

α -Oligofurans show a sizeable extent of π -conjugation as probed by Raman Spectroscopy

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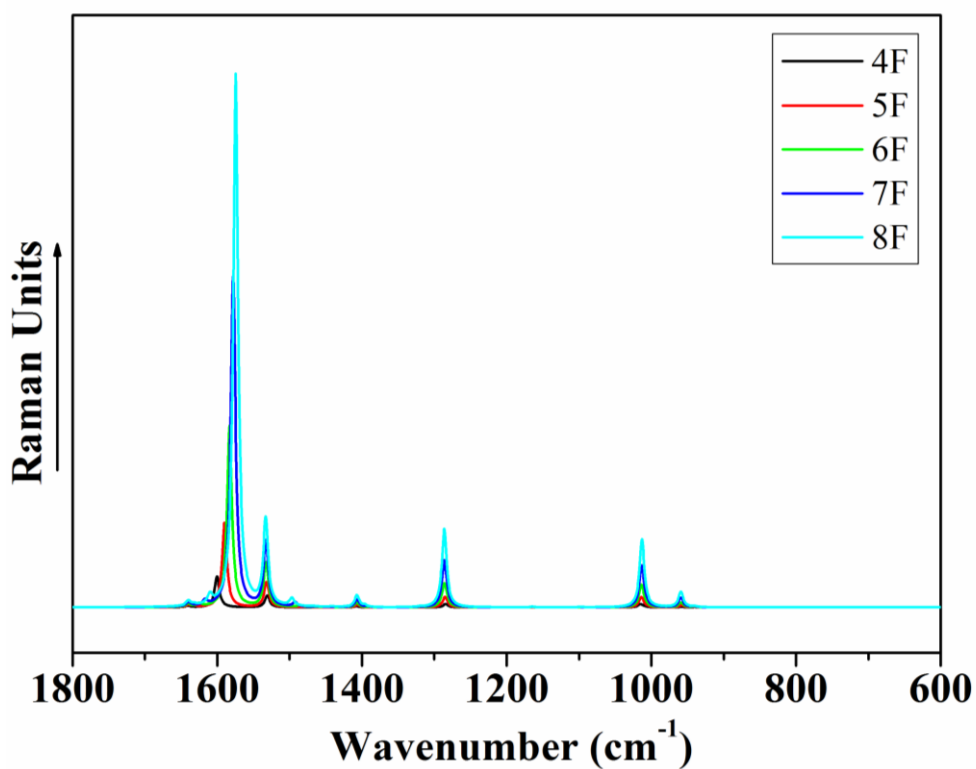


Figure S1.- Calculated Raman spectra of the various α -oligofurans at the DFT//B3LYP/6-31G(d).

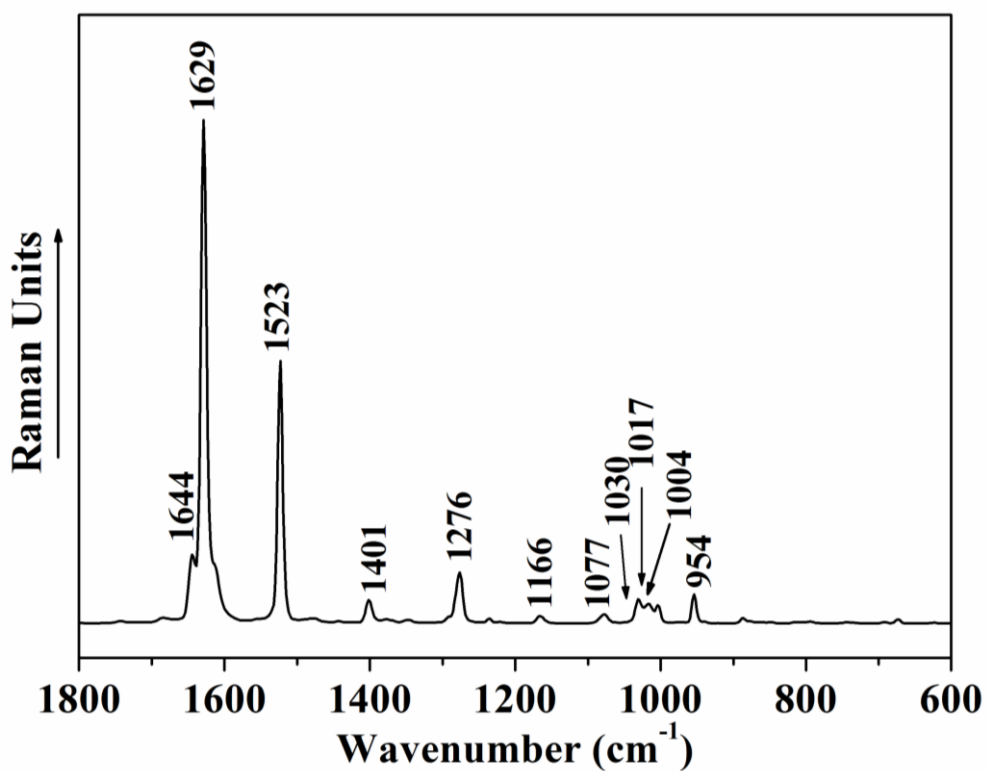


Figure S2.- FT-Raman spectra of 3F recorded with excitations at 1064 nm.

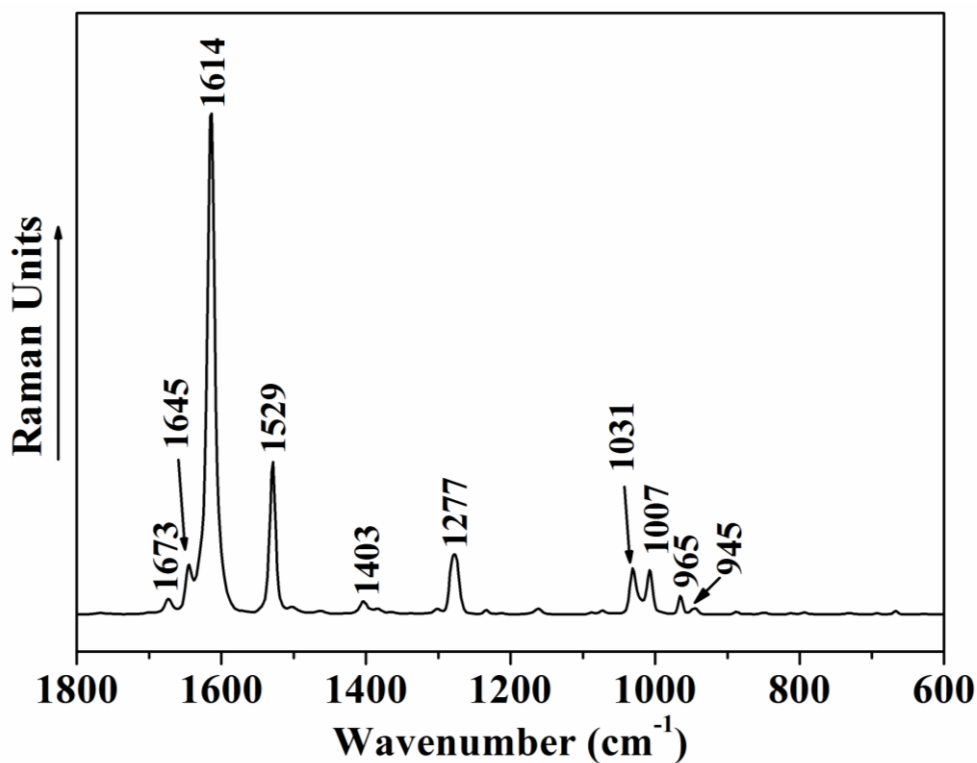


Figure S3.- FT-Raman spectra of 4F recorded with excitations at 1064 nm.

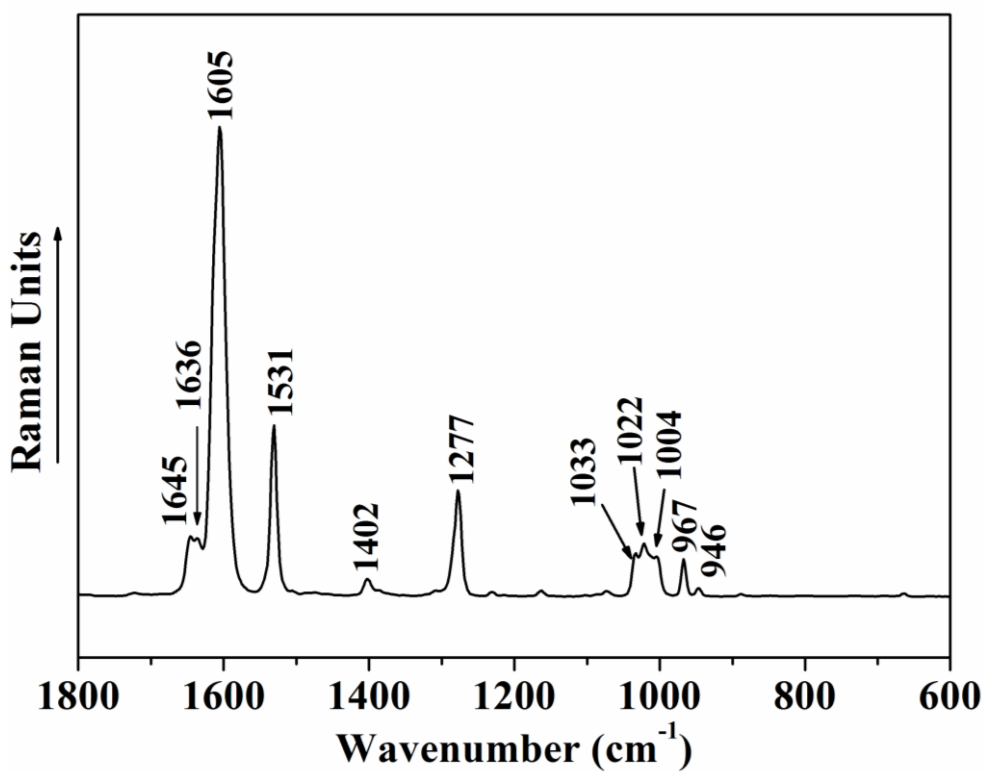


Figure S4.- FT-Raman spectra of 5F recorded with excitations at 1064 nm.

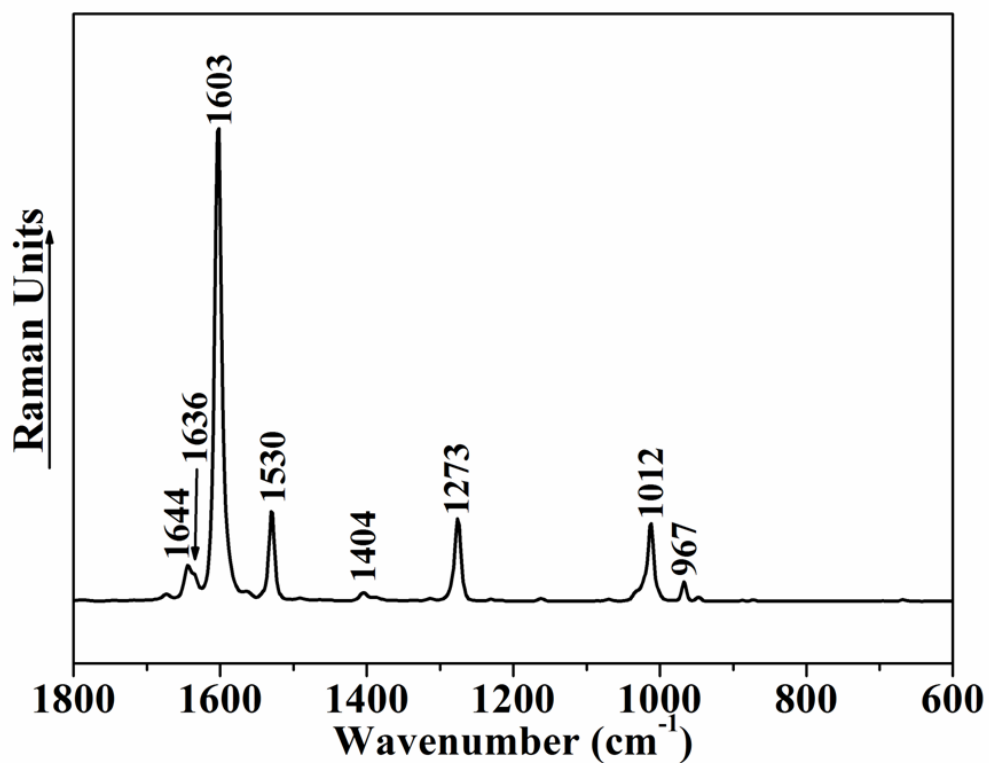


Figure S5.- FT-Raman spectra of 6F recorded with excitations at 1064 nm.

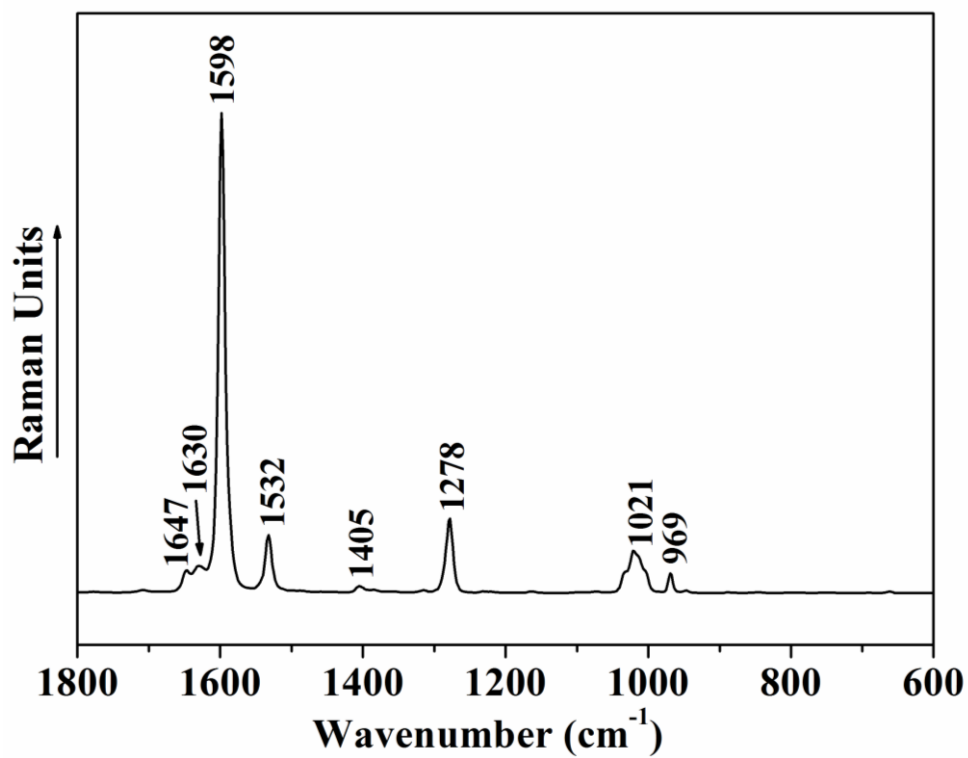


Figure S6.- FT-Raman spectra of 7F recorded with excitations at 1064 nm.

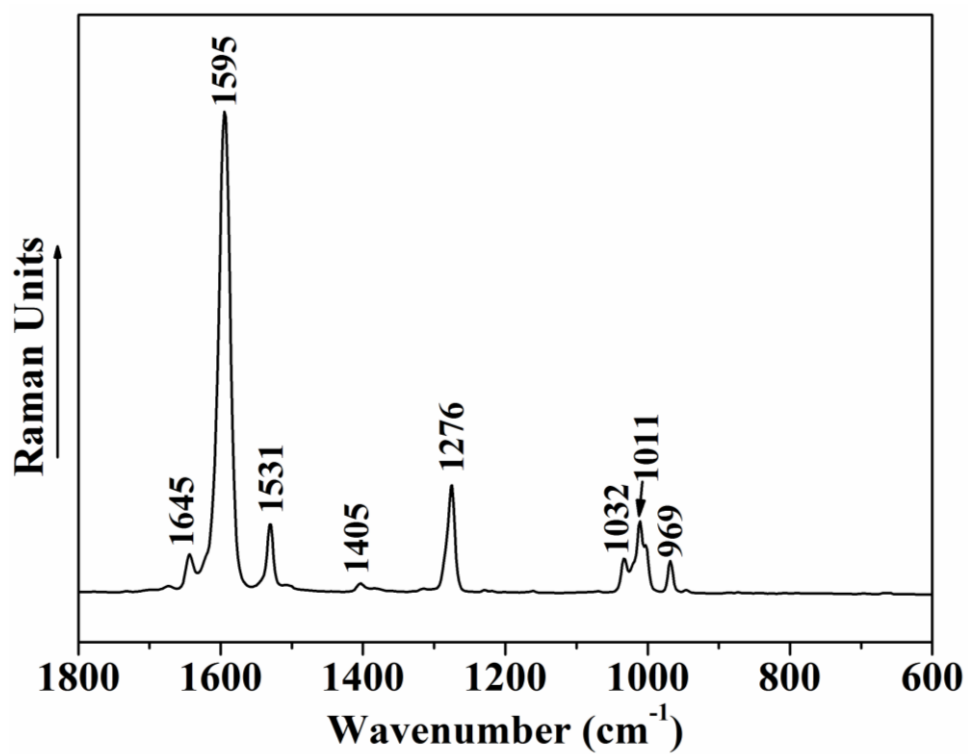
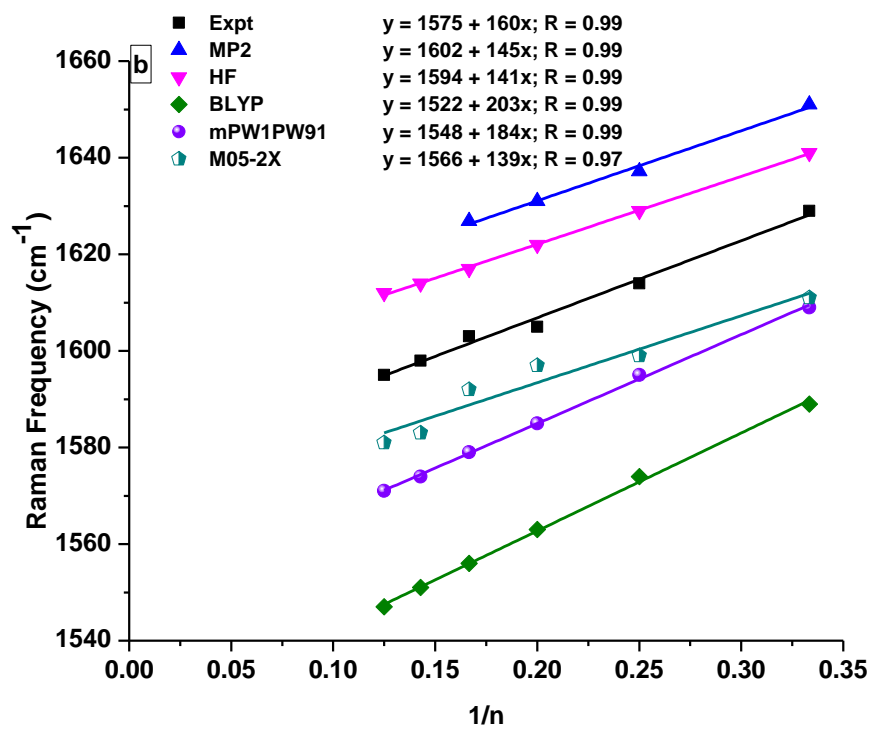
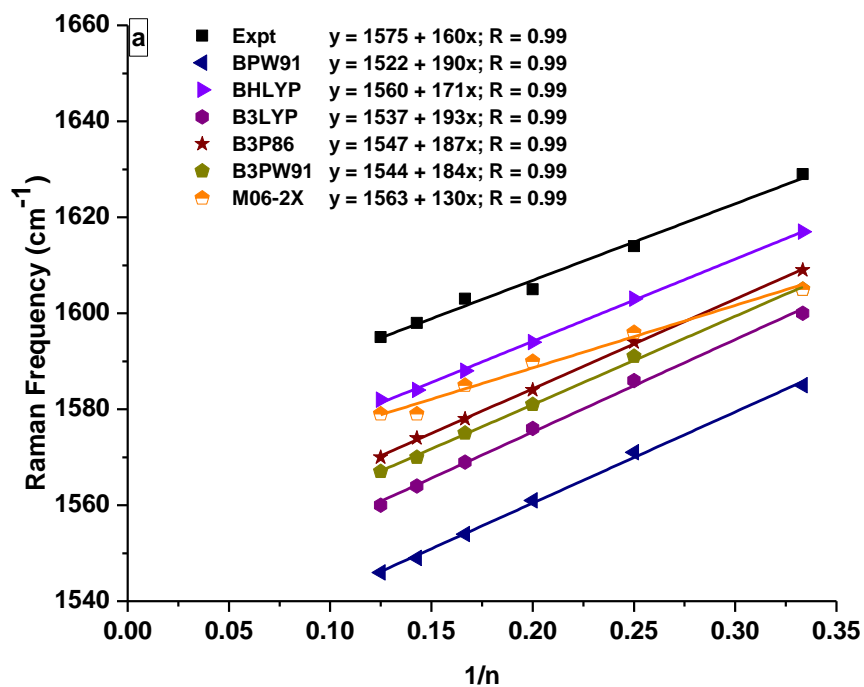


Figure S7.- FT-Raman spectra of **8F** recorded with excitations at 1064 nm.

Computational details: All calculations were carried out using Gaussian 09 program.¹ All molecules (**3F-8F**) were fully optimized without symmetry constraints using various DFT functionals (as well as HF and MP2 levels) with 6-31G(d) basis set. The functionals used for the calculations were BLYP, BHLYP, B3LYP, B3P86, B3PW91, mPW1PW91, BPW91, M05-2X and M06-2X (Figure S8). The optimized geometries were confirmed as minima by frequency calculations. In case of MP2 level, 3-21G basis set was used for geometry optimization and frequency calculations, as frequency calculations at MP2/6-31G(d) level from **4F** onwards are not feasible with modern computational power. The Raman frequency corresponding to stretching motions of C-C bonds involved in π -conjugation and having maximum intensity (\mathcal{A} mode) was taken for the plot. The calculated Raman frequencies at different methods were scaled by commonly used scaling factor. The scaling factors used for Raman frequencies for various methods involving 6-31G(d) basis set are HF (0.8953), BLYP (0.9940), BHLYP (0.9244), B3LYP (0.9613), B3P86 (0.9557), B3PW91 (0.9571), mPW1PW91 (0.9499), M05-2X (0.9373), BPW91 (0.98).^{2,3} No scaling factor was used for Raman frequencies at MP2 level. Scaling factor for M06-2X was assumed to be same as of scaling factor for M05-2X functional with 6-31G(d) basis set.



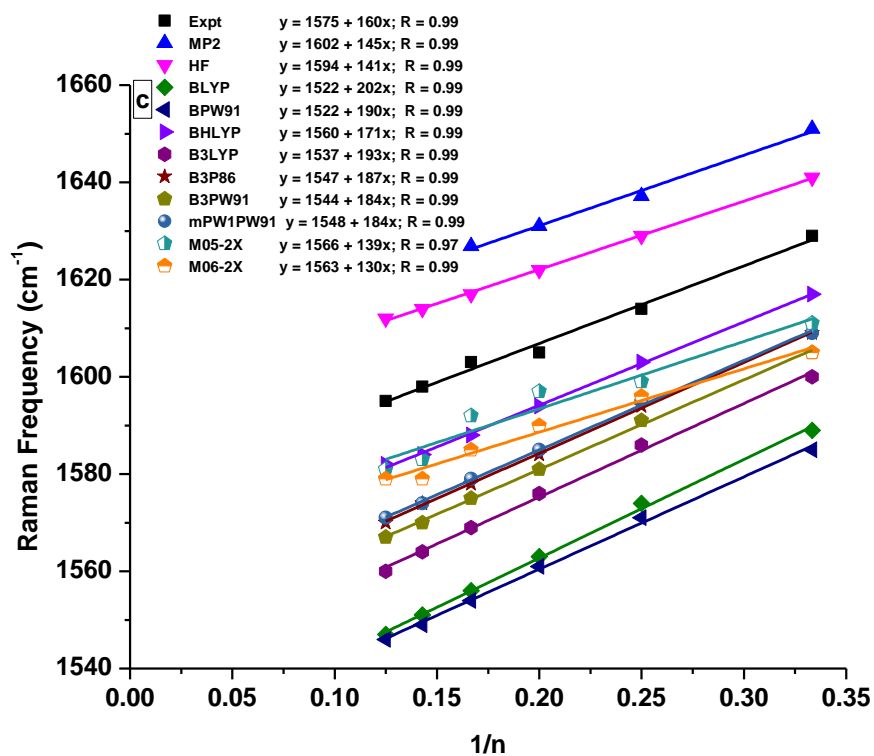


Figure S8.- Comparison of experimental and calculated (using 6-31G(d) basis set) Raman frequencies (\mathcal{R} mode) vs the reciprocal number ($1/n$) of repeat units in oligofurans **3F-8F**. Raman frequencies at MP2 level were calculated using 3-21G basis set for **3F-6F**. Graph (c) includes a complete list of the functionals studied and it is divided into graphs (a) and (b) for visual convenience.

Table S1. The slopes of linear plots of Raman frequencies (ν mode) vs the reciprocal number ($1/n$) of repeat units in oligofurans **3F-8F** with different functionals (based on Figure S8).^a

Method	Slope ($\text{cm}^{-1} \cdot n$)
Experimental	160
HF	141
B3LYP	193
B3P86	187
B3PW91	184
BHLYP	171
BLYP	202
BPW91	190
MPW1PW91	184
M05-2X	139
M06-2X	130
MP2 ^a	145

^a 6-31G(d) basis set was used for all functionals except of MP2 method where 3-21G basis set was employed.

Table S2. Absolute energies (a. u.) of optimized geometries of **3F-8F** at different levels of theory using 6-31G(d) basis set.^a

	3F	4F	5F	6F	7F	8F
HF	-683.592148	-911.075802	-1138.559441	-1366.043077	-1593.526708	-1821.010338
B3LYP	-687.700150	-916.540578	-1145.380949	-1374.221380	-1603.061772	-1831.902190
B3P86	-689.566391	-919.017205	-1148.467919	-1377.918722	-1607.369468	-1836.820253
B3PW91	-687.440640	-916.194856	-1144.948968	-1373.703172	-1602.457317	-1831.211502
BHLYP	-687.303732	-916.014294	-1144.724808	-1373.435357	-1602.145879	-1830.856417
BLYP	-687.481721	-916.253669	-1145.025576	-1373.797555	-1602.569493	-1831.341463
BPW91	-687.639974	-916.462225	-1145.284394	-1374.106660	-1602.928870	-1831.751121
mpw1pw91	-687.541857	-916.331179	-1145.120363	-1373.909657	-1602.698881	-1831.488153
M05-2X	-687.634026	-916.455491	-1145.277048	-1374.098484	-1602.919601	-1831.741027
M06-2X	-687.430750	-916.185430	-1144.939992	-1373.694488	-1602.448568	-1831.203493
MP2^a	-681.185307	-907.866895	-1134.548499	-1361.230106		

^a 3-21G basis set was employed for MP2 level.

Synthesis of oligo- and polyfuran

Oligofurans **4F-8F** were prepared according to the procedures published in ref. 4. **3F** was prepared according to ref. 5.

Polyfuran **PF** was prepared electrochemically from 0.5mM solution of terfuran **3F** in acetonitrile containing 0.1M tetrabutylammonium trifluoromethanesulfonate using a one-compartment three-electrode cell assembly. Thin film of gold on glass (area ~0.5cm×1.0cm) was used as working electrode, Pt-wire was used as counter electrode and Ag|AgCl wire was used as pseudo-reference electrode. The polymerization was done potentiostatically at 0.79 V (vs. SCE) for 30 mC.

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