

Assessment of Photosensitization Performance and Stability of Host-Guest MCM-41 Composites from the Direct Observation of Singlet Oxygen Formation and Properties

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Experimental section

Materials: the mesoporous silica MCM-41 was purchased from Sigma Aldrich and was used as received.

Synthesis of the porphyrin photosensitizers

Tetraphenylporphyrin was synthesized from benzaldehyde and pyrrole in refluxing propionic acid according to Adler method. Synthesis of water soluble free base TMPyP 4Cl was achieved from TPyP in refluxing DMF in presence of MeI followed by ion exchange ($I^- \rightarrow Cl^-$). Zinc(II) 5,10,15,20-(tetra-N-methyl-4-pyridyl)porphyrin was synthesized from 5,10,15,20-(tetra-N-methyl-4-pyridyl)porphyrin tetraiodide by the treatment with zinc acetate and sodium acetate in refluxing methanol, followed by ion-exchange ($I^- \rightarrow Cl^-$). Synthesis of TCPP was achieved from carboxybenzaldehyde and pyrrole in refluxing propionic acid. ZnTCPP was synthesized from TCPP by the treatment with zinc acetate and sodium acetate in refluxing DMF.

Synthesis of porphyrin@MCM-41 composites

5,10,15,20-tetraphenyl porphyrin/MCM-41 (1) 5,10,15,20-tetraphenyl porphyrin (5mg, 0.008 mmol) was dissolved in 40 ml dichloromethane (DCM) and stirred vigorously at room temperature. After obtaining homogeneous solution 250 mg MCM-41 was added and the mixture was stirred for one hour. The mixture was filtered and further washed with DCM several times until filtrate becomes colorless to remove weakly attached porphyrin. Slightly colored purple powder was dried at room temperature under vacuum for 12 hours to give final product. Three other porphyrin/MCM-41 complexes with higher concentrations (10 mg, 0.016 mmol; 15 mg, 0.024 mmol and 20 mg, 0.032 mmol) of porphyrin loading have been prepared with the same method.

5,10,15,20-tetraphenyl porphyrin/MCM-41 (2) Mixture of benzaldehyde (0.1 ml, 0.0009 mmol), pyrrole (0.07 ml, 0.001 mmol) was dissolved in 5 ml toluene. 250 mg MCM-41 was added and reaction mixture was refluxed during 12 hours. Solid brown powder was obtained after filtration. Brown solid was washed several times with toluene and dichloromethane to remove weakly attached porphyrin. Final product was dried at 60°C under vacuum for 12 hours to give final product.

5,10,15,20-(tetra-4-pyridyl)porphyrin/MCM-41 (3) 5,10,15,20-(tetra-4-pyridyl)porphyrin (5 mg, 0.006 mmol) was dissolved in 40 ml deionized water (DI) and stirred vigorously at room temperature for 5 minutes. After obtaining homogeneous solution 250 mg MCM-41 was added and the mixture was stirred for one hour. The mixture was filtered and further washed with DI water several times until filtrate becomes colorless to remove weakly attached porphyrin traces. Slightly colored purple powder was dried at 60°C under vacuum for 12 hours to give the final product. Three other porphyrin/MCM-41 complexes with higher concentrations (10 mg, 0.01 mmol; 15 mg, 0.018 mmol and 20 mg, 0.024 mmol) of porphyrin loading have been prepared with the same method described above.

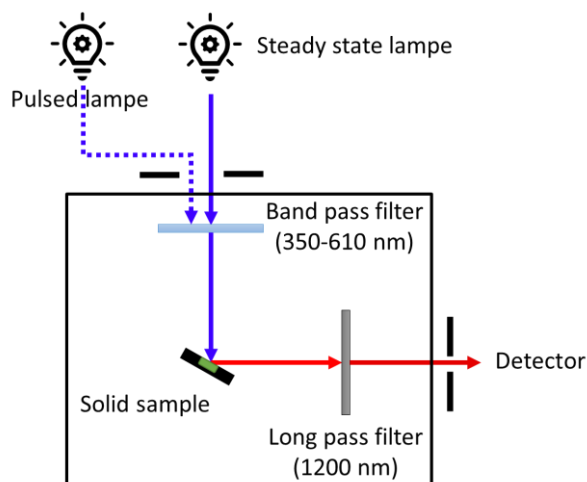
Zinc(II)5,10,15,20-(tetra-4-pyridyl)porphyrin/MCM-41 (4) Zinc(II) 5,10,15,20-(tetra-4-pyridyl)porphyrin 5mg, 0.0056 mmol was dissolved in 40 ml deionized water (DI) and further synthesis take care under the conditions described above. Three other complexes with higher concentrations (10 mg, 0.011 mmol; 15 mg, 0.017 mmol and 20 mg, 0.022 mmol) of porphyrin loading have been prepared with the same method.

5,10,15,20-(tetra-4-carboxyphenyl)porphyrin/MCM-41 (5) 5,10,15,20-(tetra-4-carboxyphenyl)porphyrin (5 mg, 0.006 mmol) was dissolved in 40 ml DMSO and stirred vigorously at room temperature for 5 minutes. After obtaining homogeneous solution 250 mg MCM-41 was added and the mixture was stirred for one hour. The mixture was filtered and slightly colored powder was dried at 60°C under vacuum for 12 hours to give the final product.

Zinc(II) 5,10,15,20-(tetra-4-carboxyphenyl)porphyrin/MCM-41 (6) Zinc(II) 5,10,15,20-(tetra-4-carboxyphenyl)porphyrin 5mg, 0.0058 mmol was dissolved in 40 ml deionized water (DI) and further synthesis take care under the conditions described above.

Instrumentation The absorption spectra in solution were measured on a Hewlett-Packard 8453 diode array spectrometer with a 0.1 s integration time. The solid-state UV-visible spectra were recorded on a Varian Cary 300 Bio UV-Vis spectrophotometer at 298 K using 8° raised-angle transmittance apparatus. Powder was dispersed between two quartz plate and placed directly on the end opening of the integration sphere. The reflectance signal was converted into absorbance. Steady state solution and solid-state emissions were acquired on a QM-400 spectrofluorometer by PTI equipped with a Ushio 75 W Xenon Short Arc Lamp and a NIR PMT R5509-43 (300 to 1400 nm) from Hamamatsu cooled with liquid nitrogen. Solid sample were placed in a homemade

sample holder and held with a homemade 3D-printed sample holder and adjusted at 38° angle from the excitation source to maximize the emission intensity of the powder samples. The excitation signal was cleaned with a band pass filter (335-610 nm) from Thorlabs directly after the excitation monochromator. Diffuse light, scattering and harmonic phenomena were filtered off in the 1225-1325 nm window with a 1200 nm longpass filter from ThorLabs placed before the emission monochromator. Scheme for the experimental setup is provided in 4. The radiative emission decay in solution was monitored at 1275 nm with a similar set up but a Hamamatsu 15 W Xenon Flash Lamp was used as an excitation source. The results were fitted with Origin software with a two-phase exponential decay function with time constant parameter model $\left(I(\lambda, t) = I_0 + A_1 e^{-\frac{t}{\tau_1}} + A_2 e^{-\frac{t}{\tau_2}}\right)$.



Experimental setup for emission measurement.

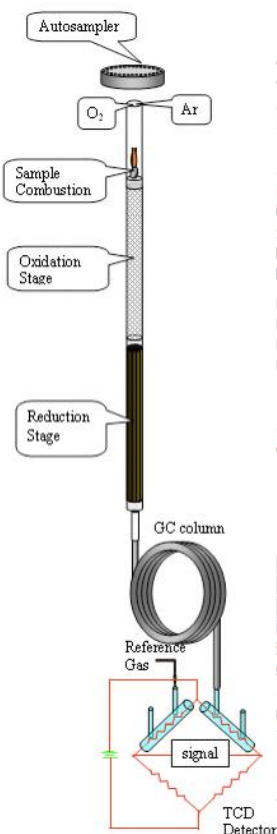
Ultraviolet Visible Spectroscopy (UV-Vis): Absorption spectra in solution were recorded on a Shimadzu-1800 UV-visible double beam spectrophotometer.

X-Ray Diffraction (XRD): Analyses are performed from $2\theta = 3^\circ$ to 50° by default. X-ray powder analysis diffraction were carried out in transmission mode unless mentioned otherwise. The samples (few milligrams) are introduced without being crushed in 1 mm diameter glass capillaries to avoid preferential orientation or between two Mylar® foil. The analysis is performed in transmission mode by using a focusing X-ray mirror with divergence slits and anti-scatter slits (aperture 0.5°), on an Empyrean diffractometer from PANalytical Company

equipped with a copper anticathode tube (wavelength $\lambda K\alpha_1 = 1.54060 \text{ \AA}$ / $K\alpha_2 = 1.54443 \text{ \AA}$) and with a PIXcel 1D detector with anti-scatter slits of 7.5 mm. The calibration of the analytical instrument is checked before each analytical batch according to quality system.

Elemental analyses Analyses are performed on Thermo Electron Flash EA1112. 1.5 md sample (solid or liquid) is introduced in a capsule (the weight of capsule is already known). After weighing (microgram precision) this capsule is delive(red) to the analyzer via a sample changer. The capsule drops into the reactor tube. It is a quartz tube with a diameter of 16 mm and a length of 500 mm previously filled with copper oxide and metallic copper.

The compound is then instantly pyrolyzed at 960°C under a stream of oxygen.



The nitrogen, carbon, hydrogen and sulfur atoms possibly present in the sample then form respectively: NO / NO₂, CO₂, H₂O and SO₂ / SO₃. Pushed by a vector gas (helium), these molecules pass over the copper oxide in granules (by completion of the oxidation). NO and NO₂ are (red)uced to N₂, SO₃ to SO₂. At the exit of the tube, we are therefore in the presence of a mixture of the following four gases: Dinitrogen, carbon dioxide, water, sulfur dioxide.

Thermogravimetric Analyses (TGA) Thermogravimetric (TGA) analyses were recorded using a Netzsch STA 409 PC thermal analyzer. The samples were heated from 298 to 1273 K with a heating rate of 5 K min⁻¹ in the 298-873 K range and 10 K min⁻¹ in the 873-1273 K range under a flow of nitrogen (30 mL min⁻¹) and oxygen (10 mL min⁻¹).

Brunauer-Emmett-Teller (BET) Nitrogen adsorption/desorption isotherms were measured at 77 K on a Belsorp maxII apparatus. The residual solvent molecules trapped inside the pores of the solids were removed by degassing the samples (60-80 mg), transferred in a pre-weighed glass, in a dynamic vacuum ($< 5 \times 10^{-3}$ mbar) at 298 K for at least 3 h before measurements. The specific surface area was determined using the Langmuir and the Brunauer-Emmett-Teller (BET) calculations, and the pore volume were obtained directly from the N₂ adsorption/desorption isotherms at $P/P_0 = 0.99$.

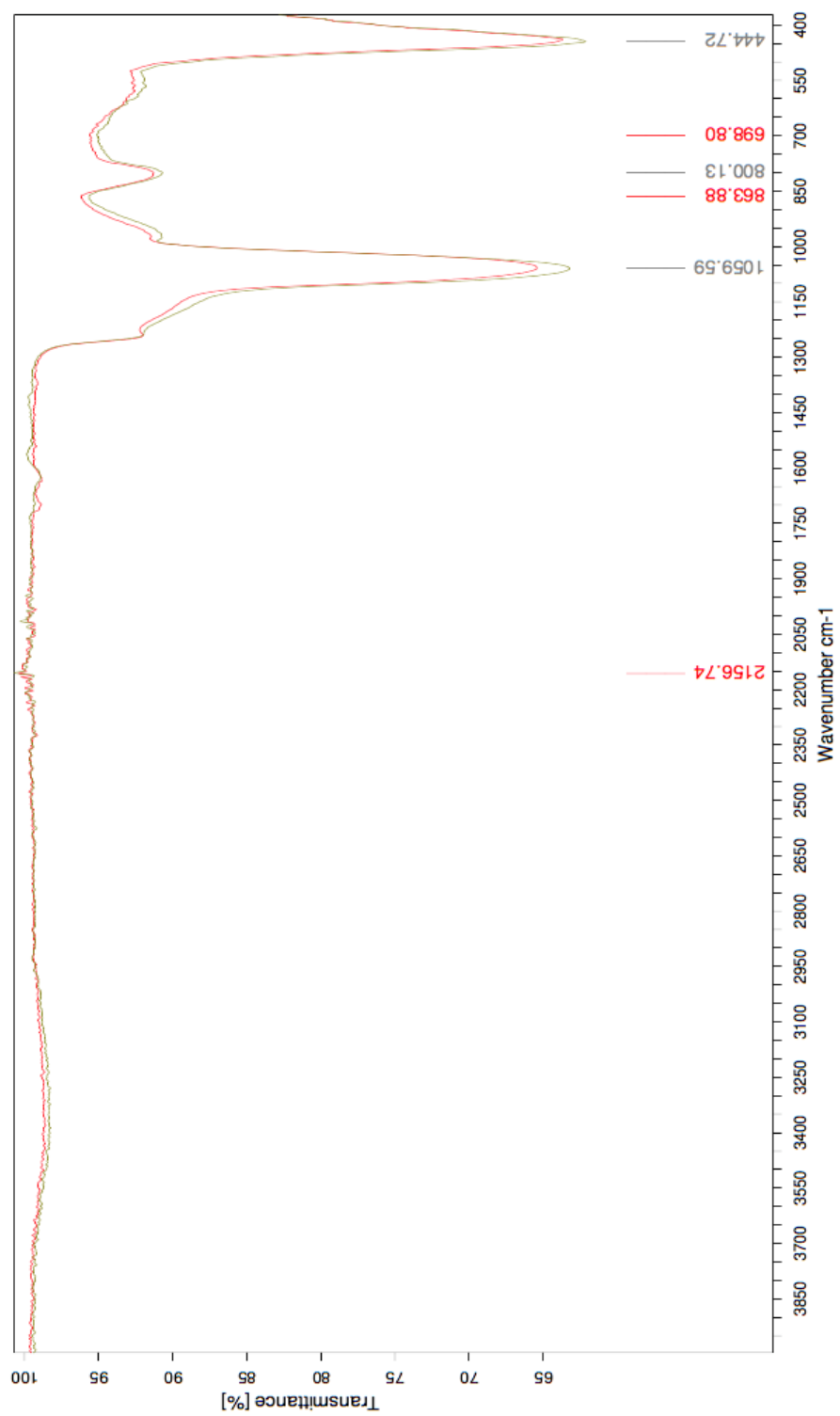


Fig. S2: IR spectra of MCM-41 (grey) and TPP@MCM-41 (red) .

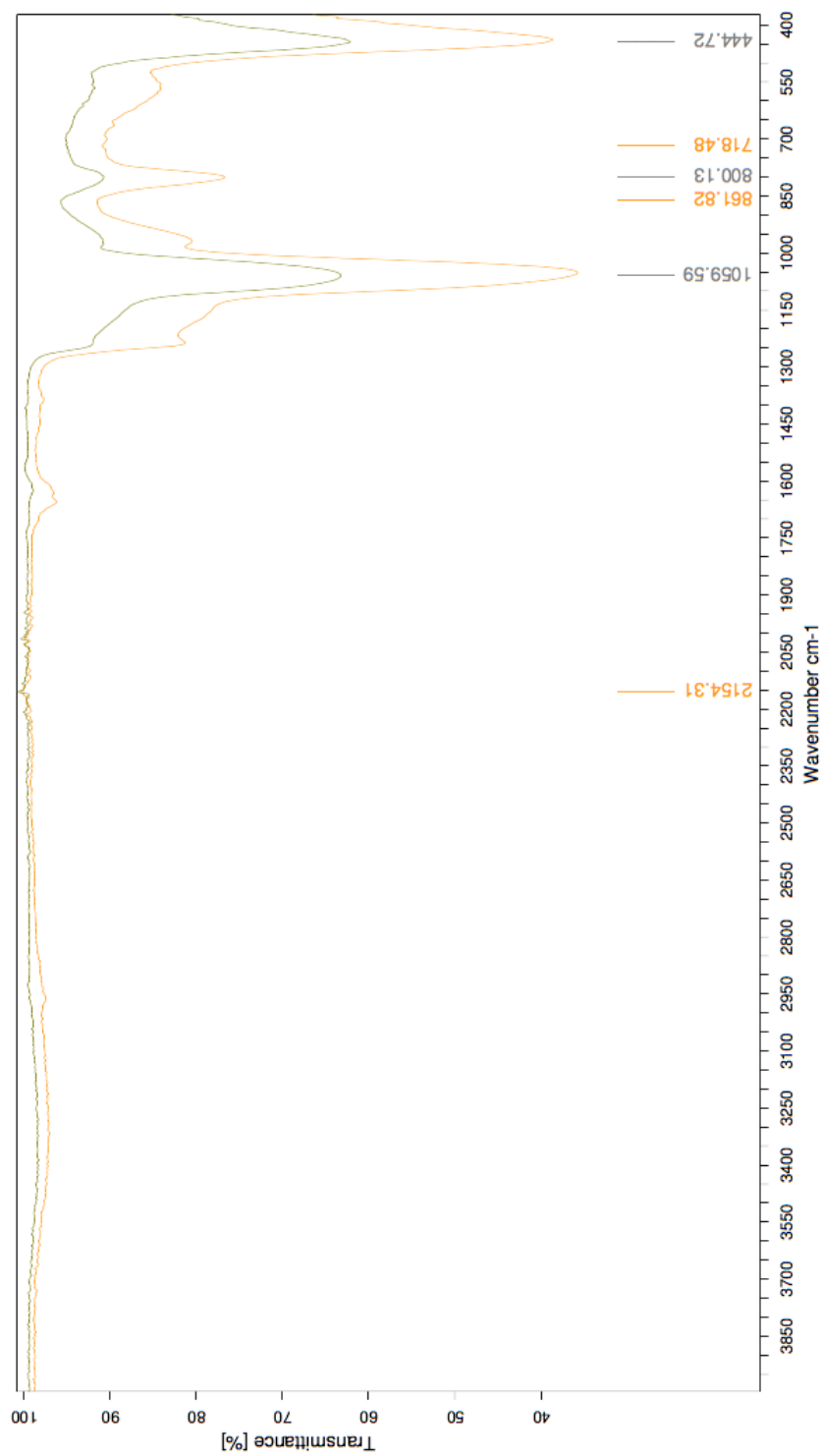


Fig. S2: IR spectra of MCM-41 (grey) and TPP@MCM-41 direct synthesis (orange).

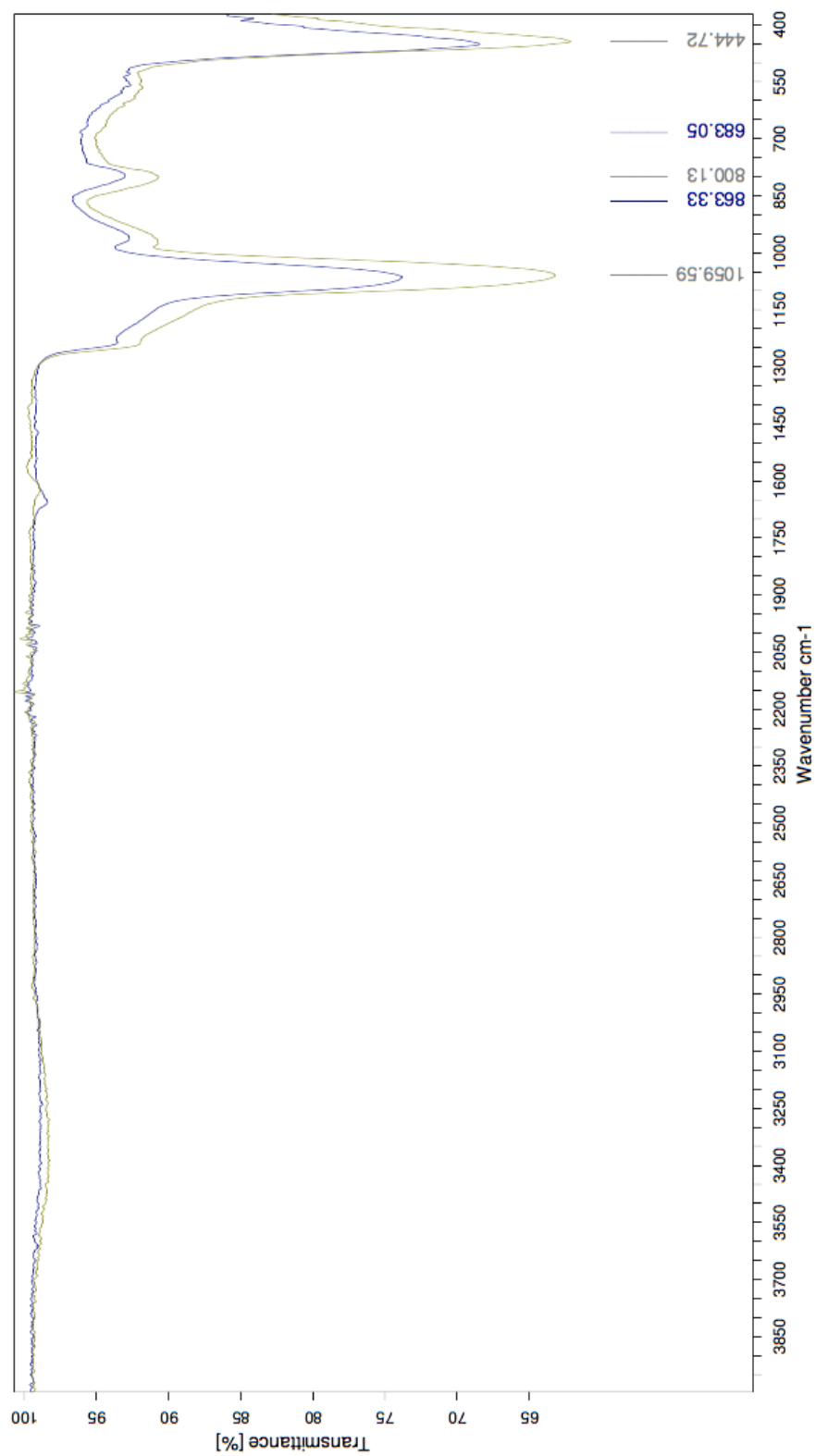


Fig. S3: IR spectra of MCM-41 (grey) and TNMPyP@MCM-41 (blue).

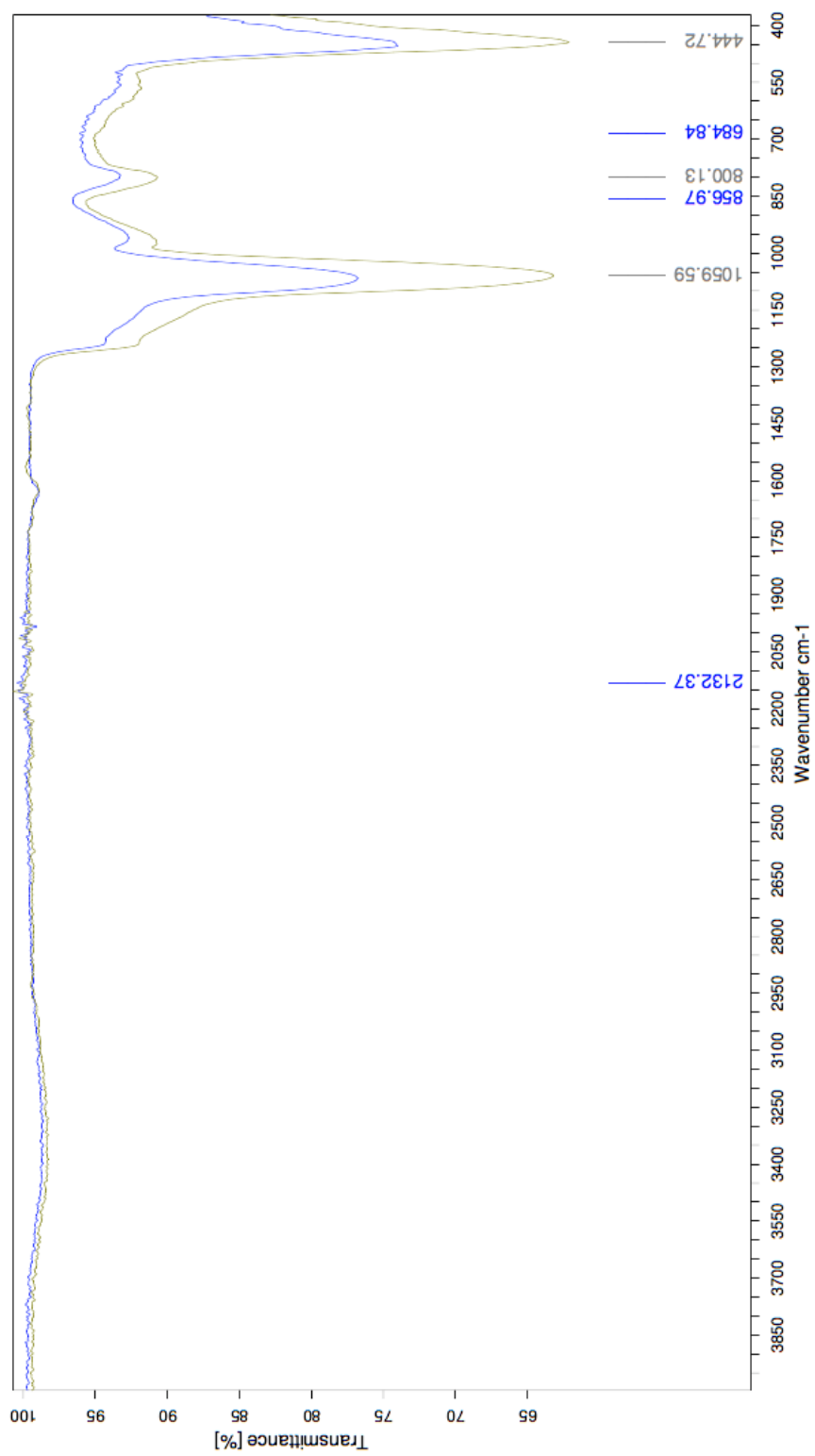


Fig. S4: IR spectra of MCM-41 (grey) and ZnTNMPyP@MCM-41 (blue).

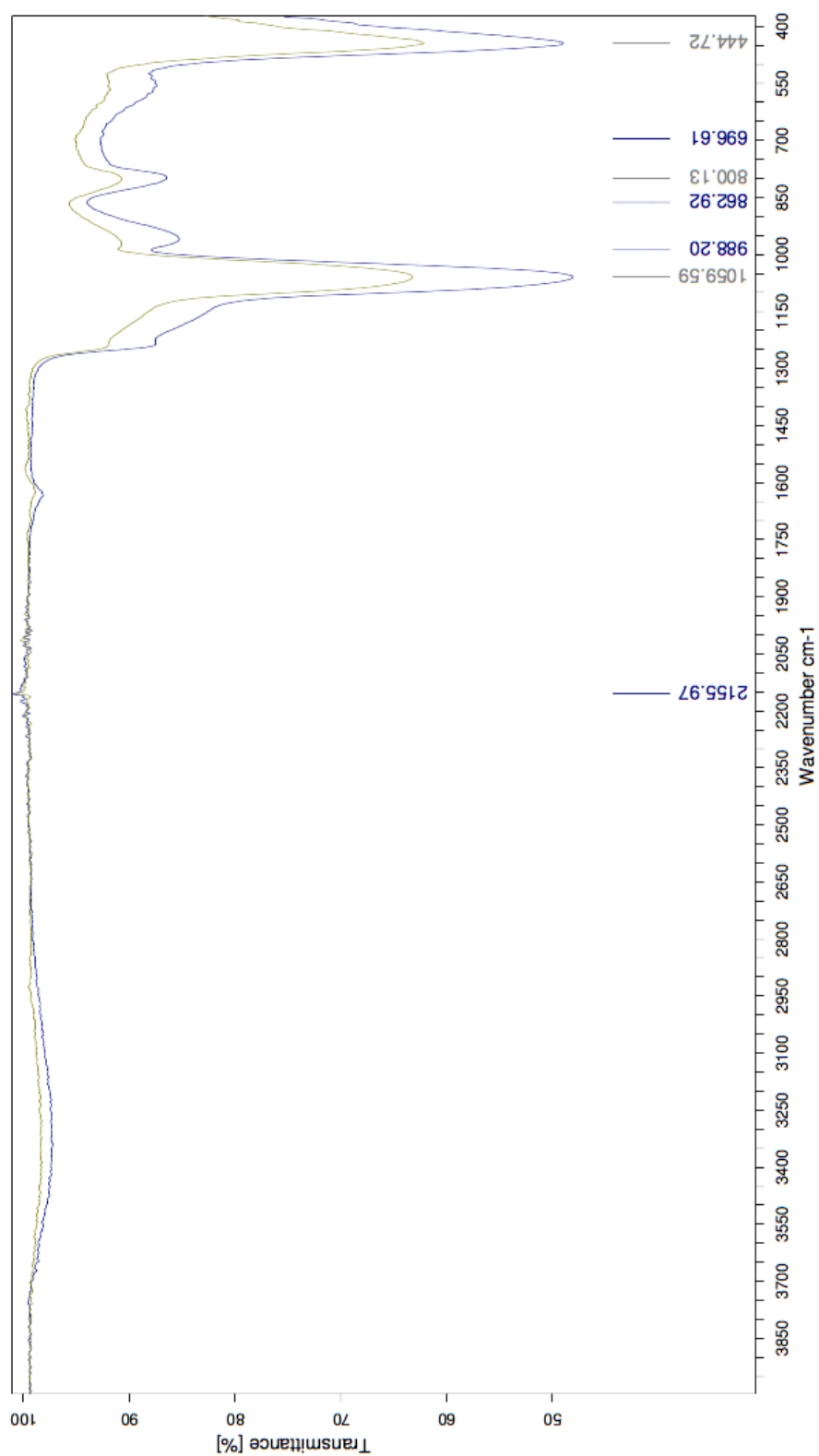


Fig. S5: IR spectra of MCM-41 (grey) and ZnTCPP@MCM-41 (blue).

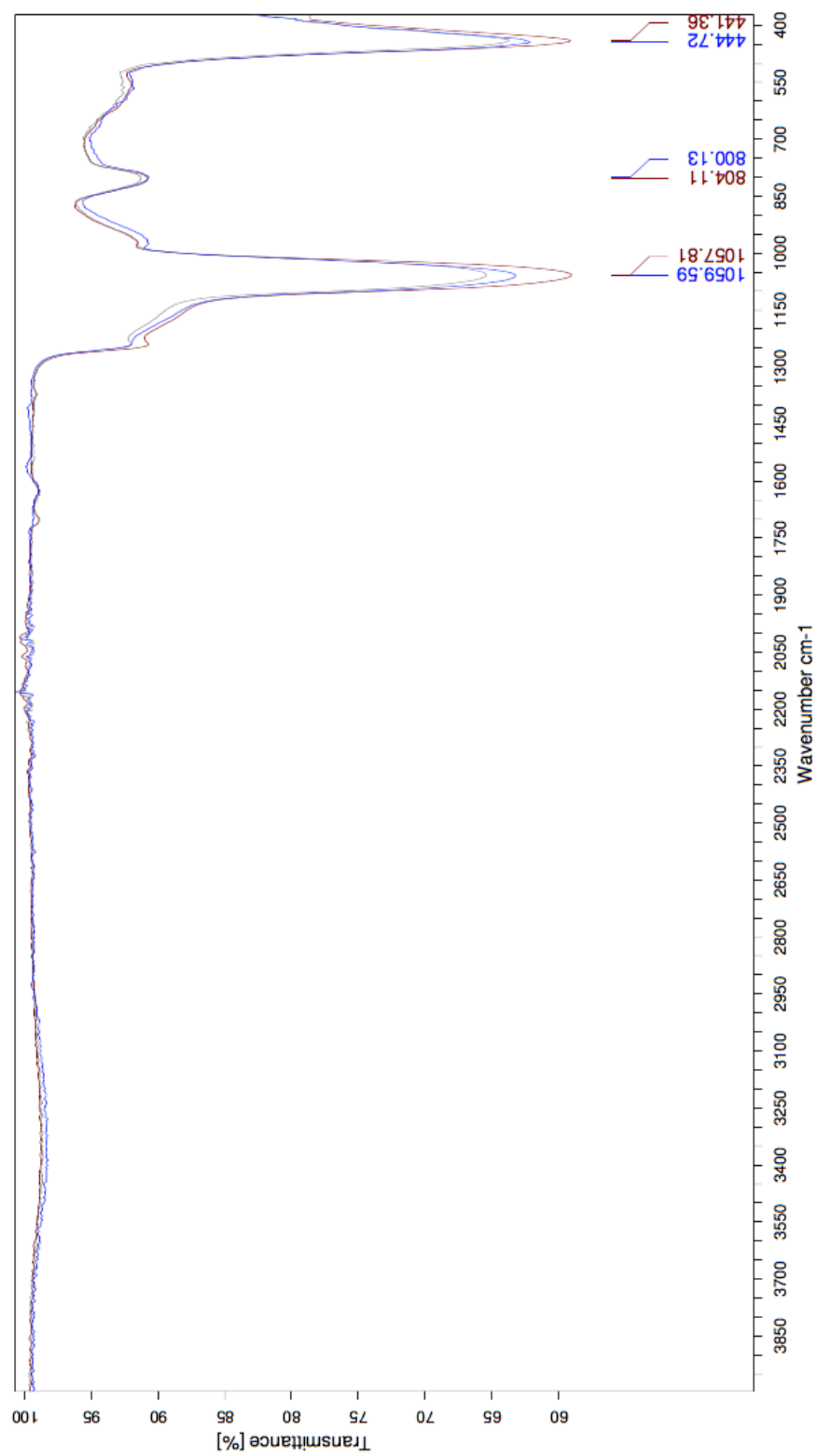


Fig. S6: IR spectra of MCM-41 (blue), TPP@MCM-41 (grey) and TPP@MCM-41 (containing a higher amount of TPP) (red).

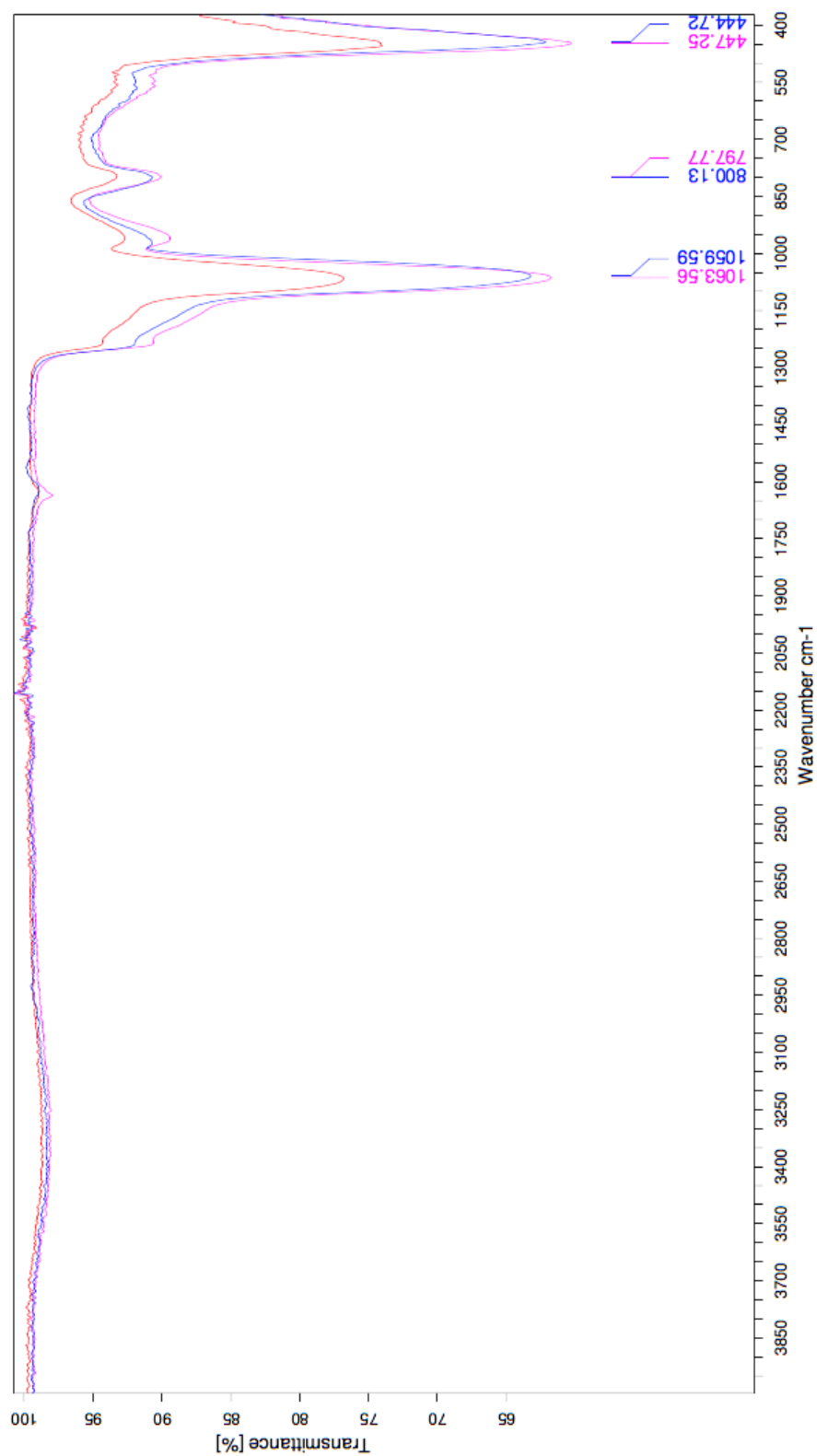


Fig. S7: IR spectra of MCM-41 (blue), ZnTNMPyP@MCM-41 (blue), and ZnTNMPyP@MCM-41 (containing higher amount of ZnTNMPyP) (violet).

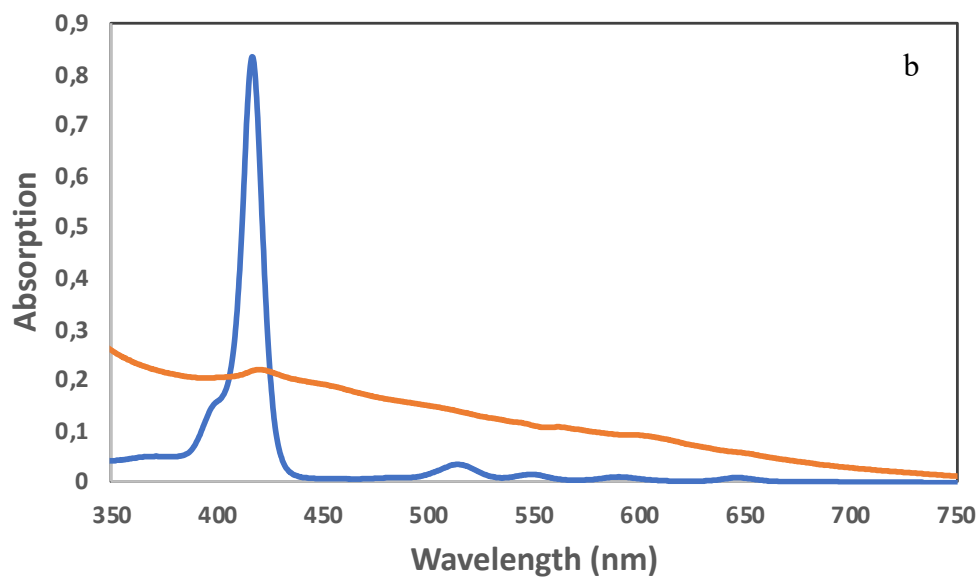
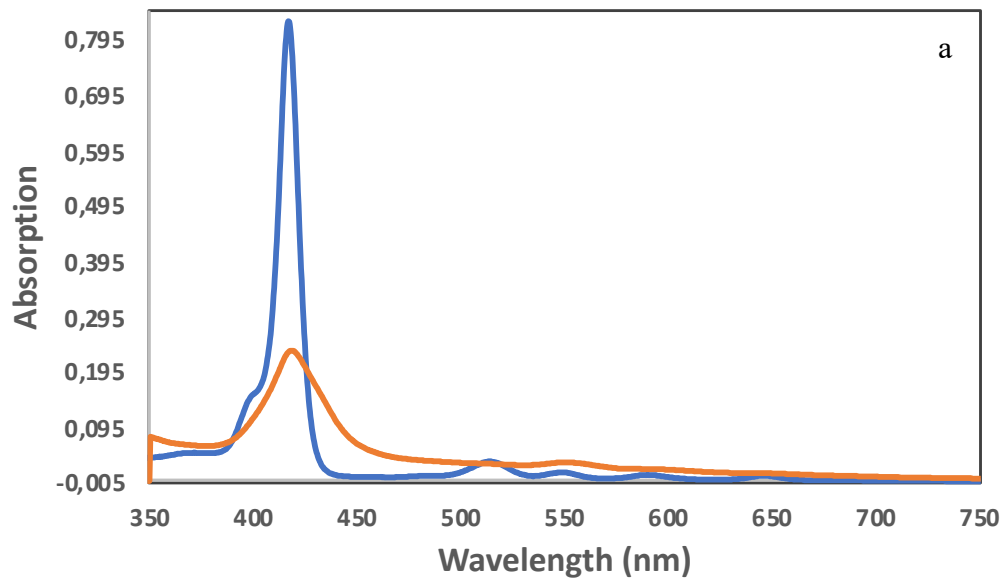


Fig. S8: UV-Vis absorption spectra of (a) TPP (blue) and TPP@MCM-41 (orange), in CH₂Cl₂, (b) TPP (blue) and TPP@MCM-41 direct synthesis (orange).

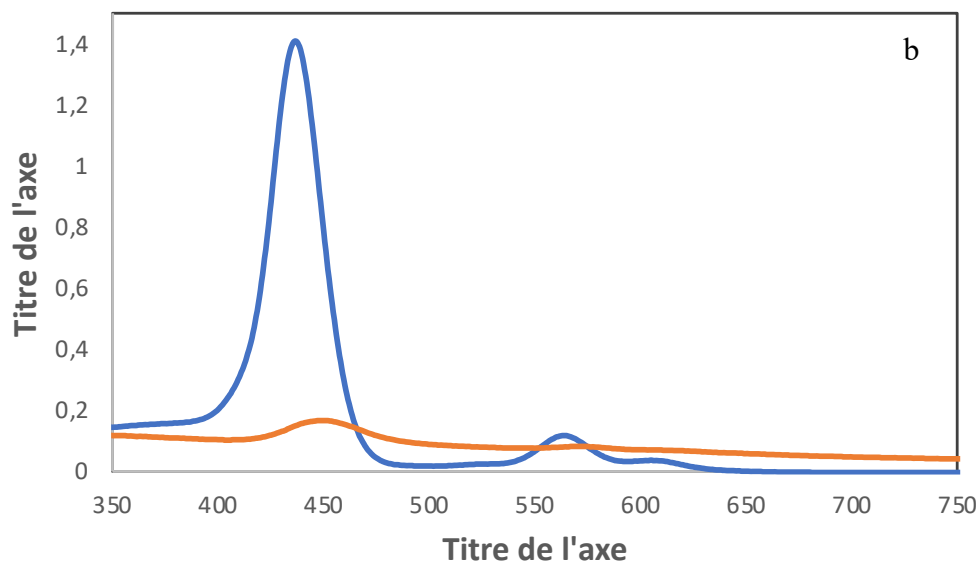
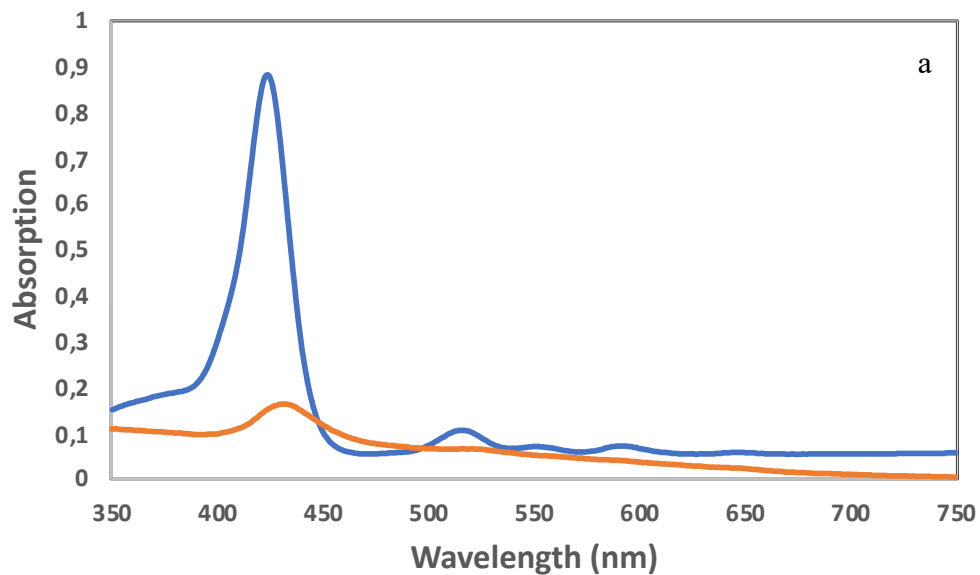


Fig. 9: UV-Vis absorption spectra of (a) TNMPyP (blue) and TNMPyP@MCM-41 in H₂O (orange), (b) ZnTNMPyP (blue) and ZnTNMPyP@MCM-41 (orange) in H₂O.

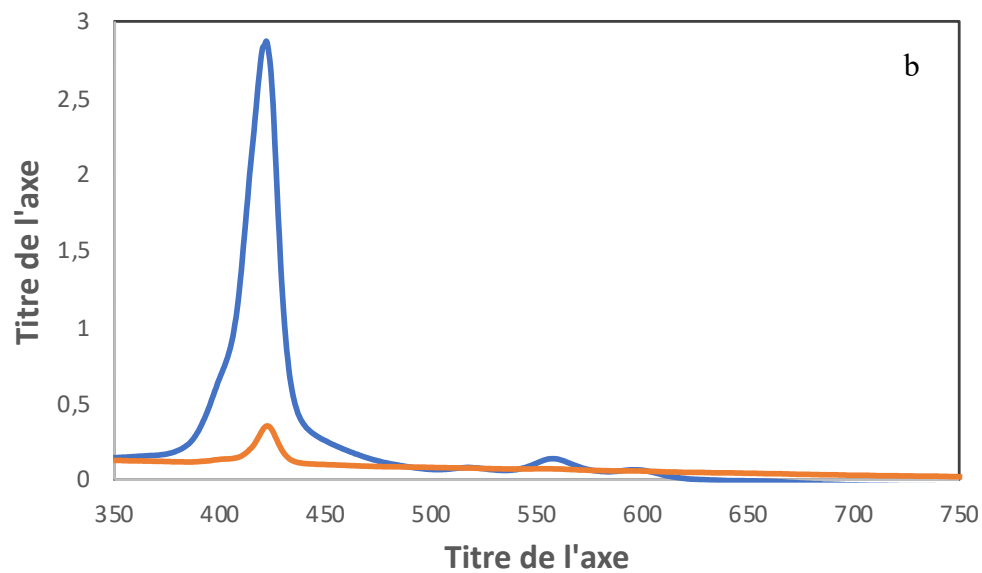
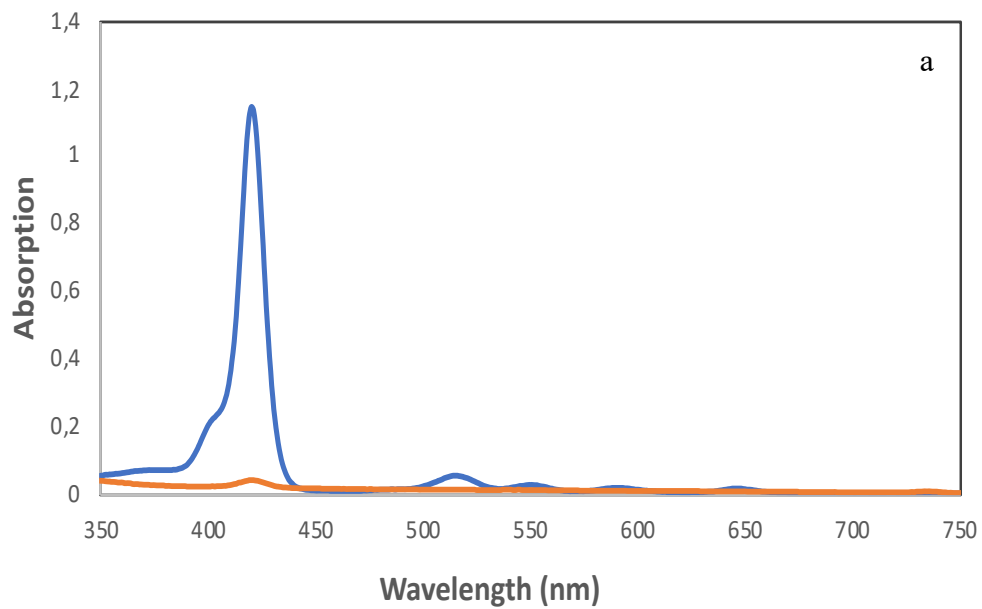


Fig. S10: UV-Vis absorption spectra of (a) TCPP (blue) and TCPP@MCM-41 (orange) in DMSO, (b) ZnTCPP (blue) and ZnTCPP@MCM-41 orange in H₂O.

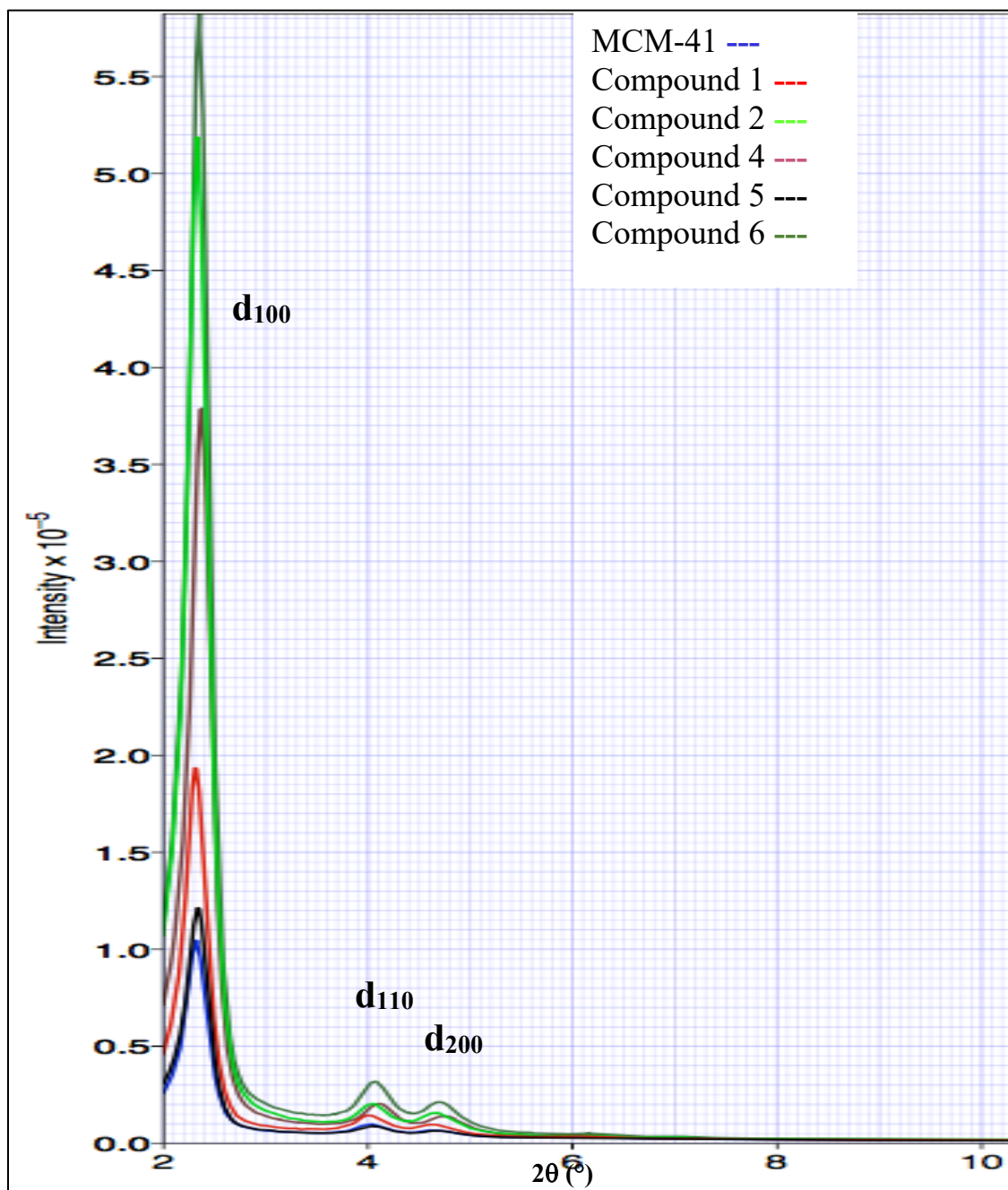


Fig. S11: X-ray diffraction spectra of MCM-41, TPP@MCM-41 (compound 1), TPP@MCM-41 (compound 2), ZnTNMPyP@MCM-41 (compound 4), ZnTCPP@MCM-41 (compound 6).

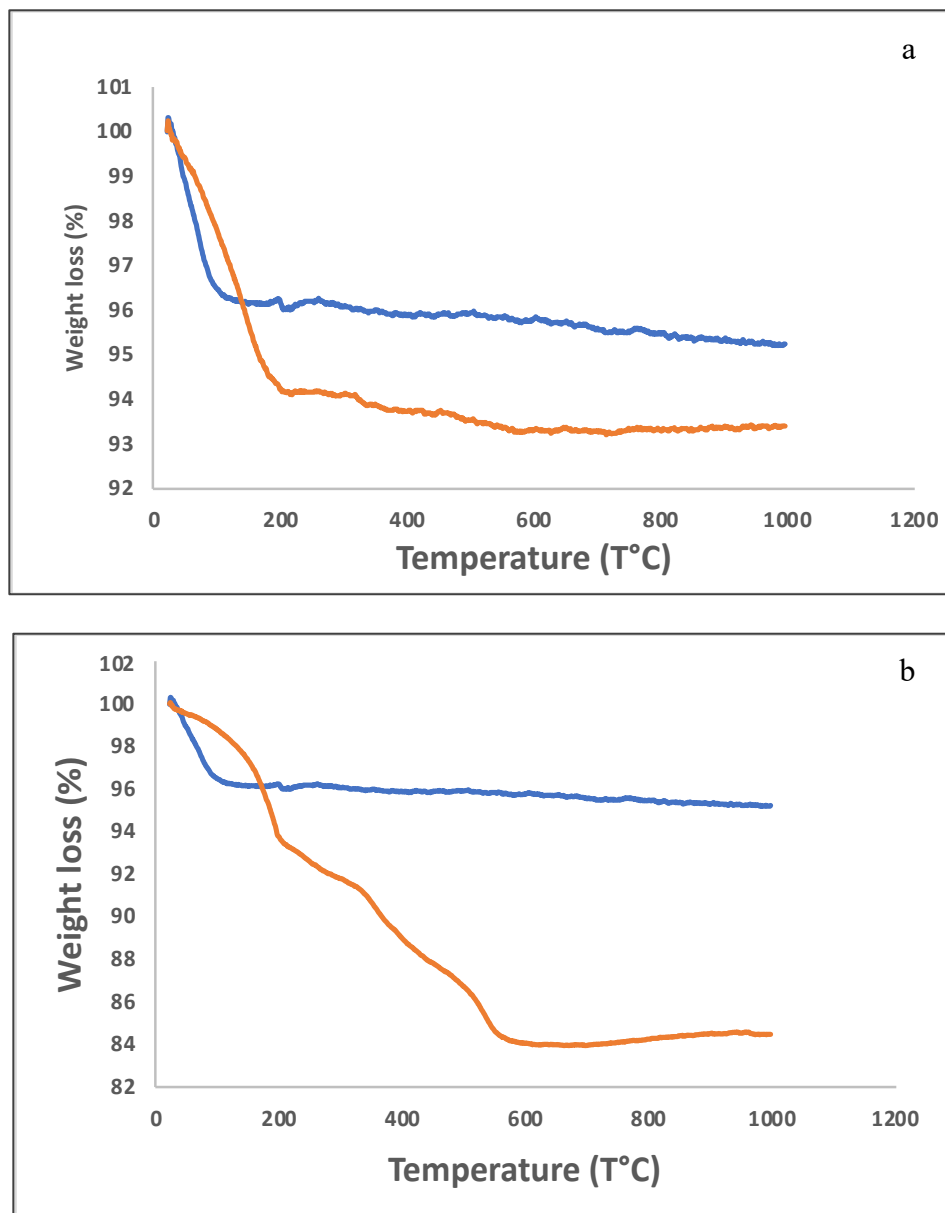


Fig. S12: TGA traces of (a) MCM-41(blue) and TPP@MCM-41(orange); (b) MCM-41(blue) and TPP@MCM-41 direct synthesis (orange).

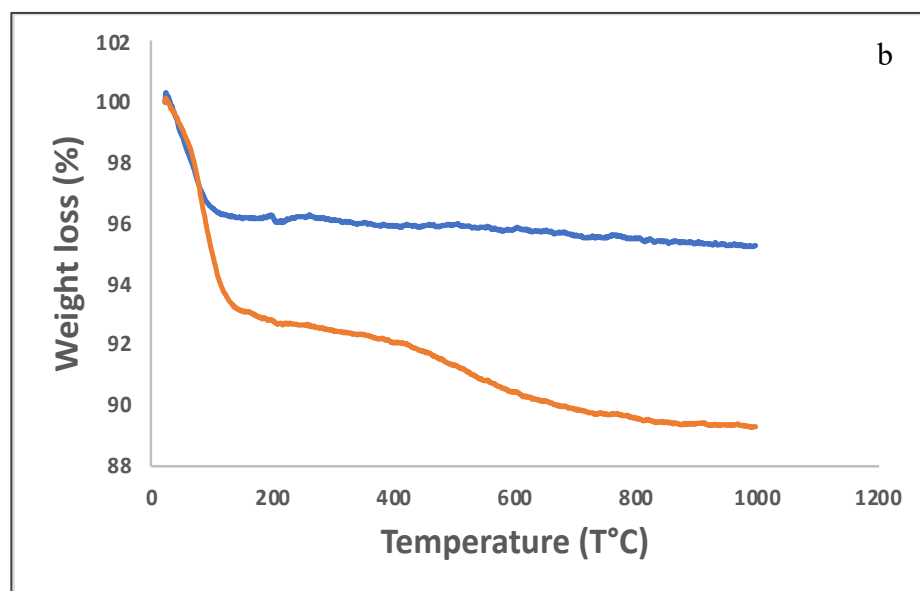
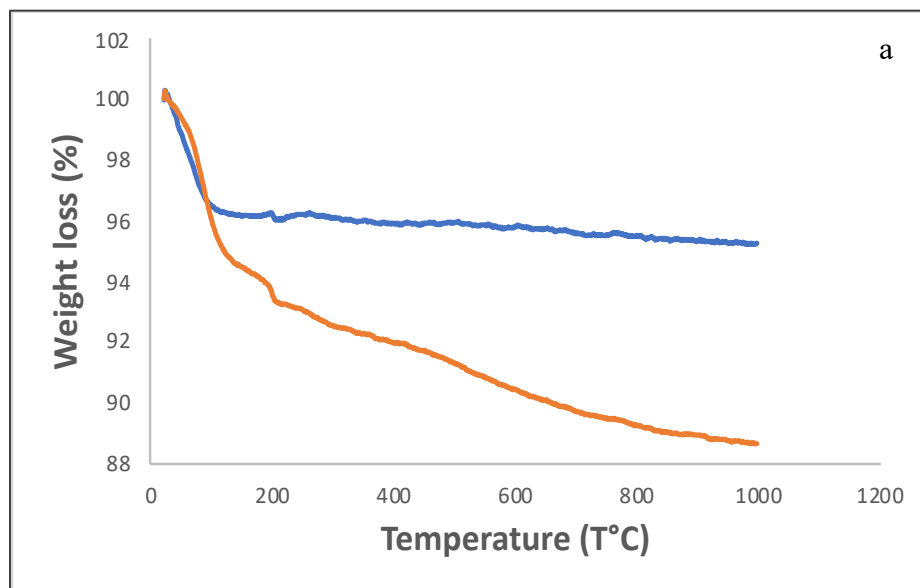


Fig. S13: TGA traces of (A) MCM-41(blue) and ZnTNMPyP@MCM-41; (b) MCM-41 and ZnTCTPP@MCM-41 (orange).

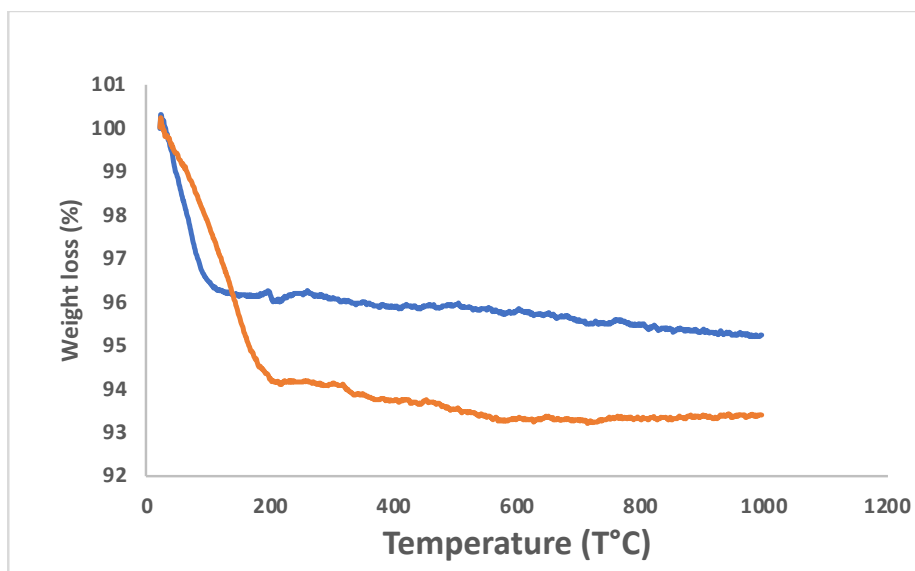


Fig. S14: TGA traces of MCM- 41(blue) and TNMPyP@MCM-41(orange).

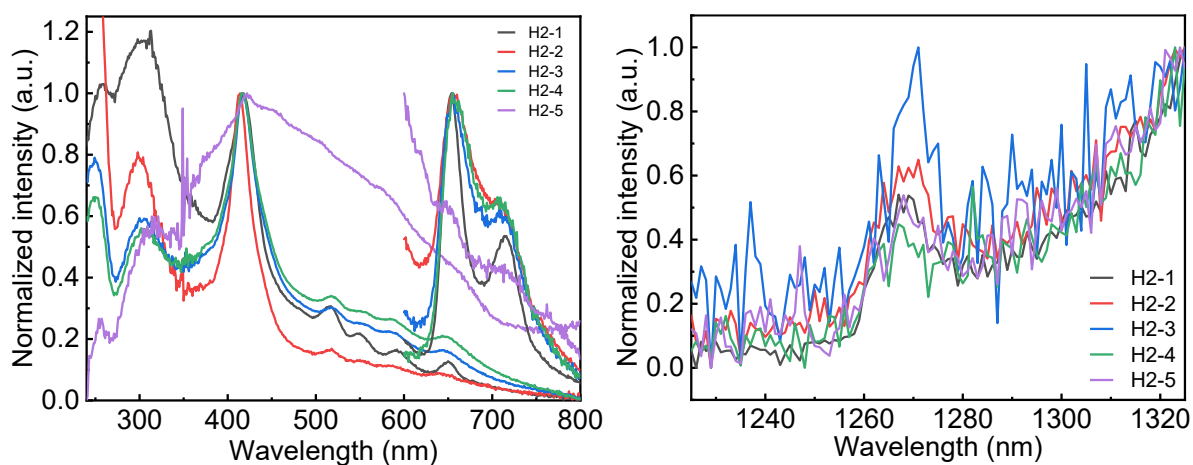


Fig. S15. Left: solid state absorption and emission of **Zn-[1-4]**. Right: $^1\text{O}_2$ emission photosensitized by **Zn-[1-4]** (solid state/air interface).

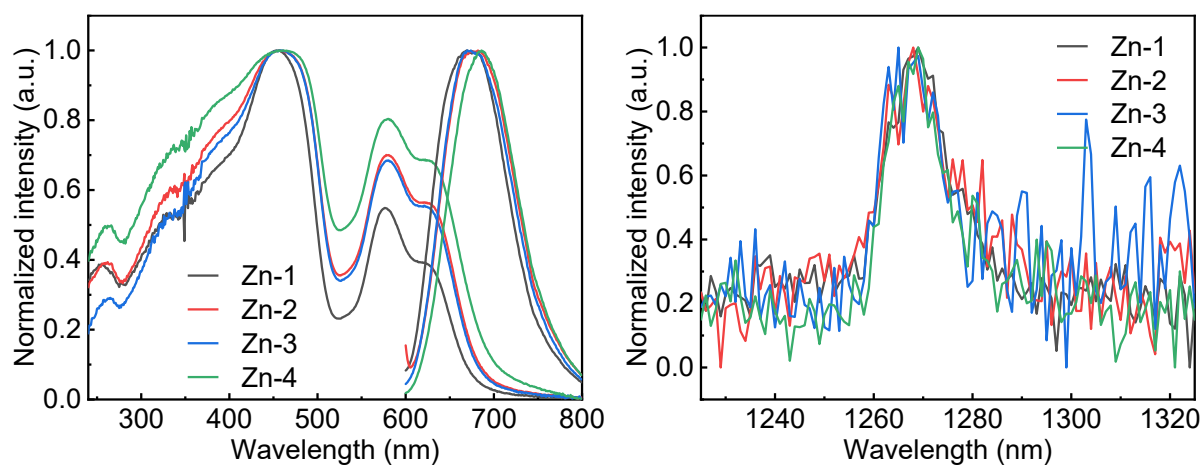


Fig. S16. Left: solid state absorption and emission of **H2-[1-4]**. Right: $^1\text{O}_2$ emission photosensitized by **H2-[1-4]** (solid state/air interface).

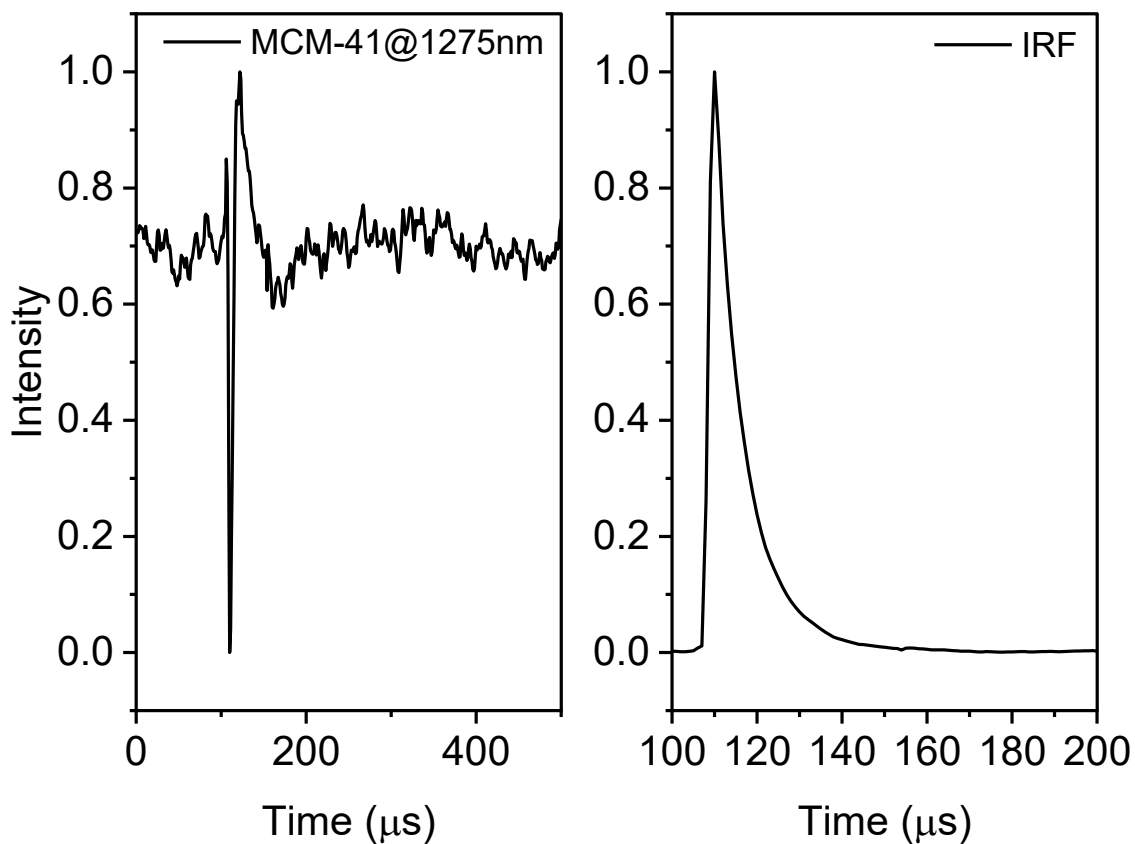


Fig. S17. Decay response at 1275 nm of MCM-41 and IRF (Instrument function response).

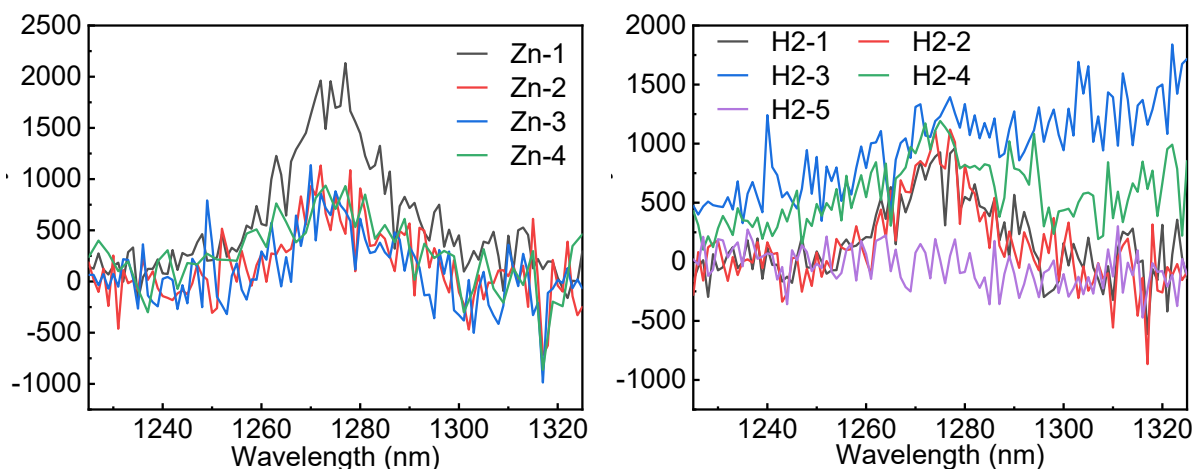


Fig. S18. $^1\text{O}_2$ emission photosensitized by **Zn-[1-4]**(left) and **H2-[1-5]** (right) suspended in CH_2Cl_2 .

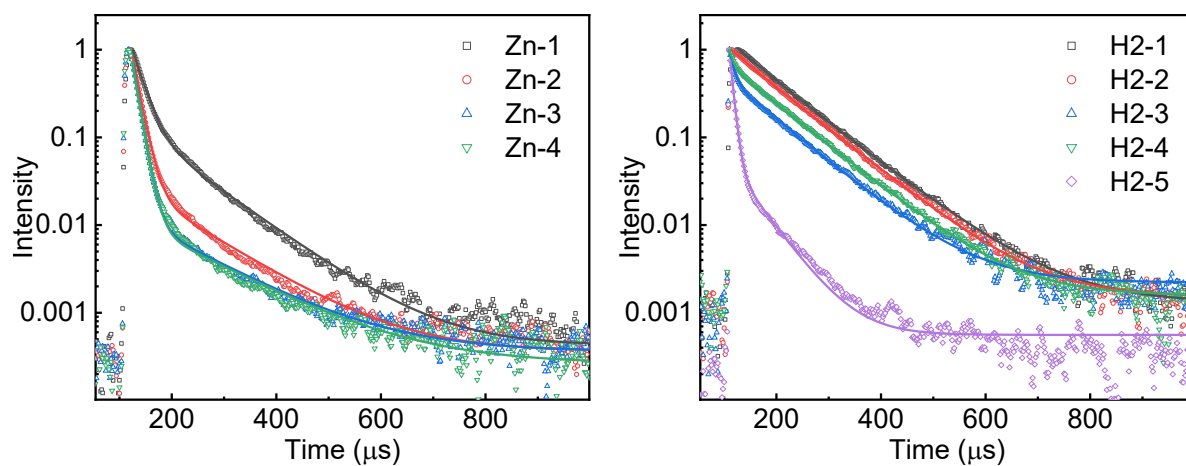


Fig. S19. Emission decays of $^1\text{O}_2$ photosensitized by **Zn-[1-4]**(left) and **H2-[1-5]** (right) suspended in DCM. Data in Table 3 of the text.

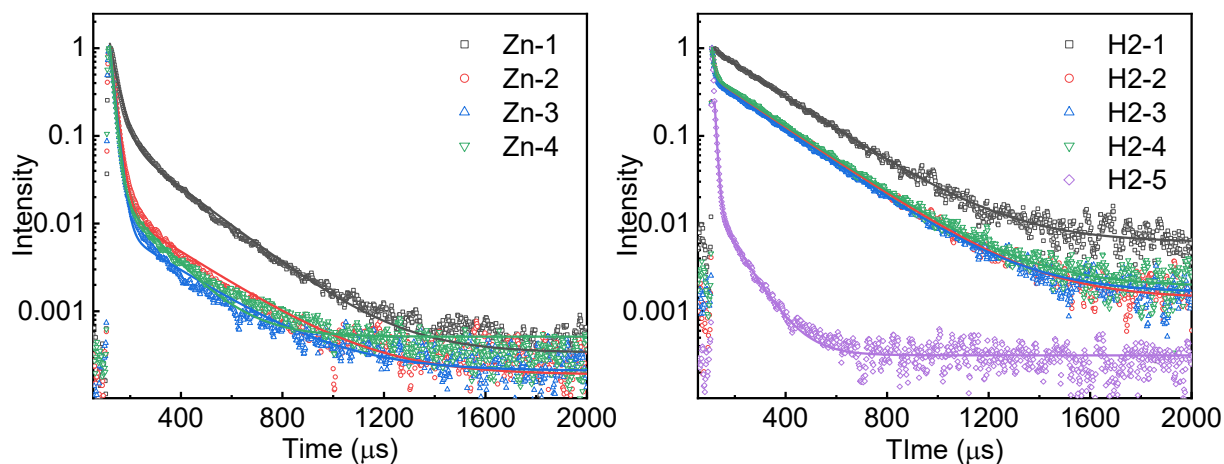


Fig. S20. Emission decays of $^1\text{O}_2$ photosensitized by **Zn-[1-4]**(left) and **H2-[1-5]** (right) suspended in CHCl_3 . Data in Table 3 of the text.