Electronic Supplementary Material (ESI) for CrystEngComm.

Tuning the Dimensionality of Organometallic-Organic Hybrid Polymers Assembled from [$Cp_2Mo_2(CO)_4(\eta^2$-$P_2)$], Bipyridyl Linkers and Ag^I Ions

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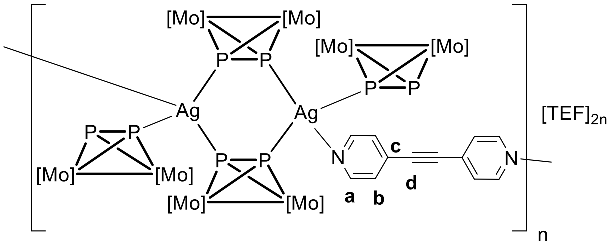
Gabor Balázs and Manfred Scheer*

1. General information:

All manipulations were carried out under an inert atmosphere of dried nitrogen using standard Schlenk techniques. The organic linker 4,4'-bipyridine (**5**) was purchased from Alfa Aesar and used as received. The ligand complex [$Cp_2Mo_2(CO)_4P_2$] (**1**),[1] Ag[Al{$OC(CF_3)_3$}$_4$][2] and the organic linkers 1,2-di(pyridin-4-yl)ethyne (**3**)[3] and 4,4'-bis(pyridin-4-ylethynyl)-1,1'-biphenyl (**4**)[4] were prepared according to literature procedures. Solvents were freshly distilled under argon from Na/K alloy (*n*-pentane) or from CaH_2 (CH_2Cl_2 and CH_3CN). IR spectra were recorded as KBr discs on varian FTS-800 spectrometer. ^1H, ^{13}C, ^{31}P and ^{19}F spectra were recorded on a Bruker Avance 300 spectrometer. ^1H and ^{13}C, ^{31}P and ^{19}F NMR chemical shifts were reported in parts per million (ppm) relative to external standard Me_4Si, H_3PO_4 (85%) or $CFCl_3$. Elemental analysis were performed by the microanalytical laboratory of the Universität Regensburg. For the ESI-MS a Finnigan ThermoQuest TSQ 7000 mass spectrometer was used.

2. Synthesis of the hybrid polymers 6-9:

2.1. Synthesis of [{$Cp_2Mo_2(CO)_4(\mu_4,\eta^{1:1:2:2}$-$P_2)$}$_2${$Cp_2Mo_2(CO)_4(\mu_3,\eta^{1:2:2}$-$P_2)$}$_2$-{$\mu,\eta^{1:1}$-$C_{12}H_8N_2$}$Ag_2$]$_n$[Al{$OC(CF_3)_3$}$_4$]$_{2n}$ (6):



6

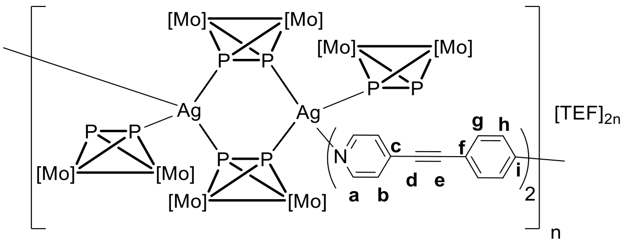
[Mo] = $CpMo(CO)_2$

[TEF] = Al{$OC(CF_3)_3$}$_4$

A solution of Ag[Al{$OC(CF_3)_3$}$_4$] (41 mg, 0.035 mmol), [$Cp_2Mo_2(CO)_4P_2$] (**1**; 35 mg, 0.07 mmol) and 1,2-di(pyridin-4-yl)ethyne (**3**; 6 mg, 0.035 mmol) in CH_2Cl_2 (10 mL) was stirred for 3h at room temperature. The mixture was then filtrated and the red-orange solution was layered with pentane and stored at room temperature. Within few days crystals of **6** × 1.45•CH_2Cl_2 suitable for single crystal X-ray diffraction analysis formed. These crystals were isolated by filtration, washed with pentane (2 × 2 mL) and dried in the vacuum. Compound **6** was finally isolated as air sensitive orange powder (53 mg, 70% yield).

^1H NMR (300 MHz, CD_3CN): δ = 5.31 (s, H_{Cp}), 7.48 (d, $^2J_{HH}$ = 5.97 Hz, H_b), 8.63 ppm (d, $^2J_{HH}$ = 5.82 Hz, H_a). $^{13}C\{^1H\}$ NMR (75.47 MHz, CD_3CN): δ = 86.1 (s, C_{Cp}), 89.7 (s, C_d), 125.1 (s, C_b), 129.4 (s, C_c), 149.8 (s, C_a), 225.6 ppm (s, C_{CO}). $^{31}P\{^1H\}$ NMR (121.49 MHz, CD_3CN): δ = -78.5 (s) ppm. $^{19}F\{^1H\}$ NMR (282.40 MHz, CD_3CN): δ = -74.7 ppm (s; CF_3). IR (KBr): $\tilde{\nu}$/cm^{-1} = 3057 (m), 3017 (m), 2960 (vw), 2162 (w), 1984 (s, CO), 1919 (s; CO), 1605 (s), 1554 (m). Positive ion ESI-MS (CH_3CN), m/z (%) = 1281.2 (8) $[Ag(\mathbf{1})_2(\mathbf{3})]^+$, 1100.1 (14) $[Ag(\mathbf{1})_2]^+$, 599.4 (68) $[Ag(\mathbf{1})]^+$, negative ion ESI-MS (CH_3CN), m/z (%) = 966.2 (100) $[Al\{OC(CF_3)_3\}_4]^-$; Elemental analysis, calcd. (%) for $Al_2Ag_2Mo_8P_8N_2F_{72}O_{24}C_{100}H_{48}$ (4314.34 g·mol^{-1}): C 27.84, H 1.12, N 0.65; found: C 27.91, H 1.19. N 0.61.

2.2 Synthesis of $[\{Cp_2Mo_2(CO)_4(\mu_4,\eta^{1:1:2:2}\text{-}P_2)\}_2\{Cp_2Mo_2(CO)_4(\mu_3,\eta^{1:2:2}\text{-}P_2)\}_2\text{-}\{\mu,\eta^{1:1}\text{-}C_{26}H_{16}N_2\}Ag_2]_n[Al\{OC(CF_3)_3\}_4]_{2n}$ (7):



7

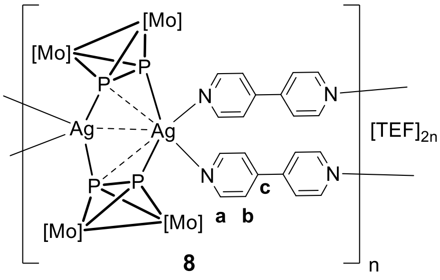
[Mo] = $CpMo(CO)_2$

[TEF] = $Al\{OC(CF_3)_3\}_4$

A solution of $Ag[Al\{OC(CF_3)_3\}_4]$ (41 mg, 0.035 mmol), $[Cp_2Mo_2(CO)_4P_2]$ (**1**; 35 mg, 0.07 mmol) and 4,4'-bis(pyridin-4-ylethynyl)-1,1'-biphenyl (**4**; 13 mg, 0.035 mmol) in CH_2Cl_2 (10 mL) was stirred for 3h at room temperature. The mixture was then filtrated and the red-orange solution was layered with pentane and stored at room temperature. Within two days crystals of **7** × 1.5•CH_2Cl_2 suitable for single crystal X-ray diffraction analysis formed. These crystals were isolated by filtration, washed with pentane (2 × 2 mL) and dried in the vacuum. Compound **7** was isolated as air sensitive orange powder (64 mg, 82% yield).

^1H NMR (300 MHz, CD_3CN): δ = 5.31 (s, H_{Cp}), 7.41 (d, $^2J_{HH}$ = 6.09 Hz, H_b), 7.67 (s, H_{g+h}), 8.59 ppm (d, $^2J_{HH}$ = 5.94 Hz, H_a). $^{13}C\{^1H\}$ NMR (75.47 MHz, CD_3CN): δ = 86.1 (s, C_{Cp}), 88.1 (s, C_e), 93.7 (s, C_d), 122.0 (s, C_f), 125.8 (s, C_b), 127.5 (s, C_h), 132.9 (s, C_g), 141.1 (s, C_i), 149.7 (s, C_c), 150.3 (s, C_a), 225.6 ppm (s, C_{CO}). $^{31}P\{^1H\}$ NMR (121.49 MHz, CD_3CN): δ = -79.3 (s) ppm. $^{19}F\{^1H\}$ NMR (282.40 MHz, CD_3CN): δ = -75.6 ppm (s; CF_3). IR (KBr): $\tilde{\nu}$/cm^{-1} = 3102 (w), 3020 (w), 2245 (m), 2220 (w), 1986 (s, CO), 1923 (s; CO), 1857 (m), 1639 (w), 1596 (w), 1539 (w), 1522 (vw). Positive ion ESI-MS (CH_3CN), m/z (%) = 1456.0 (1) $[Ag(\mathbf{1})_2(\mathbf{4})]^+$, 1100.6 (72) $[Ag(\mathbf{1})_2]^+$, 644.6 (65) $[Ag(\mathbf{1})(CH_3CN)]^+$, negative ion ESI-MS ($CH_3CN$), m/z (%) = 967.1 (100) $[Al\{OC(CF_3)_3\}_4]^-$; Elemental analysis, calcd. (%) for $Al_2Ag_2Mo_8P_8N_2F_{72}O_{24}C_{114}H_{56}$ (4490.56 g·mol^{-1}): C 30.49, H 1.26, N 0.62; found: C 30.71, H 1.44. N 0.63.

2.3 Synthesis of $[\{Cp_2Mo_2(CO)_4(\mu_4,\eta^{1:2:2:2}\text{-}P_2)\}_2\{\mu,\eta^{1:1}\text{-}C_{13}H_{14}N_2\}Ag_2]_n[Al\{OC(CF_3)_3\}_4]_{2n}$ (8):



8

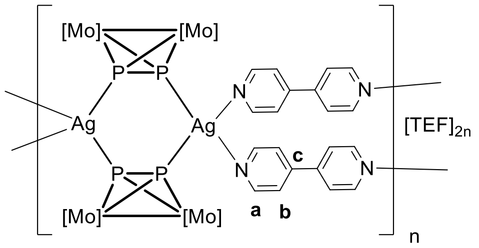
[Mo] = $CpMo(CO)_2$

[TEF] = $Al\{OC(CF_3)_3\}_4$

A solution of $Ag[Al\{OC(CF_3)_3\}_4]$ (41 mg, 0.035 mmol), $[Cp_2Mo_2(CO)_4P_2]$ (**1**; 35 mg, 0.07 mmol) and 4,4'-bipyridine (**3**; 5 mg, 0.035 mmol) in CH_2Cl_2 (10 mL) was stirred for 1h at 0°C. The mixture was then filtrated and the red-orange solution was layered with pentane and stored at room temperature. Within one day crystals of **8** × 2.4•CH_2Cl_2 suitable for single crystal X-ray diffraction analysis formed. These crystals were isolated by filtration, washed with pentane (2 × 2 mL) and dried in the vacuum. Compound **8** was isolated as air sensitive red powder (39 mg, 64% yield).

^1H NMR (300 MHz, CD_3CN): δ = 5.38 (s, H_{Cp}), 7.71 (d, $^2J_{HH}$ = 6.18 Hz, H_b), 8.71 ppm (d, $^2J_{HH}$ = 5.97 Hz, H_a). $^{13}C\{^1H\}$ NMR (75.47 MHz, CD_3CN): δ = 86.7 (s, C_{Cp}), 121.4 (s, C_b), 145.1 (s, C_c), 150.1 (s, C_a), 223.4 ppm (s, C_{CO}). $^{31}P\{^1H\}$ NMR (121.49 MHz, CD_3CN): δ = -75.9 (s) ppm. $^{19}F\{^1H\}$ NMR (282.40 MHz, CD_3CN): δ = -74.7 (s; CF_3). IR (KBr): $\tilde{\nu}$/cm^{-1} = 2982 (vw), 2936 (vw), 1960 (vs, CO), 1877 (s), 1599 (m), 1441 (m), 1358 (m), 1294 (s). IR (CH_3CN): $\tilde{\nu}$/cm^{-1} = 3126 (w), 2955 (s), 2924 (w), 1976 (vs, CO), 1948 (vs, CO), 1936 (vs, CO), 1914 (vs, CO), 1600 (m), 1535 (vw). Positive ion ESI-MS (CH_3CN), m/z (%) = 1100.4 (18) $[Ag(\mathbf{1})_2]^+$, 645.9 (46) $[Ag(\mathbf{1})(CH_3CN)]^+$, negative ion ESI-MS ($CH_3CN$), m/z (%) = 967.0 (100) $[Al\{OC(CF_3)_3\}_4]^-$; Elemental analysis, calcd. (%) for $Al_2Ag_2Mo_4P_4N_4F_{72}O_{16}C_{80}H_{36}$ (3454.39 g·mol^{-1}): C 27.81, H 1.05, N 1.62; found: C 27.85, H 1.21. N 1.62.

2.4 Synthesis of $[\{Cp_2Mo_2(CO)_4(\mu_4,\eta^{1:1:2:2}\text{-}P_2)\}_2\{\mu,\eta^{1:1}\text{-}C_{13}H_{14}N_2\}Ag_2]_n[Al\{OC(CF_3)_3\}_4]_{2n}$ (9):



9

[Mo] = $CpMo(CO)_2$
[TEF] = $Al\{OC(CF_3)_3\}_4$

A solution of $Ag[Al\{OC(CF_3)_3\}_4]$ (41 mg, 0.035 mmol), $[Cp_2Mo_2(CO)_4P_2]$ (**1**; 35 mg, 0.07 mmol) and 4,4'-bipyridine (**3**; 6 mg, 0.035 mmol) in CH_2Cl_2 (10 mL) was stirred for 1h at 60°C. The mixture was then filtrated and the red-orange solution was layered with pentane and stored at room temperature. Within few days crystals of **9** × $2{\bullet}CH_2Cl_2$ suitable for single crystal X-ray diffraction analysis formed. These crystals were isolated by filtration, washed with pentane (2 × 2 mL) and dried in the vacuum. Compound **9** was isolated as air sensitive orange powder (35 mg, 57% yield).

^1H NMR (300 MHz, CD_3CN): $\delta = 5.37$ (s, H_{Cp}), 7.70 (d, $^2J_{HH} = 6.12$ Hz, H_b), 8.71 ppm (d, $^2J_{HH} = 5.94$ Hz, H_a). $^{13}C\{^1H\}$ NMR (75.47 MHz, CD_3CN): $\delta = 86.7$ (s, C_{Cp}), 121.3 (s, C_b), 145.1 (s, C_c), 150.1 (s, C_a), 223.6 ppm (s, C_{CO}). $^{31}P\{^1H\}$ NMR (121.49 MHz, CD_3CN): $\delta = -74.3$ (s) ppm. $^{19}F\{^1H\}$ NMR (282.40 MHz, CD_3CN): $\delta = -74.7$ (s; CF_3). IR (KBr): $\tilde{\nu}$/cm^{-1} = 3002 (vw), 2003 (s, CO), 1956 (s, CO), 1607 (w), 1427 (m), 1340 (m), 1270 (m). IR (CH_3CN): $\tilde{\nu}$/cm^{-1} = 3124 (w), 2954 (s), 2924 (w), 1978 (s, CO), 1946 (s, CO), 1936 (s, CO), 1912 (s, CO), 1617 (w), 1522 (w). Positive ion ESI-MS (CH_3CN), m/z (%) = 1100.0 (97) $[Ag(\mathbf{1})_2]^+$, 599.1 (38) $[Ag(\mathbf{1})]^+$, 644.8 (16) $[Ag(\mathbf{1})(CH_3CN)]^+$, negative ion ESI-MS ($CH_3CN$), m/z (%) = 967.0 (100) $[Al\{OC(CF_3)_3\}_4]^-$; Elemental analysis, calcd. (%) for $Al_2Ag_2Mo_4P_4N_4F_{72}O_{16}C_{80}H_{36}$ (3454.39 g·mol^{-1}): C 27.81, H 1.05, N 1.62; found: C 27.80, H 1.15. N 1.63.

Note: All the formed polymers **6**-**9** show no detectable light- or air-sensitivity in the solid state for several days. However, solutions of these compounds are air-sensitive and show slight decomposition within hours and a full decomposition after few days when open to air.

3. NMR Spectra:

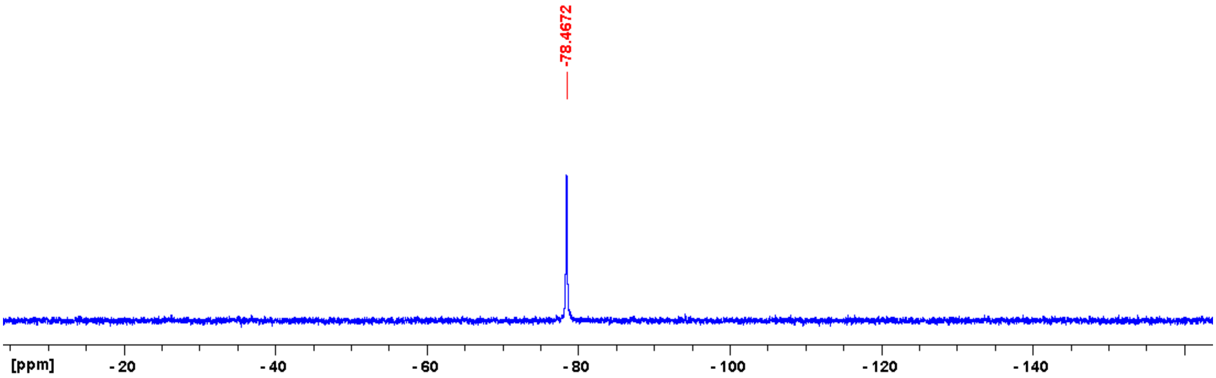


Figure S1: $^{31}P\{^1H\}$ NMR spectrum of complex **6** in CD_3CN at 121.49 MHz.

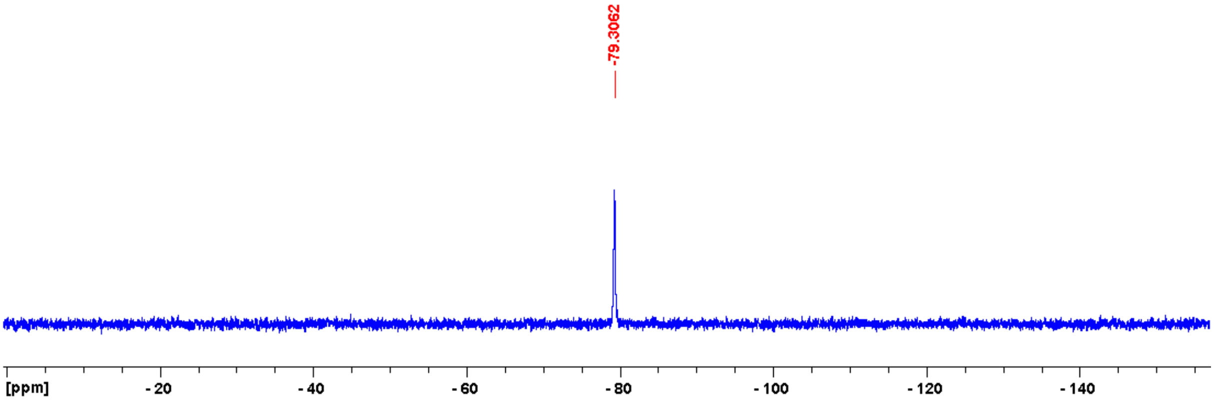


Figure S2: $^{31}P\{^1H\}$ NMR spectrum of complex **7** in CD_3CN at 121.49 MHz.

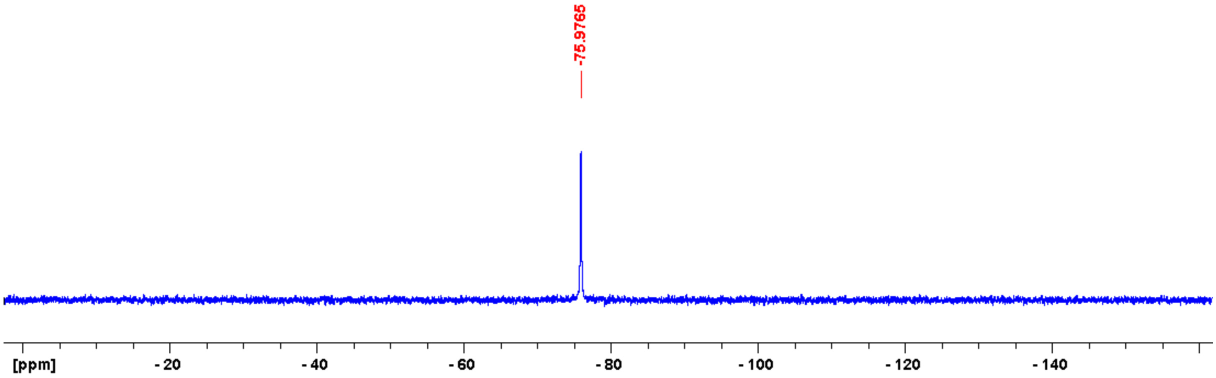


Figure S3: $^{31}P\{^{1}H\}$ NMR spectrum of complex **8** in CD_3CN at 121.49 MHz.

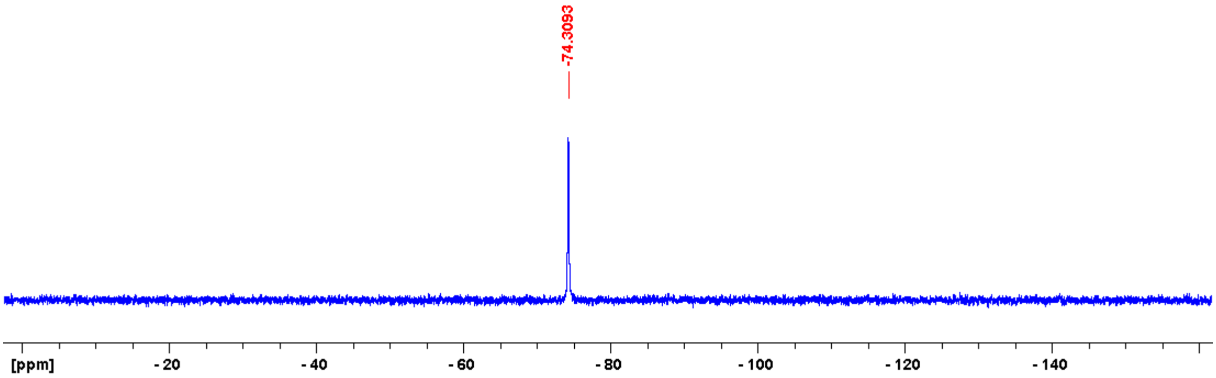


Figure S4: $^{31}P\{^{1}H\}$ NMR spectrum of complex **9** in CD_3CN at 121.49 MHz.

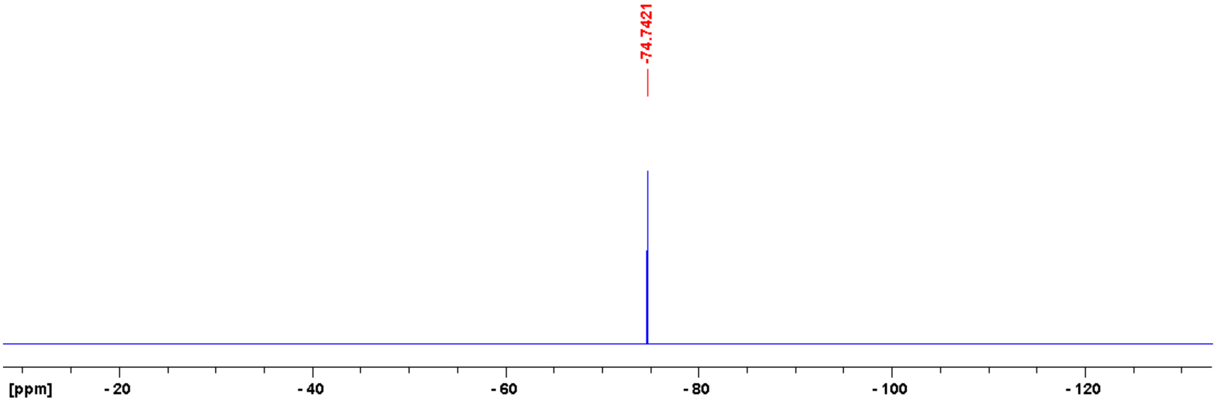


Figure S5: $^{19}F\ \{^1H\}$ NMR spectrum of complex **6** in CD_3CN at 282.40 MHz.

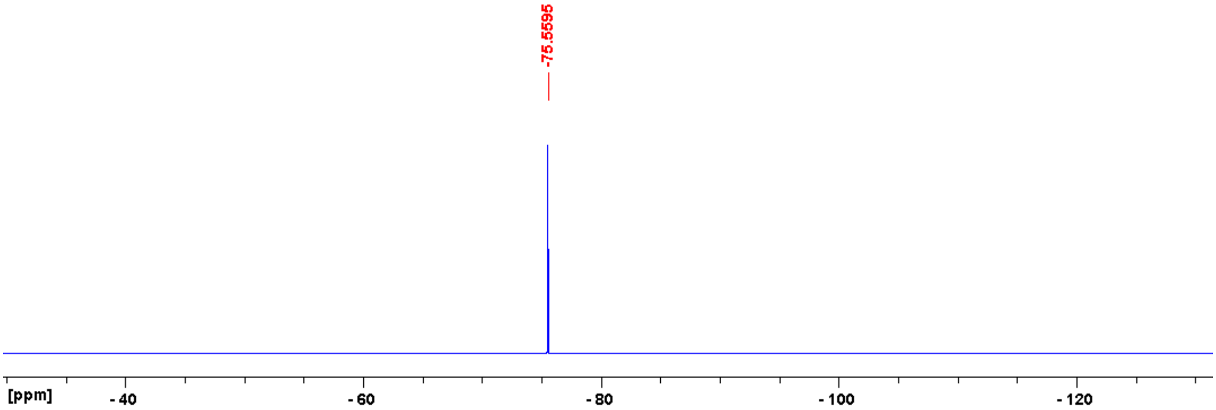


Figure S6: $^{19}F\ \{^1H\}$ NMR spectrum of complex **7** in CD_3CN at 282.40 MHz.

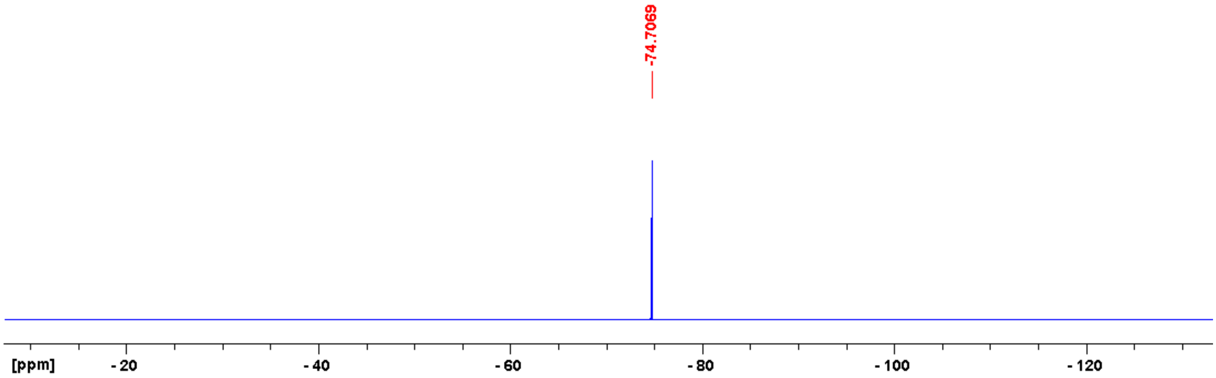


Figure S7: $^{19}F\ \{^1H\}$ NMR spectrum of complex **8** in CD_3CN at 282.40 MHz.

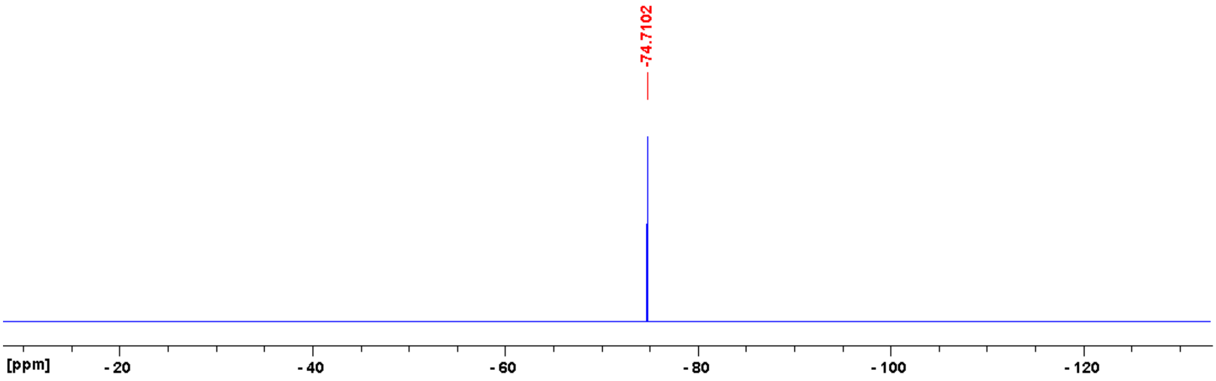
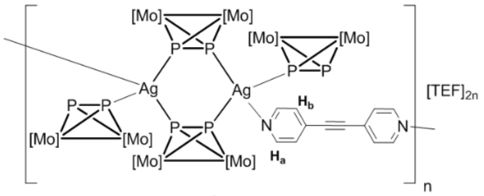


Figure S8: ${}^{19}F$ {${}^{1}H$} NMR spectrum of complex **9** in CD_3CN at 282.40 MHz.



6

[Mo] = $CpMo(CO)_2$
[TEF] = $Al\{OC(CF_3)_3\}_4$

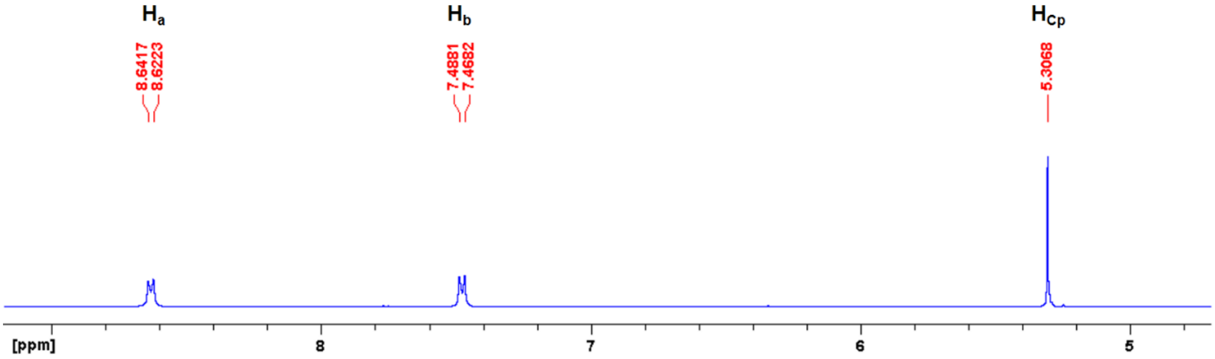
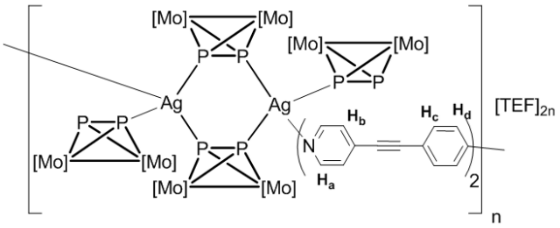


Figure S9: ${}^{1}H$ NMR spectrum of complex **6** in CD_3CN at 300 MHz.



7

[Mo] = $CpMo(CO)_2$

[TEF] = $Al\{OC(CF_3)_3\}_4$

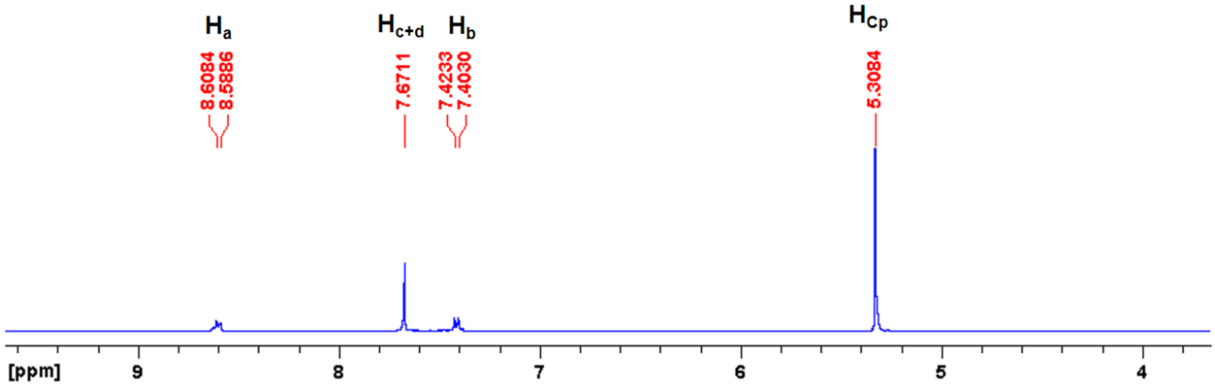
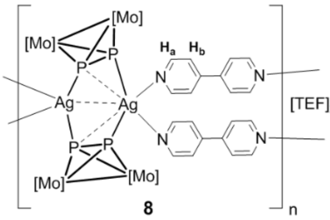


Figure S10: ^{1}H NMR spectrum of complex **7** in CD_3CN at 300 MHz.



8

[Mo] = $CpMo(CO)_2$

[TEF] = $Al\{OC(CF_3)_3\}_4$

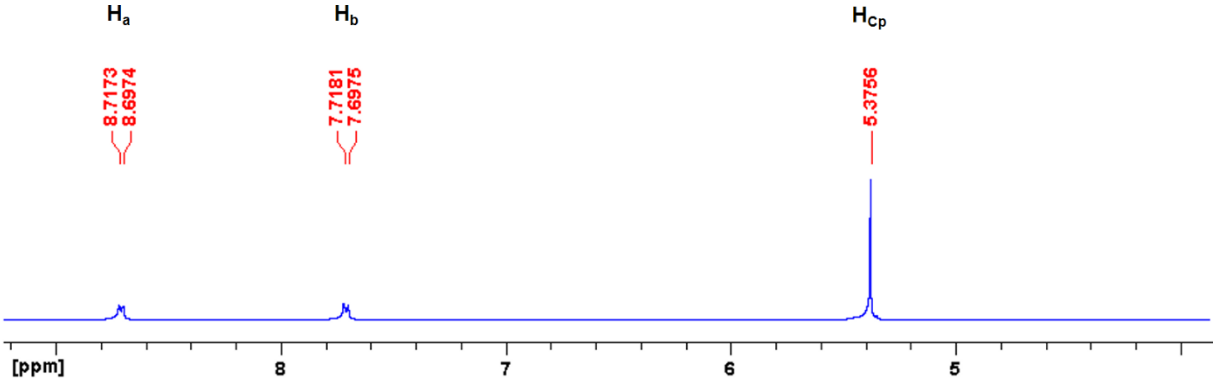
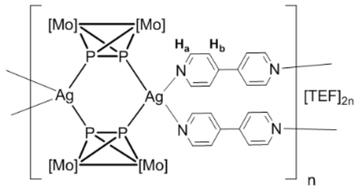


Figure S11: ^{1}H NMR spectrum of complex **8** in CD_3CN at 300 MHz.



9

[Mo] = $CpMo(CO)_2$
[TEF] = $Al\{OC(CF_3)_3\}_4$

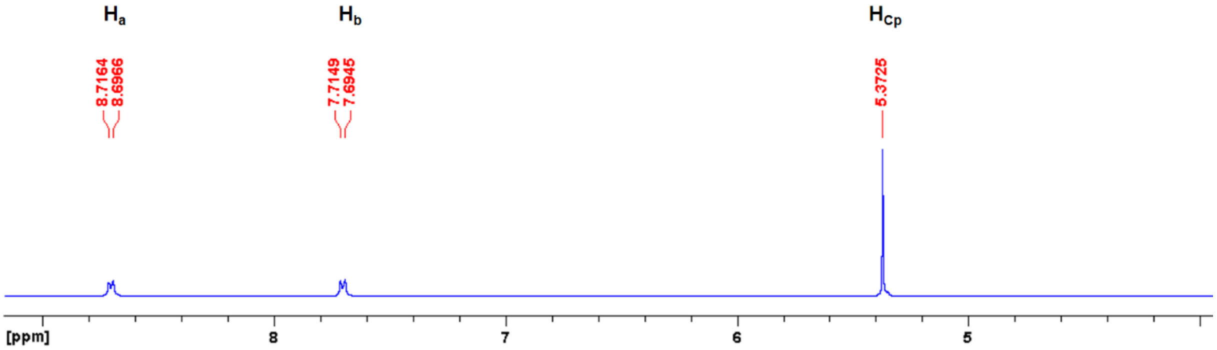
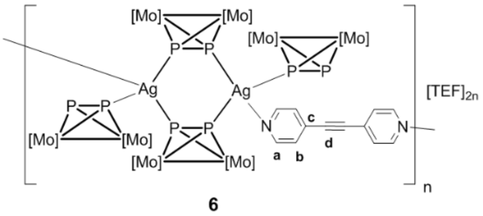


Figure S12: ^{1}H NMR spectrum of complex **9** in CD_3CN at 300 MHz.



6

[Mo] = $CpMo(CO)_2$
[TEF] = $Al\{OC(CF_3)_3\}_4$

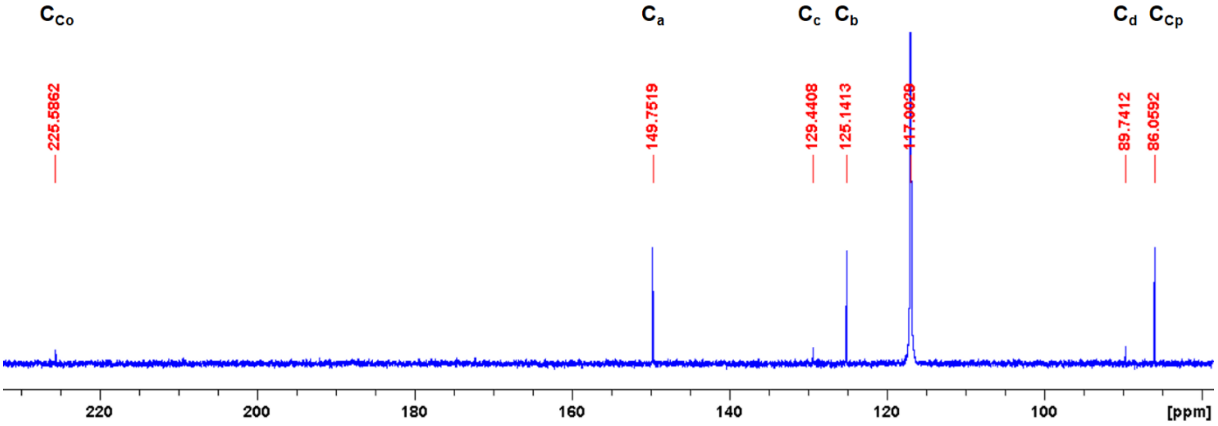
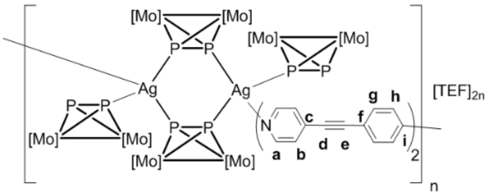


Figure S13: ^{13}C NMR spectrum of complex **6** in CD_3CN at 75.47 MHz.



7

[Mo] = CpMo(CO)$_2$
[TEF] = Al{OC(CF$_3$)$_3$}$_4$

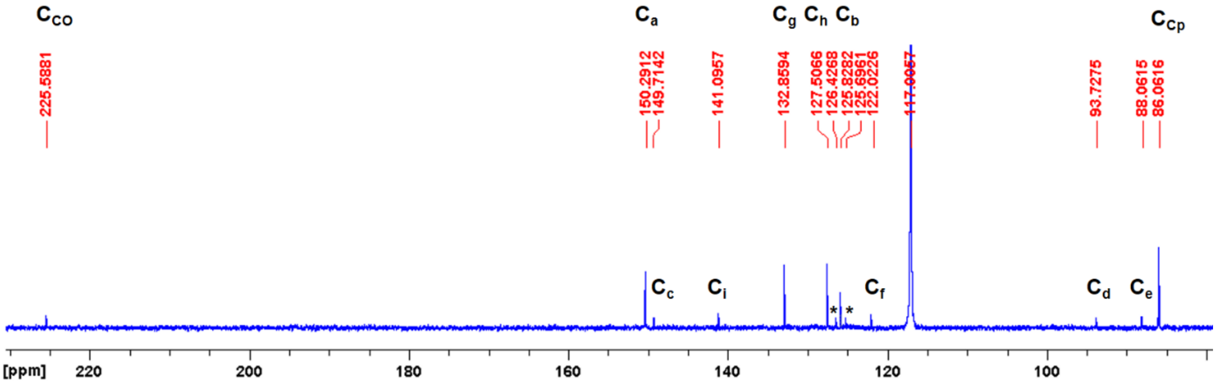
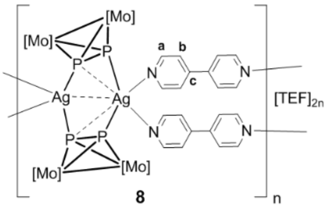


Figure S14: ^{13}C NMR spectrum of complex **7** in CD$_3$CN at 75.47 MHz.* traces of impurities



8

[Mo] = CpMo(CO)$_2$
[TEF] = Al{OC(CF$_3$)$_3$}$_4$

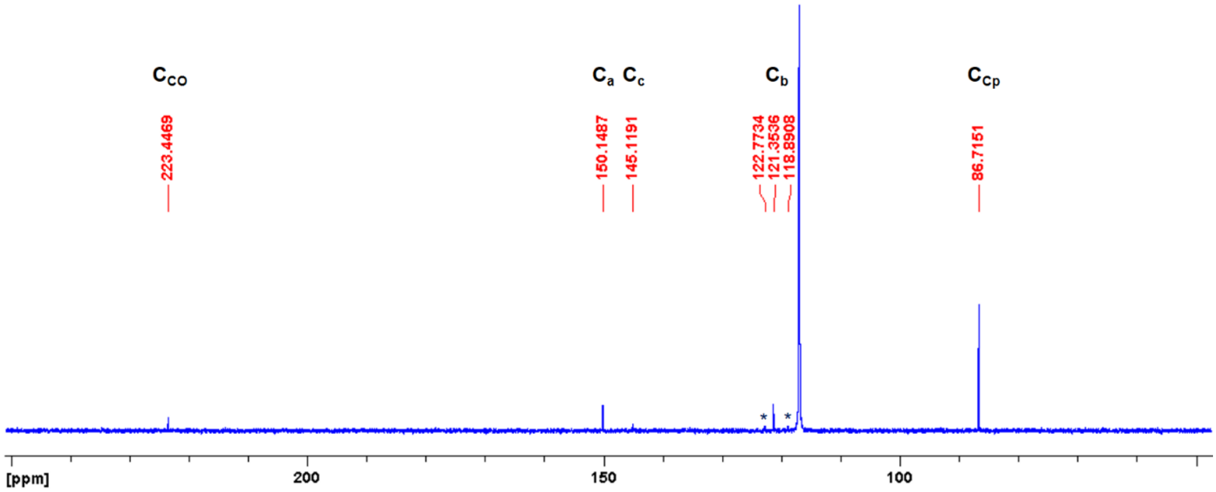
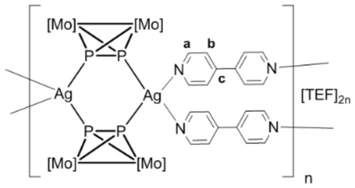


Figure S15: ^{13}C NMR spectrum of complex **8** in CD$_3$CN at 75.47 MHz.* traces of impurities



9

[Mo] = CpMo(CO)$_2$
[TEF] = Al{OC(CF$_3$)$_3$}$_4$

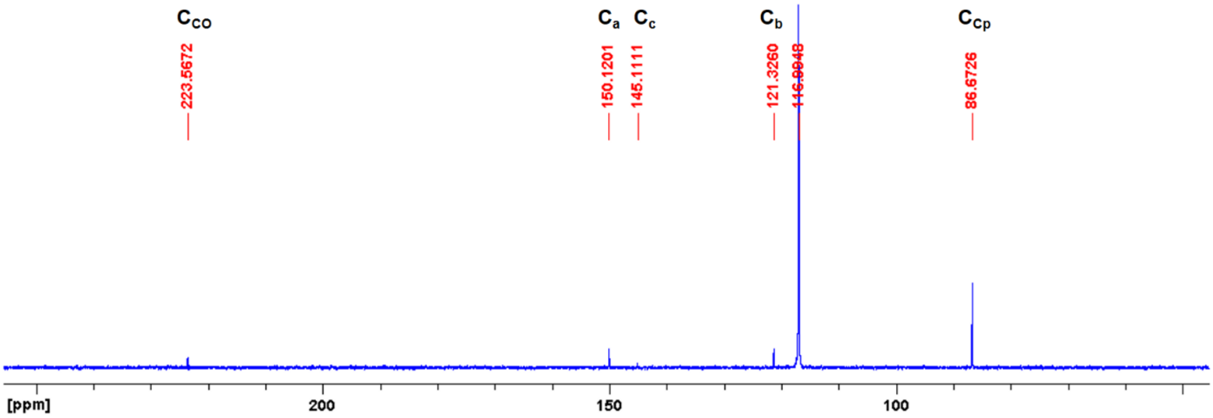


Figure S16: ^{13}C NMR spectrum of complex **9** in CD$_3$CN at 75.47 MHz.

4. DFT calculations:

The DFT calculations have been performed with the TURBOMOLE program package[5] at the RI[6]-B3LYP[7]/def2-TZVP[8] level of theory. The geometries were optimized in the gas phase using the Multipole Accelerated Resolution of Identity (MARI-J)[9] approximation during the geometry optimization steps. The solvent effects were incorporated as single point calculations (without the RI approximation) on the gas phase optimized geometries via the Conductor-like Screening Model (COSMO)[10] using the dielectric constant of CH$_2$Cl$_2$ (ε = 8.930). For the reaction energies the SCF energies, corrected for the “outlying charge” were used.

Table S1. Cartesian coordinates of the gas-phase optimized geometry of [{Cp(CO)$_2$Mo)$_2$(μ-P$_2$)}$_4$Ag$_2$Py$_4$]$^{2+}$ at the RI-B3LYP/def2-TZVP level of theory.

Atom	x	y	z
Ag	0.2049833	2.3842906	0.6805051
Ag	-0.2035061	-2.3839696	-0.6803505
Mo	4.1153319	-0.6129795	0.7765890
Mo	2.2278266	-1.0945203	3.2042651
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Mo	-2.2285383	1.0950542	-3.2028846
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P	1.6820300	-1.4757001	0.8197005
P	-1.9722275	-0.5522510	-1.2342316
P	-1.6824332	1.4757150	-0.8182409
C	3.6956320	-0.5881976	-1.1679892
C	4.2557352	-2.6038042	0.6343365
C	2.8392174	0.6777330	3.9015324
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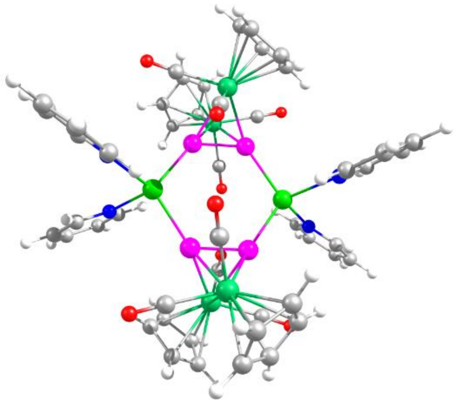

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H	6.8252000	-1.6156577	1.8573502
C	5.7255565	0.2553554	2.3622722
H	5.6302343	0.1970778	3.4326658
C	5.2963028	1.3353930	1.5442841
H	4.8058276	2.2303833	1.8887460
C	5.6759723	1.0526167	0.2093072
H	5.5346601	1.7006732	-0.6402038
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H	0.4606747	-3.3074614	4.3588704
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H	1.6068385	-1.6304675	6.1334463
C	3.4821029	-2.0278768	4.9850147
H	4.2200336	-1.4631321	5.5319792
N	-0.2356046	3.5771619	2.7068157
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H	-2.0690735	2.6821131	3.0308824
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H	-2.5314000	3.8869023	5.1415850
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C	0.5006617	5.1586283	4.3504866
H	1.2674687	5.8455785	4.6820482
C	0.6731408	4.4445369	3.1745385
H	1.5709252	4.5691226	2.5817445
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C	-1.4964210	3.0037784	-4.3638004
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O	0.7264299	0.1806978	-3.7127774
H	-6.7956788	0.6814564	0.6625927
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H	-4.6970946	3.0584314	-3.4279797
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H    -2.4766644   -7.2357629    2.6696368
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  ENERGIES [a.u.]:
    Total energy            =    -4605.7117129033
    Total energy + OC corr. =    -4605.7060179199
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Table S2. Cartesian coordinates of the gas-phase optimized geometry of $[\{Cp(CO)_2Mo)_2(\mu\text{-}P_2)\}_4Ag_2Py_4]^{2+}$ with fixed Ag-Ag distance (2.8299 Å) at the RI-B3LYP/def2-TZVP level of theory.

Atom	x	y	z
Ag	-0.1555038	1.3919983	0.1612845
Ag	0.1752115	-1.4005180	-0.1558253
Mo	4.3806615	0.5989596	-1.2883311
Mo	4.1101985	-0.0306676	1.7610556
Mo	-4.3598044	-0.6079553	1.2947085
Mo	-4.0901861	0.0207583	-1.7549901
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P	-2.9131203	1.1714675	0.1058499
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H	6.8204732	0.8546265	2.9414191
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C	0.7067820	4.3021744	1.6155263
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C	-4.5382723	-2.5912403	2.5469217
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C	-5.4299292	2.0110132	-1.9349322
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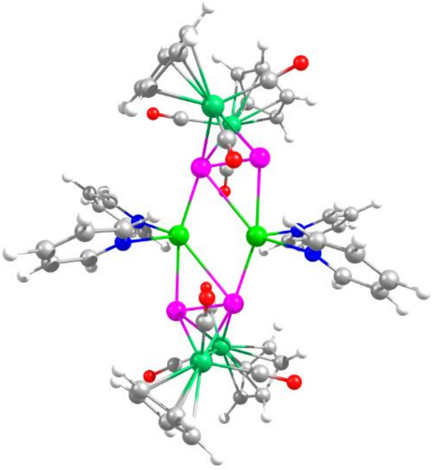

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C     1.1061273   -4.1784194    1.5409740
C     0.6645816   -4.9616612    3.7549154
H    -0.6726144   -1.9301376    3.0918623
C    -0.0413022   -3.7859401    3.9765725
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H     1.5541765   -4.2996902    0.5619730
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  ENERGIES [a.u.]:
    Total energy             =    -4605.6918913492
    Total energy + OC corr. =    -4605.6862933361
```

5. X-ray Crystallography:

5.1. Crystallographic details:

Crystals of **6 – 9** were taken from a Schlenk flask under a stream of argon and immediately covered with mineral oil or perfluorinated Fomblin® mineral oil to prevent both decomposition and a loss of solvent. The quickly chosen single crystals covered by a drop of the oil were taken to the pre-centered goniometer head with CryoMount® and directly attached to the diffractometer into a stream of cold nitrogen.

The crystal of **6** was preselected using aforesaid procedure and after checking its scattering power and quality was placed in the Dewar vessel filled with liquid nitrogen. X-ray diffraction experiment for **6** was measured using one-circle diffractometer and DECTRIS PILATUS 6M pixel array detector at the DESY PETRA III synchrotron (beamline P11) with narrow (0.3°) φ scans.[11] The measurement was performed at 10(2) K using open-flow helium cryo system Cryocool-LHe (CRYO Industries of America, Inc.). Data reduction was performed XDS software.[12]

The diffraction experiments for **7 – 9** were collected a SuperNova diffractometers (Rigaku Oxford Diffraction) equipped with micro-focus SuperNova source (CuKα radiation, λ = 1.54178 Å) and Atlas (**7**) or Titan^{S2} (**8**, **9**) CCD detectors, respectively, using ω scans of 1° frames. The measurements for **7 – 9** were performed at 123 K. Absorption corrections were applied analytically using *CrysAlis PRO* Software. [13]

The crystal structures were solved by direct methods with *SHELXT*[14] or *Olex*[15] programs and refined by full-matrix least-squares method against $|F|^2$ in anisotropic approximation using multiprocessor versions SHELX2013 or SHELX2015.[14] Hydrogen atoms were refined in calculated positions using riding on pivot atom model. In case of the disorder, the site occupation factors of disordered components were refined with their U_{iso} fixed at average U_{eq} for ordered atoms in given structure in order to avoid correlations. After refinement, occupancies were fixed at resulting values and the refinement of atomic displacement parameters was performed. The light atoms with site occupation factors less than 0.5 were refined isotropically.

The crystals of **6** and **9** proved to be inversion twins. The compound **6** crystallizes in *Pnma* space group with unit cell parameters a = 20.9607(5), b = 31.2214(11), c = 21.8852(7) Å. The first experiment at 123 K showed that two crystallographically unique [TEF] anions are severely disordered not only over mirror plane m_y but also have at least two orientations each. As a result, no acceptable model of the disorder was found. The experiment performed at the least accessible temperature in our laboratory with nitrogen as a cryogas (90 K) showed slight improvement and suggested that dynamic disorder in this structure can be suppressed by lowering the temperature. Therefore, we performed experiment at helium temperatures (10 K). At this temperature, we have found the same unit cell, but lower symmetry in the same symmetry class. The transition to *t*-subgroup $P2_12_12_1$ was accompanied by racemic twinning. The twin batches in **6** were refined to an expected 0.50(3)/0.50(3) ratio still suggesting parent pseudo centrosymmetric space group. However, the systematic absences violations for the *Pnma* and $Pna2_1$ space groups are quite significant: average $I_{hkl} = 5.3\sigma(I)$ for $hk0$, $h+k=2n+1$ (*n* glide plane $\perp x$) and $3.8\sigma(I)$ for $hk0$, $h=2n+1$ (*a* glide plane $\perp z$).

The resulting quality factors were $R_1 = 0.049$ and wR_2 (all data) = 0.136 for $d_{min} = 0.64$ Å resolution, and the residual density did not exceed 1.44 $e \cdot Å^{-3}$ compared to respective values in centrosymmetric model at 123 K $R_1 = 0.075$ and wR_2 (all data) = 0.134, and 1.2 $e \cdot Å^{-3}$ for much lower resolution (0.84 Å). As a result, non-centrosymmatric model allowed refinement of [TEF] anions with simpler disorder model and the transition can be traced to their partial ordering.

The crystal of **9** proved an inversion twin in the space group $Pna2_1$. The twin batches were refined to 0.650(7)/0.350(7). The resulting quality factors were $R_1 = 0.043$ and wR_2 (all data) = 0.117 compared to respective values without twinning model $R_1 = 0.056$ and wR_2 (all data) = 0.1568.

The $Cp_2Mo_2P_2(CO)_4$ dimers demonstrate different type of disorder. It can be rotational caused by re-orientations of Cp groups about the direction of π-bond (**6**), or positional, related to different mutual orientation of the CO, Cp ligands coordinated to Mo atoms (**6**). The tendency for the disorder is related to the linker length; the longer the linker, the more disorder of the $\{Mo_2P_2\}$ dimer occurs.

A long spacer is disordered in structure of **7** over three close positions; two of them represent bent conformation of the spacer and are related by inversion center. The other one corresponds to a linear conformation. The site occupation factors were refined as 0.4 × 2 and 0.2 for the bent and the linear case. An entire $\{Mo_2P_2\}$ dimer is also disordered following the disorder of the spacer.

In all structures except for **8**, the weakly coordinating anion [TEF] is disordered. The disorder patterns varied according to different orientations or conformations of the [TEF] anion caused by rotation around O-*tert*C (**6**, **7**, **9**) or C-C(F_3) bonds of OC_4F_9 groups (**6**, **7**, **9**). In all structures the solvent CH_2Cl_2 molecules are also either disordered or partly occupied. The disorder is illustrated in the Figures S17, S18 and S21. The crystal packings for **6** - **9** are depicted in the Figures S17, S19, S20 and S22.

The supplementary crystallographic data for this publication (Tables S3-S4: CCDC-1864891 (**6**), CCDC-1864892 (**7**), CCDC-1864893 (**8**), CCDC-1864894 (**9**)) can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: + 44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

All ORTEP drawings for **6 – 9** were made in Olex2.[15]

The investigation of connectivity and topologies of the underlying nets for **8** and **9** were performed with *TOPOSPro* program suit.[16]

The estimation of hypothetically available volume in the 3D framework of **9** was performed with PLATON. [17] The counter anions [TEF] and solvent molecules were removed from the list of atomic coordinates and resulting volume for a hypothetical void in the framework was calculated to give 7386 $Å^3$ per formula unit. The cavity is nearly spherical and reaches ~9.9 Å in diameter. Theoretically the framework could be interesting due to its porosity, if the use of the bulky anions can be avoided.

Table S3. Crystal data, data collection and refinement of **6** and **7**.

	6	**7**
CCDC Code	CCDC-1864891	CCDC-1864892
Chemical formula	$C_{68}H_{50}Ag_2Mo_8N_2O_{16}P_8 \cdot 2(AlO_4C_{16}F_{36}) \cdot 1.45(CH_2Cl_2)$	$C_{115.50}H_{59}Ag_2Al_2Cl_3F_{72}Mo_8N_2O_{24}P_8$
M_r	4439.54	4617.97
Crystal system, space group	Orthorhombic, $P2_12_12_1$	Triclinic, $P\bar{1}$
Temperature (K)	10(2)	123.0(2)
a, *b*, *c* (Å)	20.930(6), 21.739(2), 30.936(2)	15.4197(5), 15.8109(5), 17.5800(6)
α, β, γ (°)	90, 90, 90	107.136(3), 92.394(3), 90.977(2)
V (Å^3)	14076 (4)	4090.2 (2)
Z	4	1
F(000)	8564	2233
Radiation type	Synchrotron, λ = 0.6702Å	Cu Kα
μ (mm^{-1})	1.05	9.32
Crystal shape and colour	Elongated orange thin plate	Orange needle
Crystal size (mm)	0.15 × 0.05 × 0.03	0.28 × 0.12 × 0.08
Data collection		
Diffractometer	1-cycle diffractometer, P11 beamline, DESY	SuperNova, Single source at offset, Atlas
Absorption correction	-	Gaussian
T_{min}, T_{max}	-	0.232, 0.594
No. of measured, independent and observed [I > 2σ(I)] reflections	103797, 40700, 37247	30686, 16168, 12199
R_{int}	0.061	0.030
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.778	0.624
Range of *h*, *k*, *l*	*h* = -28→28, *k* = -29→29, *l* = -33→39	*h* = -19→18, *k* = -19→17, *l* = -21→20
Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.049, 0.136, 1.06	0.076, 0.242, 1.08
No. of reflections	40700	16168
No. of parameters	2685	1146
No. of restraints	141	24
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained
$\Delta\rangle_{max}$, $\Delta\rangle_{min}$ (e Å^{-3})	1.44, -1.68	2.08, -1.54
Absolute structure	Refined as an inversion twin	-
Absolute structure parameter	0.50 (3)	-

Computer programs: Petra III, P11 beamline software, *XDS*, build 20170720 (W. Kabsch), *SHELXS* (Sheldrick), *SHELXL2016*/6 (Sheldrick, 2016).

Table S4. Crystal data, data collection and refinement of **8** and **9**.

	8	**9**
CCDC Code	CCDC-1864893	CCDC-1864894
Chemical formula	$C_{48}H_{36}Ag_2Mo_4N_4O_8P_4\cdot(C_{16}AlF_{36}O_4)_2\cdot(CH_2Cl_2)_{2.4}$	$C_{82}H_{40}Ag_2Al_2Cl_4F_{72}Mo_4N_4O_{16}P_4$
M_r	3658.29	3624.32
Crystal system, space group	Monoclinic, $P2_1/c$	Orthorhombic, $Pna2_1$
Temperature (K)	123.0(2)	123.0(2)
a, *b*, *c* (Å)	18.1526(9), 18.9664(7), 18.8938(8)	28.6833(2), 25.7478(2), 15.8316(1)
α, β, γ (°)	110.424(6)	90, 90, 90
V (Å^3)	6096.0 (5)	11692.14 (14)
Z	2	4
F(000)	3537.6	7008
Radiation type	Cu *K*α	Cu *K*α
μ (mm^{-1})	8.97	9.17
Crystal shape and colour	Orange plate	Red prism
Crystal size (mm)	0.18 × 0.10 × 0.07	0.30 × 0.25 × 0.12
Data collection		
Diffractometer	SuperNova, Titan^{S2} diffractometer	SuperNova, Titan^{S2} diffractometer
Absorption correction	Gaussian	Gaussian
T_{min}, T_{max}	0.437, 0.603	0.149, 0.442
No. of measured, independent and observed [> 2σ(I)] reflections	20614, 11772, 7605	226513, 23516, 23077
R_{int}	0.061	0.107
(sin θ/λ)$_{max}$ (Å^{-1})	0.626	0.623
Range of *h*, *k*, *l*	*h* = -22→20, *k* = -23→19, *l* = -23→17	*h* = -35→35, *k* = -31→31, *l* = -19→19
Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.056, 0.154, 0.96	0.043, 0.117, 1.06
No. of reflections	11772	23516
No. of parameters	895	1880
No. of restraints	0	1
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained
$\Delta\rangle_{max}$, $\Delta\rangle_{min}$ (e Å^{-3})	1.11, -1.37	1.15, -1.18
Absolute structure	-	Refined as an inversion twin
Absolute structure parameter	-	0.650 (7)

Computer programs: *CrysAlis PRO*, Agilent Technologies, Version 1.171.37.34 (release 22-05-2014 CrysAlis171 .NET) (compiled May 22 2014,16:03:01), *SHELXL97* (Sheldrick, 1997), *SHELXL2013* (Sheldrick, 2013).

5.2. Crystallographic details for 6:

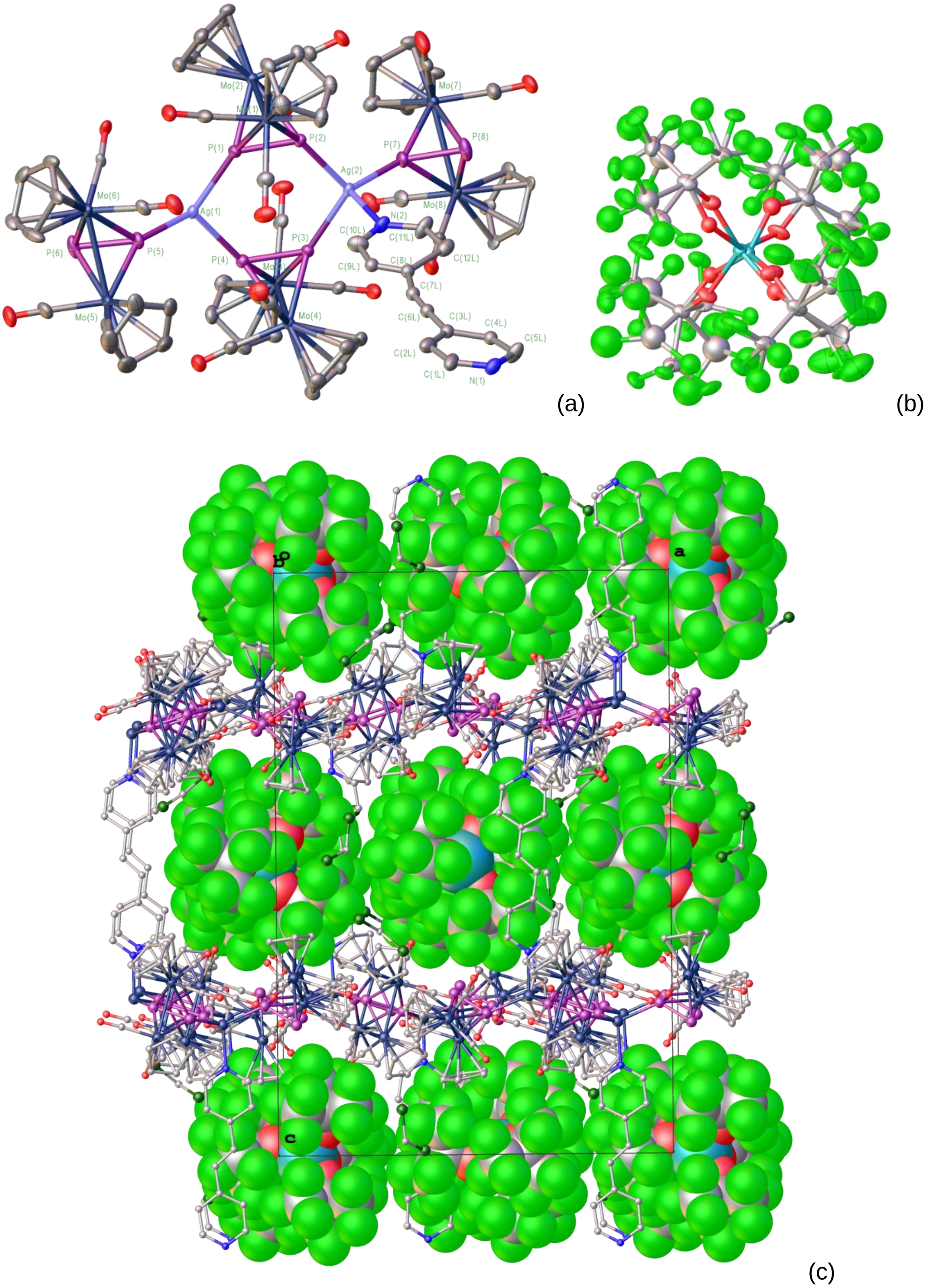

Figure S17. (a) Repeating cationic unit in **6** with enumeration scheme (*cf*. Table S5); (b) $[Al(OC_4F_9)_4]^-$ (TEF) counter anion disordered over 2 close positions (ellipsoids at 50% probability level); (c) the packing in **7** ([TEF] are shown in space filling mode).

Table S5. Selected geometric parameters (Å, º) for **6**

Ag1—N1^{i}	2.324 (6)	N1—C5L	1.334 (10)
Ag1—P5	2.4618 (19)	N1—C1L	1.346 (9)
Ag1—P4	2.5174 (17)	N2—C10L	1.324 (10)
Ag1—P1	2.5277 (17)	N2—C11L	1.354 (10)
Ag2—N2	2.335 (6)	C1L—C2L	1.372 (12)
Ag2—P7	2.4676 (19)	C2L—C3L	1.369 (13)
Ag2—P2	2.5035 (17)	C3L—C4L	1.406 (12)
Ag2—P3	2.5316 (17)	C3L—C6L	1.458 (11)
Mo1—P2	2.4504 (17)	C4L—C5L	1.410 (11)
Mo1—P1	2.5266 (19)	C6L—C7L	1.337 (10)
Mo1—Mo2	3.0372 (8)	C7L—C8L	1.493 (11)
Mo2—P1	2.4440 (17)	C8L—C12L	1.394 (12)
Mo2—P2	2.5366 (18)	C8L—C9L	1.398 (13)
Mo3—P4	2.4538 (18)	C9L—C10L	1.434 (12)
Mo3—P3	2.5257 (19)	C11L—C12L	1.374 (11)
Mo3—Mo4	3.0324 (9)	C4—C43A	1.48 (7)
Mo8—P8	2.471 (3)	C4—C41	1.545 (12)
P1—P2	2.086 (2)	C4—C43	1.562 (15)
P3—P4	2.088 (2)	C4—C41A	1.56 (2)
P5—P6	2.091 (3)	C4—C42	1.587 (12)
P7—P8	2.087 (3)	C5—C54	1.36 (4)
Mo4—P3	2.4504 (17)	C5—C53	1.494 (14)
Mo4—P4	2.5380 (18)	C5—C56	1.56 (3)
Mo5—P5	2.4206 (19)	C5—C51	1.582 (13)
Mo5—P6	2.561 (3)	C5—C52	1.584 (12)
Mo5—Mo6	3.0073 (9)	C5—C55	1.60 (2)
Mo7—P7	2.4277 (19)		
N1— Ag1—P5^{i}	112.01(16)	N2—Ag2—P7	110.40(16)
N1—Ag1— P4^{i}	100.54(15)	N2—Ag2—P2	102.15(15)
P5—Ag1—P4	120.07(6)	P7—Ag2—P2	118.57(6)
N1—Ag1—P1^{i}	97.31(16)	N2—Ag2—P3	98.81(17)
P5—Ag1—P1	114.75(6)	P7—Ag2—P3	114.83(6)
P4—Ag1—P1	108.89(6)	P2—Ag2—P3	109.49(6)

Symmetry code(s): (i) -*x*+1/2, -*y*+1, *z*+1/2.

5.3. Crystallographic details for 7:

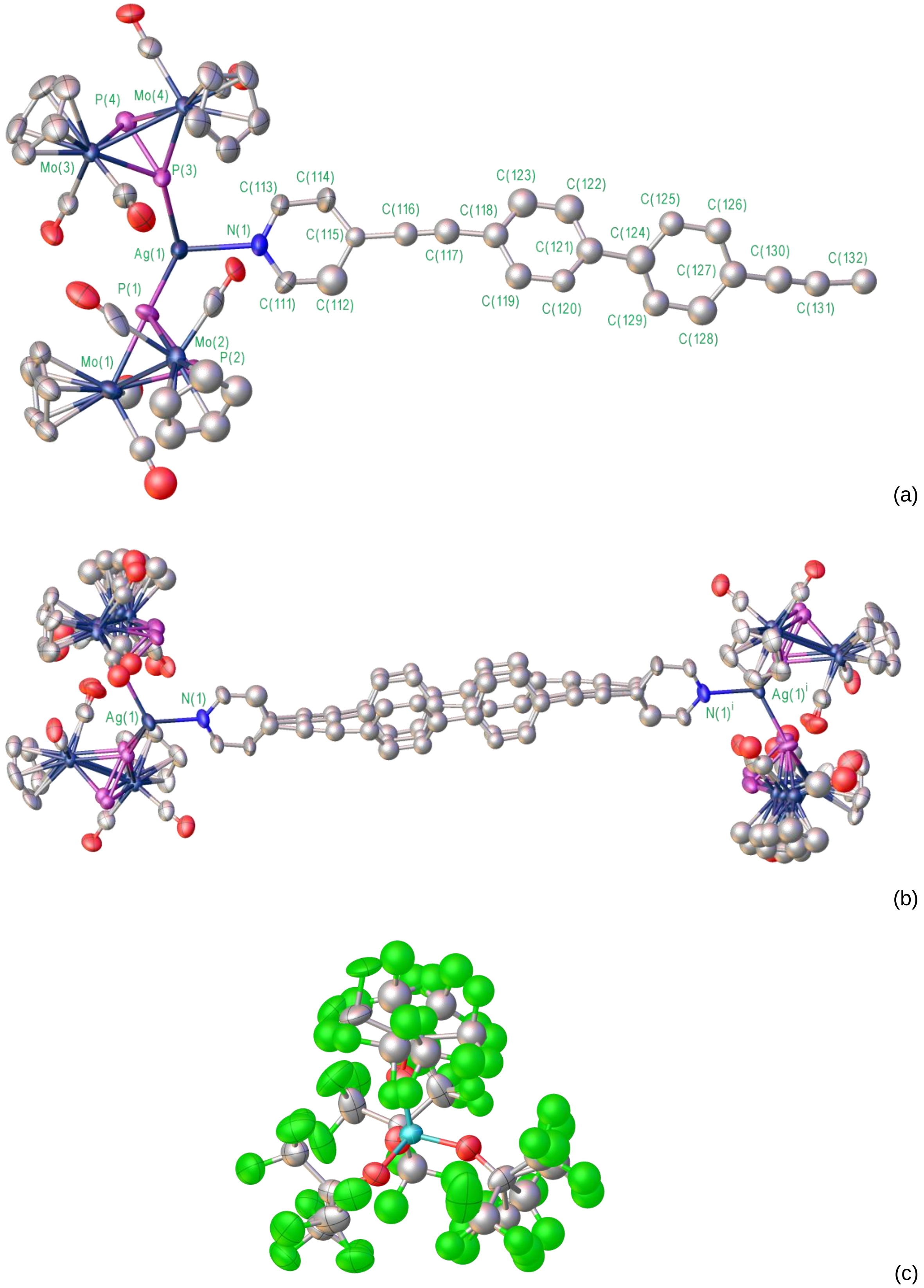

Figure S18. Disordered repeating unit of **7**: (a) enumeration scheme for the major part of the disordered cationic portion (*cf*. Table S6); (b) the model of the disorder; (c) disordered [TEF] counter anion (ellipsoids at 50% probability level).

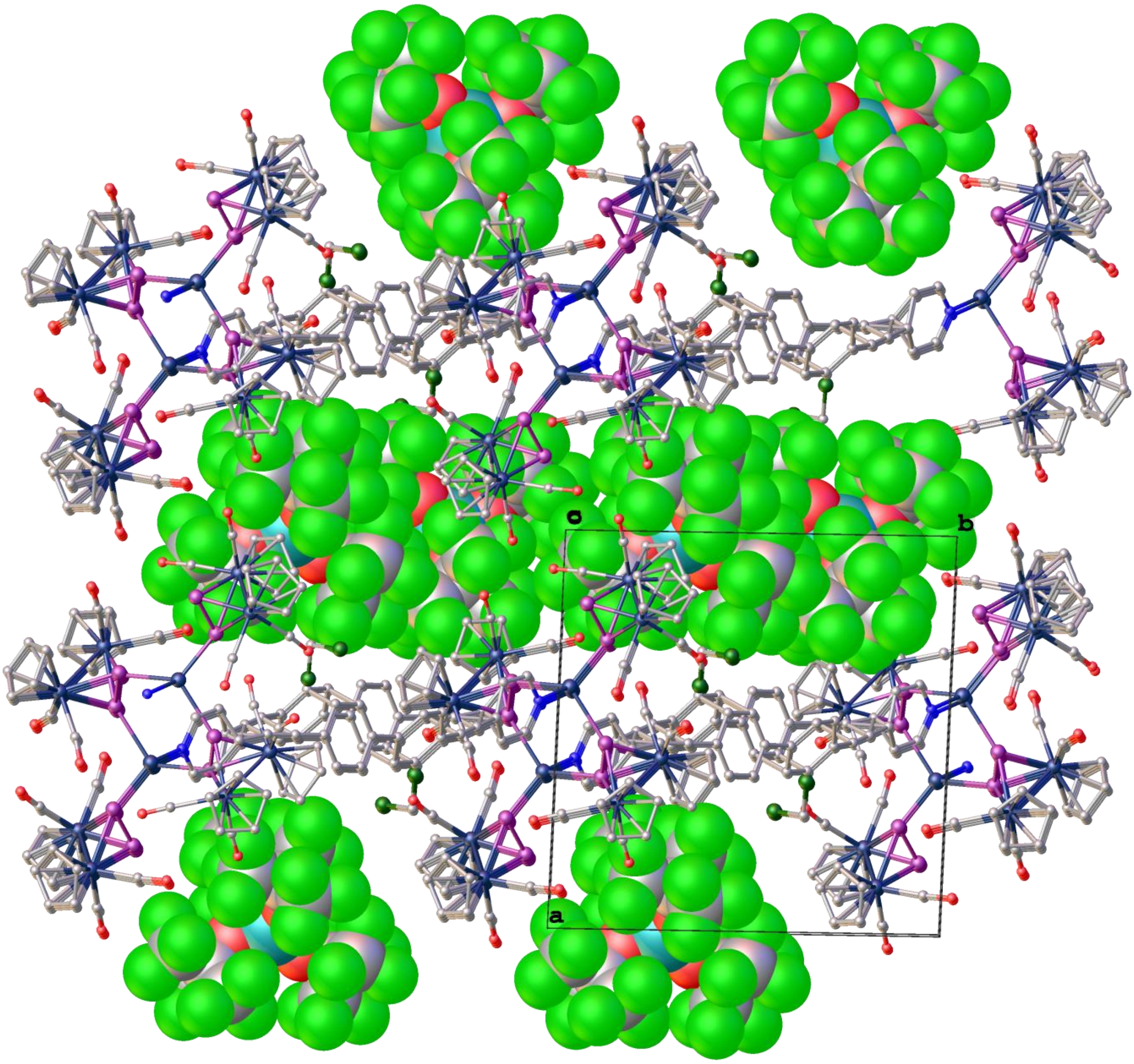

Figure S19. The packing in **7** ([TEF] are shown in space filling mode).

Table S6. Selected geometric parameters (Å, º) for **7**

Ag1—P1	2.313 (9)	P1A—Mo2A	2.444 (10)
Ag1—N1	2.337 (6)	P1A—Mo2C	2.561 (11)
Ag1—P4A^{i}	2.345 (11)	Mo2A—P2A	2.23 (2)
Ag1—P3A	2.443 (15)	Mo3—P4	2.440 (10)
Ag1—P3	2.592 (15)	Mo3—P3	2.536 (15)
Ag1—P1A	2.624 (10)	Mo3—Mo4	3.063 (8)
Ag1—P4^{i}	2.702 (11)	Mo4—P3	2.423 (17)
Mo1—C11	1.94 (3)	Mo4—P4	2.533 (17)
Mo1—C12	1.96 (2)	P3—P4	2.08 (2)
Mo1—C15	2.293 (11)	P4—Ag1^{i}	2.702 (11)
Mo1—C16	2.302 (10)	P2A—Mo2C	2.65 (2)
Mo1—C14	2.358 (11)	Mo3A—C31	1.955 (10)
Mo1—C17	2.384 (11)	Mo3A—C32	2.107 (12)
Mo1—C13	2.439 (12)	Mo3A—C33	2.348 (10)
Mo1—P2	2.491 (19)	Mo3A—C37	2.350 (10)
Mo1—P1	2.497 (12)	Mo3A—P4A	2.453 (10)
Mo1—Mo2	2.790 (7)	Mo3A—P3A	2.508 (15)
P1—P2	2.11 (2)	Mo3A—Mo4A	3.041 (8)
P1—Mo2	2.583 (9)	Mo4A—P3A	2.461 (17)
Mo2—P2	2.29 (2)	Mo4A—P4A	2.509 (16)
Mo1A—P1A	2.417 (14)	P3A—P4A	2.08 (2)
Mo1A—P2A	2.804 (19)	P4A—Ag1^{i}	2.345 (11)
P1A—P2A	2.20 (2)	Mo2B—P2B	2.18 (3)

Symmetry code(s): (i) $-x+1$, $-y+2$, $-z$.

5.4. Crystallographic details for 8:

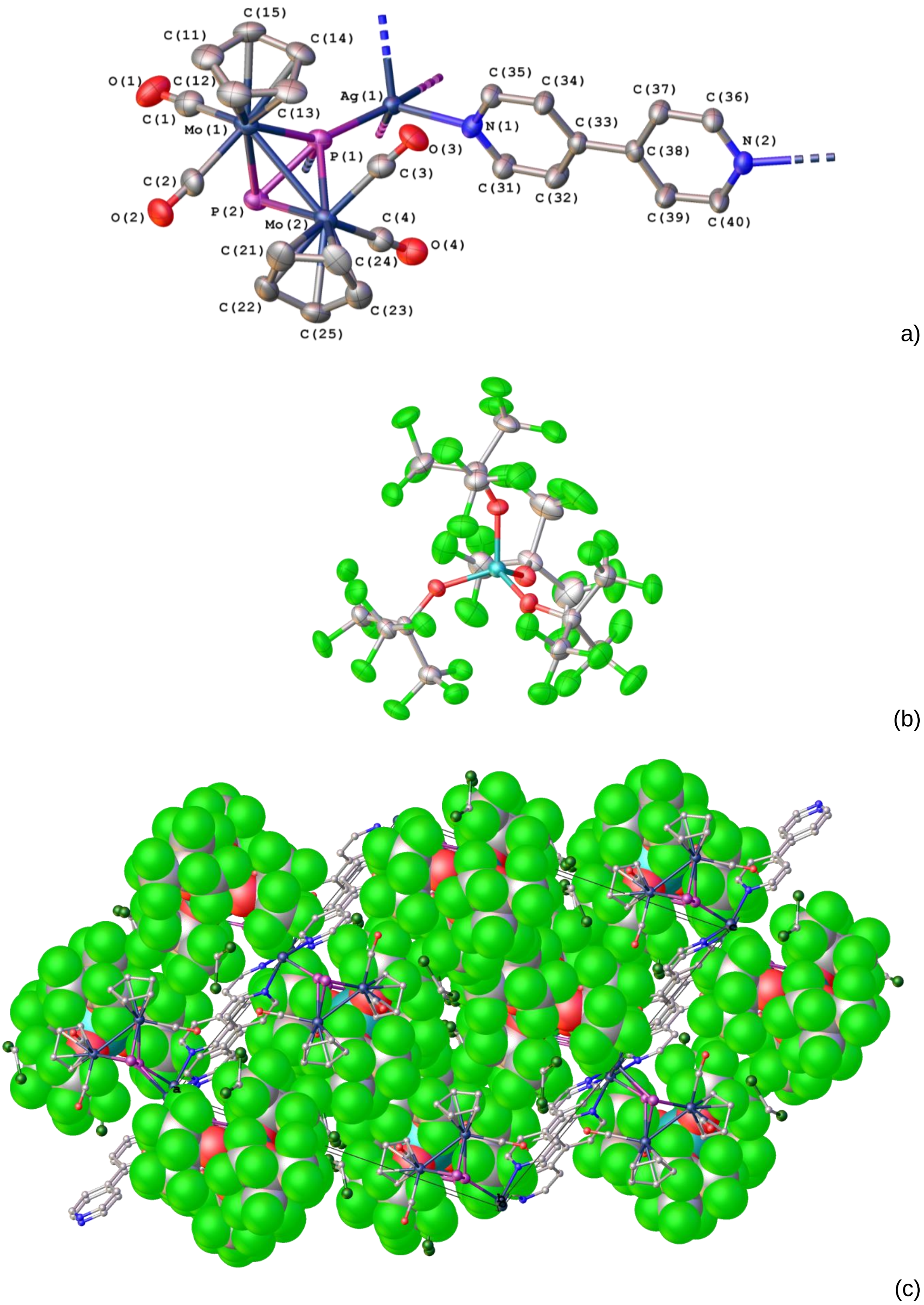

Figure S20. (a) Molecular structure of cationic repeating unit in **8** and enumeration scheme (*cf*. Table S7); (b) [TEF] counter anions (ellipsoids at 50% probability level); (c) the packing in **8** ([TEF] are shown in space filling mode).

Table S7. Selected geometric parameters (Å, º) for **8**

Ag1—N1	2.301 (6)	Mo2—C22	2.337 (8)
Ag1—N2^{i}	2.344 (6)	Mo2—C21	2.342 (9)
Ag1—P1	2.592 (2)	Mo2—P2	2.462 (2)
Ag1—P1^{ii}	2.715 (2)	Mo2—P1	2.524 (2)
Ag1—Ag1^{ii}	2.8298 (9)	P1—P2	2.123 (3)
Ag1—P2^{ii}	2.837 (2)	P1—Ag1^{ii}	2.715 (2)
Mo1—C1	1.989 (10)	P2—Ag1^{ii}	2.837 (2)
Mo1—C2	2.006 (9)	N1—C35	1.323 (9)
Mo1—C11	2.293 (8)	N1—C31	1.341 (10)
Mo1—C15	2.305 (8)	N2—C36	1.335 (9)
Mo1—C12	2.323 (9)	N2—C40	1.341 (10)
Mo1—C14	2.358 (8)	N2—Ag1^{iii}	2.344 (6)
Mo1—C13	2.362 (9)	C31—C32	1.388 (11)
Mo1—P1	2.459 (2)	C32—C33	1.389 (11)
Mo1—P2	2.550 (2)	C33—C34	1.382 (10)
Mo1—Mo2	3.0349 (9)	C33—C38	1.491 (10)
Mo2—C4	1.982 (8)	C34—C35	1.394 (10)
Mo2—C3	1.997 (9)	C36—C37	1.379 (10)
Mo2—C24	2.287 (9)	C37—C38	1.407 (10)
Mo2—C25	2.293 (8)	C38—C39	1.384 (11)
Mo2—C23	2.293 (8)	C39—C40	1.381 (11)
N1—Ag1—N2^{i}	102.6 (2)	P2—Mo2—Mo1	54.08 (5)
N1—Ag1—P1	101.71 (17)	P1—Mo2—Mo1	51.51 (5)
N2^{i}—Ag1—P1	96.06 (17)	P2—P1—Mo1	67.18 (8)
N1—Ag1—P1^{ii}	120.48 (16)	P2—P1—Mo2	63.29 (8)
N2^{i}—Ag1—P1^{ii}	116.59 (17)	Mo1—P1—Mo2	75.04 (6)
P1—Ag1—P1^{ii}	115.61 (5)	P2—P1—Ag1	133.97 (11)
N1—Ag1—Ag1^{ii}	132.26 (16)	Mo1—P1—Ag1	152.12 (8)
N2^{i}—Ag1—Ag1^{ii}	121.74 (15)	Mo2—P1—Ag1	127.83 (8)
P1—Ag1—Ag1^{ii}	59.91 (5)	P2—P1—Ag1^{ii}	70.59 (8)
P1^{ii}—Ag1—Ag1^{ii}	55.70 (4)	Mo1—P1—Ag1^{ii}	125.99 (8)
N1—Ag1—P2^{ii}	96.97 (17)	Mo2—P1—Ag1^{ii}	113.32 (7)
N2^{i}—Ag1—P2^{ii}	89.19 (17)	Ag1—P1—Ag1^{ii}	64.39 (5)
P1—Ag1—P2^{ii}	158.95 (6)	P1—P2—Mo2	66.32 (8)
P1^{ii}—Ag1—P2^{ii}	44.90 (6)	P1—P2—Mo1	62.70 (7)
Ag1^{ii}—Ag1—P2^{ii}	100.10 (5)	Mo2—P2—Mo1	74.51 (6)
P1—Mo1—Mo2	53.45 (5)	P1—P2—Ag1^{ii}	64.52 (8)
P2—Mo1—Mo2	51.41 (5)	Mo2—P2—Ag1^{ii}	111.24 (8)
P1—Mo1—P2	50.11 (6)	Mo1—P2—Ag1^{ii}	117.64 (7)

Symmetry code(s): (i) x, $-y+1/2$, $z+1/2$; (ii) $-x+2$, $-y+1$, $-z+1$; (iii) x, $-y+1/2$, $z-1/2$.

5.5. Crystallographic details for 9:

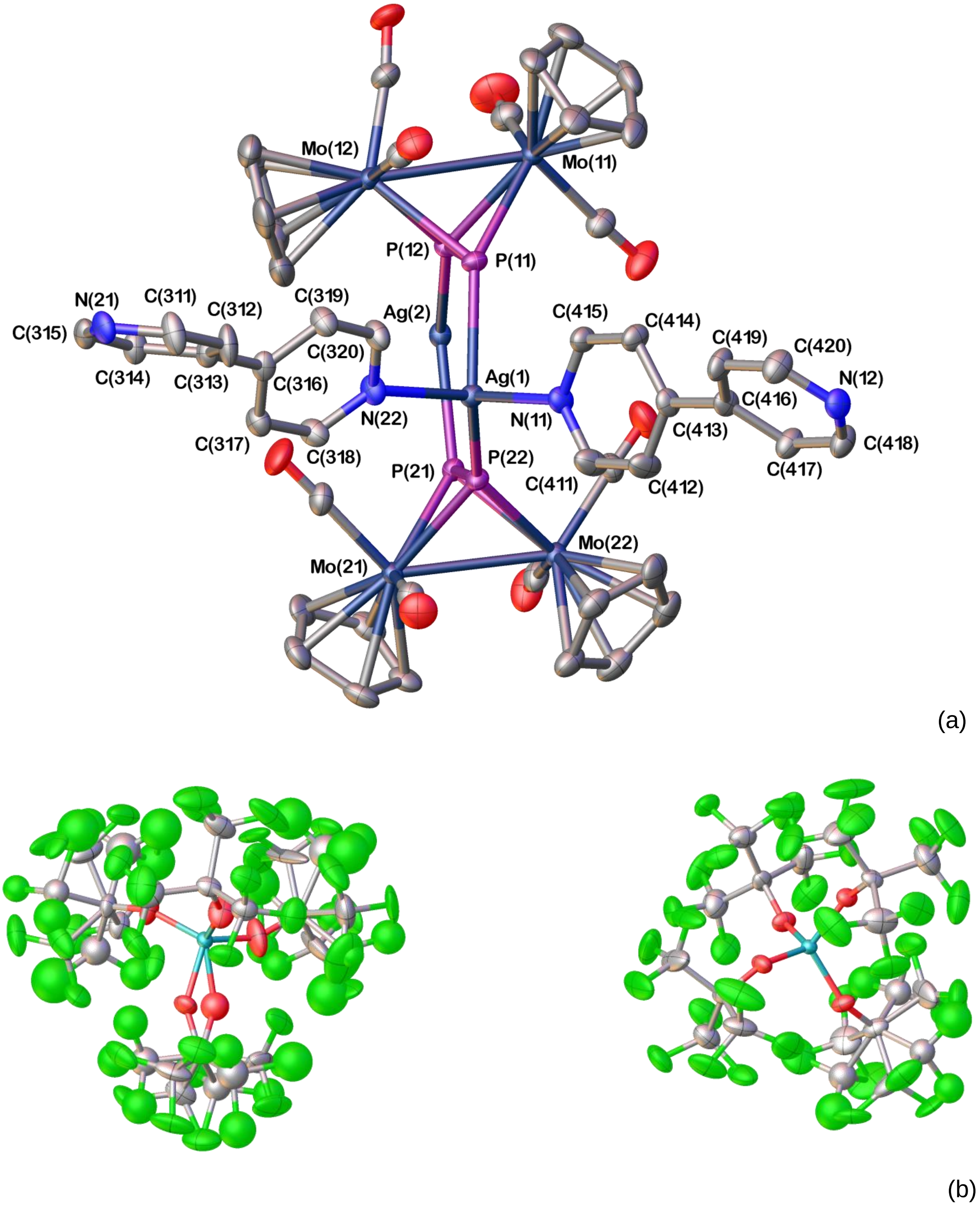

Figure S21. (a) The repeating unit and enumeration scheme for **9** (*cf*. Table S8); (b) crystallographically unique [TEF] counter anions (ellipsoids at 50% probability level).

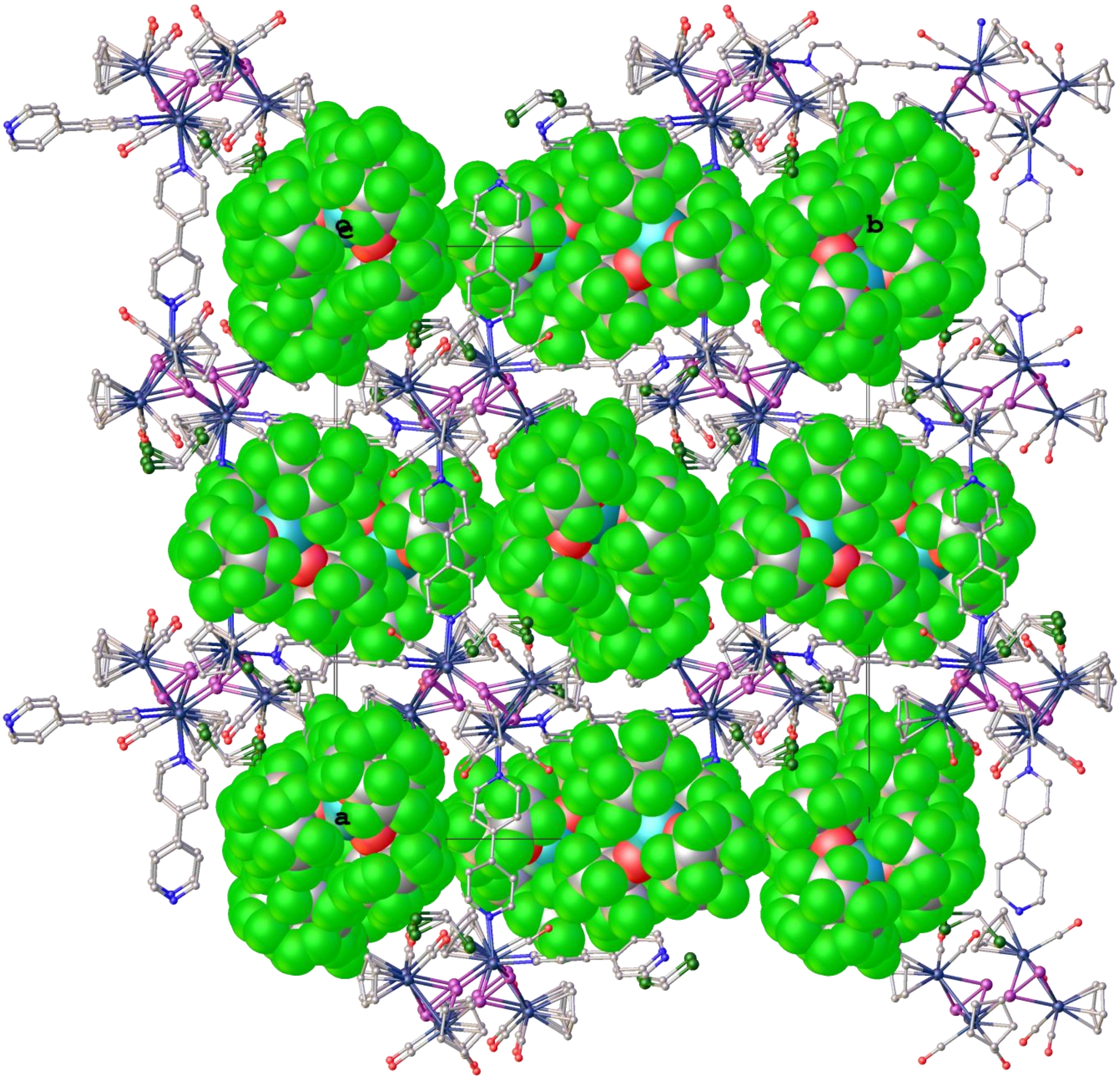

Figure S22. The packing in **9** ([TEF] are shown in space filling mode).

Table S8. Selected geometric parameters (Å, º) for **9**

Ag1—N22	2.324 (6)	Mo21—C25	2.292 (8)
Ag1—N11	2.332 (6)	Mo21—C21	2.302 (7)
Ag1—P22	2.3864 (17)	Mo21—C24	2.331 (8)
Ag1—P11	2.5417 (19)	Mo21—C22	2.352 (7)
Ag2—N21^{i}	2.310 (5)	Mo21—C23	2.369 (8)
Ag2—N12^{ii}	2.343 (6)	Mo21—P21	2.4694 (18)
Ag2—P12	2.4224 (17)	Mo21—P22	2.5175 (17)
Ag2—P21	2.5488 (19)	Mo21—Mo22	3.0478 (7)
Mo11—C1	1.999 (8)	Mo22—C7	1.994 (8)
Mo11—C2	2.013 (9)	Mo22—C8	2.014 (8)
Mo11—C14	2.282 (9)	Mo22—C26	2.293 (9)
Mo11—C13	2.303 (9)	Mo22—C30	2.308 (9)
Mo11—C15	2.312 (9)	Mo22—C27	2.310 (8)
Mo11—C12	2.351 (8)	Mo22—C28	2.341 (8)
Mo11—C11	2.370 (8)	Mo22—C29	2.354 (9)
Mo11—P12	2.4837 (18)	Mo22—P22	2.4117 (17)
Mo11—P11	2.4845 (18)	Mo22—P21	2.5418 (18)
Mo11—Mo12	3.0921 (7)	P11—P12	2.088 (2)
Mo12—C3	1.999 (9)	P21—P22	2.087 (2)
Mo12—C4	2.002 (7)	N11—C415	1.334 (10)
Mo12—C19	2.291 (8)	N11—C411	1.339 (12)
Mo12—C18	2.308 (8)	N12—C420	1.320 (11)
Mo12—C20	2.331 (8)	N12—C418	1.331 (11)
Mo12—C17	2.340 (9)	N12—Ag2^{iii}	2.343 (6)
Mo12—C16	2.352 (8)	N21—C311	1.320 (11)
Mo12—P12	2.4438 (18)	N21—C315	1.334 (10)
Mo12—P11	2.5125 (19)	N21—Ag2^{iv}	2.310 (5)
Mo21—C5	1.980 (8)	N22—C320	1.332 (10)
Mo21—C6	1.987 (9)	N22—C318	1.346 (10)
N22—Ag1—N11	96.4 (2)	P12—Mo11—P11	49.70 (6)
N22—Ag1—P22	122.39 (17)	P12—Mo11—Mo12	50.56 (4)
N11—Ag1—P22	119.41 (17)	P11—Mo11—Mo12	52.18 (4)
N22—Ag1—P11	96.54 (18)	P12—Mo12—P11	49.80 (6)
N11—Ag1—P11	100.65 (17)	P12—Mo12—Mo11	51.71 (4)
P22—Ag1—P11	116.68 (6)	P11—Mo12—Mo11	51.37 (4)
N21^{i}—Ag2—N12^{ii}	95.2 (2)	P21—Mo21—P22	49.47 (6)
N21^{i}—Ag2—P12	115.23 (17)	P21—Mo21—Mo22	53.63 (4)
N12^{ii}—Ag2—P12	118.45 (18)	P22—Mo21—Mo22	50.26 (4)
N21^{i}—Ag2—P21	100.8 (2)	P22—Mo22—P21	49.76 (6)
N12^{ii}—Ag2—P21	102.00 (18)	P22—Mo22—Mo21	53.39 (4)
P12—Ag2—P21	120.83 (6)	P21—Mo22—Mo21	51.47 (4)

Symmetry code(s): (i) *x*+1/2, -*y*+1/2, *z*; (ii) -*x*+1/2, *y*-1/2, *z*-1/2; (iii) -*x*+1/2, *y*+1/2, *z*+1/2; (iv) *x*-1/2, -*y*+1/2, *z*.

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