

# **Protonated Thiophene-based Oligomers as Formed within Zeolites: Understanding their Electron Delocalization and Aromaticity**

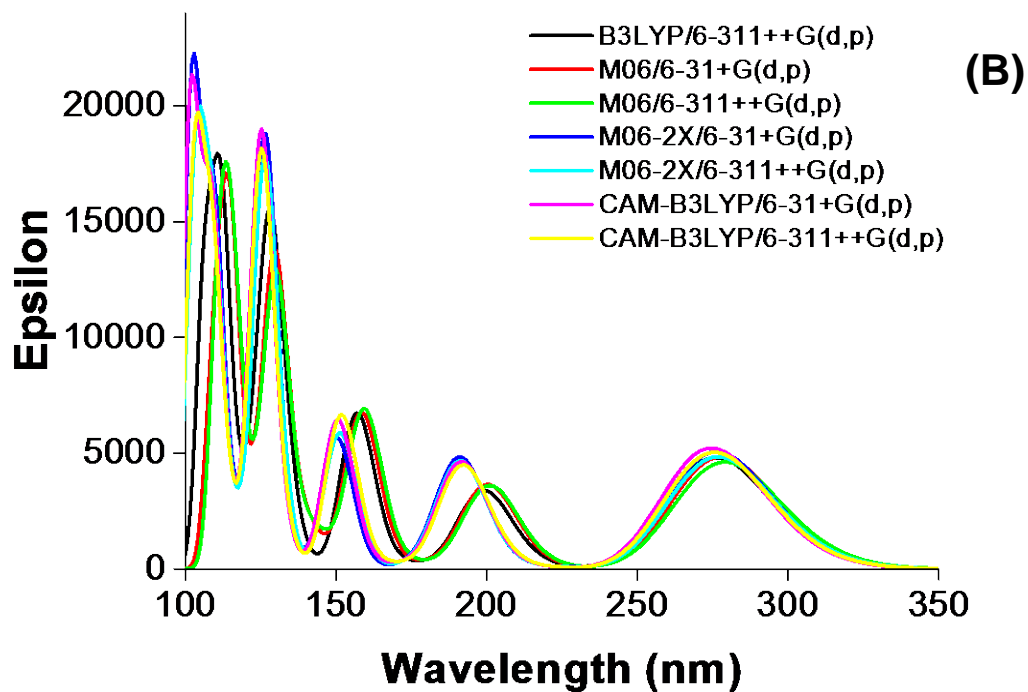
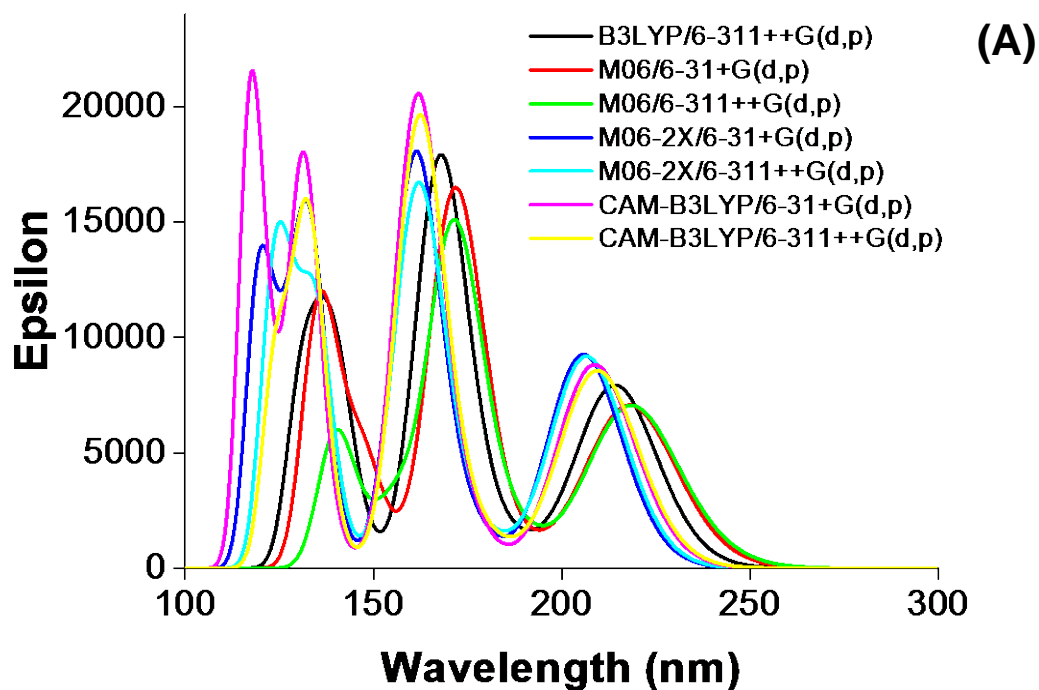
Diego Valencia, Gareth T. Whiting, Rosa E. Bulo and Bert M. Weckhuysen

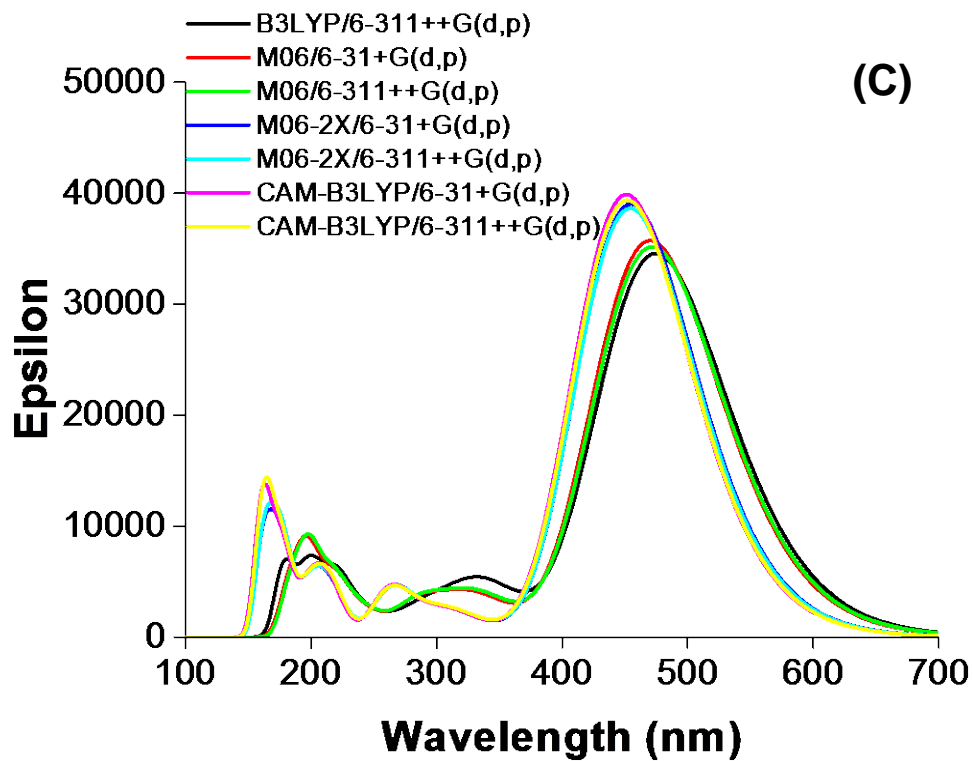
Inorganic Chemistry and Catalysis group, Debye Institute for Nanomaterials Science, Utrecht  
University, Universiteitsweg 99, 3584 CG Utrecht, The Netherlands

\* To whom correspondence should be addressed: [B.M.Weckhuysen@uu.nl](mailto:B.M.Weckhuysen@uu.nl)

## **SUPPORTING INFORMATION**

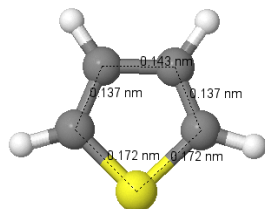
**Figure S1.** Theoretical UV-Vis spectra obtained at different levels of theory for (A) thiophene, (B) protonated thiophene and (C) protonated 3-thiophene.





**Figure S2.** Optimized geometries for non- and protonated thiophene-based oligomers at M06-2X/6-31+G(d,p). Selected bond lengths are shown and Cartesian coordinates are provided below.

**T**



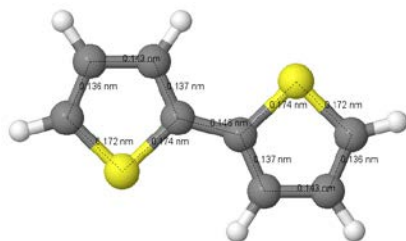
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C	-1.26958800	-0.71457200	-0.00012600
C	-1.26958700	0.71457200	0.00010200
C	-0.00731100	1.23554800	-0.00003500
S	1.19259800	0.00000000	-0.00001700
H	0.28559300	-2.27592200	0.00015100
H	-2.16498800	-1.32400400	-0.00020000
H	-2.16498800	1.32400400	0.00014900
H	0.28559500	2.27592200	-0.00005700

**T-H<sup>+</sup>**



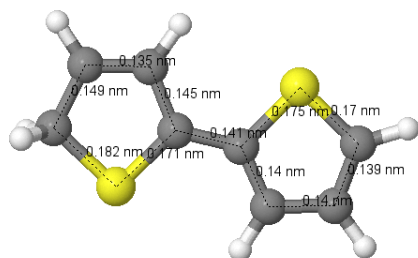
C	-0.08017200	-1.21933700	-0.00003100
C	1.27399300	-0.78870800	0.00002100
C	1.36102400	0.56952000	-0.00002400
C	0.05914900	1.26834500	0.00000500
S	-1.22125000	-0.01190200	0.00000100
H	-0.40081600	-2.25843300	0.00002300
H	2.10874300	-1.47849500	0.00006000
H	2.29016300	1.13199300	-0.00004200
H	-0.07100700	1.90816000	0.88412700
H	-0.07105000	1.90828900	-0.88401100

**2T**



C	0.71774600	-0.12134200	0.00008900
C	1.38370500	-1.32147400	0.00036200
C	2.80147500	-1.17437800	0.00026900
C	3.19153700	0.13321900	-0.00010500
S	1.84077900	1.20360900	-0.00020600
H	0.87525100	-2.27916800	0.00065100
H	3.49662800	-2.00477200	0.00045300
H	4.19539500	0.53349800	-0.00028600
C	-0.71776600	0.12133100	0.00007300
C	-1.38370800	1.32147600	0.00035400
S	-1.84078700	-1.20360600	-0.00033300
C	-2.80149800	1.17441900	0.00023600
H	-0.87518400	2.27914200	0.00066000
C	-3.19147700	-0.13324500	-0.00011300
H	-3.49671600	2.00474400	0.00042100
H	-4.19533100	-0.53353500	-0.00025800

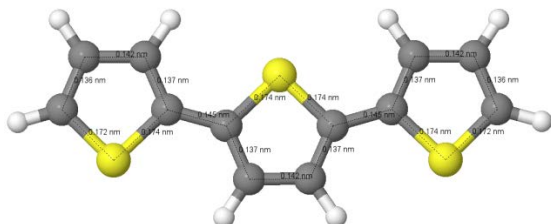
## 2T-H<sup>+</sup>



C	-0.66062800	0.06473400	0.00000400
C	-1.32033400	1.35211800	0.00017500
C	-2.66378800	1.25939000	0.00013500
C	-3.20623400	-0.12336800	-0.00000300
S	-1.77062100	-1.23510000	-0.00015700
H	-0.76619400	2.28376000	0.00028900
H	-3.33556800	2.11187900	0.00020500
H	-3.81874600	-0.32458800	0.88657300
H	-3.81886500	-0.32442300	-0.88652800
C	0.73502400	-0.13191500	0.00002700
C	1.42968600	-1.34679800	0.00019000
S	1.84827100	1.21355700	-0.00014500
C	2.81730700	-1.17843100	0.00013000

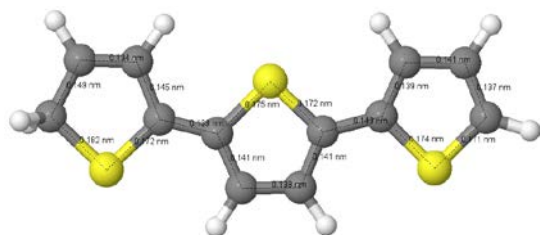
H	0.93585500	-2.31298400	0.00030500
C	3.17631000	0.15940200	-0.00001700
H	3.53709600	-1.98643400	0.00021000
H	4.17996400	0.56666900	-0.00007700

### 3T



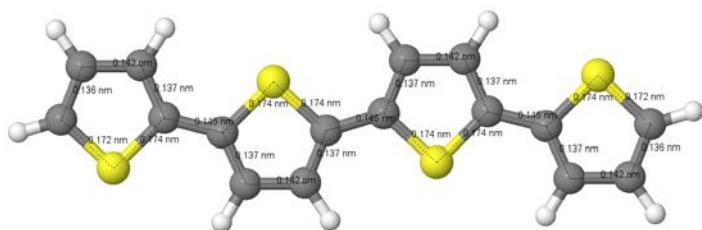
C	2.65153600	0.12906000	-0.00003300
C	3.18944800	1.39268100	-0.00009600
C	4.61438700	1.39323500	-0.00003200
C	5.13811200	0.13312100	0.00021800
S	3.90644000	-1.07249900	-0.00013300
H	2.58467500	2.29269700	-0.00019900
H	5.21978900	2.29114700	-0.00006300
H	6.17816000	-0.16058000	0.00044400
C	1.25151500	-0.26073600	-0.00001800
C	0.71013000	-1.52192600	-0.00003000
S	-0.00001800	0.94595000	0.00001600
C	-0.71022600	-1.52194000	-0.00001000
H	1.31221300	-2.42363700	-0.00005500
C	-1.25154000	-0.26076300	0.00001300
H	-1.31236600	-2.42362100	-0.00001700
C	-2.65158500	0.12910200	0.00003000
C	-3.18941400	1.39272000	0.00005700
S	-3.90642200	-1.07250000	0.00000600
C	-4.61438600	1.39331200	0.00007200
H	-2.58447300	2.29264600	0.00006800
C	-5.13798200	0.13307400	0.00006400
H	-5.21992800	2.29109700	0.00009700
H	-6.17803700	-0.16061500	0.00007700

### 3T-H<sup>+</sup>



C	-2.57217700	0.07010000	-0.00000500
C	-3.10834500	1.41762500	-0.00000100
C	-4.45179200	1.46110500	0.00000400
C	-5.13734100	0.14069900	0.00001800
S	-3.82082600	-1.11640400	-0.00000900
H	-2.46623500	2.29125600	-0.00000500
H	-5.03145700	2.37849000	0.00000200
H	-5.76584900	0.00534400	0.88696400
H	-5.76590500	0.00533900	-0.88688600
C	-1.21837900	-0.25895900	-0.00000400
C	-0.64204300	-1.54445000	-0.00000200
S	0.03518700	0.96670800	-0.00000400
C	0.73871300	-1.52881500	-0.00000200
H	-1.23580800	-2.45271300	0.00000000
C	1.27465600	-0.22607800	0.00000000
H	1.35917500	-2.41688300	-0.00000100
C	2.65912800	0.13597100	0.00000000
C	3.21163000	1.40714100	-0.00000600
S	3.90260200	-1.08006600	0.00000800
C	4.62165100	1.39106300	0.00000300
H	2.61912600	2.31591000	-0.00000900
C	5.12546400	0.11169000	-0.00000400
H	5.24392000	2.27637800	0.00000500
H	6.16462400	-0.18947300	-0.00000400

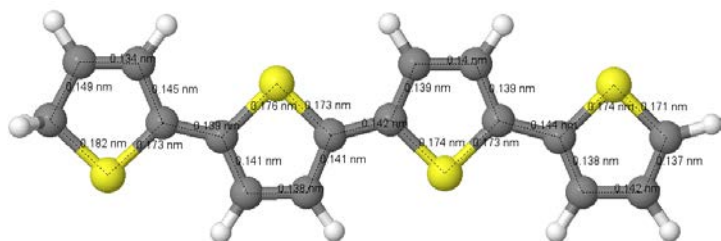
4T



C	-4.60450300	0.10212300	0.00008100
C	-5.16787200	1.35473700	0.00041300
C	-6.59243000	1.32638300	0.00030200
C	-7.09044000	0.05582000	-0.00018600
S	-5.83483300	-1.12465100	-0.00025000
H	-4.58146200	2.26683600	0.00074600
H	-7.21594600	2.21179400	0.00051900
H	-8.12432200	-0.25890500	-0.00045400
C	-3.19712600	-0.25905400	0.00005200
C	-2.63012900	-1.50932300	-0.00003800
S	-1.97066500	0.97324100	0.00013800
C	-1.21068800	-1.48093200	-0.00004000

H	-3.21399400	-2.42291100	-0.00008900
C	-0.69459900	-0.20828900	0.00005100
H	-0.59070000	-2.37043300	-0.00009700
C	0.69465000	0.20826100	0.00008100
C	1.21072300	1.48092900	0.00022700
S	1.97069300	-0.97325900	-0.00009200
C	2.63014900	1.50934000	0.00023800
H	0.59073000	2.37042200	0.00035100
C	3.19711900	0.25907600	0.00009100
H	3.21407000	2.42289800	0.00039300
C	4.60452600	-0.10214400	0.00006900
C	5.16786200	-1.35474400	0.00067700
S	5.83480600	1.12464600	-0.00077800
C	6.59243700	-1.32641100	0.00045100
H	4.58132200	-2.26677600	0.00130700
C	7.09032100	-0.05573900	-0.00033000
H	7.21607100	-2.21171100	0.00085300
H	8.12421300	0.25895900	-0.00065700

#### 4T-H<sup>+</sup>



C	4.50541500	0.04386800	-0.00001500
C	5.07697200	1.37806700	-0.00020100
C	6.42004900	1.39071500	-0.00016500
C	7.07742800	0.05431500	0.00004900
S	5.73210500	-1.17405900	0.00023600
H	4.45588200	2.26689300	-0.00034700
H	7.02011300	2.29477600	-0.00028100
H	7.70232600	-0.09416300	-0.88694800
H	7.70234800	-0.09389200	0.88707300
C	3.14983600	-0.25119100	-0.00001000
C	2.54125600	-1.52665100	0.00003800
S	1.92025700	1.00358900	-0.00006400
C	1.16592600	-1.48339300	0.00002600
H	3.11717400	-2.44629100	0.00007600
C	0.65093300	-0.16551700	-0.00001900
H	0.52754800	-2.35871100	0.00004900
C	-0.71482100	0.21539800	-0.00004600
C	-1.25102100	1.49999600	-0.00014900



S	-1.98644400	-0.97915400	0.00005200
C	-2.64752400	1.51655800	-0.00015300
H	-0.64011800	2.39660300	-0.00022900
C	-3.20801900	0.24141100	-0.00006900
H	-3.24396800	2.42098100	-0.00024300
C	-4.60595000	-0.10878900	-0.00005900
C	-5.17209600	-1.36743200	-0.00039000
S	-5.83196300	1.12211400	0.00038600
C	-6.58801200	-1.33447900	-0.00029600
H	-4.59084100	-2.28329900	-0.00072600
C	-7.07763600	-0.05457200	0.00013100
H	-7.21839800	-2.21419800	-0.00052700
H	-8.11177200	0.26162200	0.00030300

## 5T



C	-6.55131400	0.15537300	0.00001100
C	-7.08922500	1.41914100	0.00064700
C	-8.51401800	1.41955600	0.00045400
C	-9.03759900	0.15928500	-0.00044700
S	-7.80607500	-1.04632800	-0.00060800
H	-6.48459400	2.31926600	0.00125800
H	-9.11953800	2.31736900	0.00087500
H	-10.07762600	-0.13450800	-0.00090400
C	-5.15156600	-0.23409300	-0.00006900
C	-4.61008100	-1.49570200	-0.00036100
S	-3.90049600	0.97308000	0.00023500
C	-3.19051100	-1.49621600	-0.00036400
H	-5.21241600	-2.39720500	-0.00056000
C	-2.64860900	-0.23418400	-0.00006700
H	-2.58879100	-2.39818900	-0.00057600
C	-1.25149600	0.15381400	0.00001900
C	-0.70949000	1.41606900	0.00027600
S	0.00002400	-1.05385100	-0.00021700
C	0.70953500	1.41607200	0.00028200
H	-1.31151400	2.31780300	0.00045500
C	1.25154100	0.15382400	0.00003400
H	1.31158400	2.31779100	0.00047200
C	2.64867100	-0.23419100	-0.00002300

C	3.19055800	-1.49624700	-0.00013000
S	3.90051400	0.97308100	0.00006400
C	4.61012100	-1.49574200	-0.00019500
H	2.58881800	-2.39820100	-0.00019100
C	5.15153500	-0.23412400	-0.00012300
H	5.21254400	-2.39719000	-0.00035600
C	6.55133200	0.15542400	-0.00016400
C	7.08917700	1.41916900	-0.00145700
S	7.80603100	-1.04630800	0.00156300
C	8.51400700	1.41961300	-0.00107500
H	6.48436100	2.31919000	-0.00271800
C	9.03743900	0.15921800	0.00050000
H	9.11968300	2.31728300	-0.00195300
H	10.07748400	-0.13452900	0.00110200

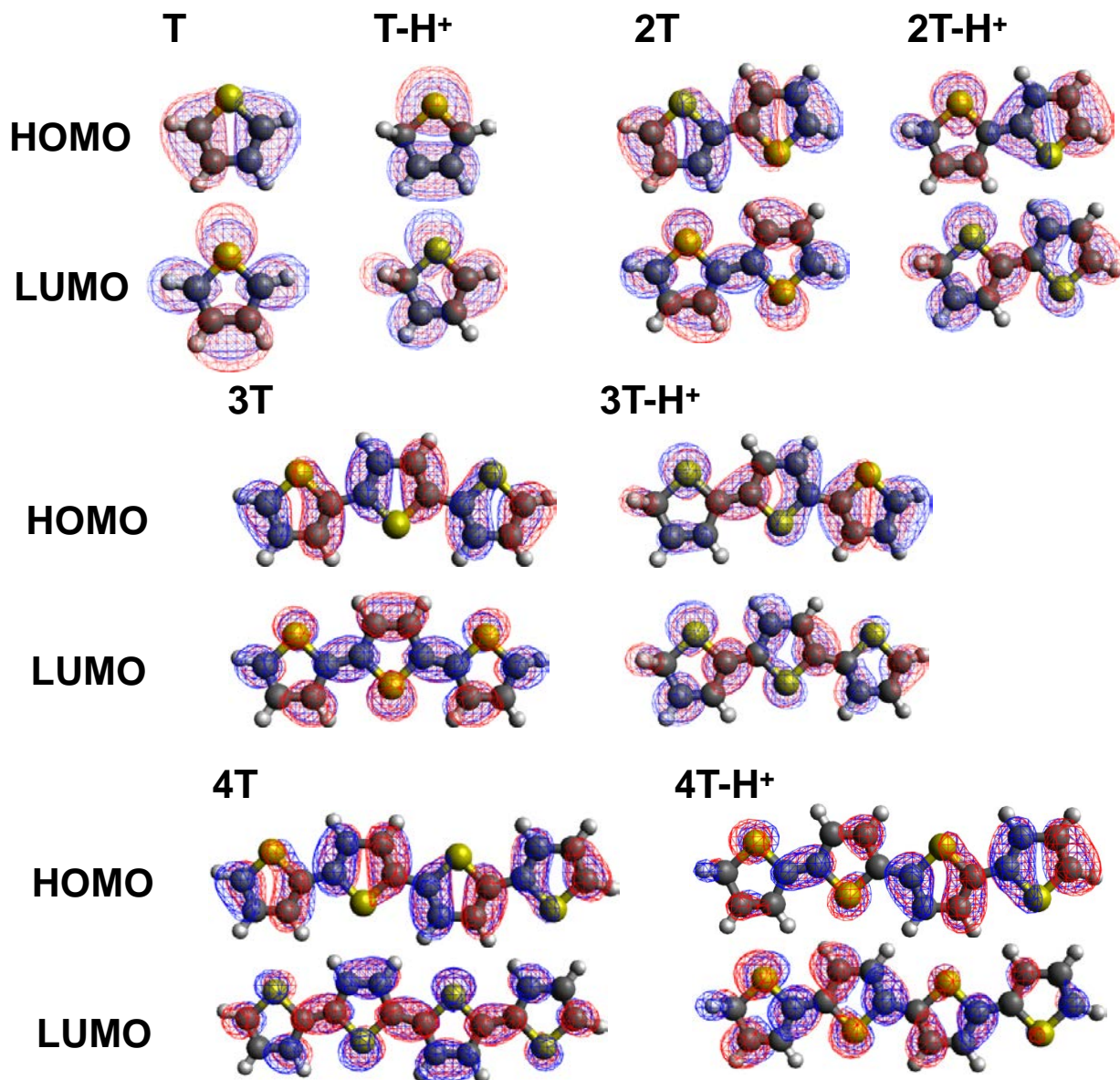
### 5T-H<sup>+</sup>



C	-6.43999300	0.09472000	0.00005300
C	-6.98883700	1.43896900	0.00037600
C	-8.33102700	1.47671800	0.00036800
C	-9.01428800	0.15250100	0.00004200
S	-7.69190700	-1.10167500	-0.00029800
H	-6.35170000	2.31643900	0.00059700
H	-8.91378900	2.39195500	0.00058300
H	-9.64172000	0.01622500	0.88703900
H	-9.64178000	0.01666600	-0.88697700
C	-5.09267200	-0.22445300	0.00000400
C	-4.50720600	-1.51304800	-0.00013100
S	-3.83733000	1.00691600	0.00011800
C	-3.13334500	-1.49756100	-0.00014000
H	-5.10194700	-2.42059400	-0.00021700
C	-2.58924400	-0.18867600	-0.00002700
H	-2.51263300	-2.38555000	-0.00022900
C	-1.22015700	0.16083300	-0.00000200
C	-0.65451300	1.43628900	0.00012800
S	0.02866300	-1.06076500	-0.00013100
C	0.73805000	1.42574200	0.00010700
H	-1.24812200	2.34446700	0.00022500
C	1.27695300	0.13622200	-0.00001700

H	1.35232500	2.31815100	0.00018600
C	2.65994700	-0.23467900	-0.00006000
C	3.20902000	-1.50442500	-0.00015200
S	3.91069000	0.97688600	0.00001400
C	4.61517400	-1.50109800	-0.00017400
H	2.61159800	-2.40990000	-0.00021200
C	5.15506800	-0.22658400	-0.00011100
H	5.22245500	-2.39844100	-0.00026500
C	6.55085400	0.15410300	-0.00012200
C	7.09157400	1.42041300	-0.00075900
S	7.79987600	-1.05233700	0.00073800
C	8.51141700	1.41559500	-0.00058100
H	6.49203600	2.32430300	-0.00137900
C	9.02718200	0.14865800	0.00021200
H	9.12292100	2.30871500	-0.00102000
H	10.06673800	-0.14824600	0.00052000

**Figure S3.** HOMO and LUMO plots of non- and protonated thiophene-based oligomers at M06-2X/6-31+G(d,p) level.



**Figure S4.** NICS values for neutral and protonated PAHs at M06-2X/6-31+G(d,p) level. NICS values for non-protonated compounds are in blue and the corresponding for protonated ones are in red. Protonated site was chosen (\*) as reported in Ref. 32.

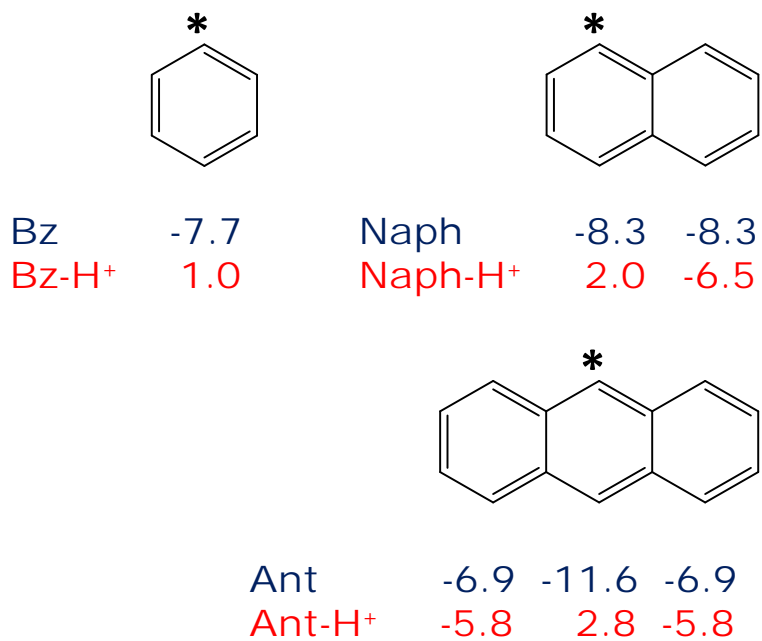
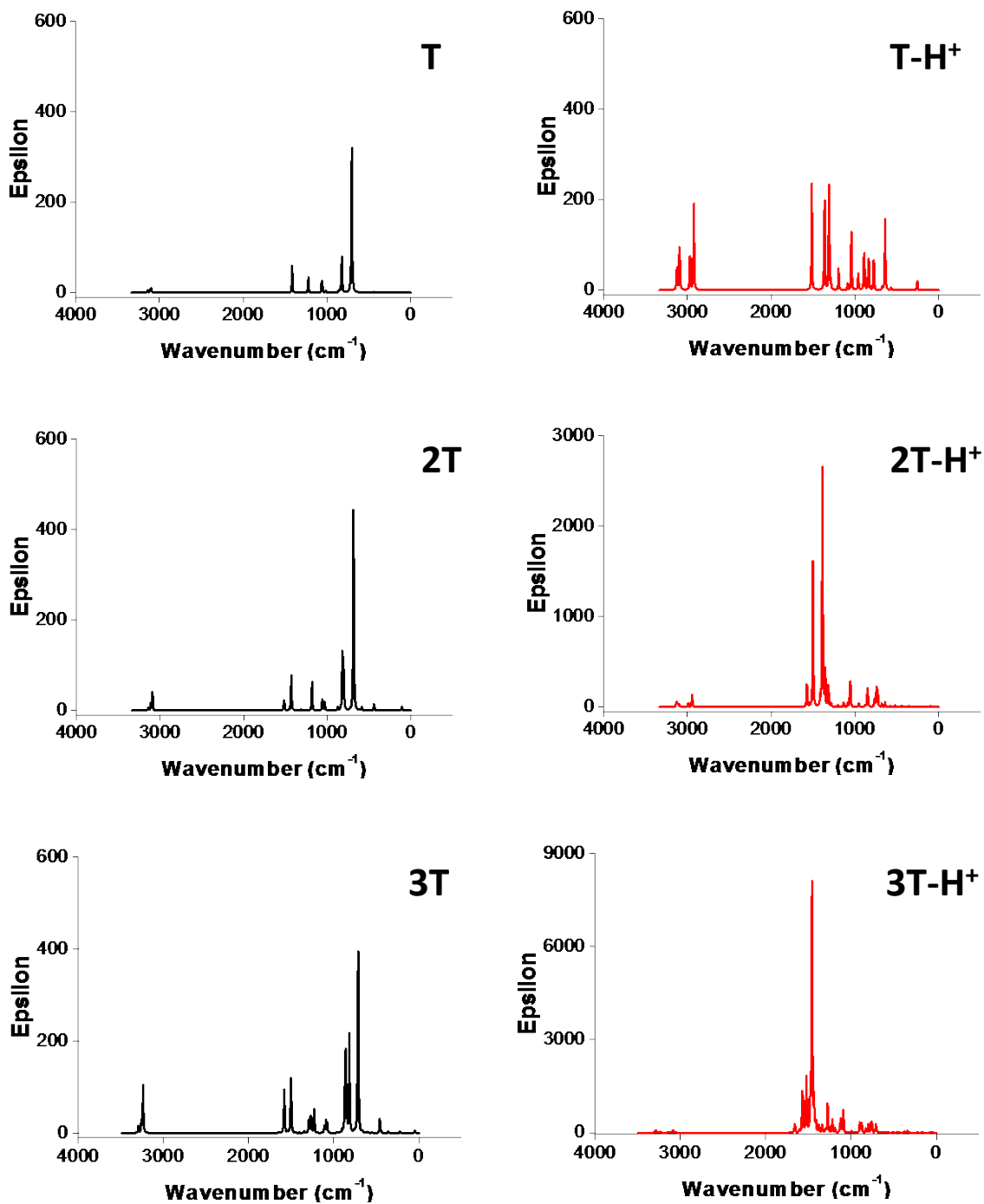
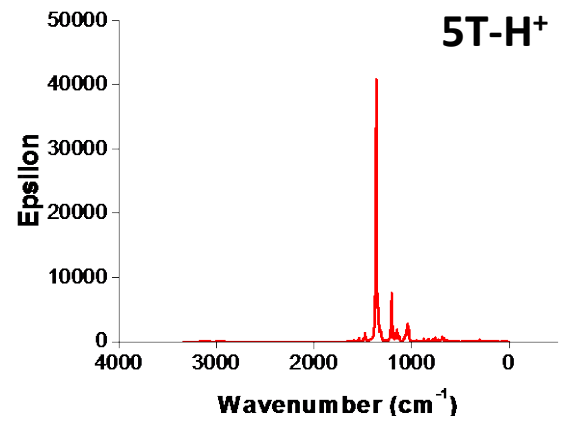
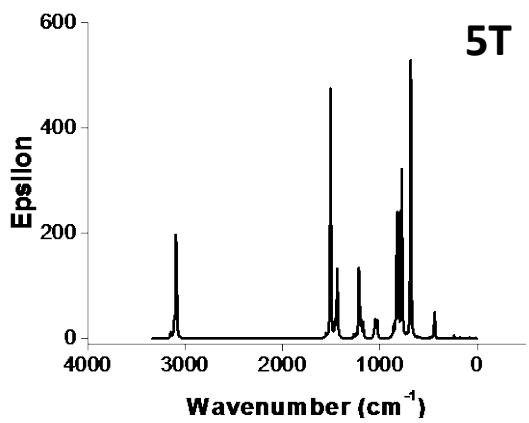
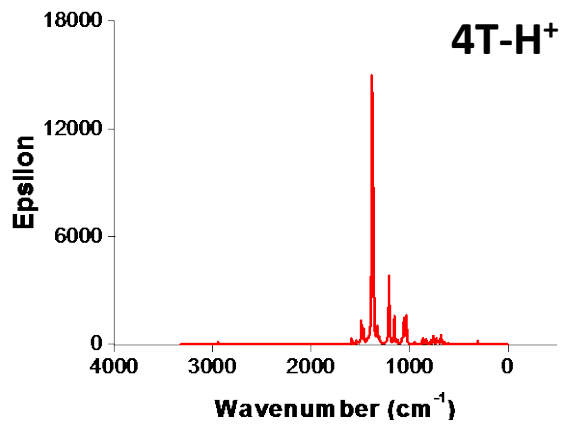
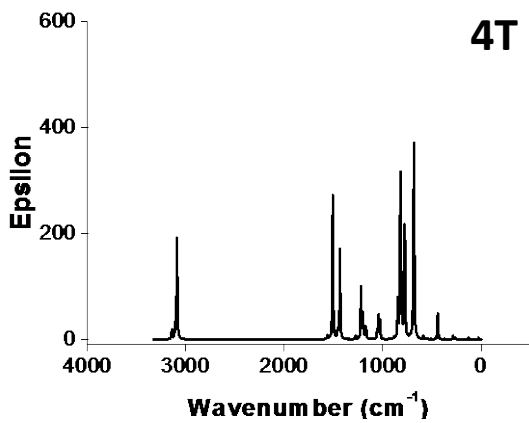


Figure S5. Theoretical IR spectra for the thiophene-based oligomers.





**Table S1.** Red-shift ( $\Delta\lambda$ ) upon protonation and dipole moments for PAHs compounds.

Compound	$\Delta\lambda^a$ (nm)	$\mu^b$ (D)	$\mu^c$ (D)
Benzene	60	0.00	0.90
Naphthalene	154	0.00	2.16
Anthracene	60	0.00	0.08

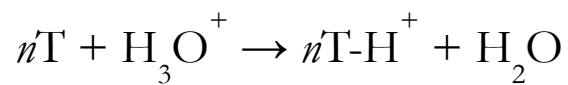
<sup>a</sup> Reported in Ref. 32.

<sup>b</sup> Theoretical dipole moment for neutral compound.

<sup>c</sup> Theoretical dipole moment for protonated compound.



**Table S2.** Protonation reaction of thiophene-based oligomers and  $\Delta G^0$  values for this reaction ( $n$  = number of thiophene monomers in the oligomers).



$n$	$\Delta G^0$ (kJmol <sup>-1</sup> )
1	-108
2	-186
3	-220
4	-231
5	-246