Electronic Supplementary Informations

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Experimental procedures

Analytical solvents were purchased at analytical grade and used without further purification. All commercially available products were used without further purification.

^{1}H, ^{13}C and ^{31}P spectra were recorded at 298 K on a Bruker AV300 spectrometer, with the solvent peak as the internal reference. In the assignment, the chemical shift is given first, followed in brackets by the multiplicity of the signal (br = broad, m = multiplet), the integration and the assignment. Mass spectrometry was performed by the Service de Spectrométrie de Masse, University of Strasbourg. Elemental analyses were performed on a Thermo Scientific Flash 2000 by the Service Commun de Microanalyse of the University of Strasbourg.

X-Ray diffraction studies on single crystals were performed on a Bruker APEX8 CCD Diffractometer equipped with an Oxford Cryosystem liquid N_2 device, at 173(2) K, using graphite-monochromated Mo-Kα (λ= 0.71073 Å) 50 radiation. For both structures, diffraction data were corrected for absorption. Structures were solved using SHELXS-97 and refined by full matrix least-squares on F^2 using SHELXL-97.[1] Powder X-ray diffraction (DRXP) patterns were recorded on a Bruker D8 AV diffractometer using Cu- Kα radiation (λ = 1.5406 Å) operating at 40 kV and 40 mA with a scanning range between 3.8 and 30° by a scan step size of 2°/min. For comparison, simulated patterns were calculated using the Mercury software. Thermo gravimetric analysis (TGA) were performed on a Pyris 6 TGA Lab System apparatus (Perkin-Elmer), using a N_2 flow of 20 mL/min and a heat rate of 5°/min.

Synthetic procedures

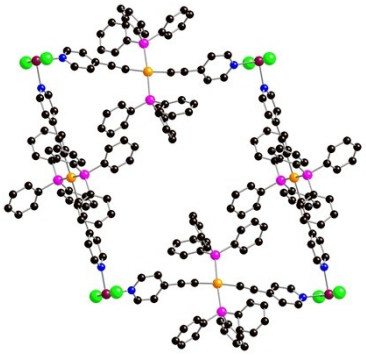
4-ethynylpyridine was synthesized as described in the literature.[2] *trans*-[Pt(C≡CPy)$_2$(PPh$_3$)$_2$] was synthesized following an adapted literature procedure.[3]

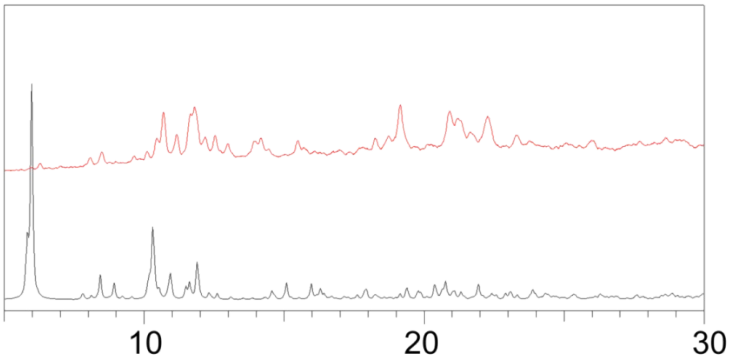
Tecton T: *cis*-Pt(PPh$_3$)$_2$Cl$_2$ (150 mg, 0.19 mmol, 1 eq.) and 4-ethynylpyridine (59 mg, 0.57 mmol, 3 eq.) were dissolved in degassed toluene/Et$_2$NH (1/1 mixture, 8 mL) and CuI (2.5 mg, 0.013 mmol, 0.07 eq.) was added. After 2 days at RT, the solution was evaporated to dryness, purified by column chromatography (SiO$_2$, CH$_2$Cl$_2$/acetone 1/0 to 1/1) and recrystallized with CH$_2$Cl$_2$/pentane to yield *trans*-[Pt(C≡CPy)$_2$(PPh$_3$)$_2$] (133 mg, 76%) as yellow needles.

^{1}H-NMR (CDCl$_3$, 300 MHz): δ (ppm) = 6.11 (br, 4H, pyr), 7.29-7.45 (m, 18H, Ph), 7.67-7.81 (m, 12H, Ph), 8.09 (br, 4H, pyr).
^{13}C-NMR (CDCl$_3$, 75 MHz): δ (ppm) = 88.6, 111.3, 125.3, 128.0, 130.6, 130.8, 135.0, 136.0, 148.5.
^{31}P-NMR (CDCl$_3$, 121.5 MHz): δ (ppm) = 18.8 ($J_{P\text{-}Pt}$ = 2600 Hz).
MS (ESI): m/z calcd for $C_{50}H_{38}N_2P_2PtH^+$ $[M + H]^+$ 1139.37 g·mol^{-1}; found 1139.37 g·mol^{-1}.
Crystallization conditions: Crystals of the networks have been obtained by diffusion of an alcoholic solution of the metal salt (*ca.* 5 mg/mL) in a solution of the bis-pyridyl compound in a chlorinated solvent (*ca.* 1 mg/mL), the two phases being separated with a buffer layer, in a glass tube (inner diameter 0.4 cm).
For the crystallization of larger amounts of the materials, the same procedure has been applied in a test tube. Yields are given based on the micro-analysis formula and the amount of starting *trans*-[Pt(C≡CPy)$_2$(PPh$_3$)$_2$] complex.

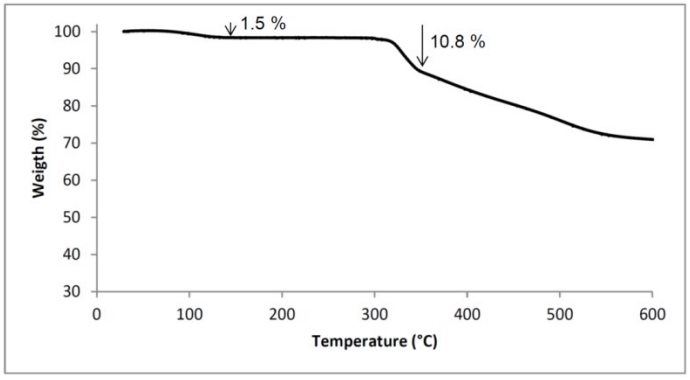
Networks characterization

(**T**,$CoCl_2$)





PXRD (black: simulated pattern; red: observed pattern)

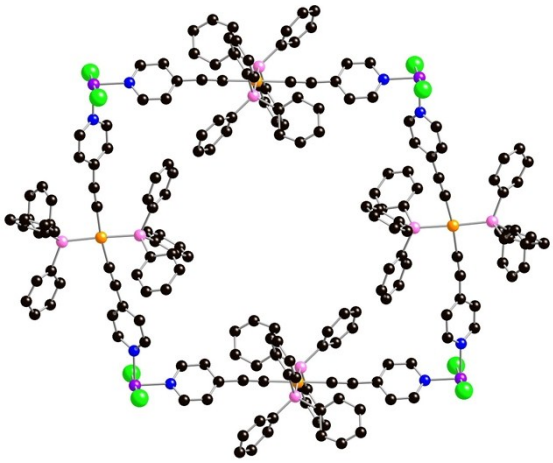


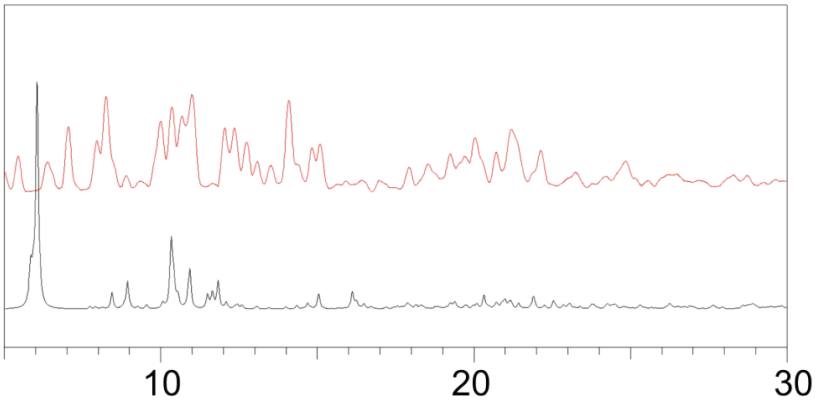
TGA trace (N_2 flow: 20 mL/min; heat rate: 5°/min)

40 % Yield: 4.6 mg

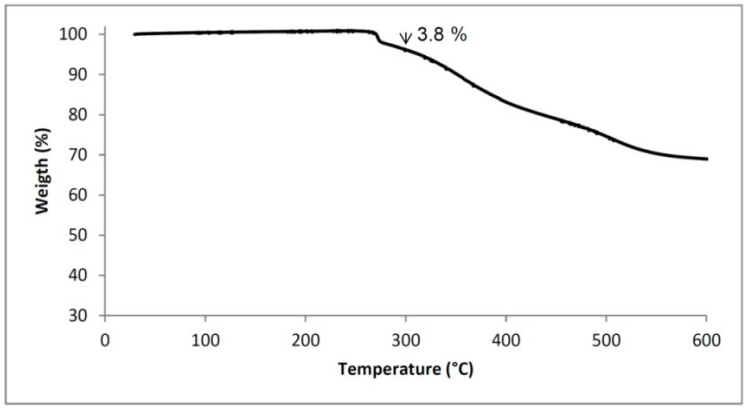
Elemental analysis: $C_{100}H_{76}Cl_2CoN_4P_4Pt_2{\cdot}CHCl_3{\cdot}3(H_2O)$: Calc. C 56.40, H 3.89, N 2.60, found C 56.47, H 3.78, 2.64.

(**T**,$NiCl_2$)





PXRD (black: simulated pattern; red: observed pattern)

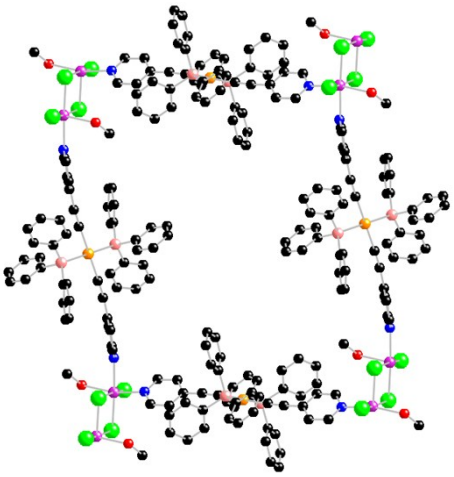


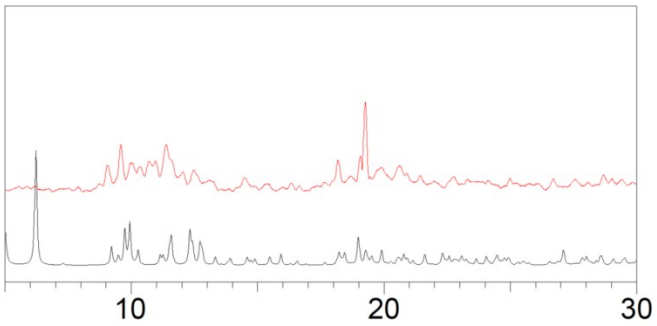
TGA trace (N_2 flow: 20 mL/min; heat rate: 5°/min)

62 %Yield, 7.0 mg

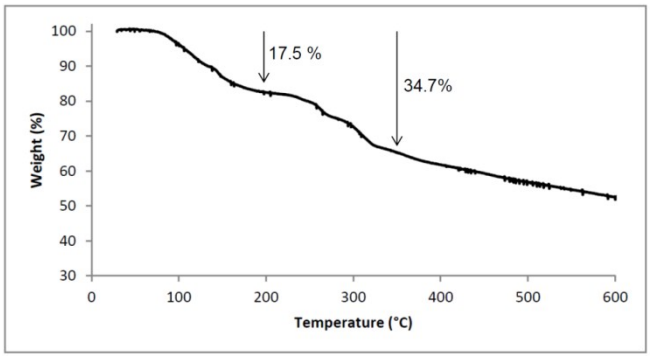
Elemental analysis: $C_{100}H_{76}Cl_2N_4NiP_4Pt_2{\cdot}CHCl_3$: Calc. C 57.86, H 3.70, N 2.67, found C 58.12, H 3.90, 2.73.

(**T**,$CdCl_2$)





PXRD (black: simulated pattern; red: observed pattern)

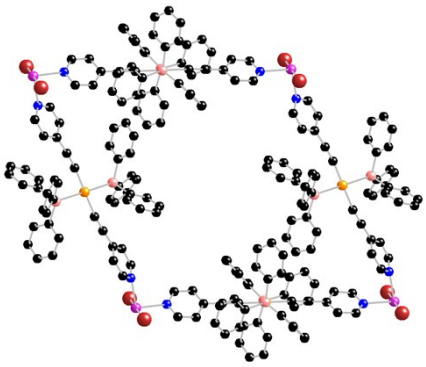


TGA trace (N_2 flow: 20 mL/min; heat rate: 5°/min)

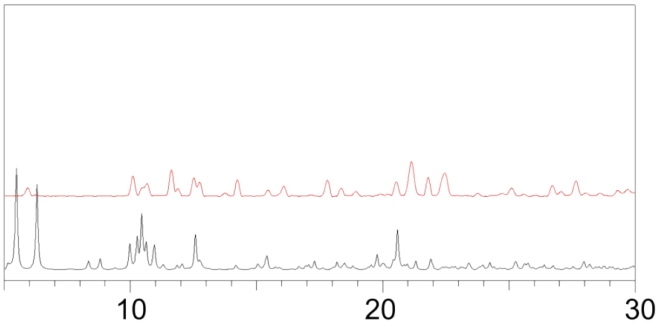
28 % Yield, 4.0 mg.

Elemental analysis: $C_{51}H_{41}CdCl_2N_2OP_2Pt{\cdot}C_2H_2Cl_4$: Calc. C 48.74, H 2.14, N 3.32, found C 48.08, H 2.62, 3.29.

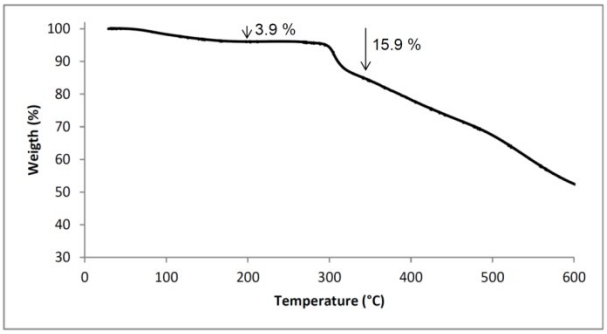
(**T**,$CdBr_2$)



$CHCl_3$/EtOH



PXRD (black: simulated pattern; red: observed pattern)

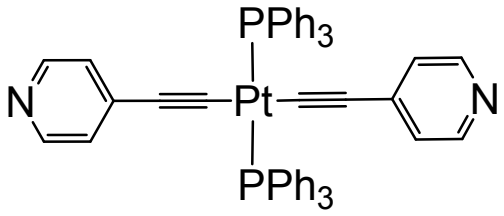


TGA trace (N_2 flow: 20 mL/min; heat rate: 5°/min)

94 % Yield, 12.9 mg.

Elemental analysis: $2(C_{100}H_{76}Br_2CdN_4P_4Pt_2)\cdot 7(CHCl_3)$: Calc. C 48.98, H 3.16, N 2.21, found C 48.93, H 3.27, 2.31.

Crystallographic datas for T



Crystallization conditions: diffusion of pentane into a solution of **T** in CH_2Cl_2.

Empirical formula	$C_{50}H_{38}N_2P_2Pt$	
Formula weight	923.85	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 9.8982(5) Å	α = 83.162(2)°.
	b = 10.2683(5) Å	β = 67.534(2)°.
	c = 10.6425(5) Å	γ = 81.896(2)°.
Volume	987.09(8) $Å^3$	
Z	1	
Density (calculated)	1.554 Mg/m^3	
Absorption coefficient	3.673 mm^{-1}	
F(000)	460	
Crystal size	0.08 x 0.06 x 0.05 mm^3	
Theta range for data collection	2.01 to 29.16°	
Index ranges	-13<=h<=13, -14<=k<=13, -13<=l<=15	
Reflections collected	10992	
Independent reflections	5285 [R(int) = 0.0360]	
Completeness to theta = 29.16°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8377 and 0.7576	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5285 / 0 / 250	
Goodness-of-fit on F^2	1.023	
Final R indices [I>2σ(I)]	R1 = 0.0354, wR2 = 0.0772	
R indices (all data)	R1 = 0.0369, wR2 = 0.0782	
Largest diff. peak and hole	1.844 and -1.204 $e.Å^{-3}$	

Crystallographic datas for (T,$CoCl_2$)

Crystallization conditions: diffusion of a $CoCl_2$ solution in MeOH (5 mg/mL) into a solution of **T** in $CHCl_3$ (1 mg/mL).

Empirical formula	$C_{101}H_{83}Cl_5CoN_4O_3P_4Pt_2 = C_{100}H_{76}Cl_2CoN_4P_4Pt_2$, $CHCl_3$, $3(H_2O)$	
Formula weight	2150.95	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 11.0755(2) Å	α = 89.7140(10)°.
	b = 17.2285(3) Å	β = 86.0250(10)°.
	c = 30.5221(6) Å	γ = 81.0480(10)°.
Volume	5739.17(18) $Å^3$	
Z	2	
Density (calculated)	1.245 Mg/m^3	
Absorption coefficient	2.789 mm^{-1}	
F(000)	2138	
Crystal size	0.06 x 0.05 x 0.05 mm^3	
Theta range for data collection	0.67 to 29.33°	
Index ranges	-15<=h<=15, -24<=k<=24, 0<=l<=43	
Reflections collected	30865	
Independent reflections	30865 [R(int) = 0.0678]	
Completeness to theta = 30.33°	98.1 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8731 and 0.8505	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	30865 / 21 / 1198	
Goodness-of-fit on F^2	1.098	
Final R indices [I>2σ(I)]	R1 = 0.0617, wR2 = 0.1987	
R indices (all data)	R1 = 0.0885, wR2 = 0.2118	
Largest diff. peak and hole	1.647 and -1.228 $e.Å^{-3}$	

Crystallographic datas for (T,$NiCl_2$)

Crystallization conditions: diffusion of a $Ni(NO_3)_2$ solution in MeOH (5 mg/mL) into a solution of **T** in $CHCl_3$ (1 mg/mL).

Empirical formula	$C_{100}H_{76}Cl_2N_4NiP_4Pt_2$	
Formula weight	1977.32	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 11.0555(4) Å	α = 90.794(2)°.
	b = 17.1663(6) Å	β = 93.971(2)°.
	c = 30.4851(10) Å	γ = 99.038(2)°.
Volume	5698.2(3) $Å^3$	
Z	2	
Density (calculated)	1.152 Mg/m^3	
Absorption coefficient	2.753 mm^{-1}	
F(000)	1964	
Crystal size	0.08 x 0.06 x 0.05 mm^3	
Theta range for data collection	1.78 to 28.00°	
Index ranges	-15<=h<=15, -24<=k<=24, 0<=l<=42	
Reflections collected	27043	
Independent reflections	27043 [R(int) = 0.0456]	
Completeness to theta = 28.00°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8746 and 0.8098	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	27043 / 0 / 967	
Goodness-of-fit on F^2	1.111	
Final R indices [I>2σ(I)]	R1 = 0.0713, wR2 = 0.2419	
R indices (all data)	R1 = 0.1317, wR2 = 0.2663	
Largest diff. peak and hole	1.075 and -1.477 $e.Å^{-3}$	

Crystallographic datas for (T,$CdCl_2$)

Crystallization conditions: diffusion of a $CdCl_2$ solution in MeOH (5 mg/mL) into a solution of **T** in $C_2H_2Cl_4$ (1 mg/mL).

Empirical formula	$C_{55}H_{45}Cl_{10}CdN_2OP_2Pt = C_{51}H_{41}Cl_2CdN_2OP_2Pt, 2(C_2H_2Cl_4)$	
Formula weight	1473.86	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 9.7730(3) Å	α = 96.5820(10)°.
	b = 18.3347(5) Å	β = 102.6170(10)°.
	c = 19.9481(6) Å	γ = 100.1690(10)°.
Volume	3389.35(17) $Å^3$	
Z	2	
Density (calculated)	1.444 Mg/m^3	
Absorption coefficient	2.851 mm^{-1}	
F(000)	1446	
Crystal size	0.06 x 0.05 x 0.05 mm^3	
Theta range for data collection	1.68 to 30.72°.	
Index ranges	-14<=h<=13, -27<=k<=26, 0<=l<=29	
Reflections collected	19923	
Independent reflections	19923 [R(int) = 0.0254]	
Completeness to theta = 30.72°	96.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8706 and 0.8476	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	19923 / 20 / 707	
Goodness-of-fit on F^2	1.054	
Final R indices [I>2σ(I)]	R1 = 0.0566, wR2 = 0.1735	
R indices (all data)	R1 = 0.0718, wR2 = 0.1835	
Largest diff. peak and hole	2.003 and -1.790 $e.Å^{-3}$	

Crystallographic datas for (T,$CdBr_2$)

Crystallization conditions: diffusion of a $CdBr_2$ solution in EtOH (5 mg/mL) into a solution of **T** in $CHCl_3$ (1 mg/mL).

Empirical formula	$C_{204}H_{170}Br_4Cd_2C_{112}N_8O_7P_8Pt_4 = 2(C_{100}H_{76}Br_2CdN_4P_4Pt_2),4(CHCl_3),7(H_2O)$	
Formula weight	4843.44	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 17.6603(4) Å	α = 113.2070(10)°.
	b = 19.2398(4) Å	β = 99.7830(10)°.
	c = 19.5076(4) Å	γ = 101.2470(10)°.
Volume	5746.7(2) $Å^3$	
Z	1	
Density (calculated)	1.400 Mg/m^3	
Absorption coefficient	3.547 mm^{-1}	
F(000)	2378	
Crystal size	0.09 x 0.07 x 0.07 mm^3	
Theta range for data collection	1.95 to 29.08°	
Index ranges	-24<=h<=24, -27<=k<=24, 0<=l<=27	
Reflections collected	30582	
Independent reflections	30582 [R(int) = 0.0547]	
Completeness to theta = 29.08°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7894 and 0.7408	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	30582 / 18 / 1174	
Goodness-of-fit on F^2	1.041	
Final R indices [I>2σ(I)]	R1 = 0.0513, wR2 = 0.1478	
R indices (all data)	R1 = 0.0716, wR2 = 0.1566	
Largest diff. peak and hole	1.890 and -1.418 $e.Å^{-3}$	

References

[1] G. M. Sheldrick, *Program for Crystal Structure Solution*, (University of Göttingen), **1997**.
[2] L. Yu, J. S. Lindsey, *J. Org. Chem.*, 2001, **66**, 7402-7419.
[3] X. Li, X. Zhao, J. Zhang, Y. Zhao, *Chem. Commun.*, 2013, **49**, 10004-10006.