Fullerene C\textsubscript{60} dianion salt, (Me\textsubscript{4}N\textsuperscript{+})\textsubscript{2}(C\textsubscript{60}\textsuperscript{2-})\textsubscript{2}·(TPC)\textsubscript{2}·2C\textsubscript{6}H\textsubscript{4}Cl\textsubscript{2}, where TPC is triptycene, obtained by a multicomponent approach†

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A multicomponent approach provided a new salt (Me\textsubscript{4}N\textsuperscript{+})\textsubscript{2}(C\textsubscript{60}\textsuperscript{2-})\textsubscript{2}·(TPC)\textsubscript{2}·2C\textsubscript{6}H\textsubscript{4}Cl\textsubscript{2} (1) containing the discrete C\textsubscript{60}\textsuperscript{2-} dianions, where TPC is triptycene. The crystal structure consists of alternating layers of closely packed zigzag fullerene chains solvated with C\textsubscript{6}H\textsubscript{4}Cl\textsubscript{2} molecules and the TPC network with Me\textsubscript{4}N\textsuperscript{+} cations. The hexagonal vacancies in the TPC network accommodate the cations and simultaneously act as a template for the formation of zigzag fullerene chains. Optical spectra support the formation of C\textsubscript{60}\textsuperscript{2-} dianions. According to the electron paramagnetic resonance technique (EPR) the C\textsubscript{60}\textsuperscript{2-} dianions have a diamagnetic singlet ground state below 140 K. The increased intensity of the EPR signal above this temperature reflects the growing thermal population of the excited triplet state. This signal has $g = 2.0003$ and a linewidth of 2.53 mT at 302 K and the estimated singlet–triplet energy gap is $674 \pm 10$ K ($468 \pm 7$ cm\textsuperscript{-1}).

Fullerene compounds possess promising conducting and magnetic properties.\textsuperscript{1-4} For example, compounds with mono-reduced fullerenes obtained by alkali metal doping,\textsuperscript{1} layered salts with hexagonal C\textsubscript{60}\textsuperscript{+} packing,\textsuperscript{2} and fullerene complexes with partial charge transfer\textsuperscript{3} show metallic conductivity whereas fullerene salt with tetrakis(dimethylamino)ethylene manifests ferromagnetic ordering of spins below 16 K.\textsuperscript{4} It is known\textsuperscript{5} that the C\textsubscript{60}\textsuperscript{+} radical anions have a strong tendency to form diamagnetic singly-bonded fullerene (C\textsubscript{60})\textsubscript{2} dimers. Therefore, an important point in the design of such compounds is to organize close packing of fullerene anions in a crystal but steric hindrances should be introduced to prevent the dimerization of fullerenes.

The effectiveness of the multicomponent approach is proved to form the abovementioned hexagonal C\textsubscript{60}\textsuperscript{+} packing. In this way, one of the components is a structure-forming molecule of large size, which defines the crystal structure of the compound and prevents fullerene dimerization. Another component is a cation of small size, which defines the charged state of fullerene. Up to now several compounds of such type have been obtained,\textsuperscript{2,6} for example, (MDABCO\textsuperscript{+})(C\textsubscript{60}\textsuperscript{+})·TPC,\textsuperscript{2} where MDABCO\textsuperscript{+} is the N-methylidiazabicyclooctanium cation and TPC is a structure-forming triptycene molecule. TPC molecules form a hexagonal network which accommodates the MDABCO\textsuperscript{+} cations and becomes a template for the formation of closely packed hexagonal fullerene layers. At the same time fullerenes are separated in the layers by TPC molecules and cannot dimerize even at short distances between them. As a result, this compound shows metallic conductivity in the fullerene layers preserved from room temperature down to liquid helium temperatures. This is a rare example of a fullerene compound with quasi-two-dimensional metallic conductivity.\textsuperscript{2} Variation of cations allows the interfullerene distances in the layers to change, and (MQ\textsuperscript{+})(C\textsubscript{60}\textsuperscript{+})·TPC with larger N-methylquinucleinidium cations transfers to the Mott insulating state.\textsuperscript{6c} Recently this approach was extended to the synthesis of layered salts\textsuperscript{7} with metal phthalocyanines allowing one to obtain compounds with strong magnetic coupling of spins in (Me\textsubscript{4}P\textsuperscript{+})[M\textsuperscript{4+}O(Pc\textsuperscript{+})\textsubscript{3}](TPC)\textsubscript{0.5}·C\textsubscript{6}H\textsubscript{4}Cl\textsubscript{2} (M = Ti and V, Pc is phthalocyanine).\textsuperscript{2b}

Despite the fact that different fullerene salts with the C\textsubscript{60}\textsuperscript{2-} dianions were obtained,\textsuperscript{8} the multi-component salts with the C\textsubscript{60}\textsuperscript{2-} dianions are still unknown. In this work we for the first time extend the multicomponent approach to the synthesis of dianion fullerene salt to obtain crystalline (Me\textsubscript{4}N\textsuperscript{+})\textsubscript{2}(C\textsubscript{60}\textsuperscript{2-})·(TPC)\textsubscript{2}·2C\textsubscript{6}H\textsubscript{4}Cl\textsubscript{2} (1) with closely packed zigzag fullerene chains. The optical and magnetic properties of 1 and the effectiveness of structural design of the multicomponent dianion salt are discussed.

The salt was synthesized using a strong reductant sodium fluorenone ketyl\textsuperscript{9} which can generate the C\textsubscript{60}\textsuperscript{2-} dianions in
solution in the presence of an excess of the Me₄N⁺ cations. Slow mixing of the obtained solution with n-hexane without TPC did not yield the crystals of the two-component salt (Me₂N)₂(C₆₀²⁻). The synthesis in the presence of an excess of TPC resulted in the crystallization of thin plates in high yield whose composition was determined by X-ray diffraction on a single crystal (using synchrotron radiation) to be (Me₄N)₂(C₆₀²⁻)(TPC)₂-2C₆H₄Cl₂ (1).

The charged state of fullerene can be unambiguously determined from the spectra in the IR- and visible-NIR ranges measured in KBr pellets prepared under anaerobic conditions. A 2:1 cation to fullerene ratio indicates a formal 2⁻ charge on the fullerene molecules, which is supported by the IR spectrum of 1. The absorption bands of C₆₀ are manifested in the spectrum of 1 at 516, 572, 1184 and 1371 cm⁻¹ assignable to the F₁u(1–4) modes, respectively. The band of the F₁u(4) C₆₀ mode is most sensitive to the presence of absorption bands at 845 and 956 nm (Fig. 1) confirming the dianionic state of C₆₀. The spectrum of 1 is characterized by a broad and relatively weak band with a maximum at 1220 nm (shown by an arrow in Fig. 1). Most probably this band can be assigned to the F₁u(4) C₆₀ mode.

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linear in the 300–180 K range allowing one to estimate the singlet–triplet energy gap in the C_{60}^{2–} dianions to be 674 ± 10 K (468 ± 7 cm^{-1}). Previously several salts containing the C_{60}^{2–} dianions manifested the diamagnetic singlet ground state and thermal population of the excited triplet state with the singlet–triplet energy gaps in the 701–1045 K or 487–730 cm^{-1} ranges.\(^{8,11}\) It is seen that the gap obtained for \(\textbf{1}\) is the smallest gap among all studied C_{60}^{2–} salts. Nevertheless, the population of the excited triplet state in \(\textbf{1}\) is less than 10% of spins from the total amount of C_{60}. This is too small even at 302 K to manifest the conductivity or promising magnetic properties.

It is evident that the multi-component approach can be used in the design of dianion fullerenes salts. As in the case of previously studied multi-component C_{60}^{2+} salts,\(^{5,6}\) TPC molecules form a hexagonal network with vacancies accommodating small Me_{4}N\(^{+}\) cations. This network becomes a template to build fullerene layers which contains closely packed zigzag fullerene chains and solvent o-C_{6}H_{4}Cl_{2} molecules. Potentially the TPC network allows the formation of hexagonal fullerene layers but in the case of the C_{60}^{2–} dianions only fragments of these layers are formed since half of fullerene positions in these layers are substituted by neutral solvent molecules to preserve the electroneutrality of the compound. It is shown that the C_{60}^{2–} dianions have the singlet ground state in \(\textbf{1}\) with the excited triplet state thermally populated above 140 K. The singlet–triplet energy gap was estimated to be 674 ± 10 K. To date this is the smallest gap among studied C_{60}^{2–} salts.

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### Notes and references

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