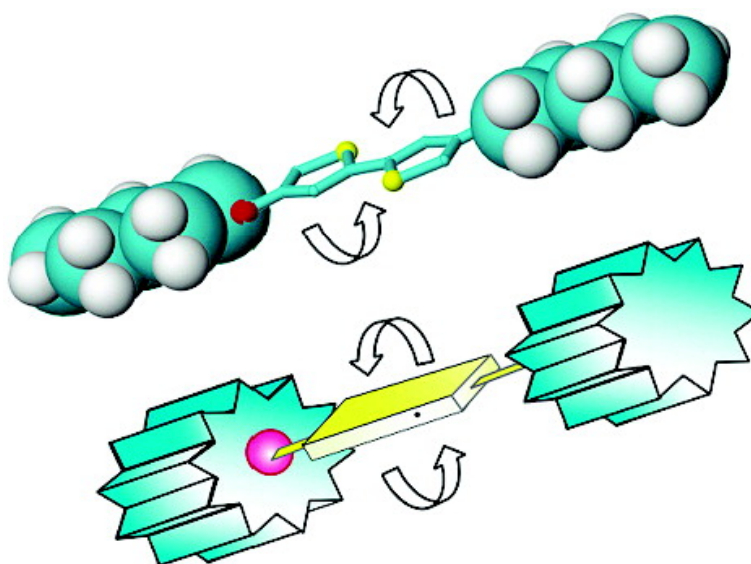


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Dynamics of Alkoxy–Oligothiophene Ground and Excited States in Nanochannels

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Abstract: Two oligothiophenes, 4,4'-dipentoxy-2,2'-dithiophene and 4,4''-dipentoxy-2,2':5',2'':5'',2'''-tetrathiophene, have been included in the nanochannels of the autoassembling host TPP (tris-*o*-phenylenedioxycyclotriphosphazene). The effect of the confinement on the structure and properties of the two dyes, as conformational arrangements, dynamics, and photophysical behavior, was addressed by the combination of high spinning speed solid-state NMR and time-resolved EPR spectroscopy. We compared the conformations of the dyes in their ground and photoexcited triplet states and described in detail the dynamics of the supramolecular adducts from 4 K to room temperature. Above 200 K surprisingly fast spinning rates of the dithiophene core were discovered, while the side chains show far slower reorientation motion, being in bulky gauche-rich conformations. These lateral plugs keep the planar core as appended in the space like a nanoscale gyroscope, allowing a reorientation in the motion regime of liquids and a long triplet lifetime at unusually high temperature. The nuclear magnetic properties of the guest dyes are also largely affected by the aromatic rings of the neighboring host, imparting an impressive magnetic susceptibility effect (2 ppm proton shift). The high mobility is due to the formation of a nanocage in a channel where aliphatic and aromatic functions isolate the thiophene moieties. Instead, two conformers of the tetrathiophene twisted on the central bond are stabilized by interaction with the host. They interconvert fast enough to be averaged in the NMR time scale.

Introduction

Molecular confinement is a growing field which focuses on the new properties of molecules when isolated one from another or aggregated in low-dimensionality files or clusters.¹ Both nanoporous and self-assembled materials, which can incorporate molecules in ordered lattices, can serve to confine the active species.² Optoelectronic and nonlinear optical properties, emission, and absorption of radiation can be modulated. In some instances it has been possible to obtain macroscopically oriented samples suitable for laser applications.³

Conventional zeolites have been largely applied for molecular confinement. Organic zeolites are now attracting much attention because of their versatility and easiness to grow crystals with a variety of molecules of high and low molecular weights.⁴ Self-

assembly allows inclusion in a single step of molecules with low volatility and diffusing slowly in preformed channels. The organic hosts arranging the guests anisotropically into nanochannels can store large amounts of chromophores without intermolecular association, preventing the interchain interactions. Self-assembled porous materials are currently of great interest for several fields in addition to molecular confinement and have an impact on nanotechnological applications.⁵

Here we describe a tight confinement and alignment of alkoxy-substituted oligothiophenes in aromatic nanochannels of

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- (1) *Comprehensive Supramolecular Chemistry*; Atwood, J. L., Davies, J. E. D., MacNicol, D. D., Vögtle, F., Lehn, J.-M., Eds.; Elsevier Science Ltd.: Oxford, 1996.
- (2) (a) Berberan-Santos, M. N.; Chopinet, P.; Fedorov, A.; Jullien, L.; Valeur, B. *J. Am. Chem. Soc.* **2000**, *122*, 11876–11886. (b) Li, G.; McGown, L. B. *Science* **1994**, *264*, 249–251. (c) Wu, C.-G.; Bein, T. *Science* **1994**, *264*, 1757–1759. (d) Spange, S. *Angew. Chem., Int. Ed.* **2003**, *42*, 4430–4432. (e) Aida, T.; Tajima, K. *Angew. Chem., Int. Ed.* **2001**, *40*, 3803–3806. (f) Macchi, G.; Meinardi, F.; Simonutti, R.; Sozzani, P.; Tubino, R. *Chem. Phys. Lett.* **2003**, *379*, 126–131. (g) Hoss, R.; König, O.; Kramer-Hoss, V.; Berger, U.; Rogin, P.; Hulliger, J. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1664–1666.

- (3) (a) Fichou, D. *Handbook of Oligo- and Polythiophenes*; Wiley-VCH: New York, 1999. (b) Rodenberger, D. C.; Hefflin, J. R.; Garito, A. F. *Nature* **1992**, *359*, 309–311. (c) Cao, Y.; Parker, I. D.; Yu, G.; Zhang, C.; Heeger, A. J. *Nature* **1999**, *397*, 414–417. (d) Friend, R. H.; Gymer, R. W.; Holmes, A. B.; Burroughes, J. H.; Marks, R. N.; Taliani, C.; Bradley, D. D. C.; Dos Santos, D. A.; Brédas, J. L.; Lögdlund, M.; Salaneck, W. R. *Nature* **1999**, *397*, 121–128. (e) Crone, B.; Dodabalapur, A.; Lin, Y.-Y.; Filas, R. W.; Bao, Z.; LaDuca, A.; Sarapeshkar, R.; Katz, H. E.; Li, W. *Nature* **2000**, *403*, 521–523. (f) Mason, W. T. *Fluorescent and Luminescent Probe for Biological Activity*; Academic Press: New York, 1999. (g) Besanger, T.; Zhang, Y.; Brennan, J. D. *J. Phys. Chem. B* **2002**, *106*, 10535–10542.
- (4) (a) Ramamurthy, V.; Caspar, J. V.; Eaton, D. F.; Kuo, E. W.; Corbin, D. R. *J. Am. Chem. Soc.* **1992**, *6*, 3882–3892. (b) Calzaferri, G.; Huber, S.; Maas, H.; Minkowski, C. *Angew. Chem., Int. Ed.* **2003**, *42*, 3732–3758; *Angew. Chem.* **2003**, *115*, 3860–3888. (c) Hulliger, J.; Weber, E.; Hertzsch, T.; Sozzani, P. Organic Zeolites. In *Encyclopedia of Supramolecular Chemistry*; Atwood, J. L., Ed.; Dekker: New York, 2004. (d) Langley, P. J.; Hulliger, J. *J. Chem. Soc. Rev.* **1999**, *28*, 279–292. (e) Sozzani, P.; Comotti, A.; Simonutti, R.; Meersmann, T.; Logan, J. W.; Pines, A. *Angew. Chem., Int. Ed.* **2000**, *39*, 2695–2699.
- (5) Chae, H. K.; Siberio-Pérez, D. Y.; Kim, J.; Go, Y.; Eddaoudi, M.; Matzger, A. J.; O'Keeffe, M.; Yaghi, O. M. *Nature* **2004**, *427*, 523–527.

the self-assembly host tris-*o*-phenylenedioxy-cyclotriphosphazene (TPP).⁶ The guest dyes have been studied by focusing on their dynamic and conformational properties in the unusual constraining environment. The transient photoexcited triplet state of the confined molecules has also been addressed. This investigation has been made possible by use of advanced magnetic resonance techniques, such as high spinning speed MAS NMR and time-resolved EPR. These two spectroscopies give comparably detailed insight into the molecular conformation and dynamics, respectively, of ground singlet and excited triplet states. Moreover, they investigate the molecular dynamics on different time scales.

Magnetic resonance spectroscopies have been used successfully by several groups for investigations on the supramolecular structure and dynamics of molecules in a number of inclusion matrices, both organic and inorganic. Several works focused on carbon, proton, and deuterium NMR to study the arrangement of low and high molecular mass guests in confining matrices, such as zeolites, urea, perhydrotriphenylene (PHTP), and cyclodextrins.⁷ The dynamics of included polymers and elongated molecules forming high-melting nanocomposites is particularly intriguing and promotes anisotropic motions and mesophases.⁸ EPR spectroscopies have been applied to stable nitroxide radicals included as guests in zeolites,⁹ to radicals and macroradicals formed by ionizing radiation in zeolites,¹⁰ and in organic hosts such as urea and PHTP.¹¹ Radicals as probes have also been produced by photolysis.¹² The photoexcited triplet state of the included guests is a paramagnetic probe allowing a TR-EPR study of supramolecular properties and of the effect of confinement on the photophysics of the dyes.¹³

The photophysical properties of poly- and oligothiophenes are interesting because of their use in molecular electronics, charge storage, and nonlinear optical applications. Oligothiophenes are widely studied both for their interest for applications and as models of polythiophenes. The conformations and decay paths of their excited states are studied by optical and

theoretical methods.^{14,15} Radiative and nonradiative decay routes are both possible, and the parameters that favor one type of decay over the other are of interest for many applications. The main decay path of the excited singlet in solution is the intersystem crossing (ISC) to the triplet state. In solids, their photophysics depends on the matrix. Intermolecular interactions between coplanar adjacent thiophene molecules, when possible, can lead to specific decay routes due to the formation of low-lying optically forbidden states. Oligothiophenes in nanochannels cannot arrange in coplanar aggregates. Therefore, their photophysics, in particular the efficiency of ISC, are mainly determined by the conformations of the ground and excited states in the ordering and confining matrix as the spin-orbit coupling depends on the symmetry of the states.^{14a,15}

The interplay of conformational arrangement, motions, and transient state properties are organically addressed in the present paper. Route of formation, structure, and decay properties of the photogenerated triplet states of the oligothiophene molecules aligned as single files in the fully aromatic pipes of TPP are of great interest as compared to the properties of the same molecules when dispersed in less confining environments.

Experimental Section

Synthesis and Sample Preparation. The inclusion compounds (ICs) with 4,4'-dipentoxo-2,2'-dithiophene (4-T2) and 4,4'-dipentoxo-2,2':5',2'':5'',2'''-tetrathiophene (4-T4) have been obtained by crystallization from *o*-xylene solutions of TPP (0.01 mol/L) and guest molecules (host:guest weight of 3:1). *o*-Xylene was previously purified from *n*-nonane impurities using molecular sieves and the TPP matrix as an entrapment agent of linear alkanes. The fraction of the guests in the IC is typically 0.12. Synthesis of TPP was carried out as follows: a solution of cathecol (10.8 g) in 27.5 mL of triethylamine and anhydrous tetrahydrofuran (90 mL) was added dropwise under stirring to sublimed hexachlorophosphazene (11.53 g) dissolved in 175 mL of tetrahydrofuran. Stirring and refluxing was applied for 40 h at 60 °C. The white precipitate was filtered off and washed with tetrahydrofuran and then distilled water, and the product was dried under vacuum. A prolonged extraction with benzene yielded the TPP/benzene IC. The IC was heated at 70 °C under vacuum (10⁻² Torr) for 0.5 h to remove the benzene and obtain the TPP sample.⁶ Synthesis of oligothiophene derivatives used in this work is described elsewhere.¹⁶

The IC's formed by TPP and oligothiophenes were checked by calorimetry. The melting temperatures of the inclusion compounds are shown by sharp DSC melting peaks up to 290–310 °C, much higher than both the melting temperatures of pure thiophenes and the TPP matrix, indicating a congruent melting of the adducts (Supporting Information). The X-ray powder diffraction pattern of the inclusion compounds with both dithiophene and tetrathiophene derivatives can be indexed considering a hexagonal cell in agreement with the channel-like structure formed by the TPP matrix with linear-chain molecules. In Figure 1 the dithiophene molecule is shown embedded in the TPP channel. The side chains, depicted in the all-trans conformation for clarity, are dynamically averaged with gauche conformations, as discussed below.

Solid-State NMR Measurements. The solid-state NMR spectra were run at 75.5 MHz on a Bruker Avance 300 instrument operating

- (6) (a) Comotti, A.; Simonutti, R.; Stramare, S.; Sozzani, P. *Nanotechnology* **1999**, *10*, 70–76. (b) Kobayashi, T.; Isoda, S.; Kubono, K. *Cyclophosphazenes, Structure and Molecular Selectivity*. *Comp. Supramol. Chem.* **1996**, 399–420. (c) Allcock, H. R.; Siegel, L. A. *J. Am. Chem. Soc.* **1964**, *86*, 5140–5144.
- (7) (a) Zaborowski, E.; Zimmermann, H.; Vega, S. *J. Am. Chem. Soc.* **1998**, *120*, 8113–8123. (b) Turro, N. J.; Lei, X.-G.; Li, W.; Liu, Z.; McDermott, A.; Ottaviani, M. F.; Abrams, L. *J. Am. Chem. Soc.* **2000**, *122*, 11649–11659. (c) Jaramillo, E.; Grey, C. P.; Auerbach, S. M. *J. Phys. Chem.* **2001**, *105*, 12319–12329. (d) Kubo, A.; Imashiro, F.; Terao, T. *J. Phys. Chem.* **1996**, *100*, 10854–10860. (e) Vold, R. L.; Hostson, G. L.; Subramanian, R. *J. Phys. Chem.* **1998**, *108*, 7305–7316. (f) Aliev, A. E.; Harris, K. D. *M. J. Phys. Chem.* **1997**, *101*, 4541–4547. (g) Schilling, F. C.; Amundson, K. R.; Sozzani, P. *Macromolecules* **1994**, *27*, 6498–6502. (h) Meersmann, T.; Logan, J. W.; Simonutti, R.; Caldarelli, S.; Comotti, A.; Sozzani, P.; Kaiser, L. G.; Pines, A. *J. Phys. Chem. A* **2000**, *104*, 11665–11670. (i) Lu, J.; Mirau, P.; Tonelli, A. *Macromolecules* **2001**, *34*, 3276–3284.
- (8) (a) Farina, M.; Di Silvestro, G.; Sozzani, P. Perhydrotriphenylene: a D₃ symmetric host. *Comp. Supramol. Chem.* **1996**, *6*, 371–398. (b) Schilling, F. C.; Amundson, K. R.; Sozzani, P. *Macromolecules* **1994**, *27*, 6498–6502.
- (9) Ottaviani, M. F.; Lei, X.-G.; Liu, Z.; Turro, N. J. *J. Phys. Chem. B* **2001**, *105*, 7954–7962.
- (10) (a) Sozzani, P.; Di Silvestro, G.; Gervasini, A. *J. Polym. Sci., Part A: Polym. Chem.* **1986**, *24*, 815–825. (b) Liu, W.; Wang, P.; Komaguchi, K.; Shiotani, M.; Michalik, J.; Lund, A. *PCCP* **2000**, *2* (11), 2515–2519.
- (11) (a) Segre, U.; Brustolon, M.; Brunel, L. C.; Maniero, A. L. *Chem. Phys. Lett.* **1999**, *308*, 408–412. (b) Brustolon, M.; Maniero, A. L.; Marcomini, A.; Segre, U. *J. Mater. Chem.* **1996**, 1723–1729. (c) Brustolon, M.; Maniero, A. L.; Segre, U. *J. Chem. Soc., Perkin Trans.* **1997**, 2519–2523. (d) Brustolon, M.; Megalini, M. L.; Bonora, M.; Maniero, A. L.; Segre, U. *Perkin Trans. 2* **1998**, 1731.
- (12) Turro, N. J.; Jockusch, S.; Lei, X.-G. *J. Org. Chem.* **2002**, *67* (16), 5779–5782.
- (13) Barbon, A.; Bortolus, M.; Brustolon, M.; Comotti, A.; Maniero, A. L.; Segre, U.; Sozzani, P. *J. Phys. Chem. B* **2003**, *107*, 3325–3331.
- (14) (a) Beljonne, D.; Shuai, Z.; Pourtois, G.; Bredas, J. L. *J. Phys. Chem. A* **2001**, *105*, 3899–3907. (b) Becker, R. S.; deMelo, J. S.; Macanita, A. L.; Elisei, F. *J. Phys. Chem.* **1996**, *100*, 18683–18695. (c) Belletête, M.; Di Césaire, N.; Leclerc, M.; Durocher, G. *Chem. Phys. Lett.* **1996**, *250*, 31–39.
- (15) Gigli, G.; Della Sala, F.; Lomascolo, M.; Anni, M.; Barbarella, G.; Di Carlo, A.; Lugli, P.; Cingolati, R. *Phys. Rev. Lett.* **2001**, *86*, 167–170.
- (16) Zotti, G.; Gallazzi, M. C.; Zerbi, G.; Meille, S. V. *Synth. Met.* **1995**, *73*, 217–231.

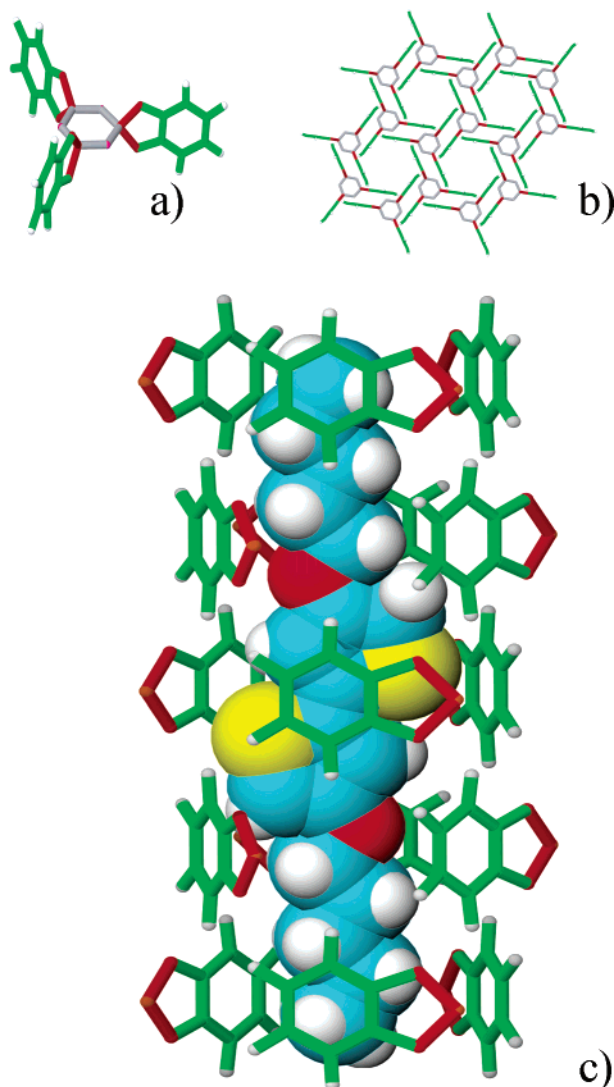


Figure 1. (a) Skeletal representation of TPP molecule. (b) Organization of TPP molecules in the hexagonal lattice of the inclusion compound (the guest is omitted for clarity). (c) Schematic representation of dithiophene (4-T_2) confined to the aromatic nanochannels formed by paddles of TPP as viewed along the channel axis (TPP paddles: C, green; O, red; P, orange; H, white). The guest molecule is represented by van der Waals radii (C, blue; S, yellow; O, red; H, white) with the alkoxy chains depicted in all-trans conformation.

at a static field of 7.04 T equipped with 4 mm zirconia rotors and double-resonance MAS probes. The samples are spun at a speed of 15 kHz, and ramped-amplitude cross-polarization (RAMP-CP)¹⁷ transfer is applied. This procedure restores a broader matching profile between proton and carbon nuclei. The ramp is obtained changing the strength of the proton RF from 80 kHz at the beginning of the contact time to a value of 60 kHz at the end of the cross-polarization period in 100 steps. The 90° pulse for proton was 2.9 μs (86 kHz). Cross-polarization (CP) MAS experiments were performed using a recycle delay of 10 s and a contact time of 2.5 ms. ^{13}C T_1 relaxation times performed at variable temperatures with Torchia sequence¹⁸ were collected between 200 K and room temperature with 7 mm ZrO_2 rotors spinning at a speed of 5–6 kHz; 90° pulse duration on the proton channel was 4.7 μs (~53 kHz).

Time-Resolved EPR Measurements. A Bruker ESP380E spectrometer with a dielectric resonator was used for time-resolved cw EPR (TR-EPR)¹⁹ by using a high quality factor (Q) of the cavity and a

(17) Metz, G.; Wu, X.; Smith, S. O. *J. Magn. Reson. A* **1994**, *110*, 219–227.
 (18) Torchia, D. A. *J. Magn. Reson.* **1978**, *30*, 613–616.

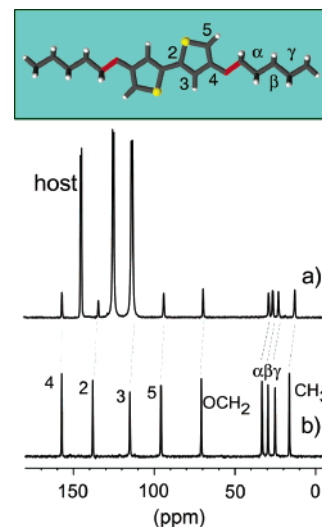


Figure 2. ^{13}C cross-polarization (RAMP-CP) MAS NMR spectra of dithiophene (4-T_2) with TPP in the IC (a) and pure dye in the solid state (b).

corresponding slow detection line. The signal generated by the laser flash under continuous microwave irradiation was taken from the detector, preamplified and digitalized from a LeCroy 3560 digital oscilloscope. The response time of the apparatus was estimated to be around 800 ns. A surface was obtained by acquiring the time decay traces for different field positions. Integration with time windows of around 400 ns allowed obtaining slices along the field. The spectra are normally obtained with the integration window centered at 1 μs .

Optical irradiation was performed by laser flashes 5 ns in width at 355 nm produced by a Nd:YAG laser equipped with second- and third-harmonic generators. The light was conveyed into the cavity through an optical window in the cryostat.

We obtained the TR-EPR of the photogenerated triplet states of 4-T_2 and 4-T_4 in a toluene frozen matrix and in the IC's. All the samples were degassed and sealed under vacuum. The oligothiophenes concentration in toluene solution was about 10^{-5} M, higher concentrations showing a modification of the spectra due to the well-known tendency of the oligothiophenes to form π dimers. The triplet spectrum of 4-T_2 has been recorded in the temperature range 4–240 K. For 4-T_4 the triplet spectrum was detected in the range 4–80 K, the signal being too weak at higher temperatures. A Oxford CF935 cryostat has been used with either liquid helium or nitrogen.

Results and Discussion

NMR. The ^{13}C MAS NMR spectra of pure 4-T_2 and the corresponding IC are reported in Figure 2. The spectrum of the pure dye in the solid state shows nine sharp resonances: four downfield resonances of thiophene rings in the aromatic region (90–160 ppm), four resonances of the aliphatic chain at 10–40 ppm, and a single resonance at about 70 ppm due to the methylene bearing the electron-attractor oxygen atom. The resonances are associated with the nine nonequivalent carbons in the unit cell and correspond to one-half of the carbons of the 4-T_2 molecule. Thus, the remarkable resolution of the spectrum allows distinguishing all the carbons that are fully assigned by comparison with the ^{13}C solution NMR spectrum (Table 1). The chemical shift values of pentoxy side chains in the crystalline

(19) (a) McLauchlan, K. A. In *Modern Pulsed And Continuous Wave Electron Spin Resonance*; Kevan, L., Bowman, L. K., Eds.; Wiley: New York, 1990.
 (b) Hirota, N.; Yamauchi, S. *J. Photochem. Photobiol., C* **2003**, *4*, 109–124.
 (c) Corvaja C.; Agostini G.; Giacometti G.; Pasimeni L. *Chem. Phys.* **1984**, *85*, 421–429.

Table 1. ^{13}C Solid-State Chemical Shifts (δ/ppm) and ^{13}C Relaxation Times (T_1/s) at Room Temperature of 4-T_2 in the Pure Dye in the Solid State and as a Guest in the TPP IC (as a reference the chemical shifts of 4-T_2 in CDCl_3 solution are reported)

assign.	^{13}C δ pure 4-T_2	^{13}C δ TPP/ 4-T_2 IC	^{13}C δ^b in CDCl_3	^{13}C Δ^c	^{13}C T_1 pure 4-T_2	^{13}C T_1 TPP/ 4-T_2 IC
CH_3	16.2	12.9	14.5	-3.3	3	2
$\gamma\text{-CH}_2$	25.2	23.0	22.9	-2.2	100	1
$\beta\text{-CH}_2$	29.5	26.5	28.7	-3.0	105	1
$\alpha\text{-CH}_2$	33.2	29.1	29.4	-4.1	147	0.8
$-\text{OCH}_2$	70.9	69.4	70.6	-1.5	290	0.7
C5	95.8	93.7	96.8	-2.1	328	0.5
C3	115.0	113.3 ^a	116.3	-1.7	293	31
C2	137.9	134.0	136.5	-3.9	282	24
C4	157.3	156.5	158.0	-0.8	294	n.d.

^a This peak overlaps the atom signal of the TPP matrix. ^b Chemical shifts of 4-T_2 in CDCl_3 solution.⁹ ^c ^{13}C Δ (ppm) = $\delta(\text{TPP}/4\text{-T}_2 \text{ IC}) - \delta(4\text{-T}_2 \text{ pure})$.

state of the pure 4-T_2 indicates the presence of trans-planar conformations, consistent with the structure resolved by X-ray diffraction.²⁰

In the spectrum of the IC (Figure 2a) three intense peaks appear due to the three independent carbons of TPP in the hexagonal phase (^{13}C NMR δ 144.7, 124.9, and 113.3 ppm). The 4-T_2 carbons resonate upfield with respect to the pure dye, showing an exceptional shift of -4.1 ppm on $\alpha\text{-CH}_2$ (Table 1). Destruction of the crystal packing of the pure 4-T_2 and confinement of the molecules in the aromatic nanochannels of the TPP matrix considerably change the immediate surroundings of each 4-T_2 molecule. Such marked upfield shifts are mainly due to two phenomena: the magnetic susceptibility generated by the aromatic paddles of the TPP matrix and the conformational changes of the guests. A previous study, performed by some of the authors on *n*-alkanes,²¹ showed that a 1.5 upfield shift due to the magnetic susceptibility is generated by the aromatic rings of TPP surrounding the guest carbons at a short distance of less than 3 Å. The amount of upfield shift is consistent with the nucleus-independent chemical-shift maps, giving the calculated chemical shifts in the space region above the plane of aromatic rings (in this case the TPP paddles).²² Taking into account this value of magnetic susceptibility due to aromatic rings we can estimate the influence of other effects (i.e., conformational) on the chemical shifts (Table 1). The resonances of most carbons of 4-T_2 in IC undergo a further upfield shift to 2 ppm due to conformations. It is well known that the γ -gauche effect causes an upfield shift of 5 ppm when the observed carbon moves from trans to gauche conformations.²³ The observed upfield shift is the result of fast averaging between trans and gauche conformations explored by the pentoxy chains of the guest molecule. Similar unusual upfield shifts were observed also in tetrathiophene 4-T_4 in TPP, as compared to the pure dye (Figure 3 and Table 2). Proton MAS NMR spectra of the oligothiophenes at the high spinning speed of 15 kHz exhibit high resolution although in the solid state. The chemical shifts of all the hydrogen species can be recognized, and in particular, the ^1H spectra of pure crystalline

(20) Meille, S. V.; Farina, A.; Bezziccheri, F.; Gallazzi, M. C. *Adv. Mater.* **1994**, *6*, 848–851.

(21) Comotti, A.; Simonutti, R.; Catel, G.; Sozzani, P. *Chem. Mater.* **1999**, *11*, 1476–1483.

(22) Von Ragué Schleyer, P.; Maerker, C.; Dransfeld, A.; Jiao, H.; Van Eikema Hommes, N. J. R. *J. Am. Chem. Soc.* **1996**, *118*, 6317–6318.

(23) Tonelli, A. E. *Macromolecules* **1978**, *11*, 565–567.

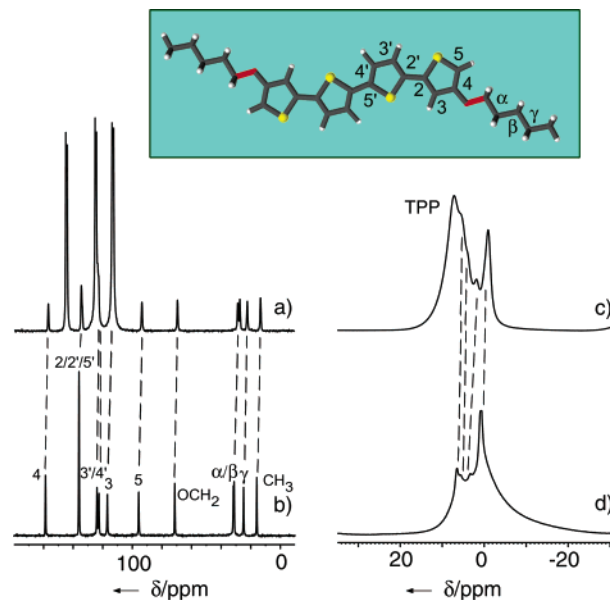


Figure 3. ^{13}C cross-polarization (RAMP-CP) MAS NMR spectra of tetrathiophene (4-T_4) with TPP in the IC (a) and pure dye in the solid state (b). ^1H MAS NMR spectra performed under high spinning speed of 15 kHz of (4-T_4) with TPP in the IC (c) and pure dye in the solid state (d).

4-T_4 and of its IC are compared in Figure 3. The striking change of the guest spectrum profile in the IC evidences a remarkable upfield shift of about 2 ppm, shifting the methyl resonances even to negative values. Nucleus-independent chemical-shift maps give the calculated chemical shifts in the region around the aromatic ring as derived from the electronic current density generated by the main magnetic field. Therefore, the hydrogens of the guest are placed 2.5 Å from the paddle of the host, suggesting the occurrence of a $\text{CH}\cdots\pi$ intermolecular interaction cooperating favorably to the stabilization of the adduct.²⁴ The existence of $\text{CH}\cdots\pi$ interactions is compatible with the size of the 5 Å nanochannels that are present in the crystal structure.

To gain a better insight into the diffusion motions of the guests confined to nanochannels, carbon spin-lattice relaxation times of 4-T_2 in TPP and in the pure form were measured (Table 1). The spin-lattice relaxation times of pure dithiophene are very long (of the order of hundreds of seconds), in agreement with the rigid conformation assumed by the molecules in the trans-planar arrangement of the crystalline state, which prevents the relaxation mechanism due to motion. In addition, the pentoxy side chains are rigid in the pure dye, except for the methyl groups with their intrinsic rotational motion. In the IC the relaxation times drastically drop by 1 or 2 orders of magnitude. The ^{13}C T_1 , on the order of a few seconds for the side chains, are very close to the minimum of the master curve reporting the theoretical T_1 vs τ_c (correlation times). This minimum corresponds to the most efficient relaxation that occurs when the motion frequencies match the observation frequency of the spectrometer (75 MHz).²⁵ On the other hand, the relaxation times of thiophene ring carbons are still on the order of tens of seconds (Table 1), consistent with one of the two opposite possibilities of very fast or very slow regimes of motion

(24) Sozzani, P.; Comotti, A.; Bracco, S.; Simonutti, R. *Chem. Commun.* **2004**, *7*, 768–769.

(25) Goldman, M. *Quantum Description of High-Resolution NMR*; Liquids, International Series of Monographs on Chemistry 15; Clarendon Press: New York, 1993.

Table 2. ^{13}C Solid-State Chemical Shifts (δ/ppm) and ^{13}C Relaxation Times (T_1/s) of 4-T₄ as Pure Dye in the Solid State and as a Guest in the TPP IC (as a reference the chemical shifts of 4-T₄ in CDCl₃ solution is reported)

assign.	^{13}C δ pure 4-T ₄	^{13}C δ TPP/4-T ₄ IC	^{13}C δ ^b 4-T ₄ in CDCl ₃	^{13}C Δ ^c	^{13}C T_1 pure 4-T ₄	^{13}C T_1 TPP/4-T ₄ IC
CH ₃	15.9	13.1	14.0	-2.8	2	2
γ -CH ₂	24.8	22.1	22.4	-2.7	3	2
β -CH ₂	31.3	27.2	28.2	-4.1	4	1.2
α -CH ₂	31.7	28.5	28.9	-3.2	4	0.9
-OCH ₂	71.3	69.5	70.2	-1.8	10	0.7
C5	95.7	93.6	97.5	-2.1	24, 148 ^e	0.2
C3	116.9	113.4 ^a	117.1	-3.5	26, 149 ^e	n.d.
C3',C4' ^d	122.6, 123.9	123.0, 123.7	125.2, 125.3	0.4,-0.2	21, 121 ^e 23, 114 ^e	n.d.
C2,C2',C5' ^d	136.0	134.0, 134.7	136.5, 137.1, 137.7	-2, -1.3	180	13
C4	158.7	157.1	158.8	-1.6	6, 131 ^e	9

^a This peak overlaps the atom signal of the TPP matrix. ^b As a reference the chemical shifts of 4-T₄ in CDCl₃ solution are reported. ^c ^{13}C Δ (ppm) = $\delta(\text{TPP}/4\text{-T}_4 \text{ IC}) - \delta(4\text{-T}_4 \text{ pure})$. ^d The overlapping of the signals prevents specific assignments. ^e Biexponential decay.

both far away from the minimum of the curve. To solve this dichotomy, relaxation times at low temperatures down to 200 K were measured, showing a progressive decrease of the values to a few seconds and therefore indicating that the extreme narrowing regime of motion is explored in the observation temperature range. Such a large change compared to the pure dye in the solid state confirms that a surprisingly fast diffusion motion of the dithiophene rings at the center of the molecule is present when confined to nanochannels. These motion frequencies are much higher than those of the side chains, generating a nanoscopic gyroscope where an extremely mobile central element spins and librates supported on two lateral hinges made by the two aliphatic chains. Considering the geometry of the channels we can conclude that the guest dyes explore anisotropic motions of rotation and libration around the channel axis. A cross-section of about 0.5 nm of the host nanochannels provides soft constraints and an exceptionally higher degree of freedom than the crystal packing in the pure dye in the solid-state phase.

Shorter spin-lattice relaxation times measured at room temperature in TPP/4-T₄ IC (Table 2), still in the fast motion regime, indicate a slower motion of the tetramer with respect to the dimer, consistent with its larger mass. However, the dynamics of the side chains are the same as in the dimer, in the nanosecond correlation time range. The same dynamics of the aliphatic chains are observed in our sample of pure 4-T₄, their arrangement being less ordered than in the crystal packing of the dimer.

Interestingly, in both ICs the relaxation times of C5 carbon follows the behavior of the aliphatic side chains, suggesting that its main relaxation mechanism is due to the side chain motion in close proximity.

TR-EPR. TR-EPR spectra of the laser photoexcited triplets of the two oligothiophenes in glassy toluene and polycrystalline IC are shown in Figures 4 and 5. The spectra are simulated by using the spin Hamiltonian²⁶

$$H = \mu_B \mathbf{S} \cdot \mathbf{g} \cdot \mathbf{B} + \mathbf{S} \cdot \mathbf{D} \cdot \mathbf{S}$$

where the two terms are, respectively, the electron Zeeman interaction and the electron-electron dipolar interaction. \mathbf{D} is the traceless spin-spin dipolar tensor with principal values X ,

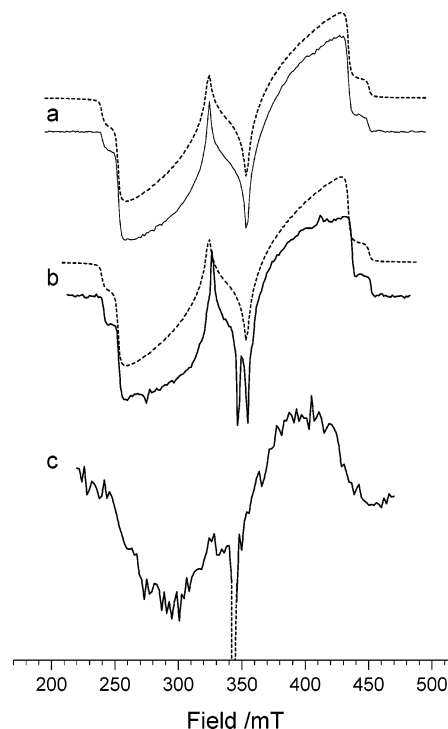


Figure 4. (a) TR-EPR spectrum together with its simulation (dotted lines) of 4-T₂ excited at 355 nm in toluene matrix at 80 K. (b) TR-EPR spectrum together with its simulation (dotted lines) of 4-T₂ excited at 355 nm in the TPP inclusion compound at 80 K and (c) 240 K.

Y , and Z . The principal directions of the \mathbf{g} and \mathbf{D} tensors are considered collinear.

For each orientation of the magnetic field with respect to the system of principal axes of the magnetic tensors we obtain the energies of the three triplet sublevels $M_s = 1, 0, -1$ by complete diagonalization of the secular determinant and calculate the resonance fields relative to the two allowed transitions $-1 \rightarrow 0$ ($B_{\text{res-}}$) and $0 \rightarrow 1$ ($B_{\text{res+}}$). The intensity of each transition depends on the nonequilibrium population difference between the two states, determined by the selective population of the zero-field triplet sublevels via intersystem crossing from the excited singlet. The total spectrum is then calculated as an integral over all the orientations.²⁷

The spectra show six features, each pair of symmetric features at low and high field corresponding to the $B_{\text{res}\pm}$ resonance fields

(26) Weil, J. A.; Bolton, J. R.; Wertz, J. E. *Electron Paramagnetic Resonance. Elementary Theory and Practical Applications*; J. Wiley & Sons: New York, 1994.

(27) Segre, U.; Pasimeni, L.; Ruzzi, M. *Spectrochim. Acta A* **2000**, *56*, 265–271.

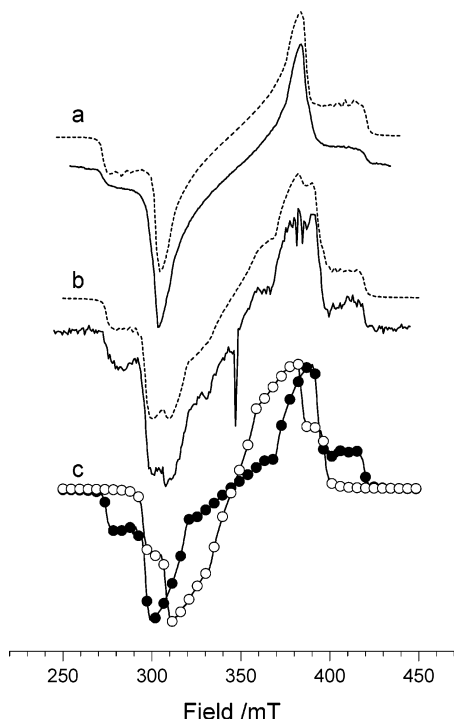


Figure 5. (a) TR-EPR spectrum together with its simulation (dotted lines) of 4-T_4 excited at 420 nm in toluene matrix at 80 K. (b) TR-EPR spectrum together with its simulation (dotted lines) of 4-T_4 excited at 420 nm in the TPP matrix at 80 K. The spectrum has been fitted as a sum of the two species shown in (c): $4\text{-T}_4\text{-A}$, 67% (●), $4\text{-T}_4\text{-B}$, 33% (○).

Table 3. Triplet-State Parameters for 4-T_2 and 4-T_4 in Toluene and as Guests in the TPP IC at 80 K: ZFS Parameters (D , E/cm^{-1}), Sublevel Population Ratio, and g -Tensor Principal Values

	D^a	E^a	$(\rho_x - \rho_y):(\rho_x - \rho_z)$	g_x, g_y, g_z
4-T_2^b	0.098	0.023	-0.77:-0.23	2.009, 2.005, 2.003
4-T_4^c	0.069	0.003	-0.35:+0.65	2.007, 2.005, 2.003
4-T_4^d A (67%)	0.068	0.007	-0.75:+0.25	2.005, 2.009, 2.003
4-T_4^d B (33%)	0.048	0.008	-0.33:+0.67	2.005, 2.007, 2.009

^a The error margin is $\pm 1 \times 10^{-3} \text{ cm}^{-1}$. ^b Toluene and IC. ^c Toluene matrix. ^d TPP IC.

when the magnetic field is aligned with one of the principal axes, ZYX/XYZ . Due to nonequilibrium spin populations the spectra are spin polarized with a polarization pattern EEA/EAA (E = emission, A = absorption). In Table 3 we report the ZFS parameters D and E obtained by the simulations, where $D = -(3/2)Z$ and $E = (1/2)(Y - X)$, and the relative spin populations P_x, P_y, P_z .

The E parameter indicates a nonaxial symmetry of the electron spin distribution. The TR-EPR spectra in IC are weaker than in the glassy toluene matrix, despite the far larger concentration of the dye in the host channels of the IC. A less efficient pathway to the triplet state by ISC can depend on many factors. In particular, chromophores organized in nanochannels show improved photoemission properties due to their organization in linear arrays^{28,29} with a reduction of the lifetime of the excited singlets.

The experimental and simulated TR-EPR spectra of 4-T_2 in toluene and in IC at 80 K are reported in Figure 4a,b. The spectra

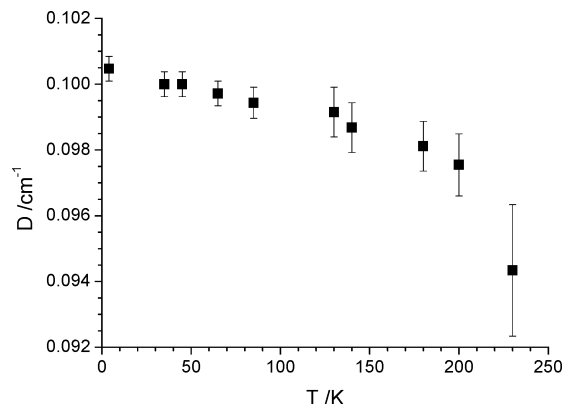


Figure 6. D -value as function of the temperature for 4-T_2 in TPP.

and the parameters (Table 3) in the two matrices are very similar. The central narrow emissive line in IC can be attributed to the formation of a polarized radical associated with photodegradation of the material.³⁰ We conclude that at low temperature the triplet state of 4-T_2 has the same electronic and geometrical structure in frozen solution and in TPP channels, despite the far different properties of the two environments. This indicates that the TPP matrix does not exert severe steric constraints on the dithiophene core, as already shown by the fast reorientational dynamics highlighted by the NMR results.

The D value of 4-T_2 agrees with that measured for the end-capped dithiophene and with the calculated value for the planar unsubstituted dithiophene.^{30,31} Therefore, 4-T_2 in the channels of TPP has the same planar conformation in both the singlet ground state, as found by NMR, and the excited triplet state.

The relative sublevel populations have been determined by considering a positive value for D . This sign cannot be obtained from the spectra but can be estimated by calculation of the ZFS parameters and by experimental determination of the symmetry of the spin distribution. The calculated D value for the planar unsubstituted dithiophene is positive.³¹ An unpublished TR-EPR study by some of the present authors on this dye in a partially oriented matrix shows that the Y and Z principal axes of the triplet are, respectively, parallel to the inter-ring C–C bond and perpendicular to the molecular plane. A positive sign of the D parameter is associated with such disklike triplet spin distribution.

In IC D decreases slightly on increasing the temperature, as shown in Figure 6, with a larger decrease for $T > 200$ K. The spectral line shape does not change up to 200 K. This is not surprising since only fast and wide molecular reorientations could average out the large magnetic anisotropies of the fine electron–electron interaction. A fast reorientation of the molecule about the axis of the channel, nearly parallel to the Y axis of the ZFS tensor, would average the X and Z principal values, giving rise to an axial spectrum with principal values X', Y, Z' , where $X' = Z' = (X + Z)/2 = -Y/2$. Due to the ZFS anisotropy, in this time scale a “fast” motion showing effects on the line shape should have a reorientation rate near 10^{10} s^{-1} .

The dramatic modification of the line shape in the temperature range 200–240 K can be attributed to fast motion of this kind. The width of the spectrum is strongly reduced, and the features

(28) Botta, C.; Trevignanti, R.; Bongiovanni, G.; Mura, A.; Tubino, R. *Synth. Met.* **1999**, *101*, 565–568.

(29) Bongiovanni, G.; Botta, C.; Di Silvestro, G.; Loi, M. A.; Mura, A.; Tubino, R. *Chem. Phys. Lett.* **2001**, *345*, 386–394.

(30) Bennati, M.; Grupp, A.; Mehring, M.; Baeuerle, P. *J. Phys. Chem.* **1996**, *100*, 2849–2853.

(31) Bennati, M.; Nemeth, K.; Surjan, P. R.; Mehring, M. *J. Chem. Phys.* **1996**, *105*, 4441–4447.

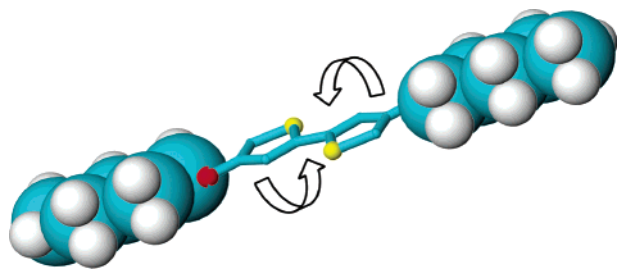


Figure 7. Cartoon of the arrangement of the dithiophene π core hanging between the two bulky alkoxy groups in TPP channels and rotating rapidly in comparison to the lateral chains.

are broadened. At 240 K the shape and width of the spectrum correspond approximately to $\langle D \rangle = -(3/2)Y$ and $\langle E \rangle = 0$, as expected for an averaged spectrum, see Figure 4c. The broad line widths show that the motional narrowing limit is not yet reached, but we can conclude that the reorientation rate in the channel at 240 K is now close to the value of 10^{10} s^{-1} indicated above. This value agrees with the NMR relaxation times that show a regime of motion in the extreme narrowing limit above 200 K. It is worth noting that the NMR results also suggest that the pentoxy chains in bulky gauche conformations are far less mobile with respect to the thiophene rings. It is likely that the conformation and dynamics of the chains are not affected by the electronic state of the π electrons on the thiophene rings. Comparing the rate of libration of the two rings (ca. 1–2 GHz at $T = 240 \text{ K}$) with that of the two chains (ca. 100 MHz at room temperature), the motion of the guest should be described as a slow reorientation of the aliphatic chains in the host channels accompanied by a very fast intramolecular rotation of the central rings (Figure 7). The joint between the pentoxy chains and the thiophene rings is the $\text{C}_4\text{--O}$ bond. It must undergo a relevant friction as the mesomeric effects give a partial double-bond character. Instead, the flexible single bonds O--CH_2 allow an almost free rotation since a particularly low potential barrier is expected in this case.³²

The unusual motional behavior of the guest in the nanochannels, as derived by EPR, is in agreement with the NMR results. The surprisingly high mobility of the core part of the molecule with respect to the aliphatic chains recalls the nanoscopic gyroscope described by Garcia-Garibay in crystalline molecular compounds.³³

The dynamics of the guest at lower temperatures (4–100 K) has been studied by echo-EPR.^{20,34} At temperatures as low as 80 K the dye in IC is librating fast around its long axis with a small angle. The weak temperature dependence of D in the range 4–200 K reported in Figure 6 could be attributed to variation of the amplitude of this libration angle as a consequence of the slightly increasing diameter of the channel. Over 200 K a different motion regime appears, as indicated by the sudden jump of the value of D and by the change in TR-EPR spectral profile.

The photoexcited triplet of 4- T_4 has been studied in IC and glassy toluene in the temperature range 4–80 K. In Figure 5a and b we report, respectively, the experimental and simulated spectra in toluene and in IC at 80 K. The parameters in toluene reported in Table 3 are very close to those of end-capped tetrathienophene in frozen solution.³⁰ Reduction of the ZFS parameters with respect to 4- T_2 is a consequence of the extended π conjugation over the four thiophene rings. The E parameter is very small, indicating a quasi-axial symmetry of the ZFS tensor. The spectra in IC (Figure 5b) are different with respect to those in frozen toluene. They show two triplet species, A and B, with relative intensities of ca. 2:1. In Figure 5c the separate simulation traces for the two species are reported. They have similar relative populations of the triplet sublevels, but triplet A has a D value very close to that in toluene, whereas triplet B shows a much lower D value (Table 3).

Oligothiophenes can have different conformations depending on the matrices due to the easiness of the internal rotations around interannular bonds. In solution more conformations with similar energy become accessible by increasing the number of linked thiophene rings. On the other hand, the T_4 oligomers prefer an almost planar conformation in rigid matrices, similar to that in the pure crystalline dye.^{14c,35} The ZFS parameter D of the triplet of 4- T_4 in toluene and of triplet A in IC is very similar to that calculated for a planar geometry,³¹ and so we assume that these two triplets are planar. The difference between their E values can be attributed to the presence of different cis–trans planar isomers in the two phases.³⁰ The D value of the B triplet is sensibly smaller. We checked the dependence of the D values on the twisting angle around the central bond of the tetramer using a simple semiempirical model.³⁶ The results of the calculations show that for 4- T_4 the D parameter decreases on increasing the twisting angle. Therefore, we assign species B to a triplet state in a strongly nonplanar twisted conformation.

Our results can be compared with those found by optical spectroscopies for the quinquethiophene molecule included in the channels of another organic host, peryhydrotriphenylene (PHTP).^{28,37} The emission spectra of that IC have been interpreted as due to two different emitting conformers of the guest, characterized by different degrees of inter-ring twisting. The authors assumed that specific interactions with the host in IC stabilize twisted conformers, as for 4- T_4 in TPP.

Several authors have studied by NMR the behavior of small molecules hosted in TPP, as perdeuterated benzene,³⁸ perdeuterated *o*- and *p*-xilenes,³⁹ perdeuterated 1,3,5-trioxane,⁴⁰ and others, in some cases in a wide range of temperatures. The main conclusions of these works are that the guests in the TPP channels perform a number of different intra- and intermolecular motions. Their fast rates show that small and unsubstituted molecules with a molecular mass of less than 100 are singularly unhindered in TPP. In some cases the dynamics of this motion has been fully determined, as for 1,3,5-trioxane.⁴⁰ The reorienta-

(32) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953.

(33) (a) Godinez, C. E.; Zepeda, G.; Garcia-Garibay, M. A. *J. Am. Chem. Soc.* **2002**, *124*, 4701–4707. (b) Schalley, C. A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1513–1515.

(34) (a) Salikhov, K. M.; Tsvetkov, Yu. D. Electron Spin–Echo Studies of Spin–Spin Interactions in Solids. In *Time Domain Electron Spin Resonance*; Kevan, L., Schwartz, R. N., Eds.; Wiley-Interscience: New York, 1979; pp 231–277. (b) Brustolon, M.; Barbon, A. EPR of Free Radicals in Solids: Trends in Methods and Applications. In *Progress in Theoretical Chemistry and Physics*; Lund, A., Shiotani, M., Eds.; Kluwer Academic Publishers: Dordrecht, 2003; Vol. 10.

(35) Di Césare, N.; Belletête, M.; Garcia, E. R.; Leclerc, M.; Durocher, G. *J. Phys. Chem. A* **1999**, *103*, 3864–3875.

(36) Barbon, A.; Bortolus, M.; Brustolon, M.; Maniero, A. L. *Phys. Chem. Chem. Phys.* **2004**, *6*, 2396–2402.

(37) Bongiovanni, G.; Botta, C.; Brédas, J. L.; Cornil, J.; Ferro, D. R.; Mura, A.; Piaggi, A.; Tubino, R. *Chem. Phys. Lett.* **1997**, *278*, 146–153.

(38) Rice, D. M.; Witebort, R. J.; Griffin, R. G.; Meirovitch, E.; Stimson, E. R.; Meinwald, Y. C.; Freed, J. H.; Scheraga, H. A. *J. Am. Chem. Soc.* **1981**, *103*, 7707–7710.

(39) Meirovitch, E.; Belsky, I. *J. Phys. Chem.* **1984**, *88*, 4308–4315.

(40) Liebelt, A.; Detken, A.; Mueller, K. *J. Phys. Chem. B* **2002**, *106*, 7781–7790.

tion rate of this guest between 200 and 240 K varies in the range from 5×10^9 to $1.7 \times 10^{10} \text{ s}^{-1}$. The intramolecular reorientation of the dithiophene core in 4-T_2 in the same temperature interval, according to our results, has the same rate. This comparison leads to the conclusion that the motion of the planar dithiophene core is determined only by the cylindrical shape of the inner surface of TPP channel, and the constraints of the bonds with the pentoxy chains are negligible. The side chains keep the planar core as hanging in the space, minimizing its interactions with the host and allowing a fast reorientation motion (Figure 7). Another consequence of this intermolecular configuration is the long lifetime of the triplet state, allowing observation of a TR-EPR spectrum in the IC at the surprisingly high temperature of 240 K.

According to this model the motion regime of the guest appearing in the temperature interval 200–240 K is characterized by the onset of a “fast” jump of the dithiophene core between the three potential wells generated by the aromatic paddles at each cross-section of the nanochannel. The fast motions of small amplitude at lower temperatures are due to librations of the dithiophene cores inside one of the potential wells.

In the case of 4-T_4 , the conformation of the tetrathiophene core is less rigid and the interactions with the host are larger than for 4-T_2 . As a consequence, the triplet decays too fast to observe a TR-EPR spectrum for $T > 80 \text{ K}$. The twisted conformers observed in IC are probably stabilized by interaction of the two halves of the tetramer with two different wells along the channel.

Conclusions

Oligothiophenes as aligned in nanochannels of crystalline inclusion compounds perform intra- and intermolecular motions in both the ground and the excited triplet state. By the combined approach of high spinning speed MAS NMR and TR-EPR spectroscopies, we could understand the intriguing mechanism of motion of 4,4'-dipentoxy-2,2'-dithiophene, which involves the alkoxy side chains and the dithiophene core. The side chains swell to form gauche-rich and bulky conformations that fill the

channel space, and the close contact $\text{CH}\cdots\pi$ interactions with the aromatic channel walls reduce the reorientation motion. Thus, the dithiophene core, planar in both the ground and the excited triplet states, undergoes reduced interactions with the nanochannel being appended to the lateral plugs and gaining much larger freedom. Considering the time scale characteristic of the TR-EPR line shape, we can conclude that at temperatures above 200 K the planar core of the molecule reorients at the surprisingly fast rate of 10^{10} s^{-1} as a rotor spinning about the flexible single O–CH₂ bonds. Thanks to the reduced interactions of the π -electron distribution in the nanochannel, the dithiophene photoexcited triplet state can be observed at far higher temperatures than usual.

Tetrathiophene shows a new conformation in the nanochannels with the two halves of the molecule twisted around the central bond.

The present study is a contribution to the intense activity pursued to modulate the conformational arrangements of polyconjugated molecules organized in nanostructured materials with the technological purpose of obtaining new photoactive and photoresponsive materials. We have shown that oligothiophene molecules, widely studied for a number of physical applications, could be engineered in such an accurate way as to achieve local dynamics in the regime of liquids despite being arranged in high-melting crystals.

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Supporting Information Available: DSC traces of pure 4-T_2 in the crystalline state and TPP/ 4-T_2 . This material is available free of charge via the Internet at <http://pubs.acs.org>.

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