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Zeolite-*like* Metal−Organic Frameworks (ZMOFs) Based on the Directed Assembly of Finite Metal−Organic Cubes (MOCs)

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The ability to control the coordination number, and thus geometry, around metal nodes through metal−ligand directed assembly permits construction of predesigned finite and rigid metal−organic polyhedra (MOPs).[1] MOPs with peripheral functionalities can be employed further as supermolecular building blocks (SBBs) in the construction of extended metal−organic frameworks (MOFs).[2] Programming such building blocks with a hierarchy of appropriate information to promote the synthesis of targeted structures, while simultaneously avoiding other easily attainable nets,[3] i.e. diamond nets for the assembly of tetrahedral building blocks, represents a significant advancement in framework design.[4] In crystal chemistry, edge transitive nets are suitable targets for such processes, since they are unique networks constructed solely from one kind of edge.[5] Herein, we report the utilization of our predesigned finite metal−organic cube (MOC)[6] as a rigid and directional SBB for the directed assembly and deliberate construction of MOFs based on edge transitive nets and having zeolite-*like* topologies.

Zeolite-*like* frameworks, based on tetrahedral nodes, are of tremendous interest due to the myriad potential applications associated with their unique structures and intrinsic pore systems.[7] Nevertheless, the scope of applications is restricted by the intricacy to construct zeolite-*like* frameworks with extra-large cavities/windows and/or periodic intraframework organic functionality.[8] Our group, among others, is continuously striving to develop new synthetic pathways and design strategies to assemble zeolite-*like* metal−organic frameworks (ZMOFs) to tackle these challenges, where the unique features of MOFs, namely facile tunability, pore size tailoring, and intra- and/or extra-framework functionalization, are combined with the distinctive confined space, ion exchange ability, and, especially, the forbidden interpenetration of zeolite structures.

Our group has recently implemented a particular approach in which nondefault structures can be targeted using heterochelation to generate rigid and directional single-metal-ion-based molecular building blocks (MBBs). For example, the utilization of rigid and directional tetrahedral building units TBU, induced through heterochelation, along with ligands having the commensurate coordination angle (∼144°) for zeolite nets has successfully permitted the assembly of nondefault ZMOFs, thus avoiding diamond nets, the default topology for the assembly of simple tetrahedral building units and flexible ditopic linkers.[9]

A particular subset of zeolite nets share a common composite building unit consisting of eight tetrahedra in a cube-like arrangement, commonly referred to as a double 4-ring, d4R.[11] Accordingly, the MOCs can be regarded as d4Rs building units and can be employed as 8-connected SBBs to construct zeolite-like frameworks related to 8-connected edge-transitive nets. The d4Rs can be connected through linear linkers to construct nets based on zeolites **LTA** and **ACO** or through 4-coordinate nodes to result in **AST**- and **ASV**-*like* topologies.

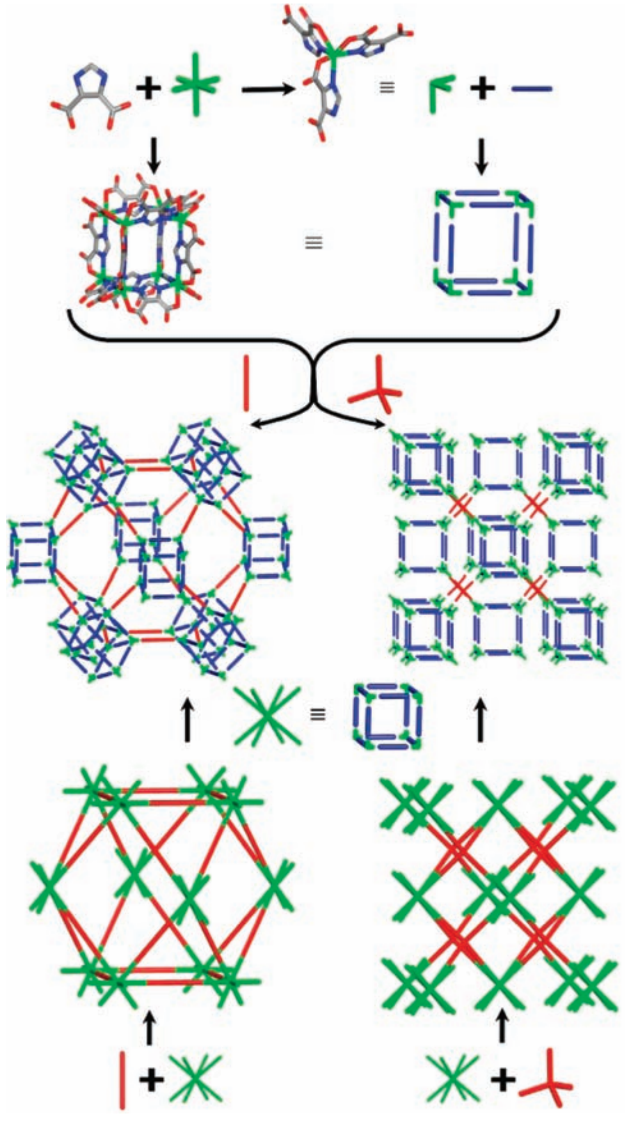

Figure 1. (Top) Single-metal-ion-based MBBs facilitate the assembly of MOCs, which are used as 8-connected SBBs to generate ZMOFs (middle). Specific zeolite nets are targeted based on relations with regular (8-connected)-based nets (bottom). The **reo** net (bottom left) corresponds to zeolite **LTA** (middle left) and **flu** (bottom right) to zeolite **AST** (middle right) when the 8-connected nodes are augmented or replaced by cubes.

The aforementioned zeolites (**ACO**, **AST**, **ASV**, and **LTA**) are especially interesting to reticular chemistry as their nets correspond to

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the augmentation of the edge-transitive nets **bcu**, **flu**, **scu**, and **reo**, respectively, where the d4Rs serve as the cube-like vertex figures.[5] Specifically, **bcu** and **reo** are both semiregular 8-connected nets, and **scu** and **flu** are edge-transitive (4,8)-connected nets. Herein, zeolitic nets that can be regarded as augmented edge-transitive (8-connected)-based nets are targeted, Figure 1, representing a strategy encompassing basic nets to target zeolite-*like* structures.

As previously described by us, the metal−organic molecular cube can be assembled through heterochelation of octahedral single-metal ions, in a *fac*-$MN_3(CO_2)_3$ manner, by ditopic bis-bidentate linkers.[6] The molecular cube consists of eight vertices occupied by triconnected nodes bridged through twelve 4,5-imidazoledicarboxylate (H_nImDC, $n = 0-1$) linkers. The MOCs possess peripheral carboxylate oxygen atoms that can potentially coordinate additional metal ions and/or participate in hydrogen bonding to construct extended structures. Accordingly, by expanding the coordination of the cube's vertices, interconnected tetrahedra similar to the d4R units in zeolites can be attained.

Indeed, reaction of 4,5-imidazoledicarboxylic acid (H_3ImDC) and $Zn(NO_3)_2 \cdot 6H_2O$ in a *N*,*N*′-dimethylformamide (DMF)/ H_2O mixture in the presence of excess zinc and guanidinium cations yields colorless polyhedral crystals containing the expected anionic zinc-based MOCs. The presence of excess zinc and guanidinium ions permits the linkage of the MOCs through the oxygen atoms of H_nImDC to form extended zeolite-*like* frameworks having **AST** topology, Figure 2. The as-synthesized compound is formulated as Zn_{12}(guanidinium)$_8$(ImDC)$_8$(HImDC)$_4 \cdot$(DMF)$_8$(H_2O)$_3$, **1**, using single-crystal X-ray diffraction studies.[13] In **1**, the anionic MOCs, formulated as [Zn_8 (ImDC)$_8$ (HImDC)$_4$]$^{16-}$, are composed of four doubly and eight triply deprotonated ligand molecules and eight Zn^{2+} ions. In the crystal structure of **1**, Figure 2a, each anionic molecular cube is concurrently connected through its edges and vertices to zinc and guanidinium ions, respectively, and further extends to 12 adjacent MOCs. Each edge connection occurs through a Zn^{2+} ion octahedrally coordinated by four carboxylate oxygen atoms (Zn−O distance of 2.07 Å) from two ImDC ligands of two MOCs and two disordered DMF solvent molecules as axial ligands (Zn−O distance of 2.1 Å). The 12 edge connections through Zn^{2+} ions can be visualized as edge-to-edge connections between the cubes. Intermolecular vertex connections occur through charge-assisted hydrogen bonds between four guanidinium ions, paneling a supramolecular tetrahedron, and carboxylate oxygen atoms (N···O distances 2.84−3.04 Å), Figures S1, S2. These H-bonds play a decisive structure-directing role and can be regarded as a tetrahedral node linking four cubes through vertices producing the zeolite-*like* **AST** topology.

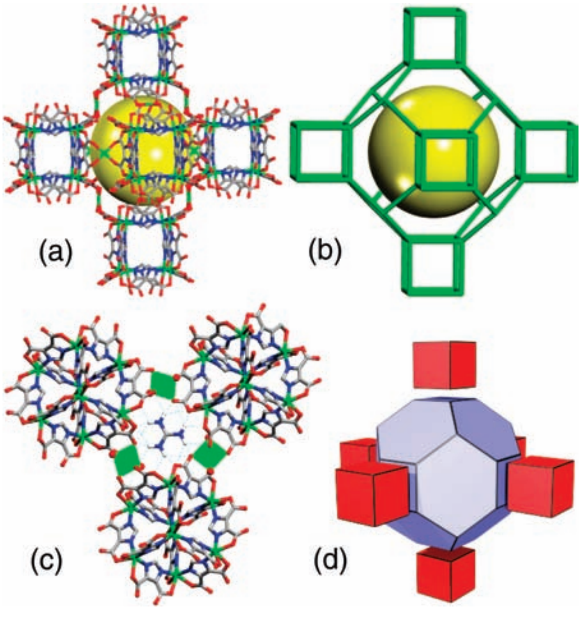

Figure 2. (a) Single-crystal structure of *ast*-ZMOF, **1** (yellow sphere represents vdw sphere of a diameter ∼15 Å that can fit into the *ast*-cage without touching vdw surfaces of the framework), with (b) zeolite **AST**-*like* network topology. (c) In **1**, the MOC-based SBBs are linked via simultaneous edge-to-edge connection through coordinated metal ions and vertex-to-vertex connectivity through charge-assisted H-bonded guanidinium ions. (d) In *ast*-ZMOFs, **1** and **2**, six MOCs (red tile) are connected to generate the **AST**-cage (blue tile).

Reaction of (H_3ImDC) and $Zn(NO_3)_2 \cdot 6H_2O$ in a DMF/H_2O mixture in the presence of potassium chloride yields colorless polyhedral crystals formulated as Zn_8K_8 (HImDC)$_{12}$(DMF)$_5$(H_2O)$_{16}$, **2**.[14] In the crystal structure of **2**, four tetrahedrally arranged K^+ ions coordinate to the oxygen atoms on the vertices of four tetrahedrally arranged MOCs, Figure S3. Each K^+ ion is coordinated by six oxygen atoms on the vertices of three cubes (two per cube, K−O bond distance of 2.72−2.82 Å) and by an additional oxygen atom of a disordered water molecule (K−O distances of 3.08−3.26 Å).

We describe the connectivity through these K^+ clusters as tetrahedral nodes linking four cubes through the vertices. The resulting MOF has the zeolitic **AST** topology and can also be represented by the **flu** net, if the SBB is viewed as an 8-coordinate node.

The same strategy as detailed above also was applied to Cd, Co, In, and Mn to result in similar extended frameworks, **4**−**8**, demonstrating a versatile and readily accessible approach toward construction of ZMOFs based on a variety of octahedrally coordinated metal ions (Supporting Information). In both **1** and **2**, the frameworks consist of one type of cages, namely the **AST**-cage, encapsulated by 6 cubes. The largest sphere that can fit into these cages without touching the van der Waals surfaces of the frameworks has a diameter of ∼15 and ∼12 Å, in **1** and **2**, respectively.

Reaction of $Cd(NO_3)_2 \cdot 4H_2O$ and H_3ImDC in the presence of Na^+ ions results in compound **3**, Figure 3a, formulated as Cd_8Na_8(HImDC)$_8$(ImDC)$_4$(H_2Pip)$_2$(EtOH)$_5$(H_2O)$_{37}$ (Pip = Piperazine, EtOH = Ethanol).[15] In the crystal structure of **3**, Figure 3a,

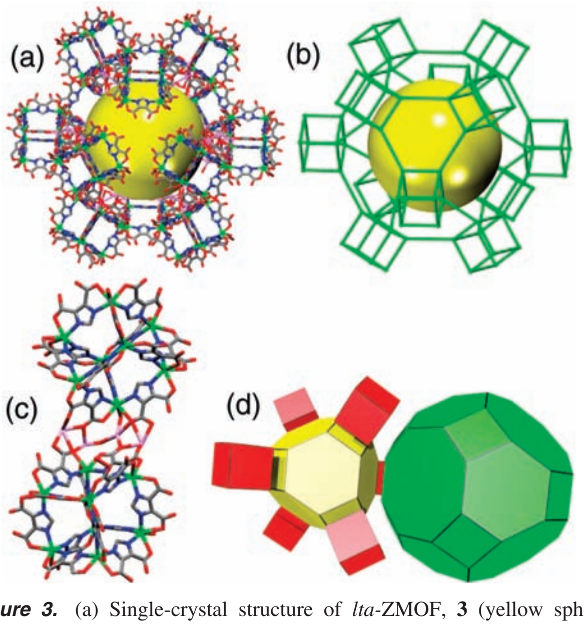

Figure 3. (a) Single-crystal structure of *lta*-ZMOF, **3** (yellow sphere represents vdw sphere), with (b) zeolite **LTA**-*like* network topology. (c) In **3**, 12 MOCs are connected through a series of sodium ions to generate (d) an α-cage (green tile) that can accommodate a sphere with a diameter of ∼32 Å, and 6 MOCs (red tile) assemble into a *β*-cage (yellow tile) that can fit a sphere of ∼8.5 Å in diameter.

each MOC is linked to eight other cubes through linear vertex-to-vertex connections. Half are connected through hydrogen bonded water molecules, and the other four vertices are connected through a series of four sodium atoms, Figure 3b. The framework consists of two types of cages, namely an α-cage encapsulated by 12 cubes and an elliptical *β*-cage enclosed by 6 cubes. The largest sphere that can fit into these cages without touching the van der Waals surface of the framework has a diameter of ~32 Å for the α-cage and ~8.5 Å for the *β*-cage. Topologically, the framework can be viewed as an **LTA**-*like* network or an augmented version of **reo** when the hydrogen-bonded and sodium-bridged vertex−vertex connections are considered. However, the structure can be interpreted as **nbo** if only connections through sodium ions are considered.

Herein, we demonstrate that the utilization of MOPs as SBBs represents an interesting approach toward rational design and synthesis of nanostructures, specifically ZMOFs. MOCs, the MOPs of significance, offer the potential to target and build zeolitic frameworks containing d4Rs. The aforementioned SBBs contain a hierarchy of information regarding the evolution of single-metal ions, with anticipated coordination geometries, deemed as rigid and directional vertices, via heterochelation, into MOPs that can be used as defined highly connected building blocks to yield zeolitic frameworks. Work is in progress to explore the potential of constructed ZMOFs as hosts for molecules with applications in catalysis and/or small molecule sensing. Additionally, we are extending this approach further to construct novel ZMOFs based on the directed assembly of the readily accessible MOCs.

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Supporting Information Available: Experimental details, figures, XRPD, FT-IR, TGA, and X-ray crystallographic data tables. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Eddaoudi, M.; Kim, J.; Wachter, J. B.; Chae, H. K.; O'Keeffe, M.; Yaghi, O. M. *J. Am. Chem. Soc.* **2001**, *123*, 4368–4369. (b) Kitagawa, S.; Kitaura, R.; Noro, S. I. *Angew. Chem., Int. Ed.* **2004**, *43*, 2334–2375. (c) Moulton, B.; Lu, J.; Mondal, A.; Zaworotko, M. *Chem. Commun.* **2001**, 863–864. (d) Yaghi, O. M.; O'Keeffe, M.; Ockwig, N. W.; Chae, H. K.; Eddaoudi, M.; Kim, J. *Nature* **2003**, *423*, 705–714. (e) Stein, A.; Keller, S. W.; Mallouk, T. E. *Science* **1993**, *259*, 1558–1564. (f) Brant, J. A.; Liu, Y.; Sava, D. F.; Beauchamp, D.; Eddaoudi, M. *J. Mol. Struct.* **2006**, *796*, 160–164. (g) Bell, Z. R.; Harding, L. P.; Ward, M. D. *Chem. Commun.* **2003**, 2432–2433. (h) Hong, M.; Zhao, Y.; Su, W.; Cao, R.; Fujita, M.; Zhou, Z.; Chan, A. S. C. *J. Am. Chem. Soc.* **2000**, *122*, 4819–4820. (i) Liu, Y.; Kravtsov, V. C.; Beauchamp, D. A.; Eubank, J. F.; Eddaoudi, M. *J. Am. Chem. Soc.* **2005**, *127*, 7266–7267.

(2) (a) Cairns, A. J.; Perman, J. A.; Wojtas, L.; Kravtsov, V. Ch.; Alkordi, M. H.; Eddaoudi, M.; Zaworotko, M. J. *J. Am. Chem. Soc.* **2008**, *130*, 1560–1561. (b) Nouar, F.; Eubank, J. F.; Bousquet, T.; Wojtas, L.; Zaworotko, M. J.; Eddaoudi, M. *J. Am. Chem. Soc.* **2008**, *130*, 1833–1835.

(3) O'Keeffe, M.; Eddaoudi, M.; Li, H.; Reineke, T.; Yaghi, O. M. *J. Solid State Chem.* **2000**, *152*, 3–20.

(4) Eddaoudi, M.; Moler, D. B.; Li, H.; Chen, B.; Reineke, T. M.; O'Keeffe, M.; Yaghi, O. M. *Acc. Chem. Res.* **2001**, *34*, 319–330.

(5) (a) Delgado-Friedrich, O.; O'Keeffe, M.; Yaghi, O. M. *Acta Crystallogr.* **2006**, *A62*, 350–355. (b) Delgado-Friedrich, O.; O'Keeffe, M.; Yaghi, O. M. *Acta Crystallogr.* **2003**, *A59*, 515–525.

(6) Liu, Y.; Kravtsov, V.; Walsh, R. D.; Poddar, P.; Srikanth, H.; Eddaoudi, M. *Chem. Commun.* **2004**, 2806–2807.

(7) (a) Davis, M. E. *Nature* **2002**, *417*, 813–821. (b) Corma, A.; Davis, M. E. *Chem. Phys. Chem.* **2004**, *5*, 304–313.

(8) (a) Yamamoto, K.; Sakata, Y.; Nohara, Y.; Takahashi, Y.; Tatsumi, T. *Science* **2003**, *300*, 470. (b) Jones, C. W.; Tsuji, K.; Davis, M. E. *Nature* **1998**, *393*, 52. (c) Davis, M. E. *Chem.*−*Eur. J.* **1997**, *3*, 1745–1750.

(9) Ockwig, N. W.; Delgado-Friedrichs, O.; O'Keeffe, M.; Yaghi, O. M. *Acc. Chem. Res.* **2005**, *38*, 176–182.

(10) Liu, Y.; Kravtsov, V. C.; Larsen, R. W.; Eddaoudi, M. *Chem. Commun.* **2006**, 1488–1490.

(11) (a) Database of Zeolite Structures. http://www.iza-structure.org/databases/. (b) Reticular Chemistry Structure Resource (RCSR), http://rcsr.anu.edu.au/home. (c) Baerlocher, Ch.; MeierW. N.; Olson. D. H. *Atlas of Zeolite Framework Types*, 5th revised ed.; Elsevier: Amsterdam, 2001. (d) O'Keeffe, M.; Peskov, M. A.; Ramsden, S. J.; Yaghi, O. M. *Acc. Chem. Res.* **2008**, *30*, 1782–1789.

(12) (a) Russell, V. A.; Etter, M. C.; Ward, M. D. *J. Am. Chem. Soc.* **1994**, *116*, 1941–1952. (b) Holman, K. T.; Pivovar, A. M.; Ward, M. D. *Science* **2001**, *294*, 1907–1911. (c) Videnova-Adrabinska, V.; Obara, E.; Lis, T. *New J. Chem.* **2007**, *31*, 287–295. (d) Abrahams, B.; Haywood, M.; Robson, R. *Polyhedron* **2007**, *26*, 300–304.

(13) Preparation of **1**: A mixture of $Zn(NO_3)_2 \cdot 6H_2O$ (0.2 mmol), H_3ImDC (0.2 mmol), and guanidinium nitrate (0.2 mmol) in 1 mL of DMF and 1 mL of H_2O was prepared. The mixture was then heated to 115 °C for 12 h after which colorless polyhedral crystals were obtained, collected, washed with DMF and ethanol, and then air dried (26.8% yield based on Zn). FT-IR (4000−600 cm^{-1}): 1654 (vs), 1557 (m), 1547 (m), 1471 (s), 1397 (s), 1359 (w), 1255 (m), 1110 (m), 867 (w), 837 (w), 818 (m), 798(w), 669 (vs). Crystal data for **1**: $C_{92}H_{128}N_{56}O_{60}Zn_{12}$, $M_r = 3761.6$, cubic, $Fm\bar{3}$, $a = 25.976(5)$ Å, $V = 17527(5)$ Å^3, $Z = 4$, $D_c = 1.475$ g cm^{-3}, $\mu = 1.650$ mm^{-1}, Final *R* indices ($I > 2\sigma(I)$): $R_1 = 0.0878$, $wR_2 = 0.228$.

(14) Preparation of **2**: A mixture of $Zn(NO_3)_2 \cdot 6H_2O$ (0.2 mmol), H_3ImDC (0.2 mmol), and potassium chloride (0.2 mmol) in 1 mL of DMF and 1 mL of H_2O was prepared. The mixture was then heated to 115 °C for 12 h after which colorless polyhedral crystals were obtained, collected, washed with DMF and ethanol, and then air dried (41% yield based on Zn). FT-IR (4000−600 cm^{-1}): 1664 (m), 1558 (w), 1486 (vs), 1413 (w), 1354 (w), 1303 (m), 1253 (m), 1116 (w), 784 (m), 661 (vs). Crystal data for **2**: $C_{75}H_{83}N_{29}O_{65}Zn_8K_8$, $M_r = 3265.7$, cubic, $Fm\bar{3}$, $a = 23.1553(15)$ Å, $V = 12415.1(14)$ Å^3, $Z = 4$, $D_c = 1.722$ g cm^{-3}, $\mu = 1.893$ mm^{-1}, Final *R* indices ($I > 2\sigma(I)$): $R_1 = 0.0795$, $wR_2 = 0.2277$.

(15) Preparation of **3**: A mixture of H_3ImDC (0.087 mmol), piperazine (0.1 mL, 0.58 M in DMF), sodium hydroxide (0.1 mL, 0.174 M in ethanol), 2,4-pentanedione (0.1 mL, 0.174 M in ethanol), and $Cd(NO_3)_2 \cdot 4H_2O$ (0.0435 mmol) in 1 mL of *N*,*N′*-diethylformamide and 0.25 mL of ethanol were added to a 25 mL scintillation vial, which was then sealed, heated to 85 °C, and cooled to room temperature at a rate of 1 °C min^{-1} to produce colorless, hexagonal prism-like crystals (67% yield based on Cd). FT-IR (4000−600 cm^{-1}): 1650.25 (w), 1622.59 (w), 1548.82 (s), 1484.49 (vs), 1437.5 (s), 1379.16 (s), 1298.34 (m), 1253.75 (m), 1217.09 (w), 1110.98 (m), 997.18 (w), 975.02 (w), 846.39 (w), 786.95 (s), 667.49 (vs), 655.87 (vs), 613.00 (s). Crystal data for **3**: $C_{70.4}H_{46}Cd_8N_{26}Na_8O_{89.72}$, $M_r = 3774.77$, trigonal, $R\bar{3}m$, $a = 40.637(5)$ Å, $c = 39.063(7)$ Å, $V = 55865(13)$ Å^3, $Z = 9$, $D_c = 1.010$ g/cm^3, $\mu = 0.751$ mm^{-1}, Final *R* indices ($I > 2\sigma(I)$): $R_1 = 0.0973$, $wR_2 = 0.2266$.

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