

Supporting Information

Tris(hydroxymethyl)aminomethane Modified Layered Double Hydroxides Largely Facilitate Polyoxometalate Intercalation

*Yang Chen,[†] Dongpeng Yan,[†] and Yu-Fei Song**

State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing 100029, P. R. China.

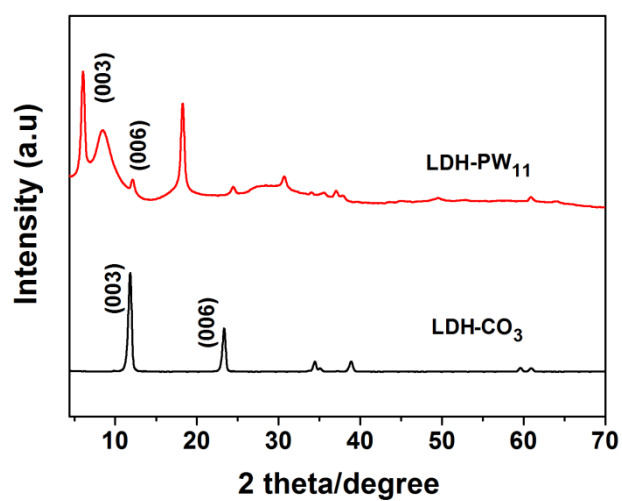


Figure S1. Powder XRD pattern of the LDH-CO₃ and LDH-PW₁₁.

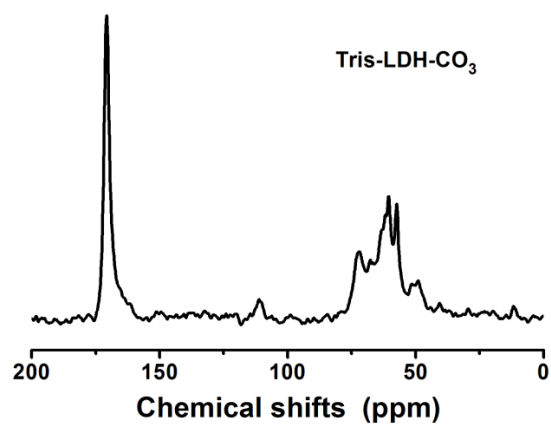


Figure S2. Solid-state ¹³C CP/MAS NMR spectra of Tris-LDH-CO₃.

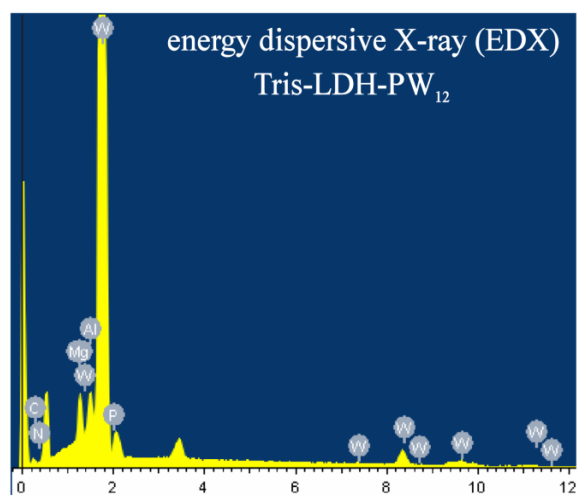


Figure S3. Energy dispersive X-ray (EDX) of Tris-LDH-PW₁₂.

Table S1. Elemental Composition of LDH Samples (mmol/g).

Sample	Mg	Al	W	N
Tris-LDH-CO ₃	7.81	3.86	—	1.13
Tris-LDH-PW ₁₂	1.67	0.74	0.27	0.23

Calculation details and analysis of Tris-LDH-CO₃ and Tris-LDH-PW₁₂.

Building of the structural model of LDH-CO₃, LDH-PW₁₂, Tris-LDH-CO₃ and Tris-LDH-PW₁₂ systems and computational method: An ideal LDH layer (Figure S4b) with R3-m space group containing 17 Mg atoms and 7 Al atoms (Mg/Al ratio of 2.48, close to the experimental value) was built. The lattice parameters of the 2-dimensional layer are $a = b = 3.05 \text{ \AA}$, which is in accordance with other literatures.^[S1] Each octahedral layer has 24 metal atoms and 48 OH groups, and a supercell was constructed with lattice parameter $a = 10.57 \text{ \AA}$, $b = 18.30 \text{ \AA}$, $c = 7.9 \text{ \AA}$ and $10.3 \text{ \AA}$ for LDH-CO₃ and LDH-PW₁₂, respectively; $\alpha = \beta = \gamma = 90^\circ$. The supercell was treated as P1 symmetry, and a three-dimensional periodic boundary condition was applied. For LDH-CO₃, four CO₃ anions were introduced into the simulated LDH supercell; for LDH-PW₁₂, one PW₁₂O₄₀ anion (Figure S4c), two CO₃ anions and one NO₃ anion were introduced into the simulated LDH supercell. As a result, the formula of the simulated structures of LDH-CO₃ and LDH-PW₁₂ can be expressed as: Mg₁₇Al₇(OH)₄₈(CO₃)₃(NO₃), Mg₁₇Al₇(OH)₄₈(PW₁₂O₄₀)(CO₃)₂. For Tris modified LDH layer, one or two tris(hydroxymethyl)aminomethane (Tris) molecules (Figure S4a) was directly anchored onto the LDH layer to form C-O-Mg or C-O-Al covalent bond, and the Tris-LDH-CO₃ and Tris-LDH-PW₁₂ can be expressed as Mg₁₇Al₇(OH)₄₅(C₄H₈NO₃)₁(CO₃)₄, Mg₁₇Al₇(OH)₄₂(C₄H₈NO₃)₂(OH)_{2-3y}(CO₃)₄, and Mg₁₇Al₇(OH)₄₅(C₄H₈NO₃)₁(PW₁₂O₄₀)(CO₃)₂, Mg₁₇Al₇(OH)₄₂(C₄H₈NO₃)₂(PW₁₂O₄₀)(CO₃)₂. All calculations were performed with the periodic density functional theory (DFT) method using Dmol3^[S2a,b] module in Material Studio software package.^[S2c] The initial configuration was first fully optimized with fixed positions for the atoms in the layer by classical molecular mechanics method employed cff91 force field,^[S2d-f] then further optimization was implemented by Perdew-Wang (PW91)^[S2g] generalized gradient approximation (GGA) method with the double numerical basis sets plus polarization function (DNP). The core electrons for metals were treated by effective core potentials (ECP). SCF converged criterion was within 1.0×10^{-5} hartree/atom and converged criterion of structure optimization was 1.0×10^{-3}

hartree/bohr. The Brillouin zone is sampled by $1 \times 1 \times 1$ k -points, and test calculations reveal that the increase of k -points does not affect the results.

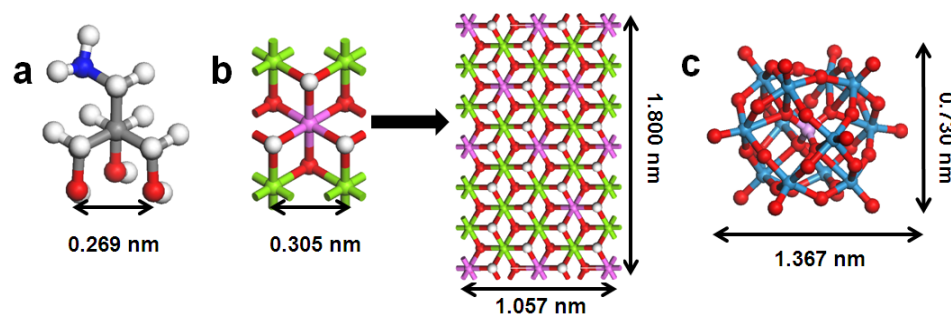


Figure S4. a). the structural model of tris(hydroxymethyl)aminomethane (Tris); b) the tetragonal superlattice model for LDH layer (color codes: white: H; red: O; pink: Al; green: Mg), c). structural model of PW_{12} , $(\text{PW}_{12}\text{O}_{40})^{3-}$.

Table S2. Calculated lattice energy of LDH- CO_3 , Tris-LDH- CO_3 , LDH- PW_{12} , and Tris-LDH- PW_{12} .

Sample	LDH- CO_3	Tris ₁ -LDH- CO_3	Tris ₂ -LDH- CO_3
Energy (hartree)	-9792.4909526	-10039.7048054	-10286.9186582
Sample	LDH- PW_{12}	Tris ₁ -LDH- PW_{12}	Tris ₂ -LDH- PW_{12}
Energy (hartree)	-14268.8953034	-14560.6598780	-14767.1701887

Tris₁-LDH- CO_3 : $\text{Mg}_{17}\text{Al}_7(\text{OH})_{45}(\text{C}_4\text{H}_8\text{NO}_3)_1(\text{CO}_3)_4$; Tris₂-LDH- CO_3 : $\text{Mg}_{17}\text{Al}_7(\text{OH})_{42}(\text{C}_4\text{H}_8\text{NO}_3)_2(\text{OH})_{2-3}(\text{CO}_3)_4$;
Tris₁-LDH- PW_{12} : $\text{Mg}_{17}\text{Al}_7(\text{OH})_{45}(\text{C}_4\text{H}_8\text{NO}_3)_1(\text{PW}_{12}\text{O}_{40})(\text{CO}_3)_2$; Tris₂-LDH- PW_{12} : $\text{Mg}_{17}\text{Al}_7(\text{OH})_{42}(\text{C}_4\text{H}_8\text{NO}_3)_2(\text{PW}_{12}\text{O}_{40})(\text{CO}_3)_2$.

To detect the influences of the different models on the calculation results, a $4 \times 3 \times 1$ Mg-Al-LDH supercell (Figure S5) was further selected to accommodate the pure PW_{12} anions in the absence of intercalated CO_3^{2-} . In this case, a new layer model (denoted as **Model 2**) containing 9 Mg atoms and 3 Al atoms was built as shown in Figure S5 (equivalent to a $4 \times 3 \times 1$ super cell), and one PW_{12} anion with -3 charges can be directly assembled into the LDH without other anions. The formula of three models can be expressed as: $\text{Mg}_9\text{Al}_3(\text{OH})_{24}(\text{PW}_{12}\text{O}_{40})$ (as Pure LDH- PW_{12}), $\text{Mg}_9\text{Al}_3(\text{OH})_{21}(\text{C}_4\text{H}_8\text{NO}_3)(\text{PW}_{12}\text{O}_{40})$ (as Pure Tris₁-LDH- PW_{12}), and $\text{Mg}_9\text{Al}_3(\text{OH})_{18}(\text{C}_4\text{H}_8\text{NO}_3)_2(\text{PW}_{12}\text{O}_{40})$ (as Tris₂-LDH- PW_{12}). All calculations were performed with the same condition in Material Studio software package.

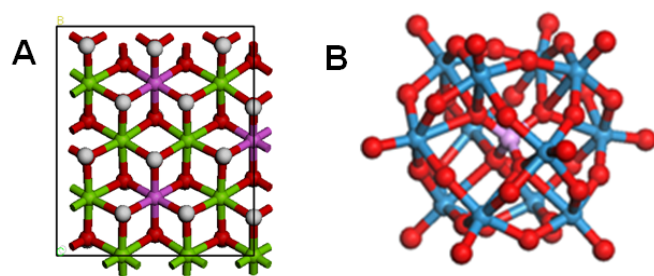


Figure S5. A). The LDH layer (denoted as **model 2**; $4 \times 3 \times 1$ super cell), and B). Structural model of PW_{12} , $(\text{PW}_{12}\text{O}_{40})^{3-}$.

Table S3. Calculated lattice energy of LDH- PW_{12} and Tris-LDH- PW_{12} (**Model 2**)

Sample	Pure LDH- PW_{12}	Pure Tris ₁ -LDH- PW_{12}	Pure Tris ₂ -LDH- PW_{12}
Energy (hartree)	-5951.1860022	-6185.4562903	-6419.3763851

Pure LDH- PW_{12} : $\text{Mg}_9\text{Al}_3(\text{OH})_{24}(\text{PW}_{12}\text{O}_{40})$; Pure Tris₁-LDH- PW_{12} : $\text{Mg}_9\text{Al}_3(\text{OH})_{21}(\text{C}_4\text{H}_8\text{NO}_3)_1(\text{PW}_{12}\text{O}_{40})$;

Pure Tris₂-LDH- PW_{12} : $\text{Mg}_9\text{Al}_3(\text{OH})_{18}(\text{C}_4\text{H}_8\text{NO}_3)_2(\text{PW}_{12}\text{O}_{40})$.

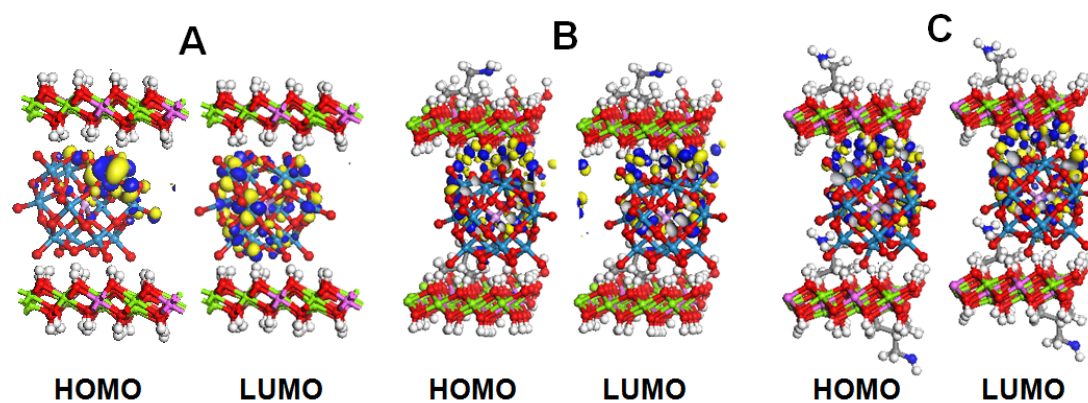


Figure S6. Frontier orbitals (HOMO and LUMO) of the DFT-optimized pure LDH- PW_{12} (A), pure Tris₁-LDH- PW_{12} (B), and pure Tris₂-LDH- PW_{12} (C) structures viewed from [010] direction; the two colors donate +/- wavefunctions.

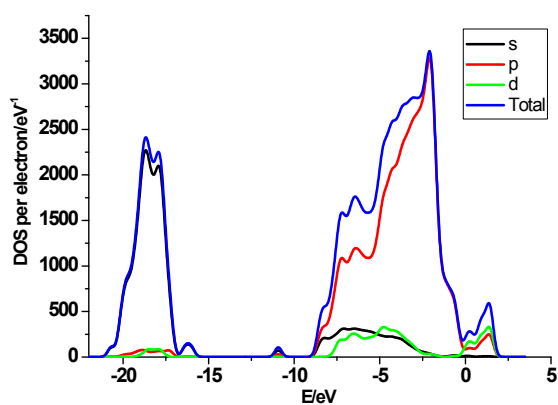


Figure S7. Total electronic densities of states (TDOS) in the LDH-PW₁₂ system. (the Fermi energy level was set as zero).

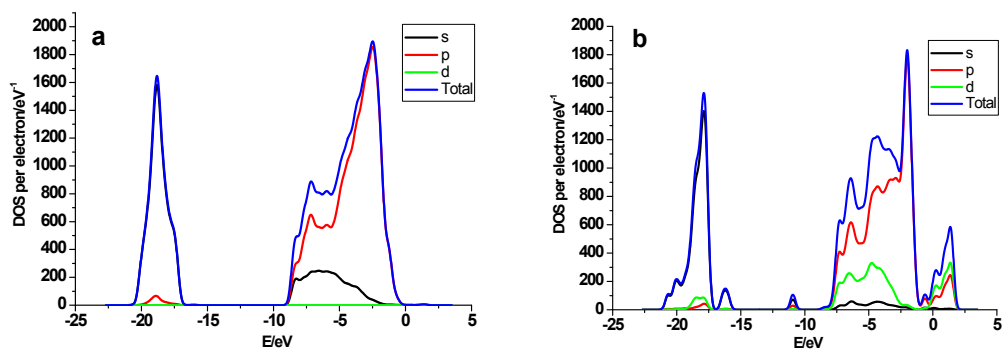


Figure S8. Partial electronic densities of states (PDOS) in the LDH-PW₁₂ system. (the Fermi energy level was set as zero).

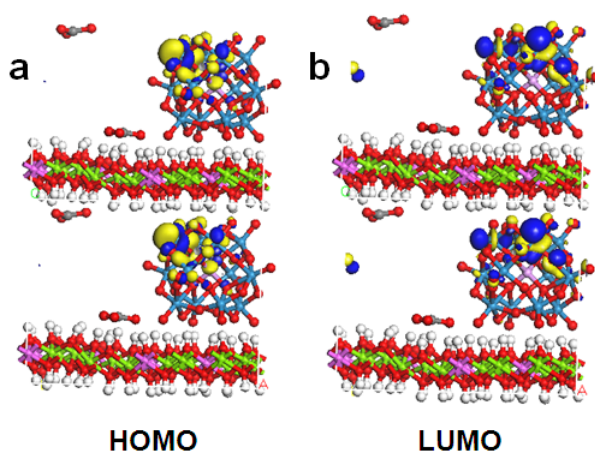


Figure S9. Frontier orbitals (HOMO (a) and LUMO (b)) of the DFT-optimized LDH-PW₁₂ structure viewed from [010] direction; the two colors denote +/- wavefunctions.

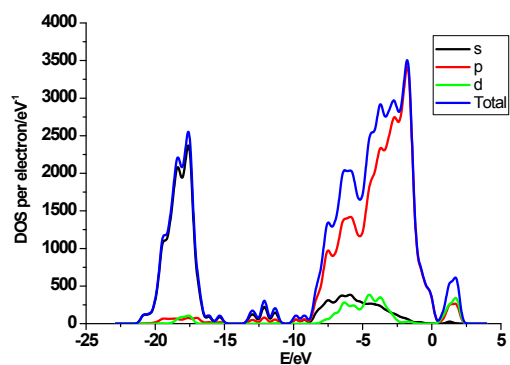


Figure S10. Total electronic densities of states (TDOS) in the Tris-LDH-PW₁₂ system. (the Fermi energy level was set as zero).

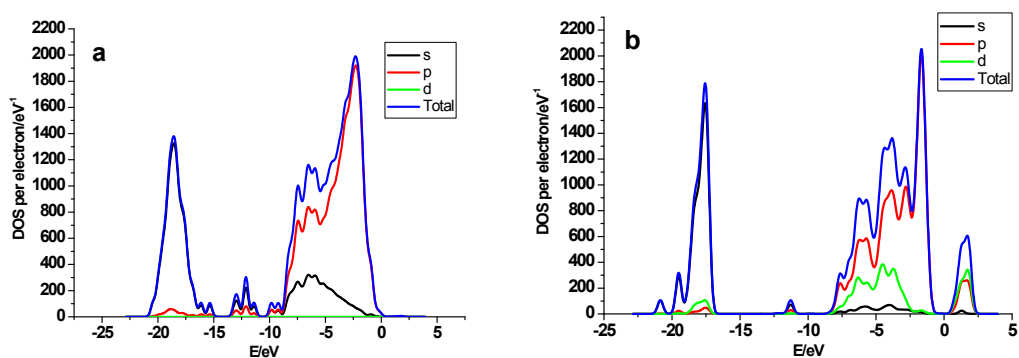


Figure S11. Partial electronic densities of states (PDOS) in the Tris-LDH-PW₁₂ system. (the Fermi energy level was set as zero).

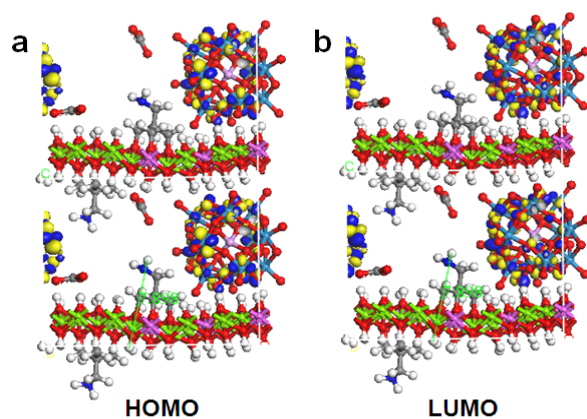


Figure S12. Frontier orbitals (HOMO (a) and LUMO (b)) of the DFT-optimized Tris-LDH-PW₁₂ structure viewed from [010] direction; the two colors donate +/- wavefunctions.

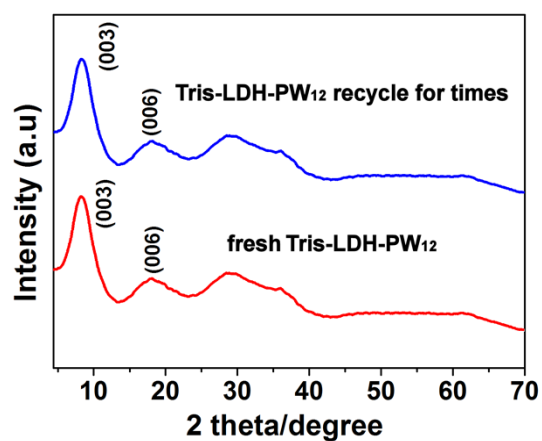


Figure S13. The XRD patterns of the Tris-LDH-PW₁₂ and the recycled Tris-LDH-PW₁₂ for ten times.

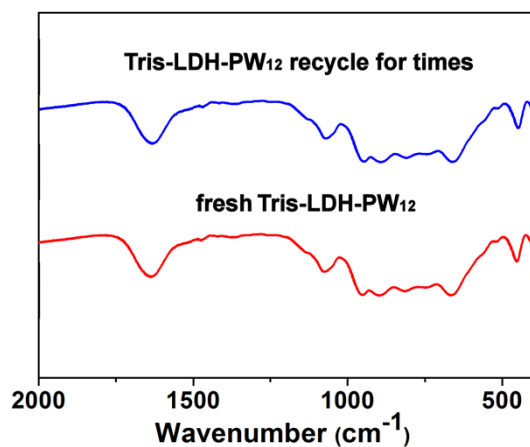


Figure S14. FT-IR spectra of the Tris-LDH-PW₁₂ and the recycled Tris-LDH-PW₁₂ for ten times.

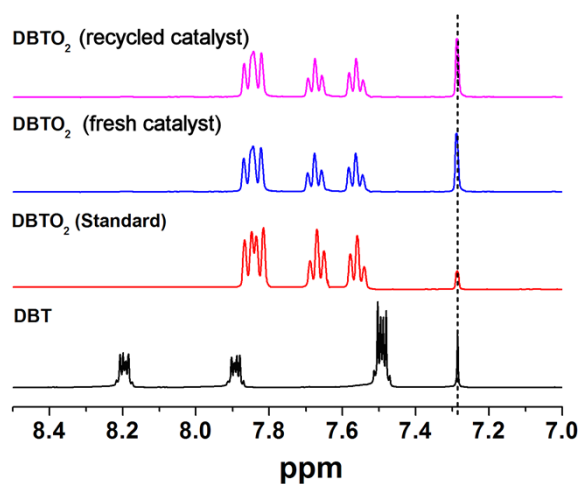


Figure S15. ¹H NMR (CDCl₃) spectra of DBT, DBTO₂ (standard), the oxidative product DBTO₂ (fresh catalyst) and DBTO₂ (the recycled catalyst for ten times).

References

- [S1] D. P. Yan, J. Lu, L. Chen, S. H. Qin, J. Ma, M. Wei, D. G. Evans, X. Duan, *Chem. Commun.*, **2010**, 46, 5912.
- [S2] a) B. Delley, *J. Chem. Phys.* **1990**, *92*, 508. b) B. Delley, *J. Chem. Phys.* **2000**, *113*, 7756. c) *Dmol3 Module, MS Modeling*, Version 2.2; Accelrys Inc.: San, Diego, CA, 2003. d) Maple, J. R.; Hwang, M.-J.; Stockfisch, T. P.; Dinur, U.; Waldman, M.; Ewig, C. S.; Hagler, A. T. *J. Comput. Chem.* **1994**, *15*, 162. e) D. P. Yan, J. Lu, M. Wei, H. Li, J. Ma, F. Li, D. G. Evans, X. Duan, *J. Phys. Chem. A* **2008**, *112*, 7671. f) D. P. Yan, J. Lu, M. Wei, J. B. Han, J. Ma, F. Li, D. G. Evans, X. Duan, *Angew. Chem., Int. Ed.*, 2009, *48*, 3073; g) J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, C. Fiolhais, *Phys. Rev. B* **1992**, *46*, 6671.