Electronic supplementary information (ESI) file of the paper

Rationale design of the solid-state synthesis of materials based on poly-aromatic molecular complexes

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Section 1: Kinetic analysis of non-isothermal data

In the literature, three different approaches for kinetic analysis in ramp conditions are described, *viz*:

1. Kennedy-Clark equation as described before;
2. Kissinger equation[i]:

$$E_a \beta \left(RT_p^{\,2} \right) = Ae^{\frac{-E_a}{RT}}$$

Where A is the frequency factor and β is the heating rate, which is expressed as β = dT/dt.

Taking the logarithm of the above equation, we obtain:

$$-\ln\left(\beta T^{2}{}_{p}\right) = -\ln\left(\frac{AR}{E_a}\right) + \left(\frac{1}{T_p}\right) \times \left(\frac{E_a}{R}\right)$$

The activation energy, E_a can be obtained by plotting $\ln(\beta T_p^2)$ as function $1/T_p$, where T_p is the peak temperature;

3. Flynn-Wall method[ii]:

This is one of the integral methods that can be used to determine the activation energy, which does not require the knowledge of reaction order.

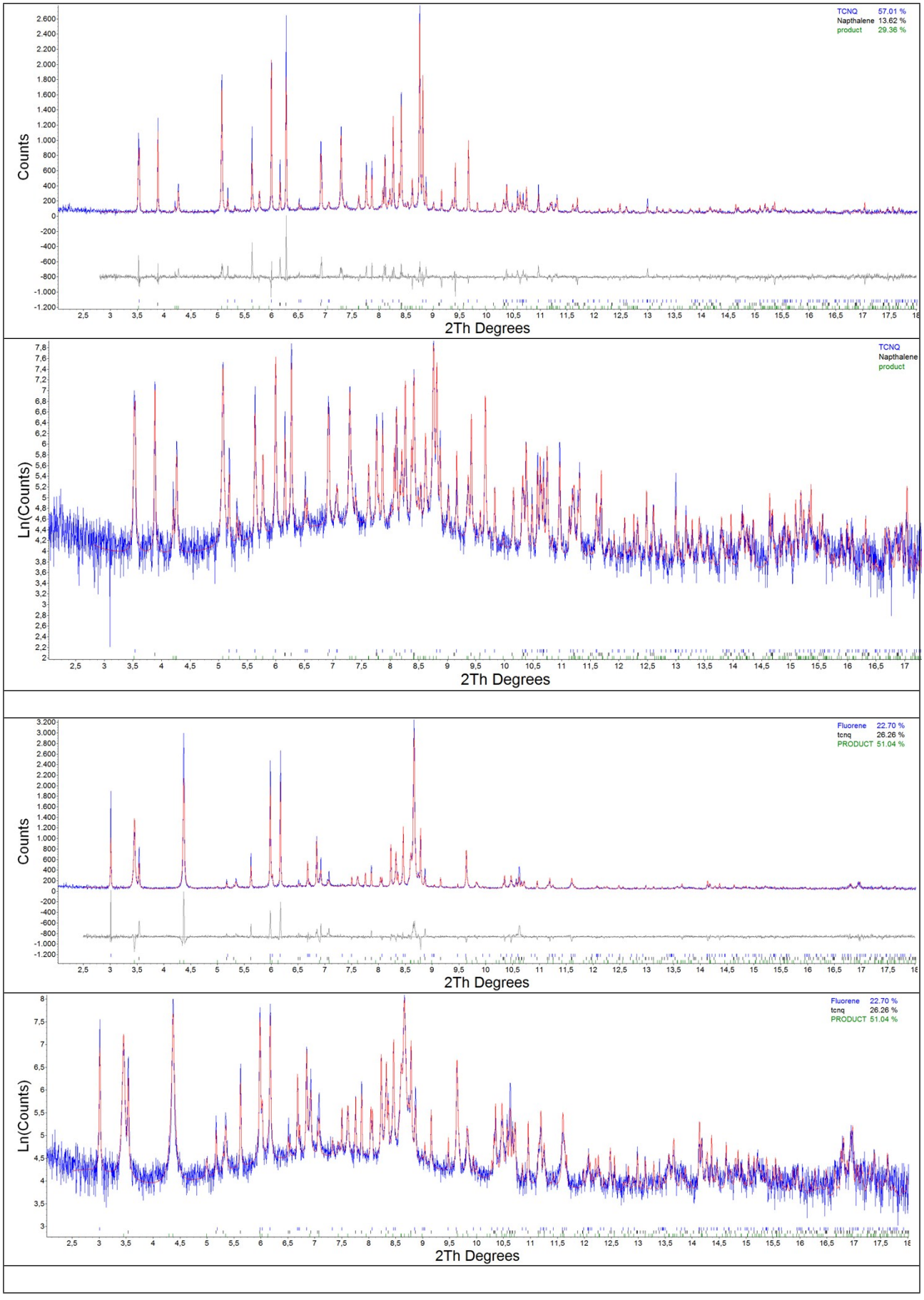
$$\log \beta = \log \frac{AE_a}{g(\alpha)R} - 2{,}315 - \frac{0{,}475E_a}{RT}$$

Where β is the heating rate, A is the frequency factor, E_a is the activation energy and T is the peak temperature. g(α) is integral function of conversion, α being the reaction coordinate.

The activation energy for different conversion values can be calculated from a log β versus 1000/T plot.

However the drawback of Kissinger and Flynn-Wall approach is that it requires at least two ramp analyses to calculate *Ea* and, since in our case we search for a less time consuming yet accurate approach applicable to a single ramp experiment, the Kennedy-Clark (KC) equation has been chosen for all the temperature ramp data analysis.

Section 2: In situ XRPD data analysis



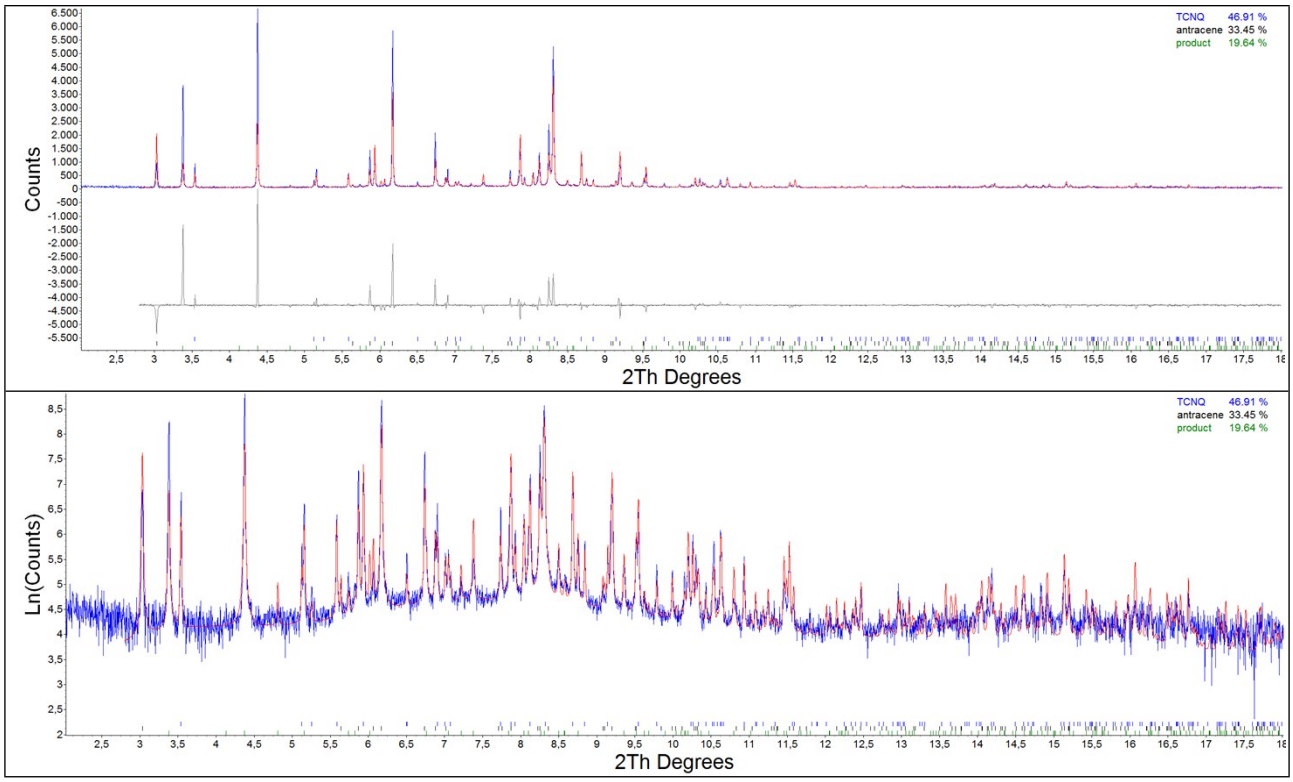


Figure SI1: Rietveld refinement for NA-TCNQ, FL-TCNQ and AN-TCNQ.

NA:TCNQ scan number	r_p	r_wp	gof
1	14,76049	17,53134	1,45266
2	14,80813	17,76226	1,469793
3	15,26986	18,1202	1,502317
4	15,1674	18,17045	1,502255
5	15,30205	18,47401	1,524059
6	14,93656	17,88208	1,476306
7	15,28633	18,50943	1,524775
8	15,57665	18,6418	1,538641
9	14,92431	18,3097	1,508666
10	16,08293	19,28161	1,585734
11	15,81568	18,59778	1,531122
12	16,04422	19,11276	1,571251
13	16,2229	19,14686	1,571346
14	16,01118	18,88485	1,55074
Average	**15,44348**	**18,45894**	**1,522119**

Table SI1: Agreement and goodness of fit factors for the Rietveld refinements of non-isothermal in situ XRPD data of NA:TCNQ

FL:TCNQ scan number	r_p	r_wp	gof
1	13,33598	15,26294	1,378052
2	13,24616	15,46804	1,593206
3	14,02287	16,10042	1,622637
4	13,46469	15,73732	1,559047
5	14,93459	17,37221	1,570877
6	15,24942	17,88394	1,606506
7	15,60374	18,48638	1,560521
8	15,32148	18,05631	1,678125
9	16,01344	18,92332	1,679315
10	15,30302	18,00339	1,659408
11	15,69731	18,38413	1,635028
12	14,55887	17,60861	1,390508
13	15,08978	17,66482	1,438725
14	14,68368	17,8748	1,394237
15	14,3725	17,41773	1,534137
16	15,37619	18,57543	1,589358
17	15,25637	18,67236	1,643707
18	15,11556	18,49151	1,605037
19	14,88753	18,33514	1,676057
Average	**14,81754**	**17,59573**	**1,569184**

Table SI2: Agreement and goodness of fit factors for the Rietveld refinements of non-isothermal in situ XRPD data of FL:TCNQ.

AN:TCNQ scan number	r_p	r_wp	gof
1	19,05507	21,59338	1,964973
2	19,17846	22,10376	2,025448
3	19,54073	22,36244	2,057452
4	19,03895	21,72123	2,162885
5	18,88597	21,63086	2,152441
6	18,91735	21,70352	2,156231
7	18,73995	21,54907	2,139821
8	18,82281	21,74655	2,154598
9	19,00575	21,93742	2,171247
10	18,94955	21,7753	2,153278
11	19,58799	22,74092	2,249875
12	19,01509	21,97335	2,174659
13	19,09778	22,23062	2,195365
14	18,99729	22,10321	2,188376
15	20,03415	23,63506	2,243826
16	19,92063	23,43481	2,308144
17	20,553	23,99002	2,366121
18	20,4153	24,22257	2,385843
19	20,91588	24,64085	2,427886
20	21,14383	24,83892	2,445988
21	21,76094	25,62776	2,52534
22	22,90611	28,31327	2,602835
24	22,62989	26,63656	2,613047
25	22,87516	26,94605	2,64065
26	23,10415	27,57424	2,693593
27	23,90359	28,51993	2,774605
28	23,59699	28,55957	2,740951
29	25,20672	30,43886	2,84897
30	25,46216	30,78718	2,888752
Average	**20,73315**	**24,32198**	**2,360455**

Table SI3: Agreement and goodness of fit factors for the Rietveld refinements of non-isothermal in situ XRPD data of AN:TCNQ

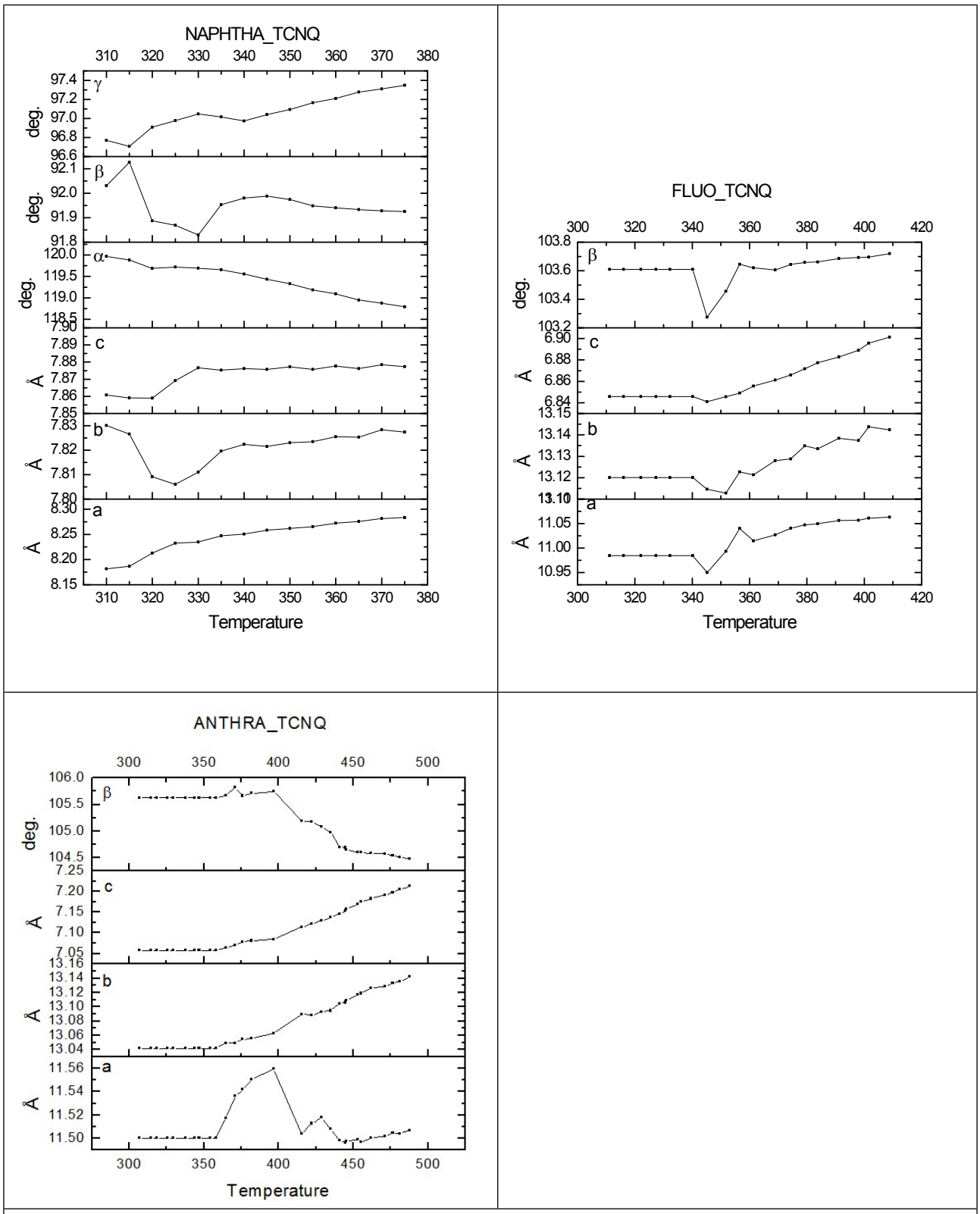


Figure SI2: Trends of the lattice parameters during Rietveld refinement of in situ XRPD data

Section 2: Kinetic analysis of isothermal in situ XRPD data

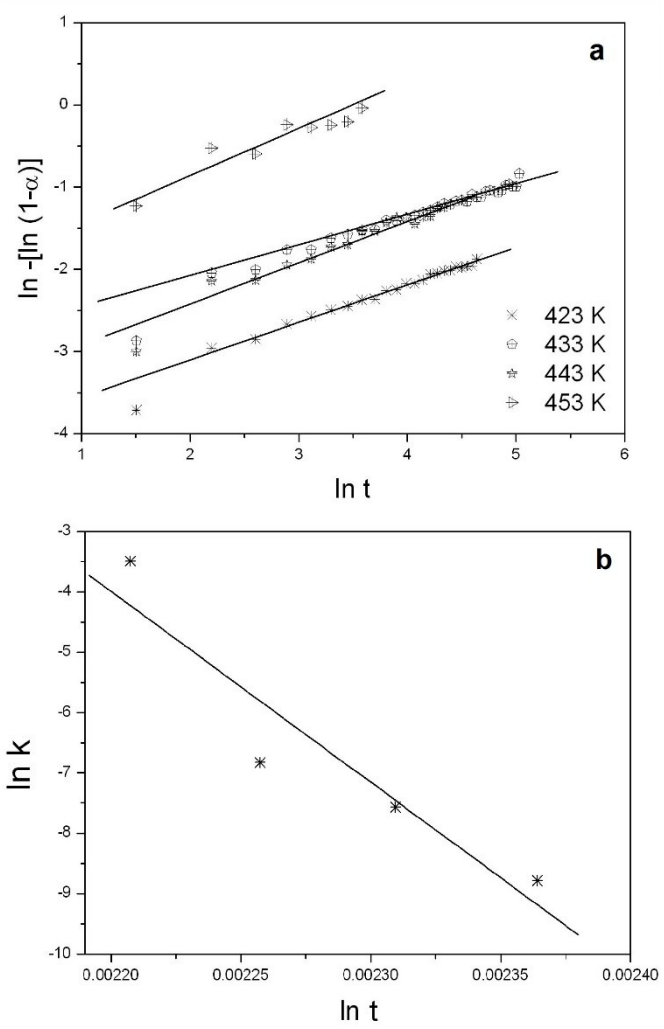
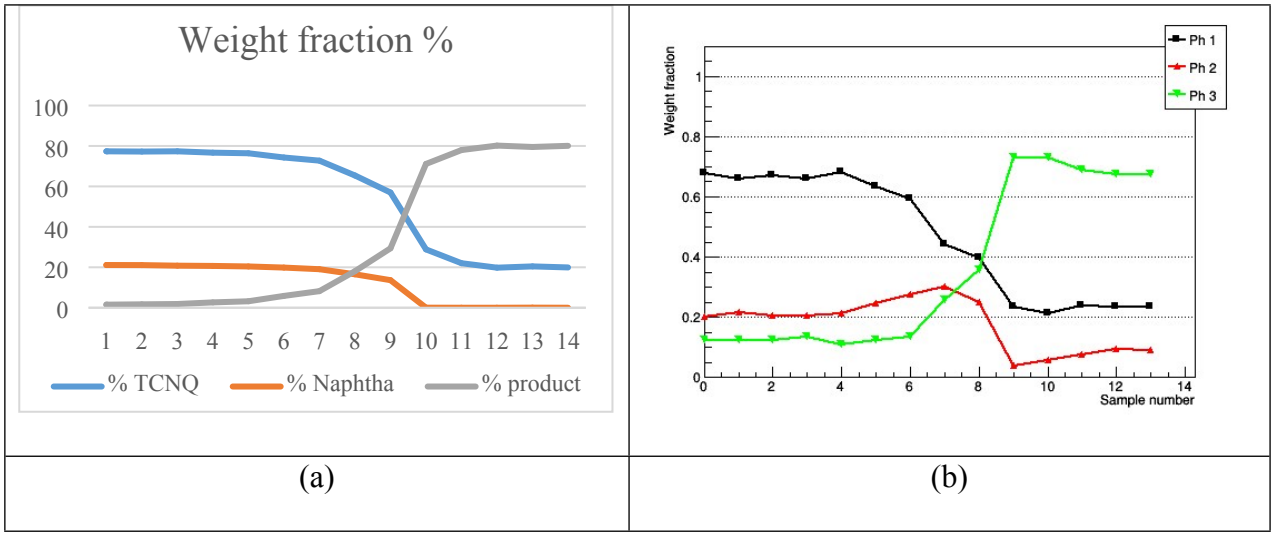


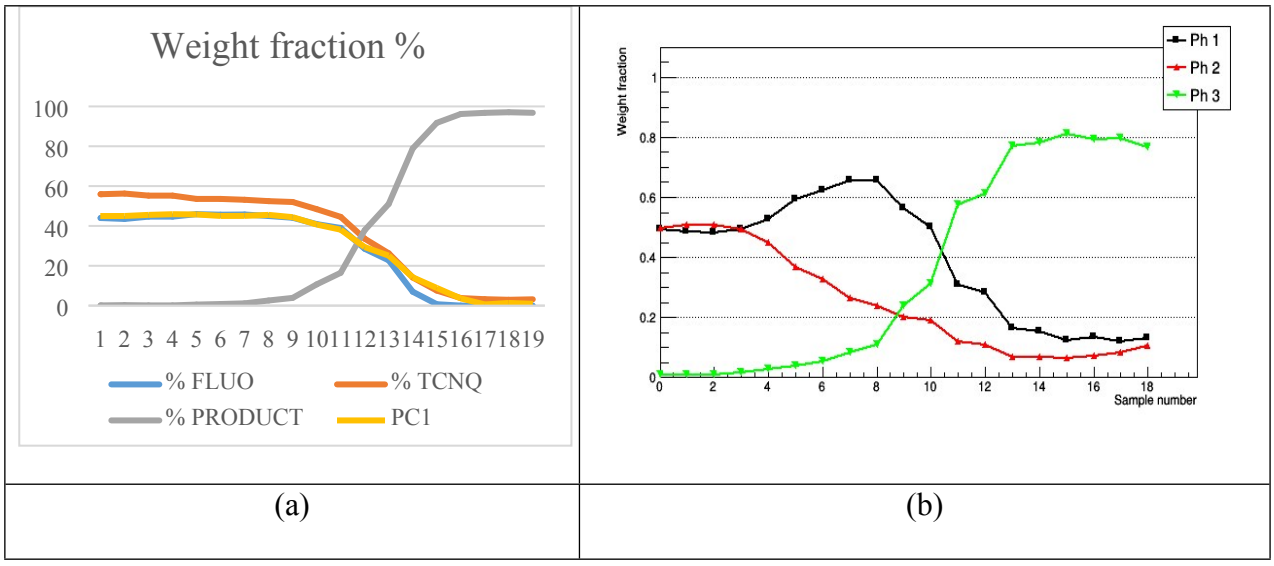
Figure SI3 Kinetic analysis of isothermal in situ XRPD data for AN-TCNQ CT complex formation with Avrami plot (a) and Arrhenius (b) plots at four isothermal temperature conditions of 423, 433, 443 and 453 K respectively.

Section 3: Principal Component Analysis (PCA)



(a) (b)

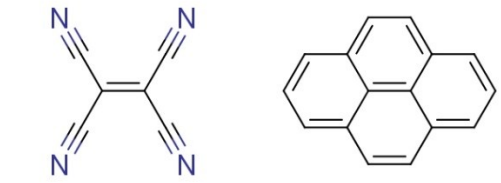
Figure SI4: Phase amount estimation by Rietveld refinement (a) and LSQ regression (b) for NA-TCNQ reaction; the agreement is not bad because the temperature change is not large and lattice variations do not affect so much the regression.



(a) (b)

Figure SI5: Phase amount estimation by Rietveld refinement (a) and LSQ regression (b) for FL-TCNQ reaction; the agreement is bad because the temperature change is larger than in NA-TCNQ case and lattice and peak shape variations become important and affect so much the regression, giving unreliable values.

Section 4: Ex-situ synthesis of NA-TCNE and PY-TCNE



Tetracyanoethylene
(TCNE)

Pyrene
(PY)

Figure SI6: Structure formula of TCNE and Pyrene

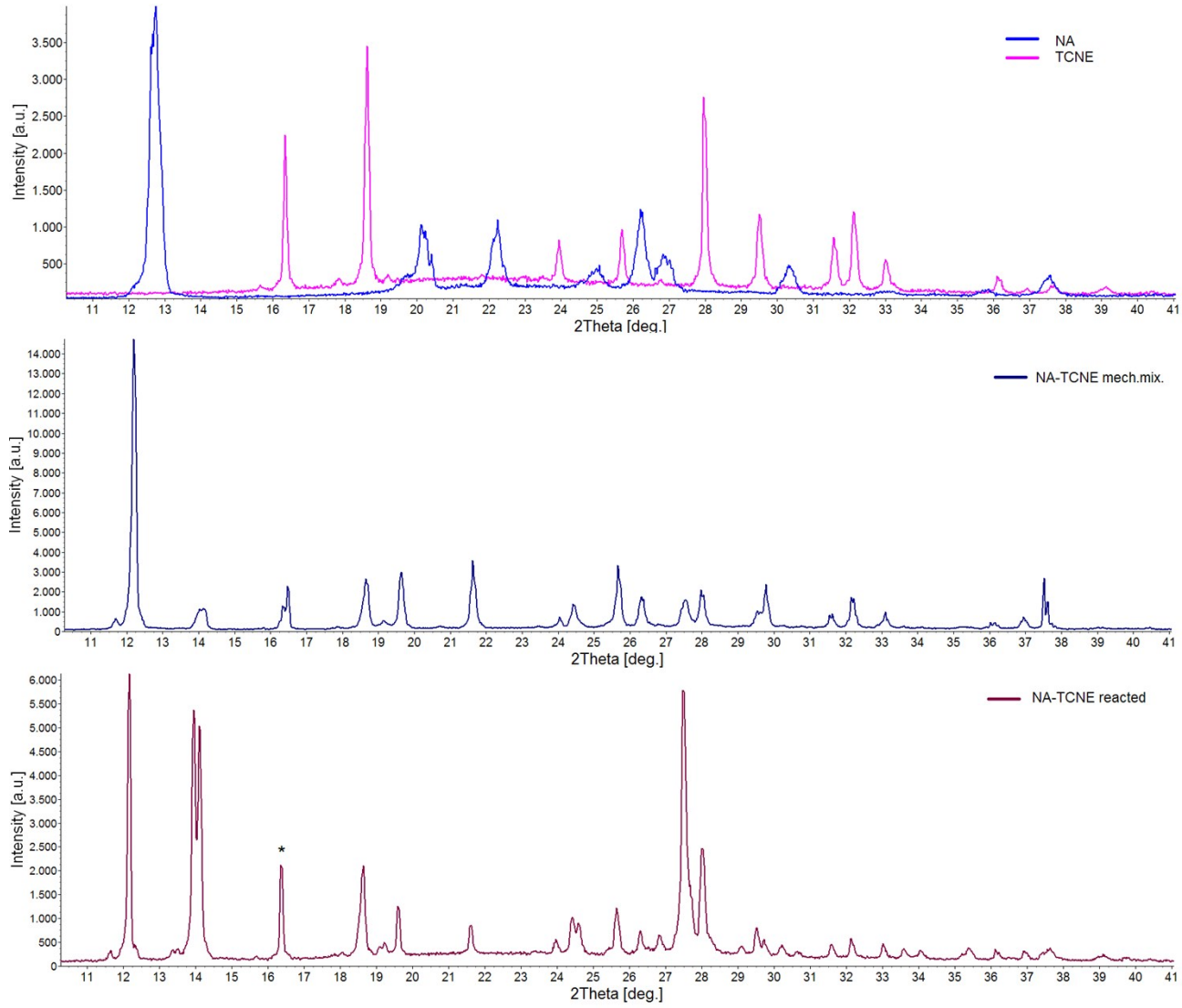


Figure SI7: XRPD patterns of the reactants Naphthalene (NA) and Tetracyanoethylene (TCNE), their mechanical mixture and NA-TCNE complex after reaction. The asterisk marks the peak of residual TCNE.

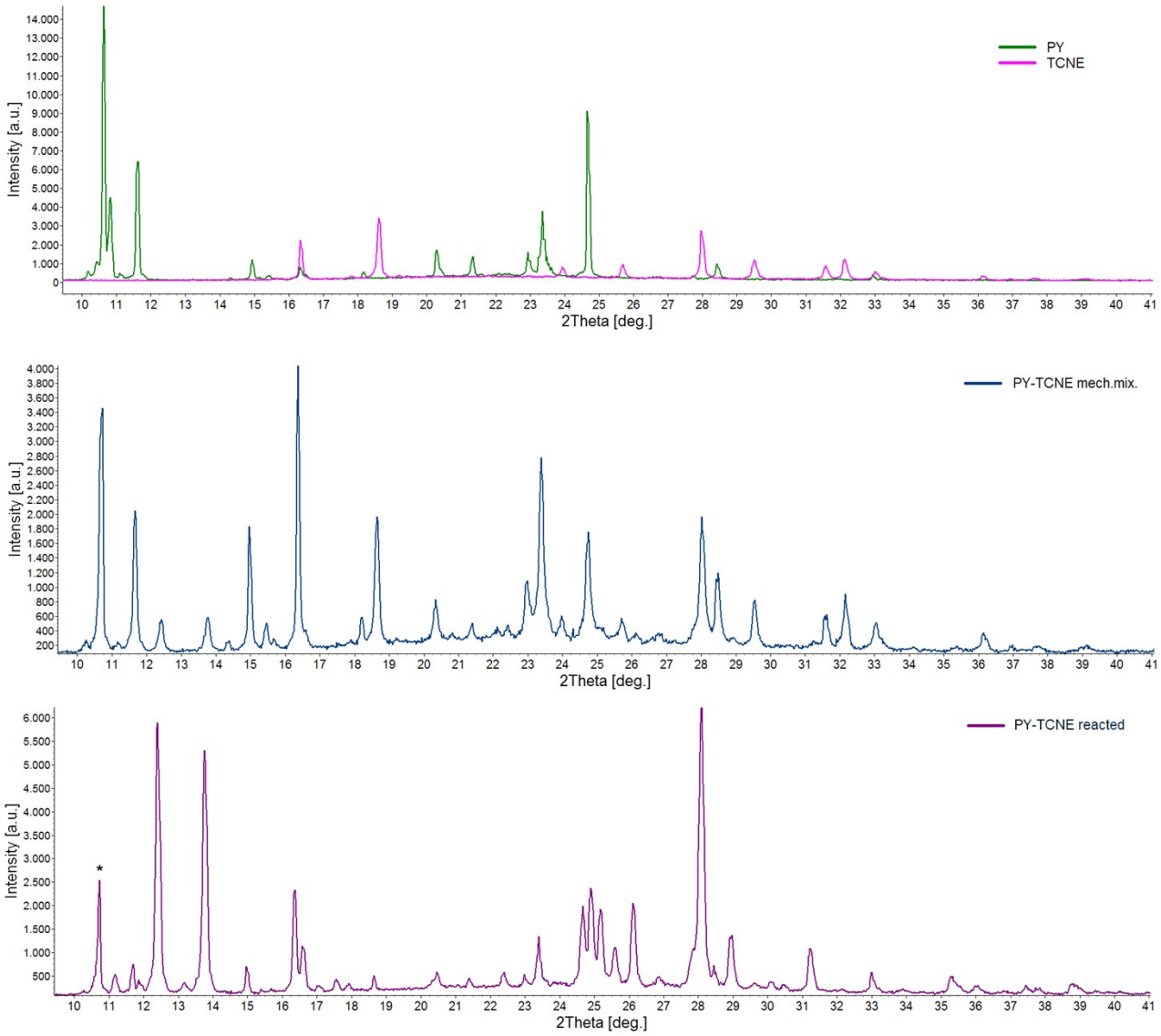


Figure SI8: XRPD patterns of the reactants Pyrene (PY) and Tetracyanoethylene (TCNE), their mechanical mixture and PY-TCNE complex after reaction. The asterisk marks the peak of residual PY.

[i] Kissinger H E. Anal Chem., **1957**, 29, pg.1702.

[ii] Flynn J H, Wall L A. J Res Nat Bur Stand A Phys Chem., **1966**, 70A.pg. 487.