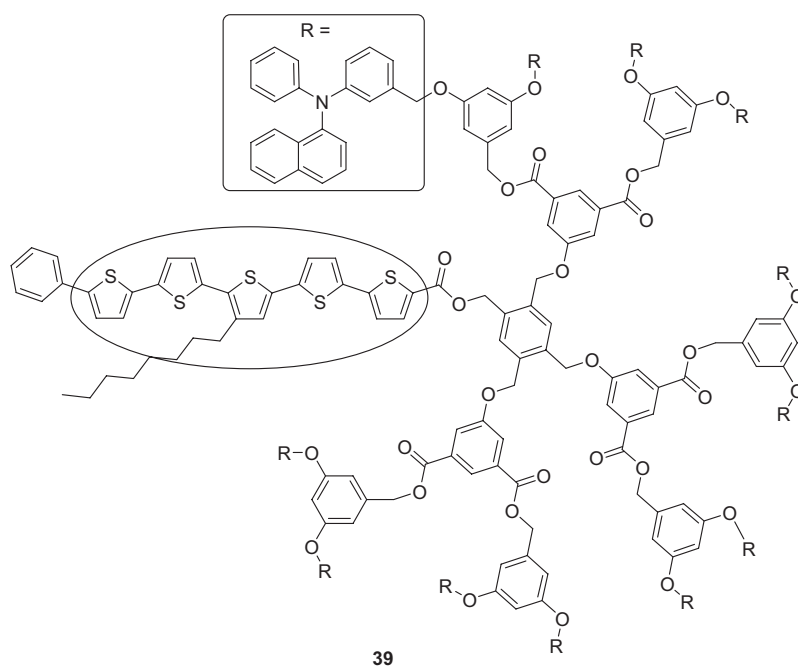


Highly ordered and crystalline low-molecular-weight oligothiophenes usually result in poorly performing LEDs, while several publications demonstrate electroluminescence from amorphous oligothiophene-based LEDs. For a deeper understanding of the correlation of effective conjugation length and the electrical properties and emission in PTs, Geiger et al. studied a series of end-capped oligothiophenes **36**.^[76] The ITO/**36**/Al devices prepared by vacuum sublimation of oligomers showed relatively low turn-on voltages of ca. 2.5 V and moderate current densities (e.g., 7 mA cm⁻²) with maximum efficiency at ca. 8 V. However, the EL efficiency was quite low (with an estimated internal efficiency of $\Phi_{EL}^{int} \approx 10^{-2}$ – 10^{-3} %). LEDs showed a red-shift in the EL peak with an increasing number of thiophene units ($n=3 \rightarrow n=5$), and a linear dependence of the EL band energy on the inverse number of monomer units. Averaging over the EL, PL, and absorbance data, the effective conjugation length was estimated as approximately 9–10 thiophene units. End-capping of terthiophene and quaterthiophene with triphenylamino groups (**37**), which led to stable amorphous glasses, can afford relatively high luminescence efficiencies of 0.03 and 1.1 lm W⁻¹, respectively (at a luminance of 300 cd m⁻²).^[77] A double-layer device with oligomer **37** ($n=3$) as an emitting layer and aluminumtris(8-hydroxyquinoline) (Alq₃) as an electron-transporting layer showed significantly improved performance, exhibiting a maximum luminance of 13 000 cd m⁻² at a driving voltage of 18 V. Undoubtedly, improving the hole-transport properties in these oligomers by end-capping with triphenylamino fragments is also an important factor. Terthiophene end-capped with 2-aminoethyl groups was also used in hybrid organ-

ic–inorganic perovskite materials. When **38** was incorporated within lead halide perovskite layers in an ITO/**38**:PbCl₄/OXD7/Mg/Ag device (OXD7: 1,3-bis(4-(*tert*-butylphenyl)-1,3,4-oxadiazolyl)phenylene), a bright green-light emission (530 nm) from the organic layer was found.^[78]



A quinquethiophene oligomer unit was used as a core in the light-emitting dendrimer **39**.^[79] In this material, an excitation of the peripheral amines at 310 nm results in energy transfer to the highly luminescent fluorophore at the core of the dendrimer with subsequent green-light emission ($\lambda_{PL} = 550$ nm) exclusively from the oligothiophene. In the LED that contains PBD as the electron-transporting material, the hole transport occurs solely through peripheral triarylaminos, whereas the



core oligothiophene plays the role of a light emitter. The EL spectrum was essentially identical to PL ($\lambda_{\text{EL}} = 560$ nm) with no emission from either PBD (390 nm) or peripheral amines (425 nm), and the maximum $\Phi_{\text{EL}}^{\text{ex}}$ was 0.12 %.

5. Oligomers and Polymers with the Thiophene-*S,S*-Dioxide Moiety as Emissive and Electron-Transport Materials

Poly- and oligothiophenes are generally *p*-type (hole-transporting) semiconductors. Recently Barbarella et al. reported a novel approach to tailoring the frontier orbitals of thiophene oligomers through chemical transformation of the thiophene ring into the corresponding thiophene-*S,S*-dioxide (via oxidation with 3-chloroperbenzoic acid).^[80,81] This modification results in “de-aromatization” of the thiophene unit and increases the electron affinity and electron-transport properties of the material. A comparison of two quaterthiophenes **40** and **41** indicates that a single thiophene-*S,S*-dioxide moiety leads to only a slight increase of the oxidation potential (from 0.95 V to 1.04 V versus Ag/AgCl), whereas the reduction potential is drastically shifted from -2.12 to -1.28 V, resulting in a bandgap contraction of more than 0.7 eV.^[80] Another feature of this modification is a reduced aggregation tendency, resulting in decreased exciton migration to the non-radiative centers. Consequently, oligomers incorporating thiophene-*S,S*-dioxide units possess good photoluminescence properties in solution and the solid state, as well as high EL efficiency (for PTs). Particularly interesting in this case are the oligomers with a centrally located thiophene-*S,S*-dioxide unit, for which the solid-state PL quantum yields were reported to be as high as 37 % for pentathiophene **42f**,^[82] 45 % for terthiophene **42d**,^[83] and even 70 % for phenylenethiophene oligomer **42c**.^[84]

Incorporation of electron-deficient thiophene-*S,S*-dioxide units into electron-rich conjugated oligomers (**42**) predictably results in reduction of the material's bandgap. This allows variation of both the absorption and PL energies over a wide range ($\lambda_{\text{max}}^{\text{abs}} \sim 310\text{--}540$ nm, $\lambda_{\text{max}}^{\text{PL}} \sim 400\text{--}725$ nm) to cover the full visible range, from the UV to the NIR (Fig. 7).^[80,84] The alternating donor-acceptor polymers obtained by chemical polymerization of

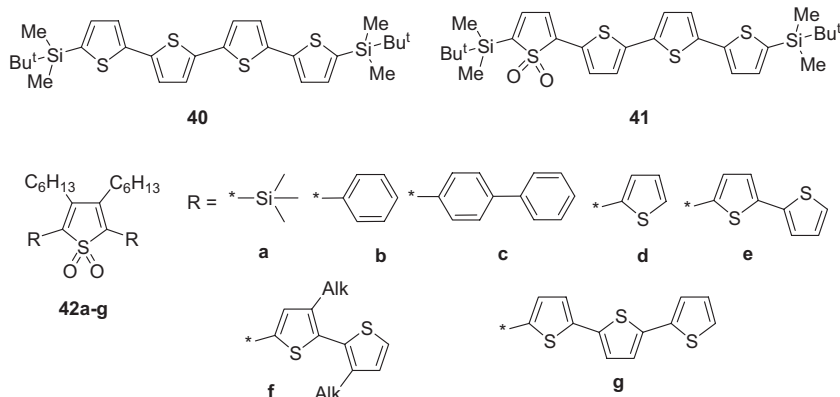


Figure 7. Emission of cast films of oligomers **42a–g** under UV irradiation. Reprinted with permission from [84]. Copyright 2000 American Chemical Society.

oligomers **42d** and **42f** with FeCl_3 showed PL in the NIR region (801 and 910 nm, respectively), although the quantum yields were not reported for these materials.^[84] A non-optimized LED with **42f** as an active layer (ITO/**42f**/Ca/Al) showed a luminance of ~ 100 cd m^{-2} at 7 V and a quite low EL efficiency of 0.03 cd A^{-1} at ~ 180 mA cm^{-2} .^[85] However, further studies showed that these parameters can be sufficiently improved by blending **42f** with PVK and introducing a PEDOT layer: the PLED built with a configuration of ITO/PEDOT/(**42f**/PVK, 85:15)/Ca/Al showed a maximum luminance of ~ 200 cd m^{-2} at 7 V and EL efficiency of ~ 0.9 cd A^{-1} at 3 mA cm^{-2} .^[82]

Thiophene–thiophene-*S,S*-dioxide copolymers **43a,b** were reported by Berlin et al.^[86] The polymers absorbed at 535 nm (bandgap energy $E_g = 2.3$ eV) in chloroform solution and in films (which is consistent with their electrochemistry: oxidation potential $E_{\text{ox}} \approx 0.40\text{--}0.50$ V and reduction potential $E_{\text{red}} \approx -1.75\text{--}1.8$ V; $\Delta E \approx 2.2\text{--}2.25$ V) and emitted at 650 nm ($\Phi_{\text{PL}}^{\text{film}} \sim 1\%$). Such a high bandgap (which exceeds that of PEDOT homopolymers by ~ 0.6 eV) strongly suggests a disruption of the conjugation, possibly due to steric interactions. The EL emission spectrum was entirely the same as PL emission, and $\Phi_{\text{EL}}^{\text{ex}} = 0.01\%$ at 100 cd m^{-2} was found for an ITO/(TPD/**43a**/PC, 40:40:20)/Ca diode (TPD: tetraphenylbenzidine, PC: bisphenol A polycarbonate).

These pioneering works stimulated recent research activities towards incorporation of the thiophene-*S,S*-dioxide unit into various copolymers, and PLEDs built with such copolymers were reported by several groups. Charas et al. studied PLEDs based on copolymer **44** (obtained by Suzuki coupling of 2,5-dibromothiophene-*S,S*-dioxide with the diboronic ester of 9,9-bis(2-ethylhexyl)fluorene^[87]) and its blends with poly(9,9-dioctylfluorene) homopolymer (PFO).^[88] Copolymer **44** emitted orange light ($\lambda_{\text{PL}}^{\text{film}} = 615$ nm), and there was a strong suppression of PL quantum yield going from solution to the solid state, suggesting strong interchain inter-



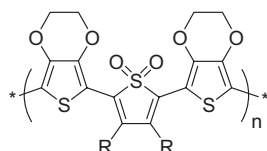
actions due to the planar backbone ($\Phi_{\text{PL}}^{\text{cyclohexane}} = 19\%$, $\Phi_{\text{PL}}^{\text{film}} = 0.5\%$). A single-layer ITO/44/Ca PLED exhibited quite low EL efficiency ($\Phi_{\text{EL}}^{\text{ex}} = 2.2 \times 10^{-4}\%$), which was attributed to a combination of low PL efficiency and charge-transport limitations. Upon inserting a hole-injection PEDOT layer, the EL efficiency was increased to $\Phi_{\text{EL}}^{\text{ex}} = 9 \times 10^{-4}\%$ and the maximum luminance increased from 0.2 cd m^{-2} to about 5.3 cd m^{-2} . The obviously unbalanced charge transport in these devices was improved by blending 44 with PFO, allowing an increase in $\Phi_{\text{EL}}^{\text{ex}}$ up to 0.21% (for an ITO/PEDOT/(PFO/44, 95:5)/PBD/Ca architecture) and a decrease in the turn-on voltage from 16 V to 5–5.5 V. Remarkably, the EL of the blend in this case was almost exclusively from the copolymer 44, in spite of the low content of the latter.

The same Suzuki methodology was used to synthesize a similar copolymer 45.^[89] The polymer showed a solvent-dependent green–yellow–light emission (from 545 nm in THF to 565 nm in chloroform), as often observed for polar chromophores. The PL QE also varied with the solvent (from 11% in THF to 21% in decalin), but, in contrast to copolymer 44, no strong decrease in emission efficiency was observed in the solid state ($\Phi_{\text{PL}}^{\text{film}} = 13\%$) that could be attributed to a hindering effect of substituents at the thiophene ring, preventing a strong aggregation. A ITO/PEDOT/45/Ca/Al LED showed

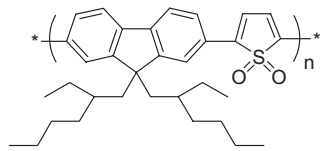
a turn-on voltage of ca. 10 V with a maximum brightness of 340 cd m^{-2} at 22 V and moderate $\Phi_{\text{EL}}^{\text{ex}} = 0.14\%$.

Beaupré and Leclerc reported fluorene–thiophene copolymers in which fluorene and thiophene-*S,S*-dioxide fragments were separated by one or two thiophene units (46 and 47, respectively).^[90] The electronic effect of an additional thiophene unit (the system can be viewed as an alternating donor–acceptor polymer) and the planarization factor known for longer oligothiophene units resulted in some bandgap contraction. These copolymers are both p- and n-dopable, as follows from their electrochemistry, with bandgaps of 2.2 and 2.0 eV for 46 and 47, respectively. The PLEDs, fabricated with the configuration ITO/LiF/polymer/PBD/LiF/Al/Ag, showed rather low turn-on voltages of 4 V, but the maximum brightnesses (120 cd m^{-2} at 7 V and 15 cd m^{-2} at 8 V, for 46 and 47, respectively) were lower than that for copolymer 45. Although highly efficient ($\Phi_{\text{PL}}^{\text{film}} \approx 40\text{--}70\%$) solid-state PL was demonstrated from some oligothiophenes and oligophenylenes containing thiophene-*S,S*-dioxide units,^[84] the efficiency of similar fluorene copolymers was much lower. The combination of thiophene and thiophene-*S,S*-dioxide units in a copolymer allows tuning of the emission color from green to pure red.^[90,91] However, the PLEDs fabricated with these materials often show a rather low $\Phi_{\text{EL}}^{\text{ex}} < 0.01\%$ that further decreases with an increasing number of thiophene units.

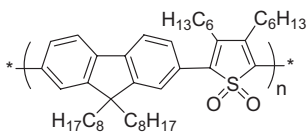
Similar results (a significant decrease of the PL QE) were observed for thiophene–thiophene-*S,S*-dioxide copolymers containing 3,6-dimethoxyfluorene (48^[92]) and carbazole units (49^[93]) (with $\Phi_{\text{PL}} = 20\text{--}25\%$ in solution).



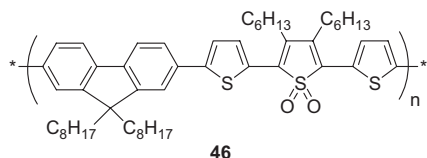
43a,b
a, R = C₆H₁₃
b, R = C₁₂H₂₅



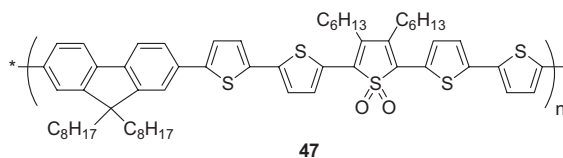
44
Abs: 445 nm, PL: 615 nm, Orange



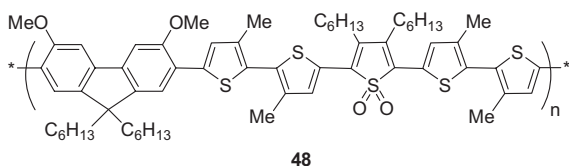
45
Abs: 411 nm, PL: 551 nm
EL: 550 nm Green-yellow



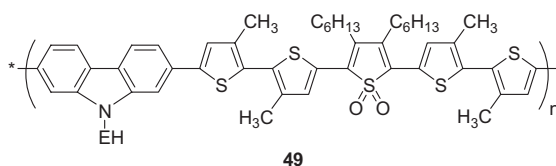
46
Abs: 509 nm, PL: 610, 660 nm, EL: 610, 650 nm, Red-orange



47
Abs: 547 nm, PL: 666, 708 nm, EL: 668, 708 nm, Red



48
UV: 392, 478 nm, PL: 662 nm, Red



49
Abs: 512 nm, PL: 671 nm, $\Phi_{\text{PL}} = 25\%$

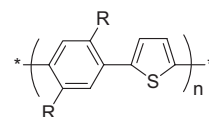
6. Copolymers of Thiophenes with Other Conjugated Moieties

The largest variety of emission wavelengths and the most efficient EL materials were created via copolymerization of thiophene with other conjugated monomers. Thus, “diluting” the thiophene units in the polymer chain with other aromatic moieties enlarges the material bandgap, affording blue-light-emitting thiophene copolymers, and in many cases suppresses aggregation in the solid state (thus improving the emission

efficiency). Copolymerization with electron-deficient comonomers results in a bandgap reduction (well-known for alternating donor (D)–acceptor (A) polymers, DADA), thus affording NIR-emitting materials. At the same time, whereas the emission wavelength in PT copolymers can be predicted reasonably well (based on the known polymer-bandgap-control principles),^[2] the solid-state PL and, particularly, the EL efficiencies are still a subject of a mostly purely empirical approach.

6.1. Thiophene-Phenylene Copolymers

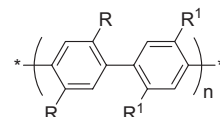
Salaneck and co-workers first reported EL from the alternating phenylene–thiophene copolymer **50a**. Its bandgap, ionization potential, and electron affinity, calculated with the valence effective Hamiltonian (VEH) method, are 3.08, 5.29, and 2.22 eV, respectively.^[94] These values are between the corresponding values for higher bandgap poly(*p*-phenylene) (PPP) (3.28, 5.43, and 2.15 eV^[95]) and lower bandgap PT **3** (2.2,^[96a] 5.0, and 3.4 eV^[96b]). Quite unexpectedly, AM1 calculations predict the interannular torsion angles in this copolymer (due to steric hindrance of the heptyl side groups) to be substantially larger (50°) than that of PPP (23°); nevertheless, its bandgap is smaller than that of PPP. Phenylene–thiophene copolymers **50b** and **50a** emit blue light at ca. 450–475 nm, with somewhat different reported $\Phi_{\text{EL}}^{\text{ex}}$ values of 0.2 %^[97] and 0.03 %,^[98] respectively, for ITO/polymer/Ca configurations. It has also been shown that the efficiency of the device can be substantially improved (up to 2 %) by blending of **50a** with substituted C7C5-PPP (1:10), which probably reduces the self-quenching effect.^[97] This is among the highest EL efficiencies reported for thiophene-based LEPS.



50a,b

a, R = C₇H₁₅; Abs: ~330 nm, PL: ~450 nm,
EL: ~475 nm, $\Phi_{\text{EL}}^{\text{ex}}$ = ~0.2%, Blue

b, R = C₅H₁₁; Abs: 335 nm, PL: 455 nm,
EL: 455 nm, $\Phi_{\text{EL}}^{\text{ex}}$ = 0.03%, Blue

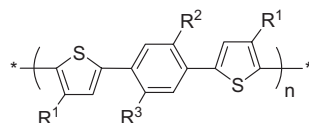


PPP, R = R¹ = H
C7C5-PPP, R = C₇H₁₅,
R¹ = OC₅H₁₁

A related series of copolymers **51** containing thiophene–phenylene–thiophene repeat units have been reported by Huang and co-workers.^[99–101] Polymers were obtained via FeCl₃ oxidation of thiophene–phenylene–thiophene trimers that were synthesized by Pd-catalyzed coupling of 1,4-R₂,R₃-2,5-dibromobenzenes with the corresponding 3-R₁-2-thienylzinc chlorides. By changing the steric effect of substituents R₁ and R₂, the polymer emission was tuned from greenish-yellow to pure green. While retaining much of the substituted PT character (e.g., good hole-transport properties and stability), these materials exhibit significantly improved fluorescence efficiency in the solid state (Φ_{PL} up to 29 %) that leads to $\Phi_{\text{EL}}^{\text{ex}}$ of up to 0.1 % for ITO/**51**/Ca PLEDs (Table 3).

Twisted 1,1-binaphthyl units in alternating oligothiophene-containing copolymers **52a–c** and **53a,b** interrupt the conjugation, which could prevent the self-quenching processes in the solid state. A variation in the length of the oligothiophene segment from one to seven thiophene rings predictably reduced the polymer bandgap and tuned the emission color from yellow–green to red (Table 4).^[102] A single-layer device, ITO/**52b**/Al, emitted orange light (λ_{EL} at 568 nm with a shoulder at 590 nm) with a turn-on voltage of 5.7 V, luminance of 25 cd m⁻² at 8.0 V, and $\Phi_{\text{EL}}^{\text{ex}}$ = 0.005 %.^[103]

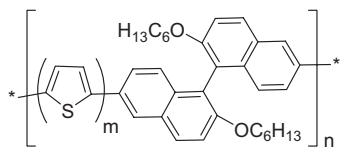
Table 3. Tuning the properties of substituted phenylenethiophene copolymers.



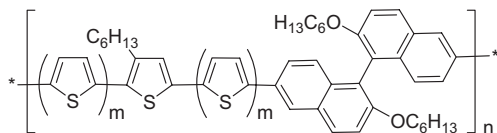
51

R ¹	R ²	R ³	M _n [g mol ⁻¹]	PDI	$\lambda_{\text{max}}^{\text{abs}}$ [nm]	$\lambda_{\text{max}}^{\text{PL}}$ [nm]	Φ_{PL} [%]	$\Phi_{\text{EL}}^{\text{ex}}$ [%]	Turn-on voltage [a] [V]	Ref.
<i>n</i> -C ₆ H ₁₃	CH ₃	CH ₃	20 400	2.92	340	477	10	0.004	17	[99]
			12 600	1.48	346	470	15 ± 1			[101]
<i>n</i> -C ₆ H ₁₃	H	H	19 700	2.74	396	524	20	0.02	13	[99]
			31 200	2.31	378	505	22 ± 2			[101]
<i>n</i> -C ₆ H ₁₃	OC ₁₀ H ₂₁	OC ₁₀ H ₂₁	14 600	1.92	430	530	29	0.1	8	[99]
			26 100	1.27	405	520	27 ± 3			[101]
<i>c</i> -C ₆ H ₁₁	CH ₃	CH ₃			360	466	6			[99]
<i>c</i> -C ₆ H ₁₁	H	H			376	495	11			[99]
<i>c</i> -C ₆ H ₁₁	OC ₁₀ H ₂₁	OC ₁₀ H ₂₁			410	505	16	0.05	9	[99]
<i>p</i> -(<i>n</i> -C ₄ H ₉)Ph	<i>n</i> -C ₁₀ H ₂₁	<i>n</i> -C ₁₀ H ₂₁	82 300	2.19	442	532	11	(~0.1)	(~7)	[100]
<i>p</i> -(<i>n</i> -C ₄ H ₉)Ph	CH ₃	2-ethylhexyl	68 500	1.51	426	538	12	(~0.1)	(~7)	[100]
<i>p</i> -(<i>n</i> -C ₄ H ₉)Ph	2-ethylhexyl	2-ethylhexyl	43 600	1.68	429	533	11	0.1	7	[100]

[a] ITO/polymer/Ca.



52a: m = 1
52b: m = 2
52c: m = 4



53a: m = 2
53b: m = 3

Table 4. Properties of binaphthyl-linked thiophene block copolymers **52a–c** and **53a,b** with different conjugation lengths in dichloromethane (DCM).

Compound	$\lambda_{\max}^{\text{abs}}$ [nm]	$\lambda_{\max}^{\text{PL}}$ (DCM) [a] [nm]	Φ_{PL} (DCM) [a,b] [%]
52a	368	421, 446, 475sh	54
52b	406	463, 498	26
52c	440	515, 549sh	23 (19)
53a	434	530, 568sh	5.4 (23)
53b	454	545, 583, 631sh	6.5 (7.2)

[a] Excitation at 380 nm (sh: shoulder). [b] Values in parenthesis correspond to excitation at the longest wavelength absorption maximum.

6.2. Thiophene–Fluorene Copolymers

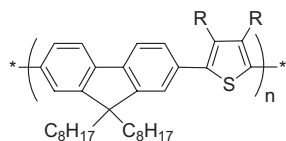
PFs are an important class of LEPs with high thermal, photo-, and environmental stability and efficient, bright blue-light emission. This last fact stimulated a number of researchers to develop fluorene–thiophene copolymers for light-emitting applications.

In addition to an expected increase of PL QE in such copolymers, such a combination of electron-rich thiophene units with relatively electron-deficient fluorene units should modify the bandgap of the material (and thus tune the emission) and improve the charge injection/transport balance compared to fluorene homopolymers.

Lévesque, Leclerc, and co-workers have efficiently tuned the emission color from blue to green and yellow by introducing various thiophene units in alternating fluorene copolymers **54–58**.^[92,104] Changing the nature of the comonomer unit from the relatively electron-deficient phenylene to very electron-rich bis(ethylenedioxy)thiophene affects the bandgap of the polymer (and thus, the emitting color) as well as the charge-transport properties, thus influencing the performance of the PLEDs based on the corresponding copolymers. The highest brightness achieved for bithiophene-based copolymer **55** was 4.5 cd m^{-2} for a neat copolymer and 18 cd m^{-2} for a blend with 20% of hole-transport material TPD, which is far too low for a practical application.

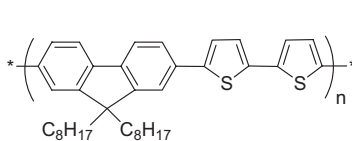
Huang's group has systematically studied the structure–property relationships of fluorene–thiophene-based conjugated polymers **59–62**.^[105,106] In contrast to PT homopolymers, the regioregularity of the bithiophene fragments in the studied copolymers show little influence on the optical bandgap (**61** and **62**, respectively: $E_g = 2.49$ and 2.58 eV ,^[106] or 2.57 and 2.60 eV ^[107,108]) or the emission maxima, but the HH copolymer **62** was significantly more thermally stable.

All copolymers showed reversible n- and p-doping in cyclic voltammetry (CV) experiments. A schematic diagram showing the HOMO and LUMO energy levels relative to the work functions of the electrode materials used in EL devices is given in Figure 8.^[108] A single-layer ITO/**62** (100 nm)/Ca device emitted green light (493, 515 nm) with a high turn-on voltage of 20 V. The introduction of a PVK hole-transport layer decreased the turn-on voltage to 8 V and increased the maximum $\Phi_{\text{EL}}^{\text{ex}}$ from 0.05% to 0.6%^[105] (although a less-pronounced increase was observed for other polymers of the



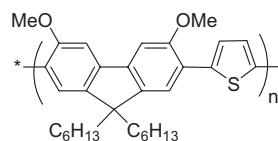
54a,b

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



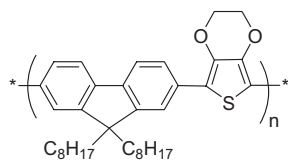
55

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



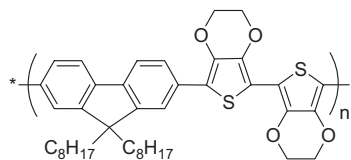
56

Abs: 446 nm, PL: 510 nm
Greenish blue



57

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



58

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

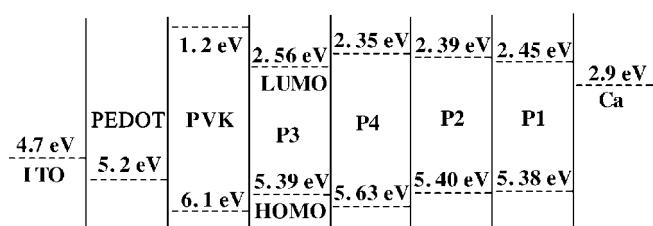
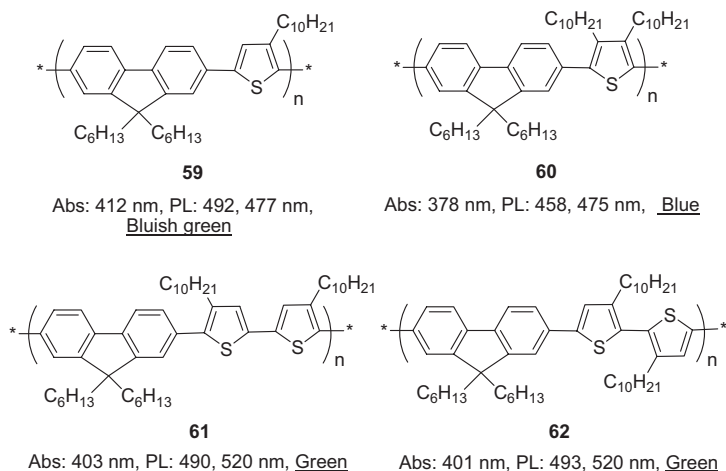
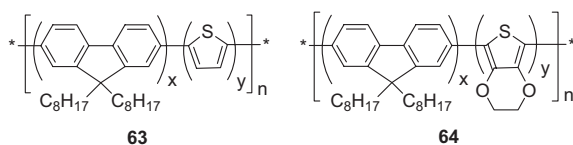


Figure 8. The schematic energy-level structures for the devices with copolymers **59** (labeled P3 on the diagram), **60** (P4), **61** (P1), and **62** (P2). Reprinted with permission from [108]. Copyright 2002 Elsevier.

series^[108]). Later, Liu et al.^[108] reported a somewhat lower $\Phi_{\text{EL}}^{\text{ex}} = 0.3\%$ for the device ITO/PVK/**62** (75 nm)/Ca/Al. The highest $\Phi_{\text{EL}}^{\text{ex}}$ in this series was reported for **59** (0.64 % for a ITO/PVK/**59**/Ca/Al device) and the lowest one was for **61** (0.07 % for a ITO/PEDOT/**61**/Ca/Al device).^[108] However, this trend has no correlation with the polymer energy levels.

Several random fluorene–thiophene copolymers such as **63**^[109] and **64**^[109,110] have been investigated. Due to low thiophene unit content (1–5 %), these materials have shown EL performance far greater than that of the corresponding alternating copolymers, and even of the PF homopolymer. Thus, the PLED ITO/PEDOT/copolymer/Ba/Al shows brightness above 2500 cd m^{-2} (at 8 V) and $\Phi_{\text{EL}}^{\text{ex}}$ of 1.2 % for **63**, and as high as 2.0 % for **64**.^[109]

Vamvounis and Holdcroft prepared a series of fluorene–thiophene copolymers **65** with a varying ratio of conjugated (2,5-thienylene) and non-conjugated (3,4-thienylene) thiophene moieties in the polymer chain (Scheme 4).^[111] Whereas the solution Φ_{PL} for either copolymer **65a** or **65f** is rather high (57 and 39 %, respectively), the PL efficiencies in films are

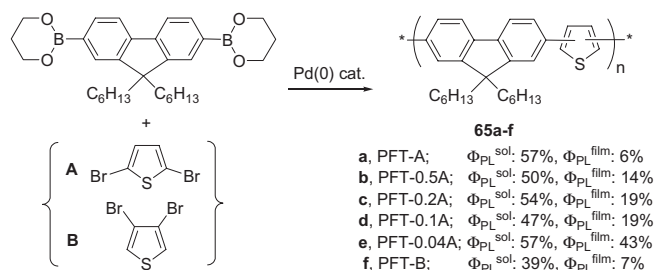


low (6 and 7 %, respectively). Substantial increases in solid-state PL efficiency were observed when mixtures of 2,5-dibromothiophene and 3,4-dibromothiophene were used in the synthesis of copolymers **65**, reaching a value of 43 % for copolymer **65e** (with a thiophene A/B ratio of 4:96, see Scheme 4). This enhanced solid-state emission was rationalized in terms of a self-forming host–guest system in which excitons formed on the PFT-B host fragments transfer their energy to electronically isolated, highly efficient PTF-A emitting fragments (Fig. 9).

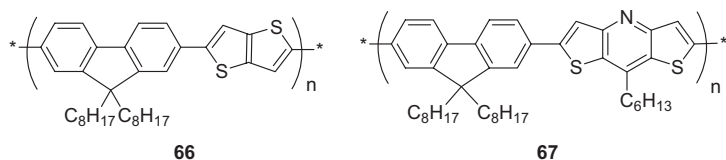
A very efficient green-light-emitting fluorene copolymer **66** was synthesized by Shim and co-workers via Suzuki coupling of dibromothieno[3,2-*b*]thiophene with 9,9-dioctylfluorene-2,7-diboronic acid bis(pinacol ester).^[112] The authors compared the EL properties of this copolymer with PFO and the PFO–bithiophene copolymer **55**. The absorption and emission spectra of **66** are red-shifted compared to PFO but slightly blue-shifted compared to the bithiophene-based copolymer **55**. A PLED fabricated in the configuration ITO/PEDOT/**66**/LiF/Al showed a pure green-light emission (CIE: $x=0.29$, $y=0.63$) close to the standard NTSC (National Television Standard Committee color specification) green color (CIE: $x=0.26$, $y=0.65$) with a very low turn-on voltage of 3.3 V. The low turn-on voltage is attributed to a better match (compared to PFO) between the HOMO

(−5.38 eV) level with the workfunction of PEDOT (5.1–5.3 eV). Interestingly, although the PL quantum yield of **66** (12 % in films, similar to **55**) is lower than that of PFO (55 %), the EL efficiency is higher, which may reflect an improved balance of electron/hole transport in this copolymer. The maximum current efficiency of **66** is 0.32 cd A^{-1} at 0.78 A cm^{-2} , exceeding the performance of similar devices fabricated with **55** or PFO (which showed 0.20 cd A^{-1} at 143 mA cm^{-2} and 0.06 cd A^{-1} at 25 mA cm^{-2} , respectively). The $\Phi_{\text{EL}}^{\text{ex}}$ of 0.1 % of **66** was twice as high as for the former polymers.

Introduction of electron-accepting bithieno[3,2-*b*:2',3'-*e*]pyridine units resulted in copolymer **67** with ca. 0.5 V lower reduction potential than the PFO homopolymer.^[113] Upon ex-



Scheme 4. Synthesis of fluorene–thiophene copolymers **65a–f** and the effect of the ratio of thienylene isomers in the copolymers on their PL efficiencies in solution and in films. Numbers in the abbreviations of copolymers denote the portion of thiophene A in the mixture of (A+B) dibromothiophenes used in the synthesis.



66
Abs: 448, 471 nm, PL: 495, 511, 548 nm
EL: 515 nm, Green CIE (0.29, 0.63)

67
Abs: 415 nm, PL: 481, 536 nm
EL: 480, 536 nm, Blue-green

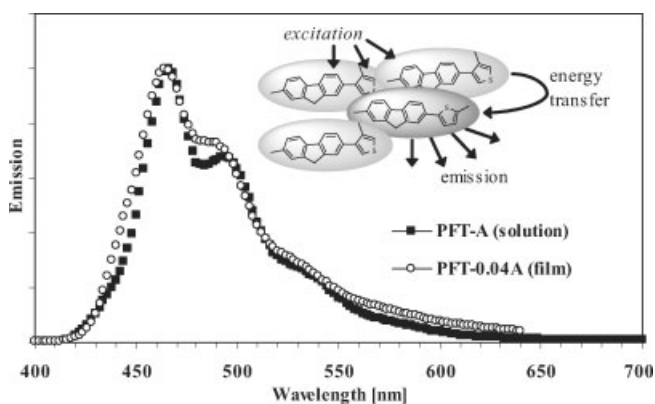
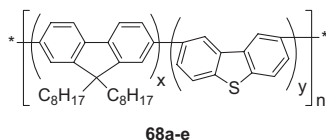


Figure 9. Solution emission of copolymer **65a** (PFT-A) and solid state emission of copolymer **65e** (PFT-0.04A). Inset: energy-transfer mechanism. Reprinted from [111].

citation at 420 nm ($\lambda_{\text{abs}}^{\text{max}} = 415$ nm), copolymer **67** exhibited blue–green–light emission with two peaks at 481 nm and 536 nm. Preliminary EL studies of an ITO/PEDOT/**67**/Al device showed two peaks equivalent to the PL spectra. The PLED exhibited a low turn-on voltage (~4 V), and at higher voltages of 6–9 V a slight relative increase of the green component was observed.

Several random fluorene–dibenzothiophene copolymers **68a–e** [114,115] have been reported. The “meta” linkage in the dibenzothiophene in copolymer **68a–e** hinders the conjugation, limiting the emission bands to the deep-blue color range ($\lambda_{\text{max}} \sim 420$ and 440 nm). [114] Furthermore, hindered conjugation as well as hindered π -aggregation suppress the parasitic green-light emission at 520 nm in the solid state of the polymer often observed in PFs.

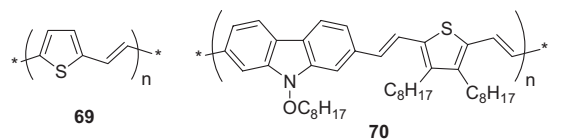


68a–e
a, x:y = 95:5; Abs: 383 nm, PL: 422 nm, Φ_{PL} : 29%, EL: 422 nm, $\Phi_{\text{EL}}^{\text{ex}}$: 0.36%
b, x:y = 90:10; Abs: 380 nm, PL: 421 nm, Φ_{PL} : 25%, EL: 421 nm, $\Phi_{\text{EL}}^{\text{ex}}$: 0.34%
c, x:y = 80:20; Abs: 373 nm, PL: 420 nm, Φ_{PL} : 18%, EL: 420 nm, $\Phi_{\text{EL}}^{\text{ex}}$: 0.22%
d, x:y = 70:30; Abs: 350 nm, PL: 419 nm, Φ_{PL} : 23%, EL: 419 nm, $\Phi_{\text{EL}}^{\text{ex}}$: 0.10%
e, x:y = 50:50; Abs: 343 nm, PL: 410 nm, Φ_{PL} : 62%, EL: 417 nm, $\Phi_{\text{EL}}^{\text{ex}}$: 0.42%
PFO, x:y = 100:0; Abs: 391 nm, PL: 422 nm, Φ_{PL} : 47%, EL: 456 nm, $\Phi_{\text{EL}}^{\text{ex}}$: 0.52%

6.3. Thiophene–Vinylene Copolymers

Oligo-2,5-thienylenevinylenes (OTVs) have been recognized as a potential class of linear conjugated systems for micro- and nanoelectronics. [116] Comparison of optical data for OTV with other classes of conjugated oligomers (oligothiophenes, oligo-2,5-thiopheneethynyls, oligo-1,4-phenylenevinyls, oligo-1,4-phenyleneethynyls, oligoacetylenes) shows that OTVs exhibit the longest effective conjugation lengths among the known systems and the smallest $\Delta E_{\text{HOMO-LUMO}}$ values, thus promising the lowest bandgaps for the corresponding polymers. We are not aware of any report of poly-(2,5-thienylenevinylene) itself (PTV, **69**) [117] being a fluorescent material, in spite of the highly emissive properties of nearly all PPV derivatives and the strong NIR photo- and electroluminescence observed in acceptor- (cyano-) substituted PTV. [118] Furthermore, blending 5–25 % of PTV **69** into PPV completely quenches the luminescence of the later. In our opinion, the behavior of **69** can be explained by the high PTV HOMO energy which allows for partial air doping (that, in turn, quenches the fluorescence), although further photo-physical studies are needed to support this hypothesis.

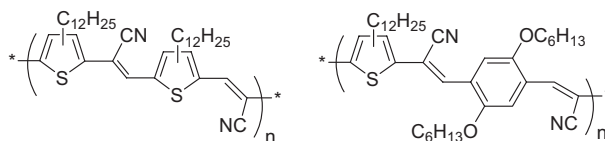
More recently, Leclerc and co-workers synthesized a 2,7-carbazolynevinylene–thienylenevinylene copolymer **70** via the Horner–Emmons reaction. [119] Whereas this material showed red emission in solution ($\lambda_{\text{PL}} = 581$ nm, $\Phi_{\text{PL}} = 16\%$) it was not fluorescent in the solid state.



69
70
Abs: 485 nm, PL: 581, 547 nm, Φ_{PL} : 16% (CHCl₃)
 E_g : 2.14 eV, HOMO: -4.96 eV, LUMO: -2.83 eV

As already mentioned, attaching a cyano group drastically improves the fluorescence of PTV materials. Two CN-PTV derivatives, **71** and **72**, synthesized by the Knoevenagel method, showed strong fluorescence in the NIR region and have been used to fabricate rarely achieved NIR PLEDs. [118]

Combining the CN-PTV structure with other conjugated moieties allows one to tune their emission into the visible region and to achieve a deep-red color. A PLED based on the fluorene–PTV copolymer **73** (ITO/LiF/**73**/PBD/LiF/Al/Ag) emitted red–orange light (brightness of 45 cd m⁻² at 10 V;



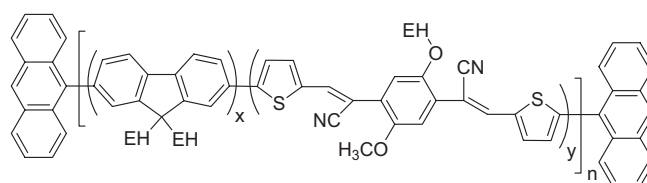
71
PL: 950 nm, $E_g = 1.55$ eV
72
PL: 840 nm, EL: 730 nm, $E_g = 1.8$ eV

turn-on voltage of 5 V).^[90] Pure red-light emission was also achieved in a similar copolymer **74**.^[92]

Fluorene–thiophene–phenylenevinylene copolymers **75–76** clearly demonstrate the effect of the exact position of CN groups in the vinylene fragment on the emission of the materials.^[120] Both absorption and emission maxima of the polymer **75** with cyano groups in the β -position with respect to the thiophene nucleus are hypsochromically shifted as compared to the polymer **76** (having the cyano group in the α -position), which can be explained by steric interactions between the cyano and alkoxy groups. Nevertheless, both copolymers **75** and **76** exhibit pure red-light emission with chromaticity values very close to standard red (CIE, $x=0.66$, $y=0.33–0.38$), although no PL quantum-yield values have been reported. An ITO/PEDOT/**75**/Ca/Al device showed a very low turn-on voltage of 2.6 V and a remarkable (for this class of materials) maximum brightness of 3100 cd m⁻² at 6 V. Its maximum $\Phi_{\text{EL}}^{\text{ex}}$ was 0.46 %, achieved at 4 V.

Following that, Shim and co-workers reported a series of random copolymers **77a–d** synthesized by Yamamoto coupling of a fluorene and thiophene-based brominated monomer with different feed ratios.^[121] All the copolymers were soluble in common organic solvents and M_n was in the range of 13 000–22 000 g mol⁻¹ (PDI=1.5–2.7). Regardless of the composition, all the copolymers showed similar absorptions with λ_{max} at \sim 380 nm, with the exception of a weak shoulder at \sim 470 nm, which was more intense for polymers with a higher thiophene content. In contrast, their emission colors were progressively red-shifted with increasing thiophene-based comonomer content. Copolymer **77a** emitted green light (540 nm), **77b** emitted yellow light (585 nm), and **77c** emitted bright red light (620 nm); all with reasonably high photoluminescent quantum yields (34–69 %). The electroluminescence spectra obtained from PLEDs fabricated as ITO/PEDOT/polymer/LiF/Al were almost identical to the PL spectra. As the ratio of thiophene monomer increased, the threshold voltage dropped from 13 to only 5 V, and the emission intensity at low voltages also increased, suggesting an improved charge-transport balance in the material. As can be calculated from the current–voltage–luminance (I – V – L) plot, luminous

efficiencies of \sim 0.7 cd A⁻¹ (at 15 V), \sim 2.4 cd A⁻¹ (at 12 V), and \sim 1.5 cd A⁻¹ (at 9.5 V) were achieved with polymers **77a,b,c**, respectively.

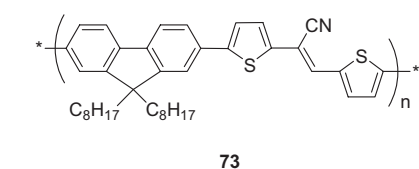
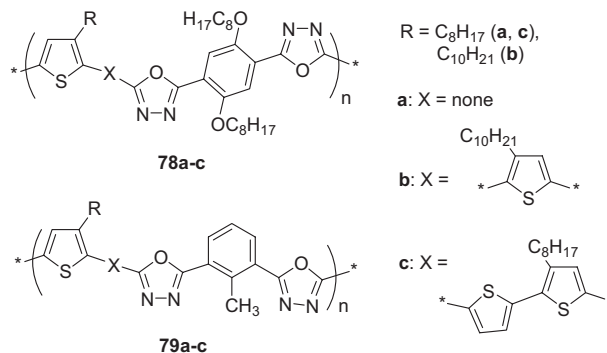


77a-d

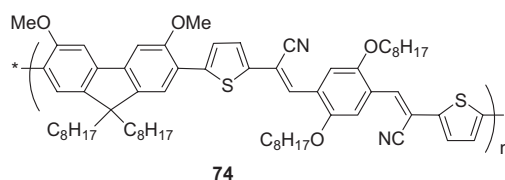
a, x:y = 99:1; Abs: 380 nm, PL: 536 nm, EL: 532 nm
b, x:y = 97:3; Abs: 380 nm, PL: 544 nm, EL: 535 nm
c, x:y = 95:5; Abs: 380 nm, PL: 583 nm, EL: 580 nm
d, x:y = 85:15; Abs: 379 nm, PL: 620 nm, EL: 630 nm

6.4. Thiophene Copolymers with Oxadiazole Moieties in the Main Chain

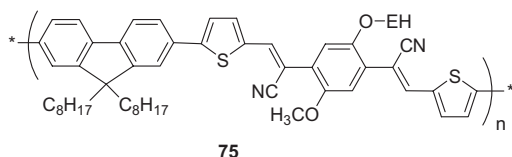
Several thiophene copolymers (**78–79**) containing electron-rich thiophene and electron-deficient 1,3,4-oxadiazole units have been reported by Huang et al.^[122,123] Structural variations, particularly different lengths of oligothiophene fragments, allowed them to tune the bandgap and PL energy of these materials: $\lambda_{\text{PL}}^{\text{film}} = 489 \text{ nm} \rightarrow 530 \text{ nm} \rightarrow 580 \text{ nm}$ (**78a** \rightarrow **b** \rightarrow **c**); $462 \text{ nm} \rightarrow (498, 526 \text{ nm}) \rightarrow 568 \text{ nm}$ (**79a** \rightarrow **b** \rightarrow **c**). Several devices fabricated with this class of materials showed very poor



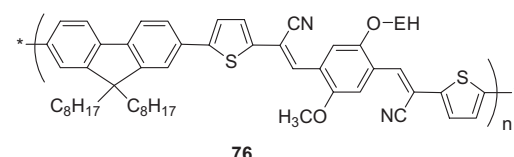
Abs: 500 nm, PL: 610 nm, EL: 610 nm, Red-orange



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



Abs: 460 nm, PL: 602 nm, EL: 604 nm, Red, CIE (0.63, 0.38)



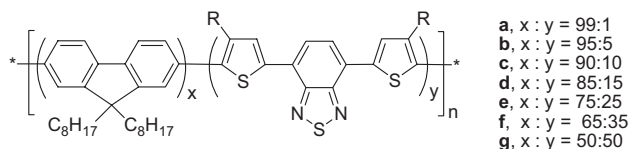
Abs: 537 nm, PL: 674 nm, EL: 674 nm, Red, CIE (0.66, 0.33)

performance ($\Phi_{EL}^{ex} \sim 0.0001\%$) that was explained by unoptimized device structure and, possibly, impurities.^[122]

6.5. Copolymers with Thiophene and Benzothiadiazole Units in the Main Chain

Narrowing the bandgap of copolymers by alternation of electron-rich thiophene and electron-deficient benzo-1,2,3-thiadiazole units was used in the design of several LEPs whose optical and electronic properties could be tuned through such a modification. Cao and co-workers synthesized copolymers **80**^[124] and **81**^[125] exploiting random copolymerization of fluorene fragments with dibromo derivatives of a thiophene-benzothiadiazole heterocycle. The absorption spectra of copolymers **80** and **81** show two maxima corresponding to oligofluorene ($\sim 370\text{--}390\text{ nm}$) and bithienylbenzothiadiazole fragments ($\sim 520\text{--}550\text{ nm}$). The intensity of the later band increases with increasing bithienylbenzothiadiazole concentration (Fig. 10). The fluorescence of oligofluorene moieties in the copolymers is quenched completely at a bithienylbenzothiadiazole unit concentration as low as 1% in the film due to efficient energy transfer to the narrow-bandgap fragment, and both copolymers emit saturated red light (Fig. 10). Decreased interchain interaction for copolymers **81**, compared to **80** (due to hexyl substituents on the thiophene rings), results in increased PL quantum yield in the solid state (44–88% for **81a–g** compared to 4–12.5% for **80a–g**). ITO/PEDOT/**80**/Ba/Al devices showed Φ_{EL}^{ex} in the range of 0.5–1.4%. The highest efficiency of 1.4% and a luminance of 256 cd m^{-2} at a bias of 5.1 V was achieved for the copolymer having a ratio $x:y$ of 85:15. This device reached a maximum luminance of 3780 cd m^{-2} at 8.2 V. An even higher $\Phi_{EL}^{ex} = 1.93\text{--}2.54\%$ was achieved with copolymers **81b** ($x:y = 95:5$ to 85:15) for the device ITO/PEDOT/PVK/**81b**/Ba/Al.^[125] These copolymers showed saturated red-light emission with $\lambda_{EL} = 634\text{--}647$ ($x = 0.66\text{--}0.67, y = 0.33\text{--}0.34$).

Cao and co-workers also prepared random 3,6-carbazole-benzothiadiazole–thiophene copolymers **82** by Suzuki coupling.^[126] The behavior of this copolymer was similar to the fluorene-containing copolymer **81**: PL and EL of the carbazole segment were completely quenched for copolymers with benzothiadiazole concentrations of 1%. Copolymers **82** emitted saturated red light (from 660 to 730 nm, depending on the stoichiometry) with a luminance of $70\text{--}631\text{ cd m}^{-2}$ and $\Phi_{EL}^{ex} = 0.55\text{--}1.48\%$. Also, a very high efficiency red-light-emitting PLED ($\lambda_{EL} = 680\text{ nm}$; CIE: $x = 0.67, y = 0.33$) was fabricated by blending small amounts of **82** ($x:y = 4:1$) into MEH-PPV. The device ITO/PEDOT/MEH-PPV:**82** (240:1)/CsF/Al showed $\Phi_{EL}^{ex} = 3.8\%$.^[127]



80a–f, R = H; Abs: 382–388, 535–551 nm, PL: 635–685 nm, Φ_{PL} : 4–12.5%, EL: 628–674 nm, Φ_{EL} : 0.5–1.4%, Red, CIE (0.67–0.70, 0.29–0.32)
81a–g, R = C_6H_{13} ; Abs: 369–383, 520–526 nm, PL: 629–678 nm, Φ_{PL} : 19–88%, EL: 613–672 nm, Φ_{EL} : 0.25–1.45%, Red, CIE (0.60–0.68, 0.32–0.38)

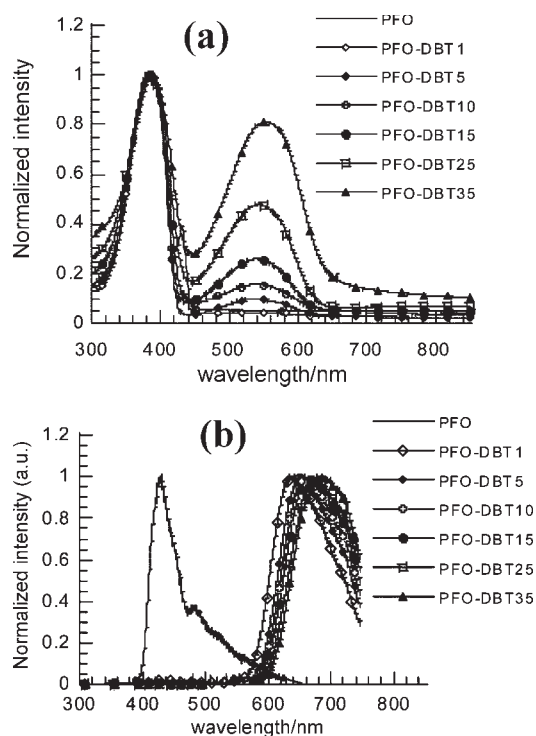
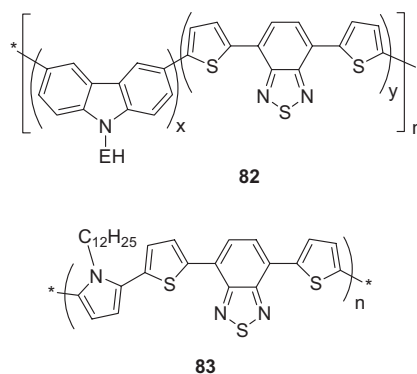


Figure 10. a) Absorption and b) PL spectra of copolymers **80** in solid-state films. DBT: 4,7-dithienyl-2,1,3-benzothiadiazole. Reprinted with permission from [124]. Copyright 2002 The Royal Society of Chemistry.

ing PLED ($\lambda_{EL} = 680\text{ nm}$; CIE: $x = 0.67, y = 0.33$) was fabricated by blending small amounts of **82** ($x:y = 4:1$) into MEH-PPV. The device ITO/PEDOT/MEH-PPV:**82** (240:1)/CsF/Al showed $\Phi_{EL}^{ex} = 3.8\%$.^[127]



Further lowering of the bandgap ($E_g \sim 1.6\text{ eV}$) was observed for bithienylbenzothiadiazole–pyrrole copolymer **83**, reflecting an increased conjugation through the 2,5-connected pyrrole units.^[128] The PLED with this material emitted in the NIR region ($\lambda_{EL} \sim 800\text{ nm}$) with a turn-on voltage less than 4 V, but with very low efficiency. Blending with poly(2-methoxy-5-(3,7-dimethyloctyloxy-1,4-phenylenevinylene)) (MDMO-PPV) to produce the device ITO/PEDOT/polymer blend/LiF/Ca sub-

stantially improved the EL efficiency (by ca. two orders of magnitude). A moderately efficient energy transfer from the higher-bandgap MDMO-PPV ($\lambda_{\text{EL}}=650$ nm) to copolymer **83** (PTPTB) ($\lambda_{\text{EL}}=830$ nm) allowed fine tuning of the emission color by changing the component ratio (Fig. 11).^[129]

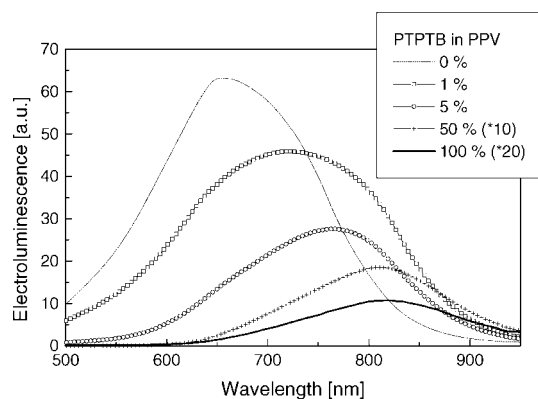
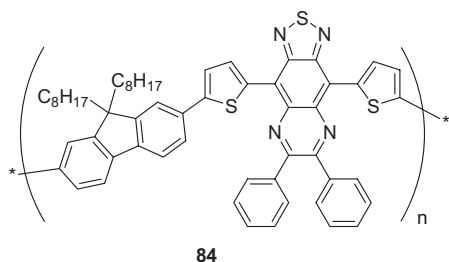


Figure 11. Electroluminescence spectra of ITO/PEDOT/active layer/LiF/Ca devices with **83** (PTPTB) and MDMO-PPV (PPV) as an active layer. Reprinted from [129].

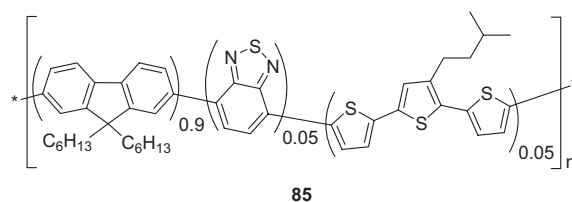
PL and EL emissions from a very-low-bandgap copolymer **84** ($E_g=1.27$ eV) was demonstrated by Swedish researchers.^[130] The material had two absorption peaks at 400 and 780 nm, and emitted light in the NIR region. The PL spectrum of thin films had one peak at 1035 nm that was blue-shifted by ca. 60 nm on annealing at 200 °C for 10 min. An ITO/PEDOT/**84**/Ca/Al diode showed EL at 1.1 V ($\lambda_{\text{EL}}=970$ nm). The $\Phi_{\text{EL}}^{\text{ex}}$ for a non-optimized device was quite low (0.03–0.05 %); nevertheless, demonstration of EL from a PLED in the NIR region can be important for communication and sensor technologies.



84
Abs: 400, 780 nm, PL: 1035 nm, EL: 970 nm, NIR, E_g : 1.27 eV

Jen's group reported a highly efficient random conjugated copolymer **85** containing dihexylfluorene, electron-deficient 2,1,3-benzothiadiazole (BT), and electron-rich terthiophene units, synthesized by Suzuki-coupling polymerization.^[131] Electron-rich units were introduced into the polymer to balance the charge-transport and charge-injection properties. Copolymer **85** showed an absorption with $\lambda_{\text{max}}=378$ nm. The luminescence properties of the copolymer were dominated by the BT unit. The copolymer had a green luminescence

($I_{\text{PL}}=540, 562$ nm ($F_{\text{PL}}=23\%$), $I_{\text{EL}}=535, 560$ nm ($F_{\text{PL}}=0.39-1.3\%$)), and the terthiophene comonomer does not contribute to the emission spectra. This can be explained by the charge-transfer or energy-transfer process between the electron-rich segments and electron-deficient BT units. The PLEDs were fabricated in a configuration ITO/HTL/copolymer/Ca, where the hole-transport layer (HTL) was either PEDOT or triarylamine/perfluorocyclobutane-containing polymer (BTPD-PFCB). In a series of fluorene–BT copolymers with different third components (terthiophene, dimethyl- and dioctyloxyphenylene), the thiophene-based copolymer **85** revealed the lowest efficiency (external QE of 1.3 %, current efficiency of 3.45 cd A⁻¹) which was attributed to the oligothiophene unit quenching effect.

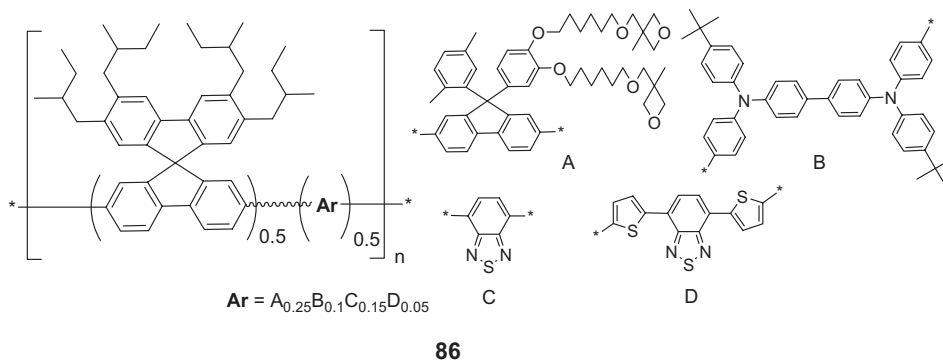


85

A further development of the approach of using multi-component PF copolymers for tuning the emission color was recently exemplified by fabrication of an RGB (red/green/blue color specification) prototype display, in which the pure red, green, and blue colors was achieved by variation of the feed ratio of several monomers (Scheme 5, Fig. 12).^[132] The key material for the red-light emission, thiophene copolymer **86**, was synthesized by Suzuki coupling, resulting in a high molecular weight ($M_n=55\,000$; PDI=2.45) yet highly soluble compound. A PLED fabricated as ITO/PEDOT/**86**/Ca/Al showed red-light emission with a switch-on voltage of 7.5 V and maximal EL efficiency of 1.1 cd A⁻¹. The presence of a photopolymerizable (in the presence of photoacid) oxetane unit in the comonomer A produced an insoluble crosslinked polymer upon photolithographic development and allowed solution-process fabrication of the PLED display bearing different emitting materials.

6.6. Thiophene Copolymers with Electron-Deficient Heterocycles as Electron-Transport Materials

Electron-deficient polyheterocycles (polyquinolines, polyquinoxalines) form a known class of n-type conjugated polymers for use as electron-transport materials in PLEDs. A number of thiophene–quinoline, thiophene–quinoxaline, and thiophene–benzobisthiazole copolymers were reported by the Jenekhe group.^[133] Although these copolymers show very weak or no PL and low performance in single-layer PLEDs ($\Phi_{\text{EL}}^{\text{ex}} < 0.02\%$), they possess good electron-transport proper-



Scheme 5. Multicomponent copolymer for RGB PLED display.

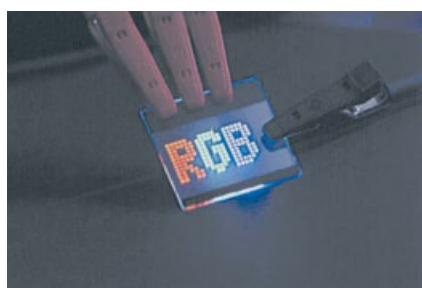


Figure 12. RGB PLED display prepared with copolymers **86**. Reprinted with permission from [132]. Copyright 2003 Nature Publishing Group.

ties and substantially increase the efficiency of double-layer PLEDs with MEH-PPV or PPV as the emissive layer ($\Phi_{EL}^{ex} \sim 0.5\text{--}1.5\%$, luminance of $300\text{--}2300\text{ cd m}^{-2}$).

7. Conclusions

PTs and their copolymers represent an important class of light-emitting polymers for LED applications. Through variation in substituent pattern and concomitant change of the backbone distortion their emission color can be tuned in a wide range, from blue to deep red and into the NIR. PTs possess a strong aggregation tendency that decreases their PL and EL emission efficiency, but this can be minimized to some extent by introducing bulky substituents. Regioregularity in monosubstituted PTs offers an additional control over the light-emitting properties of these materials. PATs have higher HOMO energies than PPVs or PFs (e.g., for P3OT: HOMO = -4.57 eV , $E_g = 1.96\text{ eV}$), thus decreasing the hole-injection barrier from ITO.

Relatively efficient blue- (polymer **24**, $\Phi_{EL}^{ex} = 0.6\%$ ^[48]), red- (polymer **21**, $\Phi_{EL}^{ex} = 0.7\%$ ^[51]) and white-light (blend of **17**, **23**, and **27**, $\Phi_{EL}^{ex} = 0.3\%$ ^[59]) emitters have been reported for thiophene homopolymers, although their performances do not rival those of the champions of other classes of LEP. A lower emission efficiency of PTs compared with other major classes of LEPs, such as PFs and PPVs, is already observed in solution.

It can be partially explained by the “heavy-element” (S) effect that facilitates intersystem crossing to the triplet state by spin-orbit coupling with concomitant loss of fluorescence efficiency. In electroluminescent devices, the problem is further emphasized by the tendency of PTs to aggregate. Another, poorly addressed, issue is quenching by oxidized states (defects). Having a high HOMO energy, many PTs can be at least partially oxidized by air, creating quenching sites. Eliminating the quenching effect by diluting the polymer or introducing other conjugated units (which can lower the HOMO energy and the aggregation tendency) could be a potential route to higher-performance PT-based LEDs. Thus, very respectable performances have been demonstrated by blends of PTs with other emitting polymers, as exemplified by a yellow-light-emitting blend of LPPP with P3DT, **9d** ($\Phi_{EL}^{ex} = 4.2\%$).^[65] Furthermore, easy functionalization of the thiophene nucleus and its electron-rich character make it attractive for design of various copolymers with other classes of aromatic/heteroaromatic systems, allowing tuning of the EL emission energy and the hole/electron transport properties of the materials. In fact, some of the best-performing LEPs contain thiophene comonomer units in the structure (e.g., the pure red-light emitter **77c**^[121]).

Finally, while the recent progress in red-light-emitting phosphorescent dye-doped PLEDs may limit the technological importance of PT homopolymers, the synthetic versatility of thiophenes make them very attractive building blocks for creating multicomponent light-emitting copolymers with tailored properties.

Regarding the barriers to development and the future of polymer LED technology as a whole, we believe that at this stage the ball is in the industrial players' court. From an academic's point of view, the fundamental concepts were shown, almost from the very beginning, to be sound. The general perception that the known problems of stability and cycle life have been overcome, propagated by one of the principal players, is still very questionable (particularly with easily oxidizable PTs). This would explain why there are still no major LEP-based consumer products available in 2005.

Received: March 5, 2005
Final version: May 11, 2005

Note Added in Proof: After this paper was submitted, several important articles describing light-emitting properties of thiophene oligomers^[134,135] and copolymers^[136–142] were published.

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