Supplementary Information for

Syntheses and characterisation of terephthalonitrile radical salts

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1. Experimental and synthetic methods

a. Experimental techniques

Single crystals X-ray diffraction (SCXRD) data were collected with a Bruker APEX II Quasar diffractometer, equipped with a graphite monochromator centred on the path of Mo K_{α} radiation ($\lambda = 0.71073$ Å). The single crystals were coated with CargilleTM NHV immersion oil and mounted on a fiber loop, followed by data collection at 120 K, then also at 250 K for Li⁺(tpn)^{•-} (THF)₂. The program SAINT was used to integrate the data, which was thereafter corrected using SADABS.^[1] The data were cut at their limit of diffraction, that is with a resolution of 0.81 Å for Na⁺(tpn)^{•-}(THF), 0.83 Å and 0.87 Å for Li⁺(tpn)^{•-}(THF)₂ at 120 K and 250 K respectively. The structures were solved using direct methods and refined by a full-matrix least-squares method on *F*² using SHELXL-2019/2.^[2] All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were assigned to ideal positions and refined isotropically using a suitable riding model.

The crystallographic data are listed in Table S1. The CIF files have been deposited at the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 2351403-2351405.

Powder X-ray diffraction (PXRD) measurements were performed at ambient temperature on the BM01 beamline at the European Synchrotron Radiation Facility (ESRF) in Grenoble, France.^[3] Samples were sealed inside 0.5 mm diameter borosilicate glass capillaries and measured with a wavelength of 0.72479 Å for Na⁺(tpn)^{•-}(THF) and 0.69387 Å for Li⁺(tpn)^{•-}(THF)₂. For the variable-temperature PXRD studies, the Li⁺(tpn)^{•-}(THF)₂ sample was cooled down from 300 K to 120 K and ramped back up to 300 K with a 6 K.min⁻¹ rate.

Electrochemistry: Cyclic voltammetry (CV) measurements were performed with a Metrohm Autolab PGSTAT101 equipped with a platinum working electrode. Ferrocene was used as an internal reference. Measurements were done in dehydrated and degassed THF (5 mL) with 0.1 M (n-Bu₄N)PF₆ as supporting electrolyte.

Elemental analyses were measured on a Elementar UNICUBE CHNS element analyzer (He carrier gas) housed at the Department of Chemistry at the University of Jyväskylä. A standard 5 mg calibration sequence for daily factor determination was used and routine blanks were performed before analyses. Additional run-in measurements were employed to ensure residual CHN values returned below background levels prior to each set of sample lot measurements. All samples were prepared inside an argon-filled glovebox equipped with inline oxygen scrubbers and a controlled atmosphere. Samples (~ 3 - 8 mg) were prepared in pre-weighed Sn capsules, doubly sealed and the weight of analyte determined by difference on an analytical balance (maximum ≤ 2 g) prior to introduction into the combustion chamber just before each analysis run to prevent any sample degradation.

Infrared spectroscopy measurements were performed on crystalline samples using an Agilent Technologies Cary 630 FT-IR spectrometer in an argon-filled glovebox with controlled atmosphere.

UV-vis spectra were recorded using a Perkin Elmer LAMBDA 950 in dry THF and MeCN mixed solvent.

Electron paramagnetic resonance (EPR) measurement was performed at room temperature using a continuous-wave X-band Bruker Elexys 500 spectrometer operating at approximately 9.75 GHz. The samples $Li^+(tpn)^{\bullet-}(THF)_2$ (1 mg) and $Na^+(tpn)^{\bullet-}(THF)$ (0.8 mg) were analyzed in the solid state. Additionally, both samples were examined as 1 mM solutions (0.1 mL) in dry THF. All the samples were sealed in a quartz tube for the analysis. To calibrate the *g* value, a reference sample of 2,2-diphenyl-1-(2,4,6-trinitrophenyl) hydrazyl (DPPH) with a known *g* value of 2.0036 was used.

Magnetic susceptibility measurements were performed on a Quantum Design SQUID magnetometer MPMS-XL at temperatures between 1.85 and 300 K in an applied dc magnetic fields between -7 T and 7 T. The data were collected on crystalline powder samples of Li⁺(tpn)⁻⁻ (THF)₂ (19.6, 10.9 and 6.0 mg) and Na⁺(tpn)^{•-}(THF) (27.2 and 25.3 mg), sealed in polypropylene bags (size ~2 × 0.5 × 0.02 cm; mass ~10-15 mg) and additional outer polyethylene bags (size ~2 × 1 × 0.02 cm; mass ~10-15 mg) in a nitrogen or argon-filled glovebox to ensure a complete protection from oxygen and moisture. Measurements on three batches of Li⁺(tpn)^{•-}(THF)₂ revealed the presence of an unidentified diamagnetic species (most likely a residual unreduced tpn ligand). Its amount was estimated to be 0.5, 1.7 and 4.2 % in the three samples measured, respectively, based on the expected magnetic susceptibility for an isolated S = 1/2 spin. The data shown in Figure 4 at 0.1 T (measured between 1.85 and 100 K) are not corrected for the 0.5% diamagnetic impurity, while the data at 1 T (measured between 10 and 300 K) have been corrected for the diamagnetic species (scaling on the 0.1 T data) to highlight the reproducibility of the χT vs T measurements. The resulting magnetic data have been systematically corrected for the sample holder and in the case of Li⁺(tpn)^{•-}(THF)₂ for the intrinsic diamagnetic contribution.

b. Syntheses

Materials and methods

The syntheses of Li⁺(tpn)^{•-}(THF)₂ and Na⁺(tpn)^{•-}(THF) were carried under a dry argon atmosphere using a glovebox, dried glassware or standard Schlenk techniques unless otherwise stated. Diethyl ether (Et₂O), acetonitrile (CH₃CN), and tetrahydrofuran (THF) were purified using an Innovative Technologies solvent purification system and kept over 4 Å molecular sieves. Measured water contents < 5 ppm were quantified by Karl-Fischer titration. Terephthalonitrile was purchased from Alfa Aesar, sodium and lithium metal were purchased from Sigma-Aldrich, and used as received.

Synthesis of Li⁺(tpn)^{•–}(THF)₂

Lithium 1,2-dihydroacenaphthylenide was prepared by stirring 185 mg (1.2 mmol) of 1,2dihydroacenaphthylene with a 10-fold excess of lithium metal (83 mg, 12 mmol) in 5 mL of THF for 3 hours at room temperature.^[4] Meanwhile, 128.3 mg of terephthalonitrile (1.0 mmol) was dissolved in 12 mL of THF to form a clear colorless solution. The dark green reducing agent ($E_{1/2} = -3.2$ V in anhydrous THF vs. F_c/F_c^+) solution was then filtered through a fine sintered glass Büchner funnel under 10⁻¹ bar static vacuum and added dropwise to the terephthalonitrile solution. This resulted in an immediate color change to dark red and the precipitation of olivegreen crystals within 10 minutes. The crystals were collected by filtration using Whatman filter paper, washed three times with 5 mL of Et₂O, and allowed to stand in an argon atmosphere for 3 minutes to dry. Yield ~35% (98 mg, 0.35 mmol) based on the ligand.

This rapid and straightforward synthesis provided reproducible yields (~35%), characterizations (IR and UV-vis spectra, powder and single crystal X-ray diffraction data, EPR in solid state and THF solution, and magnetic susceptibility), and a homogeneous product, as illustrated by the photographs in Figure S1. However, the elemental analysis remained very challenging as this material was systematically decomposed during shipment to the site where the elemental analysis was performed. After more than 20 attempts to obtain a satisfactory elemental analysis, Li⁺(tpn)^{•-}(THF)₂ was synthesized on site with a slightly different method: a 100 mL ampoule closed by a J.Young Teflon in glass valve and containing a Pyrex coated stir bar dried under dynamic vacuum (10-3 bar) and terephthalonitrile (643 mg, 5.021 mmol) was loaded into the ampoule with finely divided Li metal (34 mg, 4.900 mmol) and ~10 mol % of 1,2dihydroacenaphthylene (7.8 mg, 0.0506 mmol). Anhydrous THF (60 mL) was added to the solids and the ampoule sealed. The mixture was sonicated at 25°C for 5 min and then stirred for 24 hours to afford a dark green solution over a microcrystalline dark-yellow precipitate. The mixture was stirred for 4 days with intermittent sonication (vide supra) until all the lithium metal had been consumed. The solid was collected by filtration on fine sintered glass funnel under argon, washed 2 x 5 mL of cold THF (-20°C) and dried under reduced pressure (0.1 bar for 10 min) to afford an olive-green microcrystalline solid. Collected 1.169 g, 4.216 mmol (Yield 84 %). Both methods led to reproducible characterizations (IR spectra and powder X-ray diffraction data), and a homogeneous product.

IR (solid, $\bar{\nu}/cm^{-1}$): 2981(m), 2872(m), 2132(s), 2107(vs), 2080(s), 1690(vw), 1662(vw), 1514(vw), 1486(vw), 1455(s), 1368(vw), 1298(w), 1290(m), 1227(s), 1207(w), 1161(vw), 1110(w), 1152(s), 979(m), 962(m), 915(m), 897(m), 744(vs), 665(s), 558(w), 508(vs).

Elemental analysis found (calcd) for $C_{16}H_{20}LiN_2O_2$: C 69.30(68.81), H 7.36(7.22), N 10.25(10.03).



Figure S1. Photographs of the crystals of Li⁺(tpn)^{•–}(THF)₂ under polarized light with two different orientations.

Synthesis of Na⁺(tpn)^{•–}(THF)

Method 1: A dark green solution of sodium 1,2-dihydroacenaphtylenide was prepared by stirring 185 mg (1.2 mmol) of 1,2-dihydroacenaphtylene over a 5-fold excess of sodium metal (138 mg, 6 mmol) in 5 mL of dried THF overnight. This solution was then filtered through a 0.2 μ m PTFE syringe filter and added dropwise to a clear THF solution (12 mL) of terephthalonitrile (128.3 mg, 1.0 mmol) in 12 mL THF, the color became dark red. Subsequently, about 50 mL of Et₂O was added and a large amount of green solid precipitated at the bottom of the vial. The final product is obtained by filtering on a fine sintered glass Buchner funnel. Yield: ~38 % yield based on the ligand.

Method 2: To a colourless solution of terephthalonitrile (641 mg; 5 mmol)-in THF (27 ml), sodium metal, cut into 2-3 mm pieces, (109 mg; 4.75 mmol) were added and the resulting mixture was stirred for 20h at room temperature, slowly turning the solution orange, then green. The resulting dark green precipitate is collected by filtration under vacuum (~80 % yield based on the ligand). Hexagonal green crystals, suitable for SCXRD and elemental analysis were obtained by slow diffusion of Et₂O into a filtered saturated solution of Na⁺(tpn)^{•-}(THF) in THF.

IR (solid, $\overline{\nu}/cm^{-1}$): 2873(vw), 2854(vw), 2109(vs), 2083(vs), 1571(vs), 1552(m), 1455(s), 1364(vw), 1284(w), 1228(s), 1151(vs), 1138(s), 1125(w), 1108(w), 1042(vs), 979(m), 961(m), 923(w), 905(w), 897(m), 776(vs), 759(m), 750(vs), 658(s), 650(s), 642(s), 561(w), 512(vs), 501(m).

Elemental analysis found (calcd) for $C_{12}H_{12}N_2NaO$: C 64.33(64.57), H 5.18(5.42), N 12.62(12.55).



Figure S2. Photographs of the crystals of Na⁺(tpn)^{•–}(THF) under polarized light with two different orientations.

2. Electrochemistry



Figure S3. Cyclic voltammograms of a 5.5 mM solution of terephthalonitrile in anhydrous THF, at 100 mV.s⁻¹ (in grey) and 50 mV.s⁻¹ (in green) scan rates, using a platinum working electrode, and 0.1 M (n-Bu₄N)PF₆ as supporting electrolyte. Note that while the first redox process at - 2.25 V remains reversible down to scan rates of 50 mV.s⁻¹, the second process at $E_{1/2}$ = -3.16V is shown here at 100 mV.s⁻¹, as the reversibility of both processes is altered at lower scan rates.



3. Electron paramagnetic resonance

Figure S4. Top plot: EPR spectra of polycrystalline samples of $Li^+(tpn)^{\bullet-}(THF)_2$ in blue line and solid $Na^+(tpn)^{\bullet-}(THF)$ in red line at room temperature. Bottom plot: EPR spectra of 1 mM solution of $Na^+(tpn)^{\bullet-}(THF)$ (red line) and $Li^+(tpn)^{\bullet-}(THF)_2$ (blue line) in dry THF at room temperature.

Comments: In the solid state, the broad EPR signal of $Li^{+}(tpn)^{\bullet-}(THF)_2$ is a signature of the radical tpn^{•-}, whereas Na⁺(tpn)^{•-}(THF) exhibits a narrow signal, with a double integration value about 1.4 compared to 35 for the Li analog suggesting about 4 % of free tpn^{•-} radical-anion after normalization with the mass. In THF solutions, the spectra are very similar to what has been reported in dimethoxyethane,^[5] tetrahydrofuran^[5] or mixtures,^[6] with hyperfine interactions with the N, H, Li or Na nuclear spins.

4. Spectroscopy



Figure S5. UV-Visible spectra of diluted solutions of $Li^{+}(tpn)^{\bullet-}(THF)_2$ (blue line) and $Na^{+}(tpn)^{\bullet-}(THF)$ (red line) in dry THF at room temperature.



Figure S6. FT-IR spectra (450 to 4000 cm⁻¹) of terephthalonitrile (black line), $Li^{+}(tpn)^{\bullet-}(THF)_{2}$ (blue line), and $Na^{+}(tpn)^{\bullet-}(THF)$ (red line) at room temperature.

5. Crystallographic Studies

Compound	Li ⁺ (tpn)•-(THF) ₂	Li ⁺ (tpn) ^{•-} (THF) ₂	Na ⁺ (tpn) ^{•–} (THF)
	at 120 K	at 250 K	at 120 K
Formula	$C_{16}H_{20}LiN_2O_2$	$C_{16}H_{20}LiN_2O_2$	C ₁₂ H ₁₂ NaN ₂ O
FW (g·mol⁻¹)	279.28	279.28	223.23
Crystal color	olive green	olive green	green
Crystal size (mm)	$0.20 \times 0.14 \times 0.04$	$0.20\times0.14\times0.04$	$0.30 \times 0.30 \times 0.10$
Crystal system	monoclinic	monoclinic	monoclinic
Space group	C2/c	<i>C</i> 2/c	C2/c
Temperature (K)	120	250	120
<i>a</i> (Å)	28.5128(17)	14.939(4)	20.749(2)
b (Å)	11.9757(7)	5.9609(16)	9.4724(10)
<i>c</i> (Å)	20.7828(11)	18.837(4)	11.9937(12)
α (°)	90	90	90
β (°)	118.145(3)	101.844(15)	101.200(3)
γ (°)	90	90	90
$V(\text{\AA}^3)$	6257.4(6)	1641.7(7)	2312.4(4)
Ζ	16	4	8
μ (mm ⁻¹)	0.077	0.074	0.115
$ heta_{\min}$ - $ heta_{\max}$	1.620°-25.128°	2.786°-24.146°	2.001°-26.095°
Refl. coll. / unique	24998 / 5572	5322 / 1281	23818 / 2297
Completeness to 2θ (%)	98.0	98.0	100
R _{int}	0.0810	0.0393	0.0754
Refined param./restr.	380 / 0	96 / 0	147 / 0
Goodness-of-fit	1.022	1.118	1.033
${}^{\mathrm{a}}R_1 (I > 2\sigma(I))$	0.0585	0.0703	0.0449
${}^{b}wR_{2}$ (all data)	0.1930	0.2597	0.1272
CCDC number	2351403	2351404	2351405

 Table S1. Single-Crystal X-ray diffraction data and structure refinements.

 ${}^{a}R_{1} = \Sigma ||F_{0}| - |F_{C}||/\Sigma |F_{0}|$ and ${}^{b}wR_{2} = [\Sigma w(F_{0}{}^{2} - F_{C}{}^{2})^{2}/\Sigma w(F_{0}{}^{2})^{2}]^{1/2}$



Figure S7. Simulated and experimental powder X-ray diffractograms of $Li^{+}(tpn)^{\bullet-}(THF)_2$ at 120 and 250 K with $\lambda = 0.69387$ Å.



Figure S8. Simulated and experimental powder X-ray diffractograms of Na⁺(tpn)^{•–}(THF) at 120 K with $\lambda = 0.72479$ Å.



Figure S9. Thermal evolution of the powder X-ray diffractograms of $Li^+(tpn)^{\bullet-}(THF)_2$ between 300 and 120 K upon cooling, from $2\theta = 2.5^{\circ}$ to $25^{\circ}(top \ plot)$ and a magnified view from $2\theta = 5.5^{\circ}$ to $13^{\circ}(bottom \ plot)$, with $\lambda = 0.69387$ Å.



Figure S10. Stick representation of the packing of the 3-D network of $Na^+(tpn)^{\bullet-}(THF)$ along the c axis at 120 K. Color code: C grey, N blue, O red, Na purple, H atoms are omitted for clarity.

6. Magnetism



Figure S11. Temperature (T) dependence of the magnetic susceptibility, χ , at 0.1 T (between 1.85 and 150 K) and 1 T (between 1.85 and 300 K) for Na⁺(tpn)^{•–}(THF) (where $\chi = M/H$ is the molar magnetic susceptibility normalized per formula unit). The solid red line is the best fit of the experimental data to the Curie law.

7. References

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