# Supplemental Information

## Architectural diversity in the solid-state behavior of crown ether and [2.2.2]-cryptand complexes of $K^+TCNQ^{\bullet-}$ salts

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# Index

| **TCNQ complex** | **1** | **2** | **3** | **4** | **5** |
|---|---|---|---|---|---|
| CSD ref code | 2119874 | 2119875 | 2119876 | 2119877 | 2119878 |
| Empirical Formula | $C_{42}H_{34}KN_{10}O_6$ | $C_{48}H_{46}N_{12}KO_6$ | $C_{40}H_{32}N_8KO_6$ | $C_{44}H_{32}N_8KO_6$ | $C_{56}H_{48}N_{12}KO_6$ |
| Formula ($gmol^{-1}$) | 813.89 | 926.07 | 759.84 | 807.87 | 1024.16 |
| Crystal System, space group | Monoclinic, *$P2_1/c$* | Monoclinic, *$P2_1/n$* | Monoclinic, *$P2_1/m$* | Triclinic *P-1* | Triclinic *P-1* |
| a/Å | 8.0740(2) | 8.0104(2) | 6.4442(1) | 7.8459(3) | 7.9514(2) |
| b/Å | 31.7168(5) | 36.7367(11) | 35.1206(6) | 14.5336(4) | 9.9644(3) |
| c/Å | 16.2190(3) | 15.8116(4) | 8.0868(2) | 17.8334(4) | 16.7703(4) |
| α/° | 90 | 90 | 90 | 96.620(1) | 87.136(2) |
| β/° | 100.863(2) | 98.291(3) | 99.840(2) | 93.222(2) | 79.011(2) |
| γ/° | 90 | 90 | 90 | 101.779(2) | 80.148(3) |
| Vol/$Å^3$ | 4078.96(14) | 4604.3(2) | 1803.31(6) | 1970.77(10) | 1284.91(7) |
| Temperature (K) | 100 | 100 | 100 | 120 | 100 |
| $D_x$ ($gm^{-3}$) | 1.325 | 1.336 | 1.399 | 1.361 | 1.324 |
| Abs coeff ($mm^{-1}$) | 0.191 | 0.179 | 0.209 | 0.196 | 0.168 |
| Crystal | Shiny black | Shiny black | Dark blue | Black | Bright purple |
| Z | 4 | 4 | 2 | 2 | 1 |
| F000 | 1692.0 | 1940.0 | 790.0 | 838.0 | 535.0 |
| h,k,lmax | 10, 41, 21 | 10, 47, 20 | 8, 45, 10 | 10, 18, 23 | 10, 12, 21 |
| R (reflections) | 0.0353(7494) | 0.0688(5909) | 0.0332(3771) | 0.0842(6598) | 0.0350(5173) |
| $wR_2$ (reflections) | 0.0916(9358) | 0.1632(10319) | 0.0908(4212) | 0.1698(8943) | 0.0979(5852) |

Table S1. Crystal structure data for ionophore alkali metal TCNQ complexes (**1-5**) in this study

| Complex | TCNQ dimer | π-π separation/Å | Long-axis slippage/Å | Short-axis slippage/Å | Ref. |
|---|---|---|---|---|---|
| **1.** (at 100 K) | AC | 3.17 | 2.12 | 0.32 | This work |
| | AB | 3.38 | 1.86 | 2.39 | |
| **2.** (at 100 K) | AC | 3.08 | 1.95 | 0.15 | This work |
| | AB | 3.24 | 1.96 | 0.38 | |
| **3.** (at 100 K) | AA* | 3.18 | 1.98 | 0.028 | This work |
| **4.** (at 120 K) | AB | 3.12 | 2.15 | 0.012 | This work |
| **5.** (at 100 K) | AA' | 3.05 | 2.17 | 0.015 | This work |
| **6.** (at r.t.) | AB | 3.23 | 0.08 | 0.33 | [1, 2] |
| **7.** (ambient) | AB | 3.15 | 0.03 | 1.00 | [3] |

Table S2. Key structural data for TCNQ dimers in the complexes (**1-5**) discussed here with comparative literature data (r.t. = room temperature, see Fig 3 for the definitions of long- and short-axis slippage).

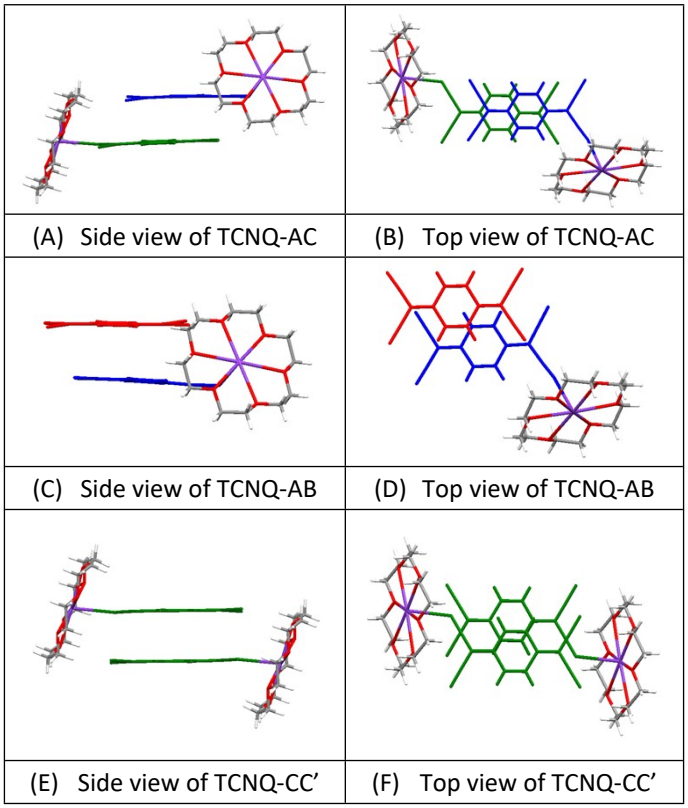



Fig S1. Side (A/C/E) and top (B/D/F) views of TCNQ units in (18-crown-6)K(TCNQ)$_{2.5}$ (**1**).

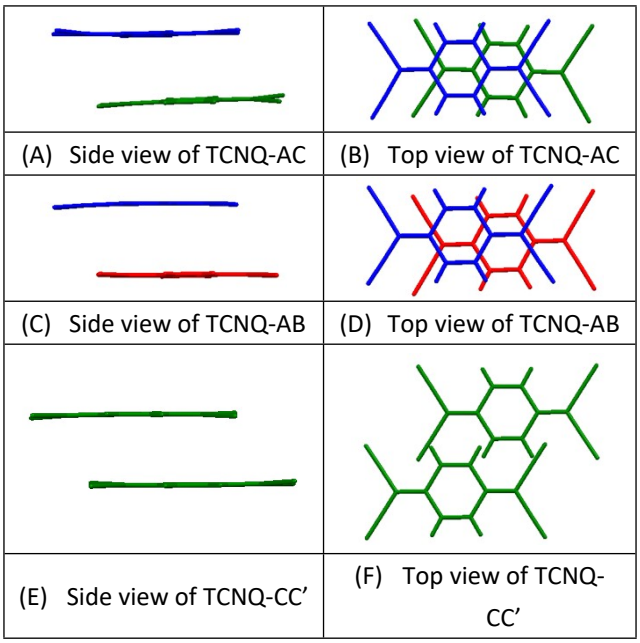
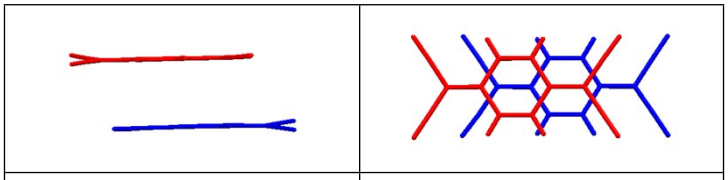
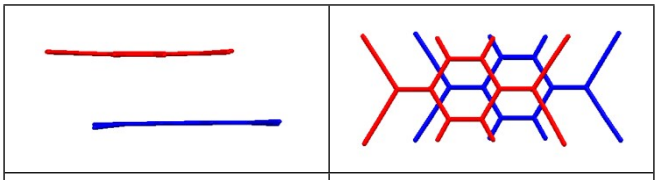



Fig S2. Side (A/C/E) and top (B/D/F) views of TCNQ units in (2.2.2-cryptand)K(TCNQ)$_{2.5}$ (**2**).



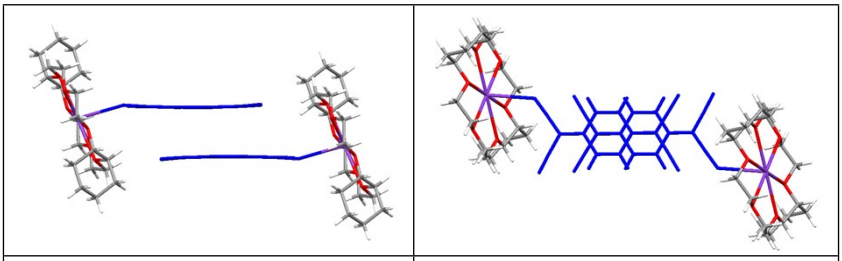
(A) Side view of TCNQ-AA* | (B) Top view of TCNQ-AA*

Fig S3. Side (A) and top (B) views of TCNQ units in (benzo-18-crown-6)K(TCNQ)$_2$ (**3**).



(A) Side view of TCNQ-AB | (B) Top view of TCNQ-AB

Fig S4. Side (A) and top (B) views of TCNQ units in (dibenzo-18-crown-6)K(TCNQ)$_2$ (**4**).



(A) Side view of TCNQ-AA' | (B) Top view of TCNQ-AA'

Fig S5. Side (A) and top (B) views of TCNQ units in (dicyclohexano-18-crown-6)K(TCNQ)$_3$ (**5**).

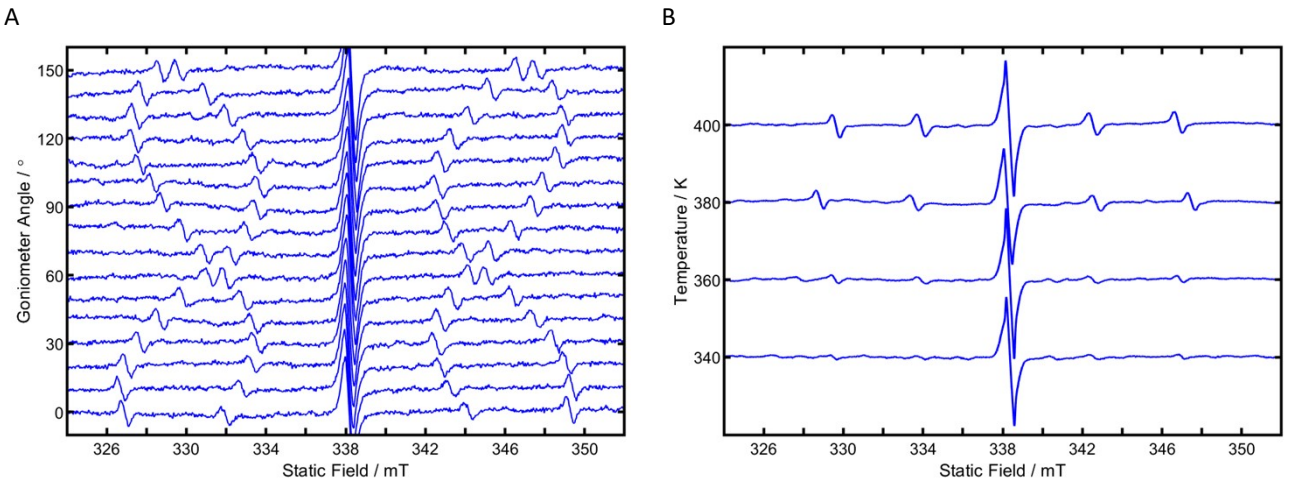



Fig S6. The EPR results of (18-crown-6)KTCNQ (**6**) re-measured for this study showing (A) angular dependence of the triplet exciton signals at 380 K and (B) growth of the triplet exciton signals with increasing temperature for an arbitrary fixed orientation. Two spectral doublets arise from the crystallographically distinct TCNQ dimer columns. In both cases microwave power was 0.8 mW in a $TM_{110}$ cavity with 0.50 mT modulation amplitude used to aid observation of the small thermally populated exciton signals. The higher signal to noise in (B) is due to increased signal averaging necessary to discern the weak exciton signals at lower temperatures. Spectra were baseline corrected in MATLAB® using the EasySpin `basecorr` command to apply a second order polynomial correction.[4]

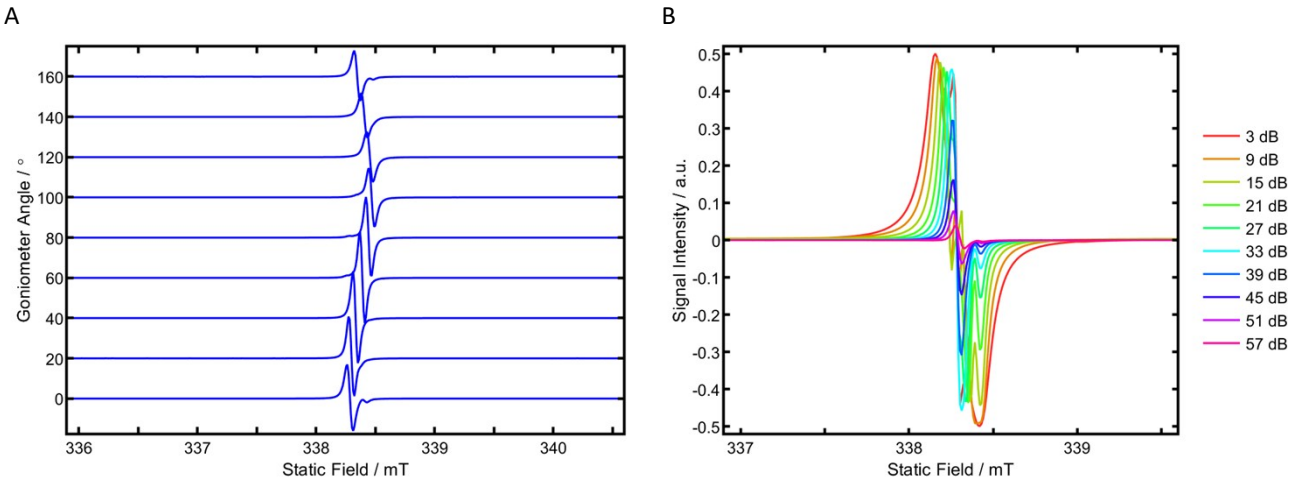



Fig S7. Preliminary EPR of (2.2.2-cryptand)K$(TCNQ)_{2.5}$ (**2**) at 295 K showing (A) weak angular dependence of the anisotropic EPR signal and (B) power saturation with microwave attenuation values as shown. The signal varies in the linear regime (double intensity for 6 dB increase in power) for attenuations of 39 dB or more and while the complex lineshape changes at higher powers (lower attenuation) have not been fully interpreted they imply multiple overlapping signals, with decreasing intensity of the central component indicative of a long relaxation time. The angular dependence data in A is recorded for 39 dB attenuation (~25 µW microwave power). In both cases spectra were recorded in a $TM_{110}$ cavity with 50 µT modulation amplitude and for clarity only the central portion of the 5.0 mT sweep is shown.

1. M. C. Grossel and S. C. Weston, *J. Phys. Org. Chem.*, 1992, **5**, 533-539.
2. R. C. Hynes, J. R. Morton, K. F. Preston, A. J. Williams, F. Evans, M. C. Grossel, L. H. Sutcliffe and S. C. Weston, *J. Chem. Soc., Faraday Trans.*, 1991, **87**, 2229-2233.
3. M. C. Grossel and S. C. Weston, *Chem. Mater.,* 1996, **8**, 977-980.
4. S. Stoll and A. Schweiger, *J. Magn. Reson.*, 2006, **178**, 42-55.