Comparison of the photophysical properties of various phenothiazine derivatives: transient detection and singlet oxygen production

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ELECTRONIC SUPPORTING INFORMATION

Section SI 01

Singlet oxygen detection. The analysis and quantification of $^1O_2$ by recording its phosphorescence emission signal[1,2] upon continuous monochromatic excitation of the photosensitizer provided the means for determining quantum yields of $^1O_2$ production (Φ_Δ) and rate constants of $^1O_2$ total quenching by the PS.[3–5] Under continuous irradiation of a PS, the quantum yield of $^1O_2$ emission is given by:

$$\Phi_e = \frac{P_e}{P_a} = \frac{CS_e}{P_0\alpha} \qquad \text{SI 01}$$

where C is a proportionality factor depending on the detection system and on specific parameters of the medium (refractive index, NIR absorbance), S_e is the $^1O_2$ signal intensity, P_0 and P_a are the incident photon flux and the photon flux absorbed by the PS ($P_a = P_0\alpha$), P_e is the photon flux emitted by singlet oxygen. α is the absorption factor with A, absorbance of the PS at the wavelength of excitation, given by:

$$\alpha = 1 - 10^{-A} \qquad \text{SI 02}$$

Φ_e may be also expressed as:

$$\Phi_e = \Phi_\Delta\, k_e\, \tau_\Delta \qquad \text{SI 03}$$

where

k_e (s^{-1}) is the rate constant of $^1O_2$ emission (negligible relative to the rate constant of quenching by the solvent in most solvents, $k_d >> k_e$),[6,7] and τ_Δ (s) is the singlet oxygen lifetime: in the absence of a quencher, $\tau_\Delta^0 = 1/\ k_d$. In ACN and CD_3OD, the two solvents used in this work, τ_Δ, is equal to 71[8] and 270[8,9] μs, respectively. In the presence of a quencher (Q), τ_Δ is given by:

$$\tau_\Delta = 1 \Big/ \left(k_d + k_t^Q[Q]\right) \qquad \text{SI 04}$$

where k_t^Q ($M^{-1}\ s^{-1}$) is the rate constant of total quenching by Q, given by the sum of the rate constants of physical quenching (k_q^Q) and chemical reaction (k_r^Q).

If the $^1O_2$ phosphorescence signals are recorded in the same solvent for the PS investigated and for a standard sensitizer of know $\Phi_\Delta{}^{R}$ (and negligible $^1O_2$ quenching: k_t^Q [Q] << k_d), the following relation is obtained by combining equations SI 01, 03 and 04 (with Q = PS):

$$\frac{S_e^R P_a^{PS}}{S_e^{PS} P_a^R} = \frac{\Phi_\Delta^R}{\Phi_\Delta^{PS}}\left(1+\tau_\Delta^0 k_t^{PS}[PS]\right) \qquad \text{SI 05}$$

It should be noted that α^{PS} and α^{R} (eq. SI 01) should not differ significantly, otherwise the geometry of the system and thus the factor C would be modified and the above relation (SI 05) would not hold.

The plot of $(S_e^R/S_e^{PS})(P_a^{PS}/P_a^R) = f([PS])$ should be linear and values of k_t^{PS} and $\Phi_\Delta^R/\Phi_\Delta^{PS}$ may be obtained from the slope and the intercept of this plot if the value of τ_Δ in the solvent used is known.

In the cases where $k_t^{PS}[PS] \ll k_d$ (negligible $^1O_2$ quenching by PS in the range of concentrations used), the quantum yield of singlet oxygen production of a PS in a given medium does not depend on the PS concentration (eq. SI 06).

$$\Phi_\Delta^{PS} = \Phi_\Delta^R \frac{S_e^{PS} P_a^R}{S_e^R P_a^{PS}} \qquad \text{SI 06}$$

The apparent values of Φ_Δ^{PS} ($\Phi_{\Delta app}^{PS}$) at given PS concentrations may be calculated from the ratio of the $^1O_2$ signal intensities (eq. SI 07).

$$\Phi_{\Delta,app}^{PS} = \Phi_\Delta^R \frac{S_e^{PS} P_a^R}{S_e^R P_a^{PS}} = \frac{\Phi_\Delta^{PS}}{1+\tau_\Delta k_t^{PS}[PS]} \qquad \text{SI 07}$$

In the cases where $k_t^{PS}[PS] \ll k_d$ (negligible $^1O_2$ quenching by the PS in the range of concentrations used), the ratio S_e^R/S_e^{PS} does not depend on the PS concentration and the quantum yield of $^1O_2$ production by the PS is equal to $\Phi_{\Delta app}^{PS}$.

The $^1O_2$ emission signals were measured at various absorbances Perinaphthenone (**PN**) that has high Φ_Δ value in a large variety of solvents, was used as standard sensitizer and was excited at 367nm.[10,1,11,12] **RB** was selected as a reference in CD_3OD (Φ_Δ = 0.76, λ_{ex} = 547 nm)[10,9] in order to minimize errors due to the irradiation of R and PS at different wavelengths.

The equipment used to monitor the *$^1O_2$ luminescence at 1270 nm upon continuous monochromatic excitation* of the PS has been custom-built and described elsewhere.[5] A cooled (-80 °C) NIR photomultiplier (Hamamatsu R5509 PMT) was used as a $^1O_2$ phosphorescence detector. The solutions containing the different PSs were irradiated at 367 nm or 547 nm with a Xe-Hg arc lamp (1 kW) through a water filter, focusing optics and a monochromator. Singlet oxygen luminescence signals were registered during a minimum of three minutes. The experimental results were the average of two to three independent series of measurements. Absorption spectra were recorded before and after irradiation on UV-Vis spectrophotometer (Hewlett-Packard 8453) to detect any sensitizer bleaching during irradiation. The incident radiant powers (W / mW) at the wavelengths of irradiation were measured using a thermopile (Laser Instrumentation, model 154): values of approx. 3.5 mW and 1.8 mW were measured at 367 nm and 547 nm, respectively.

Quantum yields of singlet oxygen production of **MV** and **NMB**$^+$ in ACN were also determined by $^1O_2$ trapping by a selective probe for singlet oxygen. The relationship between the Φ_Δ of a given PS and the rate of probe consumption is given by the following equation:

$$-\frac{\mathrm{d}[\mathrm{Q}]}{\mathrm{d}t} = P_\mathrm{a}\Phi_\Delta^\mathrm{PS}\frac{k_\mathrm{r}[\mathrm{Q}]}{k_\mathrm{d} + k_\mathrm{t}^\mathrm{PS}[\mathrm{PS}] + k_\mathrm{t}^\mathrm{Q}[\mathrm{Q}]} \qquad \text{SI 08}$$

with all the parameters described above. Rubrene selectively reacts with singlet oxygen and was used as a chemical probe.[13–19] The experimental set-up and the kinetics data concerning rubrene photosensitized oxygenation by singlet oxygen addition have already been described.[20] k_t^PS data were obtained by luminescence experiments and applied to the calculations for indirect $^1O_2$ detection.

3 mL solutions (fluorescence quartz cells) containing both the PS and rubrene, magnetically stirred at 25 °C, were irradiated with a 200W Xe-Hg Lamp; a Cornerston 260 motorized monochromator was used to select the irradiation wavelength (585 nm for **MV** and 620 for **NMB**$^+$). A Perkin Elmer double beam, double monochromator Lambda850 UV-Vis spectrometer was used for the analysis. The quartz cells were positioned directly on the support of the spectrophotometer: the decrease of rubrene absorbance was followed while irradiation took place (light source perpendicular to the analytical beam). The values of the photon flux absorbed by the PS (P_a, Einsteins $\mathrm{L}^{-1}\ \mathrm{s}^{-1}$) were calculated using eq. 8:[21] the absorbance of the PSs (A) was measured spectrophotometrically, P_0 with an International Light ILT900 spectroradiometer.

$$\sum_\lambda P_{\mathrm{a},\lambda} = \sum_\lambda P_{0,\lambda}\left(1 - 10^{-\mathrm{A}_\lambda}\right) \qquad \text{SI 09}$$

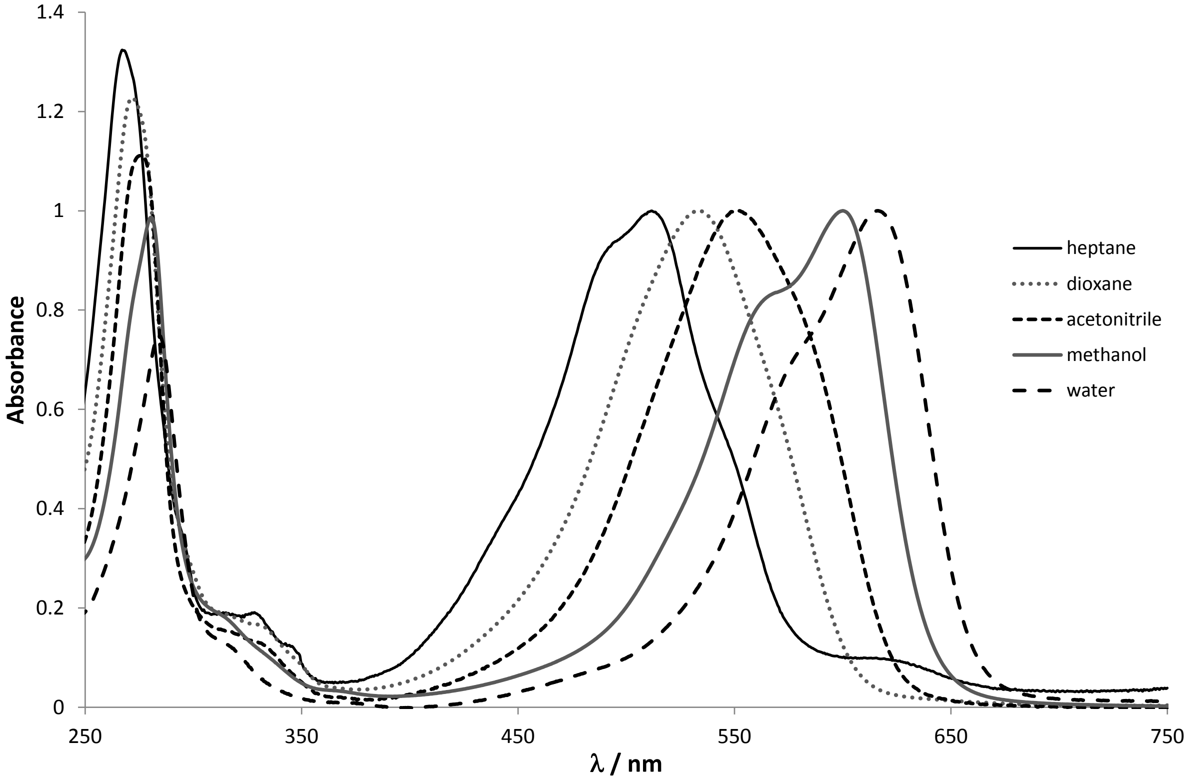

Figure SI 1 Normalized absorption spectra of **MV** in various solvents: *n*-heptane (black solid line), dioxane (grey dotted line), acetonitrile (black dashed line), methanol (grey solid line) and water (black dashehd line). Air-equilibrated solutions at room temperature.

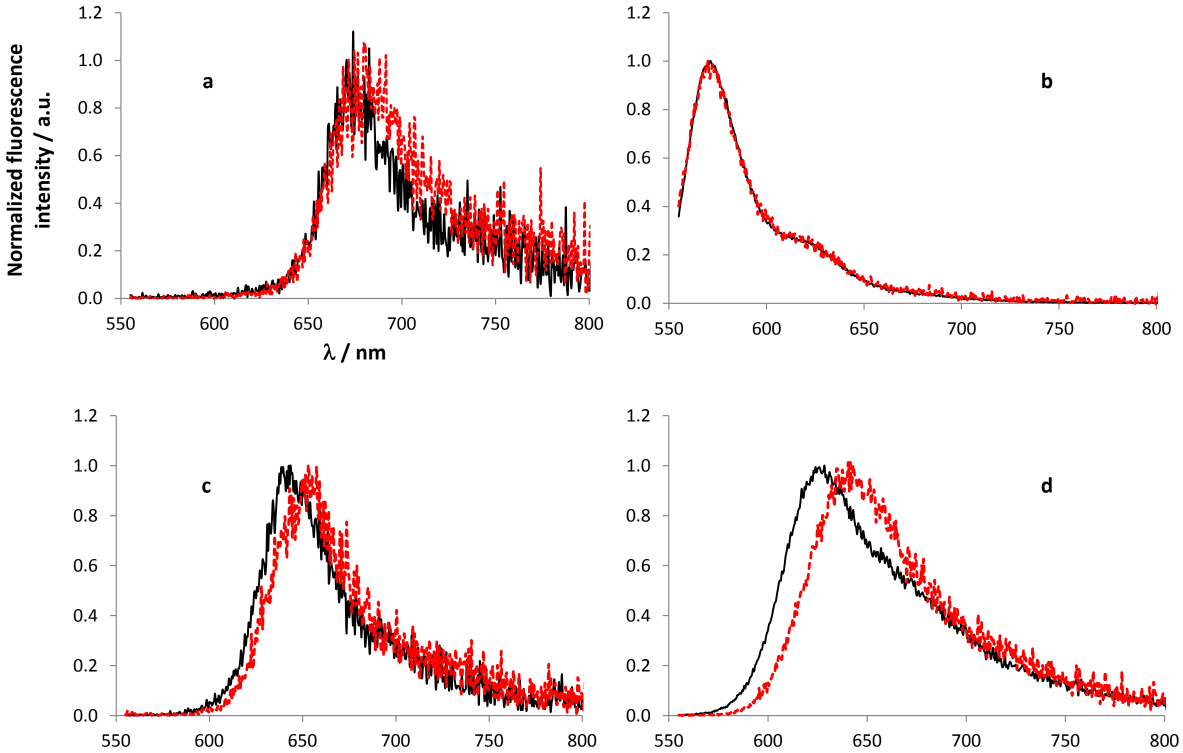

Figure SI 2 Fluorescence emission spectra (λ_{ex} = 550 nm) of **MB**$^+$ (a), **RB** (b), **NMB**$^+$ (c) and **MV** (d) in air-equilibrated MeOH (red dashed lines) and ACN (black solid lines).

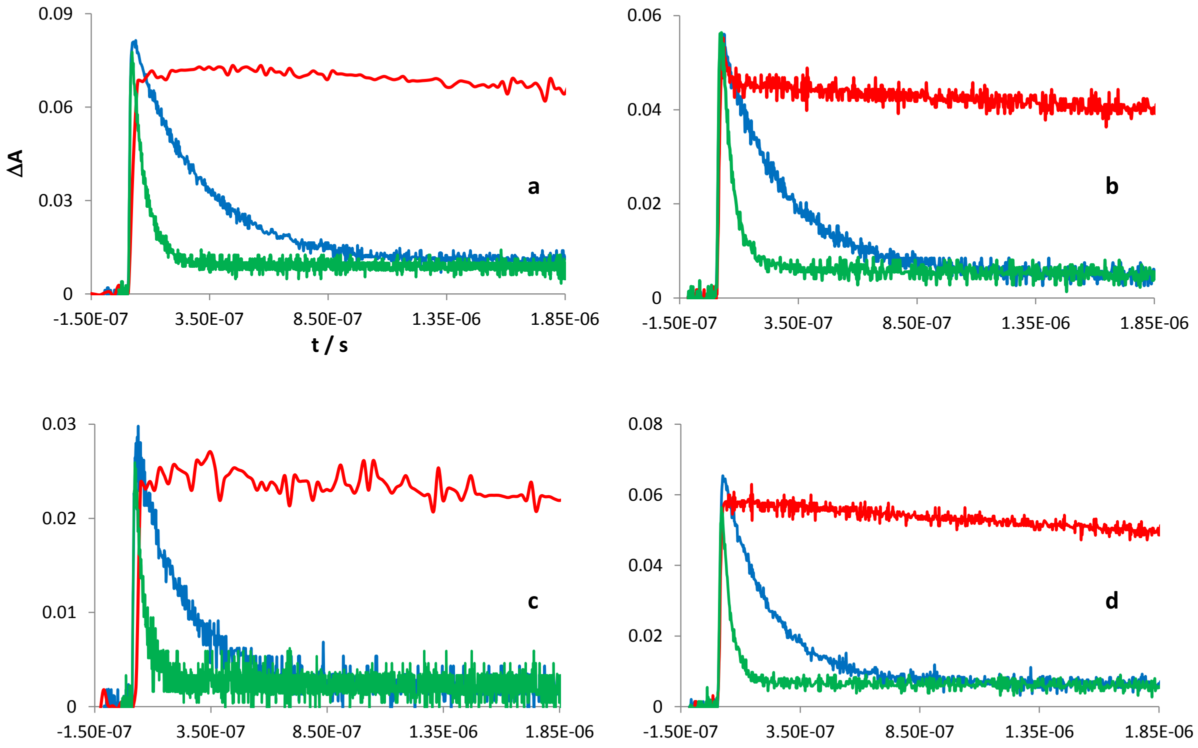

Figure SI 3 Decays of the transient absorption of **MB**$^+$ in ACN (a), **NMB**$^+$ in MeOH (b), **MV** in ACN (c) and MeOH (d) in Ar-saturated (red), air-equilibrated (blue) and oxygen-saturated (green) solutions.

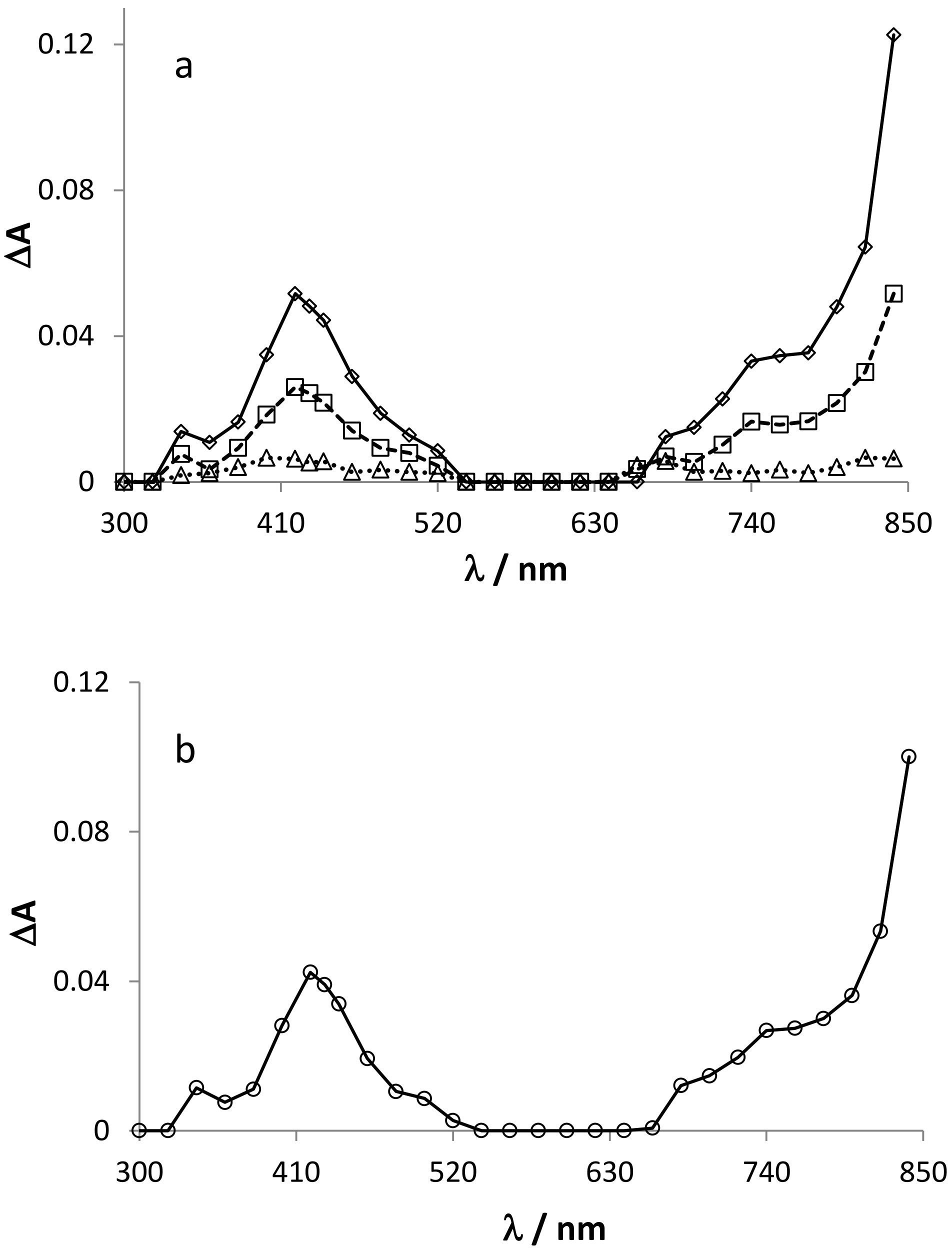

Figure SI 4 Time-evolution ((50 ns, diamonds, 250 ns, squares, and 1 μs, triangles, after the laser pulse end) of the transient spectrum obtained by laser flash photolysis of N**MB**$^+$ (1.5 × 10^{-5} M) in air-equilibrated MeOH (a) and Ar-saturated MeOH (b, 1 μs after the laser pulse).

1. C. Martí, O. Jürgens, O. Cuenca, M. Casals, and S. Nonell, *J. Photochem. Photobiol., A*, 1996, **97**, 11 – 18.
2. A. M. Braun and E. Oliveros, *Pure Appl. Chem.*, 1990, **62**, 1467–1476.
3. T. Aminian-Saghafi, G. Nasini, T. Caronna, A. M. Braun, and E. Oliveros, *Helv. Chim. Acta*, 1992, **75**, 531–538.
4. A. H. Thomas, C. Lorente, A. L. Capparelli, C. G. Martinez, A. M. Braun, and E. Oliveros, *Photochem. Photobiol. Sci.*, 2003, **2**, 245–250.
5. F. M. Cabrerizo, M. Laura Dántola, G. Petroselli, A. L. Capparelli, A. H. Thomas, A. M. Braun, C. Lorente, and E. Oliveros, *Photochem. Photobiol.*, 2007, **83**, 526–534.
6. R. D. Scurlock, S. Nonell, S. E. Braslavsky, and P. R. Ogilby, *J. Phys. Chem.*, 1995, **99**, 3521–3526.
7. L. A. Martinez, C. G. Martínez, B. B. Klopotek, J. Lang, A. Neuner, A. M. Braun, and E. Oliveros, *J. Photochem. Photobiol., B*, 2000, **58**, 94 – 107.
8. F. Wilkinson, W. P. Helman, and A. B. Ross, *J. Phys. Chem. Ref. Data*, 1995, **24**, 663.
9. C. Tournaire, S. Croux, M.-T. Maurette, I. Beck, M. Hocquaux, A. M. Braun, and E. Oliveros, *J. Photochem. Photobiol., B*, 1993, **19**, 205–215.
10. F. Wilkinson, W. P. Helman, and A. B. Ross, *J. Phys. Chem. Ref. Data*, 1993, **22**, 113–262.
11. J. Arnbjerg, M. J. Paterson, C. B. Nielsen, M. Jørgensen, O. Christiansen, and P. R. Ogilby, *J. Phys. Chem. A*, 2007, **111**, 5756–5767.
12. R. Schmidt, C. Tanielian, R. Dunsbach, and C. Wolff, *J. Photochem. Photobiol., A*, 1994, **79**, 11 – 17.
13. J. Y. Kim, D. S. Choi, and M. Y. Jung, *J. Agric. Food Chem.*, 2003, **51**, 3460–3465.
14. J. I. Kim, J. H. Lee, D. S. Choi, B. M. Won, M. Y. Jung, and J. Park, *Journal of Food Science*, 2009, **74**, C362–C369.
15. T. N. Singh-Rachford and F. N. Castellano, *J. Phys. Chem. A*, 2008, **112**, 3550–3556.
16. K. K. Chin, S.-C. Chuang, B. Hernandez, M. Selke, C. S. Foote, and M. A. Garcia-Garibay, *J. Phys. Chem.*, 2006, **110**, 13662–13666.
17. M. Neumann, M. Hild, and H.-D. Brauer, *Ber. Bunsen Phys. Chem.*, 1998, **102**, 999–1001.
18. B. F. Sels, D. E. De Vos, P. J. Grobet, F. Pierard, F. Kirsch-De Mesmaeker, and P. A. Jacobs, *J. Phys. Chem. B*, 1999, **103**, 11114–11123.
19. H. Nakazumi, H. Shiozaki, and T. Kitao, *Chem. Lett.*, 1989, **18**, 1027–1030.
20. F. Ronzani, E. Arzoumanian, S. Blanc, P. Bordat, T. Pigot, C. Cugnet, E. Oliveros, M. Sarakha, C. Richard, and S. Lacombe, *Phys. Chem. Chem. Phys.*, **in press**.
21. P. A. Hoijemberg, A. Chemtob, C. Croutxé-Barghorn, J. Poly, and A. M. Braun, *Macromolecules*, 2011, **44**, 8727–8738.