Supporting information for

Fluorescence emission anisotropy coupled to an electrochemical system: Study of exciton dynamics in conjugated polymers.

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Theoretical Calculations for the determination of the fundamental anisotropy

In order to give insight into the excitation and emission (fluorescence) of the chromophores present in the polymer, we have investigated theoretically these processes by using single-excitation configuration interaction (CIS) method with a 6-31G(d) basis set as implemented in Gaussian03 suite of programs [S1]. Concretely, we have studied the electronic and structural properties of the monomers of PFP and PPV in the ground and excited state in order to determine the fundamental anisotropy (r_0) in different conditions. We find that a high fluorescence fundamental anisotropy characterize both chromophores, and only some small deviation from the maximum anisotropy (i.e. r_0 =0.4) is present when we take into account vibrational relaxation in the excited state. Some significant amount of isotropy could be reached when excitation to higher electronic excited states (process avoided in the experimental procedure) are populated.



Fig. S1. Variation of the Mulliken charges in the excitation process (left) for PPV monomer model for ground state equilibrium geometry (charge range is expressed in atomic units). Transition vectors are shown (right) for absorption ($M_{S1} M_{S0}$) and emission ($M_{S1} M_{S0}$) for ground state and excited state equilibrium geometries respectively. S₁ state is dominated by HOMO-LUMO excitation (down).

Lowest excited state of PPV monomer is dominated by the HOMO-LUMO excitation (see Fig. S1) and presents a high oscillator strength (f=0.29), being therefore the first bright state of the chromophore. The excited state (S₁) involve the semi-occupation of π^* LUMO orbital which imply some kind of rearrangement of the π charge of the system, and therefore vibrational relaxation in this state is expected to be related mainly to stretching modes. In fact, we find that vibrational excess after excitation to this state is dissipated mainly by stretching modes relaxation (ca. 8 kcal/mol) and minor contribution is due to vinyl-phenyl torsion (ca. 2 kcal/mol). In this way, it is expected a rapid dissipation of the vibrational excess in the case of Franck-Condon transition due to the ultrafast (typically in few femtosecond time scale) relaxation along the stretching modes.

On the contrary, torsional modes contribution in the relaxation process could be, in some extent, impeded by the experimental conditions (solid matrix). Therefore, we have determined the fundamental anisotropy when stretching and/or full vibrational relaxation is taken into account. The first one, obtained by relaxing the system in the excited state keeping torsions frozen, yields a value of the angel between absorption and emission transition vectors equal to $\alpha \approx 1^{\circ}$, and therefore no significant deviation of the fundamental anisotropy from 0.4 is expected. When full relaxation in the S₁ excited state is considered, the angle increases to $\alpha \approx 3^{\circ}$, implying also a fundamental anisotropy very close to the maximum (r₀=0.398).

Participation of higher excited states (process which has been avoided in the experimental procedure) could contribute notably to the decrease of fundamental anisotropy. Concretely, the second (f=0.05) and third (f=0.86) excited states could contribute to the fundamental anisotropy with values of r_0 =0.10 and r_0 =0.36 respectively when fluorescence proceed via S₁-S₀ emission.

In the case of PFP monomer (see Fig. S2), the situation is close to that discussed for PPV monomer. When we consider vertical excitation to the first excited state (S_0S_1 excitation dominated by HOMO-LUMO transition), the vibrational excess in the excited state is associated mainly with stretching modes (ca. 9 kcal/mol) and only some small torsion (ca. 20 degrees) around the fluorene-phenyl bond yield a further relaxation of ca. 3 kcal/mol. Therefore, we have determined the fundamental anisotropy by considering partial (stretching modes) and total (stretching and torsional modes) relaxation on the

excited state. Fast stretching relaxation in the excited state implies a displacement of the emission transition vector of ca. 0.7 degrees in comparison with vertical absorption transition vector, and consequently, fundamental anisotropy remains maximum ($r_0=0.4$). Even when we take into account torsional relaxation, which should be impeded in some extent due to the experimental conditions (see discussion above), the angle between absorption and emission transition vectors remains low: $\alpha=1.6$ degrees and fundamental anisotropy essentially maximum, $r_0=0.4$.



Fig. S2. Variation of the Mulliken charges in the excitation process (left) for PFP monomer model for ground state equilibrium geometry (charge range is expressed in atomic units). Transition vectors (right) are shown for absorption ($M_{S1} M_{S0}$) and emission ($M_{S1} M_{S0}$) for ground state and excited state equilibrium geometries respectively. S₁ state is dominated by HOMO-LUMO excitation (down).

Contribution from excitations to higher excited states (excitations avoided in the experiments) close in energy to S_1 state could contribute in reducing the fundamental anisotropy when fluorescence proceeds by emission from S_1 state. For example, excitations to S_2 and S_3 , placed at ca. 8 and 19 kcal/mol respectively from S_1 state, should contribute to the fundamental anisotropy with $r_0=0.39$ and $r_0=0.19$ respectively. Nevertheless, low oscillator strengths for these transitions in comparison with the lowest S_0S_1 transition (f=0.008 and f=0.005 for S_0S_2 and S_0S_3 excitations respectively in comparison with f=0.822 for S_0S_1 excitation) prevents a significant contribution of these states in lowering the fundamental anisotropy even when these states are energetically accessible in the excitation process.

Concluding, we show that excitation to first excited state (S_1 with HOMO-LUMO excitation character) in both monomers considering both, partial (stretching modes) and total (stretching and torsional modes) vibrational relaxation, yields no significant change in the maximum fundamental anisotropy (r_0 =0.4). Eventual participation of higher low-lying excited states by using lower wavelength radiation should contribute significantly in lowering fundamental anisotropy at least in the case of PPV monomer.

Calculation of the Förster critical radius.

For the determination of the Förster critical radius we have made use of the following expression ^[S2]:

$$R_0 = 0.211 \left[Q_D \kappa^2 n^{-4} J \right]^{1/6} \tag{6}$$

Quantum yields were calculated comparing the emission of the polymers to that of a standard solution of quinine sulfate in sulphuric acid 0.1 M (Q_D = 54.6%) at 25 °C ^[S3]. Assuming the value of κ^2 =0.476 (randomly oriented chromophores in solid state ^[S4]) and a refractive index of 1.7 for both polymers.

	PFP	MDMO-PPV
$J (M^{-1} cm^{-1} nm^4)$	9.63 x10 ⁺¹³	$4.17 \text{ x} 10^{+14}$
Q_D	0.82	0.15
R_0 (Å)	29.5	28.3

Reference list:

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