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Non-symmetrical bis(aminoalkyl)phosphinates: new ligands with the enhanced binding of Cu(II) ions

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Supporting Information

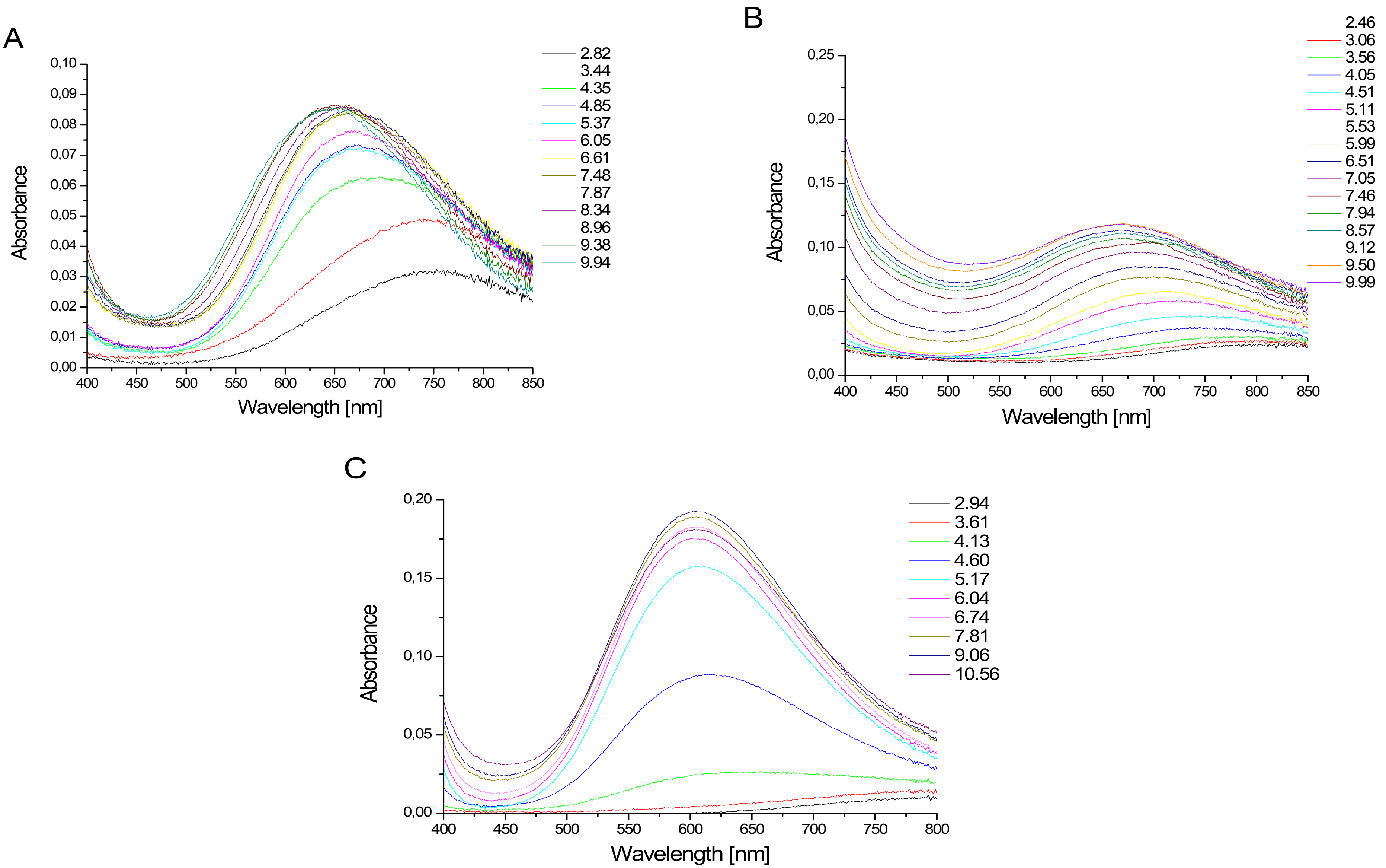

Figure S1. The UV-Vis spectra as a function of pH for Cu(II):L^{1-3} systems. A: Cu(II):L^1, [Cu(II)] = $9.09\cdot10^{-4}$M, [L^1] = $1.99\cdot10^{-3}$M; B: Cu(II):L^2, [Cu(II)] = $8.81\cdot10^{-4}$M, [L^2] = $1.94\cdot10^{-3}$M; C: Cu(II):L^3, [Cu(II)] = $6.68\cdot10^{-4}$M, [L^3] = $1.47\cdot10^{-3}$M.

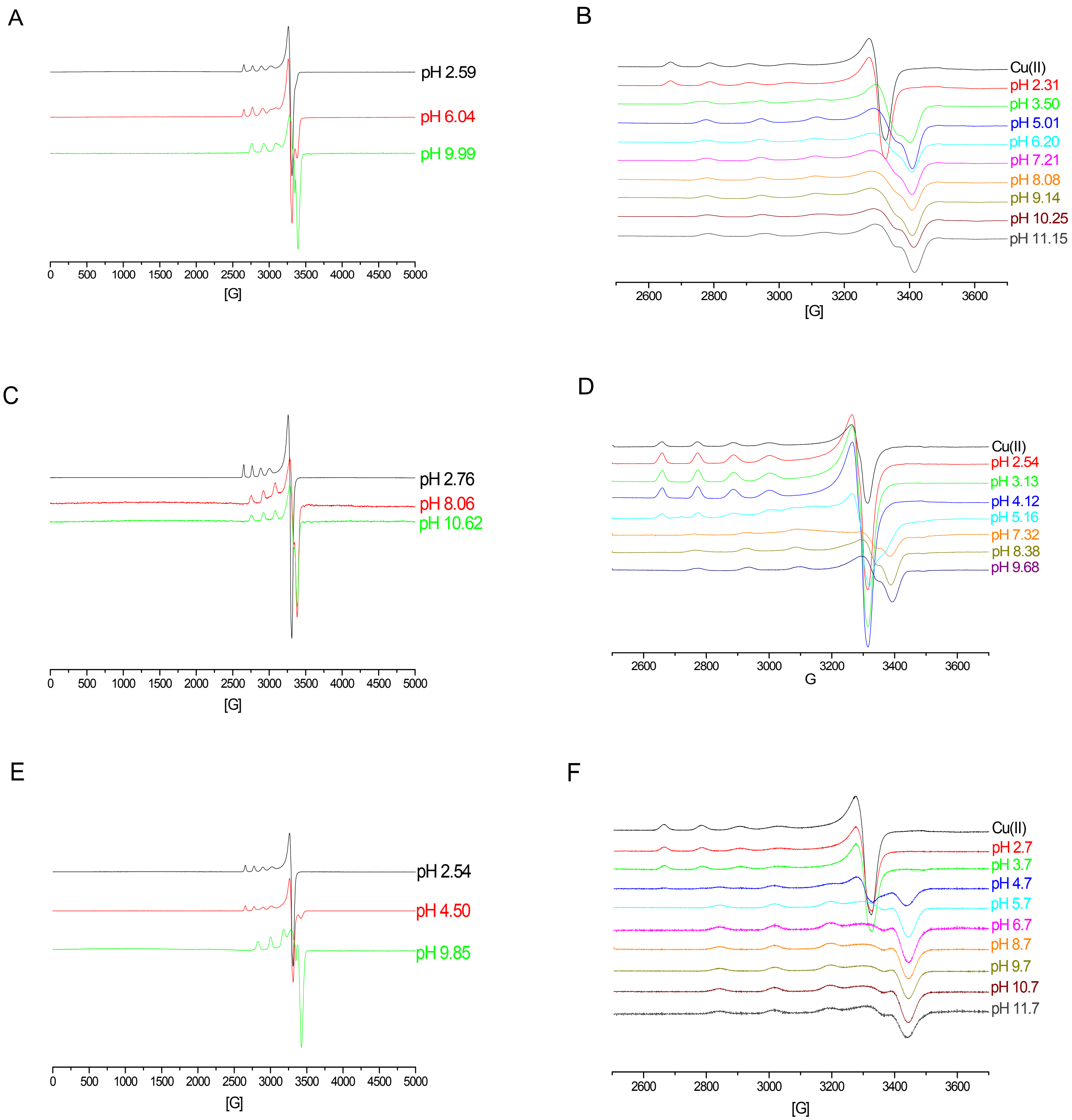

Figure S2. The EPR spectra as a function of pH for Cu(II):L^{1-3} systems. A,B: Cu(II):L^1, [Cu(II)] = 8.95·10^{-4}M, [L^1] = 1.97·10^{-3}M; C,D: Cu(II):L^2, [Cu(II)] = 9.09·10^{-4}M, [L^2] = 2.01·10^{-3}M; E,F: Cu(II):L^3, [Cu(II)] = 9.51·10^{-4}M, [L^3] = 2.09·10^{-3}M.

Table S1. Protonation constants (logK^H) of $L^1 – L^3$ ligands,[a] and selected analogous compounds.

	L1	L2	L3	apl	appg	MBAPA	AMPA	AM_2P	EDBPA	PDMBPA	PMPA	GlyDP	TEA	2,N,N-TMA	THQ
log$K$ $(NH^+)_{tertiary\ amine}$	11.11(1)											11.3	10.78		
log$K$ (NH_3^+)	9.06(1)	8.38(1)	8.75(1)	8.82	8.19	9.49	8.29	8.509							
			7.75(1)			8.80		7.071							
log$K$ $(NH^+)_{piperidine}$											8.41				
log$K$ (NH_2^+)				6.55					4.32						
									7.58						
log$K$ $(NH^+)_{piperazine}$			2.93(2)							2.622					
			5.86(2)							6.719					
log$K$ $(NH^+)_{quinoline}$		5.46(6)												5.86	5.03
log$K$ (COOH)	5.02(1)			1.98	2.79										
log$K$ (PO(OH)R)		2.12(2)				2.09	1.0	0.77							
Reference	This work	This work	This work	[1]	[1]	[2]	[3]	[4]	[5]	[6]	[6]	[7]	[8]	[9, 10]	[9]

[a] I = 0.1 M ($NaClO_4$), T = (25.0 ± 0.2) °C, solvent: H_2O for L^1 and L^3, and MeOH/H_2O 80:20 w/w for L^2.

Table S2. Equilibrium constants (logK_{ML} or pK_a) in Cu(II) complexes of of $L^1 – L^3$ ligands,[a] and selected analogous compounds.

	L1	L2	L3	apl	appg	MBAPA	AMPA	AM_2P	EDBPA	PDMBPA	PMPA
M+L=[ML]	19.37	7.21	11.55	12.08	5.66	9.87	5.45	7.64	10.10	3.18	4.91
$[M(HL)]=[ML]+H^+$	3.87			3.71	4.89			5.07			
$[ML]+H_2O=[ML(OH)]+H^+$	9.32			9.48	7.12	8.82					
$[ML(OH)]+H_2O=[ML(OH)_2]+H^+$	11.61					10.53					
$M+2HL=[M(HL)_2]$										17.79	
$[ML_2]+H^+=[MHL_2]$								6.74			
$M+2L=[ML_2]$		12.41		14.91	9.55		9.99	13.05			
$[ML_2]+H_2O=[ML_2(OH)]+H^+$							8.79	9.98			
$[ML_2]+2H_2O=[ML_2(OH)_2]+2H^+$		20.28						11.73			
Reference	This work	This work	This work	[1]	[1]	[2]	[3]	[4]	[5]	[6]	[6]

[a] I = 0.1 M ($NaClO_4$), T = (25.0 ± 0.2) °C, solvent: H_2O for L^1 and L^3, and MeOH/H_2O 80:20 w/w for L^2.

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