Electronic Supplementary Information

Zeolite encapsulated copper(II) complexes with NNO-tridentate Schiff base ligands: catalytic activity towards methylene blue (MB) degradation in a near neutral condition

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# Electronic Supplementary Information

Contents

Characterization

Characterization

NMR spectra were obtained on a Bruker 400MHz NMR spectrometer. FT-IR spectra were investigated on the Thermo-Nicolet IR200 in the range of 500-4000 cm^{-1} using KBr as a reference. The SEM-EDX analysis has been performed by using ZEISS Sigma 300 scanning electron microscope. Powder XRD patterns of the samples were investigated on the Persee XD-6 diffractometer using Cu-Kα radiation (λ = 1.542 Å). X-ray crystal structures were characterized by using a Bruker D8 VENTURE detector. The content of copper was analyzed using inductive coupled plasma mass spectrometry after the sample was treated with nitric acid. TGA analyses were studied from 40 to 800 °C at a heating rate of 10 °C·min^{-1} on a NETZSCH thermoanalyzer TG209 F3 under an atmosphere of N_2. XPS analysis was performed on a PreVac XPS-2 system by using Al Kα X-ray source (1486.6 eV). All binding energies of the samples were calibrated with the adventitious C 1s peak at 284.6 eV to compensate the charging effect. The BET surface area and pore volume have been characterized using nitrogen sorption data at 77 K with a volumetric adsorption setup (Micromeritics ASAP 2460). The electronic spectra in the solid state were obtained using Shimadzu UV-3600 plus spectrometer. UV-vis absorption spectra have been obtained on the Persee TU-1950 spectrophotometer for liquid samples. High-performance liquid chromatogram (HPLC) analysis was carried out on Waters 2695, and corresponding electrospray ionization mass spectrometry (ESI-MS) was recorded on Waters ZQ2000. High-resolution mass spectra (HRMS) were recorded on a Waters Xevo G2-XS QTof spectrometer (ESI+). Elemental analysis measurements were conducted on Elementar UNICUBE elemental analyzer.

1. Scheme S1:
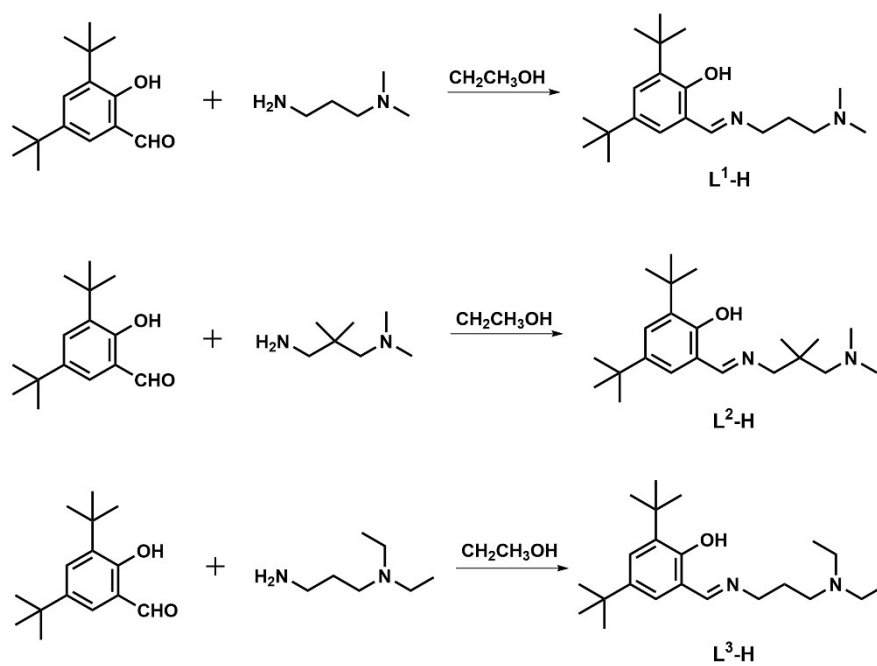
Scheme S1. Synthesis of Schiff Ligand L^1-H, L^2-H and L^3-H.

2. Figure S1:
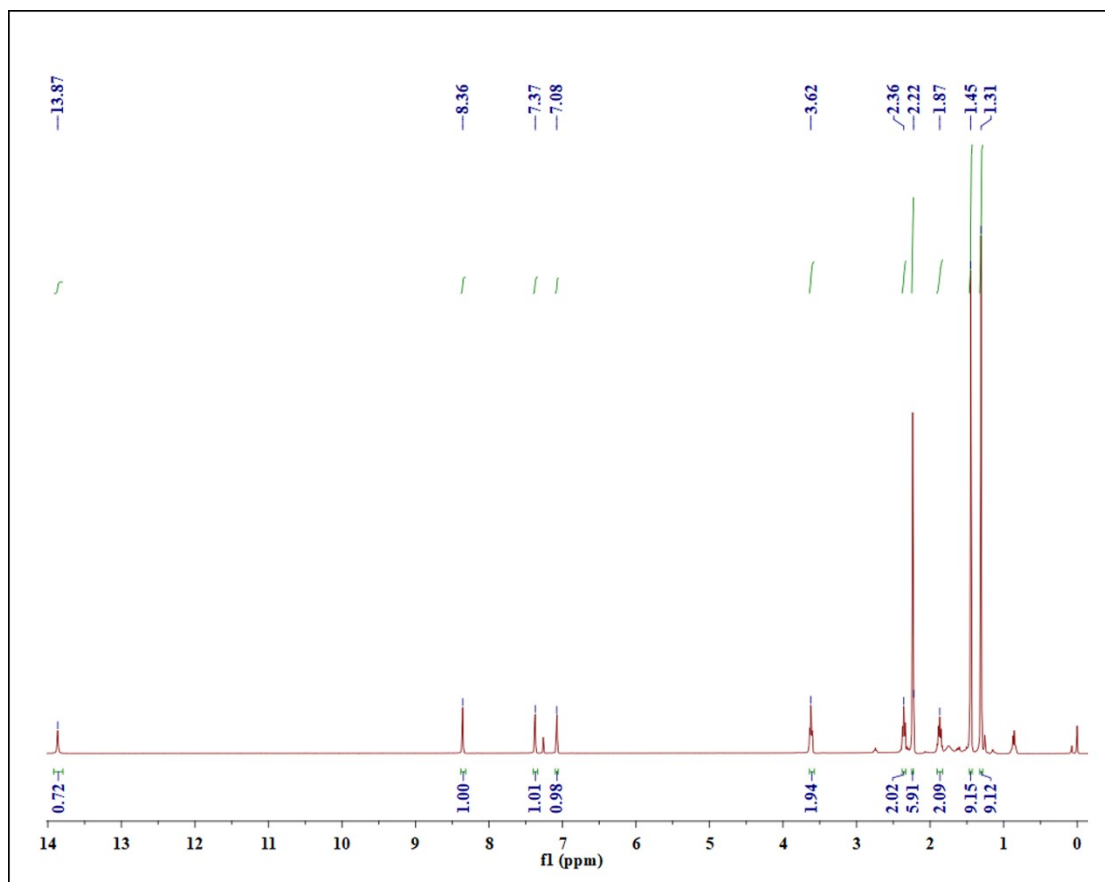
Figure S1. ^{1}H NMR of ligand L^1-H in CDCl$_3$.

3. Figure S2:
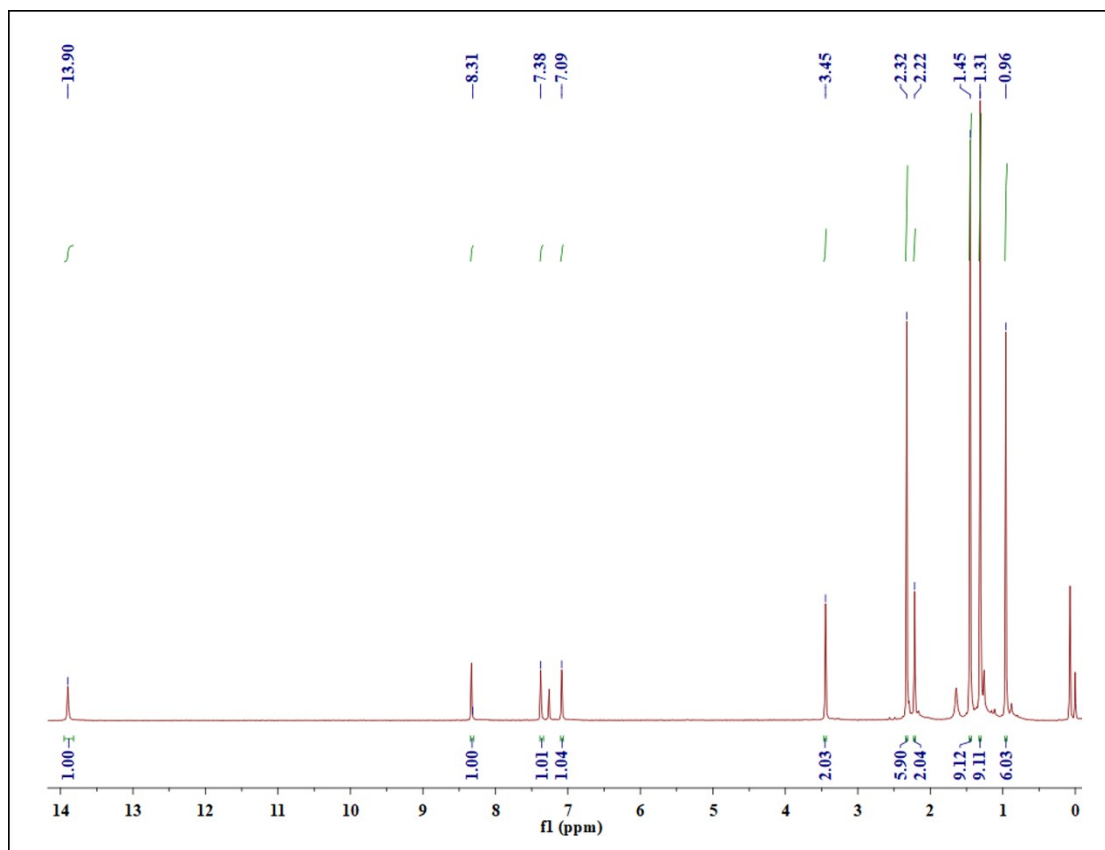
Figure S2. ^{1}H NMR of ligand L^2-H in CDCl$_3$.

4. Figure S3:
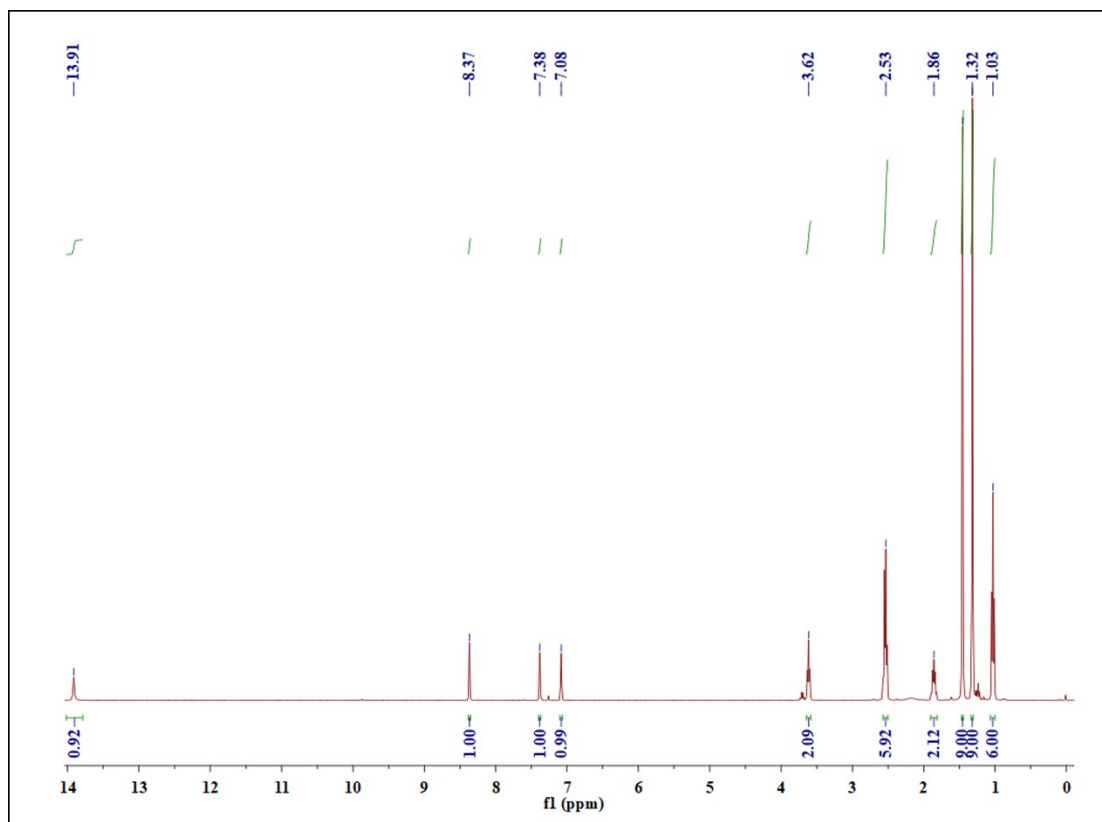
Figure S3. ¹H NMR of ligand L³-H in CDCl₃.

5. Table S1: Assignments in ¹H NMR data of Salen-type Schiff bases Lⁿ-H.

Ligand	C**H**=N	-O**H**	C**H**$_{arom}$	C**H**$_2$	C**H**$_2$CH$_3$	CH$_2$C**H**$_3$	N(C**H**$_3$)$_2$	C**H**$_3$	^{t}-Bu
L1	8.36 *s*	13.87 *s*	7.37 *s*, 7.08 *s*	3.62 *t*, 2.36 *t*, 1.87 *m*			2.22 *s*		1.45 *s*, 1.31 *s*
L2	8.31 *s*	13.90 *s*	7.39 *s*, 7.08 *s*	3.45 *s*, 2.22 *t*			2.32 *s*	0.96 *s*	1.45 *s*, 1.31 *s*
L3	8.37 *s*	13.91 *s*	7.38 *s*, 7.08 *s*	3.62 *t*, 2.53 *m*, 1.86 *t* *m*	2.53 *m*	1.03 *t*		1.03 *t*	1.46 *s*, 1.32 *s*

6. Scheme S2:
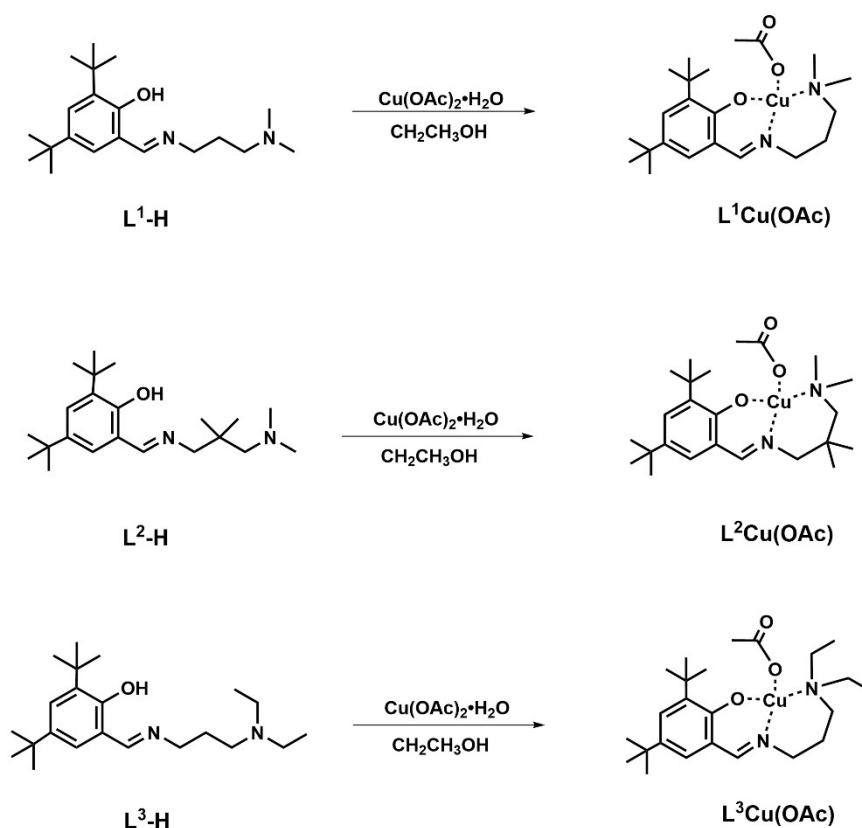
Scheme S2. Synthesis of Copper-salen complexes L^{1}Cu(OAc), L^{2}Cu(OAc) and L^{3}Cu(OAc).

Complex L^{1}Cu(OAc): Anal. Calcd for C$_{22}$H$_{36}$CuN$_2$O$_3$: N, 6.37; C, 60.04; H, 8.25%. Found: N, 6.42; C, 59.93; H, 8.72%. m/z (ESI-MS, methanol): 380.2 ([M − (CH$_3$COO)]$^+$, 100%, calcd 318.18). Characteristic IR absorptions (cm^{-1}): 1628 ($v_{C=N}$), 1533 ($v_{asymmetric\ acetate}$), 1355 ($v_{symmetric\ acetate}$).

Complex L^{2}Cu(OAc): Anal. Calcd for C$_{24}$H$_{40}$CuN$_2$O$_3$: N, 5.98; C, 61.58; H, 8.61%. Found: N, 6.08; C, 62.56; H, 8.48%. m/z (ESI-MS, methanol): 409.2 ([M − (CH$_3$COO)]$^+$, 100%, calcd 409.1). Characteristic IR absorptions (cm^{-1}): 1630 ($v_{C=N}$), 1536 ($v_{asymmetric\ acetate}$), 1343 ($v_{symmetric\ acetate}$).

Complex L^{3}Cu(OAc): Anal. Calcd for C$_{24}$H$_{40}$CuN$_2$O$_3$: N, 5.98; C, 61.58; H, 8.61%. Found: N, 5.59; C, 59.25; H, 8.20%. m/z (ESI-MS, methanol): 409.2 ([M − (CH$_3$COO)]$^+$, 100%, calcd 409.1). Characteristic IR absorptions (cm^{-1}): 1628 ($v_{C=N}$), 1540 ($v_{asymmetric\ acetate}$), 1331 ($v_{symmetric\ acetate}$).

7. Figure S4:

(a)
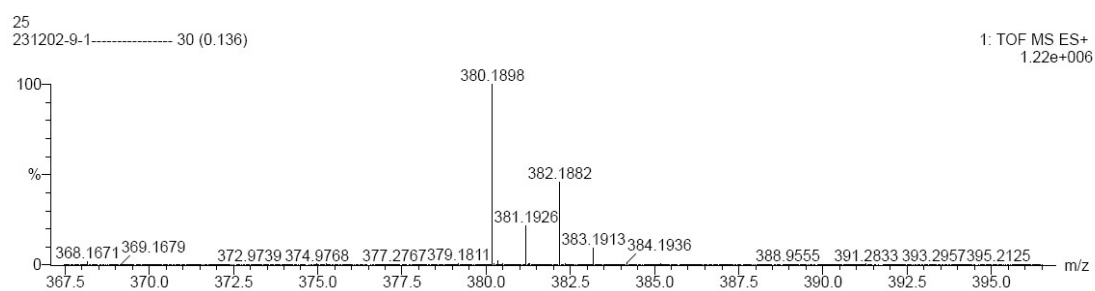
(b)
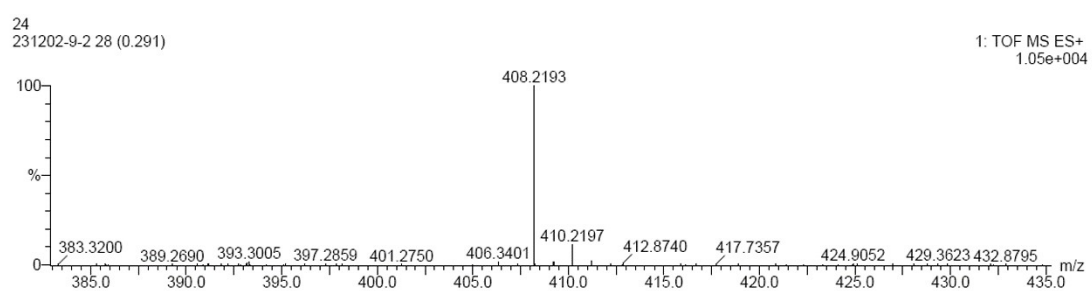
(c)
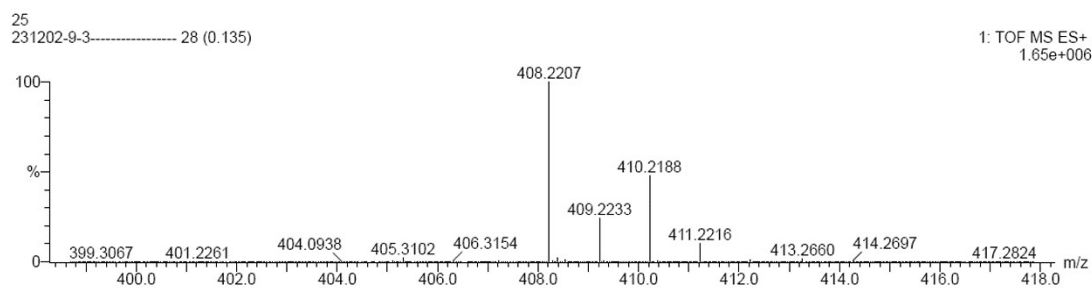
Figure S4.   Mass spectra of L^{1}Cu(OAc) (a), L^{2}Cu(OAc) (b) and L^{3}Cu(OAc) (c).

8. Figure S5:
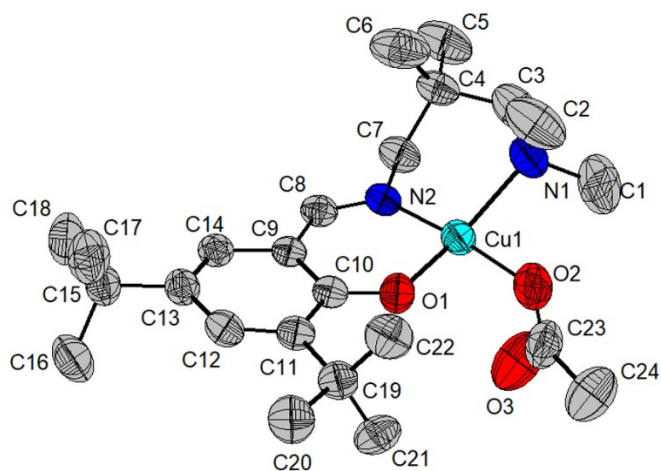
Figure S5. ORTEP drawing of complex L²Cu(OAc) with probability ellipsoids drawn at 50% level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Cu(1)-O(1) 1.8938(17), Cu(1)-N(1) 2.092(2), Cu(1)-O(2) 1.944(2), Cu(1)-N(2) 1.9336(19), O(1)-Cu(1)-N(1) 157.25(10), O(1)-Cu(1)-O(2) 85.71(8), N(1)-Cu(1)-O(2) 88.40(10), O(1)-Cu(1)-N(2) 92.71(7), N(1)-Cu(1)-N(2) 95.71(9), O(2)-Cu(1)-N(2) 172.66(10).

We tried our best to obtain the crystal of these complexes to identify the structure of copper-Schiff complexes, but unfortunately, single crystals of L¹Cu(OAc) and L³Cu(OAc) could not be obtained by accessing many methods.

9. Scheme S3:
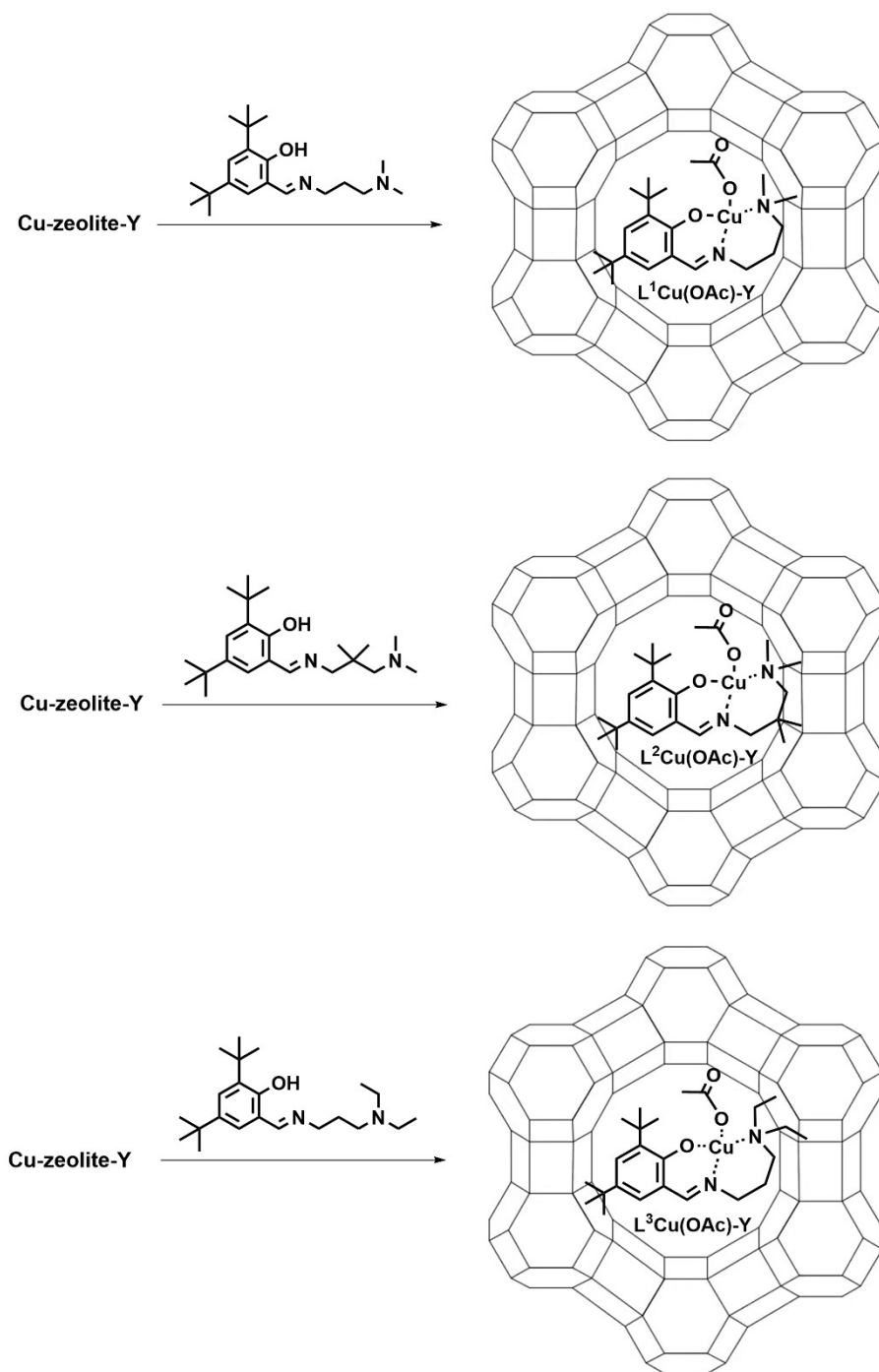
Scheme S3. Synthesis of zeolite encapsulated Copper salen complexes L¹Cu(OAc)-Y, L²Cu(OAc)-Y and L³Cu(OAc)-Y.

10. Figure S6:

(A)
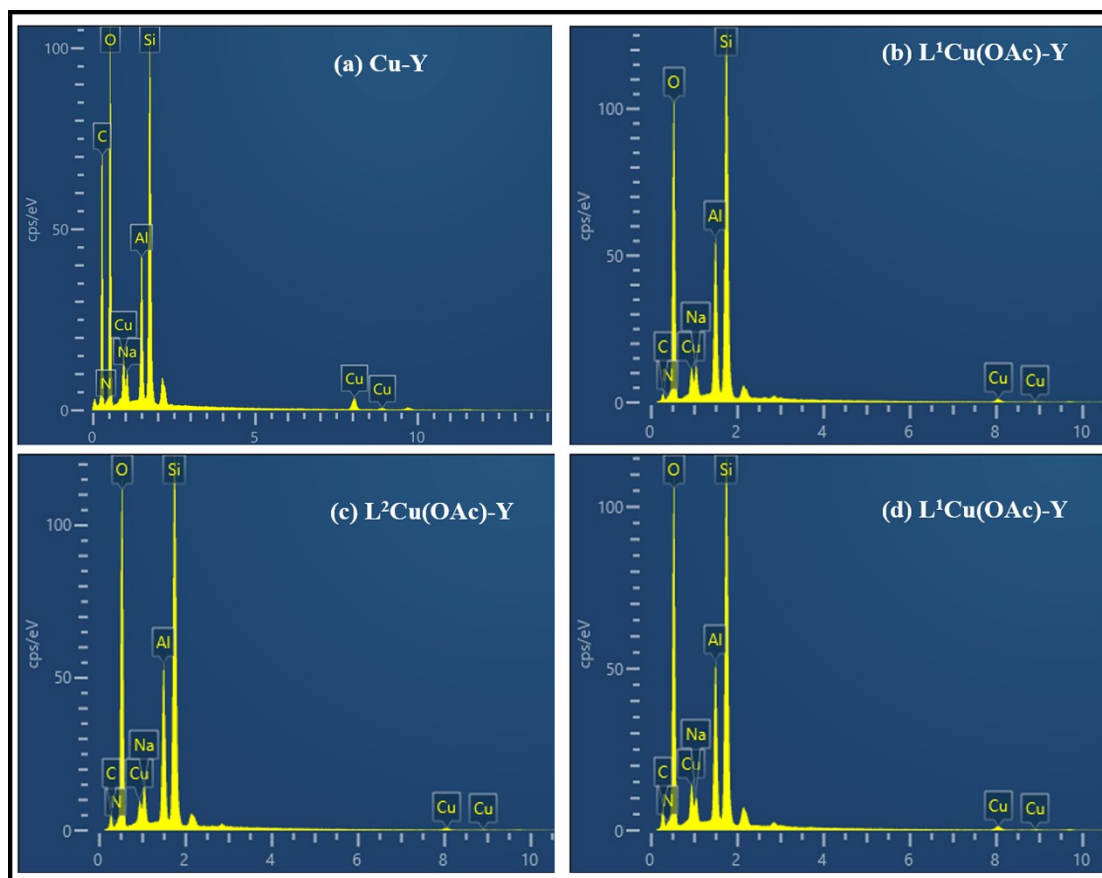
Figure S6 (A). EDX spectra of Cu-Y, L¹Cu(OAc)-Y, L²Cu(OAc)-Y and L³Cu(OAc)-Y.

(B)

L¹Cu(OAc)-Y — EDS elemental mapping (C Kα1,2; N Kα1,2; O Kα1; Na Kα1,2; Si Kα1; Al Kα1; Cu Lα1,2) and corresponding EDS spectrum.

L²Cu(OAc)-Y — EDS elemental mapping (C Kα1,2; N Kα1,2; O Kα1; Na Kα1,2; Si Kα1; Al Kα1; Cu Lα1,2) and corresponding EDS spectrum.
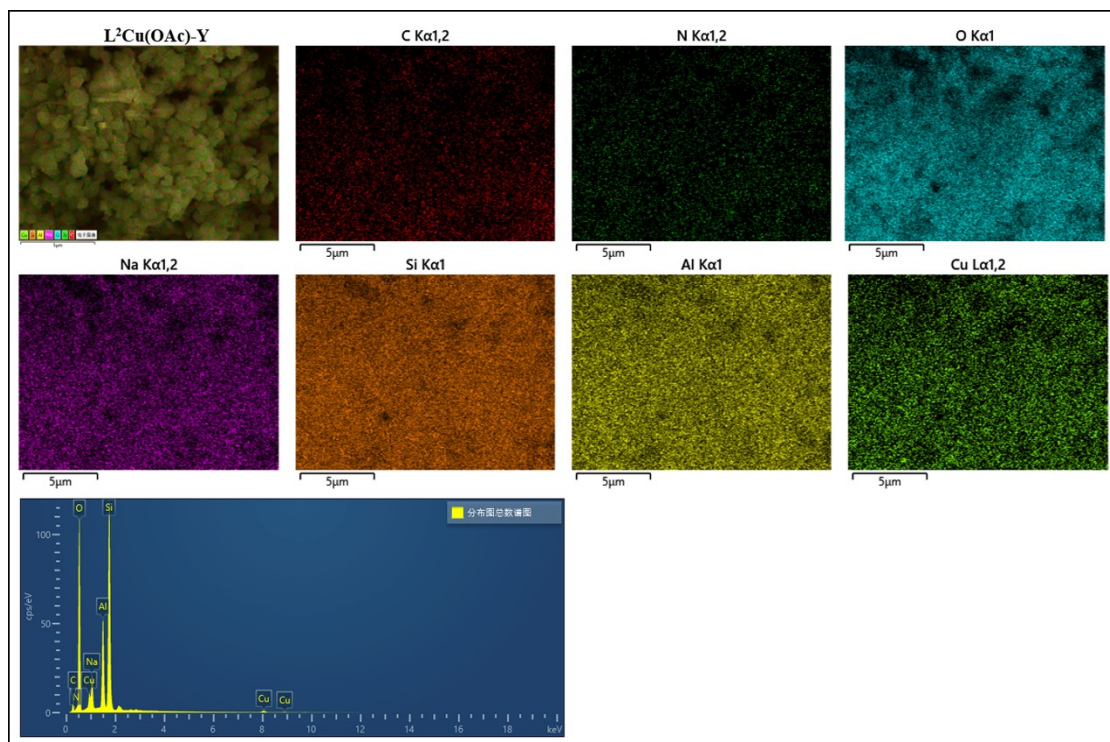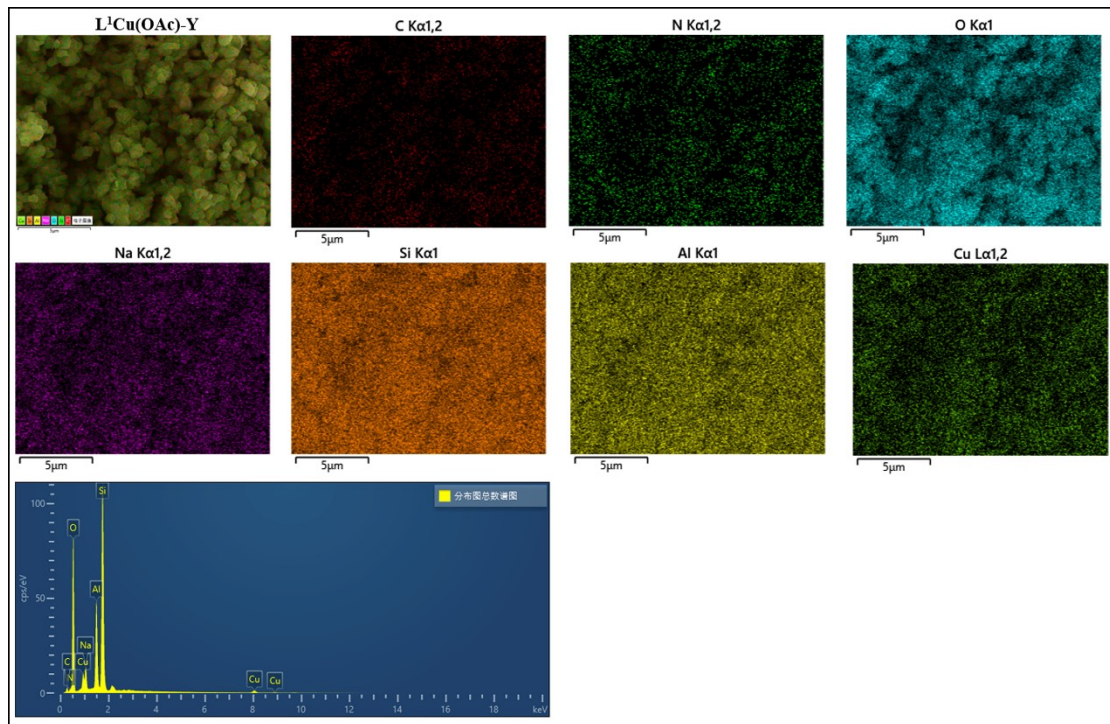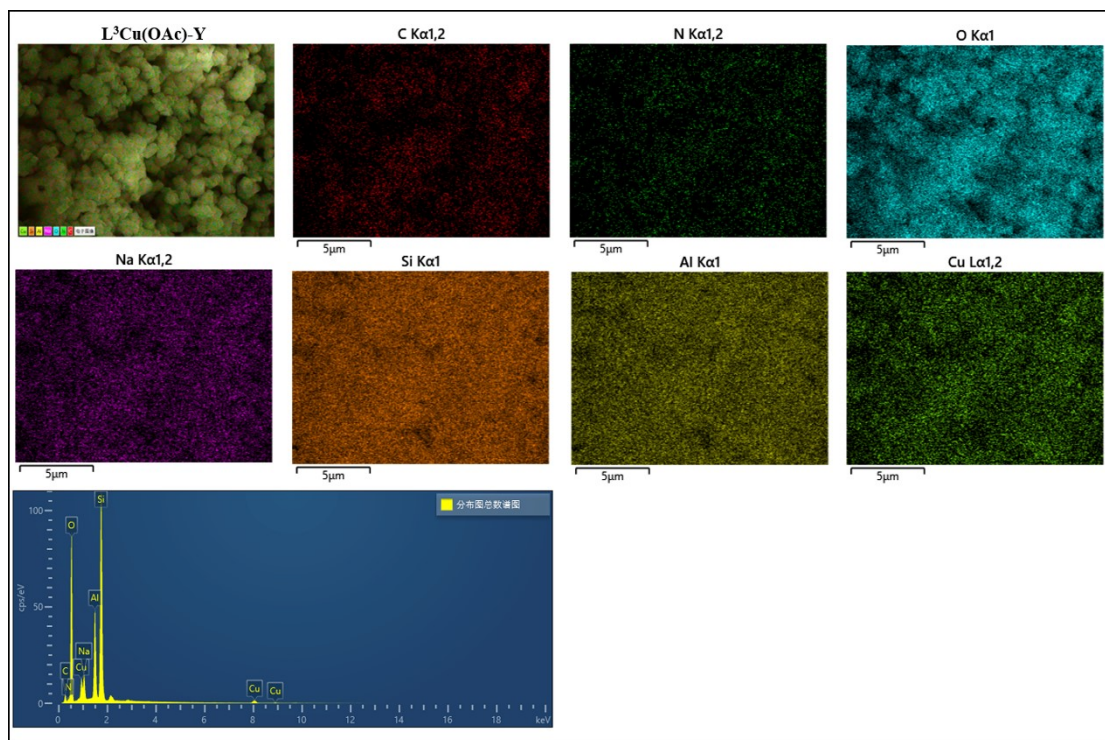
Figure S6 (B). EDX mapping of L¹Cu(OAc)-Y, L²Cu(OAc)-Y and L³Cu(OAc)-Y.

11. Figure S7:
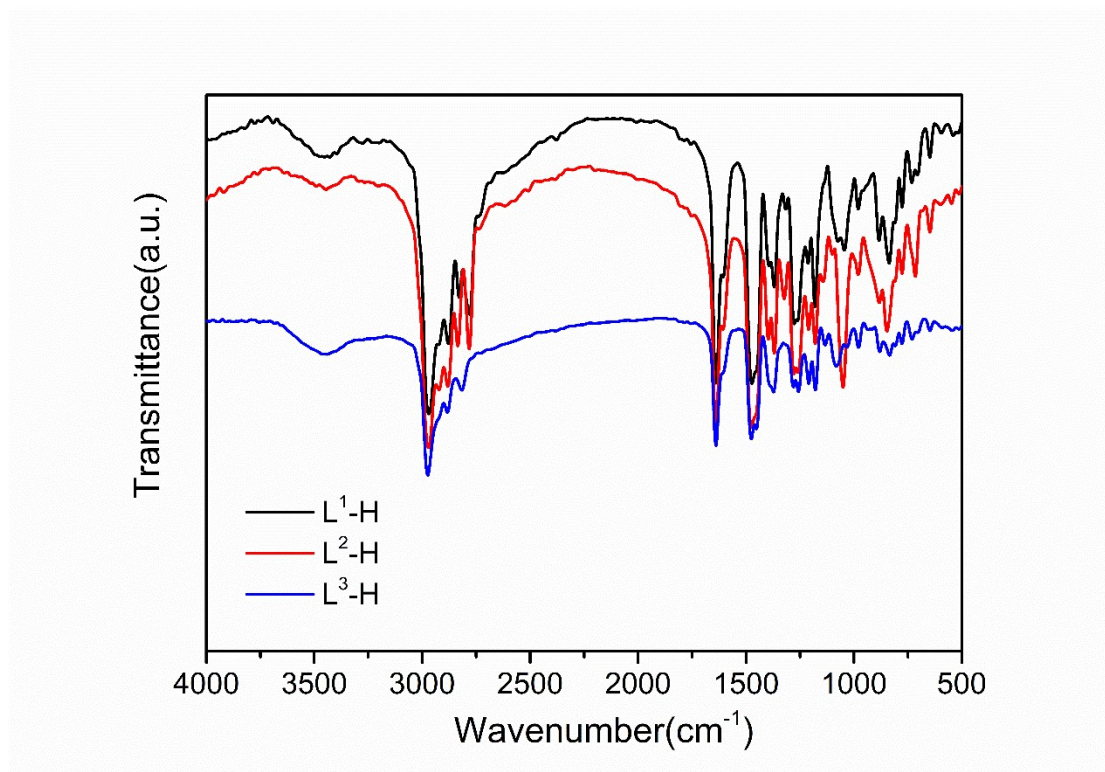
Figure S7. FTIR spectra of (a) L¹-H, (b) L²-H and (c) L³-H.

12. Figure S8:
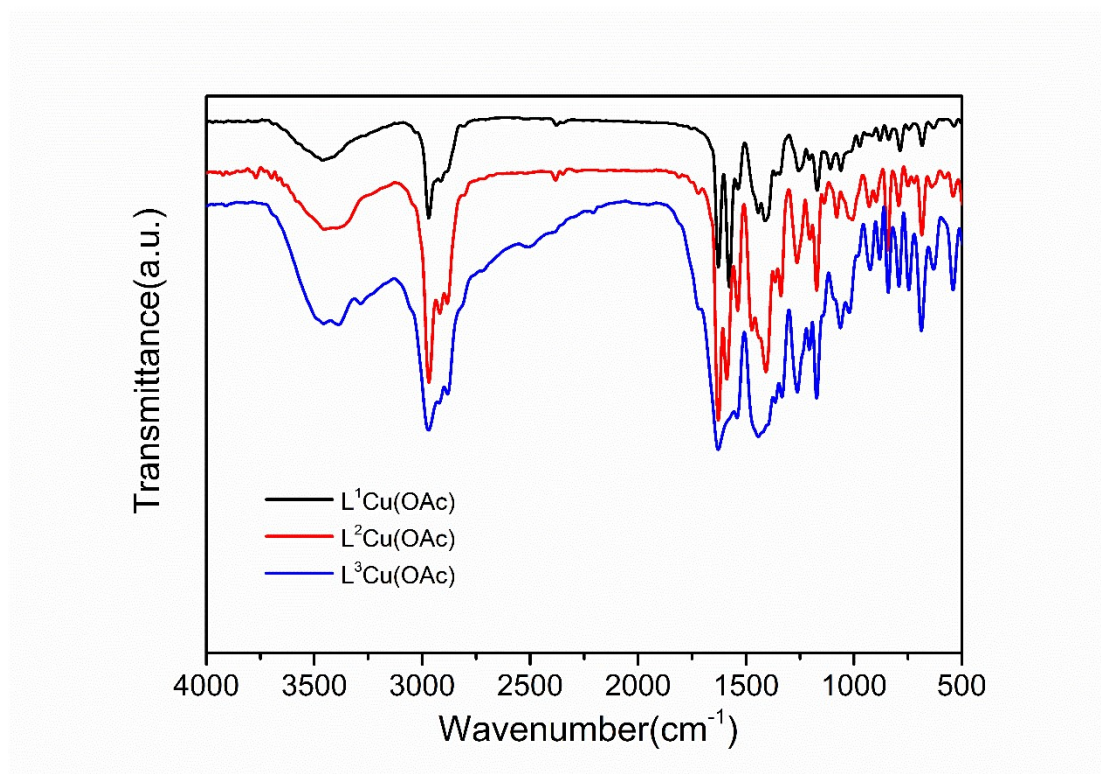
Figure S8. FTIR spectra of (a) L¹Cu(OAc), (b) L²Cu(OAc) and (c) L³Cu(OAc)

13. Table S2: FTIR spectral data (in cm⁻¹) for Ligands.

Samples	C=N stretching	C=C stretching	ν_{C-H} deformation	C-O stretching
L¹-H	1640	1604, 1472	1369	1263
L²-H	1641	1607, 1474	1368	1276
L³-H	1639	1605, 1476	1370	1246

14. Figure S9:
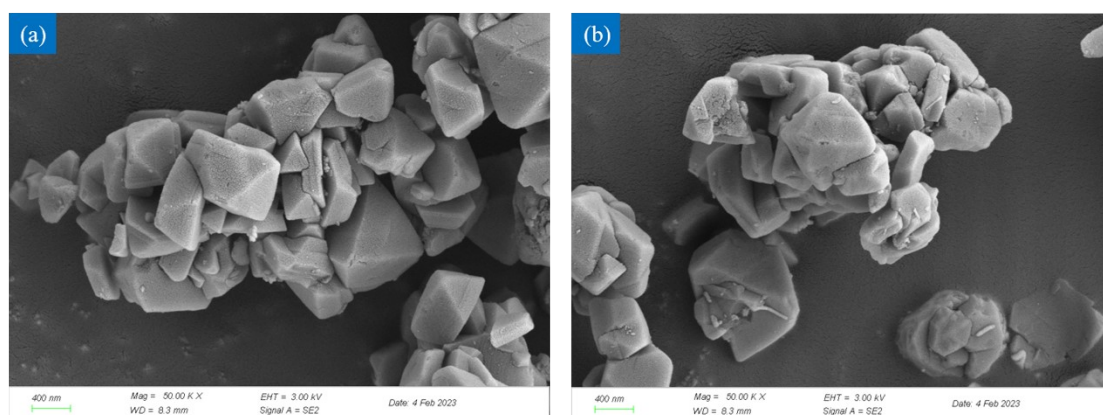
Figure S9. SEM images after Soxhlet extraction (a) L^{1}Cu(OAc)-Y and (b) L^{2}Cu(OAc)-Y.

15. Figure S10:
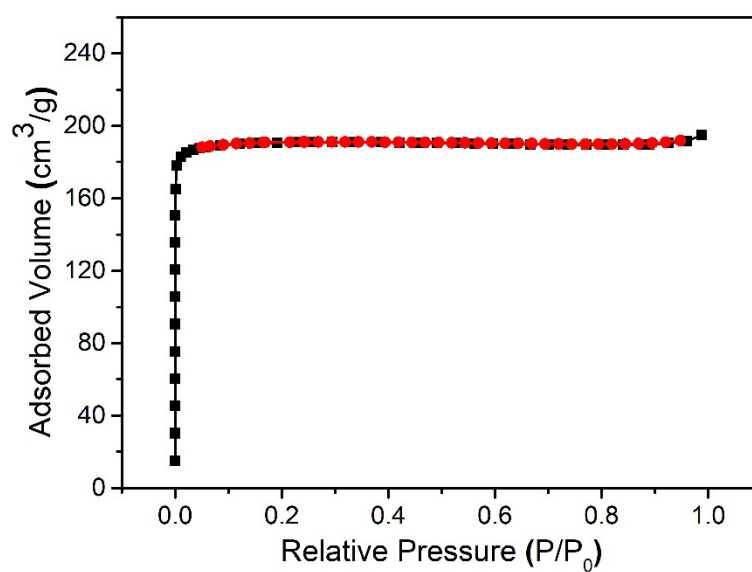
Figure S10. BET isotherms of NaY.

16. Figure S11:
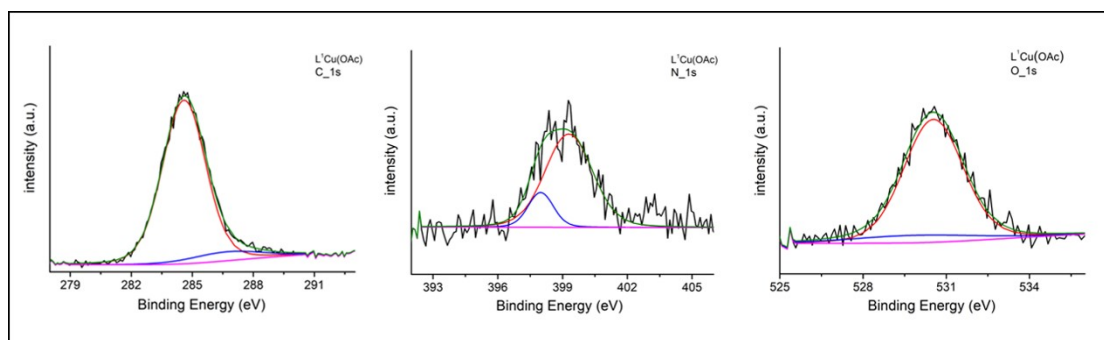
Figure S11. High resolution XPS spectra of C (1s), N (1s) and O (1s) for L¹Cu(OAc).

17. Figure S12:
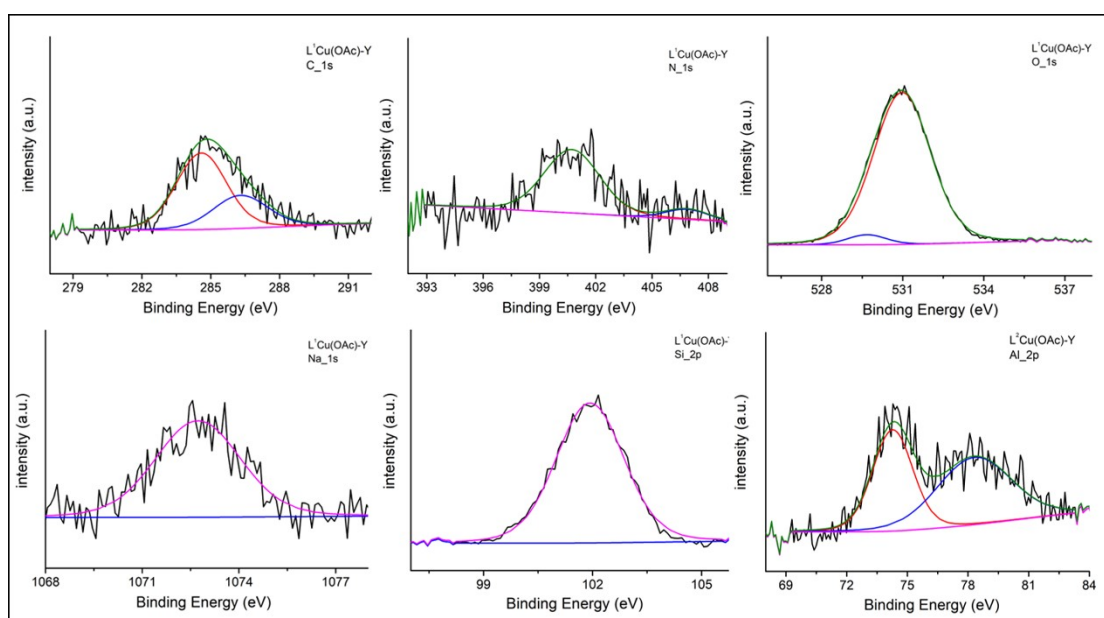
Figure S12. High resolution XPS spectra of C (1s), N (1s), O (1s), Al (2p), Si (2p) and Na (1s) for L¹Cu(OAc)-Y.

18. Figure S13:
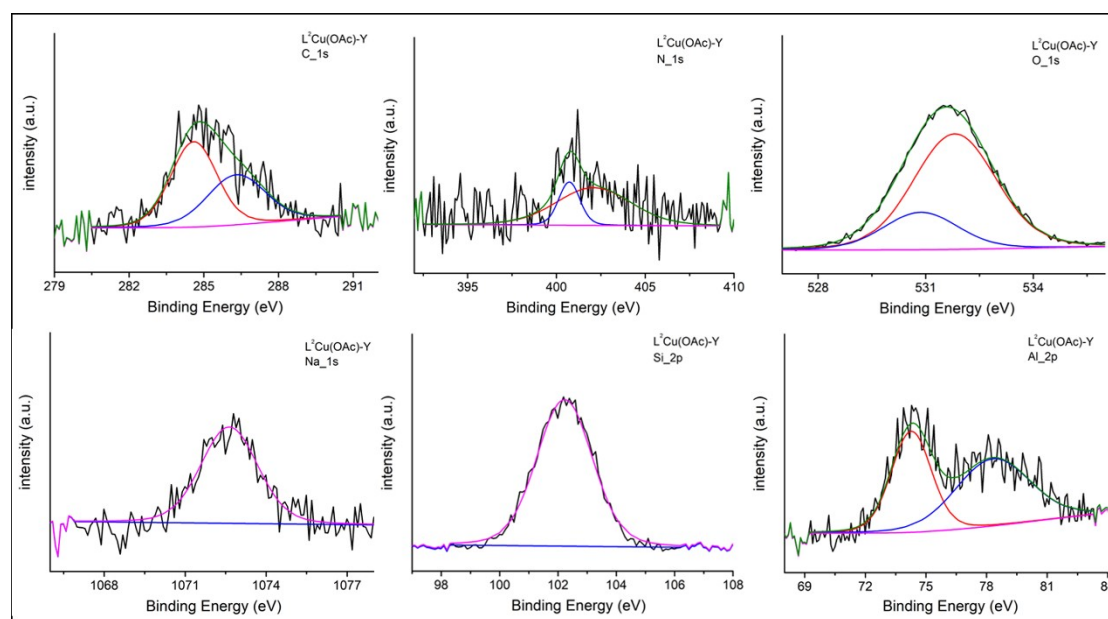
Figure S13. High resolution XPS spectra of C (1s), N (1s), O (1s), Al (2p), Si (2p) and Na (1s) for L²Cu(OAc)-Y.

19. Figure S14:
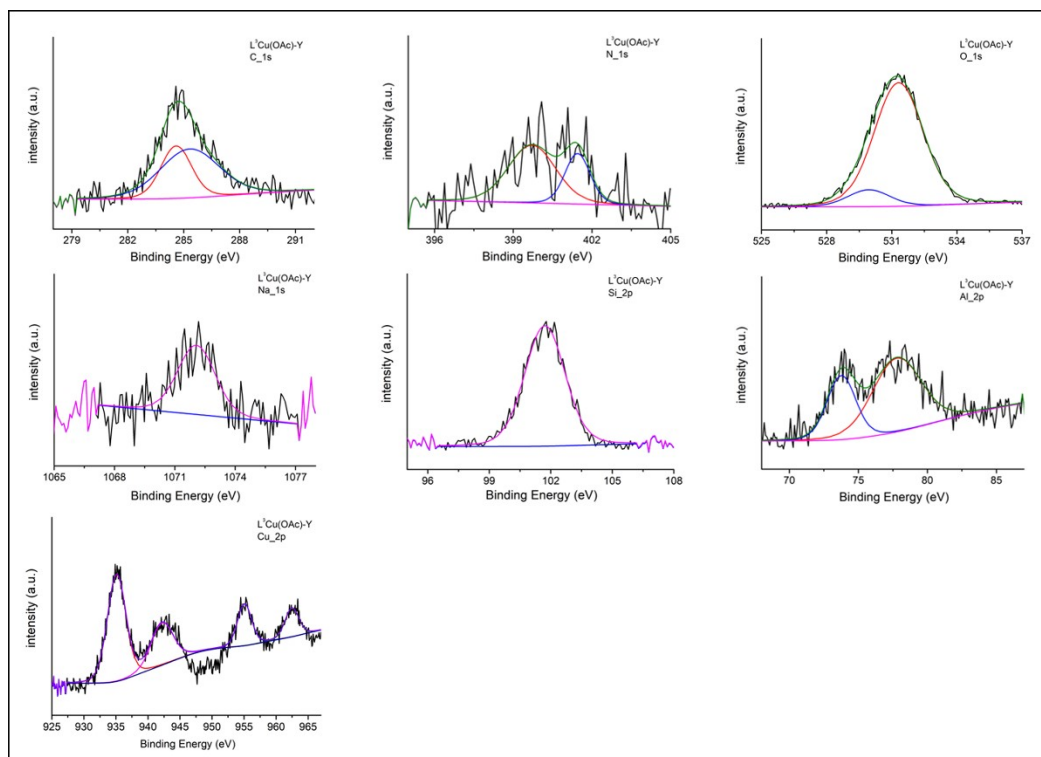
Figure S14. High resolution XPS spectra of C (1s), N (1s), O (1s), Al (2p), Si (2p), Na (1s) and Cu(2p) for L³Cu(OAc)-Y.

20. Figure S15:
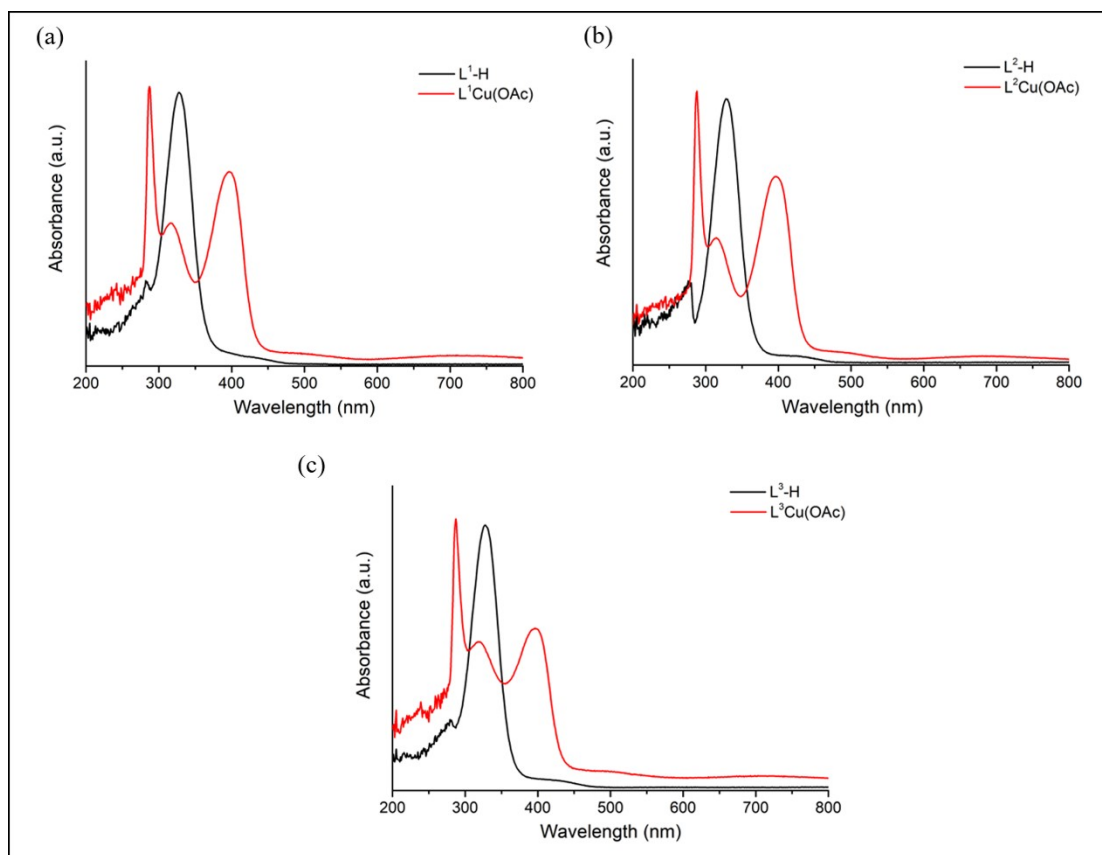
Figure S15. Solution UV-vis spectra (A) L¹-H and L¹Cu(OAc), (B) L²-H and L²Cu(OAc), (C) L³-H and L³Cu(OAc).

21. Figure. S16:

(a)

(b)

(c)
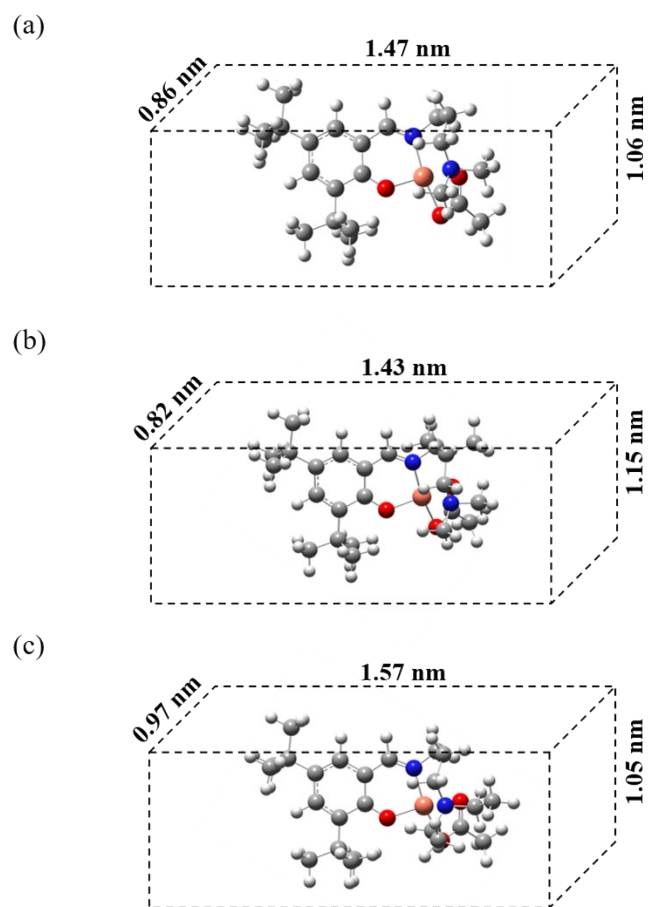
Figure. S16 Molecular dimension of free salen-complexes L¹Cu(OAc)- L³Cu(OAc) after optimization.

22. Figure S17:
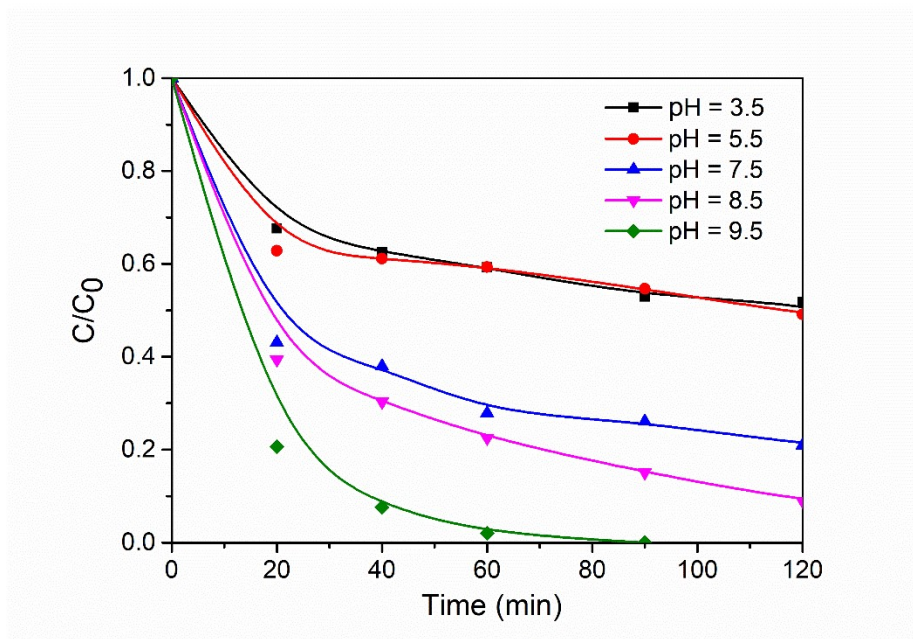
Figure S17. Effects of pH on MB degradation. Catalytic degradation performances of L³Cu(OAc)-Y with different value of pH. Reaction condition: [MB] = 25 mg·L⁻¹, catalyst = 0.5 g·L⁻¹, [H₂O₂] = 0.86 mol·L⁻¹, T = 30°C.

23. Figure S18:
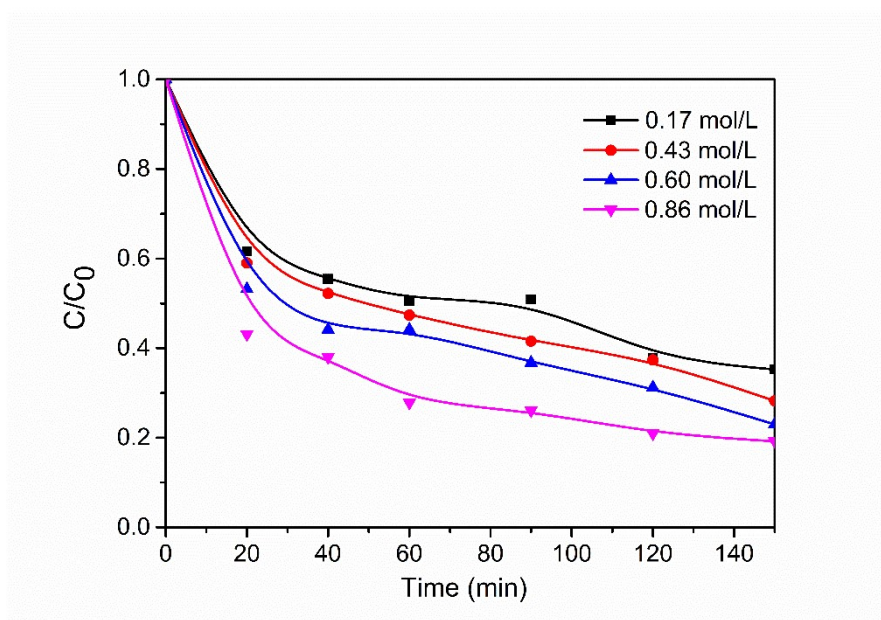
Figure S18. Effects of H₂O₂ concentration on MB degradation. Catalytic degradation performances of L³Cu(OAc)-Y with different concentration of H₂O₂. Reaction condition: [MB] = 25 mg L⁻¹, catalyst = 0.5 g·L⁻¹, T = 30°C, initial solution pH = 7.5.

24. Figure S19:
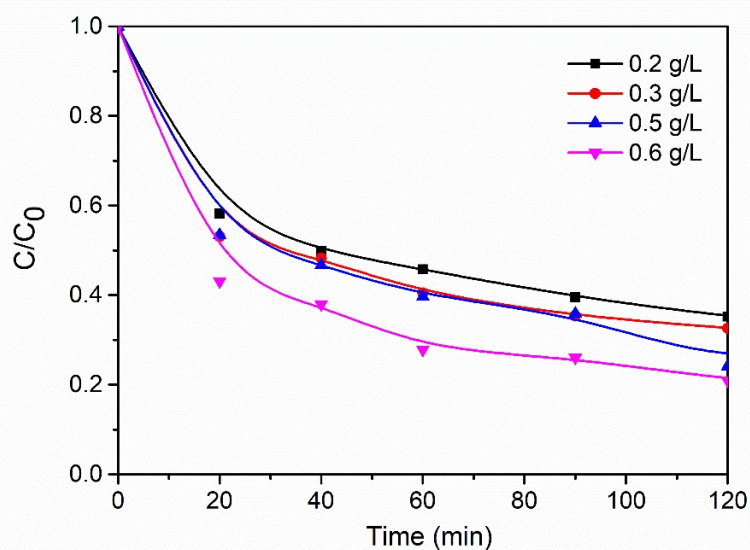
Figure S19. Effects of amout of catalyst on MB degradation. Catalytic degradation performances of L³Cu(OAc)-Y with different amount of catalyst. Reaction condition: [MB] = 25 mg·L⁻¹, [H₂O₂] = 0.86 mol·L⁻¹, T = 30°C, initial solution pH = 7.5.

25. Figure S20:
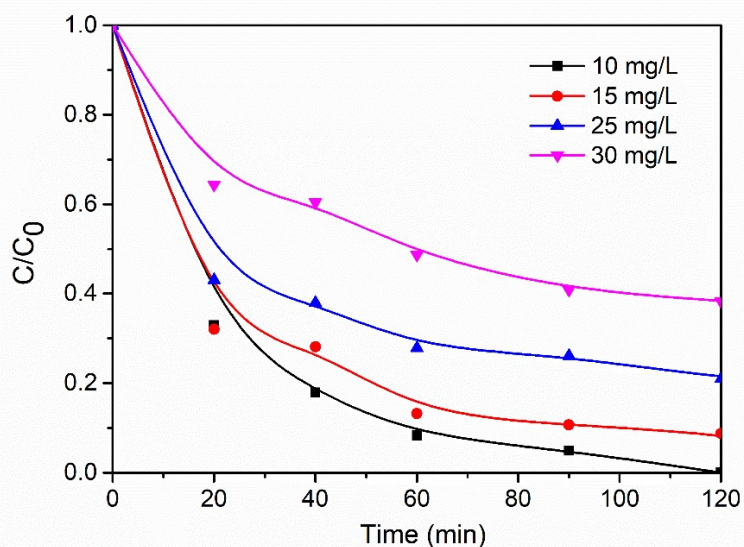
Figure S20. Effects of initial MB concentration on MB degradation. Catalytic degradation performances of L³Cu(OAc)-Y with different MB concentration. Reaction condition: [MB] = 25 mg·L⁻¹, catalyst = 0.5 g·L⁻¹, [H₂O₂] = 0.86 mol·L⁻¹, T = 30°C, initial solution pH = 7.5.

26. Table S3: Comparison of the catalytic performance of L^{3}Cu(OAc)-Y with some other catalysts.

Catalysts	Catalyst (g·L^{-1})	Objects (mg·L^{-1})	pH	Temp (°C)	Time (min)	Degradation efficiency	Ref.
Cu-NaY	0.4	2.5 AD[a]	6	30	180	85%	[1]
PS-Fe(III)BBZNH	0.5	75 XO[b]	8	-	80	63.4%	[2]
Fe@S-1	0.5	10 MB	2	60	30	90%	[3]
Molecule imprinted Fe-zeolites	0.3	9.1 MB	4	30	180	92.2%	[4]
Fe$_3$O$_4$/zeolite	0.6	50 MB	3	-	60	99%	[5]
Mn-salen-Y zeolite	0.5	2.75 AD[a]	2	30	120	60%	[6]
Cu-salen-Y zeolite	3	3 AB 113[c]	5.4	30	180	80.5%	[7]
L^{3}Cu(OAc)-Y	0.5	25 MB	7.5	30	120	80.7%	This work

[a] AD = acid dye; [b] XO= xylenol orange; [c] AB 113 = acid blue 113;

Reference

[1] N. N. Fathima, R. Aravindhan, J. R. Rao, B. U. Nair, Chemosphere, 2008, 70, 1146–1151.

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[6] R. Aravindhan, N. N. Fathima, J. R. Rao, B. U. Nair, J. Hazard. Mater, 2006, **138**, 152–159.

[7] S. L. Hailu, B. U. Nair, M. R. Abshiro, R. Aravindhan, I. Diaz, M. Tessema, J Porous Mater, 2015, **22**, 1363–1373.

27. Figure S21:

(a)

(b)

(c)
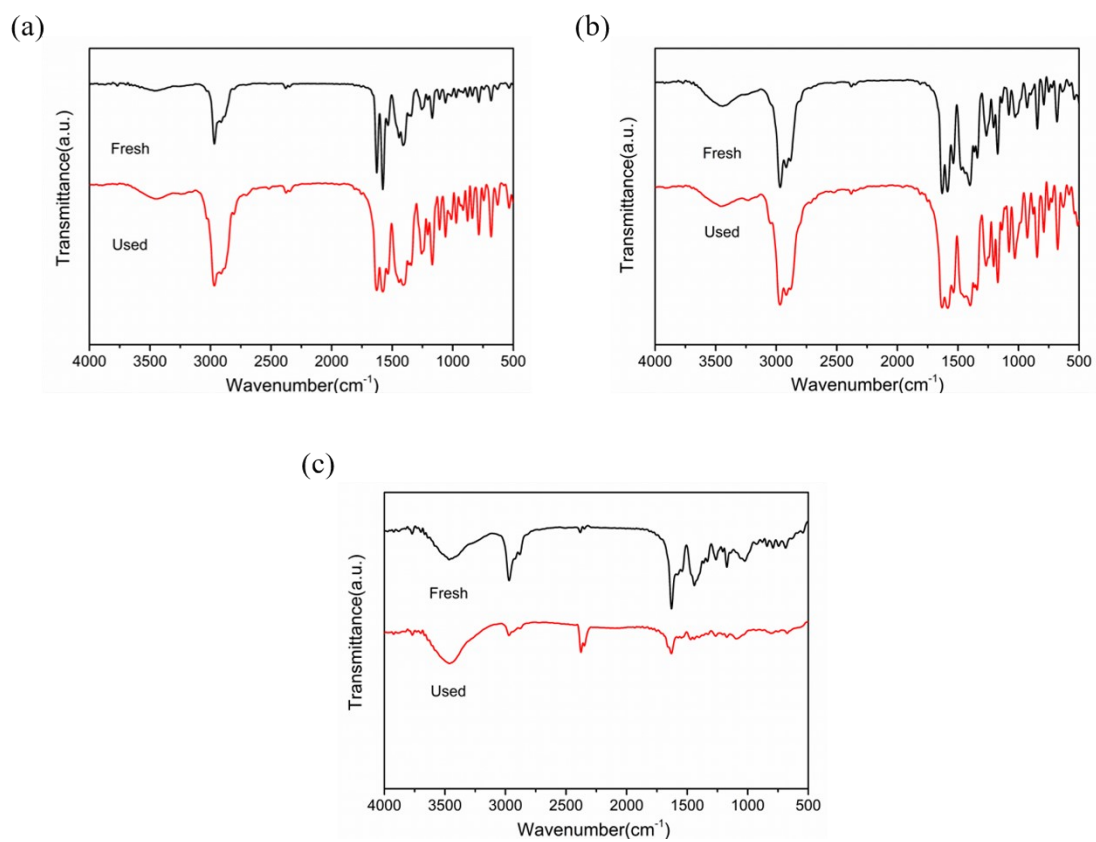
Figure S21. FT-IR spectra of fresh and used complexes of L¹Cu(OAc) (a), L²Cu(OAc) (b) and L³Cu(OAc) (c) in free states.

28. Figure S22:

(a)

(b)

(c)
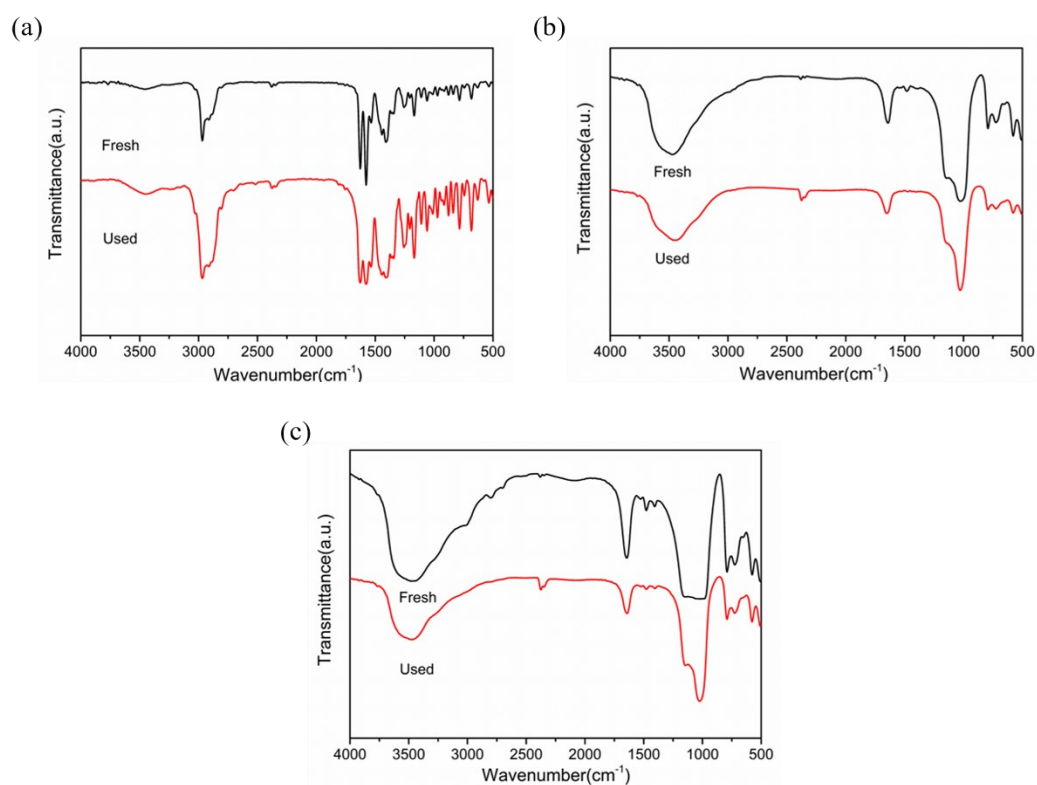
Figure S22. FT-IR spectra of fresh and used complexes of L¹Cu(OAc)-Y (a), L²Cu(OAc)-Y (b) and L³Cu(OAc)-Y (c) in encapsulated states.

29. Figure S23:
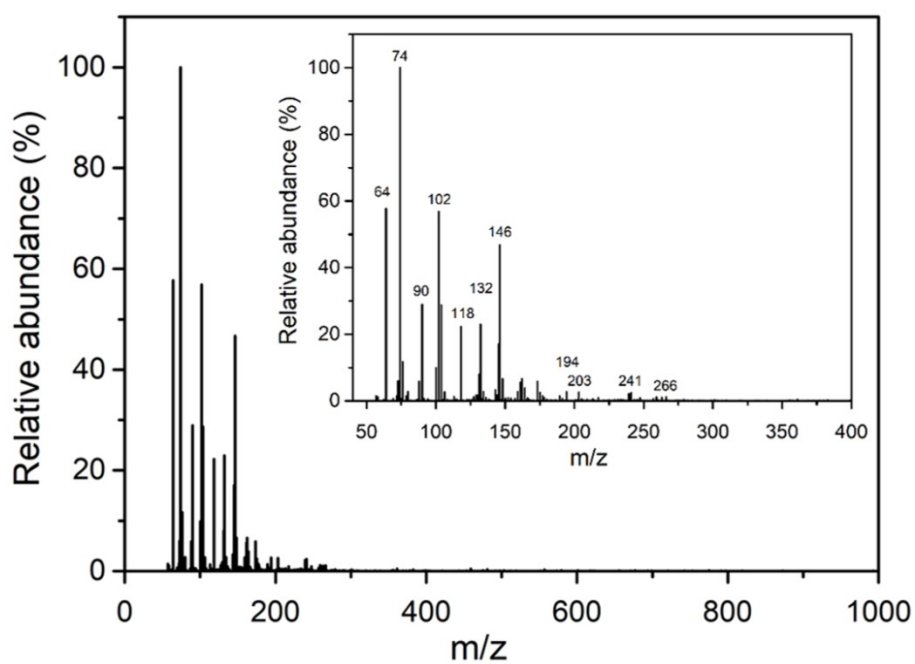
Figure S23. ESI-MS spectra of MB degradation after 120 min.

Coordinates of the studied molecules

L¹Cu(OAc)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	29	0	-1.906477	0.050533	-0.439096
2	6	0	-2.472502	-1.911181	1.910451
3	1	0	-2.913330	-2.219787	2.875506
4	1	0	-1.421768	-1.668009	2.100943
5	6	0	-2.535401	-3.103039	0.948011
6	6	0	-2.092869	-2.803182	-0.501347
7	1	0	-1.688428	-3.714520	-0.962095
8	1	0	-2.947703	-2.478350	-1.100678
9	6	0	0.151032	-1.975175	-0.490069
10	1	0	0.464849	-3.023961	-0.571365
11	6	0	1.202104	-1.017086	-0.318412
12	6	0	0.940054	0.347350	0.009361
13	6	0	2.071398	1.212741	0.219068
14	6	0	3.334122	0.674573	0.088221
15	1	0	4.183747	1.330557	0.242218
16	6	0	3.613302	-0.677097	-0.232130
17	6	0	2.529963	-1.496855	-0.423439
18	6	0	-4.536834	-0.852673	1.191351
19	1	0	-4.703581	-1.564502	0.380317
20	1	0	-4.963310	0.105559	0.884232
21	1	0	-5.063890	-1.199266	2.096962
22	6	0	-2.878828	0.406265	2.388285
23	1	0	-3.296530	1.331320	1.982880
24	1	0	-1.802904	0.551992	2.521552

25	1	0	-3.339444	0.194379	3.368111
26	7	0	-3.107320	-0.679436	1.431760
27	7	0	-1.114864	-1.728970	-0.536987
28	8	0	-0.256982	0.824953	0.143385
29	1	0	2.665073	-2.547499	-0.666299
30	6	0	1.851178	2.692419	0.568876
31	6	0	1.069403	3.389299	-0.563789
32	6	0	1.069184	2.810305	1.893106
33	6	0	3.178954	3.445217	0.747719
34	1	0	1.625118	3.327126	-1.506997
35	1	0	0.087081	2.935236	-0.704287
36	1	0	0.930489	4.450356	-0.322255
37	1	0	1.617423	2.323700	2.708823
38	1	0	0.937141	3.867035	2.156133
39	1	0	0.084001	2.349454	1.805885
40	1	0	2.967450	4.491416	0.994367
41	1	0	3.781726	3.030317	1.564387
42	1	0	3.781860	3.439537	-0.167991
43	6	0	5.068239	-1.142069	-0.343177
44	6	0	5.787810	-0.912453	0.999880
45	6	0	5.170077	-2.633336	-0.691032
46	6	0	5.781961	-0.341423	-1.449480
47	1	0	5.787809	0.144737	1.285636
48	1	0	5.299441	-1.476337	1.802342
49	1	0	6.832655	-1.239748	0.935899
50	1	0	4.698451	-2.856744	-1.654839
51	1	0	6.223485	-2.926137	-0.761788
52	1	0	4.702868	-3.260473	0.077028
53	1	0	6.826867	-0.661899	-1.541316
54	1	0	5.289389	-0.493010	-2.416219

55	1	0	5.781132	0.733139	-1.238266
56	6	0	-3.766581	1.095289	-1.509206
57	8	0	-3.548679	-0.127788	-1.747097
58	8	0	-3.001741	1.718874	-0.708989
59	6	0	-4.901830	1.820628	-2.179892
60	1	0	-5.310814	2.582825	-1.513171
61	1	0	-4.516844	2.325310	-3.072419
62	1	0	-5.677625	1.116945	-2.486774
63	1	0	-1.880875	-3.872113	1.375725
64	1	0	-3.542288	-3.534626	0.925650

L²Cu(OAc)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	29	0	-1.678727	0.535270	-0.425574
2	6	0	-2.739466	-1.572373	1.593124
3	1	0	-3.374509	-1.904384	2.435061
4	1	0	-1.725337	-1.456805	1.989361
5	6	0	-2.697563	-2.718967	0.548647
6	6	0	-2.166295	-2.247235	-0.828291
7	1	0	-1.845721	-3.127350	-1.404963
8	1	0	-2.964872	-1.755994	-1.393655
9	6	0	0.153895	-1.665412	-0.721954
10	1	0	0.358577	-2.713679	-0.973280
11	6	0	1.298547	-0.854626	-0.437098
12	6	0	1.181730	0.479800	0.057942
13	6	0	2.398663	1.183958	0.370980

14	6	0	3.596782	0.533373	0.167869
15	1	0	4.510386	1.069610	0.400056
16	6	0	3.731800	-0.789289	-0.323527
17	6	0	2.568572	-1.456654	-0.611447
18	6	0	-4.541020	-0.136777	0.743865
19	1	0	-4.682884	-0.635737	-0.214797
20	1	0	-4.798037	0.915987	0.603916
21	1	0	-5.221554	-0.571339	1.494705
22	6	0	-2.902032	0.716462	2.268934
23	1	0	-3.135656	1.727986	1.928522
24	1	0	-1.844856	0.689751	2.548531
25	1	0	-3.514498	0.474417	3.153287
26	6	0	-1.739976	-3.772872	1.132430
27	1	0	-2.061616	-4.076369	2.135586
28	1	0	-0.717827	-3.386638	1.216580
29	1	0	-1.717710	-4.669742	0.503121
30	6	0	-4.063304	-3.391004	0.338450
31	1	0	-4.809854	-2.711402	-0.079123
32	1	0	-4.451693	-3.779381	1.286645
33	1	0	-3.966326	-4.237455	-0.351698
34	7	0	-3.143652	-0.224295	1.166521
35	7	0	-1.082749	-1.293047	-0.695328
36	8	0	0.043065	1.064983	0.247149
37	1	0	2.591971	-2.476573	-0.986152
38	6	0	2.335324	2.622289	0.906367
39	6	0	1.642013	3.537131	-0.124410
40	6	0	1.559662	2.653344	2.239122
41	6	0	3.734506	3.199364	1.172309
42	1	0	2.195760	3.535352	-1.070853
43	1	0	0.617927	3.212547	-0.316244

44	1	0	1.616353	4.567845	0.250498
45	1	0	2.051405	2.017776	2.985445
46	1	0	1.531354	3.677434	2.631299
47	1	0	0.534343	2.306333	2.101406
48	1	0	3.634346	4.222228	1.551637
49	1	0	4.282751	2.621547	1.925962
50	1	0	4.340718	3.245671	0.259922
51	6	0	5.129216	-1.389990	-0.501183
52	6	0	5.857672	-1.413908	0.856411
53	6	0	5.073211	-2.826338	-1.038790
54	6	0	5.934459	-0.535312	-1.498909
55	1	0	5.968447	-0.408497	1.276149
56	1	0	5.304715	-2.020754	1.581955
57	1	0	6.861964	-1.840538	0.745266
58	1	0	4.587863	-2.871831	-2.020441
59	1	0	6.089630	-3.219158	-1.152991
60	1	0	4.535254	-3.493222	-0.355141
61	1	0	6.939526	-0.952172	-1.637028
62	1	0	5.436605	-0.507067	-2.474379
63	1	0	6.047610	0.496869	-1.150901
64	6	0	-3.253679	1.951696	-1.557081
65	8	0	-3.168277	0.761176	-1.964393
66	8	0	-2.539769	2.334263	-0.573743
67	6	0	-4.171393	2.938674	-2.228970
68	1	0	-4.623255	3.600474	-1.486346
69	1	0	-3.580974	3.558582	-2.911953
70	1	0	-4.940486	2.418868	-2.802546

L³Cu(OAc)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z

Center Number	Atomic Number	Atomic Type	X	Y	Z
1	29	0	-1.574045	0.158826	-0.787408
2	6	0	-2.332064	-1.882057	1.481865
3	1	0	-2.792863	-2.257147	2.409377
4	1	0	-1.280845	-1.679714	1.715692
5	6	0	-2.393529	-3.014417	0.447980
6	6	0	-1.838040	-2.677386	-0.953718
7	1	0	-1.426142	-3.583981	-1.417421
8	1	0	-2.636221	-2.306284	-1.601701
9	6	0	0.420589	-1.922418	-0.736337
10	1	0	0.707989	-2.978324	-0.821958
11	6	0	1.482256	-1.004387	-0.448757
12	6	0	1.235691	0.359789	-0.110196
13	6	0	2.369197	1.180434	0.226694
14	6	0	3.621081	0.603221	0.195046
15	1	0	4.473274	1.225691	0.444318
16	6	0	3.885348	-0.748484	-0.137511
17	6	0	2.798350	-1.526052	-0.447816
18	7	0	-2.915161	-0.608999	1.055484
19	7	0	-0.829027	-1.634718	-0.879894
20	8	0	0.047646	0.876532	-0.075903
21	1	0	2.921008	-2.574483	-0.706071
22	6	0	2.163921	2.656580	0.599929
23	6	0	1.514835	3.411457	-0.578395
24	6	0	1.264509	2.764755	1.848453
25	6	0	3.492287	3.357486	0.925299

26	1	0	2.154407	3.356489	-1.467343
27	1	0	0.536208	2.995390	-0.823469
28	1	0	1.387414	4.469484	-0.318014
29	1	0	1.714980	2.232773	2.695115
30	1	0	1.146429	3.817471	2.133321
31	1	0	0.275774	2.346016	1.654342
32	1	0	3.291997	4.402867	1.184446
33	1	0	4.002151	2.898467	1.780721
34	1	0	4.178021	3.357417	0.069851
35	6	0	5.329101	-1.259464	-0.130475
36	6	0	5.930394	-1.089415	1.278016
37	6	0	5.415639	-2.743750	-0.510896
38	6	0	6.165029	-0.454693	-1.144331
39	1	0	5.937467	-0.040708	1.593363
40	1	0	5.353809	-1.657417	2.016491
41	1	0	6.966024	-1.449929	1.298777
42	1	0	5.026324	-2.925975	-1.519095
43	1	0	6.461534	-3.069756	-0.495508
44	1	0	4.861623	-3.374699	0.193710
45	1	0	7.203470	-0.807636	-1.151028
46	1	0	5.757846	-0.564317	-2.155452
47	1	0	6.178514	0.613409	-0.902912
48	6	0	-3.343001	1.279749	-1.927678
49	8	0	-3.128292	0.060135	-2.191647
50	8	0	-2.617054	1.863124	-1.065000
51	6	0	-4.425859	2.040785	-2.642631
52	1	0	-4.814947	2.837257	-2.005324
53	1	0	-3.997527	2.500300	-3.539852
54	1	0	-5.225550	1.365051	-2.951769
55	6	0	-4.330938	-0.688622	0.664290

56	6	0	-5.295559	-1.418412	1.605815
57	1	0	-4.375975	-1.162109	-0.322430
58	1	0	-4.668958	0.342691	0.516021
59	1	0	-6.304993	-1.373462	1.183211
60	1	0	-5.037164	-2.476702	1.716682
61	1	0	-5.330006	-0.977299	2.604310
62	6	0	-2.584971	0.496095	1.975397
63	6	0	-3.160618	0.458855	3.393903
64	1	0	-2.890424	1.422874	1.477898
65	1	0	-1.490770	0.530527	2.032532
66	1	0	-2.683320	1.243159	3.990907
67	1	0	-4.237650	0.648923	3.406816
68	1	0	-2.972063	-0.497133	3.893731
69	1	0	-1.815305	-3.842331	0.876164
70	1	0	-3.419202	-3.382991	0.334005