A multicomponent approach provided a new salt (Me4N+)2(C602−)·(TPC)2·2C6H4Cl2 (1) containing the discrete C602− dianions, where TPC is triptycene. The crystal structure consists of alternating layers of closely packed zigzag fullerene chains solvated with C6H4Cl2 molecules and the TPC network with Me4N+ 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 C602− dianions. According to the electron paramagnetic resonance technique (EPR) the C602− 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 ± 7 cm$^{-1}$).

Fullerene compounds possess promising conducting and magnetic properties.1–4 For example, compounds with monoreduced fullerenes obtained by alkali metal doping,1 layered salts with hexagonal C60+ packing,2 and fullerene complexes with partial charge transfer3 show metallic conductivity whereas fullerene salt with tetrakis(dimethylamino)ethylen manifests ferromagnetic ordering of spins below 16 K.4 It is known5 that the C60− radical anions have a strong tendency to form diamagnetic singly-bonded fullerene (C60−)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 C60+ 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,2,6 for example, (MDABCO +)(C60−)·TPC,2 where MDABCO+ is the N-methylidiazabicyclooctanium cation and TPC is a structure-forming triptycene molecule. TPC molecules form a hexagonal network which accommodates the MDABCO+ 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.2 Variation of cations allows the interf fullerene distances in the layers to change, and (MQ)+(C60−)·TPC with larger N-methylquinuclidinium cations transfers to the Mott insulating state.6 Recently this approach was extended to the synthesis of layered salts7 with metal phthalocyanines allowing one to obtain compounds with strong magnetic coupling of spins in (Me3P)2[MIV(O(Pc+)·(TPC))]0.5 C6H4Cl2 (M = Ti and V, Pc is phthalocyanine).7b

Despite the fact that different fullerene salts with the C602− dianions were obtained,8 the multi-component salts with the C602− 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 (Me4N+)2(C602−)·(TPC)2·2C6H4Cl2 (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 fluorenenone ketyl9 which can generate the C602− 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 (Me₄N⁺)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 firms the dianionic state of C₆₀. The spectrum of presence of absorption bands at 845 and 956 nm (Fig. 1) con-

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Fig. 1 Spectrum of salt 1 in the UV-visible-NIR ranges in KBr pellets prepared under anaerobic conditions.
Fig. 3  View of the crystal structure of salt 1 along the a axis: (a) the layer containing zigzag fullerene chains and o-C6H4Cl2 molecules; (b) the layer of TPC molecules which form hexagonal vacancies to accommodate Me4N+ cations; (c) projection of the TPC layer with Me4N+ cations on the fullerene layer (o-C6H4Cl2 molecules in this layer are not shown for clarity).

Fig. 4  (a) EPR signal of polycrystalline 1 at 302 K (upper line), fitting of the signal by two Lorentzian lines is shown at the bottom; temperature dependencies of: (b) integral intensity of the signal (the inset shows the dependence of natural logarithm of integral intensity multiplied by temperature vs. reverse temperature to determine the singlet–triplet gap); (c) linewidth of the signal.

linear in the 300–180 K range allowing one to estimate the singlet–triplet energy gap in the C602− dianions to be 674 ± 10 K (468 ± 7 cm−1). Previously several salts containing the C602− 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 It is seen that the gap obtained for 1 is the smallest gap among all studied C602− salts. Nevertheless, the population of the excited triplet state in 1 is less than 10% of spins from the total amount of C60. 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 fullerene salts. As in the case of previously studied multi-component C60− salts, TPC molecules form a hexagonal network with vacancies accommodating small Me4N+ cations. This network becomes a template to build fullerene layers which contains closely packed zigzag fullerene chains and solvent o-C6H4Cl2 molecules. Potentially the TPC network allows the formation of hexagonal fullerene layers but in the case of the C602− 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 C602− dianions have the singlet ground state in 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 C602− salts.

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Notes and references

‡ Crystal data for 1: C120H60Cl4N2, F.W. 1671.50, brown plate, 0.4 × 0.4 × 0.01 mm3; 100(2) K: orthorhombic, space group Pbcn, a = 24.182(2), b = 17.718(1), c = 17.929(1) Å, V = 7681.8(9) Å3, Z = 4, dcalc = 1.445 g cm−3, μ = 0.396 mm−1, F(000) = 3448, 110 058 reflections collected, 8707 independent; R1 = 0.129 for 4947 observed data [>2σ(F)] with 702 restraints and 707 parameters; wR2 = 0.360 [all data]; G.o.F. = 1.013. CCDC 1539600.


