2716 *Macromolecules* **2005,** *38,* 2716−2721

Synthesis and Optical Properties of Simple Amine-Containing Conjugated Polymers

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Received October 13, 2004; Revised Manuscript Received January 21, 2005

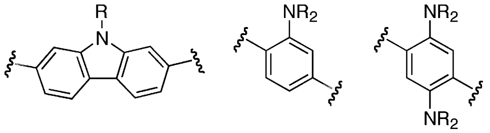
ABSTRACT: Conjugated polymers (CPs) containing amino groups have been synthesized, and their optical properties in both solution and thin film have been studied. New monomers required for the synthesis of these polymers have been readily prepared via efficient synthetic routes. These monomers have been successfully polymerized with a variety of comonomers. The spectral positions of the absorption and emission spectra correlate with the degree of electron density on the polymer chain. Polymers containing *N*-alkylcarbazole units display similar optical properties in solution to most CPs. Polymers with dialkylamino groups, however, display very different optical properties, including broadened absorbance and emission spectra, larger Stokes shifts, and longer excited state lifetimes. These results are consistent with a significant difference between the molecular geometries of the absorbing and emitting states. The solid state emission of most of the polymers is sufficient to warrant them for consideration as fluorescent sensing materials.

Introduction

Organic semiconductors have uniquely tunable optical and electronic properties that can be tailored for particular applications. Important design principles naturally depend on the application for which the conjugated polymer is intended. Sensor systems based on conjugated polymers developed in our research group and elsewhere typically rely on amplified signal transduction by electron-transfer quenching from the conjugated polymer to a bound analyte[1] or by fluorescence resonanance energy transfer from the polymer to an energy acceptor.[2] Amplification arises from the ability of delocalized photogenerated excitons to sample many potential binding sites within one excited state lifetime. Some recent important design principles in this field have included the incorporation of shape-persistent three-dimensional structures to prevent aggregation of conjugated polymer chains in the solid state,[1c,3] the introduction of electron-poor substituents to reverse the direction of electron transfer with electron-rich analytes,[4] and the taking advantage of biological binding events to give highly specific sensing.[5]

One of our recent goals has been to expand the versatility of our conjugated polymer sensors to include the ability to sense, via an amplified photoinduced electron transfer quenching scheme, analytes that have less favorable reduction potentials than nitroaromatics and quinones. This requires the development of conjugated polymers with stronger electron-donating character and smaller work functions in order to induce analyte binding and electron transfer. As part of our efforts to realize this goal, we observed that there is relatively little available literature concerning simple amine-containing conjugated polymers. Notable exceptions are carbazole-containing conjugated polymers (principally of the poly(phenylene) class), which have recently received a large degree of interest in the organic light emitting device field,[6] as well as poly(bis(dialkylamino)phenylenevinylene)s.[7] Herein we report the synthesis and photophysical properties of a series of simple amine-containing conjugated polymers, in which the amine groups are part of the conjugated system.

Chart 1. Amine-Containing Building Blocks Used



Results and Discussion

Monomer Synthesis. The three basic amine-containing synthetic building blocks used in the design and synthesis of these polymers are illustrated in Chart 1. These include the 2,7-disubstituted carbazole unit, the 2,5-disubstituted aniline unit, and the 2,5-disubstituted *p*-phenylenediamine unit. Carbazole-containing conjugated systems polymerized through the 2- and 7-positions are preferable to the more easily prepared 3,6-disubstituted systems because of a greater degree of delocalization along the polymer backbone.[6c,e] There have been efficient published syntheses of *N*-alkyl-2,7-dichloro- or dibromocarbazoles for the purpose of making polymers via metal-mediated cross-coupling chemistry.[6c,8] Scheme 1 illustrates how the 2,7-diiodide **1** can be obtained in 45% yield after recrystallization by lithiation of the corresponding dibromide[8] followed by quenching with molecular iodine.

N,*N*-Dialkylanilines containing iodides or terminal acetylenes for the synthesis of poly(phenylyeneethynylene)s, heretofore unreported in the literature, can be obtained in a straightforward and efficient manner as shown in Scheme 1. Dialkylation of 2,5-dibromoaniline using sodium hydride and the appropriate alkyl bromide gave the fully alkylated dibromoaniline in 84% yield. Transhalogenation as described above gave the diiodide **2** in 72% yield. The bis(TMS-acetylene) was isolated in 64% yield by Sonogashira cross-coupling with a small excess of (trimethylsilyl)acetylene. As a byproduct of this reaction, the monoiodide illustrated in

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10.1021/ma0478815 CCC: $30.25

Scheme 1. Synthesis of Amine-Containing Monomers for Cross-Coupling Polymerizations

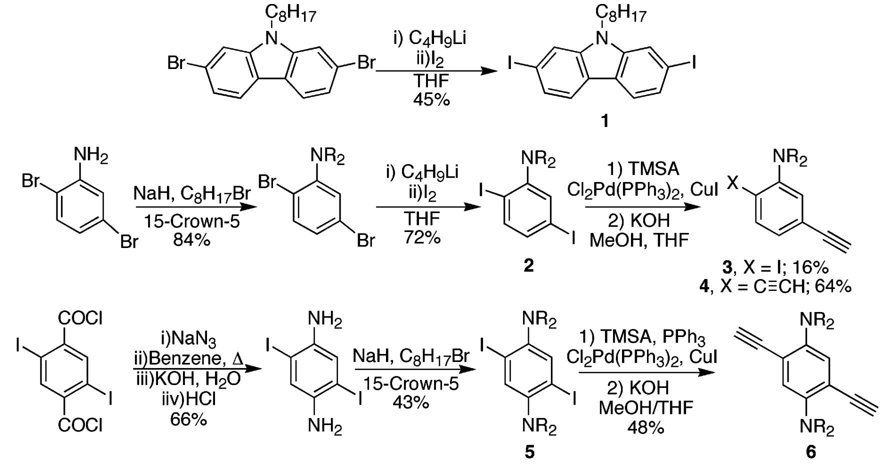
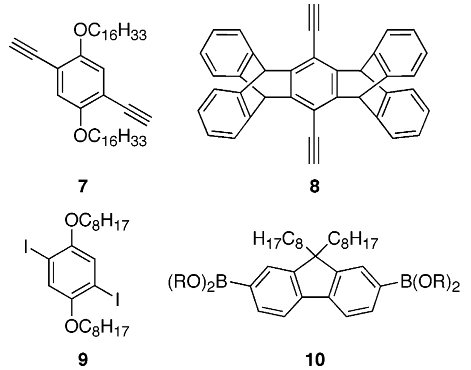


Table 1. Polymer Solution Optical Properties (THF)

polymer	M_n (DP)[a]	abs λ(onset) (nm)	abs λ(max) (nm)	emis λ(max) (nm)	Φ_f	τ_f(ns)[d]
P1	6700 (7)	490	420	458	0.28	0.6
P2	6300 (8)[b]	450	386	423	0.51	0.5
P3	11K (14)	485	350	476	0.64	1.8
P4	16K (23)	495	426	471	0.30	1.0
P5	32K (46)[c]	495	435	480	0.58	0.9
P6	20K (19)	550	353	580	0.50	3.9
P7	31K (33)	550	453	594	0.39	3.2
P8	14K (18)	415	368	413	0.86	0.6
P9	6600 (9)	425	366	453	0.57	1.9
P10	4000 (4)	445	360	512	0.22	4.2

[a] Molecular weights were determined by gel permeation chromatography (GPC) and are reported relative to polystyrene standards. [b] Reflects the molecular weight of only the soluble portion (~50%). [c] Reflects the molecular weight of only the soluble portion (~30%). [d] Reported fluorescence lifetimes are fit to a single-exponential function.

Chart 2. Comonomers Used in Cross-Coupling Polymerizations



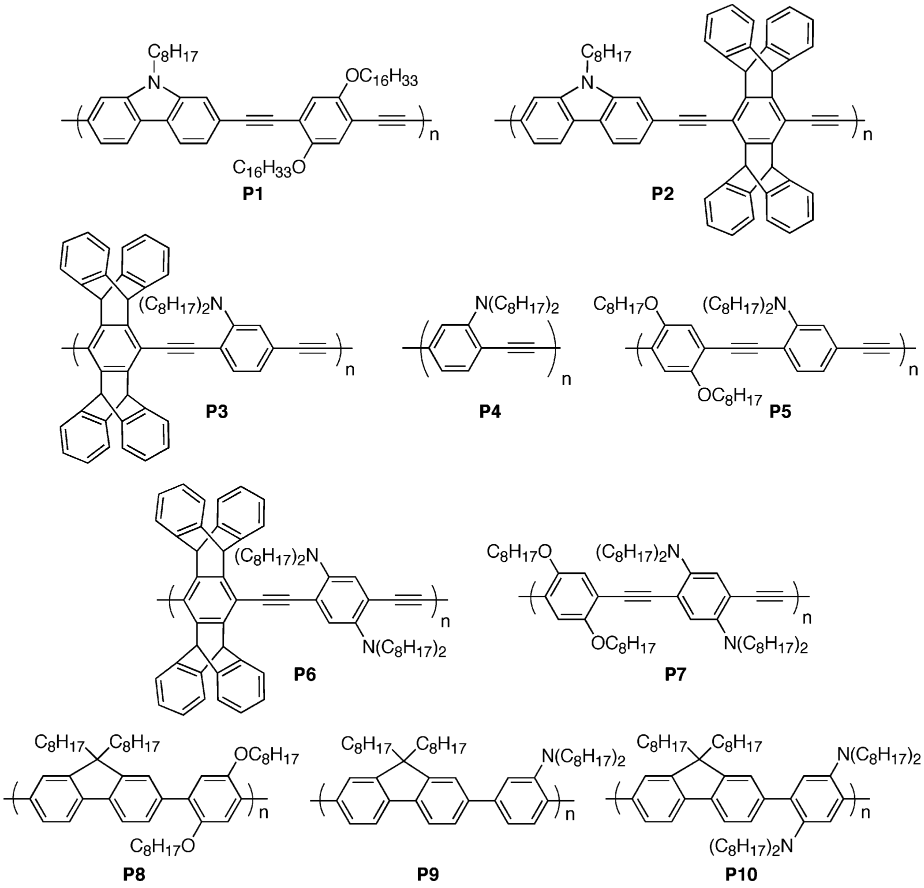
Scheme 1 was also isolated in 16% yield. The regiochemistry of this byproduct was confirmed by analysis of coupling constants and chemical shifts in the ^{1}H NMR spectrum. This is the expected byproduct, since a combination of electron-donating ability and steric influence of the amine retards cross-coupling reactions at the ortho position. Each of these monomer precursors could be readily deprotected to reveal the terminal acetylenes **3** and **4**.

Tetraalkylated diiiodophenylenediamines have been reported previously.[9] Scheme 1 shows that by carrying out a Curtius rearrangement with the diacyl azide (prepared from the corresponding diacyl chloride[1b]) the diiodophenylenediamine was efficiently prepared. Tetraalkylation with a primary bromide in the presence of sodium hydride and 15-crown-5 gave the desired diiodide monomer **5**. This was also transformed into the diacetylene monomer via a similar Sonogashira coupling/deprotection sequence as described above to give **6**.

Polymer Synthesis. These amine-containing monomers were effectively polymerized using standard cross-coupling polymerization methods. Table 1 summarizes the molecular weights and degrees of polymerization. Poly(phenyleneethynylene)s (PPEs) were prepared using tetrakis(triphenylphosphine)palladium and copper iodide catalysts in the presence of an amine solvent. It was found that a mixture of toluene and diisopropylamine was a better solvent system than morpholine, giving higher molecular weights and yields of the PPEs. Several different comonomers with different steric and electronic properties were used, as illustrated in Chart 2. Polymerization reactions with amine-containing aryl iodides were less efficient that those with amine-containing aryl alkynes, giving lower degrees of polymerization with longer reaction times and higher temperatures. Whereas polymers prepared with amine-containing dialkynes (**P5** and **P7**) could be precipitated after 6 h at 65 °C, **P3** and **P6** were polymerized for 24–48 h at 90 °C. The presence of very strong electron-donating groups on aryl halides typically has a detrimental effect on cross-coupling reactions.[10]

Similar reactivity trends were observed in the synthesis of poly(phenylene)s. These polymers **P8**, **P9**, and **P10** were prepared via biphasic Suzuki coupling using tetrakis(triphenylphosphine)palladium and potassium carbonate in the presence of a phase transfer catalyst. A diboronic ester of 9,9-dioctylfluorene was used as the comonomer in these polymerizations. Whereas using a standard *p*-dialkoxy diiodide under these conditions gave a molecular weight of 14 000 (GPC, DP = 18), using the diiodoaniline **2** gave a more modest molecular weight of 6600. The diamino diiodide **5** proved to be the

Chart 3. Polymers Synthesized in This Study



least efficient coupling partner, giving **P10** as a mixture of oligomers with a number-average molecular weight of 4000. In the case of poly(phenylene)s, optical properties were found to be very similar for fractionated (via prep-GPC) high molecular weight polymer as for bulk precipitated polymer.[6d] The structures of the polymers studied in this work are displayed in Chart 3.

Solution Electronic Spectra. UV/vis spectra of all the polymers synthesized in this study were acquired in solution. As can be observed in Figure 1 and Table 1, the absorption stretches further to red as a function of electron density in the polymer chain. This is expected since increasing electron density in a conjugated polymer reduces the oxidation potential, thereby raising the energy of the valence band. This effect is well documented for moderately electron-donating alkoxy groups.[11] Amine groups show this trend to an even greater extent.

PPEs containing carbazole in this study behave very similarly to well-known dialkoxy-PPEs. They have a relatively narrow absorption band in the near visible or ultraviolet region of the spectrum and display little solvatochromism. In contrast, the polymers that contain dialkylamino groups in general do not follow these trends. Most show very broad absorption bands with local maxima in the ultraviolet and long tails that decay well into the visible. **P3**, **P4**, **P6**, and **P7** even display what appear to be two distinct transitions in this spectral region, with one occurring at about 350 nm and the other in the visible. Initial speculation that this was due to the presence of lower molecular weight oligomers was overturned because samples (obtained via prep-GPC) of high molecular weight (DP > 15) and narrow polydispersity (PDI ~ 1.05) showed the same spectra. Similarly broad electronic spectra have been observed with a PPE containing only dialkylamino substituents.[12] This effect can be attributed to a more varied collection of polymer conformations in solution.

Also, in contrast to the carbazole-containing polymers, several of the dialkylamino polymers presented here also display solvatochromism in their absorption spectra. Table 2 displays this effect in toluene and THF. This is most easily visualized in Figure 3 with **P3**, which is a copolymer PPE with alternating aniline and pentiptycene units. The maximum absorbance shifts from 338 nm in toluene to 350 nm in tetrahydrofuran (THF) to 358 nm in *N*,*N*-dimethylformamide (DMF). Comparison of GPC traces of **P3** in THF and DMF shows the same degree of polymerization and no apparent aggregation. The observation of solvatochromic behavior typically indicates the presence of charge-transfer character. In these polymers, there are no traditional electron-withdrawing groups along the polymer chain and therefore no clear donor−acceptor CT states. This is indicative of the strong donor character of the amine in the PPE framework.

Solution State Fluorescence. Figures 1 and 2 display fluorescence spectra of several of the amino-containing polymers in THF, while Table 1 summarizes important fluorescence data of these polymers. As expected, when more electron density is injected into the polymer main chain, there is a corresponding red shift of the emission spectrum. On an absolute scale the poly(phenylene)s give blue-shifted emission spectra relative to PPEs made up of electronically similar monomers. For instance, comparing the emission spectra of **P3** and **P9** shows a 23 nm blue shift for the poly(phenylene). PPPs are known to be a more blue-emitting class of conjugated polymers relative to PPEs due to a

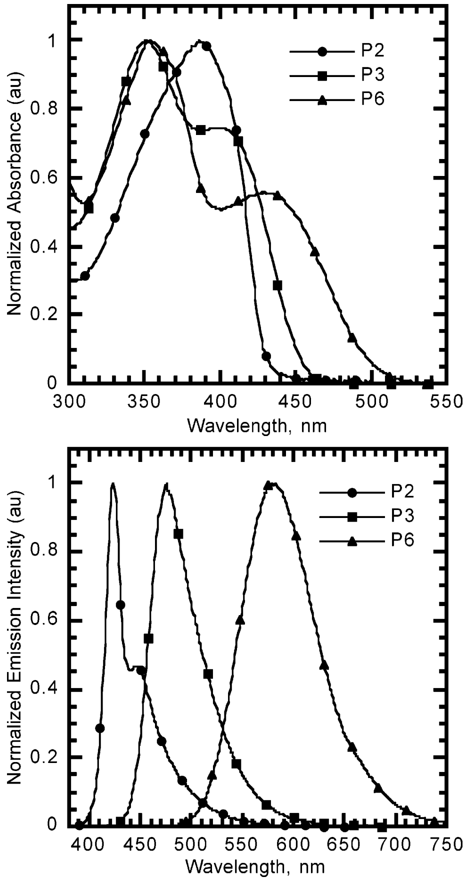


Figure 1. Absorption and emission spectra of the structurally analogous PPEs **P2** (carbazole), **P3** (monoamine), and **P6** (diamine) in THF.

Table 2. Polymer Solvatochromism

polymer	absorbance λ_{max} (nm) toluene	absorbance λ_{max} (nm) THF	emission λ_{max} (nm) toluene	emission λ_{max} (nm) THF
P3	338	350	462	475
P4	425	426	467	471
P5	434	435	478	480
P6	350	353	561	580
P7	453	453	582	594
P9	366	366	445	453
P10	350	360	500	512

decrease in effective conjugation along the polymer main chain and higher aromatic character stemming from the twisted biphenyl-type linkages.[13]

As was observed in the absorption spectra, there is significant solvatochromism in the emission spectra of some of the dialkylamino conjugated polymers studied. The solvent-dependent emission of **P3**, illustrated in Figure 3, shifts from 462 nm in toluene to 499 nm in DMF. This corresponds to a stabilization of ~0.2 eV, similar to that observed in the absorption spectra. The degree of solvatochromism is largest when the difference between the electron-donating ability of the comonomers (i.e., **P3**, **P6**, and **P10**) is maximized.

There are several other interesting and unique trends in the emission of conjugated polymers containing dialkyl amino groups. Whereas most conjugated polymers display at least some vibronic structure in their room temperature emission spectra (including the carbazole PPEs presented here), these conjugated polymers with dialkylamino groups have spectra that are comparatively broad and featureless. This is accompanied by a large Stokes shift, which is greater in magnitude for diamino polymers relative to monoamine polymers. Finally, there is a dramatic lengthening of excited state lifetime upon introduction of dialkylamino groups. This is easily observed in structurally similar polymers **P2**, **P3**, and **P6** (pentiptycene-containing PPE class, from 0.5 to 3.9 ns), **P1**, **P5**, and **P7** (dialkoxyphenylene-containing PPE class, from 0.6 to 3.2 ns), and **P8** through **P10** (PPP class, from 0.6 to 4.2 ns).

This information taken together suggests a significant conformational difference between a relatively twisted absorbing ground state and the emitting excited state, which possibly adopts a more planar excited state conformation, in the dialkylamino polymers. Large Stokes shifts accompanied by broadened emission spectra are consistent with this model.[1c,14] This is further supported by a strong correlation between the Stokes

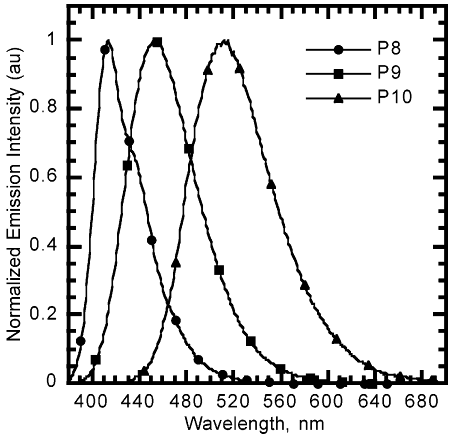


Figure 2. Emission spectra of fluorene-based poly(*p*-phenylene)s **P8**, **P9**, and **P10** in THF.

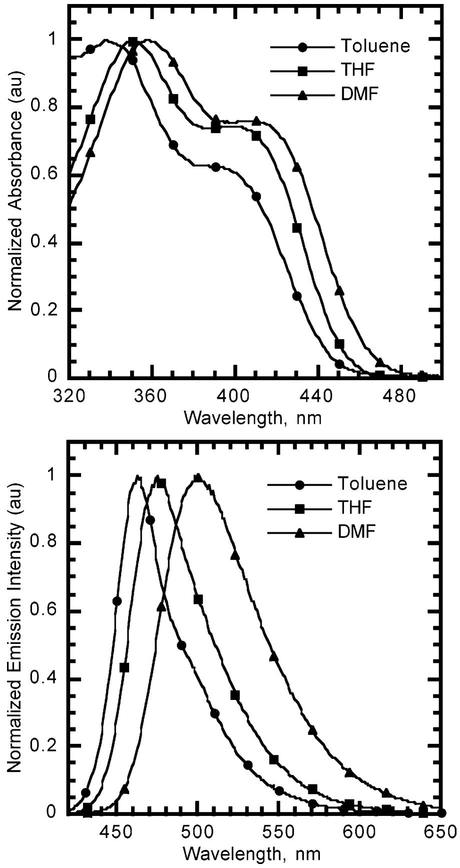


Figure 3. Solvent-dependent absorption and emission of **P3**.

Table 3. Thin Film Optical Properties

polymer	abs λ_{max} (nm)	emis λ_{max} (nm)	polymer	abs λ_{max} (nm)	emis λ_{max} (nm)
P1	420	570[a]	**P6**	356	557
P2	385	460[a]	**P7**	480	581
P3	352	472	**P8**	376	415
P4	451	518	**P9**	380	462
P5	450	486	**P10**	362	499

[a] New exciplex band in solid state.

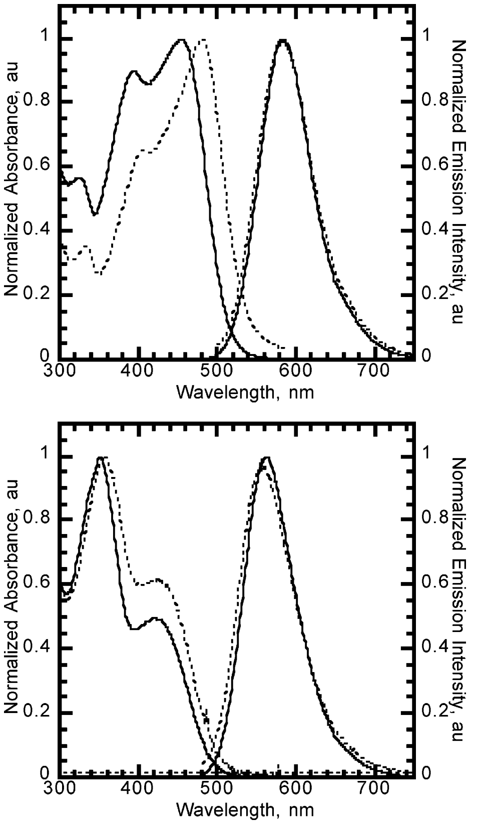


Figure 4. Toluene solution (solid line) and thin film (dotted line) absorption and emission spectra of **P7** (top) and **P6** (bottom).

shift and excited state liftetime. Longer excited state lifetimes indicate slower rates of radiative decay, also consistent with the smaller overlap of the vibronic wave functions of structurally different ground and excited states. Evidence for this significant of a structural difference between ground and excited states is not observed in more thoroughly studied dialkoxy conjugated polymers or in the carbazole-based polymers studied here.

Thin Film Behavior. Absorption and emission spectra of spun-cast thin films of these polymers from either chloroform or THF were acquired. Many of the polymers show adequate solid state brightness for use in sensory devices. Table 3 summarizes some of the optical properties of these polymers in thin film. These polymers follow some of the same trends in the solid state as in solution. For instance, polymers with more electron-donating groups are further red-shifted than those with less. Dialkylamino polymers give broad and featureless spectra, while polymers containing only alkoxy groups retain more vibronic structure in their thin film emission.

All polymers in the poly(phenylene) series display only limited aggregation behavior based on the absorption and emission spectra, in that there is minimal bathochromic shifting in the thin film relative to solution,[15] as well as retention of strong emission in the solid state. These qualities are among those that have made them so popular in PLED research.[16] The PPE series also shows interesting solid state behavior. Carbazole-based polymers **P1** and **P2** are highly quenched in thin film and also exhibit a new band that is highly red-shifted relative to the solution emission, without a corresponding change in the absorbance spectra. These results are consistent with formation of an exciplex, which carbazole is known to form with the emissive layers of OLEDs.[17]

Most of the dialkylamino PPEs, on the other hand, still retain significant solid state emission intensity upon spin-casting thin films. Excluding **P4**, the emission spectra in the solid state are very similar in spectral position and shape (shifts in spun-cast films were less than 10 nm) relative to their solution spectra. Distinct aggregation bands were not observed in the emission spectra. This is true even for polymers **P5** and **P7** that do not contain rigid pentiptycene groups. Nevertheless, those polymers with pentiptycene groups, **P3** and **P6**, show a smaller red shift in the maxima of their absorption spectra between solution and film (3−5 nm) than do **P5** and **P7**, which show a shift of 15−20 nm. This highlights the ability of the pentiptycene moiety to prevent interchain interactions in the solid state.[1c] Figure 4 illustrates these properties for several of the polymers studied. The well-behaved solid state photophysics of most of these polymers, even some of those without pentiptycene moieties, make them candidates for fluorescent chemosensing materials.

Conclusion. We have designed, synthesized, and photophysically characterized a series of new simple amine-containing conjugated polymers in which the amines are part of the conjugated system. The color of emission is easily tunable over a broad range as a function of electron density on the polymer chain, with more electron-rich polymers giving red-shifted emission. The solution optical properties of carbazole-containing PPEs are similar to most related polymers, while their high degree of self-quenching in the solid state makes them poor candidates for sensory applications. On the other hand, PPEs and PPPs containing dialkylamino groups display unique photophysical properties, including larger Stokes shifts and longer excited state lifetimes. Most are not strongly self-quenched in the solid and therefore retain a significant degree of solid state luminescence. The potential of these polymers in sensing applications, particularly for analytes that have a less favorable reduction potential than nitroaromatics or quinones, is currently being evaluated.

Acknowledgment. The authors acknowledge The Transportation Security Administration, The Technical Support Working Group, Sandia National Laboratories, and The Institute for Soldier Nanotechnologies for support as well as Mr. Jean Bouffard for the donation of 2,5-diiodo-1,4-dibenzoyl chloride.

Supporting Information Available: Experimental details for monomer and polymer synthesis as well as additional absorbance and fluorescence spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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MA0478815