Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.
This journal is © the Owner Societies 2017

Supporting Information

Experimental Evidence of Charge Transfer in a Functionalized Hexavanadate. An High Resolution X-ray Diffraction Study

Xiao Xu[a,b], Anne Spasojević-de Biré[a,b]*, Nour Eddine Ghermani[a,b,c], Yongge Wei[d], Sladjana Novaković[a,e], Nada Bošnjaković-Pavlović[a,f], Pingfan Wu[g]

[a] CentraleSupelec, Campus de Châtenay, Grande Voie des Vignes, 92295 Châtenay-Malabry, France

[b] Laboratory "Structures Propriétés et Modélisation des Solides" (SPMS), UMR CNRS 8580, Grande Voie des Vignes, 92295 Châtenay-Malabry, France

[c] Institut Galien Paris Sud, UMR CNRS 8612, Université Paris-Sud, Faculté de Pharmacie, 5, rue Jean-Baptiste Clément, 92296 Châtenay-Malabry, France

[d] Department of Chemistry, Tsinghua University, 100084 Beijing, China

[e] Laboratory for Theoretical and Condensed Matter Physics, Institute Vinča, 11000 Belgrade, Serbia

[f] Faculty of Physical Chemistry, University of Belgrade, Studentski trg 12-16, 11158 Belgrade, Serbia

[g] Institute of POM-based Materials, Hubei University of Technology, The Synergistic Innovation Center of Catalysis Materials of Hubei Province, 430086 Wuhan, Hubei Province, China

*To whom correspondence should be addressed, email: anne.spasojevic@centralesupelec.fr

Contents of Supplementary Information

Supporting Figures and Tables

1. Crystallization

The synthesis of functionalized $[(C_4H_9)_4N]_2[V_6O_{13}\{(OCH_2)_3CCH_2OCCH_2CH_3\}_2]$ (V6-C3) was reported by Wei *et al* [1]. The crystallization process is as following: The red block crystals can be obtained by diffusion of Et_2O into their solution of acetic anhydride in room temperature. The size of V6-C3 crystal for diffraction experiment is 0.3 mm × 0.28 mm × 0.20 mm.

2. X-ray Data Collection and Crystallographic Details

The data of functionalized hexavanadate V6-C3 were collected at 100.0 (1) K on a Kappa CCD APEX II diffractometer using graphite monochromated MoKα X-radiation (wavelength λ = 0.71073 Å). The data spots were recorded as ω-scans ($\Delta\omega$ = 1.0°) in order to reconstruct accurate three dimensional diffracted intensity peak profiles. The exposure times for the recorded frames vary from 10 s (low order data) to 30 s (high order data). 27889 unique reflections were collected up to a resolution of $\sin_{max} = H/2 = 1.06$ Å^{-1}, where H is the Bragg vector modulus. An empirical absorption correction was applied using SADABS[2] computer program. SORTAV[3] program was used for sorting and averaging data revealing the excellent quality of the measurements. Details of the X-ray diffraction experiment conditions and the crystallographic details for V6-C3 are given in Table S1.

3. Structural Description of V6-C3 and V10 anion

The functionalized hexavanadate V6-C3 containing functionalized V6 anion (Figure S1-a) and two tetrabutylammonium (TBA) cations (Figure S1-b). About the crystal packing, see the reference 1.

As shown in Figure S1-a, functionalized V6 anion is symmetrical, there are three chemical equivalent vanadium atoms in each unit. Around each V atom, as shown in Figure S1-c, there are four type of O atoms in V6 core: (i) terminal O atoms (**O1x**: O11, O12, O13) which have one coordinate; (ii) bridged atoms (**O2x**: O21, O22, O23) which have two coordinates; (iii) organo-bridged atoms (**O3x**: O31, O32, O33) which have three coordinates, and (iv) the central O atom (**O6x**: O61) which have six coordinates.

In V10 anion, belonging to $Na_3[V_{10}O_{28}](C_4N_3OH_5)_3(C_4N_3OH_6)_3 \cdot 10H_2O$ [4], (Figure S1-d), there are three types of vanadium atoms: the first type (type I), presents two V-O2x, two V-O3x and two V-O6x bonds; the second kind of vanadium atoms (type II) presents four V-O2x, one V-O1x and one V-O6x bond; the third type of vanadium atoms (type III) presents two V-O2x, two V-O3x, one V-O1x and one V-O6x bond. Compared to V10 anion, VII is the most similar to V atom in V6-C3.

4. Spherical and Electron Density Refinements

The crystal structure of V6-C3 was solved using SIR94 program [5] and refined using SHELX 97[6] implemented in WinGX package.[7] The electron density of V6-C3 was described using the program package MoPro,[8] which is based on the multipole formalism developed by Hansen and Coppens.[9] In this model, the total atomic electron density is treated as aspherical and is divided in three parts:

$$\rho_{tot}(r) = \rho_{core}(r) + P_{val}\kappa^3\rho_{val}(\kappa r) + \sum_{l=0}^{l_{max}} \kappa'^3 R_l(\kappa' r) \sum_{m=0}^{+l} P_{lm} d_{lm\pm}(\theta, \varphi)$$

where P_{val} is the valence population, P_{lm} are the multipole populations, κ and κ' are the contraction/expansion coefficients for spherical and aspherical valence density,

respectively. The first and second terms are the spherically averaged core and valence electron densities of an atom, which were calculated from the Hartree–Fock wave function of the free atoms. [10] The third term is a sum of angular functions $y_{lm\pm}$(l = 0 (monopole) to 4 (hexadecapole)), which are density-normalized real spherical harmonic functions, and describes the multipolar electron density. The $y_{lm\pm}$ was modulated by Slater-type radial function $R_{nl}(r) = Nr^{nl} \exp(-\xi_l r)$, where N is the normalization factor. The exponents ξ_l (in bohr^{-1}) of the radial functions are chosen equal to 3.1, 3.8 and 4.5 and n_l = 2, 2, 3 up to octupoles (l = 3) for C, N and O atoms respectively; for V atoms, ξ_l = 5.98 and = 4, 4, 4, 4 up to hexadecapoles (l = 4); ξ_l = 2.0 bohr^{-1} and n_l = 1 (dipole level, l = 1) for the H atoms. The values of kappa (κ) and multipole (κ') Coefficient are presented in Table S2.

5. Charge density refinement strategy

Vanadium element is a *3d* transition metal, which could imply some difficulties when refining the electron density because of the significantly different radial extension of the *3d* and *4s* valence orbitals. According to a previous charge density analysis performed on a decavanadate (V10), model for V atoms is based on $4s^0 3d^3$ configuration, where V^{2+} contains 18 core electrons. In order to conserve electron-neutrality, we have attributed the formal charges as follows: $[(Bu_4N)_2]^{2+}$ $[V_6O_{13}\{(OCH_2)_3CCH_2OCOCH_2CH_3\}]^{2-}$.

Strategy 1: we have not authorized a charge transfer between the anion and cation. All steps of the refinements were separated. In each step, the anion was firstly refined, then the cation. The general scheme of refinement was the following: First, scale factor, and non-hydrogen atoms anisotropic displacement parameters were refined over all data. A high-order refinement ($\sin\theta/\lambda \geq 0.8$ Å^{-1}) of the coordinates and the anisotropic displacement parameters of the non-hydrogen atoms was then performed.

Subsequently, the multipole parameters and κ parameters were introduced sequentially and refined for the non-hydrogen atoms for all data. Finally, the coordinates and anisotropic thermal displacement parameters of the non-hydrogen atoms are allowed to be refined. In the final step, the isotropic thermal displacement parameters of the hydrogen atoms were refined. Refinement of this model was stable and converged to the lowest least-squares indices. In the end of the cycles, the thermal anharmonicity parameters for V atoms were refined.

Strategy 2: Based on ***Strategy 1***, we permit the charge transfer between cation and anion. We refine the multipole populations and the corresponding κ parameters of cation and anion in the same step.

6. Residual Electron Density

The electron density, ρ(***r***), is the Fourier transform of the structure factors *F*(***H***). The residual electron density[11], $\rho_{res}(r)$, is defined as the difference between the observed and the calculated electron density. It represents the density not accounted for in the least squares refinements.

$$\Delta\rho_{res}(\boldsymbol{r}) = \rho_{obs}(\boldsymbol{r}) - \rho_{calc}(\boldsymbol{r})$$

It can be seen as an error in the electron density originating from an inaccurate model and/or errors in the observed structure factors. These maps (figure S1) should be featureless and for the ideal agreement between model and data. If the model is inadequate, the least-squares parameters will be biased such as to minimize the residual density.

7. Experimental AIM charge

As one of the goals of this paper is to analyze AIM charge distribution within the molecule we employed the XDPROP module of XD. [12] For this purpose, we used the convenient option of MoPro program to export the results in XD file format. Therefore further atomic basin charge integration was carried out with XDPROP. The V6-C3 AIM charges are summarized in Table S4.

8. Experimental Electrostatic Potential

The electrostatic potential [13] is based on the Hansen-Coppens electron density model. In the package of Mopro, VMOPRO computer program was used to generate the electrostatic potential using the following equation:

$$\Phi(\boldsymbol{r}) = \sum_{k=1}^{M} \frac{Z_k}{|\boldsymbol{R}_k - \boldsymbol{r}|} - \int \frac{\rho(\boldsymbol{r}')}{|\boldsymbol{r}' - \boldsymbol{r}|} d\boldsymbol{r}'$$

where R_k is the position and Z_k is the charge of the k-th nucleus. Sign of the potential at the given point depends on the domination of nuclei (first term) or electrons (second term). The electrostatic potential exhibits the nucleophilic (negative potential) and electrophilic (positive potential) regions of the molecule and is a good indicator of the chemical reactivity.

9. Supporting Information References

(1) Wu, P.; Xiao, Z.; Zhang, J.; Hao, J.; Chen, J.; Yin, P.; Wei, Y. *Chem. Commun.* **2011**, *47*, 5557–5559.
(2) *SADABS* (version 2.10); George Sheldrick: University of Göttingen, 2003.
(3) Blessing, R. H. *J. Appl. Crystallogr.* **1997**, *30*, 421−426.
(4) Bošnjaković-Pavlović, N.; Spasojević – de Biré, A.; Tomaz, I.; Bouhmaida, N.; Avecilla, F.; Mioc, U. B.; Pessoa, J. C.; Ghermani, N. E. *Inorg. Chem.* **2009**, *48*, 9742–9753.
(5) Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A. *J. Appl. Crystallogr*. **1993**, *26*, 343−350.

(6) (a) Sheldrick, G. M. SHELXS97 and SHELXL97: programs for crystal structure refinement; University of Gottingen: Gottingen, Germany, 1997.; (b) Sheldrick, G. M. *Acta Crystallogr.* **2008**, *A64*, 112−122.
(7) Farrugia, L. J. *J. Appl. Crystallogr*. **1999**, *32*, 837−838.
(8) (a) Guillot, B.; Viry, L.; Guillot, R.; Lecomte, C.; Jelsch, C. *J. Appl. Crystallogr*. **2000**, *34*, 214−223. (b) Jelsch, C.; Guillot, B.; Lagoutte, A.; Lecomte, C. *J. Appl. Crystallogr*. **2005**, *38*, 38−54.
(9) Hansen, N. K.; Coppens, P. *Acta Crystallogr.* **1978**, *A34*, 909–921.
(10) Clementi, E; Roetti, C. Atomic data and Nuclear data tables; Academic Press: New York, **1974**; Vol. 14, p 177.
(11) Koritsanszky, T. S.; Coppens, P. *Chem. Rev.* **2001**, *101*, 1583–1628.
(12) Volkov, A.; Macchi, P.; Farrugia, L. J.; Gatti, C.; Mallinson, P. R.; Richter, T.; Koritsanszky, T. XD2006: a Computer Program Package for Multipole Refinement, Topological Analysis of Charge Densities and Evaluation of Intermolecular Energies from Experimental and Theoretical Structure Factors, 2006.
(13) Pizzonero, M.; Keller, L.; Dumas, F.; Ourevitch, M.; Morgant, G.; Spasojević – de Biré, A.; Bogdanović, G.; Ghermani, N. E.; D'Angelo, J.; *J. Org. Chem.* **2004**, *69*, 4336-4350.
(14) Kempf, J. Y.; Rohmer, M. M.; Poblet, J. M.; Bo, C.; Bénard, M. *J. Am. Chem. Soc.* **1992**, 114, 1136-1146.

Figure S1. Structural description of V6-C3 (a, b, c) and V10 anion (d and e).

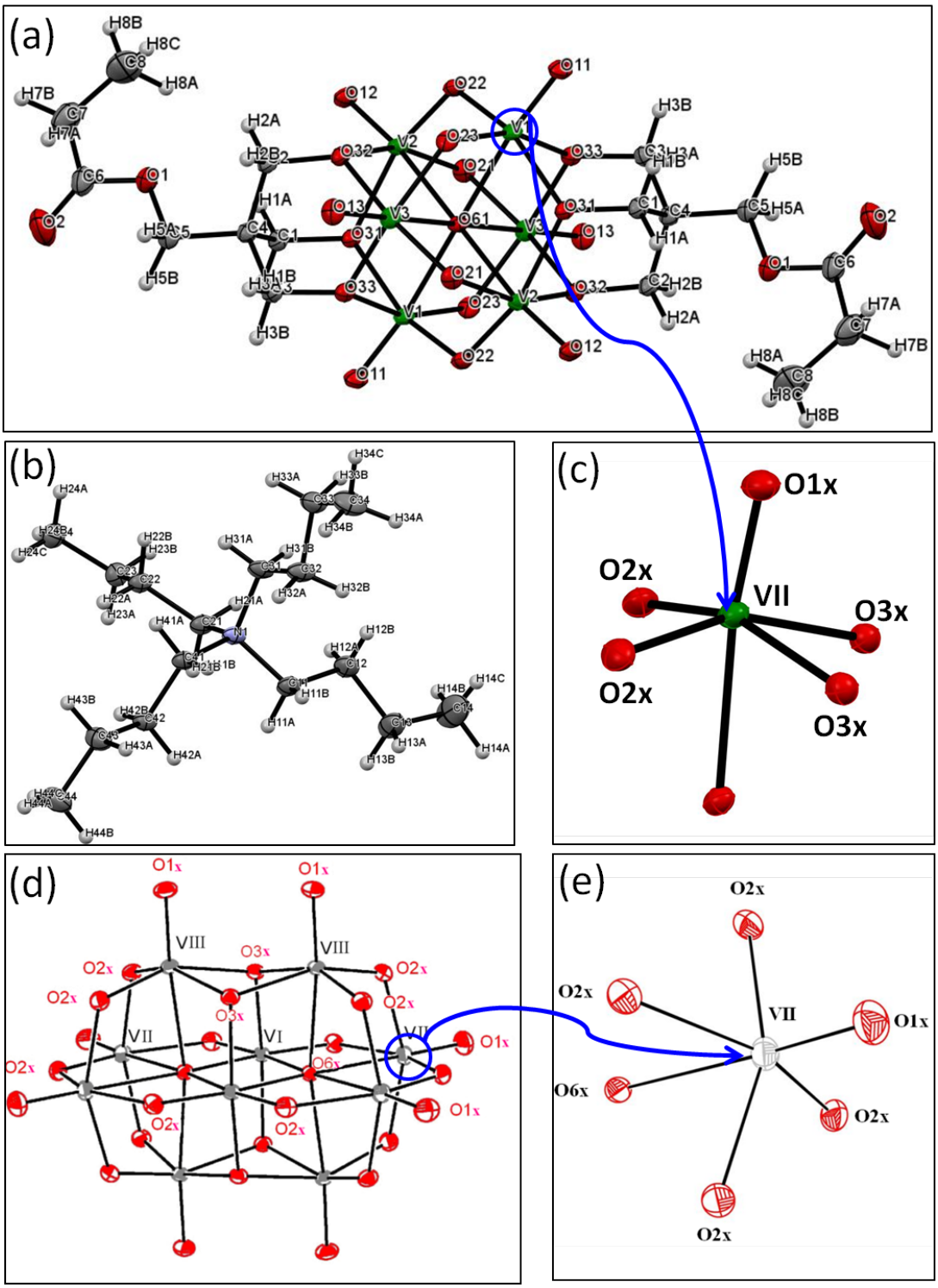

Figure S2. Residual electron density of three planes of V6 core （The contours is 0.1 eÅ^{-3}）

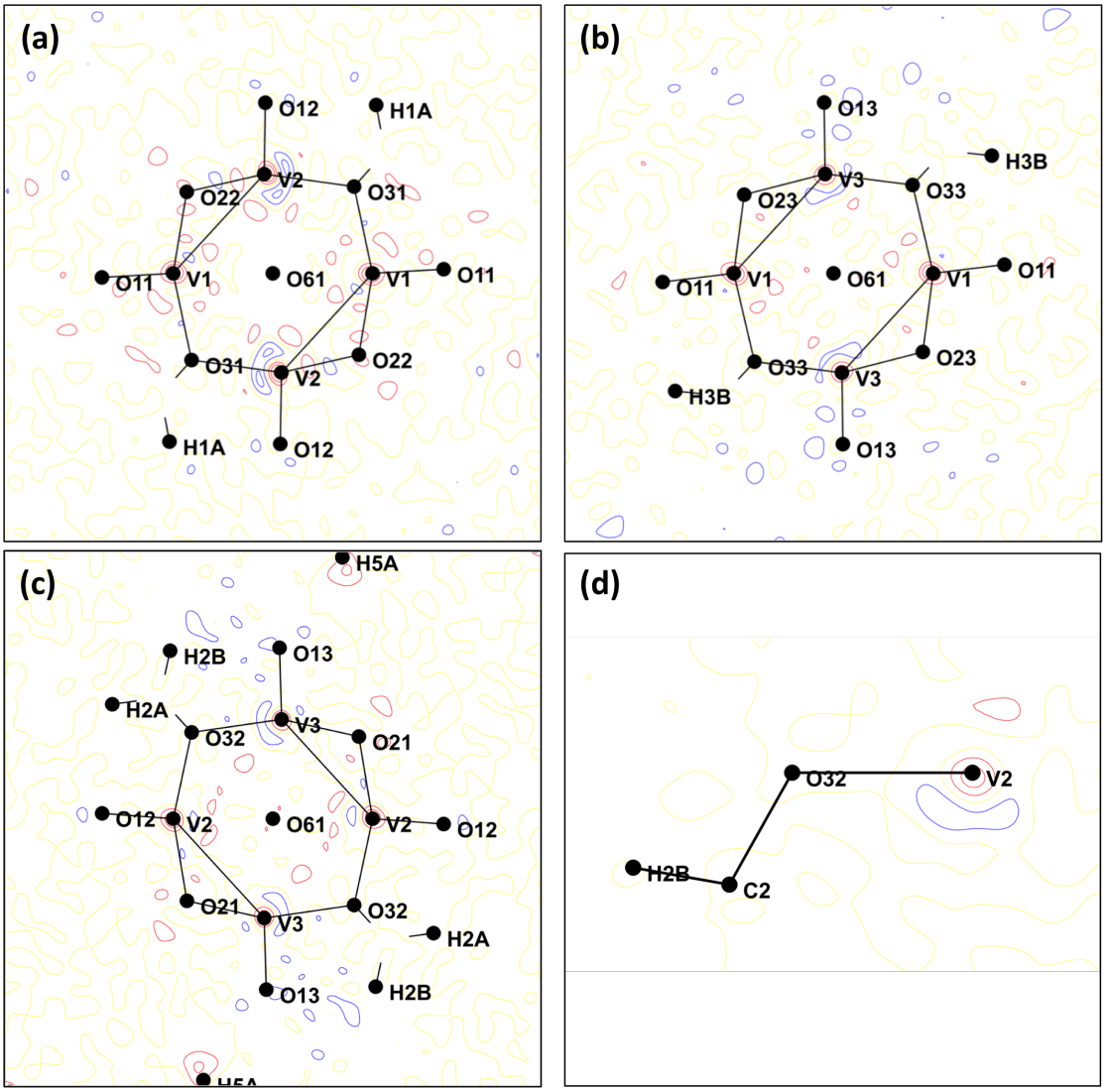

Table S1. Crystallographic details of V6-C3

Chemical formula	C48 H98 N2 O23 V6
Temperature (K)	100
Wavelength (Å)	0.71073
Cell setting, space group	monoclinic, P 21/c
Z	2
a (Å) ,b (Å), c (Å)	10.866(5),14.776(5), 19.636(5)
β (°)	97.766(5)
Volume($Å^3$)	3123.76
$[\sin\theta/\lambda]_{max}$ ($Å^{-1}$)	1.10
Number of reflexions used in SHELX : all data / unique ($F_0 > 4sigF_0$)	27889 / 20073
Spherical refinement : R(%) / R_w(%) / GOF /	2.93/ 3.27 / 1.28 /
Multipole refinement : R (%) / R_w (%) / GOF /	1.97 / 1.92 / 0.91 /

Table S2. κ contraction-expansion coefficients and spherical valence populations (refined atomic charges P_{val}) (strategy 1)

ATOM	κ	P_{val}
V1	1.042644	3.575
V2	1.062238	3.439
V3	1.061774	3.439
O61	0.949733	7.130
O11	0.969581	6.866
O12	0.972025	6.766
O13	0.958266	6.948
O21	0.952263	7.110
O22	0.965253	6.925
O23	0.955165	7.049
O31	0.969397	6.790
O32	0.967751	6.758
O33	0.965335	6.789
O1	0.970249	5.692
O2	0.96574	5.719
C1	1.019204	3.922
C2	1.005666	4.108
C3	0.989019	4.284
C4	0.995943	4.140
C5	0.975113	4.623
C6	0.992837	3.220
C7	1.001965	3.367
C8	1.025202	2.968
N1	0.974341	5.414
C11= C21= C31= C41	0.990331	4.262
C12= C22= C32= C42	0.975081	4.407
C13= C22= C33= C43	0.969193	4.365
C14= C24= C34= C44	0.984583	3.875
H1A= H1B= H3A= H3B	1.222753	0.786
H2A= H2B	1.200597	0.803
H5A = H5B	1.177487	0.865
H7A = H7B	1.10359	0.977
H8A = H8B= H8C	1.103382	1.168
H11A = H11B= H21A= H21B= H31A= H31B= H41A= H41B	1.175587	0.790
H12A = H12B= H22A= H22B= H32A= H32B= H42A= H42B	1.176615	0.755
H13A = H13B= H23A= H23B= H33A= H33B= H43A= H43B	1.118517	0.838
H14A = H14B= H14C= H24A= H24B= H24C= H34A= H34B= H44A= H44B	1.116043	0.990

Table S3. κ contraction-expansion coefficients and spherical valence populations (refined atomic charges P_{val}) (strategy 2)

ATOM	κ	P_{val}
V1	1.042644	3.622
V2	1.062238	3.483
V3	1.061774	3.485
O61	0.949733	7.152
O11	0.969581	6.889
O12	0.972025	6.786
O13	0.958266	6.974
O21	0.952263	7.13
O22	0.965253	6.951
O23	0.955165	7.069
O31	0.969397	6.817
O32	0.967751	6.787
O33	0.965335	6.816
O1	0.970249	5.871
O2	0.96574	5.678
C1	1.019204	3.948
C2	1.005666	4.147
C3	0.989019	4.311
C4	0.995943	4.165
C5	0.975113	4.605
C6	0.992837	3.184
C7	1.001965	3.302
C8	1.025202	3.021
N1	0.974341	5.427
C11= C21= C31= C41	0.990331	4.239
C12= C22= C32= C42	0.975081	4.371
C13= C22= C33= C43	0.969193	4.331
C14= C24= C34= C44	0.984583	3.898
H1A= H1B= H3A= H3B	1.222753	0.786
H2A= H2B	1.200597	0.800
H5A = H5B	1.177487	0.868
H7A = H7B	1.10359	0.969
H8A = H8B= H8C	1.103382	1.175
H11A = H11B= H21A= H21B= H31A= H31B= H41A= H41B	1.175587	0.783
H12A = H12B= H22A= H22B= H32A= H32B= H42A= H42B	1.176615	0.750
H13A = H13B= H23A= H23B= H33A= H33B= H43A= H43B	1.118517	0.840
H14A = H14B= H14C= H24A= H24B= H24C= H34A= H34B= H44A= H44B	1.116043	0.972

Table S4. AIM charges

Atom	Strategy1	Strategy2	Atom	Strategy1	Strategy2	Atom	Strategy1	Strategy2
V(1)	1.206	1.156	H(5B)	-0.097	-0.099	H(14B)	0.083	0.096
V(2)	1.332	1.288	H(7A)	0.222	0.226	H(14C)	0.083	0.096
V(3)	1.281	1.231	H(7B)	0.224	0.228	H(21A)	0.249	0.244
O(61)	-1.090	-1.111	H(8A)	-0.038	-0.037	H(21B)	0.246	0.252
O(11)	-0.762	-0.746	H(8B)	-0.042	-0.044	H(22A)	0.253	0.255
O(12)	-0.628	-0.625	H(8C)	-0.039	-0.038	H(22B)	0.252	0.245
O(13)	-0.826	-0.843	N(1)	-1.060	-1.043	H(23A)	0.210	0.212
O(21)	-1.044	-1.063	C(11)	-0.200	-0.182	H(23B)	0.210	0.208
O(22)	-0.825	-0.821	C(12)	-0.413	-0.380	H(24A)	0.078	0.091
O(23)	-0.946	-0.957	C(13)	-0.473	-0.447	H(24B)	0.079	0.093
O(31)	-1.052	-1.073	C(14)	-0.099	-0.112	H(24C)	0.078	0.092
O(32)	-0.984	-0.998	C(21)	-0.211	-0.195	H(31A)	0.247	0.247
O(33)	-1.084	-1.108	C(22)	-0.416	-0.384	H(31B)	0.245	0.241
O(1)	-0.470	-0.468	C(23)	-0.476	-0.451	H(32A)	0.254	0.255
O(2)	-0.384	-0.371	C(24)	-0.082	-0.096	H(32B)	0.255	0.256
C(1)	0.363	0.343	C(31)	-0.204	-0.186	H(33A)	0.211	0.221
C(2)	0.206	0.185	C(32)	-0.417	-0.384	H(33B)	0.210	0.211
C(3)	0.128	0.108	C(33)	-0.474	-0.444	H(34A)	0.079	0.093
C(4)	0.037	0.005	C(34)	-0.090	-0.103	H(34B)	0.078	0.092
C(5)	0.158	0.160	C(41)	-0.203	-0.186	H(34C)	0.080	0.103
C(6)	2.081	2.053	C(42)	-0.416	-0.383	H(41A)	0.246	0.252
C(7)	0.029	-0.019	C(43)	-0.479	-0.454	H(41B)	0.249	0.254
C(8)	0.590	0.560	C(44)	-0.088	-0.103	H(42A)	0.253	0.255
H(1A)	0.167	0.164	H(11A)	0.246	0.252	H(42B)	0.253	0.254
H(1B)	0.169	0.166	H(11B)	0.245	0.251	H(43A)	0.211	0.213
H(2A)	0.143	0.126	H(12A)	0.251	0.245	H(43B)	0.213	0.215
H(2B)	0.141	0.131	H(12B)	0.254	0.256	H(44A)	0.081	0.094
H(3A)	0.135	0.132	H(13A)	0.207	0.209	H(44B)	0.079	0.093
H(3B)	0.142	0.139	H(13B)	0.213	0.216	H(44C)	0.079	0.092
H(5A)	-0.114	-0.113	H(14A)	0.084	0.097			

Table S5. Experimental AIM charges (e) and EP ($eÅ^{-1}$) in V6-C3 and V10 anions. (OL = organic ligand, TBA = terbutylammonium cation)

	Functionalized V6-V3						V10		
	Refinement strategy 1			Refinement strategy 2			Refinement strategy 1		
	AIM charge (e)	Average AIM charge (e)	EP ($eÅ^{-1}$)	AIM charge (e)	Average AIM charge (e)	EP ($e Å^{-1}$)		Average AIM charge (e)	EP ($eÅ^{-1}$)
V1	1.206			1.156					
V2	1.332	1.273		1.288	1.225		VII	1.528	
V3	1.281			1.231					
O11	-0.762			-0.746					
O12	-0.628	-0.738	-0.92	-0.625	-0.738	-1.11	O1x	-0.644	-5.9
O13	-0.826			-0.843					
O21	-1.044			-1.063					
O22	-0.825	-0.938	-1.18	-0.821	-0.947	-1.40	O2x	-0.811	-7.0 to -7.5
O23	-0.946			-0.957					
O31	-1.052			-1.073					
O32	-0.984	-1.040	-1.45	-0.998	-1.060	-1.70	O3x	-0.895	-8.6
O33	-1.084			-1.108					
O61	-1.090			-1.111					
V6 core	-9.755			-10.230					
OL	+7.497			+7.071					
TBA	+0.839 x 2			+1.318 x 2					
Total [14]	-0.580			-0.522					