Supporting Information

Dalton Transactions

C$_{76}$ fullerene chlorides and cage transformations. Structural and theoretical study

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Synthesis and isolation of D_2-C_{76}

C_{76} fullerene was separated from toluene extract of fullerene soot via two-step HPLC using a Cosmosil Buckyprep column (10 mm i.d. x 250 mm, Nacalai Tesque Inc.) and toluene as eluent (5.0 mL min^{-1} flow rate, 320 nm detection wavelength). In the first step, a mixed fraction of comprised C_{76} and two isomers of C_{78} was collected, which was subjected to the second step recycling HPLC (Fig. S1). After two cycles, pure C_{76} was successfully obtained, according to MALDI-TOF MS and UV-Vis spectroscopy (Fig. S2).
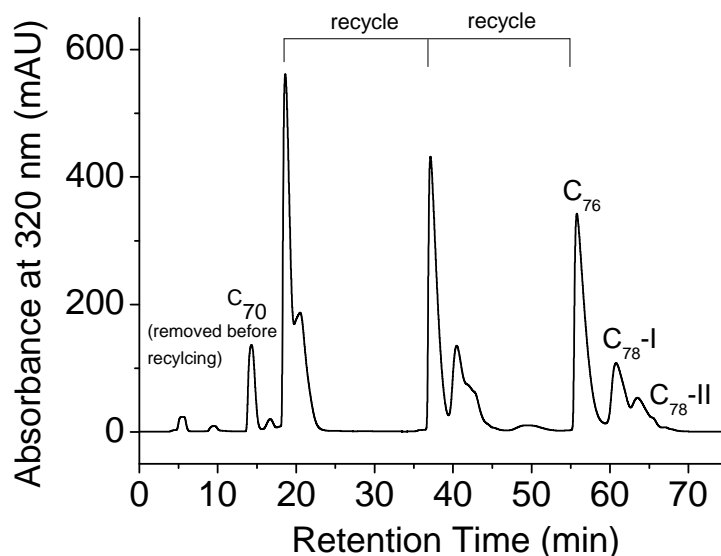
Fig. S1 The second-step isolation of C_{76} by recycling HPLC from the C_{76}-C_{78} mixture (10 x 250 mm Buckyprep column; flow rate 5.0 ml/min; injection volume 5 ml; toluene as eluent; 25°C).
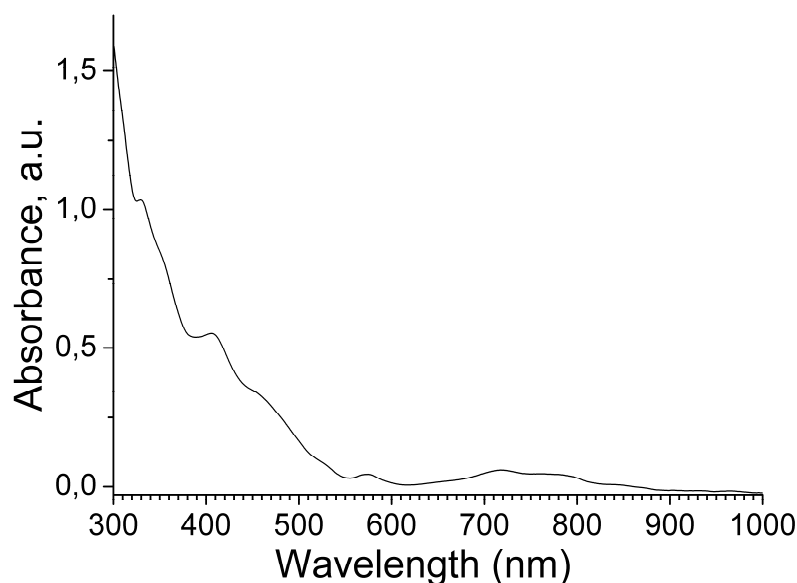
Fig. S2 UV-vis-NIR spectra of the isolated C_{76} recorded in toluene.

Synthesis of $C_{76}Cl_n$ compounds

In Table S1 we present reaction conditions and major products for the crystallographically analyzed fractions mentioned above. Sometimes, when no reaction was not clearly observed upon heating, the second heating step at higher temperature was required for successful isolation of crystals. Interestingly, one cannot see any clear correlation between products and reaction temperature or time. Probably, this is connected with co-formation and instant co-crystallization of molecules with different chlorination degrees. In particular, crystals of different composition can form simultaneously in the same ampoule experiment, which was the case for structures III, IV, and VIII.

Table S1. Reaction conditions and $C_{76}Cl_n$ products in the syntheses with VCl_4 and PCl_5

$C_{76}Cl_n$ sample	1st stage: temp, °C / time, h	2nd stage: temp, °C / time, h	Average n (x)	Major components $(n)^a$
I	290 / 6	300 / 20	24.24	24
II	250 / 120	-	26.24	26
III	200 /100	240 / 20	25.92	24(?), 26^b, 28(?)
IV	200 / 100	240 / 20	28.13	28
V	220 / 20	-	28.00	28
VI	220 / 20	-	28.00	28
VIa^c	220 / 70	240 / 30	28.00	28
VII	220 / 20	-	27.90	28
VIII	200 / 100	240 / 20	32.96	30(?), 32, 34

^{a} "(?)" stays for uncertain; ^{b} 26 Cl atoms in the structure III are distributed over those 28 positions on the C_{76} cage that are occupied in the $C_{76}Cl_{28}$ molecules from IV – VII. ^{c} The synthesis with PCl_5.

Crystallographic data and comments

The reported chlorides of C_{76} were observed to crystallize much more readily than most of the fullerene derivatives we dealt with before. As a result, some crystals deviated from exact $C_{76}Cl_{2n}$ stoichiometries due to ability of two (or more) $C_{76}Cl_{2n}$ molecules with close composition and shape to occupy equivalent crystallographic sites. This was manifested by splitting of some Cl atoms; the refinement of such atoms often required the use of restraints of anisotropic displacement parameters. Below we discuss each instance of co-crystallization of two or more compounds. In such cases, the presence of the second components was observed due to different positions of some Cl atoms. However, the corresponding carbon cage atoms from the minor components could not be observed due to low scattering at those places. For this reason, the Cl atoms from minor components appear at longer distances (by ca. 0.3 Å) from the main fullerene cage. Also, strongly disordered Cl_2 molecules were found in structures IV – VIII, as well as $POCl_3$ molecules in the interstitial sites in structure Via (see Table 1in the main text).

Structure I with overall composition of $C_{76}Cl_{24.24}$ contains the major product, $C_{76}Cl_{24}$, with some additional Cl atoms characterized by low occupancies and unusually long distances to the carbon atoms of 2.0 – 2.2 Å. The averaged molecular composition corresponds to a mixture of $C_{76}Cl_{24}$ (88%) and $C_{76}Cl_{26}$ (12%) molecules.

In structure II with the averaged composition of $C_{76}Cl_{26.24}$, the main component, $C_{76}Cl_{26}$, has two split Cl positions, whereas two additional (partially occupied) Cl atoms due to 12% admixture of $C_{76}Cl_{28}$ occupy *para* positions in a hexagon (see Fig. 2 of the main text).

In structure III with several Cl atoms split, the overall composition is $C_{76}Cl_{25.9}$. Altogether 28 carbon atoms bear Cl atoms with unit or partial occupancies. Therefore, it can be supposed that $C_{76}Cl_{24}$, $C_{76}Cl_{26}$, and $C_{76}Cl_{28}$ molecules are present in the crystal occupying the same crystallographic site. Interestingly, the unit cell is similar to that of structure VII, $C_{76}Cl_{28} \cdot 0.4\ Cl_2$ (the same space group and very similar unit cell parameters, except for shorter b).

Structures IV – VII all contain the same main molecule, $C_{76}Cl_{28}$, but their packing motifs in crystals are different thus representing four different crystalline modifications. The contents of strongly disordered Cl_2 molecules are in the range of 0.27 – 0.65. In structure IV one Cl atom is slightly disordered over two positions with 0.92(2) occupancy of the main component. The presence of one more Cl of low occupancy indicates the availability of a molecule with a slightly different addition pattern. The structure V was refined with PLATON/SQUEEZE which resulted in smoothing the residual electron density. Structures VI and VIa belong to the same crystalline modification, the latter additionally including solvated $POCl_3$ molecules. In these two structures, the $C_{76}Cl_{28}$ molecules are located on the crystallographic two-fold axes, whereas they occupy general positions in the other crystalline modifications.

From altogether 34 Cl atoms attached to the C_{76} cage in structure VIII, four have partial occupancy of 0.739(5). Obviously, $C_{76}Cl_{32}$ and $C_{76}Cl_{34}$ molecules occupy the same crystallographic site with a ratio of 1.04:0.96 resulting in the overall composition of $C_{76}Cl_{32.96}$. Also, one can consider a possible $C_{76}Cl_{30}$ molecule with all four Cl atoms missing. Two Cl atoms are disordered over two positions each with occupancies of main components being 0.815(4) and 0.920(6). This disorder corresponds to the presence of molecules with the addition pattern somewhat different from that of the main component.

Solvated Cl_2 molecules are strongly disordered over 7 atomic positions. The $C_{76}Cl_{34}$ molecule possesses non-crystallographic two-fold symmetry with C_2 axis coinciding with the shortest C_2 axis of the starting D_2-C_{76}. Note that crystal structure VIII is isotypic to $C_{76}Cl_{34}$ reported in ref. [S1], in which only one molecule type is present. However, the structure in [S1] has been determined with lower accuracy than the structure VIII because of much lower intensities of all

reflections. Additionally, residual peaks of high intensity (maximum of 2.77 e Å^{-3}) are present in difference Fourier map, which, presumably, correspond to Cl_2 molecules of solvation.

Details of DFT calculations of the IPR $C_{76}Cl_{24}$ structures

All DFT calculations mentioned in the manuscript were carried out with the use of the PRIRODA software [S2] employing an original TZ2P basis set and PBE exchange-correlation functional [S3]. Relative energies of selected (from several dozens) $C_{76}Cl_{24}$ isomers based on the D_2-C_{76} cage are presented in Table 2S. The trial structures were selected so that to incorporate aromatic fragments, preferably in the flattest regions of the carbon cage, and to have the chlorine atoms attached mostly to its highest curved regions.

Table S2 Selected most stable IPR isomers of $C_{76}Cl_{24}$ (energy in kJ mol^{-1})

0.0 kJ mol^{-1}*	37.3	49.9
67.7	70.4	71.4
78.2	81.4	87.2
88.0	94.0	96.1
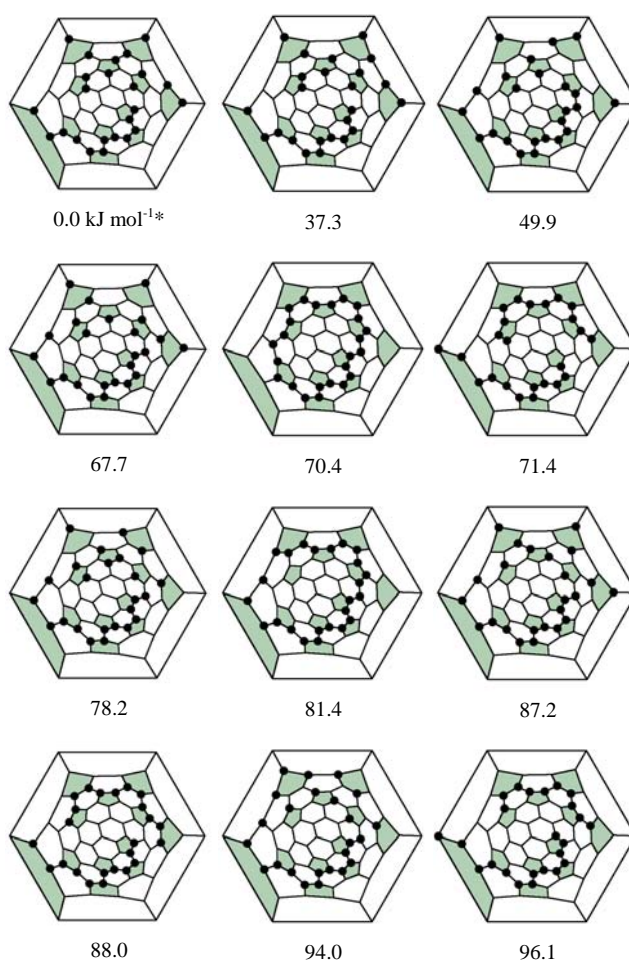
*experimental structure of $C_{76}Cl_{24}$

References

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[S3] J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.,* 1996, **77**, 3865–3868.