

Cite this: DOI: 10.1039/c0xx00000x

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ARTICLE TYPE

Supporting Information:

Excited State Characterization of a Polymeric Indigo

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Received (in XXX, XXX) Xth XXXXXXXXXX 20XX, Accepted Xth XXXXXXXXXX 20XX

DOI: 10.1039/b000000x

Table SII- Spectral and photophysical properties including quantum yields (fluorescence, ϕ_F , internal conversion, ϕ_{IC} , triplet formation, ϕ_T , and sensitized singlet oxygen formation, ϕ_Δ), lifetimes (τ_F), rate constants (k_F , k_{NR} , k_{IC} , k_{ISC}) for the polymeric indigo and indigo itself in different organic solvents at T=298 K.

| | λ_{abs}^{max} (nm) | ϵ_S ($M^{-1}cm^{-1}$) | λ_{fluo}^{max} (nm) | Δ_{SS} (nm) | ϕ_F | τ_F (ns) | ϕ_T | ϕ_Δ | ϕ_{IC} | k_F (ns^{-1}) ^[b] | k_{NR} (ns^{-1}) ^[b] | k_{IC} (ns^{-1}) ^[b] | k_{ISC} (ns^{-1}) ^[b] |
|----------------|-------------------------------|-------------------------------------|--------------------------------|-----------------------|----------|----------------------|----------|---------------|-------------|---------------------------------------|------------------------------------------|------------------------------------------|-------------------------------------------|
| Polymer | | | | | | | | | | | | | |
| DMSO | 630 | - | 681 | 51 | 0.00027 | 0.040 | 0.006 | - | | 0.00675 | 24.99 | 24.84 | 0.15 |
| DMF | 630 | - | 672 | 42 | 0.00037 | 0.050 | 0.006 | - | 0.9936 | 0.00740 | 19.99 | 19.87 | 0.12 |
| Indigo | | | | | | | | | | | | | |
| Dx | 600 | 17710 | 637 | 37 | 0.0025 | 0.126 ^[a] | | | | 0.0198 | 7.92 | | |
| DMF | 610 | 22140 | 653 | 43 | 0.0023 | 0.140 | 0.0066 | 0.0012 | 0.991 | 0.0164 | 7.12 | 7.12 | 0.0084 |

^[a] value taken from ref. ¹ from a monoexponential decay fit analysis. More recent decays obtained in our labs with a biexponential fit, lead to a value of 140 ps for the longer component.

^[b]

$$k_F = \frac{\phi_F}{\tau_F}; k_{NR} = \frac{1 - \phi_F}{\tau_F}; k_{IC} = \frac{1 - \phi_F - \phi_T}{\tau_F}; k_{ISC} = \frac{\phi_T}{\tau_F}; \phi_{IC} = 1 - \phi_F - \phi_T$$

Tables SII: spectral and photophysical data for indigo and polymeric indigo in DMSO, DMF and dioxane.

Table SI2: values of ϕ_1 obtained from PAC experiments with different energies (here seen as different values of % of transmittance).

Spectral and Photophysical Data

Table 1 includes data for the polymer indigo with data in various solvents; in the ms table 1, only the data in DMF is presented.

PAC experiments

In table SI2 the values for ϕ_1 (see experimental section) obtained with different energies (different % of transmittance obtained with different filters) are presented.

References (SI)

- J. Seixas de Melo, A. P. Moura and M. J. Melo, *J. Phys. Chem. A.*, 2004, **108**, 6975-6981.
- F. A. Schaberle, R. M. D. Nunes, M. Barroso, C. Serpa and L. G. Arnaut, *Photochemical & Photobiological Sciences*, 2010, **9**, 812-822.

Table S12. Values of ϕ_1 (obtained from the deconvolution² of the wave) for all energy measurements. Also presented is the mean value obtained.

| Transmittance | ϕ_1 |
|---------------|----------|
| 100% | 1.0839 |
| 100% | 1.0245 |
| 100% | 0.9475 |
| 100% | 0.9478 |
| 79,00% | 0.9508 |
| 79,00% | 1.0228 |
| 79,00% | 0.9287 |
| 79,00% | 0.9837 |
| 57,00% | 0.9719 |
| 57,00% | 0.8584 |
| 57,00% | 0.9221 |
| 57,00% | 0.9211 |
| 33,00% | 1.0701 |
| 33,00% | 1.0627 |
| 33,00% | 1.0759 |
| 33,00% | 1.1879 |

ϕ_1 (mean value) = 0.997 +/- 0.02