Electronic supplementary information (ESI)

for

A square-pyramidal organochromium(V) compound

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A DERIVATION OF A MODIFIED BRILLOUIN LAW TO DESCRIBE THE MAGNETIZATION AS A FUNCTION OF THE APPLIED FIELD UNDER THE ASSUMPTION OF LOW FERROMAGNETIC INTERACTION

In a simple (isotropic) paramagnet, the magnetic moment, *M*, as a function of the applied magnetic field, *H*, at a temperature, *T*, is given by the Brillouin law:

$$M = Ng\mu_B S \cdot B_S\left(\frac{g\mu_B S}{k}\frac{H}{T}\right), \tag{S1}$$

where *N* is the number of paramagnetic entities present in the sample, *S* their spin, *g* their gyromagnetic factor (which is assumed to be isotropic), μ_B the Bohr magneton and B_S the Brillouin function defined as:

$$B_S(x) = \frac{2S+1}{2S} cth\left\{\frac{2S+1}{2S}x\right\} - \frac{1}{2S} cth\left\{\frac{1}{2S}x\right\}. \tag{S2}$$

It is important to recall some elementary properties of the Brillouin function, as some use will be made of them in what follows. Firstly, note that B_S is a increasing function verifying $B_S(0) = 0$ and $B_S(x) \to 1$ as $x \to \infty$. Its Taylor expansion around $x = 0$ is given by:

$$B_S(x) = \frac{S+1}{3S}x - \frac{(S+1)\left(2S^2+2S+1\right)}{90S^3}x^3 + O\left(x^5\right) \tag{S3}$$

and its derivative is:

$$\frac{\partial B_S(x)}{\partial x} = B_S'(x) = \left(\frac{2S+1}{2S}\right)^2 \frac{1}{\sinh^2\left\{\frac{2S+1}{2S}x\right\}} - \left(\frac{1}{2S}\right)^2 \frac{1}{\sinh^2\left\{\frac{1}{2S}x\right\}} \tag{S4}$$

Going back to Eq. (S1) it is customary to introduce the magnetic moment per formula, measured in Bohr magnetons, $m = M/N\mu_B$. Additionally, since the argument of the Brillouin function only depends of the reduced field, $h = \mu_B H/kT$, a drawing of *m* against *h* results in a universal representation

$$m = gS \cdot B_S(gS \cdot h), \tag{S5}$$

which does not depend on the actual temperature.

The linear regime —that involves retaining just the first term in Eq. (S3)— is a good approximation for sufficiently low values of the applied field, *i.e.* $\mu_B H \ll kT$. Hence, the dependence of the magnetic moment with the applied field is given by:

$$M = \frac{Ng^2\mu_B^2 S(S+1)}{3kT} H, \tag{S6}$$

from which the paramagnetic susceptibility, χ_p, given by the Curie law is defined by

$$\chi_p = \frac{Ng^2\mu_B^2 S(S+1)}{3kT} = \frac{C}{T}, \tag{S7}$$

where:

$$C = \frac{Ng^2\mu_B^2 S(S+1)}{3k} \tag{S8}$$

is usually called Curie constant.

Let us consider the existence of a ferromagnetic interaction among the magnetic entities, which will be described within the molecular field approximation. In such a case, instead of just perceiving the applied magnetic field, H, the paramagnetic entities feel a local magnetic field given by $H + \gamma M$ where γ is the molecular field constant. Hence, at a given temperature in the paramagnetic phase, the magnetic moment is obtain by solving:

$$M = Ng\mu_B S \cdot B_S\left(\frac{g\mu_B S}{k}\frac{H+\gamma M}{T}\right). \tag{S9}$$

The linear regime takes place when $\mu_B(H + \gamma M) \ll kT$ and, retaining only the first term in the expansion (S3), the magnetic moment as a function of the applied field is given by:

$$M = \frac{C}{T - T_c} H, \tag{S10}$$

where the Curie temperature is defined as $T_C = \gamma C$. Consequently, the temperature dependence of the paramagnetic susceptibility (in the paramagnetic phase) follows the Curie-Weiss law:

$$\chi_p = \frac{C}{T - T_c} \tag{S11}$$

To obtain the $M(H, T)$ dependence beyond the linear regime, Eq. (S9) has to be solved for each value of the applied field and each temperature. A simple solution of such a problem is easily obtained if the ferromagnetic intermolecular interaction is weak enough, *i.e.*, if the molecular field can be considered to be sufficiently small compared with the applied field ($\gamma M \ll H$). In this case, the Taylor expansion of (S9) in powers of M can be truncated retaining only up to the linear term. So:

$$M \approx Ng\mu_B S \cdot B_S\left(\frac{g\mu_B S}{k}\frac{H}{T}\right) + Ng\mu_B S \cdot B_S'\left(\frac{g\mu_B S}{k}\frac{H}{T}\right)\frac{g\mu_B S\gamma}{kT}M \tag{S12}$$

and the magnetic moment is given as:

$$M \approx \frac{Ng\mu_B S}{1 - \dfrac{Ng^2\mu_B^2 S^2\gamma}{kT} \cdot B_S'\left(\dfrac{g\mu_B S}{k}\dfrac{H}{T}\right)} \cdot B_S\left(\frac{g\mu_B S}{k}\frac{H}{T}\right). \tag{S13}$$

Taking into account the definition of Curie temperature, T_C, and the Curie constant [Eq. (S8)], the former expression can be written as:

$$M \approx \frac{Ng\mu_B S}{1 - \left(\dfrac{3S}{S+1}\right)\left(\dfrac{T_C}{T}\right) \cdot B_S'\left(\dfrac{g\mu_B S}{k}\dfrac{H}{T}\right)} \cdot B_S\left(\frac{g\mu_B S}{k}\frac{H}{T}\right). \tag{S14}$$

At this point it is advisable to introduced a modified Brillouin function defined as:

$$B_S^{(1)}(a,x) = \frac{B_S(x)}{1 - a\left(\dfrac{3S}{S+1}\right)B_S'(x)} \tag{S15}$$

so that Eq. (S14) can be rewritten as:

$$M = Ng\mu_B S \cdot B_S^{(1)}\left(\frac{T_c}{T}, \frac{g\mu_B S}{k}\frac{H}{T}\right). \tag{S16}$$

Using the magnetic moment per formula, measured in Bohr magnetons, $m = M/N\mu_B$, and the reduced field, $h = \mu_B H/kT$, it follows:

$$m = gS \cdot B_S^{(1)}\left(\frac{T_c}{T}, gSh\right). \tag{S17}$$

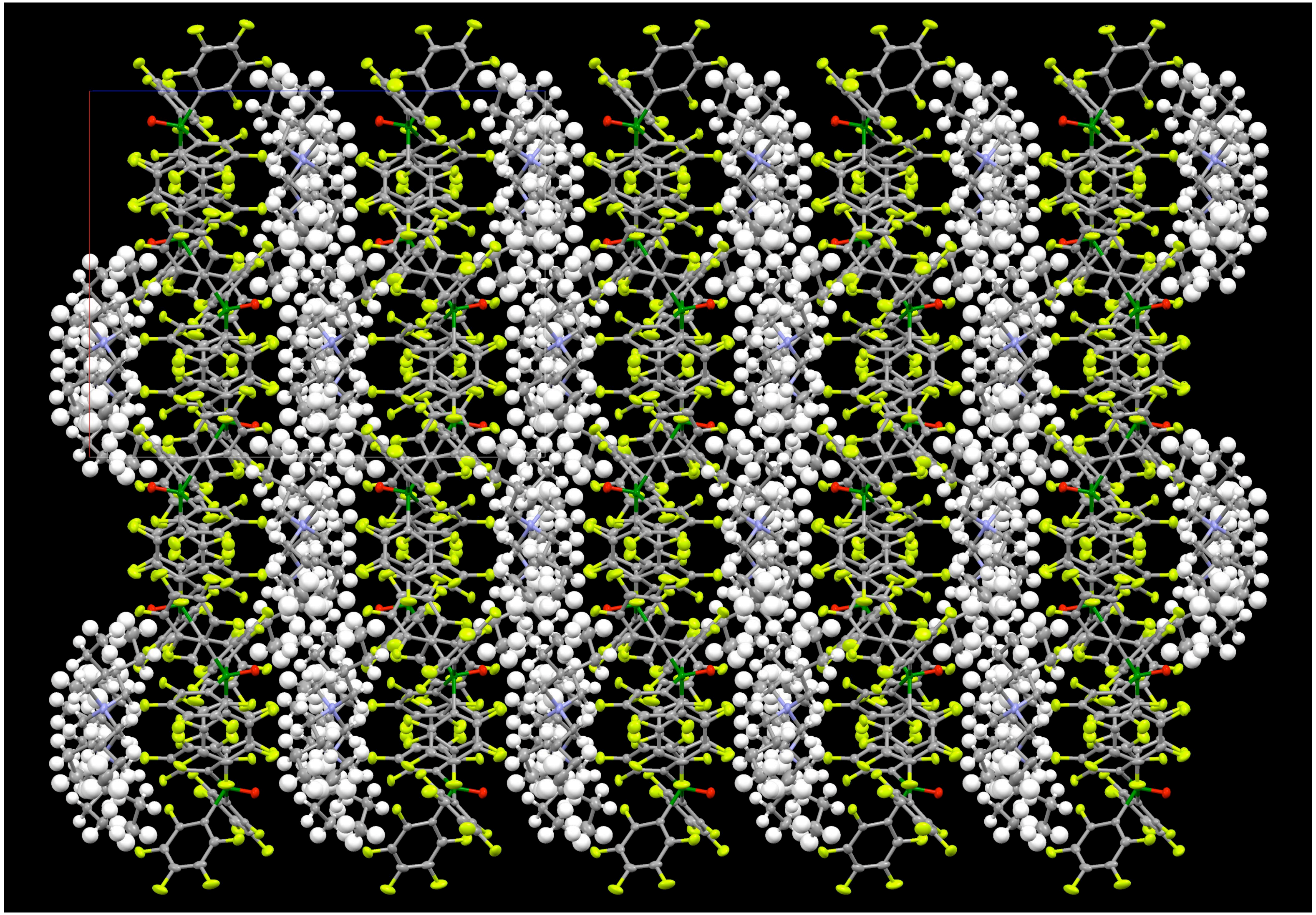

Figure S1. Structural drawing (*b* projection) showing the arrangement of $[NBu_4]^+$ cations and (*SPY*-5)-$[CrO(C_6F_5)_4]^-$ anions in alternating layers within the crystal lattice of **1**.

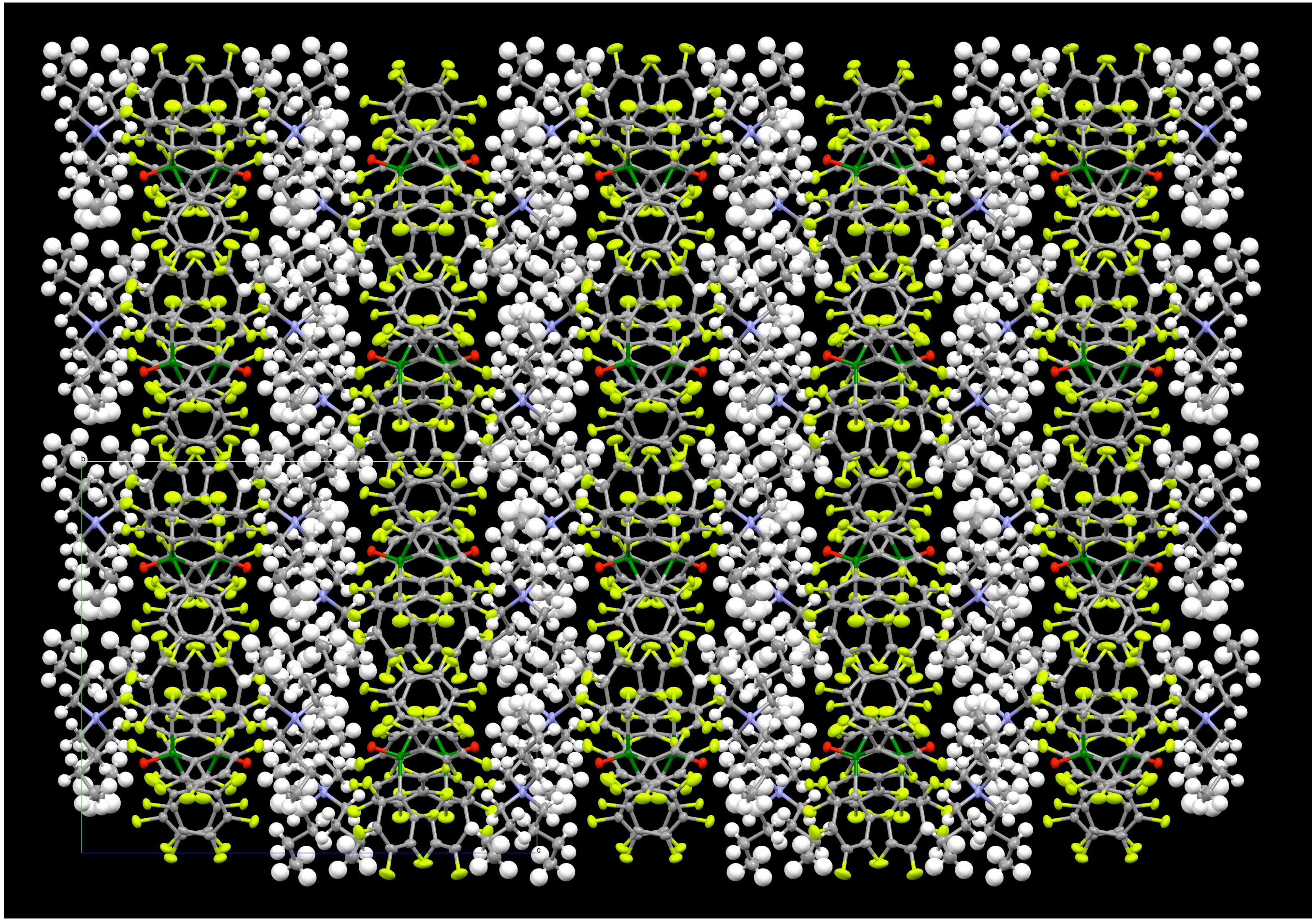

Figure S2. Structural drawing (*a* projection) showing the arrangement of $[NBu_4]^+$ cations and (*SPY*-5)-$[CrO(C_6F_5)_4]^-$ anions in alternating layers within the crystal lattice of **1**.

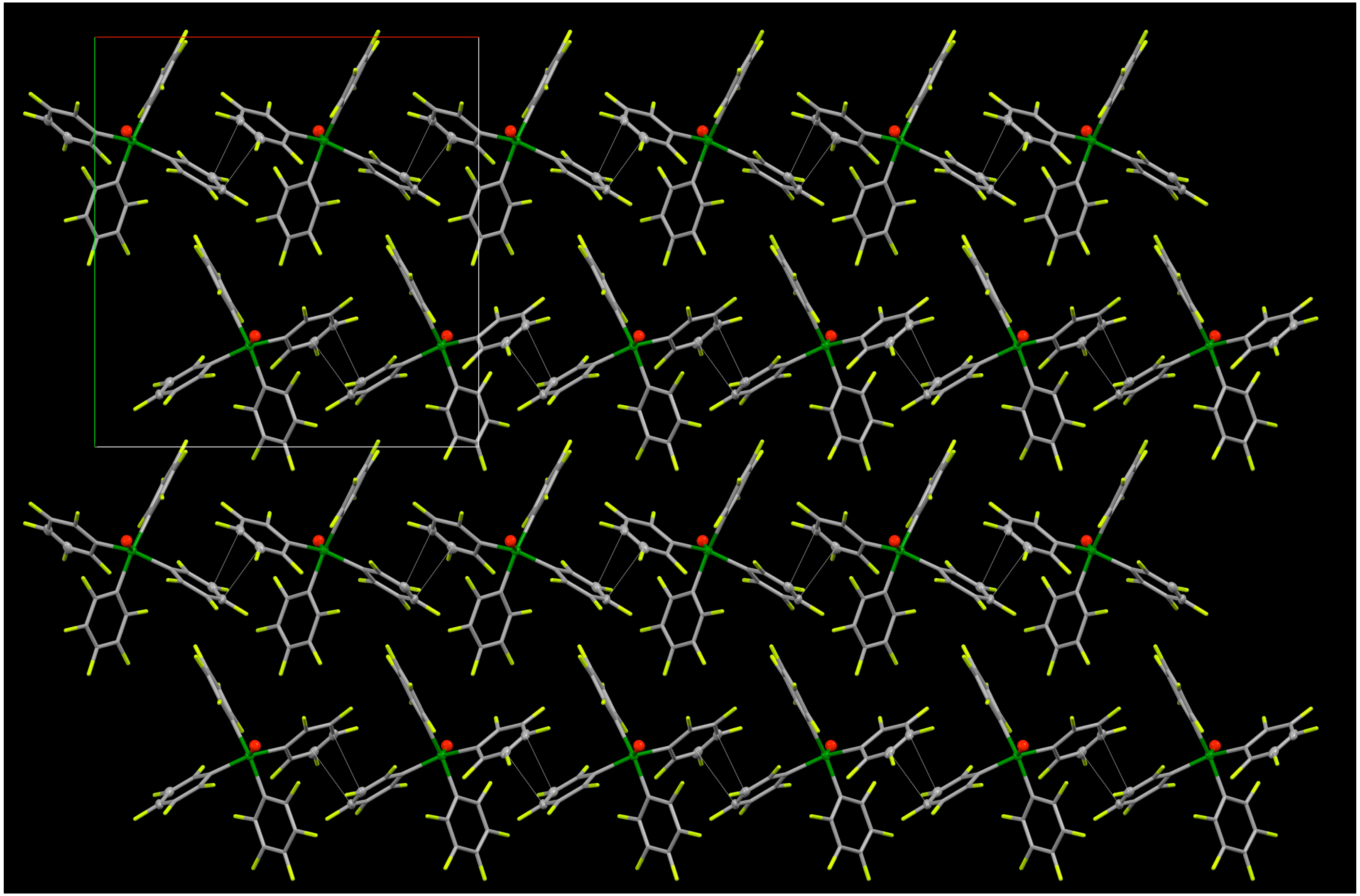

Figure S3. Extended chain arrangement of the (*SPY*-5)-[$CrO(C_6F_5)_4]^-$ anions within the anionic layer in the crystal lattice of **1**, showing the intermolecular π interactions between neighboring and nearly parallel C_6F_5 rings along the *a* axis.