A new class of easily generated $TCNQ^{2-}$-based coordination polymers

Brendan F. Abrahams*, Robert. E. Elliott, Timothy A. Hudson and Richard Robson*

School of Chemistry, University of Melbourne, Victoria 3010, Australia.

Supporting Information

Prof Richard Robson
School of Chemistry
University of Melbourne
Victoria
AUSTRALIA
Email: r.robson@unimelb.edu.au
Ph. +61 3 8344 6469
Fax: +61 3 9347 5180

Assoc. Prof. Brendan F. Abrahams
School of Chemistry
University of Melbourne
Victoria
AUSTRALIA
Email: bfa@unimelb.edu.au
Ph. +61 3 8344 0341
Fax: +61 3 9347 5180

1. Syntheses:

The general procedure used to obtain crystalline products was to place a methanolic solution containing the metal salt nitrate together with the pyridine-derived ligand over a solution of $TCNQH_2$ in dimethylformamide. Crystals, suitable for X-ray diffraction studies were generally obtained after 12 – 24 hours. Although most of the preparations could be carried out satisfactorily without precaution to exclude air, there were indications of some air oxidation in some cases where standing for several days was necessary for substantial crystal growth. We therefore routinely carried out the preparations very simply under a dinitrogen atmosphere in vials capped with subaseals, although in many cases this precaution was unnecessary. Typical procedures were as follows:

1.1 [Zn(TCNQ)(nicotinamide)$_2$]solvate: A solution of $TCNQH_2$ (20 mg, 0.097 mmol) in DMF (1 mL) was carefully layered by syringe below a solution of $Zn(NO_3)_2.6H_20$ (28.8 mg, 0.097 mmol), $LiOAc.2H_20$ (16.5 mg, 0.16 mmol) and nicotinamide (23.7 mg, 0.19 mmol) in methanol (3 mL). Pale yellow needles (8.7 mg) suitable for X-ray diffraction separated. Anal. Calcd for $C_{27}H_{23}N_9O_3Zn$, ie. [Zn(TCNQ)(nicotinamide)$_2$]1DMF, C, 55.3; H, 4..0; N, 21.5. Found: C, 54.9; H, 3.4; N, 21.2 %. IR (KBr, cm^{-1}): ν(CN) 2134 and 2195.

1.2 [Zn(TCNQ)(phenylpyridine)$_2$]solvate: A solution of $TCNQH_2$ (20 mg, 0.097 mmol) in DMF (1 mL) was carefully layered by syringe below a solution of $Zn(NO_3)_2.6H_20$ (28.8 mg, 0.097 mmol), $LiOAc.2H_20$ (16.5 mg, 0.16 mmol) and 4-phenylpyridine (30.1 mg, 0.19 mmol) in methanol (3 mL). Pale yellow crystals (27.8 mg)

suitable for X-ray diffraction separated. Anal. Calcd for $C_{34.75}H_{25}N_6O_{0.75}Zn$, ie. [Zn(TCNQ)(phenylpyridine$_2$]0.75MeOH, C, 69.1; H, 4.2; N, 13.9. Found: C, 68.8; H, 3.9; N, 14.3 %. IR (KBr, cm^{-1}): ν(CN) 2126 and 2191.

1.3 [Co(TCNQ)(quinoline$_2$]solvate: A solution of $TCNQH_2$ (10 mg, 0.048 mmol) in DMF (1 mL) was carefully layered by syringe below a solution of $Co(NO_3)_2.6H_20$ (14.4 mg, 0.049 mmol), $LiOAc.2H_20$ (16.5 mg, 0.16 mmol) and quinoline (23 μL, 0.097 mmol) in methanol (6 mL). Dark purple crystals (28.5 mg) suitable for X-ray diffraction separated. Anal. Calcd for $C_{33}H_{25}N_7O_1Co$, ie. [Co(TCNQ)(quinoline$_2$]1DMF, C, 66.7; H, 4.2; N, 16.5. Found: C, 66.1; H, 3.6; N, 16.4 %. IR (KBr, cm^{-1}): ν(CN) 2135 and 2198.

1.4 [Mn(TCNQ)(bipy)]solvate: A solution of $Mn(OAc)_2.4H_2O$ (119 mg, 0.48 mmol) in MeOH (15 ml) was diffused into a solution of $TCNQH_2$ (100 mg, 0.48 mmol) and 4,4,-bipyridine (75.7 mg, 0.48 mg) in DMF (3 mL). Orange crystals (44.0 mg) separated overnight. Anal. Calcd for $C_{22}H_{16.75}N_6O_{2.38}Mn$, ie. [Mn(TCNQ)(bipy)]2.4H_2O: C, 57.6; H, 4.3; N, 18.3. Found: C, 57.7; H, 3.7; N, 18.3 %. IR (KBr, cm^{-1}): ν(CN) 2119 and 2186.

1.5 [Cd(TCNQ)(bipy$_2$]solvate: A solution of $Cd(OAc)_2.4H_2O$ (129 mg, 0.48 mmol) in MeOH (15 ml) was diffused into a solution of $TCNQH_2$ (100 mg, 0.48 mmol) and 4,4,-bipyridine (75.7 mg, 0.48 mg) in DMF (3 mL). Orange crystals (56 mg) separated overnight. Anal. Calcd for $C_{20}H_{18.5}N_6O_{3.75}Cd$, ie. [Cd(TCNQ)(bipy)]1.4 H_2O, C, 53.1; H,

3.0; N, 16.9. Found: C, 53.1; H, 2.9; N, 16.8 %. IR (KBr, cm^{-1}): ν(CN) 2117 and 2189.

1.6 [Zn(TCNQ)(Obip)$_{1/2}$](MeOH)(DMF): To a solution of $TCNQH_2$ (100 mg, 0.48 mmol) and $Zn(NO_3)_2$. $6H_20$ (145 mg, 0.48 mmol) in DMF (6 mL) was added a solution of 4,4'-bipyridine-di-N-oxide (45.6 mg, 0.24 mmol) and $LiOAc.2H_20$ (99.0 mg, 0.96 mmol) in MeOH (10 ml). Dark red crystals separated from the solution overnight (178 mg). Anal. Calcd for $C_{20}H_{18.5}N_6O_{3.75}Zn$, ie. [Zn(TCNQ)(Obip)$_{1/2}$].DMF. $3.75H_2O$, C, 51.3; H, 4.0; N, 17.9. Found: C, 51.2; H, 3.9; N, 17.8 %. IR (KBr, cm^{-1}): ν(CN) 2127 and 2193.

2. Crystallographic details

All data were collected on an Oxford Excalibur diffractometer except for [Zn(TCNQ)(nicotinamide)]DMF which was collected at the Australian Synchrotron. Data reduction was performed using Chrysalis software. Structural solutions and refinements were performed using SHELX97[1].

In some of the structures the presence of highly disordered solvent molecules within the channels prevented sensible modeling for the solvent molecules. In these cases the SQUEEZE routine within PLATON[2] was used to generate reflection data that does not include a contribution from the diffuse solvent. The number of solvent molecules in the unit cell was estimated from the void volume and the number of electrons calculated in the solvent region.

Most of the structures showed at least some degree of twinning which, to various extents, hampered the structure determination. Often it was necessary to perform a number of data collections in order to be able to choose the data set least affected by the twinning.

In general, the strategy employed to deal with the twinning, involved excluding overlapping reflections from the data used in the solution and refinement. While this normally led to a satisfactory refinement it did impact on the completeness of data which in the case of [Zn(TCNQ)(quinoline)$_2$]DMF dropped to only 92%. In the case of [Zn(TCNQ)(pyridine)$_2$].1/2MeOH a more satisfactory refinement was achieved by using the TWIN data reduction procedure within the Crysalis software.

The structures of [Zn(TCNQ)(4-phenylpyridine)$_2$].2MeOH and [Cd(TCNQ)(bpe)].8MeOH were refined as primitive monoclinic structures. Symmetry checking software (Addsym routine within PLATON) raised the possibility that the cells were in fact C-centered in the case of [Zn(TCNQ)(4-phenylpyridine)].2MeOH or A-centred in the case of [Cd(TCNQ)(bpe)].8MeOH. Crude solutions were obtained in the centered cells but R values proved to be considerably higher. A check of the reflection data after being transformed into the respective centered cells clearly revealed the presence of reflections that should have been absent if the cells were truly centered.

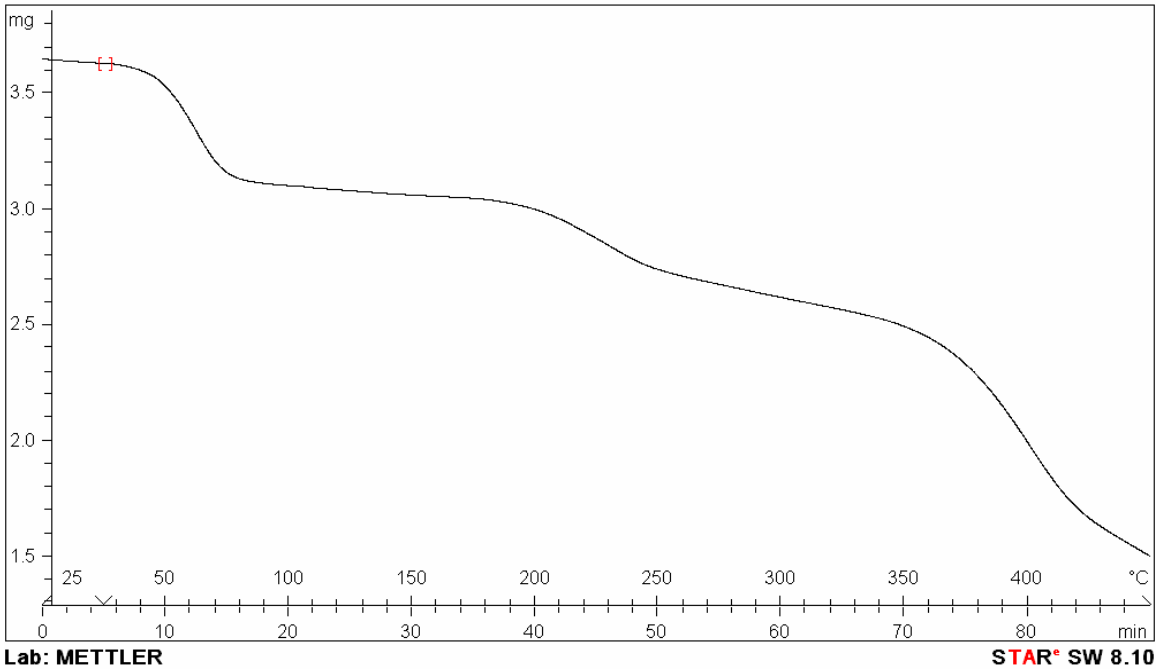
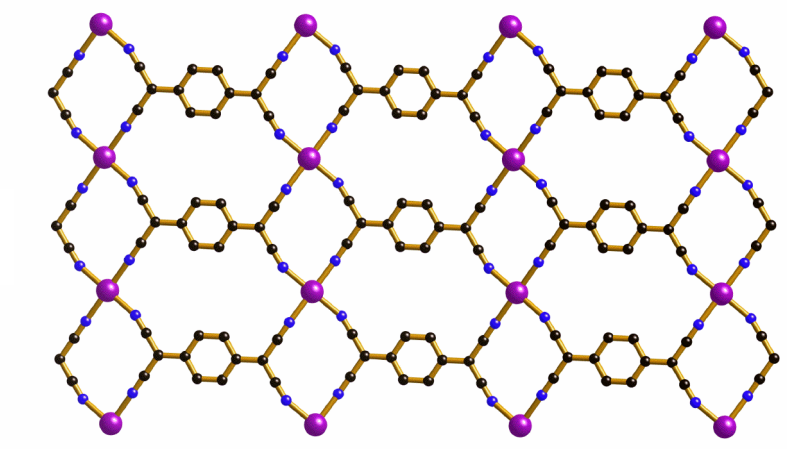


Figure S1. TGA of [Zn(TCNQ)(Obip)$_{1/2}$].MeOH.DMF.

a)



b)

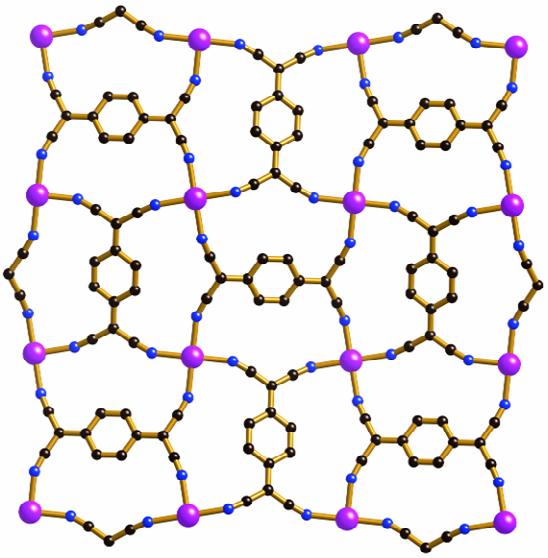


Figure S2. Representations of M^{II}(TCNQ) sheets showing the metal centres in a) square and b) rectangle arrangement.

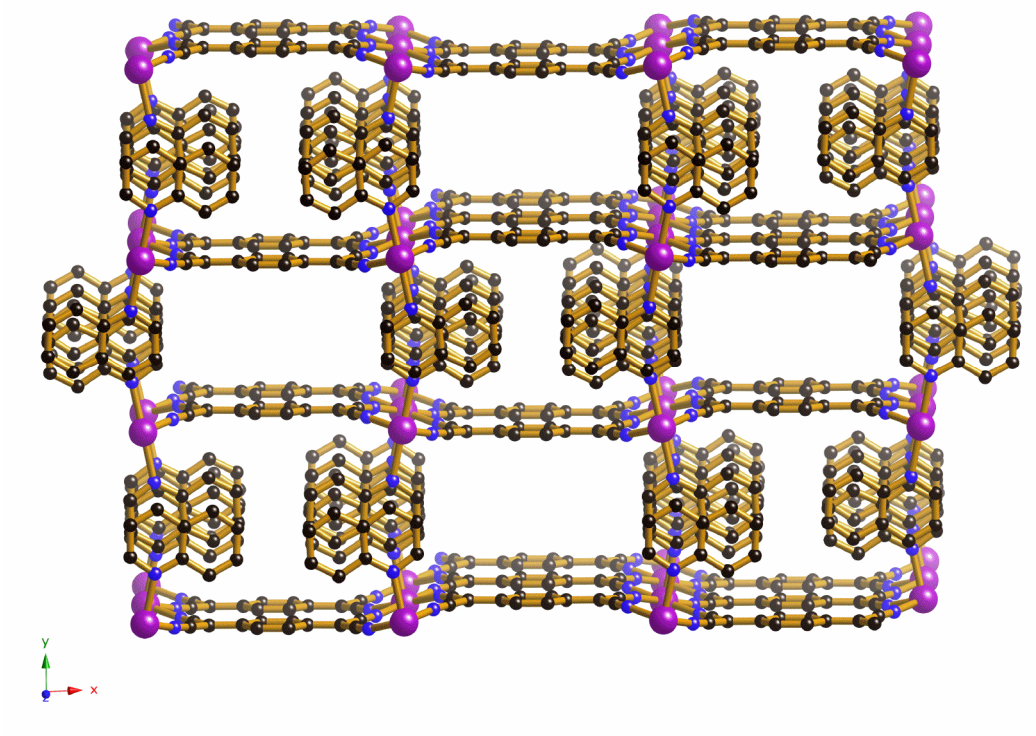


Figure S3. A view down the *z* axis of [Zn(TCNQ)(quinoline)]solvate showing the two types of channels within the network .

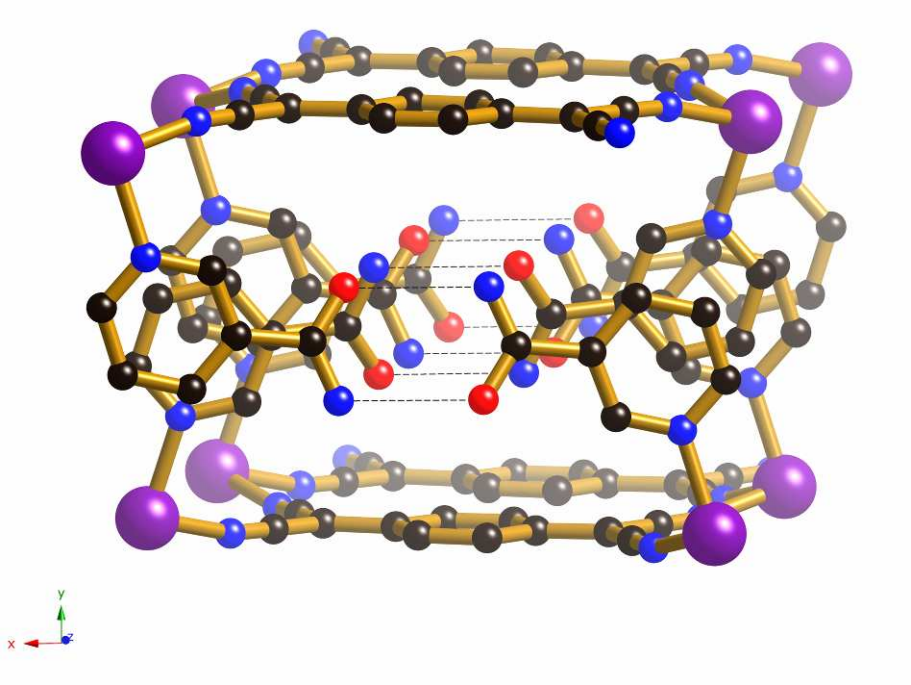


Figure S4. A view down a single channel in [Zn(TCNQ)(nicotinamide)] highlighting the complementary hydrogen bonds (represented by dashed lines) between neighbouring nicotinamide units.

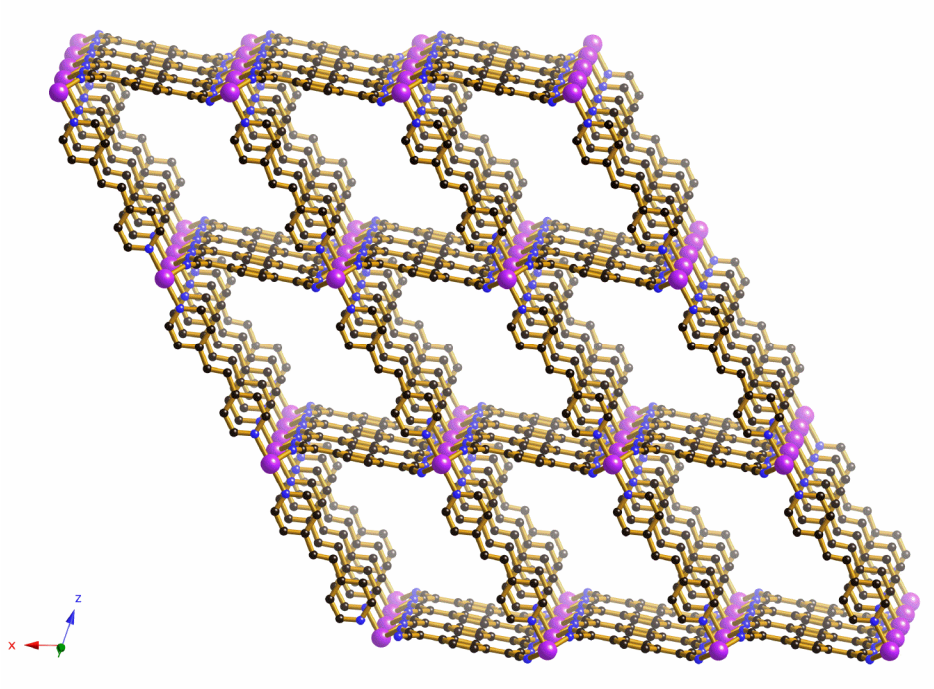


Figure S5. The [Zn(TCNQ)(bpe)] network

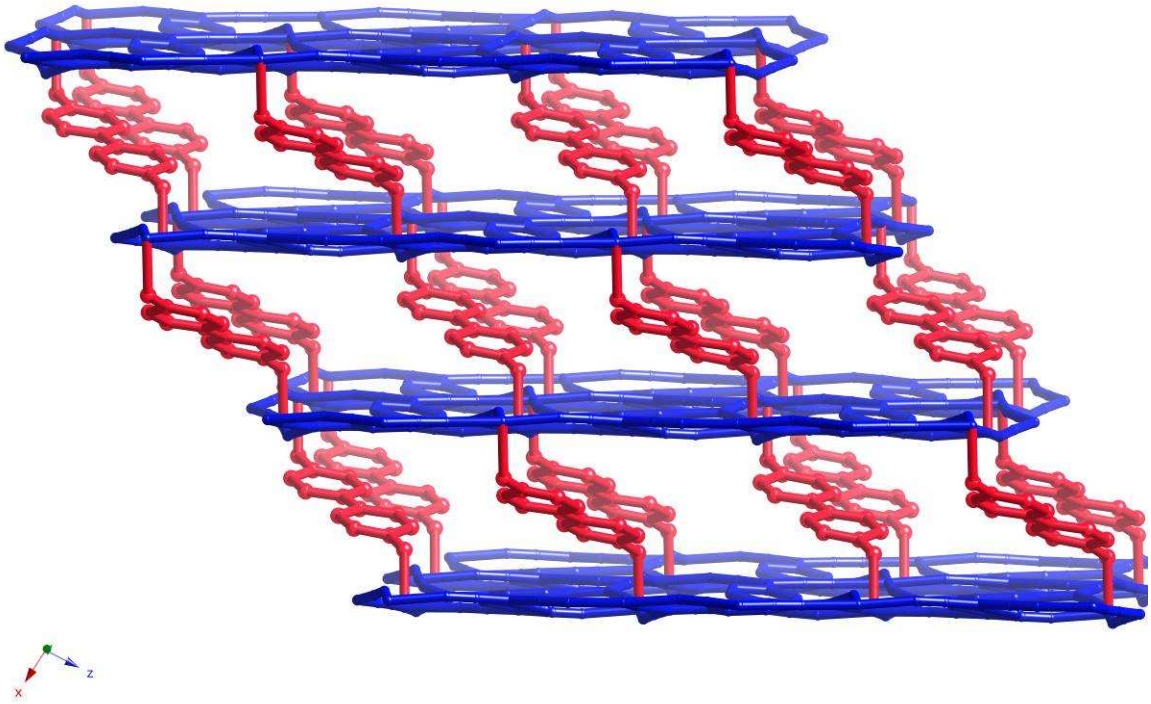


Figure S6. A representation of the [Zn(TCNQ)(Obip)] network. The [Mn(TCNQ)] are represented in blue and the Obip ligands represented in red. The coordinated MeOH molecules have been omitted.

References

(1). (a)"A short history of SHELX". Sheldrick, G.M.. Acta Cryst. **2008**, *A64*, 112 (b)

(2) Reference: A.L.Spek (2005) PLATON, A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands.

(3) L. J. Farrugia, *J. Appl. Crystallogr.*, **1999**, **32**, 837