

Electronic Supplementary Information

Stable water soluble photocatalysts based on porphyrin-carbon dots conjugates produce H₂ under visible light irradiation

Katerina Achilleos,^{†a} Anna Katsari,^{†a} Emmanouil Nikoloudakis,^{*b} Foteini Chatzipetri,^a
Dimitris Tsikritzis,^c Kalliopi Ladomenou,^{*d} Georgios Charalambidis,^{*e} Emmanuel
Stratakis,^{b,f} and Athanassios G. Coutsolelos^{*a,b}

^a Laboratory of Bioinorganic Chemistry, Chemistry Department, University of Crete,
70013 Heraklion, Crete, Greece.

^b Foundation for Research and Technology (FORTH), Institute of Electronic Structure
and Laser (IESL), 70013, Heraklion, Greece.

^c Department of Electrical & Computer Engineering, Hellenic Mediterranean
University (HMU), Heraklion, Crete 71410, Greece.

^d Hephaestus Laboratory, Department of Chemistry, School of Science, Democritus
University of Thrace, Kavala, Greece.

^e Theoretical and Physical Chemistry Institute, National Hellenic Research Foundation,
48 Vassileos Constantinou Ave., 11635, Athens, Greece.

^f Qingdao Innovation and Development Center, Harbin Engineering University,
Qingdao 266000 Shandong, P. R. China.

[†] These two authors contributed equally to this work.

Corresponding Authors

E-mail: enikoloudakis@iesl.forth.gr (E.N.), kladomenou@chem.duth.gr (K.L.),
gcharal@eie.gr (G.C.), acoutsol@uoc.gr (A.G.C)

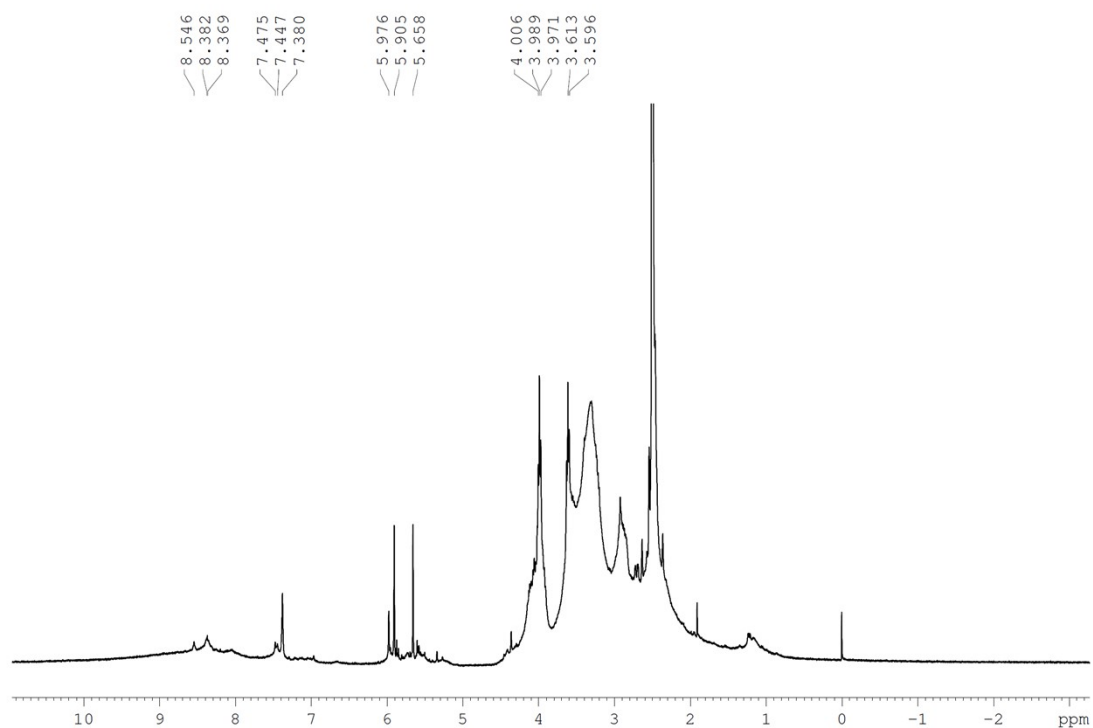


Figure S1. ^1H NMR spectrum of NCDots in d_6 -DMSO.

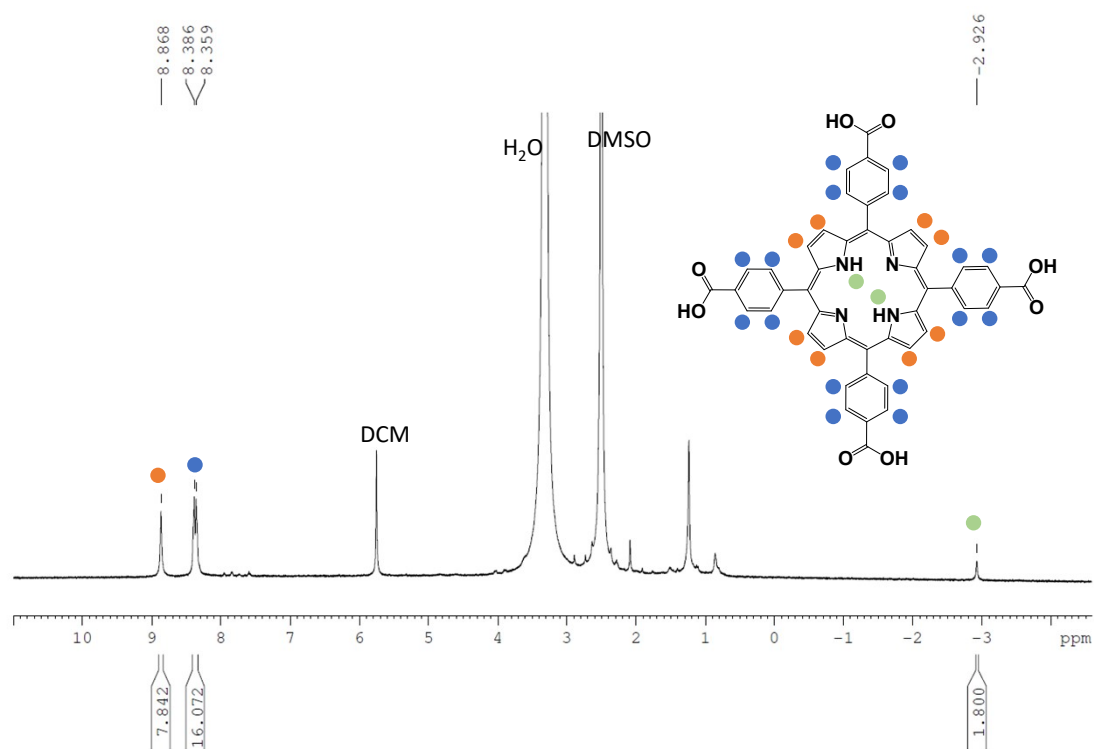


Figure S2. ^1H NMR spectrum of compound TCPP in d_6 -DMSO.

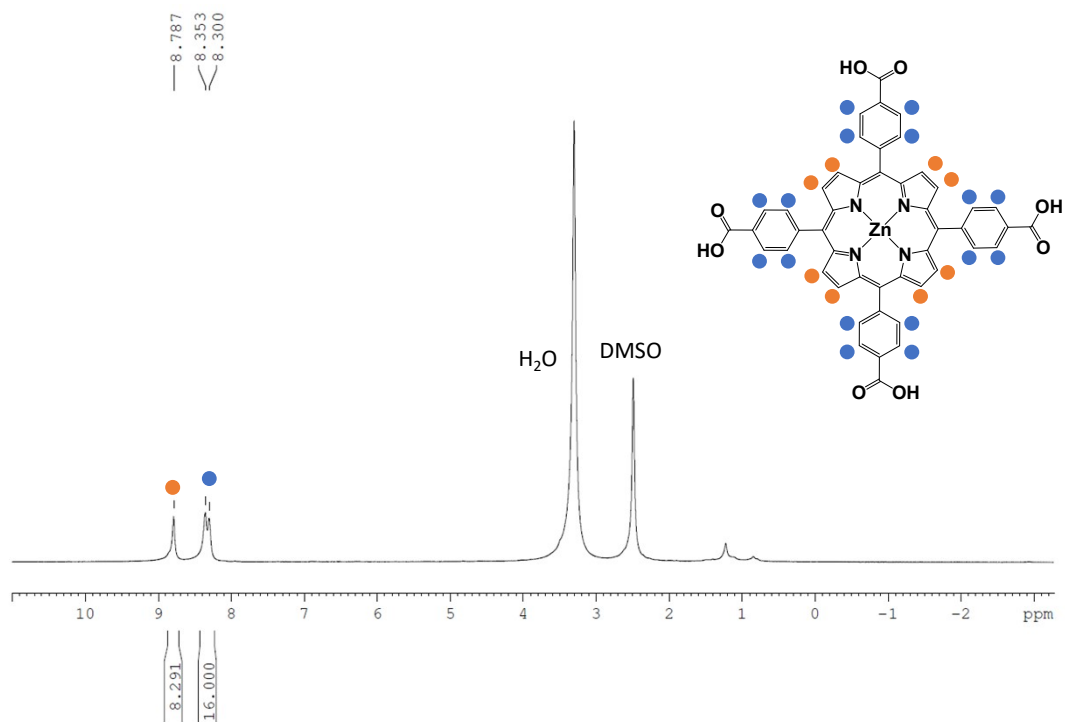


Figure S3. ^1H NMR spectrum of compound **ZnTCPP** in $\text{d}_6\text{-DMSO}$.

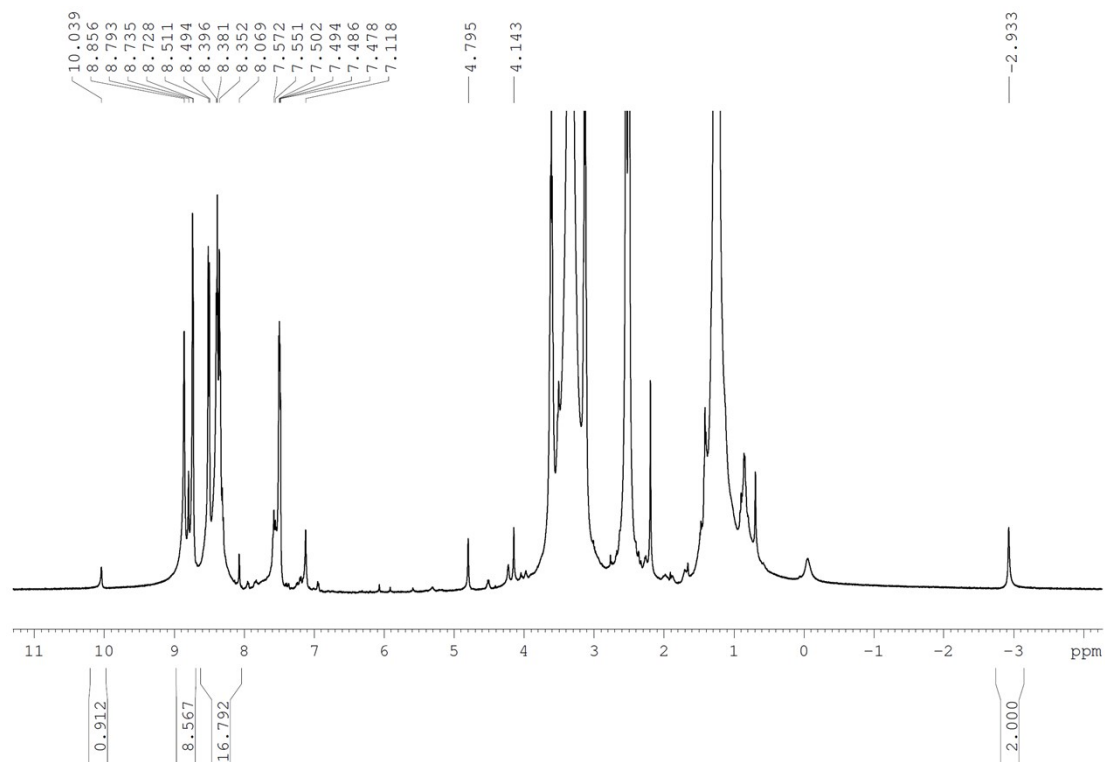


Figure S4. ^1H NMR spectrum of compound **TCPP-NCDots** in $\text{d}_6\text{-DMSO}$.

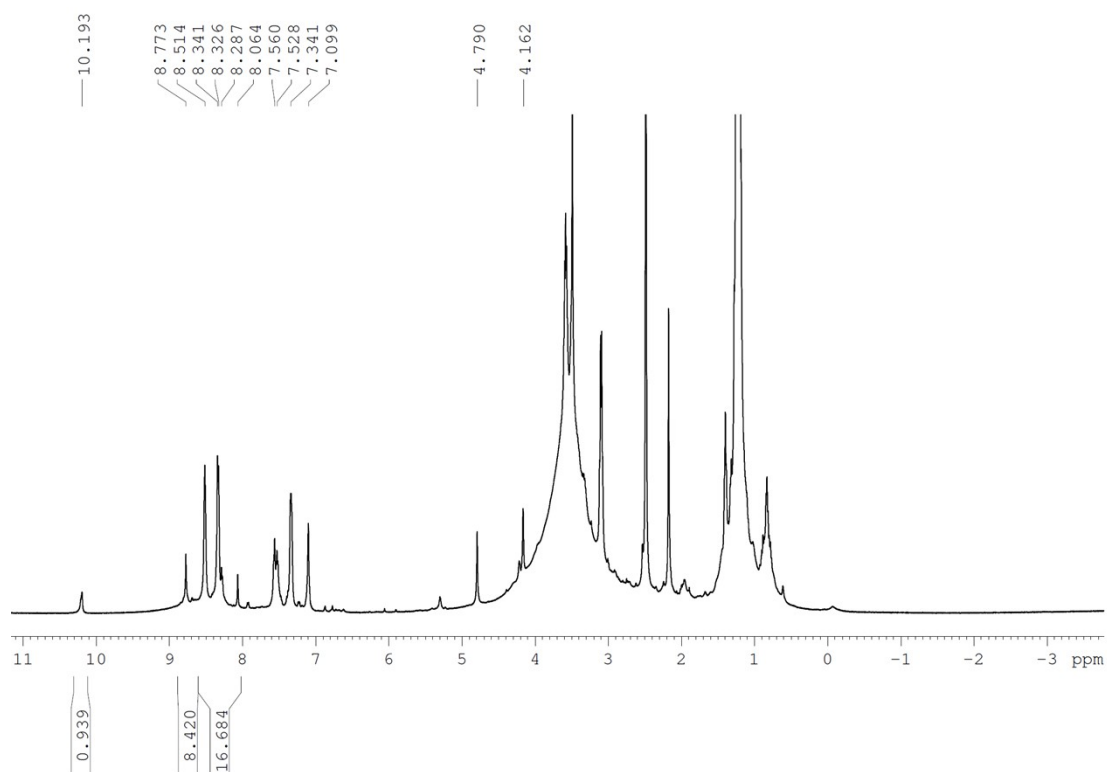


Figure S5. ^1H NMR spectrum of compound ZnTCPP-NCDots in d_6 -DMSO.

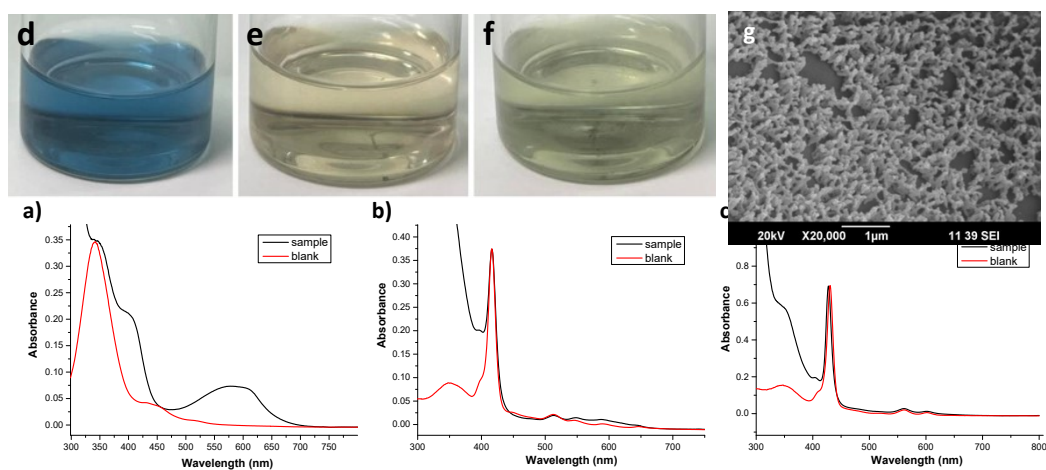


Figure S6. UV-Vis spectra of the sample with ninhydrin and the corresponding blank of Kaiser experiments for a) NCDots, b) TCPP-NCDots and c) ZnTCPP-NCDots. Photos of the samples of d) NCDots, e) TCPP-NCDots and f) ZnTCPP-NCDots. g) SEM image of NCDots.

Table S1: Table of concentration ($\mu\text{mol/g}$) and percentage of free primary amino groups of **NCDots**, **TCPP-NCDots** and **ZnTCPP-NCDots**.

Compound	$\mu\text{mol/gr}$	% Free $-\text{NH}_2$
1. NCDots	121	100%
2. TCPP-NCDots	12	9.9%
3. ZnTCPP-NCDots	13	10.7%

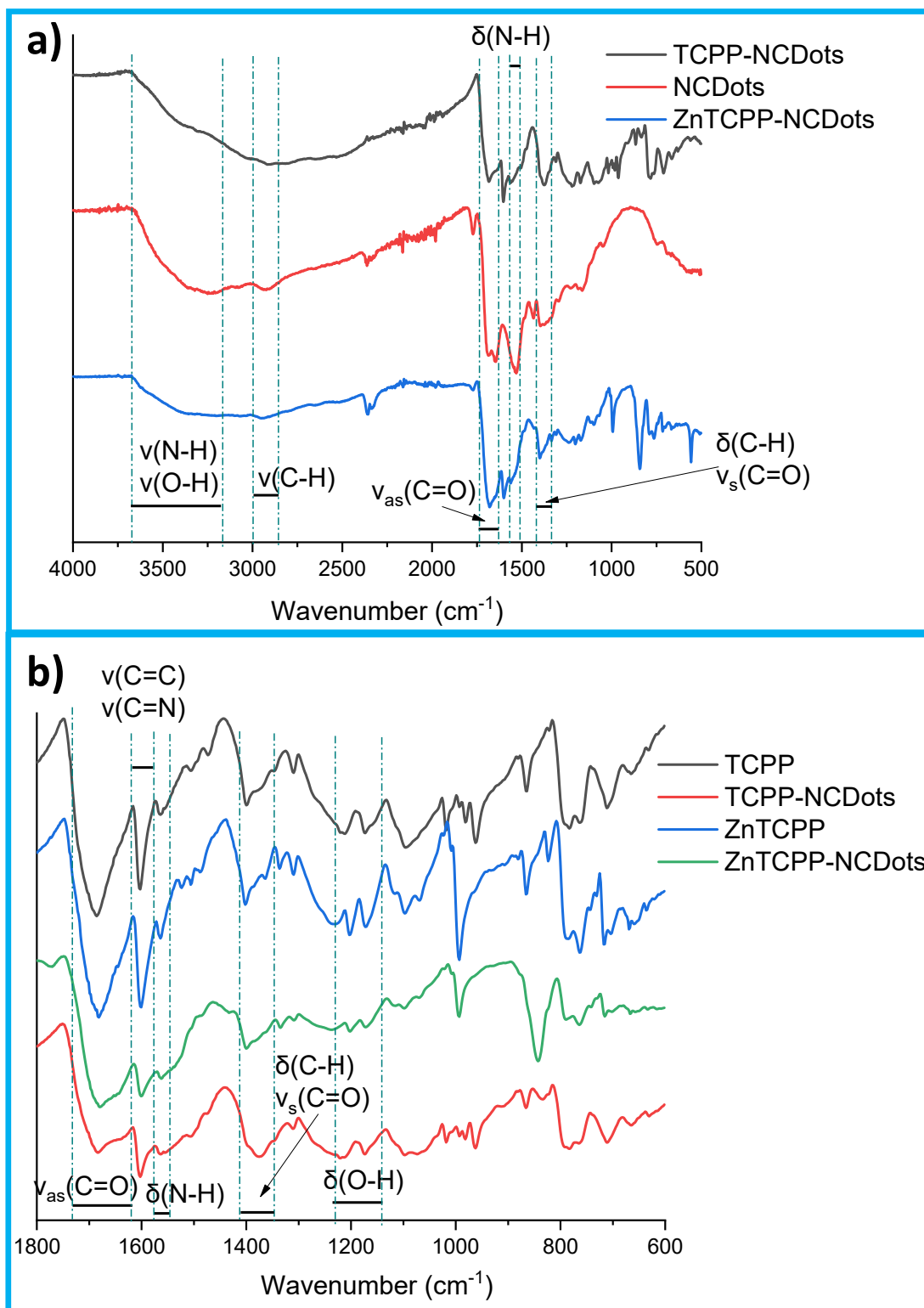


Figure S7. FT-IR spectra of TCPP-NCDots, ZnTCPP-NCDots, NCDots and the starting TCPP and ZnTCPP porphyrins.

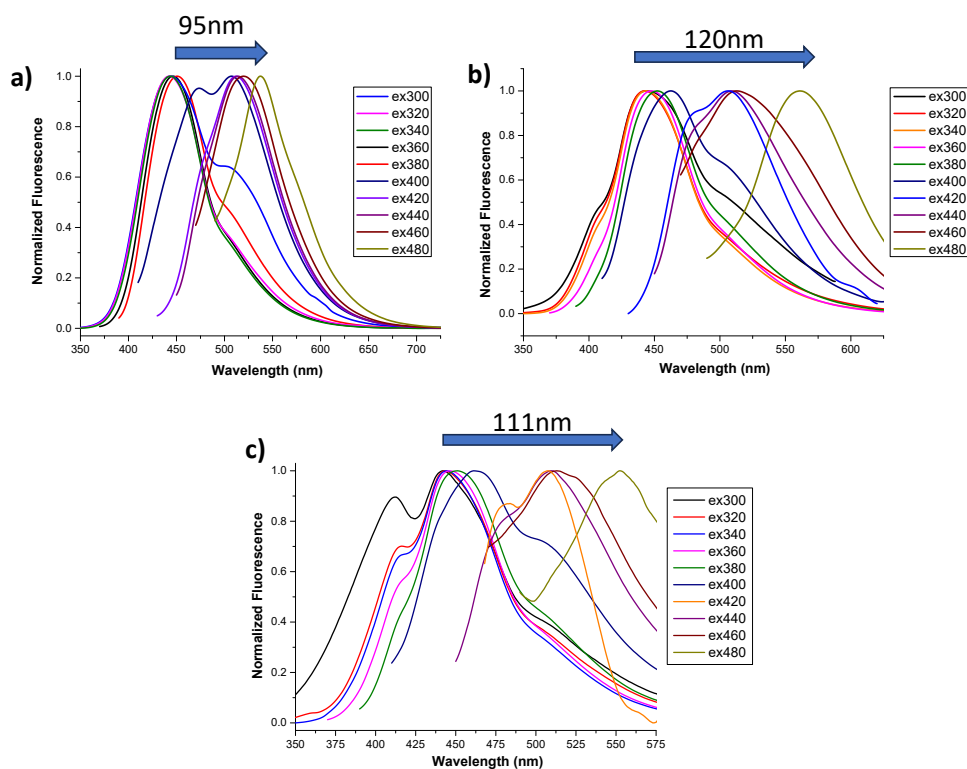


Figure S8: Normalized emission spectra in DMSO of the NCDot-originated emission band for nanomaterials a) **NCDots**, b) **TCPP-NCDots** and c) **ZnTCPP-NCDots**.

Table S2. Atomic fractions of carbon containing species.

Sample	at%					
	C-C	C-N/C-O	-C=O	-COO	π - π^*	C bonded with O/N
TCPP	74.0	11.7	5.3	6.0	3.0	23.0
ZnTCPP	75.9	10.4	4.3	6.6	2.8	21.2
NCDots	51.2	31.2	16.0	1.6		48.8
TCPP-NCDots	68.4	21.2	10.5	0	0	31.6
ZnTCPP-NCDots	66.0	22.6	10.0	1.4	0	34.0

Table S3. Binding Energies of N1s and Zn2p_{3/2} peaks.

	N1s (eV)	Zn2p _{3/2} (eV)
TCPP	398.2 & 400.1	
ZnTCPP	398.6	1022.2
NCDots	400.1	
TCPP-NCDots	400.0	
ZnTCPP-NCDots	400.1	1021.1

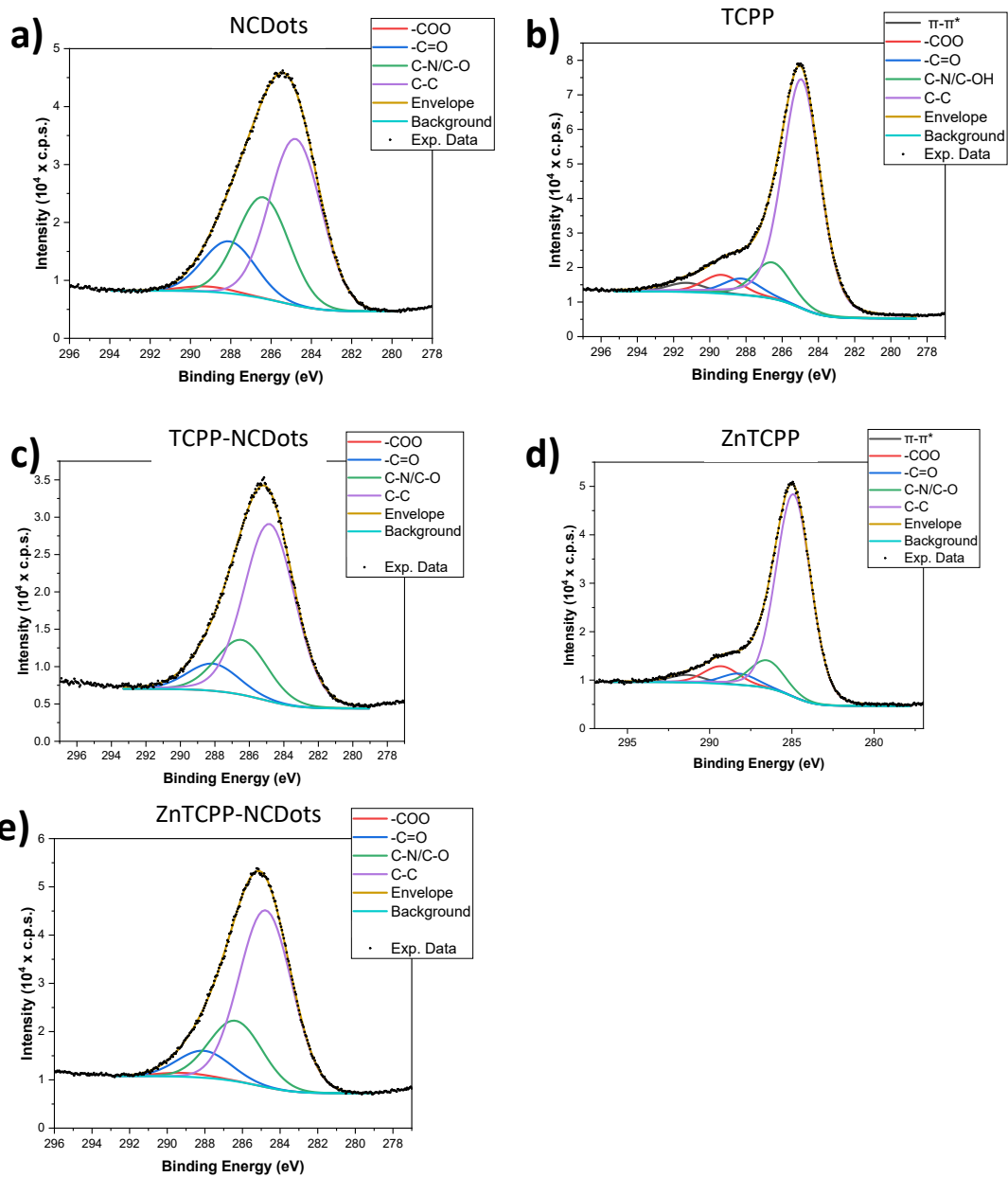


Figure S9. C1s spectra of the a) NCDots, b) TCPP, c) TCPP-NCDots, d) ZnTCPP and e) ZnTCPP-NCDots.

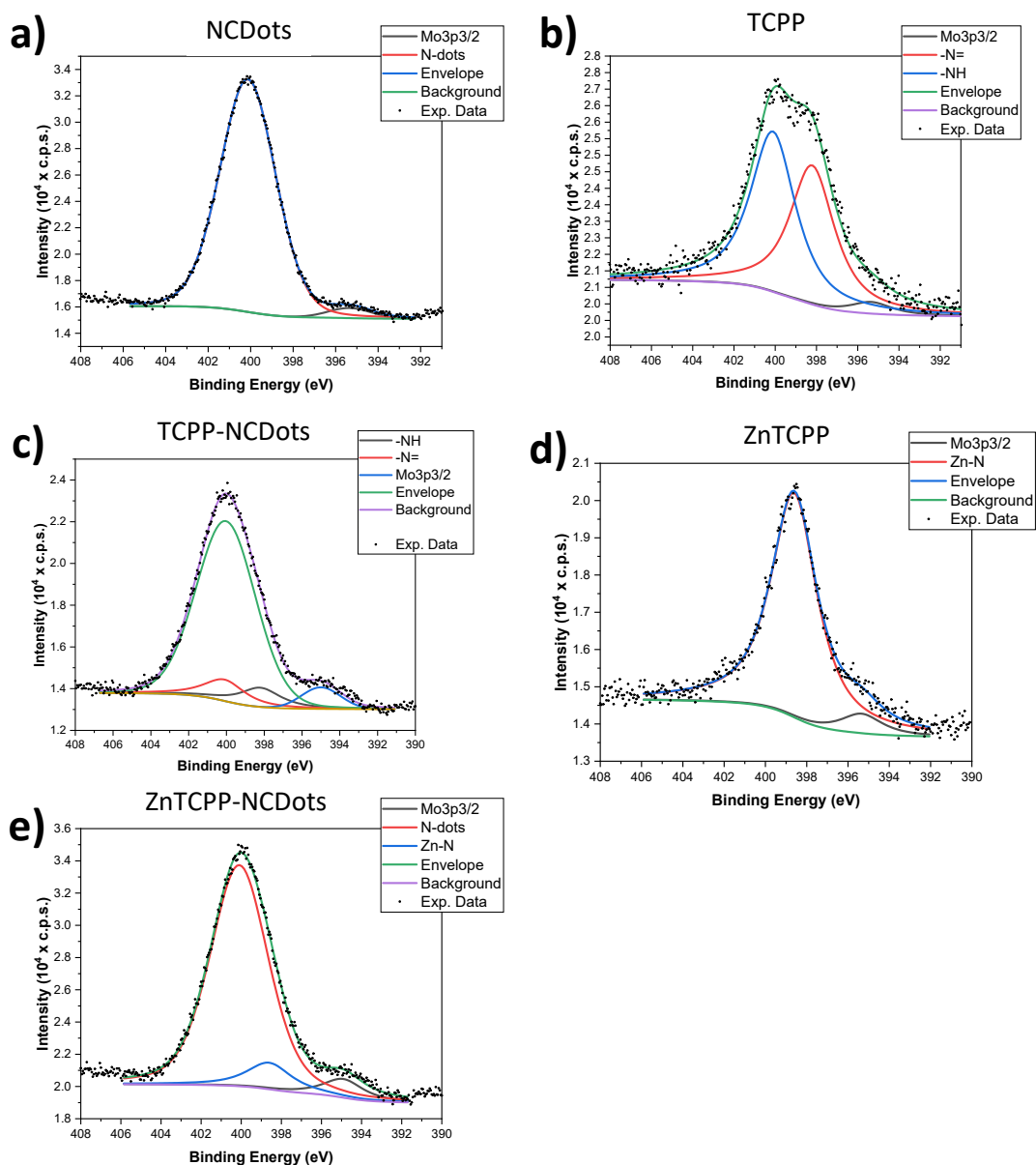


Figure S10. N1s spectra of the a) NCDots, b) TCPP, c) TCPP-NCDots, d) ZnTCPP and e) ZnTCPP-NCDots.

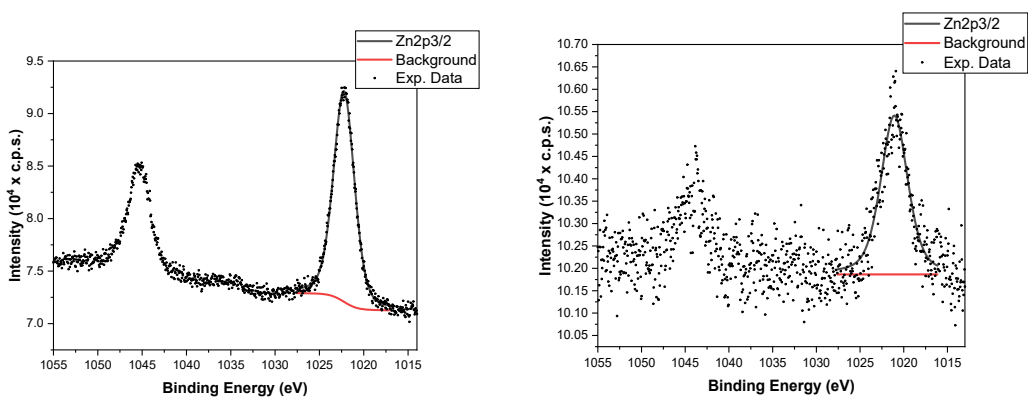


Figure S11. XPS peaks of ZnTCPP (left) and ZnTCPP-NCDots (right).

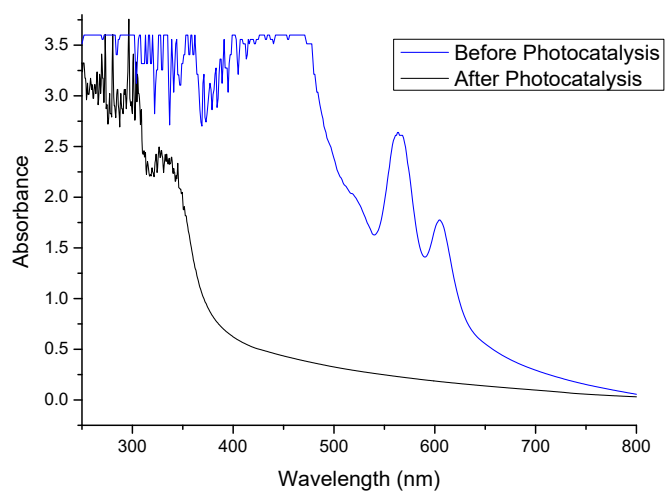


Figure S12. UV-Vis absorption spectra of the catalytic media using **ZnTCPP-NCDots** photocatalyst before and after the catalysis.

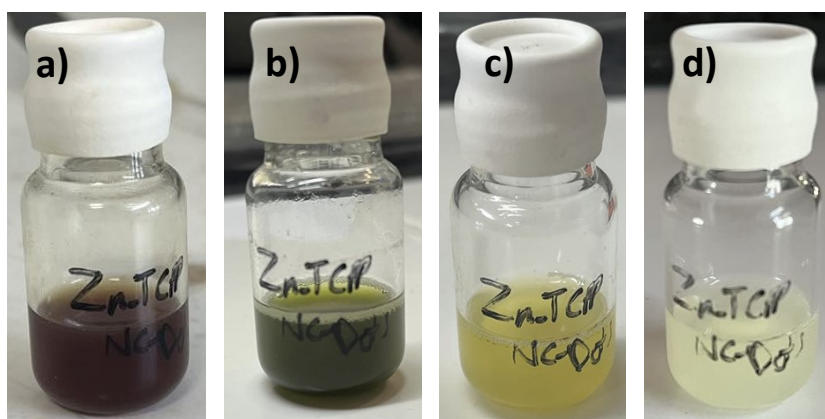


Figure S13. Photos of the catalytic media using **ZnTCPP-NCDots** photocatalyst after a) 0h, b) 24h, c) 48h and d) 72h of light irradiation.

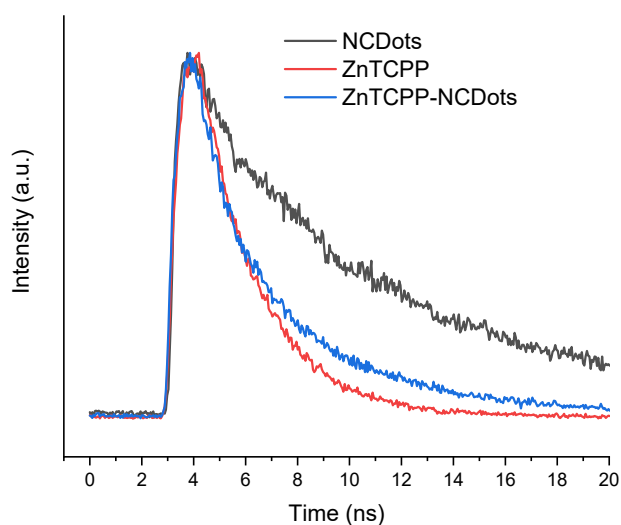


Figure S14. Histogram of lifetime fluorescence decay of **ZnTCPP**, **NCDots** and **ZnTCPP-NCDots** with a 406 nm excitation.

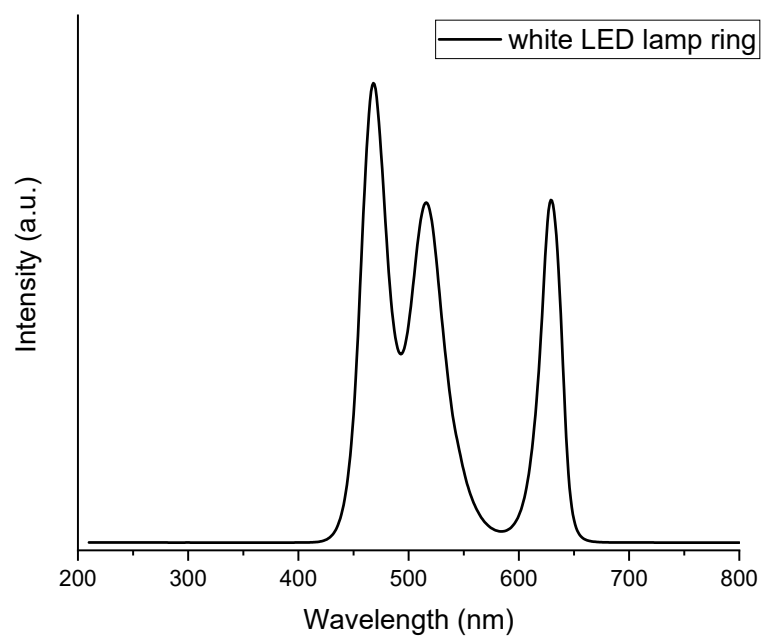


Figure S15. Spectral profile of the white LED lamp ring of 40 W with colour temperature 6400 K and lumen of 3800 LM used for the photocatalytic experiments.



Figure S16. Photo of the photoreactor used for the photocatalytic experiments.