**Supporting Information**

# Effective Conjugation in Conjugated Polymers with Strongly Twisted Backbones: a Case Study on Fluorinated MEHPPV

Rim Milad,[1,2,3] Junqing Shi,[3] Aranzazu Aguirre,[3] Antonio Cardone,[4] Begoña Milián-Medina,[3,5,*] Gianluca M. Farinola,[6] Manef Abderrabba,[1] and Johannes Gierschner[3,*]

[1] *Université de Carthage, Unité de Recherche, Laboratoire Matériaux, Molécules et applications, Institut Préparatoire aux études scientifiques et techniques IPEST, BP 51, 2070 La Marsa, Tunisia*

[2] *Université de Carthage, Faculté des sciences de Bizerte (FSB), Jarzouna, Bizerte 7021, Tunisia*

[3] *Madrid Institute for Advanced Studies, IMDEA Nanoscience, c/ Faraday 9, Ciudad Universitaria de Cantoblanco, 28049 Madrid, Spain*

[4] *Istituto di Chimica dei Composti OrganoMetallici ICCOM di Bari, Consiglio Nazionale delle Ricerche CNR, via Orabona 4, 70126-Bari, Italy*

[5] *Department for Physical Chemistry, Faculty of Chemistry, University of Valencia, Avda. Dr. Moliner 50, 46100 Burjassot (Valencia), Spain*

[6] *Dipartimento di Chimica, Università degli Studi di Bari "Aldo Moro", Via Orabona 4, Bari 70125, Italy*

* E-mail: milian@uv.es, johannes.gierschner@imdea.org

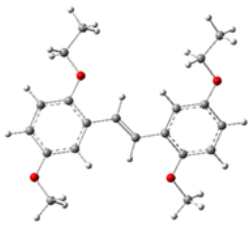
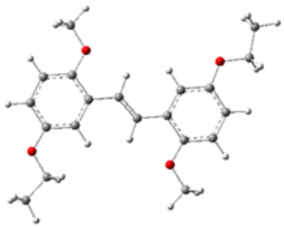
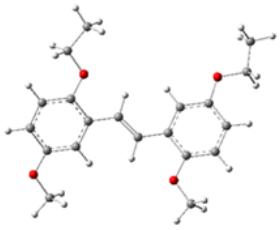
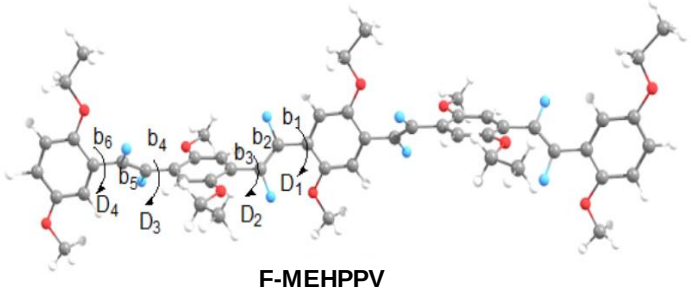
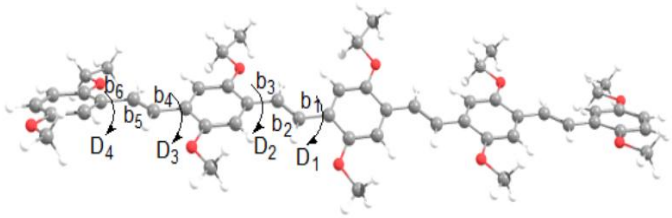
| conformer–1 | conformer–2 | conformer–3 |
|---|---|---|
|  |  |  |
| ΔE: 0 | ΔE: 0.091 | ΔE: 0.088 |

**Figure S1**: Conformers obtained for the two ring oligomer of MEHPPV with relative energies ΔE (in Kcal.mol$^{-1}$) calculated at B3LYP/6–311 G (d).




**F-MEHPPV**




**MEHPPV**

**Fig S2**: DFT (B3LYP) calculated ground state geometry of MEHPPV and F-MEHPPV oligomers with $n$ = 4, indicating bond lengths $b_i$ and torsional angle $D_i$.

**Table S1:** (TD)DFT (B3LYP) calculated phenyl-vinyl single bonds bond lengths (A°) and dihedral angles (°) calculated for MEHPPV and F-MEHPPV oligomers with $n$ = 4, in the $S_0$ and $S_1$.

| n=4 | MEHPPV | | F-MEHPPV | |
|---|---|---|---|---|
| | $S_0$ | $S_1$ | $S_0$ | $S_1$ |
| $b_1$ | 1.456 | 1.425 | 1.463 | 1.425 |
| $b_2$ | 1.351 | 1.379 | 1.341 | 1.379 |
| $b_3$ | 1.456 | 1.427 | 1.467 | 1.435 |
| $b_4$ | 1.458 | 1.438 | 1.467 | 1.450 |
| $b_5$ | 1.349 | 1.362 | 1.341 | 1.356 |
| $b_6$ | 1.461 | 1.448 | 1.468 | 1.460 |
| $D_1$ | 7.450 | 0 | 46.4 | 35.2 |
| $D_2$ | 8.4 | 0 | 46.7 | 27.6 |
| $D_3$ | 9.4 | 0 | 44.6 | 33.2 |
| $D_4$ | 10.8 | 0 | 46.2 | 39.4 |

**Table S2**: First singlet S1 excited state (vertical transitions energies) computed for MEHPPV and F-MEHPPV oligomers (*n* = number of repeat units) at different levels of theory (pl = planar geometry ; npl = non planar geometry). Singlet oscillator strength (*f*) and configuration interaction (CI) description (with contribution ≥ 5%) are listed.

| | ***n*** | **Method** | **E/ eV (λ nm)** | ***f*** | **CI description** |
|---|---|---|---|---|---|
| **MEHPPV** | 1 | TD– B3LYP // B3LYP/ npl | 3.35 (370) | 0.61 | H→L (96%) |
| | | TD– B3LYP // B3LYP/ pl | 3.31 (375) | 0.64 | H→L (96%) |
| | | TD–B3LYP// M06HF/ npl | 4.08 (303) | 0.86 | H→L (90%) |
| | | TD–M06HF // M06HF/ npl | 4.39 (282) | 0.77 | H–1→L+1(8%)<br>H→L (86%) |
| | | TD–M06HF // M06HF/ pl | 4.16 (298) | 0.84 | H–1→L+1 (5%)<br>H→L (90%) |
| | | TD–CAM–B3LYP // B3LYP/ npl | 3.74 (331) | 0.76 | H→L (94%) |
| | | TD–CAM–B3LYP// B3LYP/ pl | 3.68 (337) | 0.79 | H→L (94%) |
| | 2 | TD– B3LYP// B3LYP/ npl | 2.73 (453) | 1.48 | H→L (99%) |
| | | TD– B3LYP//B3LYP/ pl | 2.71 (456) | 1.51 | H→L (99%) |
| | | TD–B3LYP// M06HF/ npl | 3.47 (357) | 1.71 | H–1→L+1 (7%)<br>H→L (86%) |
| | | TD–M06HF//M06HF/ npl | 3.93 (315) | 1.52 | H→L (82%)<br>H–1→L+1 (8%) |
| | | TD–M06HF//M06HF/ pl | 3.65 (339) | 1.65 | H–1→L+1(7%)<br>H→L (84%) |
| | | TD–CAM–B3LYP // B3LYP/ npl | 3.13(396) | 1.64 | H→L (92%) |
| | | TD–CAM–B3LYP // B3LYP/ pl | 3.11(399) | 1.66 | H→L (92%) |
| | 3 | TD– B3LYP//B3LYP/ npl | 2.41 (513) | 2.25 | H→L (99%) |
| | | TD– B3LYP//B3LYP/ pl | 2.38 (519) | 2.29 | H→L (99%) |
| | | TD–B3LYP// M06HF/ npl | 3.21 (385) | 2.56 | H–1→L+1 (12%)<br>H→L (79%) |
| | | TD–M06HF//M06HF/ npl | 3.74 (331) | 2.29 | H–1→L+1 (12%)<br>H→L (74%) |
| | | TD–M06HF//M06HF/ pl | 3.42(362) | 2.48 | H–1→L+1 (13%)<br>H→L (77%) |
| | | TD–CAM–B3LYP// B3LYP/ npl | 2.86 (433) | 2.49 | H–1→L+1 (8%)<br>H→L (87%) |
| | | TD–CAM–B3LYP// B3LYP/ pl | 2.82 (438) | 2.52 | H–1→L+1 (8%)<br>H→L (87%) |
| | 4 | TD– B3LYP// B3LYP/ npl | 2.21 (559) | 2.95 | H→L (98.46%) |
| | | TD– B3LYP// B3LYP/ pl | 2.18 (566) | 3 | H→L (98.46%) |
| | | TD–B3LYP// M06HF/ npl | 3.07 (404) | 3.41 | H–1→L+1 (15%)<br>H→L (72%) |
| | | TD–M06HF//M06HF/ npl | 3.65 (339) | 3.08 | H–2→L+2 (5%)<br>H–1→L+1 (16%)<br>H→L (66%) |
| | | TD–M06HF//M06HF/ pl | 3.30 (375) | 3.32 | H–1→L+1 (16%)<br>H→L (69%) |
| | | TD–CAM–B3LYP // B3LYP/ npl | 2.7 (459) | 3.33 | H–1→L (11%)<br>H→L (82%) |
| | | TD–CAM–B3LYP // B3LYP/ pl | 2.66 (465) | 3.37 | H–1→L+1 (11%)<br>H→L (82%) |
| | 6 | TD– B3LYP// B3LYP/ npl | 2.03 (610) | 4.18 | H→L (96%) |
| | | TD– B3LYP// B3LYP/ pl | 1.97 (628) | 4.31 | H→L (96%) |
| | | TD–B3LYP// M06HF/ npl | 2.95 (419) | 5.06 | H–2→L+2 (8%)<br>H–1→L+1 (19%)<br>H→L (59%) |
| | | TD–M06HF//M06HF/ npl | 3.52 (352) | 4.49 | H–2→L+2 (9%)<br>H–1→L+1 (18%) |

| | | | | | |
|---|---|---|---|---|---|
| | | | | | H→L (54%) |
| | | TD–M06HF//M06HF/ pl | 3.18 (389) | 4.96 | H–2→L+2 (8%)<br>H–1→L+1 (19%)<br>H→L (56%) |
| | | TD–CAM–B3LYP // B3LYP/ npl | 2.57 (482) | 4.94 | H–2→L+2 (5%)<br>H–1→L+1 (16%)<br>H→L (70%) |
| | | TD–CAM–B3LYP // B3LYP/ pl | 2.50 (495) | 5.05 | H–2→L+2 (5%)<br>H–1→L+1 (16%)<br>H→L (72%) |
| | 9 | TD– B3LYP// B3LYP/ npl | 1.86 (664) | 6.13 | H–1→L+1 (7%)<br>H→L (90%) |
| | | TD– B3LYP// B3LYP/ pl | 1.83 (675) | 6.22 | H–1→L+1 (7%)<br>H→L (90%) |
| | | TD–B3LYP// M06HF/ npl | 2.83 (437) | 7.59 | H–3→L+3 (6%)<br>H–2→L+2 (11%)<br>H–1→L+1 (19%)<br>H→L (46%) |
| | | TD–M06HF// M06HF/ npl | 3.48 (356) | 6.90 | H–3→L+3 (7%)<br>H–2→L+2 (11%)<br>H–1→L+1 (18%)<br>H→L (40%) |
| | | TD–M06HF// M06HF/ pl | 3.10 (399) | 7.40 | H–3→L+3 (7%)<br>H–2→L+2 (11%)<br>H–1→L+1 (19%)<br>H→L (43%) |
| | | TD–CAM–B3LYP // B3LYP/ npl | 2.43(509) | 7.46 | H–2→L+2 (9%)<br>H–1→L+1 (19%)<br>H→L (58%) |
| | | TD–CAM–B3LYP // B3LYP/ pl | 2.40 (516) | 7.56 | H–2→L+2 (9%)<br>H–1→L+1 (19%)<br>H→L (58%) |
| | 12 | TD– B3LYP// B3LYP/ npl | 1.80 (687) | 8.09 | H–1→L+1 (11%)<br>H→L (83%) |
| | | TD– B3LYP// B3LYP/ pl | 1.77 ( 698) | 8.2 | H–1→L+1 (11%)<br>H→L (83%) |
| | | TD–CAM–B3LYP // B3LYP/ npl | 2.38 (520) | 10 | H–3→L+3 (6%)<br>H–2→L+2 (11%)<br>H–1→L+1 (19%)<br>H→L (47%) |
| | | TD–CAM–B3LYP // B3LYP/ pl | 2.36 (525) | 10 | H–3→L+3 (6%)<br>H–2→L+2 (11%)<br>H–1→L+1 (20%)<br>H→L (47%) |
| **F-MEHPPV** | 1 | TD– B3LYP// B3LYP/ npl | 3.58 (346) | 0.45 | H→L (98%) |
| | | TD– B3LYP// B3LYP / pl | 3.35 (369) | 0.64 | H→L (97%) |
| | | TD–B3LYP// M06HF/ npl | 4.42 (280) | 0.64 | H–1→L+1 (10%)<br>H→L (83%) |
| | | TD–M06HF// M06HF/ npl | 4.71 (264) | 0.57 | H–1→L+1 (12%)<br>H→L (80%) |
| | | TD–M06HF// M06HF/ pl | 4.31 (288) | 0.8 | H–1→L+1 (8%)<br>H→L (87%) |
| | | TD–CAM–B3LYP // B3LYP/ npl | 4.02 (308) | 0.56 | H–1→L+1 (6%)<br>H→L (90%) |
| | | TD–CAM–B3LYP // B3LYP/ pl | 3.72 (334) | 0.84 | H→L (95%) |
| | 2 | TD– B3LYP// B3LYP/ npl | 3.16 (392) | 0.97 | H→L (98%) |
| | | TD– B3LYP// B3LYP/ pl | 2.74 (452) | 1.48 | H→L (99%) |
| | | TD–B3LYP// M06HF/npl | 4.06 (305) | 1.24 | H-2→L (5%)<br>H–1→L+1 (7%) |

| | | | | | |
|---|---|---|---|---|---|
| | | | | | H–L (76%) |
| | | TD–M06HF// M06HF/ npl | 4.39(282) | 1.24 | H–2→L (7%)<br>H–1→L+1 (12%)<br>H→L (66%) |
| | | TD–M06HF// M06HF/ pl | 3.85 (322) | 1.58 | H–1→L+1 (8%)<br>H→L (81%) |
| | | TD–CAM–B3LYP // B3LYP/ npl | 3.65 (339) | 1.13 | H–1→L+1 (5%)<br>H→L (85%) |
| | | TD–CAM–B3LYP // B3LYP/ pl | 3.16 (392) | 1.70 | H→L (92%) |
| | 3 | TD– B3LYP// B3LYP/ npl | 3 (413) | 1.42 | H→L (97%) |
| | | TD– B3LYP// B3LYP/ pl | 2.42 (511) | 2.22 | H→L (99%) |
| | | TD–B3LYP// M06HF/ npl | 3.96 (313) | 1.89 | H–1→L+1 (13%)<br>H→L (66%) |
| | | TD–M06HF// M06HF/ npl | 4.29 (289) | 1.80 | H–1→L+1 (15%)<br>H→L (56%) |
| | | TD–M06HF// M06HF/ pl | 3.64 (340) | 2.46 | H–1→L+1 (13%)<br>H→L (74%) |
| | | TD–CAM–B3LYP // B3LYP/ npl | 3.54(350) | 1.73 | H–1→L+1 (10%)<br>H→L (77%) |
| | | TD–CAM–B3LYP // B3LYP/ pl | 2.89 (428) | 2.58 | H–1→L+1 (8%)<br>H→L (87%) |
| | 4 | TD– B3LYP// B3LYP/ npl | 2.87 (431) | 1.83 | H→L (95.5%) |
| | | TD– B3LYP// B3LYP/ pl | 2.24 (554) | 2.89 | H→L (98%) |
| | | TD–B3LYP// M06HF/ npl | 3.85 (322) | 2.43 | H–1→L+1 (12%)<br>H→L (62%) |
| | | TD–M06HF// M06HF/ npl | 4.20 (295) | 2.44 | H–1→L (8%)<br>H–1→L+1 (13%)<br>H→L (45%) |
| | | TD–M06HF// M06HF/ pl | 3.45 (359) | 3.53 | H–1→L+1 (16%)<br>H→L (67%) |
| | | TD–CAM–B3LYP // B3LYP/ npl | 3.42 (362) | 2.24 | H–1→L+1 (11%)<br>H→L (74%) |
| | | TD–CAM–B3LYP // B3LYP/ pl | 2.74 (452) | 3.45 | H–1→L+1 (11%)<br>H→L (81%) |
| | 6 | TD– B3LYP// B3LYP/ npl | 2.74 (452) | 2.69 | H–1→L+1 (6%)<br>H→L (90%) |
| | | TD– B3LYP// B3LYP/ pl | 2.04 (607) | 4.13 | H→L (96%) |
| | | TD–B3LYP// M06HF/ npl | 3.75 (331) | 3.61 | H–2→L+2 (7%)<br>H–1→L+1 (12%)<br>H→L (52%) |
| | | TD–M06HF// M06HF/ npl | 4.15 (299) | 3.61 | H–2→L (18%)<br>H–2→L+2 (7%)<br>H–1→L+1 (13%)<br>H→L (35%) |
| | | TD–M06HF// M06HF/ pl | 3.34 (371) | 5.28 | H–2→L+2 (9%)<br>H–1→L+1 (19%)<br>H→L (54%) |
| | | TD–CAM–B3LYP // B3LYP/ npl | 3.31 (374) | 3.36 | H–2→L+2 (6%)<br>H–1→L+1 (12%)<br>H→L (63%) |
| | | TD–CAM–B3LYP // B3LYP/ pl | 2.59 (478) | 5.16 | H–2→L+2 (5%)<br>H–1→L+1 (16%)<br>H→L (70%) |
| | 9 | TD– B3LYP// B3LYP/ npl | 2.7 (459) | 4.34 | H–1→L+1 (19%)<br>H→L (71%) |
| | | TD– B3LYP//B3LYP/ pl | 1.92 (645) | 6 | H–1→L+1 (8%)<br>H→L (90%) |
| | | TD–B3LYP// M06HF/npl | 3.72 (333) | 6.1 | H–3→L+3 (6%)<br>H–2→L+2 (9%) |

| | | | | | |
|---|---|---|---|---|---|
| | | | | | H–1→L+1 (22%)<br>H→L (31%) |
| | | TD–M06HF// M06HF/ npl | 4.10 (302) | 5.57 | H–2→L+1 (9%)<br>H–1→L (9%)<br>H→L (22%)<br>H→L+1 (6%) |
| | | TD–M06HF// M06HF/ pl | 3.37 (368) | 7.62 | H–3→L+3 (7%)<br>H–2→L+2 (11%)<br>H–1→L+1 (40%) |
| | | TD–CAM–B3LYP // B3LYP/ npl | 3.28 (377) | 5.61 | H–3→L+3 (5%)<br>H–2→L+2 (9%)<br>H–1→L+1 (24%)<br>H→L (40%) |
| | | TD–CAM–B3LYP // B3LYP/ pl | 2.50 (495) | 7.72 | H–2→L+2 (9%)<br>H–1→L+1 (19%)<br>H→L (55%) |

**Table S3**: Maximum conducive chainlength ($N_{MCC}$, $n_{MCC}$) and effective conjugation length ($N_{ECL}$, $n_{ECL}$) of F-MEHPPV, as obtained from experiment and TD-DFT calculations (for details see text).

| | $N_{MCC}$ | $n_{MCC}$ | $N_{ECL}$ | $n_{ECL}$ |
|---|---|---|---|---|
| Exp: | 26.7 | 8.2 | 5.3 | 1.1 |
| M06HF | 24.4 | 7.5 | 6.2 | 1.4 |
| B3LYP | 36 | 11.4 | 8.7 | 2.2 |

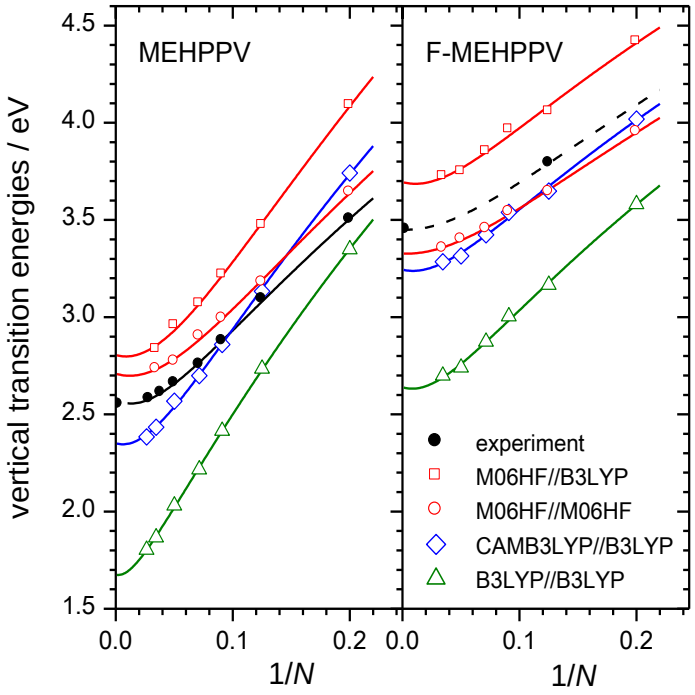



**Fig. S3**: Calculated $E_{vert}$ of F-/MEHPPV oligomers as a function of 1/ *N* for different functionals, based on B3LYP geometry optimizations. Solid lines are fits using a modified Kuhn equation.

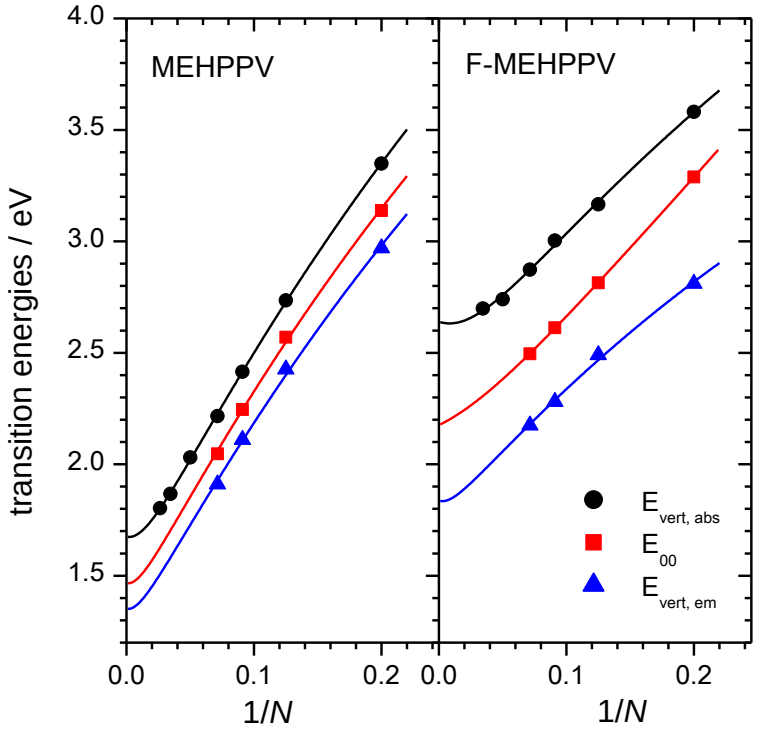



**Fig. S4**: TD-DFT calculated adiabatic ($E_{00}$) and vertical transition energies for absorption and emission ($E_{vert,abs}$, $E_{vert,em}$) of F-/MEHPPV oligomers obtained at the B3LYP//B3LYP level of theory. Solid lines are fits using a modified Kuhn equation.

**Table S4**: Calculated HOMO and LUMO energies (eV) for the studied oligomers at B3LYP level (n = number of repeat units)

| compound | n | HOMO/ eV | | LUMO/ eV | |
|---|---|---|---|---|---|
| | | B3LYP/npl | B3LYP /pl | B3LYP/npl | B3LYP/pl |
| MEHPPV | 1 | -5,048 | -5,025 | -1,385 | -1,430 |
| | 2 | -4,756 | -4,747 | -1,788 | -1,805 |
| | 3 | -4,617 | -4,601 | -1,955 | -1,977 |
| | 4 | -4,531 | -4,517 | -2,048 | -2,072 |
| | 6 | -4,457 | -4,429 | -2,124 | -2,168 |
| | 9 | -4,388 | -4,373 | -2,206 | -2,227 |
| | 12 | -4,360 | -4,350 | -2,233 | -2,253 |
| F–MEHPPV | 1 | -5,278 | -5,095 | -1,251 | -1,462 |
| | 2 | -5,198 | -4,942 | -1,611 | -1,978 |
| | 3 | -5,184 | -4,855 | -1,747 | -2,189 |
| | 4 | -5,161 | -4,808 | -1,852 | -2,307 |
| | 6 | -5,131 | -4,761 | -1,956 | -2,428 |
| | 9 | -5,122 | -4,735 | -1,988 | -2,506 |

a) pl, planar; npl, non-planar

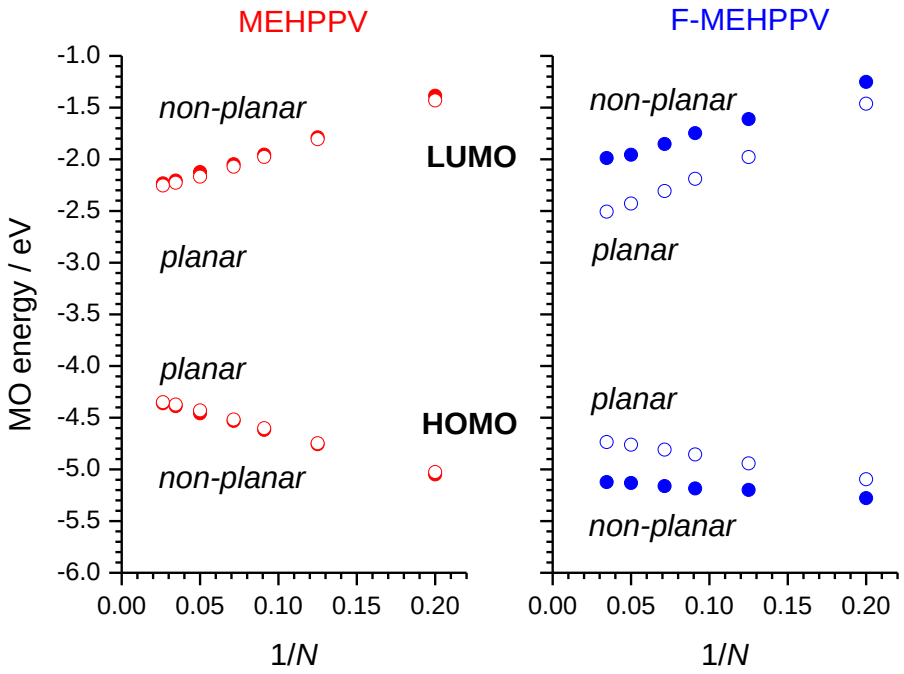



**Fig. S5**: DFT (B3LYP) calculated HOMO and LUMO energies for F-/MEHPPV oligomers with non-/planar geometries.