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Gleaned snapshots on the road to coordination polymers: heterometallic architectures based on Cu(I) metallaclips and 2,2'-bis-dipyrrin metalloligands

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Supporting Information

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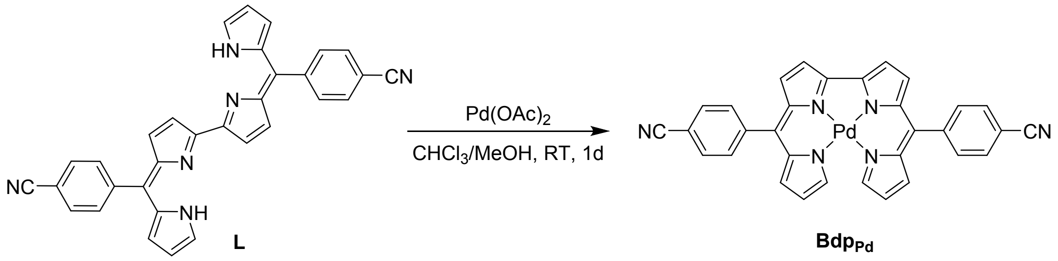
I. Experimental Section

Concerning the preparation of the ligand **Bdp$_{Pd}$**, ^{1}H- and ^{13}C-NMR spectra were recorded at 25 °C on a Bruker AV500 (500 MHz) spectrometer with the deuterated solvent as the internal reference. NMR chemical shifts and *J* values are given in parts per million (ppm) and in Hertz, respectively. Mass spectrometry was performed at the Service commun d'analyses of the University of Strasbourg. Complex **Bdp$_{Ni}$** and 2,2'-bis-dipyrrin ligand **L** were prepared as described.[1]

For the preparation of the derivatives **D**, **E** and **F**, procedures were performed under air, in a simple flask. Commercially available solvents were used as received without further purification. Commercially available reagents ($[Cu(CH_3CN)_4].PF_6$ and dppm, were obtained from Sigma-Aldrich. Dppa ligand was obtained from TCI. ^{1}H and ^{31}P{^{1}H} NMR spectra were recorded on Bruker AV300 or AV400 spectrometers. ^{1}H NMR chemical shifts were reported in parts per million (ppm) relative to Me_4Si as external standard. ^{31}P{^{1}H} NMR downfield chemical shifts were expressed with a positive sign, in ppm, relative to 85% H_3PO_4 respectively. FT-IR measurements have been performed on a Perkin Elmer Frontier spectrometer using UATR (Universal Attenuated Total Reflectance) accessory. Spectra have been recorded between 650 cm^{-1} and 4000 cm^{-1}, on pure samples.

Synthesis of ligand Bdp$_{Pd}$



A MeOH solution (15 mL) of $Pd(OAc)_2$ (95 mg, 0.40 mmol, 2 eq.) was added to a $CHCl_3$ solution (15 mL) of ligand **L** (100 mg, 0.20 mmol, 1 eq.), causing a colour change from dark-purple to dark-red. The mixture was left to stir at room temperature overnight. Upon removal of the solvent under vacuum, the residue was purified by column chromatography (SiO_2, CH_2Cl_2) to afford complex **Bdp$_{Pd}$** as red solid (90 mg, 75 %). Slow vapor diffusion of *n*-pentane into a $CHCl_3$ solution of the compound afforded crystals suitable for X-ray diffraction.

^{1}H NMR (500 MHz, $CDCl_3$) δ(ppm)= 7.74 (d, *J* = 8.2 Hz, 4H), 7.59 (d, *J* = 8.2 Hz, 4H), 7.15 (s, 2H), 6.47 (d, *J* = 4.4 Hz, 2H), 6.44 (dd, *J* = 1.0 and 4.4 Hz, 2H), 6.31 (dd, *J* = 1.0 and 4.4 Hz, 2H), 6.29 (d, *J* = 4.4 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ(ppm)= 157.77, 153.84, 143.77, 141.86, 138.16, 134.98, 134.80, 131.67, 131.27, 128.36, 118.53, 118.06, 116.31, 113.17. HR-MS (ESI) m/z $(M)^+$: calcd. for $C_{32}H_{18}N_6Pd$ 592.0634; found 592.0638. IR (ATR) ν/cm^{-1}: 2231, 2223 (CN).

Synthetic procedures of derivatives D, E and F were optimized regarding the ligands / Cu(I) fragments ratio characterized in their X-ray structures.

Synthesis of derivative D

One equivalent of $\mathbf{Bdp_{Pd}}$ ligand (0.016 g, 0.027 mmol) dissolved in 5 ml of CH_2Cl_2 was added to one equivalent of the $[Cu_2(\mu_2\text{-dppm})_2(CH_3CN)_4](PF_6)_2$ complex prepared in-situ in 10 ml of CH_2Cl_2 at room temperature from the reaction of $[Cu(CH_3CN)_4](PF_6)$ (0.020 g, 0.054 mmol) and dppm ligand (0.021 g, 0.054 mmol). A deep black limpid solution was obtained and stirred overnight at room temperature. The crude solution was then left upon pentane vapour diffusion, affording after one week of crystallization black single crystals. They were collected through filtration and dried under vacuum affording the derivative **D** (0.029 g, 0.008 mmol, 60% yield) as an air-stable black polycrystalline solid.

^1H NMR (300MHz, CD_2Cl_2) δ(ppm)= 7.75 (d, J = 8.1 Hz, 8H), 7.61 (d, J = 8.1 Hz, 8H), 7.46-7.36 (bs, 20H), 7.37-7.19 (bm, 68H), 6.51 (bt, J = 4.5 Hz, 8H), 6.37 (d, J = 4.5 Hz, 4H), 6.32(d, J = 4.5 Hz 4H), 3.48-3.36 (bs, 8H). $^{31}P\{^1H\}$ (121MHz, CD_2Cl_2) δ(ppm)= -8.9 (s, P_{dppm}), -144.3 (sept, $J_{P\text{-}F}$ = 714 Hz, P_{PF6}). IR (cm^{-1}): 690 (vs), 736 (vs), 772 (vs), 832 (vs), 984 (s), 1011 (s), 1046 (s), 1098 (s), 1222 (s), 1256 (s), 1313 (s), 1379 (s), 1436 (s), 1526 (s), 1604 (vw), 2232 (ν_{CN}, w), 2925 (w), 3054 (vw)

Synthesis of derivative E

Two equivalent of $\mathbf{Bdp_{Ni}}$ ligand (0.030 g, 0.054 mmol) dissolved in 5 ml of CH_2Cl_2 was added to one equivalent of the $[Cu_2(\mu_2\text{-dppm})_2(CH_3CN)_4](PF_6)_2$ complex prepared in-situ in 10 ml of CH_2Cl_2 at room temperature from the reaction of $[Cu(CH_3CN)_4](PF_6)$ (0.020 g, 0.054 mmol) and dppm ligand (0.021 g, 0.054 mmol). A deep black limpid solution was obtained and stirred overnight at room temperature. The crude solution was then left upon pentane vapour diffusion, affording after one week of crystallization black single crystals. They were collected through filtration and dried under vacuum affording the derivative **E** (0.039 g, 0.009 mmol, 67 % yield) as an air-stable black polycrystalline solid.

Solution NMR data were obtained by dissolving crystals of **E** in dry CD_2Cl_2:

^1H NMR (300MHz, CD_2Cl_2) δ(ppm)= 7.82 (d, J = 7.8 Hz, 4H), 7.71 (d, J = 7.8 Hz, 4H), 7.65-7.50 (bm, 6H), 7.35-7.24 (bs, 84H), 7.48-7.36 (bs, 32H), 7.20-7.10 (bm, 6H), 7.05-6.95 (bm, 6H), 6.80-6.65 (bm, 6H), 6.55-6.50 (bm, 4H), 3.40-3.35 (bs, 8H). $^{31}P\{^1H\}$ (121MHz, CD_2Cl_2) δ(ppm)= -8.6 (s, P_{dppm}), -144.3 (sept, $J_{P\text{-}F}$ = 717 Hz, P_{PF6}). IR (cm^{-1}): 690 (vs), 733 (vs), 772 (vs), 833 (vs), 987 (vs), 1044 (vs), 1098 (s), 1250 (s), 1306 (vs), 1365 (s), 1436 (s), 1526 (s), 1604 (vw), 2229 (ν_{CN}, w), 3052 (w)

Synthesis of derivative F

Two equivalents of **Bdp$_{Ni}$** ligand (0.58 g, 0.107 mmol) dissolved in 5 ml of CH_2Cl_2 was added to one equivalent of the $[Cu_2(\mu_2\text{-dppa})_2(CH_3CN)_4](PF_6)_2$ complex prepared in-situ in 10 ml of CH_2Cl_2 at room temperature from the reaction of $[Cu(CH_3CN)_4](PF_6)$ (0.040 g, 0.107 mmol) and dppa ligand (0.042 g, 0.107 mmol). A deep black limpid solution was obtained and stirred overnight at room temperature. The crude solution was then left upon pentane vapour diffusion, affording after one week of crystallization black single crystals. They were collected through filtration and dried under vacuum affording the derivative **F** (0.063 g, 0.028 mmol, 53 % yield) as an air-stable black polycrystalline solid.

Solution NMR data were obtained by dissolving crystals of **F** in dry CD_2Cl_2:

^1H NMR (300MHz, CD_2Cl_2) δ(ppm)= 7.81-7.53 (bm, 40H), 7.52-7.27 (bm, 80H), 7.23-7.06 (bs, 12H), 6.80-6.57 (bm, 12H), 6.56-6.46 (bs, 4H), 6.06-5.86 (bs, 4H), 4.27-4.06 (bs, 4H). $^{31}P\{^1H\}$ (121MHz, CD_2Cl_2) δ(ppm)= 47.5 (s, P_{dppa}), -144.4 (sept, $J_{P\text{-}F}$ = 705 Hz, P_{PF6}). IR (cm^{-1}): 693 (vs), 731 (vs), 771 (vs), 836 (vs), 987 (vs), 1044 (vs), 1100 (s), 1251 (s), 1306 (vs), 1381 (s), 1436 (s), 1526 (s), 1603 (vw), 2230 (ν_{CN}, w), 3052 (vw), 3231 (vw)

II. X-ray Crystallographic Study

Single crystal data collection for **E** and **F** were performed at 150 K with a D8 Venture Bruker AXS (Centre de Diffractométrie, Université de Rennes 1, France) with Mo-$K\alpha$ radiation (λ = 0.71073 Å). Reflections were indexed, Lorentz-polarization corrected and integrated by the *DENZO* program of the KappaCCD software package. The data merging process was performed using the SCALEPACK program.[2] Structure determinations were performed by direct methods with the solving program SIR97,[3] that revealed all the non-hydrogen atoms. SHELXL program[4] was used to refine the structures by full-matrix least-squares based on F^2. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in idealised positions and refined with isotropic displacement parameters. For **Bdp$_{Pd}$** and **D**, data were collected on a Bruker SMART CCD diffractometer with Mo-Kα radiation at 173 K. The structures were solved using SHELXS-97 and refined by full matrix least-squares on F^2 using SHELXL-2014 with anisotropic thermal parameters for all non-hydrogen atoms.[4] Single crystals of all these derivatives were always coated in paratone oil, mounted at low temperature on the diffractometer goniometer as quickly as possible and X-ray data collection were performed at low temperature.

Concerning the X-ray crystal structure resolution of **D**, 3 crystallographically independent dichloromethane molecules were identified but found to be highly disordered. The corresponding electronic density was treated using the ‘squeeze’ command.[5] Owing to the low diffracting power of the crystal, an ALERT level A remains concerning the completeness of data at maximum theta.

Concerning the X-ray crystal structure resolution of **E**, 17 included dichloromethane solvent molecules were found being highly disordered. A correct modelling of the disorder of these solvent molecules was not possible. We have therefore proceeded to a ‘squeeze’ treatment’[5] in order to remove the scattering contribution of these molecules which cannot be satisfactorily modelled. As a result, since these disordered molecules occupy a significant volume of the unit cell, an ALERT level A appear in the checkcif report since " VERY LARGE Solvent Accessible VOIDs" are present in the structure resolution.

Concerning the X-ray crystal structure resolution of **F**, 9 included dichloromethane solvent molecules and the two hexafluorophosphate counter-anions were found being highly disordered. A correct modelling of the disorder of these solvent molecules was not possible. We have therefore proceeded to a ‘squeeze’ treatment’[5] in order to remove the scattering contribution of these molecules which cannot be satisfactorily modelled. As a result, since these disordered molecules occupy a significant volume of the unit cell, an ALERT level A appear in the checkcif report since " VERY LARGE Solvent Accessible VOIDs" are present in the structure resolution.

Table S1 gives the crystallographic data for the derivatives **D**, **E** and **F** after the ‘squeeze’ treatment. Table S2 give the crystallographic data for the derivatives **D**, **E** and **F** before ‘squeeze’ treatment. Table S3 gives the crystallographic data for the derivative $\mathbf{Bdp_{Pd}}$.

Atomic scattering factors for all atoms were taken from International Tables for X-ray Crystallography.[6] CCDC reference numbers 2013354, 2013353, 2013464 and 2013465 contain the supplementary crystallographic data for the reference measurements of the X-ray crystal structures of the derivatives $\mathbf{Bdp_{Pd}}$, **D**, **E** and **F** respectively. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre.

Table S1. Crystal data and structure refinement for derivatives **D, E** and **F** after the ‘squeeze’ treatment

	D. 4 PF_6	**2E. 4 PF_6**	**F**
Molecular formula	$C_{164}H_{124}Cu_4F_{24}N_{12}P_{12}Pd_2$	$C_{228}H_{160}Cu_4F_{24}N_{24}Ni_4P_{12}$	$C_{112}H_{76}Cu_2N_{14}Ni_2P_4$
CCDC number	2013353	2013464	2013465
Molecular weight	3557.34	4552.44	1986.25
a (Å)	16.1306(10)	18.207(2)	16.697(3)
b (Å)	16.6998(11)	26.995(4)	18.050(3)
c (Å)	18.3422(12)	28.766(4)	24.093(4)
α (°)	74.727(3)	73.564(4)	94.584(6)
β (°)	77.311(3)	86.988(4)	96.139(5)
γ (°)	65.227(3)	72.007(4)	112.996(5)
V (Å^3)	4294(5)	12888(3)	6587(2)
Z	1	2	2
Dc (g cm^{-3})	1.376	1.173	1.001
Crystal system	Triclinic	Triclinic	Triclinic
Space group	P-1	P-1	P-1
Temperature (K)	173(2)	150(2)	150(2)
Wavelength Mo-$K\alpha$ (Å)	0.71073	0.71073	0.71069
Crystal size (mm)	0.11 * 0.05 * 0.04	0.21 * 0.10 * 0.08	0.33 * 0.27 * 0.09
μ (mm^{-1})	0.880	0.750	0.691
F(000)	1796	4640	2040
θ limit (°)	1.640 – 30.225	2.02 – 27.57	2.16 – 27.59
Index ranges hkl	-20 < h < 22	-23 < h < 23	-21 < h < 21
	-23 < k < 23	-35 < k < 35	-23 < k < 23
	-25 < l < 25	-37 < l < 37	-31 < l < 31
Reflections collected	189114	299483	154595
Independant reflections	22356	59120	30338
Reflections [$I>2\sigma(I)$]	12336	34792	20183
Data/restraints/parameters	22356 / 0 / 938	59120 / 0 / 2665	30338 / 0 / 1207
Goodness-of-fit on F^2	1.044	1.008	1.038
Final R indices [$I>2\sigma(I)$]	R1 = 0.0835	R1 = 0.0946	R1 = 0.0782
	wR2 = 0.1820	wR2 = 0.2674	wR2 = 0.2169
R indices (all data)	R1 = 0.1674	R1 = 0.1331	R1 = 0.1086
	wR2 = 0.2169	wR2 = 0.2957	wR2 = 0.2382
Largest diff peak and hole (e Å^{-3})	1.850 and -0.871	2.334 and -0.963	1.555 and -0.730

Table S2. Crystal data and structure refinement for derivatives **D, E** and **F** before the 'squeeze' treatment

	D. 4 PF_6, 6 CH_2Cl_2	**2E. 4 PF_6, 17 CH_2Cl_2**	**F. 2 PF_6, 9 CH_2Cl_2**
Molecular formula	$C_{170}H_{136}Cl_{12}Cu_4F_{24}N_{12}P_{12}Pd_2$	$C_{245}H_{155}Cu_4F_{24}N_{24}Ni_4P_{12}Cl_{24}$	$C_{121}H_{76}Cu_2N_{14}Ni_2P_6F_{12}Cl_{19}$
Molecular weight	4066.90	5956.87	3057.83
a (Å)	16.1306(10)	18.207(2)	16.697(3)
b (Å)	16.6998(11)	26.995(4)	18.050(3)
c (Å)	18.3422(12)	28.766(4)	24.093(4)
α (°)	74.727(3)	73.564(4)	94.584(6)
β (°)	77.311(3)	86.988(4)	96.139(5)
γ (°)	65.227(3)	72.007(4)	112.996(5)
V (Å^3)	4294.0(5)	12888(3)	6587(2)
Z	1	2	2
*D*c (g cm^{-3})	1.573	1.535	1.542
Crystal system	Triclinic	Triclinic	Triclinic
Space group	P-1	P-1	P-1
Temperature (K)	173(2)	150(2)	150(2)
Wavelength Mo-$K\alpha$ (Å)	0.71073	0.71073	0.71069
Crystal size (mm)	0.11 * 0.05 * 0.04	0.21 * 0.10 * 0.08	0.33 * 0.27 * 0.09
μ (mm^{-1})	1.071	1.111	1.129
F(000)	2048	5990	3070
θ limit (°)	1.640 – 30.225	2.02 – 27.57	2.16 – 27.59
Index ranges *hkl*	$-20 < h < 22$	$-23 < h < 23$	$-21 < h < 21$
	$-23 < k < 23$	$-35 < k < 35$	$-23 < k < 23$
	$-25 < l < 25$	$-37 < l < 37$	$-31 < l < 31$
Reflections collected	189114	299483	154595
Independant reflections	22356	59120	30338
Reflections [$I>2\sigma(I)$]	12336	34251	19882
Data/restraints/parameters	22356 / 0 / 938	59120 / 0 / 3125	30338 / 0 / 1667
Goodness-of-fit on F^2	1.057	1.525	1.884
Final *R* indices [$I>2\sigma(I)$]	R1 = 0.0890	R1 = 0.1224	R1 = 0.1517
	wR2 = 0.1953	wR2 = 0.3594	wR2 = 0.4288
R indices (all data)	R1 = 0.1811	R1 = 0.1948	R1 = 0.2026
	wR2 = 0.2357	wR2 = 0.4249	wR2 = 0.4753
Largest diff peak and hole (e Å^{-3})	1.801 and -1.101	3.727 and -1.890	5.561 and -4.659

Table S3. Crystallographic data for complex **Bdp$_{Pd}$**.

	Bdp$_{Pd}$
Molecular formula	$C_{32}H_{18}N_6Pd$
CCDC number	2013354
Molecular weight	592.92
a (Å)	9.9898(5)
b (Å)	12.0743(6)
c (Å)	12.2286(5)
α (°)	117.238(2)
β (°)	103.019(2)
γ (°)	98.413(2)
V (Å^3)	1223.63(10)
Z	2
*D*c (g cm^{-3})	1.609
Crystal system	Triclinic
Space group	P-1
Temperature (K)	173(2)
Wavelength Mo-$K\alpha$ (Å)	0.71073
Crystal size (mm)	0.08 * 0.07 * 0.06
μ (mm^{-1})	0.794
F(000)	596
θ limit (°)	1.965 – 30.311
Index ranges *hkl*	-14 < h < 14
	-17 < k < 16
	-11 < l < 16
Reflections collected	23084
Independant reflections	6698
Reflections [I>2σ(I)]	6081
Data/restraints/parameters	6695 / 0 / 352
Goodness-of-fit on F^2	1.031
Final *R* indices [I>2σ(I)]	R1 = 0.0285
	wR2 = 0.0667
R indices (all data)	R1 = 0.0323
	wR2 = 0.0692
Largest diff peak and hole (e Å^{-3})	0.471 and -0.543

Table S4. Selected bond lengths [Å], angles [°] and torsion angle of the derivatives **D**, **E**[a] and **F**.

	Cu–P	Cu–N	Cu···Cu	N-Cu-Cu[b]	Cu–N≡C-	CN-Cu-Cu-NC[b]
D	2.2343(15) 2.2441(15) 2.2635(17) 2,2785(16)	1.965(5) 1.981(5)	2.7717(10)	74.42(16) 119.13(16)	170.3(5) 178.7(5)	9.35
E[a]	2.2240(14) 2.2393(15) 2.2678(15) 2.2773(14)	1.993(5) 2.021(5)	3.262(3)	69.42 112.11	167.71 170.39	6.13
	2.2300(14) 2.2394(14) 2.2581(15) 2.2604(14)	1.970(5) 2.037(5)	3.168(3)	68.02 115.70	165.70 171.58	0.45
F	2.2378(12) 2.2412(11) 2.2495(13) 2.2516(12)	2.001(3) 2.010(4)	3.417(4)	83.02 87.15	170.5(3) 173.1(3)	28.69

[a] Two independent supramolecular rectangles are present in the unit cell. [b] within the π-stacked metallacycle units

Fig. S1. ORTEP views of the molecular structure of the derivative **Bdp$_{\mathbf{Pd}}$**. Hydrogen atoms have been omitted for clarity.

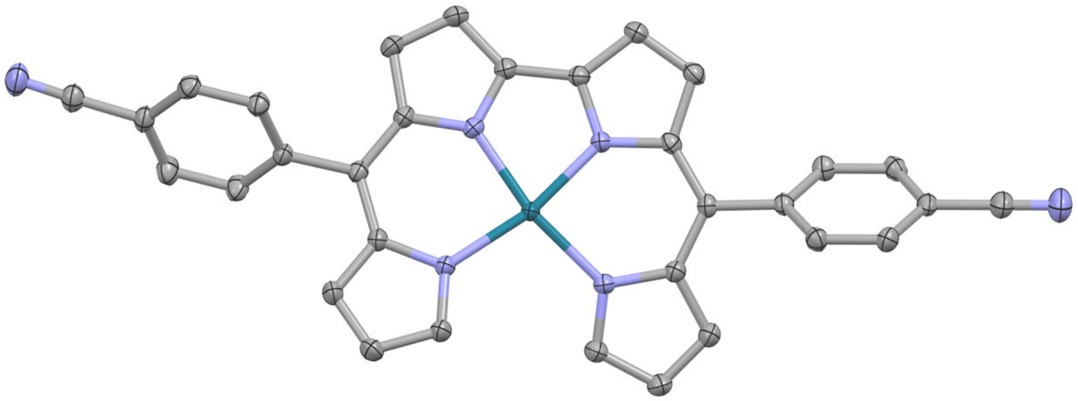


Fig. S2. ORTEP views of the molecular structure of the derivative **D**. Hydrogen atoms, included CH_2Cl_2 solvent molecules and hexafluorophosphate counter-anions have been omitted for clarity.

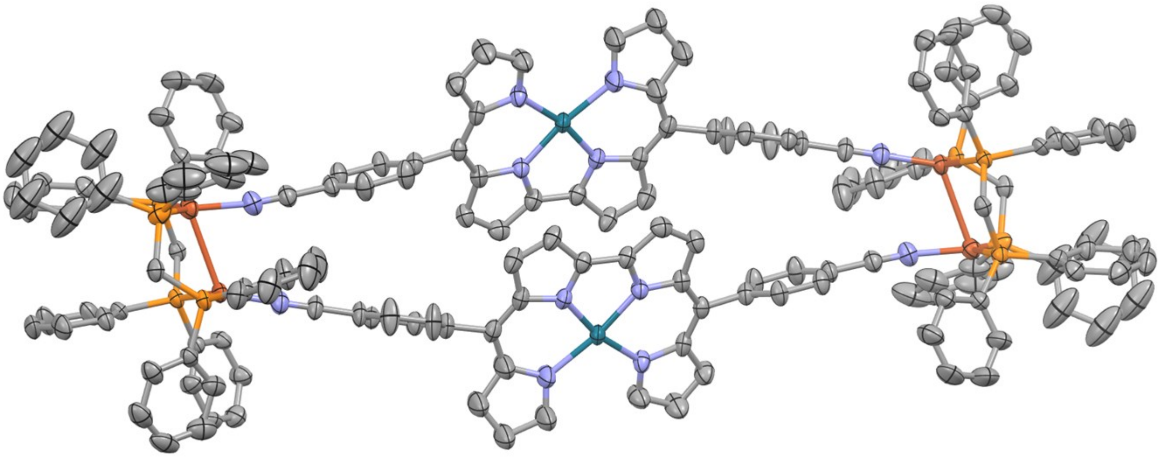


Fig. S3. ORTEP views of the molecular structure of the derivative **E**. Each of the two symmetrically independent molecules found in the unit cell are shown. Hydrogen atoms, included CH_2Cl_2 solvent molecules and hexafluorophosphate counter-anions have been omitted for clarity.

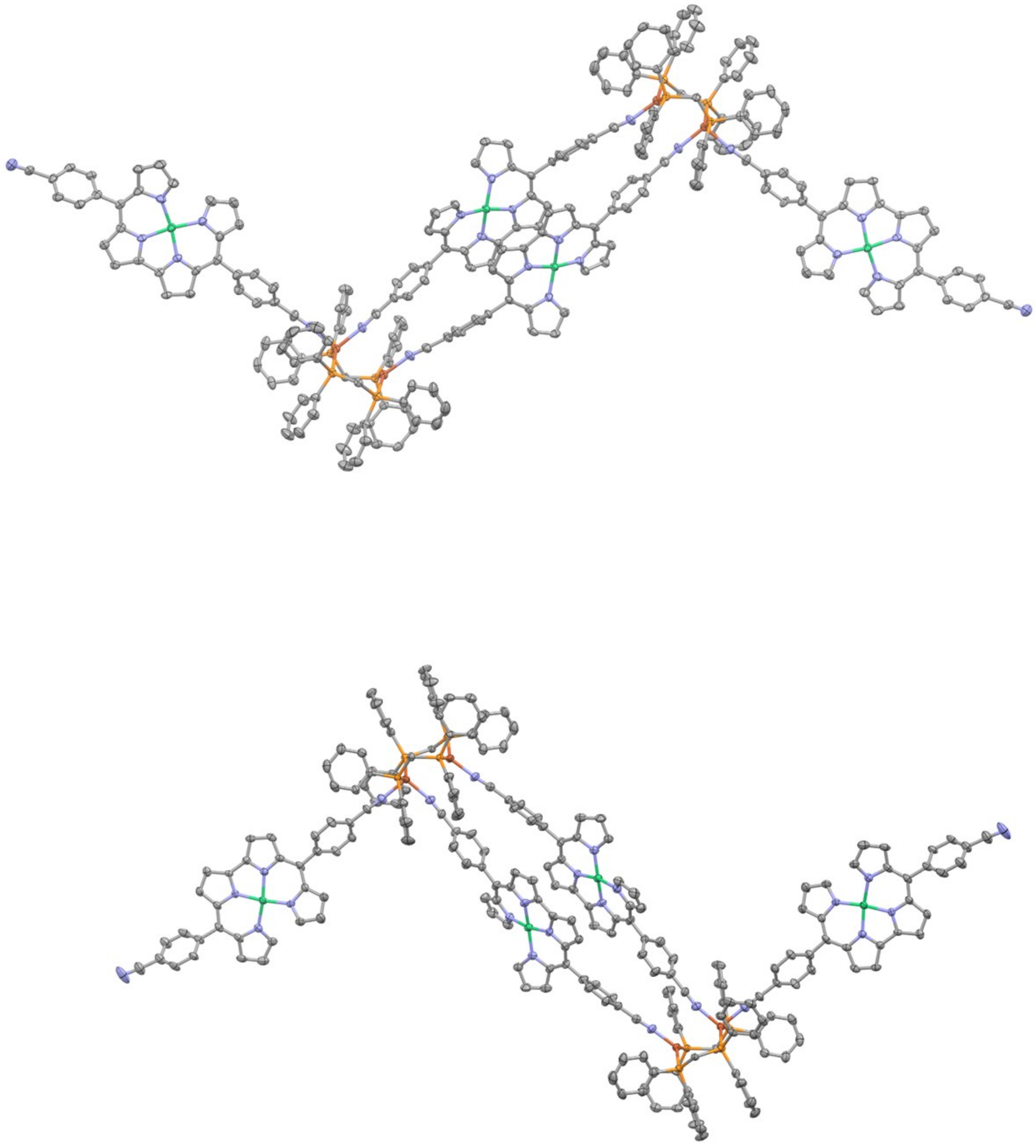


Fig. S4. ORTEP views of the molecular structure of the derivative **F**. Hydrogen atoms, included CH_2Cl_2 solvent molecules and hexafluorophosphate counter-anions have been omitted for clarity. One repetition unit is highlighted with coloured atoms while the neighbouring ones are show with atoms in white colour in order to show the 1D-ladder network scaffold.

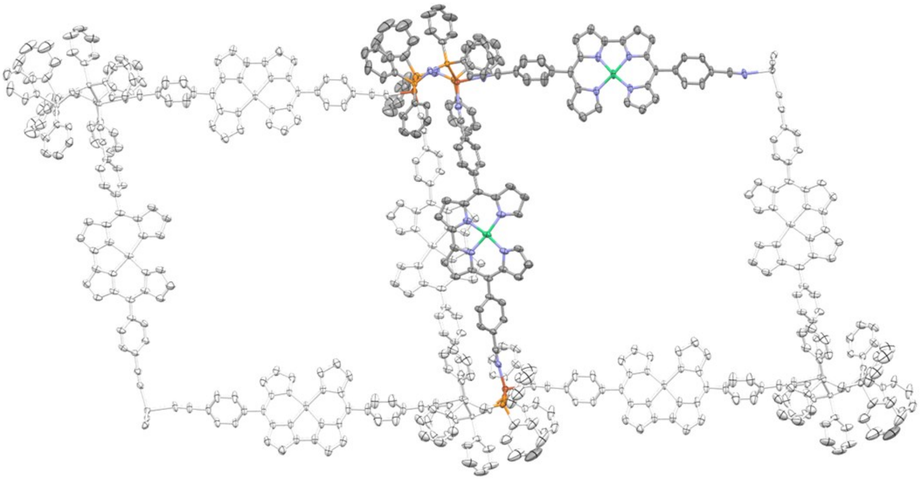
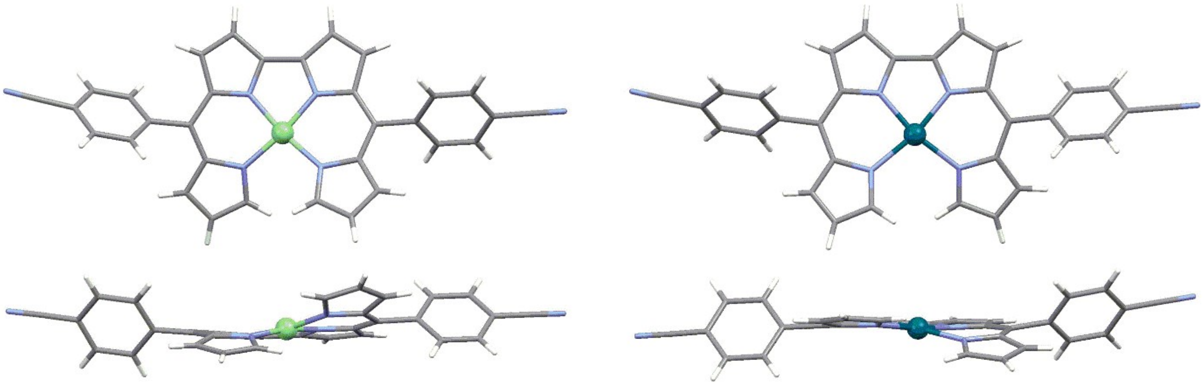
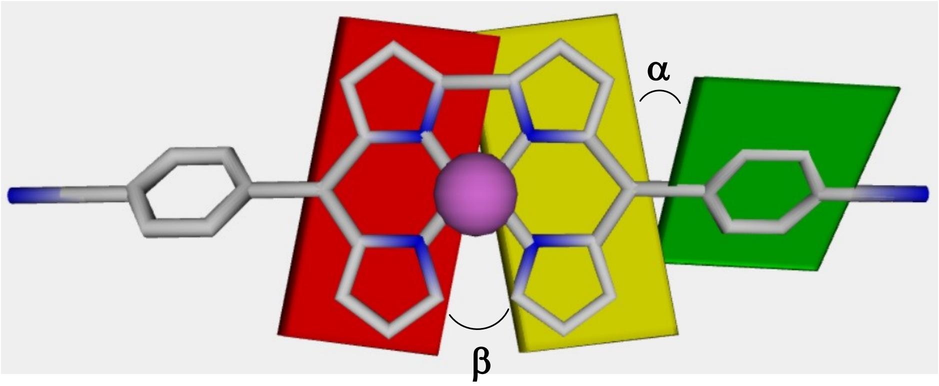


Fig. S5. Top and side views of the crystal structure of metalloligands **Bdp$_{\text{Ni}}$** (left, as reported in reference 1, CSD refcode: GIVMEF) and **Bdp$_{\text{Pd}}$** (right).



III. Representation of the torsion angles α and β 14

Fig. S6. General view of a dicyano-capped bis-dipyrrin metalloligand highlighting the location of the torsion angles α and β.



IV. References for the supplementary information file

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