

Electronic Supporting Information

Three-Dimensional Magnetic Exchange Networks in Trigonal Bisdithiazolyl Radicals.

Nathan J. Yutronkie,[†] Demetris Bates,[#] Paul A. Dube,[⊥]

Stephen M. Winter,[∇] Craig M. Robertson,[#] Jaclyn L. Brusso,^{†,} and Richard T. Oakley^{‡,*}*

[†] Department of Chemistry, University of Ottawa, Ottawa, Ontario K1N 6N5, Canada

[#] Department of Chemistry, University of Liverpool, Liverpool L69 7ZD, UK

[⊥] Brockhouse Institute for Materials Research, McMaster University, Hamilton, Ontario L8S 4M1, Canada

[∇] Institut für Theoretische Physik, Goethe-Universität, Frankfurt am Main 60438, Germany

[‡] Department of Chemistry, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada

Corresponding author e-mail addresses: jbrusso@uottawa; oakley@uwaterloo.ca

Contents (9 pages total)

Table S1. Crystal Data.	Page S2
Figure S1. Calculated and Observed PXRD Patterns for PhBPMe.	Page S3
Figure S2. FTIR spectra of α - and β -phases of PhBPMe.	Page S4
Figure S3. Curie-Weiss and HTSE Fits for α -PhBPMe.	Page S4
Figure S4. AC Magnetic Susceptibility χ' and χ'' of α -PhBPMe	Page S5
Figure S5. Heat Capacity Measurements on α -PhBPMe.	Page S5
Figure S6. Pairwise coupling of radicals in $6 \times 6 \times 6$ cell of α -PhBPMe	Page S6
High Temperature Series Expansion (HTSE) Function for α -PhBPMe.	Pages S7-S8
Theoretical Calculations.	Page S9

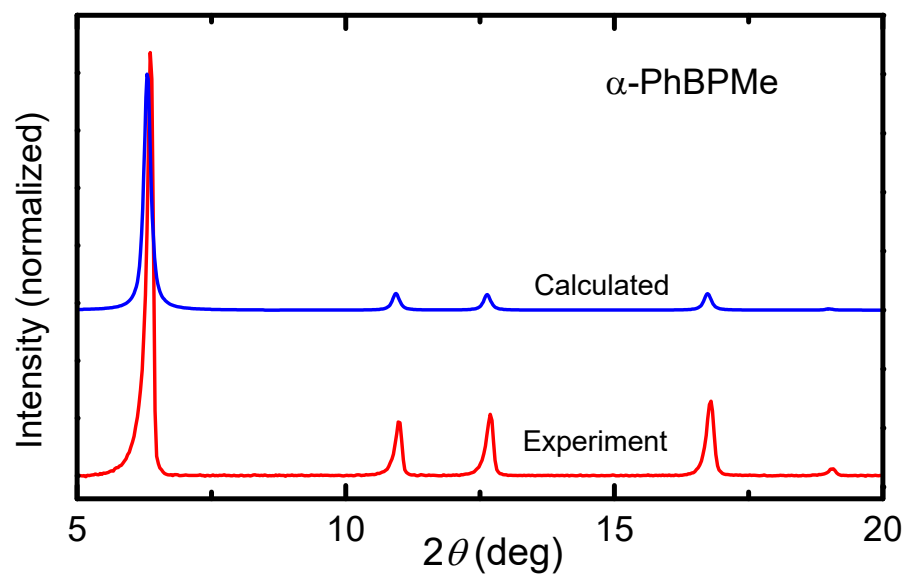
Table S1. Crystal Data.

	α -PhBPMe ^a	α -PhBPMe	β -PhBPMe	β -PhBPMe
CCDC Code	240201	1867302	1867303	1867304
Formula	C ₁₂ H ₈ N ₃ S ₄	C ₁₂ H ₈ N ₃ S ₄	C ₁₂ H ₈ N ₃ S ₄	C ₁₂ H ₈ N ₃ S ₄
<i>fw</i>	322.45	322.45	322.45	322.45
<i>a</i> (Å)	16.182(3)	16.22280(10)	21.084(4)	20.9556(6)
<i>b</i> (Å)	16.182(3)	16.22280(10)	4.0042(7)	3.8859(1)
<i>c</i> (Å)	4.2947(12)	4.17550(10)	30.170(5)	30.0859(9)
α (deg)	90	90	90	90
β (deg)	90	90	90	90
γ (deg)	120	120	90	90
<i>V</i> (Å ³)	974.0(4)	951.68(3)	2547.1(8)	2449.94(12)
ρ (calcd), g cm ⁻³	1.649	1.688	1.682	1.748
space group	<i>P</i> 3 ₁ 21	<i>P</i> 3 ₁ 21	<i>Pca</i> 2 ₁	<i>Pca</i> 2 ₁
<i>Z</i>	3	3	8	8
Temp (K)	295(2)	100(2)	293(2)	100(2)
μ (mm ⁻¹)	0.718	3.660	0.675	7.015
λ (Å)	0.71073	0.68890	0.68890	1.54178
data/restr./params.	1500/0/101	2598/0/138	5095/1/345	3847/1/345
solution method	direct methods	direct methods	direct methods	direct methods
<i>R</i> ₁ , <i>wR</i> ₂	0.0363, 0.0725	0.0166, 0.0461	0.0651, 0.1632	0.0344, 0.0813

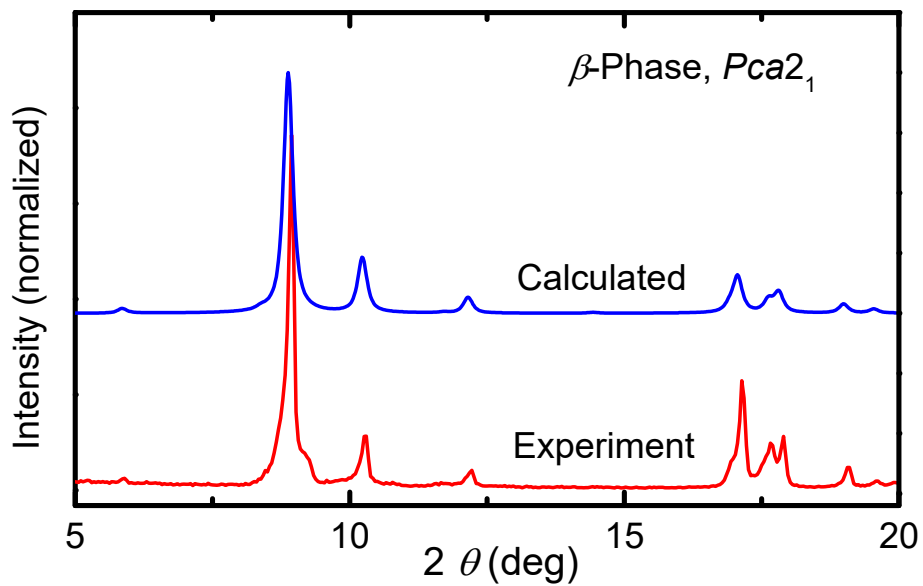
^a From ref. 13 (main text).

Figure S1. Calculated and Observed PXRD patterns ($\lambda = 1.54060 \text{ \AA}$) for PhBPMc.^a

α -Phase



β -Phase



^a Representative samples used for magnetic measurements.

Figure S2. FTIR spectra of α - and β -phases of PhBPMc.

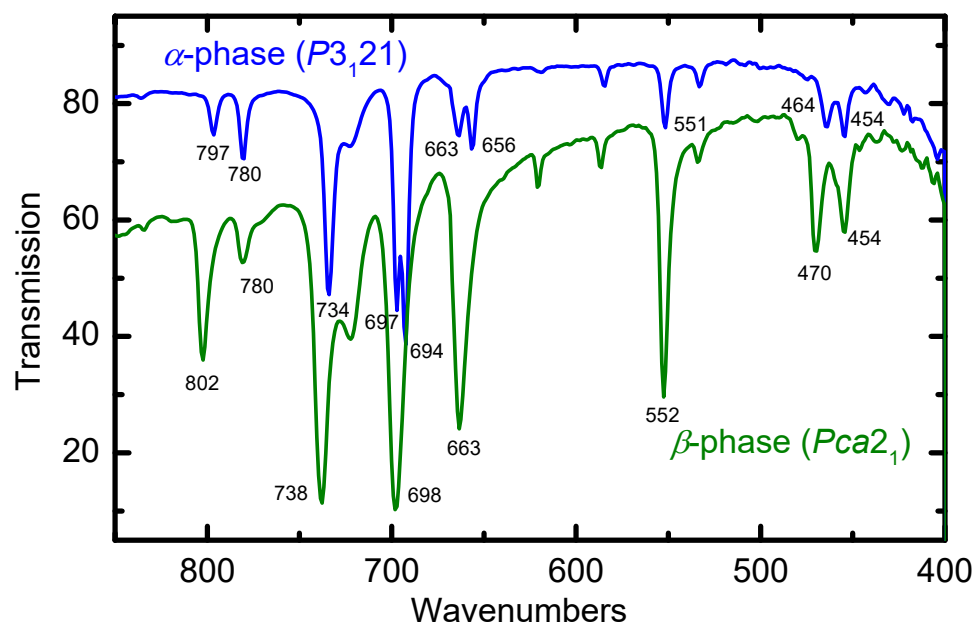


Figure S3. Curie-Weiss and HTSE Fits for α -PhBPMc.

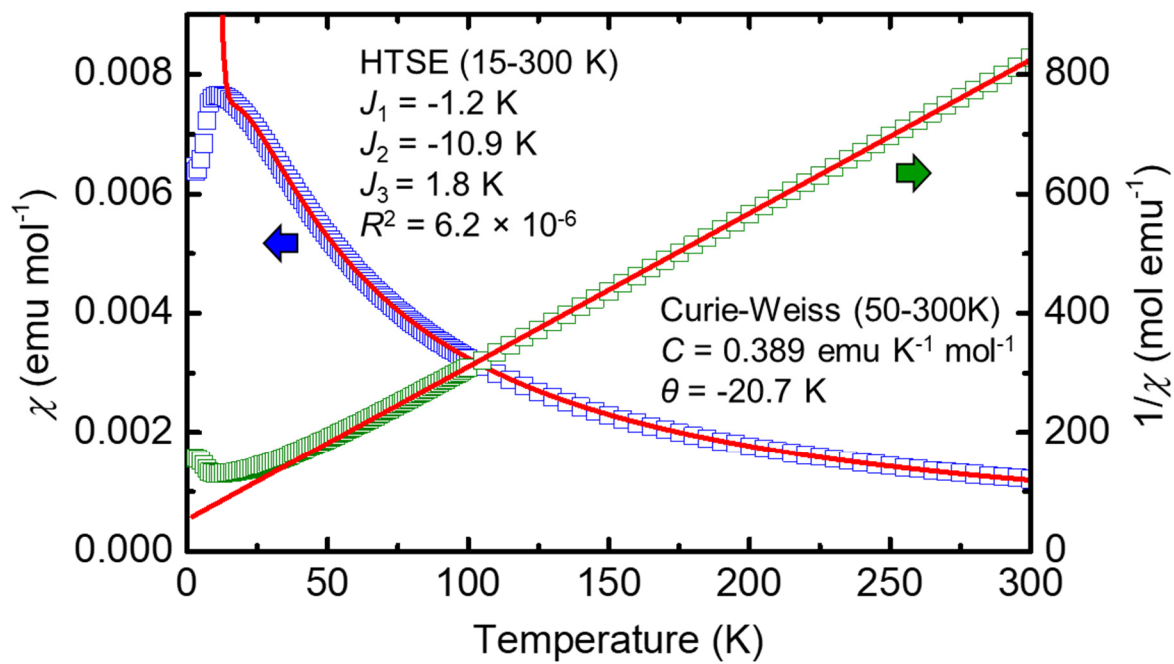
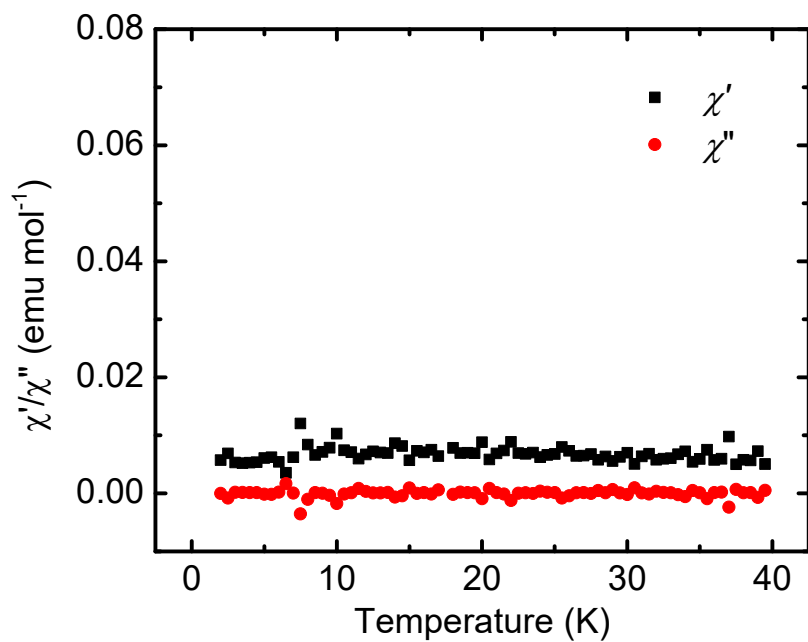


Figure S4. AC Magnetic Susceptibility χ' and χ'' of α -PhBPMc at 10 Hz.^a



^a No evidence for a magnetic phase transition was observed at any frequency from 10-1000Hz.

Figure S5. Heat Capacity Measurements on α -PhBPMc.

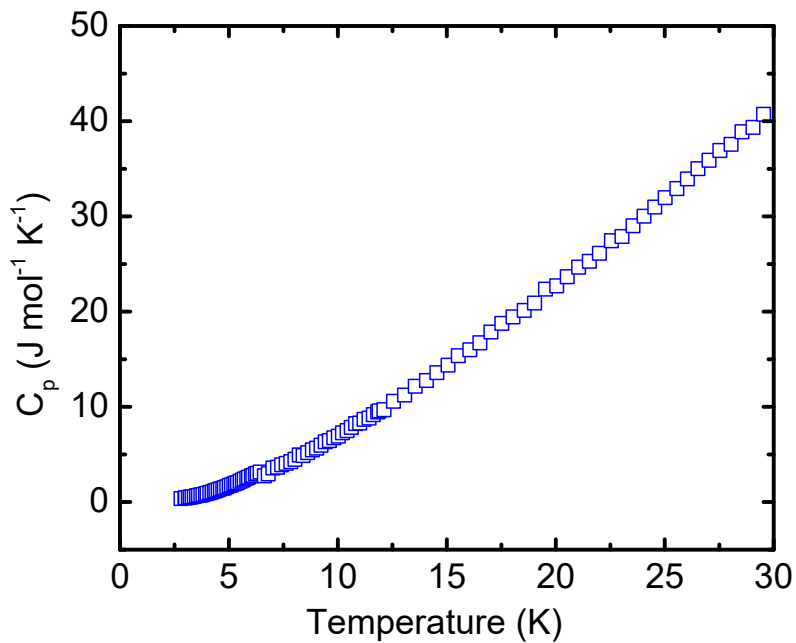
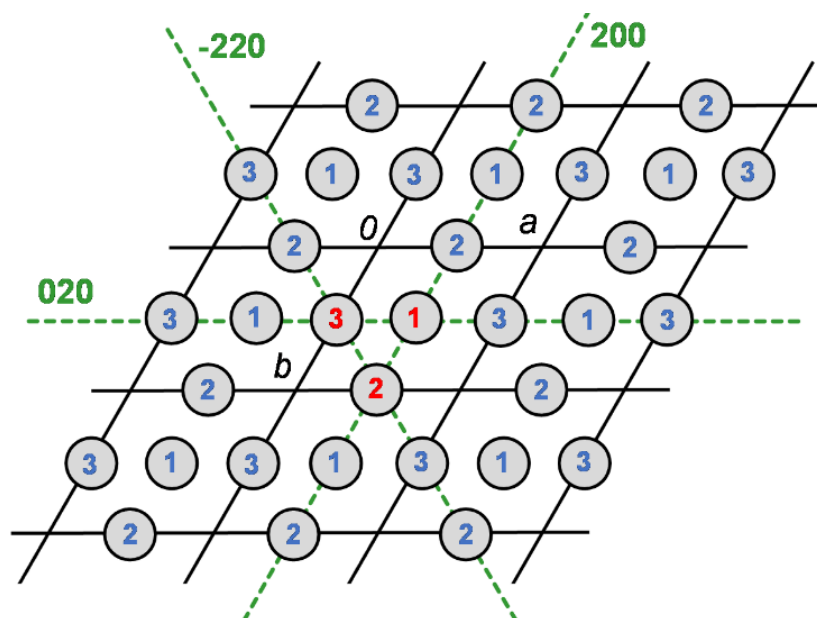


Figure S6. Pairwise coupling of radicals in $6 \times 6 \times 6$ cell of α -PhBPMe.^a



J_1 pairs	J_2 pairs	$J_3 (= J_\pi)$ pairs
1, 3	1, 3 + z	1, 1 + z
1, 3 + x	1, 3 + z + x	2, 2 + z
1, 2	1, 2 - z	3, 3 + z
1, 2 - y	1, 2 - z - y	
2, 3 + x + y + z	2, 3	
2, 3 + z	2, 3 + x + y	

^aThe three radicals labelled (in red) 1, 2 and 3 constitute the trigonal unit cell, with radicals (in blue) in neighboring cells along x , y and z . Interacting pairs are designated by their translations, for example, $(1 + x)$ indicates radical 1 in the cell shifted once along the $+x$ direction.

High Temperature Series Expansion (HTSE) Function for α -PhBPMe

Based on the expanded trigonal cell diagram shown in Figure S6, a fit function to estimate for the magnetic susceptibility χ of the trigonal phase of PhBPMe in terms of the unique pairwise exchange energies J_1 , J_2 , and J_3 ($= J_\pi$) was developed up to eighth order in $1/T$ ($n = 8$ below) according to method of Schmidt, Lohmann and Richter (ref. 27, main text). The general expression is given by:

$$\chi = C \sum_n \frac{c_n}{(k_b T)^n}$$

where C is the Curie constant and the coefficients c_n are given in terms of J_1 , J_2 , and J_3 ($= J_\pi$).

Note: In the expressions for c_n provided below, J -values are defined with respect to the Hamiltonian $H_{ex} = J_{ij} \{S_i \cdot S_j\}$. The values extracted from a fit to the data using these expressions were adjusted afterwards to conform with the convention $H_{ex} = -2 J_{ij} \{S_i \cdot S_j\}$ used in the main text.

$$c1 = 0.2500000000$$

$$c2 = -2.500000000000e-01 * J1 - 2.500000000000e-01 * J2 - 1.250000000000e-01 * J3$$

$$c3 = 1.250000000000e-01 * J1**2 + 5.000000000000e-01 * J1 * J2 + 1.250000000000e-01 * J2**2 + 2.500000000000e-01 * J1 * J3 + 2.500000000000e-01 * J2 * J3$$

$$c4 = -4.166666666667e-02 * J1**3 - 4.348958333333e-01 * J1**2 * J2 - 4.739583333333e-01 * J1 * J2**2 - 4.166666666667e-02 * J2**3 - 2.500000000000e-01 * J1**2 * J3 - 6.197916666667e-01 * J1 * J2 * J3 - 2.500000000000e-01 * J2**2 * J3 - 6.250000000000e-02 * J1 * J3**2 - 6.250000000000e-02 * J2 * J3**2 + 1.041666666667e-02 * J3**3$$

$$c5 = 2.994791666667e-02 * J1**4 + 2.269965277778e-01 * J1**3 * J2 + 7.154947916667e-01 * J1**2 * J2**2 + 2.812500000000e-01 * J1 * J2**3 + 2.994791666667e-02 * J2**4 + 1.406250000000e-01 * J1**3 * J3 + 8.190104166667e-01 * J1**2 * J2 * J3 + 8.190104166667e-01 * J1 * J2**2 * J3 + 1.536458333333e-01 * J2**3 * J3 + 1.562500000000e-01 * J1**2 * J3**2 + 2.773437500000e-01 * J1 * J2 * J3**2 + 1.562500000000e-01 * J2**2 * J3**2 - 2.083333333333e-02 * J1 * J3**3 - 2.083333333333e-02 * J2 * J3**3 + 3.255208333333e-03 * J3**4$$

$$c6 = -2.356770833333e-02 * J1**5 - 1.353624131944e-01 * J1**4 * J2 - 6.078559027778e-01 * J1**3 * J2**2 - 7.245008680556e-01 * J1**2 * J2**3 - 1.622178819444e-01 * J1 * J2**4 - 2.356770833333e-02 * J2**5 - 6.835937500000e-02 * J1**4 * J3 - 7.163628472222e-01 * J1**3 * J2 * J3 - 1.419487847222e+00 * J1**2 * J2**2 * J3 - 7.693142361111e-01 * J1 * J2**3 * J3 - 8.018663194444e-02 * J2**4 * J3 - 1.777343750000e-01 * J1**3 * J3**2 - 5.970052083333e-01 * J1**2 * J2 * J3**2 - 5.891927083333e-01 * J1 * J2**2 * J3**2 - 1.796875000000e-01 * J2**3 * J3**2 - 1.041666666667e-02 * J1**2 * J3**3 - 8.680555555556e-03 * J1 * J2 * J3**3 - 1.041666666667e-02 * J2**2 * J3**3 + 3.906250000000e-03 * J1 * J3**4 + 3.906250000000e-03 * J2 * J3**4 - 1.367187500000e-03 * J3**5$$

$$\begin{aligned}
c7 = & 4.871961805556e-03*J1^{**6} + 1.184678819444e-01*J1^{**5}*J2 + 3.957302517361e- \\
& 01*J1^{**4}*J2^{**2} + 9.856987847222e-01*J1^{**3}*J2^{**3} + 5.382541232639e-01*J1^{**2}*J2^{**4} + \\
& 1.241699218750e-01*J1*J2^{**5} + 6.092664930556e-03*J2^{**6} + 6.080729166667e- \\
& 02*J1^{**5}*J3 + \\
& 4.917263454861e-01*J1^{**4}*J2*J3 + 1.740272352431e+00*J1^{**3}*J2^{**2}*J3 + \\
& 1.789621310764e+00*J1^{**2}*J2^{**3}*J3 + 5.953667534722e-01*J1*J2^{**4}*J3 + \\
& 6.093750000000e-02*J2^{**5}*J3 + 1.187825520833e-01*J1^{**4}*J3^{**2} + 8.188368055556e- \\
& 01*J1^{**3}*J2*J3^{**2} + 1.304215494792e+00*J1^{**2}*J2^{**2}*J3^{**2} + 8.129665798611e- \\
& 01*J1*J2^{**3}*J3^{**2} + 1.282280815972e-01*J2^{**4}*J3^{**2} + 7.816840277778e-02*J1^{**3}*J3^{**3} \\
& + 1.649305555556e-01*J1^{**2}*J2*J3^{**3} + 1.687391493056e-01*J1*J2^{**2}*J3^{**3} + \\
& 7.351345486111e-02*J2^{**3}*J3^{**3} - 2.073567708333e-02*J1^{**2}*J3^{**4} - 2.479383680556e- \\
& 02*J1*J2*J3^{**4} - 2.073567708333e-02*J2^{**2}*J3^{**4} + 5.989583333333e-03*J1*J3^{**5} + \\
& 5.989583333333e-03*J2*J3^{**5} - 1.082356770833e-03*J3^{**6}
\end{aligned}$$

$$\begin{aligned}
c8 = & 6.828187003968e-04*J1^{**7} - 5.989990234375e-02*J1^{**6}*J2 - 3.101241500289e- \\
& 01*J1^{**5}*J2^{**2} - 8.564520941840e-01*J1^{**4}*J2^{**3} - 1.073144079138e+00*J1^{**3}*J2^{**4} - \\
& 3.742840802228e-01*J1^{**2}*J2^{**5} - 7.537887008102e-02*J1*J2^{**6} - 2.354213169643e- \\
& 04*J2^{**7} - \\
& 4.366590711806e-02*J1^{**6}*J3 - 3.521421079282e-01*J1^{**5}*J2*J3 - \\
& 1.631472891348e+00*J1^{**4}*J2^{**2}*J3 - 2.810948350694e+00*J1^{**3}*J2^{**3}*J3 - \\
& 1.842822265625e+00*J1^{**2}*J2^{**4}*J3 - 4.239859121817e-01*J1*J2^{**5}*J3 - \\
& 4.374547887731e-02*J2^{**6}*J3 - 7.346462673611e-02*J1^{**5}*J3^{**2} - 8.087391040943e- \\
& 01*J1^{**4}*J2*J3^{**2} - 2.089635326244e+00*J1^{**3}*J2^{**2}*J3^{**2} - \\
& 2.097923448351e+00*J1^{**2}*J2^{**3}*J3^{**2} - 8.452121310764e-01*J1*J2^{**4}*J3^{**2} - \\
& 8.492725513600e-02*J2^{**5}*J3^{**2} - 1.097819010417e-01*J1^{**4}*J3^{**3} - 4.194905598958e- \\
& 01*J1^{**3}*J2*J3^{**3} - 6.256347656250e-01*J1^{**2}*J2^{**2}*J3^{**3} - 4.042932581019e- \\
& 01*J1*J2^{**3}*J3^{**3} - 1.045875831887e-01*J2^{**4}*J3^{**3} + 1.278754340278e-02*J1^{**3}*J3^{**4} \\
& + 2.748390480324e-02*J1^{**2}*J2*J3^{**4} + 2.600685402199e-02*J1*J2^{**2}*J3^{**4} + \\
& 1.231418185764e-02*J2^{**3}*J3^{**4} - 2.522786458333e-03*J1^{**2}*J3^{**5} - 4.423466435185e- \\
& 03*J1*J2*J3^{**5} - 2.522786458333e-03*J2^{**2}*J3^{**5} + 3.634982638889e-04*J1*J3^{**6} + \\
& 3.634982638889e-04*J2*J3^{**6} + 6.200396825397e-05*J3^{**7}
\end{aligned}$$

$$\chi_{HTSE} = c1/T + c2/T + c3/T + c4/T + c5/T + c6/T + c7/T + c8/T$$

$$\chi = tip + 4*C*\chi_{HTSE}$$

Theoretical Calculations Exchange energy calculations were performed at the DFT level using the UB3LYP functional and the split-valence triple-basis set 6-311G(d,p), as contained in the Gaussian 09W suite of programs (ref. 39, main text). Tight convergence criteria were employed, and atomic coordinates were taken from the crystallographic data at 100 K. Exchange energies based on a Heisenberg Hamiltonian $H_{\text{ex}} = -2J \{S_i \cdot S_j\}$ for interacting pairs of radicals for the α - and β -phase of PhBPMc (Figure 8, main text) were computed from Eqn 2 (main text), using single-point energies of the triplet E_{TS} and broken symmetry singlet E_{BSS} states and their respective $\langle S^2 \rangle$ expectation values. These values are summarized in Table 1 of the main text.

α -Phase J -values

Interaction	E_{TS} (H)	$\langle S^2 \rangle_{\text{TS}}$	E_{BSS} Singlet (H)	$\langle S^2 \rangle_{\text{BSS}}$	J (K)
J_1 (1 step)	-4438.39622070	2.066	-4438.39620838	1.0656	3.89
J_2 (2 steps)	-4438.39807573	2.0661	-4438.39809544	1.0641	-6.21
J_π (3 steps)	-4438.39467528	2.0659	-4438.39456465	1.0641	34.87

β -Phase J -values

Interaction	E_{TS} (H)	$\langle S^2 \rangle_{\text{TS}}$	E_{BSS} Singlet (H)	$\langle S^2 \rangle_{\text{BSS}}$	J (K)
J_π (1)	-4438.39241194	2.0676	-4438.39272647	1.0477	-97.39
J_π (1)	-4438.39352196	2.066	-4438.39372783	1.0523	-64.13
J_1	-4438.39592039	2.0665	-4438.39589736	1.0664	7.27
J_2	-4438.39655709	2.0666	-4438.39653683	1.0665	6.40
J_3	-4438.39560453	2.0668	-4438.39558231	1.0666	7.02
J_4	-4438.39635168	2.0668	-4438.39635239	1.0662	-0.22