

## Supplementary Materials

# Crystal formation in TCNQ on the nanoscale: Polymorphism and progression of self-assembly

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### **Additional Characterization Experiments of reprecipitated TCNQ**

For additional characterization of the crystallized particles, several other techniques were employed. Absorption spectra of dispersions of the sample were acquired with a spectrophotometer (Ocean Optics CHEM-2000-UV-VIS). To confirm crystal formation, an XRPD pattern of a sample of freeze dried powder was obtained using a Rigaku RAPID Curved IP X-ray powder diffractometer with Cu K $\alpha$  radiation and an image plate detector.

The absorption spectra of the reprecipitated TCNQ crystals were compared to that of a TCNQ acetone solution. As shown in figure S1, the reprecipitated sample has broader absorption peaks, blue-shifted about 10 nm with respect to the solution peaks, which suggests a broader distribution of molecular energy levels of TCNQ and an increased bandgap. This may be due to the formation of H-aggregates giving rise to excitonic absorption.<sup>1</sup>

In figure S2, the XRPD patterns of the freeze dried reprecipitated sample confirms the formation of TCNQ crystals as the observed pattern follows the XRPD pattern of TCNQ in the Cambridge Structural Database. This structure was determined by Long et al. to be monoclinic, in the space group C2/c.<sup>2</sup> We also attempted to observe the particle growth of TCNQ crystals vs. time using dynamic light scattering. However, TCNQ can rapidly form large microcrystalline

structures which can intermittently enter the sampling volume and scatter strongly, so consistent autocorrelation functions of the scattered photon count could not be obtained.

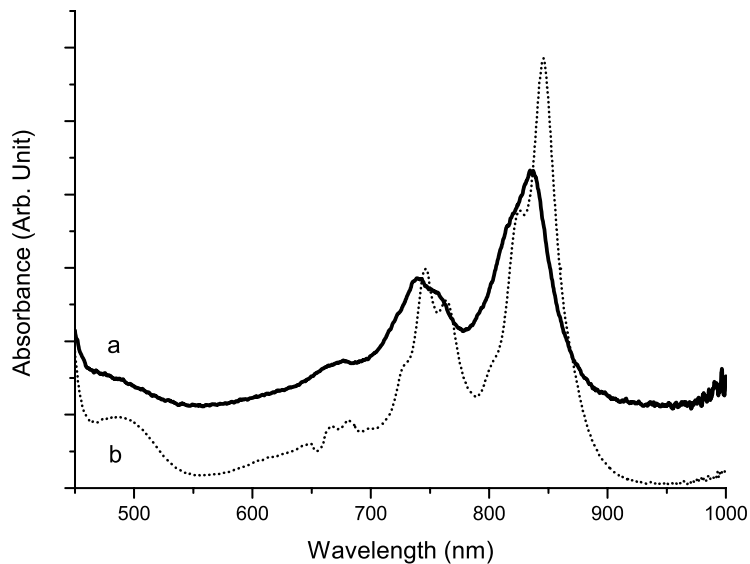


FIG. S1: Absorption spectra of (a) reprecipitated TCNQ dispersion and (b) TCNQ acetone solution.

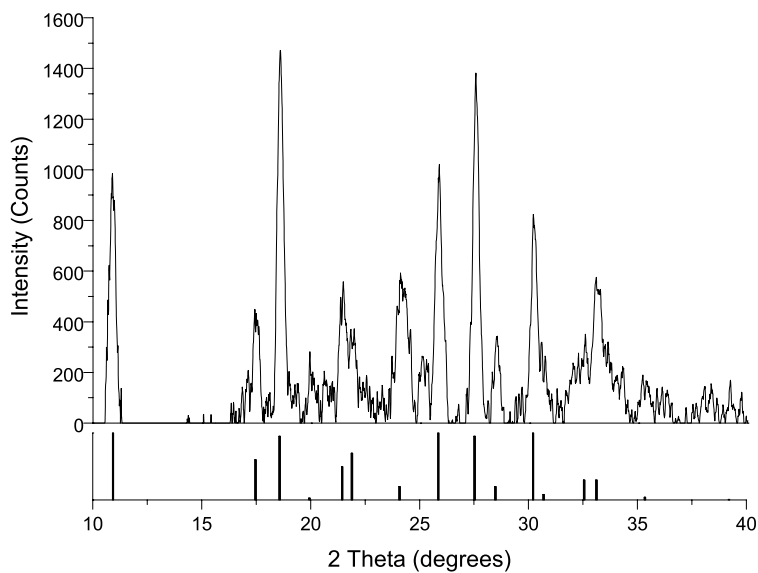
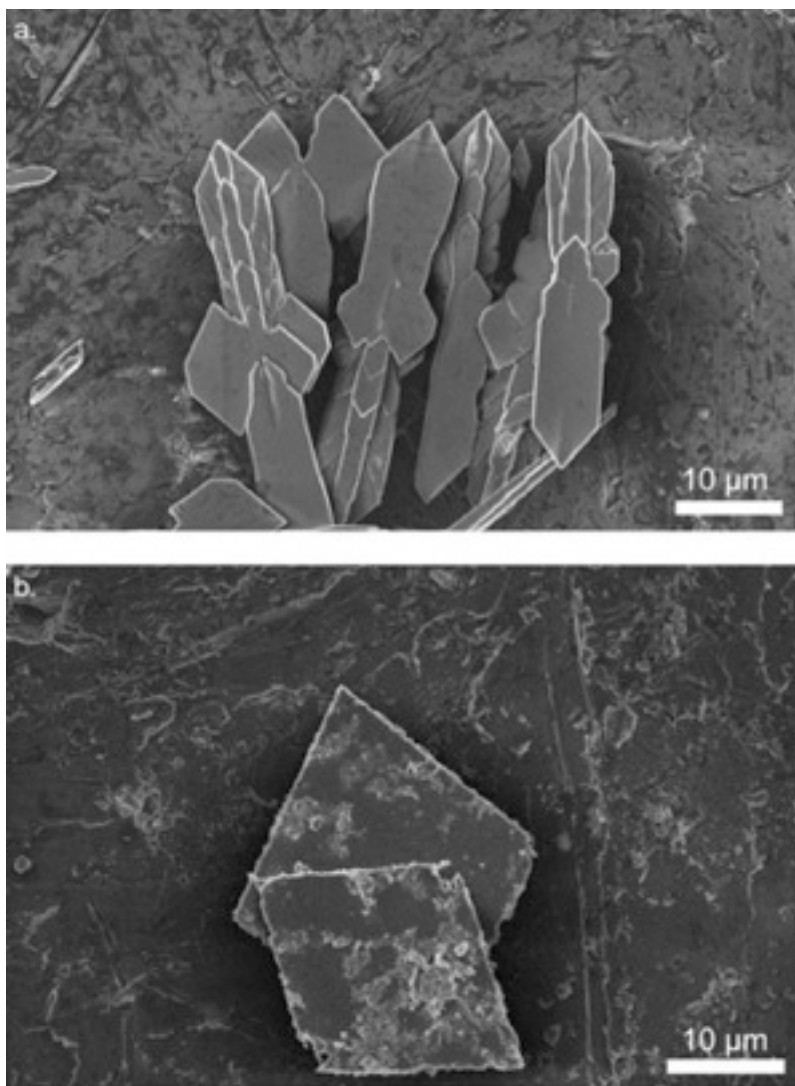


FIG. S2: XRPD pattern of TCNQ crystals (top) was examined with a peak search-match (bottom).

### SEM images of TCNQ reprecipitated in different temperatures

SEM images of TCNQ crystals prepared in different temperature environment formed different shapes of polyhedral crystal structures than that of the sample prepared at room temperature. The sample reprecipitated in cold bath formed 30  $\mu\text{m}$  long sword-like structures, and the other synthesized in hot bath had 10-30  $\mu\text{m}$  nearly perfect rhombic structures (FIG. S3).



**FIG. S3** SEM images of TCNQ crystals prepared in (a) cold and (b) hot bath.

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Reference:

1. M. Pope and C. E. Swenberg: *Electronic Processes in Organic Crystals*. (Clarendon Press, Oxford, 1982).
2. R. Long, R. Sparks, and K. Trueblood: The Crystal and Molecular Structure Of 7,7,8,8-Tetracyanoquinodimethane. *Acta Cryst.* **18**, 935 (1965).