

SUPPORTING INFORMATION

Development of phthalocyanine functionalised TiO₂ and ZnO nanofibers for photodegradation of Methyl Orange

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1. Instrumentation

Solid state spectra were measured on a Perkin-Elmer Lambda 950 UV-vis spectrophotometer. X-ray powder diffraction (XRD) patterns were recorded on a Bruker D8 Discover equipped with a LynxEye detector (proportional counter), using Cu Ka radiation ($\lambda = 1.5405 \text{ \AA}$, nickel filter) as described before [1]. FT-IR spectra were acquired using a Bruker® ALPHA FT-IR spectrometer with universal attenuated total reflectance (ATR) sampling accessory. The morphologies of the electrospun nanofibers were examined using a scanning electron microscope (SEM, JOEL JSM 840 scanning electron microscope) at an accelerating voltage of 20 kV.

Nitrogen adsorption/desorption isotherms were carried out at 77 K using a Micrometrics aSaP 2020 Surface area and Porosity analyzer. Prior to each measurement, degassing was carried out for 24 hours. The Brunauer–Emmett–Teller (BET) method was employed to determine surface area and porosity. The BET surface area and total pore volume were calculated from the isotherms obtained. The details of the setup have been previously described [1].

The electrospun fibers were obtained from an electrospinning setup consisting of a high voltage source (Glassman High Voltage. Inc.m series, 0-40 kV), a pump (Kd

Scientific, KDS-100-CE) and a plastic syringe equipped with a steel needle with a diameter of a 0.60 mm. Calcination of the nanofibers was conducted in a Labotec Precision Furnace (SNOL 3/1100).

Irradiation experiments were carried out from a halogen lamp (300 W, 120 V) with no cut off or interference filters placed in the light path before the reaction vessel (which was a glass vial). The light intensities were measured with a POWER MAX 5100 (Molelectron detector incorporated) power meter and were found to be 3.2×10^{19} photons/cm² s.

2. Calculations

2.1 Singlet oxygen quantum yield

For the determination of Φ_{Δ} of Pcs anchored on the fiber, the direct chemical method described before [2] was employed due to lack of standards. The studies were carried out in an aqueous solution, using ADMA as a chemical quencher for singlet oxygen in aqueous media. The modified fiber was suspended in the solution containing ADMA, and irradiated using the photolysis setup described above. The extinction coefficient of ADMA in water ($\epsilon = 12589$ at 380 nm [3]) was used.

First, the quantum yield of ADMA (Φ_{ADMA}) was calculated using equation (S1),

$$(\Phi_{ADMA}) = \frac{(C_o - C_t)V_R}{I_{Abs} \cdot t} \quad (\text{S1})$$

where C_o and C_t are the ADMA concentrations prior to and after irradiation, respectively; V_R is the solution volume; t is the irradiation time per cycle and I_{abs} is defined by equation (S2).

$$I_{Abs} = \frac{\alpha \cdot A \cdot I}{N_A} \quad (\text{S2})$$

where, $\alpha = 1 - 10^{-A(\lambda)}$; ($A(\lambda)$ is the absorbance of the sensitizer at the irradiation wavelength), A is the irradiated area (2.5 cm^2), I is the intensity of light 3.20×10^{16} photons/ $\text{cm}^2 \text{ s}$ and N_A is the Avogadro's constant. The singlet oxygen quantum yields (Φ_Δ) were calculated using equation (S3).

$$\frac{1}{\Phi_{ADMA}} = \frac{1}{\Phi_\Delta} + \frac{1}{\Phi_\Delta} \cdot \frac{k_d}{k_a} \cdot \frac{1}{[ADMA]} \quad (\text{S3})$$

where k_d is the decay constant of singlet oxygen and k_a is the rate constant for the reaction of ADMA with $^1\text{O}_2$ ($^1\Delta_g$). The Φ_Δ can be obtained from the intercept obtained from the plot of $1/\Phi_{ADMA}$ versus $1/[ADMA]$.

2.2 Photostability studies

The photodegradation quantum yield of complex **1** was calculated using equation (S4) as explained before [4]:

$$\Phi_{Pd} = \frac{(C_o - C_t) \times V \times N_A}{I_{abs} \times S \times t} \quad (\text{S4})$$

Where C_o and C_t in mol dm^{-3} are the concentrations of Pc in DMSO before and after irradiation, respectively. V is the volume of the Pc solution, S is the irradiated cell area (2.0 cm^2), t is the irradiation time, N is the Avogadro's number and I_{abs} is the overlap integral of the radiation source intensity and the absorption of the sample in the region of the interference filter transmittance.

3. Results

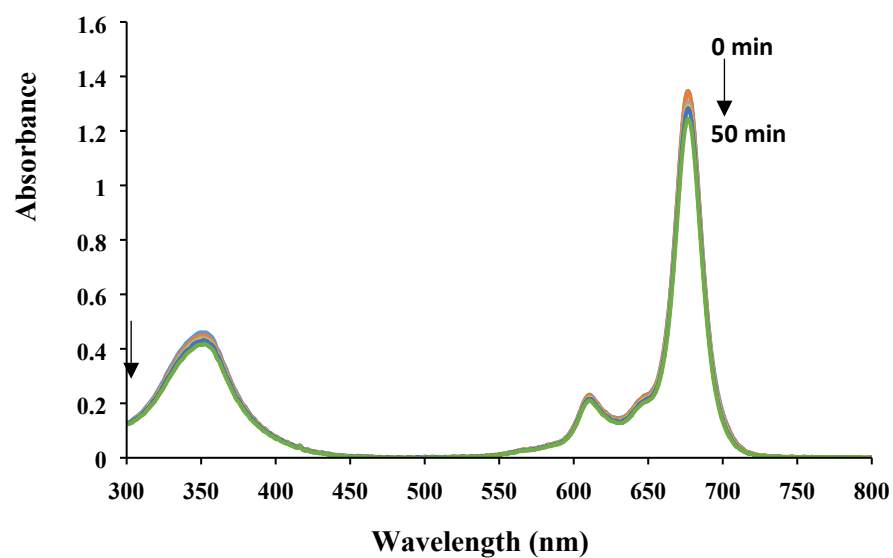


Fig. S1 Absorption spectral changes taken at 10 minute irradiation intervals during the determination of the photostability of complex **1** in DMSO.

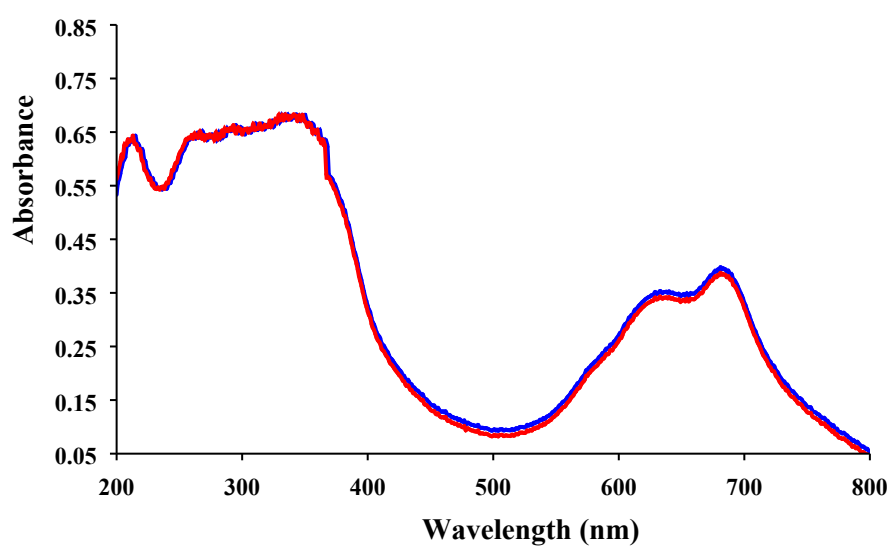


Fig. S2 Solid state UV-vis spectra of fresh (blue) and used (red) 1-TiO₂ nanofibers.

4. References:

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