Electronic Supplementary Material (ESI) for RSC Advances


# Alternant conjugated oligomers with tunable and narrow HOMO-LUMO gap as sustainable nanowires

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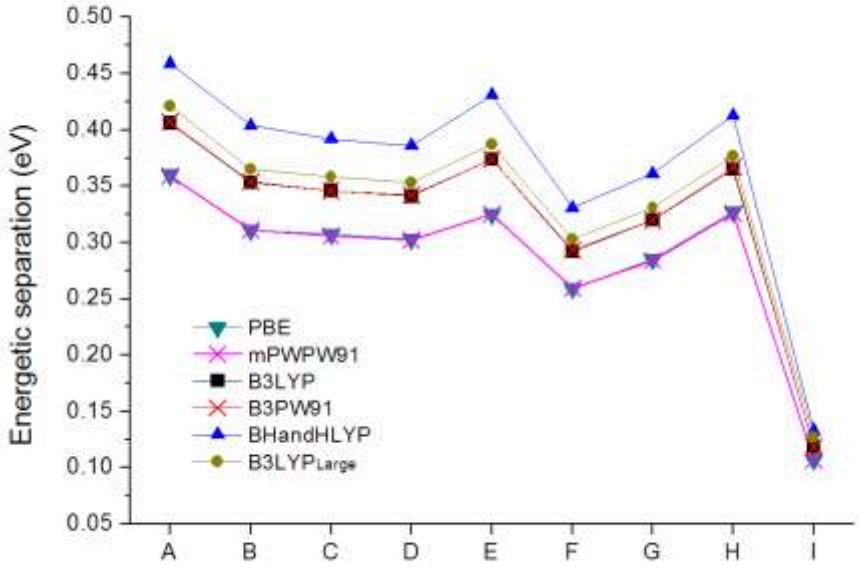



**Figure 1S.** Energetic separation between HOMO-1 and HOMO of oligomers A-I. $B3LYP_{Large}$ denotes B3LYP/6-31+G(2d,p). For all other cases, 6-31G* basis-set is used.

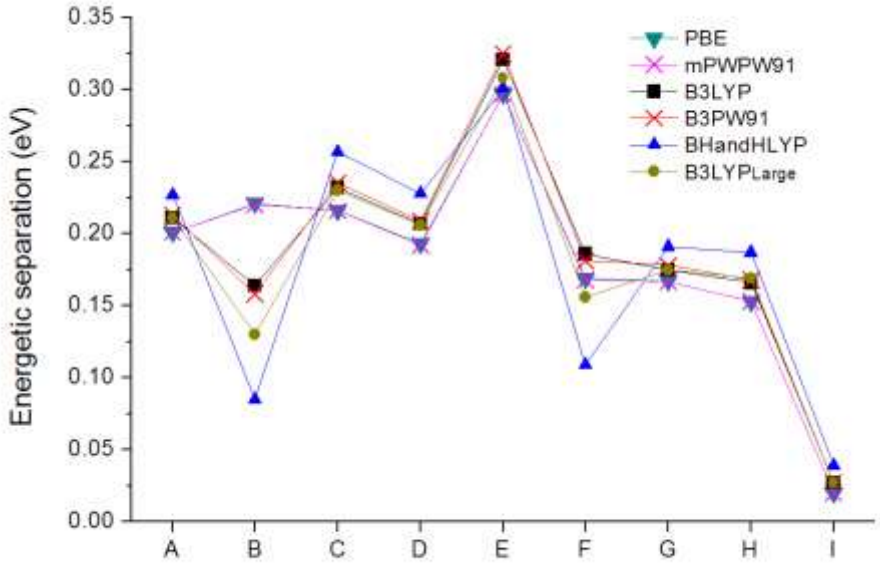
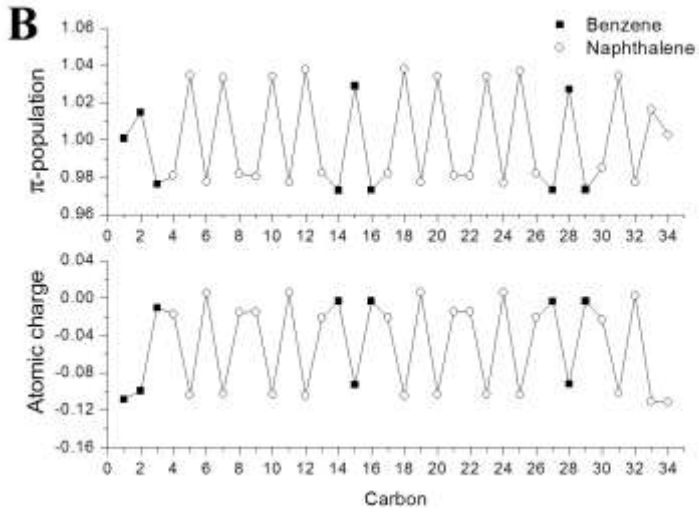
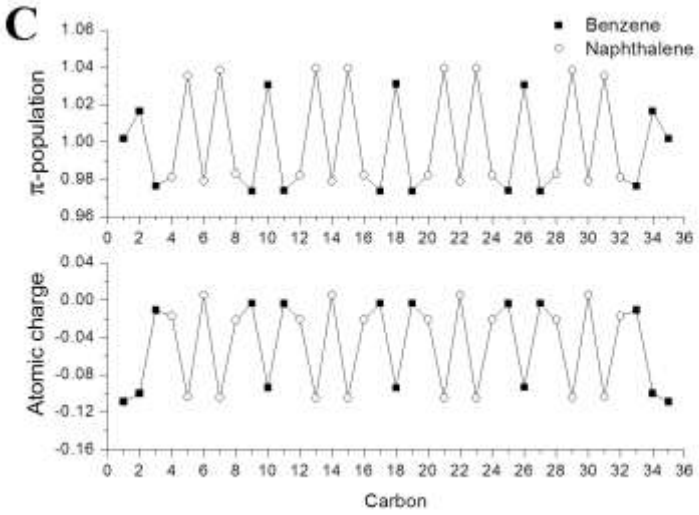
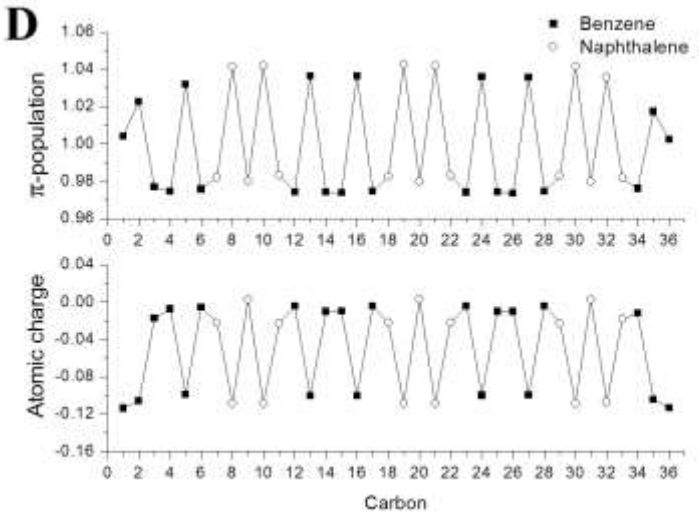
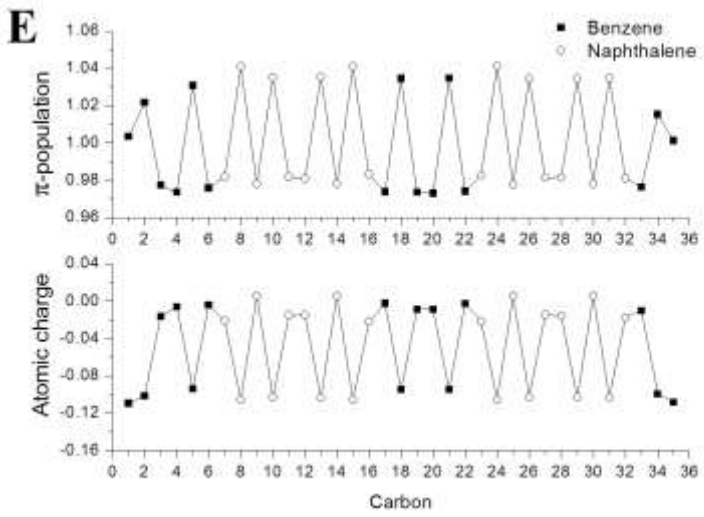


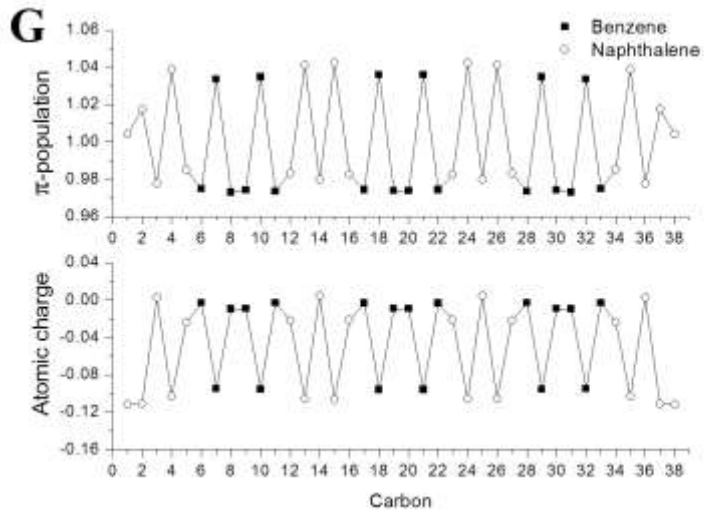

**Figure 2S.** Energetic separation between LUMO and LUMO+1 of oligomers A-I. $B3LYP_{Large}$ denotes B3LYP/6-31+G(2d,p). For all other cases, 6-31G* basis-set is used.

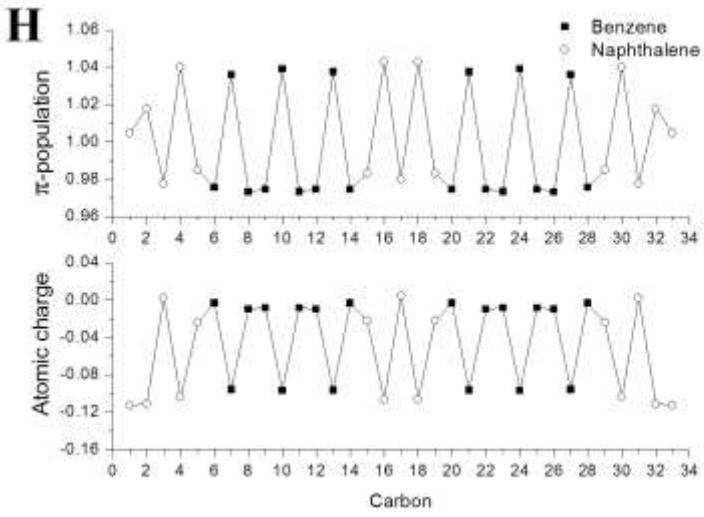




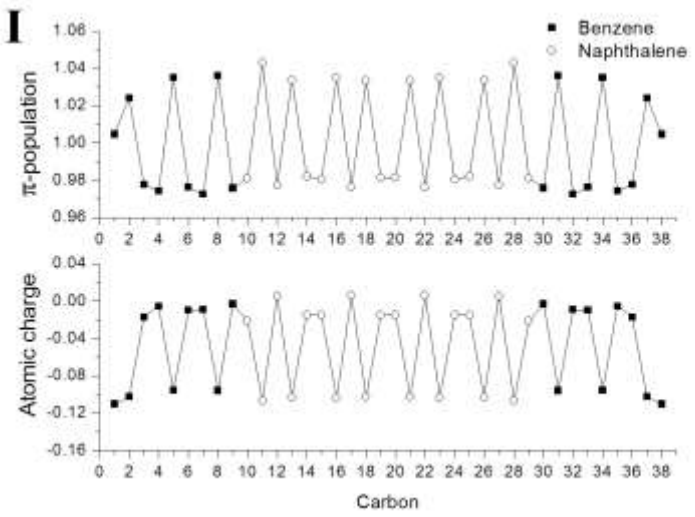
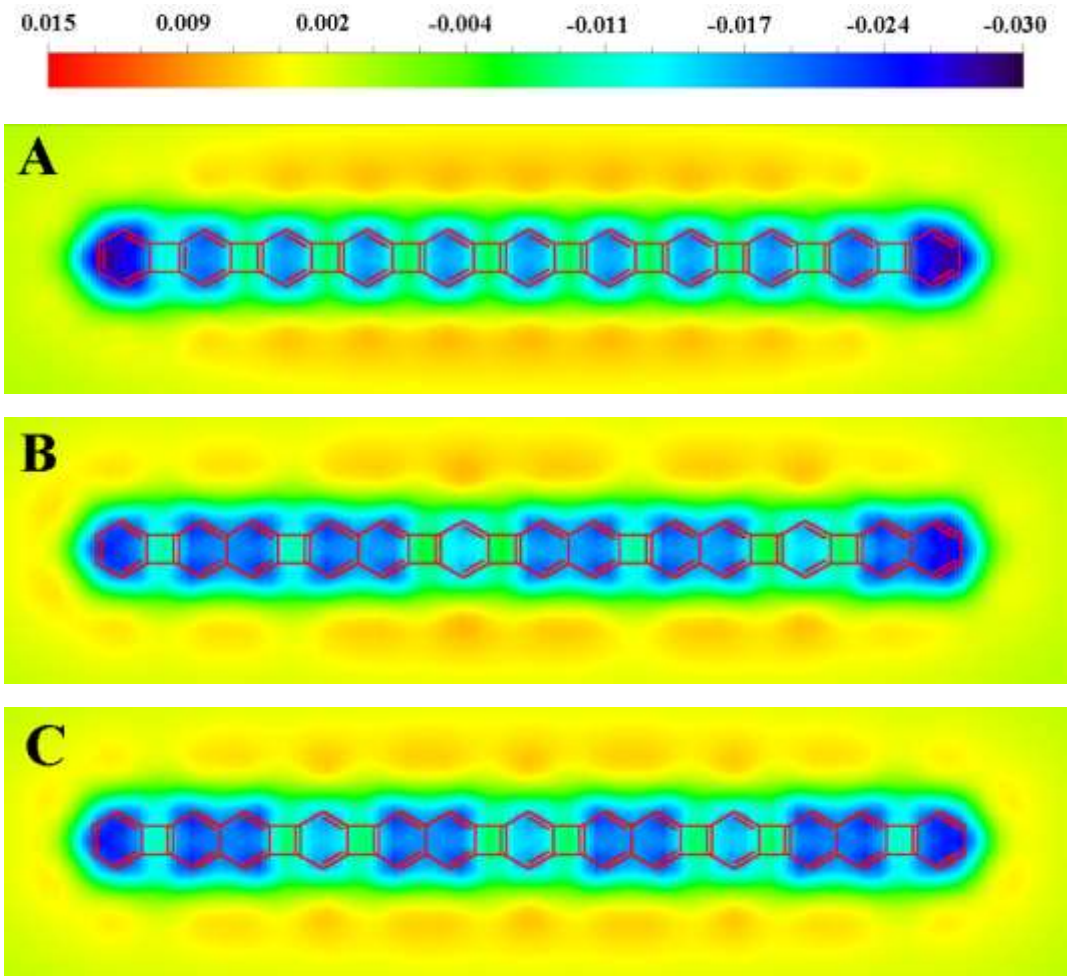



**Figure 3S.** Population of π-electrons and atomic charges of the carbons in oligomer B, C, D, E, G, H and I. The result for A and F are given in Fig. 5. The atomic numbering is described in Fig. 1.



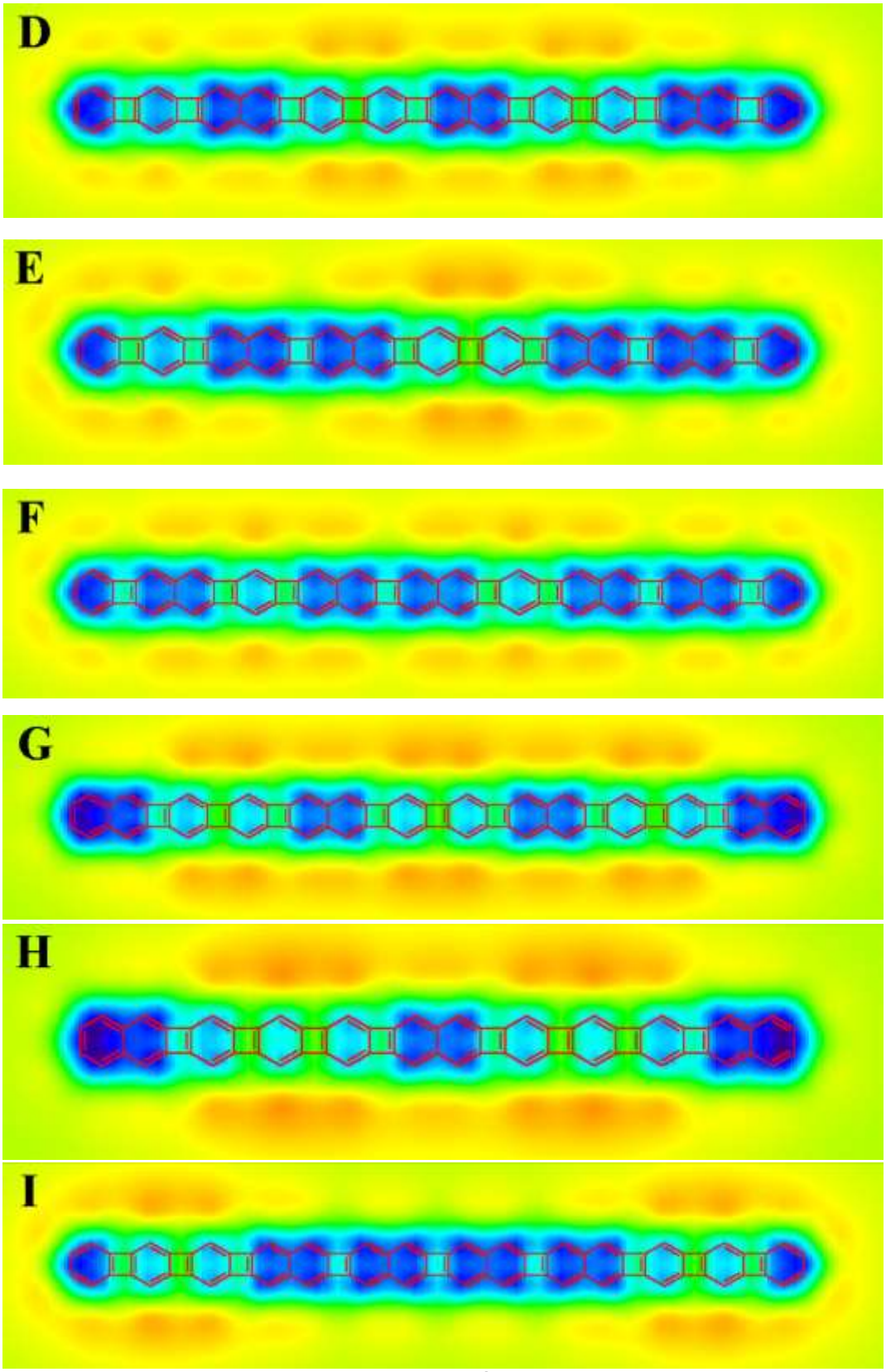



**Figure 4S.** Electrostatic potential map above 1.7Å of the oligomer planes. The values are represented by color according to the color bar. Unit is in a.u.

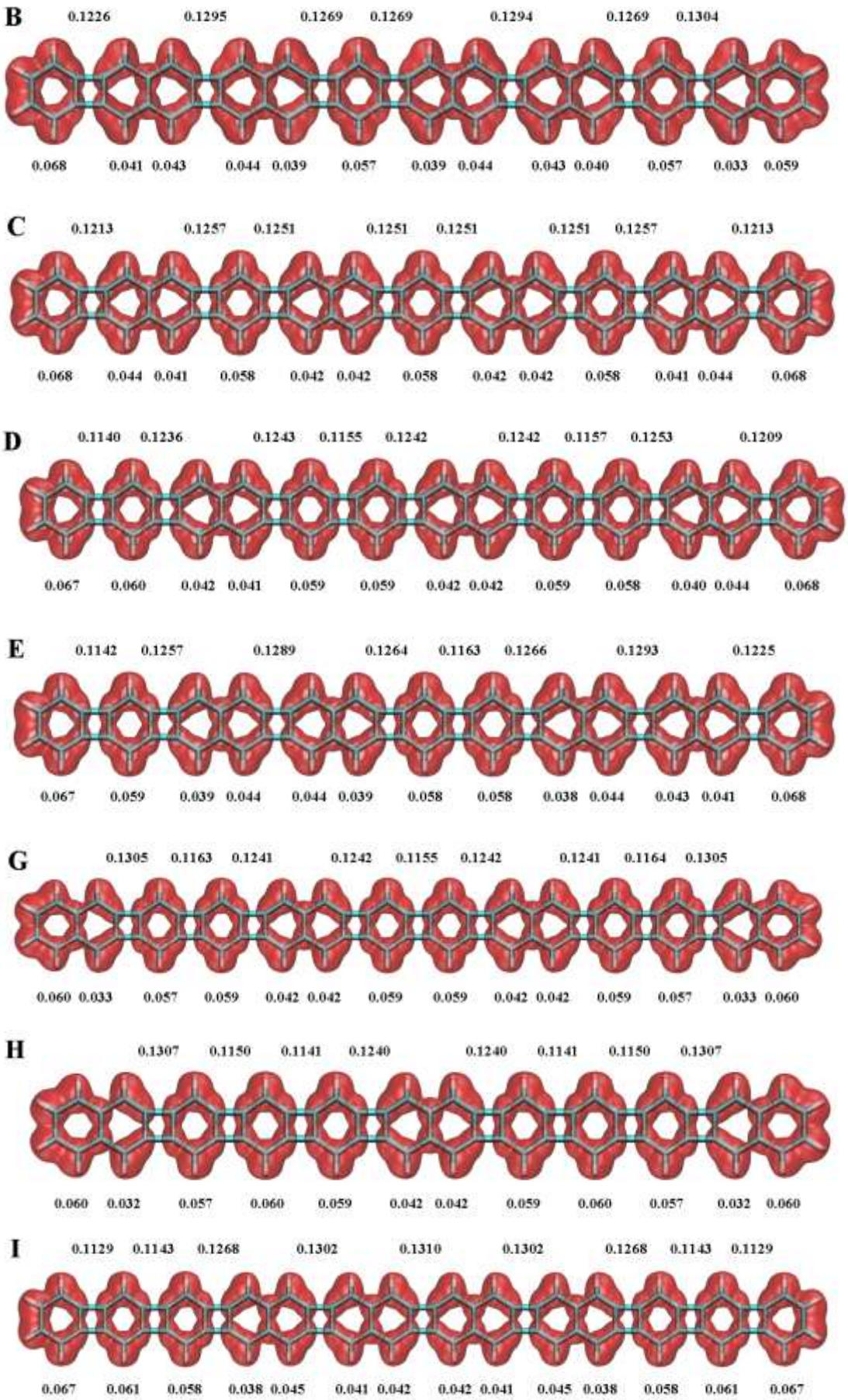


**Figure 5S.** 0.5 isosurface of ELF-π, delocalization index of the horizontal C-C bonds in the 4n rings (top) and six-center bond order of the 4n+2 rings (bottom) for oligomer B, C, D, E, G, H and I. The data for A and F are given in Fig. 6.

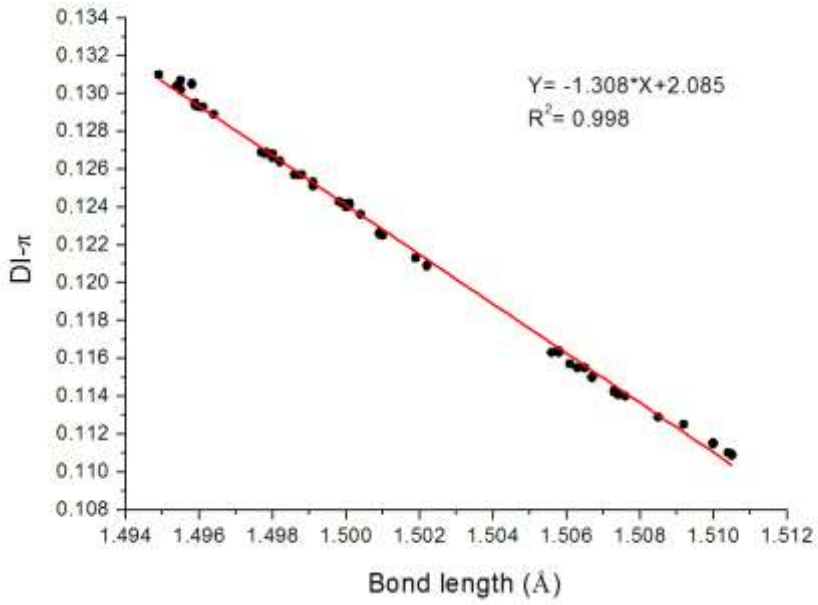



**Figure 6S.** The relationship between DI-π and bond length of the horizontal C-C bonds in the 4n units of the nine oligomers.

**Table 1S.** Statistical regression analysis of chemical composition and gap of oligomers A-I

| **HOMO-LUMO Gap versus 4n/4n+2 ratio** | | | | | |
|---|---|---|---|---|---|
| | **Coefficient** | **Std. Error** | **t** | **P** | **VIF** |
| $y_0$ | 6,7529 | 1,6309 | 4,1405 | 0,0061 | 1952,9149< |
| a | -10,5208 | 4,5498 | -2,3124 | 0,0601 | 6663,8979< |
| b | 5,1481 | 3,0918 | 1,6651 | 0,1470 | 1501,8612< |
| Eqn: | $f=y_0+ax+bx^2$ | | | | |
| | | | | | |
| Statistical tests: | | | | | |
| *Type* | *Normality Test* | *K-S Statistic* = 0,1438 | | *Constant Variance Test* | *PRESS* |
| *Factor* | Passed (P = 0,9861) | Significance Level = 0,9861 | | Passed (P 0,7086) | 0,2997 |
| $R^2$=0,9186, R=0,9585, Std. error estimate = 0,1107 | | | | | |
| **HOMO-LUMO Gap versus Napht./Benz./Cycl.** | | | | | |
| | **Coefficient** | **Std. Error** | **t** | **P** | **VIF** |
| $y_0$ | 1,4626 | 0,0972 | 15,0426 | <0,0001 | 7,0753< |
| a | 10,4954 | 1,8349 | 5,7200 | 0,0012 | 33,0323< |
| b | -25,2607 | 7,0607 | -3,5777 | 0,0117 | 16,9162< |
| Eqn: | $f=y_0+ax+bx^2$ | | | | |
| | | | | | |
| Statistical tests: | | | | | |
| *Type* | *Normality Test* | *K-S Statistic* = 0,1489 | | *Constant Variance Test* | *PRESS* |
| *Factor* | Passed (P = 0,9800) | Significance Level = 0,9800 | | Passed (P = 0,1534) | 0,1104 |
| $R^2$=0,9202, R= 0,9593, Std. error estimate = 0,1097 | | | | | |

**Table 2S.** DI-π of the horizontal C-C bonds in 4n units and the edge ones in 4n+2 units of the oligomers A-I[a]

| | Oligomer | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| # C-C bond | A | B | C | D | E | F | G | H | I |
| 1 | *0.3440* | *0.3793* | *0.3763* | *0.3530* | *0.3544* | *0.3765* | *0.4752* | *0.4741* | *0.3479* |
| 2 | *0.4997* | *0.4646* | *0.4678* | *0.4907* | *0.4892* | *0.4675* | *0.3624* | *0.3634* | *0.4956* |
| 3 | **0.1125** | **0.1226** | **0.1213** | **0.1140** | **0.1142** | **0.1213** | *0.2497* | *0.2490* | **0.1129** |
| 4 | 0.3925 | 0.5314 | 0.5218 | 0.4257 | 0.4301 | 0.5223 | *0.5687* | *0.5694* | 0.4049 |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 5 | 0.4331 | 0.2873 | 0.2962 | 0.3995 | 0.3949 | 0.2957 | **0.1305** | **0.1307** | 0.4204 |
| 6 | **0.1115** | 0.3011 | 0.2832 | **0.1236** | **0.1257** | 0.2840 | 0.3756 | 0.3698 | **0.1143** |
| 7 | 0.4058 | 0.5122 | 0.5330 | 0.5291 | 0.5403 | 0.5319 | 0.4470 | 0.4530 | 0.4443 |
| 8 | 0.4182 | **0.1295** | **0.1257** | 0.2875 | 0.2770 | **0.1257** | **0.1163** | **0.1150** | 0.3790 |
| 9 | **0.1110** | 0.5053 | 0.4095 | 0.2847 | 0.3074 | 0.4130 | 0.4304 | 0.4073 | **0.1268** |
| 10 | 0.4096 | 0.3073 | 0.4125 | 0.5315 | 0.5055 | 0.4089 | 0.3923 | 0.4157 | 0.5444 |
| 11 | 0.4140 | 0.2797 | **0.1251** | **0.1243** | **0.1289** | **0.1268** | **0.1241** | **0.1141** | 0.2727 |
| 12 | **0.1109** | 0.5363 | 0.5270 | 0.3882 | 0.5044 | 0.5363 | 0.5294 | 0.4388 | 0.3133 |
| 13 | 0.4110 | **0.1269** | 0.2884 | 0.4345 | 0.3083 | 0.2798 | 0.2865 | 0.3840 | 0.4987 |
| 14 | 0.4126 | 0.4105 | 0.2880 | **0.1155** | 0.2759 | 0.3066 | 0.2849 | **0.1240** | **0.1302** |
| 15 | **0.1109** | 0.4111 | 0.5275 | 0.4344 | 0.5407 | 0.5061 | 0.5312 | 0.5308 | 0.5189 |
| 16 | 0.4117 | **0.1269** | **0.1251** | 0.3883 | **0.1264** | **0.1293** | **0.1242** | 0.2853 | 0.2946 |
| 17 | 0.4118 | 0.5355 | 0.4110 | **0.1242** | 0.3859 | 0.5067 | 0.3879 | 0.2853 | 0.2999 |
| 18 | **0.1109** | 0.2804 | 0.4110 | 0.5304 | 0.4366 | 0.3059 | 0.4348 | 0.5307 | 0.5128 |
| 19 | 0.4125 | 0.3063 | **0.1251** | 0.2856 | **0.1163** | 0.2805 | **0.1155** | **0.1240** | **0.1310** |
| 20 | 0.4110 | 0.5063 | 0.5275 | 0.2861 | 0.4375 | 0.5354 | 0.4346 | 0.3840 | 0.5128 |
| 21 | **0.1109** | **0.1294** | 0.2880 | 0.5299 | 0.3849 | **0.1268** | 0.3881 | 0.4388 | 0.3000 |
| 22 | 0.4140 | 0.5073 | 0.2884 | **0.1242** | **0.1266** | 0.4110 | **0.1242** | **0.1141** | 0.2946 |
| 23 | 0.4096 | 0.3053 | 0.5270 | 0.3895 | 0.5419 | 0.4106 | 0.5311 | 0.4157 | 0.5190 |
| 24 | **0.1110** | 0.2817 | **0.1251** | 0.4333 | 0.2748 | **0.1269** | 0.2850 | 0.4073 | **0.1302** |
| 25 | 0.4182 | 0.5342 | 0.4126 | **0.1157** | 0.3105 | 0.5362 | 0.2865 | **0.1150** | 0.4986 |
| 26 | 0.4058 | **0.1269** | 0.4095 | 0.4372 | 0.5020 | 0.2798 | 0.5295 | 0.4530 | 0.3134 |
| 27 | **0.1115** | 0.4183 | **0.1257** | 0.3856 | **0.1293** | 0.3072 | **0.1241** | 0.3697 | 0.2726 |
| 28 | 0.4332 | 0.4032 | 0.5330 | **0.1253** | 0.5134 | 0.5054 | 0.3922 | **0.1307** | 0.5445 |
| 29 | 0.3924 | **0.1304** | 0.2831 | 0.5385 | 0.3001 | **0.1295** | 0.4305 | *0.5694* | **0.1268** |
| 30 | **0.1125** | *0.5630* | 0.2963 | 0.2783 | 0.2878 | 0.5122 | **0.1164** | *0.2489* | 0.3787 |
| 31 | *0.4998* | *0.2544* | 0.5217 | 0.2991 | 0.5309 | 0.3012 | 0.4469 | *0.3635* | 0.4445 |
| 32 | *0.3439* | *0.3585* | **0.1213** | 0.5187 | **0.1225** | 0.2872 | 0.3757 | *0.4740* | **0.1143** |
| 33 | | *0.4791* | *0.4679* | **0.1209** | *0.4650* | 0.5315 | **0.1305** | | 0.4201 |
| 34 | | | *0.3762* | *0.4692* | *0.3790* | **0.1226** | *0.5687* | | 0.4052 |
| 35 | | | | *0.3750* | | *0.4646* | *0.2497* | | **0.1129** |
| 36 | | | | | | *0.3793* | *0.3624* | | *0.4954* |
| 37 | | | | | | | *0.4751* | | *0.3481* |
| Avg. in 4n | 0.1113 | 0.1275 | 0.1243 | 0.1209 | 0.1237 | 0.1261 | 0.1229 | 0.1210 | 0.1221 |
| Avg. in 4n+2 | 0.4121 | 0.4080 | 0.4089 | 0.4098 | 0.4087 | 0.4081 | 0.4100 | 0.4106 | 0.4087 |
| Gap (eV) | 1.446 | 2.534 | 2.298 | 2.002 | 2.224 | 2.473 | 1.993 | 1.877 | 2.267 |

[a] The bolded values correspond to the horizontal C-C bonds in the 4n units. The italic values correspond to the edge C-C bonds in the boundary 4n+2 units, and the average values shown at the bottom of the table did not take them into account to avoid finite size effect.

[b] The numbering of the C-C bonds consecutively goes from leftmost side to rightmost side according to the Fig. 1 in main text.