Accepted Manuscript

Synthesis tricyanovinyl derivatives via one-pot tandem reactions with heterogeneous catalyst Au@Cu(II)-MOF



Fa-Zheng Jin, Chao-Qun Chen, Qun Zhao, Jing-Lan Kan, Yang Zhou, Gong-Jun Chen

PII:	S1566-7367(18)30137-7
DOI:	doi:10.1016/j.catcom.2018.04.006
Reference:	CATCOM 5379
To appear in:	Catalysis Communications
Received date:	8 January 2018
Revised date:	29 March 2018
Accepted date:	8 April 2018

Please cite this article as: Fa-Zheng Jin, Chao-Qun Chen, Qun Zhao, Jing-Lan Kan, Yang Zhou, Gong-Jun Chen , Synthesis tricyanovinyl derivatives via one-pot tandem reactions with heterogeneous catalyst Au@Cu(II)-MOF. The address for the corresponding author was captured as affiliation for all authors. Please check if appropriate. Catcom(2017), doi:10.1016/j.catcom.2018.04.006

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

Synthesis tricyanovinyl derivatives via one-pot tandem reactions with heterogeneous catalyst Au@Cu(II)-MOF

Fa-Zheng Jin, Chao-Qun Chen, Qun Zhao, Jing-Lan Kan, Yang Zhou^{*} and Gong-Jun Chen^{*}

College of Chemistry, Chemical Engineering and Materials Science, Collaborative Innovation Center of Functionalized Probes for Chemical Imaging in Universities of Shandong, Key Laboratory of Molecular and Nano Probes, Ministry of Education, Shandong Normal University, Jinan 250014, P. R. China. E-mail: zhouyang0404@sdnu.edu.cn, gongjchen@126.com

A Children and a chil

Abstract

In this article, the heterogeneous catalyst of Au@Cu(II)-MOF was prepared with high performance catalytic activities. By adding 5% mol Au@Cu(II)-MOF, the substrate of 2,6-di-tert-butylphenol (1) was oxidized to 2,6-di-tert-butyl-p-benzoquinone (2) with the yield of 99% using H_2O_2 as an oxidizing reagent. Moreover, treating the catalytic reaction mixture with malononitrile, new product of one 2-(3,5-di-tert-butyl-4-hydroxyphenyl)ethane-1,1,2,-tricarbonitrile (3) was obtained with the isolated yield of 87%. However, in the absence of the catalyst of Au@Cu(II)-MOF, the intermedia of 2 and malononitrile react to form a product not 3 but its isomer

2-(3,5-di-tert-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)ethane-1,1,2,-tricarbonitrile (4). At the meanwhile, in the presence of Au@Cu(II)-MOF and H_2O_2 , the product of 3 with comparable isolated yield of 86% was isolated when 1 and malononitrile directly reacted during one pot tandem reaction. Furthermore, the tautomerization of 3 and 4 was also observed in CH₂Cl₂ solution driven by trimethylamine and acetic acid.

Keywords: Heterogeneous catalyst; Tandem reaction; Proton tautomerism

1 Introduction

The development of heterogeneous catalysts is one of the major subjects in modern synthetic chemistry and industry. Owing to the features of economic, simplified and catalysts recycling [1-3], heterogeneous catalysis has received much attention in the past few decades. Inside the heterogeneous catalysis domain, Metal-organic framework (MOF) materials are relatively novel to other well-recognized porous materials like zeolites. The rational design of extended frameworks with thermal stabilities, controlled pore size and coordinative unsaturated metal sites for selective catalytic properties offers an advantageous platform to heterogeneous systems [4-7]. Au develop Nanoparticles (Au NPs) have been recognized as very active and effective catalysts and widely used in promoting many types of organic reactions such as oxidation of alcohols, reduction of nitro-aromatic compounds and so on [8-10]. Therefore, the incorporation of MOF-supports with the Au NPs would lead to an enhanced or even novel catalytic property compared to their pristine counterparts [11-12]. On the other side, tandem reactions provide incomparable opportunities for the expeditious increase of complexity and diversity. This strategy offers significant advantages over classical stepwise approaches, such as tandem cost and time timesaving, eco-friendliness, and simplified processes and low cost [13-14]. As a continuation of our work with the Au NPs-loaded materials, Cu-MOF namely Au@Cu(II)-MOF, we report herein its heterogeneous catalytic Au@Cu(II)-MOF catalyzes nature.

2,6-di-tert-butylphenol (1) to 2,6-di-tert-butyl-p-benzoquinone (2) using H_2O_2 as oxidizing reagent, malononitrile reactions in a successive manner, and furthermore, 1 with malononitrile reactions using one-pot tandem synthesis of tricyanovinyl derivatives 2-(3,5-di-tert-butyl-4-hydroxyphenyl)ethane-1,1,2,-tricarbonitrile (3). However, malononitrile Au@Cu(II)-MOF 2 and react witho ut to form 2-(3,5-di-tert-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)ethane-1,1,2,-tricarboni trile (4). The synthesis of 3 and 4 is discussed in detail and the spectroscopic

characteristics and proton tautomerism of the 3 and 4 are investigated.

2 Experimental

2.1. Materials

The reagents and solvents employed were commercially available and used without further purification. Ligand 4,4,4-trifluoro-1-(4-(pyridin-4-yl)phenyl)butane-1,3-dione (L) was synthesized according to a previous reported procedure [15-16].

2.2. Instrumentation

The powder diffractometer (XRD) patterns were collected by a D8 ADVANCEX-ray with Cu K α radiation ($\lambda = 1.5405$ Å). ICP-LC was performed on an IRIS InterpidII XSP and NU AttoM. HRTEM (High resolution transmission electron microscopy) analysis was performed on a JEOL 2100

Electron Microscope at an operating voltage of 200 kV. ¹H NMR and ¹³C NMR spectra were recorded on Bruker Avance 400 MHz spectrometer in CDCl₃. Mass spectra analysis was performed on API 200 LC/MS system (Applied Biosystems Co. Ltd). Gas chromatography (GC) analysis was performed on an Agilent 7890B GC. XPS spectra were obtained from PHI Versaprobe II.

2.3. X-ray Crystallography

Diffraction data for the complex was collected at 293 (2) K, with Agilent SuperNova X-Ray single crystal diffractometer using Cu-K α radiation (λ = 1.54178 Å) with the ω -20 scan technique. An empirical absorption correction was applied to raw intensities [17]. The structure was solved by direct methods (SHELX-97) and refined with full-matrix least-squares technique on F² using the SHELX-97 [18]. The hydrogen atoms were added theoretically, and riding on the concerned atoms and refined with fixed thermal factors.

2.4. Synthesis of Cu(II)-MOF and Au@Cu(II)-MOF

Cu(II)-MOF and Au@Cu(II)-MOF were synthesized according to previous reported procedures [15-16].

Synthesis of Cu(II)-MOF. A solution of $Cu(OAc)_2$ (2.4 mg, 0.01 mmol) in MeOH (1 mL) was layered onto a solution of L (4.8 mg, 0.02 mmol) in CH_2Cl_2 (2 mL). The solutions were left for about 3 days at room temperature, and then Cu(II)-MOF (Cu_3L_6) was obtained as bright green crystal.

Synthesis of Au@Cu(II)-MOF. Cu(II)-MOF (15 mg, 0.003 mmol) was added to a CH₃OH (10 mL) solution of chloroauric acid (20 mg, 0.2 mmol). The mixture was stirred for 1 h at room temperature. The resulting solid was isolated by centrifugation and washed with CH₂Cl₂. The obtained green-yellow crystalline solid was mixed with NaBH₄ (50 mg, 1.3 mmol) in water (4 mL) and the mixture was stirred for additional 5 h to afford a dark brown solid. This obtained crystalline solid, Au@Cu(II)-MOF, was washed with CH₃CN and EtOH and dried in air.

2.5. Synthesis of 2, 6-di-tert-butyl-1,4-benzoquinone (2) from 2,6-di-tert-butylphenol (1)

1 (21 mg, 0.1 mmol) was added to 2 mL acetonitrile solution of H_2O_2 (50 µL, 0.5 mmol). After addition of Au@Cu(II)-MOF (5 mg, 5% mol Au), the mixture was stirred at 75°C for 2 h and 25 min to afford 2 with (monitored by GC on DB-1701 column) conversion (100%) and selectivity (99%), respectively. Leaching test: Au@Cu(II)-MOF was separated from the solution by centrifugation, and the reaction solution was transferred to another reaction vial under the same conditions.

2-(3,5-di-tert-butyl-4-hydroxyphenyl)ethane-1,1,2,-tricarbonitrile (3) from 2 and malononitrile

1 (105 mg, 0.5 mmol) and H_2O_2 (250 μ L, 2.5 mmol) were added to 5 mL acetonitrile solution. After addition of Au@Cu(II)-MOF (25 mg, 5 % mol Au),

the mixture was stirred at 75°C for 2 h in air. Acetonitrile solution (5 mL) of malononitrile (115 mg, 1.75 mmol) was added to above system and then stirred for additional 8h at 75°C being monitored by TLC before cooling down to room temperature and concentrated. The crude product was purified by silica gel column chromatography (CH₂Cl₂/THF 25: 1) as eluent to give a light yellow solid **3** 158 mg with yield 87 %.

2.7.

Synthesis

of

2-(3,5-di-tert-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)ethane-1,1,2,-tricarboni trile (4) from 2 and malononitrile

1 (105 mg, 0.5 mmol) was added to acetonitrile (5 mL) solution of H_2O_2 (250 μ L, 2.5 mmol). After addition of Au@Cu(II)-MOF (25 mg, 5 % mol Au), the mixture was stirred at 75°C for 2h in air. After filtering Au@Cu(II)-MOF, the acetonitrile solution (5 mL) of malononitrile (115 mg, 1.75 mmol) was added to above system. The mixture was stirred for additional 12h at 75°C monitored by TLC and then cooled to room temperature and concentrated. The crude product was purified by silica gel column chromatography (CH₂Cl₂/THF 25: 1) as eluent to give a red solid **4** 36 mg with yield 20 %.

2.8. One-pot tandem 3 from 2,6-di-tert-butylphenol and malononitrile

A mixture of **1** (105 mg, 0.5 mmol), H_2O_2 (250 µL, 2.5 mmol), malononitrile (115 mg, 1.75 mmol) and Au@Cu(II)-MOF (25 mg, 5 % mol Au) in acetonitrile (10 mL) was stirred at 75°C for 8 h (monitored by TLC). The mixture after being cooled and concentrated, the product of **3** was purified by column

chromatography on silica gel (CH₂Cl₂/THF 25: 1) with yield 86 %.

2.9. Recycle and activation of Au@Cu(II)-MOF

Au@Cu(II)-MOF was recovered by centrifugation, washed with ethanol (3.0 mL) and dichloromethane (3.0 mL) (3 times), and then dried at 90°C in vacuum for the next run reaction under the same reaction conditions.

3 Results and Discussion

3.1. Characterization of Cu(II)-MOF and Au@Cu(II)-MOF

Cu(II)-MOF is 3D NbO network. The opposite Cu(II)····Cu(II) distance in MOF is 26.6139(4) Å. All the fluorine atoms on the framework face toward the center of the channels and the opposite F···F distance is 14.4423 (3) Å. Au@Cu(II)-MOF was prepared via the HAuCl₄ solution impregnation in Cu(II)-MOF (Scheme 1). The Au NPs-embedded Cu(II)-MOF was synthesized by the reduction of Au(III)@Cu(II)-MOF with NaBH₄ in aqueous solution. The uploaded amount of Au, as determined by inductively coupled plasma (ICP) measurement, is up to 9.3 wt. %. HRTEM was shown Au NPs highly dispersed in Cu(II)-MOF and the average particle size of ca. 2 nm. The atomic lattice with spacing of 0.23 nm fringes corresponding to Au (111) planes was observed. The oxidation state of Nano Au after reduction was checked by X-ray photoelectron spectroscopy (XPS). The observation of Au 4f_{7/2} and 4f_{5/2} peak at 83.86 and 87.46ev in XPS of Au@Cu(II)-MOF demonstrated the reduction from Au(III) to Au(0) (Fig S1). The XRPD of Au@Cu(II)-MOF is well

agreement with Cu(II)-MOF, which indicates that the structural integrity of the Cu(II)-MOF is well preserved (Fig. 1).

3.2. Synthesis of 2,6-di-tert-butyl-1,4-benzoquinone (2) from 2,6-di-tert-butylphenol (1).

We firstly examine the catalytic behavior of Au@Cu(II)-MOF for catalyzing 1 to 2, which is an important class of compounds in organic synthesis, biomedicine and materials science [19-20]. This oxidation reaction (with Au@Cu(II)-MOF, 5 % Au) was carried out using more environmentally-friendly H_2O_2 as oxidant (monitored by GC) in acetonitrile solution. As shown in Fig. 2, upon increasing the reaction time from 20 min to 2h the yield of 2 significantly is enhanced. It should be noted that an excellent yield of 99 % was achieved when the reaction was carried out at 2h, which was confirmed by GC analysis (Fig. S2 and S3). It therefore, appears that 2h is the optimum reaction time for the maximum yield of 2. The total number (TON) and turnover frequency (TOF) are 2.45 and 5.88 h⁻¹, respectively. When using tert-butyl hydroperoxid (TBHP) as the oxidant agent, the optimum reaction time for achieving the maximum yield is largely shortened to 25 minutes (Fig. S4). In order to gain insight into the heterogeneous nature of Au@Cu(II)-MOF, the hot leaching test was carried out. As indicated in Fig. 2, the yield slightly increases without Au@Cu(II)-MOF after ignition of the oxidation reaction at 60min, indicating Au@Cu(II)-MOF exhibits a typical heterogeneous catalyst nature. ICP measurement indicated that the amount of Au NPs The in Au@Cu(II)-MOF have no changes after leaching test, the amount of Au species still keep 9.3 wt. %. The catalytic activity of this oxidation reaction with only H_2O_2 (the amount five times of 1), Cu(II)-MOF (the amount two times of Au@Cu(II)-MOF) or Au@Cu(II)-MOF for was also examined under 2h,

however, **1** conversion are 20 %, 6 % and 53 %, respectively, which suggests that Nano Au is the main catalytic site (Fig. S5). The scope of the oxidation catalytic system was explored by performing the oxidation reaction. Phenol, 2, 6-Dimethylphenol and 2, 3, 5-Trimethylphenol gave 95 %, 82 % and 74 % conversion, respectively (Fig. S6). The recyclability of Au@Cu(II)-MOF was also examined. After an initial reaction, the solid catalyst was isolated from the reaction system by centrifugation and reused in additional runs. The Au@Cu(II)-MOF was be recycled for five times (Fig. 2). After each run, the solid catalyst was collected by centrifugation, washed with ethanol, dried at 90°C and reused in next run under the same conditions. The reaction yields still keep 98 % (Fig. S7), indicating almost no change of the catalytic activity of recycled Au@Cu(II)-MOF. The XRPD patterns of Au@Cu(II)-MOF and that after reused for five cycles indicated that the structural integrity of Au@Cu(II)-MOF was well preserved (Fig. S8).

3.3. Knoevenagel-Substitution reaction synthesis of 2-(3,5-di-tert-butyl-4-hydroxyphenyl)ethane-1,1,2,-tricarbonitrile (3) and 2-(3,5-di-tert-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)ethane-1,1,2,-tricarboni trile (4) from 1 and malononitrile

As one of the most prominent classes of compounds, the tricyanovinyl (TCV) compounds are strong organic electron acceptors for creating reduced band gap materials, and tricyanovinyl derivatives are also key structural motifs in photochromic active compounds and useful building blocks in the synthesis of semiconducting [21-23], as well as in intriguing nonlinear optical properties (NLO) material [24-25]. Usually, tricyanovinyl compounds are prepared by tetracyanoethylene (TCNE) with activated aromatic rings [26-27].

The catalytic behavior of Au@Cu(II)-MOF for the Knoevenagel reaction was tested. After oxidation of 1, malononitrile was added to the above system. The mixture was stirred for an additional 8 h at 75° C monitored by TLC, the product of

2-(3,5-di-tert-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)malononitrile did not generate from 2 with malononitrile (even reduce the amount of malononitrile) catalysis with Au@Cu(II)-MOF. But yellow production 3 with yield 87% was found (Scheme 2.). The structure of **3** was assigned on the basis of ESI-MS, 1 H and ${}^{13}C$ NMR. In addition, the structure of **3** is further supported by the X-ray diffraction analysis, which unambiguously confirmed its structure (Fig. S9.). Molecules of **3** are planar all atoms (excluding the butyl groups), the structure consists of one malononitrile and one cyano in the molecule of 3, Furthermore, molecule 3 forms π -stacks distance of 3.637 Å along the c-axis (CIF of 3 in Supplementary material, CCDC: 1546189). Noteworthy, after the completion of the catalytic oxidation reaction of 1 to form 2, Au@Cu(II)-MOF was filtered before malononitrile was added to the filtrate, and then a red production of 2-(3,5-di-tert-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)ethane-1,1,2,-tricarboni trile (4) (Scheme 2.) was obtained with yield 20 % (monitored by TLC) (Fig. S10). For the exclusion the influence of acetonitrile in the reaction process, using methanol instead of acetonitrile, the product is still 3 (Fig. S11). After the catalytic oxidation reactions of 1 to 2, Au@Cu(II)-MOF was filtered before Cu(II)-MOF and malononitrile were added to the filtrate, the red production 4 was also been synthesized (Fig. S12). A proposed mechanism for the reaction comprises initial oxidation of 1 to form 2, subsequent Knoevenagel reaction malononitrile attack keto group of 2 to form intermediate product 2-(3,

5-di-tert-butyl-4-oxocyclohexa-2, 5-dien-1-ylidene) malononitrile (Fig. S13). At the third stage of substitution reaction, another malononitrile molecule attacks the malononitrile middle carbon atom of intermediate product of 2-(3,5-di-tert-butyl-4-oxocyclohexa-2,5-dien-1-ylidene) malononitrile, and a cyano leave to form **3** or **4** (Scheme 3.).

3.4. The one-pot tandem synthesis of **3** from **1** and malononitrile

To further investigate the catalytic behaviour of Au@Cu(II)-MOF, the tandem reaction was expanded to 1 and malononitrile. A mixture of 1, H_2O_2 , malononitrile and Au@Cu(II)-MOF (5 % mol Au) in acetonitrile was stirred at 75°C monitored by TLC for 8 h. The product of 3 was purified by column chromatography on silica gel with yield 86 % (Fig. 3). The hot leaching test was carried out to show the heterogeneous nature of Au@Cu(II)-MOF. The yield of 3 is 48 % with Au@Cu(II)-MOF after reaction 4 hours and the yield no further increases by filtering Au@Cu(II)-MOF after 2 hours. Reusability of catalysts is very important for heterogeneous catalytic reaction. The recyclability of Au@Cu(II)-MOF was also examined. After an initial reaction, the solid catalyst was isolated from the reaction system by centrifugation and reused in additional runs. The Au@Cu(II)-MOF was be recycled five times (Fig. 3). After each run, the solid catalyst was collected by centrifugation, washed with acetonitrile, dried at 90°C and reused in next run under the same conditions. Interestingly, the reaction yield decrease slightly, as shown in Fig. 3 the XRPD patterns of Au@Cu(II)-MOF and that after reused for five cycles indicated that the structural integrity of Au@Cu(II)-MOF was well preserved. The scope of the one-pot tandem catalytic system was explored by performing the reaction phenol, 2, 6-Dimethylphenol and 2, 3, 5-Trimethylphenol with

malononitrile. Unfortunately, the reaction selectivity and the yield is very poor, the products are difficult to isolate by column chromatography, respectively.

3.5. Proton tautomerism 3 and 4

Proton tautomerism has been of sustained interest because of its importance for understanding various chemical and biochemical phenomena [28-29], many reaction mechanisms are explained by the proton tautomerism such as a keto-enol tautomerism. From physicochemical point of view, proton tautomerism can be described by an intramolecular proton transfer reaction. This implies that proton tautomerism has potential for switching the molecular properties compounds by external stimuli such as light, heat, and solvent polarity [30-35]. Initially CH₂Cl₂ solution of **3** has a light yellow color, which turns dark red upon the addition of triethylamine because of the generation of 4. After adding acetate to the solution, the color change from dark red to yellow again. Compound 3 with a hydroxyl group shows yellow color, after the addition of triethylamine, the hydrogen of hydroxyl group transfer to malononitrile group to form 4, resulting this color variation. Besides naked-eye detectable color change, the reaction progress was monitored by UV-vis spectra. As indicated in Fig. 4, the adsorption of 3 at 335 and 510 nm rapidly decreased while a concomitant increase of the peak at 425 nm. The remarkable color change of the solutions implies a presence of a proton tautomeric between keto-enol tautomer, which is further confirmed by ESI-MS data (Fig. S14 and S15).

4. Conclusions

Here we report a new one-pot tandem route for preparing the tricyanovinyl compound **3** from 2,6-di-tert-butylphenol and malononitrile using Au@Cu(II)-MOF as the catalyst in the presence of H_2O_2 oxidizing reagent, including the described highly efficient and convenient synthetic protocols, broaden the synthetic chemistry scope, as well as existed proton tautomerism between **3** and **4**. Furthermore, the distinguishingly catalytic behaviour of Au@Cu(II)-MOF in this new one-pot tandem route is successfully investigated as a heterogeneous catalyst.

Acknowledgements

We are grateful for financial support from NSFC (Grant Nos. 21301109 and 21401118), Shandong Provincial Natural Science Foundation (No. ZR2014BP011) and Jinan Science and Technology Bureau (OUT_06623).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version.

Reference

- M. Hartmann, A. G. Machoke, W. Schwieger, Chem. Soc. Rev. 45 (2016) 3313-3330.
- [2] D. Verboekend, N. Nuttens, R. Locus, J. V. Aelst, P. Verolme, J. C. Groen, J. Pérez-Ramírezc, B. F. Selsa, Chem. Soc. Rev. 45 (2016) 3331-3352.
- [3] F. Zaera, Chem. Soc. Rev. 42 (2013) 2746-2762.
- [4] J. Liu, L. Chen, H. Cui, J. Zhang, L. Zhang, C.-Y. Su, Chem. Soc. Rev. 43 (2014) 6011-6061.
- [5] X. S. Wang, R. Cao, Chem. Soc. Rev. 46 (2017) 126-157.
- [6] T. R. Cook, P. J. Stang, Chem. Rev. 15 (2015) 7001-7045.
- [7] M. Li, D. Li, M. ÓKeeffe, O. M. Yaghi, Chem. Rev. 2 (2014) 1343-1370.
- [8] X. Liu, L. He., Y. M. Liu, Y. Cao., Acc. Chem. Res. 3 (2014) 793-804.
- [9] A. Villa, N. Dimitratos, C. E. Chan-Thaw, C. Hammond, G. M. Veith, D. Wang, M. Manzoli, L. Prati, G. J. Hutchings, Chem. Soc. Rev. 45 (2016) 4953-4994.
- [10] W. Zi, F. D. Tost, Chem. Soc. Rev. 45 (2016) 4567-4589.
- [11] J. S. Wang, F. Z. Jin, H. C. Ma, X. B. Li, M. Y. Liu, J. L. Kan, G. J. Chen, Y. B. Dong, Inorg. Chem. 55 (2016) 6685-6691.
- [12] C. R. Kim, T. Uemura, S. Kitagawa, Chem. Soc. Rev. 45 (2016) 3828-3845.
- [13]J. C. Wasilke, S. J. Obrey, R. T. Baker, G. C. Bazan, Chem. Rev. 105 (2005) 1001-1020.
- [14] B. B. Touré, D. G. Hall, Chem. Rev. 109 (2009) 4439-4486.
- [15] G. J. Chen, J. S. Wang, F. Z. Jin, M. Y. Liu, C. W. Zhao, Y. A. Li, Y. B. Dong, Inorg. Chem. 55 (2016) 3058–3064.
- [16] G. J. Chen, H. C. Ma, W. L. Xin, X. B. Li, F. Z. Jin, J. S. Wang, M. Y. Liu, Y. B. Dong, Inorg. Chem. 56 (2017) 654-660.
- [17] Sheldrick. G. M. SHELXS 97, Program for the Solution of Crystal Structures, University of Götingen, Germany, 1997.
- [18] Sheldrick, G. M. SHELXL 97, Program for the Refinement of Crystal Structures, University of Götingen: Germany, 1997.

- [19] F. W. Küpper, Appl.Catal. A: Gen. 264 (2004) 253-262.
- [20] M. Hassanein, S. Gerges, M. Abdo, S. EL-Khalafy, J. Mol. Catal. A: Chem. 268 (2007) 24-28.
- [21] Z. Li, Z. Zhu, C. C. Chueh, S. B. Jo, J. Luo, S. H. Jang, A. K. Y. Jen, J. Am. Chem. Soc. 138 (2016) 11833-11839.
- [22] T. M. Pappenfus, B. J. Hermanson, T. J. Helland, G. G. W. Lee, S. M. Drew, K. RMann, K. A. McGee, S. C. Rasmussen, Org. Lett. 10 (2008) 1553-1556.
- [23] S. R. González, J. Orduna, R. Alicante, BVillacampa, K. A. McGee, J. Pina, J. S. Melo, K. M. Schwaderer, J. C. Johnson, B. A. Blackorbay, J. J. Hansmeier, V. F. Bolton, T. J. Helland, B. A. Edlund, T. M. Pappenfus, J. T. L. Navarrete, J. Casado, J. Phys. Chem. B. 115 (2011) 10573-10585.
- [24] X. Ma, F. Ma, Z. Zhao, N. Song, J. Zhang, J. Mater. Chem. 19 (2009) 2975-2985.
- [25] J. Casado, M. C. R. Delgado, M. C. R. Merchán, V. Hernández, J. T. L. Navarrete, T. M. Pappenfus, N. Williams, W. J. Stegner, J. C. Johnson, B. A. Edlund, D. E. Janzen, K. R. Mann, J. Orduna, B. Villacampa, Chem. Eur. J. 12 (2006) 5458-5470.
- [26] G. N. Sausenv, A. Engelhardntd, W. J. Middleton, J. Am. Chem. Soc. 80 (1958)2815-2822.
- [27] M. Reig, G. Bagdziunas, D. Volyniuk, J. V. Grazuleviciusb, D. Velasco, Phys. Chem. Chem. Phys. 19 (2017) 6721-6730.
- [28] Y. akane, T. akeda, N. oshino, K. Sakai, T. Akutagawa, J. Phys. Chem. A. 119 (2015) 6223-231.
- [29] D. Dahal, L. McDonald, X. Bi, C. Abeywickrama, F. Gombedza, M. Konopka, S. Paruchuri, Y. Pang, Chem. Commun. 53 (2017) 3697-3700.
- [30] A. Matwijczuk, D. Karcz, R. Walkowiak, J. Furso, B. Gładyszewska, S. Wybraniec, A. Niewiadomy, G. P. Karwasz, M. Gagos, J. Phys. Chem. A. 121 (2017) 1402-1411.
- [31] Y. H. Kim, S. -G. Roh, S. -D. Jung, M. Chung, H. K. Kim, D. W. Cho, Photochem. Photobiol. Sci. 9 (2010) 722-729.

- [32] P. Wnuk, G. Burdziński, M. Sliwa, M. Kijak, A. Grabowska, J. Sepioł, J. Kubicki, Phys. Chem. Chem. Phys. 16 (2014) 2542-2552.
- [33] H. Yamashita, J. Abe, J. Phys. Chem. A.118 (2014) 1430-1438.
- [34] J. Harada, T. Fujiwara, K. Ogawa, J. Am. Chem. Soc. 129 (2007) 16216-16221.
- [35] J. E. Kwon, S. Park, S. Y. Park, J. Am. Chem. Soc. 135 (2013) 11239-11246.

ARN SCR

Figure Captions

Scheme 1: Schematic representation of synthesis of Au@Cu(II)-MOF.

- Fig. 1. Left: HRTEM image of Au@Cu(II)-MOF. Right: XRPD patterns of Cu(II)-MOF and Au@Cu(II)-MOF.
- Fig. 2. Left: Reaction time examination and leaching test for the synthesis of 2 catalysed by Au@Cu(II)-MOF. Right: catalytic cycles. Reaction conditions: 1 (21mg, 0.1 mmol), H₂O₂ (50 μL, 0.5 mmol) and Au@Cu(II)-MOF (5 mg, 5% mol Au) in acetonitrile (2 mL) solution. The mixture was stirred at 75°C. Au@Cu(II)-MOF was recovered by centrifugation, washed with EtOH and dried at 90°C.
- Scheme 2: After oxidation of 1, malononitrile was added to the above system to synthesis of 3 and synthesis of 4.
- Scheme 3: A proposed mechanism for the reactions of 3 and 4
- Fig. 3. Recycling test: The yield obtained at 8 h in repeated runs of 3 (left) and corresponding XRPD patterns (right).
- Fig. 4. The UV-vis absorption spectra for the solution of 3 $(1 \times 10^{-3} \text{ mol in 2 ml} \text{ CH}_2\text{Cl}_2$, yellow line) in the presence of different quantity of triethylamine $(0.2 \times 10^{-3}, 0.4 \times 10^{-3}, 0.5 \times 10^{-3}, 0.8 \times 10^{-3}, 1 \times 10^{-3}, 1.2 \times 10^{-3}, 1.4 \times 10^{-3} \text{ mol})$ was added. The insert shows the color change of triethylamine and acetic acid -driven 3 and 4 tautomerism. 3 $(1 \times 10^{-3} \text{ mol})$, triethylamine in order to add $(0.2 \times 10^{-3}, 0.4 \times 10^{-3}, 0.5 \times 10^{-3}, 0.8 \times 10^{-3}, 1 \times 10^{-3}, 1.2 \times 10^{-3}, 1.4 \times 10^{-3} \text{ mol})$ and $(0.2 \times 10^{-3}, 0.4 \times 10^{-3}, 0.5 \times 10^{-3}, 0.8 \times 10^{-3}, 1 \times 10^{-3}, 1.2 \times 10^{-3}, 1.4 \times 10^{-3} \text{ mol})$ acetic acid was added again.













Graphical abstract:



Highlights

- The catalyst Au@Cu(II)-MOF exhibits a heterogeneous catalytic nature.
- Au@Cu(II)-MOF is able to catalyze one-pot tandem synthesis of compounds 3.
- Without loading the catalyst, intermedia 2 and malononitrile can form product of 4.
- The products **3** and **4** exist proton tautomerism.

Strain and the second s