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Triphenylene-Based Polymers for Blue Polymeric Light Emitting Diodes

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ABSTRACT: An efficient synthesis has been developed toward a novel series of conjugated blue emitting polymers containing triphenylene as repeating unit for PLEDs. Soluble 1,2,3,4-tetraphenyltriphenylene, 2,3-bis(4-octylphenyl)-1,4-diphenyltriphenylene, 2-heptyl-1,3,4-triphenyltriphenylene, 2-decyl-3-(4-octylphenyl)-1,4-diphenyltriphenylene, and 2,3-diheptyl-1,4-diphenyltriphenylene-based co- and homopolymers have been synthesized by the palladium-catalyzed Suzuki−Miyaura and the nickel-catalyzed Yamamoto polycondensation reactions, respectively. The photophysical properties of the polymers were studied based on the different main chains and substituents. Because of the twisted phenyl rings around the triphenylene main core, $\pi-\pi$ stacking in the polymers was prevented, resulting in almost identical photoluminescence (PL) spectra in both solutions and films. All polymers exhibited narrow emission in the range of 430−450 nm, where the human eye is most sensitive for the blue range.

Introduction

Since the discovery of electrical conductivity in π-conjugated polymers three decades ago,[1,2] semiconducting polymers have been extensively studied and become of main interest in the research activities around the globe.[3−5] Because of the simple processing, high flexibility, and ease of fabrication in large area, conjugated polymers have been incorporated as active materials into several kinds of electronic devices such as polymeric light emitting diodes (PLEDs),[6−9] organic field effect transistors (OFETs),[10,11] polymer lasers,[12] and organic photovoltaic cells.[13−15]

During the past decade PLEDs have been intensively studied because of their potential applications in a new generation of flat display and lighting technologies.[16,17] Phenylene based polymers such as poly(fluorene),[18] poly(indenofluorene),[19] poly(ladder-type pentaphenylene),[20] and ladder-type poly(*p*-phenylene)s[21] are some of the most important classes of conjugated wide band gap polymers for blue emitting PLEDs. However, these polymers suffer from problems of (i) poor charge injection and transport, and (ii) a tendency to oxidize at the bridge-head positions. The oxidation generates a ketone functionality, which leads to the appearance of a long wavelength emission band and the deterioration of device performance.[22,23] A few years ago, our group showed that replacement of the carbon with a nitrogen bridge (carbazole)[22] followed by replacement of the alkyl groups at C9-head position with aryl groups[24−27] has proved to be a successful way to obtain stable blue emission from polyfluorenes. However, one effect of aryl substituents on the physical properties of polyfluorenes is to inhibit chain packing as demonstrated by the lack of liquid crystalline phases, and the absence of any signs of organization in the polymer films when studied by atomic force microscopy (AFM).[28] Therefore, new candidates for blue emission which do not suffer from the problems of keto-functionality and low microscopic order was vital. Recently, triphenylene containing small molecules and oligomers have received considerable attention due to their discotic liquid crystalline nature and their various physical properties including one-dimensional charge migration,[29] one-dimensional energy migration,[30] electroluminescence,[31] ferroelectric switching,[32] alignment, and self-assembling behavior on surfaces.[33,34] One example is the alkoxy-substituted triphenylene which gained increased interest in the fabrication of OLEDs.[35]

In this work, we present for the first time a series of triphenylene-*alt*-arylene copolymers (P_1-P_5) and polytriphenylene homopolymers (P_6 and P_7) with different alkyl or alkoxy chains as solubilizing units. Concerning the design and the synthesis of the presented polymers, several strongly twisted phenyl rings have been introduced around the triphenylene core in order to suppress the intermolecular interactions in the solid state. Such behavior can result in self-quenching processes due to ground state aggregation and results in a reduction in the efficiency and luminescence of the PLED device.[36]

For the polymerization protocols, we decided first to use the Pd-catalyzed Suzuki−Miyaura polycondensation reaction[37,38] which is one of the most powerful methods for preparing conjugated polymers. Furthermore, Suzuki synthesis gives the ability to introduce additional arylene units between the repeating units in the polymer backbone. However, the preparation of the arylenediboronic ester derivatives requires considerable synthetic effort, especially when scale-up is needed. Moreover, such AB type polymerizations require highly accurate stoichiometries, where small deviations can lead to dramatically decreased molecular weights; this can be especially challenging for small scale reactions. These two drawbacks of the Suzuki approach to prepare copolymers motivated us to search for simpler but comparatively powerful and robust methods for the preparation of the functionalized triphenylene-based polymers.

A promising alternative was the Yamamoto polycondensation.[39] Here, dibromo-functionalized starting materials are the only monomers required and stoichiometric quantities of nickel complexes take over the role of the organometallic counterpart. Because of its simplicity, and because the Yamamoto protocol has previously shown to be highly valuable for the synthesis of constitutionally homogeneous, high molecular weight

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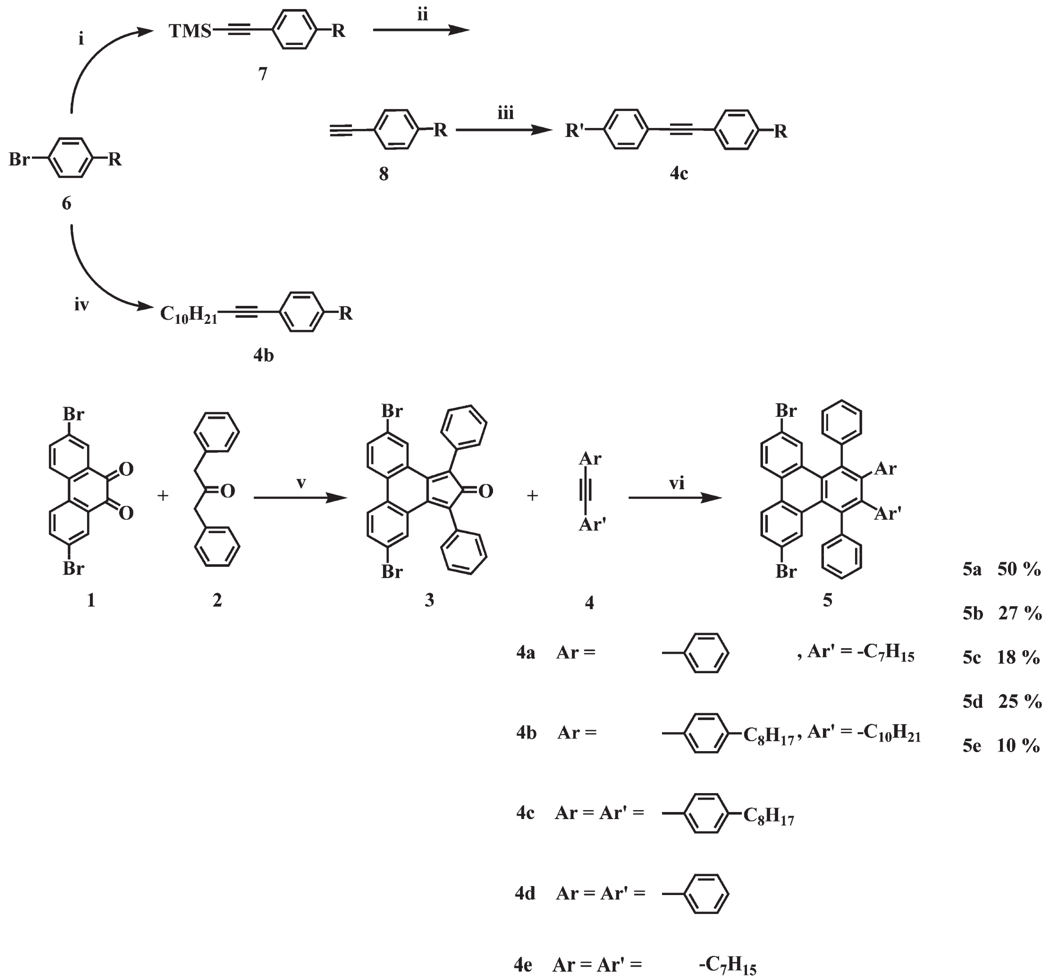
Scheme 1. Synthetic Routes of 6,11-Dibromo-1,2,3,4-*Substituted*-Triphenylene Monomers 5a−5e [a]



[a] Reagents and conditions: (i) Pd^0, ethynyltrimethylsilane, CuI, piperidine, 80 °C, 91%; (ii) TBAF, THF, 61%; (iii) Pd^0, 1-bromo-4-octylbenzene, CuI, piperidine, 70 °C, 59%; (iv) Pd^0, 1-dodecyne, CuI, piperidine, 50 °C, 70%; (v) KOH, MeOH, EtOH, 80 °C, 40%; (vi) Ph_2O, reflux.

polyaromatics,[39] we decided to utilize this method also in our synthesis. Furthermore, a direct comparison between Suzuki and Yamamoto polycondensation reactions can be available concerning their practicability, constitutional homogeneity, degrees of polycondensation, and finally the physical properties of the resulting polymers. Microwave assisted organic synthesis (MAOS) is a relatively new technique in the present-day organic synthetic world and has gained increased interest in the past decade.[40] The main advantages of MAOS are the dramatic acceleration of reactions, most often resulting in cleaner outcomes and increased yields. Herein, we present the synthesis of novel triphenylene-based polymers as promising blue light emitters for PLEDs via the microwave assisted (MA) Suzuki−Miyaura and Yamamoto polycondensation reactions.

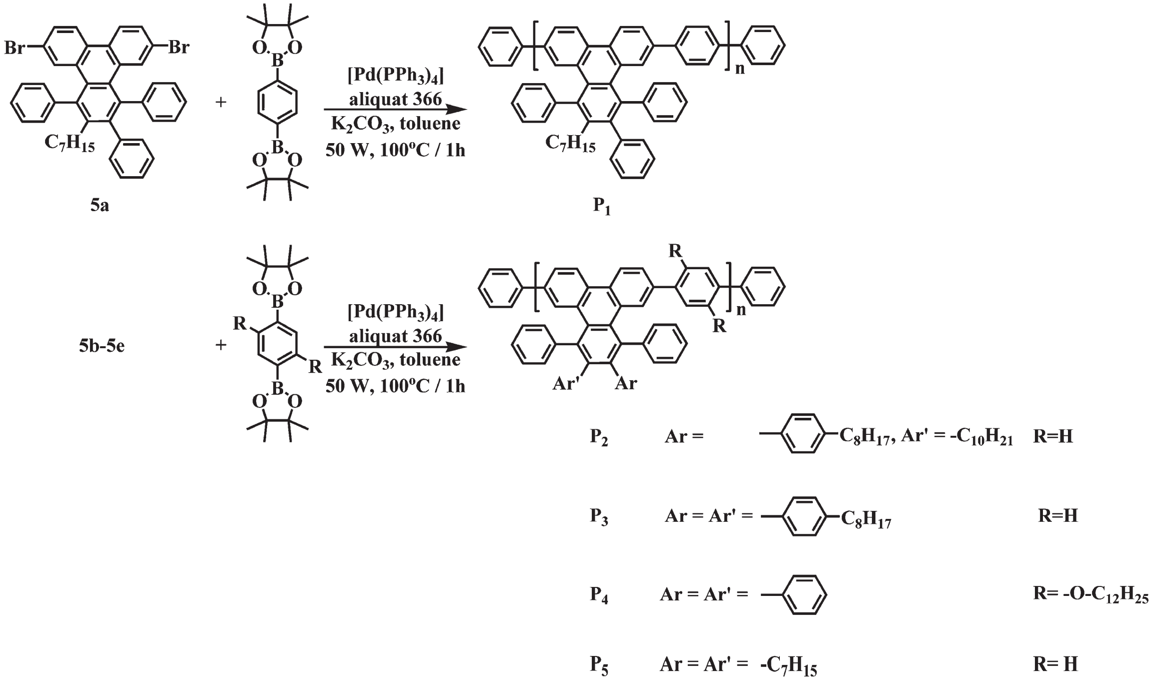
Results and Discussion

The desired triphenylene monomers were synthesized in two steps starting from the Knoevenagel condensation reaction[41] between 2,7-dibromophenanthrene-9,10-dione (**1**) and 1,3-diphenylpropan-2-one (**2**) to afford 5,10-dibromo-1,3-diphenyl-2*H*-cyclopenta[*l*]phenanthren-2-one (**3**) (Scheme 1). Following that, compound 3 was subjected to a series of Diels−Alder reactions[42] with 1,2-di-*substituted*-ethynes **4**. Utilizing different 1,2-di-*substituted*-ethynes **4** was crucial to afford the monomers with the required solubility which is needed to achieve soluble high molecular weight polymers. In addition the optical properties of the resulting polymers can be studied depending upon those different substituents. The synthesis of two new 1,2-di-*substituted*-ethynes **4b** and **4c** was accomplished by Sonogashira coupling reactions.[43]

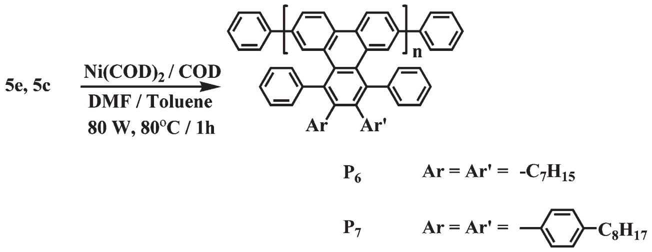
1,2-Di-*substituted*-ethynes **4** were then used for Diels−Alder reactions to give 6,11-dibromo-1,2,3,4-*substituted*-triphenylenes **5a**−**5e** (Scheme 1). Later, the triphenylene monomers were subjected to the Suzuki−Miyaura and Yamamoto polymerizations (Schemes 2 and 3).

Suzuki−Miyaura Approach. With the triphenylene monomers **5a**−**5e** in hand, our attention focused on the subsequent polymerization reactions. The MA−Suzuki−Miyaura polymerization was first applied, therefore 1,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene and its derivatives were used (Scheme 2). It was challenging to find the most suitable MA−Suzuki−Miyaura reaction conditions in terms of the applied power (50 W), temperature (100 °C), and reaction time (1 h). These complications arose from (i) the relatively low yields of the Diels−Alder reactions (10−50%) seen in Scheme 1, resulting from the steric hindrance between the aryl groups on **3** and the aryl and/or alkyl groups on **4** and the debromination of the desired product **5** due to the high temperature and the long time of the Diels−Alder reactions, (ii) the need of ultra pure monomers, and (iii) the fact that MAOS gives different results from one system to the other. Fortunately, the MA−Suzuki−Miyaura coupling reactions (Scheme 2) afforded moderate molecular weight polymers ($M_w = 15 \times 10^3$ to 63×10^3 g mol^{-1}). The

Scheme 2. Synthetic Route of Polymers via Suzuki−Miyaura Coupling Reaction



Scheme 3. Synthetic Route of Polymers via Yamamoto Coupling Reaction



molecular weights and PDI of the resulting polymers are summarized in Table 1. The GPC results for P_5 revealed unusual high PDI value due to the presence of two dominant peaks in the GPC analysis corresponding to two high molecular weight fractions which could not be separated. The smaller molecular weight fraction under the GPC curve could be attributed to the average molecular weight of the polymer while the larger molecular weight fraction could be ascribed to polymer aggregates due to the few number of the phenyl groups around the triphenylene core.

Yamamoto Approach. Utilizing the MA−Yamamoto polymerization (Scheme 3) the resulting homopolymers were of higher molecular weights (M_w = 224 × 10^3 and 112 × 10^3 g mol^{-1} for P_6 and P_7, respectively) than the copolymers (P_1−P_5) obtained by the MA−Suzuki− Miyaura polymerization (Table 1). Although polymers P_5 and P_6 have the same side chains, P_6 showed monomodal molecular weight distribution. The homopolymers were synthesized to study the effect of the direct coupling between the triphenylene repeating units on the physical properties of the final polymers.

Synthesis and Characterization. The synthetic routes of monomers **5a**−**5e** and polymers P_1−P_7 are depicted in Schemes 1−3. All of these polymers were easily dissolved in common organic solvents such as chloroform ($CHCl_3$), tetrahydrofuran (THF), dichloromethane (DCM), and toluene. In addition polymer solutions formed uniform, transparent films on quartz substrates after spin coating. The weight-average molecular weights (M_w) were measured by gel permeation chromatography (GPC), analysis was performed with SDV (PSS) columns (10^6, 10^4, and 500 Å porosity) connected to RI and UV (254 nm) detectors against 1,4-polyparaphenylene (PPP) and polystyrene standards with THF as an eluting solvent. The polydispersity index (PDI) was measured by dividing weight-average molecular weight by the number-average molecular weight (M_w/M_n). The data obtained from GPC are given in Table 1. The weight-average molecular weights (M_w) of polymers were between 15 × 10^3 and 224 × 10^3 g mol^{-1}, while the polydispersity indices (PDI) ranged from 1.4 to 3.6.

Table 1. Molecular Weights and PDI of Polymers from GPC Analysis[a] (Standard = PPP; Eluent = THF; Temperature = 25 °C)

polymer	yield (%)	M_w	PDI
P_1	68	27 × 10^3	2.7
P_2	55	36 × 10^3	1.4
P_3	67	15 × 10^3	1.9
P_4	65	18 × 10^3	1.6
P_5	81.5	63 × 10^3	3.6
P_6	93	224 × 10^3	2.7
P_7	91	112 × 10^3	2.7

[a] Refer to Synthesis and Characterization section.

Table 2. UV−Vis Absorption and PL Behavior of Monomers 5a−5e (Solvent = DCM; Concentration ~ 1 × 10^{-5} M; Temperature = 25 °C)

monomer	$\lambda_{abs.sol}$[a] (nm)	$\lambda_{PL.sol}$[b] (nm)	monomer	$\lambda_{abs.sol}$[a] (nm)	$\lambda_{PL.sol}$[b] (nm)
5a	283	405	**5d**	283	415
5b	284	408	**5e**	289	416
5c	288	411			

[a] Wavelength of the maximum absorbance. [b] Wavelength of the maximum PL.

Absorption and PL in Solution. The photophysical characteristics of the monomers as well as of the polymers were studied by UV−vis absorption and PL spectroscopy in both dilute solutions (DCM and THF, respectively) and thin films. The wavelengths of the UV−vis absorptions and PL maxima of the monomers and polymers in solutions as well

Table 3. UV−Vis Absorption, PL Behavior, and Quantum Yields (Φ_{PL}) of Polymers P_1−P_7 (Solvent = THF; Concentration ~ 1 × 10^{-5} M; Temperature = 25 °C)

polymer	$\lambda_{abs.sol}$[a] (nm)	$\lambda_{abs.film}$[a] (nm)	band gap[b] (eV)	$\lambda_{PL.sol}$[a] (nm)	$\lambda_{PL.film}$[a] (nm)	Φ_{PLfilm}[c]	$\Phi_{PLsolution}$[d]
P_1	391	387	2.87	429	430	*e*	0.65
P_2	408	392	2.91	428	428	0.34	0.84
P_3	388	389	2.90	427	427	*e*	*e*
P_4	367	380	3.02	422	420	0.34	*e*
P_5	391	391	2.83	429	459	0.31	0.66
P_6	394	401	2.91	418	458	0.21	0.67
P_7	396	398	2.90	418	424	0.17	0.85

[a] Wavelength of the maximum absorbance or PL. [b] Band gaps were calculated from the onsets of UV−vis absorption spectra of polymer solutions. [c] Relative to thin-film quantum efficiency of poly(9,9-dioctylfluorene) POF (sample polymer and reference POF were dissolved in toluene and spin coated over quartz (1 min at 2000 rpm and 15 s at 5000 rpm). [d] Determined in THF relative to 9,10-diphenylanthracene in cyclohexane (Φ_{PL} = 0.9) with excitation at 365 nm. [e] Not measured.

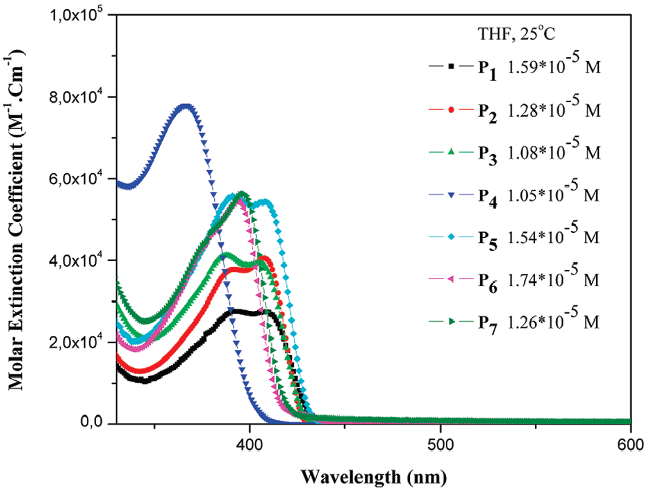


Figure 1. UV−vis spectra of polymers in THF at 25 °C.

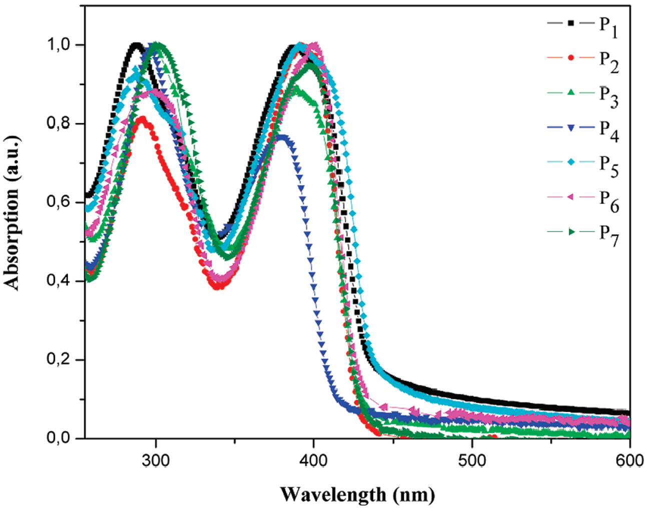


Figure 3. UV−vis spectra of polymer films.

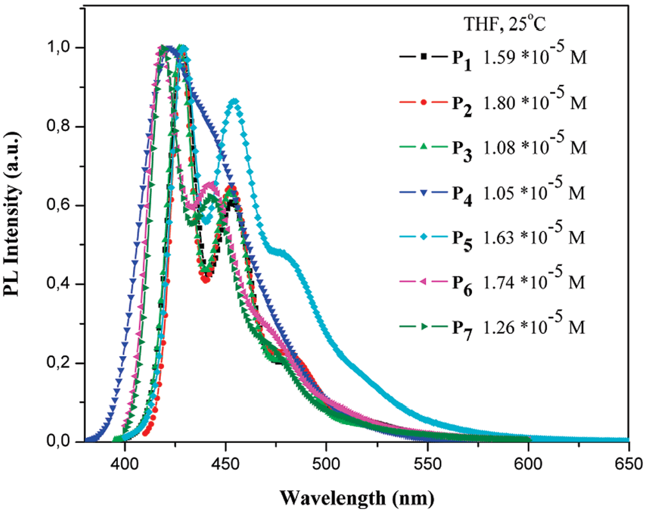


Figure 2. PL spectra of polymers in THF at 25 °C.

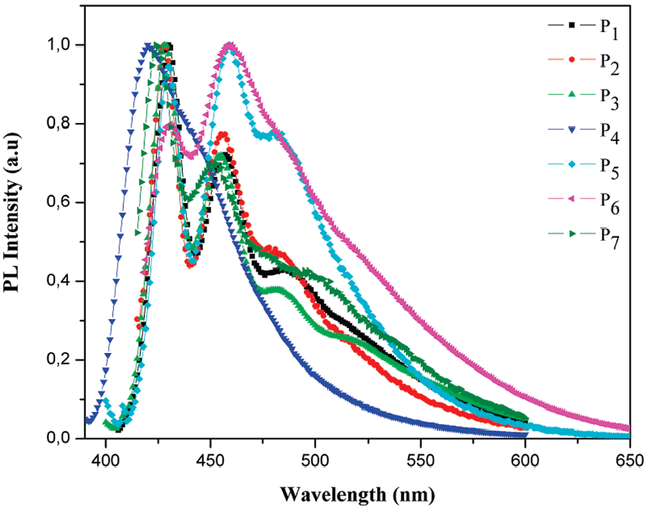


Figure 4. PL spectra of polymer films.

as in films are summarized in Tables 2 and 3 and in Figures s1 and s2 in the Supporting Information, and Figures 1−4, respectively.

The UV−vis absorption spectra of the synthesized polymers in solution (THF) are depicted in Figure 1. Polymers P_1, P_2, and P_3 exhibited two bands in the solution absorption, with the absorption maxima at 391, 408, and 388 nm, respectively, while the second bands were at 409, 392, 405 nm, respectively. These hypsochromically shifted absorption maxima for P_1 and P_3 compared to P_2 suggest a smaller conjugation length for P_1 and P_3. However the three polymers showed almost identical PL maxima in solution at 429, 428 nm, and 427 nm, respectively (Figures 1 and 2). The PL spectra were characterized by steep onsets and by well-resolved vibrationally split maxima at higher wavelengths but with lower intensities (453 and 481 nm for P_1, 453 and 480 nm for P_2, and 452 and 479 nm for P_3) which resulted from the vibrational splitting. The UV−vis spectrum of the alkoxy substituted polymer P_4 in solution was characterized by featureless $\pi-\pi^*$ transition (one band) at 367 nm which was blue-shifted compared to the absorption maxima of the other polymers. This is most probably due to the alkoxy groups on the poly(arylene)s backbone which usually lead to an increase of the dihedral angle of consecutive aromatic units, which reduces electronic conjugation leading to an increased band gap.[38]

Unlike P_1, P_2, and P_3, polymer P_4 demonstrated one PL maximum at 422 nm in solution with unresolved shoulder at 445 nm. Polymer P_5 showed absorption maxima at 391 nm with a second band at 408 nm, while the PL maximum was observed at 429 nm. P_5 exhibited also a second higher wavelength but less intense PL maximum at 454 nm which was homologous to the absorption and PL maxima of polymer P_3. Polymers P_6 and P_7 showed absorption maxima at 394 and 396 nm, respectively with PL maxima at 418 nm in solution. The PL spectra were similar to those of polymers P_1-P_5 and characterized also by steep onsets with second vibrationally split maxima at 442 and 441 nm for P_6 and P_7, respectively. Furthermore, the observed PL spectra for P_6 and P_7 suggest that decreasing the number of the aryl units around the triphenylene moiety has no significant effect in solution. The observed PL maxima of ~420 nm for P_1-P_7 compares very well with that of dialkylpolyfluorene (PL maximum ~ 415 nm)[10] which has been widely studied as an active material in blue PLED.

Absorption and PL in Thin Films. The thin films of the above polymers were prepared by spin coating from toluene solutions (~1×10^{-5} M) at 1000 rpm over quartz substrates. As shown in Figures 3 and 4, polymers P_1 and P_2 showed almost identical PL spectra in both solution and film. However the film absorption maxima were blue-shifted compared to the solution maxima by 4 and 16 nm for P_1 and P_2, respectively. Polymer P_3 exhibited an almost identical absorption and PL spectra in both solution and film. In addition a solid state related broadening of the spectra was observed in the three polymers. These results suggest that there is no significant change in the polymer conformations in going from solution to film. From that point of view P_1, P_2, and P_3 can be considered as promising blue emitters for PLED applications. While polymer P_4 gave nearly identical PL spectra in both solution and film, the film absorption maximum was red-shifted by 13 nm from the solution absorption maximum. In contrast to P_1, P_2, and P_3, polymer P_4 showed insignificant broadening in the film PL spectrum. Thus, polymer P_4 displayed a clear advantage over P_1, P_2, and P_3 in terms of more deep and pure blue emission. The absorption of polymer P_5 was nearly the same in both solution and film. However, the PL spectrum revealed a broad bathochromically shifted emission band of 30 nm in film compared to solution. This bathochromic shift suggests that polymer P_5 with fewer aryl units around the triphenylene core undergoes aggregation in the solid state.

Similar to P_5, polymer P_6 exhibited approximately the same absorption behavior in both solution and film. Nevertheless the PL spectrum showed a broader bathochromically shifted maximum of about 40 nm in film compared to solution. This resemblance to the spectra of polymer P_5, despite containing a different $\pi-$conjugated backbone (the inclusion of a phenyl spacer), gave evidence that the solublizing alkyl side chains found on monomer 5e result in the broadening and the bathochromic shift by promoting polymer aggregation. Accordingly polymers P_5 and P_6 with their more pronounced green emission can not be considered as good blue emitters.

Polymer P_7 exhibited more or less the same absorption and emission in both solution and film with a solid state related broadening in the film emission spectrum. The absorption maxima of polymer P_7 were ~9 nm red-shifted from those of polymer P_3 most probably due to the increased conjugation length in case of P_7. Moreover both polymers showed roughly identical PL behavior aside from a broadening in the PL spectra of polymer P_7. These results suggest that the direct coupling between the triphenylene repeating units in the homopolymers did not hinder the conjugation in the polymers backbones due to the probable increased twisting of the different phenyl rings on the sequential triphenylene moieties. Instead it led to analogous optical spectra for polymers P_7 and P_3.

Table 4. HOMO and LUMO Energies and Electrochemical Properties of Polymers (Corrected to Ag/AgCl Reference Electrode)

polymer	$E^{\mathrm{ox/onset}}$ (V)	$E^{\mathrm{ox/peak}}$ (V)	E^{HOMO} (eV)	E^{LUMO} (eV)
P_1	1.55	1.68	5.95	3.08
P_2	1.68	1.87	6.08	3.17
P_3	1.56	1.65	5.96	3.06
P_4	1.39	1.57	5.79	2.77
P_5	1.56	1.71	5.96	3.13
P_6	1.54	1.71	5.94	3.03
P_7	1.50	1.59	5.90	3.0

Quantum Yield. Polymers P_1, P_2, P_5, P_6, and P_7 exhibited high quantum efficiencies (Φ_{PL}) in solution, which were upon excitation at 365 nm in THF, using 9,10-diphenylanthracene ($\Phi_{\mathrm{PL}} = 0.9$) as a standard[44] found to be 0.65, 0.84, 0.66, 0.67, and 0.85, respectively. These values were close to or even in case of P_2 and P_7 higher than polyfluorene containing bis(2,2-diphenylvinyl)fluorene ($\Phi_{\mathrm{PL}} = 0.75$).[45] The values were also close and in case of P_7 equal to the quantum yield of POF ($\Phi_{\mathrm{PL}} = 0.85$).[46]

We estimated the PL quantum yield of P_2, P_4, P_5, P_6, and P_7 in films to be 0.34, 0.34, 0.31, 0.21, and 0.17, respectively. This was done by comparing their fluorescence intensity to that of a thin film sample of POF polymer that was excited at 380 nm ($\Phi_{\mathrm{PL}} = 0.55$).[45,46] The lower quantum efficiencies of P_2, P_5, P_6, and P_7 in film compared to solution might be due to the formation of intermolecular species, i.e. excimer formation or aggregates as in case of P_5 and P_6[46] which suggests that decreasing the number of aryl units around the triphenylene units in case of P_5 and P_6 was not favored.

Cyclic Voltammetry. To investigate the redox properties, cyclic voltammograms were recorded for the polymer thin films against Ag/AgCl with a ferrocene standard (Figure s3, Supporting Information). All polymers showed only anodic peaks with irreversible oxidation which was in agreement with the general case of conjugated polymers, where often only reduction or oxidation is observed or where only one process is found to be reversible.[47−49] For that reason direct estimation of the LUMO levels were not possible. Subsequently the HOMO levels, optical band gaps, and the LUMO levels of the reduced polymers (were deduced from the HOMO values and the polymers optical band gaps) were calculated as described by Janietz et al.[47] Polymers P_1-P_7 showed irreversible oxidation peaks at potentials ranging from 1.57 to 1.87 V (Table 4) and onset potentials of oxidation between 1.39 and 1.68 V in the anodic scan. This could be attributed to the electron rich nature of the polymers which may make it easier to oxidize rather than being reduced.[50,51] Compared with all polymers, the oxidation onset potential of P_4 showed the lowest value which could be due to the electron-donating property of the alkoxy group on the polymer backbone. All polymers exhibited HOMO and LUMO values in the range of 6.0 and 3.0 eV, respectively. These results were analogous to the obtained results for POF which showed HOMO and LUMO values of

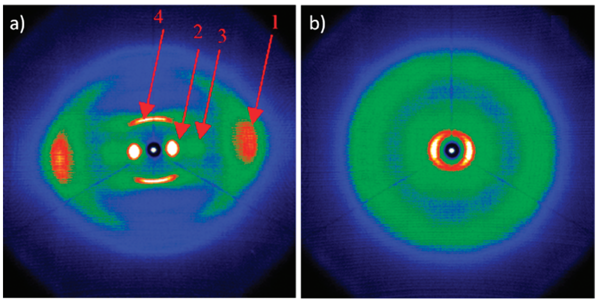


Figure 5. 2D-WAXS of (a) P_5 and (b) P_6.

5.8 and 2.85 eV (estimated),[47] respectively. The expected electron injection barrier from LiF/Al cathode was ~0.2 eV, however the expected hole injection barrier from ITO/PEDOT:PSS anode was ~0.8 eV which should consequently lead to limited charge injection into the polymers. In order to overcome this problem and to obtain better interlayer matching of the HOMO and LUMO properties in the PLED device three additives were used, the electron transporting layers t-PBD, the hole transporting material NPB, and on the top of them a Bphen layer. These additives result in better electron and hole injection into the polymer layers and thus better device performance.[53]

Structure Investigation. The supramolecular structures of polymers P_5 and P_6 have been investigated by two-dimensional wide-angle X-ray scattering (2D-WAXS) on extruded filaments.[52]

The samples were prepared as a thin filament of 0.7 mm diameter by filament extrusion using a home-built mini extruder. Polymers P_5 and P_6 were heated to 230 and 210 °C, respectively to reach a phase at which the polymer became plastically deformable and could be extruded as a thin filament.

The structure investigation was performed using a 2D wide-angle X-ray scattering (WAXS) setup, which is schematically showed in Figure 5. The sample was positioned perpendicular to the incident X-ray beam and vertical to the 2D detector.

In Figure 5 the 2D wide-angle X-ray scattering (2D-WAXS) pattern of polymers P_5 and P_6 are presented. The distinct and strong reflections for P_5 were related to a well-aligned macroscopic organization in the extruded sample, which was not obvious for P_6, confirming the influence of the chemical structure difference on the ordering of the two polymers. The presence of the arylene groups between the triphenylene repeating units in P_5 reduced the twist in the copolymer backbone and result in more ordered structures compared to P_6 in which the triphenylene moieties were directly coupled.

In case of polymer P_5, the wide-angle equatorial scattering intensity (marked in the pattern with arrows as "1") in Figure 5a was related to a stacking distance of 0.43 nm of the adjacent molecules, confirming that the polymer chains are aligned along the extrusion direction of the sample. This value is close to the distance found for different polyfluorene derivates which should result in identical charge carrier transport for this material.[53−55]

The *d*-spacing for the reflection "2" was 2.03 nm and corresponded to the interlamellae distance. The appearance of the second equatorial higher-order scattering intensity in the small-angle region (marked as "3") indicates the formation of well-defined periodic structures. The meridional reflection "4"of 1.25 nm correlates to the distance between monomer units along the polymer chain.

In contrast, the reflections for polymer P_6 were almost isotropic, indicating local order but poor macroscopic orientation (Figure 5b).

Conclusions

In conclusion, we have synthesized a novel series of blue light emitting triphenylene-based polymers in good yields, based on Suzuki−Miyaura and Yamamoto polycondensation reactions. All of the polymers showed deep blue emission in solution with PL maxima centered around 420 nm. However the film UV−vis absorption and PL spectra were diverse, that can be ascribed to the number of aryl units around the triphenylene moiety. Since in case of the less aryl substituted polymers P_5 and P_6 large bathochromic shifts of 30 and 40 nm, respectively were observed in the PL maxima (~460 nm), while in the more aryl substituted polymers P_1, P_2, P_3, P_4, and P_7 the PL maxima were centered around 430 nm to show deep blue emission. This suggests that decreasing the number of aryl units around the triphenylene moiety is not favored since it can lead to polymer aggregates. However no distinct differences were found in the solution UV−vis absorptions and PL spectra between the homopolymers and the copolymers which may suggest similar conjugation interactions along the polymers backbones. From the 2D-WAX studies, we also found that the triphenylene-*alt*-arylene copolymer P_5 was related to a well-aligned macroscopic organization in the extruded sample, which was not obvious for the polytriphenylene homopolymer P_6. This difference in the macroscopic organization can be attributed to the present extra arylene groups between the triphenylene repeating units in the copolymer which reduced the twist in the polymer backbone and result in well organized structure. Overall, the obtained results demonstrated that triphenylene-based polymers are promising candidate for blue-PLEDs. Such devices have been investigated and published elsewhere.[56]

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Supporting Information Available: Text giving the experimental information and figures showing UV-vis spectra, NMR spectra, PL spectra, cyclic voltammograms of drop-casted polymer films, and molar-mass distribution curves of polymers P_1−P_7 obtained by GPC. This material is available free of charge via the Internet at http://pubs.acs.org.

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