ABSTRACT: The charge-transfer molecular complex fluorene/7,7,8,8-tetracyanoquinodimethane (TCNQ) was obtained by an unprecedented in situ solid-state direct synthesis. The reaction advancement was monitored with Raman spectroscopy and high-resolution X-ray powder diffraction (XRPD). The experiments were performed with a novel setup (SNBL, Grenoble) capable of combining both techniques simultaneously at in situ conditions. Raman spectroscopy allowed the characterization of the reaction kinetics during the initial steps at the surface of the TCNQ crystallites, when no or very little reaction is observed by the XRPD probe. From Rietveld refinement of the synchrotron XRPD data, the time evolution of the amounts of reactants and product was obtained for the reaction proceeding into the bulk of the TCNQ crystals, together with the crystal size analysis. These data were analyzed exploiting the Avrami equation to obtain rate constants, reaction orders, and activation energies. The reaction, after starting at the surface of the TCNQ platelet-like crystals, as was also confirmed by a hot-stage microscopy experiment, proceeds toward the inner part of the crystals with a decreasing rate, because diffusion is more critical into the bulk. A full comprehension of the kinetic features of the crystal growth with a multiscale approach from the nano- to micrometer level was thus obtained.

Introduction

7,7,8,8-Tetracyanoquinodimethane (TCNQ) is a well-known organic electron acceptor,1–4 and the first charge-transfer (CT) complex, with almost metallic conductance, of TCNQ with tetrathiafulvalene was synthesized in 1973.5 Possible applications in organic photovoltaic materials were envisaged a few years later.6 Fluorene (FL) is an aromatic hydrocarbon with relevant spectrochemical features, which may be tuned by the presence of other molecular systems. FL copolymers are studied for their promising applications in polymer-based solar cells.7 Fabrication of solution-processable organic thin-film transistors (OTFTs) based on poly(9,9′-dioctylfluorene-bithiophene) (F8T2) doped with an electron-acceptor, 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4TCNQ), has been recently reported.8 The doped F8T2 device was also found to exhibit a better threshold voltage and reduced hysteresis behavior. These improvements in performance are attributed to the formation of the F8T2–F4TCNQ complex, which results in better hole injection and improved device stability. In general, FL-containing molecular complexes modulate the electronic features of the FL moiety by means of the CT interactions, hence enabling the versatile modularity of its optical and fluorescent responses.9

Recently, some complexes of FL with TCNQ (FL–TCNQ) and other electron withdrawing molecules have been synthesized and characterized by diffraction and spectroscopic techniques and by computational methods.10,11 Starting from these bases, we decided to search for new strategies to obtain this class of compounds and in particular to investigate the kinetics of the formation of the molecular complexes directly in the solid state, employing novel characterization techniques. Solid-state synthesis is a newly, rapidly emerging field in synthetic chemistry, providing both extreme purity of products, due to the absence of contaminating solvents, and null or very low environmental impacts, along with the cheap cost of preparation not only in organic synthesis scenarios12a,b but also in cocrystal chemistry.12b,c

An exhaustive characterization of the reactivity at the nanometromicrometric level is mandatory to understand the reaction mechanism and to better evaluate the applicability to possible technological devices. The availability of third generation synchrotron radiation sources and the improvements in detector performances opened the possibility of performing structural analysis under in situ conditions. However, the diffraction-based structural techniques show strong limitations when applied to disordered moieties and defective structures, thus giving little or no information on the electronic or vibrational properties. These limitations have been overcome by multitechnique experiments preferably performed simultaneously when the reactivity was investigated. The larger the complementarities of the technique combined with X-ray powder diffraction (XRPD), the greater is the obtained additional information.13 We have combined diffraction with Raman scattering and developed a novel Raman–high-resolution XRPD> experimental setup for the in situ and simultaneous investigation of the kinetics of transformations occurring at surface and bulk of materials at nonambient conditions.14 Such a combination of Raman and XRPD represents a major innovation with respect to standard in situ XRPD studies.15

In the present paper, the solid-state reaction under isothermal conditions of FL with TCNQ to form the CT molecular complex FL–TCNQ10 (Figure 1) was investigated. On one hand, the Raman probe allowed the characterization of the reaction kinetics in the first steps of the reaction at the surface of the TCNQ crystallites. On the other hand, the kinetics of the reaction in the bulk was characterized by XRPD. The Raman and XRPD complementarities were therefore fully exploited, at in situ
Formation of a Molecular Complex

conditions, by carrying out simultaneous measurements in an experiment where the in situ but separate XRPD and Raman approaches would have been hampered owing to the difficulty in synchronizing the reaction coordinates by the two probes.

Experimental and Methods

Preliminary Measurements. Equimolar amounts of FL and TCNQ (both obtained from Sigma Aldrich and used as such without further purification) were finely ground separately using an agate mortar and then mixed together in the solid state. The as-prepared reactants were then mixed together in the solid state. The as-purchased samples have a crystallite size of ca. 10 and 50 *µ*m (like the crystallite employed for the hot stage microscopy experiment), and after being crushed into a agate mortar they became smaller than 5 *µ*m (size estimated indirectly by the fact that aggregates and not single crystals can be seen on the optical microscope).

The reaction was at first tested on a conventional diffractometer employing a ThermoARL powder diffractometer XTRA, using the Debye-Sherrer geometry with Cu Kα radiation, focusing mirrors, and a solid-state Peltier cooled detector. All powder diffraction spectra were measured in continuous mode using the following conditions: 2θ angular range 5°−30°, tube power 45 kV and 40 mA, step size 0.02°/min. For the in situ experiments a furnace, working in the range 298−573 K and controlled by a thermocouple, was used (see Supporting Information Figure SM1a). The samples were treated to study the evolution of the ground reactants after mechanical mixing in isothermal conditions: (i) at RT for 48 h, with no evidence of reaction (see Supporting Information Figure SM1b) and (ii) at 348 K for 24 h with full conversion to the FL−TCNQ complex (see Supporting Information Figure SM1c). These preliminary experiments allowed finding the best reaction conditions.

UV−vis-NIR spectroscopy has been carried out with a Perkin-Elmer Lambda 900 spectrophotometer equipped with a diffuse reflectance sphere accessory. Hot stage microscopy has been carried out by a THMS600 Linkam stage as sample holder. The sample was a single crystal of TCNQ with FL crystallites deposed in the adjacent space. The vapors of FL were produced by heating the sample at 373, 383, 393, and 403 K. All the analyses gave similar results, but only the 403 K data, where the reaction is more evident, will be shown (in Figure 7 in the results and discussion section). The images and the Raman data were obtained at room temperature before and after exposure to the FL vapors by a Horiba Jobin Yvon LabRAM HR instrument, equipped with an Olympus BX41 microscope and a television camera. TCNQ, FL, and product crystals were recognized by visual analysis (FL is transparent, TCNQ is faint cyan, and FL−TCNQ is dark red) and confirmed by Raman spectroscopy. The ex situ Nd:YAG laser Raman experiment on a single crystal of FL−TCNQ was performed on a Bruker RFS100 spectrophotometer. FL, TCNQ, their 1:1 mechanical mixture and single crystals of the FL−TCNQ complex were measured in the solid state with 1 cm−1 high resolution at 50 mW irradiating laser power, averaging 500 scansions per spectrum.

In Situ Raman/XRPD Setup. The in situ simultaneous Raman-XRPD experiments were performed at the ESRF in Grenoble on BM1B Swiss-Norwegian (SNBL) beamline. High resolution powder diffraction data were collected with the standard BM1B setup. A Raman spectrophotometer is permanently integrated in the SNBL beamline and can be coupled to all available X-ray techniques. The Raman instrument is a Renishaw inVia spectrophotometer especially adapted for remote measurements. The spectrophotometer is equipped with two different Raman lasers: a green (532 nm) and a red/NIR (785 nm) source. The frequency dispersion is provided by a 1800 lines/mm grating for the 532 nm laser and a 1200 lines/mm grating for the 785 nm laser. An optical fiber cable distributes the lasers to the various instruments, and a collection fiber returns the Raman signal to the spectrophotometer. A RPF10 compact video fiber optic probe with a 100 mm long distance objective focuses the laser on the sample and collects the Raman signal back. The samples were contained in rotating quartz or glass capillaries, standard for XRPD, and also suitable for Raman measurements. The thermal treatments were carried out using a Cyberstar gas blower, controlled by a Eurotherm 902b temperature controller. The temperature was monitored by a thermocouple inserted at the blower gun opening, and the real temperature of the capillary was calibrated by monitoring, in a parallel experiment, the cell volume expansion (obtained by Rietveld analysis) of a silver wire in the temperature range from 298 to 1000 K. The calibration was also crosschecked by in situ melting of a pure FL sample. For the isothermal experiments, given the small mass of the capillary, the set temperature was reached within a few seconds after the start of the experiment on translating the preheated gas blower in the correct position to treat the sample. A detailed description of the experimental setup, together with its potentialities and limitations, is given elsewhere.

Data Collection. Five isothermal treatments were carried out on the synchrotron at 348, 358, 368, 378, and 383 K to investigate the kinetics of the reaction, by the simultaneous use of the Raman and XRPD probes. For each temperature several diffraction patterns (from 2θmin = 3.5 to 2θmax = 15.5) were collected (one every 4.5 or 9 min−1) to monitor the progress of the reaction. The XRPD patterns were collected using radiation with λ = 0.50051 Å (for the data sets at 348 and 383 K, and with λ = 0.60006(1) Å for the other isothermal analyses (the difference in wavelength pertains to the different beam time employed in separate sessions). The calibration was done using the lattice parameters of the NIST Lanthanum Hexaboride (LaB6) standard (SRM 660b; nominal a = 4.15695(6) Å at RT) with the standard SNBL experimental setup.

Raman data were collected with the green (532 nm) laser at 358, 368, 378, and 383 K and with a red/NIR (785 nm) laser at 348 K. The Raman grating calibration was systematically controlled by checking the position of a Si standard at 520 cm−1, and a resolution between 1.5 and 4 cm−1, depending on the spectral region of interest, was achieved. The Raman data sets were averaged by summing together a restricted number of adjacent and inseparable (i.e., without clear evidence of the evolution of the reaction) data sets to improve the signal-to-noise ratio. A background baseline correction of the spectra and an appropriate peak fitting by the OPUS software were carried out to obtain the best peak positions.

Rietveld Refinement of the XRPD Patterns. The powder patterns were individually refined by the Rietveld method using the GSAS/EXPGUI software to carry out the quantitative analysis (see mole fraction vs time plots in Supporting Information, Figure SM2) and to obtain the crystallite dimensions of reactants and products. The structural models of FL, TCNQ, and the FL−TCNQ complex reaction product were taken from the literature.

The values of the goodness of fit parameter (χ2), along with those of the agreement parameters wRp and Rp, for the 18 scans at 358 K are reported in Table SM1 of the Supporting Information and indicate a reasonably good fit between the calculated and the observed intensities (χ2 ∼ 2, wRp (fitted) ∼ 0.19, Rp (fitted) ∼0.16, wRp (background) ∼ 0.18, Rp (background) ∼ 0.14), thus confirming the results of a previous paper where it was demonstrated that, despite the rather short data acquisition time (between 4.5 and 9 min for a complete XRPD scan), the data were of good enough quality for performing a meaningful Rietveld refinement. The reliability of the current refinement has been supported by the selection of Rietveld refinement plots reported in the Supporting Information (Figure SM3). A similar agreement is observed for all the other data sets.

Figure 1. The formation of the FL−TCNQ molecular complex.
The crystallite size (Å) was calculated for each diffraction pattern by the formula:

$$\rho(i) = \frac{18000K\lambda}{\pi LX_{\text{SAMPLE}}(i)}$$

where $K$ is the Scherrer parameter assumed as constant ($K = 0.89$).\(^{21}\)

The wavelength is denoted by $\lambda$, and $LX_{\text{SAMPLE}}(i) = LX_{\text{REF}}(i) - LX_{\text{IB}}$ is the Lorentzian component of the sample-induced broadening of the peak profile (depending on $(\cos \theta)^{-1}$), taking into account the instrumental broadening ($LX_{\text{IB}}$). The values of $LX_{\text{EFF}}(i)$ are obtained by the Rietveld refinement of the profile parameters of each scan ($i$). $LX_{\text{IB}}$ is the instrumental broadening and was evaluated by refining the profile parameters of a LaB$_6$ standard sample (with no refinement of the cell parameters). For our synchrotron setup an average value of $LX_{\text{IB}} = 1.11$ was obtained.

**Kinetic Analysis of XRPD and Raman Data.** The reaction coordinate for the XRPD data, $\alpha_{\text{XRPD}}$, used to evaluate the kinetic trend of the reaction, was calculated as a ratio between the moles of product ($\text{FL} - \text{TCNQ}$ complex) at each scan ($\text{mole}_i$) and the moles of TCNQ available at the beginning of the reaction ($\text{mole}_0$) as obtained by Rietveld least-squares analysis:

$$\alpha_{\text{XRPD}} = \frac{\text{mole}_i}{\text{mole}_0}$$

Similarly, the Raman reaction coordinate, $\alpha_{\text{Raman}}$, is defined as the ratio between the area (i.e., the integral) of the Raman peak of TCNQ set at $1600 \pm 2$ and $1595 \pm 2$ cm$^{-1}$ in the product and in the reactant respectively at each scan $i$, divided by maximum value of these integral ratios, used as a normalization factor:

$$\alpha_{\text{Raman}} = \frac{\int TCNQ_{\text{product}}}{\int TCNQ_{\text{reactant}}}$$

The reaction order $n$ and the rate constant $k$ were obtained using the Avrami\(^{23}\) equation for both XRPD and Raman data:

$$R = 1 - e^{-(kt)^n}$$

and the interpolation of the data was carried out using its linear form:

$$\ln[-\ln(1 - \alpha)] = n \ln t + n \ln k$$

where $\alpha$ is the reaction coordinate, $k$ is the rate constant, $t$ is the considered until reaction time, and $n$ is the empirical reaction order.

From the fitting of the data with the Avrami equation (see Results and Discussion) the values of $n$ and $k$ were obtained. The $k$ values at different temperatures were finally used to obtain the activation energy using the Arrhenius equation.

Finally, in order to gain some insight into the actual reaction mechanism, we fitted the data with kinetic equations related to phenomenological models, such as the contracting volume, the contracting area model, also known as 2D advancing interface (2D-AI) model\(^{23}\) turned out to be the best one fitting our XRPD experimental data. This model is described by the equation:

$$kt = 1 - (1 - \alpha)^{0.5}$$

that can be expressed in the linear form:

$$\ln k + ln t = \ln[1 - (1 - \alpha)^{0.5}]$$

where the variables assume the same meanings described above.

From the statistical point of view, considering the preliminary experiments on the laboratory diffractometer and Raman, every experiment was carried out between 2 and 3 times with consistent results and acceptable reproducibility. Because of the limited machine time allocated by the ESRF and the reproducibility of the preliminary experiments only one data set for each temperature was collected. However, the good fit of the different points (3–5 isothermal reactions) in the Arrhenius plots ensures the statistical significance of the obtained kinetic results (i.e., the obtained reaction orders and activation energies).

**Results and Discussion**

**The Collected XRPD and Raman Data.** The FL–TCNQ molecular complex\(^{10}\) was obtained for the first time by solid-state synthesis, according to the reaction illustrated in Figure 1, by heating the reactants sealed in a capillary and the kinetics of its formation were investigated. This solid-state synthesis strategy, despite its simplicity, has been seldom used to obtain molecular organic complexes.\(^{12}\)

The first mixing experiments of the finely ground powder of FL and TCNQ, in a 1:1 molar ratio at room temperature, showed that the reaction is initiated immediately, as indicated by the change in color from the lightly colored reactants to dark brown.\(^{10}\) Experimentally, the weakening of the FL green-laser Raman bands in the range 1599–1605 cm$^{-1}$ just after mixing at RT indicated that the reaction had started, but the lack of product peaks in the XRPD patterns even after 48 h (see Figure SM1b, Supporting Information) demonstrated that it only occurred at the molecular level on the surface of the TCNQ crystals. A parallel XRPD experiment conducted at 348 K (See Supporting Information SM1c) revealed a complete transformation to product FL–TCNQ after 48 h of data collection. This result shows the importance of temperature in driving the reaction to completion at the bulk level. Concordantly, the separate Nd:YAG NIR (1064 nm) laser Raman experiment, conducted at RT on the dark brown crystalline powders of the FL–TCNQ mechanical mixture, displayed the unreacted separated molecular counterparts; hence, the colored matter corresponds necessarily to a minimal thin surface layer of the generated product.

Then a series of combined Raman–XRPD experiments was performed to shed light on the features of the reaction in the bulk of the crystals (XRPD), on the crystal surface (green-laser Raman), and at the micrometric level by crystallite size analysis. Rietveld analysis of the diffraction patterns allowed obtaining the amounts of reactants and product at each step of the reaction. The results are reported as reaction coordinate (related to the product mole fraction as in eq 1) versus time in Figure 2a. The full mole fraction data for the reactants, compared to those of the product at 348, 358, 368, and 378 K, are available in Figure SM2, Supporting Information. The results obtained at the four isothermal conditions and the trends of the reaction coordinate evolutions in Figure 2a gave a clear indication of a thermally activated reaction. Thus, a full kinetic analysis was carried out on the XRPD and Raman data collected during the in situ isothermal runs. The lattice parameters of the three compounds, controlled at the end of the 358 K experiment, remained almost unchanged, with just small variations in those of FL and TCNQ, probably due to their evolution toward a nanocrystalline form (Figure SM4, Supporting Information). The simultaneously collected Raman data shown in Figure 2b were fitted with standard curves simply to highlight the trends, but the kinetic analysis was carried out by fitting the experimental points using solid-state kinetic eqs 4 and 6 (see discussion below).

A small loss of FL was observed during some experiments, due to a temperature gradient in the sealed capillary between the hotter central part (where the gas blower is more efficient) and the cooler lateral parts. A separate experiment, on a conventional diffractometer with a different reaction chamber, designed in such a way that the hot points are in the lateral parts of the capillary and the cold point in the center (where
the X-ray beam hits the sample), indicated that FL sublimation occurred without material loss and the reaction subsequently proceeded until complete TCNQ consumption (Supporting Information SM1c).

At the very beginning of the isothermal runs, when no reaction product was detected by the XRPD probe, the analysis of the Raman spectra showed a very high sensitivity to minute changes in molecular environment. More precisely, the observed immediate variations of the bands at 1204 cm$^{-1}$ (C–CN stretching), 1450 cm$^{-1}$, and 1600 cm$^{-1}$ (ring deformations) highlighted the early formation of the complex and the slow disappearance of isolated TCNQ. These data showed a clear interaction of the more volatile FL with the TCNQ crystals, indicating that the sublimated FL first reacts with TCNQ on the crystal surface, and henceforth the reaction advances from the surface toward the inner part.

The Surface Sensitivity of the Green Laser Raman Probe. The red and green laser Raman probes provided different indications when applied to the same reactions. The RED/NIR (785 nm) Raman data gave a reaction constant and a reaction coordinate as defined in eq 1 (to save time the measurements were stopped when the reaction coordinate becomes larger than 0.5); (b) evolution of the Raman reaction coordinate as defined in eq 2. The qualitative trends are highlighted by interpolation with polynomial function (continuous line).

The small energy difference alone between red and green radiation cannot explain the observed dramatic difference, which must be ascribed to the different optical absorption efficiency toward different laser radiations shown by the FL–TCNQ molecular complex. As it can be seen in the reflectivity spectra of Figure 3, the absorption edge of the product is located at around 650 nm, in between the green (532 nm) and red (785 nm) wavelengths. Thus, the larger absorption of the green radiation resulted in a reduced penetration depth. The absorbed energy with the resonant green laser was mostly degraded by fluorescence. One can state this because the fluorescence background increased at a similar rate as the growth rate of the reaction product. Because the radiation is completely extinguished beyond the very surface of the crystallites by molecular absorption, the surface sensitivity was effectively enhanced. An ex situ UV-vis-NIR experiment was also carried out by measuring the absorption of the green radiation on the mechanical mixture sealed inside a capillary and treated at 348 K with data collected every 15 min for 2 h. A significant absorption of the 532 nm radiation was observed after 15 min and remained constant up to the end of the solid-state reaction, thus confirming a constant surface sensitivity of the Raman probe during the reaction and the possibility of a quantitative estimation of the reaction coordinate at the surface from the Raman intensities. Conversely, the red laser was found to have a drastically reduced electronic absorption and was therefore able to further penetrate and probe the reaction advancement into the bulk of crystals.

An ex situ Raman experiment, operated by using the 1.064 mm Nd:YAG laser NIR source, is further supportive of this hypothesis. In the NIR spectral region of the FL–TCNQ complex, which is completely transparent to the irradiating Raman light, the examination of the 1:1 solid-state reacting brown mixture revealed the bulk presence of the two separate molecular reactants, with no modification of their respective spectral features. For comparison, the peculiar spectroscopic aspects of the molecular complex were observed on FL–TCNQ macroscopic single crystals grown from solution (Nd:YAG laser Raman spectra are presented in Figures SM6, SM7, SM8, Supporting Information). It is worth noting that the solid-state reacting mixture, made of the apolar FL and the polar TCNQ phases, experiences a remarkable hampering of the absolute Raman intensity for the apolar unit, that is, the FL molecule.

Figure 2. Evolution of the reaction with time (minutes). (a) Evolution of the reaction coordinate derived from the amount of formed product as obtained from the Rietveld analysis of the diffraction data as defined in eq 1 (to save time the measurements were stopped when the reaction coordinate becomes larger than 0.5); (b) evolution of the Raman reaction coordinate as defined in eq 2. The qualitative trends are highlighted by interpolation with polynomial function (continuous line).

Figure 3. UV-vis-NIR spectrum of FL, TCNQ, and FL–TCNQ (product) complex product showing a remarkable change in reflectance in going from the green laser region (before 650 nm) to the red laser region (after 750 nm). Raman experiments were carried out at 532 nm (green laser) and 785 nm (red/NIR laser), highlighted by the colored vertical arrows.
This abatement is observable in different situations of intermolecular interactions.\textsuperscript{10,14a,24} The spatial nearness with a locally polar structure, such as the carbonitrilic TCNQ, determines a decrease of the FL polarizability, due to the possible quenching of the electron motions throughout the molecular frame caused by electrostatic weak interactions.\textsuperscript{24} The effect operates not only in presence of established intermolecular interactions, such as in molecular\textsuperscript{10} or inclusion\textsuperscript{24} complexes, but also in the case of finely and homogeneously mixed solid-state powders, where only long-range dipolar interactions are present.

Hereafter, the separate Nd:YAG laser experiment undoubtedly states that, apart from the surface-absorbed sources, a transparent wavelength laser frequency penetrates into the bulk of a crystallite, providing a description of the core crystal situation.

Finally, it is worth pointing out that the green Raman laser indicated that the reaction at the surface was completed after 60 min at 358 and after 5 min at 368 K (Figure 2b), whereas the bulk XRPD probe (Figure 2a) detected a slow advancement of the reaction in the bulk even after 2–4 h, when the average crystallite size exceeded the micrometer especially for the lower T isothermal reaction. The growth of the crystallites beyond the micrometer size is indicated by (i) the possibility of seeing the single crystallites of the product in an optical microscope and (ii) by the fact that, in the second part of the reaction, the amount of product increased (XRPD reaction coordinate) but no further peak broadening occurred, indicating that no new crystallites were created. A rough estimate of the penetration depth of the green Raman probe can be obtained observing that when the Raman probe indicated the end of the reaction, the crystallite size is evaluated in the range 300–500 nm. Thus, the green Raman laser, is much more surface-sensitive, and for this reason, the green laser Raman was employed in all the experiments to perform the kinetic analysis, in order to fully exploit its complementarities with the XRPD probe. It should be noted that the surface reaction at 383 K was too fast for the surface green laser Raman probe, which indicated that only 10 s (the collection time of the first Raman spectrum) were enough to complete the reaction, and therefore the data were not sufficiently reliable to be used into the surface kinetic analysis.

**Kinetic Analysis of the XRPD and Raman Data.** The Raman and XRPD data turned out to fit with an acceptable error the general Avrami model, and the XRPD data fitted the phenomenological 2D advancing interface model.\textsuperscript{23} Previous studies have demonstrated that the Avrami equation can be successfully employed to investigate the kinetics of the formation of molecular compounds by spectroscopic data.\textsuperscript{25} In the present paper, we applied for the first time the equation in a simultaneous study of both bulk (XRPD) and surface (Raman) kinetics.

Using the XRPD data, the slope and intercept coefficients of the fitted lines in the Avrami plots of Figure 4a allowed us to calculate the values of the reaction order ($n \approx 1$) (slope in eq 4) and of the rate constant $k$ (Table 1) for the isothermal runs at 348, 358, 368, and 378 K (383 K data were not used since only two experimental points from the plateau region depicting an almost completed reaction were available). The $k$ values observed by the Raman probe increase with $T$ at a faster rate; that is, $k$ obtained by Raman analysis at 358 K is smaller than $k$ obtained by XRPD, but exceeds $k$ by XRPD at higher temperature data sets, because of the deceleration of the reaction in the bulk, where diffusion of FL plays a more important role, thus becoming the rate limiting step. Thus, the values of ln $k$ obtained were then plotted vs the inverse of the temperature to obtain the Arrhenius plot of Figure 5a and to calculate the activation energy for the complex formation. A small curvature can be observed and deviation of the linear fit in the data collected at a higher acquisition time as shown in Figure 4.
pertaining to the slowing down of the reaction tending to plateau conditions. This is in agreement with the known behavior of the Avrami equation, that usually best fits the data if the reaction coordinate is smaller than 0.85. However, its robustness (double logarithm) ensures that, despite the observed curvature, reliable kinetic parameters can be extracted. Anyhow, to avoid any possible bias, we ensured that the obtained kinetic parameters (k, n, and the activation energy) only changed within the e.s.d’s of the reaction coordinate values obtained from the Rietveld refinement of the diffraction data.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>k (XRPD fixed slope = 1) [obtained n values]</th>
<th>k (Raman532 nm fixed slope = 2) [obtained n values]</th>
</tr>
</thead>
<tbody>
<tr>
<td>348</td>
<td>0.0054 [0.95]</td>
<td>N/A</td>
</tr>
<tr>
<td>358</td>
<td>0.0108 [1.19]</td>
<td>0.0084 [2.70]</td>
</tr>
<tr>
<td>368</td>
<td>0.0501 [1.09]</td>
<td>0.0625 [1.86]</td>
</tr>
<tr>
<td>378</td>
<td>0.1918 [0.74]</td>
<td>0.8885 [2.99]</td>
</tr>
<tr>
<td>383</td>
<td>0.2442 [N/A]</td>
<td>N/A (value &gt;1) [N/A]</td>
</tr>
</tbody>
</table>

* Raman data not available (N/A) at 348 K, because the red laser (785 nm) was employed, and at 383 K, when the reaction was too fast to analyze.

Figure 5. Arrhenius plot from XRPD data (a) and from green laser Raman data (b).
data indicates that at the surface the sublimated FL molecules have a higher degree of freedom and requires the entropic loss of extra translational and rotational energy in order to orient themselves in the correct position to allow the charge transfer complex formation, thus confirming the sensitivity of the vibrational spectroscopy probe toward solid–solid reaction interface, where the conformational freedom is important.27

**Investigation of the Reactivity at the Micrometric Level.** The sharpening of the product peaks and the broadening of the reactant peaks in the diffraction patterns, due to the increase of the crystallite size of the product and its decrease for the reactants, was also used to derive kinetic information at the nanometer and micrometer scale (Figure 6). The 358, 368, and 378 K data sets (Figure 6b) show a nice increasing behavior that can be interpolated by a polynomial fit (continuous line in Figure 6b). Conversely, the large spread of the crystallite size values at 348 K in Figure 6a is probably due to the effects of the simultaneous presence of small and larger (favored by the slower growth at smaller temperature) crystallites, with large crystallites causing also preferred orientation problems. However, a trend line (broken line in Figure 6a) can still be found to highlight the increasing behavior of the crystallite sizes (sizes smaller than 200 nm prevail in the first 30 min, while points above 400 nm prevailed beyond 150 min as shown in Figure 6). When the average crystallite size reaches about 300±500 nm, the crystal size becomes too large to produce crystallite size induced broadening, and thus the peak full width at half-maximum (fwhm) is determined mainly by the instrumental setup. This limiting value was reached after about 165 min at 348 K and after 56 min at 358 K, well before the end of the reaction. At higher temperatures (368 and 378 K) crystallite dimensions of the same order of magnitude were reached after 30 and 10 min, respectively, as shown in Figure 6, reporting the variation of the estimated product crystallite size during the four isothermal scans. It is worth noting that the reaction proceeds without the formation of new crystallites (that would induce observable peak broadening also at higher reaction times), and therefore the crystallite size must grow beyond the 300±500 nm to sizes not observable by the XRPD peak broadening analysis. However, the analysis with an optical microscope of a FL–TCNQ mixture treated ex situ at 358 K for 24 h indicated crystals that can be seen with the optical microscope and resulted therefore much larger than the 500 nm limit observable by the XRPD data.

**The Reaction Mechanism of the FL–TCNQ Complex Formation.** The kinetic data on the FL–TCNQ solid-state reaction allowed us to unravel the reaction mechanism as depicted in Figure 7, together with the picture of a TCNQ crystal before (a) and after (b) exposure to FL vapors (a full collection of pictures taken during the reaction by hot stage microscopy experiment is reported in Figure SM9 of Supporting Information). The complex formation resulted thermodynamically controlled by the sublimation of FL, which is practically absent at room temperature (thus the reaction does not proceed beyond the surface), becomes relevant at 360 K, and rapidly increases as the temperature increases from 368 to 383 K and approaches the melting point of FL (385–388 K). FL sublimation plays a relevant role in the formation of the FL–TCNQ complex. Given the enthalpy of sublimation28 ($\Delta H_{\text{sub}} = 83 \pm 1 \text{kJ} \cdot \text{mol}^{-1}$) and the vapor pressure at 298 K ($p_1 = 0.0886 \text{Pa}$)29 of FL and using the Clausius–Clapeyron equation we can compute the vapor pressures due to sublimation at different temperatures, as shown in Table 2.

The kinetic analysis of the solid-state reaction to obtain the FL–TCNQ molecular complex, carried out from the XRPD data analysis, indicated an activation energy of 114 (±15) kJ·mol$^{-1}$, exceeding the enthalpy of sublimation of FL (83.1 kJ·mol$^{-1}$)
by approximately 30 kJ·mol⁻¹ and other rate limiting effects must be taken into account. In particular, there could be two most likely rate limiting steps: (i) the repulsion of the electronic clouds of the two approaching aromatic molecules forming the CT complex, and (ii) the diffusion of FL through product layers to reach the nonreacted inner parts of the TCNQ crystals. Instead, the activation energy of 250 kJ·mol⁻¹ derived from the green laser Raman data, probing the reactivity at the surface, is much higher, suggesting that for the initial stages of the reaction a larger energy is needed, which is dependent on the two reacting species FL and TCNQ, as shown by the observed smaller rate constant (k) from the Avrami plots at the lowest temperature (Table 1). Then the reaction at the surface accelerates at higher temperatures, becoming faster than in the bulk (as indicated by the k values in Table 1). It can be concluded that the faster reaction observed by Raman was not due to local overheating induced by the laser beam, because the reaction did not occur at room temperature under Raman irradiation only; that is, the mechanical mixture of FL and TCNQ was stable under the green laser for days. Moreover, a hot local overheating occurred without any actual change in the kinetics, the reaction coordinate by the Raman probe would have resulted into an Avrami plot with the same slope (i.e., same reaction order and mechanism) but with a larger intercept value. Instead, the Raman probe indicated a reaction order of two suggesting a reaction advancing on a planar surface, which is consistent with nuclei of product (not detectable by diffraction) formed on the surface of the TCNQ crystallites and expanding (as indicated by the hot stage microscopy) to coalesce into a nanometer scale layer (as indicated by the crystallite size analysis). Furthermore, the growth of the product layer (and of the size of the product crystallites) continues on the surface of the TCNQ crystals, according to the mechanism depicted in Figure 7 (confirmed by the hot stage microscopy experiment pictures). Figure 7a,b shows the images obtained before (a) and after (b) exposure to FL vapors (Figure SM9 of the Supporting Information). The black arrows indicates parts of the TCNQ crystals that were clearly transparent before the exposure to FL vapors and assumed a typical dark color of the FL—TCNQ complex after exposure.

At this point, the product layer is thicker and its crystallites have reached the micrometer size with the reaction speed becoming smaller (Table 1) because the amount of FL available for reaction progress is limited by its diffusion in the thick and more compact product.

Thus, the optimum amount of FL needed to complete the conversion of TCNQ into the product will depend from the reaction temperature, reaction time, reaction vessel volume, and ambient pressure. Even though a small but significant amount of FL is already available to start the reaction at the surface also at RT, its partial pressure is not enough to promote the reaction into the bulk. A higher temperature is required not only to yield a larger amount of available sublimated FL, but principally to increase the mobility and diffusivity of FL into the product layers to finally react with the TCNQ molecules, according to the model depicted in Figure 7.

Furthermore, we verified that several different poly condensed aromatic building blocks exhibit an efficient solid-state reactivity with kinetic features similar to those of FL and TCNQ, thus opening wide possibilities for the reported synthesis strategies in the field of molecular complexes. For all the molecular complexes examined (obtained by solid-state reaction of naphthalene, FL, and anthracene as electron-donating counterparts with TCNQ as electron-withdrawing counterparts) the most apt temperature \( T_{\text{REACT}} \) (expressed in Kelvin) to carry out the solid-state reaction (i.e., with yield close to 100%, reaction time less than 24 h and good crystallinity) was experimentally found to be equal to:

\[
T_{\text{REACT}} = T_M - T_M(15/100)
\]

where \( T_M \) is the melting temperature of the of the electron-donating counterpart.

Conclusions

An alternative solvent-free synthesis route to obtain crystalline molecular complexes formed by poly condensed aromatic building blocks was tested and its kinetics and reaction mechanism was fully characterized by the simultaneous Raman/XRPD approach to obtain quantitative information on both surface and bulk reactivity at once. The study of the solid-state kinetics is interesting because wider applications of this synthesis route may be envisaged in particular for this class of compounds, and more generally in materials chemistry. Some well-known advantages of solid-state synthesis are (i) cost saving due the use of very simple reaction chambers, (ii) high purity of products, and (iii) absence of dangerous waste solvents. The largest advantage of employing a simultaneous Raman/XRPD multitechnique characterization approach is given by the perfect synchronization between the reaction coordinates obtained by the two probes which eliminates the possible bias caused by different sample holders and conditioning modes used in traditional “in situ but separate” approaches. The Rietveld analysis of the XRPD data provided the information on the crystal growth at the nanoscale level and the peak profile analysis provided micrometer-scale data about the crystallite sizes. At the same time, surface reactivity was investigated by Raman spectroscopy employing an optically absorbed laser source (i.e., in the experiment, the green frequency). This information, together with the ability to predict the ideal temperature for the reaction (eq 7), will help the design and discovery of new materials by an high throughput screening of possible complexes, simply by heating the reactant mixtures at the calculated temperature of reaction. From the technologic point of view, the observed kinetic features of the product formation indicate that the growth of thin films (rather common in opto-electronic devices) by a very cheap chemical vapor deposition process at atmospheric pressure is actually possible.

Further studies of FL derivatives and/or alternative electron donors coupled with TCNQ for their CT behavior are currently under progress. Worth noting is the possibility of studying memory effects in these CT complexes, as reported for a TCNQ containing organometallic compound.

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Supporting Information Available: Ex situ XRPD and Raman data, mole fractions from Rietveld analysis, Rietveld refinements details and plots, comparison of XRPD, red and green laser Raman kinetic data.
plots, and full set of images from the hot stage microscopy experiment. This information is available free of charge via the Internet at http://pubs.acs.org.

References

(17) The experiments were carried out in two different shifts at the ESRF synchrotron, and in the second shift the detector operated faster thus allowing reliable XRPD patterns with 4.5 min data collections.
(21) This is a widely used, albeit rather crude, approximation because the Scherrer parameter actually varies with the shape of the grain-size distribution, which is never constant for real samples. In our case, the assumption of a constant $K$ can be accepted because we are mainly interested in the relative trend of the ordered domain size.

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