Supporting Information

Calix[*n*]arene-based Polyradicals: Enhancing Ferromagnetism by Avoiding Edge Effects

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1.- Mapping expressions for linear, helical and circular arrangements.

From a general point of view, and assuming the physics of the problem can be described correctly by means of the HDVV spin Hamiltonian, the procedure used to extract the coupling constant consists in mapping the diagonal elements of the HDVV Hamiltonian to the energy expectation value of the high spin and of the different broken symmetry (BS) solutions. Within the present approach the number of different broken symmetry (BS) solutions for a given multiplicity can be calculated using the binomial coefficient $C_{N,i}$ where N is the number of magnetic centres and i the number of beta spin densities. For instance, for a $N = 6$ system, the spin multiplicities range from septet, quartet and doublet, which corresponds to $i = 0, 1\ and\ 2$. Thus, there are $C_{6,1} = \frac{6!}{1!(6-1)!} = 6$ different ways of having one beta density in a six-membered system. As usual the high spin state is referred to as ferromagnetic (FM) and the different BS solutions correspond to antiferromagnetic (AFM) arrangements.

Due to the large amount of AFM solutions which are possible for each of the cases studied it is convenient to find a way to express the energy differences between the FM and AFM solutions in a more compact manner, applicable to all investigated systems. To this end we make use of three convenient choices. First, we refer all energy differences to the FM solution. Second, we assume that all AFM_i solutions correspond to situations in which we progressively increase the number of consecutive spin-down (beta) densities (located at the extreme of the molecules for linear and helical cases); i indicates the number of beta densities in the molecule. Thus, AFM_5 would correspond to a state with 5 consecutive beta densities at one of the extremes of the molecule. Third, we also assume that the number of centres present in the molecule allows for the same number of second nearest neighbour interactions in linear and circular cases and fourth nearest neighbour interactions for the helix. This is fulfilled for $N \geq 4$ and $N \geq 7$ for linear and helical cases, respectively. Using only these solutions, the energy differences between FM and $AFM_{(i)}$ can be expressed in terms of the coefficients presented in table SI1 as discussed in more detail below.

Table SI1. Coefficients to use in eq(2), eq(4) and eq(6).

A_i^j		j			
		1	2	3	4
i	1	1	1	1	1
	2	1	2	2	2
	3	1	2	3	3
	4	1	2	3	4
	5	1	2	3	4

Index j is associated to the order of the nearest interacting neighbour whereas index i refers to how many consecutive beta centres are in the extreme. In order to clarify the choice of $N \geq 4$ and $N \geq 7$ for linear and helical cases, let us take the case of $N = 6$ in a linear arrangement. In this situation we would have the following solutions: $FM = |\alpha\alpha\alpha\alpha\alpha\alpha\rangle$, $AFM_1 = |\beta\alpha\alpha\alpha\alpha\alpha\rangle$, $AFM_2 = |\beta\beta\alpha\alpha\alpha\alpha\rangle$, $AFM_3 = |\beta\beta\beta\alpha\alpha\alpha\rangle$. It is then clear that for AFM_3, the third consecutive β-spin does not have a fourth nearest neighbour, which makes the entries in Table SI1 not applicable. For $N < 4$ and $N < 7$ in linear and helical cases, the energy expressions are obtained in the same manner; it is just that there is not a unified expression for all of them.

The DFT-calculated solutions not always correspond to consecutive β densities at one of the extremes. Common scenarios involve consecutive β densities in the middle of the molecule (in linear and helical cases), consecutive β density sets at each of the extremes or randomly alternated β densities. Those are generically labelled as AFM_{i^*} and the correct ordering of α and β densities is indicated where appropriate.

1.1. Systems with borders: linear and helical.

Linear case.

Assuming second neighbours interactions only, the HDVV Hamiltonian can be expressed as

$$\hat{H}_{linear}^{HDVV} = -\sum_{\langle i,j \rangle} J_{ij}\ \hat{\boldsymbol{S}}_i \cdot \hat{\boldsymbol{S}}_j \tag{1}$$

Which translates into the following energy difference expressions for any linear system

$$\langle FM|\hat{H}_{linear}^{HDVV}|FM\rangle - \langle AFM_i|\hat{H}_{linear}^{HDVV}|AFM_i\rangle = -\frac{1}{2}\left[A_i^1 \cdot J_1 + A_i^2 \cdot J_2\right] \tag{2}$$

Where the coefficients A can be obtained from Table SI1 and J_1 and J_2 are the first and second nearest neighbours exchange coupling constants, respectively. It is important to recall that all $AFM_{(i)}$ solutions correspond to situations in which we progressively increase the number of consecutive beta densities located at the extreme of the molecules.

Helical case.

Assuming fourth neighbours interactions only, the HDVV Hamiltonian can be expressed as

$$\hat{H}_{helix}^{HDVV} = -\sum_{\langle i,j=i+1,2,3,4\rangle} J_{ij}\ \hat{\boldsymbol{S}}_i \cdot \hat{\boldsymbol{S}}_j \tag{3}$$

Which translates into the following energy difference expressions for any helical system

$$\langle FM|\hat{H}_{helix}^{HDVV}|FM\rangle - \langle AFM_i|\hat{H}_{helix}^{HDVV}|AFM_i\rangle = \\ = -\frac{1}{2}\left[A_i^1 \cdot J_1 + A_i^2 \cdot J_2 + A_i^3 \cdot J_3 + A_i^4 \cdot J_4\right] \tag{4}$$

Where the coefficients A_i^j can be obtained from Table SI1 and J_1, J_2, J_3 and J_4 are the first, second, third and fourth nearest neighbours exchange coupling constants, respectively. Again, we have to recall that all AFM_i solutions correspond to situations in which we progressively increase the number of consecutive beta densities located at the extreme of the molecules.

1.2 Systems without borders: Rings.

Here the A coefficients can be also obtained from Table SI1 and J_1 and J_2 are the first and second nearest neighbours exchange coupling constants, respectively. It is important to recall that all $AFM_{(i)}$ solutions correspond to situations in which we progressively increase the number of consecutive beta densities located at the extreme of the molecules.

Assuming second neighbours interactions only, the HDVV Hamiltonian can be expressed as

$$\hat{H}_{ring}^{HDVV} = -\sum_{\langle i,j=i+1,2\rangle} J_{ij}\ \hat{\boldsymbol{S}}_i \cdot \hat{\boldsymbol{S}}_j \tag{5}$$

Which translates into the following energy difference expressions for any circular system

$$\left\langle FM\middle|\hat{H}_{ring}^{HDVV}\middle|FM\right\rangle - \left\langle AFM_{(i)}\middle|\hat{H}_{ring}^{HDVV}\middle|AFM_{(i)}\right\rangle = -\left[A_i^1 \cdot J_1 + A_i^2 \cdot J_2\right] \tag{6}$$

Where J_1 and J_2 are the first and second nearest neighbours exchange coupling constants, respectively. Note that Eq. (6) is just twice Eq. (2).

***2. Linear*:**

Table SI2. Absolute energies (a.u.) and energy differences (cm^{-1}) of FM and AFM_i solutions. N stands for the number of magnetic centres; *i* refers to the number of spin-down centres; AFM_{i^*} refers to a AFM solution with the beta densities at each extremes of the molecule, except for AFM_{i^*} for $N = 10$.

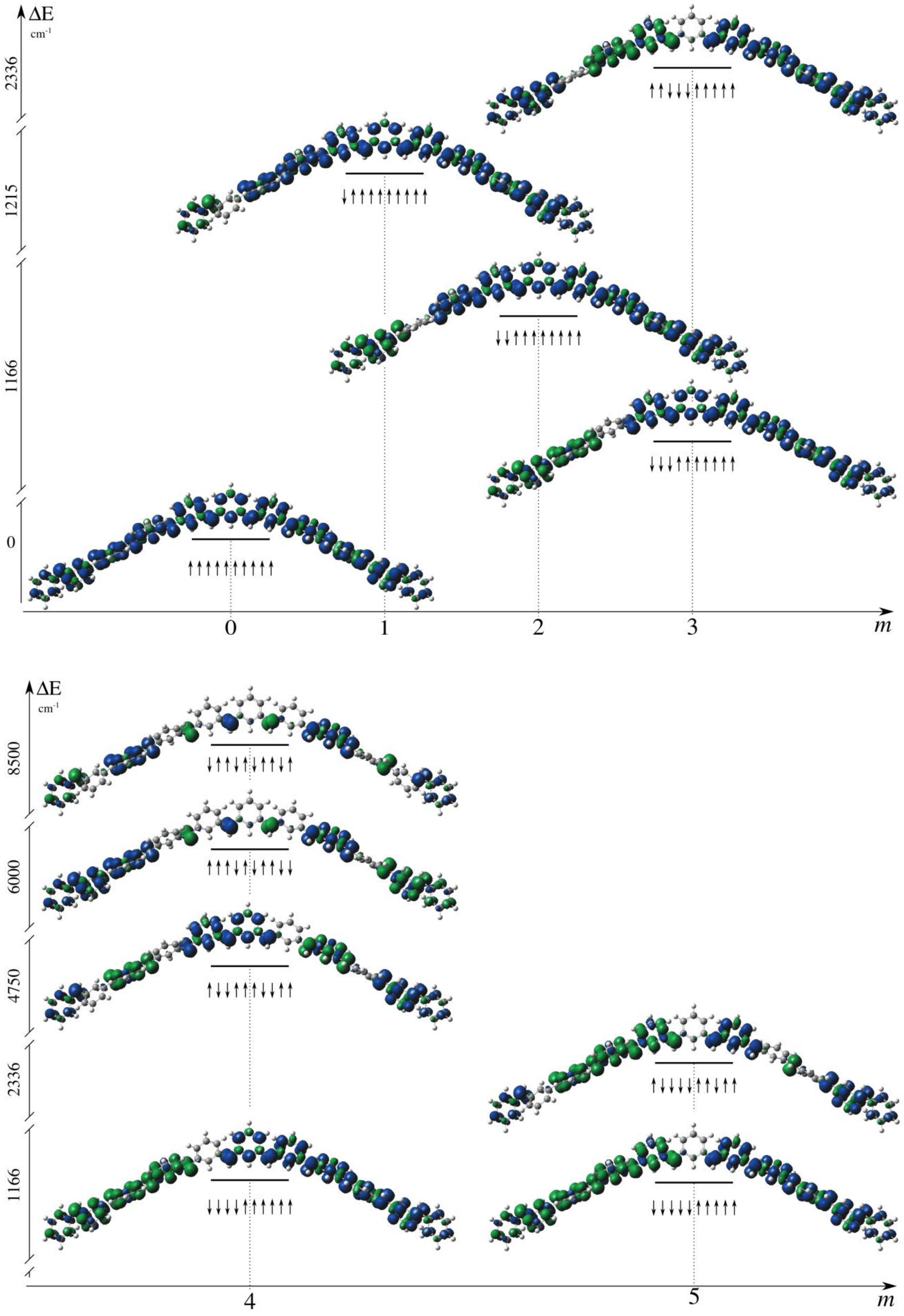
	$N = 4$		$N = 5$		$N = 6$	
	Energy	$\Delta E_{FM-AFM_{(i)}}$	Energy	$\Delta E_{FM-AFM_{(i)}}$	Energy	$\Delta E_{FM-AFM_{(i)}}$
FM	-1311.2931		-1581.0503		-1850.8077	
AFM_1	-1311.2875	-1214	-1581.0448	-1213	-1850.8022	-1212
AFM_2	-1311.2878	-1166	-1581.0450	-1164	-1850.8024	-1166
AFM_3					-1850.8024	-1167
AFM_{2^*}			-1581.0393	-2427	-1850.7966	-2425
AFM_{3^*}					-1850.7969	-2379

	$N = 7$		$N = 8$		$N = 9$	
	Energy	$\Delta E_{FM-AFM_{(i)}}$	Energy	$\Delta E_{FM-AFM_{(i)}}$	Energy	$\Delta E_{FM-AFM_{(i)}}$
FM	-2120.5649		-2390.3223		-2660.0796	
AFM_1	-2120.5594	-1214	-2390.3167	-1217	-2660.0740	-1210
AFM_2	-2120.5596	-1170	-2390.3170	-1166	-2660.0742	-1165
AFM_3	-2120.5596	-1170	-2390.3170	-1162	-2660.0742	-1168
AFM_4			-2390.3170	-1164	-2660.0742	-1165
AFM_{2^*}	-2120.5539	-2425	-2390.3112	-2434	-2660.0685	-2420
AFM_{3^*}	-2120.5541	-2382	-2390.3114	-2383	-2660.0687	-2375
AFM_{4^*}			-2390.3116	-2332	-2660.0689	-2330

	$N = 10$		$N = 12$		$N = 13$	
	Energy	$\Delta E_{FM-AFM_{(i)}}$	Energy	$\Delta E_{FM-AFM_{(i)}}$	Energy	$\Delta E_{FM-AFM_{(i)}}$
FM	-2929.8368		-3469.3514		-3739.1087	
AFM_1	-2929.8313	-1216	-3469.3459	-1215	-3739.1032	-1213
AFM_2	-2929.8315	-1166	-3469.3461	-1167	-3739.1034	-1168
AFM_3	-2929.8315	-1165	-3469.3461	-1163	-3739.1034	-1166
AFM_4	-2929.8315	-1169	-3469.3461	-1168	-3739.1034	-1166
AFM_5	-2929.8315	-1170	-3469.3461	-1169	-3739.1034	-1165
AFM_6			-3469.3461	-1168	-3739.1034	-1167
AFM_{2^*}						
AFM_{3^*}	-2929.8262	-2336				
AFM_{4^*}	-2929.8153	-4716				
AFM_{5^*}	-2929.8151	-4768				
AFM_6						

	$N = 14$	
	Energy	$\Delta E_{FM-AFM_{(i)}}$
FM	-4008.8660	
AFM_1	-4008.8605	-1215
AFM_2	-4008.8607	-1165
AFM_3	-4008.8607	-1169
AFM_4	-4008.8607	-1172
AFM_5	-4008.8607	-1166
AFM_6	-4008.8607	-1164
AFM_7	-4008.8607	-1166

Figure SI1. Density plots (α-blue; β-green) of the different FM and AFM_i ($1 \leq i \leq 5$) found for the linear $N = 10$ case. y-axis represents the energy difference referred to the FM ground state and x-axis the number of carbon-centred radicals with beta density. As observed, each phenyl ring without spin density implies a ~1000 cm^{-1} of destabilization.



3. ***Helical***:

Table SI 3. Absolute energies and energy differences of FM and AFM_i solutions. N stands for the number of magnetic centres; i refers to the number of β centres. $*$ indicates that the corresponding solutions were not obtained.

	$N = 4$		$N = 5$		$N = 6$	
	Energy	$\Delta E_{FM-AFM(i)}$	Energy	$\Delta E_{FM-AFM(i)}$	Energy	$\Delta E_{FM-AFM(i)}$
FM	-1311.3080		-1581.0752		-1850.8424	
AFM_1	-1311.3041	-866	-1581.0710	-928	-1850.8382	-918
AFM_2	-1311.3048	-701	-1581.0714	-825	-1850.8389	-772
AFM_3					-1850.8400	-517
AFM_{1^*}						
AFM_{2^*}			-1581.0662	-1981	-1850.8329	-2078
AFM_{3^*}						

	$N = 7$		$N = 8$		$N = 9$	
	Energy	$\Delta E_{FM-AFM(i)}$	Energy	$\Delta E_{FM-AFM(i)}$	Energy	$\Delta E_{FM-AFM(i)}$
FM	-2120.6105		-2390.37858		-2660.1463	
AFM_1	-2120.6064	-906	-2390.37443	-912	-2660.1422	-920
AFM_2	-2120.6071	-751	-2390.37522	-738	-2660.1425	-853
AFM_3	-2120.6077	-616	$*$	$*$	-2660.1443	-457
AFM_4			$*$	$*$	-2660.1432	-684
AFM_{1^*}			-2390.36955	-1982		
AFM_{2^*}	-2120.6023	-1809	-2390.36927	-2042	-2660.1378	-1837
AFM_{3^*}	-2120.6027	-1712	-2390.37156	-1541	-2660.1286	-3904
AFM_{4^*}			-2390.37218	-1404	-2660.1283	-3967

	$N = 10$		$N = 12$		$N = 13$	
	Energy	$\Delta E_{FM-AFM(i)}$	Energy	$\Delta E_{FM-AFM(i)}$	Energy	$\Delta E_{FM-AFM(i)}$
FM	-2929.9141		-3469.4506		-3739.21864	
AFM_1	$*$	$*$	-3469.4457	-1076	$*$	$*$
AFM_2	$*$	$*$	-3469.4478	-602	$*$	$*$
AFM_3	$*$	$*$	-3469.4478	-596	$*$	$*$
AFM_4	$*$	$*$	-3469.4480	-556	$*$	$*$
AFM_5	$*$	$*$	-3469.4477	-618	$*$	$*$
AFM_6	$*$	$*$	-3469.4482	-527	$*$	$*$
AFM_{1^*}	-2929.9046	-2085			-3739.2096	-1985
AFM_{2^*}	-2929.9062	-1730	-3469.4457	-1076	-3739.2115	-1574
AFM_{3^*}	-2929.9073	-1493	-3469.4365	-3081	-3739.2125	-1352
AFM_{4^*}	-2929.9075	-1452	-3469.4383	-2682	-3739.2134	-1157
AFM_{5^*}	-2929.9077	-1407	-3469.4381	-2742	-3739.2135	-1135
AFM_{6^*}			-3469.4379	-2775	-3739.2131	-1223

	$N = 14$	
	Energy	$\Delta E_{FM-AFM(i)}$
FM	-4008.9865	
AFM_1	$*$	$*$
AFM_2	$*$	$*$
AFM_3	$*$	$*$
AFM_4	$*$	$*$
AFM_5	$*$	$*$
AFM_6	$*$	$*$
AFM_7	$*$	$*$

AFM_{1^*}	-4008.9773	-2031
AFM_{2^*}	-4008.9797	-1510
AFM_{3^*}	-4008.9800	-1439
AFM_{4^*}	-4008.9794	-1575
AFM_{5^*}	-4008.9803	-1362
AFM_{6^*}	-4008.9813	-1159
AFM_{7^*}	-4008.9767	-2155

Now, by taking the case in which $i \geq 4$, for an helix with more than 8 centres, all AFM_i are degenerate according to Eq (3). However, by looking at Table SI3, the entry for $N = 12$ clearly shows that this is not the case. Therefore, one should consider higher order terms like three- or four-body interactions, which is currently under investigation.

In order to facilitate the explanation, we take as an example the case with $N = 9$. For this system, AFM_{2^*}, AFM_{3^*} and AFM_{4^*} correspond to the solutions $|\beta\alpha\alpha\alpha\alpha\alpha\alpha\alpha\beta\rangle$, $|\beta\alpha\alpha\alpha\beta\alpha\alpha\alpha\beta\rangle$ and $|\beta\alpha\alpha\alpha\beta\beta\alpha\alpha\beta\rangle$, respectively. The reported values in the main text have been obtained using the set of equations

$$\langle FM|\hat{H}_{helix}^{HDVV}|FM\rangle - \langle AFM_1|\hat{H}_{helix}^{HDVV}|AFM_1\rangle$$

$$\langle FM|\hat{H}_{helix}^{HDVV}|FM\rangle - \langle AFM_2|\hat{H}_{helix}^{HDVV}|AFM_2\rangle$$

$$\langle FM|\hat{H}_{helix}^{HDVV}|FM\rangle - \langle AFM_{3^*}|\hat{H}_{helix}^{HDVV}|AFM_{3^*}\rangle$$

$$\langle FM|\hat{H}_{helix}^{HDVV}|FM\rangle - \langle AFM_{4^*}|\hat{H}_{helix}^{HDVV}|AFM_{4^*}\rangle$$

It is worth noting that using the different available sets of equations provides a different set of magnetic coupling constants; whereas J_1 and J_2 remain the same, J_3 and J_4 present important variations ranging from -1245 and 454 to -679 and 113 cm^{-1}. Similar variations are also found for the rest of helical structures.

Also, let us highlight the form of AFM_{i^*} solutions for the case of $N = 14$. Assuming the same ordering of radical centres along the molecule, those would be $|\alpha\alpha\alpha\alpha\alpha\alpha\alpha\beta\alpha\alpha\alpha\alpha\alpha\alpha\rangle$, $|\alpha\alpha\alpha\alpha\alpha\alpha\beta\beta\alpha\alpha\alpha\alpha\alpha\alpha\rangle$, $|\alpha\alpha\alpha\alpha\alpha\alpha\beta\beta\beta\alpha\alpha\alpha\alpha\alpha\rangle$, $|\alpha\alpha\alpha\alpha\alpha\beta\beta\beta\beta\alpha\alpha\alpha\alpha\alpha\rangle$, $|\alpha\alpha\alpha\alpha\beta\beta\beta\beta\beta\alpha\alpha\alpha\alpha\alpha\rangle$, $|\alpha\alpha\alpha\alpha\beta\beta\beta\beta\beta\beta\alpha\alpha\alpha\alpha\rangle$ and $|\alpha\alpha\alpha\alpha\beta\beta\beta\beta\beta\beta\alpha\alpha\alpha\beta\rangle$.

Table SI 4 presents the calculated exchange coupling constant values for some representative cases in the series although this is not the main issue here due to the lack of experimental data to compare with. For the linear cases, we consider first and second nearest neighbour interactions ($\langle i, j = i + 1{,}2 \rangle$) whereas for the helical case it is required to include up to the fourth nearest neighbour ($\langle i, j = i + 1{,}2{,}3{,}4 \rangle$). This is due to the corresponding short distance between the magnetic centres in the helix (~5, ~6, ~4 and ~4.5 Å, for 1st, 2nd, 3rd and 4th nearest neighbour respectively). For more detailed information on the different magnetic solutions, the reader is referred to sections 2 and 3 of the supporting information. As observed, the magnetic coupling constants in the linear molecules remain practically the same throughout the series, where J_1 is an order of magnitude larger than J_2 and of opposed sign. These values are also consistent when using AFM solutions that display alternate spin down centres. The situation is less clear for the helical arrangement, as there is a significant variation in the magnitude and sign of the different two body terms with the number of centres. This might indicate possible differential effects associated with odd and even number of unpaired electrons. Additionally, depending on which DFT-computed energies are used to solve the spectrum, one finds a large variation on J_3 and J_4 (see section 3 in the SI). This is consistent with the fact that the topological AFM solutions that should be degenerate according to the present mapping, show considerable splitting when the corresponding solutions are numerically obtained. These results point to the fact that the low-lying magnetic states of these helical structures cannot be described by the simple HDVV model spin Hamiltonian. A more accurate description would then require including higher order terms in the spin model Hamiltonian such as four body terms, and perhaps anisotropic D tensor to account for the spin-spin contribution to magnetic anisotropy. The crucial point here is, however, the consistent prediction of a helical-induced stabilization of the FM ground state in all cases that can be safely addressed considering the HDVV spin model Hamiltonian to classify and compare the different spin solutions.

Table SI 4. Energy difference (in cm^{-1}) between the FM ground state and lowest excited AFM solutions, calculated per number of magnetic centres (N) in each of the linear and helical minima. Middle column shows the stabilization energy (in kcal mol^{-1}) per magnetic centre gained when the helical conformation is adopted as compared to the linear arrangement. Rightmost column presents the calculated magnetic coupling constants (in cm^{-1}) for both linear and helical systems. * indicates that solutions with all consecutive spin-down in one of the chain extremes were not converged.

	ΔE_{FM-AFM}		Helical stabilization	linear		helical			
N	linear	helical		J_1	J_2	J_1	J_2	J_3	J_4
4	-291	-175	2.3						
5	-283	-165	3.1	2525	-98	2630	-546	341	-568
6	-194	-86	3.6	2516	-92	2879	-672	-511	516
7	-167	-88	4.1	2514	-87				
8	-145	*	4.4	2535	-101	2170	459	-489	-318
9	-130	-51	4.7	2510	-90	1972	50	-70	-113
10	-117	*	4.9	2530	-99				
12	-97	-44	5.2	2524	-95	3100	-938	69	-80
13	-90	*	5.3	2517	-91				
14	-83	*	5.4	2528	-99	2552	-450	-207	136

4. Ring

Table SI 5. Absolute energies (a.u.) and energy differences (cm^{-1}) of FM and AFM_i solutions for each of the lowest in energy stationary points. N stands for the number of magnetic centres; *i* refers to the number of β centres.

	$N = 4$		$N = 5$		$N = 6$	
	Energy	$\Delta E_{FM-AFM_{(i)}}$	Energy	$\Delta E_{FM-AFM_{(i)}}$	Energy	$\Delta E_{FM-AFM_{(i)}}$
FM	-1079.02150		-1348.7816		-1618.5418	
AFM_1	-1079.01078	-2353	-1348.7699	-2557	-1618.5315	-2264
AFM_2	-1079.011076	-2287	-1348.7727	-1936	-1618.5302	-2541
AFM_3					-1618.5318	-2206
AFM_{2^*}	-1078.999431	-4843				
AFM_{3^*}						

	$N = 7$		$N = 8$		$N = 9$	
	Energy	$\Delta E_{FM-AFM_{(i)}}$	Energy	$\Delta E_{FM-AFM_{(i)}}$	Energy	$\Delta E_{FM-AFM_{(i)}}$
FM	-1888.293495		-2158.05793		-2427.796774	
AFM_1	-1888.281783	-2570	-2158.04740	-2311	-2427.785624	-2447
AFM_2	-1888.283687	-2153	-2158.04750	-2289	-2427.786289	-2301
AFM_3	-1888.284999	-1865	-2158.04760	-2267	-2427.787405	-2056
AFM_4			-2158.04707	-2384	-2427.786822	-2184
AFM_{2^*}	-1888.271828	-4756	-2158.03704	-4586		
AFM_{3^*}			-2158.03636	-4735		
AFM_{4^*}						

	$N = 10$		$N = 12$		$N = 15$	
	Energy	$\Delta E_{FM-AFM_{(i)}}$	Energy	$\Delta E_{FM-AFM_{(i)}}$	Energy	$\Delta E_{FM-AFM_{(i)}}$
FM	-2697.573153		-3237.067639		-4046.337946	
AFM_1	-2697.562049	-2437	-3237.056248	-2500	-4046.326924	-2419
AFM_2	-2697.5633	-2162	-3237.056267	-2496	-4046.327283	-2340
AFM_3	-2697.563797	-2053	-3237.057781	-2164	-4046.328854	-1995
AFM_4	-2697.563176	-2190	-3237.057929	-2131	-4046.328104	-2160
AFM_5	-2697.563564	-2104	-3237.056682	-2405	-4046.328079	-2166
AFM_6			-3237.055433	-2679	-4046.327891	-2207
AFM_7					-4046.327851	-2216
AFM_{2^*}	-2697.55178	-4691			-4046.316079	-4799
AFM_{3^*}	-2697.552322	-4572	-3237.046241	-4696	-4046.308293	-6508
AFM_{4^*}	-2697.552789	-4469	-3237.036897	-6747	-4046.307541	-6673
AFM_{5^*}	-2697.553652	-4280	-3237.025269	-9299	-4046.305886	-7036
AFM_{6^*}			-3237.024709	-9422	-4046.30753	-6675
$AFM_{6^{**}}$					-4046.318734	-4217
AFM_{7^*}					-4046.318686	-4227

Table SI 6. Specification of the determinants and corresponding HDVV expressions associated with each of the ferro- and antiferromagnetic solutions for the cases with 4, 7, 10 and 15 radical centres, for which exchange coupling constants are discussed in the main text. α stands for spin-up and β for spin-down (positive and negative spin densities at each of the radical centres respectively. These expressions are to be compared with the calculated absolute energies presented in Table SI4.

	$N = 4$		$N = 7$	
	Function $\|i\rangle$	$\langle i\|\hat{H}_{ring}^{HDVV}\|i\rangle$	Function $\|i\rangle$	$\langle i\|\hat{H}_{ring}^{HDVV}\|i\rangle$
FM	$\|\alpha\alpha\alpha\alpha\rangle$	$-J_1 - J_2$	$\|\alpha\alpha\alpha\alpha\alpha\alpha\alpha\rangle$	$-7/4J_1 - 7/4J_2$
AFM_1	$\|\beta\alpha\alpha\alpha\rangle$	0	$\|\beta\alpha\alpha\alpha\alpha\alpha\alpha\rangle$	$-3/4J_1 - 3/4J_2$
AFM_2	$\|\beta\beta\alpha\alpha\rangle$	$-J_2$	$\|\beta\beta\alpha\alpha\alpha\alpha\alpha\rangle$	$-3/4J_1 + 1/4J_2$
AFM_3			$\|\beta\beta\beta\alpha\alpha\alpha\alpha\rangle$	$-3/4J_1 + 1/4J_2$
AFM_{2^*}	$\|\beta\alpha\beta\alpha\rangle$	$+J_1 - J_2$	$\|\beta\alpha\beta\alpha\alpha\alpha\alpha\rangle$	$+1/4J_1 - 3/4J_2$

	$N = 10$		$N = 15$	
	Function $\|i\rangle$	$\langle i\|\hat{H}_{ring}^{HDVV}\|i\rangle$	Function $\|i\rangle$	$\langle i\|\hat{H}_{ring}^{HDVV}\|i\rangle$
FM	$\|\alpha\alpha\alpha\alpha\alpha\alpha\alpha\alpha\alpha\alpha\rangle$	$-10/4J_1 - 10/4J_2$	$\|\alpha\alpha\alpha\alpha\alpha\alpha\alpha\alpha\alpha\alpha\alpha\alpha\alpha\alpha\alpha\rangle$	$-15/4J_1 - 15/4J_2$
AFM_1	$\|\beta\alpha\alpha\alpha\alpha\alpha\alpha\alpha\alpha\alpha\rangle$	$-6/4J_1 - 6/4J_2$	$\|\beta\alpha\alpha\alpha\alpha\alpha\alpha\alpha\alpha\alpha\alpha\alpha\alpha\alpha\alpha\rangle$	$-11/4J_1 - 11/4J_2$
AFM_2	$\|\beta\beta\alpha\alpha\alpha\alpha\alpha\alpha\alpha\alpha\rangle$	$-6/4J_1 - 2/4J_2$	$\|\beta\beta\alpha\alpha\alpha\alpha\alpha\alpha\alpha\alpha\alpha\alpha\alpha\alpha\alpha\rangle$	$-11/4J_1 - 7/4J_2$
AFM_3	$\|\beta\beta\beta\alpha\alpha\alpha\alpha\alpha\alpha\alpha\rangle$	$-6/4J_1 - 2/4J_2$	$\|\beta\beta\beta\alpha\alpha\alpha\alpha\alpha\alpha\alpha\alpha\alpha\alpha\alpha\alpha\rangle$	$-11/4J_1 - 7/4J_2$
AFM_4	$\|\beta\beta\beta\beta\alpha\alpha\alpha\alpha\alpha\alpha\rangle$	$-6/4J_1 - 2/4J_2$	$\|\beta\beta\beta\beta\alpha\alpha\alpha\alpha\alpha\alpha\alpha\alpha\alpha\alpha\alpha\rangle$	$-11/4J_1 - 7/4J_2$
AFM_5	$\|\beta\beta\beta\beta\beta\alpha\alpha\alpha\alpha\alpha\rangle$	$-6/4J_1 - 2/4J_2$	$\|\beta\beta\beta\beta\beta\alpha\alpha\alpha\alpha\alpha\alpha\alpha\alpha\alpha\alpha\rangle$	$-11/4J_1 - 7/4J_2$
AFM_6			$\|\beta\beta\beta\beta\beta\beta\alpha\alpha\alpha\alpha\alpha\alpha\alpha\alpha\alpha\rangle$	$-11/4J_1 - 7/4J_2$
AFM_7			$\|\beta\beta\beta\beta\beta\beta\beta\alpha\alpha\alpha\alpha\alpha\alpha\alpha\alpha\rangle$	$-11/4J_1 - 7/4J_2$
AFM_{2^*}	$\|\beta\alpha\alpha\alpha\alpha\beta\alpha\alpha\alpha\alpha\rangle$	$-2/4J_1 - 2/4J_2$	$\|\beta\alpha\alpha\beta\alpha\alpha\alpha\alpha\alpha\alpha\alpha\alpha\alpha\alpha\alpha\rangle$	$-7/4J_1 - 7/4J_2$
AFM_{3^*}	$\|\beta\beta\alpha\alpha\alpha\alpha\alpha\beta\alpha\alpha\rangle$	$-2/4J_1 + 2/4J_2$	$\|\beta\alpha\alpha\beta\alpha\beta\alpha\alpha\alpha\alpha\alpha\alpha\alpha\alpha\alpha\rangle$	$-3/4J_1 - 7/4J_2$
AFM_{4^*}	$\|\beta\beta\beta\alpha\alpha\beta\alpha\alpha\alpha\alpha\rangle$	$-2/4J_1 + 2/4J_2$	$\|\beta\alpha\beta\alpha\alpha\beta\beta\alpha\alpha\alpha\alpha\alpha\alpha\alpha\alpha\rangle$	$-3/4J_1 - 3/4J_2$
AFM_{5^*}	$\|\beta\beta\beta\alpha\alpha\alpha\beta\beta\alpha\alpha\rangle$	$-2/4J_1 + 6/4J_2$	$\|\beta\alpha\beta\beta\alpha\alpha\alpha\beta\beta\alpha\alpha\alpha\alpha\alpha\alpha\rangle$	$-3/4J_1 + 1/4J_2$
AFM_{6^*}			$\|\beta\beta\beta\alpha\alpha\alpha\beta\alpha\alpha\alpha\beta\beta\alpha\alpha\alpha\rangle$	$-3/4J_1 + 5/4J_2$
$AFM_{6^{**}}$			$\|\beta\beta\beta\alpha\beta\beta\beta\alpha\alpha\alpha\alpha\alpha\alpha\alpha\alpha\rangle$	$-7/4J_1 - 3/4J_2$
AFM_{7^*}			$\|\beta\beta\beta\alpha\beta\beta\beta\beta\alpha\alpha\alpha\alpha\alpha\alpha\alpha\rangle$	$-7/4J_1 - 3/4J_2$

Table SI 7. Exchange coupling constants extracted from different sets of equations for the cases with 4, 7, 10 and 15 radical centres.

$N =$	Expression used	J_1	J_2
4	$\langle FM\|\hat{H}_{ring}^{HDVV}\|FM\rangle - \langle AFM_1\|\hat{H}_{ring}^{HDVV}\|AFM_1\rangle$ $\langle FM\|\hat{H}_{ring}^{HDVV}\|FM\rangle - \langle AFM_2\|\hat{H}_{ring}^{HDVV}\|AFM_2\rangle$	2287	65
	$\langle FM\|\hat{H}_{ring}^{HDVV}\|FM\rangle - \langle AFM_1\|\hat{H}_{ring}^{HDVV}\|AFM_1\rangle$ $\langle FM\|\hat{H}_{ring}^{HDVV}\|FM\rangle - \langle AFM_{2^*}\|\hat{H}_{ring}^{HDVV}\|AFM_{2^*}\rangle$	2422	-70
7	$\langle FM\|\hat{H}_{ring}^{HDVV}\|FM\rangle - \langle AFM_1\|\hat{H}_{ring}^{HDVV}\|AFM_1\rangle$ $\langle FM\|\hat{H}_{ring}^{HDVV}\|FM\rangle - \langle AFM_2\|\hat{H}_{ring}^{HDVV}\|AFM_2\rangle$	2987	-417
	$\langle FM\|\hat{H}_{ring}^{HDVV}\|FM\rangle - \langle AFM_1\|\hat{H}_{ring}^{HDVV}\|AFM_1\rangle$ $\langle FM\|\hat{H}_{ring}^{HDVV}\|FM\rangle - \langle AFM_3\|\hat{H}_{ring}^{HDVV}\|AFM_3\rangle$	3275	-705
	$\langle FM\|\hat{H}_{ring}^{HDVV}\|FM\rangle - \langle AFM_1\|\hat{H}_{ring}^{HDVV}\|AFM_1\rangle$ $\langle FM\|\hat{H}_{ring}^{HDVV}\|FM\rangle - \langle AFM_{2^*}\|\hat{H}_{ring}^{HDVV}\|AFM_{2^*}\rangle$	2186	384
10	$\langle FM\|\hat{H}_{ring}^{HDVV}\|FM\rangle - \langle AFM_1\|\hat{H}_{ring}^{HDVV}\|AFM_1\rangle$ $\langle FM\|\hat{H}_{ring}^{HDVV}\|FM\rangle - \langle AFM_2\|\hat{H}_{ring}^{HDVV}\|AFM_2\rangle$	2712	-275
	$\langle FM\|\hat{H}_{ring}^{HDVV}\|FM\rangle - \langle AFM_1\|\hat{H}_{ring}^{HDVV}\|AFM_1\rangle$ $\langle FM\|\hat{H}_{ring}^{HDVV}\|FM\rangle - \langle AFM_3\|\hat{H}_{ring}^{HDVV}\|AFM_3\rangle$	2821	-384
	$\langle FM\|\hat{H}_{ring}^{HDVV}\|FM\rangle - \langle AFM_1\|\hat{H}_{ring}^{HDVV}\|AFM_1\rangle$ $\langle FM\|\hat{H}_{ring}^{HDVV}\|FM\rangle - \langle AFM_4\|\hat{H}_{ring}^{HDVV}\|AFM_4\rangle$	2684	-247
	$\langle FM\|\hat{H}_{ring}^{HDVV}\|FM\rangle - \langle AFM_1\|\hat{H}_{ring}^{HDVV}\|AFM_1\rangle$ $\langle FM\|\hat{H}_{ring}^{HDVV}\|FM\rangle - \langle AFM_{3^*}\|\hat{H}_{ring}^{HDVV}\|AFM_{3^*}\rangle$	2739	-302
	$\langle FM\|\hat{H}_{ring}^{HDVV}\|FM\rangle - \langle AFM_1\|\hat{H}_{ring}^{HDVV}\|AFM_1\rangle$ $\langle FM\|\hat{H}_{ring}^{HDVV}\|FM\rangle - \langle AFM_{5^*}\|\hat{H}_{ring}^{HDVV}\|AFM_{5^*}\rangle$	2734	-297
15	$\langle FM\|\hat{H}_{ring}^{HDVV}\|FM\rangle - \langle AFM_1\|\hat{H}_{ring}^{HDVV}\|AFM_1\rangle$ $\langle FM\|\hat{H}_{ring}^{HDVV}\|FM\rangle - \langle AFM_2\|\hat{H}_{ring}^{HDVV}\|AFM_2\rangle$	2498	-79
	$\langle FM\|\hat{H}_{ring}^{HDVV}\|FM\rangle - \langle AFM_1\|\hat{H}_{ring}^{HDVV}\|AFM_1\rangle$ $\langle FM\|\hat{H}_{ring}^{HDVV}\|FM\rangle - \langle AFM_{3^*}\|\hat{H}_{ring}^{HDVV}\|AFM_{3^*}\rangle$	1670	749
	$\langle FM\|\hat{H}_{ring}^{HDVV}\|FM\rangle - \langle AFM_1\|\hat{H}_{ring}^{HDVV}\|AFM_1\rangle$ $\langle FM\|\hat{H}_{ring}^{HDVV}\|FM\rangle - \langle AFM_{5^*}\|\hat{H}_{ring}^{HDVV}\|AFM_{5^*}\rangle$	2640	-221
	$\langle FM\|\hat{H}_{ring}^{HDVV}\|FM\rangle - \langle AFM_1\|\hat{H}_{ring}^{HDVV}\|AFM_1\rangle$ $\langle FM\|\hat{H}_{ring}^{HDVV}\|FM\rangle - \langle AFM_{6^*}\|\hat{H}_{ring}^{HDVV}\|AFM_{6^*}\rangle$	2710	-291
	$\langle FM\|\hat{H}_{ring}^{HDVV}\|FM\rangle - \langle AFM_1\|\hat{H}_{ring}^{HDVV}\|AFM_1\rangle$ $\langle FM\|\hat{H}_{ring}^{HDVV}\|FM\rangle - \langle AFM_{6^{**}}\|\hat{H}_{ring}^{HDVV}\|AFM_{6^{**}}\rangle$	3040	-621

Note that for any N, according to HDVV the different AFM solutions showing an increasing number of consecutive β densities are degenerate. However, the calculated energies presented in Table S. I. 4 indicate that there are ~300 cm^{-1} deviations, which translates into the different J values in Table S. I. 6. This is most likely due to the assumption that the distance between second neighbours is constant, which is not always true.

Table SI 8. Exchange coupling constants (cm^{-1}) calculated on the different local minima for the circular arrangement.

N	J_1	J_2	J_1	J_2	J_1	J_2	J_1	J_2
	1		**2**		**3**		**4**	
4	2422	-70						
5	3179	-621						
6	2323	-59	901	-370				
7	2987	-417	1882	-229				
8	2333	-22	2566	-124	1770	172		
9	2593	-146	1325	519	1222	427	1451	466
10	2712	-275						
12	2504	-4						
15	2498	-79						

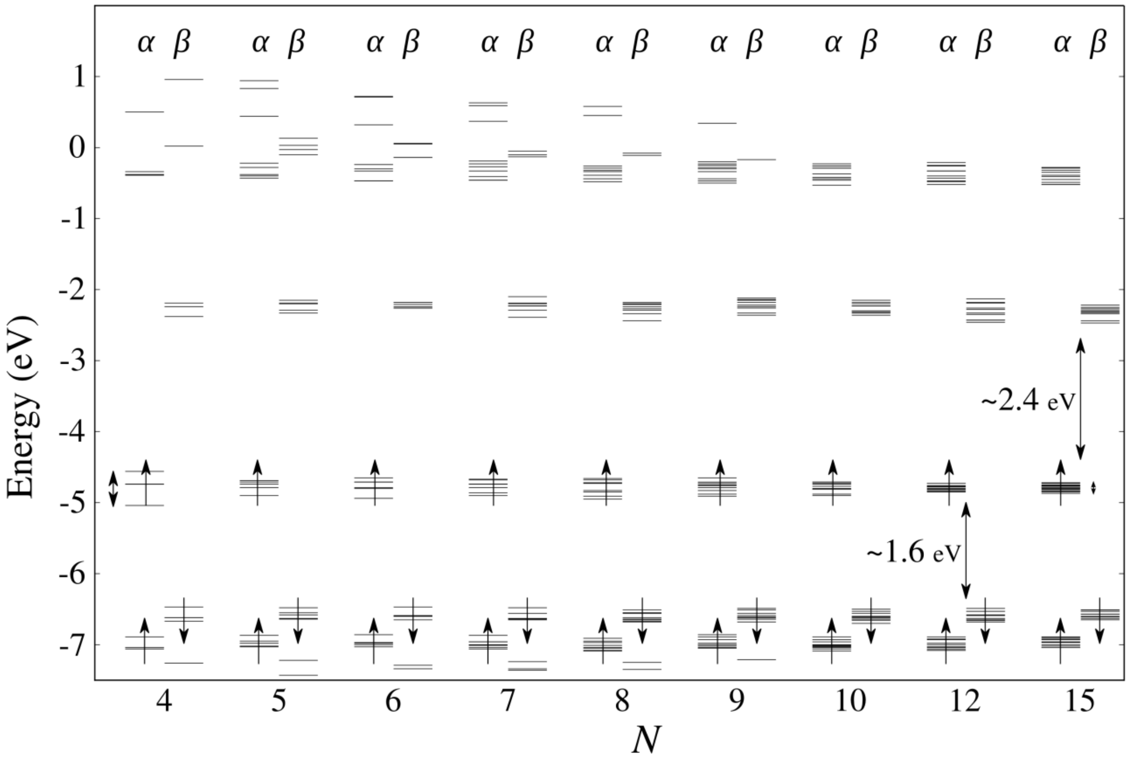
Table SI 9. Energy difference (in cm^{-1}) between the ferromagnetic ground state (FM) and lowest excited antiferromagnetic (AFM) solutions, calculated per number of magnetic centres (N) for the differently substituted ring systems. The characterized minima are indicated in bold. Middle column shows the energy difference (in kcal mol^{-1}) between the different minima for a given ring with N magnetic centres, being minimum **1** the lowest in energy. Rightmost columns presents the calculated magnetic coupling constants (in cm^{-1}) for the lowest energy minima.

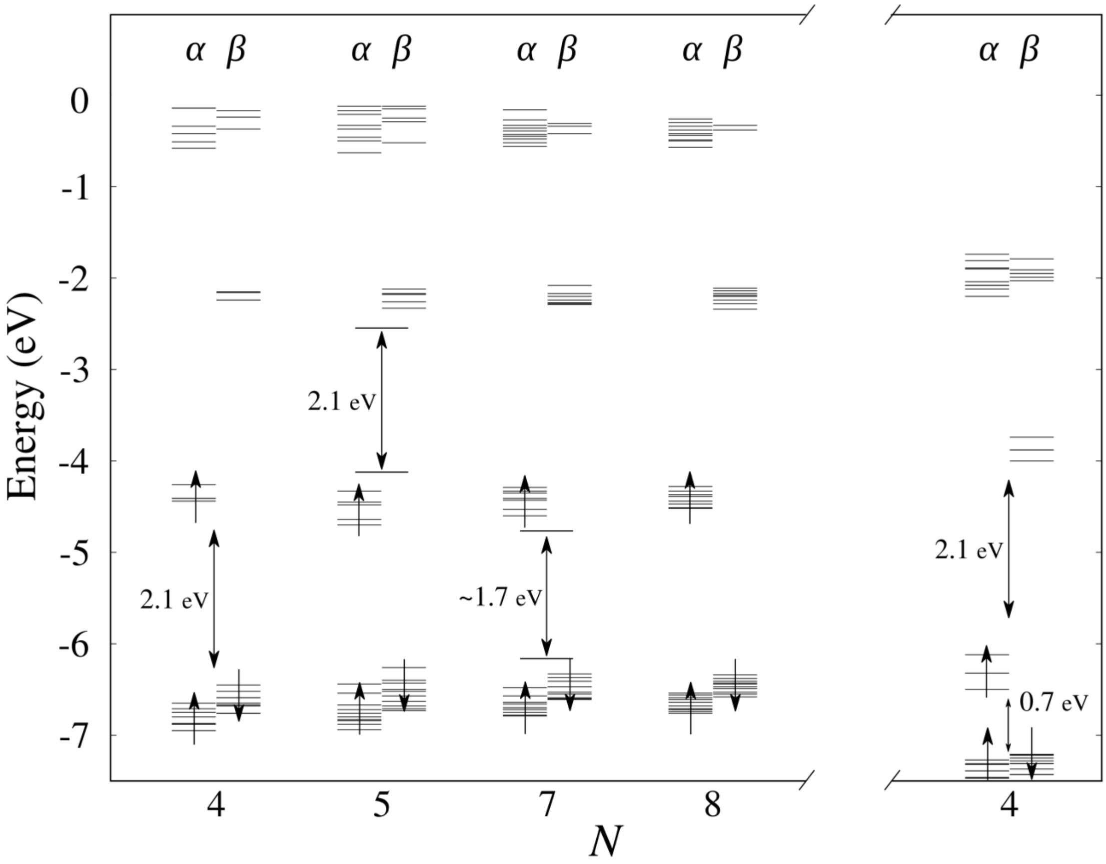
	ΔE_{FM-AFM} (cm^{-1})				ΔE between minima (Kcalmol^{-1})				
								J_1	J_2
N	**1**	**2**	**3**	**4**	**1 → 2**	**1 → 3**	**1 → 4**	**1**	
a)	$R = H$ or arylmethyl-derivatives								
4	-572							2422	-70
5	-387	-454	-353		-8.2	-17.0		3179	-621
6	-367	-27			-17.5			2323	-59
7	-266	-203			-35.2			2987	-417
8	-283	-270	-269	-209	-1.3	-24.0	-34.2	2333	-22
9	-228	-205	-184	-213	-1.0	-6.6	-17.4	2593	-146
10	-205	-233	-180		-1.1	-25.6		2712	-275
12	-178							2504	-4
15	-133							2498	-79
b)	$R = Phenyl$ or triphenylmethyl-derivatives								
4	-256	-34.5			-15.8			1078	-26
5	-236								
7	-120	-44	-217		-8.7	-22.2		800	40
8	-156							1637	-60
c)	PTM-derivatives								
4	-106	-34			-15.8			429	-4

Table SI 10. Energy difference (in cm^{-1}) between the ferromagnetic ground state (FM) and lowest excited antiferromagnetic (AFM) solutions, calculated per number of magnetic centres (N) for the ring type systems. The characterized minima are indicated in bold. For the lowest energy minima, magnetic coupling constants (in cm^{-1}) are also presented. Rightmost column shows the energy difference (in kcal mol^{-1}) between the different minima for a given ring with N magnetic centres, being minimum **1** the lowest in energy.

N	ΔE_{FM-AFM}				J_1	J_2	ΔE between minima		
	1	**2**	**3**	**4**	**1**		**1 → 2**	**1 → 3**	**1 → 4**
4	-572				2422	-70			
5	-387	-454	-353		3179	-621	-8.2	-17.0	
6	-367	-27			2323	-59	-17.5		
7	-266	-203			2987	-417	-35.2		
8	-283	-270	-269	-209	2333	-22	-1.3	-24.0	-34.2
9	-228	-205	-184	-213	2593	-146	-1.0	-6.6	-17.4
10	-205	-233	-180		2712	-275	-1.1	-25.6	
12	-178				2504	-4			
15	-133				2498	-79			

Figure SI2. Energy diagram showing the relative position of the molecular orbitals for the lowest in energy structures found. *N* represents the number of radical centres in the ring-like structures.





5. Effect of functional and basis set: the case of 7-membered ring.

For the 7-centres ring, we have investigated the effect of the functional on the predicted structures and the energy differences between the ferro- and the relevant antiferromagnetic solutions. For the latter, we have also studied the impact introduced by a triple-ζ polarized quality basis set. Table SI 11 presents the results.

Table SI 11. a) RMDS values in Å comparing the predicted optimized geometries by the different functionals with respect B3LYP, using a 6-31G(d,p) basis set, for minimum **1**. The following three lines indicate the energy difference in cm^{-1} between the ferro- and the antiferromagnetic solutions with consecutive β-spin densities obtained with 6-31G(d,p) / cc-pVTZ basis sets. Last row indicates the energy difference per number of magnetic centres in cm^{-1} between the ground ferromagnetic state and the lowest in energy antiferromagnetic solution. b) RMDS values in Å comparing the predicted optimized geometries by the different functionals with respect B3LYP, using a 6-31G(d,p) basis set, for minimum **2**. Last row indicates the energy difference in Kcal/mol between the predicted local minima **1** to **2**, as predicted by the different functionals with the 6-31G(d,p) basis set.

a)

1					
	B3LYP	TPSS	PBE0	M06-2X	LC-ωPBE
RMSD	-	0.06	0.02	0.08	0.05
ΔE_{FM-AFM_1}	-2570	-1765 / -1733	-3025 / -2933	-2230 / -2264	-5027 / *
ΔE_{FM-AFM_2}	-2153	-1713 / -1682	-2504 / -2433	-1776 / -1800	-4002 / *
ΔE_{FM-AFM_3}	-1865	-1498 / -1477	-2144 / -2088	-1501 / -1520	-3356 / *
Per centre	-266	-214 / -211	-306 / -298	-214 / -217	-479 / *

b)

2					
RMSD	-	0.07	0.06	0.19	0.26
ΔE **1** → **2**	-35.2	-33.8	-35.4	-35.2	-35.1