Supplementary information

Assembly of a Trapped Valent Ce[III/IV] -TCNQ Complex through Metal-Ligand Redox Cooperativity

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General Methods: All synthetic work and subsequent manipulations were performed under anaerobic, anhydrous, and strictly inert atmosphere (N_2) using standard Schlenk techniques or in a glovebox equipped with a molecular sieves 13X/Q5 Cu-0226S catalyst purifier system. All glassware were oven-dried at 150 °C overnight prior to use. Elemental analyses were performed on a Costech ECS 4010 analyzer at the University of Pennsylvania.

Materials: Toluene and Dichloromethane (DCM or CH_2Cl_2) were purchased from Fisher Scientific. The solvents were sparged for 30 minutes with dry Argon and dried using a commercial two-column solvent purification system comprising columns packed with Q5 reactant and neutral alumina respectively. The collected solvents were stored over 3 Å sieves for at least 24 h prior to use. Tetracyanoquinodimethane (TCNQ) was received from Sigma Aldrich and purified by sublimation as shiny orange crystals. $Cp_3Ce(THF)$ was prepared as previously described.[1]

Synthetic Details for 1.

In a 20 ml vial, TCNQ (10.0 mg, 0.049 mmol, 1 equiv) was dissolved in 2 ml CH_2Cl_2 and 14 ml of a toluene/CH_2Cl_2 mixture (2/1 v:v) was carefully layered on top of the CH_2Cl_2 solution without disturbing it. In a second vial $Cp_3Ce(THF)$ (79.8 mg, 0.196 mmol, 4 equiv) was suspended in 4 ml of a toluene/CH_2Cl_2 mixture (2/1 v:v) that was stirred for 10 min and filtered using a Kimwipe plug in glass pipette. This filtered solution was carefully layered on top of the TCNQ solution and set undisturbed in a glove box freezer at -20 °C for 10 d. Brown-black crystals appeared in the bottom and on the walls of the vial and were collected by filtration over a fine frit. The crystals were rinsed with 2 ml CH_2Cl_2, followed by multiple washes with 2 ml toluene until the color of the filtrate was colorless. The crystalline solid was dried under reduced pressure and isolated in 71% yield. The product is essentially insoluble in organic solvents including toluene, CH_2Cl_2, and Et_2O and decomposes in CH_3CN and THF. FT-IR (v_{CN}): 2098, 2177 cm^{-1}. Anal. Calc. for $(C_{72}H_{64}Ce_4N_4).(C_7H_8)$: C, 57.93; H, 4.43; N, 3.42 Found: C, 58.35; H, 4.15; N, 3.30

IR Spectroscopy:

FT-IR Spectroscopy data of TCNQ and **1** was collected on a Bruker Invenio-S FT-IR spectrometer. KBr mixture of compounds were finely grounded and pressed with a pellet press to create homogeneous circular pellets then transferred to the spectrometer for measurement.
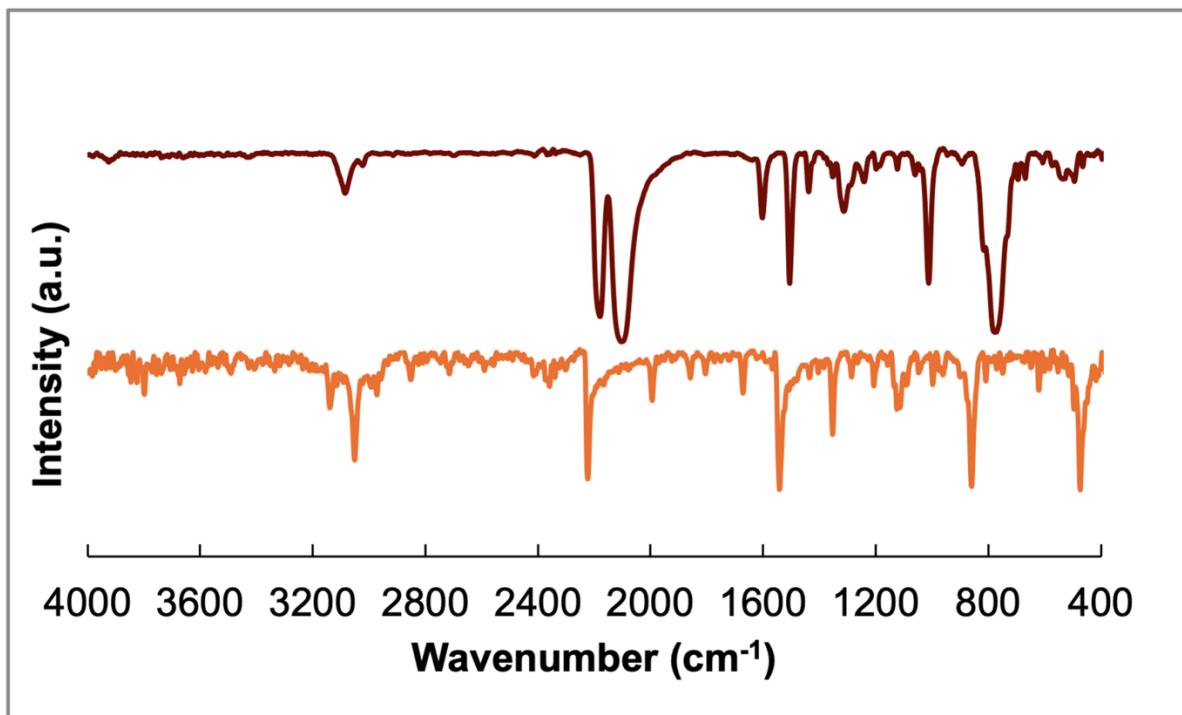

Fig. S1 IR data comparison for **1** (top) and TCNQ (bottom) collected in KBr matrix.

Raman Spectroscopy:

Raman data was collected on JASCO NRS-5500 Raman Spectrometer using a 532 nm laser. Si substrate was used to calibrate the instrument. Single crystals of **1** and TCNQ were sealed in a 1 mm cuvettes in a N_2 filled glove box. Then cuvettes were taken out of the glove box and placed on the instrument stage. The measurements were performed at the confocal mode with a 20x objective lens, 60 sec exposure time and single accumulation on each compound. Other typical parameters used are: L1200/500 nm grating, 200×1000 μm slit, d-4000 μm aperture. Laser power was kept at 0.3 mW at 5% or below to avoid any sample decomposition during measurement. These data were collected on multiple crystals to eliminate any artifact possibility.
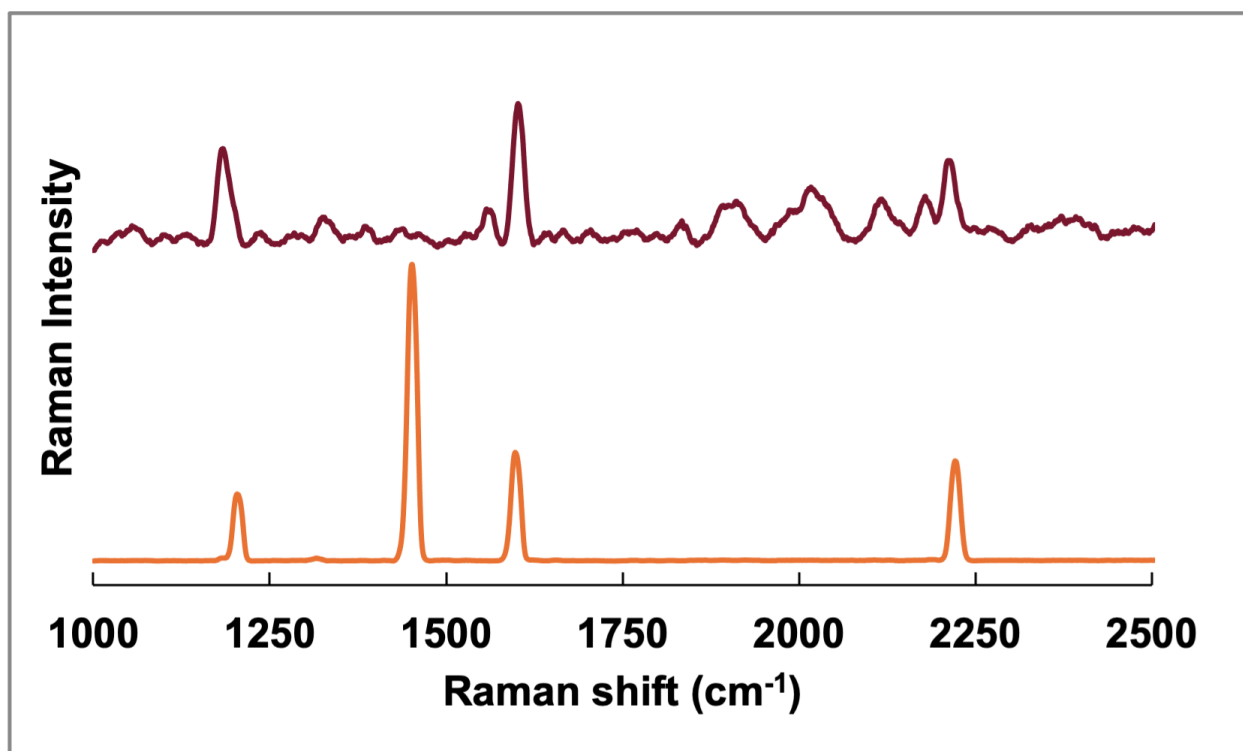

Fig. S2 Raman data comparison for **1** (top) and TCNQ (bottom) collected on single crystals.

Magnetic Measurements:

Magnetic susceptibility and magnetization data were collected using a Quantum Design MPMS-7 SQUID magnetometer. Samples were prepared in a N_2 filled glovebox (Vacuum Atmospheres, Inc. Nexus II) under inert conditions. Polycrystalline samples of $Cp_3Ce(THF)$ and **1** were loaded into polyethylene bags using disposable spatulas to avoid impurities. Furthermore, ceramic forceps were used to handle the polybag to avoid direct touch of the glove with the loaded bag and these bags were subsequently sealed using a Ziploc v159 Vacuum Sealer System. The bags were then folded, inserted, and immobilized in a plastic drinking straw at specific length using disposable Q-tips and removed from the glovebox to mount in the SQUID magnetometer. Saturation magnetization measurements were performed at 2 K varying the applied field from 0 to 7 T. Magnetic susceptibility data were collected at temperatures ranging from 2 to 300 K at an applied field of 2 T. Data were corrected for the diamagnetic contributions of the sample holder and bag by subtracting empty containers; corrections for the sample were calculated from Pascal's constants.[2]
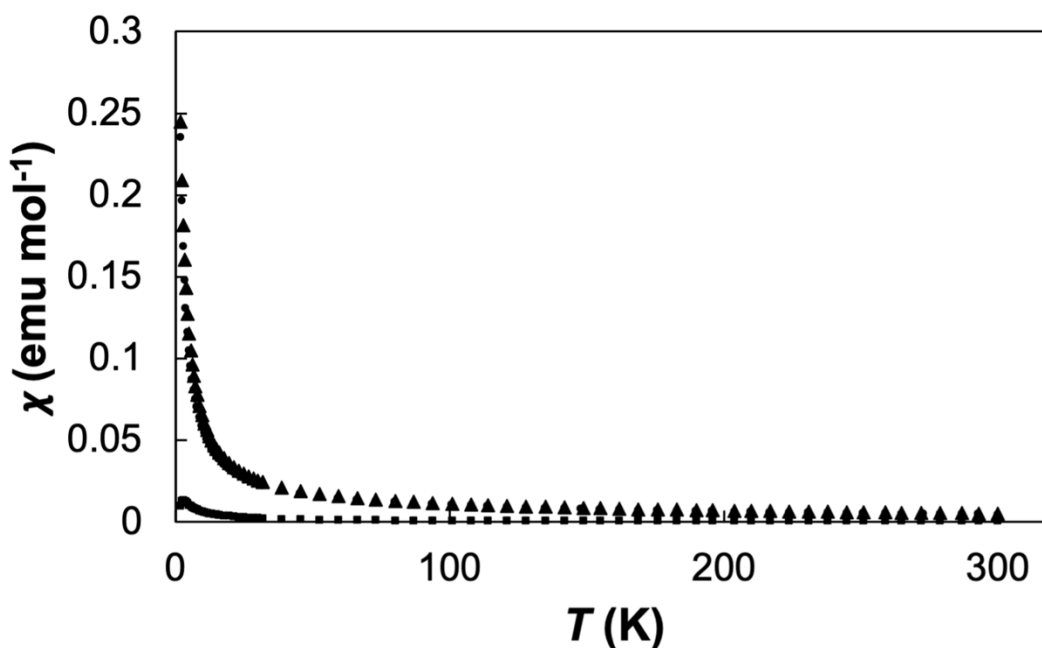

Fig. S3 Variable temperature susceptibility measurements plots of **1** (triangle markers) and $2 \times \chi$ for $Cp_3Ce(THF)$ (circle markers) plotted along with the difference between **1** and $2 \times \chi$ for $Cp_3Ce(THF)$ (square markers).
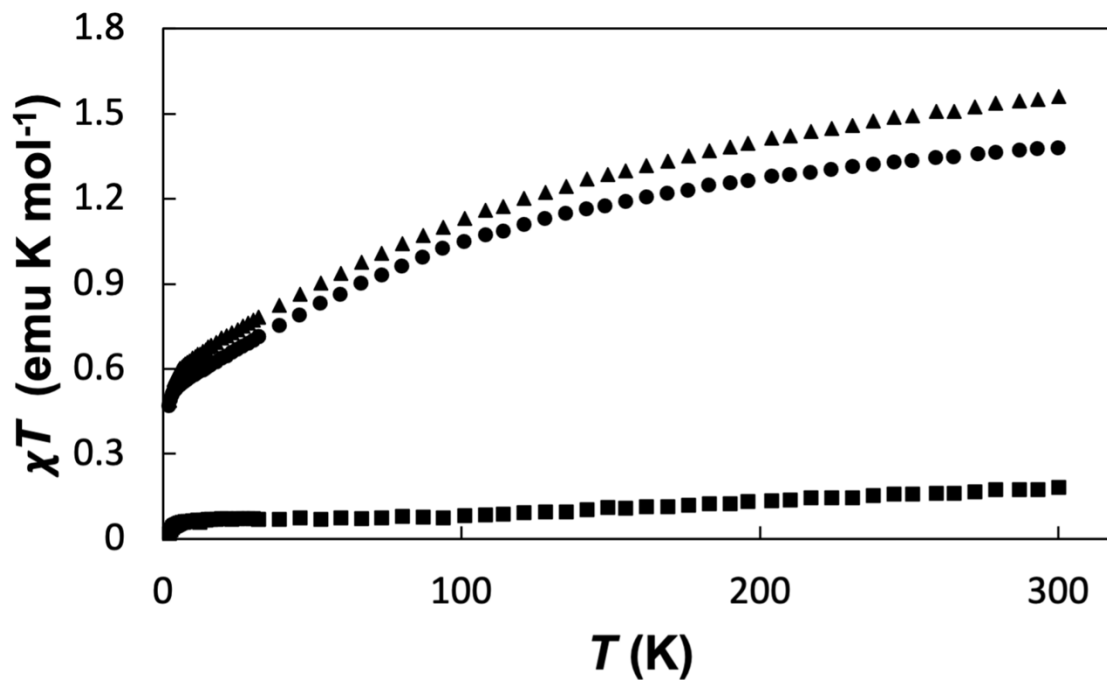
Fig. S4 Variable temperature susceptibility measurements plots of **1** (triangle markers) and 2 × χT for Cp$_3$Ce(THF) (circle markers) plotted along with the difference between **1** and 2 × χT for Cp$_3$Ce(THF) (square markers).

Photophysical Studies:

10 mm path length quartz cells fused with a J-Young valve were used luminescence studies of air and moisture sensitive compounds. Emission and excitation spectra were collected on Fluorolog®-3 spectrofluorometer (HORIBA Jobin Yvon, Inc.) using an R928 PMT detector.
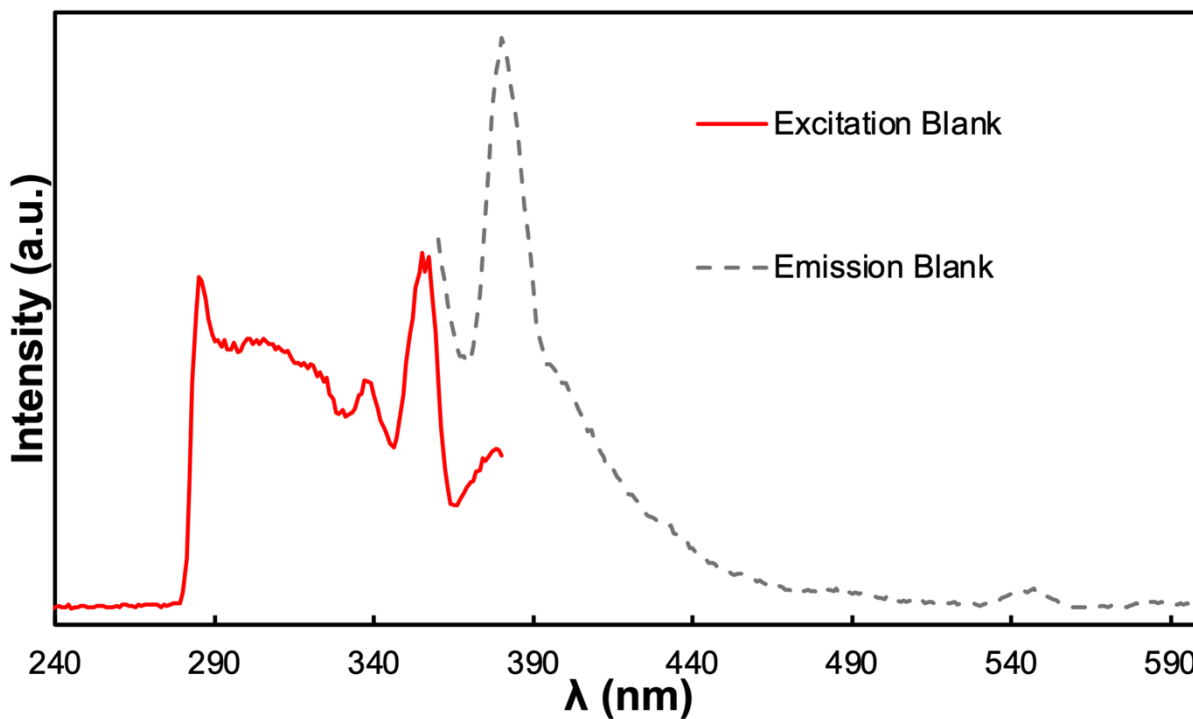
Fig. S5. Photoluminescence spectrum of blank toluene. The emission spectrum at 340 nm excitation is shown as grey dashed traces. The excitation spectrum at 420 nm emission is shown as a red trace.
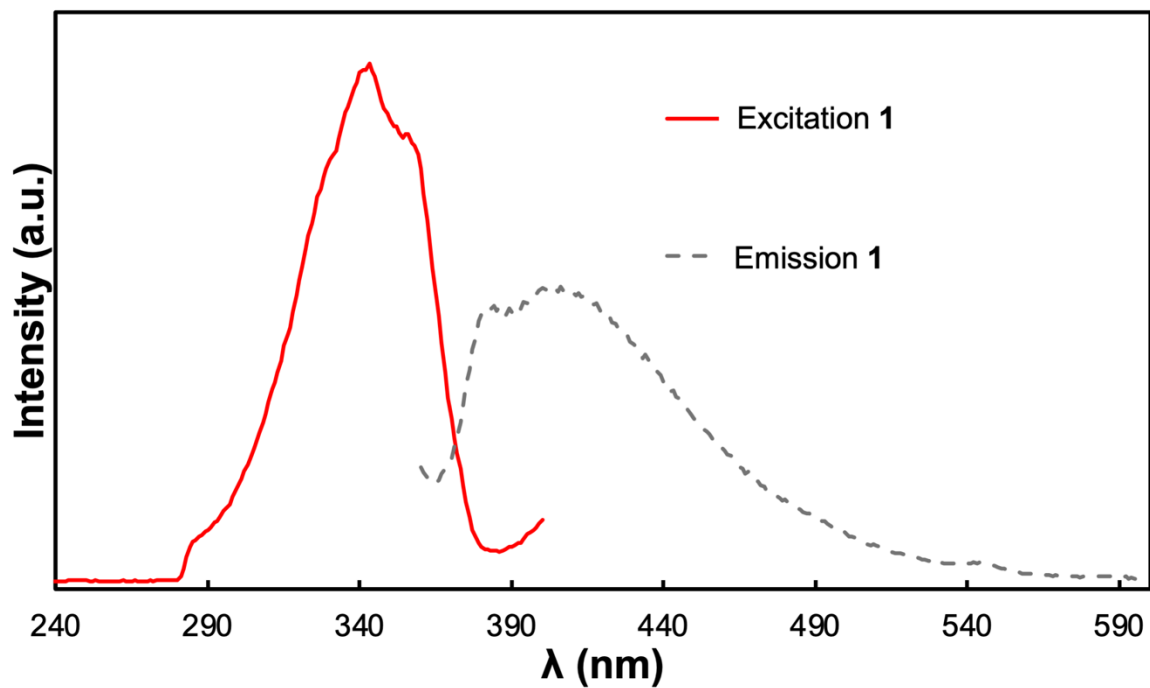
Fig. S6. Photoluminescence spectra of **1** as a suspension in toluene. The emission spectra at 340 nm excitation are shown as grey dashed traces. The excitation spectra at 420 nm emission are shown as a red trace.

Fig. S7. Photoluminescence spectra of Cp$_3$Ce(THF) as a a 0.005 mM solution. The emission spectra at 340 nm excitation are shown as grey dashed traces. The excitation spectra at 420 nm emission are shown as a red trace.
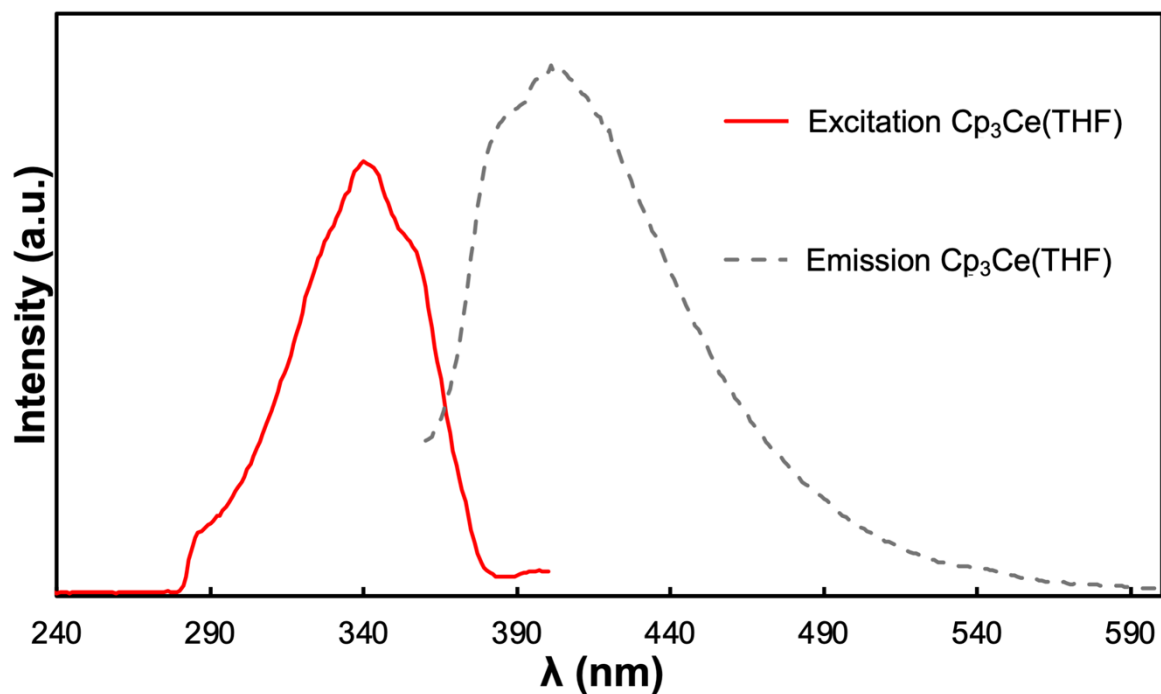
Single Crystal X-ray Diffraction:

X-ray intensity data were collected on a Rigaku XtaLAB Synergy-S diffractometer[3] equipped with an HPC area detector (HyPix-6000HE) and employing confocal multilayer optic-monochromated Cu-Kα radiation (λ=1.54184 Å) at a temperature of 100K. Preliminary indexing was performed from a series of sixty 0.5° rotation frames with exposures of 0.25 seconds for θ = ±47.434° and 1 second for θ = 113.25°. A total of 4796 frames (44 runs) were collected employing ω scans with a crystal to detector distance of 34.0 mm, rotation widths of 0.5° and exposures of 0.31 seconds for θ = ±47.542° and 1.23 seconds for θ = -90° and 113.25°.

Rotation frames were integrated using CrysAlisPro[3], producing a listing of unaveraged F^2 and $\sigma(F^2)$ values. A total of 61439 reflections were measured over the ranges 5.996 ≤ 2θ ≤ 149.006°, -10 ≤ h ≤ 9, -21 ≤ k ≤ 21, -33 ≤ l ≤ 33 yielding 7821 unique reflections (Rint = 0.0615). The intensity data were corrected for Lorentz and polarization effects and for absorption using SCALE3 ABSPACK (minimum and maximum transmission 0.27259, 1.00000).[4] The structure was solved by dual space methods – SHELXT.[5] Refinement was by full-matrix least squares based on F^2 using SHELXL.[6] All but 6 reflections were used during refinement due to being labeled outliers. The weighting scheme used was $w=1/[\sigma^2(F_o^2) + (0.0466P)^2 + 4.6224P]$ where $P = (F_o^2 + 2F_c^2)/3$. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined using a riding model. Refinement converged to R1=0.0280 and wR2=0.0739 for 7312 observed reflections for which F > 4σ(F) and R1=0.0304 and wR2=0.0769 and GOF =1.036 for all 7821 unique, non-zero reflections and 474 variables. The maximum Δ/σ in the final cycle of least squares was 0.003 and the two most prominent peaks in the final difference Fourier were +1.26 and -0.77 e/Å[3]. This report has been created with Olex2.[7] Table 1 lists cell information, data collection parameters, and refinement data. The asymmetric unit has half a molecule of the Ce-complex lying about an inversion centre and 1.5 toluene molecules (one in a general position and the other lying about an inversion centre).

Table 1. Summary of Structure Determination of Compound 1

|	
Empirical formula	$C_{93}H_{88}Ce_4N_4$
Formula weight	1822.15
Diffractometer	Rigaku XtaLAB Synergy-S (HyPix-6000HE)
Temperature/K	100
Crystal system	Monoclinic
Space group	$P2_1/c$
a	8.09830(10)Å
b	17.55890(10)Å
c	27.1102(2)Å
α	90°
β	90.1720(10)°
γ	90°
Volume	3854.98(6)Å^3
Z	2
d_{calc}	1.570 g/cm^3
M	18.257 mm^{-1}
F(000)	1812.0
Crystal size, mm	0.22 × 0.11 × 0.01
2θ range for data collection	5.996 - 149.006°
Index ranges	-10 ≤ h ≤ 9, -21 ≤ k ≤ 21, -33 ≤ l ≤ 33
Reflections collected	61439
Independent reflections	7821[R(int) = 0.0615]
Data/restraints/parameters	7821/42/474
Goodness-of-fit on F^2	1.036
Final R indexes [I>=2σ (I)]	$R_1 = 0.0280$, $wR_2 = 0.0739$
Final R indexes [all data]	$R_1 = 0.0304$, $wR_2 = 0.0769$
Largest diff. peak/hole	1.26/-0.77 eÅ^{-3}

Crystallographic Analysis:
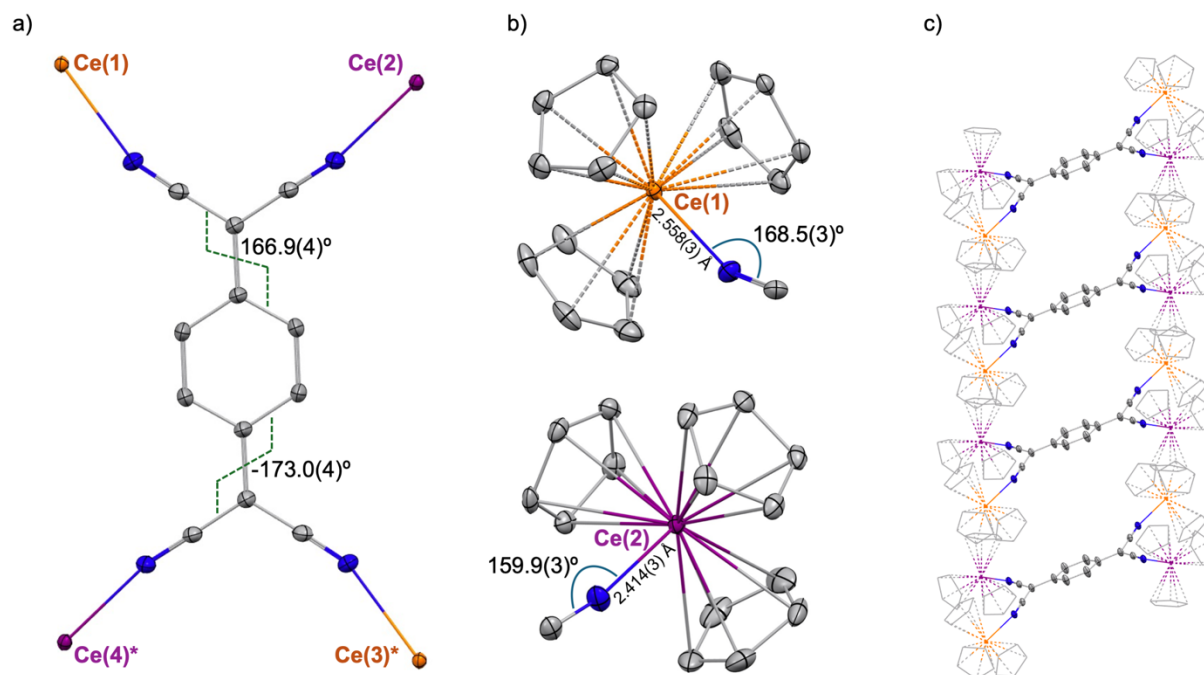
Fig. S8 Fractions of complex **1** presented with focus on a) torsional angles b) key bond length and angles c) insignificant TCNQ intermolecular interactions.
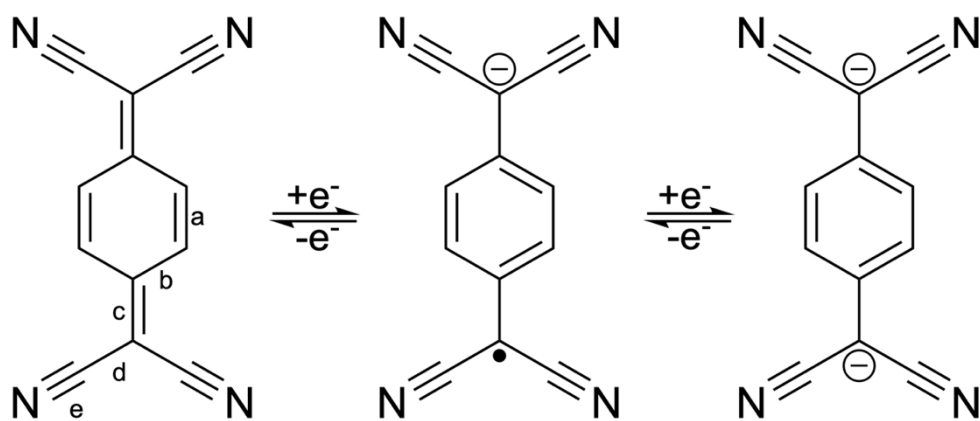

Fig. S9 TCNQ Structures in three redox states (neutral, radical anion and dianion).

Kistemacher equation:

The empirical Kistenmacher equation[8] is used to estimate the extent of charge transfer (q) on TCNQ molecules that is calculated from the following equation:

$$q = -A[c/(b+d)] + B$$

Where A = -41.667 and B = 19.818. The b, c, d values bond lengths in TCNQ assigned in following figure.

	a	B	c	d	q
$(CeCp_3)_4$TCNQ	1.375(5)	1.394(5), 1.399(5)	1.468(5)	1.375(5), 1.394(5)	−2.2
TCNQ	1.346(3)	1.446(4)	1.374(3)	1.441(4)	0.0

References:

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