Electronic Supplementary Material (ESI) for RSC Advances

Reusable surface confined semi-conducting metal-TCNQ and metal-TCNQF$_4$ catalysts for electron transfer reactions†

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Supplementary Information

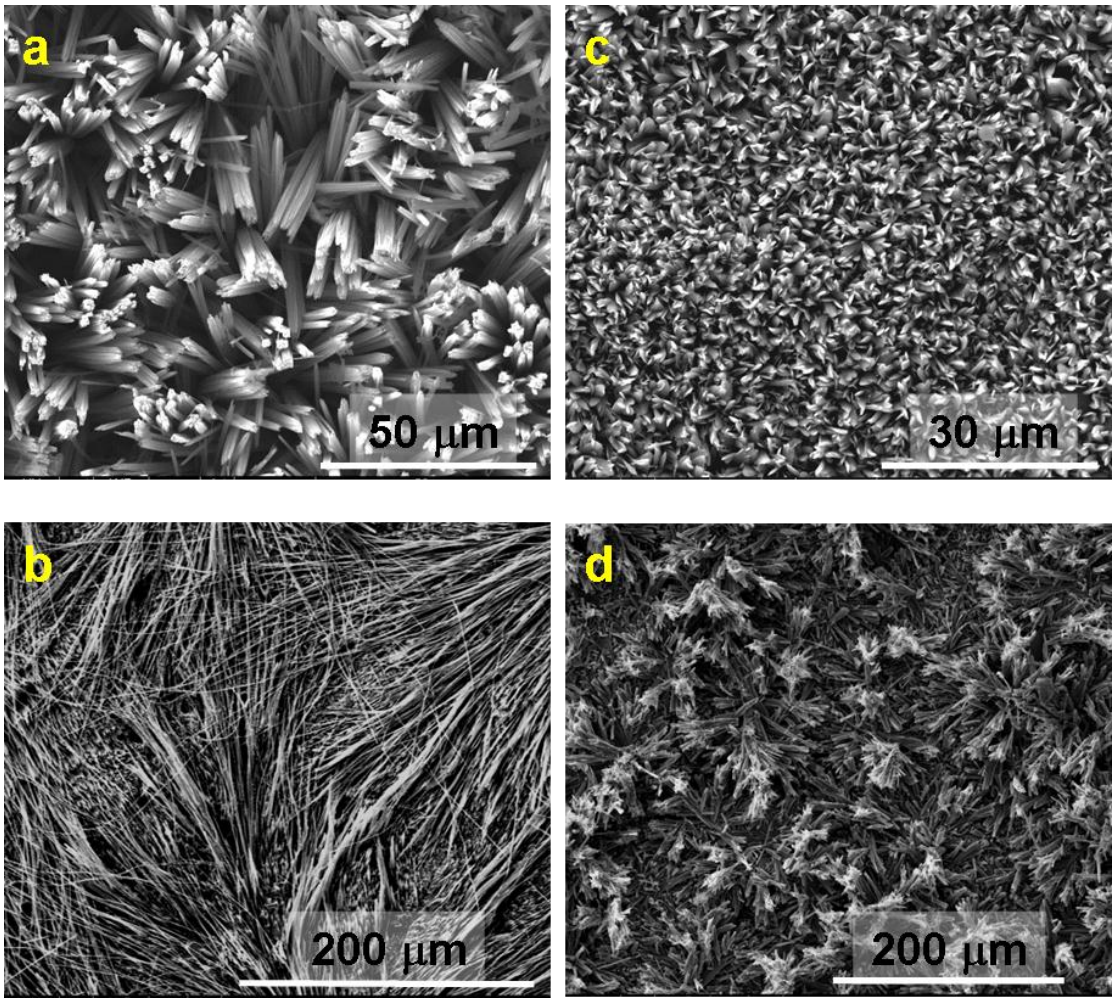

Figure S1: SEM images of (a) CuTCNQ phase I, (b) AgTCNQ, (c) CuTCNQF$_4$ and (d) AgTCNQF$_4$

Table S1. FT-IR data for TCNQ and $TCNQF_4$ materials

Sample	***FT-IR***			***Raman***			
	ν(C≡N) (cm^{-1})	ν (C=C) (cm^{-1})	δ(C-H) (cm^{-1})	ν(C≡N) (cm-1)	ν(C=C) (cm^{-1})	δ (C-CN) (cm-1)	Δ(C=CH) (cm-1)
TCNQ	2221	1541		2222	1597	1449	1204
CuTCNQ I	2206, 2172	1509, 1359	823	2205	1604	1378	1204
CuTCNQ II	2210, 2172	1502	825	2212	1598	1379	1196
AgTCNQ	2198, 2162	1509	821	2209	1604	1384	1204
TCNQF4	2226	1493		2223	1662	1452	
CuTCNQF4	2215	1502		2220	1642	1438	
AgTCNQF4	2197	1497		2224	1644	1448	

Table S2: FT-IR data for TCNQ and $TCNQF_4$ materials after catalysis

	FT-IR data After Catalysis		
	ν(C≡N) (cm^{-1})	**ν (C=C) (cm^{-1})**	**Δ(C-H) (cm^{-1})**
CuTCNQ I	2204, 2172	1509, 1355	821
CuTCNQ II	2211, 2170	1509	826
AgTCNQ	2198, 2160	1509	821
CuTCNQF4	2211	1496	
AgTCNQF4	2198	1501	

Table S3: Raman data for MTCNQ and $MTCNQF_4$ materials after catalysis

	RAMAN data After Catalysis		
	ν(C≡N) (cm^{-1})	**ν (C=C) (cm^{-1})**	**Δ(C-CN) (cm^{-1})**
CuTCNQ I	2203	1604	1382
AgTCNQ	2212	1604	1387
CuTCNQF4	2221	1641	1439
AgTCNQF4	2218	1644	1452

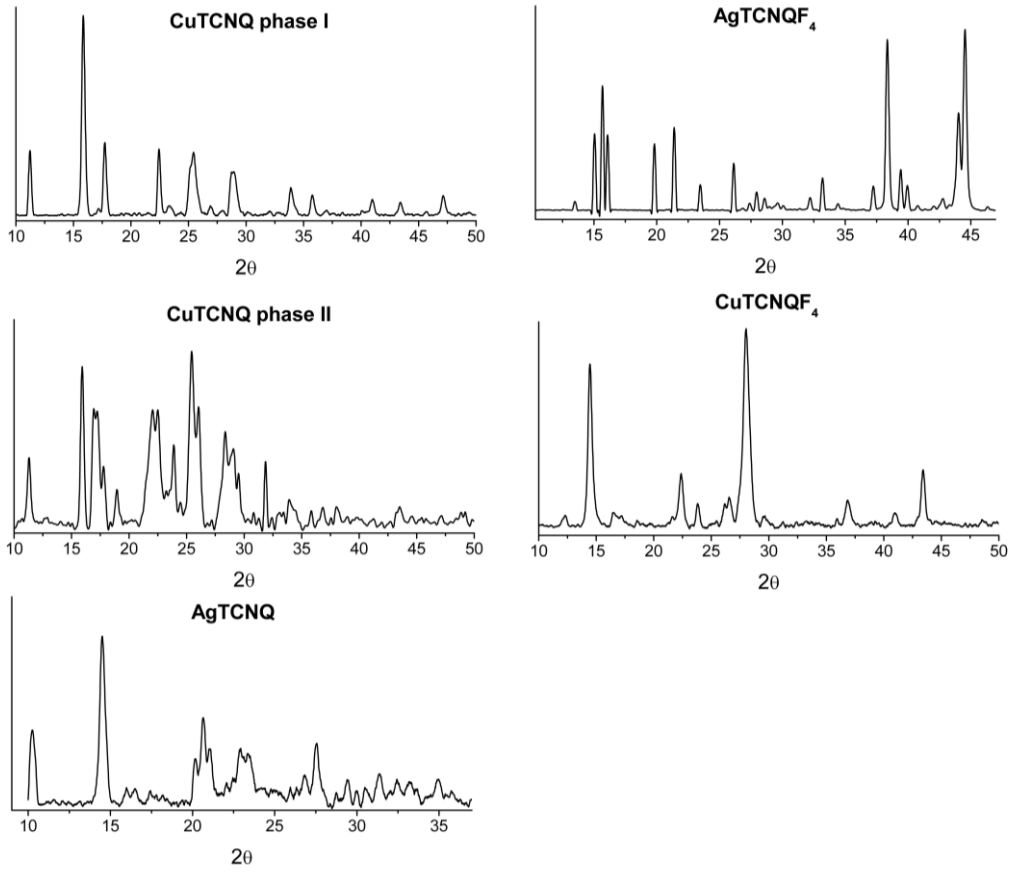

Figure S2: XRD patterns for CuTCNQ phase I, CuTCNQ phase II, AgTCNQ, $AgTCNQF_4$ and $CuTCNQF_4$.

For CuTCNQ phase I the diffraction pattern is consistent with that reported by Dunbar [1] and is indexed in the tetragonal crystal system. The XRD pattern is significantly changed in the case of CuTCNQ phase II when compared to CuTCNQ phase I, and is indicative of a monoclinic unit cell which is again consistent with Dunbar's work. The XRD pattern of $CuTCNQF_4$ is shown, however to the best of our knowledge there is no known XRD pattern of this material available in the literature. However from the FT-IR and Raman data it is clear that $CuTCNQF_4$ is formed.
For AgTCNQ the XRD pattern is also consistent with previous reports and is indicative of the tetragonal unit cell [2]. The XRD pattern for $AgTCNQF_4$ is consistent with previous studies [2] and is indicative of a monoclinic crystal system.

[1] R. A. Heintz, H. Zhao, X. Ouyang, G. Grandinetti, J. Cowen, K. R. Dunbar, *Inorg. Chem.* **1999**, *38*, 144.
[2] S. A. O'Kane, R. Clerac, H. Zhao, X. Ouyang, J. R. Galan-Mascaros, R. Heintz, K. R. Dunbar, *J. Solid State Chem.* **2000**, *152*, 159

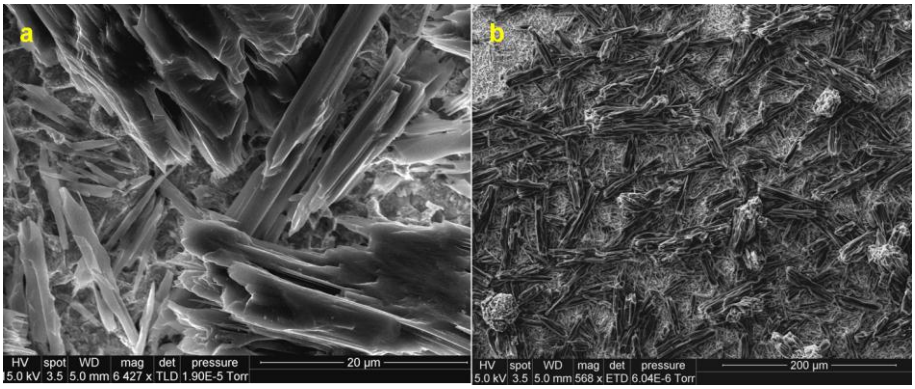

Figure S3: SEM images of $AgTCNQF_4$ after complete reaction of 1 mM $[Fe(CN)_6]^{3-}$ with 0.1 M $S_2O_3^{2-}$ in 30 ml of solution under stirring conditions.

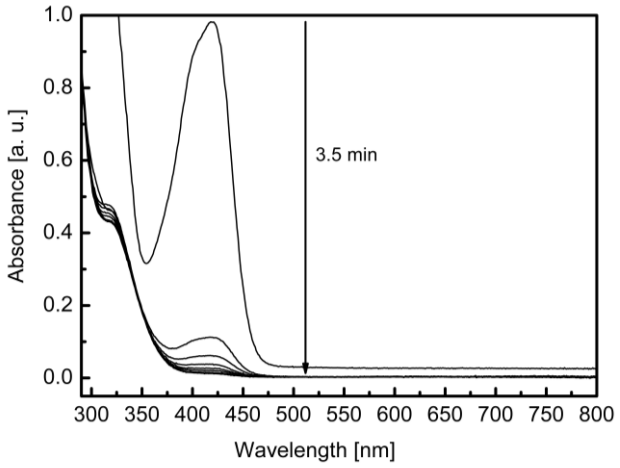

Figure S4: Time dependent UV-vis spectra recorded for the reduction of 1 mM of $Fe(CN)_6^{3-}$ with 0.1 M $S_2O_3^{2-}$ in a total volume of 30 ml catalysed by $AgTCNQF_4$.

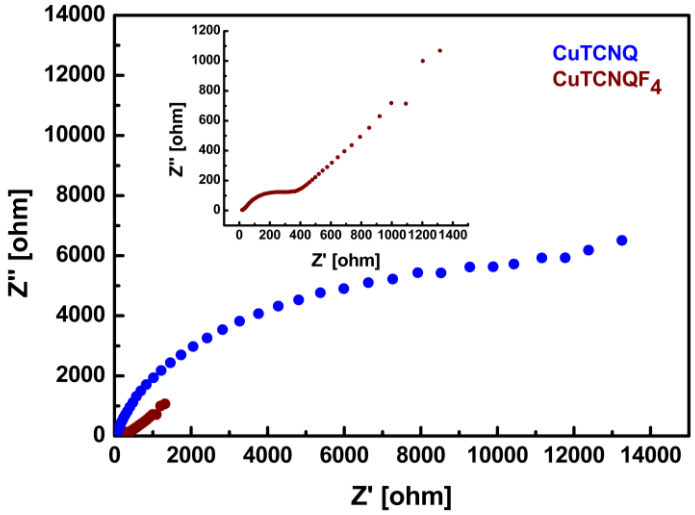

Figure S5: Nyquist plots obtained in 0.1 M $S_2O_3^{2-}$ and 0.1 M NaCl at OCP for CuTCNQ phase I (–) and $CuTCNQF_4$ (–).