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Highly Efficient Tuning of Ferromagnetic Spin Interactions in High-Spin Arylamine Structures by Incorporation of Spin Bearing Carbazole Units

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ABSTRACT

Arylamine moieties oxidized to radical cations are considered promising spin bearing units in high-spin type compounds. Here, we report the first use of carbazole-3,6-diamine units as efficient rigid spin containing units. The use of rigid spin bearing units enhances significantly spin exchange interactions. The design using DFT calculations shows the progressive increase of the exchange coupling constant dependent on the considered model molecules. Two of the most representative molecules containing flexible (dimer 1) and rigid spin coupling unit (dimer 2) were synthesized. Electrochemical and pulsed-EPR nutation studies showed that both dimers can be oxidized to yield a majority of di-cationic di-radicals exhibiting S = 1 ground states. The high values of the dimer 2 exchange coupling constant obtained both computationally ($J/k_B = 145$ K; $H_{Heis.} = -J S_1.S_2$) and experimentally ($J/k_B = 90-100$ K) indicates the beneficial role of the carbazole moiety incorporated into spin bearing units.

INTRODUCTION

An extensive development in the field of organic electronics, mainly associated with OLED, OFET and OPV technologies¹⁻³ has directed the attention to the search of organic magnetic materials which can be applied in molecular electronics,^{4,5} spintronics ^{6,7} or in biomedicine as MRI contrasts.⁸⁻¹⁰ The key feature of organic magnetic materials is the formation of high-spin states, which was originally carried out based on a polaronic model.¹¹ At present, the research in the field of high-spin molecules is focused on reaching high spin states governed by coextensive spin densities¹² spread over the entire molecule and tuning the magnetic exchange coupling constant *J* value to achieve as strong spin – spin interactions as possible.¹³

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The number of high spin organic molecules is gradually increasing including various π conjugated systems e.g. linear oligomers,¹⁴⁻²⁰ cyclophanes ²¹⁻³⁰ and polymers.^{13,30-33} Within these
structures, the total spin and exchange coupling constant enlargement is accomplished by a
progressive extension of the π -conjugation with simultaneous rigidification of the molecular
backbone.^{13,14,16} Since the exchange coupling constant value is extremely sensitive to the
changes in local conformations Rajca and co-workers proposed to use ring-fused polycyclic
structures¹⁴ including spin bearing units connected through *m*-phenylene to form a planar crossconjugated π system.^{16,19} Reaching even higher values of *J* was possible by moving from various
aminyl radicals^{14,16} to aza-*m*-xylylene derivatives,³⁴⁻³⁷ where extended π -conjugation was
diminished, and radical stability was provided by bulk substituents in close proximity to the
radical. The essential increase of the *J* value provided by rigidification of the molecular
backbone around the *m*-phenylene moiety was also observed by our group in the case of
arylamine-based compounds (both dimer and polymer) oxidized to radical cations.¹³

In terms of structure rigidification, one of the unexploited solution to the polaronic model mentioned above consists in providing a new type of reduced flexibility, namely that of the conjugated spin bearing moiety, for example by using planar carbazole type units. Recent study revealed that, under certain conditions, radicals localized on carbazole nitrogen may present an enhanced stability.³⁸ However, the incorporation of carbazole into the 5,7,12,14-tetrahydroquinolino[3,2-b]acridine moiety, which served as the background for both radical¹⁶ and radical cation-based¹³ high-spin systems must be carried out with caution as too extensive delocalization over the spin coupling unit, the nature of the connecting groups or even the addition of peripheral electro-donor groups may strongly modulate (sometimes unfavorably) the resulting ferromagnetic spin interactions (see Ref.¹⁶). In this study we present how structure

rigidification in the form of carbazole-3,6-diamine moiety readily enhances ferromagnetic spin interactions and associated exchange coupling constant values (dimer 1, Scheme 1). We then introduced additional molecular stiffening by incorporating a rigid coupling unit in between rigid spin bearing units (dimer 2, Scheme 1). Before presenting experimental data pertaining to these two dimers, we present the relevant DFT calculations which led us to them.



Scheme 1. Chemical structures of the studied compounds: dimer 1 and dimer 2 and the model compounds D2 and QA (for comparison).

EXPERIMENTAL SECTION

For any experimental details on the supply of chemicals, synthesis, pulsed EPR and SQUID measurements as well as DFT calculations see Supporting Information

RESULTS AND DISCUSSION

DFT calculations

The rigidification of arylamine structures may have a crucial impact on their magnetic properties. To understand beforehand structural and electronic contributions to spin - spin interactions we performed DFT calculations for various dimer **1** and dimer **2** models. In **Table 1** we first show plots of the magnetic orbitals for the experimental dimer **1** for which we computed $J/k_B = 44$ K. We also show the corresponding magnetic orbital for the dimer $2_{An,C<Me}$ modelling the experimental dimer **2** ($J/k_B = 204$ K)¹. Because of this last high *J* magnitude, special attention has been paid to dimer **2** model compounds: **Table S1** shows magnetic orbitals and exchange coupling constants *J* for gradually more complex dimer **2** models.

Table 1. Plots of the DFT-BS computed (left-end dimer sides) magnetic orbitals for model dimer 1 (left) and model dimer 2An,C<Me, (right) closest to the experimental dimer 1 and dimer 2, respectively. The equivalent magnetic orbitals for the right-end dimer sides can be deduced by symmetry for these symmetrical dimers. Isodensity value set to 0.03 a.u.

dimer 1

dimer 2_{An,C<Mec}

¹ Several compounds derived from dimers **1** and **2** that were studied by DFT calculations (see Table S2). They are named "dimer nSub1,Sub2". Here, n (=1 or 2) stands for the parent dimer structure. Sub1 stands for the substituent of the N atoms and can be: H atom ("H"), Phenyl group ("Ph"), or Anisyl group ("An"). Sub2 stands for the group that possibly connects the central *meta*-phenyl group with adjacent aromatic rings: no connecting group (no subscript), CH2 connecting group (">CH"), CMe2 connecting group (">CMe").



The striking difference between J values computed for both model dimers lies in the extension of the spin density at the level of the spin couplers. Magnetic orbitals must be mutually orthogonal to cancel the antiferromagnetic contribution to J but must still occupy the same region of space (*i.e.* at the coupler) to increase the ferromagnetic contribution.

To better understand what contributes to such a high J/k_B magnitude in the case of dimer $2_{An,C<Me}$ (204 K) compared to both dimer 1 (44 K) but also to the previously published QA dimer $(J/k_B = 42 \text{ K})$, we planned on treating the different effects separately (rigidification of the coupler and/or of the spin bearer and increasing complexity of the peripheral ligands (see Table S2). We therefore computed *J* coupling constants for equivalent dimer 1 models and discuss at length in Supporting Information all *J* constants in Table S2 (see also FigureS8; no magnetic orbital plots are shown for dimer 1 models beside the one in Table 1). The lessons learned from

Table S2 are the following: i) rigidifying the spin coupler optimizes the ferromagnetic contribution to the exchange coupling constant by enforcing the bearer-coupler-bearer unit to behave as strict alternant hydrocarbons; ii) however, electron-donor groups pouring out electron density toward the coupler have (it would seem) to be avoided, as this increases the antiferromagnetic contribution to *J* expected to be proportional to the square of the residual overlap of the magnetic orbitals (represented in **Table 1**); iii) however, the same alternant hydrocarbon network rigidifying the spin bearers also modulates the electron density present at the coupler, *i.e.* enforcing planarity upon the spin bearers withdraws some of the electronic density provided by electro-donor groups away from the coupler (*contra* point ii above). Further DFT calculations would be necessary to investigate this delicate balance between the extent of a dimer's planarity on the one hand and the presence of electro-donor groups at various positions on the other hand (out of the scope of the present paper).

We now turn to the experimental results.

Synthesis

To verify the theoretical conclusions drawn from the DFT calculations presented above, we synthesized two dimers containing carbazole moiety as the spin bearer (see **Scheme 1**).

All studied compounds containing carbazole-3,6-diamine moiety have been prepared using catalyzed C-N coupling reactions (Scheme 2 and 3). In the first step 9-(4'- methoxyphenyl)carbazole, **3** was obtained by a standard method in the reaction of carbazole and 4-iodoanisole in the presence of CuI/(\pm)-*trans*-1,2-diaminocyclohexane with 81% yield after the recrystallization. The carbazole **3** was brominated with NBS which led to dibromo derivative **4**. Then the compound **4** was reacted with 4-anisidine to give monoamino derivative **5** using Pd₂dba₃/BINAP catalyst (34% yield), then the coupling with 1,3-diiodobenzene in the presence

of Pd(dba)₂/t-Bu₃P, led to the derivarive 6 containing two active bromine sites. It was converted into the dimer 1 in the reaction with bis(4-methoxyphenyl)amine with 49% yield. It should be underlined that other routes to prepare the dimer 1 were also tested but the overall yield was lower than that reached in the method presented in Scheme 2.



Scheme 2. The synthesis of the dimer 1: (i) 4-iodoanisole, CuI, (\pm)-*trans*-1,2diaminocyclohexane, K₃PO₄, anhydrous 1,4-dioxane, 110 °C, Ar, 24 h (ii) NBS, anhydrous THF, anhydrous DMF, 0 °C, Ar, 1.5 h (iii) 4-methoxyaniline, Pd₂(dba)₃, BINAP, *t*-BuONa, anhydrous 1,4-dioxane, 110 °C, Ar, 24 h (iv) 1,3-diiodobenzene, Pd(dba)₂, P(*t*-Bu)₃, *t*-BuONa, anhydrous toluene, 90 °C, Ar, 24 h (v) bis(4-methoxyphenyl)amine, Pd(dba)₂, P(*t*-Bu)₃, *t*-BuONa, anhydrous toluene, 110 °C, Ar, 24 h.

Dimer **2** was synthesized in an 8-steps synthetic route. First, the intermediate compound, namely N^3 , N^3 , 9-tris(4-methoxyphenyl)-9*H*-carbazole-3, 6-diamine was prepared (see Supporting Information, Scheme S1). The synthetic route consists of subsequent nitration, selective reduction of nitro groups and then Cu catalyzed substitution and Pd catalyzed coupling amination. Finally, reduction with hydrazine and palladium on activated charcoal gave unsymmetrical carbazole derivative **11**, which was used in the following synthesis of final dimer **2**, presented in **Scheme 3**. The reaction between **11** and 1,5-dibromo-2,4-di(prop-1-en-2-yl)benzene, catalyzed by Pd(dba)₂ combined with bulky ligand (QPhos) allowed the formation of **12** with a very high yield (90%). Then, acidic cyclization with AcOH/H₃PO₄ yielded amine **13** (77%), where 5,8,10,13,18,20-hexahydroindolo[3,2-*a*]indolo[3',2':5,6]qinolino[2,3-*i*]acridine core was formed. The target dimer **2** was obtained *via* substitution of **13** at N8 and N10 positions with on-site prepared 1-iodo-4-((2-octyldodecyl)oxy)benzene (77% yield).



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Scheme 3. Synthesis of dimer 2: (i) [Pd₂(dba)₃], QPhos, *t*-BuONa, anhydrous toluene, 110 °C, Ar, 24 h (ii) H₃PO₄, AcOH, 100 °C, Ar, 24 h (iii) 1-iodo-4-((2-octyldodecyl)oxy)benzene, [Pd₂(dba)₃], P(*t*-Bu)₃, *t*-BuONa, 1,4-dioxane, 110 °C, Ar, 24 h.

Spins generation

Arylamine compounds are efficient spins bearers due to their easy oxidation to radical cations. Arylamine compounds can be oxidized by electrochemical or chemical means. The electrochemical properties of the dimers 1 and 2 were studied by cyclic voltammetry in dichloromethane (1) and THF (2) with 0.1 M Bu₄NBF₄ as a supporting electrolyte.

The cyclic voltammograms (CV) (Supporting Information) and differential pulse voltammograms (DPV) (**Figure 1**) of both dimers were very similar and showed reversible waves corresponding to the successive oxidation of amine groups.

Considering the chemical structures of the dimers **1** and **2** one can suppose that the electrochemical properties of both compounds should be comparable to those of previously studied arylamine dimers such as **D2** (flexible one corresponding to dimer **1**) and **QA** (rigid one corresponding to dimer **2**).¹³ However, the incorporation of planar carbazole moieties into the structures of the compounds studied presently changed the electrochemical behavior of both dimers. In the initial stage of the oxidation process, DPV of the dimer **1** showed only one peak at 0.05 V (vs. Fc/Fc⁺) (**Figure 1**).



Figure 1. Differential pulse voltammograms obtained for the dimers 1 (A) and 2 (B) in CH_2Cl_2 and THF solutions, respectively (the concentration of the compounds was $c = 1 \cdot 10^{-3}$ M)

containing an electrolyte – 0.1 M Bu₄NBF₄, (modulation time 50 ms, modulation amplitude 10 mV, step potential 5 mV). The peak was large ($\Delta E_1 = 107$ mV), indicating that multi-electron oxidation process took place

and can be attributed to the oxidation of two lateral amine groups into radical cations. By contrast, the DPV of dimer 2 showed two oxidation peaks at 0.06 V ($E_{1,1}$) and 0.137 V ($E_{1,2}$) (vs. Fc/Fc^+). These two peaks can be related to the formation of one radical cation in each conjugated segments and located mainly on the lateral amine sites. The difference in the electrochemical behavior between dimers 1 and 2 as well as with dimer OA reported previously can be due to their chemical structures. In the case of the dicationic dimer 2, the magnetic orbitals computed by DFT show that the hole is born by each lateral diamine groups (corresponding to a Mülliken charge of about 0.4|e|), leaving about 0.6 for each coupler's sides. By contrast, in the case of the dicationic dimer 1, each hole is more lateralized. This can explain the increase of the electrostatic repulsion between adjacent holes in dimer 2 and, therefore, the oxidation potential for the formation of a second radical cation shifted by 77 mV. The further oxidations differ from those observed previously for D2 and QA.¹² Thus, the DPV of dimer 1 showed two well resolved peaks at 0.29 and 0.46 V (vs. Fc/Fc⁺) which can be attributed to the formation of a second radical cation in each conjugated segments. The resonant nature of conjugated units causes the increase of the oxidation potential. Thus, the separation between the first and the second oxidation peaks equal to 0.24 V confirms the location of radical cations within the same unit. Then the separation between the second and the third peaks in DPV of dimer 1 was equal to 0.17 V indicating the generation of radical cations in two adjacent units linked via the *m*-phenylene coupler.

On the other hand, it should be emphasized that the DPV of dimer 2 showed similar character but differs significantly for the intermediate oxidation state. The peaks corresponding to the

subsequent oxidation appeared at 0.27 V (E_2) and 0.436 V (E_3) (vs. Fc/Fc⁺). The separation between the second ($E_{1,2}$) and the third (E_2) oxidation waves was of only 133 mV and both peaks overlapped at a potential value around 0.2 V. At last, the separation between the first and the third peaks was equal to 0.21 V suggesting the formation of a second radical cation within the same conjugated unit.

Pulsed-EPR nutation – Spin states

Samples of dimers 1 and 2 oxidized with 2 equivalents of oxidant per dimer were studied by pulsed-EPR nutation spectroscopy. In the nutation spectra shown in Figure 2, one can see that for both dimers, the most intense signals are due to S = 1 states, consistent with the ferromagnetic coupling of spins born by both conjugated units in a given dimer. The rather diluted sample of dimer 1 (Figure 2, upper frame) exhibited also weaker signals due to S = 1/2 as well as to spin states higher that S = 1. In a more concentrated sample of dimer 1 (Figure 2, middle frame) the signal of S = 1 spins is still the most intense, but signals of S = 3/2 and S = 2 spin states are clearly observed and more intense than in the case for the diluted dimer 1 sample. In the case of dimer 2 (Figure 2, lower frame), besides dominant S = 1 signal, signals from higher S = 3/2 may be also observed, even though with much less intensity than for dimer 1.

These S = 3/2 and S = 2 signals have higher intensity relative to S = 1 signals in spectra recorded at higher temperatures (see SI Figure S3 for dimer 1) so they correspond to weak antiferromagnetic interactions that are tentatively attributed to intermolecular magnetic coupling between two dimer molecules. This would be consistent with the fact that coupled S = 3/2 and S = 2 states are better observed at higher concentration for dimer 1 samples.

From these experiments it is clear that it is difficult to obtain a concentrated sample of dimer 1 containing a pure S = 1 spin state suitable for measuring unambiguously the intramolecular exchange coupling constant by SQUID magnetometry. Dimer 2 seemed to be a better candidate and was selected for the SQUID magnetometry investigations.



Figure 2. Pulsed-EPR nutation spectra recorded at T = 7 K for samples of oxidized dimer 1 and 2 at different concentrations. Nutation frequency of S = 1/2 varies slightly, 4.95 MHz (down), 5.5 MHz (middle) and 5.3 MHz (top) due to variation of EPR cavity tuning for the different samples.

Magnetization measurements

The SQUID measurements of the dimer **2** were performed for the samples diluted in a polystyrene matrix (denoted as DS) and for concentrated samples (powder form, non-diluted samples, NDS).

For both types of the samples, the paramagnetic contribution shows typical Brillouin-type behavior: at low temperatures magnetization tends to saturate with magnetic field H, while at higher temperatures it is almost linear with H and decreases with increasing temperature (see Supporting Information, Fig. S4: magnetization measured as a function of magnetic field at different temperatures). **Figure 3** shows the magnetization M of DS samples as a function of magnetic field divided by temperature H/T (for the NDS see Supporting Information Fig. S5). The experimental points obtained at 2, 5 and 10 K in the M vs. H/T coordinates are located between the curves calculated by the standard Brillouin function (SBF) for spins S = 1 (x = 87.5%, where x is expressed as the concentration of spin S) and spins S = 1/2 (x = 175%), respectively. The three experimental curves almost mutually overlap, which suggests the absence or the presence of very week only *intermolecular interaction*.

The inset in **Figure 3** shows the experimental data at T = 2 K, which can be described in a qualitative manner using the effective Brillouin function (EBF). Namely, in EBF, for temperature *T* is substituted by $T - \theta$, where θ is paramagnetic Neel/Curie temperature, treated as an additional parameter (for the sense of θ parameter see Supporting Information). The inset in **Figure 3** shows that magnetization of DS samples measured at 2 K can be well approximated with the EBF with S = 1, $\theta = -0.27$ K and x = 87.7%.





Figure 3 Magnetization of the dimer 2 (DS samples) versus magnetic field over temperature, H/T at T = 2, 5, 10 K. In the inset: magnetization *vs.* magnetic field *H* at T = 2 K.

From this fit it appears that the oxidation efficiency would be *ca.* \cong 87%, thus the highest efficiency observed to date for high-spin arylamine compounds. However, it should be emphasized that this estimated concentration of *S* = 1 states could actually be smaller than $x \cong$ 87%, causing the θ value to be also overestimated, as a small number of molecules with only one unpaired electron (*S* = 1/2) may be present. Overall the magnetization measurements reported in **Figure 3** are fully consistent with the presence of dominant triplet ground state created after oxidation of the dimer **2** to radical cations.

To investigate further the oxidized dimer 2, magnetization was measured as a function of temperature at $H = 10^4$ Oe. To demonstrate prevalent interactions between magnetic centers for both type of samples the products of the magnetization and temperature $M \cdot T vs$. temperature T at $H = 10^4$ Oe were shown in **Figure 4** (for only NDS samples see SI, Fig. S6).



Figure 4. Product of magnetization and temperature *M*·*T versus* temperature *T* at $H = 10^4$ Oe obtained for the dimer **2** (the blue squares - the samples diluted in polystyrene matrix, DS, the red circles non-diluted samples, NDS). The black dashed curve is calculated for non-interacting unpaired electrons S = 1/2 and x = 170% by SBF. The simulated curves correspond to the simplest model (mix of S = 1 and S = 1/2 states) with parameters shown in the legend. The model curves were calculated using Eq. S3 with Heisenberg exchange $-J \cdot S_1 \cdot S_2$.

The shape of *M*·*T vs.* temperature in the temperature range between 20 K and 300 K clearly reflects *intramolecular* ferromagnetic interaction between spins of radical cations. These experimental data were compared to the calculated model curves (Supporting Information, Eq. S3 with Heisenberg exchange $-J \cdot S_1 \cdot S_2$) based on the concept of the effective temperature with $J/k_B = 70$ K, 90 K and 100 K. For all the simulated curves a fraction (from 16% to 26%) of S = 1/2 spin state was included, which is consistent with the spin states identified by pulsed EPR

nutation. The curves computed for $J/k_B = 90$ K and 100 K both exhibit a good agreement with experimental data in the 40–300 K range, while $J/k_B = 70$ K exhibits a slightly better agreement in lower temperature range (2–40 K). Overall these simulations confirm the presence of a large majority of S = 1 states and provide an estimation of J/k_B exchange coupling constants close to 70–100 K. This value is lower, but still close enough to the value ($J/k_B \approx 145$ K) predicted for dimer **2** by DFT calculations after proper correction performed on the basis of previous works (see **Table S3** and **Figure S10**).

CONCLUSIONS

To the best of our knowledge this is the first study exhibiting ferromagnetic interactions between spins located on carbazole spin bearing moieties. Based on a series of DFT calculations of relevant structures (see **Tables S1-2** and **Figure S9**), dimer **2**, and dimer **1** for the sake of comparison, were selected as good candidates as DFT predicted a significant increase of the magnitude of *J* from **D2** (35 K) and dimer **1** (44 K) to dimer **2** (204 K) (see Tables S2-3). This strategy using DFT predictively lead to an estimated *J* coupling constant as high as $J/k_B \approx 145$ K (after correction) for dimer **2**. Dimers **1** and **2** were successfully prepared by multistep synthesis. Electrochemical and pulsed-EPR nutation studies showed that both dimers can be easily oxidized to yield a majority of di-cationic di-radicals exhibiting S = 1 ground states. The relatively high *J* value measured experimentally ($J/k_B = 90-100$ K) for not-diluted dimer **2**, is close enough to the (still higher) value predicted by DFT calculations and confirms the trend predicted by DFT.

Overall this study demonstrates quantitatively that, introducing rigid carbazole moieties combined with restricted conformational mobility in high spin organic dimers (such as dimer 2) significantly increases the J coupling constant by a factor 3 compared with non-rigid arylamine

analogues (**D2**). These results pave the way for exploring this new class of carbazole-based rigid structures and for designing high spin oligo- and polymers with improved magnetic properties.

ASSOCIATED CONTENT

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Supporting Information Available. DFT calculations, synthesis procedures, additional electrochemical studies, chemical oxidation procedures, and experimental details of pulsed-EPR nutation experiments and magnetization measurements. This information is available free of charge via the Internet at <u>http://pubs.acs.org</u>.

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