

Electronic Supplementary Information for:

Organo-Functionalized Metal-Oxide Clusters: Synthesis and Characterization of the Reduced Cationic Species $[\text{NaV}^{\text{IV}}_6\text{O}_6\{(\text{OCH}_2\text{CH}_2)_2\text{NH}\}_6]^+$

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FTIR spectrum of $\text{NaV}^{\text{IV}}_6\text{O}_6[(\text{OCH}_2\text{CH}_2)_2\text{NH}]_6 \cdot (\text{OH})_{0.5} \cdot \text{Cl}_{0.5} \cdot (\text{HOCH}_2\text{CH}_2)_2\text{N}(\text{CH}_2\text{CH}_2\text{NH}_2)$ (**C2**).

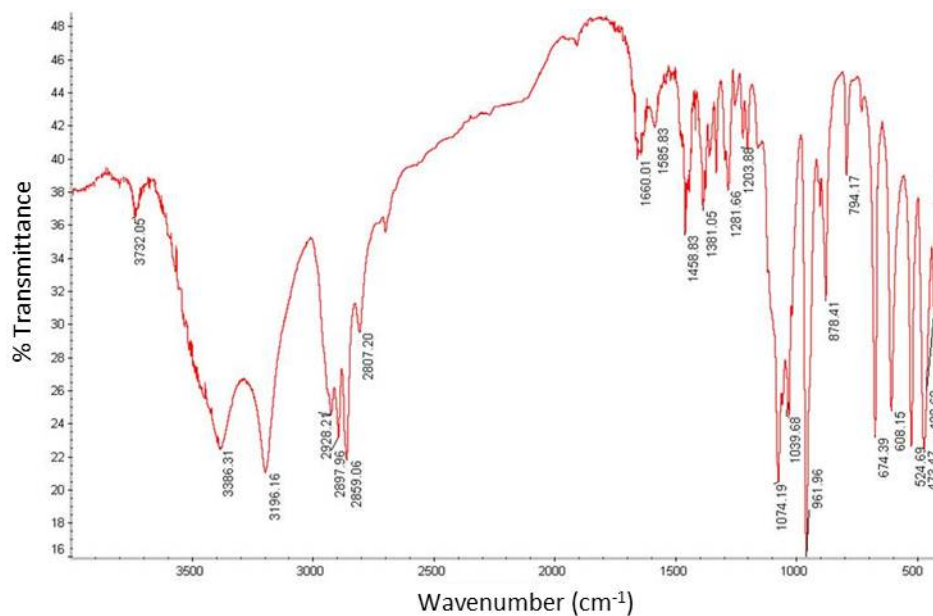


Fig. S1 FTIR spectrum of $\text{NaV}^{\text{IV}}_6\text{O}_6[(\text{OCH}_2\text{CH}_2)_2\text{NH}]_6 \cdot (\text{OH})_{0.5} \cdot \text{Cl}_{0.5} \cdot (\text{HOCH}_2\text{CH}_2)_2\text{N}(\text{CH}_2\text{CH}_2\text{NH}_2)$ (**C2**).

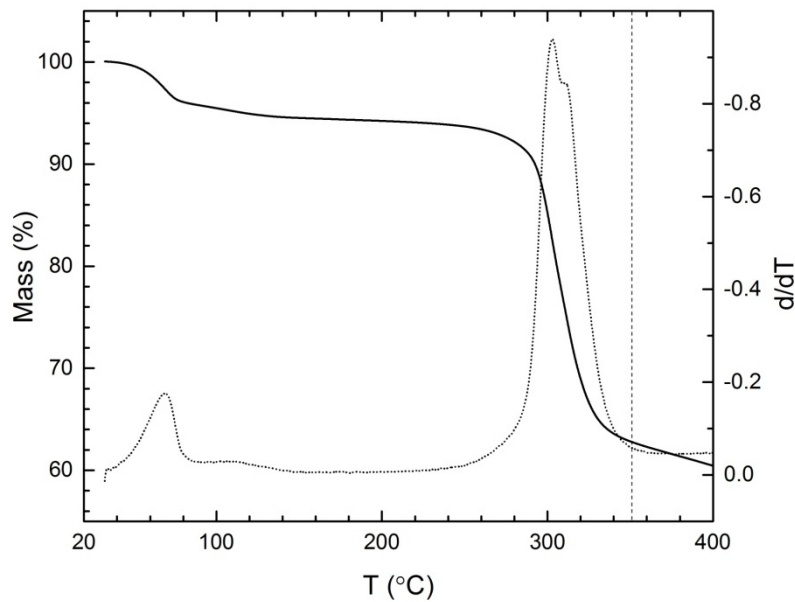


Fig. S2 TGA curve of a polycrystalline (powder) sample of $\text{NaV}_6\text{O}_6[(\text{OCH}_2\text{CH}_2)_2\text{NH}]_6 \cdot (\text{OH})_{0.5} \cdot \text{Cl}_{0.5} \cdot 3(\text{H}_2\text{O})$ (**C3**) and derivative of mass loss (.....). **C3** loses about 4.5 wt. % at 100 °C and an additional 1.2 wt. % by 200 °C, which we attribute to water of crystallization and strongly held water, respectively. The mass % loss from 200 to 351 °C (31.4 %) corresponds to the mass % of C and H associated with the functionalized cationic core of **C3**. (3°C/min, 100 SCCM Ar)

Cyclic Voltammetry—determination of the nature of the shoulder appearing in cyclic voltammogram of C3 (Fig. 2).

The shoulder appearing in the cyclic voltammogram of **C3** (Fig. 3) may be conceivably caused by adsorption of the oxidized species. In such a case, the adsorption energy lowers the effective activation energy of the electrochemical oxidation process, resulting in a reduced oxidation potential for the fraction of **C3** that is oxidized *and* adsorbed as compared to the fraction of **C3** that is oxidized but not adsorbed. A shoulder (or “pre-peak”) appears in such a case.¹ Such adsorptive currents have a linear scan rate dependence,² while the current associated with the non-adsorptive case has a linear square root scan rate dependence due to mass-transport effects.³ Therefore the origin of the shoulder is investigated by plotting the peak current (I_p) associated with the shoulder versus the scan rate and square root of the scan rate. We found the best linear relationship and most ideal y-intercept value for the I_p versus square root case, indicating that the shoulder is not due to adsorption of the oxidized species. Peak currents were obtained from Gaussian curves fit to the background-subtracted data.

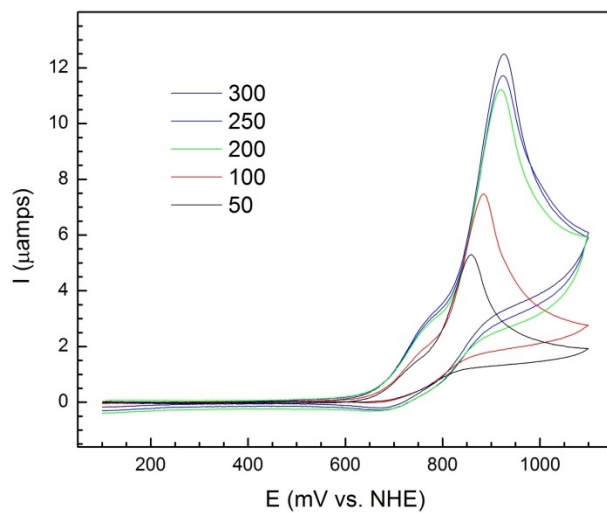


Fig. S3 Background-subtracted cyclic voltammograms of C3 at the scan rates indicated in the figure.

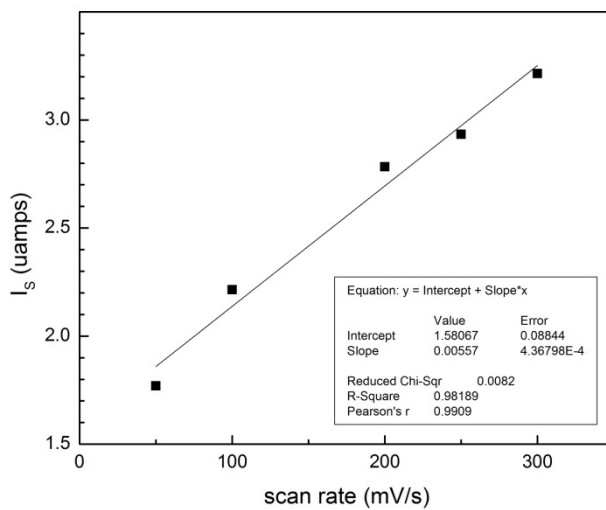


Fig. S4 The shoulder currents (I_s) of Fig. S3 versus the scan rate.

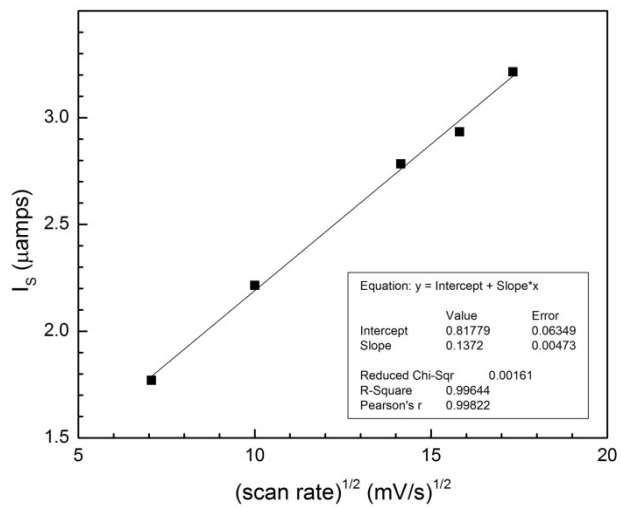


Fig. S5 The shoulder currents (I_s) of Fig. S3 versus the square root of the scan rate.

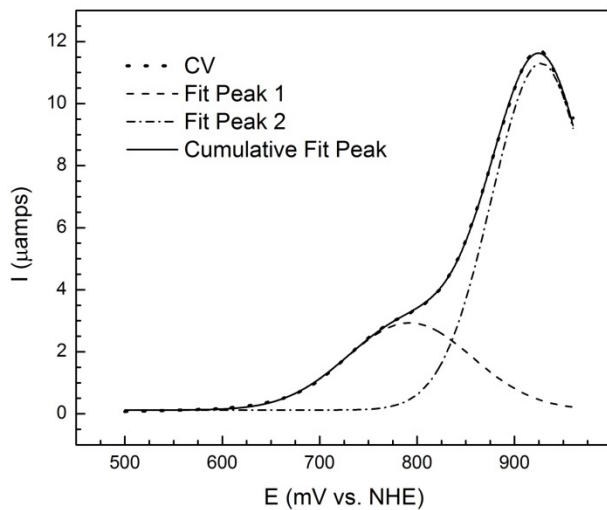


Fig. S6 Sample peak fitting (scan rate = 250 mV/s). Gaussian peaks were fit to the portion of the background-subtracted anodic scan indicated in the figure in order to determine the peak current associated with the leading shoulder indicated in the scan rate dependent CVs (Fig. S3).

Cyclic Voltammetry—C1/C3 oxidation potential comparison

In the general case, the peak position (mV) is a function of the intrinsic redox potential of the species, its distance from the electrode, and mass transport parameters (species diffusion coefficient). In the present case, we may assume that the intrinsic redox potentials of **C1** and **C3** are (nearly) equivalent, due to the isomorphous nature of the respective cationic cores of **C1** and **C3** with respect to the V=O_t bond (Fig. 1). This assumption is supported by the strong correspondence of the main aqueous phase charge transfer band (V=O_t) observed in the UV-vis spectra (Fig. 4). With respect to mass transport, the larger **C1**, with its six pendant ethanolic arms, is expected to have a lower diffusion coefficient than **C3**. All other things being equal, this factor would order the oxidative potentials as **C3** > **C1**.⁴ Therefore we attribute the observed order (**C1** > **C3**) to an increase in charge transfer distance caused by the pendant ethanolic arms of **C1**.

1. Bard, A. *Electrochemical Methods: Fundamentals and Applications*, 2nd ed.; John Wiley & Sons: New York, 2001; pp. 595-601.
2. Ibid.
3. Ibid.
4. Ibid., pp. 234-236.

Table 1. Crystal data and structure refinement for **C3**.

Empirical formula	C ₁₆ H ₃₆ N ₄ Na _{0.67} O ₁₄ V ₄	
Formula weight	727.57	
Temperature	88(2) K	
Wavelength	0.71073 Å	
Crystal system	Cubic	
Space group	P2 ₁ 3 (#198)	
Unit cell dimensions	a = 18.316(2) Å	α = 90°.
	b = 18.316(2) Å	β = 90°.
	c = 18.316(2) Å	γ = 90°.
Volume	6144(2) Å ³	
Z	6	
Density (calculated)	1.180 Mg/m ³	
Absorption coefficient	0.939 mm ⁻¹	
F(000)	2228	
Crystal size	0.25 x 0.22 x 0.10 mm ³	
Theta range for data collection	1.93 to 28.27°.	
Index ranges	-23 ≤ h ≤ 23, -24 ≤ k ≤ 24, -24 ≤ l ≤ 24	
Reflections collected	74709	
Independent reflections	5107 [R(int) = 0.0466]	
Completeness to theta = 28.27°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7457 and 0.6748	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	5107 / 1 / 179	
Goodness-of-fit on F ²	1.125	
Final R indices [I > 2σ(I)]	R1 = 0.0439, wR2 = 0.1380	
R indices (all data)	R1 = 0.0484, wR2 = 0.1408	
Absolute structure parameter	-0.01(3)	
Largest diff. peak and hole	0.685 and -0.353 e.Å ⁻³	

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **C3**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
V(1)	5008(1)	9683(1)	2345(1)	25(1)
V(2)	6526(1)	10497(1)	1835(1)	26(1)
Na(1)	5922(1)	9078(1)	922(1)	24(1)
O(1)	5404(1)	8607(1)	1958(1)	26(1)
O(2)	5446(1)	10121(1)	1440(1)	26(1)
O(3)	4195(1)	9145(1)	1804(1)	29(1)
O(4)	5992(1)	9970(1)	2650(1)	30(1)
O(5)	4462(1)	10298(1)	2672(1)	34(1)
O(6)	7137(1)	10830(1)	2377(1)	33(1)
N(1)	5113(2)	9067(1)	3352(1)	31(1)
N(2)	5907(2)	11504(1)	1741(2)	32(1)
C(1)	5602(2)	9522(2)	3804(2)	35(1)
C(2)	6253(2)	9778(2)	3356(2)	31(1)
C(3)	5379(2)	8293(2)	3232(2)	35(1)
C(4)	5801(2)	8243(2)	2530(2)	31(1)
C(5)	5149(2)	11399(2)	1478(2)	34(1)
C(6)	5081(2)	10676(2)	1058(2)	31(1)
C(7)	6371(2)	11955(2)	1252(2)	40(1)
C(8)	3487(2)	9391(2)	1616(2)	37(1)
O(11)	3737(5)	8971(5)	4235(5)	85(2)
O(12)	3232(6)	11247(6)	2535(6)	85(2)
O(13)	1864(12)	11202(13)	3296(13)	85(2)

Table 3. Bond lengths [\AA] and angles [$^\circ$] for **C3**.

V(1)-O(5)	1.621(2)
V(1)-O(4)	1.958(2)
V(1)-O(2)	2.008(2)
V(1)-O(3)	2.043(2)
V(1)-N(1)	2.170(3)
V(1)-O(1)	2.216(2)
V(1)-Na(1)	3.2894(5)
V(2)-O(6)	1.616(2)
V(2)-O(3)#1	1.949(2)
V(2)-O(1)#1	2.003(2)
V(2)-O(4)	2.028(2)
V(2)-N(2)	2.170(3)
V(2)-O(2)	2.216(2)
V(2)-Na(1)	3.2829(5)
Na(1)-O(1)	2.290(2)
Na(1)-O(2)	2.304(2)
O(1)-C(4)	1.438(4)
O(1)-V(2)#2	2.003(2)
O(2)-C(6)	1.402(4)
O(3)-C(8)	1.416(4)
O(3)-V(2)#2	1.949(2)
O(4)-C(2)	1.424(4)
N(1)-C(1)	1.478(4)
N(1)-C(3)	1.514(4)
N(2)-C(5)	1.483(4)
N(2)-C(7)	1.485(4)
C(1)-C(2)	1.521(5)
C(3)-C(4)	1.504(4)
C(5)-C(6)	1.536(4)
C(7)-C(8)#1	1.498(5)
C(8)-C(7)#2	1.498(5)
O(5)-V(1)-O(4)	106.03(11)
O(5)-V(1)-O(2)	105.86(11)

O(4)-V(1)-O(2)	76.19(9)
O(5)-V(1)-O(3)	93.69(11)
O(4)-V(1)-O(3)	159.85(9)
O(2)-V(1)-O(3)	94.79(9)
O(5)-V(1)-N(1)	95.86(11)
O(4)-V(1)-N(1)	79.40(10)
O(2)-V(1)-N(1)	150.92(10)
O(3)-V(1)-N(1)	103.01(10)
O(5)-V(1)-O(1)	159.71(10)
O(4)-V(1)-O(1)	91.62(9)
O(2)-V(1)-O(1)	87.76(8)
O(3)-V(1)-O(1)	69.79(8)
N(1)-V(1)-O(1)	77.29(9)
O(5)-V(1)-Na(1)	147.19(10)
O(4)-V(1)-Na(1)	81.27(7)
O(2)-V(1)-Na(1)	43.75(6)
O(3)-V(1)-Na(1)	79.87(6)
N(1)-V(1)-Na(1)	116.95(8)
O(1)-V(1)-Na(1)	44.01(6)
O(6)-V(2)-O(3)#1	106.01(11)
O(6)-V(2)-O(1)#1	106.57(11)
O(3)#1-V(2)-O(1)#1	76.26(9)
O(6)-V(2)-O(4)	93.47(10)
O(3)#1-V(2)-O(4)	160.26(9)
O(1)#1-V(2)-O(4)	95.45(9)
O(6)-V(2)-N(2)	95.20(12)
O(3)#1-V(2)-N(2)	79.51(10)
O(1)#1-V(2)-N(2)	151.00(10)
O(4)-V(2)-N(2)	102.23(10)
O(6)-V(2)-O(2)	159.45(10)
O(3)#1-V(2)-O(2)	91.31(9)
O(1)#1-V(2)-O(2)	87.97(8)
O(4)-V(2)-O(2)	70.28(8)
N(2)-V(2)-O(2)	76.83(9)
O(6)-V(2)-Na(1)	147.67(10)
O(3)#1-V(2)-Na(1)	81.25(7)

O(1)#1-V(2)-Na(1)	43.48(6)
O(4)-V(2)-Na(1)	80.53(7)
N(2)-V(2)-Na(1)	117.13(8)
O(2)-V(2)-Na(1)	44.50(6)
O(1)-Na(1)-O(1)#1	100.74(9)
O(1)-Na(1)-O(2)#1	179.86(14)
O(1)-Na(1)-O(2)	79.31(7)
O(2)#1-Na(1)-O(2)	100.57(9)
O(1)-Na(1)-V(2)#1	137.73(8)
O(2)-Na(1)-V(2)#1	142.95(8)
O(1)-Na(1)-V(2)	90.87(6)
O(1)#1-Na(1)-V(2)	37.00(5)
O(2)#1-Na(1)-V(2)	89.09(5)
O(2)-Na(1)-V(2)	42.38(5)
V(2)#1-Na(1)-V(2)	119.901(4)
O(1)-Na(1)-V(1)	42.24(5)
O(1)#1-Na(1)-V(1)	89.06(5)
O(2)#1-Na(1)-V(1)	137.64(7)
O(2)-Na(1)-V(1)	37.07(5)
V(2)-Na(1)-V(1)	60.059(13)
V(2)-Na(1)-V(1)#2	179.92(9)
O(1)-Na(1)-V(1)#1	142.98(8)
O(2)-Na(1)-V(1)#1	90.97(6)
V(2)-Na(1)-V(1)#1	60.132(13)
V(1)-Na(1)-V(1)#1	119.908(4)
C(4)-O(1)-V(2)#2	121.11(18)
C(4)-O(1)-V(1)	110.17(17)
V(2)#2-O(1)-V(1)	102.47(9)
C(4)-O(1)-Na(1)	124.72(18)
V(2)#2-O(1)-Na(1)	99.52(9)
V(1)-O(1)-Na(1)	93.75(8)
C(6)-O(2)-V(1)	120.74(19)
C(6)-O(2)-V(2)	111.24(17)
V(1)-O(2)-V(2)	102.14(9)
C(6)-O(2)-Na(1)	125.16(18)
V(1)-O(2)-Na(1)	99.18(9)

V(2)-O(2)-Na(1)	93.12(8)
C(8)-O(3)-V(2)#2	119.62(19)
C(8)-O(3)-V(1)	129.24(19)
V(2)#2-O(3)-V(1)	111.13(11)
C(2)-O(4)-V(1)	120.12(18)
C(2)-O(4)-V(2)	128.67(19)
V(1)-O(4)-V(2)	111.16(10)
C(1)-N(1)-C(3)	114.4(3)
C(1)-N(1)-V(1)	103.7(2)
C(3)-N(1)-V(1)	113.11(19)
C(5)-N(2)-C(7)	114.3(3)
C(5)-N(2)-V(2)	113.89(19)
C(7)-N(2)-V(2)	102.8(2)
N(1)-C(1)-C(2)	110.3(2)
O(4)-C(2)-C(1)	107.6(3)
C(4)-C(3)-N(1)	110.2(3)
O(1)-C(4)-C(3)	109.6(3)
N(2)-C(5)-C(6)	110.4(3)
O(2)-C(6)-C(5)	109.7(3)
N(2)-C(7)-C(8)#1	110.2(3)
O(3)-C(8)-C(7)#2	108.5(3)

Symmetry transformations used to generate equivalent atoms:

#1 $z+1/2, -x+3/2, -y+1$ #2 $-y+3/2, -z+1, x-1/2$

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **C3**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$

	U11	U22	U33	U23	U13	U12
V(1)	26(1)	25(1)	25(1)	-3(1)	3(1)	-2(1)
V(2)	26(1)	27(1)	24(1)	-5(1)	1(1)	-5(1)
Na(1)	24(1)	24(1)	24(1)	-2(1)	2(1)	-2(1)
O(1)	27(1)	28(1)	23(1)	-1(1)	2(1)	-2(1)
O(2)	28(1)	23(1)	27(1)	-2(1)	1(1)	0(1)
O(3)	26(1)	26(1)	35(1)	-4(1)	4(1)	-1(1)
O(4)	32(1)	35(1)	22(1)	1(1)	-1(1)	-7(1)
O(5)	33(1)	29(1)	39(1)	-5(1)	8(1)	-2(1)
O(6)	31(1)	38(1)	31(1)	-7(1)	0(1)	-8(1)
N(1)	35(1)	32(1)	27(1)	-2(1)	5(1)	-3(1)
N(2)	38(1)	23(1)	35(1)	-7(1)	2(1)	-4(1)
C(1)	41(2)	37(2)	27(2)	-5(1)	4(1)	-5(2)
C(2)	36(2)	38(2)	20(1)	-3(1)	-3(1)	-5(1)
C(3)	53(2)	28(2)	25(2)	-2(1)	-2(1)	-6(1)
C(4)	33(2)	29(1)	30(2)	-3(1)	-3(1)	2(1)
C(5)	38(2)	23(1)	41(2)	-1(1)	3(1)	4(1)
C(6)	34(2)	25(1)	35(2)	0(1)	-3(1)	0(1)
C(7)	47(2)	26(2)	47(2)	-4(1)	14(2)	-3(1)
C(8)	23(1)	38(2)	50(2)	-10(2)	4(1)	-1(1)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **C3**.

	x	y	z	U(eq)
H(1)	4678	9048	3567	37
H(2)	5891	11716	2177	38
H(1A)	5776	9235	4228	42
H(1B)	5330	9950	3990	42
H(2A)	6484	10206	3592	37
H(2B)	6621	9384	3319	37
H(3A)	5695	8145	3645	42
H(3B)	4956	7957	3214	42
H(4A)	6286	8474	2591	37
H(4B)	5875	7724	2398	37
H(5A)	5011	11809	1154	41
H(5B)	4810	11396	1899	41
H(6A)	4560	10546	1001	38
H(6B)	5297	10730	566	38
H(7A)	6802	12133	1525	48
H(7B)	6091	12384	1081	48
H(8A)	3518	9756	1219	45
H(8B)	3252	9624	2043	45