

Supporting information for to the manuscript:

**Reversible dissociation of singly-bonded $(C_{60}^-)_2$ dimers in $(MV^{\bullet+})_2(C_{60}^-)_2$ ·Solvent salt
containing paramagnetic methyl viologen $MV^{\bullet+}$ radical cations**

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Supporting information

EXPERIMENTAL

Materials. Methyl viologen ($\{\text{MV}\}\text{Cl}_2$, >98%) was purchased from TCI reagents. C_{60} of 99.98% purity was used from MTR Ltd. without further purification. Cesium anthracene ($\text{Cs}^+(\text{C}_{14}\text{H}_{10}^{\bullet-})$) was obtained by direct interaction of metallic cesium and anthracene in toluene. *o*-Dichlorobenzene ($\text{C}_6\text{H}_4\text{Cl}_2$) was distilled over CaH_2 under reduced pressure; *n*-hexane was distilled over Na/benzophenone. All operations on the synthesis of the crystals of **1** and their storage were carried out in a MBraun 150B-G glove box with controlled atmosphere in which water and oxygen content was less than 1 ppm. The solvents were degassed and stored in a glove box. KBr pellets for IR- and UV-visible-NIR measurements were prepared in the glove box. Polycrystalline sample of **1** placed in 2 mm quartz tubes in anaerobic conditions for EPR and SQUID measurements was sealed under ambient pressure of argon.

General. UV-visible-NIR spectra were measured in KBr pellets with a PerkinElmer Lambda 1050 spectrometer in the 250-2500 nm range. FT-IR spectra ($400\text{-}7800\text{ cm}^{-1}$) were measured in KBr pellets with a PerkinElmer Spectrum 400 spectrometer. EPR spectra were recorded for polycrystalline sample of **1** from room temperature down to 4.3 K and from room temperature up to 407 K with a JEOL JES-TE 200 X-band ESR spectrometer equipped with a JEOL ES-CT470 cryostat. Integral intensity of EPR signal from **1** was estimated relative to that of EPR signal from weighted amount of $\text{CuSO}_4\cdot 5\text{H}_2\text{O}$.

Synthesis.

For preparation of $(\text{MV}^{\bullet+})_2(\text{C}_{60}^-)_2\cdot 2.5\text{C}_6\text{H}_4\text{Cl}_2\cdot 0.5\text{C}_6\text{H}_6$ (**1**), 27 mg of cesium anthracene ($\text{Cs}^+(\text{C}_{14}\text{H}_{10}^{\bullet-})$) (0.087 mmol) was added to 10.8 mg of $(\text{MV})\text{Cl}_2$ (0.042 mmol) in 6 mL of benzene. Stirring of this solution during two hours at 60°C provided dissolution of initially insoluble orange powder and black ($\text{Cs}^+(\text{C}_{14}\text{H}_{10}^{\bullet-})$) and the formation of weakly coloured red-brown solution presumably containing MV^0 . This solution was cooled down to room temperature

and was filtered into a flask containing 30 mg of C₆₀ (0.042 mmol) in 10 ml of *o*-dichlorobenzene. The obtained solution was stirred during one day at 60°C providing the formation of deep blue solution. This solution was cooled down to room temperature and filtered into a tube for diffusion with a ground glass plug of 50 mL volume. *n*-Hexane was layered over the obtained solution and slow mixing of two solutions during 2 months produced crystals on the walls of the tube. Then the solvent was decanted from the crystals, and they were washed with *n*-hexane to yield black plates up to 1×0.8×0.2 mm³ in size in 58% yield. Composition of the crystals was determined from X-ray diffraction analysis on single crystals. We tested several crystals from the synthesis which showed the same unit cell parameters and belonged to one crystal phase. Elemental analysis could not be applied to confirm the composition of this compound due to high air-sensitivity of both MV^{•+} and C₆₀^{•-} ions.

X-ray Crystallographic study.

Crystal data for **1** at 100(2) K: C₁₆₂H₄₁Cl₅N₄, F.W. 2220.24, black plate, 0.50×0.18×0.3 mm³; 100(2) K, triclinic, space group $P\bar{1}$, $a = 9.8950(6)$, $b = 14.1098(10)$, $c = 17.6549(14)\text{\AA}$, $\alpha = 98.039(6)$, $\beta = 91.161(6)$, $\gamma = 110.473(6)^\circ$, $V = 2280.2(3)\text{\AA}^3$, $Z = 1$, $d_{\text{calcd}} = 1.617\text{ M gm}^{-3}$, $\mu = 0.235\text{ mm}^{-1}$, $F(000) = 1126$, $2\theta_{\text{max}} = 51.356^\circ$; 9678 reflections collected, 9678 independent; $R_1 = 0.0955$ for 4701 observed data [$> 2\sigma(F)$] with 3558 restraints and 1856 parameters; $wR_2 = 0.2642$ (all data); final G.o.F. = 0.972. CCDC 2036459.

The intensity data for the structural analyses of the crystal of **1** were collected on an Oxford diffraction "Gemini-R" CCD diffractometer with graphite monochromated MoK_α 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-2013.² Non-hydrogen atoms were refined in the anisotropic approximation. Positions of hydrogen atoms were calculated geometrically. There is a half of independent (C₆₀⁻)₂ dimer in **1** which is disordered between three orientations with the 0.364(3)/0.319(3)/0.317(3) occupancies. There are two positions of

solvent molecules. One general position is shared by $C_6H_4Cl_2$ and C_6H_6 solvent molecules at a 0.75/0.25 ratio, respectively. The second one in the inverse centre is occupied by disordered $C_6H_4Cl_2$ at a 0.5/0.5 ratio in accordance with the symmetry of position. To keep fullerene and solvent geometry close to reasonable one in the disordered groups, the restraints and constraints were applied using the SAME and AFIX66 SHELXL instructions. To keep the anisotropic thermal parameters of the fullerene atoms within reasonable limits the displacement components were restrained using SIMU, DELU and ISOR SHELXL instructions. That results in relatively great number of restraints used for the refinement of the crystal structures of **1**.

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

	(MV^{2+}) $(\text{Cl}^-)_2$	C_{60}	$\text{C}_6\text{H}_4\text{Cl}_2$	$(\text{MV}^{\bullet+})_2(\text{C}_{60}^{\bullet-})_2$ $\cdot 2.5\text{C}_6\text{H}_4\text{Cl}_2 \cdot 0.5\text{C}_6\text{H}_6$ (1) monomeric phase at RT
MV	464s 486m 706m 714m 790m 811vs 1028m 1113w 1180m 1194w 1222w 1271m 1334w 1418w 1436w 1458m 1523w 1635s 1654m 1696m 2852w - 2961w 3021m 3058w			- - - 726s 780w 801m 1024s 1101m 1190s 1202w 1214w 1262m 1335w 1412m 1432w 1452w* 1508w 1632vs - - 2850w 2924w 2962w - 3059w
C_{60}		526s 576m 1181w 1429s		524w 576s - 1390s
$\text{C}_6\text{H}_4\text{Cl}_2$			657w 748s 1030m 1122m 1453m	658w 745w 1030m - 1452w*

*bands coincide, w - weak, m – middle, s – strong, vs- very strong intensity.

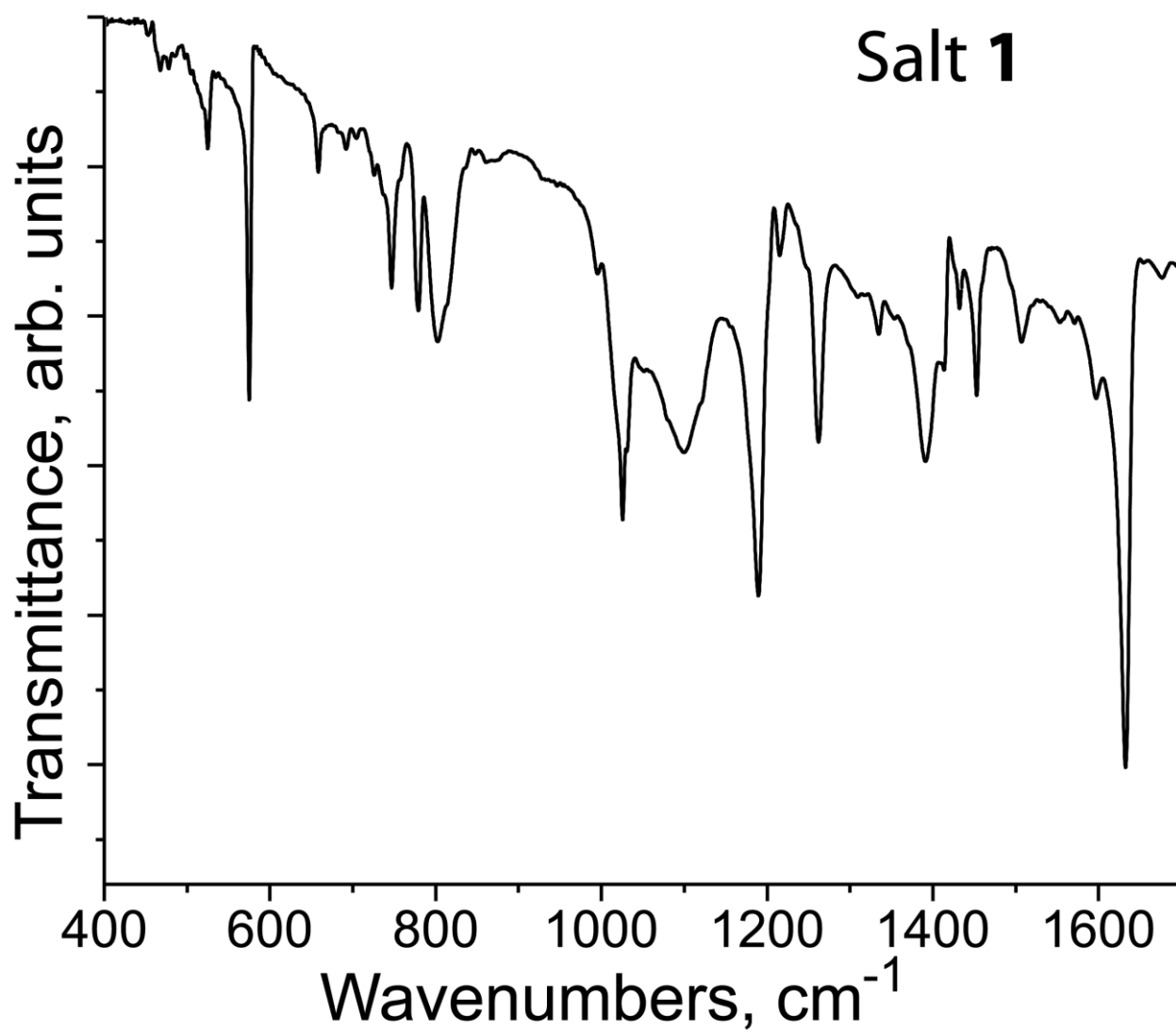


Figure S1. IR-spectrum of $(MV^{\bullet+})_2(C_{60}^{\bullet-})_2 \cdot 2.5C_6H_4Cl_2 \cdot 0.5C_6H_6$ (**1**) in a KBr pellet prepared in anaerobic conditions.

Crystal structure of $(MV^{\bullet+})_2(C_{60}^-)_2 \cdot 2.5C_6H_4Cl_2 \cdot 0.5C_6H_6$ (**1**) salt at 100(2) K.

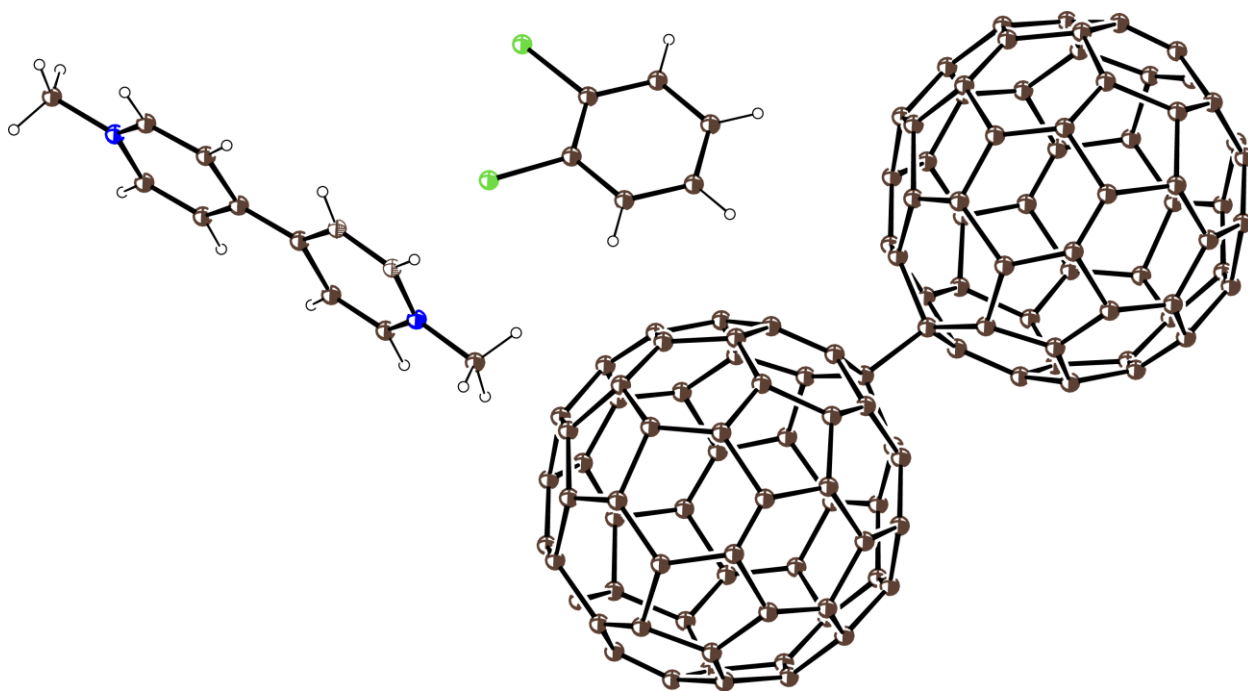


Fig. S2. Independent units in $(MV^{\bullet+})_2(C_{60}^-)_2 \cdot 2.5C_6H_4Cl_2 \cdot 0.5C_6H_6$ (**1**) salt: half of single bonded $(C_{60}^-)_2$ dimer; the $MV^{\bullet+}$ radical cation and solvent $C_6H_4Cl_2$ molecule. Dimer is disordered between three orientations. One position of solvent is shared by $C_6H_4Cl_2$ and benzene molecules at a 0.75/0.25 ratio, respectively (in this case only $C_6H_4Cl_2$ molecules are shown). Solvent $C_6H_4Cl_2$ molecule with half occupancy in the inversion center is omitted.

EPR signals from salt 1.

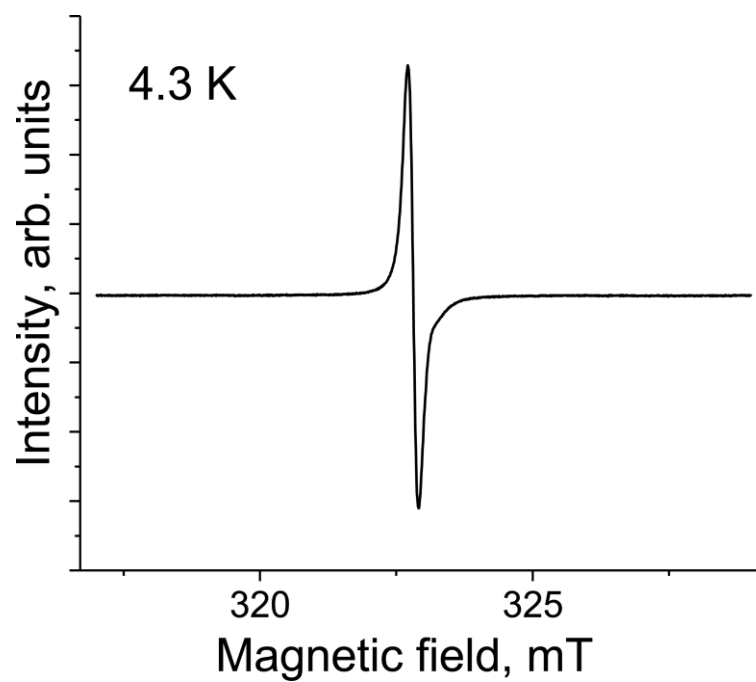


Fig. S3. EPR signal from polycrystalline **1** at 4.3 K.

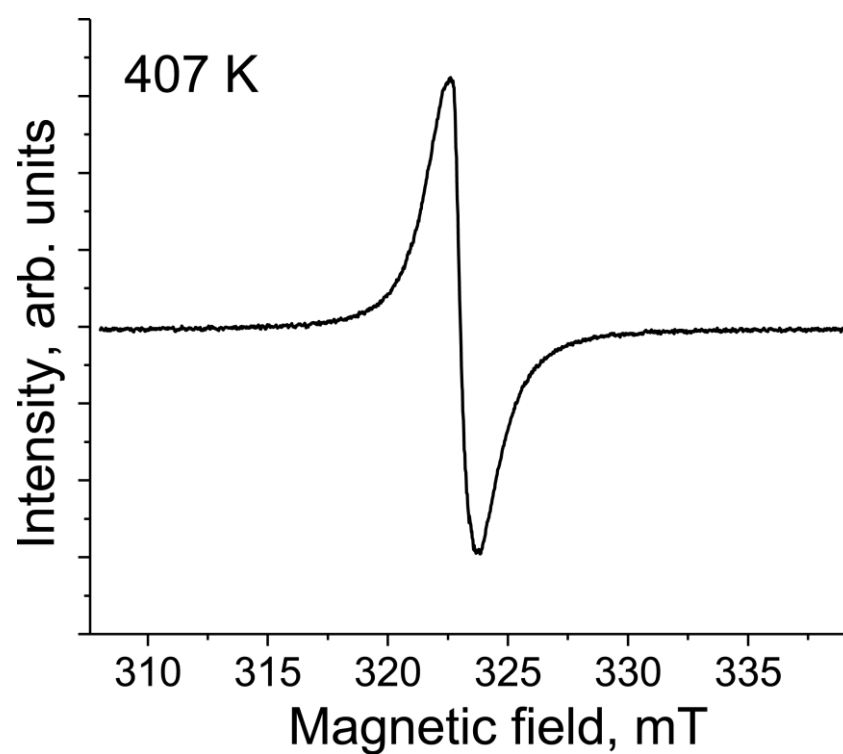


Fig. S4. EPR signal from polycrystalline **1** at 407 K.

References

1. CrysaliS Bruker AXS Inc., Madison, Wisconsin, USA.
2. G. M. Sheldrick, *Acta Crystallogr., Sect. A: Fundam. Crystallogr.* **2008**, *64*, 112 – 122.