Electronic Supporting Informa

Information for

Postsynthetic modification of a zirconium metal-organic framework at the inorganic secondary building unit with diphenylphosphinic acid for increased photosensitizing

properties and stability

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1. General Information for Experiments

Materials. 5,10,15,20-Tetrakis(4-carboxyphenyl)porphyrin (TPPC, Porphychem), ZrOCl₂·8H₂O, 9,10-diphenyl anthracene, and diphenylphosphinic acid (all Sigma-Aldrich), DMF and formic acid 98% (Penta, Czech Republic), and acetone (Lachner, Czech Republic) were used as purchased. Synthesis of PCN-222/MOF-545. The parent PCN-222 was synthesized by the modified procedure published previously.¹ 150 mg ZrOCl₂·8H₂O (465 μ mol) was dissolved in 40 mL of DMF by 30 min sonication. Then, 116 mg of TPPC (147 μ mol) was added and the solution was further sonicated for 10 min followed by addition of formic acid (20 mL, 90%). The mixture was transferred to a PTFE autoclave (Berghoff DAB-3) and heated at 130 °C for 3 days. The resulting precipitate was centrifuged (Hettich Rotina 35, 10000 rpm, 10 min), washed three times with DMF and three times with acetone. The obtained purple solid was air-dried at room temperature.

Postsynthetic modification of PCN-222. Four different Ph₂PO₂H:Zr molar ratios were prepared by addition of varying amounts of Ph₂PO₂H. Typically 100 mg of PCN-222 was suspended in 15 mL solution of Ph₂PO₂H dissolved in mixture DMF/water 2:1. The amount of Ph₂PO₂H was 16.7, 33.3, 100, and 166.7 mg for **MOF-A**, **B**, **C**, and **D**, respectively. The suspension was shaken for 4 h, centrifuged and washed twice with DMF and twice with water. The samples were either directly air-dried at 150°C (water dried samples) or additionaly washed twice with acetone and air-dried at room temperature (acetone-dried samples).

Stability of MOF-A-D in trifluoracetic acid (TFA) solution. Stability tests were made by similar procedure published previously.² 10 mg of **MOF-A-D** were suspended in 3 ml of 0.2M TFA solution and shaken for 24 hours at room temperature. Then, samples were centrifuged and purified three times with water and three times with acetone. Solid samples were air-dried at room temperature. In order to obtain more reliable data, the stability tests were done in two consecutive runs.

Singlet oxygen mediated oxidation reaction of diphenylanthracene.

The photosensitizing ability was tested using the reaction of 9,10-diphenyl anthracene with photoproduced $O_2(^1\Delta_g)$ forming the corresponding endoperoxide. The progress of the reaction was monitored by the UV/Vis spectroscopy where 9,10-diphenyl anthracene absorbs in the region between 230 – 410 nm. In each experiment, the amount of MOF was adjusted to an equal content of porphyrin and was dispersed in 20 mL of 10^{-4} M 9,10-diphenyl anthracene in acetonitrile (Chromasolv Plus, Sigma-Aldrich) and placed in a quartz cuvette. After sonication for 10 s, the dispersion was stirred with a magnet bar and continuously irradiated by a 300 W Xe lamp (ozone free, Newport) equipped with a water filter and a glass filter (cuton at 435 nm, Newport) for 3 h. In regular time intervals, the mixture was centrifuged (10000 rpm, 10 min), filtered through a 0.2 µm Millipore microfilter, and inserted into a 10×10 mm quartz cell to measure the corresponding UV/Vis spectrum.

In the blank experiment, the solution of 9,10-diphenyl anthracene without the MOF photosenzitizer was irradiated and monitored identically as in normal experiments.

2. Instrumental Methods

Powder X-ray diffraction (XRD) was recorded using a PANalytical X'Pert PRO diffractometer in the transmission setup equipped with a conventional Cu X-ray tube (40 kV, 30 mA). Qualitative analysis was performed with the HighScorePlus software package (PANalytical, Almelo, The Netherlands, version 3.0) and the JCPDS PDF-2 database.³ The porosity and sorption properties were determined by measuring the nitrogen adsorption isotherms at the boiling point of liquid nitrogen (ca 77 K) with a Micromeritics ASAP 2010 apparatus. Prior to the adsorption experiment, the samples were evacuated at 80 °C overnight. The total surface area of porous samples was determined using the BET equation in the range of relative pressures typically of 0.05-0.3. The pore size distribution was calculated from the nitrogen isotherms using the NLDFT method for cylindrical pores. The presence of micropores was tested using the Broekhoff – de Boer t-plot and α_8 methods. Fourier transform infrared spectra (FTIR) were collected with a Nicolet NEXUS 670-FT spectrometer using KBr pellets. The UV/vis absorption spectra were recorded using a PerkinElmer Lambda 35 spectrometer.

The content of P and Zr was determined on an ICP-OES spectrometer IRIS Intrepid II, Thermo Electron Corp. equipped with an axial plasma and ultrasonic CETAC nebulizer, model U-5000AT+. The samples were mineralized by microwave irradiation (250 W, 90 min) in mixture of HNO₃ and HF.

¹³C NMR cross-polarization spectra under the magic angle spinning conditions (CP/MAS NMR) and ³¹P MAS NMR were recorded using a JEOL 600 MHz NMR spectrometer at 20 kHz MAS rate. For measurement of ¹³C CP/MAS spectra contact time was set to 10 ms and relaxation delay was 5 s. In the case of ³¹P MAS spectra measurement relaxation delay was 60 s.

3. Characterization data for MOF-A-D

Sample	As prepared		Molar ratio P:Z treatment	Zr ₆ after TFA
	Molar ratio	Molar ratio	1 st cycle	2 nd cycle
	Zr:P	P:Zr ₆		
MOF-A	3.26	1.84	1.79	1.45
MOF-B	2.18	2.75	2.43	2.45
MOF-C	1.95	3.07	2.87	2.79
MOF-D	1.91	3.14	2.96	2.86

Table S1. Elemental analysis of MOF-A-D.



Figure S1. XRD patterns of **MOF-A-D** and the parent PCN-222 activated from acetone. The diffractograms are vertically shifted in order to avoid overlaps. For clarity, in the range 11-20° 2θ the intensities are multiplied by 5.



Figure S2. Adsorption isotherms of parent

PCN-222 and MOF-A-D activated from acetone (A) and water (B).



Figure S3. Pore size distribution for **MOF-C** and parent PCN-222 activated from water and acetone.



Figure S4. ¹³C CP/MAS NMR spectra of PCN-222 and MOF-A-D.



Figure S5. ³¹P MAS NMR spectra of PCN-222 and **MOF-A-D**.





Figure S6. Infrared spectra of PCN-222 modified with DPPA in the range of 400-1800 cm⁻¹ (top) and 1800-4000 cm⁻¹ (bottom).



Figure S7. XRD patterns of **MOF-C**, **MOF-C** treated with TFA, and the parent PCN-222. The diffractograms are vertically shifted in order to avoid overlaps. For clarity, in the range $11-20^{\circ} 2\theta$ the intensities are multiplied by 5.

4. Molecular Dynamics Calculation

Molecular mechanics and classical molecular dynamics were carried out in Materials Studio modelling environment.⁴ The crystal structure of PCN-222 was taken from ref [5]. The cell parameters were following: a = b = 42.680 Å, c = 16.660 Å. $\alpha = \beta = 90^{\circ}$, $\gamma = 120^{\circ}$; the space group was P6/mmm. The DPPA molecule was built and optimized in Compass forcefield.⁶ The experimental measurements revealed that each SBU unit contained 2 - 3 DPPA molecules bonded to Zr atoms. Thus, the water molecules bonded to Zr atoms of SBU units were deleted and replaced by two or three DPPA molecules. Two types of structure models were built: (i) all DPPA molecules exhibited a bridging coordination, i.e. each oxygen atom of DPPA was bonded to two neighbouring Zr atoms; and (ii) all DPPA molecules exhibited a chelate coordination, i.e. each oxygen atom of DPPA molecule was bonded to the same Zr atom of the SBU unit. The charges were calculated by qeq method (charge equilibrium approach).⁷ The geometry of the models was optimized in Universal forcefield,⁸ the structure of MOF except of MOF hydrogen atoms was kept rigid and atomic positions of DPPA were variable. The electrostatic interactions were calculated by Ewald method, van der Waals energy was calculated using a Lennard – Jones potential with a cutoff distance of 12.5 Å. Quench molecular dynamics was done in an NVT statistical ensemble (N - constant number of particles, V - constant volume, T - constant temperature) at 298 K. One step was 1 fs and 10^6 steps were carried out. The models with the lowest value of energy were collected to obtain final structure models. The total energy values for bridging and chelating coordination were calculated from interactions of DPPA molecule using identical functional terms.

Generally, the values of bonded and non-bonded interactions and their sum (E_{total}) help us to choose the most probable conformation and the most stable model from a set of optimized models by the relative comparison of their energy values. The bonded interactions include the bond stretching, bond angle bending, dihedral angle torsion, and inversion terms. The non-bonded interactions consist of electrostatic and van der Waals terms.⁸

In order to being able to compare the total energies of the models, energy of each of the DPPA molecule per SBU was calculated separately, see Table S2. Specifically, three types of

models containing 1, 2, and 3 DPPA molecules per SBU unit were constructed and the total energy E_{total} for each DPPA molecule per SBU unit was calculated in the following way:

$$E_{total} = \frac{E_i - E_j}{n_i - n_j}$$

where E_i is the total energy of the model containing *i* DPPA molecules per SBU unit and E_j is the total energy of the model containing *j* DPPA molecules per SBU unit, n_i and n_j is the number of DPPA molecules in the model with *i* and *j* DPPA molecules per SBU unit, respectively. The energy of MOF structure was not included in the E_{total} , *i.e.*, $E_0=0$. E_{total} was calculated for the following couples (*i*,*j*): (1,0), (2,1), (3,2). Each model contained 6 SBU units and therefore in all cases $n_i - n_j = 6$, *i.e.*, the model with 1, 2, and 3 DPPA per SBU unit contained 6, 12, and 18 DPPA molecules, respectively.

The first and the second DPPA molecule have the same energy because of the symmetry of the system. However, the third DPPA molecule is located in different bonding environment. The difference in the total energies within the bridging vs. the chelate coordination can be explained by a higher variability of DPPA molecule location in a chelate coordination and lower steric hindrance in comparison with bridging coordination, see Figure S8 and S9.

Coordination mode		E _{total} / kcal mol ⁻¹	Non-bonded/ kcal mol ⁻¹	Bonded/ kcal mol ⁻¹
	1 st DPPA	126	-168	294
bridging	2 nd DPPA	126	-168	294
	3 rd DPPA	174	-123	297
	1 st DPPA	276	-82	358
chelate	2 nd DPPA	276	-82	358
	3 rd DPPA	275	-82	357

Table S2. The comparison of the total energy for structure models with bridging and chelating coordination of DPPA molecules calculated per one DPPA molecule. The bonded energy includes the bonded interactions within DPPA molecules and the bonded interactions between the DPPA molecules and the SBUs). The non-bonded energy includes the non-bonded interactions within the DPPA, between the neighbouring DPPA molecules, and between the MOF structure and DPPA molecules. The bonded and the non-bonded interactions within the MOF structure are not included in E_{total} .

The higher values of bonded interaction energies in chelating coordination models with respect to bridging coordination models indicate that the way of bonding in bridging coordination models is more favourable than in the chelating coordination models. On the other hand, the higher values of non-bonded interactions in chelating coordination models with respect to bridging coordination models indicate a better crystal packing in bridging coordination models. Finally, the higher values of E_{total} in chelating coordination models with respect to bridging coordination models indicate higher stability and therefore higher probability of occurrence of the bridging models in comparison with the chelating coordination models.

Bridging and chelating coordination of DPPA molecule to SBU unit is shown in Figures 3A and S8-S10. In the case of bridging coordination the orientation of DPPA with respect to SBU unit is given by the positions of Zr atoms in the SBU unit and the existence of two bonds between DPPA and two different Zr atoms does not allow high variability of DPPA orientation. A line connecting the two carbons bonded to the P atom of DPPA via O atoms. In the case of chelating coordination, the DPPA molecules adopt different orientation and location with respect to SBUs. Moreover, the DPPA molecules can slightly rotate around the P-Zr line as shown in Figure S10. A different bonding of DPPA to Zr atoms and different orientation of DPPA molecules with respect to SBUs, in comparison with bridging coordination enables variability in DPPA location, see Figure S9 and S10.



Figure. S8. Orientation of DPPA molecule with respect to SBU unit in a bridging coordination.



Figure. S9. Orientation of DPPA molecule with respect to SBU unit for chelate coordination.



Figure. S10. Orientation of three DPPA molecules for chelate coordination.

- ⁴ Materials Studio Modeling Environment, Release 4.3 Documentation. Accelrys Software Inc., San Diego, CA, 2003.
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³ JCPDS PDF-2 database, International Centre for Diffraction Data, Newtown Square, PA, release 54, 2004.

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