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Structure, Optical, and Magnetic Properties of (PPN+)2(C70^2−)·2 C6H4Cl2, which Contains Dianionic Polymeric (C70^2−)n Chains

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Abstract: A new salt, (PPN+)2 (C70^2−)·2 C6H4Cl2 (**1**), which contains C70^2− dianions, has been obtained as single crystals (PPN+ = bis(triphenylphosphine)iminium cation). The C70^2− dianions form polymeric zigzag (C70^2−)n chains, in which the fullerene units are bonded through single C−C bonds of length 1.581(5)–1.586(6) Å. The distance between the centers of neighboring C70^2− units is 10.441 Å. The optical and magnetic properties of (C70^2−)n have also been studied. Decreasing the symmetry of C70 in the polymer activate about 20 new IR bands in addition to the 10 IR-active bands of the starting C70. The polymeric structure shows absorptions in the visible and NIR regions, with three main bands at 890,

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1200, and 1550 nm, instead of one band of isolated C70^2− dianions at 1165–1184 nm. We concluded that the (C70^2−)n polymer was diamagnetic, with a negative molar magnetic susceptibility of −3.82 × 10^−4 emu mol^−1 per C70^2− dianion. The polymer is EPR silent and a weak narrow EPR signal in salt **1** is due to impurities, which only constitute 0.84 % of spin $S = 1/2$ of the total amount of fullerene C70.

Introduction

Ionic fullerene compounds have evoked great interest owing to their promising conducting and magnetic properties[1–4] and to the large variety of developed dimeric and polymeric structures of fullerene anions, which show different physical properties.[5–16] The intercalation of C60 by alkali metals in a 1:1 molar ratio has yielded radical anion salts KC60, RbC60, and CsC60.[5–7] Slow cooling of the intercalation products results in the polymerization of the C60^·− anion radicals,
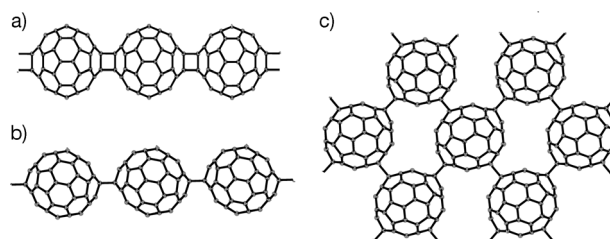

Figure 1. a) Linear (C60^−)x polymer in MC60 (M = K, Rb, and Cs);[5–7] b) linear (C60^3−)x polymer in Na2RbC60;[8] c) 2D (C60^4−)x polymer in Na4C60.[11]

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through [2+2] cycloaddition reactions, and to the formation of linear polymeric chains (Figure 1a). These air-stable polymers are not soluble in tetrahydrofuran (THF) and their depolymerization is only observed at $T > 320$°C. [KC60]n is a 3D metal down to 4 K,[5] whereas [RbC60]n and [CsC60]n are quasi-1D metals. These two latter salts transform into the diamagnetic state below 50 K and 40 K, respectively, owing to the antiferromagnetic ordering of spins in the polymer chains.[6,7]

The C60^3− trianions also polymerize in Na2RbC60,[8] Na2CsC60,[9] and Li3CsC60,[10] thus forming linear chains in which each C60^3− unit is bonded to its neighboring fullerenes through two single C−C bonds (Figure 1b). The starting phases, which contain monomeric C60^3− units, are superconducting. It was supposed that polymerization decreases the superconducting transition temperature in Na2CsC60 by 3 K, but the polymeric Na2RbC60 phase does not transfer into the superconducting state.[9] A 2D polymer is formed in Na4C60, in which each C60^4− anion is connected to the neighboring

fullerenes through four single C−C bonds (Figure 1 c). It was shown that this polymer is a strongly correlated metal without a transition into the superconducting state.[11]

A 2D polymer is formed in Li_4C_{60}, even at room temperature. This polymer contains linear chains that are formed by [2+2] cycloaddition reactions, similar to the polymeric chains in the KC_{60}, RbC_{60}, and CsC_{60} salts. These chains are bonded into the 2D polymer through single C−C bonds and the polymer has the properties of a nonmagnetic insulator.[12] Further studies have shown that this phase possesses relatively high ionic conductivity, owing to the high mobility of the Li^+ ions.[13] Because all of the polymers with negatively charged fullerenes are exclusively formed in the doped fullerene phases, the polymeric C_{60} structures can only be studied by powder X-ray diffraction.

Only several negatively charged polymers are known for fullerene C_{70}. However, in contrast to C_{60}, all of these compounds that contained C_{70} polymers have been studied by single-crystal X-ray diffraction.[14–16] These compounds were obtained by exchange reactions of alkali metal salts of C_{70} di- and trianions with metal cations (Ba^{2+}, Sr^{2+}, Ca^{2+}, Yb^{2+}, and Eu^{2+}) in liquid ammonia. Whereas the molecular structures and Raman spectra of the $(C_{70}^{2-})_n$ polymers have been reported,[14,15] their spectroscopic properties in the IR and UV/Vis/NIR regions, as well as their magnetic properties, still remain unknown.

Recently, we developed a convenient method for the preparation of different salts with fullerene C_{60} dianions.[17] The strong reducing agent sodium fluorenone selectively generates C_{60}^{2-} dianions in o-dichlorobenzene ($C_6H_4Cl_2$) in the presence of salts of organic cations. Significantly, the C_{60}^{3-} trianions are not formed, even in an excess of the reducing agent. For example, the reduction of C_{60} by sodium fluorenone in the presence of PPN^+Cl^- (PPN^+=bis(triphenylphosphine)iminium cation), followed by precipitation with n-hexane, allowed us to obtain $(PPN^+)_2$ $(C_{60}^{2-})\cdot 2 C_6H_4Cl_2$ (**2**).[17] Herein, we report the use of sodium fluorenone in the presence of PPN^+Cl^- for the reduction of C_{70}. A new salt, $(PPN^+)_2(C_{70}^{2-})\cdot 2 C_6H_4Cl_2$ (**1**), was obtained and precipitated in the form of single crystals by the diffusion of n-hexane. In contrast to the monomeric C_{60}^{2-} dianions in compound **2**, the C_{70}^{2-} dianions in salt **1** form infinite $(C_{70}^{2-})_n$ chains. This discussion concerns the molecular structure of the $(C_{70}^{2-})_n$ polymer, its spectroscopic properties in the IR and UV/Vis/NIR regions, and its magnetic properties, which have been studied for the first time.

Results and Discussion

Spectra of Compound 1 in the IR and UV/Vis/NIR Regions

The IR spectrum of $(PPN^+)_2(C_{70}^{2-})\cdot 2 C_6H_4Cl_2$ (**1**), together with that of $(PPN^+)_2(C_{60}^{2-})\cdot 2 C_6H_4Cl_2$ (**2**) obtained previously, is shown in Figure 2 a. Because both salts contain the same species (PPN^+ cation, fullerene, and solvent $C_6H_4Cl_2$ molecules), the positions of the bands that originate from the $(C_{70}^{2-})_n$ polymer can be unambiguously determined by

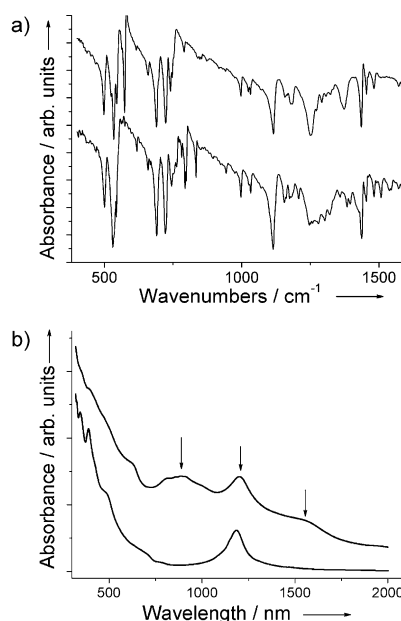Figure 2. a) IR spectra of $(PPN^+)_2(C_{60}^{2-})\cdot 2 C_6H_4Cl_2$ (**2**) with isolated C_{60}^{2-} dianions (top)[17] and of $(PPN^+)_2(C_{70}^{2-})\cdot 2 C_6H_4Cl_2$ (**1**) with the $(C_{70}^{2-})_n$ polymer (bottom); b) spectrum of compound **1** in the UV/Vis/NIR region (top) and a spectrum of isolated C_{70}^{2-} dianions in o-dichlorobenzene (bottom).

comparison of these spectra. Monomeric C_{60}^{2-} dianions in the spectrum of compound **2** only show four IR-active bands, with a shift of the $F_{1u}(4)$ mode from 1429 cm^{-1} (in neutral C_{60}) to 1373 cm^{-1}.[17] The IR-active bands of the $(C_{70}^{2-})_n$ polymer in the spectrum of compound **1** are listed in the Supporting Information. About 30 bands can be attributed to $(C_{70}^{2-})_n$, whereas the starting C_{70} only shows 10 IR-active bands.[18] These changes may be due to the activation of many silent modes, because polymerization decreases the molecular symmetry of C_{70}. Some of the bands of C_{70} are also split into several bands. For example, a weak band at 1413 cm^{-1} and a stronger band at 1429 cm^{-1} are observed in the spectrum of molecular C_{70} in the region 1350–1450 cm^{-1}. Instead of two bands, four bands of weak intensity appear in the spectrum of compound **1** at 1358, 1384, 1395, and 1427 cm^{-1}, which may be due to a shift of the main band at 1429 cm^{-1} to smaller wavenumber (a similar shift is observed upon the formation of C_{60}^{2-} dianions) and to the splitting of this band into several bands.

It is known that monomeric C_{70}^{2-} dianions only have one band in their solution-state Vis/NIR spectrum, at about 1165–1184 nm.[19,20] In fact, the C_{70}^{2-} dianions that are generated by reduction with sodium fluorenone in o-dichlorobenzene in the presence of PPN^+Cl^- exhibit this band at 1184 nm (Figure 2 b). The $(C_{70}^{2-})_n$ polymer shows broad absorption in the UV/Vis/NIR region in its solid-state spectrum, with three major bands at 890, 1200, and 1550 nm (Figure 2 b). The spectrum of the polymer is notably different from that of isolated C_{70}^{2-} dianions (Figure 2 b), thus indicating that the polymerization strongly affects the electronic structure of C_{70}. The appearance of a new, broad low-

energy band can be attributed to electron transfer between the C_{70}^{2-} dianions within the polymer chain. Previously, we also found that dimerization of the $C_{70}^{\bullet-}$ radical anions caused a change in the NIR region of the spectrum and resulted in the appearance of two broad bands for the $(C_{70}^-)_2$ dimers at 880 and 1240 nm, instead of one band for $C_{70}^{\bullet-}$ at 1363–1386 nm.[21–23]

Crystal Structure

The crystal structure of compound **1** contains four crystallographically independent PPN⁺ cations, two C_{70}^{2-} dianionic units, and four solvent *o*-dichlorobenzene molecules. Thus, the composition of compound **1** can be presented as $(PPN^+)_2(C_{70}^{2-})\cdot 2\,C_6H_4Cl_2$. Both crystallographically independent C_{70}^{2-} dianionic units and four PPN⁺ cations are fully ordered, whereas most solvent $C_6H_4Cl_2$ molecules are disordered between two positions.

The dianionic C_{70}^{2-} units form polymeric chains parallel to the *c* axis (Figure 3 and Figure 4a). Separate C_{70}^{2-} units are bound together through single C−C bonds (1.581(5) Å in one chain and 1.586(6) Å in another; averaged value:
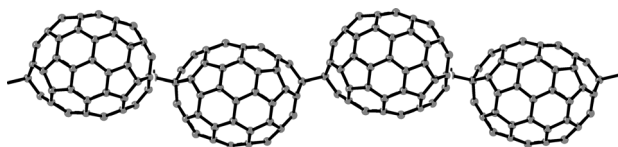
Figure 3. Polymeric $(C_{70}^{2-})_n$ chain in the crystal structure of compound **1**.

1.583(5) Å) between C_{70} cage pentagons that belong to the apical pentagons of undistorted D_{5h} C_{70} molecules. The polymer chains zigzag slightly in the *bc* plane, with an angle of 152.2° between the centers of neighboring C_{70}^{2-} units. The bond angles between intercage and C_{70}-cage C−C bonds lie within the narrow range of 111.1–113.3°, thus indicating sp³ hybridization of the bridging atoms. The distances between the centers of neighboring C_{70}^{2-} units in the polymeric chains are 10.447 and 10.435 Å in two crystallographically independent chains. The overall symmetry of the C_{70}^{2-} unit in the polymeric chain is lowered from D_{5h} in the starting C_{70} molecule to (non-crystallographic) C_2 symmetry. Apparently, this symmetry lowering is responsible for a more complicated IR spectrum of the polymeric structure in comparison with that of the starting C_{70} molecule (see previous section). The geometric parameters of the $(C_{70}^{2-})_n$ polymeric chains in compound **1** show close similarity to the chains in the structures of $[(Ba^{2+})(NH_3)_7](C_{70}^{2-})\cdot 9\,NH_3$ and $[(Sr^{2+})-(NH_3)_8](C_{70}^{2-})\cdot 3\,NH_3$, as previously described.[14,15] The polymeric chains in the latter salt have the following geometric parameters: The intercage C−C bond length is 1.575(3), the distance between the centers of neighboring C_{70}^{2-} is 10.493 Å, and the angle in the zigzag chains is 153.2°,[15] which are very close to the corresponding values in structure **1**. Interestingly, singly bonded $(C_{70}^-)_2$ dimers have virtually the same lengths of the intercage C−C bonds (1.583(2)–
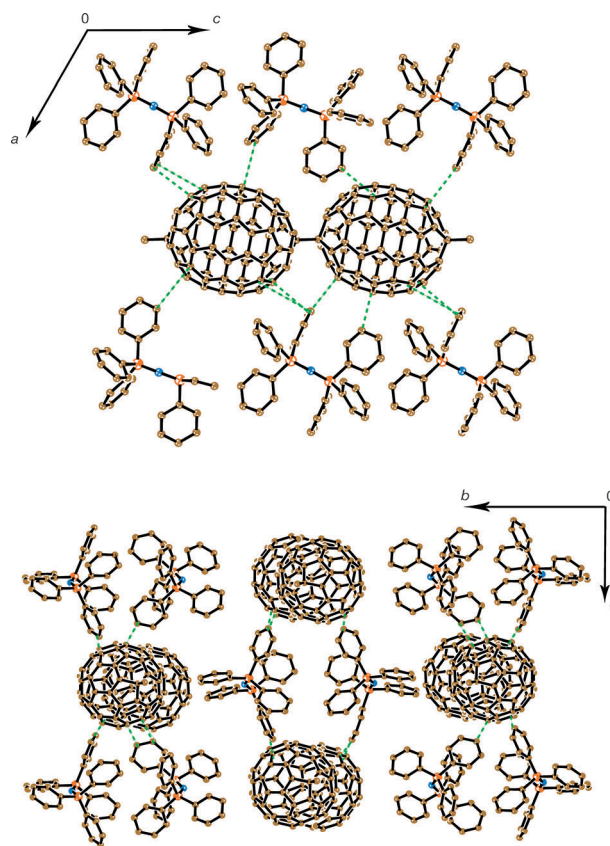
Figure 4. Projections of the crystal structure of compound **1** along the *b* (a) and *c* axes (b); H atoms and solvent molecules are omitted for clarity. Van der Waals C···C interactions between the $(C_{70}^{2-})_n$ polymeric chains and the PPN⁺ cations are denoted by dashed green lines.

1.586(3) Å) and the distances between the centers of neighboring C_{70}^- units (10.47-10.51 Å).[21–25] Slightly longer intercage C−C bonds (1.616(4) Å) were found in the positively charged singly bonded $(C_{70}^+)_2$ dimers.[26]

Polymer chains are well-separated from each other by bulky PPN⁺ cations: The shortest distance between the centers of C_{70}^{2-} units of neighboring polymer chains exceeds 17 Å. Each C_{70}^{2-} unit is surrounded by eight PPN⁺ cations. Phenyl groups on the PPN⁺ cations form some van der Waals H···C and C···C contacts with C_{70}^{2-} dianions at distances of 2.63–2.86 Å and 3.29–3.51 Å, respectively (Figure 4). Solvent o-$C_6H_4Cl_2$ molecules occupy channels that are directed parallel to the *c* axis, that is, also parallel to the $(C_{70}^{2-})_n$ chains.

Magnetic Properties

A polycrystalline sample of compound **1** was studied by SQUID and electron paramagnetic resonance (EPR) techniques. The salt is diamagnetic with a negative temperature-independent molar magnetic susceptibility of $\chi_0 = -0.00124\,emu\,mol^{-1}$ in the temperature range 70–300 K (Figure 5). The core temperature-independent diamagnetic contributions from the PPN⁺ cations and solvent $C_6H_4Cl_2$ molecules, as calculated by using Pascal constants, are
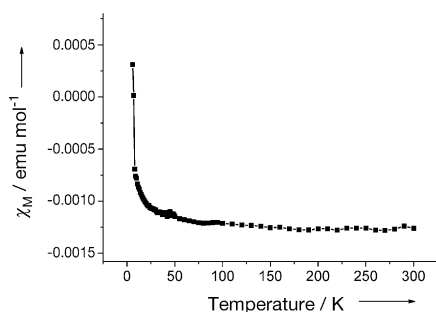
Figure 5. Temperature dependence of the molar magnetic susceptibility of compound **1** in the range 1.9–300 K.

-6.80×10^{-4} and -1.78×10^{-4} emu mol^{-1} for two PPN$^+$ cations and two $C_6H_4Cl_2$ molecules, respectively. Therefore, the $(C_{70}^{2-})_n$ polymer is diamagnetic, with a negative molar magnetic susceptibility of -3.82×10^{-4} emu mol^{-1} per C_{70}^{2-} dianionic unit. This value is rather close to the experimentally determined molar magnetic susceptibilities of neutral C_{60} (-2.52×10^{-4} emu mol^{-1}) and C_{70} (-4.96×10^{-4} emu mol^{-1}).[27] The contribution from the Curie impurities in compound **1** was estimated to be only 0.84% with spin $S = 1/2$ of the total amount of C_{70}. The diamagnetism of this polymer is explained by the presence of two electrons per C_{70}^{2-} dianion, both of which are involved in the formation of two intercage C–C bonds. Similarly, the singly bonded $(C_{70}^-)_2$ dimer is diamagnetic because one electron of the C_{70}^- anion is involved in the formation of one intercage C–C bond in the dimer.[21–25]

Salt **1** shows a narrow, weak EPR signal at room temperature, which can be fitted well by two lines with $g_1 = 2.0034$ (linewidth $(\Delta H) = 0.255$ mT) and $g_2 = 2.0044$ ($\Delta H = 0.150$ mT, Figure 6). The integral intensities of both lines correspond to a contribution of about 0.8% of the spins from the total amount of fullerene. The lines have an almost temperature-independent linewidth and a pure paramagnetic temperature dependence of the intensity at Weiss temperatures of close to zero. Thus, the major part of the C_{70}^{2-} dianions in the $(C_{70}^{2-})_n$ polymer is EPR silent, in accordance with the diamagnetic ground state of the polymer. This weak EPR signal can be attributed to impurities that are formed in the sample, owing to the slight oxidation of the highly air-sensitive C_{70}^{2-} dianions. In fact, similar weak narrow signals are always observed in the samples that con-
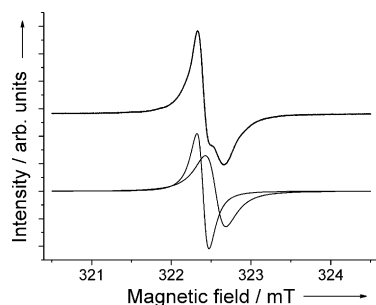
tain diamagnetic singly bonded $(C_{60}^-)_2$ and $(C_{70}^-)_2$ dimers (up to 5% of paramagnetic impurities).[21,23,28–32]

Conclusions

A new salt of dianionic C_{70}, $(PPN^+)_2(C_{70}^{2-})\cdot 2\,C_6H_4Cl_2$ (**1**), was obtained in which singly bonded C_{70}^{2-} dianions formed polymeric zigzag $(C_{70}^{2-})_n$ chains. The structure of these polymeric chains is close to those found in alkali-earth ammonia complexes $[(Ba^{2+})(NH_3)_7](C_{70}^{2-})(NH_3)_9$ and $[(Sr^{2+})(NH_3)_8]$ $(C_{70}^{2-})(NH_3)_3$.[14,15] The IR and Vis/NIR spectra and magnetic properties of the salt that contains polymeric $(C_{70}^{2-})_n$ chains are reported for the first time. Many IR-silent bands of the starting C_{70} become IR active and several of the IR bands are split, owing to the symmetry lowering of C_{70} in the polymeric structure of compound **1**. In addition, three main bands at 890, 1200, and 1550 nm appear in the Vis/NIR spectrum of salt **1** instead of the one band of isolated C_{70}^{2-} dianions (at 1165–1184 nm). The diamagnetism of salt **1** and of the $(C_{70}^{2-})_n$ polymer was explained by the involvement of both electrons in the C_{70}^{2-} units in the formation of intercage C–C bonds. Therefore, the polymer is EPR silent, whereas the observed weak EPR signal is attributed to impurities.

Experimental Section

Materials

PPNCl was purchased from Aldrich. C_{70} (98% purity) was purchased from NeoTech. Sodium fluorenone was obtained according to a literature procedure.[33] Solvents were purified under an argon atmosphere. *o*-Dichlorobenzene ($C_6H_4Cl_2$) was distilled over CaH$_2$ under reduced pressure; *n*-hexane was distilled over Na/benzophenone. The solvents were degassed and stored in the glove box. All of the synthetic operations of highly air-sensitive compound **1** were performed in an MBraun 150B-G glove box under a controlled atmosphere with water and oxygen content of less than 1 ppm. The as-prepared crystals were stored in a glove box. The polycrystalline sample was placed under anaerobic conditions in 2 mm quartz tubes for the EPR and SQUID measurements. KBr pellets of compound **1** for the IR and Vis/NIR measurements were prepared in the glove box.

General

UV/Vis/NIR spectra were recorded as KBr pellets on a Perkin–Elmer Lambda 1050 spectrometer in the range 250–2500 nm. FTIR spectra were obtained for KBr pellets on a Perkin–Elmer Spectrum 400 spectrometer (400–7800 cm^{-1}). EPR spectra were recorded from 293 K to 4 K on a JEOL JES-TE 200 X-band ESR spectrometer. A Quantum Design MPMS-XL SQUID magnetometer was used to measure the static molar magnetic susceptibility (χ_M) of compound **1** in a 100 mT magnetic field under cooling and heating conditions from 300 K to 1.9 K and back from 1.9 K to 300 K. A contribution from the sample holder was subtracted from the experimental values.

Synthesis

The preparation of crystals of $(PPN^+)_2(C_{70}^{2-})\cdot 2\,C_6H_4Cl_2$ (**1**) was accomplished by using a diffusion technique. Typically, C_{70} (28 mg, 0.033 mmol), PPNCl (2 equiv, 38 mg, 0.084 mmol), and sodium fluorenone (16 mg, 0.077 mmol) were stirred in *o*-dichlorobenzene (16 mL) at 80°C for 2 h. The red solution of the salt was cooled to RT and filtered. The NIR spec-

Figure 6. EPR spectrum of compound **1** at 295 K (top) and the fitting of the signal by two Lorentzian lines (bottom).

trum of the solution indicated the reduction of C_{70} into the -2 charge state (Figure 2b, bottom). The obtained solution was placed in a glass tube (capacity: 50 mL, diameter: 1.8 cm) with a ground glass plug and *n*-hexane (30 mL) was layered on top of the solution. Leaving the mixture to stand for one and half months yielded black plate-like crystals of the salt (up to $1 \times 1 \times 0.2$ mm^3) on the walls of the tube. The solvent was decanted from the crystals and they were washed with *n*-hexane. The composition of salt **1**, which was obtained in 72% yield, was determined by single-crystal X-ray diffraction. Several crystals that were tested from the synthesis showed the same unit-cell parameters.

X-ray Crystallography

X-ray diffraction data for a single crystal of compound **1** of size $0.4 \times 0.4 \times 0.3$ mm^3 were collected on an Oxford diffraction "Gemini-R" CCD diffractometer with graphite-monochromated MoKα radiation ($\lambda = 0.71073$ Å) at 130 K by using an Oxford Instrument Cryojet system. The raw data reduction to F^2 was performed on CrysAlisPro software (Oxford Diffraction Ltd.). Empirical absorption correction was applied by using spherical harmonics ($T_{min}/T_{max} = 0.89477{:}1.0000$). The structure was solved by using direct method and refined by the full-matrix least-squares method against F^2 with SHELXS97 and SHELXL97, respectively.[34] The structure can be successfully solved in both monoclinic space groups $P2/c$ and Pc. However, the refinement in the centrosymmetric space group was accompanied by orientational disorder of many phenyl groups of the PPN$^+$ cations, which is very atypical for most known structures that contain this cation. On the contrary, no disorder of the phenyl groups was observed during the refinement in the non-centrosymmetric space group Pc, which was chosen for final structure refinement. This space group also allowed the disorder of the solvated molecules of *o*-dichlorobenzene to be modeled much more easily. All of the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in the geometrically calculated positions and refined in a riding mode.

*Crystal Data for Salt **1***

$C_{154}H_{68}Cl_4N_2P_4$; $M_w = 2211.78$; monoclinic; space group Pc; $a = 20.1611(16)$, $b = 28.3842(18)$, $c = 20.1871(14)$ Å; $\beta = 118.679(9)°$; $V = 10135.0(15)$ Å^3; $Z = 4$; $\rho_{calcd} = 1.450$ g cm^{-3}; $\mu = 0.245$ mm^{-1}; $F(000) = 4536$; $\theta_{max} = 30.03°$; reflections measured 105327; unique reflections 41945; reflections with $I > 2\sigma(I)$ 23969; parameters refined 3058; restraints 128; $R_1 = 0.077$, $wR_2 = 0.193$; GOF $= 1.025$.

CCDC 918232 (**1**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements

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