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Supplementary Information

"Tetrathiafulvalene: A Gate to the Mechanochemical Mechanisms of Electron Transfer Reactions"

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I. Quantitative phase analysis from laboratory X-ray powder diffraction data:

The internal standard method was used for quantitative phase analysis (QPA) [1]. The samples to be analyzed were doped with a known and constant amount of a reference material or *internal standard*. Then, the weight fraction of the phase *j* in the doped material, wf_j', is:

$$\boldsymbol{wf_j' = wf_j\,(1 - wf_s)} \quad (1)$$

where wf_s is the weight fraction of the internal standard, 0.05 (or 5 %) in our measurements, and wf_j is the weight fraction of the phase *j* in the non-doped specimen. Then, the ratio of two intensities of non-overlapping peaks in the powder diffraction pattern, $S_{j,s}$, one peak belonging to the sample and other to the standard, is independent of the specimen absorption (μ^*):

$$\boldsymbol{S_{j,s} = \frac{I_{i,j}}{I_{h,s}} = \frac{K_{i,j}\,wf_j\,(1-wf_s)}{K_{h,s}\,wf_s}} \quad (2)$$

the indexes *i* and *j* correspond to the analyte, while *h* and *s* correspond to the internal standard. $K_{i,j}$ and $K_{h,s}$ are constants. Thus, since wf_s is constant, the weight fraction of the analyte in the non-doped specimen, wf_j, is a linear function of the intensity ratio $S_{j,s}$, which is a measurable quantity from the X-ray powder diffraction (XRPD) data.

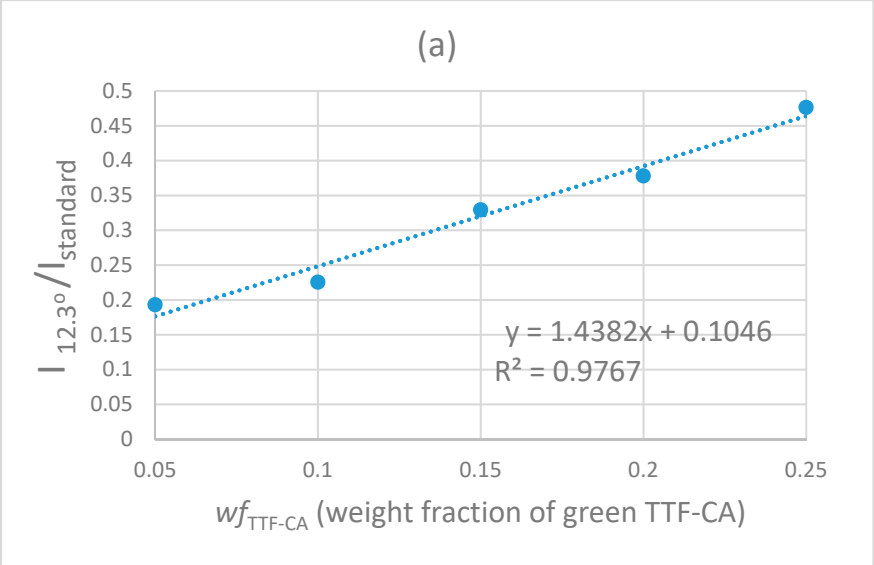
I.1. Neat mechanochemical reaction

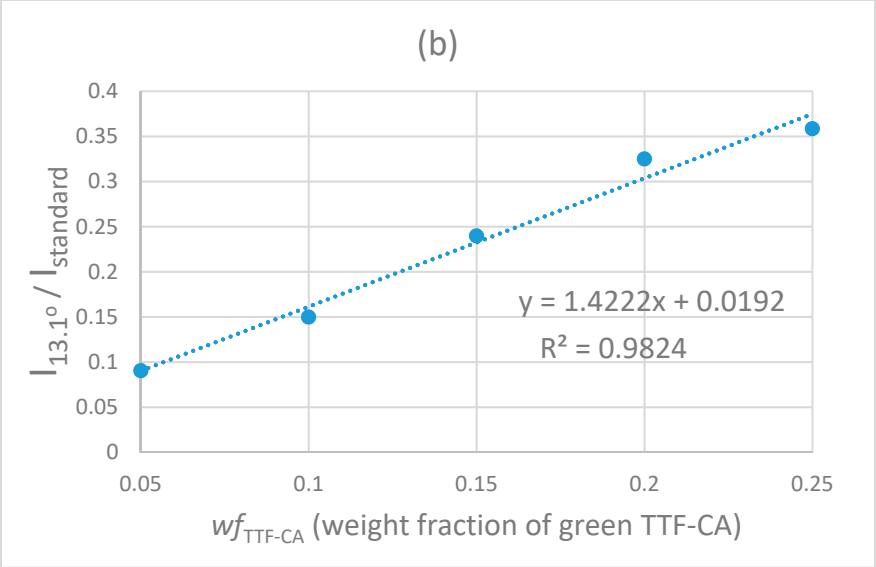
Three calibration curves were done using three different peaks of the mechanochemical product (at 2θ=12.3°, 13.1° and 16.9°), and the most intense diffraction peak of the standard (at 22.0°). The equations for straight lines (the small intercepts are acceptable [1]) were calculated using Microsoft Excel.

Peak heights were used rather than integrated intensities due to a small overlap of the peak of the standard with another peak. The graphs of $S_{j,s}$ as a function of wf_j are shown in Figure S1. The mixtures for the calibration curves had all 0.1000 g total mass and were composed of green TTF-CA synthesized by neat grinding in an agate mortar, 0.0050 g of NIST standard and ground glass. The compositions are shown in Table S1.

Table S1. Composition (in mass) of the mixtures used to measure the calibration curves shown in Figure S1 and the calculated weight fractions of green TTF-CA, $wf_{\text{TTF-CA}}$.

Green TTF-CA (g)	Ground glass (g)	SiO_2 standard (g)	$wf_{\text{TTF-CA}}$
0.0050	0.0900	0.0050	0.0500
0.0100	0.0850	0.0050	0.1000
0.0150	0.0800	0.0050	0.1500
0.0200	0.0750	0.0050	0.2000
0.0250	0.0700	0.0050	0.2500


(a)
0.5
0.45
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
I 12.3° /I standard
y = 1.4382x + 0.1046
R² = 0.9767
0.05
0.1
0.15
0.2
0.25
wf TTF-CA (weight fraction of green TTF-CA)


(b)
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
I13.1° / I standard
y = 1.4222x + 0.0192
R² = 0.9824
0.05
0.1
0.15
0.2
0.25
wf TTF-CA (weight fraction of green TTF-CA)

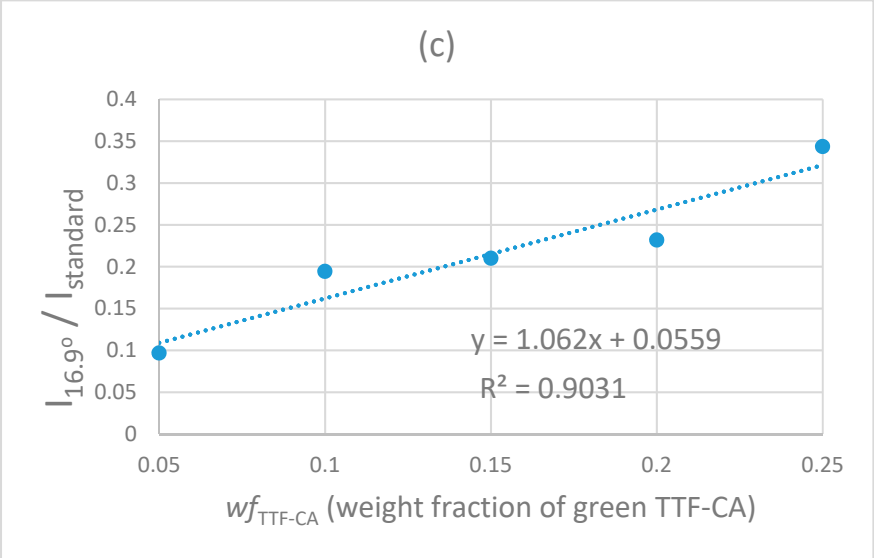


Figure S1. Calibration curves for QPA of the green form of TTF-CA (as reaction product under neat conditions) using the peaks at: (a) 12.3°, (b) 13.1° and (c) 16.9°. The equations of the linear relationships are shown in the graphs.

I.2. Liquid assisted grinding reaction with diethyl ether (1 μL/mg)

The above procedure was repeated under liquid assisted grinding (LAG) with diethyl ether conditions. The same peaks were used for QPA, but this time the product used to prepare the calibration curves was prepared by LAG with diethyl ether (1 μL/mg), as the analyte.

The graphs of $S_{j,s}$ as a function of wf_j are shown in Figure S2. The mixtures for the calibration curves had all 0.1000 g total mass and were composed of green TTF-CA, 0.0050 g of NIST standard and ground glass. The compositions are shown in Table S2.

Table S2. Composition (in mass) of the mixtures used to measure the calibration curves shown in Figure S2 and the calculated weight fractions of green TTF-CA, wf_{TTF-CA}.

Green TTF-CA (g)	Ground glass (g)	SiO_2 standard (g)	wf_{TTF-CA}
0.0050	0.0900	0.0050	0.0500
0.0100	0.0850	0.0050	0.1000
0.0200	0.0750	0.0050	0.2000
0.0250	0.0700	0.0050	0.2500

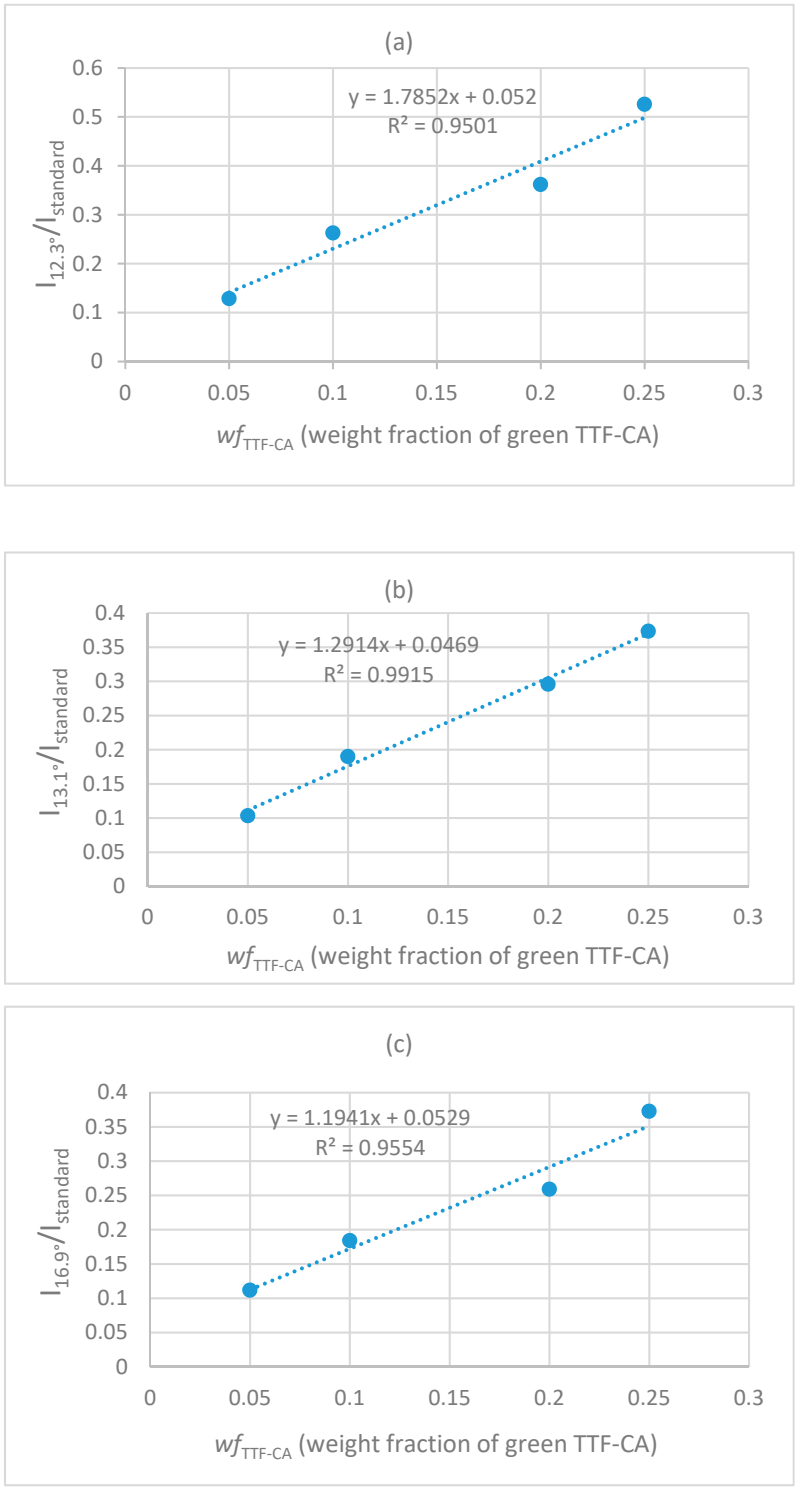


Figure S2. Calibration curves for QPA of the green form of TTF-CA (as reaction product) in the LAG reaction with diethyl ether (1 µL/mg), using the peaks at: (a) 12.3°, (b) 13.1° and (c) 16.9°. The equations of the linear relationships are shown in the graphs.

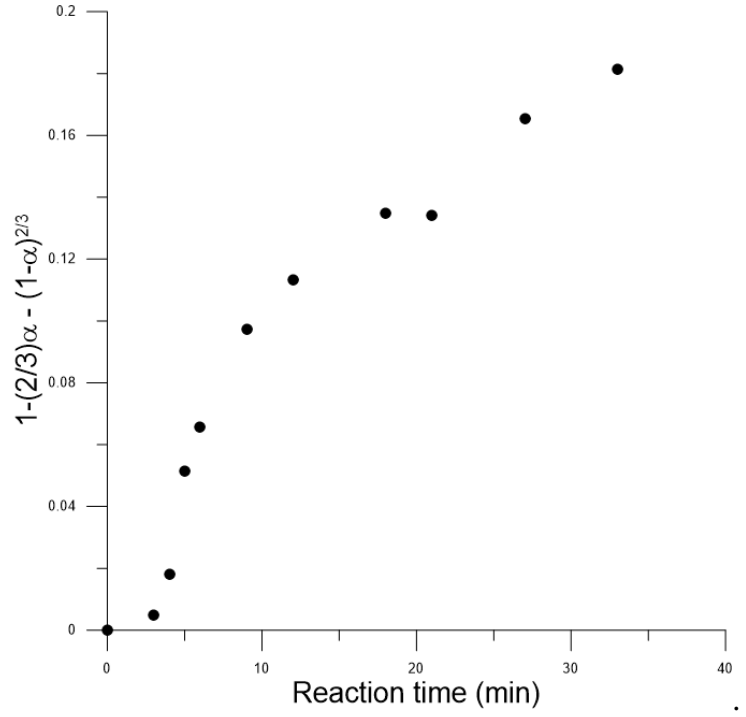


Figure S3. Functional dependence given by the Ginstling-Brounshtein 3D diffusion-controlled reaction model (vertical axis) applied to the conversion fraction (α) corresponding to the neat mechanochemical data for the reaction of TTF and CA, as a function of the reaction time.

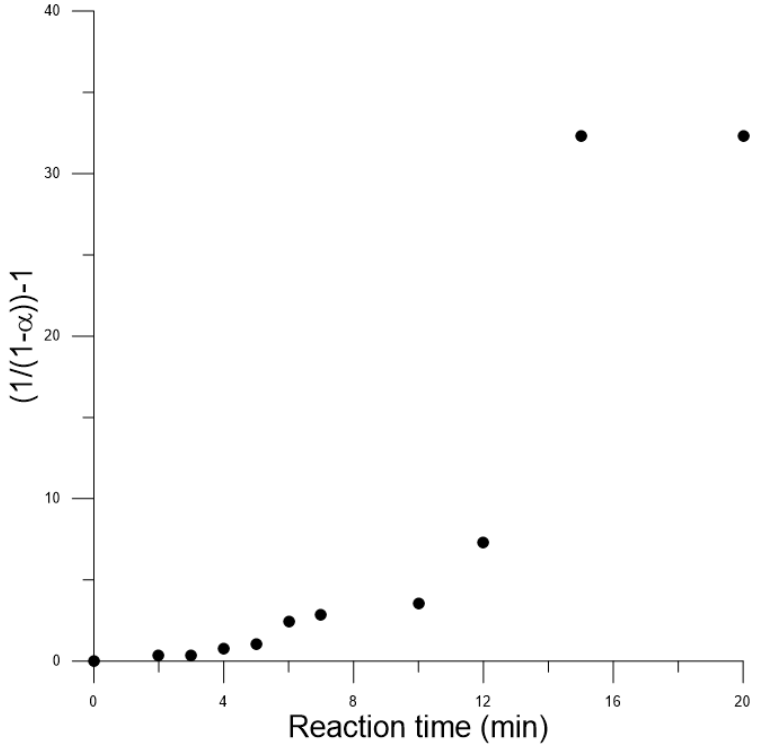


Figure S4. Functional dependence given by the second order reaction model (vertical axis) applied to the conversion fraction (α) corresponding to the LAG reaction of TTF and CA (diethyl ether, 1 µL/mg), as a function of the reaction time.

References

[1].- Zevin, G. and Kimmel, L. S. *Quantitative X-ray diffractometry*; Springer, NY: USA, 1995.



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