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Molecular structure, optical and magnetic properties of free-base tetrapyrazinoporphyrazine in various reduction states

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Supporting information

IR- spectra

Table S1. IR-spectra (cm⁻¹ in KBr) of starting compounds and salts **1-3**.

Components	cryptand[2.2.2]	Cp ₂ Fe ₂ (CO) ₄	C ₆ H ₄ Cl ₂	H ₂ TPyzPz	1	2	3
H ₂ TPyzPz				444m	444m	444m	444w
				571w	571w*	571w*	562w*
				633s	635m	634m	636m
				669w	-	668m	-
				726s	732m*	735m*	735m*
				752s	752w*	758m*	750w*
				800s	800m	790m	791m
				864m	865w	859w	-
				891s	890w	882w	882w
				-	950m	950s	948m
				993m	-	-	-
				1040s	1031m*	1028m*	1031m*
				-	-	1052s	1052m
				1084w	-	1084s	1087s
				1121s	1124s*	-	1133s*
				-	1149m	1141s	1145s
				1157m	1160s	1158s	1158s
				1198s	1198s	-	-
				1264w	1260s	1260s	1260s
				1294w	1293m*	1300s*	1299s*
				1364s	1358s*	1354s*	1355s*
				-	-	1415s	1410s
				-	1474m	1476m	1478w
				1501m	1507w	1498w*	1505w
				1560w	1562w	1569m	1563w
				-	-	1586s	1586s
				-	-	1606m	1606m
				3051w	3059w	3045w	3058w
			3286w	3302w	3337w	3336w	
cryptand[2.2.2]	476w				468w	-	-
	528w				522w	525w	522w
	581w				571w*	571w*	-
	735m				732m*	735m	734m*
	922m				932m	933m*	932w
	1038w				1031m*	1028m*	1031m*
	1071m				-	-	-
	1100s				1101s	1103s	1103s

	1127s				1124s*	-	1133s*
	1213w				-	1211m	1210m
	1295m				1293m*	1300s*	1299s*
	1329m				-	1332w	1333w
	1360s				1358s*	1354s*	1355s*
	1446m				1445s	1443w	1443w
	1462m				1453s*	1458w*	1456m*
	2790w				-	-	-
	2877w				2875m	2883m	2880m
	2943w				-	-	-
C ₆ H ₄ Cl ₂			653m		658m	655w	649m*
			757m		752w*	758m*	750w*
			1035w		1031m*	1028m*	1031m*
			1456s		1453s*	1458w*	1456m*
Cp ₂ Fe ₂ (CO) ₄		542w					544w
		565w					562w*
		595w					-
		648m					649m*
		830w					833w
		1016w					-
		CO					CO
		1756s					1765s
		1771s					-
		1936s					1930m
		1956s					1975s
		CH					CH
		3113w					-

* - bands are coincided

w – weak intensity, m –middle intensity, s – strong intensity

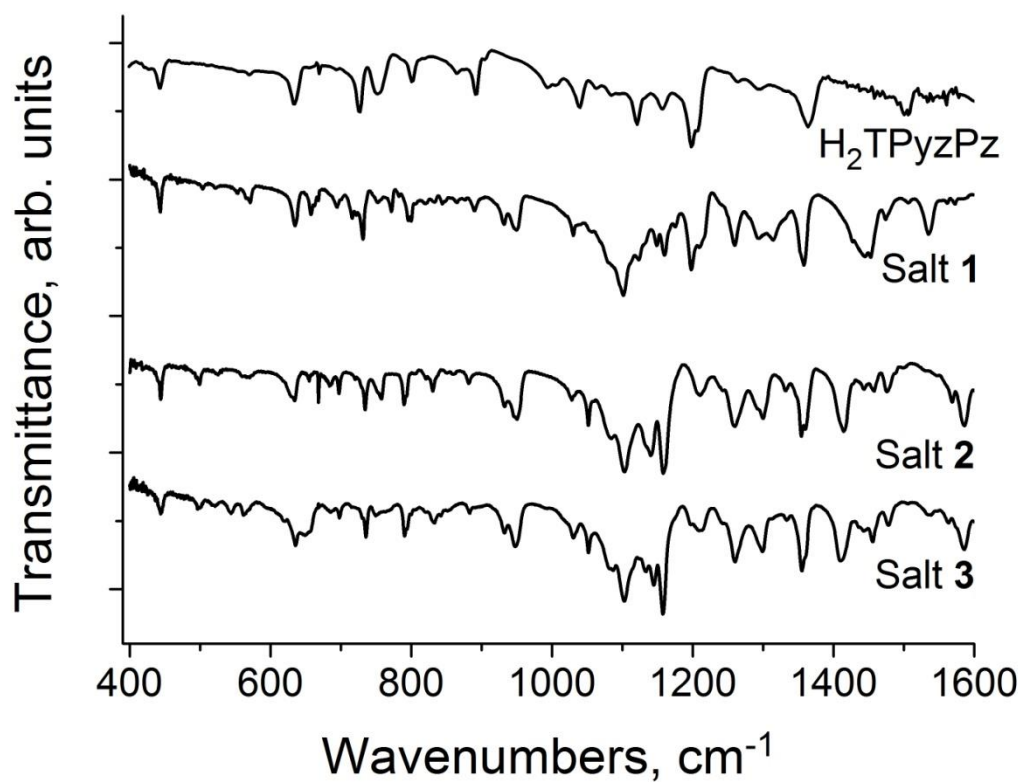


Figure S1. IR spectra of neutral H₂TPyzPz and salts 1-3 in KBr pellets prepared in anaerobic condition.

Table S2. Geometric parameters for phthalocyanine and tetrapyrroline macrocycles in different compounds and according to DFT calculations.

Compound	Charge state of the macro cycle	Average length of the bonds, Å, and bond angles in °.		
		C-N _{pyr} , angle CN _{pyr} C (in pyrrole ring*)	C-N _{pyr} , angle CN _{pyr} C (in pyrroline ring*)	C-N _{meso} short/long, difference
Pristine H ₂ Pc [1]	0	1.373(4), 109.77°	1.373(4), 108.03°	1.327(2)
(Bu ₄ N ⁺) ₂ (H ₂ Pc ^{•-})(Br ⁻) [2]	-1	1.381(9), 112.06°	1.370(9), 106.58°	1.303(8)/1.363(8), 0.060
(Pr ₄ N ⁺) ₂ (H ₂ Pc ^{•-})(Br ⁻) [2]	-1	1.389(3), 112.39°	1.373(3), 106.47°	1.309(3)/1.367(3), 0.058
Salt 1 for two of three independent macrocycles	-1	1.369(3), 110.87° 1.367(3), 110.26°	1.364(3), 108.53° 1.364(3), 108.35°	1.324(3)/1.335(3), 0.011 1.325(3)/1.334(3), 0.009
Salt 2	-2	1.395(4), 113.03° 1.395(4), 113.40°	1.373(4), 107.67° 1.374(4), 107.22°	1.291(4)/1.378(4), 0.087 1.290(4)/1.382(4), 0.092
Salt 3	-2	1.398(2), 112.98° 1.390(3), 112.66°	1.370(2), 107.60° 1.367(3), 108.17°	1.289(2)/1.374(2), 0.085 1.297(3)/1.371(3), 0.074
Salt 4 [3]	-2	1.384(2)		1.284(2)/1.376(2), 0.092
Pristine H ₂ TPyzPz (DFT) [3]	0	1.386, 113.38°	1.374, 107.82°	1.318/1.336, 0.018
H ₂ TPyzPz ^{•-} (DFT) [3]	-1	1.388, 113.66°	1.381, 108.17°	1.325/1.338, 0.013
H ₂ TPyzPz ²⁻ (DFT) [3]	-2	1.403, 113.32°	1.378, 108.86°	1.303/1.367, 0.064
*pyrrole ring contains nitrogen atoms with hydrogen pyrroline ring contains nitrogen atoms without hydrogen				

EPR measurements

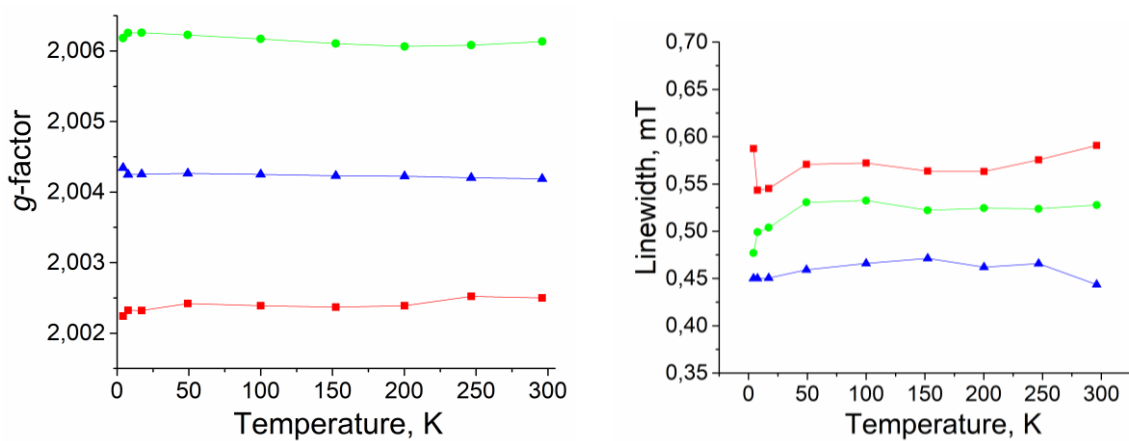


Figure S2. Temperature dependence of g-factor and linewidth of lines manifested in the EPR spectrum of salt **1**.

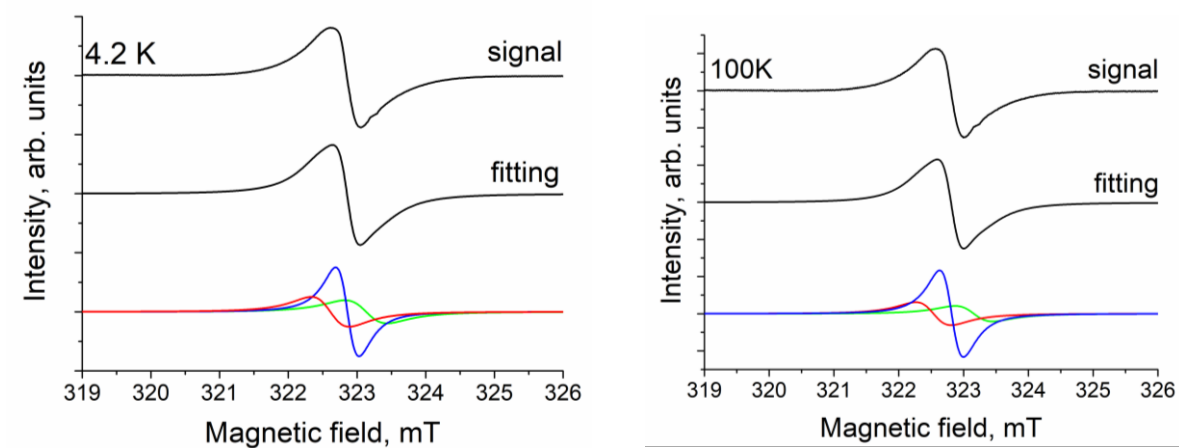


Figure S3. Examples of EPR spectra of polycrystalline **2** at 4.2 and 100 K.

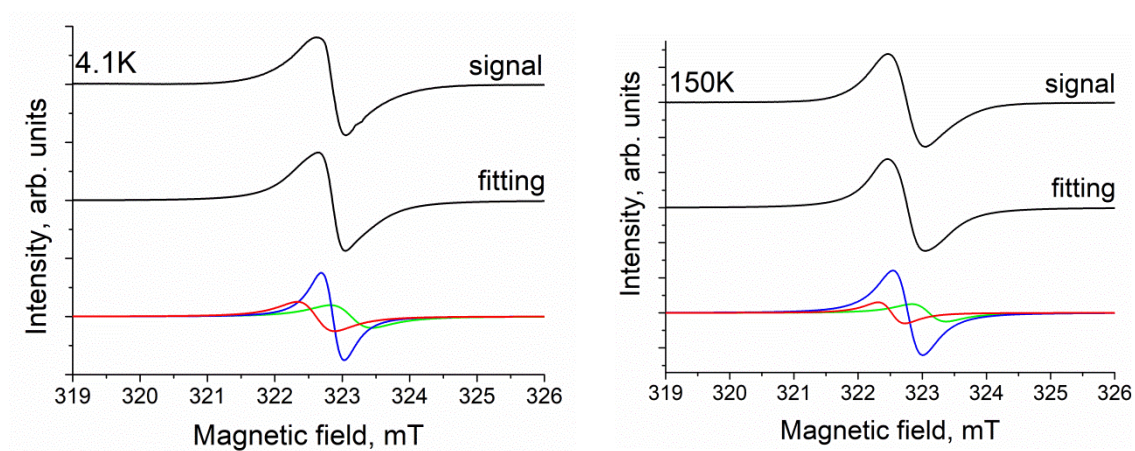


Figure S4. Examples of EPR spectra of polycrystalline **3** at 4.2 and 150 K.

References

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