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Highly Emissive Conjugated Polymer Excimers

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Abstract: Conjugated polymers often display a decrease of fluorescence efficiency upon aggregation due in large part to enhanced interpolymer interactions that produce weakly emissive species generally described as having excimer-like character. We have found that poly(phenylene ethynylene)s with fused pendant [2.2.2] ring structures having alkene bridges substituted with two ester groups function to give highly emissive, broad, and red-shifted emission spectra in the solid state. To best understand the origin of this new solid-state emissive species, we have performed photophysical studies of a series of different materials in solution, spin-coated thin films, solid solutions, and Langmuir films. We conclude that the new, red-shifted, emissive species originate from excimers produced by interchain interactions being mediated by the particular [2.2.2] ring system employed. The ability to design structures that can reliably produce highly emissive conjugated polymer excimers offers new opportunities in the emission tailoring of electroluminescence and sensory devices.

Introduction

Interchain interactions often play a dominant role in determining the photophysical properties of conjugated polymers (CPs).[1] Most often strong electronic couplings between the delocalized portion of the polymer's backbone give rise to low fluorescence quantum yields, and researchers have focused on strategies for solid-state organizations that discourage these interactions. Strong interchain interactions are most prevalent in CPs having large band gaps and presumably more localized wave functions. For example, poly(phenylene ethynylene)s (PPEs) are a class of polymers with a particularly high tendency to produce interchain interactions relative to lower band gap poly(phenylene vinylene) homologues. Strong interchain interactions in PPEs produce a red-shift in the CP's absorbance spectrum that is due to both planarization and cofacial π-electron delocalization, and these effects have been studied in precisely organized PPE monolayers at an air−water interface.[2] The red-shifted emission spectra from CP aggregates are often referred to as having excimer-like character due to their broad featureless spectral character, reduced quantum yields, and longer excited-state lifetimes.[3] The interchain spacing of PPE aggregates has been studied in organized Langmuir monolayers, and it was found that excimer-like features dominate when the interchain spacing is less than 4.3 Å.[4] It is also found that the absorption spectrum is red-shifted by these close interactions. With few exceptions,[5] strong interactions between the delocalized states of CPs produce greatly diminished quantum yields.

In small-molecule photophysics the term "excimer" is reserved for excited-state dimeric complexes that display a repulsive intermolecular interaction in their ground state. As mentioned, typical CP aggregates have strong ground-state interactions with significant interchain mixing of the wave functions. Classical excimers wherein the CP's ground states and their associated absorption spectra are unaffected by the neighboring polymer chains are less common. We had previously discovered a singular example of excimer behavior in systems with elaborated pentiptycene frameworks appended to the polymer.[6] In this case we found that rigid bicyclic [2.2.2] scaffolds with naphthalenes constituting one of the bridging groups displayed excimer behavior. We suggested that this rigid scaffold, which was designed to prevent strong interactions between the polymer backbones, might itself associate via the naphthalene with a neighboring polymer's backbone to produce an excited-state complex.

This report details new polymer structures also having [2.2.2] ring systems that faithfully prevent strong ground-state interactions. We detail how a series of PPEs (**1**, **3**, and **7**, Chart 1) and a related poly(phenylene diethynylene) (**5**, Chart 1), which all contain a [2.2.2] ring system having a bridge disubstituted with esters, display bright excimer emissions. These systems were initially of interest to us as systems wherein we could use hyperconjugative and inductive interactions of the electron-poor

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(1) Jenekhe, S. A.; Osaheni, J. A. *Science* **1994**, *265*, 765−768.

(2) (a) Kim, J.; Swager, T. M. *Nature* **2001**, *411*, 1030−1034. (b) Kim, J.; Levitsky, I. A.; McQuade, D. T.; Swager, T. M. *J. Am. Chem. Soc.* **2002**, *124*, 7710−7718.

(3) (a) Cornil, J.; dos Santos, D. A.; Crispin, X.; Silbey, R.; Brédas, J.-L. *J. Am. Chem. Soc.* **1998**, *120*, 1289−1299. (b) Blatchford, J. W.; Jessen, S. W.; Lin, L.-B.; Gustafson, T. L.; Fu, D.-K.; Wang, H.-L.; Swager, T. M.; MacDiarmid, A. G.; Epstein, A. J. *Phys. Rev. B* **1996**, *54*, 9180−9189.

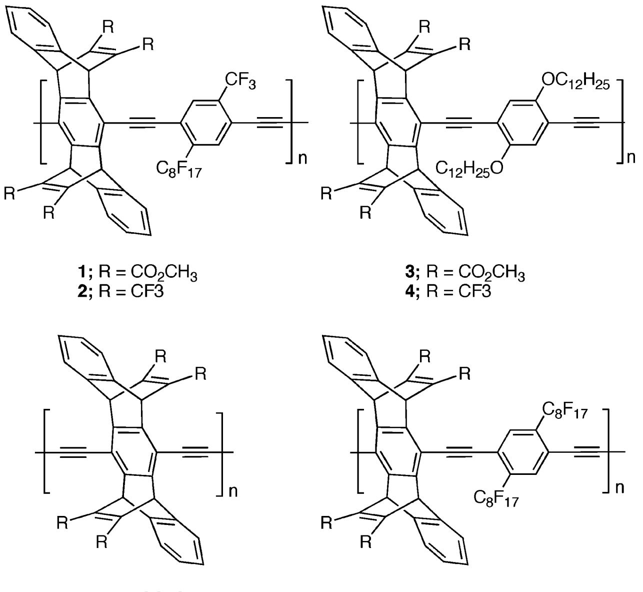
(4) McQuade, D. T.; Kim, J.; Swager, T. M. *J. Am. Chem. Soc.* **2000**, *122*, 5885−5886.

(5) We have found that systems having an apparent oblique orientation between polymer chains can display strong red-shifts in their absorption and emission and also maintain high quantum yields. (a) Deans, R.; Kim, J.; Machacek, M.; Swager, T. M. *J. Am. Chem. Soc.* **2000**, *122*, 8565−8566. (b) Zahn, S.; Swager, T. M. *Angew. Chem., Int. Ed.* **2002**, *41*, 4225−4230.

(6) Yang, Y.-S.; Swager, T. M. *J. Am. Chem. Soc.* **1998**, *120*, 11864−11873.

10.1021/ja053893+ CCC: $30.25

Chart 1



1; R = CO_2CH_3
2; R = CF3

3; R = CO_2CH_3
4; R = CF3

5; R = CO_2CH_3
6; R = CF3

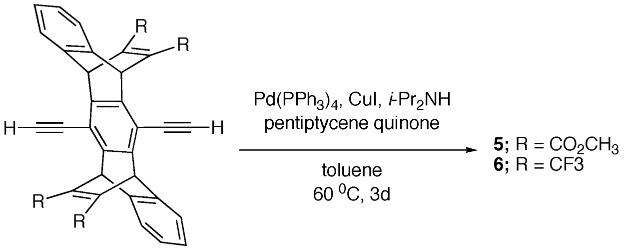
7; R = CO_2CH_3

alkene in the [2.2.2] system to tune the electronics of the polymers and employ the ester groups in biological conjugation chemistries.[7] However, as reported herein we have come to recognize this [2.2.2] ring system common to **1**, **3**, **5**, and **7** to be an important structure for producing strong excimer emissions in a variety of phenylene ethynylene-containing polymers. The special nature of this structure is revealed in that homologues also having electron-withdrawing trifluoromethyl-substituted bridging olefins (**2**, **4**, and **6**, Chart 1) exhibited indistinguishable absorption spectra but gave no evidence of excimer formation. Elucidation of the factors that can produce excimers in these systems is of interest for extending the utility and basic photophysics of CPs in optoelectronic devices and sensors.

Results and Discussion

Synthesis. The preparation of polymers **1**−**4** was reported elsewhere,[8] and their respective number average molecular weights are 17 000 (PDI = 2.0, DP = 15), 18 000 (PDI = 1.2, DP = 15), 21 000 (PDI = 1.8, DP = 20), and 28 000 (PDI = 2.0, DP = 26). Poly(phenylene diethynylene)s **5** and **6** were synthesized from homopolymerization[9] (Scheme 1) of diacetylene monomers **8** and **9**, which were also used in the preparation of polymers **1**−**4**. Neither polymer **5** nor **6** is adorned, as is typical for soluble CPs, with long flexible side chains, yet both are completely soluble in common organic solvents such as chloroform, THF, and dichloromethane. High solubility in polymers having [2.2.2] ring systems has been attributed to the fact that strong intermolecular interactions are blocked by the rigid scaffolds.[10] The molecular weights (M_n) were 15 000 (PDI = 1.3, DP = 24) and 12 000 (PDI = 1.4, DP = 19) for polymers **5** and **6**, respectively.

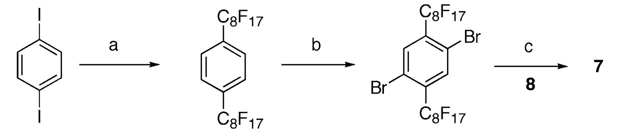
Scheme 1



5; R = CO_2CH_3
6; R = CF3

8; R = CO_2CH_3
9; R = CF3

Scheme 2 [a]



10 **11**

[a] Reagents and conditions: (a) $C_8F_{17}I$, Cu, DMSO, 140 °C, 3 d, 35%. (b) H_2SO_4/TFA (0.3 v/v), NBS, 70 °C, 2 d, 30%. (c) CuI, Pd(PPh$_3$)$_4$, (*i*-Pr)$_2$NH/toluene (1:2), 70 °C, 3 d, 61%.

In an effort to add bulk to the polymer backbone that will be unfavorable to interchain contacts, we prepared polymer **7** having bis-perfluorooctyl groups as shown in Scheme 2. Monomer **11** is obtained in 11% overall yield by a copper-promoted coupling reaction between perfluorooctyl iodide and 1,4-diiodobenzene in DMSO followed by bromination. The low synthetic yield of monomer **11** is attributed to its low solubility and that of its intermediate. Polymer **7** prepared by Sonogashira−Hagihara cross-coupling reaction exhibits good solubility in common organic solvents (M_n = 14 000, PDI = 1.5, DP = 9).

Photophysical Properties. The absorption and emission spectra of these polymers were investigated in solution and in the solid state (Figure 1). The most striking result is that all of the polymers containing ester-appended double bonds as one bridge in the [2.2.2] bicyclic rings (polymer **1**, **3**, **5**, and **7**) display new intense solid-state emission peaks that are red-shifted from their solution spectra. In contrast, the polymers containing trifluoromethyl-substituted olefins (**2**, **4**, and **6**) display solid-state spectra that are very similar to those obtained in solution.

To probe the origin of the red-shifted emissive peak, we investigated the effect of the film thickness on the emission spectra. As the thickness of polymer **1** film increases (Figure 2a), so does the intensity of the long-wavelength emission relative to that of shorter wavelength emission (I_{496}/I_{438}). Two factors may contribute to the enhanced long-wavelength emission in thicker films. In thin films interfaces can dictate polymer organization and create conformations unfavorable to the long-wavelength emission. Hence, with thicker films the amount of polymer away from the interfaces increases, and if this material is organized in a way that gives the new emission we expect an enhancement. Alternatively, in addition to this organizational explanation, energy migration may be enhanced in thicker films.[11] In this case we must infer that the energy of the polymer segments responsible for the low-energy emission is favorable (i.e. lower energy than its surroundings) for energy transfer to occur. We additionally studied spin-cast films wherein polymer **1** is interned within a poly(methyl methacrylate) (PMMA)

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(7) Kim, Y.; Zhu, Z.; Swager, T. M. *J. Am. Chem. Soc.* **2004**, *126*, 452−453.
(8) Kim, Y.; Whitten, J.; Swager, T. M. *J. Am. Chem. Soc.* **2005**, *127*, 12122−12310.
(9) Williams, V. E.; Swager, T. M. *J. Polym. Sci. A* **2000**, *38*, 4669−4676.
(10) Williams, V.; Swager, T. M. *Macromolecules* **2000**, *33*, 4069−4073.
(11) Levitsky, I. A.; Kim, J.; Swager, T. M. *J. Am. Chem. Soc.* **1999**, *121*, 1466−1472.

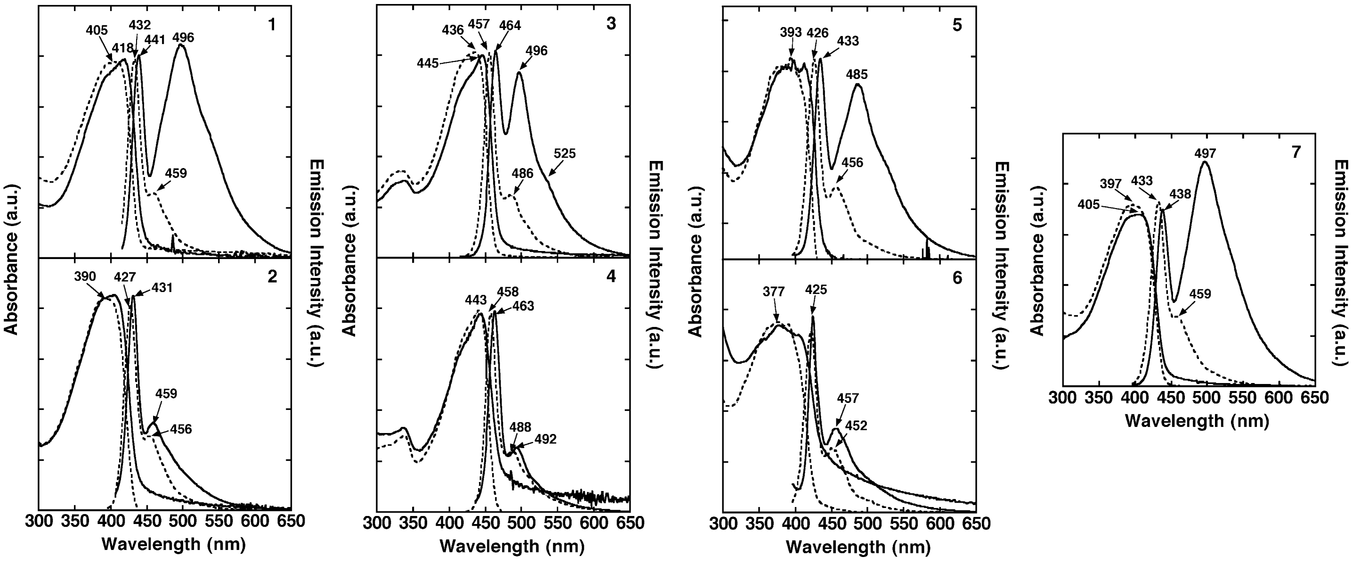

Figure 1. Normalized absorption and emission spectra of polymers **1**−**7** in chloroform (dotted line) and solid films (solid line). Polymers **1**, **2**, **5**, **6**, and **7** were excited at 380 nm, and polymers **3** and **4** were excited at 420 nm.

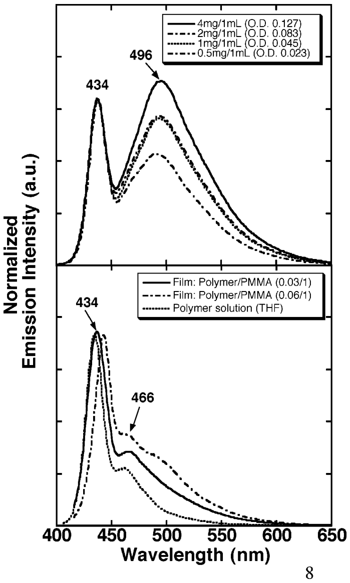

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Figure 2. Emission spectra of polymer **1** films as a function of film thickness (top) and normalized emission spectra of polymer **1** in THF and as spin-cast films in PMMA (OD is 0.05 for 0.03/1 and 0.3 for 0.06/1) (bottom). Films and solutions were excited at 400 and 390 nm, respectively.

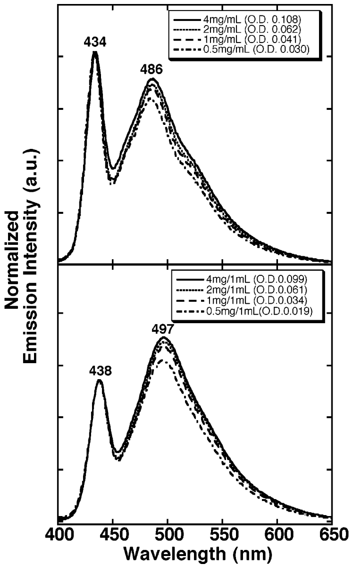

Figure 3. Emisssion spectra of polymer **5** (top) and polymer **7** (bottom) films as a function of film thickness.

matrix with different weight ratios (polymer **1**/PMMA). As shown in Figure 2b, mixed films wherein the polymer **1**/PMMA ratio is less than 0.03 behave like a solution, demonstrating that long-wavelength emission may be avoided by reducing interchain interactions. Therefore, PMMA films containing small amounts of polymer **1** exhibit a strong blue fluorescence, whereas films of pure polymer **1** exhibit a strong green fluorescence due to the new emission.

The concentration dependence of the emission characteristics of polymer **1** in solution shows a behavior similar to that of small-molecule excimers. In dilute THF solutions (5×10^{-6}–5×10^{-5} M), polymer **1**'s spectroscopic characteristics were constant: the emission spectra displayed an emission maximum at 432 nm with a vibrational band at 459 nm ($\Delta E^{\circ 1} = 1362$ cm^{-1}) and the emission intensity scales linearly with concentration, indicating that the emission is emanating from an isolated chain singlet excited state, A*. However, at high concentrations (0.1 wt % in THF) of **1** a new red-shifted emission peak was observed that is consistent with emission from a singlet excimer excited state, AA*. Unlike most CP aggregates, which experience significant red-shifts in both their emission and absorption, a new red-shifted peak of polymer **1** film was not observed in its absorption spectra at any concentration or in thin films. Moreover, the absorption and excitation spectra of polymer **1** film are identical. Hence, these solution studies and the thin-film investigations clearly point toward the new long-wavelength emission being characterized as an excimer.

The photophysical studies of other polymers were similarly carried out in solution and in the solid state. The same trends displayed by polymer **1** were observed for the polymers having alkenes bearing esters as one of the bridges in the [2.2.2] bicyclic ring system (**3**, **5**, **7**). Similar film thickness behaviors are consistently observed for these polymers**,** as shown in Figure 3. We emphasize that none of these behaviors were observed

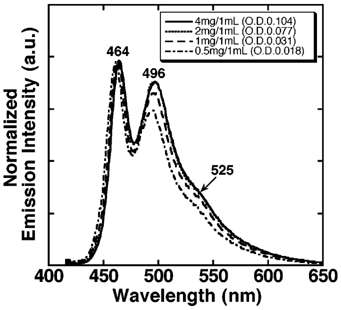

Figure 4. Emission spectra of polymer **3** films as a function of film thickness.

for polymers **2**, **4**, and **6** films at any thicknesses prepared (>OD 0.15).

In considering the structure of polymer **1**, it is tempting to suggest that the new excimer emission is due to an association involving the more sterically accessible phenylene that lacks the [2.2.2] ring system. However, polymer **5** that has only [2.2.2] substituted phenylenes in the polymer backbone still displays excimer behavior in thin films, although with weaker intensity (I_{AA*}/I_{A*}) than those observed for films of polymer **1** with similar optical density. Moreover, polymer **7**, bearing two bulky perfluorooctyl groups, which was originally prepared to reduce interchain contacts, exhibits a stronger tendency for excimer formation (larger I_{AA*}/I_{A*}) than polymer **1** (Figure 3). The stabilization energy of the excimers, which is the energy difference between the single chain A* and excimer AA* emission maxima, is almost the same for films of polymers **1** (0.33 eV), **5** (0.31 eV), and **7** (0.33 eV). These values are also consistent with the stabilization energies for excimers of conjugated polymers reported in the literature.[4,12]

Polymer **3** differs significantly from polymers **1** and **7** in that it has electron-donating alkoxy substituents instead of perfluoroalkyl groups attached to alternating phenylenes. The oxygen groups tend to raise HOMO levels, and hence **3** has a lower band-gap than the other polymers and further displays an excimer emission which, in concert with **1**, **5**, and **7**, increases in intensity with film thickness (Figure 4) but is generally less intense and has a smaller stabilization energy (0.25 eV) than the other excimer-forming polymers. However, due to the smaller excimer stabilization energy associated with polymer **3**, the exciplex emission may overlap with higher-order vibronic transitions associated with a single-chain emission, and as a consequence the relative contributions of each of these species to the red-shifted emission remain undetermined.

To rule out the possibility that our excimer emission is not merely a vibrational band enhanced by certain nuclear coordinates of the polymers in thin films and concentrated solutions, we measured time-resolved photoluminescence decay dynamics of polymer **1** and **2** in solution and thin films using a streak camera technique (Figure 5).[13] In particular the observation of different lifetimes for the two emission peaks observed will confirm that they are not from the same emissive state. Polymer **2** does not display the excimer behavior in thin films, and hence it serves as a reference. In dilute solution (ca. 10^{-6} M $CHCl_3$), wherein we observe emission strictly from isolated chains, A*, both polymers **1** and **2** exhibited a single-exponential decay with lifetimes of 0.44 and 0.39 ns, respectively. The excited-state decay dynamics of thin films of CPs are typically shorter and multiexponential in character, which is an indication of different organizations and energy-transfer processes. Thin films of polymer **2** (OD = 0.08 ± 0.01) were found to have a single-exponential lifetime of 0.11 ns at 436 nm and biexponential lifetimes of 0.09 ns (91.5%) with a small portion (8.5%) of a longer-lived excited state (0.47 ns) at 466 nm. The PL decay dynamics of polymer **1** are more interesting, and thin films (OD = 0.08 ± 0.01) were best described by a single-exponential lifetime of 0.05 ns at 444 nm and biexponential lifetimes of 0.10 and 1.14 ns at 502 nm, respectively. In this case the contribution of the longer-lived excited state at 502 nm is increased (36.8%). The faster decays at shorter wavelength for both polymer **1** and **2** films are suggestive of fast exciton diffusion to low-energy sites. The longer-lived emitting species at 502 nm for polymer **1** film is consistent with the expected longer radiative lifetimes typical of excimers, and its large difference from the 444 nm emission clearly confirms that it is a different emissive state.

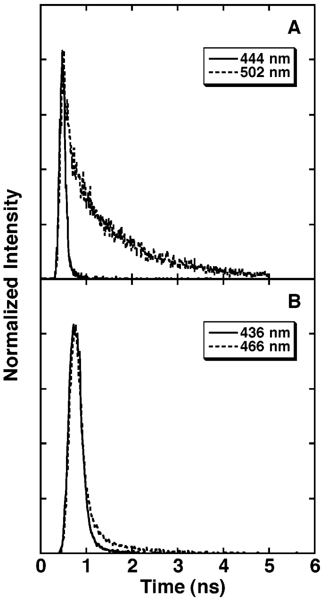

Figure 5. Time-resolved emission decays of polymer films (A) **1** and (B) **2**. Polymer **1** exhibits a single-exponential decay that was fit to 0.05 ns at 444 nm and a biexponential decay giving lifetimes of 0.10 ns (63.2%) and 1.14 ns (36.8%) for 502 nm. Polymer **2** gave a single-exponential decay that was fit to a lifetime of 0.11 ns for 436 nm, and a biexponential decay yielded lifetimes of 0.09 ns (91.5%) and 0.47 ns (8.5%) for 466 nm.

One of the most striking features of the excimers reported herein is their relatively high quantum yields that are apparent from casual inspection. The quantum yields for polymers **1** and **2** are similar in solution (0.87 and 0.84, respectively) and in the solid state (0.21 and 0.22, respectively). This result indicates that excimer emission from polymer **1** thin film does not affect its quantum yield more than would be expected from a solid-state structure devoid of excimers. We also determined the quantum yield of polymer **1**:PMMA films at concentrations below those producing excimers (2 wt % polymer **1**/PMMA) to be 0.81, which compares favorably with the solution values. Of the excimer-forming materials, polymer **3** stands out as having lower quantum yields both in solution (0.59) and in the

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(12) Li, H.; Powell, D. R.; Hayashi, R. K.; West, R. *Macromolecules* **1998**, *31*, 52−58.

(13) Osaheni, J. A.; Jenekhe, S. A. *Macromolecules* **1994**, *27*, 739−742. The samples were excited at 391 nm with the doubled light. The laser repetition rate was 250 kHz, the pulse width was about 150 fs, and the average power was 15.4 μW.

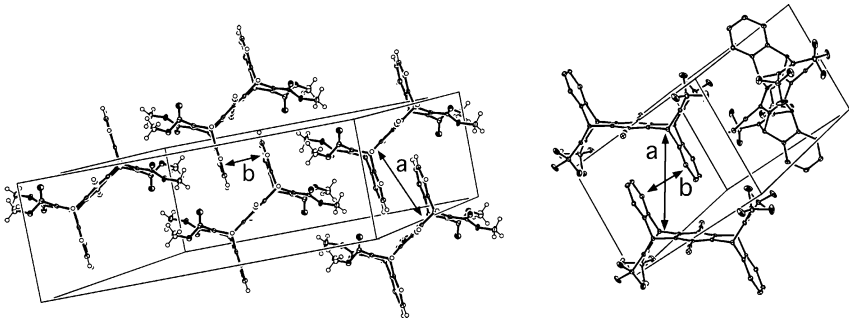

Figure 6. Perspective view of crystal packing of monomers **8** (left) and **9** (right). Hydrogen atoms in the crystal structure of monomer **9** were omitted for clarity.

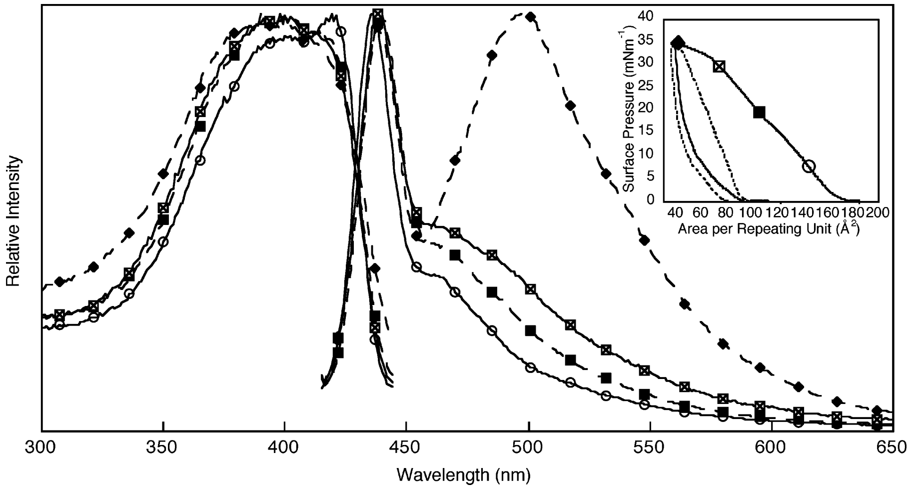

Figure 7. Normalized fluorescence excitation and emission spectra of Langmuir monolayers of polymer **7** of during cycles of compressions and expansions. The inset presents the pressure−area (*P*−*A*) isotherms of polymer **7**, first (solid line) and second (dashed line) compression cycles, and the pressure locations where the specific spectra were taken.

solid state (0.05). It is possible that the donation properties of the alkoxy groups give rise to nonradiative transitions having charge-transfer characteristics.

Central to understanding interchain interactions in CPs is the determination of the structure of aggregates. Given the pivotal nature of the [2.2.2] ring system in excimer formation, we sought to investigate if any unusual interactions could be identified in crystals of the monomers **8** and **9**. Although both the syn and anti isomers are produced in approximately 1:1 ratio in the synthesis, we found that the anti isomers gave crystals suitable for X-ray diffraction studies. As shown in Figure 6, the perpendicular distances (*a*) for **8** and **9** between two central aromatic rings in neighboring molecules are similar, with values of 8.456 and 8.483 Å, respectively. The most interesting aspect of the structures is the parallel alignment and close spacing (*b*) of 4.029 Å for **8** and 4.228 Å for **9** between phenylenes constituting one of the bridges of the [2.2.2] bicyclic system. The closer spacing of 4.029 Å in **8** is sufficient to cause intermolecular electronic coupling,[1,3] and we note that this monomer is responsible for producing excimer properties. This feature suggests that electronic interactions with the pendant groups of the [2.2.2] ring system are responsible for the excimers observed for polymers **1**, **3**, **5**, and **7**. The greater steric demands of the trifluoromethyl groups in monomer **9** may prevent interactions, and we see no evidence of strong interpolymer electronic interactions for polymers **2**, **4**, and **6**.

Structural correlations in polymer aggregates are complicated by the disorder that is inherent to polymers assembling from solution random coil conformations. However, the conformational disorder in PPEs can be greatly restricted by confining them to a monolayer at the air−water interface. When densely assembled in this two-dimensional state the polymer chains exhibit high persistence length,[14] and the adjacent polymer chains are organized in a parallel fashion. As a result, Langmuir−Blodgett techniques have proven their utility in the study of conjugated polymers and in controlling the structure of their self-assembled films,[15] and we have shown that in situ spectroscopic measurements can be used to better understand inter- and intrachain effects.[1] To utilize these methods to elucidate the interactions generating excimers, we have studied polymer **7**, which forms highly stable and luminescent Langmuir monolayers with an extrapolated area of 170 Å^2 per repeating unit (Figure 7). Perfluoroalkyl side chains such as those present in polymer **7** are best known for their hydrophobicity,[16] and hence they are predicted to remain outside the water subphase. Given their para substitution, we would expect the phenylene to organize with a *face-on* orientation of the arene ring coplanar to the air−water interface. The preferred orientation of the arene

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(14) PPEs have a relatively high persistence length of 15 nm in solution: Cotts, P. M.; Swager, T. M.; Zhou, Q. *Macromolecules* **1996**, *29*, 7323−7328.

(15) (a) Wegner, G. *Thin Solid Films* **1992**, *216*, 105−116. (b) Robitaille, L.; Leclerc, M. *Macromolecules* **1994**, *27*, 1847−1851. (c) Kim, J.; McHugh, S.; Swager, T. M. *Macromolecules* **1999**, *32*, 1500−1507. (d) Rietzel, N.; Greve, D. R.; Kjaer, K.; Howes, P. B.; Jayaraman, M.; Savoy, S.; McCullough, R. D.; McDevitt, J. T.; Bjornholm, T. *J. Am. Chem. Soc.* **2000**, *122*, 5788−5800.

(16) Hong, X. M.; Tyson, J. C.; Collard, D. M. *Macromolecules* **2000**, *33*, 3502−3504.

ring bearing the more hydrophilic ester-substituted bicyclic framework is not as easily predicted. However, the characteristic bathochromic shifts observed in the fluorescence excitation (24 nm) and emission (7 nm) maxima of polymer **7** in Langmuir films (Figure 7) with respect to their solution values are consistent with an extended effective conjugation length associated with an entirely *face-on* organization of the polymer main chain at the air−water interface. As the monolayer is compressed, the surface pressure increases until the monolayer folds into multilayers at 33 mN m^{-1}. As indicated by the P−A isotherm for polymer **7** (Figure 7, inset), the folding into multilayers is largely irreversible, possibly due to the formation of aggregates promoted by the association of perfluoroalkyl side chains that are more conformationally rigid than simple alkanes. The fluorescence excitation and emission spectra of Langmuir monolayers of polymer **7** show minimal variations as the surface pressure is increased and do not present an excimer emission band at 497 nm. However, as the monolayer is folded into multilayers, a strong excimer emission appears. We interpret these observations to be consistent with the requirement for coincident orientation of the polymers and subtle organizations between adjacent polymer chains to give rise to the excimer emission. We further find this observation to be consistent with our earlier suggestion based on **8**'s crystal structure that the fused pendant arene groups defining the [2.2.2] ring systems are responsible for the excimer emission. Below the pressure at which the monolayer collapses into multilayers, the arene rings of the polymer main chain are constrained to the plane of the air−water interface due to its *face-on* structure. As the monolayer collapses into multilayers, this conformational restriction is released and face-to-face interaction between pendant arene units on adjacent polymer chains becomes possible.

Conclusion

In summary, spectroscopic results showed the existence of highly emissive excimers in polymer **1**, **3**, **5**, and **7** films with ester groups appended on [2.2.2] bicyclic ring systems. The photophysical behaviors from these systems are consistent with classical exciplexes known for low-molecular-weight systems. Our present investigations suggests that the pendant arene groups of the [2.2.2] bicyclic ring system are responsible for intermolecular interactions that produce a bright excimer emission. The ability to design excimers on demand has important ramifications for the development of sensors as well as light-emissive devices. The [2.2.2] bicyclic ring system reported herein represents a significant advance to that goal by faithfully generating excimer emission in four different polymers. Our ongoing investigations are directed at discovering other excimer-promoting structures and exploiting this behavior in sensory schemes.

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Supporting Information Available: Detailed synthetic procedures and characterization of all compounds (PDF, CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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