Exploitation of knowledge databases in the synthesis of zinc(II) malonates with photo-sensitive and photo-insensitive \(N,N'\)-containing linkers

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### Table S1  Previously Reported Zinc(II) Malonate Complexes with 4,4'-Bipyridine and its Analogs.

| Complex | L : Zn | CCF | net | Refcode |
|---------|--------|-----|-----|---------|
| [Zn₂(bipy)(Memal)$_2$(H$_2$O)$_2$] | 0.5 | A$_2$B$^2$K$^{21}$M$^1_2$ | ins | GAKVEV |
| [Zn₂(bipy)(cbdc)$_2$(H$_2$O)$_2$] | 0.5 | A$_2$B$^2$K$^{21}$M$^1_2$ | ins | IHEFIM |
| [Zn₂(bipy)(cbdc)$_2$(H$_2$O)$_2$] | 0.5 | A$_2$B$^2$K$^{21}$M$^1_2$ | ins | IHEFIM01 |
| [Zn₂(bipy)(mal)$_2$(H$_2$O)$_2$] · 0.5H$_2$O | 0.5 | A$_2$B$^2$K$^{21}$M$^1_2$ | ins | JIQKIE |
| [Zn₂(bipy)(mal)$_2$(H$_2$O)$_2$] · MeCN · H$_2$O | 0.5 | A$_2$B$^2$K$^{21}$M$^1_2$ | ins | KEXKAB |
| [Zn₂(pdd)(mal)$_2$(H$_2$O)$_2$] · 2MeCN | 0.5 | A$_2$B$^2$K$^{21}$M$^1_2$ | ins | KEXKEF |
| [Zn₂(bpe)(mal)$_2$(H$_2$O)$_2$] · 2MeCN | 0.5 | A$_2$B$^2$K$^{21}$M$^1_2$ | ins | KEXPIO |
| [Zn₂(bpa)(mal)$_2$(H$_2$O)$_2$] · 2MeCN | 0.5 | A$_2$B$^2$K$^{21}$M$^1_2$ | ins | KEXPOU |
| [Zn₂(bpe)(Memal)$_2$(H$_2$O)$_2$] | 0.5 | A$_2$B$^2$K$^{21}$M$^1_2$ | ins | TEMTIQ |
| [Zn₂(bpa)(Memal)$_2$(H$_2$O)$_2$] | 0.5 | A$_2$B$^2$K$^{21}$M$^1_2$ | ins | TEMTOW |
| [Zn₂(bpa)(cbdc)$_2$(H$_2$O)$_2$] | 0.5 | A$_2$B$^2$K$^{21}$M$^1_2$ | ins | YAMYIX |
| [Zn(bipy)(Ph(CH$_2$)$_3$mal)$_2$(H$_2$O)$_2$] · 4H$_2$O | 1 | AB$^{2\Pi}$T$^{11}$M$^1$ | sql | ZEQJAI |

*a* Memal = methylmalonate; cbcd = cyclobutane-1,1-dicarboxylate; mal = malonate; pdd = 4,4’-(propane-1,3-diyldipyridine.
Table S2  The most probable complexes and their coordination formulas and networks in the Zn$^{II}$ : An$^2$ (or HAn$^-$) : L : H$_2$O mixtures

Ratio - ratio of L and Zn$^{II}$; CN - coordination number of Zn$^{II}$; CP - coordination polyhedron; CF - coordination formula; possible nets are taken from previously reported databases of networks obtained for coordination polymers [S1-S3] or taken for a database of zinc(II) complexes with bipy, bpe or bpa.

| Ratio | CN | CP | CF | Complex | nets | Examples |
|-------|----|----|----|---------|------|----------|
| 0.5   | 4  | NO$_3$ | A$_2$B$^2$M$_6^{14}$ | [Zn$_2$L(H$_2$O)$_6$] | dimer | [Zn$_2$(bpe)(Et$_2$mal)$_2$(bpe)$_2$] (5) - hcb; {CIXNAZ} - hcb; {KEFTER} - 4$^4$(0,2); {LEDLA} - srs; {LEVPA} - etb; {MENMAU} - 4$^4$(0,2); {PIXWID} 4$^4$(0,2); {TOFLO} - 2C1; {TUBBA} - hcb; {VIXV} - hcb; {UNAWUC} hcb; {WAJGEU} - hcb; {XIZLIC} - 4$^4$(0,2); {YOQMUO} - hcb. |
|       |    |     | A$_2$B$^2$B$^2$M$_2^{12}$ | [Zn$_2$LAn$_2$(H$_2$O)$_2$] | | |
|       |    |     | A$_2$B$_2$T$_2^{12}$ | [Zn$_2$LAn$_2$] | dimer | |
|       |    |     | A$_2$B$_2$T$_2^{11}$ | [Zn$_2$LAn$_2$] | | |
| 5     | NO$_4$ | A$_2$B$^2$M$_8^{14}$ | [Zn$_2$L(H$_2$O)$_8$] | dimer | 2C1 (1D), 4$^4$(0,2) (1D) hcb (2D), sq (2D), 3,3L5 (2D), 3,3,3T9 (3D), etb (3D) | |
|       |    |     | A$_2$B$^2$B$^2$M$_4^{14}$ | [Zn$_2$LAn$_2$(H$_2$O)$_4$] | | [UYASOD] - 4$^4$(0,2) |
|       |    |     | | | | |
|       |    |     | | | | |
| 6     | NO$_5$ | A$_2$B$^2$M$_{10}^{14}$ | [Zn$_2$L(H$_2$O)$_{10}$] | dimer | 2C1 (1D), 4$^4$(0,2) (1D) hcb (2D), sq (2D), 3,3L5 (2D), 3,3,3T9 (3D), etb (3D) | |
|       |    |     | A$_2$B$^2$B$^2$M$_{6}^{14}$ | [Zn$_2$LAn$_2$(H$_2$O)$_6$] | | |
|       |    |     | A$_2$B$_2$T$_2^{12}$ | [Zn$_2$LAn$_2$] | | |
|       |    |     | A$_2$B$_2$T$_2^{11}$ | [Zn$_2$LAn$_2$] | | |

- Indicates not applicable or insufficient information.
| 1 | 4 | NO₃ | AM⁺M₄⁺ | [ZnL(H₂O)₃]²⁺ | 0D | 0D | dimer, 2C1 (1D) | dimer, tetramer, 2C1 (1D) | [Zn(bpe)(HMe₂mal)] (3); {DAYCEM} {DAZYEI} {EBITEQ} {EDUNOH} {FADWAK} {FIXFAU} {GOLTAD} {GOXKUZ} {GOYRAN} {HUVJOZ} {ICOVAZ} {IXAJAT} {IXOTAR} {JESRUV} {JOKKIF} {JOMWUF} {LIGYUX} {MAHROF} {MOPNIQ} {MOYGIR} {MUFTOX} {MUFTUD} {MUZNOM} {PASNOO} {PIHKEX} {REFLAR} {RILIU} {SENKAY} {SUSWAF} {TEGTII} {TEGTII} {TUSKUN} {TUSLAI} {UBOCIX} {UBOCOD} {UBOTUI} {VIYQAX} {XOBWIV} {ZAWREW} {ZAWRIA} {ZAZDAH} {CASHOU} - 2C1 for all
| 5 | NO₄ | AM⁺M₄⁺ | [ZnL(H₂O)₄]²⁺ | 0D | 0D | dimer, 2C1 (1D) | dimer, 2C1 (1D) | [Zn(bpe)(Me₂mal)] (2) - zst; [Zn(bpa)(Me₂mal)] (4) - zst, [Zn(bpe)(Et₂mal)]·0.5bpe (7) - igc²; [Zn(bpe)₀,₇₅(tpcb)₀,₂₅(Et₂mal)] (7a) - igc²; [Zn(bpa)(Et₂mal)] (9) - igc¹; {CUWGAD} - sql; {CUYKEN} - dia; {IWEPF} - dia; {IWEPJI} - dia; {UHOMIP} - cds; {VAJTEH} - neb; {ZARZAV} - dia
| Formula | Description |
|---------|-------------|
| \(\text{AM}^4\text{K}^{21}\) | 4\(^{\text{th}}\) (0,2) (1D), \text{hcb} (2D), \text{fes} (2D), 3,4L13 |
| \(\text{N}_2\text{O}_3\) | dimer, 2C1 (1D) |
| \(\text{AB}^2\text{M}^1\) | 4\(^{\text{th}}\) (0,2) (1D), \text{sql} (2D), \text{kgl} (2D), 4L1 (2D), \text{dia}(3D), \text{pts} (3D), \text{lon} (3D), \text{dmp} (3D), \text{qtz} (3D), \text{cds} (3D), \text{uoc} (3D), 4T12 (3D), \text{mnt} (3D), \text{neb} (3D), \text{nbo} (3D) |
| \(\text{AB}^2\text{B}^3\text{M}^1\) | dimer, 2C1 (1D) |
| \(\text{AB}^2\text{T}^1\) | \text{sql} (2D), 4L1 (2D), 4L2 (2D) |
| \(\text{NO}_5\) | 0D |
| \(\text{AM}^4\text{M}^5\) | dimer, 2C1 (1D) |
| \(\text{AM}^4\text{B}^2\text{M}^1\) | 0D |
| \(\text{AM}^4\text{B}^3\text{M}^3\) | Dimer |
| \(\text{AM}^4\text{B}^{11}\text{M}^2\) | dimer, tetramer, 2C1 (1D) |
| \(\text{AM}^4\text{T}^{11}\text{M}^2\) | \text{hcb} (2D), \text{fes} (2D) |
| \(\text{AM}^4\text{K}^{21}\) | 4\(^{\text{th}}\) (0,2) (1D), \text{hcb} (2D), \text{fes} (2D), 3,4L13 |
| AB^2B^01M_2 | [ZnLAn(H2O)] | neb (3D), nbo (3D) | dimer, 2C1 (1D) | - |
| AB^2B^11M | [ZnLAn(H2O)] | sql (2D), 4L1 (2D), 4L2 (2D) | - |
| AB^2T^11M | [ZnLAn] | sql (2D), 4L1 (2D), 4L2 (2D) | [ZEQJAI] - sql |
| AB^2T^21 | [ZnLAn] | 3.4L83, 3.5L2, gek1 | - |
| AB^2K^21 | [ZnLAn] | 3.5L2 3.4L83 4^4(0,4) (1D), 4^4(1,4) (1D), sql (2D), dia (3D), neb-e (3D), fet (3D) | {SUJQOE} - fet; {SUJQUK} - fet |

| N_2O_2 | AM^12M^01_2 | [ZnL_2(H_2O)_2]^{2+} | 0D | - |
| AM^12B^2 | [ZnL_2(HAn)] | dimer, 2C1 (1D) | - |
| AM^12B^01 | [ZnLAn] | 0D | - |

| N_2O_3 | AM^12M^01_3 | [ZnL_2(H_2O)_3]^{2+} | 0D | - |
| AM^12B^2M^01 | [ZnLAn(H_2O)] | dimer, 2C1 (1D) | - |
| AM^12B^01M^1 | [ZnL_2(HAn)] | 0D | - |

| N_2O_4 | AM^12M^01_4 | [ZnL_2(H_2O)_4]^{2+} | 0D | [Zn(H_2O)_3(bpe)]_2(HEt_2mal)_2 (8) {ESIXEL} {CERFIP} {DOFWEB} {GASWAA} {GATXII} {KESNIH} |
| AM^12B^01M^1 | [ZnL_2(HAn)]_2(H_2O)_2 | - |

| N_4 | AB^2_2 | [ZnL_2]^{2+} | 4^4(0,2) (1D), sql (2D), kgl (2D), 4L1 (2D), dia (3D), pts (3D), lon (3D), dmp (3D), qtz (3D), cds (3D), uoc (3D), 4T12 (3D), mmt (3D), neb (3D), nbo (3D) | - |

| N_4 | AB^2_2 | [ZnL_2]^{2+} | 4^4(0,2) (1D), sql (2D), kgl (2D), 4L1 (2D), dia (3D), pts (3D), lon (3D), dmp (3D), qtz (3D), cds (3D), uoc (3D), 4T12 (3D), mmt (3D), neb (3D), nbo (3D) | - |

| N_4 | AB^2_2 | [ZnL_2]^{2+} | 4^4(0,2) (1D), sql (2D), kgl (2D), 4L1 (2D), dia (3D), pts (3D), lon (3D), dmp (3D), qtz (3D), cds (3D), uoc (3D), 4T12 (3D), mmt (3D), neb (3D), nbo (3D) | - |
| Chemical Formula | Structure | Description | Notes |
|------------------|-----------|-------------|-------|
| AM$^{1+2}$B$^{2-}$M$^{1-2}$ | [ZnL$_2$An(H$_2$O)$_2$] | dimer, 2C1 (1D) | 0D |
| AM$^{1+2}$B$^{0-1}$M$^{1-2}$ | | | |
| AM$^{1+2}$B$^{1+}$M$^{1-1}$ | [ZnL$_2$An(H$_2$O)] | dimer | |
| AM$^{1+2}$T$^{2+1}$ | [ZnL$_2$An] | hcb (2D), fes (2D) | 4$^4$(0,2) (1D), hcb (2D), fes (2D), 3,4L13 |
| AM$^{1+2}$K$^{2+1}$ | | | |
| N$_2$O$_2$ AB$^{2+3}$M$^{1-2}$ | [ZnL$_2$(H$_2$O)$_2$]$^{2+}$ | 4$^4$(0,2) (1D), sql (2D), kgl (2D), 4L1 (2D), dia(3D), pts (3D), lon (3D), dmp (3D), qtz (3D), cds (3D), uoc (3D), 4T12 (3D), mmt (3D), neb (3D), nbo (3D) | |
| AB$^{2+3}$B$^{2-}$ | [ZnL$_2$An] | 2C-1 (1D) sql (2D) pcu (3D), jsm (3D) | |
| AB$^{2+3}$B$^{0+1}$ | [ZnL$_2$An] | 4$^4$(0,2) (1D), sql (2D), kgl (2D), 4L1 (2D), dia(3D), pts (3D), lon (3D), dmp (3D), qtz (3D), cds (3D), uoc (3D), 4T12 (3D), mmt (3D), neb (3D), nbo (3D) | |
S1. Experimental

S1.1. Coordination Formulas and Their Applications

Let us denote mono-, bi-, tri- or tetradenate ligands with M, B, T or K letters. The way in which metal atoms A surround the ligand is denoted by numerical superscripts (mbtk). The superscripts define the ‘partial’denticity of the ligand with respect to any A atom (m – mono-, b – bi-, t – tri-, k – tetradenticity). The number of A atoms with respect to the ligand that exhibits the corresponding partial denticity is denoted by the numerical value of the corresponding superscript. Then the coordination type of an i-th ligand is given as $D^{mbtk}$. A few examples of tridentate ligands coordinated by one, two or three metal atoms are given in Fig. S1, as well as the corresponding coordination-type symbols.

![Coordination modes](image)

**Figure S1** Selected coordination modes of bpe or malonate anion and its derivatives in zinc(II) complexes.

The symbol for the ligand coordination type also denotes the total number of complexing atoms (Z) which surround the ligand, and the total number of chemical bonds that the ligand makes with the central atom ($N_B$) as $Z = m + b + t + k$ and $N_B = 1m + 2b + 3t + 4k$.

For example, for a chelate ligand $B^{01}$, $Z = 1 (0 + 1)$ and $N_B = 2 (1\cdot0 + 3\cdot1)$, while for a bridge-chelate $K^{21}$ ligand $Z = 3 (2 + 1)$ and $N_B = 4 (1\cdot2+2\cdot1)$ (Fig. S1).

Provided that the coordination types of all the ligands in a complex are determined, the coordination formula (CF) of the complex can be written. Any CF includes the coordination types of all the ligands with the same chemical formula (with the exception of counterions and molecules). The subscripts denote the stoichiometric composition with respect to any equivalent ligand and a metal A atom. Using the chemical and crystallochemical formulae of a complex together allows the environment of the central atom to be
characterized in order to calculate the coordination number (CN) and the number of ligands in the first coordination sphere \( (N_A) \) without any diagrammatical or text description.

\[
CN(A) = \sum_i v_i(m + 2b + 3t + 4k), \quad N_A = \sum_i v_i(m + b + t + k),
\]

For example, a complex with composition \([\text{ZnLAn(H}_2\text{O)}_2]\) may have CF AM\(^{11}\)B\(^{3}\)M\(^{1}\)\(_2\) and AM\(^{11}\)B\(^{1}\)M\(^{1}\)\(_2\) if L acts as monodentate ligand, and An is bridge or bridge-chelate ligand, or AB\(^{3}\)B\(^{3}\)M\(^{1}\)\(_2\) if both L and An are bridge ligands. Calculation of CN and CP as possible diagrammatical representations of corresponding architectures are given in Scheme S1.

| CF                | CN(Zn) | CP     |
|-------------------|--------|--------|
| [ZnLAn(H\(_2\)O)\(_2\)] | AM\(^{11}\)B\(^{3}\)M\(^{1}\)\(_2\) | 1 + 2 + 1\cdot 2 = 5 | \( NO_4 \) |
|                   | AM\(^{11}\)B\(^{1}\)M\(^{1}\)\(_2\) | 1 + (1\cdot 1 + 1\cdot 2) + 1\cdot 2 = 6 | \( NO_5 \) |
|                   | AB\(^{3}\)B\(^{3}\)M\(^{1}\)\(_2\) | 2 + 2 + 1\cdot 2 = 6 | \( N_2O_4 \) |

Scheme S1. Some coordination formulas for a complex with composition \([\text{ZnLAn(H}_2\text{O)}_2]\), calculation of coordination number of central atom, its polyhedron and possible architectures.
S1.2. Analysis of Previously Reported Zinc(II) Complexes with *bipy*, *bpe* and *bpa*.

Distribution of zinc(II) coordination numbers and composition of coordination polyhedra has been calculated for 1473 complexes containing both zinc(II) and at least one of *bipy*, *bpe* or *bpa* ligands. Distribution of zinc(II) coordination numbers is given on Fig. S2; and distribution of various coordination polyhedra for the most widespread coordination numbers 4 - 6 is depicted on Fig. S3. Note, that the number of coordination polyhedra $O_4$, $O_5$ and $O_6$ is substantially non-zero, but these were excluded from analysis as we were interested only in mixed complexes containing L ligands. The number of polyhedra containing three and more nitrogen atoms is also high, but these can appear only if $L : Zn^{II} = 2 : 1$ and more.

Figure S2  Distribution of coordination numbers for zinc(II) atoms in Zn$^{II}N_xO_y$ coordination polyhedra found in 1473 X-rayed complexes with *bipy*, *bpe* or *bpa* ligands.

Figure S3  Distribution of various coordination polyhedra for CN(Zn) = 4 (left), 5 (middle) and 6 (right).

Among all zinc(II) complexes with *bipy* analogs, 220 compounds containing 298 symmetrically independent *bpe* ligands (as the target photosensitive ligand) were taken to determine possible coordination modes of this linker and probable Zn : L ratios. *bpe* acts as an uncoordinated molecule, terminal ligand or linker in 15, 22 and
261 cases; for bpa corresponding values are equal to 4, 9 and 192. The L : Zn$^{II}$ ratio is equal to 0.5, 1 or 2 in 29, 49 and 8% of complexes. The other values do not exceed 3%.

**Table S3** Distribution of L : Zn ratio in previously reported bpe and bpa complexes.

| L : Zn | 0.25 | 0.33 | 0.50 | 0.67 | 0.75 | 1.00 | 1.33 | 1.50 | 1.67 | 2.00 | 2.50 | 3.00 |
|-------|------|------|------|------|------|------|------|------|------|------|------|------|
| N     | 8    | 11   | 118  | 7    | 4    | 199  | 1    | 10   | 1    | 31   | 1    | 14   |
| %     | 0.02 | 0.03 | **0.29** | 0.02 | 0.01 | **0.49** | 0.00 | 0.02 | 0.00 | **0.08** | 0.00 | 0.03 |
S1.3. Synthetic procedures

**General Details:** Commercially available reagents were used as received, in particular, Zn(OAc)$_2$·2H$_2$O («Roth», Germany, 99%), Zn(NO$_3$)$_2$·6H$_2$O (Chimmed, Russia, «pure»), H$_2$Me$_2$Mal («Sigma Aldrich», Switzerland, 98%), H$_2$Et$_2$Mal («Sigma Aldrich», Switzerland, «pure»), 4,4'-bipyridine («Alfa Aesar», Germany, 98%), 1,2-bis(4-pyridyl)ethane («Sigma Aldrich», Germany, 99%), 1,2-bis(4-pyridyl)ethylene («Sigma Aldrich», Germany, 97%). IR spectra were measured by using a Perkin–Elmer Spectra 65 instrument by the attenuated total reflection (ATR) method in the range 4000–400 cm$^{-1}$. CHN analysis was performed by using an automatic CHNS analyzer EuroEA3000 at the Center of Collective Use of IGIC RAS.

**Synthesis of new compounds**

$[\text{Zn}_2(\text{H}_2\text{O}-\kappa\text{O})_2(\mu-\text{bipy})(\mu-\text{Me}_2\text{mal}-\kappa^2\text{O},\text{O'})_2]_n$ (1):

A water solution (4 mL) of Zn(OAc)$_2$·2H$_2$O (0.033 g, 0.15 mmol) and dimethylmalonic acid (0.020 g, 0.15 mmol) was placed at the bottom of a test tube. Then, a water interphase (6 mL) was carefully layered. A 4 mL acetonitrile solution of 4,4'-bipyridine (0.047 g, 0.3 mmol) was carefully added on the top. The test tube was covered and allowed to stand at room temperature for a week. The resulting colorless crystals are suitable for X-ray diffraction analysis. Crystals of 1 were filtered, washed by water and dried in air at room temperature. IR-spectrum (ATR method), $\nu$/cm$^{-1}$: 3183 m, 2995 m, 2944 m, 2225 w, 1606 s, 1562 s, 1535 s, 1491 m, 1469 m, 1431 s, 1410 m, 1330 m, 1218 m, 1204 m, 1181 m, 1158 m, 1079 m, 1049 m, 1011 m, 969 m, 945 m, 872 m, 838 m, 813 s, 801 m, 751 s, 733 m, 688 s, 678 s, 630 s, 594 m, 516 m, 498 s, 461 m, 442 m. Calculated (%) for Zn$_2$C$_{20}$H$_{24}$N$_2$O$_{10}$: %: C, 41.19; H, 4.15; N, 4.8; found (%): C, 41.07; H, 5.30; N, 4.93. The yield of 1 is 0.019 g (44% counting per Zn).

Complexes 2-9 were obtained by a procedure similar to that used in the synthesis of complex 1.

$\{[\text{Zn}(\mu-bpe)(\mu-\text{Me}_2\text{mal})] \cdot \text{H}_2\text{O}\}_n$ (2):

Amounts of reagents: water solution of (10 mL) Zn(OAc)$_2$·2H$_2$O (0.100 g, 0.45 mmol) and dimethylmalonic acid (0.060 g, 0.45 mmol), 5 mL of water interphase, acetonitrile solution (10 mL) of bis(4-pyridyl)ethylene (0.166 g, 0.90 mmol). The colorless crystals were grown after 8 days. IR-spectrum (ATR method), $\nu$/cm$^{-1}$: 3546 m, 3481 w, 3044 w, 3021 w, 2975 w, 2929 w, 2895 w, 2859 w, 1985 w, 1714 w, 1615 s, 1592 s, 1576 s, 1511 m, 1459 m, 1449 m, 1432 s, 1393 s, 1354 m, 1312 m, 1256 m, 1227 w, 1210 m, 1191 m, 1165 m, 1072 m, 1029 s, 996 w, 974 m, 964 m, 887 m, 841 s, 830 s, 802 m, 777 m, 693 m, 590 m, 572 s, 553 s, 460 s, 422 m, 412 m. Calculated (%) for ZnC$_{17}$H$_{18}$N$_2$O$_5$: C, 51.60; H, 4.58; N, 7.08; found (%): C, 51.64; H, 4.69; N, 7.25. The yield of 2 is 0.158 g (88% counting per Zn).

$[\text{Zn}(\mu-bpe)(\mu-\text{Me}_2\text{mal})]_3[\text{Zn}_2(\text{tpcb})(\text{Me}_2\text{mal})]_2 \cdot \text{H}_2\text{O}$ (2a):

A single crystal or powder pattern of 2 was irradiated over 6 hours with Xe laser ($\lambda$ = 365 nm; 200 W source used with 40 % of the full intensity; see the next Section for details). Reaction product was characterized with
single-crystal and powder diffractions techniques, and $^1$H NMR. The conversion of 2 to 2a is 30% based on XRD and $^1$H NMR data.

$\text{[Zn(μ-bpe)(HMe}_2\text{mal)}]_n$ (3):

Amounts of reagents: water solution (10 mL) of Zn(NO$_3$)$_2$·6H$_2$O (0.100 g, 0.34 mmol) and dimethylmalonic acid (0.044 g, 0.33 mmol), 5 mL of water interphase, acetonitrile solution (10mL) of bis(4-pyridyl)ethylene (0.122 g, 0.67 mmol). The colourless crystals were grown after a two week. IR-spectrum (ATR method), ν/cm$^{-1}$: 3544 w, 3480 w, 3082 w, 3044 w, 2975 w, 2935 w, 2863 w, 2039 w, 1616 s, 1590 s, 1576 m, 1511 w, 1459 w, 1449 w, 1432 m, 1392 m, 1313 m, 1256 w, 1227 w, 1191 m, 1161 w, 1073 w, 1029 s, 996 w, 974 m, 964 m, 887 m, 573 s, 552 s, 453 m, 444 m, 424 m, 405 m. Calculated (%) for ZnC$_{22}$H$_{24}$N$_2$O$_8$: C, 51.83; H, 4.74; N, 5.49; found (%): C, 52.20; H, 4.86; N, 6.25. The yield of 3 is 0.123 g (72% counting per Zn).

$\text{[Zn(μ-bpa)(μ-Me}_2\text{mal)}] ∙ H$_2$O}$ (4):

Amounts of reagents: water solution (0.5 mL) of Zn(OAc)$_2$·2H$_2$O (0.033 g, 0.15 mmol) and dimethylmalonic acid (0.020 g, 0.15 mmol), 1.3 mL of water interphase, acetonitrile solution (0.6 mL) of 1,2-bis(4-pyridyl)ethane (0.055 g, 0.30 mmol). The colorless crystals were grown after a week. IR-spectrum (ATR method), ν/cm$^{-1}$: 3557 w, 3484 w, 2983 w, 2930 w, 2865 w, 2225 w, 1619 s, 1576 s, 1595 s, 1510 m, 1460 m, 1450 m, 1432 s, 1388 s, 1348 s, 1306 m, 1246 s, 1228 m, 1191 m, 1168 m, 1074 m, 1032 m, 949 s, 886 m, 834 s, 821 m, 777 m, 693 m, 590 m, 559 m, 543 s, 493 m, 426 m. Calculated (%) for ZnC$_{17}$H$_{20}$N$_2$O$_5$: C, 51.34; H, 5.07; N, 7.04.; found (%): C, 51.02; H, 4.64; N, 7.08. The yield of 4 is 0.038 g (63 % counting per Zn).

$\text{[Zn(bipy)(μ-bipy)}_{0.5}(μ-Et}_2\text{mal)}] ∙ H$_2$O}$ (5)

Amounts of reagents: water solution (10 mL) of Zn(OAc)$_2$·2H$_2$O (0.027 g, 0.12 mmol) and diethylmalonic acid (0.020 g, 0.12 mmol), 1.3 mL of water interphase, acetonitrile solution (10mL) of 4,4'-bipyridine (0.039 g, 0.25 mmol). The colourless crystals were grown after a two week. IR-spectrum (ATR method), ν/cm$^{-1}$: 3513 w, 3393 w, 3081 w, 3047 w, 2968 w, 2935 w, 2879 w, 1588 s, 1532 s, 1492 m, 1459 m, 1443 m, 1420 m, 1409 s, 1385 s, 1301 m, 1271 m, 1220 m, 1181 w, 1166 w, 1143 w, 1081 m, 1070 m, 1046 m, 1022 w, 996 m, 964 w, 939 w, 888 w, 878 w, 855 w, 839 w, 810 s, 767 m, 750 m, 731 m, 701 m, 678 m, 643 m, 626 s, 597 m, 576 m, 539 m, 476 s, 430 m, 415 m, 404 s. Calculated (%) for ZnC$_{22}$H$_{24}$N$_2$O$_5$: C, 55.53; H, 5.07; N, 8.83; found (%): C, 55.52; H, 5.32; N, 9.1. The yield of 5 is 0.023 g (38% counting per Zn).

$\text{[Zn(H}_2$O-$κO)]_{4}(μ-bipy)}_{2}(\text{HEt}_2\text{mal)}_{2} ∙ bipy$· 2H$_2$O} (6):

Amounts of reagents: water solution (10 mL) of Zn(NO$_3$)$_2$·6H$_2$O (0.037 g, 0.12 mmol) and diethylmalonic acid (0.02 g, 0.12 mmol), 4 mL of water interphase, acetonitrile solution (10 mL) of 4,4'-bipyridine (0.039 g, 0.25 mmol). The colourless crystals were grown after a month. IR-spectrum (ATR method), ν/cm$^{-1}$: 3542 m, 3465 m, 3162 m, 3097 m, 3063 m, 2970 m, 2932 m, 2878 m, 2343 w, 1963 w, 1698 w, 1671 m, 1607 s, 1596 s, 1536 m, 1490 m, 1453 m, 1408 s, 1378 s, 1307 s, 1227 m, 1182 m, 1133 m, 1104 m, 1072 m, 1039 m, 1008 m, 996 m, 982 m, 930 m, 833 s, 804 s, 764 s, 730 s, 632 s, 616 s, 570 s, 483 s, 450 s, 413 s. Calculated (%) for
ZnC₃H₅₀N₅O₁₄: C, 50.78; H, 6.27; N, 6.97; found (%): C, 51.02; H, 6.43; N, 7.15. The yield of 6 is 0.037 g (38% counting per Zn).

{(Zn(μ-bpe)(μ-Et₂mal))·0.25bpe}ₙ (7):

Amounts of reagents: water solution of (10 mL) Zn(OAc)₂·2H₂O (0.100 g, 0.45 mmol) and diethylmalonic acid (0.073 g, 0.45 mmol), 4 mL of water interphase, acetonitrile solution (10 mL) of bis(4-pyridyl)ethylene (0.166 g, 0.90 mmol). The pale-yellow crystals were grown after a week. IR-spectrum (ATR method), ν/cm⁻¹: 3044 w, 3017 w, 2958 w, 2937 w, 2874 w, 1602 s, 1512 m, 1438 m, 1375 m, 1361 m, 1335 m, 1287 m, 1263 m, 1212 m, 1164 m, 1141 m, 1074 m, 1030 m, 991 m, 967 m, 880 w, 844 m, 803 m, 768 w, 750 w, 699 m, 599 m, 574 m, 549 s, 492 w, 469 w, 430 m, 417 w, 404 w. Calculated (%) for ZnC₂₂H₂₅N₂.5O₂: C, 58.55; H, 5.02; N, 7.76; found (%): C, 58.37; H, 4.91; N, 7.51. The yield of 7 is 0.168 g (82% counting per Zn).

[Zn(μ-bpe)₀.₇₅(μ-tpcb)₀.₂₅(μ-Et₂mal)]ₙ(7a):

A single crystal or powder pattern of 7 was irradiated over 6 hours with Xe laser (λ = 365 nm; 200 W source used with 40 % of the full intensity; see the next Section for details). Reaction product was characterized with single-crystal and powder diffractions techniques, and ¹H NMR. The conversion of 7 to 7a is 100% based on XRD and ¹H NMR data.

[Zn(H₂O-κO)₄(bpe)₂](HEt₂mal)₂ (8)

Amounts of reagents: water solution (10 mL) of Zn(NO₃)₂·6H₂O (0.100 g, 0.33 mmol) and diethylmalonic acid (0.054 g, 0.33 mmol), 5 mL of water interphase, acetonitrile solution (10 mL) of bis(4-pyridyl)ethylene (0.123 g, 0.67 mmol). The pale-yellow crystals were grown after a week. IR-spectrum (ATR method), ν/cm⁻¹: 3040 w, 2957 w, 2937 m, 2933 w, 2874 w, 1603 s, 1512 m, 1483 m, 1375 m, 1361 m, 1335 m, 1287 m, 1263 m, 1212 m, 1164 m, 1141 m, 1074 m, 1030 s, 992 m, 966 m, 951 m, 879 w, 844 m, 803 m, 767 w, 750 w, 699 m, 598 m, 574 m, 549 s, 495 m, 429 m, 420 m, 403 m. Calculated (%) for ZnC₃₈H₄₈N₄O₁₂: C, 55.78; H, 5.91; N, 6.85; found (%): C, 55.57; H, 5.64; N, 6.72. The yield of 8 is 0.119 g (43 % counting per Zn).

[Zn(H₂O-κO)₄(bpe)₂]₀.₁₅[Zn(H₂O)₄(tpcb)]₀.₈₅(HEt₂mal)₄ (8a):

A single crystal or powder pattern of 8 was irradiated over 6 hours with Xe laser (λ = 365 nm; 200 W source used with 40 % of the full intensity; see the next Section for details). Reaction product was characterized with single-crystal and powder diffractions techniques, and ¹H NMR. The conversion of 8 to 8a is 90% based on XRD and ¹H NMR data.

{(Zn(μ-bpa)(μ-Et₂mal))·0.38H₂O}ₙ (9):

Amounts of reagents: water solution of (10 mL) Zn(OAc)₂·2H₂O (0.100 g, 0.45 mmol) and diethylmalonic acid (0.073 g, 0.45 mmol), 2 mL of water interphase, acetonitrile solution (5 mL) of 1,2-bis(4-pyridyl)ethane (0.168 g, 0.9 mmol). The colorless crystals were grown after 8 days. IR-spectrum (ATR method), ν/cm⁻¹: 3066 w, 3043 w, 2957 m, 2933 w, 2874 w, 1603 s, 1506 m, 1456 m, 1432 m, 1373 s, 1337 m, 1289 m, 1266 m, 1225 m, 1211 m, 1163 m, 1137 w, 1072 m, 1032 s, 954 w, 883 w, 837 s, 804 s, 703 m, 597 m, 545 s, 499 m, 424 m, 417
Calculated (%) for ZnC_{19}H_{22.75}N_{2.38}O_{4.38}: C, 55.04; H, 5.53; N, 6.76; found (%): C, 55.37; H, 5.38; N, 6.86. The yield of 9 is 0.110 g (58% counting per Zn).
S1.4. Crystallography

Single crystals of 1-9 were obtained from reaction mixtures. The intensities of reflections were measured with a Bruker Apex II DUO CCD diffractometer using graphite monochromated MoKα radiation (λ = 0.71073 Å) at 120.0(2) K. Intensity data for 2a were collected at the K4.4 station of the Kurchatov Center for Synchrotron Radiation and Nanotechnology in Moscow (Russia) at a wavelength of 0.9699 Å using a MAR CCD 165 detector and merged using SCALA. Data collection was performed at low temperature [100 K] using an Oxford CryoJet from Oxford Cryosystems Ltd. The structures were solved by the direct method and refined by full-matrix least squares against F². Non-hydrogen atoms were refined anisotropically except some disordered atoms. The disordered fragments, particularly, one carbon atom of bipy in 1, solvent bpe molecule in 7, one ethyl fragment in 9, a methyl group and all carbon atoms of bpe and tcpb ligands in 2a were refined isotropically. A number of EADP, ISOR, SADI, RIGU and DFIX instructions were applied to refine some moieties, especially, in crystals of 2a, 7, 8a disordered by symmetry or containing disordered fragments. TWIN/BASF refinement was performed for 9. Positions of hydrogen atoms were calculated and all were included in the refinement by the riding model with Uiso(H) = 1.5Ueq(X) for methyl groups and water molecules, and Uiso(H) = 1.2Ueq(X) for other atoms. All calculations were made using the SHELXL2014 and OLEX2 program packages. Experimental details and crystal parameters are listed in Tables S4 and S5.

Then, single crystals 2, 7 and 8 containing closely packed bpe ligands were irradiated over 6 hours with Xe laser (λ = 365 nm; 200 W source used with 40 % of the full intensity) on air. XRD confirmed that these compounds underwent single-crystal-to-single-crystal photoreactions to afford, respectively, 2a, 7a and 8a, accompanied with loss of some uncoordinated water by 2a. Careful inspection of occupancies of carbon atoms of ethylene or cyclobutane fragments indicated that only 7a underwent 100% conversion. 8a contained 15 % of initial substance, and 2a contained 50% of 2.
Table S4  Crystallographic Data and Refinement Parameters for Zinc(II) Dimethylmalonates

| Compound | [Zn₂(H₂O)₂(bipy)(Me₂mal)] [Zn(bpe)(Me₂mal)] | [Zn(bpe)(Me₂mal)]₂[Zn₂(tpeb)(Me₂mal)] [Zn₂(H₂O)₂](1) | [Zn(bpe)(Me₂mal)] [Zn₂(tpeb)(Me₂mal)] [Zn₂(H₂O)₂] (2) | [Zn(bpe)(Me₂mal)] [Zn₂(tpeb)(Me₂mal)] [Zn₂(H₂O)₂] (2a) | [Zn(bpe)(HMe₂mal)] (3) | [Zn(bpe)(Me₂mal)] [Zn₂(H₂O)₂](4) |
|----------|------------------------------------------------|---------------------------------------------|------------------------------------------------|------------------------------------------------|----------------|---------------------------------
| CCDC     | 1568619                                        | 1568620                                    | 1568621                                           | 1568622                                           | 1568623       |
| Formula  | C₂₀H₂₄N₂O₁₀Zn₂                                | C₁₇H₁₈N₂O₁₀Zn                                | C₁₇H₁₉N₂O₁₂₅Zn                                    | C₂₂H₁₈N₂O₅Zn                                    | C₁₇H₂₀N₂O₅Zn  |
| Fw       | 583.15                                         | 395.70                                      | 382.69                                             | 509.80                                            | 397.72         |
| Crystal System | Orthorhombic                                      | Monoclinic                                    | Orthorhombic                                        | Monoclinic                                        | Monoclinic    |
| Space group | P n n m                                              | P 2₁/c                                      | P n n a                                            | C 2/c                                              | P 2₁/c          |
| Wavelength | h (Å)                                             | 0.71073                                      | 0.71073                                            | 0.9699                                            | 0.71073        |
| a (Å)    | 7.4159(16)                                      | 8.2852(11)                                   | 8.3000(17)                                         | 18.0211(8)                                        | 8.4434(14)     |
| b (Å)    | 19.318(4)                                       | 10.4999(14)                                  | 10.400(2)                                          | 5.8795(2)                                         | 10.381(18)     |
| c (Å)    | 7.3457(16)                                      | 21.684(3)                                    | 19.740(4)                                          | 21.7192(12)                                       | 21.551(4)      |
| β (°)    | 90                                              | 117.282(3)                                   | 90                                                  | 113.890(1)                                        | 115.928(4)     |
| V (Å³)   | 1052.3(4)                                       | 1676.5(4)                                    | 1704.0(6)                                          | 2104.10(17)                                       | 1698.8(5)      |
| Z        | 2                                               | 4                                            | 4                                                   | 4                                                  | 4              |
| dₑ (g/cm³)| 1.840                                           | 1.568                                        | 1.492                                              | 1.609                                             | 1.555          |
| μ (mm⁻¹) | 2.343                                           | 1.496                                        | 3.318                                              | 1.222                                             | 1.476          |
| F(000)   | 596                                             | 816                                          | 788                                                | 1056                                              | 824            |
| lₐhl    | 15845 / 2674                                    | 19935 / 5502                                 | 10296 / 1696                                       | 6512 / 2296                                       | 25908 / 7954   |
| col/uniq | 0.094                                           | 0.061                                        | 0.087                                              | 0.044                                             | 0.053          |
| Rint    | 0.054                                           | 0.087                                        | 0.026                                              | 0.026                                             | 0.070          |
| Nobs     | 1859 / 103                                       | 4217 / 236                                   | 976 / 117                                          | 2562 / 150                                        | 6155 / 232     |
| R₁[2σ(I)] | 0.066                                           | 0.051                                        | 0.093                                              | 0.026                                             | 0.070          |
| Rw[2σ(I)] | 0.145                                           | 0.101                                        | 0.214                                              | 0.069                                             | 0.153          |
| GOF      | 1.04                                           | 1.00                                         | 1.07                                               | 1.13                                              | 1.00           |

\(^{a}R = \sum | |F_o| - |F_c| |/\sum |F_o|

\(^{b}R_w = [\sum (w(F_o^2 - F_c^2)^2) / \sum (w(F_o^2))]^{1/2}

\(^{c}GOF = [\sum w(F_o^2 - F_c^2)^2 / (N_{obs} - N_{param})]^{1/2}\)
Table S5  Crystallographic data and refinement parameters for zinc(II) diethylmalonates

| Compound | [Zn(bipy)$_{1.5}$ (Et$_2$mal)] · H$_2$O (5) | [Zn(H$_2$O)$_4$(bipy)] · 2HEt$_3$mal · bipy (6) | [Zn(bpe)(Et$_2$mal)] · 0.25bpe (7) | [Zn(bpe)$_{0.75}$(tpcb)$_{0.25}$ (Et$_2$mal)] (7a) | [Zn(H$_2$O)$_4$(bpe)$_2$] (HEt$_2$mal)$_2$ (8) | [Zn(H$_2$O)$_4$(bpe)$_2$]$_{0.15}$ (HEt$_2$mal)$_{0.85}$ | [Zn(bpa)(Et$_2$mal)] · 0.38H$_2$O (9) |
|-----------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|
| CCDC      | 1568624                         | 1568625                         | 1568626                         | 1568627                         | 1568628                         | 1568629                         | 1568630                         |
| Formula   | C$_{22}$H$_{24}$N$_2$O$_5$Zn    | C$_{34}$H$_{30}$N$_4$O$_{14}$Zn | C$_{22}$H$_{22.5}$N$_{2.5}$O$_4$Zn | C$_{22}$H$_{22.5}$N$_{2.5}$O$_4$Zn | C$_{38}$H$_{48}$N$_4$O$_{12}$Zn | C$_{38}$H$_{48}$N$_4$O$_{12}$Zn | C$_{10}$H$_{22.75}$N$_2$O$_4.38$Zn |
| Fw        | 475.81                          | 804.15                          | 451.29                          | 451.29                          | 818.17                          | 818.17                          | 414.51                          |
| Crystal   | Monoclinic                      | Monoclinic                      | Orthorhombic                    | Orthorhombic                    | Monoclinic                      | Monoclinic                      | Orthorhombic                    |
| System    |                                 |                                 |                                 |                                 |                                 |                                 |                                 |
| Space group | P 2$_1$/c                       | C 2/c                          | C m c m                         | P b c n                         | C 2/m                           | C 2/c                           | C 2 2 2 1                       |
| Wavelength (Å) | 0.71073                        | 0.71073                         | 0.71073                         | 0.71073                         | 0.71073                         | 0.71073                         | 0.71073                         |
| a (Å)     | 11.1832(8)                      | 22.6008(12)                     | 9.8266(5)                       | 9.845(8)                        | 22.881(2)                       | 26.8028(19)                      | 24.6623(3)                      |
| b (Å)     | 8.2422(6)                       | 11.4154(6)                      | 22.0654(12)                     | 22.082(17)                      | 6.8976(6)                       | 6.8933(5)                        | 37.180(5)                       |
| c (Å)     | 23.8320(17)                     | 17.1552(9)                      | 22.1641(11)                     | 21.905(17)                      | 14.1573(12)                     | 23.0690(17)                      | 8.7826(12)                      |
| β (°)     | 99.143(2)                       | 120.308(1)                      | 90                              | 90                             | 117.532(2)                      | 110.021(1)                       | 90                              |
| V (Å$^3$) | 2168.8(3)                       | 3821.1(4)                       | 4805.8(4)                       | 4762(6)                         | 1981.3(3)                       | 4004.6(5)                        | 8053.0(19)                      |
| Z         | 4                               | 4                               | 8                               | 8                              | 2                               | 4                               | 4                               |
| d$_e$ (g/cm$^3$) | 1.457                          | 1.398                          | 1.247                          | 1.259                          | 1.371                          | 1.357                          | 1.368                          |
| μ (mm$^{-1}$) | 1.171                          | 0.713                          | 1.050                          | 1.059                          | 0.686                          | 0.679                          | 1.247                          |
| F(000)    | 988                             | 1696                           | 1872                           | 1872                           | 860                            | 1720                           | 3452                           |
| I$_{hk0}$ / uniq | 23649 / 6785                  | 27960 / 7041                   | 22224 / 3498                   | 40353 / 7285                   | 17312 / 4490                   | 25740 / 6154                    | 41027 / 12430                  |
| R$_{int}$ | 0.073                           | 0.029                          | 0.082                          | 0.202                          | 0.039                          | 0.050                          | 0.103                          |
| Obs. refl. / N | 4755 / 282                    | 5947 / 264                     | 2496 / 209                     | 3089 / 252                     | 3929 / 182                     | 3847 / 314                     | 7821 / 461                     |
| R, a % [I > 2σ(I)] | 0.047                          | 0.029                          | 0.052                          | 0.114                          | 0.052                          | 0.055                          | 0.065                          |
| R$_{w}$, b % | 0.103                          | 0.075                          | 0.140                          | 0.237                          | 0.132                          | 0.176                          | 0.150                          |
| GOF$^c$   | 1.01                            | 1.02                            | 1.01                            | 1.01                            | 1.18                           | 1.03                           | 1.02                           |
| Flack     | -                               | -                               | -                               | -                               | -                              | -                              | 0.01(2)                        |

$^aR = \Sigma | F_o | - | F_c | / \Sigma | F_o | . \quad ^bR_w = [\Sigma (w(F_o^2 - F_c^2)^2)/\Sigma (w(F_o^2))]^{1/2}. \quad ^cGOF = [\Sigma w(F_o^2 - F_c^2)^2/(N_{obs} - N_{param})]^{1/2}$
S1.5. Powder X-Ray diffraction.

Phase composition of the bulk samples was confirmed with powder XRD. Powder patterns were measured on a Bruker D8 Advance diffractometer at room temperature with LynxEye detector and Ge(111) monochromator, $\lambda$(CuK$_\alpha$) = 1.54060 Å, $\theta$/2$\theta$ scan from 4° to 60°. The powder patterns were modeled with the Rietveld method using Bruker TOPAS® software. Fundamental parameters approach (Cheary & Coelho, 1992) was used for profile fitting. The preferred orientation was taken into account with the spherical harmonics approach (Järvinen, 1993).

Figure S4 The experimental (blue) and calculated (red) powder patterns for [Zn$_2$(H$_2$O)$_2$(bipy)(Me$_2$mal)$_2$] (1) and their difference (grey). Smooth residual curve indicates purity of the sample; high $R_{wp}$/$R_{bragg}$ = 20.28/4.95 % values are related to prominent preferred orientation.

Figure S5 The experimental (blue) and calculated (red) powder patterns for [Zn(bpe)(Me$_2$mal)] · H$_2$O (2) and their difference (grey). $R_{wp}$/$R_{bragg}$ = 6.04/1.42 % indicate purity of the sample.

Figure S6 The experimental (blue) and calculated (red) powder patterns for [Zn(bpe)(Me$_2$mal)] · H$_2$O (2) irradiated for 6 hours. Rietveld analysis indicates that the sample contains the [Zn(bpe)(Me$_2$mal)] · H$_2$O and [Zn(bpe)(Me$_2$mal)$_2$][Zn$_2$(tpcb)(Me$_2$mal)$_2$] · H$_2$O phases in 1 : 1 ratio. $R_{wp}$ = 3.479% and $R_{bragg}$ = 0.387/0.481%. The blue line is the experimental pattern, the fuchsia line is the calculated pattern, and the grey line is the difference curve.
Figure S7  XRD pattern for [Zn(μ-bpa)(μ-Me₂mal)] · H₂O]ₙ (4). Rietveld analysis indicates purity of the sample. R_{wp}/R_{bragg} = 6.195/1.106 %. The blue line is the experimental pattern, the fuchsia line is the calculated pattern, and the grey line is the difference curve.

Figure S8  The experimental (blue) and calculated (red) powder patterns for [Zn(bipy)₁₅(Et₂mal)] · H₂O (5) and their difference (grey). R_{wp}/R_{bragg} = 3.32/0.67 % indicate purity of the sample.

Figure S9  The experimental (blue) and calculated (red) powder patterns for [Zn(H₂O)₄(bipy)](HEt₂mal)₂ · bipy · 2H₂O (6) and their difference (grey). Although some impurity is present in the sample, R_{wp}/R_{bragg} = 4.98/1.16 % indicate that the sample consists mainly of the target product.

Figure S10  The experimental (blue) and calculated (red) powder patterns for [Zn(bpe)(Et₂mal)] (7) and their difference (grey). Smooth residual curve and R_{wp}/R_{bragg} = 17.73/3.88 % indicate that the
sample exhibit strong preferred orientation and consists mainly from the target substance. Some impurity is present that we failed to determine.

**Figure S11** The experimental (blue) and calculated (red) powder patterns for [Zn(bpe)(Et₂mal)] (7) irradiated for 6 hours. Rietveld analysis indicates purity of the sample. $R_{wp} = 5.296\%$ and $R_{bragg} = 1.030\%$. The blue line is the experimental pattern, the fuchsia line is the calculated pattern, and the grey line is the difference curve.

**Figure S12** The experimental (blue) and calculated (red) powder patterns for [Zn(H₂O)₄(bpe)₂](HEt₂mal)₂ (8) and their difference (grey). Rietveld analysis indicates that the sample consists mainly from the target substance. Some impurity is present that we failed to determine.

**Figure S13** The experimental (blue) and calculated (red) powder patterns for [Zn(H₂O)₄(bpe)₂](HEt₂mal)₂ (8) irradiated for 6 hours. Rietveld analysis indicates that the sample consists of [Zn(H₂O)₄(bpe)₂](HEt₂mal)₂ and [Zn(H₂O)₄(bpe)₂]₀.15[Zn(H₂O)₄(tpcb)]₀.₈₅(HEt₂mal)₄ in 1 : 9 ratio and contains some impurity. $R_{wp} = 3.193\%$ and $R_{bragg} = 0.215/0.304\%$. The blue line is the experimental pattern, the fuchsia line is the calculated pattern, and the grey line is the difference curve.
**Figure S14** The experimental (blue) and calculated (red) powder patterns for [Zn(hpa)(Et₂mal)] · 0.38H₂O (9) and their difference (grey). Although some impurity is present in the sample, $R_{wp}/R_{bragg} = 6.31/1.00\ %$ indicate purity of the sample.
S1.6. $^1$H NMR Analysis of acidified 2a, 7a and 8a in $d_6$-DMSO

$^1$H NMR spectra were recorded on a 300 MHz Bruker FT-NMR spectrometer with TMS as an internal reference. As even moderate heating of $d_6$-DMSO solutions of reaction products 2a, 7a and 8a causes cleavage of tcpb, the samples were dissolved using a drop of HNO$_3$ at room temperature.

**Figure S15** $^1$H NMR spectrum of 2a dissolved in $d_6$-DMSO using a drop of HNO$_3$. 
Figure S16 $^1$H NMR spectrum of 7a dissolved in $d_6$-DMSO using a drop of HNO$_3$. 
Figure S17 $^1$H NMR spectrum of 8a dissolved in $d_6$-DMSO using a drop of HNO$_3$. 
S2. Systre INPUT files for all 2D and 3D coordination polymers

1

crystal
name 0.5(C40 H48 N4 O20 Zn4)
cell 7.4159 19.3180 7.3457 90.0000 90.0000 90.0000
group Pnnm
atom 1 3 0.75138 0.81710 0.50000
edge 1 0.4886 0.7189 0.5000
edge 1 0.9886 0.7811 1.0000
edge 1 0.9886 0.7811 0.0000
atom 2 4 0.48860 0.71895 0.50000
edge 2 0.7514 0.8171 0.5000
edge 2 0.2514 0.6829 0.0000
edge 2 0.2514 0.6829 1.0000
edge 2 1.5114 0.2811 0.5000
end

2

crystal
name C17 H16 N2 O4 Zn, H2 O
cell 8.2852 10.4999 21.6840 90.0000 117.280 90.0000
group P121/c1
atom 1 4 0.05990 0.49185 0.31425
edge 1 -0.0599 0.9918 0.1858
edge 1 -0.0599 -0.0082 0.1858
edge 1 0.9401 1.5082 0.6858
edge 1 -0.0599 0.4918 0.6858
end

2a - novel topology
Coordination sequences
----------------------
Ti1: 1 2 3 4 5 6 7 8 9 10
Num 4 11 24 49 82 128 180 235 302 377
Cum 5 16 40 89 171 299 479 714 1016 1393
----------------------
Zn1: 1 2 3 4 5 6 7 8 9 10
Num 4 12 28 50 84 130 180 240 302 372
Cum 5 17 45 95 179 309 489 714 1031 1403
----------------------
Zn2: 1 2 3 4 5 6 7 8 9 10
Num 4 9 20 43 78 122 172 227 292 369
Cum 5 14 34 77 155 277 449 676 968 1337
----------------------
TD10=1377

Vertex symbols for selected sublattice
--------------------------------------
Ti1 Point symbol:{4.6^4.8}
Extended point symbol: [4.8(5).6.6.6.6]

Zn1 Point symbol: {6^5.8}
Extended point symbol: [6.6.6.6.6(2).8(2)]

Zn2 Point symbol: {4^3.6^3}
Extended point symbol: [4.4.4.6(2).6.6]

Point symbol for net: {4.6^4.8}{4^3.6^3}{6^5.8}
4,4,4-c net with stoichiometry (4-c)(4-c)(4-c); 3-nodal net

Crystal name C17 H16 N2 O4 Zn, H2 O / B2 to K4
Cell 8.2852 10.4999 21.6840 90.000 117.280 90.000
Group P21
Atom 1 4 0.75000 0.50000 0.75000
Edge 1 0.9401 0.9919 0.9358
Edge 1 0.9401 -0.0081 0.9358
Edge 1 0.0599 1.0082 0.5642
Edge 1 1.0599 0.0082 0.5642
Atom 2 4 0.05990 0.00815 0.56425
Edge 2 -0.0599 -0.4918 0.4358
Edge 2 -0.0599 0.5082 0.4358
Edge 2 0.7500 -0.5000 0.7500
Edge 2 -0.2500 0.5000 0.7500
Atom 3 4 0.94010 0.99185 1.0642
Edge 3 1.0599 1.4919 1.0642
Edge 3 1.0599 0.4919 1.0642
Edge 3 0.7500 0.5000 0.7500
Edge 3 0.7500 1.5000 0.7500

Crystal name C17 H18 N2 O4 Zn, H2 O
Cell 8.4434 10.3811 21.5510 90.000 115.930 90.000
Group P121/c1
Atom 1 4 0.93529 0.99201 0.18412
Edge 1 1.0647 0.4920 0.3159
Edge 1 1.0647 1.4920 0.3159
Edge 1 1.0647 0.0080 -0.1841
Edge 1 0.0647 2.0080 -0.1841

Crystal name C22 H22 N3 O4 Zn, H2 O
Cell 11.1832 8.2422 23.8320 90.000 99.140 90.000
Group P121/c1
atom 1 3 0.55981 0.07828 0.32295
edge 1 0.4402 0.5783 0.1770
edge 1 0.4402 -0.4217 0.1770
edge 1 0.4402 0.9217 0.6770
end

7 - novel topology
Structure consists of 3D framework with Zn

Coordination sequences
-----------------------------
Zn1:  1  2  3  4  5  6  7  8  9  10
Num  4 12 30 70 130 212 315 430 545 682
Cum  5 17 47 117 247 459 774 1204 1749 2431
-----------------------------
Zn2:  1  2  3  4  5  6  7  8  9  10
Num  4 12 30 70 130 212 315 430 545 682
Cum  5 17 47 117 247 459 774 1204 1749 2431
-----------------------------
Zn3:  1  2  3  4  5  6  7  8  9  10
Num  4 12 30 70 130 212 315 430 545 682
Cum  5 17 47 117 247 459 774 1204 1749 2431
-----------------------------
Zn4:  1  2  3  4  5  6  7  8  9  10
Num  4 12 30 70 130 212 315 430 545 682
Cum  5 17 47 117 247 459 774 1204 1749 2431
-----------------------------
Zn5:  1  2  3  4  5  6  7  8  9  10
Num  4 12 30 70 130 212 315 430 545 682
Cum  5 17 47 117 247 459 774 1204 1749 2431
-----------------------------
Zn6:  1  2  3  4  5  6  7  8  9  10
Num  4 12 30 70 130 212 315 430 545 682
Cum  5 17 47 117 247 459 774 1204 1749 2431
-----------------------------
Zn7:  1  2  3  4  5  6  7  8  9  10
Num  4 12 30 70 130 212 315 430 545 682
Cum  5 17 47 117 247 459 774 1204 1749 2431
-----------------------------
Zn8:  1  2  3  4  5  6  7  8  9  10
Num  4 12 30 70 130 212 315 430 545 682
Cum  5 17 47 117 247 459 774 1204 1749 2431
-----------------------------
TD10=2431

Vertex symbols for selected sublattice
--------------------------------------
Zn1 Point symbol:{6^5.8}
Extended point symbol:{6.6.6.6(2).8(2)}
--------------------------------------
Zn2 Point symbol: \{6^{5.8}\}
Extended point symbol: \{6.s.6.s.6.s.6.2.8.2(2)\}

Zn3 Point symbol: \{6^{5.8}\}
Extended point symbol: \{6.s.6.s.6.s.6.2.8.2(2)\}

Zn4 Point symbol: \{6^{5.8}\}
Extended point symbol: \{6.s.6.s.6.s.6.2.8.2(2)\}

Zn5 Point symbol: \{6^{5.8}\}
Extended point symbol: \{6.s.6.s.6.s.6.2.8.2(2)\}

crystal
name C19 H20 N2 O4 Zn
cell 22.1641 9.8266 22.0654 90.000 90.000 90.000
group P1
atom 1 4 0.45563 0.00000 0.20098
edge 1 0.5444 -0.5000 0.2990
edge 1 0.5444 0.5000 0.2990
edge 1 0.5444 -1.0000 -0.2010
edge 1 0.0444 1.0000 0.2010
atom 2 4 0.95563 0.00000 0.79902
edge 2 1.0444 -0.5000 0.7010
edge 2 1.0444 0.5000 0.7010
edge 2 1.0444 -1.0000 1.2010
edge 2 0.5444 1.0000 0.7990
atom 3 4 0.04437 0.50000 0.70098
edge 3 -0.0444 0.5000 0.2990
edge 3 -0.0444 -0.5000 0.2990
edge 3 0.4556 1.5000 0.7010
atom 4 4 0.54437 0.50000 0.29902
edge 4 0.4556 0.0000 0.2990
edge 4 0.4556 1.0000 0.2010
edge 4 0.4556 -0.5000 0.7010
edge 4 0.9556 1.5000 0.2990
atom 5 4 0.45563 0.50000 0.70098
edge 5 0.5444 1.0000 0.7990
edge 5 0.5444 0.0000 0.7990
edge 5 0.5444 1.5000 0.2990
edge 5 0.0444 -0.5000 0.7010
atom 6 4 0.95563 0.50000 0.29902
edge 6 1.0444 1.0000 0.2010
edge 6 1.0444 0.0000 0.2010
edge 6 1.0444 1.5000 0.7010
edge 6 0.5444 -0.5000 0.2990
atom 7 4 0.04437 0.00000 0.20098
edge 7 -0.0444 0.5000 0.2990
edge 7 -0.0444 -0.5000 0.2990
edge 7 -0.0444 1.0000 -0.2010
edge 7 0.4556 -1.0000 0.2010
atom 8 4 0.54437 0.00000 0.79902
edge 8 0.4556 0.5000 0.7010
edge 8 0.4556 -0.5000 0.7010
edge 8 0.4556 1.0000 1.2010
edge 8 0.9556 -1.0000 0.7990
end

8 - novel topology, igc2
(as obtained after simplification of the structure from Cmcm to P1 space group and adjacency matrix correction to obtain the AB²B' 3D network)

Coordination sequences

|     |        |        |        |        |        |        |        |        |        |        |
|-----|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
|     | Zn1    | Zn2    | Zn3    | Zn4    | Zn5    | Zn6    | Zn7    | Zn8    |
|     | Num    | Cum    | Num    | Cum    | Num    | Cum    | Num    | Cum    |
| 1   | 4      | 5      | 4      | 5      | 4      | 5      | 4      | 5      |
| 2   | 12     | 17     | 12     | 17     | 12     | 17     | 12     | 17     |
| 3   | 30     | 47     | 30     | 47     | 30     | 47     | 30     | 47     |
| 4   | 70     | 117    | 70     | 117    | 70     | 117    | 70     | 117    |
| 5   | 130    | 247    | 130    | 247    | 130    | 247    | 130    | 247    |
| 6   | 212    | 459    | 212    | 459    | 212    | 459    | 212    | 459    |
| 7   | 315    | 774    | 315    | 774    | 315    | 774    | 315    | 774    |
| 8   | 430    | 1204   | 430    | 1204   | 430    | 1204   | 430    | 1204   |
| 9   | 545    | 1749   | 545    | 1749   | 545    | 1749   | 545    | 1749   |
| 10  | 682    | 2431   | 682    | 2431   | 682    | 2431   | 682    | 2431   |

TD10=2431

Vertex symbols for selected sublattice

Zn1 Point symbol:{6^5.8}
Extended point symbol: [6.6.6.6.6(2).8(2)]

--------------------------------------
Zn2 Point symbol: {6^5.8}
Extended point symbol: [6.6.6.6.6(2).8(2)]

--------------------------------------
Zn3 Point symbol: {6^5.8}
Extended point symbol: [6.6.6.6.6(2).8(2)]

--------------------------------------
Zn4 Point symbol: {6^5.8}
Extended point symbol: [6.6.6.6.6(2).8(2)]

--------------------------------------
Zn5 Point symbol: {6^5.8}
Extended point symbol: [6.6.6.6.6(2).8(2)]

--------------------------------------
Zn6 Point symbol: {6^5.8}
Extended point symbol: [6.6.6.6.6(2).8(2)]

--------------------------------------
Zn7 Point symbol: {6^5.8}
Extended point symbol: [6.6.6.6.6(2).8(2)]

--------------------------------------
Zn8 Point symbol: {6^5.8}
Extended point symbol: [6.6.6.6.6(2).8(2)]

--------------------------------------
Point symbol for net: {6^5.8}
4-c net; uninodal net

crystal
name C19 H20 N2 O4 Zn
cell 22.1641 9.8266 22.0654 90.0000 90.0000 90.0000
group P1
atom 1 4 0.45563 0.00000 0.20098
edge 1 0.5444 -0.50000 0.2990
edge 1 0.5444 0.50000 0.2990
edge 1 0.5444 -1.00000 -0.2010
edge 1 0.0444 1.00000 0.2010
atom 2 4 0.95563 0.00000 0.79902
edge 2 1.0444 -0.50000 0.7010
edge 2 1.0444 0.50000 0.7010
edge 2 1.0444 -1.00000 1.2010
edge 2 0.5444 1.00000 0.7990
atom 3 4 0.04437 0.50000 0.70098
edge 3 -0.0444 0.00000 0.7990
edge 3 -0.0444 1.00000 0.7990
edge 3 -0.0444 -0.50000 0.2990
edge 3 0.4556 1.50000 0.7010
atom 4 4 0.54437 0.50000 0.29902
edge 4 0.4556 0.00000 0.2010
edge 4 0.4556 1.00000 0.2010
edge 4 0.4556 -0.50000 0.7010
edge 4 0.9556 1.50000 0.2990
atom 5 4 0.45563 0.50000 0.70098
dge 5 0.5444 1.0000 0.7990
dge 5 0.5444 0.0000 0.7990
dge 5 0.5444 1.5000 0.2990
dge 5 0.0444 -0.5000 0.7010
atom 6 4 0.95563 0.50000 0.29902
dge 6 1.0444 1.0000 0.2010
dge 6 1.0444 0.0000 0.2010
dge 6 1.0444 1.5000 0.7010
dge 6 0.5444 -0.5000 0.2990
atom 7 4 0.04437 0.00000 0.20098
dge 7 -0.0444 0.5000 0.2990
edge 7 -0.0444 -0.5000 0.2990
edge 7 -0.0444 1.0000 -0.2010
edge 7 0.4556 -1.0000 0.2010
atom 8 4 0.54437 0.00000 0.79902
dge 8 0.4556 0.5000 0.7010
dge 8 0.4556 -0.5000 0.7010
dge 8 0.4556 1.0000 1.2010
dge 8 0.9556 -1.0000 0.7990
end

8a - as obtained after UV irradiation of 8 for 6 hours - novel topology, ige2

Coordination sequences
----------------------
Zn1:  1  2  3  4  5  6  7  8  9  10
Num   4 12 30  70 130 212 315  430  545  682
Cum   5 17 47 117 247 459 774 1204 1749 2431
----------------------
TD10=2431

Vertex symbols for selected sublattice
--------------------------------------
Zn1 Point symbol:{6^5.8}
Extended point symbol:[6.6.6.6.6(2).8(2)]
--------------------------------------
Point symbol for net: {6^5.8}
4-c net; uninodal net

crystal
name ort_a.res in Pbcn
cell 9.8454 21.9051 21.9051 90.0000 90.0000 90.0000
group Pbcn
atom 1 4 0.49776 0.29674 0.45427
dge 1 0.9978 0.2033 0.5457
dge 1 -0.0022 0.2033 0.5457
dge 1 1.5022 0.2967 0.0457
dge 1 -0.4978 0.7033 0.5457
end
9 - novel topology, **igc1**

Coordination sequences

|         | Zn1: |         | Zn2: |         | Zn3: |
|---------|------|---------|------|---------|------|
| Num     | 1    | 2       | 3    | 4       | 5    | 6    | 7    | 8    | 9    | 10   |
|         | 4    | 12      | 30   | 70      | 128  | 216  | 332  | 466  | 598  | 742  |
| Cum     | 5    | 17      | 47   | 117     | 245  | 461  | 793  | 1259 | 1857 | 2599 |
|         | 4    | 12      | 30   | 70      | 130  | 220  | 334  | 466  | 606  | 747  |
| Cum     | 5    | 17      | 47   | 117     | 247  | 467  | 801  | 1267 | 1873 | 2620 |
|         | 4    | 12      | 30   | 70      | 126  | 212  | 334  | 466  | 608  | 748  |
| Cum     | 5    | 17      | 47   | 117     | 243  | 455  | 789  | 1255 | 1863 | 2611 |
| TD10=2612 |

Vertex symbols for selected sublattice

|         | Zn1 Point symbol: |{6^5.8} |
|---------|-------------------|---------|
|         | Extended point symbol:| [6.6.6.6.(2).8(2)] |
|         | Zn2 Point symbol: |{6^5.8} |
|         | Extended point symbol:| [6.6.6.6.(2).8(2)] |
|         | Zn3 Point symbol: |{6^5.8} |
|         | Extended point symbol:| [6.6.6.6.(2).8(2)] |

Point symbol for net: {6^5.8}
4,4,4-c net with stoichiometry (4-c)(4-c)2(4-c); 3-nodal net

crystal
name C19 H22 N2 O4 Zn, 0.38(H2 O)
cell 24.6620 37.1800 8.7826 90.000 90.000 90.000
group C2221
atom 1 4 0.43029 0.50000 0.50000
edge 1 0.5697 0.5000 1.0000
edge 1 0.5697 0.5000 0.0000
edge 1 0.2403 0.2914 -0.5961
edge 1 0.2403 0.7086 1.5961
atom 2 4 0.24034 0.29141 0.40389
edge 2 0.2597 0.2086 -0.0961
edge 2 0.2597 0.2086 0.9039
edge 2 0.0000 0.4566 -0.7500
edge 2 0.4303 0.5000 1.5000
atom 3 4 0.00000 0.45663 0.25000
edge 3 0.0000 0.5434 0.7500
edge 3 0.0000 0.5434 -0.2500
edge 3 -0.2403 0.2914 -0.9039
edge 3 0.2403 0.2914 1.4039
end

_____________________________________


References

S1. T. G. Mitina and V. A. Blatov, *Cryst. Growth Des.*, 2013, 13, 1655.
S2. E. V. Alexandrov, A. P. Shevchenko, A. A. Asiri and V. A. Blatov, *CrystEngComm*, 2015, 17, 2913.
S3. A. P. Shevchenko, I. A. Blatov, E. V. Kitaeva and V. A. Blatov, *Cryst. Growth Des.*, 2017, 17, 774.
S4. Winn, M. D., Ballard, C. C., Cowtan, K. D., Dodson, E. J., Emsley, P., Evans, P. R., Keegan, R. M., Krissinel, E. B., Leslie, A. G. W., McCoy, A., McNicholas, S. J., Murshudov, G. N., Pannu, N. S., Potterton, E. A., Powell, H. R., Read, R. J., Vagin, A., Wilson, K. S., *Acta. Cryst.*, 2011, D67, 235.
S5. Sheldrick, G. M., *Acta Crystalogr.*, 2015, C71, 3.
S6. Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K., Puschman, H., *J. Appl. Cryst.*, 2009, 42, 339.
S7. *Bruker TOPAS 5 User Manual*, Bruker AXS GmbH, Karlsruhe, Germany, 2014.
S8. R. W. Cheary, A. Coelho, *J. Appl. Crystallogr.* 1992, 25, 109.
S9. M. Järvinen, *J. Appl. Crystallogr.* 1993, 26, 525.