Supporting Information for

Structural diversity in Cu(I) complexes of the PNP ligand: from pincer to binuclear coordination modes and their effects upon the electrochemical and photophysical properties

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Contents :

Figures:

Figure S1:	¹ H-NMR spectrum of $[Cu^{I}(PNP)_{2}](ClO_{4})$, (1), in CD ₃ CN at 300 K. Inset : ³¹ P-NMR spectrum.
Figure S2:	Right.: COSY of (1) in CD ₃ CN. Left.: proton numbering and observed cosy.
Figure S3:	Arrhenius plot for the fluxional behavior of (1) in CD_3CN . Ea = 47.42 kJ/mol.
Figure S4:	Proton numbering of the complex $[Cu^{I}_{2}(PNP)_{2}(phen)](ClO_{4})_{2}$, (2).
Figure S5:	¹ H-NMR spectrum of the complex (2) in $C_2Cl_4D_2$ at 300K.
Figure S6:	COSY spectrum of (2) in $C_2Cl_4D_2$ at 300K.
Figure S7:	³¹ P-NMR spectrum of (2) in $C_2Cl_4D_2$ at 300K.

- Figure S8: NOESY spectrum of (2) in $C_2Cl_4D_2$ at 300K. Green lines indicate Noesy interaction between protons on the pyridine ring and the phen ligand. Other Noesy between phosphine-protons and phen are observed at higher intensity of signals, which agree with the helical conformation in solution, similar to the crystal structure.
- Figure S9: ¹H-NMR spectrum of $[Cu^{I}(PNP)(PPh_{3})](ClO_{4})$, (3), in $C_{2}Cl_{4}D_{2}$ at 300 K. Inset : ³¹P-NMR spectrum.
- Figure S10: Right.: COSY of (3). Left.: proton numbering and observed cosy.
- Figure S11: ¹H-NMR spectrum of $[Cu^{I}(PNP)(dmp)](ClO_4)$, (4), in $C_2Cl_4D_2$ at 300K. Inset : ³¹P-NMR spectrum.
- **Figure S12:** Left: ³¹P VT-NMR of (4) in CD₃CN at temperature range 224-280K. Right: ³¹P signal (black) and deconvolution of the experimental signal (blue), at 228K.
- Figure S13: Deconvoluted emission spectra of complex (4). A fourth Gaussian centered at 630 nm is associated to the radiative relaxation of $Cu(I) \rightarrow dmp$ MLCT excited state.
- Figure S14: Deconvoluted emission spectra of complex (3). The addition of the three individual peaks (black dotted line) perfectly fits with the experimental spectrum (blue dotted line).
- Figure S15: Deconvoluted emission spectra of complex (2). Two Gaussians overlap to produce a single Gaussian with higher amplitude centered at 406 nm. A fourth Gaussian centered at 601 nm is associated to the radiative relaxation of Cu(I)→phen MLCT excited state.
- Figure S16: Deconvoluted emission spectra of ligand PNP. The addition of the three individual peaks (black dotted line) perfectly fits with the experimental spectrum (blue dotted line).

Tables :

Table S1:Chemical shift and ¹H-NMR assignment for (2).



Figure S1: ¹H-NMR spectrum of $[Cu^{I}(PNP)_{2}](ClO_{4})$, (1), in CD₃CN at 300K. Inset : ³¹P-NMR spectrum.



Figure S2: Right.: COSY of (1) in CD₃CN. Left.: proton numbering and observed COSY



Figure S3: Arrhenius plot for the fluxional behavior of (1) in CD_3CN . Ea = 47.42 kJ/mol.



Figure S4: Proton numbering of the complex $[Cu_2^I(PNP)_2(phen)](ClO_4)_{2,}$ (2).

	1		1		
Proton	δ (ppm)	Proton	δ (ppm)	Proton	δ (ppm)
N1H (2H)	4.91 (s)	H2β (4H)	7.07 (t)	Η4α, Η4γ (6Η)	7.66 (s)
H3' (2H)	5.94 (d)	Н3α, Н3γ (6Н)	7.16 (m)	H4β (4H)	7.96 (s)
H5' (2H)	6.29 (d)	N2H (2H)	7.25 (s)	H3, H8 (2H)	8.11 (dd)
H1α (4H)	6.63 (d)	H3β (4H)	7.31 (m)	H5, H6 (2H)	8.27 (s)
H2α (4H)	6.74 (d)	Η1γ, Η2γ (4Η)	7.31 (m)	H4, H7 (2H)	8.77 (d)
H1β (4H)	6.97 (t)	H4' (4H)	7.31 (m)	H2, H9 (2H)	9.00 (d)

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Figure S5: ¹H-NMR spectrum of the complex (2) in $C_2Cl_4D_2$ at 300K.



Figure S6: COSY spectrum of (2) in $C_2Cl_4D_2$ at 300 K.



Figure S7: 31 P-NMR spectrum of (2) in C₂Cl₄D₂ at 300K.



Figure S8: NOESY spectrum of (2) in $C_2Cl_4D_2$ at 300K. Green lines indicate Noesy interaction between protons on the pyridine ring and the phen ligand. Other Noesy between phosphine-protons and phen are observed at higher intensity of signals, which agree with the helical conformation in solution, similar to the crystal structure.



Figure S9: ¹H-NMR spectrum of $[Cu^{I}(PNP)(PPh_{3})](ClO_{4})$, (3), in $C_{2}Cl_{4}D_{2}$ at 300 K. Inset : ³¹P-NMR spectrum.



Figure S10: Right.: COSY of (3). Left.: proton numbering and observed COSY.



Figure S11: ¹H-NMR spectrum of $[Cu^{I}(PNP)(dmp)](ClO_4)$, (4), in $C_2Cl_4D_2$ at 300K. Inset : ³¹P-NMR spectrum.



Figure S12: Left: ³¹P VT-NMR of (4) in CD₃CN at temperature range 224-280K. Right: ³¹P signal (black) and deconvolution of the experimental signal (blue), at 228K.



Figure S13: Deconvoluted emission spectra of ligand PNP. The addition of the three individual peaks (black dotted line) perfectly fits with the experimental spectrum (blue dotted line).



Figure S14: Deconvoluted emission spectra of complex (2). Two Gaussians overlap to produce a single Gaussian with higher amplitude centered at 406 nm. A fourth Gaussian centered at 601 nm is associated to the radiative relaxation of Cu(I)-phen MLCT excited state.



Figure S15: Deconvoluted emission spectra of complex (3). The addition of the three individual peaks (black dotted line) perfectly fits with the experimental spectrum (blue dotted line).



Figure S16: Deconvoluted emission spectra of complex (4). A fourth Gaussian centered at 630 nm is associated to the radiative relaxation of $Cu(I) \rightarrow dmp$ MLCT excited state.