Supporting information

Bactericidal nanofabrics based on photoproduction of singlet oxygen

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Experimental Details

Materials

Polyurethane (PUR): Larithane LS 1086^{TM}, $M_W \approx 50\,000$, aliphatic elastomer based on 2000 M_W linear polycarbonated diol, isophorone diisocyanate and extended isophorone diamine), Novotex, Italy;
Tetraethylammonium bromide (TEAB), 9,10-antracenediyl-bis(methylene)dimalonic acid, all Fluka;
5,10,15,20-tetraphenylporhyrin (TPP), Porphyrin Systems, Germany;
5-bromo-4-chloro-3-indolyl-β-D-galactopyranoside (X-gal, Invitrogen, CA, USA);
Bacteria DH5α (Invitrogen, CA, USA);
Plasmid pGEM11Z (Promega, WI, USA);
Uric acid, tryptophan, N,N-dimethylformamide (DMF), sodium dodecyl sulfate (SDS), D_2O, KI, NaN_3 and other inorganic salts, all Aldrich, were used as received.

Preparation of nanofabrics

The nanofiber layers were produced using an electrospinning device (Figure S1) consisting of a roller immersed in a tank containing a polymer solution in DMF. A polypropylene spun-bond textile moves along a grounded counter-electrode and serves as the supporting textile for the continuous nanofiber layer. The area weight of the nanofiber layer (*ca.* 2 g/m^2) is easily controlled by linear velocity of the supporting material (18 g/m^2).

The nanofiber layers were prepared using following solutions:
i) 15 % PUR, 1.2 % TEAB in DMF (porphyrin-free nanofibers)
ii) 15 % PUR, 1.2 % TEAB, 0.12 % TPP in DMF
iii) 15 % PUR, 1.2 % TEAB, 0.12 % TPP, 0.6 % SDS in DMF

Methods

The UV/VIS absorption spectra were measured on a Unicam 340 and Perkin Elmer Lambda 35 spectrometers. The fluorescence emission spectra were recorded using a Perkin Elmer LS 50B luminescence spectrophotometer. All fluorescence spectra were corrected for the characteristics of the detection monochromator and photomultiplier using a recently described procedure (Gardecki, J. A.; Maroncelli, M. *Appl. Spectroscopy* **1998**, *52*, 1179).

Time-resolved photophysical measurements

Laser flash photolysis experiments were performed with a Lambda Physik FL 3002 dye laser (425 nm, output energy 0.1-3 mJ/pulse, pulse width ~ 28 ns). The time profiles of the porphyrin triplet states were probed at 460 nm using a 250 W Xe lamp equipped with a pulse unit and a R928 photomultiplier. The recorded time profiles were analyzed by nonlinear least-squares fitting procedure giving the lifetime of the triplet states τ_T under conditions used. The formation of singlet oxygen was followed using time-resolved near-infrared emission at 1270 nm. The emission was monitored with a germanium diode (Judson J16-8SP-R05M-HS, USA) after being selected by a 1270 nm band-pass filter (Laser Components, Olching, Germany). The lifetime of $^1O_2$ was calculated from the averaged kinetic traces using the simplified fitting function with τ_Δ and A ($\sim \Phi_\Delta$) as free parameters

$$S(t) = A \frac{\tau_\Delta}{\tau_T - \tau_\Delta} (\exp(-t/\tau_T)-\exp(-t/\tau_\Delta)),$$

where τ_T and τ_Δ are lifetimes of the triplet states and of $O_2(^1\Delta_g)$, respectively. Delayed fluorescence was monitored at 650 nm that is the maximum of the monomer fluorescence emission band. All traces were accumulated 20 - 500 times to improve the signal-to-noise statistics. Where appropriate, the experiments were performed in argon or oxygen atmosphere and in argon-, air- or oxygen-saturated solutions.

Continuous irradiation experiments

A piece of the porphyrin-doped nanofabric was peeled off from the polypropylene supporting textile and placed into a thermostatted 10 mm quartz cell (22 °C) containing an aqueous solution of a substrate (0.1M I^-, 10^{-4} M, 9,10-antracenediyl-bis(methylene)dimalonic acid, 2.25×10^{-4} M uric acid). The cell was irradiated by a 300W stabilized halogen lamp under continuous stirring. The UV/VIS absorbance changes due to the formation of an oxidized substrate were recorded in regular time intervals and compared with those of a blank solution of the same composition kept in the dark.

A piece of the porphyrin-doped nanofabric was peeled off from the polypropylene supporting textile and placed on X-gal bacterial agar plates inoculated with bacteria *Escherichia coli* DH5α containing plasmid pGEM11Z producing β-galactosidase. The agar plates were either illuminated with cold white light from a 150W halogen bulb for 60 minutes, or kept in the dark. The plates were then incubated overnight in the dark at 37ºC to allow individual bacteria to grow and form visible blue-green colonies. Blue-green color of the colonies was due to an indolyl dye produced from X-gal substrate (5-bromo-4-chloro-3-indolyl-β-D galactopyranoside) by the bacterial β-galactosidase.

Figure S1. Electrospinning device. 1 – tank with polymer solution, 2 – polymer solution, 3 – rotating spinning roller (charged), 11 – polymer solution inlet, 12 – polymer solution outflow, 40 – grounded electrode, 5 – cover, 6 – vacuum duct, 90 – air duct, 9 – air, 20 – flying nanofibers, 72 – polypropylene spun-bond supporting material, 81 – unwinding, 82 – take-up mechanism.

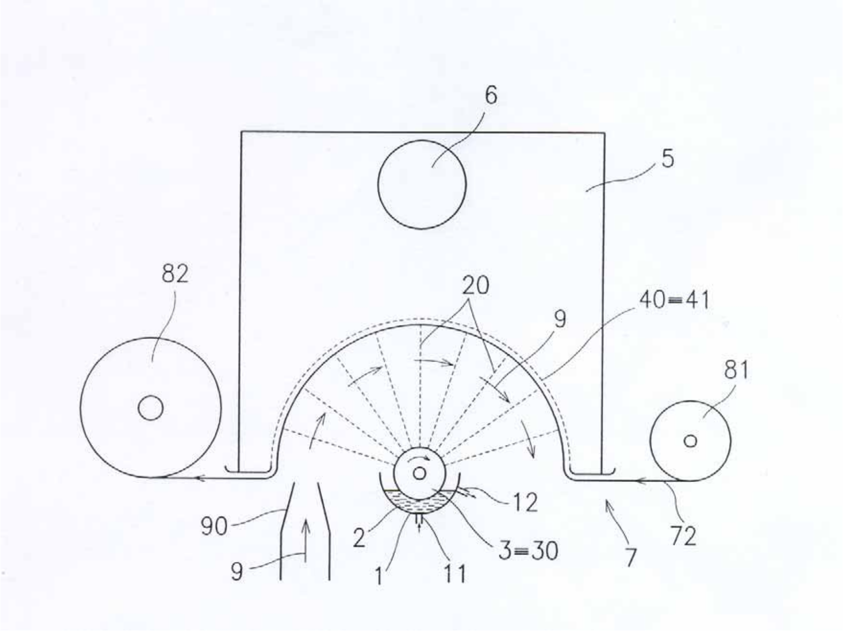

Figure S2. Time-resolved absorption of the triplet states of **2** monitored at 460 nm in the given atmosphere (λ_{exc}= 425 nm, average of 20 traces)

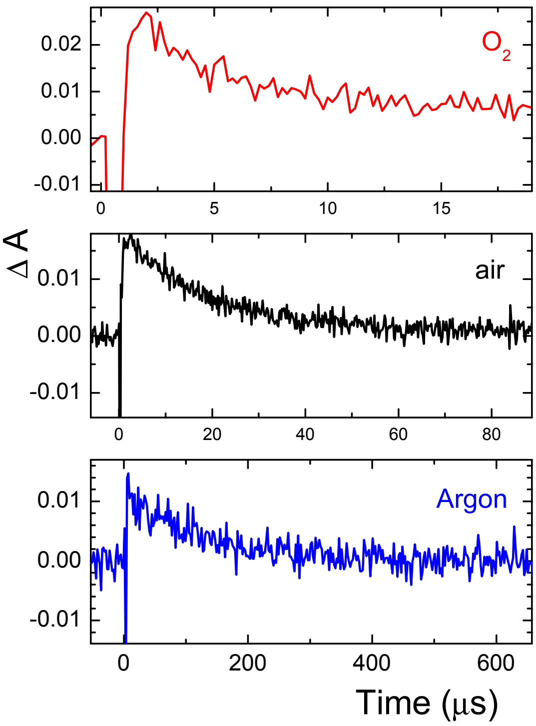

Figure S3. Linear dependence of the rate constants k_{O2} of the triplet states in **2** on partial pressure of oxygen p_{O2}. The straight line gives the bimolecular rate constant of 2.5 s^{-1} Pa^{-1}.

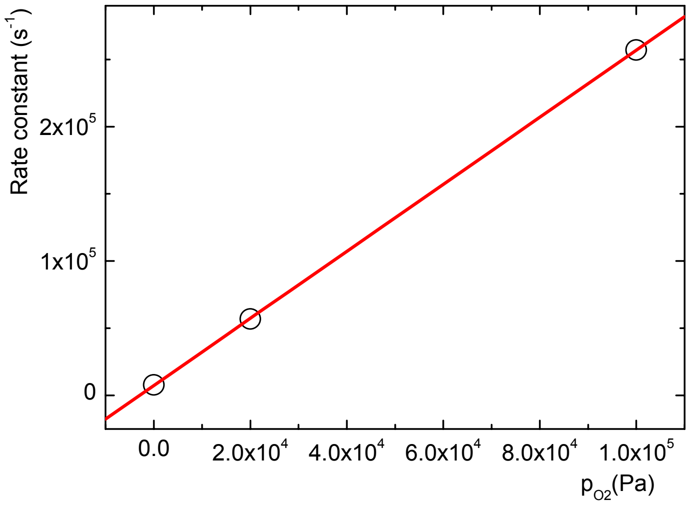

Figure S4. Time-resolved luminescence of $^1O_2$ generated by irradiation of **2** in air atmosphere (λ_{exc}= 425 nm, average of 20 traces), and after immersing **2** into H_2O, D_2O and 10^{-2} M NaN_3 (a). Typical fitting curves of singlet oxygen luminescence (b) and triplet states (c) in air-saturated H_2O.

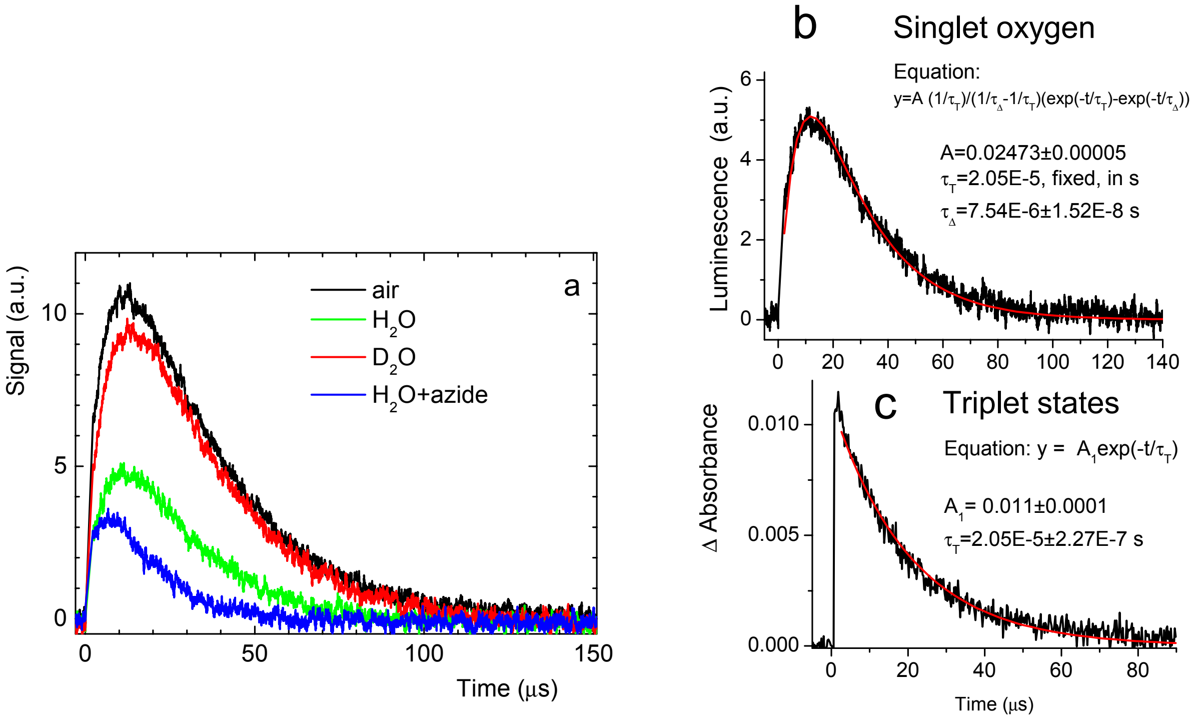

Figure S5. Time-resolved delayed fluorescence of **2** at 650 nm as a function of partial pressure of oxygen p_{O2}. In argon atmosphere only prompt fluorescence (τ_f ~ 10 ns) was detected (black line). The amplitude of delayed fluorescence increases with oxygen content whereas the lifetime decreases. The nanofabric **2** was irradiated by a Lambda Physik FL3002 dye laser (425 nm, fwhm 28 ns, energy 1.1 mJ/pulse).

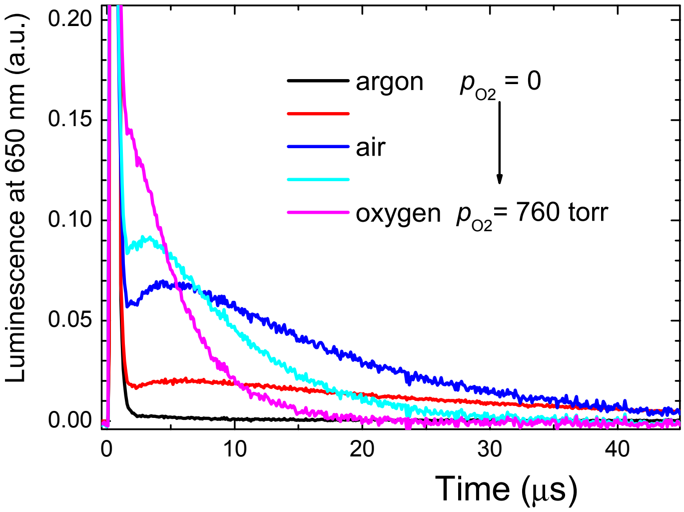

Figure S6. Absorption changes of 3 ml of air-saturated aqueous solution of 0.1M I^- containing a piece of **1** (1 cm^2) during continuous irradiation for 60 min by a stabilized 300W halogen lamp at 22°C. The increasing bands at 287 and 351 nm correspond to photoproduced I_3^-. The amount of I_3^- is directly proportional to the concentration of $O_2(^1\Delta_g)$. Inset: Concentration of I_3^-, expressed by absorbance at 351 nm, produced by irradiation of air-saturated (a) and oxygen-free (b) iodide solutions.

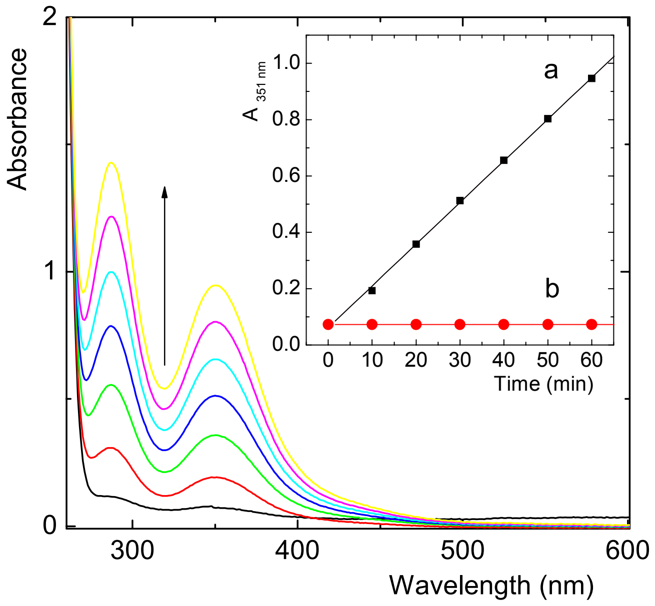

Figure S7. Photodegradation of uric acid during 60 min irradiation of 3 ml of 2.25×10^{-4} mol l^{-1} uric acid containing a piece of **1** (1 cm^2) by a stabilized 300W halogen lamp at 22°C. The arrows indicate the course of photooxidation. Air-saturated 0.02 mol l^{-1} phosphate buffer, pH = 7.0. Inset: Comparison of actual concentrations of uric acid in air- (a) and argon-saturated (b) solutions during irradiation.