



Cite this: *New J. Chem.*, 2017, **41**, 4779

Received 3rd April 2017,
Accepted 11th May 2017

DOI: 10.1039/c7nj01096f

rsc.li/njc

Fullerene C₆₀ dianion salt, (Me₄N⁺)₂(C₆₀^{2−})·(TPC)₂·2C₆H₄Cl₂, where TPC is triptycene, obtained by a multicomponent approach†

Dmitri V. Konarev,^a Sergey I. Troyanov,^b Akihiro Otsuka,^{cd} Hideki Yamochi,^{cd} Gunzi Saito^{ef} and Rimma N. Lyubovskaya^a

A multicomponent approach provided a new salt (Me₄N⁺)₂(C₆₀^{2−})·(TPC)₂·2C₆H₄Cl₂ (**1**) containing the discrete C₆₀^{2−} 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 C₆₀^{2−} dianions. According to the electron paramagnetic resonance technique (EPR) the C₆₀^{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 ± 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)ethylene 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*-methyldiazabicyclooctanium 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 interfullerene distances in the layers to change, and (MQ⁺)(C₆₀^{•−})·TPC with larger *N*-methylquinuclidinium cations transfers to the Mott insulating state.^{6c} 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 (Me₄P⁺)[M^{IV}O(Pc^{3−})]^{•−}(TPC)_{0.5}·C₆H₄Cl₂ (M = Ti and V, Pc is phthalocyanine).^{7b}

Despite the fact that different fullerene salts with the C₆₀^{2−} dianions were obtained,⁸ the multi-component salts with the C₆₀^{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 (Me₄N⁺)₂(C₆₀^{2−})·(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 fluorenone ketyl⁹ which can generate the C₆₀^{2−} dianions in

^a Institute of Problems of Chemical Physics RAS, Chernogolovka, 142432, Russia.
E-mail: konarev3@yandex.ru; Fax: +7-496-522-18-52

^b Moscow State University, Leninskie Gory, 119991 Moscow, Russia

^c Research Center for Low Temperature and Materials Sciences, Kyoto University, Sakyo-ku, Kyoto 606-8501, Japan

^d Division of Chemistry, Graduate School of Science, Kyoto University, Sakyo-ku, Kyoto 606-8502, Japan

^e Faculty of Agriculture, Meijo University, 1-501 Shiogamaguchi, Tempaku-ku, Nagoya 468-8502, Japan

^f Toyota Physical and Chemical Research Institute, 41-1, Yokomichi, Nagakute, Aichi 480-1192, Japan

† Electronic supplementary information (ESI) available: IR spectra of starting compounds and salt **1**. CCDC 1539600. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c7nj01096f



solution in the presence of an excess of the Me_4N^+ cations.^{8f} Slow mixing of the obtained solution with *n*-hexane without TPC did not yield the crystals of the two-component salt $(\text{Me}_4\text{N}^+)_2(\text{C}_{60}^{2-})$. 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 $(\text{Me}_4\text{N}^+)_2(\text{C}_{60}^{2-}) \cdot (\text{TPC})_2 \cdot 2\text{C}_6\text{H}_4\text{Cl}_2$ (**1**).

The charged state of fullerene can be unambiguously determined from the spectra in the IR- and visible-NIR ranges¹⁰ 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 C_{60} are manifested in the spectrum of **1** at 516, 572, 1184 and 1371 cm^{-1} assignable to the $\text{F}_{1u}(1-4)$ modes, respectively. The band of the $\text{F}_{1u}(4)$ C_{60} mode is most sensitive to charge transfer to the fullerene molecule and is shifted from 1429 cm^{-1} (neutral state) to 1388–1396 cm^{-1} in the spectra of the salts with the $\text{C}_{60}^{\bullet-}$ radical anions and to 1370–1374 cm^{-1} in the spectra of the salts with the C_{60}^{2-} dianions.¹⁰ The position of this band at 1371 cm^{-1} in the spectrum of **1** clearly indicates the formation of C_{60}^{2-} . Fullerene C_{60} anions in each charged state show characteristic spectra in the near-IR range.^{10d,e} The presence of absorption bands at 845 and 956 nm (Fig. 1) confirms the dianionic state of C_{60} . The spectrum of **1** also contains 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 attributed to the interfullerene charge transfer process in closely packed zigzag fullerene chains (see the crystal structure section). Generally, such charge transfer bands are manifested in the spectra of the salts containing closely packed fullerene anions.^{6c}

The crystal structure of **1** was determined at 100 K.[‡] The independent components are shown in Fig. 2. The C_{60}^{2-} dianion is located on a twofold axis and is statistically disordered between two orientations. Salt **1** has a layered structure which is characteristic of all the compounds obtained by the

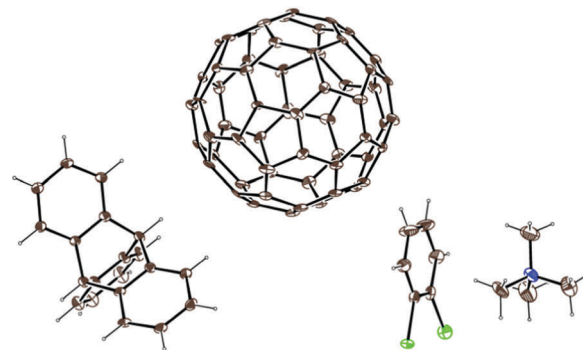


Fig. 2 Independent components in salt **1**. Ellipsoids are shown with the 25% probability.

multi-component approach with $\text{TPC}^{2,6c,7}$ (Fig. 3). The organic layer contains a hexagonal TPC network which accommodates one small Me_4N^+ cation in each vacancy (Fig. 3b). The network is not ideally hexagonal as in the case of $(\text{MDABCO}^+)(\text{C}_{60}^{\bullet-}) \cdot \text{TPC}$ with the MDABCO⁺ cations² but is slightly distorted. The triangles formed by three nitrogen atoms of Me_4N^+ in this network have the sides of 9.01, 9.87 and 10.30 Å. Fullerene C_{60}^{2-} dianions are partially penetrated into the hexagonal TPC network which becomes a template to build fullerene layers. Fullerene layers contain zigzag fullerene chains arranged along the *c* axis and alternate with the *o*- $\text{C}_6\text{H}_4\text{Cl}_2$ molecules along the *b* axis (Fig. 3a). These chains can be considered as fragments of closely packed hexagonal fullerene layers since the zigzag angle is close to 120° and the center-to-center interfullerene distances are only 10.015 and 10.031 Å (very close to those in the closely packed hexagonal fullerene layers of $(\text{MDABCO}^+)(\text{C}_{60}^{\bullet-}) \cdot \text{TPC}$ – 10.07 Å at 300 K).² However, hexagonal fullerene layers are not formed in **1** since there are two hexagonal vacancies occupied by Me_4N^+ per one fullerene unit due to the dianion state of fullerenes. As a result, one of two fullerenes in the hexagonal layer is substituted by two neutral $\text{C}_6\text{H}_4\text{Cl}_2$ molecules to retain the electroneutrality of the compound. In **1**, the zigzag fullerene chains with an angle of 120° are the resultant packing patterns of fullerene dianions.

The magnetic properties of the salt were studied by the EPR technique for a polycrystalline sample of **1** sealed in the quartz tube. Only a weak narrow EPR signal is observed below 140 K with a nearly temperature independent *g*-factor of 1.9999 and a linewidth (ΔH) of 0.4–0.5 mT. The integral intensity of this signal corresponds to the contribution of less than 2% of spins from the total amount of C_{60} . This indicates the diamagnetic singlet ground state for the C_{60}^{2-} dianions in **1**. Above 140 K a new signal grows in intensity and it is strongly broadened with the temperature increase (Fig. 4b and c). The intensity increases more than 3 times and the signal has *g* = 2.0003 and ΔH = 2.53 mT at 302 K (Fig. 4a). Such behaviour can be attributed to the thermal population of the excited triplet state of the C_{60}^{2-} dianions. The triplet features of the signal are not manifested at high temperature (*T* > 140 K) most probably due to averaging effects. The plot of natural logarithm of integral intensity multiplied by temperature vs. reverse temperature is

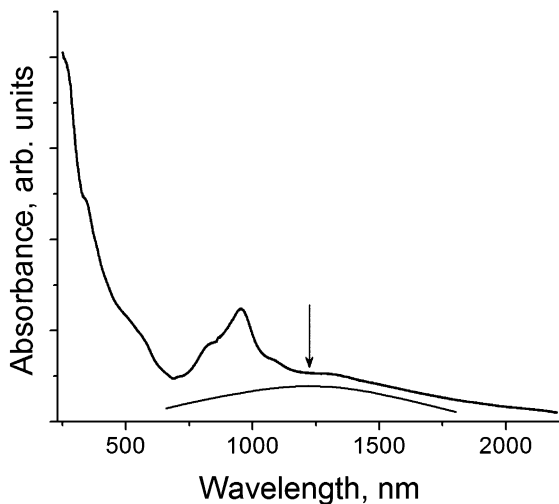


Fig. 1 Spectrum of salt **1** in the UV-visible-NIR ranges in KBr pellets prepared under anaerobic conditions.



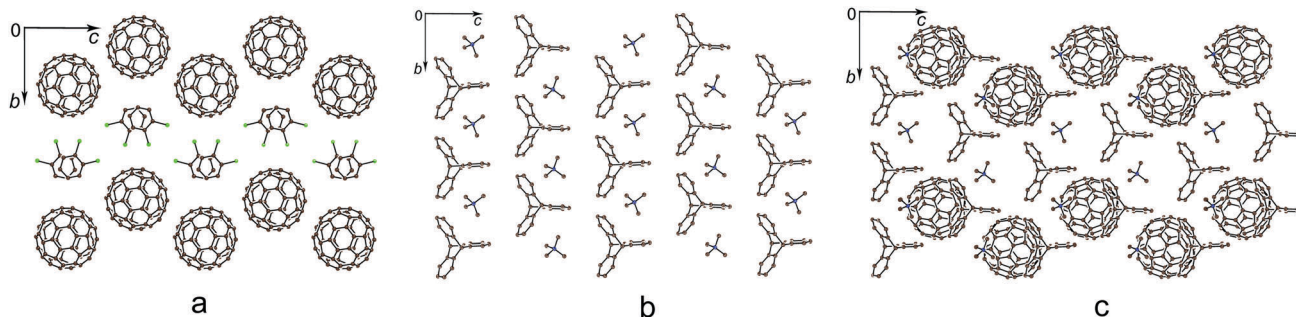


Fig. 3 View of the crystal structure of salt **1** along the *a* axis: (a) the layer containing zigzag fullerene chains and *o*-C₆H₄Cl₂ molecules; (b) the layer of TPC molecules which form hexagonal vacancies to accommodate Me₄N⁺ cations; (c) projection of the TPC layer with Me₄N⁺ cations on the fullerene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

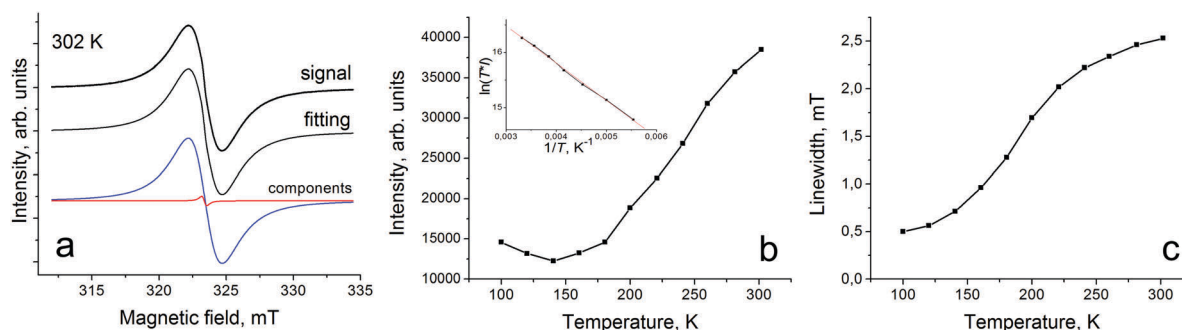


Fig. 4 (a) EPR signal of polycrystalline **1** at 302 K (upper line), fitting of the signal by two Lorentzian lines is shown at the bottom; temperature dependencies of: (b) integral intensity of the signal (the inset shows the dependence of natural logarithm of integral intensity multiplied by temperature 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 C₆₀^{2−} dianions to be 674 ± 10 K (468 ± 7 cm^{−1}). Previously several salts containing the C₆₀^{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.^{8j,l} It is seen that the gap obtained for **1** is the smallest gap among all studied C₆₀^{2−} 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^{2,6} 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 C₆₀^{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 C₆₀^{2−} 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 C₆₀^{2−} salts.

This work was supported by FASO Russia, state task #0089-2014-0036 and JSPS KAKENHI Grant Numbers JP23225005 and JP26288035.

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, *d*_{calcd} = 1.445 g cm^{−3}, *μ* = 0.396 mm^{−1}, *F*(000) = 3448, 110 058 reflections collected, 8707 independent; *R*₁ = 0.129 for 4947 observed data [*> 2σ*(*F*)] with 702 restraints and 707 parameters; *wR*₂ = 0.360 (all data); G.o.F. = 1.013. CCDC 1539600.

- (a) P. W. Stephens, G. Bortel, G. Faigel, M. Tegze, A. Jánosy, S. Pekker, G. Oszlanyi and L. Forró, *Nature*, 1994, **370**, 636; (b) F. Bommeli, L. Degiorgi, D. Wachter, Ö. Legeza, A. Jánosy, G. Oszlanyi, O. Chauvet and L. Forro, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1995, **51**, 14794; (c) M. J. Rosseinsky, *J. Mater. Chem.*, 1995, **5**, 1497.
- D. V. Konarev, S. S. Khasanov, A. Otsuka, M. Maesato, G. Saito and R. N. Lyubovskaya, *Angew. Chem., Int. Ed.*, 2010, **49**, 4829.
- D. V. Konarev, S. S. Khasanov, M. Ishikawa, E. I. Yudanov, A. F. Shevchun, M. S. Mikhailov, P. A. Stuzhin, A. Otsuka, H. Yamochi, G. Saito and R. N. Lyubovskaya, *ChemistrySelect*, 2016, **1**, 323.
- P. W. Stephens, D. Cox, J. W. Lauher, L. Mihaly, J. B. Wiley, P.-M. Allemand, A. Hirsch, K. Holczer, Q. Li, J. D. Thompson and F. Wudl, *Nature*, 1992, **355**, 331.



- 5 (a) D. V. Konarev, S. S. Khasanov, G. Saito, A. Otsuka, Y. Yoshida and R. N. Lyubovskaya, *J. Am. Chem. Soc.*, 2003, **125**, 10074; (b) D. V. Konarev, S. S. Khasanov and R. N. Lyubovskaya, *Russ. Chem. Bull.*, 2007, **56**, 371; (c) G. A. Domrachev, Y. A. Shevelev, V. K. Cherkasov, G. V. Markin, G. K. Fukin, S. Ya. Khorshev, B. S. Kaverin and V. L. Karnatchevich, *Russ. Chem. Bull.*, 2004, **53**, 2056; (d) N. V. Kozhemyakina, K. Y. Amsharov, J. Nuss and M. Jansen, *Chem. – Eur. J.*, 2011, **17**, 1798.
- 6 (a) D. V. Konarev, A. Y. Kovalevsky, S. S. Khasanov, G. Saito, A. Otsuka and R. N. Lyubovskaya, *Eur. J. Inorg. Chem.*, 2005, 4822; (b) D. V. Konarev, S. S. Khasanov, G. Saito, A. Otsuka and R. N. Lyubovskaya, *J. Mater. Chem.*, 2007, **17**, 4171; (c) D. V. Konarev, S. S. Khasanov, A. Otsuka, M. Maesato, M. Uruichi, K. Yakushi, A. Shevchun, H. Yamochi, G. Saito and R. N. Lyubovskaya, *Chem. – Eur. J.*, 2014, **20**, 7268.
- 7 (a) D. V. Konarev, S. S. Khasanov, M. Ishikawa, A. Otsuka, H. Yamochi, G. Saito and R. N. Lyubovskaya, *Inorg. Chem.*, 2013, **52**, 3851; (b) D. V. Konarev, S. S. Khasanov, A. V. Kuzmin, Y. Nakano, M. Ishikawa, A. Otsuka, H. Yamochi, G. Saito and R. N. Lyubovskaya, *Cryst. Growth Des.*, 2017, **17**, 753.
- 8 (a) P. Paul, Z. Xie, R. Bau, P. D. W. Boyd and C. A. Reed, *J. Am. Chem. Soc.*, 1994, **116**, 4145; (b) J. Hong, M. P. Shores and C. M. Elliott, *Inorg. Chem.*, 2010, **49**, 11378; (c) K. Himmel and M. Jansen, *Eur. J. Inorg. Chem.*, 1998, 1183; (d) K. Himmel and M. Jansen, *Chem. Commun.*, 1998, 1205; (e) K. Himmel and M. Jansen, *Z. Anorg. Allg. Chem.*, 1998, **624**, 1; (f) K. Himmel and M. Jansen, *Inorg. Chem.*, 1998, **37**, 3437; (g) H. Brumm and M. Jansen, *Z. Anorg. Allg. Chem.*, 2001, **627**, 1433; (h) T. F. Fässler, A. Spiekermann, M. E. Spahr and R. Nesper, *Angew. Chem., Int. Ed.*, 1997, **36**, 486; (i) S. D. Hoffmann and T. F. Fässler, *Z. Naturforsch., B: Chem. Sci.*, 2004, **59**, 1579; (j) D. V. Konarev, S. S. Khasanov, I. I. Vorontsov, G. Saito, Y. M. Antipin and R. N. Lyubovskaya, *Inorg. Chem.*, 2003, **42**, 3706; (k) D. V. Konarev, S. S. Khasanov, G. Saito and R. N. Lyubovskaya, *J. Porphyrins Phthalocyanines*, 2008, **12**, 1146; (l) D. V. Konarev, A. V. Kuzmin, S. V. Simonov, S. S. Khasanov, E. I. Yudanov, G. Saito and R. N. Lyubovskaya, *Phys. Chem. Chem. Phys.*, 2013, **15**, 9136.
- 9 R. O. Loutfy, K. Hsiaob, S. Ong and B. Keoshkeria, *Can. J. Chem.*, 1984, **62**, 1877.
- 10 (a) M. S. Dresselhaus, G. Dresselhaus and P. C. Eklund, *Science of Fullerenes and Carbon Nanotubes*, Academic Press, San Diego, 1996; (b) T. Picher, R. Winkler and H. Kuzmany, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1994, **49**, 15879; (c) V. N. Semkin, N. G. Spitsina, S. Krol and A. Graja, *Chem. Phys. Lett.*, 1996, **256**, 616; (d) C. A. Reed and R. D. Bolskar, *Chem. Rev.*, 2000, **100**, 1075; (e) D. V. Konarev and R. N. Lyubovskaya, *Russ. Chem. Rev.*, 2012, **81**, 336.

