# DFT study of the ambipolar character of polymers based on s-tetrazine and aryl rings

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# Supplementary Materials

**Table 1S.** Calculated optical band gap energies (eV) within the oligomeric approximation along with experimental maximum of absorption ($E_{exp}$ in eV) reported for some monomers (solvent in parenthesis).

| Oligomer | n | TD-B3LYP | TD-M06-2X | TD-PBE0 | TD-CAM-B3LYP |
|---|---|---|---|---|---|
| | 1 | 3.954 | 4.429 | 4.142 | 4.407 |
| | 3 | 3.094 | 3.756 | 3.243 | 3.753 |
| | 5 | 2.907 | 3.601 | 3.056 | 3.602 |
| $(PhTz)_nPh$ | 7 | 2.840 | 3.541 | 2.987 | 3.542 |
| | 10 | 2.796 | 3.501 | 2.943 | 3.503 |
| | 15 | 2.770 | 3.475 | 2.915 | 3.477 |
| | n→∞[a] | 2.794±0.029 | 3.499 ± 0.028 | 2.939 ± 0.029 | 3.500 ± 0.028 |
| *$E_{exp}$* | *n = 1* | *4.18 (n-hexane)[b]* | *4.08 ($CCl_4$)[b]* | *4.16 ($CCl_4$)[c]* | |
| | 1 | 3.623 | 4.059 | 3.731 | 4.060 |
| | 3 | 2.650 | 3.277 | 2.777 | 3.291 |
| | 5 | 2.390 | 3.085 | 2.572 | 3.103 |
| $(FuTz)_nFu$ | 7 | 2.292 | 3.009 | 2.432 | 3.028 |
| | 10 | 2.231 | 2.958 | 2.371 | 2.978 |
| | 15 | 2.193 | 2.924 | 2.331 | 2.944 |
| | n→∞[a] | 2.222 ± 0.037 | 2.952 ± 0.036 | 2.362 ± 0.039 | 2.972 ± 0.036 |
| | 1 | 3.507 | 3.895 | 3.617 | 3.896 |
| | 3 | 2.574 | 3.108 | 2.708 | 3.110 |
| | 5 | 2.239 | 2.917 | 2.395 | 2.932 |
| $(PyTz)_nPy$ | 7 | 2.159 | 2.838 | 2.307 | 2.855 |
| | 10 | 2.102 | 2.784 | 2.247 | 2.802 |
| | 15 | 2.065 | 2.784 | 2.201 | 2.766 |
| | n→∞[a] | 2.081 ± 0.023 | 2.793 ± 0.027 | 2.224 ± 0.027 | 2.798 ± 0.042 |
| *$E_{exp}$* | *n = 1* | *3.44 ($CH_3$-CN)[d]* | | | |
| | 1 | 3.470 | 3.941 | 3.600 | 3.935 |
| | 3 | 2.580 | 3.216 | 2.723 | 3.223 |
| | 5 | 2.343 | 3.040 | 2.495 | 3.051 |
| $(ThTz)_nTh$ | 7 | 2.253 | 2.970 | 2.409 | 2.982 |
| | 10 | 2.198 | 2.924 | 2.353 | 2.936 |
| | 15 | 2.163 | 2.893 | 2.317 | 2.906 |
| | n→∞[a] | 2.189 ± 0.034 | 2.919 ± 0.033 | 2.345 ± 0.036 | 2.932 ± 0.032 |
| *$E_{exp}$* | *n = 1* | *3.57 ($CCl_4$)[c]* | *3.57 ($CH_3$-CN)[d]* | | |
| | 1 | 3.004 | 3.539 | 3.137 | 3.532 |
| | 3 | 2.307 | 2.974 | 2.457 | 2.992 |
| | 5 | 2.129 | 2.843 | 2.287 | 2.864 |
| $(TeTz)_nTe$ | 7 | 2.063 | 2.791 | 2.223 | 2.812 |
| | 10 | 2.021 | 2.756 | 2.182 | 2.778 |
| | 15 | 1.995 | 2.733 | 2.155 | 2.755 |
| | n→∞[a] | 2.016 ± 0.026 | 2.754 ± 0.026 | 2.177 ± 0.028 | 2.775 ± 0.024 |
| | 1 | 3.043 | 3.624 | 3.192 | 3.614 |
| | 3 | 2.377 | 3.125 | 2.538 | 3.125 |
| | 5 | 2.219 | 3.007 | 2.380 | 3.008 |
| $(TaTz)_nTa$ | 7 | 2.151 | 2.960 | 2.320 | 2.970 |
| | 10 | 2.113 | 2.929 | 2.282 | 2.931 |
| | 15 | 2.088 | 2.909 | 2.257 | 2.911 |
| | n→∞[a] | 2.109 ± 0.026 | 2.926 ± 0.022 | 2.282 ± 0.026 | 2.931 ± 0.024 |
| | 1 | 4.044 | 4.610 | 4.182 | 4.580 |
| $(PdTz)_nPd$ | 3 | 3.230 | 3.883 | 3.358 | 3.882 |
| | 5 | 3.030 | 3.736 | 3.180 | 3.739 |
| | 7 | 2.966 | 3.679 | 3.116 | 3.683 |

| | | | | | |
|---|---|---|---|---|---|
| | 10 | 2.924 | 3.641 | 3.075 | 3.645 |
| | 15 | 2.900 | 3.616 | 3.048 | 3.621 |
| | n→∞[a] | 2.921 ± 0.024 | 3.642 ± 0.030 | 3.071 ± 0.034 | 3.646 ± 0.030 |
| $E_{exp}$ | *n = 1* | *4.17 (MeOH)*[e] | | | |
| | 1 | 4.043 | 4.565 | 4.175 | 4.566 |
| | 3 | 3.242 | 3.915 | 3.383 | 3.908 |
| | 5 | 3.056 | 3.765 | 3.201 | 3.761 |
| $(PzTz)_nPz$ | 7 | 2.990 | 3.707 | 3.135 | 3.704 |
| | 10 | 2.950 | 3.669 | 3.093 | 3.667 |
| | 15 | 2.923 | 3.644 | 3.066 | 3.612 |
| | n→∞[a] | 2.947 ± 0.028 | 3.666 ± 0.028 | 3.091 ± 0.030 | 3.653 ± 0.042 |

[a] Values for the limit polymer were obtained from a fitting to Meier´s equation , $E(n) = E_\infty + (E_1 - E_\infty) \exp[-a(n-1)]$. The error corresponds to ± 2σ where σ is the standard deviation with respect to the fitting.

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**Table 2S.** Calculated optical band gaps at the TD-B3LYP/6-31G* level for oligomers of different chain length (n).

| Polymer | n | Energy / eV | *f* | Main component of transition (MO / % contribution) |
|---|---|---|---|---|
| $(PhTz)_nPh$ | 1 | 3.954 | 1.020 | HOMO-1 → LUMO+1 (72%) |
| | 3 | 3.094 | 2.661 | HOMO-3 → LUMO (89%) |
| | 5 | 2.907 | 4.210 | HOMO-3 → LUMO (85%) |
| | 7 | 2.840 | 5.869 | HOMO-2 → LUMO (75%) |
| | 10 | 2.796 | 8.467 | HOMO-4 → LUMO (56%) |
| | 15 | 2.770 | 12.797 | HOMO-4 → LUMO (32%) |
| | n→∞[a] | 2.794±0.029 | | |
| $(FuTz)_nFu$ | 1 | 3.623 | 1.050 | HOMO → LUMO+1 (100%) |
| | 3 | 2.650 | 2.299 | HOMO → LUMO+3 (43%) |
| | 5 | 2.390 | 3.524 | HOMO → LUMO (94%) |
| | 7 | 2.292 | 4.826 | HOMO → LUMO (86%) |
| | 10 | 2.231 | 6.942 | HOMO → LUMO (68%) |
| | 15 | 2.193 | 10.581 | HOMO → LUMO (40%) |
| | n→∞[a] | 2.222 ± 0.037 | | |
| $(PyTz)_nPy$ | 1 | 3.507 | 0.959 | HOMO → LUMO+1 (95%) |
| | 3 | 2.574 | 2.303 | HOMO → LUMO +3 (77%) |
| | 5 | 2.239 | 2.138 | HOMO → LUMO (89%) |
| | 7 | 2.159 | 4.303 | HOMO → LUMO (85%) |
| | 10 | 2.102 | 6.676 | HOMO → LUMO (66%) |
| | 15 | 2.065 | 10.504 | HOMO → LUMO (35%) |
| | n→∞[a] | 2.081 ± 0.023 | | |
| $(ThTz)_nTh$ | 1 | 3.470 | 0.849 | HOMO → LUMO+1 (95%) |
| | 3 | 2.580 | 2.348 | HOMO → LUMO (98%) |
| | 5 | 2.343 | 3.763 | HOMO → LUMO (94%) |
| | 7 | 2.253 | 5.204 | HOMO → LUMO (85%) |
| | 10 | 2.198 | 7.518 | HOMO → LUMO (67%) |
| | 15 | 2.163 | 11.456 | HOMO → LUMO (40%) |
| | n→∞[a] | 2.189 ± 0.034 | | |
| $(TeTz)_nTe$ | 1 | 3.004 | 1.277 | HOMO → LUMO+1 (96%) |
| | 3 | 2.307 | 3.469 | HOMO → LUMO (96%) |
| | 5 | 2.129 | 5.452 | HOMO → LUMO (89%) |
| | 7 | 2.063 | 7.567 | HOMO → LUMO (76%) |

| | | | | |
|---|---|---|---|---|
| | 10 | 2.021 | 10.903 | HOMO → LUMO (54%) |
| | 15 | 1.995 | 16.478 | HOMO → LUMO (25%)<br>HOMO-2 → LUMO (31%) |
| | n→∞[a] | 2.016 ± 0.026 | | |
| $(TaTz)_nTa$ | 1 | 3.043 | 1.127 | HOMO → LUMO (94%) |
| | 3 | 2.377 | 3.052 | HOMO → LUMO (97%) |
| | 5 | 2.219 | 4.843 | HOMO → LUMO (88%) |
| | 7 | 2.151 | 6.742 | HOMO → LUMO (75%) |
| | 10 | 2.113 | 90.706 | HOMO → LUMO (53%) |
| | 15 | 2.088 | 14.639 | HOMO → LUMO (26.5%)<br>HOMO-2 → LUMO (28%) |
| | n→∞[a] | 2.109 ± 0.026 | | |
| $(PdTz)_nPd$ | 1 | 4.044 | 0.919 | HOMO-1 → LUMO+1 (98%) |
| | 3 | 3.230 | 1.348<br>1.160 | HOMO-3 → LUMO (68%)<br>HOMO-3 → LUMO+1 (68%) |
| | 5 | 3.030 | 3.968 | HOMO-5 → LUMO (89%) |
| | 7 | 2.966 | 5.559 | HOMO-7 → LUMO (76%) |
| | 10 | 2.924 | 8.043 | HOMO-10 → LUMO (50%) |
| | 15 | 2.900 | 12.159 | HOMO-15→LUMO (28%) |
| | n→∞[a] | 2.921 ± 0.024 | | |
| $(PzTz)_nPz$ | 1 | 4.043 | 0.921 | HOMO-3 → LUMO+1 (90%) |
| | 3 | 3.242 | 2.459 | HOMO-5 → LUMO (97%) |
| | 5 | 3.056 | 3.890 | HOMO-7 → LUMO (89%) |
| | 7 | 2.990 | 5.417 | HOMO-9 → LUMO (77%) |
| | 10 | 2.950 | 7.794 | HOMO - 12→ LUMO (59%) |
| | 15 | 2.923 | 11.784 | HOMO - 19→ LUMO (19%) |
| | n→∞[a] | 2.947 ± 0.028 | | |

[a]Data obtained from a fitting to Meier´s equation , $E(n) = E_\infty + (E_1 - E_\infty) \exp[-a(n-1)]$. The error corresponds to ±2σ where σ is the standard deviation with respect to the first order exponential fitting.

**Table 3S.** Calculated optical bands gap at the TD-PBE0/6-31G* level for oligomers of different chain length (n).

| Polymer | n | Energy / eV | *f* | Main component of transition (MO / % contribution) |
|---|---|---|---|---|
| $(PhTz)_nPh$ | 1 | 4.142 | 0.626 | HOMO-1 → LUMO+2 (61%) |
| | 3 | 3.243 | 2.852 | HOMO-2 → LUMO (87%) |
| | 5 | 3.056 | 4.611 | HOMO-2 → LUMO (80%) |
| | 7 | 2.987 | 6.445 | HOMO-2 → LUMO (68%) |
| | 10 | 2.943 | 9.252 | HOMO-2 → LUMO (51%) |
| | 15 | 2.915 | 13.880 | HOMO-2 → LUMO (30%) |
| | n→∞a | 2.943 ± 0.36 | | |
| $(FuTz)_nFu$ | 1 | 3.731 | 1.079 | HOMO → LUMO+1 (100%) |
| | 3 | 2.777 | 2.434 | HOMO → LUMO (97%) |
| | 5 | 2.572 | 3.826 | HOMO → LUMO (90%) |
| | 7 | 2.432 | 5.295 | HOMO →LUMO (78%) |
| | 10 | 2.371 | 7.591 | HOMO → LUMO (60%) |
| | 15 | 2.331 | 11.447 | HOMO → LUMO (35%) |
| | n→∞[a] | 2.362 ± 0.039 | | |
| $(PyTz)_nPy$ | 1 | 3.617 | 1.042 | HOMO → LUMO+1 (97%) |
| | 3 | 2.708 | 2.267 | HOMO → LUMO+3 (63%) |
| | 5 | 2.395 | 3.179 | HOMO → LUMO (89%) |
| | 7 | 2.307 | 5.068 | HOMO → LUMO (78%) |
| | 10 | 2.247 | 7.547 | HOMO → LUMO (58%) |
| | 15 | 2.201 | 11.579 | HOMO → LUMO (30%) |
| | n→∞[a] | 2.224 ± 0.027 | | |
| $(ThTz)_nTh$ | 1 | 3.600 | 0.905 | HOMO → LUMO+1 (97%) |
| | 3 | 2.723 | 2.507 | HOMO → LUMO (97%) |

| | | | | |
|---|---|---|---|---|
| | 5 | 2.495 | 4.072 | HOMO → LUMO (89%) |
| | 7 | 2.409 | 5.685 | HOMO → LUMO (78%) |
| | 10 | 2.353 | 8.184 | HOMO → LUMO (59%) |
| | 15 | 2.317 | 12.355 | HOMO → LUMO (35%) |
| | n→∞[a] | 2.345 ± 0.036 | | |
| $(TeTz)_nTe$ | 1 | 3.137 | 1.354 | HOMO → LUMO+1 (97%) |
| | 3 | 2.457 | 3.705 | HOMO → LUMO (94%) |
| | 5 | 2.287 | 5.939 | HOMO → LUMO (83%) |
| | 7 | 2.223 | 8.267 | HOMO → LUMO (68%) |
| | 10 | 2.182 | 11.823 | HOMO → LUMO (46%) |
| | 15 | 2.155 | 17.695 | HOMO → LUMO (22%)<br>HOMO-2 → LUMO (28%) |
| | n→∞[a] | 2.177 ± 0.028 | | |
| $(TaTz)_nTa$ | 1 | 3.192 | 1.068 | HOMO → LUMO (82%) |
| | 3 | 2.538 | 3.263 | HOMO → LUMO (94%) |
| | 5 | 2.380 | 5.271 | HOMO → LUMO (82%) |
| | 7 | 2.320 | 7.357 | HOMO → LUMO (67%) |
| | 10 | 2.282 | 10.522 | HOMO → LUMO (46%) |
| | 15 | 2.257 | 15.747 | HOMO → LUMO (24%)<br>HOMO-2 → LUMO (25%) |
| | n→∞[a] | 2.282 ± 0.026 | | |
| $(PdTz)_nPd$ | 1 | 4.182 | 0.964 | HOMO-1 → LUMO+1 (98%) |
| | 3 | 3.358 | 2.625 | HOMO-3 → LUMO (94%) |
| | 5 | 3.180 | 4.373 | HOMO-5 → LUMO (84%) |
| | 7 | 3.116 | 6.134 | HOMO-7 → LUMO (69%) |
| | 10 | 3.075 | 8.843 | HOMO-10 → LUMO (37%) |
| | 15 | 3.048 | 13.233 | HOMO-15 → LUMO (25%) |
| | n→∞[a] | 3.071 ± 0.034 | | |
| $(PzTz)_nPz$ | 1 | 4.175 | 0.963 | HOMO-3 → LUMO+2 (47%)<br>HOMO-3 → LUMO+1 (52%) |
| | 3 | 3.383 | 2.652 | HOMO-5 → LUMO (95%) |
| | 5 | 3.201 | 4.275 | HOMO-7 → LUMO (84%) |
| | 7 | 3.135 | 5.972 | HOMO-9 → LUMO (70.5%) |
| | 10 | 3.093 | 8.383 | HOMO-11 → LUMO (51%) |
| | 15 | 3.066 | 12.823 | HOMO-17 → LUMO (32%) |
| | n→∞[a] | 3.091 ± 0.030 | | |

[a] Data obtained from a fitting to Meier´s equation, $E(n) = E_\infty + (E_1 - E_\infty) \exp[-a(n-1)]$. The error corresponds to ± 2σ where σ is the standard deviation with respect to the first order exponential fitting.

**Table 4S.** Calculated optical band gap at the TD-M06-2X/6-31G* level for oligomers of different chain length (n).

| **Polymer** | **n** | **Energy / eV** | ***f*** | **Main component of transition (MO / % contribution)** |
|---|---|---|---|---|
| **$(PhTz)_nPh$** | 1 | 4.429 | 1.088 | HOMO → LUMO+1 (96%) |
| | 3 | 3.756 | 3.248 | HOMO → LUMO (81%) |
| | 5 | 3.601 | 5.391 | HOMO → LUMO (63%) |
| | 7 | 3.541 | 7.521 | HOMO → LUMO (49%) |
| | 10 | 3.501 | 10.684 | HOMO → LUMO (35%) |
| | 15 | 3.475 | 15.922 | HOMO → LUMO (22%) |
| | n→∞[a] | | | |
| **$(FuTz)_nFu$** | 1 | 4.059 | 1.075 | HOMO → LUMO+1 (97%) |
| | 3 | 3.277 | 2.615 | HOMO → LUMO (84%) |

| | | | | |
|---|---|---|---|---|
| | 5 | 3.085 | 4.287 | HOMO → LUMO (68%) |
| | 7 | 3.009 | 5.971 | HOMO → LUMO (54%) |
| | 10 | 2.958 | 8.478 | HOMO → LUMO (38%) |
| | 15 | 2.924 | 12.624 | HOMO → LUMO (23%) |
| | $n \rightarrow \infty$[a] | 2.952 ± 0.036 | | |
| **$(PyTz)_nPy$** | 1 | 3.895 | 1.098 | HOMO → LUMO+1 (97%) |
| | 3 | 3.108 | 2.401 | HOMO → LUMO (76%) |
| | 5 | 2.917 | 4.388 | HOMO → LUMO (68%) |
| | 7 | 2.838 | 6.186 | HOMO → LUMO (54%) |
| | 10 | 2.784 | 8.841 | HOMO → LUMO (37%) |
| | 15 | 2.784 | 13.206 | HOMO → LUMO (21%) |
| | $n \rightarrow \infty$[a] | 2.793 ± 0.027 | | |
| **$(ThTz)_nTh$** | 1 | 3.941 | 0.943 | HOMO → LUMO+1 (95%) |
| | 3 | 3.216 | 2.733 | HOMO → LUMO (83%) |
| | 5 | 3.040 | 4.564 | HOMO → LUMO (67%) |
| | 7 | 2.970 | 6.393 | HOMO → LUMO (53%) |
| | 10 | 2.924 | 9.117 | HOMO → LUMO (38%) |
| | 15 | 2.893 | 13.614 | HOMO → LUMO (23%) |
| | $n \rightarrow \infty$[a] | 2.919 ± 0.033 | | |
| **$(TeTz)_nTe$** | 1 | 3.539 | 1.077 | HOMO → LUMO (54%)<br>HOMO → LUMO+1 (41%) |
| | 3 | 2.974 | 4.048 | HOMO → LUMO (76%) |
| | 5 | 2.843 | 6.625 | HOMO → LUMO (58%) |
| | 7 | 2.791 | 9.181 | HOMO → LUMO (43%) |
| | 10 | 2.756 | 12.977 | HOMO → LUMO (29%) |
| | 15 | 2.733 | 19.222 | HOMO → LUMO (15.5%)<br>HOMO-2 → LUMO (15.5%) |
| | $n \rightarrow \infty$[a] | 2.754 ± 0.026 | | |
| **$(TaTz)_nTa$** | 1 | 3.624 | 1.174 | HOMO→ LUMO (94%) |
| | 3 | 3.125 | 3.460 | HOMO → LUMO (75%) |
| | 5 | 3.007 | 5.221 | HOMO → LUMO (51.5%) |
| | 7 | 2.960 | 7.934 | HOMO → LUMO (42%) |
| | 10 | 2.929 | 11.269 | HOMO → LUMO (29%) |
| | 15 | 2.909 | 16.734 | HOMO →LUMO (16%)<br>HOMO-2→ LUMO (14%) |
| | $n \rightarrow \infty$[a] | 2.926 ± 0.022 | | |
| **$(PdTz)_nPd$** | 1 | 4.610 | 1.035 | HOMO-1 → LUMO (93%) |
| | 3 | 3.883 | 3.027 | HOMO-2 → LUMO (81%9 |
| | 5 | 3.736 | 5.124 | HOMO-2 → LUMO (62%) |
| | 7 | 3.679 | 7.186 | HOMO-2 → LUMO (47%) |
| | 10 | 3.641 | 10.268 | HOMO-1 → LUMO (32%) |
| | 15 | 3.616 | 15.256 | HOMO-2 → LUMO (19%) |
| | $n \rightarrow \infty$[a] | 3.642 ± 0.030 | | |
| **$(PzTz)_nPz$** | 1 | 4.565 | 0.749 | HOMO-1 → LUMO (56%)<br>HOMO-1 → LUMO+1 (58%) |
| | 3 | 3.915 | 3.015 | HOMO-3 → LUMO (79%) |
| | 5 | 3.765 | 5.001 | HOMO-3 → LUMO (62%) |
| | 7 | 3.707 | 6.980 | HOMO-4 → LUMO (48%) |
| | 10 | 3.669 | 9.926 | HOMO-6 → LUMO (34%) |
| | 15 | 3.644 | 14.789 | HOMO-8 → LUMO (22%) |
| | $n \rightarrow \infty$[a] | 3.668 ± 0.028 | | |

[a] Data obtained from a fitting to Meier´s equation, $E(n) = E_\infty + (E_1 - E_\infty) \exp[-a(n-1)]$. The error corresponds to $\pm 2\sigma$ where $\sigma$ is the standard deviation with respect to the first order exponential fitting.

**Table 5S.** Calculated optical band gap at the TD-CAM-B3LYP/6-31G* level for oligomers of different chain length (n).

| Polymer | n | Energy / eV | *f* | Main component of transition (MO / % contribution) |
|---|---|---|---|---|
| **$(PhTz)_nPh$** | 1 | 4.407 | 1.061 | HOMO → LUMO+1 (94%) |
| | 3 | 3.753 | 3.240 | HOMO → LUMO (77%) |
| | 5 | 3.602 | 5.394 | HOMO → LUMO (59%) |
| | 7 | 3.542 | 7.537 | HOMO → LUMO (46%) |
| | 10 | 3.503 | 10.723 | HOMO → LUMO (32%) |
| | 15 | 3.477 | 15.977 | HOMO → LUMO (20%) |
| | $n\rightarrow\infty$[a] | 3.499 ± 0.028 | | HOMO → LUMO+1 (96%) |
| **$(FuTz)_nFu$** | 1 | 4.060 | 1.079 | HOMO → LUMO+1 (96%) |
| | 3 | 3.291 | 2.631 | HOMO → LUMO (81%) |
| | 5 | 3.103 | 4.323 | HOMO → LUMO (64%) |
| | 7 | 3.028 | 6.020 | HOMO → LUMO (50%) |
| | 10 | 2.978 | 8.546 | HOMO → LUMO (36%) |
| | 15 | 2.944 | 12.722 | HOMO → LUMO (22%) |
| | $n\rightarrow\infty$[a] | 2.972 ± 0.036 | | |
| **$(PyTz)_nPy$** | 1 | 3.896 | 1.101 | HOMO → LUMO+1 (96%) |
| | 3 | 3.110 | 2.005 | HOMO → LUMO (80%) |
| | 5 | 2.932 | 4.357 | HOMO → LUMO (64%) |
| | 7 | 2.855 | 6.191 | HOMO → LUMO (50%) |
| | 10 | 2.802 | 8.866 | HOMO → LUMO (34%) |
| | 15 | 2.766 | 13.254 | HOMO → LUMO (19%) |
| | $n\rightarrow\infty$[a] | 2.798 ± 0.042 | | |
| **$(ThTz)_nTh$** | 1 | 3.935 | 0.944 | HOMO → LUMO+1 (94%) |
| | 3 | 3.223 | 2.735 | HOMO → LUMO (80%) |
| | 5 | 3.051 | 4.585 | HOMO → LUMO (63%) |
| | 7 | 2.982 | 6.425 | HOMO → LUMO (49%) |
| | 10 | 2.936 | 9.160 | HOMO → LUMO (35%) |
| | 15 | 2.906 | 13.671 | HOMO → LUMO (21%) |
| | $n\rightarrow\infty$[a] | 2.932 ± 0.032 | | |
| **$(TeTz)_nTe$** | 1 | 3.532 | 1.355 | HOMO → LUMO+1 (59%)<br>HOMO → LUMO (37%) |
| | 3 | 2.992 | 4.064 | HOMO → LUMO (72%) |
| | 5 | 2.864 | 6.661 | HOMO → LUMO (54%) |
| | 7 | 2.812 | 9.225 | HOMO → LUMO (40%) |
| | 10 | 2.778 | 13.034 | HOMO → LUMO (27%) |
| | 15 | 2.755 | 19.319 | HOMO → LUMO (15%) |
| | $n\rightarrow\infty$[a] | 2.775 ± 0.024 | | |
| **$(TaTz)_nTa$** | 1 | 3.614 | 1.175 | HOMO → LUMO (91%) |
| | 3 | 3.125 | 3.469 | HOMO → LUMO (71%) |
| | 5 | 3.008 | 5.734 | HOMO → LUMO (53%) |
| | 7 | 2.970 | 7.862 | HOMO → LUMO (38%) |
| | 10 | 2.931 | 11.302 | HOMO → LUMO (27%) |
| | 15 | 2.911 | 16.787 | HOMO → LUMO (16%) |
| | $n\rightarrow\infty$[a] | 2.930 ± 0.024 | | |
| **$(PdTz)_nPd$** | 1 | 4.580 | 1.019 | HOMO -1 → LUMO +1 (92%) |
| | 3 | 3.882 | 3.030 | HOMO -3 → LUMO (77%) |
| | 5 | 3.739 | 5.148 | HOMO -3 → LUMO (58%) |
| | 7 | 3.683 | 7.214 | HOMO -4 → LUMO (44%) |
| | 10 | 3.645 | 10.280 | HOMO -5 → LUMO (30%) |
| | 15 | 3.621 | 15.329 | HOMO -8 → LUMO (18%) |
| | $n\rightarrow\infty$[a] | 3.646 ± 0.030 | | |

| | | | | |
|---|---|---|---|---|
| **$(PzTz)_nPz$** | 1 | 4.566 | 0.922 | HOMO -1 → LUMO (62%) |
| | 3 | 3.908 | 3.015 | HOMO -3 → LUMO (75%) |
| | 5 | 3.761 | 5.019 | HOMO -5 → LUMO (58%) |
| | 7 | 3.704 | 7.009 | HOMO -7 → LUMO (44%) |
| | 10 | 3.667 | 9.970 | HOMO -9 → LUMO (32%) |
| | 15 | 3.612 | 14.845 | HOMO -13 → LUMO (20%) |
| | $n \rightarrow \infty$[a] | 3.653 ± 0.042 | | |

[a] Data obtained from a fitting to Meier´s equation, $E(n) = E_\infty + (E_1 - E_\infty) \exp[-a(n-1)]$. The error corresponds to $\pm 2\sigma$ where $\sigma$ is the standard deviation with respect to the first order exponential fitting.

**Table 6S**. Data obtained from the fit of the band gap values to mono-exponential Meier-like equation, $E(n) = E_\infty + (E_1 - E_\infty) \exp[-a(n-1)]$

| Polymer | Method | $E_\infty$ / eV | $E_1 - E_\infty$ / eV | a | $r^2$ |
|---|---|---|---|---|---|
| **p(PhTz)** | TD-B3LYP | 2.794 | 1.157 | 0.631 | 0.998 |
| | TD-PBE0 | 2.939 | 1.197 | 0.661 | 0.998 |
| | TD-M06-2X | 3.499 | 0.928 | 0.609 | 0.997 |
| | TD-CAM-B3LYP | 3.500 | 0.904 | 0.604 | 0.997 |
| **p(FuTz)** | TD-B3LYP | 2.222 | 1.397 | 0.566 | 0.998 |
| | TD-PBE0 | 2.362 | 1.361 | 0.545 | 0.995 |
| | TD-M06-2X | 2.952 | 1.103 | 0.579 | 0.997 |
| | TD-CAM-B3LYP | 2.972 | 1.084 | 0.579 | 0.997 |
| **p(PyTz)** | TD-B3LYP | 2.081 | 1.425 | 0.532 | 0.999 |
| | TD-PBE0 | 2.224 | 1.395 | 0.517 | 0.999 |
| | TD-M06-2X | 2.793 | 1.099 | 0.599 | 0.999 |
| | TD-CAM-B3LYP | 2.798 | 1.094 | 0.588 | 0.996 |
| **p(ThTz)** | TD-B3LYP | 2.189 | 1.277 | 0.566 | 0.998 |
| | TD-PBE0 | 2.345 | 1.253 | 0.569 | 0.998 |
| | TD-M06-2X | 2.919 | 1.019 | 0.584 | 0.997 |
| | TD-CAM-B3LYP | 2.932 | 1.000 | 0.584 | 0.997 |
| **p(TeTz)** | TD-B3LYP | 2.016 | 0.985 | 0.584 | 0.998 |
| | TD-PBE0 | 2.177 | 0.959 | 0.584 | 0.998 |
| | TD-M06-2X | 2.754 | 0.783 | 0.600 | 0.997 |
| | TD-CAM-B3LYP | 2.775 | 0.755 | 0.855 | 0.997 |
| **p(TaTz)** | TD-B3LYP | 2.109 | 0.931 | 0.591 | 0.998 |
| | TD-PBE0 | 2.282 | 0.912 | 0.596 | 0.998 |
| | TD-M06-2X | 2.926 | 0.695 | 0.594 | 0.997 |
| | TD-CAM-B3LYP | 2.931 | 0.681 | 0.592 | 0.997 |
| **p(PdTz)** | TD-B3LYP | 2.921 | 1.121 | 0.623 | 0.999 |
| | TD-PBE0 | 3.071 | 1.106 | 0.649 | 0.998 |
| | TD-M06-2X | 3.642 | 0.969 | 0.659 | 0.997 |
| | TD-CAM-B3LYP | 3.646 | 0.932 | 0.651 | 0.997 |
| **p(PzTz)** | TD-B3LYP | 2.947 | 1.094 | 0.629 | 0.998 |
| | TD-PBE0 | 3.091 | 1.083 | 0.624 | 0.998 |
| | TD-M06-2X | 3.666 | 0.896 | 0.609 | 0.998 |
| | TD-CAM-B3LYP | 3.653 | 0.910 | 0.594 | 0.995 |

**Table 7S.** Calculated HOMO energy (in eV) for the n-mers of the studied systems (n is the number of repeat units) at B3LYP/6-31+G*//B3LYP/6-31G* levels. The HOCO energy for the infinite polymer chains was fitted using the mono-exponential Meier-like equation, $E(n) = E_\infty + (E_1 - E_\infty) \exp[-a(n-1)]$.

| | $E_{HOMO}$ | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| **n** | **$(PhTz)_nPh$** | **$(FuTz)_nFu$** | **$(PyTz)_nPy$** | **$(ThTz)_nTh$** | **$(TeTz)_nTe$** | **$(TaTz)_nTa$** | **$(PdTz)_nPd$** | **$(PzTz)_nPz$** |
| **n=1** | -6.480 | -6.298 | -5.798 | -6.379 | -6.007 | -6.807 | -6.394 | -6.776 |
| **n=3** | -6.629 | -6.246 | -5.787 | -6.317 | -5.995 | -6.782 | -6.562 | -6.883 |
| **n=5** | -6.655 | -6.258 | -5.811 | -6.326 | -6.012 | -6.793 | -6.587 | -6.915 |
| **n=7** | -6.661 | -6.269 | -5.830 | -6.337 | -6.023 | -6.802 | -6.593 | -6.922 |
| **n=9** | -6.662 | -6.278 | -5.842 | -6.344 | -6.031 | -6.808 | -6.595 | -6.924 |
| **n=11** | – | – | -- | – | -6.036 | -6.811 | -6.594 | -6.925 |
| **$n\rightarrow\infty$** [a] | -6.662 ± 0.001 | -6.340 ± 0.028 | -5.876 ± 0.016 | -6.421 ± 0.262 | -6.047 ± 0.004 | -6.804 ± 0.006 | -6.593 ± 0.002 | -6.925 ± 0.012 |

[a] The error corresponds to ± 2σ where σ is the standard deviation with respect to the first order exponential fitting.

**Table 8S.** Calculated LUMO energy (in eV) for the n-mers of the studied systems (n is the number of repeat units) at B3LYP/6-31+G* // B3LYP/6-31G* levels. The LUCO energies for the infinite polymer chain were fitted using a mono-exponential Meier-like equation, $E(n) = E_\infty + (E_1 - E_\infty) \exp[-a(n-1)]$.

| | $E_{LUMO}$ | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| **n** | **$(PhTz)_nPh$** | **$(FuTz)_nFu$** | **$(PyTz)_nPy$** | **$(ThTz)_nTh$** | **$(TeTz)_nTe$** | **$(TaTz)_nTa$** | **$(PdTz)_nPd$** | **$(PzTz)_nPz$** |
| **n=1** | -2.967 | -2.911 | -2.842 | -2.981 | -2.976 | -3.505 | -2.948 | -2.967 |
| **n=3** | -3.242 | -3.310 | -3.092 | -3.432 | -3.391 | -4.084 | -3.533 | -3.242 |
| **n=5** | -3.430 | -3.536 | -3.254 | -3.648 | -3.564 | -4.243 | -3.717 | -3.430 |
| **n=7** | -3.505 | -3.634 | -3.349 | -3.741 | -3.637 | -4.309 | -3.792 | -3.505 |
| **n=9** | -3.542 | -3.684 | -3.401 | -3.789 | -3.674 | -4.342 | -3.841 | -3.542 |
| **n=11** | – | – | – | – | -3.695 | -4.361 | -3.852 | -3.541 |
| **$n\rightarrow\infty$** [a] | -3.605 ± 0.056 | -3.745 ± 0.028 | -3.494 ± 0.022 | -3.829 ± 0.008 | -3.701 ± 0.008 | -4.350 ± 0.022 | -3.849 ± 0.022 | -3.578 ± 0.040 |

[a] The error corresponds to ± 2σ where σ is the standard deviation with respect to the first order exponential fitting.

**Table 9S**. Data obtained from the fit of the HOCO and LUCO energies values to a mono-exponential Meier-Like equation, $E(n) = E_\infty + (E_1 - E_\infty) \exp[-a(n-1)]$

| Polymer | Energy Level | $E_\infty$ / eV | $E_1 - E_\infty$ / eV | a | $r^2$ |
|---|---|---|---|---|---|
| **p(PhTz)** | HOCO | -6.662 | 0.182 | 0.852 | 0.999 |
| | LUCO | -3.605 | 0.642 | 0.304 | 0.998 |
| **p(FuTz)** | HOCO | -6.340 | 0.094 | 0.069 | 0.999 |
| | LUCO | -3.745 | 0.835 | 0.336 | 0.999 |
| **p(PyTz)** | HOCO | -5.876 | 0.089 | 0.161 | 0.999 |
| | LUCO | -3.494 | 0.653 | 0.248 | 0.999 |
| **p(ThTz)** | HOCO | -6.421 | 0.105 | 0.051 | 0.996 |
| | LUCO | -3.829 | 0.848 | 0.382 | 0.999 |
| **p(TeTz)** | HOCO | -6.047 | 0.052 | 0.195 | 0.999 |
| | LUCO | -3.701 | 0.724 | 0.419 | 0.999 |
| **p(TaTz)** | HOCO | -6.820 | 0.039 | 0.182 | 0.998 |
| | LUCO | -4.350 | 0.843 | 0.553 | 0.999 |
| **p(PdTz)** | HOCO | -6.593 | 0.199 | 0.927 | 0.999 |
| | LUCO | -3.849 | 0.899 | 0.503 | 0.999 |
| **p(PzTz)** | HOCO | -6.925 | 0.149 | 0.641 | 0.999 |
| | LUCO | -3.578 | 0.616 | 0.334 | 0.996 |

**Table 10S.** AIP, VIP, AEA, VEA, $\lambda^+$ and $\lambda^-$ calculated at B3LYP/6-31+G* level on the corresponding B3LYP/6-31G* geometries for oligomers with different number of repeat units.

| **AIP / eV** | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| **Polymer** | **n=1** | **n=3** | **n=5** | **n=7** | **n=9** | **n=11** | **n=13** | **n →∞[a]** |
| **(PhTz)$_n$Ph** | 7.70 | 7.43 | 7.30 | 7.20 | 7.14 | | | 7.07 ± 0.03 |
| **(FuTz)$_n$Fu** | 7.70 | 7.17 | 6.97 | 6.86 | 6.78 | | | 6.76 ± 0.06 |
| **(PyTz)$_n$Py** | 7.17 | 6.86 | 6.51 | 6.41 | 6.37 | | | 6.22 ± 0.29 |
| **(ThTz)$_n$Th** | 7.69 | 7.18 | 6.99 | 6.89 | 6.82 | | | 6.79 ± 0.06 |
| **(TeTz)$_n$Te** | 7.11 | 6.72 | 6.57 | 6.48 | 6.42 | | | 6.39 ± 0.05 |
| **(TaTz)$_n$Ta** | 7.96 | 7.53 | 7.37 | 7.27 | 7.21 | 7.16 | | 7.15 ± 0.04 |
| **(PdTz)$_n$Pd** | 7.70 | 7.41 | 7.25 | 7.16 | 7.11 | | | 7.06 ± 0.01 |
| **(PzTz)$_n$Pz** | 8.12 | 7.76 | 7.57 | 7.47 | 7.39 | | | 7.33 ± 0.03 |
| **VIP / eV** | | | | | | | | |
| **Polymer** | **n=1** | **n=3** | **n=5** | **n=7** | **n=9** | **n=11** | **n=13** | **n →∞[a]** |
| **(PhTz)$_n$Ph** | 8.32 | 7.68 | 7.44 | 7.31 | 7.23 | | | 7.20 ± 0.06 |
| **(FuTz)$_n$Fu** | 7.83 | 7.24 | 7.02 | 6.89 | 6.81 | | | 6.77 ± 0.06 |
| **(PyTz)$_n$Py** | 7.29 | 6.76 | 6.56 | 6.44 | 6.36 | | | 6.33 ± 0.06 |
| **(ThTz)$_n$Th** | 7.84 | 7.27 | 7.05 | 6.93 | 6.85 | | | 6.82 ± 0.06 |
| **(TeTz)$_n$Te** | 7.24 | 6.79 | 6.61 | 6.51 | 6.44 | | | 6.41 ± 0.05 |
| **(TaTz)$_n$Ta** | 8.09 | 7.60 | 7.41 | 7.30 | 7.23 | 7.18 | | 7.17 ± 0.04 |
| **(PdTz)$_n$Pd** | 8.18 | 7.64 | 7.42 | 7.29 | 7.21 | | | 7.18 ± 0.05 |
| **(PzTz)$_n$Pz** | 8.47 | 7.90 | 7.67 | 7.54 | 7.46 | | | 7.42 ± 0.05 |
| **$\lambda^+$ / eV** | | | | | | | | |
| **Polymer** | **n=1** | **n=3** | **n=5** | **n=7** | **n=9** | **n=11** | **n=13** | **n →∞[a]** |
| **(PhTz)$_n$Ph** | 1.245 | 0.516 | 0.329 | 0.236 | 0.184 | | | 0.192 ± 0.046 |
| **(FuTz)$_n$Fu** | 0.261 | 0.162 | 0.103 | 0.074 | 0.059 | | | 0.038 ± 0.008 |
| **(PyTz)$_n$Py** | 0.263 | 0.161 | 0.102 | 0.073 | 0.069 | | | 0.052 ± 0.016 |
| **(ThTz)$_n$Th** | 0.295 | 0.178 | 0.112 | 0.081 | 0.064 | | | 0.044 ± 0.006 |
| **(TeTz)$_n$Te** | 0.259 | 0.145 | 0.091 | 0.066 | 0.054 | | | 0.044 ± 0.001 |
| **(TaTz)$_n$Ta** | 0.268 | 0.149 | 0.094 | 0.069 | 0.056 | 0.046 | | 0.043 ± 0.002 |
| **(PdTz)$_n$Pd** | 1.051 | 0.476 | 0.331 | 0.254 | 0.176 | | | 0.193 ± 0.070 |
| **(PzTz)$_n$Pz** | 0.859 | 0.309 | 0.19 | 0.134 | 0.105 | | | 0.115 ± 0.030 |
| **AEA /eV** | | | | | | | | |
| **Polymer** | **n=1** | **n=3** | **n=5** | **n=7** | **n=9** | **n=11** | **n=13** | **n →∞[a]** |
| **(PhTz)$_n$Ph** | 1.51 | 2.36 | 2.72 | 2.91 | 3.03 | | | 3.09±0.06 |
| **(FuTz)$_n$Fu** | 1.42 | 2.39 | 2.79 | 3.00 | 3.13 | | | 3.19 ± 0.07 |
| **(PyTz)$_n$Py** | 1.43 | 2.15 | 2.51 | 2.71 | 2.85 | | | 2.97 ± 0.05 |
| **(ThTz)$_n$Th** | 1.56 | 2.54 | 2.93 | 3.13 | 3.26 | | | 3.31 ± 0.07 |
| **(TeTz)$_n$Te** | 1.72 | 2.63 | 2.96 | 3.12 | 3.23 | | | 3.26 ± 0.07 |
| **(TaTz)$_n$Ta** | 2.32 | 3.31 | 3.62 | 3.79 | 3.89 | 3.96 | 4.01 | 3.94 ± 0.09 |
| **(PdTz)$_n$Pd** | 1.46 | 2.62 | 2.99 | 3.18 | 3.33 | | | 3.34 ± 0.11 |
| **(PzTz)$_n$Pz** | 1.94 | 3.04 | 3.39 | 3.59 | 3.71 | 3.79 | 3.90 | 3.83 ± 0.09 |
| **VEA / eV** | | | | | | | | |
| **Polymer** | **n=1** | **n=3** | **n=5** | **n=7** | **n=9** | **n=11** | **n=13** | **n →∞[a]** |
| **(PhTz)$_n$Ph** | 1.23 | 2.26 | 2.65 | 2.86 | 2.99 | | | 3.03± 0.09 |
| **(FuTz)$_n$Fu** | 1.13 | 2.28 | 2.72 | 2.94 | 3.07 | | | 3.13 ± 0.09 |
| **(PyTz)$_n$Py** | 1.09 | 2.06 | 2.46 | 2.68 | 2.82 | | | 2.89 ± 0.07 |
| **(ThTz)$_n$Th** | 1.26 | 2.45 | 2.86 | 3.08 | 3.22 | | | 3.25 ± 0.09 |
| **(TeTz)$_n$Te** | 1.41 | 2.55 | 2.89 | 3.08 | 3.19 | | | 3.21 ± 0.09 |
| **(TaTz)$_n$Ta** | 2.19 | 3.22 | 3.56 | 3.74 | 3.86 | 3.93 | 3.99 | 3.96 ± 0.07 |
| **(PdTz)$_n$Pd** | 1.29 | 2.51 | 2.92 | 3.13 | 3.28 | | | 3.30 ± 0.11 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| **$(PzTz)_nPz$** | 1.79 | 2.93 | 3.33 | 3.59 | 3.71 | 3.75 | 3.87 | 3.81 ± 0.09 |
| | | | | **$\lambda^-$ / eV** | | | | |
| **Polymer** | **n=1** | **n=3** | **n=5** | **n=7** | **n=9** | **n=11** | **n=13** | **n →∞[a]** |
| **$(PhTz)_nPh$** | 0.624 | 0.192 | 0.126 | 0.091 | 0.071 | | | 0.083 ± 0.022 |
| **$(FuTz)_nFu$** | 0.672 | 0.215 | 0.154 | 0.111 | 0.086 | | | 0.103 ± 0.032 |
| **$(PyTz)_nPy$** | 0.759 | 0.231 | 0.109 | 0.081 | 0.063 | | | 0.067 ± 0.008 |
| **$(ThTz)_nTh$** | 0.662 | 0.199 | 0.138 | 0.098 | 0.076 | | | 0.091 ± 0.030 |
| **$(TeTz)_nTe$** | 0.690 | 0.171 | 0.113 | 0.080 | 0.062 | | | 0.076 ± 0.024 |
| **$(TaTz)_nTa$** | 0.264 | 0.198 | 0.129 | 0.092 | 0.071 | 0.059 | 0.050 | 0.026 ± 0.022 |
| **$(PdTz)_nPd$** | 0.333 | 0.201 | 0.133 | 0.097 | 0.074 | | | 0.050 ± 0.004 |
| **$(PzTz)_nPz$** | 0.304 | 0.225 | 0.146 | 0.106 | 0.084 | 0.069 | 0.051 | 0.035.± 0.022 |

[a] Values for the limit polymer were obtained from a fitting to Meier´s equation [, $E(n) = E_\infty + (E_1 - E_\infty) \exp[-a(n-1)]$. The error corresponds to ± 2σ where σ is the standard deviation with respect to the first order exponential fitting.

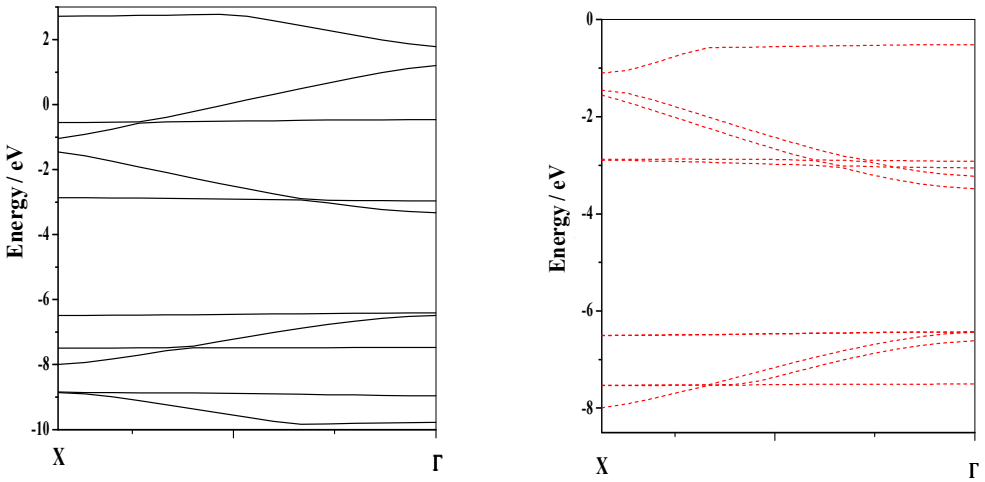
**Table 11S**. Data obtained from the fit of the AIP, VIP, AEA, VEA, $\lambda^+$ and $\lambda^-$ values to mono-exponential equation, $E(n) = E_\infty + (E_1 - E_\infty) \exp[-a(n-1)]$, at B3LYP/6-31G+*//B3LYP/6-31G* level.

| Polymers | Property | $E_\infty$ / eV | $E_1 - E_\infty$ / eV | a | $r^2$ |
|---|---|---|---|---|---|
| **p(PhTz)** | **AIP** | 7.070 | 0.631 | 0.264 | 0.999 |
| | **VIP** | 7.201 | 1.101 | 0.409 | 0.999 |
| | **$\lambda^+$** | 0.192 | 1.05 | 0.563 | 0.998 |
| | **AEA** | 3.093 | -1.579 | 0.370 | 0.999 |
| | **VEA** | 3.034 | -1.803 | 0.406 | 0.999 |
| | **$\lambda^-$** | 0.083 | 0.540 | 0.768 | 0.997 |
| **p(FuTz)** | **AIP** | 6.760 | 0.940 | 0.394 | 0.998 |
| | **VIP** | 6.773 | 1.051 | 0.386 | 0.998 |
| | **$\lambda^+$** | 0.038 | 0.223 | 0.302 | 0.999 |
| | **AEA** | 3.196 | -1.769 | 0.382 | 0.999 |
| | **VEA** | 3.135 | -2.002 | 0.410 | 0.999 |
| | **$\lambda^-$** | 0.103 | 0.568 | 0.767 | 0.996 |
| **p(PyTz)** | **AIP** | 6.212 | 0.970 | 0.354 | 0.984 |
| | **VIP** | 6.328 | 0.961 | 0.382 | 0.998 |
| | **$\lambda^+$** | 0.052 | 0.212 | 0.349 | 0.998 |
| | **AEA** | 2.967 | -1.531 | 0.306 | 0.999 |
| | **VEA** | 2.889 | -1.785 | 0.369 | 0.999 |
| | **$\lambda^-$** | 0.067 | 0.692 | 0.713 | 0.999 |
| **p(ThTz)** | **AIP** | 6.794 | 0.890 | 0.393 | 0.998 |
| | **VIP** | 6.815 | 1.016 | 0.386 | 0.998 |
| | **$\lambda^+$** | 0.044 | 0.251 | 0.320 | 0.999 |
| | **AEA** | 3.308 | -1.746 | 0.399 | 0.999 |
| | **VEA** | 3.251 | -1.981 | 0.432 | 0.999 |
| | **$\lambda^-$** | 0.091 | 0.570 | 0.793 | 0.996 |
| **(TeTz)** | **AIP** | 6.392 | 0.717 | 0.370 | 0.998 |
| | **VIP** | 6.413 | 0.827 | 0.375 | 0.998 |
| | **$\lambda^+$** | 0.043 | 0.216 | 0.376 | 1.000 |
| | **AEA** | 3.255 | -1.529 | 0.430 | 0.999 |
| | **VEA** | 3.202 | -1.791 | 0.480 | 0.998 |
| | **$\lambda^-$** | 0.076 | 0.613 | 0.902 | 0.998 |
| **(TaTz)** | **AIP** | 7.183 | 0.772 | 0.375 | 0.998 |
| | **VIP** | 7.200 | 0.884 | 0.376 | 0.998 |
| | **$\lambda^+$** | 0.046 | 0.222 | 0.383 | 0.999 |
| | **AEA** | 3.943 | -1.611 | 0.432 | 0.997 |

| | | | | | |
|---|---|---|---|---|---|
| | **VEA** | 3.873 | -1.675 | 0.448 | 0.998 |
| | **$\lambda^-$** | 0.019 | 0.242 | 0.204 | 0.995 |
| **p(PdTz)** | **AIP** | 7.059 | 0.641 | 0.303 | 0.999 |
| | **VIP** | 7.176 | 0.997 | 0.371 | 0.999 |
| | **$\lambda^+$** | 0.193 | 0.854 | 0.513 | 0.994 |
| | **AEA** | 3.336 | -1.868 | 0.452 | 0.998 |
| | **VEA** | 3.298 | -1.996 | 0.444 | 0.998 |
| | **$\lambda^-$** | 0.050 | 0.283 | 0.321 | 0.999 |
| **p(PzTz)** | **AIP** | 7.332 | 0.781 | 0.297 | 0.999 |
| | **VIP** | 7.421 | 1.042 | 0.370 | 0.999 |
| | **$\lambda^+$** | 0.115 | 0.743 | 0.645 | 0.998 |
| | **AEA** | 3.719 | -1.775 | 0.459 | 0.998 |
| | **VEA** | 3.691 | -1.892 | 0.437 | 0.998 |
| | **$\lambda^-$** | 0.027 | 0.280 | 0.201 | 0.996 |

**Table 12S**. Lattice Parameters for the studied periodic systems calculated at HSE06/6-31G* levels

| | **a / Å** | **b / Å** | **c / Å** | **α / º** | **β / º** | **γ / º** |
|---|---|---|---|---|---|---|
| **p(PhTz)** | 8.319 | 7.305 | 5.805 | 65.440 | 42.269 | 55.267 |
| **p(FuTz)** | 14.251 | 10.321 | 7.063 | 36.488 | 62.784 | 71.747 |
| **p(PyTz)** | 14.320 | 10.562 | 7.072 | 37.429 | 62.651 | 72.080 |
| **p(ThTz)** | 15.451 | 10.170 | 7.029 | 43.725 | 56.061 | 83.032 |
| **p(TeTz)** | 10.003 | 8.005 | 6.187 | 54.650 | 36.335 | 47.459 |
| **p(TaTz)** | 9.7962 | 6.074 | 4.369 | 122.617 | 83.410 | 77.286 |
| **p(PdTz)** | 8.2457 | 7.7581 | 6.035 | 59.940 | 40.427 | 48.227 |
| **p(PzTz)** | 8.180 | 11.126 | 4.771 | 65.621 | 55.439 | 36.182 |




(a) (b)

**Figure 1S.** Electronic band structures of p(PhTz) for (a) an isolated periodic chain and (b) two cofacially stacked periodic chains calculated at the B3LYP/6-31G*//HSE06/6-31G* level. Points of high symmetry in the first Brillouin zone are labelled as Γ (0,0,0) and X(0.5,0,0), all in reciprocal space coordinates.

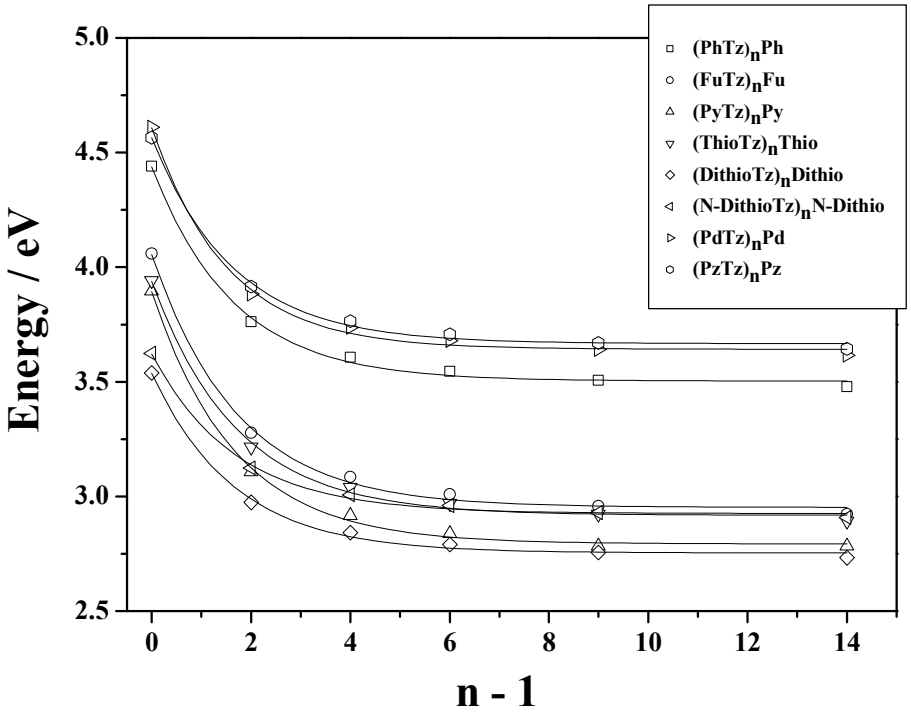



**Figure 2S.** Band gap values calculated for all the studied oligomers at the TD-M06-2X/6-31G* level and fits to the equation proposed by Meier *et al*. ($E(n) = E_\infty + (E_1 - E_\infty) \exp[-a(n-1)]$).

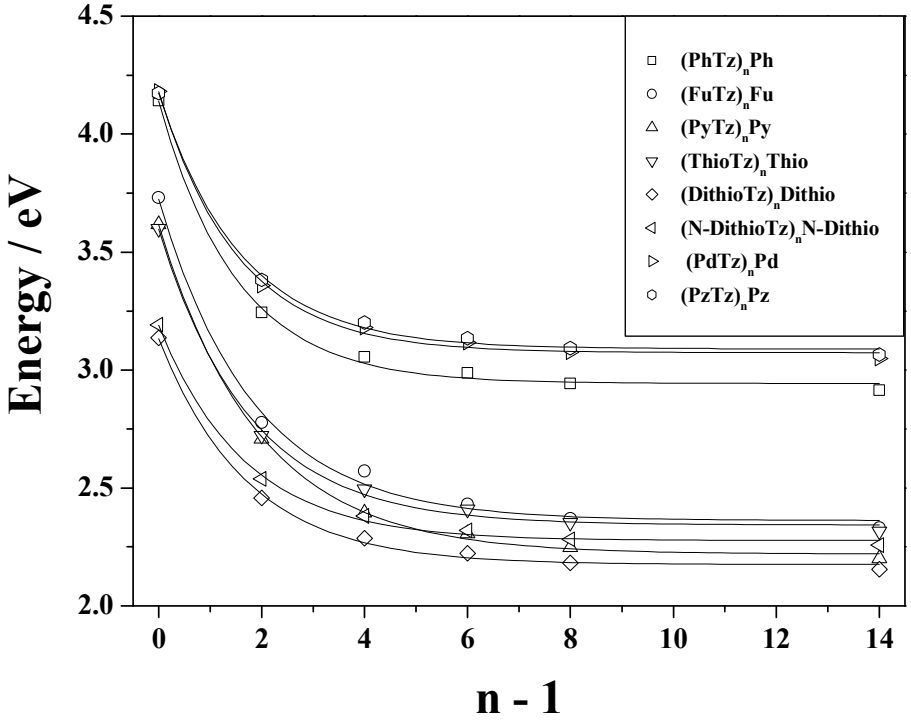



**Figure 2S.** Band gap values calculated for all the studied oligomers at the TD-PBE0/6-31G* level and fits to the equation proposed by Meier *et al*. ($E(n) = E_\infty + (E_1 - E_\infty) \exp[-a(n-1)]$).

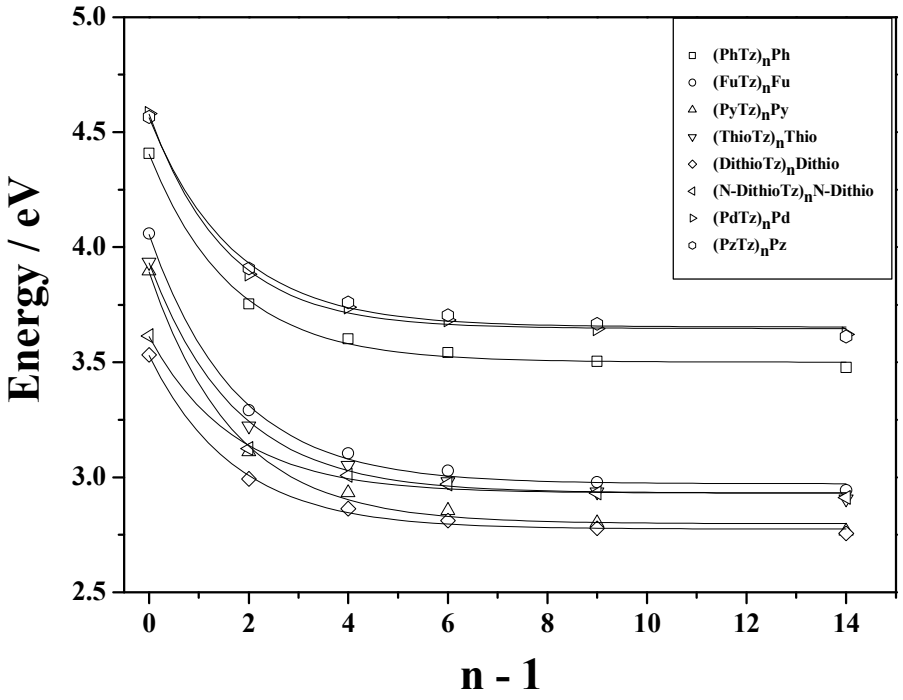



**Figure 2S.** Band gap values calculated for all the studied oligomers at the TD-CAM-B3LYP/6-31G* level and fits to the equation proposed by Meier *et al*. ($E(n) = E_\infty + (E_1 - E_\infty) \exp[-a(n-1)]$).