Supporting Information

Novel Copper Photoredox Catalysts for Polymerization: In-situ Synthesis of Metal Nanoparticles

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Experimental part

All reagents and solvents were purchased from Aldrich and used as received without further purification. Elemental analyses (EA) (C, H, N and Cl) were determined using atomic absorption with a Perkin-Elmer 2380 spectrophotometer. The IR spectra using a Perkin-Elmer 1430 infrared spectrometer were measured as KBr discs in range 4000-200 cm^{-1}. Electronic absorption spectra in the 200-900 nm region were recorded on a Perkin-Elmer 550 spectro-photometer. The Gouy method was used to measure magnetic susceptibilities at room temperature. A Bibby conductometer MCl was used for conductance measurements. Thermal analyses (TGA/DTG) were carried out by using a Shimadzu DTG/TG-50 thermal Analyzer with a heating rate of 10°C/min in nitrogen atmosphere with a flowing rate of 20/ml.

Synthesis of 3-Hydroxy-N′-(1-(6-methyl-2,4-dioxo-3,4-dihydro-2H-pyran-3-yl)ethylidene)-2,4 dinitrophenylhydrazone (HL)

A 30ml ethanolic solution 3-acetyl-2-hydroxy-6-methyl-4H-pyran-4-one (DHA) (0.01mol) was added to an equimolar ethanolic solution of 2,4 dinitrophenylhydrazine (0.01mol) dropwise and refluxed for 5 hr. The resulting pale red colored precipitates were filtered and dried in a vacuum desiccator over anhydrous calcium chloride Scheme (1).Yield: 90%; m.p: °C; Selected IR data (KBr,v/cm−1): 3441 cm^{-1}b (O-H str), 3098 m(N-H str), 2926 cm^{-1} m (aromatic C-H str), 2852 m, 2922 m v (aliphatic C-H str), 1716 cm^{-1}s v(C=O str), 1613 cm^{-1}s v(C=N), 1H NMR (400MHz, DMSO-d6): 2.26 (s, CH_3), 2.45 (s, CH_3), 6.21 (s, CH arm.), 8.4–7.8 (m, Ar-CH phenyl, 9.0(s,NH),10.9 (s, OH) ppm. ESI MS(m/z):348,333,313,306,291,267,260,245,227,219,198, 181,167,151,126,115,109,85,77,67 and 35. Anal. Calc. for $C_{14}H_{12}O_7N_4$ (348): C, 48.27; H, 3.45; N, 16.0. Found: C, 48.27; H, 3.31; N, 15.94%.

Synthesis of copper II complex of 3-hydroxy- N′-(1-(6-methyl-2,4-dioxo-3,4-dihydro-2H-pyran-3-yl) ethylidene) 2,4 dinitrophenylhydrazone [HLCuCl]

The copper complex was prepared by reacting 1:1 stoichiometric ratio of the ligand and copper chloride. An ethanolic solution of the respective copper chloride (0.01 mol) was added to 15 ml ethanolic solution of the hydrazine (H_2L) (0.01mol) while being stirred. The reaction was refluxed for 4hr. The resulting precipitates were filtered off, washed with cold ethanol and dried in vacuum desiccator over anhydrous calcium chloride. Yield: 80%; m.p: 130°C; Selected IR data (KBr,v/cm−1): 3445 cm^{-1}b (O-H str),3165 cm^{-1} m(N-H str), 2927 cm^{-1} m (aromatic C-H str), 2927 cm^{-1} m (aromatic C-H str), 1713 cm^{-1}s v(C=O str), 1614 cm^{-1}s v(C=N), 555 cm^{-1}m(Cu-O), 517 cm^{-1}m(Cu-N), 449 cm^{-1}w(Cu-Cl). Anal. Calc. for Cu $C_{14}H_{11}O_7N_4$ Cl (447): C, 37.6; H, 2,5; N,12. 5. Found: C,37.1;H,3.1;N,12.2 μeff (BM): 1.73. Molar conductance (Ω−1cm2mol−1): 10.3.

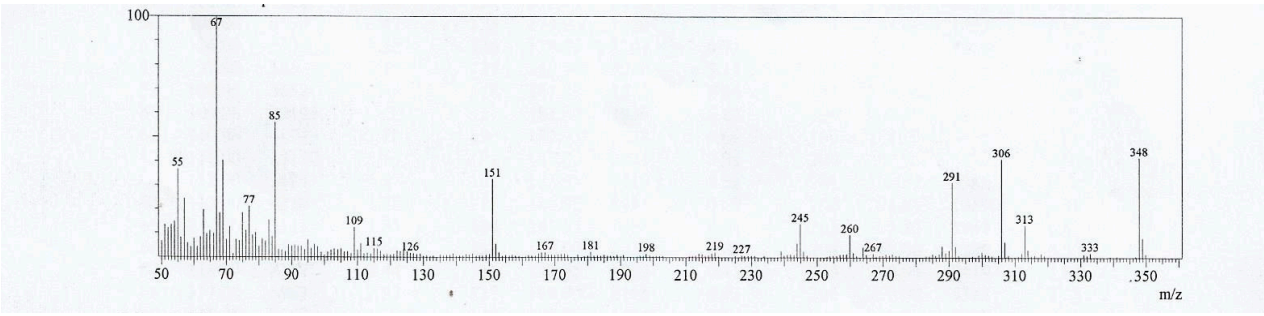


Figure S1. Mass spectrum of the ligand (HL)

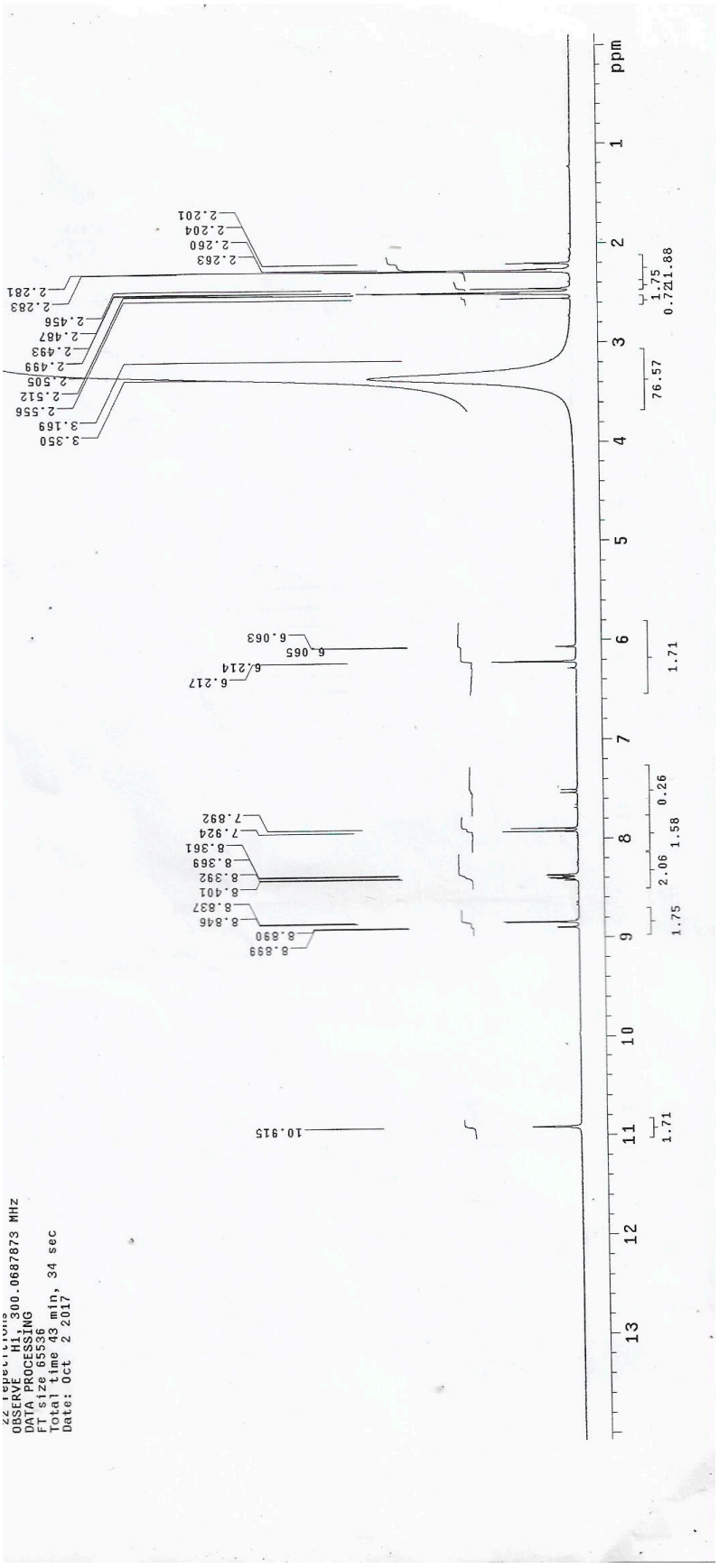


Figure S2. H^1NMR spectrum of the ligand (HL)

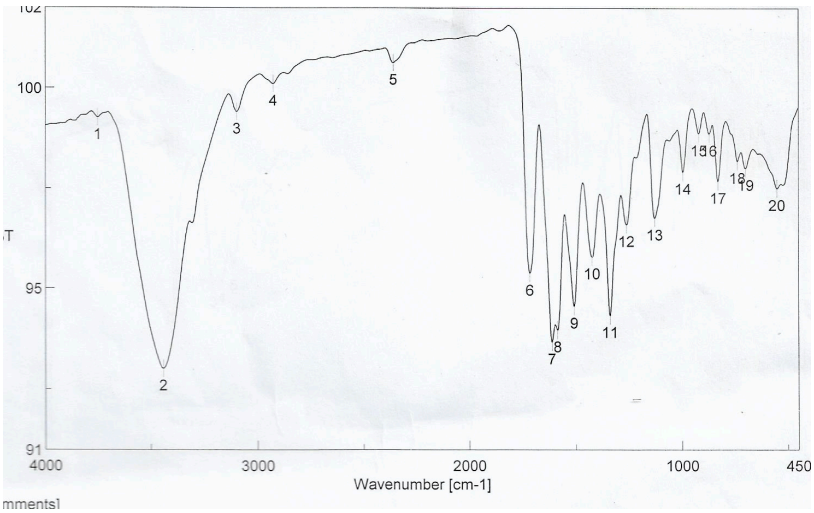


Figure S3. IR .spectrum of the ligand (HL)

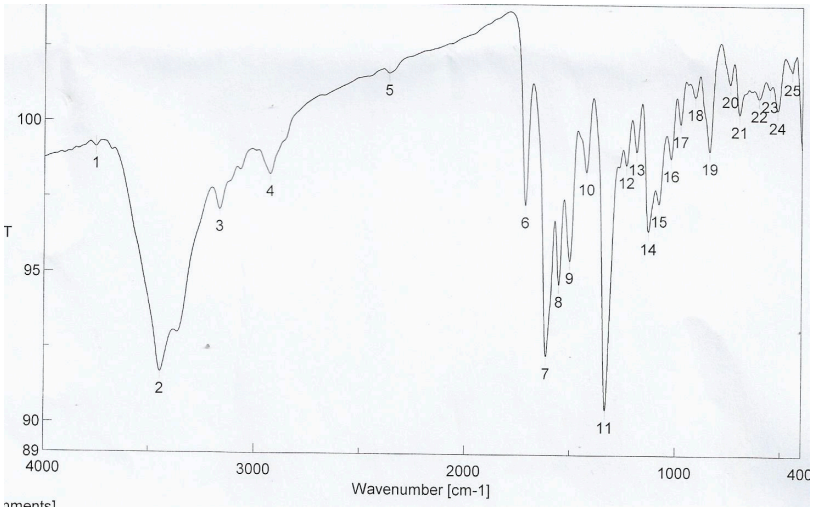
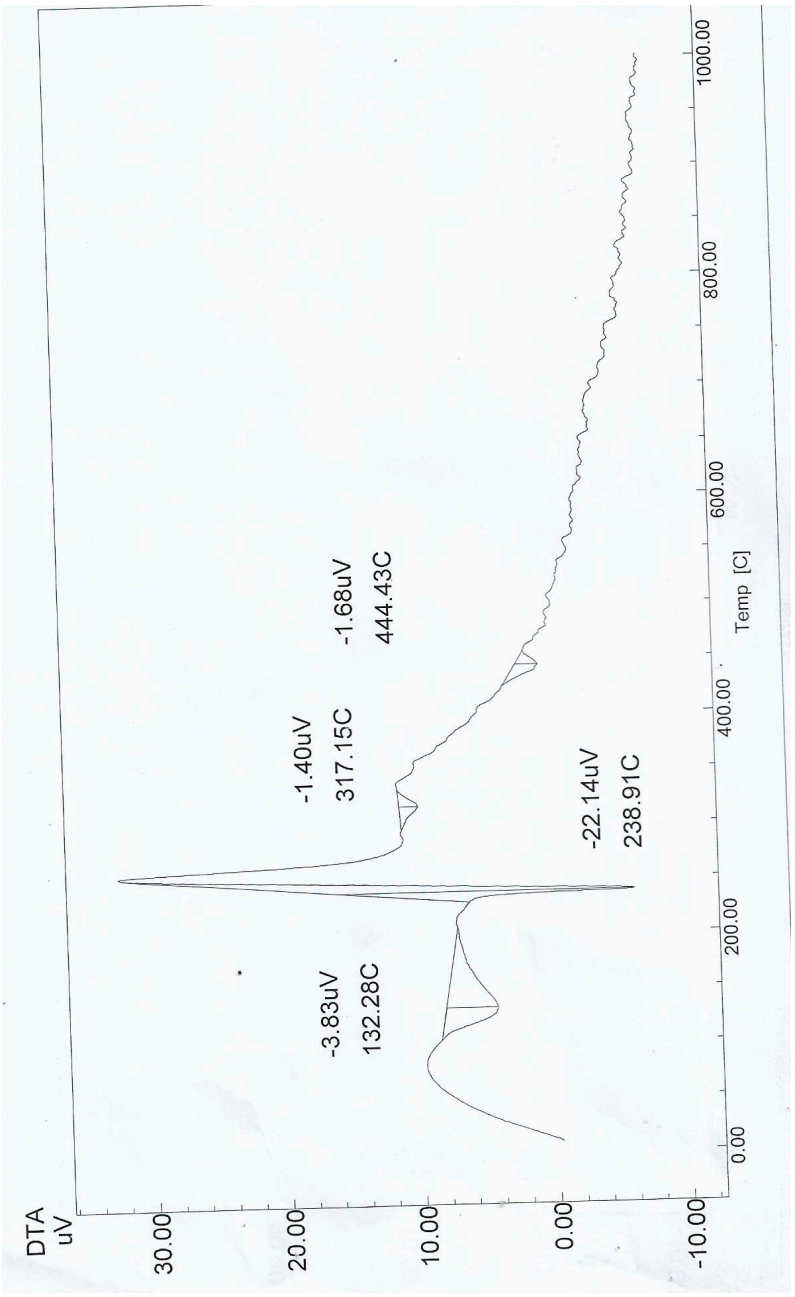
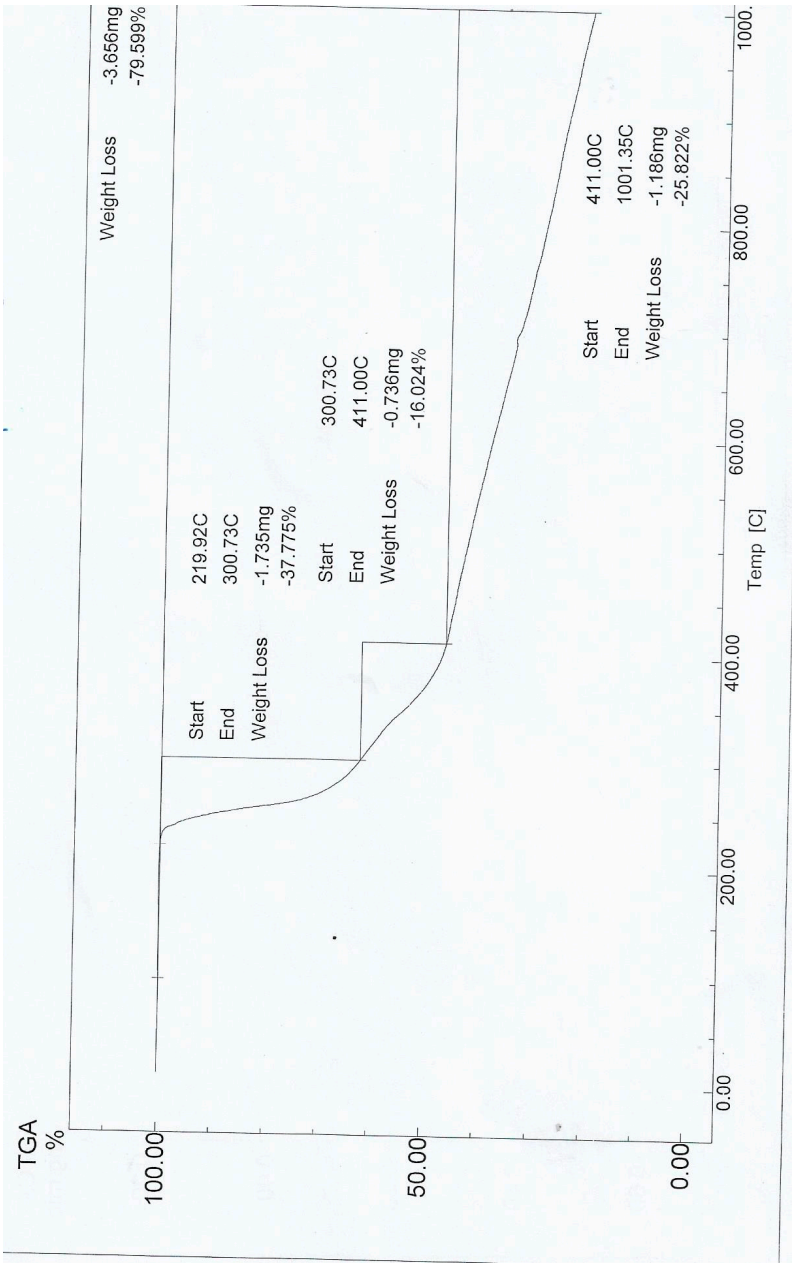


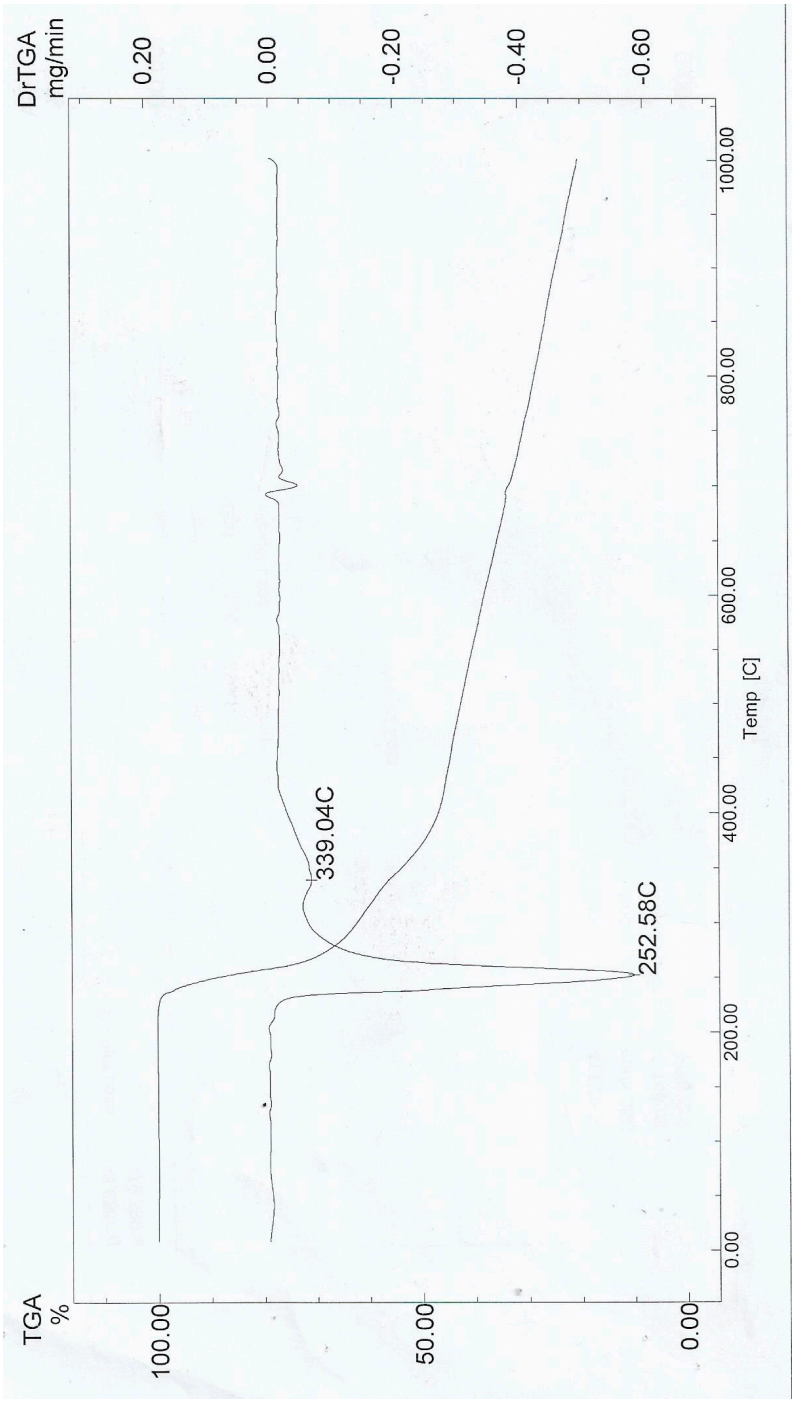
Figure S4. IR .spectrum of the copper complex


DTA
uV
30.00
20.00
10.00
0.00
-10.00
0.00
200.00
400.00
600.00
800.00
1000.00
Temp [C]
-3.83uV
132.28C
-1.40uV
317.15C
-1.68uV
444.43C
-22.14uV
238.91C

(**a**)

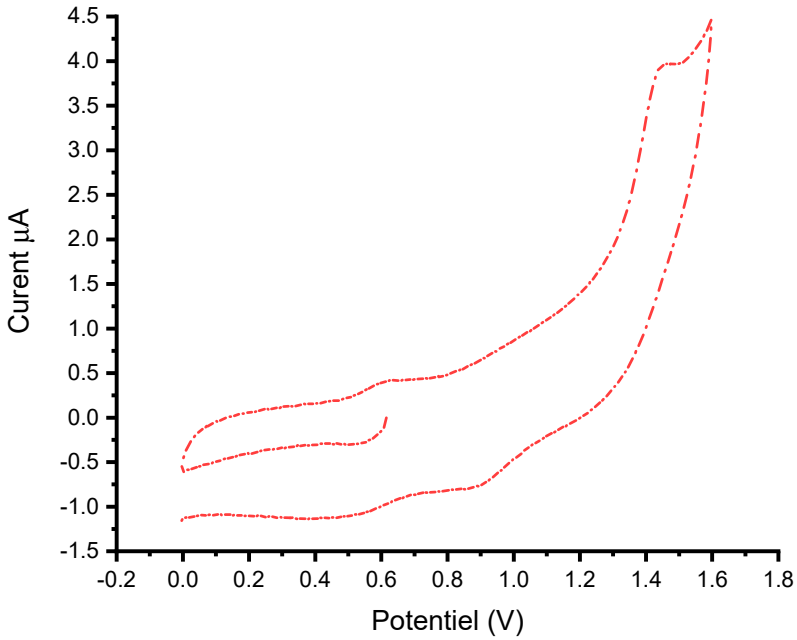

TGA
%
100.00
50.00
0.00
0.00
200.00
400.00
600.00
800.00
1000.
Temp [C]
Weight Loss -3.656mg
-79.599%
Start 219.92C
End 300.73C
Weight Loss -1.735mg
-37.775%
Start 300.73C
End 411.00C
Weight Loss -0.736mg
-16.024%
Start 411.00C
End 1001.35C
Weight Loss -1.186mg
-25.822%

(**b**)



(**c**)

Figure S5. DTA, TGA and DrTGA of the ligand (HL).



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106 **Figure S6.** Cyclic voltammogram of HLCuCl in acetonitrile.

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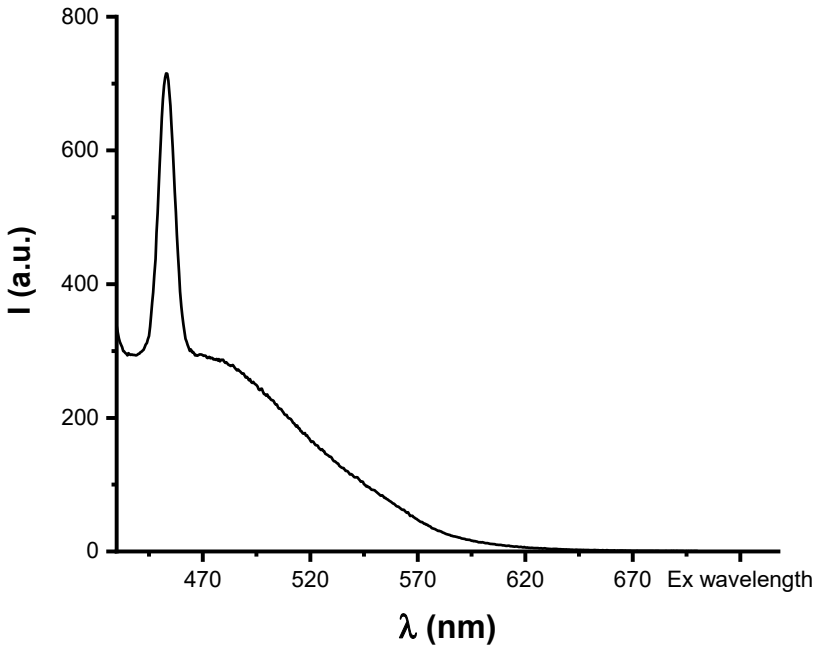

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109 **Figure S7.** Photoluminescence of HLCuCl in DMF

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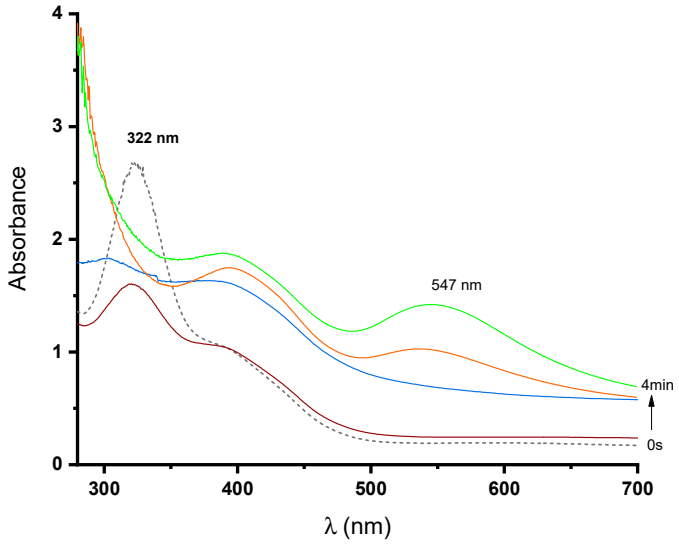

Figure S8. Evolution of the absorption spectra of irradiated mixtures (λ_{irr} = 419 nm). Solution: HLCuCl 0.05 wt% and gold Chloride 4wt% dissolved in 25 ml DMF.