Electronic Supplementary Information

Molecular recognition in curved π-systems: Effects of π-lengthening of tubular molecules on thermodynamics and structures

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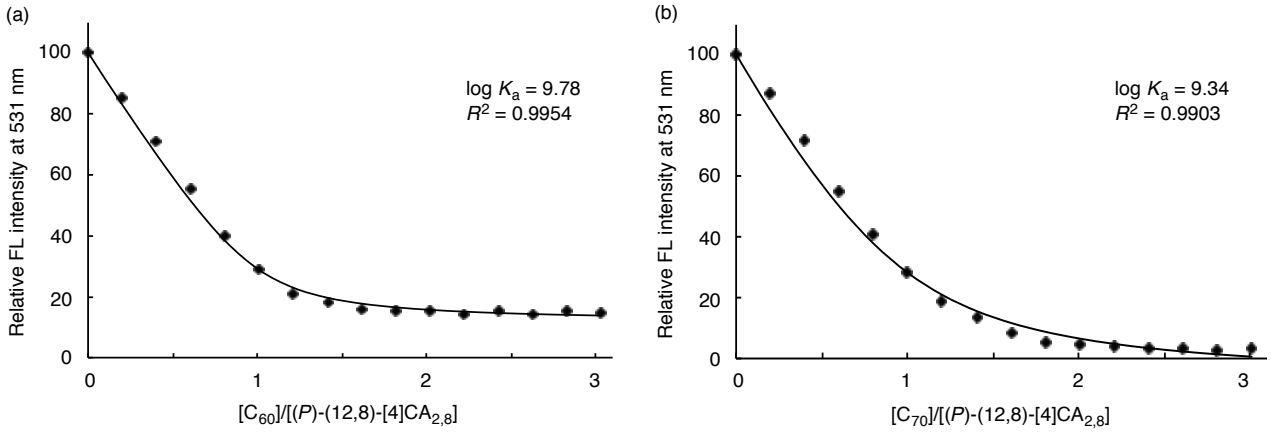

Fig. S1. Curve-fitting analysis from fluorescence quenching titrations. A curve from the fitting analysis is shown along with the log K_a value and the R^2 measure for the goodness-of-fit. (a) Curve fitting for (*P*)-(12,8)-[4]CA⊃C_{60}. (b) Curve fitting for (*P*)-(12,8)-[4]CA⊃C_{70}. See Fig. 2 for the fluorescence spectra.

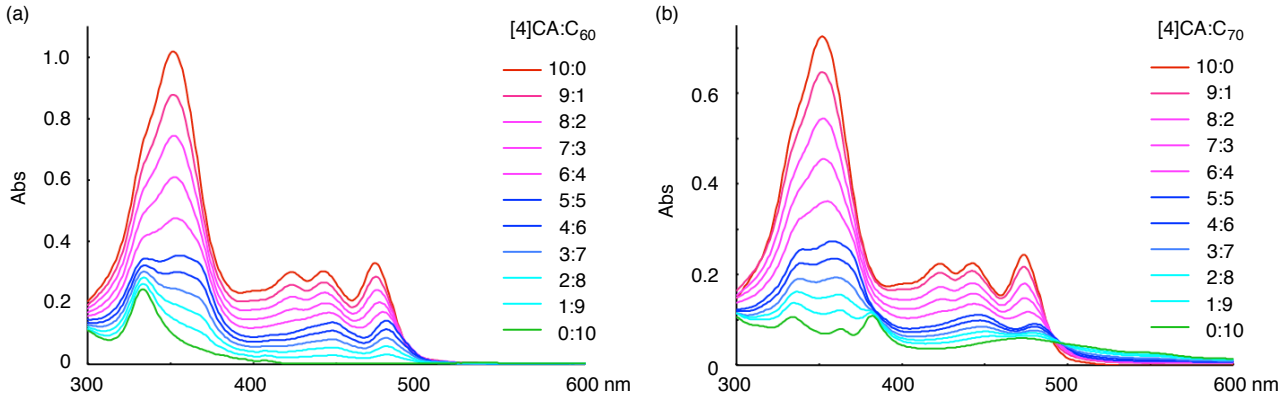

Fig. S2. UV-vis spectra for Job plot analysis. (a) Spectra for (*P*)-(12,8)-[4]CA⊃C_{60}. (b) Spectra for (*P*)-(12,8)-[4]CA⊃C_{70}. See Fig. 2 for the Job plot.

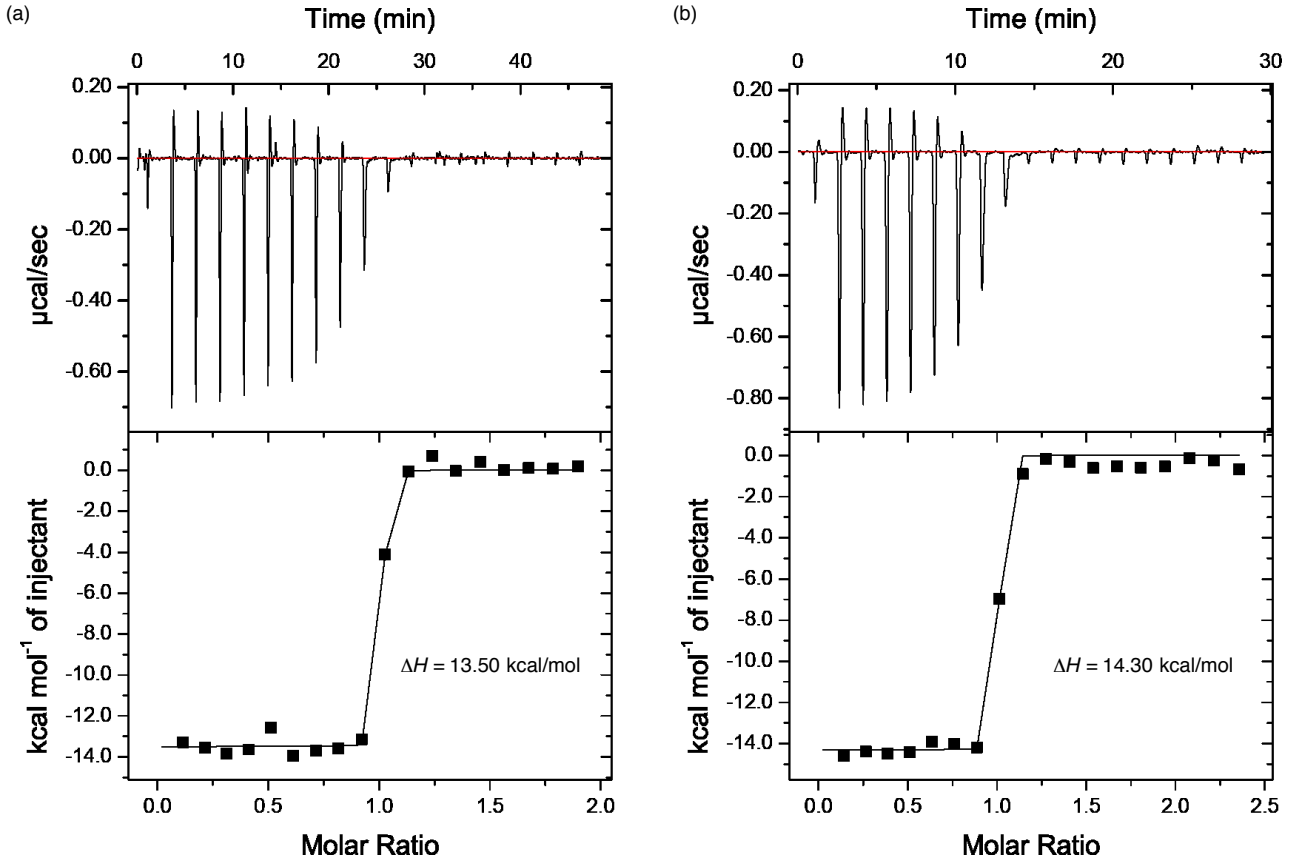

Fig. S3. Representative ITC diagrams for (*P*)-(12,8)-[4]CA⊃fullerene in *o*DCB. Titration raw data (above) and curve fitting analysis (below) from ORIGIN program of the instrument are shown. (a) (*P*)-(12,8)-[4]$CA_{2,8}$⊃C_{60}. (b) (*P*)-(12,8)-[4]$CA_{2,8}$⊃C_{70}.

Table S1. Thermodynamics data for (*P*)-(12,8)-[4]CC⊃C_{60} after corrections of the molar amount by combustion elemental analysis.[1]

solvent	log K_a	ΔG (kcal/mol)	ΔH (kcal/mol)	ΔS (cal/mol•K)
1-methylnaphthalene	8.9 ± 0.0	–12.1 ± 0.0	–7.4 ± 0.3	15.9 ± 1.0
*o*DCB	9.5 ± 0.2	–13.0 ± 0.3	–7.7 ± 0.2	17.6 ± 1.6
PhCN	10.0 ± 0.2	–13.6 ± 0.3	– 8.0 ± 0.2	18.9 ± 1.6
PhCl	10.5 ± 0.1	–14.3 ± 0.1	– 9.0 ± 0.2	17.8 ± 1.1
CH_2Cl_2	10.9 ± 0.0	–14.9 ± 0.3	–11.6 ± 0.4	10.9 ± 1.3
$CHCl_3$	10.9 ± 0.2	–14.9 ± 0.3	–10.3 ± 0.2	15.3 ± 1.6
toluene	11.6 ± 0.2	–15.8 ± 0.3	–11.3 ± 0.1	15.2 ± 1.3
benzene	12.2 ± 0.1	–16.6 ± 0.1	–13.6 ± 0.4	10.2 ± 1.8

1. For the original data and detailed discussion, see H. Isobe, S. Hitosugi, T. Yamasaki, R. Iizuka, *Chem. Sci.,* 2013, **4**, 1293-1297.

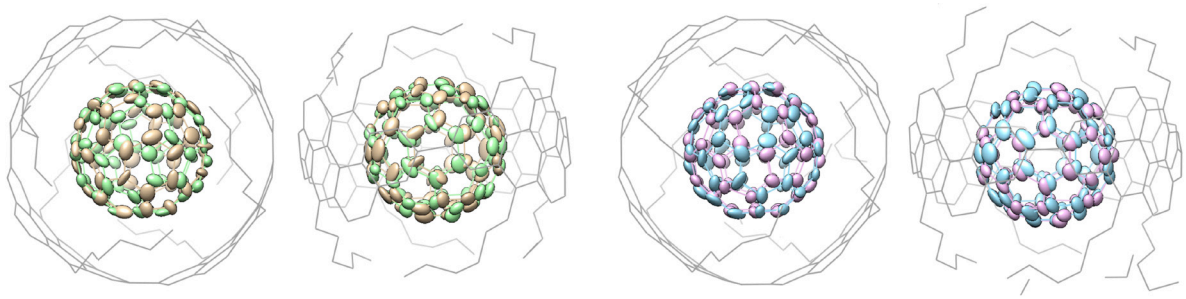

Fig. S4. Molecular structures of (*P*)-(12,8)-[4]CA⊃C_{60}. Two disordered C_{60} molecules were found in each peapod. Occupancies are 63% (green), 37% (light brown), 51% (pink) and 49% (blue), respectively. Thermal ellipsoids of C_{60} are drawn at 20% level. Hydrogen atoms are omitted for clarity.

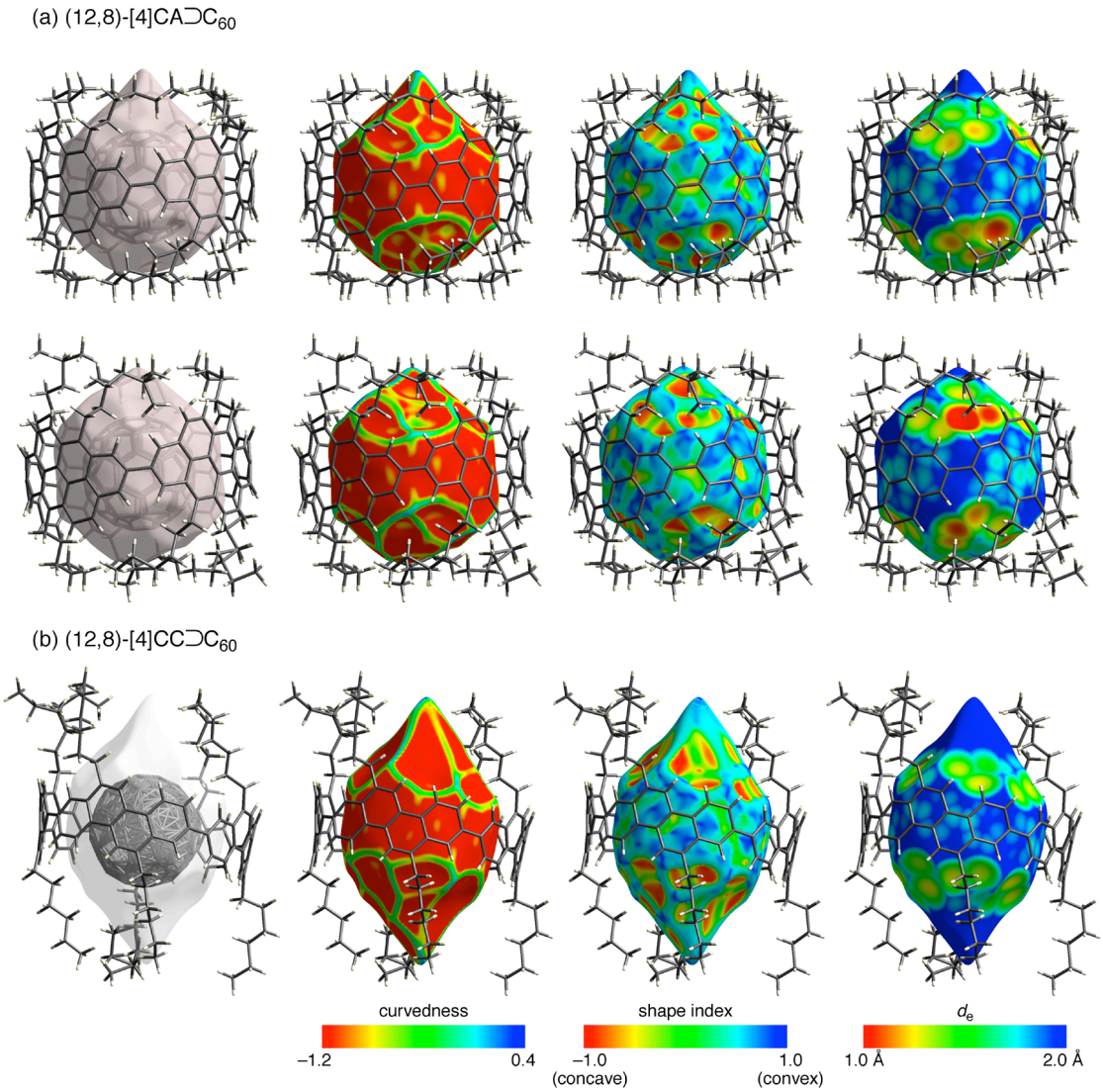

Fig. S5. Hirshfeld surfaces of molecular peapods. (a) (*P*)-(12,8)-[4]CA⊃C_{60}. Two non-identical structures are shown. (b) (*M*)-(12,8)-[4]CC⊃C_{60} (data taken from ref. 2).

2. S. Sato, T. Yamasaki, H. Isobe, *Proc. Natl. Acad. Sci. U.S.A.,* 2014, **111**, 8374-8379.

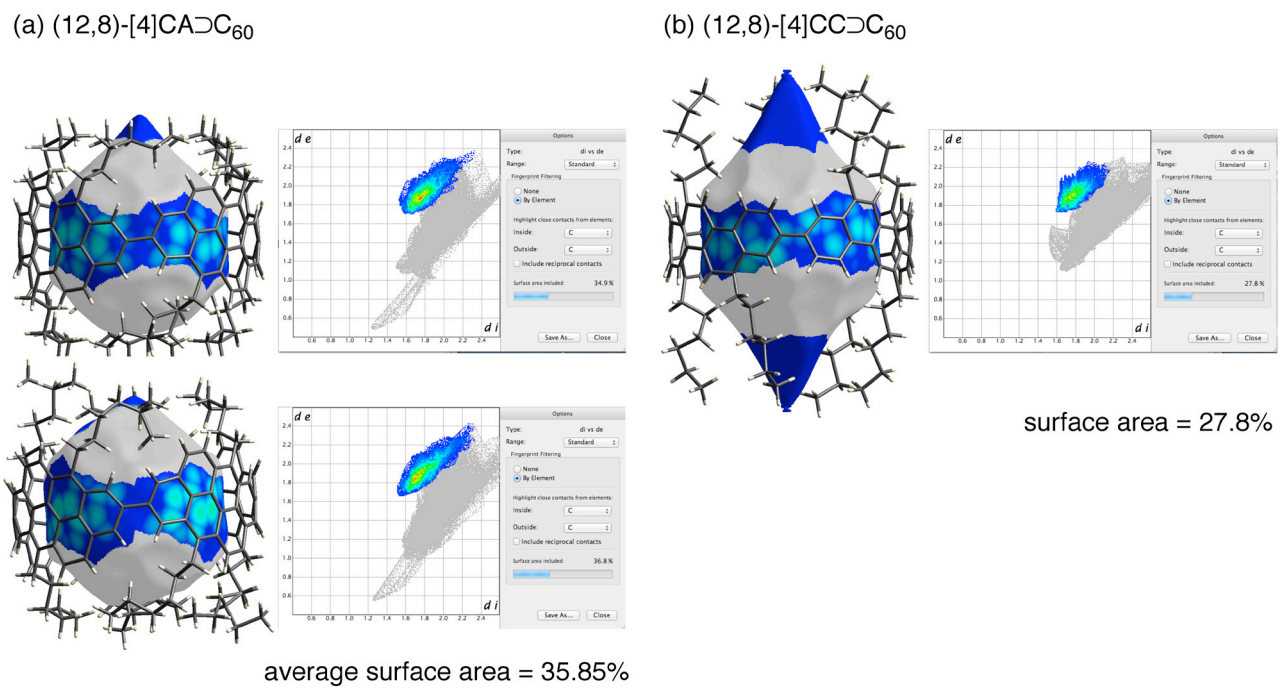

Fig. S6. Hirshfeld surface with d_e color mapping for C-C contacting areas. (a) (*P*)-(12,8)-[4]CA⊃C_{60}. (b) (*M*)-(12,8)-[4]CC⊃C_{60}.

Table S2. Crystal data and structure refinement for (*P*)-(12,8)-[4]CA⊃C_{60}.

CCDC No.	1018830	
Empirical formula	$C_{197.82}H_{137.82}$ $C_{l5.46}$	
Formula weight	2708.42	
Temperature	95.0(2) K	
Wavelength	0.96000 Å	
Crystal system	Monoclinic	
Space group	*C* 2	
Unit cell dimensions	a = 53.108(11) Å	α = 90°.
	b = 21.244(4) Å	β = 98.53(3)°.
	c = 26.197(5) Å	γ = 90°.
Volume	29229(10) $Å^3$	
Z	8	
Density (calculated)	1.231 Mg/m^3	
Absorption coefficient	0.364 mm^{-1}	
F(000)	11341	
Crystal size	0.07 × 0.07 × 0.02 mm^3	
Theta range for data collection	1.05 to 33.06°.	
Index ranges	-58<=h<=59, -24<=k<=24, -29<=l<=29	

Reflections collected	80181
Independent reflections	39425 [R(int) = 0.0606]
Completeness to theta = 33.06°	94.8 %
Absorption correction	Empirical
Max. and min. transmission	0.9928 and 0.9750
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	39425 / 2725 / 4351
Goodness-of-fit on F^2	1.500
Final R indices [I>2σ (I)]	R_1 = 0.1420, wR_2 = 0.3558
R indices (all data)	R_1 = 0.1605, wR_2 = 0.3849
Absolute structure parameter	0.25(12)
Largest diff. peak and hole	0.365 and -0.560 e•Å^{-3}

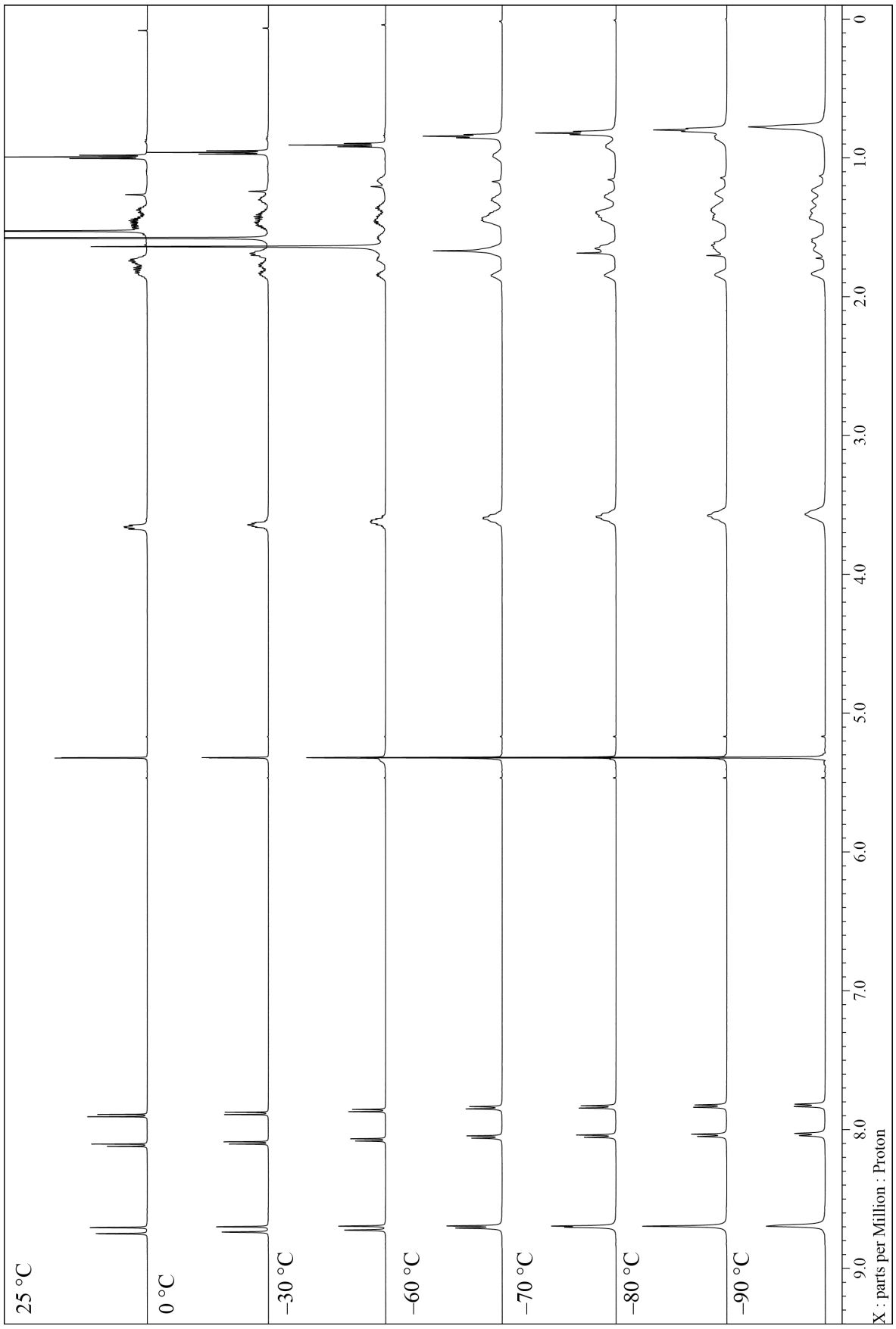

Fig. S7. Variable temperature NMR spectra of (*P*)-(12,8)-[4]CA⊃C_{60} in CD_2Cl_2.

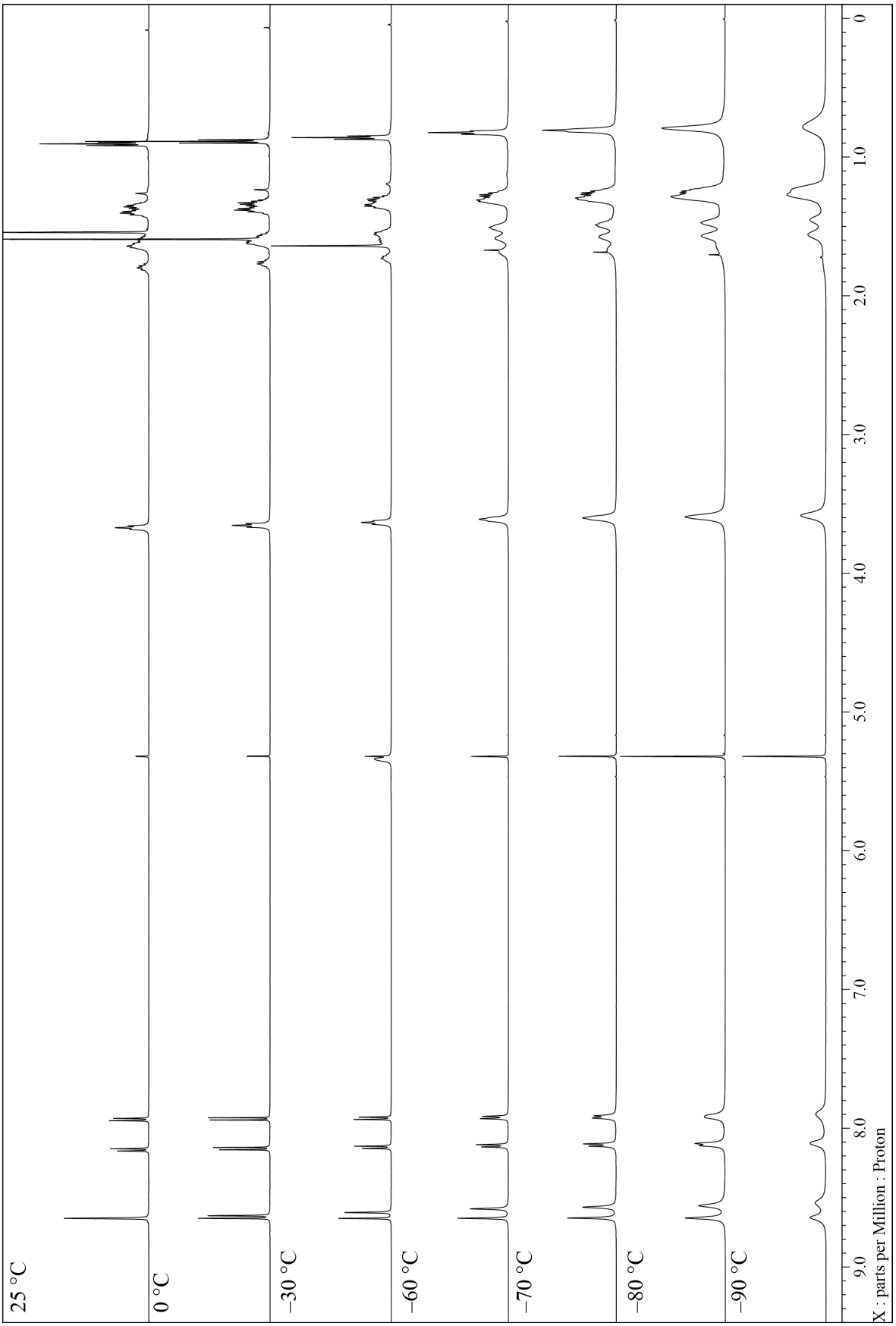

Fig. S8. Variable temperature NMR spectra of (*P*)-(12,8)-[4]CA in CD_2Cl_2.

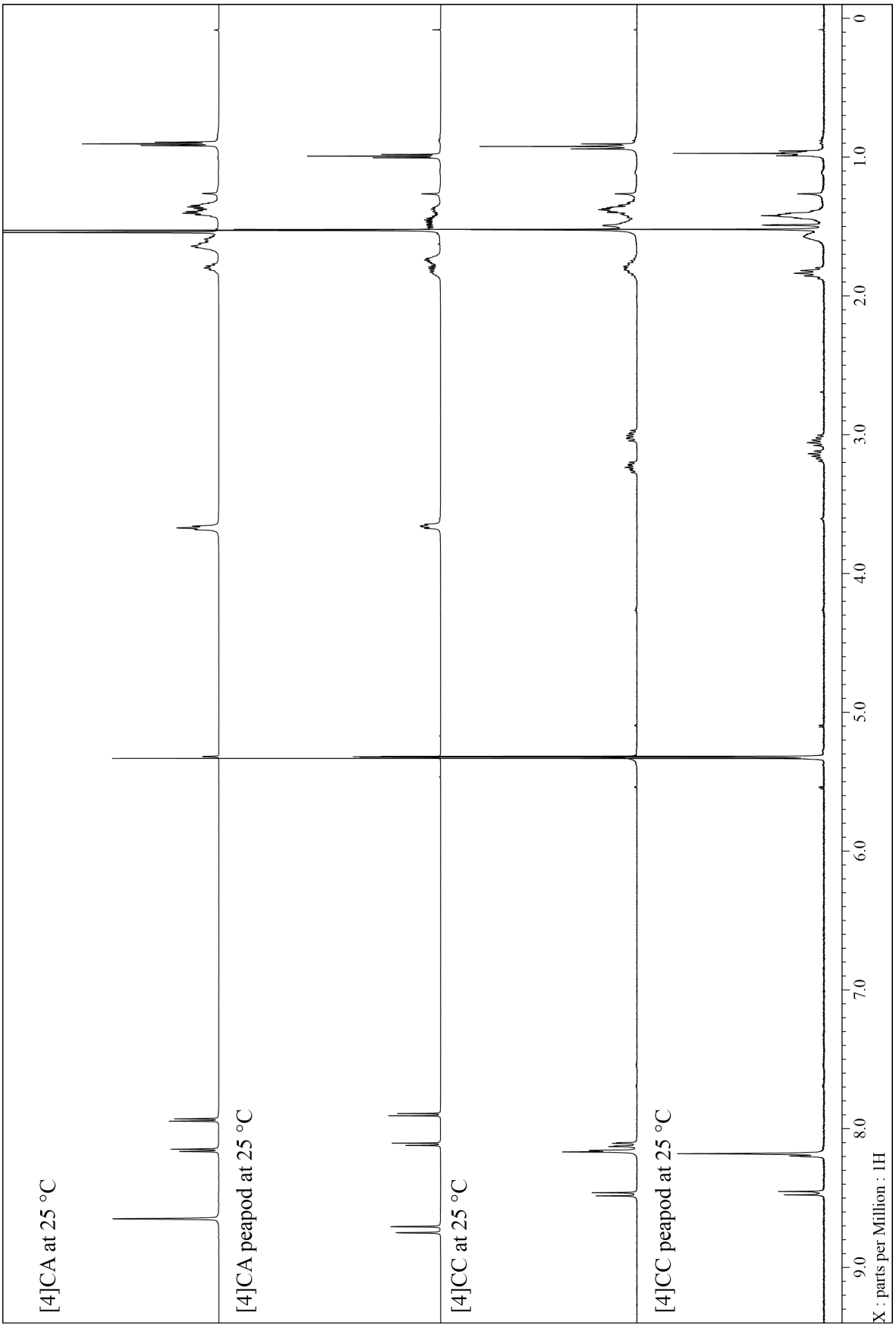

Fig. S9. NMR spectra of (*P*)-(12,8)-[4]CA, (*P*)-(12,8)-[4]CA⊃C_{60}, (*P*)-(12,8)-[4]CC and (*P*)-(12,8)-[4]CC⊃C_{60} in CD_2Cl_2. Spectra of [4]CC were taken from ref. 1.

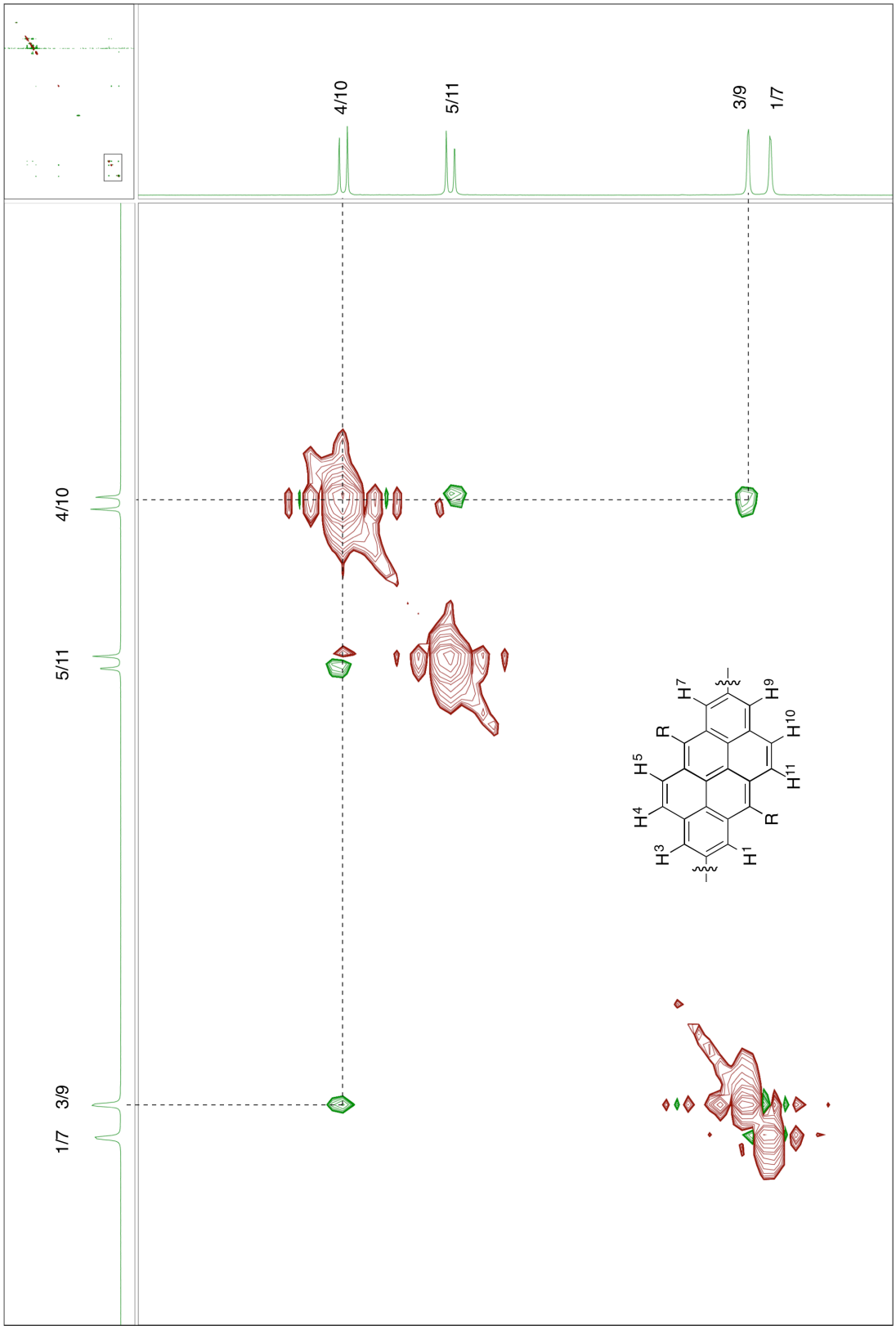

Fig. S10. A phase-sensitive NOESY spectrum of (*P*)-(12,8)-[4]CA⊃C_{60} in CD_2Cl_2 with positive correlations shown in green and negative correlations in red. The correlations between 3/9 and 4/10 protons allowed for the assignment of aromatic resonances.