

## Invited Article

# (INVITED) Stable solution emission of 2,3,5,6-Tetrafluoro-7,7,8,8-tetracyanoquinodimethane

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## ABSTRACT

In the research field on materials for energy solutions, the exploitation of organic compounds and polymers is of great interest, especially in view of a more eco-sustainable development. In this context, the 2,3,5,6-Tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4TCNQ) molecule actively participates in the optimization of many optoelectronic devices based on such elements, thanks to its electrical properties. In this paper, we report a study on its optical properties, in particular demonstrating fluorescence emission from solutions containing F4TCNQ. This phenomenon is equally relevant, together with the effects on electrical conductivity, in the design of systems for energy technology. The results we present here offer new insights in the phenomenological picture of this molecule and can sharpen its applicability.

## 1. Introduction

The 4-fold fluorinated derivative of 7,7,8,8-Tetracyanoquinodimethane, F4TCNQ, is a molecule that has found extensive use in recent technological developments of organic-based electronics [1–6]. Its diffuse use derives from its properties as electron acceptor with a rather high electron affinity [7]. This characteristic makes this molecule particularly interesting in improving the electrical conductivity of optoelectronic devices such as OLEDs, transistors and sensors, but also in the doping of hole transporting materials, in photovoltaics [8–13]. The F4TCNQ molecule offers the ability to form charge transfer complexes (CTC) with normally electron donor organic compounds as in the case of the well-known parent species, the TCNQ [14]. Optically, these charge transfer complexes are characterized by new energy transitions in the UV–Vis-IR. The spectral position of these new bands also depends on the structure of the electron-donor compound. In the case, for example, of poly (3-hexylthiophene-2,5-diyl) (P3HT) three new absorption bands, one in the NIR (~0.6 eV), one in the visible (~2.0 eV) and one in the UV (~3.4 eV), appear after doping with F4TCNQ [15]. Furthermore, the formation of these donor-acceptor complexes has given access to new electrical and magnetic properties in organic compounds [16,17], starting with the first demonstration of “metallic” conductivity of the TTF-TCNQ [18]. More recently the synthesis of the same complex but in nanostructured form has revealed excellent electromagnetic absorption

(EMA) and electromagnetic interference shielding (EMI) [14]. The formation of CTCs from pyrene and F4TCNQ brought anisotropic magneto-electric coupling [19], while conjugating pyrene with 2,3-di-O-methyl cellulose and TCNQ as acceptor, allowed to obtain emission properties in the red and NIR range, in biocompatible systems [20]. At the same time, the electronic transfer can induce a photoluminescence quenching, when the F4TCNQ interacts with an emitter [21–23]. This phenomenon can be generally a diagnostic tool in the photo-physical study of luminescent materials but also implies a typical technological dichotomy, being both useful, as in the case of solar cells and detrimental, for example in light emitting systems. Therefore, considering the application potential of this molecule and the strong impulse in materials science towards a more effective and sustainable energy technology, a fundamental analysis of the materials is equally necessary in order to optimize its exploitation. In this work, we present a spectroscopic study of the behavior of the F4TCNQ molecule and in particular the analysis of its fluorescence emission. Some previous reports on F4TCNQ solid crystals and TCNQ liquid solutions investigated their emission properties [24,25]. In this study, we report static photoluminescence measurements of F4TCNQ dissolved in different solvents revealing strong emission from F4TCNQ solution.

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## 2. Experimental

### 2.1. Materials and solutions

Taking into account the main role of the F4TCNQ molecule in materials science, which concerns above all, the p-type doping of organic compounds and polymers, we analyzed liquid systems dissolving the molecule in the most commonly used solvents also convenient for polar molecules, i.e. chloroform, toluene and acetonitrile. In particular, we purchased F4TCNQ from Ossila and used it without any further purification, Chloroform (anhydrous and non-anhydrous) and Toluene from Sigma Aldrich and Acetonitrile from MerckMillipore. The solvent choice also allows some consideration on the different polarity, which has already been shown to be an influential parameter in the behavior of these species [24]. As a reference for the preparation of all three solutions, we used a concentration of 787  $\mu\text{M}$  in order to avoid any saturation problem [26]. The F4TCNQ solubility decreases, in order, passing from Acetonitrile to Chloroform to Toluene [27]. Nonetheless, for the specific analysis the samples were prepared in the cuvette solution with a concentration of 7.8  $\mu\text{M}$  to circumvent any aggregation phenomena. In any case, we ensured sufficient absorption signal, in each system. For the spectroscopic analysis of the three samples, in fact, we initially examined the absorption spectra.

### 2.2. Optical measurements

Optics measurements were performed using a quartz cuvette with  $10 \times 10$  mm optical path and 4 optical windows both for optical density and luminescence characterization. We recorded absorption spectra using a Agilent Cary 5000 UV-Vis-NIR while for the photoluminescence we made use of the Agilent Cary Eclipse spectrophotometer. Photoluminescence and excitation measurements were performed in right angle geometry. After preparation, all samples were stored in ambient conditions.

## 3. Results and discussions

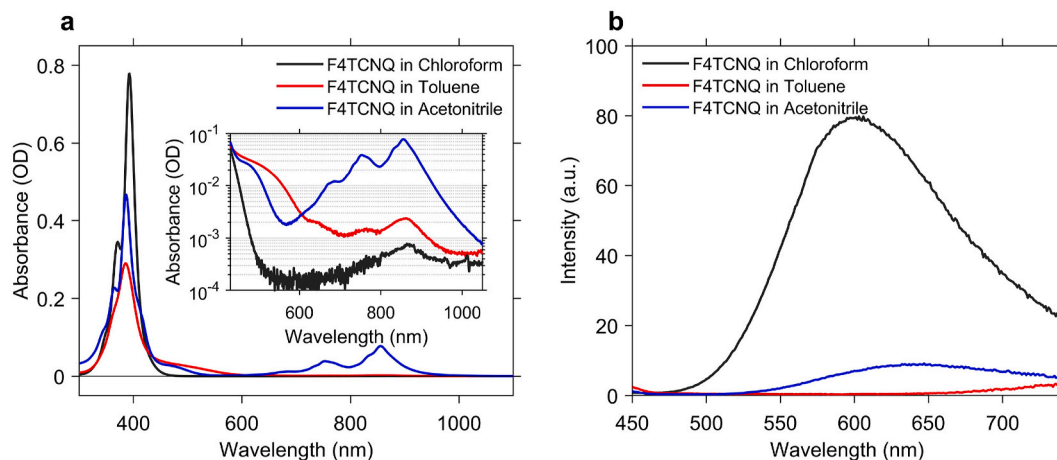
### 3.1. F4TCNQ solutions spectroscopy

The comparison between the optical densities of the three types of solutions revealed, as first, the different chemical stability of F4TCNQ in the three solvents. As reported in Fig. 1a, the spectral dependence of the absorption in the three samples shows three different shapes. The main peak, with a maximum of intensity centered at 390 nm, is generally

assigned to the absorption of the F4TCNQ molecule in its neutral conformation [25]. In such conditions, the absorption curve takes the spectral form of a double peak with a second contribution to the blue. As can be seen in the figure, the F4TCNQ solution in Chloroform perfectly reproduces this behavior. In the case of molecules dissolved in Toluene, two effects stand out from the recorded spectra. First, the main absorption peak undergo a spectral shift towards shorter wavelengths with respect to the same peak in chloroform. In addition, absorption peaks in the spectral region between 600 nm and 900 nm become evident together with an absorption band around 500 nm. The aforementioned contributions become even more intense in the case of the sample prepared in Acetonitrile. This absorption difference has already been reported previously and is usually related to the ionization of the molecule in the form of anion and/or dianion [28]. F4TCNQ molecule demonstrates to be more stable in Chloroform.

Subsequently, we conducted photoluminescence measurements on the same set of samples shown in Fig. 1a and we were able to record emission spectra both in the case of samples prepared in Chloroform and in Acetonitrile. On the other hand, as shown in Fig. 1b, the solution prepared in Toluene did not show any fluorescence. The spectra recorded in the two cases of Chloroform and Acetonitrile solutions present a red shift from the first one to the latter. As it has already been observed in the case of TCNQ solutions [24], the emission of its fluorinated derivative is also highly dependent on the solvent and in particular on its polarity. A series of non-aromatic solvents were examined in the TCNQ study and the increased polarity demonstrated a quenching effect on the photoluminescence intensity. In our case the same behavior emerges in the comparison between chloroform and acetonitrile. The case of Toluene instead differs from this trend considering that it is a non-polar solvent in which, however, the emission of F4TCNQ is completely quenched. However, an explanation can be traced back to a certain character of polarizability given by the presence of the aromatic ring together with the possible  $\pi$ -type interactions offered by the same electronic cloud. A similar quenching effect originating from the presence of aromatic solvents has in fact already been observed in the case of other molecules such as 3,5-diphenyl-8-CF<sub>3</sub>-BODIPYs or fullerene [29, 30].

In order to analyse the origin of the luminescence, we investigated the spectral evolution of the photoexcitation by measuring the fluorescence excitation of samples in Chloroform and Acetonitrile, at the peak wavelength of their emission, i.e. 600 nm and 620 nm, respectively. In both cases, the result (Figure S1) resembles the typical absorption spectrum of the neutral F4TCNQ species. In particular, as regards the molecule dissolved in acetonitrile, it can be observed that the band that



**Fig. 1.** (a) Absorption and (b) emission spectra of F4TCNQ in Chloroform (black lines), Toluene (red lines) and Acetonitrile (blue lines). Inset of panel (a) shows the contribution of the ionized species to the overall F4TCNQ absorption. Concentration of the three solution was set to 7.8  $\mu\text{M}$ . Emission spectra were recorder with excitation wavelength of 390 nm. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

contributes to the absorption at wavelengths longer than 400 nm is not present in the photo-excitation curve. This is a further indication that this absorption comes from the formation of an anionic species that does not produce any luminescence. We also want to point out that in the fluorescence excitation, the intensity of the absorption peaks in the blue region is slightly different from the absorption spectra. As this occurs for the sample in both solvents, we exclude any contamination factor.

After the emission experiments, we again analyzed the absorption of the three species subjected to the same photoexcitation conditions. In Fig. 2 we report the comparison among the absorption of samples prepared in Chloroform, Toluene and Acetonitrile before and after the fluorescence measurements. We noticed, in particular in the case of the Chloroform solution, the appearance of a new contribution in the optical density, around 500 nm. This feature may be associated, in particular, to

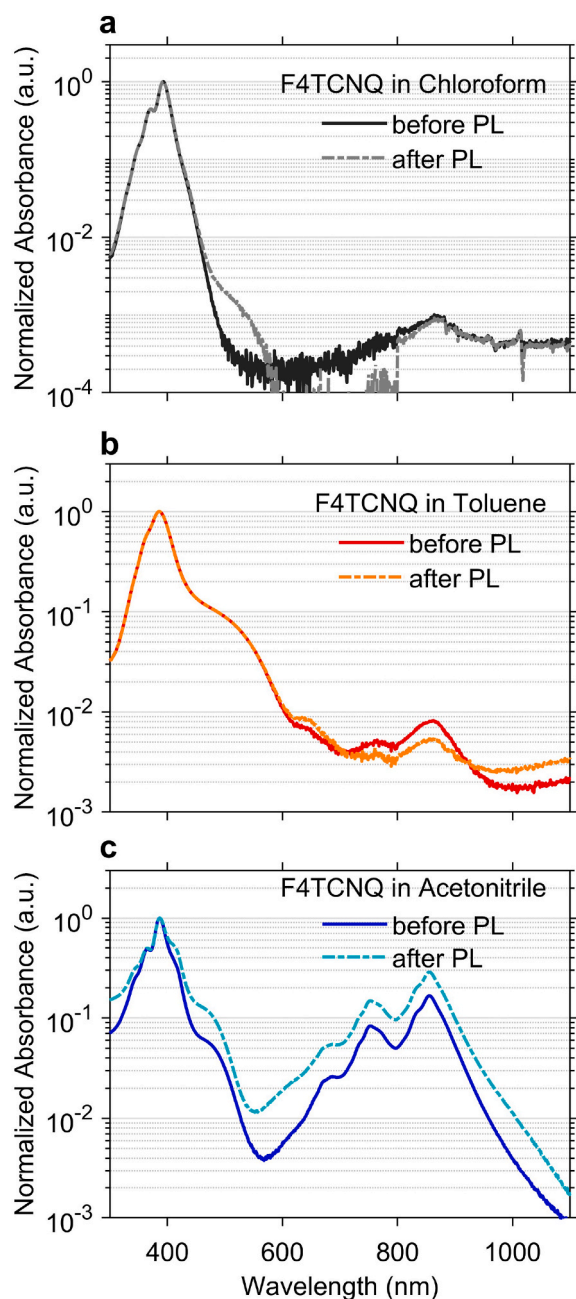


Fig. 2. Normalized absorbance spectra of F4TCNQ in (a) Chloroform, (b) Toluene and (c) Acetonitrile before and after the photoluminescence (PL) measurements. Excitation was set to 390 nm.

its ionization. As already reported in the case of solid crystals, in fact, these molecules can incur a photo-induced self-ionization [25].

### 3.2. Time and concentration effects

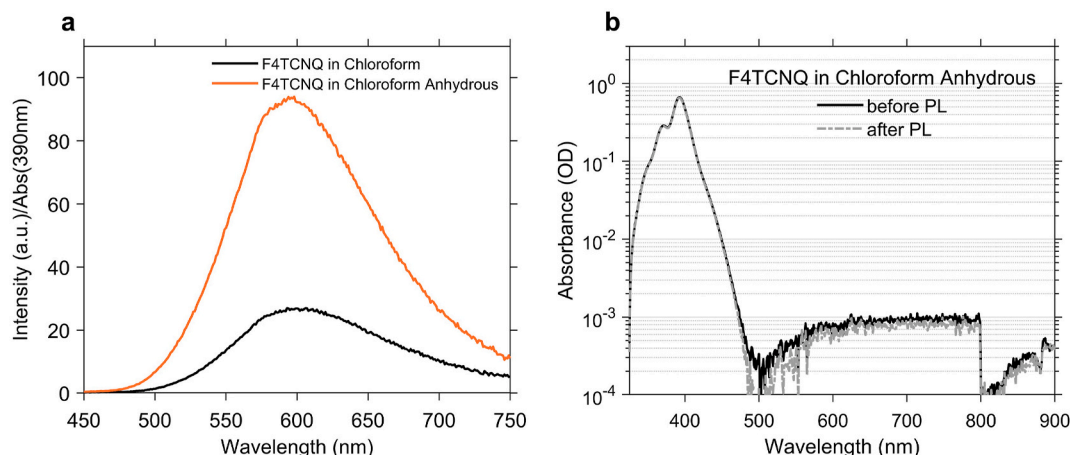
To further investigating this aspect, we tracked the evolution over time of this sample. Absorption measurements carried out after 48 h demonstrated how this phenomenon is irreversible. As illustrated in Figure S2, the intensity of the main peak decreases by about 50%. At the same time, the photoluminescence, in addition to undergoing a decrease in intensity corresponding to the decrease in the absorption, displays a slight shift to the red (see Figure S2b).

In order to overcome the problem of long-term stability of the F4TCNQ solution we explored a variation of the solvent, using anhydrous Chloroform. As indicated in Fig. 3, the use of anhydrous Chloroform and the preparation of the sample in an inert atmosphere in a  $N_2$  filled glovebox, has brought to light a considerable improvement, not only in terms of stability, but more generally, in the spectroscopic response of the F4TCNQ molecule. Fig. 3a shows the comparison of the photoluminescence recorded for the same molecule dissolved in anhydrous and non-anhydrous Chloroform, having normalized the emission intensity to the corresponding maximum absorption values. The sample prepared in the anhydrous solvent revealed an increase in the intensity of the emission of about 3.5 times. Furthermore, as shown in Fig. 3b, the shape of the absorption peak of this species does not undergo any change induced by the photoexcitation, contrary to what happens in the non-anhydrous case (see Fig. 3a). The anhydrous solvent seems to allow preserving the F4TCNQ molecule chemical stability. Moreover, from tracking down time evolution of both absorption and emission we observed a much smaller variation than in the previous case. As can be seen in Figure S2c, the intensity of the absorption peak decreases by less than 10% in the same time range and the fluorescence spectrum (Figure S2d) does not reveal any red shift as in non-anhydrous Chloroform.

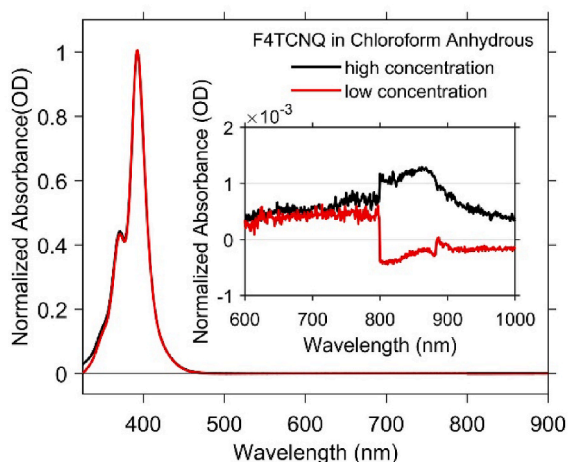
Ultimately, we also analyzed concentration-dependent behavior. For this purpose, we prepared a starting solution about 1.2 mM (in anhydrous Chloroform). Again, in this case, in order to record the absorption spectra, dilutions up to 12  $\mu$ M were prepared to obtain a sample as clean as possible. In Fig. 4 we report the normalized optical densities of the two samples with distinct concentration. As can be seen from the magnification in the red region of the spectrum, the sample prepared starting from the most concentrated solution reveals a relevant contribution from the anionic species. This result points to the fact that the increase in concentration favors the formation of ionized molecules. This behavior is in accordance with what has already been reported in the case of the TCNQ [31].

## 4. Conclusions

In conclusion, this study demonstrates that the F4TCNQ is capable of emitting photoluminescence in the visible spectral range. This behavior is strongly dependent, both in intensity and in the spectral position, on the polarity of the solvent. In the same way, the choice of the solvent affects both the chemical stability of the molecule and its photosensitivity. This analysis is helpful considering that the charge transfer of the p-dopant can vary quantitatively depending on whether it is in the neutral, mono-anionic or di-anionic state. It is therefore important to know the starting point in each solvent. In this case, we have shown how Chloroform can ensure the presence of only the neutral species, which can then conduct a single or double transfer. Furthermore, however, we observed that it is preferable to work with anhydrous solvents. The irreversible transformation of the starting species under illumination is an effect that can further complicate the use of the F4TCNQ. For the same reasons it is also important to keep the concentration of the materials under particular control in order not to incur any modification of the original state of the molecule, as we have shown. This set of



**Fig. 3.** (a) Emission of F4TCNQ in Chloroform (black line) and Chloroform anhydrous (orange line). The emission intensity is normalized to the corresponding absorption values at the excitation wavelength (390 nm). (b) Absorbance of F4TCNQ dissolved in Chloroform anhydrous before and after the emission measurement. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)



**Fig. 4.** Normalized absorbance spectra of F4TCNQ dissolved in Chloroform anhydrous in the limit of high and low concentration. The high concentration solution reveals traces of ionized F4TCNQ (inset).

characterizations first demonstrate how the F4TCNQ compound deserves a deeper analysis. However, the intent of this study is also to serve as a guide in particular in applications where the F4TCNQ is used as an analysis tool, such as titration or quenching methods, and in the development of devices for optoelectronics.

#### CRedit authorship contribution statement

**Andrea Rubino:** Conceptualization, Investigation, Writing – original draft. **Andrea Camellini:** Conceptualization, Investigation, Writing – review & editing. **Ilka Kriegel:** Conceptualization, Supervision, Funding acquisition, Writing – review & editing.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.omx.2021.100081>.

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