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Impact of terminal substituents on electronic, vibrational and optical properties of thiophene-phenylene co-oligomers

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Abstract

Owing to combination of efficient charge transport and bright luminescence, thiophene-phenylene cooligomers (TPCOs) are promising materials for organic light-emitting devices such as diodes, transistors and lasers. The synthetic flexibility of TPCOs enables facile tuning of their properties. In this study, we address the effect of various electron-donating and electron-withdrawing symmetric terminal substituents (fluorine, methyl, trifluoromethyl, methoxy, tert-butyl, and trimethylsilyl) on frontier polarizabilities, orbitals, charge distribution, static molecular vibrations, bandgaps and photoluminescence quantum yields of 5,5'-diphenyl-2,2'-bithiopene (PTTP). By combining DFT calculations with cyclic voltammetry, absorption, photoluminescence, and Raman spectroscopies, we show that symmetric terminal substitution tunes the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energies of the TPCO within the range of ~0.7 eV, shifts the frequencies of the vibrational modes associated with the phenyl rings, changes the photoluminescence quantum yield in about twice and slightly changes the bandgap by ~ 0.1 eV. We demonstrate that these effects are governed by two factors: the Hammet constant of the substituents and their involvement into the π -conjugation/hyperconjugation described by the effective conjugation length of the substituted oligomer. The microscopic picture underlying the effect of terminal substituents on the electronic, vibrational and optical properties of TPCOs is presented. Overall, the unraveled relationships between the structure and the properties of the substituted PTTPs should facilitate the rational design of π -conjugated (co-)oligomers for efficient organic optoelectronic devices.

1. Introduction

Organic optoelectronic devices, e.g., organic light-emitting diodes (OLEDs), organic light-emitting transistors (OLETs) and electric-driven lasers, require materials with high charge-carrier mobility and luminescence efficiency. However, combination of these two properties is rarely observed. Thiophene-phenylene co-oligomers (TPCOs) constitute one of a few lucky exceptions — they show photoluminescence quantum yield (PLQY) up to ~80-90 % in the solid state^{1,2} approaching that in solution along with considerable charge-carrier mobility.^{1,3} Their benefits are also facile crystallization from either vapor or solution phase, with large⁴ and high-quality⁵ single crystals as an outcome. Various organic

(opto)electronic devices based on TPCOs, including light-emitting diodes (OLEDs),⁶ solar cells,⁷ field-effect transistors (OFETs),³ light-emitting transistors (OLETs)^{1,2} and lasers⁸ have been demonstrated. Moreover, bendable⁹ and monolayer^{10,11} devices with TPCO-based active layers have recently been reported. The synthetical flexibility of TPCOs enables their prompt chemical modification, e.g., introduction of electron-donating or electron-withdrawing substituents.³ For several oligomer and co-oligomer series, e.g., for distyrylbenzenes¹² and furan-phenylene co-oligomers,^{9,13} it was shown that substitution can dramatically alter the properties of both the isolated molecules and the corresponding solid-state phase. Importantly, many of the structural, electronic, and optical properties of organic semiconductors are directly related to those of the molecules constituting them. For instance, the emission spectra and PLQYs of the ultrapure TPCO shave been synthesized and studied to date,^{3, 10, 15, 16} the impact of their molecular structure on the electronic and optical properties has not been systematically investigated yet. Such a study is highly desired since it can reveal important structure-property relationships for the rational design of TPCOs and related materials for organic optoelectronics.

Combination of experiment and quantum-chemical modeling is the most appropriate way for systematic studies of the organic semiconductors at the molecular level.^{17,18} Modeling provides excessive information about various molecular properties; however, it is frequently model-dependent and hence is not always reliable.^{19, 20} On the contrary, experiment often provides very limited and indirect information; nevertheless, the experimental data can verify the modeling results. Thus, combination of theory and experiment is highly desired to establish the structure-properties relations in organic semiconductor materials.

In this work, we perform a combined experimental and theoretical study of TPCO series with a 5,5'-diphenyl-2,2'-bithiopene (PTTP) π -conjugated core and various symmetric terminal substituents including electron-donating or electron-withdrawing ones (Fig. 1): fluorine (F), methyl (Me), trifluoromethyl (TFM), methoxy (MeO), tert-butyl (tertBu), and trimethylsilyl (TMS). The impact of these substituents on different molecular properties including the frontier orbital energies, vibrational spectra, bandgaps and PLQY is addressed with the use of cyclic voltammetry (CV), optical absorption, photoluminescence (PL), and Raman spectroscopies combined with density functional theory (DFT) calculations. The results obtained allowed us to draw a microscopic picture of the effect of terminal substituents on the electronic, vibrational and optical properties of TPCOs, which is important for the rational design of TPCOs and other linear π -conjugated systems.

2. Methods

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2.1. Materials

Chemical structures of the TPCOs investigated are shown in Fig. 1; for Raman measurements, paraquaterphenyl (4P) and 2,2':5',2'':5'',2'''-quaterthiophene (4T) were also used. Purification of the target compounds was made by a vacuum sublimation. Gel permission chromatography (GPC) analysis showed that all of them are monodisperse individual compounds. The purity and molecular structures of all synthesized oligomers were confirmed by ¹H NMR spectroscopy, GPC and elemental analysis; see Supporting information (SI) for details. ¹³C NMR measurements were performed for tertBu-PTTP-tertBu only because of its good solubility in CDCl₃.

2.2. Experimental details

Cyclic voltammetry (CV) measurements were performed in CH_2Cl_2 solution (concentration of ~0.1 g/l) by using a computer controlled potentiostat (P-8nano, Elins) in combination with three-electrode cell (Gamry); 0.1 M tetrabutylammonium hexafluorophosphate was used as a supporting electrolyte. The Pt,

Pt wire and Ag/AgCl were used as working, counter and reference electrodes, respectively. The measurements were standardized by measuring the redox potential of ferrocene after each compound analysis. The HOMO energy levels were estimated using the onset oxidation potentials according to equation: E_{homo} = -(E_{ox}^{onset} +4.8) (eV). Raman measurements in oligomer powders were conducted using a Raman microscope (inVia, Renishaw) with an excitation wavelength of 633 nm provided by a He-Ne laser. Absorption spectra were recorded using a spectrophotometer (UV-2501PC, Shimadzu) in a standard 10-mm-thick photometric quartz cuvette filled with THF solutions with the concentrations of 10⁻⁵ M. A scanning spectrofluorimeter (ALS01M)²¹ was used for the registration of PL spectra. The PL excitation wavelengths were set to the absorption maxima. PL measurements were performed in 90°-geometry for several optical densities in the range from 0.06 to 0.12 absorbance units in a 10-mm-thick quartz cuvette. The PLQY was measured by comparing the integral PL intensity of 10⁻⁶ M diluted solutions of TPCOs in tetrahydrofuran (THF) with the integral PL intensity of the standard as described elsewhere.²² As a standard in measuring the PLQY (Φ), a diluted solution of 1,4-bis(5-phenyloxazol-2-yl)benzene (POPOP) in cyclohexane (Φ =1) was used.

2.3. Computational details

All DFT calculations were performed using GAMESS package^{23,24} at B3LYP/6-31G(d,p) level, which provides a reasonable tradeoff between the calculation time and accuracy. HOMO/LUMO energies, optical bandgaps and oscillator strengths were also calculated using 6-311G(d,p) basis set; the comparison of the results for the two basis sets is given in SI, Section S2. The geometry of the isolated molecules was fully optimized, and its correspondence to the previous calculations was checked (see Fig. S2).²⁵ The frequency analysis was used to check the absence of imaginary frequencies in the optimized structures. The electron density at various atoms for HOMO/LUMO was estimated as the sum of the squared coefficients for all the basis vectors centered at these atoms in the HOMO/LUMO wavefunctions. Raman spectra were calculated in the off-resonance regime from the static polarizabilities. Time-dependent DFT (TDDFT) calculations implemented in GAMESS package by Chiba et al.²⁶ were performed to address the optical properties of the studied molecules:²⁷ energies of the lowest excited states (optical bandgaps) and oscillator strengths for absorption and luminescence.

3. Results and discussion

3.1. Synthesis



Fig. 1. Chemical structure of the TPCOs investigated.

For preparation of 5,5'-diphenyl-2,2'-bithiophene (PTTP), 5,5'-*bis*[4-methylphenyl]-2,2'-bithiophene (Me-PTTP-Me), 5,5'-*bis*[4-methoxylphenyl]-2,2'-bithiophene (MeO-PTTP-OMe) and 5,5'-*bis*(4-*tert*-butylphenyl)-2,2'-bithiophene (tertBu-PTTP-tertBu) novel synthetic schemes were elaborated. The oligomers with methyl (Me-PTTP-Me) and methoxyl terminal groups (MeO-PTTP-OMe) were prepared by the Kumada coupling reaction of 5,5'-dibromo-2,2'-bithiophene with *p*-tolylmagnesium bromide or *p*-anisole magnesium bromide, respectively (Fig. S1a). The reaction yield was 83% for Me-PTTP-Me and 86% for MeO-PTTP-OMe (as determined by GPC analysis), and the isolated yield was 63% and 58%,

respectively. In both cases, purification was carried out by column chromatography on silica gel followed by vacuum sublimation.

PTTP and tertBu-PTTP-tertBu were prepared in two steps (Fig. S1b). First, 2-phenylthiophene (PT) and 2-(4-tert-butylphenyl)thiophene (tertBu-PT) were synthesized by the Kumada reaction between 2-thienylmagnesium bromide, prepared *in situ* from 2-bromothiophene, magnesium, and bromobenzene or 1-bromo-4-tert-butylbenzene, respectively. Second, PTTP and tertBu-PTTP-tertBu were obtained by lithiation of PT or tertBu-PT followed by oxidative coupling reaction in presence of CuCl₂ (Fig. S1b). These reactions proceeded with high efficiency, with the yields between 78% and 84% (as determined by GPC analysis of the reaction mixture). The synthetic details are given in the SI.

5,5'-*bis*[4-fluorophenyl]-2,2'-bithiophene (F-PTTP-F), 5,5'-*Bis*[4-(trifluoromethyl)phenyl]-2,2'bithiophene (TFM-PTTP-TFM) and 5,5'-*bis*(4-trimethylsilyl-phenyl)-2,2'-bithiophene (TMS-PTTP-TMS) were synthesized according to the methods described previously.⁵ 4P and 4T were synthesized according to the methods described in Refs. [28] and [29], respectively.

3.2. Electronic properties

3.2.1. Frontier orbitals

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Fig. 2 collates the HOMO energies for the investigated TPCOs estimated from CV analysis (see SI, Section S3, for details) and calculated by DFT at B3LYP/6-31G(d,p) level. The experimental and theoretical data, except for fluorine-containing substituents (F and TFM), are in good agreement considering a systematic bias of ~0.2 eV for calculated HOMO energies, which can be attributed to the solvent effect: the calculations were performed for isolated molecules, while the experimental data were recorded for solutions. To check this hypothesis, we also performed the calculations in solution (CH₂Cl₂) using a polarizable continuum model (SI, Section S2). In the latter case, for all the TPCOs except for TFM-PTTP-TFM, the HOMO energies indeed decreased by ~0.1 eV as compared to the isolated molecules (Fig. S4a). However, the observed differences between the calculated and experimental HOMO energies became not systematic, which probably should be assigned to oversimplified treatment of the solvent effect in the polarizable continuum model. Because of this, we will use below the calculations for isolated molecules, which involve less approximations. The second source of the difference between the theoretical and experimental HOMO energies is in the moderate size of the basis set used, 6-31G(d,p). Using the extended basis set (6-311G(d,p)) provided the HOMO energies closer to the experimental data, as shown in SI, Section S2. However, the vibrational analysis with this extended basis set yielded imaginary frequencies, which we could not eliminate. Since vibrational properties constitute an essential part of this study, we will use below the data calculated with the 6-31G(d,p) basis set. Comparison of the molecular properties calculated with the 6-31G(d,p) and 6-311G(d,p) basis sets (SI, Section S2) shows that the trends discussed below are similar for both basis sets. Thus, the extension of the basis set does not affect the conclusions of this study.

For the fluorine-containing substituents (F and TFM), the relative HOMO energies as compared to PTTP are in less agreement with the experiment than for the other studied compounds (considering the abovementioned systematic bias of ~0.2 eV). Specifically, F increases the experimental HOMO energy as compared to the unsubstituted TPCO (PTTP) by ~0.1 eV but should decrease it according to the calculations. For TFM, the experimental decrease of the HOMO energy as compared to PTTP is reproduced by the calculations; however, the calculated decrease is stronger and amounts to 0.43 eV (0.1 eV in the experiment). Considering well-known strong electron-withdrawing properties of F- and TFM-substituents, which should decrease the HOMO energy,³⁰ we assume that the deviation of the CV data from the calculated HOMO energies is because of the essentially different charge distribution patterns for the fluorine-containing TPCOs as compared to the other TPCOs studied: F and TFM groups bear large negative electrical charges (Fig. 3c) in contrast to positive charges at the substituents for the other investigated

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oligomers. Therefore, F-PTTP-F and TFM-PTTP-TFM have a larger quadrupole moment, which could strongly modify the arrangement of solvent molecular dipoles (CH₂Cl₂). As a result, the Arsolvent reorganization energies for F-PTTP-F and TFM-PTTP-TFM (and their corresponding cations) will substantially differ from those of the other TPCOs studied. These changes could facilitate electron detachment from the molecule. However, detailed investigation of the solvation effects on the CV data is beyond the scope of this work.

As Fig. 2a shows, TFM results in the largest decrease of both the HOMO and LUMO energies (0.43 eV in theory, 0.1 eV in experiment), whereas MeO results in the largest increase of these energies (0.27 eV in calculations, 0.28 eV in experiment). Me and tertBu substituents also increase the energies of the frontier orbitals, although to a lesser extent (0.1 eV in theory, ~0.2 eV in experiment) than MeO group. From the calculations, TMS has a negligible effect on the HOMO and LUMO energies, while F slightly decreases both HOMO and LUMO energies. Fig. 2b shows that the calculated HOMO values are in excellent correspondence with the Hammet constants of the substituents, ³⁰ σ , which describe the ability of the group to donate/withdraw the electron density to/from the conjugated core. The similar correspondence is observed for LUMO (SI, Fig. S4b). This means that the HOMO and LUMO energies of a terminal-substituted PTTP can be rather accurately predicted just from the σ values of the substituents. Fig. 2c-h presents the HOMO and LUMO patterns, as well as the histograms of the estimated HOMO electron densities at various atoms, for PTTP and its derivatives showing the strongest effect of the substituents – MeO-PTTP-MeO and TFM-PTTP-TFM. It clearly shows that both the HOMO and LUMO are concentrated at the PTTP core, mostly at the thiophene rings. Specifically, outermost α -carbon atoms of the thiophene rings (labeled as 2 and 5 in Fig. 2c) bear the largest π -electron density (HOMO and LUMO). Among the phenyl ring atoms, the largest π -electron density is located at the terminal atom (labeled as 9 in Fig. 2c). As a result of hyperconjugation,³¹ the substituents bear small π -electron (HOMO and LUMO) density, which explains the fact that the substituents slightly affect the HOMO/LUMO and optical bandgaps (see Fig. 7b). Although the substituents (except for MeO) are formally not involved into the π conjugated system, the small π -electron density at the substituents for the oligomers investigated affects significantly the radiative decay rate and PLQY as shown below.



Fig. 2. Effect of symmetric terminal substituents of PTTP on the frontier orbitals. (a) Calculated HOMO (rer.) and LUMO (blue) energies and experimental HOMO energies (black). Dashed lines indicate the calculated HOMO and LUMO levels of unsubstituted PTTP. The TPCOs in the investigated series are arranged in order of increasing the molecular length, from the shortest (PTTP) to the longest (TMS-PTTP-TMS). (b) Correlation between the calculated HOMO energy and Hammet constant of the substituent (for para-substitution, taken from Ref. [30]). The line is a linear fit. (c-h) HOMO patterns (c,e,g) and estimated electron density at HOMO (d,f,h) for PTTP, MeO-PTTP-MeO and TFM-PTTP-TFM. The bars indicate the HOMO electron density. Atoms belonging to thiophene rings, phenyl (phenylene for the substitued PTTPs) rings, and substituents are highlighted with blue, green, and red frames, respectively.



3.2.2. Charge distribution, conjugation length and molecular polarizability

Fig. 3. Comparison of charge distribution in unsubstituted, MeO, and TFM substituted PTTP. (a) Mulliken charges for PTTP. (b,c) Difference in Mulliken charges for MeO-PTTP-MeO (b) and TFM-PTTP-TFM (c) as compared to PTTP. Red (blue) color denotes positive (negative) Mulliken charge. Note that color scheme is different for panels (a) and (b,c): dark blue (red) corresponds to -0.25e (+0.25e) at (a) but to -0.025e (+0.025e) at (b) and (c). Black labels at (b,c) denote the difference between the Mulliken charge for substituted and unsubstituted PTTPs; grey labels denote the Mulliken charges for substituents atoms. Fig. 4. Calculated conjugation lengths (a) and static electronic polarizabilities along the longest molecular axis (b) for the TPCOs investigated.

To get a deeper understanding of the effect of substituents on the electronic properties of substituted PTTP, we analyzed changes in the charge distribution, effective conjugation length of the molecule, and molecular polarizability with substitution. Fig. 3 compares the Mulliken charges for PTTP and its substituted counterparts. In PTTP, the hydrogen and sulfur atoms bear positive charges, while the carbon atoms are negatively charged. As follows from Fig. 3b,c, terminal substitution affects mostly the charge density at the aromatic rings adjacent to the substituents (phenylenes) and has a negligible impact on the more distant aromatic rings (thiophenes). Fig. 3b also shows that MeO substitution provides an extra negative charge to the conjugated core so that the electron affinity and ionization potential decrease, and the frontier orbital energies increase (Fig. 2a). On the contrary, TFM substitution (Fig. 3c) results in extra positive charge on the conjugated core – this should increase the electron affinity and ionization potential, i.e., decrease the HOMO and LUMO energies as observed in Fig. 2a.

To quantify the involvement of the substituents into π -conjugation/hyperconjugation, we estimated the conjugation lengths for HOMO and LUMO as $l_{H,L} = \sqrt{\sum_{i} c_i^2 r_i^2} / \sqrt{\sum_{i} c_i^2}$, where c_i are the

coefficients of the *i*-th atom wavefunctions in the corresponding molecular orbitals (see Fig. S5b), and then obtained the effective conjugation length as $l = \sqrt{l_H \cdot l_L}$. Fig. 4a presents *l* for the investigated

TPCOs. It increases from PTTP to TMS-PTTP-TMS, i.e., with the increase of the substituent size and hence the molecule length. For MeO-PTTP-MeO, *I* is larger than for all the other investigated TPCOSTIGNED should be attributed to a significant involvement of the oxygen atoms of MeO groups into π -conjugation (see Fig. 2e,f and Fig. S5a).

Fig. 4b shows the calculated static electronic polarizabilities of PTTP and its substituted counterparts. The polarizability gradually increases within the investigated series from PTTP to TMS-PTTP-TMS. This fact can be naturally assigned to the *l* increase. Noteworthily, in contrast to *l*, the polarizability does not reach maximum for MeO-PTTP-MeO, probably because of an additional contribution in the polarizability of the bulky tertBu and TMS groups to the overall polarizability of the molecule. For TPCOs with the similar sizes of the substituents – PTTP and F-PTTP-F, as well as Me-PTTP-Me and TFM-PTTP-TFM, – the polarizabilities are nearly equal. The variation of the polarizability in the TPCOs series affects the radiative lifetime as described below.

3.3. Vibrational properties

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Changes in the vibrational spectra with substitution can elucidate changes in the molecular geometry and π -electron density distribution, since the frequencies of the vibrational modes are determined by the force constants sensitive to the molecular geometry and charge density, whereas the Raman intensities are determined by the vibrational modulation of the π -conjugated electronic system.^{32, 33} In this section, first of all, we compare Raman spectra of PTTP and oligomers comprised of either only thiophene or only phenyl (phenylene) aromatic rings – quaterphenyl (4P) and quaterthiophene (4T), and distinguish the vibrational modes with dominant motion of thiophene rings from that of phenyl (phenylene) ones. Then, we analyze the effect of the substituents on the Raman frequencies/intensities.

3.3.1. Thiophene- and phenyl-associated vibrational modes

Fig. 5 collates the experimental and calculated Raman spectra for 4P, 4T, and PTTP in the frequency range of 900-1700 cm⁻¹, which contains the most part of the intensive Raman modes. The experimental and theoretical spectra are in good agreement strongly supporting the reliability of the calculated molecular geometries and vibrational modes. To match the theoretical and experimental spectra, the calculated vibrational frequencies were multiplied by a factor of 0.97. Such vibrational frequency scaling is a common practice for DFT calculations, and the scaling factor chosen is close to the values of 0.961-0.969 recommended for the DFT functional used in this study (B3LYP).³⁴ The scaled calculated vibrational frequencies will be used below.

As follows from Fig. 5, seven modes are the most intensive in the PTTP Raman spectrum. Among them, positions and relative intensities of the experimental (calculated) bands at ~1060 (1052) and ~1462 (1463) cm⁻¹ are similar to the bands of 4T, whereas those at ~1000(985) and 1600 (1606) cm⁻¹ are close to the bands of 4P. The atomic vibrational displacements (vibrational pattern) shown in Fig. S9 indicate that all these modes correspond to the collective motion of atoms in the conjugated molecular core. These displacements confirm that the bands at ~1060 (1052) and ~1462 (1463) cm⁻¹ of PTTP are indeed associated mainly with vibration of the thiophene rings (similar to 4T), whereas bands at ~1000 (985) and 1600 (1606) cm⁻¹ are associated with vibration of the phenyl moieties (similar to 4P). On the other hand, some PTTP modes, e.g., at ~1440 (1441) and 1500 (1494) cm⁻¹, incorporate comparable contributions from the vibrations of both phenyl and thiophene moieties.

To quantify the contributions of vibrations of thiophene and phenyl moieties to the *i*-th vibrational mode of PTTP, we introduce the quantities

$$T_{i} = \frac{\sum_{j,thiophene} m_{j} \Delta r_{ij}^{2}}{\sum_{j,all} m_{j} \Delta r_{ij}^{2}}, \qquad P_{i} = \frac{\sum_{j,phenyl} m_{j} \Delta r_{ij}^{2}}{\sum_{j,all} m_{j} \Delta r_{ij}^{2}}$$

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where m_j is the mass of atom j and Δr_{ij} is the vibrational displacement of this atom for the studied vibrational mode. Summation in the numerator of T_i and P_i runs over carbon and sulfur atoms in thiophene and phenyl rings, respectively; summation in the denominators runs over all the carbon and sulfur atoms in the molecule. We omitted summation over hydrogens as they are practically not involved in the π conjugation/hyperconjugation. The larger the T_i (P_i) value, the larger the contribution from the atoms of the thiophene (phenyl) rings to the given vibrational mode. We will refer to the modes with dominating contribution of thiophene atoms motion (large T_i) as to "thiophene modes", and to that with dominating contribution of phenyl atoms motion (large P_i) as to "phenyl modes". The calculated values of T_i and P_i are shown in Fig. 5 as blue and red bars, respectively.



Fig. 5. Experimental (line) and calculated (bars) Raman spectra of 4P (a), 4T (b), PTTP (c). The experimental spectra were recorded for polycrystalline powders, the calculations were performed for isolated molecules. The calculated intensity bars for PTTP are divided to show the contribution of thiophene (blue) and phenyl (red) atoms motions to the corresponding modes. Dashed lines are guides to the eye, they indicate positions of the most intensive calculated Raman bands for 4P and 4T for their comparison with PTTP.

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3.3.2. Impact of substituents on Raman spectra

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Fig. 6 illustrates the effect of substituents on the Raman spectra of the TPCOs studied. The calculated and experimental frequencies as well as the corresponding relative intensities are in close agreement. Most of the PTTP modes are retained in the spectra of the substituted oligomers; however, some modes show considerable frequency and intensity variations with the substituent.

The most pronounced changes were observed for PTTP experimental (calculated) Raman bands at ~1000 (982), 1440 (1441), 1500 (1494) and 1600 (1606) cm⁻¹. All these modes have large P_i and small T_i (see Fig. 5), whereas the modes with large T_i and small P_i are much less sensitive to substituents. In the experimental Raman spectra of the substituted PTTPs (Fig. 6a), the former two modes (~1000 and 1440 cm⁻¹) are significantly shifted (see SI, Section S4) and nearly disappeared. Similar changes were observed in calculations except for MeO-PTTP-MeO. These two modes in PTTP contain significant contributions from the motion of the atoms at the terminals of PTTP, namely C and H, as shown in Fig. S10. Therefore, the substituents restrict the motion of the terminal C atoms resulting in changes in the corresponding vibrational patterns. The modes at 1500 (1494) and 1600 (1606) cm⁻¹ of PTTP do not show such a pronounced reduction in the intensity but demonstrate significant frequency shifts (Fig. 6a). Fig 6b shows that the shift of the peak frequencies for experimental (calculated) bands at ~1500 (1494) cm⁻¹ and 1600 (1606) cm⁻¹ correlates well with the absolute value of the Hammet constant of the substituent, $|\sigma|$: these frequencies increase for either electron-donating (Me, MeO, tertBu) or electron-withdrawing (F, TFM) substituents. The frequency increase can be attributed to the altered charge distribution at the phenylene moieties, which makes the structure more quinoid-like. In fact, as shown for both the strongest electrondonating/withdrawing (MeO/TFM) substituents in Table S1, the bond lengths between atoms 7-8 and 10-11 shorten, whereas those between atoms 8-9 and 9-10 (see Fig. 2c for atoms numbers) lengthen. In contrast, the bond lengths within the thiophene rings are unaltered. The results obtained confirm our suggestion that terminal substituents affect mostly the π -electron density on the adjacent phenylene rings, while the electronic structure of the thiophene rings remains nearly unaffected.



Fig. 6. The effect of substituents on the Raman spectra of PTTP oligomers. (a) Experimental (lines) and calculated (bars) Raman spectra. The modes showing a pronounced frequency shift with substitution are labeled with arrows. (b) Positions of the experimental Raman bands at ~1600 (top) and 1500 cm⁻¹ (bottom) as a function of the absolute value of the Hammet constant, $|\sigma|$.

3.4. Optical properties



Fig. 7. (a) Experimental absorption and PL spectra of PTTP, F-PTTP-F and MeO-PTTP-MeO in THF solution. (b) Calculated HOMO-LUMO gaps, E_{HL} (red), and optical bandgaps for absorption (blue) and luminescence (green). Dashed lines are guides to the eye showing E_{HL} and E_g for PTTP.

Fig. 7a presents the experimental absorption and PL spectra of PTTP and its substituted counterparts with the widest (F) and the narrowest (MeO) bandgaps. Experimental spectra of the other investigated process are given in Fig. S12. All the absorption (PL) spectra have very similar shapes: the absorption spectra are unstructured, while the PL spectra show a vibrational structure with a few vibrational subbands. The relative intensities of the subbands do not change significantly with substitution. Therefore, the nearly identical spectral shapes for all the TPCOs studied indicate that the substituents do not considerably affect the molecular geometry both in the ground (S_0) and in the first excited (S_1) states.

The substituents slightly affect the bandgap, E_a : the differences in absorption and emission maxima positions for the investigated TPCOs amount to 20 nm (0.1 eV). This is in good agreement with our calculations, which predict that the HOMO-LUMO gap (Fig. 2a) and E_g (Fig. 7b) are slightly affected by the substituents. The experimental and calculated E_g values for the investigated TPCOs are in the reasonable correspondence with each other (see Fig. S13). Some discrepancies should be attributed to the limited accuracy of the DFT technique, which hardly exceeds 25 meV.²⁰ The narrowest experimental absorption and emission bandgaps within the investigated series are observed for TMS-PTTP-TMS and MeO-PTTP-MeO (see Fig. 7 and Fig. S12), whereas PTTP and F-PTTP-F show the widest bandgaps. The DFT results for the HOMO-LUMO gaps and optical bandgaps shown in Figs. 2a and 7b are in line with the experimental data, except for lower calculated absorption E_a for tertBu-PTTP-tertBu and TFM-PTTP-TFM than for MeO-PTTP-MeO. The possible reason of the latter discrepancy can be a more planar conformation of MeO-PTTP-MeO in solution (experiment) than in vacuum (calculations); this suggestion is in line with the fact that the calculations reproduce much narrower luminescence E_a (which is associated with the nearly planar excited-state geometry) for this compound as compared to the other TPCOs studied. Low E_a for MeO-PTTP-MeO and TMS-PTTP-TMS most likely stem from the noticeable involvement of MeO and TMS groups into π -conjugation and hyperconjugation, respectively; this results in the longest effective conjugation length, *l*, for these TPCOs (see Fig. 2g,h and Fig. 4a). On the contrary, F-PTTP-F and PTTP have the shortest / values. Among the investigated TPCOs, only F substituent resulted in a blueshift of the experimental absorption and PL spectra, which was reproduced by the calculations for absorption. The moderate effect of substituents on E_g and the HOMO-LUMO gap (variation in the range of ~0.1-0.2 eV) can be explained by small π -electron density at the substituents as follows from Fig. 2c-h, Fig. S3 and Fig. S5.

3.4.2. Radiative decay rates and PL quantum yields

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Involvement of the substituents into a π -conjugated system of PTTP affects also the oscillator strengths, *f*, of the S₀ \rightarrow S₁ (absorption) and S₁ \rightarrow S₀ (luminescence) transitions:

$$f = \frac{2m_e}{3e^2\hbar^2} E_g \left| \mathbf{d} \right|^2, \tag{2}$$

where m_e is the electron mass, \hbar is the reduced Planck constant, and **d** is the corresponding transition dipole moment. The calculated f values are shown in Fig. 8a. They are the lowest ones for the unsubstituted and F-substituted PTTPs and the highest ones for tertBu- and TMS-substituted counterparts. The f values increase with the molecular polarizability (Fig. 4b), which in turn increases with the effective conjugation length of the TPCO due to the presence (albeit weak) of π -electron density at the substituents (see Fig. 2c-h and Fig. S5). From the calculated E_g and f values, the radiative decay rates k_r were obtained according to formula:

$$k_r = \frac{e^2 E_g^2 f}{2\pi\varepsilon_0 \hbar^2 m_e c^3},$$

where ε_0 is the vacuum permittivity, *e* is the elementary charge, and *c* is the speed of light. Fig. 8b presents the calculated k_r values for the investigated TPCO series. These values are in the range of 3.8-10⁸LtS-10⁸ s⁻¹, which is in reasonable correspondence with the available experimental data: k_r =4.3·10⁸ s⁻¹ for PTTP³⁵ and 6.5·10⁸ s⁻¹ for TMS-PTTP-TMS.³⁶ Note that higher k_r for TMS-PTTP-TMS than for PTTP obtained in the experiment is reproduced in the calculations. As follows from Fig. 8b, the substituents slightly affect the k_r values (up to 20%), which can be attributed to different involvement of the substituents into the π -conjugated system and hence the effective conjugation length (which affects *f* as mentioned above). Like the *f* values, the calculated k_r values are the lowest ones for unsubstituted and F-substituted TPCOs and the highest ones for tertBu- and TMS-substituted TPCOs.

PLQY, Φ , is governed by the interplay of the radiative decay quantified by k_r and various non-radiative decay pathways characterized by rate constant k_{nr} :

$$\Phi = \frac{k_r}{k_r + k_{nr}}.$$
(4)

The experimental Φ data for the investigated TPCOs plotted in Fig. 8b as a function of k_r is well described by Eq. (4) with the best-fit k_{nr} value (2.3±0.2)·10⁹ s⁻¹, which is ~4 times higher than k_r . These values are in line with the experimental k_{nr} values: 2.9·10⁹ s⁻¹ for PTTP³⁵ and 2.6·10⁹ s⁻¹ for TMS-PTTP-TMS.³⁶ However, k_{nr} calculated directly using Eq. (4) from k_r and Φ for the substituted PTTP studied slightly differ as shown in Fig. S14. Specifically, the lowest k_{nr} is observed for TMS-PTTP-TMS (1.77·10⁹ s⁻¹) and tertBu-PTTP-tertBu (1.95·10⁹ s⁻¹), while the highest k_{nr} is observed for Me-PTTP-Me (3.1·10⁹ s⁻¹) and F-PTTP-F (2.9·10⁹ s⁻¹). Probably, the lowest k_{nr} for TMS-PTTP-TMS and tertBu-PTTP-tertBu stem from the strongest π -electron delocalization among the TPCOs studied. The stronger delocalization could decrease the internal conversion and intersystem crossing rates since it decreases the Huang-Rhys factors (reorganization energy)³⁷ and the charge density at heavier atoms (sulfur); however, detailed investigation of the nonradiative deactivation pathways is beyond the scope of the current study.



Fig. 8. Impact of terminal substituents of PTTP on the oscillator strength and PL quantum yield. (a) Calculated oscillator strengths of $S_0 \rightarrow S_1$ (black) and $S_1 \rightarrow S_0$ (red) transitions. (b) Experimental PLQY (Φ) as a function of the calculated luminescence rate. The red line is the fit with Eq. (4), and the green line is a linear fit.

3.5. Extension to other TPCOs

To check whether our conclusions on the effect of terminal substituents are relevant for other TPCOs, we addressed the frontier orbitals, optical bandgaps and oscillator strengths for TPCOs with 5-ring conjugated core, PTPTP. TPCOs with this conjugated core are actively studied in OFETs and light-emitting devices.^{3, 38, 39} The results are given in SI, Section S4. As follows from Fig. S15, the impact of the substituents

on the HOMO and LUMO energies of the substituted PTPTPs is quite similar to that on the studied PTTPs and correlates well with the Hammet constants of the substituents. Specifically, TFM-Viandtic MeDe substituted PTPTPs show the lowest and highest HOMO/LUMO energies, respectively, in line with the results for the PTTP series. Analogously, the substituents alter the E_g and f values of PTPTPs in a similar fashion as in the PTTPs studied (see Fig. S16); e.g., the largest f is observed for TMS-PTPTP-TMS. The positive impact of TMS group on the f value is also in line with the observed increase in PLQY upon substitution of PTPTP.⁴⁰ Although further studies on other π -conjugated oligomers series are required, we anticipate that the revealed effects of the substituents are general for this class of organic semiconductor materials.

4. Conclusions

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The impact of various terminal substituents on the frontier orbitals, charge distribution, molecular polarizability, Raman spectra, optical bandgaps, radiative decay rates and PLQY was investigated for TPCOs series with 5,5'-diphenyl-2,2'-bithiopene (PTTPs) π -conjugated core. Electron-donating or electronwithdrawing substituents resulted in tuning of the HOMO and LUMO energy levels within about 0.7 eV in the calculations and 0.4 eV in the experiment in accordance with the Hammet constants of the substituents. The substitution considerably changed the electron density at the phenylenes but did not affect it at the central 2,2'-bithiophene moiety. As a result, vibrational (Raman-active) modes associated mainly with the motion of the phenyl rings showed a significant frequency shift with substitution, while those related mostly to the thiophene rings remained nearly unaffected. The substituents were found to be weakly involved in the π -conjugated system of the PTTP core, which resulted in weak changes in the absorption and emission maxima (within 0.1 eV) with substitution. However, subtle spreading of the frontier orbitals over the substituents can nearly double the photoluminescence quantum yield as observed for TMS- and tertBu-substituted PTTPs. Thus, two main factors governing the impact of the substituent were identified: the Hammet constant of the substituent and its involvement in π -conjugation (or hyperconjugation) quantified by the effective conjugation length of the substituted molecule. The revealed effect of the terminal substituents is anticipated to be general for various other TPCOs and related co-oligomers, e.g. furan-phenylene ones,^{9,41} making the established structure-property relationships valuable for the rational design of functional materials for optoelectronic applications.

Conflicts of interest

There are no conflicts of interest to declare.

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TOC entry

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Two main factors governing the effect of terminal substituents on the properties of thiophenephenylene co-oligomers are revealed.