Theoretical study of conformational aspects, excited states and directional energy transfer: The Terphenylene, Diphenylhexatriene and Quinquethiophene triad included in PHTP nanochannels

Sergio O. Vásquez *, Carmen Gaete-Acuña

Departamento de Ciencia de los Materiales, Facultad de Ciencias Físicas y Matemáticas, Universidad de Chile, Tupper 2069, Santiago, Casilla 2777, Santiago, Chile

ARTICLE INFO

ABSTRACT

The limited one-dimensional space of nanochannels of the supramolecular Perhydrotriphenylene (PHTP) matrix host induce changes on the structure of included molecules that affect some of their properties. A combination of Density Functional Theory and semi-empirical methodologies is used to study the structural changes, the electronic excited states and the energy transfer processes between the triad of oligomers Terphenylene (P3), Diphenylhexatriene (DPH) and Quinquethiophene (T5) included in PHTP. Details of the conformational aspects of the oligomeric guest species have been obtained assuming a rigid matrix approach for the PHTP host. Optimal geometries were considered to study excited states and processes for the P3 → DPH → T5 chain of two-steps transfer of energy from the UV to the visible. Trends for the dominant directional mechanism for the energy transfer have been resolved from a theoretical point of view.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

Nanoscience focus attention on the relationship between the structure and the properties of a given material at a nanometric scale and one of the most interesting topics in this field is the study of confinement effects. Examples of nanometric structures that clearly show confinement effects are those with nanochannel architectures where the low dimensional and small diameter cavities could be filled by molecules of proper dimensions and selected properties. Supramolecular compounds that have channel-like architectures are of particular interest to study the effects of confinement on luminescence and energy transfer processes between guest molecules of appropriate dimensions. Moreover, the fact that the channel have a high length to diameter ratio allow the filling with a chain of guest molecules that are separated between them and not bound to the inner wall of the channel architecture, behaving as almost isolated molecules in this tight vacuum-like space. Well known examples are self-assembly inclusion compounds (ICs) derived from Perhydrotriphenylene (PHTP), cyclodextrines or cyclotriphosphazines [1–4].

Experimental work of several authors [5–7] has focused attention on the conformational aspects of these ICs. On the other hand, results on theoretical calculations [8,9], show that the most important role of the host channel is to modify the geometry of the more flexible guest molecules, adapting them to the details of the innermost wall of the channel.

Botta et al. [10] carried out studies on the co-inclusion compound (co-IC) grown with PHTP and the triad of guests: Terphenylene (P3), Diphenylhexatriene (DPH) and Quinquethiophene (T5). Observation of relatively efficient and directional energy transfer processes P3 → DPH → T5 are facilitated by the relative separation between the oligomers in different channels, a fact that inhibits the aggregation effects observed in condensed state pure oligomeric solutions.

This study deals with conformational aspects of the P3, DPH and T5 included molecules, their excited states, as well of an estimation of the relative energy transfer rates in this co-IC, based on excited states ab initio calculations.

2. Computational aspects

In a previous work [8] we have developed a three-steps strategy to study these type of systems: (I) modelling of the PHTP channel under a simplified chiral structure that is representative of the

---

* Corresponding author. Tel.: +56 2 9784488; fax: +56 2 6994119.
  E-mail address: ovasquez@dqb.uchile.cl (S.O. Vásquez).

crystallographic available information [11], (II) calculation of the ground state of the molecular guests in an isolated gas phase condition, (III) modelling of the host matrix and included guests system (PHTP:T5), (PHTP:DPH) and (PHTP:P3), under the assumption of a rigid PHTP host, and relaxation of the geometry of the more flexible lineal molecular guests. Afterwards, we have added calculations on the excited states of the guests in order to study donor–acceptor energy transfer phenomena in the ICs [9]. The model systems of inclusion compounds have the following overall compositions: $C_{174}H_{406}$ for (PHTP:P3), $C_{198}H_{466}$ for (PHTP:DPH) and $C_{176}H_{402}S_5$ for (PHTP:T5).

In this study, we have improved the level of calculation using Density Functional Theory (DFT): details of the ground state of P3, DPH and T5 have been studied using the Becke, Lee, Yang and Parr B3LYP hybrid functional for exchange and correlation and the 6-311G+(d,p) basis set. In relation to step (III), relaxation of the geometry within ICs has also been improved and a two-layer ONIOM methodology with the guest molecule treated as the high layer (DFT/B3LYP/6-311+(d,p)) and the whole PHTP channel is considered in the low level (semi-empirical PM3) of the calculation. The choice of a semi-empirical treatment for the low level calculation is *justified* by the size of the systems (~600 + atoms). Another interesting aspect that has also been included in step (III) is the mapping of the energetic barriers for displacements of the guest molecules inside the PHTP channel. Considering the optimized geometry found in the initial ONIOM calculations and bearing in mind that the focus of this part of the study is just to have a qualitative idea of the freedom of movements of the guests inside the channels we have performed single point calculations of the model systems under 0.1 Å translations and 5° rotations of the guests inside the PHTP channel. The complete study was done at a simpler semi-empirical PM3 level, although we have checked results for some few selected configurations using the ONIOM methodology mentioned above. This choice is analyzed and validated later in the results section.

Excited state calculations were carried out with Time Dependent Density Functional Theory (TD-DFT). Vertical absorption transitions on the ground state optimized geometry of the ICs were studied performing TD-DFT/B3LYP/6-311G+(d,p) calculations. In the case of emission transitions a previous search for the correct geometry of the excited state of the guests was done using the Configuration Interaction Singles methodology and a 6-31G+(d,p) basis set, improving previous works [9,12]. Subsequently, the emissive transition is calculated with this geometry and the TD-DFT/B3LYP/6-311G+(d,p) methodology.

Finally, a simple calculation on energy transfer rates is made using the calculated oscillator strengths for the P3-DPH and DPH-T5 interacting pairs of the triad of guest molecules, in order to search directional behaviour of the transfer processes.

The *Gaussian* 03 code was used to perform all the calculations [13].

3. Conformational details of the guest within the nanochannels

One of the relevant geometric data in the analysis of the ground stete geometry of the oligomeric guests in isolated gas phase condition is the dihedral angle between aromatic rings of the molecules (see Table 1). In general, good agreement with the corresponding experimental data is found, in particular for T5 and P3 that are non-planar molecules as well as DPH that is found to be planar.

Once included in the channel, oligomers behave like isolated molecules in a tight vacuum-like space and confinement effects tend to distort them, as they are much more flexible entities than the PHTP host matrix. The ONIOM methodology is a good choice for this kind of systems, as there is no formal chemical bonds

Table 1
Characteristic dihedral angles (degrees) for P3, DPH and T5 molecules in gas phase and as inclusion compounds (IC) in PHTP channel.[a]

| Dihedral angles[b]	P3 (gas phase/ground state)	P3 (IC/ground state)
Terphenylene		
D1	139.67°	120.14°
D2	139.67°	121.09°
	DPH (gas phase/ground state)	DPH (IC/ground state)
Diphenylhexatriene		
D1	180.0°	178.42°
D2	180.0°	178.67°
	T5 (gas phase/ground state)	T5 (IC/ground state)
Quinquethiophene		
D1	154.31°	178.93°
D2	156.90°	171.16°
D3	156.90°	169.34°
D4	154.310°	179.52°

[a] See Fig. 1 for details.
[b] For P3: $D_1 = (C_1–C_3–C_4–C_5)$; D_2 is mirror symmetric to D_1 in gas phase P3. For DPH: $D_1 = (C_6–C_5–C_4–C_3)$; D_2 is mirror symmetric to D_1 in gas phase DPH. For T5: $D_1 = (S_3–C_8–C_7–S_2)$; $D_2 = (S_2–C_4–C_3–S_1)$; D_4 and D_3 are a mirror symmetric to D_1 and D_2 respectively in gas phase T5.

between the guest (high layer) and host matrix (low layer). Fig. 2 is a frontal view of the model channel-guest molecule system for (PHTP:P3), (PHTP:T5) and (PHTP:DPH). This shows a general situation in agreement to the experimental facts and the most significant alteration observed is the change for dihedral angles. The most striking observed feature is the almost planar geometry of the T5 guest in (PHTP:T5), as well as the reduction in dihedral angles of P3 in (PHTP:P3) from 140° to about 120°. On the contrary, DPH remain in an almost planar geometry and all the guests show a relatively close coaxial alignment to the channel. All these changes are the result of the details of the innermost structure of the PHTP channel: a chiral structure of threefold symmetry that in average consist of alternated stacks of *R*-PHTP and *S*-PHTP.
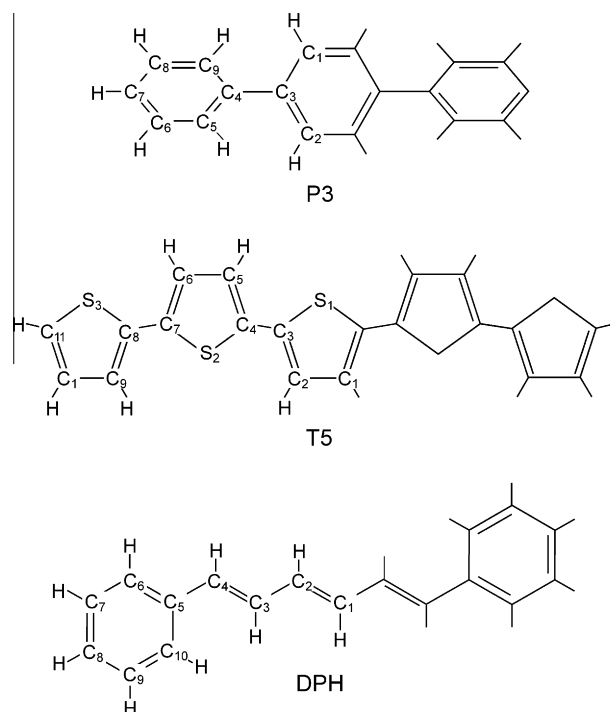
Fig. 1. Geometrical data and total electric dipole moment μ for P3, T5 and DPH in gas phase.
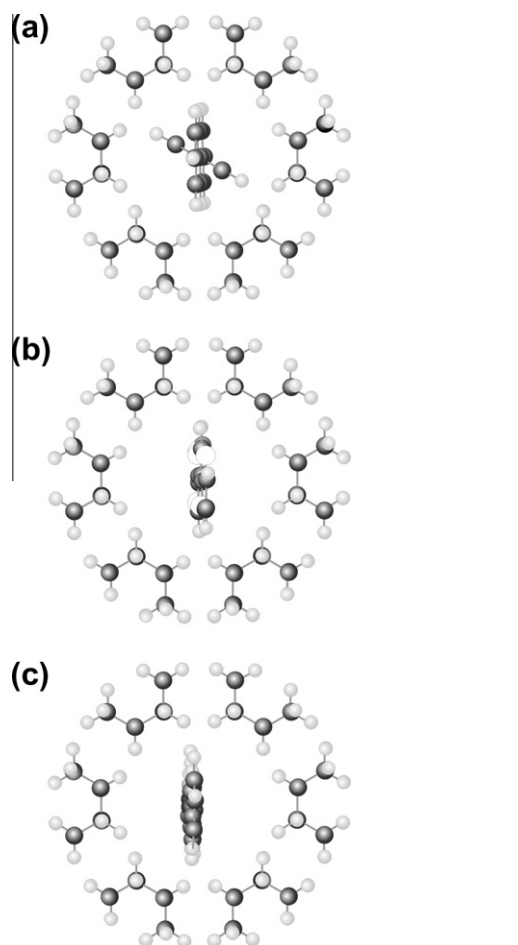
Fig. 2. Frontal view of the IC models: (a) (PHTP:P3), (b) (PHTP:T5) and (c) (PHTP:DPH). Oligomeric guests after optimization of geometry. In (b), sulphur atoms are in white.

The role of the bonded hydrogen atoms at the surface of the innermost wall of the channel is very significant. The distribution of electronic densities of these atoms and the interaction with the peripheral atoms of the oligomers must determine much of the observed geometrical changes and allocation of the included oligomers inside the channel, driving their terminal atoms toward zones of low electronic density in the channel and lowering the total repulsion in the host–guest system.

The degree of localization and stability of the relative positions of the guests inside the channel can be analyzed studying the energetic barriers for rotational and translational displacements of these molecules. Fig. 3 show that translational and rotational movements of the included guests are very limited. In Fig. 3, we have represented the relative $\left(\Delta E_{tras}/\Delta E_{tras}^{max}\right)$ and $\left(\Delta E_{rot}/\Delta E_{rot}^{max}\right)$ ratios for translations along the channel and rotations of the guest, respectively. Maxima and minima of Fig. 3a–c show a periodic pattern dictated by the crystallographic characteristics of the PHTP crystals: channels are built by the threefold symmetry arrangement of long homo-chiral stacks formed by replication of the corresponding R or S unit of PHTP on the crystallographic c-axis and keeping an interlayer distance of $c = 4.78$ Å. There is also a displacement between the R homo-chiral stacks and the S homo-chiral stacks of $c/2$. Axial displacements $\Delta x = \pm 4.8$ Å place the guest in an environment that is a perfect replication of the original at $\Delta x = 0$. This is clearly observed for DPH, while P3 and T5 have also local secondary minima at $c/2$, which could be ascribed as a plausible pseudo-stable condition. In the other hand, rotational barriers show more intricate patterns of $\left(\Delta E_{rot}/\Delta E_{rot}^{max}\right)$ as a function of the rotation relative to the optimal geometry. For rota-

tions, the threefold symmetry of the alternated R-PHTP and S-PHTP stacks explain the energetic barriers by the simple fact that rotations in $\pm 120°$ along the channel's axis repeat the chemical ambient at $0°$. This is the rule for the almost planar and coaxial T5 and DPH molecules with two more absolute minima at $\pm 120°$. In the case of P3 and as a consequence of a non-coaxial absolute minima (see Fig. 2), rotation at $\pm 120°$ leads to secondary minima slightly higher in energy. Rotations at $\pm 60°$ and $\pm 180°$ invert the chiral order of the stacks with respect to the guest and the observation of local minima or maxima depends on the number and strength of the host–guest interactions.

In reference to semi-empirical PM3 calculations on the ICs, the ΔE_{tras}^{max} and ΔE_{rot}^{max} are 6.5 (kcal mol^{-1}) for P3, about 10 (kcal mol^{-1}) in the case of T5 or up to 22.5 (kcal mol^{-1}) for DPH. The corresponding selected values obtained from the ONIOM calculations are somewhat lower (4.3 (kcal mol^{-1}) for P3, about 6.2 (kcal mol^{-1}) in the case of T5 or up to 13.2 (kcal mol^{-1}) for DPH), but when represented as relative $\left(\Delta E/\Delta E^{max}\right)$ they show a good agreement to the straightforward and faster semi-empirical calculations. The particular behaviour of ΔE_{tras} and ΔE_{rot} as a function of the axial or angular displacements depend on the number, the nature and relative distance of the several interactions between the hydrogen atoms of the innermost wall of the PHTP channel and the peripheral atoms of the guests. All these results are indicative of very stable conformations and positions inside the channel for temperatures ca. 300 K (where $kT \sim 0.53$ (kcal mol^{-1})) and higher under the assumptions of the model.

As the geometry of the guest molecules evolves inside the channel, changes on the carbon–carbon and carbon–sulphur bond lengths are indicative of an increment of delocalization of the π electronic densities of the guests. The general trend is that the carbon–carbon bonds that in the isolated gas phase molecule have a more single bond character become shorter in the inclusion compound, for instance C_3–C_4 in P3 and T5, as well as C_2–C_3 or C_4–C_5 for DPH (see Table 2). This effect is stronger for carbon–carbon bonds between aromatic rings and is followed by a simultaneous stretching of the alternate carbon–carbon bonds with a more double bond character in the gas phase (see C_4–C_5 for P3, C_2–C_3 and C_4–C_5 for T5 and C_3–C_4 for DPH). However, these opposite effects compensate and the included molecules do not exhibit notorious changes on their total size. From Table 2, we could infer that in practice the total length of P3 remains almost unchanged (0.5% shorter), that DPH become 1.4% shorter as the result of the more flexible behaviour of the six bonded carbons of the hexatriene segment between the opposite phenyl rings and finally that T5 stretches 2.1% mostly due to the planarization of the molecule. All these different behaviours are the result of a compromise on sizes of the guest molecules that tend to accommodate their different aromatic rings between the $c = 4.78$ Å space of two successive PHTP units in the homo-chiral stacks of the matrix host. For instance, in P3 the distance between baricentres of phenyl groups is 4.26 Å, which is close to c, thus allowing an easy placement of P3 in a $3 \times c$ length space of the channel. Longer molecules like DPH and T5 need volumes of $4 \times c$ and $5 \times c$ length of the channel, respectively.

The guest molecules also experience a reduction of symmetry with respect to the condition of phase gas, from C_s (T5) and C_{2h} (P3 and DPH) to C_1, due to the details of the interactions with the hydrogen decorated innermost wall of the channel, producing slight differences in bond lengths and bond angles for mirror-image equivalent atoms of the oligomers.

4. Excited states

In Table 3, we include results for the vertical absorption energies of the $S_0 \rightarrow S_1$ most intense singlet–singlet transitions, calcu-
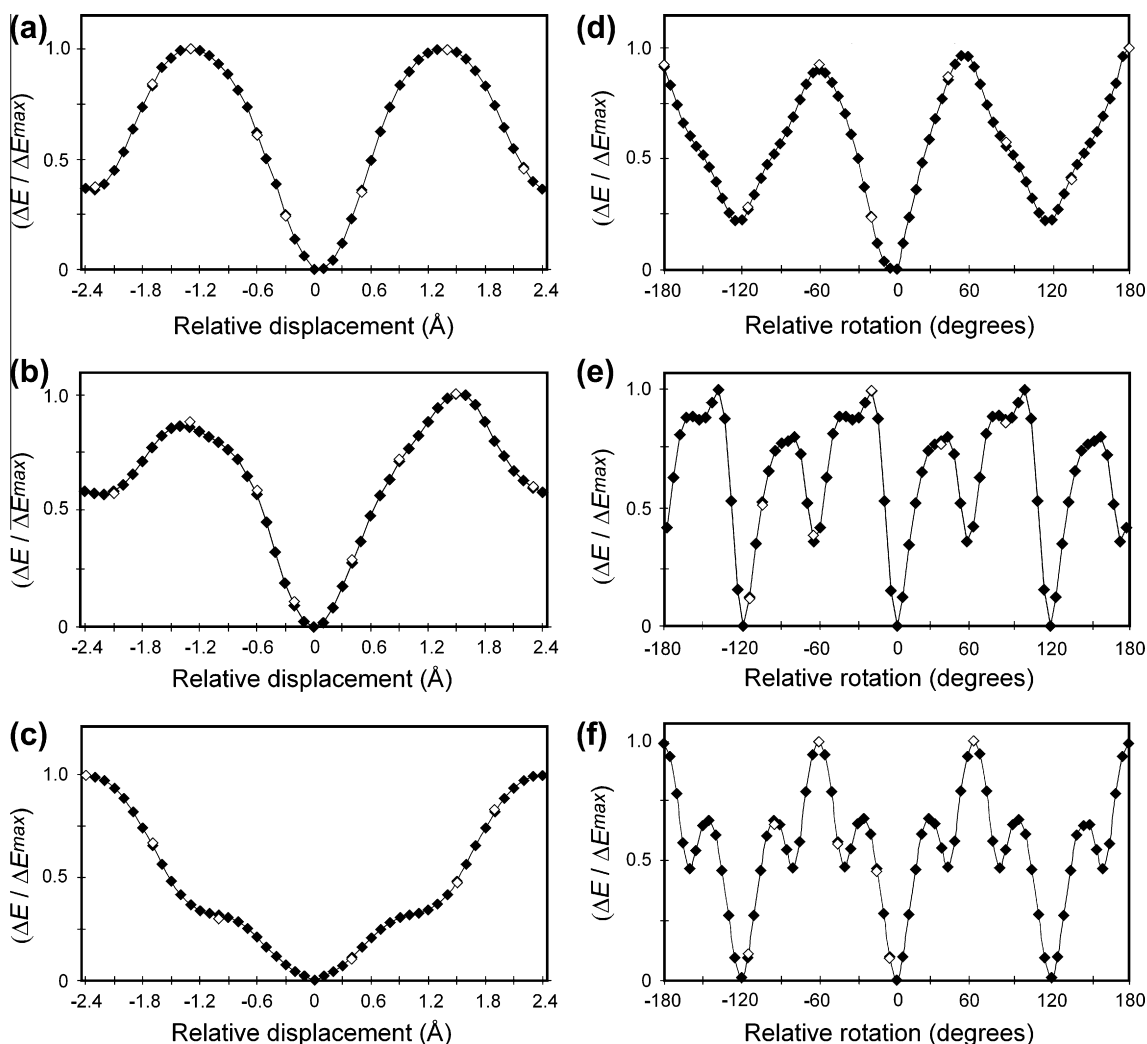
Fig. 3. $(\Delta E/\Delta E^{\max})$ energetic barrier ratios for movements of guest molecules inside the channel. Translational barriers: (a) P3, (b) T5 and (c) DPH. Rotational barriers: (d) P3, (e) T5 and (f) DPH. The reference is the optimal conformation of the guest inside the channel. Black squares for PM3 calculations; white squares for ONIOM calculations.

lated under time dependent Density Functional Theory (TD-DFT) framework for the three oligomers. Although we do not expect results that match experimental data, quantitative agreement is found regarding to experimental absorption spectra [2,10].

In order to compute energy transfer rates, in addition to oscillator strengths for vertical absorption transitions we need to calculate energies and oscillator strengths for emissive fluorescent transitions. In fact and as explained later on, the P3 → DPH → T5 global ET process have a transfer rate that must consider a first transfer step P3 → DPH and the calculation needs of an estimation of the fluorescent $S_1 \rightarrow S_0$ transition of P3 and the corresponding $S_0 \rightarrow S_1$ vertical absorption for DPH. The second step consider the DPH → T5 transfer of energy, in this case evaluating the in fluorescent $S_1 \rightarrow S_0$ transition of DPH and the corresponding $S_0 \rightarrow S_1$ vertical absorption for T5 in a similar procedure.

Emission processes are computed following the procedure explained in Section 2. Changes on geometries in the S_1 excited state depends on the molecule, for instance P3 becomes a more planar structure characterized by opened dihedral angles: P3 change from ∼121° (see Table 1) to 171.2°, as well as T5 which increase dihedral close to 180° and DPH which remains a planar structure with 180° dihedrals. Red shifts of the $S_1 \rightarrow S_0$ transitions and increments of the oscillator strengths respect to the vertical absorption transitions were computed for the three oligomers, although we showed only the relevant cases in Table 3.

5. Directionality of energy transfer processes

Energy transfer (ET) processes are the result of weak electromagnetic coupling between a pair of molecules consisting of a donor molecule (D) and the complementary acceptor (A) molecule. Within the Förster theory of resonant energy transfer and an electric dipole type mechanism, the rate of such transfer process is given by:

$$w_{DA} = \frac{1}{R^6} |\mu_{d'd}|^2 |\mu_{aa'}|^2 \Gamma_{DA} \int g_{D^*}(E) g_A(E) dE \qquad (1)$$

where $\mu_{d'd}$ is the transition electric dipole moment for the donor $d' \rightarrow d$ excited to ground state transition and $\mu_{aa'}$ the corresponding for a $a \rightarrow a'$ excitation at the acceptor. R is the distance between the molecular baricentres of the D–A pair which in this type of systems is long enough to assume the simpler point dipole approximation.

The $\mu_{d'd}$ and $\mu_{aa'}$ transition electric dipole moments are proportional to the oscillator strength of an emission process in the donor and an absorption transition in the acceptor and the integral expression in Eq. (1) is the normalized overlap between emission–absorption spectra of the donor and the acceptor. In Eq. (1) Γ_{DA} is the geometrical factor that accounts for the relative orientation of the transition dipole moment vectors between the donor and the acceptor with a general form [14]:

Table 2
Characteristic bond lengths and total longitudinal length for P3, T5 and DPH molecules in gas phase and as inclusion compounds (IC) in PHTP channel.[a]

Bond lengths (Å)	P3 (gas phase/ground state)	P3 (IC/ground state)
Terphenylene		
C_3–C_4	1.48562	1.46915
C_4–C_5	1.40657	1.40624
C_5–C_6	1.39578	1.40161
Total length (Å)	13.643	13.579
	DPH (gas phase/ground state)	DPH (IC/ground state)
Diphenylhexatriene		
C_2–C_3	1.43763	1.42685
C_3–C_4	1.35264	1.36374
C_4–C_5	1.46082	1.44603
C_5–C_6	1.40667	1.41107
C_6–C_7	1.39141	1.39350
Total length (Å)	16.434	16.202
	T5 (gas phase/ground state)	T5 (IC/ground state)
Quinquethiophene		
C_3–C_4	1.44415	1.42058
C_4–C_5	1.37794	1.38821
C_5–C_6	1.41513	1.41314
S_1–C_3	1.75448	1.76272
S_2–C_7	1.75343	1.76318
S_3–C_8	1.75392	1.76725
Total length (Å)	20.087	20.508

[a] See Fig. 1 for details.

Table 3
Relevant absorption and fluorescence energies calculated for P3, DPH and T5 as guests in the (PHTP: P3,DPH,T5) co-inclusion compound.[a]

P3	DPH	T5	
Fluorescence	Absorption	Fluorescence	Absorption
E (eV)	E (eV)	E (eV)	E (eV)
3.5159 (1.1607)	3.2849 (1.8483)	2.8881 (2.0890)	2.5755 (1.5527)

[a] Oscillator strengths are in parenthesis.

$$\Gamma_{DA} = \frac{(\cos\theta - 3\cos\phi\cos\gamma)^2}{16\pi^2\varepsilon_o^2} \tag{2}$$

After initial excitation in the UV range of wavelengths, the P3 → DPH → T5 global ET process is a two step composed mechanism: firstly, a pair interaction that involves the P3 (donor) and DPH (acceptor) oligomers, relaxes P3 to the S_0 ground state and promotes DPH to the S_1 excited state. A subsequent second transfer step, where the DPH acts as a donor and T5 is the final acceptor, excite the T5 oligomer to its own S_1 excited state which finally relaxes with emission in the yellow. In a first place this study is focused on a comparison between the $w_{P3\text{-}DPH}$ and the $w_{DPH\text{-}T5}$ step rates in order to establish relative ratios of the total energy transfer rate for different routes of the P3 → DPH → T5 transfer in the PHTP matrix host.

In the co-inclusion compound, the oligomeric guests could fill the channels in random positions and the global energy transfer do occur following several different pathways that depend on the relative angular orientation and distances between the P3, DPH and T5 trio.

The highest global energy transfer rates do occur for nearest neighbor oligomers within the co-inclusion compound. Relative to the channels axis, there are three different spatial arrangements of the P3-DPH-T5 trio that fulfill this condition (see Fig. 4):

(1) Fully longitudinal ET : $w_{P3\text{-}DPH}^{longitudinal} \rightarrow w_{DPH\text{-}T5}^{longitudinal}$

(2) Fully perpendicular ET : $w_{P3\text{-}DPH}^{perpendicular} \rightarrow w_{DPH\text{-}T5}^{perpendicular}$

(3) Mixed ET : $w_{P3\text{-}DPH}^{longitudinal} \rightarrow w_{DPH\text{-}T5}^{perpendicular}$ or $w_{P3\text{-}DPH}^{perpendicular} \rightarrow w_{DPH\text{-}T5}^{longitudinal}$.

As transition dipole moment vectors are co-linear to the molecular axis for the three oligomers under study, for longitudinal transfers the angles θ, ϕ and γ are $\theta = 0$, $\phi = \gamma = 180°$ and $\Gamma_{DA,180°} = 1/4\pi^2\varepsilon_o^2$. For perpendicular orientations, the interacting DA pair is located in nearest neighbor channels with baricentres in a 90° angle, then $\theta = 0$, $\phi = \gamma = 90°$ and $\Gamma_{DA,90°} = 1/16\pi^2\varepsilon_o^2$. A nodal conic region for energy transfer with $\Gamma_{DA} = 0$ is found for $\gamma = 125.26°$ and other angles show $0 \leqslant \Gamma_{DA,180°} \leqslant 1/4\pi^2\varepsilon_o^2$ geometrical factors.

In relation to the guest–guest distance in the co-inclusion compound, a pair of nearest neighbors oligomers in the same channel reach a stable configuration when carbon terminal atoms are separated by about 5.2 Å [9]. Then the baricentres representative distance for the pairs P3-DPH and DPH-T5 are $R_{P3\text{-}DPH}$ = 18.09 Å and $R_{DPH\text{-}T5}$ = 21.56 Å.

The ($w_{P3\text{-}DPH}/w_{DPH\text{-}T5}$) ratio of the two step of the transfer between the triad P3-DPH-T5 could be easily inferred from these data:
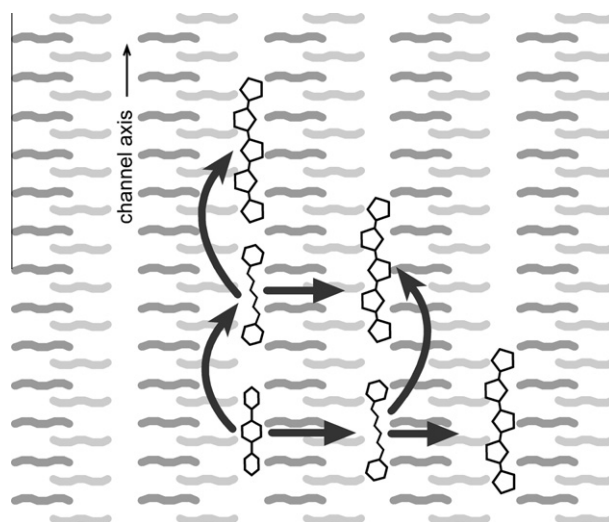
Longitudinal transfers:

$$\frac{w_{P3\text{-}DPH}^{longitudinal}}{w_{DPH\text{-}T5}^{longitudinal}} = \left(\frac{R_{DPH\text{-}T5}}{R_{P3\text{-}DPH}}\right)^6 \times \frac{|\mu_{d'd}^{P3}|^2|\mu_{aa'}^{DPH}|^2}{|\mu_{d'd}^{DPH}|^2|\mu_{aa'}^{T5}|^2}$$
$$\times \frac{\left(\int g_{D^*}(E)g_A(E)dE\right)_{P3\text{-}DPH}}{\left(\int g_{D^*}(E)g_A(E)dE\right)_{DPH\text{-}T5}} \tag{3}$$

Replacing $R_{P3\text{-}DPH}$ and $R_{DPH\text{-}T5}$ figures, oscillator strengths (proportional to the transition electric dipole moments) and considering the experimental report of an almost complete overlap between emission and absorption spectra for both the P3-DPH and DPH-T5 interacting pairs $\frac{\left(\int g_{D^*}(E)g_A(E)dE\right)_{P3\text{-}DPH}}{\left(\int g_{D^*}(E)g_A(E)dE\right)_{DPH\text{-}T5}} \simeq 1$ [10], it is obtained $\frac{w_{P3\text{-}DPH}^{longitudinal}}{w_{DPH\text{-}T5}^{longitudinal}} = 1.26$.

Fig. 4. Scheme of the different pathways for ET processes between the P3-DPH-T5 trio within the nanochannels of PHTP. Fully longitudinal transfers follow the channel axis direction. Pathways for fully perpendicular and mixed transfers are also showed.

Perpendicular transfers: In this case the distances $R_{P3\text{-}DPH}$ and $R_{DPH\text{-}T5}$ are exactly the same (14 Å, distance between contiguous channels [9]) then the $(w_{P3\text{-}DPH}^{perpendicular})/(w_{DPH\text{-}T5}^{perpendicular})$ ratio depends only on oscillator strengths and $\frac{w_{P3\text{-}DPH}^{perpendicular}}{w_{DPH\text{-}T5}^{perpendicular}} = 0.438$.

From this analysis, we observe that for longitudinal transfers inside the channel the second step (DPH-T5 transfer rate) controls the global P3→DPH→T5 ET rate, a result in agreement to averaged experimental results of Ref. [10]. In the case of perpendicular transfers between the P3-DPH-T5 triad in parallel channels, the global ET rate is mostly controlled by the first step (i.e. the P3-DPH transfer rate), due to the magnitudes of the oscillator strengths calculated by us.

On the other hand, the total energy transfer rate for the global process is $W_{ET}^{total} = w_{P3\text{-}DPH} \times w_{DPH\text{-}T5}$ and the relative total energy transfer rates ratio between the different pathways are:

$$\frac{W_{ET\text{-}longitudinal}^{total}}{W_{ET\text{-}perpendicular}^{total}} = \left(\frac{(R_{P3\text{-}DPH} \times R_{DPH\text{-}T5})_{perpendicular}}{(R_{P3\text{-}DPH} \times R_{DPH\text{-}T5})_{longitudinal}} \right)^6 \times \left(\frac{\Gamma_{DA,180°}}{\Gamma_{DA,90°}} \right)^2$$
$$= 0.258$$

and

$$\frac{W_{ET\text{-}mixed}^{total}}{W_{ET\text{-}perpendicular}^{total}} = \left(\frac{14}{(R_{DA})_{longitudinal}} \right)^6 \times \frac{\Gamma_{DA,180°}}{\Gamma_{DA,90°}} = 0.86 \ or \ 0.30$$

depending on which D–A pair is filling the same channel.

In summary, the global energy transfer rates increase as $W_{ET\text{-}longitudinal}^{total} < W_{ET\text{-}mixed}^{total} < W_{ET\text{-}perpendicular}^{total}$.

Other pathways of the transfer of energy for oligomers located at greater distances and/or relative orientation have lower W_{ET}^{total}.

From these results based on the point dipole approximation, we conclude that the most efficient ET processes in (PHTP:P3,DPH,T5) do occur as a two-step interaction between channels, propagating the excitation in a direction perpendicular to the long channel axis of the matrix host, although the mixed $(P3 \rightarrow DPH)_{longitudinal}$ and $(DPH \rightarrow T5)_{perpendicular}$ pathway is also a very competive contribution to the ET rate.

6. Results and conclusions

A theoretical study of models of the (PHTP:P3,DPH,T5) co-inclusion compound allow a detailed explanation of the conformational aspects that govern the self-assembly of these crystals. Despite of the fact that the oligomeric units are not chemically bonded to the PHTP matrix host and within the assumptions of the model, it has been observed that P3, DPH and T5 units are much localized inside the channels adopting geometries somewhat different to the isolated gas phase case. Confinement dictated by the size and spatial details of the inner electronic densities of the channel determined optima geometries for the included oligomeric units as well as energetic barriers to displacements and rotations within the channel. Excited state calculations lead to estimation of the most efficient energy transfer processes that occur in this system. From the geometric and excited states information, some simple criteria show that the UV to yellow two-step down conversion between the (P3:DPH:T5) trio tends to propagate preferentially in directions that are perpendicular to the c-axis of the crystals. Development of this kind of systems, by including other selected oligomers of different lengths and spectroscopic features, could lead to useful functionalized materials for electro optical devices.

References

[1] G. Bongiovanni, C. Botta, G. Di Silvestro, M.A. Loi, A. Mura, R. Tubino, Chem. Phys. Lett. 345 (2001) 386.
[2] G. Bongiovanni, C. Botta, J.E. Communal, F. Cordella, L. Magistrelli, A. Mura, G. Patrinoiu, P. Picouet, G. Di-Silvestro, Mater. Sci. Eng. C 23 (2003) 909.
[3] L. Rabara, M. Aranyosiov, D. Velic, Appl. Surf. Sci. 252 (2006) 7000.
[4] M.A. Hunt, D.-W. Jung, M. Shamsheer, T. Uyar, A.E. Tonelli, Polymer 45 (2004) 1345.
[5] C. Botta, R. Bosisio, G. Bongiovanni, A. Mura, R. Tubino, Synth. Met. 84 (1997) 535.
[6] G. Bongiovanni, C. Botta, J.L. Brédas, J. Cornil, D.R. Ferro, A. Mura, A. Piaggi, R. Tubino, Chem. Phys. Lett. 278 (1997) 146.
[7] F. Meinardi, A. Borghesi, M. Cerminara, A. Sasella, S. Tavazzi, R. Tubino, M. Gurioli, A. Mura, G. Bongiovanni, Synth. Met. 121 (2001) 1355.
[8] S.O. Vásquez, Comput. Mater. Sci. 37 (4) (2006) 572.
[9] S.O. Vásquez, Phys. Chem. Chem. Phys. 10 (35) (2008) 5459.
[10] C. Botta, G. Patrinoiu, P. Picouet, S. Yunus, J.E. Communal, F. Cordella, F. Quochi, A. Mura, G. Bongiovanni, M. Pasini, S. Destri, G. Di Silvestro, Adv. Mater. 16 (19) (2004) 1716.
[11] D.M. McCann, P.J. Stephens, J.R. Cheeseman, J. Org. Chem. 69 (2004) 8709.
[12] F. Martínez, G. Neculqueo, S.O. Vásquez, R. Letelier, M.T. Garland, A. Ibañez, J.C. Bernede, J. Mol. Struct. 973 (2010) 56.
[13] Gaussian 03, Revisión B.05, M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery, Jr., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gilí, B. Johnson, W. Chen, M.W. Wong, C. González, J.A. Pople, Gaussian, Inc., Pittsburgh PA, 2003.
[14] G.J. Daniels, R.D. Jenkins, D.S. Bradshaw, D.L. Andrews, J. Chem. Phys. 119 (2003) 2265.