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Cu(II) Coordination Polymers as Vehicles in the A³ Coupling

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Supporting Information

ABSTRACT: A family of benzotriazole based coordination compounds, obtained in two steps and good yields from commercially available materials, formulated as $[Cu^{II}(L^1)_2(MeCN)_2] \cdot 2ClO_4 \cdot MeCN$ (1), $[Cu^{II}(L^1)(NO_3)_2] \cdot MeCN$ (2), $[Zn^{II}(L^1)_2(H_2O)_2] \cdot 2ClO_4 \cdot 2MeCN$ (3), $[Cu^{II}(L^1)_2Cl_2]_2$ (4), $[Cu^{II}_5(L^1)_2Cl_{10}]$ (5), $[Cu^{II}_2(L^1)_4Br_2] \cdot 4MeCN \cdot Cu^{II}_2Br_6$ (6), $[Cu^{II}(L^1)_2(MeCN)_2] \cdot 2BF_4$ (7), $[Cu^{II}(L^1)_2(CF_3SO_3)_2]$ (8), $[Zn^{II}(L^1)_2(MeCN)_2] \cdot 2CF_3SO_3$ (9), $[Cu^{II}_2(L^2)_4(H_2O)_2] \cdot 4CF_3SO_3 \cdot 4Me_2CO$ (10), and $[Cu^{II}_2(L^3)_4(CF_3SO_3)_2] \cdot 2CF_3SO_3 \cdot Me_2CO$ (11), are reported. These air-stable compounds were tested as homogeneous catalysts for the A³ coupling synthesis of propargylamine derivatives from aldehyde, amine, and alkyne under a noninert atmosphere. Fine tuning of the catalyst resulted in a one-dimensional (1D) coordination polymer (CP) (8) with excellent catalytic activity in a wide range of substrates, avoiding any issues that would inhibit its performance.



■ INTRODUCTION

Coordination polymers (CPs) are compounds constructed from metal centers and polytopic organic ligands through coordination bonds, in order to form structures that extend into one, two, or three dimensions.¹ These species have received tremendous attention due to their use in gas sorption,² drug delivery,^{3,4} luminescence,⁵ magnetism,⁶ sensing,⁷ and catalysis.⁸ The last application has been thoroughly studied for porous three-dimensional CPs, also known as metal-organic frameworks (MOFs); however, there is a significant effect on their preparation and handling.⁹ One-dimensional (1D) CPs are typically easy to synthesize and their composition may be easily tuned, via variation of ligand/metal/counterion, in order to optimize their application potential,^{10–12} of which most interestingly their catalytic properties have been scarcely studied.^{13–18}

The metal-catalyzed multicomponent reaction (MCR) of an aldehyde, an amine, and an alkyne, also known as the A³ coupling, has gathered significant interest.^{19–27} This coupling reaction yields propargylamines, which have been proposed as key intermediates in the synthesis of nitrogen-containing biologically active compounds such as acrylamidines,²⁸ oxazoles,^{29,30} pyrroles,³¹ and pyrrolidines³² as well as natural products.^{33,34} Due to this importance, a large variety of metal sources have been employed to catalyze this reaction such as Au(I)/Au(III),^{35–37} Ag(I),^{38–41} Cu(I),^{26,42–45} In(III),⁴⁶ and Rh(III).⁴⁷ More common transition metals, such as Cu-(II),^{48–50} Fe(III),^{51–53} Ni(II),⁵⁴ and Zn(II),⁵⁵ have also been occasionally employed, albeit with higher catalyst loadings and under inert conditions.

Benzotriazole has been extensively used in organic transformations as an auxiliary⁵⁶ or to yield other heterocycles.⁵⁷ More importantly in the context of this work, its derivatives provide enormous coordination versatility in combination with transition-metal ions,⁵⁸ to yield coordination polymers^{59–63} or coordination clusters.^{64,65} Our previous studies focused on the catalytic potential of one- and two-dimensional CPs⁶⁶ and were focused in semirigid benzotriazole-based ligands.^{67,68} As the organic ligand 1,2-bis((1H-benzo[d][1,2,3]triazol-1-yl)methyl)benzene (L¹, Scheme 1) has not been extensively used in coordination chemistry, we recently used it to synthesize three 1D CPs, formulated as $[Cu^{II}(L^1)_2(MeCN)_2]$. $2ClO_4 \cdot MeCN$ (1), $[Cu^{II}(L^1) (NO_3)_2] \cdot MeCN$ (2), and $[Zn^{II}(L^1)_2(H_2O)_2] \cdot 2ClO_4 \cdot 2MeCN$ (3).⁶⁹ Astonishingly, only 1 was found to catalyze the one-pot synthesis of N-substituted dihydropyridines, from azines and ethyl propiolate,⁶⁹ whereas 2 and 3 were catalytically inactive. This great discrepancy in catalytic activity can be explained by the different coordination environments (1 and 2) as well as metal centers (1 and 3). Moreover, the catalytic performance of 1 is inhibited due to its conversion to the catalytically inactive $[Cu^{I}(L^{1})Cl](1')$ species $(ClO_4^-$ is converted to Cl^-), as confirmed by single-crystal Xrav analysis.

Encouraged by our recent study, we decided on further exploring the coordination capabilities of L^1 and its derivatives L^2 and L^3 with other Cu salts to characterize new coordination polymers (Scheme 1) and use them as catalysts toward

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Scheme 1. Organic Ligands (L¹-L³) Used in This Study



chemical transformations of current high interest. The ultimate goal of this research is to establish a library of 1D coordination polymers as catalysts and, by fine-tuning their composition, to be able to optimize their catalytic performance as well as to gain useful mechanistic insights. To the best of our knowledge, 1D Cu(II) CPs have not been employed as catalysts for the A³ coupling so far. Therefore, we report the synthesis and characterization of eight new compounds formulated as $[Cu^{II}(L^1)_2Cl_2]_2$ (4), $[Cu^{II}_5(L^1)_2Cl_1_0]$ (5), $[Cu^{II}_2(L^1)_4Br_2]$. 4MeCN·Cu^{II}_2Br₆ (6), $[Cu^{II}(L^1)_2(MeCN)_2]$ ·2BF₄ (7), $[Cu^{II}(L^1)_2(CF_3SO_3)_2]$ (8), $[Zn^{II}(L^1)_2(MeCN)_2]$ ·2CF₃SO₃ (9) $[Cu^{II}_2(L^3)_4(CF_3SO_3)_2]$ ·2CF₃SO₃·4Me₂CO (10) and $[Cu^{II}_2(L^3)_4(CF_3SO_3)_2]$ ·2CF₃SO₃·Me₂CO (11), as well as the catalytic application of 1–11 in to the A³ coupling reaction among aldehydes, alkynes, and amines yielding the corresponding propargylamine derivatives.

EXPERIMENTAL SECTION

Materials. Chemicals (reagent grade) were purchased from Sigma-Aldrich, Acros Organics, and Alfa Aesar. Materials and solvents were used with no further purification. Ligand L^1 and compounds 1-3 were synthesized according to the reported procedure.⁶⁹ Safety note: perchlorate salts are potentially explosive; such compounds should be used in small quantities and handled with caution and utmost care at all times.

Instrumentation. IR spectra of the samples were recorded over the range of 4000-650 cm⁻¹ on a PerkinElmer Spectrum One FT-IR spectrometer fitted with a UATR polarization accessory. EI-MS was performed on a VG Autospec Fissions instrument (EI at 70 eV). TGA analysis was performed on a TA Instruments Q-50 model (TA, Surrey, U.K.) under nitrogen and at a scan rate of 10 °C/min. NMR spectra were measured on a Varian VNMRS solution-state spectrometer at 30 °C. Chemical shifts are quoted in parts per million (ppm). Coupling constants (J) are recorded in hertz (Hz). UV-vis measurements were performed on a Thermo Scientific Evolution300 UV-vis spectrophotometer, and the collected data were processed using the Vision Pro software. Cyclic voltammetry studies were performed using a BASi-Epsilon potentiostat under computer control. iR drop was compensated using the feedback method. Cyclic voltammetry experiments were performed using a three-electrode configuration with a glassy-carbon disk (7.0 mm^2) as the working electrode, a Pt wire as the counter electrode, and Ag wire as the pseudoreference electrode. Sample solutions were prepared by dissolving the analyte (ca. 5 mM) in DMSO (1 mL) followed by addition of 0.05 M of the supporting electrolyte $[{}^{n}Bu_{4}\dot{N}][PF_{6}]$. The reported half-potentials are referenced to the $FeCp_{2}^{+/0}$ redox couple, which was measured by adding ferrocene (ca. 1 mg) to the sample solution. Magnetic measurements were performed on crushed crystalline samples using a Quantum Design MPMS XL7 SQUID magnetometer.

X-ray Crystallography. Data for compounds 4, 5, and 9 were collected (ω scans) at the University of Sussex using an Agilent Xcalibur Eos Gemini Ultra diffractometer with CCD plate detector under a flow of nitrogen gas at 173(2) K and Cu K α radiation ($\lambda = 1.54184$ Å). CRYSALIS CCD and RED software were used respectively for data collection and processing. Reflection intensities were corrected for absorption by the multiscan method. Data for 6–8 and 10 were collected at the National Crystallography Service,

University of Southampton.⁷⁰ All structures were determined using Olex2,⁷¹ solved using SHELXT,^{72,73} and refined with SHELXL-2014.⁷⁴ All non-H atoms were refined with anisotropic thermal parameters, and H atoms were introduced at calculated positions and allowed to ride on their carrier atoms. Compound 9 is isostructural with 8 (a unit cell comparison is given in the Supporting Information), and its formula was confirmed by ESI-MS, TGA, and CHN analysis. However, it was not possible to refine the lattice OTf molecules with anisotropic parameters; therefore, the SQUEEZE method was applied to remove them. For compound 11, three different crystallographic data sets (University of Sussex, National Crystallography Service, University of Southampton, Diamond Source) confirmed the synthesis of the proposed formula, also suggested from ESI-MS, TGA, and CHN analysis (see the Supporting Information). However, despite producing large block-shaped green crystals, none of these data sets fulfilled the publication criteria and therefore the CIF file is not provided; a figure of the structure showing connectivity is provided in the Supporting Information. Crystal data and structure refinement parameters for newly reported compounds are given in Tables S1 and S2 in the Supporting Information. Geometric/crystallographic calculations were performed using PLATON,75 Olex2,7 and WINGX⁷⁴ packages; graphics were prepared with Crystal Maker and MERCURY.⁷⁶ Each of the crystal structures (4-10) has been deposited at the CCDC as file numbers 1522927-1522931, 1538190, and 1538191.

Synthetic Procedures. General Catalytic Protocol for A^3 Coupling. A mixture of aldehyde (1 mmol), amine (1.1 mmol), alkyne (1.2 mmol), Cu catalyst (2 mol %, based on aldehyde amount), and 2-propanol (5 mL) was placed in a sealed tube and stirred at 90 °C for a selected time. The reaction was monitored by thin-layer chromatography (TLC). After completion, the slurry was filtered upon a short pad of silica (to withhold the catalyst) and the filtrate was evaporated under vacuum. The resulting residue was then loaded into a flash column chromatograph and the product propargylamine was isolated through silica gel using a hexane/EtOAc mixture in a ratio of 10/1 as the eluent.

Synthesis of 1-(2-((5-Methyl-1H-benzo[d][1,2,3]triazol-1-yl)methyl)benzyl)-5-methyl-1H-benzo[d][1,2,3]triazole (L²). 5-Methyl-1H-benzotriazole (2.796 g, 21.0 mmol) was dissolved in acetone (40 mL), and then potassium carbonate (6 g, 43 mmol) and potassium iodide (0.50 g, 3.01 mmol) were added. After the mixture was stirred for 30 min, solid α , α' -dichloro-*o*-xylene (1.75 g, 10.0 mmol) was added slowly. The mixture was refluxed for 5 h. After it was cooled, the solution was filtered and the filtrate was evaporated to dryness. The resulting colorless syrup was then dissolved in 20 mL of methanol, after which a white microcrystalline precipitate was formed. Yield: 33% (1.2 g). Selected IR peaks (cm⁻¹): 2972 (w), 1624 (w), 1501 (m), 1455 (m), 1311 (w), 1278 (m), 1265 (w), 1222 (s), 1163 (w), 1135 (w), 1117 (m), 1103 (m), 1075 (m), 1039 (w), 951 (m), 930 (m), 860 (m), 801 (s), 757 (s), 740 (s), 722 (s), 693 (m), 664 (w), 616 (m). HRMS for C₂₂H₂₁N₆ [M + H]: theor 369.1827 m/z, calcd 369.1822 m/z.

Synthesis of 1-(2-((5,6-Dimethyl-1H-benzo[d][1,2,3]triazol-1-yl)methyl)benzyl)-5,6-dimethyl-1H-benzo[d][1,2,3]triazole (L^3). 5,6-Dimethyl-1H-benzotriazole monohydrate (1.3 g, 8 mmol) was dissolved in acetone (30 mL), and then potassium carbonate (2.2 g, 16 mmol) and potassium iodide (0.50 g, 3.01 mmol) were added. After the mixture was stirred for 30 min, solid α, α' -dichloro-o-xylene (0.65 g, 3.75 mmol) was added slowly. The mixture was refluxed for 5 h. After

Entry	Compound	Coordination Environment	Coordination Mode	Dimensionality		
1	1	N N N N N N S	А	1D		
2	2		А	2D		
3	3	N - N N - N N - N	А	1D		
4	4		В	0D		
5	5		С	2D		
6	6		D	0D		
7	7		А	1D		
8	8		А	1D		
9	9	N, - N N, - N N, - N S	А	1D		
10	10		D	0D		
11	11		D	0D		
mode A		mode B	mode C	mode D		

Table 1. Overview of the Coordination Characteristics (Ligand Conformation, Coordination Geometry of the Metal) of the Compounds Used in This Study (S = Solvent)

it was cooled, the solution was filtered and the filtrate was evaporated to dryness, after which a brown microcrystalline precipitate was formed. Yield: 93% (1.38 g). Selected IR peaks (cm⁻¹): 2974 (w), 1630 (w), 1493 (m), 1449 (m), 1372 (w), 1314 (w), 1284 (m), 1259 (w), 1222 (s), 1158 (w), 1117 (m), 1102 (m), 1070 (m), 1049 (w), 1023 (w), 999 (m), 934 (m), 846 (s), 784 (w), 746 (s), 718 (s), 685 (m), 664 (w), 606 (m). HRMS for $C_{24}H_{25}N_6$ [M + H]: theor 397.2140 *m/z*, calcd 397.2135 *m/z*.

Synthesis of $[Cu^{ll}(L^1)Cl_2]_2$ (4). A 0.12 mmol portion (0.041 g) of L¹ and 0.12 mmol (0.016 g) of anhydrous CuCl₂ were dissolved in 8 mL of MeCN with stirring to produce a yellow solution. After a further 15 min of stirring, the solution was filtered, stored in a glass vessel, and heated at 75 °C for 18 h to produce large green block crystals. Selected IR peaks (cm⁻¹): 1590 (w), 1492 (w), 1455 (m), 1315 (m), 1290 (w), 1235 (w), 1145 (w), 1015 (w), 1006 (w), 952 (m), 900 (w), 778 (m), 770 (m), 729 (s), 661 (m). Yield: 18% (based on Cu). Anal. Calcd for C₄₀H₃₂Cl₄Cu₂N₁₂: C, 50.74; H, 3.41; N, 17.76. Found: C, 50.79; H, 3.46; N, 17.89.

Synthesis of $[Cu^{l}_{5}(L^{1})_{2}Cl_{10}]$ (5). A 0.12 mmol portion (0.041 g) of L¹ and 0.36 mmol (0.048 g) of anhydrous CuCl₂ were dissolved in 8 mL of MeCN with stirring to produce a yellow solution. After a further 15 min of stirring, the solution was filtered, stored in a glass vessel, and heated at 95 °C for 18 h to produce good-quality brown block crystals.

Selected IR peaks (cm⁻¹): 1589 (w), 1492 (w), 1452 (m), 1370 (w), 1331 (m), 1313 (w), 1278 (w), 1231 (m), 1165 (w), 1144 (w), 1002 (w), 970 (w), 961 (w), 841(w), 792 (w), 779 (w), 752 (m), 738 (s), 711 (m), 668 (m). Yield: 33% (based on Cu). Anal. Calcd for $C_{40}H_{32}Cl_{10}Cu_5N_{12}$: C, 35.70; H, 2.40; N, 12.50. Found: C, 35.59; H, 2.46; N, 12.43.

Synthesis of $[Cu^{l}_{2}(L^{1})_{4}Br_{2}]$ ·4MeCN· $Cu^{l}_{2}Br_{6}$ (6). Anhydrous CuBr₂ was used as the metal salt in a procedure similar to the synthesis of 4. The resultant dark green solution was stored in a vial at room temperature. Small green crystals were obtained after 3 days. Selected IR peaks (cm⁻¹): 1594 (w), 1494 (s), 1456 (m), 1321 (w), 1283 (w), 1233 (m), 1167 (m), 1144 (m), 1002 (w), 966 (w), 843 (w), 789 (m), 736 (s), 670 (w), 628 (m). Yield: 11% (based on Cu). Anal. Calcd for C₈₈H₇₆Br₈Cu₄N₂₈: C, 43.69; H, 3.17; N, 16.21. Found: C, 43.81; H, 3.13; N, 16.11.

Synthesis of $[Cu^{ll}(L^1)_2(MeCN)_2]\cdot 2BF_4$ (7). A 0.24 mmol portion (0.082 g) of L¹ was dissolved in 10 mL of MeCN with stirring to produce a colorless solution. A solution containing 0.48 mmol (0.170 g) of Cu(BF_4)_2.6H_2O in MeCN (7.5 mL) was slowly added. The resulting green solution was filtered and stored at room temperature. Green block crystals were obtained after 1 day. Selected IR peaks (cm⁻¹): 3468 (w), 3508 (w), 1651 (w), 1592 (w), 1495 (w), 1454 (m), 1320 (m), 1282 (m), 1234 (m), 1172 (m), 1159 (w), 1060 (s),

1017 (s), 969 (m), 953 (w), 853 (w), 793 (w), 780 (m), 757 (s), 748 (s), 739 (s), 672 (w). Yield: 49% (based on Cu). Anal. Calcd for $C_{44}H_{38}B_2CuF_8N_{14}$: C, 52.84; H, 3.83; N, 19.62. Found: C, 52.92; H, 3.86; N, 19.70.

Synthesis of $[Cu^µ(L¹)_2(CF_3SO_3)_2]$ (8). A 0.24 mmol portion (0.082 g) of L¹ and 0.48 mmol (0.180 g) of Cu(OTf)₂·H₂O were dissolved in 15 mL of Me₂CO with stirring to produce a dark green solution. After it was stirred for 1 h, the solution was filtered and then layered over *n*-hexane in a 1/2 ratio to produce large blue block crystals after 7 days. Selected IR peaks (cm⁻¹): 1589 (w), 1492 (w), 1457 (m), 1320 (m), 1275 (m), 1244 (m), 1163 (w), 1140 (m), 1023 (s), 952 (w), 848 (w), 779 (m), 746 (s), 669 (m). Yield: 11% (based on Cu). Anal. Calcd for C₄₂H₃₂CuF₆N₁₂O₆S₂: C, 48.41; H, 3.10; N, 16.14. Found: C, 48.53; H, 3.04; N, 16.07.

Synthesis of $[Zn^{ll}(L^1)_2(MeCN)_2] \cdot 2CF_3SO_3$ (9). A 0.24 mmol portion (0.082 g) of L¹ was dissolved in 15 mL of MeCN with stirring to produce a colorless solution. A 0.12 mmol portion (0.044 g) of $Zn(OTf)_2$ was then added. After it was stirred for a further 30 min, the resulting colorless solution was filtered and then layered over Et₂O in a 1/2 ratio. Large colorless block crystals were obtained after 2 weeks. Selected IR peaks (cm⁻¹): 3434 (br), 1654(w), 1592 (w), 1494 (w), 1456 (m), 1372 (w), 1319 (m), 1269 (m), 1226 (s), 1153 (m), 1094 (w), 1025 (s), 951 (w), 880 (w), 843 (w), 766 (w), 740 (s), 714 (w), 669 (m). Yield: 38% (based on Zn). Anal. Calcd for C₄₆H₃₈F₆N₁₄O₆S₂Zn: C, 49.04; H, 3.40; N, 17.42. Found: C, 49.11; H, 3.53; N, 17.38.

Synthesis of $[Cu^{l}_{2}(L^{2})_{4}(H_{2}O)_{2}]\cdot 4CF_{3}SO_{3}\cdot 4Me_{2}CO$ (10). A 0.1 mmol portion (0.036 g) of L² and 0.1 mmol (0.037 g) of $Cu(OTf)_{2}\cdot H_{2}O$ were dissolved in 15 mL of acetone with stirring to produce a turquoise solution. The solution was filtered and then layered over *n*-hexane in a 1/2 ratio to produce green needlelike crystals after a few hours. Selected IR peaks (cm⁻¹): 1592 (w), 1504 (w), 1457 (m), 1279 (m), 1223 (s), 1158 (m), 1027 (s), 868 (w), 805 (m), 758 (w), 721 (w), 636 (s). Yield: 23% (based on Cu). Anal. Calcd for $C_{104}H_{108}Cu_{2}F_{12}N_{24}O_{18}S_{4}$: C, 50.65; H, 4.42; N, 13.64. Found: C, 50.73; H, 4.36; N, 13.63.

Synthesis of $[Cu^{II}_{2}(L^{3}_{4}(CF_{3}SO_{3})_{2}]\cdot 2CF_{3}SO_{3}\cdot Me_{2}CO$ (11). A 0.12 mmol portion (0.048 g) of L³ and 0.24 mmol (0.089 g) of Cu(OTf)₂· H₂O were dissolved in 15 mL of acetone with stirring to produce a dark green solution. The solution was filtered and then layered over *n*-hexane in a 1/2 ratio to produce small green block crystals after 10 days. Selected IR peaks (cm⁻¹): 3436 (br), 1707 (w), 1631 (w), 1590 (w), 1559 (w), 1494 (w), 1456 (m), 1252 (m), 1235 (s), 1221 (s), 1153 (m), 1026 (s), 1003 (m), 965 (w), 901 (w), 845 (m), 785 (w), 748 (m). Yield: 10% (based on Cu). Anal. Calcd for C₁₀₃H₁₀₂Cu₂F₁₂N₂₄O₁₃S₄: C, 52.25; H, 4.35; N, 14.21. Found: C, 52.33; H, 4.41; N, 14.34.

RESULTS

Synthetic Aspects. A crystalline material was obtained through a variety of techniques: leaving the sample undisturbed at room temperature (1, 3, 6, 7), solvothermal conditions (4, 5), or liquid diffusion (2, 8-11). All reactions, with the exception of compounds 4 and 5, are not sensitive to the Cu(II):L molar ratio; ratios from 3:1 to 1:3 yield the same compound in comparable yields and purity. In the case of 4 and 5, the final product depends on the appropriate ratio of starting materials (1:1 and 3:1, respectively) and temperature (75 and 95 °C, respectively). The metal center (Cu(II) or Zn(II)) is not coordinated to the N2 nitrogen atom of the benzotriazole molecules in any of the compounds; this may be attributed to the steric effects of the bulky CH2-C6H4-CH2 unit. All compounds are soluble in DMF and slightly soluble in other common organic solvents (e.g., acetonitrile, methanol, and THF); their solubility in these solvents increases greatly on heating. However, they are insoluble in water.

Crystal Structure Description. The crystal structures of 1-3 were recently reported; however, they will be described in detail to facilitate discussion and comparison with compounds 4-11.

Compound 1 crystallizes in the triclinic space group $P\overline{1}$ and contains one molecule in the asymmetric unit. The unit consists of a Cu(II) center, one organic ligand molecule, a perchlorate lattice anion, and two acetonitrile solvent molecules, out of which one acts as a terminal ligand and one is in the lattice; the latter will not be further discussed. In this conformation of the ligand (Table 1, mode A), the angle between the planes of the benzotriazole molecules is $123.00(5)^\circ$. As a result, the structure extends to one dimension along the *a* axis, forming a 1D framework with small voids (Figure 1). Cu(II) is coordinated



Figure 1. (top) Asymmetric unit of **1**. H atoms are omitted for clarity. (bottom) Part of the one-dimensional framework of **1**. H atoms, certain perchlorate anions, and solvent molecules are omitted for clarity. Color code: Cu (blue), C (black), N (light blue), Cl (green), O (red).

to six nitrogen atoms and possesses a distorted-octahedral geometry, in which the axial positions are occupied by the acetonitrile nitrogen atoms. The relevant N–Cu–N bond angles range from 87.02(7) to 92.98(7)°. As for the relevant bond lengths, the mean Cu– N_{ligand} distances are 2.0815(16) and 2.0133(17) Å, significantly shorter than the respective Cu– $N_{acetonitrile}$ distance, which was measured at 2.422(2) Å. No strong hydrogen bonds or other supramolecular interactions are observed. Additionally, compounds 3, 7, and 9 were found to be isostructural with 1; in 7 (Figure S3 in the Supporting

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Figure 2. Part of the two-dimensional framework of 2. H atoms are omitted for clarity. Color code: Cu (blue), C (black), N (light blue), O (red).

Information) the counteranion is BF_4^- instead of ClO_4^- . 3 was synthesized using $Zn(ClO_4)_2 \cdot 6H_2O$ and shows an identical 1D framework; however, the two coordinating acetonitrile moieties are replaced by H_2O molecules (Figure S2 in the Supporting Information). 9 is another Zn(II) compound that is a similar 1D CP and contains $CF_3SO_3^-$ anions in the lattice (Figure S4 in the Supporting Information). As a result, these structures will not be described further.

In compound 2 the complex crystallizes in the monoclinic $P2_1/n$ space group. Its asymmetric unit consists of a Cu(II) center, one organic ligand molecule, two nitrate anions, and one acetonitrile solvent molecule (Figure S1 in the Supporting Information). The coordination mode of the ligand is the same as the mode in 1 (Table 1, mode A). The presence of the chelating and bridging nitrate moieties leads to the formation of an unusual dimeric Cu₂ unit, as the structure extends in two dimensions along the b0c plane (Figure 2). A search of the Cambridge Structure Database⁷⁷ reveals no other example of a Cu₂ unit based on nitrates. The metal center has a coordination environment of $\{N_2O_5\}$ and possesses a pseudo-octahedral geometry; five nitrate oxygen atoms occupy the equatorial positions of the pseudo-octahedron, while two nitrogen atoms from ligand molecules occupy the axial positions. The mean Cu-N distances are 1.9849(6) and 1.9916(6) Å, while the Cu-O distances range from 1.9813(6) to 2.6587(6) Å. The relevant N-Cu-O bond angles range from 85.32(4) to 95.66(4)°.

Compound 4 crystallizes in the triclinic $P\overline{1}$ space group and consists of two $[Cu_2L_2Cl_4]$ units. All metal centers in the structure show a distorted trigonal bipyramidal geometry through a coordination environment of $\{N_2Cl_3\}$ ($\tau = 0.46$ for Cu1, 0.40 for Cu2).⁷⁸ The basal plane in the geometries of both metal centers consists of chloride atoms, while ligand nitrogen atoms are in the axial positions. These units are not further linked through intermolecular interactions, and each ligand adopts a syn conformation regarding the position of the benzotriazole groups (Table 1, mode B). This accounts for the eventual formation of zero-dimensional dimeric units (Figure 3, top). The mean Cu–N distances are 2.015(4) and 2.028(4) Å. Cl–Cu–Cl bond angles range from 93.65(4) to 154.33(6)°,



Figure 3. Structures of compounds **4** (zero-dimensional dimer, top) and **5** (two-dimensional framework, bottom). H atoms are omitted for clarity. Color code: Cu (blue), C (black), N (light blue), Cl (green).

while the respective values for the N–Cu–N angles are 177.47(17) and $178.44(17)^{\circ}$.

Compound **5** also crystallizes in the triclinic $P\overline{I}$ space group. However, in this case the asymmetric unit contains two fulloccupancy and one half-occupancy Cu(II) centers, as well as one ligand molecule and five chlorine atoms. Two of the metal centers (Cu2, Cu3) are coordinated to the ligand and to chlorine atoms, while the third (Cu1) is only coordinated to chlorine atoms and bridges the $[Cu_2L_2]$ nodes. The ligand adopts the same conformation as in mode A, but a different coordination mode (Table 1, mode C). All of the above lead to the formation of an unusual two-dimensional coordination polymer which extends along the a0c plane, as shown in Figure 3 (bottom). The coordination environment and geometries of the metal centers are also varied. Cu1 is coordinated to five chlorine atoms and exhibits a distorted-square-pyramidal geometry ($\tau = 0.15$).⁷⁸ The basal plane in this geometry has a mean deviation of 0.129 Å. Cu2 is also coordinated to five atoms and possesses a distorted-square-pyramidal geometry (τ = 0.09;⁷⁸ however, in this case the basal plane consists of three chlorine atoms and one ligand nitrogen atom, while the axial position is occupied by another ligand nitrogen atom, resulting in a $\{N_2Cl_3\}$ coordination environment. In this case, the respective plane has a deviation of 0.151 Å. Finally, Cu3 shows a $\{N_2Cl_4\}$ coordination environment, consistent with an octahedral geometry, in which the ligand nitrogen atoms occupy the axial positions while chlorine atoms form the basal plane. The mean Cu–Cl bond distances range from 2.2671(12) to 2.6348(10) Å, while the respective Cu-N bond lengths range from 2.016(3) to 2.425(3) Å.

Compound **6** was synthesized using CuBr_2 and crystallizes in the monoclinic C2/c space group. The main core of the structure consists of a $[\text{Cu}_2\text{L}_4\text{Br}_2]^{2+}$ dicationic dimer. A dianionic $[\text{Cu}_2\text{Br}_6]^{2-}$ unit is also present and completes the charge balance for all Cu(II) centers. In a fashion similar to that for **4**, this dimer does not form any intermolecular interactions and thus the structure is zero-dimensional (Figure 4). In this



Figure 4. Structure of compound 6. H atoms and solvent molecules are omitted for clarity. Color code: Cu (blue), C (black), N (light blue), Br (brown).

case the angle between the planes of the benzotriazole molecules of the ligand was measured at 125.4(4)°, similar to that in mode A. However, a concurrent rotation of the nonrigid C–N bond is also observed, leading to a different conformation mode (Table 1, mode D). The metal center that shows ligand coordination (Cu1) possesses a distorted-trigonal-bipyramidal ($\tau = 0.65$)⁷⁸ geometry through a {N₄Br} environment. The bromine atom and two nitrogen atoms from ligand molecules constitute the basal plane, with the relevant angles ranging from 102.2(5) to 139.0(3)°. The two remaining nitrogen atoms are

also derived from ligand molecules and occupy the axial positions of the bipyramid.

Compound 8 crystallizes in the triclinic $P\overline{1}$ space group, and its asymmetric unit contains a Cu(II) center, one organic ligand molecule, and one triflate anion molecule. The metal center is coordinated to a total of six atoms and possesses an octahedral geometry through a $\{N_4O_2\}$ coordination environment. The complex shows a one-dimensional framework identical with that of compounds 1, 3, 7, and 9; the only difference is that the axial positions of the octahedron are now occupied by triflate oxygen atoms instead of acetonitrile nitrogen (Figure 5).



Figure 5. Part of the one-dimensional framework of **8**. H atoms are omitted for clarity. Color code: Cu (blue), C (black), N (light blue), O (red), S (yellow), F (light green).

Consequently, the ligand adopts the same coordination mode as in the aforementioned compounds (mode A). The mean Cu–O distance was measured at 2.536(4) Å, while the Cu–N bond lengths are 2.009(5) and 2.013(7) Å. No strong hydrogen bonds or other supramolecular interactions are observed.

Compound 10 was prepared using L^2 and crystallizes in the monoclinic C2/c space group. The structure is similar to that of compound 6, as it contains a dicationic dimer, $[Cu_2L_4(H_2O)_2]^{2+}$, as the main core. Four triflate anions are present in the lattice to complete the charge balance for all metal centers. As a result, the structure is zero-dimensional (Figure 6) and the dimer is further stabilized through the formation of two strong O-H…O hydrogen bonds, each formed between a water molecule and a triflate anion. The L² ligand behaves similarly to L^1 in the case of compound 6, adopting the same conformation and coordination mode (Table 1, mode D). Each metal center shows a $\{N_4O\}$ coordination environment through four ligand nitrogen atoms and one oxygen atom from the water molecule, possessing a distorted-square-pyramidal ($\tau = 0.29$)⁷⁸ geometry. The basal plane of this pyramid consists of three nitrogen atoms and one oxygen and shows a mean deviation of 0.149 Å. Compound 11 may be considered as isoskeletal with 10, as it contains a similar dimeric core; in this case the two coordinating water molecules are replaced by triflate anions (Figure S5 in the Supporting Information). Due to the similarities, the resulting zerodimensional structure will not be described further.

Characterization of Compounds 1–11. Magnetic measurements for 1 and 2 in the solid state are consistent with octahedral S = 1/2 Cu(II) centers with $g \approx 2.2$. For 1 there are negligible interactions along the chain (Figure S6 in the Supporting Information), while for 2 we observe a weak short-range ferromagnetic exchange within the dimeric repeat unit of ca. 1 cm⁻¹ (Figure S7 in the Supporting Information).



Figure 6. Structure of compound **10**. Lattice solvent molecules, lattice anions, and certain H atoms are omitted for clarity. Color code: Cu (blue), C (black), N (light blue), O (red), H (light pink).

Furthermore, given that the compounds are soluble in most common organic solvents, a range of techniques was used to determine their behavior in solution. ESI-MS (positive-ion mode) in methanolic solution for all Cu(II) complexes (1, 2, 4-8, 10, 11) reveals two main peaks which perfectly correspond to the respective $[Cu(L)]^+$ and $[Cu(L)_2]^+$ fragments. Additional peaks are also observed in each spectrum, and the main peaks correspond perfectly to metal-ligand-anion fragments. The most common fragments found were [Cu(L)- $X^{+}_{,}$ [Cu₂(L)X]⁺, [Cu(L)₂X]⁺, [Cu(L)₃X]⁺, where X is the anion present in each compound. Similar fragments were obtained for the Zn(II) compounds (3 and 9). ESI-MS spectra, along with a detailed analysis of the fragments, are presented in Figures S8-S18 in the Supporting Information. These results indicated that the CPs of this study could retain their polymeric structure in solution. To further clarify this, the same method was applied to a DMF solution of 1, given that generally DMF molecules can easily coordinate to the metal center. Indeed, the mass spectrum showed peaks identical with those above, as well as an additional peak at 575.07 m/z, corresponding perfectly to $[Cu(L^1)(DMF)(ClO_4)]^{1+}$ (Figure S8). Additionally, the UV-vis spectra of 1, 7, 8, 10, and 11 in

Additionally, the UV–vis spectra of 1, 7, 8, 10, and 11 in MeOH show a broad peak which is characteristic of a Jahn–Teller effect and consistent for a Cu(II) center with an octahedral $\{N_4O_2\}$ geometry (Figure S19 in the Supporting Information).

TGA measurements were also conducted to examine the thermal stability of all complexes. In all cases (Figures S20–S30 in the Supporting Information), the first mass loss corresponds to the loss of any existing solvent molecules or the counteranions. The stability of the remaining core is then retained up to the region of \sim 300–400 °C, where gradual decomposition takes place. A detailed analysis of the TGA graphs is presented in the Supporting Information.

Catalytic Studies. In order to test the possible catalytic activity of 1–11, we studied the application of these catalytic systems in the A^3 coupling of benzaldehyde, pyrrolidine, and phenylacetylene (Table 2). During initial experiments with 1 as catalyst we managed to isolate a yellow crystalline material after the end of the reaction, on the basis of TLC. X-ray crystallography showed that this material corresponds to the Cu(I) coordination polymer [Cu^I(L¹)Cl] (1'), which has already been reported and found to inhibit the catalytic performance of 1.⁶⁹ To avoid the conversion issue, we therefore employed 8 in the following optimization procedures.

Furthermore, after screening a variety of solvents for the title reaction, we found 2-propanol (iPrOH, an environmentally friendly solvent)⁷⁹ to provide excellent yields when the reaction mixture was heated to 90 °C (Table S3, entry 6, in the Supporting Information), while other common organic solvents (such as DMF, acetonitrile, and DCM) afforded lower yields. In addition, the reaction was found to be catalyzed by only 0.02 mmol of the catalyst (on a 1 mmol reaction scale of benzaldehyde), at 90 °C and in an air atmosphere (TON = 44.5, TOF = 3.71 h^{-1}).

To evaluate the catalytic activity of our compound, several control experiments with common Cu(II) salts were performed for the same A^3 reaction, and the results are summarized in Table 3. In all cases, the corresponding Cu(II) salts afforded significantly lower yields, ranging from 55 to 65%, at a higher catalyst loading of ca. 10 mol %, on the basis of the benzaldehyde amount (Table 3, entries 1–8). Moreover, the use of Cu(II) salts as catalysts in this A^3 coupling with other para-substituted benzaldehydes (such as 4-chloro, 4-trifluoromethyl, and 4-methoxy), instead of benzaldehyde, gave the corresponding product in low yields (10–15%), showcasing their limited catalytic efficiency. In the absence of catalyst no reaction was observed, a result which supports the catalytic behavior of the studied multicomponent coupling.

We then explored the scope of the reaction by employing a variety of aldehydes, amines, and alkynes. The results are presented in Scheme 2. Using different aldehydes, pyrrolidine as the amine, and phenylacetylene under the aforementioned conditions, a variety of alkyl- and aryl-substituted propargylamines (1a-k) were formed in moderate to high isolated yields. In particular, saturated aliphatic aldehydes react with higher isolated yields (98-100%), in comparison to the aromatic aldehydes, which show slightly lower reactivity with moderate yields in the range of 57-89%. Consequently, the results of the amine screening (1l-u) indicate that only secondary amines lead to reaction completion, in contrast to primary amines in which no reaction was observed. In general, cyclic aliphatic and aromatic secondary amines afford the corresponding propargylamine products in excellent yields, ranging from 98 to 100%; acyclic secondary amines were found to be slightly less effective. Finally, the employment of 1-hexyne and (4-(trifluoromethyl)phenyl)acetylene in the reaction process (1v-x) demonstrated that both alkynes react with the produced imine, forming the corresponding propargyl products in good to excellent yields.

Mechanistic Aspects. In order to investigate the role of CPs in the reaction and shed light on the reaction mechanism, we focused on synthesizing a variety of Cu(II) CPs with the same ligand by fine-tuning their composition; this would enable us to optimize their catalytic performance and see how factors such as the metal geometry or the different anions in the compounds would affect the catalytic activity. Our previous

Enter	Compound	Coordination	Viald ^a , b
Entry	Compound	Environment	rielu
1	1	S	68%
		N L N ZCU.	
		N´ I `N S	
2	2	N N	<5%
		N N	
3	3	S N. I. N	<10%
4		Ś	NDC
4	4		INK
5	5	N N	NR ^c
Ū.	C C	ପ୍ଟ୍ରା ପ୍ଟ୍ରାଦ୍ର	
6	6	Br	NR^{c}
		N L N Cu	
7	7	N N S	64%
7	7	N T N Cu	0470
		N I N	
8	8	, O	89%(85%) ^d
9	9	S N. I. N	21%
10	10	Ś	570/
10	10	N L N	5/%
		N ^{Cu} s	
11	11	N = N	44%

Table 2. Overview of the Characteristics and Catalytic Activity of the Coordination Polymers in This Study

^{*a*}Isolated yields based on aldehyde. ^{*b*}Reaction conditions: benzaldehyde (102 μ L, 1 mmol), pyrrolidine (90 μ L, 1.1 mmol), phenylacetylene (132 mL, 1.2 mmol), catalyst (2 mol %), iPrOH (5 mL), *T* = 90 °C, 12 h stirring. ^{*c*}No reaction. ^{*d*}The reaction was performed in the presence of 10% TEMPO.

Table 3. Evaluation of Various Cu Salts as Catalysts in the Multicomponent Coupling of Phenylacetylene, Pyrrolidine, and Benzaldehyde

entry	catalyst	[product], ^a %
1	CuCl ₂	64
2	$Cu(NO_3)_2 \cdot 2.5H_2O$	65
3	$Cu(ClO_4)_2 \cdot 6H_2O$	60
4	CuBr ₂	64
5	CuBF ₂ ·6H ₂ O	55
6	$Cu(OAc)_2 \cdot H_2O$	58
7	$Cu(OTf)_2 \cdot H_2O$	53
8	$Cu(OTf)_2 \cdot H_2O^c$	55
9	no catalyst	NR ^b

^{*a*}Reaction conditions: benzaldehyde (102 μ L, 1 mmol), pyrrolidine (90 μ L, 1.1 mmol), phenylacetylene (132 μ L, 1.2 mmol), catalyst (10 mol %), iPrOH (5 mL), heated at 90 °C for 12 h. Isolated yields based on aldehyde. ^{*b*}No reaction. ^{*c*}Two equivalents of L¹ was added to the reaction mixture.

experience and familiarity with the ligand proved critical for this targeted synthesis, and as a result we obtained compounds which possess the desired characteristics (these are further detailed in Tables 1 and 2). **2** was synthesized using $Cu(NO_3)_2$. 2.5H₂O, and the metal center has a coordination environment of $\{N_2O_5\}$, possessing a pseudo-octahedral geometry. The

resulting 2D CP, however, only accounted for disappointing yields when it was tested as a catalyst (Table 2, entry 2). The employment of halogen copper sources afforded complexes 4-6, which show considerable differences. The presence of a coordinating anion once again affects the resulting coordination environments ({N₂Cl₃}, {N₂Cl₄}, {N₄Br}) and geometries (trigonal bipyramidal, octahedral), which can be found in further detail in Table 1 (entries 4-6). Nevertheless, none of the compounds show any catalytic activity in the tested reaction. Furthermore, by using Cu(II) sources with traditionally noncoordinating anions (as in the case of our initial catalyst, 1), we were able to isolate compounds 7 and 8. Both compounds show an identical 1D framework and solution behavior in comparison to 1, and only the present anion is different. The use of 7 as a catalyst (Table 2, entry 7) provided results similar to those for 1. This indicated that a similar Cu(I) species (analogous to 1') is generated, possibly through the conversion of BF_4^- to F^- (further supported by the ESI-MS analysis of 7, in which several peaks containing F⁻ as the anion were observed), and inhibits the performance of the catalyst. To our delight, however, 8 showed very good catalytic activity in the tested reaction, with yields similar to those of the initial catalyst (Table 2, entry 8). To investigate its electron-donating capabilities, the electrochemistry of 8 was studied by cyclic voltammetry (CV). CV in the cathodic direction over several

Scheme 2. Catalytic Activity of 8 in the A³ Coupling among Aldehydes, Amines, and Substituted Acetylenes toward Propargylamine Derivative Synthesis



cycles showed a quasi-reversible reduction process at -0.423 V vs Fc^{+/0} ($i_a/i_c = 1.5$) (Figure 7) vs FeCp₂^{+/0} and a nonreversible reduction process⁸⁰ at -1.156 V vs Fc^{+/0}. The former may be assigned to the [Cu^{II}] \leftrightarrow [Cu^I] couple, further supporting the formation of a Cu(I) intermediate during the catalytic reaction. Additional control experiments were then performed to investigate the importance of the redox potential. Given that Zn(II) has lower potential than Cu(II), we employed compounds 3 and 9; both are 1D Zn(II) CPs with the same framework and have similar thermal and solution behavior. In the case of 3, the corresponding propargylamine was afforded only at 10% yield (Table 2, entry 3). Interestingly, compound 9 (Zn(II)), which is isostructural with 8 (Cu(II)), was found to catalyze the title reaction in only 21% yield, as determined by ¹H NMR (Table 2, entry 9).

The use of the modified benzotriazole derivatives in position 5 (L^2) or positions 5 and 6 (L^3) yielded the corresponding dimers, **10** and **11**, and not the anticipated 1D CP. The latter were found to moderately catalyze the reaction (Table 2, entries 10 and 11). In both structures, each Cu(II) center coordinates to four N atoms (from four different ligands) and one O atom, adopting a distorted-square-pyramidal geometry. However, the UV-vis spectra show that the Cu(II) centers in **10** and **11** adopt an octahedral geometry (4N + 2O) and



Figure 7. Overlaid CV scans (two cycles) of 8 in 0.05 M $[^nBu_4N][PF_6]/DMSO$ (scan rate 300 mV $s^{-1}).$

possibly upon solvation four N atoms and two O atoms, from four ligands and two MeOH solvated molecules (catalysis takes place in iPrOH), occupy the equatorial and axial positions, respectively. In this way, the adaptation of the symmetrical $\{N_{4}\}$ plane in solution yields the anticipated 1D CP and this transformation may explain the catalytic activity of 10 and 11. However, the poorer catalytic performance of 10 and 11 in comparison to 8 may be explained by the following factors or a combination of them. (A) The aforementioned "in situ" geometry transformation is required for 10 and 11 to behave as catalysts. (B) Substitution in position(s) 5(6) of the benzotriazole moieties may attribute a second coordination sphere effect to Cu centers. (C) The presence of different axial ligands H_2O (10) or Br (6) vs OTf (8) may disrupt the aforementioned "in situ" transformation or decrease the reactivity of the catalysts.^{81,82} Finally, the use of Cu^ICl as the metal source resulted in the synthesis of the catalytically inactive species $[Cu^{I}(L^{1})Cl]$ (1'). It is also worth noting that the addition of 10 mol % of TEMPO did not affect the reaction yield, showcasing the absence of a clear radical process containing (Table 2, entry 8) the Cu(I) complex species and supporting the plausible in situ formation of the copper(I) acetylide intermediate, which is responsible for the catalytic cycle (Scheme S1 in the Supporting Information).

On the basis of the above observations, the presence of a Cu(II) center in the solution featuring an octahedral geometry with four nitrogen atoms occupying the equatorial positions is important in order to promote catalytic activity. Furthermore, the choice of the proper anion is critical. The desired catalytically active motif (4N + 2O) can be reproduced by the use of noncoordinating anions. In contrast, the use of other anions results in different coordination geometries and dimensionalities, with zero catalytic activity. These observations are also consistent with the commonly suggested mechanism of the A^3 coupling, which involves the activation of the alkyne by the catalyst (Scheme S1 in the Supporting Information). The planar $\{N_4\}$ geometry of Cu(II) promotes the coordination of the alkyne with concomitant activation of the C-H bond and the formation of the corresponding Cu(I) acetylide (the acetylenic hydrogen might be abstracted from the hydroxyl anions produced from the iminium ion formation). Consequently, the symmetrical $\{N_4\}$ plane accounts for adequate electron delocalization to ensure the reduction of Cu(II) to Cu(I), which is further promoted by the redox potential of Cu(II). Finally, addition of the Cu(I) acetylide to the in situ generated iminium ion yields the corresponding propargylamine derivative and water and regeneration of the catalyst. The proposed catalytic pathway can be supported, in part, by the recently reported kinetic studies on the effect of alcoholic solvents to Cu(II) Schiff base complexes⁸¹ and Cu(II)catalyzed aerobic oxidation of benzylic alcohols in an imidazole containing an N₄ ligand framework.⁸²

CONCLUSION

In this work, we have introduced a system of 1D Cu(II) CPs that can catalyze the multicomponent reaction of aldehydes, amines, and alkynes to produce propargylamine derivatives. In particular, fine tuning of the catalyst allowed us to generate a 1D CP with excellent catalytic activity, avoiding any issues that would inhibit its performance. The method uses relatively mild conditions and provides results for a broad range of substrates, especially when aliphatic aldehydes and secondary amines are employed. Furthermore, it eliminates the need for expensive

metal salts, inert atmosphere, or high loadings. We have also attempted to shed more light on the mechanism of the reaction, from an inorganic point of view; through a thorough synthesis and study of targeted CPs, we evaluated how factors such as coordination geometry, anion, and ligand tuning affect the catalytic activity. The results are consistent with the suggested mechanism. We envision that this work demonstrates the catalytic potential of the rarely used 1D CPs. As such, our future efforts will be dedicated to (a) synthesizing variations of 8 with the use of substituted benzotriazole derivatives with electron-donating or -withdrawing groups, (b) using the present library of catalysts for other chemical transformations, and (c) employing CPs of other metals in the given A^3 coupling reaction.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.6b03084.

Crystallographic data, additional figures of certain structures, magnetic measurements, ESI-MS analysis for 1-11, UV-vis spectra, thermogravimetric analysis for 1-11, evaluation of catalytic conditions, and characterization data for A³-coupling products (¹H and ¹³C NMR and HRMS spectra) (PDF) Crystallographic data (CIF)

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Notes

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