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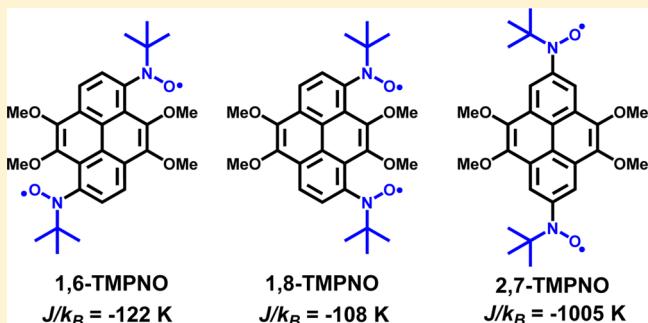
Positional Isomers of Tetramethoxypyrene-based Mono- and Biradicals

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Supporting Information

ABSTRACT: The positional isomers of *tert*-butylnitroxide (NO) substituted 4,5,9,10-tetramethoxypyrene-based mono- and biradical are synthesized. While the biradical 2,7-TMPNO in which two NO radical moieties are attached at the nodal plane of pyrene adopts a semiquinoid structure, the 1,6- and 1,8-isomers of the same exist in biradical form. The tuning of the antiferromagnetic exchange interactions is achieved by synthesizing the positional isomers of the biradical while maintaining the same radical moiety as well as the π spacer.



1. INTRODUCTION

Among the family of stable organic radicals,^{1–3} the aminoxyls⁴ are of special interest owing to their exceptional stability and ability to coordinate to metal ions.^{5,6} Lately the stable aminoxy radical attached to several polycyclic aromatic hydrocarbons (PAHs) have been synthesized and proved their application in rechargeable batteries, sensors, organic field effect transistors, and quantum magnets.^{7–12} The PAH-bearing aminoxy radical moieties are also found to exhibit photoexcited high spin states.^{13,14} The enhanced photostability of pentacene was achieved by attaching the nitronylnitroxide moiety.¹⁵ The physical properties of these PAHs highly depend on the type of radical moiety and its position on the polycyclic core.^{16,17}

Recently we have shown how magnetic exchange interaction and the physical properties of 2,7-disubstituted, 4,5,9,10-tetramethoxypyrene (TMP)-based biradicals can be tuned by changing the radical moieties (Figure 1).¹⁷ While the fine-tuning of magnetic exchange interaction was achieved by replacing one of the nitronylnitroxide (NN) radical moiety by an iminonitroxide (IN) (Figure 1 molecules 1, 2, and 3), the *tert*-butylnitroxide (NO) derivative (molecule 4) showed exceptionally large coupling constant. Later molecule 4 was found to exist in a semiquinoid form, exhibiting biradical and quinoidal character simultaneously.^{18,19} Moreover the structural transformation was observed upon temperature variation. Therefore, it was intriguing to synthesize the positional isomers of biradicaloid molecule 4 and study the influence of the position of the NO radical moieties on the TMP core.

Herein we report the analysis of the influence of the position of NO radical moiety on the stability, electrochemical, optical, and magnetic properties of TMP-based mono- and biradical system (Figure 2).

2. MONORADICALS 1-TMPNO AND 2-TMPNO

The monoradicals, 1-TMPNO and 2-TMPNO were synthesized in two steps from the 1-bromo and 2-bromo TMP. The UV-vis spectra of 1-TMPNO and 2-TMPNO showed distinct features for the pyrene as well as radical absorption pattern (Figure 3). While 1-TMPNO showed absorption band for pyrene at 339 and 356 nm, 2-TMPNO displayed the same at 312 and 354 nm with different extinction coefficients, as shown in Figure 3. Both of the radicals exhibited the characteristic $n-\pi^*$ transition for NO radical moiety that appeared as a shoulder of the pyrene absorption peak in 1-TMPNO and as a distinguished peak in 2-TMPNO. The UV-vis analysis clearly signaled the influence of the position of the radical moiety on the electronic structure of the pyrene core. This was also further reflected in EPR measurements (Table 1).

The room-temperature EPR spectrum of 1-TMPNO in toluene consisted of three lines having equal intensity due to hyperfine coupling (hfc) with nitrogen (Figure 4). The obtained hfc constant from the spectral simulation was $a_N = 1.6 \text{ mT}$ at a g value of 2.0068. Interestingly, 2-TMPNO provided an EPR spectrum that comprises triplet of triplet because of hfc with the two aminoxy nitrogens and two ortho protons (Figure 4). The spectral simulation gave the hfc constant values $a_N = 1.23 \text{ mT}$ and $a_H = 0.196 \text{ mT}$ at a g value of 2.0067. Thus, the EPR analysis indicated that the extent of spin delocalization is higher in the case of 2-TMPNO than in 1-TMPNO.

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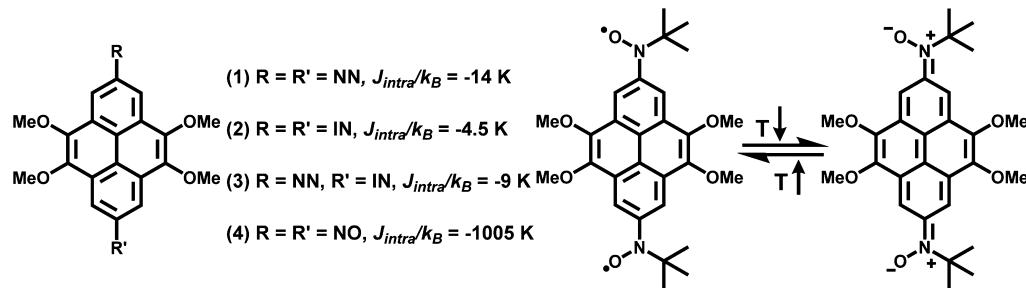


Figure 1. Tuning of exchange interactions by changing the radical moiety.

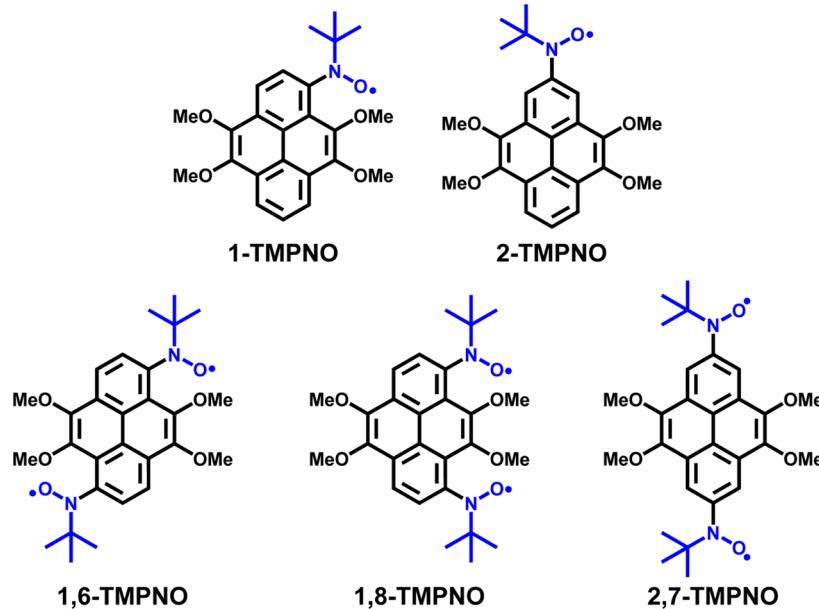
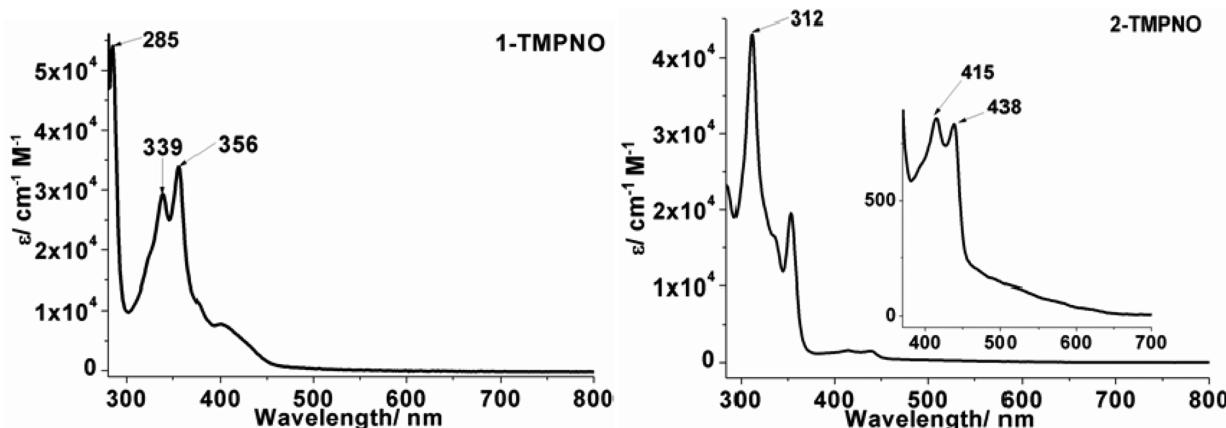
Figure 2. Monoradicals 1-TMPNO and 2-TMPNO and 1,6-, 1,8-, and 2,7- positional isomers of TMP based *tert*-butylnitroxide biradicals.

Figure 3. UV-vis spectra of 1-TMPNO and 2-TMPNO.

Table 1. Summary of EPR Parameters

radical	spectral width (mT)	hfc (mT)	g_s ($\Delta M_S = 1$) 290 K	$2D_s$ (mT) 140 K	d (Å)
1-TMPNO	3.2	1.6 (a_N)	2.0068		
2-TMPNO	2.4	1.23 (a_N), 0.196 (a_H)	2.0067		
1,6-TMPNO	3.2	1.6 (a_N)	2.0068	11.6	7.85
1,8-TMPNO	3.2	1.6 (a_N)	2.0068	18.4	6.74

Single crystals of both the mono radicals were successfully obtained by slow diffusion of hexane to the DCM solutions of both compounds (CCDC numbers, 1057029 and 1057030). Single-crystal X-ray analysis revealed that 1-TMPNO and 2-TMPNO crystallized in triclinic and monoclinic space groups, respectively. The crystal packing analysis indicated no short contacts between radical centers, ruling out the presence of any substantial intermolecular magnetic exchange interactions. Notably, a very significant difference was observed in the

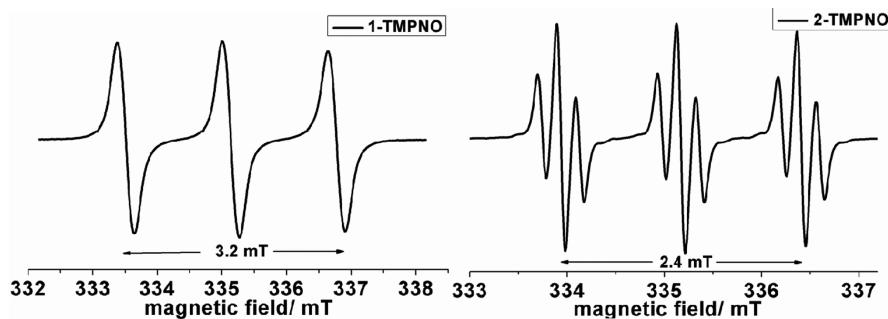


Figure 4. EPR spectra of 1-TMPNO and 2-TMPNO in toluene at room temperature.

torsion angle of the aminoxy group with the pyrene core in both isomers. The radical moiety was nearly in-plane with the pyrene core for 2-TMPNO (torsion angle 13°) and out-of-plane for 1-TMPNO (torsion angle 60°) (Figure 5). Using the

oxoammonium cation, while the reduction peak was due to delocalization of the aminoxy anion. Therefore, it can be concluded that the position of the radical moiety influences not only the electronic structure of pyrene but also the affinity of the radical moiety toward oxidation or reduction.

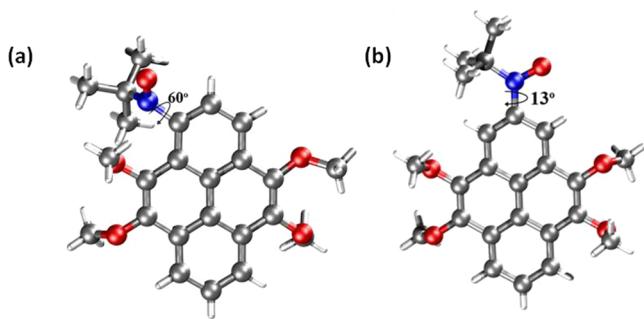


Figure 5. Crystal structures of (a) 1-TMPNO and (b) 2-TMPNO.

single-crystal geometries the spin densities were calculated with DFT. In concurrence with EPR measurements, the spin density was localized on nitroxide in 1-TMPNO but highly delocalized over the nitroxide and pyrene in 2-TMPNO, although the radical moiety was attached to the nodal plane of pyrene (Figure 6).

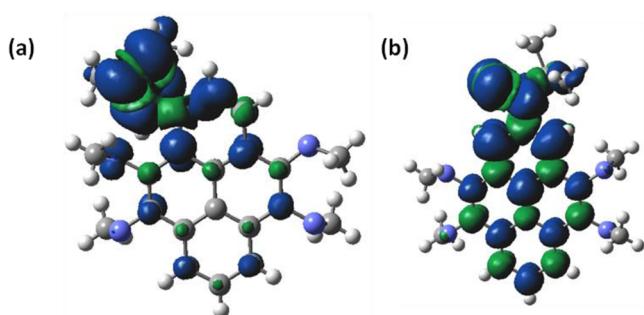


Figure 6. Spin density distributions in (a) 1-TMPNO and (b) 2-TMPNO.

To probe the influence of the position of the radical moiety on the electrochemical property of TMPNO, cyclic voltammetry (CV) measurements were carried out. The CV plots were measured in acetonitrile using ferrocene as an internal standard. While 2-TMPNO gave a reversible oxidation ($E^{1/2}(\text{ox}) = 0.94$ V) and reduction wave ($E^{1/2}(\text{red}) = -0.91$ V), the 1-TMPNO displayed a reversible oxidation ($E^{1/2}(\text{ox}) = 0.79$ V) and a nonreversible reduction wave (Figure 7). The oxidation peak could be assigned to resonance delocalization of

3. BIRADICALS, 1,6-, 1,8-, AND 2,7-TMPNO

TMP can be efficiently brominated by Br_2 in CCl_4 as a solvent at room temperature. Depending on the equivalence of bromine used and reaction time, mono-, di-, tri-, or tetrabromo-4,5,9,10-tetramethoxypyrene can be synthesized.²⁰ Dibromo-4,5,9,10-tetramethoxypyrene (DBrTMP) was obtained in 10 min after the addition of 2 M bromine in CCl_4 to the solution of TMP in CCl_4 , as a mixture of 1,6- and 1,8-isomers (Scheme 1), which even could not be separated by column chromatography. The mixture of both isomers DBrTMP was purified, however, on silica gel column, and only then applied in the next step for the synthesis of biradicals. Reaction of DBrTMP with $n\text{-BuLi}$ in diethyl ether and subsequent addition of 2-methyl-2-nitrosopropane gave bishydroxylamine, which was also used for further reaction without separating the isomers. Oxidation of bishydroxylamine yielded the desired biradicals. Both isomers showed poor stability on silica gel column but could be well-separated over the alumina column. The limited stability of 1,6- and 1,8-TMPNO allowed their characterization and analysis only by FD-Mass, EPR, UV-vis spectroscopy, and DFT calculations. The isomers were distinguished by low-temperature EPR measurements in toluene glass matrix. The synthesis and detailed characterization of isomer 2,7-TMPNO was previously reported.¹⁹ The 2,7-TMPNO exhibited exceptionally high stability in solution as well as in solid state under ambient conditions.

1,6-TMPNO and 1,8-TMPNO displayed similar UV-vis spectra as monoradical 1-TMPNO. Both biradicals showed the pyrene absorption around 360 nm, and the absorption due to radical moiety appeared as a shoulder to the pyrene absorption (Figure 8). This indicated, unlike found for 2,7-TMPNO, that 1,6-TMPNO and 1,8-TMPNO exist in complete biradicaloid structure.

The room-temperature EPR spectra of biradicals in toluene consisted of five lines due to hyperfine coupling of two equivalent nitrogen atoms (Figure 9). The spectral simulation gave the hfc constant $a_N = 1.6$ mT, as for the mono radical 1-TMPNO at a g value of 2.0068, just the line spacing is half due to the strong exchange interactions where J is much larger than the hfc constant ($J \gg a_N$). The EPR measurement of biradicals in toluene glass matrix at 140 K gave distinct fine structure spectra, as shown in Figure 9b,d. The zero-field splitting was observed due to dipolar (anisotropic) interaction of unpaired

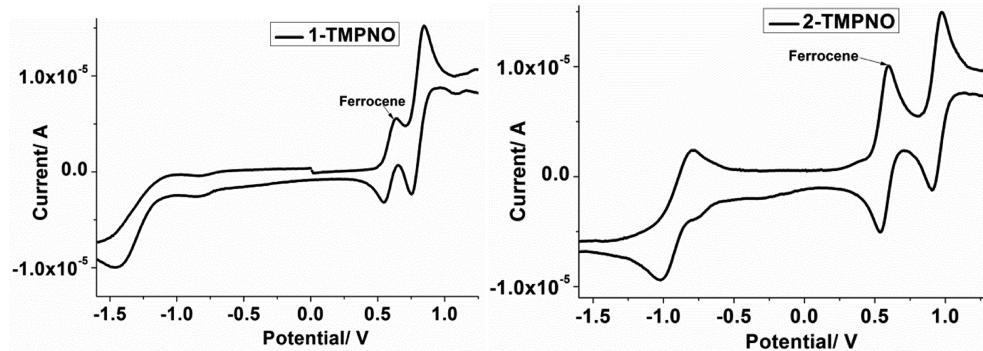


Figure 7. Cyclic voltammetry curves of 1-TMPNO and 2-TMPNO recorded in acetonitrile (Bu_4NPF_6 (0.1 M), scan rate of 100 mV/s).

Scheme 1. Synthesis of 1,6- and 1,8-TMPNO

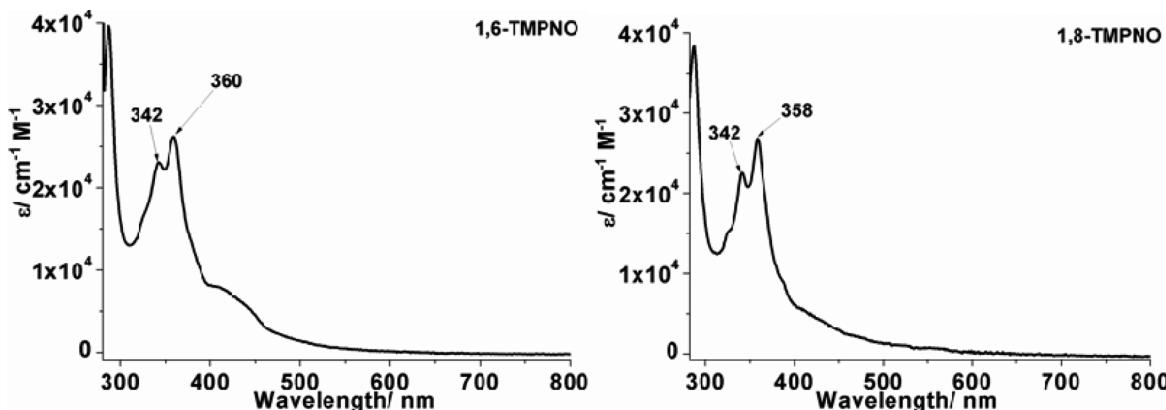
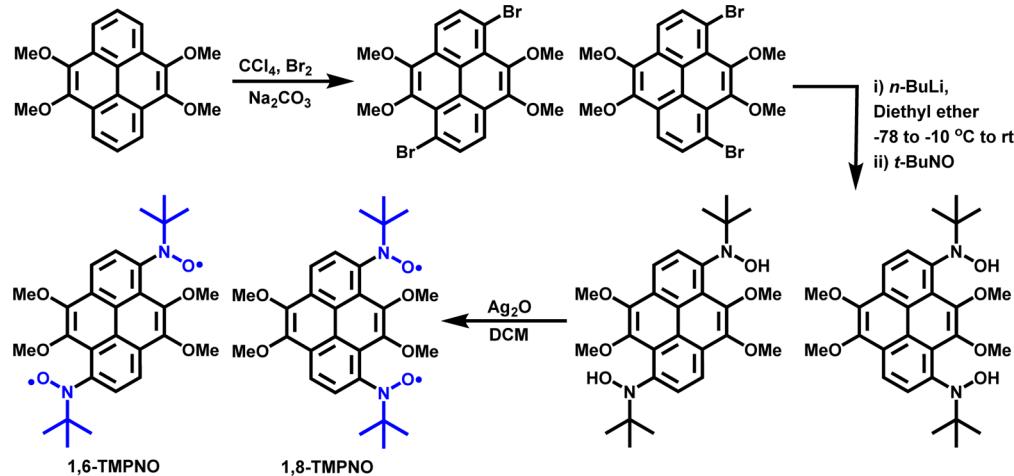


Figure 8. UV-vis spectra of 1,6-TMPNO and 1,8-TMPNO.

electrons in the molecules. The observed spectra in frozen toluene matrix are quite complex and difficult to reproduce by spectral simulation and only by adding up different simulations (see also Figures S2 and S3 in the SI). This is mainly caused by the different possible orientations of the radical moieties with respect to each other (E,Z, and further rotated isomers) in the frozen solution. For an axial symmetric system the magnitude of the *zfs* parameter *D* is related to the intraradical distance (*d*) by $1/d^3$. The *D* value increases as the distance between the radical center decreases. The average intraradical distance can be obtained by using the formulas, $d = 0.318/|D|^{1/3}$, where *d* and *D* are in nm and cm^{-1} units, respectively. The 1,6- and 1,8-

biradical isomers of TMPNO were distinguished from the magnitude of *D*. From the point dipole calculations using the above formula, the *D* value should be larger for the 1,8-isomer compared with the 1,6-isomer. Thus, the EPR spectrum with *D* value 9.2 mT was assigned to 1,8-TMPNO and with *D* value of 5.8 mT assigned to 1,6-TMPNO. The calculated average intraradical distances were 6.74 and 7.85 Å for 1,6-TMPNO and 1,8-TMPNO, respectively. Additionally, a $\Delta M_s = 2$ transition at half magnetic resonance field was also observed for both radicals supporting the biradical nature of the molecules.

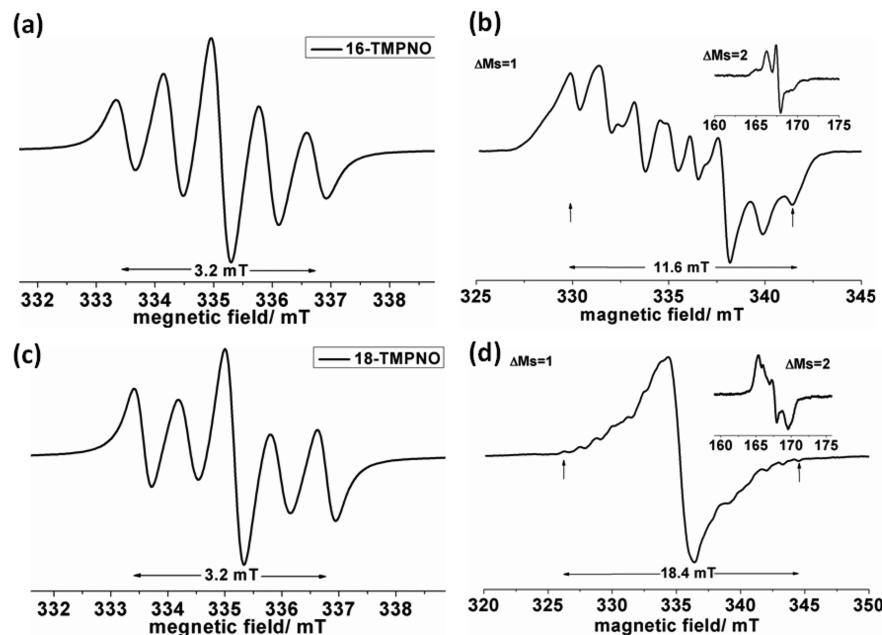


Figure 9. EPR spectra of 1,6-TMPNO in toluene (a) at room temperature and (b) in frozen state at 140 K and 1,8-TMPNO in toluene (c) at room temperature and (d) in frozen state at 140 K.

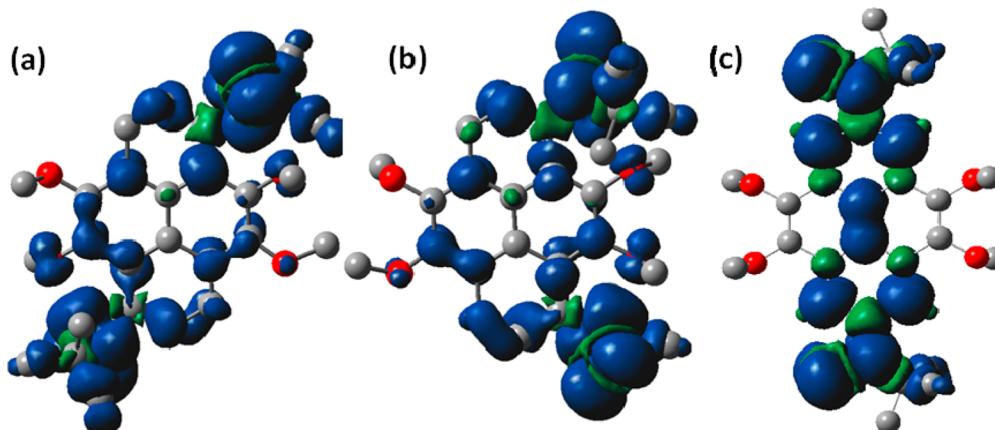


Figure 10. Spin density distribution of the triplet states of (a) 1,6-, (b) 1,8-, and (c) 2,7-TMPNO calculated at UBLYP/6-31G(d) level of theory. Hydrogen atoms are omitted for clarity.

4. DFT CALCULATIONS

The broken-symmetry DFT calculations were performed to get an insight into magnetic exchange interactions operating between radical moieties in biradicals 1,6-, 1,8-, and 2,7-TMPNO.^{21,22} The calculations were executed with the Gaussian 09 program package²³ employing the unrestricted²⁴ BLYP functional^{25–27} and the 6-31G(d) basis set.²⁸ The geometry of biradical 2,7-TMPNO was taken from X-ray diffraction determinations without further optimization. The X-ray structure geometry of monoradical 1-TMPNO was used for 1,6-TMPNO and 1,8-TMPNO by including one more radical moiety with same bond lengths and torsion angles at the desired positions. While the biradicals 1,6-TMPNO and 1,8-TMPNO showed similar triplet state spin density distribution, they showed large difference compared with the biradical 2,7-TMPNO (Figure 10). The biradical 2,7-TMPNO, which exists in semiquinoid form showed larger spin density distribution along the nodal plane of pyrene giving rise to extremely strong antiferromagnetic intramolecular exchange interaction, ex-

change coupling constant $J_{\text{intra}} = -1005 \text{ K}$.²⁴ The biradicals 1,6-TMPNO and 1,8-TMPNO displayed spin density distribution along the periphery of the pyrene core while nearly no spin density in the central part. The moderate exchange coupling constant (J_{intra}) values -121.6 and -108.1 K were obtained for 1,6-TMPNO and 1,8-TMPNO, respectively. It should be noted that although the distance between two radical moieties is in the order 2,7-TMPNO $>$ 1,6-TMPNO $>$ 1,8-TMPNO, the calculated J_{intra} , however, follows the order 2,7-TMPNO \gg 1,6-TMPNO $>$ 1,8-TMPNO (Table 2). In contrast with our

Table 2. Summary of DFT Calculations

molecule	$E, \text{ eV (BS)} (\langle S^2 \rangle)$	$J_{\text{intra}} (\text{K})$	$\Delta E_{\text{ST}} (\text{K})^a$	$d_{\text{rr}} (\text{\AA})^b$
1,6-TMPNO	-44806.60482 (0.99)	-121.6	-243	8.6
1,8-TMPNO	-44808.97459 (0.99)	-108.1	-216	7.2
2,7-TMPNO	-44813.72592 (0.82)	-1005.0	-2010	9.8

^aSinglet-triplet energy gap = $2J/k_B$. ^bEstimated distance between two N centers of biradical.

previous observation, here the exchange interactions decreases with decreasing the distance between the spin centers. The only logical reason came from consideration of the spin density distribution. These findings showed that in these biradical systems the exchange interactions operated more through bond than space and highly depend on the position of the radical moiety on the pyrene core and the spin density distribution along the π spacer.

5. SUMMARY

We have successfully synthesized the positional isomers of TMP-based mono- and biradicals. The structure–property analysis of isomeric mono- and biradicals showed that position of radical moiety highly influences the electronic structure of the aromatic core as well as the stability of radical moiety. While the 2,7-TMPNO exists in semiquinoid structure, the 1,6-TMPNO and 1,8-TMPNO exist in the biradical form. The calculated exchange coupling constant J_{intra} follows the order 2,7-TMPNO \gg 1,6-TMPNO $>$ 1,8-TMPNO, which shows that the exchange interactions highly depend on the distribution of spin density. Tuning of the exchange interactions was achieved in positional isomers maintaining the same radical moiety and π spacer.

■ ASSOCIATED CONTENT

Supporting Information

Detailed synthetic procedures. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcb.5b03056.

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Notes

The authors declare no competing financial interest.

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■ ABBREVIATIONS

DCM, dichloromethane; DFT, density functional theory; EPR, electron paramagnetic resonance; IN, iminonitroxide; NN, nitronylnitroxide; NO, *tert*-butylnitroxide; PAH, polyaromatic hydrocarbons; TMP, 4,5,9,10-tetramethoxypyrene

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