

# Enhanced Coherence by Coupling Spins through a Delocalized $\pi$ -System: Vanadyl Porphyrin Dimers

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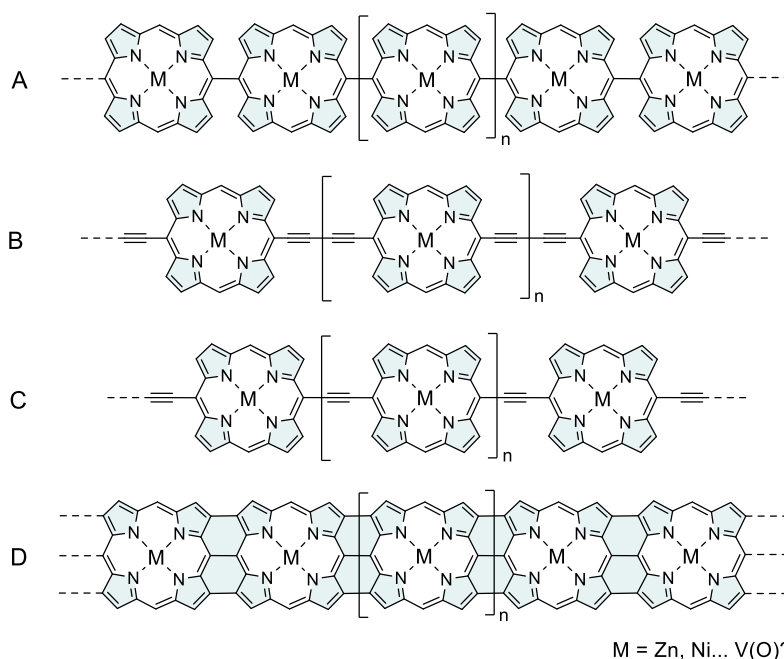
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**Abstract:** Vanadium(IV) magnetic centers are prime candidates as molecular quantum units. One longstanding question is how to obtain a scaffold that connects multiple centers and allows two communication modalities: magnetic and electronic. We have synthesized and studied a selection of vanadyl porphyrin dimers, as models of the most synthetically accessible linear porphyrin arrays. We show that a strongly  $\pi$ -conjugated backbone places the magnetic system in the strong coupling regime and protects the quantum coherence against electron pair flip-flop processes at low temperatures (<10 K). This result is a fundamental step towards the design of molecular materials for single-molecule devices controlled by microwaves with electrical readout.

## Introduction

Transition metal complexes offer many examples of interesting magnetic behavior. For example,  $V^{4+}$  complexes<sup>1-4</sup> (particularly vanadyl derivatives)<sup>5-8</sup> have extremely long coherence times,<sup>9,10</sup> hyperfine coupling in a range suitable for microwave manipulation,<sup>11</sup> and the possibility of creating air-stable complexes and tunable scaffolds.<sup>10</sup> A central question is how to achieve magnetic coupling between multiple metal centers via a molecular backbone. The development of scaffolds that allow the transfer of electrons, and that can be extended to multiple centers by direct chemical design, is urgently needed. While electron transport is facilitated by the presence of delocalized  $\pi$ -orbitals in organic materials, the influence of a conjugated backbone on the magnetic properties remains difficult to anticipate. Moreover, the proximity of several spin centers often has detrimental effects on the quantum coherence.<sup>12-14</sup> Studies of non-molecular systems, e.g. Si quantum dots and Ti atoms, show that exchange coupled spins via quantum mediators can suppress decoherence.<sup>15-20</sup> Observing such effects in  $\pi$ -conjugated molecules would lead to better designs for functional magnetic materials.<sup>21,22</sup> With the purpose of exploring this issue, molecular magnets have been immobilized onto or into carbon nanotubes<sup>23-29</sup> and  $\pi$ -conjugated backbones have been combined with magnetic centers, such as open-shell graphenoids<sup>30-32</sup> or graphene nanoribbons.<sup>33,34</sup> In this context  $\pi$ -conjugated porphyrin polymers<sup>35-43</sup> appear to be ideal scaffolds: they offer a single delocalized channel linking multiple metallic centers, such as copper(II)<sup>44-46</sup> or lanthanides,<sup>47,48</sup> each placed at a precise distance and location.



**Figure 1.** Porphyrin polymers: a) singly-linked, b) butadiyne-linked, c) ethyne-linked, and d) edge-fused. (Solubilizing side chains not shown.)

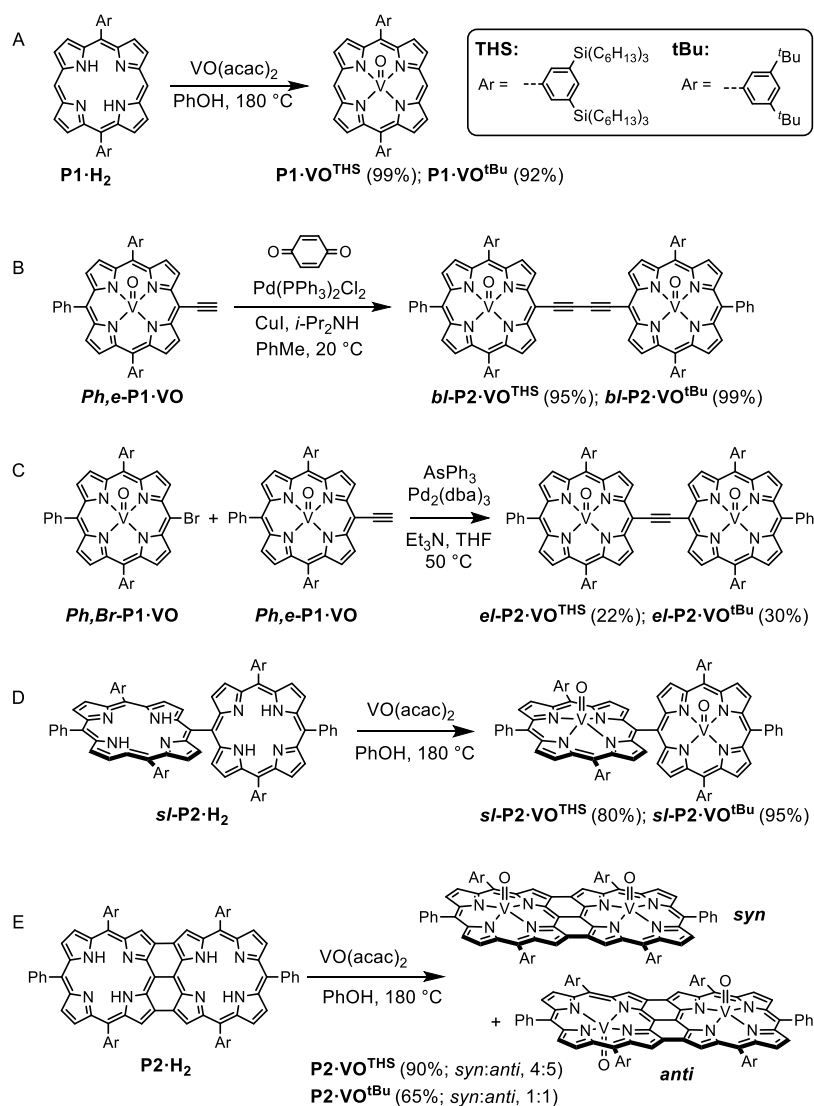
Zinc(II) porphyrin oligomers have been widely investigated as molecular wires.<sup>35-43</sup> The chemical structures of the most synthetically accessible porphyrin polymers, all of which could potentially be synthesized with vanadyl centers, are shown in Figure 1. Two experimental approaches have been used to probe the strength of  $\pi$ -conjugation in these oligomers: a) measurement of the UV-vis-NIR spectra of discrete oligomers, to test how the HOMO-LUMO gap decreases with increasing chain length,<sup>37,38</sup> and b) measurement of the single-molecule conductances, to evaluate the attenuation of conductance as a function of molecular length.<sup>41-43</sup> Both approaches show that the polymers represented in Figure 1 exhibit increasingly strong  $\pi$ -delocalization in the order A<B<C<D. Singly *meso-meso*-linked chains a) are not  $\pi$ -conjugated because the planes of neighboring porphyrins are almost orthogonal, whereas edge-fused chains d) have highly delocalized electronic structures. To date, the influence of  $\pi$ -conjugation on the quantum coherence of vanadyl units in porphyrin arrays remains elusive, despite recent studies of edge-fused and singly-linked vanadyl dimers.<sup>49,50</sup>

*Meso*-aryl substituents are commonly used to tune the solubility of porphyrin polymers. *t*-Bu-substituted aryls are useful for growing crystals for X-ray diffraction analysis, whereas flexible side chains, such as Si(C<sub>6</sub>H<sub>13</sub>)<sub>3</sub>, confer higher solubility and prevent aggregation. Here we test the effect of these solubilizing groups on the magnetic relaxation times of several different  $\pi$ -conjugated or non-conjugated porphyrin backbones. We show that porphyrin scaffolds can connect vanadyl centers without producing a drastic loss of coherence by investigating intermetallic interactions in dimers, as minimal models for synthetically accessible porphyrin arrays. These systems shed light on the relationship between the chemical structure and the relative strength of the magnetic interactions. They reveal how different substituents affect the phase memory time ( $T_m$ ), providing insights into the structure-property relationships that govern the quantum performance of vanadyl porphyrin polymers.

In this article, we use rational codes to designate the porphyrin derivatives, as illustrated in Scheme 1. For example, in ***bl*-P2-VO<sup>THS</sup>**, the prefix *bl* denotes “butadiyne-linked”, P2 indicates two porphyrins, VO signifies that the porphyrins are coordinated by vanadyl, and the super index THS specifies the sidechain (THS for tri(*n*-hexyl)silyl or *t*Bu for *tert*-butyl). When no solubilizing group is specified we refer to compounds with both side chains. The other prefixes used for the porphyrin dimers are ethyne-linked (*el*), singly-linked (*sl*), syn-periplanar (*syn*) and anti-periplanar (*anti*).

## Experimental Results

**Synthesis and Chemical Characterization.** The vanadyl porphyrin monomers **P1·VO<sup>THS</sup>** and **P1·VO<sup>tBu</sup>** were prepared in almost quantitative yield by heating vanadyl acetylacetonate with the free-base porphyrins in phenol (Scheme 1).<sup>6,51-53</sup> We attempted to synthesize the alkyne-linked dimers **bl-P2·VO<sup>tBu</sup>** and **el-P2·VO<sup>tBu</sup>** from the corresponding free-base dimers under the same reaction conditions, but this resulted in decomposition, so we inserted the vanadyl ion at an earlier stage in the synthesis (SI, Section 1.2 and 1.3 for the compounds containing THS and *t*-Bu groups, respectively). Butadiyne-linked dimers (**bl-P2·VO**) were obtained in high yields (>95%) by Pd-mediated Glaser coupling of **Ph,*a*-P1·VO** (Scheme 1). By contrast, the ethyne-linked dimers (**el-P2·VO**) were synthesized in moderate yields by copper-free Sonogashira coupling, using triphenylarsine as ligand to avoid competing Glaser coupling.<sup>54</sup> The singly-linked dimers **sl-P2·VO** were synthesized by direct insertion of vanadyl ions into the free-base dimers in 80% and 95% yields for the THS and *t*-Bu aryl substituted groups, respectively. The edge-fused dimers **syn-P2·VO<sup>THS</sup>** and **anti-P2·VO<sup>THS</sup>** were obtained in a 90% yield (4:5, *syn:anti*) from the corresponding free-bases by treatment with VO(acac)<sub>2</sub> in phenol at 180 °C, and separated by column chromatography on silica, with the *syn*-isomers being more polar (lower *R<sub>f</sub>*). The analogous compounds **syn-P2·VO<sup>tBu</sup>** and **anti-P2·VO<sup>tBu</sup>** were prepared under the same reaction conditions. Full conversion was observed by TLC, but the yield of the two isomers was only a 65% (1:1, *syn:anti*, separated by chromatography on SiO<sub>2</sub>) due to their poor solubility in common organic solvents.

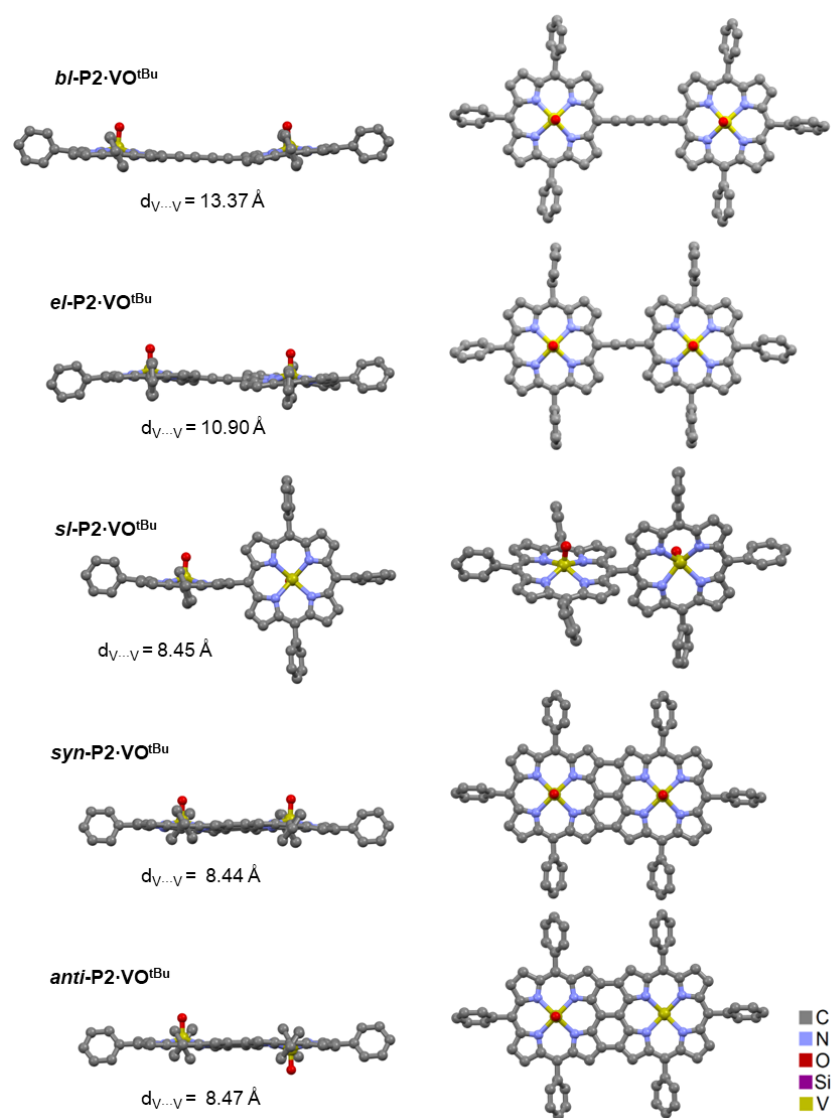


**Scheme 1.** Synthesis of: a) **P1·VO**, b) **bl-P2·VO**, c) **el-P2·VO**, d) **sl-P2·VO**, and e) **syn-P2·VO** and **anti-P2·VO**, with the different side chains in the aryl substituted groups.

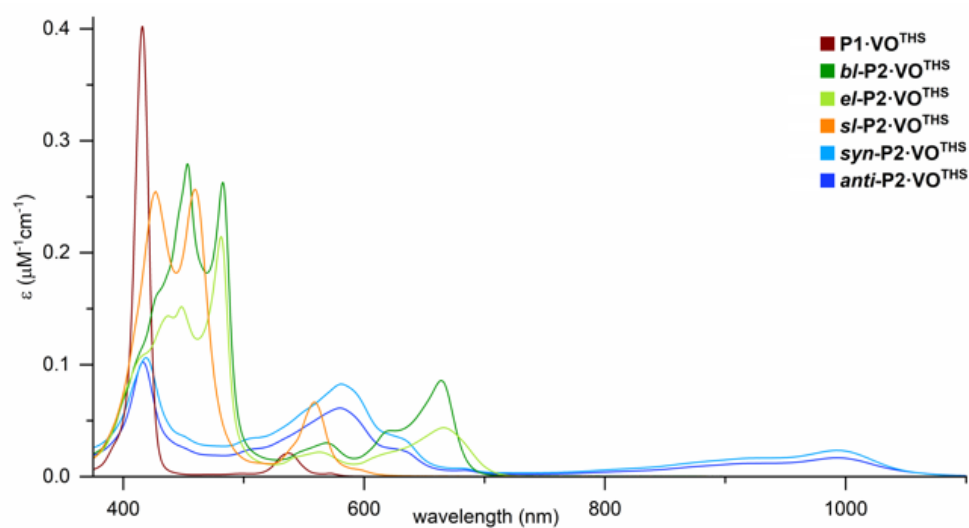
Single-crystal X-ray diffraction was used to determine the structures of **P1·VO<sup>THS</sup>**, **P1·VO<sup>tBu</sup>**, **bl-P2·VO<sup>tBu</sup>**, **el-P2·VO<sup>tBu</sup>**, **sl-P2·VO<sup>tBu</sup>**, **syn-P2·VO<sup>tBu</sup>** and **anti-P2·VO<sup>tBu</sup>** (Figure 2, SI, Section 5). In every structure, the asymmetric unit consists of one complete molecule, except for **anti-P2·VO<sup>tBu</sup>**, in which case the asymmetric unit is half a porphyrin dimer. All these vanadyl porphyrins show V–O distances in the normal range for vanadyl porphyrins (1.56–1.64 Å), and the distances of the vanadium atoms from the plane of the porphyrin are in the range 0.49–0.59 Å.<sup>55–57</sup> In general, flexible THS substituents prevent formation of suitable crystals for X-ray analysis, however suitable crystals of **P1·VO<sup>THS</sup>** were grown by cooling a solution in acetamide. The intramolecular V···V distances in the dimers are: **bl-P2·VO<sup>tBu</sup>**: 13.367(1) Å; **el-P2·VO<sup>tBu</sup>**: 10.896(1) Å; **sl-P2·VO<sup>tBu</sup>**: 8.445(1) Å; **syn-P2·VO<sup>tBu</sup>**: 8.402(6) Å; **anti-P2·VO<sup>tBu</sup>**: 8.466(3) Å. The alkyne-linked dimers **bl-P2·VO<sup>tBu</sup>** and **el-P2·VO<sup>tBu</sup>** crystallize in *syn*-periplanar conformations, with both vanadyl groups on the same face of the dimer, possibly due to the packing. The angle between the planes of the porphyrins are 8.6° and 3.5°, in **bl-P2·VO<sup>tBu</sup>** and **el-P2·VO<sup>tBu</sup>**, respectively. Coplanar conformations are often observed in crystal structures of butadiyne-linked<sup>38</sup> and ethyne-linked porphyrin dimers,<sup>58,59</sup> although a wide range of conformational angles is populated in solution.<sup>60</sup> The singly-linked dimer **sl-P2·VO<sup>tBu</sup>** has a twisted conformation, as expected; the angle between the mean planes of the two porphyrin units is 83.4°. Recently, two polymorphs of a closely related singly-linked vanadyl porphyrin dimer (Ar = Ph) were reported by Lorenzo Sorace and coworkers,<sup>50</sup> in these structures the angles between planes of the porphyrins is 67.8° and 72.5°. The crystal structures of *syn*- and *anti*-**P2·VO<sup>tBu</sup>** show disorder of the VO groups. In each case, the disorder could be modelled assuming the presence of just one isomer, and the sites of highest occupancy confirm the *syn*- and *anti*-stereochemistry. Both  $\pi$ -conjugated scaffolds are nearly planar; the root-mean-square deviation from planarity for the 48-atom cores are 0.10 Å for **syn-P2·VO<sup>tBu</sup>** and 0.08 Å for **anti-P2·VO<sup>tBu</sup>**.

The alkyne-linked dimers, **bl-P2·VO<sup>tBu</sup>** and **el-P2·VO<sup>tBu</sup>** form dimers-of-dimer  $\pi$ - $\pi$  stacks in the solid state, suggesting a potential mode of aggregation in solution. These bimolecular stacks are centrosymmetric, with the V=O units pointing outwards, away from the center of the aggregate. The mean separation between the 48-atom porphyrin dimer planes in these stacks are 3.729 Å and 3.467 Å for **bl-P2·VO<sup>tBu</sup>** and **el-P2·VO<sup>tBu</sup>**, respectively. In both cases, the molecules are stacked in a parallel arrangement, offset along the alkyne axis, with interdigitated aryl sidechains, as reported in related aggregates.<sup>58,61</sup> In the case of **el-P2·VO<sup>tBu</sup>**, the center of one porphyrin sits directly above the central alkyne unit of the other dimer.

The UV-vis-NIR spectra of the THS-substituted compounds are shown in Figure 3. Changing the solubilizing group from THS to *t*-Bu has a negligible effect on the absorption spectra in dilute solution. The spectra of these vanadyl complexes are broadly similar to those of the corresponding porphyrin complexes of other first-row transition metals such as Zn<sup>II</sup>, Cu<sup>II</sup> or Ni<sup>II</sup> (SI, Section 3). The absorption maxima are **P1·VO**: 414 and 536 nm;<sup>54</sup> **bl-P2·VO**: 453, 482, 619 and 662 nm;<sup>47</sup> **el-P2·VO**: 482 and 673 nm;<sup>54</sup> **sl-P2·VO**: 419, 456 and 558 nm;<sup>48</sup> *syn*- and *anti*-**P2·VO**: 420, 580, and 995 nm.<sup>39–43,48</sup> Comparison the lowest energy absorption bands shows that **el-P2·VO** is slightly more conjugated than **bl-P2·VO**, and that both are more conjugated than **sl-P2·VO**. This observation was expected due to the almost perpendicular geometry of **sl-P2·VO**, as observed in the X-ray structure (Figure 2b). The absorption spectra of butadiyne- and ethyne-linked porphyrins reflect their flexible structures in solution,<sup>36,60</sup> beyond the approximately coplanar conformations in the crystalline states. The IR spectra of all the vanadyl porphyrins exhibit intense peaks at around 1004–1009 cm<sup>-1</sup> due to V=O bond stretching (see SI, Section 3).



**Figure 2.** X-ray structure of *bl*-P2·VO<sup>tBu</sup>, *el*-P2·VO<sup>tBu</sup>, *sl*-P2·VO<sup>tBu</sup>, *syn*-P2·VO<sup>tBu</sup> and *anti*-P2·VO<sup>tBu</sup>. Hydrogens, *t*-Bu groups, and low-occupancy disordered atoms were omitted for clarity.



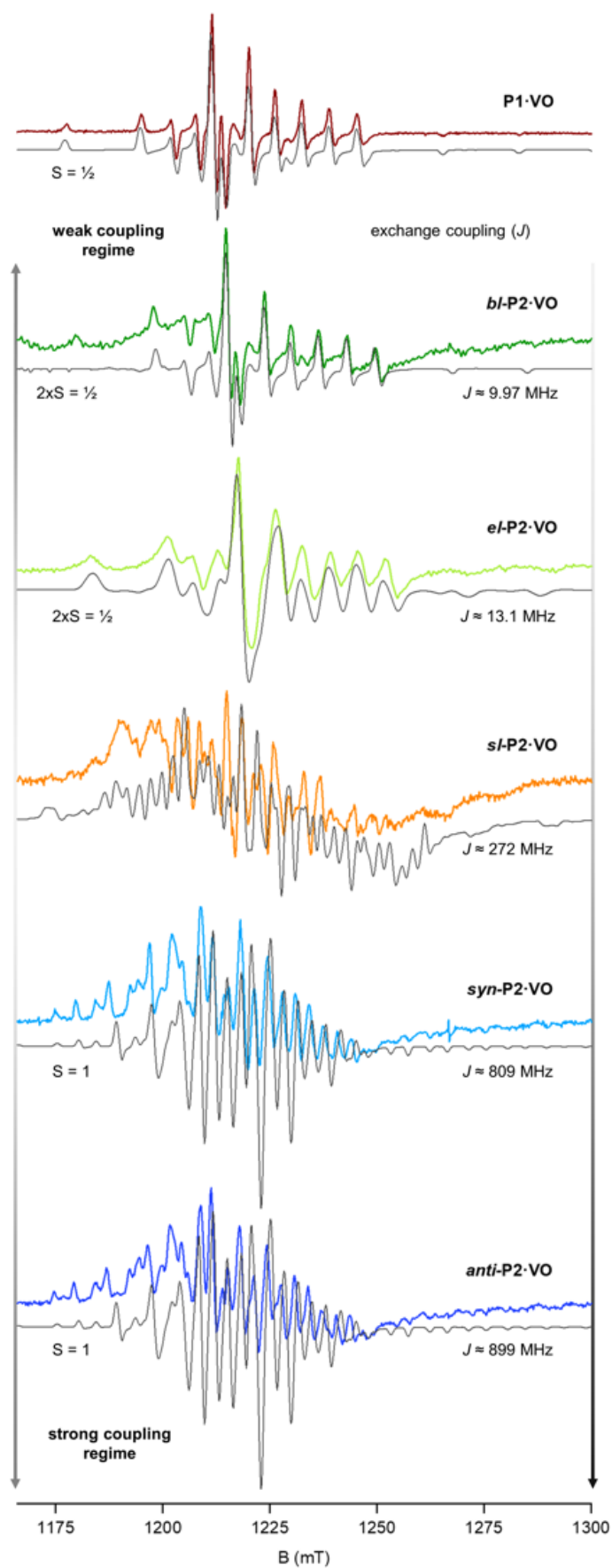
**Figure 3.** UV-vis-NIR absorption spectra of P1·VO<sup>THS</sup>, *bl*-P2·VO<sup>THS</sup>, *el*-P2·VO<sup>THS</sup>, *sl*-P2·VO<sup>THS</sup>, and *syn*-P2·VO<sup>THS</sup> and *anti*-P2·VO<sup>THS</sup>, in dichloromethane at 25 °C.

**Magnetic Properties.** CW EPR spectra were recorded at X-band and Q-band (Figure 4 and SI, Section 6) at 1 mM concentration in deuterated toluene frozen at 140 K for all the vanadyl porphyrins, except for **syn-P2·VO<sup>tBu</sup>** and **anti-P2·VO<sup>tBu</sup>** due to their poor solubility. Pairs of compounds that differ only in the solubilizing group (THS vs. *t*-Bu) gave practically identical spectra, and they were simulated using the same parameters (collected in Table 1). Figure 4 shows the spectra of selected vanadyl porphyrins and their simulations (in black). The spectrum of **P1·VO<sup>tBu</sup>** is similar to those of previously reported vanadyl porphyrin monomers,<sup>62</sup> with  $g_{xy} = 1.9612 \pm 0.0001$  and  $g_z = 1.9840 \pm 0.0002$  for in- and off-plane contributions,<sup>63</sup> and anisotropic hyperfine coupling, **A**,<sup>64,65</sup> to the <sup>51</sup>V nucleus ( $I = 7/2$ ) with  $A_{xy} = 477$  MHz and  $A_z = 170$  MHz. The alkyne-linked dimers **bl-P2·VO** and **el-P2·VO** present similar CW spectra with **g** and **A** values  $g_{xy} = 1.9612 \pm 0.0001$  and  $g_z = 1.9840 \pm 0.0002$ ,  $A_{xy} = 477 \pm 2$  MHz and  $A_z = 170 \pm 1$  MHz, close to those observed for the monomer (Table 1 and Figure 4). The major differences arise from the small effect of exchange and dipolar interactions (**bl-P2·VO**:  $D = 10.74 \pm 0.04$  MHz,  $J = 9.97 \pm 0.04$  MHz; and **el-P2·VO**:  $D = 14.67 \pm 0.02$  MHz,  $J = 13.07 \pm 0.01$  MHz, antiferromagnetic coupling). The singly-linked dimers **sl-P2·VO** are in an intermediate situation, being not weakly interacting doublets nor pure triplets, as recently reported for an analogous molecule.<sup>50</sup> The best simulation was achieved assuming the behavior as two weakly interacting doublets with the following set of parameters:  $g_{xy} = 1.9612 \pm 0.0001$  and  $g_z = 1.9840 \pm 0.0002$ ,  $A_{xy} = 477 \pm 2$  MHz and  $A_z = 170 \pm 1$  MHz,  $D = 84 \pm 1$  MHz, and  $J = 272 \pm 1$  MHz, with antiferromagnetic coupling. The values obtained in this way are in good agreement with those reported for a magnetically equivalent system.<sup>50</sup>

**Table 1.** EPR parameters for vanadyl porphyrins<sup>a</sup>

	<b>P1·VO</b>	<b>bl-P2·VO</b>	<b>el-P2·VO</b>	<b>sl-P2·VO</b>	<b>syn-P2·VO</b>	<b>anti-P2·VO</b>
spin	½	S1 = ½ S2 = ½	S1 = ½ S2 = ½	S1 = ½ S2 = ½	1	1
$g_{xy}$	1.9612 ±0.0001	1.9612 ±0.0001	1.9612 ±0.0001	1.9612 ±0.0001	1.9636 ±0.0003	1.9636 ±0.0003
$g_z$	1.9840 ±0.0002	1.9840 ±0.0002	1.9840 ±0.0002	1.9840 ±0.0002	1.9874 ±0.0002	1.9874 ±0.0002
$A_{xy}$ (MHz)	477±2	477±2	477±2	477±2	261.587 ±0.001	261.587 ±0.001
$A_z$ (MHz)	170±1	170±1	170±1	170±1	85.2983 ±0.0001	85.2983 ±0.0001
$D$ (MHz)		10.74±0.04	14.67±0.02	84±1	186±7	186±7
$J$ (MHz)		9.97±0.04	13.07±0.01	272±1	809±30 <sup>b</sup>	899±30 <sup>b</sup>

<sup>a</sup> $g$ : Landè factor;  $A$ : hyperfine coupling;  $J$ : exchange coupling;  $D$ : dipolar coupling. All five dimers exhibit antiferromagnetic coupling. <sup>b</sup> $J$  not included in the EPR simulation. The approximate values included in the table were obtained by SQUID magnetometry.



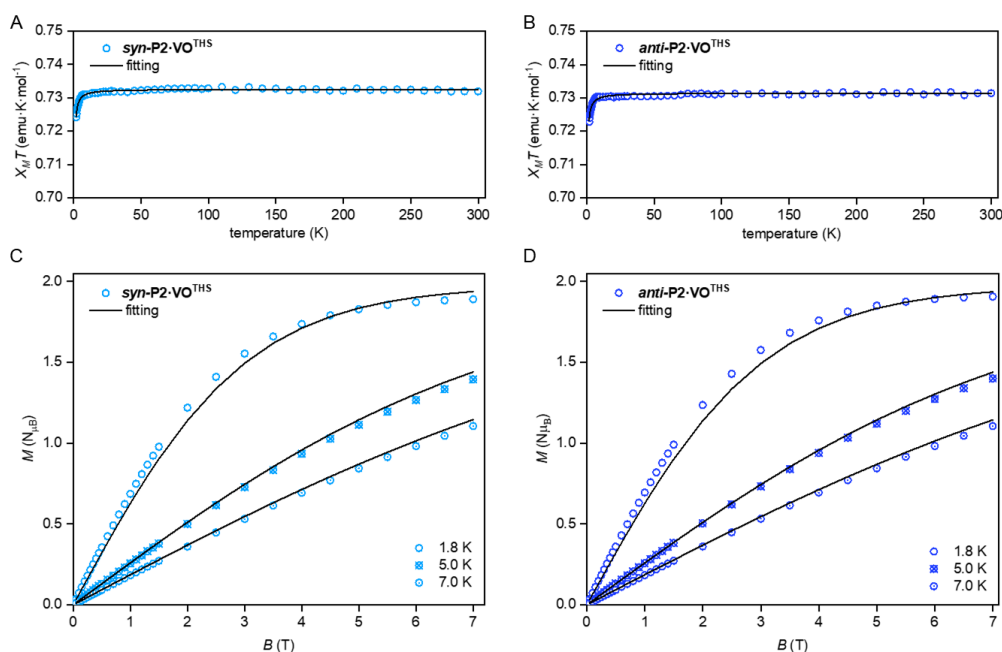
**Figure 4.** CW-EPR spectra of  $\text{P1}\cdot\text{VO}^{\text{tBu}}$ ,  $\text{bl-P2}\cdot\text{VO}^{\text{tBu}}$ ,  $\text{el-P2}\cdot\text{VO}^{\text{tBu}}$ ,  $\text{sl-P2}\cdot\text{VO}^{\text{tBu}}$ ,  $\text{syn-P2}\cdot\text{VO}^{\text{THS}}$  and  $\text{anti-P2}\cdot\text{VO}^{\text{THS}}$ . Simulations are shown in black. All spectra recorded at 140 K at 33.9 GHz in frozen deuterated toluene solutions (1 mM). EPR parameters used for the simulations are listed in Table 1.

The Landé factors  $g_{xy} = 1.9636 \pm 0.0003$  and  $g_z = 1.9874 \pm 0.0002$  of **anti-P2·VO<sup>THS</sup>** and **syn-P2·VO<sup>THS</sup>** are similar to those of **P1·VO<sup>THS</sup>**, confirming that the much more complex EPR spectra of the dimers can be interpreted in terms of two coupled monomers. The splitting produced by the hyperfine coupling drastically depends on the exchange regime.<sup>65</sup> If the strongest interaction is the hyperfine coupling rather than the exchange interaction ( $A \gg J$ ), then the overall spectral shape follows that for a typical vanadyl porphyrin monomer, such as **P1·VO<sup>THS</sup>**, as is the case for previously reported vanadyl dimers.<sup>66,67</sup> On the other hand, if exchange coupling dominates ( $J \gg A$ ), the unpaired electrons interact equally with both nuclear spins. In this case, the spectrum is expected to display halved  $A$  values<sup>65,68-70</sup> and two sets of hyperfine splitting, with 15 lines each ( $2NI + 1$ , where  $N = 2$  and  $I = 7/2$ ) with higher intensities in the center and distortions from other interactions, such as dipolar coupling, as discussed below. This scenario causes extremely complex patterns and, to the best of our knowledge, experimental values for the parameters involved are unreported. The exchange coupling  $J \approx 1$  GHz deduced from magnetic susceptibility measurements (discussed below) suggests that **syn-P2·VO<sup>THS</sup>** and **anti-P2·VO<sup>THS</sup>** are in this strong-exchange regime, dominated by the  $J$  interaction. This places the conjugated vanadyl dimers in a regime that is different from previous non-conjugated molecular architectures,<sup>50,66,67</sup> which are paired quantum mechanically by dominant hyperfine and dipole-dipole interactions, rather than exchange coupling. Simulation of the spectra was achieved by considering that  $J$  is the dominant contribution and the hyperfine coupling values should be roughly half those of the monomer, with the Hamiltonian:

$$H = \mu_B \sum_{i=1}^2 \mathbf{B} g_i \hat{S}_i + \sum_{k,j=1,2} \hat{S}^k A \hat{I}^j + \hat{S}_1 D \hat{S}_2 - 2 \hat{S}_1 J \hat{S}_2 \quad (1)$$

where  $\mu_B$  is the Bohr magneton,  $\mathbf{B}$  is the external magnetic field,  $\hat{S}$  and  $\hat{I}$  are the electron and nucleus spin operators and there are two overlapping hyperfine patterns of 15 lines with constants  $A_x^1 = A_y^1 = A_x^2 = A_y^2 = 261.587 \pm 0.001$  MHz,  $A_z^1 = A_z^2 = 85.2983 \pm 0.0001$  MHz centered at  $g_{xy} = 1.9636 \pm 0.0003$  and  $g_z = 1.9874 \pm 0.0002$  respectively, and further split by  $D = 186 \pm 7$  MHz; see simulated spectra (black) in Figure 4. This experimental value of  $D$  was compared with the calculated value obtained using the point-dipole approximation (this model is known to underestimate  $D$  for a determined distance),<sup>71</sup> leading to values of 128 and 131 MHz for the distances of 8.400 and 8.465 Å, in good agreement with our simulation. The broad features underlying the spectra can probably be attributed to  $J$  anisotropy.<sup>68-70</sup> Approximate values of  $J$  in **syn-P2·VO<sup>THS</sup>** and **anti-P2·VO<sup>THS</sup>** isomers were obtained by SQUID magnetometry, because these parameters could not be determined from the CW EPR spectra, as their values are too large for the EPR window. The molar magnetic susceptibilities of the dimers **syn-P2·VO<sup>THS</sup>** and **anti-P2·VO<sup>THS</sup>** at room temperature ( $T = 300$  K;  $c_M T = 0.732$  and  $0.731$  emu K mol<sup>-1</sup>, respectively) are in agreement with the expected value for two weakly interacting unpaired electrons (0.750 emu K mol<sup>-1</sup>), and approximately twice the value of the monomer **P1·VO<sup>THS</sup>** (0.372 emu K mol<sup>-1</sup>) (see Figure 5A and B, and SI for more details of SQUID magnetometry studies, Section 7).<sup>72</sup> Magnetization measurements at variable field are shown in Figure 5C and D. When  $H \gg kT$ , magnetization saturates at around  $2N\mu_B$ , as the expected for  $S = 1$  species.<sup>72</sup> Simultaneous fitting (of  $c_M T$  and  $M$ ) of the temperature-dependance reveals a Landé factor  $g = 1.97 \pm 0.01$  and  $g = 1.98 \pm 0.01$ , and a spin-spin coupling of  $899 \pm 60$  and  $809 \pm 30$  MHz for **anti-** and **syn-P2·VO<sup>THS</sup>**, respectively, with antiferromagnetic coupling. Dipolar,  $D$ , and exchange,  $J$ , interactions cannot be distinguished experimentally here. The exchange coupling  $J$  is thus in the order of 1 GHz, which is stronger than in previously reported bis-vanadyl complexes with similar inter-spin distances,<sup>50,66,67</sup> but two orders of magnitude weaker than in the analogous Cu(II) porphyrin dimer.<sup>44,45</sup>

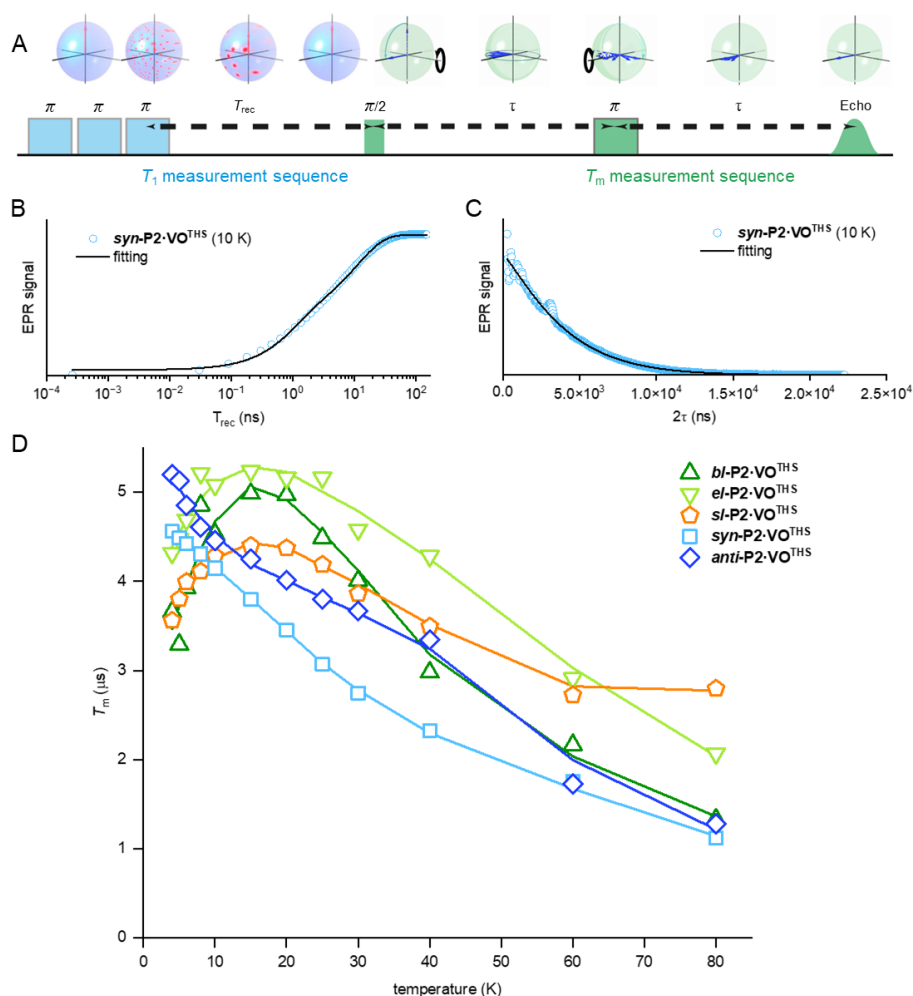




**Figure 5.** Temperature dependence of the  $c_M T$  product for a) *syn-P2-VO*<sup>THS</sup> and b) *anti-P2-VO*<sup>THS</sup>. Magnetization ( $M$ ) vs magnetic field b) plot for c) *syn-P2-VO*<sup>THS</sup> and d) *anti-P2-VO*<sup>THS</sup>. Fittings are shown in black, and obtained parameters  $g$  and  $J$  listed in Table 1.

**Pulsed Electron Paramagnetic Resonance.** The quantum behavior of the vanadyl porphyrins was studied by pulse-EPR. The spin-lattice relaxation time ( $T_1$ ) was determined by fitting the Picket-Fence recovery traces with a bi-exponential model (Figure 6 B, for more details see: SI, Section 6.1), yielding values on the order of milliseconds for the selected vanadyl porphyrins (*P1-VO*<sup>THS</sup>, *bl-P2-VO*<sup>tBu</sup>, *el-P2-VO*<sup>tBu</sup>, *sl-P2-VO*<sup>tBu</sup>, *syn-P2-VO*<sup>THS</sup> and *anti-P2-VO*<sup>THS</sup>). The temperature-dependence of  $T_1^{-1}$  reveals similar phonon-mediated relaxation processes for all the compounds: direct processes below 20 K and Raman processes between 20 and 80 K, as reported for other V(IV) complexes (SI, Section 6, Figure S64).<sup>10</sup>

**Spin Phase Memory Time.** The phase memory times ( $T_m$ ) were determined using a Hahn Echo sequence (Figure 6A), fitting echo decay traces (e.g. Figure 6C) with a stretched exponential model (SI, Section 6).  $T_m$  values of vanadyl porphyrin dimers containing THS chains are shown in Figure 6D. The five vanadyl pairs exhibit increasing  $T_m$  values with decreasing temperature (80 to 20 K). The dimers in the weak coupling regime (*bl-P2-VO*<sup>THS</sup>, *el-P2-VO*<sup>THS</sup>, and *sl-P2-VO*<sup>THS</sup>) reach a maximum between 10 to 20 K, and suffer a pronounced drop of  $T_m$  on lowering the temperature (below 10 K). Surprisingly, *syn-P2-VO*<sup>THS</sup> and *anti-P2-VO*<sup>THS</sup> isomers display a different behavior, increasing continuously from 80 K with maximum values at 4 K (4.6 and 5.2  $\mu$ s respectively). Apparently, the dominant exchange coupling via a delocalized channel leads to suppression of decoherence at low temperatures (<10 K), as previously observed in Si quantum dots and Ti atoms.<sup>16-20</sup> This behavior has not been reported previously for molecular systems, and, may be attributed to the strong  $\pi$ -conjugation in *syn*- and *anti-P2-VO*<sup>THS</sup>. Interestingly, the magnetic behavior is not the same for both isomers: *syn-P2-VO*<sup>THS</sup> shows shorter  $T_m$  times (up to 30% at 40 K) and a less-marked coherence-improvement than *anti-P2-VO*<sup>THS</sup>. Although *syn-P2-VO*<sup>THS</sup> lacks a molecular inversion center, the two vanadyl atoms are related by a virtual mirror plane, so that the difference cannot be assigned to local environmental distortions, and the origin must lie in the fact that  $J$  is slightly lower for *syn-P2-VO*<sup>THS</sup>, so that decoherence suppression is less effective.

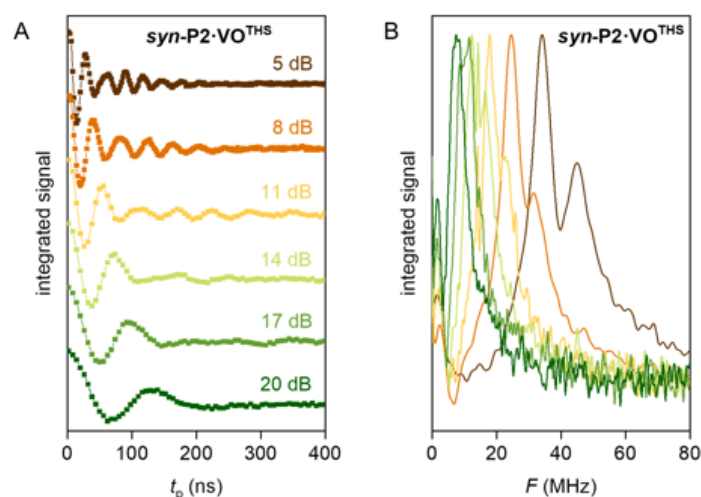


**Figure 6.** a) Pulse sequences used to measure the characteristic relaxation times and Bloch sphere depiction. b) Picket-Fence recovery trace and a fit with a bi-exponential function (black line, discussed in the SI) of  $syn-P2-VO^{THS}$  at 10 K. c) The Hahn echo decay trace and a fit with a stretched exponential function of  $syn-P2-VO^{THS}$  at 10 K. d) Temperature dependence of the phase memory times ( $T_m$ ) of vanadyl dimers containing THS (solid trend lines are included as visual guide). All measurements at Q-band, at 33.9 GHz and in frozen deuterated toluene solutions (1 mM).

At low temperatures, the phase memory time ( $T_m$ ) can be affected by small-angle molecular motions in glassy organic solvents (librations)<sup>73</sup> and spin-spin interactions (spin-spin interactions).<sup>74</sup> We studied the *t*-Bu-substituted dimers;  $bl-P2-VO^{tBu}$ ,  $el-P2-VO^{tBu}$ , and  $sl-P2-VO^{tBu}$ , which exhibited the same pronounced coherence drop below 10 K as the corresponding THS-containing analogs (SI, Figure S63B). Compounds containing THS chains are more flexible and practically double the molecular weight of those containing *t*-Bu groups, hence libration movements in these systems are less probable, and it is unlikely that both families of compounds (THS and *t*-Bu) will be equally affected by this type of relaxation. Intramolecular spin-spin interactions due to hyperfine couplings are not expected to be significantly different in the two families of compounds because the H nuclei on the porphyrin backbones are practically the same for all the systems and within spin-diffusion barrier.<sup>74</sup> The H nuclei in the THS chains seem to produce 1–2  $\mu s$  lower  $T_m$  values than the analogous compounds with *t*-Bu substituents across the whole temperature range (SI, Figure S63A and B). For these reasons, the coherence loss below 10 K of the compounds in the weak coupling regime can be attributed to the electron pair flip-flops.<sup>74</sup> Importantly, this effect is not relevant in compounds in the strong coupling regime ( $syn$ - and  $anti-P2-VO^{THS}$ ), demonstrating that the presence of a dominant exchange interaction ( $J$ ) leads to the suppression of decoherence. Furthermore, the dominant exchange coupling is inevitably related with the presence of the  $\pi$ -delocalized backbone, allowing us

to establish a clear relationship between chemical structure, magnetic interactions, and quantum coherence: strong  $\pi$ -conjugation/dominant exchange coupling/longer  $T_m$  (below 10 K).

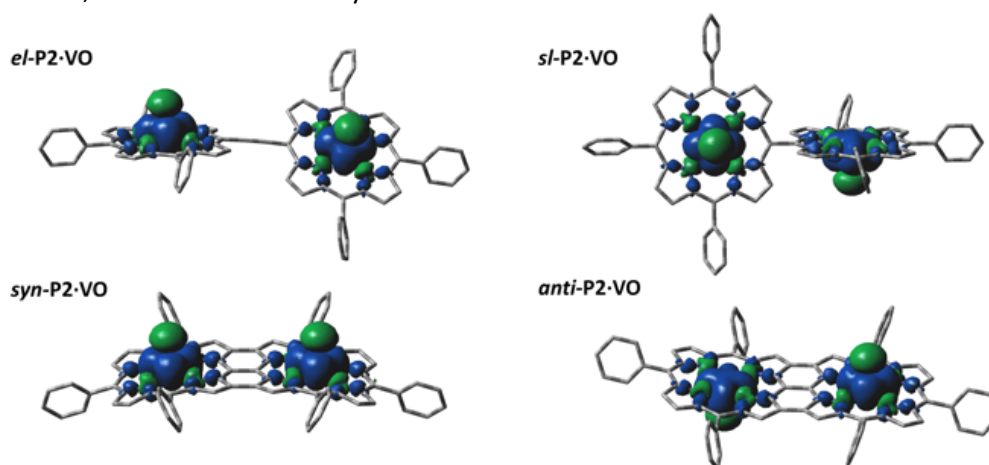
The study of Rabi oscillations was used to investigate whether the system can be placed in a quantum superposition and reveal other potential decoherence channels. Transient nutation experiments were performed for selected vanadyl porphyrins (*bl-P2-VO*<sup>tBu</sup>, *el-P2-VO*<sup>tBu</sup>, *sl-P2-VO*<sup>tBu</sup>, *syn-P2-VO*<sup>THS</sup> and *anti-P2-VO*<sup>THS</sup>) yielding similar results (see SI, Section 6). Figure 7 shows the Rabi oscillations for *syn-P2-VO*<sup>THS</sup>. Their Fourier transform show linear  $B_1$ -dependance of the Rabi frequency of the main peaks and does not present any constant feature. This observation indicates that the hyperfine couplings (e.g. with the peripheral hydrogens) do not introduce alternative decoherence pathways to those previously mentioned in this article (phonon-mediated processes; direct and Raman, and electron pair flip-flops).



**Figure 7.** a) Rabi oscillations at different power attenuation, *syn-P2-VO*<sup>THS</sup>,  $T = 10$  K,  $\nu = 9.5$  GHz. b) Fourier transform of the oscillation.

## Discussion

The spin density maps, calculated with DFT, B3LYP6-31G(d,p) show that the unpaired electrons are located in  $3d_{xy}$  orbitals of the vanadium atoms, as previously reported for vanadyl porphyrins<sup>62</sup> and as expected for a  $d^1$  configuration (Figure 8).<sup>75</sup> The  $d_{xy}$  orbital is aligned between the nitrogen atoms of the porphyrin core, minimizing interactions of the unpaired spin with the porphyrin or with the environment, which favors a long phase memory time<sup>7</sup> and a relatively weak exchange coupling. The stronger exchange coupling in the analogous Cu(II) porphyrins arises because in that case the  $d^9$  configuration places the unpaired spin in a  $d_{x^2-y^2}$  orbital, which has a direct interaction with the nitrogen atoms, and thus with the  $\pi$ -systems.<sup>44,45</sup>



**Figure 8.** Spin density surfaces of *el-P2-VO*, *sl-P2-VO*, *syn-P2-VO* and *anti-P2-VO*.

Counterintuitively, **sl-P2·VO** dimers have a stronger exchange interaction ( $J = 272$  MHz) than the  $\pi$ -conjugated alkyne-linked dimers **bl-P2·VO** and **el-P2·VO** ( $J = 10.0$  MHz and  $J = 13.1$  MHz, respectively, from the CW-EPR simulations, which implies that significant exchange interaction occurs through the  $\sigma$ -bond, and that the shorter metal-metal distance in **sl-P2·VO** compensates for its lack of  $\pi$ -conjugation. However, in the strongly conjugated systems, which have similar V...V distances, **syn-** and **anti-P2·VO**, the exchange coupling is drastically increased, surpassing the strength of the hyperfine coupling and placing these compounds in the strong coupling regime. The structural and magnetic analysis of the molecules is crucial to study their quantum performance.<sup>76,77</sup> While compounds in the weak coupling regime have similar trends, with maxima values of phase memory time ( $T_m$ ) at 10–20 K, the compounds in the strong coupling regime exhibit a continuous increase in phase memory time with decreasing the temperature. The comparison between magnetically equivalent compounds with different substituents is essential to study the main decoherence pathways at different temperatures and allow us to identify that the different trends below 10 K are related with electron spin flip-flop processes, which are one of the most relevant decoherence sources in solid physics. These observations indicate that the dominant exchange coupling can be used to suppress the decoherence originated by this cause in molecular spin systems.

Conjugated quantum mediators can transport electrons in conduction channels while preserving magnetic information, and be operated on chip by applying magnetic fields or microwaves.<sup>78-87</sup> When considering recent results on fused<sup>39-42,88</sup> and magnetic porphyrins,<sup>10,44-48,89</sup> together with the chemical structure/quantum coherence relationships reported in this article, these results demonstrate the suitability of magnetic porphyrin materials for quantum applications; the integration into single-electron transistors seems practicable, with the perspective to create molecular systems that can be used in single-molecule devices with magnetic control and electrical readout, and with potential applications in quantum information processing, as spin valves, or spin filters.<sup>29,86-91</sup> The suppression of decoherence at low temperatures by molecular design is crucial because the magnetic states are very close in energy (usually  $< 1$  meV), and thus, their electrical read-out is necessarily available only at temperatures below 10 K.<sup>92,93</sup> With that regard, extended materials based on **P2·VO** might offer an interesting platform, having a conduction channel available while keeping long phase memory times at low temperatures. These results constitute a fundamental step for the development of spin-electronic molecular quantum units.

## Conclusions

We report the synthesis of twelve vanadyl porphyrins; two monomeric systems and ten dimers. The characterization of these compounds was performed by standard methods (e.g. mass spectrometry, IR, UV-vis-NIR spectroscopy), accurate structural information was achieved by X-ray diffraction analysis and study their  $\pi$ -conjugation was probed by UV-vis-NIR spectroscopy. CW-EPR spectra show that dimers **bl-P2·VO** and **el-P2·VO** behaving as two weakly interacting vanadyl centers. Compounds **sl-P2·VO** present a mixed spin state, as recently reported for an analogous compound,<sup>50</sup> with a relatively high exchange coupling despite the lack of  $\pi$ -conjugation, which indicates significant exchange coupling through the sigma bond between *meso-meso*-linked porphyrins. In contrast, **syn-** and **anti-P2·VO** are strongly  $\pi$ -conjugated with efficient electron-electron communication through the multiply-connected  $\pi$ -system, with an intermetallic distance of 8.4–8.5 Å. The combined use of EPR spectroscopy and SQUID magnetometry allowed us to quantify the magnetic interactions in these systems, describing for the first time vanadyl pairs in the strong coupling regime.

These systems all exhibit spin-lattice relaxation times ( $T_1$ ) in the millisecond range with similar phonon-mediated decoherence pathways. The study of the phase memory time ( $T_m$ ) at different temperatures shows that the compounds in the weak coupling regime (**bl-P2·VO**, **el-P2·VO** and **sl-P2·VO**) have a coherence drop below 10 K, whereas the compounds in the strong coupling regime (**syn-** and **anti-P2·VO**) exhibit increasing  $T_m$  with decreasing temperature. This difference is attributed to the influence of electron pair flip-flop processes by comparing magnetically equivalent systems

with different substituents (THS and *t*-Bu). The immersion of vanadyl units in a strongly  $\pi$ -conjugated scaffold places the systems in the strong coupling regime, increasing their exchange interaction and protecting the phase memory time, as previously observed in non-molecular systems. The use of 2D electron gases to connect spins without suppressing their coherence has been observed in surface nanostructures made of semiconductors,<sup>94-97</sup> and the origins of this effect remain subject to debate.<sup>98,99</sup> Our observation of this effect at the molecular scale can now prompt a rigorous theoretical analysis, in systems where every atomic position is known and that can be modelled in detail. We thus expect these results to impact not only the synthetic community, but also on theoreticians working on quantum systems.

These results show that the chemistry of porphyrin polymers can be used to create conducting molecular materials with multiple quantum units linked together, tuning the spin-spin couplings in a rational manner, which are in the range of suitable values for quantum information processing. We demonstrate that the use of a conjugated backbone produces multiple spin centers that communicate efficiently but do not suffer from decoherence issues that traditionally plague interacting quantum systems. This combination of features is appealing for the design of functional magnetic materials for single-molecule devices. Having multiple spins that interact coherently is the first step in creating molecular devices where quantum operations can be performed. The systems presented here can be integrated into molecular junction devices<sup>100,101</sup> where the spin levels can be read electrically.<sup>90</sup> They thus offer an excellent platform for the full control of molecular systems in transport devices, controlled by microwave irradiation at low temperatures.

### **Experimental Procedures**

Full experimental procedures are available in the Supplemental Information.

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### **Author Contributions**

I.P., L.B. and H.L.A. conceived the project. Z.H., F.L. and M.S. carried out the EPR measurements, analysis, and simulations. W.K.M. provided assistance and support with EPR experiments. I.P. and J.-R.D. conducted the synthesis and chemical characterization. I.P. and F.K. performed the theoretical calculations. D.A. carried out SQUID magnetometry. W.S., P.N.H. and S.J.C. performed X-ray crystallography. I.P., L.B. and H.L.A. coordinated and supervised the project. All authors contributed to the manuscript.

### **Declaration of Interests**

The authors declare no competing interests.

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$$D = (-3/2) (\mu_0 (g_e \beta_e)^2) / (4 \pi h r^3)$$
where  $\mu_0 = 4\pi \times 10^{-7}$  (H/m),  $g_e = 2.0023$ ,  $\beta_e = 9.27 \times 10^{-24}$  (J/T),  $h$  is the Planck constant, and  $r$  is the distance between metal centers, 8.466 and 8.402 Å from the X-ray crystallography.
72.  $\chi_{MT} = (Ng^2 \beta^2) / 3k S(S+1)$ , where  $\chi_{MT}$  is the molar magnetic susceptibility at 300 K,  $N$  is the number of spins,  $g$  is the Landé Factor,  $\beta$  is the Bohr magneton and  $k$  the Boltzmann constant, and  $M(N\mu_B) = gS$ , where  $g$  is the Landé Factor and  $S$  the spin number. See Khan, O. (1993). *Molecular Magnetism*. Wiley-VCH. ISBN 3-527-89566-3.
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