

SUPPLEMENTARY MATERIAL FOR:

1,3-Dipolar Cycloaddition of a Nitronyl Nitroxide-substituted Alkyne to Heteroaromatic *N*-imines

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Crystal Structure of nitroxide **4b**

The crystal structure of **4b** is composed of infinite π -stacks with the distances between aromatic ring planes from 3.470(2) to 3.550(2) Å. In solid **4b**, there are two type of stacks formed respectively by two independent molecules, say, **A** and **B** (Fig. 1S). The main difference in geometry of **A** and **B** is the dihedral angle between planes of the paramagnetic and aromatic moieties (2.9° and 23.7°, respectively). The independent molecules adopt such conformations to achieve the densest packing of the methyl groups of the molecules belonging to the adjacent stacks, that is clear seen from Fig. 2S.

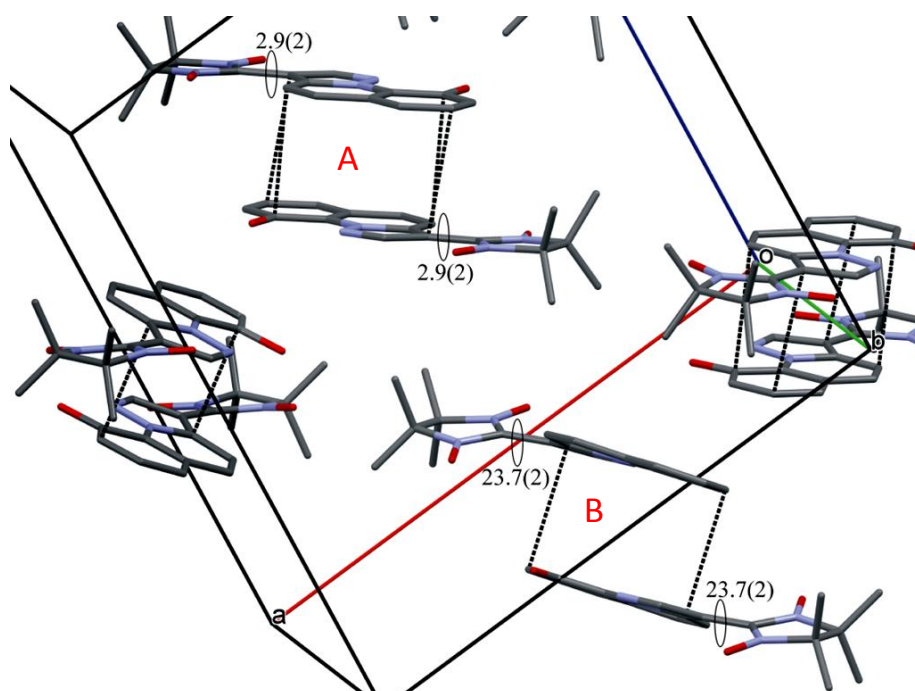


Fig. 1S. Fragment of the crystal packing of **4b** showing π -stacking of molecules and dihedral angle between planes of the nitronyl nitroxide and pyrazolo[1,5-a]quinoline moieties (H-atoms are omitted).

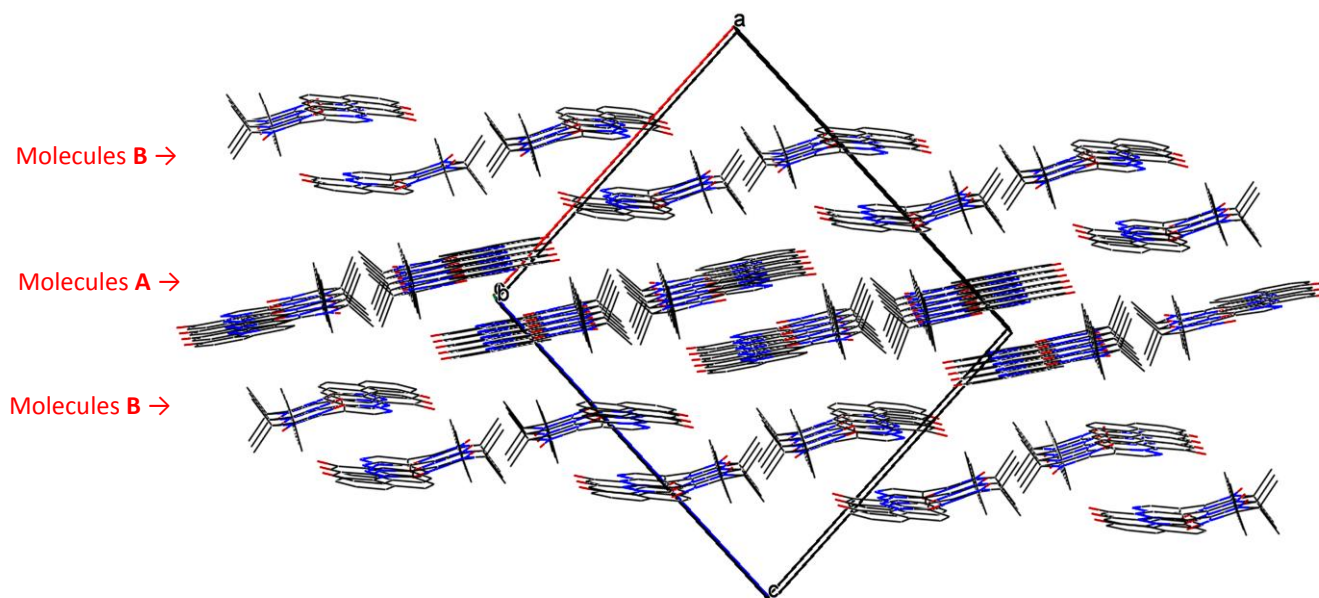


Fig. 2S. Packing motif of the independent molecules **A** and **B** in solid **4b**.

Experimental

General Methods

4,4,5,5-Tetramethyl-2-[2-(trimethylsilyl)ethynyl]imidazolidine-1,3-diol (**2**),^[1] 2-ethynyl-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazole-3-oxide-1-oxyl (**1**),^[2] *N*-aminopyridinium tetrafluoroborate (**3a**) and *N*-amino-8-hydroxyquinolinium mesitylenesulfonate (**3b**)^[3] were prepared according to the published procedures. All the solvents were of reagent quality. All of them were removed under reduced pressure, and all the commercial reagents were used without additional purification. The reactions were monitored by TLC on silica gel 60 F₂₅₄ aluminium sheets from Merck. The yields are given for pure substances obtained after recrystallisation. Infrared (IR) spectra were recorded on a Bruker VECTOR 22 infrared spectrometer. Melting points were determined with a Boetius melting point apparatus. Microanalyses were performed by means of a Carlo Erba 1106 analyser. Mass spectra were acquired on a Finnigan MAT-8200 instrument by the electron impact ionisation technique (70 eV).

2-(Pyrazolo[1,5-*a*]pyridine-3-yl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazole-3-oxide-1-oxyl

4a

MnO₂ (218 mg, 2.5 mmol) was added to a solution of **2** (128 mg, 0.5 mmol) in EtOH (5 mL). The resulting reaction mixture was stirred at room temperature for 30 min and filtered, and the solvents were evaporated (bath temp. ~30 °C). The residue was dissolved in CH₃CN (5 mL), and *N*-aminopyridinium tetrafluoroborate (**3a**) (82 mg, 0.45 mmol) and K₂CO₃ (310 mg, 2.3 mmol) were added to the solution. The reaction mixture was stirred for 1 h (TLC), then was loaded onto a chromatographic column (20 × 1.5 cm, a CH₂Cl₂:AcOEt mixture as an eluent). The column was eluted with CH₂Cl₂ and then with AcOEt, and a deep blue fraction of radical **4a** was collected. The solution was concentrated (bath temp. ~30 °C), and the residue was recrystallised from a CH₂Cl₂:hexane mixture to obtain the title compound. Yield 84 mg (61 %); dark blue crystals; m.p. 87–88 °C. UV/Vis (EtOH), λ_{max} (ε, M⁻¹ cm⁻¹): 204 (16007), 223 (16265), 268 (6040), 315 sh. (15416), 367 (3087), 664 (116) nm. IR (KBr): 424(m), 462(w), 484(w), 541(m), 567(w), 657(vw), 761(s), 867(m), 889(w), 1012(w), 1064(w), 1124(m), 1139(m), 1172(m), 1213(s), 1255(m), 1301(m), 1344(vs), 1363(vs), 1398(s), 1427(m), 1444(m), 1457(m), 1496(m), 1533(m), 1579(s), 1631(s), 2927(m), 2979(w), 3444(w) cm⁻¹. ESR: g_{iso} = 2.0074; A_N(2N) = 0.75 mT. C₁₄H₁₇N₄O₂ (273.31) calcd. C 61.52, H 6.27, N 20.50; found C 61.49, H 6.19, N 20.44.

2-(9-Hydroxypyrazolo[1,5-a]quinolin-3-yl)-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazole-3-oxide-1-oxyl **4b**

MnO₂ (218 mg, 2.5 mmol) was added to a solution of **2** (128 mg, 0.5 mmol) in EtOH (5 mL). The resulting reaction mixture was stirred at room temperature for 30 min and then filtered, and the solvents were evaporated (bath temp. ~30 °C). The residue was dissolved in CH₃CN (5 mL), and *N*-amino-8-hydroxyquinolinium mesitylenesulfonate (**3b**) (162 mg, 0.45 mmol) and K₂CO₃ (310 mg, 2.3 mmol) were added to the solution. The reaction mixture was stirred for 1 h (TLC), then was loaded onto a chromatographic column (20 × 1.5 cm, a CH₂Cl₂:AcOEt mixture as an eluent). The column was eluted with CH₂Cl₂ and then with AcOEt, and a deep blue fraction of radical **4b** was collected. The solution was concentrated (bath temp. ~30 °C), and the residue was recrystallised from a CH₂Cl₂:hexane mixture to obtain the title product. Yield 92 mg (54 %); dark blue crystals; m.p. 73–74 °C. UV/Vis (EtOH), λ_{max} (ε, M⁻¹ cm⁻¹): 205 (22000), 213 (22151), 284 (18700), 327 sh. (14331), 652 (550). IR (KBr): 478(w), 522(w), 540(w), 588(w), 609(vw), 653(w), 671(w), 719(m), 773 (w), 871(w), 954(w), 1033(w), 1135(s), 1170(m), 1191(s), 1218(m), 1272(s), 1299(vs), 1429(m), 1456(s), 1487(m), 1529(w), 1573(s), 1616(m), 2929(w), 2991(m), 3114(w) cm⁻¹. ESR: g_{iso} = 2.0074; A_N(2N) = 0.75 mT. C₁₈H₁₉N₄O₃ (339.37) calcd. C 63.70, H 5.64, N 16.51; found C 63.65, H 5.78, N 16.52.

Synthesis of complexes [Cu(hfac)₂4a]_n

Hexane (3 mL) was added to a solution of Cu(hfac)₂ (23.3 mg, 0.0488 mmol) and **4a** (13.4 mg, 0.0488 mmol) in CH₂Cl₂ (1 mL). The resulting solution was kept in an open vessel at 4 °C for 1 week. Needle-like dark blue crystals that formed were filtered off, washed with cold hexane and dried in air. The yield was 21.5 mg (58%). M.p. 150–152 °C (decomp.). IR (KBr): 424(vw), 457(vw), 495(w), 536(w), 594(m), 680(m), 754(m), 796(m), 815(w), 86(vw), 896(vw), 1020(vw), 1068(w), 1106(m), 1151(vs), 1214(s), 1259(w), 1309(m), 1344(m), 1363(m), 1396(w), 1446(m), 1465(w), 1486(m), 1527(m), 1556(m), 1581(m), 1645(s), 2998(vw), 3135(vw), 3432(vw) cm⁻¹. Found (%): C, 38.05; H, 2.58; F, 30.81; N, 7.42. C₂₄H₁₉N₄O₆Cu₁F₁₂. Calculated (%): C, 38.39; H, 2.55; F, 30.36; N, 7.46.

Crystallography

For compounds **4a** and **4b**, the X-ray diffraction experiments were carried out on a Bruker P4 diffractometer, and for [Cu(hfac)₂4a]_n, on a Bruker Kappa Apex II CCD diffractometer (graphite-monochromated Mo Kα radiation, λ = 0.71073 Å). The structures were solved by direct methods using the SHELXS-97 software and were refined by the anisotropic (except H atoms) full-matrix least-squares method against F² of all reflections in SHELX-97.^[4] The H atom

positions were calculated by means of the riding model. Absorption corrections were applied empirically using *SADABS* software. In the $[\text{Cu}(\text{hfac})_2\mathbf{4a}]_n$ complex, one trifluoromethyl group is disordered by two positions in a 0.69:0.31(3) occupation ratio. Crystallographic data for the structures of compounds **4a**, **4b** and $[\text{Cu}(\text{hfac})_2\mathbf{4a}]_n$ were deposited at the Cambridge Crystallographic Data Centre; CCDC numbers are 1539841, 1539842 and 1553473, respectively. A copy of the data can be obtained free of charge, on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: +44 122 3336033 or e-mail: deposit@ccdc.cam.ac.uk; Internet: www.ccdc.cam.ac.uk).

Crystallographic data for **4a**: $\text{C}_{14}\text{H}_{17}\text{N}_4\text{O}_2$, monoclinic, $P2_1/c$, a 9.979(1), b 11.483(1), c 13.298(2) Å, β 111.29(1)°, V 1419.8(3) Å³, Z 4, D_{calcd} 1.279 g cm³, $\mu(\text{Mo-K}\alpha)$ 0.089 mm⁻¹, $F(000)$ 580, (θ 2.19–24.99°, completeness 100.0%), T 296(2) K, black prism (0.60 × 0.30 × 0.2) mm³, 2644 measured reflections in index range $0 \leq h \leq 11$, $0 \leq k \leq 13$, $-15 \leq l \leq 14$, 2492 independent (R_{int} 0.0156), 182 parameters, R_1 0.0473 (for 1600 observed $I > 2\sigma(I)$), wR_2 0.1368 (all data), *GOOF* 1.054, largest diff. peak and hole 0.167 and -0.179 e·Å⁻³.

Crystallographic data for **4b**: $\text{C}_{18}\text{H}_{19}\text{N}_4\text{O}_3$, monoclinic, $P2_1/n$, a 16.196(2), b 11.341(1), c 18.305(2) Å, β 95.84(1)°, V 3344.8(6) Å³, Z 8, D_{calcd} 1.348 g cm³, $\mu(\text{Mo-K}\alpha)$ 0.094 mm⁻¹, $F(000)$ 1432, (θ 2.52–25.50°, completeness 99.8%), T 297(2) K, black prism-needle (0.65 × 0.15 × 0.10) mm³, 6435 measured reflections in index range $-19 \leq h \leq 0$, $-13 \leq k \leq 0$, $-22 \leq l \leq 22$, 6206 independent (R_{int} 0.0513), 454 parameters, R_1 0.0668 (for 2680 observed $I > 2\sigma(I)$), wR_2 0.1510 (all data), *GOOF* 1.141, largest diff. peak and hole 0.263 and -0.270 e·Å⁻³. The crystal structure of **4b** is formed by two crystallographically independent molecules.

Crystallographic data for $[\text{Cu}(\text{hfac})_2\mathbf{4a}]_n$: $\text{C}_{24}\text{H}_{19}\text{N}_4\text{O}_6\text{Cu}_1\text{F}_{12}$, orthorhombic, $P2_12_12_1$, a 9.1824(4), b 15.9474(6), c 20.6708(6) Å, V 3026.9(2) Å³, Z 4, D_{calcd} 1.648 g cm³, $\mu(\text{Mo-K}\alpha)$ 0.840 mm⁻¹, $F(000)$ 1504, (θ 3.22–25.02°, completeness 99.7%), T 296(2) K, black prism (0.35 × 0.25 × 0.07) mm³, 29303 measured reflections in index range $-10 \leq h \leq 10$, $-18 \leq k \leq 18$, $-24 \leq l \leq 24$, 5300 independent (R_{int} 0.0553), 453 parameters, R_1 0.0494 (for 4655 observed $I > 2\sigma(I)$), wR_2 0.1782 (all data), *GOOF* 1.049, largest diff. peak and hole 0.871 and -0.677 e·Å⁻³.

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