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Photodegradation of Emissive Conjugated Copolymers and Oligomers Containing Thienopyrazine

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ABSTRACT: The thieno[3,4-*b*]pyrazine moiety in conjugated copolymers and model compounds degrades upon UV irradiation in air, in both solution and the solid state. The photodegradation is evidenced by the substantial changes in the photophysical, electroluminescent, and structural properties of thieno[3,4-*b*]pyrazine-containing emissive conjugated copolymers and oligomers upon their exposure to UV radiation. Depending on the irradiation time, partial or complete quenching of the intramolecular charge transfer absorption and emission bands of the copolymers and oligomers is observed in dilute toluene solutions and in thin films, clearly pointing to a selective photodegradation of the thieno[3,4-*b*]pyrazine moiety in the emissive materials. ^{1}H NMR and FTIR spectroscopies on a thieno[3,4-*b*]pyrazine-containing oligomer revealed changes in the molecular structure of the thieno[3,4-*b*]pyrazine ring upon photoirradiation. It appears that the C═N bonds in the thieno[3,4-*b*]pyrazine ring are broken down to form a secondary amine, destroying the native electron-accepting property of the thieno[3,4-*b*]pyrazine ring. The observed poor photochemical stability of the thieno[3,4-*b*]pyrazine moiety has implications for the performance and durability of organic solid-state devices based on thieno[3,4-*b*]pyrazine-containing semiconductors, including light-emitting diodes, solar cells, and thin film transistors.

Introduction

Semiconducting π-conjugated oligomers and polymers are extensively being investigated as the active elements in various organic electronic and optoelectronic devices, including organic light-emitting diodes (OLEDs),[1] organic solar cells,[2] and organic thin film transistors (OTFTs).[3] Photochemical instability of the organic semiconductors, particularly in the presence of ambient oxygen and moisture, is one of the main factors currently limiting the performance and lifetime of organic devices on the path toward their commercial scale applications.[1b,c,f] Several studies of the photodegradation of technologically relevant classes of materials have been reported,[4] including poly(alkylthiophene)s (PATs),[5] poly(*p*-phenylenevinylene)s (PPVs),[6,7] poly(*p*-phenyleneethynylene)s (PPEs),[7] poly(dialkylfluorene)s (PFs),[8] and conducting poly(3,4-ethylenedioxythiophene) (PEDOT).[9] Understanding of the effects of photoirradiation on the optical and optoelectronic properties of organic semiconductors and of the underlying photodegradation mechanisms is needed to guide the design of new environmentally robust materials and improve the durability of organic electronic and optoelectronic devices.

Conjugated copolymers and oligomers containing electron-deficient (n-type) thieno[3,4-*b*]pyrazine moiety are currently of much interest as emissive materials for red and white OLEDs,[10] as small band gap donor−acceptor polymers with near-infrared absorption for efficient light harvesting in solar cells,[11] and as semiconductors for ambipolar thin film transistors.[12] The thieno[3,4-*b*]pyrazine moiety has also been demonstrated as an excellent building block for the development of small band gap conducting polymers.[13−17] Because of its growing significance as an n-type building block in developing organic semiconductors for diverse applications, knowledge of the photochemical stability of thieno[3,4-*b*]pyrazine-containing molecules and polymers should be of broad interest. However, nothing is currently known about its photochemistry and photochemical stability; only the basic photophysical properties of thieno[3,4-*b*]pyrazine derivatives have been reported.[18]

In this paper, we report studies of the effects of UV irradiation on the optical absorption, photoluminescence, and electroluminescence of thieno[3,4-*b*]pyrazine-containing emissive conjugated copolymers and oligomers. The materials investigated, whose structures are shown in Chart 1, include new model polyfluorene copolymers containing 10-hexylphenoxazine (HPO)[19] or 9-fluorenone (FLO)[8,20] and thieno[3,4-*b*]pyrazine (TP) that were synthesized by Suzuki coupling polymerization. The synthetic strategy ensured achievement of well-defined molecular structures in which each HPT, FLO, or TP moiety is isolated within the poly(9,9-dioctylfluorene) (PFO) chains. The polymers studied include a PFO copolymer containing 2 mol % TP (2FTP),[10b] a PFO copolymer containing 2 mol % TP and 0.1 mol % FLO (FFOTP), and a PFO copolymer containing 1 mol % each of TP and HPO (FPOTP). We also investigated two thieno[3,4-*b*]pyrazine model compounds, viz., 5,7-bis(3-dodecylthiophen-2-yl)thieno[3,4-*b*]pyrazine (BTTP) and 5,7-bis(5-bromo-3-dodecylthiophen-2-yl)thieno[3,4-*b*]pyrazine (BTTPBr), whose structures are shown in Chart 1. Selective photodegradation of the thieno[3,4-*b*]pyrazine moiety was observed in all the materials using optical absorption, photoluminescence, NMR, and FTIR spectroscopies. The results presented herein have broad implications for thieno[3,4-*b*]pyrazine-based organic/polymer semiconductors being developed for applications in OLEDs, solar cells, and OTFTs.

Experimental Section

Materials. The three polyfluorene copolymers containing thieno[3,4-*b*]pyrazine, 2FTP, FFOTP, and FPOTP were synthesized by the Suzuki coupling polymerization using procedures reported in the literature.[10b,c] The two thieno[3,4-*b*]pyrazine model compounds, BTTP and BTTPBr, were synthesized using reported procedures.[11a]

Sample Preparation. Dilute (1×10^{-5} M) solutions of the copolymers or the model compounds were made in spectroscopic

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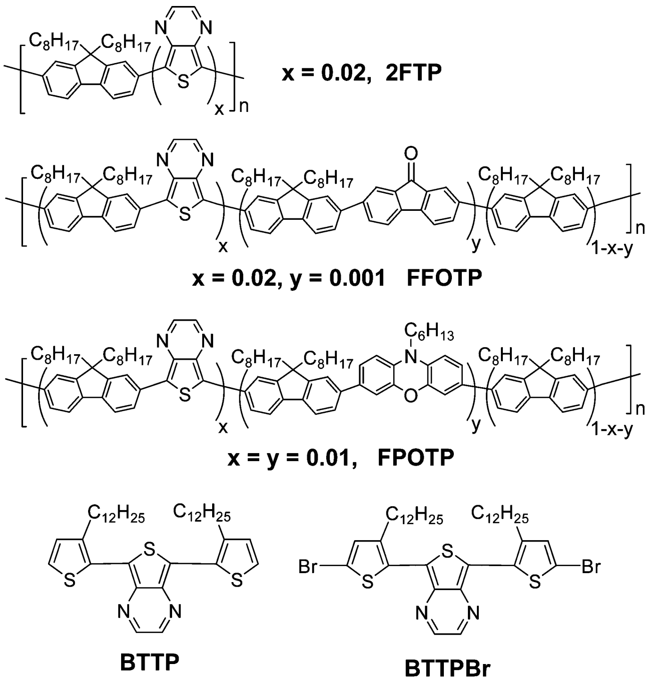
Chart 1



grade toluene that was not deoxygenated before use. For studies in the solid state, optically clear thin films (30−40 nm thick) of the copolymers were made on glass substrates by spin-coating from their ∼0.5 wt % solutions in toluene. The solvent was removed by drying the films in a vacuum at 60 °C for at least 8 h. In the case of the model compounds, their neat thin films spin-coated on glass slides tended to crystallize after drying in vacuum. To minimize their crystallization, the model compounds were dispersed in a 75 wt % polystyrene matrix. The resulting films spin-coated from the blend solution of polystyrene (75 wt %) and model compound (25 wt %) in toluene remained optically clear after drying.

Single-layer light-emitting diodes based on the copolymers were fabricated on ITO-coated glass substrates. A 65 nm thick poly(ethylenedioxythiophene)/poly(styrenesulfonate) blend (PEDOT) hole injection layer was spin-coated on top of ITO and dried at 200 °C for 15 min under a vacuum. 30−40 nm thick films of the copolymers were deposited on top of the PEDOT layer by spin-coating from their ∼0.5 wt % solutions in toluene and dried in a vacuum at 60 °C for at least 8 h. Finally, a 2 nm LiF and a ∼120 nm thick aluminum layer were sequentially deposited through a shadow mask in a vacuum evaporator (Edwards Auto 306) at base pressures of $<8 \times 10^{-7}$ Torr to form active diode areas of 0.2 cm^2. The details of the device fabrication and characterization have been reported previously.[21]

Photodegradation. The photodegradation of the materials was done in two ways. In the first method, the copolymers and model compounds were irradiated with UV radiation ex-situ for varying amounts of time with a Spectroline UV lamp (model ENF-280c; Spectronics Corp., Westbury, NY) emitting UV-A radiation at 365 nm with a peak intensity of ∼0.5 mW/cm^2. The copolymer or model compound solution in toluene (1×10^{-5} M) was put in a capped vial (5 mL), and the vial was placed within 3 in. of the UV lamp, ensuring that the entire solution volume is uniformly irradiated. The solution was not deoxygenated before sealing the vial. The photodegradation in the solid state was accomplished by exposing the thin films to the 365 nm UV radiation for 1 h in air. In the case of the LEDs, the copolymer thin films on ITO/PEDOT were similarly irradiated using the UV lamp for 1 h in air before loading the substrates in the vacuum evaporator for cathode deposition.

In the second method, the UV irradiation was performed in-situ in a Photon Technology International (PTI) Inc. model QM-2001-4 spectrofluorimeter. This was only done for thin films of the materials and not for solution. Monochromatic radiation at 380 nm was incident on the thin films by focusing the excitation light to a rectangular beam (∼10 mm × 2 mm) that had an intensity of ∼0.5 mW/cm^2 where it hit the copolymer thin films on glass. The 380 nm radiation served as the excitation wavelength as well that enabled simultaneous acquisition of the PL spectra of the emissive thin films every 4−5 min for an overall period of 1 h. The irradiation was done in air at room temperature.

Spectroscopy. Optical absorption spectra were recorded using a Perkin-Elmer model Lambda 900 UV/vis/near-IR spectrophotometer. Solution spectroscopy was performed in quartz cuvettes with 1 cm path length. Steady-state PL emission spectra were acquired on the PTI Inc. model QM-2001-4 spectrofluorimeter. In solution, the PL emission was detected in the right-angle geometry. Thin films were positioned at an angle of ∼22° with respect to the excitation beam, with the emission detector fixed at 90° with respect to the excitation beam. ^{1}H NMR spectra were recorded on a Bruker-AF300 spectrometer at 300 MHz. Spectra of the thienopyrazine model compound BTTPBr in toluene-d_8 ($\sim 10^{-2}$ M) were acquired after 25 and 49 h of UV (365 nm) irradiation on the UV lamp. The NMR tube containing the solution was placed in front of the UV lamp. The solution in the NMR tube was not deoxygenated before capping the tube. FT-IR spectra were taken on a Perkin-Elmer 1720 FTIR spectrophotometer with KBr pellets on the nonirradiated and irradiated BTTPBr samples. After the 49 h of UV exposure of BTTPBr toluene solution in the NMR tube, the toluene solvent was evaporated, and the resultant solid powder of the photodegraded BTTPBr was ground into a KBr pellet for spectra acquisition.

Results and Discussion

Thieno[3,4-*b*]pyrazine-Containing Polymers. a. Solutions. Figure 1a shows the optical absorption spectra of dilute (10^{-5} M) toluene solutions of copolymer 2FTP as a function of time of UV irradiation (365 nm) with the UV lamp. The spectrum of the nonirradiated solution has an absorption maximum at 387 nm (absorbance, $A = 0.377$) and a very weak low-energy band at ∼525 nm ($A = 0.006$). The former band is associated with the $\pi-\pi^*$ transition of the polyfluorene backbone while the latter is related to the intramolecular charge-transfer (ICT) transition between fluorene and thieno[3,4-*b*]pyrazine moieties.[10b] Because of the low concentration (2 mol %) of thieno[3,4-*b*]pyrazine, this ICT absorption band is very weak. It is clearer in the absorption spectra shown on an expanded scale in the inset of Figure 1a. With increasing irradiation time, the intensities of both absorption bands steadily decrease. The absorbance at 387 nm is 0.342, 0.333, 0.329, and 0.328 after 1, 2, 3, and 13 h of UV irradiation, respectively. The ICT band is almost completely quenched after 13 h of UV irradiation, suggesting selective degradation of the thienopyrazine moieties on the copolymer chains. Figure 1b shows the PL emission spectra of the same dilute (10^{-5} M) 2FTP toluene solutions under 380 nm excitation. The spectrum of the nonirradiated solution has two well-resolved blue emission peaks at 414 and 436 nm. In addition to these two peaks, there is a red emission band at 645 nm which is very weak compared to the blue emission. The blue emission arises from the parent PFO backbone, whereas the red emission originates from the ICT excited state. With increasing irradiation time, the emission in the blue region increases at the expense of gradual decrease in intensity of the red emission band. This decrease in the red emission is clearly seen in the inset of Figure 1b, which shows the emission spectra under selective excitation of the ICT absorption band at 525 nm. The 645 nm band steadily decreases with increasing irradiation time, finally disappearing completely after 13 h of irradiation. The observed quenching of the red emission band along with the decrease of the 525 nm ICT absorption band clearly indicates the selective photodegradation of the thienopy-

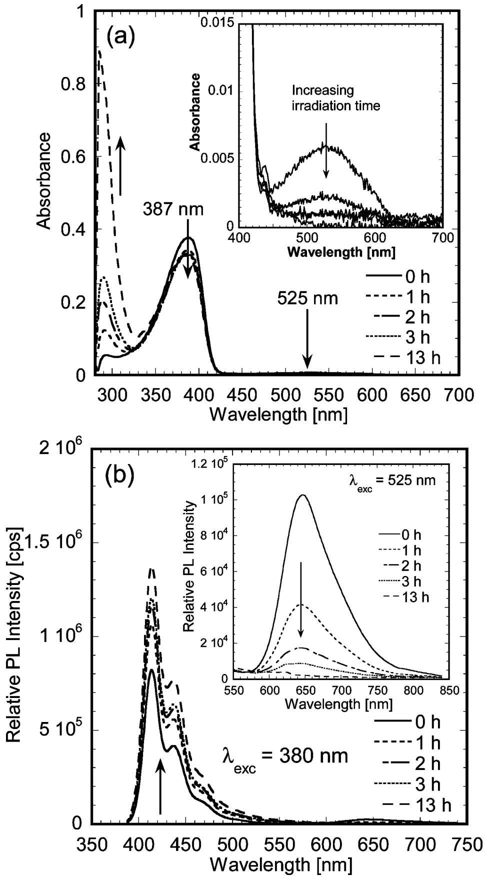


Figure 1. (a) Changes in the optical absorption spectra of 10^{-5} M solutions of 2FTP in toluene with time of UV (365 nm) irradiation on a UV lamp. The inset shows the same absorption spectra on an expanded scale. (b) Changes in the PL emission spectra of 10^{-5} M solutions of 2FTP in toluene with time of UV (365 nm) irradiation. Excitation wavelength = 380 nm. The inset shows the PL emission spectra of the same irradiated polymer solutions using a 525 nm excitation wavelength.

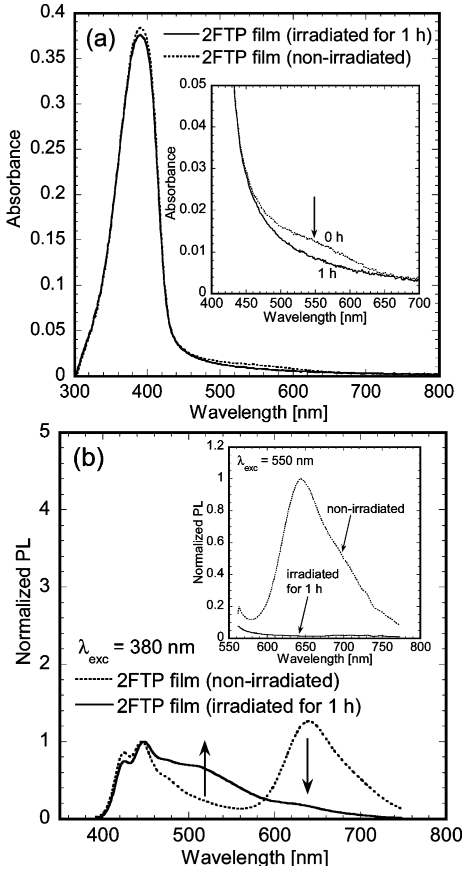


Figure 2. (a) Changes in the optical absorption spectra of 2FTP thin film after 1 h of UV (365 nm) irradiation on a UV lamp. The inset shows the same absorption spectra on an expanded scale. (b) Changes in the PL emission spectra of 2FTP thin film after 1 h of UV (365 nm) irradiation on a UV lamp. Excitation wavelength = 380 nm. The inset shows the PL emission spectra of the same irradiated thin film using a 550 nm excitation wavelength.

razine moieties on the 2FTP copolymer chains under UV irradiation. The overall integrated PL emission intensity of the 13 h irradiated solutions is enhanced by ~80% relative to the nonirradiated solution. This implies that thieno[3,4-*b*]pyrazine moieties act as low-energy quenching sites for the blue emission from the PFO backbone; their selective elimination by photodegradation leads to enhanced blue emission from the resulting "trap-free" PFO backbone.

b. Thin Films. To investigate the photodegradation in the solid state, thin films of the copolymers on glass substrates were exposed to UV radiation (365 nm) for 1 h using the UV lamp. The optical absorption spectra of thin films of copolymer 2FTP, before and after 1 h of UV irradiation, are shown in Figure 2a. As in solution, there are two absorption features. The main absorption band is at 390 nm, and the weak ICT band is at ~550 nm. The absorbance of the 390 nm band decreases slightly from 0.383 to 0.376 after 1 h of irradiation. The broad ICT band is completely quenched after the UV irradiation, as shown in the inset of Figure 2a. The effects of the UV irradiation on the thin film PL emission spectra are shown in Figure 2b. Under 380 nm excitation, the nonirradiated 2FTP film has blue emission bands at 425 and 445 nm, in addition to the red ICT band at 640 nm, which is 1.26 times the intensity of the 445 nm band. The reason for the enhanced red emission in the thin film compared to dilute solution is the efficient solid-state three-dimensional energy transfer from the fluorene segments to the thienopyrazine-containing segments.[10b,20] After 1 h of irradiation, this red band is nearly completely quenched; additionally, a new green emission band at ~515 nm emerges. The green emission is likely due to the formation of fluorenone moieties on the copolymer chains due to UV-induced photo-oxidation of the fluorene moieties.[8,20] Such isolated fluorenone defects in polyfluorenes are known to give rise to efficient green emission as seen here.[8,20] The emission spectra under selective excitation of the ICT band at 550 nm (inset of Figure 2b) clearly shows the disappearance of the red emission band after 1 h of irradiation. Similar results were observed for thin films of FFOTP (see Supporting Information, Figure S1). Similar to the solution results, it appears that the thienopyrazine moieties on the polyfluorene chains are selectively degraded by the UV irradiation in the solid state as well. Also, the integrated PL emission intensity of the irradiated film was larger than that of the nonirradiated film by a factor of 2. Such enhancements in the PL emission intensity upon photoirradiation have been observed previously for PPV thin films.[22]

To better monitor the changes in the PL emission at shorter time intervals (4−5 min), we obtained the emission spectra of the copolymer thin films with in-situ UV (380 nm) irradiation in the spectrofluorimeter. Figure 3a shows the emission spectra of a thin film of 2FTP acquired every 4 min for a total time of 60 min under continuous UV irradiation. With increasing irradiation time, the dominant red emission band at 640 nm steadily decreases in intensity and slightly blue-shifts along with an increase in the blue emission bands at 425 and 445 nm. Additionally, there is an increase in the green emission feature

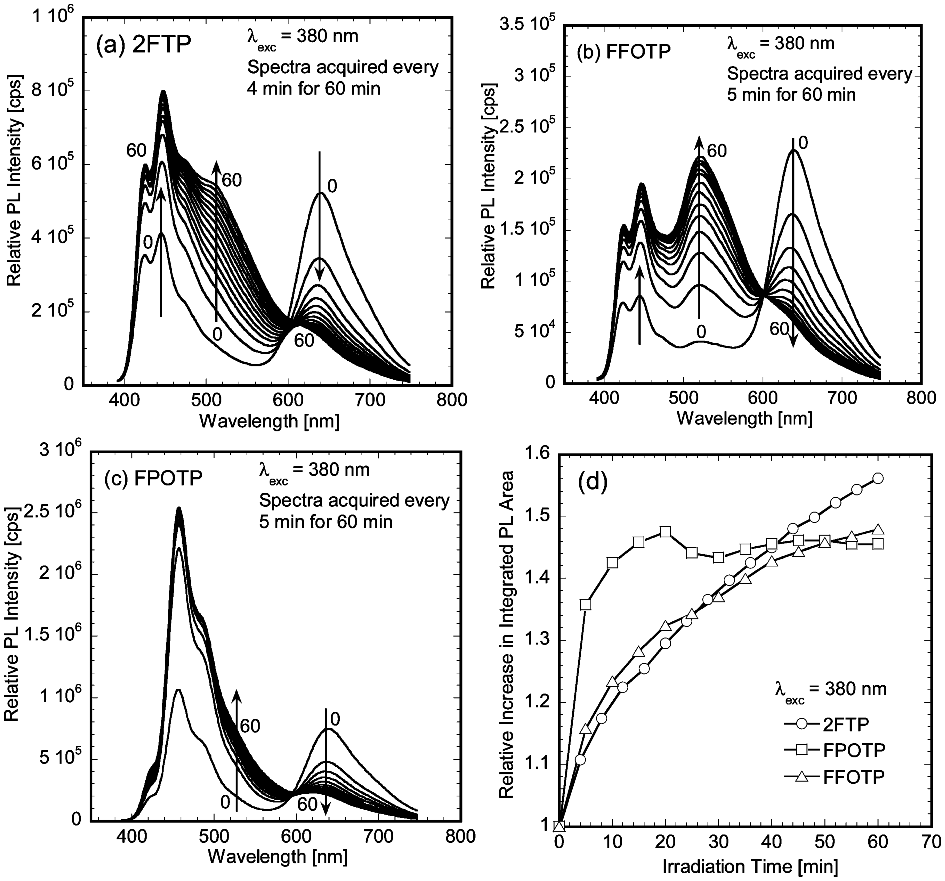


Figure 3. Changes in the PL emission spectra of 2FTP (a), FFOTP (b), and FPOTP (c) thin films with time of in-situ UV (380 nm) irradiation in the spectrofluorimeter. (d) Variation in the integrated PL emission intensity of thin films of 2FTP, FFOTP, and FPOTP with time of in-situ UV (380 nm) irradiation. The lines merely serve as a guide to the eye.

at ~510 nm due to fluorenone formation.[8,20] There appears to be an isobestic-like ("iso-emissive") point at ~610 nm which suggests the presence of two competing emissive sites, with the blue emission increasing at the expense of the red emission. Similar effects were observed in the case of thin films of FFOTP and FPOTP, as shown in parts b and c of Figure 3, respectively. The relative increase in the integrated PL emission intensity of all three copolymer thin films with irradiation time is plotted in Figure 3d. The rate of increase is different for the three copolymers. After 5 min of irradiation, the integrated emission intensity of FFOTP increases by 15%, whereas that of FPOTP is enhanced by 35%. The rate of increase is very steep for FPOTP films in the initial 30 min, with eventual saturation beyond 40 min. In the case of 2FTP, the PL intensity continues to increase with time, becoming 1.56 times the intensity of the nonirradiated film after 60 min of in-situ irradiation. Overall, it is amply evident that the thieno[3,4-*b*]pyrazine moiety is selectively being photodegraded in all the copolymers upon their exposure to UV radiation in air, resulting in partial or complete quenching of the red PL emission band at 640 nm.

To investigate the effects of this photodegradation on the electroluminescence of the emissive copolymers, we fabricated simple single-layer LEDs based on both nonirradiated and irradiated films. Figure 4a shows the normalized EL spectra of a diode based on a nonirradiated 2FTP film. The EL spectra have two emission features, a blue band at 420 nm and a red band at 635 nm, the former being the dominant emission. The intensity of the red band relative to the blue increases with increasing applied voltage. The red:blue EL ratio increases from 0.05:1 at 6 V to 0.2:1 at 9 V. Compared to the PL emission of 2FTP thin film (Figure 2b), the intensity of the red band in the EL emission is much lower. This is likely a result of the competing dynamics of charge carrier trapping and radiative recombination on the thienopyrazine segments vs the high-energy PFO chain segments. The EL spectra of the diode containing a 2FTP film that has been irradiated for 1 h with the UV (365 nm) lamp are shown in Figure 4b. The most striking characteristic is the complete absence of the red emission band at all applied voltages. The dominant emission is still at 420 nm, and there is additional emission in the green region (515 nm) due to the fluorenone moieties formed by photo-oxidation.[8,20] On the basis of the aforementioned PL emission results, the disappearance of the red emission band in EL suggests complete degradation of the thieno[3,4-*b*]pyrazine moieties on the copolymer chains. This results in a substantial change in the CIE emission color coordinates of the diode, which is a highly undesirable feature in emissive polymers. Figure 4c shows the normalized EL spectra of a diode based on a nonirradiated FFOTP film while Figure 4d shows the EL spectra of the diode containing a FFOTP film that has been irradiated for 1 h with the UV (365 nm) lamp. Here, too, complete quenching of the red EL emission band (635−640 nm) was observed for the photodegraded films. In both cases, the maximum brightness of the irradiated devices was twice as large compared to the nonirradiated devices, consistent with the observed PL enhancement upon irradiation of the polymer thin films (Figure 3d). However, the observed lack of photochemical stability in the current thieno[3,4-*b*]pyrazine-containing emissive copolymers does not bode well for their targeted applications in red and white OLEDs.[10]

Thieno[3,4-*b*]pyrazine Model Compounds. Figure 5a shows the changes in the optical absorption spectra of dilute (10^{-5} M)

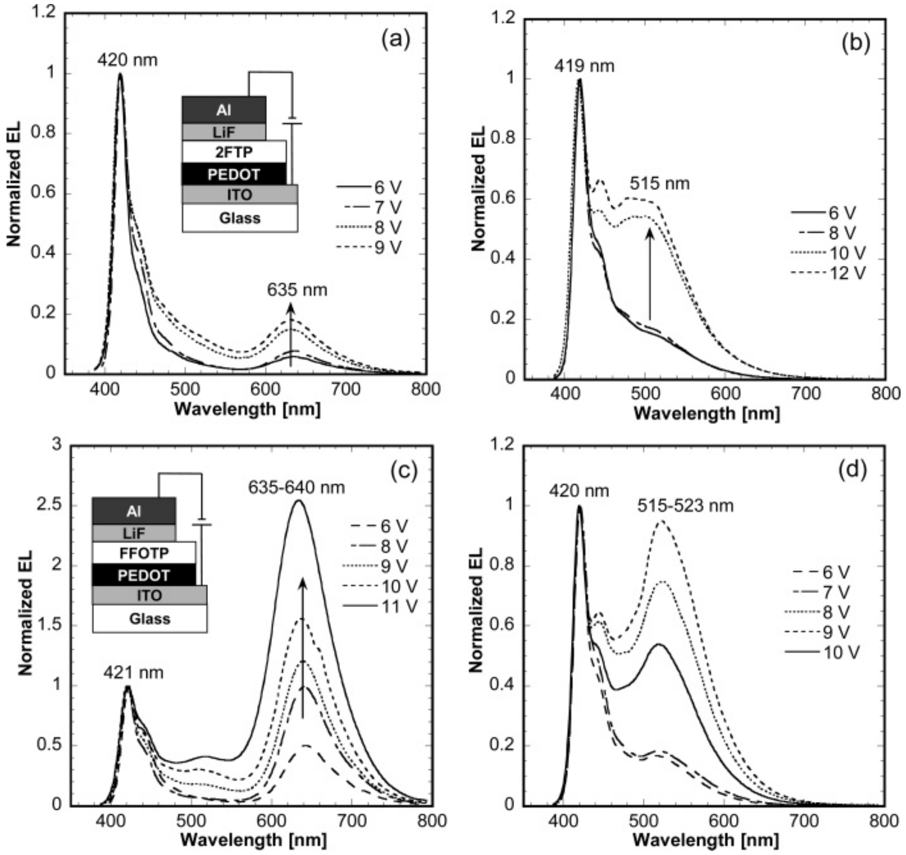


Figure 4. Normalized EL spectra of single-layer diodes of the type ITO/PEDOT/copolymer/LiF/Al: (a) nonirradiated 2FTP film, (b) 2FTP film after 1 h of UV (365 nm) irradiation on a UV lamp, (c) nonirradiated FFOTP film, and (d) FFOTP film after 1 h of UV (365 nm) irradiation on a UV lamp. The inset shows the device schematic.

toluene solution of the model compound BTTPBr with time of UV irradiation (365 nm) by a UV lamp. The nonirradiated solution has a low-energy absorption maximum at 535 nm ($A = 0.0855$) due to the ICT transition between donor thiophene and acceptor thieno[3,4-*b*]pyrazine. The high-energy absorption band at ~315 nm is likely associated with the thieno[3,4-*b*]pyrazine moiety.[18] With increasing time of irradiation, the absorbance of the ICT band steadily decreases from 0.081 to 0.076 to 0.011 after 1, 2, and 13 h of UV irradiation, respectively. Figure 5b shows the PL emission spectra of the same BTTPBr toluene solutions under 530 nm excitation. BTTPBr emits weak red light with a maximum at 672 nm which is an ICT transition. With increasing irradiation time, a steady decrease in the PL emission intensity is observed without any changes in the spectral shape. After 13 h of UV exposure, the integrated PL emission intensity drops by 85% compared to the nonirradiated solution. Similar results were observed upon photoirradiation of dilute toluene solutions of BTTP (see Supporting Information, Figure S2). This observed decrease in the ICT absorption band and the red emission band upon UV irradiation points to photodegradation of the thieno[3,4-*b*]pyrazine moieties in the molecule, similar to what was found in the thienopyrazine-containing copolymers. Photodegradation effects were also observed for thin films of the model compounds. We monitored the changes in the PL emission spectra of a blend thin film containing 25 wt % BTTP in a 75 wt % polystyrene matrix under in situ UV irradiation (380 nm) in the spectrofluorimeter (see Supporting Information, Figure S3). Very weak red emission was observed in the nonirradiated film with peaks at 687 and 705 nm. The PL emission intensity decreased with increasing irradiation time without any noticeable changes in the shape of the spectrum. After 60 min of UV exposure, the integrated PL intensity dropped by 18% relative to the fresh film.

Changes in Molecular Structure upon Photodegradation. In an effort to further gain insights into the structural changes accompanying the photodegradation of the thieno[3,4-*b*]pyrazine moiety and the underlying photodegradation mechanisms, we acquired ^{1}H NMR and FTIR spectra of the model compound BTTPBr both before and after UV irradiation. The ^{1}H NMR spectra of the nonirradiated BTTPBr sample in toluene-d_8 and those after 25 and 49 h of exposure to UV light (365 nm) on the UV lamp are shown in Figure 6. In the spectrum of the nonirradiated sample, three singlet resonances at 6.77, 7.86, and 2.76 ppm (labeled a, b, and c, respectively) were observed. These were assigned to the two protons in the thiophene ring, the protons adjacent to the imine nitrogen atoms in the thieno[3,4-*b*]pyrazine ring, and the α-methylene protons of the dodecyl chains, respectively. Upon exposure to UV radiation for 2 h, new peaks at 6.64, 7.80, and 2.93 ppm were observed in the NMR spectrum which had very low intensity (not shown). The intensity of these new resonances was found to increase with the UV exposure time. After 25 h irradiation, the resonances labeled a, b, and c were significantly suppressed, and the additional peaks at 6.64, 7.80, and 2.93 ppm (labeled a′, b′, and c′, respectively) grew in intensity. The original peaks (labeled a, b, and c) completely disappeared from the NMR spectrum after 49 h of irradiation. These results indicate a significant change in the molecular structure of BTTPBr upon UV irradiation. On the basis of the observed changes in the absorption and emission properties of the copolymers and the model compounds, we speculate that the C═N bonds in the thieno[3,4-*b*]pyrazine ring are broken upon UV exposure.

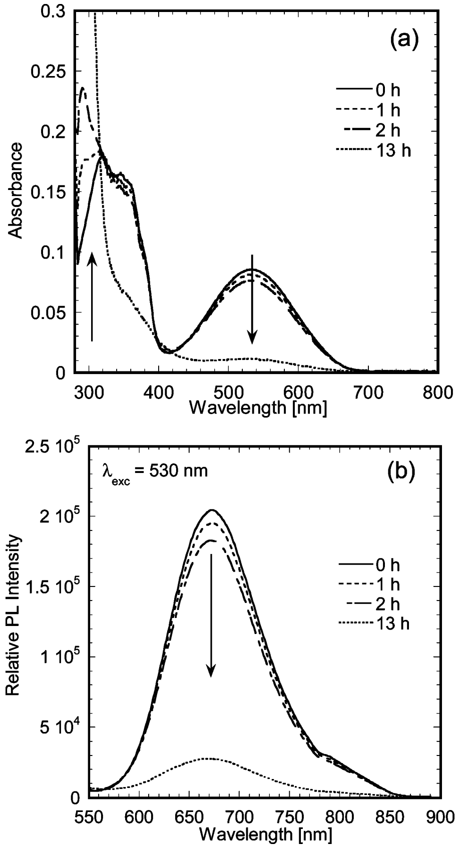


Figure 5. (a) Changes in the optical absorption spectra of 10^{-5} M solution of BTTPBr in toluene with time of UV (365 nm) irradiation on a UV lamp. (b) Changes in the PL emission spectra of 10^{-5} M solution of BTTPBr with time of UV (365 nm) irradiation on a UV lamp. Excitation wavelength = 530 nm.

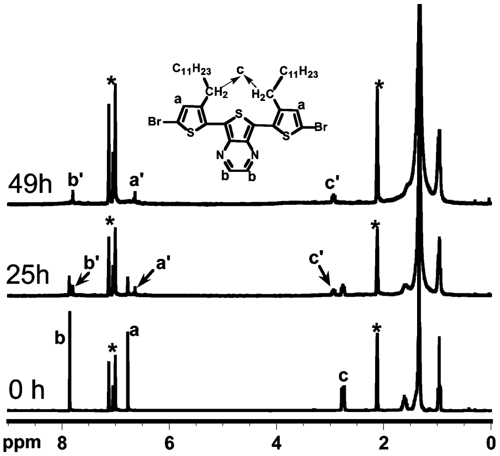


Figure 6. ^{1}H NMR spectra of BTTPBr in toluene-d_8 of the nonirradiated sample and after 25 and 49 h of UV (365 nm) irradiation on a UV lamp. The peaks labeled with an asterisk are due to the solvent.

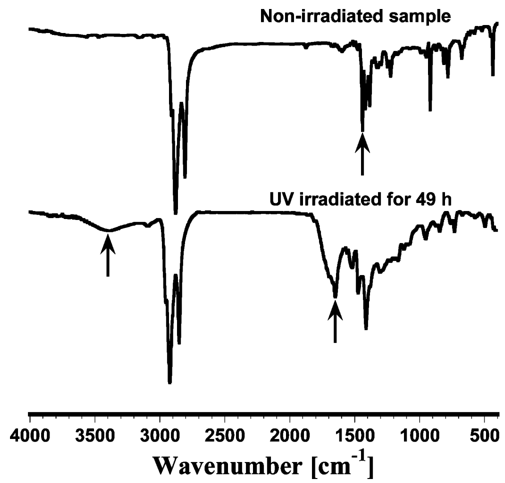


Figure 7. Changes in the FTIR spectrum of BTTPBr after 49 h of UV (365 nm) irradiation on a UV lamp.

To confirm this hypothesis, we obtained the FT-IR spectra of nonirradiated BTTPBr and the sample after 49 h of UV exposure, which are shown in Figure 7. In the fresh sample, the vibrational bands at 1485 cm^{-1} (indicated by an arrow) are due to stretching vibrations of the C=N bond and are characteristic of the thieno[3,4-*b*]pyrazine ring. After 49 h of irradiation, two new broad bands emerged at 3400 and 1640 cm^{-1} in the FT-IR spectrum. These new peaks could likely be attributed to the presence of a secondary amine which normally has an N−H stretching vibration at 3300−3500 cm^{-1} and an N−H in-plane bending at 1640−1560 cm^{-1}. These observations lead us to believe that a plausible scenario is the breaking down of the C=N bonds in the thieno[3,4-*b*]pyrazine ring of BTTPBr upon UV exposure, ultimately resulting in the formation of a secondary amine. Given that oxygen has invariably been identified as the main culprit in the photodegradation of most conjugated polymers,[4−9] further studies investigating the role of oxygen in the degradation of the thieno[3,4-*b*]pyrazine moiety are needed to develop a clear understanding of the underlying photodegradation mechanisms. Also of interest in future studies is investigation of whether aromatic or alkyl substituents on the thieno[3,4-*b*]pyrazine ring can retard or eliminate the photodegradation.

Conclusions

We have investigated the effects of UV irradiation on the photophysical, electroluminescent, and structural properties of thieno[3,4-*b*]pyrazine-containing emissive conjugated copolymers and oligomers. The thieno[3,4-*b*]pyrazine moiety was found to rapidly photodegrade upon UV irradiation in air, both in solution and in the solid state, resulting in drastic undesirable changes in the absorption, photoluminescence, and electroluminescence of the emissive materials. Selective photodegradation of the thieno[3,4-*b*]pyrazine moiety was evidenced by way of partial or complete quenching of the intramolecular charge transfer absorption and red emission bands associated with the thieno[3,4-*b*]pyrazine moiety, upon UV exposure of the emissive materials for varying lengths of time. Preliminary NMR and FTIR studies on one of the model compounds reveal the breaking of the C=N bond in the thieno[3,4-*b*]pyrazine ring to form a secondary amine as one of the possible degradation mechanisms. The consequences of the observed poor photochemical stability of the thieno[3,4-*b*]pyrazine moiety are very important for the performance and durability of many solid-state devices including OLEDs, solar cells, and OTFTs based on thienopyrazine-containing organic semiconductors.

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Supporting Information Available: Absorption and PL emission spectra of FFOTP thin film and BTTP solution and thin film under UV irradiation. This material is available free of charge via the Internet at http://pubs.acs.org.

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