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Nitroxide radicals appended to phthalonitriles: synthesis, structural characterization and photophysical properties

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Nitroxide Radical-Appended Phthalonitriles: Synthesis, Structural Characterization, and Photophysical Properties

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Table of Contents	page
1. General Information	S2
2. Synthetic Procedures	S4
3. FT-IR and Mass Spectra of Compounds	S5
4. Absorption Spectroscopy	S8
5. Electron Paramagnetic Resonance (EPR) Spectroscopy	S22
6. Magnetic Measurements	S24
7. X-ray Diffraction Analysis	S25
8. References	S27

GENERAL INFORMATION

Reagents and solvents: All reagents, purchased from fine chemical suppliers Aldrich, Merck, Alfa Aesar, and Fluka, were used without further purification unless otherwise stated. Solvents were either used as commercially supplied or used as purified by standard techniques.

Methods: Nonaqueous reactions were performed in oven-dried glassware under argon atmosphere at reported temperature. Microwave reactions were carried out in open vessels at specified conditions using Milestone Start S Microwave Labstation for Synthesis. Reactions were monitored by thin layer chromatography on Merck silica gel 60 F254 precoated aluminum sheets. Spots were visualized either by UV 254 nm light or by staining with acidic ninhydrin solution. Column chromatography was performed on Merck silica gel 60 (230-400 mesh size) using the appropriate solvent system as eluent.

Melting Points: Melting points were obtained using Stuart SMP3 melting point apparatus and were uncorrected.

Infrared Spectroscopy: Infrared spectra were recorded on a PerkinElmer Spectrum 100 FT-IR spectrometer with an attenuated total reflection (ATR) accessory featuring diamond/ZnSe plate. Samples were deposited as neat on ATR module and absorption maxima (ν_{\max}) were quoted in wavenumbers (cm^{-1}) in the range of 4000-650 cm^{-1} . Intensities of absorptions are abbreviated as s, strong; m, medium; and w, weak.

Mass Spectra: Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectra were recorded on a BRUKER Microflex LT spectrometer using reported matrixes.

Elemental Analysis: Elemental Analysis was performed on Thermo Finnigan Flash 1112 Series Elemental Analyzer operated at The Scientific and Technological Research Council of Turkey (TUBITAK), Marmara Research Center, Institute of Chemical Technology.

Absorption Spectroscopy: Absorption spectra were recorded at room temperature on a Shimadzu UV-2600 UV-vis spectrometer using a 1 cm path length quartz cuvette between 200 and 900 nm. Solutions were prepared in spectro-grade solvents. Molar extinction coefficients (ϵ) were determined by measurement of the absorption of at least six solutions of differing concentration for each radical, followed

by determination of the slope.

Electrochemical Analyses: Electrochemical measurements were carried out on a CH Instruments 842B model work station. The setup was a conventional three-electrode cell equipped with a glassy carbon working electrode, platinum wire counter electrode, and Ag/AgNO₃ reference electrode. The glassy carbon electrode was polished routinely with 0.05 μm alumina powder/water slurry on pads before running experiments. All measurements of samples were recorded as reported analyte concentration in 0.1 M n-Bu₄NBF₄ electrolyte solutions of acetonitrile. Solutions were deaerated with argon purge for 5 min and kept under a blanket of argon during the experiments. All electrochemical measurements were performed at ambient temperature. Ferrocene was used as internal reference, and all potentials were referenced to a ferrocene/ferrocenium (Fc/Fc⁺) redox couple ($E_{1/2}$: 0.416 V vs SCE (Ranchet *et al.*, 1998)). All potentials as $E_{1/2} = (E_{pa} + E_{pc})/2$ were reported versus saturated calomel electrode (SCE). Scan rate was 100 mV/s for all cyclic voltammetry (CV) experiments.

The 3mm-diameter glassy carbon working electrode (CHI104), nonaqueous Ag/Ag⁺ reference electrode with porous Teflon tip (CHI112), platinum wire counter electrode (CHI115), and electrode polishing kit (CHI120) were purchased from CH Instruments. Supporting electrolyte, n-Bu₄NBF₄ was purchased from Alfa Aesar and dried overnight at 70°C under vacuum. Ferrocene was supplied by Fluka, AgNO₃ by Carlo Erba, and anhydrous acetonitrile by VWR.

Electron Paramagnetic Resonance (EPR) Spectroscopy: The EPR solution spectra were recorded with a Jeol JES FA 300 X-band (9.6 GHz) spectrometer, with 100 kHz magnetic field modulation. Modulation amplitude was kept below the estimated peak-to-peak width for all spectra. Spectra were simulated using the Jeol IsoSimu computer program to obtain the value of g, isotropic hyperfine coupling constants (a_N), and linewidth (ΔH_{p-p}). Typical concentration of the radicals is 10⁻⁴ M in the dichloromethane-toluene (1:1) mixture. Solutions in spectro-grade solvent mixture were degassed by bubbling argon through the solutions for 30 min. Spectra for degassed solutions of the radicals were recorded at the reported temperature.

Magnetic Measurements: Magnetic susceptibility data were collected on a polycrystalline sample on a Quantum Design MPMS-XL SQUID magnetometer under an applied magnetic field of 0.1 T and temperature range 2-300 K. All data were corrected for the contribution of the sample holder, and the

diamagnetism of the samples was estimated from Pascal's constants (Pascal, 1910).

1. SYNTHETIC PROCEDURES

4-nitrophthalonitrile was purchased from Aldrich. **1** was synthesized according to already published method (Fidan *et al.*, 2017). Syntheses of phthalonitriles were performed on the basis of reference procedures (Korkut *et al.*, 2016).

Phthalonitriles 3 and 4: 4-nitrophthalonitrile (**2**) (1.0 eq., 1.5 mmol, 0.2595 g), 2-(4-Hydroxyphenyl)-4,4,5,5-tetramethyl-2-imidazoline-3-oxide-1-oxyl (**1**) (1.1 eq., 1.65 mmol, 0.4125 g), and K₂CO₃ (4.4 eq., 4 eq. for each –OH, 6.6 mmol, 0.910 g) were charged into a microwave tube. DMF (10 mL) was added, then purged with argon. The tube was placed in the cavity and stirred efficiently. Tube content was subjected to microwave irradiation (maximum energy 300 Watt) at 50 °C for 2 hours under argon. Reaction mixture was poured into water (200 mL). Blue mixture was extracted with CH₂Cl₂ (150 mL). Blue organic phase was washed with aqueous solution of K₂CO₃ (3x100 mL), then with H₂O (3x100 mL). Resulting blue solution was dried over Na₂SO₄, evaporated to dryness. TLC analysis revealed that crude product contains both phthalonitriles **3** and **4**, which were separated with column chromatography on silica gel eluting with hexane-ethyl acetate mixture. Column purification gave 0.323 g blue powder of **3** in 57.4% yield and 0.052 g brownish-red powder of **4** in 9.7% yield.

Phthalonitrile **3**: mp. 190-192 °C. FT-IR (ATR, ν_{\max} , cm⁻¹): 3094w, 3039w, 2971w, 2937w, 2226m, 1592s, 1574m, 1562s, 1518m, 1491s, 1466s, 1450m, 1418s, 1388s, 1361s, 1308s, 1296s, 1257s, 1217s, 1180s, 1162s, 1129s, 1090m, 1013m, 958s, 917m, 859s, 840s, 822m, 812m, 715m, 696w, 616s.

MALDI-TOF MS (*trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile): *m/z* for C₂₁H₁₉N₄O₃ [calculated]: 375, [found]: 374 [M-1]⁺. Elemental Analysis for C₂₁H₁₉N₄O₃ [calculated]: C, 67.19; H, 5.10; N, 14.92. [found]: C, 66.48; H, 5.18; N, 15.13.

Phthalonitrile **4**: mp. 122-124 °C. FT-IR (ATR, ν_{\max} , cm⁻¹): 3107w, 3077w, 3043w, 2981w, 2930w, 2231m, 1593s, 1564s, 1484s, 1423m, 1407m, 1375m, 1367m, 1282s, 1250s, 1208s, 1159s, 1138s, 1090m, 1014m, 951s, 892m, 880s, 854s, 837s, 772m, 747w, 716w, 666s, 625w. MALDI-TOF MS (*trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile): *m/z* for C₂₁H₁₉N₄O₂ [calculated]: 359, [found]: 360 [M+H]⁺. Elemental Analysis for C₂₁H₁₉N₄O₂ [calculated]: C, 70.18; H, 5.33; N, 15.59. [found]: C, 70.36; H, 5.69; N, 15.51.

2. FT-IR AND MASS SPECTRA OF COMPOUNDS

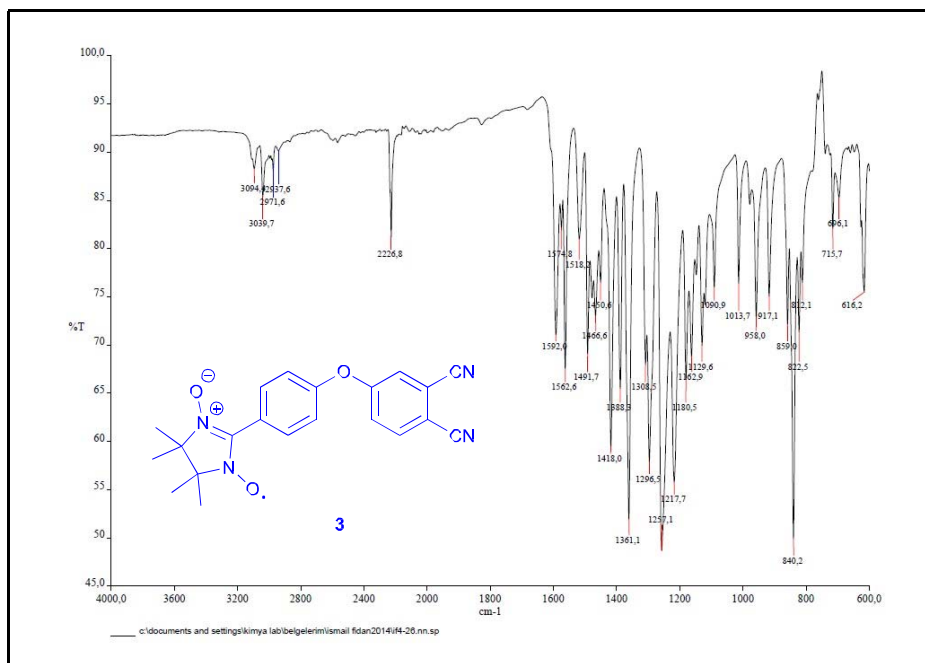


Figure S1: FT-IR Spectrum of 3.

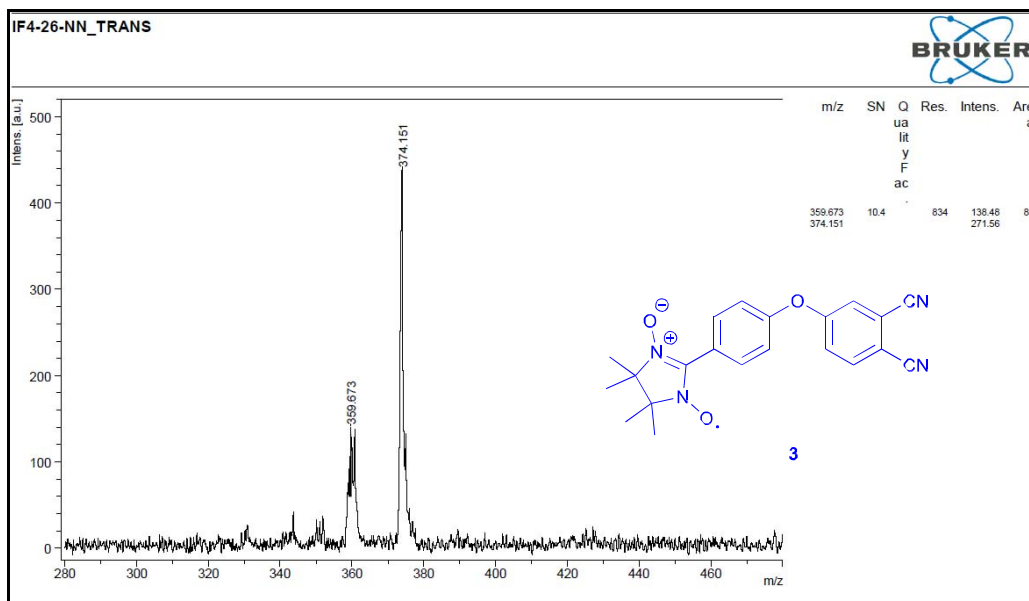


Figure S2: MALDI-TOF MS Spectrum of 3.

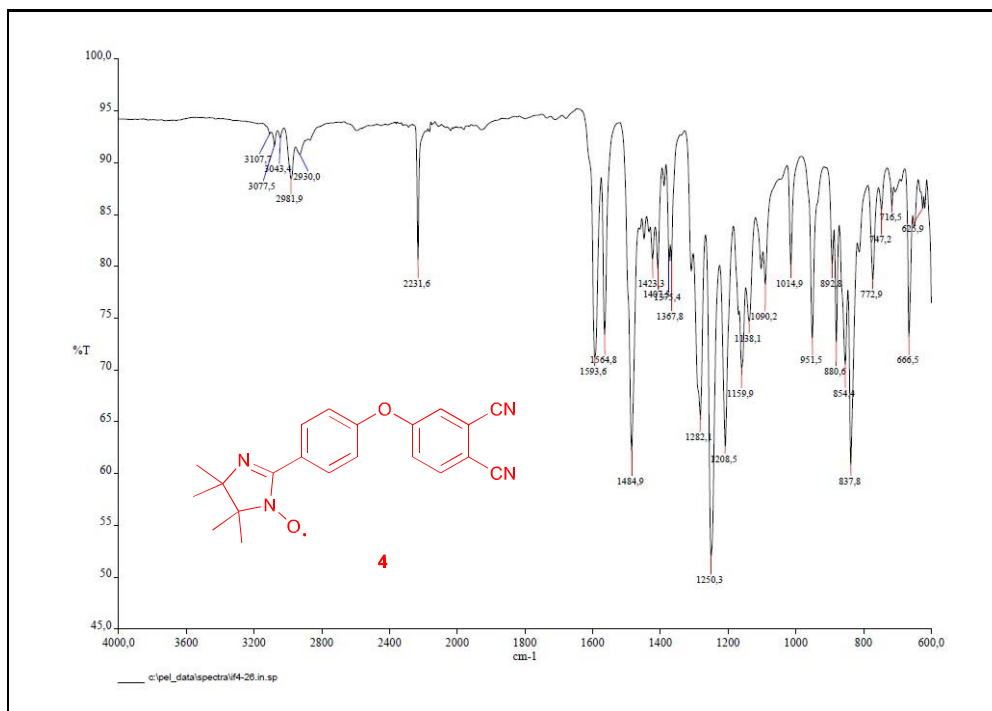


Figure S3: FT-IR Spectrum of 4.

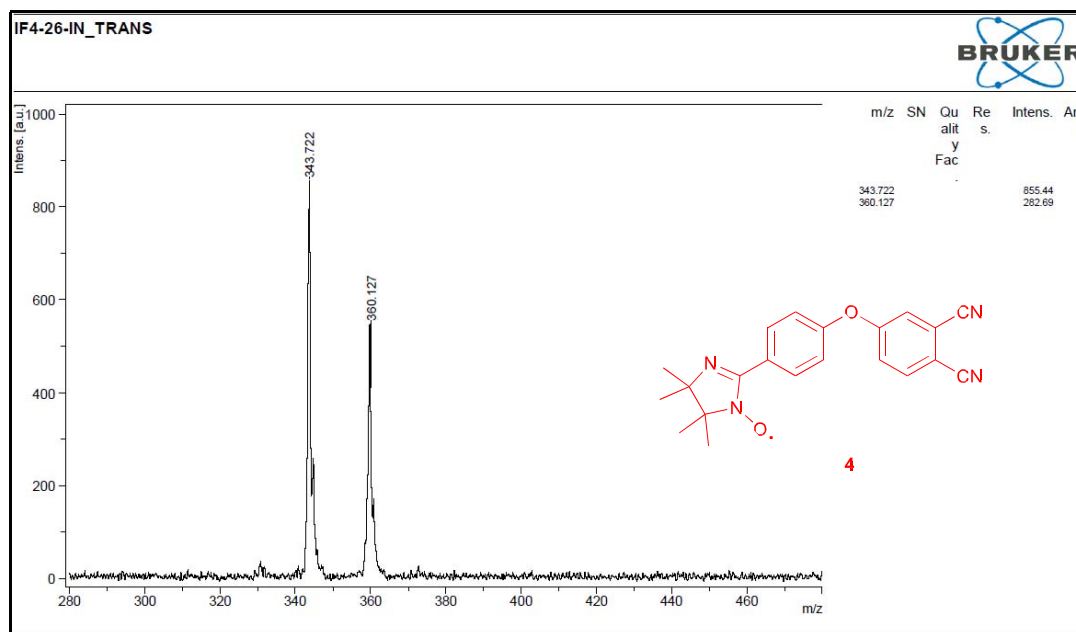


Figure S4: MALDI-TOF MS Spectrum of **4**.

3. ABSORPTIONSPECTROSCOPY

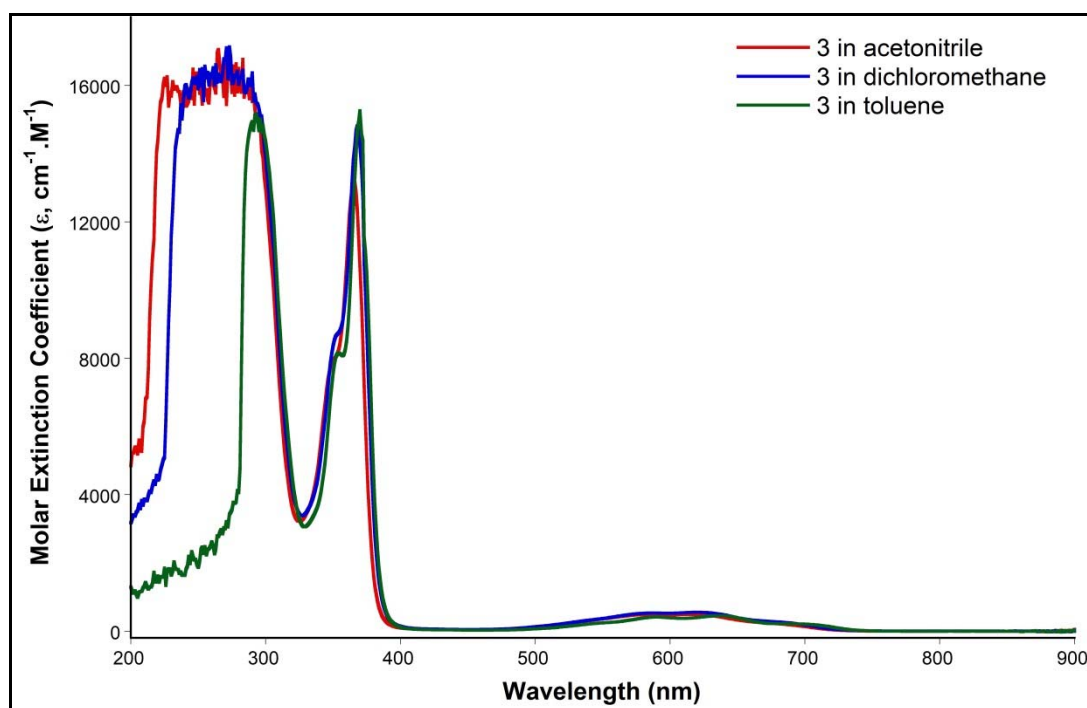


Figure S5: UV-vis Spectra of 3 in Acetonitrile, Dichloromethane and Toluene.

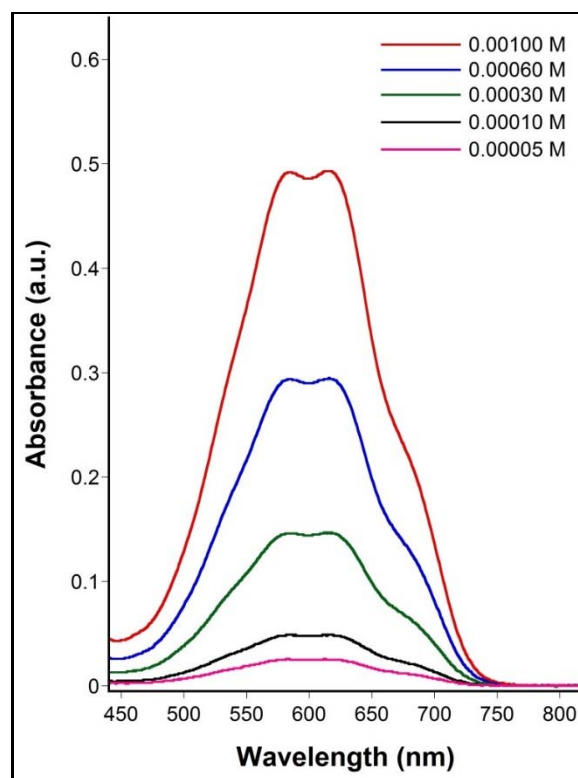
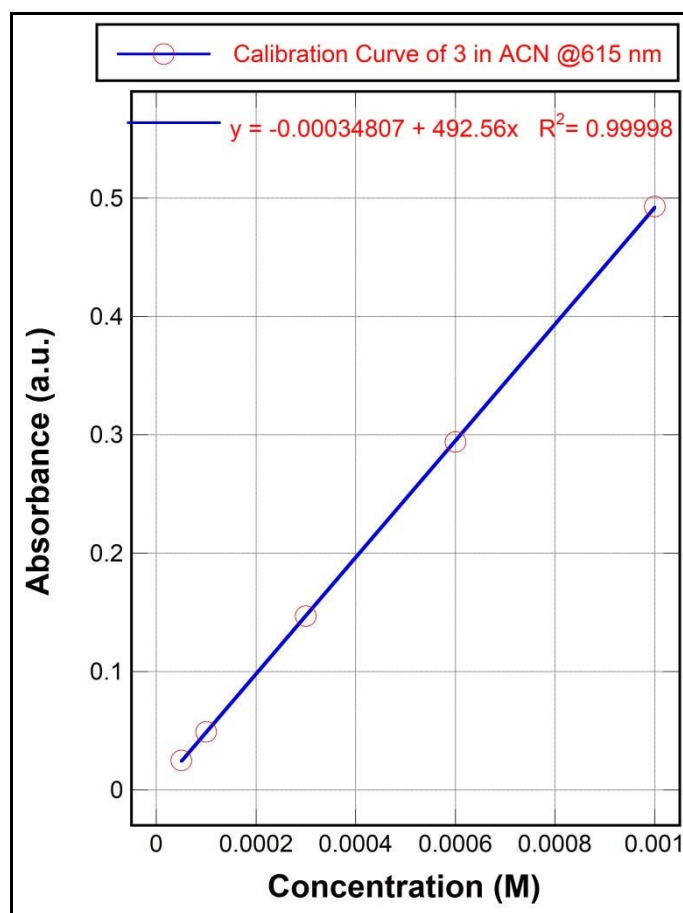


Figure S6: UV-Vis Spectra for $n \rightarrow \pi^*$ Transitions of **3** in Acetonitrile.

Figure S7: Calibration Curve of **3** in Acetonitrile at 615 nm.

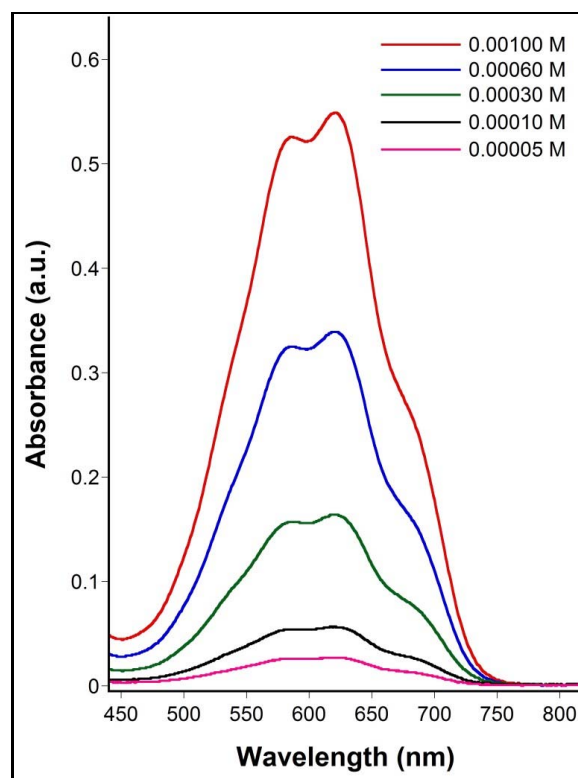


Figure S8: UV-Vis Spectra for $n \rightarrow \pi^*$ Transitions of **3** in Dichloromethane.

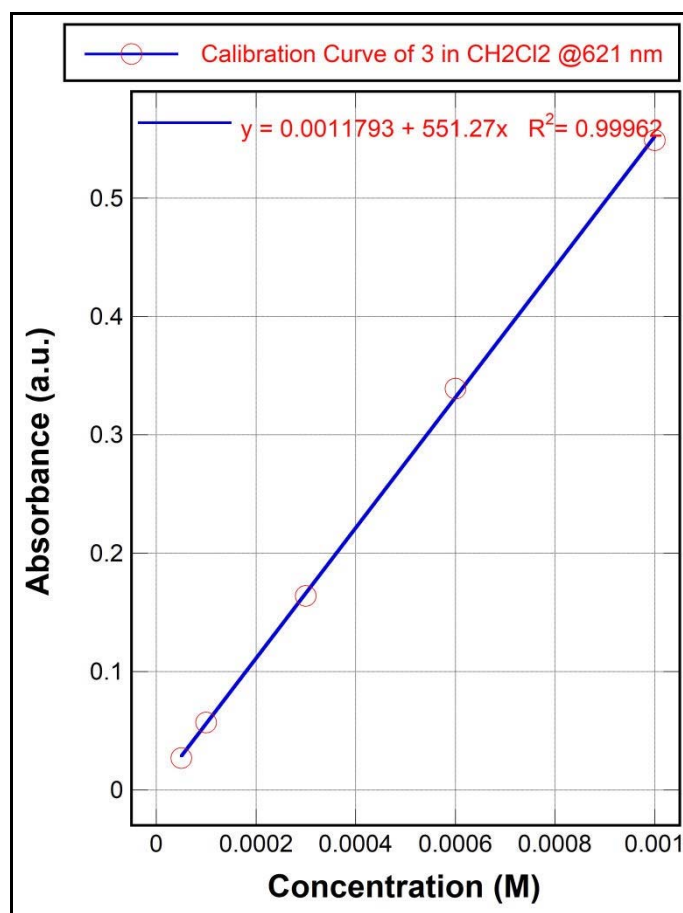


Figure S9: Calibration Curve of **3** in Dichloromethane at 621 nm.

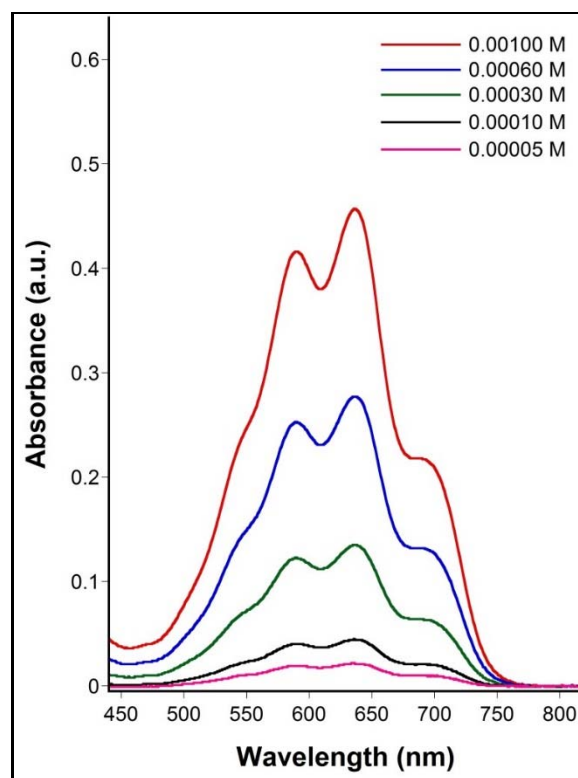
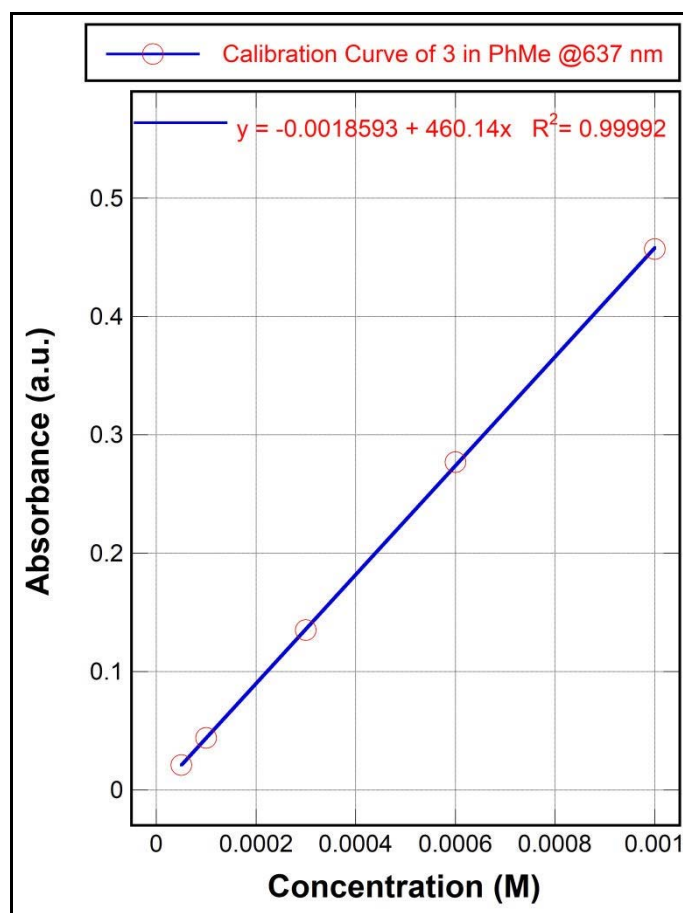


Figure S10: UV-Vis Spectra for $n \rightarrow \pi^*$ Transitions of **3** in Toluene.

Figure S11: Calibration Curve of **3** in Toluene at 637 nm.

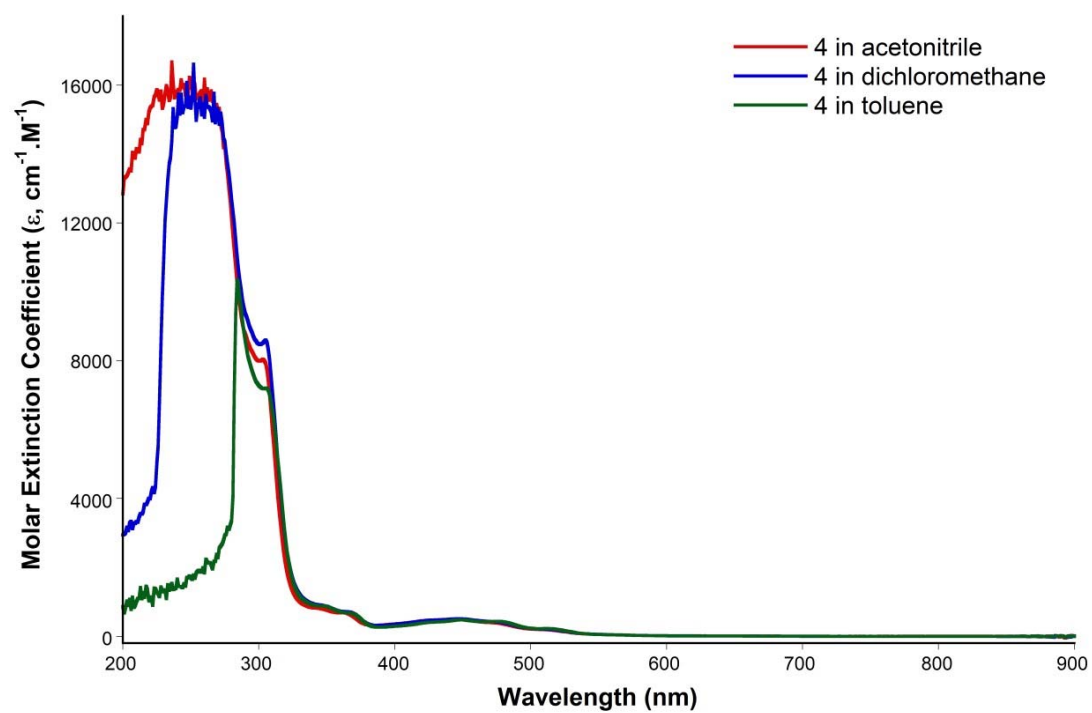


Figure S12: UV-vis Spectra of **4** in Acetonitrile, Dichloromethane and Toluene.

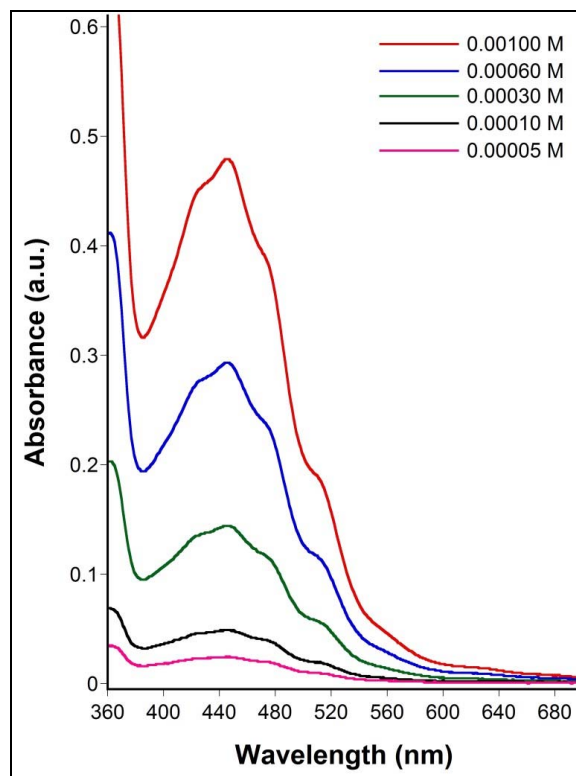


Figure S13: UV-Vis Spectra for $n \rightarrow \pi^*$ Transitions of **4** in Acetonitrile.

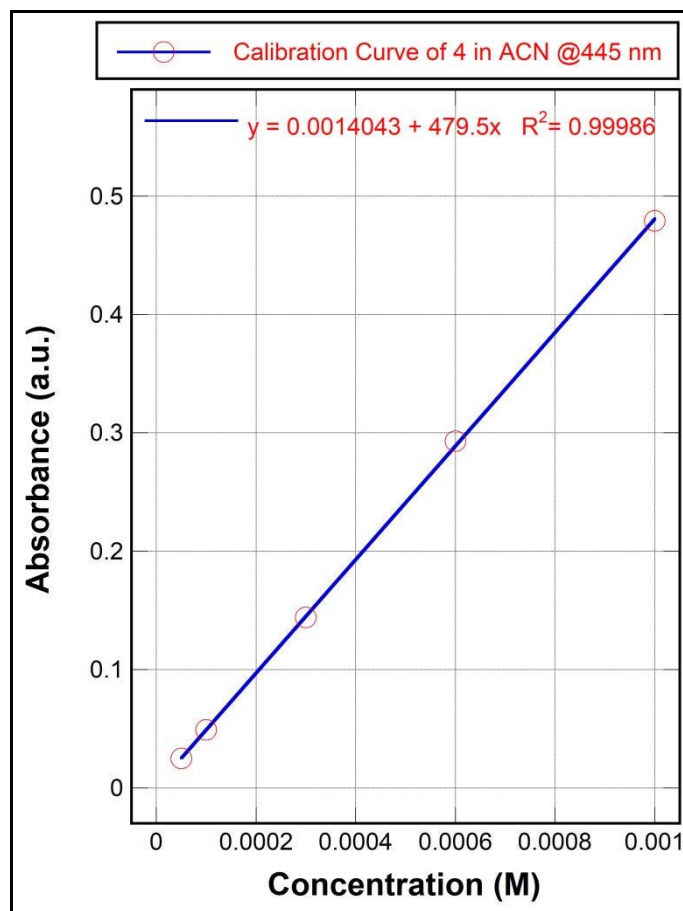


Figure S14: Calibration Curve of 4 in Acetonitrile at 445 nm.

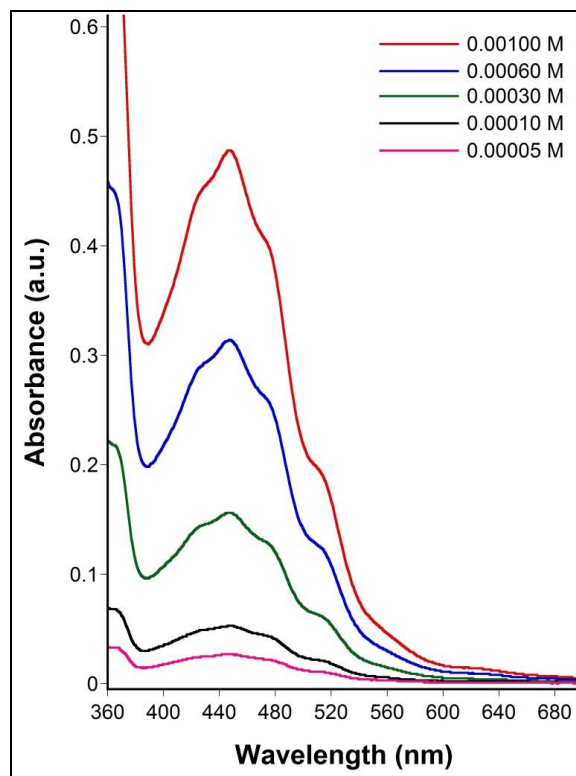


Figure S15: UV-Vis Spectra for $n \rightarrow \pi^*$ Transitions of **4** in Dichloromethane.

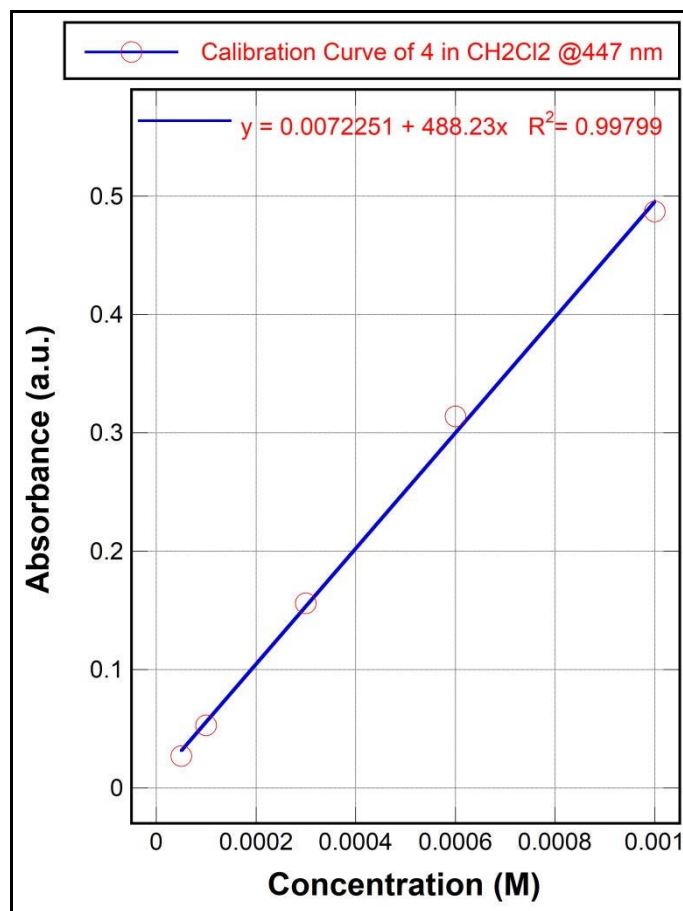


Figure S16: Calibration Curve of **4** in Dichloromethane at 447 nm.

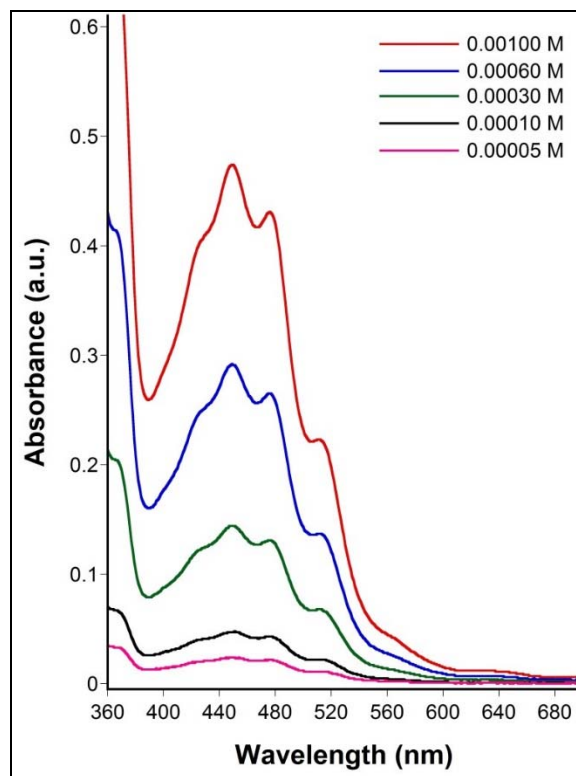


Figure S17: UV-Vis Spectra for $n \rightarrow \pi^*$ Transitions of **4** in Toluene.

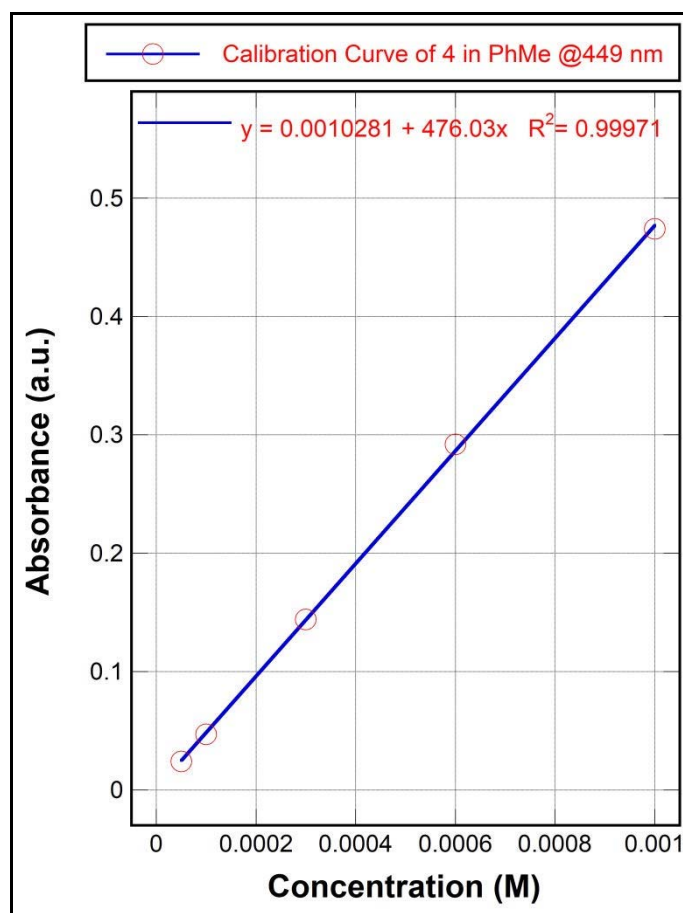


Figure S18: Calibration Curve of 4 in Toluene at 631 nm.

4. ELECTRON PARAMAGNETIC RESONANCE (EPR) SPECTROSCOPY



Figure S19: X-band EPR Spectra of 3×10^{-4} M in Dichloromethane-Toluene (1:1) Solution at Different Temperature.

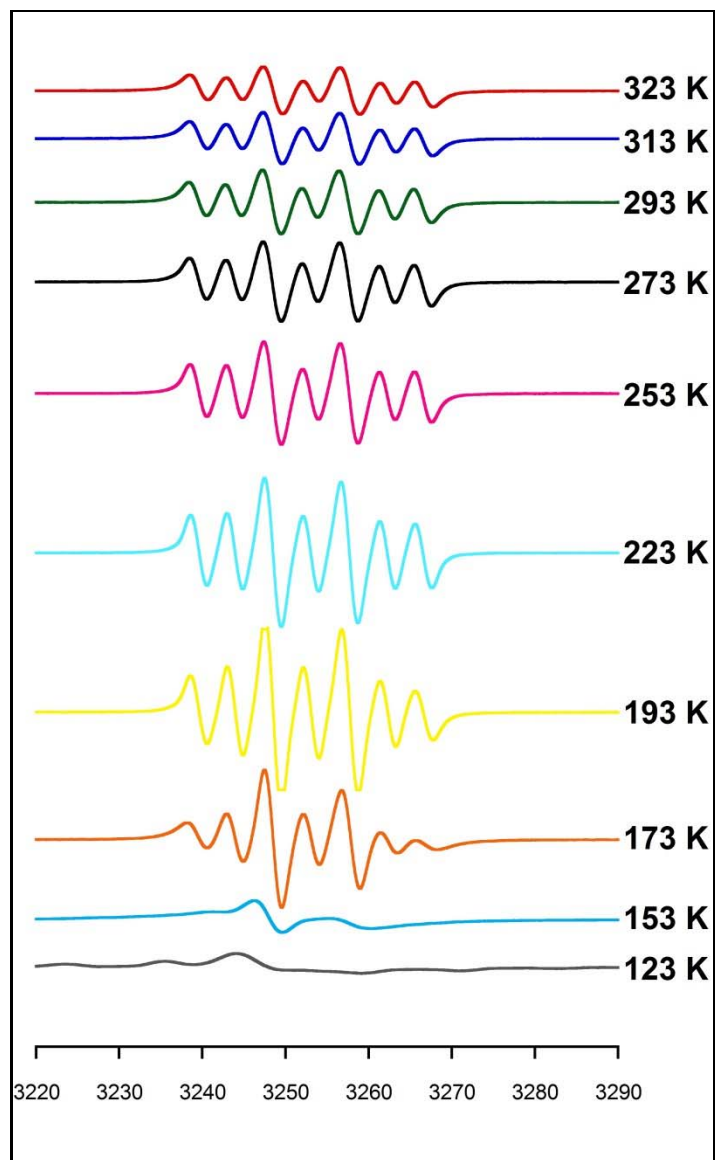


Figure S20: X-band EPR Spectra of 4×10^{-4} M in Dichloromethane-Toluene (1:1) Solution at Different Temperature.

5. MAGNETIC MEASUREMENTS

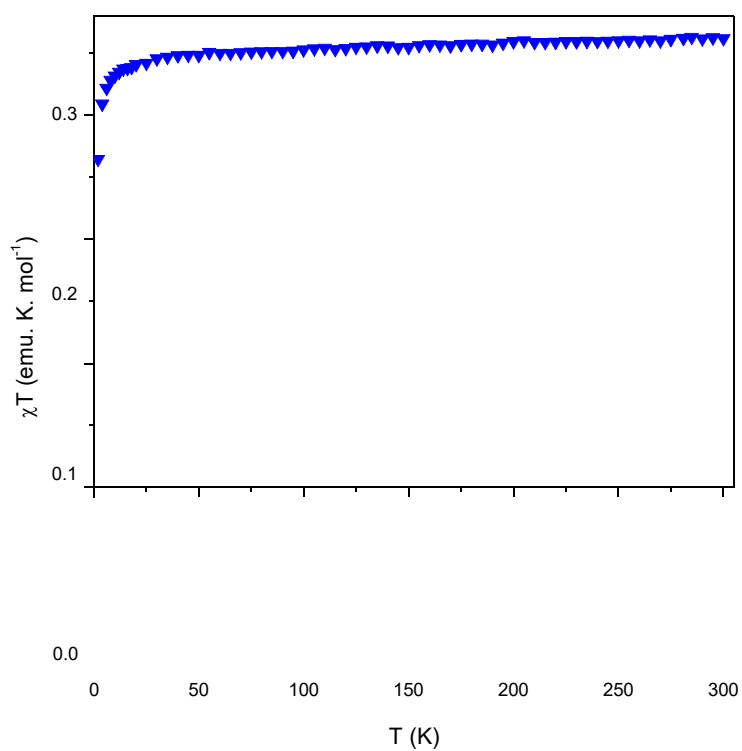
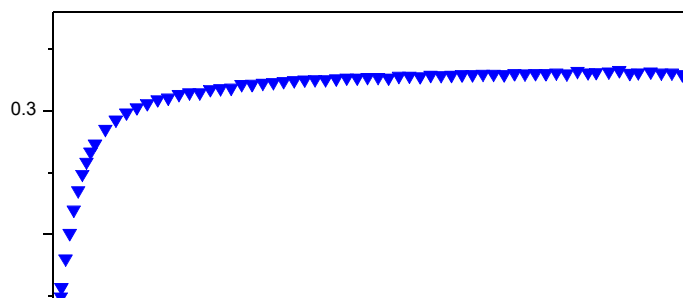


Figure S21: Temperature dependence of the product of the magnetic susceptibility with temperature (χT) for phthalonitrile 3.



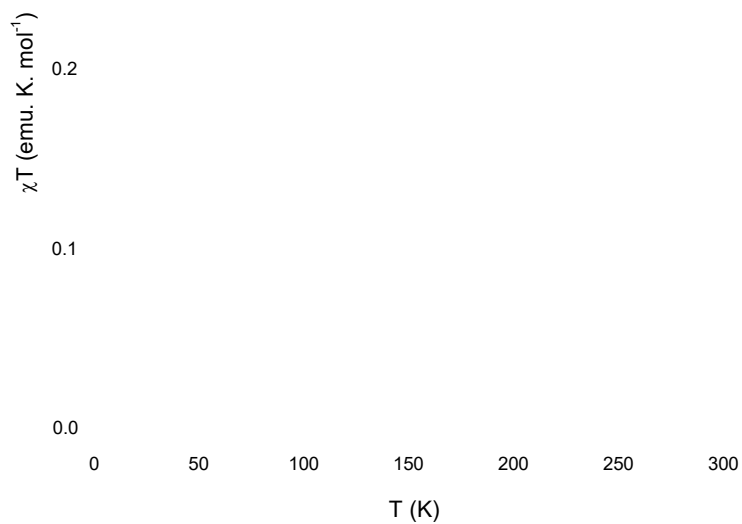


Figure S22: Temperature dependence of the product of the magnetic susceptibility with temperature (χT) for phthalonitrile **4.**

6. X-RAY DIFFRACTION ANALYSIS

Table S1: Crystal data and structure refinement details for 3.

CCDC	1913919
Chemical Formula	C ₂₁ H ₁₉ N ₄ O ₃
Formula weight (g. mol ⁻¹)	375.40
Temperature (K)	173.15
Wavelength (Å)	0.71073
Crystal system, Space Group	Monoclinic, P2 ₁ /c
<i>a</i> (Å)	10.575(3)
<i>b</i> (Å)	17.149(5)
<i>c</i> (Å)	10.615(3)
α(°)	90
β(°)	108.434(14)
γ(°)	90
Crystal size (mm ³)	0.237 × 0.15 × 0.082
<i>V</i> (Å ³)	1826.3(9)
<i>Z</i>	4
ρ _{calcd} (g. cm ⁻³)	1.365
μ (mm ⁻¹)	0.094
F(000)	788.0
θ range for data collection (°)	4.06 to 50.132
<i>h</i> / <i>k</i> / <i>l</i>	-12 ≤ <i>h</i> ≤ 12, -20 ≤ <i>k</i> ≤ 20, -12 ≤ <i>l</i> ≤ 12
Reflections collected	12874
Independent reflections	3237 [R _{int} = 0.0840, R _{sigma} = 0.0791]
Data/restraints/parameters	3237/0/257
Goodness-of-fit on F ²	1.061
R[F ² > 2σ(F ²)], wR(F ²)	R ₁ = 0.0631, wR ₂ = 0.1539
Largest diff. peak and hole (e.Å ⁻³)	0.30/-0.26

Table S2. Selected bond lengths (Å) and bond angles (°) for the compound **3**.

Bond lengths (Å)			
Phthalonitrile moiety		Nitronyl nitroxide moiety	
O1-C107	1.372(4)	O2-N7	1.281(3)
O1-C109	1.394(4)	O3-N8	1.289(3)
N5-C101	1.142(4)	N7 C115	1.352(4)
N6-C102	1.146(4)	N8 C115	1.350(4)
C101-C103	1.440(5)	N7-C117	1.510(4)
C102-C104	1.438(5)	N8-C116	1.499(4)
Bond angles (°)			
Phthalonitrile moiety		Nitronyl nitroxide moiety	
C104-C103-C101	120.6(3)	O2 N7 C115	126.2(3)
C103-C104-C102	118.9(3)	O2 N7 C117	121.3(3)
C107-O1-C109	123.2(3)	O3 N8 C115	125.9(3)
		O3 N8 C116	121.2(3)

Table S3: The intermolecular C-H \cdots X (X: O, N) interaction parameters (Å and °) for **3**.

DH \cdots A	Symmetry	d (D-H)	d (H \cdots A)	d (D-H \cdots A)	D-H \cdots A
C118-H11C \cdots N5	-1+x,y,1+z	0.98	2.57	3.469(6)	153
C105-H105 \cdots O3	x,y,-1+z	0.95	2.43	3.282(4)	149
C108-H108 \cdots O2	1+x,y,z	0.95	2.59	3.476(4)	155
C111-H111 \cdots O2	-	0.95	2.39	2.940(4)	117
C113-H113 \cdots O3	-	0.95	2.27	2.859(4)	119

Table S4: The intermolecular N-O \cdots π and C-N \cdots π interaction parameters (Å and °) for compound **3**.

Y-X \cdots π	Symmetry	X \cdots π (Å)	Y-X \cdots π (°)	Y \cdots π (Å)
N7-O2 \cdots Cg1	1-X,-Y,1-Z	3.563(3)	136.66(19)	4.580(4)
N8-O3 \cdots Cg2	X,1/2-Y,1/2+Z	3.729(3)	142.93(19)	4.820(4)
C101-N5 \cdots Cg2	2-X,-Y,1-Z	3.612(4)	114.0(3)	4.208(4)
C102-N6 \cdots Cg1	X,1/2-Y,-1/2+Z	3.268(4)	128.6(3)	4.082(4)

Cg1 and Cg2 are the centroids of the C103-C108 and C109-C114 rings, respectively.

7. REFERENCES

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- (2) Korkut, S. E., Akyuz, D., Ozdogan, K., Yerli, Y., Koca, A. & Sener, M. K. (2016). *Dalton Trans.*, (3) **45**, 3086-3092.
- (4) Ranchet, D., Tommasino, J.B., Vittori, O. & Fabre, P.L. (1998). *J. Solution Chem.*, **27(11)**, 979-991.
- (5) Pascal, M.P. (1910). *Ann. Chim. Phys.*, **19**, 5.