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Molecular-Level Control of the Photoluminescence from PPV Nanostructured Films

Valtencir Zucolotto, Ângelo D. Faceto, Felipe R. Santos, Cleber R. Mendonça, Francisco E. G. Guimarães, and Osvaldo N. Oliveira Jr.*

IFSC, USP, CP 369, 13560-970, São Carlos, SP, Brazil

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The fabrication of varied molecular architectures in layer-by-layer (LbL) films is exploited to control the photoluminescence (PL) of poly(*p*-phenylene vinylene) (PPV) in an unprecedented way. This was achieved by controlling the Förster energy transfer between PPV layers (donors) and layers of a commercial azodye, Brilliant Yellow (BY) (acceptors). Energy transfer was controlled by inserting spacer layers of inert polymers between PPV and BY layers and by photoaligning the BY molecules via *trans*–*cis*–*trans* isomerization. The PPV/BY LbL films displayed polarized PL whose intensity could be varied almost continuously by changing the time of photoalignment, which was carried out by impinging a linearly polarized laser light simultaneously to the PL experiments. For PPV/BY films with no spacer layers, PL was completely quenched, but its intensity increased with the number of spacing layers. Further increase in PL was obtained by photoaligning the BY molecules perpendicularly to the PPV molecules. This minimizes energy transfer, since Förster processes are directional, dipole-dependent resonant transfers. Energy transfer is also controlled by imparting a preferential orientation of the PPV chains on PPV/BY LbL films deposited onto flexible Teflon substrates that may be stretched.

1. Introduction

The layer-by-layer (LbL) technique has been widely exploited for fabricating heterostructures where interactions between the components are controlled at the molecular level.^{1–7} For instance, the intensity of photoluminescence in LbL films of poly(*p*-phenylene vinylene) (PPV) has been controlled by electron transfer between PPV and an electron acceptor layer, viz., C₆₀ or poly(thiophene acetic acid) (PTAA).³ Recovery of the fluorescence signal was obtained by interposing inert spacer layers between PPV and the electron acceptor layers, in a process that could be modeled with electron transfer theories.⁴ In LbL films of PPV and poly(*p*-phenylene) (PPP), fluorescence quenching was caused by energy transfer rather than electron transfer,⁸ which could also be recovered using spacer layers. Förster energy transfer processes were used to explain the experimental data. Control over energy transfer in resonant systems is also useful to tune the color of emission in dye-doped PPV films.⁹

In this work, the molecular control of luminescence was achieved in nanostructured films where PPV layers were alternated with layers of an azodye, Brilliant Yellow (BY),¹⁰ which acts at the receiving end of energy transferred from photoexcited PPV molecules via the Förster transfer mechanism.¹¹ The intensity of photoluminescence from the PPV LbL films is controlled by interposing inert bilayers of polyelectrolytes between PPV and BY layers. The novelty lies in the possibility of photoaligning BY molecules which makes it possible to further control photoluminescence as the energy transfer is hampered when the BY orientation¹² is perpendicular to the electric field of the polarized emission from PPV. The PPV LbL films were deposited onto quartz and polymeric Teflon substrates. After film deposition, the Teflon + PPV films were subjected to mechanical stretching, which imparted a preferential

orientation of PPV chains, leading to an increase in the polarization of the emitted light. A host of applications are envisaged with such fine control of luminescence properties, including optical switches, displays, and antenna devices.

2. Experimental Section

Poly(allylamine hydrochloride) PAH, poly(vinyl sulfonic acid) (PVS), and poly(xylylidenetetrahydrothiophenium chloride) (PTHT) were purchased from Aldrich Co. PTHT was purified before use, and the others were used as received. Brilliant Yellow (BY) was purchased from TCI. The PPV layers were deposited using PTHT, a polycationic PPV precursor, assembled with long chain ions of a sodium salt of dodecylbenzenesulfonate (DBS).⁹ The chemical structures of the materials employed are shown in Figure 1. PTHT/DBS bilayers were deposited from aqueous solution at pH 5.0 and a deposition time of 1 min. The acceptor layers comprised PAH/BY bilayers adsorbed from pH 8.0 solutions with 3 min of deposition. These experimental conditions also applied to the PAH/PVS spacer inert layers. The deposition times employed here were chosen on the basis of previous studies¹⁶ and were appropriate for the assembly of good optical-quality films. The final architecture of the films corresponds to four blocks of PTHT/DBS and four blocks of PAH/BY, where each block contained five bilayers of PTHT/DBS or PAH/BY deposited onto quartz or Teflon substrates. The PAH/PVS spacing layers were interposed between the blocks. After assembly, the films were treated at 110 °C for 20 min under vacuum to allow the thermal conversion of PTHT into PPV. Photoluminescence (PL) measurements were carried out with a He–Cd linearly polarized laser operating at 441 nm as excitation light. The emitted light was collected by a monochromator. The analyses were performed at room temperature under vacuum to avoid photodegradation.

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

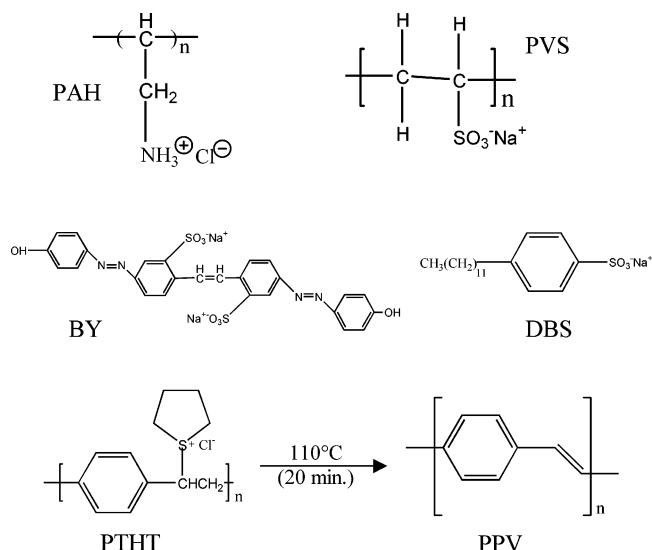


Figure 1. Chemical structures of the materials employed in the PPV/BY LbL films.

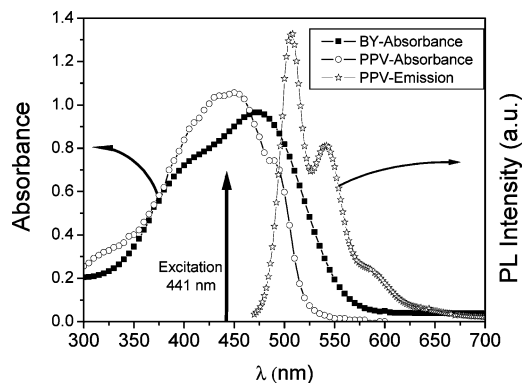


Figure 2. UV-vis spectra from PPV and BY films and emission spectrum of the PPV film.

3. Results and Discussion

Figure 2 depicts the electronic absorption spectra from PPV and BY, along with the PPV emission spectrum. Since the absorption spectra from BY and the fluorescence from PPV overlap, the resonant energy transfer (RET) process is expected to depend on the distance between the donor (PPV) and acceptor (BY) species, as described by the Förster RET theory.¹¹

The RET process was confirmed using supramolecular structures such as those depicted in Figure 3A, where PAH and PVS bilayers were deposited between PPV and BY layers. PL increases with the number of spacer PAH/PVS layers (~ 2 nm per bilayer), similarly to what has been reported in the literature.^{3,4,8} For the PPV/BY system studied here, quenching is also caused by energy transfer, with PL being recovered as the distance between PPV and BY (donor and acceptor layers, respectively) increased, as shown in Figure 3B.

While the control of fluorescence emission in PPV LbL layers by introducing spacer layers had already been done, as mentioned above, a much finer control is demonstrated here by photoaligning the azobenzene chromophores in the BY layers. Figure 4 shows that PL increases with the time of irradiation with a linearly polarized He-Cd laser that photoaligns the BY chromophores (for films deposited onto quartz slides). As expected, the process depends on the laser power, as shown in the inset of Figure 4. For a power of 8 W/cm^2 , the PL increases 4 times and saturates after ~ 500 s of illumination. Because the process is continuous, the control over the final

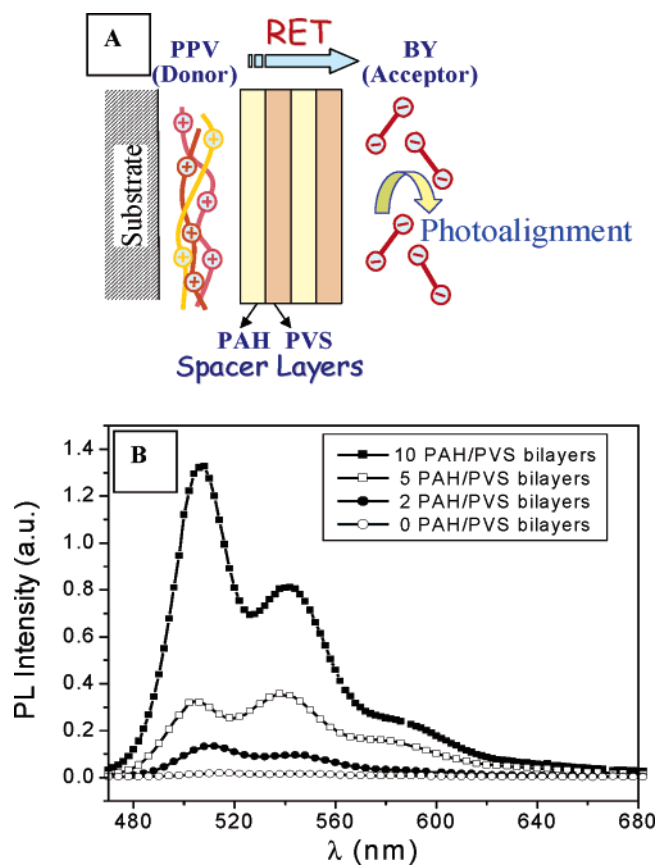


Figure 3. (A) Schematic diagram of PPV/BY LbL films with PAH/PVS spacer layers. In the BY layers, the azobenzene chromophores are represented to indicate that the layer may be modified by photoaligning the chromophores. (B) PL increases with the number of PAH/PVS layers.

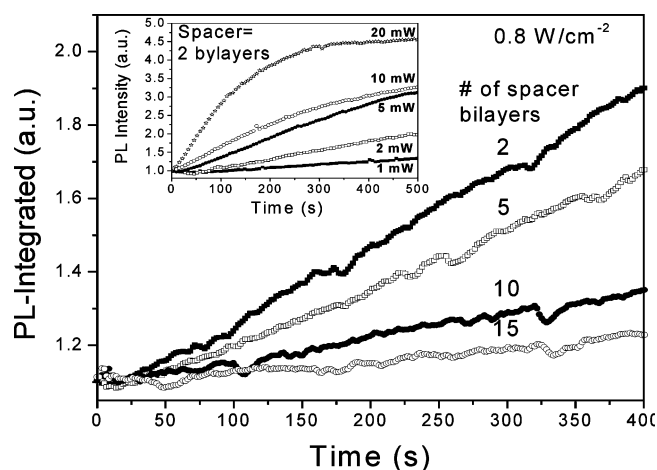


Figure 4. PL as a function of time of writing for the photoalignment of BY chromophores, in PPV/BY LbL films with different numbers of PAH/PVS spacer layers. Excitation of PPV and photoalignment of the BY molecules was performed simultaneously using the same laser beam at 441 nm from an He-Cd laser operating at 20 mW. The inset shows the PL increase for a film containing five spacer layers as a function of the laser power.

fluorescence properties is extremely fine. Fluorescence increases with the photoalignment, since the chromophores are being oriented in such a way as to hamper the energy transfer from PPV molecules, which ultimately leads to the quenching. It is known that PPV emission is more efficient in a direction parallel to the polarization of the incident light, when a linearly polarized light is used as excitation.¹³ On the other hand, azodyes such

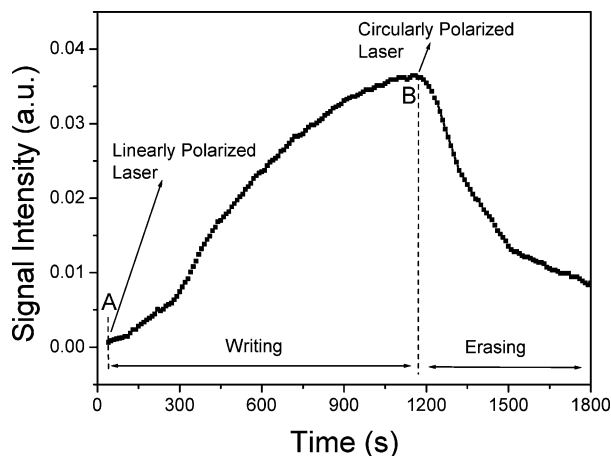


Figure 5. Complete optical storage cycle (writing and erasing) performed on PPV/BY LbL films containing five PAH/PVS spacer layers (the same used in the PL experiments from Figure 4). The increase in the signal intensity is due to the photoalignment of the BY chromophores perpendicular to the direction of laser polarization. Erasing (i.e., randomization of the BY chromophores) was achieved upon shining the sample with a circularly polarized laser light. A detailed description of the experimental setup employed in the optical storage experiments can be found in ref 12 (and references therein). as BY molecules tend to align in a direction perpendicular to the linearly polarized light,^{12,14} resulting in the so-called optical storage (photoinduced birefringence).

It is worth noting that chromophore photoalignment can yield an effective decrease on the RET rate via different mechanisms, such as the in-plane or out-of-plane reorientation of the chromophore. The former process, however, is most likely to occur, as confirmed by optical storage experiments performed on the PPV/BY films. This is shown in Figure 5, which shows the transmitted light across the sample and crossed polarizers as a function of time (a full description of optical storage experiments is found in ref 12 and references therein). If there is no birefringence in the film, no light is detected (point A). As the birefringence is photoinduced with a linearly polarized laser, the transmitted signal increases until reaching saturation. At point B, the linearly polarized laser was switched off and replaced by a circularly polarized light that randomized the chromophores and therefore reduced the birefringence—represented by the decrease in the transmitted light. Note that the times involved in photoaligning the chromophores are comparable to those for the buildup of PL, shown in the inset of Figure 4. In summary, the results in Figure 5 indicate that the BY chromophores in the PPV/BY film can be reversibly photoaligned. Thus, the PL increase in Figure 4 is due to alignment of the BY molecules perpendicular to the laser polarization direction, and consequently perpendicular to the PPV emission direction, which minimizes RET and increases PL.

Obviously, the effects are relatively larger for samples having a lower number of spacer layers (two PAH/PVS bilayers, see Figure 4) because quenching (i.e., energy transfer) was stronger. Fluorescence recovery is also observed for other numbers of spacers, as indicated in Figure 4. PL increases until chromophore alignment is saturated. As the BY layer thicknesses were held constant for all samples in Figure 4, the different rates of intensity increase cannot be accounted for by changes in the BY absorption along the excitation polarization due to alignment of the chromophores in the perpendicular direction. Note that the results depend on the polarization of the writing laser responsible for the photoalignment, which represents a further parameter to control the final film properties.

The fine control of fluorescence in the PPV/BY LbL films can be explained with the Förster energy transfer model, according to which energy transfer responsible for fluorescence quenching depends not only on the distance between donor and acceptor but also on the relative angle between their transition dipole moments.^{11,15} This is represented in eq 1, which gives the average rate of energy transfer from an excited donor to an acceptor molecule:

$$k_{\text{DA}} = a \frac{Q_{\text{D}}}{n^4 \tau} \left(\frac{\kappa^2}{r_{\text{DA}}^2} \right) \int_0^\infty \frac{f(\tilde{\nu}) \epsilon(\tilde{\nu})}{\tilde{\nu}^4} d\tilde{\nu} \quad (1)$$

where a is a numerical constant, τ and Q_{D} are the lifetime and the quantum yield of the donor in the absence of transfer, n is the scalar refractive index of the medium, and r_{DA} is the separation between the two molecules. The integral is the overlap between the fluorescence intensity, $f(\tilde{\nu})$, of the donor and the absorption coefficient of the acceptor, $\epsilon(\tilde{\nu})$, in the wavenumber range $\tilde{\nu} + d\tilde{\nu}$ for $\int_0^\infty f(\tilde{\nu}) d\tilde{\nu} = 1$. The orientational factor, κ , depends on the unit vectors, μ_{D} and μ_{A} , defining the orientation of the transition dipole moments among donor and acceptor and the donor–acceptor separation unit vector, \hat{r}_{DA} , at a time, t , that is, $\kappa = \mu_{\text{D}} \cdot \mu_{\text{A}} - 3(\mu_{\text{D}} \cdot \hat{r}_{\text{DA}})(\mu_{\text{A}} \cdot \hat{r}_{\text{DA}})$. As the excitation light is perpendicular to the donor and acceptor layers which are very thin and parallel, this parameter is almost zero when the transition dipole moment of the BY chromophore is perpendicular; that is, the Förster energy transfer rate, κ_{DA} , vanishes after the BY alignment by laser excitation. The directional energy transfer may be also controlled if the PPV molecules are made to emit light with a preferential polarization. Indeed, strong polarized emission has been reported for PPV films built with the Langmuir–Blodgett (LB)¹³ and the LbL technique,¹⁶ which have been proven to be anisotropic. The degree of anisotropy is increased if the PPV/BY films containing five PAH/PVS spacer layers are deposited onto flexible Teflon substrates, as the latter can now be stretched. The idea behind such an approach¹⁷ was to verify if an increase in the polarization degree of the light emitted by PPV would result in an increase in the efficiency of the RET process. Upon stretching the Teflon substrate and increasing the drawing ratio, L/L_0 , from 1 to the values 1.2 and 1.4, we observed that PL was affected. In these experiments, the excitation light was polarized parallel to the stretching direction and PL was continuously collected in all directions (in the sample plane) after the light passed through a polarizer. The angle between the polarizer and the excitation light direction was continuously varied within a time interval of 10 min. The results shown in Figure 6 indicate that the PL collected in a direction parallel to the excitation direction (upper part of the curves, corresponding to analyzer angles of 0°, 180°, 360°, etc.) is much higher than that collected in a direction perpendicular to the excitation direction (lower part of the curves corresponding to angles of 90°, 270°, etc.).

Such anisotropy, or the polarization degree of PL, greatly increases with stretching. In addition, PL increases with time, similarly to what was observed for the LbL film on a quartz substrate of Figure 4. Now, the increase in PL is significantly higher for highly stretched substrates. The increase in PL was 2.6 and 3.4 times the initial value for a nonstretched film and for a film stretched with $L/L_0 = 1.2$, respectively. For a film stretched up to $L/L_0 = 1.4$, the increase in PL was ~ 4.4 times its initial value, after 10 min. For higher drawing ratios, the efficiency of the energy transfer is optimized. Thus, with the

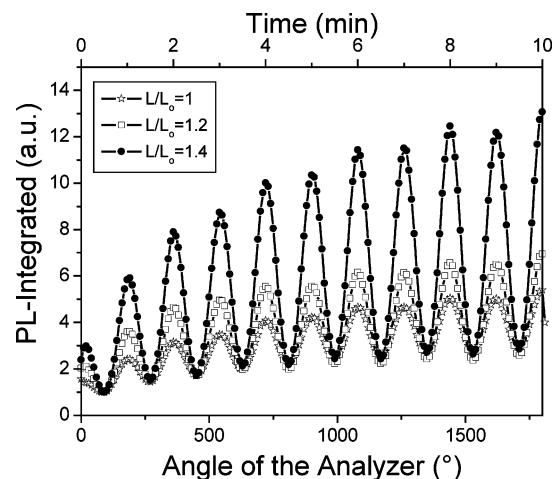


Figure 6. Integrated PL vs angle of the analyzer when PL is collected from PPV/BY LbL films adsorbed onto Teflon substrates containing five spacer layers. The substrates were stretched and had their length increased by 0, 2, and 4 mm.

photoalignment of the chromophores in a direction perpendicular to the PL polarization, the RET process is weaker and PL increases.

4. Conclusions

The possibility of controlling the molecular architecture of LbL films has been exploited to vary the luminescence of PPV layers almost continuously, with the further advantage of obtaining polarized emission. This was made possible by combining the luminescent PPV polymer with the azobenzene BY, which functions both as the acceptor in the energy transfer mechanism and as the photoaligned entities that allow fine control of the energy transferred.

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