Topologically Unique 2D Heterometallic Cu^{II}/Mg Coordination Polymer: Synthesis, Structural Features, and Catalytic Use in Alkane Hydrocarboxylation

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Supporting Information

Supporting Information contains materials and methods, refinement details for single-crystal X-ray analysis, procedure for alkane hydrocarboxylation studies, supporting references, Figures S1−S4 with additional structural representations of **1**, results of thermal analysis (Figure S5, Table S1), and additional catalytic tests (Figure S6, Table S2).

1. Materials and Methods

All synthetic work was performed in air. The reagents and solvents were obtained from commercial sources and used as received. C, H, and N elemental analyses were carried out by the Microanalytical Service of the Instituto Superior Técnico. Infrared spectra ($4000–400$ cm^{-1}) were recorded on a BIO-RAD FTS 3000MX instrument in KBr pellets (abbreviations: vs − very strong, s − strong, m – medium, w – weak, br – broad, sh – shoulder). Differential thermal analysis was run with a Perkin-Elmer STA 6000 Instrument (air atmosphere, 10 ℃/min heating rate, 30−750 ℃ temperature interval). Gas chromatography (GC) analyses were performed on a Fisons Instruments GC 8000 series gas chromatograph with a DB WAX (J&W) capillary column (30 m × 0.25 mm × 0.25 μm; helium carrier gas), and by using Jasco-Borwin v.1.50 software.

2. Refinement Details for Single-crystal X-ray Analysis

The X-ray quality single crystal of **1** was mounted in inert oil within the cold gas stream of the diffractometer. The X-ray diffraction data were collected with a Nonius Kappa CCD diffractometer at 120 K. The Denzo–Scalepack[S1] program package was used for cell refinements and data reduction. The structure was solved by direct methods by using the SIR-97 program.[S2] A multiscan absorption correction based on equivalent reflections (Xprep in SHELXTL v.6.14-1)[S3] was applied to all data. The structure was refined with SHELXL-97[S3] and the WinGX graphical user interface.[S4] Two of the crystallization water molecules were disordered and refined over two positions with occupancies 0.5. The H$_2$O/OH hydrogen atoms were located from the difference Fourier map but constrained to ride on their parent atom, with U_{iso} = 1.5 U_{eq}(parent atom). Other hydrogen atoms were positioned geometrically and were also constrained to ride on their parent atoms, with C−H = 0.95−0.99 Å, and U_{iso} = 1.2 U_{eq}(parent atom). Diamond and TOPOS software packages[S5] were used for structural visualization.

3. Alkane Hydrocarboxylations

In a typical experiment the reaction mixtures were prepared as follows: to 4.0 µmol of the catalyst precursor **1** contained in a 13.0 mL stainless steel autoclave, equipped with a Teflon-coated magnetic stirring bar, were added 1.50 mmol of K$_2$S$_2$O$_8$, 2.0 mL of H$_2$O, 4.0 mL of MeCN (total solvent volume was 6.0 mL), and 1.00 mmol of alkane. Then the autoclave was closed and flushed with CO three times to remove the air, and finally pressurized with 20 atm of CO. The reaction mixture was stirred for 4 h at 60 ℃ using a magnetic stirrer and an oil bath, whereupon it was cooled in an ice bath, degassed, opened, and transferred to a flask. Diethyl ether (9.0 mL) and 90 µL of cycloheptanone (typical GC

17

internal standard) were added. In the case of cycloheptane hydrocarboxylation, cyclohexanone (90 μL) was used as a GC standard. The obtained mixture was vigorously stirred for 10 min, and the organic layer was analyzed by gas chromatography (internal standard method), revealing the formation of the corresponding monocarboxylic acids as the dominant products. In the reactions with cycloalkane substrates, cyclic ketones and alcohols were also formed as by-products of partial alkane oxidation, whereas in the transformations of linear alkanes the generation of the corresponding oxygenates was negligible (their overall yields did not exceed 1.0%).

Blank tests indicated that the hydrocarboxylations also proceed in the metal-free systems,[19] although typically leading to 3−7 times inferior yields of carboxylic acids in comparison with the Cu-catalyzed transformations. The acetonitrile solvent is nonreactive in the present systems, since no generation of acetic or propionic acids from MeCN was detected when the reactions were repeated in the absence of alkane. Furthermore, the alkane hydrocarboxylations do not proceed either in sole H_2O or MeCN solvent.

4. Supporting References

S1 Otwinowski, Z.; Minor, W. *Processing of X-ray Diffraction Data Collected in Oscillation Mode. Methods in Enzymology, Macromolecular Crystallography, Part A* (Eds.: Carter Jr., C. W.; Sweet, M.), Academic Press, New York, **1997**; vol. 276, pp. 307−326.

S2 Altomare, A.; Burla, M. C.; Camalli, M. C.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R. *J. Appl. Crystallogr.* **1999**, *32*, 115.

S3 Sheldrick, G. M. *Acta Crystallogr.* **2008**, *A64*, 112.

S4 Farrugia, L. J. *J. Appl. Crystallogr.* **1999**, *32*, 837.

S5. (a) Brandenburg, K. *Diamond.* Crystal Impact GbR, Bonn, Germany, **2006**. (b) Blatov, V. A. *IUCr CompComm Newsletter*, **2006**, *7*, 4.

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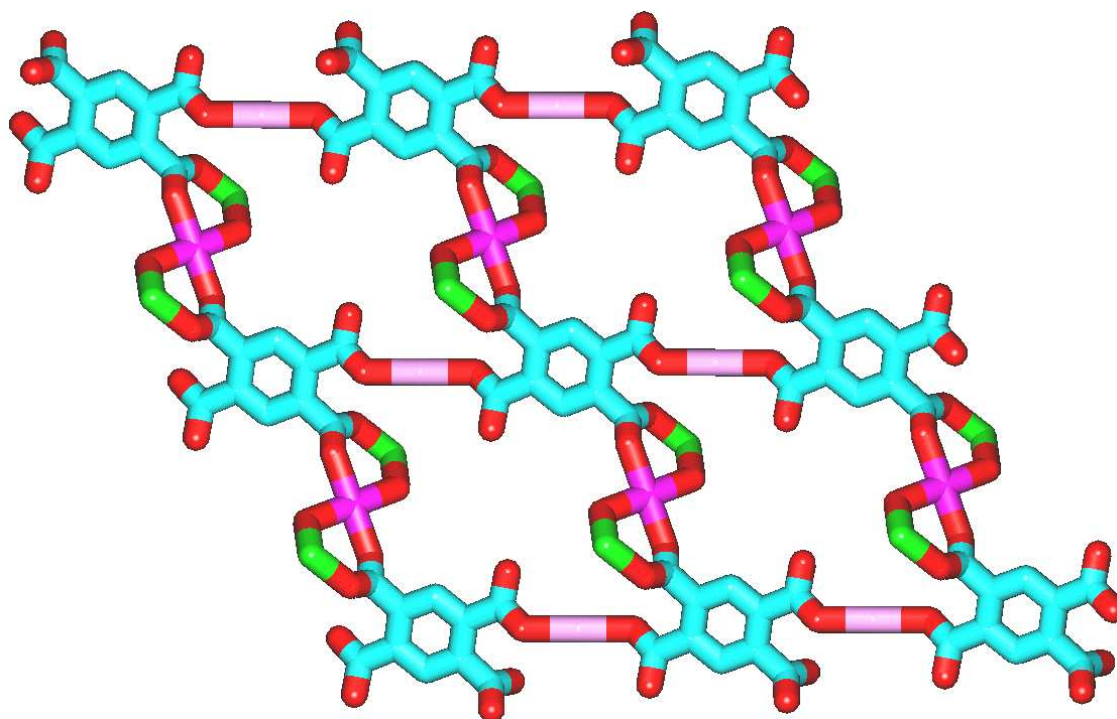## 5. Supporting Figures

Figure S1. Simplified representation of an infinite 2D metal-organic layer in **1** showing its "rhombic grid" network composed of "windows" formed by two Cu_2Mg cores, two Mg2 linkers, and four pma spacers. H atoms, H_2O molecules, and Htea moieties (apart from the O1 atoms) are omitted for clarity. Color codes: Cu (green), Mg1 (magenta), Mg2 (pale pink), O (red), C (cyan).
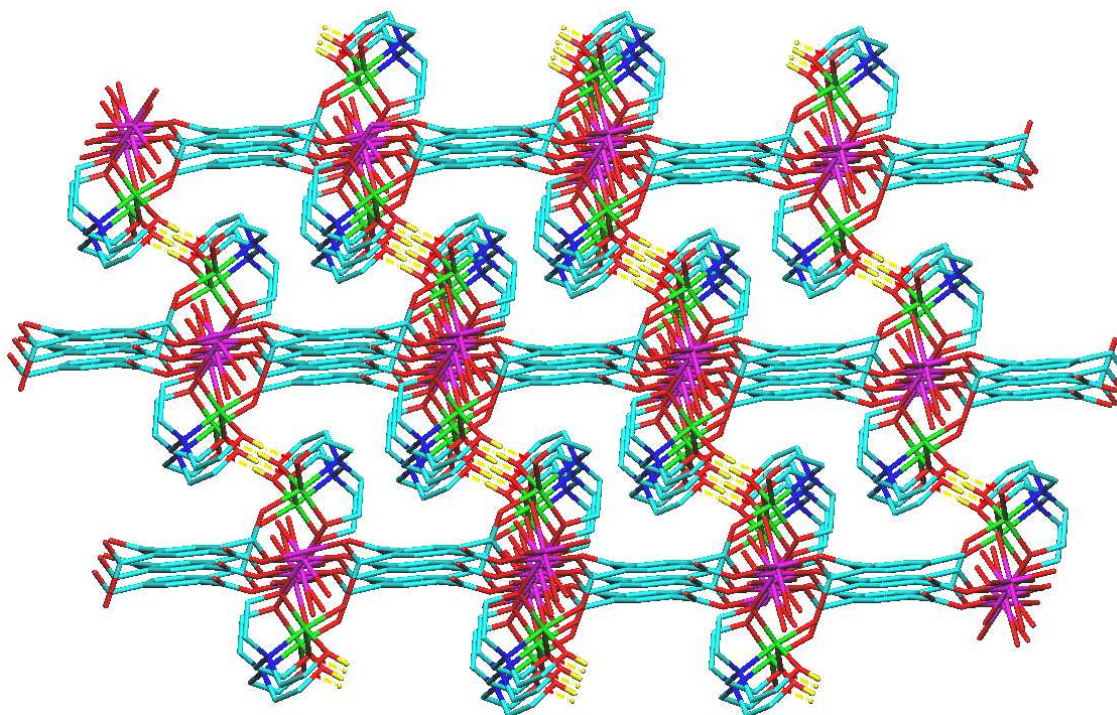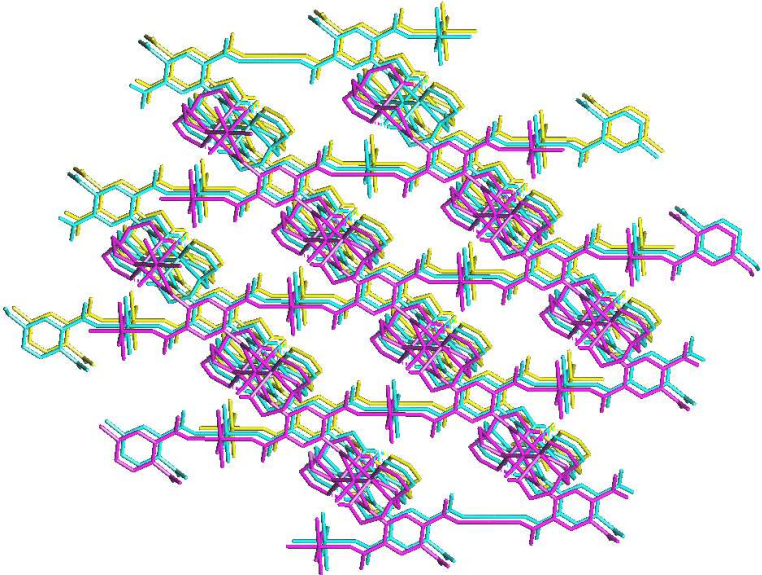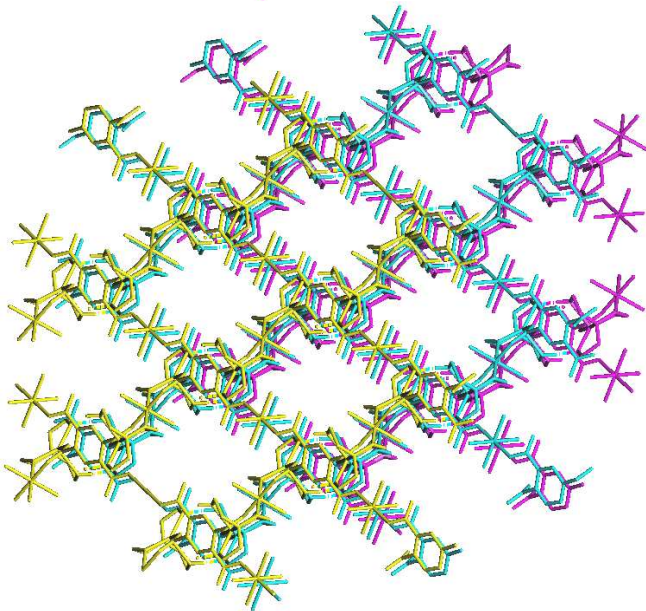

Figure S2. Crystal packing diagram of **1** (rotated view along the *c* axis) showing the relative arrangement (side view) and interdigitation of three adjacent 2D metal-organic layers, as well as their extension (2D→3D) into a 3D supramolecular framework through the multiple interlayer O2−H2O···O3^{vi} [2.520(3) Å, 170.8º] hydrogen bonds (yellow-red dashed lines). H atoms (apart from those of OH groups) and crystallization H_2O molecules are omitted for clarity. Color codes: Cu (green), Mg (magenta), O (red), C (cyan), H (yellow).

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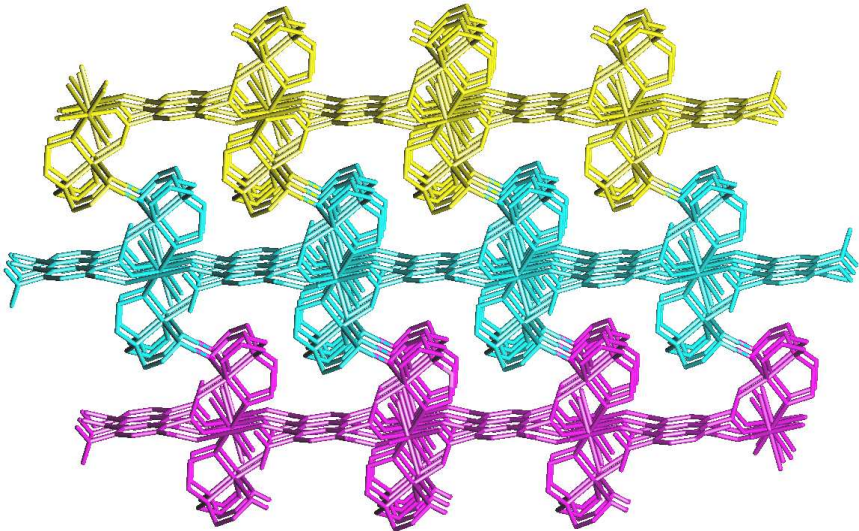51
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(a)

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(c)

Figure S3. Fragments of the crystal packing diagrams of **1** [rotated views along the *a* (a), *b* (b) and *c* (c) axes] showing the relative arrangement of three adjacent 2D metal-organic layers represented by different colors. H atoms (apart from those of OH groups) and crystallization H$_2$O molecules are omitted for clarity.
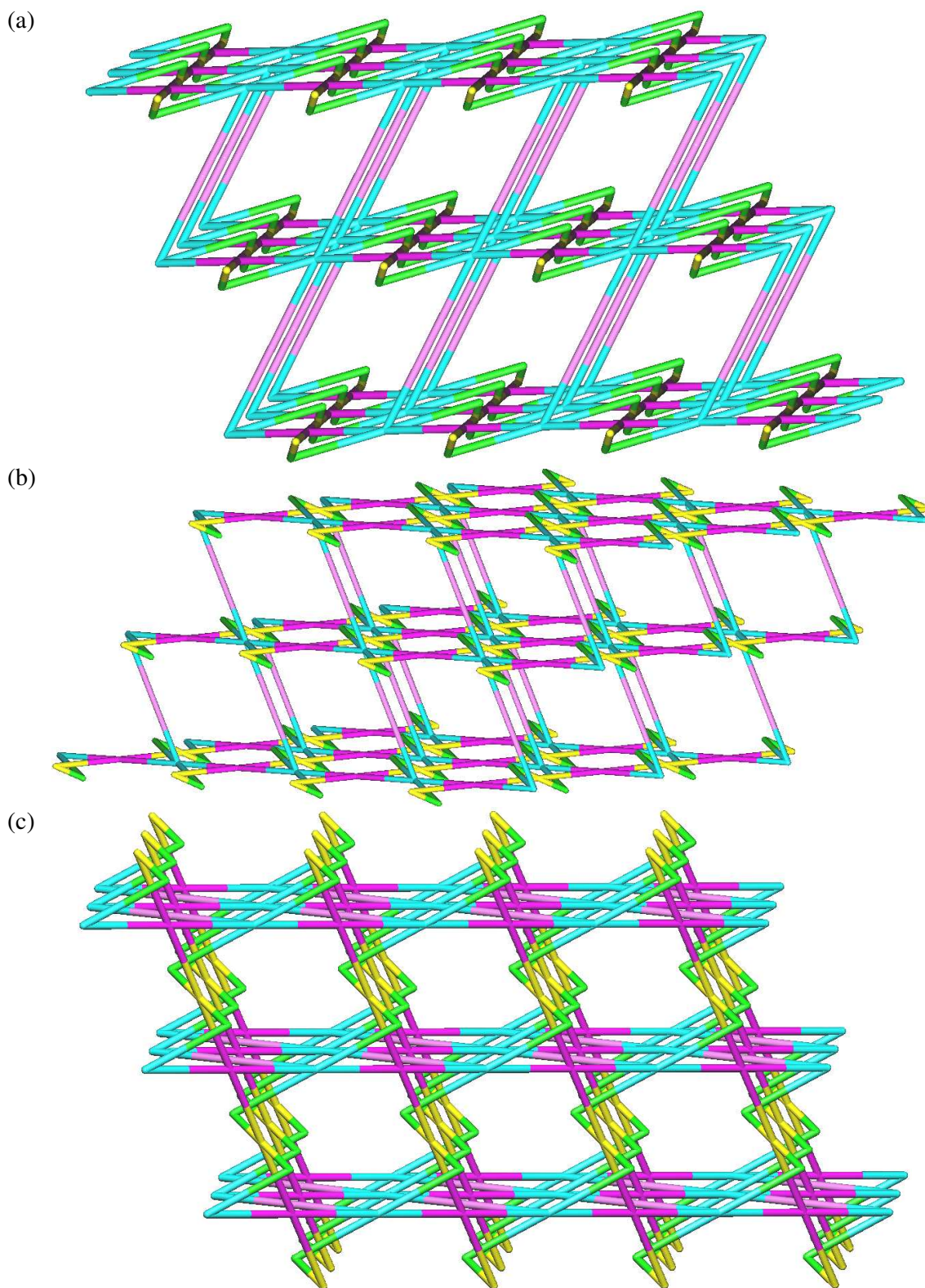
Figure S4. 3D supramolecular framework in **1**: topological representations [rotated views along the *a* (a), *b* (b), and *c* (c) axes] of underlying binodal 4,6-connected net with an unprecedented topology defined by the point symbol of $(3^2.6^{10}.7^2.8)(3^2.6^3.7)_2$. Color codes: centroids of 6-connected pma (cyan) and 4-connected (Htea)$_2$ nodes (yellow), 4-connected Mg1 nodes (magenta), 2-connected Mg2 (pale pink) and Cu1 (green) linkers.
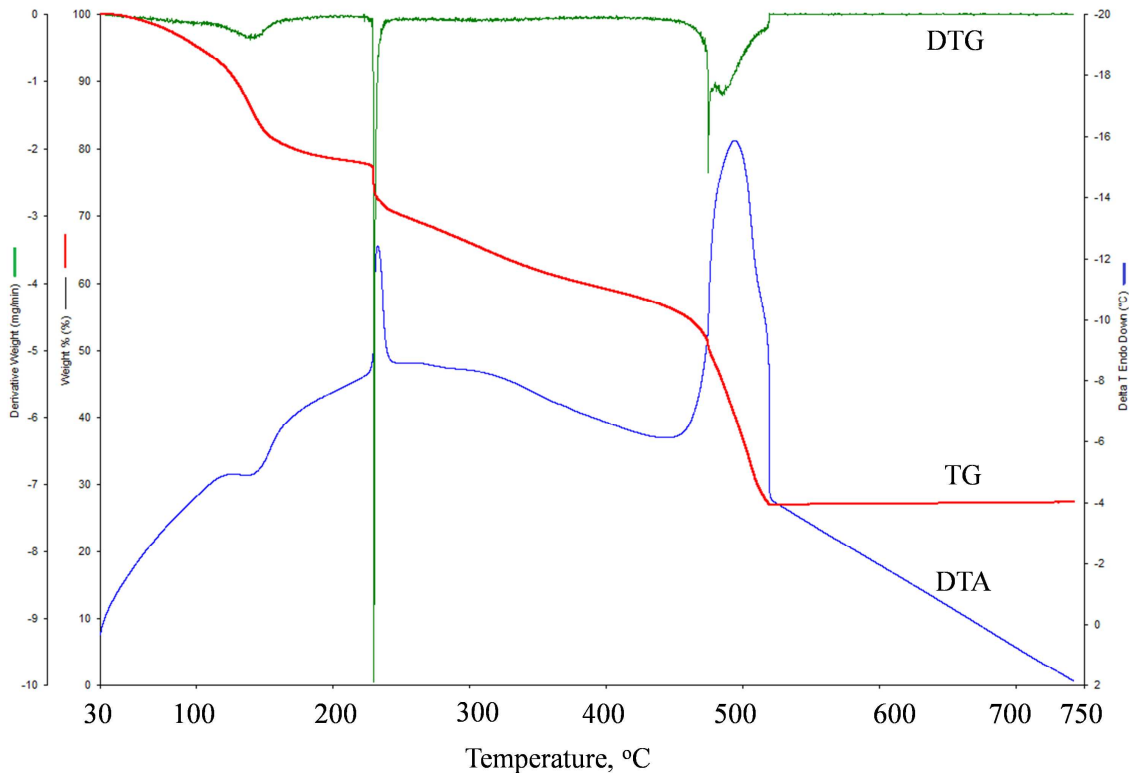
6. Thermal Analysis Data

Figure S5. Differential thermal analysis plots of **1**.

Table S1. Summary of Differential Thermal Analysis of **1**.[a]

Thermal effect	Temperature, °C		Mass loss, % of initial weight
	interval	maximum	
I (endothermic)	30–210	140	22.6 (23.1)[b]
II[c] (exothermic)	210–250	230	31.1
III (exothermic)	250–520	495	74.0 (74.7)[d]

[a] Allocation of thermal effects is based on the DTA curve. [b] Calculated value for elimination of $12H_2O$. [c] Beginning of the multi-step complex decomposition. [d] Calculated value for decomposition until $2CuMgO_2$.
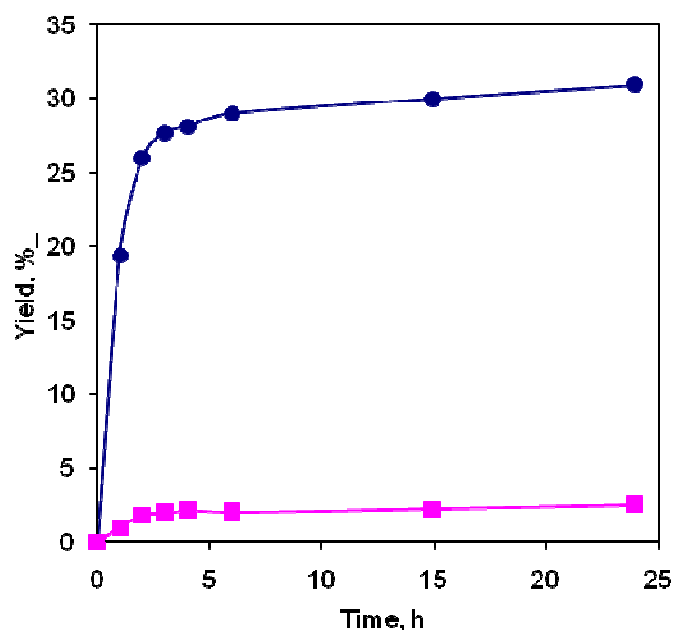
7. Additional Catalytic Data

Figure S5. Accumulation of products over time in the hydrocarboxylation of cyclohexane. Yield of cyclohexanecarboxylic acid – blue circles; total yield of cyclohexanol and cyclohexanone by-products – pink squares. The reaction conditions are those of Table S2.

Table S2. Single-pot Hydrocarboxylation of Cyclohexane Catalyzed by **1**.[a]

Entry	Time, h	Yield of products, %[b]			
		Cyclohexane-carboxylic acid	Cyclohexanol	Cyclohexanone	Total[c]
1	1	19.4	0.5	0.5	20.4
2	2	26.0	0.5	1.3	27.8
3	3	27.7	0.5	1.4	29.6
4	4	28.1	0.6	1.5	30.2
5	6	29.0	0.5	1.5	31.0
6	15	30.0	0.5	1.7	32.2
7	24	30.9	0.5	2.0	33.4

[a]Reaction conditions: cyclohexane (1.0 mmol), $p(CO)$ = 20 atm (1 atm = 0.266 mmol); compound **1** (4.0 µmol); $K_2S_2O_8$ (1.5 mmol). H_2O (2.0 mL)/MeCN (4.0 mL); 60 °C, 13.0 mL autoclave. [b]Moles of product/100 moles of alkane. [c]Yield of all products.