Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.


# First Principles study of Organic sensitizers for Dye Sensitized Solar Cells: Effects of Anchoring Groups on optoelectronic properties and Dye aggregation

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**Table S1.** The calculated absorption energies (λ, in nm) for the model dye L1 at different DFT functionals using 6-31G* basis set at acetonitrile medium.

| **Methods** | **L1** | | **L2** | |
|---|---|---|---|---|
| | **λ** | **Exp.[a]** | **λ** | **Exp.[a]** |
| TDB3LYP//B3LYP | 560.7 | 404 | 615.6 | 427 |
| TDBHandHLYP//B3LYP | 441.0 | | 483.4 | |
| TDCAM-B3LYP//B3LYP | 440.3 | | 479.7 | |
| TDM062X//B3LYP | 445.6 | | 485.5 | |
| TDωB97XD//B3LYP | 426.0 | | 463.7 | |
| TDBHandHLYP//BHandHLYP | 414.9 | | 452.2 | |
| TDCAM-B3LYP//CAM-B3LYP | 414.9 | | 449.0 | |
| TDM062X//M062X | 421.2 | | 455.9 | |
| **TDωB97XD//ωB97XD** | **397.1** | | **430.6** | |

[a]taken from Ref.

**Table S2.** The calculated most representative absorption energies (λ, in nm), oscillator strengths (*f* in a.u.), and the corresponding MO transitions of designed dyes with $PO_3H_2$ anchoring group at TD ωB97XD//ωB97XD/6-31G* level of theory.

| Dyes | State | λ | *f* | Transition assignment |
|---|---|---|---|---|
| **Dπ-CDM** | S0→S1 | 642.8 | 0.12 | H-1->L+0 (67%) |
| | S0→S3 | 343.0 | 1.55 | H-0->L+1 (28%), H-1->L+1 (25%) |
| **Dπ-$^{CN}$CDM** | S0→S1 | 630.5 | 0.18 | H-1->L+0 (64%), H-0->L+0 (19%) |
| | S0→S3 | 357.3 | 1.47 | H-1->L+1 (35%), H-0->L+1 (19%) |
| **Dπ-TP** | S0→S1 | 487.7 | 0.84 | H-0->L+0 (51%), H-1->L+0 (44%) |
| | S0→S3 | 339.5 | 0.35 | H-1->L+0 (27%), H-0->L+0 (23%), H-0->L+1 (21%) |
| | S0→S4 | 300.2 | 0.54 | H-0->L+1 (37%), H-1->L+1 (25%) |
| **Dπ-$^{CN}$TP** | S0→S1 | 511.1 | 1.00 | H-0->L+0 (52%), H-1->L+0 (43%) |
| | S0→S4 | 312.4 | 0.49 | H-1->L+1 (45%), H-0->L+1 (31%) |
| **Dπ-CDT** | S0→S1 | 385.8 | 1.99 | H-0->L+0 (43%), H-1->L+0 (42%) |
| **Dπ-$^{CN}$CDT** | S0→S1 | 412.0 | 1.98 | H-1->L+0 (52%), H-0->L+0 (32%) |

*H and L represent HOMO and LUMO, respectively.

**Table S3.** The calculated most representative absorption energies (λ, in nm), oscillator strengths (*f* in a.u.), and the corresponding MO transitions of designed dyes with $SO_3H$ anchoring group at TD ωB97XD//ωB97XD/6-31G* level of theory.

| Dyes | State | λ | *f* | Transition assignment |
|---|---|---|---|---|
| **Dπ-CDM** | S0→S1 | 637.3 | 0.14 | H-1->L+0 (64%) |
| | S0→S3 | 346.8 | 1.63 | H-1->L+1 (26%), H-0->L+1 (24%), H-0->L+2 (21%) |
| **Dπ-$^{CN}$CDM** | S0→S1 | 630.8 | 0.21 | H-1->L+0 (61%), H-0->L+0 (19%) |
| | S0→S3 | 364.7 | 1.48 | H-1->L+1 (36%), H-0->L+1 (20%) |
| **Dπ-TP** | S0→S1 | 493.9 | 0.91 | H-0->L+0 (50%), H-1->L+0 (45%) |
| | S0→S3 | 345.7 | 0.22 | H-1->L+0 (30%), H-0->L+0 (28%) |
| | S0→S4 | 302.7 | 0.63 | H-0->L+1 (36%), H-1->L+1 (30%) |
| **Dπ-$^{CN}$TP** | S0→S1 | 521.9 | 1.06 | H-0->L+0 (52%), H-1->L+0 (43%) |
| | S0→S4 | 315.1 | 0.50 | H-1->L+1 (47%), H-0->L+1 (29%) |
| **Dπ-CDT** | S0→S1 | 392.7 | 2.02 | H-1->L+0 (48%), H-0->L+0 (35%) |
| **Dπ-$^{CN}$CDT** | S0→S1 | 422.1 | 1.97 | H-1->L+0 (53%), H-0->L+0 (29%) |

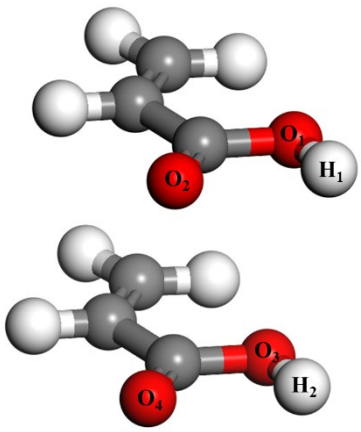
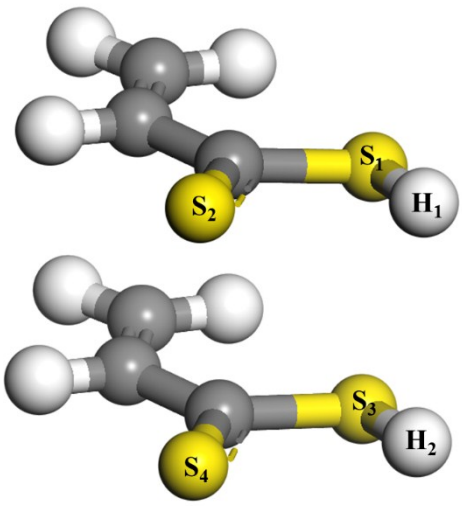
*H and L represent HOMO and LUMO, respectively.

**Table S4.** The calculated dihedral angle values ( θ in degrees) between different units for the face-to-face dimeric configurations including isolated monomer and individual monomers in dimer. ( See figure 8 for dihedral angle definition)

| Anchoring group | Acceptor group | Type* | $\theta_1$ | $\theta_2$ | $\theta_3$ |
|---|---|---|---|---|---|
| **COOH** | CDM | IM | 0.51 | 0.96 | -26.49 |
| | | M1 | 17.06 | 6.36 | 11.67 |
| | | M2 | -12.97 | -5.94 | 27.17 |
| | TP | IM | -0.02 | 0.09 | -1.14 |
| | | M1 | -12.24 | -3.43 | -10.89 |
| | | M2 | -4.19 | 11.71 | 2.73 |
| | CDT | IM | -0.02 | 0.07 | -29.33 |
| | | M1 | 16.56 | 2.99 | 17.59 |
| | | M2 | -13.51 | -6.73 | 29.14 |
| **CSSH** | CDM | IM | -0.30 | 0.71 | -26.08 |
| | | M1 | -1.04 | 2.34 | -8.71 |
| | | M2 | -3.82 | 1.16 | 10.98 |
| | TP | IM | -0.12 | -0.01 | -1.90 |
| | | M1 | -5.85 | -0.41 | -7.30 |
| | | M2 | -4.42 | -0.19 | 5.08 |
| | CDT | IM | 1.32 | 1.21 | -23.32 |
| | | M1 | -7.82 | -1.26 | -18.25 |
| | | M2 | -5.19 | 0.58 | -4.29 |

*IM, M1 and M2 are Isolated monomer dye, individual monomer dye 1 in dimer and individual monomer dye 2 in dimer, respectively.

**Table S5.** The calculated hydrogen bond distances (in Å) between individual monomers of Head-to-Head dimeric configuration of designed dyes.

| System | Acceptor group | R1 | R2 | R3 | R4 |
|---|---|---|---|---|---|
|  | CDM | 4.52 | 5.94 | 3.83 | 1.98 |
| | TP | 2.07 | 3.86 | 3.53 | 3.77 |
| | CDT | 4.52 | 5.92 | 3.83 | 1.99 |
|  | CDM | 4.62 | 4.23 | 3.76 | 5.50 |
| | TP | 4.71 | 4.29 | 3.65 | 5.51 |
| | CDT | 3.26 | 4.75 | 4.83 | 5.01 |

R1, R2, R3 and R4 are distances of $O_1\cdots H_2$, $O_2\cdots H_2$, $O_3\cdots H_1$ and $O_4\cdots H_1$ for COOH and $S_1\cdots H_2$, $S_2\cdots H_2$, $S_3\cdots H_1$ and $S_4\cdots H_1$ for CSSH dyes.

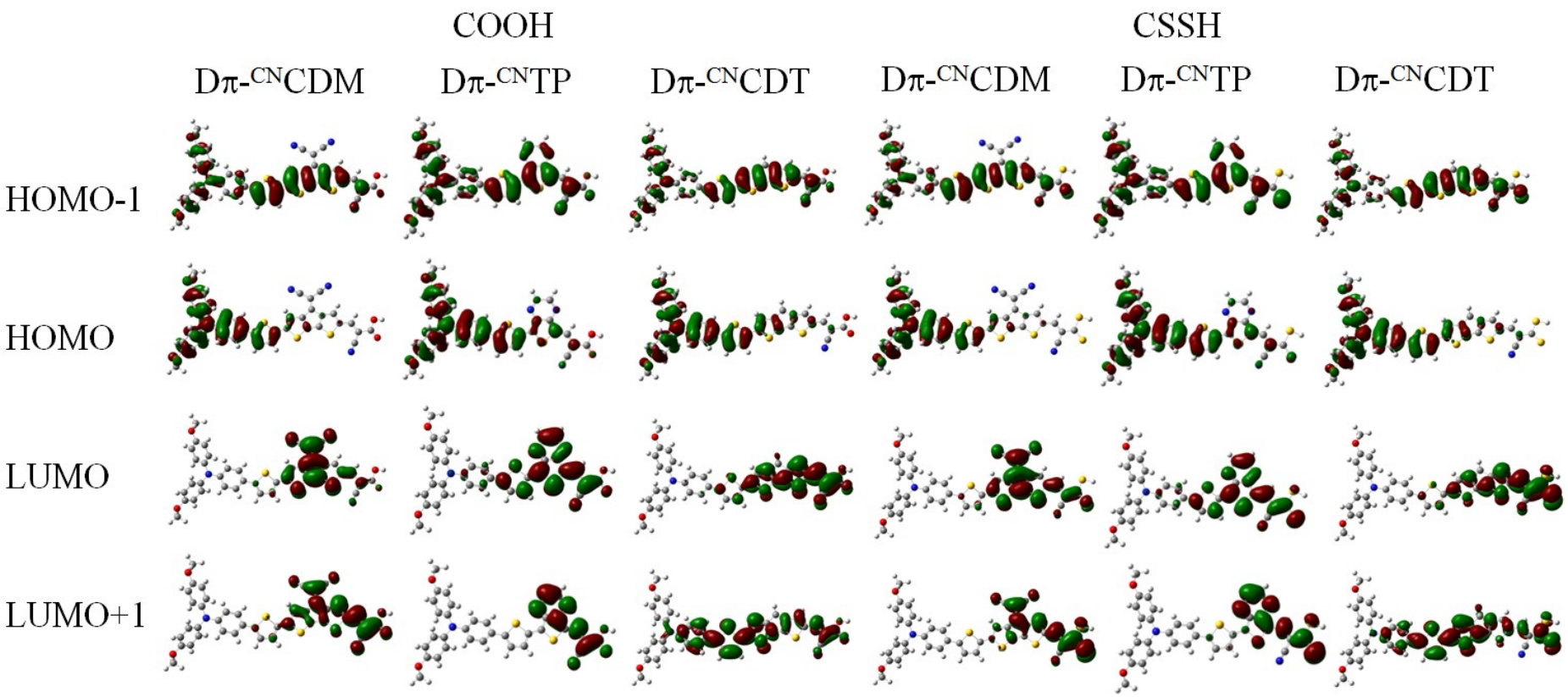



**Figure S1.** Isodensity plots of selected frontier molecular orbitals of the designed dyes with different acceptors and anchoring groups containing CN. The calculations were performed by ωB97XD/6-31G* level of theory and the isovalue is 0.02 a.u.

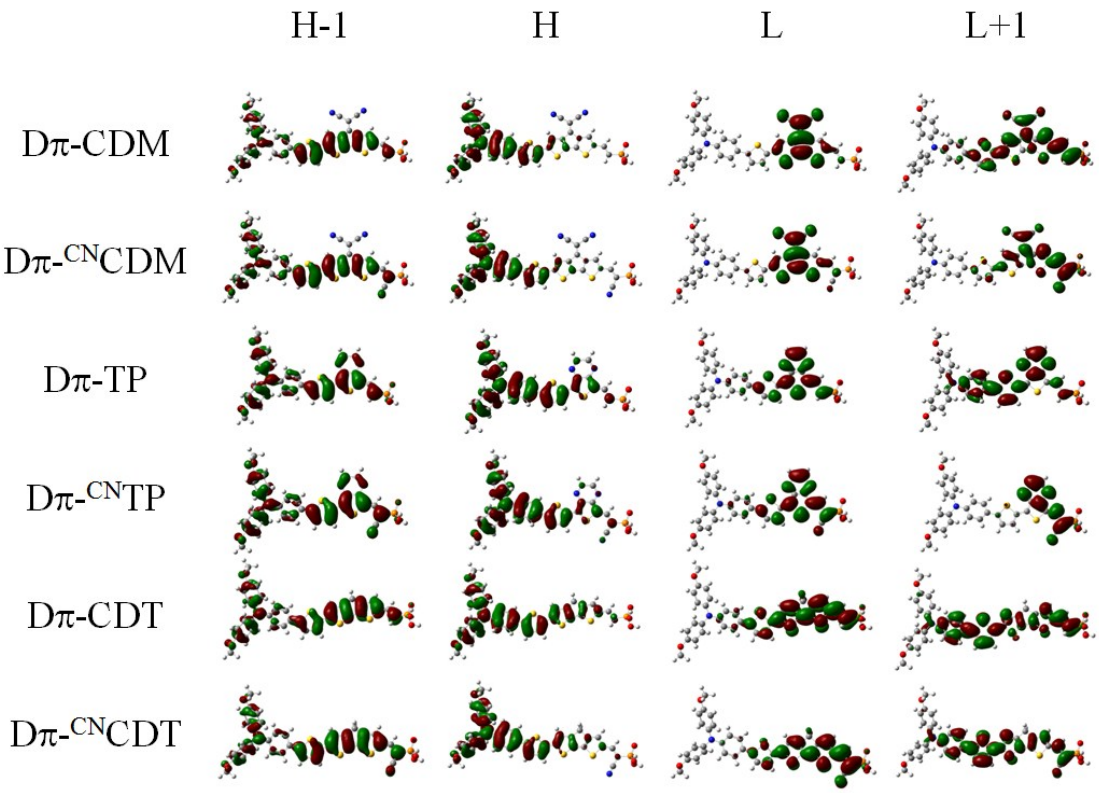



**Figure S2.** Isodensity plots of selected frontier molecular orbitals of the designed dyes with different acceptors and $PO_3H_2$ anchoring group. The calculations were performed by ωB97XD/6-31G* level of theory and the isovalue is 0.02 a.u.

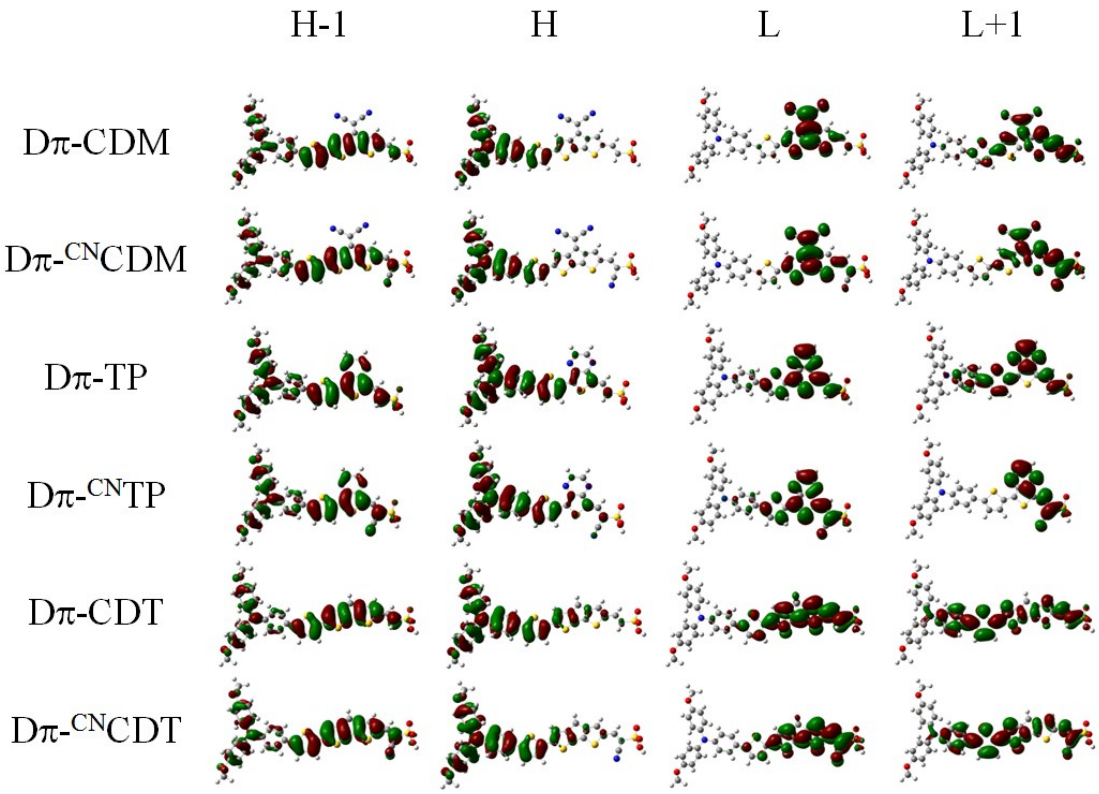



**Figure S3.** Isodensity plots of selected frontier molecular orbitals of the designed dyes with different acceptors and $SO_3H$ anchoring group. The calculations were performed by ωB97XD/6-31G* level of theory and the isovalue is 0.02 a.u.