

Folding of a supramolecular framework based on a tetrametallic clips driven by π - π interactions.

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Supporting Information

I. Experimental Section

All experiments were performed under an atmosphere of dry argon using standard Schlenk techniques. Commercially available reagents were used as received without further purification. Solvents were freshly distilled under argon from sodium/benzophenone (diethylether, THF) or from phosphorus pentoxide (dichloromethane). ^1H and ^{13}C NMR spectra were recorded on Bruker AV300, DPX200 or AV500 spectrometers. ^1H and ^{13}C NMR chemical shifts were reported in parts per million (ppm) relative to Me_4Si as external standard. Elemental analyses were performed by the "CRMPO", University of Rennes 1 or the "Centre de Microanalyse du CNRS" at Vernaison, France. *p*-Phenylenebis(dichlorophosphine)^[S1] was synthesized according to procedure previously published. The BF_4^- salt of the molecular bis-clip **2** was prepared according to the same route than the PF_6^- salts using $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{BF}_4$ as Cu(I) source instead of $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{PF}_6$.^[S2]

Synthesis of ligand 1: 300 mg (1.22 mmol) of 1,8-di(2-pyridyl)octa-1,7-diyne and 356 mg (1.22 mmol) of Cp_2ZrCl_2 were degassed for 30 mn at room temperature and then dissolved in 25 ml of THF. This solution was then cooled to -80°C and 2.5 mmol (1 ml, 2.5 M in hexane) of *n*-Buli were slowly added. The resulting solution stayed for one hour at -80°C and then allowed to warm to room temperature overnight. Then the brown solution was cooled to -80°C and 143 mg (0.51 mmol) of *p*-phenylenebis(dichlorophosphine) dissolved in 5 ml of diethylether were added slowly. The solution was left at for one hour at -80°C and allowed to warm to room temperature (ca 4 hours). The solution was then filtrated under inert atmosphere over basic Al_2O_3 and extracted with 40 ml of THF. The solvent from the filtrate was evaporated and the residue was washed with 20 ml of pentane affording **1** as a bright yellow powder (171 mg, 51 % yield).

^1H NMR (200 MHz, CDCl_3): δ = 1.57-1.90 (m, 8H, $\text{C}=\text{C}-\text{CH}_2-\text{CH}_2$), 2.65-2.88 (m, 4H, $\text{C}=\text{C}-\text{CH}_2$), 3.13-3.34 (m, 4H, $\text{C}=\text{C}-\text{CH}_2$), 6.85-6.96 (m, 8H, pyridyl H_4 and pyridyl H_5), 7.36 (bd, 4H, $^3J_{\text{PH}} = 8.3$ Hz H-Ph), 7.49 (bt, 4H, $^3J_{\text{HH}} = 7.7$ Hz, pyridyl H_3), 8.41 (bd, 4H, $^3J_{\text{HH}} = 4.7$ Hz, pyridyl H_6); $^{13}\text{C}\{^1\text{H}\}$ NMR (75.46 MHz, CDCl_3): δ = 23.7 (s, $\text{C}=\text{C}-\text{CH}_2-\text{CH}_2$), 29.3 (s $\text{C}=\text{C}-\text{CH}_2$), 121.2 (s, pyridyl C_5), 124.4 (d, $^3J_{\text{PC}} = 9.4$ Hz, pyridyl C_3), 132.8 (d, $^1J_{\text{PC}} = 9.4$ Hz, phenyl *ipso*-C), 133.7 (dd, $^2J_{\text{PC}} = 18.0$ Hz, $^3J_{\text{PC}} = 7.0$ Hz, phenyl -CH), 136.5 (s, pyridyl C_4), 144.2 (d, $^1J_{\text{PC}} = 4.7$ Hz, P-C=C), 148.5 (d, $^2J_{\text{PC}} = 11.0$ Hz, P-C=C), 150.0 (s, pyridyl C_6), 156.4 (d, $^2J_{\text{PC}} = 19.6$ Hz, pyridyl C_2). $^{31}\text{P}\{^1\text{H}\}$ NMR (121.5 MHz, CDCl_3): δ = +12.3 ppm.

HR-MS (ESI) m/z calcd for $\text{C}_{42}\text{H}_{36}\text{N}_4\text{P}_2\text{Na}$ $[\text{M}+\text{Na}]^+$: 681.23074; found : 681.2305.

Elemental analysis calcd (%) for $\text{C}_{42}\text{H}_{36}\text{N}_4\text{P}_2$ (658.71 g/mol): C 76.58, H 5.51, N 8.51; found C 76.45, H 5.67, N 8.59.

Synthesis of complex 2: 104 mg (0.157 mmol) of ligand **1** were dissolved in 20 ml of CH₂Cl₂ and mixed at room temperature with 257 mg (0.691 mmol) of [Cu(CH₃CN)₄]PF₆ dissolved in 20 ml of CH₂Cl₂. The resulting yellow is left upon stirring for one hour then the solvent is evaporated. The resulting residue is washed with 2*5 ml of THF (in order to remove the excess of [Cu(CH₃CN)₄]PF₆) then left under vacuum for one night at 40 °C affording the complex **2** as a bright yellow powder (254 mg, 89 % yield). Single crystals of the complex **2** were obtained upon diethylether vapour diffusion onto a CH₂Cl₂ solution of complex **2**.

¹H NMR (200 MHz, CDCl₃): δ = 2.1 (s, 24 H, CH₃CN), 2.15-2.35 (m, 8H, C=C-CH₂-CH₂), 2.50-3.35 (m, 8H, C=C-CH₂), 6.90 (bs, 4H, pyridyl H₅), 7.18 (bs, 4H, H-Ph), 7.35 (m, 4H, pyridyl H₄), 7.75 (m, 4H, pyridyl H₃), 8.18 (bs, 4H, pyridyl H₆);

¹³C{¹H} NMR (75.46 MHz, CDCl₃): δ = 1.1 (s, CH₃CN), 23.7 (s, C=C-CH₂-CH₂), 29.3 (s C=C-CH₂), 120.0 (s, CH₃CN), 121.2 (s, pyridyl C₅), 124.4 (d, ³J_{PC} = 9.4 Hz, pyridyl C₃), 132.8 (d, ¹J_{PC} = 9.4 Hz, phenyl *ipso*-C), 133.7 (dd, ²J_{PC} = 18.0 Hz, ³J_{PC} = 7.0 Hz, phenyl -CH), 136.5 (s, pyridyl C₄) 144.2 (d, ¹J_{PC} = 4.7 Hz, P-C=C), 148.5 (d, ²J_{PC} = 11.0 Hz, P-C=C), 150.0 (s, pyridyl C₆), 156.4 (d, ²J_{PC} = 19.6 Hz, pyridyl C₂).

³¹P{¹H} NMR (121.5 MHz, CDCl₃): δ = -2.2 ppm (μ-P), -142.7 ppm (sept, ¹J_{PF} = 707.1 Hz, PF₆⁻).

Elemental analysis calcd (%) for C₅₈H₆₀Cu₄F₂₄N₁₂P₆ (1821,17 g/mol): C 38.25, H 3.32, N 9.23; found C 38.41, H 3.11, N 9.59.

It is noteworthy that supramolecular derivatives **4** and **6** can also be obtained in similar isolated yields by simply mixing all their simple molecular components (ie. Cu⁺: dppm: **1** : linkers **3** or **5** in a 4 : 2 : 1 : 2 molar ratio) in CH₂Cl₂ followed by pentane vapor diffusion.

Synthesis of derivative 4: 48 mg (0.03 mmol) of 'bis-clip' **2** (X = BF₄), 23 mg (0.06 mmol) of dppm and 5 mg (0.06 mmol) of fumaronitrile (linker **3**) were dissolved in 20 ml of CH₂Cl₂ at room temperature. The resulting yellow clear solution was left upon stirring at room temperature for four hours. A yellow precipitate was then observed and removed by filtration. The filtrate was then exposed to pentane vapour diffusions leading after one week to the formation of a homogeneous batch of yellow crystals of the CP **4**. These crystals were collected, left under vacuum at room temperature for one night affording the CP **4** as a bright yellow powder (34.2 mg, 53% yield).

³¹P{¹H} NMR (81.02 MHz, CDCl₃): δ = +15.0 ppm (t, ²J_{PP} = 83.7 Hz, 1P, μ-P), -0.1 ppm (d, ²J_{PP} = 83.7 Hz, 2P, P_{dppm}).

Elemental analysis calcd (%) for C₁₀₂H₈₈Cu₄F₁₆N₈P₆B₄Cl₄ (2354,90 g/mol): C 52.02, H 3.77, N 4.76; found C 52.19, H 3.41, N 4.41.

Synthesis of derivative 6 (one pot procedure): 20 mg (0.03 mmol) of ligand **1**, 38 mg (0.12 mmol) of [Cu(CH₃CN)₄]BF₄, 23 mg (0.06 mmol) of dppm and 14 mg (0.06 mmol) of the linker **5** were dissolved in 20 ml of CH₂Cl₂ at room temperature. The resulting yellow clear solution was left upon stirring at room temperature for eight hours. A yellow precipitate was then observed and removed by filtration. The filtrate was then exposed to pentane vapour diffusions leading after one week to the formation of a homogeneous batch of yellow crystals of the CP **6**. These crystals were collected, left under vacuum at room temperature for one night affording the CP **6** as a bright yellow powder (43.8 mg, 58 % yield).

³¹P{¹H} NMR (81.02 MHz, CDCl₃): δ = +12.9 ppm (bt, ²J_{PP} = 74.5 Hz, 1P, μ-P), -1.1 ppm (bd, ²J_{PP} = 74.5 Hz, 2P, P_{dppm}).

Elemental analysis calcd (%) for C₁₂₇H₁₀₆Cu₄F₁₆N₈P₆B₄Cl₆ (2744.22 g/mol): C 55.58, H 3.89, N 4.08; found C 55.87, H 4.03, N 3.87.

II. X-ray Crystallographic Study :

X-ray Crystallographic Study: Single crystals suitable for X-Ray crystal analysis were obtained by slow diffusion of vapours of pentane into a dichloromethane solution of coordination complex **2** and of the coordination polymers **4** and **6** at room temperature. Single crystal data collection were performed at 100 K with an APEX II Bruker-AXS (Centre de Diffractométrie, Université de Rennes 1, France) with Mo-K α radiation ($\lambda = 0.71073$ 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.^[S3] Structure determinations were performed by direct methods with the solving program SIR97,^[S4] that revealed all the non hydrogen atoms. SHELXL program^[S5] 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. In the crystal lattices of the coordination polymers studied, dichloromethane (and one pentane molecule in the case of the coordination polymer **6**) solvent molecules were found in addition to the cationic coordination polymers and to their counter-anions. These solvent molecules have a strong tendency to leave the bulk crystal via evaporation once the crystals are removed from their mother solution, a process that induce a rapid degradation of the single-crystal integrity of the crystals investigated. In order to slow down this process, single crystals of all these derivatives were always coated in paratone oil once removed from the mother solution, mount at low temperature (100 K) as quickly as possible on the diffractometer goniometer and X-ray data collection were performed at low temperature (100 K). In most of the case, X-ray crystal structure resolution revealed these solvent molecules highly disordered. In the case of the coordination polymer **4**, modelling of the disorder of these solvent molecules was possible leading to rather high anisotropic displacement parameters for some of their atoms. Nevertheless, anisotropic displacement parameters associated to the atoms of the cationic coordination complexes are always satisfactory. Table S1 gives the crystallographic data for the derivatives **2** and **4**. In the case of the coordination polymer **6**, single crystals were very tiny and very sensitive to included solvent evaporation and collapsed very quickly once removed from the mother solvent, even though they were handled in paratone oil. After several attempts, we have been able to mount a single crystal of **6** having a very weak but satisfactory diffraction pattern. In addition, in this derivative, CH₂Cl₂, one pentane molecules, and counter-anions are highly disordered and delocalized and it was not possible to correctly localize them. We have proceeded to a 'squeeze' treatment in order to remove the scattering contribution of these molecules (CH₂Cl₂ molecules and counter-anions) which can not be satisfactory modelled. Table S1 gives the crystallographic data for the coordination polymer **6** after this 'squeeze' treatment. Table S2 gives the crystallographic data for the derivatives **6** before such 'squeeze' treatment. The number of solvent molecule indicated correspond to the number of disordered dichloromethane molecules that could be identified. In addition, due to the poor quality of the X-ray data collection for the crystals of **6** due to the tiny size of the single crystal measured and the rapid desolvation of the included solvent molecules, some of the carbon atoms had to be refined with isotropic displacement parameters. For these reasons, final agreement (R) factors for **6** were determinate with modest values and several alerts level A appear in the checkcif file for derivative **6**. Atomic scattering factors for all atoms were taken from International Tables for X-ray Crystallography.^[S6] CCDC reference numbers 789214, 789215 and 789216 contain the supplementary crystallographic data for derivatives **2**, **4** and **6** respectively. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Center, 12 union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk

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Table S1 . Crystal data and structure refinement for the coordination complex **2**, for the derivative **4** and for the derivative **6** after the ‘squeeze’ treatment.

	2 · 4PF ₆	4 · 2BF ₄ · 5CH ₂ Cl ₂	6
Molecular formula	C ₅₈ H ₆₀ Cu ₄ F ₂₄ N ₁₂ P ₆	C ₅₅ H ₅₂ Cu ₂ F ₈ N ₄ P ₃ B ₂ Cl ₁₀	C ₁₂₄ H ₁₀₀ Cu ₄ N ₈ P ₆
CCDC number	789214	789215	789216
Molecular weight	1821.16	1517.12	2142.10
<i>a</i> [Å]	9.9984(4)	12.849(2)	15.367(4)
<i>b</i> [Å]	24.3664(10)	12.981(2)	18.717(4)
<i>c</i> [Å]	15.1535(6)	20.113(3)	27.879(7)
α [°]	90	73.033(5)	97.301(2)
β [°]	95.606(2)	90.042(5)	98.417(2)
γ [°]	90	86.256(5)	105.936(2)
<i>V</i> [Å ³]	3674.1(3)	3201.2(9)	7509(3)
<i>Z</i>	2	2	2
ρ_{calcd} [Mg m ⁻³]	1.646	1.574	0.947
crystal system	Monoclinic	Triclinic	Triclinic
space group	P2 ₁ /c	P-1	P-1
<i>T</i> [K]	100(2)	100(2)	100(2)
Wavelength Mo- <i>K</i> α (Å)	0.71069	0.71069	0.71069
Crystal size [mm]	0.1 * 0.08 * 0.06	0.1 * 0.08 * 0.07	0.1 * 0.08 * 0.02
μ (Mo- <i>K</i> α) [cm ⁻¹]	1.380	1.221	0.661
<i>F</i> (000)	1828	1530	2212
θ limit (°)	2.48 – 27.50	1.06 – 26.48	1.53 – 26.40
Index ranges <i>hkl</i>	-12 ≤ <i>h</i> ≤ 12, -16 ≤ <i>k</i> ≤ 31, -19 ≤ <i>l</i> ≤ 19	-16 ≤ <i>h</i> ≤ 16, -16 ≤ <i>k</i> ≤ 16, -25 ≤ <i>l</i> ≤ 25	-19 ≤ <i>h</i> ≤ 19, -23 ≤ <i>k</i> ≤ 23, -34 ≤ <i>l</i> ≤ 34
Reflections collected	36469	48036	73746
Independant reflections	8380	13137	30290
Reflections [<i>I</i> > 2 σ (<i>I</i>)]	5598	11247	7146
Data/restraints/parameters	8380 / 0 / 473	13137 / 0 / 776	30290 / 0 / 944
Goodness-of-fit on <i>F</i> ²	1.024	1.125	0.828
Final <i>R</i> indices	<i>R</i> 1 = 0.0562	<i>R</i> 1 = 0.0534	<i>R</i> 1 = 0.1327
[<i>I</i> > 2 σ (<i>I</i>)]	<i>wR</i> 2 = 0.1372	<i>wR</i> 2 = 0.1537	<i>wR</i> 2 = 0.3239
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0962	<i>R</i> 1 = 0.0650	<i>R</i> 1 = 0.2622
	<i>wR</i> 2 = 0.1570	<i>wR</i> 2 = 0.1702	<i>wR</i> 2 = 0.3571
Largest diff peak and hole (e Å ⁻³)	1.567 and -0.551	1.368 and -1.024	1.229 and -1.020

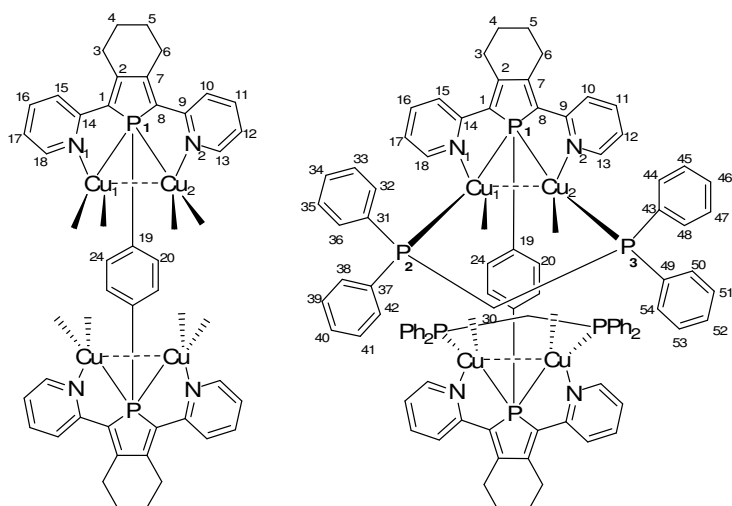
Table S2 . Crystal data and structure refinement for the derivative **6** before the ‘squeeze’ treatment

	6 4BF ₄ · 9CH ₂ Cl ₂ · C ₅ H ₁₂
Molecular formula	C ₁₃₈ H ₁₂₂ Cu ₄ N ₈ P ₆ Cl ₁₈ B ₄ F ₁₆
Molecular weight	3317.76
<i>a</i> [Å]	15.367(4)
<i>b</i> [Å]	18.717(4)
<i>c</i> [Å]	27.879(7)
α [°]	97.301(2)
β [°]	98.417(2)
γ [°]	105.936(2)
<i>V</i> [Å ³]	7509(3)
<i>Z</i>	2
ρ_{calcd} [Mg m ⁻³]	1.467
crystal system	Triclinic
space group	P-1
<i>T</i> [K]	100(2)
Wavelength Mo- <i>K</i> α (Å)	0.71069
Crystal size [mm]	0.1 * 0.08 * 0.02
μ (Mo- <i>K</i> α) [cm ⁻¹]	1.014
<i>F</i> (000)	3364
θ limit (°)	1.53 – 26.40
Index ranges <i>hkl</i>	-19 ≤ <i>h</i> ≤ 19, -23 ≤ <i>k</i> ≤ 23, -34 ≤ <i>l</i> ≤ 34
Reflections	74083
collected	
Independant reflections	30362
Reflections [<i>I</i> > 2 σ (<i>I</i>)]	9275
Data/restraints/parameters	30362 / 0 / 1712
Goodness-of-fit on <i>F</i> ²	1.282
Final <i>R</i> indices	<i>R</i> 1 = 0.2037
[<i>I</i> > 2 σ (<i>I</i>)]	<i>wR</i> 2 = 0.4621
<i>R</i> indices (all data)	<i>R</i> 1 = 0.3763
	<i>wR</i> 2 = 0.5389
Largest diff peak and hole (e Å ⁻³)	1.672 and -1.313

Table S3. Selected bond lengths [Å] and angles [°] of the Cu₂(μ -NPN) moieties of complexes **A**, **B** and **2**, and CPs **4** and **6**.

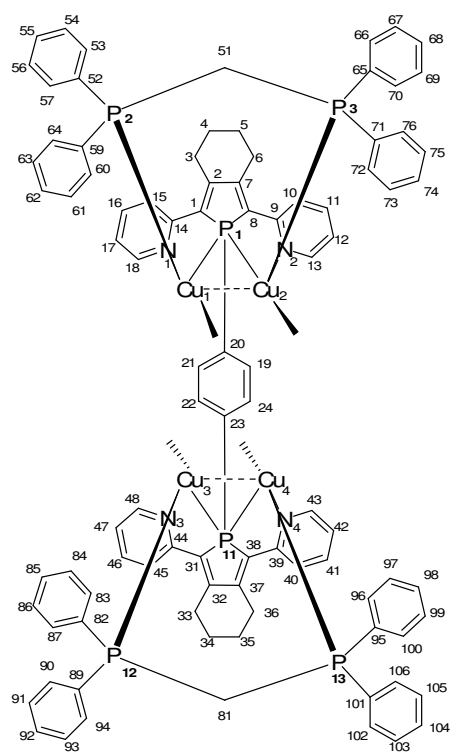
	Cu- μ P	Cu-N	Cu ^{··} Cu	N-Cu- μ P
A	2.324(1)	2.040(4)	2.568(1)	85.29(1)
	2.314(1)	2.041(5)	-	85.55(1)
B	2.413(8)	2.077(2)	2.6822(9)	81.39(6)
	2.402(8)	2.062(2)	-	82.79(6)
2	2.2997(12)	2.044(4)	2.5730(8)	85.65(10)
	2.3265(12)	2.064(4)		86.42(11)
4	2.3576(12)	2.040(3)	2.6415(11)	84.83(9)
	2.3850(11)	2.040(3)		84.91(10)
6	2.391(4)	2.027(7)	2.670(3)	81.9(2)
	2.411(4)	2.030(6)		81.9(3)
	2.355(4)	2.062(8)	2.676(3)	82.3(3)
	2.425(4)	2.076(8)		83.4(3)

Scheme S1. Labelling scheme adopted for the atoms of the derivatives **2**, **4** and **6**.



Derivative 2

Derivative 4



Derivative 6

Figure S1. Molecular structure of the cationic part of the derivative **2** (thermal ellipsoids 50% probability). Hydrogen atoms and PF_6^- counter anion have been omitted for clarity.

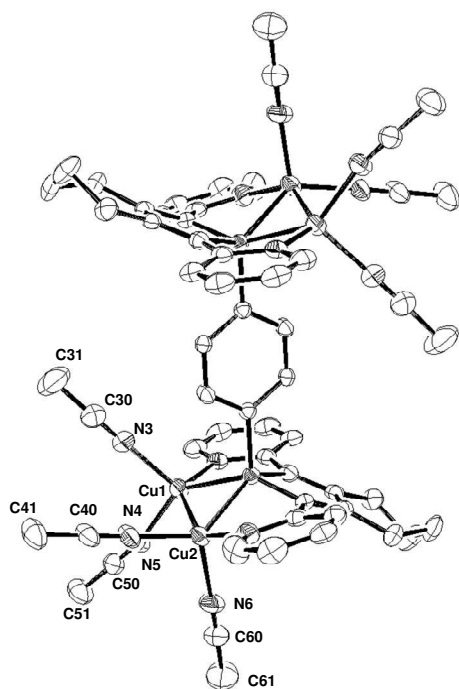


Figure S2. Molecular structure of the cationic part of the derivative **4** (thermal ellipsoids 50% probability). Hydrogen atoms and BF_4^- counter anion and dichloromethane solvent molecules have been omitted for clarity.

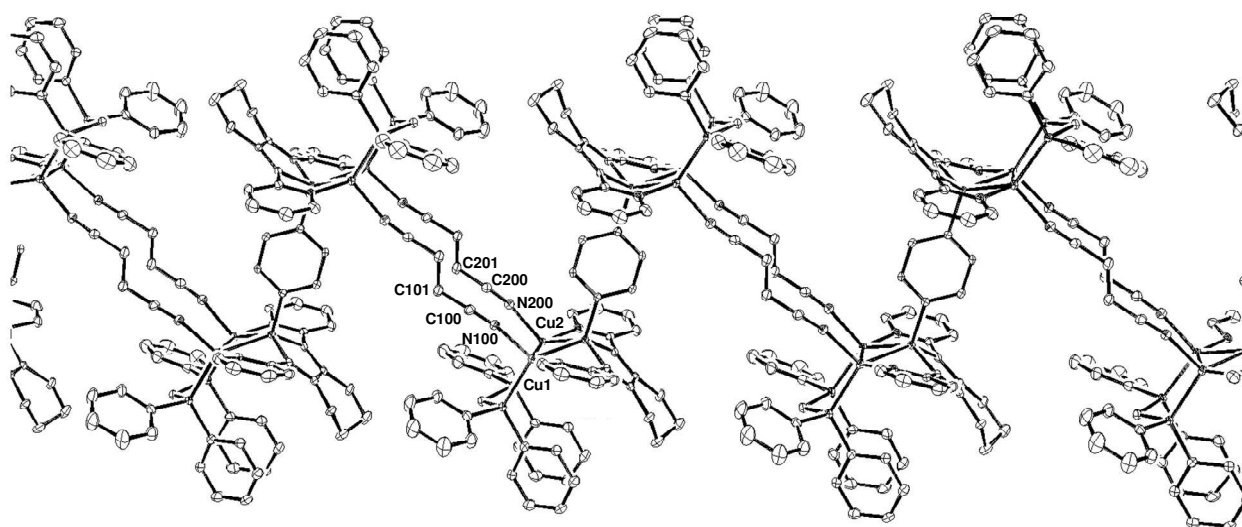


Figure S3. Molecular structure of the cationic part of the derivative **6** (thermal ellipsoids 50% probability).

