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Supporting Information

Disatereoselective solid-state crossed photocycloaddition of olefins in a 3D Zn(II) coordination polymer

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Experimental

General methods

Commercially available reagents were used as received, in particular, $Zn(OAc)_2{\cdot}2H_2O$ («Roth», Germany, 99%), allylmalonic acid («abcr», Germany, 98%), 1,2-bis(4-pyridyl)ethylene («Sigma Aldrich», Germany, 97%). IR spectra were measured by using a Perkin–Elmer Spectrum 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. ^1H NMR spectra were recorded on a 400 MHz Bruker FT-NMR spectrometer with TMS as an internal reference. Reaction products have poor solubility, thus, were dissolved at d_6-DMSO using a drop of HNO_3 at room temperature.

Synthesis

1: A water solution (10 mL) of $Zn(OAc)_2{\cdot}2H_2O$ (0.030 g, 0.14mmol) and allylmalonic acid (0.020 g, 0.14mmol) was placed at the bottom of a test tube. Then, a water/acetonitrile interphase (4/4mL) was carefully layered. A 10 mL acetonitrile solution of 1,2-bis(4-pyridyl)ethylene (0.050 g, 0.27mmol) 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. ^1H NMR (400 MHz, d_6-DMSO): for bpe δ 9.01 (d, J = 6.0 Hz, 4H), 8.32 (d, J = 6.0 Hz, 4H), 8.13 (s, 2H); for Amal δ 5.74 (ddt, J = 17.0, 10.2, 6.7 Hz, 1H), 5.10 – 4.94 (m, 2H), 3.29 (t, J = 7.5 Hz, 1H), 2.43 (t, J = 7.2 Hz, 2H). IR-spectrum (ATR method), ν/cm^{-1}: 3207m.w, 3079 w, 3046 w, 2949 w, 2912 w, 1629 m, 1585 s, 1560 s, 1511 m, 1437m, 1424 m, 1328 s, 1298 m, 1274 m, 1253 m, 1220 m, 1206 m, 1196 m, 1132 w, 1114 w, 1100 w, 1070 m, 1018 m, 979 m, 967 m, 950 m, 926 w, 909 m, 882 w, 859 m, 845 m, 817 m, 798 m, 743 m, 712 s, 671 m, 648 m, 599 m, 549 s, 470 m. Calculated (%) for $C_{24}H_{26}N_2O_{10}Zn_2$: %: C, 45.52; H, 4.14; N, 4.42; found (%): C, 45.73; H, 4.37; N, 4.30. The yield of **1** is 0.0249 g (57.5 % counting per Zn).

1→2: A single crystal of $[Zn_2(H_2O)_2(Amal)_{1.25}(Bpcbmal)_{0.75}(bpe)_{0.25}]$ (**2**) was obtained by UV irradiation of a single crystal of **1** for 16 hours. At ^{1}H NMR spectra signals corresponding to bpe, Amal and Bpcbmal are present. For Bpcbmal ^{1}H NMR (400 MHz, d$_6$-DMSO): δ8.89 (d, J = 6.0 Hz, 2H), 8.84 (d, J = 6.0 Hz, 2H), 8.07 (d, J = 6.0 Hz, 2H), 7.94 (d, J = 6.0 Hz, 2H), 4.02 (q, J = 9.3 Hz, 1H), 3.76 (t, J = 9.2 Hz, 1H), 3.14 (t, J = 7.5 Hz, 1H), 2.62–2.53 (m, 2H), 2.05 (tm, J = 7.2 Hz, 2H), 1.98 (dm, J = 10.2 Hz, 1H). Conversion rate calculated based on bpe and Amal is equal to, respectively, 81 and 80 %. ^{1}H NMR spectra of **1** irradiated for 48 hours coincide with those of the complex irradiated for 20 hours and give the same conversion rate.

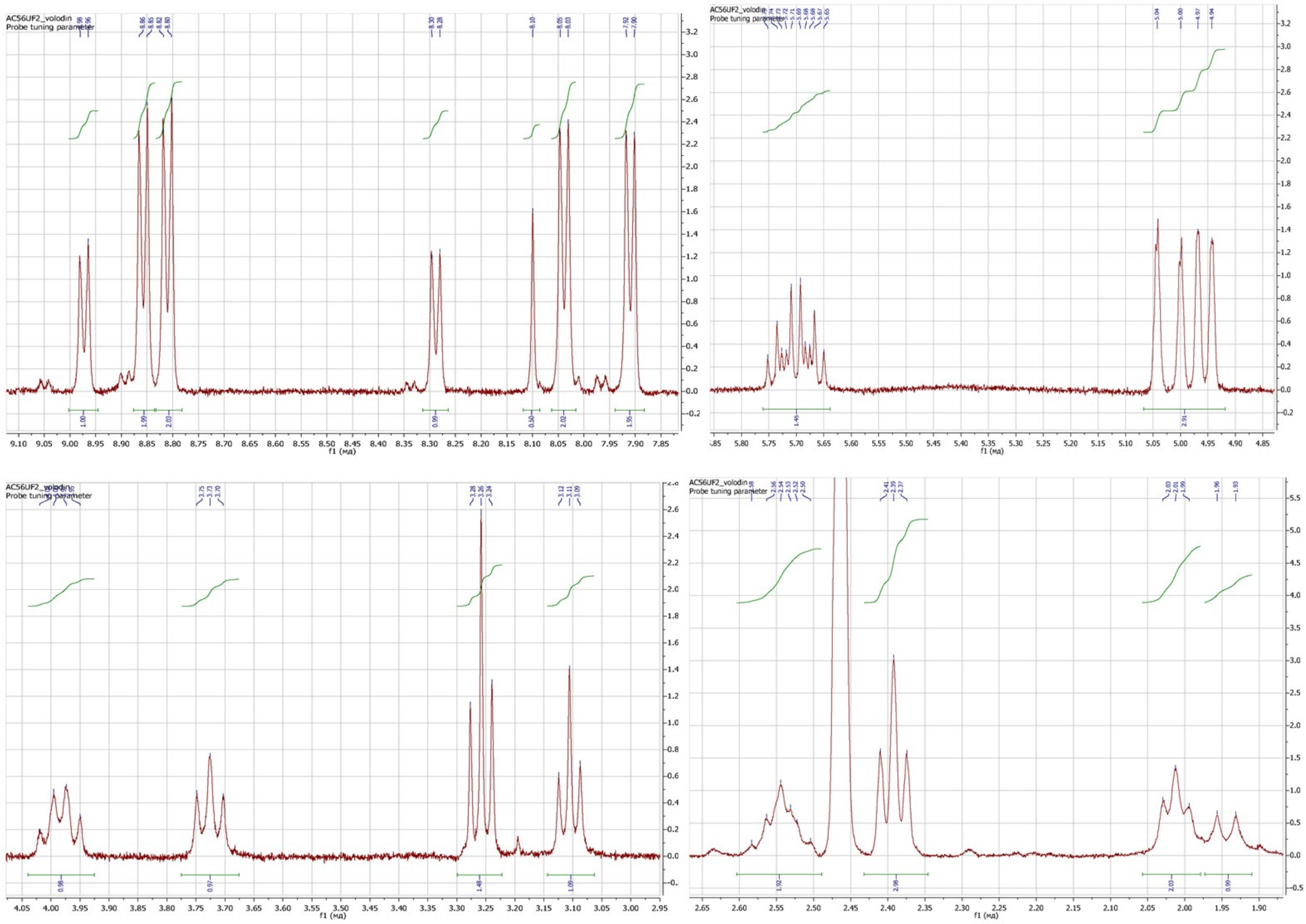
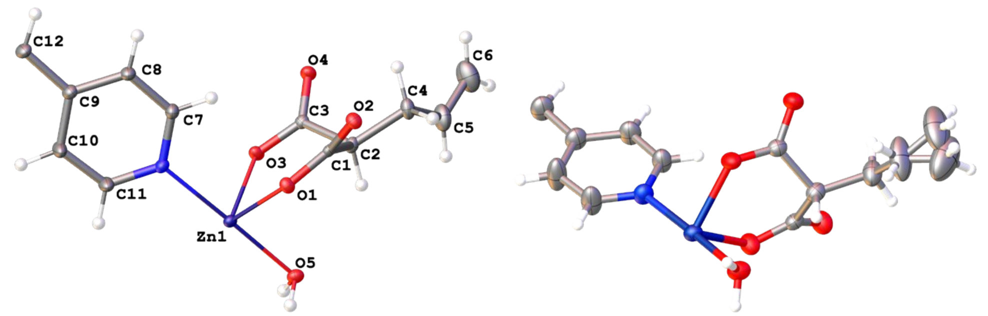


Figure S1. ^{1}H NMR spectrum of powder **1** irradiated for 20 hours dissolved in d$_6$-DMSO using a drop of HNO_3.

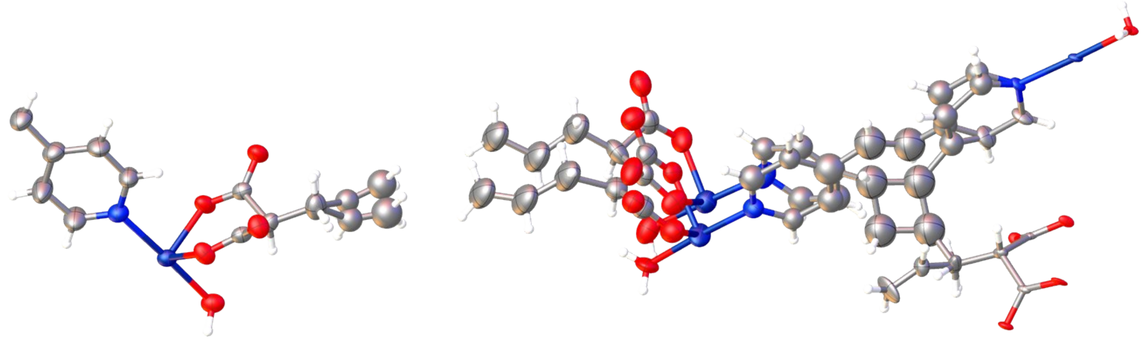
Crystallography

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), 300.0(2) and 375.0(2) K for **1** and at 120.0(20 K for **2**. The structures were solved with SHELXT method[S1] and refined by full-matrix least squares against F^2. Non-hydrogen atoms were refined anisotropically except some disordered atoms. The disordered carbon atoms of the allyl group in complex **1** studied at 375.0(2) K and those of bpe in complex **2** were refined isotropically. A single crystal of **2** contains both reagents and reaction product, thus one of two zinc atoms, two of three anions, and a bpe molecule are disordered over two sites. Free refinement of site occupancies gives approximately 3 : 1 ratio of product and reagents, thus occupancies of these fragments were fixed at, respectively, 0.75 and 0.25. A number of EADP, ISOR, SADI and DFIX instructions were applied to refine some disordered fragments. Positions of hydrogen atoms were calculated and all were included in the refinement by the riding model with $U_{iso}(H) = 1.5U_{eq}(O)$ and $U_{iso}(H) = 1.2U_{eq}(C)$. All calculations were made using the SHELXL2014[S2] and OLEX2[S3] program packages. The best available single crystal of **2** was a twin. For a number of crystals we obtained similar disorder, but another conversion rate; thus, composition, ion' connectivities and mutual disposition of cations and anions arise no doubts. CCDC 1868491-1868492 and 1876402-1876403 contain the crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via https://www.ccdc.cam.ac.uk/structures/



1, 120 K

1, 300 K

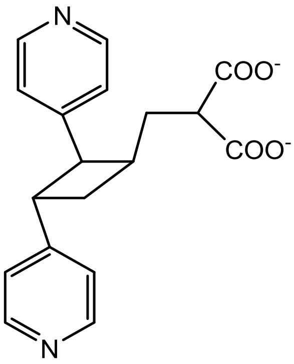


1, 375 K

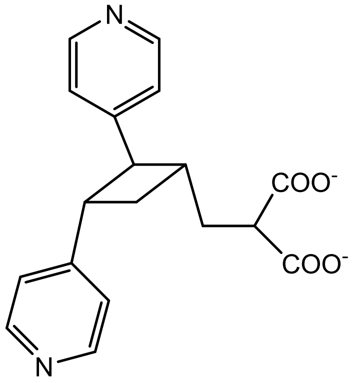
2, 120 K

Figure S2. Asymmetric unit of **1** and **2** in representation of atoms with thermal ellipsoids.

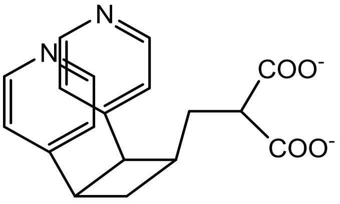
Possible diastereoisomers of 2-((2,3-di(pyridin-4-yl)cyclobutyl)methyl)malonate



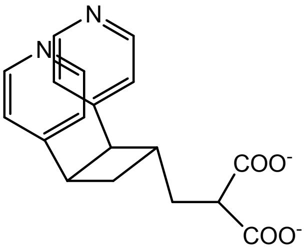
(*1R,2S,3S*)



(*1S,2S,3S*)



(*1R,2S,3R*)



(*1S,2S,3R*)

Analysis of molecular Voronoi polyhedra of bpe molecules

Within the Voronoi approach, all points within an atomic domain are closer to the inner atom than to any external one.[S4]Molecular Voronoi domain is a sum of its' atomic domains. Within this approach to investigate solids, a pair of atoms that does not share any surface is not bonded. This approach demonstrated good qualitative and semi-quantitative correlation with selected QTAIM atomic and bonding descriptors[S5-S7] and was previously applied to analyze ion migration paths[S8] and multicentered bonding.[S7] Recently, we demonstrated that photoreactive molecules are connected with bond path and share molecular Voronoi surface in the region of olefin bonds.[S9]

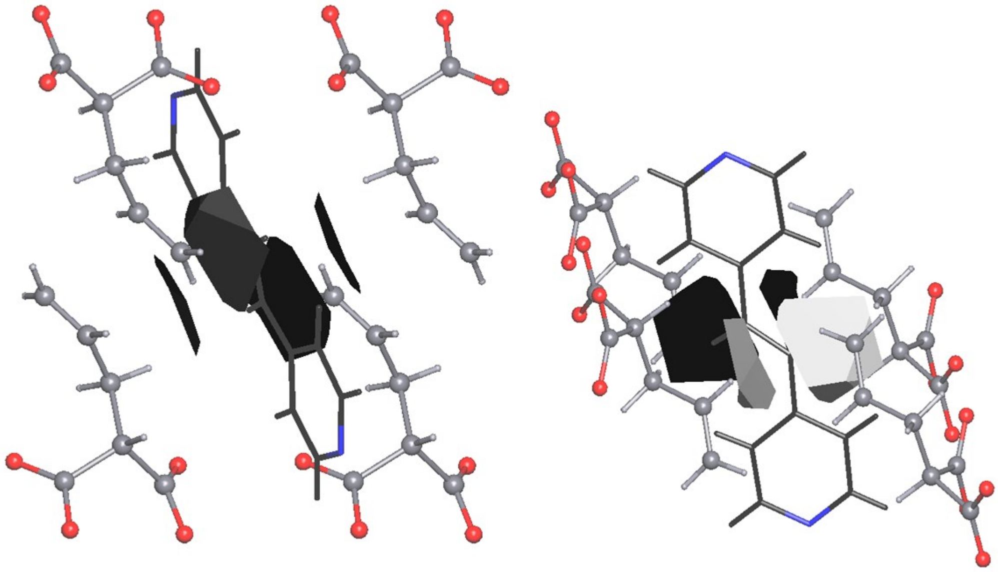


Figure S3. Closest neighborhood of a bpe molecule and fragment of its' molecular Voronoi surface corresponding to interactions of olefin bonds.

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, $\lambda(\mathrm{CuK}\alpha_1) = 1.54060$ Å, $\theta/2\theta$ scans in 2θ range 4° - 60°. The powder patterns were modeled within the Rietveld method using Bruker TOPAS4.2[S10] software. Fundamental parameters approach[S11] was used for profile fitting. Preferred orientation of crystallites was taken into account with the spherical harmonics approach[S12]. In all cases only the background, parameters of microstructure, preferred orientation and unit cell parameters were refined while atomic coordinates were fixed on the values obtained with the corresponding single-crystal experiments.

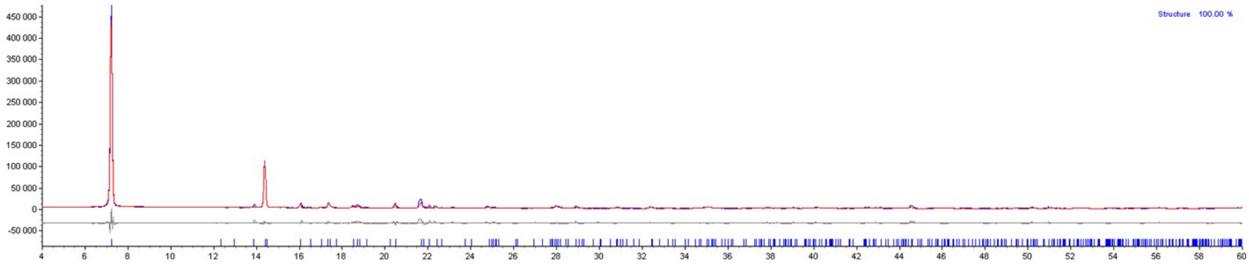


Figure S4. XRD pattern for a sample of **1**. Rietveld analysis indicates that the sample is a pure phase with $R_{\mathrm{bragg}} = 1.849\%$, $R_{\mathrm{wp}} = 12.629\%$. The blue line is the experimental pattern, the fuchsia line is the calculated pattern, and the grey line is the difference curve.

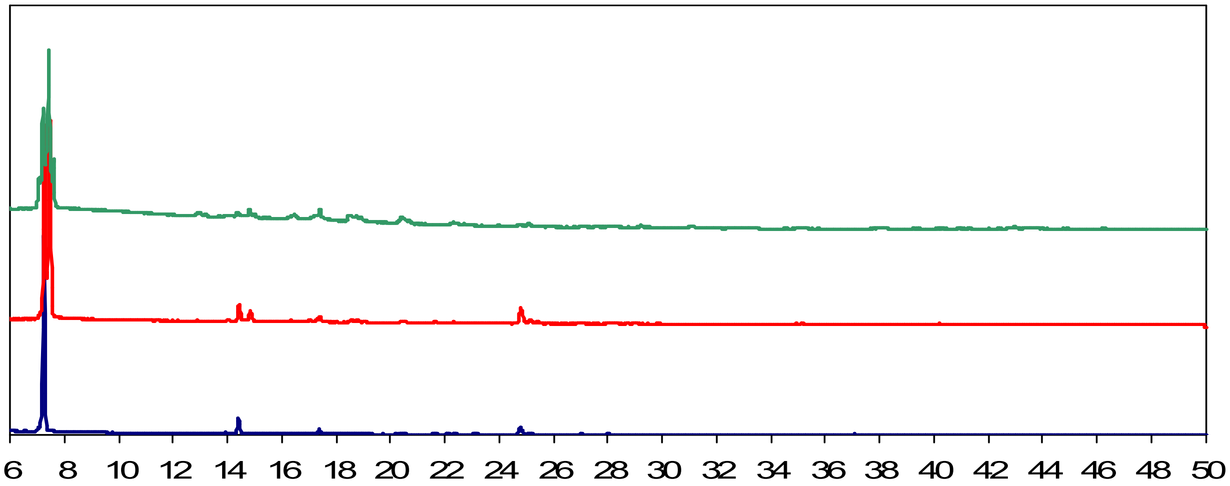


Figure S5. XRD pattern for a sample of **1** before irradiation (blue), and after irradiation for 16 h (red) and 48 h (teal).

References

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Input Systre files for [$Zn_2(H_2O)_2(Amal)_2(bpe)$] and hypothetical [$Zn_2(H_2O)_2(Amal)(Bpcbmal)$] complex

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name 1
cell 7.1598 24.1618 10.4735 90.000 134.260 90.000
group P121/c1
atom 1 3 0.56917 0.69884 0.69892
edge 1 0.3141 0.7782 0.4448
edge 1 1.3141 0.7218 0.9448
edge 1 0.3141 0.7218 0.9448
atom 2 4 0.31414 0.77815 0.44482
edge 2 0.5692 0.6988 0.6989
edge 2 -0.4308 0.8012 0.1989
edge 2 0.5692 0.8012 0.1989
edge 2 1.6859 1.2218 1.5552
end

crystal
name 2
cell 7.1981 24.0696 7.4585 90.000 90.750 90.000
group Pn
atom 1 5 0.45916 0.67312 0.50624
edge 1 0.2067 0.5294 0.8608
edge 1 0.7067 0.4706 0.3608
edge 1 0.2067 0.5294 -0.1392
edge 1 1.2067 0.5294 0.8608
edge 1 0.2089 0.9692 0.9377
atom 2 3 0.21341 0.05022 0.68415
edge 2 0.2089 -0.0308 0.9377
edge 2 0.7089 0.0308 0.4377
edge 2 -0.2911 0.0308 0.4377
atom 3 4 0.20670 0.52941 0.86082
edge 3 0.4592 0.6731 0.5062
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edge 3 0.4592 0.6731 1.5062
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Topological analysis of underlying net for hypothetical [$Zn_2(H_2O)_2$(Amal)(Bpcbmal)] complex

```
 -------------------------
Structure consists of 3D framework with Zn2TiSc

Coordination sequences
----------------------
Sc1:  1  2  3   4   5   6   7   8   9   10
Num   5 13 30  51  81 112 161 201 254  319
Cum   6 19 49 100 181 293 454 655 909 1228
----------------------
Ti1:  1  2  3  4   5   6   7   8   9   10
Num   3  9 20 37  64  92 135 181 248  287
Cum   4 13 33 70 134 226 361 542 790 1077
----------------------
Zn1:  1  2  3  4   5   6   7   8   9   10
Num   4 14 27 50  79 120 150 204 261  310
Cum   5 19 46 96 175 295 445 649 910 1220
----------------------
Zn2:  1  2  3  4   5   6   7   8   9   10
Num   4 10 23 44  66 104 146 196 241  316
Cum   5 15 38 82 148 252 398 594 835 1151
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TD10 = 1169

Vertex symbols for selected sublattice
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Ti1 Point symbol:{6^3}
Extended point symbol:[6.6.6(2)]
--------------------------------------
Zn1 Point symbol:{4^2.6^4}
Extended point symbol:[4.6(3).4.6(4).6(2).6(4)]
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Zn2 Point symbol:{6^5.8}
Extended point symbol:[6.6.6.6.6.8(5)]
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Point symbol for net: {4^2.6^4}{4^2.6^6.8^2}{6^3}{6^5.8}
3,4,4,5-c net with stoichiometry (3-c)(4-c)(4-c)(5-c); 4-nodal net
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