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Exciplex dynamics and emission from nonbonding energy levels in electronic polymer blends and bilayers

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Photoexcited bound exciplexes generated at interfaces in bilayers and blends of hole and electron transporting polymers are unusual and differ from bound excitons formed by photoexcitations of bulk polymers. We present a unique exciplex system we found present for interfaces involving a π molecular orbital on one polymer with a nonbonding N-orbital on another polymer. The exciplex emission occurs in an unexpected energy region intermediate to that of emission of each of the isolated layers. Our data show that the photophysics of this exciplex differs from that of excimers and aggregates. The exciplex emission has greater similarity to exciton emission than excimer emission, reflecting the role of symmetry breaking at the interface of two dissimilar polymers. We present the first temperature and wavelength dependent studies of exciplex photoluminescence decays and propose a model based on the unique role of the nonbonding orbital in these N-containing polymers. We demonstrate that this type of exciplex is characteristic of a broad class of materials.

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I. INTRODUCTION

Interest in the photophysics of electronic polymers has increased this past decade owing to the report of electroluminescence in poly(*p*-phenylene vinylene) (PPV) and the activities toward commercialization of displays based on this class of materials.[1] Controversy still remains concerning the binding of excitons in arylene–vinylene-based polymers such as PPV.[2–11] Emission from excited states delocalized over two dissimilar molecules or polymers, though relatively rare, has been reported for a few systems.[12–17] However, there have been no comprehensive reports of the temporal, spectral, or temperature dynamics of these unusual excited states.

We have previously reported studies of a class of conjugated polymers analogous to PPV polymers, poly(*p*-pyridine) (PPy) and poly(*p*-pyridyl vinylene) (PPyV) shown in Fig. 1. These are promising materials for use in light emitting diode applications.[2,4,18–21] The nitrogen heteroatom renders the polymer soluble in weak acidic solvents such as *m*-cresol and formic acid, thus making them easily processed into thin films.[2,19,20] Adding side chains to form poly(pyridyl vinylene phenylene vinylene) (PPyVPR$_2$V) improves solubility so the polymer can be dissolved into common organic solvents.[22] Due to their electron-deficient nature the nitrogen-containing polymers are less susceptible to oxidation than PPV and may possess improved transport abilities.[2,19–22] Also, the inclusion of the nitrogen atom introduces nonbonding orbitals and breaks the symmetry of the electronic structure.[23]

Usually, energy migration to defects and traps and interchain interactions result in excimer formation or emission from aggregates, hindering efficiency of polymer devices. In the thin film configuration, interchain interactions are more likely to occur than intrachain interactions, such as exciton formation and emission.[12,16] Blending other polymers into electronic polymers and designing polymers with "straps" to increase distance between polymer backbones are examples of schemes that have been developed in order to reduce or prevent interchain interactions.[24] Exciplexes, in contrast to

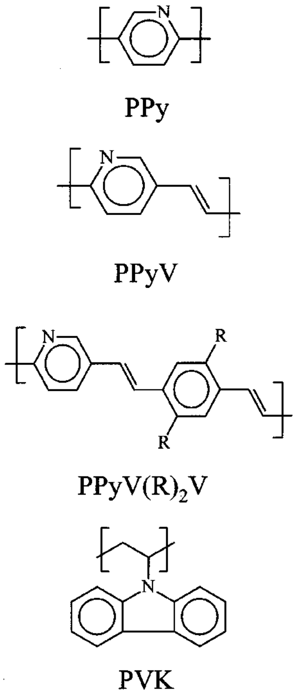

FIG. 1. Repeat units of several polymers. For PPyVPR$_2$V, R $=C_{12}H_{25}$ or R$=OC_{16}H_{33}$.

other interchain interactions, possess higher efficiencies and have been used as the primary emitter in light emitting devices.[13–15] With the implementation of multilayer devices incorporating electron and hole transporting polymers it is important to understand the formation and decay of exciplex states.[12,14,15,20] Though the excited state wave function of the two molecules or polymers forming the exciplex interact, the ground state wave function of the two units does not interact.[25,26] Interchain interactions between two dissimilar polymer chains are more likely to occur in bilayer with the exciton diffusion length for the individual homopolymer layers greater than the layer thickness. One can then use the interchain exciplex interaction as the primary emitter in a device design.

In this paper, we report on the detailed behavior of an exciplex system formed between hole transporting poly(vinyl carbazole) (PVK) and electron/hole transporting PPyVPR$_2$V (R$=$C$_{12}$H$_{25}$) shown in Fig. 1. PPyVPR$_2$V is a semiconducting polymer with similar photoluminescence (PL) time dynamics to other poly(*p*-pyridine) (PPy) systems and PPV systems.[2,18,27,28] In general, the exciplex emission is a broad, structureless band that is redshifted from the emission of each of the molecule or polymer units that make up the interface. In contrast, the exciplex emission band from the blends and bilayers used in this study occur between the emission bands from the homopolymers. To our knowledge, it is the first known exciplex of this type. We have demonstrated this class of exciplex to be effective in electroluminescent devices.[13,14] We propose that the exciplex state is formed by the interaction of the initially lowest unoccupied molecular orbitals (LUMOs) of the PVK and the PPyVPR$_2$V and the initially highest occupied molecular orbitals (HOMOs) of PVK and the nonbonding molecular orbital (NBMO) due to the nitrogen atom of PPyVPR$_2$V. We report the first spectral, temporal, and temperature time-resolved photoluminescence $[\mathrm{PL}(\lambda,T,t)]$ for this class of exciplex systems.

II. EXPERIMENT

The synthesis procedure for PPyVPR$_2$V is described elsewhere.[29] The PVK was obtained from Aldrich Chemical Co. We prepared thin films by spin casting the polymers and their blend solutions from toluene onto a quartz substrate. We collected steady state absorption spectra using a Perkin Elmer Lambda 20 UV/Vis spectrometer. We obtained steady state fluorescence emission spectra using a PTI QM1 spectrometer, while PL(t) was determined by time-correlated single-photon counting.[30,31] Our apparatus has been described previously.[32,33] Briefly, a Nd-YAG (Coherent Antares 76-s) or a Nd-YLF (Coherent Antares 76-YLF) laser system pumps a synchronously pumped, cavity dumped dye laser (Coherent 700 Series). The dye laser utilizes two different dyes (stilbene and rhodamine 6-G) in order to obtain different excitation energies. The stilbene dye laser provided excitation energies in the region from 2.7 to 3.1 eV while the Rhodamine 6-G (R6G) generated 2.0-eV radiation. An angle tuned KDP crystal frequency doubled the 2.0-eV radiation in order to provide 4.0-eV excitation. A liquid nitrogen cooled cryostat was used to study the temperature dependence of the fluorescence decays at various emission energies. We measured the quantum efficiency of the thin film with an integrating sphere and a lock-in amplifier.[7]

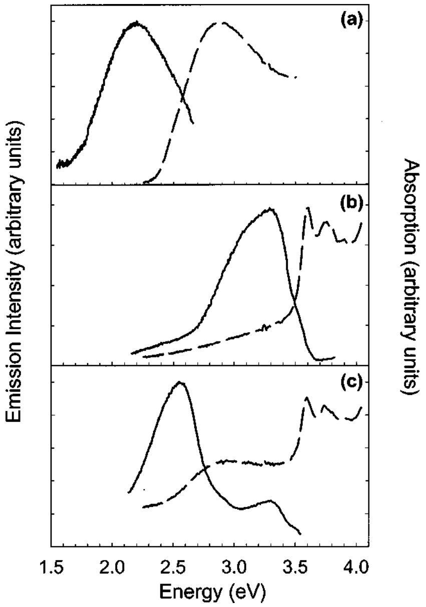

FIG. 2. Room temperature emission(—) and absorption spectra(---) shown for the thin films of (a) PPyVPR$_2$V, (b) PVK, and (c) PPyVPR$_2$V/PVK.

III. RESULTS

The absorption spectrum of the blend shown in Fig. 2(c) is approximately a linear combination of the absorption spectra of PPyVPR$_2$V in Fig. 2(a) and PVK in Fig. 2(b) with no new absorption bands. Exciting a single layer of PPyVPR$_2$V at 2.9 eV gives rise to the emission spectrum in Fig. 2(a), a single peak at 2.0 eV. Exciting a single layer of PVK at 4.0 eV gives rise to the emission spectrum in Fig. 2(b). Exciting the blend sample of PPyVPR$_2$V and PVK at 4.0 eV gives rise to an emission spectrum in Fig. 2(c).

In order to compare the exciplex with other excited state species, we collected fluorescence decays from the PPyVPR$_2$V homolayer, the PVK homolayer, and the PPyVPR$_2$V/PVK blend and bilayer thin film samples. Figure 3(a) shows decays collected from the PPyVPR$_2$V homolayer at emission energies of 2.1 and 2.4 eV, following excitation at 2.9 eV. We obtained lifetimes from the fluorescence decays by fitting to a sum of exponentials, giving lifetime distributions. Table I gives the percent contributions for the principal decay components for each thin film composition. At room temperature, the 1-ns component of PPyVPR$_2$V for 2.1-eV emission contributes about 60% of the radiative emission. The time dynamics from the PVK homolayer and the PVK excited in the blend are similar. In Fig. 3(b), we show the decays from the PVK homolayer at emission energies of 2.6 and 3.1 eV, following excitation at 4.0 eV. The 1-ns lifetime contributes only $\sim$17% of emission, with the majority of the emission due to longer-lived ($>$10 ns) excimer species. Figure 3(c) shows the decays from the blend sample

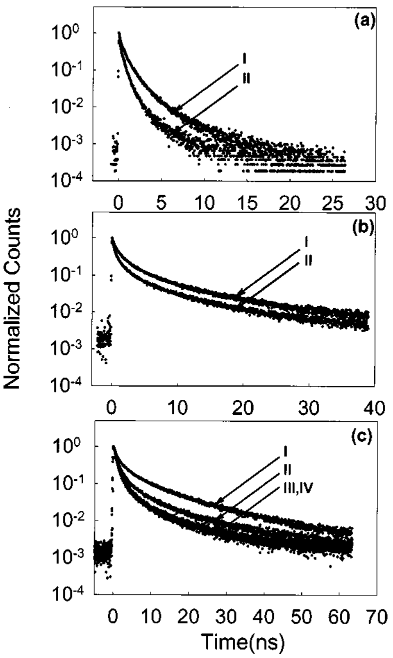

FIG. 3. Room temperature photoluminescence decays shown for (a) $PPyVPR_2V$ homolayer excited at 2.9 eV at emission energies of 2.1 eV(I) and 2.4 eV(II), (b) PVK homopolymer excited at 4.0 eV at emission energies of 2.6 eV(I) and 3.1 eV(II), and (c) $PPyVPR_2V$/PVK blend excited at 4.0 eV at emission energies of 3.1 eV(I), 2.7 eV(II), 2.6 eV(III), and 2.5 eV(IV).

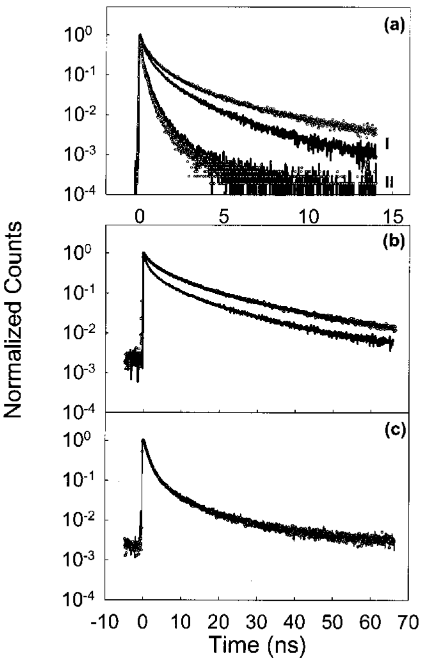

FIG. 4. Photoluminescence decays shown for room temperature(—) and 77 K(○) for (a) $PPyVPR_2V$ excited at 2.9 eV at emission energies of 2.1 eV(I) and 2.5 eV(II), (b) $PPyVPR_2V$/PVK blend excited at 4.0 eV at an emission energy of 3.1 eV, and (c) $PPyVPR_2V$/PVK blend excited at 4.0 eV at an emission energy of 2.5 eV.

excited at 4.0 eV and collected at emission energies of 2.5, 2.6, 2.7, and 3.1 eV. The decays collected at 3.1 eV in the homolayer and blend are essentially superimposable.

We collected PL decays at various temperatures from the $PPyVPR_2V$ homopolymer, the PVK emission band in the blend, and the exciplex emission band in the blend. In Fig. 4(a), the decays are shown for the $PPyVPR_2V$ sample at two emission energies, 2.5 and 2.1 eV, at room temperature and 77 K. In Table I, we show that the 1-ns component contributes to 40% of the emission at 77 K, increasing to ~60% at room temperature. In Fig. 4(b), the decays are presented for the PVK emission band at 3.1 eV in the blend sample at 77 K and room temperature; the majority of the emission is due to a long-lived species (>10 ns), Table I. At 77 K the long-lived species contribute to 80% of the emission, while at room temperature they only contribute to 50% of the emission. In Fig. 4(c), the 77 K and room temperature PL(t) decays are presented from the blend sample at 2.5 eV, the exciplex emission band. In contrast to the decays collected at 3.1 eV, the decays have *identical* lifetimes at all temperatures. The ~1-ns component contributes to 55% of the emission at both temperatures (Table I). Figure 5(a) shows the temperature dependence of the $PPyVPR_2V$ homolayer steady state emission; it decreases with an increase in temperature as expected for phonon induced quenching. Figures 5(b) and 5(c) show the exciplex emission at various temperatures for two different $PPyVPR_2V$ ($R_2{=}C_{12}H_{25}$ and $OC_{16}H_{33}$) polymers with PVK thin films.

TABLE I. The percent contribution of photoluminescent decay lifetimes collected at emission energy (in parentheses) from $PPyVPR_2V$, PVK, and $PPyVPR_2V$/PVK blend thin film samples at 300 and 77 K.

	$PPyVPR_2V$ (2.1 eV)	PVK (3.1 eV)	$PPyVPR_2V$/PvK (2.6 eV)
300 K	~1 ns (60%)	~1 ns (17%)	~1 ns (55%)
300 K		>10 ns (50%)	>10 ns (17%)
77 K	~1 ns (40%)	~1 ns (5%)	~1 ns (55%)
77 K		>10 ns (80%)	>10 ns (23%)

IV. DISCUSSION

Evidence for the existence of the exciplex in the blend and bilayer includes the absence of a unique feature in the steady state absorption spectrum and the presence of a unique emission band in the blend samples. The emission band in Fig. 2(c) at 3.3 eV is assigned to emission within PVK because of its wavelength, time, and temperature dependencies. The second emission band at 2.6 eV does not correspond to the emission of either bulk polymer and hence is assigned to an exciplex formed at $PPyVPR_2V$/PVK interface. The exciplex steady state emission spectra and time-resolved photoluminescence decays demonstrate minimal emission energy or temperature dependence.

The exciplex emission occurs at an unexpected emission energy between the emissions of the two homopolymers. In Fig. 6(a) we observe that the emission from the homopoly-

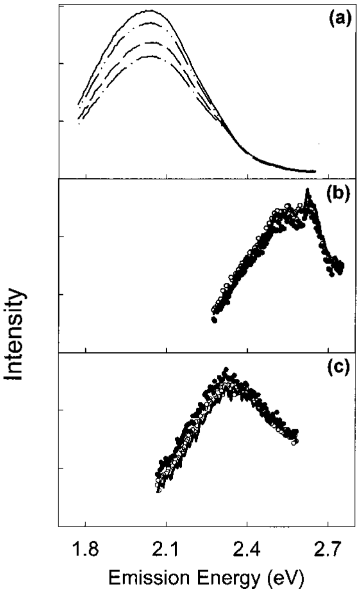

FIG. 5. Temperature dependence of (a) $\mathrm{PPyVPR_2V}$ ($\mathrm{R} = \mathrm{C_{12}H_{25}}$) homolayer photoluminescence emission spectra excited at 2.9 eV at 77 K(▲), 150 K(□), 250 K(○), and 300 K(●), (b) $\mathrm{PPyVPR_2V(R=C_{12}H_{25})/PVK}$ exciplex emission spectra excited at 4.0 eV at 77 K(○), 180 K (●), and 298 K(—), and (c) $\mathrm{PPyVPR_2V(R=OC_{16}H_{33})/PVK}$ exciplex emission spectra excited at 4.0 eV at 77 K(○), 125 K (●), and 298 K(—).

mers occurs at 3.29 eV for PVK and 2.00 eV for $\mathrm{PPyVPR_2V}$. Figure 6(b) depicts how a conventional exciplex forms between the π orbitals of each polymer. However, the exciplex emission would have to be lower in energy than either homopolymer, if this were the case. Figure 6(c) describes the proposed scheme for the exciplex formation and decay based on the central role of the nonbonded orbital of the nitrogen atom incorporated in the $\mathrm{PPyVPR_2V}$. During exciplex formation, the LUMO of the PVK interacts with the LUMO of the $\mathrm{PPyVPR_2V}$ to form a more stable excited state. The HOMO of the PVK interacts with the nonbonding molecular orbital (NBMO) of the $\mathrm{PPyVPR_2V}$ to form another state. It has been shown theoretically that the HOMO level of an anthracene-like molecule can interact with the NBMO level of an adjacent molecule.[34] The exciplex transition occurs from the interaction between the LUMO state to the HOMO–NBMO state. The nonbonding energy level of the $\mathrm{PPyVPR_2V}$ is either below or above the π energy level depending on conjugation length.[23] As conjugation length increases, the $\pi-\pi^*$ energy gap decreases and the n orbital remains constant. At a long enough conjugation length, the n energy level lies beneath the π energy level allowing photoluminescence. The difference between the π energy level and the n energy level is 1.45 eV in a PPy sample.[23] As the n energy level lies below the π energy level, the $\mathrm{PPyVPR_2V}$ $\pi-\pi^*$ energy gap will be smaller than the energy gap between the LUMOs and NBMO–HOMO levels and the exciplex emission will occur at a lower energy than the $\mathrm{PPyVPR_2V}$ homolayer emission. Thus, the exciplex emission will be intermediate of the emission from the two homopolymers.

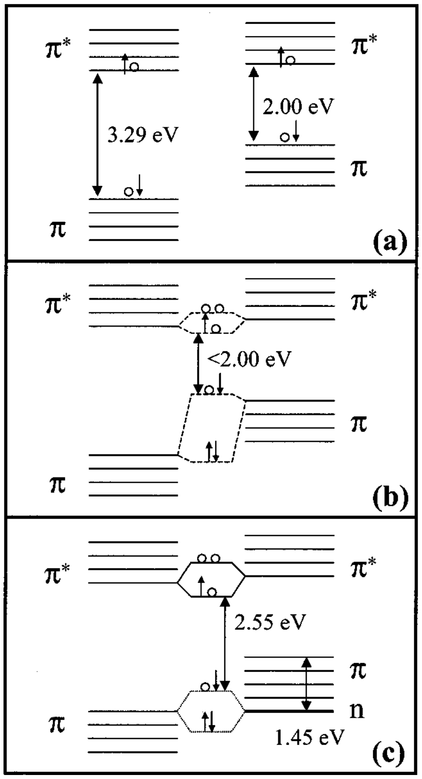

FIG. 6. (a) Schematic of exciton luminescence for the homolayers, PVK (3.29 eV) and PPyVPV (2.00 eV). (b) Schematic of conventional exciplex formation (<2.00 eV). (c) Schematic of N-orbital exciplex formation emission (2.55 eV).

A key question that arises is the possible generality of this n-orbital exciplex luminescence. Figure 7 shows a similar exciplex emission observed in another $\mathrm{PPyVPR_2V}$ ($\mathrm{R{=}OC_{16}H_{33}}$) system. The photoluminescence decays shown in the inset of Fig. 7 are not emission energy depen-

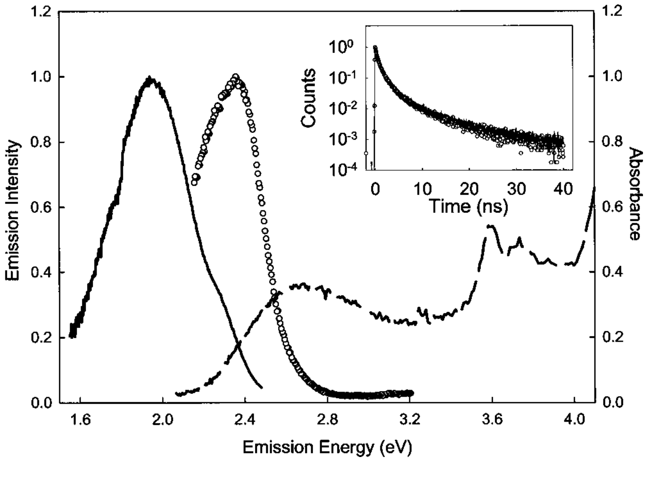

FIG. 7. Room temperature emission spectra shown for the thin films of the blend ($\mathrm{PPyVPR_2V(R=OC_{16}H_{33})/PVK}$)(○) excited at 4.0 eV and $\mathrm{PPyVPR_2V(R=OC_{16}H_{33})}$ (—) excited at 2.6 eV. Absorption spectrum(---) for the blend thin film. Inset: Photoluminescence decays of the $\mathrm{PPyVPR_2V(R=OC_{16}H_{33})/PVK}$ blend excited at 4.0 eV at emission energies of 2.25 eV (○) and 2.48 eV (●).

dent similar to the time dynamics of the exciplex formed from PPyVPR$_2$V (R$=$C$_{12}$H$_{25}$). The steady state spectra in Fig. 5(c) displays minimal temperature dependence similar to the exciplex emission formed from PPyVPR$_2$V (R$=$C$_{12}$H$_{25}$) in Fig. 5(b). Our model also explains exciplexes reported in earlier work on other nitrogen-containing systems.[35,36] In contrast, we have been unable to observe *n*-orbital exciplex luminescence emission in PPy polymers with low molecular weights, i.e., smaller conjugation lengths, nonconjugated N-containing polymers, oligomers with nitrogen atoms, or conjugated polymers without nitrogen. In order to observe the exciplex, there must be a nitrogen atom and the conjugation length must be large enough to allow the nonbonding energy level to lie beneath the π energy level.

The majority of the exciplex emission and the PPyVPR$_2$V homolayer emission arise from fast ($\sim$1 ns) components. We observe a spectral shift in the PPyVPR$_2$V homolayer time resolved PL, indicative of aggregate formation.[2,4,18] The lifetimes are shorter than the decays collected from the PVK homolayer. In addition, the exciplex possesses a quantum efficiency of 11%, comparable to a single layer of PPyVPR$_2$V.[2,4] The PVK emission is due to excimers, an excited state complex formed between two identical molecules.[37–39] We have demonstrated that though the formation of the exciplex is similar to that of an excimer in arising from the interaction of adjacent polymer chromophores, the emissive properties of the exciplex and excimer states are quite different. PVK excimer emission features longer lifetimes, emission energy dependence, and temperature dependence. Since the excimer is formed between two identical polymer chain chromophores, the wave function of the excited state species is symmetric with the ground state, making the transition forbidden.[40] Therefore, the excimer's lifetime is longer and it is a weak emitter. In contrast, the exciplex is formed between two dissimilar polymers. The breakdown of symmetry makes the exciplex less stable against radiative decay and the radiative transition of the exciplex back to ground state is more probable.[41] The lifetime of the exciplex is shorter and the quantum yield is equivalent to PPyVPR$_2$V, an exciton-based PL producer. Therefore, the time dynamics of the exciplex are closer to those of an exciton rather than an excimer.

We observe a lack of emission energy and temperature dependence in the exciplex emission compared to the homolayer emissions. The emission intensity and the time dynamics are similar regardless of temperature or emission energy. We propose that the unexpected lack of temperature and emission energy dependencies are due to the highly localized nature of an exciplex formed with a NBMO. If the exciplex is confined to very few sites, then low energy, long wavelength phonons will be less effective in inducing nonradiative decay.

V. CONCLUSIONS

In summary, we have studied the exciplex formed between pairs of electronic polymers one of which contains a nonbonded N orbital. We used time-resolved fluorescence decays at various emission energies and temperatures. The emission spectrum occurs between the two emission spectra of the polymers instead of to the red of both as is typically observed in other exciplex systems. The unique emission is assigned to the HOMO of the PVK interacting with the nonbonding state of the PPyVPR$_2$V instead of the HOMO of the PPyVPR$_2$V. The time dynamics of the exciplex have been compared to that of excimers and excitons. The exciplex has a fast, exciton-like emission, and it is localized. The localization of the exciplex is supported by the lack of temperature and emission energy dependence in the fluorescence decay. Nitrogen-containing electronic polymers give an opportunity for an exciplex emission pathway that is temperature independent with potentially high quantum efficiency through the use of nonbonding orbitals. The new type of excitation may find uses in new electroluminescent and lasing device architectures.

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[1] J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. MacKay, R. H. Friend, P. L. Burns, and A. B. Holmes, Nature (London) **347**, 539 (1990).

[2] J. W. Blatchford, S. W. Jessen, L. B. Lin, J. J. Lih, T. L. Gustafson, A. J. Epstein, D. K. Fu, M. J. Marsella, T. M. Swager, A. G. MacDiarmid, S. Yamaguchi, and H. Hamaguchi, Phys. Rev. Lett. **76**, 1513 (1996).

[3] I. D. W. Samuel, G. Rumbles, and C. J. Collison, Phys. Rev. B **52**, R11 573 (1995).

[4] J. W. Blatchford, T. L. Gustafson, A. J. Epstein, D. A. Vanden Bout, J. Kerimo, D. A. Higgins, P. F. Barbara, D. K. Fu, T. M. Swager, and A. G. MacDiarmid, Phys. Rev. B **54**, R3683 (1996).

[5] G. J. Denton, N. Tessler, N. T. Harrison, and R. H. Friend, Phys. Rev. Lett. **78**, 733 (1997).

[6] S. V. Frolov, M. Liess, P. A. Lane, W. Gellermann, Z. V. Vardeny, M. Ozaki, and K. Yoshino, Phys. Rev. Lett. **78**, 4285 (1997).

[7] N. C. Greenham, I. D. W. Samuel, G. R. Hayes, R. T. Phillips, Y. A. R. R. Kessener, S. C. Moratti, A. B. Holmes, and R. H. Friend, Chem. Phys. Lett. **241**, 89 (1995).

[8] U. Lemmer, S. Heun, R. F. Mahrt, U. Scherf, M. Hopmeier, U. Siegner, E. O. Gobel, K. Mullen, and H. Bassler, Chem. Phys. Lett. **240**, 373 (1995).

[9] M. Yan, L. J. Rothberg, E. W. Kwock, and T. M. Miller, Phys. Rev. Lett. **75**, 1992 (1995).

[10] M. Yan, L. J. Rothberg, F. Papadimitrakopoulos, M. E. Galvin, and T. M. Miller, Phys. Rev. Lett. **72**, 1104 (1994).

[11] J. M. Leng, S. Jeglinski, X. Wei, R. E. Benner, Z. V. Vardeny, F. Guo, and S. Mazumdar, Phys. Rev. Lett. **72**, 156 (1994).

[12] S. A. Jenekhe and J. A. Osaheni, Science **265**, 765 (1994).

[13] D. D. Gebler, Y. Z. Wang, D. K. Fu, M. Swager, and A. J. Epstein, J. Chem. Phys. **108**, 7842 (1998).

[14] D. D. Gebler, Y. Z. Wang, J. W. Blatchford, S. W. Jessen, D.-K.

Fu, T. M. Swager, A. G. MacDiarmid, and A. J. Epstein, Appl. Phys. Lett. **70**, 1644 (1997).

[15] D. D. Gebler, Y. Z. Wang, S. W. Jessen, J. W. Blatchford, A. G. MacDiarmid, T. M. Swager, D.-K. Fu, and A. J. Epstein, Synth. Met. **85**, 1205 (1997).

[16] S. A. Jenekhe, Adv. Mater. **7**, 309 (1995).

[17] N. L. Vekshin, *Energy Transfer in Macromolecules* (SPIE−The International Society for Optical Engineering, Bellingham, 1997).

[18] J. W. Blatchford, S. W. Jessen, L.-B. Lin, T. L. Gustafson, D.-K. Fu, H.-L. Wang, T. M. Swager, A. G. MacDiarmid, and A. J. Epstein, Phys. Rev. B **54**, 9180 (1996).

[19] J. W. Blatchford, S. W. Jessen, L.-B. Lin, J.-J. Lih, D. D. Gebler, Y. Z. Wang, T. L. Gustafson, A. J. Epstein, H. L. Wang, T. M. Swager, A. G. MacDiarmid, T. Yuzawa, T. Tahara, S. Yamaguchi, and H. Hamaguchi, in *Time-Resolved Vibrational Spectroscopy VII*, edited by R. B. Dyer *et al.* (Los Alamos Conference Proceedings, LA-13290, 1997), p. 77.

[20] D. D. Gebler, Y. Z. Wang, J. W. Blatchford, S. W. Jessen, L. B. Lin, T. L. Gustafson, H. L. Wang, T. M. Swager, A. G. MacDiarmid, and A. J. Epstein, J. Appl. Phys. **78**, 4264 (1995).

[21] A. J. Epstein, J. W. Blatchford, Y. Z. Wang, S. W. Jessen, D. D. Gebler, L. B. Lin, T. L. Gustafson, H. I. Wang, Y. W. Park, T. M. Swager, and A. G. MacDiarmid, Synth. Met. **78**, 253 (1996).

[22] M. Fahlman, D. D. Gebler, N. Piskun, T. M. Swager, and A. J. Epstein, J. Chem. Phys. **109**, 2031 (1998).

[23] J. W. Blatchford, T. L. Gustafson, and A. J. Epstein, J. Chem. Phys. **105**, 9214 (1996).

[24] A. J. Epstein, N. V. Piskun, I. V. Lebendenko, S. W. Jessen, T. L. Gustafson, D.-K. Fu, and T. M. Swager, Proc. SPIE **3145**, 316 (1997).

[25] M. Pope and C. E. Swenberg, *Electronic Processes in Organic Crystals* (Oxford University Press, New York, 1982).

[26] J. B. Birks, Nature (London) **214**, 1187 (1967).

[27] I. D. W. Samuel, G. Rumbles, C. J. Collison, R. H. Friend, S. C. Moratti, and A. B. Holmes, Synth. Met. **84**, 497 (1997).

[28] L. Smilowitz, A. Hays, A. J. Heeger, G. Wang, and J. E. Bowers, Synth. Met. **55**, 249 (1993).

[29] Dian Kui Fu, Bing Xu, and Timothy M. Swager, Tetrahedron **53**, 15 487 (1997).

[30] J. N. Demas, *Excited State Lifetime Measurements* (Academic, New York, 1983).

[31] D. V. O'Connor and D. Phillips, *Time-Correlated Single Photon Counting* (Academic, London, 1984).

[32] J. S. Buterbaugh, J. P. Toscano, W. L. Weaver, J. R. Gord, C. M. Hadad, T. L. Gustafson, and M. S. Platz, J. Am. Chem. Soc. **119**, 3580 (1997).

[33] Heather G. Johnston, Jun Wang, Stuart V. Ruffle, Richard T. Sayre, and Terry L. Gustafson, J. Phys. Chem. B **104**, 4777 (2000).

[34] M. Glenn Horner and James R. Larson, J. Photochem. Photobiol., A **55**, 145 (1990).

[35] J. A. Osaheni and S. A. Jenekhe, Macromolecules **27**, 739 (1994).

[36] Maksudul M. Alam and Samson A. Jenekhe, J. Phys. Chem. B **105**, 2479 (2001).

[37] Walter Klopffer and Herbert Bauser, Z. Phys. Chem. (Munich) **101**, 25 (1976).

[38] M. Yokoyama, T. Tamamura, M. Atsumi, M. Yoshimura, Y. Shirota, and H. Mikawa, Macromolecules **8**, 101 (1975).

[39] N. Piskun, Ph.D. dissertation, The Ohio State University, 2001.

[40] E. M. Conwell, Phys. Rev. B **57**, 14 200 (1998).

[41] R. S. Mulliken and W. B. Person, *Molecular Complexes* (Wiley, New York, 1969).