Supporting Information

Polystyrene-Bound Thioxanthone – A Heterogenous Photocatalyst for Alcohol Oxidation via Singlet Oxygen Production

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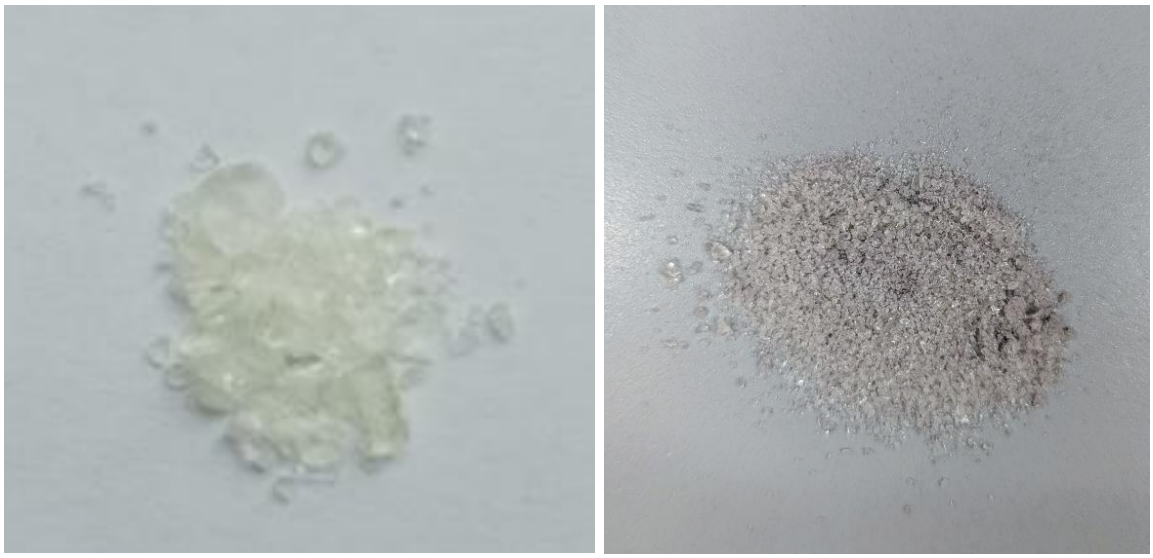
Photos of Reference Polystyrene Systems



Scheme S1. Photograph of polystyrene (left) and polystyrene heated in sulfuric acid at 65° C for 3 hours (right) rationalizing that the colour change in **TX@PS** is due to the formation of covalently bound thioxanthone moieties

ATR-IR Spectra

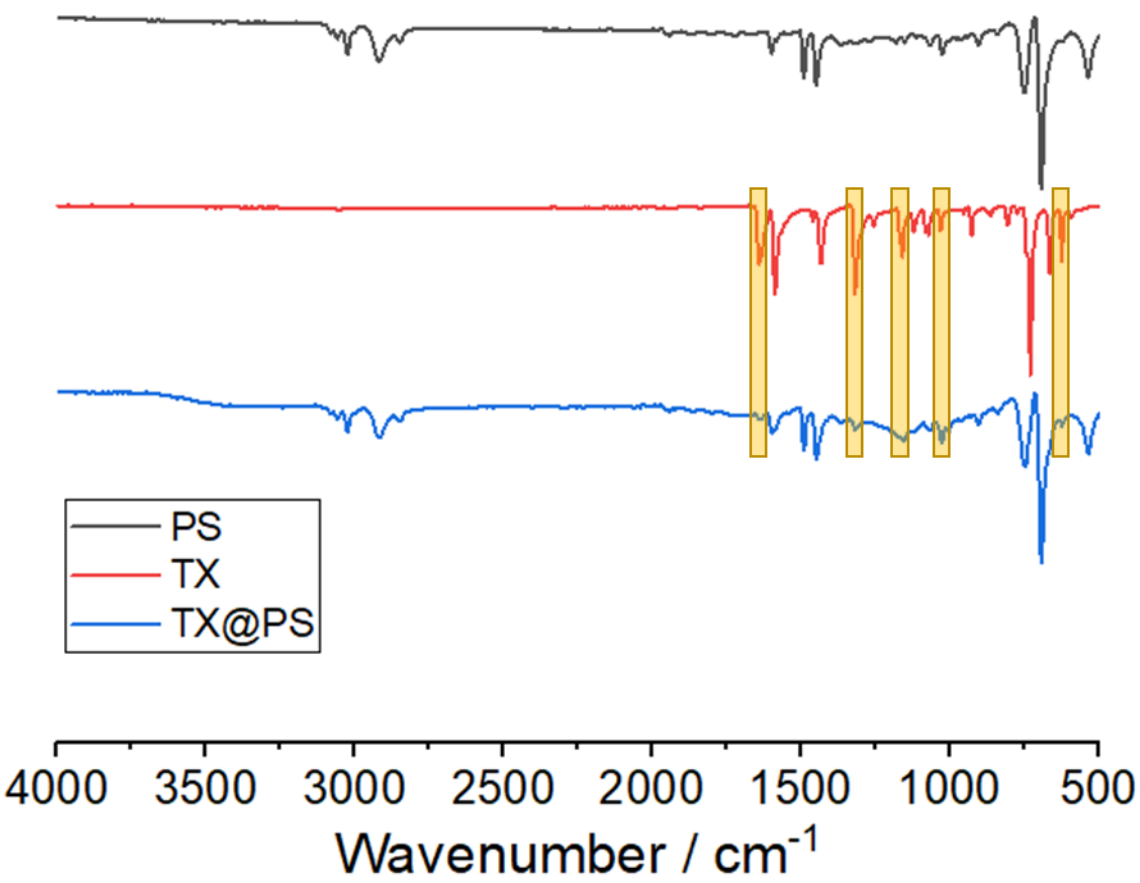


Figure S1. FT-IR of **PS** (black), **TX** (red) and **TX@PS**; all spectra were recorded in solid state in reflectance mode – yellow lines indicate characteristic vibrations corresponding to **TX** rationalizing the formation of photo-active moieties on the PS backbone

^{1}H NMR Spectra

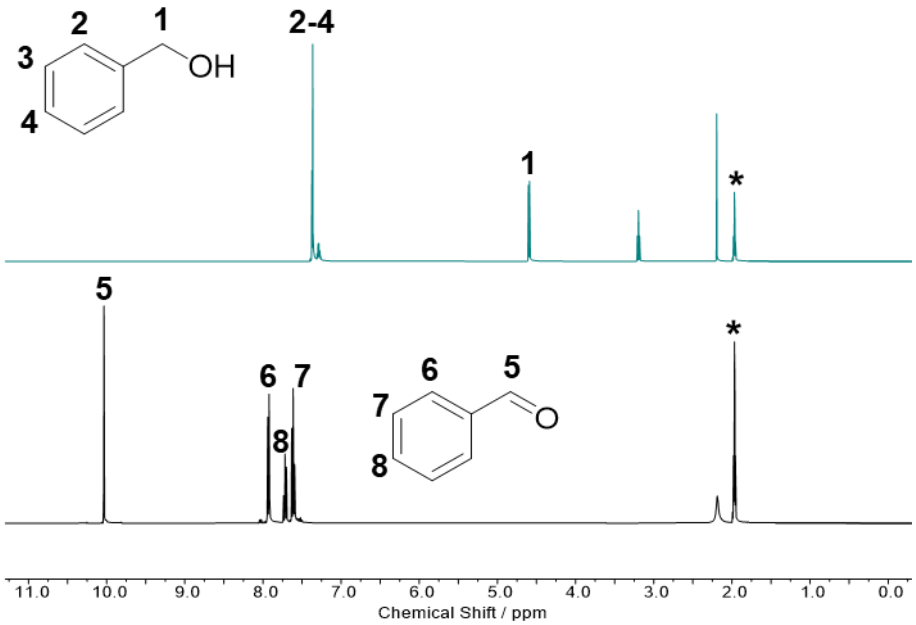


Figure S2. Refence ^{1}H-NMR spectra and signal assignment of benzyl alcohol (top; signals labelled 1-4) and benzaldehyde (bottom, signals labelled 5 - 8) in CH_3CN-d_3; the solvent peak is denoted by an asterisk

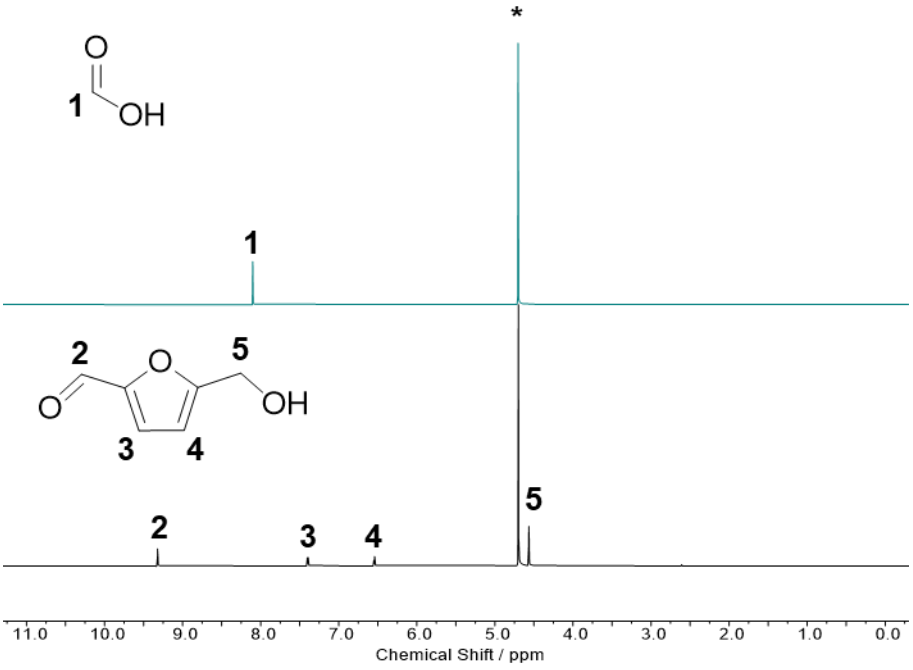


Figure S3. Refence ^{1}H-NMR spectra and signal assignment of formic acid (top, signal labelled 1) and 5-HMF (bottom, signals labelled 2-5) in H_2O-d_2; the solvent peak is denoted by an asterisk

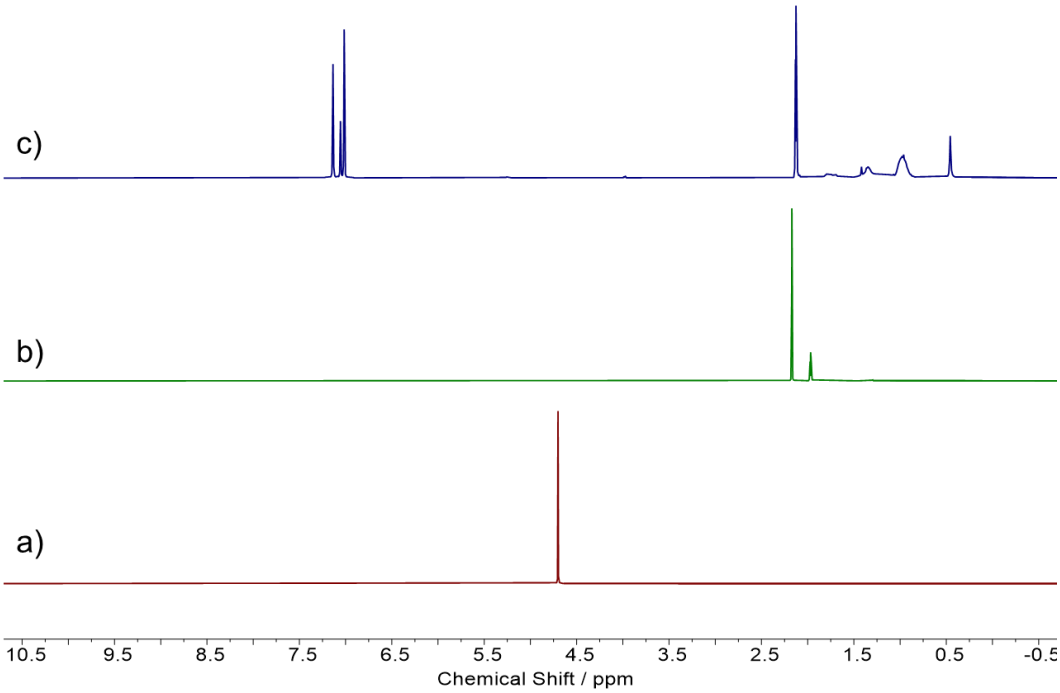


Figure S4. ^{1}H-NMR spectra of **TX@PS** after storage in a) H_2O-d_2, b) CH_3CN-d_3 or c) toluene-d_8 at 70°C for 24 h; in H_2O-d and CH_3CN-d_3, only solvent peaks are detected, rationalizing the stability of **TX@PS,** whilst in new peaks are detected, indicating that **TX@PS** is not stable under these experimental conditions

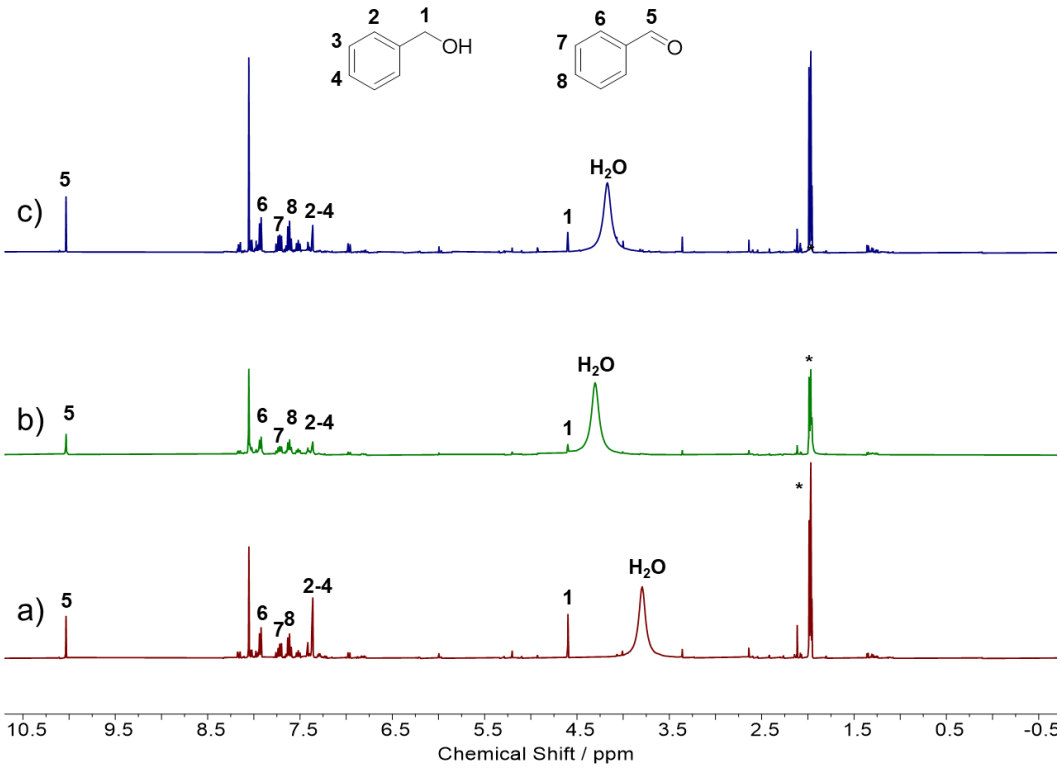


Figure S5. ^{1}H-NMR spectra of **TX@PS** in the presence of benzyl alcohol upon irradiation (18h, 405 nm) with a) fresh catalyst, b) re-used catalyst (once) or c) re-used catalyst (twice); signals labelled 1 – 4 correspond to the educt benzyl alcohol, signals labelled 5 – 8 correspond to the product benzaldehyde; spectra were recorded in CH_3CN-d_3; the solvent peak is denoted by an asterisk

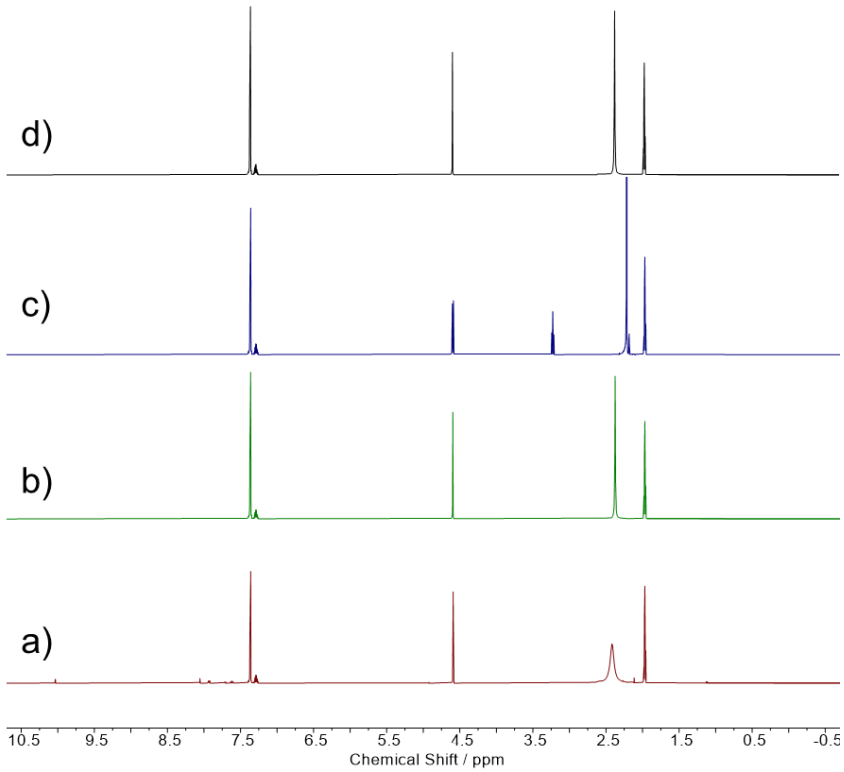


Figure S6. Reference ^{1}H-NMR spectra of benzyl alcohol; a) in the presence of **TX@PS** upon irradiation for 4h; b) in the presence of **TX@PS** without irradiation (18h); c) in the absence of **TX@PS** upon irradiation (18h); d) in the presence of **TX@PS** without irradiation (18h) at elevated temperature (T = 70°C); spectra were recorded in CH_3CN-d_3

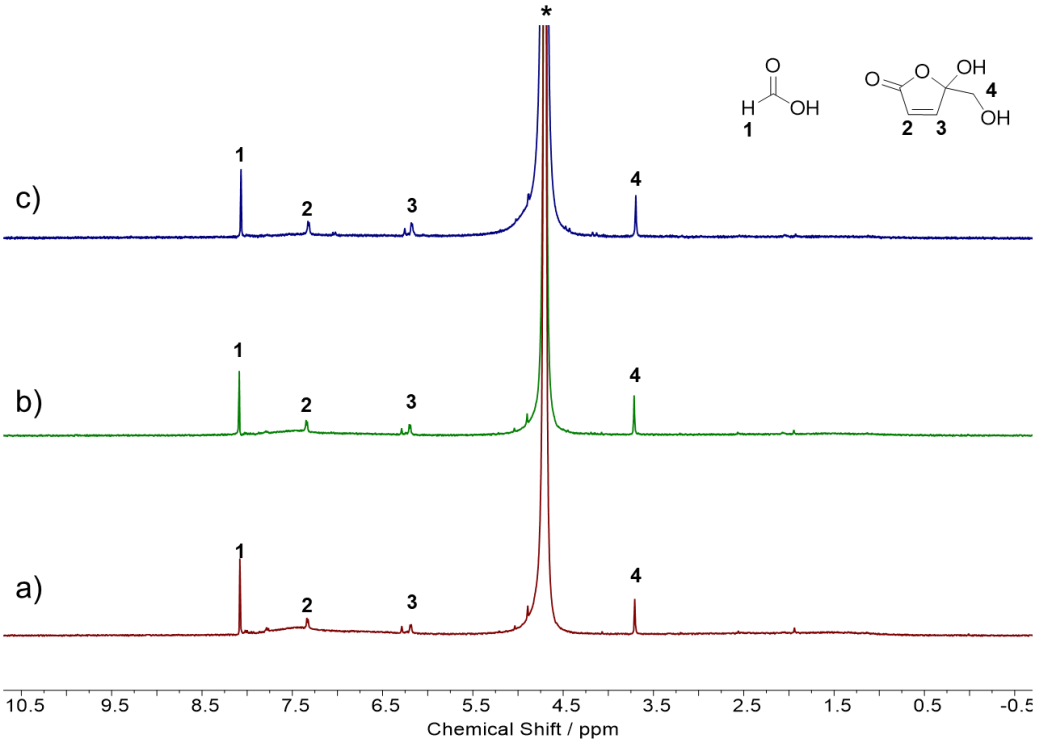


Figure S7. ^{1}H-NMR spectra of **TX@PS** in the presence of **5-HMF** upon irradiation (18h, 405 nm) with a) fresh catalyst, b) re-used catalyst (once) or c) re-used catalyst (twice); the signals labelled 1 correspond to the product formic acid, signals labelled 1 - 4 correspond to the product 5-(hydroxymethyl)-5-hydroxyfuran-2(5H)-one[1]; no signals corresponding to the educt **5-HMF** are detected, indicating full conversion; spectra were recorded in H_2O-d_2; the solvent peak is denoted by an asterisk

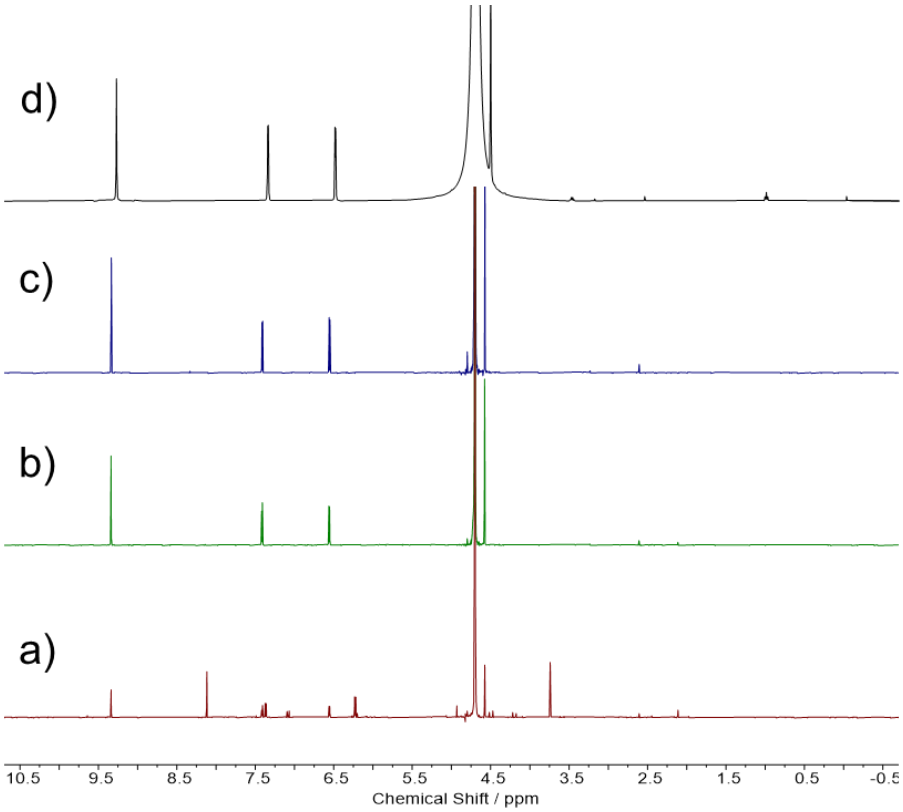


Figure S8. Reference ^{1}H-NMR spectra of 5-HMF; a) in the presence of **TX@PS** upon irradiation for 4h; b) in the presence of **TX@PS** without irradiation (18h); c) in the absence of **TX@PS** upon irradiation (18h); d) in the presence of **TX@PS** without irradiation (18h) at elevated temperature (T = 70° C); spectra were recorded in D_2O-d_2

EPR Spectra

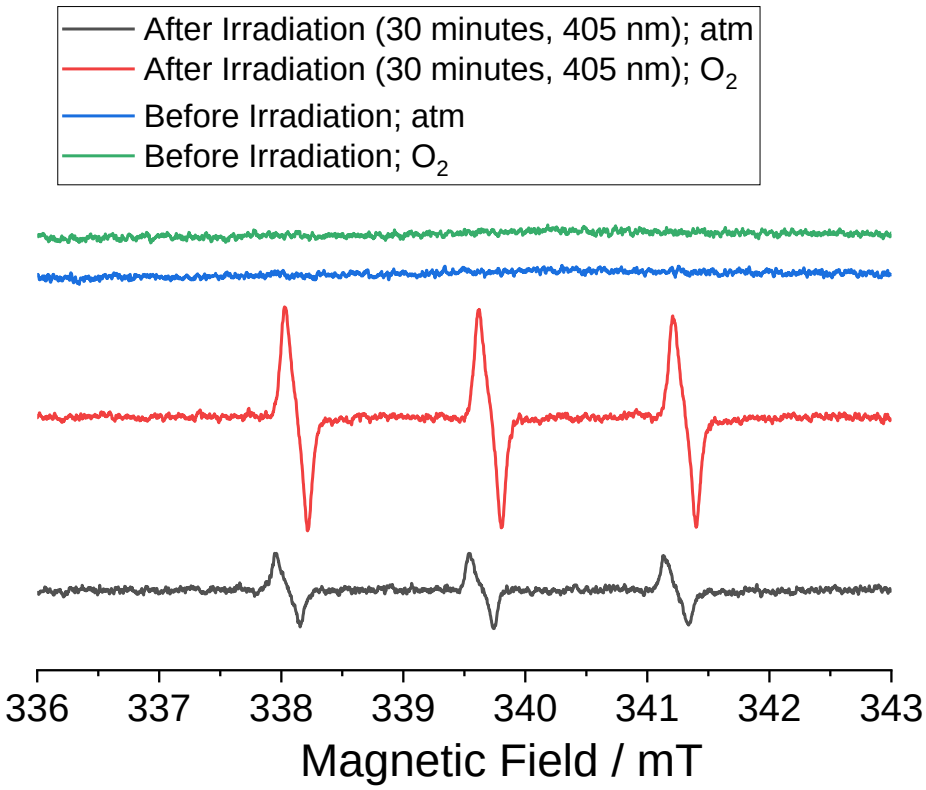


Figure S9. EPR spectra of **TX@PS** in the presence of TEMP before and after irradiation for 30 minutes inside a photoreactor (λ_{max} = 405 nm) and under atmospheric conditions or under O_2 atmosphere; the appearance of signals only after irradiation rationalizes the mechanism discussed in the main text

Gas Sorption Measurements

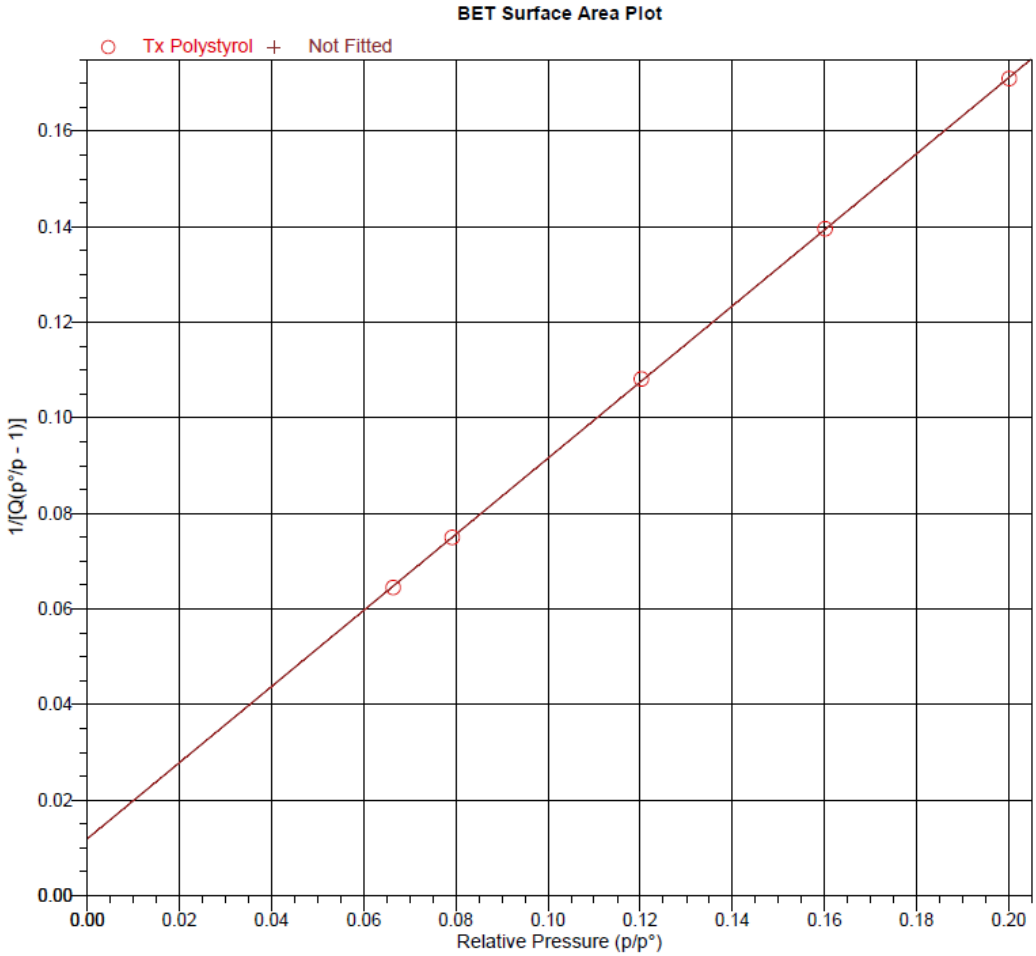


Figure S10. Brunauer-Emmett-Teller (BET) analysis of freshly prepared **TX@PS**

References

1 T. S. A. Heugebaert, C. V. Stevens and C. O. Kappe, *ChemSusChem*, 2015, 8, 1648–1651.