

Supporting Information

Cu(II) conjugation along the transformation of Vitamin K₃ derivative to dinaphthoquinone methide radical

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GSH activity calculations:

1. The net rate of decrease in A_{340} for the sample was calculated by subtracting the rate observed for a blank (where water is used instead of sample) from the rate observed for each sample.

2. The net A_{340} /min for the test sample was converted to NADPH consumed using the following relationship:

1 unit of Glutathione Reductase causes the formation of 1 mmol NADP + form NADPH per min at pH 7.0 at 25° C.

Extinction coefficient for NADPH is $0.00622 \text{ mM}^{-1} \text{ cm}^{-1}$ at 340 nm.

3. Activity of GR is expressed as International Unit/Liter (U/L) of the sample or in terms of the protein or hemoglobin content.

4. A theoretical unique factor is determined to convert change in absorbance per minute (Δ /min) to the corresponding units of enzyme activity. This factor is calculated using the following equation:

$U/L = \Delta A/\text{minute} \times F$; where $F =$ factor

$F = (TV/SV) \times 10^3 / 6.22$, where

TV = Total Volume in ml

SV = Sample Volume in ml

$10^3 =$ converts ml to L

6.22 = millimolar absorbance coefficient

For this assay, with a 1 cm light path, the factor calculates to be 4455. This factor can be programmed into the spectrophotometer and the machine directly converts the change in absorbance at 340 nm ($\Delta A/\text{min}$) to activity in U/L, or alternately, results can be calculated manually.

Table S1. Crystal data and structure refinement for 1,1'-methide-bi-Vitamin K₃.

Identification code	1,1'-methide-bi-Vitamin K ₃	
Empirical formula	C ₂₂ H ₁₆ O ₂	
Formula weight	312.35	
Temperature	123(2) K	
Wavelength	1.54184 Å	
Crystal system	Triclinic	
Space group	<i>P</i> -1̄	
Unit cell dimensions	a = 7.5080(4) Å	α = 82.421(5)°.
	b = 9.0339(7) Å	β = 87.073(4)°.
	c = 12.3483(7) Å	γ = 65.899(6)°.
Volume	757.85(8) Å ³	
Z	2	
Density (calculated)	1.369 Mg/m ³	
Absorption coefficient	0.685 mm ⁻¹	
F(000)	328	
Crystal size	0.54 x 0.18 x 0.08 mm ³	
Theta range for data collection	5.40 to 73.60°.	
Index ranges	-9 ≤ h ≤ 6, -11 ≤ k ≤ 10, -14 ≤ l ≤ 15	
Reflections collected	4872	
Independent reflections	2978 [R(int) = 0.0152]	
Completeness to theta = 67.50°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.81280	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	2978 / 0 / 219	
Goodness-of-fit on F ²	1.068	
Final R indices [I > 2σ(I)]	R1 = 0.0489, wR2 = 0.1381	
R indices (all data)	R1 = 0.0523, wR2 = 0.1420	
Largest diff. peak and hole	0.400 and -0.193 e.Å ⁻³	
CCDC	801765	

Lattice energy calculations:

The inspection of crystal structure from PLATON using KPI (Kitaigorodskii packing index) function revealed a high value for packing index (73.0%). The lattice energies using the OPIX program^[18b] turns out to be -181.0 kJ mol⁻¹. These were obtained by adding atom–atom pair-wise potential energies derived from the UNI force field.^[a, b] The contribution of intermolecular interaction from C20–H20···O1 interactions to the lattice energies was estimated to be -22.3 kJ mol⁻¹ which is in the range of those reported in the literature.^[c, d] The π···π interactions those stem from zipping of two layers engaging both rings of naphthoquinone (Cg···Cg = 3.904(1) Å) have intermolecular potential of -57.3 kJ mol⁻¹. The assessment of intermolecular potentials associated with π···π interactions between the benzenoidal phenyl rings within the layered assembly (Cg···Cg = 3.531(1) Å) and stitching of the layered structure (Cg···Cg = 3.604(1) Å) were found to be -42.1 kJ mol⁻¹ and -39.2 kJ mol⁻¹ respectively. These values point to the unusual strength of π···π interactions in molecular packing.

- a] G. Filippini, A. Gavezzotti, *Acta Crystallogr.*, **1993**, B49, 868-880;
b] A. Gavezzotti, G. Filippini, *J. Phys. Chem.*, **1994**, 98, 4831-4837; c] K. M. Sureshan, R. G. Gonnade, *Cryst. Eng. Comm.*, **2013**, 15, 1676-1679; d] C. F. Macrae, I. J. Bruno, J. A. Chisholm, P. R. Edgington, P. McCabe, E. Pidcock, L. Rodriguez-Monge, R. Taylor, J. van de Streek, P. A. Wood, *J. Appl. Crystallogr.*, **2008**, 41, 466-470.

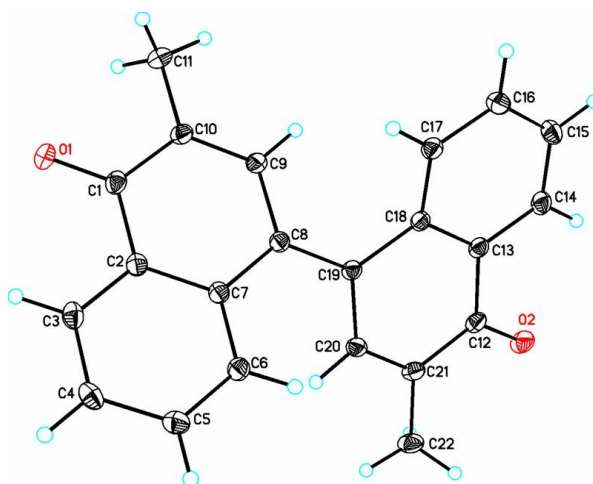
Cu estimation results:

- 1) Blank solution- Nil.
- 2) **B** (M:L :: 1:1) - 29.29 ppm in 20.3 mg **B**
- 3) **B** (M:L :: 0.25:1) - 27.26 ppm in 20.1 mg **B**

Average Cu required to get 70% yield of DNQM = 28.275 ± 1.015 ppm \equiv $\sim 0.14\%$
 \therefore 100 g DNQM \equiv 0.14 g Cu or after 100 moles of DNQM 0.688 mole of Cu

X-ray structural studies:

ORTEP of 1,1'-methide-bi-vitamin K₃ (DNQM) product (B)



Mol. Wt.: 312.37 Mol Formula: C₂₂H₁₆O₂ M.P.=185 °C
Molecular Composition: C 84.59 % , H 5.26 % , O 10.24 %

Elemental Analyses result of B:

Element	% Expected	% Observed
C	84.59	84.75
H	5.26	5.45

Computational / Theoretical studies:

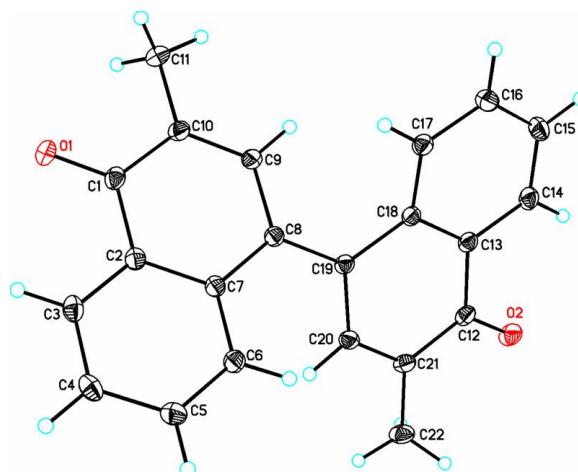


Figure. S1: The numbering schemes in **B**. Carbons are depicted in gray color, oxygens are red and hydrogens are cyan color.

Optimized structures from B3LYP/6-31G (d,p) theory.

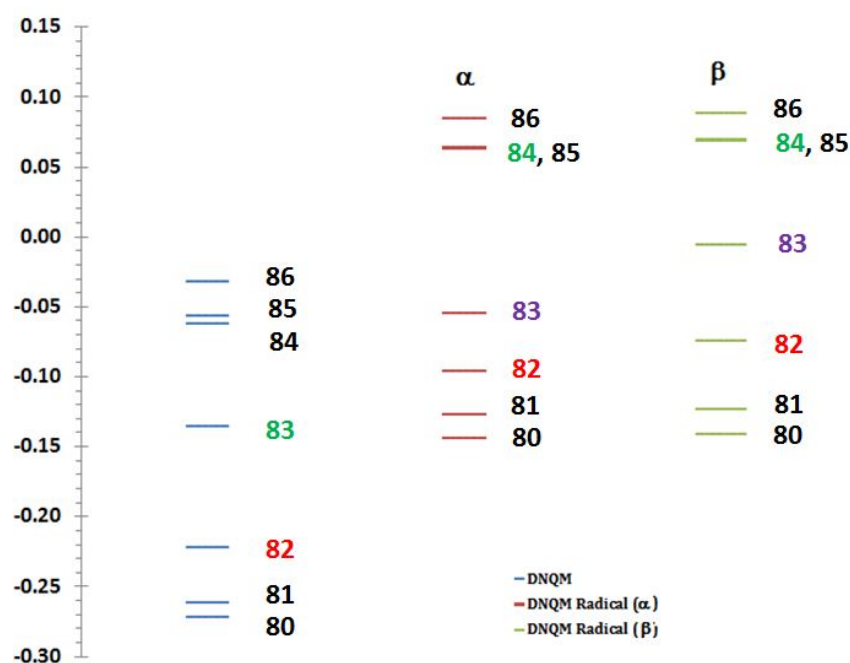


Figure S2: Correlation diagram between the energy eigenvalues of selected MOs calculated for DNQM and DNQM radical in their groundstates. The HOMO and LUMO of the **B** are represented by red and green colours, respectively. The SOMO of the **B** radical is represented by the lavender (83) colour.

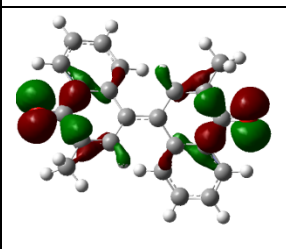
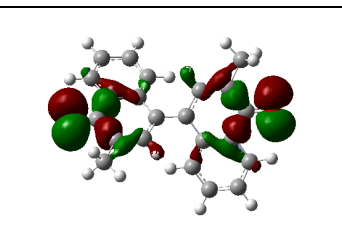
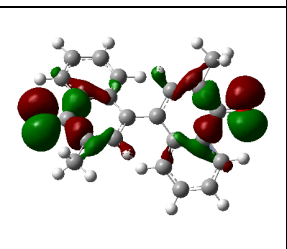
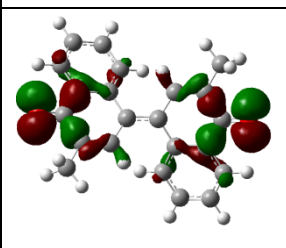
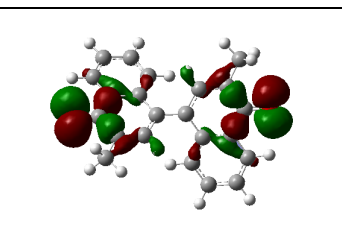
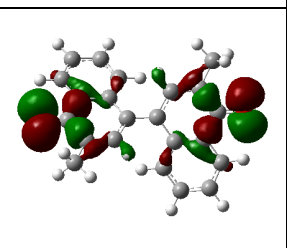
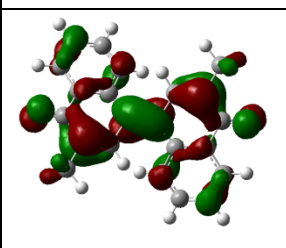
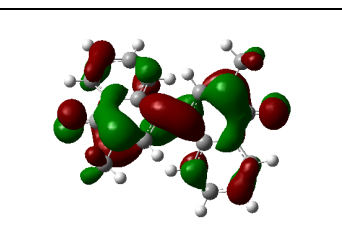
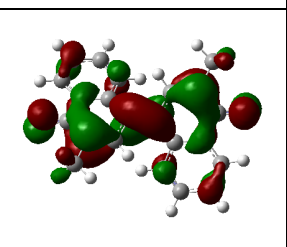
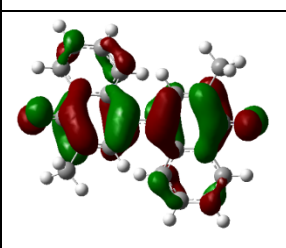
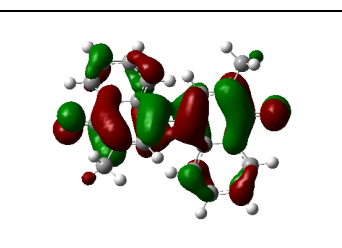
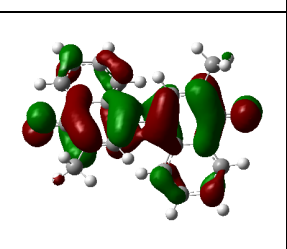
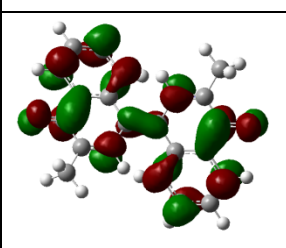
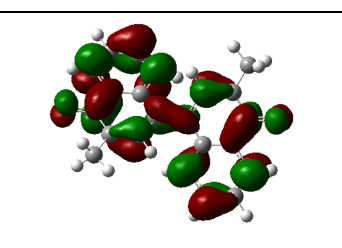
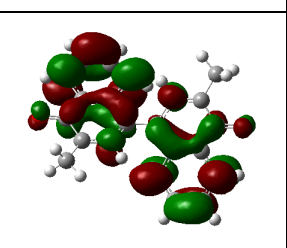
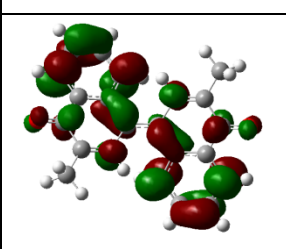
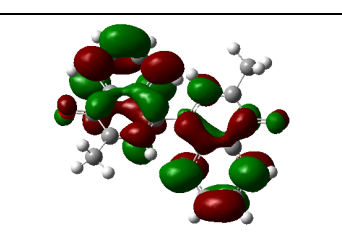
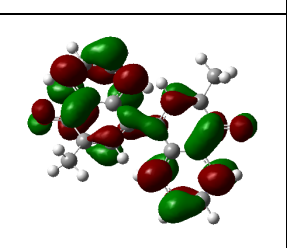
MO	B (neutral)	B (radical)	
		Alpha	Beta
80			
81			
82			
83			
84			
85			

Figure S3: The MOs in **B** (neutral) and **B** (radical) forms.

Sr.	Atom	FC	Sr.	Atom	FC
1	C	-1.61	21	C	4.92
2	C	1.51	22	C	-1.43
3	C	-1.27	23	O	-5.05
4	C	1.78	24	O	-5.05
5	C	-0.83	25	H	0.28
6	C	1.25	26	H	-1.10
7	C	-1.45	27	H	0.18
8	C	5.35	28	H	-0.90
9	C	-1.43	29	H	0.19
10	C	4.92	30	H	3.45
11	C	-1.43	31	H	4.41
12	C	-1.61	32	H	0.03
13	C	1.51	33	H	0.28
14	C	-1.27	34	H	-1.10
15	C	1.78	35	H	0.18
16	C	-0.83	36	H	-0.90
17	C	1.25	37	H	0.19
18	C	-1.45	38	H	3.45
19	C	5.35	39	H	4.41
20	C	-1.43	40	H	0.03

Table S2: The Fermi contact coupling constant (FC) (in G) for atoms in the radical form.

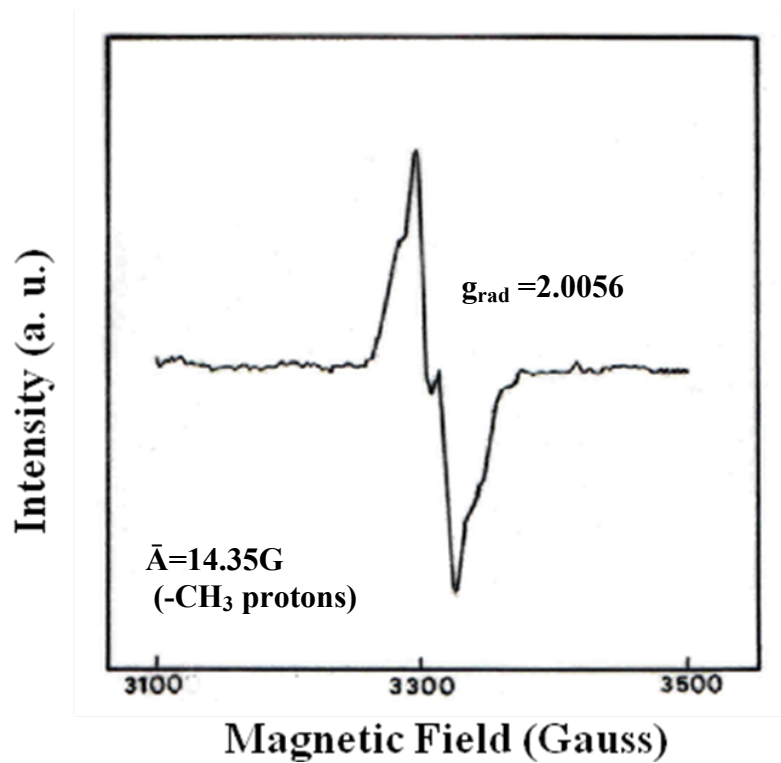


Figure S4: Frozen glass X-band ESR spectrum of **B** in DMSO at 70 K.

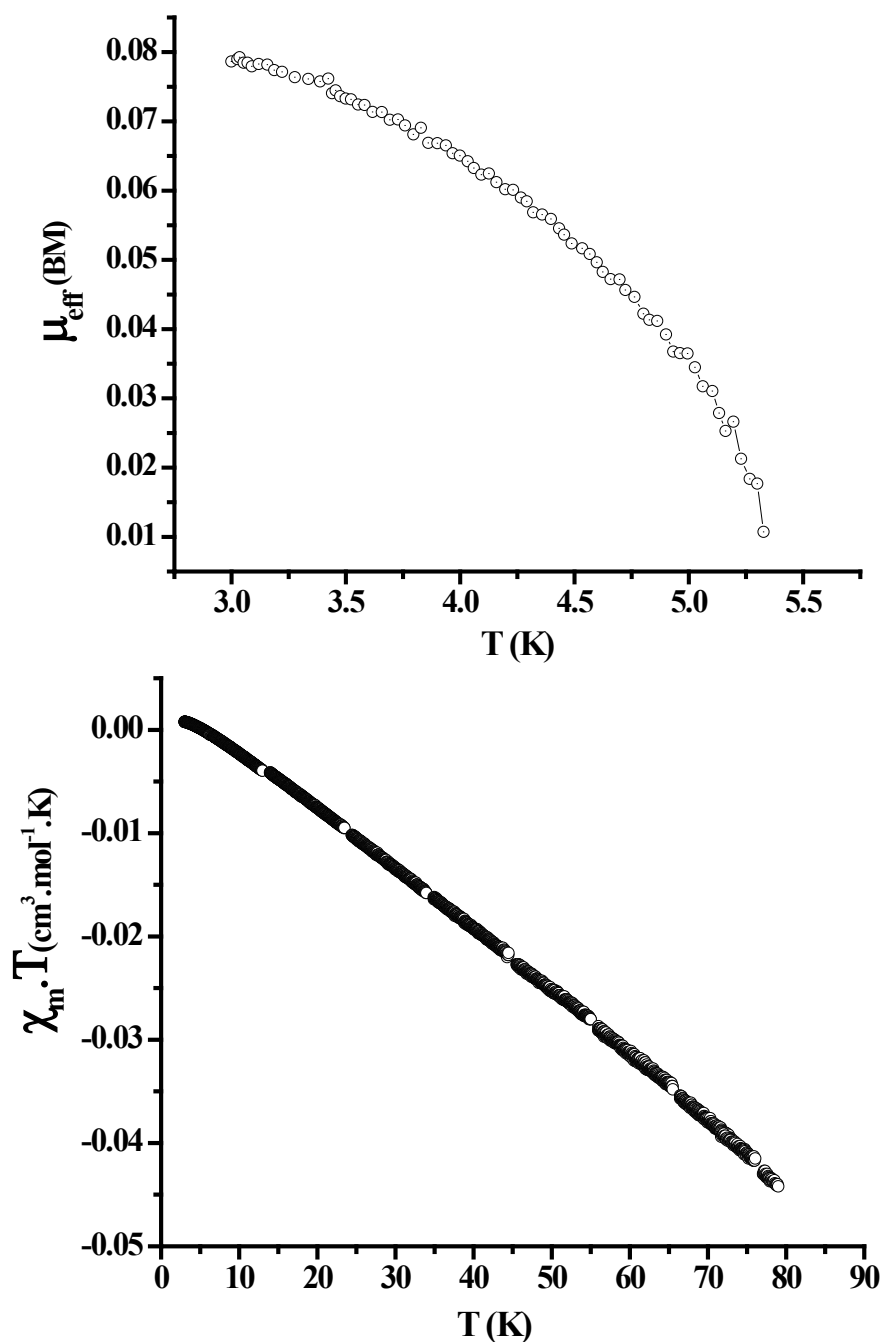


Figure S5: (a) Plot of μ_{eff} (BM) vs. T (K) and (b) Plot of $\chi_m^{\text{corr}} \cdot T$ ($\text{cm}^3 \text{mol}^{-1} \cdot \text{K}$) vs. T (K) of **B**.

The μ_{eff} at 3K is ~ 0.08 B.M. at 1T applied field which is nearly half of phthiocoloxime^[24]. Such radical dimers showing weak ferromagnetic behavior at liq. He temperature are reported by Palacio *et. al* and Murphy *et. al* (A.J. Banister, N. Bricklebank, I. Lavender, J.M. Rawson, C.I. Gregory, B.K. Tanner, W. Clegg, M.R.J. Elesgood, F. Palacio, *Angew. Chem. Int. Ed. Engl.* 1996, **35**, 2533, A. Alberola, R.J. Less, C.M. Pask, J.M. Rawson, F. Palacio, P. Oliete, C. Paulsen, A. Yamaguchi, R. Farley, D.M. Murphy, *Angew. Chem. Int. Ed. Engl.* 2003, 42, 4782). **S9**