**Supporting Information for**

# Shape dependent photocatalytic $H_2$ evolution of a zinc porphyrin

Emmanouil Orfanos,[a] Kalliopi Ladomenou,[b]* Panagiotis Angaridis,[c] Athanassios G. Coutsolelos[a,d]*

[a] *University of Crete, Department of Chemistry, Laboratory of Bioinorganic Chemistry, Voutes Campus, 70013, Heraklion, Crete, Greece.*

[b] *International Hellenic University, Department of Chemistry, Laboratory of Inorganic Chemistry, Agios Loucas, 65404, Kavala Campus, Greece.*

[c] *Aristotle University of Thessaloniki, Department of General and Inorganic Chemistry, Faculty of Chemistry, GR-54124 Thessaloniki, Greece.*

[d] *Institute of Electronic Structure and Laser (IESL)Foundation for Research and Technology - Hellas (FORTH), Vassilika Vouton, GR 70013 Heraklion, Crete, Greece*

Corresponding Authors

E-mail: acoutsol@uoc.gr (A.G.C.); kladomenou@chem.ihu.gr (K.L.); panosangaridis@chem.auth.gr (P.A.); manosorf17@gmail.com (E.O.)

**Experimental Procedure**

In a typical procedure the photosensitizers were prepared as following: 5 mgr of **ZnTPP** was placed in a small vial and 0.5 ml of a "good" solvent was added. When **ZnTPP** was fully dissolved 2 ml of methanol was inserted. The solution was stirred vigorously with sonication for one minute, then the mixture was capped and left to stand at r.t. After 48 h the solvents were removed in vacuum oven. In order to perform the photocatalytic experiment in the same vial, 5 ml of ascorbic acid and 5% w/w $Na_2PtCl_6.6H_2O$ were added. The mixture was irradiated with a 100 W white led lamp. The same process was repeated for the three different "good" solvents THF, $CHCl_3$, Tol.

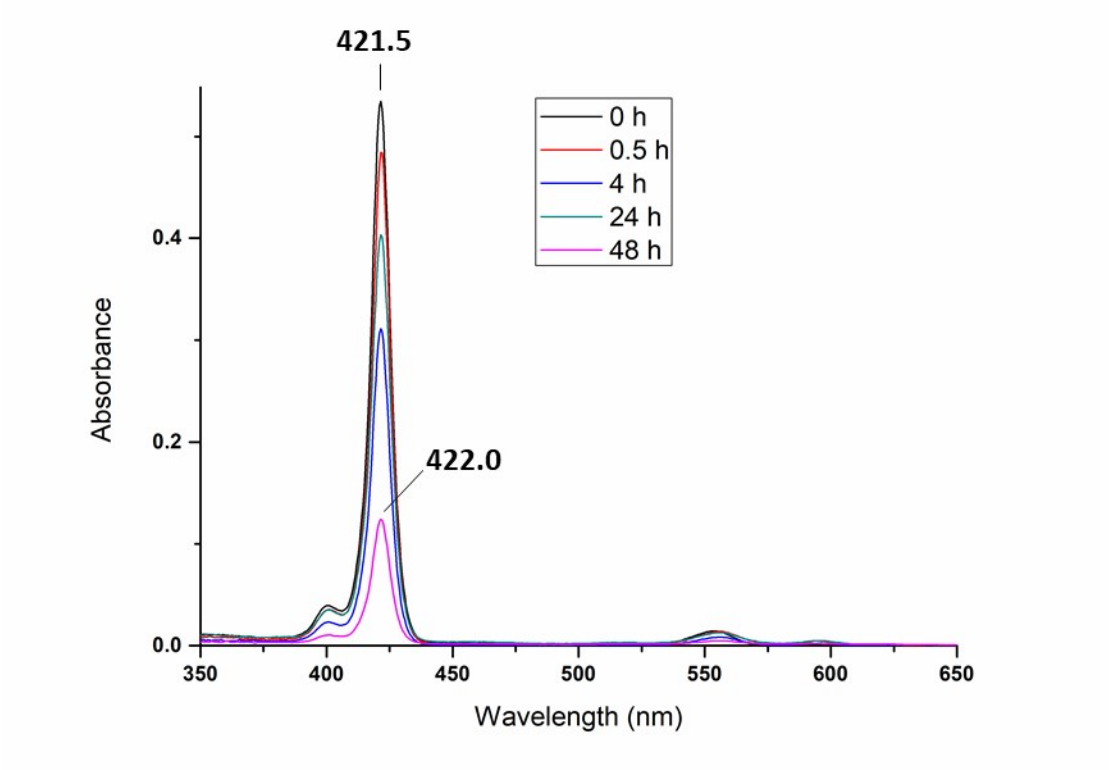


**Figure S1.** UV-Vis spectra of octahedral (THF/MeOH 1:4) in solution at various time intervals 0 h, 0.5 h, 4 h, 24 h, 48 h.

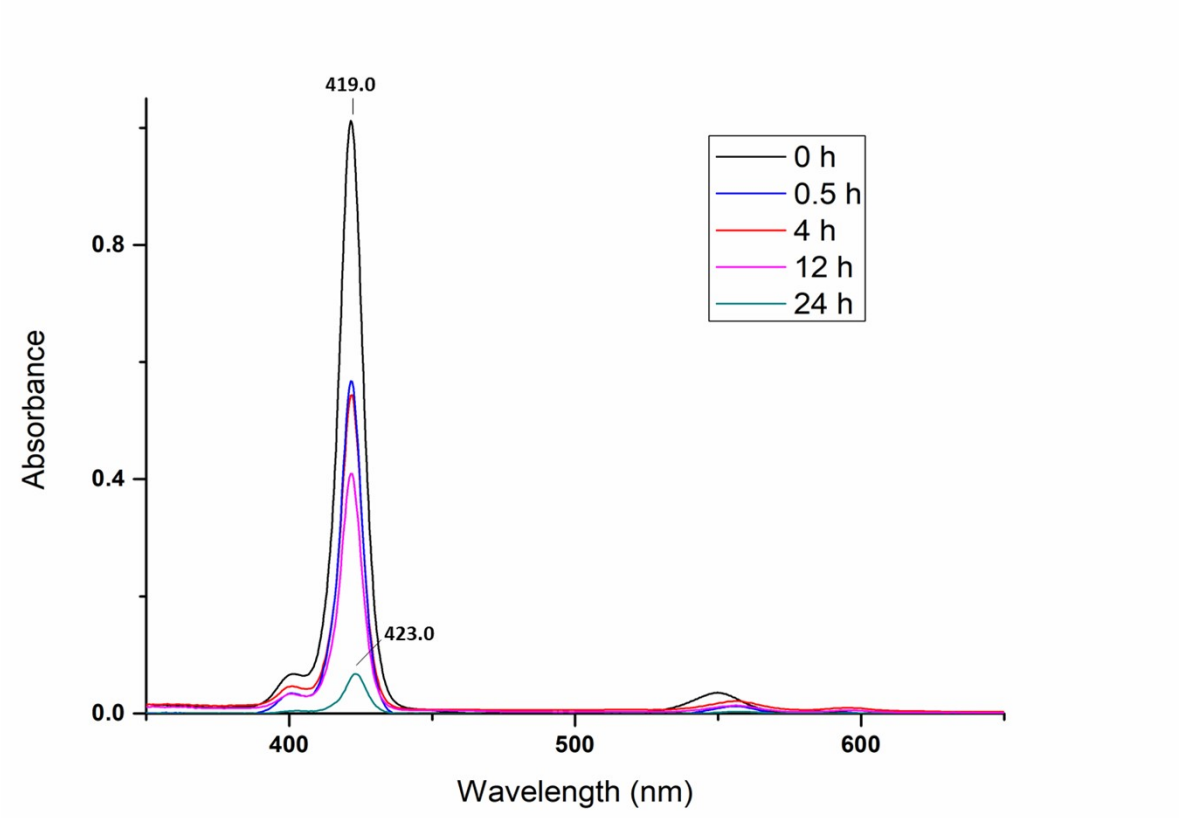


**Figure S2.** UV-Vis spectra of flowers ($CHCl_3$/MeOH 1:4) in solution at various time intervals 0 h, 0.5 h, 4 h, 24 h, 48 h.

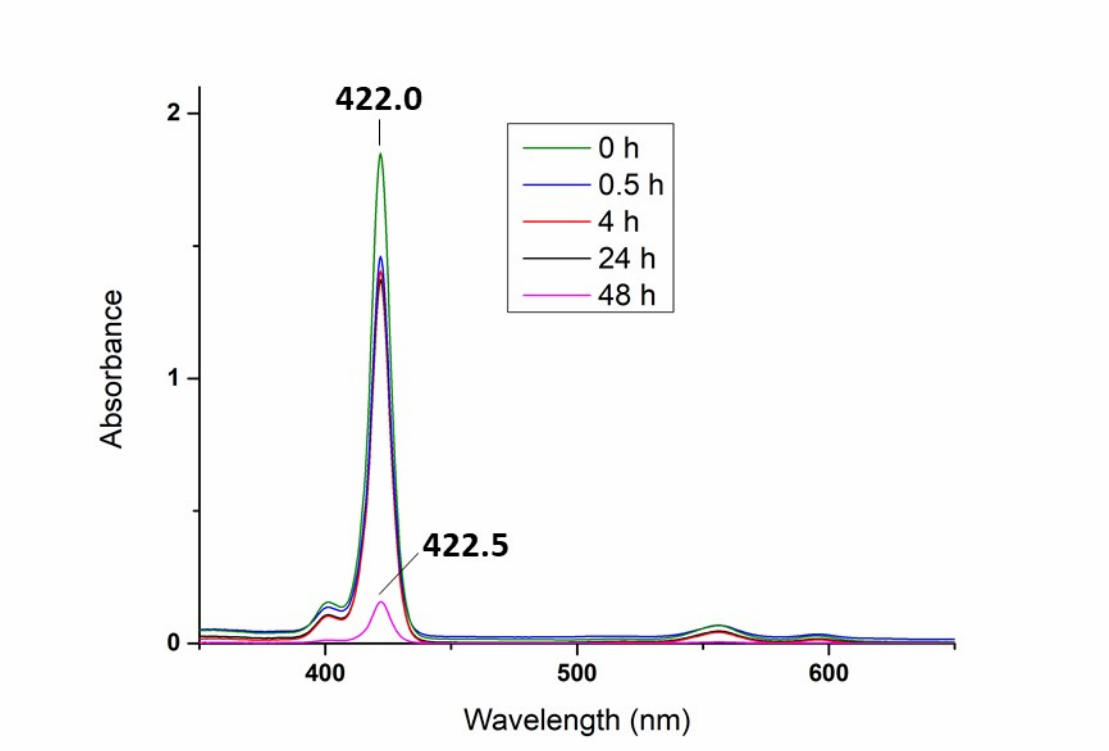


**Figure S3.** UV-Vis spectra of manta-ray (Tol/MeOH 1:4) in solution at various time intervals 0 h, 0.5 h, 4 h, 24 h, 48 h.

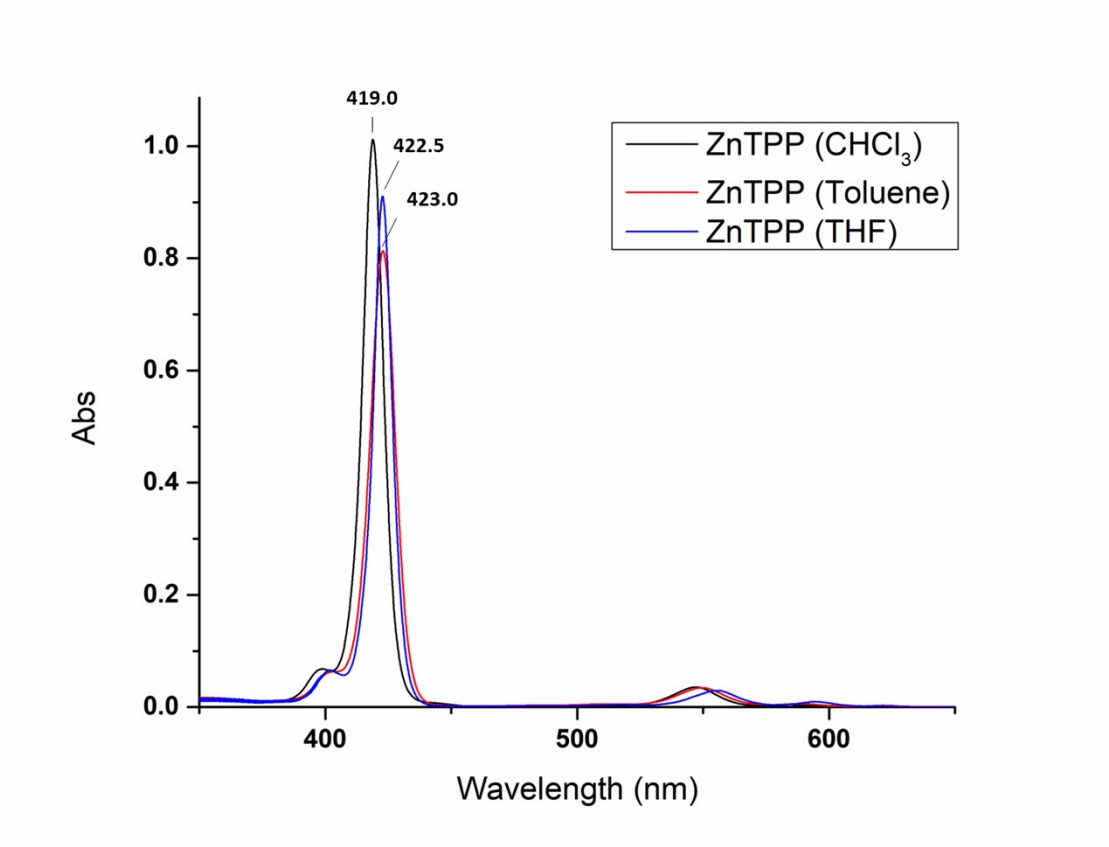


**Figure S4.** UV-Vis spectra of **ZnTPP** in $CHCl_3$, Toluene and THF.

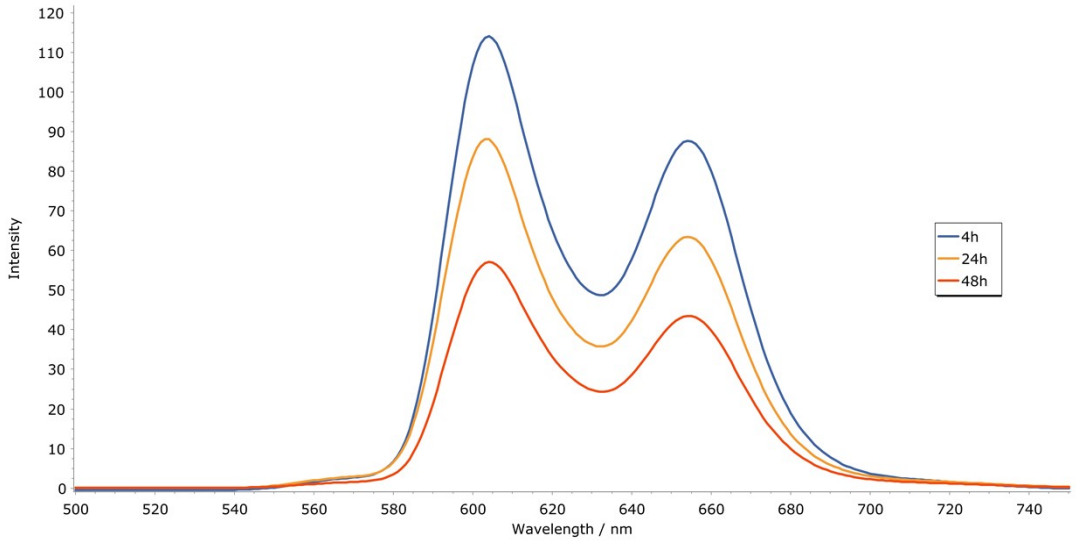


**Figure S5.** Fluorescence spectra of octahedral (THF/MeOH 1:4) in solution at various time intervals 4 h, 24 h, 48 h.

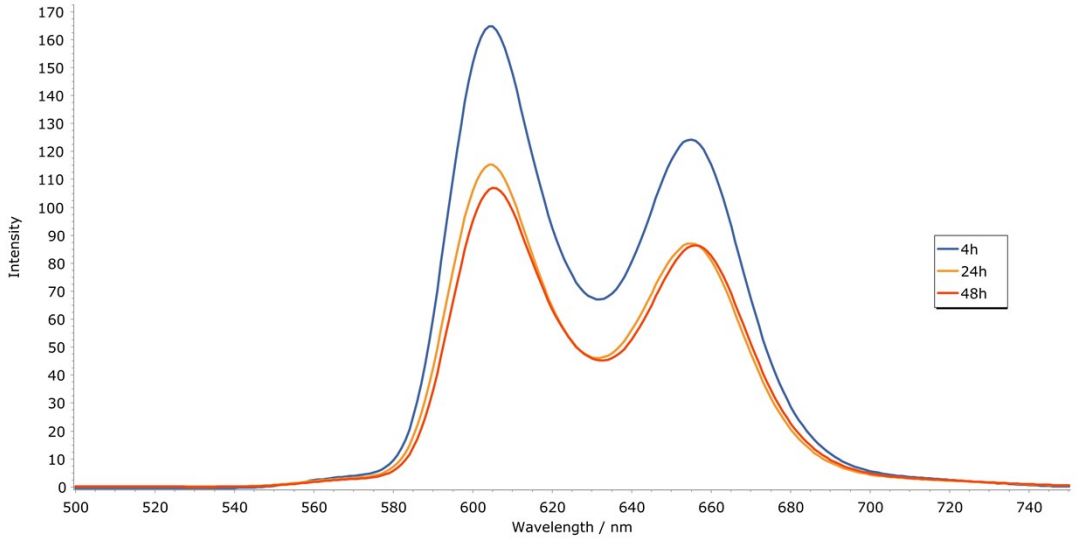


**Figure S6.** Fluorescence spectra of flowers ($CHCl_3$/MeOH 1:4) in solution at various time intervals 4 h, 24 h, 48 h.

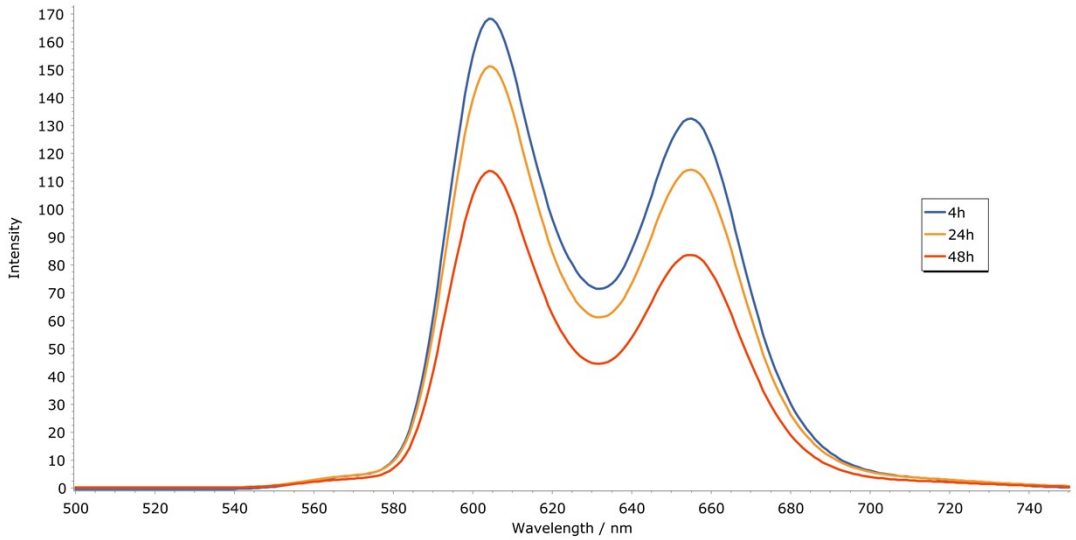


**Figure S7.** Fluorescence spectra of manta-ray (Tol/MeOH 1:4) in solution at various time intervals 4 h, 24 h, 48 h.

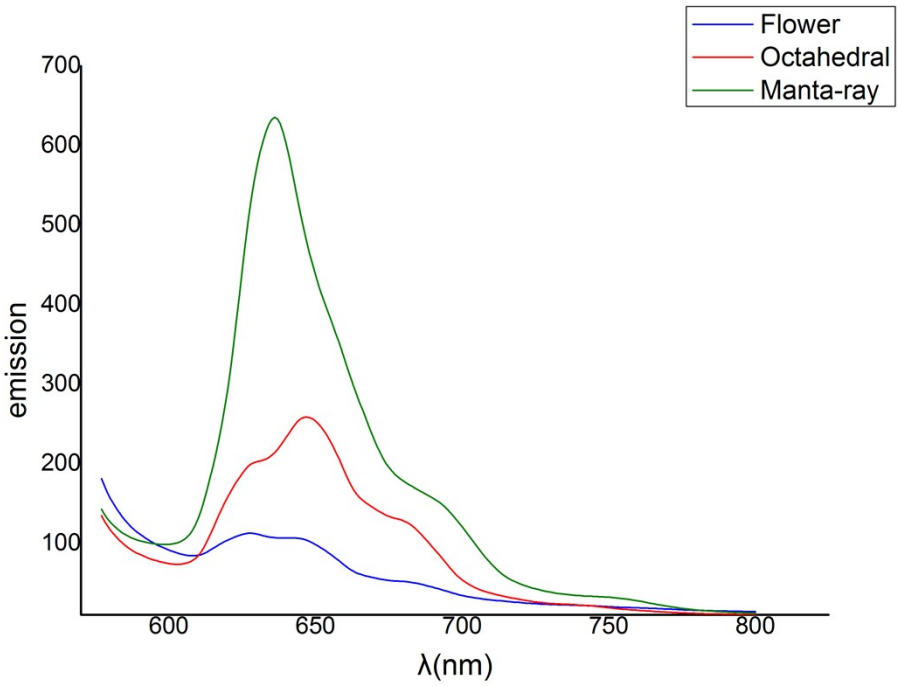


**Figure S8.** Fluorescence spectra of **ZnTPP** in solid state upon its formation of different structures.

**Table S1.** Lifetime decay fluorescence measurements of **ZnTPP** in different solid structures and in solution.

| **Photosensitizer** | **Lifetime ($\tau_1$) (ns)** | **Lifetime ($\tau_2$) (ns)** |
|---|---|---|
| Octahedral (solid) | 0.58 (70%) | 1.96 (30%) |
| "flower" (solid) | 0.70 (66%) | 2.46 (34%) |
| "manta-ray" (solid) | 0.76 (60%) | 2.49 (40%) |
| **ZnTPP** (in $CH_2Cl_2$) | | 1.97 (100%) |
| **ZnTPP** (24 h, solution of $CHCl_3$/MeOH, 1:4 mixture) | | 2.10 (100%) |
| **ZnTPP** (48 h, solution of $CHCl_3$/MeOH, 1:4 mixture) | | 2.20 (100%) |

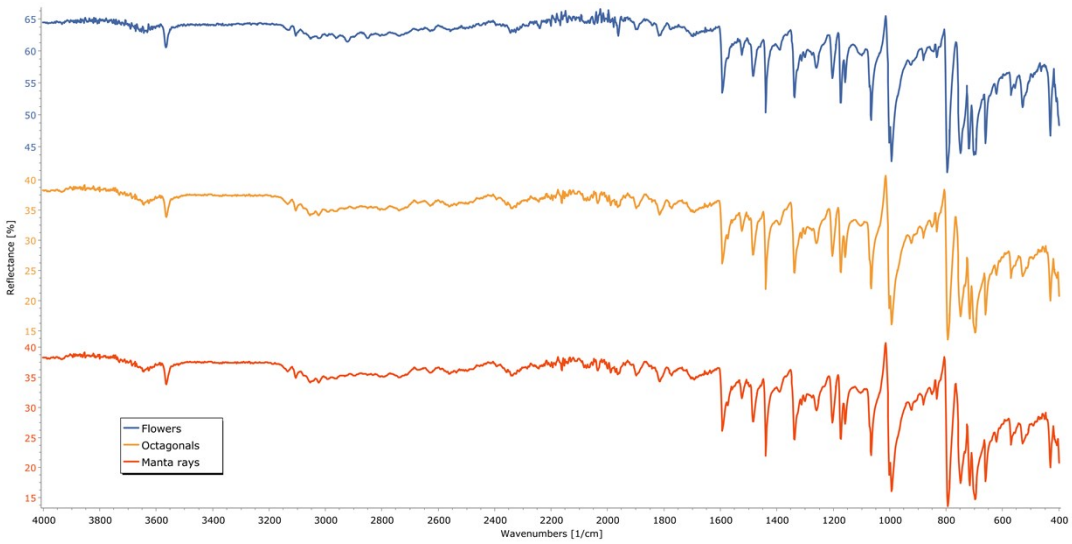


**Figure S9**. IR spectra of a) octahedral (THF/MeOH 1:4), b) flowers ($CHCl_3$/MeOH) and c) manta-ray (Tol/MeOH)

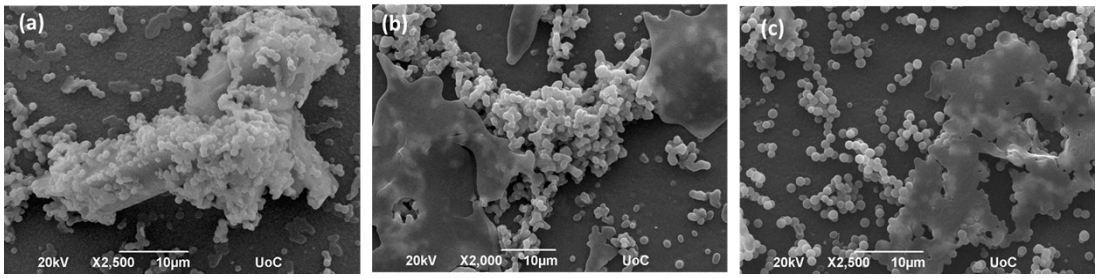


**Figure S10**. SEM images of supramolecular architectures with different morphologies of **ZnTPP** formed after 8 h of light irradiation in good/bad solvent: a) octahedral (THF/MeOH 1:4), b) flower ($CHCl_3$/MeOH 1:4), c) manta-ray (Tol/MeOH 1:4).

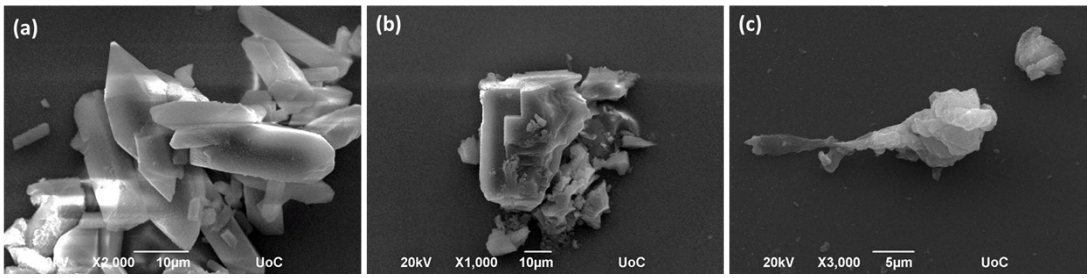


**Figure S11**. SEM images of supramolecular architectures with different morphologies of **ZnTPP** formed in water and in the presence of 5% w/w Pt and ascorbic acids 1 M, after 8 h in the dark: a) octahedral (THF/MeOH 1:4), b) flower ($CHCl_3$/MeOH 1:4), c) manta-ray (Tol/MeOH 1:4).

**Single crystal X-ray diffraction analysis**

**Experimental**

Single crystals of **ZnTPP**$(THF)_2$ were obtained by slow evaporation of a THF/$CH_3OH$ solution of the compound at room temperature over a period of two weeks.[1] A suitable crystal was selected and mounted on a STOE IPDS diffractometer. The crystal was kept at 293(2) K during data collection. Using Olex2 1.3 [2], the structure was solved with the SHELXS [3] structure solution program using Direct Methods and refined with the SHELXL 2018/3 [4] refinement package using Least Squares minimization.

Summary of Crystal Data for **ZnTPP**$(THF)_2$. Formula $C_{52}H_{44}N_4O_2Zn$ ($M_r$ = 822.28 g/mol): triclinic, space group P-1, a = 9.6632(19) Å, b = 11.266(2) Å, c = 11.812(2) Å, α = 65.13(3)°, β = 76.23(3)°, γ = 64.73(3)°, V = 1052.4(5) $Å^3$, Z = 2, T = 293(2) K, μ(MoKα) = 0.63 $mm^{-1}$, 3938 reflections measured (1.9° ≤ θ ≤ 25.6°), 2347 unique ($R_{int}$ = 0.0661, $R_{sigma}$ = 0.1242) which were used in all calculations. The final $R_1$ was 0.038 (I > 2σ(I)) and wR2 was 0.072 (all data).

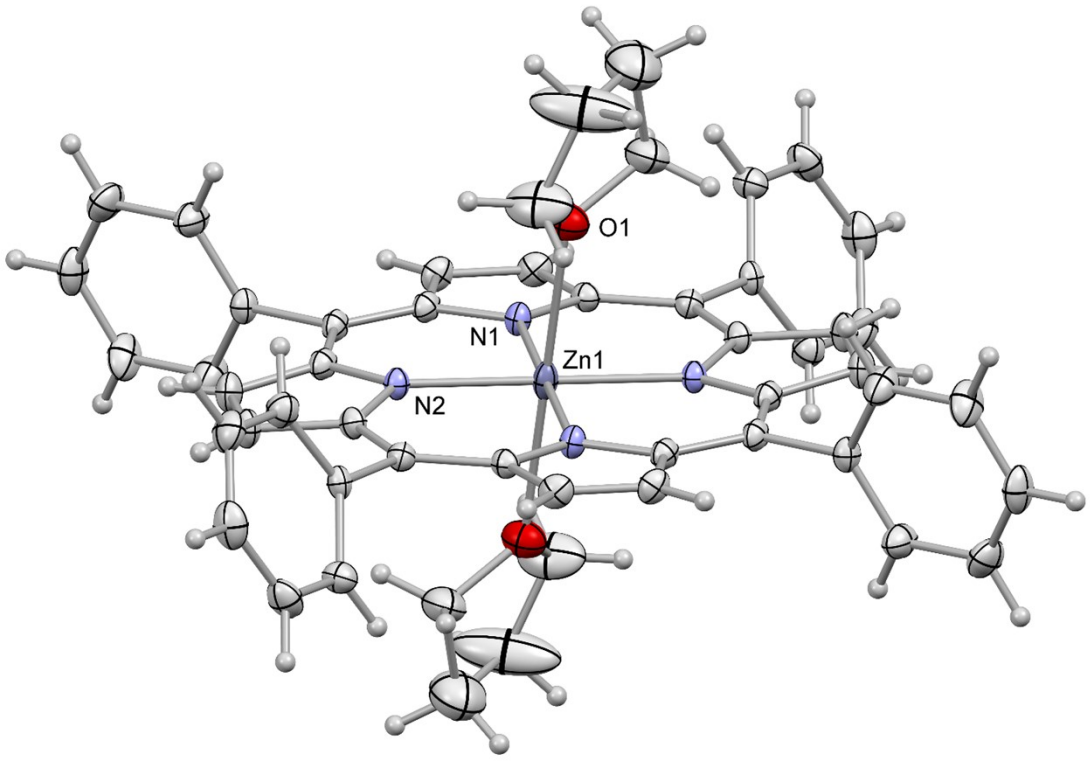


**Figure S9.** View of the crystal structure of **ZnTPP**$(THF)_2$ with displacement ellipsoids shown in the 35% probability level (Color code: C atoms, dark gray ellipsoids; O atoms, red ellipsoids; N atoms, blue ellipsoids; Zn, light mauve ellipsoid; H atoms, gray spheres of arbitrary radius).

**Table S2.** Experimental details for **ZnTPP**$(THF)_2$

| | |
|---|---|
| *Crystal data* | |
| Moiety formula | $C_{52}H_{44}N_4O_2Zn$ |
| $M_r$ | 822.28 |
| Crystal system, space group | Triclinic, *P*-1 |
| *a*, *b*, *c* (Å) | 9.6632 (19), 11.266 (2), 11.812 (2) |
| α, β, γ (°) | 65.13 (3), 76.23 (3), 64.73 (3) |
| *V* (Å$^3$) | 1052.4 (5) |
| *Z* | 1 |
| $\rho_{calc}$ (g cm$^{-3}$) | 1.298 |
| *F*(000) | 430 |
| Radiation type | Mo *K*α (λ = 0.71073 Å) |
| Temperature (K) | 293 |
| μ (mm$^{-1}$) | 0.630 |
| Crystal size (mm) | 0.6 × 0.2 × 0.07 |
| *Data collection* | |
| Diffractometer | STOE IPDS |
| No. of measured, independent and observed [$I > 2\sigma(I)$] reflections | 3938, 3938, 2347 |
| $R_{int}$ | 0.0661 |
| $\vartheta$ range for data collection (°) | 1.9 to 25.6 |
| *Refinement* | |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S* | 0.038, 0.072, 0.74 |
| No. of reflections | 3938 |
| No. of parameters | 268 |
| H-atom treatment | H-atom parameters constrained |
| $\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å$^{-3}$) | 0.42, -0.30 |

**Table S3.** Selected Bond Lengths for **ZnTPP**$(THF)_2$.

| **Atom** | **Atom** | **Length/Å** |
|---|---|---|
| Zn1 | N1 | 2.072 (2) |
| Zn1 | N2 | 2.060 (2) |
| Zn1 | O1 | 2.419 (3) |

**Table S4.** Selected Bond Angles for **ZnTPP**$(THF)_2$.

| Atom | Atom | Atom | Angle/° |
|---|---|---|---|
| N1 | Zn1 | N1$^{i}$ | 180.0 |
| N1 | Zn1 | N2 | 89.40 (8) |
| N1 | Zn1 | O1$^{i}$ | 93.24 (8) |
| N1 | Zn1 | O1 | 86.76 (8) |
| N1 | Zn1 | N2$^{i}$ | 90.60 (8) |
| N2 | Zn1 | N2$^{i}$ | 180.0 |
| N2 | Zn1 | N1$^{i}$ | 90.60 (8) |
| N2 | Zn1 | O1$^{i}$ | 87.11 (9) |
| N2 | Zn1 | O1 | 92.89 (9) |
| O1$^{i}$ | Zn1 | O1 | 180.00 (10) |

[1] (i) −x, −y, −z

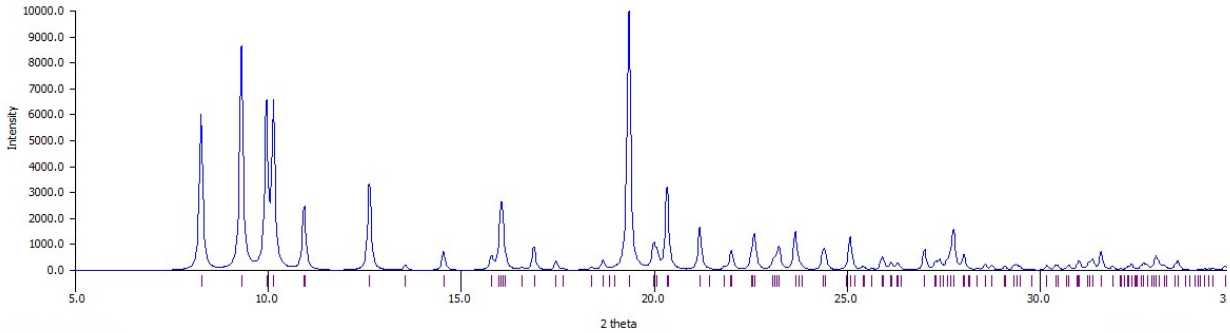


**Figure S10**. Simulated PXRD pattern obtained from the single-crystal X-ray structure of **ZnTPP**$(THF)_2$.

## References


1. Coutsolelos A. G., Orfanos E., Ladomenou K., Angaridis P., CCDC 2153314: Experimental Crystal Structure Determination, 2022, DOI: 10.5517/ccdc.csd.cc2b8pr2
2. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
3. Sheldrick, G. M. (2008). Acta Cryst. A64, 112-122

4. Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.