"Supporting Information"

A dinuclear extension to constrained heteroleptic Cu(I) systems

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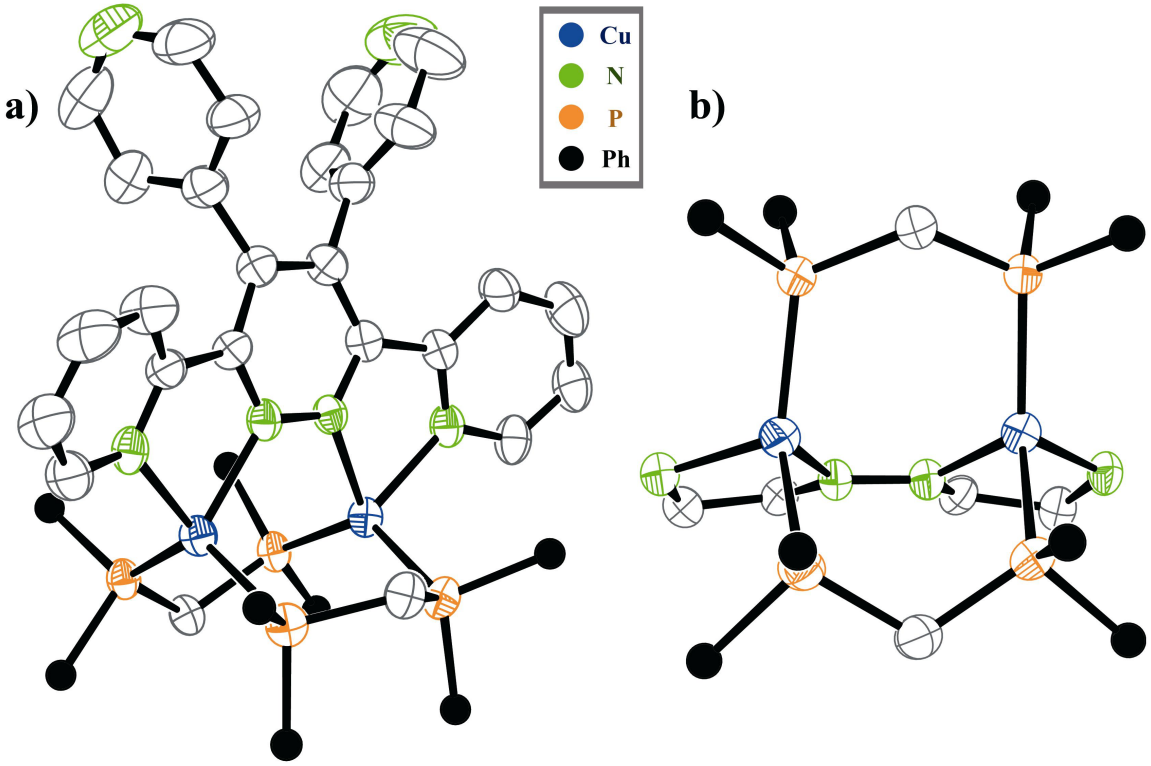

Figure S1: a) View of the structure of $[Cu_2(\mu\text{-dppm})_2\mathbf{L_B}]^{2+}$ with the hydrogen atoms and the phenyl rings of the dppm omitted for clarity. b) The boat-chair conformation of the $[Cu(\mu\text{-dppm})]_2$ ring

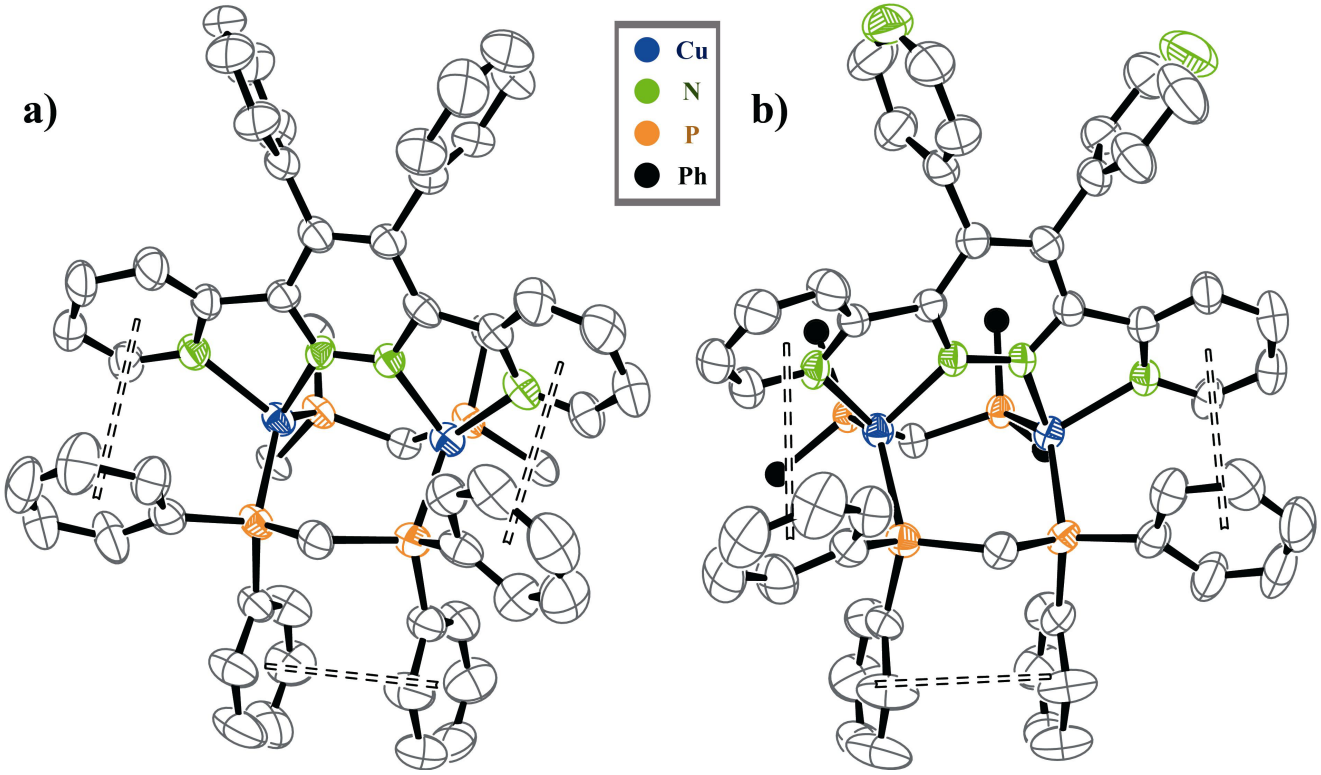

Figure S2: Weak intramolecular π···π interactions between phenyl rings on the same *dppm* ligand and between the phenyl rings of the *dppm* and both pyridine rings of the *bppn* L for $[Cu_2(\mu\text{-dppm})_2\mathbf{L_A}]^{2+}$ (a) and $[Cu_2(\mu\text{-dppm})_2\mathbf{L_B}]^{2+}$ (b)

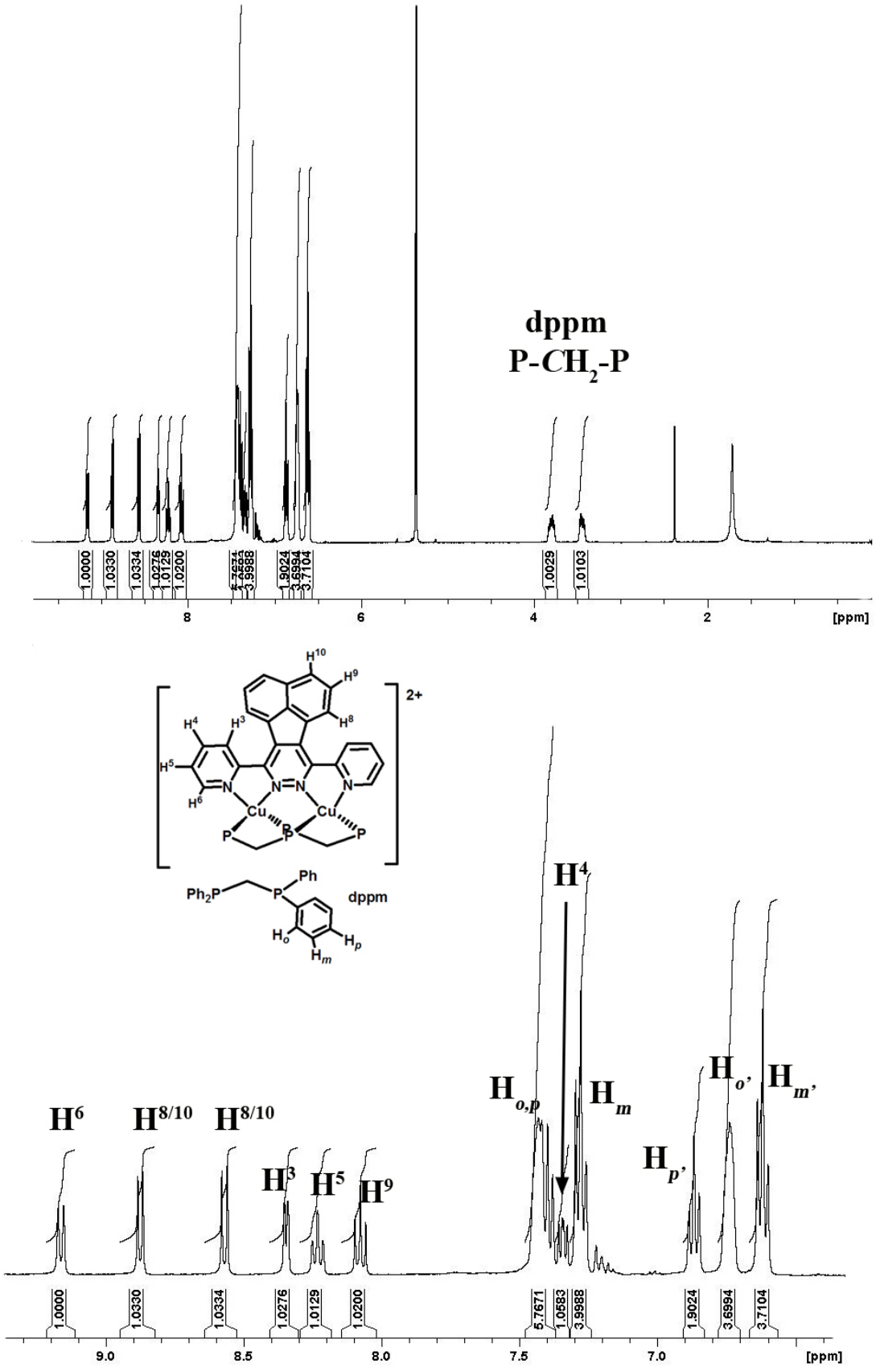

Figure S3: ^{1}H NMR spectrum of $[Cu_2(\mu\text{-dppm})_2(\mu\text{-}\mathbf{L_C})](NO_3)_2$ in $CDCl_3$

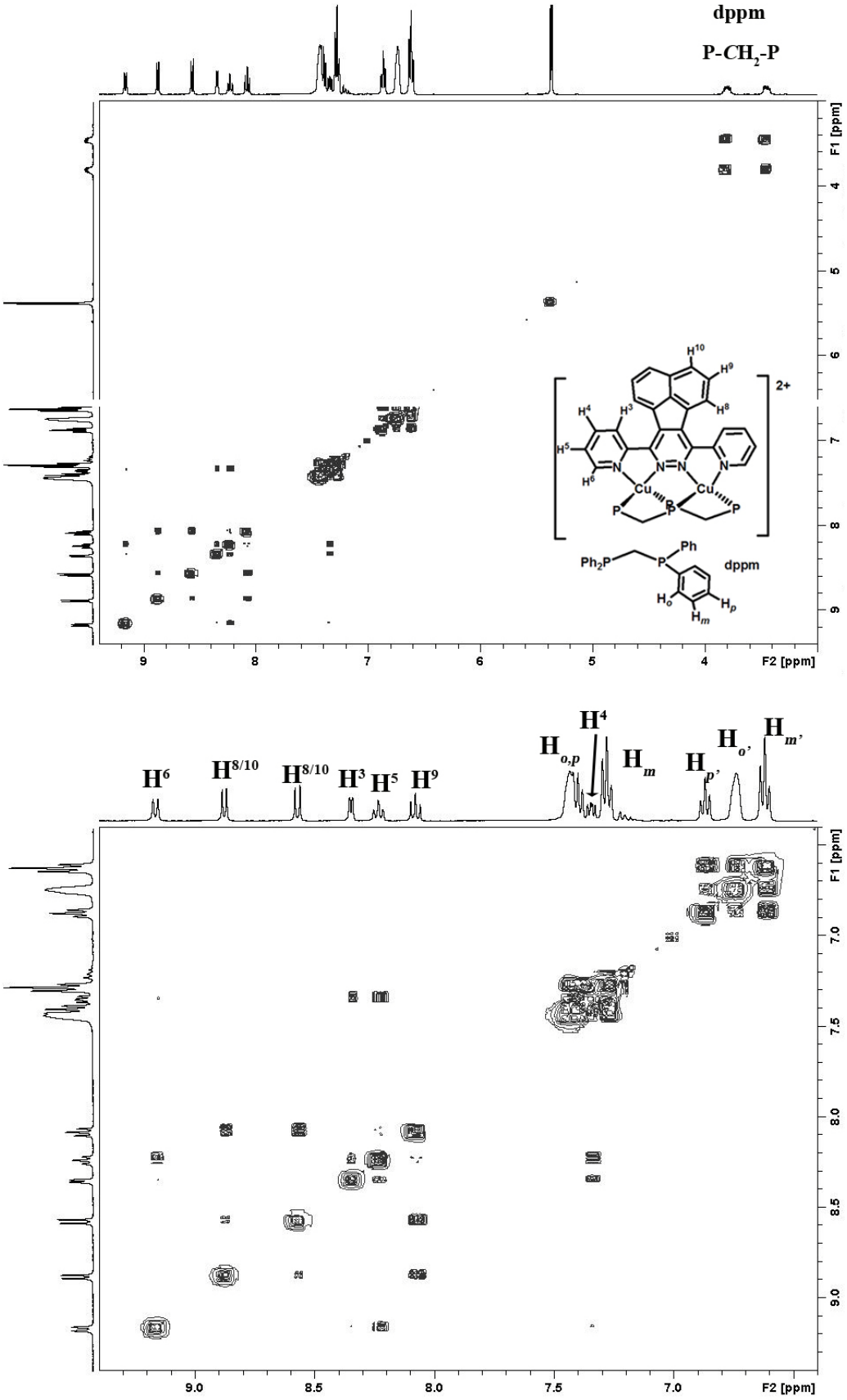

Figure S4: ^{1}H-^{1}H correlation NMR spectrum of $[Cu_2(\mu\text{-dppm})_2(\mu\text{-}\mathbf{L_C})](NO_3)_2$ in $CDCl_3$

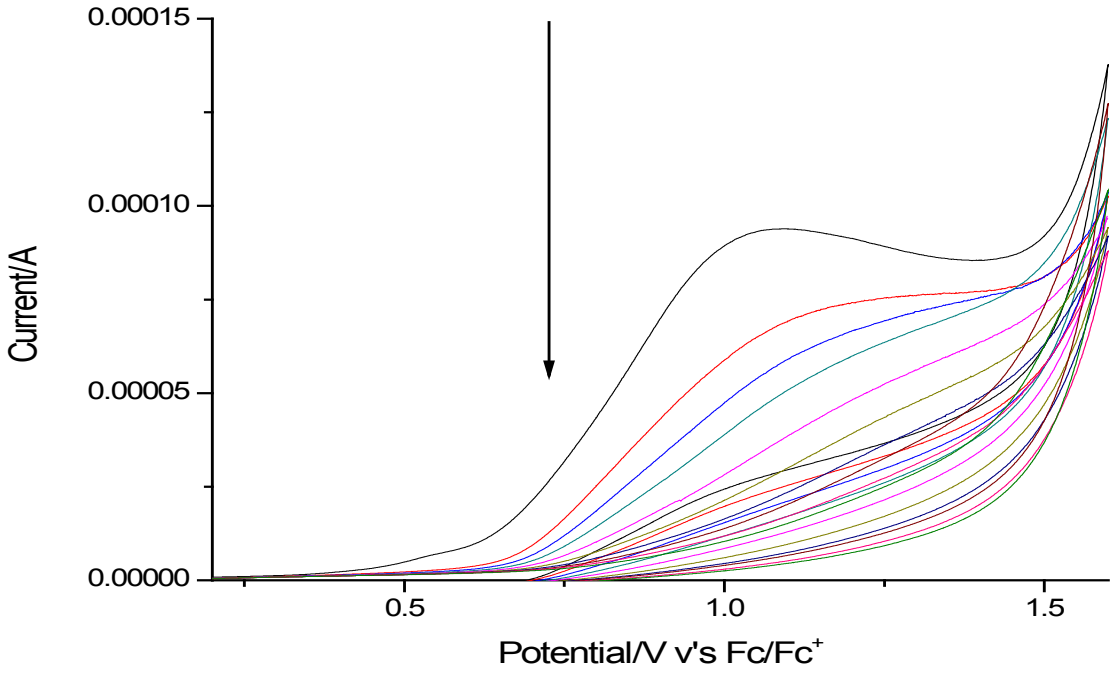

Figure S5: Cyclic Voltammogram (repetitive scans at 2s intervals) on $[Cu_2(\mu\text{-dppm})_2(\mu\text{-}\mathbf{L_B})_2]^{2+}$. Conditions as per experimental details: scan rate 100 mV s^{-1}, 1 mM solution CH_2Cl_2, 0.1 M $TBAPF_6$, Fc/Fc^+ as internal standard.

Table S1: Comparative Photophysical data of the ligands *bppn* **L**

		T [K]	λem [nm]	τ [ns]
L_A	solid	298	356*sh*, 372, 396*sh* (λ_{exc} 320 nm)	33.5 (97%) (λ_{exc} 295 -λ_{em} 370)
		77	362_{max}, 396*sh*, 411*sh* (λ_{exc} 300 nm)	
	DCM, 10^{-3}M	298	384*sh*, 393_{min}, 404, 505_{max} (λ_{exc} 350 nm)	18.0 (33%), 2.3 (67%) (λ_{exc} 340 -λ_{em} 400)
				1478.6 (26%), 318.4 (73%) (λ_{exc} 370 -λ_{em} 505)
		77	394, 415, 495_{max} (λ_{exc} 350 nm)	
L_B	solid	298	345*sh*, 360, 390*sh* (λ_{exc} 310 nm)	34.5 (97%) (λ_{exc} 295 -λ_{em} 360)
		77	358_{max}, 393*sh*, 414*sh* (λ_{exc} 305 nm)	
	DCM, 10^{-3}M	298	376, 397_{min}, 404, 495_{max} (λ_{exc} 360 nm)	19.1 (59%), 3.4 (41%) (λ_{exc} 340 -λ_{em} 400)
				1170.2 (25%), 7777.3 (70%) (λ_{exc} 370 -λ_{em} 500)
		77	394, 415, 437, 477_{max}, 552, 574 (λ_{exc} 350 nm)	
L_C	solid	298	488_{max}, 516*sh*, 570, 602_{min} (λ_{exc} 400 nm)	89.3 (93%), 7.6 (7%) (λ_{exc} 370 -λ_{em} 490)
				470.4 (92%), 70.5 (8%) (λ_{exc} 370 -λ_{em} 600)
		77	467*sh*, 490_{max}, 522, 575, 608_{min} (λ_{exc} 400 nm)	
	DCM, 10^{-3}M	298	428, 513_{max} *br* (λ_{exc} 370 nm)	4.8 (53%), 10.7 (47%) (λ_{exc} 370 -λ_{em} 510)
		77	417, 440, 480*sh*, 555_{max}, 574, 604, 625*sh* (λ_{exc} 370 nm)	