

SUPPORTING INFORMATION FOR

Photophysics of Xanthene Dyes at High
Concentrations in Solid Environments: Charge
Transfer Assisted Triplet Formation

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Table S1. Sample concentrations ($\mu\text{mol g}^{-1}$) and sample color convention.

| | Eosin Y (EoY) | Phloxine B (PhB) |
|---|---------------|------------------|
| 1 | 0.042 | 0.053 |
| 2 | 0.090 | 0.11 |
| 3 | 0.16 | 0.16 |
| 4 | 0.32 | 0.32 |
| 5 | 0.64 | 0.77 |
| 6 | 1.3 | 1.5 |
| 7 | 2.7 | 3.0 |
| 8 | 4.2 | 4.2 |

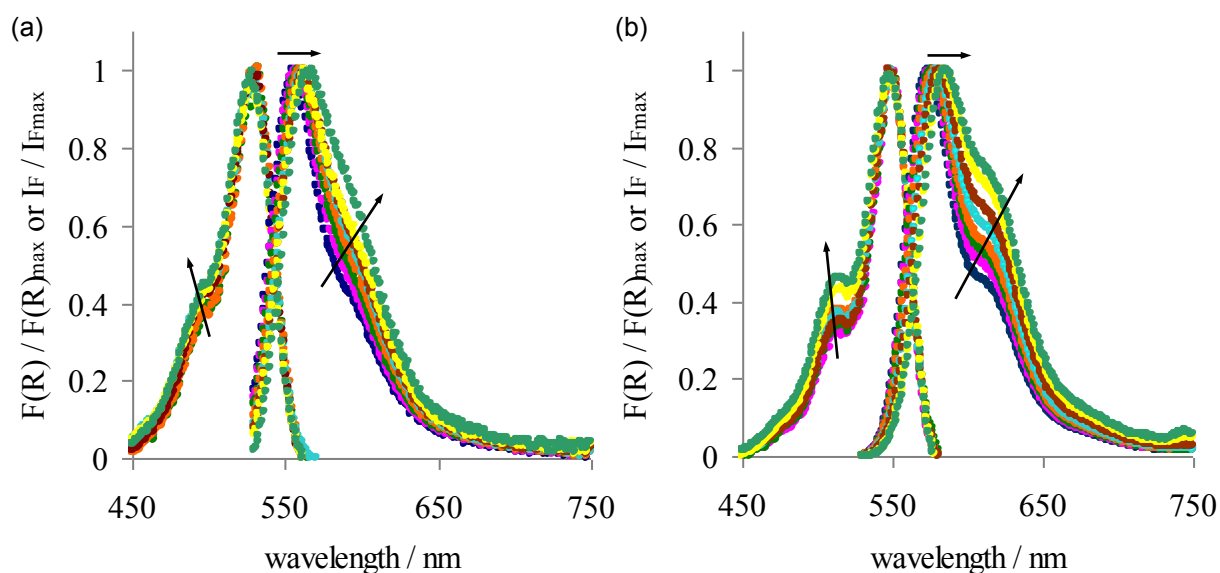


Figure S1. (a) Normalized remission function ($[\text{dye}] > 0.1 \mu\text{mol g}^{-1}$) and fluorescence (all, $\lambda_{\text{ex}} = 505$ nm) spectra of optically thick layers of EoY. Arrows indicate increasing concentrations. Data was adapted from [Rodríguez, H. B., E. San Román, P. Duarte, I. Ferreira Machado, and L. F. Vieira Ferreira (2012) Eosin Y triplet state as a probe of spatial heterogeneity in microcrystalline cellulose. *Photochem. Photobiol.* **88**, 831-839]. **(b)** Normalized remission function ($[\text{dye}] > 0.1 \mu\text{mol g}^{-1}$) and fluorescence (all, $\lambda_{\text{ex}} = 500$ nm) spectra of optically thick layers of PhB. Arrows indicate increasing concentrations.

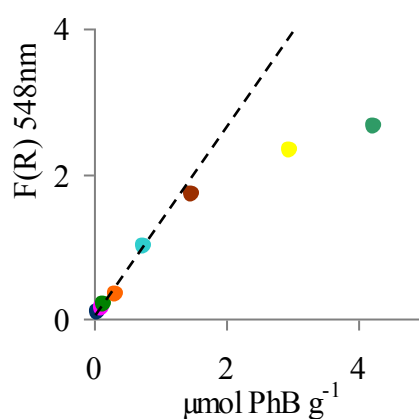


Figure S2. Remission function at maximum for PhB as a function of dye concentration.

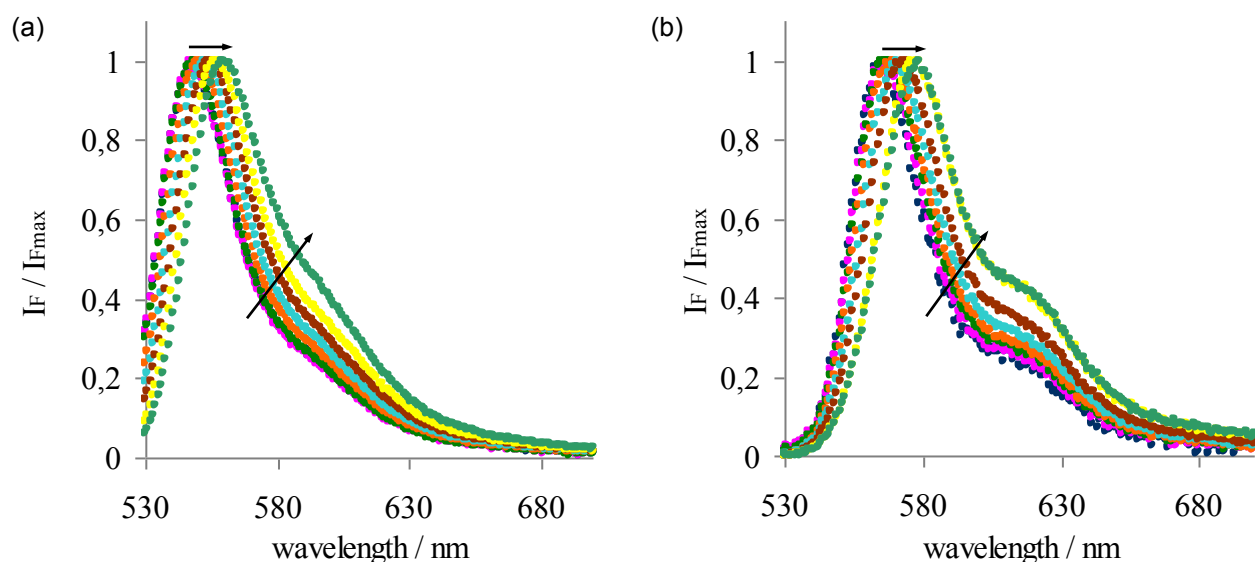


Figure S3 (a) Normalized fluorescence spectra of thin layers of EoY (all, $\lambda_{ex} = 505$ nm). Arrows indicate increasing concentrations. Data was adapted from [Rodríguez, H. B., E. San Román, P. Duarte, I. Ferreira Machado, and L. F. Vieira Ferreira (2012) Eosin Y triplet state as a probe of spatial heterogeneity in microcrystalline cellulose. *Photochem. Photobiol.* **88**, 831-839]. **(b)** Normalized fluorescence spectra of thin layers of PhB (all, $\lambda_{ex} = 500$ nm). Arrows indicate increasing concentrations.

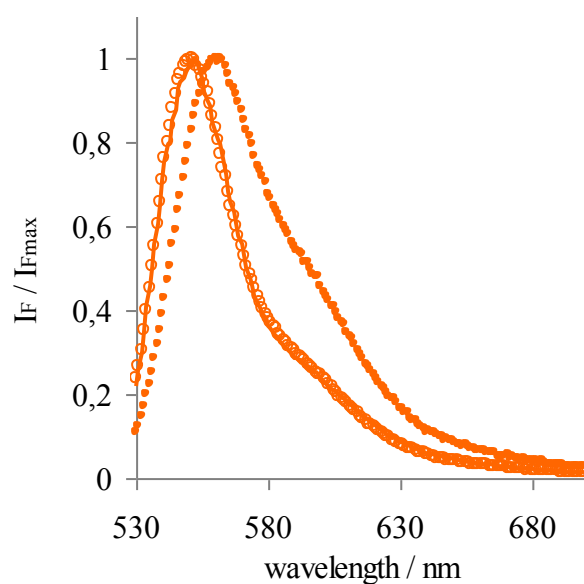


Figure S4. Normalized fluorescence spectra of thin layer (hollow circles), thick layer (filled circles) and thick layer corrected by reabsorption (full line) for EoY $0.32 \mu\text{mol g}^{-1}$ ($\lambda_{ex} = 500$ nm). Corrections are performed according to ref. [Lagorio, M. G., L. E. Dicelio, M. I. Litter, and E. San Román (1998) Modeling of fluorescence quantum yields of supported dyes. Aluminum carboxyphthalocyanine on cellulose. *J. Chem. Soc. Faraday Trans.* **94**, 419-425].

Table S2. Observed and corrected fluorescence quantum yields.

| | $\Phi_{F,obs}$ EoY | Φ_F EoY | $\Phi_{F,obs}$ PhB | Φ_F PhB |
|---|--------------------|--------------|--------------------|--------------|
| 1 | 0.670±0.017 | 0.733±0.014 | 0.601±0.017 | 0.751±0.030 |
| 2 | 0.539±0.017 | 0.634±0.016 | 0.600±0.020 | 0.730±0.030 |
| 3 | 0.412±0.018 | 0.506±0.013 | 0.599±0.021 | 0.717±0.028 |
| 4 | 0.549±0.028 | 0.640±0.033 | 0.557±0.021 | 0.662±0.026 |
| 5 | 0.404±0.025 | 0.495±0.032 | 0.311±0.014 | 0.395±0.019 |
| 6 | 0.148±0.010 | 0.199±0.012 | 0.097±0.015 | 0.131±0.021 |
| 7 | 0.089±0.015 | 0.121±0.020 | 0.101±0.015 | 0.132±0.019 |
| 8 | 0.062±0.013 | 0.083±0.018 | 0.000±0.009 | 0.000±0.020 |

Table S3. Observed and corrected triplet quantum yields obtained by LIOAS.

| | $\Phi_{T,obs}$ EoY | Φ_T EoY | $\Phi_{T,obs}$ PhB | Φ_T PhB |
|---|--------------------|--------------|--------------------|--------------|
| 1 | 0.27±0.05 | 0.24±0.04 | 0.33±0.06 | 0.26±0.05 |
| 2 | 0.43±0.09 | 0.35±0.07 | 0.39±0.02 | 0.31±0.02 |
| 3 | 0.50±0.12 | 0.43±0.10 | 0.36±0.04 | 0.27±0.03 |
| 4 | 0.30±0.07 | 0.25±0.06 | 0.39±0.07 | 0.31±0.05 |
| 5 | 0.20±0.06 | 0.18±0.05 | 0.48±0.13 | 0.42±0.12 |
| 6 | 0.29±0.09 | 0.28±0.08 | 0.42±0.11 | 0.40±0.11 |
| 7 | 0.13±0.09 | 0.13±0.09 | 0.24±0.10 | 0.24±0.10 |
| 8 | 0.11±0.08 | 0.11±0.08 | 0.21±0.10 | 0.21±0.10 |

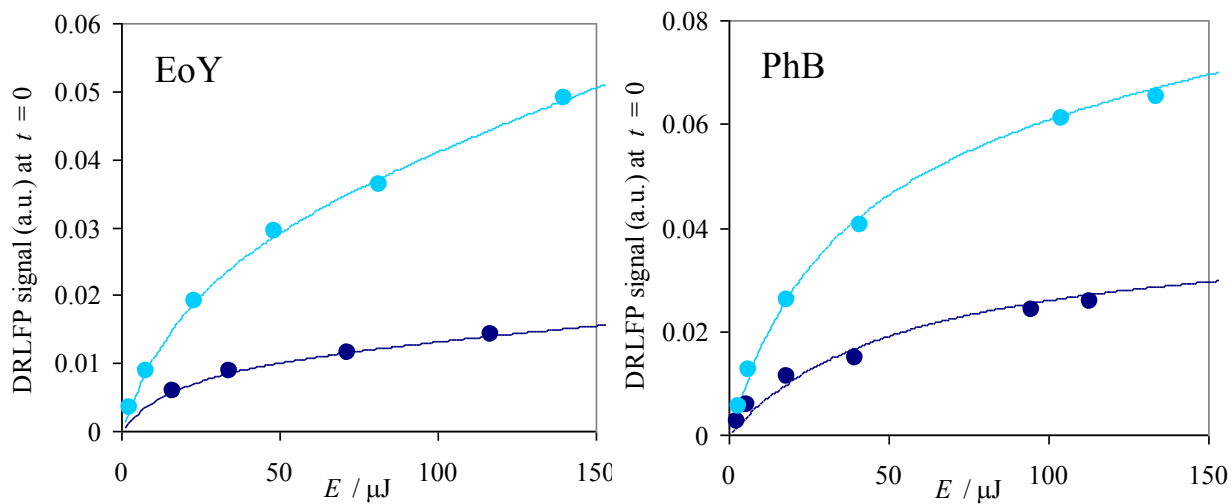


Figure S5. DRLFP signals extrapolated at $t = 0$ as a function of the laser pulse energy for selected samples of EoY (left panel) and PhB (right panel). Full lines are fits to a hyperbolic equation without physical meaning.