

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/223168237>

# Energy Transfer in Nanostructured Films Containing Poly(p-phenylene vinylene) and Acceptor Species

ARTICLE in THE JOURNAL OF PHYSICAL CHEMISTRY C · JUNE 2009

Impact Factor: 4.77 · DOI: 10.1021/jp9000785

CITATIONS

12

READS

26

5 AUTHORS, INCLUDING:



**Valtencir Zucolotto**

University of São Paulo

163 PUBLICATIONS 2,674 CITATIONS

SEE PROFILE



**Fernando Dias**

Durham University

66 PUBLICATIONS 1,440 CITATIONS

SEE PROFILE



**Andy Monkman**

Durham University

416 PUBLICATIONS 9,835 CITATIONS

SEE PROFILE



**Osvaldo N Oliveira**

University of São Paulo

531 PUBLICATIONS 8,953 CITATIONS

SEE PROFILE

# Energy Transfer in Nanostructured Films Containing Poly(*p*-phenylene vinylene) and Acceptor Species

Bruna B. Postacchini,<sup>†</sup> Valtencir Zucolotto,<sup>†</sup> Fernando B. Dias,<sup>‡</sup> Andy Monkman,<sup>‡</sup> and Osvaldo N. Oliveira, Jr.<sup>\*,†</sup>

*Instituto de Física de São Carlos, USP, 369 Trabalhador Saocarlene Avenue, 13560-970 Brazil, and Organic Electroactive Materials Research Group, Department of Physics, Durham University, South Road, Durham, DH1 3LE U.K.*

*Received: January 5, 2009; Revised Manuscript Received: March 19, 2009*

The combination of luminescent polymers and suitable energy-accepting materials may lead to a molecular-level control of luminescence in nanostructured films. In this study, the properties of layer-by-layer (LbL) films of poly(*p*-phenylene vinylene) (PPV) were investigated with steady-state and time-resolved fluorescence spectroscopies, where fluorescence quenching was controlled by interposing inert polyelectrolyte layers between the PPV donor and acceptor layers made with either Congo Red (CR) or nickel tetrasulfonated phthalocyanine (NiTsPc). The dynamics of the excited state of PPV was affected by the energy-accepting layers, thus confirming the presence of resonant energy transfer mechanisms. Owing to the layered structure of both energy donor and acceptor units, energy transfer varied with the distance between layers,  $r$ , according to  $1/r^n$  with  $n = 2$  or 3, rather than with  $1/r^6$  predicted by the Förster theory for interacting point dipoles.

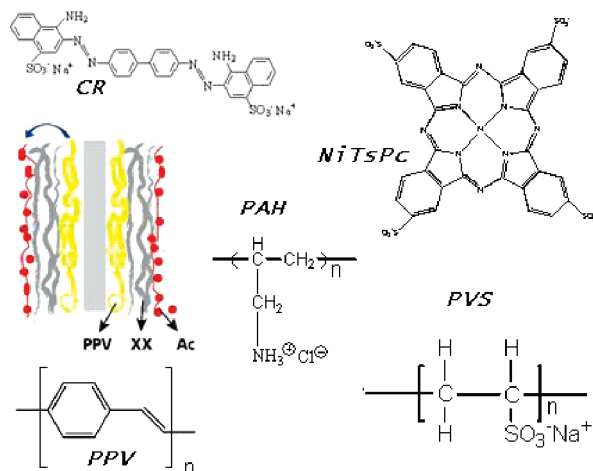
## Introduction

Energy transfer processes on the nanometric scale have been widely investigated in molecular-level control of optoelectronic properties in devices, including photovoltaic cells,<sup>1,2</sup> light-emitting diodes, and sensors.<sup>3,4</sup> In these applications, there has been a trend toward the combined use of nanocrystals,<sup>5–7</sup> metallic nanoparticles, and polymers.<sup>8–13</sup> Conjugated polymers, in particular, are advantageous owing to their tunable electrical and optical properties,<sup>14</sup> allied to easy processability. Understanding energy transfer in polymers is by no means straightforward, though, for interchain as well as intrachain processes must be considered.<sup>15,16</sup> The first models to deal with resonant energy transfer were proposed by Perrin and Förster (apud<sup>17</sup>), who explained excitation transfer mechanisms in terms of dipole interactions between donors and acceptors. The rate of energy transfer ( $k_{ET}$ ) depends on the spectral overlap between the absorption spectrum of the acceptor and the emission spectrum of the donor, in addition to the distance ( $r$ ) and the relative orientation of donors and acceptors. According to the Fermi golden rule approximation,  $k_{ET} \approx F_D F_A$ , with the interaction between donor ( $F_D$ ) and acceptor ( $F_A$ ) depending on the geometry.<sup>18</sup> For instance,  $F \approx 1/r^3$  for single dipoles,  $F \approx 1/r$  for a 2D dipole array, and  $F \approx \text{constant}$  for a 3D dipole array. For two single dipoles randomly oriented in solution, the Förster model yields a distance dependence for the energy transfer rate  $F \approx (1/r^3)(1/r^3) \approx 1/r^6$ . For solid films, this point-to-point interaction does not give suitable results and the energy transfer rate depends on the geometry of the structures.<sup>17,19</sup> Detailed knowledge is therefore gained only if the molecular architecture is controlled, which may be achieved by placing donors and acceptors in layers separated by spacing or inert layers.

## Experimental Section

In this study, we employ the layer-by-layer (LbL) method to fabricate multilayers of poly(*p*-phenylene vinylene) (PPV)<sup>20–22</sup> with controlled architectures, as shown in Scheme 1. The luminescent

**SCHEME 1: Chemical Structures of Molecules Used in LbL Films, in Addition to a Schematic Architecture for a PPV/XX/Ac LbL Film<sup>a</sup>**



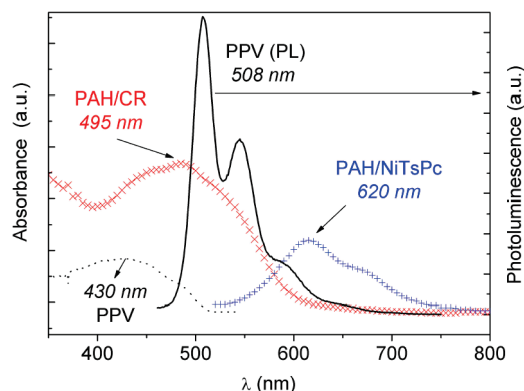
<sup>a</sup> Ac stands for the acceptor molecules, which were CR in series 1 and NiTsPc in series 2.

unit contained a four-bilayer LbL film made with a water-soluble PPV precursor,<sup>23</sup> poly(xylylidene tetrahydrothiophenium chloride) (PTHT), and an anionic solution of the sodium salt of dodecylbenzenesulfonic (DBS) (Scheme 1), alternately adsorbed on glass substrates. After thermal conversion from PTHT into PPV, the final PPV–PTHT copolymer film acted as the donor in energy transfer processes,<sup>24</sup> in which the acceptor block (Ac) comprised a single bilayer of poly(allylamine hydrochloride) (PAH) alternated with either Congo Red (CR) azodye or nickel phthalocyanine (NiTsPc). The distance between the donor and the acceptor units was controlled by inserting spacing layers of PAH and poly(vinyl sulfonic acid) (PVS). PTHT was synthesized according to the procedures of ref 25, while DBS, CR, PAH, and PVS were purchased from Aldrich. The solutions to produce LbL films were prepared by mixing the solute in Milli-Q water at a concentration of 0.5 mg mL<sup>-1</sup>. PTHT molecules in a four-bilayer PTHT/DBS

\* Corresponding author. E-mail: chu@ifsc.usp.br.

<sup>†</sup> Instituto de Física de São Carlos.

<sup>‡</sup> Durham University.



**Figure 1.** Photoluminescence emission (solid line) and optical absorption spectra for LbL films of PPV (dashed line), PAH/CR ( $\times$ ), and PAH/NiTsPc ( $+$ ).

film were converted into PPV via thermal treatment under vacuum at 110 °C for 30 min. Two series of samples were prepared. In the absence of an acceptor, they are referred to as PPV<sub>4</sub>/XX, while the samples containing an energy acceptor layer are PPV<sub>4</sub>/XX/CR<sub>1</sub> (series 1) and PPV<sub>4</sub>/XX/NiTsPc<sub>1</sub> (series 2), where XX is the number of spacing bilayers increasing from 00 (absence of spacers) to 40 bilayers. The thickness of the spacers was 1.3 nm per bilayer.<sup>26</sup>

Film absorption spectra were recorded using a Hitachi U-2001 UV–vis spectrometer. The photoluminescence spectra (PL) in the steady-state were measured with a spectrofluorimeter (Shimadzu RF-5301 PC) using a xenon lamp as excitation source. Time-resolved fluorescence decays were collected using the picosecond time correlated single photon counting (TCSPC) technique (instrument response function 24 ps, 76 MHz repetition rate). The samples were excited by a second harmonic pulse from a mode-locked Ti: sapphire laser from Coherent Inc., with vertical polarization. The emission was detected through a double-subtractive monochromator (SpectraPro-2300i), and an MCP detector (Hamamatsu model R3809U-50) was used to collect decays at 508 nm. A streak camera (model C5680 from Hamamatsu; IRF = 10 ps) was also used to collect time-resolved spectra. Both PL emission measurements were performed under vacuum, with front-face arrangement and excitation at 375 nm, corresponding to the PPV absorption band to ensure a sufficiently large spectral separation between excitation and emission wavelengths.

## Results and Discussion

Figure 1 shows absorption and photoluminescence (PL) spectra for PPV and the absorption spectra for CR and NiTsPc films. The unresolved vibronic structure in the absorption spectrum of PPV is due to a large distribution of sizes of conjugated segments in the copolymer, with a broad band at 430 nm assigned to  $\pi \rightarrow \pi^*$  transitions.<sup>23</sup> An excitation migration process from the smaller to the larger segments results in a well-resolved PL spectrum. The absorption spectra of CR and NiTsPc overlapped the PPV emission spectrum.

Strong quenching (90% for CR and 70% for NiTsPc) of PPV fluorescence occurred when an acceptor bilayer was adsorbed directly on the PPV film, with no spacing bilayers, as indicated in Figure 2. Quenching was not accompanied by changes in the PPV absorption spectra, which rules out chemical changes and charge transfer between PPV and acceptor units. Even though the spacing bilayers were inert, with no absorption or emission, their incorporation decreased both absorption and emission of PPV. This may be attributed to increased degradation induced by interaction between the polyelectrolytes and PPV, though the precise mechanism for

degradation could not be established. To avoid artifacts, we considered the PPV/XX system as the reference, so that the conclusions drawn about energy transfer processes are not affected by the above-mentioned degradation. The insets in Figure 2 show that fluorescence recovered with increasing number of bilayers, but full PL recovery was not always achieved, probably because some of the emitted light was lost through reabsorption or scattering.

Although steady-state PL measurements allow us to investigate the quenching, they cannot provide a definite conclusion about the mechanisms. With the overlap in the spectra, the most plausible hypothesis is energy transfer, but the trivial mechanism of reabsorption by the acceptor of emitted light cannot be ruled out. To distinguish between the two possibilities, we employed time-resolved spectroscopy measurements. The PL decays were obtained at room temperature collected at 506 nm, the maximum emission on the first vibronic band. These decays were best fitted to a multiexponential function, requiring three lifetimes ( $\tau_i$ ).

$$I(t) = \sum_i a_i \exp(-t/\tau_i) \quad (1)$$

It is not possible to assign physical processes to the distinct lifetimes, but subsidiary measurements using partially converted PPV showed that more than one process occurs when energy transfer among segments corresponding to distinct band gaps takes place, for example. For the sake of analysis, we calculated a representative  $\tau$  as an amplitude-weighted lifetime

$$\tau = \langle t \rangle = \int_0^\infty I(t) dt = \sum_i \alpha_i \tau_i \quad (2)$$

where  $\alpha_i$  is the amplitude (normalized contribution). This lifetime in absence of acceptor was  $\tau_D = 190 \pm 25$  ps for the samples in series 1 and  $\tau_D = 200 \pm 40$  ps for series 2. In a separate analysis, we confirmed that these lifetimes were not strongly affected by the method through which they were calculated, either by fitting the steady-state emission or fitting the time-resolved fluorescence spectra measured with TCSPC or streak camera. Moreover, it should be noted that the number of processes (i.e., lifetimes) to explain the fluorescence decay does not depend on the use of spacer layers, and therefore, the problems associated with degradation mentioned above do not affect the interpretation of the data. In the presence of an acceptor the dynamics was still multiexponential but clearly shorter, indicating a new nonradiative pathway for the PPV excitation. Figure 3a shows the PPV emission decay dynamics becoming slower as the number of spacing bilayers increases, consistent with steady-state PL measurements. Both excited state lifetime changes and distance dependence point to a resonant energy transfer process (RET).

With the time-resolved fluorescence data the energy transfer efficiency

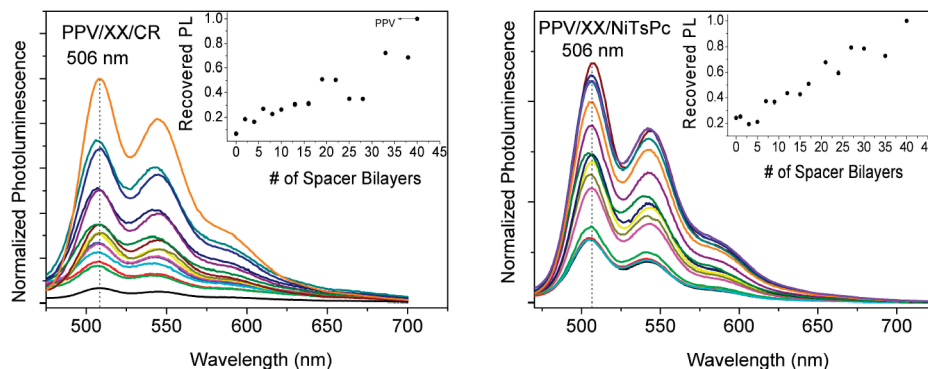
$$\Phi_{ET} = 1 - \tau_{DA}/\tau_D \quad (3)$$

could be obtained as a function of  $\tau_{DA}$  and  $\tau_D$ , the lifetimes for PPV in the presence and absence of the acceptor. Figure 4 shows the energy transfer efficiency ( $\Phi_{ET}$ ) vs D/A distance. In general, the efficiency may be written as

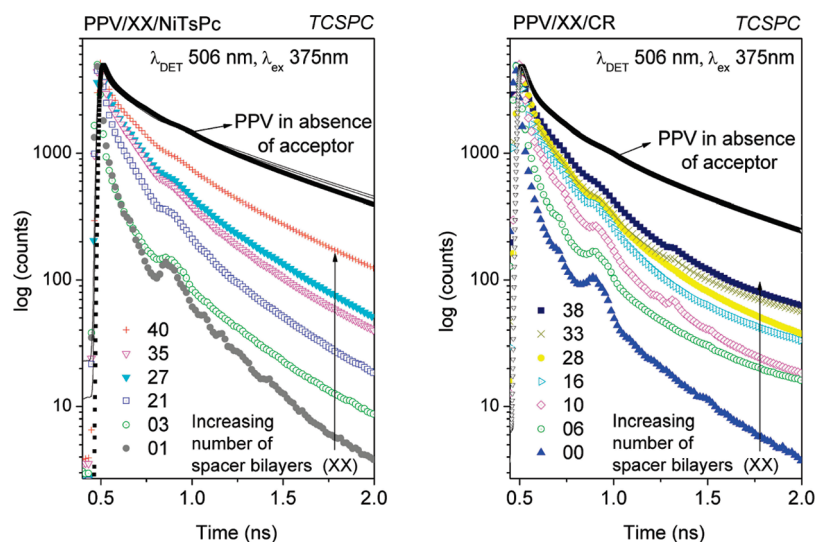
$$\Phi_{\text{ET}} = [1 + (r/r_0)^n]^{-1} \quad (4)$$

where  $r$  is the distance between donor and acceptor,  $r_0$  is the critical distance (energy transfer and fluorescence rate are equally probable), and  $n$  gives the distance-dependence. Theoretical curves with best fitting of the data are shown in Figure 4 for  $n = 2, 3, 4$ , and  $6$  for both series (CR and NiTsPc acceptors). The experimental points were taken from an average of these several measurements of lifetime obtained using single photon counting, with the data presenting considerable dispersion, as indicated by the large error

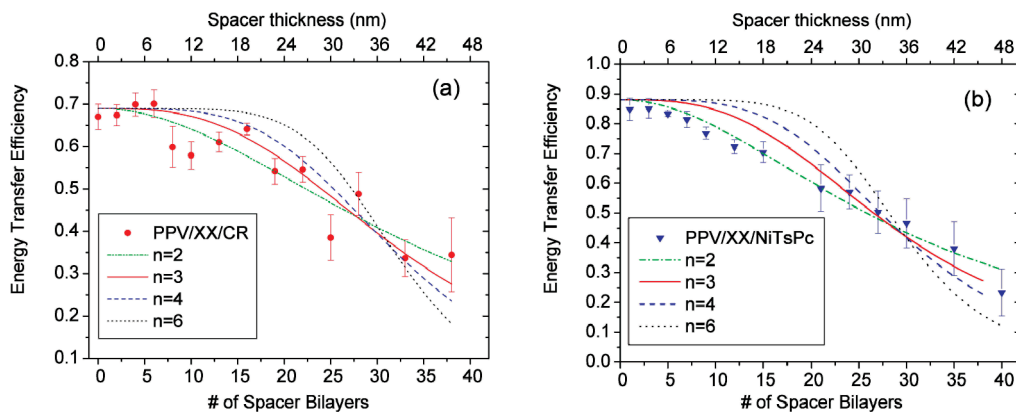
bars in Figure 4. Such large dispersion is not only due to the limitations in measuring the lifetimes but also due to the different ways to calculate the quantum efficiency and the possible interpenetration among the LbL film layers, which brings uncertainties as to the precise distance between donor and acceptor layers. Considering the distance dependence obtained from Figure 4 and steady-state fluorescence measurements (not shown), one infers that  $n = 2$  or  $n = 3$  provides the best fits, with the smallest  $\chi^2$ , as shown in Tables 1 and 2. The  $1/r^6$  characteristic of dipole–dipole interaction can be ruled out. As for the  $1/r^4$  dependence typical of



**Figure 2.** PL intensity spectra in PPV/XX/CR and PPV/XX/NiTsPc LbL films for various numbers (XX) of spacing bilayers. Measurements were obtained with steady-state spectroscopy. The insets show the increase in fluorescence at 506 nm with the number of spacing bilayers.



**Figure 3.** Time decay curves for PPV/XX/CR and PPV/XX/NiTsPc films with increasing the number of spacer bilayers (XX). Each spacer layer is estimated to be 1.3 nm thick. The black, solid curve represents decay for a pristine PPV film.



**Figure 4.** Distance dependence of the energy transfer efficiency evaluated with measurements of excited state lifetime. The thickness per spacer layer is estimated as 1.3 nm.<sup>26</sup>



**TABLE 1: Values of the Critical Radius ( $r_0$ ) Obtained from the Fitting of the Time-Resolved Fluorescence Data to Eq 4 Using  $n = 2, 3, 4$ , and 6**

$n$	$r_0$ (nm)	$\chi^2$ <sup>a</sup>
PPV/XX/CR		
6	30 ± 9	0.007 46
4	30 ± 6	0.004 01
3	30 ± 4	0.002 61
2	31 ± 4	0.002 19
PPV/XX/NiTsPc		
6	28 ± 9	0.018 70
4	28 ± 6	0.009 73
3	27 ± 4	0.005 29
2	28 ± 3	0.002 69

<sup>a</sup>  $\chi^2$  values represent the standard deviation for the fitting.

**TABLE 2: Values of the Critical Radius ( $r_0$ ) Obtained from the Fitting of the Steady-State PL Data to Eq 4 Using  $n = 2, 3, 4$ , and 6**

$n$	$r_0$ (nm)	$\chi^2$ <sup>a</sup>
PPV/XX/CR		
6	28 ± 11	0.021 78
4	27 ± 7	0.013 51
3	26 ± 5	0.009 46
2	26 ± 4	0.006 84
PPV/XX/NiTsPc		
6	23 ± 9	0.022 8
4	22 ± 4	0.012 7
3	21 ± 3	0.007 32
2	20 ± 2	0.004 41

<sup>a</sup>  $\chi^2$  values represent the standard deviation for the fitting.

interaction between a point dipole and a plane of acceptors,<sup>23,27</sup> while it cannot be completely discarded, it seems less likely than the dependences with  $n = 2$  or 3. The dependence  $1/r^2$  is associated with interacting dipoles in a plane-to-plane arrangement,<sup>23,28,29</sup> whereas  $1/r^3$  is related to a plane-to-slab geometry.<sup>22,30</sup> The latter differs from the former in that a thickness should be ascribed to the slab, in contrast to the plane.

The distance dependence mentioned above was only to be expected from the molecular architecture of the LbL films used. The layer of acceptors (CR or NiTsPc) may be considered as a plane, while the energy donors were arranged in a four-layer PPV film that could behave either as a plane or slab for the interaction.

The critical radius for energy transfer estimated from the lifetime, using  $n = 2$  (Table 1), is  $r_0 = 30 \pm 4$  spacing bilayers for CR and  $28 \pm 2$  spacing bilayers for NiTsPc. It is larger for CR because of the stronger spectral overlap. When the steady-state PL intensity was used to evaluate the energy transfer efficiency, fitting with  $n = 2$  led to  $r_0 = 26 \pm 4$  bilayers for CR and  $20 \pm 2$  bilayers for NiTsPc (Table 2). We verified that the critical distance depends only weakly on  $n$ . This may be the reason why the Förster radius evaluated in films using  $n = 6$  may give good results, even though the  $1/r^6$  dependence should not hold, as demonstrated here. Also worth discussing is the large value for the distance, where energy transfer still occurs, which is considerably larger than the typical Förster radii and the distance estimated for LB films investigated by Hill et al.<sup>28</sup> This is explained by the influence of the geometry in energy transfer within the LbL films and the ease with which energy is transferred among conjugated polymer segments with distinct conjugation degrees. Significantly, the larger distance

should be taken into account in the design of devices depending on energy transfer, as is the case of light harvesting in photovoltaic cells.

## Conclusion

We have unequivocally demonstrated nanoscale control of energy transfer in LbL films of PPV, where a clear deviation exists from the usually assumed  $1/r^6$  dependence. The possible control of molecular architecture provided by the LbL method was crucial in this context, with which a plane and slab geometry could be established. While this study contributed to addressing fundamental issues in energy-transfer mechanisms, the conclusions drawn may have some bearing on the design of stacked organic light emitting diodes (OLEDs) and stacked photovoltaic cells,<sup>1,2</sup> as energy transfer will be dominant.

**Acknowledgment.** Financial support from CNPq, CAPES, and FAPESP (Brazil) is gratefully acknowledged.

## References and Notes

- (1) Scully, S. R.; Armstrong, P. B.; Edder, C.; Fréchet, J. M. J.; McGehee, M. D. *Adv. Mater.* **2007**, *19*, 2961.
- (2) Liu, Y.-X.; Summers, M. A.; Scully, S. R.; McGehee, M. D. *J. Appl. Phys.* **2006**, *99*, 093521.
- (3) Parkinson, P.; Aharon, E.; Chang, M. H.; Dosche, C.; Frey, G. L.; Köhler, A.; Herz, L. M. *Phys. Rev. B* **2007**, *75*, 165206.
- (4) Posson, D. J.; Ge, P.; Miller, C.; Bezanilla, F.; Selvin, P. R. *Nature* **2005**, *436*, 848.
- (5) Allan, G.; Delerue, C. *Phys. Rev. B* **2007**, *75*, 195311.
- (6) Ueda, A.; Tayagaki, T.; Kanemitsu, Y. *Appl. Phys. Lett.* **2008**, *92*, 133118.
- (7) Rinnerbauer, V.; Egelhaaf, H.-J.; Hingerl, K.; Zimmer, P.; Werner, S.; Warming, T.; Hoffmann, A.; Kovalenko, M.; Heiss, W.; Hesser, G.; Schaffler, F. *Phys. Rev. B* **2008**, *77*, 085322.
- (8) Åsberg, P.; Nilsson, P.; Inganäs, O. *J. Appl. Phys.* **2004**, *96*, 3140.
- (9) Zucolotto, V.; Faceto, A. D.; Santos, F. R.; Mendonça, C. R.; Guimarães, F. E. G.; Oliveira, O. N., Jr. *J. Phys. Chem. B* **2005**, *109*, 7063.
- (10) Favarim, H. R.; Spadacio, D.; Faceto, A. D.; Zucolotto, V.; Oliveira, O. N., Jr.; Guimarães, F. E. G. *Adv. Funct. Mater.* **2007**, *17*, 2862.
- (11) Bhowmick, S.; Saini, S.; Shenoy, V. B.; Bagchi, B. *J. Chem. Phys.* **2006**, *125*, 181102.
- (12) Markov, D. E.; Blom, P. W. M. *Phys. Rev. B* **2005**, *72*, 161401.
- (13) Jennings, T. L.; Singh, M. P.; Strouse, G. F. *J. Am. Chem. Soc.* **2006**, *128*, 5462.
- (14) Heeger, A. J. *Rev. Mod. Phys.* **2001**, *73*, 281.
- (15) Schwartz, B. J. *Annu. Rev. Phys. Chem.* **2003**, *54*, 141.
- (16) Hennebicq, E.; Pourtois, G.; Scholes, G. D.; Herz, L. M.; Russel, D. M.; Silva, C.; Setayesh, S.; Grimsdale, A. C.; Müller, K.; Brédas, J.-L.; Beljonne, D. *J. Am. Chem. Soc.* **2005**, *127*, 4744.
- (17) Kuhn, H. *J. Chem. Phys.* **1970**, *53*, 101.
- (18) Yun, C. S.; Javier, A.; Jennings, T.; Fisher, M.; Hira, S.; Petersons, S.; Hopkins, B.; Reich, N. O.; Strouse, G. F. *J. Am. Chem. Soc.* **2005**, *127*, 3115.
- (19) Baumann, J.; Fayer, M. D. *J. Chem. Phys.* **1986**, *85*, 4087.
- (20) Decher, G. *Science* **1997**, *277*, 1232.
- (21) Marletta, A.; Gonçalves, D.; Oliveira, O. N., Jr.; Faria, R. M.; Guimarães, F. E. G. *Adv. Mater.* **2005**, *12*, 69.
- (22) Marletta, A.; Castro, F. A.; Borges, C. A. M.; Oliveira, O. N., Jr.; Faria, R. M.; Guimarães, F. E. G. *Macromolecules* **2002**, *35*, 9105.
- (23) Marletta, A.; Castro, F. A.; Gonçalves, D.; Oliveira, O. N., Jr.; Faria, R. M.; Guimarães, F. E. G. *Synth. Met.* **2001**, *121*, 1447.
- (24) Lakowicz, J. R. In *Principles of Fluorescence Spectroscopy*, 3th ed.; Springer: Singapore, 2006; Vol. 1.
- (25) Lenz, R. W.; Han, C. C.; Stenger-Smith, J. D.; Karasz, F. E. *J. Polym. Sci. Polym. Chem. Ed.* **1988**, *26*, 3241.
- (26) Lvov, Y.; Decher, G.; Moehwald, H. *Langmuir* **1993**, *9*, 481.
- (27) Baur, J. W.; Rubner, M. F.; Reynolds, J. R.; Kim, S. *Langmuir* **1999**, *15*, 6460.
- (28) Hill, J.; Heriot, S. Y.; Worsfold, O.; Richardson, T. H.; Fox, A. M.; Bradley, D. D. C. *Phys. Rev. B* **2004**, *69*, 041303 (R).
- (29) Nakahara, H.; Fukuda, K.; Möbius, D.; Kuhn, H. *J. Phys. Chem.* **1986**, *90*, 6144.
- (30) Haynes, D. R.; Tokmakoff, A.; George, S. M. *J. Chem. Phys.* **1994**, *100*, 1968.