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2,7-Carbazole-Based Conjugated Polymers for Blue, Green, and Red Light Emission

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ABSTRACT: Light-emitting 2,7-carbazole-based homopolymers and copolymers were prepared by Yamamoto or Suzuki cross-coupling reaction. Poly(*N*-(2-ethylhexyl)-2,7-carbazole) (PEHC), poly(*N*-octadecyl-2,7-carbazole) (PODC), and poly(*N*-(2-ethylhexyl)-2,7-carbazole-*alt*-4-heptyl-2,5-pyridine) (PCPy) emit blue light while poly(*N*-(2-ethylhexyl)-2,7-carbazole-*alt*-2,3-diheptyl-5,8-quinoxaline) (PCQ) and poly(*N*-(2-ethylhexyl)-2,7-carbazole-*alt*-3,3′,4‴,3⁗-tetramethyl-3″,4″-dihexyl-2,2′:5′,2″:5″,2‴:5‴,2⁗-quinquethiophene-1″, 1″-dioxide) (PCPTO) emit green and red light, respectively. The fluorescence quantum yield in chloroform solution ranges from 25% for PCPTO to 83% for PCQ. All these 2,7-carbazole-based polymers do not show any evidence of excimer formation in the solid state. Most of these polymers exhibit a glass transition at ca. 60−70 °C with a degradation temperature above 385 °C. These new polymeric materials should allow the development of efficient blue-, green-, and red-light-emitting diodes with improved optical stability.

Introduction

Conjugated polymers are now considered as a very important class of electroactive and photoactive materials. Some of these polymers exhibit physical properties which lend themselves to the development of display devices, transistors, sensors, etc.[1−7] Among these applications, the development of flexible and tunable polymeric light-emitting diodes (PLEDs) has received a great deal of attention from both academic and industrial laboratories.[4−7] In its simplest configuration, polymeric light-emitting diodes consist of a positive, transparent, hole-injecting electrode with a high work function, such as indium tin oxide (ITO); a negative, electron-injecting electrode with a low work function, such as Al, Mg, or Ca; and the light-emitting polymer film sandwiched between the two electrodes. In this layered structure, the injected holes and electrons migrate across the polymer layer, combine to form excitons, which then decay with photon emission. The utilization of conjugated polymers in light-emitting diodes offers several important advantages over inorganic and molecular organic materials. The polymers, in principle, can be processed into flexible films with good mechanical properties and large surface areas. Their spectral response can be adjusted through synthetic modifications. It is believed that the next generation of flat panel displays could be made from such light-emitting polymers.

Not surprisingly, many recent studies have been devoted to the development of blue-, green-, and red-light-emitting polymeric materials.[5−7] Along these lines, polyfluorene derivatives (homopolymers and copolymers) are very interesting because of their excellent solubility, good film-forming property, high luminescence quantum yield, and color tunability.[7] However, blue-light-emitting polyfluorenes show poor optical stability in the solid state due to $\pi-\pi$ stacking, which results in the formation of excimers or aggregates that shift emission spectra at longer wavelengths and decrease fluorescence quantum yields.[7] Both excimer and aggregate formations in such fluorene-based conjugated polymers can be avoided by the use of spiro-bifluorene unit,[8] rod−coil block copolymers,[9] random copolymers,[10] asymmetric fluorene units,[11] and sterically hindered side groups[12] or by introducing flexible spacers between the chromophores.[13] However, these different approaches are long and complicated from a synthetic point of view. Moreover, polyfluorenes are subject to oxidative electro- and photodegradation that form carbonyl-containing species, namely fluorenone, when nonsubstituted or monosubstituted fluorene units are present in the polymer main chain.[14,15] A very low concentration (as few as 0.1 mol %) of fluorenone can induce significant optical changes.[14]

As an alternative, we recently briefly reported the first syntheses of electroactive and photoactive poly(2,7-carbazole) derivatives.[16] Interestingly, this class of materials is not subject to the formation of ketone defects. The synthetic strategy was based on a prefunctionalization at the 2,7-positions, followed by ring closure and polymerization (Yamamoto, Suzuki, Stille) reactions. Their electrical, electrochemical, and magnetic properties have been investigated in detail,[17] and promising properties were observed for the development of blue-light-emitting diodes.[18] Poly(2,7-carbazole) derivatives are a particularly suitable class of materials for applications in light-emitting devices because they contain a rigid biphenyl unit (which leads to a large band gap with efficient blue emission), and the facile substitution at the remote N-position provides the possibility of improving the solubility and processability of polymers without significantly increasing the steric interactions in the polymer backbone. To complete investigations on processable poly(2,7-carbazole) derivatives, we report herein the synthesis and characterization of the thermal and optical properties of 2,7-carbazole-based conjugated homopolymers and alternating

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copolymers, namely poly(*N*-(2-ethylhexyl)-2,7-carbazole) (PEHC), poly(*N*-octadecyl-2,7-carbazole) (PODC), poly(*N*-(2-ethylhexyl)-2,7-carbazole-*alt*-4-heptyl-2,5-pyridine) (PCPy), poly(*N*-(2-ethylhexyl)-2,7-carbazole-*alt*-2,3-diheptyl-5,8-quinoxaline) (PCQ), and poly(*N*-(2-ethylhexyl)-2,7-carbazole-*alt*-2,2⁗-diiodo-3,3′,4‴,3⁗-tetramethyl-3″,4″-dihexyl-2,2′:5′,2″:5″,2‴:5‴,2⁗-quinquethiophene-1″,1″-dioxide) (PCPTO). These polymers seem excellent candidates for the future development of blue-, green-, and red-light-emitting diodes.

Experimental Section

Materials. Chloroform (spectrograde) and tetrahydrofuran (HPLC grade) were purchased from Aldrich and used as received. Tetrakis(triphenylphosphine)palladium(0) was synthesized following the procedure reported in the literature[19] and stored under argon in the dark.

All 2,7-functionalized carbazole derivatives were synthesized as previously described.[16,17] 2,5-Dibromo-4-heptylpyridine,[20] 5,8-dibromo-2,3-diheptylquinoxaline,[21] and 2,2⁗-diiodo-3,3′,4‴,3⁗-tetramethyl-3″,4″-dihexyl-2,2′:5′,2″:5″,2‴:5‴,2⁗-quinquethiophene-1″,1″-dioxide[22] were synthesized following procedures reported in the literature. Yamamoto coupling reactions were achieved using the same procedure to that previously reported for the synthesis of 2,7-carbazole-based polymers.[16] Suzuki cross-coupling reactions were achieved using an equimolar ratio of diboronic functionnalized unit and dihalogeno- or ditriflate derivatives.[16,17] Polymerization reactions were carried out in well-degassed THF/2 M $K_2CO_{3(aq)}$ (3:1) with 0.02 equiv of $Pd(PPh_3)_4$ as catalyst at reflux under argon for 3 days. All polymers were purified by precipitation in cold methanol followed by washing with acetone in a Soxhlet apparatus for 48 h. The polymers were redissolved in $CHCl_3$ and filtered on 0.2 μm filter paper.

Characterization. Number-average (M_n) and weight-average (M_w) molecular weights were determined by size exclusion chromatography (SEC) with an HPLC pump using a Waters UV−vis detector. The calibration curve was made with a series of monodispersed polystyrene standards in THF (HPLC grade, Aldrich). UV−vis absorption spectra were recorded on a Hewlett-Packard diode-array spectrophotometer (model 8452A) using 1 cm path length quartz cells. Optical band gaps were calculated from the onset of the UV−vis absorption band. For solid-state measurements, polymer solutions in chloroform were cast on quartz plates. The fluorescence spectra were measured using an Aminco Bowman Series 2. For fluorescence analyses in solution, the polymer concentration was about 10^{-6} M. For solid-state fluorescence analyses, the polymer was cast from a solution on a triangular quartz cell and placed at 45° with respect to the incident beam. The fluorescence quantum yields (ϕ_F) were determined in argon-saturated solutions at 298 K in chloroform against 9,10-diphenylanthracene (Aldrich) in cyclohexane as the standard ($\phi_F = 0.90$) excepted for PCQ and PCPTO where poly(3′,4″-didecyl-2,2′:5′,2″:5″,2‴-quaterthiophene)[23] ($\phi_F = 0.11$) and tris(2,2-bipyridyl)dichlororuthenium(II) ($\phi_F = 0.28$) were used, respectively. All corrected fluorescence excitation spectra were found to be equivalent to their respective absorption spectra. Differential scanning calorimetry (DSC) analyses were performed on a Perkin-Elmer (DSC-7) instrument, calibrated with ultrapure indium. Glass transition temperatures (T_g), melting temperatures (T_m), and enthalpies of fusion (ΔH_m) were measured at a scanning rate of 20 °C/min, under a nitrogen flow. Thermogravimetric measurements (TGA) were carried out with a TC-15 Mettler-Toledo apparatus. The heating rate was 10 °C/min under a nitrogen atmosphere. The temperature of degradation (T_d) corresponds to a 5% weight loss.

Results and Discussion

Synthesis and Characterization. Scheme 1 describes the reactions utilized in the synthesis of the present poly(2,7-carbazole) derivatives. PEHC was first synthesized using the standard Yamamoto coupling reaction using N-substituted, 2,7-ditriflate carbazoles or 2,7-dichloro carbazoles, Ni(0) as catalyst, and cyclooctadiene (COD) as ligand.[21a] As shown in Table 1, both polymeric samples exhibit similar low values of molecular weight (about 2600 and 2200), corresponding to a degree of polymerization of ca. 8−10. To obtain higher molecular weights, Suzuki cross-coupling reaction between *N*-(2-ethylhexyl)-2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)carbazole and *N*-(2-ethylhexyl)-2,7-bis(trifluoromethanesulfonyl)carbazole was carried out. However, this approach made no difference in terms of molecular weights (see Table 1). Introduction of longer substituents (i.e., octadecyl group, see PODC in Table 1) led to essentially similar degrees of polymerization. Finally, a recent study from Zhang et al.,[24] for the synthesis of high molecular weight poly(*N*-alkyl-3,6-carbazole)s, has reported that the slow addition of catalytic nickel solution into monomer solution (a reverse order compared to standard Yamamoto procedures) leads to a stable nickel species that undergoes disproportionation reaction (aryl−aryl coupling) more efficiently without significant hydrolysis or decomposition reaction. However, in our case, this methodology did not lead to any increase of molecular weights for poly(*N*-alkyl-2,7-carbazole)s. All these results could therefore be explained by the relatively low solubility of poly(*N*-alkyl-2,7-carbazole)s in DMF or THF/water mixture, resulting in rapid precipitation of these polymers. Nevertheless, all these relatively low molecular weight homopolymers can be easily processed by spin-coating or simple casting on various substrates to yield thin polymer films with good mechanical properties.

To increase molecular weight in 2,7-carbazole-based conjugated polymers, copolymerization with more substituted aromatic units might be a good approach. Moreover, as recently reported for polyfluorene derivatives,[7] this approach may allow the tuning of the optical properties over the entire visible range. The synthesis of alternating copolymers was then achieved using Suzuki cross-coupling reaction. Since polymerization using boronic functionalized thiophenes or electron-deficient units results generally in low molecular weight polymers,[25] boronic esters were introduced onto the carbazole unit. Therefore, *N*-ethylhexyl-2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)carbazole[17] was used in the presence of 2,5-dibromo-4-heptylpyridine, 5,8-dibromo-2,3-diheptylquinoxaline, and 2,2⁗-diiodo-3,3′,4‴,3⁗-tetramethyl-3″,4″-dihexyl-2,2′:5′,2″:5″,2‴:5‴,2⁗-quinquethiophene-1″,1″-dioxide for the synthesis of the corresponding PCPy, PCQ, and PCPTO. As shown in Table 1, these alternating copolymers exhibit slightly higher degrees of polymerization (M_n from 5000 to 10 000) than those reported for the homopolymers.

Interestingly, all 2,7-carbazole-based homopolymers and alternating copolymers (with the notable exception of PODC, discussed below) are amorphous with glass transition temperatures around 60−70 °C (118 °C for PCPTO), and most of them are stable up to temperatures around 400 °C (see Table 1). PCPTO is less stable, and that might be related to the relative thermal instability of the thiophene moieties. PODC exhibits a melting temperature around 108 °C, presumably due to the crystallization of the side chains. Similar thermal phenomena have been reported for some alkyl-substituted polythiophenes.[26] The plasticizing effect of the

Scheme 1. Syntheses of the Polymers

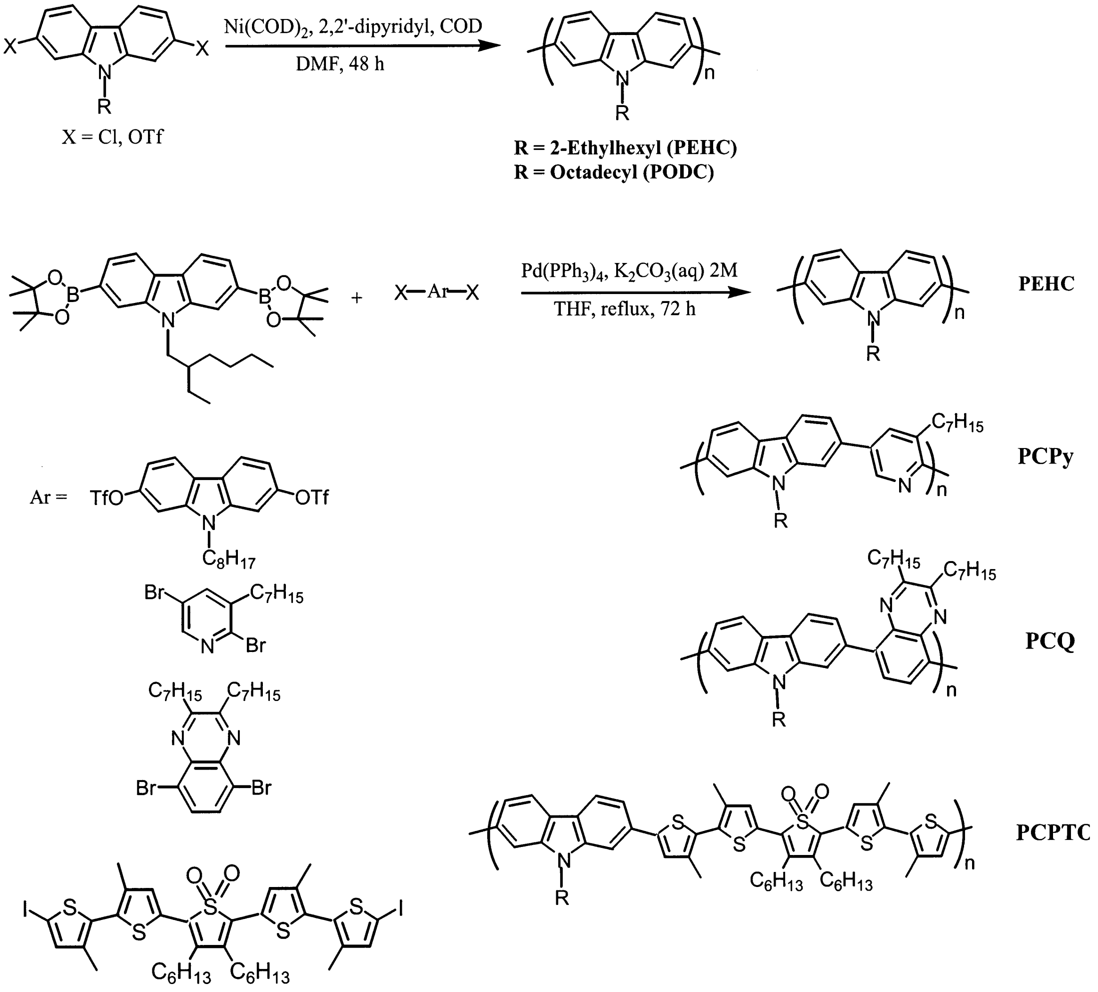

Table 1. Polymerization Yields, Molecular Weights, and Thermal Properties of the Polymers

polymer	yield (%)	M_n (g/mol)	M_w/M_n	T_g (°C)	T_m (°C)	ΔH_m (J/g)	T_d (°C)	method[a]
PEHC	77	2200	1.9					1
PEHC	71	2600	1.5					2
PEHC	67	2000	1.3	68			385	3
PODC	69	3700	1.3	54	108	23	432	2
PCPy	48	5000	2.3	66			400	1
PCQ	45	10000	2.8	61			403	1
PCPTO	74	8600[b]	4.8	118			315	1

[a] Suzuki coupling (1), Yamamoto using dichloro derivatives (2), and Yamamoto using ditriflate derivatives (3). [b] Molecular weight determined in $CHCl_3$.

relatively long substituent may also explain the relatively low glass transition temperature at 54 °C.

Optical Properties. The UV−vis absorption and photoluminescence properties of these processable 2,7-carbazole-based conjugated polymers are summarized in Table 2. All blue-light-emitting homopolymers (PEHC, PODC) show essentially similar properties, and as an example, solution and solid-state absorption and emission spectra of PEHC are reported in Figure 1. The absorption maximum, both in chloroform solution and in the solid state, is around 380 nm. These similar optical properties seem to indicate that carbazole-based homopolymers exhibit very similar conformations in both states. Photoluminescence spectra of these homopolymers show a maximum of emission around 420 nm in chloroform solution and 440 nm in solid state. This slight difference might be attributed to weak interchain interactions. These emission spectra show also a vibronic fine structure, generally associated with a rigid and well-defined backbone in the excited state.[27] Moreover, these polymers exhibit very high fluorescence quantum yields (up to 0.80; see Table 2) in solution, similar to those reported for poly(9,9-dialkyl-2,7-fluorene)s.[7] Interestingly, despite relatively low degrees of

Table 2. Optical Properties of the Polymers

	solution λ_{max} (nm)[a]		thin film λ_{max} (nm)[b]		ϕ_F	E_g
polymer	abs	emi	abs	emi	sol	(eV)
PEHC[c]	381	420 (440)	383	440 (468)	0.76	2.83
PEHC[d]	380	417 (439)	383	439 (459)	0.80	2.83
PEHC[e]	380	417 (442)	382	442 (465)	0.76	2.83
PODC	374	418 (440)	380	437 (460)	0.80	2.83
PCPy	354	407 (426)	362	430	0.40	3.02
PCQ	(324) 402	500 (487)	(328) 412	502	0.83	2.59
PCPTO	(377) 480	638	(388) 512	671	0.25	1.84

[a] Spectra in chloroform. [b] Polymer cast from a chloroform solution. [c] PEHC made from method 1. [d] PEHC made from method 2. [e] PEHC made from method 3.

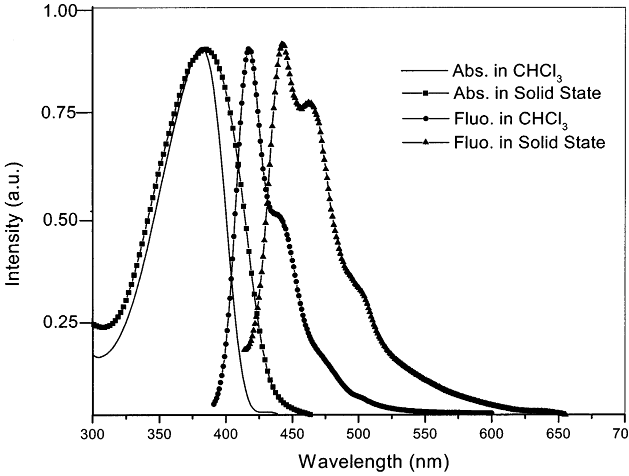

Figure 1. UV−vis absorption and fluorescence spectra of PEHC both in $CHCl_3$ and in the solid state.

polymerization, the nature of the end groups does not seem to influence the fluorescence quantum yields. However, in contrast to polyfluorene derivatives,[7,14] these poly(2,7-carbazole)s do not show any evidence of excimer formation or so-called aggregation emission peak in the solid state and do not seem to lead to the formation of oxidized sites. Preliminary measurements did not reveal any significant shift of the emission spectrum as a function of time and/or temperature. These features are particularly promising for the future development of stable, polymeric blue-light-emitting devices.

With solid-state absorption and emission maxima at 362 and 430 nm, the optical properties of PCPy are slightly blue-shifted with respect to PEHC. This weak blue shift is partially due to the more important steric hindrance induced by the heptyl chain (required for solubility) onto the pyridine unit, resulting in a more twisted backbone. The choice of pyridine as a comonomer for blue emission was motivated by their electron-deficient character, which generally leads to good electron transport properties. The combination of carbazole units (good hole transport units) and pyridine moieties should lead to efficient and balanced transport of both charge carriers and consequently to high electroluminescence quantum yields.

The optical properties of PCQ are summarized in Figure 2. The solution and solid-state absorption spectra of this polymer show a maximum at 402 and 412 nm, respectively. The presence of a peak at 320 nm is presumably due to the diimine function of the quinoxaline unit. The red shift of the optical properties of PCQ compared to PEHC is attributed to the presence of an intramolecular donor−acceptor phenomenon between quinoxaline,[28] a strong electron-withdrawing group, and carbazole, an electron-rich unit, which decrease the $\pi-\pi^*$ energy gap. This polymer is an efficient green emitter both in solution ($\phi_F = 0.83$, in solution) and in the solid state. In a previous communication,[16] we reported that poly(*N*-alkyl-2,7-carbazole-*alt*-5,5′-(2,2′-bithiophene)) (PCBT) is also a green emitter in solution, but in contrast to PCQ, the luminescence of PCBT is almost totally quenched in the solid state (the solid-state fluorescence spectrum cannot be recorded). These different behaviors could be explained by a coplanar conformation (which favors strong interchain interactions which are known to enhance nonradiative deactivation pathways[29]) for PCBT and by a nonplanar conformation for PCQ in the solid state. This information is important for the future design of solid-state luminescent poly(2,7-carbazole) derivatives.

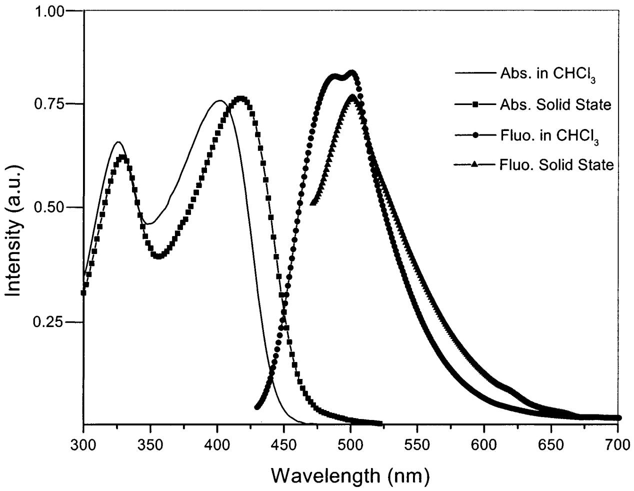

Figure 2. UV−vis absorption and fluorescence spectra of PCQ both in $CHCl_3$ and in the solid state.

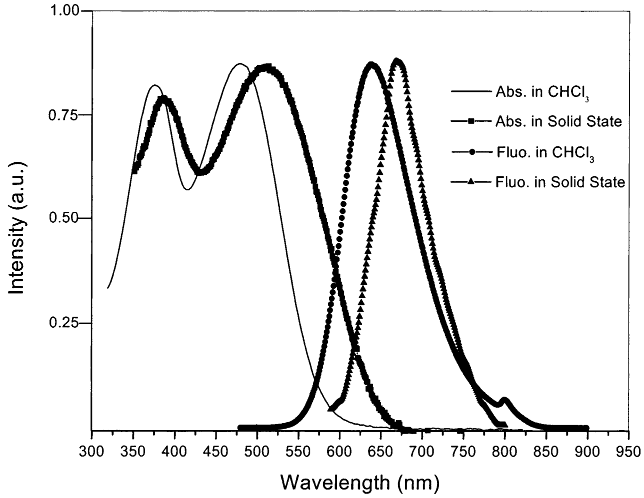

Figure 3. UV−vis absorption and fluorescence spectra of PCPTO both in $CHCl_3$ and in the solid state.

On the basis and in agreement with previous studies from Barbarella et al.[22] on low-band-gap oligothiophenes and Beaupré and Leclerc[30] on low-band-gap alternating polyfluorene derivatives, red light emission was obtained with PCPTO. As shown in Figure 3, its solid-state absorption spectrum shows absorption maxima at 392 and 512 nm corresponding to a n,σ^*_{S-O} and $\pi-\pi^*$ transition, respectively. The fluorescence spectra in both solid state and solution show a relatively narrow band centered at 671 and 638 nm, respectively, with a fluorescence quantum yield of 25% in solution. Therefore, by combining different comonomers, it is possible to develop 2,7-carbazole-based conjugated polymers that emit colors spanning the entire visible range with high efficiency.

Conclusion

This study reports the synthesis and characterization of luminescent 2,7-carbazole-based homopolymers and alternating copolymers that cover the blue, green, and red range. These amorphous polymers exhibit good thermal stabilities and processability together with interesting and stable optical properties. Moreover, the possibility of a fine-tuning of the transport and luminescence properties clearly indicates that 2,7-carbazole-based conjugated polymers are highly promising materials for the development of stable, full-color, electroluminescent polymers. This new class of conjugated polymers will be soon tested in different light-emitting devices.

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