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Theoretical Study of Very High Spin Organic π-Conjugated Polyradicals[†]

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Different forms of π-conjugated polyarylmethyl systems, such as diradicals, polyradicals, spin clusters, and polymers, were studied with valence bond (VB) calculations within the density matrix renormalization group (DMRG) framework. For these systems, the energy gap between the high-spin ground state and the lowest low-spin excited state ($\Delta E_{\mathrm{L-H}}$) was computed and found to correlate well with their stability. On the basis of our analysis, medium-sized polyarylmethyl cycles are suggested to be potential key building blocks of very high spin spin clusters and polymers.

I. Introduction

The discovery of a high-spin ground state in dicarbene[1,2] in the late 1960s signaled the beginning of an attractive research field—organic molecular magnet design. From a theoretical point of view, in this design, one aims at strong couplings between unpaired electrons through the exchange interaction, which is needed (a) to attain a magnetic ordering for the unpaired electrons and (b) to preserve this magnetic ordering at (or even above) room temperature. Many ferro- and ferrimagnets are based on the couplings between s and p orbitals, such as the crystalline solids of small radicals (nitroxides especially) or charge-transfer salts.[3−9]

Alternatively, one can turn to the coupling between unpaired π electrons in organic conjugated systems.[10] Compared with the through-space interactions (between s and p orbitals) in molecular solids of organic radicals, the exchange interaction between unpaired electrons through a π-conjugated system is expected to be stronger, thus opening the possibility of better preserving the magnetic ordering at or above room temperature.[11] Accordingly, there has been a lot of interest in the molecular design of very high spin π-conjugated polyradical molecules and polymers in recent years.[11−36]

For a period of time, the design of very high spin conjugated organic molecular magnets had been hindered by their chemical instability or by structural defects in the polyradical systems generated during the synthesis process. These structural defects can break the radical coupling paths and reduce the whole system into weakly coupled smaller groups, each with a very small magnetic moment. The situation was significantly improved several years ago by Rajca and his colleagues, who successfully synthesized a series of polyarylmethyl polymers with very large magnetic moments (spin quantum number S can be as high as 5000).[25] Their carefully designed polymers are believed to supply a network with multiple coupling channels between the radical centers, thus suppressing the structural defect effect. Of course, having such a multichannel polymer network alone does not lead us toward a stable high-spin organic magnet. It is also important, as stressed earlier, to have strong coupling between radical centers, which, for a given system, can depend on the actual topology of its network, the functional groups on its network backbone, the side chains, and so forth.

Today, it is well-established that theoretical studies can be very helpful in the understanding of the chemical and physical properties of molecular systems. The spin multiplicity of the molecular ground state and its stability with respect to the low-lying excited states are analyzed routinely through the use of many commercial theoretical chemistry software packages. A quantity of particular concern is $\Delta E_{\mathrm{L-H}}$, which is the energy difference between the high-spin ground state and the lowest-energy low-spin excited state. This energy difference is often utilized to estimate the spin-coupling strength between the neighboring radicals. When the energy gap is small enough (typically less than 1 kcal/mol), it is believed that a fast equilibrium can be achieved between the two spin states, causing both states to contribute significantly to the observed physical and chemical properties.

Since the 1980s, much theoretical work has been published characterizing the ferromagnetic or antiferromagnetic coupling in π-conjugated polyradical molecules.[37−58] Nevertheless, it is still computationally challenging to quantitatively predict $\Delta E_{\mathrm{L-H}}$ for medium- to large-size polyradicals. At one end, high-level ab initio calculations can, in principle, provide the most reliable information, but due to their prohibitive computational cost, they are often not applicable to medium- to large-size molecules. Next one can resort to computationally more-feasible methods, such as the spin-unrestricted Hartree−Fock (HF) or density functional theory (DFT) methods. However, for high-spin systems, both HF and DFT often suffer from the spin-contamination problem, which makes it difficult to resolve different spin states. A practical alternative is the semiempirical valence bond (VB) theory, which has been well-recognized in the studies of π-conjugated organic radicals[37,55−57] because it has a much lower cost than that of high-level correlation methods and because there is no spin contamination. Although it is a semiempirical model, the VB theory can correctly predict the topological dependence of the ferromagnetic spin-coupling strength for a series of medium-size bi- and polyradicals.[55−57] Unfortunately, it can still be quite costly to directly solve the VB Hamiltonian for large systems due to the explosive increase of the dimension of the configuration space.[59,60] For larger

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molecules, one has to utilize one numerical technique or another to approximately solve the VB Hamiltonian. Popular numerical techniques include (a) truncation of the configuration space through random selection (such as in the quantum Monte Carlo method[61]) or according to the additivity and locality in chemical systems (such as in the elongation method),[62,63] (b) linear-scaling quantum chemistry methods,[64] (c) density matrix renormalization group methods,[65,66] and so forth.

The density matrix renormalization group (DMRG) method[65,66] has been proven to be extremely successful in solving the many-electron models for one-dimensional or quasi-one-dimensional systems[67] and has been incorporated into the VB model to study polyacenes, polyphenanthrenes, and other one-dimensional benzenoid hydrocarbons of medium to infinite sizes by our group.[68,69] In the present work, we extend our VB studies to high-spin conjugated organic polyradical molecules with up to hundreds of carbon atoms.

II. Computational Methodology

A. Valence Bond Hamiltonian. The classical VB model used in conjugated systems can be written as

$$H = \sum_{\langle ij\rangle} J\left(2S_iS_j - \frac{1}{2}\right) \tag{1}$$

where $\langle ij\rangle$ denotes summation restricted to a bonded atom pair in the π-conjugated backbone of the molecule, S_i represents the spin operator of the ith site, and J is an (positive) empirical exchange parameter with variant values for different molecules, typically about 1−4 eV.[68,70,71,73] The wave function can be written as a linear combination of Slater determinants of atomic states limited to the subspace of the conserved z-component of total spin, namely

$$\Psi = \sum_i c_i \psi_i \tag{2}$$

We note that Malrieu and co-workers introduced fourth- and sixth-order corrections to the above VB Hamiltonian and found such corrections to be quite useful to describe small conjugated molecules, especially those containing four-membered rings.[70,71] Meanwhile, such high-order corrections become much less effective as the system size increases.[72,73] As we intend to carry out a systematic investigation of medium- to large-size systems, we choose to stick to the classic VB model in eq 1.

B. Density Matrix Renormalization Group Method. The real-space DMRG method is an extremely effective and accurate technique for solving strongly correlated Hamiltonians. It has been demonstrated and widely accepted that the accuracy of the DMRG can be comparable to exact calculations for one-dimensional or quasi-one-dimensional systems.[67] Here, we give a very brief description of the technique.

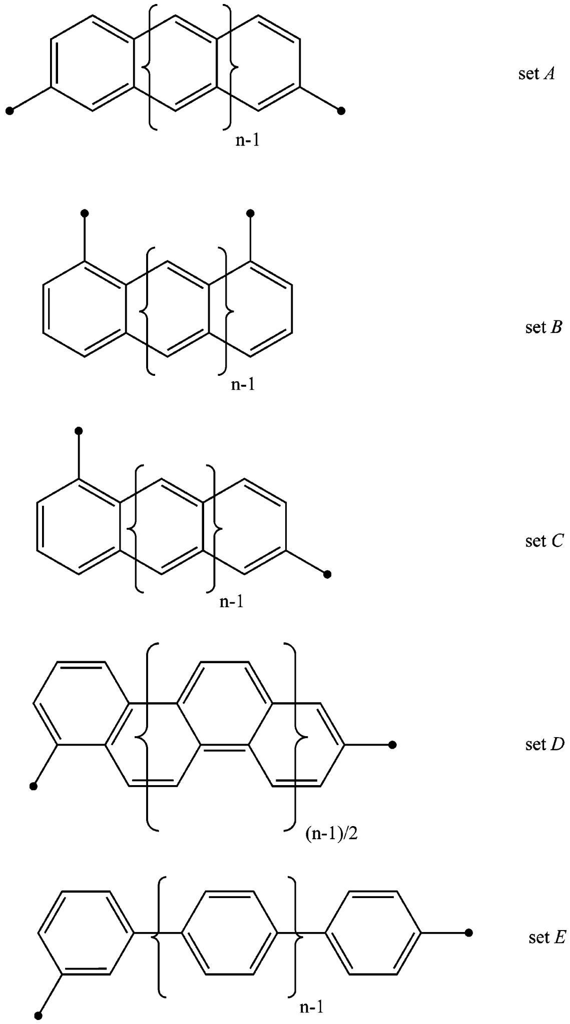

Figure 1. Diradicals.

TABLE 1: Calculated Singlet−Triplet Energy Gaps ΔE_{ST} (in Units of *J*) for Selected Diradical Systems in Figure 1

	1	2	3	4	5	6	7	8
set A	0.522	0.390	0.298	0.232	0.184	0.146	0.117	0.094
set B	0.560	0.388	0.289	0.224	0.176	0.140	0.114	0.092
set C	0.530	0.386	0.292	0.226	0.180	0.143	0.115	0.094
set D	0.528	0.366	0.256	0.182	0.130	0.094	0.069	0.050
set E	0.240	0.098	0.042	0.018	0.008			

The DMRG method is very similar to Wilson's numerical renormalization group method,[74] in which a limited number of bases of the fragments of a system is retained for later computation of larger systems. However, they are dramatically different when it comes to which bases to keep for the best reproduction of the properties of the larger system. In the numerical renormalization group method, the eigenstates corresponding to the lowest eigenvalues in the fragment are retained, which implies that the interaction of the environment with this fragment is completely neglected. This approximation leads to the failure of the numerical renormalization method in handling correlation models. In DMRG, the interaction between different fragments is taken into account by always handling a "superblock" AB, which is composed of a "system block" A and an "environment block" B connected by one or more conjugated bonds.

Given a specific state for the superblock

$$\Psi = \sum_{ij} \psi_{ij} |i\rangle |j\rangle \tag{3}$$

where $|i\rangle$'s are bases for the system block and $|j\rangle$'s are bases for the environment block, we can define a reduced density matrix ρ, where the elements are defined as

$$\rho_{ii'} = \sum_j \psi_{ij} \psi_{i'j} \tag{4}$$

The importance of each basis in the system block can be analyzed through diagonalizing this reduced density matrix. Following the definition of the density matrix, the eigenvectors corresponding to larger eigenvalues of density matrix ρ are the

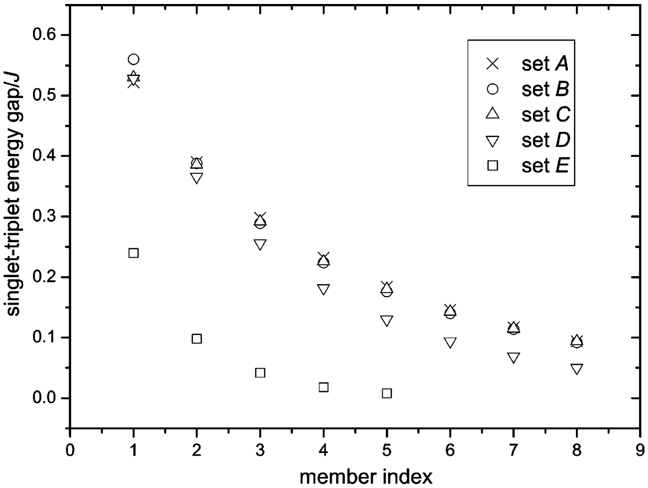

Figure 2. Plot of the singlet−triplet energy gap against the member index of diradicals.

more probable configurations of the system block. Therefore, we can retain only the m largest eigenstates which span a truncated space for the system block. All of the operators (e.g., H) are transformed into this new representation through the orthogonal transformation, $H' = OHO^+$, where the columns of matrix O are the retained eigenvectors of ρ.

A typical real-space DMRG computation is divided into two stages. The first stage employs the infinite system algorithm, during which, starting from a small fragment of a targeting system, the system is enlarged by a few atoms within each iteration until the superblock reaches the size of the targeting system. The second stage adopts the finite system algorithm, where the basis set for the system and environment blocks are further optimized to improve the accuracy, while the size of the superblock is kept constant.

A very recent modification of the standard DMRG procedure was that, instead of adding one new site to both the system block and the environment block, in each step, the modified procedure adds a new site only to the system block.[75] The new procedure is named “the single site algorithm”. It was found that the single site is more convenient for applying to quasi-two-dimensional systems, which run faster and improve the accuracy. Therefore, in the present work, we adopt the single site algorithm, which is very suitable for studying the topologically complicated structures like macrocyclic polyradicals and spin clusters.

III. Results and Discussion

A. Diradicals. In order to study the through-bond spin coupling in conjugated organic molecular or polymeric magnets, it is convenient to start from biradicals, in which two radical centers are linked together with a conjugated spin-coupling unit. Actually, diradicals have been thoroughly investigated both experimentally and theoretically, and the progresses in this field have been well-documented.[11] This section is included mainly to demonstrate and validate the application of the DMRG method in solving the VB model for radical-containing systems. Five typical sets of diradicals are shown in Figure 1, and we will use them to investigate the influence of topological features of the spin-coupling unit on the spin coupling in diradicals. Among these structures, sets A−C have the same type of spin-coupling units, which are polyacene oligomers of different lengths. The only difference among the three sets is the end sites of where the two methylene groups are attached to the backbone. Set D uses the polyphenanthrene oligomers as the coupling unit. Set E, which contains a coupling unit of the polyphenylene type, is different from all other structures in the topological character; while sets A−D can be regarded as the simple multiple spin-coupling channel diradicals, the backbone in set E supplies only one channel, the single connecting bond between two adjacent benzene rings. It is not surprising that set E will show much weaker spin-coupling strength when compared with that of all other sets. In our calculations, the benzene rings along the backbone chain are assumed to be coplanar.

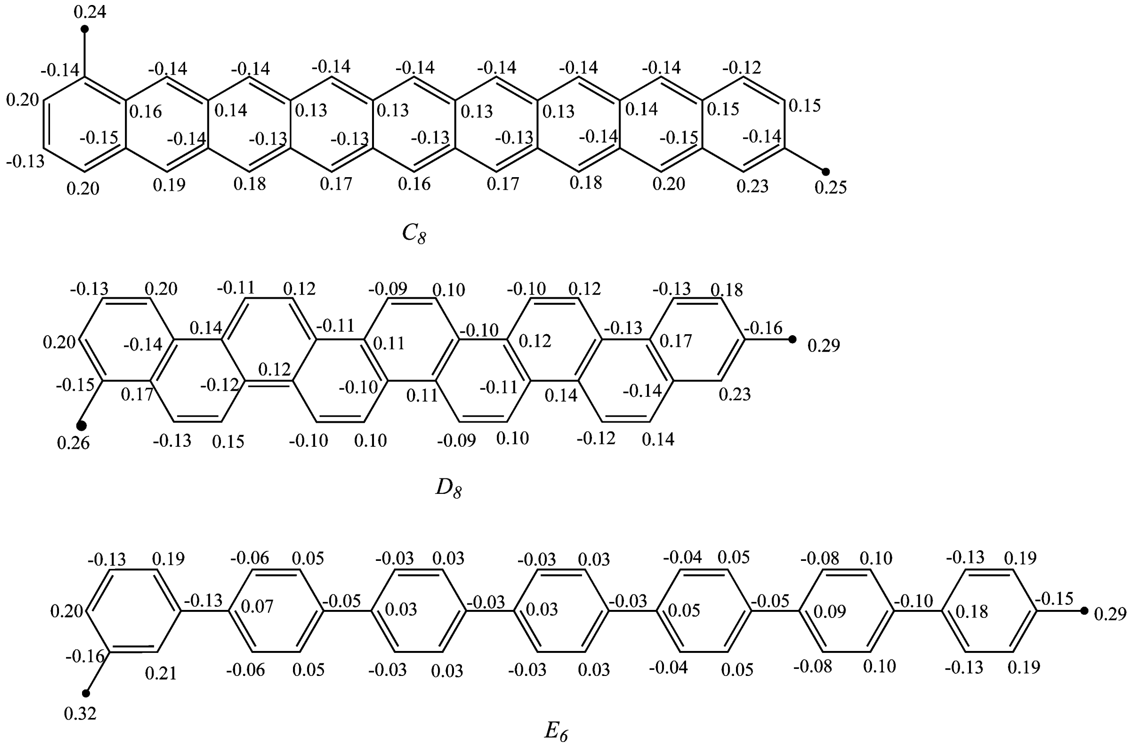

Figure 3. Calculated spin density distribution for diradicals.

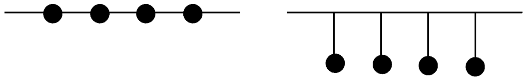
Class I
Class II

Figure 4. Spin-coupling patterns among multiple radical centers.

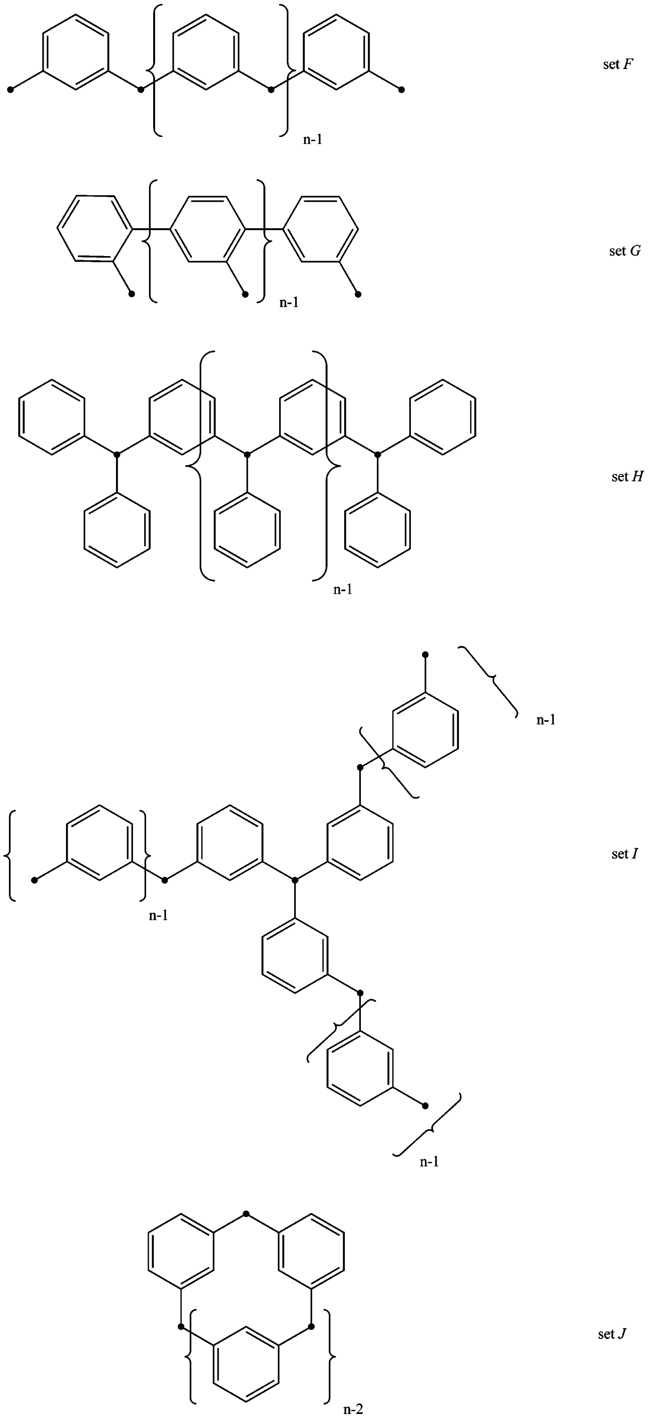

Figure 5. Linear polyradicals, branched polyradicals, and macrocyclic polyradicals.

TABLE 2: Calculated Energy Gaps ΔE_{L-H} (in Units of *J*) between the Ground and Lowest Excited States and *S* of the Ground State for Selected Polyradical Systems in Figure 5

	set F		set G		set H		set I		set J	
n	*S*	ΔE_{L-H}	*S*	ΔE_{L-H}	*S*	ΔE_{L-H}	*S*	ΔE_{L-H}	*S*	ΔE_{L-H}
1							2	0.223		
2	1.5	0.245	1	0.270	1	0.562	3.5	0.075		
3	2	0.129	1.5	0.170	1.5	0.138	5	0.041	1.5	0.578
4	2.5	0.080	2	0.111	2	0.084	6.5	0.032	2	0.374
5	3	0.055	2.5	0.076	2.5	0.056	8	0.025	2.5	0.261
6	3.5	0.040	3	0.043	3	0.041			3	0.191
7	4	0.031	3.5	0.042	3.5	0.031			3.5	0.145
8	4.5	0.025	4	0.033	4	0.025			4	0.114

In Table 1, the calculated triplet−singlet energy gap ($\Delta E_{ST} = E_S - E_T$) for all of the five sets of diradicals are listed. For a more clear illustration, the energy gaps ΔE_{ST} are plotted against the length of the backbone in Figure 2. With the increase of the length of the coupling unit, the energy gap decreases almost exponentially, which implies a rapid decrease of the coupling strength. Since sets A−C possess identical backbone structures, their plots have very similar patterns, with the differences among them being negligibly small. Overall, the meaning of these results is twofold to us. On one hand, since the coupling strength decrease exponentially with respect to the distance between the two radical-center radicals, one would need to pay enough attention to the radical distance when designing high-temperature organic magnets; on the other hand, even more attention should be paid to the design of the backbone structure itself. In contrast to sets A−C, set D shows a more rapid decrease of ΔE_{ST}, largely as a result of a different backbone structure. The energy gaps for set E decrease even more rapidly. As a matter of fact, the energy gap is already approaching the thermal energy (*RT*) when there are five repeated units between the two radical centers in set E, and the average magnetic moment can be reduced considerably due to the thermodynamic equilibrium between the high- and low-spin electronic states. All of these results for the five sets can, to some extent, be understood on the basis of the aromaticity of the backbones. A more aromatic system usually carries more delocalized π electrons, leading to less spin polarization and therefore weaker spin couplings and smaller energy gaps. The spin distribution patterns of these sets, as illustrated by one moderately sized member for each set, are shown in Figure 3. It was well-accepted that polyphenanthrenes are more stable and aromatic than polyacenes;[68] therefore, weaker spin coupling is anticipated for diradicals with polyphenanthrene backbones.

B. Linear Polyradicals, Branched Polyradicals, and Macrocyclic Polyradicals. High-spin polyradicals have multiple radical centers, which are coupled by the exchange interaction to yield large net values of *S* in the ground state. Generally, polyradicals can be divided into two classes according to the relationship between multiple radical centers and the spin-coupling units, as illustrated in Figure 4. In Class I polyradicals, the radical centers are embedded in the main chain, such as in sets F, H, I, and J shown in Figure 5, while in Class II polyradicals, the radical centers are attached to the π-conjugated backbone, such as in set G (also see Figure 5). On the other hand, the structure can also be classified according to the structure of the coupling units. In sets F, G, and H, which possess a linear backbone as the coupling unit, and set I, which comes with a branched linear backbone, there is only one coupling path between any two radical centers; set J, on the other hand, has a macrocyclic backbone, which supplies two coupling paths, one clockwise and the other counterclockwise.

In Table 2, we summarize the calculated energy gaps ΔE_{L-H} for all of these sets of polyradicals. The energy gaps were found to decrease very rapidly with the system size for the linear polyradicals, sets F, G, and H. For branched polyradicals, set I, the energy was relatively larger (for the same *S* value) but still decreased rapidly with the system size (ΔE_{L-H} is less than thermal energy for systems with more than 10 radical centers). All of these agree with the fact that only relatively low values

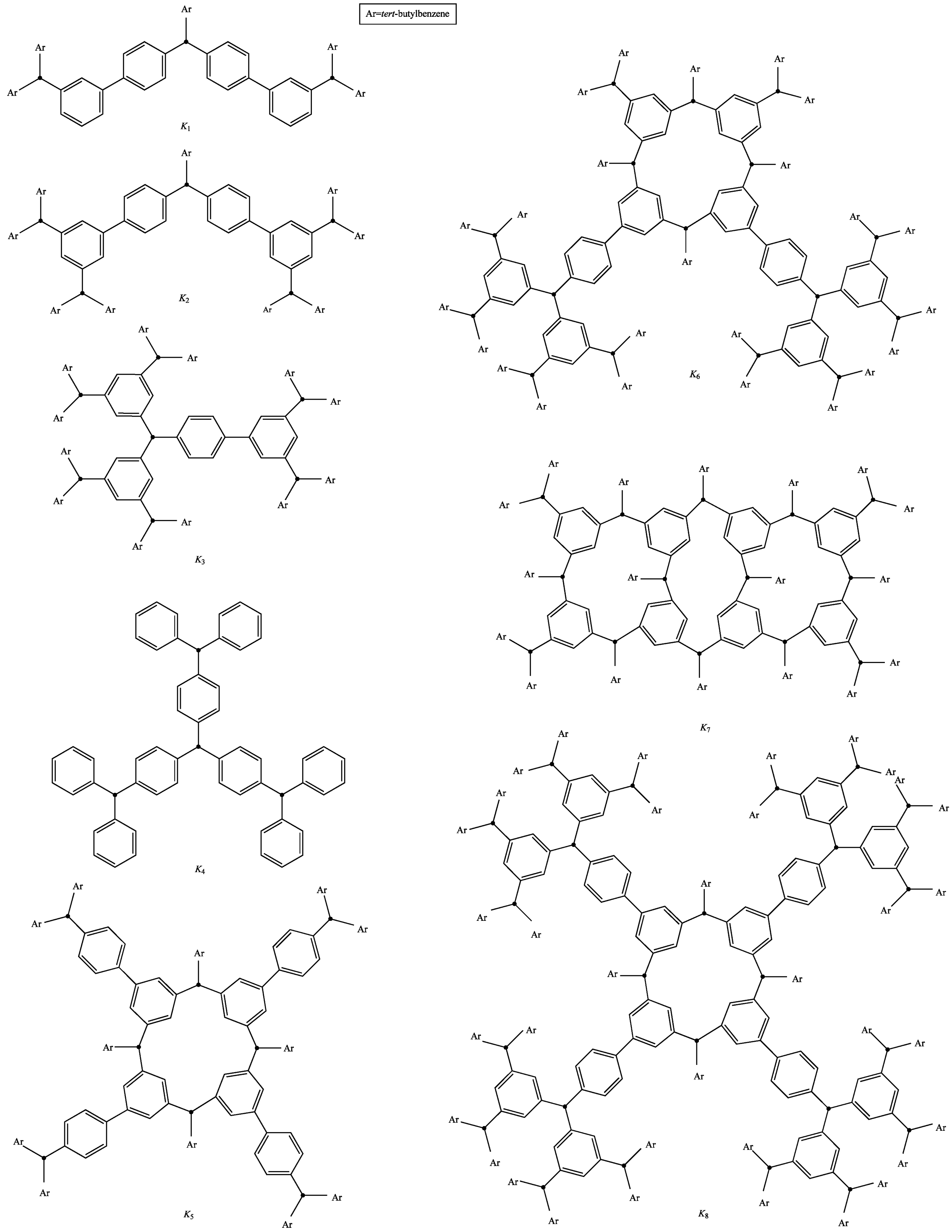

Figure 6. Spin clusters.

of spin $S \leq 5$ have been experimentally observed for linear and branched polyradicals.[14] In fact, I_3 is the model compound of the largest branch-structured polyradical ever synthesized, which has an undecet ($S = 5$) ground state.[14] In contrast, set J comes not only with a much larger $\Delta E_{\mathrm{L-H}}$ than the other sets, but its $\Delta E_{\mathrm{L-H}}$ value also decreases much slower with the system size. This can potentially give us some directions in the design of larger high-spin polyradical systems.

To us, the macrocyclic compounds like those in set J can come with two advantages. One, unlike the linear or branched polyradicals where the sole spin-coupling channel can be easily broken with a chemical defect (which then complicates the synthesis of very high spin linear or branched polyradicals),[26,32] the multiple coupling paths in a macrocyclic molecule lead to larger singlet−triple gaps and thus extra chemical stability for the high-spin ground state. Second, one can benefit from additional conformational constraints in the ring formation, which essentially reduce out-of-plane twists and make the macrocyclic molecule fairly planar. A more planar structure can then lead to stronger through-bond coupling and finally to a higher stability for the high-spin ground state. Having said this, though, we also expect to gradually lose the conformational advantage as the ring becomes bigger and bigger and approaches the limit of a linear system. So in the end, only the medium-sized polyarylmethyl cycles appear to us to be the most promising building blocks for very high spin polyradicals.

TABLE 3: Calculated Energy Gaps ΔE_{L-H} (in Units of J) between the Ground and Lowest Excited States and Calculated and Experimental S of the Ground State for Selected Spin Cluster Systems in Figure 6

compound	S_{exp}	S_{cal}	ΔE_{L-H}	compound	S_{exp}	S_{cal}	ΔE_{L-H}
K_1	1.3[a]	1.5	0.077	K_5	3.8[c]	4	0.143
K_2	2.4[a]	2.5	0.054	K_6	7.2[a]	8	0.019
K_3	3.28[a]	3.5	0.066	K_7	6.2[d]	7	0.074
K_4	1[b]	1	0.178	K_8	10.0[c]	12	0.023

[a] From ref 19. [b] From ref 33. [c] From ref 29. [d] From ref 18.

C. Spin Clusters. Modification of the macrocyclic backbone by attaching additional radical groups, which results in structures commonly named as spin clusters, is an alternative approach to designing high-spin polyradicals. Since the magnetic ordering can be preserved in extended two-dimensional or three-dimensional conjugated systems if only the radical centers are properly positioned, understanding the spin coupling in organic spin clusters may serve as a milestone on the way to the ultimate target of designing conjugated polymer-based magnets.

In Table 3, we summarize our calculated results and experimentally determined spin state S for some reported spin clusters shown in Figure 6. It can be clearly seen that the stability of the high-spin state can be reasonably predicted by the VB-calculated ΔE_{L-H}. Generally, the larger the energy gap, the more stable the high-spin state. In most cases with large ΔE_{L-H}, such as K_1-K_5, the experimentally determined S_{exp} is very consistent with the theoretically predicted S_{cal}. Meanwhile, the S_{exp} of K_6, K_7, and K_8, which are experimentally determined to be 7.2, 6.2, and 10.0, respectively, are somewhat lower than the calculated highest spin (8, 7, and 12). This phenomenon can be related to the calculated small energy gaps for these three molecules. For K_6 and K_8, ΔE_{L-H} is less than thermal energy, indicating that, due to thermal equilibrium, the high-spin ground state can be mixed substantially with a low-spin state. As a result of spin mixing, S_{exp} is, of course, expected to become lower.

D. Very High Spin Polyarylmethyl Polymers. In polymer L,[28] the $S = 3$ component spins of the calix[4]arene macrocycles are exchange-coupled with the $S = 1/2$ spins of the bis(3,4′-biphenylene)methyl linkers. Similarly, polymer M[22,25] consists of $S = 2$ calix[4]arene macrocycles and cross-linking $S = 1/2$ modules, as shown in Figure 7. In the above section of macrocyclic polyradicals, the ΔE_{L-H}'s of J_4 (the backbone of the calix[4]arene macrocycle in polymers L and M) have been calculated to be 1.18 eV, which implies very strong ferromagnetic spin couplings, and we have drawn the conclusion that medium-sized polyarylmethyl cycles can be the key building block of very high spin polyradicals. Therefore, as illustrated in Figure 7, polymer L can be seen as a "quasi-linear" chain of unequal spins of $S = 3$ and 1/2, and similarly, polymer M can be seen as a "quasi-linear" chain of $S = 2$ and 1/2 spins. When these spin components are ferromagnetically coupled, polymers L and M will have $S = 3.5n$ and $3n$ ground states, respectively; even in the worst cases, when they are ferrimagnetically coupled, polymers L and M will still have $S = 2.5n$ and n, respectively. Accordingly, polymers L and M can be anticipated to have very large magnetic moments and magnetic order if these polymers with large value of n can be synthesized.

In Table 4, we also summarize the calculated energy gaps ΔE_{L-H} for polymers L and M. It can be found that the ΔE_{L-H}'s for polymer L are much smaller than those for polymer M and decrease more rapidly than those for polymer M. This may be related to the newly formed calix[8]arene macrocycles in

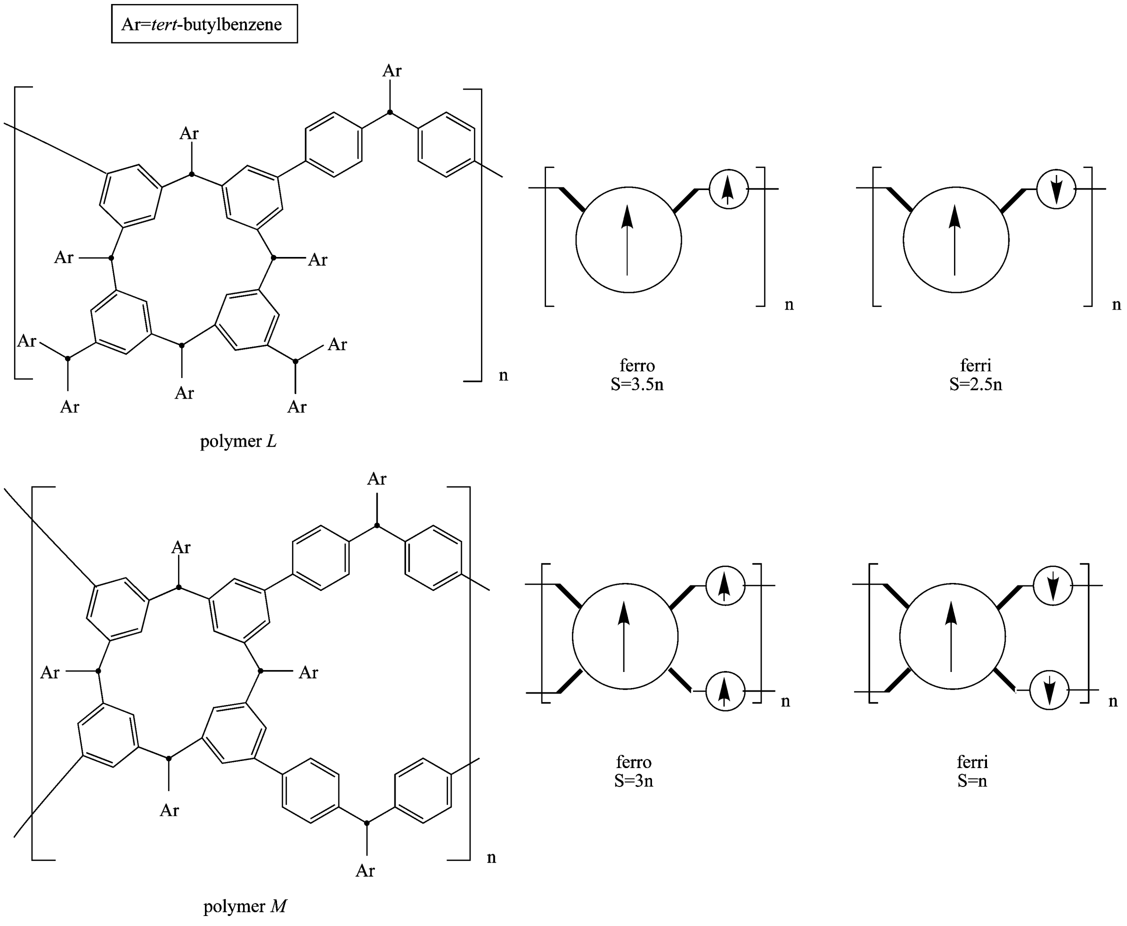

Figure 7. High-spin polymers.

TABLE 4: Calculated Energy Gaps ΔE_{L-H} (in Units of J) between the Ground and Lowest Excited States and S of the Ground State for High-Spin Polyarylmethyl Polymers in Figure 7

	polymer L		polymer M	
n	S	ΔE_{L-H}	S	ΔE_{L-H}
1	3.5	0.059	3	0.122
2	7	0.015	6	0.039
3	10.5	0.015	9	0.022
4	14	0.013	12	0.019

polymer M, which provides multiple spin-exchange coupling paths. Therefore, polymer L should have lower spin than that of polymer M. It is consistent with the experimental observations that polymers L and M possess an average value of $S \approx 18$[28] and S = 40,[22] respectively. When polymerization is stopped near the gel point, polymer M has values of $S = 600-1500$; for a longer polymerization time, values of $S = 3000-7000$ are obtained.[25] From Table 4, we can also find that for both polymers, ΔE_{L-H} decrease rapidly to values below the thermal energy when the chain elongates. This indicates that, besides an all-ferromagnetically coupled spin state, other lower spin states will also contribute significantly. Experimental determinations of $M_{sat} \approx 0.4 - 0.6\ \mu_B$ for polymer L[28] and $M_{sat} \approx 0.5\ \mu_B$ for polymer M[25] also indicate the presence of only approximately 40−60 and 50% of the unpaired electrons at low temperature for polymers L and M, respectively.

IV. Conclusion

Valence bond calculations of high-spin organic π-conjugated diradicals, polyradicals, spin clusters, and polymers were presented by virtue of the density matrix renormalization group method. The energy gap between the ground high-spin state and the excited low-spin states (ΔE_{L-H}) was calculated, and this was employed to explain the stability of polyradical molecules and polymers. For diradicals, a less aromatic backbone can induce stronger spin couplings. In order to achieve a very high spin state, cycle structures are very important due to the fact that they can provide multiple spin-coupling channels and conformational restrictions to prevent significant out-of-plane twisting. Therefore, medium-sized polyarylmethyl cycles are expected to be key building blocks of very high spin spin clusters and polymers.

However, it should be pointed out that the present method (VB−DMRG) does not account for the out-of-plane twisting of the π systems, which may reverse the order of the spin states.[15,21,45] Thus, our VB−DMRG results for seriously twisted systems, such as polyphenylene, should be taken with caution. Another concern is that the underestimation of electron delocalization by the VB model may lead to the incorrect prediction of magnetic coupling. In fact, electron delocalization may destabilize the high-spin ground state. Therefore, further studies by high-level ab initio or semiempirical approaches (such as the Pariser−Parr−Pople model), which can treat electron localization and electron delocalization in balance, are desired to give more reliable information on molecular magnetism.

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