Supporting Information

Non-classical (*NC*), heptagon-containing fullerenes obtained via chlorination-promoted cage transformations: C_{76}(*NC*2a)Cl_{24} and C_{76}(*NC*2b)Cl_{28}

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Synthesis and isolation of C_{76} chlorofullerenes.

The samples of C_{76}(1) and C_{80}(2) fullerenes were obtained by HPLC separation as described previously in refs.[S1–2]. Procedures of fullerenes chlorination with inorganic chlorides, $SbCl_5$ and VCl_4, were described more detailed in refs.[S1,3]. The chlorination products of C_{76}(1) with $SbCl_5$ were dissolved in toluene and subjected to HPLC separation in toluene using a semipreparative *Cosmosil Buckyprep* column (10 mm I.D. x 25 cm, *Nacalai Tesque Inc.*) at a flow rate 4.6 mL·min^{-1} (**Figure *S*1**). The composition of the collected fractions was controlled by recording MALDI TOF mass spectra, which revealed the presence of $C_{76}Cl_n$ compounds with n ranging from 22 to 26. The negative ion MALDI mass spectrum of fraction containing $C_{76}Cl_{24}$ is shown on **Figure *S*2**. This fraction gave crystals of C_{76}(*NC*2a)Cl_{24} by slow concentration of the toluene solution. Tiny, orange coloured crystals of C_{76}(*NC*2b)Cl_{28} were obtained after removal of an excess of VCl_4 and VCl_3 from the products of C_{80}(2) chlorination.

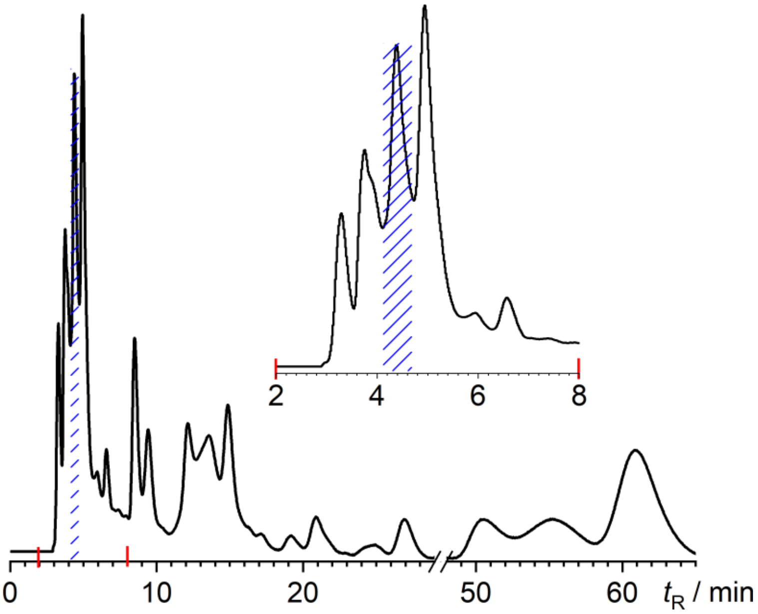

Figure *S*1. HPLC separation of the chlorination products of fullerene C_{76}(1) with $SbCl_5$ (*Cosmosil Buckyprep* column, 10 mm I.D. x 25 cm, toluene, 4.6 mL·min^{-1}). Inset show the enlarged region of HPLC traces (2–8 min). Crystals were obtained from fraction marked as blue dashed area.

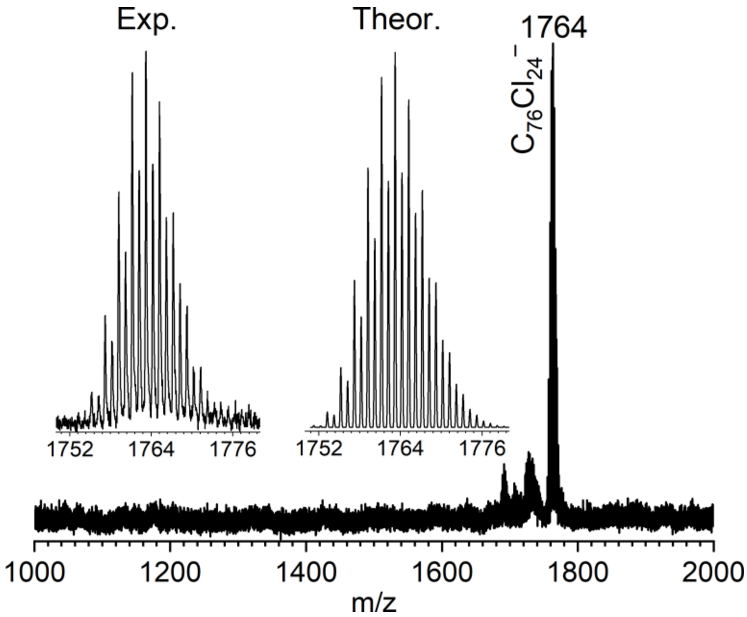

Figure *S*2. Negative-ion MALDI mass spectrum of fraction containing $C_{76}Cl_{24}$.

X-ray crystallography

Synchrotron X-ray data were collected at 100 K on BL14.3 and BL14.2 at the BESSY storage ring (Berlin, Germany) using a MAR225 CCD detector (λ = 0.8950 Å and λ = 0.8551 Å). All structures were solved and anisotropically refined using the SHELX package. Selected crystallographic data, some details of data collection and refinement, and CCDC deposition numbers are given in Table *S*1.

Table *S*1. Selected crystallographic data for non-classical C_{76} chlorofullerenes.

Compound	**$C_{76}(NC2a)Cl_{24}$**	**$C_{76}(NC2b)Cl_{28}$**
Solvate molecule	PhMe	–
Molecular Formula	$C_{83}H_8Cl_{24}$	$C_{76}Cl_{24}$
M_r	1855.69	1905.36
crystal system	monoclinic	monoclinic
space group	*C*2/*c*	*C*2/*c*
a [Å]	23.672(1)	17.137(1)
b [Å]	21.259(1)	23.973(2)
c [Å]	16.433(1)	15.008(1)
α [°]	90	90
β [°]	131.763(9)	90.389(8)
γ [°]	90	90
V [Å^3]	6168.5(8)	6165.5(8)
Z	4	4
D_c [g cm^{-3}]	1.998	2.053
refls collected / R_{int}	47561 / 0.062	46192 / 0.041
data / parameters	6854 / 514	7328 / 508
$R_1(I \geq 2\sigma(I)$ / wR_2(all)	0.042 / 0.119	0.045 / 0.106
$\Delta\rho_{max / min}$ [e Å^{-3}]	0.72 / –0.57	1.10 / –0.57
CCDC	2303657	1014799

Quantum-chemical calculations

Molecular geometry of C_{76} chlorofullerenes was optimized by TINKER v. 8 molecular mechanic package with MM2 parameter sets.[S4] Preliminary optimization of molecular geometry was carried out at the AM1 level of theory with the use of the Firefly 8.2.0 program[S5] partly based on the GAMESS(US) software.[S6] Finally, molecular geometry formation energy of C_{76} chlorofullerenes was reoptimized at the DFT level of theory with the use of the PRIRODA software[S7] employing an original TZ2p basis set[S8]and PBE exchange–correlation functional.[S9] The applicability of this calculation approach for fullerenes and their derivatives was confirmed in many previous reports.

References

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