



A study of energy transfer processes in zinc–porphyrin films using Monte Carlo simulation of fluorescence decay

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Abstract

Energy transfer in thin films of zinc tetra(-octylphenyl)-porphyrin (ZnTOPP) doped with the copper (CuTOPP) or free-base (H₂TOPP) analogues were investigated by time-resolved fluorescence and Monte Carlo simulations, applied to a single domain model of parallel porphyrin stacks. Rate constants for intra- and inter-stack energy transfer are $(0.8\text{--}1.1) \times 10^{12}$ and $(71\text{--}91) \times 10^9 \text{ s}^{-1}$, respectively. The fluorescence lifetimes for ZnTOPP and H₂TOPP films are $(1.80\text{--}1.88) \times 10^{-9}$ and $(6.8\text{--}7.3) \times 10^{-9} \text{ s}$. The rate constant for H₂TOPP to ZnTOPP back transfer is $(8.8\text{--}9.4) \times 10^6 \text{ s}^{-1}$. The results agree with those of a previous analytical analysis [1]. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

Recently, dye films have gained much interest since these are promising materials for constructing organic solar cells [2–5]. For such cells to be efficient, energy transfer, further denoted as ET, through the film must be optimized [6–8]. There are at least two reasons why the analysis of ET in molecular films is far from simple since: (i) the films may contain different types of aggregates, e.g., linear or cyclic chains or ordered domains [1,9–11] with different spectroscopic properties, and (ii) the ET rate constants depend on the nature and strength of the inter-molecular interactions at the aggregate and domain level [12–14]. These interactions depend again on the detailed film structure.

This paper reports and discusses the results of a study of ET processes in thin, spincoated films of a self-organizing porphyrin, ZnTOPP (Fig. 1) on quartz substrates. The films have been intentionally doped with known amounts of effective fluorescence quenchers, i.e., CuTOPP or H₂TOPP (Fig. 1). Optical spectroscopy of these films [1] has shown that they consist of layers of one-dimensional stacks in a ‘slipped deck of cards’ configuration. The porphyrin planes within the stacks are oriented perpendicular to the substrate. The long axes of the stacks, which form ordered domains, are parallel to the substrate. The domain orientations are randomly distributed in the substrate plane. The fluorescence decay of these films cannot be described by a single exponential, most likely indicating energy transfer/migration within the domains. Analysis of the fluorescence decay of the ZnTOPP films using analytical models has shown that the spectroscopic properties of the films are best described by

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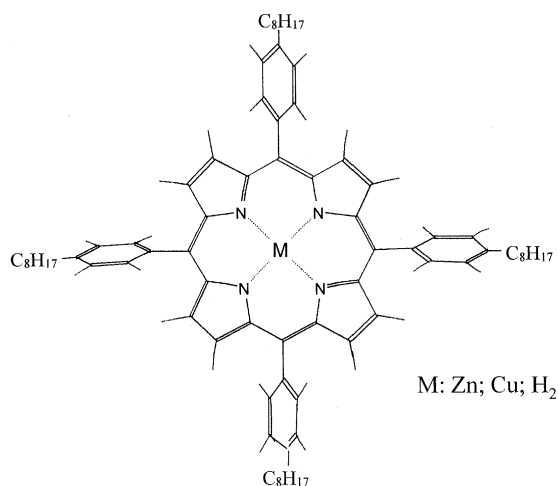


Fig. 1. Molecular structure of Zn-, Cu-, and H₂TOPP.

quasi-one-dimensional, diffusion limited energy transfer [1]. This analysis yields a rough estimate of $(0.1\text{--}1.0) \times 10^{12}$ and $0.07 \times 10^{12} \text{ s}^{-1}$ for the inter- and intra-stack energy transfer rate constants, respectively. The results of that study also showed that the undoped films contain a non-negligible fraction of non-intentionally incorporated traps, but again only an estimate could be given.

An alternative and effective approach for retrieving the energy transfer characteristics from the fluorescence decay is the Monte Carlo simulation method [15–17], in the following denoted as MC. We applied this simulation to the fluorescence data of the film using a model of the porphyrin film, which assumes that the film consists of domains containing a number of parallel porphyrin stacks. In principle for this model at least two ET rate constants should be found, corresponding to intra- and inter-stack energy transfer within each domain. Considering their excited state energies, also back transfer from H₂TOPP to ZnTOPP is expected to occur, and therefore has been incorporated in the model and the MC simulations.

2. Experimental

2.1. Materials

ZnTOPP and CuTOPP were prepared by metallization of H₂TOPP by refluxing in DMF with

ZnCl₂ (Merck, p.a.) and CuCl₂ · 2H₂O (Merck, p.a.), respectively [18]. H₂TOPP was synthesized by condensation of 4-(*n*-octyl)benzaldehyde (Kodak, 99%) with pyrrole (Janssen Chimica, 99%) in refluxing propionic acid (Merck, z.s.) [19]. All porphyrins were purified by chromatography on silica (Merck, silica gel 60) with toluene as eluent. As duplicate samples ZnTOPP purchased from Porphyrin Products was used. Results obtained with purchased or home-synthesized ZnTOPP were identical. All porphyrins are estimated to be >99% pure as shown by thin-layer chromatography and absorption- as well as fluorescence spectroscopy.

Thin films of ZnTOPP doped with various concentrations of CuTOPP and H₂TOPP as well as undoped films on quartz plates (Suprasil, Ø 15 and 1 mm thickness) were prepared by spin coating from 5×10^{-2} M toluene solutions. As the solutions already contain the appropriate amounts of ZnTOPP and CuTOPP, it may be assumed that in the films the CuTOPP molecules are distributed statistically among the ZnTOPP molecules. Before spin coating the quartz plates were subsequently rinsed with aqua regia, water, methanol and toluene and blown dry with nitrogen. All solvents were p.a. quality, if not stated otherwise.

For the time-resolved fluorescence measurements we used ZnTOPP films with the following composition: (i)–(iv): 0, 1, 2, 3 × 10⁻² molar fraction of CuTOPP; (v)–(vii): 1, 2, 3 × 10⁻² molar fraction of H₂TOPP.

3. Equipment

The instrumentation for time-resolved fluorescence measurement is time-correlated single photon counting equipment which has been described in detail elsewhere [1,20]. A mode-locked continuous wave Nd:YLF laser (Coherent model Antares 76-YLF), equipped with a LBO frequency doubler (Coherent model 7900 SHGTC) and BBO frequency tripler (Coherent model 7950 THG) was used to synchronously pump a continuous wave dye laser (Coherent radiation model CR 590). As a dye Coumarin 460 was used for excitation at 465

nm. A setup with electro-optic modulators in a dual pass configuration was used to reduce the pulse rate to 594 kHz [21]. The final pulse duration of excitation pulses was ~ 4 ps FWHM and the maximum pulse energy ~ 100 pJ. The spincoated samples were fixed on a thermostated, spring-loaded holder at an angle of 15° with respect to the direction of excitation. Data were collected using a multichannel analyzer (MCA board Nuclear Data model Accuspec B, in a PC) with a time window of 8192 channels at 3.125 ps/channel. To obtain a favorable dynamic instrumental response (~ 50 ps FWHM) for deconvolution purposes, the scatter of a rough-hewn, uncoated quartz substrate of 1 mm thickness was measured at the excitation wavelength.

The porphyrin films were measured at room temperature. Excitation was at 465 nm and detection was at 580 and 725 nm for the ZnTOPP and H₂TOPP fluorescence, respectively.

4. MC simulations

As previously found [1], ZnTOPP porphyrins on a quartz substrate are self-organizing into domains. Inside each domain the ZnTOPP monomers are presumably assembled in parallel stacks oriented along one of the domain axes (Fig. 2). The center-to-center distances between the nearest neighbor ZnTOPPs in a stack and in nearby stacks

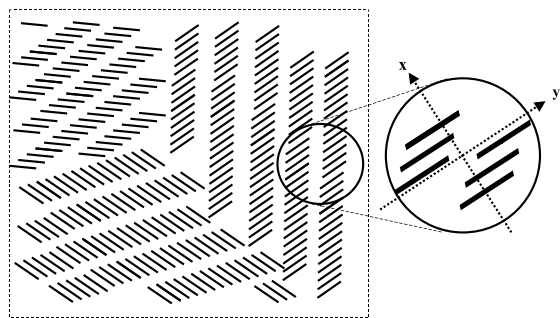


Fig. 2. Schematic 2D fragment of self-organized ZnTOPP film; magnified part: schematic fragment of a single porphyrin domain used in the Monte Carlo simulations; x and y are axes parallel and perpendicular to the long stack axis.

are ~ 5 and ~ 10 – 50 Å, respectively, the latter distance depending on the particular domain structure. As follows from the fluorescence- and fluorescence anisotropy decay measurements [1], and in agreement with a lamellar film structure [22,23], ET in the films is two-dimensional (2D). Three dominant ET pathways are expected in a 2D domain: (i) intra-stack ET along the porphyrin stack; (ii) inter-stack ET between adjacent stacks; (iii) inter-domain ET between adjacent stacks in two neighboring domains.

In ZnTOPP films doped with H₂TOPP or CuTOPP the latter are acting as traps in both film types. The long tail of the ZnTOPP fluorescence decay at 580 nm (see Fig. 5) indicates a relatively slow back transfer from H₂TOPP to ZnTOPP [1].

The presence of a non-intentional impurity, possibly H₂TOPP as a residue of the ZnTOPP preparation, results in non-exponential fluorescence decay of the undoped ZnTOPP films. This non-intentional impurity also acts as an energy trap and is assumed to have a constant concentration in all experiments. We also assume that singlet–singlet annihilation can be neglected at the low excitation rates that were used. Finally, we neglect ET between adjacent domains as compared to intra- and inter-stack ET.

The MC model for ET processes in the ZnTOPP films was based on a single domain of 200 parallel porphyrin stacks, each containing 1000 molecules. This domain size was chosen as large as possible maintaining a practical CPU time. Associating the x and y axes in the simulation model with the parallel and perpendicular directions to one of domain axes (Fig. 2), then the intra-stack ET rate constants in the x and in y directions are denoted as k_{ET}^x and k_{ET}^y , respectively. Furthermore, N_{H_2P} , N_{H_2P} and N_{imp} define the molar fractions of CuTOPP, H₂TOPP, and the non-intentional impurity molecules, respectively. The parameter k^{Back} is the ET rate constant for the intra-stack back transfer from H₂TOPP to ZnTOPP and τ_{ZnP} and τ_{H_2P} indicate the isolated, monomeric ZnTOPP and H₂TOPP fluorescence lifetimes, respectively. The parameters k_{ET}^x , k_{ET}^y , $(\tau_{ZnP})^{-1}$, k^{Back} and $(\tau_{H_2P})^{-1}$ are proportional to the probabilities P_{ET}^x , P_{ET}^y , and

P_{τ}^{ZnP} , P^{Back} and $P_{\tau}^{\text{H}_2\text{P}}$, used in the simulation model related by

$$P_{\text{ET}}^x + P_{\text{ET}}^y + P_{\tau}^{\text{ZnP}} = 1, \quad (1)$$

$$P^{\text{Back}} + P_{\tau}^{\text{H}_2\text{P}} = 1. \quad (2)$$

The following assumptions have been made to construct the simulation model:

(i) Rate constants for ‘left’ and ‘right’ ET from excited ZnTOPP to neighboring ground state ZnTOPP or CuTOPP traps in the x direction are equal as well as for ‘up’ and ‘down’ ET in the y direction (Fig. 2). Furthermore, the probability for ET from excited ZnTOPP to a neighboring ground state H₂TOPP trap is assumed to be 1, considering the relative energies of the lowest excited singlet state of ZnTOPP and H₂TOPP, as well as the spectral overlap between the fluorescence and absorption spectra of both compounds.

(ii) The rate constant k_{ET}^x , corresponding to nearest neighbor transfer, is at least one order of magnitude larger than the rate constant for transfer to the next nearest neighbor or more distant molecules, i.e., ET beyond one or more neighboring molecules is neglected.

(iii) The rate constant k_{ET}^y is a statistical mean value covering all ET pathways to the nearest nearby stack.

(iv) The back transfer from CuTOPP to ZnTOPP is neglected.

(v) The inter-stack back transfer from H₂TOPP to ZnTOPP is neglected.

Finally, the simulation model has the following set of parameters:

(a) k_{ET}^x , k_{ET}^y and N_{imp} , and τ_{ZnP} for the undoped ZnTOPP film.

(b) k_{ET}^x , k_{ET}^y , N_{CuP} , N_{imp} , and τ_{ZnP} for the CuTOPP doped ZnTOPP film.

(c) k_{ET}^x , k_{ET}^y , $N_{\text{H}_2\text{P}}$, N_{imp} , t_{ZnP} , k^{Back} , and $\tau_{\text{H}_2\text{P}}$ for the H₂TOPP doped ZnTOPP film.

A flow diagram for one run of the simulation model is shown in Fig. 3a. The molecular sites are numbered as $i = 1, \dots, 1000$ in the x direction and $j = 1, \dots, 200$ in the y direction, respectively. Since the ZnTOPP domain system is considered to be a homogeneous system and to keep the excitation within a domain the so-called ‘mirror rejection’

method has been used to define the boundary conditions. The position (i_0, j_0) of the first excited molecule, the positions (i^k, j^k) , $k = 1, \dots, 1000 \cdot N_{\text{CuP}}/N_{\text{H}_2\text{P}}$ of the $N_{\text{CuP}}/N_{\text{H}_2\text{P}}$ impurity traps and the positions (i^l, j^l) , $l = 1, \dots, 1000 \cdot N_{\text{imp}}$ of the N_{imp} non-intentional impurity traps are randomly generated using a uniform standard number generator [26] at the start of every simulation run (block 1). After checking whether the first excited molecule is a trap (block 2), the events of the fluorescence emission or ET in the x or the y directions are simulated in block 5 according to the discrete probability distribution, defined by P_{ET}^x , P_{ET}^y , and P^{ZnP} , using a random number R , generated in block 4. The time of the excitation energy transfer is considered to be a continuous random variable, distributed exponentially. Thus, the time Δt for ET from one molecule to its next neighbor is given by [17]

$$\Delta t = -(k_{\text{ET}}^q)^{-1} \ln(R), \quad (3)$$

where q is x or y , and R is a new uniformly distributed random number in $[0; 1]$. Random travel of excitation energy is simulated in blocks 4–15 until the fluorescence event (block 18) or trapped by a CuTOPP or H₂TOPP site or non-intentional impurity in blocks 3, 16, and 17. If the trap is CuTOPP or a non-intentional impurity molecule then the simulation run stops there without Δt having been determined, otherwise, Δt for the events of back ET or emission by a H₂TOPP trap is generated in blocks 3, 16 and 17 using a discrete exponential probability distribution for P^{Back} and $P_{\tau}^{\text{H}_2\text{P}}$ (Fig. 3b). The final, simulated time Δt_{ET} is recorded in a histogram [17] representing the simulated decay. The simulation runs are repeated many times – typically more than 10^6 runs are made to record one simulated decay. The simulation program is stopped when the simulated decay has reached an acceptable signal-to-noise ratio.

This simulation-based parametric fitting [16,24] was applied to the fluorescence decay of ZnTOPP films. A time shift due to the convolution of the decay curve with the instrumental response function was simulated using a published algorithm [25]. Global analysis was then applied to analyze the fluorescence decay and its change with different

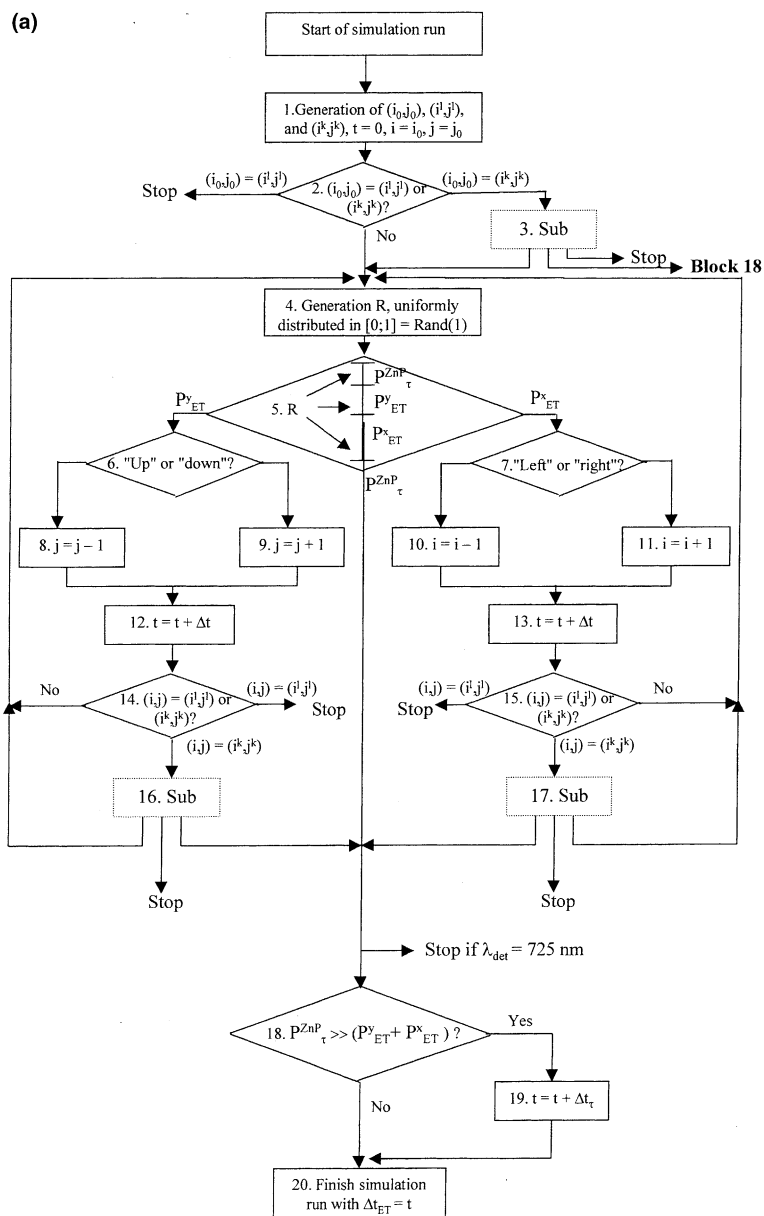


Fig. 3. (a) Flow diagram of one simulation run and (b) its subroutine.

molar fractions of the doped CuTOPP and H₂TOPP molecules. Since the fluorescence decays for different concentrations of impurity traps should result in the same values for the isolated, monomeric ZnTOPP- and H₂TOPP lifetimes and the corresponding ET rate constants, these parameters were globally linked and fitted.

The number of channels in the simulated histograms is 8096. The statistical χ^2 criterion as well as the plots of the weighted residuals and auto-correlation function were used to judge the quality of the fits. The 95% confidence intervals for the best fitted parameters were estimated using the method of asymptotic standard errors [26]. All

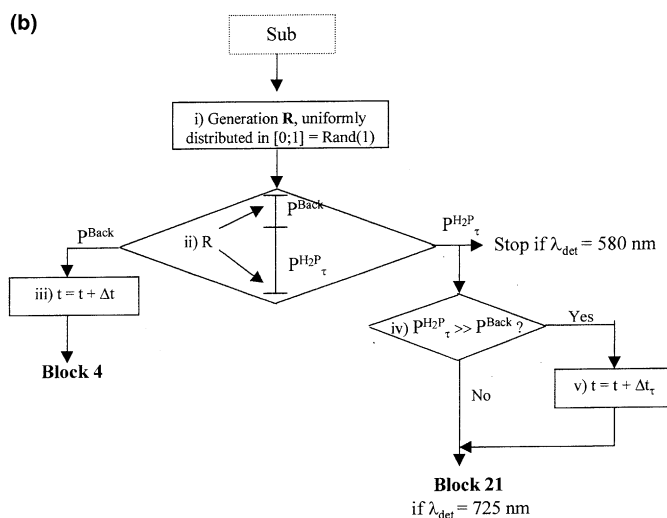


Fig. 3. (Continued)

computer simulations were performed on an IBM Pentium III 366 MHz PC.

To produce a simulated fluorescence decay with an acceptable signal-to-noise ratio typically 10^8 photon runs were needed to get stable χ^2 values, and requiring at the same time, a reasonably short simulation time.

5. Results and discussion

The experimental fluorescence decay of all ZnTOPP films can be nicely fitted by the simulated decay curves. Fig. 4 shows the best fits of the ZnTOPP fluorescence with different molar fractions of CuTOPP traps and similarly Fig. 5 for H₂TOPP traps. The parameters corresponding to the best fits are collected in Table 1.

The 580 nm fluorescence intensity of the ZnTOPP films is due to the contribution of ZnTOPP $Q(0,0)$ fluorescence with a maximum at 580 nm. At $\lambda_{\text{det}} = 725$ nm the ZnTOPP fluorescence emission is much weaker and its contribution to the fluorescence decay is negligible as compared with that of the H₂TOPP traps with a 725 nm $Q_x(0,1)$ maximum. The 725 nm fluorescence decay therefore originates from H₂TOPP traps. Then, a global analysis of the 580 and 725 nm fluorescence decay of the doped ZnTOPP films

minimizes the uncertainty in some parameters, mainly related H₂TOPP traps. Finally, this analysis creates a complete picture of the ET processes in the film.

The fluorescence lifetime of isolated, monomeric ZnTOPP resulting from MC simulations is found to be in the 1.80–1.88 ns range for all ZnTOPP films, close to the 1.81 ± 0.03 ns experimental fluorescence lifetime of ZnTOPP in toluene, typical for a zinc porphyrin in organic solvents [27–29]. The intra-stack ET rate constant of $(0.8\text{--}1.1) \times 10^{12} \text{ s}^{-1}$ is almost one order of magnitude larger than the value of $(71\text{--}91) \times 10^9 \text{ s}^{-1}$ for the inter-stack rate constant. The calculated molar fractions of CuTOPP and H₂TOPP were found to be in accordance with those in the solution, used for spin coating. The simulated fluorescence lifetime of isolated, monomeric H₂TOPP is 6.8–7.3 ns, somewhat shorter than 9.2 ± 0.5 ns for H₂TOPP in toluene. The rate constant for H₂TOPP to ZnTOPP back transfer turns out to be $(8.8\text{--}9.4) \times 10^6 \text{ s}^{-1}$. Although the back transfer is much slower than intra- or inter-stack ET, this process will result in a delay of the ZnTOPP fluorescence, as also follows from MC simulation. The simulated initial rise of the H₂TOPP fluorescence at $\lambda_{\text{det}} = 725$ nm nicely fits the experimental data (Fig. 5).

Finally, the simulations reveal a $(0.4\text{--}0.6) \times 10^{-2}$ molar fraction of non-intentional impurity

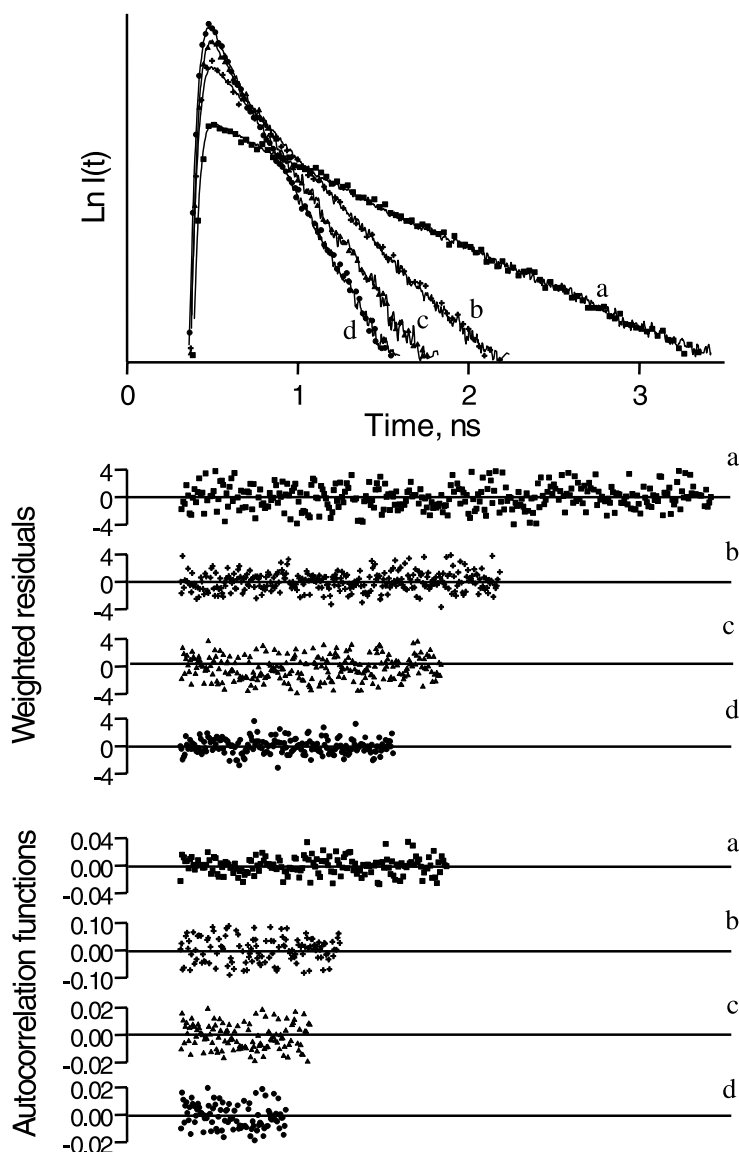


Fig. 4. Parametric fit of the experimental ZnTOPP fluorescence decays (—) with 0 (a, ■), 1×10^{-2} (b, +), 2×10^{-2} (c, ▲), and 3×10^{-2} (d, ●) molar fractions of CuTOPP; $\lambda_{\text{exc}} = 465$ nm; $\lambda_{\text{det}} = 580$ nm.

molecules, a more accurate number than could be determined by the analytical method [1].

6. Conclusions

- Monte Carlo simulation of the energy transfer processes in an undoped, self-organized

ZnTOPP film, using a physical model of its structure and excited state kinetics, has been demonstrated to be a successful method to extract the relevant kinetic parameters from the experimental complex fluorescence decay of the film. The simulated fluorescence decay nicely fits the experimental three-exponential fluorescence decay, with fast intra-stack and

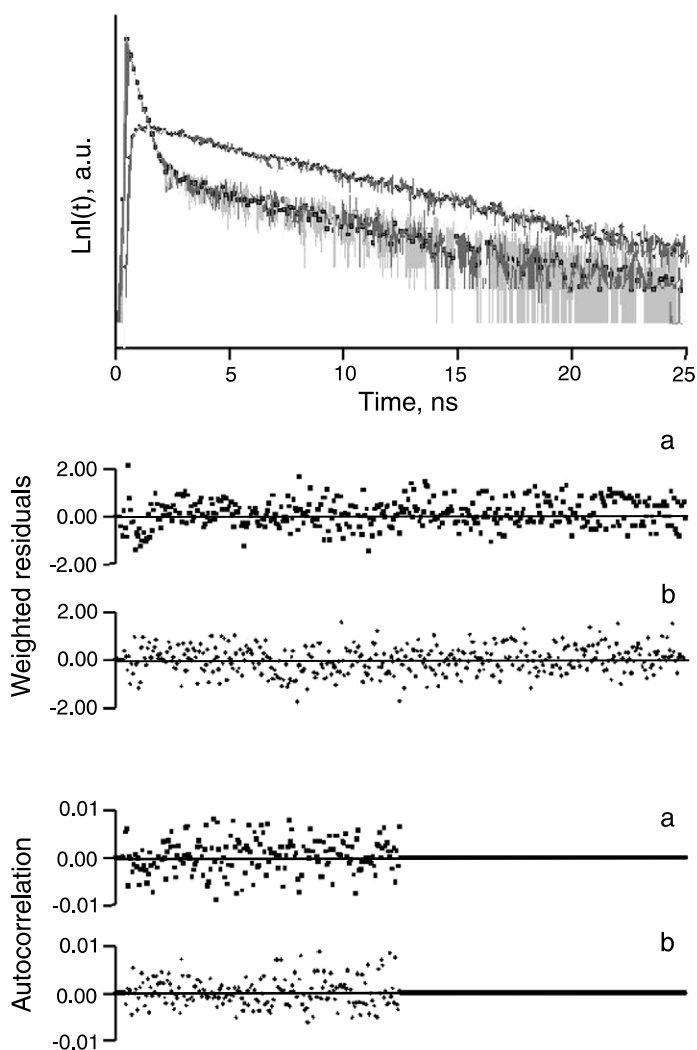


Fig. 5. Parametric fit of the experimental ZnTOPP fluorescence decays (—) for a 1×10^{-2} molar fraction of H₂TOPP; $\lambda_{\text{exc}} = 465$ nm; (a, ■): $\lambda_{\text{det}} = 580$ nm; (b, ●): $\lambda_{\text{det}} = 725$ nm.

much slower inter-stack energy transfer as the result.

- Notwithstanding the non-exponential experimental fluorescence decay the fluorescence lifetimes of 1.80–1.88 and 6.8–7.3 ns for ZnTOPP and H₂TOPP films, respectively, have been determined in a 95% confidence interval with quite good accuracy.
- The different rate constants for intra-stack and inter-stack energy transfer in the ZnTOPP film

of $(0.8\text{--}1.1) \times 10^{12}$ and $(71\text{--}91) \times 10^9 \text{ s}^{-1}$, respectively, as well as the molar fractions of intentional and non-intentional traps, obtained from the Monte Carlo simulations, support the results and conclusions of previous work [1].

- Generally, the reported method combining Monte Carlo simulation with simultaneous parameter fitting is not limited to the specific process or system as in this work. It is expected to

Table 1

Fluorescence lifetimes, molar fraction, ET parameters and corresponding 95% confidence intervals^a determined by MC simulation of experimental fluorescence decay of undoped, CuTOPP- and H₂TOPP-doped ZnTOPP films

System	λ_{det} (nm)	τ_{ZnP} ($\times 10^{-9}$ s)	N_{Imp} ($\times 10^{-2}$)	N_{CuP} ($\times 10^{-2}$)	$N_{\text{H}_2\text{P}}$ ($\times 10^{-2}$)	k^{Back} ($\times 10^6$ s ⁻¹)	$\tau_{\text{H}_2\text{P}}$ ($\times 10^{-9}$ s)	k_{ET}^{X} ($\times 10^{12}$ s ⁻¹)	k_{ET}^{Y} ($\times 10^9$ s ⁻¹)
Undoped ZnTOPP	580	1.80 [1.76;1.84]	0.6 [0.5;0.7]					1.1 [0.9;1.3]	71 [63;79]
ZnTOPP/ CuTOPP	580	1.81 [1.78;1.84]	0.5 [0.4;0.6]	1.0 [0.9;1.1] 2.0 [1.9;2.1] 3.0 [2.9;3.1]				0.9 [0.7;1.1]	81 [68;94]
ZnTOPP/ H ₂ TOPP	580	1.84 [1.82;1.86]	0.5 [0.4;0.6]		1.0 [0.9;1.1] 2.0 [1.9;2.1] 3.0 [2.9;3.1]	9.4 [6.0;12.8]	6.8 [6.5;7.1]	0.8 [0.6;1.0]	91 [71;111]
ZnTOPP/ H ₂ TOPP	725	1.88 [1.80;1.96]	0.4 [0.3;0.5]		1.0 [0.9;1.1] 2.0 [1.9;2.1] 3.0 [2.9;3.1]	8.8 [5.7;11.9]	7.3 [7.0;7.6]	1.0 [0.8;1.2]	71 [56;96]

^a Between square brackets.

be equally effective, when applied to other, more complex systems and/or different processes involving excited states, as long as an appropriate physical model can be constructed, which contains the essential parameters of the processes occurring in these systems.

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References

- [1] H. Donker, R.B.M. Koehorst, A. van Hoek, W. van Schaik, M.M. Yatskou, T.J. Schaafsma, *J. Phys. Chem. B* (in press).
- [2] B.A. Gregg, M.A. Fox, A.J. Bard, *J. Phys. Chem.* 93 (1989) 4227.
- [3] T.J. Schaafsma, *Sol. Energy Mater. Sol. Cells* 38 (1995) 349.
- [4] I. Leray, M.C. Vernières, R. Pansu, C. Bied-Charreton, J. Faure, *Thin Solid Films* 303 (1997) 295.
- [5] N. Kanayama, T. Kanbara, H. Kitano, *J. Phys. Chem. B* 104 (2000) 271.
- [6] M. Quillec (Ed.), *Materials for Optoelectronics*, Kluwer Academic Publishers, Boston, 1996.
- [7] S. Donati, *Photodetectors, Devices, Circuits and Applications*, Plenum Press, New York, 2000.
- [8] K.L. Chopra, S.R. Das, *Thin Film Solar Cells*, Plenum Press, New York, 1983.
- [9] E.K.L. Yeow, K.P. Giggino, J.H.N. Reek, M.J. Crossley, A.W. Bosman, A.P.H.J. Schenning, E.W. Meijer, *J. Phys. Chem. B* 104 (2000) 2596.
- [10] D. Markovitsi, A. Germain, P. Millié, P. Lécuyer, L.K. Gallos, P. Argyrakis, H. Bengs, H. Ringsdorf, *J. Phys. Chem.* 99 (1995) 1005.
- [11] N. Kometani, H. Nakajima, K. Asami, Y. Yonezawa, O. Kajimoto, *J. Phys. Chem. B* 104 (2000) 9630.
- [12] N. Kanayama, T. Kanbara, H. Kitano, *J. Phys. Chem. B* 104 (2000) 271.
- [13] N. Sato, S. Ito, K. Sugiura, M. Yamamoto, *J. Phys. Chem. A* 103 (1999) 3402.
- [14] L.M.S. Loura, M. Prieto, *J. Chem. Phys. B* 104 (2000) 6911.

- [15] B. Kalman, L.B.Å. Johansson, M. Lindberg, S. Engström, *J. Phys. Chem.* 93 (1989) 8371.
- [16] M.M. Yatskou, H. Donker, E.G. Novikov, R.B.M. Koehorst, A. van Hoek, V.V. Apanasovich, T.J. Schaafsma, *J. Phys. Chem. A* (in press).
- [17] L. Andrews, A. Demidov (Eds.), *Resonance Energy Transfer*, Wiley, New York, 1999.
- [18] A.D. Adler, F.R. Longo, F. Kampas, J. Kim, *J. Inorg. Nucl. Chem.* 32 (1970) 2443.
- [19] A.D. Adler, F.R. Longo, W.J. Shergalis, *Am. Chem. Soc.* 86 (1964) 3145.
- [20] A.J.W.G. Visser, P.A.W. van den Berg, N.V. Visser, A. van Hoek, H.A. van den Burg, D. Parsonage, A. Claiborne, *J. Phys. Chem. B* 102 (1998) 10431.
- [21] A. van Hoek, A.J.W.G. Visser, *Rev. Sci. Instrum.* 52 (1981) 1199.
- [22] Y. Shimizu, M. Miya, A. Nagata, K. Ohta, I. Yamamoto, S. Kusabayashi, *Liq. Cryst.* 14 (1993) 795.
- [23] Y. Shimizu, T. Higashiyama, T. Fuchita, *Thin Solid Films* 331 (1998) 279.
- [24] V.V. Apanasovich, E.G. Novikov, N.N. Yatskov, *Proc. SPIE* 2980 (1997) 495.
- [25] F.N. Chowdhury, Z.S. Kolber, M.D. Barkley, *Rev. Sci. Instrum.* 62 (1991) 47.
- [26] P.R. Bevington, *Data Reduction and Error Analysis for the Physical Sciences*, McGraw-Hill, New York, 1969.
- [27] N.C. Maiti, S. Mazumdar, N. Periasamy, *J. Phys. Chem.* 99 (1995) 10708.
- [28] P. López-Cornejo, S.M.B. Costa, *Langmuir* 14 (1998) 2042.
- [29] H.N. Fonda, J.V. Gilbert, R.A. Cormier, J.R. Sprague, K. Kamioka, J.S. Connolly, *J. Phys. Chem.* 97 (1993) 7024.