Supporting Information

Effect of temperature and ligand protonation on the electronic ground state in Cu(II) polymers having unusual secondary interactions: Magnetic and Catechol oxidase study

Sandeepta Saha[a,b], Niladri Biswas[c], Ashok Sasmal[b], Carlos J. Gómez-Garcia[d], Eugenio Garribba[e], Antonio Bauza[f], Antonio Frontera[f], Guillaume Pilet[g], Georgina M. Rosair[h], Samiran Mitra[b+], Chirantan Roy Choudhury[c]*

[a] Sripur High School, Madhyamgram Bazar, Madhyamgram, Kolkata – 700130, India

[b] Department of Chemistry, Jadavpur University, Raja S.C. Mullick Road, Kolkata-700032, West Bengal, India

[c] Department of Chemistry, West Bengal State University, Barasat, Kolkata 700126, India

[d] Instituto de Ciencia Molecular (ICMol), Dpto. QuímicaInorgánica. Universidad de Valencia, C/ Catedrático José Beltrán, 2. 46980 Paterna, Spain

[e] Department of Chemistry and Pharmacy, University of Sassari, Via Vienna 2, I-07100 Sassari, Italy

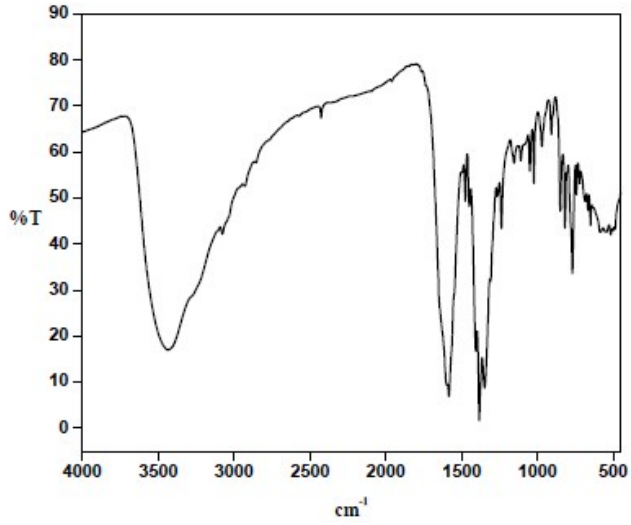
[f] Departament de Química, Universitat de les Illes Balears, Crta. deValldemossa km 7.5, 07122 Palma de Mallorca, Baleares, Spain

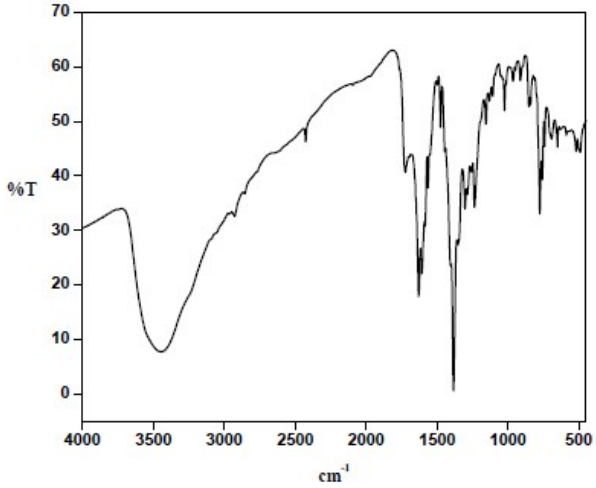
[g] Groupe de Crystallographieet Ingénierie Moléculaire, Laboratoire des Multimatériaux et Interfaces, UMR 5615 CNRS-Université Claude Bernard Lyon 1, Bât. Chevreul, 43 bd du 11 Novembre 1918, 69622 Villeurbanne Cedex, France

[h] Institute of Chemical Sciences, School of Engineering and Physical Sciences, Heriot Watt University, Edinburgh EH14 4AS, UK

[+] Deceased

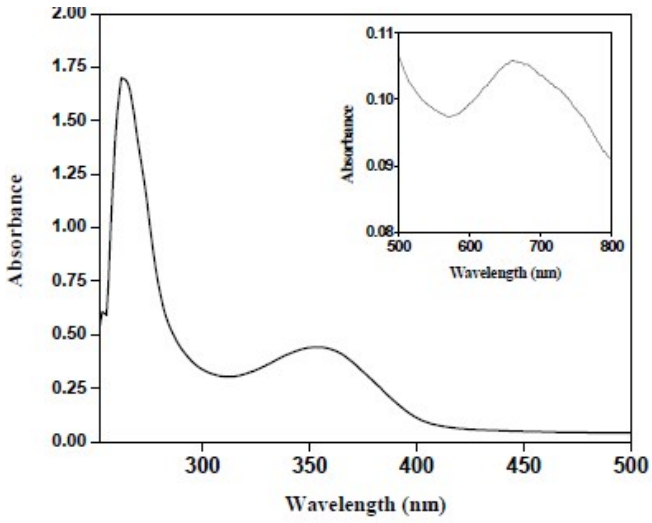
* Corresponding author: Tel: +91-9836306502
fax: +91-33-25241977
E-mail address: crchoudhury2000@yahoo.com (Chirantan Roy Choudhury)

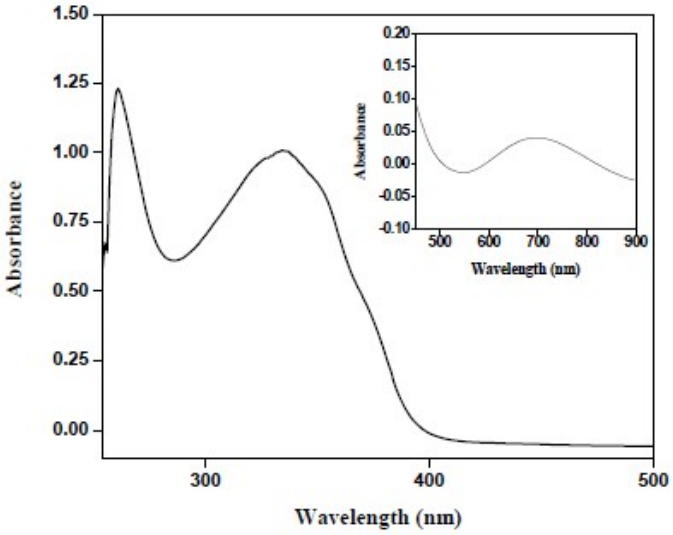




(A) **(B)**

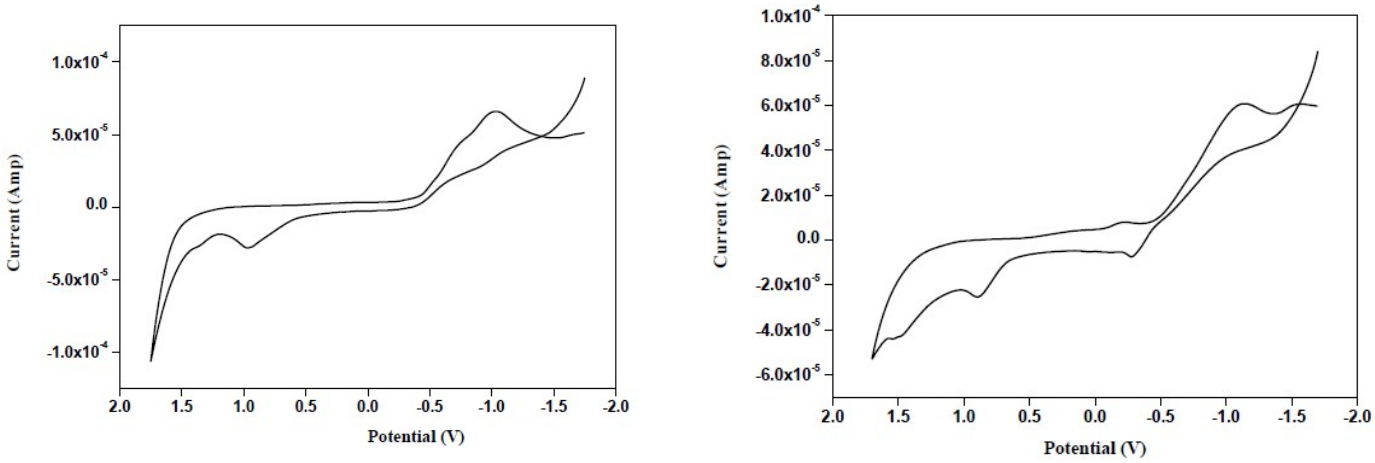
Fig. S1 Infrared spectra of the complexes **1(A)** and **2 (B)** in solid KBr discs at 300K.





(A) **(B)**

Fig. S2 UV-Vis spectra of complexes **1 (A)** and **2 (B)** in DMSO medium at 300K. The inset shows d-d transition bands.

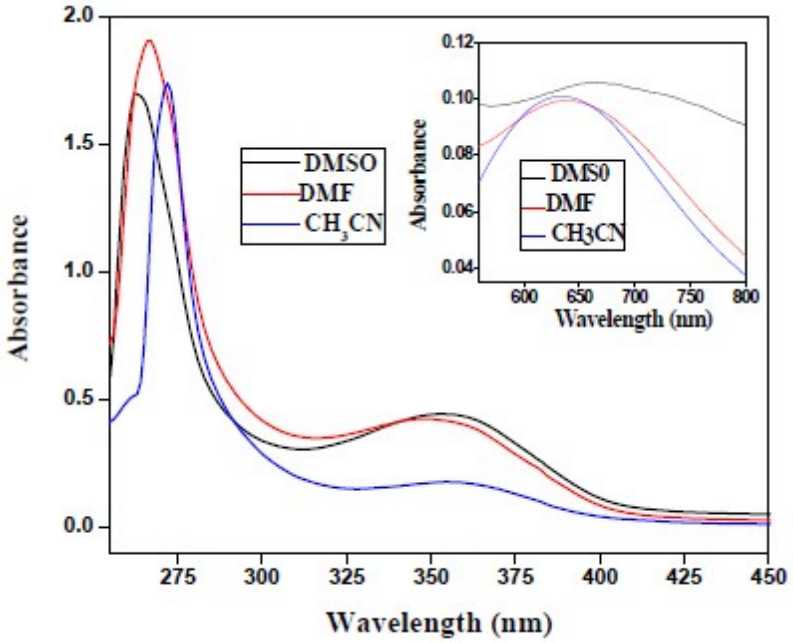


(A) **(B)**

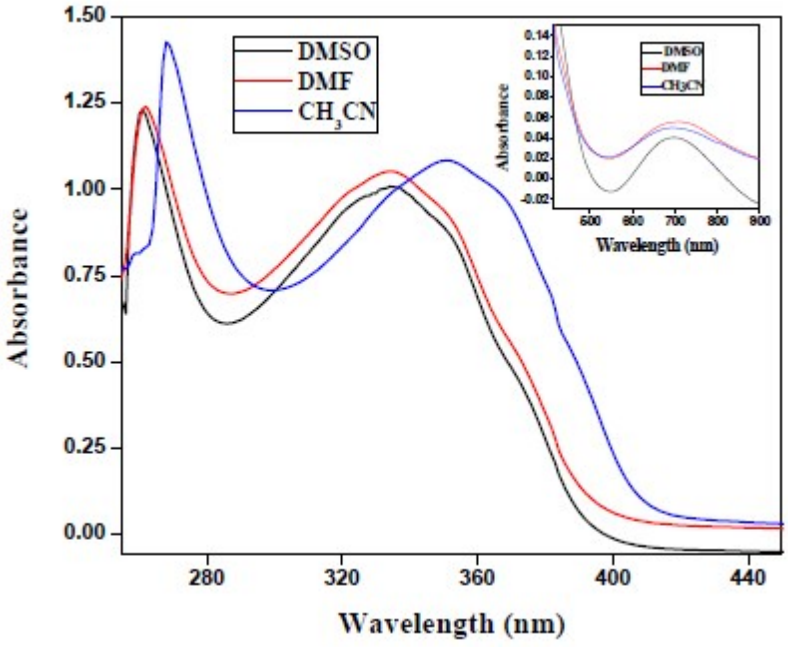
Fig. S3 The cyclic voltammograms of 1 mM concentration of complex **1 (A)** and **2 (B)** in acetonitrile medium containing 0.1 M TBAP on SCE as reference at a scan rate of 50 mV sec^{-1}.

Stability of the complexes 1 and 2 in solution

Both complexes **1** and **2** displayed characteristic IR, UV-Vis absorption bands and cyclic voltammograms also exhibited various phenomenons like Magnetic, Theoretical analysis, EPR spectral analysis and Catechol oxidase study. Therefore, the stability of both **1** and **2** provide significant importance in all above experiments. In order to verify the stability of **1** and **2**, UV-Vis absorption measurements were investigated in three different solvents (DMSO, DMF and acetonitrile). It was well noticed that UV-Vis spectra of **1** and **2** in three different solvents were superimposed with little shift. The above observations clearly indicate that complexes **1** and **2** were stable in both solid and solution form.



(A) Complex 1



(B) Complex 2

Solvents/			

medium used	DMSO		DMF		Acetonitrile	
Complexes	**(1)**	**(2)**	**(1)**	**(2)**	**(1)**	**(2)**
UV-Vis bands	661 (d-d)	697 (d-d)	638 (d-d)	707 (d-d)	633 (d-d)	697 (d-d)
	353 (CT)	335 (CT)	348 (CT)	334 (CT)	355 (CT)	351 (CT)
	263 (CT)	261 (CT)	266 (CT)	262 (CT)	272 (CT)	268 (CT)

Table T1 UV-Vis band positions of complexes (**1**) and (**2**) in DMSO, DMF and acetonitrile medium.

Table S1 H-bonding interactions in compound $\{[Cu(HPymat)(H_2O)](NO_3)\}_n$ (**1**)

Atom 1	Atom 2	Symm. op. 1	Symm. op. 2	Length (Å)
O3	C4	1-x,2-y,1/2+z	1-x,2-y,1/2+z	2.347
O10	O32	x,y,z	1-x,1-y,-1/2+z	2.596
O3	O1	x,y,z	1-x,2-y,-1/2+z	2.717
O3	C5	1-x,2-y,1/2+z	1-x,2-y,1/2+z	2.737
O1	O41	x,y,z	1-x,2-y,-1/2+z	2.805
O41	O32	x,y,z	x,y,z	2.882
O3	N20	x,y,z	1-x,2-y,-1/2+z	2.895
O33	O51	x,y,z	x,y,1+z	2.908
O9	O51	x,y,z	-1/2+x,1.5-y,z	2.953
O1	O51	x,y,z	x,y,z	2.982
O41	O51	x,y,z	1-x,2-y,1/2+z	2.994
O3	C19	x,y,z	1-x,2-y,-1/2+z	3.106
C14	O34	x,y,z	x,y,-1+z	3.152

Table S2 H-bonding interactions in compound $[Cu_2(Pymat)_2(H_2O)_3]$ (**2**)

Atom 1	Atom 2	Symm. op. 1	Symm. op. 2	Length (Å)
O7	O6	x,y,-1+z	-1+x,y,-1+z	2.743

O4	O3W	x,y,-1+z	x,y,z	2.772
O1W	O2W	x,y,z	1-x,1-y,1-z	2.800
O2W	O3W	x,y,z	x,y,z	2.816
O7	N3	x,y,-1+z	-1+x,y,-1+z	2.876
O5	N4	x,y,-1+z	x,1/2-y,-1.5+z	2.889
O8	O1W	x,y,-1+z	-1+x,y,-1+z	2.917
O1	N2	x,y,-1+z	x,1/2-y,-1/2+z	2.982
O7	O1W	x,y,-1+z	-1+x,1/2-y,-1/2+z	2.952
O1	O2	x,y,-1+z	x,1/2-y,-1/2+z	3.010
O5	O6	x,y,-1+z	x,1/2-y,-1.5+z	3.012
O1	O3	x,y,-1+z	x,1/2-y,-1/2+z	3.039
O4	C6	x,y,-1+z	-x,1-y,1-z	3.078
O7	C28	x,y,-1+z	-1+x,y,-1+z	3.087
O6	C14	x,y,-1+z	1+x,y,-1+z	3.138
C2	O2W	x,y,-1+z	x,y,-1+z	3.142

Table S3 EPR parameters of compounds **1** and **2** in solid state at 298 and 77 K and in DMF, DMSO and CH_3CN solutions.

Compound	$\mathbf{g_x}$	$\mathbf{g_y}$	$\mathbf{g_z}$	$\mathbf{A_x\ (cm^{-1})}$	$\mathbf{A_y\ (cm^{-1})}$	$\mathbf{A_z\ (cm^{-1})}$
1-298 K	2.151	2.151	2.055			
1-77 K	2.231	2.141	2.045			
1-DMF	2.062	2.062	2.267	12.0×10^{-4}	12.0×10^{-4}	179.4×10^{-4}
1-DMSO	2.063	2.063	2.268	13.0×10^{-4}	13.0×10^{-4}	178.1×10^{-4}
1-CH_3CN	2.176	2.176	2.064		-	-
2-298 K	2.249	2.144	2.037			
2-77 K	2.282	2.139	2.023			
2-DMF	2.062	2.062	2.270	12.0×10^{-4}	12.0×10^{-4}	174.5×10^{-4}
2-DMSO	2.063	2.063	2.271	12.0×10^{-4}	12.0×10^{-4}	176.0×10^{-4}
2-CH_3CN	2.064	2.064	2.281	13.0×10^{-4}	13.0×10^{-4}	178.5×10^{-4}