

Supporting information for the manuscript:

**Monomers and dimers of C₆₀ and C₇₀ in the radical anion salts with dyes,
(astrophloxine⁺)₂(C₆₀^{•-})₂ and (astrophloxine⁺)₂(C₇₀⁻)₂: suppression of the C₆₀^{•-}
dimerization by π -stacking**

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Supporting information.

Table S1. IR-spectra (cm⁻¹ in KBr pellets) of starting compounds and salts **1** and **2**.

Components	C ₆₀	C ₇₀	astrophloxine	C ₆ H ₄ Cl ₂	(astrophloxine ⁺) ₂ (C ₆₀ ^{•+}) ₂ ·C ₆ H ₄ Cl ₂ · C ₆ H ₁₄ (1)	(astrophloxine ⁺) ₂ (C ₇₀ ^{•+}) ₂ (2)
C ₆₀	524s 574s 1180s 1427s				524w 574s - 1396s	
C ₇₀		457w 534s 564m 576s 642m 673m 794m 1132w 1413w 1429s				- 530m* - 576m - 680w 801m 1127m - 1399m 1427s*
Astrophloxine			423m 460m 467m 532w; 542w 548w 666s 681w 688w 725m 736m 750s 767s 868s 910s 936s 962s 1006s 1029m 1064s 1074w 1102s 1111m 1144w 1174m 1181s 1222m 1239s 1268 1298w 1323m 1356s 1412s 1443s 1478m 1539s		425w - 476w 512w; 525w - - 680m 693w 725w 745s 754s 772s 855m 924s 940w 962w 1019m 1031w 1075s 1084m - 1114s; 1126s 1155m 1174m - 1230m 1252m 1273m 1305w 1338m 1368m 1428s 1454s 1477m 1556s	424w - 474w 530w* - 667w 680w - - 749m 757w 774s 858w 922s 942w 962w 1019m - 1075s 1088m - 1114s; 1127s 1159m 1175m - 1230m 1252m 1275m 1305w 1337m 1366m 1427s* 1456s 1477m 1557s
C ₆ H ₄ Cl ₂				663w 751s 1035m 1120s 1462m	659w 753w 1032w - 1465w	

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

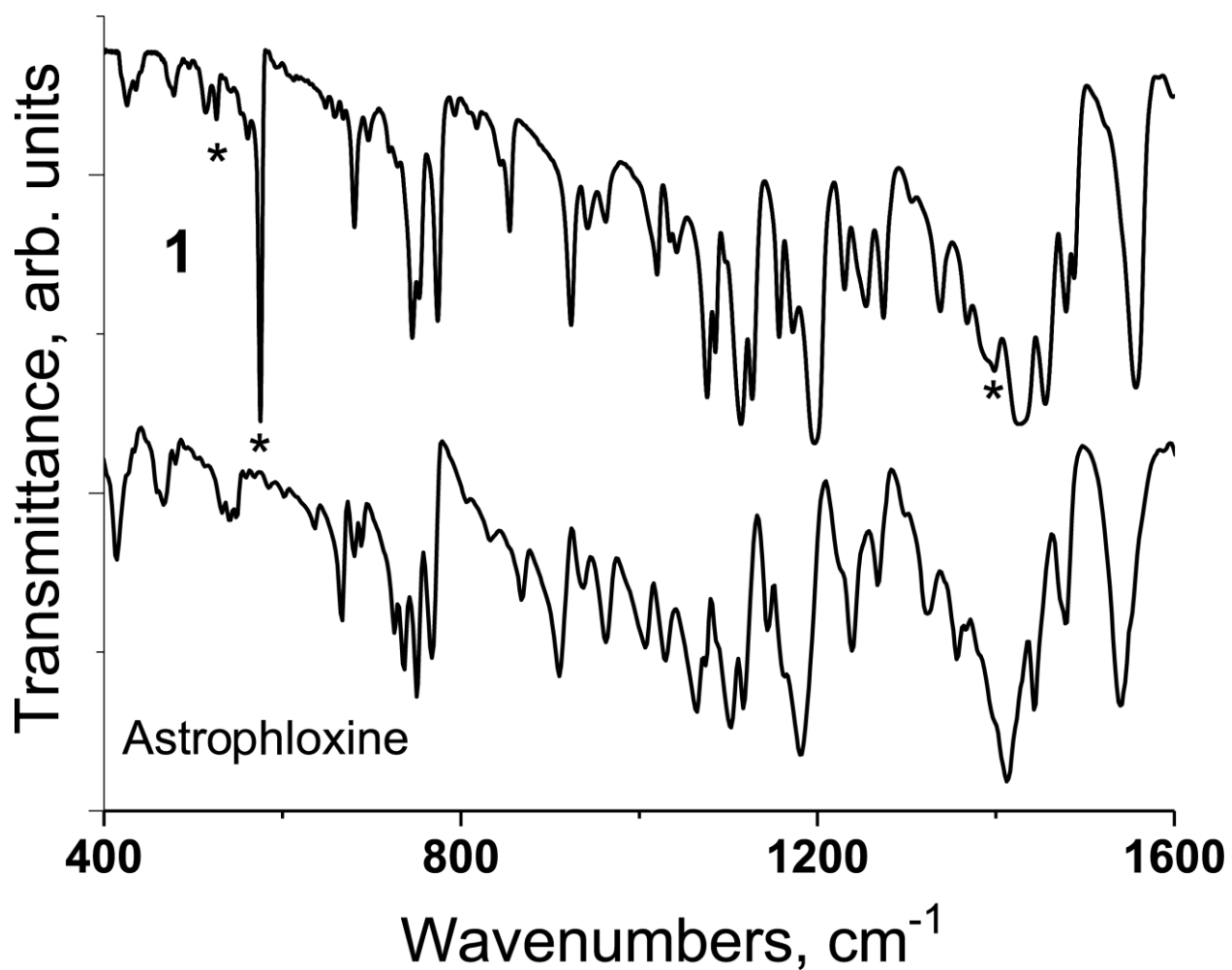


Fig. S1. Spectrum of $(\text{astrophloxine}^+)_2(\text{C}_{60}^{\bullet-})_2 \cdot \text{C}_6\text{H}_4\text{Cl}_2 \cdot \text{C}_6\text{H}_{14}$ (**1**) in a KBr pellet prepared in anaerobic conditions. Spectrum of starting astrophloxine in KBr pellet is given for comparison. Bands of C_{60} are marked by asterisk “*”.

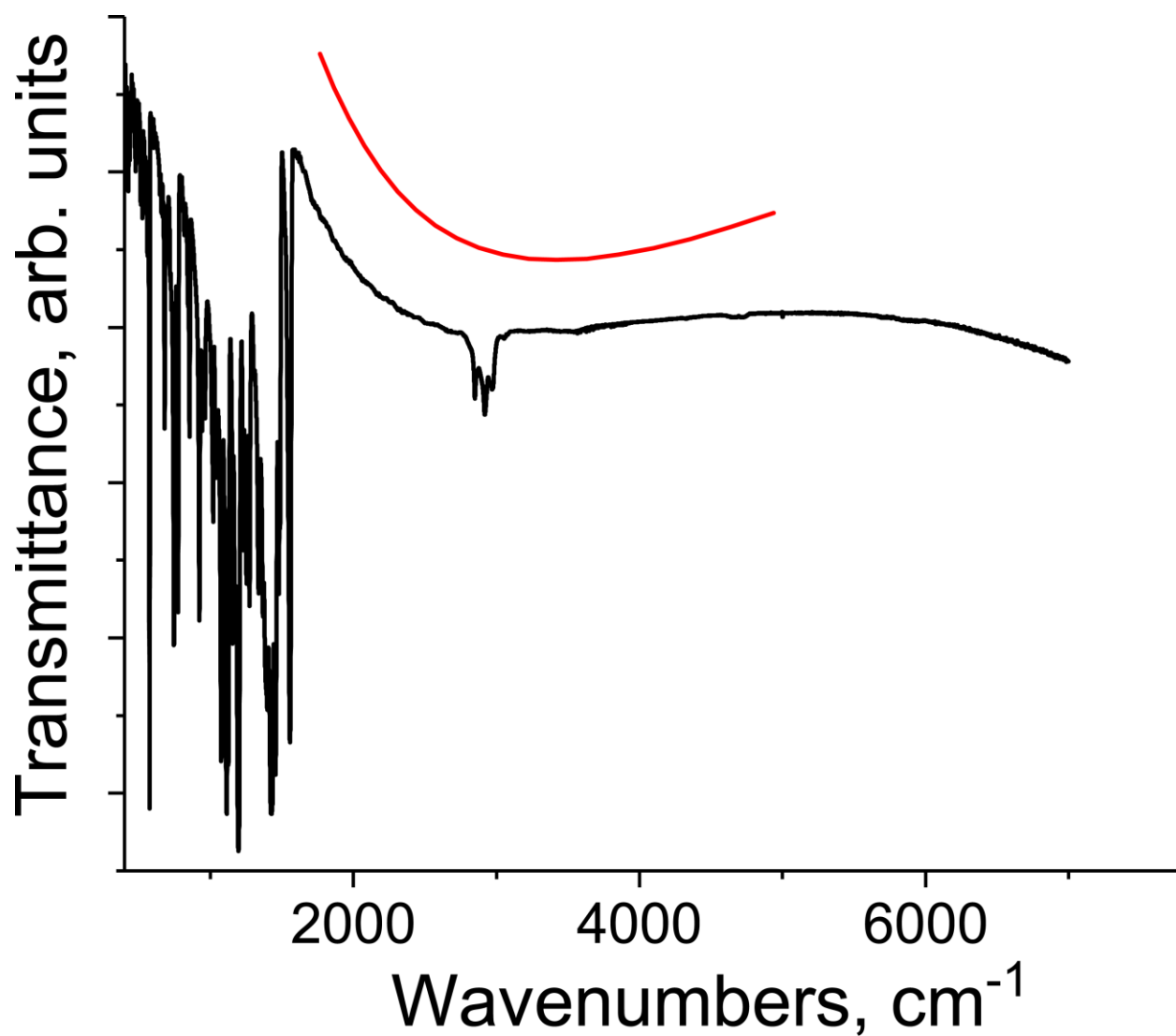


Fig. S2. Spectrum of (astrophloxine⁺)₂(C₆₀^{•-})₂·C₆H₄Cl₂·C₆H₁₄ (**1**) in a KBr pellet prepared in anaerobic conditions in the 400-7800 cm⁻¹ range. Charge transfer band with maximum at about 3300 cm⁻¹ is shown by red line.

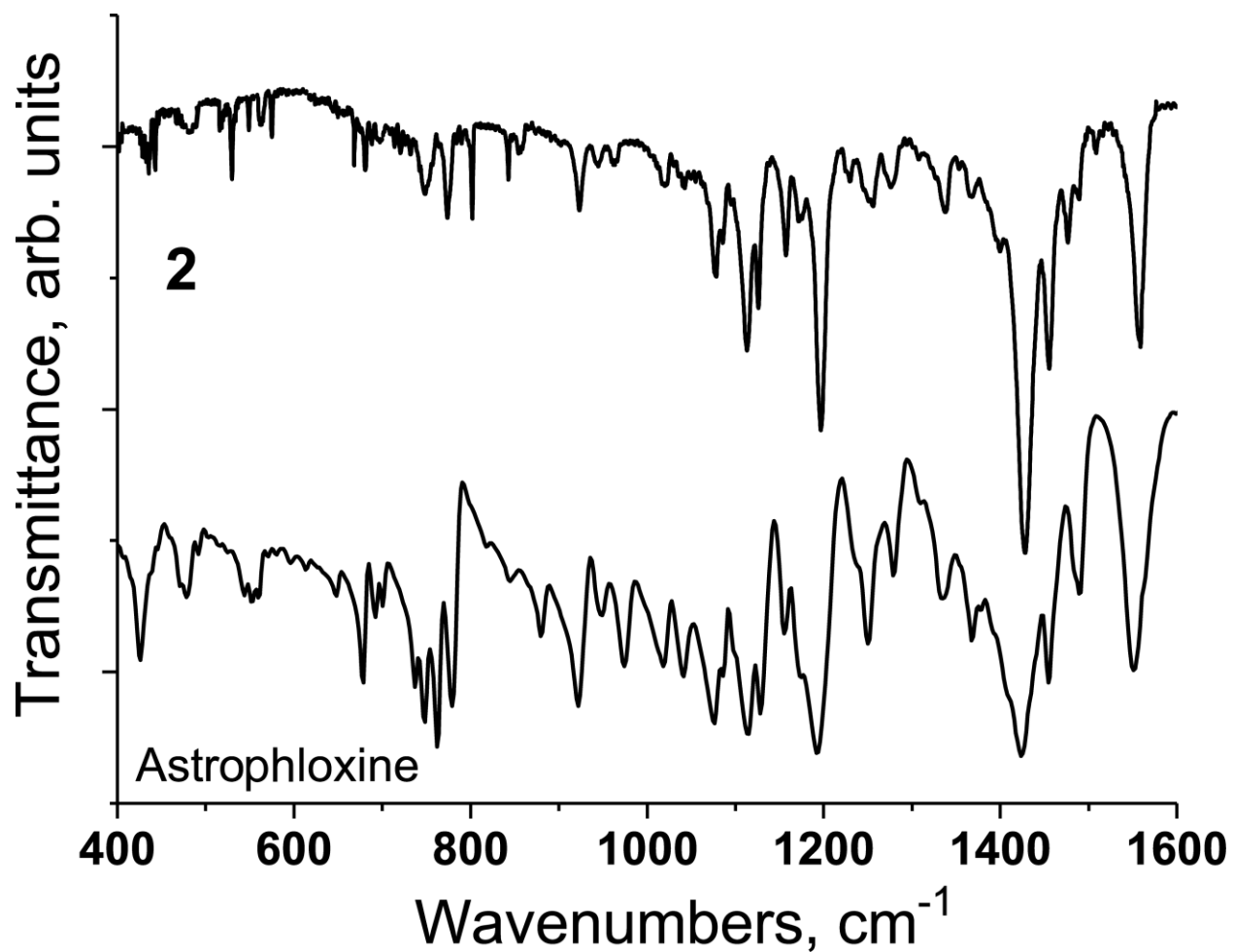


Fig. S3. Spectrum of $(\text{astrophloxine}^+)_2(\text{C}_{70}^-)_2$ (**2**) in a KBr pellet prepared in anaerobic conditions. Spectrum of starting astrophloxine in a KBr pellet is given for comparison.

The formation of contacts between fullerene dimers and cations

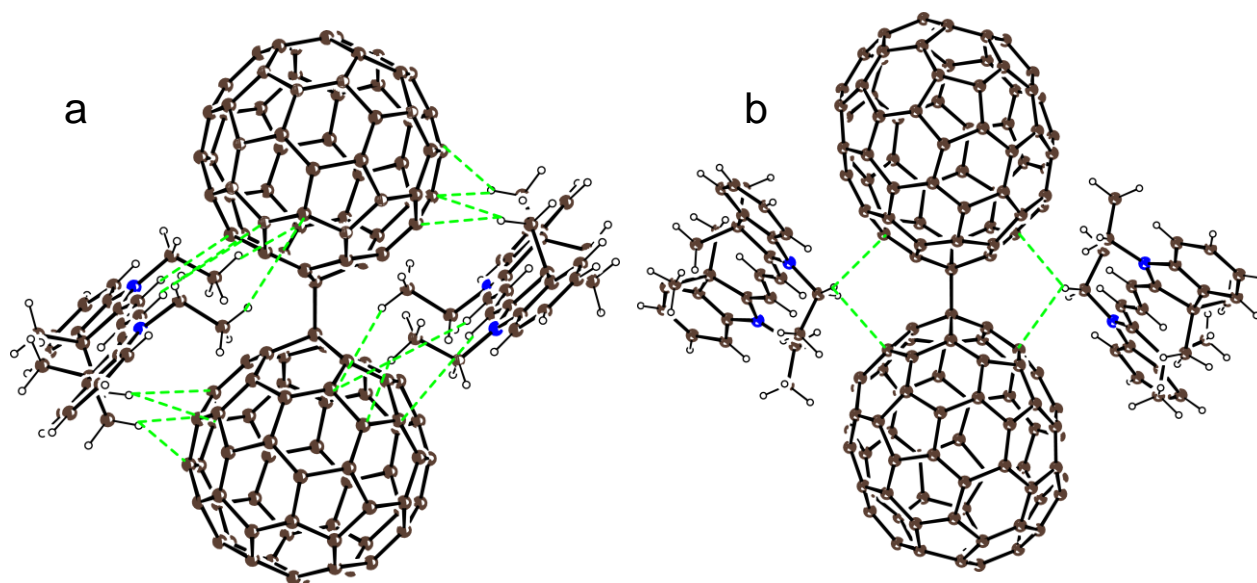


Fig. S4. Formation of short H(astrophloxine⁺)...C(Fullerene dimer) contacts in the crystal structure of **1** (for the dimeric (C₆₀)₂ form in type I with the 58% occupancy) (a) and **2** (b). These contacts are shown by green dashed lines.

Fitting of SQUID data

Singlet-triplet (isolated dimer) model with Heisenberg Hamiltonian

$$\mathbf{H} = -2J(\mathbf{S}_1 \cdot \mathbf{S}_2)$$

$$\chi = \frac{2 N_A g^2 \mu_B^2}{3 k_B T} \times \frac{1}{1 + \frac{1}{3} \exp\left(-\frac{2J}{k_B T}\right)}$$

References are given in the main text.

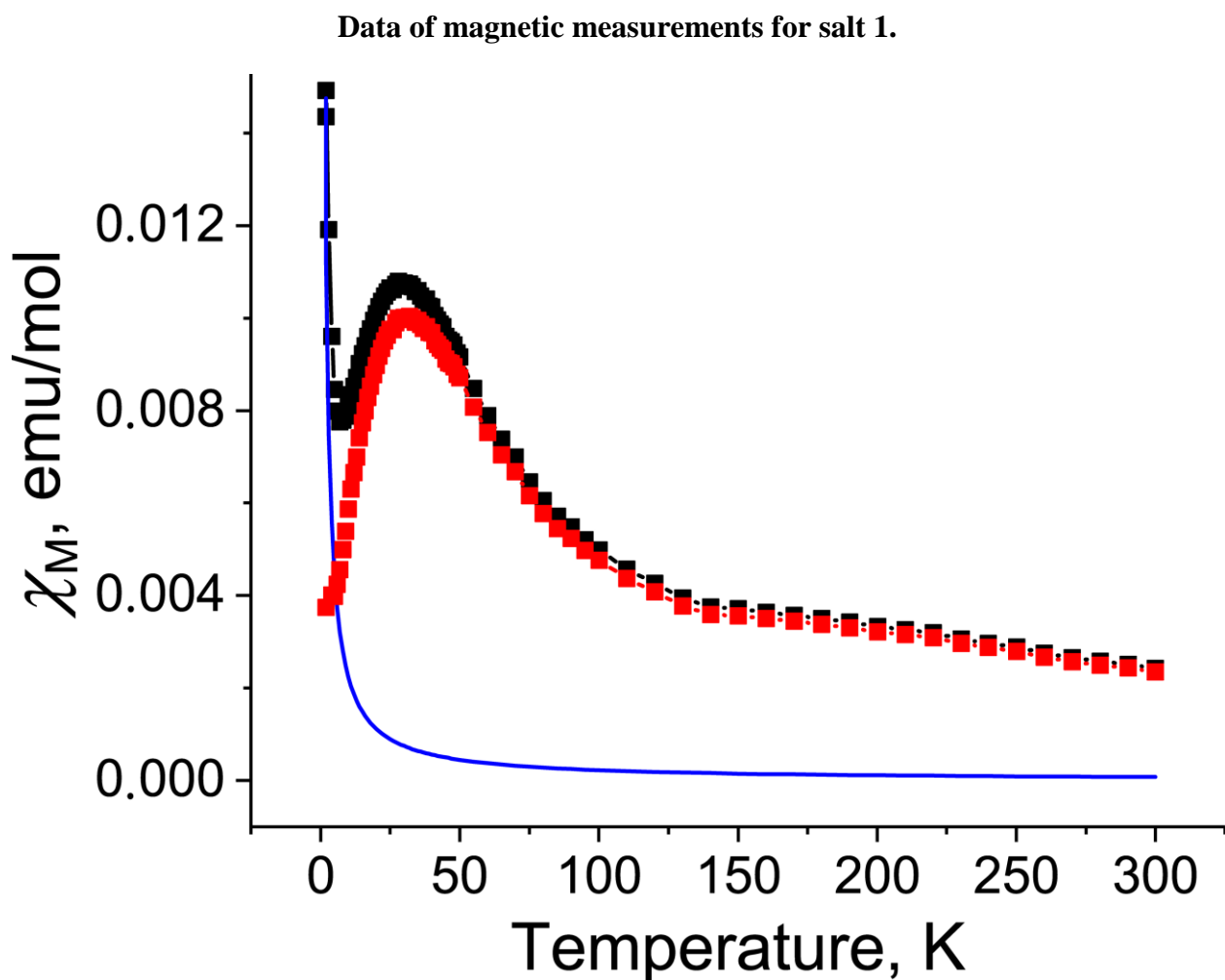


Fig. S5. Temperature dependence of molar magnetic susceptibility for polycrystalline **1** measured in the 1.9-300 K range (black squares). Two contributions can be resolved: from the Curie impurities (blue curve) originated from 3.8% of $S = 1/2$ spins and from the sample (red curve with squares). The latter contribution is obtained by the subtraction of the contribution from the Curie impurities from the experimental curve.

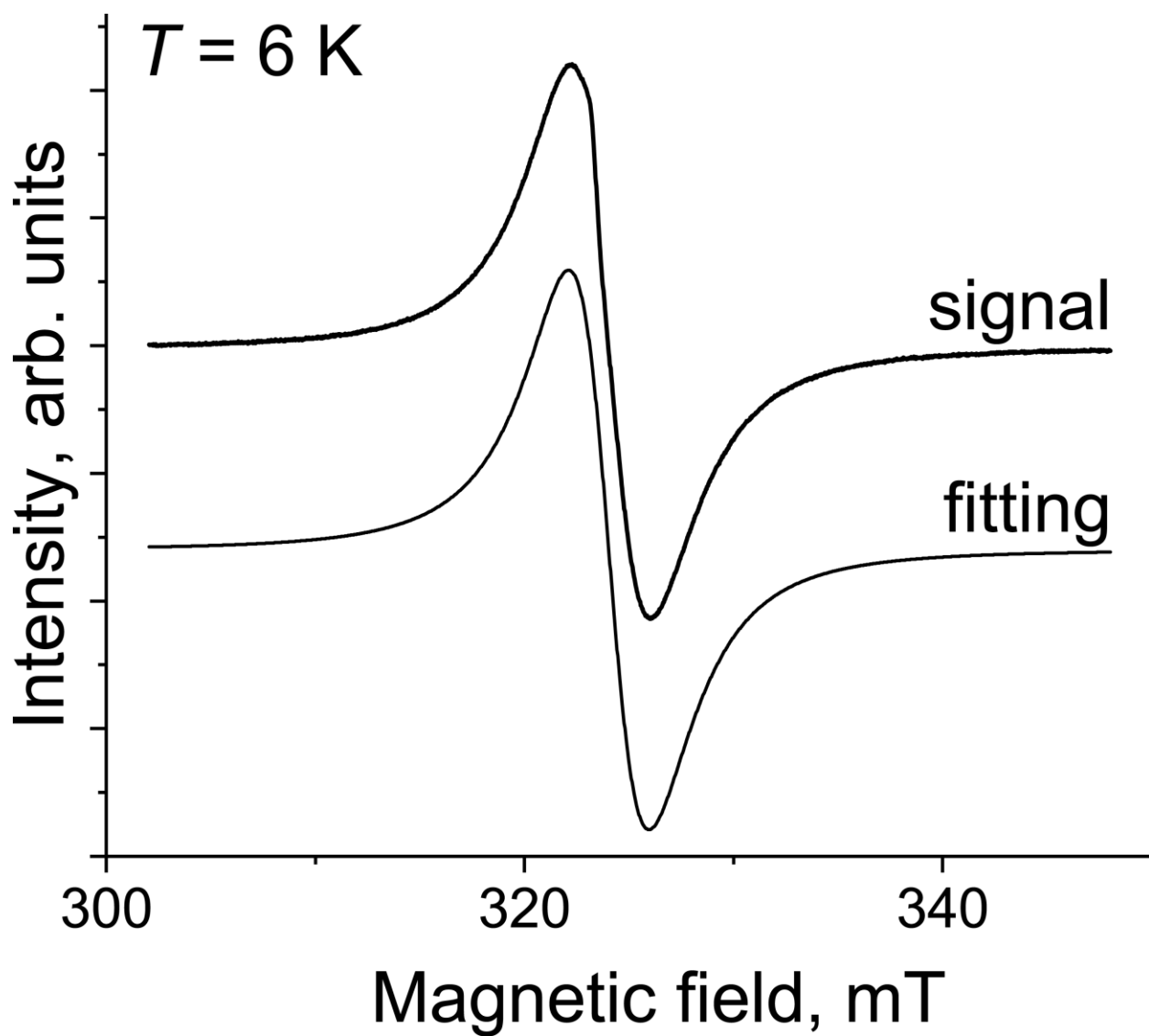


Fig. S6. EPR signal from polycrystalline **1** measured at 6 K. Signal was fitted by one Lorentzian line as shown below, parameters of this line are given in the main text.

Data of EPR measurements for salt 2.

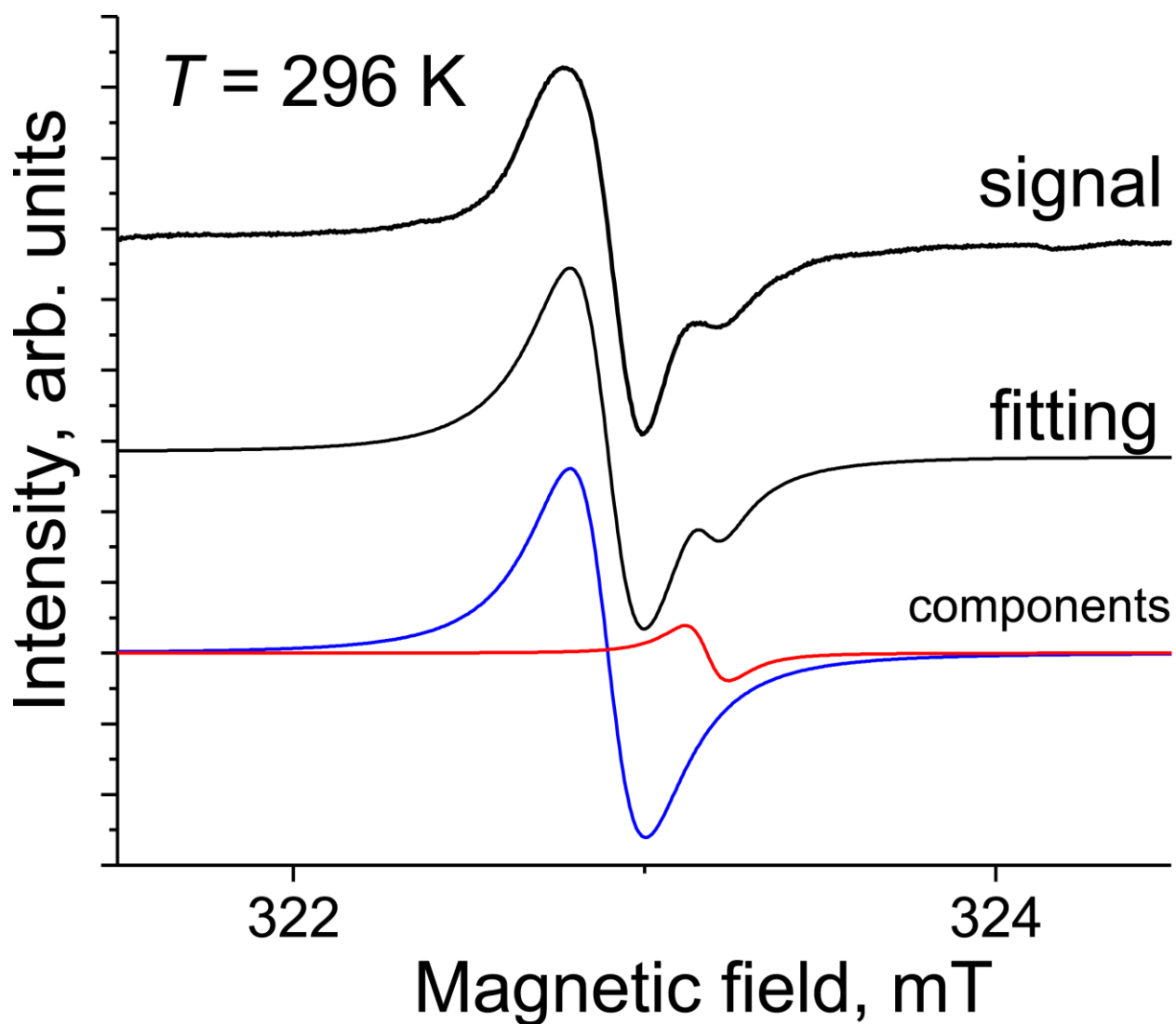


Fig. S7. EPR signal from polycrystalline **2** at 296 K, the signal was fitted by two narrow lines with $g_1 = 2.0025$ and the linewidth of 0.21 mT and $g_2 = 2.0008$ and the linewidth of 0.12 mT. This signal can be attributed to the paramagnetic impurities localized on fullerene C_{70} since integral intensity of the signal corresponds to the contribution of less than 1% of $S = 1/2$ spins per one C_{70} anion.