Charge-transfer character of excitons in poly[2,7-(9,9-di-*n*-octylfluorene)$_{(1-x)}$-co-4,7-(2,1,3-benzothiadiazole)$_{(x)}$]

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Quantum-chemical calculations performed on poly[2,7-(9,9-di-*n*-octylfluorene)$_{(1-x)}$-co-4,7-(2,1,3-benzothiadiazole)$_{(x)}$] copolymers ($0 \le x \le 0.5$) show that the lowest unoccupied molecular orbital is always highly localized on the benzothiadiazole (BT) units while the highest occupied molecular orbital is delocalized over the whole chain. Chains with a low BT content are characterized by a reduced oscillator strength of the lowest optical transition and by an increased charge-transfer character of the exciton. These results are supported experimentally by a blueshift of the lowest energy absorption band upon reduction in the BT ratio, lower photoluminescence efficiency, longer excited state lifetimes, and greater solvent dependence of the emission properties. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3177327]

Organic light-emitting diodes (LEDs) have been the subject of extensive research since the first demonstration of electroluminescence in conjugated polymers.[1] Much recent work on organic LEDs has focused on single-polymer systems[2–4] combining electron- and hole-transporting groups and emissive species within each polymer chain. Advantages of single-polymer systems include ease of processing and better control over the thin-film morphology compared to polymer blends. Properties such as the energies of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) as well as emission spectra, and charge-carrier mobilities can be tuned by adjusting the proportions of each group within the polymer chain.[5–7] Understanding the effects of electron withdrawing/donating units is thus essential in the rational design of such donor-acceptor systems. Here, we study the electronic and optical properties of a series of poly[2,7-(9,9-di-*n*-octylfluorene)$_{(1-x)}$-co-4,7-(2,1,3-benzothiadiazole)$_{(x)}$] copolymers for values of *x*, the proportion of benzothiadiazole (BT) units (by number), between 0 and 0.5 in order to investigate the effects of introducing a small amount of the strongly electron-accepting BT unit into the poly[2,7-(9,9-di-*n*-octylfluorene)] (F8) polymer backbone [chemical structures of F8 and BT units are shown in Fig. 1(a)].

F8BT ($x=0.5$) has been used extensively as an electron-transporting material in LEDs (Ref. 8) and photovoltaic cells[9] and as an ambipolar material in light-emitting field-effect transistors.[10,11] It has been shown that the BT unit is

crucial in determining the charge-transport and energy-transfer properties of F8BT.[12–15] The large separation in energy between the LUMOs of the F8 and BT monomers as well as the weak electronic density on the connecting atoms in the LUMO of BT (Ref. 13) induces a strong localization of the LUMO of F8BT on the BT unit. Conversely, the HOMOs of the F8 and BT monomers are much closer in energy and exhibit a significant electronic density on the connecting atoms; their stronger interaction gives rise to a more delocalized HOMO level in F8BT.[13,14] Interchain electron transport has been shown to occur more easily when the BT units on one F8BT chain are aligned with other BT units, as opposed to F8 units, on neighboring polymer chains. The rate of interchain energy transfer, dependent on the optical coupling between final and initial states, also increases when the BT units of neighboring polymer chains face one another.[13,14]

Poly[2,7-(9,9-di-*n*-octylfluorene)$_{(1-x)}$-co-4,7-(2,1,3-benzothiadiazole)$_{(x)}$] was synthesized by the Suzuki coupling reaction from 50 mol % of fluorene bis boronic acid and 50 mol % of arylhalide (fluorene+BT) using a Pd(0) catalyst [tetrakis(triphenylphosphine)-palladium (0.04 g, 0.036 mmol)]. The polymer was end capped with bromobenzene and phenylboronic acid to yield benzene end groups. This polymerization method implies that F8 units may be bonded to either F8 or BT units but BT units may only be bonded to F8 units; blocks of BT units are thus not present in these polymer chains. The proportion of BT units in the polymer chains (*x*) was between 6.0% and 49.7%; samples of F8 ($x=0$) were also included for comparison (details of the polymers are shown in Table I).

Absorption spectra were taken using a Hewlett–Packard diode array spectrometer. Photoluminescence (PL) spectra

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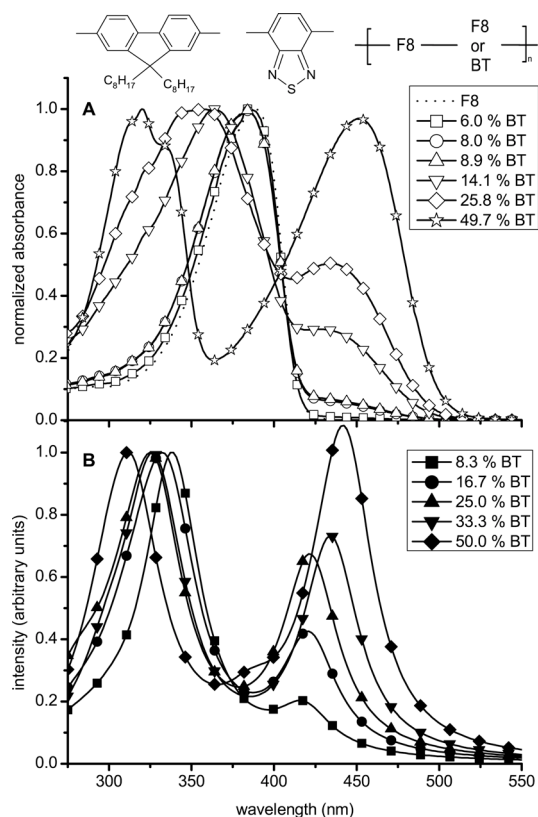
FIG. 1. (a) Absorption spectra of $F8_{(1-x)}BT_x$ copolymers in dilute solution (100 mg/l in chloroform). The inset above the graph shows chemical structures of F8 and BT units and repeat unit of copolymer. (b) Absorption spectra of $F8_{(1-x)}BT_x$ copolymers in the optimized geometry determined by quantum-chemical calculations. All absorption spectra have been normalized to the peak of the higher energy absorption band at ~ 320–380 nm.

were measured in an integrating sphere with 325 nm excitation and PL efficiencies calculated as described elsewhere.[16] HOMO and LUMO energy levels were determined by cyclic voltammetry using a platinum auxiliary electrode, Ag/Ag$^+$ nonaqueous reference electrode, and glassy-carbon working electrode. Excited-state lifetimes were measured using a time-correlated single photon counting (TCSPC) experiment with 470 nm excitation from a pulsed diode laser and emission was measured using a microchannel plate photomultiplier (Hamamatsu) coupled to a monochromator and TCSPC electronics (Edinburgh Instruments).[17] The time resolution of

TABLE I. BT content, molecular weight, and polydispersity of $F8_{(1-x)}BT_x$ copolymers used in the experimental part of this study. Copolymer compositions were determined by elemental analysis using the nitrogen content as standard.

BT content, by number (%)	Molecular weight (kg/mol)	Polydispersity
0.0	25.0	
6.0	13.6	2.4
8.0	15.8	1.9
8.9	12.8	2.6
14.1	8.7	1.2
25.8	7.5	1.7
49.7	11.9	3.0

TABLE II. BT content and structure of the model oligomers generated for the theoretical simulations.

BT content, by number (%)	Structure
8.3	F8-F8-F8-F8-F8-BT-F8-F8-F8-F8-F8-F8
16.7	F8-F8-BT-F8-F8-F8-F8-F8-BT-F8-F8-F8
25.0	F8-F8-BT-F8-F8-F8-BT-F8-F8-F8-BT-F8
33.3	F8-BT-F8-F8-BT-F8-F8-BT-F8-F8-BT-F8
50.0	F8-BT-F8-BT-F8-BT-F8-BT-F8-BT-F8-BT

the TCSPC experiment is ~ 200 ps. All spectra were measured in dilute solutions.

Model oligomers were generated for the theoretical simulations by linking 12 monomer units, with different ratios of F8 versus BT units and no BT blocks, see Table II. The ground-state geometries were optimized in the gas phase with the semiempirical Hartree–Fock Austin model 1 (AM1) method[18] as implemented in AMPAC. The calculations yield torsion angles around 40° between F8 units and around 50° between F8 and BT units. The absorption spectra were then simulated with the semiempirical Hartree–Fock intermediate neglect of differential overlap method, using Zerner's parametrization, coupled to a single configuration interaction scheme; the active space encompasses in all cases the highest 50 occupied and lowest 50 unoccupied molecular orbitals. The spectra were broadened with a Gaussian distribution with a full width at half maximum of 40 nm.

Figure 1(a) shows the absorption spectra of dilute solutions of $F8_{(1-x)}BT_x$ copolymers. The lowest energy absorption band increases in intensity with increasing BT content and shifts to longer wavelengths, from ~ 430 nm for all copolymers in the range of 8.0%–25.8% BT with a step to 451 nm for 49.7% BT. This evolution is fully supported by the quantum-chemical calculations; Fig. 1(b) shows the increase in the calculated intensity of the lowest energy absorption band with increasing BT content and accompanying redshift from ~ 420 nm for the copolymers in the range of 8.3%–25.0% BT to 436 nm for 33.3% BT and further to 445 nm for 50.0% BT.

In order to rationalize the evolution of the absorption spectra, we have first characterized the electronic structure of the copolymers. Whatever the BT fraction is, the HOMO and lower-lying occupied orbitals are delocalized over the entire backbone. The LUMOs are divided into two bands, the first originating from the combination of the LUMOs of the BT units and the second dominantly from the LUMOs of the fluorene units. Each band has a number of orbitals equal to the number of corresponding units in the chain. For a fraction of BT of 33.3% in our oligomer, there are four unoccupied orbitals mostly localized on the BT units (forming a narrow band around -1.35 eV) and eight unoccupied orbitals mostly localized on the fluorene units (forming a wider band from -0.20 to 0.32 eV) (Fig. 2). As the fraction of BT increases, the first band broadens (up to 0.1 eV for 50.0% BT) while the second band narrows following the disruption of the polyfluorene backbone (down to 0.15 eV for 50.0% BT).
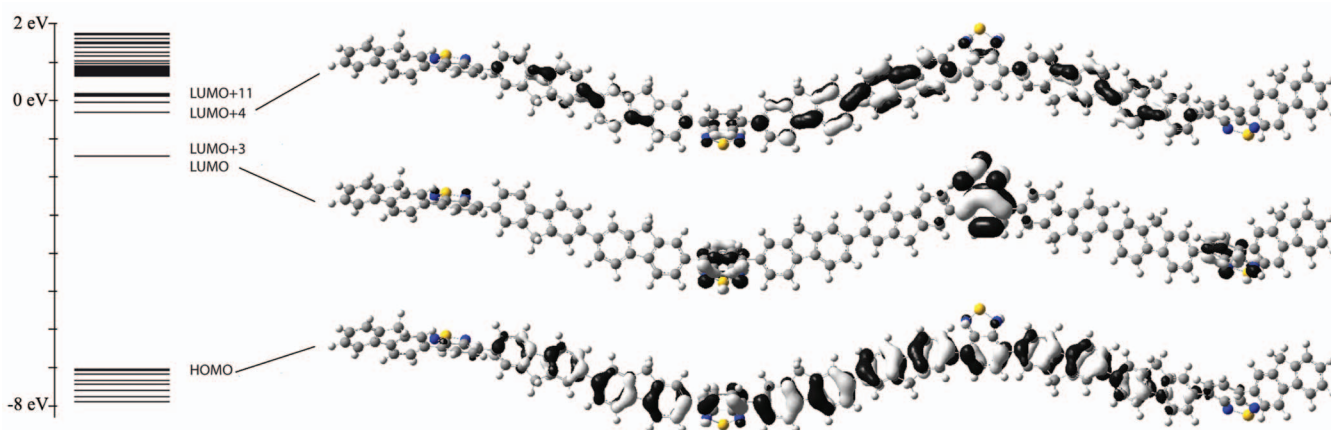
FIG. 2. Schematic electronic structure of a copolymer with 33.3% BT units showing the existence of two distinct bands for the unoccupied orbitals. The shapes of the HOMO (bottom), LUMO (middle), and LUMO +4 (top) levels are also shown. The surface represents an isovalue plot of the electronic density (for 0.002 electron/bohr^3) visualized in GAUSVIEW. The color (black/white) represents the sign of the wave function. The color and size of the spheres represent the sign and amplitude of the LCAO (linear combination of atomic orbitals) coefficients, respectively.

The lowest absorption band is described in all cases by a mixing of transitions from the HOMOs to the first band of unoccupied orbitals localized on the BT units; the latter can be delocalized over several BT units, especially at high BT content. The non-negligible weight of high-energy one-electron transitions contributes to the high energy of the excited state. When the BT ratio increases, the role of the deep occupied levels is reduced leading to the progressive redshift observed experimentally; note, however, that a small increase in the energy of the HOMOs with the BT content slightly counterbalances this trend, especially at high BT content. The increase in the oscillator strength of the lowest absorption band with the fraction of BT units is driven by a better spatial overlap between the occupied and unoccupied orbitals. Since the lowest unoccupied levels exhibit a small electronic density on the adjacent fluorene unit(s) directly linked to the contributing BT units, the larger the number of BT units, the larger is the spatial overlap with the delocalized occupied levels.

The higher energy absorption bands are made of different excited states within a small range of wavelengths, with oscillator strengths dependent on the BT content of the co-polymers. These excited states are described by transitions between occupied levels delocalized over the entire oligomer and unoccupied levels lying in the second band that are mostly localized on fluorene units. When the fraction of BT increases, the molecular orbitals of the second band are destabilized due to the disruption of the conjugation in the polyfluorene backbone leading to an overall blueshift of the higher energy absorption band. Note that the increase in energy of the absorption maximum (from 3.68 eV at 8.3% to 3.94 eV at 50.0%) is fully consistent with the increase in energy of the unoccupied levels (i.e., from −0.313 to −0.060 eV for the lowest unoccupied orbital of the second band). At low BT content the calculated position of the higher energy absorption band is also slightly blueshifted relative to the position measured experimentally. This blueshift could be due to the smaller sizes of the fluorene domains in the model oligomers compared to the polymer

chains at low BT contents, or to differences in the torsion angle between fluorene units in the gas-phase calculations and the polymer chains measured experimentally.

Experimentally determined HOMO and LUMO energies [Fig. 3(a)] show that the LUMO level of F8 is much closer to the vacuum level (−2.1 eV) than those of any of the $F8_{(1-x)}BT_x$ copolymers (−2.9 eV for 49.7% BT) and that
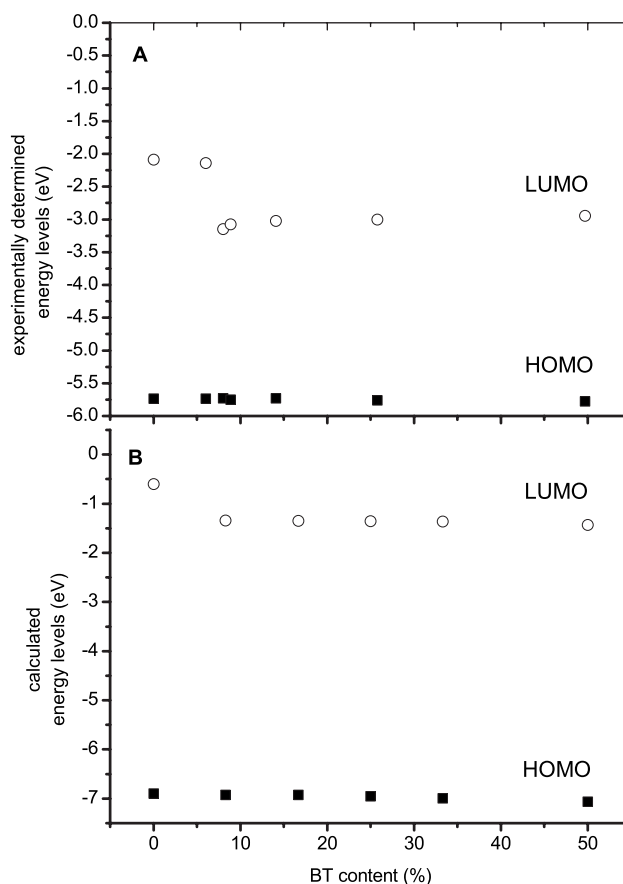

FIG. 3. (a) HOMO and LUMO energy levels of F8 and $F8_{(1-x)}BT_x$ copolymers measured by cyclic voltammetry. (b) HOMO and LUMO energy levels calculated in the optimized geometry. Values for F8 were obtained from literature (Ref. 13) for oligomers with five fluorene units.

there is very little variation of the LUMO energy level with BT content above ~8% BT (−3.1 eV for 8.0% BT compared to −2.9 eV for 49.7% BT). Our measured value of the LUMO energy of $F8_{(1-x)}BT_x$ ($x > 0.08$) is consistent with the use of F8BT ($x = 0.5$) as an electron-transporting material.[8,9] The HOMO level is slightly stabilized with increasing BT content (−5.7 eV for F8 and −5.8 eV for 49.7% BT) although this change is much smaller than the difference in LUMO energies between F8 and F8BT. The difference between the HOMO and LUMO energies (2.9 eV for 49.7% BT) is larger than the absorption band edge of the $F8_{(1-x)}BT_x$ copolymers (2.3 eV). Calculated HOMO and LUMO energies [Fig. 3(b)] follow similar trends compared to the experimental values: The LUMO energy of F8 is closest to the vacuum level and we see a large change upon adding a BT unit to the F8 chain. There is little variation in the LUMO energies among the $F8_{(1-x)}BT_x$ copolymers due to the strong localization of the LUMO over the weakly interacting BT units. In contrast, the HOMO energy does not change significantly between F8 and F8BT due its delocalized nature.

The excited states of many alternating and random copolymers and co-oligomers are known to show a charge-transfer (CT) character, particularly in polar solvents.[19–21] We will now discuss the steady-state and time-resolved PL properties of the $F8_{(1-x)}BT_x$ copolymers in different solvents in order to investigate how the proportion of BT units affects the nature of the excited state.

A significant difference in the shape of the emission from the $F8_{(1-x)}BT_x$ copolymers as a function of BT content is observed in Fig. 4(a). The PL spectrum of F8 has strong peaks at 420 and 440 nm which remain strong in $F8_{(1-x)}BT_x$ copolymers with low BT content but are very weak in copolymers with ≥14.1% BT. The strength of the F8-BT emission (~550 nm) increases with increasing BT content and is the strongest feature in the PL spectra for all $F8_{(1-x)}BT_x$ copolymers with BT content ≥8.0%. This indicates that inter- and intrachain energy transfers from the F8 to F8-BT species are significant even with a small number of BT units in the polymer chains. It is interesting to note that we do observe blue emission in the copolymers in spite of the good overlap between the PL spectrum of F8 and the F8BT absorption. This observation is entirely reasonable considering that the $F8_{(1-x)}BT_x$ copolymers with low proportions of BT units contain blocks of F8 units extending much further than the Förster radius for energy transfer from F8 to F8BT [estimated at about 4 nm (Refs. 22–24)]. F8 excitons created in these regions therefore have a significant chance of decaying radiatively rather than being transferred to the F8BT species.

While the shape of the F8BT emission band is the same for all $F8_{(1-x)}BT_x$ copolymers studied here, the PL efficiency increases with increasing BT content from 68% for 6.0% BT to 78% for 49.7% BT [Fig. 4(b)]. Figure 4(c) shows the time-resolved intensity of emission from the F8BT species (550 nm) for $F8_{(1-x)}BT_x$ copolymers dissolved in o-xylene and in chloroform. In each solvent the exciton lifetime is shorter for the copolymer with 49.7% BT units compared to the other $F8_{(1-x)}BT_x$ copolymers studied (≤25.8% BT); there is no dependence of the exciton lifetime on BT content

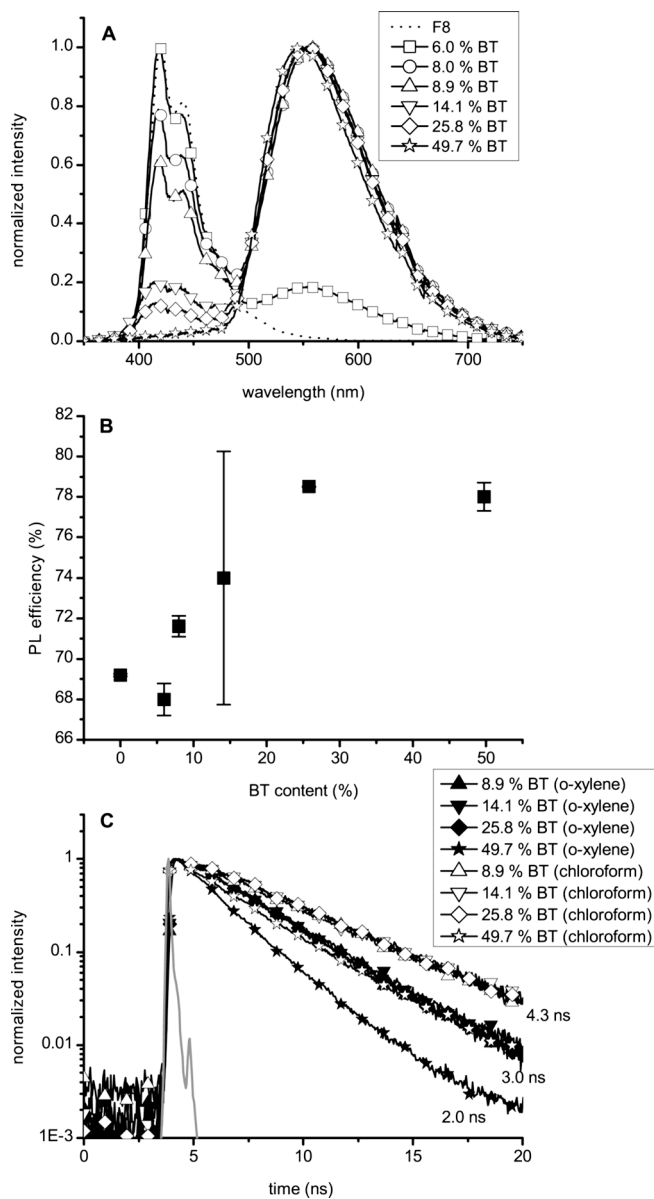FIG. 4. (a) Normalized PL spectra and (b) PL efficiencies of F8 and $F8_{(1-x)}BT_x$ copolymers (6.0%–49.7% BT) in dilute solution (15 mg/l in chloroform) after excitation at 325 nm. (c) Normalized intensity of emission from F8-BT species measured at 550 nm after excitation at 470 nm for $F8_{(1-x)}BT_x$ copolymers (8.9%–49.7% BT) in dilute solution (10 mg/l in chloroform and o-xylene) measured by TCSPC. All curves can be fitted with a single exponential, confirming that only one emissive species contributes to the emission at 550 nm. No dependence of the lifetime on the detection wavelength was found over the range of 480–680 nm. Excitation of the F8 species at 407 nm also did not change the lifetime of the emission from the F8-BT species since energy transfer from F8 to F8-BT occurs very quickly. The instrument response function is shown in gray.

within the range of 8.9%–25.8% BT units. The shorter exciton lifetime of the 49.7% BT copolymer indicates stronger coupling of the excited state to the ground state compared to the copolymers with lower BT contents. The increase in PL efficiency of the copolymers with increasing BT content [Fig. 4(b)] is also explained by the larger oscillator strength of the lowest optical absorption band in copolymers with more BT units. In Fig. 4(c), we also see that for each of the $F8_{(1-x)}BT_x$ copolymers, the exciton lifetime is longer in a more polar solvent [chloroform, dielectric constant $\varepsilon = 4.8$
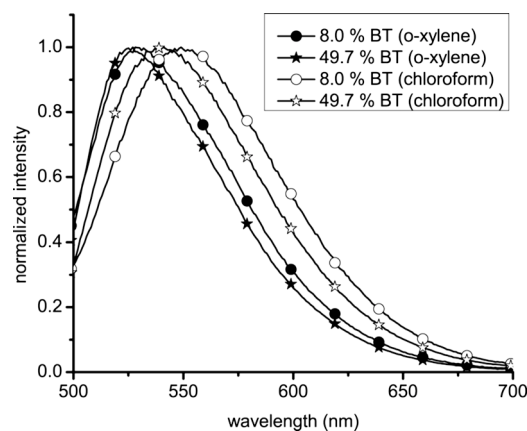
FIG. 5. Normalized PL spectra of F8$_{(1-x)}$BT$_x$ copolymers (8.0% and 49.7% BT) in dilute solutions (10 mg/l in chloroform and o-xylene) after excitation at 407 nm.

(Ref. 25)] compared to a less polar solvent [o-xylene, ε = 2.6 (Ref. 25)]. Figure 5 shows normalized steady-state PL spectra from F8$_{(1-x)}$BT$_x$ copolymers in two different solvents. We observe a redshift of the F8BT emission for the copolymers in chloroform compared to o-xylene and there was also a reduction in PL intensity. There are no significant differences in the absorption spectra of the polymers between the two solvents. The increased exciton lifetime, redshift, and reduced PL intensity in the more polar solvent are characteristics of an exciton with a CT character stabilized by the more polar environment. The F8$_{(1-x)}$BT$_x$ copolymers with lower BT content exhibit a larger redshift in PL and greater change in exciton lifetime than copolymers with higher BT content indicating a stronger CT character of excitons in the copolymers with smaller proportions of BT units. This is consistent with the theoretical calculations showing that the total charge transferred from the fluorene to the BT units upon photoexcitation remains constant as the BT fraction increases (around 0.35 $|e|$). When the BT fraction increases, this charge is delocalized over a larger number of units, thus reducing the local CT character of the excited state by dilution effects and hence the stabilization of the excited state by the medium.

In conclusion, we see that not only are excitons in F8$_{(1-x)}$BT$_x$ copolymers strongly CT in character but that the strength of this CT character increases when the proportion of BT units in the polymer chains is small. Incorporation of the strongly electron-accepting BT unit, even in small proportions, into the F8 polymer chain results in localization of the LUMO on the BT units. There are no significant changes in the HOMO and LUMO energies with BT content leading to the same shape of the F8BT emission in the PL spectrum for all F8$_{(1-x)}$BT$_x$ copolymers studied. Increased coupling of the excited state to the ground state at higher BT content results in shorter exciton lifetime and higher PL efficiency.

The increased CT character of the excitons in lower-BT-content copolymers is also seen in the stronger solvent dependence of the emission spectra and excited state lifetimes of these copolymers.

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