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Reduction of Parasexiphenyl with Organometallic Compounds in THF: Resonance Raman Scattering and Vibrational Analysis

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A systematic characterization of chemically reduced Parasexiphenyl ($\varnothing_6$) by radical anions such as biphenyl and naphthylsodium or potassium in tetrahydrofuran (THF) is presented, and the vibrational properties of this phenylene oligomer have been studied. Resonance Raman scattering coupled with a theoretical vibrational analysis leads to the conclusion that a quinoid structure takes place in the sexiphenyl molecules upon reduction with an enhancement of the external phenyl polarizability as compared to neutral molecules. However, this enhancement as well as the quinoid character of ($\varnothing_6$) is strongly dependent on the presence or absence of THF.

I. Introduction

The electronic structure and the vibrational properties of conducting polymers have been the subject of intense research activity during the past decade.[1] Much work on polythiophene and derivatives, poly(phenylenevinylene), polyaniline, and polyphenylene (PPP) has been done in different groups[2,3] and our laboratory[4] since the first publication on PPP.[5] Among experimental methods, resonance Raman scattering (RRS) was shown to be quite useful to characterize self-localized excitations, such as polarons or bipolarons, which induce upon doping structure transformation at the molecular level in nondegenerate ground state polymers.[6] It was also demonstrated that the use of oligomers as model compounds is crucial to get reliable assignments for vibrational IR and Raman modes.[3] Some preliminary results of calculations using a dynamical model based on valence force field applied to p-doped, i.e., oxidized, parasexiphenyl were already published.[7] They showed that a quinoid structure has to be postulated to account for the change in the vibrational spectra of such an oligomer. However, this work was carried out with the oxidant being in the gas phase, the oxidation reaction leading to some deficiency on doped $\varnothing_6$ molecules. In the present work, we attempt to see whether reduction, consisting in electron enrichment of $\varnothing_6$ molecules, induces the same change on their vibrational properties and if a polar molecule like THF plays a role in their vibrational spectra, i.e., in electronic densities of chemical bonds. In this report, we will restrict ourselves to the $\varnothing_6$ dianion.

II. Experimental Section

A. Materials. Parasexiphenyl ($\varnothing_6$) was synthesized according to the already published procedure,[8] which involves the electrocoupling of monobromoterphenyl. The produced oligomer was then characterized by spectroscopic methods[9] after purification. Solutions of biphenyl and naphthylsodium or potassium in tetrahydrofuran (THF) were obtained using a vacuum line and break seal technique.[10] Their concentration was about 4×10^{-2} mol L^{-1}. They were collected in glass ampules sealed under vacuum. The $\varnothing_6$ doping was carried out in a glass cell specially designed to be installed on spectrometers. This cell allowed the $\varnothing_6$ powder to be pretty easily either THF dried by liquid nitrogen or kept in suspension in THF. After thorough washings in situ by cryogenic transfer of THF, the $\varnothing_6$ powder showed a golden black color for heavily reduced samples. Elemental analysis indicate 0.5−0.6 alkali ion per $\varnothing_6$ molecule, and EPR showed a very low susceptibility, in the range 10^{-3} spins per molecule, consistent with diamagnetic dianions.

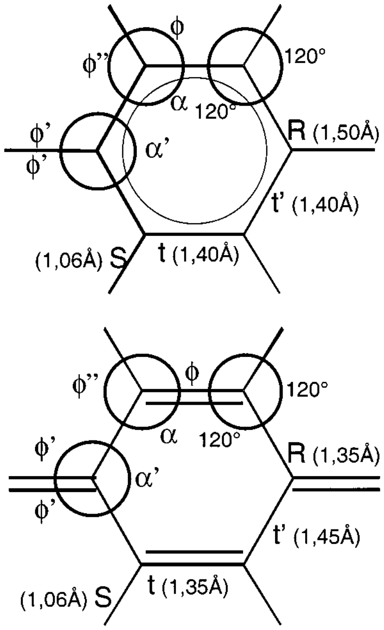

Figure 1. Internal coordinates used in our calculations for neutral and doped $\varnothing_6$.

B. Resonance Raman Scattering. Raman spectra of samples were obtained in the visible range with excitation lines at 457.9, 514.5, and 676.4 nm (argon and krypton lasers) on a multichannel Jobin-Yvon T64000 spectrometer connected to a cooled CCD detector, and the laser beam power was limited to 10 mW in order to avoid irreversible damage on the doped samples. For the near-IR excitation line at 1064 nm, a FT Raman Bruker RFS100 was used. A 90° scattering geometry allowed collection

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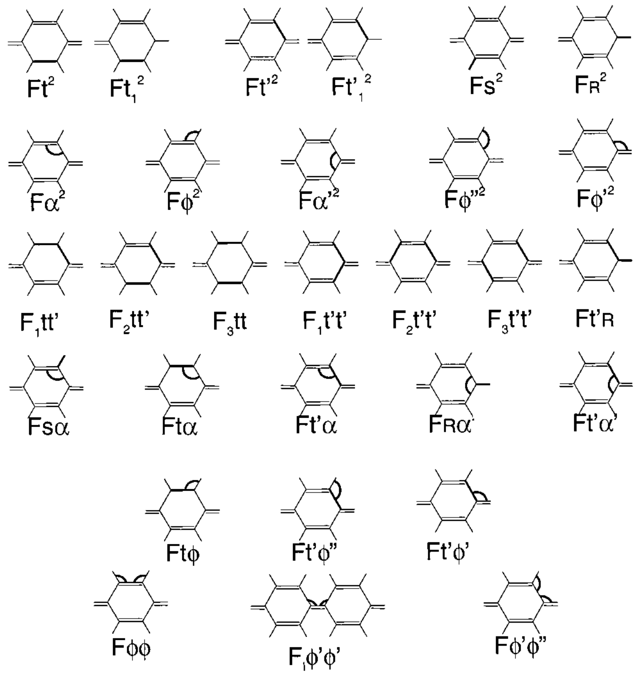

Figure 2. Set of doped $\varnothing_6$ parameters, 29 force constants.

of the signal, except for FT Raman where a backscattering configuration was imposed. In both cases, the spectral resolution was 4 cm^{-1}.

III. Calculations

Calculations of the force field and frequencies were carried out on the basis of the dynamic matrix.[4] Since $\varnothing_6$ possesses a center of symmetry, there is mutual exclusion of the activity of infrared and Raman modes. The calculations require the knowledge of geometrical parameters such as bond angles and bond lengths (Figure 1), which were taken from already published data.[7] However, $\varnothing_6$ molecules, either neutral or doped, were considered to be planar, and only in-plane vibrations were calculated. Figure 2 collects the force constants used for the simulation of doped $\varnothing_6$ spectra (dianionic species[11]). It must be noted that, for neutral $\varnothing_6$, the force constants t_1, t'_1, and t' were not discriminated from t, reducing the number of force constants to 21 as compared to the 29 used in doped $\varnothing_6$.

IV. Results and Discussion

In Figure 3, we present Raman spectra of dried, THF-free, $\varnothing_6$ heavily doped with naphthylsodium, at different excitation wavelengths (curves a–d), as well as the Raman spectrum of neutral (curve e) recorded with $\lambda_L = 1064$ nm for comparison. Several observations can be made in view of these spectra.

(i) Reduction of $\varnothing_6$ molecules induces changes in species symmetry and therefore changes in Raman band activity. It is thus not surprising to observe additional bands in dianionic $\varnothing_6$ spectra, such as those peaked at 1312 and 1338 cm^{-1}.

(ii) The mode located near 1220 cm^{-1} in neutral $\varnothing_6$ is almost not modified in frequency and intensity whatever λ_L, in contrast with those near 1280 and 1600 cm^{-1}.

(iii) In fact, the 1277 cm^{-1} disappears whatever λ_L, whereas a new mode at 1287 cm^{-1} shows up for $\lambda_L = 676$ and 1064 nm. If present, its intensity is weak for $\lambda_L = 457.9$ and 514.5 nm.

(iv) The mode peaked at 1592 cm^{-1} in neutral $\varnothing_6$ shifts slightly downward (1590 and 1588 cm^{-1} in curves a and b for $\lambda_L = 457.9$ and 514.5 nm, respectively) and splits into two

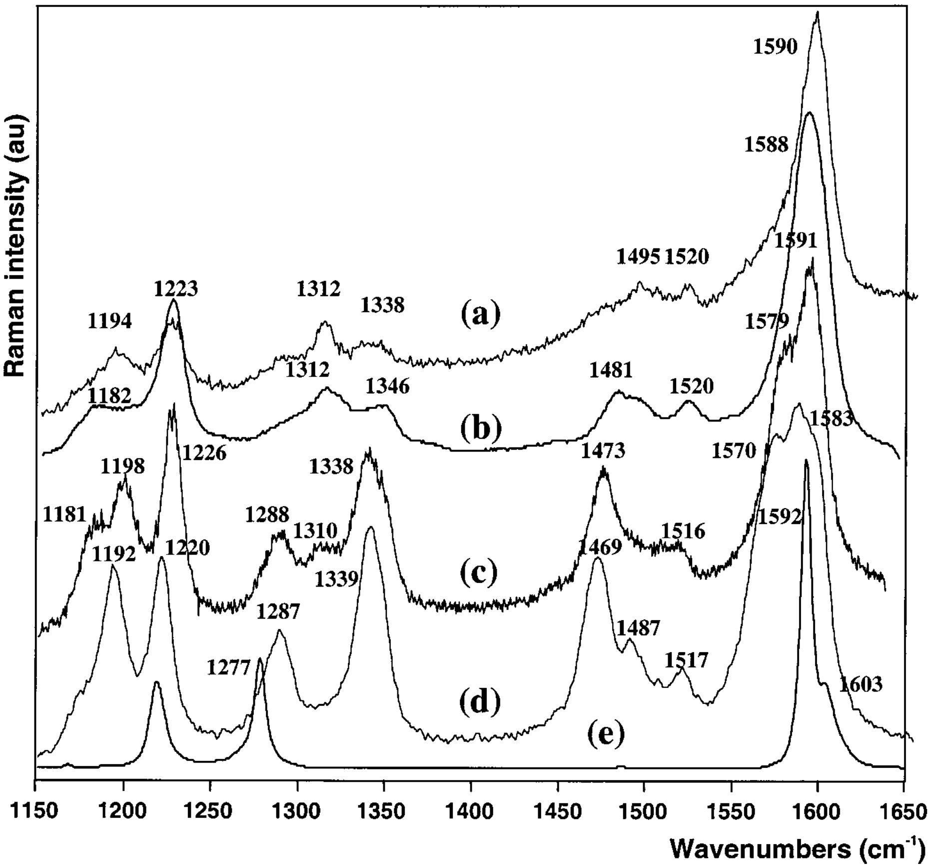

Figure 3. Raman spectra of doped sexiphenyl (a–d) in absence of THF and neutral sexiphenyl (e) with different wavelengths: (a) 475; (b) 514; (c) 676; (d,e) 1064 nm. The laser power is set at 10 mW and the spectral resolution is 4 cm^{-1}.

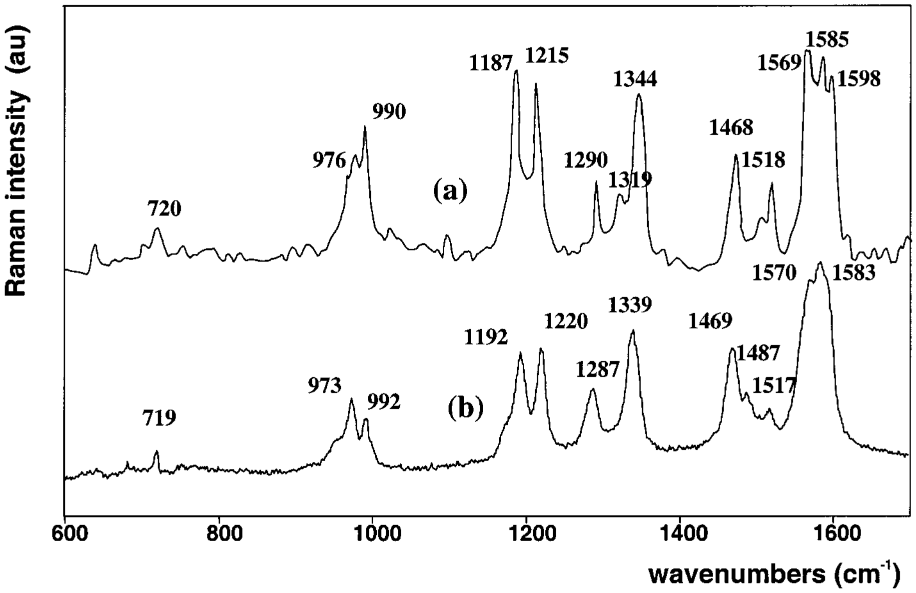

Figure 4. FT Raman spectra (1064 nm) of sexiphenyl doped with naphthylsodium: (a) with THF; (b) dry. The laser power is set at 10 mW and the spectral resolution is 4 cm^{-1}.

components for excitation wavelengths in the red range (1583 and 1570 cm^{-1} for $\lambda_L = 1064$ nm, curve d).

(v) Additional modes, whose intensities depend strongly on the excitation wavelengths, are observed in the intermediate frequency range, at 1312 and 1338 cm^{-1} for $\lambda_L = 457.9$ nm and at 1339 cm^{-1} for $\lambda_L = 1064$ nm, for example.

According to Furukawa et al.,[2] the optical absorption attributed to dianions should be located at 1170 nm; therefore, a resonance Raman scattering effect is expected when the heavily doped $\varnothing_6$ is illuminated with a 1064 nm excitation line. This is indeed observed in Figure 3 where a clean spectrum is obtained at this excitation wavelength denoting a high dianion concentration in this sample. With other excitation lines, spectra are not as easy to obtain. This is the signature of a low radical anion concentration in the sample, since resonance Raman effects should occur with a 514.5 nm excitation wavelength[7] to reveal those species.

Figure 4 shows resonance Raman spectra of heavily doped $\varnothing_6$ with naphthylsodium obtained with an excitation wavelength at 1064 nm. Some differences arise from the comparison of either THF wet or cryogenically dried samples. Small shifts are evident (modes close to 975−990 cm^{-1}, 1190−1220 cm^{-1}, 1290−1345 cm^{-1}) as well as some changes of intensity of those modes. However, the striking feature is the occurrence of new modes coming from the separation of the former ones essentially at 1569, 1585, 1598 cm^{-1} in the THF wet sample instead of 1570 and 1583 cm^{-1} in the dried one.

The assignments of the main bands present in Raman spectra of neutral and doped $\varnothing_6$ are collected in Table 1. The shift observed on vibrational modes of doped $\varnothing_6$, compared to modes of neutral sexiphenyl, may be accounted for by changes in force constants used of some chemical bonds. It is thus important to know which bonds are modified upon doping. Following the method now well established, the calculations provide a set of force constants for the neutral $\varnothing_6$, due to the good accuracy of FT Raman spectra (Figure 5), gathered in Table 2. To fit the modes present in Raman spectra of doped $\varnothing_6$, it was necessary to separate the two external benzene rings with force constants Ft_1^2 and Ft'^2_1 (see Experimental Section). The set of force constants thus obtained is given in Table 2. It is confirmed that reduction induces a tendency to quinoid structure since Ft^2 is enhanced going from 6.21 to 6.77 mdyn Å^{-1} for internal rings and 6.40 mdyn Å^{-1} for the two external rings. Ft'^2 decreases from 6.21 to 5.68 mdyn Å^{-1} for internal rings and 5.76 mdyn Å^{-1} for the external rings. FR^2 increases from 5.19 to 6.23 mdyn Å^{-1}. We observed differences between force constants of external and internal rings in the range of 5% (Ft'^2_1 and Ft'^2, Ft_1^2 and Ft^2).

TABLE 1: Experimental and Calculated Frequencies (cm^{-1}) of In-Plane Raman Modes A_g in Neutral and Doped $\varnothing_6$ with Their Assignments with Reference to Wilson Notation

neutral			doped		
benzene[a]	expt	calcd	benzene[a]	expt	calcd
ν_{8a}	1592	1592	ν_{8a}	1583	1583
			ν_{8a}	1570	1569
ν_{19a}	1486	1483	ν_{19a}	1517	1516
			ν_{19a}	1487	1487
			ν_{19a}	1469	1470
	1277	1279		1287	1287
ν_{9a}	1218	1183	ν_{9a}	1220	1219
			ν_{9a}	1192	1195
			ν_{9a}	1173	1174
ν_{18a}	1041	1038			
ν_{18a}	1033	1032			
ν_2,ν_{12}	1003	1002	ν_2,ν_{12}	992	992
ν_2,ν_{12}	994	996	ν_2,ν_{12}	973	973
			ν_2,ν_{12}	954	953
ν_{6a}	793	791	ν_{6a}	719	721
ν_{6a}	738	739			

[a] Corresponding benzene modes in Wilson notation.

The quinoid structure is not complete since the FR^2 value ranges between that of Ft^2 and that found for the vinylic −CH=CH− in PPV.[4] Furthermore, it is to be noted that the quinoid character in dianionic $\varnothing_6$ is reinforced as compared to what is observed in oxidized $\varnothing_6$ as mentioned in Table 3 where are collected values of force constants Ft^2, Ft'^2, and FR^2 for $\varnothing_6$ either reduced or oxidized with AsF_5 and for PPV reduced with alkali metal vapor.[4] This result should be connected to the different behavior of PPP electrochemically reduced or oxidized, which shows asymmetry in terms of magnetic susceptibility evolution between reduction and oxidation.[12] Altogether, calculations on $\varnothing_6$ dianion shed light on the experimental results. The inter-ring vibration is reinforced, which leads to an upshift

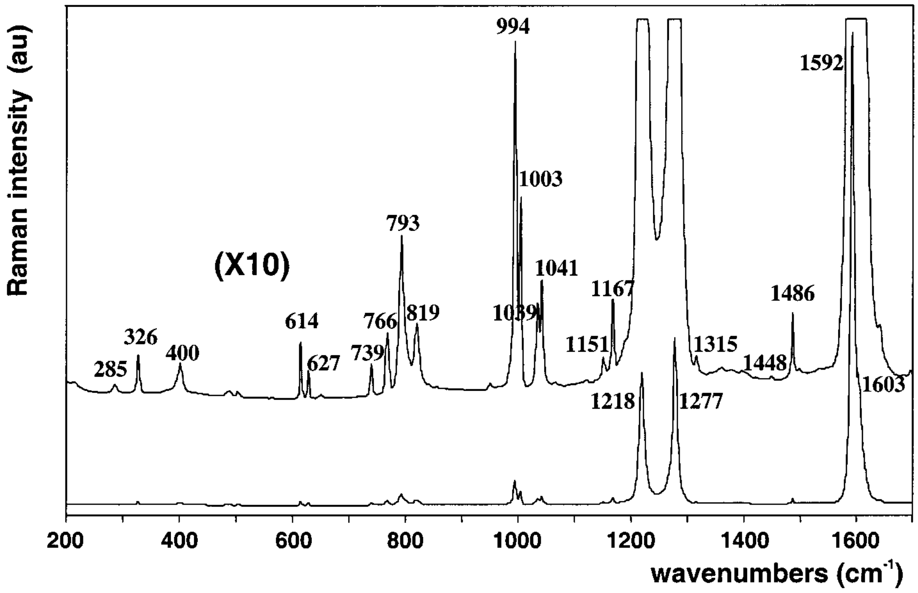

Figure 5. Raman spectra of neutral sexiphenyl with an excitation wavelength at 1064 nm from 200 to 1700 cm^{-1}. The laser power is 100 mW and the spectral resolution is 4 cm^{-1}.

TABLE 2: Values of Force Constant Used for the Calculation of Neutral and Doped $\varnothing_6$^{a}

type	Ft^2	Ft'^2	FR^2	Ft_1^2	$Ft_1'^2$	F_1tt'	F_2tt'	$F_1t't'$	$F_2t't'$	$F_3t't'$	F_3tt	$Fs\alpha$	$Ft\phi$	$F\phi\phi$	$F\phi'^2$
neutral	6.208	6.208	5.194	6.208	6.208	0.854	−0.312	0.854	−0.312	0.330	0.330	−0.126	0.161	0.019	0.634
doped	6.766	5.680	6.229	6.404	5.758	0.854	−0.283	0.854	−0.312	0.330	0.372	−0.126	0.161	0.019	0.634

type	$Ft'\alpha'$	$Ft'\phi'$	$Ft'R$	$FR\alpha'$	$Ft\alpha$	$F_I\phi'\phi'$	Fs^2	$F\alpha^2$	$F\phi^2$	$F\alpha'^2$	$F\phi''^2$	$Ft'\phi$	$F\phi'\phi''$	$Ft'\alpha$
neutral	0.161	0.128	0.359	−0.500	0.112	0.071	5.087	1.041	0.498	0.883	0.518	0.161	0.070	0.112
doped	0.173	0.128	0.373	−0.731	0.112	0.071	5.087	1.130	0.518	0.533	0.518	0.180	0.070	0.160

[a] Interaction units: bond−bond, mdyn Å^{-1}; bond−angle, mdyn rad^{-1}; angle−angle, mdyn Å rad^{-2}.

TABLE 3: Values of Main Force Constant for Neutral, n-Doped Either Dry or Wet with THF and p-Doped $\varnothing_6$ and for n-Doped PPV^a

		this work: $\varnothing_6^{(2-)}$			
type	neutral $\varnothing_6$	"dry"	"wet with THF"	p-doped[7] $\varnothing_6^{(2+)}$	n-doped[4] PPV
Ft^2	6.21	6.77	6.52	6.51	6.50
Ft'^2	6.21	5.68	5.70	5.84	5.88
Ft_1^2	6.21	6.40	6.24	6.51	6.50
$Ft'_1{}^2$	6.21	5.76	5.87	5.84	5.88
FR^2	5.19	6.23	5.88	5.74	5.55

[a] Interaction units: bond−bond, mdyn Å^{-1}; bond−angle, mdyn rad^{-1}; angle−angle, mdyn Å rad^{-2}.

of the frequency of the corresponding mode, and the polarizability of the two external rings is enhanced.

Concerning the presence or absence of THF, which causes the 1600 cm^{-1} mode splitting, it is well-known that sodium or potassium cations can easily be solvated by these polar molecules. In this case, calculations were performed following the same model as for dianions, and the new set of force constants can be visualized in Table 3 in comparison with those of neutral $\varnothing_6$ and reduced $\varnothing_6$ (dianion). It is interesting to note that the quinoid character of $\varnothing_6$ dianion is attenuated by the presence of a solvent molecule (like THF).

The vibrational modes of $\varnothing_6$ with THF are identical to those without THF, the dry species, except the three modes located at higher wavenumbers 1598, 1585, and 1569 cm^{-1} (calculated at 1597, 1585, and 1568 cm^{-1}, Figure 6). The intense mode of neutral $\varnothing_6$ close to 1600 cm^{-1} comes from in-phase vibration of the six benzene rings in this molecule, whereas here, three modes of $^1/_3$ intensity each appear. These new three modes correspond to three ring couples. The two external rings show a decrease of the quinoid character according to the $Ft'_1{}^2$ and Ft_1^2 values, as a consequence of a weaker localization of charges on external rings.

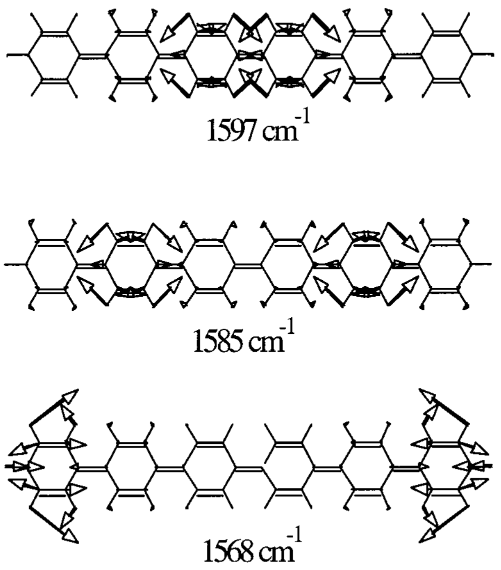

Figure 6. A_g vibrational modes in doped sexiphenyl coming from benzene ν_{1a}.

V. Conclusion

Comparison of the force constant values shows that a quinoid character is induced in n-doped $\varnothing_6$ as was expected, but it is higher at the center of the molecule, in agreement with Hückel calculations simply performed on $\varnothing_6$ bianion.[13] Moreover, according to these data and corroborated by vibrational analysis, it seems that the presence of solvent molecules, like THF, induces a tendency to smooth out the quinoid structure over the whole molecule. This is the signature of a more delocalized electronic density.

Furthermore, it is interesting to note that n-doped $\varnothing_6$ in the presence of THF exhibits force constant values fairly close to those of either p-doped $\varnothing_6$ or n-doped PPV, whereas n-doped $\varnothing_6$ in the dry state is concerned by a pretty large enhancement of its quinoid character.

The exact role of THF molecules in this process is not clear so far. Do they act as a screen toward the electric charge of cations and if so how do they induce a modification of the electronic density all over the $\varnothing_6$ molecule. The answer to these questions is not straightforward and it is necessary to make sure that no crystalline phase modification of $\varnothing_6$ in the presence of THF occurs.

References and Notes

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