#### Supporting information.

### Quantum chemical calculations

Theoretical calculations were performed using PBE density functional method<sup>1</sup> and A2 basis<sup>2</sup> of cc-pVTZ quality. Atomic distribution of charge and spin density was determined by the Hirschfeld method.<sup>4</sup> All calculations were performed using the PRIRODA program package<sup>3</sup> at Joint Supercomputer Center of the Russian Academy of Sciences. This approach allows geometry of the dimer in **1** to be well reproduced. Mean deviation of calculated bond lengths from experimental ones is no more than 0.01 Å, for exception of bridging Cr-O bond, which are larger on 0.03 and 0.06 A. Dihedral S-C-C-S and O-C-C-O angles -16.0 and -15.7°, respectively correspond to experimental data -19.2 and -18.6° as well. Experimental and theoretical IR spectra are in a good agreement (see Fig. S10). TD-DFT approach was used for calculations of electronic spectra.

Chemistry of the reactions between thioindigo (TI) and  $Cp*_2Cr$  is greatly affected by a rather low energy difference between ground *trans*-form and *cis*-conformer with respect to indigo. These values are equal to 11.6 (16.7) and 13.4 (20.6) kcal/mol for neutral and negatively charged TI molecule, respectively, corresponding values for indigo are presented in brackets. The reason is the absence of short H-H contacts for *cis*-TI.

The calculated structures of *trans*-TI (a), *cis*-TI (b) and corresponding structures for the radical anion of TI in *trans*- (c), *cis*-forms (d) are shown in Fig. S1. All of them are flat in



**Figure S1.** Calculated structures of isomeric forms of TI molecule in neutral (a, b) and radical anion (c, d) states. Interatomic distances are given in Å and angles are given in degrees.

contrast to indigo<sup>5</sup>. Dianion of TI has practically only one planar *trans*-conformation (Fig. S2a). Nonplanar *cis*-conformation with a dihedral S-C-C-S angle of -16.0° (see Fig. S2b) has by 13.1 kcal/mol higher energy and a negligible energy barrier of 1.2 kcal/mol of transformation into the ground *trans*-form. In the transition state of isomerization, the dihedral S-C-C-S angle is equal to -38.1°.

At the interaction of Cp\*<sub>2</sub>Cr with TI, a triplet outer-sphere charge transfer complex  $(Cp*_2Cr^+)(trans-TI^{\bullet-})$  (I) is formed with an energy gain of 8.5 kcal/mol. Its structure is shown in Fig. S3a. The presence of a large dipole moment D(T) = 10.4 D indicates intermolecular charge transfer in this complex. The initial centrosymmetric molecules of *trans*-TI and Cp\*<sub>2</sub>Cr do not have a dipole moment. Spin density at the Cr atom of I is 2.29 indicating the contribution of two states close to energy  $|T_1>$ , with charge transfer, and  $|T_2>$ , without charge transfer, to the ground triplet state of a system:

$$|T > = c_1 |T_1 > + c_2 |T_2 >$$
 (1)

Individual triplet state  $|T_1\rangle$  is formed at the antiparallel orientation of spins on the Cr(III) center with the high-spin d<sup>3</sup> configuration and the TI<sup>-</sup> radical anion. It is a superposition of the configurations

$$|T_1 \rangle = (3|d_1\alpha \ d_2\alpha \ d_3\alpha \ \pi\beta \rangle - |d_1\beta \ d_2\alpha \ d_3\alpha \ \alpha \ \pi\rangle - |d_1\alpha \ d_2\beta \ d_3\alpha \ \pi \ \alpha \rangle - |d_1\alpha \ d_2\alpha \ d_3\beta \ \pi \ \alpha \rangle)/\sqrt{12}$$

where  $d_1$ ,  $d_2$ ,  $d_3$  is the lower triplet of the single-occupied d-orbitals of Cr (III) and  $\pi$  is LUMO thioindigo, and  $|T_2\rangle = |d_1\alpha d_1\beta d_2\alpha d_3\alpha \rangle$ . Taking into account small overlapping of wave functions of the subsystems in the outer-sphere complex, the theoretical value of spin on the Cr(III) atom is equal to 2.5 for  $|T_1\rangle$  and 2 for  $|T_2\rangle$ . Coefficients  $c_1$  and  $c_2$  in the superposition (1) can be estimated approximately from the dipole moments.

The quintet state  $|Q\rangle = |d_1 \alpha d_2 \alpha d_3 \alpha \pi \alpha \rangle$  of outer-sphere complex I with parallel orientation of Cr(III) spin and the TI<sup>-</sup> radical anion is higher in energy by 7.9 kcal/mol. In this case, spin density on the Cr atom = 3.02, and charge on the Cp\*<sub>2</sub>Cr fragment increases from 0.31 to 0.57.



**Figure S2.** Calculated structures of isomeric forms of TI dianion (a, b). Interatomic distances are given in Å and angles are given in degrees.

Accordingly, the dipole moment increases to 18.3 D. Based on calculated charges and dipole moments, it is possible to find the effective length of the dipole arising during charge transfer, 7.0 and 6.7 Å for the triplet and quintet complex, respectively, which is in complete agreement with the difference in the Cr-O interatomic distances, 4.8 and 4.4 Å, in these complexes. Since the dipole moment is small for a state without charge transfer, then we can assume  $(c_1)^2 = D(T)/D(Q)$ , if the cross term is neglected, taking into account the weak overlapping of the wave functions of the subsystems in outer-sphere complex I.

For fixed geometry of a triplet complex, D(Q) = 19.9. This gives the value  $(c_1)^2 = 0.523$ , which spin density on the Cr 2.26 atom follows from. The energy of the formation of a similar complex with *cis*-TI (Cp\*<sub>2</sub>Cr<sup>+</sup>)(*cis*-TI<sup>•-</sup>) (**II**) increases to 11.8 kcal/mol due to a closer approach of two carbonyl groups to the Cr atom (see Fig. S3b). This energy exceeds the isomerization energy of the TI molecule. As a result, this complex has small stability of 0.2 kcal/mol relative the main isomer *trans*-TI and Cp\*<sub>2</sub>Cr complex. This is a significant difference in stability as compared to similar outer-sphere charge transfer complexes with the indigo (Ind) molecule. As



**Figure S3.** Calculated structures of outer-sphere complexes  $(Cp*_2Cr^+)(trans-TI^{\bullet-})$  (I) (a)  $(Cp*_2Cr^+)(cis-TI^{\bullet-})$  (II) (b) and the transition state of their interconversion (c). The H atoms of the C-H bonds are omitted for clarity. Interatomic distances are given in Å and angles are given in degrees.

the previous theoretical investigation shows<sup>5</sup> in this case both  $(Cp*_2Cr^+)(Ind^{\bullet-})$  complexes of type I and II turn out to be metastable with respect noninteracting  $Cp*_2Cr$  and *trans*-Ind.

The *cis*-TI molecule has a dipole moment of 3.72 D, and this moment is directed opposite to the dipole moment of outer-sphere complex **II** with charge transfer of 8.05 D. Thus, we can estimate the dipole moment for charge transfer 11.77 D and find the effective dipole length 6.8 Å taking into account the 0.36 charge on the Cp\*<sub>2</sub>Cr fragment. The increase in charge transfer is accompanied by the increase in spin density on the Cr atom to 2.41. The outer-sphere complex with the opposite orientation of the *cis*-TI molecule (**III**) is unfavorable for the ion-dipole interaction. It leads to the increase in its energy by 9.0 kcal/mol and the decrease in charge transfer to 0.23. Taking into account the dipole moment of the cifective dipole length 7.7 Å, which agrees with the mean Cr-S distance of 6.13 Å in the complex. In the outer-sphere complexes, the



**Figure S4.** Calculated structures of the (*trans*-TI-*O*)Cp\*<sub>2</sub>Cr (**IV**) complexes in triplet (a) and quintet states (b); and that of the (*cis*-TI-*O*)Cp\*<sub>2</sub>Cr complex (**V**) in quintet state (c) and the transition state (d) of interconversion of outer-sphere (*cis*-TI<sup>•–</sup>)(Cp\*<sub>2</sub>Cr<sup>+</sup>) complex **II** with triplet state into (*cis*-TI-*O*,*O*)Cp\*<sub>2</sub>Cr (**VI**). The H atoms of the C-H bonds are omitted for clarity. Interatomic distances are given in Å and angles are given in degrees.

geometry of the subsystems is intermediate between the geometry of  $Cp*_2Cr$  (mean Cr-C(Cp\*) distance is 2.177 Å and  $Cp*_2Cr^+$  (mean Cr-C(Cp\*) distance is 2.228 Å) and the corresponding isomer of the TI molecule and its radical anion (see Fig. S1) and qualitatively agrees with the degree of intramolecular charge transfer.

Note that isomerization of the TI molecule from *trans*- to *cis*-form in the outer-sphere complex requires a significant activation energy, namely, 27.2 kcal/mol. The structure of the transition state is shown in Fig. S3c. The Cr-O distance decreases to 4.39 Å and charge transfer increases to 0.44 in the transition state.

The entry of the TI-ligand into the internal coordination sphere of chromium leads to the formation of one Cr-O coordination bond of 2.35 Å length providing the  $\eta^5$ - $\eta^3$ -shift of both rings (see Fig. 4a), and therefore, it is accompanied by an increase in energy. Nevertheless, it is more stable by 4.1 kcal/mol than noninteracting components. The corresponding quintet complex has practically the same energy (higher by 0.1 kcal/mol) and a close geometry (see Fig. S4b). For both complexes, spin density on the Cr atom of 2.83 and 2.86, respectively, and charge on Cp\*<sub>2</sub>Cr of +0.48 are close. When the quintet *trans*-complex is isomerized into *cis*-complex (see Fig. S4c) with one coordination Cr-O bond, its energy slightly increases by 3.6 kcal/mol. The complex of similar structure in a triplet state (see Fig. S4d) is positioned below the quintet state by 0.7 kcal/mol, but it turns out to be a transition state of transformation of outer-sphere *cis*-complex II (see Fig. S3b) into *cis*-complex VI with two Cr-O coordination bonds (See Figure S5a). That indicates different topology of the potential energy surface of triplet and quintet states.



**Figure S5.** Calculated structures of triplet complex (*cis*-TI-O,O)Cp\*<sub>2</sub>Cr (**VI**) (a) and of transition state of interconversion of quintet (*trans*-TI-O)Cp\*<sub>2</sub>Cr complex (**IV**) into (*cis*-TI-O,O)Cp\*<sub>2</sub>Cr (**V**) (b). The H atoms of the C-H bonds are omitted for clarity. Interatomic distances are given in Å and angles are given in degrees.

Transition state of the interconversion of quintet (*trans*-TI-O)Cp\*<sub>2</sub>Cr complex (**IV**) into quintet (*cis*-TI-O,O)Cp\*<sub>2</sub>Cr (See Fig. S4b) is located by 18.8 kcal/mol higher than quintet (*trans*-TI-O)Cp\*<sub>2</sub>Cr complex (**IV**).

The transition state for the transformation of triplet (*trans*-TI-*O*)Cp\*<sub>2</sub>Cr complex (**IV**) into triplet complex (cis-TI-*O*,*O*)Cp\*<sub>2</sub>Cr (**VI**) failed to localize. It should be assumed that it is lower in energy of the above quintet transition state according to the Polanyi-Semenov rule, since in this conversion the energy decreases by 5.8 kcal/mol and does not increase. One of the Cp\* rings is in the  $\eta^1$ -coordination in (*cis*-TI-*O*,*O*)Cp\*<sub>2</sub>Cr (**VI**) complex and therefore is weakly bound.

It was found from the calculations that the interaction of the *trans*-TI molecule with Cp\*<sub>2</sub>Cr to form (*trans*-TI<sup>•-</sup>)(Cp\*<sub>2</sub>Cr<sup>+</sup>) complex (I) is accompanied by a decrease in energy by 8.5 kcal/mol. Its transformation into a (*cis*-TI-O,O)Cp\*<sub>2</sub>Cr (II) complex leads to a slight increase in energy by 2.5 kcal/mol. The change in standard enthalpy of the system is +2.0 kcal/mol. Therefore, it can be expected that the equilibrium concentration of (*cis*-TI-O,O)Cp\*<sub>2</sub>Cr complex (VI) will be sufficient for bimolecular reactions of transformation of this complex into binuclear complex 1 with the abstraction of two Cp\* rings in the form of (Cp\*)<sub>2</sub> dimer . This process proceeds with a noticeable energy gain of 33.6 kcal/mol, which explains the formation of the observed product. For the (*cis*-Ind-O,O)Cp\*<sub>2</sub>Cr complex, the analogous process with the formation of {[Ind-( $\mu_2$ -O),( $\mu$ -O)]Cp\*Cr}<sub>2</sub>, which is analog of complex 1, also has a significant energy gain. The absence of such a product is caused by the thermodynamic disadvantage of the formation of an intermediate (*cis*-Ind-O,O)Cp\*<sub>2</sub>Cr complex. As a result, its effective concentration is low and only bimolecular processes of substitution of the Cp\* ligand for the chloride ion by the reaction with {Rh(cod)Cl]<sub>2</sub>, which is present in high concentration, are possible.

#### **Optical spectra**

HOMOs filled by  $\alpha$ - and  $\beta$ -electrons are localized predominantly on thioindigo ligands in complex **1**, but LUMOs of  $\alpha$  and  $\beta$  type are localized mainly on metal atoms. The calculated spectra of *trans*-TI molecules (red line) and dianion *cis*-TI (blue line) are shown in Fig. S6. It shows the red shift of the transitions in the near-UV and optical ranges, and the appearance of negative charge as well as a noticeable drop in intensity of the UV transitions.

It was also found that Coulomb field of the cation in the pair complex {cryptand[2,2,2](Na<sup>+</sup>)} (TI<sup>•-</sup>) affects strongly on the optical spectrum of TI<sup>•-</sup>. The most intense transitions at 836, 567, 326 and 322 nm of *cis*-TI<sup>•-</sup> change to transitions 616, 565, 510, 493, 402, 400, 382 and 365 nm in the complex {cryptand[2,2,2](Na<sup>+</sup>)}(cis-TI<sup>•-</sup>). The same picture is

observed for *trans*-TI<sup>•-</sup>: new lines at 810, 633, 615, 609, 570, 536, 520 and 370 nm appear in the complex {cryptand[2,2,2](Na<sup>+</sup>)}(*trans*-TI<sup>•-</sup>) instead of lines at 835, 618, 554, 349 and 320 nm for free TI<sup>•-</sup> radical anion. These results demonstrate strong effect of surroundings of TI<sup>•-</sup> in the lattice which may be correctly taken into account in rather complicated models. At the same time appearance of large number of new lines qualitatively correspond to complex structure of optical spectrum of **2**.

It is interesting that the *cis*-TI<sup>•-</sup> radical anions have higher interaction energy with the {cryptand[2,2,2](Na<sup>+</sup>)} cation. As a result energy difference for free TI<sup>•-</sup> isomers of 13.4 kcal/mol decreases to 3.9 kcal/mol for TI<sup>•-</sup> isomers in the pair complex {cryptand[2,2,2](Na<sup>+</sup>)}(TI<sup>•-</sup>).



Figure S6. Calculated UV-visible spectra of *trans*-TI (red line) and the *cis*-TI dianion (blue line)

## **IR** spectra

Calculated vibrations observable in the IR spectra of Cp<sub>2</sub>\*Cr, {[TI-( $\mu_2$ -O),( $\mu$ -O)]Cp\*Cr}<sub>2</sub>, trans-TI, cis-TI molecules and cis-TI<sup>2-</sup> dianion in the region over 400 cm<sup>-1</sup> are presented in Table S2. The CO stretch vibrations are marked by #. These values of 1584 and 1655 cm<sup>-1</sup> for trans-TI well correspond to the experimental data 1588 and 1657 cm<sup>-1</sup>. Theoretical IR spectrum of the {[TI-( $\mu_2$ -O),( $\mu$ -O)]Cp\*Cr}<sub>2</sub> complex agrees with the experimental one (see Fig. S10). Most intense CO vibrations at 1350 and 1369 cm<sup>-1</sup> correspond to strong absorption peak in the same region. However, these vibrations are not pure and are mixed with skeleton vibrations of five and six-membered rings. Other mixed vibrations at 1354, 1373, 1405, 1410, 1461 and 1464 cm<sup>-1</sup> with noticeable contribution of CO modes have lower IR intensities. Rather strong red shift of CO vibrations in the complex **1** with respect to *cis*-thioindigo<sup>2-</sup> dianion (1540 and 1584 cm<sup>-1</sup>) is due to strong elongation of C-O bonds. In *cis*-TI<sup>2-</sup> this elongation is small because only small portion -0.19 of additional charge -2 is localized on each oxygen atom of the CO groups. Additional calculation of IR spectrum of monoprotonated

Components	Cp* <sub>2</sub> Cr	Thioindigo	Cryptand[2,2,2]	{[TI-( <i>µ</i> <sub>2</sub> - <i>O</i> ),( <i>µ</i> - <i>O</i> ]	$\{cryptand[2,2,2](Na^+)\}$
species c	species <i>cis</i> -TIH <sup>-</sup> with the C-O bonds of 1.336 and 1.292 Å length showed also large red shift of				
the CO vibrations up to 1300 and 1512 cm <sup>-1</sup> . The same behaviour was found for the complex of					
<i>cis</i> -TILi <sup>-</sup> with the C-O bonds 1.308 Å length and the CO vibrations at 1453 and 1485 cm <sup>-1</sup> which					
correspon	correspond the general rule of the effect of the bond length on the stretch vibration frequency.				

## References

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				$(Cp*Cr)$ <sub>2</sub> · $C_{6}H_{14}(1)$	(TI•-) ( <b>2</b> )
Cation				Cp*Cr	Cryptand[2,2,2](Na <sup>+</sup> )
	419w		476w	425w	501w
	_		528w	434w	535w
	585w		581w	568m	581w
	1022s		735m	1014s*	725s*
	1068w		922m	1067w	932s
	1262w		948w	1278w*	947m*
	1316s		982m	1319w*	-
	1375s		1071m	1373s	1079s*
	1414w		1127s	_	1134s*
	1423m		1213w	1425m	-
	1448w		1295m	1441w	1277m
	1634m		1329m	-	1319w*
	2852w		1360s	2852w	1356s 1364m
	2899w		-	2912w	1397m
	2955w		1446m	2956w 2977w	1445m
			1462m		1467m
			1490w		1482m
			2790w		2812w
			2877w		2876w
			-		2894m
			2943w		2970w
Thioindigo		421		425*	421
Thiomago		421W		425W*	421W 403w
		495W		493W	473W 535W*
		505w		504m	500w
		595W		594III 678m	599W
		097W		727m 739s	- 725s*
		751w		72/11/398 752m 761m	7255 756m
		972m		/ J2III / 01III 956g	-
		875w		8305	891w
		058w		02811	947m*
		1020 w		1014s	1012m
		1052s		10145	1048m
		10325		10558	1079s*
		10735		_	1103s
		1110w		1116w 1125w	1134s*
		-		1160w	1174s
		1224m		1215m	1230w
		-		-	1261m
		12898		1278w*	1301s
		1317w		1319w*	1319w*
		1451m		1453m	1456m
		-		14838 15158	1503s
		1588s		1562w	1564w
		16578		1586w	1586m
		3066w		3054w	3059w
	1				

# **IR-** spectra

 Table S1. IR-spectra (cm<sup>-1</sup> in KBr) of starting compounds, complex 1 and salt 2.

 $\ast$  Bands are overlapped, w - weak intensity, m – middle intensity, s – strong intensity.



Figure S7. IR spectrum of pristine *trans*-TI.



**Figure S8.** IR spectrum of salt {cryptand[2,2,2](Na<sup>+</sup>)}(TI<sup> $\bullet$ -</sup>) (2). Spectrum is measured in KBr pellet prepared in anaerobic conditions.



**Figure S9.** IR spectrum of coordination compound  $\{(TI-(\mu_2-O),(\mu-O)(Cp^*Cr))\}_2$  (1) in KBr pellet prepared in anaerobic conditions.

Cp <sub>2</sub> *Cr		
v, cm <sup>-1</sup>	μ	I, km/mol
437	6.16	8.4
578	4.05	5.9
997	1.36	35.1
1005	1.42	21.4
1009	1.39	47.5
1052	1.88	10.5
1360	1.20	11.6
1360	1.22	12.8
1361	1.20	13.1
1406	2.26	19.5
1418	1.79	10.4
1440	1.11	52.1
1456	1.29	12.6
1472	1.93	11.6
2936	1.05	66.2
2936	1.05	44.4
2937	1.05	91.1
2938	1.05	78.4
2942	1.04	55.4
2943	1.04	69.2
2944	1.04	34.0
2946	1.04	47.6
2948	1.04	38.9
2949	1.04	43.2
3003	1.09	22.3
3004	1.09	23.6
3005	1.09	21.7
3036	1.10	52.8
3036	1.10	76.8
3036	1.10	19.2
3036	1.10	15.6

ν, cm <sup>-1</sup>	μ	I, km/mol
409	5.07	20.1
424	8.36	34.6
483	8.71	29.4
513	8.12	78.1
556	10.32	25.4
582	9.25	23.7
627	7.49	19.0
668	8.03	36.8
719	1.64	29.2
726	1.88	96.1
752	2.64	16.0
842	7.32	74.6
1005	1.41	25.8
1009	3.47	97.2
1015	2.18	54.3
1025	3.40	66.2
1056	3.10	23.3
1107	2.22	22.3
1264	1.99	18.8
1327	4.09	27.9
1349	1.52	36.3
1350 #	3.56	293.4
1358	5.96	55.9
1369 #	4.75	109.4
1410	2.94	129.0
1418	3.81	27.0
1419	3.75	14.2
1436	1.12	18.2
1440	2.46	47.5
1450	1.14	77.5
1464	4.30	172.8
1470	2.22	39.6
1481	2.90	29.5
1484	7.94	272.2
2955	1.05	25.3
2955	1.05	26.9
2958	1.05	27.0
2958	1.05	20.3
2958	1.05	26.2
2960	1.05	16.9
2964	1.04	20.9
3116	1.09	31.5
3123	1 10	39.5
3123	1 10	33.8
3125	1 10	35.8
J 1 4 1	1.10	22.0

<i>Trans</i> -TI			
ν, cm <sup>-1</sup>	μ	I, km/mol	
414	10.50	18.5	
495	4.07	8.25	
530	10.78	46.1	
684	4.79	19.6	
685	6.74	19.9	
732	1.52	97.1	
770	6.97	11.6	
888	12.57	173.7	
1016	2.32	28.3	
1072	3.91	337.5	
1151	1.15	10.6	
1207	2.41	96.2	
1269	1.92	232.2	
1353	8.28	37.2	
1434	2.36	126.8	
1443	2.60	35.6	
1570	6.65	24.7	
1584 #	6.39	208.2	
1655 #	12.84	204.1	
3118	1.09	10.2	
3128	1.10	40.0	
3128	1.10	9.1	

Cis-TI		
ν, cm <sup>-1</sup>	μ	I, km/mol
424	11.23	22.3
517	10.29	38.2
611	9.29	24.2
668	5.08	15.8
692	6.76	12.6
731	1.62	96.0
762	7.29	32.2
771	2.72	12.2
1016	2.46	89.7
1040	5.18	577.1
1149	1.14	12.9
1191	2.64	7.5
1194	2.71	99.3
1258	1.68	177.4
1356	8.45	21.9
1439	2.39	133.8
1494	11.15	172.0
1578	7.00	27.9
1582 #	6.41	160.9
1686	13.00	28.9
1713 #	12.99	195.4
3120	1.09	14.1
3128	1.10	60.2

<i>Cis</i> -TI <sup>2–</sup> dianion			
ν, cm <sup>-1</sup>	μ	I, km/mol	
508	10.41	14.9	
633	4.70	23.6	
679	1.33	74.3	
804	8.44	26.0	
989	2.04	228.1	
1044	3.38	40.1	
1076	1.63	189.4	
1113	1.36	14.2	
1128	4.19	52.3	
1195	2.35	37.7	
1233	2.44	162.2	
1354	7.88	21.1	
1360	5.01	23.9	
1369	5.83	16.0	
1407	2.51	101.7	
1420	3.41	16.5	
1495	5.43	84.2	
1501	5.49	12.6	
1540 #	6.09	598.1	
1547	6.59	75.4	
1550	11.18	154.4	
1584 #	11.31	363.9	
3033	1.08	71.4	
3045	1.09	23.0	
3045	1.09	63.7	
3063	1.09	50.0	
3063	1.09	91.1	
3072	1.10	473.6	

Bands attributed to the CO bond vibrations are marked by #.



Figure S10. Experimental (top) and theoretical (bottom) spectra of complex 1

Crystal structure of 1.



**Figure S11.** View on the  $\{(TI-(\mu_2-O),(\mu-O)(Cp^*Cr))\}_2$  dimers in **1**. Average C(Cp\*)-Cr, the O-Cr bond lengths, the Cr…Cr distance and the dihedral angle in thioindigo are shown.

Crystal structure of 2.



**Figure S12.** View on the crystal structure of **2** along the *a* axis and channels formed by four TI<sup>•-</sup> radical anions and occupied by the {cryptand[2,2,2](Na<sup>+</sup>)} cations.



Figure S13. Possible orientations of *cis*- and *trans*-configurations for the TI<sup>-</sup> radical anions in salt 2.

One of the independent TI molecules has the occupancy for the disordered S and CO groups of 0.607/0.393 and 0.861/0.139, the major occupations are being of *trans*-configuration. To calculate minimal portion of *trans*-conformation, this configuration can be decomposed into three configurations, 2 *cis* and 1 *trans* ones (see Fig. S13). One *cis* conformation occupation factor would be 0.607, another one -0.139, and 0.746 in sum. The rest *trans*-conformation would be of 0.254 occupation. In the same way we can calculate the minimal value of the *cis*-conformation content taking into consideration 2 *trans* and 1 *cis* conformations. The sum of *trans*-conformations would be 0.532, consequently minimal portion of *cis*-conformation would be 0.468. Similar calculations for second independent TI molecules gives the lowest possible occupancies are 0.114 and 0.124 for the *trans*- and *cis*-conformations, respectively.



Figure S14. Temperature dependence of effective magnetic moment of salt 2 in the 1.9-300 K range.



Figure S15. Temperature dependence of reciprocal molar magnetic susceptibility 2 in the 1.9-300 K range.



Figure S16. EPR signal from polycrystalline salt 2 at 250 K.



Figure S17. EPR signal from polycrystalline salt 2 at 4.2 K.



**Figure S18.** Temperature dependence of the linewidth of EPR signal from salt **2** with the TI<sup>--</sup> radical anions in the 4.2- 295 K range.



Magnetic data for complex 1.

Figure S19. Temperature dependencies of effective magnetic moment of polycrystalline 1.



Figure S20. EPR spectrum of polycrystalline 1 at 140 K.



Figure S21. EPR spectrum of polycrystalline 1 at 59 K.



**Figure S22.** EPR spectrum of polycrystalline **1** at 6.5 K. Since dimer transfers to diamagnetic state at 6.5 K, the observed signal at 6.5 K originates from impurities.