Supporting Information for:

A stable open-shell redox active ditopic ligand

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Experimental Section

General considerations. All reagents were commercially available and used as received unless otherwise stated. Anhydrous solvents were obtained from a PureSolv solvent purification system. ¹H/¹³C-NMR spectra at room temperature were recorded on a Bruker Avance 400 MHz spectrometer using deuterated solvents. Variable temperature ¹H/-NMR spectra were recorded in d^8 -tolunene using a Bruker Avance AV 600 Digital FT-IR spectra were recorded on a Shimadzu IRAffinity NMR spectrometer. UV-Vis measurements were recorded on a Shimadzu 3600 spectrometer as KBr discs. UV-Vis-NIR spectrophotometer in CH₂Cl₂ solution using quartz cuvettes. Cyclic voltammetry (CV) experiments were performed with a Bioanalytical Systems Inc. (BASI) Epsilon electrochemical workstation. Compound 2 and 3 were dissolved in anhydrous solvent (DMF) and deoxygenated by sparging with N₂ gas for 15 min. Solution concentrations were approximately 10⁻³ M in analyte containing approximately 0.5 M supporting electrolyte (Bu_4NPF_6). A typical three-electrode set-up was used including a glassy carbon working electrode, Ag/AgCl reference electrode, and a platinum wire auxiliary electrode. The scan rate for all CV experiments was 100 mV/s. LC-MS experiments were recorded on an Agilent 1260 Infinity liquid chromatograph/6530 accurate mass Q-TOF in high-resolution mode with 70:30 HPLC grade acetonitrile/water using positive mode electrospray ionization. EI mass spectra were acquired on a ThermoFisher high resolution double focusing magnetic sector mass spectrometer system. EPR measurements on 3 were conducted at X-band frequencies (9.3–9.4 GHz) with a Bruker EMXplus spectrometer using a PremiumX microwave bridge and HS resonator. Low temperature measurements used a Bruker ER 4112HV

helium temperature control system and continuous-flow cryostat. EPR measurements on 2 were recorded using a Bruker Elexsys E580 pulse spectrometer operating in CW mode. EPR sample was prepared by dissolving 2 in toluene. The solution was placed in Suprasil EPR sample tube (4 mm o.d.) and was degassed by several freeze-pump-thaw cycles and then sealed under vacuum. Spectra were recorded at room temperature and 100 K. Microanalyses were performed by Canadian Microanalytical Service, Ltd, Delta, BC, Canada.

Computational details. All DFT calculations were performed using the Gaussian09 (Revision D.01) package¹ using the B3LYP hybrid functional^{2,3} and the 6-31G(d,p) basis set for the geometry optimizations and frequency calculations or the def2-TZVP basis set for single point energy calculations. The converged wave functions were tested to confirm that they correspond to the ground state surface. Tight SCF convergence criteria were used for all calculations. The program Chemissian⁴ was used to generate the spindensity and molecular orbitals figures. The intensities of the 40 lowest-energy electronic transitions were calculated by TD-DFT^{5,6} in DCM using the polarized continuum model (PCM) with the same functional/basis set combination employed for the single-point calculations.

Synthesis

2,6-Diiodo-4-(*tert***-butyl)phenol.** To a round-bottom flask containing MeOH (330 mL) and concentrated H_2SO_4 (7 mL) was added 4-*tert*-butylphenol (10g, 67 mmol) and KI (22.1g, 133 mmol). An aqueous solution of H_2O_2 (30%, 27 mL) was added and the reaction mixture was stirred for 2h at 40°C and then was let cool to room temperature. The reaction contents were diluted with CH_2Cl_2 and poured into a separatory funnel and

washed with NaHSO₃ (0.1 M) and H₂O. The organic layer was evaporated to dryness and the residue was dissolved into hexanes (80 mL) and stored in a refrigerator overnight. The resulting crystals were collected by vacuum filtration. Yield (22.6 g, 75%). Note that at this point the crystals are stained red due to the presence of residual iodine, which does not interfere with the subsequent steps. However, the crystals can be purified by flash chromatography (hexanes/EtoAc, 49:1). Characterization of the product was consistent with the reported data.⁸

1,3-Diiodo-2-methoxy-5-(*tert***-butyl)benzene.** A round bottom flask equipped with a magnetic stir bar was charged with 2,6-diiodo-4-(*tert*-butyl)phenol (20 g, 42 mmol), iodomethane (5.2 mL, 84 mmol) and K₂CO₃ (17.4 g, 126 mmol). The reaction mixture was refluxed for 12 h, cooled to room temperature and then diluted with CH_2Cl_2 and washed with water. The aqueous layer was separated and extracted twice with CH_2Cl_2 . The combined organic fractions were dried over MgSO₄ and then filtered. The solvent was evaporated under reduced pressure to afford the product. Yield (20.3g, 99%). Characterization was consistent with literature values.⁸

2-Methoxy-1,3-*bis*(8-quinolylamino)-5-(*tert*-butyl)benzene (1). A Schlenk flask containing dry, deoxygenated toluene (180 mL) was loaded with 1,3-diiodo-2-methoxy-5-(*tert*-butyl)benzene (7.0 g, 16 mmol), palladium acetate (0.19 g, 5 mol%, 0.86 mmol), BINAP (1.05 g, 1.71 mmol), Cs₂CO₃ (24.6 g, 75.4 mmol) and 8-aminoquinoline (5.44 g, 37.6 mmol) under a flow of N₂. The mixture was heated to 100°C with vigourous stirring for approximately 11 d. The reaction is monitored by TLC (20:1 Hex/EtOAc) and approximately 40 mg of palladium acetate was added periodically in order for the spot corresponding to 1,3-diiodo-2-methoxy-5-(*tert*-butyl)benzene to be completely

consumed. When total consumption of 1,3-diiodo-2-methoxy-5-(*tert*-butyl)benzene was indicated by TLC, the reaction mixture was filtered and the precipitated solids were washed with acetone (40 mL). The filtrate was concentrated to dryness and the residue was dissolved into 40:1 (Hex/EtOac) and loaded onto a large diameter column packed with silica gel. After approximately 100 mL of eluent has been collected, the eluent is changed to 25:1 Hex/EtoAc and fractions are collected resulting in the isolation of a yellow mono-substituted product [HR-MS (ESI+): calc'd for C₂₀H₂₁IN₂O (MH+) 433.077, found 433.0795]. A red product will immediately follow the collection of the first yellow band. Once the red band has exited the column, 20:1 (Hex/EtoAc), is used to separate the desired product 1 (the next yellow band) from unreacted 8-aminoquinoline. Yield (6.2g, 82%). ¹H NMR (400MHz, CDCl₃) = 8.86 δ (dd, 2H, J = 8.7 Hz), 8.65 (s, 2H), 8.16 (d, 2H, J = 8.2 Hz), 7.54 (d, 4H), 7.48 (m, 2H), 7.39 (s, 1H), 7.28 (d, 2H, J =9.6 Hz), 3.84 (s, 3H), 1.40 (s, 9H) ppm. ¹³C NMR (100 MHz, CDCl₃) = δ 147.7, 140.3, 140.3, 139.1, 136.2, 135.1, 129.0, 127.5, 121.7, 116.6, 110.3, 108.3, 60.3, 35.0, 31.7 ppm. FT-IR (Nujol) = 3370 (w), 2922 (s), 2852 (s), 1570 (m), 1517 (m), 1458 (m), 1377 (m), 1328 (w), 1267 (w), 1225 (w), 1171 (w), 1111 (w), 1066 (w), 1003 (w), 820 (w), 789 (w), 744 (w), 721 cm⁻¹ (w). UV-Vis (CH₂Cl₂): $\lambda_{max} = 383$ nm. HR-MS (ESI+): Calc'd for C₂₉H₂₈N₄O (MH+) 449.2341, found 449.2342.

2,6-Bis(8-quinolylamino)-4-(*tert***-butyl)phenol (2).** A Schlenk flask containing dry, deoxygenated dichloromethane (150 mL) was cooled to 0°C in ice-water and loaded with **1** (6.0 g, 13 mmol). To the cooled solution of **1** was added dropwise a 1 M solution of BBr₃ in dichloromethane (33.5 mL, 33.6 mmol). The reaction mixture was left in the ice bath and allowed to warm to room temperature gradually over the course of 12 h. The

reaction contents were diluted with dichloromethane and water and separated. The aqueous layer was extracted three times with dichloromethane and the combined organic fractions were washed with brine and dried over anhydrous MgSO₄. Yield (5.7g, 97% yield). ¹H NMR (600 MHz, d^{8} -toluene, 268 K): δ 10.03 (1H), 8.66 (2H), 8.15 (2H), 7.43 (4H), 7.24 (2H), 7.19 (2H), 6.81 (2H), 6.49 (2H), 1.28 (9H). FT-IR (KBr): 3364 (w), 3044 (w), 2958 (m), 2902 (w), 2864 (w), 1593 (m), 1571 (s), 1537 (m), 1514 (s), 1498 (m), 1471 (m), 1421 (m), 1377 (s), 1330 (m), 1269 (w), 1215 (m), 1170 (w), 1103 (m), 999 (w), 950 (w), 887 (w), 856 (w), 817 (m), 786 (m), 746 cm⁻¹ (m). UV-Vis (CH₂Cl₂): $\lambda_{max} = 373$ nm. HRMS (ESI+): Calc'd for C₂₈H₂₆N₄O (MH+) 435.2185, found 435.2182. HRMS (EI+): Calc'd for C₂₈H₂₆N₄O (MH+) 434.2101. Calc'd for C₂₈H₂₆N₄O•0.5CH₂Cl₂ (found): C, 71.8 (71.7); H, 5.7 (5.6); N, 11.7 (11.7). Our data suggests that **2** is in equilibrium with a paramagnetic isomer with a structure that is currently unknown.

2,6-bis-(8-quinolylamino)-4-(*tert***-butyl)phenoxyl radical (3, BQAP)**. To a methanol (60 mL) solution of **2** (0.22 g, 0.50 mmol) was added excess triethylamine (12 drops) and the resulting yellow solution was stirred for approximately 2 min before the addition of a warm aqueous solution (5 mL) of NaIO₄ (222 mg, 1.03 mmol). The solution immediately turned green, concomitant with the formation of a forest green precipitate. The mixture was stirred for 20 min and the green product was collected by vacuum filtration, washed with methanol (30 mL), warm water (30 mL) and dried. Yield (145 mg, 72% yield). Crystals suitable for X-ray diffraction were obtained over 3 months by slow evaporation of a THF solution. HRMS (ESI+): Calc'd for C₂₈H₂₅N₄O (M+) 433.2028, found 433.2024. FT-IR (KBr): 3257 (w), 3041 (w), 2960 (w), 2902 (w), 2866 (w), 1614 (w),

1591 (m), 1573 (m), 1529 (s), 1471 (s), 1431 (m), 1408 (m), 1381 (m), 1367 (m), 1334 (m), 1282 (m), 1273 (m), 1222 (w), 1200 (m), 1170 (w), 1114 (w), 1064 (w), 1022 (w), 954 (w), 817 (m), 786 (m), 738 (m). UV-Vis (CH₂Cl₂): λ_{max} nm (ϵ (M⁻¹ cm⁻¹)) = 1127 (2.6 × 10³), 490 (2.1 × 10³), 425 (1.1 × 10⁴), 305 (8.0 × 10³). Calc'd for (found) C₂₈H₂₅N₄O•0.35CH₃OH (precipitated powder from methanol): C, 76.2 (76.6); H, 6.0 (5.6); N, 12.6 (12.5). Calc'd for (found) C₂₈H₂₅N₄O•C₄H₈O (single crystals from THF): C, 76.0 (75.4); H, 6.6 (6.8); N, 11.1 (11.2).



Figure S1. Packing diagram 3 in ac plane.

Table S1.	Crystal data and structure refinement for 3 .	
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Identification code	d15105		
Empirical formula	C32 H33 N4 O2		
Formula weight	505.62		
Temperature	147(2) K		
Wavelength	1.54178 Å		
Crystal system	Monoclinic		
Space group	P2 ₁ /c		
Unit cell dimensions	a = 13.6166(3) Å	<i>α</i> =90°.	
	b = 12.5766(3) Å	β=112.1190(10)°.	
	c = 16.6119(4) Å	$\gamma = 90^{\circ}$.	
Volume	2635.43(11) Å ³		
Ζ	4		
Density (calculated)	1.274 Mg/m ³		
Absorption coefficient	0.637 mm ⁻¹		
F(000)	1076		
Crystal size	0.160 x 0.130 x 0.020 mm ³		
Theta range for data collection	3.504 to 67.317°.		
Index ranges	-16<=h<=16, -14<=k<=14, -19<=l<=19		
Reflections collected	51605		
Independent reflections	4682 [R(int) = 0.0574]		
Completeness to theta = 67.317°	99.1 %		
Absorption correction	Semi-empirical from equivalents		
Max. and min. transmission	0.7529 and 0.6688		
Refinement method	Full-matrix least-squares on F ²		
Data / restraints / parameters	4682 / 0 / 382		
Goodness-of-fit on F ²	1.029		
Final R indices [I>2sigma(I)]	R1 = 0.0517, $wR2 = 0.1350$		
R indices (all data)	R1 = 0.0678, $wR2 = 0.1490$		
Extinction coefficient Largest diff. peak and hole0.553 and -0.225 e.Å ⁻³	n/a		



Figure S2. ¹H NMR spectrum of 1 in CDCl_{3.}



Figure S3. ¹³C NMR spectrum of 1 in CDCl₃.



Figure S4. Variable temperature EPR of a frozen 1 mM solution of **3** in DCM. Top to bottom: 20 K, 40 K, 50 K, 75 K and 100 K. Frequency = 9.38 GHz, microwave power = 2 mW, modulation amplitude = 5 G.



Figure S5. Anodic CV of 3 in DMF (containing 0.5 M $^{n}Bu_4NPF_6$ with 100 mV/s scan rate).



Figure S6. Cathodic CV of 3 in DMF (containing 0.5 M $^{n}Bu_{4}NPF_{6}$ with 100 mV/s scan rate).



Figure S7. βHOMO (left) and βLUMO (right) of **3**. Iso-value is 0.020.



Figure S8. α HOMO (left) and α LUMO (right) of 3. Iso-value is 0.020.

Calculated wavelength (nm)	Oscillator strength	Transition
1025	0.16	βНОМО → βLUMO
528	0.08	αHOMO → αLUMO $ αHOMO-1 → αℤUMO+1 $ $ βHOMO-5 → βLUMO$
452	0.274	αHOMO → αLUMO $ βHOMO-2 → βLUMO$
385	0.86	αHOMO-1 → αLUMO+1 βHOMO → βLUMO+2 βHOMO-4 → βLUMO
332	0.213	αHOMO →αLUMO+4

 Table S2. Calculated electronic transitions for 3.



Figure S9. LCMS traces showing 2 (top, major peak at 730 sec acquisition time) and 2 with paramagnetic isomer growing in (bottom). The m/z of each peak is identical.



Figure S10. UV-visible spectrum of **2** (initial trace is red) and after 24 hr (blue trace) showing establishment of equilibrium of **2** with paramagnetic isomer.



Figure S11. Anodic CV of **2** in DMF (containing 0.5 M ⁿBu₄NPF₆ with 100 mV/s scan rate).



Figure S12. Cathodic CV of **2** in DMF (containing 0.5 M ⁿBu₄NPF₆ with 100 mV/s scan rate).



Figure S13. ¹H NMR spectrum of 2 in d⁸-toluene at 235 K.



Figure S14. EPR spectra of **2** in toluene solution at 298 K (red trace) and 100 K (blue trace).

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