Electronic Supplementary Material (ESI) for Chemical Communications.

Approaching the limit of Cu^{II}/Cu^{I} mixed valency in a $Cu^{I}Br_2$-*N*-methylquinoxalinium hybrid compound

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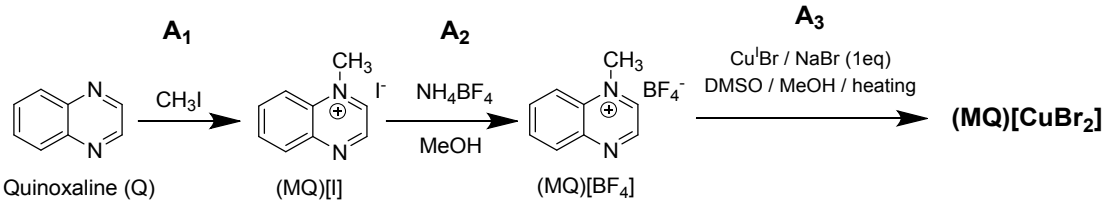
Supporting Information

A - Synthesis

$(MQ)[CuBr_2]_\infty$ salt is obtained according to the following steps :



A_1- (MQ)[I]

Quinoxaline (5 mL, 4.32 10^{-2} mol) and methyliodide (4 mL, 6.42 10^{-2} mol) are mixed with 10 mL of DCM and the solution is left standing 3 weeks after sealing. The orange-red crystals formed are filtered, washed with Et_2O and dried under vacuum to afford 9.263 g (79%) of the title compound.

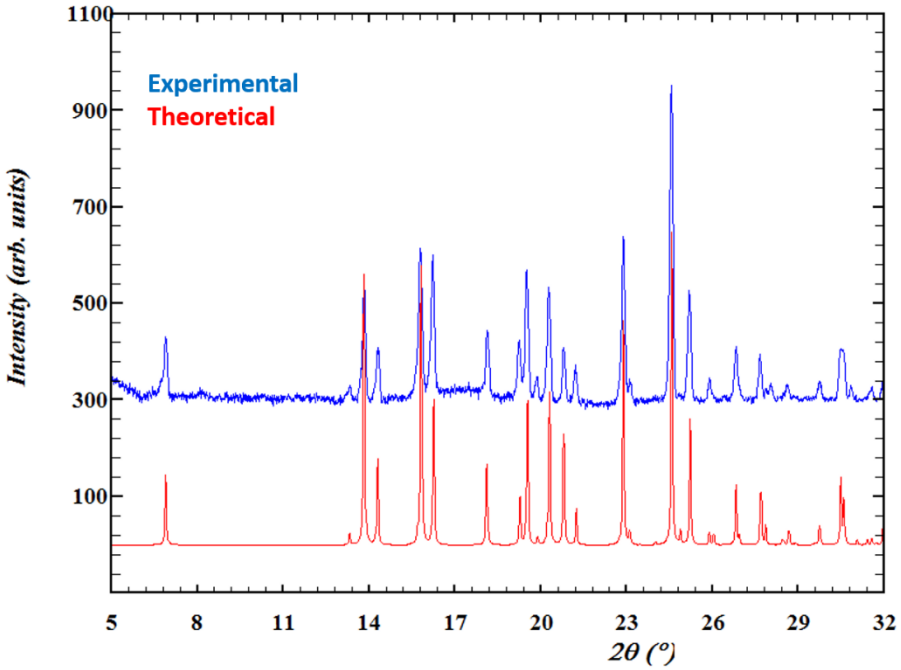
^1H NMR (500 MHz, DMSO-d^6): δ= 9.73 (d, J= 2.8 Hz, 1H), 9.67 (d, J= 2.8 Hz, 1H), 8.64 (d, J=8.5 Hz, 1H), 8.54 (dd, J=8.4, 1.3 Hz, 1H), 8.37 (ddd, J =8.7, 7.1, 1.5 Hz, 1H), 8.31 (ddd, J = 8.3, 7.1, 1.2 Hz, 1H), 4.73 (s, 3H).

A_2-(MQ)[BF_4]

(MQ)[I] (2.721 g, 10^{-2} mol) and NH_4BF_4 (5.242 g, 5 10^{-2} mol) are added into 150 mL of MeOH. The mixture is heated up to the boiling point and subsequently filtered through a paper filter. The red filtrate is then stored overnight in the freezer at -20°C. The mixture of crystals formed is collected in a filter paper and dried. To separate the residual NH_4BF_4 salt, (MQ)[BF_4] crystals are dissolved with 10 mL of ACN giving a red solution. Et_2O (100 mL) is then added resulting of a crystalline yellow precipitate. The precipitate is repeatedly recrystallized from MeOH at -20°C, giving 1.034 g (44 %) of the title compound as white flakes.

^{1}H NMR (500 MHz, DMSO-d^{6}): δ= 9.57 (d, J= 2.1 Hz, 1H), 9.10 (d, J= 2.6 Hz, 1H), 8.55 (dd, J=8.5, 1.4 Hz, 1H), 8.47 (d, J=8.6, 1H), 8.36 (ddd, J = 8.8, 7.1, 1.5 Hz, 1H), 8.31 (ddd, J = 8.2, 7.1, 1.2 Hz, 1H), 4.69 (s, 3H).

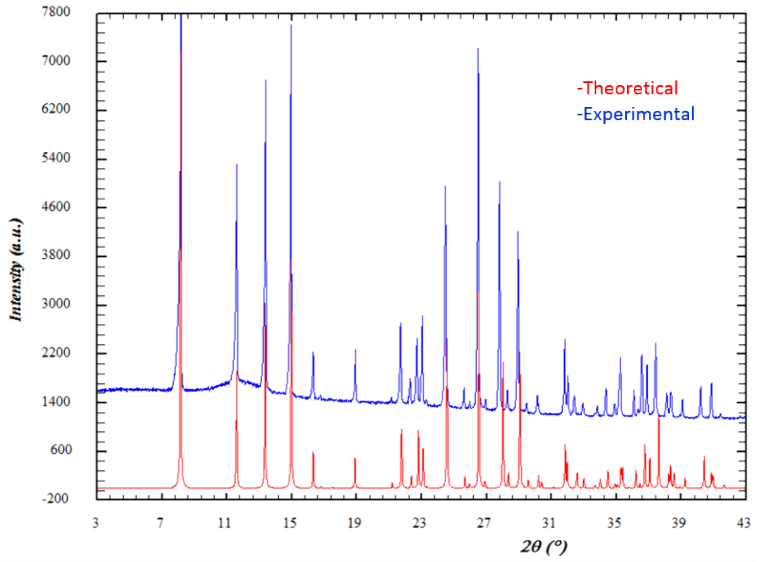
XRPD of (MQ)[BF_4]: theoretical (red) and experimental (blue)



A_3-(MQ)[$CuBr_2$]$_\infty$

Under aerobic conditions, in a pillbox is mixed a stoichiometric (2.10^{-3} mol) amount of Cu^{I}Br (143 mg), NaBr (106 mg) and (MQ)[BF_4] (232 mg) in 2.5 mL of DMSO. The compounds are completely dissolved under slightly heating, leading to a brown solution. After cooling to room temperature, the pillbox is covered with an aluminium foil pierced with 4 "syringes" holes and then inserted in a bigger one filled with MeOH for liquid/gas diffusion. After few hours dark brown crystals of the title compound were formed in a pure phase (257 mg, 35%).

XRPD of (MQ)[$CuBr_2$]$_\infty$: theoretical (red) and experimental (blue)



B- Single crystal X-ray diffraction analysis for $(MQ)[CuBr_2]_\infty$ and $(MQ)[BF_4]$

B-I- $(MQ)[CuBr_2]_\infty$

Summary of crystallographic data

Empirical formula	C9 H9 Br2 Cu N2
Formula weight	368.54
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, C 2/m
Unit cell dimensions	a = 15.373(2) A alpha = 90 deg. b = 6.4099(7) A beta = 96.692(12) deg. c = 10.9646(18) A gamma = 90 deg.
Volume	1073.1(3) A^3
Z, Calculated density	4, 2.281 Mg/m^3
Absorption coefficient	9.441 mm^-1
F(000)	704
Crystal size	0.362 x 0.185 x 0.081 mm
Theta range for data collection	3.447 to 27.308 deg.
Limiting indices	-19<=h<=19, -8<=k<=7, -11<=l<=14
Reflections collected / unique	2530 / 1265 [R(int) = 0.0216]
Completeness to theta = 25.242	94.9 %
Absorption correction	Integration
Max. and min. transmission	0.4145 and 0.1832
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1265 / 0 / 92
Goodness-of-fit on F^2	1.322
Final R indices [I>2sigma(I)]	R1 = 0.0290, wR2 = 0.0792
R indices (all data)	R1 = 0.0328, wR2 = 0.0912
Extinction coefficient	0.012(2)
Largest diff. peak and hole	0.390 and -0.582 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3).
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
C(1)	7633(4)	5000	8930(5)	59(1)
C(2)	7516(3)	5000	6666(4)	46(1)
C(3)	8428(3)	5000	6711(5)	54(1)
C(4)	8783(4)	5000	5629(6)	64(1)
C(5)	8264(4)	5000	4487(6)	67(1)
C(6)	7373(4)	5000	4436(5)	61(1)
C(7)	6979(3)	5000	5528(5)	53(1)
C(8)	5741(3)	5000	6494(6)	62(1)
C(9)	6240(3)	5000	7645(5)	56(1)
N(1)	7100(2)	5000	7716(4)	49(1)
N(2)	6083(3)	5000	5466(5)	63(1)
Cu(1)	10000	7336(1)	10000	66(1)
Br(2)	9281(1)	5000	11400(1)	54(1)
Br(1)	9046(1)	10000	8769(1)	52(1)

Table 3. Bond lengths [A] and angles [deg].

C(1)-N(1)	1.480(6)
C(1)-H(1B)	1.10(5)
C(1)-H(1C)	0.77(8)
C(2)-N(1)	1.381(6)
C(2)-C(3)	1.397(6)
C(2)-C(7)	1.414(7)
C(3)-C(4)	1.362(8)
C(3)-H(3)	0.9300
C(4)-C(5)	1.405(9)
C(4)-H(4)	0.9300
C(5)-C(6)	1.364(9)
C(5)-H(5)	0.9300
C(6)-C(7)	1.403(8)
C(6)-H(6)	0.9300
C(7)-N(2)	1.372(6)
C(8)-N(2)	1.298(8)
C(8)-C(9)	1.398(8)
C(8)-H(8)	0.9300
C(9)-N(1)	1.315(6)
C(9)-H(9)	0.9300
Cu(1)-Br(2)#1	2.4935(6)
Cu(1)-Br(2)	2.4935(6)
Cu(1)-Br(1)#2	2.5347(6)
Cu(1)-Br(1)	2.5347(6)
Cu(1)-Cu(1)#1	2.9946(15)
Br(2)-Cu(1)#1	2.4934(6)
Br(1)-Cu(1)#2	2.5347(6)

N(1)-C(1)-H(1B)	110(3)
N(1)-C(1)-H(1C)	108(5)
H(1B)-C(1)-H(1C)	109(3)
N(1)-C(2)-C(3)	122.1(4)
N(1)-C(2)-C(7)	117.1(4)
C(3)-C(2)-C(7)	120.8(5)
C(4)-C(3)-C(2)	118.1(5)
C(4)-C(3)-H(3)	120.9
C(2)-C(3)-H(3)	120.9
C(3)-C(4)-C(5)	122.2(5)
C(3)-C(4)-H(4)	118.9
C(5)-C(4)-H(4)	118.9
C(6)-C(5)-C(4)	120.0(5)
C(6)-C(5)-H(5)	120.0
C(4)-C(5)-H(5)	120.0
C(5)-C(6)-C(7)	119.7(5)

C(5)-C(6)-H(6)	120.1
C(7)-C(6)-H(6)	120.1
N(2)-C(7)-C(6)	119.2(5)
N(2)-C(7)-C(2)	121.6(5)
C(6)-C(7)-C(2)	119.2(5)
N(2)-C(8)-C(9)	123.3(5)
N(2)-C(8)-H(8)	118.3
C(9)-C(8)-H(8)	118.3
N(1)-C(9)-C(8)	119.6(5)
N(1)-C(9)-H(9)	120.2
C(8)-C(9)-H(9)	120.2
C(9)-N(1)-C(2)	120.7(4)
C(9)-N(1)-C(1)	120.1(5)
C(2)-N(1)-C(1)	119.2(4)
C(8)-N(2)-C(7)	117.5(5)
Br(2)#1-Cu(1)-Br(2)	106.19(3)
Br(2)#1-Cu(1)-Br(1)#2	117.514(17)
Br(2)-Cu(1)-Br(1)#2	110.314(17)
Br(2)#1-Cu(1)-Br(1)	110.314(17)
Br(2)-Cu(1)-Br(1)	117.513(16)
Br(1)#2-Cu(1)-Br(1)	95.29(3)
Br(2)#1-Cu(1)-Cu(1)#1	53.094(15)
Br(2)-Cu(1)-Cu(1)#1	53.094(16)
Br(1)#2-Cu(1)-Cu(1)#1	132.354(15)
Br(1)-Cu(1)-Cu(1)#1	132.354(15)
Cu(1)#1-Br(2)-Cu(1)	73.81(3)
Cu(1)-Br(1)-Cu(1)#2	84.71(3)

Symmetry transformations used to generate equivalent atoms:
#1 -x+2,-y+1,-z+2 #2 -x+2,-y+2,-z+2

Table 4. Anisotropic displacement parameters (A^2 x 10^3).
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
C(1)	58(3)	79(4)	41(2)	0	5(2)	0
C(2)	51(2)	43(2)	46(2)	0	8(2)	0
C(3)	48(2)	59(3)	55(3)	0	7(2)	0
C(4)	58(3)	61(3)	78(4)	0	23(3)	0
C(5)	96(4)	56(3)	55(3)	0	31(3)	0
C(6)	87(4)	48(2)	46(2)	0	5(2)	0
C(7)	55(2)	45(2)	57(3)	0	1(2)	0
C(8)	44(2)	70(3)	71(3)	0	4(2)	0
C(9)	48(2)	57(3)	65(3)	0	13(2)	0
N(1)	47(2)	46(2)	53(2)	0	6(2)	0
N(2)	55(2)	62(2)	70(3)	0	-7(2)	0
Cu(1)	68(1)	65(1)	65(1)	0	13(1)	0
Br(2)	58(1)	55(1)	50(1)	0	13(1)	0
Br(1)	48(1)	57(1)	50(1)	0	3(1)	0

checkCIF/PLATON report (basic structural check)

No syntax errors found. CIF dictionary
Please wait while processing .... Interpreting this report

Datablock: shelx

```
Bond precision:      C-C = 0.0080 A               Wavelength=0.71073
Cell:          a=15.373(2)     b=6.4099(7)     c=10.9646(18)
               alpha=90        beta=96.692(12) gamma=90
Temperature: 293 K
                    Calculated                      Reported
Volume              1073.1(3)                       1073.1(3)
Space group         C 2/m                           C 2/m
Hall group          -C 2y                           -C 2y
Moiety formula      Br2 Cu, C9 H9 N2                Br2 Cu, C9 H9 N2
Sum formula         C9 H9 Br2 Cu N2                 C9 H9 Br2 Cu N2
Mr                  368.53                          368.54
Dx,g cm-3           2.281                           2.281
Z                   4                               4
Mu (mm-1)           9.441                           9.441
F000                704.0                           704.0
F000'               703.38
h,k,lmax            19,8,14                         19,8,14
Nref                1325                            1265
Tmin,Tmax           0.134,0.465                     0.183,0.414
Tmin'               0.030
Correction method= # Reported T Limits: Tmin=0.183
Tmax=0.414 AbsCorr = INTEGRATION
Data completeness= 0.955        Theta(max)= 27.308
R(reflections)= 0.0290( 1133)      wR2(reflections)= 0.0912( 1265)
S = 1.322              Npar= 92
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

PLAT019_ALERT_1_C _diffrn_measured_fraction_theta_full/_max < 1.0
0.994 Report
PLAT341_ALERT_3_C Low Bond Precision on C-C Bonds 0.0080
Ang.
PLAT350_ALERT_3_C Short C-H (X0.96,N1.08A) C1 - H1C ... 0.76
Ang.

Alert level G

PLAT004_ALERT_5_G Polymeric Structure Found with Maximum Dimension
1 Info
PLAT164_ALERT_4_G Nr. of Refined C-H H-Atoms in Heavy-Atom Struct. 2
Note
PLAT199_ALERT_1_G Reported _cell_measurement_temperature ..... (K)
293 Check
PLAT200_ALERT_1_G Reported _diffrn_ambient_temperature ..... (K) 293
Check
PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X) Br1 -- Cu1 .. 34.6 su
PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X) Br2 -- Cu1 .. 25.4 su
PLAT380_ALERT_4_G Incorrectly? Oriented X(sp2)-Methyl Moiety C1
Check
PLAT764_ALERT_4_G Overcomplete CIF Bond List Detected (Rep/Expd) .
1.19 Ratio

0 **ALERT level A** = Most likely a serious problem - resolve or explain
0 **ALERT level B** = A potentially serious problem, consider carefully
3 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight

8 **ALERT level G** = General information/check it is not something unexpected

B-II- (MQ)[BF_4]

Summary of crystallographic data

Empirical formula	C9 H9 B F4 N2
Formula weight	231.99
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P 21/a
Unit cell dimensions	a = 13.372(2) A alpha = 90 deg. b = 6.2221(9) A beta = 112.232(11) deg. c = 13.8278(19) A gamma = 90 deg.
Volume	1064.9(3) A^3
Z, Calculated density	4, 1.447 Mg/m^3
Absorption coefficient	0.136 mm^-1
F(000)	472
Crystal size	0.204 x 0.176 x 0.102 mm
Theta range for data collection	3.066 to 27.398 deg.
Limiting indices	-17<=h<=17, -7<=k<=8, -17<=l<=14
Reflections collected / unique	4693 / 2357 [R(int) = 0.0315]
Completeness to theta = 25.242	98.5 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2357 / 0 / 191
Goodness-of-fit on F^2	0.716
Final R indices [I>2sigma(I)]	R1 = 0.0362, wR2 = 0.0764
R indices (all data)	R1 = 0.1415, wR2 = 0.0992
Extinction coefficient	0.028(4)
Largest diff. peak and hole	0.082 and -0.074 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3).
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
C(1)	4436(2)	859(5)	850(2)	138(1)
C(2)	5109(2)	1408(4)	2769(2)	86(1)
C(3)	5727(2)	-443(4)	2935(3)	117(1)
C(4)	6337(2)	-1021(5)	3935(4)	141(1)
C(5)	6356(2)	184(6)	4765(3)	133(1)
C(6)	5767(2)	1985(5)	4621(2)	117(1)
C(7)	5113(2)	2642(4)	3608(2)	90(1)
C(8)	3923(2)	4979(4)	2523(3)	119(1)
C(9)	3894(2)	3816(5)	1652(2)	107(1)
N(1)	4475(2)	2075(4)	1782(2)	95(1)
N(2)	4508(2)	4450(3)	3476(2)	114(1)
F(1A)	5868(4)	5765(10)	1375(4)	132(2)
F(1B)	6040(30)	5110(70)	1760(50)	264(12)
F(2A)	7269(17)	4510(30)	2513(7)	263(5)
F(2B)	7750(9)	4962(11)	2483(7)	138(4)
F(3A)	7261(10)	6550(20)	1372(16)	274(6)
F(3B)	7345(3)	6009(14)	1001(6)	152(3)
F(4A)	6742(6)	3290(20)	882(10)	166(4)
F(4B)	6773(10)	2716(18)	1440(30)	157(7)
B(1)	6847(2)	4896(5)	1564(3)	83(1)

Table 3. Bond lengths [A] and angles [deg].

C(1)-N(1)	1.478(3)
C(1)-H(1A)	0.9600
C(1)-H(1B)	0.9600
C(1)-H(1C)	0.9600
C(2)-N(1)	1.370(3)
C(2)-C(3)	1.385(3)
C(2)-C(7)	1.390(3)
C(3)-C(4)	1.361(4)
C(3)-H(3)	0.9300
C(4)-C(5)	1.363(4)
C(4)-H(4)	0.9300
C(5)-C(6)	1.341(4)
C(5)-H(5)	0.9300
C(6)-C(7)	1.402(3)
C(6)-H(6)	0.9300
C(7)-N(2)	1.357(3)
C(8)-N(2)	1.295(3)
C(8)-C(9)	1.392(4)
C(8)-H(8)	0.9300
C(9)-N(1)	1.305(3)
C(9)-H(9)	0.9300
F(1A)-F(1B)	0.64(7)
F(1A)-B(1)	1.348(5)
F(1B)-B(1)	1.220(15)
F(1B)-F(2A)	1.62(6)
F(2A)-F(2B)	0.719(17)
F(2A)-B(1)	1.240(9)
F(2A)-F(4B)	1.77(3)
F(2B)-B(1)	1.383(9)
F(2B)-F(3A)	1.732(18)
F(3A)-F(3B)	0.659(19)
F(3A)-B(1)	1.244(11)
F(3B)-B(1)	1.387(6)
F(4A)-F(4B)	0.838(17)
F(4A)-B(1)	1.344(7)
F(4B)-B(1)	1.366(12)

N(1)-C(1)-H(1A)	109.5

N(1)-C(1)-H(1B)	109.5
H(1A)-C(1)-H(1B)	109.5
N(1)-C(1)-H(1C)	109.5
H(1A)-C(1)-H(1C)	109.5
H(1B)-C(1)-H(1C)	109.5
N(1)-C(2)-C(3)	121.5(3)
N(1)-C(2)-C(7)	118.0(2)
C(3)-C(2)-C(7)	120.5(3)
C(4)-C(3)-C(2)	118.6(3)
C(4)-C(3)-H(3)	120.7
C(2)-C(3)-H(3)	120.7
C(3)-C(4)-C(5)	121.6(3)
C(3)-C(4)-H(4)	119.2
C(5)-C(4)-H(4)	119.2
C(6)-C(5)-C(4)	120.8(3)
C(6)-C(5)-H(5)	119.6
C(4)-C(5)-H(5)	119.6
C(5)-C(6)-C(7)	120.1(3)
C(5)-C(6)-H(6)	120.0
C(7)-C(6)-H(6)	120.0
N(2)-C(7)-C(2)	122.1(2)
N(2)-C(7)-C(6)	119.4(3)
C(2)-C(7)-C(6)	118.5(3)
N(2)-C(8)-C(9)	123.8(3)
N(2)-C(8)-H(8)	118.1
C(9)-C(8)-H(8)	118.1
N(1)-C(9)-C(8)	119.4(3)
N(1)-C(9)-H(9)	120.3
C(8)-C(9)-H(9)	120.3
C(9)-N(1)-C(2)	120.1(2)
C(9)-N(1)-C(1)	118.8(3)
C(2)-N(1)-C(1)	121.2(2)
C(8)-N(2)-C(7)	116.6(2)
F(1B)-F(1A)-B(1)	64.6(17)
F(1A)-F(1B)-B(1)	87(4)
F(1A)-F(1B)-F(2A)	129(2)
B(1)-F(1B)-F(2A)	49.3(18)
F(2B)-F(2A)-B(1)	85.4(15)
F(2B)-F(2A)-F(1B)	126(2)
B(1)-F(2A)-F(1B)	48.2(18)
F(2B)-F(2A)-F(4B)	105.1(14)
B(1)-F(2A)-F(4B)	50.3(9)
F(1B)-F(2A)-F(4B)	69.1(11)
F(2A)-F(2B)-B(1)	63.4(11)
F(2A)-F(2B)-F(3A)	103.4(15)
B(1)-F(2B)-F(3A)	45.4(4)
F(3B)-F(3A)-B(1)	87.9(14)
F(3B)-F(3A)-F(2B)	106.3(19)
B(1)-F(3A)-F(2B)	52.3(7)
F(3A)-F(3B)-B(1)	63.7(12)
F(4B)-F(4A)-B(1)	73.4(13)
F(4A)-F(4B)-B(1)	70.5(11)
F(4A)-F(4B)-F(2A)	112.1(17)
B(1)-F(4B)-F(2A)	44.3(8)
F(1B)-B(1)-F(2A)	82(4)
F(1B)-B(1)-F(3A)	117(2)
F(2A)-B(1)-F(3A)	109.1(15)
F(1B)-B(1)-F(4A)	112.0(11)
F(2A)-B(1)-F(4A)	118.8(10)
F(3A)-B(1)-F(4A)	113.7(13)
F(1B)-B(1)-F(1A)	28(3)
F(2A)-B(1)-F(1A)	107.6(8)
F(3A)-B(1)-F(1A)	96.0(9)
F(4A)-B(1)-F(1A)	109.0(4)
F(1B)-B(1)-F(4B)	96.2(18)
F(2A)-B(1)-F(4B)	85.4(16)
F(3A)-B(1)-F(4B)	144.3(14)
F(4A)-B(1)-F(4B)	36.0(8)
F(1A)-B(1)-F(4B)	110.8(6)
F(1B)-B(1)-F(2B)	109(3)
F(2A)-B(1)-F(2B)	31.2(8)
F(3A)-B(1)-F(2B)	82.3(8)
F(4A)-B(1)-F(2B)	119.4(6)
F(1A)-B(1)-F(2B)	127.7(5)
F(4B)-B(1)-F(2B)	98.1(11)

F(1B)-B(1)-F(3B)	137(3)
F(2A)-B(1)-F(3B)	124.7(13)
F(3A)-B(1)-F(3B)	28.4(9)
F(4A)-B(1)-F(3B)	85.5(9)
F(1A)-B(1)-F(3B)	109.2(4)
F(4B)-B(1)-F(3B)	117.0(12)
F(2B)-B(1)-F(3B)	93.6(6)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for shelx.
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
C(1)	139(2)	189(3)	98(2)	-52(2)	60(2)	-35(2)
C(2)	74(1)	95(2)	88(2)	-16(2)	31(1)	-9(1)
C(3)	96(2)	115(2)	136(3)	-29(2)	40(2)	3(2)
C(4)	107(2)	111(2)	183(4)	-13(3)	31(2)	10(2)
C(5)	109(2)	124(2)	134(3)	16(2)	10(2)	-4(2)
C(6)	112(2)	131(2)	97(2)	-19(2)	28(2)	-19(2)
C(7)	90(1)	91(2)	88(2)	-16(2)	31(1)	-8(1)
C(8)	108(2)	106(2)	134(3)	-7(2)	35(2)	8(2)
C(9)	96(2)	124(2)	94(2)	5(2)	28(2)	-16(2)
N(1)	87(1)	109(2)	97(2)	-18(1)	43(1)	-22(1)
N(2)	120(2)	105(2)	110(2)	-23(1)	36(1)	6(1)
F(1A)	110(2)	122(3)	174(6)	-32(2)	66(3)	14(2)
F(1B)	174(14)	173(15)	530(30)	-80(20)	230(19)	-60(11)
F(2A)	191(10)	469(17)	115(4)	66(7)	41(5)	57(7)
F(2B)	122(5)	158(7)	112(5)	-25(4)	19(3)	-3(3)
F(3A)	374(15)	240(8)	290(12)	-104(11)	218(14)	-184(10)
F(3B)	117(4)	227(6)	129(4)	18(4)	66(3)	-5(3)
F(4A)	136(3)	176(7)	164(6)	-80(4)	31(3)	30(4)
F(4B)	107(5)	103(5)	244(19)	-11(7)	46(9)	-10(4)
B(1)	75(2)	83(2)	97(3)	-4(2)	37(2)	-9(2)

checkCIF/PLATON report (basic structural check)

No syntax errors found. CIF dictionary
Please wait while processing .... Interpreting this report

Datablock: shelx

```
Bond precision:      C-C = 0.0047 A                Wavelength=0.71073
Cell:          a=13.372(2)    b=6.2221(9)      c=13.8278(19)
               alpha=90       beta=112.232(11) gamma=90
Temperature: 293 K
                    Calculated                        Reported
Volume              1065.0(3)                         1064.9(3)
Space group         P 21/a                            P 21/a
Hall group          -P 2yab                           -P 2yab
Moiety formula      C9 H9 N2, B F4                    C9 H9 N2, B F4
Sum formula         C9 H9 B F4 N2                     C9 H9 B F4 N2
Mr                  231.99                            231.99
Dx,g cm-3           1.447                             1.447
Z                   4                                 4
Mu (mm-1)           0.136                             0.136
F000                472.0                             472.0
F000'               472.36
h,k,lmax            17,8,17                           17,8,17
Nref                2419                              2357
Tmin,Tmax           0.973,0.986
Tmin'               0.973
Correction method= Not given
Data completeness= 0.974        Theta(max)= 27.398
R(reflections)= 0.0362( 707)       wR2(reflections)= 0.0992( 2357)
S = 0.716              Npar= 191
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level B

PLAT026_ALERT_3_B Ratio Observed / Unique Reflections too Low .... 30 %
PLAT242_ALERT_2_B Low Ueq as Compared to Neighbors for ..... B1 Check

Alert level C

GOODF01_ALERT_2_C The least squares goodness of fit parameter lies outside the range 0.80 <> 2.00
Goodness of fit given = 0.716
PLAT234_ALERT_4_C Large Hirshfeld Difference F3A -- B1 .. 0.23 Ang.
PLAT241_ALERT_2_C High Ueq as Compared to Neighbors for ..... C4 Check
PLAT340_ALERT_3_C Low Bond Precision on C-C Bonds ..... 0.0047 Ang.

Alert level G

PLAT128_ALERT_4_G Alternate Setting for Input Space Group P21/a P21/c Note
PLAT199_ALERT_1_G Reported _cell_measurement_temperature ..... (K) 293 Check
PLAT200_ALERT_1_G Reported _diffrn_ambient_temperature ..... (K) 293 Check
PLAT230_ALERT_2_G Hirshfeld Test Diff for F3B -- B1 .. 6.2 su
PLAT301_ALERT_3_G Main Residue Disorder ..... Percentage = 25 Note
PLAT432_ALERT_2_G Short Inter X...Y Contact F4A .. C9 .. 2.97 Ang.
And 2 other PLAT432 Alerts

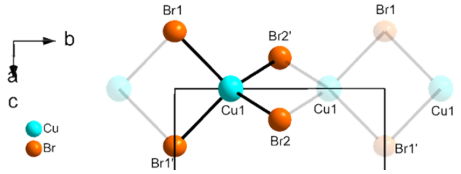
More ...
PLAT764_ALERT_4_G Overcomplete CIF Bond List Detected (Rep/Expd) .
1.35 Ratio
PLAT779_ALERT_4_G Suspect or Irrelevant (Bond) Angle in CIF .... # 55
Check
B1 -F4B -F2A 1.555 1.555 1.555 44.30 Deg.
PLAT779_ALERT_4_G Suspect or Irrelevant (Bond) Angle in CIF .... # 62
Check
F1B -B1 -F1A 1.555 1.555 1.555 28.00 Deg.
PLAT779_ALERT_4_G Suspect or Irrelevant (Bond) Angle in CIF .... # 69
Check
F4A -B1 -F4B 1.555 1.555 1.555 36.00 Deg.
PLAT779_ALERT_4_G Suspect or Irrelevant (Bond) Angle in CIF .... # 72
Check
F2A -B1 -F2B 1.555 1.555 1.555 31.20 Deg.
PLAT779_ALERT_4_G Suspect or Irrelevant (Bond) Angle in CIF .... # 79
Check
F3A -B1 -F3B 1.555 1.555 1.555 28.40 Deg.

---

0 **ALERT level A** = Most likely a serious problem - resolve or explain
2 **ALERT level B** = A potentially serious problem, consider carefully
4 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
14 **ALERT level G** = General information/check it is not something unexpected

C-Supplementary Tables

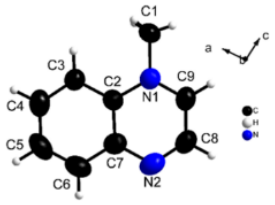
Table S1: View of the $[CuBr_2]_\infty$ chain with the corresponding selected Bond distances [Å] and Angles (deg.)



Bond Distances	Cu_1-Br_1 = 2.535 (1)	*0.021*	Deviation from ideal tetrahedral geometry (abs value)
	Cu_1-Br_2 = 2.493 (1)	*0.021*	
Bridging Angles	Cu_1-Br_1-Cu_1=84.708(3)	*14.178*	
	Cu_1-Br_2-Cu_1=73.810(3)	*3.280*	
Interligand Dihedral Angles	$Br_1Cu_1Br_1$'-$Br_2Cu_1Br_2$'= 84.426(10)	*5.574*	
	$Br_1Cu_1Br_2$'-Br_1'Cu_1Br_2= 77.678(7)	*12.322*	
	$Br_1Cu_1Br_2$-Br_1'Cu_1Br_2'= 83.078(8)	*6.922*	
Edge Central Angles	Br_1-Cu_1-Br_1'= 95.292 (3)	*14.208*	
	Br_2-Cu_1-Br_2'= 106.190 (4)	*3.310*	
	Br_1-Cu_1-Br_2' = 110.314 (4)	*0.814*	
	Br_1-Cu_1-Br_2 = 117.513 (6)	*8.013*	
Face-Edge-Face Angles[(a)]	Br_1'(Br_2'Br_2)Br_1=60.372(10)	*10.157*	
	Br_2(Br_1'Br_1)Br_2'=63.529(9)	*7.000*	
	Br_1(Br_2Br_1')Br_2'=70.362(10)	*0.167*	
	Br_1'(Br_2'Br_1)Br_2=70.369(9)	*0.160*	
	Br_1'(Br_2Br_1)Br_2'=78.854(9)	*8.325*	

a(bc)d: dihedral angle between the abc and bcd planes, (bc) being the common shared-edge

Table S2: Thermal ellipsoid view of the MQ moiety of $(MQ)[CuBr_2]_\infty$ with its corresponding selected Bond distances [Å] and Angles (deg.). Comparison with those measured in $(MQ)[BF_4]$ and reported in $(MQ)_2\{H_2\text{-}[Fe^{II}(CN)_6]\}$.[7]



		$(MQ)[CuBr_2]_\infty$	$(MQ)[BF_4]$ (ESI†)	$(MQ)_2\{H_2\text{-}[Fe^{II}(CN)_6]\}$[7]
Bond Distances	C_1-N_1 =	1.480 (6)	1.478 (3)	1.476 (7)
	C_9-N_1 =	1.315 (6)	1.305 (3)	1.364 (6)
	C_9-C_8 =	1.398 (8)	1.392 (4)	1.288 (8)
	C_8-N_2 =	1.298 (8)	1.295 (3)	1.331 (6)
	C_7-N_2 =	1.372 (6)	1.357 (3)	1.389 (5)
	C_7-C_2 =	1.414 (7)	1.390 (3)	1.355 (6)
	C_2-C_3 =	1.397 (6)	1.385 (3)	1.440 (6)
	C_3-C_4 =	1.362 (8)	1.361 (4)	1.342 (7)
	C_4-C_5 =	1.405 (9)	1.363 (4)	1.331 (8)
	C_5-C_6 =	1.364 (9)	1.341 (4)	1.388 (7)
	C_6-C_7 =	1.403 (8)	1.402 (3)	1.440 (6)
Planar angles	C_1-N_1-C_2 =	119.2 (4)	121.2 (3)	122.8 (3)
	C_9-N_1-C_2 =	120.7 (4)	120.1 (2)	115.0 (3)
	N_1-C_9-C_8 =	119.6 (5)	119.4 (3)	123.4 (4)
	C_9-C_8-N_2 =	123.3 (5)	123.8 (3)	125.2 (5)
	C_8-N_2-C_7 =	117.5 (5)	116.6 (2)	112.9 (3)
	N_2-C_7-C_2 =	121.6 (5)	122.1 (2)	124.0 (3)
	C_7-C_2-N_1 =	117.1 (4)	118.0 (2)	119.0 (3)
	C_7-C_2-C_3 =	120.8 (5)	120.5 (3)	119.2 (4)
	C_2-C_3-C_4 =	118.1 (5)	118.6 (3)	117.8 (4)
	C_3-C_4-C_5 =	122.2 (5)	121.6 (3)	123.7 (5)
	C_4-C_5-C_6 =	120.0 (5)	120.8 (3)	121.5 (5)
	C_5-C_6-C_7 =	119.7 (5)	120.1 (3)	116.2 (4)

C_6-C_7-C_2 =	119.2 (5)	118.5 (3)	121.2 (3)

Table S3: Average Interplanar distances between two consecutives cations in some cationic π-deficient heterocycles with a similar stacking arrangement.

Compound Formula[a]	Temperature (K)	Interplanar distance [Å] [b]	Ref.
$(NMP)_2[Pd(C_2O_4)_2]$	295	3.25[c]	11a
$(NMP)_2[Cu(mnt)_2]$	295	3.33	11b
$(NMP)_2[Pd(NO_2)_4]$	295	3.33	11c
$(NMP)[Ni(S_2C_6H_4)_2]$	295	3.36	11d
(NMP)[TCNQ]	295	3.36	11e
$(NMP)[Ni(mnt)_2]$	295	3.38	11f
$(NMP)[2,5\text{-}Cl_2TCNQ]$	296	3.42	11g
$(NMP)_2[Ni(mmt)_2]$	295	3.42	11h
$(Q)_4[Ge_1Mo_{12}O_{39}OH]$	295	3.42	11i
$(Q)_4[PMo_9W_3O_{40}\cdot 2DMF]$	295	3.44	11j
$(Q)[Co(Co)_4]$	295	3.46	11k
$(MQ)_2\{H_2\text{-}[Fe^{II}(CN)_6]\}$	295	3.47	7
$(N\text{-}MeA)_2[Ni(mnt)_2]$	291	3.52	11l
$(N\text{-}MeA)[X]$, H_2O ($X=Cl^-$, Br^-)	295	3.52^{Cl}, 3.54^{Br}	11m

(a) NMP=N-Methylphenazinium, Q=N-Methylquinolinium, MQ=N-methylquinoxalinium, N-MeA=N-Methylacridinium. *(b)* Average distance measured between two consecutive planes which contain only the phenazine or quinoxaline core. (*c)* Specific distance measured in a NMP/NMP/$[Pb(C_2O_4)_2]$ tryad

D-Supplementary Figures

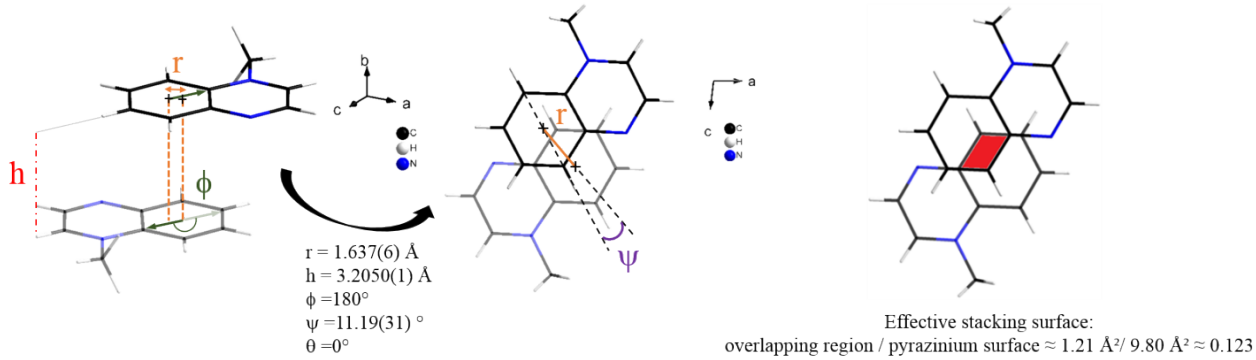


Figure S1. Stacking parameters within the organic sub-network of (MQ)[$CuBr_2$]$_\infty$: Interplanar distance (h), shift distance between the centres of the two phenyls (*r*), inclination angle between two MQ moieties (θ), twist angle between two MQ (ϕ), direction of the shift *r* along the N^+-CH_3 direction (ψ). Calculated effective stacking surface (red) of about 12%.

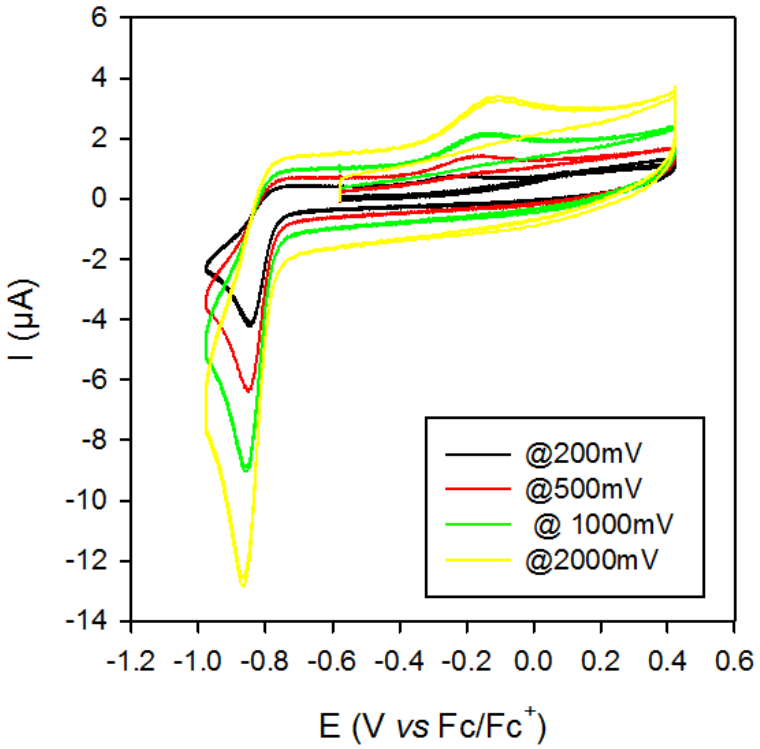


Figure S2. Cyclic Voltammogram of (MQ)[BF4] (0.65mM) in DMF, with TBAP (0.1 M) as supporting electrolyte on Pt, at different scan rates.

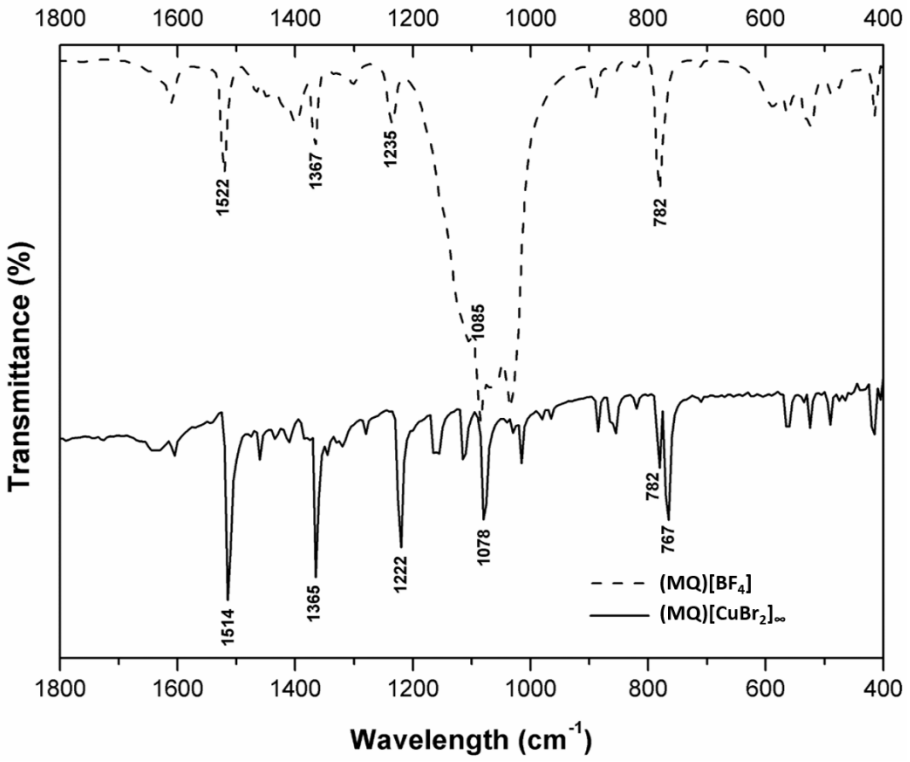


Figure S3. Infrared spectra $(MQ)[CuBr_2]_\infty$ (solid line) and $(MQ)[BF_4]$ (dashed line).

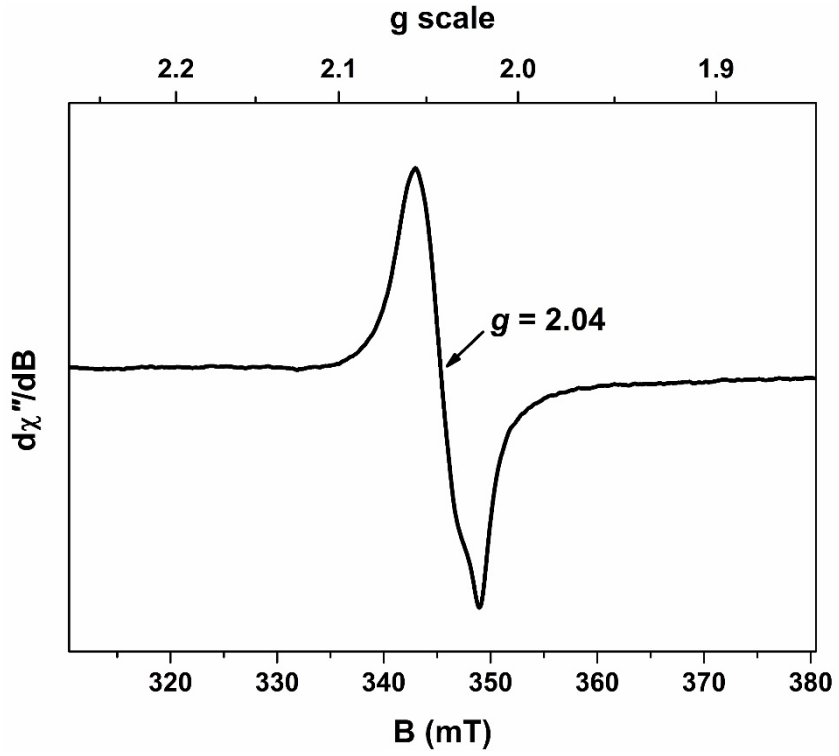


Figure S4. X-band EPR spectrum of polycrystalline $(MQ)[CuBr_2]_\infty$ recorded at ambient temperature (experimental conditions: frequency, 9.4471 GHz; power, 20.0 mW; modulation, 0.2 mT).

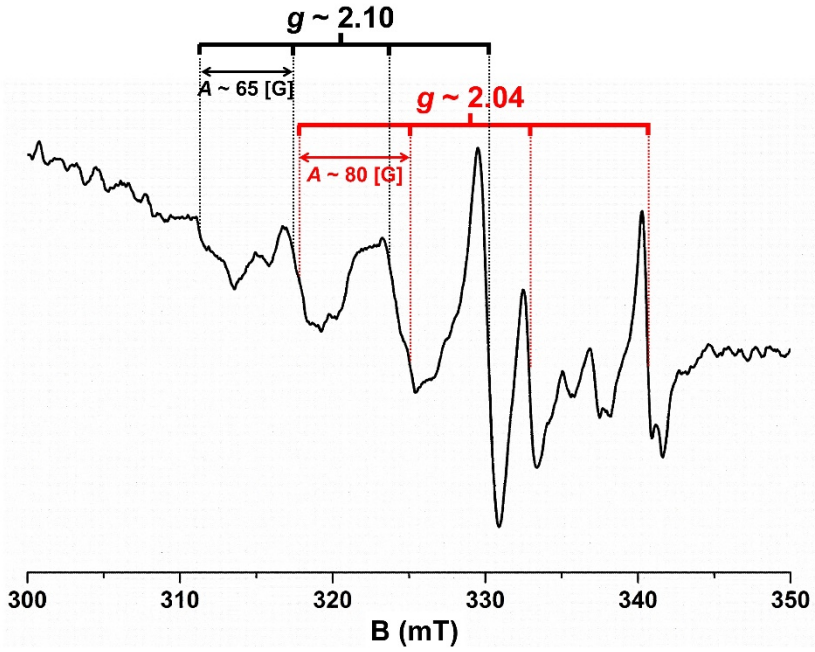


Figure S5. X-band EPR spectrum of (MQ)[$CuBr_2$] recorded in DMSO solution at 333 K (experimental conditions: frequency, 9.4235 GHz; power, 50.3 mW; modulation, 0.6 mT). Two identifiable four-line Cu(II) signals are indicated above the spectrum.

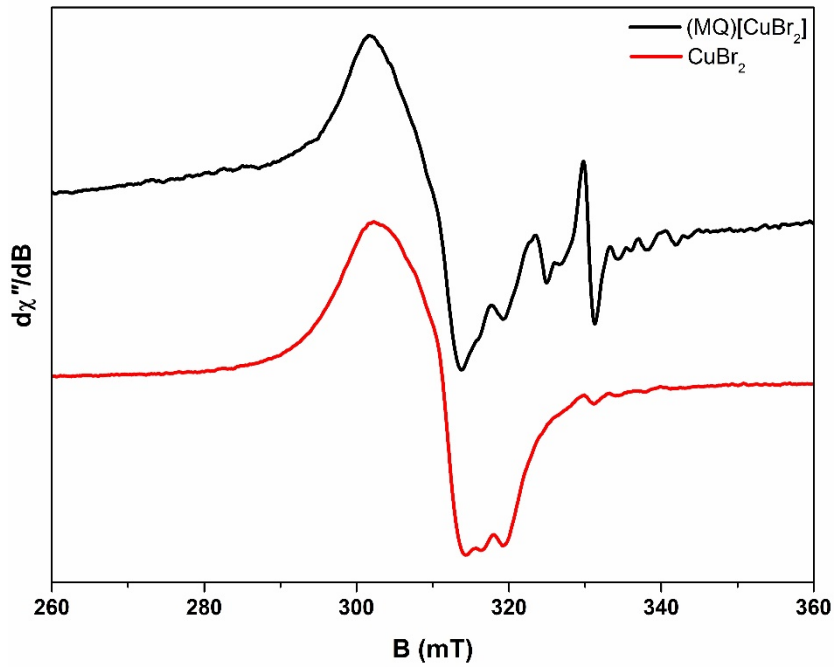


Figure S6. Comparison of the EPR spectra of 'exposed' (MQ)[$CuBr_2$] (black) and $CuBr_2$ (red) in DMSO solution at 293 K (experimental conditions: frequency, 9.4248 GHz; power, 15.0 mW; modulation, 0.6 mT).

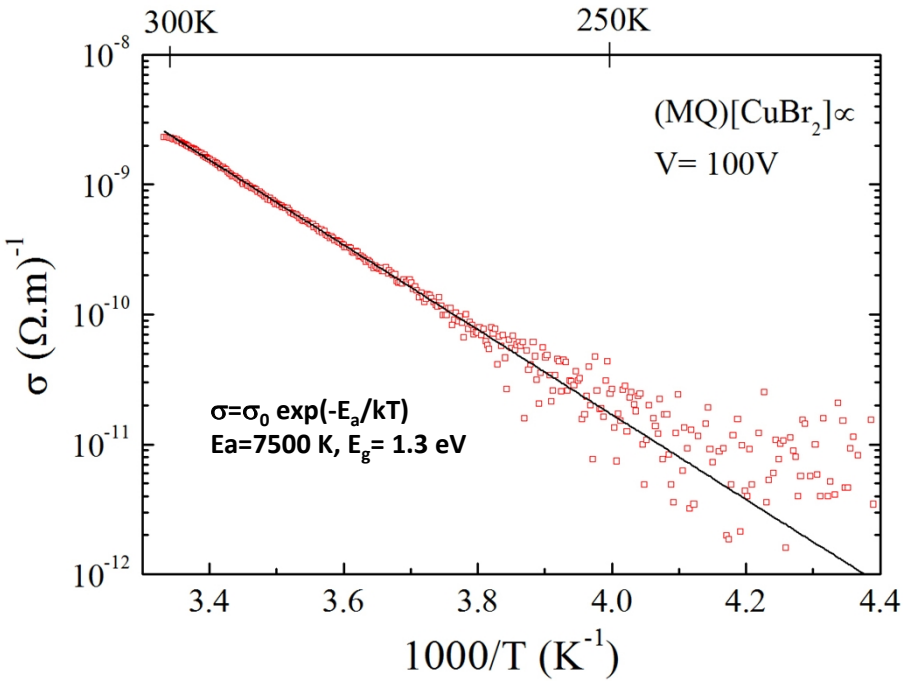


Figure S7. Conductivity of single crystal along the *b* axis of $(MQ)[CuBr_2]_\infty$ plotted as a function of the inverse temperature. The black line is the fit of the data with an activation law.

E-Further experimental techniques

Resistivity measurements. Gold wires were attached with silver paint on the corresponding small faces of the plate-like single crystals. Because of very high resistance values, two-probe DC measurements were performed under vacuum, applying a constant voltage in the range 100 - 200V and measuring the current using a Keithley 6487 Picoammeter / Voltage Source. The temperature dependence of the resistivity has been measured in a Quantum Design PPMS.