

**Redox Chemistry of an Anionic Dithiolene Radical**

Journal:	<i>Dalton Transactions</i>
Manuscript ID	Draft
Article Type:	Communication
Date Submitted by the Author:	n/a
Complete List of Authors:	Wang, Yuzhong; University of Georgia, Department of Chemistry Xie, Yaoming; University of Georgia, Center for Computational Quantum Chemistry Wei, Pingrong; University of Georgia, Department of Chemistry Schaefer, Henry; University of Georgia, Computational Chemistry Robinson, Gregory ; University of Georgia,



The University of Georgia

Gregory H. Robinson
*Foundation Distinguished
Professor of Chemistry*

Department of Chemistry

413-Chemistry Annex
Athens, Georgia 30602-2556
Voice: 706.542.1853/2040
Fax: 706.542.9454/1972
email: robinson@uga.edu

18 December 2018

Professor Marta E. G. Mosquera, Guest Editor

Professor Zachariah M. Heiden, Guest Editor

Professor Harkesh B. Singh, Guest Editor

Dr. Andrew Shore, Editor

Dalton Transactions

Themed Issue: *Inorganic Chemistry of the p-Block Elements*

Royal Society of Chemistry

Thomas Graham House,

Milton Road, Science Park, Cambridge, CB4 0WF, United Kingdom

Dear Editors:

On behalf of my co-authors, I hereby submit the associated manuscript entitled:

Redox Chemistry of an Anionic Dithiolene Radical

for consideration for publication as a *Communication* in the themed *Dalton Transactions* issue:

Inorganic Chemistry of the p-Block Elements

Largely due to unusual optical, conductive, magnetic, and catalytic properties, transition metal dithiolenes may be traced the 1960s. This is largely due to the unique non-innocence character of dithiolene ligands. While the radical character of transition metal dithiolene complexes has been extensively explored, highly reactive transition metal-free anionic dithiolene radicals have only been studied by theoretical methods or EPR. This laboratory recently synthesized the first structurally characterized anionic dithiolene radical (**1**[•]) (*J. Am. Chem. Soc.*, 2017, **139**, 6859-6862). Notably, boron dithiolene radicals were recently obtained via **1**[•] (*Angew. Chem. Int. Ed.*, 2018, **57**, 7865-7868). The considerable stability of **1**[•] may prove advantageous for probing the redox chemistry of dithiolene radical anions. In the submitted work, we explore the exciting redox chemistry of the anionic dithiolene radical (**1**[•]). While one-electron reduction of **1**[•] by Cp₂Co or KC₈ affords the corresponding dithiolate dimers **2** and **3**, respectively, one-electron oxidation of **1**[•] by Ph₃C⁺BF₄⁻ (or O₂) conveniently gives **4**, the neutral dithiolene dimer.

We feel that the submitted contribution will nicely complement the exciting themed *Dalton Transactions* issue, *Inorganic Chemistry of the p-Block Elements*.

Thank you for your time and consideration.

Sincerely,

Gregory H. Robinson



Journal Name

COMMUNICATION

Redox Chemistry of an Anionic Dithiolene Radical

Yuzhong Wang, Yaoming Xie, Pingrong Wei, Henry F. Schaefer III, and Gregory H. Robinson*

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

The redox chemistry of the first stable anionic dithiolene radical **1**[•] was investigated by both reactivity and cyclic voltammetry studies. While one-electron reduction of **1**[•] by Cp₂Co or KC₈ affords the corresponding dithiolate dimers **2** and **3**, respectively, one-electron oxidation of **1**[•] by Ph₃C⁺BF₄[−] (or O₂) conveniently gives **4**, the neutral dithiolene dimer.

Largely due to unusual optical, conductive, magnetic, and bio-inspired properties, studies of transition metal dithiolene complexes may be traced to the 1960s.^{1–13} While molybdenum- and tungsten-dithiolene complexes have shown enzymatic activity,^{2,5,12} other transition metal bis-dithiolenes have demonstrated remarkable potential as optoelectronic materials.^{4,7,10,11} The non-innocent nature of dithiolene ligands (Fig. 1) plays a pivotal role in the intriguing redox chemistry of transition metal dithiolenes.³

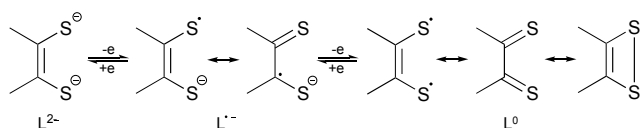
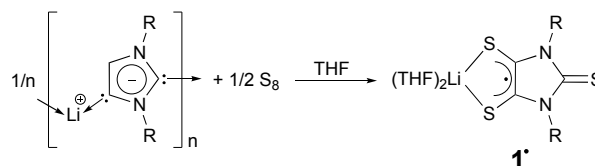


Fig. 1 Redox non-innocence of a dithiolene ligand.¹⁴

While the radical character of dithiolene ligands (L^{•−}) in transition metal complexes was well documented,^{8,15–27} highly reactive transition metal-free anionic dithiolene radicals have only been investigated using theoretical methods and electron paramagnetic resonance.^{28–31} Notably, the electronic absorption spectrum of the prototype anionic dithiolene radical (C₂H₂S₂^{•−}) was studied in a low-temperature matrix.³² Recently, the first structurally characterized anionic dithiolene radical **1**[•] was synthesized by this laboratory *via* trisulfurization of the corresponding anionic N-heterocyclic dicarbene³³ (Scheme 1).³⁴ It was anticipated that this discovery could

provide a unique platform for accessing the largely unexplored chemistry of main group dithiolene radicals (*e.g.*, boron dithiolene radicals were achieved *via* **1**[•]).³⁵ Moreover, the considerable stability of **1**[•] would be advantageous for probing the redox chemistry of dithiolene radical anions (L^{•−} in Fig. 1). To this end, we report the syntheses,³⁶ molecular structures³⁶ and computations³⁶ of compounds **2**, **3**, and **4**, all obtained *via* one-electron redox reactions of **1**[•].



Scheme 1. Previously reported synthesis of **1**[•] (R = 2,6-diisopropylphenyl).³⁴

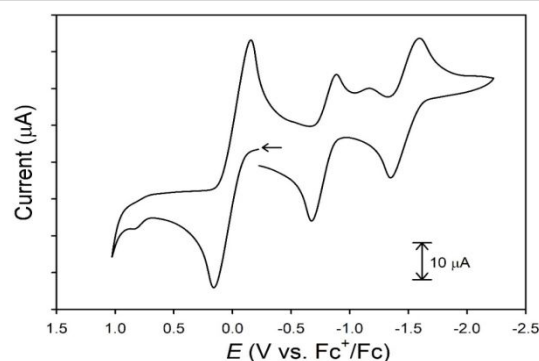


Fig. 2 Cyclic voltammogram of **1**[•] (6.45 mM) with Fc internal standard (4.5 mM; E_{1/2} set to 0 V) in THF (scan speed: 100 mV/s, 0.1 M ⁿBu₄NPF₆ supporting electrolyte, glassy carbon working electrode, Pt-wire counter electrode, RT). Arrow indicates direction of the scan.

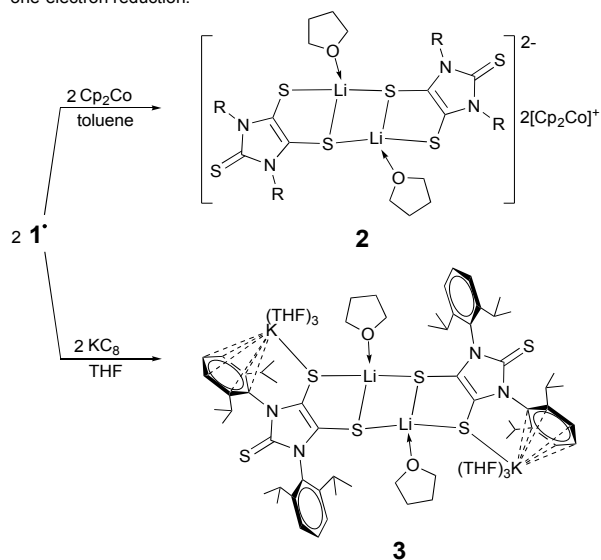
The cyclic voltammogram of **1**[•] was recorded (Fig. 2), potentials are reported in THF versus an internal ferrocene/ferrocenium (Fc/Fc⁺) standard. Radical **1**[•] exhibits two electrochemically quasi-reversible, diffusion-controlled couples at E_{1/2} = −0.78 V (ΔE_p = 0.22 V) and E_{1/2} = −1.47 V (ΔE_p = 0.26 V), which are assigned to [L⁰/L^{•−}] and [L^{•−}/L^{2−}] ligand reduction events, respectively. The 1:1 reaction of **1**[•] with

* Department of Chemistry, The University of Georgia, Athens, Georgia 30602-2556, United States. E-mail: robinson@uga.edu

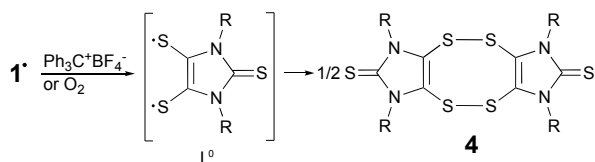
Electronic Supplementary Information (ESI) available: Synthetic and computational details and structural and spectral characterization. Crystallographic details in .cif format. CCDC 1881413–1881415. See DOI: 10.1039/x0xx00000x

cobaltocene (Cp_2Co), a well known one-electron reducing agent,³⁷ quantitatively affords dimeric dithiolate **2** (as a green powder) (Scheme 2). Compound **2** is insoluble in toluene, slightly soluble in THF, and moderately soluble in acetonitrile. Although turquoise-coloured X-ray quality crystals of **2** were obtained from acetonitrile, the significantly broadening of the ^1H NMR spectrum pattern of **2** in CD_3CN and THF-d_8 suggests the partial dissociation of **2**. Consequently, ideal NMR data of **2** could not be obtained in polar solvents. In addition, potassium graphite (KC_8) reduction of **1**[•] in THF quantitatively provided the lithium-potassium mixed alkali metal dithiolate dimer **3** (Scheme 2). However, trace amounts of O_2 results in the oxidation of **3**, yielding unidentified products with the colour change from colourless to purple.

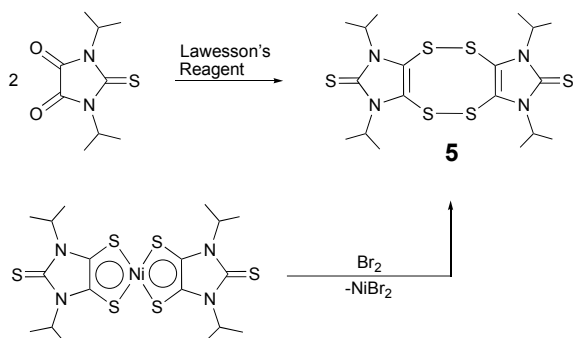
one-electron reduction:



one-electron oxidation:



Scheme 2. Synthesis of compounds **2**, **3**, and **4** ($\text{R} = 2,6\text{-diisopropylphenyl}$).



Scheme 3. Previously reported synthetic routes of **5**.³⁸⁻⁴⁰

Reaction of **1**[•] with $\text{Ph}_3\text{C}^+\text{BF}_4^-$ (in a 1:1 ratio) in toluene leads to one-electron oxidation of **1**[•],³⁷ giving orange-red crystals of **4** (a dimer of the neutral dithiolene ligand; L^0 in Fig. 1) in 55.3% yield (Scheme 2). Alternatively, **4** may also be obtained by dioxygen oxidation of **1**[•]. Notably, compound **5**, the analogue of **4**, has been synthesized as previously reported *via* two unique routes (Scheme 3): (1) sulfurization of imidazole-based dione with Lawesson's reagent;^{38,39} and (2) oxidation of the nickel bis-dithiolene complex by Br_2 .^{38,40} Compounds **4** and **5** may serve as convenient platforms to access metal dithiolene complexes *via* reductive cleavage of the S-S bonds.⁴⁰

X-ray structural analysis³⁶ of **2** (Fig. 4) shows that the $[\text{2}]^{2-}$ moieties contains two lithium dithiolene units dimerized through two Li-S bonds. With THF-coordination, each lithium atom is four-coordinate and adopts a distorted tetrahedral geometry. The central Li_2S_2 ring is planar, in which the bridging Li-S bond [2.396(15) Å] is ca. 0.13 Å shorter than those in the neighbouring LiS_2C_2 ring [2.525(16) Å]. The LiS_2C_2 rings in **2** are somewhat more bent than that in **1**[•] [the bend angle (η) between the LiS_2 plane and the S_2C_2 plane = 17.6° for **2** vs. 14.2° for **1**[•]].³⁴ By comparison with **1**[•] [$d_{\text{C-C}} = 1.417(3)$ Å; $d_{\text{C-S}} = 1.677(3)$ Å, av],³⁴ compound **2** exhibits shorter olefinic C-C bonds [1.362(8) Å] and concomitant longer C-S bonds [1.729(8) Å, av]. These distances compares well to those for the free dithiolate ligand $(\text{NMe}_4)_2(\text{C}_3\text{S}_5)$ ⁴¹ [$d_{\text{C-C}} = 1.371(8)$ Å; $d_{\text{C-S}} = 1.724(6)$ Å] and the theoretical values for the simplified $[\text{2-Me}]^{2-}$ model ($d_{\text{C-C}} = 1.375$ Å; $d_{\text{C-S}} = 1.754$ Å).³⁶ The ligand-based HOMO of dimeric dithiolate $[\text{2-Me}]^{2-}$ (Fig. 3b) mainly involves C-C π -bonding and C-S π -antibonding character, which is relevant to the SOMO of its radical precursor $[\text{1-Me}]^{\bullet}$ (Fig. 3a) and consistent with the C-C and C-S bond distance change of the C_2S_2 units in **2** in comparison with those for **1**[•].³⁴ Similar to that in $[\text{1-Ph}]^{\bullet}$,³⁴ the LiS_2C_2 rings in $[\text{1-Me}]^{\bullet}$ and $[\text{2-Me}]^{2-}$ are nearly planar in the gas phase.

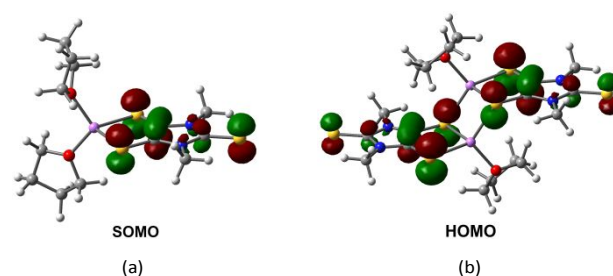


Fig. 3 Selected molecular orbitals of the simplified models $[\text{1-Me}]^{\bullet}$ (a) and $[\text{2-Me}]^{2-}$ (b).

Compound **3** is a Li-K mixed metal dithiolate dimer in the solid state.³⁶ The central $[\text{C}_2\text{S}_2\text{Li}(\text{THF})_2]_2$ core in **3** shows similar geometry and bonding parameters to that in **2** (see the caption of Fig. 4). The potassium cation in **3** is σ -bonded to a sulphur atom and coordinated to three THF molecules. The potassium-phenyl centroid distance (2.990 Å) in **3** compares well with that [3.034(9) Å] in $[\{\text{K}\{2,6\text{-iPr}_2\text{C}_6\text{H}_3\text{N}_2\text{CH}_2\}_2\text{K}(\text{THF})_2\}_n] \cdot n\text{THF}$,⁴² which suggests the presence of cation- π interaction between the potassium cation and the phenyl ring.⁴³ The S-K bond distance for **3** [3.1490(13) Å] is comparable to that in $[\{\text{Ce}(\text{Cp}^*)_2(\text{dddt})\text{K}(\text{thf})_2\}_2]$ (dddt = 5,6-dihydro-1,4-dithiin-2,3-

dithiolate)⁴⁴ [3.26(5) Å] and in the simplified model **3-Ph** (3.210 Å).³⁶ The Wiberg bond indices of the K–S bonds in **3-Ph** are 0.11, suggesting their strong ionic character. In the solid state,³⁶ the central eight-membered C₄S₄ ring of **4** (Fig. 4) adopts a chair conformation as suggested by torsion angles [*i.e.*, C(2)–S(2)–S(3A)–C(3A), 97.81°; C(2)–C(3)–S(3)–S(2A), 75.50°], which are similar to those reported for **5** [C–S–S–C, 101.8(6)°; S–S–C–C, –82(1) and 79(1)°].³⁹ The C–C bonds

1.348(3), C(2)–S(2) 1.739(2), C(3)–S(3) 1.739(2), S(3)–S(2A) 2.0728(9); S(2)–C(2)–C(3) 129.74(17), C(2)–S(2)–S(3A) 104.28(8).

[1.348(3) Å] and C–S bonds [1.739(2) Å] in the C₂S₂ units of **4** are also similar to those in **5** [*d*_{C–C} = 1.36(2) Å; *d*_{C–S} = 1.75(1) Å, *av.*].³⁹ The S–S bond in **4** [2.0728(9) Å] is a typical single bond, involving predominant 3p character (92.50%).³⁶

Conclusions

While reactions of stable lithium dithiolene radical **1**[•] with Cp₂Co or KC₈ give the corresponding one-electron reduction product **2** and **3**, respectively, combination of **1**[•] with Ph₃C⁺BF₄[–] (or O₂), *via* one-electron oxidation, leads to the isolation of **4**. Further application of these neutral (**4**), monanionic (**1**[•]), and dianionic (**3**) dithiolene species in main group chemistry is being investigated in this laboratory.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

We are grateful to the National Science Foundation for support: CHE-1565676 (G.H.R., Y.W.) and CHE-1361178 (H.F.S.). We also want to thank Mr. Phan T. Truong for his assistance with the cyclic voltammetric measurements.

Notes and references

- 1 J. A. McCleverty, *Prog. Inorg. Chem.*, 1968, **10**, 49–221.
- 2 E. I. Stiefel, Ed., *Dithiolene Chemistry: Synthesis, Properties, and Applications*, John Wiley & Sons, Hoboken, NJ, 2004.
- 3 R. Eisenberg and H. B. Gray, *Inorg. Chem.*, 2011, **50**, 9741–9751.
- 4 R. Kato, *Chem. Rev.*, 2004, **104**, 5319–5346.
- 5 F. J. Hine, A. J. Taylor and C. D. Garner, *Coord. Chem. Rev.*, 2010, **254**, 1570–1579.
- 6 S. Rabaca and M. Almeida, *Coord. Chem. Rev.*, 2010, **254**, 1493–1508.
- 7 B. Garreau-de Bonneval, K. I. M. C. Ching, F. Alary, T. T. Bui and L. Valade, *Coord. Chem. Rev.*, 2010, **254**, 1457–1467.
- 8 S. Sproules and K. Wieghardt, *Coord. Chem. Rev.*, 2011, **255**, 837–860.
- 9 S. Sproules, *Prog. Inorg. Chem.*, 2014, **58**, 1–144.
- 10 A. Kobayashi, E. Fujiwara and H. Kobayashi, *Chem. Rev.*, 2004, **104**, 5243–5264.
- 11 D. Espa, L. Pilia, S. Attar, A. Serpe and P. Deplano, *Inorg. Chim. Acta*, 2018, **470**, 295–302.
- 12 S. Leimkuhler, *Biol. Chem.*, 2017, **398**, 1009–1026.
- 13 R. H. Holm, P. Kennepohl and E. I. Solomon, *Chem. Rev.*, 1996, **96**, 2239–2314.
- 14 B. S. Lim, D. V. Fomitchev and R. H. Holm, *Inorg. Chem.*, 2001, **40**, 4257–4262.

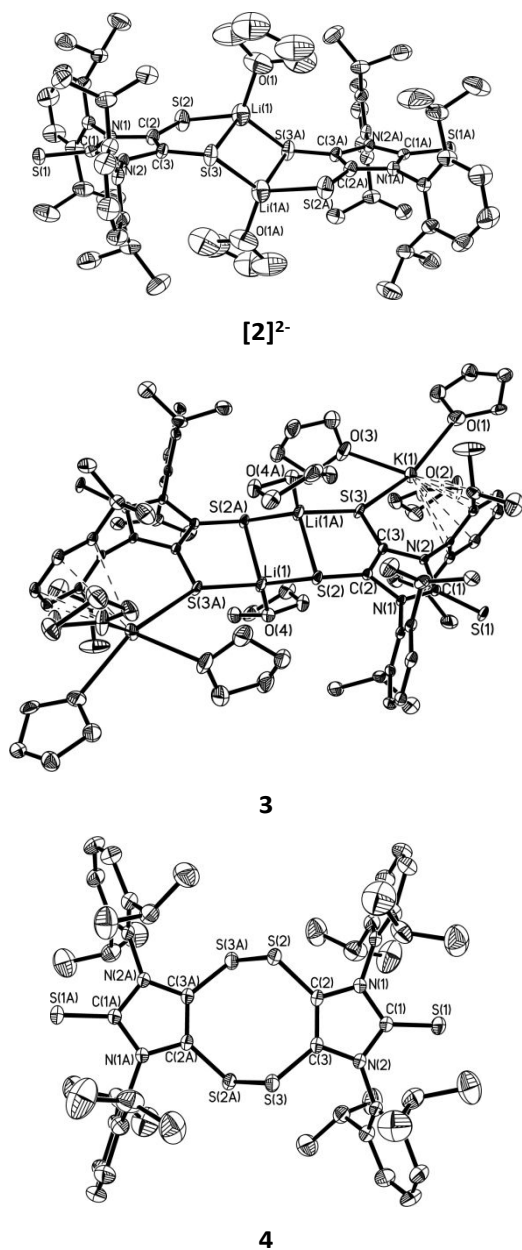


Fig. 4 Molecular structures of **[2]**^{2–}, **3**, and **4**. Thermal ellipsoids represent 30% probability; hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°) are as follows. For **[2]**^{2–}, C(1)–S(1) 1.680(6), C(2)–C(3) 1.362(8), C(2)–S(2) 1.724(6), C(3)–S(3) 1.733(6), S(2)–Li(1) 2.434(15), S(3)–Li(1) 2.525(16), S(3A)–Li(1) 2.396(15), O(1)–Li(1) 1.961(18); S(2)–C(2)–C(3) 131.1(5), C(2)–S(2)–Li(1) 92.0(4), S(2)–Li(1)–S(3) 93.6(5), S(3)–Li(1)–S(3A) 111.7(7), O(1)–Li(1)–S(2) 120.5(8). For **3**, C(1)–S(1) 1.701(3), C(2)–C(3) 1.366(5), C(2)–S(2) 1.733(3), C(3)–S(3) 1.732(4), S(2)–Li(1) 2.416(8), S(2)–Li(1A) 2.531(7), S(3)–Li(1A) 2.407(7), S(3)–K(1) 3.1490(13), O(4)–Li(1) 1.960(9); S(2)–C(2)–C(3) 130.7(3), C(2)–S(2)–Li(1A) 90.09(19), S(2)–Li(1A)–S(3) 94.2(2), S(2)–Li(1A)–S(2A) 110.8(3), C(3)–S(3)–K(1) 115.01(12). For **4**, C(1)–S(1) 1.655(2), C(2)–C(3)

- 15 H. B. Gray and E. Billig, *J. Am. Chem. Soc.*, 1963, **85**, 2019-2020.
- 16 E. I. Stiefel, J. H. Waters, E. Billig and H. B. Gray, *J. Am. Chem. Soc.*, 1965, **87**, 3016-3017.
- 17 S. Kokatam, K. Ray, J. Pap, E. Bill, W. E. Geiger, R. J. LeSuer, P. H. Rieger, T. Weyhermuller, F. Neese and K. Wieghardt, *Inorg. Chem.*, 2007, **46**, 1100-1111.
- 18 J. E. Huyett, S. B. Choudhury, D. M. Eichhorn, P. A. Bryngelson, M. J. Maroney and B. M. Hoffman, *Inorg. Chem.*, 1998, **37**, 1361-1367.
- 19 C. Milsman, E. Bothe, E. Bill, T. Weyhermuller and K. Wieghardt, *Inorg. Chem.*, 2009, **48**, 6211-6221.
- 20 C. Milsman, G. K. Patra, E. Bill, T. Weyhermuller, S. D. George and K. Wieghardt, *Inorg. Chem.*, 2009, **48**, 7430-7445.
- 21 R. K. Szilagy, B. S. Lim, T. Glaser, R. H. Holm, B. Hedman, K. O. Hodgson and E. I. Solomon, *J. Am. Chem. Soc.*, 2003, **125**, 9158-9169.
- 22 R. Sarangi, S. D. George, D. J. Rudd, R. K. Szilagy, X. Ribas, C. Rovira, M. Almeida, K. O. Hodgson, B. Hedman and E. I. Solomon, *J. Am. Chem. Soc.*, 2007, **129**, 2316-2326.
- 23 R. R. Kapre, E. Bothe, T. Weyhermuller, S. D. George and K. Wieghardt, *Inorg. Chem.*, 2007, **46**, 5642-5650.
- 24 K. Ray, S. D. George, E. I. Solomon, K. Wieghardt and F. Neese, *Chem. - Eur. J.*, 2007, **13**, 2783-2797.
- 25 N. Tenn, N. Bellec, O. Jeannin, L. Piekara-Sady, P. Auban-Senzier, J. Iniguez, E. Canadell and D. Lorcy, *J. Am. Chem. Soc.*, 2009, **131**, 16961-16967.
- 26 A. Filatre-Furcate, N. Bellec, O. Jeannin, P. Auban-Senzier, M. Fourmigue, A. Vacher and D. Lorcy, *Inorg. Chem.*, 2014, **53**, 8681-8690.
- 27 T. J. Morsing, S. N. MacMillan, J. W. H. Uebler, T. Brock-Nannestad, J. Bendix and K. M. Lancaster, *Inorg. Chem.*, 2015, **54**, 3660-3669.
- 28 G. A. Russell and M. Zaleta, *J. Am. Chem. Soc.*, 1982, **104**, 2318.
- 29 G. A. Russell, W. C. Law and M. Zaleta, *J. Am. Chem. Soc.*, 1985, **107**, 4175-4182.
- 30 D. Buddensiek, B. Koepke and J. Voss, *Chem. Ber.*, 1987, **120**, 575-581.
- 31 B. Roth, H. Bock and H. Gotthardt, *Phosphorus, Sulfur Relat. Elem.*, 1985, **22**, 109-119.
- 32 M. Yamaguchi and T. Shida, *J. Phys. Chem. A*, 2016, **120**, 3570-3577.
- 33 Y. Wang, Y. Xie, M. Y. Abraham, P. Wei, H. F. Schaefer, III, P. v. R. Schleyer and G. H. Robinson, *J. Am. Chem. Soc.*, 2010, **132**, 14370-14372.
- 34 Y. Wang, H. P. Hickox, Y. Xie, P. Wei, S. A. Blair, M. K. Johnson, H. F. Schaefer, III and G. H. Robinson, *J. Am. Chem. Soc.*, 2017, **139**, 6859-6862.
- 35 Y. Wang, Y. Xie, P. Wei, S. A. Blair, D. Cui, M. K. Johnson, H. F. Schaefer, III and G. H. Robinson, *Angew. Chem., Int. Ed.*, 2018, **57**, 7865-7868.
- 36 See the supporting information for synthetic, computational, and crystallographic details.
- 37 N. G. Connelly and W. E. Geiger, *Chem. Rev.*, 1996, **96**, 877-910.
- 38 P. Deplano, M. L. Mercuri, G. Pintus and E. F. Trogu, *Comments Inorg. Chem.*, 2001, **22**, 353-374.
- 39 F. Bigoli, P. Deplano, F. A. Devillanova, J. R. Ferraro, V. Lippolis, P. J. Lukes, M. L. Mercuri, M. A. Pellinghelli, E. F. Trogu and J. M. Williams, *Inorg. Chem.*, 1997, **36**, 1218-1226.
- 40 F. Bigoli, S. Currelli, P. Deplano, L. Leoni, M. L. Mercuri, M. A. Pellinghelli, A. Serpe and E. F. Trogu, *J. Chem. Soc., Dalton Trans.*, 2002, 1985-1991.
- 41 J. G. Breitner, A. I. Smirnov, L. F. Szczepura, S. R. Wilson and T. B. Rauchfuss, *Inorg. Chem.*, 2001, **40**, 1421-1429.
- 42 A. G. M. Barrett, M. R. Crimmin, M. S. Hill, P. B. Hitchcock, G. Kociok-Kohn and P. A. Procopiu, *Inorg. Chem.*, 2008, **47**, 7366-7376.
- 43 S. L. De Wall, L. J. Barbour and G. W. Gokel, *J. Am. Chem. Soc.*, 1999, **121**, 8405-8406.
- 44 M. Roger, L. Belkhir, P. Thuery, T. Arliguie, M. Fourmigue, A. Boucekkine and M. Ephritikhine, *Organometallics*, 2005, **24**, 4940-4952.

**SUPPORTING INFORMATION of SYNTHESSES, STRUCTURES,
AND COMPUTATIONS**

Redox Chemistry of an Anionic Dithiolene Radical

*Yuzhong Wang, Yaoming Xie, Pingrong Wei, Henry F. Schaefer III, and
Gregory H. Robinson**

*Department of Chemistry and the Center for Computational Chemistry, The
University of Georgia, Athens, Georgia 30602-2556, United States.*

To whom correspondence should be addressed. Email: robinson@uga.edu

SUPPORTING INFORMATIONS of SYNTHESSES

Materials and Methods

General.

The syntheses of air-sensitive compounds were performed under purified argon using Schlenk techniques and an inert atmosphere drybox (M-Braun LabMaster SP). Chemicals were purchased from Aldrich and Strem and used as received. The solvents were dried and distilled under argon from Na/benzophenone prior to use. ^1H NMR and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were recorded on a Bruker Avance III HD 400 MHz spectrometer and a Varian Unity Inova 500 MHz spectrometer. X-ray intensity data for **2**, **3**·(THF), and **4**·(THF)₂ were collected on a Bruker D8 Quest PHOTON 100 CMOS X-ray diffractometer system with Incoatec Microfocus Source (I μ S) monochromated Mo K α radiation ($\lambda = 0.71073$ Å, sealed tube) using phi and omega-scan technique. Electrochemical measurements (CV, DPV) were performed on a Eco Chemie B.V. μ Autolab Type III potentiostat controlled by the Autolab GPES software. The electrode system consisted of a non-aqueous Ag/Ag⁺ (0.01 M AgNO₃/0.1 M ⁿBu₄NPF₆ in MeCN) reference electrode, Pt wire counter electrode, and a glassy-carbon working electrode (diameter = 2 mm). Measurements were performed at ambient temperature using 7.1 mM analyte in THF under Ar containing 0.1 M ⁿBu₄NPF₆ as the supporting electrolyte. Analyte potentials were referenced against an internal ferrocene (4.5 mM) standard; $E_{1/2} = 0.224$ V in THF vs. the Ag/Ag⁺ reference electrode.

Compound **2**: 5 mL toluene solution of Cp₂Co (0.03 g, 0.16 mmol) was added to a Schlenk tube containing 5 mL of toluene solution of **1**⁺ (0.10 g, 0.16 mmol) at room temperature, which was then stirred for 2h and resulted in a green slurry. Filtration, washing with 10 mL of toluene, and drying in vacuo gave **2** as a green solid in a quantitative yield. X-ray quality crystals of **2** were observed after crystallization of **2** in acetonitrile at room temperature. Mp: gradually decomposed (>266 °C). Crystal data for **2**: C₈₂H₁₀₄Co₂Li₂N₄O₂S₆, fw = 1501.78, monoclinic, $P2_1/n$, $a = 14.1048(15)$ Å, $b = 15.2174(16)$ Å, $c = 19.0290(19)$ Å, $\beta = 90.200(3)^\circ$, $V = 4084.3(7)$ Å³, $Z = 2$, $R1 = 0.0994$ for 5305 data ($I > 2\sigma(I)$), $wR_2 = 0.2373$ (all data).

Compound **3**: 10 mL of THF was added to a Schlenk tube containing **1**⁺ (0.10 g, 0.16 mmol) and KC₈ (0.03 g, 0.22 mmol) at room temperature. One hour reaction gave an amber color solution and white precipitate. TMEDA was added dropwise to the mixture until white precipitate disappeared. After filtration, the volatiles were removed under vacuum, giving **3** as an off-white solid in a quantitative yield. Colorless X-ray quality crystals of **3** were obtained by concentrating the parent THF/TMEDA solution of **3** at room temperature. Mp: gradually decomposed (>180 °C) and melt (> 290 °C). ^1H NMR (499.80 MHz, THF-*d*₈): δ 1.25 [d, 24H, CH(CH₃)₂], 1.27 [d, 24H, CH(CH₃)₂], 1.77

(THF), 2.92 [m, 8H, CH(CH₃)₂], 3.62 (THF), 7.09 [d, 8H, Ar-*H*], 7.19 [t, 4H, Ar-*H*]. ¹³C{¹H} NMR (125.69 MHz, THF-*d*₈): δ 24.65, 24.77 [CH(CH₃)₂], 26.55 (THF), 29.96 [CH(CH₃)₂], 68.39 (THF), 123.31 [NCCN], 128.13, 129.97, 138.52, 148.37 [Ar-*C*], 160.17 [NC(=S)N]. Crystal data for **3**·(THF): C₉₀H₁₄₀K₂Li₂N₄O₉S₆, fw = 1706.50, monoclinic, *P*2₁/n, *a* = 12.5227(9) Å, *b* = 29.009(2) Å, *c* = 13.0842(9) Å, β = 98.110(2)°, *V* = 4705.5(6) Å³, *Z* = 2, *R*₁ = 0.0780 for 6664 data (*I* > 2σ(*I*)), w*R*₂ = 0.2127 (all data).

Compound **4**: 50 mL of toluene was added to a Schlenk flask containing **1**⁺ (0.50 g, 0.79 mmol) and Ph₃C⁺BF₄[−] (0.26 g, 0.79 mmol) at room temperature. The resulting mixture was sonicated until the color changed from dark purple to orange-red. After filtration, the volatiles were removed under vacuum. The resulting orange-red solid was combined with 10 mL of toluene in a Schlenk tube and then heated until to achieve a homogeneous dark red solution, which was kept stationary under ambient temperature over three days, giving red crystalline solid of **4** (0.21 g, 55.3% yield). X-ray quality single crystals of **4** were achieved by recrystallization in THF. Mp: gradually decomposed (>139 °C) and melt at 269 °C. ¹H NMR (400.14 MHz, THF-*d*₈): δ 1.07 [d, 12H, CH(CH₃)₂], 1.15 [d, 12H, CH(CH₃)₂], 1.32 [d, 12H, CH(CH₃)₂], 1.40 [d, 12H, CH(CH₃)₂], 2.14 [m, 4H, CH(CH₃)₂], 3.08 [m, 4H, CH(CH₃)₂], 7.23 [d, 4H, Ar-*H*], 7.32 [d, 4H, Ar-*H*], 7.41 [t, 4H, Ar-*H*]. ¹³C{¹H} NMR (100.63 MHz, THF-*d*₈): δ 24.15, 24.32, 24.59 [CH(CH₃)₂], 30.23, 30.58 [CH(CH₃)₂], 125.01 (NCCN), 125.29, 131.50, 132.11, 133.15, 147.57, 148.04 [Ar-*C*], 170.18 [NC(=S)N]. Crystal data for **4**·(THF)₂: C₆₂H₈₄N₄O₂S₆, fw = 1109.68, triclinic, *P*-1, *a* = 9.1839(8) Å, *b* = 14.0016(11) Å, *c* = 14.4200(12) Å, α = 62.605(4)°, β = 72.521(4)°, γ = 86.256(4)°, *V* = 1564.5(2) Å³, *Z* = 1, *R*₁ = 0.0557 for 4706 data (*I* > 2σ(*I*)), w*R*₂ = 0.1558 (all data).

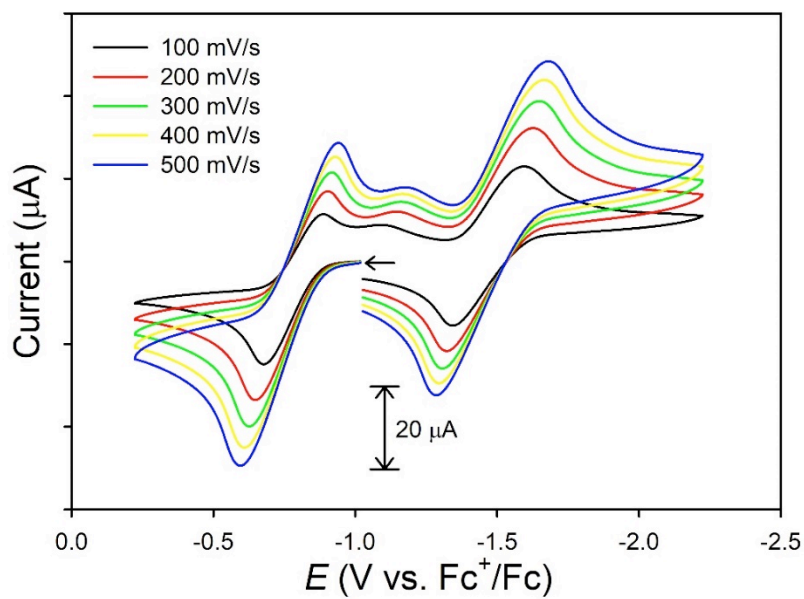


Figure S1. CVs of **1•** (7.10 mM) in THF at various scan speeds (0.1 M $n\text{-Bu}_4\text{NPF}_6$ supporting electrolyte, glassy carbon working electrode, Pt-wire counter electrode, RT). Arrow indicates direction of the scan.

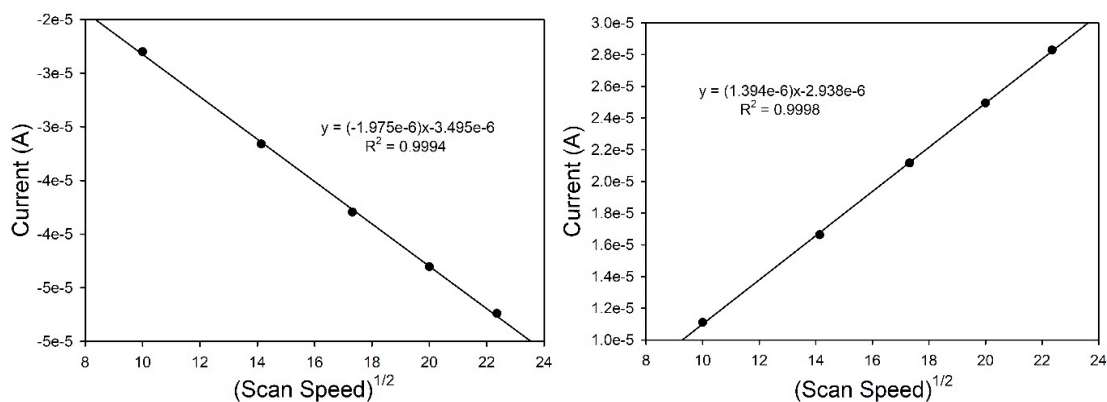


Figure S2. Plots of the square root of scan speed vs. current (A) for the anodic (left) and the cathodic (right) currents for $1^\bullet$ at $E_{1/2} = -0.78$ V (vs. Fc^+/Fc).

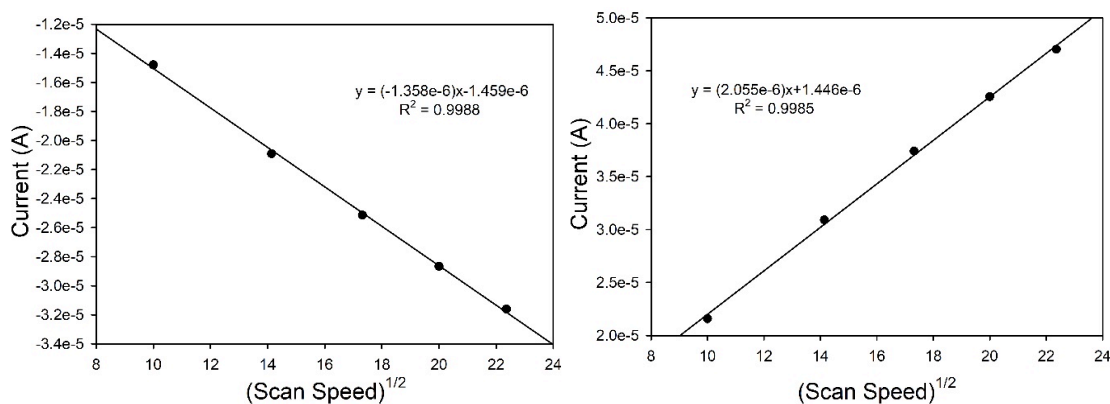


Figure S3. Plots of the square root of scan speed vs. current (A) for the anodic (left) and the cathodic (right) currents for $1^\bullet$ at $E_{1/2} = -1.47$ V (vs. Fc^+/Fc).

SUPPORTING INFORMATIONS of COMPUTATIONS

All computations employed the Gaussian09 programs:

For Gaussian 09: 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. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. 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, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, *Gaussian 09*, revision D.01; Gaussian, Inc., Wallingford CT, 2013.

Table S1. Coordinates of the B3LYP/6-311G** optimized geometry of [1-Me]⁺.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	16	0	5.410781	-0.232118	-0.087304
2	16	0	0.303594	0.006033	1.832664
3	16	0	0.204418	-0.259365	-1.737406
4	7	0	2.929621	-0.096041	1.071469
5	7	0	2.869141	-0.260107	-1.115245
6	6	0	3.736472	-0.196595	-0.043589
7	6	0	1.589317	-0.094509	0.724014
8	6	0	1.550002	-0.201474	-0.698834
9	3	0	-1.425630	0.006435	0.088261
10	8	0	-2.449660	1.684292	-0.014152
11	6	0	-2.537566	2.452640	-1.246454
12	1	0	-3.372456	2.067171	-1.836618
13	1	0	-1.609106	2.294863	-1.800159
14	6	0	-2.726664	3.913967	-0.823928
15	1	0	-3.789039	4.171296	-0.786859
16	1	0	-2.236343	4.605072	-1.511101
17	6	0	-2.124869	3.939931	0.589591
18	1	0	-1.035341	4.016714	0.544852
19	1	0	-2.503658	4.759549	1.202721
20	6	0	-2.530483	2.572553	1.126495
21	1	0	-1.864080	2.183110	1.896530
22	1	0	-3.560286	2.577270	1.503602
23	8	0	-2.673718	-1.478369	0.222508
24	6	0	-4.060012	-1.512272	-0.184941
25	1	0	-4.118956	-1.282822	-1.254908
26	1	0	-4.597891	-0.742169	0.370354
27	6	0	-4.536827	-2.933847	0.107717
28	1	0	-5.362235	-3.236526	-0.538878
29	1	0	-4.867554	-3.019675	1.146780
30	6	0	-3.256337	-3.752241	-0.116491
31	1	0	-3.271185	-4.721082	0.385243
32	1	0	-3.095920	-3.923657	-1.184613
33	6	0	-2.178165	-2.826490	0.443956
34	1	0	-2.035738	-2.965403	1.519597
35	1	0	-1.213150	-2.916371	-0.056000
36	6	0	3.418009	-0.005366	2.438296
37	1	0	3.075211	0.926000	2.891940
38	1	0	3.032596	-0.841559	3.023816
39	1	0	4.504362	-0.033707	2.405427
40	6	0	3.281466	-0.375288	-2.505090
41	1	0	4.368146	-0.400754	-2.528186
42	1	0	2.869879	-1.288594	-2.937634
43	1	0	2.908592	0.478752	-3.072808

Table S2. Coordinates of the B3LYP/6-311G** optimized geometry of [2-Me]²⁻ (in C_i symmetry).

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	16	0	1.002841	6.812710	-0.590183
2	16	0	-0.279683	2.328397	2.426274
3	16	0	-0.721531	1.560374	-1.099088
4	7	0	0.409227	4.670796	1.079870
5	7	0	0.172620	4.220861	-1.027428
6	6	0	0.520588	5.214627	-0.166810
7	6	0	-0.018315	3.326173	1.012506
8	6	0	-0.168060	3.038208	-0.324143
9	3	0	-0.888504	0.358086	1.130492
10	8	0	-2.783752	-0.301535	1.261065
11	6	0	-3.794556	0.671736	0.958126
12	1	0	-3.340281	1.654593	1.079534
13	1	0	-4.618917	0.561365	1.678225
14	6	0	-4.259096	0.364872	-0.480746
15	1	0	-5.348078	0.434978	-0.564240
16	1	0	-3.806324	1.068123	-1.179924
17	6	0	-3.738424	-1.073285	-0.747762
18	1	0	-4.519254	-1.749430	-1.105963
19	1	0	-2.934838	-1.061330	-1.485236
20	6	0	-3.184167	-1.518782	0.611508
21	1	0	-2.309826	-2.163555	0.546154
22	1	0	-3.956723	-2.010785	1.221364
23	16	0	-1.002841	-6.812710	0.590183
24	16	0	0.279683	-2.328397	-2.426274
25	16	0	0.721531	-1.560374	1.099088
26	7	0	-0.409227	-4.670796	-1.079870
27	7	0	-0.172620	-4.220861	1.027428
28	6	0	-0.520588	-5.214627	0.166810
29	6	0	0.018315	-3.326173	-1.012506
30	6	0	0.168060	-3.038208	0.324143
31	3	0	0.888504	-0.358086	-1.130492
32	8	0	2.783752	0.301535	-1.261065
33	6	0	3.794556	-0.671736	-0.958126
34	1	0	3.340281	-1.654593	-1.079534
35	1	0	4.618917	-0.561365	-1.678225
36	6	0	4.259096	-0.364872	0.480746
37	1	0	5.348078	-0.434978	0.564240
38	1	0	3.806324	-1.068123	1.179924
39	6	0	3.738424	1.073285	0.747762
40	1	0	4.519254	1.749430	1.105963
41	1	0	2.934838	1.061330	1.485236
42	6	0	3.184167	1.518782	-0.611508
43	1	0	2.309826	2.163555	-0.546154
44	1	0	3.956723	2.010785	-1.221364
45	6	0	0.684181	5.375073	2.312945
46	1	0	-0.218895	5.427594	2.926739
47	1	0	1.447195	4.841861	2.884849
48	1	0	1.026392	6.375700	2.052419

49	6	0	0.150899	4.375065	-2.467193
50	1	0	-0.121916	3.410355	-2.892865
51	1	0	-0.577414	5.136746	-2.759013
52	1	0	1.132654	4.690647	-2.828505
53	6	0	-0.150899	-4.375065	2.467193
54	1	0	0.577414	-5.136746	2.759013
55	1	0	0.121916	-3.410355	2.892865
56	1	0	-1.132654	-4.690647	2.828505
57	6	0	-0.684181	-5.375073	-2.312945
58	1	0	-1.447195	-4.841861	-2.884849
59	1	0	0.218895	-5.427594	-2.926739
60	1	0	-1.026392	-6.375700	-2.052419

Table S3. Coordinates of the B3LYP/6-311G** optimized geometry of **3-Ph** (in C_i symmetry).

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	19	0	-0.500191	-0.137124	-5.965517
2	16	0	-2.259342	-5.580785	-2.882096
3	16	0	0.451823	-1.919556	0.300552
4	16	0	0.641282	-0.853403	-3.117414
5	7	0	-0.960468	-3.890187	-1.129353
6	7	0	-0.797631	-3.267808	-3.211157
7	6	0	-1.336532	-4.245718	-2.400818
8	6	0	-0.194503	-2.687648	-1.136430
9	6	0	-0.090524	-2.299055	-2.443587
10	6	0	-0.851767	-3.296839	-4.629100
11	6	0	-2.079003	-3.233697	-5.292946
12	6	0	-2.117975	-3.260198	-6.686110
13	1	0	-3.075973	-3.235219	-7.193624
14	6	0	-0.935745	-3.344843	-7.423422
15	1	0	-0.968786	-3.381136	-8.506570
16	6	0	0.288832	-3.408516	-6.757542
17	1	0	1.211044	-3.491692	-7.321806
18	6	0	0.332773	-3.389013	-5.364266
19	6	0	-1.313628	-4.643110	0.033362
20	6	0	-2.161610	-4.092009	0.992876
21	6	0	-2.519926	-4.844450	2.109663
22	1	0	-3.188261	-4.416825	2.849464
23	6	0	-2.037016	-6.141576	2.270337
24	1	0	-2.328369	-6.729311	3.134264
25	6	0	-1.182649	-6.683323	1.311629
26	1	0	-0.805701	-7.693603	1.425649
27	6	0	-0.818569	-5.935758	0.195537
28	8	0	1.989904	0.567126	-6.768489
29	6	0	3.110371	-0.013885	-6.065735
30	1	0	2.733237	-0.434139	-5.131596
31	1	0	3.547038	-0.818480	-6.673020
32	6	0	4.094354	1.137415	-5.894870
33	1	0	5.115424	0.798049	-5.711006
34	1	0	3.786211	1.771799	-5.059050
35	6	0	3.938266	1.879291	-7.232542
36	1	0	4.213404	2.933640	-7.173987
37	1	0	4.565332	1.411588	-7.996442
38	6	0	2.447962	1.682778	-7.563596
39	1	0	1.848415	2.556501	-7.290569
40	1	0	2.280336	1.465745	-8.622969
41	8	0	-1.896825	0.645912	-8.225403
42	6	0	-2.401953	-0.109914	-9.348302
43	1	0	-2.748149	-1.072781	-8.965660
44	1	0	-1.590119	-0.292087	-10.059812
45	6	0	-3.542371	0.722708	-9.969181
46	1	0	-3.202631	1.216745	-10.883114
47	1	0	-4.408857	0.110908	-10.224716
48	6	0	-3.845559	1.769573	-8.883145

49	1	0	-4.266497	2.692886	-9.285630
50	1	0	-4.541355	1.369667	-8.140247
51	6	0	-2.469611	1.966629	-8.256949
52	1	0	-1.848475	2.628119	-8.877715
53	1	0	-2.475420	2.340439	-7.233149
54	8	0	-1.452947	2.265559	-5.023698
55	6	0	-0.658930	3.473255	-4.904828
56	1	0	-0.871882	4.098570	-5.779465
57	1	0	0.400993	3.203541	-4.917242
58	6	0	-1.075258	4.147772	-3.592054
59	1	0	-0.409765	3.855457	-2.778627
60	1	0	-1.064824	5.236089	-3.666210
61	6	0	-2.475082	3.570675	-3.336932
62	1	0	-3.239004	4.111986	-3.904966
63	1	0	-2.737142	3.588181	-2.278324
64	6	0	-2.318488	2.150410	-3.865348
65	1	0	-3.252923	1.693276	-4.200188
66	1	0	-1.838941	1.503799	-3.123654
67	3	0	-1.122309	-0.131054	0.939237
68	8	0	-3.014682	-0.596685	0.519711
69	6	0	-3.375736	-0.812047	-0.868809
70	1	0	-3.720837	-1.845056	-0.986627
71	1	0	-2.480433	-0.671064	-1.475055
72	6	0	-4.492560	0.188334	-1.150404
73	1	0	-4.069257	1.167318	-1.389089
74	1	0	-5.135947	-0.127005	-1.974404
75	6	0	-5.221013	0.239408	0.200823
76	1	0	-5.807064	1.149722	0.340408
77	1	0	-5.893479	-0.617872	0.300642
78	6	0	-4.064038	0.140150	1.198092
79	1	0	-3.665738	1.121397	1.468919
80	1	0	-4.324829	-0.398536	2.111816
81	19	0	0.500191	0.137124	5.965517
82	16	0	2.259342	5.580785	2.882096
83	16	0	-0.451823	1.919556	-0.300552
84	16	0	-0.641282	0.853403	3.117414
85	7	0	0.960468	3.890187	1.129353
86	7	0	0.797631	3.267808	3.211157
87	6	0	1.336532	4.245718	2.400818
88	6	0	0.194503	2.687648	1.136430
89	6	0	0.090524	2.299055	2.443587
90	6	0	0.851767	3.296839	4.629100
91	6	0	2.079003	3.233697	5.292946
92	6	0	2.117975	3.260198	6.686110
93	1	0	3.075973	3.235219	7.193624
94	6	0	0.935745	3.344843	7.423422
95	1	0	0.968786	3.381136	8.506570
96	6	0	-0.288832	3.408516	6.757542
97	1	0	-1.211044	3.491692	7.321806
98	6	0	-0.332773	3.389013	5.364266
99	6	0	1.313628	4.643110	-0.033362
100	6	0	2.161610	4.092009	-0.992876
101	6	0	2.519926	4.844450	-2.109663
102	1	0	3.188261	4.416825	-2.849464
103	6	0	2.037016	6.141576	-2.270337
104	1	0	2.328369	6.729311	-3.134264

105	6	0	1.182649	6.683323	-1.311629
106	1	0	0.805701	7.693603	-1.425649
107	6	0	0.818569	5.935758	-0.195537
108	8	0	-1.989904	-0.567126	6.768489
109	6	0	-3.110371	0.013885	6.065735
110	1	0	-2.733237	0.434139	5.131596
111	1	0	-3.547038	0.818480	6.673020
112	6	0	-4.094354	-1.137415	5.894870
113	1	0	-5.115424	-0.798049	5.711006
114	1	0	-3.786211	-1.771799	5.059050
115	6	0	-3.938266	-1.879291	7.232542
116	1	0	-4.213404	-2.933640	7.173987
117	1	0	-4.565332	-1.411588	7.996442
118	6	0	-2.447962	-1.682778	7.563596
119	1	0	-1.848415	-2.556501	7.290569
120	1	0	-2.280336	-1.465745	8.622969
121	8	0	1.896825	-0.645912	8.225403
122	6	0	2.401953	0.109914	9.348302
123	1	0	2.748149	1.072781	8.965660
124	1	0	1.590119	0.292087	10.059812
125	6	0	3.542371	-0.722708	9.969181
126	1	0	3.202631	-1.216745	10.883114
127	1	0	4.408857	-0.110908	10.224716
128	6	0	3.845559	-1.769573	8.883145
129	1	0	4.266497	-2.692886	9.285630
130	1	0	4.541355	-1.369667	8.140247
131	6	0	2.469611	-1.966629	8.256949
132	1	0	1.848475	-2.628119	8.877715
133	1	0	2.475420	-2.340439	7.233149
134	8	0	1.452947	-2.265559	5.023698
135	6	0	0.658930	-3.473255	4.904828
136	1	0	0.871882	-4.098570	5.779465
137	1	0	-0.400993	-3.203541	4.917242
138	6	0	1.075258	-4.147772	3.592054
139	1	0	0.409765	-3.855457	2.778627
140	1	0	1.064824	-5.236089	3.666210
141	6	0	2.475082	-3.570675	3.336932
142	1	0	3.239004	-4.111986	3.904966
143	1	0	2.737142	-3.588181	2.278324
144	6	0	2.318488	-2.150410	3.865348
145	1	0	3.252923	-1.693276	4.200188
146	1	0	1.838941	-1.503799	3.123654
147	3	0	1.122309	0.131054	-0.939237
148	8	0	3.014682	0.596685	-0.519711
149	6	0	3.375736	0.812047	0.868809
150	1	0	3.720837	1.845056	0.986627
151	1	0	2.480433	0.671064	1.475055
152	6	0	4.492560	-0.188334	1.150404
153	1	0	4.069257	-1.167318	1.389089
154	1	0	5.135947	0.127005	1.974404
155	6	0	5.221013	-0.239408	-0.200823
156	1	0	5.807064	-1.149722	-0.340408
157	1	0	5.893479	0.617872	-0.300642
158	6	0	4.064038	-0.140150	-1.198092
159	1	0	3.665738	-1.121397	-1.468919
160	1	0	4.324829	0.398536	-2.111816

161	1	0	-1.274958	3.446512	4.835711
162	1	0	2.990682	3.193816	4.712558
163	1	0	0.170669	6.352781	0.563927
164	1	0	2.528501	3.081540	-0.868517
165	1	0	-2.990682	-3.193816	-4.712558
166	1	0	1.274958	-3.446512	-4.835711
167	1	0	-2.528501	-3.081540	0.868517
168	1	0	-0.170669	-6.352781	-0.563927

Table S4. Coordinates of the B3LYP/6-311G** optimized geometry of **4-Me** (in C_i symmetry).

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	16	0	-0.024668	0.591363	5.584990
2	16	0	-1.784407	-0.903580	0.594331
3	16	0	1.777231	-0.907062	0.610435
4	7	0	-1.110567	-0.103193	3.170542
5	7	0	1.081672	-0.105390	3.180474
6	6	0	-0.017849	0.129592	3.978308
7	6	0	-0.697190	-0.500280	1.903414
8	6	0	0.678995	-0.501661	1.909646
9	16	0	0.024668	-0.591363	-5.584990
10	16	0	1.784407	0.903580	-0.594331
11	16	0	-1.777231	0.907062	-0.610435
12	7	0	1.110567	0.103193	-3.170542
13	7	0	-1.081672	0.105390	-3.180474
14	6	0	0.017849	-0.129592	-3.978308
15	6	0	0.697190	0.500280	-1.903414
16	6	0	-0.678995	0.501661	-1.909646
17	6	0	-2.477972	0.035583	3.652347
18	1	0	-2.634479	1.051669	4.016064
19	1	0	-3.157732	-0.182989	2.832677
20	1	0	-2.648365	-0.656442	4.478498
21	6	0	2.444930	0.030548	3.674668
22	1	0	3.131636	-0.188978	2.861065
23	1	0	2.600082	1.046176	4.040229
24	1	0	2.606546	-0.662156	4.502016
25	6	0	-2.444930	-0.030548	-3.674668
26	1	0	-2.600082	-1.046176	-4.040229
27	1	0	-3.131636	0.188978	-2.861065
28	1	0	-2.606546	0.662156	-4.502016
29	6	0	2.477972	-0.035583	-3.652347
30	1	0	3.157732	0.182989	-2.832677
31	1	0	2.634479	-1.051669	-4.016064
32	1	0	2.648365	0.656442	-4.478498

SUPPORTING INFORMATIONS of X-RAY

Compound 2

Table S5. Sample and crystal data for 2.

Identification code	2
Chemical formula	$\text{C}_{82}\text{H}_{104}\text{Co}_2\text{Li}_2\text{N}_4\text{O}_2\text{S}_6$
Formula weight	1501.78 g/mol
Temperature	297(2) K
Wavelength	0.71073 Å
Crystal size	0.100 x 0.160 x 0.250 mm
Crystal system	monoclinic
Space group	$P2_1/n$ (No. 14)
Unit cell dimensions	$a = 14.1048(15) \text{ Å}$ $\alpha = 90^\circ$ $b = 15.2174(16) \text{ Å}$ $\beta = 90.200(3)^\circ$ $c = 19.0290(19) \text{ Å}$ $\gamma = 90^\circ$
Volume	$4084.3(7) \text{ Å}^3$
Z	2
Density (calculated)	1.221 g/cm^3
Absorption coefficient	0.606 mm^{-1}
F(000)	1592

Table S6. Data collection and structure refinement for **2**.

Theta range for data collection	2.14 to 25.25°
Index ranges	-16≤h≤16, -18≤k≤18, -22≤l≤22
Reflections collected	88772
Independent reflections	7314 [R(int) = 0.0946]
Max. and min. transmission	0.7457 and 0.5147
Structure solution technique	direct methods
Structure solution program	SHELXS-97 (Sheldrick 2008)
Refinement method	Full-matrix least-squares on F ²
Refinement program	SHELXL-2014/7 (Sheldrick, 2014)
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	7314 / 294 / 527
Goodness-of-fit on F²	1.043
Final R indices	5305 data; R1 = 0.0994, wR2 = 0.2218 I>2σ(I)
	all data R1 = 0.1275, wR2 = 0.2373
Weighting scheme	w=1/[σ ² (F _o ²)+(0.0451P) ² +30.9033P] where P=(F _o ² +2F _c ²)/3
Largest diff. peak and hole	2.334 and -0.509 eÅ ⁻³
R.M.S. deviation from mean	0.096 eÅ ⁻³

Table S7. Bond lengths (Å) for **2**.

S1-C1	1.680(6)	S2-C2	1.724(6)
S2-Li1	2.434(15)	S3-C3	1.733(6)
S3-Li1	2.396(15)	S3-Li1	2.525(16)
N1-C1	1.361(7)	N1-C2	1.406(8)
N1-C16	1.430(7)	N2-C1	1.357(7)
N2-C3	1.417(7)	N2-C4	1.437(7)
C2-C3	1.362(8)	C4-C9	1.378(9)
C4-C5	1.381(9)	C5-C6	1.391(9)
C5-C13	1.511(10)	C6-C7	1.361(11)
C7-C8	1.377(11)	C8-C9	1.399(10)
C9-C10	1.509(10)	C10-C12	1.522(12)
C10-C11	1.525(11)	C13-C15	1.507(11)
C13-C14	1.526(11)	C16-C17	1.395(9)
C16-C21	1.395(9)	C17-C18	1.395(10)
C17-C25	1.514(10)	C18-C19	1.354(12)
C19-C20	1.361(12)	C20-C21	1.399(11)
C21-C22	1.515(11)	C22-C24	1.517(14)
C22-C23	1.524(13)	C25-C26	1.506(11)
C25-C27	1.527(11)	Li1-O1	1.961(18)
Li1-S3	2.396(15)	Li1-Li1	2.77(4)
O1-C31'	1.477(19)	O1-C28'	1.474(19)
O1-C28	1.449(16)	O1-C31	1.469(16)
C28-C29	1.516(18)	C29-C30	1.513(17)
C30-C31	1.488(17)	C28'-C29'	1.51(3)
C29'-C30'	1.51(2)	C30'-C31'	1.48(2)
Co1-C41	1.960(18)	Co1-C39	1.977(19)

Co1-C34	1.922(13)	Co1-C35	2.002(11)
Co1-C32	2.013(10)	Co1-C40	1.98(2)
Co1-C37	1.97(2)	Co1-C36	2.017(10)
Co1-C33	2.009(11)	Co1-C38	1.96(2)
Co1-C37'	2.08(3)	Co1-C41'	2.09(3)
C32-C33	1.349(16)	C32-C36	1.406(14)
C33-C34	1.336(16)	C34-C35	1.401(16)
C35-C36	1.370(16)	C37-C41	1.42(3)
C37-C38	1.38(3)	C38-C39	1.41(2)
C39-C40	1.42(2)	C40-C41	1.38(2)
C37'-C41'	1.42(3)	C37'-C38'	1.38(3)
C38'-C39'	1.41(2)	C39'-C40'	1.41(2)
C40'-C41'	1.37(2)		

Table S8. Bond angles (°) for **2**.

C2-S2-Li1	92.0(4)	C3-S3-Li1	116.5(4)
C3-S3-Li1	90.4(4)	Li1-S3-Li1	68.3(7)
C1-N1-C2	112.0(5)	C1-N1-C16	122.2(5)
C2-N1-C16	125.6(5)	C1-N2-C3	111.4(5)
C1-N2-C4	124.5(5)	C3-N2-C4	124.0(5)
N2-C1-N1	104.3(5)	N2-C1-S1	127.7(4)
N1-C1-S1	128.0(4)	C3-C2-N1	106.0(5)
C3-C2-S2	131.1(5)	N1-C2-S2	122.8(4)
C2-C3-N2	106.2(5)	C2-C3-S3	130.1(5)
N2-C3-S3	123.5(5)	C9-C4-C5	124.2(6)
C9-C4-N2	118.1(6)	C5-C4-N2	117.7(6)
C4-C5-C6	117.0(7)	C4-C5-C13	122.5(6)
C6-C5-C13	120.4(6)	C7-C6-C5	120.4(7)
C6-C7-C8	121.6(7)	C7-C8-C9	119.9(7)
C4-C9-C8	116.8(7)	C4-C9-C10	122.1(6)
C8-C9-C10	121.1(6)	C9-C10-C12	111.5(7)
C9-C10-C11	114.5(7)	C12-C10-C11	109.9(7)
C5-C13-C15	112.9(7)	C5-C13-C14	111.2(7)
C15-C13-C14	111.5(7)	C17-C16-C21	121.7(6)
C17-C16-N1	119.3(6)	C21-C16-N1	119.0(6)
C16-C17-C18	117.6(7)	C16-C17-C25	119.6(6)
C18-C17-C25	122.8(7)	C19-C18-C17	121.3(8)
C18-C19-C20	120.8(8)	C21-C20-C19	121.0(8)
C16-C21-C20	117.5(7)	C16-C21-C22	121.0(6)
C20-C21-C22	121.4(7)	C21-C22-C24	109.8(8)
C21-C22-C23	112.8(8)	C24-C22-C23	111.3(9)
C17-C25-C26	110.5(7)	C17-C25-C27	112.6(7)
C26-C25-C27	110.7(7)	O1-Li1-S2	120.5(8)
O1-Li1-S3	117.3(8)	S2-Li1-S3	103.2(5)
O1-Li1-S3	108.2(6)	S2-Li1-S3	93.6(5)
S3-Li1-S3	111.7(7)	C31'-O1-C28'	104.(2)

C28-O1-C31	106.0(17)	C31'-O1-Li1	119(3)
C28'-O1-Li1	125(4)	C28-O1-Li1	113.3(16)
C31-O1-Li1	113.6(14)	O1-C28-C29	105.1(17)
C30-C29-C28	105.0(19)	C31-C30-C29	105.3(19)
C30-C31-O1	108.4(18)	O1-C28'-C29'	108(2)
C30'-C29'-C28'	106(2)	C29'-C30'-C31'	105(2)
O1-C31'-C30'	108(3)	C41-Co1-C39	69.4(9)
C41-Co1-C34	106.1(8)	C39-Co1-C34	165.2(9)
C41-Co1-C35	116.6(9)	C39-Co1-C35	126.4(8)
C34-Co1-C35	41.8(5)	C41-Co1-C32	164.9(7)
C39-Co1-C32	120.8(9)	C34-Co1-C32	66.9(6)
C35-Co1-C32	67.9(5)	C41-Co1-C40	40.8(6)
C39-Co1-C40	41.9(7)	C34-Co1-C40	125.7(8)
C35-Co1-C40	105.5(7)	C32-Co1-C40	154.2(7)
C41-Co1-C37	42.3(8)	C39-Co1-C37	69.2(9)
C34-Co1-C37	117.6(9)	C35-Co1-C37	152.4(11)
C32-Co1-C37	127.5(8)	C40-Co1-C37	70.1(8)
C41-Co1-C36	151.0(9)	C39-Co1-C36	108.6(8)
C34-Co1-C36	68.0(6)	C35-Co1-C36	39.9(5)
C32-Co1-C36	40.8(4)	C40-Co1-C36	118.1(7)
C37-Co1-C36	166.1(10)	C41-Co1-C33	127.1(7)
C39-Co1-C33	153.9(9)	C34-Co1-C33	39.7(5)
C35-Co1-C33	68.2(5)	C32-Co1-C33	39.2(5)
C40-Co1-C33	163.6(8)	C37-Co1-C33	108.1(7)
C36-Co1-C33	67.5(5)	C41-Co1-C38	70.9(10)
C39-Co1-C38	41.9(8)	C34-Co1-C38	151.5(10)
C35-Co1-C38	165.1(10)	C32-Co1-C38	108.4(8)
C40-Co1-C38	71.3(9)	C37-Co1-C38	41.3(8)
C36-Co1-C38	128.0(9)	C33-Co1-C38	118.7(9)
C34-Co1-C37'	133.5(10)	C35-Co1-C37'	175.3(10)
C32-Co1-C37'	111.0(10)	C36-Co1-C37'	141.9(12)
C33-Co1-C37'	107.9(9)	C34-Co1-C41'	117.7(11)
C35-Co1-C41'	139.6(12)	C32-Co1-C41'	146.6(11)
C36-Co1-C41'	171.0(10)	C33-Co1-C41'	121.5(10)

C37'-Co1-C41'	39.7(10)	C33-C32-C36	108.5(12)
C33-C32-Co1	70.3(7)	C36-C32-Co1	69.7(6)
C32-C33-C34	107.8(11)	C32-C33-Co1	70.6(7)
C34-C33-Co1	66.6(7)	C35-C34-C33	110.5(13)
C35-C34-Co1	72.2(7)	C33-C34-Co1	73.7(8)
C36-C35-C34	105.4(11)	C36-C35-Co1	70.7(6)
C34-C35-Co1	66.1(7)	C35-C36-C32	107.6(11)
C35-C36-Co1	69.5(7)	C32-C36-Co1	69.4(6)
C41-C37-C38	108.4(18)	C41-C37-Co1	68.4(11)
C38-C37-Co1	68.8(13)	C39-C38-C37	106.9(18)
C39-C38-Co1	69.8(12)	C37-C38-Co1	69.9(13)
C40-C39-C38	109.0(16)	C40-C39-Co1	69.4(11)
C38-C39-Co1	68.3(13)	C39-C40-C41	106.9(16)
C39-C40-Co1	68.8(11)	C41-C40-Co1	68.6(11)
C37-C41-C40	108.8(18)	C37-C41-Co1	69.3(10)
C40-C41-Co1	70.5(11)	C41'-C37'-C38'	107(2)
C41'-C37'-Co1	70.8(19)	C38'-C37'-Co1	70.9(19)
C39'-C38'-C37'	108.(2)	C39'-C38'-Co1	66.3(18)
C37'-C38'-Co1	70(2)	C40'-C39'-C38'	107.7(18)
C40'-C39'-Co1	72.3(19)	C38'-C39'-Co1	73.3(19)
C41'-C40'-C39'	107.2(18)	C41'-C40'-Co1	72.0(18)
C39'-C40'-Co1	66.9(18)	C40'-C41'-C37'	109(2)
C40'-C41'-Co1	69.6(19)	C37'-C41'-Co1	69.5(18)

Compound 3·(THF)**Table S9.** Sample and crystal data for **3·(THF)**.

Identification code	3·(THF)	
Chemical formula	$\text{C}_{90}\text{H}_{140}\text{K}_2\text{Li}_2\text{N}_4\text{O}_9\text{S}_6$	
Formula weight	1706.50 g/mol	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal size	0.070 x 0.140 x 0.250 mm	
Crystal system	monoclinic	
Space group	$P2_1/n$ (No. 14)	
Unit cell dimensions	$a = 12.5227(9)$ Å	$\alpha = 90^\circ$
	$b = 29.009(2)$ Å	$\beta = 98.110(2)^\circ$
	$c = 13.0842(9)$ Å	$\gamma = 90^\circ$
Volume	$4705.5(6)$ Å ³	
Z	2	
Density (calculated)	1.204 g/cm ³	
Absorption coefficient	0.289 mm ⁻¹	
F(000)	1840	

Table S10. Data collection and structure refinement for **3·(THF)**.

Theta range for data collection	2.11 to 26.02°	
Index ranges	-15≤h≤15, -35≤k≤35, -16≤l≤15	
Reflections collected	140881	
Independent reflections	9268 [R(int) = 0.1118]	
Max. and min. transmission	0.7454 and 0.5102	
Structure solution technique	direct methods	
Structure solution program	SHELXS-97 (Sheldrick 2008)	
Refinement method	Full-matrix least-squares on F ²	
Refinement program	SHELXL-2014/7 (Sheldrick, 2014)	
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	9268 / 537 / 645	
Goodness-of-fit on F²	1.071	
Final R indices	6664 data; I>2σ(I)	R1 = 0.0780, wR2 = 0.1934
	all data	R1 = 0.1123, wR2 = 0.2127
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0928P)^2+9.9471P]$	
	where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	0.737 and -0.517 eÅ ⁻³	
R.M.S. deviation from mean	0.079 eÅ ⁻³	

Table S11. Bond lengths (Å) for **3•(THF)**.

K1-O3'	2.637(9)	K1-O1	2.712(9)
K1-O3	2.689(9)	K1-O2	2.752(10)
K1-O1'	2.711(11)	K1-O2'	2.751(9)
K1-S3	3.1490(13)	K1-C8	3.246(4)
K1-C7	3.258(4)	K1-C6	3.287(4)
K1-C9	3.301(3)	K1-C4	3.336(3)
S1-C1	1.701(3)	S2-C2	1.733(3)
S2-Li1	2.416(8)	S2-Li1	2.531(7)
S3-C3	1.732(4)	S3-Li1	2.407(7)
N1-C1	1.351(4)	N1-C2	1.417(4)
N1-C16	1.438(4)	N2-C1	1.350(4)
N2-C3	1.406(4)	N2-C4	1.430(4)
C2-C3	1.366(5)	C4-C9	1.396(5)
C4-C5	1.395(5)	C5-C6	1.404(5)
C5-C13	1.511(6)	C6-C7	1.377(6)
C7-C8	1.377(6)	C8-C9	1.389(5)
C9-C10	1.511(6)	C10-C11	1.520(7)
C10-C12	1.514(7)	C13-C15	1.521(7)
C13-C14	1.517(7)	C16-C17	1.391(5)
C16-C21	1.400(5)	C17-C18	1.394(5)
C17-C25	1.511(6)	C18-C19	1.381(6)
C19-C20	1.371(6)	C20-C21	1.396(5)
C21-C22	1.512(6)	C22-C24	1.520(6)
C22-C23	1.534(6)	C25-C27	1.539(7)
C25-C26	1.516(6)	O1-C31	1.405(12)
O1-C28	1.475(12)	C28-C29	1.439(12)
C29-C30	1.472(14)	C30-C31	1.497(12)
O1'-C31'	1.401(14)	O1'-C28'	1.459(13)
C28'-C29'	1.439(14)	C29'-C30'	1.453(16)
C30'-C31'	1.477(15)	O2-C35	1.380(13)
O2-C32	1.414(12)	C32-C33	1.491(16)
C33-C34	1.587(16)	C34-C35	1.457(14)

O2'-C35'	1.386(12)	O2'-C32'	1.415(11)
C32'-C33'	1.503(15)	C33'-C34'	1.599(15)
C34'-C35'	1.466(13)	O3-C36	1.441(16)
O3-C39	1.422(14)	C36-C37	1.486(17)
C37-C38	1.43(2)	C38-C39	1.484(16)
O3'-C36'	1.392(15)	O3'-C39'	1.439(14)
C36'-C37'	1.527(14)	C37'-C38'	1.398(19)
C38'-C39'	1.491(14)	Li1-O4	1.960(9)
Li1-S3	2.407(7)	Li1-S2	2.531(7)
Li1-Li1	2.812(16)	O4-C40	1.449(6)
O4-C43	1.453(6)	C40-C41	1.508(7)
C41-C42	1.519(8)	C42-C43	1.480(9)
O5-C47	1.397(13)	O5-C44	1.429(13)
C44-C45	1.584(15)	C45-C46	1.509(14)
C46-C47	1.610(16)		

Table S12. Bond angles (°) for **3·(THF)**.

O1-K1-O3	111.5(5)	O1-K1-O2	80.2(7)
O3-K1-O2	76.7(5)	O3'-K1-O1'	101.4(5)
O3'-K1-O2'	76.5(4)	O1'-K1-O2'	81.6(7)
O3'-K1-S3	84.7(3)	O1-K1-S3	144.1(6)
O3-K1-S3	80.5(3)	O2-K1-S3	135.6(5)
O1'-K1-S3	136.9(7)	O2'-K1-S3	140.3(3)
O3'-K1-C8	172.8(3)	O1-K1-C8	76.7(4)
O3-K1-C8	171.0(3)	O2-K1-C8	101.8(4)
O1'-K1-C8	74.0(4)	O2'-K1-C8	107.9(3)
S3-K1-C8	94.93(7)	O3'-K1-C7	161.4(3)
O1-K1-C7	78.4(4)	O3-K1-C7	150.7(3)
O2-K1-C7	78.1(4)	O1'-K1-C7	78.8(4)
O2'-K1-C7	85.2(3)	S3-K1-C7	108.04(7)
C8-K1-C7	24.45(10)	O3'-K1-C6	144.4(3)
O1-K1-C6	100.0(4)	O3-K1-C6	129.6(3)
O2-K1-C6	71.0(4)	O1'-K1-C6	101.6(5)
O2'-K1-C6	80.4(3)	S3-K1-C6	96.53(7)
C8-K1-C6	42.85(11)	C7-K1-C6	24.28(10)
O3'-K1-C9	154.0(3)	O1-K1-C9	96.5(4)
O3-K1-C9	150.1(3)	O2-K1-C9	119.8(4)
O1'-K1-C9	92.1(5)	O2'-K1-C9	127.9(3)
S3-K1-C9	70.47(7)	C8-K1-C9	24.47(9)
C7-K1-C9	43.19(9)	C6-K1-C9	50.23(10)
O3'-K1-C4	140.5(3)	O1-K1-C4	118.8(4)
O3-K1-C4	129.7(3)	O2-K1-C4	111.2(4)
O1'-K1-C4	115.3(4)	O2'-K1-C4	121.2(3)
S3-K1-C4	58.85(6)	C8-K1-C4	42.28(9)
C7-K1-C4	49.23(9)	C6-K1-C4	42.24(9)
C9-K1-C4	24.27(9)	C2-S2-Li1	116.0(2)
C2-S2-Li1	90.09(19)	Li1-S2-Li1	69.2(3)

C3-S3-Li1	92.9(2)	C3-S3-K1	115.01(12)
Li1-S3-K1	151.89(17)	C1-N1-C2	110.7(3)
C1-N1-C16	123.5(3)	C2-N1-C16	125.7(3)
C1-N2-C3	111.1(3)	C1-N2-C4	123.8(3)
C3-N2-C4	125.0(3)	N2-C1-N1	105.8(3)
N2-C1-S1	126.2(3)	N1-C1-S1	128.0(3)
C3-C2-N1	106.1(3)	C3-C2-S2	130.7(3)
N1-C2-S2	123.2(3)	C2-C3-N2	106.3(3)
C2-C3-S3	130.4(3)	N2-C3-S3	123.3(3)
C9-C4-C5	123.1(3)	C9-C4-N2	118.7(3)
C5-C4-N2	118.2(3)	C9-C4-K1	76.46(19)
C5-C4-K1	78.6(2)	N2-C4-K1	117.52(19)
C6-C5-C4	117.1(4)	C6-C5-C13	120.5(3)
C4-C5-C13	122.4(3)	C6-C5-K1	75.2(2)
C4-C5-K1	77.4(2)	C13-C5-K1	116.7(2)
C5-C6-C7	120.9(4)	C5-C6-K1	80.4(2)
C7-C6-K1	76.6(2)	C6-C7-C8	120.2(4)
C6-C7-K1	79.1(2)	C8-C7-K1	77.3(2)
C9-C8-C7	121.6(4)	C9-C8-K1	80.0(2)
C7-C8-K1	78.2(2)	C8-C9-C4	117.1(3)
C8-C9-C10	121.5(4)	C4-C9-C10	121.4(3)
C8-C9-K1	75.6(2)	C4-C9-K1	79.27(19)
C10-C9-K1	116.2(2)	C9-C10-C11	110.5(4)
C9-C10-C12	112.2(4)	C11-C10-C12	111.1(5)
C5-C13-C15	110.3(4)	C5-C13-C14	112.1(4)
C15-C13-C14	112.2(4)	C17-C16-N1	118.9(3)
C17-C16-C21	122.5(3)	N1-C16-C21	118.6(3)
C18-C17-C16	117.7(4)	C18-C17-C25	120.5(4)
C16-C17-C25	121.8(3)	C17-C18-C19	120.8(4)
C18-C19-C20	120.6(4)	C21-C20-C19	120.9(4)
C20-C21-C16	117.5(4)	C20-C21-C22	120.8(4)
C16-C21-C22	121.7(3)	C21-C22-C24	111.9(3)
C21-C22-C23	110.4(4)	C24-C22-C23	111.2(4)
C17-C25-C27	110.9(3)	C17-C25-C26	111.6(4)

C27-C25-C26	111.6(4)	C31-O1-C28	109.1(8)
C31-O1-K1	114.9(9)	C28-O1-K1	135.2(9)
C29-C28-O1	108.5(9)	C28-C29-C30	103.2(10)
C31-C30-C29	107.9(9)	O1-C31-C30	104.9(9)
O1-C31-K1	44.0(6)	C30-C31-K1	146.3(8)
C31'-O1'-C28'	109.6(10)	C31'-O1'-K1	122.0(11)
C28'-O1'-K1	125.2(15)	C29'-C28'-O1'	107.7(11)
C28'-C29'-C30'	106.4(12)	C31'-C30'-C29'	108.9(11)
O1'-C31'-C30'	105.8(11)	C35-O2-C32	109.5(10)
C35-O2-K1	126.4(11)	C32-O2-K1	124.0(11)
O2-C32-C33	107.8(11)	C34-C33-C32	97.1(12)
C35-C34-C33	101.7(12)	O2-C35-C34	107.5(12)
C35'-O2'-C32'	110.4(9)	C35'-O2'-K1	122.7(11)
C32'-O2'-K1	122.0(9)	O2'-C32'-C33'	105.2(10)
C34'-C33'-C32'	97.5(11)	C35'-C34'-C33'	100.5(11)
O2'-C35'-C34'	107.8(10)	C36-O3-C39	105.5(9)
C36-O3-K1	123.3(9)	C39-O3-K1	128.3(10)
O3-C36-C37	107.1(11)	C38-C37-C36	102.3(12)
C37-C38-C39	109.8(12)	C38-C39-O3	105.7(12)
C36'-O3'-C39'	108.4(9)	C36'-O3'-K1	110.8(10)
C39'-O3'-K1	119.8(8)	O3'-C36'-C37'	105.9(9)
O3'-C36'-K1	46.7(7)	C37'-C36'-K1	121.0(9)
C38'-C37'-C36'	101.1(11)	C37'-C38'-C39'	105.4(11)
C38'-C39'-O3'	104.3(11)	O4-Li1-S2	121.3(3)
O4-Li1-S3	120.5(4)	S2-Li1-S3	104.8(3)
O4-Li1-S2	101.4(3)	S2-Li1-S2	110.8(3)
S3-Li1-S2	94.2(2)	O4-Li1-Li1	128.7(5)
S2-Li1-Li1	57.3(3)	S3-Li1-Li1	106.6(4)
S2-Li1-Li1	53.5(2)	C40-O4-C43	108.2(4)
C40-O4-Li1	110.9(3)	C43-O4-Li1	114.9(4)
O4-C40-C41	106.1(4)	C42-C41-C40	102.8(5)
C43-C42-C41	102.1(4)	O4-C43-C42	106.8(4)
C47-O5-C44	106.0(10)	O5-C44-C45	110.2(11)
C46-C45-C44	105.2(12)	C47-C46-C45	99.7(14)

O5-C47-C46 114.4(13)

Compound 4·(THF)₂**Table S13.** Sample and crystal data for 4·(THF)₂.

Identification code	4·(THF)₂	
Chemical formula	C ₆₂ H ₈₄ N ₄ O ₂ S ₆	
Formula weight	1109.68 g/mol	
Temperature	297(2) K	
Wavelength	0.71073 Å	
Crystal size	0.080 x 0.110 x 0.230 mm	
Crystal system	triclinic	
Space group	P-1(No. 14)	
Unit cell dimensions	a = 9.1839(8) Å	α = 62.605(4)°
	b = 14.0016(11) Å	β = 72.521(4)°
	c = 14.4200(12) Å	γ = 86.256(4)°
Volume	1564.5(2) Å ³	
Z	1	
Density (calculated)	1.178 g/cm ³	
Absorption coefficient	0.262 mm ⁻¹	
F(000)	596	

Table S14. Data collection and structure refinement for **4·(THF)₂**.

Theta range for data collection	2.42 to 27.10°	
Index ranges	-11≤h≤11, -17≤k≤17, -18≤l≤18	
Reflections collected	98726	
Independent reflections	6898 [R(int) = 0.0789]	
Max. and min. transmission	0.7456 and 0.5969	
Structure solution technique	direct methods	
Structure solution program	SHELXS-97 (Sheldrick 2008)	
Refinement method	Full-matrix least-squares on F ²	
Refinement program	SHELXL-2014/7 (Sheldrick, 2014)	
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	6898 / 193 / 380	
Goodness-of-fit on F²	1.028	
$\Delta/\sigma_{\max}$	0.001	
Final R indices	4706 data; I>2σ(I)	R1 = 0.0557, wR2 = 0.1358
	all data	R1 = 0.0943, wR2 = 0.1558
	$w=1/[\sigma^2(F_o^2)+(0.0795P)^2+0.5388P]$ where $P=(F_o^2+2F_c^2)/3$	
Weighting scheme		
Largest diff. peak and hole	0.317 and -0.264 eÅ ⁻³	
R.M.S. deviation from mean	0.045 eÅ ⁻³	

Table S15. Bond lengths (Å) for **4•(THF)₂**.

S1-C1	1.655(2)	S2-C2	1.739(2)
S2-S3	2.0727(9)	S3-C3	1.739(2)
S3-S2	2.0728(9)	N1-C1	1.371(3)
N1-C2	1.397(3)	N1-C16	1.444(3)
N2-C1	1.375(3)	N2-C3	1.391(3)
N2-C4	1.448(3)	C2-C3	1.348(3)
C4-C5	1.393(3)	C4-C9	1.391(3)
C5-C6	1.388(3)	C5-C13	1.513(4)
C6-C7	1.359(4)	C7-C8	1.373(4)
C8-C9	1.399(4)	C9-C10	1.509(4)
C10-C12	1.529(4)	C10-C11	1.527(4)
C13-C14	1.513(5)	C13-C15	1.529(5)
C16-C17	1.397(3)	C16-C21	1.395(4)
C17-C18	1.390(4)	C17-C25	1.510(4)
C18-C19	1.362(5)	C19-C20	1.360(5)
C20-C21	1.391(4)	C21-C22	1.507(4)
C22-C23	1.523(5)	C22-C24	1.515(6)
C25-C26	1.511(5)	C25-C27	1.520(5)
O1-C31	1.410(13)	O1-C28	1.497(14)
C28-C29	1.471(14)	C29-C30	1.557(13)
C30-C31	1.474(12)	O1'-C31'	1.406(15)
O1'-C28'	1.526(14)	C28'-C29'	1.467(18)
C29'-C30'	1.540(17)	C30'-C31'	1.457(13)

Table S16. Bond angles (°) for 4•(THF)₂.

C2-S2-S3	104.28(8)	C3-S3-S2	103.40(8)
C1-N1-C2	109.94(17)	C1-N1-C16	124.66(18)
C2-N1-C16	125.04(18)	C1-N2-C3	109.95(17)
C1-N2-C4	123.39(17)	C3-N2-C4	126.42(17)
N1-C1-N2	105.27(18)	N1-C1-S1	127.01(16)
N2-C1-S1	127.71(17)	C3-C2-N1	107.31(18)
C3-C2-S2	129.74(17)	N1-C2-S2	122.93(16)
C2-C3-N2	107.50(18)	C2-C3-S3	129.53(17)
N2-C3-S3	122.97(16)	C5-C4-C9	123.5(2)
C5-C4-N2	117.9(2)	C9-C4-N2	118.6(2)
C4-C5-C6	116.6(3)	C4-C5-C13	123.7(2)
C6-C5-C13	119.7(2)	C7-C6-C5	121.8(3)
C6-C7-C8	120.4(3)	C7-C8-C9	121.2(3)
C4-C9-C8	116.5(2)	C4-C9-C10	123.1(2)
C8-C9-C10	120.4(3)	C9-C10-C12	110.2(2)
C9-C10-C11	112.2(2)	C12-C10-C11	111.8(3)
C5-C13-C14	111.5(3)	C5-C13-C15	110.7(3)
C14-C13-C15	110.8(3)	C17-C16-C21	123.8(2)
C17-C16-N1	117.8(2)	C21-C16-N1	118.4(2)
C16-C17-C18	116.1(3)	C16-C17-C25	122.8(2)
C18-C17-C25	121.1(3)	C17-C18-C19	121.2(3)
C20-C19-C18	121.5(3)	C21-C20-C19	120.9(3)
C20-C21-C16	116.4(3)	C20-C21-C22	120.4(3)
C16-C21-C22	123.2(2)	C23-C22-C21	112.2(3)
C23-C22-C24	109.7(3)	C21-C22-C24	111.4(3)
C26-C25-C17	111.1(3)	C26-C25-C27	110.5(3)
C17-C25-C27	112.5(3)	C31-O1-C28	97.1(14)
O1-C28-C29	97.2(13)	C30-C29-C28	95.9(11)
C29-C30-C31	108.4(11)	O1-C31-C30	94.0(11)
C31'-O1'-C28'	101.6(12)	C29'-C28'-O1'	98.9(13)

C30'-C29'-C28'	83.4(15)	C29'-C30'-C31'	93.8(13)
O1'-C31'-C30'	99.8(12)		