Table 1S. Crystal data, data collection, structure solution and refinement parameters for **4a** and **4b**.

Data	**4a**	**4b**
Empirical formula	$C_{48}H_{52.26}ClN_{32}O_{21.63}$	$C_{98}H_{123}Br_{1.53}Cl_{2.47}N_{52}O_{43.38}$
Formula weight	1459.01	2933.39
Crystal size, mm	0.26 × 0.14 × 0.14	0.42 × 0.18 × 0.12
Crystal system	Tetragonal	Monoclinic
Space group	$P4_2/ncm$	$P2_1/n$
a, Å	26.2548(8)	15.5210(7)
b, Å	26.2548(8)	25.5665(11)
c, Å	12.7555(5)	32.4483(14)
β, deg		101.039(2)
V, Å^3	8792.6(5)	12637.8(10)
Z	4	4
Density (calc.), g/cm^3	1.102	1.542
$\mu(MoK_\alpha)$, mm^{-1}	0.121	0.658
Temperature, K	120.0(2)	120.0(2)
θ range, deg	1.10 to 27.00	1.02 to 28.00
Index ranges	$-33 \le h \le 30$	$-20 \le h \le 20$
	$-33 \le k \le 30$	$-33 \le k \le 33$
	$-16 \le l \le 16$	$-42 \le l \le 42$
Refl. collected	60288	150412
Independent refl.	4966 [R(int) = 0.0964]	30519 [R(int) = 0.2618]
Data/parameters	4966 / 266	30519 / 1679
Goodness-of-fit on F^2	1.941	0.921
Final Rs [$I > 2\sigma(I)$]	R_1 = 0.1903,	R_1 = 0.1253,
	wR_2 = 0.4958	wR_2 = 0.3255
Rs (all data)	R_1 = 0.2546,	R_1 = 0.3045,
	wR_2 = 0.5266	wR_2 = 0.3702
Largest diff. peak and hole, e·A^{-3}	2.063 and –0.589	1.773 and –1.773

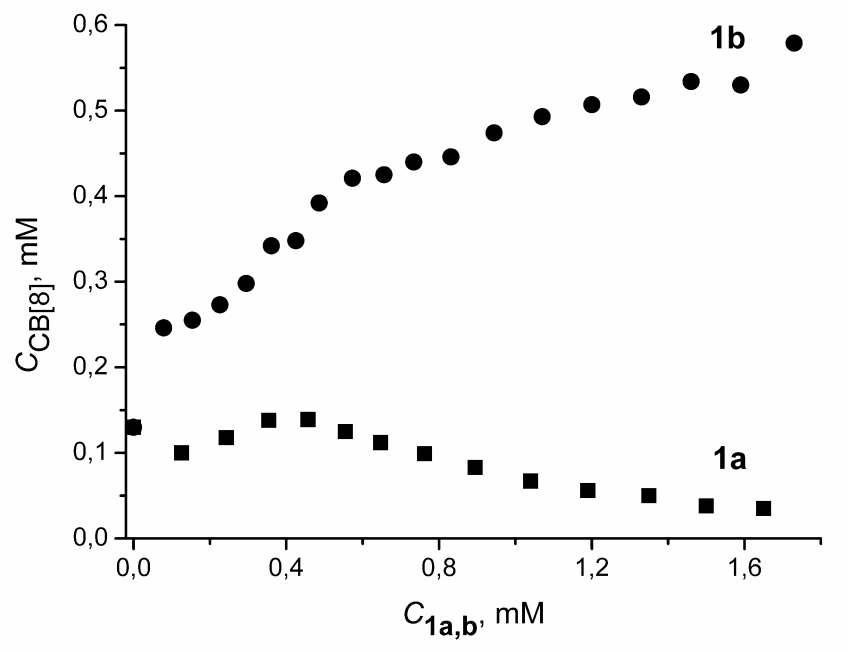

Fig. 1S. Dependence of the CB[8] solubility on **1a,b** concentration in D_2O/CD_3CN (10 : 1) at 30°C.

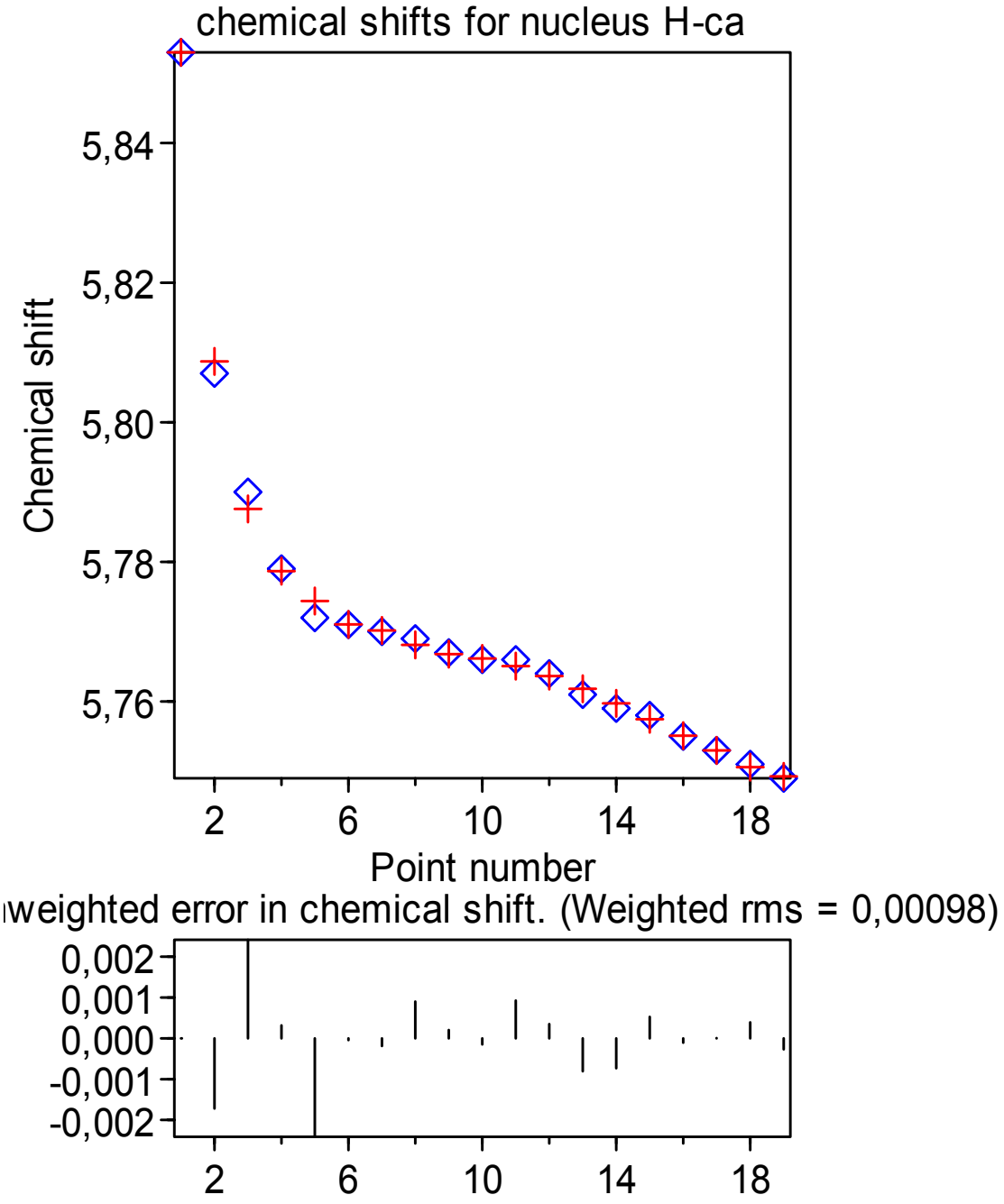

Fig. 2S. The HYPNMR plot of ^{1}H NMR titration in the CB[8]/(*E*)-**1b** system. Blue rhombs show the dependence of δ_H of the low-field CH_2 signals of CB[8] on amount of added **1b** and red crosses – the best fit to the system of three equilibria with stability constants $\lg K_{1:1} = 4.6$, $\lg K_{2:1} = 3.2$, and $\lg K_{1:2} = 3.0$.

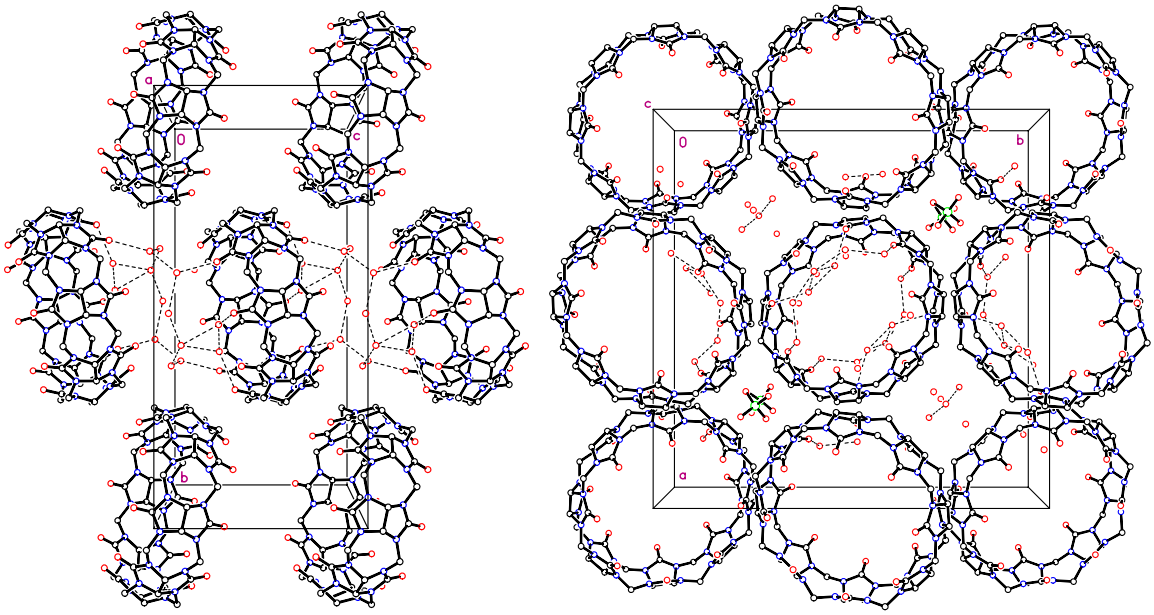

Fig. 3S. Two different projections of crystal packing of **4a**.