Supporting Information

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

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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).



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 .

- 4	MEH	IPPV	F-MEHPPV	
11=4	\mathbf{S}_0	\mathbf{S}_1	\mathbf{S}_0	\mathbf{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 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 S₀ and S₁.

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 $\ge 5\%$) are listed.

$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$		11	Method	E/ eV		CI description
3 TD-B3LYP // B3LYP /pl 3.35 (370) 0.61 HL (96%) 1 TD-B3LYP // B3LYP /pl 3.31 (375) 0.64 HL (90%) TD-B3LYP // M06HF /pl 4.08 (303) 0.86 HL (90%) TD-M06HF // M06HF /pl 4.16 (298) 0.84 H-1-L+1 (15%) TD-M06HF // M06HF /pl 4.16 (298) 0.84 H-1-L+1 (15%) TD-CAM-B3LYP // B3LYP /pl 3.74 (331) 0.76 HL (90%) TD-CAM-B3LYP // B3LYP /pl 3.73 (453) 1.48 HL (99%) TD-B3LYP // B3LYP /pl 2.73 (453) 1.48 HL (99%) TD-B3LYP // B3LYP /pl 3.47 (357) 1.71 H-1-L(17%) TD-B3LYP // B3LYP /pl 3.31 (396) 1.65 H-1-L(17%) TD-M06HF //M06HF /pl 3.65 (339) 1.65 H-1-L(17%) TD-CAM-B3LYP // B3LYP /pl 3.11(399) 1.66 HL (92%) TD-CAM-B3LYP // B3LYP /pl 3.13(396) 1.64 HL (17%) TD-B3LYP //B3LYP /pl 2.38 (519) 2.29 H-1-L(17%) TD-B3LYP //B3LYP /pl 3.42 (352) <		n	Method	(λ nm)	J	CI description
$A = \frac{1}{1} \begin{bmatrix} \frac{10 - B3LYP / B3LYP / pl}{TD - B3LYP / M06HF / npl} & 4.08 (303) & 0.86 & H \rightarrow L (90%) \\ \hline TD - M06HF / M06HF / npl & 4.39 (282) & 0.77 & H \rightarrow U (91%) \\ \hline TD - M06HF / M06HF / pl & 4.16 (298) & 0.84 & H \rightarrow U (90%) \\ \hline TD - CAM - B3LYP / B3LYP / npl & 3.74 (311) & 0.76 & H \rightarrow U (94%) \\ \hline TD - CAM - B3LYP / B3LYP / npl & 2.73 (453) & 1.48 & H \rightarrow U (99%) \\ \hline TD - B3LYP / B3LYP / pl & 2.71 (456) & 1.51 & H \rightarrow U (99%) \\ \hline TD - B3LYP / M06HF / npl & 3.47 (357) & 1.71 & H \rightarrow U (94%) \\ \hline TD - B3LYP / M06HF / npl & 3.47 (357) & 1.71 & H \rightarrow U (82%) \\ \hline TD - B3LYP / M06HF / npl & 3.43 (315) & 1.52 & H \rightarrow U (82%) \\ \hline TD - M06HF / M06HF / npl & 3.43 (357) & 1.71 & H \rightarrow U (82%) \\ \hline TD - M06HF / M06HF / npl & 3.13 (396) & 1.64 & H \rightarrow U (92%) \\ \hline TD - CAM - B3LYP / B3LYP / npl & 3.11 (399) & 1.66 & H \rightarrow U (92%) \\ \hline TD - CAM - B3LYP / B3LYP / npl & 3.11 (399) & 1.66 & H \rightarrow U (92%) \\ \hline TD - CAM - B3LYP / B3LYP / npl & 3.11 (399) & 1.64 & H \rightarrow U (92%) \\ \hline TD - B3LYP / B3LYP / npl & 3.21 (385) & 2.56 & H \rightarrow U (99%) \\ \hline TD - B3LYP / B3LYP / npl & 3.21 (385) & 2.56 & H \rightarrow U (99%) \\ \hline TD - B3LYP / M06HF / npl & 3.74 (331) & 2.29 & H \rightarrow U (99%) \\ \hline TD - CAM - B3LYP / B3LYP / npl & 2.86 (433) & 2.49 & H \rightarrow U + 11 (12%) \\ \hline TD - CAM - B3LYP / B3LYP / npl & 2.86 (633) & 4.41 & H \rightarrow U + 11 (2%) \\ \hline TD - CAM - B3LYP / B3LYP / npl & 2.86 (633) & 2.49 & H \rightarrow U + 11 (2%) \\ \hline TD - CAM - B3LYP / B3LYP / npl & 2.86 (633) & 2.49 & H \rightarrow U + 11 (2%) \\ \hline TD - CAM - B3LYP / B3LYP / npl & 2.18 (566) & 3 & H \rightarrow U + 18 (566) \\ \hline TD - B3LYP / B3LYP / npl & 2.18 (566) & 3 & H \rightarrow U + 11 (1%) \\ \hline TD - B3LYP / B3LYP / npl & 2.18 (566) & 3 & H \rightarrow U + 11 (1%) \\ \hline TD - B3LYP / B3LYP / npl & 2.20 (559) & 2.95 & H \rightarrow U (9846\%) \\ \hline TD - M06HF / M06HF / npl & 3.00 (375) & 3.32 & H \rightarrow U + 11 (1%) \\ \hline TD - B3LYP / B3LYP / npl & 2.03 (610) & 4.18 & H \rightarrow U (9846\%) \\ \hline TD - CAM - B3LYP / B3LYP / npl & 2.03 (610) & 4.18 & H \rightarrow U (98\%) \\ \hline TD - CAM - B3LYP / B3LYP / npl & 2.03 (610) & 4.18 & H \rightarrow U (98\%) \\ \hline TD - CAM - B3LYP / B3LYP / npl & 2.03 (610) & 4.18 & H \rightarrow U (98\%) \\ \hline TD - CA$			TD-B3LYP // B3LYP/ npl	3.35 (370)	0.61	H→L (96%)
$\begin{tabular}{ c c c c c c c c c c c c c c c c c c c$			TD– B3LYP // B3LYP/ pl	3.31 (375)	0.64	H→L (96%)
$ {\rm MH} = \frac{1}{1} = \frac{1}{10-M06HF / M06HF / npl} = \frac{4.39 (282)}{4.39 (282)} = 0.77 = \frac{H-1-L+1(8\%)}{H-L(86\%)} + \frac{H-1-L+1(8\%)}{H-L(86\%)} + \frac{H-1-L+1(8\%)}{H-L(90\%)} + \frac{H-1-L+1(8\%)}{H-L(90\%)} + \frac{H-1-L+1(8\%)}{H-L(90\%)} + \frac{H-1-L+1(8\%)}{H-L(90\%)} + \frac{H-1-L+1(9\%)}{H-L(90\%)} + \frac{H-1-L+1(9\%)}{H-L(90\%)} + \frac{H-1-L+1(9\%)}{H-L(90\%)} + \frac{H-1-L+1(7\%)}{H-L(86\%)} + \frac{H-1-L+1(7\%)}{H-1-L+1(7\%)} + \frac{H-1-L+1(7\%)}{H-1-L+1(7\%)} + \frac{H-1-L+1(7\%)}{H-1-L+1(7\%)} + \frac{H-1-L+1(7\%)}{H-1-L(86\%)} + \frac{H-1-L+1(17\%)}{H-1-L(86\%)} + \frac{H-1-L+1(17\%)}{H-1-L(17\%)} + \frac{H-1-L+1(17\%)}{H-1-L(17\%)} + \frac{H-1-L+1(17\%)}{H-1-L(117\%)} + \frac{H-1-L+1(12\%)}{H-1-L+1(12\%)} + \frac{H-1-L+1(12\%)}{H-1-L(12\%)} + \frac{H-1-L+1(12\%)}{H-1-L(12\%)} + \frac{H-1-L+1(12\%)}{H-1-L(12\%)} + \frac{H-1-L+1(12\%)}{H-1-L+1(12\%)} + \frac{H-1-L+1(12\%)}{H-1-L(12\%)} + \frac{H-1-L+1(12\%)}{H-1-L(12\%)} + \frac{H-1-L+1(12\%)}{H-1-L(12\%)} + \frac{H-1-L+1(12\%)}{H-1-L(12\%)} + \frac{H-1-L+1(12\%)}{H-1-L+1(12\%)} + H-1-L+1(12\%)$			TD-B3LYP// M06HF/ npl	4.08 (303)	0.86	H→L (90%)
$ { $			TD MOCHE // MOCHE/ mal	4 20 (282)	0.77	$H-1\rightarrow L+1(8\%)$
$A H = \frac{1}{10^{-0.00} \text{GeV} / \text{B3LYP} / \text{B3LYP} / \text{pl}}{10^{-0.00} \text{B3LYP} / \text{B3LYP} / \text{B3LYP} / \text{pl}}{10^{-0.00} \text{B4LYP} / \text{B3LYP} / \text{pl}}{10^{-0.00} $		1	ID-MUGHF // MUGHF/ npi	4.39 (282)	0.77	H→L (86%)
$ { $			TD MOCHE // MOCHE/ -1	4.16 (200)	0.94	$H-1 \rightarrow L+1 (5\%)$
$A = \frac{1}{10^{$			пд-моонг // моонг/ рі	4.10 (298)	0.84	H→L (90%)
$ I = \frac{TD-CAM-B3LYP//B3LYP/pl}{TD-B3LYP//B3LYP/pl} 2.73 (453) 1.48 H \rightarrow L (99%) \\ TD-B3LYP//B3LYP/pl 2.71 (456) 1.51 H \rightarrow L (99%) \\ TD-B3LYP//M06HF/pl 3.47 (357) 1.71 H \rightarrow L (8%) \\ TD-B3LYP//M06HF/npl 3.93 (315) 1.52 H \rightarrow L (8%) \\ TD-M06HF//M06HF/npl 3.93 (315) 1.52 H \rightarrow L (18%) \\ TD-M06HF//M06HF/pl 3.65 (339) 1.65 H \rightarrow L (92%) \\ TD-M06HF//M06HF/pl 3.13 (396) 1.64 H \rightarrow L (92%) \\ TD-CAM-B3LYP//B3LYP/npl 3.11 (399) 1.66 H \rightarrow L (92%) \\ TD-B3LYP//B3LYP/npl 2.41 (513) 2.25 H \rightarrow L (99%) \\ TD-B3LYP//B3LYP/npl 2.41 (513) 2.25 H \rightarrow L (99%) \\ TD-B3LYP//B3LYP/npl 3.11 (399) 1.66 H \rightarrow L (92%) \\ TD-B3LYP//B3LYP/npl 3.21 (385) 2.56 H \rightarrow L (99%) \\ TD-B3LYP//B3LYP/npl 3.21 (385) 2.56 H \rightarrow L (17%) \\ H \rightarrow L (79%) \\ TD-M06HF//M06HF/npl 3.74 (331) 2.29 H \rightarrow L (17%) \\ H \rightarrow L (79%) \\ TD-M06HF//M06HF/npl 3.74 (331) 2.29 H \rightarrow L (17%) \\ H \rightarrow L (79%) \\ TD-M06HF//M06HF/npl 3.74 (331) 2.29 H \rightarrow L (17%) \\ H \rightarrow L (79%) \\ TD-M06HF//M06HF/npl 3.74 (331) 2.29 H \rightarrow L (17%) \\ H \rightarrow L (79%) \\ TD-M06HF//M06HF/npl 3.74 (331) 2.29 H \rightarrow L (17%) \\ H \rightarrow L (79%) \\ TD-M06HF//M06HF/npl 3.74 (331) 2.29 H \rightarrow L (17%) \\ H \rightarrow L (79%) \\ TD-M06HF//M06HF/npl 3.74 (331) 2.29 H \rightarrow L (17%) \\ H \rightarrow L (79%) \\ TD-M06HF//M06HF/npl 3.74 (331) 2.29 H \rightarrow L (17%) \\ H \rightarrow L (111) \\ H \rightarrow L + 1 (12%) \\ H \rightarrow L (75%) \\ TD-M06HF//M06HF/npl 3.74 (331) 2.29 H \rightarrow L (17%) \\ H \rightarrow L (111) \\ H \rightarrow L + 1 (12%) \\ H \rightarrow L (111) \\ H \rightarrow L + 1 (12\%) \\ H \rightarrow L (111) \\ H \rightarrow L + 1 (12\%) \\ H \rightarrow L (111) \\ H \rightarrow L + 1 (12\%) \\ H \rightarrow L (111) \\ H \rightarrow L + 1 (115\%) \\ H \rightarrow L (111) \\ H \rightarrow L + 1 (115\%) \\ H \rightarrow L (111) \\ H \rightarrow L + 1 (115\%) \\ H \rightarrow L (111) \\ H \rightarrow L + 1 (115\%) \\ H \rightarrow L (111) \\ H \rightarrow L + 1 (115\%) \\ H \rightarrow L (111) \\ H \rightarrow L + 1 (115\%) \\ H \rightarrow L (111) \\ H \rightarrow L + 1 (115\%) \\ H \rightarrow L (111) \\ H \rightarrow L + 1 (115\%) \\ H \rightarrow L (111) \\ H$			TD-CAM-B3LYP // B3LYP/ npl	3.74 (331)	0.76	H→L (94%)
APP TD=B3LYP//B3LYP/pl 2.73 (453) 1.48 H→L (99%) TD=B3LYP//B3LYP/pl 2.71 (456) 1.51 H→L (99%) TD=B3LYP//B3LYP/pl 2.71 (456) 1.51 H→L (87%) TD=M06HF//M06HF/npl 3.93 (315) 1.52 H→-L (87%) TD=M06HF//M06HF/pl 3.65 (339) 1.65 H→-L (17%) TD=CAM=B3LYP // B3LYP / npl 3.13(396) 1.64 H→-L (27%) TD=CAM=B3LYP // B3LYP / npl 2.41 (513) 2.25 H→-L (12%) TD=B3LYP//B3LYP / pl 2.38 (519) 2.29 H→-L (12%) TD=B3LYP//B3LYP / pl 3.21 (385) 2.56 H→-L+1+1 (12%) H→D=M6HF//M06HF/ npl 3.21 (385) 2.56 H→-L+1+1 (12%) TD=M06HF//M06HF/ npl 3.42 (362) 2.48 H→-L (7%) TD=M06HF//M06HF/ npl 3.42 (362) 2.48 H→-L (12%) TD=CAM=B3LYP// B3LYP/ npl 2.86 (433) 2.49 H→-L+1+1 (13%) H→D=CAM=B3LYP// B3LYP/ npl 2.86 (433) 2.49 H→-L+1+1 (18%) TD=CAM=B3LYP// B3LYP/ npl 2.85 (339) 3.08			TD-CAM-B3LYP// B3LYP/ pl	3.68 (337)	0.79	H→L (94%)
AFF TD=B3LYP//B3LYP/pl 2.71 (456) 1.51 H→L (99%) TD=B3LYP//M06HF/npl 3.47 (357) 1.71 H→L (82%) TD=M06HF//M06HF/npl 3.93 (315) 1.52 H→L (82%) TD=M06HF//M06HF/pl 3.65 (339) 1.65 H→-L (82%) TD=CAM=B3LYP // B3LYP/npl 3.13(396) 1.64 H→-L (84%) TD=CAM=B3LYP // B3LYP/npl 3.11(399) 1.66 H→-L (92%) TD=CAM=B3LYP // B3LYP / npl 2.31(35) 2.25 H→-L (92%) TD=B3LYP //B3LYP / npl 2.38 (519) 2.29 H→-L (92%) TD=B3LYP //B3LYP / npl 3.21 (385) 2.56 H→-L (79%) TD=M06HF//M06HF / npl 3.74 (331) 2.29 H→-L (79%) TD=CAM=B3LYP // B3LYP / npl 2.86 (433) 2.49 H→-L (79%) TD=CAM=B3LYP // B3LYP / npl 2.86 (433) 2.49 H→-L (18%) TD=CAM=B3LYP // B3LYP / npl 2.86 (433) 2.49 H→-L (79%) TD=CAM=B3LYP // B3LYP / npl 2.86 (433) 2.49 H→-L (48%) TD=B3LYP // B3LYP / npl 2.86 (433) 2.49 </td <td></td> <td></td> <td>TD-B3LYP//B3LYP/npl</td> <td>2.73 (453)</td> <td>1.48</td> <td>H→L (99%)</td>			TD-B3LYP//B3LYP/npl	2.73 (453)	1.48	H→L (99%)
At 1 TD-B3LYP//M06HF/npl 3.47 (357) 1.71 H-1→L+1 (7%) H→L (82%) 2 TD-M06HF//M06HF/npl 3.93 (315) 1.52 H-1→L+1 (8%) TD-M06HF//M06HF/pl 3.65 (339) 1.65 H-1→L+1 (7%) 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%) TD-B3LYP//B3LYP/pl 2.31 (355) 2.25 H→L (99%) TD-B3LYP//B3LYP/pl 2.38 (519) 2.29 H→L (12%) TD-B3LYP//B3LYP/pl 2.38 (519) 2.29 H→L (12%) TD-B3LYP//B3LYP/pl 2.38 (519) 2.29 H→L (12%) TD-M06HF//M06HF/npl 3.74 (331) 2.29 H→L (7%) TD-M06HF//M06HF/pl 3.42(362) 2.48 H→L (7%) TD-CAM-B3LYP//B3LYP/pl 2.86 (433) 2.49 H→L (14%) H→L (8%) H→L (8%) H→L (8%) H→L (8%) TD-CAM-B3LYP//B3LYP/pl 2.86 (433) 2.49 H→L (14%) TD-B3LYP//B3LYP/pl 2.18 (566) 3 H→L (08%) </td <td></td> <td></td> <td>TD-B3LYP//B3LYP/ pl</td> <td>2.71 (456)</td> <td>1.51</td> <td>H→L (99%)</td>			TD-B3LYP//B3LYP/ pl	2.71 (456)	1.51	H→L (99%)
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$			TD D2I VD// MOCHE/ mml	2 47 (257)	1 71	H−1→L+1 (7%)
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$			TD-B3LYP// MU6HF/ npl	3.47 (357)	1./1	H→L (86%)
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$		2		2.02 (215)	1.50	H→L (82%)
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$		2	ID-MUOHF//MUOHF/ npl	3.93 (313)	1.52	H−1→L+1 (8%)
$ \mathbf{H} = \frac{10^{-M(06HF/M(06HF/pl)} - \frac{3.03(339)}{3.13(396)} - \frac{1.63}{1.64} + H \rightarrow L(84\%)}{H \rightarrow L(92\%)} \\ \hline \mathbf{TD} = CAM = B3LYP // B3LYP / pl - 3.11(399) - 1.66 + H \rightarrow L(92\%) \\ TD = B3LYP // B3LYP / pl - 2.41(513) - 2.25 + H \rightarrow L(99\%) \\ TD = B3LYP // B3LYP / pl - 2.38(519) - 2.29 + H \rightarrow L(99\%) \\ TD = B3LYP // M06HF / npl - 3.21(385) - 2.56 + H -1 \rightarrow L + 1(12\%) \\ H \rightarrow L(79\%) + H -1 \rightarrow L + 1(12\%) \\ H \rightarrow L(79\%) + H -1 \rightarrow L + 1(12\%) \\ H \rightarrow L(77\%) + H -1 \rightarrow L + 1(12\%) \\ H \rightarrow L(77\%) + H -1 \rightarrow L + 1(12\%) \\ H \rightarrow L(77\%) + H -1 \rightarrow L + 1(12\%) \\ H \rightarrow L(77\%) + H -1 \rightarrow L + 1(12\%) \\ H \rightarrow L(77\%) + H -1 \rightarrow L + 1(12\%) \\ H \rightarrow L(77\%) + H -1 \rightarrow L + 1(12\%) \\ H \rightarrow L(87\%) + H -1 \rightarrow L + 1(12\%) \\ H \rightarrow L(87\%) + H -1 \rightarrow L + 1(12\%) \\ H \rightarrow L(87\%) + H -1 \rightarrow L + 1(12\%) \\ H \rightarrow L(87\%) + H -1 \rightarrow L + 1(12\%) \\ H \rightarrow L(87\%) + H - L(11\%) \\ H \rightarrow L(11\%) L(11\%) \\ H $			TD MOGUE/MOGUE/ ml	2 65 (220)	1 65	$H-1\rightarrow L+1(7\%)$
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$			D-MOORF//MOORF/ pi	3.03 (339)	1.05	H→L (84%)
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$			TD-CAM-B3LYP // B3LYP/ npl	3.13(396)	1.64	H→L (92%)
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$			TD–CAM–B3LYP // B3LYP/ pl	3.11(399)	1.66	H→L (92%)
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$			TD-B3LYP//B3LYP/ npl	2.41 (513)	2.25	H→L (99%)
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$			TD-B3LYP//B3LYP/ pl	2.38 (519)	2.29	H→L (99%)
$\begin{array}{ c c c c c c c c c c c c c c c c c c c$			TD D2I VD// M06UE/ mp1	2 21 (295)	2.56	H−1→L+1 (12%)
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$			ID-BSLIP// MOOHF/ lipi	5.21 (585)		H→L (79%)
$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	Λ	3	TD $M06HE/M06HE/np1$	3.74 (331)	2 20	H−1→L+1 (12%)
$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	ΡP				2.29	H→L (74%)
$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	IHI		TD_M06HF//M06HF/ pl	3 42(362)	2.48	H−1→L+1 (13%)
$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	ME			5.42(502)		H→L (77%)
$4 \begin{bmatrix} 1D - CAM - B3LYP / B3LYP / pl \\ TD - CAM - B3LYP / B3LYP / pl \\ 2.82 (438) \\ 2.52 \\ H - 1 \rightarrow L (87\%) \\ H \rightarrow L (87\%) \\ TD - B3LYP / B3LYP / pl \\ 2.18 (566) \\ 3 \\ H \rightarrow L (98.46\%) \\ TD - B3LYP / M06HF / npl \\ 3.07 (404) \\ 3.41 \\ H - 1 \rightarrow L + 1 (15\%) \\ H \rightarrow L (72\%) \\ H \rightarrow L (72\%) \\ H \rightarrow L (72\%) \\ H - 2 \rightarrow L + 2 (5\%) \\ H \rightarrow L (66\%) \\ TD - M06HF / M06HF / pl \\ 3.30 (375) \\ 3.32 \\ H - 1 \rightarrow L + 1 (16\%) \\ H \rightarrow L (66\%) \\ TD - CAM - B3LYP / B3LYP / pl \\ 2.7 (459) \\ 3.33 \\ H - 1 \rightarrow L + 1 (16\%) \\ H \rightarrow L (82\%) \\ TD - CAM - B3LYP / / B3LYP / pl \\ 2.66 (465) \\ 3.37 \\ H - 1 \rightarrow L + 1 (11\%) \\ H \rightarrow L (82\%) \\ TD - B3LYP / B3LYP / pl \\ 2.95 (419) \\ TD - B3LYP / M06HF / npl \\ H \rightarrow L (96\%) \\ H - 1 \rightarrow L + 1 (19\%) \\ H \rightarrow L (96\%) \\ H - 1 \rightarrow L + 1 (19\%) \\ H - 1 \rightarrow L +$	Ι		TD_CAM_B3I YP// B3I YP/ npl	2.86 (433)	2.49	H−1→L+1 (8%)
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$						H→L (87%)
$4 \qquad \begin{array}{ c c c c c c c c c c c c c c c c c c c$			TD-CAM-B3LYP//B3LYP/pl	2.82 (438)	2.52	$H-1 \rightarrow L+1 (8\%)$
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$				2.02 (150)	2.32	H→L (87%)
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$			TD–B3LYP//B3LYP/npl	2.21 (559)	2.95	H→L (98.46%)
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$			TD–B3LYP//B3LYP/pl	2.18 (566)	3	H→L (98.46%)
$\begin{array}{ c c c c c c c c c c c c c c c c c c c$			TD-B3LYP// M06HF/ npl	3.07 (404)	3.41	$H-1 \rightarrow L+1 (15\%)$
$4 \qquad TD-M06HF/M06HF/ npl \qquad 3.65 (339) \qquad 3.08 \qquad \begin{array}{c} H-2 \rightarrow L+2 (5\%) \\ H-1 \rightarrow L+1 (16\%) \\ H\rightarrow L (66\%) \\ H\rightarrow L (66\%) \\ H\rightarrow L (66\%) \\ H\rightarrow L (69\%) \\ TD-CAM-B3LYP // B3LYP / npl \qquad 2.7 (459) \qquad 3.33 \qquad \begin{array}{c} H-1 \rightarrow L+1 (11\%) \\ H\rightarrow L (69\%) \\ H\rightarrow L (82\%) \\ H\rightarrow L (82\%) \\ H\rightarrow L (82\%) \\ \hline TD-CAM-B3LYP // B3LYP / pl \qquad 2.66 (465) \qquad 3.37 \qquad \begin{array}{c} H-1 \rightarrow L+1 (11\%) \\ H\rightarrow L (82\%) \\ H\rightarrow L (82\%) \\ \hline TD-B3LYP // B3LYP / npl \qquad 2.03 (610) \qquad 4.18 \qquad H\rightarrow L (96\%) \\ \hline TD-B3LYP // B3LYP / pl \qquad 1.97 (628) \qquad 4.31 \qquad H\rightarrow L (96\%) \\ \hline TD-B3LYP // M06HF / npl \qquad 2.95 (419) \qquad 5.06 \qquad \begin{array}{c} H-2 \rightarrow L+2 (8\%) \\ H-1 \rightarrow L+1 (19\%) \\ H\rightarrow L (59\%) \\ \hline H\rightarrow L (59\%) \\ \hline TD-M06HF //M06HF / npl \qquad 3.52 (352) \qquad 4.49 \qquad \begin{array}{c} H-2 \rightarrow L+2 (9\%) \\ H-1 \rightarrow L+1 (18\%) \\ \hline H\rightarrow L (11\%) \\ H\rightarrow L$						$H \rightarrow L (72\%)$
$\begin{array}{ c c c c c c c c c c c c c c c c c c c$				3.65 (339)	• • • •	$H-2\rightarrow L+2(5\%)$
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$			TD–M06HF//M06HF/ npl		3.08	$H-1\rightarrow L+1 (16\%)$
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$		4				$H \rightarrow L (66\%)$
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$			TD-M06HF//M06HF/ pl	3.30 (375)	3.32	$H-1 \rightarrow L+1 (16\%)$
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$			1 			$H \rightarrow L (69\%)$
$\begin{array}{ c c c c c c c c c c c c c c c c c c c$			TD-CAM-B3LYP // B3LYP/ npl	2.7 (459)	3.33	$H-I \rightarrow L(11\%)$
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$						$H \rightarrow L (82\%)$
$\begin{array}{c c c c c c c c c c c c c c c c c c c $			TD–CAM–B3LYP // B3LYP/ pl	2.66 (465)	3.37	$H-I \rightarrow L+I(11\%)$
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$			TD_D2I_VD// D2I_VD/1	2.02 (610)	1 10	$\Pi \rightarrow L (\delta 2\%)$
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$			TD = BSL TP//BSL TP//IIII	2.03 (610)	4.18	$H \rightarrow L (96\%)$
$\begin{array}{c cccc} 6 & TD-B3LYP//M06HF/npl & 2.95 (419) & 5.06 & H-2 \rightarrow L+2 (8\%) \\ & H-1 \rightarrow L+1 (19\%) \\ & H\rightarrow L (59\%) \\ \hline TD-M06HF//M06HF/npl & 3.52 (352) & 4.49 & H-2 \rightarrow L+2 (9\%) \\ & H-1 \rightarrow L+1 (18\%) \\ \hline \end{array}$			D-DJIF//BJLIF/ pl	1.97 (028)	4.31	$\Pi \rightarrow L (90\%)$
U U		6	TD D2I VD// MOGUE/ mal	2.95 (419)	5.04	$\Pi - 2 \rightarrow L + 2 (8\%)$
TD-M06HF/M06HF/ npl $3.52 (352)$ 4.49 $H-2 \rightarrow L+2 (9\%)$ $H-1 \rightarrow L+1 (18\%)$		0	TD–B3LYP// M06HF/ npl		5.06	$\Pi - I \rightarrow L \pm I (19\%)$ $\Pi \rightarrow I (50\%)$
TD-M06HF//M06HF/ npl $3.52 (352)$ 4.49 $H_{-1} \rightarrow L^{+2} (9\%)$ $H_{-1} \rightarrow L^{+1} (18\%)$						$\Pi \rightarrow L (39\%)$
			TD-M06HF//M06HF/ npl	3.52 (352)	4.49	$H_{-1} \rightarrow L^{+2} (970)$ $H_{-1} \rightarrow L^{+1} (18\%)$

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

					H–L (76%)
		TD-M06HF// M06HF/ npl	4.39(282)	1.24	$H-2 \rightarrow L (7\%)$ $H-1 \rightarrow L+1 (12\%)$ $H \rightarrow L (66\%)$
		TD-M06HF// M06HF/ pl	3.85 (322)	1.58	$H-1 \rightarrow L+1 (8\%)$ $H \rightarrow L (81\%)$
		TD–CAM–B3LYP // B3LYP/ npl	3.65 (339)	1.13	H−1→L+1 (5%) H→L (85%)
		TD-CAM-B3LYP // B3LYP/ pl	3.16 (392)	1.70	H→L (92%)
		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	$H-1 \rightarrow L+1 (13\%)$ $H \rightarrow L (66\%)$
	3	TD-M06HF// M06HF/ npl	4.29 (289)	1.80	$H-1 \rightarrow L+1 (15\%)$ $H \rightarrow L (56\%)$
	5	TD-M06HF// M06HF/ pl	3.64 (340)	2.46	H–1→L+1 (13%) H→L (74%)
		TD–CAM–B3LYP // B3LYP/ npl	3.54(350)	1.73	H–1→L+1 (10%) H→L (77%)
		TD–CAM–B3LYP // B3LYP/ pl	2.89 (428)	2.58	H−1→L+1 (8%) H→L (87%)
		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%) H→L (62%)
	4	TD-M06HF// M06HF/ npl	4.20 (295)	2.44	$H-1 \rightarrow L (8\%)$ $H-1 \rightarrow L+1 (13\%)$ $H \rightarrow L (45\%)$
		TD-M06HF// M06HF/ pl	3.45 (359)	3.53	H−1→L+1 (16%) H→L (67%)
		TD–CAM–B3LYP // B3LYP/ npl	3.42 (362)	2.24	H–1→L+1 (11%) H→L (74%)
		TD–CAM–B3LYP // B3LYP/ pl	2.74 (452)	3.45	$H-1 \rightarrow L+1 (11\%)$ $H \rightarrow L (81\%)$
		TD-B3LYP//B3LYP/npl	2.74 (452)	2.69	$H \to L + 1 (6\%)$ $H \to L (90\%)$
		TD-B3LYP//B3LYP/pl	2.04 (607)	4.13	H→L (96%)
	6	TD-B3LYP// M06HF/ npl	3.75 (331)	3.61	$H-2 \rightarrow L+2 (7\%)$ $H-1 \rightarrow L+1 (12\%)$ $H \rightarrow L (52\%)$
		TD–M06HF// M06HF/ npl	4.15 (299)	3.61	$\begin{array}{l} H-2 \rightarrow L \ (18\%) \\ H-2 \rightarrow L+2 \ (7\%) \\ H-1 \rightarrow L+1 \ (13\%) \\ H \rightarrow L \ (35\%) \end{array}$
		TD-M06HF// M06HF/ pl	3.34 (371)	5.28	$H-2 \rightarrow L+2 (9\%)$ $H-1 \rightarrow L+1 (19\%)$ $H \rightarrow L (54\%)$
		TD–CAM–B3LYP // B3LYP/ npl	3.31 (374)	3.36	$H-2 \rightarrow L+2 (6\%)$ $H-1 \rightarrow L+1 (12\%)$ $H \rightarrow L (63\%)$
		TD–CAM–B3LYP // B3LYP/ pl	2.59 (478)	5.16	$H-2 \rightarrow L+2 (5\%)$ $H-1 \rightarrow L+1 (16\%)$ $H \rightarrow L (70\%)$
		TD-B3LYP//B3LYP/npl	2.7 (459)	4.34	H−1→L+1 (19%) H→L (71%)
	9	TD-B3LYP//B3LYP/ pl	1.92 (645)	6	H−1→L+1 (8%) H→L (90%)
		TD-B3LYP// M06HF/npl	3.72 (333)	6.1	H–3→L+3 (6%) H–2→L+2 (9%)

					H−1→L+1 (22%) H→L (31%)
	TD-M06HF// M06HF/ npl	4.10 (302)	5.57	$H-2 \rightarrow L+1 (9\%)$ $H-1 \rightarrow L (9\%)$ $H \rightarrow L (22\%)$ $H \rightarrow L+1 (6\%)$	
	TD-M06HF// M06HF/ pl	3.37 (368)	7.62	$H-3 \rightarrow L+3 (7\%)$ $H-2 \rightarrow L+2 (11\%)$ $H-1 \rightarrow L+1 (40\%)$	
	TD–CAM–B3LYP // B3LYP/ npl	3.28 (377)	5.61	H-3→L+3 (5%) H-2→L+2 (9%) H-1→L+1 (24%) H→L (40%)	
	TD–CAM–B3LYP // B3LYP/ pl	2.50 (495)	7.72	H-2→L+2 (9%) H-1→L+1 (19%) 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}	$N_{ m ECL}$	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.

		HOMO/ eV		LUMO/ eV	
compound	n	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

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

a) pl, planar; npl, non-planar



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