The effect of broken conjugation on the excited state: Ether linkage in the cyano-substituted poly(*p*-phenylene vinylene) conjugated polymer poly(2,5,2′,5′-tetrahexyloxy-8,7′-dicyano-di-*p*-phenylene vinylene)

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We investigate the effect of broken conjugation on the excited state dynamics of excimers in cyano-substituted phenylene-vinylene polymers. We compare previous studies on the well-characterized poly(2,5,2′,5′-tetrahexyloxy-8,7′-dicyano-di-*p*-phenylene vinylene) (CN-PPV) with poly[oxa-1,4-phenylene-1,2-(1-cyano)-ethenylene-2,5-dioctyloxy-1,4-phenylene-1,2-(2-cyano)-ethenylene-1,4-phenylene] (CN-ether-PPV), in which the conjugation is disrupted by the insertion of an oxygen atom within the polymer backbone. Despite the broken conjugation, the spectroscopic behavior of the two materials is similar, indicating that the cyano group dominates the photophysics in these materials. The emission in CN-ether-PPV is due to a single-chain exciton in solution and due to an interchain excimer in thin film, as previously reported for CN-PPV; however, the excimer absorption and emission in thin film are blueshifted by ~0.2 eV relative to CN-PPV, implying that the excimer in CN-ether-PPV is less stable. Furthermore, substitution of an ether group along the chain results in decay times in both solution and film that are twice as long than in CN-PPV due to the broken conjugation which restricts the exciton within a conjugation segment and reduces its access to internal quenching sites. These properties result in a decay time of 14 ns for CN-ether-PPV film, one of the longest decay times observed in a conjugated polymer film. The long lifetime indicates a large exciton diffusion length, making these species particularly vulnerable to quenching by other materials. This work has implications for the design of conjugated polymers for efficient optoelectronic devices, such as photovoltaics. © *2006 American Institute of Physics.*
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I. INTRODUCTION

The future of molecular and polymer electronics rests in some part upon the ability to tune materials for color, band gap, efficiency, and other characteristics necessary to optimize their use for a particular application (photovoltaics, transistors, light-emitting diodes, etc.). As such, much time has been spent investigating the relationship between molecular structure and the nature of the excited state species in the poly(phenylene vinylene) (PPV) derivatives which are popularly used in optoelectronics.[1–4] Because of the strong intermolecular interactions in these thin films, interchain interactions (such as dimers, excimers, and exciplexes), in addition to the intrachain exciton, may play an important role in the electronic properties of these materials. Polymers with a high electron affinity are relatively rare, and a thorough understanding of the excited state carriers in these materials is of particular importance in light-emitting diodes and photovoltaics, which often rely upon D/A blends to achieve high efficiencies. In the current work, we use time-resolved photoluminescence to investigate the effects of side groups upon the nature of these species in two electron-transporting PPV derivatives.

The time rate of decay of the luminescence of a material (in film or solution) upon photoexcitation depends upon the efficiency of radiative and nonradiative decay rates, k_r and k_{nr},

$$\tau = \frac{1}{k_r + k_{nr}},$$

where each rate constant is reciprocally related to its respective lifetime. Thus, photoluminescence decay is a valuable tool in determining the decay pathways of excited state species. Different lifetimes may be measured for single-chain versus interchain species, or for either species in a variety of chain locations, resulting in multiexponential decay fits. The photoluminescence efficiency is related to the efficiency with which the radiative decay competes with nonradiative decay,

$$\phi = \frac{bk_r}{k_r + k_{nr}} = \frac{b\tau}{\tau_r},$$

where $\tau_r = 1/k_r$ is the natural radiative lifetime and b is the fraction of absorbed photons generating the emissive species.

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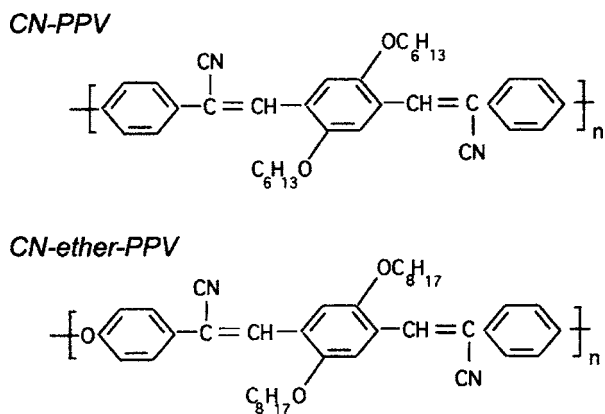b)Electronic mail: sacarter@ucsc.edu

FIG. 1. Chemical structures of CN-PPV and CN-ether-PPV.

These results may be used as a tool in understanding the nature of the excited state species.

The conjugated polymer poly(2,5,2′,5′-tetrahexyloxy-8,7′-dicyano-di-*p*-phenylene vinylene) or CN-PPV (see Fig. 1) has been studied extensively. CN-PPV is a highly luminescent cyano-substituted derivative of PPV which serves as an electron acceptor and electron transporter, though recent work suggests that bipolar charge transport may occur in this material.[5] The cyano group confers a higher electron affinity while the oxyalkyl group confers solubility. CN-PPV produces efficient photovoltaic devices when blended with the hole-transporting polymer poly(2-methoxy,5-(2-ethyl-hexyloxy)-*p*-phenylene vinylene) (MEH-PPV)[6] or poly(3-hexylthiophene) (P3HT) [7] due to its higher electron affinity.

The photoexcitations in CN-PPV have been found to consist quite clearly of interchain species (i.e., excimers or polaron pairs). The cyano substitution results in a broad, featureless emission spectrum with a large Stokes' loss,[1,4] and a long-lived photoexcitation in film of ~5.6 ns which is much longer than that in solution.[3,4,8] The long radiative lifetime of 16 ns[1] suggests that the radiative transition in CN-PPV film is not fully allowed, as would be expected of an interchain excitation with low wave function overlap and a transition that is disallowed by symmetry. This is in contrast to other conjugated polymers such as MEH-PPV or PPV which show clear vibronic structure in their emission spectrum, slight shifts in the emission spectrum, and a short lifetimes (0.3 −0.5 ns) in both solution and film, suggesting a short radiative lifetime of about 1 ns.[2,9–11] It is likely that the primary photoexcitation in both cases (MEH-PPV and CN-PPV) is the hot intrachain exciton, which can vibrationally relax and then decay directly or migrate to form interchain species.[1,3]

The preferential formation of emissive interchain species in CN-PPV is likely due to the relatively short interchain distance of 0.34 nm,[12,13] as well as a slipped-chain cofacial/lamellar stacking of the molecules (i.e., the cyano group from one chain overlapping the edge of an aromatic ring in a neighboring chain),[12,14] resulting in a more crystal-like order[15] than in other PPV's. The increased chain coupling in CN-PPV is due to the high electron affinity of this polymer[13] as well as more extended chain conformations as observed in symmetrically substituted PPV's.[16] This reduced interchain

distance results in a matrix element for emission that is 16–20 times larger for excimers in CN-PPV as opposed to MEH-PPV.[13]

The predominance of interchain excitations results in an increased quantum yield and decay lifetime in CN-substituted polymers.[4] The mobility of these interchain *excitonic* species is likely to be high compared to single-chain species,[17] whereas the mobility of *charged* carriers (electrons, holes) is greater along the chain than between chains.[18] The formation of interchain excitations, with a long radiative lifetime[19] and high mobility, may be advantageous to photovoltaic device performance since it increases the chances for decaying via nonradiative means, such as charge transfer at a suitably provided heterojunction. Thus, an understanding of the effects of polymer structure upon these excitations is of interest to the field.

Poly [oxa-1, 4-phenylene-1, 2-(1-cyano)-ethenylene-2, 5-dioctyloxy-1, 4-phenylene-1, 2-(2-cyano)-ethenylene-1, 4-phenylene] or CN-ether-PPV (see Fig. 1) is a derivative of CN-PPV and is designed to increase solubility and electron affinity relative to CN-PPV. It has highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels of 3.5 and 5.9 eV, respectively, a number-average molecular weight (MW) of 28 100 as determined by gel permeation chromatography (GPC) analysis, and a glass transition temperature of 61 °C.[20] When blended or layered with M3EH-PPV (an alternating copolymer of MEH-PPV) it results in photovoltaic devices with short-circuit currents of 3 mA/cm^2 and power conversion efficiencies of ~1.0% under 0.80 mA/cm^2 illumination.[21,22] It is similar in structure to polyoxa-1,4-phenylene-1–cyano-1,2-vinylene-2-methoxy-5-3,7- dimethyloctyloxy-1,4-phenylene-1,2-2-cyanovinylene-1,4-phenylene, or PCNEPV, which has been the subject of recent studies.[23,24] The addition of an ether linkage along the backbone in CN-ether-PPV is likely to disrupt the conjugation and affect the chain packing morphology due to increased flexibility in the chain at the sites of conjugation breaks. Broken conjugation has been found to disrupt energy and charge migration in conjugated polymers.[25] We have investigated the photophysics of CN-ether-PPV and compared it to the past work on CN-PPV in order to explore these effects on the excited state.

II. METHODS

CN-ether-PPV was obtained courtesy of the University of Jena in Germany and synthesized as described elsewhere.[26] Thin-film samples were spin coated from chlorobenzene solution on quartz substrates to thicknesses of 100–150 nm. Dilute solutions were prepared in chlorobenzene with optical densities <0.2 at the peak absorption wavelength to ensure that reabsorption effects are minimized.

Steady-state photoluminescence spectra were recorded using a Fluorolog-3 (JYHoriba) spectrometer that utilized a liquid N$_2$ cooled charge-coupled device (CCD) detector. Monochromatic excitation light was generated by a xenon arc lamp with double monochromator. Fluorescence was collected at 90° to excitation for solution and at 22° for thin film

TABLE I. Decay parameters for a variety of PPV's, both measured (as in case of CN-ether-PPV decay) and extracted from literature values. CN-ether-PPV decays are detected at the low energy edge (650 nm for solution, 700 nm for film). CN-ether-PPV film is 150 nm thick.

	ϕ	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)	Average τ (ns)	τ_r (ns)	τ_{nr} (ns)
CN-PPV solution[a]	0.52	0.9				1.7	1.9
CN-PPV film[a]	0.35	5.6				16	8.6
CN-ether-PPV solution	0.55[b]	1.8 (87%)	0.7 (8%)	11.3 (5%)	1.8		
CN-ether-PPV film	0.45[b]	14 (69%)	6.2 (31%)		11.6	23–53	
PPV film[c]	0.27	0.32				1.2	0.5
MEH-PPV film[d]	0.26	0.15–0.20				1.1	

[a]References 8 and 34.
[b]Reference 26.
[c]Reference 35.
[d]References 2 and 11.

relative to the excitation beam, passed through a single monochromator containing a 300 lines/mm grating and imaged on the liquid nitrogen cooled CCD array. All photoluminescence (PL) spectra were corrected for the spectral output of the excitation source and for the spectral response of the detection optics.

Fluorescence decay signals were measured using the technique of time correlated single photon counting (TCSPC).[27] The spectrometer comprised a pulsed, picosecond diode laser (IBH NanoLED-10) operating at a wavelength of 438 nm and a repetition rate of 1 MHz. Emission was detected at 90° to excitation for solution and at 45° for thin film by focusing the emission onto the slits of a 0.25 m monochromator (SPEX minimate) and subsequently detected by a photon counting photomultiplier tube (Hamamatsu H6279). The instrument response function (IRF) from this system when scattering the excitation light from a dilute solution of colloidal silica was determined to be 220 ps. Using a nonlinear, least squares iterative deconvolution procedure employing the Marquardt minimization routine, the influence of the IRF could be removed from the measured luminescence decay curves to reproduce the true decay kinetics with a temporal resolution of ~30 ps.

III. RESULTS

A. CN-ether-PPV in solution

CN-PPV has been well characterized in previous studies. In solution, the absorption of CN-PPV peaks at 450 nm and the photoluminescence peaks at 555 nm, in film, absorption peaks at 490 nm and photoluminescence at 690 nm.[3,8] CN-PPV is highly photoluminescent and is characterized by a long decay time; it has a luminescence quantum yield of 0.52 and a decay time of 0.9 ns.[3,8] See Table I for a comparison of several PPV's.

CN-either-PPV is similar to CN-PPV except for the addition of an ether group (a single oxygen) along the conjugation length, which is expected to disrupt the conjugation

and affect chain packing. Steady-state absorption and photoluminescence for films and solution of CN-either-PPV are shown in Fig. 2.

As in CN-PPV, photoluminescence in solution is narrow with clear vibronic peaks. Despite the broken conjugation, the spectral positions of CN-ether-PPV solution are almost completely consistent with CN-PPV[3] (Fig. 2, unfilled arrows).

The PL for solution shows a dependence on excitation wavelength; when excited at 400 nm it no longer resembles the steady-state spectrum for CN-PPV, due to the enhancement of the vibronic peak at 2.4 eV. Even though solutions were optically dilute, this could be due to reabsorption effects. Another possibility is that excitation at 400 nm results in a short effective conjugation length (analogous to an increase in temperature leading to conformational disorder) since excitons are restricted by the broken conjugation; this leads to an increase in the high-energy vibronic peak due to a corresponding shift in the Huang-Rhys parameter,[28] indicative of a change in the coupling strength between the ground and excited states. These effects are being reevaluated.

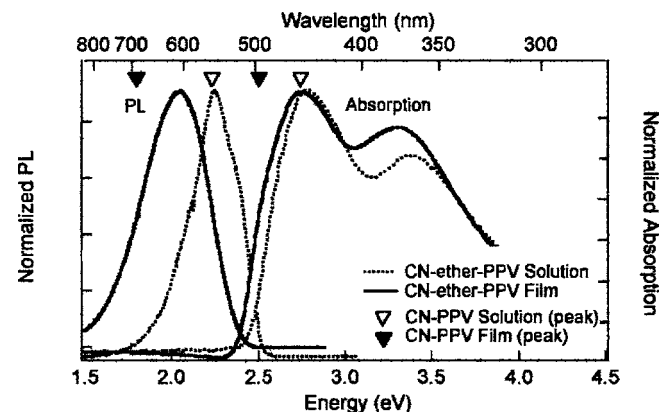The time decay of CN-either-PPV is plotted in Fig. 3.

FIG. 2. Steady-state photoluminescence and absorption for CN-ether-PPV film and solution at 500 nm excitation. Position of spectral peaks in CN-PPV (Ref. 3) are indicated by filled (film) and unfilled (solution) arrows.
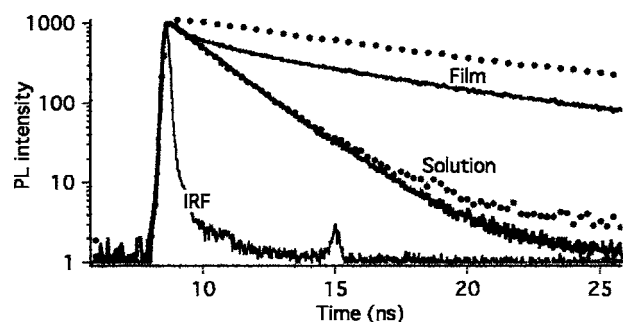
FIG. 3. Time decay of CN-ether-PPV film and dilute solution. Circles correspond to detection at the low-energy edge (650 nm in solution, 700 nm in film) and thick lines correspond to detection at the high-energy edge (550 nm for both film and solution).

Results of multiexponential fits are reported in Table I; these decay times are measured at the red edge of the PL emission, which we take to represent the characteristic decay time of the excited state species following energetic relaxation and migration to longer, low energy, conjugation segments. All fits were characterized by reduced chi-square $\leqslant 1.2$ and Durbin-Watson $\geqslant 1.8$.[27] Decay times for CN-ether-PPV increased as the emission energy decreased, consistent with diffusion from shorter to longer conjugation segments and the relaxation of hot singlet excitons to form lower energy excimers with time.

CN-ether-PPV solution was dominated by a decay time of 1.8 ns (87%), which we take to be the characteristic decay time of the isolated intrachain singlet exciton. This is twice as long as the previously measured lifetime for CN-PPV in solution,[3] and indicates that single-chain excitons are confined by the break in conjugation, reducing their ability to visit quenching sites. There was evidence for additional decay components, including an 11 ns component (5%) at low emission energy, which we assign to excimer emission due to self-coiling of the polymer chain.[29]

B. CN-ether-PPV films

The behavior of CN-PPV in film is qualitatively different from that in solution. The photoluminescence spectra are narrow with clear vibronic peaks in solution, but redshifted, broad, and featureless for film. There is no corresponding shift in the absorption spectra, indicating that the spectral shift is due to an excited state species, i.e., an excimer. CN-PPV film has a luminescence quantum yield of 0.35 and a long decay time of 5.6 ns.[3,8] This makes CN-PPV one of the most luminescent conjugated polymers with a lifetime about 20 times longer than that observed in related PPV's, indicating a very small rate of nonradiative decay.

In the ether-substituted CN-ether-PPV both absorption and photoluminescence curves are substantially blueshifted (to higher energy) by about 0.2 eV relative to CN-PPV film (Fig. 2, filled arrows). This shift contrasts with the spectral similarity of the two polymers in solution. The reduced Stokes' loss from solution to film in CN-ether-PPV could be explained by the presence of excimers in CN-ether-PPV that are less stable relative to CN-PPV. Broken conjugation has been found to reduce excimer emission in MEH-PPV,[30] sup-

porting this possibility. The spectral shift may also be due to preferential weighting towards shorter, high-energy chain segments due to the disruption of the conjugation. Both mechanisms would result in greater confinement of the excited state species and thus a shift to higher energy.

At 700 nm the decay of CN-ether-PPV film was dominated by a long component of 14.0 ns (69%), which we take to be the interchain exciton or excimer. The assignment of the 14.0 ns component to an excimer is based upon arguments from previous studies of temperature dependence and photoluminescence in film and solution of CN-PPV,[1,3,9] the broad featureless redshifted steady-state spectrum, the longer lifetime of film compared to solution, and the fact that the 14 ns component is easily quenched in heterojunctions with both electron and hole transporters.

We also see a secondary 6.2 ns component (31%), suggesting that, as with CN-PPV, at least two species are present in the excited state.[31] Our measured PL lifetimes are similar to those measured for a similar ether-substituted version of CN-PPV termed PCNEPV.[24] Unlike CN-PPV, there is still a sizeable intrachain component at low energies (4 ns at 20% yield), suggesting that the restriction of the exciton between the ether groups in CN-ether-PPV reduces the efficiency of interchain interactions in favor of intrachain interactions.

The 14.0 ns excimer decay is more than double the 5.6 ns dominant decay of CN-PPV,[3] and the secondary decay is similarly twice as long as that measured in CN-PPV,[31] suggesting that the breakage in the conjugation along the backbone imposed by the ether linkage significantly affects the dynamics of the excited state. As in films of CN-PPV, we measure high photoluminescence in the steady state and a long excited state lifetime. Based on previous studies,[20] the quantum yield of CN-ether-PPV in solution nearly matches that of CN-PPV (0.55), but in CN-ether-PPV film is slightly more photoluminescent (0.45 vs 0.35 in CN-PPV).[3] This gives $\tau_r = 26$ ns for CN-ether-PPV on average and $\tau_r = 31$ ns for the dominant 14 ns component—about twice that measured for CN-PPV.

The long radiative lifetime indicates that k_r is small, whereas the high quantum yield indicates that $k_{nr} \ll k_r$, and thus nonradiative decay in CN-ether-PPV must be extremely inefficient. Both radiative and nonradiative processes are less efficient than in CN-PPV. Because the exciton is confined to the portion of the chain between the ether groups, the effective exciton diffusion length is small. Thus, it is more difficult for excitations to visit quenching sites and recombination is low, leading to the long exciton lifetime and high photoluminescence. Chain packing could also be less efficient in CN-ether-PPV, resulting in both poorer nonradiative decay due to an inability to visit quenching sites, as well as a smaller matrix element for emission of the excimer state.

Longer time decay and higher photoluminescence have been previously reported for poorly conjugated PPV.[32] It is interesting that the same behavior is found in a cyano-substituted PPV, which is dominated by interchain excitonic species. The radiative lifetime of CN-ether-PPV is one of the longest natural radiative lifetimes ever measured in a photoluminescent polymer and, because it is significantly longer than that of other PPV's, indicates that this radiative transi-
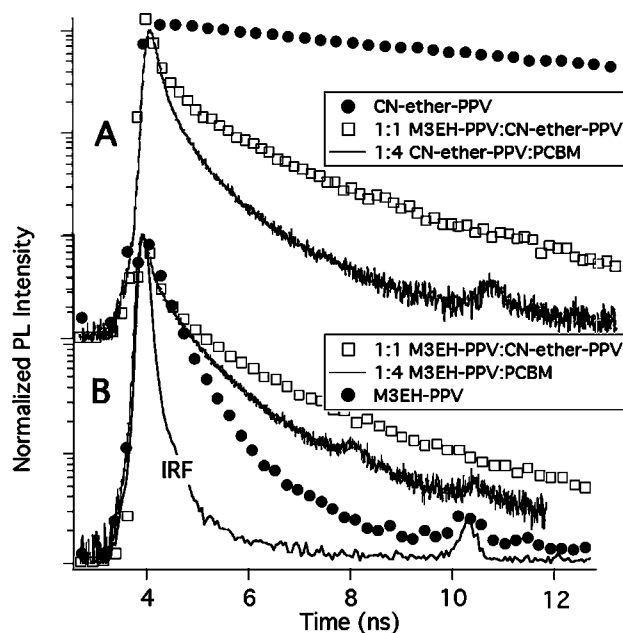
FIG. 4. Time decay of heterojunctions of (A) CN-ether-PPV and (B) M3EH-PPV. Emission is detected at 650 nm. CN-ether-PPV is more easily quenched by PCBM and other PPV's than is M3EH-PPV.

Measured decay components in solution and thin film were at least twice as long as those previously measured for CN-PPV. These results suggest that the broken conjugation in this polymer confines the exciton or excimer, reducing its ability to visit quenching sites and resulting in a long lifetime and efficient photoluminescence for both the intrachain exciton in solution and the interchain exciton (excimer) in film. The excimer in CN-ether-PPV is less stable than that in CN-PPV, as evidenced by a blueshift of the photoluminescence and a large percent yield of an intrachain decay component at low energies. In general, however, the photophysics of CN-ether-PPV is remarkably similar to that of CN-PPV. Thus, the effect of high electron affinity cyano group dominates the nature of the excited state in these materials.

Steady-state emission and the dominant 14 ns decay component in CN-ether-PPV are easily and (generally) completely quenched by blending with a variety of electron- and hole-accepting materials, suggesting that despite a reduction in internal quenching mechanisms, the confined excitons are vulnerable to quenching by external agents. Excited state species with long lifetimes and diffusion lengths, that are easily quenched by charge transfer, may be advantageous to devices, such as photovoltaics.

tion is not fully allowed, consistent with the presence of an excimer. Thus the photoluminescence from excitons formed in CN-ether-PPV should be much easier to quench than those in most PPV's. We find this to be true—the steady-state photoluminescence and the 14.0 ns component are easily quenched by a variety of external quenchers, including another soluble PPV, P3HT, the fullerene derivative 6,6-phenyl C61-butyric acid methyl ester, or PCBM, and TiO$_2$ (SSPL only), whereas the decay components of a copolymer of MEH-PPV [i.e., M3EH-PPV.[22,33]] are far more robust, as shown in Fig. 4. Charge transfer from CN-ether-PPV to PCBM is extremely efficient, despite a published HOMO/LUMO offset of only 0.2 eV, such that the photoluminescence of CN-ether-PPV is quenched by three orders of magnitude, and emission from PCBM itself is observed. This implies a very low binding energy for the unstable excimer species. Thus, CN-ether-PPV may serve as an efficient provider of photogenerated charges for photovoltaic devices.

IV. CONCLUSIONS

We have investigated the effects of ether linkage on the photophysics and excited state dynamics of a well-characterized conjugated polymer, CN-PPV. CN-PPV in solution is dominated by intrachain singlet excitons, whereas the film is dominated by interchain species, such as excimers. The ether-substituted version, CN-ether-PPV, has broken conjugation which is likely to affect the excited state. Despite the break in conjugation, the behavior of the two materials is surprisingly similar. Emission in thin film is broad, featureless, and redshifted compared to solution, and the decay in film is longer than solution. A very long decay component of 14 ns dominated the decay in film, suggesting a radiative lifetime of 31 ns, one of the longest measured in a photoluminescent polymer.

ACKNOWLEDGMENTS

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