Identification of supramolecular structure in a semiconductor mixture of two organic compounds: curcumin and paracetamol

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Abstract

This study refers to experimental investigations about the semiconductor material (P-wt50%/C-wt50%)-mw obtained from pure curcumin and paracetamol starting molecules when physically mixed together and treated by microwaves in water. After some analysis aimed to understand the chemical structure of the resulting (P-wt50%/C-wt50%)-mw mixture performed by ¹H- and ¹³C-NMR techniques, some more FT-IR and UV-Vis analysis have been performed in order to investigate deep the way in which the precursors interact each other in the bulk semiconductor system. After the explanation that only admitting the existence of a peculiar supramolecular structure among the two pure materials, our study proceeded performing some morphological analysis. The SEM observations obtained so far show the presence of flaking planes which could slide on each other and, as consequence, could be responsible for the pronounced semiconducting properties shown by (P-wt50%/C-wt50%)-mw mixture. XRD spectra show a modification of the crystal organization of the mixture when obtained in the presence of microwaves.

Graphical abstract

Keywords Curcumin · Paracetamol · Organic semiconductor · Supramolecular structure

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1 Introduction

Following the discovery, in the late 1970s, of a high-conductivity phase of metallic type in doped polyacetylene (PA) [1], which is a conjugated linear polymer, enormous research has been undertaken in order to understand the origin and the mechanism of this conduction, by developing new polymer materials which have an increasing conductivity. These conductive materials as a whole have certain fundamental characteristics which are responsible for this high conductivity: (a) a structure which exhibits a delocalization of π -electrons on a large number of recurring units; (b) the HOMO–LUMO gap of the molecule that is directly related to the structure of the conjugate system.

Among the most well-known conductive polymers, mention may be made of polyaniline (PANI) [2], polypyrrole (PPy) [3], and polythiophene (PT) [4, 5].

Parallel to the development of the conductive properties of these polymers, the properties of organic semiconductors (OSCs) are of great interest to the scientific community and form the basis of electronics. Now these OSCs have important applications in the fields of display (light-emitting diodes) [6], low-voltage lighting (white light emission) [7], microelectronics (transistors Field effect) [8], or the conversion of solar energy (photovoltaic cells) [9].

In a paper, Tomasz et al. [10] studied some derivatives of diketopyrrolopyrroles symmetrically disubstituted with bi- or terthiophenes (DPPnT). These latter compounds exhibit a very interesting semiconductor behavior by having a small optical band gap, a tunable photoluminescence of high quantum yield and high charge carrier mobilities for both electrons and holes. In their study, they focused on the 2D supramolecular organization of the monomolecular layers of DPPnT derivatives with different lengths and positions of alkyl substituents and different sizes of thiophene segments. The results obtained by STM (Scanning Tunnel Microscopy) reveal that all these compounds show a strong tendency to form ordered monolayers of regular lattice-like structure. However, the specific characteristics of their organization depend on their molecular topology. The differences observed in the supramolecular organization revealed two specific characteristics of crucial importance: (a) a clear effect of the position of the alkyl substituent (central core with respect to the terminal thiophene ring) on the alkyl group interdigitation pattern; (b) an influence of the position of the alkyl substituents in the terminal thiophene ring on the conformation of the molecule and the resulting 2D supramolecular organization.

In a recent work, some of us have studied the electrical and optical properties of a material composed of

a mixture of two organic products, curcumin and paracetamol, in a ratio of 50–50 wt% with UV–Visible and impedancemetry [11]. The results show that this material exhibits good semiconductor behavior. These properties are comparable to those of the already available organic and inorganic semiconductors. It may even be considered the ideal candidate to replace inorganic semiconductors in some applications, which have some shortcomings in recent years. Among these properties, mention may be made of: (a) electrical conductivity that increases exponentially with increasing temperature; (b) an activation energy (E_a) of 0.49 eV; (c) an optical gap energy of the material equal to 2.60 eV and 2.46 eV for the direct and indirect band difference, respectively; (d) low permittivity of 6.77 at room temperature; (e) high transmittance of about 98%.

This led us to ask a lot of questions about the structure of this material and the type of reaction that associates these two organic compounds composing this mixture. In the current work, we conduct a study by NMR, FT-IR, UV–Vis absorption and scanning electron microscopy (SEM) in order to understand how curcumin and paracetamol are reorganized in the mixture.

2 Experimental

2.1 Reagents and solvents

All the reagents used in this work were of analytical grade and were used without further purification: p-aminophenol (Biochem Chemopharma, purity $\geq 98\%$), acetic anhydride (Sigma-Aldrich, purity $\geq 99\%$) and commercial curcumin (Sigma-Aldrich, purity $\geq 65\%$).

The solvents CDCl_3 (99.96 at.% D) and CD_3OD (≥ 99.8 at.% D) for NMR analysis have been purchased from Merck (Sigma-Aldrich).

2.2 Synthesis of acetaminophen (paracetamol)

Acetaminophen (paracetamol) was prepared by mixing 2.7 g (24.7 mmol) of p-aminophenol and 25 mL distilled water in a glass flask equipped with a condenser. The solution obtained was maintained at a temperature of 80 °C in a water bath with magnetic stirring. After cooling to room temperature, a volume of 3.5 mL (37 mmol) of acetic anhydride was added drop-wise and cautiously. The reaction mixture was left at a temperature of 60 °C with magnetic stirring for a further 10 min. After cooling in an ice bath the crystals of acetaminophen obtained were filtered, washed and air-dried in an oven overnight.

2.3 Preparation of samples mixtures

Two samples were prepared by mixing 1 g of powdered curcumin (commercial, MW 368.38) with 1 g of acetaminophen (synthesized, MW 151.16) [50–50 wt%]. An amount of 7 ml of distilled water was added to each sample and was thoroughly mixed. One of these two samples was placed into a microwave oven at 300 W for 10 min to get a homogenous semiconductor material. Finally, using a mortar, the mixture was crushed until a fine powder was obtained. The samples are labeled P for paracetamol, C for curcumin, (P-wt50%/C-wt50%)-mw for mixture of paracetamol and curcumin with microwaves and (P-wt50%/C-wt50%) for mixture of paracetamol and curcumin without microwaves. In a previous work was done where the parameters of the solvent, the power of the microwave and the treatment time were optimized [11]. For the power of the microwave oven and the treatment time, the only values that allow to observe a semiconductor behavior of the Curcumin-Paracetamol mixture are 300 W and 10 min. For the choice of solvent, water and acetone were used in the preparation. The same semiconductor behavior of the material was observed for both solvents.

2.4 Characterizations

The ^1H - and ^{13}C -NMR (Nuclear Magnetic Resonance) spectra were recorded by a Varian INOVA 500 spectrometer using tetramethylsilane as an internal standard. Multiplicities are reported as follows: singlet (s), broaden singlet (bs), doublet (d), multiplet (m) at 500 MHz by using CD_3OD and CDCl_3 as solvents.

The FT-IR spectra were recorded with a Jasco FT-IR-430 Fourier Transform Infrared Spectrometer in the 400–4000 cm^{-1} range. The powders have been collected as thin uniform film on top of a sticky tape and the substrate background have been acquired as blank spectrum and automatically subtracted by software from the spectra belonging to each sample under analysis. Every measurement has been acquired in transmission mode. This sample setup has been used in order to avoid any mixing with other compounds (such as KBr) with the aim to preserve as much as possible the environment around compounds and, in case, to preserve the supramolecular structure among curcumin and paracetamol in the mixtures.

The UV–Vis absorption spectra of the powder were recorded with a Jasco V-570 UV/Vis/NIR Spectrophotometer in the 300–700 nm range. The powders have been collected as thin uniform film on top of a sticky tape and the substrate background have been acquired as blank spectrum and automatically subtracted by software from the spectra belonging to each sample under analysis. Every measurement has been acquired in absorption mode. This

sample setup has been used in order to avoid the samples' dissolution into solvents with the aim to preserve as much as possible the environment around compounds and, in case, to preserve the supramolecular structure among curcumin and paracetamol in the mixtures.

Scanning electron microscopy (SEM) images were taken using an ESEM FEI Company XL-30 instrument with a LaB6 source, operating at 20 kV. Samples have been prepared by pressing slightly each powder material into the sample holder's cavity. Each sample has been then metalized with gold in order to establish an electric contact.

XRD spectra were recorded using Rigaku miniflex 600, anticathode: Cu(K α). Step size was 0.02° while speed scan was 4°/min.

3 Results and discussion

^1H - and ^{13}C -NMR (500 MHz) spectra of pure curcumin (C), paracetamol (P), P-wt50%/C-wt50% and (P-wt50%/C-wt50%)-mw samples in solution have been performed. Since a satisfactory solubility of these samples in methanol and chloroform has been found, they have been studied by NMR using CDCl_3 (chloroform-*d*) and CD_3OD (methanol-*d*₄) as solvents. From the analysis of (P-wt50%/C-wt50%)-mw molecular system in CD_3OD , all the characteristic signals coming from the different parts of the molecules have been found with the exclusion of the enol proton belonging to curcumin moiety as it has been shown in Fig. 1 and Table 1.

Since this evidence could be ascribable to a proton exchange with the methanol solvent, it has been thought to perform the measurements in an aprotic solvent such as chloroform. Indeed, in this way we had the possibility to fully characterize not only the composite systems (P-wt50%/C-wt50%)-mw, P-wt50%/C-wt50%, but C and P as well, comparing their results (Fig. 2). First of all it has been found that while P-wt50%/C-wt50%, (P-wt50%/C-wt50%)-mw and C samples show a satisfactory solubility in chloroform, the sample P has a lower solubility but still good enough to acquire ^1H - and ^{13}C -NMR spectra. In chloroform, we have been able to find the enol proton peak characterized by its diagnostic signal at around 16 ppm belonging to (P-wt50%/C-wt50%)-mw material. Therefore, the curcumin does not chemically react thorough its enol proton with the paracetamol counterpart.

In addition, no evidences of any other new covalent bond have been ascertained from ^1H - and ^{13}C -NMR analysis of samples (P-wt50%/C-wt50%)-mw and P-wt50%/C-wt50% in CDCl_3 .

From a quantitative point of view, the studied mixtures show a peculiar curcumin/paracetamol ratio. Despite the molar ratio among mixed curcumin and paracetamol

Fig. 1 ¹H-NMR spectrum related to (P-wt50%/C-wt50%)-mw in CD₃OD solvent. The inset shows the aromatic region

Table 1 (P-wt50%/C-wt50%)-mw, ¹H-NMR, CD₃OD assignments, chemical shifts (δ), constant couplings (J) and numbers of protons

H-position	δ (ppm)	J	Numbers of Hs
P1	2.07 (s)	–	3
P3	7.20 (s)	–	1
P5, P5'	7.31–7.29 (d)	10 Hz	2
P6, P6'	6.73–6.72 (d)	10 Hz	2
P8	4.86 (s)	–	1
1	5.95–5.94 (d)	5 Hz	1
3, 3'	6.63–6.60 (d)	15 Hz	2
4, 4'	7.58–7.55 (d)	15 Hz	2
6, 6'	6.83–6.81 (d)	10 Hz	2
7, 7'	7.49–7.47 (d)	5 Hz	2
10, 10'	7.11–7.09 (d)	5 Hz	2
11	3.91 (s)	–	6
12	–	–	–
13	–	–	–

s Singlet, d doublet

should be expected of 1:2.4 (taking into account that a fifty–fifty mixture in weight has been prepared), from our quantitative evaluations coming from NMR analysis,

different ratios have been found. For sample (P-wt50%/C-wt50%) an almost 1:3 ratio has been determined, while, for sample (P-wt50%/C-wt50%)-mw a 1:4 ratio have been evaluated among curcumin/paracetamol mixture, respectively.

In our opinion, this is a suggestion that what we are seeing from the samples (P-wt50%/C-wt50%) and (P-wt50%/C-wt50%)-mw is something different from a simple mixture of them, rather a particular kind of supra-molecular organization among curcumin and paracetamol has been reached thanks to the chosen experimental conditions and/or the microwave treatment performed during their preparation.

Considering the FTIR spectra, in literature, the characteristic region of phenolic OH stretching vibrations (Ar–OH) of the curcumin was found to be at 3595 cm^{−1} [12]. In our case, its value is (at 3665 cm^{−1}) shifted to higher wavenumbers most probably due to the involvement of intra-molecular H-bondings among curcumin molecules [13]. The Ar–OH stretching mode for paracetamol has been found (at 3660 cm^{−1}) more or less in the same region. In (P-wt50%/C-wt50%) and (P-wt50%/C-wt50%)-mw systems this broad and low intense band is shifted as well and appears at 3625 and 3667 cm^{−1}, respectively. In conclusion, among all the molecule here studied, the

Fig. 2 ¹H-NMR spectrum related to (P-wt50%/C-wt50%)-mw in CDCl₃ solvent. The inset shows the aromatic region

greatest 3667 cm^{−1} stretching vibration belonging to (P-wt50%/C-wt50%)-mw indicates its greatest tendency to form intra-molecular H-bondings involving Ar–OH moiety. Anyway, it cannot be excluded a somehow inter-molecular interaction of these phenolic hydroxyls with paracetamol. Explaining why this shift appears more strongly in (P-wt50%/C-wt50%)-mw than in (P-wt50%/C-wt50%), it can be stated that, most probably, the microwave treatment could lead to a quite different environment/supramolecular organization in its system. The Ar–OH groups are less available because involved not only in intra-molecular bonds but probably also to some kind of supramolecular and/or inter-molecular interactions among pure curcumin and paracetamol counterparts.

On the other side, the enolic OH stretching mode (R–OH) is predicted to be a strong band at around 3300–2000 cm^{−1} region. Such band did not appear experimentally in our case, in perfect agreement with what has been already published in literature by Tayyari et al. [14, 15] and Chiavassa et al. [16] for curcumin and similar compounds. In general, the intensity and broadness of this band depend on the strength of the intra-molecular hydrogen bonds. Upon increasing the hydrogen bond strength its intensity decreases, while its broadness considerably increases [17–20]. In our case, the enolic

OH band appears as a very broad band and characterized by a very low intensity at around 3534 cm^{−1} for C, 3540 cm^{−1} for (P-wt50%/C-wt50%)-mw, and 3538 cm^{−1} for (P-wt50%/C-wt50%) mixture; however, for paracetamol this enolic stretching band has been found at 3581 cm^{−1}. Note that the (P-wt50%/C-wt50%)-mw mixture gives the more shifted signal toward higher wavenumbers than (P-wt50%/C-wt50%) mixture if compared with pure curcumin.

In some published works [14, 15], they studied the dibenzoylmethane, a β-diketone system similar to curcumin. It has been suggested that π-systems, such as that belonging to phenyl groups, have the characteristic of increasing the H-bond strength thanks to a better conjugation with the central enol group. Moreover, the hydroxyl and methoxy groups belonging to the phenyl rings of curcumin are electron donating systems. They are expected to cause stronger hydrogen bond effect and this H bond is even more stronger because of the presence of hydroxyl groups on phenyl ring belonging to paracetamol pure system. This leads us to think that, most probably, the interaction among curcumin and paracetamol could develop through the enolic OH group involved both in intra- and/or inter-molecular H bonding in the mixtures (P-wt50%/C-wt50%) and (P-wt50%/C-wt50%)-mw.

From literature, it is known that the assignment of the experimental bands to the calculated normal modes in the C–H stretching region ($3200\text{--}2700\text{ cm}^{-1}$) is not obvious because there are fewer bands in the experimental spectrum than predicted by calculations [13]. Anyway, based on our FT-IR spectra, in the $2958\text{--}2909\text{ cm}^{-1}$ region, some sharp and very intense signals have been found for all the systems under analysis. The highest wavenumber experimental bands observed in the FT-IR spectra ($2969\text{--}2945\text{ cm}^{-1}$) can be assigned to the aromatic C–H stretches (Ar–C–H); while, the lower wavenumber bands ($2927\text{--}2909\text{ cm}^{-1}$) are attributed to aliphatic C–H (R–C–H) stretching modes related to the methyl group motions belonging to the molecule.

Curcumin molecule possesses one of the most prominent functional group (the keto-enol group) in the central part, which develops a high driving force to give interactions with other molecular systems. This is due to the co-existence of keto and enol groups in curcumin molecules by its tautomeric equilibrium. Moreover, it has been theoretically and experimentally demonstrated that a particular kind of tautomerism is possible in water among different tautomers of curcumin characterized by a negligible energy difference among them and shown in Fig. 3 [21].

The keto-enol tautomer (KE) is linear, bearing intramolecular hydrogen bonding, while in the diketo tautomer (KK) the carbonyl groups are in β -position, forming two non-conjugated fragments separated by one carbon atom. In agreement with these literature knowledge, it is not surprising to have an interaction, be it weak or strong, of curcumin tautomers with paracetamol.

Furthermore, all the FT-IR spectra measured in this study show the typical peaks related to the carbonyl region ($1800\text{--}1650\text{ cm}^{-1}$). In particular, two stretching C=O signals ascribable to KK form have been found at around 1740 and 1730 cm^{-1} related to symmetric and

Fig. 3 Chemical structures of the two most abundant tautomers of curcumin: KE (keto-enol) and KK (keto-keto) forms

Fig. 4 Focus on the $1760\text{--}1250\text{ cm}^{-1}$ region of FT-IR spectra about C, P, (P-wt50%/C-wt50%) and (P-wt50%/C-wt50%)-mw molecular systems

asymmetric modes of vibration, respectively (see FT-IR spectra reported in Fig. 4).

Moving away from this region, two more bands at around 1876 and 1832 cm^{-1} have been found. They were attributed to vibrations of C–H bond involved in alkene groups ($=\text{C}\text{--}\text{H}$) related to curcumin, (P-wt50%/C-wt50%) and (P-wt50%/C-wt50%)-mw systems (see Table 2 for all signals and specific assignments).

Furthermore, around $1671\text{--}1673\text{ cm}^{-1}$ strong peaks related to mixed --C=C-- and C=O stretching vibrations have been found for all the molecules, as already predicted by Kolev et al. [13]. In particular, these authors predict these mixed kind of vibration for the diketo form of curcumin skeleton.

At around $1161\text{--}1170\text{ cm}^{-1}$ the C–O–C stretching vibrations have been moreover found.

One particular difference came up from the FT-IR spectrum of (P-wt50%/C-wt50%)-mw: a new band at 1456 cm^{-1} appears in its spectrum. According to literature [22], this peak should be related predominantly to bending deformation vibrations of $\text{--C}\text{--}\text{H}$ bonds related to the methyl groups. Anyway, most bands in the $1450\text{--}1300\text{ cm}^{-1}$ region are highly mixed and could also be related to olefinic C–H in-plane ($=\text{C}\text{--}\text{H}$) bending vibrations of curcumin [23].

Table 2 Main assignments of FT-IR peaks coming from spectra related to curcumin (C), (P-wt50%/C-wt50%), (P-wt50%/C-wt50%)-mw, paracetamol (P)

FT-IR assignments	C (cm ⁻¹)	(P-wt50%/C-wt50%) (cm ⁻¹)	(P-wt50%/C-wt50%)-mw (cm ⁻¹)	P (cm ⁻¹)	FT-IR assignments
Str Ar–O–H	3665	3625	3667	3660	Str Ar–O–H
Str R–OH	3534	3538	3540	3581	Str R–OH
Str Ar–C–H–	2958	2958	–	2969	Str Ar–C–H
	2955	2955	2954	2958	
	2945	–	–	–	
Str R–C–H–	2927	2927	2927	–	Str R–C–H–
	2924	2924	2924	2924	
	2913	2913	2913	2913	
	2909 Shoulder	2909	2909 Shoulder	–	
	–	–	–	2909	
Str =C–H–	1840	1838	1832	–	–
	1876	1876	1870	–	
Str C=O symm	1740	1740	1739	1740	Str C=O amidic
Str C=O asym	1730	1729	1730	1729	
Mixed Str –C=C– + Str C=O	–	1673	1671	1672	Mixed Str C=C + Str C=O
Bend –C–H (CH ₃) Bend =C–H–	–	–	1456	–	
Str C–O–C	1166	1169	1170	1166	Str. C–O–C
			1161		

Surprisingly, this peak is not present nor in the pure curcumin nor in the (P-wt50%/C-wt50%) mixture. One possible explanation of this peculiar behavior of (P-wt50%/C-wt50%)-mw mixture could be related to the hypothesis that in this mixture the methyl belonging to the phenyl rings are much more available than in (P-wt50%/C-wt50%) and in pure curcumin samples. In turn, it can be responsible for a better electron-donating force toward central KE tautomer so that the (P-wt50%/C-wt50%)-mw mixture could be involved in stronger intra- and/or inter-molecular H bond interactions by involving itself and paracetamol molecules, respectively.

The UV–Vis absorption spectra of samples are presented in Fig. 5 and the most important absorption peaks are given in the Table 3. From these results, the peak 1 is characteristic of paracetamol compound and it has been found also in (P-wt50%/C-wt50%) and (P-wt50%/C-wt50%)-mw mixtures; the peaks 2 and 3 are common both in C and P pure molecules and appear also in (P-wt50%/C-wt50%) and (P-wt50%/C-wt50%)-mw mixtures at around 420 and 449 nm, respectively. The more interesting behavior has been found for the peak 4: a pronounced red-shift related to this (P-wt50%/C-wt50%)-mw absorption band appears at 527 nm, in contrast with the 503 nm of the same peak belonging to curcumin. This peak is even more red-shifted if compared with the corresponding small peak of paracetamol at 518 nm. In particular, the peak 4 has been attributed to

Fig. 5 UV–Vis absorption spectra on powders of C, P, (P-wt50%/C-wt50%) and (P-wt50%/C-wt50%)-mw molecular systems**Table 3** Main absorption peaks of C, P, (P-wt50%/C-wt50%) and (P-wt50%/C-wt50%)-mw molecular systems

Peak	P (nm)	C (nm)	(P-wt50%/C-wt50%) (nm)	(P-wt50%/C-wt50%)-mw (nm)
1	367	–	367	367
2	428	420	420	428
3	457	449	449	456
4	518	503	503	527

the HOMO–LUMO (or valence-to-conduction band) transition of (P-wt50%/C-wt50%)-mw mixture with its energy gap elsewhere evaluated [11] from this absorption peak. In general, the red-shifting of HOMO–LUMO absorption band is characteristic of a better semiconductor material. In fact, the higher wavelength of this valence-to-conduction band is related to a smaller energy needed for its associated transition and therefore to a better semiconductor property. So far, it can be concluded that the observed red-shift of HOMO–LUMO absorption band is in perfect agreement with the better semiconducting properties already known for (P-wt50%/C-wt50%)-mw material. It is still to understand if this smaller energy gap is due to a lowering of LUMO (conduction) state or to the increasing of the HOMO (valence) band. This depends strongly also on the electronic characteristics induced by the paracetamol molecule into the mixture system. Anyway, what we can assess for sure is that the red-shift of the absorption band observed for peak 4, could be associated with an aromaticity increase of the (P-wt50%/C-wt50%)-mw mixture promoted by a better delocalization of π -electron density between the curcumin and paracetamol interacting units.

The SEM images at low magnification (200 $\times$) are depicted in Fig. 6a–d. Some differences among the samples have been found.

As already reported in literature [24], the curcumin SEM (Fig. 6a) appears like large and inhomogeneously distributed chunks forming undefined shape. After the curcumin loading on the sample holder, the roughness of the obtained surface is high.

The same kind of sample loading for the (P-wt50%/C-wt50%)-mw mixture (Fig. 6b) allowed us to assess that the characteristic morphology belonging to curcumin is not present anymore. On the contrary, a very smooth surface has been found at the same magnification and experimental conditions. So far, the (P-wt50%/C-wt50%)-mw physical mixture seems to be more keen to form extended compact layers of material than curcumin and (P-wt50%/C-wt50%) mixture (Fig. 6d). Indeed, in the same conditions, more or less the almost same smooth-like surface has been found also in the case of (P-wt50%/C-wt50%) material. In this case, the surface seems to be less regular and, in some points, the smoothness seems to be broken on the contrary of (P-wt50%/C-wt50%)-mw. On the other hand, pure paracetamol seems to be characterized by its prismatic

Fig. 6 SEM images powders of: **a** C; **b** (P-wt50%/C-wt50%)-mw; **c** P and **d** (P-wt50%/C-wt50%). Magnification: $\times 200$, voltage: 20 kV

shaped crystal structure (Fig. 6c). Comparing paracetamol to the other samples, its presence in both physical mixtures cannot be ascertained by our SEM images.

Figure 7a–d shows the SEM images of the samples investigated at a 1000× magnification. At this magnification it is more evident the curcumin morphology (Fig. 7a) as rough surface on which a wide distribution of smaller particles is spread.

For the (P-wt50%/C-wt50%)-mw semiconducting sample (Fig. 7b) a less roughness has been evidenced on top of surface where a much less number of small particles are superficially distributed. Also the (P-wt50%/C-wt50%) mixture (Fig. 7d) is characterized by a rough surface but much more similar to that of curcumin.

Comparing our paracetamol SEM image (Fig. 7c) with already published data [25], the morphology of paracetamol crystal could be attributed to the known Form I (monoclinic) or Form II (orthorhombic) crystal structure.

The most interesting observations have been found at a 10,000× magnification (Fig. 8b). In this case, the surface of (P-wt50%/C-wt50%)-mw mixture seems to be clearly organized in sheets or lamellar structures much more extended and regular than pure curcumin. In particular,

flaking planes are clearly visible coming up from the smooth surface of the semiconductor material. These flaking planes could slide on each other and, as consequence, could be responsible for the pronounced semiconducting properties shown by (P-wt50%/C-wt50%)-mw mixture. From the picture, it can be observed that each single plane has a thickness of about 100 nm. These flaking planes could be the layers by which each single molecule overlap regularly thanks to probable π – π interactions.

At the highest magnification (Fig. 9), it has been possible to have a clearer view of the extended and regular flaking planes characterizing (P-wt50%/C-wt50%)-mw material.

XRD spectra are showed in Fig. 10. Curcumin is an amorphous material in agreement with the tautomeric equilibria present in this compound. Paracetamol is a monoclinic structure [26]. The (P-wt50%/C-wt50%) material showed a peak at 5.2 Å that allows to consider a shift of paracetamol from monoclinic to orthorhombic structure. This peak is present also in (P-wt50%/C-wt50%)-mw material. However, in this case, the peak 5.7 Å (1175 counts) shifted at 5.85 Å (2682 counts). Both the shift and the increase of this peak can be attributable to a different supramolecular

Fig. 7 SEM images powders of: **a** C; **b** (P-wt50%/C-wt50%)-mw; **c** P and **d** (P-wt50%/C-wt50%). Magnification: ×1000, voltage: 20 kV

Fig. 8 SEM images powders of: **a** C; **b** (P-wt50%/C-wt50%)-mw. Magnification: $\times 10,000$, voltage: 20 kV

Fig. 9 SEM image powder of (P-wt50%/C-wt50%)-mw. Magnification: $\times 20,000$, voltage: 20 kV

crystalline structure of paracetamol in the mixture. It is not possible at this stage to understand what type of modification occurs, but it is a clear evidence that this modification is present.

4 Conclusion

Starting from the experimental evaluation that all the typical NMR signals belonging to curcumin and paracetamol have been evidenced in the semiconductor mixture (P-wt50%/C-wt50%)-mw, the initial hypothesis of a new chemical bond among the two starting precursors have been totally excluded. So far, this study has been carried on toward the investigation of a possible organized supramolecular structure among curcumin

Fig. 10 XRD spectra

and paracetamol taking into account what happens when a physical C–P 50–50% wt mixture is prepared by dissolution in water with and without microwaves treatment giving the semiconductor (P-wt50%/C-wt50%)-mw and (P-wt50%/C-wt50%) molecular systems, respectively. The resulting (P-wt50%/C-wt50%)-mw system shows peculiar characteristics related to its high semiconducting properties investigated in the present paper by FT-IR, UV–Vis and by SEM measurements to study in depth the morphological structure belonging to the bulk (P-wt50%/C-wt50%)-mw system.

Looking to the FT-IR spectrum of (P-wt50%/C-wt50%)-mw a characteristic band at 1456 cm^{-1} appears. This band has been assigned predominantly to bending deformation vibrations of –C–H bonds related to the two methyl groups. This means that the methyl groups belonging to phenyl rings are much more available in (P-wt50%/C-wt50%)-mw than in (P-wt50%/C-wt50%) or, even worse, in pure curcumin samples. It can be responsible for a better electron-donating force toward the central part of the molecule. So far, the (P-wt50%/C-wt50%)-mw mixture could be involved in stronger intra- and inter-molecular hydrogen bond interactions among curcumin itself and involving also paracetamol molecules.

From a morphological point of view, the most interesting observations by SEM have been found at the highest magnification of (P-wt50%/C-wt50%)-mw system. In this case, the surface of (P-wt50%/C-wt50%)-mw seems to be clearly organized in lamellar structures characterized by a thickness of about 100 nm that appear such as extended and regular flaking planes. These flaking planes could slide on each other and, as consequence, could be responsible for the pronounced semiconducting properties evaluated for the (P-wt50%/C-wt50%)-mw mixture. These flaking planes could be the layers by which each single molecule overlaps regularly thanks to strong and efficient π – π interactions and inter-molecular hydrogen bonds among curcumin tautomers and paracetamol. XRD spectra showed a shift from 5.7 to $5.85\text{ \AA}$ and increase of intensity in agreement with a different crystal organization of paracetamol in the mixture.

More detailed analysis is going to be performed in order to better investigate the nature of this supramolecular peculiar organization among curcumin and paracetamol starting materials.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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