Supporting Information

Enhanced Anion Binding by Heteroatom Replacement in Bambusurils

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General methods. Commercially available chemicals were purchased from Sigma-Aldrich and used as received. ¹H and ¹³C NMR spectra were recorded with the solvents indicated by using AVIII400 Bruker spectrometer. Chemical shifts (δ) are given in ppm relative to TMS. The residual solvent signals were used as references and the chemical shifts were converted to the TMS scale: CDCl₃: δ_{H} = 7.26 ppm, δ_{C} = 77.16 ppm, [D₆]DMSO: δ_{H} = 2.50 ppm, δ_{C} = 39.5 ppm. For clarity, the ¹³C NMR quartet at 125.5, 122.3, 119.1 and 115.9 ppm assigned for the CF₃ group of the triflate anions were omitted from the ¹³C NMR data. Mass spectra were recorded on a Waters LCT Premier microMax spectrometer (TOF-ESI, in 7:3 acetonitrile:water at a flow rate of 0.25 mL/min).

All structure and energy calculations were carried out using Gaussian 09-D.01.^[1] All minima were characterized with analytical Hessian calculations to ensure real minima (n_{imag}=0) and for obtaining the zero-point energy (ZPE) corrections and thermochemical data. NBO charges were calculated using NBO version 3.1.^[2] NEDA calculations were performed on GAMESS-13-BLW^[3] with NBO version 6.0.^[4]

Crystal structure analysis. The crystal structures of **5b** and **5c** were obtained by slow evaporation from solution using a methanol/chloroform mixture affording colorless plates. The single crystal of **5b** were mounted on a ApexDuo, Bruker-AXS CCD diffractometer equipped with a Imus micro focus monochromator and data were collected using the multi-scan method (SADABS) with a scan range of 1° at low temperature (110 K) using cryostream low temperature device. The single crystals of **5c** was mounted on a Nonius KappaCCD diffractometer equipped with a graphite monochromator with Mo- K_{α} radiation (λ = 0.71073) at 200 K.

Data reduction of **5b** was performed using Bruker SAINT Software package using a narrowframe algorithm. The structures were solved by direct methods using SHELXTL-2014 and refined by full-matrix least squares on F² with anisotropic displacement parameters for the non-H atoms using SHELXL-2014/7.^[5] The hydrogen atoms were calculated in ideal positions with isotropic displacement parameters set to 1.2-1.5xUeq of the attached atom. All ellipsoid figures were generated using SHELXTL.

The following program was used for data collection and reduction of **5c**: Nonius 1997 Collect,^[6] and DENZO HKL 2000.^[7] Structures were solved by direct methods using the program package maXus^[8] and refined in the usual way using SHELXL97.^[5] Non-hydrogen atoms were refined anisotropically and hydrogen atoms isotropically.

Data can be obtained free of charge from the Cambridge Crystallographic Data Center via www.ccdc.cam.ac.il/data_request/cif. Tables of positional and thermal parameters, bond angles, torsion angles, figures and lists of observed and calculated structure factors are located in the CIF documents available from the Cambridge Crystallographic Centre *via* quoting CCDC numbers 1058391 and 1064130. The CIF files also contain details of the crystal data, data collection and structure refinement.

	5b	5c
CCDC No.	1064130	1058391
empirical formula	$C_{10}H_{18}N_5O * CF_3SO_3$	$C_{11}H_{20}N_5O * CF_3SO_3$
Mw	361.35	387.39
crystal size (mm ³)	0.20×0.20×0.4	0.27×0.24×0.21
T (K)	110(2)	200(2)
crystal system	monoclinic	triclinic
space group	<i>P</i> -1 21/n 1	<i>P</i> -1
a (Å)	6.56300(10)	6.4770(5)
b (Å)	14.3405(3)	10.5840(11)
<i>c</i> (Å)	15.7391(4)	12.7780(14)
α (°)	90	85.883(5)
β (°)	94.2250(10)	86.565(6)
γ(°)	90	75.600(6)
V (Å ³)	1477.29(5)	845.45(14)
Ζ	4	2
d / (g×cm ⁻³)	1.625	1.522
R indices	R1 = 0.0307	R1 = 0.0892
(all data)	wR2 = 0.0756	wR2 = 0.2240
Final R indices	R1 = 0.0289	R1 = 0.0834
$(> 2\sigma())$	wR2 = 0.0743	wR2 = 0.2142
quality-of-fit	1.046	1.208

Table S1. Pertinent crystallographic data and refinement details for 5b and 5c.

Synthetic procedures and characterization:



Scheme S1. Synthesis of *semiaza*-glycolurils. Reagents and conditions: a) NaH, THF, RT, 24 h; b) MeOTf, CH_2Cl_2 , RT, 2 h; c) NH_3 , $MeNH_2$ or allylamine in THF, reflux, 12 h for the synthesis of **5a**, **5b** or **5c** respectively.

N,N,N,N-Tetramethyl semithio-glycoluril, 8. N,N-Dimethyl semithio-glycoluril, $1^{[9]}$ (1.86 g, 10 mmol) was added to a stirred suspension of NaH (1.58 g, 33 mmol) in THF (50 mL) and the mixture was stirred at RT for 30 min. Methyl iodide (MeI) (2.3 mL, 37 mmol) was added and the mixture was stirred at RT for 24 h, then quenched with water, extracted with ethyl acetate, washed with brine and dried over Na₂SO₄. The residue obtained after removal of the solvent was suspended in hexane and the resulting precipitate was washed with Et₂O and dried in vacuum to afford **8** (1.32 g, 62%) as yellow solid. ¹H NMR (400 MHz, CDCl₃): δ

= 5.18 (s, 2H), 3.24 (s, 6H), 2.975 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ = 182.7; 158.1, 75.1, 34.0, 30.1. HRMS (TOF/ESI+), *m*/z calcd for C₈H₁₅N₄OS [M+H]⁺ 215.0967; found: 215.0972.

Genera; procedure for the synthesis of N,N,N,N-Tetramethyl-semiaza-glycolurils, 5a-c.

To a stirred suspension of 8 (100 mg, 0.46 mmol) in dichloromethane (DCM, 20 mL) was added MeOTf (50 μ L, 0.5 mmol) and the reaction mixture was stirred at RT for 2 h. After solvent removal under reduced pressure and drying under vacuum, 1,3,4,6-tetramethyl-5-oxohexahydroimidazo[4,5-d]imidazol-2(1H)-ylidene(methyl)sulfonium

trifluoromethanesulfonate, **9** was obtained and used in following step without further purification.

Crude **9** was suspended in THF (2 mL). The amine of choice, either NH₃ in THF solution (0.4 M, 1.75 mL, 0.7 mmol), methylamine in THF (2 M, 0.35 mL, 0.7 mmol) or allyamine (38 mg, 0.7 mmol) was added. The reaction mixture was refluxed for 12h and then was allowed to cool to room temperature. The white precipitate was filtered, washed with THF and dried under vacuum to afford *N*,*N*,*N*,*N*-tetramethyl-*semiaza*-bambus[4]uril, **10**, (120 mg ,74%), *N*,*N*,*N*-tetramethyl-*semi(methyl)aza*-bambus[4]uril, **11**, (110 mg ,65%) and *N*,*N*,*N*,*N*-tetramethyl-*semi(allyl)aza*-bambus[4]uril, **5**, (130 mg ,72%). All three compounds were obtained in the form of iminium triflate salt.

Compound 5a. ¹H NMR (400 MHz, [D₆]DMSO): δ = 8.32 (bs, 2H), 5.35 (s, 2H), 3.05 (s, 6H), 2.86 (s, 6H); ¹³C NMR (100 MHz, [D₆]DMSO) δ = 158.2, 157.2, 75.0, 31.4, 30.2; HRMS (TOF/ESI+), m/z calcd for C₈H₁₆N₅O [M+H]⁺ 198.1355; found: 198.1314.

Compound 5b. ¹H NMR (400 MHz, [D₆]DMSO): δ = 8.09 (bs, 1H), 5.36 (s, 2H), 3.13 (s, 6H), 3.03 (s, 3H), 2.86 (s, 6H); ¹³C NMR (100 MHz, [D₆]DMSO) δ = 158.3, 158.0, 76.1, 33.3, 30.4, 30.0; HRMS (TOF/ESI+), m/z calcd for C₉H₁₈N₅O [M+H]⁺ 212.1511; found: 212.1523.

Compound 5c. ¹H NMR (400 MHz, [D₆]DMSO): δ = 8.24 (bs, 1H), 6.00-5.91 (m, 1H), 5.36 (s, 2H), 5.31-5.26 (m, 2H), 4.05 (s, 2H), 3.12 (s, 6H), 2.86 (s, 6H); ¹³C NMR (100 MHz, [D₆]DMSO) δ = 158.2, 158.0, 134.4, 116.7, 76.1, 45.4, 33.3, 30.0; HRMS (TOF/ESI+), m/z calcd for C₁₁H₂₀N₅O [M+H]⁺ 238.1668; found: 238.1662.



Figure S1: ¹H NMR (top) and ¹³C NMR (bottom) of Compound 8.



Figure S2: ¹H NMR (top) and ¹³C NMR (bottom) of Compound 10.



Figure S3: ¹H NMR (top) and ¹³C NMR (bottom) of Compound 11.



Figure S4: ¹H NMR (top) and ¹³C NMR (bottom) of Compound 5.

Table S2. NBO analysis (M06-2x/6-311+g^{**}) between chloride orbitals and the σ^* orbitals in glycolurils, **2a**, **2b** and **2d**:

2a:

Donor NBO (i)	Acceptor NBO (j)	E(kcal/mol)	E(j)-E(i) (a.u.)	F(I,j) (a.u.)
CR (2)Cl 24	BD*(1) C 1 - H 2	0.07	10.49	0.024
CR (2)Cl 24	BD*(1) C 3 - H 4	0.07	10.49	0.024
LP (1)CI 24	BD*(1) C 1 - H 2	0.22	1.23	0.015
LP (1)CI 24	BD*(1) C 3 - H 4	0.22	1.23	0.015
LP (3)CI 24	BD*(1) C 1 - H 2	1.02	0.73	0.024
LP (3)CI 24	BD*(1) C 3 - H 4	1.02	0.73	0.025
LP (4)Cl 24	RY*(3) C 1	0.13	1.29	0.012
LP (4)Cl 24	RY*(3) C 3	0.13	1.29	0.012
LP (4)Cl 24	BD*(1) C 1 - H 2	2.18	0.81	0.038
LP (4)CI 24	BD*(1) C 1 - N 5	0.16	0.70	0.009
LP (4)Cl 24	BD*(1) C 1 - N 7	0.15	0.70	0.009
LP (4)Cl 24	BD*(1) C 3 - H 4	2.18	0.81	0.038
LP (4)CI 24	BD*(1) C 3 - N 6	0.16	0.70	0.009
LP (4)CI 24	BD*(1) C 3 - N 8	0.15	0.70	0.009
2b:				
Donor NBO (i)	Acceptor NBO (j)	E(kcal/mol)	E(j)-E(i) (a.u.)	F(I,j) (a.u.)
CR (2)Cl 24	BD*(1) C 1 - H 2	0.07	10.49	0.025
CR (2)Cl 24	BD*(1) C 3 - H 4	0.07	10.49	0.025
LP (1)CI 24	BD*(1) C 1 - H 2	0.25	1.22	0.016
LP (1)CI 24	BD*(1) C 3 - H 4	0.24	1.22	0.016
LP (2)CI 24	BD*(1) C 1 - N 5	0.05	0.60	0.005
LP (2)CI 24	BD*(1) C 1 - N 7	0.05	0.62	0.005
LP (2)Cl 24	BD*(1) C 3 - N 6	0.05	0.60	0.005
LP (2)Cl 24	BD*(1) C 3 - N 8	0.05	0.62	0.005
LP (3)Cl 24	BD*(1) C 1 - H 2	1.14	0.73	0.026

LP (3)CI 24	BD*(1) C	3 - H	4	1.15	0.73	0.026
LP (4)Cl 24	RY*(3) C	1		0.15	1.30	0.013
LP (4)Cl 24	RY*(3) C	3		0.15	1.29	0.013
LP (4)Cl 24	BD*(1) C	1 - H	2	2.36	0.80	0.039
LP (4)Cl 24	BD*(1) C	1 - N	5	0.16	0.68	0.009
LP (4)Cl 24	BD*(1) C	1 - N	7	0.18	0.70	0.010
LP (4)Cl 24	BD*(1) C	3 - H	4	2.34	0.80	0.039
LP (4)Cl 24	BD*(1) C	3 - N	6	0.16	0.68	0.009
LP (4)Cl 24	BD*(1) C	3 - N	8	0.18	0.70	0.010
2d:						
Donor NBO (i)	Accepto	r NBO	(j)	E(kcal/mol)	E(j)-E(i) (a.u.)	F(I,j) (a.u.)
CR (2)Cl 23	BD*(1) C	1 - H	2	0.06	10.49	0.023
CR (2)Cl 23	BD*(1) C	3 - H	4	0.06	10.49	0.023
LP (1)CI 23	BD*(1) C	1 - H	2	0.21	1.23	0.014
LP (1)CI 23	BD*(1) C	3 - H	4	0.21	1.23	0.014
LP (3)CI 23	BD*(1) C	1 - H	2	0.99	0.73	0.024
LP (3)CI 23	BD*(1) C	3 - H	4	1.00	0.73	0.024
LP (4)Cl 23	RY*(3) C	1		0.14	1.30	0.012
LP (4)Cl 23	RY*(3) C	3		0.14	1.30	0.012
LP (4)CI 23	BD*(1) C	1 - H	2	2.05	0.81	0.037
LP (4)Cl 23	BD*(1) C	1 - N	5	0.16	0.71	0.010
LP (4)Cl 23	BD*(1) C	1 - N	7	0.15	0.71	0.009
LP (4)Cl 23	BD*(1) C	3 - H	4	2.05	0.81	0.037
LP (4)Cl 23	BD*(1) C	3 - N	6	0.16	0.71	0.010
LP (4)Cl 23	BD*(1) C	3 - N	8	0.15	0.71	0.009

 Table S3. Selected NBO charges (atomic units) in 3a, 3b and 3d using calculations.



Comp.	3a	3a&Cl⁻	Diff	3b	3b&Cl⁻	Diff	3d	3d&Cl⁻	Diff
X	-0.642	-0.661	-0.019	-0.192	-0.247	-0.055	-0.760	-0.784	-0.024
H (NH)	-	-	-	-	-	-	0.345	0.338	-0.007
C (C=X)	0.873	0.874	0.001	0.328	0.344	0.016	0.665	0.669	0.004
Ν	-0.564	-0.560	0.004	-0.541	-0.539	0.002	-0.559	-0.554	0.006
C (CH)	0.203	0.188	-0.015	0.210	0.214	0.004	0.200	0.188	-0.012
H (CH)	0.214	0.236	0.022	0.220	0.237	0.017	0.214	0.239	0.025
N'	-0.567	-0.564	0.003	-0.566	-0.571	-0.005	-0.566	-0.564	0.002
C (C=O)	0.875	0.876	0.001	0.875	0.875	0.000	0.877	0.878	0.001
0	-0.691	-0.692	-0.001	-0.693	-0.692	0.001	-0.697	-0.702	-0.005
CI		-0.934			-0.954			-0.950	



Figure S5. Computed structure of a two possible binding modes between **4** and chloride (M062X/6-311+g**): **A**. Top and side view of four short contacts based binding mode, and **B**. Top and side view of three short contacts based binding mode. Mode A is more stable than mode B by 2.3 kcal/mol.



Figure S6: Calculated electronic properties of bambus[6]uril, **3a**: **A**. The electrostatic potential surface of the molecule, **B**. HOMO orbital and **C**. LUMO orbital. The range of electrostatic potential energy (kcal/mol) represented by color-coded scale ranging from red (-28.2 kcal/mol) to blue (37.6 kcal/mol).



Figure S7: Calculated electronic properties of bambus[6]uril analog, **3b**: **A**. The electrostatic potential surface of the molecule, **B**. HOMO orbital and **C**. LUMO orbital. The range of electrostatic potential energy (kcal/mol) represented by color-coded scale ranging from red (-20.7 kcal/mol) to blue (43.9 kcal/mol).



Figure S8: Calculated electronic properties of bambus[6]uril analog, **3c**: **A**. The electrostatic potential surface of the molecule, **B**. HOMO orbital and **C**. LUMO orbital. The range of electrostatic potential energy (kcal/mol) represented by color-coded scale ranging from red (-30.5 kcal/mol) to blue (25.1 kcal/mol).



Figure S9: Calculated electronic properties of bambus[6]uril analog, **3d**: **A**. The electrostatic potential surface of the molecule, **B**. HOMO orbital and **C**. LUMO orbital. The range of electrostatic potential energy (kcal/mol) represented by color-coded scale ranging from red (-28.9 kcal/mol) to blue (31.5 kcal/mol).



Figure S10: Calculated electronic properties of bambus[6]uril analog, **3e**: **A**. The electrostatic potential surface of the molecule, **B**. HOMO orbital and **C**. LUMO orbital. The range of electrostatic potential energy (kcal/mol) represented by color-coded scale ranging from red (229.0 kcal/mol) to blue (269.8 kcal/mol).







Figure S11: Structures of the chloride complexes of 3: A. 3a; B. 3b; C. 3c; D. 3d; E. 3e.



Figure S12: Calculated electrostatic potential energies along the z axis of **A.** bambus[6]uril derivatives, **3a-d** and **B**. including **3e**.

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