

## Supporting Information

### Synthetic Precursors for TCNQF<sub>4</sub><sup>2-</sup> Compounds: Synthesis, Characterization and Electrochemical Studies of (Pr<sub>4</sub>N)<sub>2</sub>TCNQF<sub>4</sub> and Li<sub>2</sub>TCNQF<sub>4</sub>

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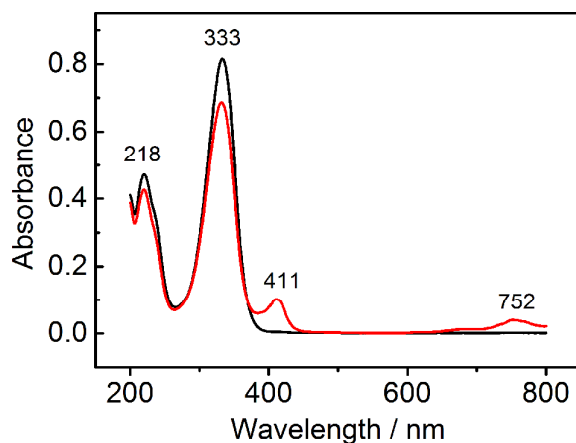
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### Stability of Li<sub>2</sub>TCNQF<sub>4</sub>

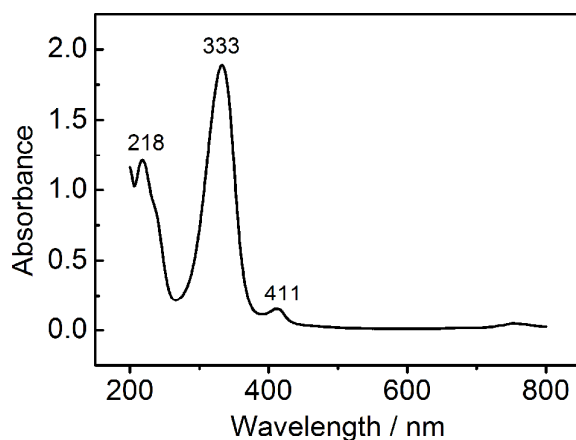
The UV-vis spectrum for freshly synthesized Li<sub>2</sub>TCNQF<sub>4</sub> dissolved in acetonitrile has two absorption bands at  $\lambda_{\text{max}} = 333$  and 218 nm (Figure S1 - black curve), which is characteristic of TCNQF<sub>4</sub><sup>2-</sup>.<sup>S1</sup> However, on exposure of the Li<sub>2</sub>TCNQF<sub>4</sub> solid to air over 15 days before dissolution in acetonitrile, two new bands appear with  $\lambda_{\text{max}} = 411$  and 752 nm (Figure S1 - red curve), which indicates that the Li<sub>2</sub>TCNQF<sub>4</sub> has been partially converted to TCNQF<sub>4</sub><sup>•-</sup>-based material.<sup>S1</sup> This is in contrast to the (Pr<sub>4</sub>N)<sub>2</sub>TCNQF<sub>4</sub> which is stable over months.



**Figure S1.** UV-vis spectra for Li<sub>2</sub>TCNQF<sub>4</sub>; black curve is for the freshly prepared solid dissolved in acetonitrile (0.02 mM) and the red curve is after 15 days exposure to the air.

### UV-vis Study of a Mixture of Li<sub>2</sub>TCNQF<sub>4</sub> and LiTCNQF<sub>4</sub>

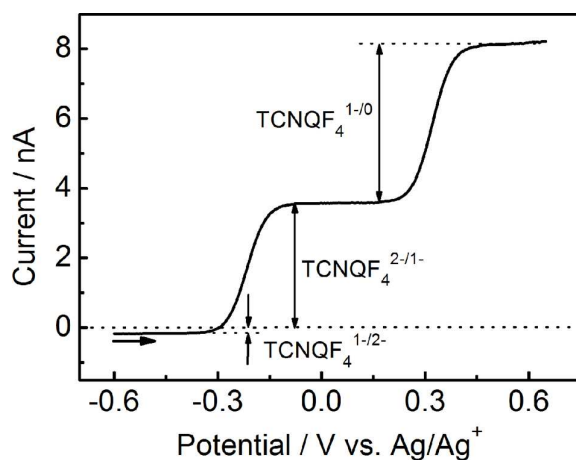
Absorption (UV-vis) spectroscopy was used for the quantitative determination of both TCNQF<sub>4</sub><sup>2-</sup> and TCNQF<sub>4</sub><sup>•-</sup> present in a mixture of Li<sub>2</sub>TCNQF<sub>4</sub> and LiTCNQF<sub>4</sub>. The absorption bands at 333 and 411 nm<sup>S1</sup> were used to calculate the amount of LiTCNQF<sub>4</sub> or Li<sub>2</sub>TCNQF<sub>4</sub> in a mixture. Figure S2 shows a typical experiment in which the crude product, generated via Pathway 1 (Scheme 1) using a 3:1 molar ratio of LiI and TCNQF<sub>4</sub> contained ~95% of TCNQF<sub>4</sub><sup>2-</sup> and ~5% of TCNQF<sub>4</sub><sup>•-</sup> (mole percent).



**Figure S2.** UV-vis spectrum in acetonitrile of the crude LiTCNQF<sub>4</sub> product from the reaction of a 3:1 molar ratio of LiI and TCNQF<sub>4</sub> as shown in Pathway 1 (Scheme 1).

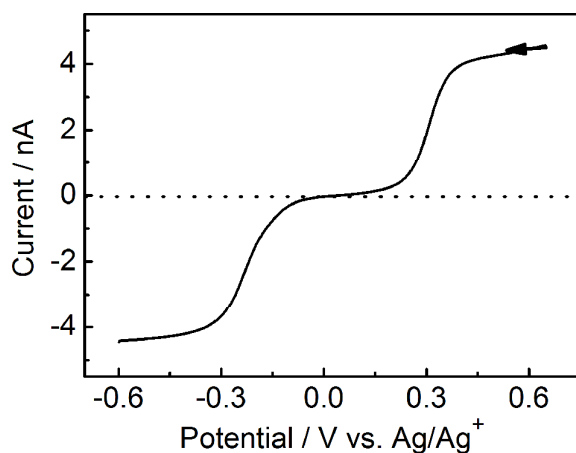
#### Electrochemical Study of a Mixture of Li<sub>2</sub>TCNQF<sub>4</sub> and LiTCNQF<sub>4</sub>

Steady-state voltammetry was also used to quantify the proportion of Li<sub>2</sub>TCNQF<sub>4</sub> and LiTCNQF<sub>4</sub> present in the mixture generated by Pathway 1 (Scheme 1) and also studied by UV-vis in Figure S2 (above). In the steady-state voltammetry the fact that there is a cathodic (reduction) current in solution at the initially applied potential (-0.6 V) reflects the presence of TCNQ<sup>•-</sup> in the initial solution, i.e. causing the reduction current. The limiting current both TCNQF<sub>4</sub><sup>2-/-•-</sup> and TCNQF<sub>4</sub><sup>•-/0</sup> waves upon anodic (oxidative) scan reflects the integrity of the TCNQF<sub>4</sub> redox processes in this solution; no competing chemical reactions are occurring. Furthermore the limiting current is proportional to concentration, hence together with the position of zero current can be used to quantify the molar percentage of TCNQF<sub>4</sub><sup>•-</sup> and TCNQF<sub>4</sub><sup>2-</sup> in the initial mixture (Figure S3). This method is a sensitive and quantitative confirmation of the data and conclusion from the UV-vis spectroscopy, i.e. that the crude product contained ~95% of Li<sub>2</sub>TCNQF<sub>4</sub> and ~5% of LiTCNQF<sub>4</sub>.



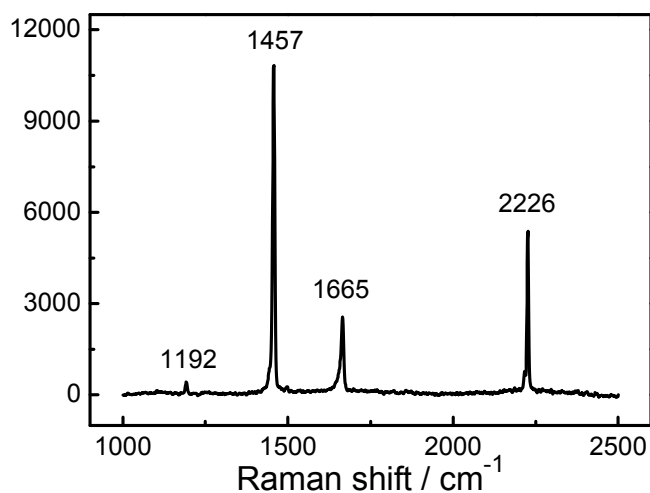
**Figure S3.** Near steady-state voltammogram for the product, synthesized via Pathway 1 (Scheme 1) using a 3:1 molar ratio of LiI and TCNQF<sub>4</sub> in acetonitrile (0.1 M Bu<sub>4</sub>NPF<sub>6</sub>) obtained with a 12.0  $\mu\text{m}$  diameter carbon fiber microelectrode at a scan rate of 20  $\text{mV s}^{-1}$ .

#### Electrochemistry of Pr<sub>4</sub>NTCNQF<sub>4</sub>



**Figure S4.** Near steady-state voltammogram for a 1.0 mM solution of Pr<sub>4</sub>NTCNQF<sub>4</sub> in acetonitrile (0.1 M Bu<sub>4</sub>NPF<sub>6</sub>) obtained with a 12.0  $\mu\text{m}$  diameter carbon fiber microelectrode at a scan rate of 20  $\text{mV s}^{-1}$ .

## Raman Spectrum of TCNQF<sub>4</sub>.



**Figure S5.** Raman spectrum for the neutral TCNQF<sub>4</sub> solid.

## X-ray Crystallographic Data

**Table S1.** Bond distances (Å) and angles (°) of hydrogen bonds for relevant crystallographic interactions for (Pr<sub>4</sub>N)<sub>2</sub>TCNQF<sub>4</sub>. The identity of each atom is shown in Figure 1a. D represents donor atom and A is the acceptor atom.

D-H----A	d(D-H) (Å)	d(H-A) (Å)	d(D-A) (Å)	<(DHA) (°)	Symmetry code
C12-H12C----F1	0.980	2.620	3.582	166.9	$\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$
C15-H15C----F1	0.980	2.629	3.584	164.9	$2-x, 1-y, -z$
C13-H13A----N1	0.990	2.707	3.512	138.7	$x, y-1, \frac{1}{2}-z$
C7-H7A----N2	0.990	2.559	3.509	161.1	$3/2-x, y-\frac{1}{2}, \frac{1}{2}-z$
C12-H12A----N2	0.980	2.744	3.652	154.4	$x, y-1, z$
C16-H16B----N2	0.990	2.603	3.503	151	$3/2-x, y-\frac{1}{2}, \frac{1}{2}-z$

**Table S2.** Bond distances (Å) and angles (°) of hydrogen bonds for relevant crystallographic interactions for Pr<sub>4</sub>NTCNQF<sub>4</sub>. The identity of each atom is shown in Figure 1a. D represents donor atom and A is the acceptor atom.

D–H---A	d(D–H) Å	d(H–A) Å	d(D–A) Å	<(DHA) °	Symmetry code
C22–H22A----F1	0.990	2.609	3.589	170.5	x, y, z
C21–H21B----F3	0.980	2.571	3.308	132.0	1–x, 1–y, –z
C19–H19A----N2	0.990	2.574	3.497	160.8	2/3–x, 1/2+y, 1/2–z
C19–H22B----N2	0.990	2.455	3.431	168.8	2/3–x, 1/2+y, 1/2–z
C15–H15C----N3	0.980	2.724	3.611	174.5	1+x, y, z
C18–H18B----N4	0.980	2.731	3.629	152.3	x, y, z
C23–H23A----N5	0.990	2.610	3.404	137.2	1/2+x, 3/2–y, 1/2+z

Crystal data for (Pr<sub>4</sub>N)<sub>2</sub>TCNQF<sub>4</sub> (CCDC: 831469): C<sub>18</sub>H<sub>28</sub>F<sub>2</sub>N<sub>3</sub>, *M* = 324.43, colorless block, 0.22 × 0.19 × 0.15 mm<sup>3</sup>, monoclinic, space group *P*2<sub>1</sub>/*n* (No. 14), *a* = 10.591(2), *b* = 11.791(2), *c* = 14.954(3) Å, *β* = 103.94(3)°, *V* = 1812.5(6) Å<sup>3</sup>, *Z* = 4, *D*<sub>c</sub> = 1.189 g/cm<sup>3</sup>, *F*<sub>000</sub> = 700, MoKα radiation, *λ* = 0.77343 Å, *T* = 123(2)K, 2*θ*<sub>max</sub> = 50.0°, 11403 reflections collected, 2478 unique (*R*<sub>int</sub> = 0.0352). Final *GoF* = 1.054, *R*1 = 0.0445, *wR*2 = 0.1078, *R* indices based on 2902 reflections with *I* > 2*sigma*(*I*) (refinement on *F*<sup>2</sup>), 212 parameters, 0 restraints. Lp and absorption corrections applied, *μ* = 0.085 mm<sup>–1</sup>.

Crystal data for Pr<sub>4</sub>NTCNQF<sub>4</sub> (CCDC: 831468): C<sub>24</sub>H<sub>28</sub>F<sub>4</sub>N<sub>5</sub>, *M* = 462.51, blue needle, 0.09 × 0.03 × 0.01 mm<sup>3</sup>, monoclinic, space group *P*2<sub>1</sub>/*n* (No. 14), *a* = 14.946(3), *b* = 7.1680(14), *c* = 22.136(4) Å, *β* = 103.01(3)°, *V* = 2310.6(8) Å<sup>3</sup>, *Z* = 4, *D*<sub>c</sub> = 1.330 g/cm<sup>3</sup>, *F*<sub>000</sub> = 972, ADSC Quantum 210r Detector, Synchrotron radiation, *λ* = 0.77343 Å, *T* = 123(2)K, 2*θ*<sub>max</sub> = 50.0°, 14654 reflections collected, 3145 unique (*R*<sub>int</sub> = 0.0478). Final *GoF* = 1.048, *R*1 = 0.0426, *wR*2 = 0.1087, *R* indices based on 3582 reflections with *I* > 2*sigma*(*I*) (refinement on *F*<sup>2</sup>), 302 parameters, 0 restraints. Lp and absorption corrections applied, *μ* = 0.103 mm<sup>–1</sup>.

## Reference

(S1) Le, T. H.; Nafady, A.; Qu, X.; Martin, L. L.; Bond, A. M. *Anal. Chem.* **2011**, 83, 6731-6737.