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Regioregular Di(2′-(thienyl))furan- and Di(2′-thienyl))benzene-Based Polymers: Steric and Heavy-Atom Effects on the Luminescence of Conjugated Systems

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Poly(3-alkylthiophenes) (P3ATs) are a promising class of polymer for electroluminescence (EL)[1] due to their ease of preparation, versatility, and tunable band gap,[2] but their solid-state luminescent efficiency is too low.[3] This low efficiency is attributed to internal conversion of excitation through molecular aggregates and the existence of sulfur in the thienyl moiety which promotes intersystem crossing via spin−orbital coupling, i.e., the heavy atom effect.[4] Replacing a fraction of the thienylene moieties with groups possessing lighter atoms, e.g., phenylene and furylene, or introducing steric constraints to reduce molecular aggregation should significantly enhance solid-state luminescence, while retaining the desirable versatility of P3ATs. It has been reported that the fluorescent quantum efficiency for a solution of 2,5-di(2′-thienyl)furan (DTF) ($\Phi_f = 50\%$) is significantly higher than that for the corresponding α-terthiophene (α-3T, $\Phi_f = 8\%$).[5] More recently, Yu and co-workers[4] demonstrated that EL efficiency in a simple single-layer device using poly(phenylene-*co*-furan) (PPF) was 0.1%, much larger than the corresponding polymer, poly(phenylene-*co*-thiophene) (PPT) (0.03%). The lower EL efficiency for PPT was attributed to the heavy atom effect. Chan and co-workers[6] synthesized poly(1,4-di-(2′-(3′-alkylthienyl)benzenes) (PDATBs) with different alkyl side chains. The PDATBs were only partially soluble in common organic solvents. The soluble fractions of the polymers were found to be stronger emitters than analogous P3ATs. Reynolds and co-workers reported syntheses and characterization of a series of poly-(di-2-thienyl-2,5-dialkyl(alkoxy)phenylenes).[7] Yoshino and co-workers found these polymers to be highly luminescent, but no quantitative data were reported.[8]

There are numerous quantitative reports on EL of conjugated polymers but relatively few on solid-state photoluminescence (PL). The latter, however, are necessary in order to understand the role of polymer structure and morphology on EL efficiency since the latter is complicated by polymer/electrode, and other interfacial, processes. In this paper, a systematic investigation of PL quantum yields (solution and solid state) of regiochemically controlled polymers of 1,4-di(2′-(hexylthienyl))benzene (DHTB), 2,5-di(2′-(hexylthienyl))furan (DHTF), and 2,5-di(2′-(3′-hexylthienyl))thiophene (3,3′-DHTT) is reported.

Table 1. Absorption and Fluorescence Characteristics of Heteroaromatic Trimers in Hexanes

trimer	λ_{max}(abs) (nm)	λ_{max}(em) (nm)	Φ_f (%)
DTF	350	400	57 ± 6
α-3T	352	423	8.1 ± 0.8
3,3′-DHTF (**6a**)	340	407	36 ± 4
4,4′-DHTF (**6b**)	355	407	56 ± 6
3,3′-DHTB (**8a**)	300	381	19 ± 2
4,4′-DHTB (**8b**)	330	386	53 ± 6
3,3′-DHTT (**9**)	340	426	4.6 ± 0.5

DTF was prepared following a modified literature procedure.[9] The syntheses of DHTF, DHTB, and 3,3′-DHTT monomers are outlined in Schemes 1 and 2 and will be reported in detail elsewhere. In addition to other confirmatory analyses, proton NMR analysis of 3,3′-DHTF (**6a**) gave peaks due to the α-methylene (2.81 ppm), furylene (6.49 ppm), and thienyl moieties (6.91, 7.16 ppm, $J = 5.1$ Hz).[10] For 4,4′-DHTF (**6b**), the corresponding resonance peaks were found at 2.64, 6.52, 6.85, and 7.17 ppm, with $J = 1.0$ Hz for thienyl protons. For 3,3′-DHTB (**8a**), peaks were observed for α-methylene (2.69 ppm) and phenylene (7.46 ppm). Two doublets at 7.00 and 7.24 ppm ($J = 5.2$ Hz) were assigned to the thienyl moieties. The corresponding peaks for **8b** were observed at 2.62, 7.56, 6.85, and 7.14 ppm ($J = 1.0$ Hz). For **9**, peaks were observed at 2.78, 6.94, 7.05, and 7.18 ppm ($J = 5.2$ Hz).

Chemical oxidation of **8a**, **8b**, **6b**, and **9** by iron(III) chloride in carbon tetrachloride yielded the corresponding polymers: poly(di(2′-(3′-hexylthienyl))benzene) (P33-DHTB), poly(di(2′-(4′-hexylthienyl))benzene) (P44DHTB), poly(di(2′-(4′-hexylthienyl))furan) (P44DHTF), and poly-(di(2′-(3′-hexylthienyl))thiophene) (P33DHTT).[6,11] Poly-(di(2′-(3′-hexylthienyl))furan) (P33DHTF) was prepared by the McCullough method.[3d] The polymers were extensively purified by Soxhlet extraction and their structures confirmed by spectroscopic analyses. FTIR analyses showed a weak peak at 1654 cm^{-1} for both P33DHTF and P44DHTF and was assigned to carbonyl groups that resulted from partial ring opening of the furylene moiety during polymerization. GPC analyses against a poly(3-hexylthiophene) calibration curve[3a] indicated M_n in the range 4000−8000 (10−20 trimeric units).

UV−vis absorption (Carey 3E) and fluorescence spectra (PTI QuantumMaster model QM-1) were taken at ambient temperature. Solutions (OD = 0.05−0.10) were deoxygenated by purging with argon. Fluorescence quantum yields (≤10% error) were measured by using 2-aminopyridine ($\Phi_f = 0.60$ in 0.1 N H_2SO_4) and quinine bisulfate ($\Phi_f = 0.546$ in 1.0 N H_2SO_4) as secondary standards for trimers and polymers, respectively. Solid-state fluorescent measurements were performed on spin-cast films (OD = 0.15−0.50) under an oxygen-free nitrogen atmosphere. Quantum yields (≤30% error) were determined relative to 9,10-diphenylanthracene ($<10^{-3}$ M) in PMMA glass ($\Phi_f = 0.83$). Absorption and fluorescence characteristics of the trimers are summarized in Table 1.

The absorption spectra (not shown) of the heteroaromatic trimers were broad and featureless. λ_{max} ranged from 300 nm for 3,3′-DHTB to 352 nm for α-3T. Placement of the hexyl groups at the 3,3′-positions of the thienyl moiety does not appear to significantly

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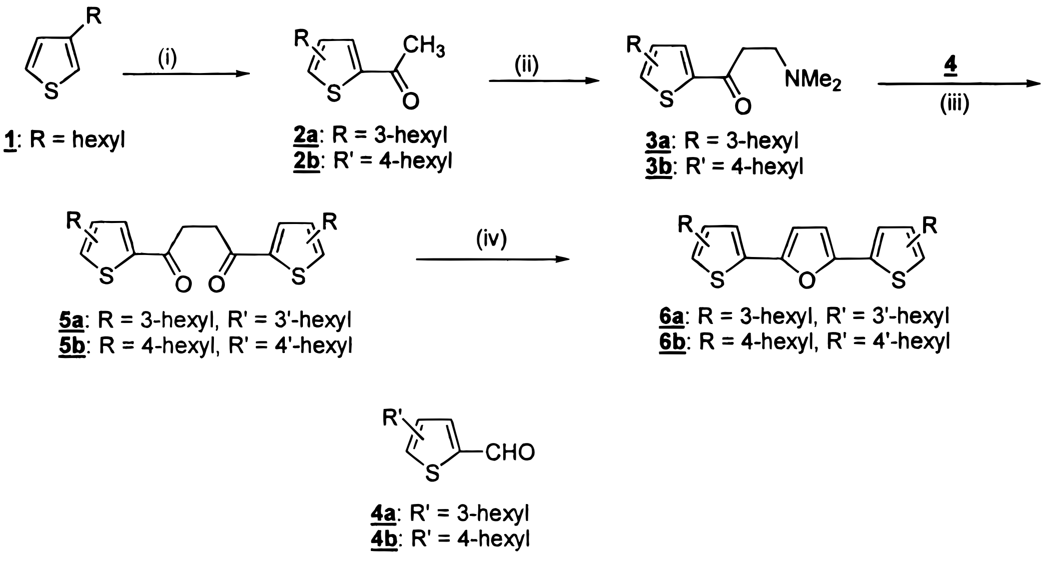
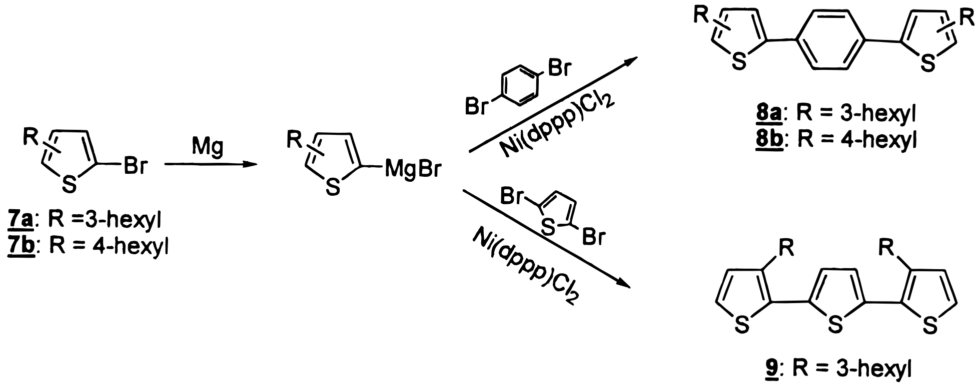
Scheme 1



(1) $CH_3COCl/SnCl_4$; (ii) $(H_2CO)n/Me_2NHCl/C_2H_5OH$; (iii) thiazolium salt or NaCN; (iv) HCl gas/$(CH_3CO)_2O$

Scheme 2



reduce the effective conjugation between adjacent rings for dithienylfuran- and terthienyl-based trimers, but it does for dithienylbenzene analogues. As expected, the introduction of the phenylene unit appears to reduce the effective conjugation of the molecule by increasing the torsional angle. The value of 8.1% for Φ_f of α-3T is consistent with previous reports which indicate that the fluorescent efficiency for thiophene oligomers is relatively low[5,12] and can be attributed to the presence of the bulky sulfur atom, which renders the thienylene ring less rigid and which favors internal conversion through skeleton relaxation. Furthermore, the relatively heavy sulfur atom enhances intersystem crossing (ISC) due to spin−orbital coupling. Φ_{ISC} for α-3T is reported to be greater than 90%.[13] Fluorescence yields of DTF, 4,4′-DHTF, and 4,4′-DHTB were found to be 7 times greater than that of α-3T. Steric arguments cannot explain this difference since 4,4′-DHTB is a relatively twisted molecule whereas 4,4′-DHTF is not. The data are consistent with a reduction in the number of sulfur atoms, i.e., a heavy-atom effect.

The addition of hexyl groups at the 3,3′- and 4,4′-position in the α-3T and the DTF has only a little effect on the effective conjugation length of the molecule. This is in contrast to DHTB polymers wherein substitution at the 3,3′-position reduces the rigidity of the trimer and lowers Φ_f. DTF and 4,4′-DHTF possess very similar values of Φ_f, indicating that the hexyl groups do not interfere with the excited state in this configuration. Severe steric hindrance of the 3,3′-alkyl groups in 3,3′-DHTB forces the trimer to adopt a significantly more twisted conformation than 4,4′-DHTB, an effect which results in Φ_f being relatively smaller.

Absorption and fluorescent characteristics of the polymers in solution and in solid state are summarized in Table 2. Absorption maxima in THF solution range from 383 nm for P44DHTB to 470 nm for P33DHTF, indicating a difference in their effective conjugation length. Fluorescence from P33DHTB solutions is greenish-blue and Φ_f is 54%, one of the highest fluorescent efficiencies for a solution of thiophene-based polymers reported to date.[14] Φ_f for P44DHTB solutions is half that of P33DHTB, due to the severe steric interaction between adjoining trimeric units, i.e., a head-to-head coupling, and the resulting decrease in rigidity of the polymer in solution. On the basis of the fluorescent studies of the trimers, an even higher value of Φ_f for DHTF-based polymers would have been expected because of increased conjugation resulting from polymerization. The lower than expected values are attributed to the existence of carbonyl defects which efficiently quench luminescence of conjugated polymers.[15] Φ_f for

Table 2. Absorption and Fluorescence Characteristics of Polymers in THF Solution and in Solid State

polymer	solution			solid state		
	λ_{max}(abs) (nm)	λ_{max}(em) (nm)	Φ_f (%)	λ_{max}(abs) (nm)	λ_{max}(em) (nm)	Φ_f (%)
P33DHTB	395	490	54 ± 5	410	511	18 ± 6
P44DHTB	383	484	25 ± 3	385	500	20 ± 7
P33DHTF	470	567	42 ± 4	520	625	0.5 ± 0.2
P44DHTF	398	519	28 ± 3	410	542	0.8 ± 0.3
P33DHTT	450	562	37 ± 4	530	649	1.6 ± 0.6

P33DHTT in solutions is 37%, which is consistent with that for an extensively purified regioregular P3HT sample.[16]

The polymers strongly emit in the solid state. P44DHTB and P33DHTBs show emission bands at 500 and 511 nm, respectively. Φ_f values of 20% and 18% for P44DHTB and P33DHTB films are orders of magnitude higher than P3ATs. Steric hindrance between thienylene and phenylene moieties prevents the polymers from achieving long-range order in the solid state, as evidenced by the absence of DSC and X-ray diffraction peaks associated with semicrystalline conjugated polymers. In addition, only a modest difference in λ_{max} between solution to solid state is evident, inferring that the PDHTB chains cannot adopt a planar conformation in the solid state. In combination with the reduced heavy-atom effect, the twisted conformation and amorphous morphology prevents radiationless relaxation channel through π-stacking and enables the polymers to maintain a high Φ_f in the solid state. The high luminescent efficiencies of the DHTB polymers make them very good candidates as emissive materials for LEDs.

P44DHTF showed a weak and broad emission band at 542 nm in the solid state. Structured emission bands at 625 and 649 nm were observed for P33DHTF and P33DHTT in the solid state, respectively. It is known that fluorescent quantum yields for thiophene polymers are usually 1−2 orders of magnitude lower in the solid state than that in solution, due to π-stacking.[3a] The recorded Φ_f value of 1.6% for P33DHTT is consistent with that reported for P3ATs. Similar to P33DHTT, the very low fluorescence efficiencies found for the DHTF polymers appear to be attributed to π-stacking. This assertion is made because DHTF segments are relatively planar; even the 3,3′-DHTF trimeric unit, with its two alkyl chains directed toward the central ring, can adopt a high degree of coplanarity as indicated by its spectral properties. Despite these observations, if the deleterious aggregation of luminescent centers can be reduced and the existence of carbonyl defects eliminated, dithienylfuran-based polymers have the potential to be highly luminescent, perhaps more luminescent than dithienylbenzene-based polymers.

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