Electronic Supplementary Material (ESI) for Chemical Communications

Cadmium TCNQ-Based Semiconductor with Versatile Binding Modes and Non-Integer Redox States

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Supporting information

Figure S1-5.

X-ray crystallographic details.

Table S1-2.

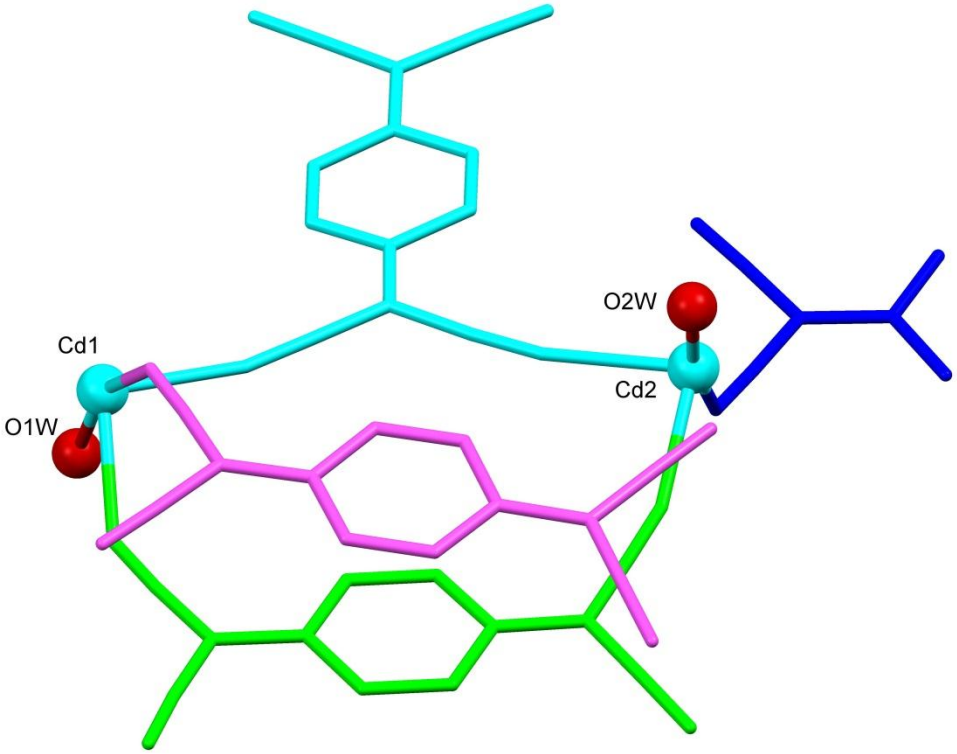


Figure S1. The asymmetric unit with half of an *anti*-*anti*-μ^2-TCNQ (in blue) lying across an inversion centre. Color-coding is the same as in Fig. 2.

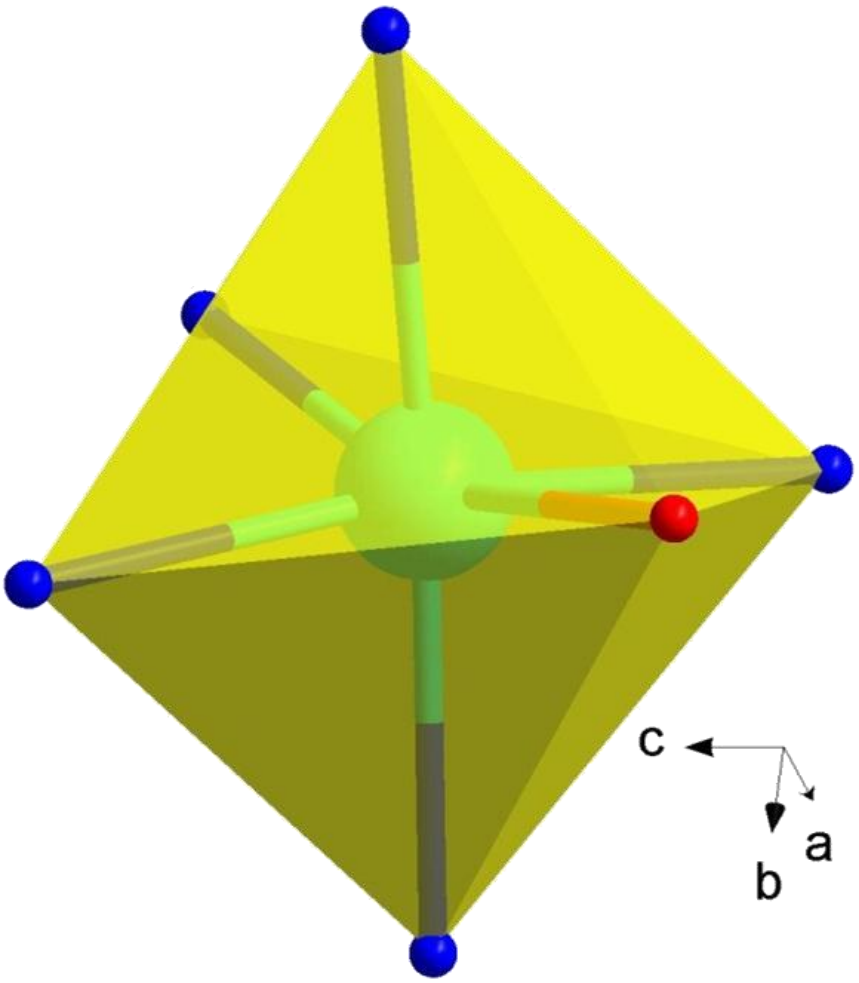


Figure S2. The coordination sphere of Cd showing the highly distorted octahedral geometry. Cd: turquoise; N: blue; O: red.

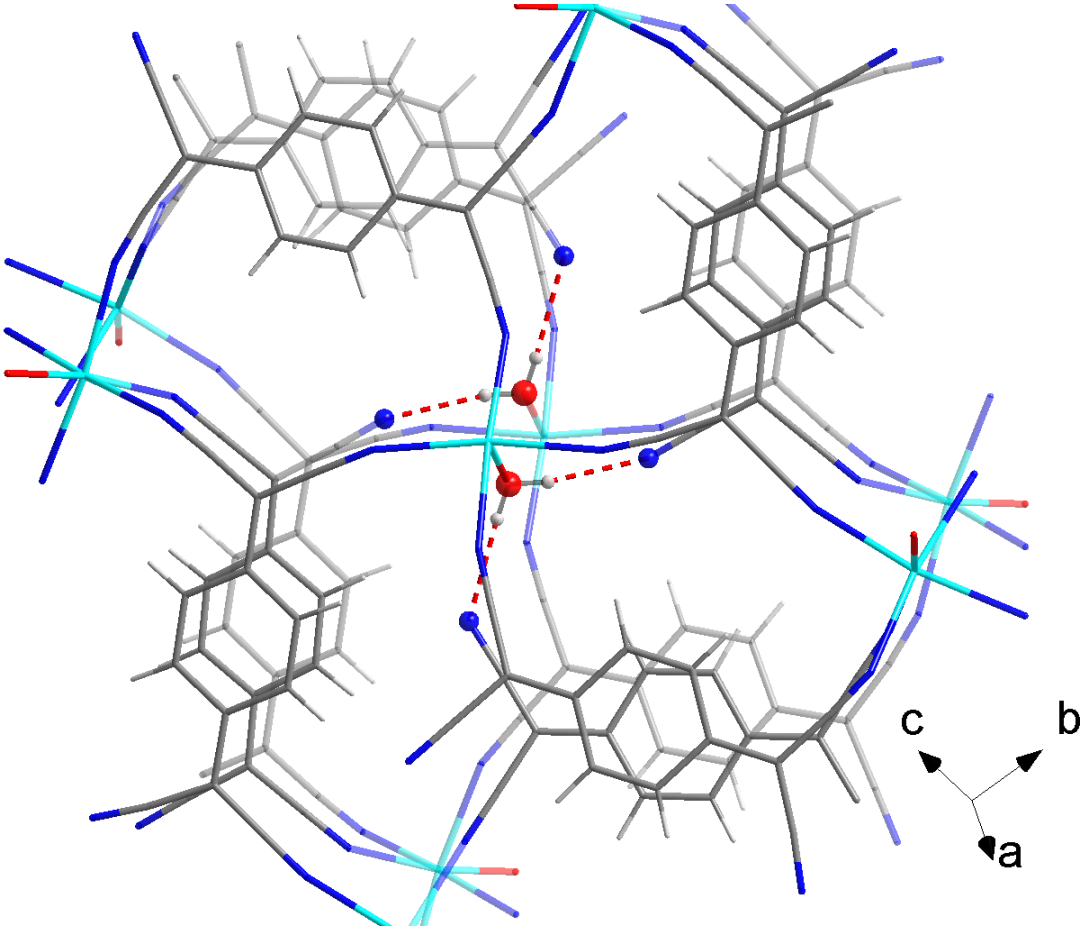


Figure S3. Packing diagram highlighting the hydrogen bonding interactions between water molecules and the nitrogen atoms of the TCNQ species in the structure. The O-N distances are ~2.8 angstroms.

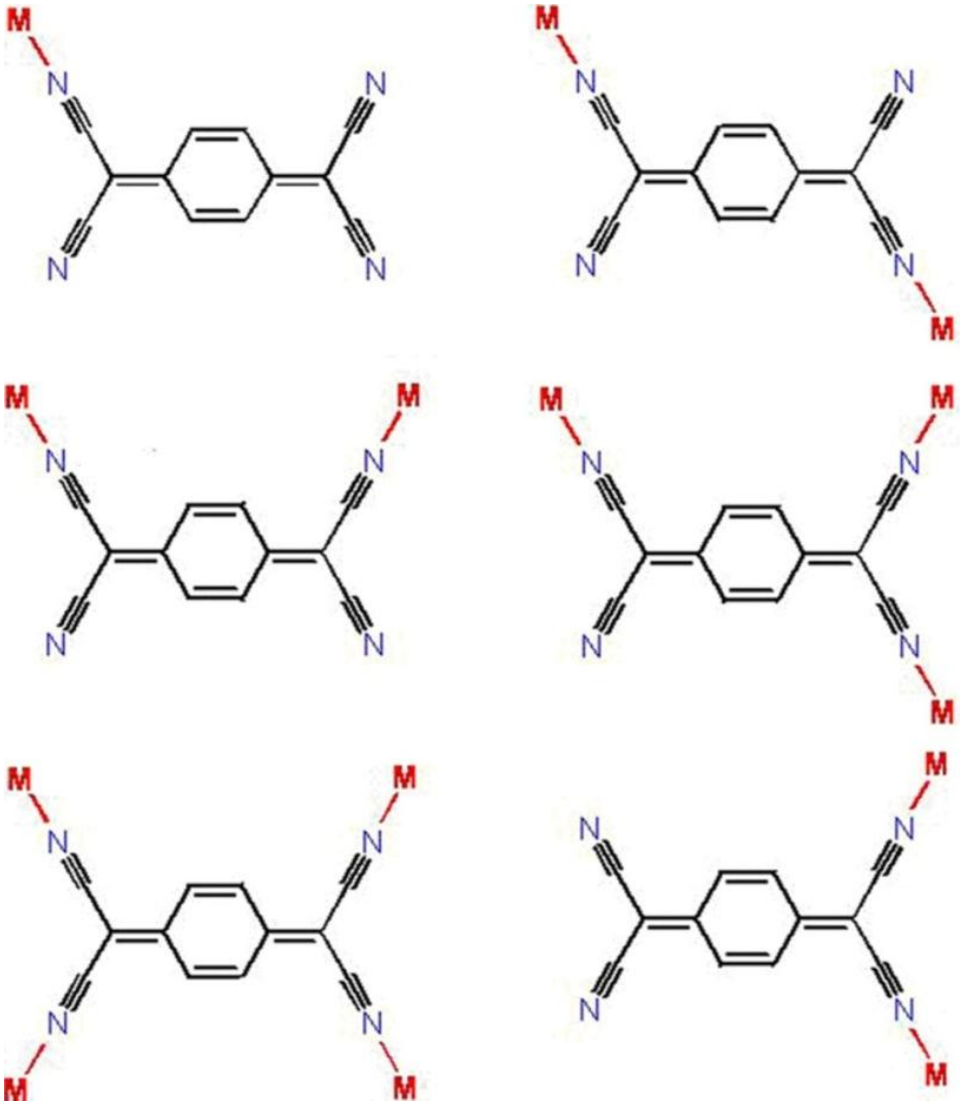


Figure S4. Possible binding modes for TCNQ.

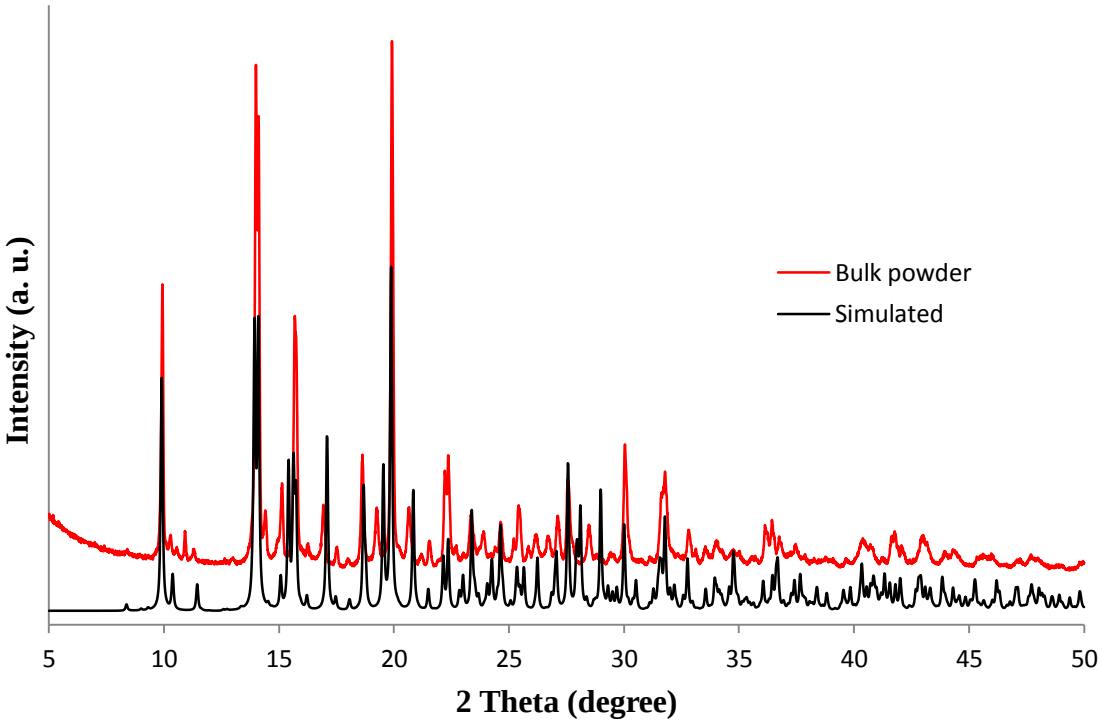


Figure S5. The powder X-ray diffraction pattern of the bulk phase in red compared to the simulated pattern of the single crystal in black.

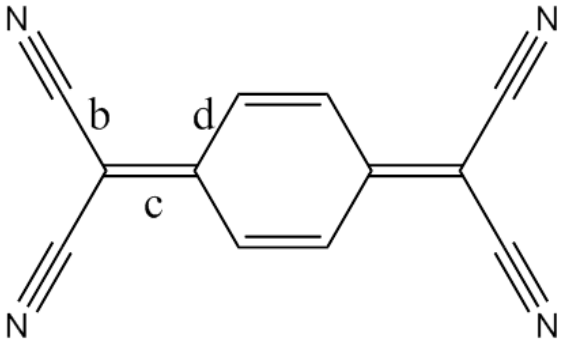
X-ray Crystallography

Single-crystal X-ray data were collected at 110 K on a Bruker APEX CCD diffractometer equipped with a graphite monochromated MoKα radiation source (λ=0.71073 Å). A dark purple crystal was affixed onto a nylon loop with Paratone oil and place in a cold steam of N_2(g) at 110(2) K. The data sets were recorded as three ω-scans of 606 frames each, at 0.3° step width, and integrated with the Bruker SAINT[1] software package. The absorption correction (SADABS)[2] was based on fitting a function to the empirical transmission surface as sampled by multiple equivalent measurements. Solution and refinement of the crystal structures were carried out using the SHELX[3] suite of programs and the graphical interface X-SEED.[4] Preliminary indexing of the data established a monoclinic unit cell. And systematic extinctions indicated a space group $P2_1/c$. The structure was solved by direct methods that resolved the positions of the metal atoms and most of the C and N atoms. The remaining non-hydrogen atoms were located by alternating cycles of least-squares refinements and difference Fourier maps. Hydrogen atoms were placed at calculated positions. The final refinement was carried out with anisotropic thermal parameters for all non-hydrogen atoms. A summary of pertinent information relating to the unit cell parameters are provided in Table S1. CCDC 885983 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S1. Crystal data and details of the refinement parameters for the compound.

Formula	$C_{42}H_{18}Cd_2N_{14}O_2$
Formula Mass	975.50 g/mol
Space group	P2(1)/c (No. 14)
Unit cell	a = 19.061(4) Å b = 12.717(3) Å c = 15.548(3) Å β = 95.24(3)°
Unit cell volume, V	3753(1)Å^3
Z	4
Density, ρ_{calc}	1.726 g/cm^3
Abs. coeff., μ	1.193 mm^{-1}
Crystal color and habit	Dark purple needle
Crystal size	0.15 x 0.09 x 0.07 mm
Temperature	110 K
Radiation, λ	Mo-Kα, 0.71073 Å
Reflections collected	32182
Independent reflections	5785
Data/parameters/restraints	5487 / 557 / 0
R [$F_o > 4\sigma(F_o)$]	R_1 = 0.0206 wR_2 = 0.0523
G.o.f. on F^2	1.020
Maximum and minimum residual densities, e·Å^{-3}	0.36, -0.36

Table S2. The charges (ρ) of different TCNQ species in $[Cd_2(TCNQ)_{3.5}(H_2O)_2]_\infty$ estimated from Kistenmacher's formula.[5]



	b	c	d	ρ
A	1.422	1.403	1.430	-0.66
B	1.419	1.420	1.420	-1.00
C	1.413	1.424	1.419	-1.11
D	1.408	1.448	1.410	-1.57

References

1. SMART and SAINT, Siemens Analytical X-ray Instruments Inc., Madison, WI, 1996.
2. SADABS, Sheldrick, G. M. University of Gottingen, Gottingen, Germany, 1996.
3. SHELXS-97 and SHELXL-97, Sheldrick, G. M. University of Gottingen Gottingen, Germany, 1997.
4. Barbour, L. J. *Journal of Supramolecular Chemistry* **2001**, *1*, 189.
5. Kistenmacher, T. J.; Emge, T. J.; Bloch, A. N.; Cowan, D. O. *Acta Crystallographica Section B* **1982**, *38*, 1193.