Terminal Group Engineering of Dipyran-based Non-Fullerene Acceptors: A Computational Approach for High Performance Organic Solar Cells

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Four hybrid functionals namely B3LYP,[1] CAM-B3LYP,[2] MPW1PW91,[3] and wB97XD[4] were initially tested with the 6-31G(d,p)[5] basis set for ground state optimizations and molar absorptivity calculations of the reference molecule.[6] The optimized DPCT-4F system exhibited λ_{max} values of 812 nm (B3LYP), 559 nm (CAM-B3LYP), 768 nm (MPW1PW91), and 534 nm (wB97XD). Comparison with the experimental λ_{max} (764 nm)[7] revealed deviations of 48 nm, 205 nm, 4 nm, and 230 nm, respectively, confirming MPW1PW91/6-31G(d,p) as the most accurate functional. The graphical representation of λ_{max} is shown in **Fig. S1**. DOS analysis was conducted using PyMOlyze 1.1[8] to probe the contributions of donor and acceptor fragments to the absorption features. The transition density matrix (TDM)[9]maps were generated with Multiwfn 3.8[10] to visualize the nature of electronic excitations. Reorganization energies (λ) were computed at the MPW1PW91/6-31G(d,p) level, separating internal and external contributions.[11,12] Electron (λ_e) and hole (λ_h) reorganization energies were calculated using the Marcus theory equations:[13,14]

$$\lambda_e = \left[E^{-}_{\circ} - E_{-}\right] + \left[E^{\circ}_{-} - E_{\circ}\right] \quad (1)$$

$$\lambda_h = \left[E^{+}_{\circ} - E_{+}\right] + \left[E^{\circ}_{+} - E_{\circ}\right] \quad (2)$$

λ_e and λ_h is the reorganization energy of an electron and hole, respectively. $E_{\circ}$ is neutral ground state energy, E_{-} and E_{+} correspond to optimized anionic and cationic total energies. E°_{-} and E°_{+} are neutral energies computed at optimized anionic and cationic geometries. $E^{-}_{\circ}$ and $E^{+}_{\circ}$ are single-point energies of the anion and cation at the neutral geometry.

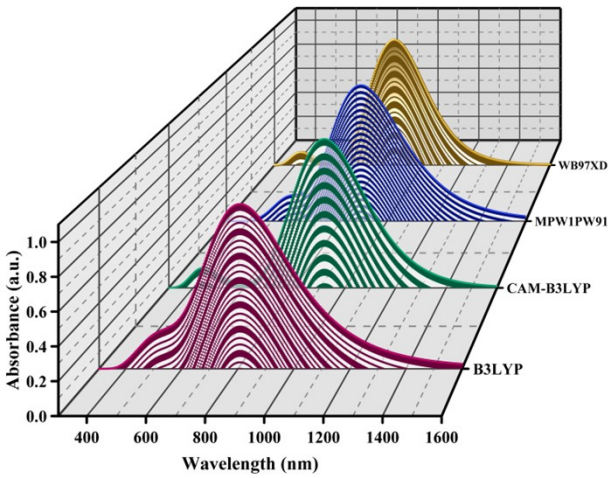

Fig. S1 Comparison of four distinct functionals (B3LYP, CAM-B3LYP, wB97X-D, MPW1PW91) used for method selection

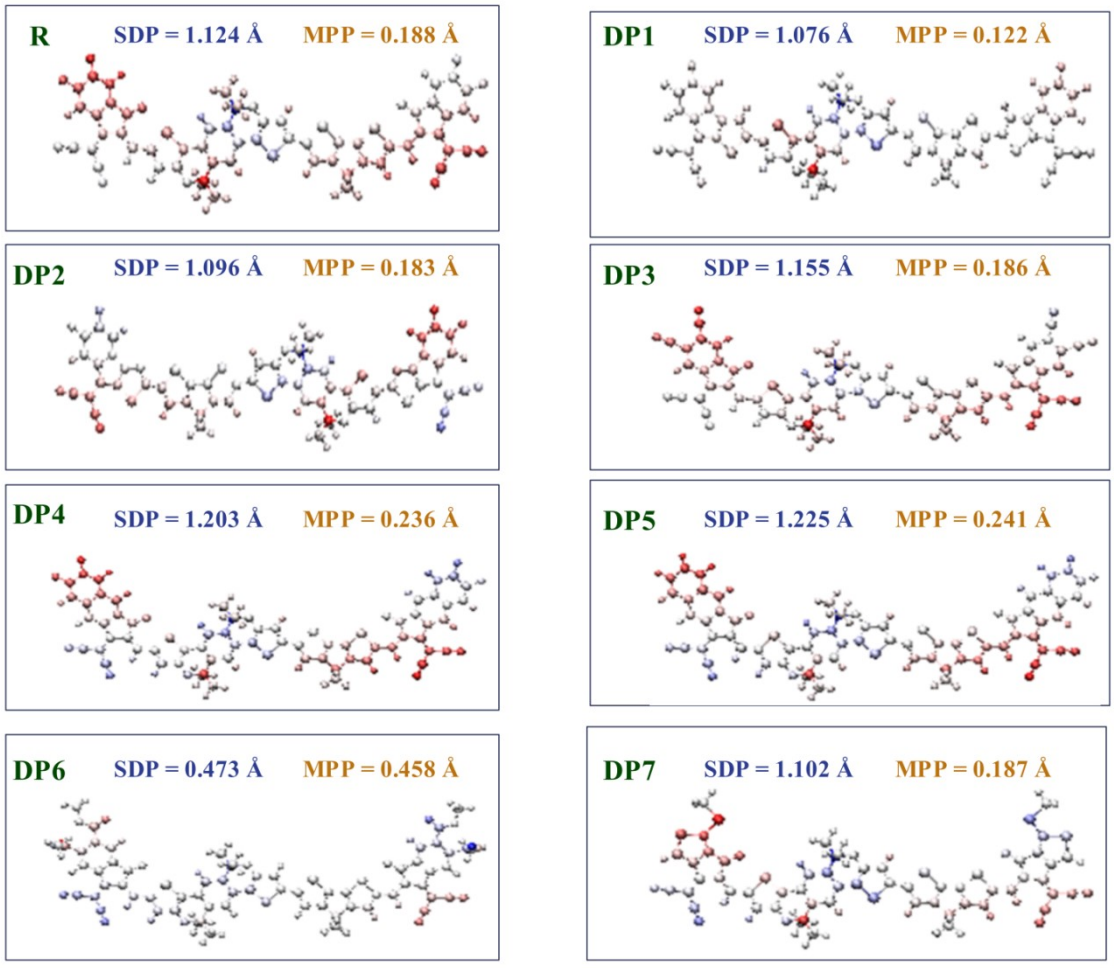

Fig. S2 Representation of the molecular planarity parameter (MPP) and span of deviation from the plane (SDP) for the reference molecule R and the designed molecules (DP1-DP7)

Table S1 Calculated energies of HOMO, LUMO, and E_g for R and DP1-DP7

Molecule	E_{HOMO} (eV)	E_{LUMO} (eV)	E_g (eV)
R	-5.61	-3.47	2.14
DP1	-5.36	-3.51	1.85
DP2	-5.47	-3.61	1.86
DP3	-5.95	-3.94	2.01
DP4	-5.57	-3.47	2.10
DP5	-5.47	-3.35	2.12
DP6	-5.67	-3.59	2.08
DP7	-5.44	-3.30	2.14

Table S2 Calculated percentage involvement of donor, π-bridge, and terminal acceptors.

Molecule	Excitation energy state	Percentage contribution of donor (%)	Percentage contribution of π-bridge (%)	Percentage contribution of acceptor (%)
R	HOMO	55.2	27.4	17.4
	LUMO	26.7	17.0	56.3
DP1	HOMO	53.0	29.6	17.4
	LUMO	11.0	4.40	84.6
DP2	HOMO	54.5	28.8	16.7
	LUMO	11.9	4.20	83.9
DP3	HOMO	55.2	26.1	18.7
	LUMO	24.2	12.7	63.1
DP4	HOMO	54.2	27.1	18.7
	LUMO	25.9	16.2	57.8
DP5	HOMO	54.0	27.4	18.6
	LUMO	26.1	16.8	57.1
DP6	HOMO	55.2	26.7	61.5
	LUMO	24.2	14.0	18.9
DP7	HOMO	53.7	27.4	18.9
	LUMO	26.8	17.4	55.8

Table S3 The Dipole moment (D) of reference molecule R and designed acceptor molecules

Molecule	Dipole moment in gas phase (D)	Dipole moment in solvent phase (D)
R	1.403	1.612
DP1	4.938	6.812
DP2	1.070	1.470
DP3	9.296	11.417
DP4	2.941	3.587
DP5	7.093	8.284
DP6	1.696	1.512
DP7	7.821	9.060

Table S4 Calculated values of excitation energy (E_x) and oscillator strength (f) of molecule R and designed acceptor molecules in gas phase

Molecule	Excitation energy (E_x) (eV)	Oscillator strength (f)
R	1.7947	2.832
DP1	1.5516	1.807
DP2	1.5531	1.737
DP3	1.6844	2.719
DP4	1.7539	3.044
DP5	1.7724	3.054
DP6	1.7344	2.787
DP7	1.7882	2.887

Table S5 Calculated values of excitation energy (E_x) and oscillator strength (f) of molecule R and designed acceptor molecules in Solvent

Molecule	Excitation energy (E_x) (eV)	Oscillator strength (f)
R	1.6131	3.089
DP1	1.4020	2.079
DP2	1.3956	1.962
DP3	1.5159	2.786
DP4	1.6117	3.260
DP5	1.6281	3.269
DP6	1.5764	2.928
DP7	1.6474	3.124

Table S6 Calculated Light harvesting efficiency (LHE) of molecule R and designed acceptor molecules

Molecule	LHE (gas)	LHE (Solvent)
R	0.998528	0.999185
DP1	0.984404	0.991663
DP2	0.981677	0.989086
DP3	0.998090	0.998363
DP4	0.999096	0.999450
DP5	0.999117	0.999462
DP6	0.998367	0.998820
DP7	0.998703	0.999248

Table S7 Binding energies (E_b) values of of molecule R and designed acceptor molecules in both phases

Molecule	Binding energy in gas phase (eV)	Binding energy in solvent (eV)
R	0.36	0.53
DP1	0.30	0.45
DP2	0.31	0.46
DP3	0.33	0.49
DP4	0.35	0.49
DP5	0.35	0.49
DP6	0.35	0.50
DP7	0.35	0.49

Table S8 Calculated values of electron mobility (λ_e) and hole mobility (λ_h) of molecule R and designed acceptor molecules

Molecule	λ_e (eV)	λ_h (eV)
R	0.0061873	0.0086137
DP1	0.0041269	0.007939
DP2	0.0040141	0.0039555
DP3	0.0041649	0.0083167
DP4	0.005495	0.0084726
DP5	0.0055294	0.0083542
DP6	0.0055698	0.0091092
DP7	0.0061609	1.008308

Table 9 Calculated V_{OC} and fill factor values of molecule R and designed acceptors molecules

Molecule	V_{oc} (V)	FF %
R	1.54	91.6
DP1	1.5	91.4
DP2	1.4	90.9
DP3	1.07	88.8
DP4	1.54	91.6
DP5	1.66	99.1
DP6	1.42	91.0
DP7	1.71	92.3

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