Supplementary Information

for

Heterogeneous formulation of the tricopper complex for efficient catalytic conversion of methane into methanol under ambient temperature and pressure

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A. Synthesis of ligands and preparation of tricopper complexes

Preparation of 3,3'-[1,4-diazepane-1,4-diyl]bis(1-chloropropan-2-ol) (1). A solution of epichlorohydrin (1.85 g, 20 mmol) dissolved in methanol (15.0 ml) was added drop-wise to a solution of homopiperazine (1.02 g, 10 mmol) dissolved in methanol (30.0 ml) and stirred at 5 °C. After stirring for 72 h at 5 °C, the resulting mixture was purified by column chromatography on silica gel using a mixed solvent (8% CH_3OH in CH_2Cl_2) as the eluent. Compound **1** was obtained in 88% yield (2.50 g).

Synthesis of the ligand (3,3'-(1,4-diazepane-1,4-diyl)bis[1-(4-ethylpiperazine-1-yl) propan-2-ol]) (7-N-Etppz). K_2CO_3 (4.15 g, 30 mmol) was added to a CH_3CN (15.0 ml) solution containing compound **1** (4.28 g, 15 mmol), and 1-ethylpiperazine (3.46 g, 30 mmol). The mixture was then heated to 70-80 °C for 48 h under a N_2 atmosphere. After cooling to room temperature, the solution was filtered, and upon evaporation of the filtrate to dryness, the ligand **7-N-Etppz** was obtained. ^{1}H NMR ($CDCl_3$, 300 MHz): 1.8 (t, 2H, CH_3); 2.05-2.93 (m, CH_2); 3.6 (s, 2H, CH), 4.4 (s 2H, CH). ^{13}C NMR (300 MHz, $CDCl_3$): the major peaks appeared at 11.74, 11.82, 27.10, 52.0, 52.5, 53.2, 54.4, 55.3, 62.2, 62.4, and 64.7. The ESI-MS (positive ion): m/z 441.

Synthesis of the ligand (3,3'-(1,4-diazepane-1,4-diyl)bis[1-(4-ethylhomopiperazine -1-yl)propan-2-ol]) (7-N-Ethppz). Following the same procedure as above, **7-N-Ethppz** was prepared by mixing compound **1** (4.29 g, 15 mmol) with 1-ethylhomopiperazine (3.80 g, 30 mmol). Yield: 80% (5.6 g). ^{1}H NMR ($CDCl_3$, 300 MHz): 1.11 (s, 4H, CH_3), 1.14 (m, 4H CH_2), 1.15 (d, 6H, CH_2), (m, 16H, CH_2), 2.41-2.88 (m, 8H, CH_2), 3.13 (d, 2H, CH). ^{13}C NMR (300 MHz, $CDCl_3$): 12.2, 25.4, 46.2, 52.3, 52.5, 52.7, 54.2, 62.0 and 65.5. The ESI-MS (positive ion): m/z 469.

Preparation of the $Cu^{II}Cu^{II}Cu^{II}$ tricopper complex, Cu_3(7-N-Etppz). A anhydrous CH_3CN solution (25 ml) containing **7-N-Etppz** (2.205 g, 5.0 mmol) and three equivalents of $Cu^{II}(ClO_4)_2 \cdot 6H_2O$ (5.49 g, 15.1 mmol) were mixed and stirred for 1 h to give a deep green solution, which was filtered, washed with CH_2Cl_2, and dried in vacuum to give a green powder. The calculated yield was 4.00 g (95%). The elemental analysis of $C_{23}H_{46}O_{11}N_6Cl_2Cu_3$ gave C, 32.77; H, 5.50; N, 9.94%, which were the same as the calculated values within experimental uncertainty: C, 32.72; H, 5.49; N, 9.96%. The ESI-MS (positive ion): m/z 844.02.

Preparation of the $Cu^{II}Cu^{II}Cu^{II}$ tricopper complex, Cu_3(7-N-Ethppz). A anhydrous CH_3CN solution (25 ml) containing **7-N-Ethppz** (2.345 g, 5.0 mmol) and three equivalents of $Cu^{II}(ClO_4)_2 \cdot 6H_2O$ (5.49 g, 15.1 mmol) were mixed and stirred for 1 h to give a blue solution, which was filtered, washed with CH_2Cl_2, and dried in vacuum to give a blue powder. The calculated yield was 4.23 g (97%). The elemental analysis of $C_{25}H_{50}O_{11}N_6Cl_2Cu_3$ gave C, 34.48; H, 5.82; N, 9.60%, which were the same as the calculated values within experimental uncertainty: C, 34.42; H, 5.78; N, 9.63%. The ESI-MS (positive ion): m/z 872.09.

B. Supplementary Figures S1-S7

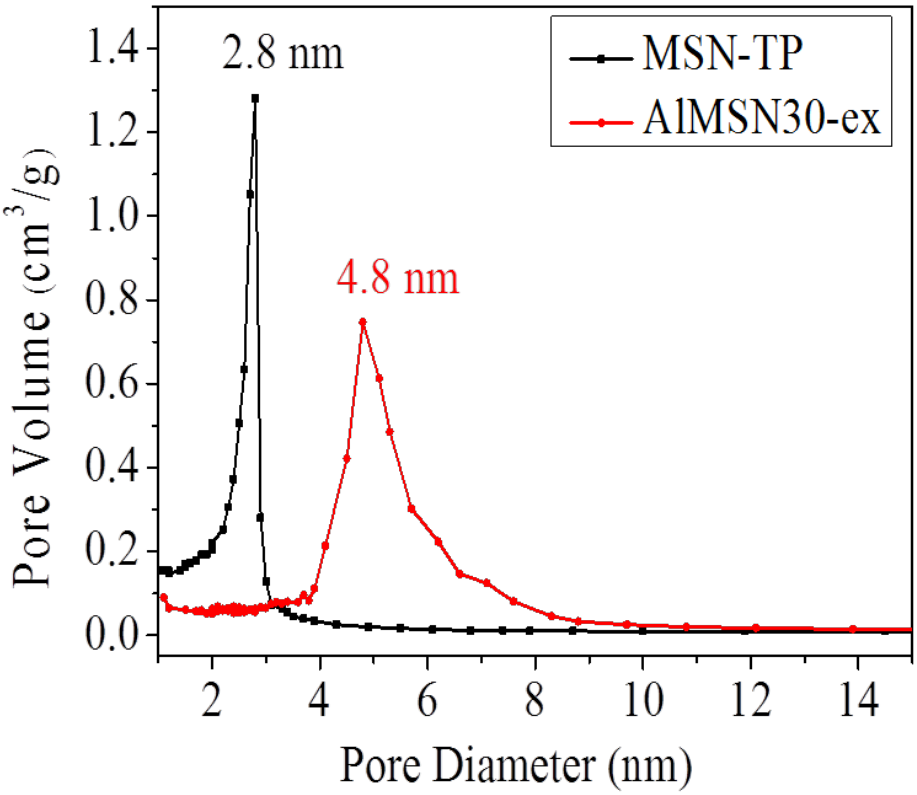

Fig. S1. Plots of the pore size distribution of the MSN-TP and AlMSN30-ex samples. The pore size is 2.8 ± 0.14 nm for the MSN-TP sample and is 4.8 ± 0.57 nm for the AlMSN30-ex sample.

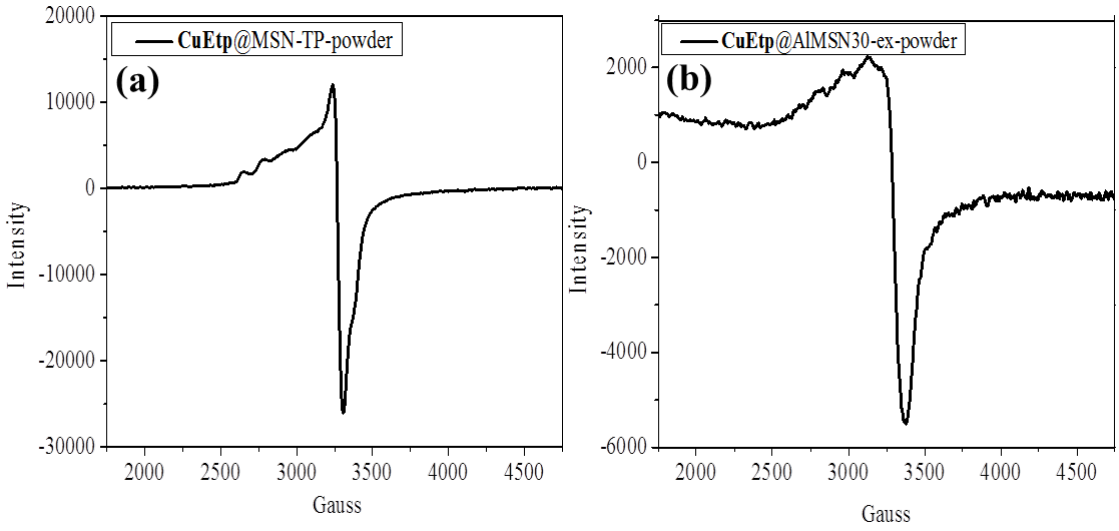

Fig. S2. X-band EPR spectra of MSN samples at 77 K: (**a**) **CuEtp**@MSN-TP; and (**b**) **CuEtp**@AlMSN30-ex. Conditions: Microwave frequency: 9.45 GHz; microwave power: 10 mW; and modulation amplitude: 8 G.

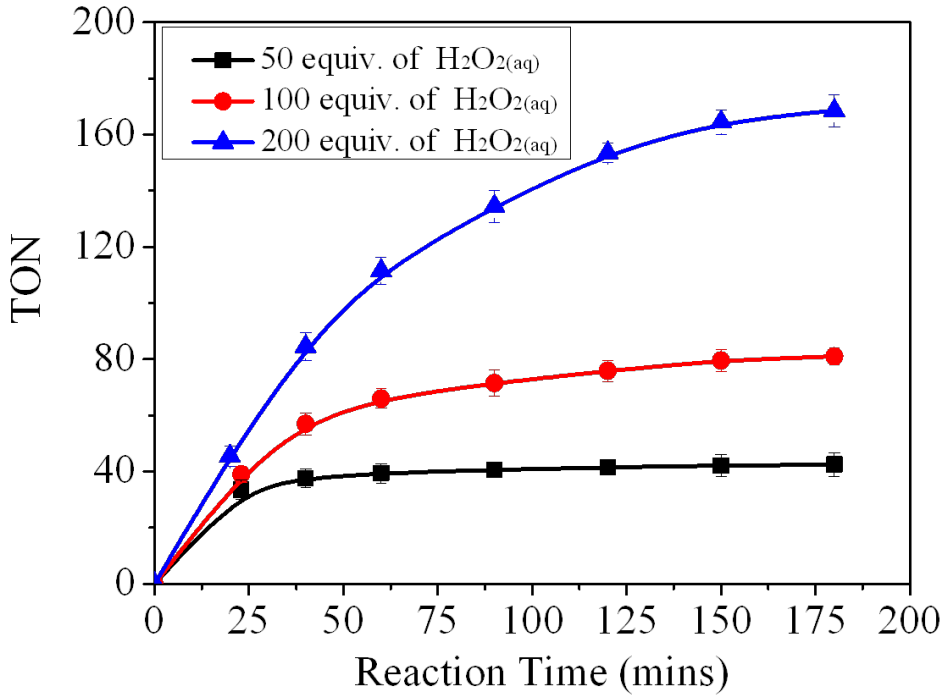

Fig. S3. Time course of the TONs for the methane oxidation reaction catalyzed by the best performing catalyst, **CuEtp**@AlMSN30-ex, at room temperature using different amounts of H_2O_2 (equiv.) to drive the catalytic turnover.

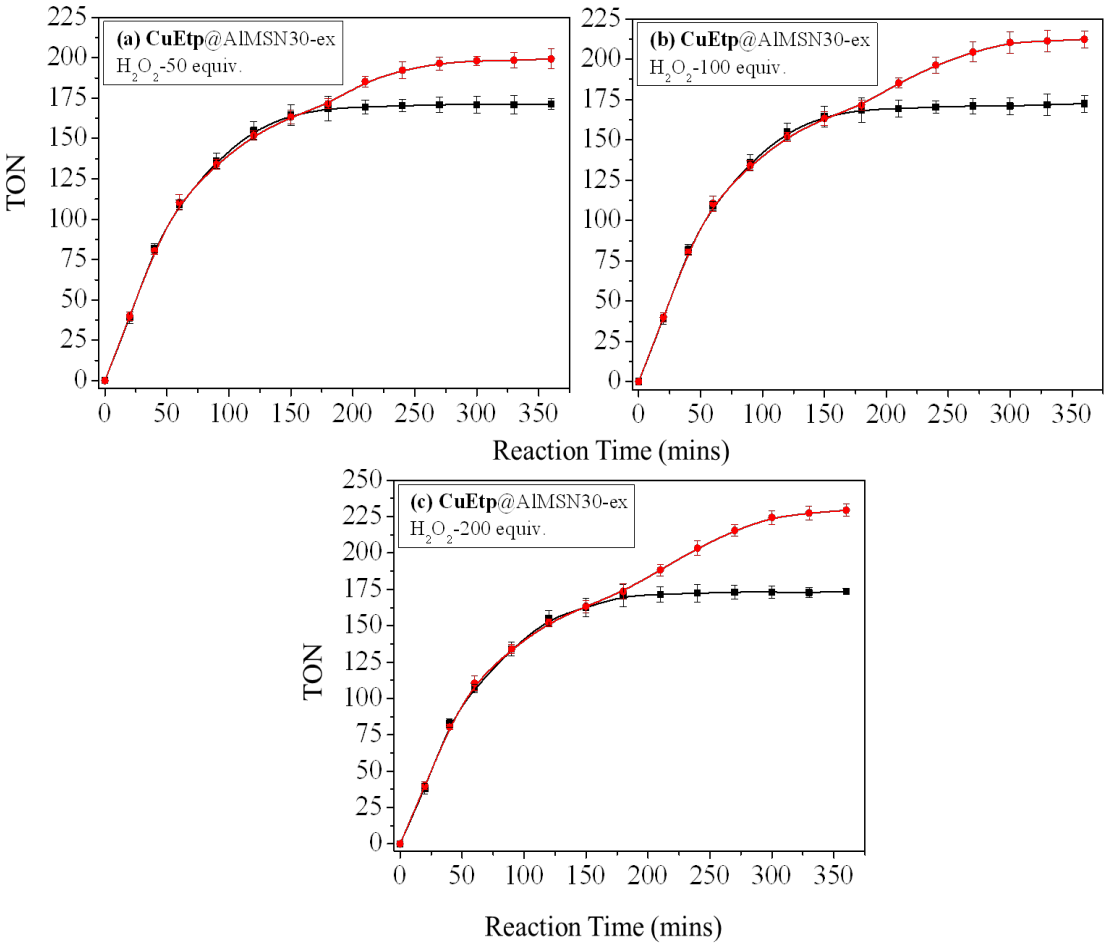

Fig. S4. Sustaining the catalytic turnover of the tricopper complex toward methane oxidation mediated by $[Cu^{I}Cu^{I}Cu^{I}(\textbf{7-N-Etppz})]^{1+}$ immobilized in the **CuEtp**@AlMSN30-ex formulation. The turnover was first initiated by 200 equiv. of H_2O_2 in the presence of 100 ml of CH_4 (986 equiv.) and 10 ml of O_2 (98.6 equiv.), and the time course of the TON for the methane oxidation reaction was monitored for 3 h at room temperature. At the end of this period, the sample was re-purged with 50 equiv. of methane and the TON monitored up to 6 h without the introduction of additional H_2O_2 (black line); or with the introduction of additional H_2O_2: (**a**) 50 equiv.; (**b**) 100 equiv.; and (**c**) 200 equiv. Adding 50 equiv. of methane (black line) did not increase the turnover number of methanol because the H_2O_2 used to initiate the original turnover had already been consumed during the first 3 h. However, further methane oxidation was observed up to 6 h with the injection of a new aliquot of H_2O_2.

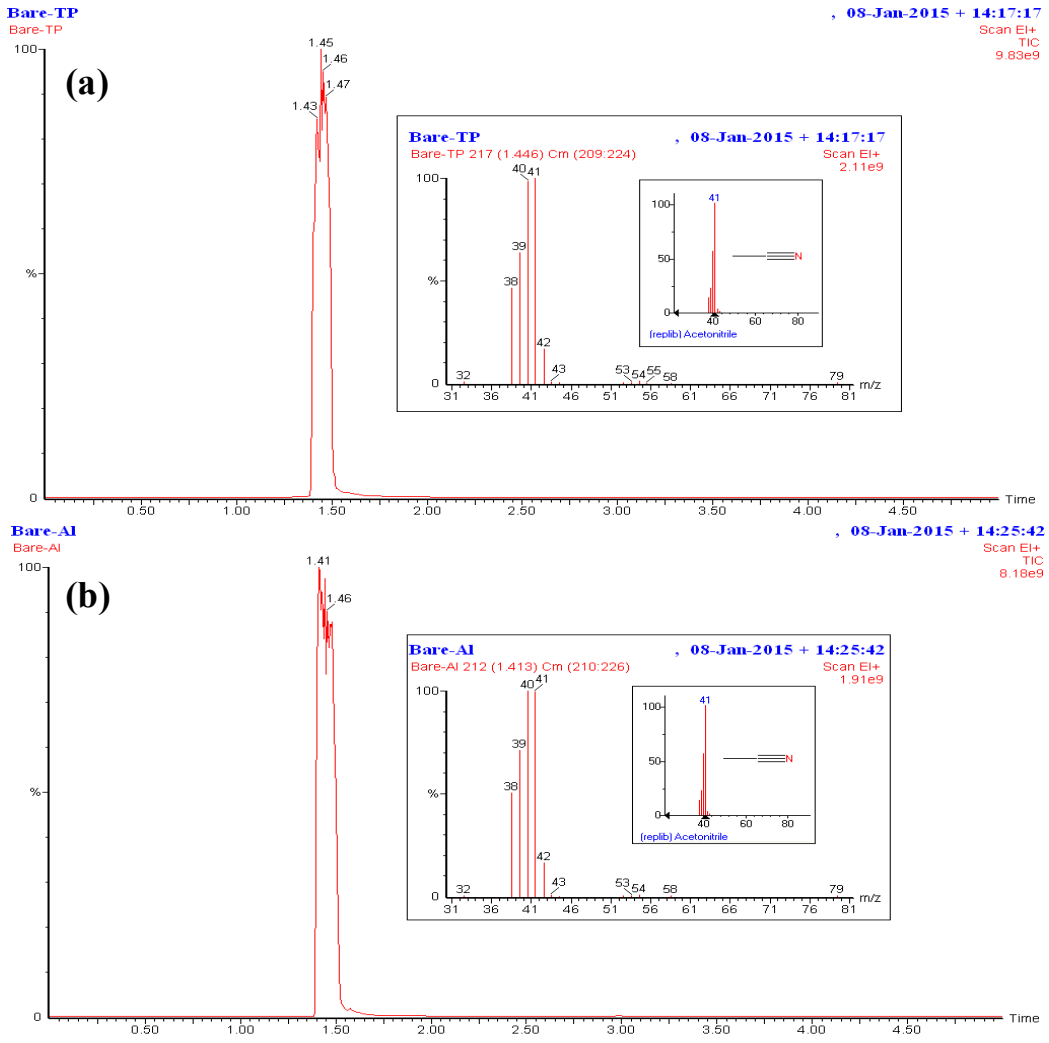

Fig. S5. GC-MS spectra of the products observed in the methane oxidation reaction attempted using the (**a**) bare MSN-TP sample, and (**b**) bare AlMSN30-ex sample, for 3 h. These control experiments were performed according to the same procedures used in the methane oxidation reaction mediated by the *quasi*-heterogeneous tricopper complex formulations. 20 mg of the bare MSN-TP or bare AlMSN30-ex samples was first suspended in O_2-free acetonitrile (5 ml) in a 50 ml Schlenk flask. The samples were then purged with O_2 (10 ml at STP, 0.44 mmol) and CH_4 (100 ml STP, 4.4 mmol). Finally, an aliquot of 200 equiv. of H_2O_2 was injected into the sample after adding the amounts of sodium ascorbate solution typically used in the methane oxidation with the tricopper complex-immobilized MSN samples. The heterogeneous mixture suspension was then stirred vigorously at room temperature for 3 h and analyzed by using GC-MS. No oxidation products were observed. *Inset*: The fitted MS spectrum from the built-in MS database software.

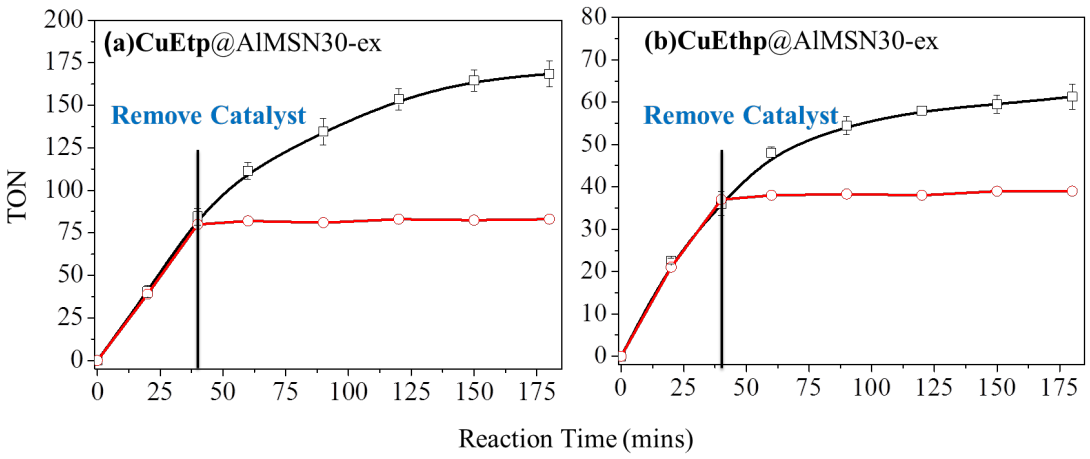

Fig. S6. Time course of the TONs for the methane oxidation reaction catalyzed by (**a**) **CuEtp**@AlMSN30-ex, and (**b**) **CuEthp**@AlMSN30-ex samples at room temperature with 200 eq. of H_2O_2 (black line). In each case, a parallel experiment was also conducted under the same conditions, except that the catalytic turnover was interrupted 40 min into the experiment to quickly separate and remove the MSNs from the liquid phase by centrifugation. Measurement of the catalytic activity was then continued on the supernatant until the end of the 3-h experiment (red line). No catalytic activity was observed for the supernatant.

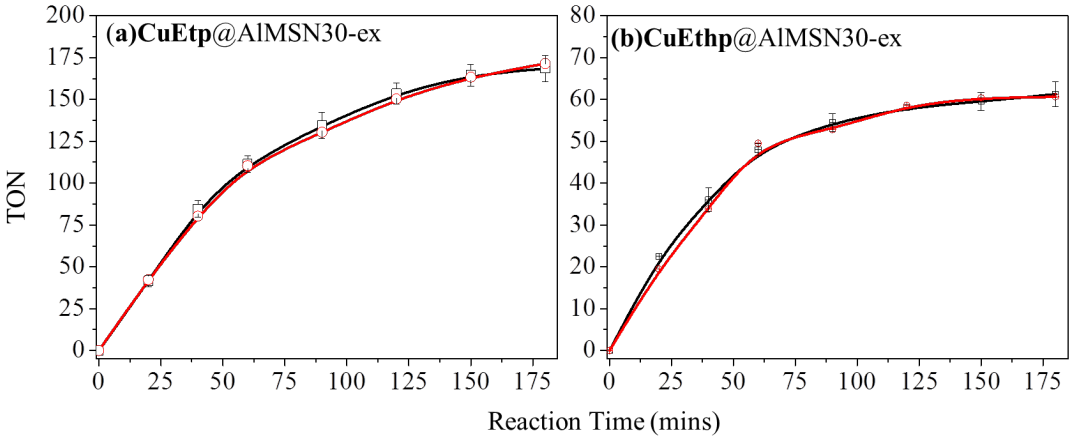

Fig. S7. Comparison of the time courses of the methane oxidation reaction mediated by (**a**) **CuEtp**@AlMSN30-ex, and (**b**) **CuEthp**@AlMSN30-ex at room temperature in the absence (black line) and presence (red line) of the radical trapping agent 2,6-di-*tert*-butyl-*p*-cresol (1 equiv., based on the amount of the immobilized tricopper complexes in the AlMSN30-ex samples). The TONs of the products are expressed in terms of the moles of product formed per mole of the tricopper complex in each case.

Supplementary Table

Table S1. Time course of leaching of the tricopper $Cu^{II}Cu^{II}Cu^{II}$ complexes from the MSNs at 25 ^{o}C.

Sample	**CuEtp@MSN-TP**	**CuEthp@MSN-TP**	**CuEtp@AlMSN30-ex**	**CuEthp@AlMSN30-ex**
Time (h)	Released (ppm)	Released (ppm)	Released (ppm)	Released (ppm)
0	0	0	0	0
0.5	4	4	2	3
1.0	6	7	5	6
2.0	10	12	8	11
4.0	14	15	11	13
6.0	16	20	13	16
8.0	18	24	16	18
10.0	22	26	18	20