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Vapochromic Behaviour of Polycarbonate Films Doped with a Luminescent Molecular Rotor

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Abstract

We report on vapochromic films suitable for detecting volatile organic compounds (VOCs), based on polycarbonate (PC) doped with 4-(triphenylamino)phthalonitrile (**TPAP**), a fluorescent molecular rotor sensitive to solvent polarity and viscosity. PC films of variable thickness (from 20 up to 80 μm) and containing small amounts of **TPAP** (0.05 wt.%) were prepared and exposed to a saturated atmosphere of different VOCs. **TPAP**/PC films showed a gradual decrease and red-shift of the emission during the exposure to solvents with high polarity index and favourable interaction with the polymer matrix such as THF, CHCl_3 , and acetonitrile. In the case of the most interacting solvents (THF and CHCl_3), **TPAP**/PC films also showed a fluorescence increase at longer exposure times, as a consequence of an irreversible, solvent-induced crystallization process of the polymeric matrix. The vapochromism of **TPAP**/PC films is rationalized on the basis of alterations of the rotor intramolecular motion upon solvent uptake by PC and polarity effects of the microenvironment. Interestingly, the fluorescence response of the **TPAP**/PC films shows a non-trivial, tuneable dependence on film thickness during the second solvent-exposure stage. The latter effect is attributed to a variable extent of the crystallization process occurring in the PC films. This observation promptly suggests, in turn, an effective procedure to modulate the spectroscopic response in such functionalized polymeric materials through the precise control of the film thickness.

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Keywords

polycarbonate films; fluorescent molecular rotors; volatile organic compounds; vapochromism

1 Introduction

The detection of volatile organic compounds (VOCs) is of great concern because of the VOCs undesirable impact on both environment and human health.[1] VOCs side-effects on human organism include acute and chronic respiratory effects, eye and throat infection, etc. [2] Among others, a simple and effective way to detect VOCs is based on plastic films doped with fluorophores suitable to sense vapours of different organic solvents, as recently proposed. Such fluorophores belong to the category of vapochromic fluorescent dyes since they display a significant emission change upon exposure to VOCs of different nature.[3,4] A special class of these vapochromic fluorophores is known as fluorescent molecular rotors (FMRs).[5–9] FMRs exhibit viscosity-dependent emission properties when dissolved in solvents with different viscosity or dispersed in plastic films.[10,11] Usually, the exposure of FMR/polymer films to an atmosphere of well-interacting VOCs causes a significant drop of the FMR fluorescence due to the favoured non-emissive decay from the excited state, usually an intramolecular charge-transfer (ICT) state. In general, the success of vapour sensing polymer films is largely due to the ability of volatile compounds to spread rapidly inside the polymer matrix and interact with the embedded molecules giving a fast and reliable fluorescence response. Such emission changes are the result of the increased mobility of the macromolecular chains upon solvent uptake which, in turn, leads to an enhanced FMR flexibility, thus favouring non-radiative deactivation pathways.[12–15]

Some FMRs, like 4-(diphenylamino)phthalonitrile (**DPAP**), exhibit both viscosity- and polarity-dependent emission properties when dispersed in plastic films and exposed to saturated atmosphere of polar and well-interacting VOCs.[16–18] Such dye-enriched films show a significant variation of the emission due to solvent-induced changes in the local polarity and viscosity of the polymeric matrix. The observed vapochromism of **DPAP**-doped films was attributed to alterations of the rotor intramolecular motion and polarity effects stemming from the environment, which, in concert, influence the deactivation pathways of the rotor intramolecular charge-transfer state.

While vapochromic polymer films based on viscosity- and polarity-sensitive fluorophores have been already confirmed as effective VOCs sensing systems,[19–25] there are still a number of physico-chemical properties and effects concerning these materials that have not been fully investigated. Here, we focused on the emission properties of a newly synthesized FMR, namely 4-(triphenylamino) phthalonitrile (**TPAP**, Figure 1a) in PC films of different thickness as a function of exposure time to different solvent vapours. **TPAP** is a highly-flexible FMR with strong polarity and viscosity sensitivity.[26] In addition, **TPAP** has an extended π -conjugated system that results in a significant distance between the electron-accepting cyano and the electron-donating amino groups, which, in turn, affects its electronic and spectroscopic features with respect to solvent polarity and viscosity. In particular, in the present study we have investigated, in some detail, the effect of the

thickness on the vapochromic response of **TPAP**/PC films, in terms of both the spectral signal features and the kinetics of its response.

2 Experimental

Materials

TPAP (Figure 1a) was prepared following a standard, transition metal-catalysed cross-coupling reaction between 4-iodo-phthalonitrile and 4-boronic acid-triphenylamine.[26] Chloroform (CHCl_3) was purchased from Sigma-Aldrich and used as received. Random copolymer polycarbonate-polysiloxane LEXAN® EXL 1414T (PC, SABIC, Mw = 220,000 g/mol with 1.5 wt.% Si) was used as received.

Preparation of TPAP/PC films

500 mg of PC were dissolved in 2 mL of chloroform under stirring for 10 minutes. Then, **TPAP** (0.05 wt.%) was added and the resulting viscous solution poured into clean glass dishes. A ZUA 2000 Universal Applicator (Zehntner Testing Instruments) was used to distribute the mixture over the glass in order to obtain 20-80 μm thick films after complete solvent evaporation (Figure 1b).

Apparatus and Methods

Fluorescence spectra ($\lambda_{\text{exc}} = 380 \text{ nm}$) of **TPAP**/polymer films were measured on a Horiba Jobin-Yvon Fluorolog®-3 spectrofluorometer at room temperature in the dark by using the F-3000 Fibre Optic Mount apparatus coupled with optical fibre bundles. Light generated from the excitation spectrometer is directly focused to the **TPAP**/PC sample using an optical fibre bundles. Emission from the sample is then directed back through the bundle into the collection port of the sample compartment. The emission response of the **TPAP**/PC films was tested by exposing a 2×2 cm portion of the film, attached to an aluminium foil covering a 50 mL closed container (Figure 1c)[17,21], to 20 mL of organic solvents of different polarities, namely, *n*-hexane, THF, CHCl_3 , and CH_3CN , at 20 °C and atmospheric pressure. The experiments were carried out after solvent saturation was reached. The concentrations of about 10^4 ppm for toluene and 10^5 ppm for the other solvents were estimated taking into consideration their vapour pressures (Table S1).

Microscopy images and lifetime measurements were collected by using a Leica TCS SP5 SMD inverted confocal microscope (Leica Microsystems AG, Wetzlar, Germany) equipped with an external pulsed diode laser (PicoQuant GmbH, Berlin, Germany) for excitation at 405 nm. The laser repetition rate was set to be 40 MHz. Each of the image sizes were 512×512 pixels and acquired with a scan speed of 400 Hz (lines per second). The pinhole aperture was set at 1.00 Airy. **TPAP**/PC films fixed on microscope glass slides were viewed with a 100 × 1.3 NA oil immersion objective (Leica Microsystems). The images were collected using low excitation power at the sample (10-20 μW). Emissions were monitored in the 430-490 nm range by acousto-optical tuneable beam splitter (AOBS) based built in detectors. Acquisition lasted until about 100-200 photons per pixel were collected, at photon counting rates of 100-500 kHz. Emission lifetime images (FLIM) of the **TPAP**/PC were elaborated using Picoquant Symphotime software for FLIM analysis.

Differential scanning calorimetry (DSC) measurements were done by using Perkin–Elmer DSC 4000 under nitrogen atmosphere coupled with an Intracooler SP VLT 100, heating from 30 to 280 °C at a rate of 10 °C min⁻¹. Indium and lead samples were used to calibrate the DSC unit. PC crystalline content (f_c) was evaluated from the measured melting enthalpy (ΔH_m) taking into account the melting enthalpy of the perfect PC crystal ($\Delta H_m^0 = 132$ J/g) [27] using the equation 1:

$$f_c = \frac{\Delta H_m}{\Delta H_m^0} \cdot 100 \quad (\text{eq. 1})$$

3 Results and Discussions

TPAP (Figure 1a) is a FMR showing a solvent-insensitive absorption with a broad band peaked at 392 nm and a noteworthy fluorescence sensitivity to viscosity[26]. As a result, by hampering the **TPAP** intramolecular rotations through a highly viscous medium, enhanced fluorescence intensity is generally obtained. In the film preparation, **TPAP** was dispersed in PC films at a concentration of 0.05 wt.%. The latter concentration was chosen to maximize the spectroscopic response of the resulting polymer films avoiding any spurious effect due to aggregation, self-quenching, self-absorption, etc.

Highly homogeneous **TPAP**/PC films with controlled thickness of 80 µm were prepared (Figure 1b). Note that PC is an amorphous polymer, characterized by a glass transition temperature (T_g) of about 150 °C, in which the **TPAP** intramolecular rotations are strongly hampered. Under such conditions, the radiative decay of **TPAP** is expected to dominate its photophysics. In line with these assumptions, **TPAP**/PC films gave rise to a bright blue emission characterized by a single unstructured broad band peaked at about 450 nm (Figure 2) with an emission lifetime of 4.2 ns (Figure S1).

The **TPAP**/PC films were exposed to solvent vapours with different vapour pressure and polarity index. We used a semi-empirical relationship to predict solvent/PC interactions, which takes into account the solubility parameter difference δ , that is, the measure of the attractive strength between molecules of the material.[28] Notably, the δ ($\delta = \delta_{PC} - \delta_{\text{solvent}}$) is small for effective solvent/PC interactions (Table S1).

In Figure S2, the emission spectra of **TPAP**/PC films upon exposure to *n*-hexane vapours as a function of time are presented. No appreciable alterations in terms of their emission maximum and intensity even after 25 min. of vapours exposure are observed, being *n*-hexane the least polar and interacting solvent with PC.

A more evident change in the emission is observed for **TPAP**/PC films exposed to CH₃CN vapours (Figure S3), a solvent with the highest polarity index (Table S1). The emission of the **TPAP**/PC film experiences a significant quenching and red-shift (34 nm). Note that in the glassy state the PC matrix is characterized by a large fraction of free volume, generally in the form of channels and cavities reaching molecular dimensions. Considering that solvent vapours may fill up such empty spaces, diffusion and swelling of the polymer starts

from the outer surface layers inwards. As a consequence, an overall decrease of the local microviscosity evolves.[29] This phenomenon leads to an increase of **TPAP** mobility, which, in turn, favours its non-radiative deactivation from the non-emissive ICT state. Moreover, a red-shifted emission of more than 30 nm is observed due the polar nature of CH₃CN.[17]

A striking vapochromic response was recorded when THF and CHCl₃ were used as solvents (Figure 2), i.e. solvents which present a favourable combination of polarity index and δ parameter (Table S2). During the first 10 min, the decrease in the **TPAP**/PC emission is mainly ascribed to the viscosity sensitivity of **TPAP** with increasing solvent molecules uptake by the PC matrix. After the initial drop in **TPAP**/PC emission intensity, a marked fluorescence enhancement was observed in both cases (Figure 2). Both fluorescence intensity variations and wavelength shifts appear slightly more pronounced when the **TPAP**/PC film is exposed to THF vapours, notwithstanding the similar polarity index and δ parameter of THF and CHCl₃.

It was reported that the exposure of PC to strongly interacting organic solvents ($\delta = 0.7$ for THF and 0.5 for CHCl₃) in the vapour or liquid state effectively enhances the polymer crystallization rate due to the role of the absorbed solvents as plasticizers.[30–32] As a result of the solvent uptake, the mobility of the polymeric segments increases, triggering the crystallization of the polymer that can occur at room temperature under such conditions. This crystallization process due to THF and CHCl₃ exposures reduces the flexibility of the polymer-embedded **TPAP**, hampering its internal motions and, in turn, enhancing its radiative decay process.

Emission imaging studies were carried out investigating the morphology of **TPAP**/PC films before (Figure 3a) and after (Figure 3b) CHCl₃ exposure. In particular, the films were subjected to CHCl₃ vapours for 25 min and analysed by means of confocal scanning laser fluorescence microscopy using a laser source at 405 nm and an emission in the 430–490 nm range. Before CHCl₃ vapours exposure, the film surface appeared smooth and homogeneous (Figure 4a). Conversely, after solvent molecules exposure, the area of the film placed in contact with CHCl₃ vapours revealed a strong modification of its texture with the formation of micro-sized granules, in agreement with the polymer crystallization process in the plastic film (Figure 4b).[33]

The original **TPAP**/PC emission maximum was almost completely recovered upon solvent desorption (465 nm (Figure S4, red spectrum) versus 461 nm (Figure 2b, blue spectrum) for CHCl₃-exposed and pristine **TPAP**/PC films, respectively). In other words, when CHCl₃ starts to desorb from the doped matrix, the film emission is accordingly shifted to lower wavelengths in line with the different effective polarity of PC and CHCl₃. Upon solvent vapours desorption of the **TPAP**/PC films, a second and a third cycle of THF and CHCl₃ exposure were also carried out. Fluorescence studies on these films showed a similar trend in the fluorescence variation to the one observed for the first cycle, that is, a film fluorescence emission drop flanked by a red-shift of the emission maximum. However, in this case, and differently from the first cycle, no fluorescence enhancement was observed increasing the exposure to the solvent vapours (Figure S5). From these results we can conclude that the

expected kinetically-irreversible crystallization process occurring in the **TPAP/PC** films can be considered mostly completed after the first 25 min of CHCl_3 vapours exposure.[17]

In order to give an insight into the nature of the investigated phenomenon, the effect of film thickness on the vapochromic behaviour of **TPAP/PC** films was investigated. Following the procedure described in the preceding section, highly homogeneous **TPAP/PC** films with different and controlled thickness in the range between 20 and 60 μm were prepared. CHCl_3 was selected as the solvent due to the most favourable δ parameter. The emission spectra of **TPAP/PC** films exposed to CHCl_3 vapours are reported in Figure 4 as a function of exposure time. Four different film thicknesses were considered, namely 20 μm , 25 μm , 40 μm and 60 μm .

In all cases, the **TPAP/PC** fluorescence was observed to change upon solvent vapours exposure. During the first 5 min, the decrease in the **TPAP/PC** emission is mainly ascribed to the viscosity sensitivity of **TPAP** with increasing CHCl_3 uptake by the polymer matrix. It is worth noticing that the increase in film thickness strongly affects the extent of emission variation within the first 5 min of CHCl_3 exposure. More specifically, **TPAP/PC** films with lower thickness give rise to higher fluorescence variation within the same time interval, as a result of a more complete sorption process with respect to thicker films.

Interestingly, the extent of fluorescence recovery of **TPAP/PC** films, i.e. the difference between the emission intensity at $t = 25$ min and that at $t = 5$ min, appeared influenced by film thickness. More specifically, thinner films presented smaller fluorescence variations with respect to thicker films, possibly due to differences in the solvent-induced crystallization process. Notably, **TPAP/PC** films with 20-25 μm thickness showed at the end of the vapour exposure ($t = 25$ min) an emission wavelength about 7-8 nm blue-shifted with respect to their thicker counterparts. This phenomenon could be also explained in terms of the faster CHCl_3 desorption occurring in thin films, leading to an overall lower polarity of the material.

Optical inspection of the **TPAP/PC** films immediately after CHCl_3 exposure under near-UV light (366 nm) revealed a clear change of the fluorescence from blue to green (Figure 5), thus allowing the detection of the vapochromic response with a naked eye. Notably, the **TPAP/PC** film with higher thickness (60 μm , figure 3b, against 20 μm , figure 3a) possibly revealed a more evident vapochromic response with the emission variation from blue to green.

These findings can be related to the differences in emission intensity and frequency, as observed by spectroscopic investigations, comparing the spectra of **TPAP/PC** films with thickness of 20 μm and 60 μm (Figures 4a and 4d, respectively).

To further validate our findings, we eventually probed the thermal properties of **TPAP/PC** films at variable thickness, before and after CHCl_3 vapours exposure, by comparing their first heating DSC scans (Figure 6). During the first heating scan, both pristine and CHCl_3 -exposed films displayed a T_g at around 150 $^\circ\text{C}$. However, in contrast to the pristine **TPAP/PC** films which may be regarded essentially as amorphous materials, the solvent-

exposed system displayed the progressive formation of endothermic peaks from 140 up to 240 °C with two main signals at around 185 °C and 220 °C which support the co-existence of a crystalline phase, as similarly observed after acetone exposure of PC-based samples. [30] After cooling, during the second heating scan, all the samples appeared as completely amorphous showing only the T_g at around 150 °C. (Figure 6a).

It is worth noticing that upon CHCl₃ exposure, the crystallinity of **TPAP**/PC films progressively increases upon increasing the film thickness (Figure 6b and Table 1). This result can be related to the fact that in thinner **TPAP**/PC films the diffusion of CHCl₃ into the amorphous polymer is nearly complete before the crystallization process is completed. Furthermore, as crystallization proceeds, solvent is rejected from the crystalline regions of the polymer, thus limiting the crystallization process.[34]

In Figure 7, the crystallinity content in PC films with different thickness is compared with the fluorescence intensity variation $(I-I_0)/I_0$, where I and I_0 are the fluorescence intensities after 25 min and 5 min of CHCl₃ exposure, respectively. As expected, the fluorescence increase does agree quite well with the PC film crystalline content, suggesting that the vapochromic response is governed by morphology variations in the PC film bulk.

Conversely, the apparent slight decrease in the fluorescence of the thickest PC film (60 μm) is likely due to the micro-phase separation of **TPAP** molecules which occurs in the PC bulk during the crystallization process. Indeed, such a phenomenon can adversely affect the homogeneous fluorescence response of the macroscopic film.

Conclusions

We have demonstrated that a recently synthesized FMR, namely **TPAP**, characterized by a high sensitivity toward solvent polarity and viscosity, once embedded into PC films, confers interesting vapochromic features to the resulting films. In particular, **TPAP** exhibits viscosity- and polarity-dependent emission properties when dispersed at low loadings (0.05 wt.%) in PC plastic films and exposed to a saturated atmosphere of VOCs, such as CH₃CN, THF and CHCl₃, which present a favourable combination of polarity index and solubility parameter difference δ . The obtained dye-enriched films showed a decrease and red-shift of emission due to solvent-induced changes in the local polarity and viscosity of the polymeric matrix. Moreover, for THF and CHCl₃ as solvents, the optical response was accompanied by an increase in the film fluorescence intensity at longer solvent-exposure time. This effect is attributed to a PC crystallization process in the plastic films upon solvent molecules uptake, which causes a significant increase in the matrix viscosity. This process reduces the flexibility of the embedded **TPAP**, specifically hampering the intramolecular rotational motions and, in turn, enhancing the radiative decay pathway. Notably, the vapochromic behaviour of such films was strongly influenced by the film thickness. More specifically, the increase in film thickness strongly affects the extent of emission variation within the first 5 min of CHCl₃ exposure. **TPAP**/PC films with smaller thickness resulted in higher fluorescence variation within the same time interval, possibly due to a more complete sorption process with respect to thicker films. On the other hand, thicker films determined the largest fluorescence intensity variation during the second stage of solvent exposure,

allowing a more defined vapochromic behaviour with colour emission changes from blue to green. This effect is attributed to a more complete crystallization process occurring in thicker films. It is worth noting that the observed variable kinetics with film thickness might be exploited for the realization of functional materials with controllable spectroscopic response. These findings consistently support the effective preparation and use of a new class of vapochromic plastic materials with tuneable properties. Further work will be focused on the determination of the sensitivity and the detection limit of the dye/polymer films.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1. (a) Molecular structure of 4-(triphenylamino) phthalonitrile (**TPAP**); (b) schematic representation of the film preparation and (c) of the setup used to study the vapochromic behaviour of **TPAP/PC** films.

Figure 2.

Progressive changes in the emission of 0.05 wt% **TPAP/PC** films as a function of exposure to (a) THF and (b) CHCl_3 vapours ($\lambda_{\text{exc}} = 325$ nm). The spectra were collected for 25 min with a time interval of 1 min.

Figure 3.

Confocal microscope images of 80 μm thick **TPAP/PC** films with emission collection in the 430–490 nm range (a) before and (b) after exposure to CHCl₃ vapours for 25 min. In this latter case, after the CHCl₃ vapour exposure, the **TPAP/PC** film was placed at room temperature and atmospheric pressure for 40 min. allowing the desorption of the trapped solvent molecules from the polymeric matrix. Note that the emission images are in pseudocolors.

Figure 4.

Emission of 0.05 wt.% **TPAP/PC** films as a function of exposure time to CHCl_3 vapours ($\lambda_{\text{exc}} = 325 \text{ nm}$). PC film thickness: a) 20 μm ; b) 25 μm ; c) 40 μm ; d) 60 μm . The spectra were collected during 25 min with a time interval of 1 min and normalized at the emission maximum after 25 min of exposure. All the spectra were normalized to the emission maxima

Figure 5.

(a) Picture of **TPAP/PC** films (about 1 x 2 cm) with a thickness of (a) 20 µm and (b) 60 µm after 25 min of exposure to CHCl_3 vapours. The picture was taken under the illumination at 366 nm. Films areas exposed and unexposed to the CHCl_3 vapours are clearly distinguishable.

Figure 6.

(a) DSC scans of pristine and CHCl_3 -treated 60 μm thick (both first and second heating) 0.05 wt.% **TPAP/PC** films. (b) First heating DSC scans of pristine PC pellet and 0.05 wt.% **TPAP/PC** films with different thickness. The CHCl_3 -treated films were prepared exposing the **TPAP/PC** films to CHCl_3 vapours for 25 min and the resulting films let to stand at room temperature and atmospheric pressure for 1 hour in order to eliminate solvent molecules trapped in the polymeric matrix.

Figure 7. Crystallinity (black circles) and fluorescence intensity variation (black squares) of CHCl_3 -exposed **TPAP/PC** films with different thickness.

Table 1

Crystallinity (f_c) calculated for PC pellet and **TPAP**/PC films with different thickness unexposed or exposed for 25 min to CHCl_3 vapours.

<i>Sample</i>	f_c (%)
PC pellet ^a	0
60 μm TPAP /PC film ^a	0
20 μm TPAP /PC film ^b	5.70
25 μm TPAP /PC film ^b	6.30
40 μm TPAP /PC film ^b	7.40
60 μm TPAP /PC film ^b	8.80

^a unexposed

^b exposed to CHCl_3 vapours