Electronic Supplementary Material (ESI) for ChemComm.

Bidentate Nitroxide Ligands Stable Toward Oxidative Redox Cycling and their Complexes with Cerium and Lanthanum

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Supporting Information

Experimental Procedures

General methods. All reactions and manipulations were performed under an inert atmosphere (N2) using standard Schlenk techniques or in a Vacuum Atmospheres, Inc. Nexus II drybox equipped with a molecular sieves 13X / Q5 Cu-0226S catalyst purifier system. Glassware was oven-dried overnight at 150 °C prior to use. ^{1}H NMR and ^{13}C NMR were obtained on a Bruker DMX-300 and a Bruker AM–500 Fourier transform NMR spectrometer at 300 MHz and 126 MHz, respectively. Chemical shifts were recorded in units of parts per million downfield from residual proteo solvent peaks (^{1}H) or characteristic solvent peaks (^{13}C{1H}). Elemental analyses were performed at Complete Analysis Laboratories, Inc. using a Carlo Erba EA 1108 analyzer. UV-Vis data were collected on a Cary 5000 spectrometer in methylene chloride in 1 mm path length air-free quartz cuvettes. The infrared spectra were obtained from 400–4000 cm-1 using a Perkin Elmer 1600 series infrared spectrometer.

Materials. THF, CH_2Cl_2, dimethoxyethane (DME), pyridine and hexanes were purchased from Fisher Scientific. These solvents were sparged for 30 min with dry argon and dried using a commercial two-column solvent purification system comprising columns packed with Q5 reactant and neutral alumina respectively (for hexanes), or two columns of neutral alumina (for THF, CH_2Cl_2 and pyridine). Deuterated solvents were purchased from Cambridge Isotope Laboratories, Inc. and stored over either 3 Å molecular sieves or potassium mirror overnight prior to use. Ce[N(SiHMe$_2$)$_2$]$_4$,[1] Ce(O*t*Bu)$_4$(py)$_2$[1] La[N(SiMe$_3$)$_2$]$_3$[2] and [*n*Pr$_4$N][B(3,5-CF$_3$-C$_6$H$_3$)$_4$] ([*n*Pr$_4$N][BAr^F$_4$])[3] were prepared by following published literature procedures. The 2-methyl-2-nitrosopropane was prepared by a modified procedure.[4] The 2.5 M *n*BuLi in hexanes solution was used as received from Acros Organics. The 1,3-bis(2´-bromophenyl)-benzene were prepared by a modified procedure.[5] In this procedure, the crude 1,3-bis(2´-bromophenyl)-benzene was purified by flash chromatography using 20/80 ether/hexanes eluent to remove triphenylphosphine (TPP) and triphenylphosphine oxide (TPPO). The product was eluted as a first portion. When the TPP was still remained by ^{1}H NMR, the resulting product was further purified by chromatography, eluted by 1/99 toluene/hexanes. Then the resulting product was dried at 50 ˚C under reduced pressure while it was solidified as white solid, yielding 71 %.

Electrochemistry. Cyclic Voltammetry experiments (CV) were performed using a CH Instruments 620D Electrochemical Analyzer/Workstation and the data were processed using CHI software v9.24. All experiments were performed in an N_2 atmosphere drybox using electrochemical cells that consisted of a 4 mL vial, glassy carbon working electrode, a platinum wire counter electrode, and a silver wire plated with AgCl as a quasi-reference electrode. The working electrode surfaces were polished prior to each set of experiments. Potentials were reported versus ferrocene, which was added as an internal standard for calibration at the end of each run. Solutions employed during these studies were ~1 mM in analyte and 0.1 M [*n*Pr$_4$N][BAr^F$_4$] in methylene chloride. All data were collected in a positive-feedback IR compensation mode.

Computational details. Gaussian '09 Rev. A.02 was used in electronic structure calculations.[6] The B3LYP hybrid DFT method was employed with a 28-electron small core pseudopotential on cerium with published segmented natural orbital basis sets incorporating quasi-relativistic effects[7] and the 6-31G* basis set on all other atoms. Geometry optimizations were carried out starting from the coordinates of the crystal structures while the geometry optimization on the cationic portion of $\mathbf{1}^+$ was carried out starting from the optimized coordinates of **1**. The frequency calculations indicated that the geometries were the minima (no imaginary frequencies). Molecular orbitals were rendered with the program Chemcraft v1.6 at an isovalue of 0.03.[8] Natural population analysis was performed using the IOp(6/80 = 1) keyword in Gaussian '09.

X-ray crystallography. X-ray intensity data were collected on a Bruker APEXII CCD area detector employing graphite-monochromated Mo-Kα radiation (λ=0.71073 Å) at a temperature of 100(1) K. Preliminary indexing was performed from a series of thirty-six 0.5° rotation frames with exposures of 10 seconds. Rotation frames were integrated using SAINT,[9] producing a listing of unaveraged F^2 and $\sigma(F^2)$ values which were then passed to the SHELXTL[10] program package for further processing and structure solution. The intensity data were corrected for Lorentz and polarization effects and for absorption using SADABS.[11] The structure was solved by direct methods (SHELXS-97[12]). Refinement was by full-matrix least squares based on F^2 using SHELXL-97.[12] All reflections were used during refinement. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined using a riding model.

Synthetic details and characterization of H_2arene-diNOx, 1 and 2

Preparation of H_2arene-diNOx. In the 50 ml schlenk flask charged with 1,3-bis(2′-bromophenyl)-benzene (786.5 mg, 2.03 mmol) and stir bar purged with N_2 three times, dry diethyl ether (30 ml) was added and cooled down to –100 ºC in diethyl ether/dry ice bath. *n*BuLi in hexane solution (1.71 ml, 4.26 mmol, 2 equiv) was added dropwise with syringe at –100 ºC stirring then the reaction mixture was stirred at –100 ºC for 3 h. Then 2-methyl-2-nitrosopropane (741.7 mg, 4.26 mmol) in diethyl ether (10 ml) solution was added by syringe dropwise at –100 ºC. The reaction mixture was stirred for 18 h slowly warming up to room temperature. The reaction was quenched with a saturated aqueous NH_4Cl solution. The organic layer was extracted with Et_2O, three times, dried over $MgSO_4$, then filtered. Volatiles were removed under reduced pressure and the product further purified by recrystallization in methylene chloride/hexane. The white powder was isolated by filtration and washed by hexane. Yield 487 mg, 59 %. ^1H NMR (300 MHz, C_6D_6) δ: (Ar-*H*) 7.81 (m, 2H), 7.74 (m, 1H), 7.49 (m, 2H), 7.34 (m, 3H) 7.16 (m, overlapping with C_6D_6, 2H), 7.07 (m, 2H), 4.29 (s, –NOH, 2H), 0.97 (s, *t*Bu, 18H). ^{13}C NMR (126 MHz, acetone-d_6) δ: (Ar) 149.3, 142.7, 139.8, 132.3, 131.1, 129.2, 127.9, 127.7, 126.6, 68.2 (THF), 61.8 ($\mathit{C}(CH_3)_3$), 26.3 (overlapping with THF, $C(C\mathit{H_3})_3$). Melting point: 135.9–137.2 ºC. High res. mass spec.: Calc'd 404.2464 $[M+H]^+$, Found 405.2523.

Preparation of $Ce(arene\text{-}diNOx)_2$ (1).

Start from $Ce[N(SiHMe_2)_2]_4$ In 20 ml scintillation vial charged with dark red solution of $Ce[N(SiHMe_2)_2]_4$ (200mg, 0.300 mmol) in 2 ml THF and stir bar, H_2arene-diNOx (272.4 mg, 0.600 mmol) was added as solid. The reaction mixture was stirred 30 min, while the solution turned to dark orange. Volatiles were removed under reduced pressure. Dark orange crystals were grown in THF/hexanes mixture at –35 ˚C. Yield 195.6 mg, 70 %.

Start from Ce(O*t*Bu)(pyr)$_2$ In 20 ml scintillation vial charged with a yellow solution of Ce(O*t*Bu)(pyr)$_2$ (85.9 mg, 0.145 mmol) in 1 ml THF and stir bar, H_2arene-diNOx (117.7 mg, 0.291 mmol) in 1 ml THF was added dropwise, while stirring. The reaction was changed color to dark brown-orange solution and stirred 15 min. The volatiles were removed by applying reduced pressure. Then ~2 ml THF and ~3 ml hexane was added and concentrated to ~2 ml. Dark orange crystals were grown at –35 ºC overnight. The crystals that precipitated from the solution were shown to have the formula Ce(arene-diNOx)$_2$•(THF)$_2$ by X-ray diffraction. The product was isolated by filtration and dried under reduced pressure. From these steps, the product was shown to have the formula Ce(arene-diNOx)$_2$•(THF)$_{0.5}$ by combustion analysis. Yield 103.3 mg, 72 %. ^1H NMR (300 MHz, C_6D_6) δ: (Ar-*H*) 8.75 (s, 2H), 7.77 (m, 2H), 7.74 (m, 2H), 7.28 (m, 8H), 7.03 (m, 4H), 6.72 (m, 4H), 6.34 (m, 2H), 3.58 (THF), 1.42 (THF), 1.36 (s, *t*Bu, 18H) 0.86 (s, *t*Bu, 18H). ^1H NMR (300 MHz, CD_2Cl_2) δ: 8.38 (m, 2H), 7.55–7.44 (m, 4H), 7.29–7.18 (m, 10H), 7.01–6.99 (m, 2H), 6.91–6.86 (m, 2H), 6.45–6.44 (m, 4H), 3.68 (THF), 1.82 (THF), 1.21 (s, *t*Bu, 18H), 0.62 (s, *t*Bu, 18H). ^{13}C NMR (126 MHz, C_6D_6) δ: (Ar) 149.4, 148.5, 143.4, 142.8, 139.9, 138.6, 134.9, 132.3, 129.5, 129.2, 127.8, 127.6, 126.9, 126.8, 126.5, 126.4, 126.3, 68.1 (THF), 67.6 ($\mathit{C}(CH_3)_3$), 65.3 ($\mathit{C}(CH_3)_3$), 28.5 (THF), 27.5 ($C(C\mathit{H_3})_3$), 26.1 ($C(C\mathit{H_3})_3$). Anal. Calc'd. Ce(arene-diNOx)$_2$•(THF)$_{0.5}$: C 66.10; H 6.57; N 5.71 Found: C 65.95; H 6.68; N 5.57.

Preparation of $[(py)_2K(18\text{-}crown\text{-}6)][La(arene\text{-}diNOx)_2]$ (2).

$K(DME)_2[La(arene\text{-}diNOx)_2]$ (2′). In 20 ml scintillation vial charged with H_2arene-diNOx (0.645 mmol, 2 equiv.) in 5 ml dimethoxyethane and stir bar, $La[N(SiMe_3)_2]_3$ (202 mg, 0.326 mmol) in 1 ml dimethoxyethane was added while stirring. The solution was changed to colorless solution to yellow solution and stirred 5 min. Then $KN(SiMe_3)_2$ (0.322 mmol, 1 equiv.) was added as solid. The reaction mixture was stirred 14 h. The solvent was concentrated to ~2 ml while the pale yellow product was precipitated as a solid.. The pale yellow powder was collected by filtration and washed by hexanes to remove $HN(SiMe_2)_2$ and any residual $La[N(SiMe_2)_2]_3$. The pale yellow crystals were grown from pyridine/hexanes with a couple of drops of DME. Yield 276.7 mg, 74 %. ^1H NMR (300 MHz, pyridine-d_5) δ: (Ar-*H*) 9.17 (s, 2H), 8.37 (d, 2H), 7.59-7.51 (m, overlapping with py, 4H), 7.39-7.32 (m, 8H), 7.22-7.16 (m, overlapping with py, 4H), 6.91 (m, 2H), 6.57 (m, 2H), 3.51 (DME), 3.28 (DME), 1.38 (s, *t*Bu, 18H), 1.01 (s, *t*Bu, 18H). ^{13}C NMR (126 MHz, pyridine-d_5) δ: (Ar) 153.68, 152.30, 144.50, 144.11, 140.22, 138.31, 135.63, 130.84, 129.78, 128.80, 128.61, 128.53, 127.88, 127.06, 126.92, 126.65, 124.56, 72.51 (DME), 63.42 (*C*(CH_3)$_3$), 63.12 (*C*(CH_3)$_3$), 59.10 (DME), 28.87 (C(C*H_3*)$_3$), 27.73 (C(C*H_3*)$_3$)., Anal. Calc'd.: C 61.95; H 6.93; N 4.82 Found: C 61.76; H 6.82; N 4.98.

[(py)$_2$K(18-crown-6)][La(arene-diNOx)$_2$] (2). In 20 ml scintillation vial, K(DME)$_2$[La(arene-diNOx)$_2$] (**2′**) (200 mg, 0.172 mmol) was charged. 18-crown-6 (45.4 mg, 0.172 mmol, 1 equiv) was added as solid. ~1 ml pyridine was added and stirred until the solids were fully dissolved. Then 15 ml hexanes were layered over the pyridine solution. The yellow crystals were grown and collected by filtration. Yield 201.5 mg, 83 %. ^{1}H NMR (300 MHz, pyridine-*d_5*) δ: (Ar-*H*) 9.05 (s, 2H), 8.41 (d, 2H), 7.55 (d, 2H), 7.50 (m, 2H), 7.39 (m, 2H), 7.34 (m, 4H), 7.27–7.20 (overlapping, 4H), 7.11 (m, 2H), 6.94 (m, 2H), 6.67 (m, 2H), 3.46 (s, 18-crown-6, 24H), 1.58 (s, ^{t}Bu, 18H), 1.13 (s, ^{t}Bu, 18H). ^{13}C NMR (126 MHz, pyridine-*d_5*) δ: (Ar) 153.94, 153.32, 145.61, 144.03, 139.58, 139.31, 131.59, 129.48, 128.99, 128.69, 127.96, 126.94, 126.59, 126.32, 126.25, 124.55, 123.28, 70.87 (18-crown-6), 63.40 (*C*(CH_3)$_3$), 62.78 (*C*(CH_3)$_3$), 28.88 (C(C*H_3*)$_3$), 27.82 (C(C*H_3*)$_3$). Anal. Calc'd.: C 63.23; H 6.74; N 5.98 Found: C 62.97; H 6.64; N 5.89.

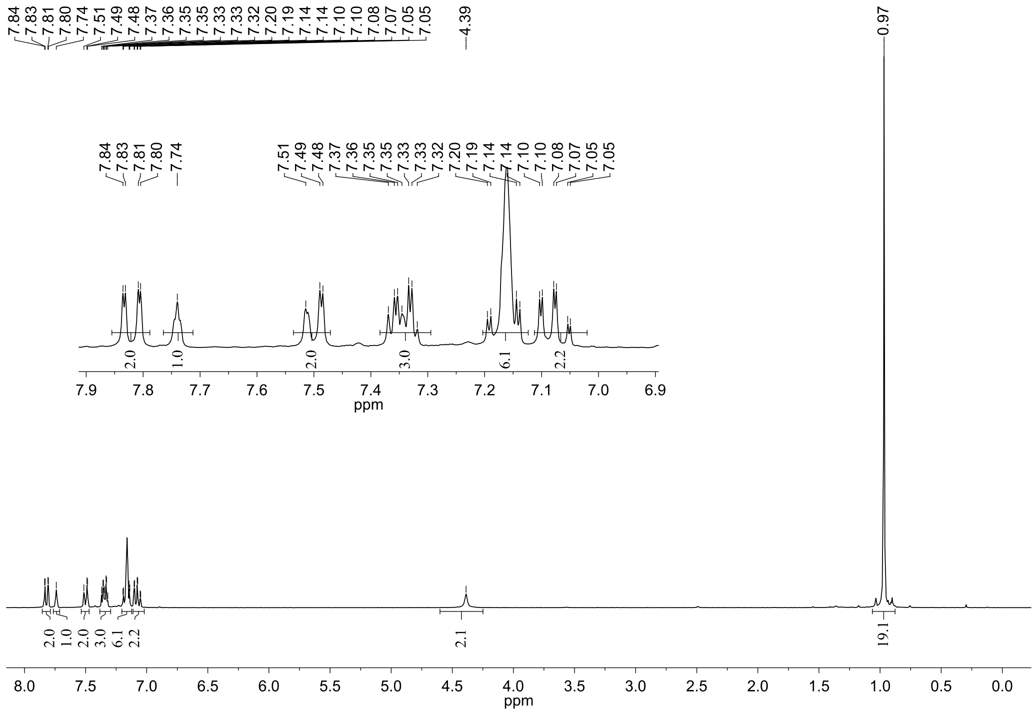

Figure S1a. ^{1}H NMR spectrum of H$_2$arene-diNOx in benzene-d_6.

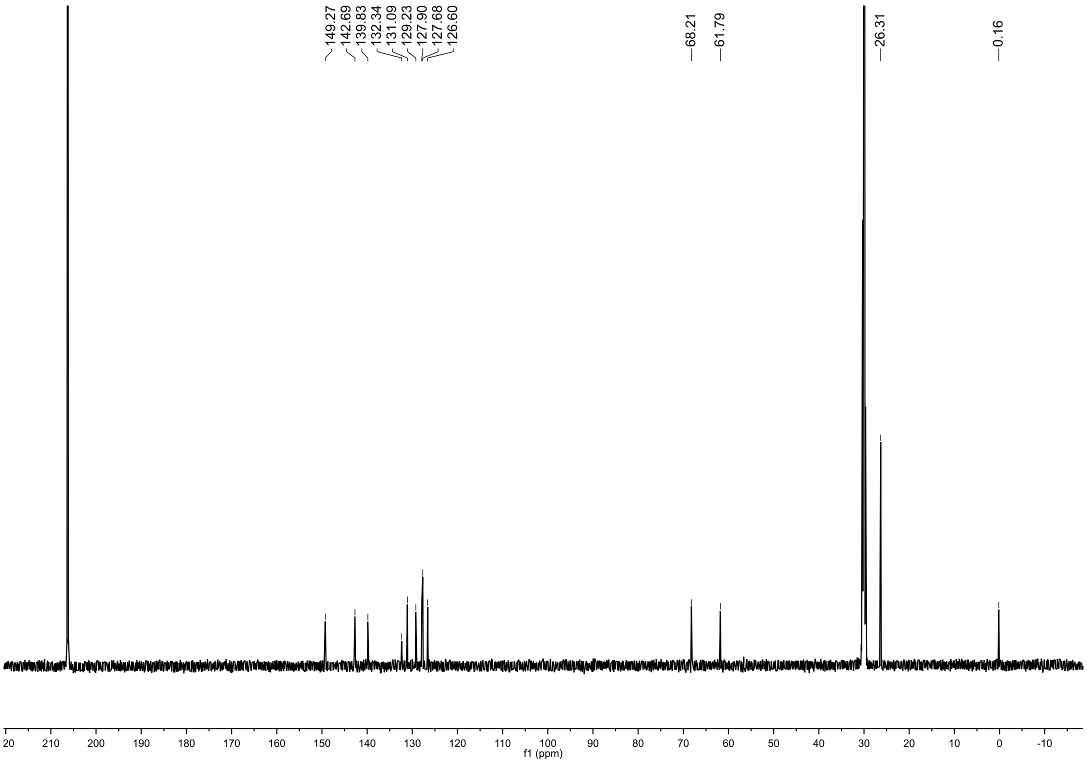

Figure S1b. ^{13}C NMR spectrum of H$_2$arene-diNOx in acetone-d_6.

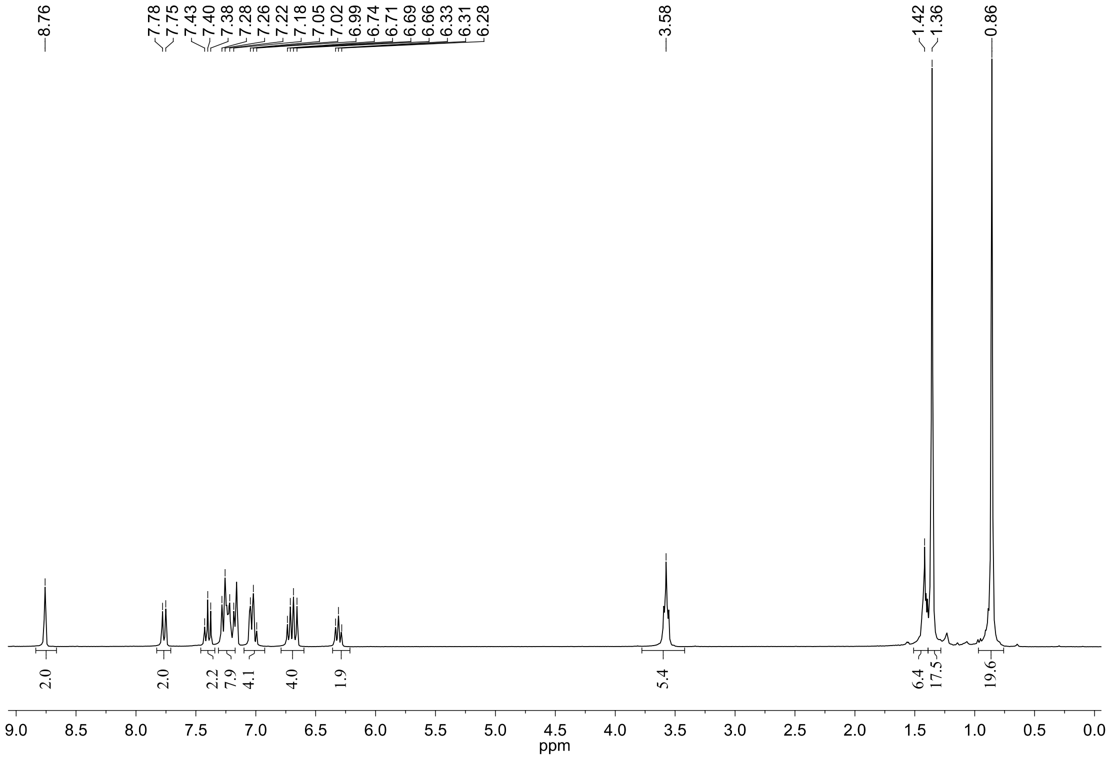

Figure S2a. ^{1}H NMR spectrum of Ce(arene-diNOx)$_2$ (**1**) in benzene-d_6.

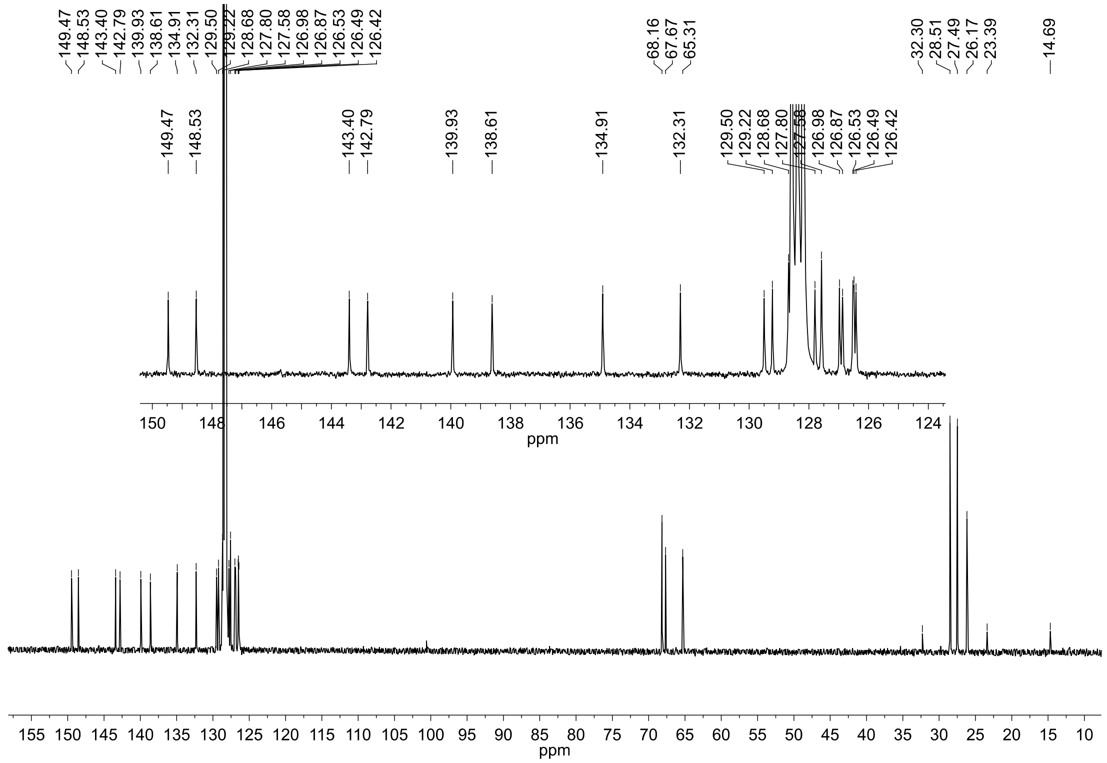

Figure S2b. ^{13}C NMR spectrum of Ce(arene-diNOx)$_2$ (**1**) in benzene-d_6.

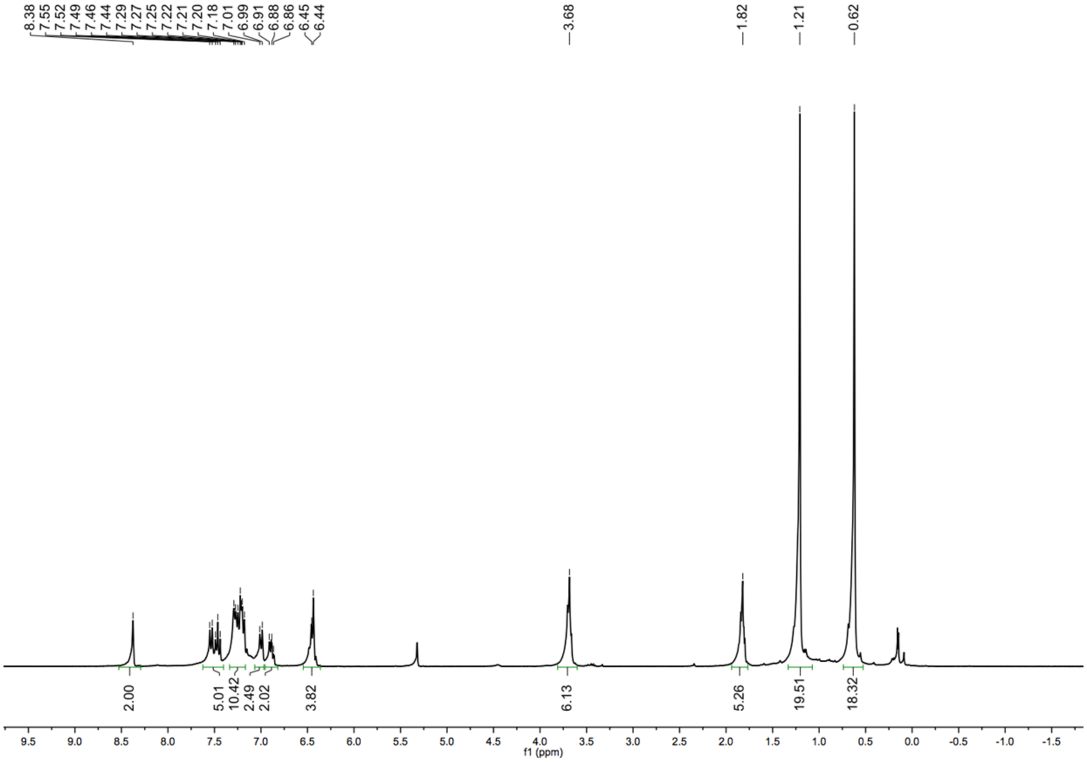

Figure S3. ^{1}H NMR spectrum of Ce(arene-diNOx)$_2$ (**1**) in methylene chloride-*d*$_2$.

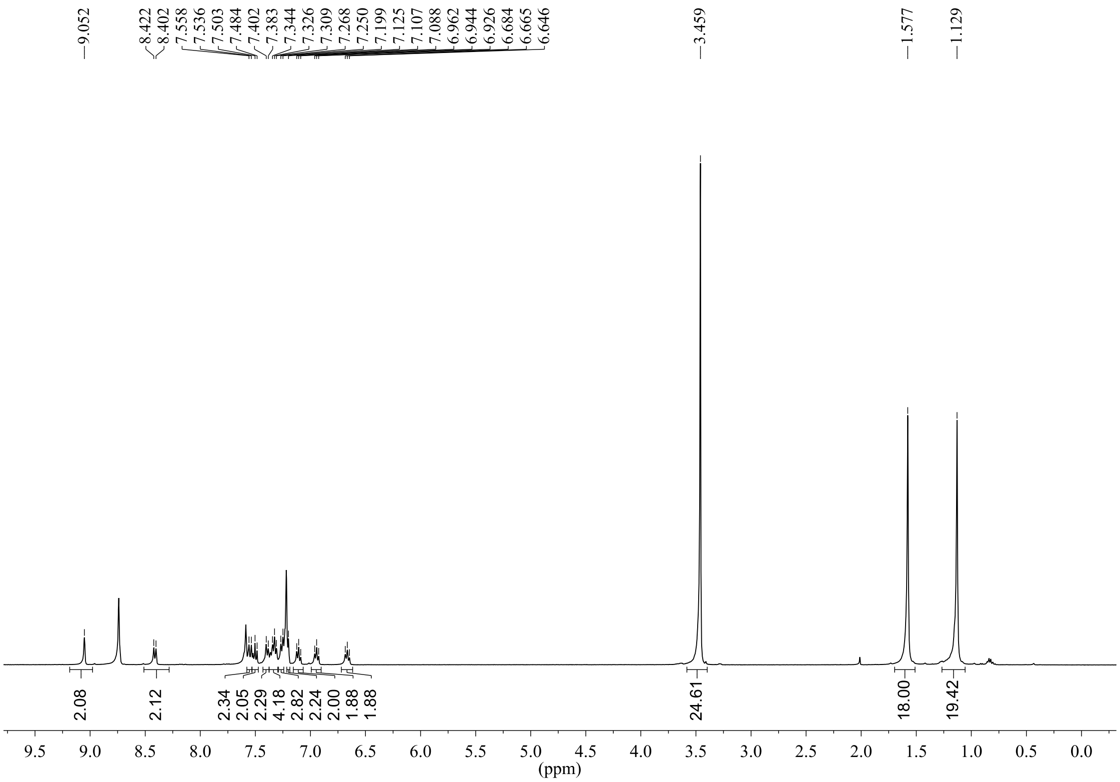

Figure S4a. ^{1}H NMR spectrum of K(18-crown-6)[La(arene-diNOx)$_2$] (**2**) in pyridine-*d*$_5$.

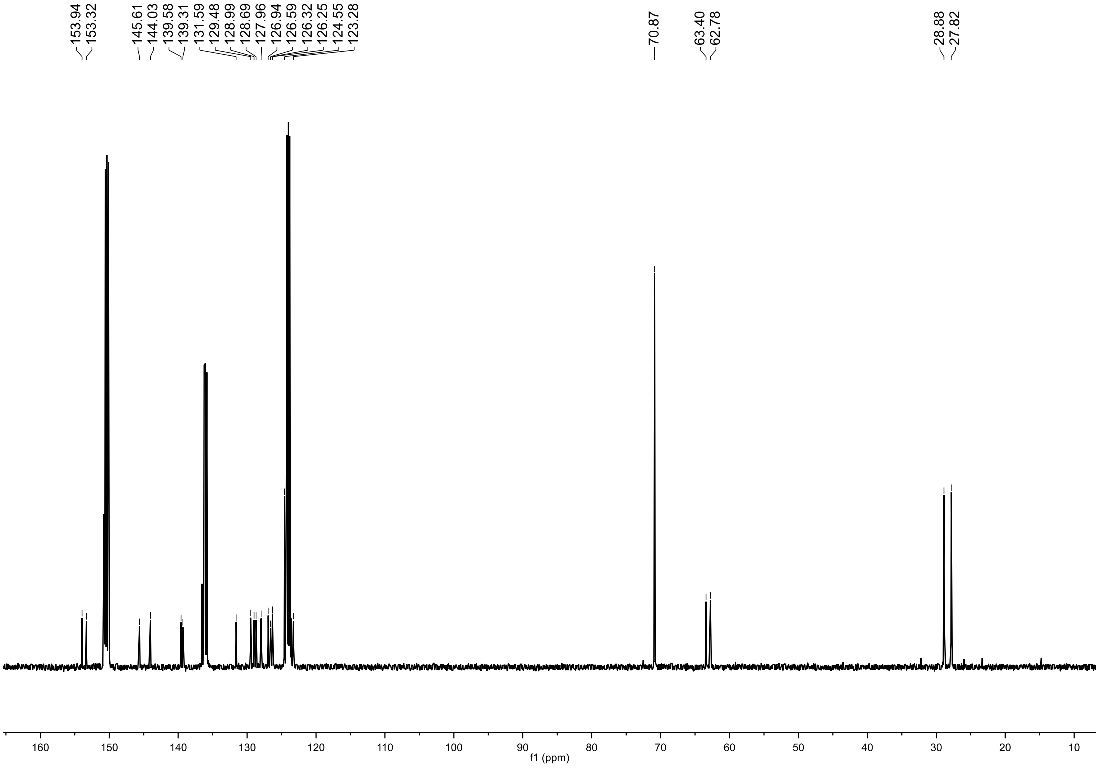

Figure S4b. ^{13}C NMR spectrum of K(18-crown-6)[La(arene-diNOx)$_2$] (**2**) in pyridine-*d*$_5$.

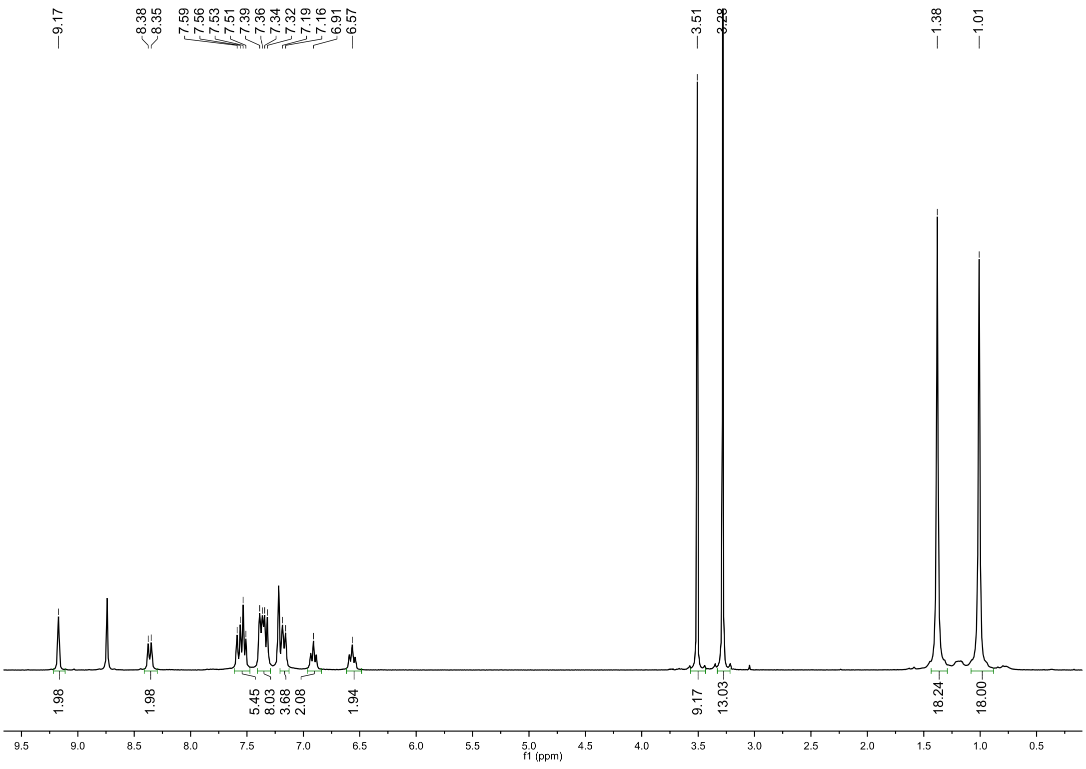

Figure S5a. ^{1}H NMR of K(DME)[La(arene-diNOx)$_2$] (**2′**) in pyridine-*d*$_5$.

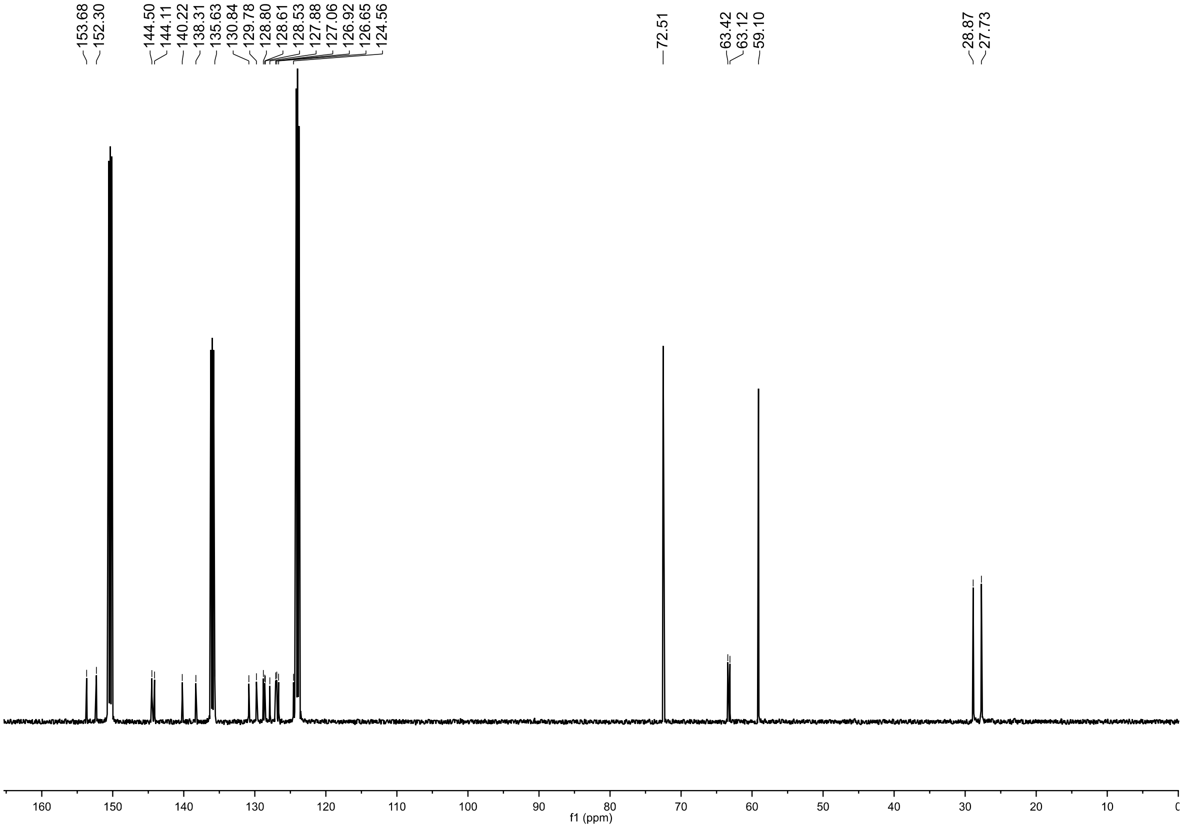

Figure 5b. ^{13}C spectrum of K(DME)$_2$[La(arene-diNOx)$_2$] (**2′**) in pyridine-*d*$_5$.

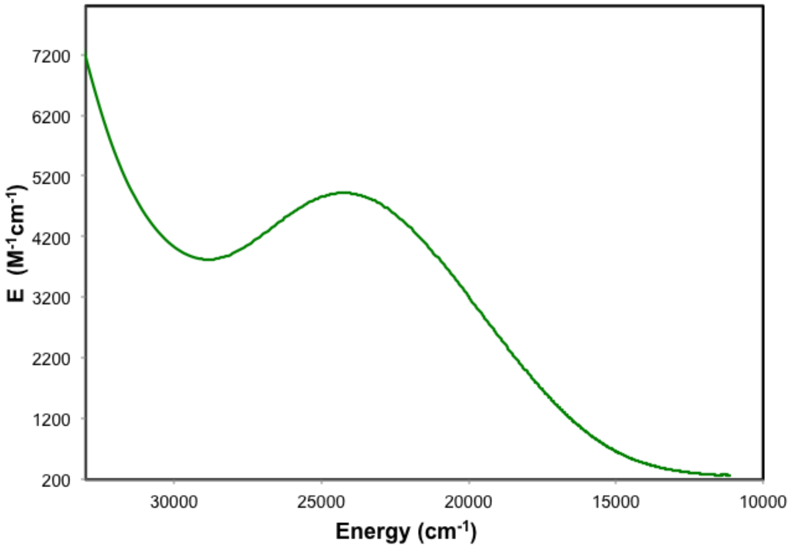

Figure S6. LMCT band by UV-Vis spectrum of Ce(arene-diNOx)$_2$ (**1**) in methylene chloride.

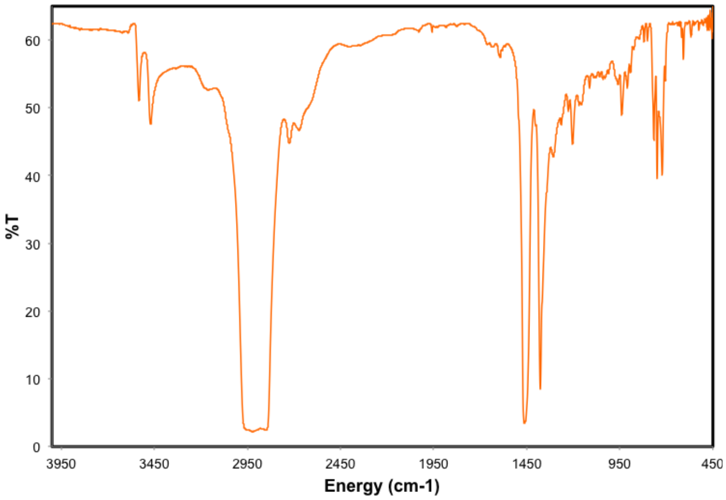

Figure S7. IR spectrum of H$_2$arene-diNOx in nujol.

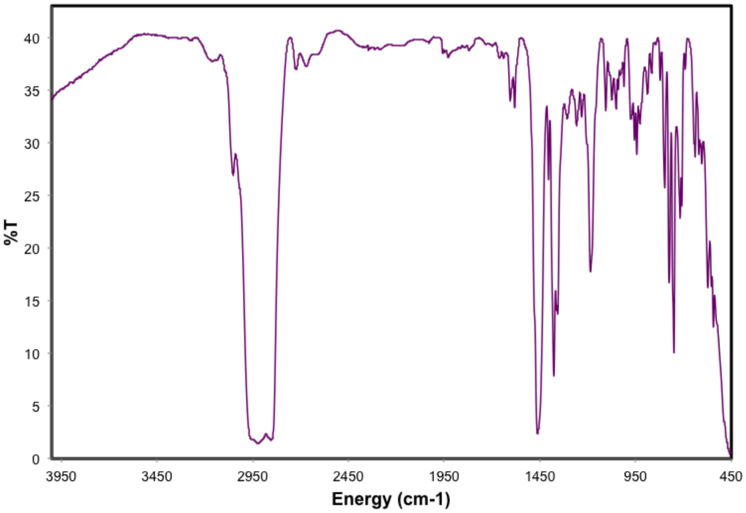

Figure S8. IR spectrum of Ce(arene-diNOx)$_2$ (**1**) in nujol.

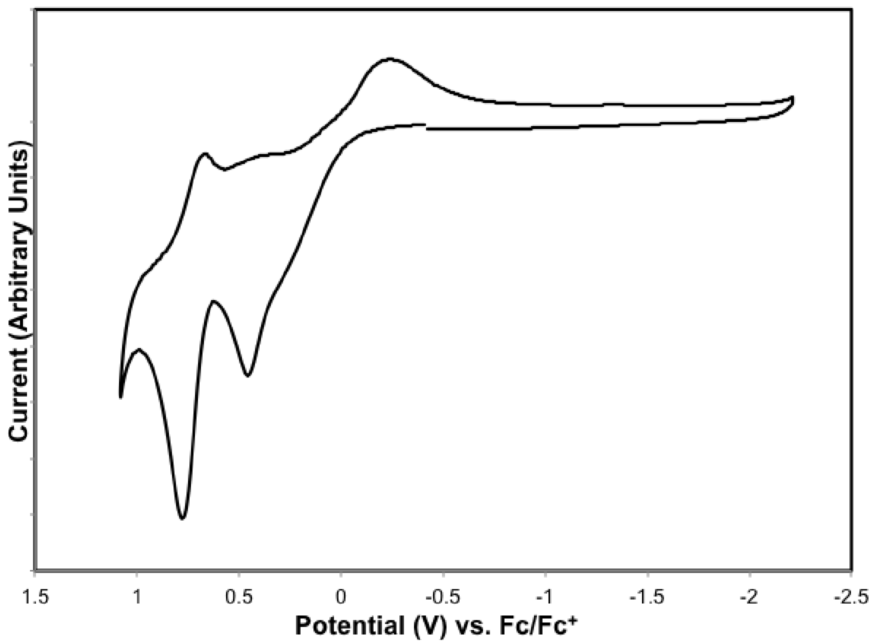

Figure S9a. Full scan cyclic voltammograms of H_2arene-diNOx in methylene chloride with 0.1 M [*n*Pr_4N][$BAr^F{}_4$] at ν =100 mV/s (ν= scan rate).

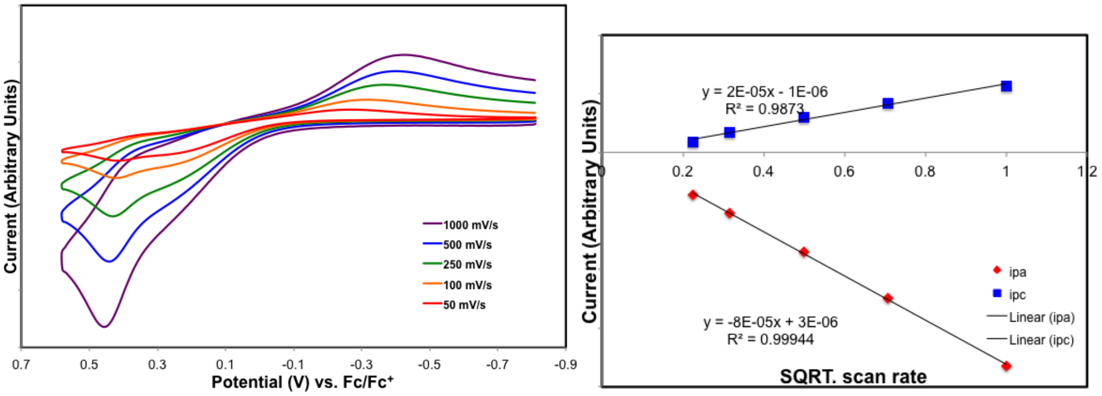

Figure S9b. Left: Isolated [N–OH]/[N–O•] couple at varying scan rates. Right: Current versus $\nu^{1/2}$ (ν = scan rate) plot from the scan rate dependence of the isolated [N–OH]/[N–O•] couple. Cathodic features are shown in blue and anodic features are shown in red. Linearity shows that the redox couple is diffusion controlled according to the Randles-Sevcik equation.

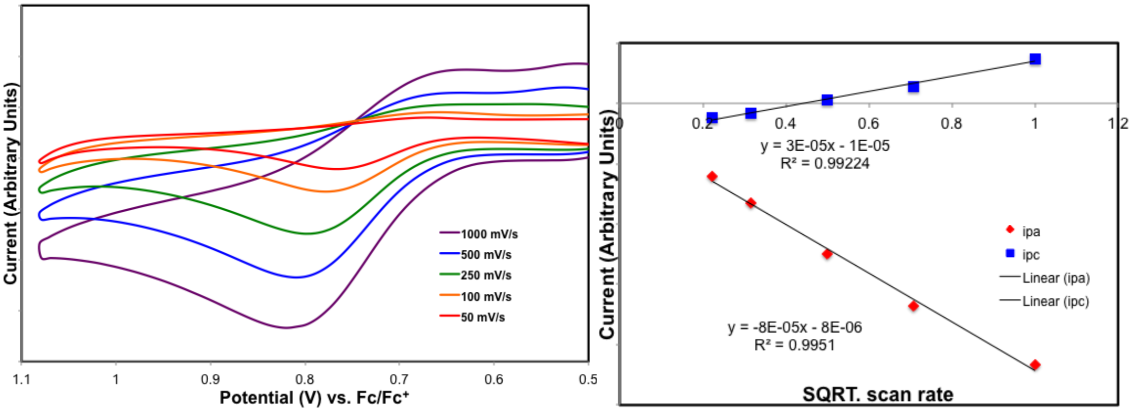

Figure S9c. Left: Isolated [N–O•]/[N=O$^+$] couple at varying scan rates. Right: Current versus $\nu^{1/2}$ (ν = scan rate) plot from the scan rate dependence of the isolated [N–OH]/[N–O•] couple. Cathodic features are shown in blue and anodic features are shown in red. Linearity shows that the redox couple is diffusion controlled according to the Randles-Sevcik equation.

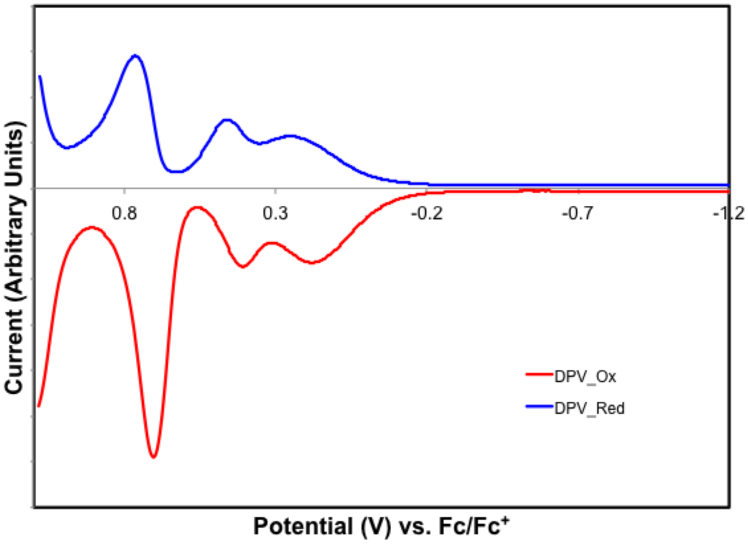

Figure S9d. Differential pulse voltammogram of H_2arene-diNOx in methylene chloride.

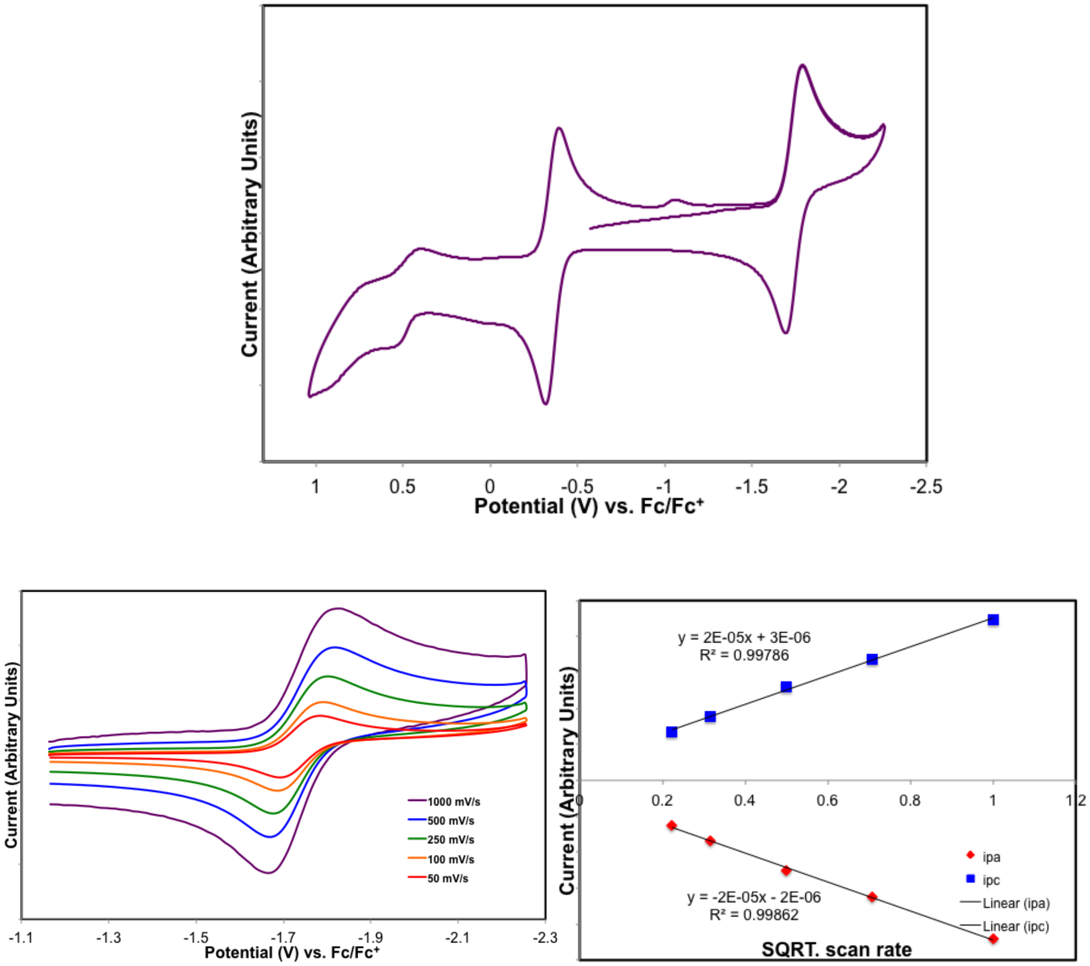

Figure S10a. Top: Full scan cyclic voltammograms of Ce(arene-diNOx)$_2$ (**1**) in methylene chloride with 0.1 M [*n*Pr$_4$N][BAr$^F{}_4$] at ν =100 mV/s (ν= scan rate). Bottom left: Isolated cerium(III/IV) redox couple at varying scan rates. Bottom right: Current versus ν$^{1/2}$ plot from the scan rate dependence of the isolated cerium(III/IV) couple. Cathodic features are shown in blue and anodic features are shown in red. Linearity shows that the redox couple is diffusion controlled according to the Randles-Sevcik equation.

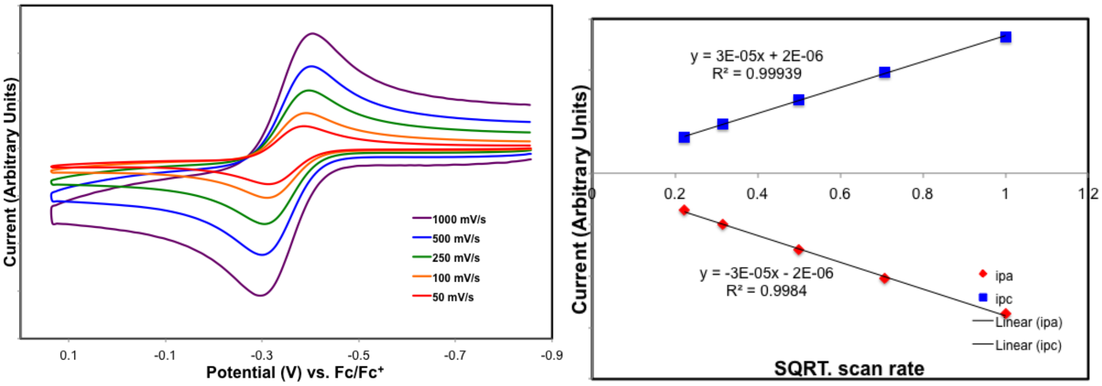

Figure S10b. Left: Isolated [N–O$^-$]/[N–O•] couple at varying scan rates. Right: Current versus ν$^{1/2}$ (ν = scan rate) plot from the scan rate dependence of the isolated [N–O$^-$]/[N–O•] couple. Cathodic features are shown in blue and anodic features are shown in red. Linearity shows that the redox couple is diffusion controlled according to the Randles-Sevcik equation.

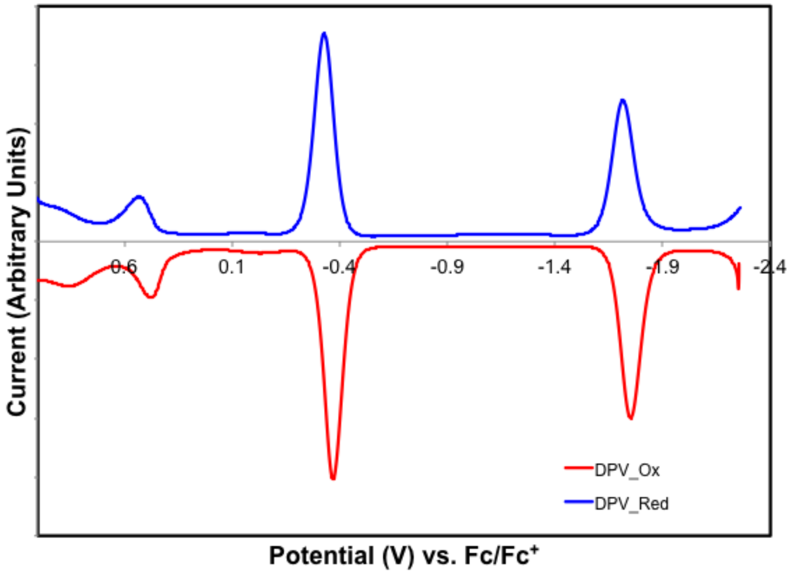

Figure S10c. Differential pulse voltammogram of Ce(arene-diNOx)$_2$ (**1**) in methylene chloride.

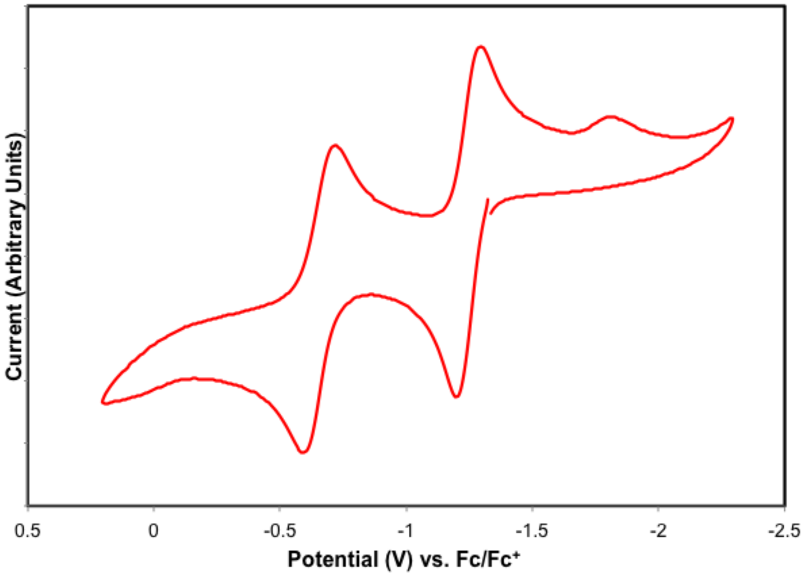

Figure S11a. Full scan cyclic voltammograms of $[(\mathrm{py})_2\mathrm{K}(18\text{-crown-6})][\mathrm{La}(\text{arene-diNOx})_2]$ (**2**) in methylene chloride with 0.1 M $[n\mathrm{Pr}_4\mathrm{N}][\mathrm{BAr^F}_4]$ at ν =100 mV/s (ν= scan rate).

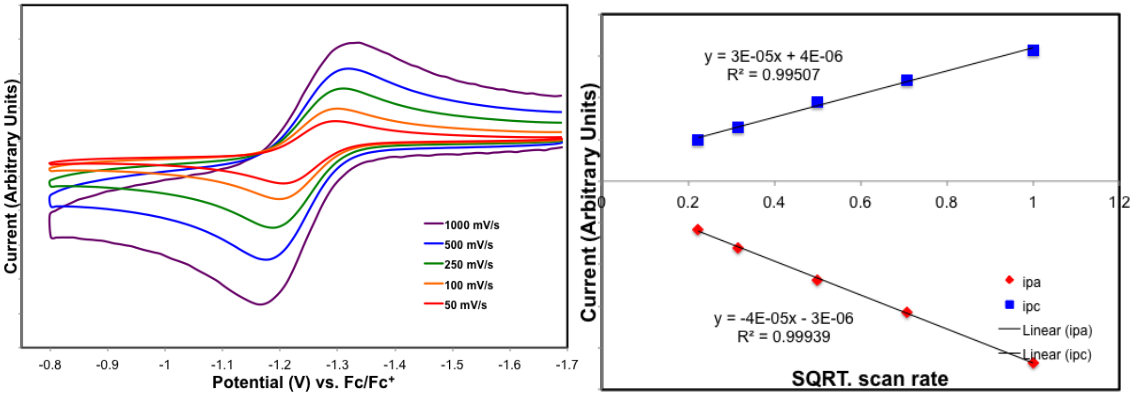

Figure S11b. Left: Isolated first wave as $[\mathrm{N–O^-}]/[\mathrm{N–O\bullet}]$ couple at varying scan rates. Right: Current versus $\nu^{1/2}$ (ν = scan rate) plot from the scan rate dependence of the isolated $[\mathrm{N–O^-}]/[\mathrm{N–O\bullet}]$ couple. Cathodic features are shown in blue and anodic features are shown in red. Linearity shows that the redox couple is diffusion controlled according to the Randles-Sevcik equation.

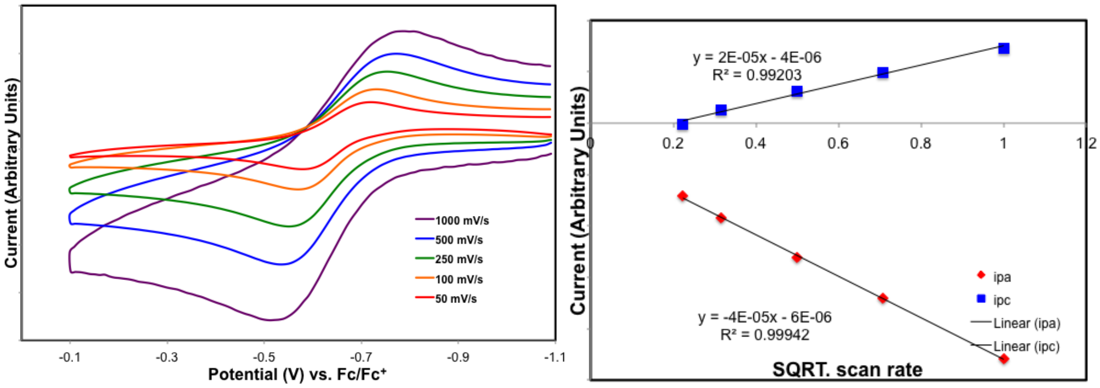

Figure S11c. Left: Isolated second wave as $[\mathrm{N–O^-}]/[\mathrm{N–O\bullet}]$ couple at varying scan rates. Right: Current versus $\nu^{1/2}$ (ν = scan rate) plot from the scan rate dependence of the isolated $[\mathrm{N–O}]/[\mathrm{N–O\bullet}]$ couple. Cathodic features are shown in blue and anodic features are shown in red. Linearity shows that the redox couple is diffusion controlled according to the Randles-Sevcik equation.

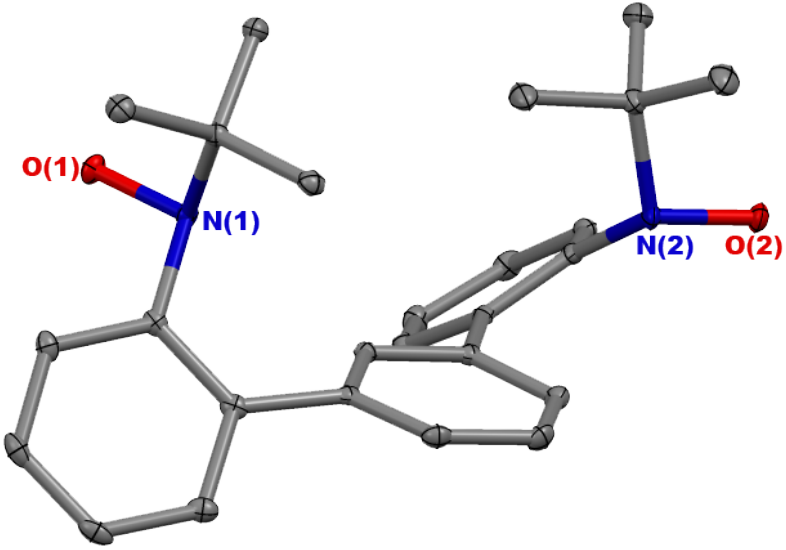

Figure S12. Thermal ellipsoid plot of H_2arene-diNOx at 30 % probability. Hydrogen atoms and interstitial solvent were omitted for clarity.

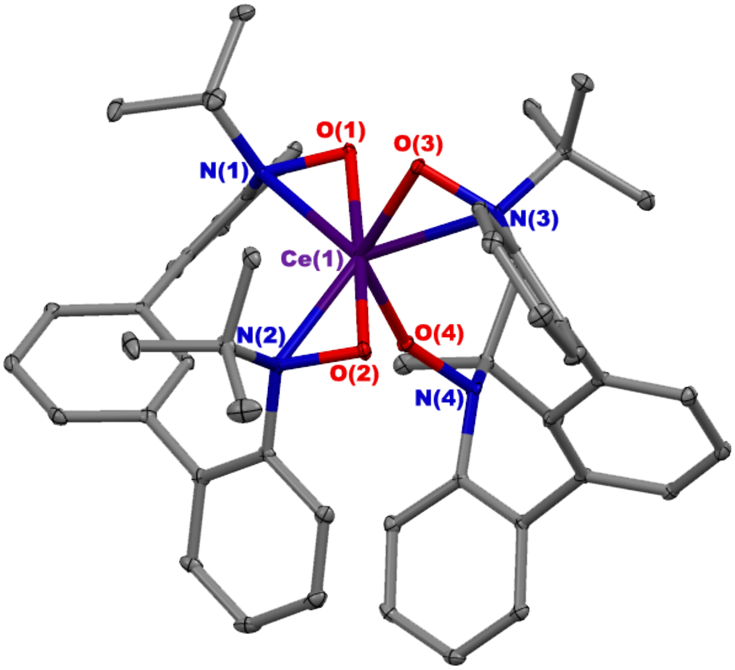

Figure S13. Thermal ellipsoid plot of Ce(arene-diNOx)$_2$ (**1**) at 30 % probability. Hydrogen atoms and interstitial solvent were omitted for clarity.

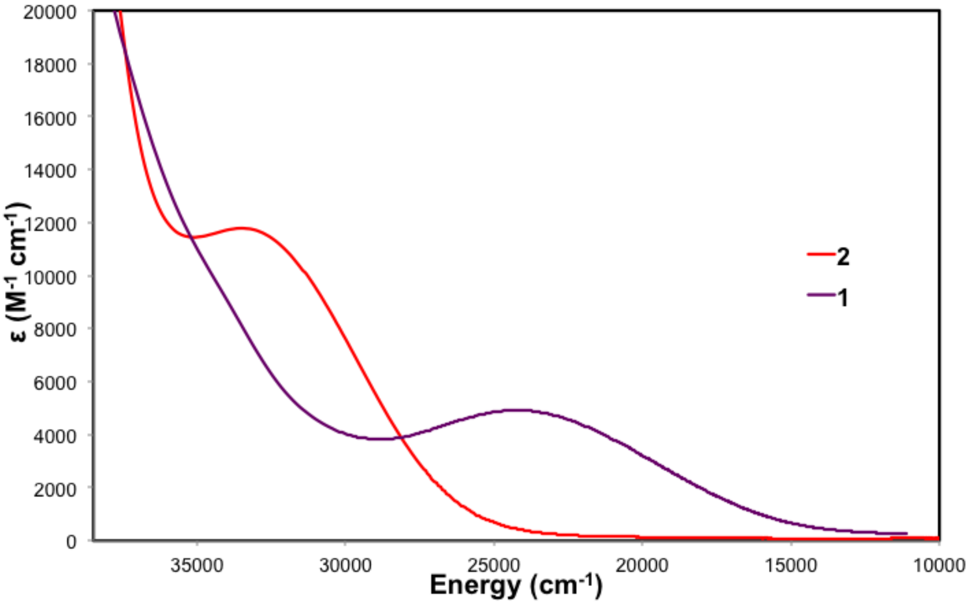

Figure S14. UV-Vis spectra of K(18-crown-6)[La(arene-diNOx)$_2$] (**2**) and Ce(arene-diNOx)$_2$ (**1**) in methylene chloride.

Table S1. Geometry optimized coordinates of Ce(arene-diNOx)$_2$ (**1**).

Ce	0.246436000	-0.882205000	0.183884000
O	-0.834253000	0.349931000	1.677928000
O	1.420066000	-2.288764000	-1.078266000
O	-1.078789000	-2.534415000	0.702799000
O	0.135138000	0.610544000	-1.354132000
N	0.352946000	0.734661000	2.351630000
N	2.649475000	-1.932590000	-0.469557000
N	-2.302817000	-2.189425000	0.058929000
N	-0.754907000	1.215755000	-2.278404000
C	3.032720000	1.958635000	1.764964000
C	3.106938000	1.219868000	0.576653000
H	2.268336000	1.251669000	-0.114414000
C	4.264817000	0.520194000	0.212739000
C	5.389313000	0.603127000	1.047756000
H	6.301797000	0.080834000	0.774459000
C	5.337634000	1.351652000	2.225128000
H	6.213857000	1.411694000	2.865013000
C	4.169328000	2.026388000	2.584776000
H	4.135856000	2.605593000	3.503255000
C	1.803206000	2.748909000	2.065145000
C	0.523232000	2.179390000	2.244883000
C	-0.594973000	3.018774000	2.360034000
H	-1.575544000	2.566269000	2.438608000
C	-0.457016000	4.404549000	2.372396000
H	-1.338095000	5.032789000	2.468431000
C	0.812494000	4.976411000	2.267475000
H	0.935796000	6.055579000	2.284513000
C	1.921797000	4.150319000	2.104378000
H	2.907011000	4.588800000	1.971453000
C	0.288429000	0.231991000	3.802946000
C	1.503766000	0.747964000	4.587044000
H	1.492932000	1.835583000	4.701097000
H	2.442629000	0.456583000	4.108442000
H	1.483711000	0.307625000	5.589901000
C	-1.008935000	0.680143000	4.500213000
H	-1.886468000	0.359353000	3.933549000
H	-1.048200000	1.765478000	4.629531000
H	-1.055642000	0.226125000	5.496117000
C	0.344845000	-1.300578000	3.771761000
H	0.260239000	-1.693670000	4.790553000
H	1.302220000	-1.642158000	3.364868000
H	-0.468593000	-1.725424000	3.178024000
C	4.318775000	-0.178927000	-1.105457000
C	3.499493000	-1.274273000	-1.457420000
C	3.510005000	-1.744953000	-2.779526000
H	2.832090000	-2.546010000	-3.045778000
C	4.361390000	-1.195570000	-3.734896000
H	4.353526000	-1.582291000	-4.750296000
C	5.224980000	-0.157679000	-3.378733000
H	5.900659000	0.275659000	-4.110726000
C	5.189838000	0.343295000	-2.079728000
H	5.823427000	1.183019000	-1.807759000

C	3.274573000	-3.191162000	0.148371000
C	3.462759000	-4.302590000	-0.900972000
H	4.200008000	-4.026638000	-1.660166000
H	2.515855000	-4.533951000	-1.395966000
H	3.822245000	-5.209942000	-0.403423000
C	4.628116000	-2.838740000	0.780291000
H	4.529212000	-2.039395000	1.519591000
H	5.365397000	-2.532217000	0.032533000
H	5.019964000	-3.726352000	1.288857000
C	2.332795000	-3.696024000	1.249733000
H	2.731859000	-4.623506000	1.674114000
H	1.331888000	-3.904570000	0.863539000
H	2.258821000	-2.970163000	2.065449000
C	-4.379795000	0.016946000	-0.310996000
C	-3.352185000	0.938159000	-0.539427000
H	-2.483014000	0.930130000	0.107974000
C	-3.450725000	1.923019000	-1.534609000
C	-4.613355000	1.981675000	-2.315185000
H	-4.708062000	2.741489000	-3.086577000
C	-5.646362000	1.064303000	-2.102645000
H	-6.544439000	1.111447000	-2.713060000
C	-5.537533000	0.094924000	-1.105010000
H	-6.350871000	-0.606481000	-0.939424000
C	-4.307476000	-0.913757000	0.858069000
C	-3.302815000	-1.887589000	1.073895000
C	-3.280578000	-2.589669000	2.290084000
H	-2.481920000	-3.302022000	2.454093000
C	-4.248697000	-2.384053000	3.269593000
H	-4.204176000	-2.945869000	4.198872000
C	-5.275668000	-1.466016000	3.043576000
H	-6.043479000	-1.295863000	3.793188000
C	-5.291146000	-0.745424000	1.852229000
H	-6.062887000	0.001517000	1.687482000
C	-2.684370000	-3.347199000	-0.867342000
C	-2.845417000	-4.668676000	-0.092220000
H	-1.939604000	-4.897083000	0.475948000
H	-3.020979000	-5.485490000	-0.801185000
H	-3.694204000	-4.637614000	0.597580000
C	-3.991851000	-3.014717000	-1.599426000
H	-4.840964000	-2.933979000	-0.915032000
H	-4.211614000	-3.822089000	-2.306608000
H	-3.908856000	-2.081245000	-2.162054000
C	-1.568147000	-3.505285000	-1.907909000
H	-1.423187000	-2.575541000	-2.464012000
H	-1.847714000	-4.286523000	-2.623667000
H	-0.619028000	-3.784070000	-1.446765000
C	-2.366570000	2.941047000	-1.643226000
C	-1.023223000	2.577791000	-1.881799000
C	-0.015221000	3.546451000	-1.759327000
H	1.020856000	3.251257000	-1.876266000
C	-0.331684000	4.878847000	-1.497936000
H	0.461443000	5.617205000	-1.417354000
C	-1.667968000	5.260031000	-1.350945000
H	-1.925180000	6.298721000	-1.161971000
C	-2.670429000	4.293380000	-1.409216000
H	-3.705944000	4.575349000	-1.237782000

C	-0.287978000	1.010384000	-3.694659000
C	-1.277857000	1.734655000	-4.624766000
H	-2.307416000	1.423242000	-4.418959000
H	-1.043675000	1.481602000	-5.664676000
H	-1.218056000	2.822392000	-4.522942000
C	1.147318000	1.506333000	-3.965490000
H	1.210948000	2.598209000	-3.958454000
H	1.475165000	1.165819000	-4.954477000
H	1.842464000	1.106107000	-3.222172000
C	-0.364700000	-0.498080000	-3.979869000
H	0.308189000	-1.061744000	-3.329108000
H	-0.082428000	-0.696335000	-5.020204000
H	-1.386965000	-0.859709000	-3.828245000

Table S2. Comparison of calculated and crystallographically determined bond lengths and angles in **1**.

	Bond lengths (exp.)	Bond lengths (calc'd.)	Natural charges	MBO
Ce(1)			1.89	
O(1)	2.2208(15)	2.2246	-0.63	0.74
O(2)	2.2100(15)	2.2177	-0.63	0.71
O(3)	2.1813(15)	2.1807	-0.66	0.78
O(4)	2.0940(15)	2.1462	-0.67	0.92
N(1)	2.5510(18)	2.7028	-0.23	0.28
N(2)	2.5976(18)	2.7064	-0.24	0.29
N(3)	2.5931(18)	2.8676	-0.22	0.26
N(4)	–	3.3863	-0.18	0.12
O(2)–Ce(1)–O(1)	172.37(6)˚	172.14˚		
O(4)–Ce(1)–O(3)	134.80(6)˚	131.76˚		

Table S3. Geometry optimized coordinates of [Ce(arene-diNOx)$_2$]$^+$ (**1**$^+$).

Ce	0.218895017	-1.017257079	0.078218006
O	-0.870322068	-0.171728013	1.751070134
O	1.430573108	-1.977128151	-1.447299109
O	-0.955198072	-2.806713212	0.261259020
O	-0.073708006	0.967324073	-1.286794099
N	0.286955022	0.141261011	2.509412189
N	2.667686204	-1.735370133	-0.800546063
N	-2.123336163	-2.286787172	-0.357708028
N	-0.528064041	1.920446145	-2.028897154
C	2.888311222	1.601517124	2.161531166
C	2.999040228	1.123210086	0.850415065
H	2.161655163	1.255924094	0.170770013
C	4.190046318	0.577663046	0.356520027
C	5.311432430	0.546269039	1.198362093
H	6.249113454	0.139747011	0.830712066
C	5.223140397	1.034404079	2.503619191
H	6.096822486	1.007791077	3.148739238
C	4.022829308	1.560480121	2.985640227
H	3.963976304	1.940210148	4.001531304
C	1.619706126	2.253604171	2.596579197
C	0.374686029	1.592340121	2.661968201
C	-0.791111060	2.331144180	2.912627224
H	-1.745347135	1.819191137	2.908190221
C	-0.732522058	3.699634282	3.164727244
H	-1.647769126	4.250601325	3.360566256
C	0.502506038	4.350669330	3.173837242
H	0.563832040	5.415104392	3.380731259
C	1.658119129	3.630235278	2.882570221
H	2.616371199	4.140016318	2.839091219
C	0.234531018	-0.624938048	3.845964295
C	1.424414109	-0.200536015	4.718160360
H	1.358916105	0.845449065	5.029741384
H	2.375261179	-0.354423027	4.200878322
H	1.427036108	-0.817555063	5.622810431
C	-1.085251085	-0.362235028	4.592369350
H	-1.946990147	-0.613767047	3.968658306
H	-1.171857091	0.678482054	4.915866378
H	-1.116658083	-0.990245073	5.489055431
C	0.359398028	-2.123991163	3.545690270
H	0.288435022	-2.687773207	4.481438341
H	1.333284103	-2.352049179	3.099750236
H	-0.435678033	-2.478244189	2.883922221
C	4.265077328	0.167515013	-1.075276084
C	3.478830264	-0.858461068	-1.641938127
C	3.493136264	-1.056764082	-3.030772231
H	2.845422216	-1.812772138	-3.456770262
C	4.320819330	-0.298009023	-3.855143293
H	4.319463329	-0.472940036	-4.927197375
C	5.153262393	0.674131053	-3.296707252
H	5.810829436	1.265851099	-3.926833300
C	5.112754388	0.903027069	-1.923465149
H	5.722069425	1.689818127	-1.488032115

C	3.330970256	-3.082151235	-0.467504036
C	3.522506268	-3.946063300	-1.726438134
H	4.247831325	-3.508426269	-2.417662184
H	2.574285198	-4.089935312	-2.251928171
H	3.900525295	-4.929868376	-1.428895108
C	4.686033358	-2.820524215	0.203807016
H	4.576586348	-2.194399170	1.093365082
H	5.398411390	-2.343984179	-0.475315036
H	5.113288391	-3.780371288	0.512335039
C	2.424779184	-3.823875294	0.522430040
H	2.876399220	-4.788120365	0.776690059
H	1.433925112	-4.023219306	0.105018008
H	2.319665177	-3.258890250	1.453912110
C	-4.179527322	0.024103002	-0.394312030
C	-3.212537244	1.037305081	-0.361237028
H	-2.395777185	0.967392072	0.348268027
C	-3.326459253	2.184692164	-1.161033088
C	-4.436431340	2.321968178	-2.007004155
H	-4.542386347	3.211958245	-2.621074198
C	-5.406007412	1.318646103	-2.050583155
H	-6.266095493	1.426635108	-2.705339208
C	-5.285119404	0.185051014	-1.246225095
H	-6.055336472	-0.580243044	-1.273582098
C	-4.139706316	-1.109396083	0.586683046
C	-3.175535245	-2.142678163	0.649101048
C	-3.227853248	-3.071779234	1.700163129
H	-2.462554189	-3.835758292	1.749962132
C	-4.227861324	-3.021601229	2.667489202
H	-4.240807323	-3.756315287	3.467595265
C	-5.210825400	-2.034474153	2.592097198
H	-6.003262467	-1.981869151	3.333026253
C	-5.155165394	-1.098515082	1.563202119
H	-5.899112447	-0.308426023	1.517411115
C	-2.484936191	-3.214424243	-1.531674114
C	-2.694049206	-4.659704356	-1.045158082
H	-1.808761138	-5.028418383	-0.520311040
H	-2.872188218	-5.305352395	-1.911732146
H	-3.559378270	-4.746039365	-0.381660029
C	-3.759768285	-2.709316208	-2.217923167
H	-4.632418352	-2.765053210	-1.561913117
H	-3.958617300	-3.344570254	-3.087489237
H	-3.648560279	-1.680004127	-2.567802194
C	-1.334393100	-3.177311243	-2.544836193
H	-1.176516089	-2.162341167	-2.921919222
H	-1.590792119	-3.811803290	-3.399933260
H	-0.399312031	-3.543702272	-2.118524164
C	-2.326124177	3.282844252	-1.021491079
C	-0.971178076	3.130588236	-1.368789103
C	-0.037144003	4.146661319	-1.144566087
H	1.004389076	3.988532303	-1.401619106
C	-0.454138035	5.359875432	-0.598379044
H	0.270457021	6.149122450	-0.424393033
C	-1.801543139	5.551321442	-0.287321022
H	-2.136560165	6.497277475	0.127495010
C	-2.719839210	4.521500345	-0.491036037
H	-3.761957285	4.661957354	-0.220133017

C	-0.284759022	1.836524142	-3.520058268
C	-1.214510095	2.824454213	-4.237423324
H	-2.266923171	2.597440200	-4.043161308
H	-1.040682079	2.734476210	-5.313931417
H	-1.016368077	3.860854295	-3.952160300
C	1.194742092	2.182507165	-3.783913289
H	1.413512110	3.226302245	-3.540553271
H	1.407182108	2.033969154	-4.847536371
H	1.857484144	1.531379119	-3.207677243
C	-0.586024046	0.399249031	-3.966139300
H	0.100911008	-0.314689024	-3.507271266
H	-0.468363036	0.338366026	-5.052173388
H	-1.614194126	0.119407009	-3.716603281

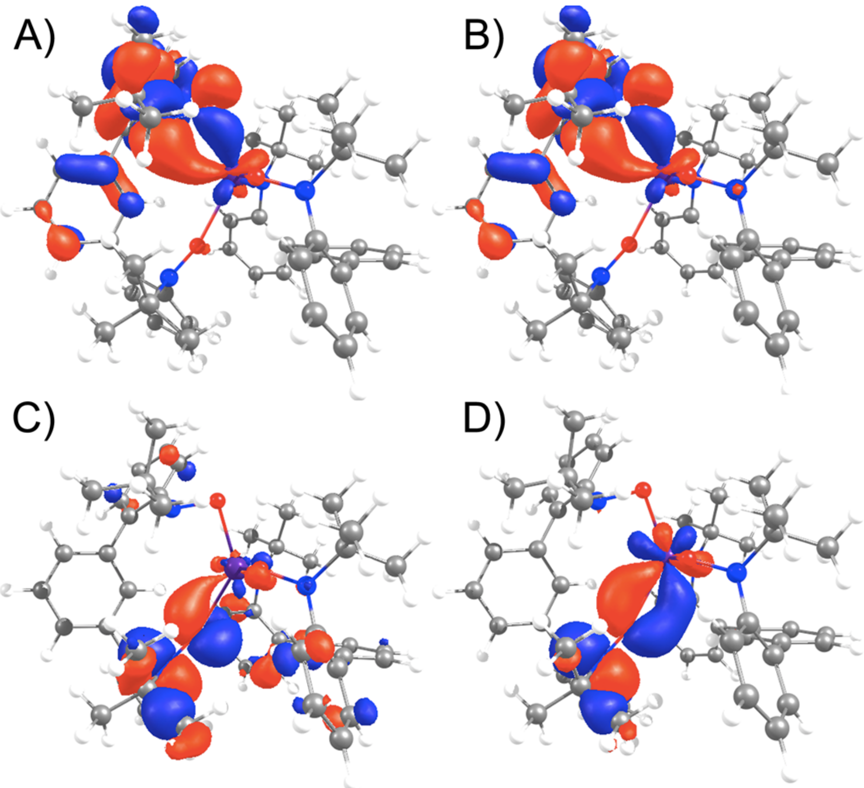

Figure S16. α-HOMO (A), β-HOMO (B), α-HOMO–7 (C) and β-LUMO (D) of calculated beta molecular orbitals of [Ce(arene-diNOx)$_2$]$^+$ (**1**$^+$). The α and β HOMOs were degenerate, localized on a fully reduced nitroxide group. The singly occupied molecular orbital, SOMO was α-HOMO–7 (C) and the corresponding empty orbital was β-LUMO (D).

Table S4. Comparison of calculated and crystallographically determined bond lengths in **1** and **1**$^+$.

	Bond lengths in **1** (exp., Å)	Bond lengths in **1** (calc'd., Å)	Bond lengths in **1**$^+$ (calc'd., Å)	Spin density
Ce				0.03
O(1)	2.2208(15)	2.2246	2.1718	0.00
O(2)	2.2100(15)	2.2177	2.1679	0.00
O(3)	2.1813(15)	2.1807	2.1481	0.00
O(4)	2.0940(15)	2.1462	2.4264	0.35
avg. N–aO	1.430(2)	1.41713	1.4186	0.00
N(4)–O(4)	–	–	1.2906	0.94 (0.59 on N(4))

Table S5. Spin density of **1**$^+$.

	Spin density
Ce	0.03
O(1)	0.00
O(2)	0.00
O(3)	0.00
O(4)	0.35
N(1)	0.00
N(2)	0.00
N(3)	0.00
N(4)	0.59

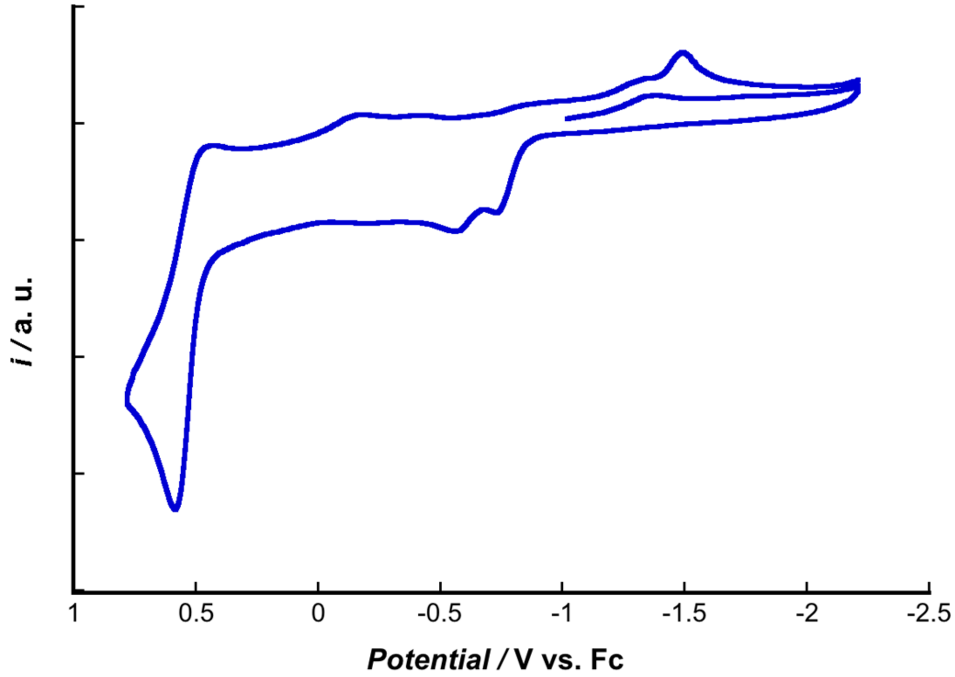

Figure S18. Cylic voltammograms of [K(18-crown-6)(py)$_2$][La[2-(*t*BuNO)py]$_4$] in 0.1 M [Pr$_4$N][BAr^F$_4$] in methylene chloride. Synthesis and characterization of [K(18-crown-6)(py)$_2$][La[2-(*t*BuNO)py]$_4$] was reported in Bogart, J. A. et al., *Inorg. Chem.*, **2015**, 54, 2830-2837 (in the Supporting information).

Table S6. Summary of structural determination of compound H$_2$arene-diNOx and **1**.

	H$_2$arene-diNOx	**1**
Empirical formula	$C_{30}H_{40}N_2O_3$	$C_{60}H_{76}N_4O_6Ce$
Formula weight	476.64	1089.37
Temperature	100(1) K	100(1) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
Cell constants:		
a	10.0002(4) Å	15.1376(7) Å
b	9.8745(4) Å	13.3253(7) Å
c	27.4051(10) Å	26.6562(12) Å
α	–	–
β	96.384(2)°	99.733(2)°
γ	–	–
Volume	2689.39(18) Å^3	5299.5(4) Å^3
Z	4	4
Density (calculated)	1.177 Mg/m^3	1.365 Mg/m^3
Absorption coefficient	0.075 mm^{-1}	0.914 mm^{-1}
F(000)	1032	2280
Crystal size	0.30 × 0.12 × 0.08 mm^3	0.15 × 0.15 × 0.10 mm^3
Theta range for data collection	12.05 to 25.40°	1.36 to 27.63°
Index ranges	$-12 \leq h \leq 12$, $-11 \leq k \leq 11$, $-33 \leq l \leq 33$	$-18 \leq h \leq 19$, $-17 \leq k \leq 17$, $-34 \leq l \leq 34$
Reflections collected	55475	70825
Independent reflections	4833 [R(int) = 0.0386]	12139 [R(int) = 0.0355]
Completeness to theta = 27.59°	97.9 %	98.5 %
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.7452 and 0.6944	0.7456 and 0.6858
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	4833 / 0 / 325	12139 / 0 / 653
Goodness-of-fit on F^2	1.159	1.083
Final R indices [I>2sigma(I)]	R1 = 0.0479, wR2 = 0.1068	R1 = 0.0307, wR2 = 0.0688
R indices (all data)	R1 = 0.0568, wR2 = 0.1104	R1 = 0.0386, wR2 = 0.0717
Largest diff. peak and hole	0.211 and -0.221 e.Å^{-3}	1.392 and -1.033 e.Å^{-3}

Reference:

1 U. J. Williams, D. Schneider, W. L. Dorfner, C. Maichle-Mossmer, P. J. Carroll, R. Anwander and E. J. Schelter, *Dalton Trans.*, 2014, **43**, 16197.

2 D. C. Bradley, J. S. Ghotra and F. A. Hart, *J. Chem. Soc., Dalton Trans.*, 1973, 1021.

3 R. K. Thomson, B. L. Scott, D. E. Morris and J. L. Kiplinger, *C. R. Chim.*, 2010, **13**, 790.

4(a) J. C. Stowell, *J. Org. Chem.*, 1971, **36**, 3055; (b) J. A. Bogart, H. B. Lee, M. A. Boreen, M. Jun and E. J. Schelter, *J. Org. Chem.*, 2013, **78**, 6344.

5(a) S. T. Chao, N. C. Lara, S. Lin, M. W. Day and T. Agapie, *Angew. Chem. Int. Ed.*, 2011, **50**, 7529; (b) D. E. Herbert, N. C. Lara and T. Agapie, *Chem. Eur. J.*, 2013, **19**, 16453.

6 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, N. J. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian, Inc., Wallingford, CT, USA, 2009.

7 M. Dolg, H. Stoll and H. Preuss, *J. Chem. Phys.*, 1989, **90**, 1730.

8 G. A. Zhurko and D. A. Zhurko, http://chemcraftprog.com/.

9 Bruker, *SAINT*, Bruker AXS inc., Madison, Wisconsin, USA, 2009.

10 *SHELXTL*, Bruker AXS Inc., Madison, Wisconsin, USA 2009.

11 G. M. Sheldrick, *SADABS*, University of Gottingen, Germany, 2007.

12 G. M. Sheldrick, *Acta Cryst.*, 2008, **A64**, 112.