

**Reaction of Ga<sup>III</sup>ClPc, Sn<sup>IV</sup>Cl<sub>2</sub>TPP and B<sup>III</sup>ClSubPc with cyanide anions: reduction of  
macrocycles vs formation of cyano-containing macrocyclic anions.**

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## SUPPORTING INFORMATION

**Table S1.** IR spectra of starting compounds and salts **1** and **2**.

Components	Cryptand [2.2.2]	Ga <sup>III</sup> ClPc	{crypt(K <sup>+</sup> )} {Ga <sup>III</sup> CN(Pc <sup>3-</sup> )} <sup>•-</sup> ·0.5C <sub>6</sub> H <sub>4</sub> Cl <sub>2</sub> ( <b>1</b> )	Sn <sup>IV</sup> Cl <sub>2</sub> TPP	{crypt(K <sup>+</sup> )} {Sn <sup>IV</sup> (CN) <sub>2</sub> [TPP(CN) <sub>3</sub> ] <sup>-</sup> } <sup>-</sup> ( <b>2</b> )
Metal macrocycle		430w	438w	439w	438w
		507w	503w	475w	490w*
		572w	570w	534w	-
		733s	712s 718s	560w	550w
		755m	753s*	615w	628w
		780m	766s	660w	660w
		897m	892w	702s	704s
		1062s	1054m	753s	758s 771m
		1121s	1118s*	802s	792m
		1169m	1169s	846w	844w
		1288m	1267w	1025s	1015m 1018m
		1332s	1327s*	1073s	1067s
		1423m	1422s	1109w	1107s*
		1467w	1466s	1175w	1158w 1177w
		1484w	-	1210m	1205w
		1506m	1512w	1237w	1240w 1266m
		1608w	-	1304w	1300m*
		-	CN (2179w)	1346w	1352w
		3050w	CH (3050w)	1382w	1372m
				1440m	1420s 1440m*
				1472m	1474vs*
				1518w	1540m 1574w
				-	1596w
				-	CN (2150w)
				-	CN (2240w)
				2851w	2884w*
				2923w	2920w
			3056w	3056w	
Cryptand(M <sup>+</sup> )	476w	-	-	-	490w*
	528w	-	-	-	-
	581w	-	586w	-	-
	735m	-	735w	-	932w
	922m	-	925m	-	951m
	948w	-	940w	-	-
	982m	-	999w	-	1031w
	1038w	-	-	-	-
	1071m	-	1089s	-	1107s*
	1100s	-	1101s	-	1135m
	1127s	-	1118s*	-	1223w
	1213w	-	-	-	1300m*
	1295m	-	1292m 1300m	-	1327w
	1329m	-	1327s*	-	1360w
	1360s	-	1355m 1381m	-	1440m
	1446m	-	-	-	1447m
	1462m	-	1454s*	-	1474vs*
	1490w	-	-	-	-
2790w	-	2820w	-	2812w	
2877w	-	2868w	-	2884w*	
2943w	-	2960w	-	2957w	
C <sub>6</sub> H <sub>4</sub> Cl <sub>2</sub>			659w		
			753s*		
			-		
			1454s*		

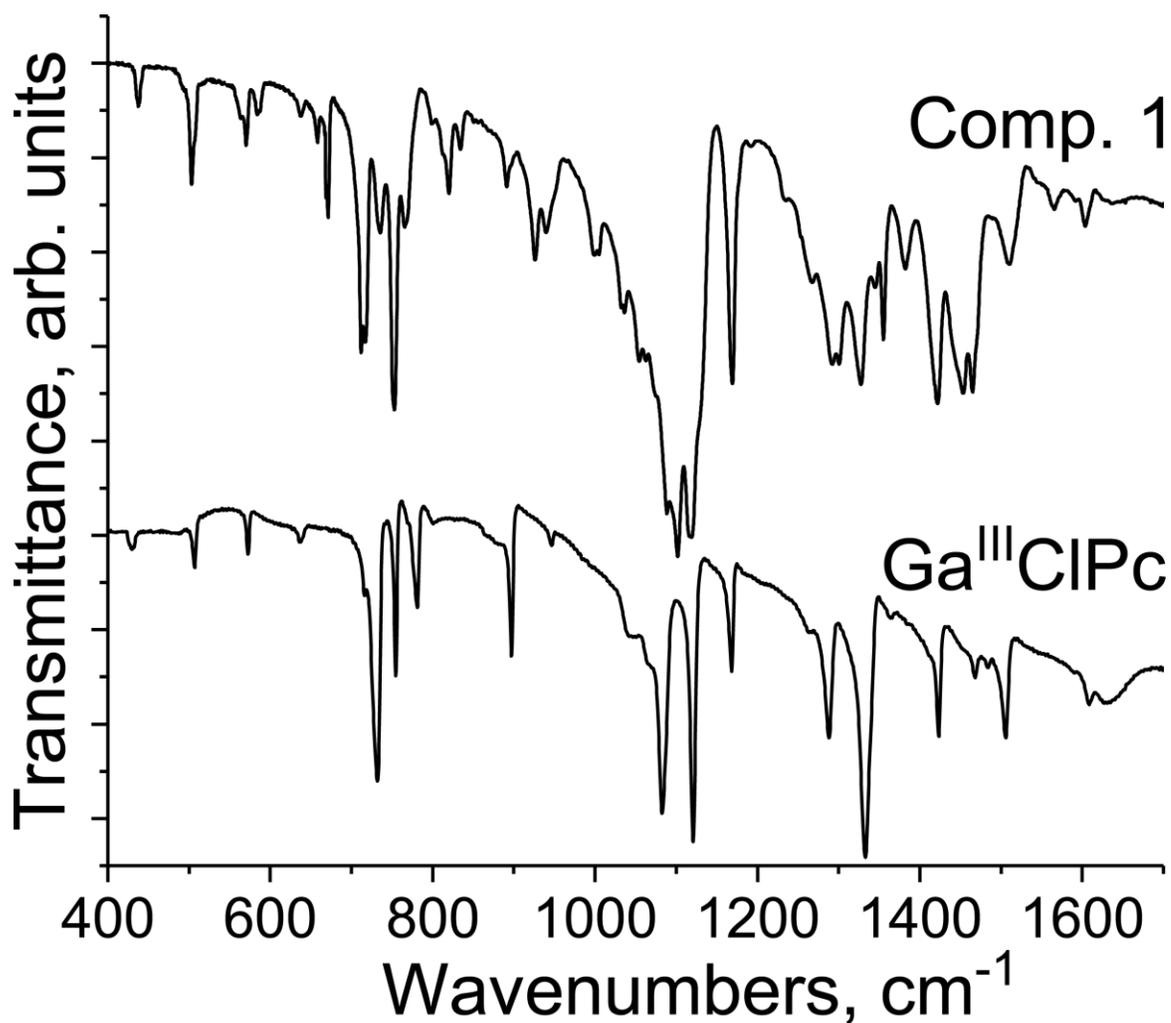
\* - bands coincide; w – weak intensity, m –middle intensity, s – strong intensity

**Table S2.** IR spectra of starting compound and salt **3**.

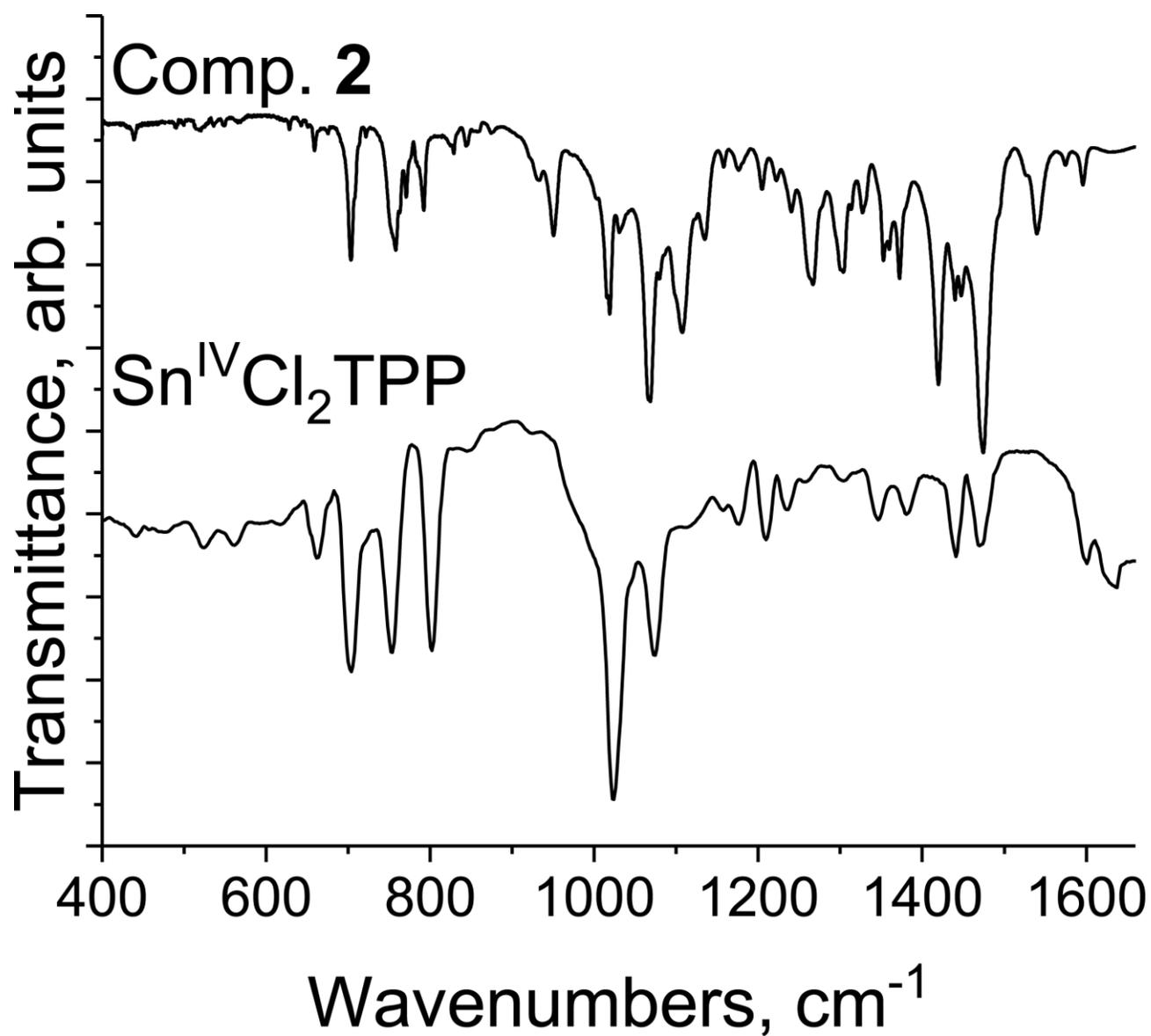
Components	B <sup>III</sup> ClSubPc	{crypt(K <sup>+</sup> )} <sub>2</sub> {B <sup>III</sup> (CN) (SubPc(CN) <sub>2</sub> ) <sub>2</sub> } <sub>2</sub> <sup>2-</sup> ·3C <sub>6</sub> H <sub>4</sub> Cl <sub>2</sub> ( <b>3</b> )
Metal macrocycle	444w	441w
	631w	-
	697w	681w
	750vs	740s*
	758m	750s*
	797w	772m
	880w	877w
	951m	951s*
	960m	976w*
	1088w	1080s*
	1130s	1132s*
	1150w	-
	1196w	-
	1231m	1259w
	1281s	1283w
	1321w	1324m*
	1386m	1384m
	1432s	-
	1440s	-
	1453s	1456m*
	1491w	1471m*
	-	1580m
	-	1613s 1640s
	-	CN (2130w)
	-	CN (2170w)
	-	CN(2233w)
	2853w	2885w
2925w	-	
3058w	3058w	
Cryptand(K <sup>+</sup> )		-
		525w
		-
		740s*
		931m
		951s*
		976w*
		1032w*
		1080s*
		1102vs
		1132s*
		-
		1300w
		1324m*
		1355s 1360s
	-	
	1456m*	
	1471m*	
	2815w	
	2886w	
	2950w	
C <sub>6</sub> H <sub>4</sub> Cl <sub>2</sub>		658w
		750s*
		1032w*
		1456m*

\* - bands coincide, w – weak intensity, m –middle intensity, s – strong intensity

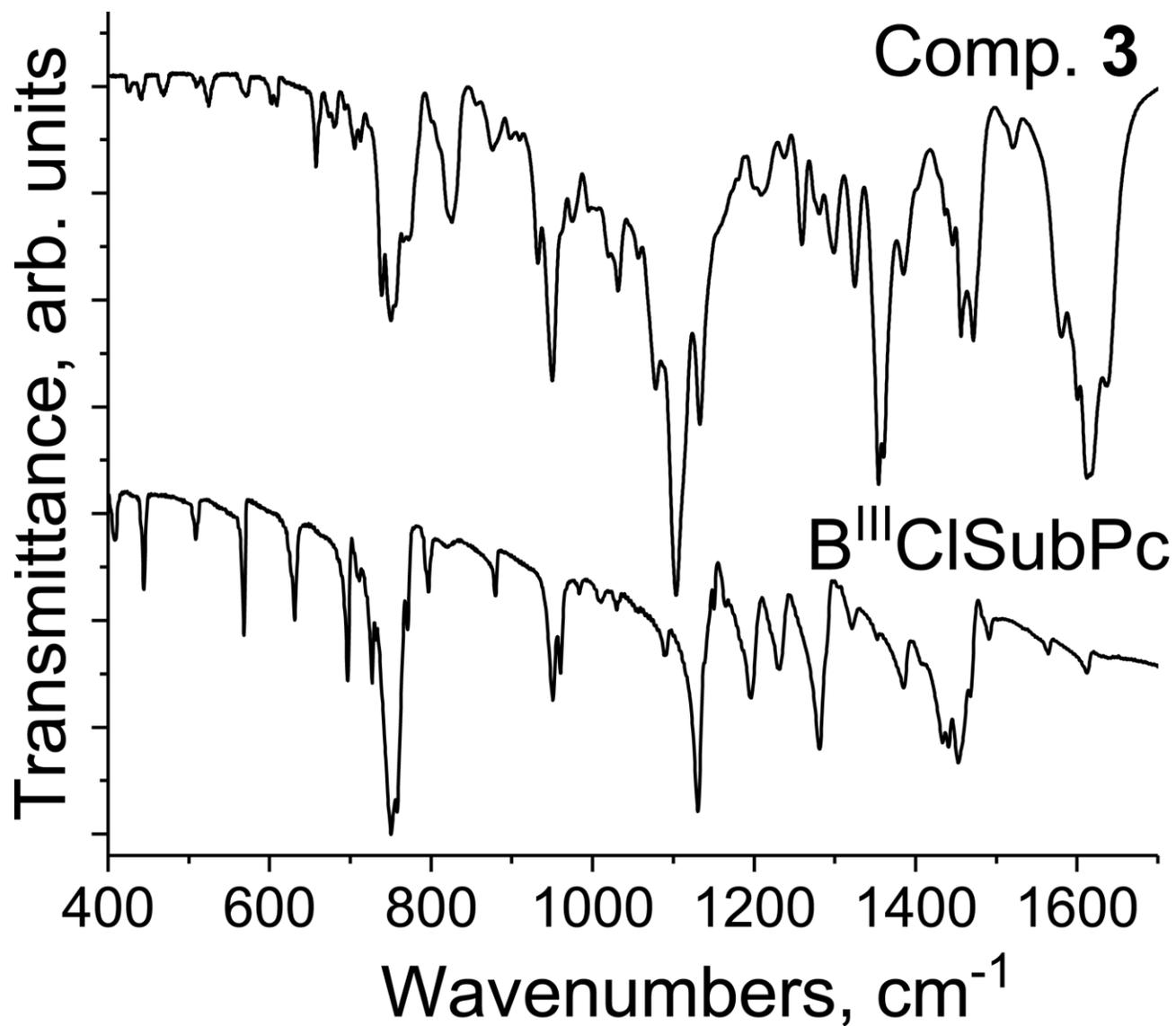
IR spectra of starting metal phthalocyanines and obtained salts.



**Figure S1.** IR spectra of pristine gallium(III) chloride phthalocyanine  $\text{Ga}^{\text{III}}\text{Cl}(\text{Pc}^{2-})$  and  $\{\text{crypt}(\text{K}^+)\}\{\text{Ga}^{\text{III}}\text{CN}(\text{Pc}^{\bullet 3-})\}^{\bullet-} \cdot 0.5\text{C}_6\text{H}_4\text{Cl}_2$  (**1**) in KBr pellets. Pellet for **1** was prepared in anaerobic conditions.



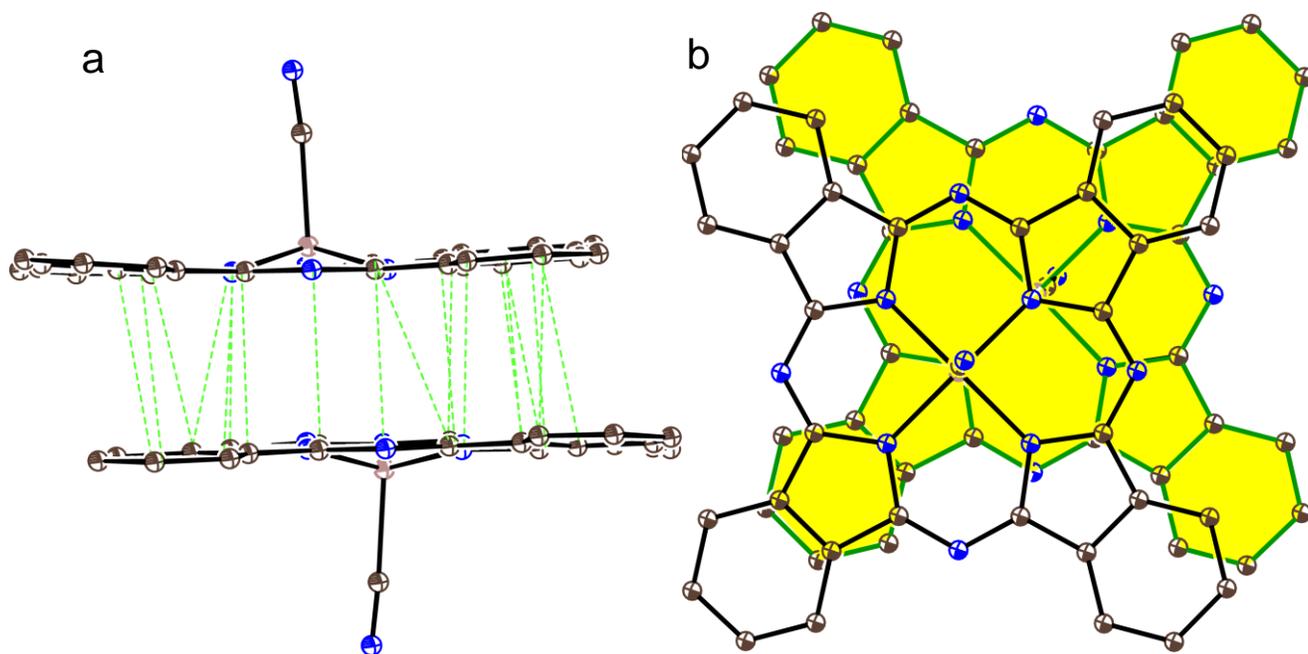
**Figure S2.** IR spectra of pristine Sn<sup>IV</sup>Cl<sub>2</sub>(TPP<sup>2-</sup>) and {crypt(K<sup>+</sup>)}{Sn<sup>IV</sup>(CN)<sub>2</sub>[TPP(CN)<sup>3-</sup>]}<sup>-</sup> (**2**) in KBr pellets. Pellet for **2** was prepared in anaerobic conditions.



**Figure S3.** IR spectra of pristine B<sup>III</sup>Cl(SubPc<sup>2-</sup>) and {crypt(K<sup>+</sup>)<sub>2</sub>[B<sup>III</sup>(CN){SubPc(CN)<sub>2</sub>]}<sub>2</sub><sup>2-</sup>·3C<sub>6</sub>H<sub>4</sub>Cl<sub>2</sub> (**3**) in KBr pellets. Pellet for **3** was prepared in anaerobic conditions.

## Crystal structures

### Compound 1.



**Fig. S4.** View on (a) and along (b) the  $\pi$ -stacking dimer from the  $[\text{Ga}^{\text{III}}(\text{CN})(\text{Pc}^{\bullet 3-})]^{-}$  radical anions. The most distant radical anion of two ones is shown by green bonds and yellow color. Short van der Waals contacts between the radical anions are shown by green dashed lines.

Compound 3.

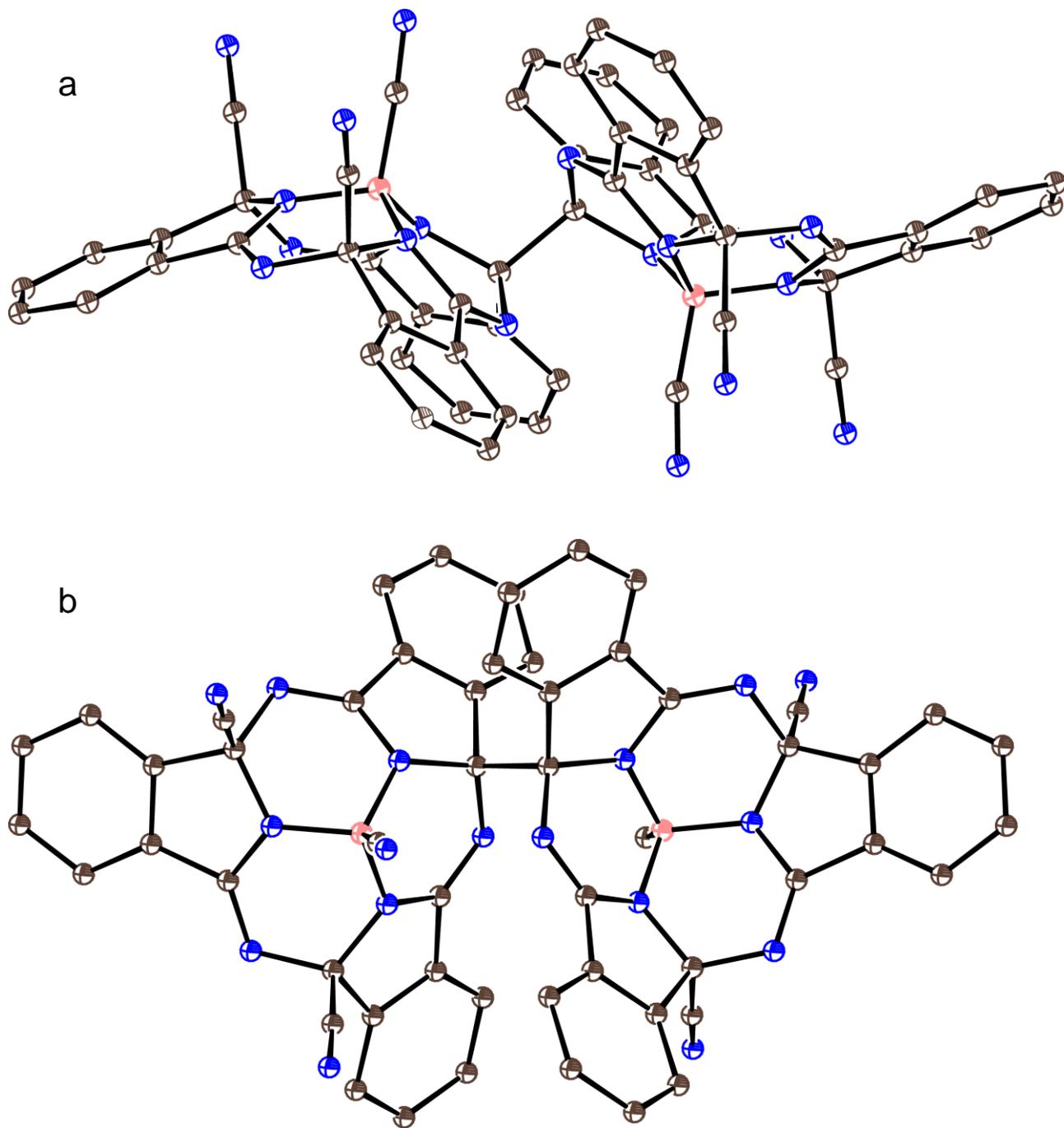
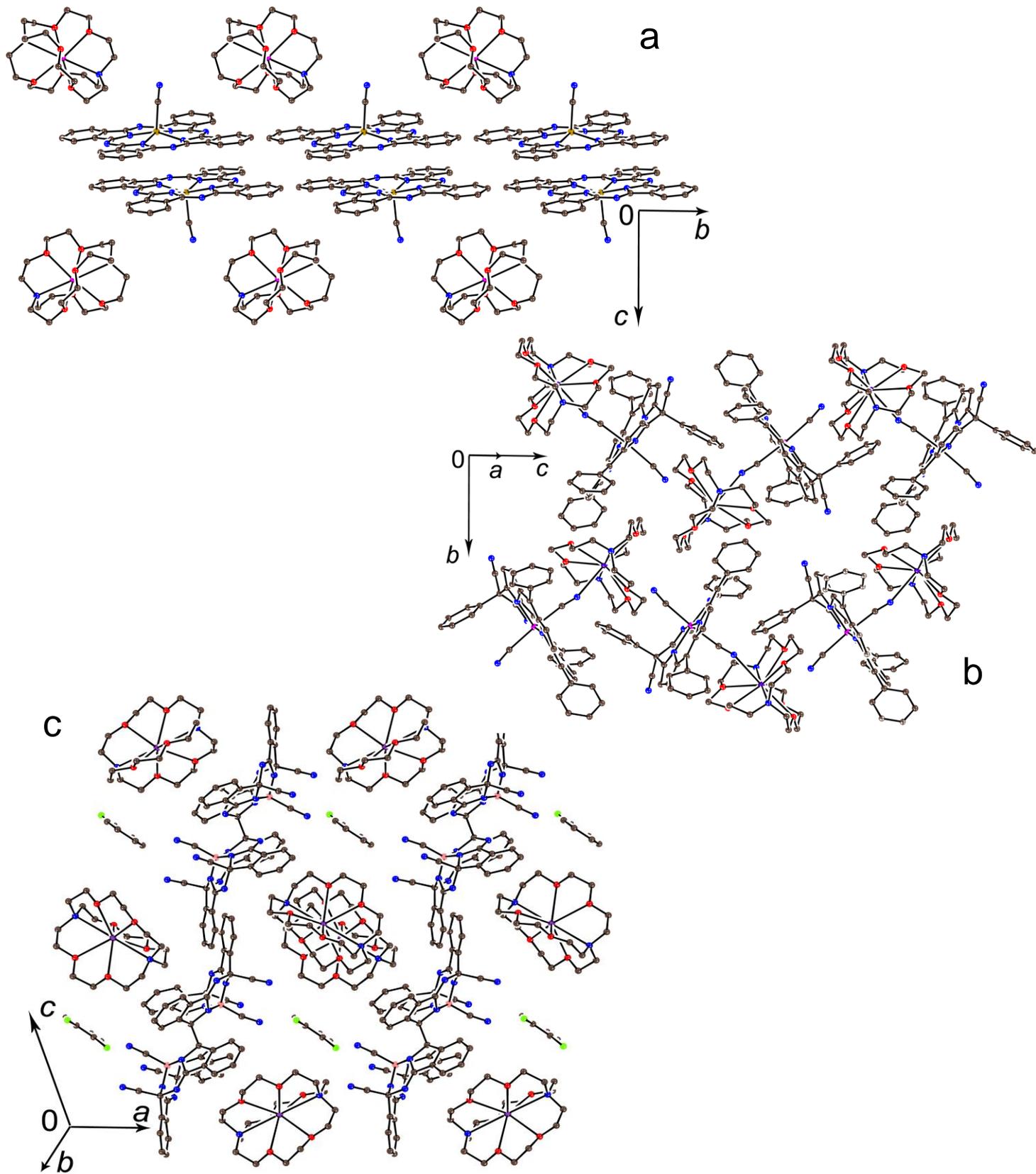
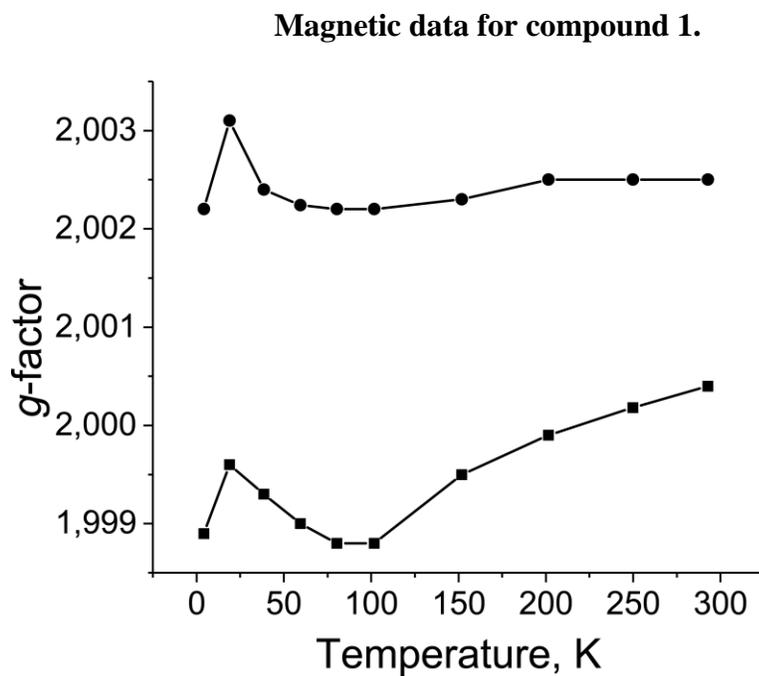


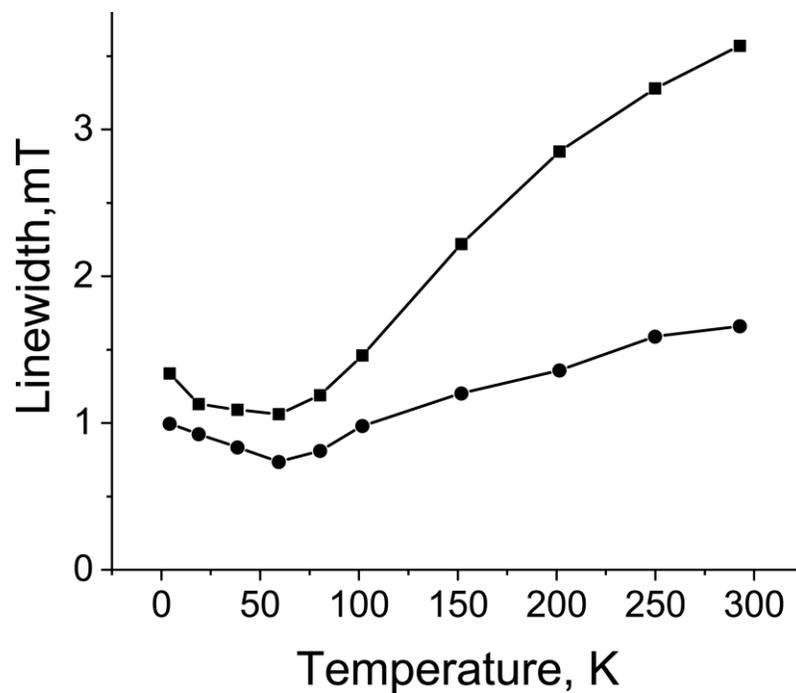
Fig. S5. View on the  $\{B^{III}(CN)[SubPc(CN)_2]\}_2^{2-}$  dimer (a and b).



**Fig. S6.** Crystal structure of compounds: **1** (a); **2** (b); and **3** (c).



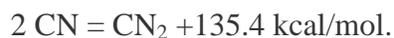
**Fig. S7.** Temperature dependence of  $g$ -factors of two components of EPR signal from polycrystalline **1**.



**Fig. S8.** Temperature dependence of linewidth of two components of EPR signal from polycrystalline **1**.



Substitution of  $\text{Cl}^-$  by  $\text{CN}^-$  in  $\text{Ga}^{\text{III}}\text{Cl}(\text{Pc}^{2-})$  gives the energy gain of 5.4 kcal/mol. Complex  $\text{Ga}^{\text{III}}(\text{CN})(\text{Pc}^{2-})$  (Fig. S9) has high electron affinity of 2.6 eV. However, this value is essentially lower than electron affinity of  $\text{CN}^-$  (3.56 eV). Therefore, reduction of  $\text{Ga}^{\text{III}}(\text{CN})\text{Pc}$  by the  $\text{CN}^-$  anion is thermodynamically possible only in the case of the dimerization of CN.



Cyanide-anion can add to the carbon atom closest to *meso*-nitrogen atom of the  $\text{Pc}^{2-}$  macrocycle with the energy gain of 37.1 kcal/mol, and the  $\{\text{Ga}^{\text{III}}(\text{CN})[\text{Pc}(\text{CN})]^{3-}\}^-$  anions are formed (Fig S10). This gain decreases to 16.3 kcal/mol when calculations were carried out together with the  $\text{crypt}(\text{K}^+)$  counter cation. Addition of second  $\text{CN}^-$  to  $\{\text{Ga}^{\text{III}}(\text{CN})[\text{Pc}(\text{CN})]^{3-}\}^-$  is thermodynamically forbidden since in this case the energy loss is 45.3 kcal/mol.

Energy of the C-CN bond cleavage in  $\{\text{Ga}^{\text{III}}(\text{CN})[\text{Pc}(\text{CN})]^{3-}\}^-$  derived from the calculations is 62.5 kcal/mol and 58.4 kcal/mol when calculations were carried out with or without the counter cation, respectively. Therefore, the  $\{\text{Ga}^{\text{III}}(\text{CN})[\text{Pc}(\text{CN})]^{3-}\}^-$  anion is metastable towards the CN cleavage and their following dimerization:

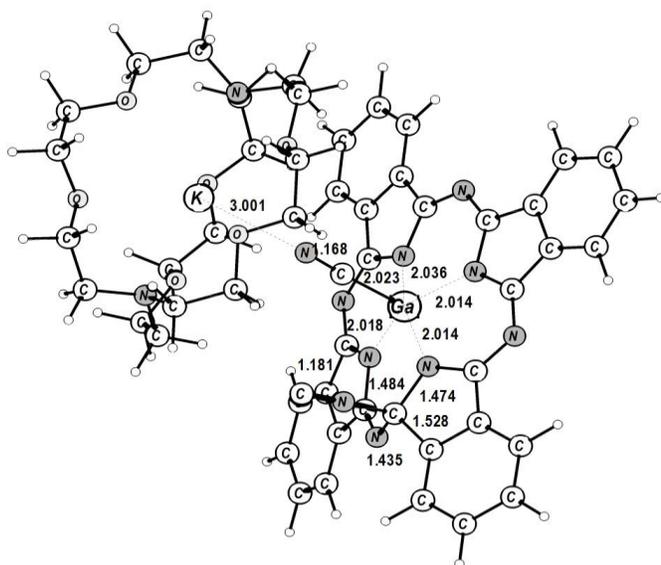


However, this bimolecular reaction cannot occur due to strong shielding of the reaction centers – carbon atoms of the CN substituents.

It should be noted that  $\text{CN}^-$  anions potentially can add to the macrocycle also by nitrogen atom as shown in Fig. S11. In this case energy gain is smaller being only 19.3 kcal/mol. This reaction is almost thermoneutral in the presence of  $\{\text{crypt}(\text{K}^+)\}$  cation:



According to the calculations triplet state of this compound is higher in energy by 16.3 kcal/mol than the ground singlet state. The energy of the C-NC bond cleavage in this compound is 44.2 and 40.6 kcal/mol according to the calculations with or without the counter cation, respectively. However, in this case the reaction centers – carbon atoms of the CN substituents become unshielded.



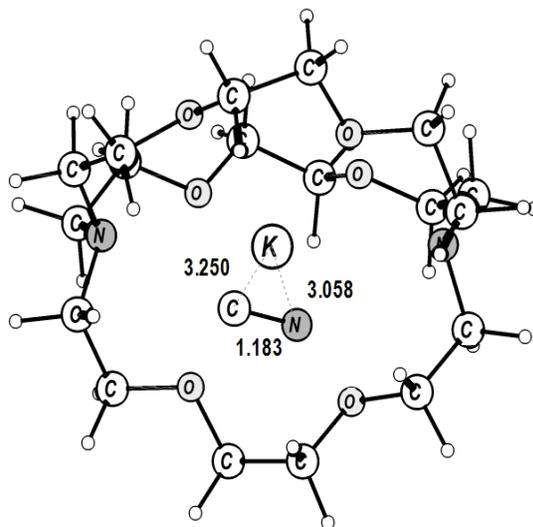
**Fig. S11.** Structure of  $\{\text{crypt}(\text{K}^+)\}\{\text{Ga}^{\text{III}}(\text{CN})[\text{Pc}(\text{NC})]^{3-}\}^-$ .

In this case bimolecular reaction accompanied by the C-NC bond cleavage, the formation of  $\text{Pc}^{\bullet 3-}$  and dimerization of CN occurs with essential energy gain.



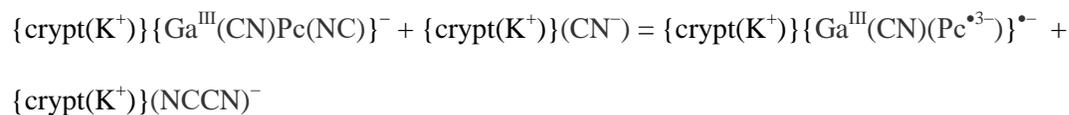
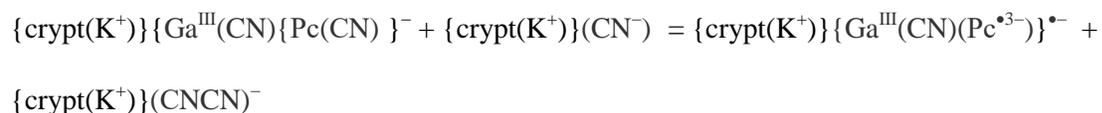
Considering the ionic  $\{\text{crypt}(\text{K}^+)\}(\text{CN}^-)$  pairs in Fig. S12, it is seen that the K-C and K-N distances are close. Configuration with the K-C(N)-N(C) angle =  $180^\circ$  is a transition state for the rotation of  $\text{CN}^-$  in the ionic pair and the energy of this state is higher by several kcal/mol relative to the basic structure shown in Fig. S12. The C and N atoms of  $\text{CN}^-$  are unshielded in the transition state and obviously less shielded in comparison with the terminal C or N atoms of the cyano-group linked to the macrocycle in  $\{\text{Ga}^{\text{III}}(\text{CN})\{\text{Pc}(\text{NC or CN})\}^{3-}\}^-$ . As a result, the reaction of cleavage of

the C-CN bond by the CN<sup>-</sup> anion in the ionic pair is sterically less hindered in comparison with the direct interaction of two {Ga<sup>III</sup>(CN){Pc(NC)}<sup>3-</sup> anions.



**Fig. S12.** Calculated structure of the ionic {crypt(K<sup>+</sup>)}(CN<sup>-</sup>) pair.

As a result, reduction of the macrocycle can occur after the C-CN bond cleavage by CN<sup>-</sup> in the following reactions:

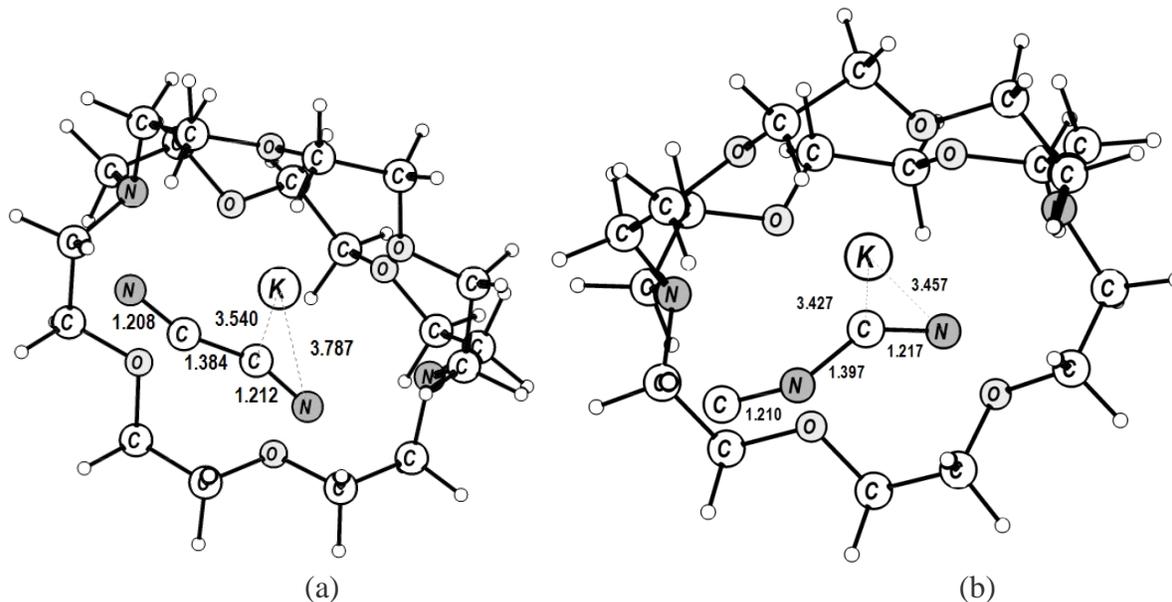


Taking into account the reactions:



it can be concluded that the {Ga<sup>III</sup>(CN)[Pc(NC)]<sup>3-</sup> or {Ga<sup>III</sup>(CN)[Pc(CN)]<sup>3-</sup> anions can eliminate the CN group in the presence of third equivalent of {crypt(K<sup>+</sup>)}(CN<sup>-</sup>) independently on type of the

initial addition of  $\text{CN}^-$  to the macrocycle. Both routes of the  $\text{CN}^-$  addition yield the same reduction product  $\{\text{crypt}(\text{K}^+)\}\{\text{Ga}^{\text{III}}(\text{CN})(\text{Pc}^{\bullet 3-})\}^{\bullet -}$  but probably different side products (shown in Fig. S13).



**Fig. S13.** Structure of ionic pairs  $\{\text{crypt}(\text{K}^+)\}(\text{NCCN})^-$  (a) and  $\{\text{crypt}(\text{K}^+)\}(\text{NCNC})^-$  (b).

### The formation of dimeric complex at cyanation of $\text{B}^{\text{III}}\text{Cl}(\text{SubPc})$ .

Dissolution of  $\text{KCN}$  in *o*-dichlorobenzene in the presence of cryptand[2.2.2] yields soluble ionic  $\{\text{crypt}(\text{K}^+)\}(\text{CN}^-)$  pairs. Calculated energy of the  $\text{CN}^-$  bonding in these pairs is 79.4 kcal/mol.

Substitution of  $\text{Cl}^-$  at the boron(III) atom of  $\text{B}^{\text{III}}\text{Cl}(\text{SubPc}^{2-})$  by  $\text{CN}^-$  is a thermodynamically favorable reaction:



The addition of first  $\text{CN}^-$  to  $\text{B}^{\text{III}}(\text{CN})(\text{SubPc}^{2-})$  yields the  $[\text{B}^{\text{III}}(\text{CN})\{\text{SubPc}(\text{CN})\}]^{3-}$  anion with the large energy gain of 39.5 kcal/mol. On the contrary, the energy loss is 32.5 kcal/mol at the addition of second  $\text{CN}^-$  and the formation of the  $[\text{B}^{\text{III}}(\text{CN})\{\text{SubPc}(\text{CN})_2\}]^{4-}$  dianions. These dianions are strong electron donors since elimination of one electron from them gives the energy gain of 0.7 eV.

As a result, addition of two cyanide anions with simultaneous elimination of one electron provides rather large energy gain of 22.9 kcal/mol in total providing the formation of the  $[B^{III}(CN)\{SubPc(CN)_2\}^{\bullet 3-}]^{\bullet -}$  radical anions. However, according to the calculations these radical anions cannot dimerize due to essential Coulomb repulsion between them, and their dimerization is unfavorable (the energy loss at the dimerization is 23.6 kcal/mol).

In contrast to the  $\{Ga^{III}(CN)[Pc(CN)]^{3-}\}^-$  anion, the C-CN bond energy in the  $[B^{III}(CN)\{SubPc(CN)\}^{3-}]^-$  anion is very high being 72.5 kcal/mol, and it cannot be compensated by the dimerization energy of two CN radicals. In the  $[B^{III}(CN)\{SubPc(CN)_2\}^{4-}]^{2-}$  dianion the C-CN bond energy becomes even higher being 74.7 kcal/mol. Thus, there is only one possible way of the dianion transformation, namely, electron transfer to surrounding solvent molecules.

Taking into account the interaction of the obtained anions or dianions with the  $\{crypt(K^+)\}$  counter cations, both  $CN^-$  additions to  $B^{III}(CN)(SubPc^{2-})$  become thermodynamically possible and even second addition of  $CN^-$  becomes almost a thermoneutral reaction:



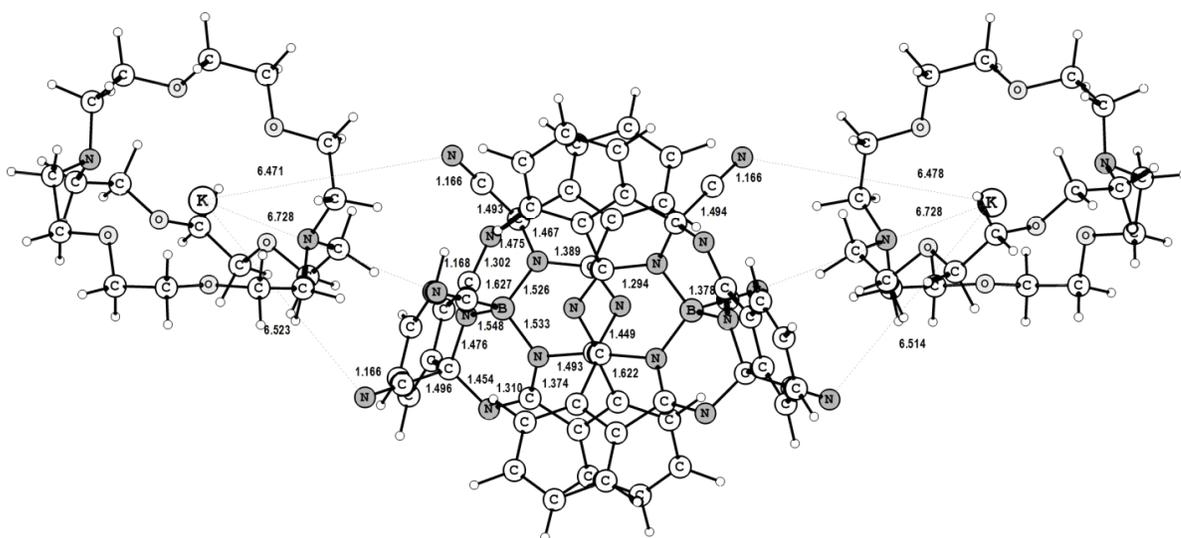
Calculated structures of the salts obtained in these reactions are shown in Fig. S14.



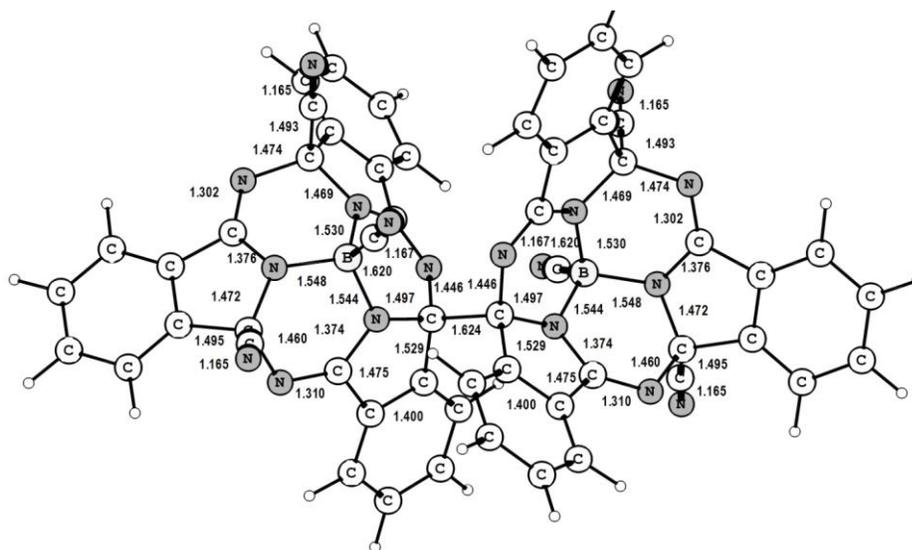
Dimerization in the presence of the {crypt(K<sup>+</sup>)} counter cations which neutralize the effects of Coulomb repulsion also becomes energetically favorable.



Structure of the dimeric product shown in Fig. S15 is close to the experimental structure of the [B<sup>III</sup>(CN){SubPc(CN)<sub>2</sub>}<sup>3-</sup>]<sub>2</sub><sup>2-</sup> dianion. Fig. S16 shows the structure of this dianion whose geometry was optimized without counter cations. It is seen that the structure with or without the counter cations has close geometry indicating a weak effect of counter cations on their geometry.

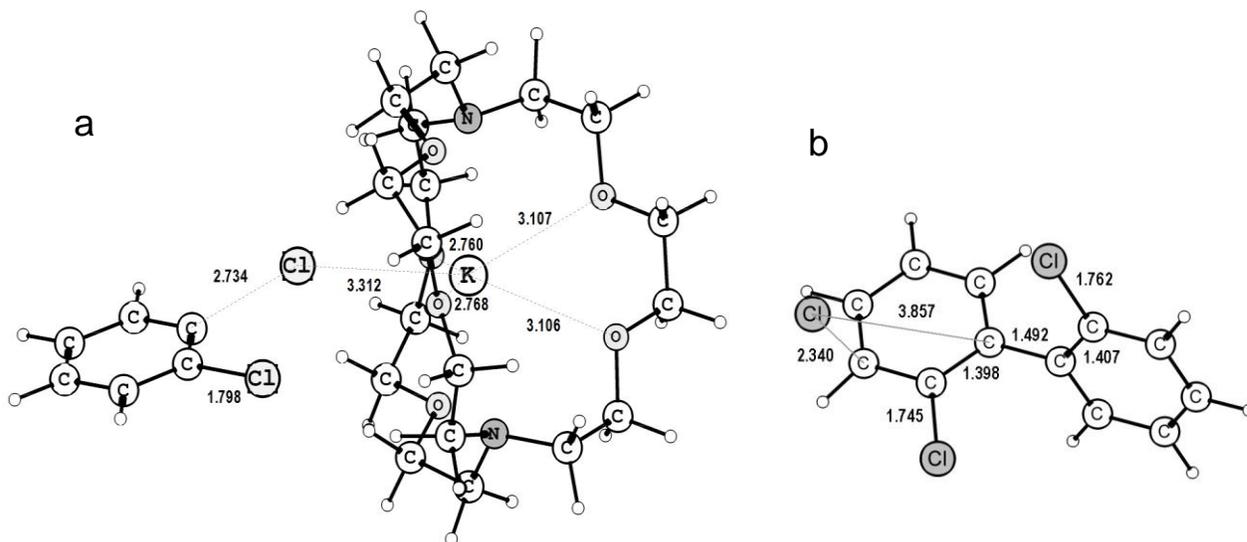


**Fig. S15.** Calculated structure of  $\{\text{crypt}(\text{K}^+)\}_2[\text{B}^{\text{III}}(\text{CN})\{\text{SubPc}(\text{CN})_2\}^{3-}]_2^{2-}$ .



**Fig. S16.** Structure of the  $[\text{B}^{\text{III}}(\text{CN})\{\text{SubPc}(\text{CN})_2\}^{3-}]_2^{2-}$  dianion optimized without counter cations.

The  $[\text{B}^{\text{III}}(\text{CN})\{\text{SubPc}(\text{CN})_2\}^{4-}]^{2-}$  dianion is a strong donor of electron and we suppose that solvent *o*-dichlorobenzene molecules ( $\text{C}_6\text{H}_4\text{Cl}_2$ ) accept an electron from these dianions. The  $(\text{C}_6\text{H}_4\text{Cl}_2)^{\bullet-}$  anions formed at such electron transfer have high interaction energy (71.7 kcal/mol) with the counter cations in ionic pairs (Fig. S17). Pristine  $\text{C}_6\text{H}_4\text{Cl}_2$  has two equal C-Cl bonds of about 2.089 Å length. However, the C-Cl bonds have different length in the reduction product of  $\text{C}_6\text{H}_4\text{Cl}_2$  (Fig. S17a). Interaction with the counter cation leads to decrease of C-Cl dissociation energy from 13.4 to 5.3 kcal/mol. Addition of the  $\text{C}_6\text{H}_4\text{Cl}_2^{\bullet-}$  radical to the solvent  $\text{C}_6\text{H}_4\text{Cl}_2$  molecule is more favorable to the chlorinated carbon atom of  $\text{C}_6\text{H}_4\text{Cl}_2$ , (Fig. S17b) giving the energy gain of 27.2 kcal/mol. Finally, this way leads to the formation of corresponding dichlorobiphenyl.



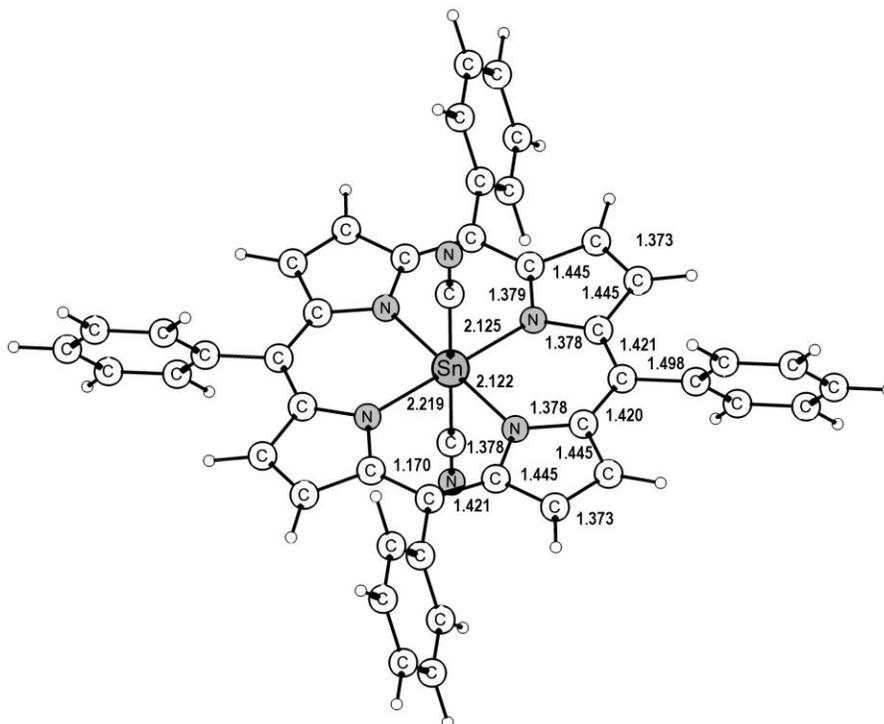
**Fig. S17.** (a) Structure of the ionic  $\{\text{crypt}(\text{K}^+)\}(\text{C}_6\text{H}_4\text{Cl}_2)^-$  pair; (b) structure of the product of  $\text{C}_6\text{H}_4\text{Cl}_2^{\bullet-}$  addition to  $\text{C}_6\text{H}_4\text{Cl}_2$ .

As we discussed above, addition of two  $\text{CN}^-$  with simultaneous elimination of one electron from the formed dianion provides large energy gain even excluding the effect of counter cation. Energy gain of this reaction can be even increased when the effect of counter cations is taken into account. Electron transfer from  $[\text{B}^{\text{III}}(\text{CN})\{\text{SubPc}(\text{CN})_2\}^{4-}]^{2-}$  to  $\text{C}_6\text{H}_4\text{Cl}_2$  requires rather small energy loss of

only 9.4 kcal/mol. Taking into account essential energy gains at the dimerization of  $C_6H_4Cl_2^-$  and the  $[B^{III}(CN)\{SubPc(CN)_2\}^{3-}]^{\bullet-}$  radical anions, it can be concluded that reaction of the formation of dimeric  $[B^{III}(CN)\{SubPc(CN)_2\}^{3-}]_2^{2-}$  bonded by a single C-C bond is very favorable and it becomes irreversible proceeding with large energy release.

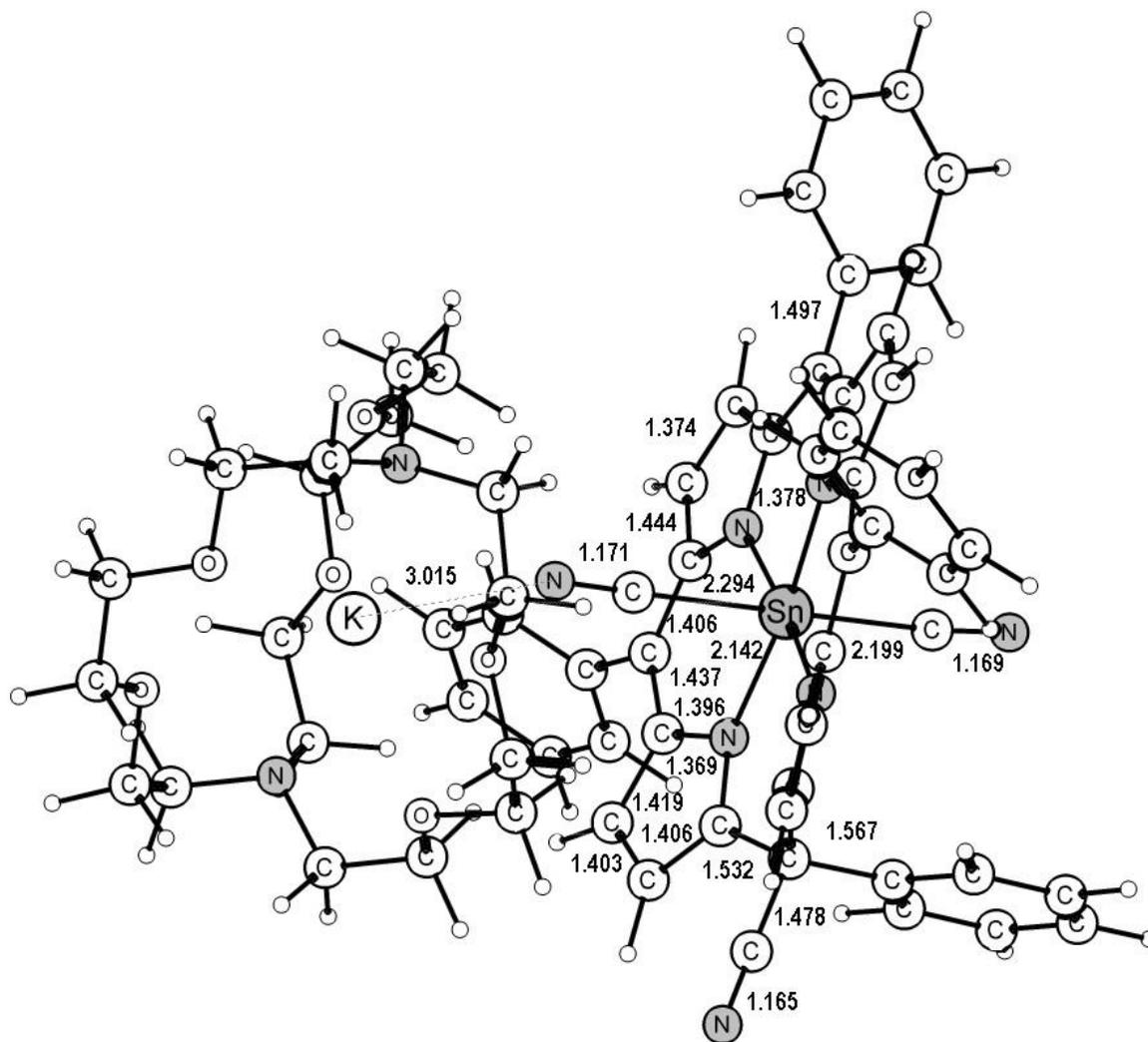
**Reaction of  $\{Sn^{IV}(CN)_2[TPP]^{2-}\}$  with KCN in the presence of cryptand[2.2.2].**

$\{Sn^{IV}(CN)_2[TPP]^{2-}\}$  porphyrin (Fig. S18) has high electron affinity of 2.3 eV. Addition of  $CN^-$  to *meso*-position of this porphyrin gives energy gain of 41.3 kcal/mol. Addition of the second  $CN^-$  anion leads to the formation of metastable system with the energy increase by 31.7 kcal/mol. Detachment of  $CN^-$  from the  $\{crypt(K^+)\}(CN^-)$  pair is also thermodynamically favorable in the presence of counter cation:



**Fig. S18.** Structure of  $\{Sn^{IV}(CN)_2[TPP]^{2-}\}$ .

The structure of the product is shown in Fig 19. Similarly to boron(III) subphthalocyanine,  $\text{Sn}^{\text{IV}}(\text{CN})_2[\text{TPP}(\text{CN})]^{3-}]^-$  has high energy of 69.6 kcal/mol for the elimination of CN radical which cannot be compensated by the dimerization energy of two CN radicals.  $\{\text{Sn}^{\text{IV}}(\text{CN})_2[\text{TPP}(\text{CN})]^{3-}\}^-$  has the singlet ground state with a singlet-triplet gap of 14 kcal/mol.



**Fig. S19.** Structure of  $\{\text{crypt}(\text{K}^+)\}\{\text{Sn}^{\text{IV}}(\text{CN})_2[\text{TPP}(\text{CN})]^{3-}\}^-$ .

## References

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2. W. J. Stevens, H. Basch, M. Krauss *J. Chem. Phys.* 1984, **81**, 6026.
3. D. N. Laikov, *Chem. Phys. Lett.* 1997, **281**, 151.