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ACS Appl. Mater. Interfaces, **Just Accepted Manuscript** • DOI: 10.1021/acsami.0c09386 • Publication Date (Web): 15 Sep 2020

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Organic PolyRadicals as Redox Mediators: Effect of Intramolecular Radical Interactions in their Efficiency.

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ABSTRACT: The spin-spin interactions between unpaired electrons in organic (poly)radicals, especially nitroxides, are largely investigated and are of crucial importance for their applications in areas such as organic magnetism, molecular charge transfer or multiple spin labeling in structural biology. Recently, TEMPO and polymers functionalized with nitroxides have been described as successful redox mediators in several electrochemical applications, however, the study of spin-spin interactions effect in such an area is absent. This communication reports the preparation and study of a novel family of discrete polynitroxide molecules, with the same number of radical units but different arrangement to study how intramolecular spin-spin interactions affect on their electrochemical potential and their use as oxidation redox mediators in a Li-oxygen battery. We find that the intensity of interactions, as measured by the d_1/d EPR parameter, progressively lowers the reduction potential, This allows to tune the charging potential of the battery and so optimize its energy efficiency.

Introduction

The spin-spin interactions between unpaired electrons in organic diradicals and polyradicals are of crucial importance in many areas such as organic magnetism,[1–5] molecular charge transfer,[6] or multiple spin labeling in structural biology.[7] When unpaired electrons are in close proximity, the dominant interaction is likely to be spin-exchange coupling and dipole-dipole interactions. The origin of such radical-radical interactions could be intra- and/or intermolecular; that is, between radicals of the same molecule or radicals from different species. Intramolecular interactions exist when radical units within a structure are close enough, and are detected at both low and high concentrations, while intermolecular interactions exist only at high concentrations, due to the higher proximity between molecules. Among organic radicals, nitroxides have the advantage that are stable under ambient conditions and can be easily synthesized, functionalized, and manipulated. Di- and polynitroxides have shown improved properties with respect to mononitroxides as organic ferromagnets, labels in electron magnetic resonance imaging, radiation protectors during whole brain radiotherapy or as polarizing agents in dynamic nuclear polarization (DNP).[8] For example, when used as electron spin agents for DNP, dinitroxides can enhance the sensitivity of nuclear magnetic resonance signals by orders of magnitude compared with mononitroxides. Among other factors, the intramolecular exchange interactions and electron-electron dipolar coupling are possible spin relaxation enhancement pathways.[9–11] We are not aware of effects reported beyond magnetic properties. Nitroxide radicals also have relevant electrochemical properties, and have been used as redox charge mediators.

Redox mediation is a mechanism ubiquitous in nature, used to transport electrons in solution phase, usually to connect a catalytic center to another one or to a reactant. In general, the redox mediator (RM) is a soluble component able to exchange an electron with a redox center, to diffuse to a different redox center and to exchange again an electron to restore its initial state. In the cell respiratory system for example, nicotinamide adenine dinucleotide hydrogen (NADH) shuttles electrons through the membrane, and three distinct complexes are involved in the electron transport chain in the mitochondria before reducing oxygen to water.[12,13] In photosynthesis, different quinones play similar roles between the reactive complexes involved.[14] In part inspired by such systems, several chemical and electrochemical energy conversion or storage systems rely or are improved by the use of redox mediators (*i.e.* artificial photosynthesis, organic dye-sensitized solar cells, pseudocapacitors, redox flow, lithium-sulfur and metal-oxygen batteries).[15] Nitroxides, and in particular, 2,2,6,6-tetramethylpiperidinyloxyl monoradical (TEMPO) have been widely studied in the past two decades in energy storage,[16,17] either as part of the cathode[18] or in the electrolyte.[19] Being part of the cathode TEMPO could be used for instance as active material in an organic-based paper battery[20] or to tune conductivity in conjugated radical polymer battery.[21,22] On the other hand, it could be used in the electrolyte as catholyte for redox flow batteries[23] or as soluble oxidation mediator in metal-oxygen batteries.[24] This wide use is due to its appropriate potential, kinetics and availability.[25] Some polynitroxide compounds, such as polymers functionalized with nitroxides, have been described exhibiting high mediation of charge.[26,27]

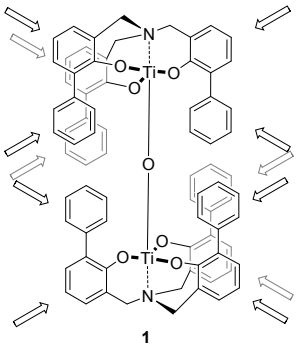
Aim of this study is to functionalize molecule in Scheme 1 to obtain a polynitroxide. To the best of our knowledge, mediation has not been reported with discrete molecules presenting several identical (nitroxides) redox centers with well-defined arrangement and the effect of intramolecular radical interactions still remains a challenging mechanism to understand. In addition, a comparison between polynitroxides and mononitroxides is also absent. The intensity of the intramolecular spin-spin interactions increase mainly with the proximity of the radical units and the number of interacting radicals, and can be detected and studied by electron paramagnetic resonance (EPR) spectroscopy.[28,29] In this work, we study the effect of intramolecular spin-spin interactions in polynitroxide molecules on their electrochemical potential and their use as redox mediators, in particular as charge mediators in aprotic lithium-oxygen batteries. These batteries present high theoretical capacities due to a reaction between pure lightweight elements (Li and O_2) with solid product (Li_2O_2), but are affected by several issues related to the formation of reactive intermediates and passivation by Li_2O_2.[30]

Mediators are critical in two different processes of metal-air batteries: they allow to delay electrode passivation during discharge and assist peroxide removal during charge.[31,32] Using mediators with redox potential below the oxygen reduction potential (E^0 = 2.96 V vs. Li/Li^+) results in an oxygen reduction reaction (ORR) with enhanced kinetics and discharge capacity.[33–36] When instead its redox potential is above the equilibrium potential, the mediator is active during charge, where it is oxidized at the electrode, diffuses to Li_2O_2, with which it chemically reacts to give place to oxygen evolution (oxygen evolution reaction OER).[24,31,37–40] Thus, in the case of the TEMPO nitroxide we have the following catalytic scheme:

$$2TEMPO \rightarrow 2TEMPO^+ + 2e^-$$

$$Li_2O_2 + 2TEMPO^+ \rightarrow 2Li^+ + O_2 + 2TEMPO \qquad (1).$$

For efficient operation, apart from the appropriate reduction potential, a mediator requires stability to cell components and intermediates,[39] reactivity with Li_2O_2[41] and moderate diffusivity.[32] The latter is necessary to minimize shuttling to the anode, and is favored by larger compounds, while nitroxides are regarded as one of the most stables functional groups among halogenides, quinones, and several other organic molecules.[42]



SCHEME 1 Reported μ-oxo dinuclear titanium complex **1** with indicated the possible functionalization positions.

To obtain the target molecules aim of the present study, we have used as scaffold triphenolamines[43] and in particular a μ-oxo dinuclear titanium complex **1** (Scheme 1).[44]

In recent years, we reported about the use of tetradentate metal complexes in catalysis,[45–48] molecular recognition,[49–54] and as molecular scaffolds for multiple functionalization. Among the different structures, μ-oxo dinuclear titanium complex **1** represent the ideal architecture to become a scaffold for multiple functionalisation (Scheme 1). This system, which spontaneously forms starting from two titanatranes units via selective hydrolysis, has a well-defined geometry and it is stable even in the presence of water. The overall stability combined by the defined geometry make this molecular structure idea for multiple functionalization with redox mediators.

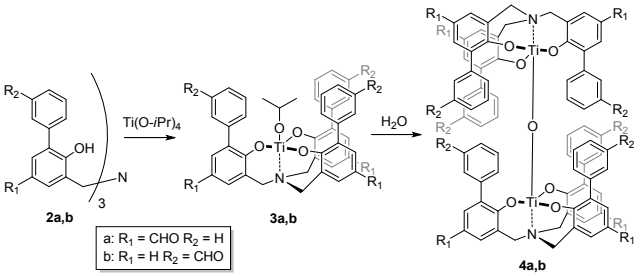
In the present paper, we report about: *i*) the synthetic evolution of the system in order to obtain a molecular scaffold suitable for multiple functionalization, *ii*) the preparation of defined molecular systems containing the same number of radical units with different arrangement, some with closer and others with more distant radicals disposition *iii*) the study of the intramolecular interactions strength among radicals in the different arrangements and *iv)* the effect of such radical interactions on their

electrochemical behavior and redox mediators' capabilities.

Results and Discussion

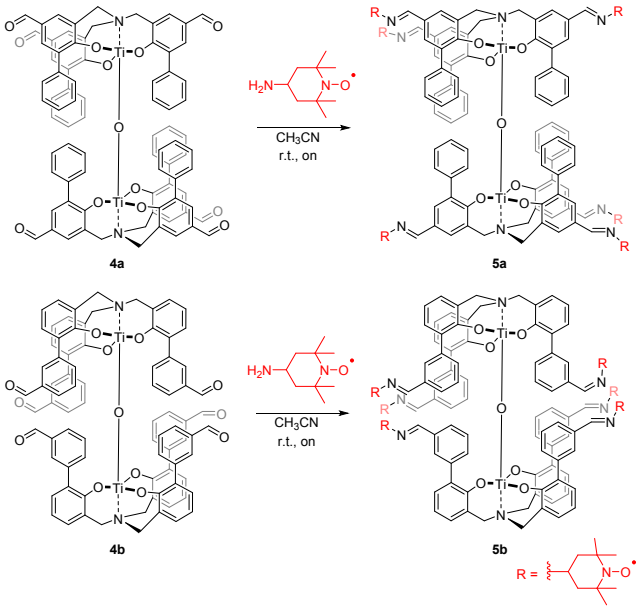
Synthesis of multiple radical molecular architectures

As shown in our previous paper, titanatranes with bulky phenyl substituents in *ortho* positions spontaneously form highly stable μ-oxo dinuclear complexes in the presence of traces of water.[44] We took advantage of this chemistry to synthetize a series of novel μ-oxo complexes **4a-b**, bearing aldehydes in different positions (Scheme 2). Aldehydes were chosen as possible anchoring points for the subsequent introduction of amino-TEMPO units via imine condensation reaction. The parent ligands **2a-b** were prepared with a newly developed synthesis (See Supporting Info, Chapter S1).

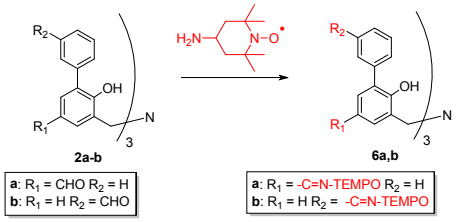


SCHEME 2 μ-oxo complexes **4a-b** can be obtained from the corresponding phenol derivatives **2a-b** by reaction with Ti(O-*i*Pr)$_4$. The mononuclear titanatrane systems **3a-b** evolve spontaneously to the corresponding **4a-b** in the presence of traces of water**.**

This takes advantage of either a direct three-fold formylation of a preformed ligand, for the functionalization of the phenol' *para* positions (*viz.* **2a**), and/or of a Suzuki coupling with formyl-arylboronic acid for the functionalization of the upper substituted phenyl ring (*viz.* **2b**). Reaction between the amine triphenolates **2a-b** and Ti(O-*i*Pr)$_4$ gave the *in situ* formation of the C_3 mononuclear Ti(IV) complexes **3a-b** which rapidly and spontaneously self-assemble, in the presence of traces of water, into the dinuclear μ-oxo **4a-b**, as the only S_6-symmetric system (Scheme 2). Complexation and formation of the dinuclear μ-oxo titanium (IV) complexes can be easily followed by ^{1}H-NMR spectroscopy. As an example, by addition of one equivalent of Ti(O-*i*Pr)$_4$ to **2b**, the ^{1}H-NMR in $CDCl_3$ shows the formation of a single set of signals at 3.69 ppm for the methylene protons in α to the nitrogen of **3b** (See Supporting Info Figure S12). Upon addition of few amount of water, **3b** rapidly evolves into the dinuclear μ-oxo complex **4b** which precipitates over time from the solution. ^{1}H-NMR spectrum of **4b** shows the formation of an AB system at 4.40 and 3.31 ppm, corresponding to the methylene protons (See Supporting Info Figure S13). Moreover, the aromatic protons of the peripheral aryl rings together with the aldehydic signal are shifted up field (for CHO from 9.94 to 9.20 ppm), because of the intercalation of the rings around the μ-oxo bridge. The formation of the dimeric complexes **4a-b** is also confirmed by ESI-MS analysis. As example for **4b**, the spectra both in positive and negative modes clearly display the characteristic isotopic distribution for the formation of [M]$^-$ (*m/z* = 1041.2) or of the complex having Na$^+$ counterion (*m/z* = 1423.4).



Scheme 3. Synthesis of TEMPO functionalized dinuclear μ-oxo Titanium (IV) complexes **5a-b.**



Scheme 4. Synthesis of TEMPO functionalized ligands **6a-b.**

Condensation between **4a-b** and radical 4-amino-TEMPO has allowed to obtain compounds **5a-b** (Scheme 3). The handling of radicals in solution was carried out under dark and anhydrous conditions to avoid, respectively, the possible degradation of the radicals and imine bond hydrolysis. This post-functionalization leads to the construction of stable and spatially ordered structures with multiple mediator functionalities disposed in a controlled way into space. Similarly, to have a comparison with a less spatially defined system, radical carriers **6a-b** were prepared starting from ligands **2a-b** (Scheme 4). The novel μ-oxo complexes 5**a-b** and ligands **6a-b** were characterized by ESI-MS, FTIR, elemental analysis and Electron Paramagnetic Resonance spectroscopy (EPR). In the ESI-MS spectra, all experimental isotopic clusters were in agreement with the theoretical ones. The FTIR measurements for all the systems showed the disappearance of the characteristic carbonyl stretching of the aldehyde (at ca. 1700 cm^{-1}) and the appearance of the stretching peak of the C=N bond (at ca. 1600 cm^{-1}). The full functionalization with radicals of all compounds was

quantitatively determined by EPR spectroscopy (see Supporting Info Table S1).

The X-ray structure of **5b** unambiguously confirmed the dimer formation as well as the condensation between the radical 4-amino-TEMPO and the aldehyde moieties present in **4b** (Figure 1). The molecular structure of this radical functionalized dinuclear system **5b** shows a C_3-symmetry in the solid state instead of the S_6-symmetric system in solution that was observed for **4b**.

Ligands **6a-b** and the corresponding μ-oxo complexes **5a-b** were investigated by EPR, to gather information on the relative arrangement of the radicals in solution. The results obtained were then correlated to their electrochemical properties evaluated by cyclic voltammetry and finally to the OER redox mediators for Li-O_2 batteries. The same concentration has been used in each pair.

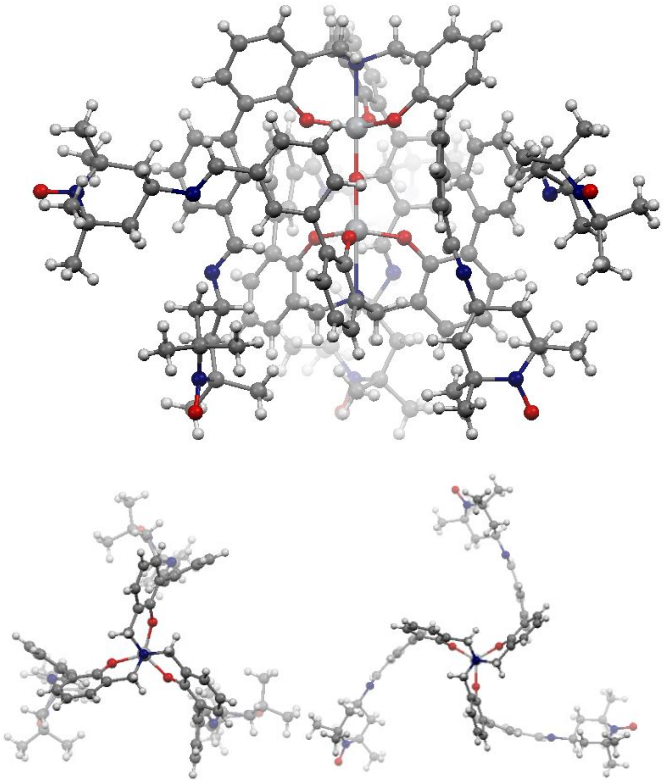


Figure 1. The X-ray single crystal structure of **5b**, and detail of the relative orientations of the two titanatranes units in μ-oxo system.

*EPR spectroscopy for polyradical species **5a-b** and **6 a-b**.*

The EPR study was done in diluted conditions to focus on intramolecular radical interactions. The EPR spectra of the polyradical species at 300 K (Figure 2) showed mainly a three-line pattern like TEMPO free radical, although with broader lines and a selective decrease of the high-field line due to the hindered motion of the radicals attached to a big molecule. In addition, some signs related to the radical interactions were observed. In the EPR spectra of the corresponding **b** species (**6b** and **5b**), some little alternating linewidth effect compared with their respective **a** species (**6a** and **5a**) was observed. This means some spin-exchange interaction among radicals in such compounds. In fact, radicals in **b** conformations present more degrees of freedom than in **a**, favoring their mobility and hence, their proximity.

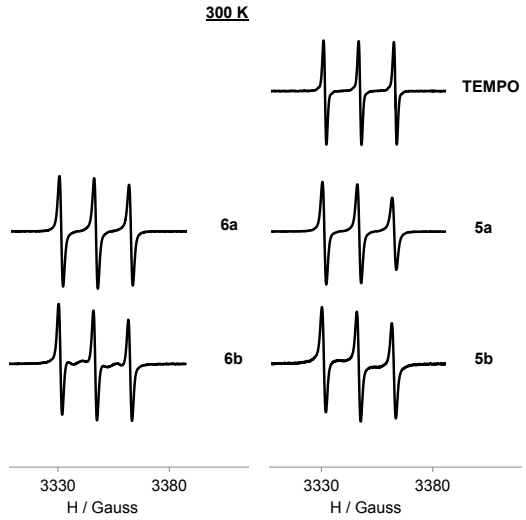


Figure 2. Normalized EPR spectra of TEMPO, ligands **6a-6b** and μ-oxo complexes **5a-5b** in DCM:toluene 1:1, at 300 K and 1 mM.

In frozen solution, 120 K, the EPR spectra shape changes completely. Under these anisotropic conditions, the spectra shape is sensitive to the distance between neighboring nitroxides up to ca. 2 nm and a convenient measure of the strength of the dipole-dipole interactions is therefore given by the empirical ratio of peak heights d_1/d value (Figure 3).[55] The higher the ratio, the shorter the distance between the radical centers, and hence the higher the radical interactions. Table 1 displays the calculated d_1/d value for all compounds from their corresponding frozen solution spectra (shown in Figure 3 and Supporting Info Figures S15-S16). The d_1/d ratio was 0.51 for monoradical TEMPO where intramolecular interactions are absent, while for all the polyradical species this ratio was much higher. This suggested that all of them presented intramolecular dipolar interactions, and that some of their radicals should be located at distances lower than 2 nm. This compares well with the 7.846 Å radical-radical distance found in the crystal structure. In detail, both in the ligands and μ-oxo complexes pairs, higher d_1/d values, i.e. closer radicals, in their corresponding **b** arrangement (0.85 and 0.81 for **6b** and **5b** in front of 0.69 and 0.68 for **6a** and **5a**, respectively) were observed. In addition, under these conditions, all polyradical compounds showed a $|\Delta m_s| = 2$ transition at half-field. This signal is characteristic of dipolar coupled spins and a direct evidence of the presence of a high-spin state. It is mainly generated by the presence of two radical units closer than a critical distance and its intensity depends on the average distance between them and the number of interacting pairs of radicals. Therefore, the half-filed signal intensity was used as a second independent parameter to quantify the radical interactions in our compounds. In Table 1 are also reported the normalized half-field signal intensities of all compounds and in Figures 3 (and Supporting Info Figure S17), their corresponding EPR spectra.

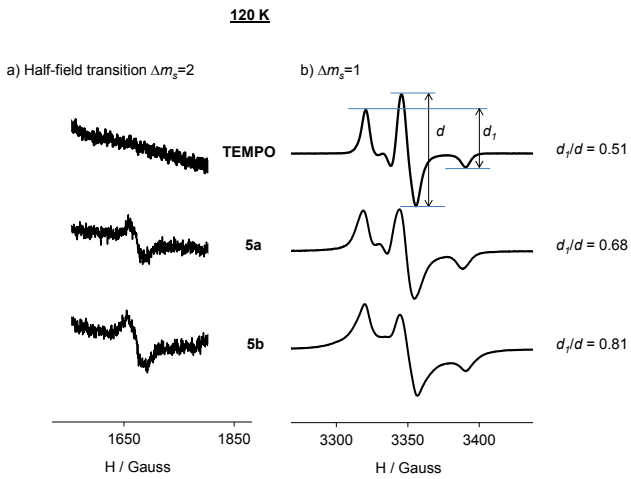


Figure 3. a) $|\Delta m_s|$= 2 transition at half-field EPR spectra and b) $|\Delta m_s|$= 1 EPR spectra of TEMPO and μ-oxo complexes **5a-5b** in DCM:toluene 1:1 at 120 K and 1 mM.

Table 1. EPR and electrochemical parameters of compounds **5a-b** and **6a-b**.

	d_1/d	$\|\Delta m_s\|$= 2 intensity	$E_{1/2}$ (V) vs Ag/AgCl	Voltage (V) vs Li^+/Li at 0.05 mA/cm^2
6a	0.69	1.0	0.86	3.94
6b	0.85	1.05	0.84	3.83
5a	0.68	1.3	0.86	3.89
5b	0.81	1.6	0.83	3.81

Measures replicates shows variations in the range of +/- 2 mV for $E_{1/2}$ and +/- 0,001 for d1/d.

Following the same trend, the half-field intensity was also larger in the **b** species. This difference in intensity is significant in the μ-oxo complexes pair (**5a** *vs* **5b**) and can be explained taking into account the different location of the radicals in the scaffold. In **5b** the radicals of both titanatranes are disposed in closer proximity than in **5a**. In fact, the **5b** X-ray structure displays three close enough (7.846 Å) pairs of radicals (each pair with radicals of both titanatranes). The corresponding EPR study of TEMPO free radical in frozen solution is explained in the SI.

*Cyclic voltammetries of compounds **5a-b** and **6a-b***

The electrochemical properties of the polyradical species under study and TEMPO free radical were evaluated by cyclic voltammetry (CV) in DMF with 0.1 M of tetrabutylammonium hexafluorophosphate (TBAHFP) as electrolyte. The corresponding cyclic voltammograms are shown in Figure 4 (see also Supporting Info Figure S18-S20 and Figure S21 for CV at different scan rates) and the half-wave potential $E_{1/2}$ are included in Table 1. The polyradical compounds exhibited a reversible redox wave at lower potential values than monoradical TEMPO ($E_{1/2}$ ~ 0.9 V, see Supporting Info Table S2). Focusing on the different polynitroxides, it can be observed that the **b** species (**6b** and **5b**) exhibited lower $E_{1/2}$ potential than their corresponding homologues with the **a** arrangement (**6a** and **5a**, respectively). These relations are a clear indication of the mutual interactions between the redox centers existing in these polyradical species (absent in monoradical TEMPO) and can be explained by means of intramolecular electron-electron interaction effects. As previously reported,[56] in the polyradical species with closer radical disposition (higher interactions) this shift was higher. As shown in Fig. 5 we observe a interesting correlation between the $E_{1/2}$ potential and the d1/d parameter. This suggests that the same

interactions caused by the close distance forced by the ligand geometry on one hand are reflected in the magnetic radical coupling, and on the other destabilize the electronic level of the radical state, resulting in a lower reduction potential.

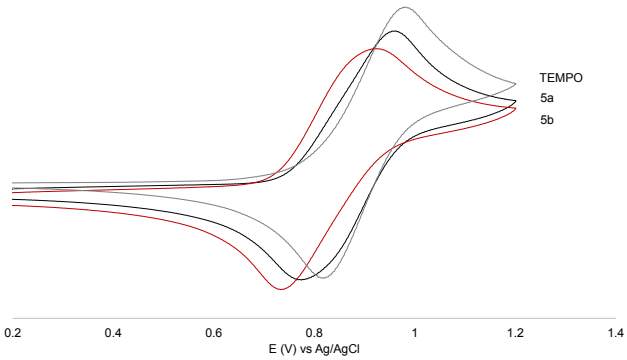


Figure 4. Cyclic voltammetry of TEMPO and μ-oxo complexes **5a-5b** at 1 mM in DMF with 0.1 M HFPTBA, vs Ag/AgCl at the scan rate of 200 mV/s.

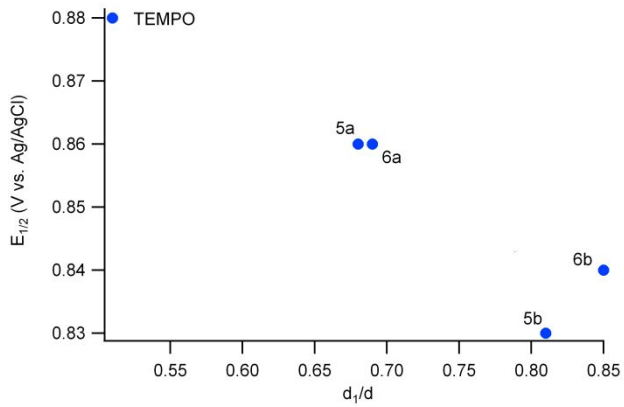


Figure 5. Half-wave potential E1/2 versus d_1/d of TEMPO and polynitroxides **6a-b** and **5a-b** at the same molecular concentration of 1 mM.

*Compounds **5a-b** and **6a-b** as redox charge mediators*

Ligands **6a-b** and their corresponding μ-oxo complexes (**5a-b**) were tested as redox charge mediators for Li-O_2 batteries. Typical galvanostatic discharge and charge profiles are reported in Figure 6 (see also Supporting Info Figure S22 for the complete dataset and corresponding polarization curves). Table 1 reports their corresponding cell voltages *vs* Li^+/Li when a charging current of 0.05 mA/cm^2 was applied. Comparing to the electrolyte without additives we clearly observe mediation of charge, with general tendencies consistent with the potential shifts obtained by cyclic voltammetry, as graphically also shown in Figure S24. This implies that the larger molecular size does not affect the mediation activity as much as the redox potential.

Remarkably, we can observe that by using TEMPO mononitroxide at different concentrations, from 1 to 12 mM, we measured systematically higher charge voltages than those obtained with the polynitroxide species under study (Supporting Info Figure S23 and Tables S2-S3). Although there was a tendency towards lower charge voltage by increasing TEMPO radical concentration, which was also reported elsewhere,[25] even at double radical concentration than polynitroxides (12 mM), the TEMPO charge voltage was still higher (see Supporting Info Table S2). In addition, the charge potential decreases from **6a** to **5b** much more than the corresponding $E_{1/2}$ variation even if the same radical concentration has been used. This suggests that intramolecular interactions also have a direct impact in the kinetic efficiency of polynitroxides as charge mediators, which sums to the thermodynamic variation of redox potential.

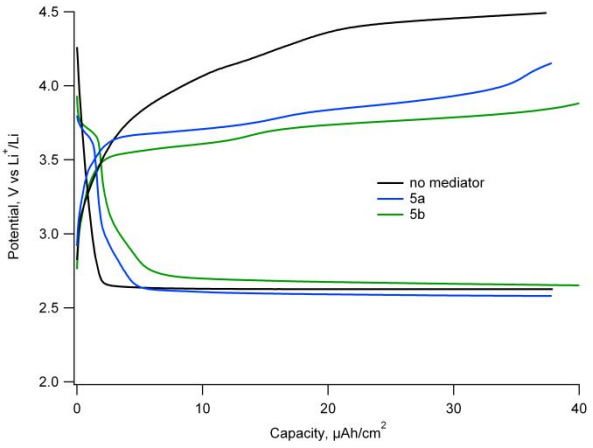


Figure 6. Charge and discharge galvanostatic pulses with electrolyte without additives and using **5a-b** mediators at 1 mM at current densities of 0.05 mA/cm^2.

Conclusions

Triphenolamines and μ-oxo dinuclear Ti(IV) complexes with versatile multiple functionalization and a well-defined geometry have been synthesized and characterized. These molecular scaffolds have permitted us to anchor up to six redox active TEMPO radical units in two different arrangements (some with closer and others with more distant radicals disposition) to study the influence of the intramolecular radical interactions on their electrochemical and OER mediator behavior. These polyradical species have been synthesized and characterized. We studied by EPR and X-ray diffraction the arrangement of the radical units in such molecular scaffolds, and their mutual interactions, and quantified their electrochemical behavior by cyclic voltammetry and their radical efficiency as redox mediator, by the charge voltage in a Li/O_2 battery.

We can conclude that multiple TEMPO redox species in the same discrete molecular scaffold favour the efficiency as OER mediator compared with monoradical species. In particular, the better performances observed are related to the closer disposition of the radical units and the higher number of pairs of radicals that can interact intramolecularly. Such intramolecular interactions seem to decrease the half-wave potential of the electroactive TEMPO radical units. In a Li—O_2 battery this allows to tune the charging potential towards lower values, making more efficient the OER mediator redox process. In fact, the smaller difference between dicharge and charge potential increase the energy efficiency, and the lower overpotential decreases the probability of secondary reactions. Thus, this study suggests a correlation between the radical efficiency as redox mediator and the intramolecular radical interactions quantified by EPR. Further studies are in progress to evaluate such effects with a bigger family of polynitroxide systems.

ASSOCIATED CONTENT

Supporting Information. Supporting Information containing the compound synthesis and charachterisation, EPR and galvanostatica and Xray data is available free of charge via the Internet at http://pubs.acs.org."

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ACKNOWLEDGMENT

This work was supported by DGICT-MINECO (MAT2016-80826-R, MAT2017-91404-EXP, RTI2018-09273-B-I00), AGAUR (2017 SGR 918, 2014 SGR 1505, 2017 SGR 1687). ICMAB acknowledges Spanish MINECO through the Severo Ochoa Centres of Excellence Programme Grant SEV- 2015-0496 and Songbai Zhang his CSC grant.

REFERENCES

(1) Iwamura, H.; Koga, N. Studies of Organic Di-, Oligo-, and Polyradicals by Means of Their Bulk Magnetic Properties. *Acc. Chem. Res.* **1993**, *26* (6), 346–351. https://doi.org/10.1021/ar00030a008.

(2) Rajca, A. *The Physical Organic Chemistry of Very High-Spin Polyradicals*; 2005; Vol. 40. https://doi.org/10.1016/S0065-

3160(05)40004-0.

(3) Rajca, A.; Wongsriratanakul, J.; Rajca, S. Magnetic Ordering in an Organic Polymer. *Science (80-.).* **2001**, *294* (5546), 1503 LP – 1505. https://doi.org/10.1126/science.1065477.

(4) Rajca, A.; Shiraishi, K.; Vale, M.; Han, H.; Rajca, S. Stable Hydrocarbon Diradical, An Analogue of Trimethylenemethane. *J. Am. Chem. Soc.* **2005**, *127* (25), 9014–9020. https://doi.org/10.1021/ja052002v.

(5) Fukuzaki, E.; Nishide, H. Room-Temperature High-Spin Organic Single Molecule: Nanometer-Sized and Hyperbranched Poly[1,2,(4)-Phenylenevinyleneanisylaminium]. *J. Am. Chem. Soc.* **2006**, *128* (3), 996–1001. https://doi.org/10.1021/ja0569611.

(6) Chernick, E. T.; Mi, Q.; Kelley, R. F.; Weiss, E. A.; Jones, B. A.; Marks, T. J.; Ratner, M. A.; Wasielewski, M. R. Electron Donor−Bridge−Acceptor Molecules with Bridging Nitronyl Nitroxide Radicals: Influence of a Third Spin on Charge- and Spin-Transfer Dynamics. *J. Am. Chem. Soc.* **2006**, *128* (13), 4356–4364. https://doi.org/10.1021/ja0576435.

(7) Altenbach, C.; Oh, K.-J.; Trabanino, R. J.; Hideg, K.; Hubbell, W. L. Estimation of Inter-Residue Distances in Spin Labeled Proteins at Physiological Temperatures: Experimental Strategies and Practical Limitations. *Biochemistry* **2001**, *40* (51), 15471–15482. https://doi.org/10.1021/bi011544w.

(8) Huang, L.; Yan, C.; Cui, D.; Yan, Y.; Liu, X.; Lu, X.; Tan, X.; Lu, X.; Xu, J.; Xu, Y.; Liu, R. Organic Radical Contrast Agents Based on Polyacetylenes Containing 2,2,6,6-Tetramethylpiperidine 1-Oxyl (TEMPO): Targeted Magnetic Resonance (MR)/Optical Bimodal Imaging of Folate Receptor Expressing HeLa Tumors in Vitro and in Vivoa. *Macromol. Biosci.* **2015**, *15* (6), 788–798. https://doi.org/10.1002/mabi.201400403.

(9) Matsuki, Y.; Maly, T.; Ouari, O.; Karoui, H.; Le Moigne, F.; Rizzato, E.; Lyubenova, S.; Herzfeld, J.; Prisner, T.; Tordo, P.; Griffin, R. G. Dynamic Nuclear Polarization with a Rigid Biradical. *Angew. Chemie Int. Ed.* **2009**, *48* (27), 4996–5000. https://doi.org/10.1002/anie.200805940.

(10) Song, C.; Hu, K.-N.; Joo, C.-G.; Swager, T. M.; Griffin, R. G. TOTAPOL: A Biradical Polarizing Agent for Dynamic Nuclear Polarization Experiments in Aqueous Media. *J. Am. Chem. Soc.* **2006**, *128* (35), 11385–11390. https://doi.org/10.1021/ja061284b.

(11) Pinto, L. F.; Marín-Montesinos, I.; Lloveras, V.; Muñoz-Gómez, J. L.; Pons, M.; Veciana, J.; Vidal-Gancedo, J. NMR Signal Enhancement of >50 000 Times in Fast Dissolution Dynamic Nuclear Polarization. *Chem. Commun.* **2017**, *53* (26), 3757–3760. https://doi.org/10.1039/C7CC00635G.

(12) Green, D. E.; Tzagoloff, A. The Mitochondrial Electron Transfer Chain. *Arch. Biochem. Biophys.* **1966**, *116* (1), 293–304. https://doi.org/10.1016/0003-9861(66)90036-1.

(13) Kracke, F.; Vassilev, I.; Krömer, J. O. Microbial Electron Transport and Energy Conservation – the Foundation for Optimizing Bioelectrochemical Systems . *Frontiers in Microbiology* . 2015, p 575.

(14) Crofts, A. R.; Wraight, C. A. The Electrochemical Domain of Photosynthesis. *Biochim. Biophys. Acta - Rev. Bioenerg.* **1983**, *726* (3), 149–185. https://doi.org/https://doi.org/10.1016/0304-4173(83)90004-6.

(15) Boschloo, G.; Hagfeldt, A. Characteristics of the Iodide/Triiodide Redox Mediator in Dye-Sensitized Solar Cells. *Acc. Chem. Res.* **2009**, *42* (11), 1819–1826. https://doi.org/10.1021/ar900138m.

(16) Kim, J.; Kim, J. H.; Ariga, K. Redox-Active Polymers for Energy Storage Nanoarchitectonics. *Joule* **2017**, *1* (4), 739–768. https://doi.org/10.1016/j.joule.2017.08.018.

(17) Friebe, C.; Lex-Balducci, A.; Schubert, U. S. Sustainable Energy Storage: Recent Trends and Developments toward Fully Organic Batteries. *ChemSusChem* **2019**, *12* (18), 4093–4115. https://doi.org/10.1002/cssc.201901545.

(18) Xie, Y.; Zhang, K.; Monteiro, M. J.; Jia, Z. Conjugated Nitroxide Radical Polymers: Synthesis and Application in Flexible Energy Storage Devices. *ACS Appl. Mater. Interfaces* **2019**, *11* (7), 7096–7103. https://doi.org/10.1021/acsami.8b21073.

(19) Lai, Y. Y.; Li, X.; Zhu, Y. Polymeric Active Materials for Redox Flow Battery Application. *ACS Appl. Polym. Mater.* **2020**, *2* (2), 113–128. https://doi.org/10.1021/acsapm.9b00864.

(20) Suga, T.; Konishi, H.; Nishide, H. Photocrosslinked Nitroxide Polymer Cathode-Active Materials for Application in an Organic-Based Paper Battery. *Chem. Commun.* **2007**, No. 17, 1730–1732. https://doi.org/10.1039/B618710B.

(21) Li, F.; Wang, S.; Zhang, Y.; Lutkenhaus, J. L. Electrochemical Energy Storage in Poly(Dithieno[3,2-b:2′,3′-d]Pyrrole) Bearing Pendant Nitroxide Radicals. *Chem. Mater.* **2018**, *30* (15), 5169–5174. https://doi.org/10.1021/acs.chemmater.8b01775.

(22) Wang, S.; Li, F.; Easley, A. D.; Lutkenhaus, J. L. Real-Time Insight into the Doping Mechanism of Redox-Active Organic Radical Polymers. *Nat. Mater.* **2019**, *18* (1), 69–75. https://doi.org/10.1038/s41563-018-0215-1.

(23) Wei, X.; Xu, W.; Vijayakumar, M.; Cosimbescu, L.; Liu, T.; Sprenkle, V.; Wang, W. TEMPO-Based Catholyte for High-Energy Density Nonaqueous Redox Flow Batteries. *Adv. Mater.* **2014**, *26* (45), 7649–7653. https://doi.org/10.1002/adma.201403746.

(24) Bergner, B. J.; Schürmann, A.; Peppler, K.; Garsuch, A.; Janek, J. TEMPO: A Mobile Catalyst for Rechargeable Li-O2 Batteries. *J. Am. Chem. Soc.* **2014**, *136* (42), 15054–15064. https://doi.org/10.1021/ja508400m.

(25) Bergner, B. J.; Hofmann, C.; Schürmann, A.; Schröder, D.; Peppler, K.; Schreiner, P. R.; Janek, J. Understanding the Fundamentals of Redox Mediators in Li–O2 Batteries: A Case Study on Nitroxides. *Phys. Chem. Chem. Phys.* **2015**, *17* (47), 31769–31779. https://doi.org/10.1039/C5CP04505C.

(26) Vlad, A.; Rolland, J.; Hauffman, G.; Ernould, B.; Gohy, J.-F. Melt-Polymerization of TEMPO Methacrylates with Nano Carbons Enables Superior Battery Materials. *ChemSusChem* **2015**, *8* (10), 1692–1696. https://doi.org/10.1002/cssc.201500246.

(27) Nishide, H.; Iwasa, S.; Pu, Y.-J.; Suga, T.; Nakahara, K.; Satoh, M. Organic Radical Battery: Nitroxide Polymers as a Cathode-Active Material. *Electrochim. Acta* **2004**, *50* (2), 827–831. https://doi.org/https://doi.org/10.1016/j.electacta.2004.02.052.

(28) Badetti, E.; Lloveras, V.; Muñoz-Gómez, J. L.; Sebastián, R. M.; Caminade, A. M.; Majoral, J. P.; Veciana, J.; Vidal-Gancedo, J. Radical Dendrimers: A Family of Five Generations of Phosphorus Dendrimers Functionalized with TEMPO Radicals. *Macromolecules* **2014**, *47* (22), 7717–7724. https://doi.org/10.1021/ma502062q.

(29) Badetti, E.; Lloveras, V.; Scaramuzzo, F. A.; Wurst, K.; Veciana, J.; Vidal-Gancedo, J.; Licini, G.; Zonta, C. Tris-Pyridylmethylamine (TPMA) Complexes Functionalized with Persistent Nitronyl Nitroxide Organic Radicals. *Dalt. Trans.* **2020**, *49* (29), 10011–10016. https://doi.org/10.1039/D0DT01553A.

(30) Christensen, J.; Albertus, P.; Sanchez-Carrera, R. S.; Lohmann, T.; Kozinsky, B.; Liedtke, R.; Ahmed, J.; Kojic, A. A Critical Review of Li/Air Batteries. *J. Electrochem. Soc.* **2011**, *159* (2), R1–R30. https://doi.org/10.1149/2.086202jes.

(31) Lim, H.-D.; Lee, B.; Zheng, Y.; Hong, J.; Kim, J.; Gwon, H.; Ko, Y.; Lee, M.; Cho, K.; Kang, K. Rational Design of Redox Mediators for Advanced Li-O2 Batteries. *Nat. Energy* **2016**, *1* (6). https://doi.org/10.1038/nenergy.2016.66.

(32) Landa-Medrano, I.; Lozano, I.; Ortiz-Vitoriano, N.; Ruiz de Larramendi, I.; Rojo, T. Redox Mediators: A Shuttle to Efficacy in Metal–O2 Batteries. *J. Mater. Chem. A* **2019**, *7* (15), 8746–8764. https://doi.org/10.1039/C8TA12487F.

(33) Lacey, M. J.; Frith, J. T.; Owen, J. R. A Redox Shuttle to Facilitate Oxygen Reduction in the Lithium Air Battery. *Electrochem. commun.* **2013**, *26*, 74–76. https://doi.org/https://doi.org/10.1016/j.elecom.2012.10.009.

(34) Matsuda, S.; Hashimoto, K.; Nakanishi, S. Efficient Li2O2 Formation via Aprotic Oxygen Reduction Reaction Mediated by Quinone Derivatives. *J. Phys. Chem. C* **2014**, *118* (32), 18397–18400. https://doi.org/10.1021/jp504894e.

(35) Tesio, A. Y.; Blasi, D.; Olivares-Marín, M.; Ratera, I.; Tonti, D.; Veciana, J. Organic Radicals for the Enhancement of Oxygen Reduction Reaction in Li–O2 Batteries. *Chem. Commun.* **2015**, *51* (99), 17623–17626. https://doi.org/10.1039/C5CC07242E.

(36) Gao, X.; Chen, Y.; Johnson, L.; Bruce, P. G. Promoting Solution Phase Discharge in Li–O2 Batteries Containing Weakly Solvating Electrolyte Solutions. *Nat. Mater.* **2016**, *15* (8), 882–888. https://doi.org/10.1038/nmat4629.

(37) Chen, Y.; Freunberger, S. A.; Peng, Z.; Fontaine, O.; Bruce, P. G. Charging a Li-O_2 Battery Using a Redox Mediator. *Nat. Chem.* **2013**, *5* (6), 489–494. https://doi.org/10.1038/nchem.1646.

(38) Sun, D.; Shen, Y.; Zhang, W.; Yu, L.; Yi, Z.; Yin, W.; Wang, D.; Huang, Y.; Wang, J.; Wang, D.; Goodenough, J. B. A Solution-Phase Bifunctional Catalyst for Lithium–Oxygen Batteries. *J. Am. Chem. Soc.* **2014**, *136* (25), 8941–8946. https://doi.org/10.1021/ja501877e.

(39) Kwak, W.-J.; Hirshberg, D.; Sharon, D.; Shin, H.-J.; Afri, M.; Park, J.-B.; Garsuch, A.; Chesneau, F. F.; Frimer, A. A.; Aurbach, D.; Sun, Y.-K. Understanding the Behavior of Li–Oxygen Cells Containing LiI. *J. Mater. Chem. A* **2015**, *3* (16), 8855–8864. https://doi.org/10.1039/C5TA01399B.

(40) Landa-Medrano, I.; Olivares-Marín, M.; Bergner, B.; Pinedo, R.; Sorrentino, A.; Pereiro, E.; Ruiz de Larramendi, I.; Janek, J.; Rojo, T.; Tonti, D. Potassium Salts as Electrolyte Additives in Lithium–Oxygen Batteries. *J. Phys. Chem. C* **2017**, *121* (7), 3822–3829. https://doi.org/10.1021/acs.jpcc.7b00355.

(41) Chen, Y.; Gao, X.; Johnson, L. R.; Bruce, P. G. Kinetics of Lithium Peroxide Oxidation by Redox Mediators and Consequences for the Lithium–Oxygen Cell. *Nat. Commun.* **2018**, *9* (1), 767. https://doi.org/10.1038/s41467-018-03204-0.

(42) Kwak, W.-J.; Park, J.; Kim, H.; Joo, J. M.; Aurbach, D.; Byon, H. R.; Sun, Y.-K. Oxidation Stability of Organic Redox Mediators as Mobile Catalysts in Lithium–Oxygen Batteries. *ACS Energy Lett.* **2020**, *5* (6), 2122–2129. https://doi.org/10.1021/acsenergylett.0c00883.

(43) Licini, G.; Mba, M.; Zonta, C. Amine Triphenolate Complexes: Synthesis, Structure and Catalytic Activity. *J. Chem. Soc. Dalt. Trans.* **2009**, No. 27. https://doi.org/10.1039/b822653a.

(44) Bernardinelli, G.; Seidel, T. M.; Kündig, E. P.; Prins, L. J.; Kolarovic, A.; Mba, M.; Pontini, M.; Licini, G. Stereoselective Dimerization of Racemic C3-Symmetric Ti(Iv) Amine Triphenolate Complexes. *Dalt. Trans.* **2007**, No. 16, 1573–1576. https://doi.org/10.1039/B702958F.

(45) Miceli, C.; Rintjema, J.; Martin, E.; Escudero-Adán, E. C.; Zonta, C.; Licini, G.; Kleij, A. W. Vanadium(V) Catalysts with High Activity for the Coupling of Epoxides and CO<inf>2</Inf>: Characterization of a Putative Catalytic Intermediate. *ACS Catal.* **2017**, *7* (4). https://doi.org/10.1021/acscatal.7b00109.

(46) Amadio, E.; González-Fabra, J.; Carraro, D.; Denis, W.; Gjoka, B.; Zonta, C.; Bartik, K.; Cavani, F.; Solmi, S.; Bo, C.; Licini, G. Efficient Vanadium-Catalyzed Aerobic C−C Bond Oxidative Cleavage of Vicinal Diols. *Adv. Synth. Catal.* **2018**, *360* (17). https://doi.org/10.1002/adsc.201800050.

(47) Badetti, E.; Gjoka, B.; Nagy, E. M.; Bernardinelli, G.; Kündig, P. E.; Zonta, C.; Licini, G. Mononuclear Iron(III) Complexes as Functional Models of Catechol Oxidases and Catalases. *Eur. J. Inorg. Chem.* **2015**, *2015* (21). https://doi.org/10.1002/ejic.201403225.

(48) Mba, M.; Pontini, M.; Lovat, S.; Zonta, C.; Bernardinelli, G.; Kündig, P. E.; Licini, G. C<inf>3</Inf> Vanadium(V) Amine Triphenolate Complexes: Vanadium Haloperoxidase Structural and Functional Models. *Inorg. Chem.* **2008**, *47* (19). https://doi.org/10.1021/ic8015113.

(49) Badetti, E.; Lloveras, V.; Romano, F.; Di Lorenzo, R.; Veciana, J.; Vidal-Gancedo, J.; Zonta, C.; Licini, G. Discrimination of Octahedral versus Trigonal Bipyramidal Coordination Geometries of Homogeneous Ti^{IV}, V^{V}, and Mo^{VI}Amino Triphenolate Complexes through Nitroxyl Radical Units. *Eur. J. Inorg. Chem.* **2016**, *2016* (31). https://doi.org/10.1002/ejic.201600649.

(50) Zardi, P.; Wurst, K.; Licini, G.; Zonta, C. Concentration-Independent Stereodynamic g-Probe for Chiroptical Enantiomeric Excess Determination. *J. Am. Chem. Soc.* **2017**, *139* (44), 15616–15619. https://doi.org/10.1021/jacs.7b09469.

(51) Zonta, C.; Kolarovic, A.; Mba, M.; Pontini, M.; KÜndig, E. P.; Licini, G. Enantiopure Ti(IV) Amino Triphenolate Complexes as NMR Chiral Solvating Agents. *Chirality* **2011**, *23* (9). https://doi.org/10.1002/chir.20994.

(52) Bravin, C.; Badetti, E.; Scaramuzzo, F. A.; Licini, G.; Zonta, C. Triggering Assembly and Disassembly of a Supramolecular Cage. *J. Am. Chem. Soc.* **2017**, *139* (18). https://doi.org/10.1021/jacs.7b02341.

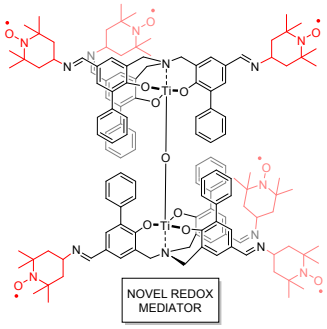
(53) Bravin, C.; Licini, G.; Hunter, C. A.; Zonta, C. Supramolecular Cage Encapsulation as a Versatile Tool for the Experimental Quantification of Aromatic Stacking Interactions. *Chem. Sci.* **2019**, *10* (5). https://doi.org/10.1039/c8sc04406f.

(54) Bravin, C.; Licini, G.; Zonta, C.; Hunter, C. A. Hetero Co-Encapsulation within a Supramolecular Cage. Moving Away from the Statistical Distribution of Different Guests. *Chem. – A Eur. J.* **2020**, *n/a* (n/a). https://doi.org/10.1002/chem.202000574.

(55) Kulikov, A. V; Likhtenstein, G. I. The Use of Spin Relaxation Phenomena in the Investigation of the Structure of Model and Biological Systems by the Method of Spin Labels. *Adv. Mol. Relax. Interact. Process.* **1977**, *10* (1), 47–79. https://doi.org/https://doi.org/10.1016/0378-4487(77)80013-7.

(56) Lloveras, V.; Liko, F.; Pinto, L. F.; Muñoz-Gómez, J. L.; Veciana, J.; Vidal-Gancedo, J. Tuning Spin-Spin Interactions in Radical Dendrimers. *ChemPhysChem* **2018**, *19* (15), 1895–1902.

https://doi.org/10.1002/cphc.201800372.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