

## Supporting Information for publication

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

Andrey Yu. Sosorev<sup>1,2</sup>, Muzaffar K. Nuraliev<sup>1</sup>, Elizaveta V. Feldman<sup>1</sup>, Dmitry R. Maslennikov<sup>1,2</sup>, Oleg V. Borshchev<sup>3</sup>, Maxim S. Skorotetcky<sup>3</sup>, Nikolay M. Surin<sup>3</sup>, Maxim S. Kazantsev<sup>4,5</sup>, Sergei A. Ponomarenko<sup>3,6\*</sup>,  
Dmitry Yu. Paraschuk<sup>1\*\*</sup>

<sup>1</sup>Faculty of Physics and International Laser Center, Lomonosov Moscow State University, Leninskie Gory 1/62, Moscow 119991, Russia

<sup>2</sup>Institute of Spectroscopy, Russian Academy of Sciences, Fizicheskaya 5, Troitsk, Moscow 108840, Russia

<sup>3</sup>Enikolopov Institute of Synthetic Polymeric Materials, Russian Academy of Science, Profsoyuznaya 70, Moscow 117393, Russia

<sup>4</sup>N.N. Vorozhtsov Novosibirsk Institute of Organic Chemistry, Lavrentieva 9, Novosibirsk 630090, Russia

<sup>5</sup>Novosibirsk State University, Pirogova 2, Novosibirsk 630090, Russia

<sup>6</sup>Department of Chemistry, Lomonosov Moscow State University, Leninskie Gory 1/3, Moscow 119991, Russia

#### 1. Synthetic details

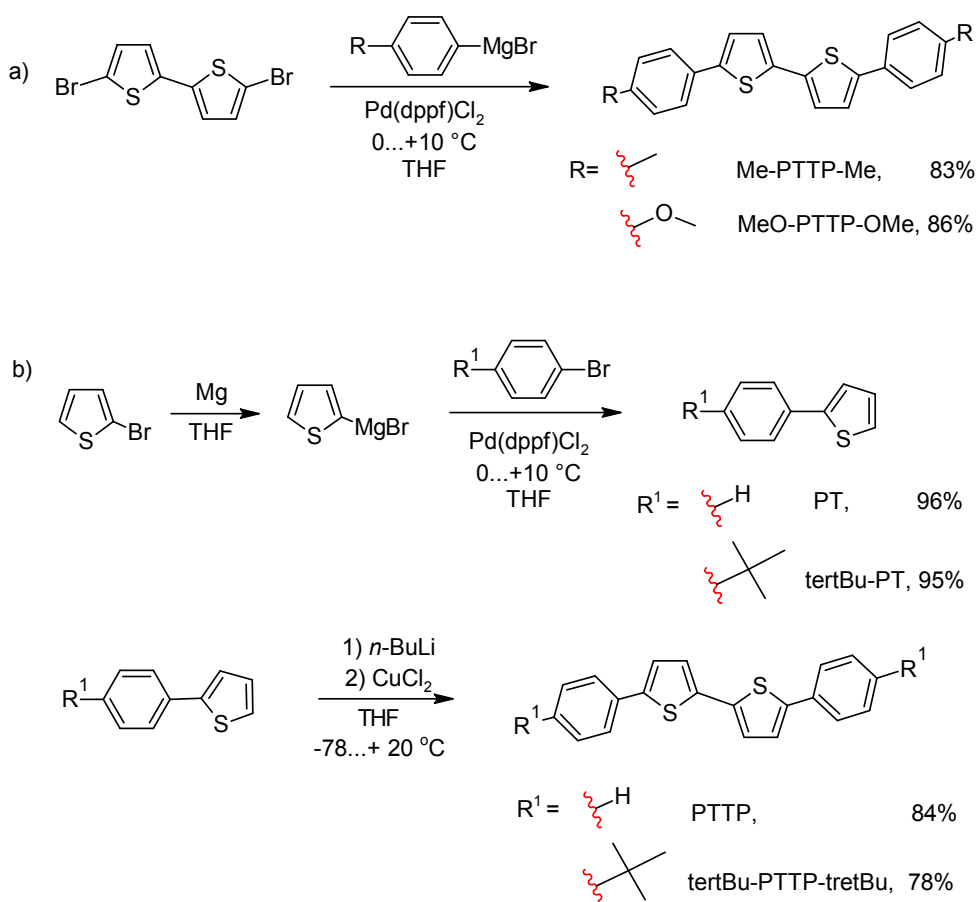


Fig. S1. Synthesis of substituted PTTPs.

**2-Phenylthiophene (PT)** [1]. A solution of 2-bromothiophene (3.42 g, 21.0 mmol) in anhydrous THF (30 mL) was added dropwise to a suspension of magnesium (0.52 g, 22.0 mmol) in THF (5 mL). The reaction mixture was refluxed during 1 h to yield 2-thienylmagnesium bromide, cooled to room temperature and added dropwise to an ice cooled solution of bromobenzene (3.00 g, 19.1 mmol) and Pd(dppf)Cl<sub>2</sub> (0.15 g, 0.21 mmol) in anhydrous THF (50 mL). Then the cooling bath was removed, and stirring was continued for 5 h at room temperature. Afterwards the reaction mixture was poured into water (500 mL), and extracted twice with freshly distilled diethyl ether (400 mL). The organic phase was separated, washed with water, dried over sodium sulfate and evaporated. The product was purified by column chromatography on silica gel (eluent toluene) to give pure **PT** (2.94 g, 96%). <sup>1</sup>H-NMR (250 MHz, CDCl<sub>3</sub>): δ (ppm) 7.10 (dd, J<sub>1</sub> = 4.9 Hz, J<sub>2</sub> = 3.7 Hz, 1H), 7.30-7.51 (overlapping peak, 5H), 7.65 (d, J = 7.3, 2H).

**2-(4-Tert-butylphenyl)thiophene (tertBu-PT)** [2]. The same procedure as above was used to give a white solid **tertBu-PT** (yield = 95%). <sup>1</sup>H-NMR (250 MHz, CDCl<sub>3</sub>): δ (ppm) 1.36 (s, 9H), 7.08 (dd, J<sub>1</sub> = 4.9 Hz, J<sub>2</sub> = 3.7 Hz, 1H), 7.24-7.31 (overlapping peak, 2H), 7.42 (d, J = 8.2, 2H), 7.57 (d, J = 8.5, 2H).

**5,5'-bis[4-methylphenyl]-2,2'-bithiophene (Me-PTTP-Me)** [3]. A solution of 4-bromotoluene (2.6 g, 15.2 mmol) in anhydrous THF (30 mL) was added dropwise to a suspension of magnesium (0.52 g, 22.0 mmol) in THF (5 mL). The reaction mixture was refluxed during 1 h to yield *p*-tolylmagnesium bromide, cooled to room temperature and added dropwise to an ice cooled solution of 5,5'-dibromo-2,2'-bithiophene (2.34 g, 7.2 mmol) and Pd(dppf)Cl<sub>2</sub> (0.08 g, 0.11 mmol) in anhydrous THF (40 mL). Then the cooling bath was removed, and stirring was continued for 5 h at room temperature. Afterwards the reaction mixture was poured into water (500 mL) and extracted twice with toluene (400 mL). The organic phase was separated, washed with water, dried over sodium sulfate and evaporated to give 2.62 g of crude product, containing 83% of **Me-PTTP-Me** (GPC). The crude product was filtered through a silica gel pad with hot toluene followed vacuum sublimation under reduced pressure to give pure yellow solid **Me-PTTP-Me** (1.75 g, 70%). mp 250–251 °C. <sup>1</sup>H-NMR (250 MHz, CDCl<sub>3</sub>): δ (ppm) 2.37 (s, 6H), 7.12-7.22 (overlapping peak, 8H), 7.49 (d, J = 8.1, 4H). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ (ppm) 21.11, 123.32, 124.38, 125.69, 129.65, 131.58, 136.50, 137.57, 143.52. Anal. Calcd for C<sub>22</sub>H<sub>18</sub>S<sub>2</sub> (346.51): C, 76.26; H, 5.24. Found: C, 76.32; H, 5.26.

**5,5'-Bis[4-methoxyphenyl]-2,2'-bithiophene (MeO-PTTP-OMe)** [4]. The same procedure as that for **Me-PTTP-Me** was used. The reaction mixture contained 86% of **MeO-PTTP-OMe**, according to the GPC analysis data. The crude product was purified by vacuum sublimation to yield a yellow solid (yield = 68%). mp 271–272 °C. **MeO-PTTP-OMe** was not soluble enough for NMR measurements in CDCl<sub>3</sub>. Anal. Calcd for C<sub>22</sub>H<sub>18</sub>O<sub>2</sub>S<sub>2</sub> (378.51): C, 69.81; H, 4.79; S, 16.94. Found: C, 70.21; H, 4.88; S, 16.74.

#### **5,5'-Diphenyl-2,2'-bithiophene (PTTP)** [5]

A 1.6 M solution of *n*-butyllithium in hexane (3.35 mL, 5.4 mmol) was added dropwise to a solution of 2-phenylthiophene **PT** (0.86 g, 5.4 mmol) in anhydrous THF (30 mL), keeping the temperature below -70 °C. The reaction mixture was stirred for 10 minutes at -75 °C, then the cooling bath was removed and the mixture was allowed to warm to 0 °C. After that the reaction mixture was cooled to -78 °C and CuCl<sub>2</sub> (1.44 g, 10.7 mmol) was added in one portion. Then the reaction mixture was stirred for 30 min at -78 °C, and the temperature was slowly allowed to rise to room temperature. After completion of the reaction, 500 mL of toluene and 200 mL of water were added. The organic phase was separated, washed with water

twice, dried over sodium sulfate, and the solvent was evaporated by a Rotavapor. The reaction mixture contained 84% of **PTTP**, according to the GPC analysis data. The reaction mixture was filtered through a silica gel pad with hot toluene. The crude product was purified by recrystallization from toluene followed by vacuum sublimation to give pure **PTTP** as a yellowish solid (0.144 g, 28%),  $m_p = 240-241$  °C.  $^1\text{H-NMR}$  (250 MHz,  $\text{CDCl}_3$ ): 7.10-7.45 (overlapping peak, 10H), 7.63 (d,  $J = 7.9$ , 4H). Anal. Calcd for  $\text{C}_{20}\text{H}_{14}\text{S}_2$  (318.46): C, 75.43; H, 4.43; S, 20.14. Found: C, 76.01; H, 4.52; S, 20.10.

**5,5'-Bis(4-tert-butylphenyl)-2,2'-bithiophene (tertBu-PTTP-tertBu)** [5]. The same procedure as that for **PTTP** was used. The reaction mixture contained 78% of **tertBu-PTTP-tertBu**, according to the GPC analysis data. The crude product was purified by vacuum sublimation to yield a yellow solid (yield = 65%).  $m_p = 282-283$  °C.  $^1\text{H-NMR}$  (250 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 1.36 (s, 18H), 7.14 (d,  $J = 3.8$ , 2H), 7.18 (d,  $J = 3.8$ , 2H), 7.40 (d,  $J = 8.5$ , 4H), 7.54 (d,  $J = 8.22$ , 4H).  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  (ppm) 31.31, 34.67, 123.40, 124.39, 125.53, 125.88, 131.52, 136.58, 143.41, 150.94. Anal. Calcd for  $\text{C}_{28}\text{H}_{30}\text{S}_2$  (430.69): C, 78.09; H, 7.02; S, 14.89. Found: C, 78.16; H, 7.09; S, 14.81 .

For the synthesis, hexane solutions of 1.6M n-butyllithium (CAUTION: solution can ignite in contact with water and carbon dioxide <sup>6</sup>), 2-bromothiophene, bromobenzene, 4-bromotoluene, 4-bromoanisole, 1-bromo-4-tert-butylbenzene, magnesium, copper (II) chloride, 1,1'-bis(diphenylphosphino) ferrocene palladium (II)  $\text{Pd}(\text{dppf})\text{Cl}_2$  were obtained from Sigma–Aldrich Co. and used without further purification. 5,5'-Dibromo-2,2'-bithiophene was synthesized as described in Ref. <sup>7</sup>. All reactions, unless stated otherwise, were carried out in an inert atmosphere using anhydrous solvents.

The purity and molecular structures of all oligomers synthesized were confirmed by  $^1\text{H NMR}$ , GPC spectroscopy and elemental analysis. The  $^1\text{H NMR}$  spectra were recorded on a Bruker AC-250 spectrometer (250 MHz) using the residual signal of  $\text{CDCl}_3$  ( $\delta$  7.27 ppm) as the internal standard. The  $^{13}\text{C NMR}$  spectra were recorded on a Bruker AVII-300 spectrometer at working frequencies 75 MHz. Elemental analysis of C, H elements was carried out using CHN automatic analyzer CE1106 (Italy). The settling titration using  $\text{BaCl}_2$  was applied to analyze sulphur. Experimental error is 0.30–0.50%. GPC analysis was performed on a Shimadzu instrument with a RID10A<sup>VP</sup> refractometer and a SPD-M10A<sup>VP</sup> diode matrix as detectors using  $7.8 \times 300$  mm<sup>2</sup> Phenomenex columns (USA) filled with the Phenogel sorbent with pore size of 500 Å and THF as the eluent.

## 2. Electronic properties

### Equilibrium geometry

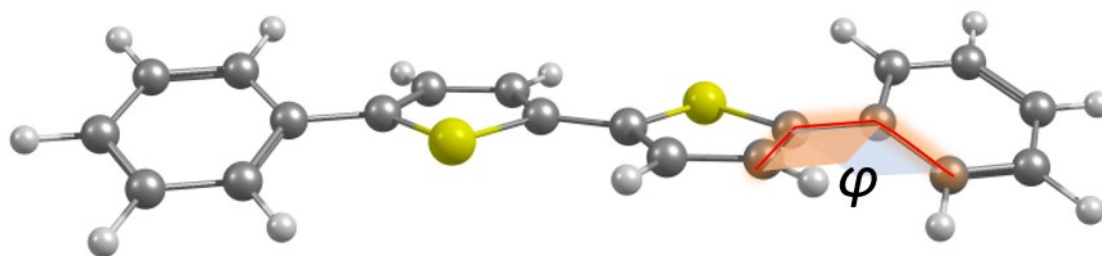


Fig. S2. Equilibrium geometry of PTPP obtained using DFT at B3LYP/6-31g(d,p) level.

Fig. S2 presents the optimized geometry of PTPP molecule. In line with previous observations,<sup>8</sup> the planes of phenyl rings are twisted with respect to the thiophene ones. The twist angle,  $\varphi$ , amounts  $\sim 26^\circ$  in vacuum and  $\sim 17^\circ$  in  $\text{CH}_2\text{Cl}_2$ .

### Calculated frontier molecular orbitals

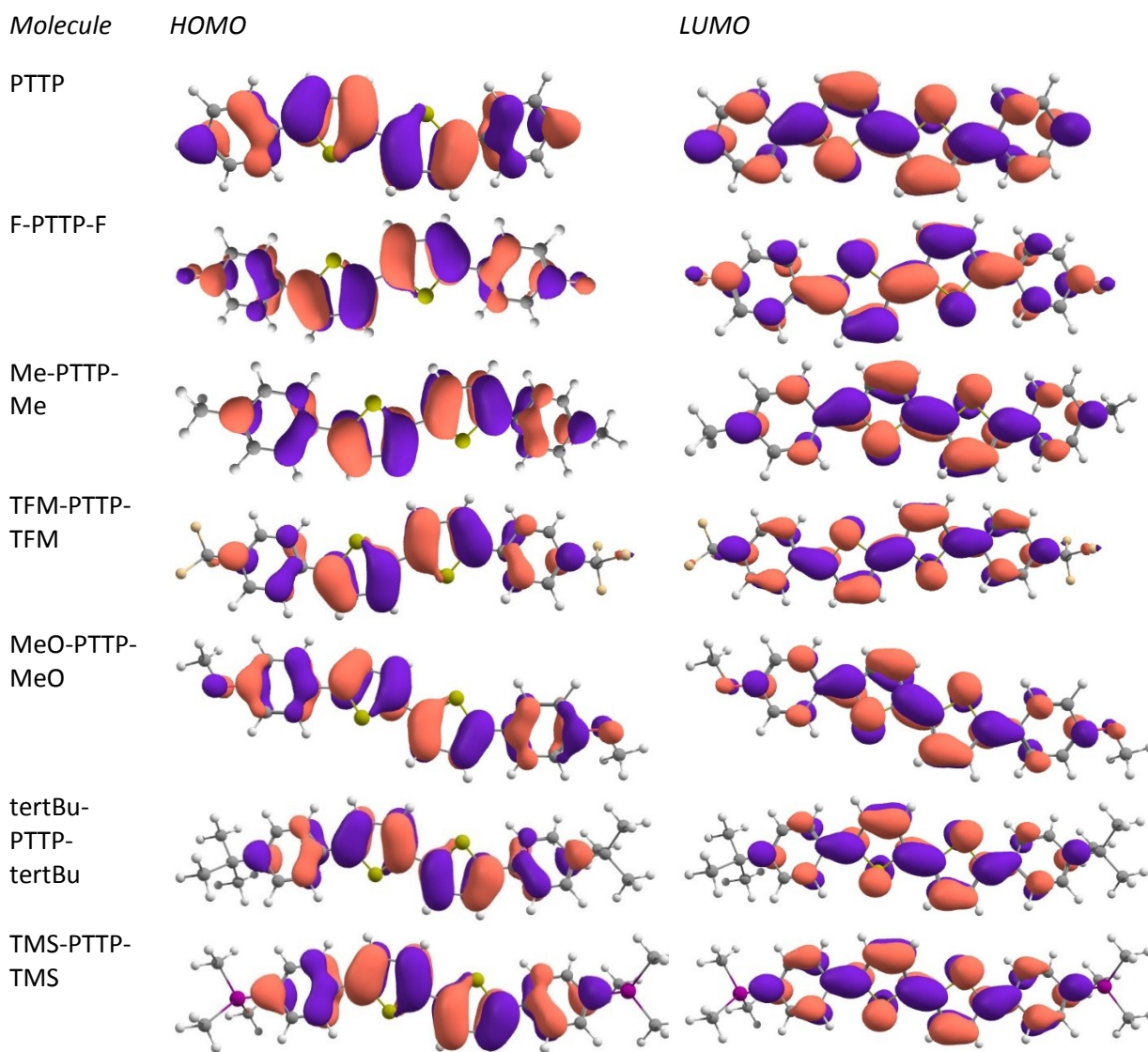


Fig. S3. HOMO and LUMO patterns of the investigated TPCOs.

a)

b)

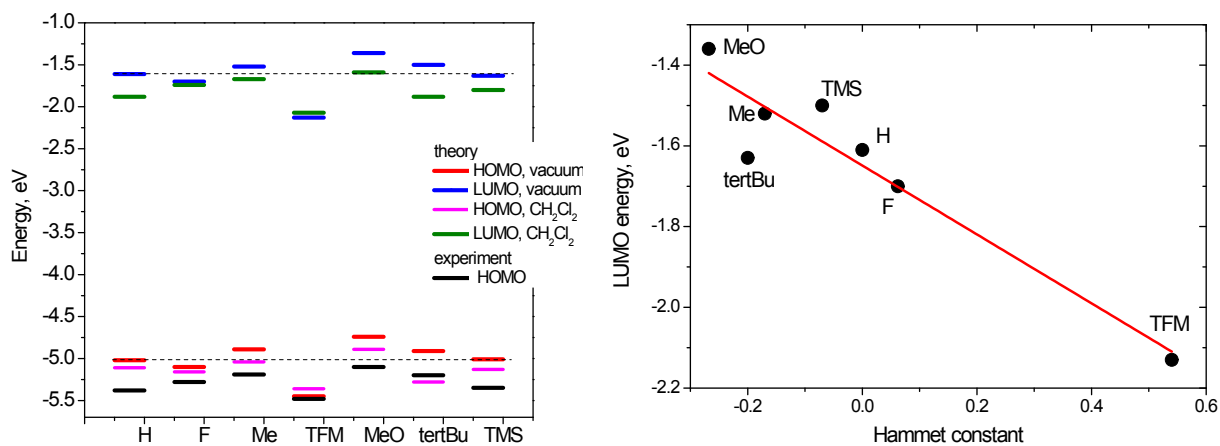


Fig. S4. Experimental and calculated energies of HOMO and LUMO for the PTPT series with various symmetric terminal substituents. (a) Effect of solvent on frontier orbital energies. (b) Correlation between the calculated LUMO energies and the Hammett constants of the substituents.

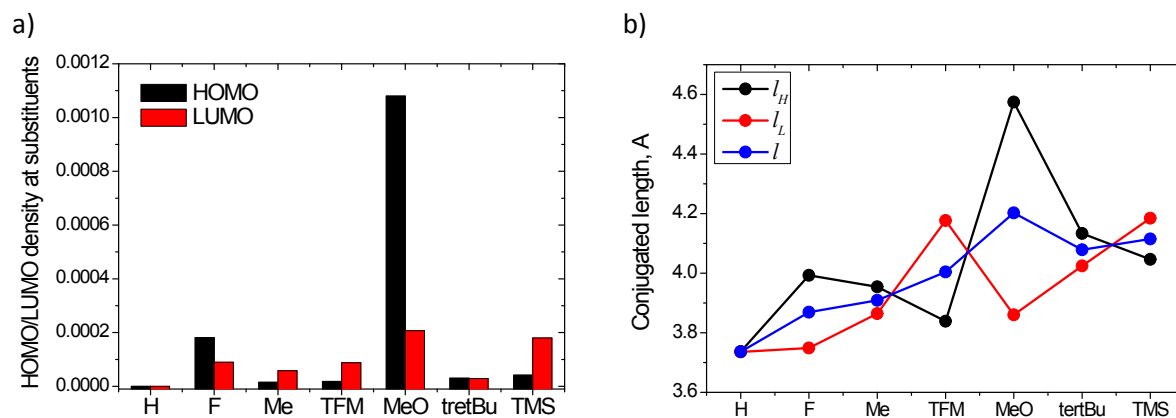
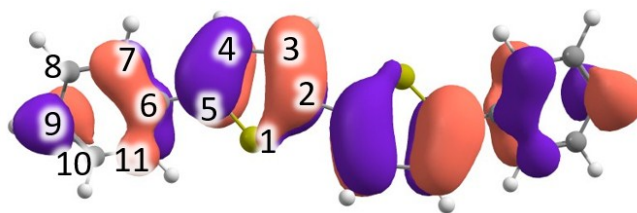


Fig. S5. Electron densities for the HOMO and LUMO at the substituents (sum over all atoms) for the TPCOs studied (a) and conjugated length for HOMO,  $l_H$ , LUMO,  $l_L$ , and their geometrical average  $l = \sqrt{l_H \cdot l_L}$  (b).

## Bond lengths



Atom pair	H	TFM	MeO
Phenyl ring			
7 – 8	1.393	1.389	1.394
10 – 11	1.393	1.391	1.386
6 – 7	1.408	1.409	1.404
6 – 11	1.407	1.407	1.410
8 – 9	1.397	1.399	1.400
9 – 10	1.396	1.396	1.403
Thiophene ring			
1 – 2	1.756	1.755	1.758
1 – 5	1.756	1.755	1.757
4 – 5	1.378	1.379	1.378
3 – 4	1.417	1.416	1.418
2 – 3	1.381	1.381	1.380

Table S1. Selected bond lengths for PTTP and substituted PTTPs with the strongest electron-donating/accepting (MeO/TFM) substituents. The atoms numbers are given above the table. All lengths are in Å.

Comparison of results obtained using 6-31G(d,p) and 6-311G(d,p) basis sets

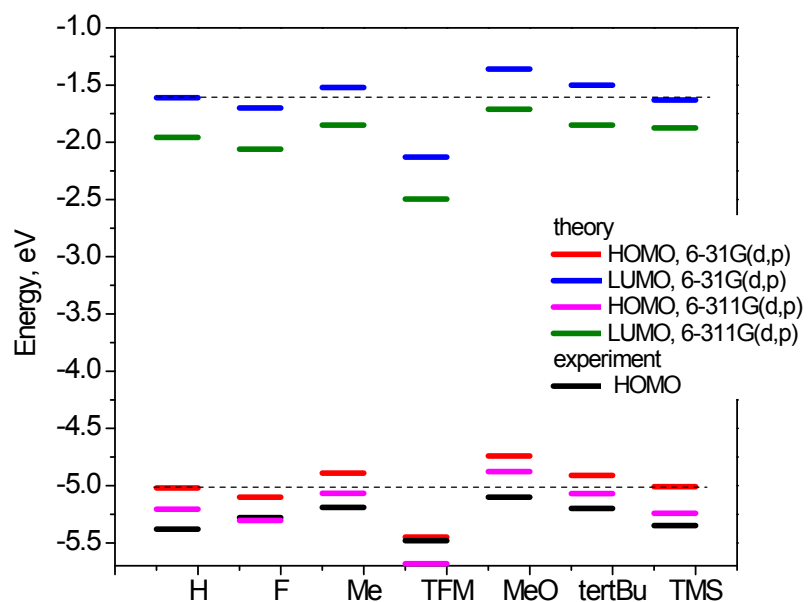


Fig. S6. Frontier orbitals energies of the studied TPCOs in 6-31G(d,p) and 6-311G(d,p) basis sets compared to the cyclic voltammetry data.

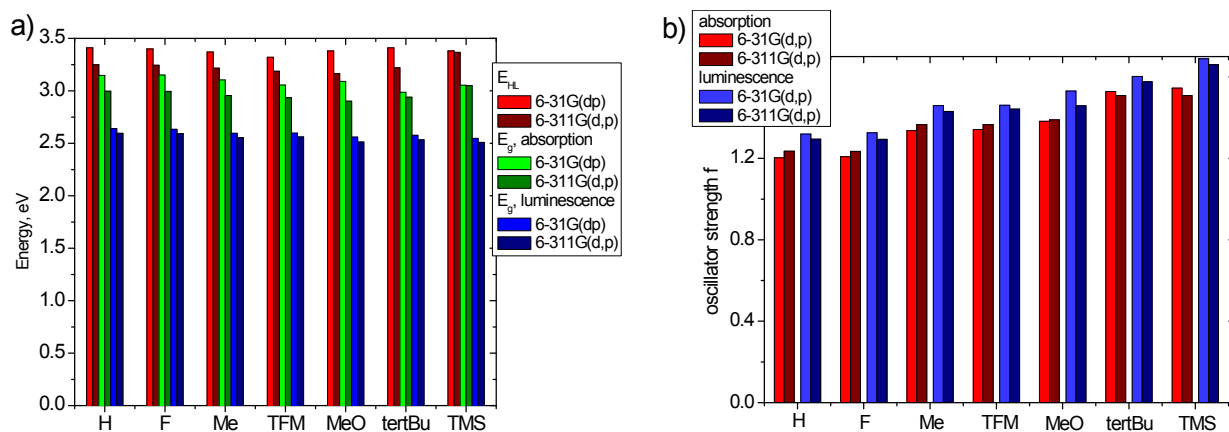


Fig. S7. HOMO-LUMO gaps,  $E_{HL}$  (red), and optical bandgaps for absorption (blue) and luminescence (green) calculated using 6-31G(d,p) and 6-311G(d,p) basis sets.

Figs. S6 and S7 collates the frontier orbitals energies, optical bandgaps and oscillator strength obtained using 6-31G(d,p) and 6-311G(d,p) basis sets. From Fig. S6 it follows that the latter basis set yields HOMO energies  $\sim 0.15$ - $0.2$  eV lower and LUMO energies  $\sim 0.2$ - $0.3$  eV lower than the former one and better reproduces the cyclic voltammetry data. Fig. S7a shows that optical bandgaps in the 6-311G(d,p) basis set are slightly lower than in the 6-31G(d,p) one. Fig. S7a indicates that the oscillator strengths of some compounds are slightly lower in 6-311G(d,p) basis set, and for the others in 6-31G(d,p) one. Nevertheless, the general trends established in this study for 6-31G(d,p) basis set are retained in the 6-311G(d,p) one.

### 3. Cyclic voltammetry details

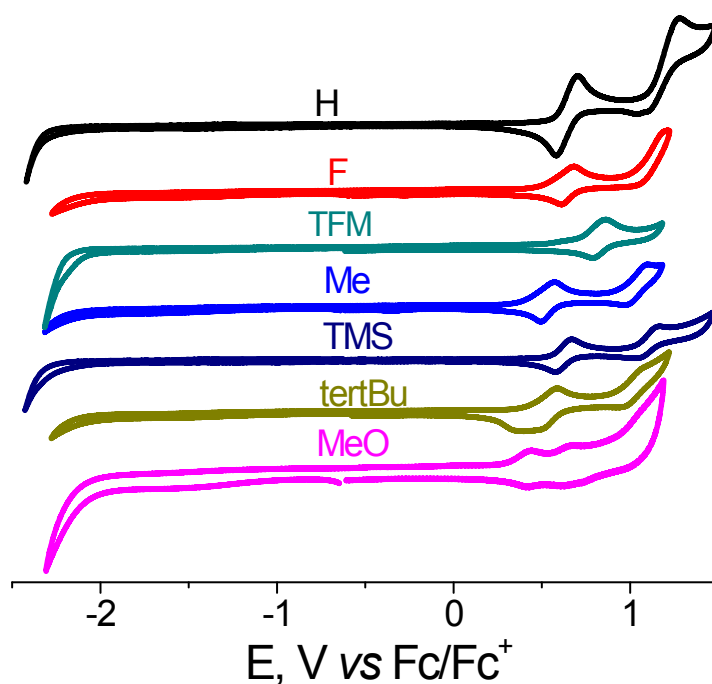


Fig. S8. Cyclic voltammograms of PTPP with various terminal substituents in  $\text{CH}_2\text{Cl}_2$  solution.

#### 4. Vibrations

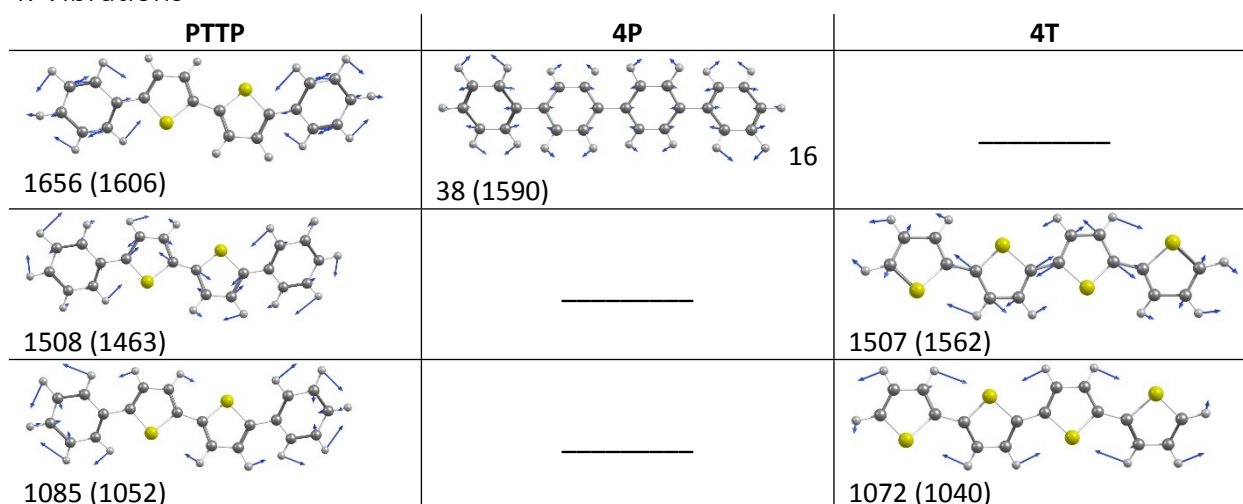
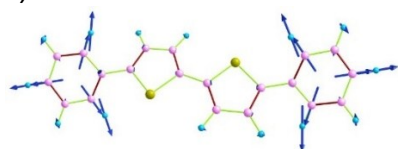


Fig. S9. Comparison of vibrational patterns in PTTP with those in 4P and 4T for three modes. The left column shows vibrations of PTTP with dominating contributions of phenyl rings motion (top), thiophene rings motion (middle) and their combination (bottom). The right panel displays the corresponding vibrations of 4P and 4T. Vibrational frequencies multiplied by 0.97 are given in parenthesis.

For PTTP, the most intensive vibration at  $\sim 1462\text{ cm}^{-1}$  is an in-phase symmetric  $\nu(\text{C}=\text{C})$  stretching spreading over the whole oligothiophene backbone; vibration at  $\sim 1499\text{ cm}^{-1}$  is the in-phase antisymmetric  $\nu(\text{C}=\text{C})$  vibration mostly localized on the outer rings of the oligothiophene chain; mode at  $\sim 1442$  is a collective symmetric  $\nu(\text{C}=\text{C})$  vibration, mostly localized on the inner thiophene rings;<sup>9</sup> mode at  $\sim 1600\text{ cm}^{-1}$  is localized mostly at the peripheral phenyl rings (see Fig. S8). The atomic displacements shown in Fig. S8 confirm our suggestion that peaks at  $\sim 1442\text{ cm}^{-1}$  and  $\sim 1030\text{ cm}^{-1}$  for PTTP correspond to vibration of the inner thiophene rings (similar to 4T), while peaks at  $\sim 1000\text{ cm}^{-1}$  and  $\sim 1600\text{ cm}^{-1}$  corresponds to the vibration of phenyl moieties (similar to 4P). On the other hand, some PTTP vibrations, e.g.  $1060\text{ cm}^{-1}$  (calc) and  $1491$  (calc), incorporate comparable contributions from the vibrations of both phenylene and thiophene moieties.

The most pronounced changes are for PTTP modes at  $\sim 1000$  and  $1440\text{ cm}^{-1}$ . In the Raman spectra of the PTTP derivatives (Fig. 7), these modes seem to disappear. However, the comparative analysis of the DFT results for PTTP, TMS-PTTP-TMS and TFM-PTTP-TFM yields that these modes are just significantly altered. Specifically, the experimental (calculated) band at  $\sim 1442$  ( $1441$ )  $\text{cm}^{-1}$  shifts to  $\sim 1410$  ( $1411$ )  $\text{cm}^{-1}$  for TFM-PTTP-TFM and  $\sim 1395$  ( $1396$ )  $\text{cm}^{-1}$  for TMS-PTTP-TMS, with strong intensity reduction. The mode at  $\sim 1000$  ( $983$ )  $\text{cm}^{-1}$  mixes with the mode at  $1030$  ( $1027$ )  $\text{cm}^{-1}$  and provides a new one at  $\sim 1020\text{ cm}^{-1}$  for both TFM-PTTP-TFM ( $1002\text{ cm}^{-1}$ , calculated) and TMS-PTTP-TMS ( $1004\text{ cm}^{-1}$ , calculated), whose intensity is very weak.

a)  $985\text{ cm}^{-1}$



b)  $1441\text{ cm}^{-1}$

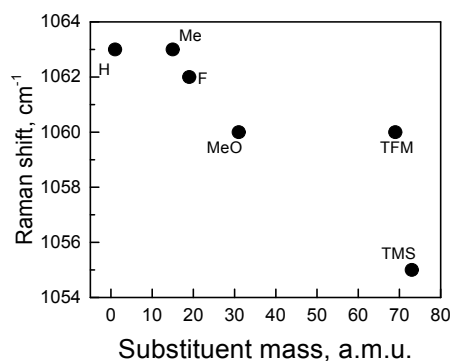
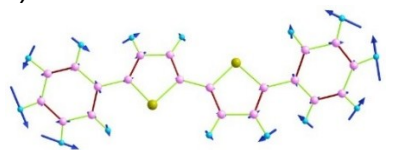




Fig. S10. Atom displacement vectors for calculated modes 985 and 1441  $\text{cm}^{-1}$  of PTPP.

Fig. S11. Experimental peak position for 1063  $\text{cm}^{-1}$  mode as a function of the substituent mass.

## 5. Optical properties

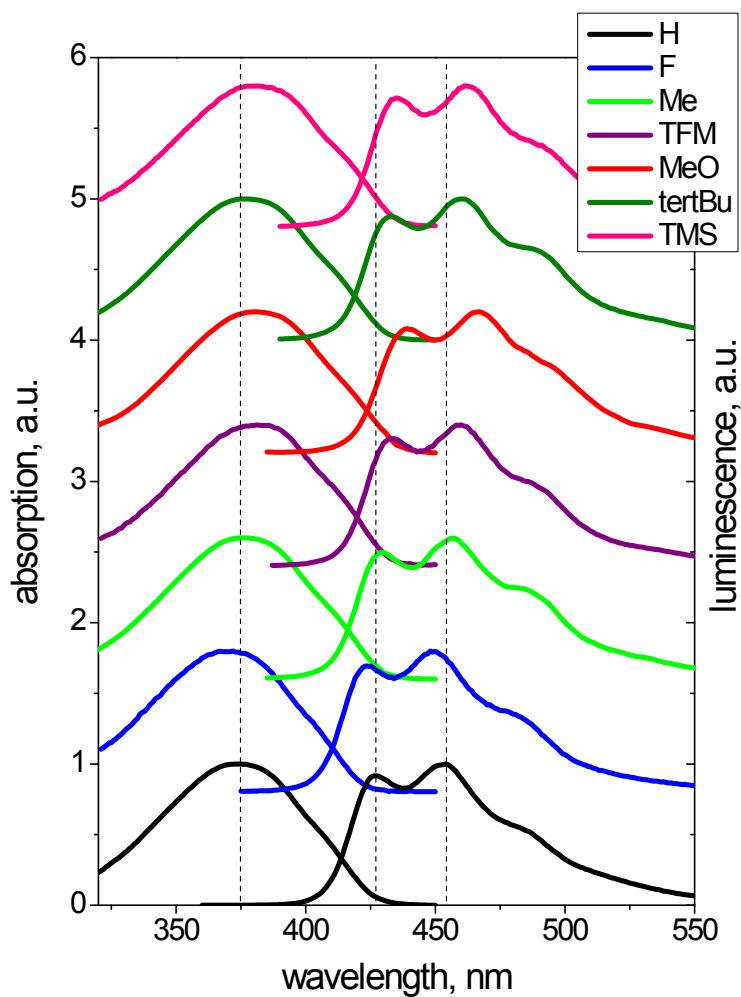


Fig. S12. Absorption and PL spectra of the investigated PTPPs. Dashed lines are guides to the eye depicting positions of the PTPP absorption maximum and two PL maxima.

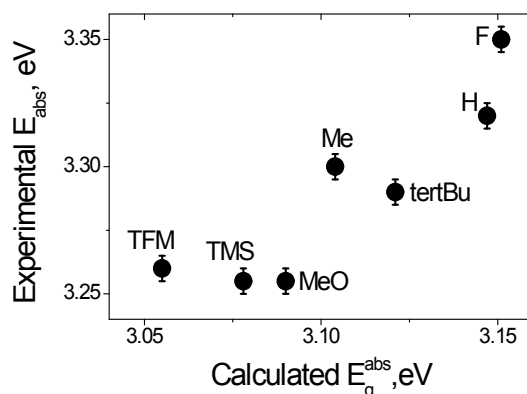


Fig. S13. Correlation between the experimental energy of the absorption maximum and calculated absorption  $E_g$  for the PTPPs studied.

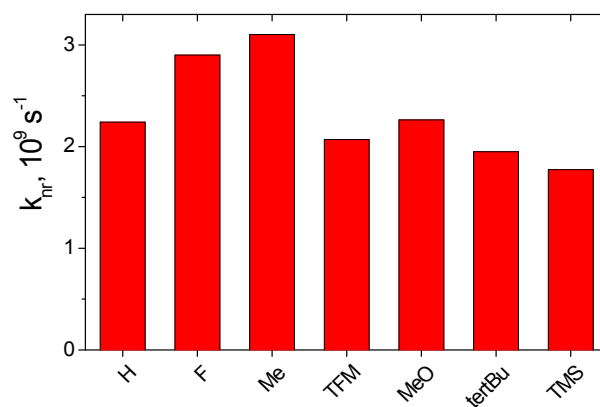


Fig. S14. Non-radiative decay rates,  $k_{nr}$ , for the investigated TPCOs evaluated from calculated  $k_r$  and experimental PLQY.

## 6. Comparison of PTPP and PTPTP series

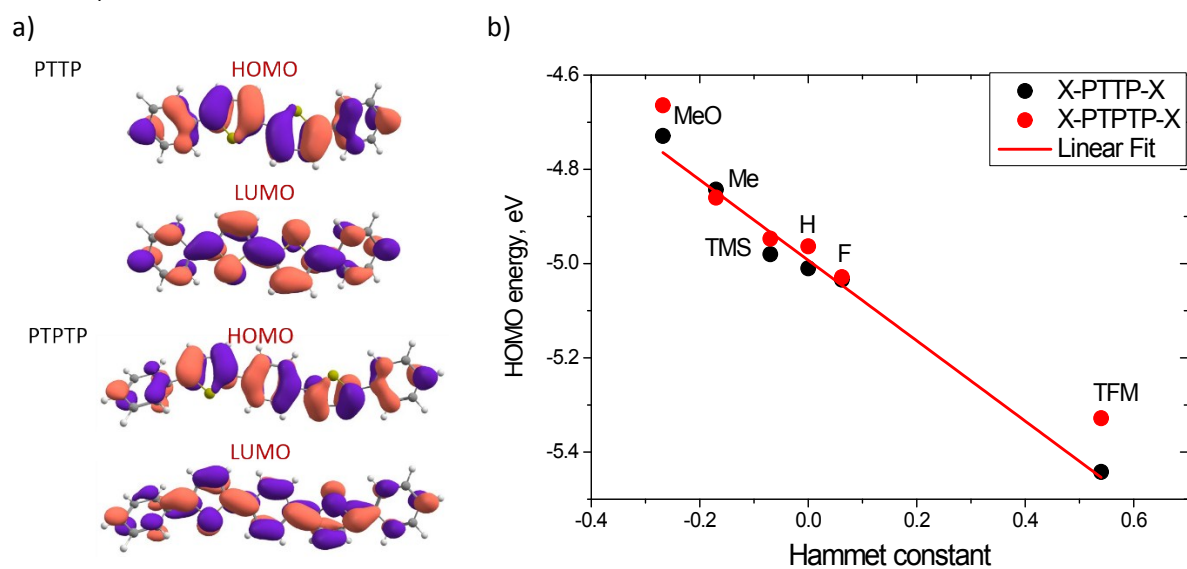


Fig. S15. Frontier orbitals of PTPP and PTPTP (a) and correlations between the Hammett constant of the substituent and the calculated HOMO energy (b).

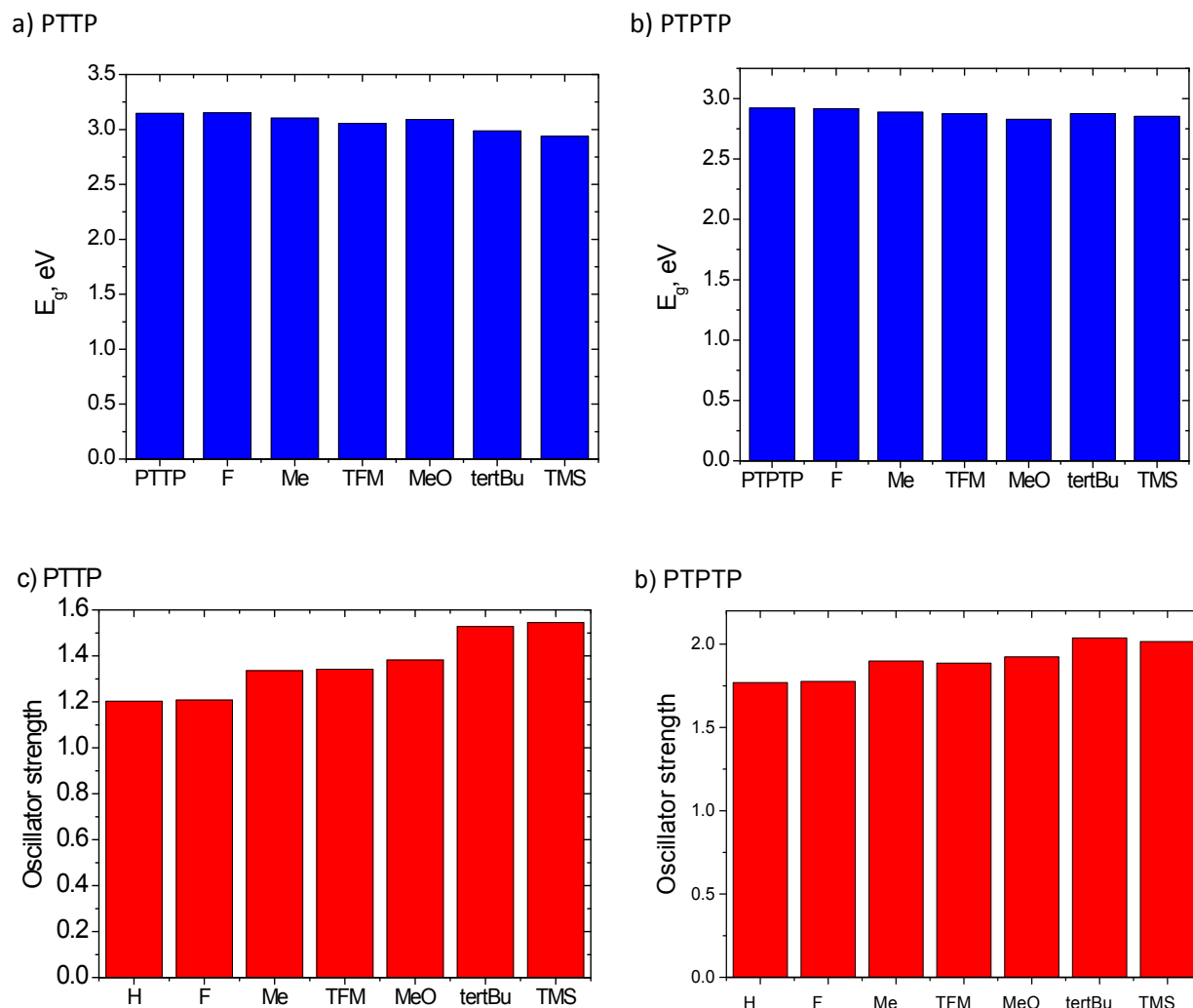


Fig. S16. Calculated optical bandgaps (a,b) and oscillator strengths (c,d) of S0-S1 transition for PTTP (a,c) and PTPTP (b,d) derivatives.

## References

1. Tsai, F.-Y.; Lin, B.-N.; Chen, M.-J.; Mou, C.-Y.; Liu, S.-T.. *Tetrahedron* **2007**, *63* (20), 4304-4309.
2. Johansson Seechurn, C. C. C.; Parisel, S. L.; Colacot, T. J. *J. Org. Chem.* **2011**, *76* (19), 7918-7932.
3. Li, Y.; Wang, J.; Huang, M.; Wang, Z.; Wu, Y.; Wu, Y. *J. Org. Chem.* **2014**, *79* (7), 2890-2897.
4. Sung, A.; Ling, M. M.; Tang, M. L.; Bao, Z.; Locklin, J. *Chem. Mater.* **2007**, *19* (9), 2342-2351.
5. Yokooji, A.; Satoh, T.; Miura, M. *Tetrahedron* **2004**, *60* (32), 6757-6763.
6. *Bretherick's Handbook of Reactive Chemical Hazards (7-th Edition)*, Ed.: P.G. Urban. Academic Press: Oxford, 2007.
7. Getmanenko, Y. A.; Twieg, R. J. *J. Org. Chem.* **2008**, *73* (3), 830-839.
8. S. A. Lee, S. Hotta and F. Nakanishi. *J. Phys. Chem. A* 2000, **104**, 1827.

9. Castro, C. M.; Delgado, M. C. R.; Hernandez, V.; Hotta, S.; Casado, J.; Navarrete, J. T. L. *J. Chem. Phys.* **2002**, *116* (23), 10419-10427.