Oligothiénylenevinylene Polarons and Bipolarons Confined Between Hostile Electron Accepting Perchlorotriphenylmethyl Radicals

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ABSTRACT: A detailed analysis of positive charged species generated on a series of thienylenevinylene (nTV) wires terminally substituted with two perchlorotriphenylmethyl (•PTM) radical acceptors groups, •PTM-nTV-PTM• (n = 2-7), has been carried out. Motivated by the counterintuitively key role played by holes in the nTV bridges on the operating mechanism of electron transfer in their radical-anion mixed-valence derivatives, a wide combination of experimental and theoretical techniques have been used, aiming to get further insights on their structural location. As a result, contributions of the •PTM units for the stabilization of the radical cations and hole localization, particularly in the case of the shortest molecular wire, have been probed. In this sense, the formation of a quinoidal ring segments, resulted from the coupling of the unpaired electron of the •PTM radical site with the ones generated along the nTV chains, has been found. Additionally, open-shell dications, described by the recovery of the central aromaticity and two terminal quinoidal segments, assisted by the •PTM units, have been detected.

INTRODUCTION

Molecular wires are examples of through-bond charge transport phenomena, permitting the electron flow to occur between the different elements of a molecular electronic device.¹ Among the organic molecular wires, aromatic oligothiophenes (nT) are common building blocks widely used in the field of molecular electronics. A related family of compounds, thienylenevinylene derivatives (i.e., nTV) are considered even better wires. Two main advantages can be enumerated for nTV compared to nT: *i*) The introduction of vinylene units between consecutive thiophenes minimizes the electronically perturbing torsional angle among the rings.^{2,3} Thus, the increase of the degree of coplanarity implies a reduction of the overall thiophene aromatic character and a further extension of the conjugation length. Concomitantly, a series of electronic properties, such as electron and charge transmission along the nTV molecular wire, are benefited;⁴⁻⁸ and *ii*) The release of steric congestion by vinylene insertion allows a more versatile degree of functionalization at the 3,4 positions of the thiophenes units, pursuing the increment of processability without sacrificing electronic features.^{9,10} Additionally, just as their parent nT compounds, substitution at the terminal 2,2' positions of the thiophenes with electronically active groups represents a common method to extensively tune the electronic properties of the nTV.¹¹ Combination of these advantages and terminal substitution has led nTV derivatives to become excellent molecular wires, acting as efficient conducting bridges between terminal redox units (i.e. with electron donor or acceptor character).¹²⁻¹⁵

In a recent work,¹⁶ a series of six nTV molecular wires terminally substituted with two perchlorotriphenylmethyl (•PTM) radical acceptors, abbreviated as •PTM-nTV-PTM• (Chart 1a) was studied in the context of the mixed-valence (MV) behavior generated by partial reduction to their radical-anion species, [PTM-nTV-PTM]^{•-} (see transient polaron in Scheme

1). Operating mechanisms for the intramolecular electron transfer/transport between the terminal •PTM radical and PTM⁻ anion units in the ground state through the nTV wire of such mixed-valence derivatives, were determined. Unexpectedly, holes on the nTV bridges played a key role assisting the transport of electrons (see Scheme 1).

Chart 1. Chemical structures of the studied compounds.

(a) •PTM-nTV-PTM• series, where n = x+1 = 2-7, and (c) mono-radical reference, •PTM-2TV together with their corresponding hydrogenated derivatives, (b) (αH,α'H)-PTM-nTV-PTM and (d) (αH)-PTM-2TV. R = -hexyl chains.

Scheme 1. State of the art of the research in charge structure of molecular polarons and bipolarons (negative and positive) of the •PTM-nTV-PTM• series.

Species labelled as **a** and **b** indicates those studied in a previous and the current work, respectively. PTM units in different oxidation states are represented by green circles and nTV bridges by pink rectangles. Blue circles represent the corresponding counteranions.

Figure 1. Cyclic voltammograms of (a) $\bullet$ PTM-2TV-PTM $\bullet$, (b) $(\alpha\text{H},\alpha'\text{H})$ -PTM-2TV-PTM, (c) $\bullet$ PTM-7TV-PTM $\bullet$, (d) $(\alpha\text{H},\alpha'\text{H})$ -PTM-7TV-PTM. See footnote of Table 1 for experimental details.

Now, a follow up research is reported. The focus is turned into the analysis of where holes generated in $\bullet$ PTM-*n*TV-PTM $\bullet$ are located when formed in a hostile environment such as that provided by the electron-withdrawing $\bullet$ PTM radical units (see cations in Scheme 1). Hence, taking into account the donor nature of the *n*TV moiety,^{17–21} their ability to stabilize positive charged species will be explored. Thus, oxidations of $\bullet$ PTM-*n*TV-PTM $\bullet$ series to their radical cation and dication states ($[\bullet\text{PTM-}n\text{TV-PTM}\bullet]^{\bullet+}$ and $[\bullet\text{PTM-}n\text{TV-PTM}\bullet]^{2+}$ respectively), as molecular models analogue of polarons and bipolarons, will be carried out (Scheme 1, species denoted as **b**). To this end, a detailed UV-Vis-NIR electronic absorption spectroscopy study will be conducted in combination with electronic spin resonance (ESR) and resonant Raman spectroscopies and theoretical DFT calculations.

RESULTS AND DISCUSSION

Optical and electrochemical properties. Firstly, it is interesting to start with the evaluation of the electronic features of the wires in the absence of positive charges (i.e., unperturbed neutral wires) to explore the influence of the $\bullet$ PTM units on the neutral bridges. For that purpose, the optical properties of $\bullet$ PTM-*n*TV-PTM $\bullet$ series were studied in terms of Meier's equation²² and compared with those of: *i*) their corresponding hydrogenated derivatives $(\alpha\text{H},\alpha'\text{H})$ -PTM-*n*TV-PTM and *ii*) the unfunctionalized thienylenevinylene bridges, *n*TV family.^{6,8} It turns out that a similar chain-length saturation is found in the two terminally substituted series (λ_{∞} = 596.7 and

587.7 nm respectively), whereas λ_{∞} = 600.8 nm is found in the *n*TV series, revealing the small role of the electron withdrawing effect of the $\bullet$ PTM units in terms of improving π -conjugation, as far as for the longest wires is concerned (see Section 2 of ESI for further details).

Electrochemical properties were also investigated. Figure 1 depicts the cyclic voltammograms of two representative members (*n* = 2 and 7) of the $\bullet$ PTM-*n*TV-PTM $\bullet$ and $(\alpha\text{H},\alpha'\text{H})$ -PTM-*n*TV-PTM series (see also Figures S5–7), whereas Table 1 summarizes all redox data together with those of the monosubstituted analogue of $\bullet$ PTM-2TV-PTM $\bullet$, either in its radical (i.e., $\bullet$ PTM-2TV) and hydrogenated form (i.e., (αH) -PTM-2TV) forms (see Chart 1 for chemical structures). $\bullet$ PTM-*n*TV-PTM $\bullet$ and $\bullet$ PTM-2TV exhibit a reduction process, around -0.17 V, associated with the generation of the carbanionic species on the $\bullet$ PTM units.^{23–25} For the $\bullet$ PTM-*n*TV-PTM $\bullet$ series, besides the bielectronic reduction process, three main electrochemical features can be noticed depending on the *n*TV length: *i*) a shift toward lower values of the two first oxidation potentials when the size of *n*TV core is increased; *ii*) the decrease of the difference between the potential values of these two first oxidation waves as the *n*TV enlarges, reaching coalescence in the longest *n*TVs; and *iii*) the appearance of additional waves involving higher oxidation states than dications for the longer *n*TV bridges, although our study here is focused only in the first two oxidation states. Overall, these behaviors again reveal the enhancement of the conjugation length with the increase of the number of TV units. On the other hand, the $(\alpha\text{H},\alpha'\text{H})$ -PTM-*n*TV-PTM series shows similar values for the first two oxidation potentials compared to the unsubstituted *n*TV oligomers, i.e. $(\alpha\text{H},\alpha'\text{H})$ -PTM-4TV-PTM/ 4TV: 0.60/ 0.63 and 0.79/0.84 V. It is important to note that, for a given chain length, $(\alpha\text{H},\alpha'\text{H})$ -PTM-*n*TV-PTM exhibit a larger number of redox processes than *n*TV.

Table 1. CV data (in V vs Ag/AgCl) of $\bullet$ PTM-*n*TV-PTM $\bullet$ series¹⁶ together with $\bullet$ PTM-2TV (named as $\bullet$ R) (top) and their hydrogenated $(\alpha\text{H},\alpha'\text{H})$ -PTM-*n*TV-PTM homologues (bottom).

<i>n</i>	$E_{red}^{1/2}$	$E_{Ox1}^{1/2}$	$E_{Ox2}^{1/2}$	$E_{Ox3}^{1/2}$	$E_{Ox4}^{1/2}$	$E_{Ox5}^{1/2}$	$E_{Ox6}^{1/2}$
$\bullet$ R	-0.17	0.80	1.54	-	-	-	-
2	-0.18	0.78	1.37	-	-	-	-
3	-0.17	0.65	1.07	-	-	-	-
4	-0.16	0.57	0.83	1.34	-	-	-
5	-0.19	0.51	0.68	1.14	1.48	-	-
6	-0.17	0.51	0.61	0.99	1.61	1.74	-
7	-0.15	0.51	0.86	1.11	1.42	1.69	-

<i>n</i>	$E_{red}^{1/2}$	$E_{Ox1}^{1/2}$	$E_{Ox2}^{1/2}$	$E_{Ox3}^{1/2}$	$E_{Ox4}^{1/2}$	$E_{Ox5}^{1/2}$	$E_{Ox6}^{1/2}$
αHR	-	0.99	1.43	-	-	-	-
2	-	0.96	1.42	-	-	-	-
3	-	0.69	1.04	1.63	-	-	-
4	-	0.60	0.79	1.55	1.79	-	-
5	-	0.57	0.72	1.32	1.55	1.77	-
6	-	0.55	0.62	1.10	1.28	1.68	-
7	-	0.54	0.93	1.09	1.49	1.62	-

0.1 M Bu₄NPF₆/CH₂Cl₂ solutions. Electrodes: Pt wires, reference electrode Ag/AgCl. Scan rate 0.1 V/s. $(\alpha\text{H},\alpha'\text{H})$ -PTM-*n*TV-PTM data were acquired from OSWV (See Figure S7).

Figure 2. UV-Vis-NIR electronic absorption spectra of the electrochemically oxidized species ($c = 10^{-3}$ M) in 0.1 M TBA-PF₆/DCM solutions at room temperature for: (a) **•PTM-2TV-PTM•**, (b) **•PTM-3TV-PTM•**, (c) **•PTM-4TV-PTM•**, (d) **•PTM-5TV-PTM•**, (e) **•PTM-6TV-PTM•** and (f) **•PTM-7TV-PTM•**. Neutral diradical compounds correspond to black curves, radical cations to red and dications to blue curves.

Indeed, the formation of a tri- and tetracation was observed for (α H, α' H)-PTM-4TV-PTM (at 1.55 and 1.79 V respectively), while in 4TV, such higher oxidation states were not possible to stabilize.⁶ This can be simply due to the blockade of the terminal reactive sites, which allows more processes to take place inside the core.

From the comparison of the **•PTM-nTV-PTM•** and (α H, α' H)-PTM-nTV-PTM series, a general decrease of the oxidation potential values is observed, going from the hydrogenated to the diradical molecules. This is especially noticeable in the case of the shortest members, **•PTM-2TV-PTM•** vs (α H, α' H)-PTM-2TV-PTM, where the formation of the radical cation and dication occur at 0.78/1.37 in the diradical derivative and at 0.98/1.42 V in the corresponding hydrogenated compound. In this sense, it is clear that the radical nature of terminal **•PTM** units contributes to the stabilization of both charged species, being more pronounced in the radical cation. This is rather counterintuitive since one would expect that, by

lowering the electron withdrawing effect of the terminal groups, oxidation should become facilitated.

Spectro(electro)chemical properties. In order to gain further insights, the study of these positive charged species was carried out by means of spectrochemistry, by a stepwise addition of a FeCl₃ solution, and spectroelectrochemistry, by progressively increasing the anodic potential (see Sections 4-5 of SI).

In **Figure 2** the UV-Vis-NIR electronic absorption spectra of the oxidized samples of all members of the **•PTM-nTV-PTM•** family, obtained electrochemically, are plotted (see **Table S1** for the actual absorption maxima). The clean generation of the radical cations, [**•PTM-nTV-PTM•**]^{•+}, can be easily identified by the appearance of the bands related to their SOMO-LUMO and HOMO-SOMO electronic transitions, in decreasing order of energy, respectively.^{26,27} In all cases, the transformation of neutral compounds into their corresponding radical cations was accompanied by neat isosbestic points between the electronic absorption spectra of ones and others. Intermolecular π -dimerization was not observed at room temperature²⁸ during this first oxidation step, even when solutions of high concentration were analyzed. This fact can be ascribed to the steric hindrance imparted by the alkyl chains in the β -positions of the thiophene rings²⁹ and by the bulky terminal PTM groups.

The complete disappearance of the nTV centered π - π^* absorption band of the neutral species during first oxidation process is concomitantly accompanied, in **•PTM-2TV-PTM•**, with the decrease of the absorbance of the band assigned to **•PTM** unit¹⁶ (**Figure 2** (a) inset) up to half its initial absorbance, a dual evolution that was not observed in the longer compounds. Additionally, in **Figure 3** (a), the transition energies (in eV, taken at the energy peak maxima) are plotted as a function of the reciprocal number of thiophene rings for the above mentioned π - π^* HOMO-SOMO electronic transition of [**•PTM-nTV-PTM•**]^{•+}. A slight non-negligible deviation of [**•PTM-2TV-PTM•**]^{•+} from the perfect alignment along the linear regression of the other members of the series was observed.

Aiming to gain further insights into the phenomenon underlying these observations, the reference **•PTM-2TV** was also analyzed. The electrochemically obtained spectrum of [**•PTM-2TV**]^{•+} features the total disappearance of the so called **•PTM** band of the neutral radical during the first oxidation in **Figure 3** (b). This result might be explained in terms of the formation of a closed-shell quinoidal structure³⁰ by electron pairing between the pre-existing radical of the **•PTM** group and that newly formed of the radical cation. Thus, in order to keep a coherent nomenclature, [**•PTM-2TV**]^{•+} will be named from now on as [**PTM-2TV**]⁺. In analogy to this, the radical cation of **•PTM-2TV-PTM•** would give rise to the formation of a radical cation on the 2TV bridge (tri-radical cation). Then, it would evolve by electron pairing with one **•PTM** unit producing a stable quinoidal radical cation (i.e., [**•PTM-2TV-PTM•**]^{•+} should be better named as [**•PTM-2TV-PTM**]^{•+}). This is in good agreement with the fact that the total absorbance of the **•PTM** band is reduced to half-absorbance during the one-electron oxidation of **•PTM-2TV-PTM•**, which is in line with the removing of the radical character of one of two **•PTM** units (**Figure 2** (a) inset). Interestingly, the formation of these quinoidal structures extending over the **•PTM** acceptors in the radical cations of the longer compounds was not detected, [**•PTM-nTV-PTM•**]^{•+}.

Figure 3. (a) Plots of the electronic transition energies (eV) vs the reciprocal number of thiophene rings for the electronic transitions (SOMO-LUMO: white circles, $y = 0.97x + 0.89$; HOMO-SOMO: black circles, $y = 1.72x + 0.29$) of [**•PTM-nTV-PTM(•)**]^{(*)+} and of [**•PTM-nTV-PTM(•)**]²⁺ (black squares, $y = 3.38x + 0.24$) together with their linear regression fittings ($R^2 > 0.99$ in all cases). (b). UV-Vis-NIR electronic absorption spectra of the electrochemically oxidized species obtained in 0.1 M TBA-PF₆/DCM solutions at room temperature for **•PTM-2TV**. Neutral radical compound corresponds to the black curve while the cationic species to the grey one.

Following with the electrochemical oxidation of **•PTM-nTV-PTM•** series, by increasing the applied potentials, dication species of all members, [**•PTM-nTV-PTM(•)**]²⁺, were obtained (Figure 2). These are characterized by a new electronic absorption band appearing in the NIR spectral region and attributed to their HOMO-LUMO electronic excitations (also plotted in Figure 3 (b)). The spectroscopic behavior of these dications can be summarized as follows: *i*) in the case of the shorter nTV wires ($n \leq 3$), these absorptions appeared blue-shifted regarding the SOMO-LUMO electronic transition bands of their respective radical cations. Due to the withdrawing nature of **•PTM** units, the two positive charges should be repelled and confined over the nTV bridge, thus increasing the charge repulsion and consequently, the excitation energies; *ii*) in the longer nTV wires the new band is placed in between those of the cations, given the release of electronic repulsion in the longer bridges.

ESR measurements and theoretical modeling. Cationic species derived from **•PTM-nTV-PTM•** series were examined by ESR spectroscopy (see section 6 of ESI file). Firstly, ESR spectrum of [(aH)-**PTM-2TV**]⁺ was registered in order to isolate the fingerprint of the radical unit on the nTV bridge from the influence of the **•PTM** site. A broad and poorly resolved ESR signal with weak intensity was observed at $g_{iso} = 2.0029$ (Figure S11), in accordance with the spectrum reported by Roncali *et al.* for [4TV]⁺.²⁹ However, in the case of [**PTM-2TV**]⁺, neither this signal nor that corresponding to the **•PTM** unit were observed. In fact, the ESR signal of the neutral **•PTM-2TV** disappeared when the radical cation was formed (Figure S12 (a)). This is in good agreement with the disappearance of the UV-Vis band at 390 nm of the **•PTM** chromophore, previously described, and with the formation of a closed-shell ESR silent [**PTM-2TV**]⁺ species.

Moving on to **•PTM-nTV-PTM•** series, the spectrum of neutral **•PTM-2TV-PTM•** shows, at g_{iso} of 2.0027 (Figure 4 (a)),

Figure 4. Evolution of the ESR spectra of (a) **•PTM-2TV-PTM•** and (b) **•PTM-4TV-PTM•** after stepwise addition of a FeCl₃ solution. Neutral diradical compounds correspond to black spectra and light grey to the one obtained when an excess of FeCl₃ is present.

Table 2. DFT/(U)B3LYP/6-31G energy differences between the highest and lowest solutions for the cationic and dicationic species of •PTM-2TV, •PTM-2TV-PTM• and •PTM-4TV-PTM•.**

	$E_T - E_{SOS}$	$E_{SOS} - E_{SCS}$
[(•PTM-2TV)] ^{(*)+}	4,62	0,00
	$E_Q - E_{DOS}$	$E_{DOS} - E_{PCS}$
[•PTM-2TV-PTM(•)] ^{(*)+}	5,17	0,00
[•PTM-4TV-PTM(•)] ^{(*)+}	1,72	0,00
	$E_Q - E_{SOS}$	$E_{SOS} - E_{SCS}$
[(•PTM-2TV-PTM)] ²⁺	7,69	0,00
[(•PTM-4TV-PTM(•))] ^{2(*)+}	2,22	0,00

T: triplet, Q: quartet, S: Singlet, D: Doublet, OS: Open-Shell and CS: Closed-Shell.

three overlapped ESR lines that were attributed to the coupling of one unpaired electron with two equivalent protons. The coupling constant, $a(2H)$, is 0.9 G which is half of the value showed by a **•PTM** monoradical attached to one vinylene bridge ($a(1H) = 2$ G). The appearance of three symmetrical lines indicates the magnetic interaction between the two electrons of the **•PTM** groups, with a magnetic exchange coupling constant, J , that fulfils the condition $|J| \gg |a_i|$.³¹ After generation of [**•PTM-2TV-PTM**]⁺, the spectrum of the sample evolved towards 2 overlapped lines of lower intensity, which points out the presence of only one **•PTM** radical coupled with only one vinyl hydrogen.

Quantum chemical calculations were carried out for the different electronic configurations of [**PTM-2TV**]⁺ and [**•PTM-2TV-PTM**]⁺ and the most relevant data are summarized in Table 2 (see Section 7 of ESI for further details). According to them, the cationic species of **•PTM-2TV** and **•PTM-2TV-PTM** present a closed-shell singlet and an open-shell doublet ground-state structures, [**PTM-2TV**]⁺ and [**•PTM-2TV-PTM**]⁺ respectively, having their lowest energy lying highest multiplicity states at 4.62 (triplet) and 5.17 (quartet) Kcal/mol. Additionally these smaller low-to-high spin gap implies a partial contribution of open-shell singlet configuration to the overall electronic structures of the ground electronic state of [**PTM-2TV**]⁺ (see Scheme 2) and equivalently for [**•PTM-2TV-PTM**]⁺.

Scheme 2. Generation of the quinoidal structure of [PTM-2TV]⁺

Alkyl-chains have been omitted for clarity.

As a consequence, theory supports the formation of a sizeable quinoidal structure in the π -conjugated backbone, whose extent depends on the strength of the electronic bonding between the paired electrons (more marked in the closed-shell and lighter in the open-shell form).

Going back to ESR results, the formation of the radical cation of $\bullet$ PTM-3TV-PTM $\bullet$ also resulted in a decreased intensity of the starting signal. However, it did not show two overlapped lines but only a broad one (Figure S12 (c)). Thus, either the interaction between the $\bullet$ PTM and the nTV cation radicals observed in $[\bullet$ PTM-2TV-PTM] $^{+}$ is null in the longer cations or this become really small. This is in accordance with the fact that the UV-Vis band at 390 nm related to the $\bullet$ PTM unit scarcely diminishes its intensity upon oxidation (Figure 2 (b)). Therefore, the formation of a radical cation rather isolated in the central thiophene rings is the most plausible case. In this regard, the observed ESR signal for this cationic species should be related to a tri-radical cation species.

Aiming to analyze the structural nature of the longer series members to an affordable computational cost, charged species for $\bullet$ PTM-4TV-PTM $\bullet$ were chosen for their theoretical modelling. According to the results shown in Table 2, also in this case, the most stable situation is the one leading to the coupling between $\bullet$ PTM site and the generated radical of the cation of the nTV segment, giving rise to a partially quinoidal open-shell doublet ground electronic state (i.e., a doublet $[\bullet$ PTM-4TV-PTM] $^{+}$). However, unlike in the shorter member of the family, the energy difference between this state and its corresponding highest multiplicity one (i.e., a quartet, $[\bullet$ PTM-4TV-PTM] $^{+}$) is only 1.72 kcal/mol being this, therefore, accessible at room temperature and thus contributing to the broad ESR signal observed such as described now.

The corresponding ESR spectra of $[\bullet$ PTM-nTV-PTM] $^{+}$, with $n = 4-6$, see Figure 4 (b) and Figure S12 (d-f), exhibited a very similar signal shape compared to that of the $[\bullet$ PTM-3TV-PTM] $^{+}$ indicating the formation of increasingly magnetically-active doublet states with progressively small low-to-high spin gaps as the nTV radical cation spatially separate from the $\bullet$ PTM external radicals in oligomers of longer size.

Table 2 (and Tables S4-5) also summarizes the quantum chemical calculations for the dications of $\bullet$ PTM-2TV-PTM $\bullet$ and $\bullet$ PTM-4TV-PTM $\bullet$. Accordingly, the ground electronic states are singlets, revealing a significant bonding coupling between the two radical cations generated in the central 2TV and the two of the $\bullet$ PTMs, $[\text{PTM-2TV-PTM}]^{2+}$. The same situation is predicted for the dication of $\bullet$ PTM-4TV-PTM $\bullet$, $[\text{PTM-4TV-PTM}]^{2+}$. However, a distinctive increment of the diradical character for the ground electronic state of this and

longer dications is revealed by the lowering of the energy gap to the highest multiplicity states placed at 7.69 and 2.22 kcal/mol above the ground electronic state for $[\bullet$ PTM-2TV-PTM] $^{+}$ and $[\bullet$ PTM-4TV-PTM] $^{+}$ respectively.

Raman Spectroscopy. Raman spectroscopy is a very useful technique to explore the molecular structure in the electronic ground state of π -electron conjugated molecules. This can be realized by evaluating the changes on the vibrational Raman frequencies of the strongest Raman bands, due to the $\nu(\text{C}=\text{C})_{\text{vinyl}}$ stretching vibrational modes, among the series. To corroborate this spectroscopic assignment, theoretical Raman spectra of representative members of the family with different chain lengths were calculated.

Figure S15 shows a comparison of the experimental and DFT/UB3LYP/6-31G** theoretical Raman spectra of $[\bullet$ PTM-2TV-PTM] $^{+}$. The vibrational eigenvectors associated with the most relevant bands are collected in Table S6. From this comparison, the two main experimental Raman bands in the 1600-1500 cm^{-1} region can be ascribed to $\nu(\text{C}=\text{C})_{\text{vinyl}}$ modes: i) The

Figure 5. (a) Raman spectra of radical cations of $\bullet$ PTM-nTV-PTM $\bullet$ series: (i) $[\bullet$ PTM-2TV-PTM] $^{+}$, (ii) $[\bullet$ PTM-3TV-PTM] $^{+}$, (iii) $[\bullet$ PTM-4TV-PTM] $^{+}$, (iv) $[\bullet$ PTM-5TV-PTM] $^{+}$, (v) $[\bullet$ PTM-6TV-PTM] $^{+}$ and (vi) $[\bullet$ PTM-7TV-PTM] $^{+}$. Additionally, $[(\alpha\text{H}, \alpha'\text{H})\text{-PTM-2TV-PTM}]^{+}$ has been included (black dotted line). (b) Raman spectra of dications of longer members of $\bullet$ PTM-nTV-PTM $\bullet$ series: (i) $[\text{PTM-4TV-PTM}]^{2+}$, (ii) $[\text{PTM-5TV-PTM}]^{2+}$, (iii) $[\text{PTM-6TV-PTM}]^{2+}$ and (iv) $[\text{PTM-7TV-PTM}]^{2+}$. All the spectra were obtained under resonant conditions ($\lambda = 1064$ nm), at room temperature from chemically oxidized DCM solutions. (See section 10 in ESI for further details)

Scheme 3. Proposed chemical structures for the charged species of •PTM-nTV-PTM• series, according to experimental results.

Quinoidal ring segments have been highlighted with dashed lines. Alkyl-chains have been omitted for clarity.

, +.

intense band at 1547 cm^{-1} (theoretically at 1540 cm^{-1}) belongs to the stretch of the central bond, $\nu(\text{C}=\text{C})_{\text{vinyl-central}}$; and *ii*) the weak band at 1590 cm^{-1} (theoretically at 1553 cm^{-1}) corresponds to the stretch of the external vinylene units, $\nu(\text{C}=\text{C})_{\text{vinyl-external}}$. It now follows the study of the Raman spectroscopic properties of the radical cations and dications, derived from $(\alpha\text{H},\alpha'\text{H})\text{-PTM-nTV-PTM}$ and $\bullet\text{PTM-nTV-PTM}\bullet$ series in connection with their molecular structures³².

From $[(\alpha\text{H},\alpha'\text{H})\text{-PTM-nTV-PTM}]^{+\bullet}$ data (Figure S17 (top)), two main effects must be highlighted: *i*) the most intense Raman bands of spectra of the radical cations show significant downshifts regarding the same bands in the neutral samples; and *ii*) the Raman peak positions of these cationic species are almost insensitive to the molecular length of the nTV bridge.

In particular, the evolution of the $\nu(\text{C}=\text{C})_{\text{vinyl}}$ Raman bands in the neutral species upon oxidation occurred from $1586/1576\text{ cm}^{-1}$ for $(\alpha\text{H},\alpha'\text{H})\text{-PTM-2TV-PTM}/(\alpha\text{H},\alpha'\text{H})\text{-PTM-7TV-PTM}$ to $1547/1547\text{ cm}^{-1}$ $[(\alpha\text{H},\alpha'\text{H})\text{-PTM-2TV-PTM}]^{+\bullet}/[(\alpha\text{H},\alpha'\text{H})\text{-PTM-7TV-PTM}]^{+\bullet}$. This is explained by the $\text{C}-\text{C}=\text{C}-\text{C}$ conversion of the vinylene bridges to $\text{C}=\text{C}-\text{C}=\text{C}$ moiety with single bond character, a vinylene bond weakening that is accompanied by the transformation of the aromatic benzene/thiophene into quinoidal ring shapes.

On the other hand, the constant position of these bands in the Raman spectra of the $[(\alpha\text{H},\alpha'\text{H})\text{-PTM-nTV-PTM}]^{+\bullet}$ series, around 1547 cm^{-1} , no matter the length of the wire, indicates the formation of quinoidal ring segments affecting similar number of thiophene units. This fact can be related to the repulsion exerted by the electron-deficient $\bullet\text{PTM}$ groups towards the injected positive charges that confine these in the nTV bridge in a similar way, aside the nTV length. Other effects favoring the local confinement of the charges are the torsional disorder between consecutive aromatic rings and the unfavorable energy cost of breaking aromaticity when spreading the quinoidal structure over more rings³³.

Figure 5 (a) depicts the Raman spectra of the radical cations of $\bullet\text{PTM-nTV-PTM}\bullet$, $[\bullet\text{PTM-nTV-PTM}(\bullet)]^{(\bullet)+}$. More bands

are displayed in the $\nu(\text{C}=\text{C})_{\text{vinyl}}$ region in the case $[\bullet\text{PTM-2TV-PTM}]^{+\bullet}$ compared with the others. In particular, there are two clear features at 1590 and 1547 cm^{-1} , in contrast with only one dominant at $1540\text{--}1550\text{ cm}^{-1}$ in the longer derivatives. Furthermore, as it was previously commented, the spectrum of the non-radicaloid $[(\alpha\text{H},\alpha'\text{H})\text{-PTM-2TV-PTM}]^{+\bullet}$ (also included in **Figure 5 (a)**) shows only one main band at 1547 cm^{-1} . This comparison highlights that the formation of a quinoidal structure with the phenyl ring of one $\bullet\text{PTM}$ in $[\bullet\text{PTM-2TV-PTM}]^{+\bullet}$ provokes an asymmetry in the cation that pushes the 1590 cm^{-1} band to emerge. On the other hand, both compounds have identical 1547 cm^{-1} feature in the spectra, meaning that the charge defect (the structural deformation by accommodation of the positive charge) is very similar. This is interesting, given that, while the quinoidal structure is promoted by the spin pairing of the radicals, this bonding does not impulse a charge drift.

For the others $[\bullet\text{PTM-nTV-PTM}\bullet]^{+\bullet}$, very weak bands (i.e., significantly different than the 1590 cm^{-1} one in $[\bullet\text{PTM-2TV-PTM}]^{+\bullet}$) are detected at 1571 , 1570 , 1573 and 1576 cm^{-1} in $[\bullet\text{PTM-4TV-PTM}\bullet]^{+\bullet}$, $[\bullet\text{PTM-5TV-PTM}\bullet]^{+\bullet}$, $[\bullet\text{PTM-6TV-PTM}\bullet]^{+\bullet}$ and $[\bullet\text{PTM-7TV-PTM}\bullet]^{+\bullet}$, respectively. However in $[\bullet\text{PTM-3TV-PTM}(\bullet)]^{(\bullet)+}$ this band is at 1590 cm^{-1} , such as in $[\bullet\text{PTM-2TV-PTM}]^{+\bullet}$, in accordance with the fact that this compound slightly maintains the spin pairing of the radicals and, consequently, a partial quinoidization of the phenyl PTM ring. The strongest bands at $1542\text{--}1549\text{ cm}^{-1}$ in the series of cations reveal the similar nature of the charge defects in all due to the confinement of the charge in the nTV segments.

Figure 5 (b) also displays the Raman spectra of the dicationic species, starting with that of the tetramer and longer. Such as in the case of the cations, DFT/UB3LYP/6-31G** theoretical Raman spectra of the dication of $\bullet\text{PTM-4TV-PTM}\bullet$ were calculated and discussed in **Figure S16** and **Table S7** to affirm the assignments of the $\nu(\text{C}=\text{C})_{\text{vinyl}}$ bands in the $1500\text{--}1600\text{ cm}^{-1}$ region. The spectrum of the dication of $\bullet\text{PTM-4TV-PTM}\bullet$ significantly changes regarding its cation: differences consisting on the emergence of a new 1592 cm^{-1} band and the

upshift of the 1545 cm^{-1} cationic band up to 1554 cm^{-1} in the dication. The new 1592 cm^{-1} feature can result from the formation of a quinoidal structure in the benzenes of the two •PTMs, a structural change accompanied by a mitigation of the structural perturbation in the nTV bridge (revealed by the $1545\rightarrow 1554\text{ cm}^{-1}$ upshift). This means that the insertion of two charges in •PTM-4TV-PTM• can be viewed as resulting by the injection of two cation radicals, each one forming a quinoidal structure by spin pairing with the two PTM radicals. As a consequence, a singlet structure for the ground electronic state is revealed, in agreement with the quantum chemical calculations. The stabilization of the singlet ground electronic state by quinoidal bonding (i.e., the radical pairing) in this dication is preferred compared to the high spin triplet where charge repulsion is smaller but no bonding is feasible. Furthermore in this singlet state, a slight increase of the spatial separation of the two positive charge should take place provoking a slight recovery of the former aromatic structure in the molecular nTV center at the origin of the detected Raman frequency upshift. For the other dications, the enlargement of the nTV segment mitigates the electrostatic repulsion between the positive charges and the Raman bands recover the frequency positions of the cations. The weak bands at $1607\text{--}1616\text{ cm}^{-1}$ also indicate the recovery of the double bond character of the external C=C bonds in agreement with the confinement of the charges and spins in the nTV moiety. **Scheme 3** resumes all the proposed chemical structures for the charged species of •PTM-nTV-PTM• series, according to experimental results.

SUMMARY AND CONCLUSIONS

An exhaustive study, combining theoretical and experimental techniques, including UV-Vis-NIR electronic absorption, electron spin resonance (ESR) and resonant Raman spectroscopies, revealed the key role of the terminal •PTM units of the diradical •PTM-nTV-PTM• series for the stabilization of positively charged species generated on the nTV bridges. For comparisons, their corresponding hydrogenated derivatives, ($\alpha\text{H},\alpha'\text{H}$)-PTM-nTV-PTM, have been also studied.

In the case of radical cations, two main structures have been found, depending on the location of the quinoidal ring segment along the molecular wire: *i*) *symmetrical diradical cation* and *ii*) an *asymmetrical radical cation*. Common symmetrical structures were found for the series members with longer bridges (i.e. $n \geq 3$), where the quinoidal segments were confined in the center of the molecules, leading to *triradical-cation* species (i.e., a quartet ground electronic state, [•PTM-nTV-PTM•] $^{+}$). However, in the case of •PTM-2TV-PTM• an asymmetrical structure was deduced. Thus, the limited extension of the molecular wire promoted the coupling of the unpaired radical of one of the •PTM sites with the one generated along the nTV chain after the removal of an electron, [•PTM-2TV-PTM] $^{+}$. This fact is in good agreement with the closed-shell ground state cation obtained for the monoradical reference upon oxidation, •PTM-2TV, [PTM-2TV] $^{+}$. Dicationic species of longer series members (i.e. $n \geq 4$) were also analyzed. In line with the case of radical cations, a closed-shell ground states, with the recovery of the central aromaticity and terminal quinoidal segments, assisted by the •PTM units, was described for [PTM-4TV-PTM] $^{2+}$, while thiophene pseudo-aromatized tetradicals were ascribed to longer nTV bridges [•PTM-nTV-PTM•] $^{2+}$.

In conclusion, •PTM-nTV-PTM• series represents a special case of A-D-A triads where, despite the electron-withdrawing or hole repelling nature of the PTM building blocks, a counterintuitive effect is that the nTV bridges (i.e., donors) and the terminal •PTM sites (i.e., acceptors) all contribute to the stabilization of positive charged states.

ASSOCIATED CONTENT

UV-Vis-NIR electronic absorption characterizations, EPR measurements of the radical cation and dications, Raman spectra of charged species of ($\alpha\text{H},\alpha'\text{H}$)-PTM-nTV-PTM series and details of the quantum-chemical calculations, together with a complete list of authors for some references. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

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REFERENCES

- 1 T. A. Su, M. Neupane, M. L. Steigerwald, L. Venkataraman and C. Nuckolls, *Nat. Rev. Mater.*, 2016, **1**, 16002.
- 2 J. L. Brédas, G. B. Street, B. Thémans and J. M. André, *J. Chem. Phys.*, 1985, **83**, 1323–1329.
- 3 J. Nakayama and T. Fujimori, *Heterocycles*, 1991, **32**, 991.
- 4 C. Krzeminski, C. Delerue, G. Allan, V. Haguët, D. Stiévenard,

- P. Frère, E. Levillain and J. Roncali, *J. Chem. Phys.*, 1999, **111**, 6643–6649.
- 5 J. Roncali, *Macromol. Rapid Commun.*, 2007, **28**, 1761–1775.
- 6 I. Jestin, P. Frère, P. Blanchard and J. Roncali, *Angew. Chemie Int. Ed.*, 1998, **37**, 942–945.
- 7 J. Roncali, I. Jestin, P. Frère, E. Levillain and D. Stievenard, *Synth. Met.*, 1999, **101**, 667–670.
- 8 I. Jestin, P. Frère, N. Mercier, E. Levillain, D. Stievenard and J. Roncali, *J. Am. Chem. Soc.*, 1998, **120**, 8150–8158.
- 9 D. Fichou, *Handbook of Oligo- and Polythiophenes*, Wiley-VCH Verlag GmbH, Weinheim, Germany, 1998.
- 10 I. F. Perepichka and D. F. Perepichka, *Handbook of thiophene-based materials: applications in organic electronics and photonics*, Wiley, 2009.
- 11 J. Roncali, *Acc. Chem. Res.*, 2000, **33**, 147–156.
- 12 S. Prasanthkumar, A. Gopal and A. Ajayaghosh, *J. Am. Chem. Soc.*, 2010, **132**, 13206–13207.
- 13 F. Oswald, D.-M. S. Islam, Y. Araki, V. Troiani, R. Caballero, P. de la Cruz, O. Ito and F. Langa, *Chem. Commun. (Camb.)*, 2007, **106**, 4498–4500.
- 14 J. J. Apperloo, C. Martineau, P. A. van Hal, J. Roncali and R. A. J. Janssen, *J. Phys. Chem. A*, 2002, **106**, 21–31.
- 15 C. Videtot, J. Ackermann, P. Blanchard, J.-M. Raimundo, P. Frère, M. Allain, R. de Bettignies, E. Levillain and J. Roncali, *Adv. Mater.*, 2003, **15**, 306–310.
- 16 C. Franco, P. M. Burrezo, V. Lloveras, R. Caballero, I. Alcón, S. T. Bromley, M. Mas-Torrent, F. Langa, J. T. López Navarrete, C. Rovira, J. Casado and J. Veciana, *J. Am. Chem. Soc.*, 2017, **139**, 686–692.
- 17 Y. Fu, H. Cheng and R. L. Elsenbaumer, *Chem. Mater.*, 1997, **9**, 1720–1724.
- 18 E. H. Elandaloussi, P. Frère, P. Richomme, J. Orduna, J. Garin and J. Roncali, .
- 19 B. Lim, K.-J. Baeg, H.-G. Jeong, J. Jo, H. Kim, J.-W. Park, Y.-Y. Noh, D. Vak, J.-H. Park, J.-W. Park and D.-Y. Kim, *Adv. Mater. (Weinheim, Ger.)*, 2009, **21**, 2808–2814.
- 20 E. H. Elandaloussi, P. Frère and J. Roncali, *Chem. Commun.*, 1997, 301–302.
- 21 E. Zhou, J. Cong, K. Hashimoto and K. Tajima, *Energy Environ. Sci.*, 2012, **5**, 9756.
- 22 H. Meier, *Angew. Chemie Int. Ed.*, 2005, **44**, 2482–2506.
- 23 C. Sporer, I. Ratera, D. Ruiz-Molina, Y. Zhao, J. Vidal-Gancedo, K. Wurst, P. Jaitner, K. Clays, A. Persoons, C. Rovira and J. Veciana, *Angew. Chemie Int. Ed.*, 2004, **43**, 5266–5268.
- 24 J. Veciana, C. Rovira, N. Ventosa, M. I. Crespo and F. Palacio, *J. Am. Chem. Soc.*, 1993, **115**, 57–64.
- 25 R. G. (Robin G. Hicks and Wiley InterScience (Online service), *Stable radicals: fundamentals and applied aspects of odd-electron compounds*, Wiley-Blackwell, 2010.
- 26 J. L. Bredas and G. B. Street, *Acc. Chem. Res.*, 1985, **18**, 309–315.
- 27 J. A. E. H. Van Haare, E. E. Havinga, J. L. J. Van Dongen, R. A. J. Janssen, J. Cornil and J. L. Brédas, *Chem. - A Eur. J.*, 1998, **4**, 1509–1522.
- 28 P. M. Burrezo, B. Pelado, R. P. Ortiz, P. De La Cruz, J. T. L. Navarrete, F. Langa and J. Casado, *Chem. - A Eur. J.*, 2015, **21**, 1713–1725.
- 29 J. J. Apperloo, J. Raimundo, P. Frère, J. Roncali and R. A. J. Janssen, *Chem. - A Eur. J.*, 2000, **6**, 1698–1707.
- 30 M. Ballester, J. Riera, J. Castaner, C. Carreras, J. J. Ubierna, C. Badia, C. Miravittles and E. Molins, *J. Org. Chem.*, 1989, **54**, 4611–4615.
- 31 J. A. (John A. Weil and J. R. Bolton, *Electron paramagnetic resonance: elementary theory and practical applications.*, Wiley-Interscience, 2007.
- 32 S. Rodríguez González, M. C. Ruiz Delgado, R. Caballero, P. De la Cruz, F. Langa, J. T. López Navarrete and J. Casado, *J. Am. Chem. Soc.*, 2012, **134**, 5675–5681.
- 33 P. M. Burrezo, X. Zhu, S.-F. Zhu, Q. Yan, J. T. López Navarrete, H. Tsuji, E. Nakamura and J. Casado, *J. Am. Chem. Soc.*, 2015, **137**, 3834–3843.

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