

SUPPLEMENTARY INFORMATION

What is the maximum charge uptake of Lindqvist-type polyoxovanadates in organic-inorganic heterostructures?

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I. Charge distribution in the POV6 *without* compensating counterions

The charge distribution during sequential addition of electrons to the dicationic POV6 core in the presence of 2^+ counterion (Mg) or two 1^+ counterions (NH_4) is studied. To investigate the influence of ligand and cation type, various combinations of ligands and cations are considered for this simulation (Fig. S1): the system with type I ligands and Mg cation (Type_I_Mg), the system with type I ligands and two NH_4 cations (Type_I_NH₄) and the system with type III ligands and Mg cation (Type_III_Mg).

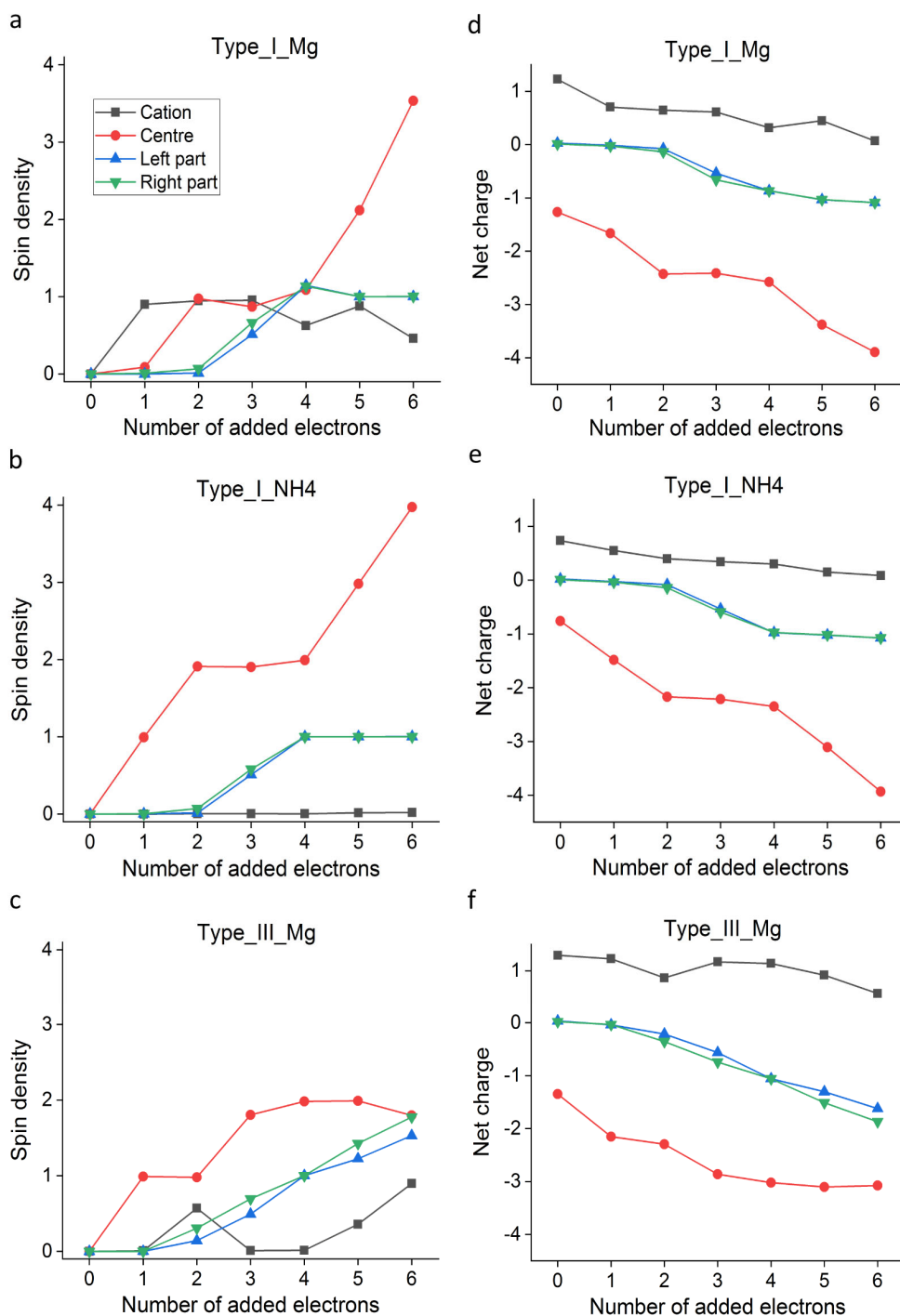


Fig. S1 Spin density (a)-(c) and net charge (d)-(f) of the system parts during sequential addition of electrons (charging). Number of added electrons is the number of extra electrons added to the system. Each curve shows the sum of spin density or net charge (respectively) on all atoms in the corresponding part of the POV6. Color code: grey – cation (Mg or NH_4), red – central part, blue – left-hand ligand, green – right-hand ligand.

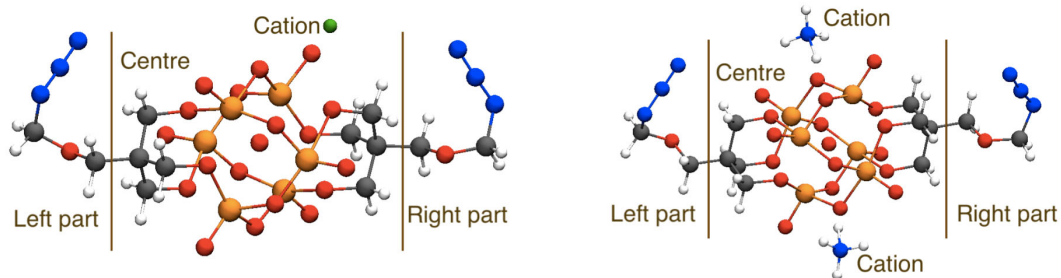


Fig. S2 System parts notation. Color code is the same as in Fig. 1, green – magnesium.

II. Charge distribution in the POV6 in the presence of counterions

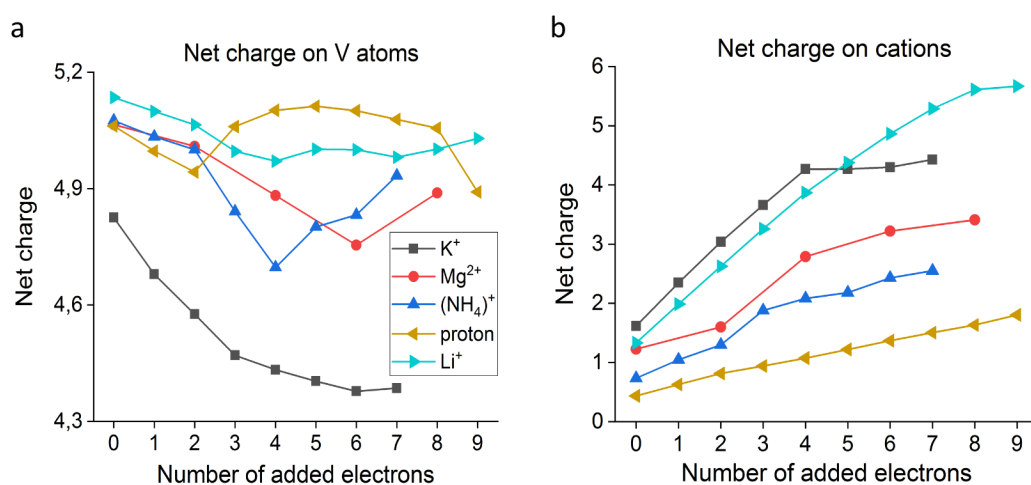


Fig. S3 Net charge during simultaneous addition of electrons and cations for different types of cations. Each curve shows the sum of net charge on all vanadium atoms (a) or all cations (b) in the system. Color code: grey – K cations, red – Mg cations, blue – NH₄ cations, yellow – H cations (protons), cyan – Li cations. POV6 with type I ligand is considered.

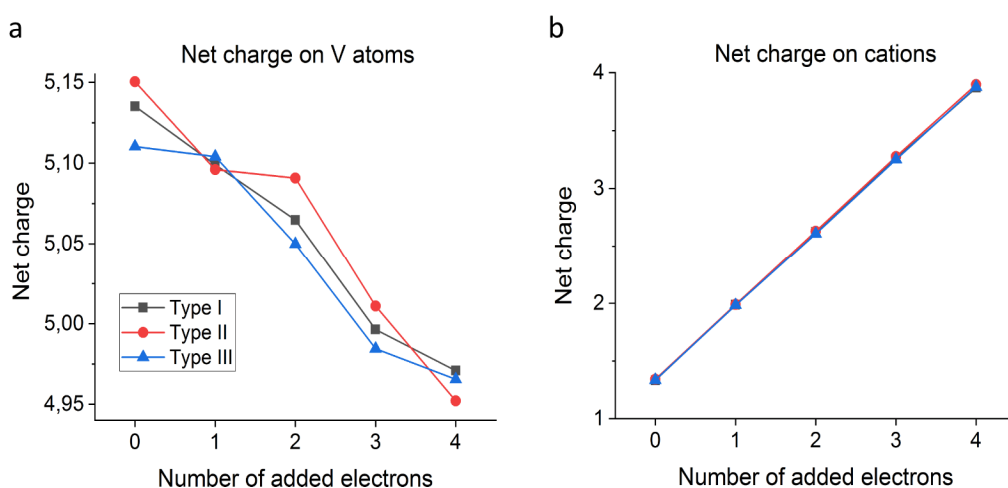


Fig. S4 Net charge during simultaneous addition of electrons and cations for different types of POV6 ligands. Each curve shows the sum of net charge on all vanadium atoms (a) or all cations (b) in the system. Color code: grey – ligand type I, red – ligand type II, blue – ligand type III. In all systems Li counterions are used.

III. Structural integrity of the bisligated POV6 complexes in the presence of counterions

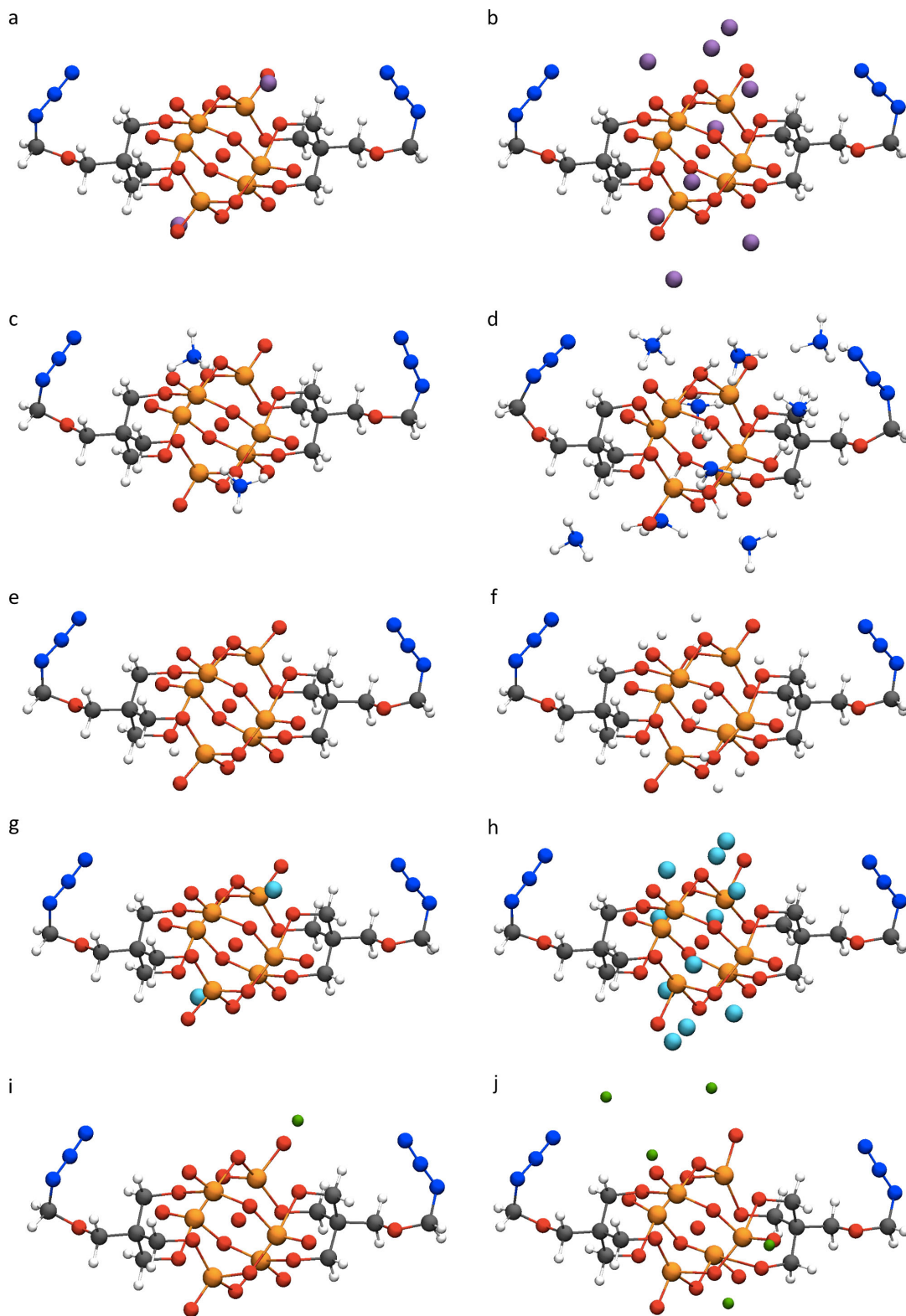


Fig. S5 Structure of the systems with different type and number of cations. (a) 2 K cations, (b) 9 K cations, (c) 2 NH_4 cations, (d) 9 NH_4 cations, (e) 2 H cations, (f) 11 H cations, (g) 2 Li cations, (h) 11 Li cations, (i) 1 Mg cation, (j) 5 Mg cations. Colour code is the same as in Fig. 1, cyan – lithium.

IV. Change of V–O bond length

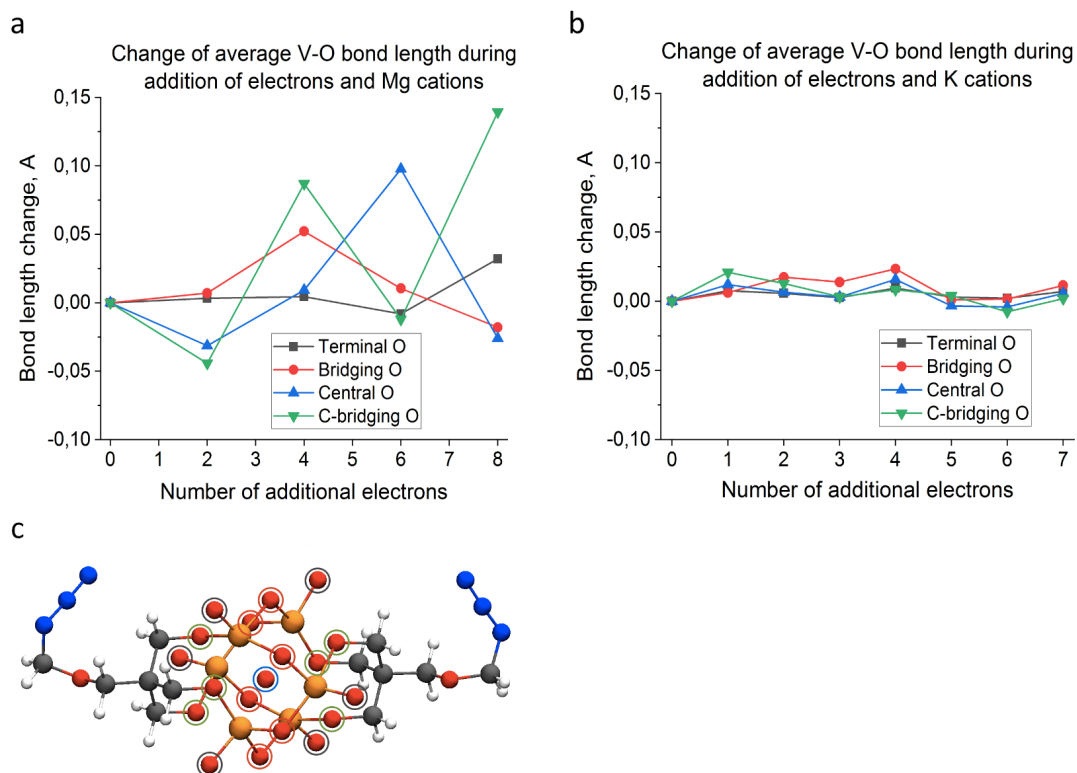


Fig. S6 Change of V–O bond length during simultaneous addition of electrons and Mg (a) and K (b) cations. Each point shows the difference between average V–O bond length for n and $n-1$ additional electrons for various types of O atom. (c) Notation of O atom types: grey – terminal oxygen atoms, red – bridging oxygen atoms, blue – central oxygen atoms, green – C-bridging oxygen atoms.

V. Energy decomposition analysis for the bisligated POV6 core with K counterions

Table S1 Energy decomposition analysis: contribution of Pauli repulsion, electrostatic and orbital interaction to the total bonding energy.

Additional electrons	Energy, eV				% of total energy		
	Total bonding energy	Pauli repulsion	Electrostatic interaction	Orbital interaction	Pauli repulsion	Electrostatic interaction	Orbital interaction
0	-0.0873	-0.0031	-0.0009	-0.0834	3.55	1.03	95.53
1	19.3709	0.2035	-0.1257	19.2937	1.05	0.65	99.60
2	30.3819	0.7577	-0.4074	30.0325	2.49	1.34	98.85
3	44.6768	1.0985	-0.6501	44.2301	2.46	1.46	99.00
4	60.7035	1.7378	-1.0242	59.9923	2.86	1.69	98.83
5	79.8077	4.4241	-2.2911	77.6770	5.54	2.87	97.33

V. Broken symmetry state

To study the effect of different spin orientation i.e., different multiplicity, simulations of the broken symmetry states were performed. For this purpose, in systems with K as cation and 2 to 5 additional electrons (which corresponds to 4 to 7 additional K atoms) a flip of one or two spins of electrons located at V atoms was performed. The usage of this approach instead of simply specifying the lower multiplicity allows to flip the spins on different V atoms. The energy differences between high spin (all electrons on V are α -electrons) and lower spin (both α - and β -electrons are present on one or two V atoms) states for these systems are shown in Fig. S4. The exact values of total spin for each system are given in Table S2. It can be seen that spin state with the minimal energy varies for different additional electrons number. Namely, in case of 5 K cations the high spin state energy is smaller than that of low spin state, while in case of 6 and 7 cations the minimum is reached at the first lower spin states which means that these states are more stable. Besides, the absolute value of the energy difference changes with the number of cations and spin state: it is almost zero for the case of 4 cations, has similar values for the first lower symmetry states of 5, 6 and 7 cations and intermediate values for the second lower symmetry states of 6 and 7 cations.

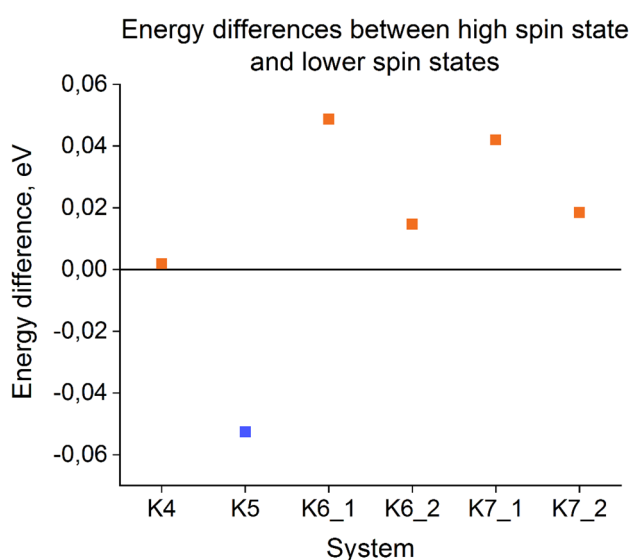


Fig. S7 Energy differences between high spin and lower spin states for systems with various number of additional electrons and cations. First number on each tick on x axis shows a number of cations, second number (where presented) corresponds to the first or second lower symmetry state. Orange marks are the positive energy differences, blue mark is a negative energy difference.

Table S2 Total spin of high and low spin states for systems with different number of cations.

System	Total spin of the high spin state	Total spin of the low spin state
K4	1	0
K5	3/2	1/2
K6_1	2	1
K6_2	2	0
K7_1	5/2	3/2
K7_2	5/2	1/2

VI. Spin densities at V atoms calculated with PBE and PBE0

Table S3 Mulliken spin densities at Vanadium atoms for Type I structure with different number of cations, calculated using local DFT PBE potential and hybrid PBE0 potential.

	K2	K3	K4	K5	K6
PBE					
V ₁	0	0.347928	0.602778	0.636228	0.917831
V ₂	0	0.22886	0.47481	0.563328	0.599788
V ₃	0	0.354463	0.134695	0.44195	0.549913
V ₄	0	0.125638	0.127589	0.671327	0.700797
V ₅	0	0.185671	0.369234	0.520495	0.730226
V ₆	0	0.113863	0.705154	0.65606	0.839106
SUM	0	1.356423	2.41426	3.489388	4.337661
PBE0					
V ₁	0	0.691183	1.043863	1.011876	1.098474
V ₂	0	0.101239	0.182144	0.342235	0.637507
V ₃	0	0.678497	0.095178	0.276394	0.263576
V ₄	0	0.022165	0.074667	0.988825	0.812331
V ₅	0	0.102419	0.102681	0.287761	1.017791
V ₆	0	0.024969	1.090014	0.990919	1.057487
SUM	0	1.620472	2.588547	3.89801	4.887166