Computational study of 4, 4'- dimethoxy triphenylamine donor linked with low band gap π spacers by single and double bond for DSSC applications

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Content:

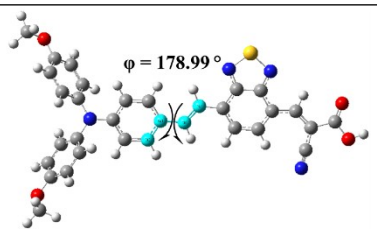
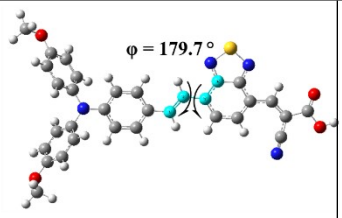
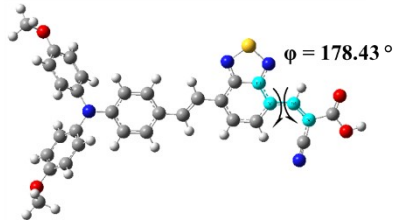
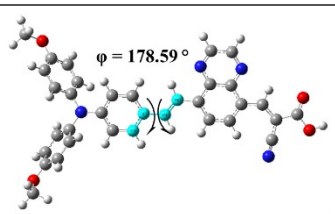
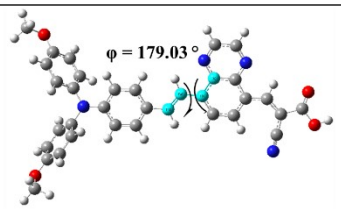
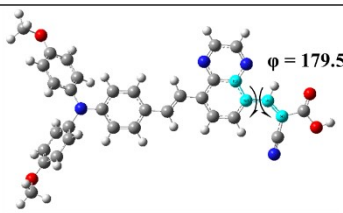
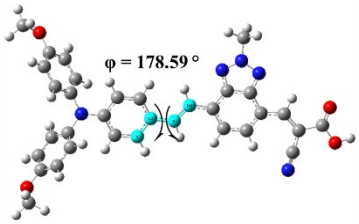
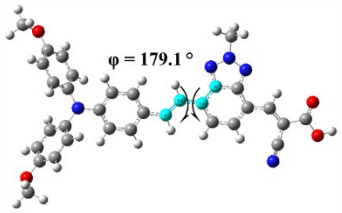
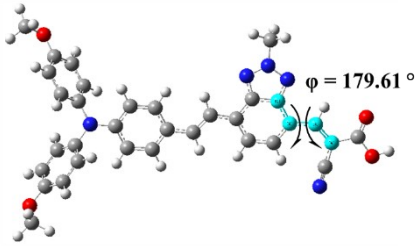
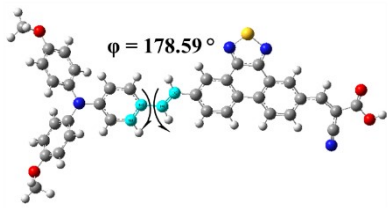
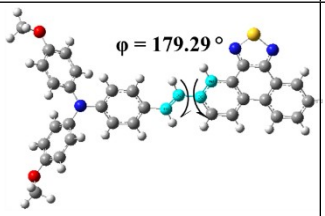
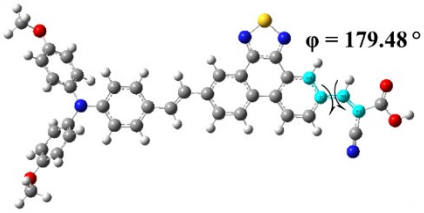
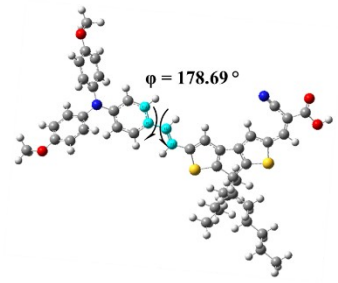
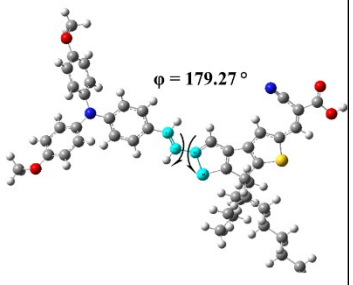
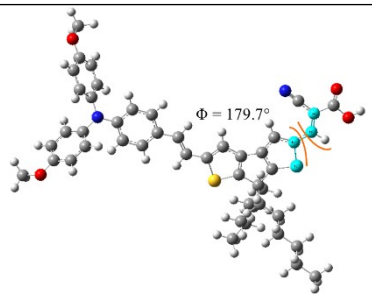
Dyes	Dihedral angle	
	W.r.t Donor – π-Spacer	W.r.t π-Spacer - Acceptor
TC1”	 	
TC2”	 	
TC3”	 	
TC4”	 	
TC5”	 	

Fig. S1 The dihedral angle obtained from ground state optimized structures of the dyes (TC1”-TC5”) obtained using B3LYP/6-311+G (d,p) method in dichloromethane solvent

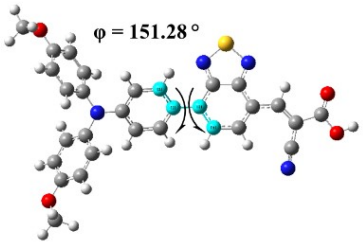
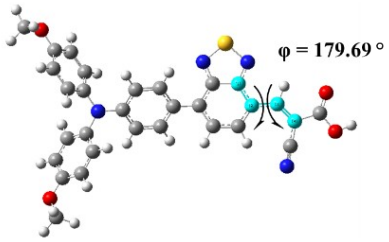
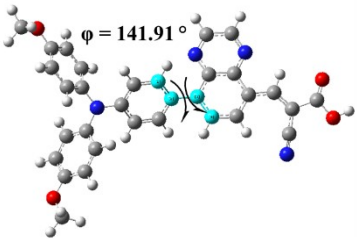
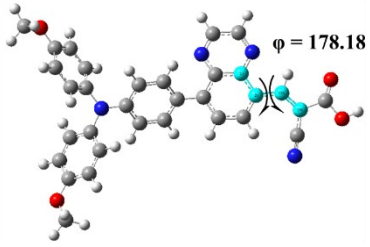
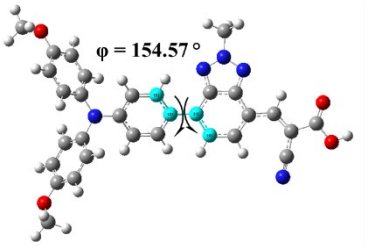
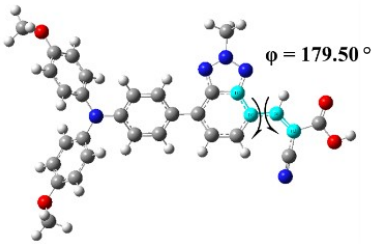
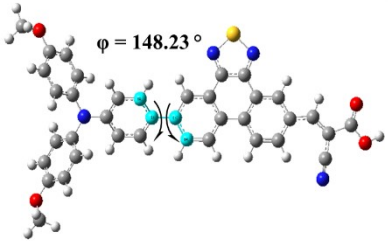
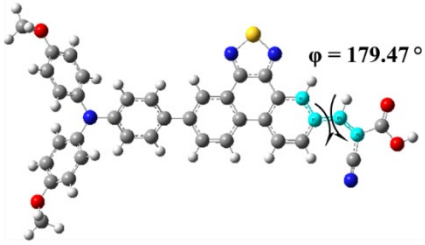
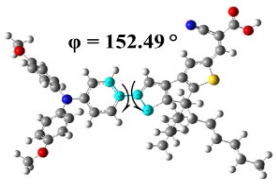
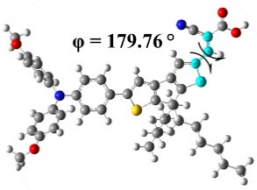
Dyes	Dihedral angle	
	W.r.t Donor – π-Spacer	W.r.t π-Spacer - Acceptor
TC1		
TC2		
TC3		
TC4		
TC5		

Fig. S2 The dihedral angle obtained from ground state optimized structures of the dyes (TC1”-TC5”) obtained using B3LYP/6-311+G (d,p) method in dichloromethane solvent

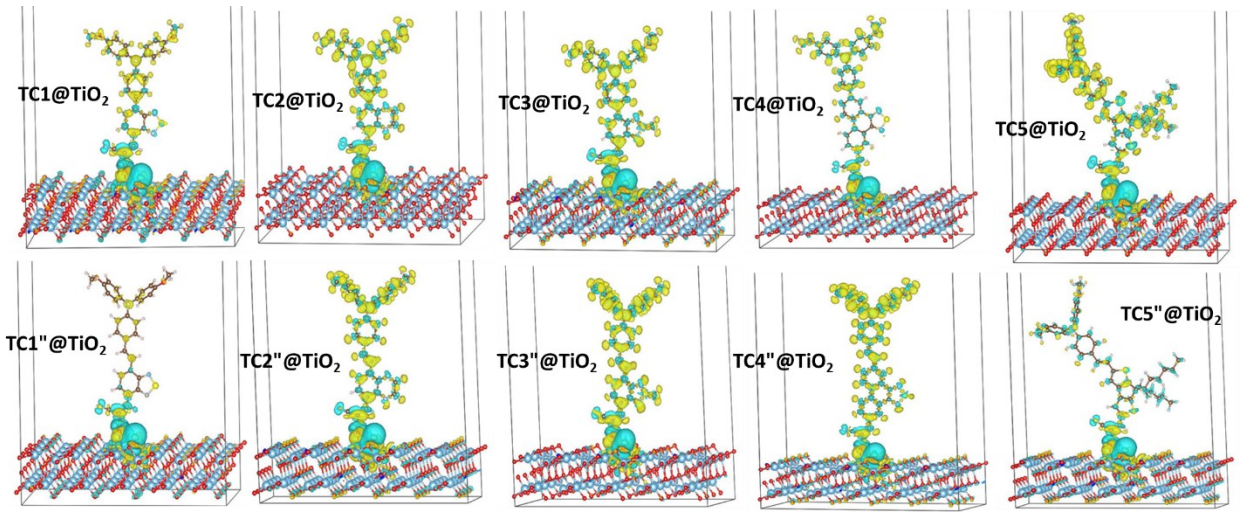


Fig S3. 3D charge density difference plot of the TC1-TC5 and TC1”-TC5” on TiO_2 surface.

Table S1 Ground state optimization followed by frequency calculations via different functional

Functional	Basis set	HOMO /eV	LUMO /eV	HOMO-LUMO Energy gap /eV
Experimental	NA	**-5.08**	**-3.19**	**1.89**
B3LYP	6-31G(d,p)	-4.76	-2.63	2.13
B3LYP	6-31+G(d,p)	-5.01	-2.93	2.08
B3LYP	6-311G(d,p)	-5	-2.81	2.19
B3LYP	6-311+G(d,p)	-5.07	-2.95	2.12
CAM-B3LYP	6-31G(d,p)	-6.02	-1.44	4.58
CAM-B3LYP	6-31+G(d,p)	-6.26	-1.77	4.49
CAM-B3LYP	6-311G(d,p)	-6.26	-1.63	4.63
CAM-B3LYP	6-311+G(d,p)	-6.32	-1.79	4.53
M06	6-31G(d,p)	-5.09	-2.49	2.6
M06	6-31+G(d,p)	-5.3	-2.76	2.54
M06	6-311G(d,p)	-5.32	-2.65	2.67
M06	6-311+G(d,p)	-5.37	-2.76	2.61
M06-2X	6-31G(d,p)	-5.96	-1.78	4.18
M06-2X	6-31+G(d,p)	-6.16	-2.05	4.11
M06-2X	6-311G(d,p)	-6.17	-1.95	4.22

M06-2X	6-311+G(d,p)	-6.22	-2.07	4.15
PBE1PBE	6-31G(d,p)	-5	-2.54	2.46
PBE1PBE	6-31+G(d,p)	-5.19	-2.79	2.4
PBE1PBE	6-311G(d,p)	-5.18	-2.68	2.5
PBE1PBE	6-311+G(d,p)	-5.23	-2.8	2.43
TPSSH	6-31G(d,p)	-4.44	-2.89	1.55
TPSSH	6-31+G(d,p)	-4.64	-3.14	1.5
TPSSH	6-311G(d,p)	-4.63	-3.03	1.6
TPSSH	6-311+G(d,p)	-4.68	-3.15	1.53
WB97XD	6-31G(d,p)	-6.6	-0.92	5.68
WB97XD	6-31+G(d,p)	-6.8	-1.19	5.61
WB97XD	6-31G(d,p)	-6.8	-1.07	5.73
WB97XD	6-31+G(d,p)	-6.85	-1.19	5.66

Table S2 The simulated absorption spectra parameters by TDDFT calculations by different functionals and basis set

	Basis sets {Wavelength (nm) / oscillator strength}			
Functional (TC5)	**6-31G(d,p)**	**6-31+G(d,p)**	**6-311G(d,p)**	**6-311+G(d,p)**
B3LYP	671/0.0355, 459/0.2209	696/0.0443, 471/0.2365	669/0.0439, 461/0.2428	691/0.0491, 472/0.2458
CAM-B3LYP	398/0.4447	412/0.4646	403/0.482	413/0.4866
M06	573/0.049, 428/0.3263	589/0.0614, 439/0.3417	568/0.066, 430/0.3541	582/0.0728, 439/0.3573
M06-2X	406/0.3373	418/0.3657	410/0.3858	420/0.3929
PBE1PBE	599/0.0436, 431/0.2978	618/0.053, 441/0.313	598/0.0542, 433/0.3212	614/0.0595, 441/0.3225
TPSSH	844/0.0264, 507/0.1321	874/0.0324, 519/0.1444	837/0.0319, 507/0.1484	864/0.0354, 519/0.1517
WB97XD	382/0.6524	392/0.6708	387/0.6756	394/0.6828
Experimental	**553**			