Supporting Information

Chiral binaphthylbisbipyridine-based copper(I) coordination polymer gels as supramolecular catalysts

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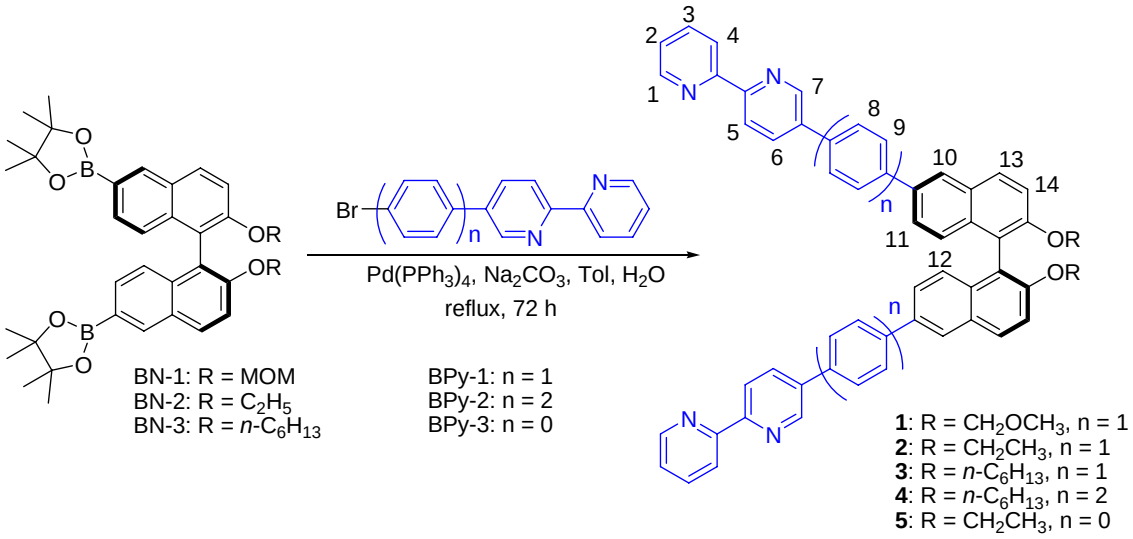
1. General remark

All reagents and solvents were obtained from commercial supplies and used directly without further purification unless otherwise stated. The solvents for spectroscopic studies were purified according to standard methods. Chromatographic purification was conducted using 100-200 mesh silica gel. TLC was performed on aluminum TLC-layers silica gel GF254 and visualized using UV light.

Melting points (M.p.s) were determined by using a DSC Q100 TA instrument under a nitrogen atmosphere at heating rates of 5 $^{o}Cmin^{-1}$. Optical rotations were measured on a 341LC polarimeter. ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker AV400 or AV600 spectrometer. Chemical shifts were reported downfield from TMS (δ = 0.00 ppm) for ^{1}H NMR. For ^{13}C NMR spectra, chemical shifts were reported on the scale relative to deuterated solvent as internal standard ($CDCl_3$, δ = 77.00 ppm). The coupling constants were reported in hertz. IR spectra were performed on a Bruker Vertex 70 spectrometer with KBr pellets. Mass spectra (MALDI-TOF-MS or ESI-MS) were recorded with a Thermo Finnigan LCQ instrument. Elemental analyses (C, H, N) were carried out with a VarioEL instrument. UV-vis spectra were recorded on an UV-2500 UV-vis spectrophotometer using a 1 cm cuvette. The gel samples were prepared by sandwiching samples between two quartz glass plates. The fluorescent spectra were recorded on Perkin-Elmer LS 50B

fluorescence spectrophotometer. Circular dichroism (CD) spectra were recorded on JASCO J-815 CD spectrophotometer. SEM pictures were taken using an XL 30 ESEM FEG field emission scanning electron microscope with 20 kV operating voltage. Cyclic voltammetry (CV) experiments were carried out with a CHI660a electrochemical analyzer with a three electrode cell in a solution of 0.1 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) dissolved in dichloromethane-acetonitrile (1/1) at a scan rate of 100 mVs^{-1}. A platinum disk was used as a working electrode. This electrode was polished prior to use with diamond paste and rinsed thoroughly with water and acetone. A Pt wire was used as a counter electrode. All potentials were referenced to a SCE electrode.

2. Synthetic procedure and characterization of the compounds 1-5



Scheme S1 Synthesis of the compounds (*S*)-**1**-**5**.

(*S*)-6,6'-Bis(4-(2,2'-bipyridin-5-yl)phenyl)-2,2'-dimethoxymethoxy-1,1'-binaphthyl (*S*)-**1**

To a degassed solution of 5-(4-bromophenyl)-2,2'-bipyridine (2.00 g, 6.43 mmol) in toluene (60 mL) is added $Pd(PPh_3)_4$ (0.18 g, 0.16 mmol) under a nitrogen atomosphere. After the resulting mixture is stirred for 10 minutes at room temperature, 2,2'-bis(methoxymethoxy)-1,1'-binaphhyl-6,6'-diboronic acid pinacol ester (2.00 g, 3.21 mmol) and 1M Na_2CO_3 (38.6 mL) are added sequentially into the mixture. Then the mixture is refluxed for 3 days under nitrogen. After removal of the solvent, the resulting residue is extracted with chloroform (80 mL × 3), washed

with brine (80 mL) and dried over anhydrous $MgSO_4$. Evaporation of the solvent gives a yellow residue which is purified by flash silica gel column chromatography (THF), following by recrystallization in CH_2Cl_2, to afford pure (*S*)-**1** in 84% yield as a yellow powder.

M.p. 224-226 °C; $[\alpha]_D^{20}$ 214.5 (*c* = 0.076 in CH_2Cl_2); FT-IR (KBr, cm^{-1}): 1587, 1573, 1485, 1476, 1458, 1434, 1368, 1346, 1240, 1196, 1188, 1149, 1091, 1076, 1046, 1022, 1000, 959, 920, 823, 796, 750; ^{1}H NMR ($CDCl_3$, 600.1 MHz) δ (ppm): 8.980 (d, *J* = 1.8 Hz, 2H), 8.700 (d, *J* = 4.2 Hz, 2H), 8.491 (d, *J* = 8.4 Hz, 2H), 8.450 (d, *J* = 7.8 Hz, 2H), 8.166 (d, *J* = 1.8 Hz, 2H), 8.062 (m, 4H), 7.819 (m, 6H), 7.744 (d, *J* = 7.8 Hz, 4H), 7.655 (d, *J* = 9.6 Hz, 2H), 7.574 (dd, *J* = 9.6 Hz, 1.8 Hz, 2H), 7.311 (m, 4H), 5.130 (d, *J* = 7.2 Hz, 2H), 5.042 (d, *J* = 7.2 Hz, 2H), 3.211 (s, 6H); ^{13}C NMR ($CDCl_3$, 150.9 MHz) δ (ppm): 155.85, 154.91, 153.04, 149.21, 147.48, 140.87, 136.94, 136.28, 135.98, 135.88, 135.01, 133.41, 130.13, 129.87, 127.85, 127.45, 126.26, 125.83, 125.78, 123.68, 121.07, 121.05, 117.81, 95.24, 55.90; MS (ESI) (*m/z*) Calcd for $C_{56}H_{42}N_4O_4$: 834.3, Found: 835.1; Anal. Calcd for $C_{56}H_{42}N_4O_4$: C, 80.55; H, 5.07; N, 6.71, Found: C, 80.57; H, 4.99; N, 6.80%.

Compound (*S*)-**2**-**5** were prepared according to the method of the (*S*)-**1**.

(*S*)-6,6'-Bis(4-(2,2'-bipyridin-5-yl)phenyl)-2,2'-diethoxy-1,1'-binaphthyl (*S*)-**2**

M.p. 298-300 ºC; $[\alpha]_D^{20}$ 260.0 (*c* = 0.06 in CH_2Cl_2); FT-IR (KBr, cm^{-1}): 1587, 1465, 1456, 1433, 1238, 1053, 826, 802, 796, 749; ^{1}H NMR ($CDCl_3$, 400.0 MHz) δ (ppm): 9.000 (d, *J* = 1.6 Hz, 2H), 8.723 (d, *J* = 4.8 Hz, 2H), 8.535 (d, *J* = 8.0 Hz, 2H), 8.490 (d, *J* = 8.0 Hz, 2H), 8.152 (s, 2H), 8.108 (dd, *J* = 8.4 Hz, 1.6 Hz, 2H), 8.051 (d, *J* = 9.2 Hz, 2H), 7.880 (t, *J* = 7.6 Hz, 2H), 7.838 (d, *J* = 8.4 Hz, 4H), 7.761 (d, *J* = 8.4 Hz, 4H), 7.562 (dd, *J* = 9.2 Hz, 1.2 Hz, 2H), 7.497 (d, *J* = 9.2 Hz, 2H), 7.349 (t, *J* = 6.0 Hz, 2H), 7.291 (d, *J* = 8.8 Hz, 2H), 4.115 (m, 4H), 1.120 (t, *J* = 6.8 Hz, 6H); ^{13}C NMR ($CDCl_3$, 150.9 MHz) δ (ppm): 154.69, 149.18, 147.47, 141.16, 137.04, 136.08, 135.22, 135.08, 133.59, 129.62, 129.46, 127.84, 127.44, 126.21, 125.84, 125.59, 123.72, 121.12, 120.38, 116.27, 65.20, 15.03; MS (ESI) (*m/z*) Calcd for $C_{56}H_{42}N_4O_2$: 802.3, Found: 803.4; Anal. Calcd for $C_{56}H_{42}N_4O_2$: C, 83.77; H, 5.27; N, 6.98, Found: C, 83.78; H, 5.33; N, 6.91%.

(*S*)-6,6'-Bis(4-(2,2'-bipyridin-5-yl)phenyl)-2,2'-dihexyloxy-1,1'-binaphthyl (*S*)-**3**

M.p. 136-138 ºC; $[\alpha]_D^{20}$ 180.9 (*c* = 0.084 in CH_2Cl_2); FT-IR (KBr, cm^{-1}): 2950, 2926, 2855,

1589, 1575, 1487, 1459, 1435, 1343, 1278, 1244, 1092, 1068, 1054, 1031, 1001, 822, 797, 750; ^{1}H NMR ($CDCl_3$, 600.1 MHz) δ (ppm): 8.992 (s, 2H), 8.710 (d, J = 4.2 Hz, 2H), 8.503 (d, J = 8.4 Hz, 2H), 8.462 (d, J = 7.8 Hz, 2H), 8.141 (s, 2H), 8.084 (dd, J = 6.6 Hz, 2.4 Hz, 2H), 8.032 (d, J = 9.0 Hz, 2H), 7.817-7.853 (m, 6H), 7.754 (d, J = 7.8 Hz, 4H), 7.553 (d, J = 8.4 Hz, 2H), 7.476 (d, J = 9.0 Hz, 2H), 7.305-7.320 (m, 4H), 3.967-4.022 (m, 4H), 1.432-1.464 (m, 4H), 0.971-1.064 (m, 12H), 0.726 (t, J = 7.2 Hz, 6H); ^{13}C NMR ($CDCl_3$, 150.9 MHz) δ (ppm): 154.93, 149.19, 147.47, 141.23, 137.01, 136.11, 136.04, 135.17, 135.06, 133.64, 129.55, 129.46, 127.83, 127.42, 126.21, 125.81, 125.53, 123.70, 121.11, 120.42, 116.25, 69.75, 31.33, 29.37, 25.35, 22.47, 13.91; MS (ESI) (*m/z*) Calcd for $C_{64}H_{58}N_4O_2$: 914.46, Found: 915.22; Anal. Calcd for $C_{64}H_{58}N_4O_2$: C, 83.99; H, 6.39; N, 6.12, Found: C, 83.89; H, 6.42; N, 6.11%.

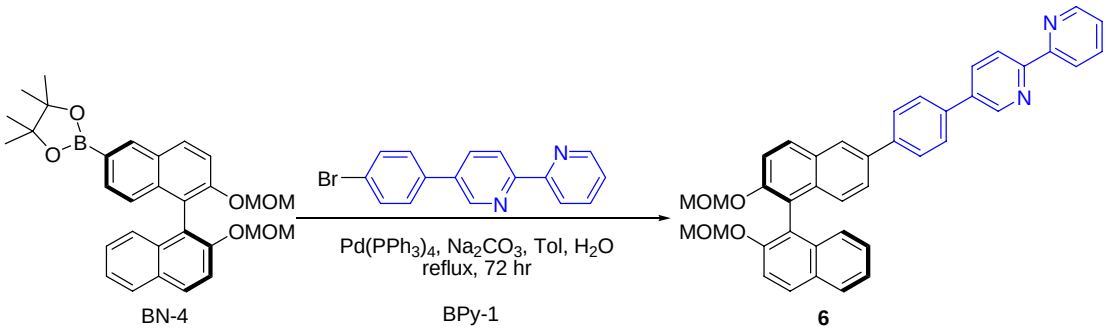
(*S*)-6,6'-Bis(4'-(2,2'-bipyridin-5-yl)biphen-4-yl)-2,2'-dihexyloxy-1,1'-binaphthyl (*S*)-**4**

M.p. 258-260 ºC; $[\alpha]_D^{20}$ 193.3 (c = 0.104 in CH_2Cl_2); FT-IR (KBr, cm^{-1}): 1588, 1573, 1484, 1458, 1435, 1342, 1273, 1244, 1188, 1145, 1091, 1052, 1036, 1022, 1002, 817, 795, 750; ^{1}H NMR ($CDCl_3$, 600.1 MHz) δ (ppm): 8.998 (s, 2H), 8.720 (d, J = 3.6 Hz, 2H), 8.523 (d, J = 7.8 Hz, 2H), 8.477 (d, J = 7.8 Hz, 2H), 8.144 (s, 2H), 8.097 (d, J = 7.8 Hz, 2H), 8.033 (d, J = 9.0 Hz, 2H), 7.859 (t, J = 7.2 Hz, 2H), 7.748-7.814 (m, 16H), 7.564 (d, J = 8.4 Hz, 2H), 7.477 (d, J = 9.0 Hz, 2H), 7.339 (t, J = 6.0 Hz, 2H), 7.315 (d, J = 9.0 Hz, 2H), 3.980 (m, 4H), 1.451 (m, 4H), 0.973-1.059 (m, 12H), 0.732 (t, J = 7.2 Hz, 6H); ^{13}C NMR ($CDCl_3$, 150.9 MHz) δ (ppm): 154.86, 149.20, 147.49, 140.67, 140.59, 138.86, 137.03, 136.40, 136.05, 135.39, 135.09, 133.58, 129.50, 127.68, 127.63, 127.47, 127.40, 126.17, 125.71, 125.60, 123.73, 121.12, 120.48, 116.24, 69.77, 31.34, 29.38, 25.36, 22.48, 13.92; MS (ESI) (*m/z*) Calcd for $C_{76}H_{66}N_4O_2$: 1066.52, Found: 1067.34; Anal. Calcd for $C_{76}H_{66}N_4O_2$: C, 85.52; H, 6.23; N, 5.25, Found: C, 85.49; H, 6.26; N, 5.25%.

(*S*)-6,6'-Bis(2,2'-bipyridin-5-yl)-2,2'-diethoxyl-1,1'-binaphthyl (*S*)-**5**

M.p. 186-188 ºC; $[\alpha]_D^{20}$ 235.6 (c = 0.10 in CH_2Cl_2); FT-IR (KBr, cm^{-1}): 1622, 1588, 1572, 1550, 1490, 1467, 1456, 1434, 1335, 1278, 1244, 1113, 1091, 1056, 1031, 943, 796, 746; ^{1}H NMR ($CDCl_3$, 600.1 MHz) δ (ppm): 9.083 (d, J = 1.2 Hz, 2H), 8.757 (d, J = 4.2 Hz, 2H), 8.543 (d, J = 8.4 Hz, 2H), 8.505 (d, J = 7.8 Hz, 2H), 8.220 (s, 2H), 8.168 (dd, J = 8.4 Hz, 2.4 Hz, 2H), 8.113 (d,

J = 9.0 Hz, 2H), 7.881 (t, *J* = 7.8 Hz, 2H), 7.602 (dd, *J* = 9.0 Hz, 1.2 Hz, 2H), 7.558 (d, *J* = 9.0 Hz, 2H), 7.362 (m, 4H), 4.167 (m, 4H), 1.178 (t, *J* = 7.2 Hz, 6H); ^{13}C NMR ($CDCl_3$, 150.9 MHz) δ (ppm): 155.90, 154.91, 154.53, 149.18, 147.63, 136.92, 136.50, 135.13, 133.76, 132.39, 129.73, 129.35, 126.40, 126.13, 125.20, 123.60, 121.02, 120.16, 116.27, 65.11, 14.99; MS (ESI) (*m/z*) Calcd for $C_{44}H_{34}N_4O_2$: 650.27, Found: 651.31; Anal. Calcd for $C_{44}H_{34}N_4O_2$: C, 81.21; H, 5.27; N, 8.61, Found: C, 81.24; H, 5.31; N, 8.59%.



Scheme S2 Synthesis of the compound **6**.

To a degassed solution of 5-(4-bromophenyl)-2,2'-bipyridine (0.35 g, 1.12 mmol) in toluene (20 mL) is added $Pd(PPh_3)_4$ (115.6 mg, 0.10 mmol) under a nitrogen atomosphere. After the resulting mixture is stirred for 10 minutes at room temperature, 2,2'-bis(methoxymethoxy)-1,1'-binaphhyl-6-boronic acid pinacol ester (0.50 g, 1.00 mmol) and 1M Na_2CO_3 (6.0 mL) are added sequentially into the mixture. Then the mixture is refluxed for 3 days under nitrogen. After removal of the solvent, the resulting residue is extracted with chloroform (40 mL × 3), washed with brine (40 mL) and dried over anhydrous $MgSO_4$. Evaporation of the solvent gives a yellow residue which is purified by silica gel column chromatography (CH_2Cl_2/THF = 50/1) to afford (*S*)-**6** in 92% yield as an off-white powder.

Mp: 226-228 ºC; $[\alpha]_D^{20}$ -29.4 (*c* = 0.102 in CH_2Cl_2); FTIR (KBr, cm^{-1}): 2925, 1589, 1458, 1435, 1240, 1197, 1148, 1071, 1031, 1013, 958, 921, 823, 796, 749; ^{1}H NMR ($CDCl_3$, 600.1 MHz) δ (ppm): 8.990 (s, 1H), 8.715 (d, *J* = 4.2 Hz, 1H), 8.512 (d, *J* = 7.8 Hz, 1H), 8.468 (d, *J* = 7.2 Hz, 1H), 8.148 (s, 1H), 8.086 (d, *J* = 6.6 Hz, 1H), 8.036 (d, *J* = 9.0 Hz, 1H), 7.975 (d, *J* = 9.0 Hz, 1H), 7.893 (d, *J* = 8.4 Hz, 1H), 7.851 (t, *J* = 7.2 Hz, 1H), 7.817 (d, *J* = 8.4 Hz, 2H), 7.753 (d, *J* = 8.4 Hz, 2H), 7.629 (d, *J* = 9.0 Hz, 1H), 7.603 (d, *J* = 9.0 Hz, 1H), 7.548 (d, *J* = 8.4 Hz, 1H), 7.363 (t, *J* =

7.2 Hz, 1H), 7.342 (t, *J* = 5.4 Hz, 1H), 7.242-7.272 (m, 2H), 7.207 (d, *J* = 8.4 Hz, 1H), 5.109 (d, *J* = 6.6 Hz, 2H), 5.010 (t, *J* = 7.2 Hz, 2H), 3.191 (s, 3H), 3.169 (s, 3H); ^{13}C NMR ($CDCl_3$, 150.9 MHz) δ (ppm): 155.79, 154.82, 152.97, 152.71, 149.18, 147.46, 140.92, 137.00, 136.20, 136.02, 135.79, 135.05, 133.99, 133.42, 130.09, 129.90, 129.74, 129.48, 127.90, 127.84, 127.43, 126.36, 126.30, 125.77, 125.67, 125.47, 124.10, 123.69, 121.23, 121.11, 121.10, 117.77, 117.31, 107.90, 95.27, 95.17, 67.61, 55.84; MS (ESI) (*m/z*) Calcd for $C_{40}H_{32}N_2O_4$: 604.24, Found: 605.25; Anal. Calcd for $C_{40}H_{32}N_2O_4$: C, 79.45; H, 5.33; N, 4.63, Found: C, 79.46; H, 5.32; N, 4.66%.

3. Gelation test of the complexes Cu(I)·1-5 and Cu(I)·6_2 in mixed solvents at room temperature

A mixture of equimolar compound (*S*)-**1-5** (1.6×10^{-2} mmol) or two equivalent of compound **6** (3.2×10^{-2} mmol), $Cu(CH_3CN)_4BF_4$ (5.0 mg, 1.6×10^{-2} mmol) and mixed solvent (v/v, 1/1, 1.0 mL) were charged with a glass test tube (35 mm × 15 mm), which was capped and sonicated for a few minutes using sonoreactor (0.26 Wcm^{-1}, 40 kHz). If the gel cannot be formed, the mixture was heated in an oil bath (*T* = 120 ºC) until the mixture was dissolved in the solvent. After the solution was allowed to stand at room temperature (25 ± 5 ºC) for 30 min, the state of the mixture was evaluated by the "stable to inversion of test tube" method. The gel-forming abilities of the complexes Cu(I)·**1-5** and Cu(I)·$\mathbf{6}_2$ were summarized in Table S1.

The complexes Cu(I)·**1-3** formed gels in CH_2Cl_2-CH_3CN (1:1) in 5 minutes, while the complex Cu(I)·**4** required longer time - 9 minutes - to gelate the mixed solvents. The gel Cu(I)·**4** in CH_2Cl_2-CH_3CN (1:1) can be damaged by vigorous shake with hand.

Table S1 Gel abilities of complexes Cu(I)·**1-5** and Cu(I)·$\mathbf{6}_2$ at mixed solvents (v/v, 1/1) at 25 ºC.[a]

Mixed solvents	Cu(I)·**1**	Cu(I)·**2**	Cu(I)·**3**	Cu(I)·**4**	Cu(I)·**5**	Cu(I)·$\mathbf{6}_2$
CH_2Cl_2-CH_3CN	G (G*)	G	G	G	S	S
$CHCl_3$-CH_3CN	P (G*)	P	P	P	S	S
THF-CH_3CN	G (G*)	G	G	G	S	S
dioxane-CH_3CN	G (G*)	G	G	G	S	S

[a] G: gel formed by heating-cooling process, G*: gel formed via sonication, S: solution, P: precipitate, $c = 1.6 \times 10^{-2}$ $molL^{-1}$.

No collapse was observed when various solvent such as CH_2Cl_2, $CHCl_3$, THF, dioxane, Et_2O, CH_3CN, EtOAc, acetone, toluene, hexane, MeOH, DMF, DMAc, or HOAc (1.0 mL) was placed over the metallogel Cu(I)·**1** (Fig. S1a, c = 1.6 × 10^{-2} molL^{-1}, 1.0 mL) overnight (Fig. S1b). But when pyridine (1.0 mL) was placed over the metallogel, the gel slowly turned into yellow (Fig. S1c) and finally green (Fig. S1d) solution with a small amount of precipitate.

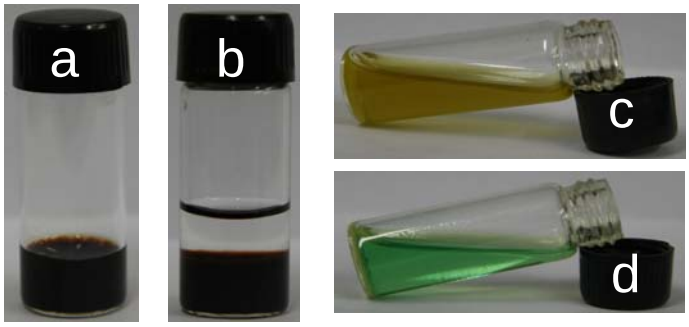


Fig. S1 The stabilities of the CH_2Cl_2-CH_3CN (1/1) gel Cu(I)·**1** to various solvents at room temperature.

The redox-responsive properties of gel Cu(I)·**1**: When $NOBF_4$ (1.0 equiv.) was added at the top of preformed gel Cu(I)·**1** (c = 1.6 × 10^{-2} molL^{-1} in CH_2Cl_2-CH_3CN (1/1)) and then the system was heated and subsequently cooled to room temperature, the dark red gel turned into the light green solution (Fig. S2b). Afterward, excess ascorbic acid (6.0 equiv.) was added to the solution and the resulting mixture was heated until the color of the solution turned into deep red. The gel was re-formed upon cooling to room temperature with a small amount of liquid (Fig. S2a).

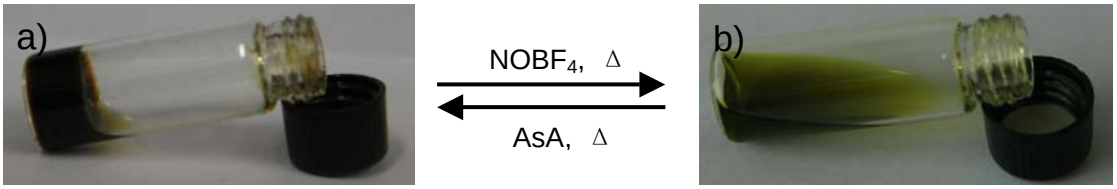


Fig. S2 Phase transition behaviour of the complex Cu(I)·**1** triggered by heat-aided chemical redox reaction.

4. FTIR spectra of the compounds 1-4 and their corresponding xerogels Cu(I)•1-4.

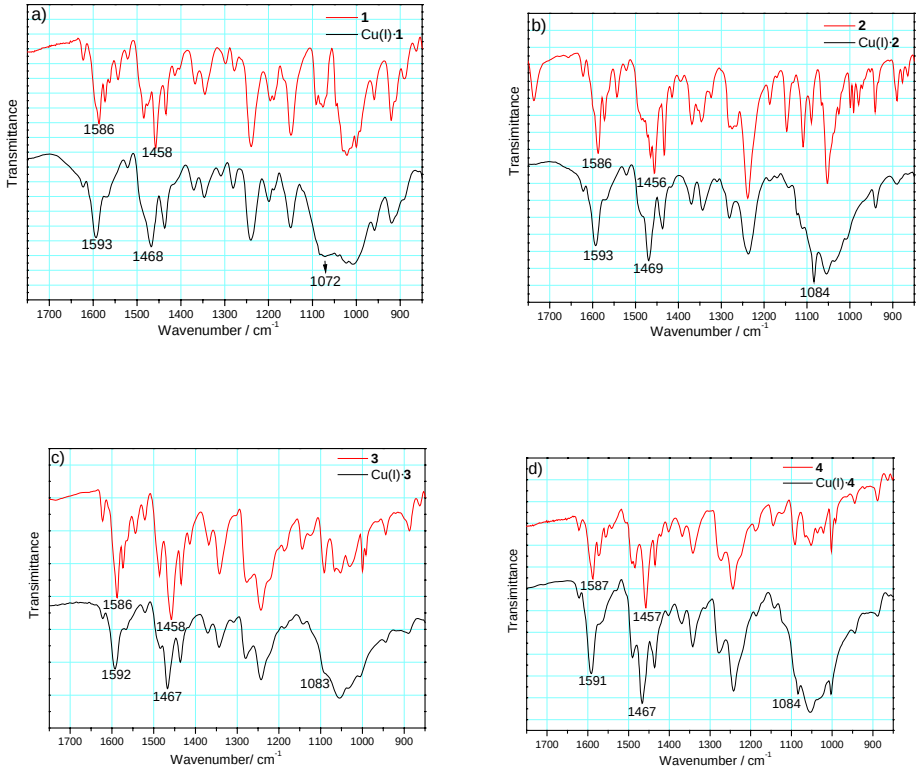
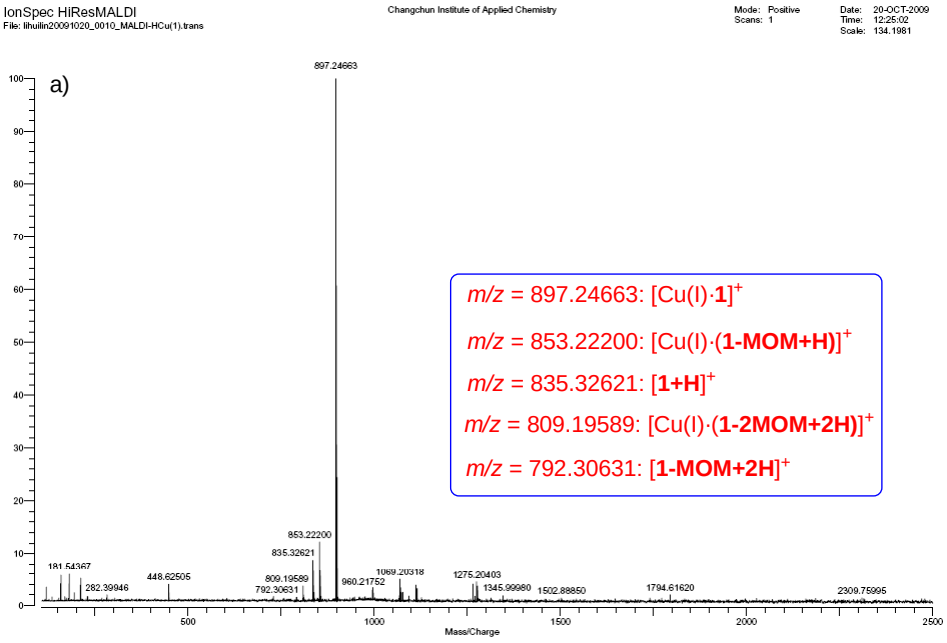
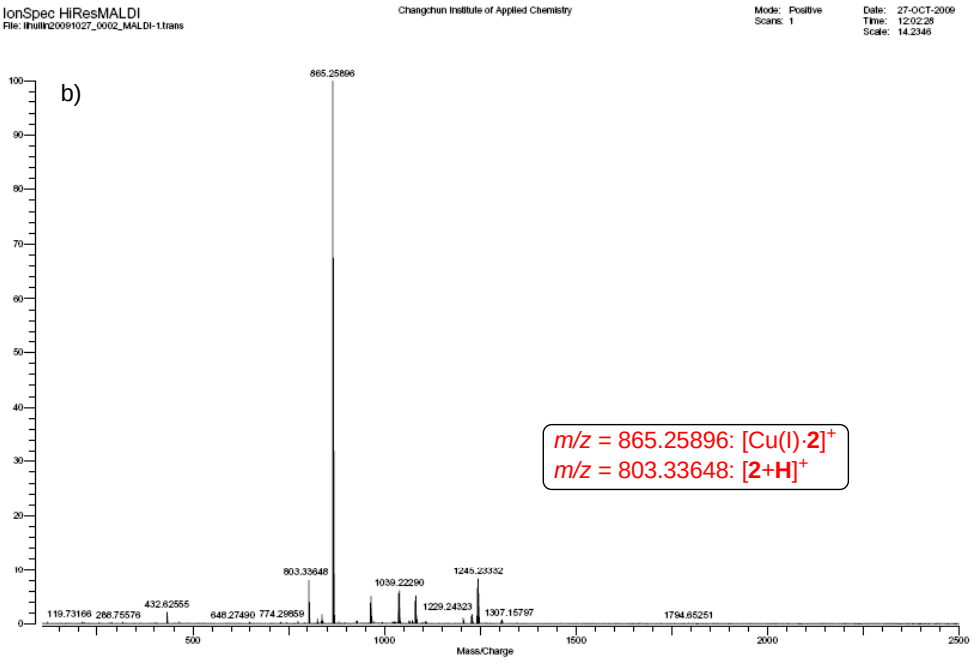


Figure S3 Comparison of FTIR spectra between the compounds **1-4** and their corresponding complexes Cu(I)·**1-4**.

5. MALDI-TOF-MS spectra of complexes Cu(I)•1-4





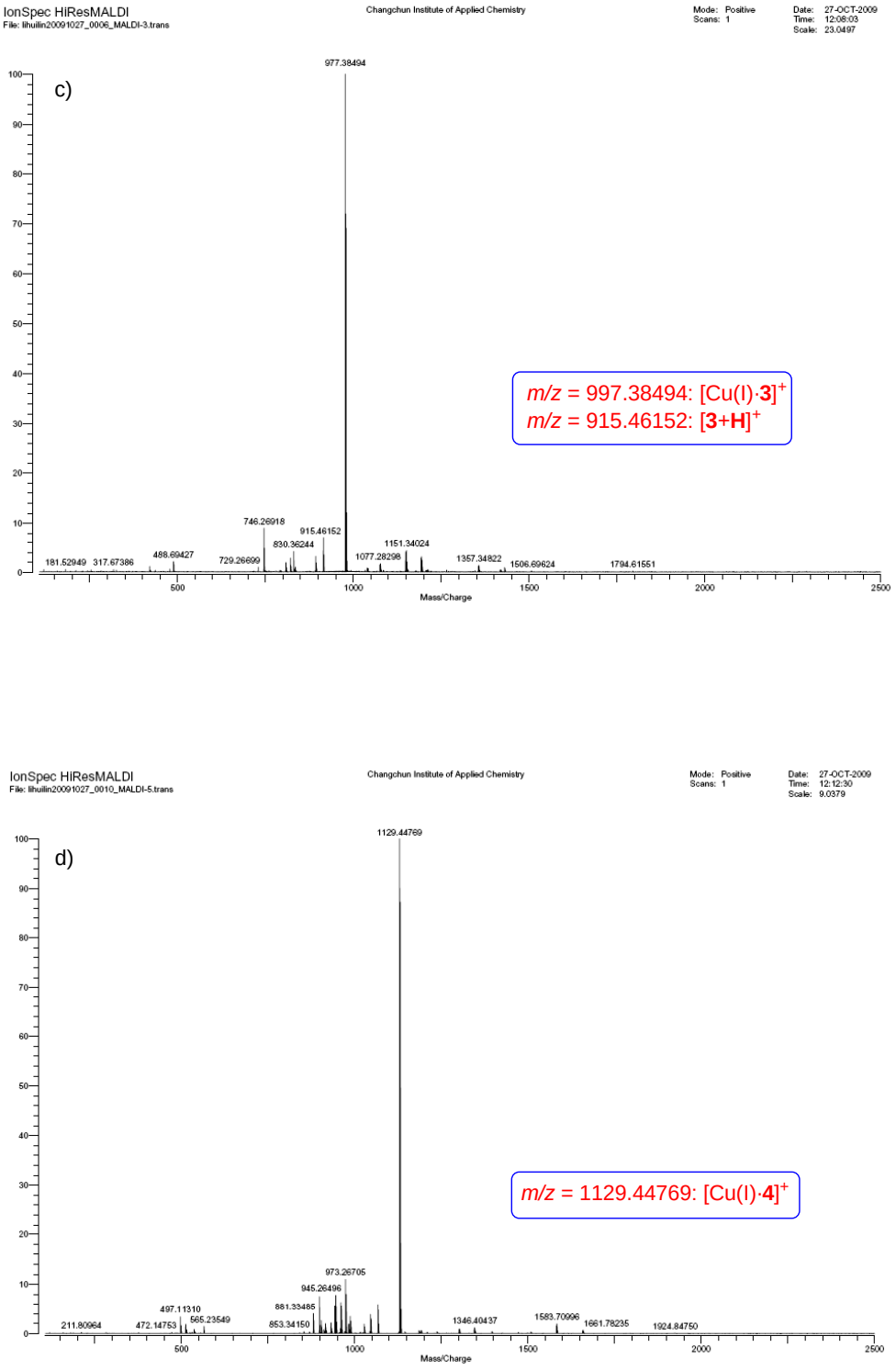


Figure S4 MALDI-TOF-MS spectra of the complexes Cu(I)•**1** (a), Cu(I)•**2** (b), Cu(I)•**3** (c), and Cu(I)•**4** (d). $c = 1 \times 10^{-3}$ molL^{-1}.

6. Job plot analysis of the complexation of 1 and Cu(I) ion

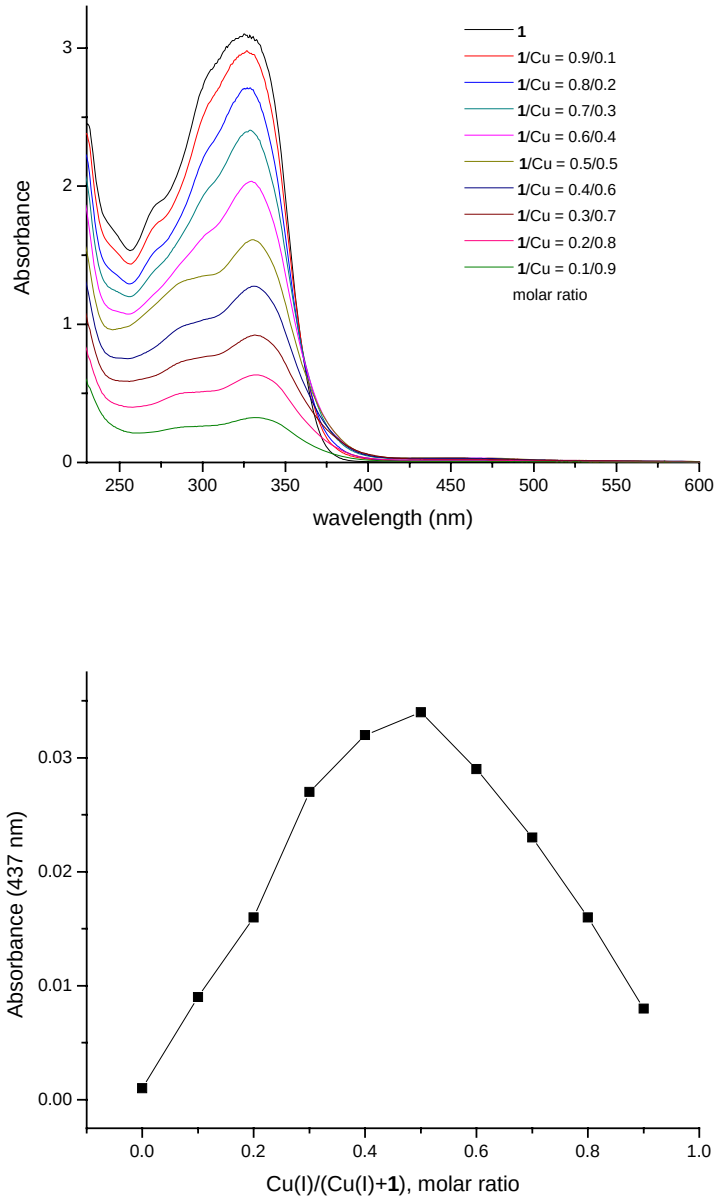


Figure S5 A Job plot analysis at 437 nm of the complexation of **1** and $Cu(CH_3CN)_4BF_4$ by UV-vis spectroscopy at room temperature. The total molar concentration is 4×10^{-5} M in CH_3CN-CH_2Cl_2 (v/v, 1/1) .

7. CD spectra of the compounds (*S*)-1, (*R*)-1 and their corresponding complexes

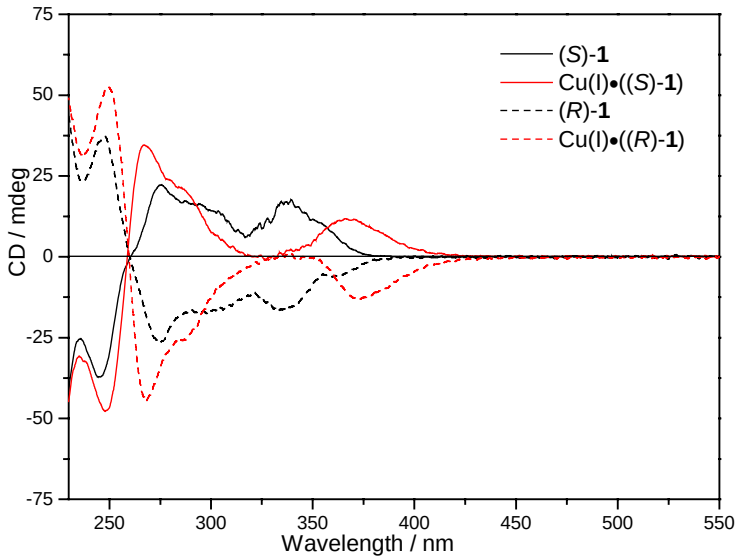
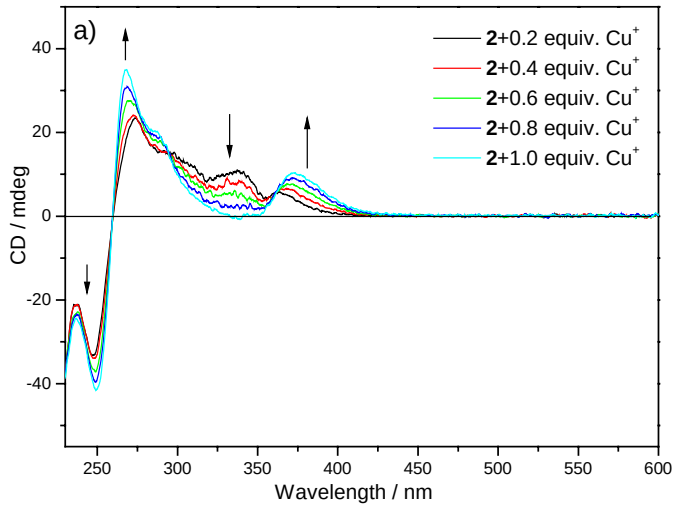


Figure S6 CD spectra of the compounds (*S*)-**1**, (*R*)-**1** and their corresponding complexes in CH_2Cl_2-CH_3CN (1:1) solution, $c = 2 \times 10^{-4}$ molL^{-1}.

8. Circular dichroism (CD) spectroscopic titration



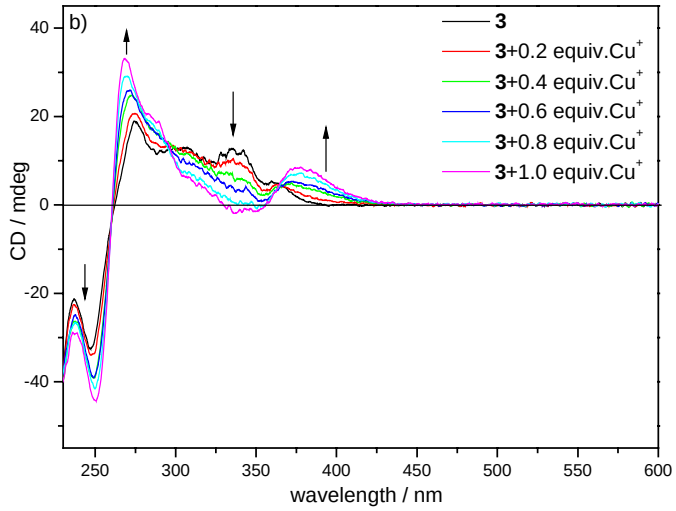


Figure S7 CD spectroscopic titration of the complexes Cu(I)•**2** (a) and Cu(I)•**3** (b) in CH_2Cl_2-CH_3CN (v/v, 1/1) solution, $c = 2 \times 10^{-4}$ molL^{-1}.

9. The SEM images of xerogels of complexes Cu(I)•2-4

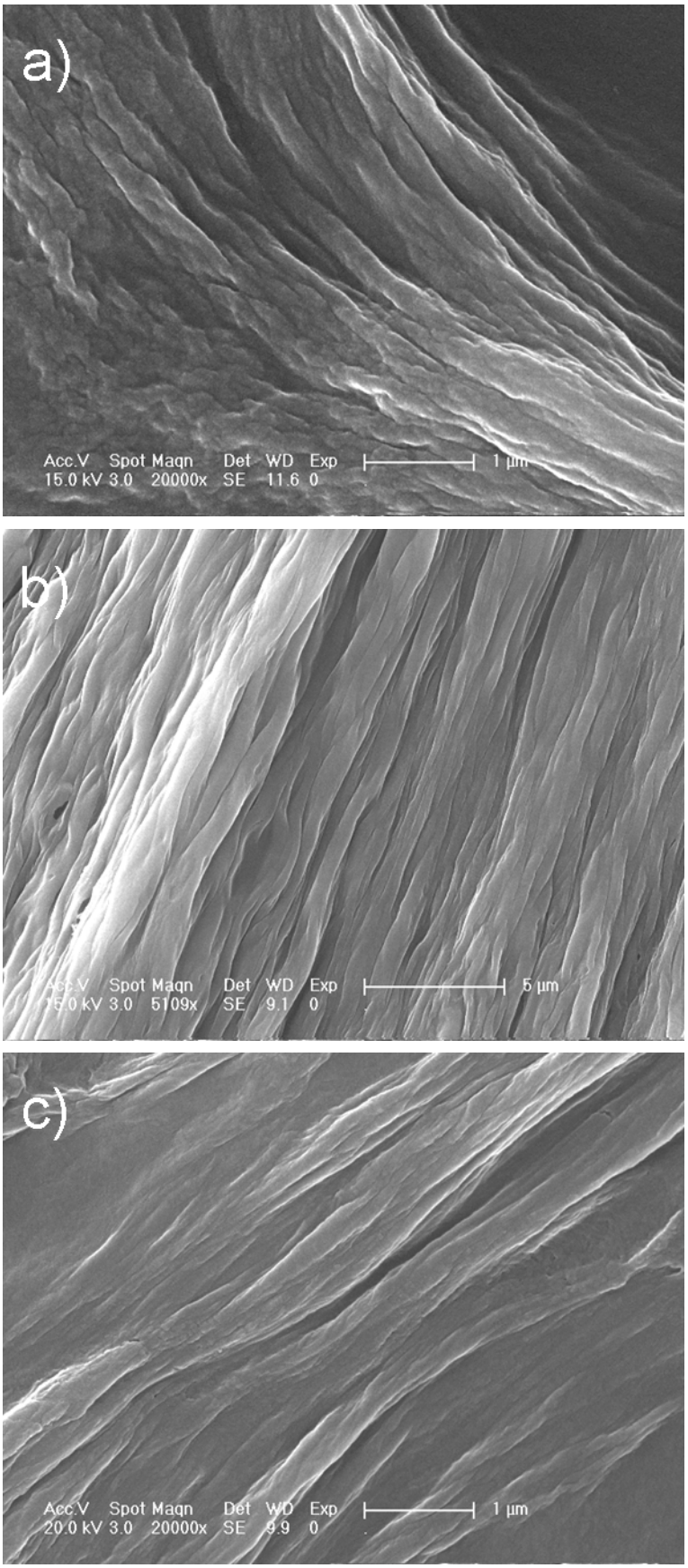


Figure S8 SEM images of xerogels Cu(I)•**2 (**a), Cu(I)•**3** (b) and Cu(I)•**4** (c).

10. **DSC curves of gels Cu(I)•1-4**

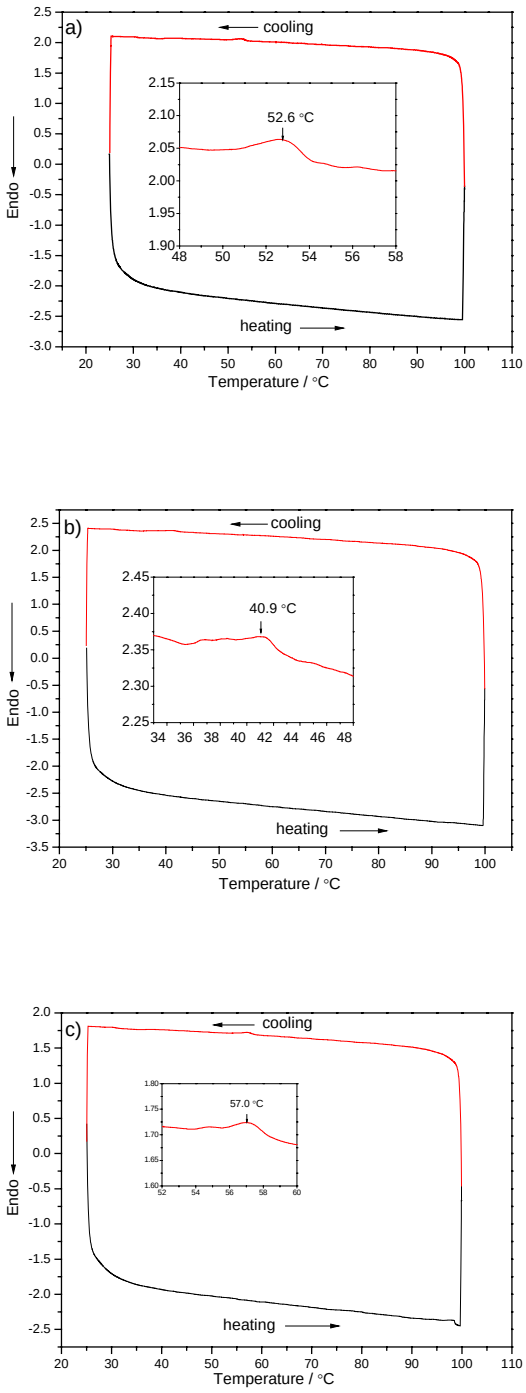


Figure S9 DSC thermograms of CH_2Cl_2-CH_3CN (v/v, 1/1) gels Cu(I)•**1** (a), Cu(I)•**2** (b) and Cu(I)•**3** (c), c = 1.6 × 10^{-2} molL^{-1}, heating and cooling rate: 5 ºCmin^{-1}. Repeated heating and cooling cycle shows similar transition behaviour.

11. CV Curves of the complexes Cu(I)•1-4

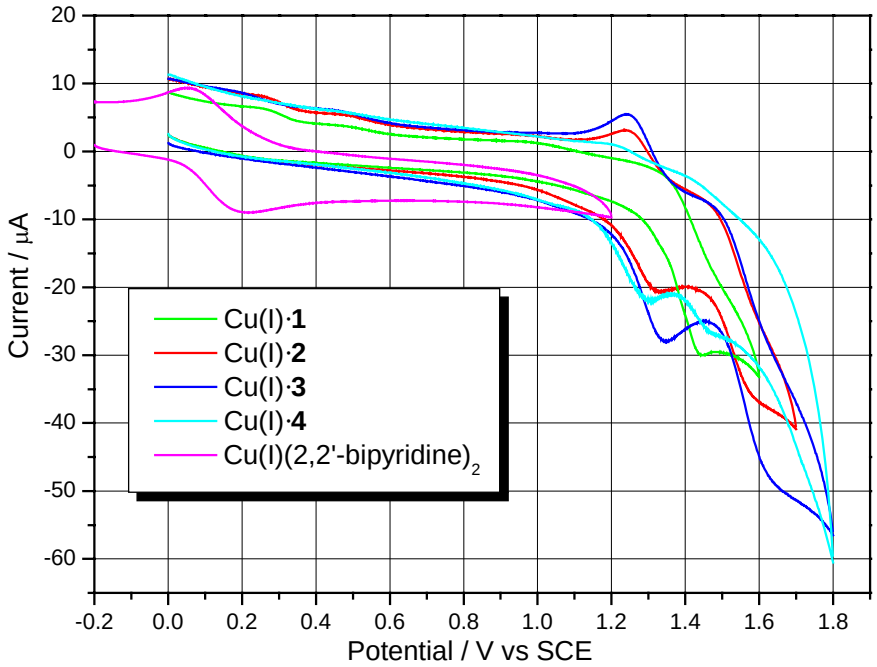


Figure S10 CV Curves of the complexes Cu(I)•**1-4** and Cu(I)(2,2'-bipyridine)$_2$ in CH_2Cl_2-CH_3CN (v/v, 1/1), c = 2.0 × 10^{-3} molL^{-1}, Scan rate = 0.1 Vs^{-1}.

12. UV-Vis spectra change of the phase transition triggered by chemical redox reaction

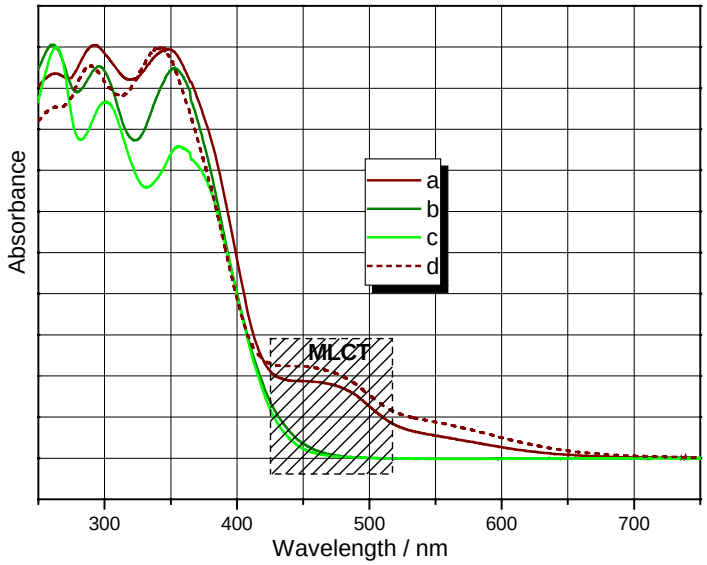
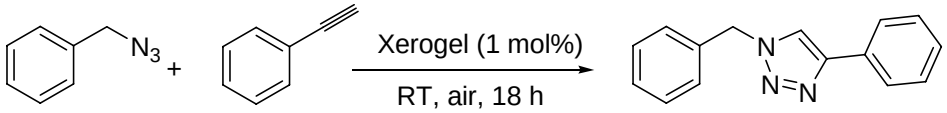


Fig. S11 UV-vis spectra of the gel in CH_2Cl_2-CH_3CN (1/1) (a), the oxidized solution sample (b), the solution of Cu(Ⅱ) •**1** (c) and the re-formed gel sample (d).

13. Xerogel catalyzed Huisgen cycloaddition reaction

Xerogel **1**-**4** (0.01 mmol), alkyne **8a-d** (1.2 mmol), benzyl azide **7** (1.0 mmol), and solvent (2.0 mL) were added to a 10 mL flask and the mixture was stirred at RT in air over a required duration. EtOAc (8 mL) and H_2O (2 mL) were added to the resultant mixture, and the catalyst was filtered off. The organic layer was separated from the aqueous portion. The organic extract was dried over anhydrous $MgSO_4$, filtered, and analyzed by GC–MS. It was then concentrated in vacuum and purified by silica gel column chromatography (petroleum ether / ethyl acetate). The results of screening solvents and catalysts were shown in Table S2. Using water as solvent and xerogel Cu(I)•**3** as catalyst gave the best result. For recovering, the catalyst was separated by simple filtration. The separated solid catalyst was recharged with water and substrates again for the next run of click reaction. The results of recycling and reuse of the xerogel catalyst Cu(I)•**1** were shown in Table S3.

Table S2 Huisgen cycloaddition reactions of benzyl azide and phenylacetylene with xerogels as catalysts in different solvents.[a]

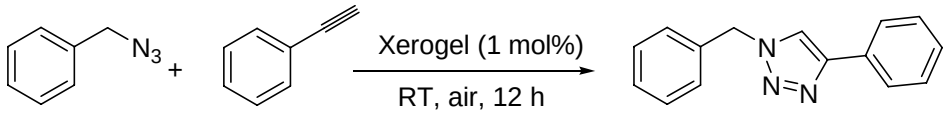


7 **8a** **9a**

Solvents	Xerogel Cu(I)•**1**	Xerogel Cu(I)•**2**	Xerogel Cu(I)•**3**	Xerogel Cu(I)•**4**
CH_2Cl_2	81.1%	73.5%	64.0%	87.0%
CH_3CN	78.4%	62.1%	58.7%	83.6%
CH_3CN-H_2O (1:1)	65.7%	76.7%	55.7%	87.1%
H_2O	78.3%	73.1%	**100%**	96.5%

[a] Rection condition: alkyl azide **7** (1.0 mmol), phenylacetylene **8a** (1.2 mmol), xerogel (0.01 mmol), solvent (2.0 mL), RT, air; GC yield.

Table S3 Recycling and reuse of the xerogel catalyst Cu(I)•**1** in Huisgen cycloaddition reactions.[a]



7 **8a** **9a**

Run	1st	2nd	3rd	4th
Yield (%)[b]	100	100	100	99.5

[a] Reaction condition: **7** (1.0 mmol), **8a** (1.2 mmol), xerogel Cu(I)•**1** (0.01 mmol), water (2.0 mL), RT, air; [b] Yield was determined by GC.

9a: ^{1}H NMR ($CDCl_3$, 400.0 MHz) δ (ppm): 7.797-7.818 (m, 2H), 7.666 (s, 1H), 7.369-7.419 (m, 5H), 7.308-7.335 (m, 3H), 5.583 (s, 2H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ (ppm): 148.14, 134.65, 130.50, 129.07, 128.72, 128.08, 127.98, 125.63, 119.46, 54.12.

9b: ^{1}H NMR ($CDCl_3$, 400.0 MHz) δ (ppm): 7.684 (d, J = 8.0 Hz, 2H), 7.614 (s, 1H), 7.371 (m, 3H), 7.296-7.315 (m, 2H), 7.202 (d, J = 8.0 Hz, 2H), 5.560 (s, 2H), 2.360 (s, 3H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ (ppm): 148.27, 138.00, 134.71, 129.45, 129.12, 128.74, 128.04, 127.67, 125.60, 119.11, 54.20, 21.24.

9c: ^{1}H NMR ($CDCl_3$, 400.0 MHz) δ (ppm): 7.658 (s, 1H), 7.642 (s, 1H), 7.569 (d, J = 8.0 Hz, 1H), 7.363-7.407 (m, 3H), 7.298-7.317 (m, 2H), 7.269 (d, J = 7.6 Hz, 1H), 7.129 (d, J = 7.6 Hz, 1H), 5.570 (s, 2H), 2.380 (s, 3H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ (ppm): 148.31, 138.48, 134.68, 130.34, 129.14, 128.94, 128.76, 128.68, 128.05, 126.38, 122.80, 119.43, 54.23, 21.37.

9d: ^{1}H NMR ($CDCl_3$, 600.1 MHz) δ (ppm): 8.536 (d, J = 4.2 Hz, 1H), 8.185 (d, J = 7.8 Hz, 1H), 8.070 (s, 1H), 7.772 (td, J = 7.8 Hz, 1.2 Hz, 1H), 7.327-7.393 (m, 5H), 7.211 (m, 1H), 5.584 (s, 2H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ (ppm): 150.14, 149.21, 148.60, 136.73, 134.26, 129.02, 128.68, 128.16, 122.70, 121.81, 120.06, 54.21.

14. Comparison of ^{1}H NMR spectra between the compound 1 and its corresponding complex Cu(I)•1.

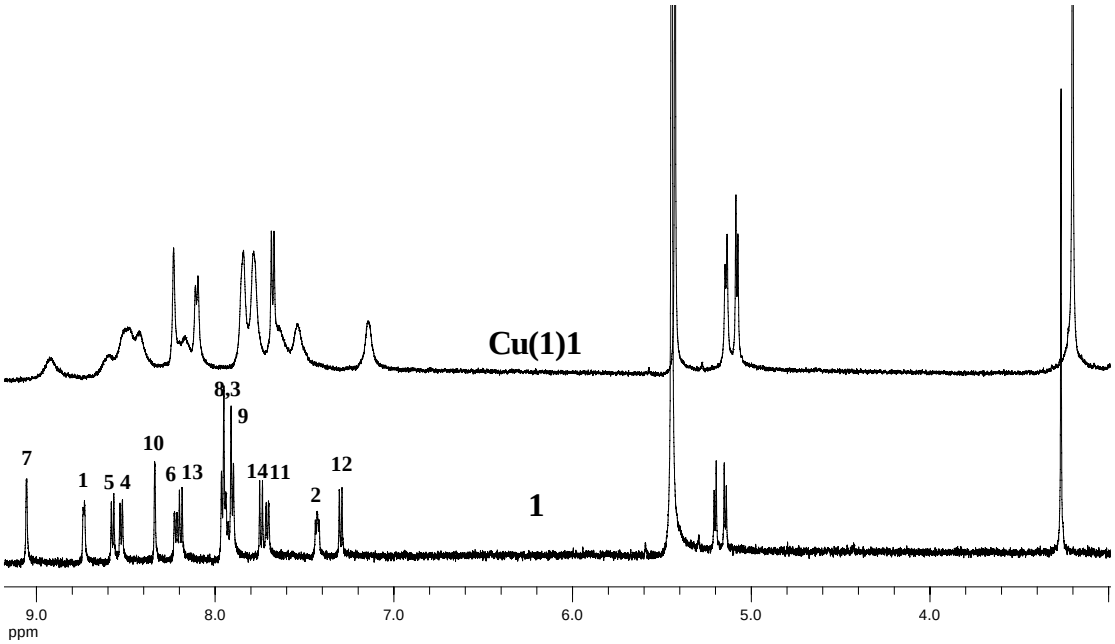


Figure S12 ^{1}H NMR spectra (600.1 MHz, 298 K, CD_2Cl_2/CD_3CN (1/1)) of the compound **1** (top) and **1** + 1.0 equiv. $Cu(CH_3CN)_4BF_4$ (bottom). Numbering of the atoms is according to Scheme S1 and signals are assigned on the basis of ^{1}H-^{1}H COSY NMR experiment. $c = 3.7 \times 10^{-3}$ molL^{-1}.

15. Temperature-dependent ^{1}H NMR spectra of the complex Cu(I)•1 in CD_2Cl_2-CH_3CN

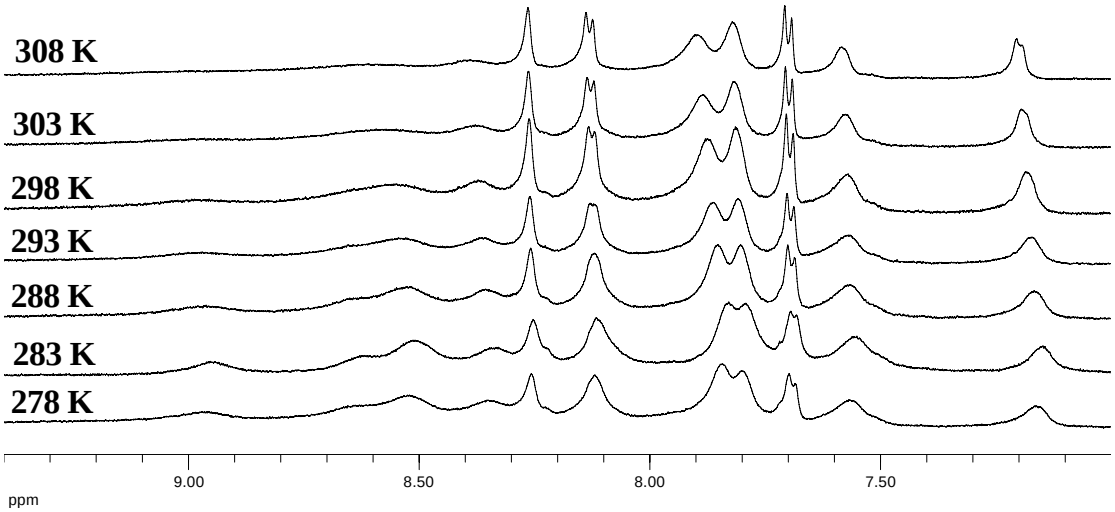
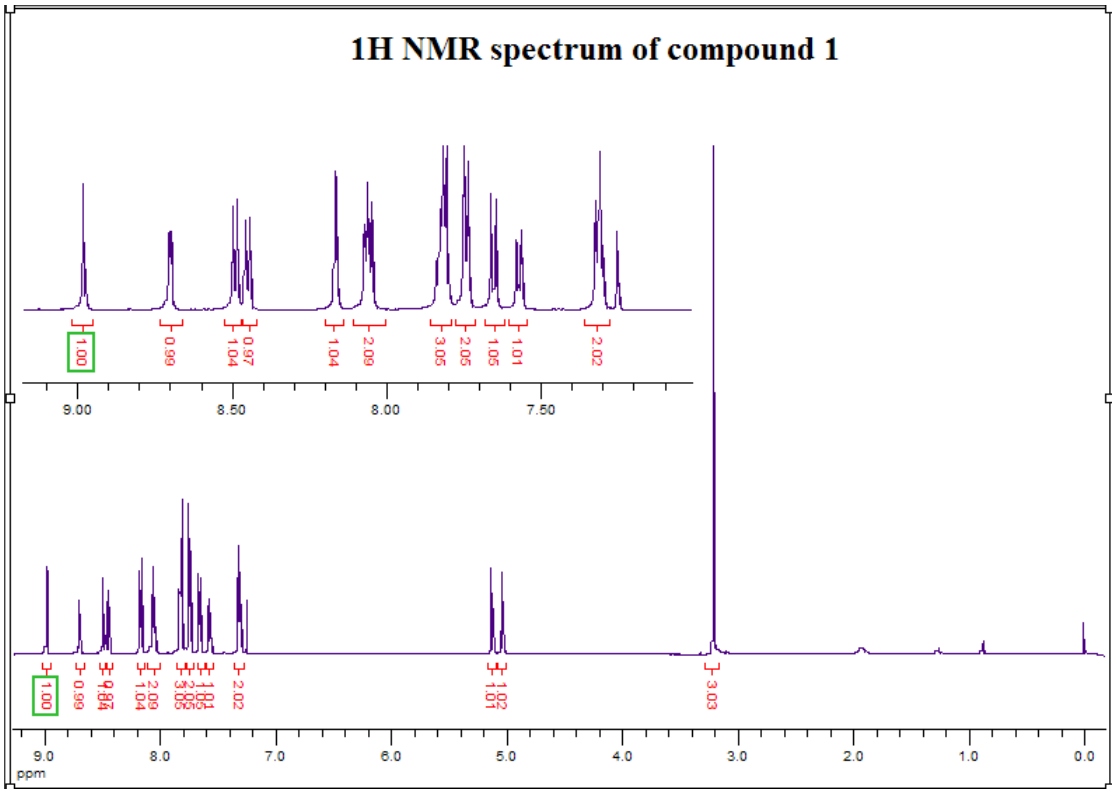
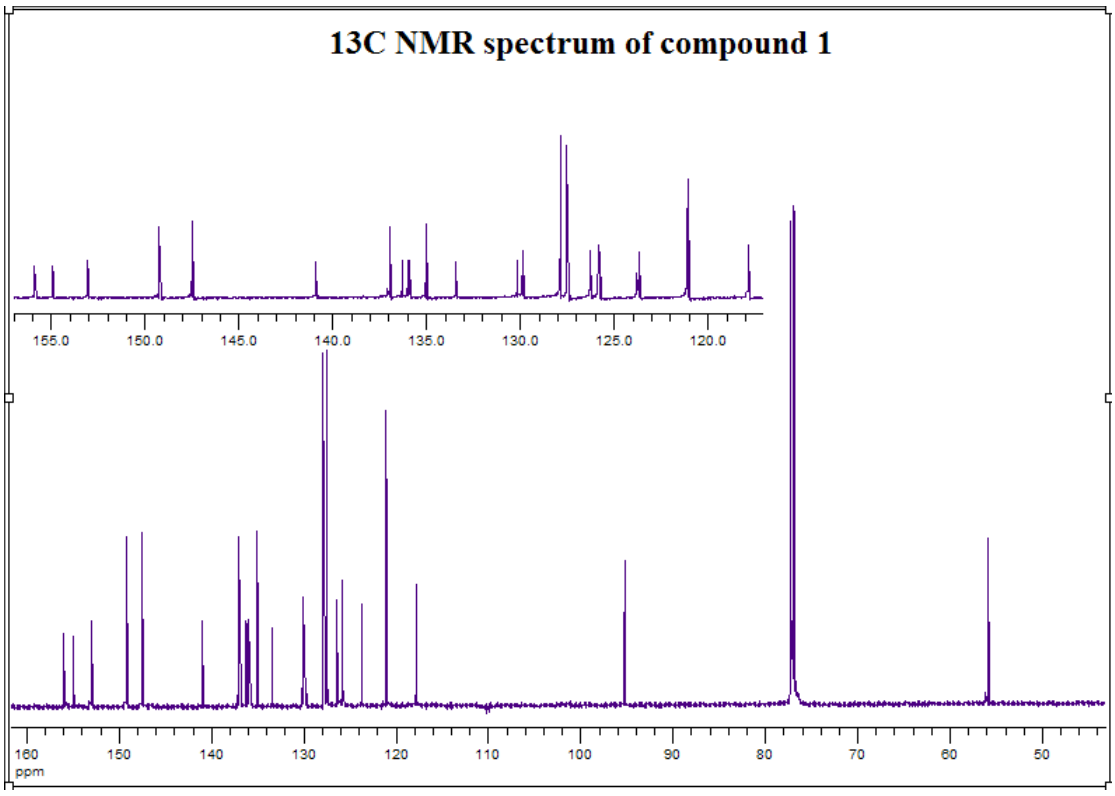
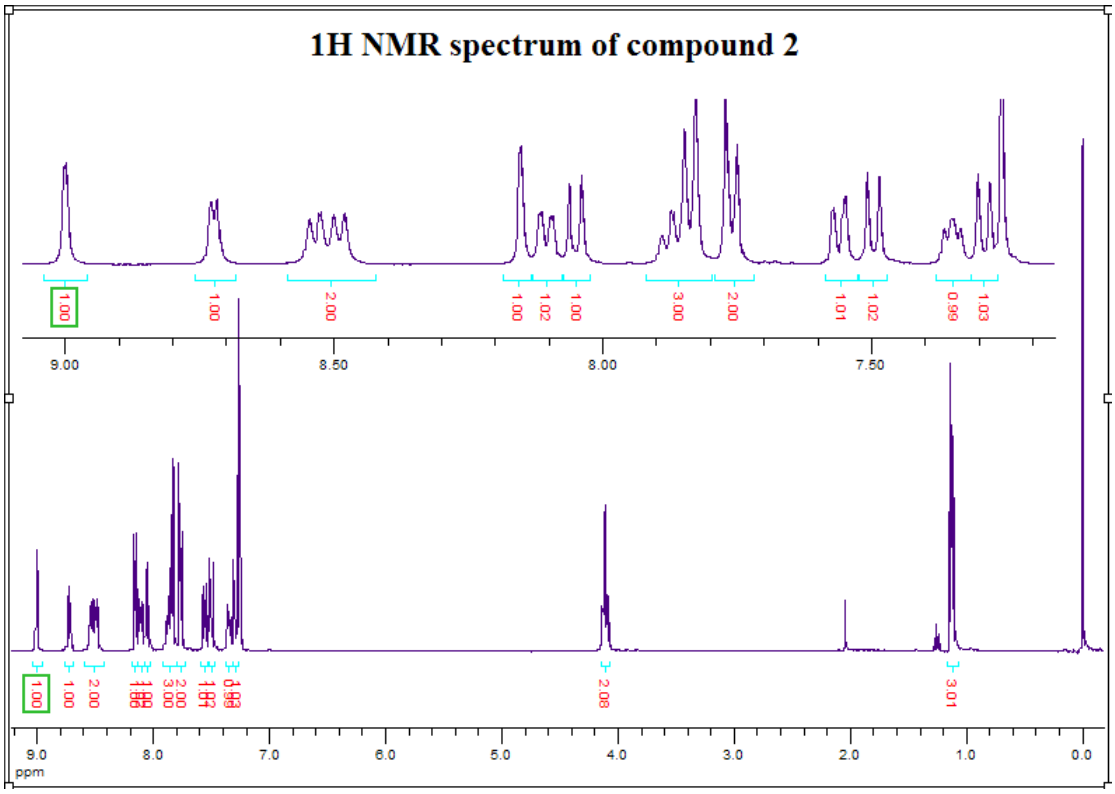


Figure S13 Temperature-dependent ^{1}H NMR spectrum of complex Cu(I)•**1** in CD_2Cl_2-CD_3CN (1/1).

16. ^{1}H NMR and ^{13}C NMR of the compounds investigated (*S*)-1-5.



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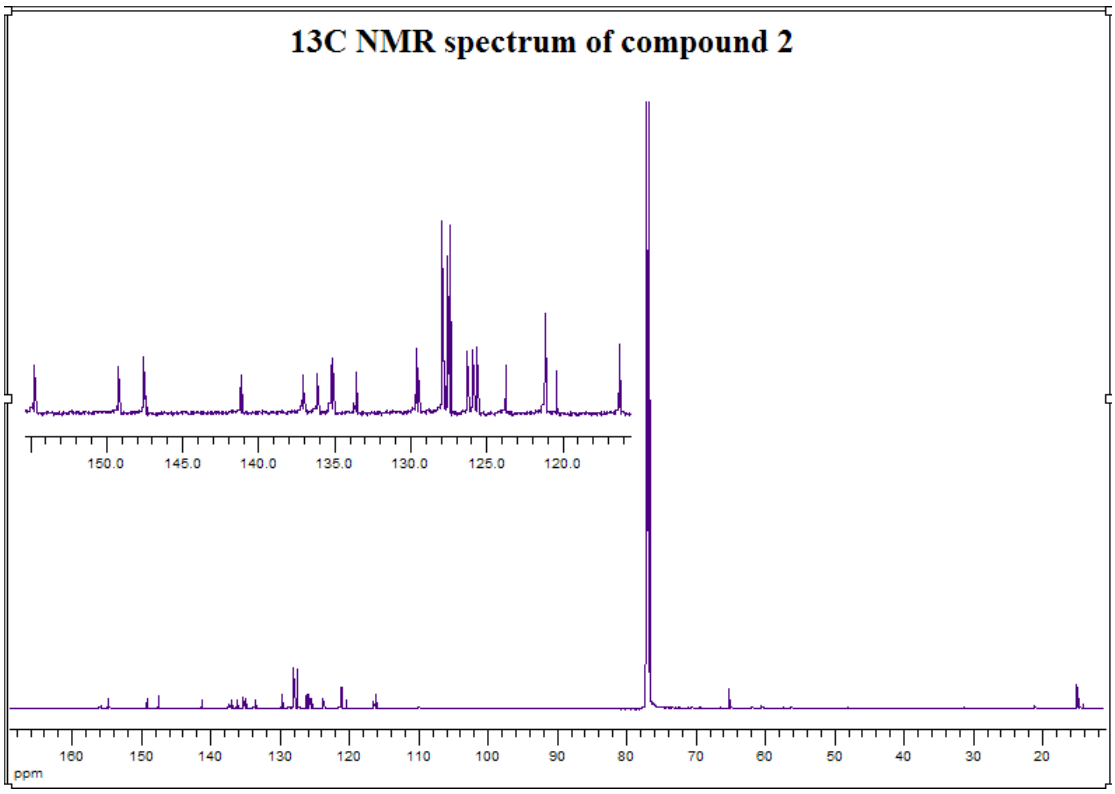
2.00
1.00
1.02
1.00
3.00
2.00
1.01
1.02
0.99
1.03
9.00
8.50
8.00
7.50
1.00
1.00
2.00
3.00
2.00
2.08
3.01
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm


13C NMR spectrum of compound 2
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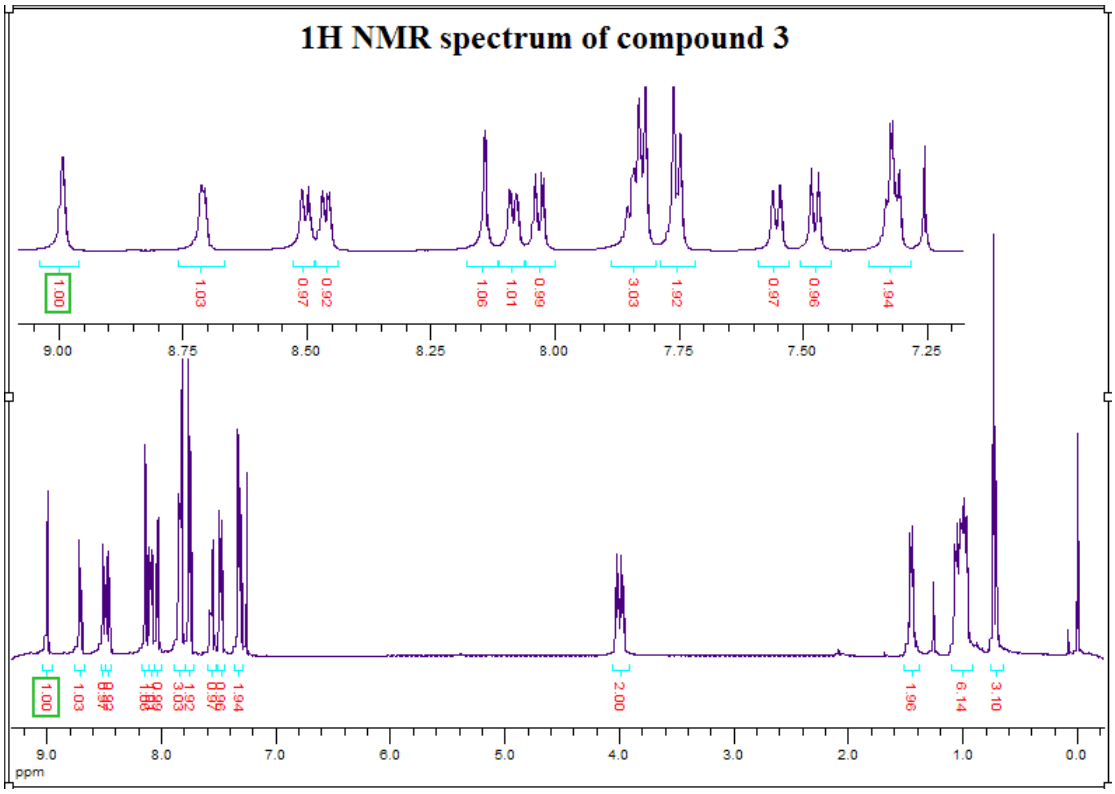
90
80
70
60
50
40
30
20
ppm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3.03
1.92
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0.96
1.94
9.00
8.75
8.50
8.25
8.00
7.75
7.50
7.25
1.00
1.03
3.03
1.94
2.00
1.96
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6.0
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3.0
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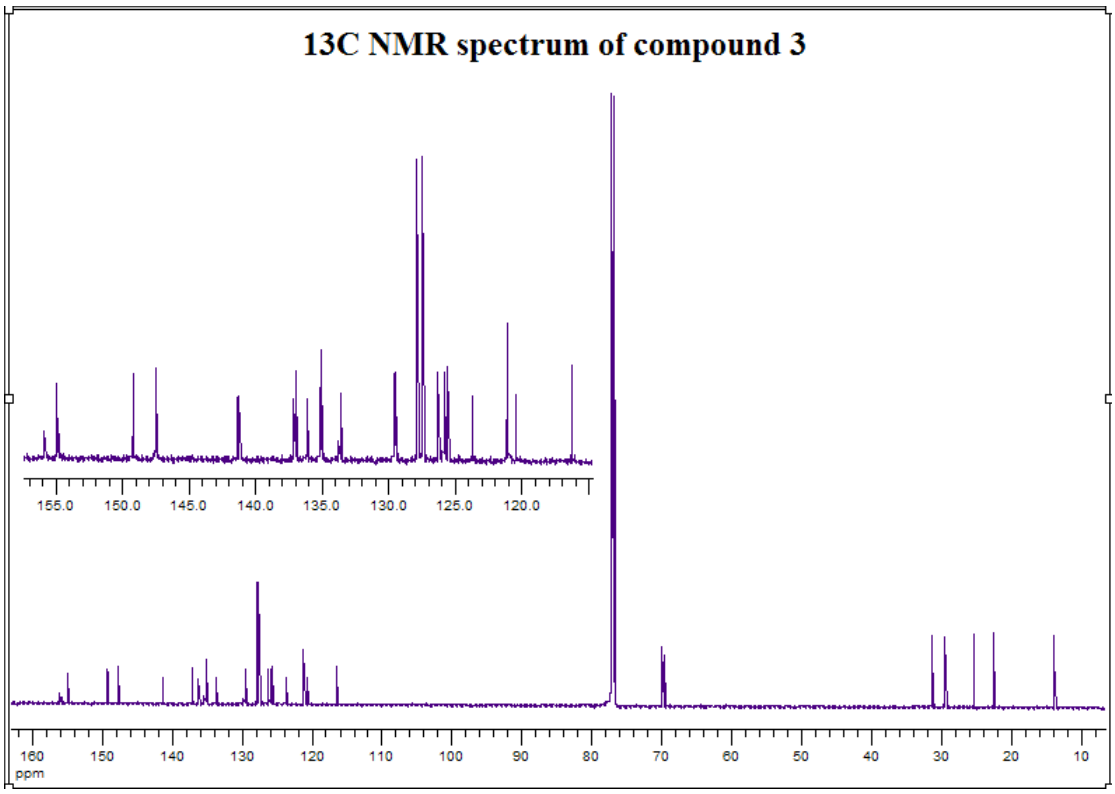
1.0
0.0
ppm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70
60
50
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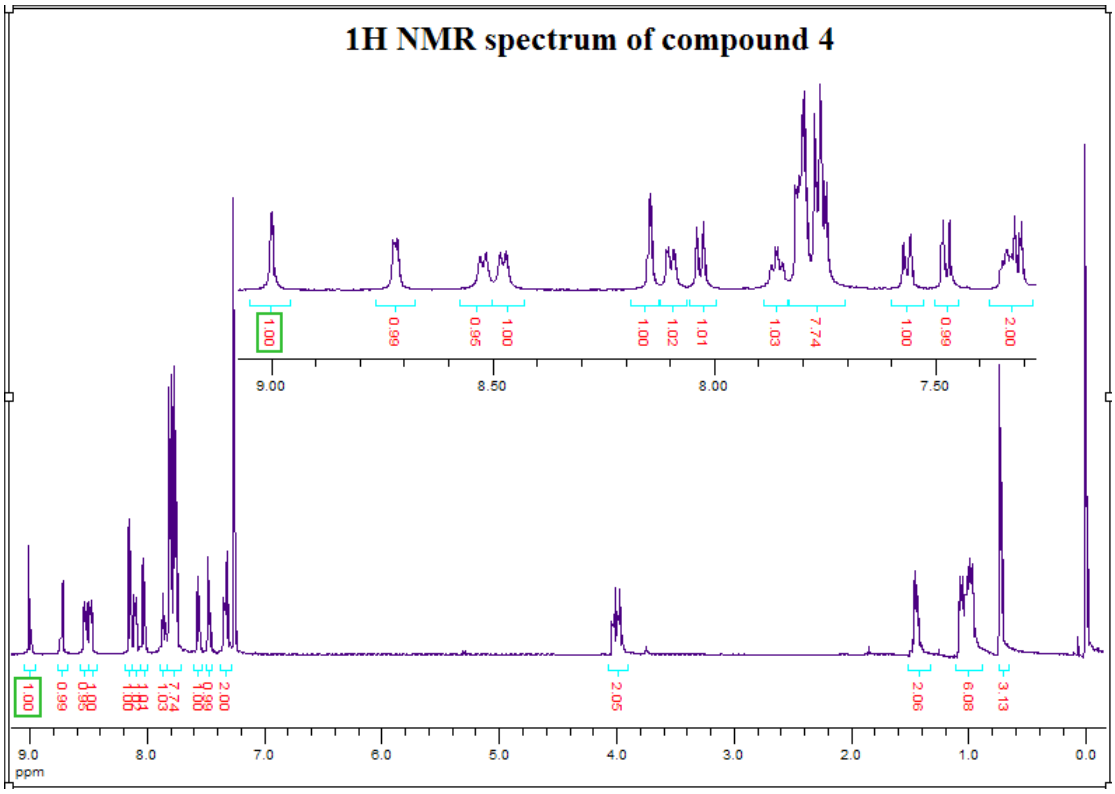
30
20
10
ppm


1H NMR spectrum of compound 4
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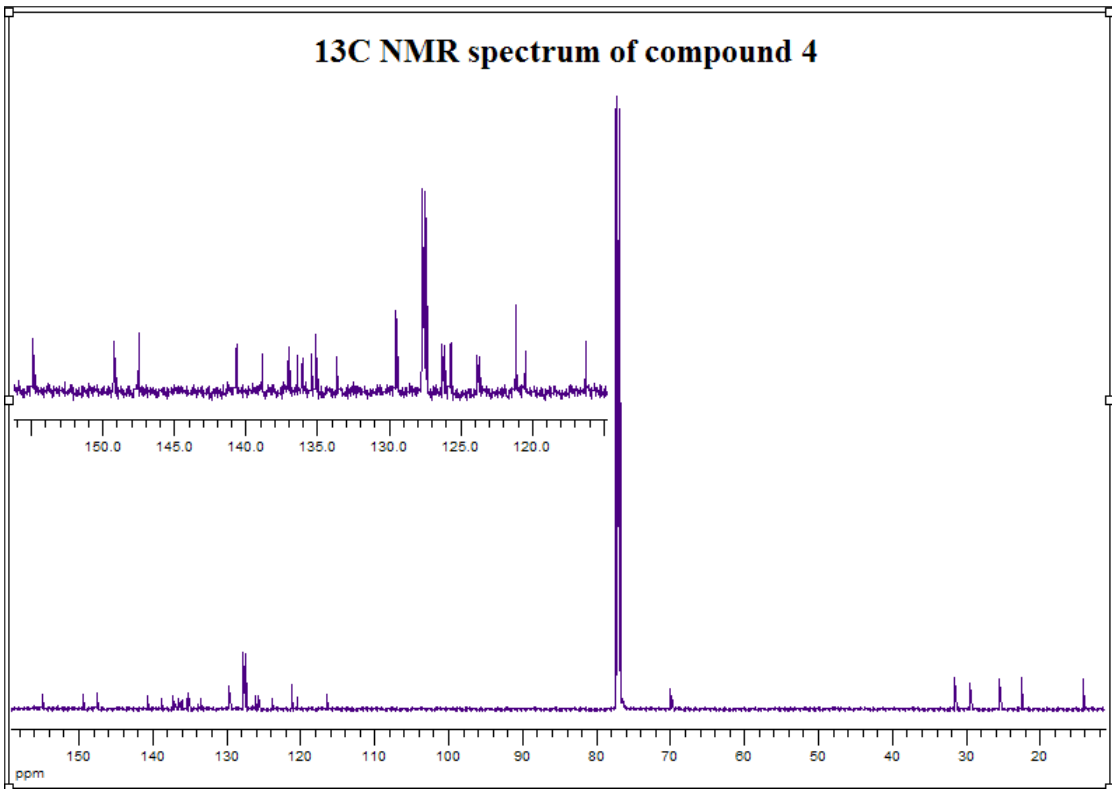
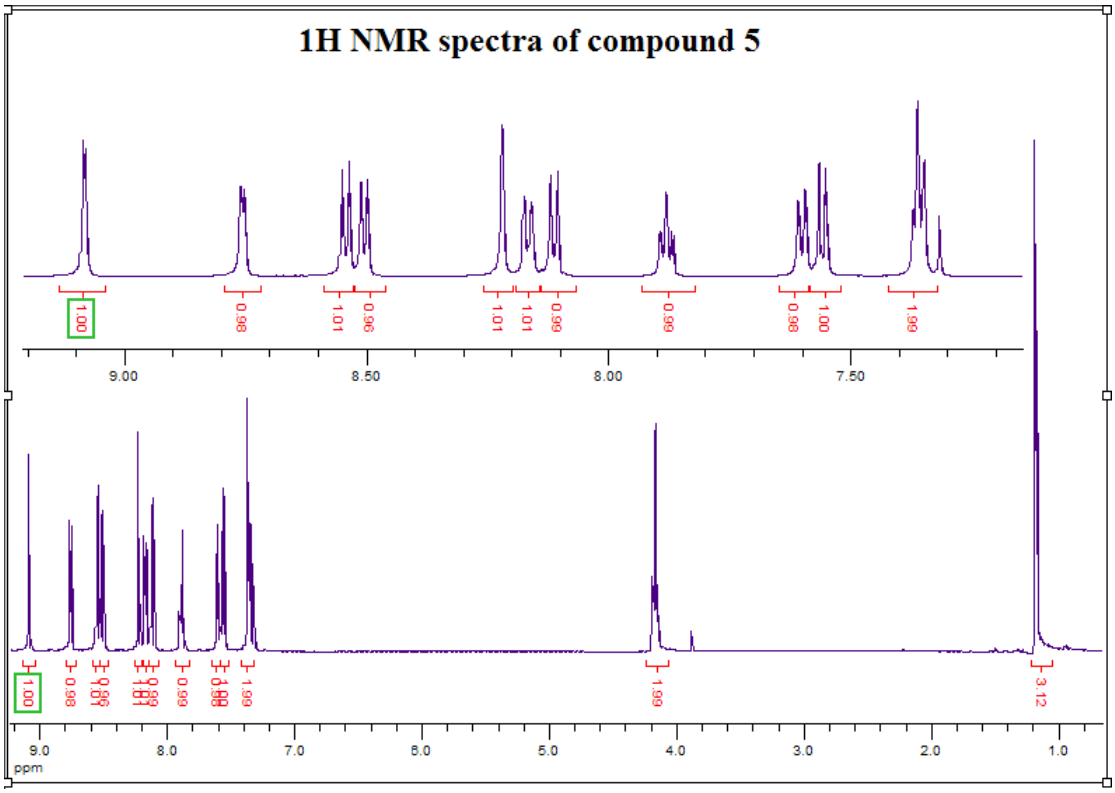

13C NMR spectrum of compound 4
ppm


1H NMR spectra of compound 5
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8.00
7.50
1.00
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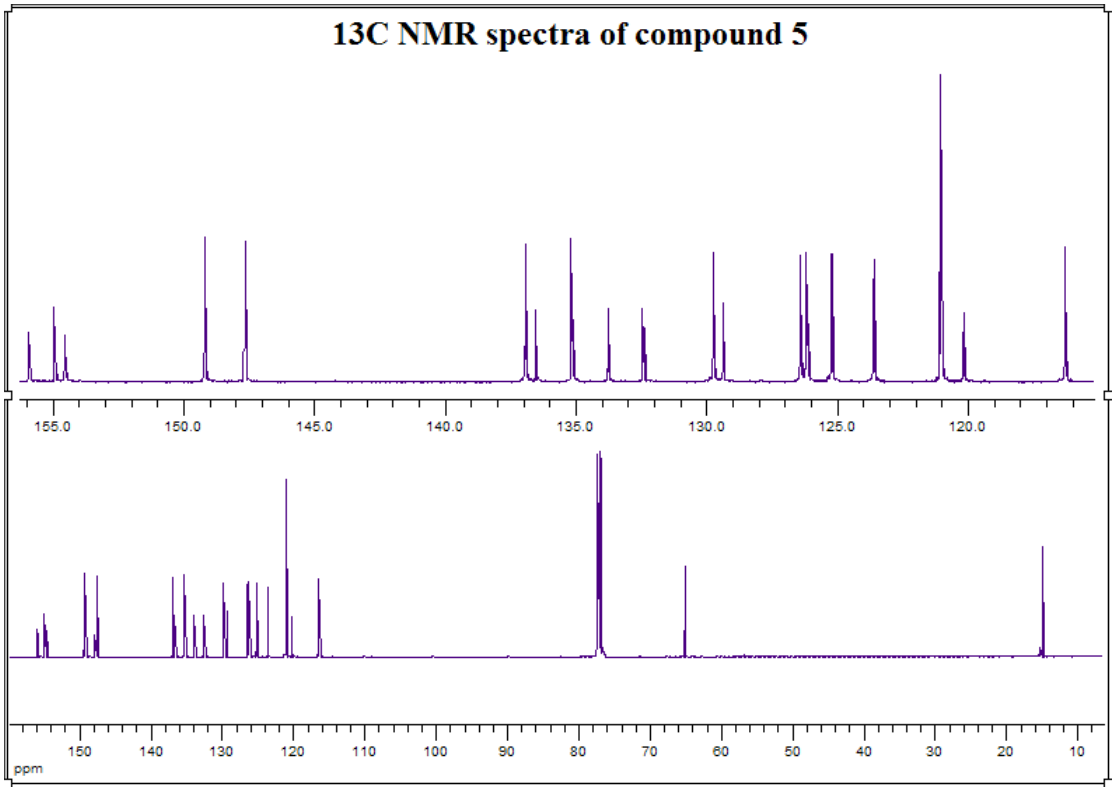
ppm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50
40
30
20
10
ppm