

A Perylenediimide-based Zinc-Coordination Polymer for Photosensitized Singlet-Oxygen Generation

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1. Analytical Methods

Surface Area Determination (BET)

Adsorption measurements with N₂ (99.999 vol%) at 77 K were carried out on a 3Flex Physisorption from Micromeritics Instrument Corp., which uses a manometric method to determine the amount adsorbed under an equilibrated gas pressure.

Adsorption data was processed using the 3Flex Software Version 5.01 by Micromeritics Instrument Corp. and plotted in OriginPro 2019b by OriginLab Corp. To create open access data, prevent issues with data mining, and facilitate machine learning, all isotherms are presented as adsorption information files in the SI [1]. The conversion of measurement files was performed using an open access web application. [2]

The activated samples were transferred into pre-weighed sample tubes and capped with Micromeritics Check Seals. The samples were subsequently heated at 60 °C for 12 hours under a dynamic vacuum of ~ 10–3 mbar using SmartVac Prep by Micromeritics Instrument Corp. to ensure the absence of unwanted adsorbates and identical pre-measurement states of all the samples. The mass of the adsorbent was then recorded. The free space of the sample tube was determined prior to measuring each adsorption isotherm using helium (99.999 vol%). A water bath was used to maintain temperatures from 5–25 °C; a liquid nitrogen bath was used for measurements at 77 K.

Nuclear Magnetic Resonance Spectroscopy (NMR)

¹H-NMR spectra were recorded on a BRUKER AVIII 400 US with 400 MHz (¹H). The chemical shifts δ were referenced on the residue of the proton signals of the used solvents and specified in parts per million (ppm). The determined data are shown in the following presented sequence: chemical shift in ppm (multiplicity, coupling constant, integral, and assignment). The following abbreviations were used in the assignment of the signals: s – singulett, m – multipllett.

Powder X-Ray Diffraction (PXRD)

Powder X-ray diffraction measurements were carried out on a Rigaku MiniFlex 600-C diffractometer. The diffractometer is equipped with a 600 W X-ray tube and a D/teX Ultra silicon strip detector and a scan width of $2\Theta = 3\text{--}50^\circ$.

Solid State UV/Vis (SS-UV/Vis)

The UV/Vis spectra of solids were recorded on a UV-3600 Plus from SHIMADZU at a wavelength range of 200 nm–800 nm. The sample was sandwiched between two quartz microscope plates from Alfa Aesar and measured at room temperature.

UV/Vis Spectroscopy

UV/Vis spectra were measured on a Lambda 365 UV/Vis Spectrometer from Perkin Elmer at a wavelength range of 0–900 nm. The spectrometer uses a tungstenhalogen and deuterium interface.

Elemental Analysis

The elemental analysis was carried out in the Microanalytical Laboratory at the Technical University of Munich. The analyses for carbon, chlorine hydrogen, nitrogen, and zinc were carried out with a flash 88 combustion method at 1800 °C with an ELEMENTAL analyzer from HEK-ATECH. All data are presented in %.

Thermogravimetric Analysis (TGA)

The TGA was carried out with a TGA/DSC 3+ STAR system from METTLER TOLEDO, to which a gas analysis system from THERMOSstar was connected. The sample was filled into a crucible, which was tared beforehand, and the sample was weighed in the device.

Single-Crystal X-Ray Diffraction (SC-XRD)

X-ray intensity data of the compound was collected at 100(2)K using a Bruker D8 Venture diffractometer equipped with a Helios optic monochromator, a Photon 2 CPAD detector, and a Mo IMS micro source (Mo-K α radiation) (compound 2) or a Photon 100 CMOS detector and a TXS rotating anode (Mo-K α radiation) (compound 3). The raw area detector data frames were reduced and corrected for absorption effects using the SAINT and SADABS programs with multi-scan absorption correction. Final unit cell parameters were determined by fast Fourier transform refinement of the respective independent reflections obtained from the data sets. The structure was solved using SHELXT. Difference Fourier calculations and full-matrix least-squares refinements against F² were performed by SHELXL-2014/7 (Sheldrick, 2014). All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were calculated in ideal positions using a riding model.

Fluorescence Spectroscopy

A FS5 Spectrofluorometer from Edinburgh Instruments was used for the fluorescence measurements. As the light source, a 150 W CW ozone-free xenon arc lamp was used and a Czerny–Turner design monochromator with a dual grating turret. The detector used was a Photomultiplier R928P with a spectral coverage of 200 nm–900 nm.

2. Synthetic Procedures

1,6,7,12-tetrachloro-perylene-3,4,9,10-tetracarboxylic anhydride 1: the synthesis was performed according to a literature-known synthesis. [18] In a 100 mL Schlenk flask, 1 g of perylene-3,4,9,10-tetracarboxylic acid anhydride 1 (2.5 mmol, 1 eq.) and 0.17 g of iodine (0.68 mmol, 0.27 eq.) in 6.55 mL of chlorosulfonic acid were stirred for 2 days at 70 °C under argon atmosphere. After completion, the reaction mixture was slowly poured into 500 mL of ice water. Subsequently, the precipitating orange solid was filtered, washed with water, and dried to produce a bright orange powder (1.32 g, 2.49 mmol, 99%). ¹H-NMR (400 MHz, CDCl₃): δ (ppm) = 8.74 (s, 4H).

1,6,7,12-tetrachloroperylene-diimide-N,N'-di-benzoic acid (H₂tpbd) 2: the synthesis was performed with a modified literature synthesis [19]. In a 100 mL round bottom flask, 1 g of 1 (1.89 mmol, 1 eq.) and 3.88 g 4-aminobenzoic acid 3 (28.3 mmol, 15 eq.) were dissolved in 25 mL of propionic acid and stirred for 2 days at 160°C. After the completion of the reaction, the reaction mixture was poured into 100 mL of water and subsequently filtered off. The filtrate was washed with 100 mL of water/methanol (1:1), and afterwards the orange solid was dried to constant weight (1.1 g, 1.89 mmol, 82%).

¹H-NMR (400 MHz, DMSO-d₆): δ (ppm) = 13.20 (s, 2H, COOH), 8.64 (s, 4H), 8.21–8.05 (m, 4H), 7.65–7.56 (m, 4H).

Zn(tpdb)(DMF)₃ 3: in a 4 mL screw-cap vial, Zn(NO₃)₂ (15.0 mg, 0.05 mmol, 3.8 eq.) and H₂tpbd 2 (10.0 mg, 0.013 μ mol, 1 eq.) were dissolved in 3 mL of DMF. Afterwards, the solution was sonicated and placed for 96 h at 90°C in an oven. The precipitated solid was then filtered and dried to constant weight to produce orange needles of Zn(tpdb)(DMF)₃ 3 (4.13 mg, 0.0039 mmol, 30%)

Elemental analysis (%) calc. for Zn(tpdb)(DMF)₃: C, 53.17; H, 3.17; N, 6.66; Zn, 6.22; Cl, 13.49; found C, 53.57; H, 2.78; N, 6.03; Zn, 6.2; Cl, 13.0.

¹O₂-Evolution Experiments

In a glovebox, a 20 mL phototube was filled with 1.25 mg (4.62 mmol, 1 eq.) of DBPF and 1 eq. of the respective photosensitizer **2** or **3**. A total of 5 mL of dried acetonitrile was added with argon counter flow and subsequently the suspension was stirred for 30 minutes in the dark to achieve the adsorption/desorption equilibrium under oxygen atmosphere. Afterwards, an LED with a wavelength of 512 nm was turned on and, at defined time intervals, aliquots of the reaction solution were obtained, diluted, and investigated, and UV/Vis spectra were recorded.

3. Supplementary Figures

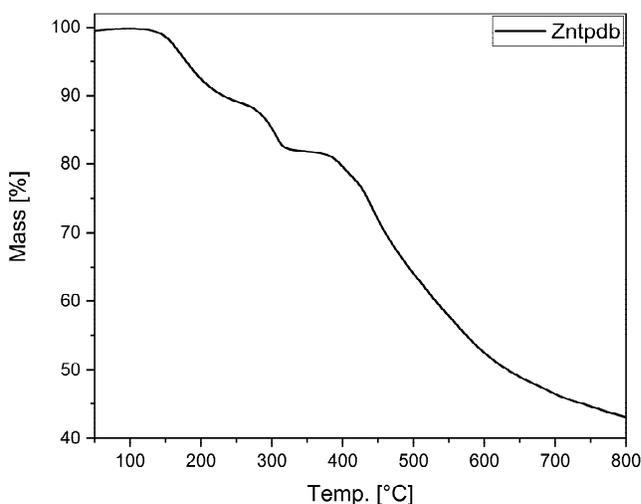


Figure S1. Thermal gravimetric analysis of Zn(tpdb)(DMF)₃ from 25°C to 800°C with a rate of 10 K min⁻¹. The weight loss of 10% starting at 150°C indicates that the loss in the structure included water. The subsequent weight loss of 5% starting at 300°C corresponds to the stored DMF in the structure. The MOF structure is then stable until 400°C. At this temperature, the MOF starts to decompose.

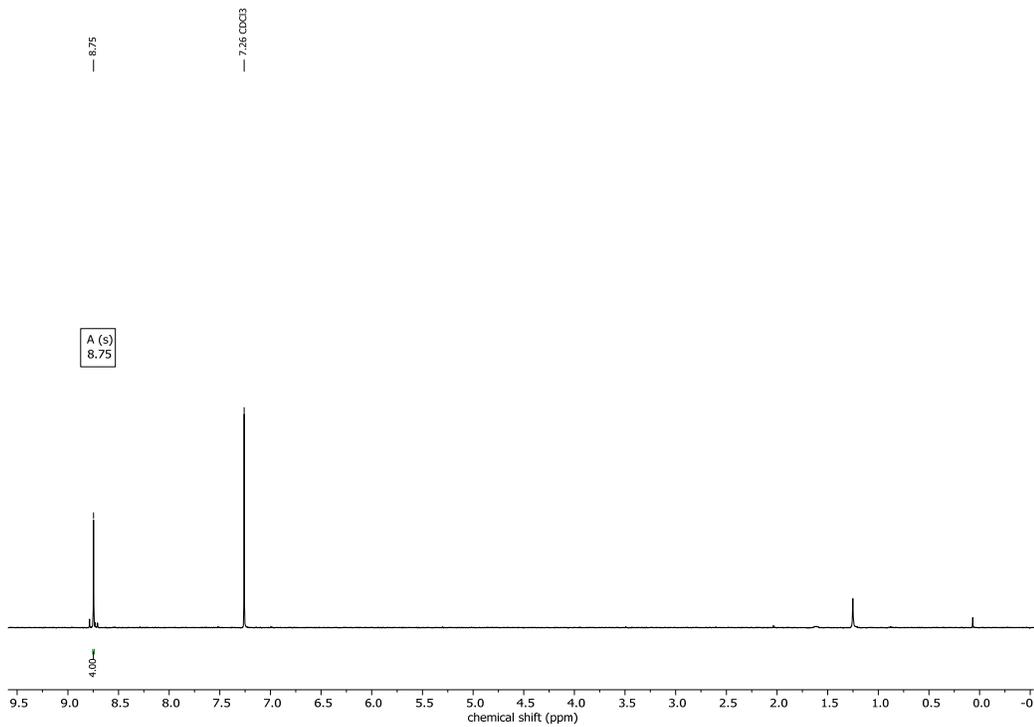


Figure S2. $^1\text{H-NMR}$ of 1,6,7,12-tetrachloro-perylene-3,4,9,10-tetracarboxylic anhydride (**1**) in CDCl_3 showing a single singlet, according for the H atoms in the bay area of the perylene.

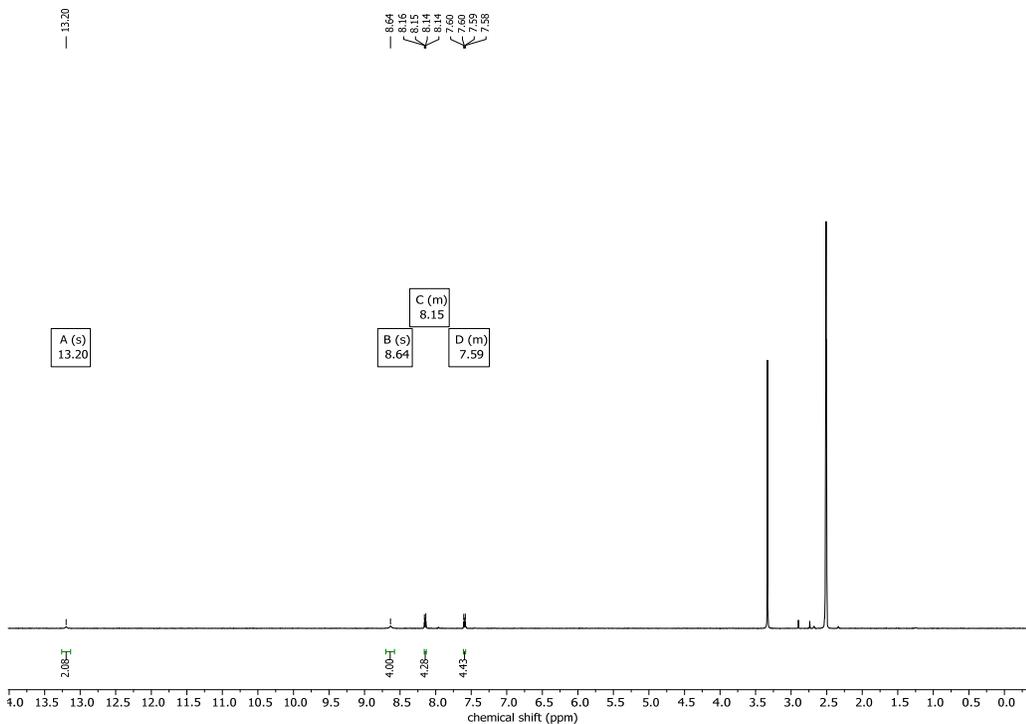


Figure S3. $^1\text{H-NMR}$ of 1,6,7,12-tetrachloroperylene diimide- $\text{N,N}'$ -di-benzoic acid (**2**) in DMSO-d_6 showing a singlet at 13.2 ppm for the carboxylic acid groups, and an additional singlet at 8.64 ppm for the H atoms in the bay area of the perylene. Additionally, two multiplets can be seen, accounting for the aromatic H atoms of the benzoic acid at 8.15 ppm and 7.59 ppm.

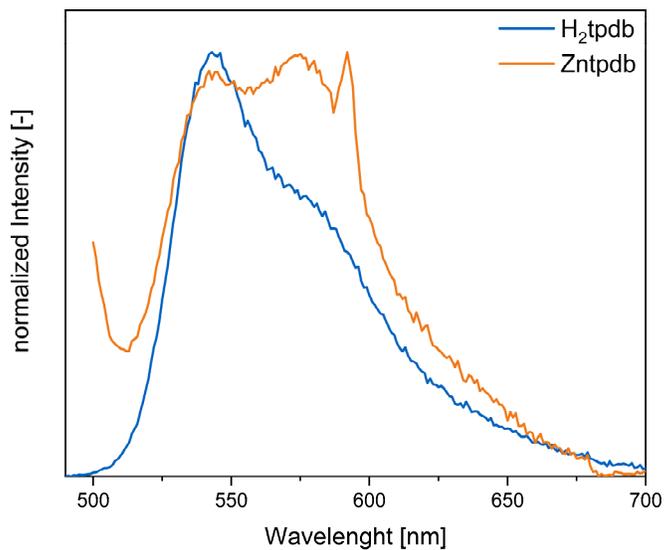


Figure S4. Comparison of the emission behavior of **2** and **3**. The linker shows a much stronger emission than the MOF (compare $QY(H_2tpbd) = 0,9$ vs. $QY(Zn(tpbd)) = < 0,01$), suggesting H-type aggregated perylenes, which show a high n-type mobility and quenching of the absorbed light energy, not allowing for directed energy transfer.

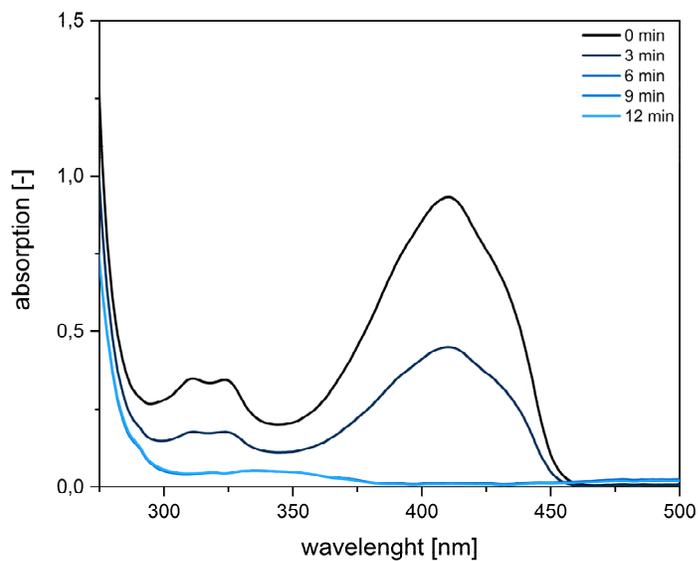


Figure S5. UV/Vis of the decrease in the absorption intensity of DBPF during the reaction with 1O_2 produced by **2**.

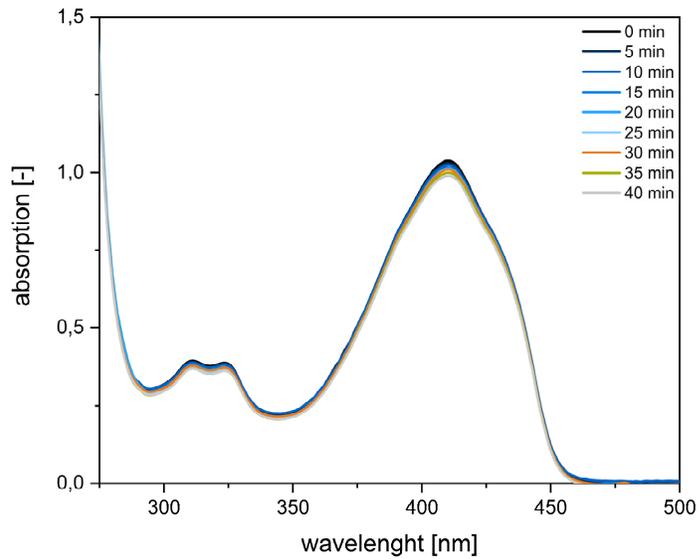


Figure S6. Control experiment of DBPF with 3 and without light irradiation over the duration of 40 minutes.

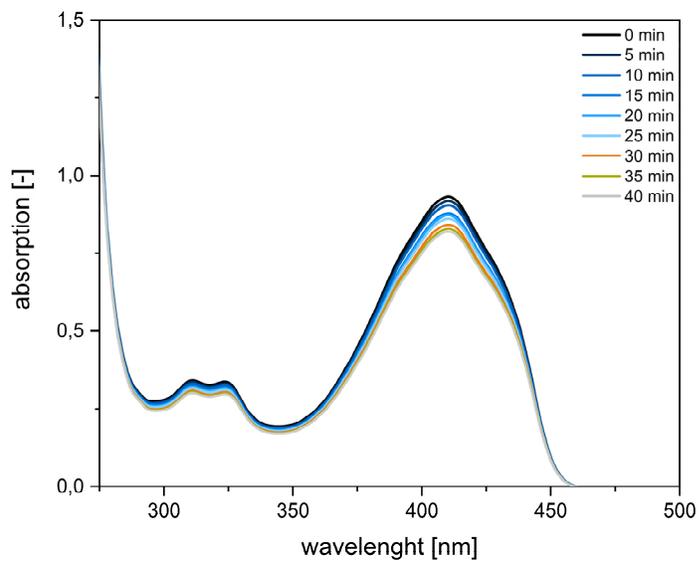


Figure S7. Control experiment of DBPF without 3 and with light irradiation over the duration of 40 minutes.

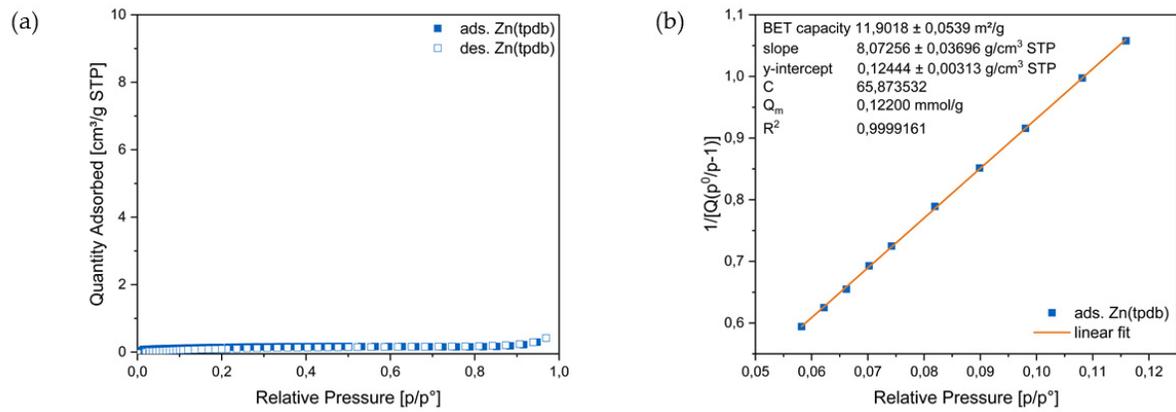


Figure S8: BET data of $\text{Zn}(\text{tpdb})(\text{DMF})_3$ showing the low surface area of it because of missing pores and the layer structure of the 2D coordination polymer. (a) Semi-log plot of the nitrogen isotherm at 77 K of $\text{Zn}(\text{tpdb})$. (b) BET plot with linear-fit control parameters and calculated monolayer capacity (Q_m).

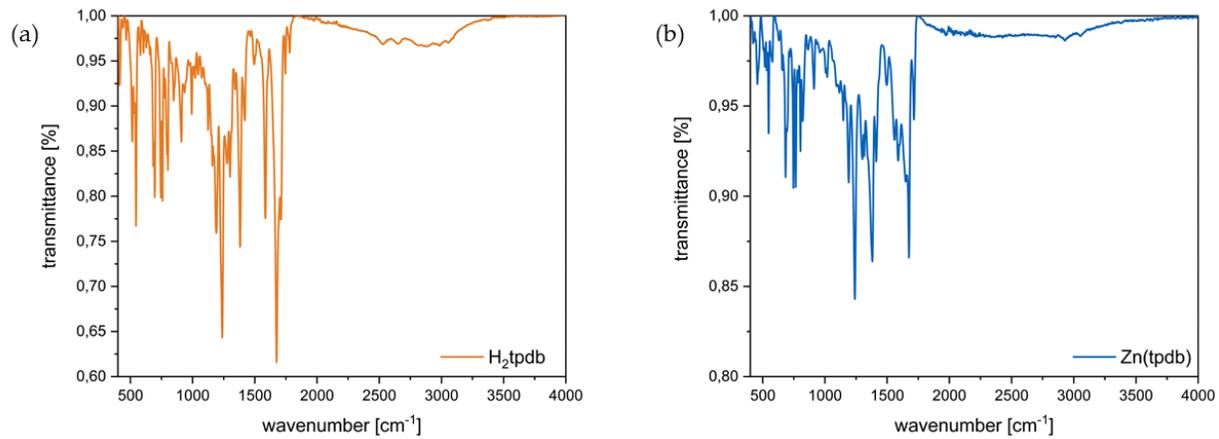


Figure S9: IR data of (a) linker 2 and (b) MOF 3.

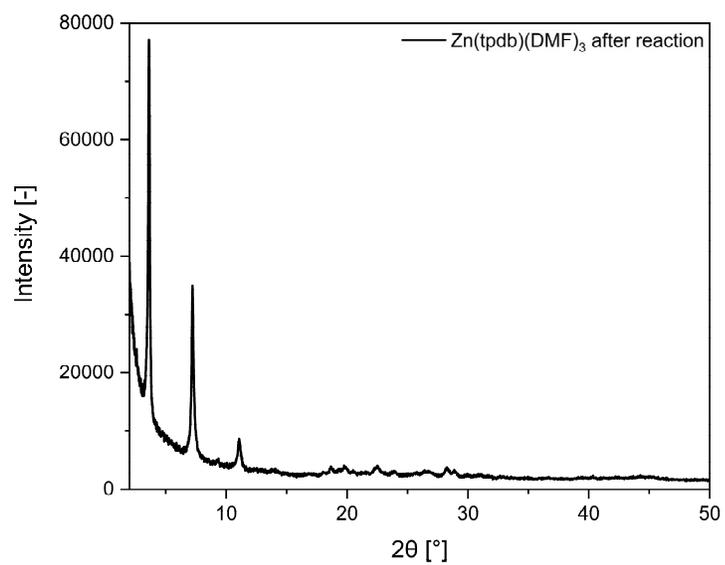


Figure S10: PXRD of **3** after $^1\text{O}_2$ evolution studies.

4. Single-Crystal X-Ray Diffraction Experiments

4.1 H2tpdb (CCDC: Deposition Number 2153020)

Crystal data	
Chemical formula	C ₃₈ H ₁₄ Cl ₄ N ₂ O ₈ ·2(C ₄ H ₈ O)
<i>M_r</i>	912.52
Crystal system, space group	Monoclinic, <i>C2/c</i>
Temperature (K)	100
<i>a</i> , <i>b</i> , <i>c</i> (Å)	35.229 (4), 12.3677 (13), 21.757 (3)
β (°)	119.954 (6)
<i>V</i> (Å ³)	8213.3 (18)
<i>Z</i>	8
Radiation type	Mo Kα
μ (mm ⁻¹)	0.35
Crystal size (mm)	0.23 × 0.09 × 0.06
Data collection	
Diffractometer	Bruker Photon CMOS
Absorption correction	Multi-scan SADABS 2016/2, Bruker, 2016
<i>T_{min}</i> , <i>T_{max}</i>	0.692, 0.745
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	150702, 8080, 7369
<i>R_{int}</i>	0.070
(sin θ/λ) _{max} (Å ⁻¹)	0.617
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.078, 0.156, 1.22
No. of reflections	8080
No. of parameters	655

No. of restraints	121
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
	$W = 1/[\Sigma^2(FO^2) + (0.0321P)^2 + 60.8212P]$ WHERE $P = (FO^2 + 2FC^2)/3$
$\Delta\rho_{\max}, \Delta\rho_{\min}$ (e Å ⁻³)	0.60, -0.77

Computer programs: APEX III Control Software (Bruker, 2016), SAINT (Bruker, 2017), SHELXT (Sheldrick, 2015), SHELXL (Sheldrick, 2017), SHELXLE (Huebschle, 2011), PLATON (Spek, 2011), and enCIFer (Allen, 2014).

4.2 Zntpdb(DMF)₃ (CCDC: Deposition Number 2153019)

Crystal data	
Chemical formula	C ₈₅ H ₄₁ Cl ₈ N ₇ O ₁₉ Zn ₂ (C ₃ H ₇ NO)
<i>M_r</i>	1965.81
Crystal system, space group	Monoclinic, C2/c
Temperature (K)	123
<i>a</i> , <i>b</i> , <i>c</i> (Å)	50.894 (3), 19.9711 (12), 16.310 (1)
β (°)	91.825 (2)
<i>V</i> (Å ³)	16569.2 (17)
<i>Z</i>	8
Radiation type	Mo Kα
μ (mm ⁻¹)	0.92
Crystal size (mm)	0.28 × 0.10 × 0.05
Data collection	
Diffractometer	Bruker Photon CMOS
Absorption correction	Multi-scan SADABS 2016/2, Bruker, 2016
<i>T_{min}</i> , <i>T_{max}</i>	0.689, 0.736
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	204129, 16317, 11889
<i>R_{int}</i>	0.101

$(\sin \theta/\lambda)_{\max}$ (\AA^{-1})	0.617
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.080, 0.233, 1.04
No. of reflections	16317
No. of parameters	1143
No. of restraints	48
H-atom treatment	H-atom parameters constrained
	$W = 1/[\Sigma^2(FO^2) + (0.1242P)^2 + 156.7946P]$ WHERE $P = (FO^2 + 2FC^2)/3$
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ ($e \text{\AA}^{-3}$)	3.35, -1.81

Computer programs: *APEX III* Control Software (Bruker, 2016), *SAINT* (Bruker, 2017), *SHELXT* (Sheldrick, 2015), *SHELXL* (Sheldrick, 2017), *SHELXLE* (Huebschle, 2011), *PLATON* (Spek, 2011), and *enCIFer* (Allen, 2014).

5. References

- [1] <https://doi.org/10.1021/acs.langmuir.1c00122>
 [2] <https://raw2aif.herokuapp.com/>