Supporting Information (SI) for the manuscript:

Synthesis, Crystal Structure and Magnetic Properties of $(H_2tppz)[ReCl_6]$ and $[Cu(bpzm)_2(\mu\text{-}Cl)ReCl_3(\mu\text{-}ox)Cu(bpzm)_2(\mu\text{-}ox)ReCl_3(\mu\text{-}Cl)]_n$

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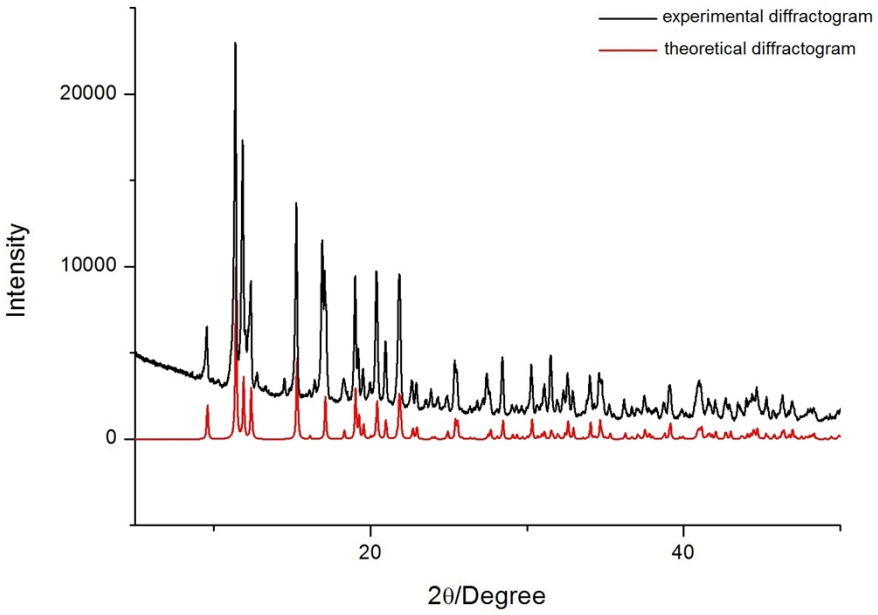

Figure S1. The X-ray powder diffraction pattern of compound **1** (experimental - black) and the simulation of the powder pattern of **1** from the crystal structure (red).

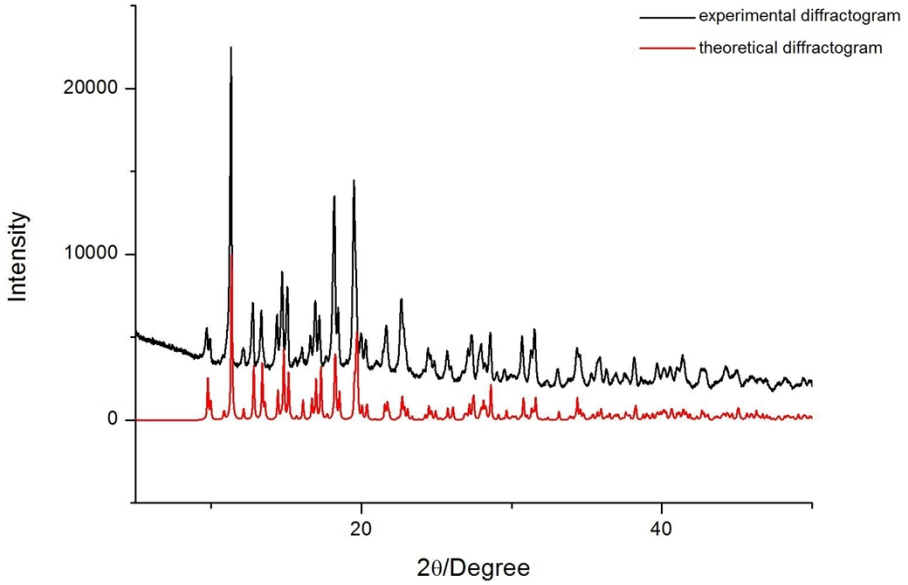

Figure S2. The X-ray powder diffraction pattern of compound **2** (experimental - black) and the simulation of the powder pattern of **2** from the crystal structure (red).

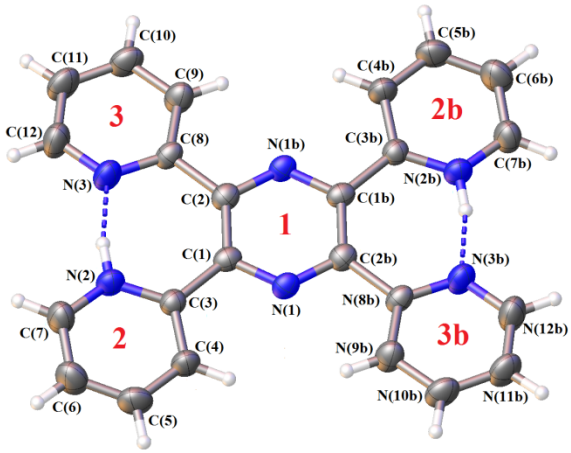

Figure S3. View of the H_2tppz^{2+} dication in **1** showing the hydrogen bonds N—H•••N (blue dotted lines) [symmetry code: (b) = 1-*x*, 1-*y*, 1-*z*].

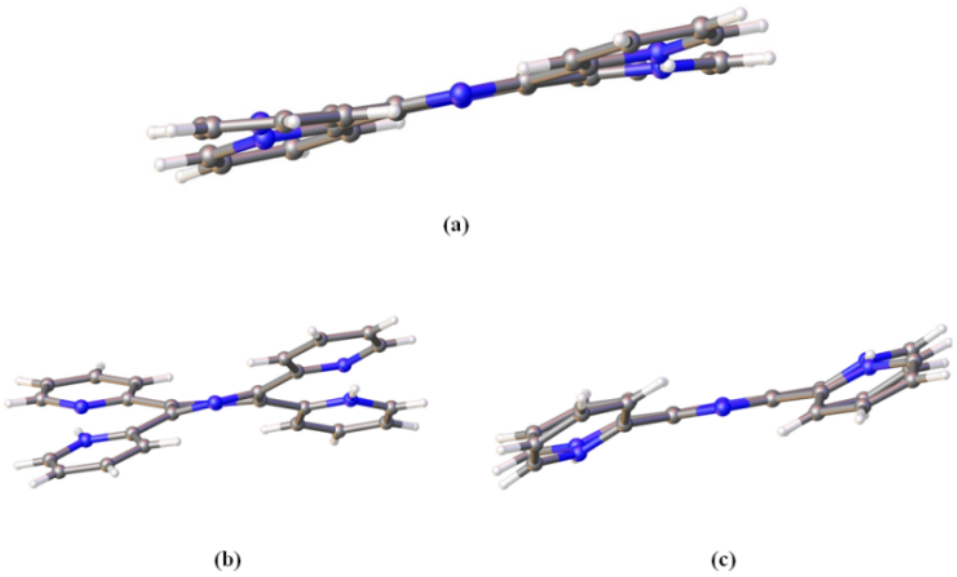

Figure S4. View of conformations of the cation H_2tppz^{2+} found in **1** (a), $H_2tppz(I_2 \cdot I_3)_2$ (b) and $H_2tppz[B(C_6H_5)_4]_2$ (c).

Table S1. Short intra- and intermolecular contacts detected in structures **1** and **2*.**

D–H	A	D—H [Å]	H•••A [Å]	D•••A [Å]	D—H•••A [°]
			1		
N(2)	N(3)	0.88	1.69	2.549(4)	164.5(2)
C(4)	N(1)	0.93	2.38	2.701(5)	99.9(2)
C(5)	Cl(2k)	0.93	2.81	3.737(4)	171.4(3)
C(7)	Cl(3l)	0.93	2.81	3.687(3)	158.2(2)
C(9)	N(1m)	0.93	2.36	2.689(4)	100.3(2)
C(11)	Cl(3n)	0.93	2.76	3.515(4)	138.5(3)
C(12)	Cl(3l)	0.93	2.79	3.684(4)	161.3(3)
			2		
C(4)	O(4)	0.97	2.24	2.967(16)	130.8(8)
C(4)	Cl(2o)	0.97	2.74	3.654(12)	156.7(7)
C(7)	Cl(3p)	0.93	2.82	3.412(15)	122.3(9)
C(10)	Cl(4q)	0.93	2.82	3.554(13)	136.1(8)
C(10)	O(4r)	0.93	2.57	3.248(19)	130.5(9)
C(11)	O(4r)	0.97	2.24	3.130(17)	152.3(8)
C(11)	Cl(1)	0.97	2.74	3.608(13)	149.5(8)

*Symmetry transformations used to generate equivalent atoms: (k) = -1+x,y,-1+z; (l) = 1-x,-1/2+y,1/2-z; (m) 1-x,1-y,1-z; (n) = x,1/2-y,1/2+z; (o) = x,1+y,z; (p) = 1-x,2-y,2-z; (q) = 1+x,-1+y,z; (r) = x,-1+y,z

Table S2. The selected bond lengths [Å] and angles [°] for **1***

Bond lengths		Bond angels	
Re(1)–Cl(1)	2.3487(9)	Cl(1)–Re(1)–Cl(2)	89.12(3)
Re(1)–Cl(2)	2.3539(9)	Cl(1)–Re(1)–Cl(3)	90.20(3)
Re(1)–Cl(3)	2.3634(9)	Cl(1)–Re(1)–Cl(2)	90.88(4)
		Cl(1a)–Re(1)–Cl(1)	180.00(3)
		Cl(1)–Re(1)–Cl(3a)	89.80(3)
		Cl(2)–Re(1)–Cl(3)	88.96(3)
		Cl(2)–Re(1)–Cl(3a)	91.04(3)
		Cl(2)–Re(1)–Cl(2a)	180.000(1)
		Cl(3)–Re(1)–Cl(3a)	180.0

*Symmetry transformations used to generate equivalent atoms: (a) = 2-*x*, 1-*y*, 1-*z*.

Table S3. Selected structural data for compounds of general formula $(Cat)_2[ReX_6]$.

$(Cat)_2[ReCl_6]$[a]	**Re–Cl**	**The shortest Cl•••Cl interaction**	**The shortest Re•••Re interaction**	**Ref.**
$[Fe(C_5H_5)_2]_2[ReX_6]$	2.349(3) 2.353(3) 2.361(5) 2.343(3) 2.361(5) 2.369(4)	3.382(4)	8.072(1)	9
$[Fe(C_5Me_5)_2]_2[ReX_6]$	2.328(3) 2.374(3) 2.363(3)	3.836(5)	8.4908(3)	9
$(MePPh_3)_2[ReCl_6]$	2.323 (1) 2.364 (2) 2.365 (2)	6.006(5)	9.144(3)	12
$(BEDT\text{-}TTF)_4[ReCl_6]\cdot PhCN$	2.365(3) 2.371(3) 2.361(2)	5.211(5)	9.455(2)	6
$(p\text{-rad})_2[ReCl_6]$	2.338(2) 2.339(2) 2.357(2)	6.448(7)	9.0302(7)	11
$(m\text{-rad})_2[ReCl_6]$	2.352(3) 2.354(2) 2.348(3)	5.651(5)	9.1135(9)	11
$[(DM\text{-}BEDT\text{-}TTF]_4[ReCl_6]$	2.367(3) 2.358(3) 2.362(2) 2.374(3) 2.356(2) 2.348(3)	5.942(4)	9.195(1)	15
$[N(CH_3)_4]_2[ReCl_6]$	2.360 (2)	5.684(18)	9.023 (2)	4
$(Hpy)_2[ReCl_6]$	2.354(1) 2.375(1) 2.352(2)	4.199(3)	7.280(4)	7
$(Hqy)_2[ReCl_6]\cdot 2H_2O$	2.353(1) 2.360(1) 2.358(1)	3.893(1)	7.160(2)	7
$(4,4'\text{-}dmbpy)_2[ReCl_6]$	2.356(2) 2.365(2) 2.370(2)	4.908(3)	7.991 (3)	10
$H_4biim[ReCl_6]\cdot 4H_2O$	2.3536(5) 2.3711(5) 2.3520(5)	3.584(1)	7.963(1)	14
$[RuCl(NH_3)_5]_2[ReCl_6]Cl_2$	2.370(1) 2.341(1) 2.345(1)	3.322(1)	6.9252(3)	15

$[RuCl_2(en)_2]_2[ReCl_6]\cdot 2CH_3CN$	2.319(5) 2.353(5) 2.341(5) 2.346(5) 2.360(5) 2.357(4)	3.814(6)	8.450(1)	15

[a]Abbreviation for the ligands: BEDT-TTF = bis(ethylenedithio)tetrathiafulvalene, *p*-rad = 2-(4-N-methylpyridinium)-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazol-1-oxyl-3-N-oxide, *m*-rad = 2-(3-N-methylpyridinium)-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazol-1-oxyl-3-N-oxide, DM-BEDT-TTF = dimethylbis-(ethylenedithio)tetrathiafulvalene, py = pyridine, qy = quinoline, 4,4'-dmbpy = 4,4'-dimethyl-2,2'-bipyridinium, H_2biim = 2,2'-biimidazole and en = 1,2-ethylenediamine.

Table S4. Geometric parameters of the H_2tppz^{2+} cation.

Compound[a]	Dihedral angles 2/3(4/5)[b] (°)	Dihedral angles 1/2 and 1/3(1/4 and 1/5)[b] (°)	N_{pyr}–H•••N_{pyr},[a] (Å)	C_{pyz}–C_{pyz} [a] (Å)	C_{pyz}–C_{pyr} (Å)	N_{pyz}–C_{pyz}–C_{pyz} (°)	N_{pyz}–C_{pyz}–C_{pyr} (°)	C_{pyz}–C_{pyz}–C_{pyr} (°)	N_{pyr}–C_{pyr}–C_{pyz} (°)	Ref.
$H_2tppz(I_2•I_3)_2$	11.1(3)	18.53(16)	2.563(5)	1.441(11)	1.484(7)	117.0(4)	113.2(5)	129.6(4)	120.8(6)	57
$H_2tppz(Hca)_2$ 295(K)	29.41(4)	19.73(5) 19.17(5)	2.551(1)	1.426(1)	1.487(1) 1.501(1)	118.61(8)	111.77(7) 111.90(7)	129.57(9) 130.19(9)	120.38(8) 119.99(8)	58
$H_2tppz(Hca)_2$ 100(K)	24.27(3) 35.41(3)	16.20(3) 16.56(3) 22.31(3) 23.57(3)	2.5345(8) 2.5694(8)	1.4312(8) 1.4248(8)	1.4976(9) 1.4913(10) 1.4869(10) 1.4925(9)	118.25(6) 117.91(7) 118.22(7) 118.42(6)	112.10(5) 111.43(5) 112.43(5) 111.30(5)	129.62(7) 130.66(6) 129.35(6) 130.23(7)	119.94(5) 120.19(5) 120.77(5) 119.46(5)	58
$H_2tppz(Hba)_2$ 370 (K)	31.24(8)	19.88(8) 21.31(8)	2.5451(12)	1.4224(12)	1.4955(17) 1.4892(17)	118.32(10) 118.48(10)	111.53(8) 111.94(8)	130.09(12) 129.58(11)	120.10(9) 119.45(9)	58
$H_2tppz(Hba)_2$ 200 (K)	26.61(9) 35.79(9)	17.01(8) 18.51(8) 23.43(8) 23.41(8)	2.5294(12) 2.5571(12)	1.4263(12) 1.4204(12)	1.492(2) 1.4933(19) 1.4916(19) 1.487(2)	118.43(13) 118.10(12) 118.31(12) 118.52(14)	111.40(9) 111.83(9) 111.36(9) 112.45(9)	130.17(13) 130.03(14) 130.28(14) 129.03(13)	119.74(9) 119.87(9) 120.70(10) 112.45(9)	58
$H_2tppz(ICl_2)_2$	35.9(2)	22.5(2) 22.7(2)	2.528(7)	1.399(8)	1.486(9) 1.516(7)	118.9(5) 119.7(5)	111.3(5) 110.0(5)	129.7(5) 130.4(5)	120.1(5) 118.0(5)	59
$H_2tppz[B(C_6H_5)_4]_2$	32.60 (9)	20.67(11) 25.95(11)	2.527(3)	1.419(2)	1.495(2) 1.497(3)	118.96(15) 118.76(17)	111.41(14) 111.31(14)	129.62(17) 129.92(17)	119.40(15) 118.7(2)	60
$H_2tppz[AuCl_4]_2$	34.14(9)	20.79(10) 25.11(10)	2.538(3)	1.414(3)	1.491(4) 1.494(3)	118.8(3) 118.7(3)	111.43(19) 111.3(2)	129.6(2) 130.0(3)	119.55(9) 119.3(2)	61
$H_2tppz[ReCl_6]$	9.48(16)	6.03(19) 4.95(18)	2.549(4)	1.422(5)	1.504(5) 1.497(4)	118.2(3) 117.7(3)	111.1(3) 110.8(3)	130.7(3) 131.5(3)	121.3(3) 119.2(3)	this work

[a] Abbreviations: H_2ca = chloranilic acid, H_2ba = bromanilic acid, pyr = pyridine and pyz = pyrazine.

[b] Values of the dihedral angles corresponding to the ring planes of the following structural drawing:

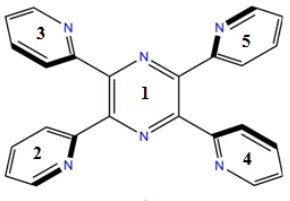

Table S5. The structural parameters for heterometallic compounds [$Re^{IV}Cl_4(\mu\text{-ox})Cu^{II}$].

Compound[a]	Type of bridge	Cu–O [Å]	Cu–Cl [Å]	$Re–O_{av}$ [Å]	$Re–Cl_{av}$ [Å]	Re•••Cu *via* ox-bridge [Å]	Re•••Cu *via* Cl-bridge [Å]	Ref.
[Re Cl_4(μ-ox)Cu(bipy)$_2$]	$\mu_{1,2,3}$	2.650(2)	3.352(2)	2.047(5)	2.339(2)	4.798(1)	4.658(1)	19
[$ReCl_4$(μ-ox)Cu(phen)$_2$]	$\mu_{1,2,3,4}$	2.355(6) 2.465(8)	–	2.058(6)	2.325(4)	5.628(2)	–	20
[$ReCl_4$(μ-ox)Cu(phen)$_2$]·MeCN	$\mu_{1,2,3,4}$	2.41(2) 2.41(2)	–	2.06(2)	2.329(8)	5.649(3)	–	20
[$ReCl_4$(μ-ox)Cu(terpy)(H_2O)][$ReCl_4$(*μ*-ox)Cu(terpy)(CH_3CN)]	$\mu_{1,2,3,4}$ and $\mu_{1,2,3}$	2.05(1) 2.48(1) 2.40(1)	3.077(2)	2.06(1) 2.05(1)	2.328(5) 2.338(5)	5.504(3) 5.436(2)	4.763(2)	20
[$ReCl_4$(μ-ox)Cu(pyim)$_2$]	$\mu_{1,1,2}$	2.681(2)	3.483(1)	2.056(2)	2.333(1)	4.544(1)	4.805(1)	27
(NBu_4)$_2$[{$ReCl_4$(μ-ox)}$_2$Cu(Him)$_2$]	$\mu_{1,2,3,4}$	2.041(4) 2.354(4)	-	2.069(4)	2.318(7)	5.536(1)	–	25
[CuL_β][$ReCl_4$(ox)]·DMF	$\mu_{1,2,3}$	2.580(4) 2.655(3)	-	2.038(2)	2.339(2)	5.568(2) 5.870(2)	–	22
[CuCuL][$ReCl_4$ox]$_2$·2DMF	terminal	–	3.147(3)	2.041(5)	2.339(3)	-	4.904(2)	23
{(CuL_α)[$ReCl_4$(ox)]}$_n$	terminal	–	2.9912(9) 2.9767(9)	2.021(2)	2.3477(9)	-	4.7177(3) 4.6840(3)	26
{(CuL_α)[$ReCl_4$(μ-ox)]}$_n$	$\mu_{1,2,3}$	2.581(6)	2.997(3)	2.083(6)	2.386(3)	6.029(4)	4.769(3)	34
[Cu(bpzm)$_2$(μ-Cl)$ReCl_3$(μ-ox)Cu(bpzm)$_2$(μ-ox)$ReCl_3$(μ-Cl)]$_n$	$\mu_{1,2,3}$	2.599(11)	3.068(4)	2.051(8)	2.338(6)	6.478(10)	4.898(4)	here

[a]Abbreviation for the ligands: ox = oxalate dianion, bipy = 2,2'-bipyridine, phen = 1,10-phenanthroline, terpy = 2,2':6,2"- terpyridine, pyim = 2-(2-pyridyl)imidazole, NBu_4^+= tetra-*N*-butylammonium cation, Him = imidazole; L_β = *N-dl*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene, DMF = *N, N* -dimethylformamide, L = 6,13-bis(dodecylaminomethylidene)-1,4,8,11-tetraazacyclotetradeca-4,7,11,14-tetraene, L_α = N-*meso*-5,12-Me_2-7,14-Et_2-[14]-4,11-dieneN_4,