Electronic Supplementary Material (ESI) for Catalysis Science & Technology

Supporting Information

Developing an efficient catalyst for controlled oxidation of small alkanes under ambient conditions

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Methods Summary

The synthesis and spectroscopic characterization of the **7-N-Etppz** ligand as well as the preparation of the [$Cu^ICu^ICu^I$(**7-N-Etppz**)](ClO_4) complex have been described earlier.[1] We have also followed the oxidation of the $Cu^ICu^ICu^I$ complex by O_2 in the absence of substrate by UV-visible spectroscopy. The spectral results support the formation of the [$Cu^{II}Cu^{II}$(μ-O)Cu^{II}(**7-N-Etppz**)](ClO_4)$_2$ species (Figure S1) as has been reported previously.[2-4]

As the reduced tricopper complex is extremely air sensitive, it is necessary to perform the substrate oxidation experiments under a purified nitrogen atmosphere inside the glove box. The reaction mixture is vigorously stirred with a magnetic stirring bar for various times up to 1 h using different sample bottles. At designated intervals, a sample bottle is removed from the glove box for identification of the products and determination of product yields by GC. 3 μl of nitrobenzene is added to the solution to provide an internal stranded (IS) for quantitation of the products (Figure S2).

References:

1 S. I. Chan, Y. J. Lu, P. Nagababu, S. Maji, M. C. Hung, M. M. Lee, I. J. Hsu, P. D. Minh, J. C. H. Lai, K. Y. Ng, S. Ramalingam, S. S.-F. Yu and M. K. Chan, *Angew. Chem. Int. Ed.*, 2013, **52**, 3731–3735.

2 S. I. Chan, C. Y.-C. Chien, C. S.-C. Yu, P. Nagababu, S. Maji and P. P.-Y. Chen, *J. Catal.*, 2012, **293**, 186–194.

3 P. P.-Y. Chen, R. B.-G. Yang, J. C.-M. Lee and S. I. Chan, *Proc. Nat. Acad. Sci. USA*, 2007, **104**, 14570–14575.

4 P. Nagababu, S. Maji, M. P. Kumar, P. P.-Y. Chen, S. S.-F. Yu and S. I. Chan, *Adv. Synth. Catal.* 2012, **354**, 3275–3282.

GC Analysis of Oxidation Products

Before product analysis of the solutions by GC after hydrocarbon oxidation, the solutions were passed through a flash chromatography column (silica gel) to remove the metal complexes. GC analyses were performed on a HP6890 plus equipped with a flame ionization detector. For gas substrates (methane, ethane, propane and *n*-butane), the conditions were as follows: HP5 column (60 m × 0.25 mm × 0.25 mm film thickness); carrier gas, nitrogen at a flow rate of 1 ml/min; oven temperature, isothermal at 30 °C; pulsed splitless injection at 280 °C, (25.0 psi for 30 sec and 17.5 psi for the rest of the acquisition time); and FID detector at 300 °C. For liquid substrates (*n*-pentane, *n*-hexane, cyclohexane and cyclohexene), the conditions were as follows: HP5 column (60 m × 0.25 mm × 0.25 mm film thickness); carrier gas, nitrogen at a flow rate of 1 ml/min; oven temperature, isothermal at 120 °C; splitless injection at 280 °C, (36.9 psi for 30 sec and 10 psi for the rest of the acquisition time); and FID detector at 300 °C.

Control Experiments

1. Control experiments were performed according to the procedures described in the text without the ligand **7-N-Etppz** but with the complex $[Cu(MeCN)_4](ClO_4)$. No oxidation of methane or ethane was observed. Only very low reactivity was observed with the remaining substrates. (Table S1 and Figure S3)

2. Control experiments were also performed with H_2O_2 alone, without either the ligand **7-N-Etppz** or the complex $[Cu(MeCN)_4](ClO_4)$. No oxidation of substrate was evident. (Table S1).

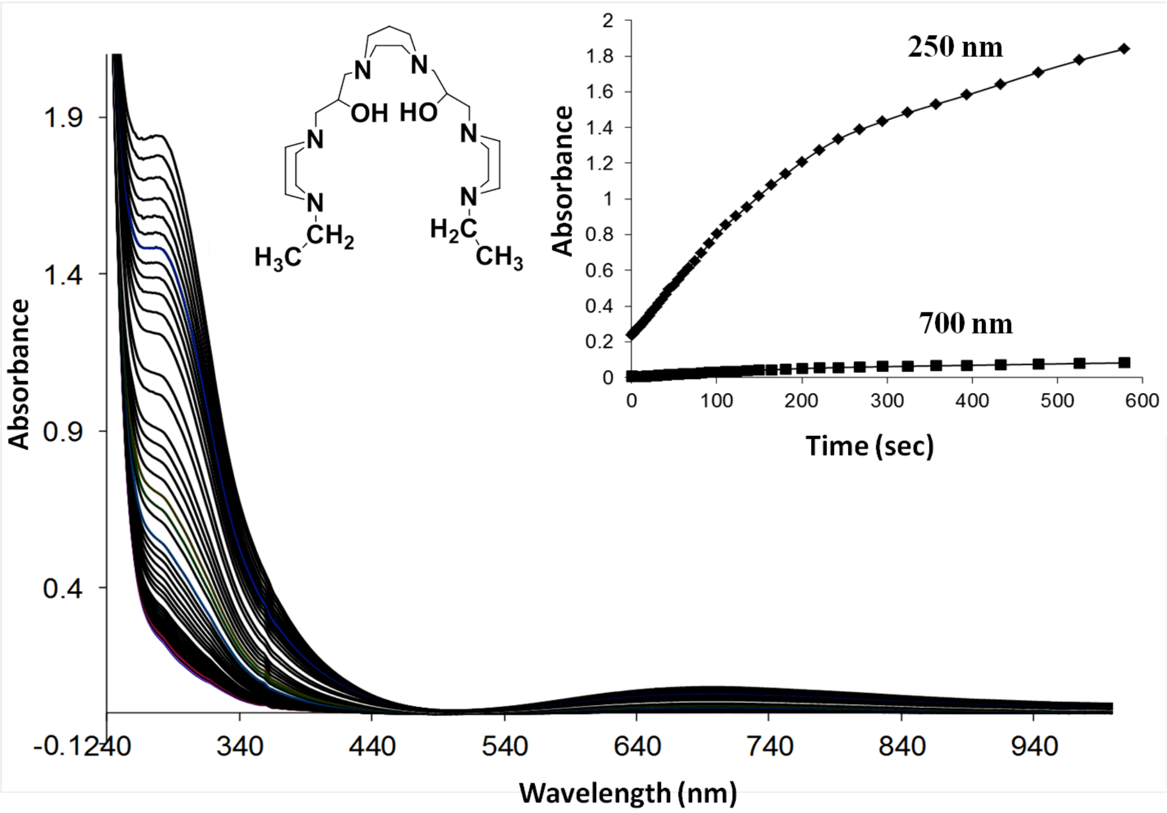
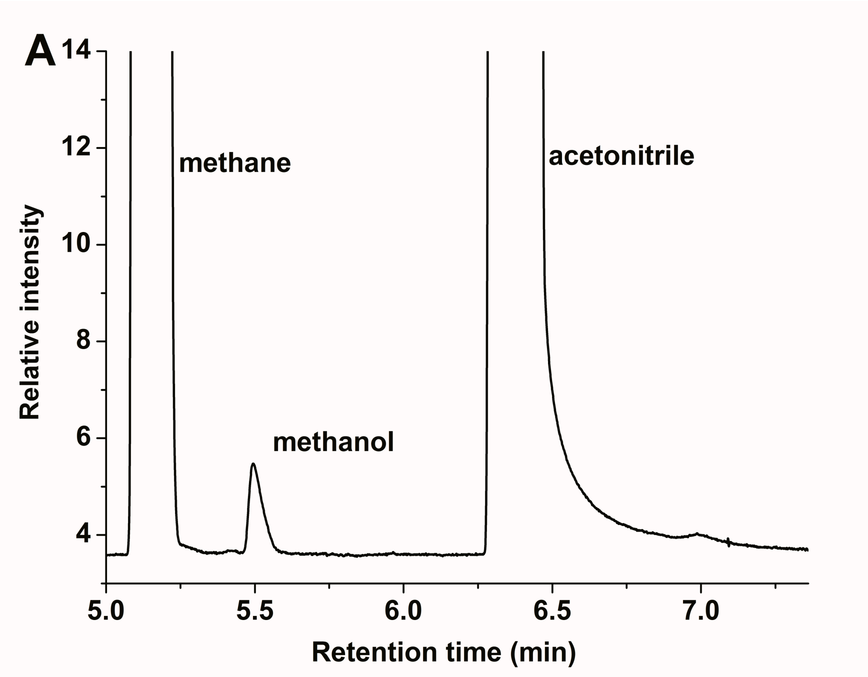
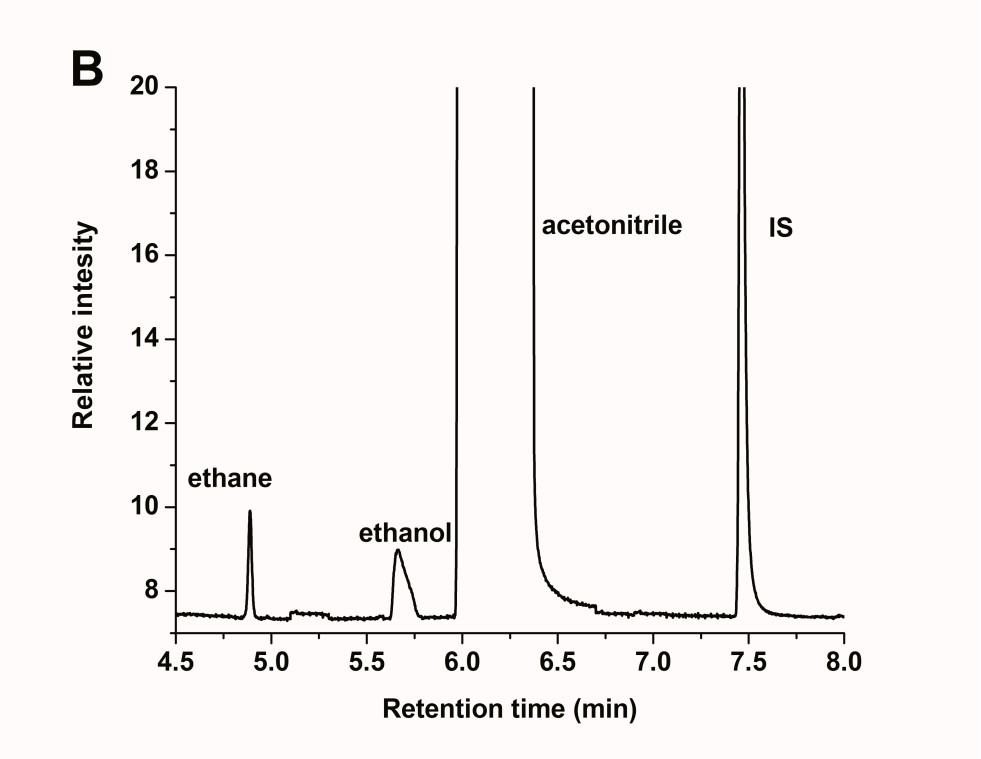
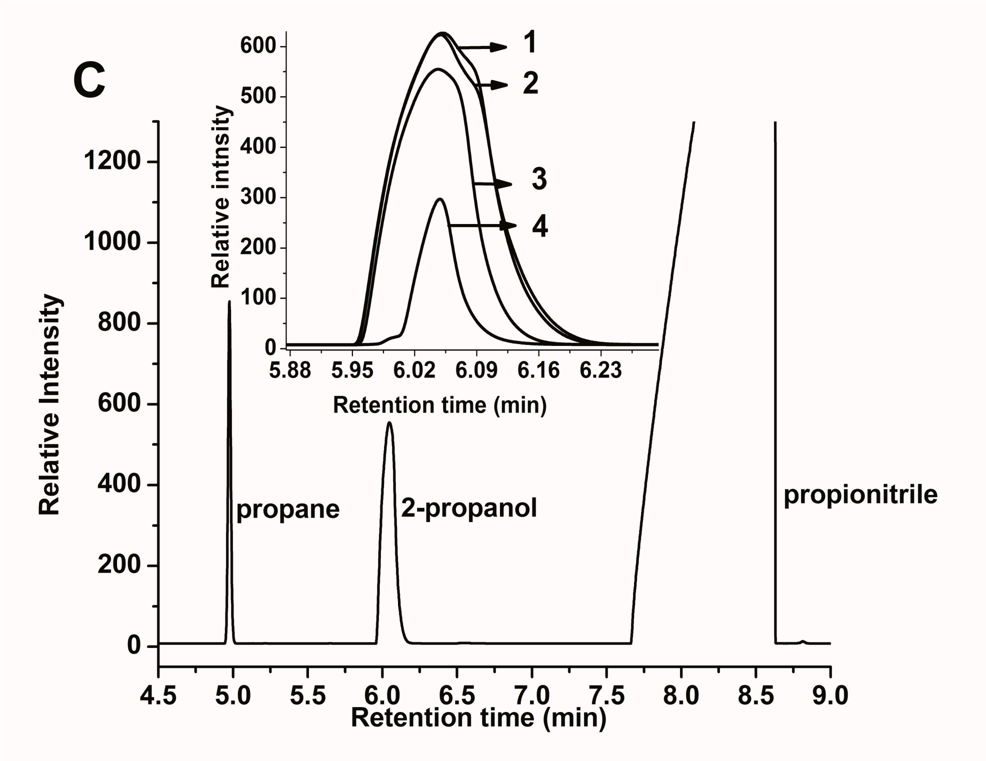
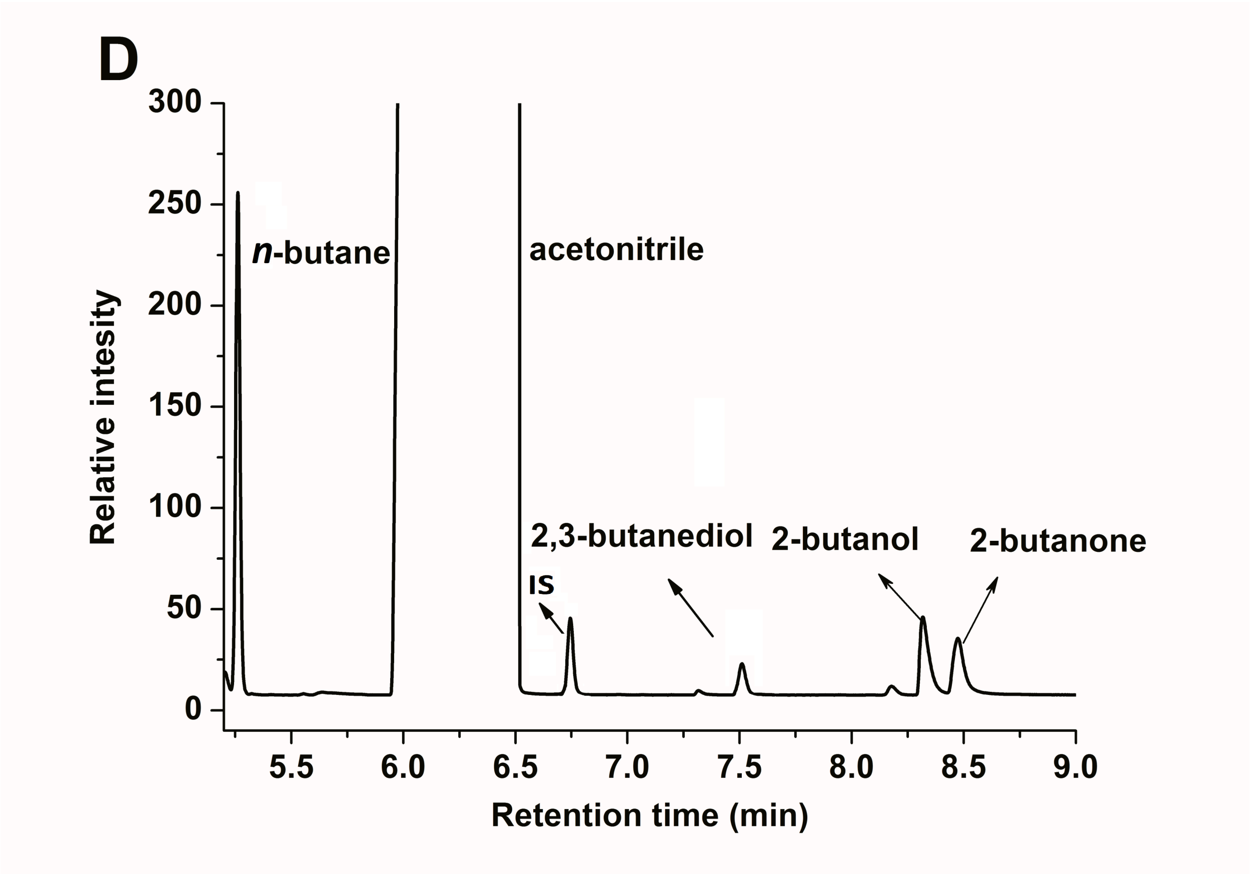


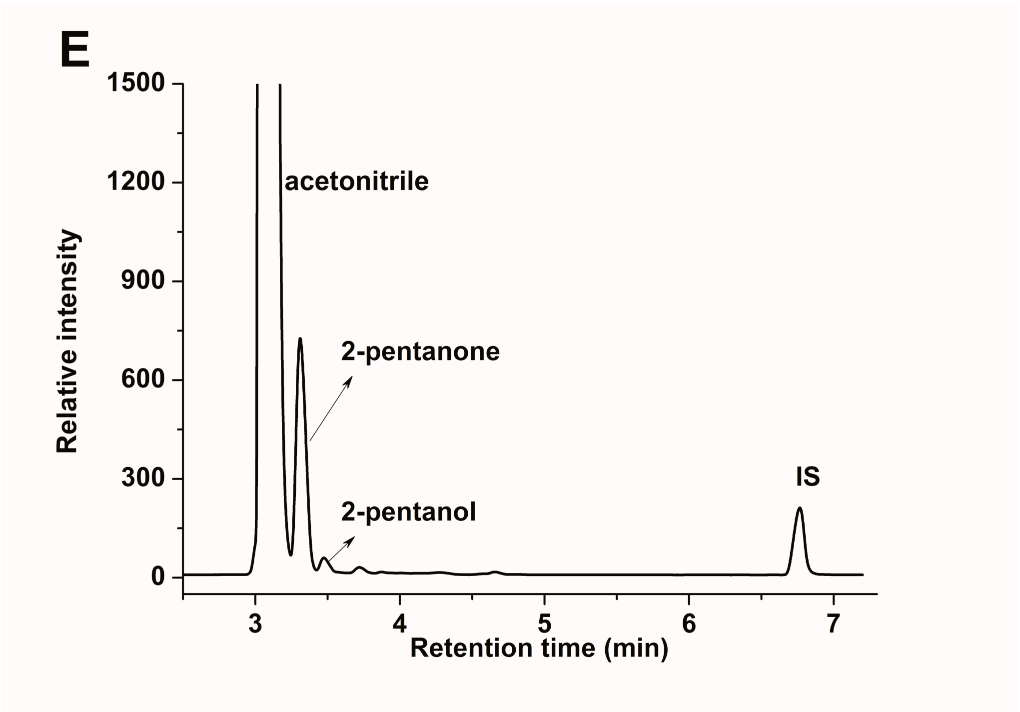
Figure S1 | Spectral changes observed in the UV-visible region upon mixing of O_2-saturated MeCN with a 0.5 mM solution of [Cu^{I}Cu^{I}Cu^I(**7-N-Etppz**)](ClO$_4$) (total volume 3 ml) at room temperature.

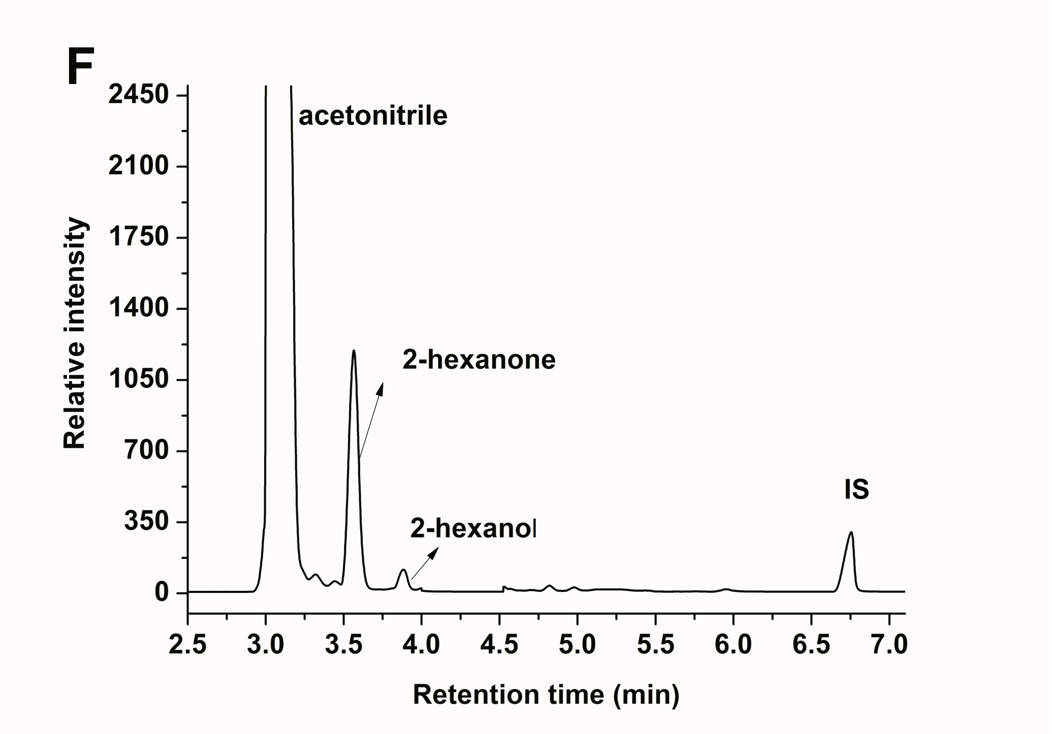

A
14
12
10
8
6
4
Relative intensity
methane
methanol
acetonitrile
5.0
5.5
6.0
6.5
7.0
Retention time (min)

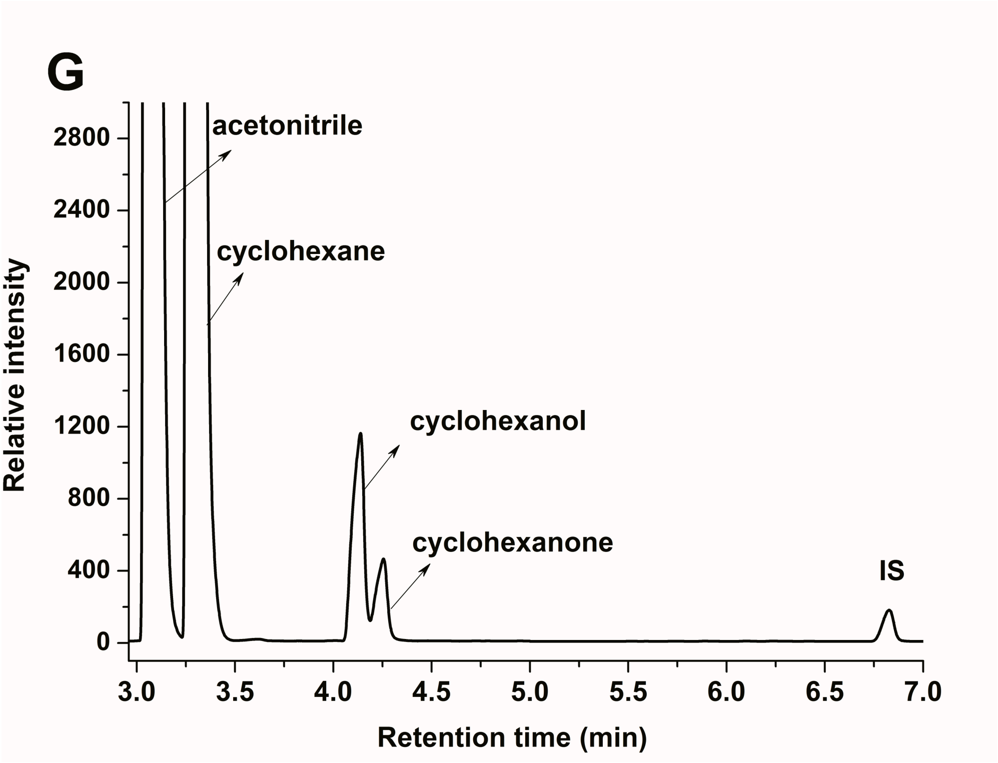

B
20
18
16
14
12
10
8
Relative intesity
ethane
ethanol
acetonitrile
IS
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
Retention time (min)


C
Relative Intensity
0
200
400
600
800
1000
1200
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
Retention time (min)
propane
2-propanol
propionitrile
Relative intnsity
0
100
200
300
400
500
600
5.88
5.95
6.02
6.09
6.16
6.23
Retention time (min)
1
2
3
4


D
Relative intesity
0
50
100
150
200
250
300
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
Retention time (min)
n-butane
acetonitrile
IS
2,3-butanediol
2-butanol
2-butanone


E
1500
1200
900
600
300
0
Relative intensity
acetonitrile
2-pentanone
2-pentanol
IS
3
4
5
6
7
Retention time (min)


F
2450
2100
1750
1400
1050
700
350
0
Relative intensity
acetonitrile
2-hexanone
2-hexanol
IS
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
Retention time (min)


G
acetonitrile
cyclohexane
cyclohexanol
cyclohexanone
IS
Relative intensity
0
400
800
1200
1600
2000
2400
2800
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
Retention time (min)

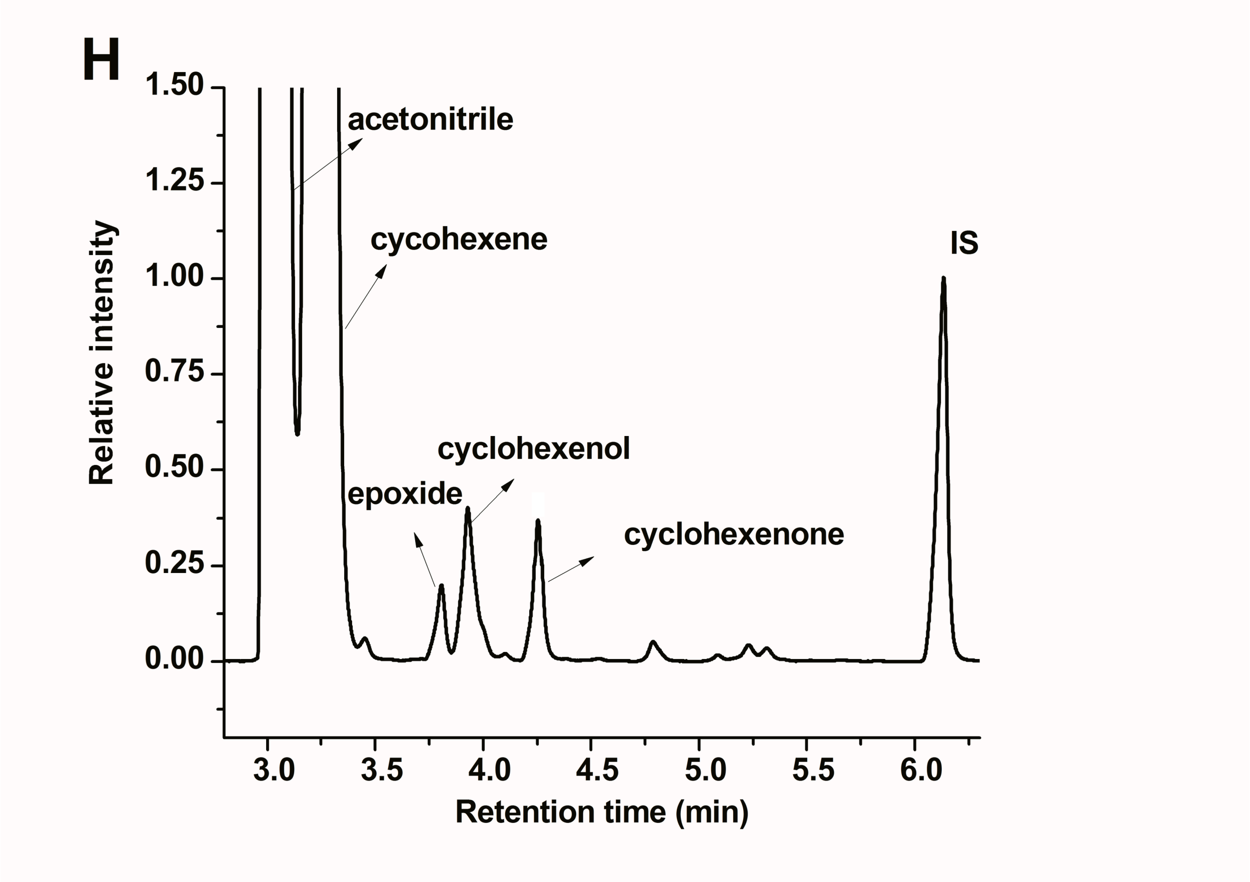

H
acetonitrile
cycohexene
epoxide
cyclohexenol
cyclohexenone
IS
Relative intensity
0.00
0.25
0.50
0.75
1.00
1.25
1.50
3.0
3.5
4.0
4.5
5.0
5.5
6.0
Retention time (min)

Figure S2 | GC-chromatograms showing the oxidation of different hydrocarbon substrates by H_2O_2 mediated by 22.7 μmoles (1 equiv.) of [Cu^{I}Cu^{I}Cu^I(**7-N-Etppz**)**]**(ClO$_4$). (**A**) Conversion of methane to methanol (t_R: 5.54 min) in the presence of 20 equiv. of H_2O_2; (**B**) ethane to ethanol (t_R: 5.6 min) in the presence of 100 equiv. of H_2O_2; (**C**) propane to 2-propanol (t_R: 6.04 min) in the presence of 100 equiv. of H_2O_2; EtCN is used as the solvent in this experiment due to interference between the product (2-propanol) peak and the solvent peak with MeCN; time course of the oxidation is shown in *inset*: **4**, after 5 min; **3**, after 10 min; **2**, after 20 min; and **1**, after 30 min; (**D**) *n*-butane to 2-butanol (t_R: 8.39 min), 2-butanone (t_R: 8.55 min), and 2,3-butanediol (t_R: 7.65 min) in the presence of 100 equiv. of H_2O_2 ; (**E**) *n*-pentane to 2-pentanol (t_R: 3.47 min) and 2-pentanone (t_R: 3.32 min) in the presence of 200 equiv. of H_2O_2; (**F**) *n*-hexane to 2-hexanol (t_R: 3.8 min) and 2-hexanone (t_R: 3.56 min) in the presence of 200 equiv. of H_2O_2; (**G**) cyclohexane to cyclohexanol (t_R: 4.1 min) and cyclohexanone (t_R: 4.2 min) in the presence of 200 equiv. of H_2O_2; and (**H**) cyclohexene to cyclohexene oxide (t_R: 3.94 min), cyclohexenol (t_R: 4.09 min), and cyclohexenone (t_R: 4.48 min) in the presence of 200 equiv. of H_2O_2. Quantification of the products is determined by co-injection of a nitrobenzene ($C_6H_6NO_2$) internal standard (IS).

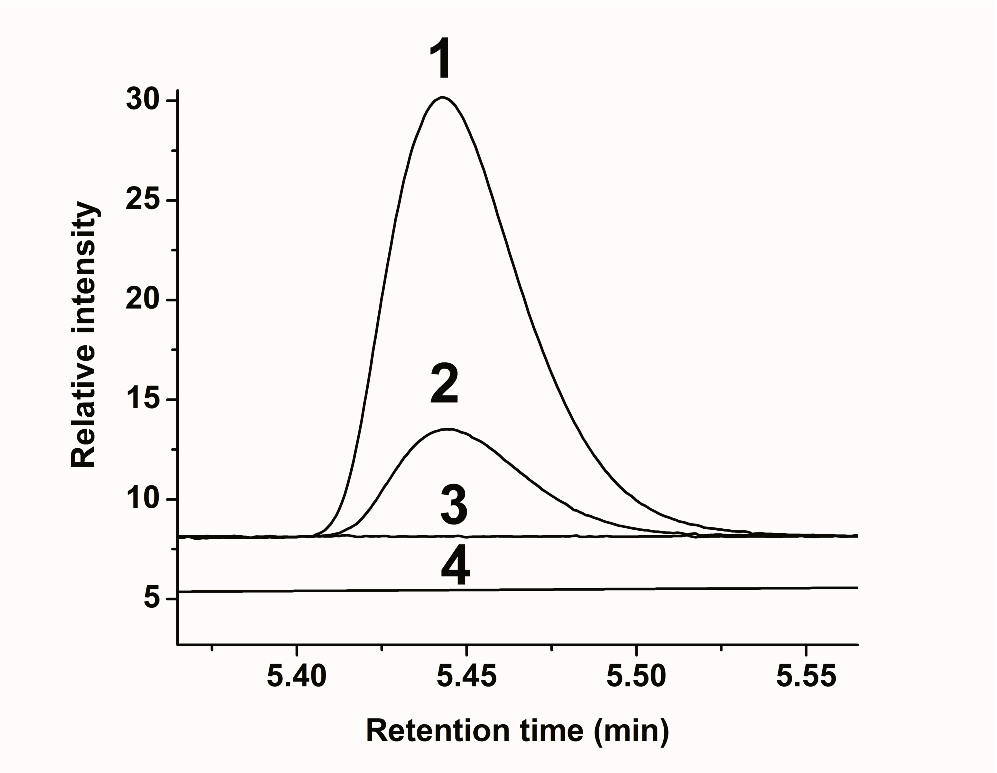


Figure S3 | Control experiments on the oxidation of methane. **1**: methanol (2.4×10^{-5} mole) in MeCN (3 ml); **2**: a reaction mixture containing initially 1 equiv. (22.7 μmoles) of [Cu^{I}Cu^{I}Cu^{I}(**7-N-Etppz**)**]**(ClO_4), 4.17×10^{-3} moles of methane, and 20 equiv. of H_2O_2 in MeCN (3 ml) after 1 h; **3**: a reaction mixture containing initially 1 equiv. of [Cu(**MeCN**)$_4$**]**ClO_4, 4.17×10^{-3} moles of methane, and 20 equiv. of H_2O_2 in MeCN (3 ml) after 1 h; and **4**: 4.17×10^{-3} moles of methane and 20 equiv. of H_2O_2 in MeCN (3 ml) after 1 h of incubation.

Table S1. Control experiments on the oxidation of hydrocarbons

Conditions	**Substrate**	**TON**
$Cu^I[(CH_3CN)_4](ClO_4)$ (10 mg) + H_2O_2 (100 equiv.) in MeCN (3 ml) only (without the **7-N-Etppz** ligand) 1 h incubation	methane	××[a]
	ethane	××[a]
	propane	1
	n-butane,	1
	n-pentane	1.3
	n-hexane	1.7
	cyclohexane	2.2
	cyclohexene	2.6
H_2O_2 (100 equiv.) in MeCN (3 ml) only (without the $Cu^ICu^ICu^I$(**7-N-Etppz**) complex) 1 h incubation	methane, ethane, propane and *n*-butane, *n*-pentane, *n*-hexane, cyclohexane and cyclohexene	××[a]

[a] No products detected.