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Supporting information for the manuscript:

Optical and magnetic properties of *trans*-indigo$^{\bullet-}$ radical anions. Magnetic coupling between *trans*-indigo$^{\bullet-}$ (S = 1/2) mediated by intermolecular hydrogen N-H···O=C bonds.

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Materials

Indigo (>97%) was purchased from TCI. Potassium graphite (KC_8) was purchased from Strem and cryptand[2.2.2] (98%) was purchased from Acros. *o*-Dichlorobenzene ($C_6H_4Cl_2$) was distilled over CaH_2 under reduced pressure; *n*-hexane was distilled over Na/benzophenone. All operations on the synthesis of **1** and their storage were carried out in a MBraun 150B-G glove box with controlled atmosphere and water and oxygen content less than 1 ppm. The solvents were degassed and stored in the glove box. KBr pellets for IR- and UV-visible-NIR measurements were prepared in the glove box. Polycrystalline sample of **1** was placed in 2 mm quartz tubes in anaerobic conditions for EPR and SQUID measurements and sealed under ambient pressure of argon gas.

General

UV-visible-NIR spectra were measured in KBr pellets on a Perkin Elmer Lambda 1050 spectrometer in the 250-2500 nm range. FT-IR spectra (400-7800 cm^{-1}) were measured in KBr pellets with a Perkin-Elmer Spectrum 400 spectrometer. EPR spectra were recorded for polycrystalline samples of **1** with a JEOL JES-TE 200 X-band ESR spectrometer equipped with a JEOL ES-CT470 cryostat working between room and liquid helium temperatures. A Quantum Design MPMS-XL SQUID magnetometer was used to measure static magnetic susceptibility of **1** at 100 mT magnetic field in cooling and heating conditions in the 300 − 1.9 K range. A sample holder contribution and core temperature independent diamagnetic susceptibility (χ_d) were subtracted from the experimental values. The χ_d values were estimated by the extrapolation of the data in the high-temperature range by fitting the data with the following expression: $\chi_M = C/(T - \Theta) + \chi_d$, where C is Curie constant and Θ is Weiss temperature. Effective magnetic moment (μ_{eff}) was calculated with the following formula: $\mu_{eff} = (8 \cdot \chi_M \cdot T)^{1/2}$.

Synthesis

The crystals of $\{\text{cryptand[2.2.2]}(K^+)\}_6\{\textit{trans}\text{-indigo}\}_7 \cdot 5.5C_6H_4Cl_2$ (**1**) were obtained by the following procedure. 11 mg of indigo (0.043 mmol) was reduced by large excess of potassium graphite (20 mg, 0.148 mmol) in the presence of one equivalent of cryptand[2.2.2] (16 mg, 0.028 mmol) in 16 mL of *o*-dichlorobenzene. Indigo is completely dissolved during several hours to form red-violet solution.

Intense stirring is carried out at 80°C during 24 hours. The solution was cooled down to room temperature and filtered into the 50 mL glass tube of 1.8 cm diameter with a ground glass plug, and 30 mL of *n*-hexane was layered over the solution. The crystals were precipitated on the walls of the tube during 1 month. Then the solvent was decanted from the crystals and they were washed with *n*-hexane to yield black prisms with characteristic copper luster up to 0.6×0.4×0.3 mm^3 in size in 63% yield. Composition of the crystals was determined from X-ray diffraction analysis on single crystals. We tested several crystals from the synthesis and all of them show the same unit cell parameters. Therefore, they belonged to one crystal phase. Composition of **2** was confirmed by elemental analysis: $C_{253}H_{308}Cl_{11}K_6N_{26}O_{50}$, F.W. 5137.79, Calc., C = 59.14; H = 6.00; Cl = 7.60; N = 7.11; O = 15.60; K = 4.55; Found, C = 58.44; H = 5.71; Cl = 7.52; N = 6.92.

X-ray crystal structure determination

The intensity data for the structural analysis were collected on an Oxford diffraction "Gemini-R" CCD diffractometer with graphite monochromated MoK$_\alpha$ radiation using an Oxford Instrument Cryojet system. Raw data reduction to F^2 was carried out using CrysAlisPro, Oxford Diffraction Ltd.[1] The structures were solved by direct method and refined by the full-matrix least-squares method against F^2 using SHELX-2016/6.[2] Non-hydrogen atoms were refined in the anisotropic approximation. Positions of hydrogen atoms were calculated geometrically.

Crystal data for **1**: $C_{253}H_{308}Cl_{11}K_6N_{26}O_{50}$, F.W. 5137.79, black prism, 0.435×0.234×0.135 mm^3; 120.0(2) K: triclinic, space group $P\bar{1}$, a = 15.2735(5), b = 17.5699(5), c = 25.9540(6) Å, α = 97.646(2), β = 98.970(2), γ = 106.968(3)°, V = 6461.6(3) Å^3, Z = 1, d_{calcd} = 1.320 M gm^{-3}, μ = 0.294 mm^{-1}, $F(000)$ = 2709, $2\theta_{max}$ = 58.888°; 49133 reflections collected, 31762 independent; R_1 = 0.0742 for 15231 observed data [> 2σ(F)] with 3176 restraints and 2132 parameters; wR_2 = 0.1746 (all data); final G.o.F. = 1.005. CCDC 1897094.

There are four independent indigo molecules in **1**: three molecules with full and one molecule with half occupancies. One indigo molecule has two positions of carbonyl oxygen atom with the 0.6/0.4 occupancies. Another indigo molecule has phenylene substituent statistically disordered between two positions. There are three independent cryptand[2.2.2] cations with full occupancies. Cation in one position is statistically disordered between two positions. There are also three independent $C_6H_4Cl_2$ molecules. One molecule is ordered, whereas another molecule is disodered between four orientations with the 0.35/0.25/0.2/0.20 occupancies. There is also $C_6H_4Cl_2$ molecule with 0.75 occupancy and this molecule is disordred between three positions with 0.30/0.25/0.20 occupancies. To keep the anisotropic thermal parameters of the disordered atoms within reasonable limits, the displacement components were restrained using SHELXL instructions of ISOR, SIMU and DELU. That resulted in the 3176 restraints used for the refinement of crystal structure of **1.**

IR- spectra.

Table S1. IR-spectra (cm^{-1} in KBr) of starting compounds and salt **1**.

Components	Cryptand[2.2.2]	Indigo	$C_6H_4Cl_2$	{Cryptand[2.2.2](K)}$_6$ (Indigo)$_7$·5.5$C_6H_4Cl_2$ (**1**)
Cryptand[2.2.2]	423w			428w
	476w			-
	528w			529w
	581w			-
	735m			738s*
	922m			933m
	948w			948m
	982m			-
	1038w			1032w*
	1071m			1080s*
	1100s			1101s*
	1127s			1132s*
	1213w			-
	1295m			1298m*
	1329m			-
	1360s			1344m 1355s 1361m split
	1446m			1444m
	1462m			1462m*
	1490w			1511m
	2790w			2811w
	2877w			2880w
	2943w			2960w
Indigo		563w		
		643w		564w
		699w		-
		714w		698w
		745w sh		-
		755m		738s*
		859w		-
		879w		858w
		1012w		883w
		1071s		1004w
		1096w		1080s*
		1107w		1101s*
		1129s		-
		1173s		1132s*
		1200s		1174w
		1298m		1199w
		1318m		1298m
		1392m		1318w
		1409w sh		1396w
		1462s		-
		1483m		1462m*
		-		1482m
		1586w		1566w
		1613s		1586w
		1627s		1614w
		3040w		1625m
		3058w		3049w
		3250w		3250w
$C_6H_4Cl_2$		3270m		-
			657w	-
			748s	738s*
			1030m	1032w*
			1122m	1132s*
			1453m	1462m*

*Bands are overlapped, w - weak intensity, m – middle intensity, s – strong intensity

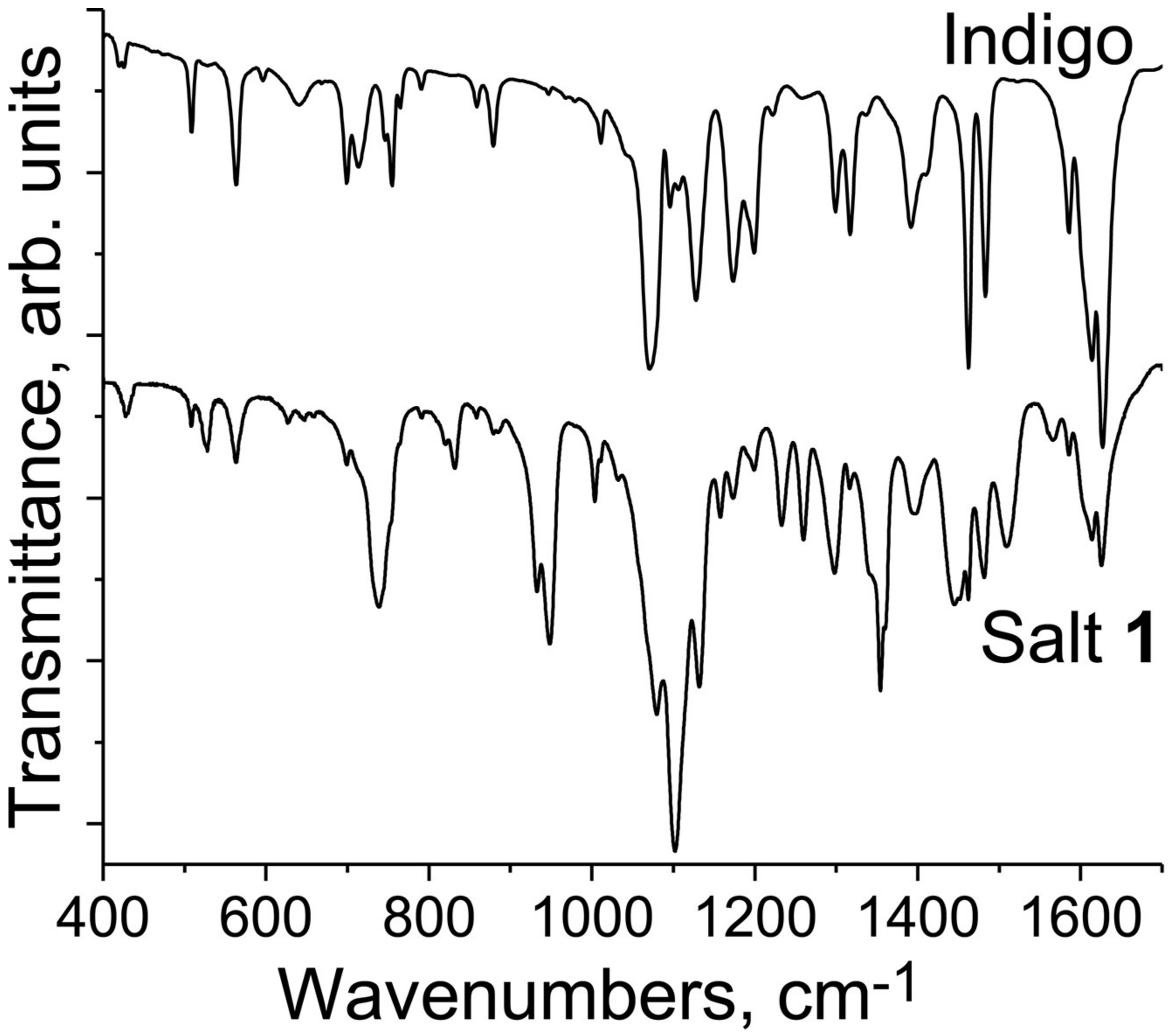

Fig. S1. IR spectra of pristine *trans*-indigo and the radical-anion salt {Cryptand[2.2.2](K$^+$)}$_6$ (Indigo$^{\bullet-}$)$_7$·5.5C$_6$H$_4$Cl$_2$ (**1**) measured in KBr pellets. Pellet of **1** was prepared in anaerobic conditions.

EPR data.

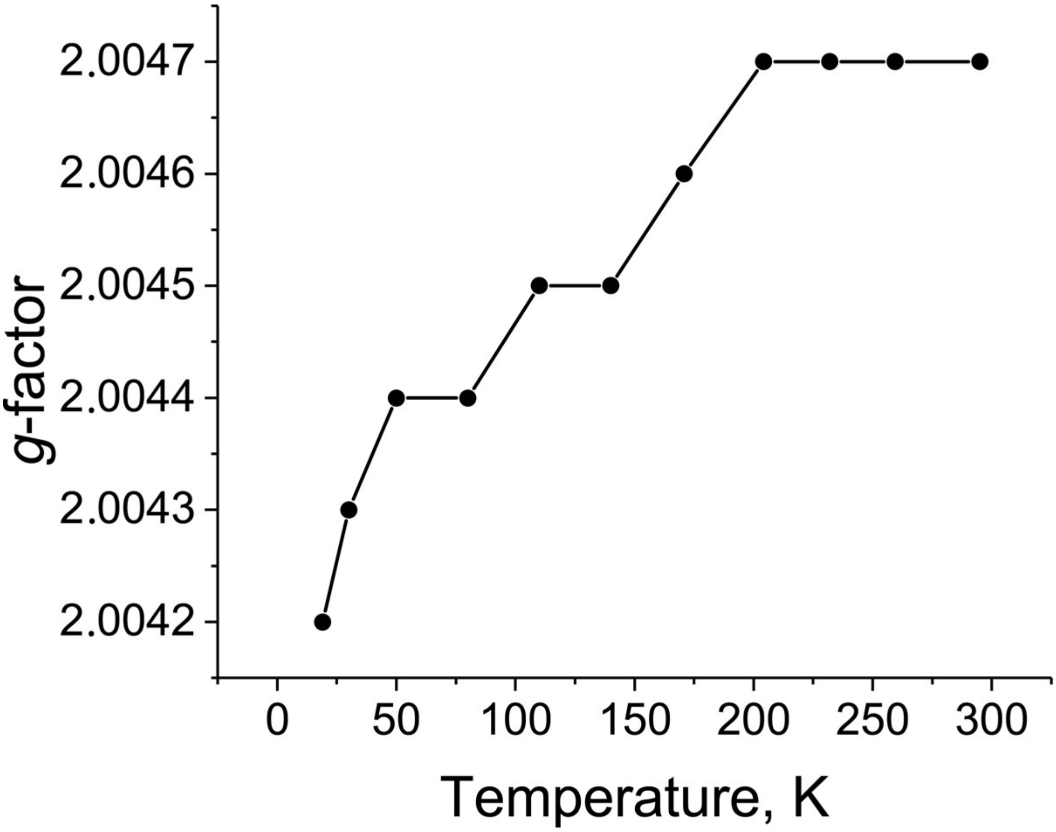

Fig. S2. Temperature dependence of *g*-factor of EPR signal from polycrystalline **1**.

Fitting of magnetic data by the Van-Vleck and the Bleaney-Bowers approximations.

The Van-Vleck expression[3] used in the paper is derived from the general exchange Hamiltonian:

$$\hat{H} = -2JS_1 \cdot S_2 - j(S_1 \cdot S_2)^2,$$

where j is a biquadratic exchange constant. These types of models proved to be useful for a number of different spin systems.[4] The Bleaney-Bowers equation[5], which is the second-order approximation of the Van-Vleck expression, was also used and yielded a better fit (see paper).

The attempt to extract a second *intra*-chain magnetic coupling constant closely followed the approach suggested by *Johnston et al.*[6]

References

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