Electronic Supplementary Information

Effect of "push-pull" sensitizers with modified conjugation bridges on the performance of p-type dye-sensitized solar cells

Fengying Zhang, Pei Yu, Wei Shen, Ming Li, Rongxing He*

Key Laboratory of Luminescence and Real-Time Analytical chemistry (Southwest University), Ministry of Education, College of Chemistry and Chemical Engineering, Southwest University, Chongqing 400715, China

* To whom correspondence should be addressed. E-mail: herx@swu.edu.cn.

Table Captions

Table S1 Calculated molecular orbital energy levels (HOMO and LUMO, eV) for sensitizer T-D-1S-A-1S with different functionals.

Table S2 Calculated wavelength of maximum absorption λ_{max}(nm) and corresponding energy $E_{\lambda max}$(eV) of T-D-1S-A-1S in acetonitrile solution with PBE0/6-31G(d) geometries.

Table S3 Electronic transition data obtained at BMK/6-31G(d) level for Q band and B band of sensitizers, respectively.

Table S4 Electron density difference plots of electronic transition in Q band for all the dyes binding with NiO or $(NiO)_9$, which are performed in acetonitrile solvent using BMK functional together with 6-31G(d) basis set.

Figure Captions

Fig. S1 Geometries of all the dyes binding with NiO or $(NiO)_9$, which are optimized at PBE0/6-31G(d) level.

Fig. S2 The diagram of several important performance parameters for designed sensitizers. (a) The light-harvesting efficiency at maximum wavelength. (b) The fraction of electron exchange in the process of electron transfer. (c) The driving force of hole injection. (d) The driving force of regeneration. (e) The driving force of recombination.

Table S1 Calculated molecular orbital energy levels (HOMO and LUMO, eV) for sensitizer T-D-1S-A-1S with different functionals.

Scheme	HOMO (eV)	LUMO (eV)
Exp [a]	-5.53	-3.35
M062X/6-31G(d)	-6.38	-2.14
LC-WB97XD/6-31G(d)	-7.01	-1.28
PBE0/6-31G(d)	-5.53	-3.17
B3LYP/6-311G(d, p)	-5.51	-3.15

[a] Experimental value from Ref 25.

Table S2 Calculated wavelength of maximum absorption λ_{max}(nm) and corresponding energy $E_{\lambda max}$(eV) of T-D-1S-A-1S in acetonitrile solution with PBE0/6-31G(d) geometries.

Scheme	λ_{max} (nm)	$E_{\lambda max}$ (eV)
Exp [a]	488/369	2.54/3.36
PBE0/6-31G(d)	573/381	2.16/3.25
CAM-B3LYP/6-31G(d)	454/335	2.73/3.70
BMK/6-31G(d)	498/344	2.49/3.60

[a] Experimental value from Ref 25.

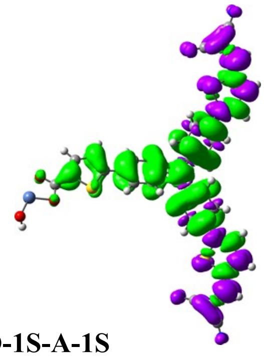
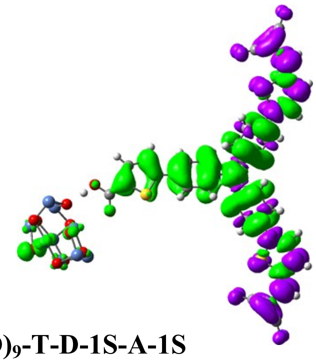
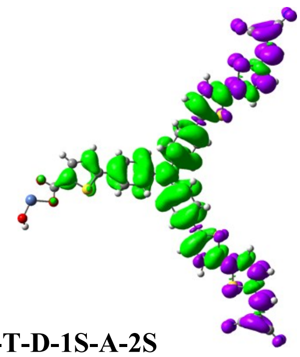
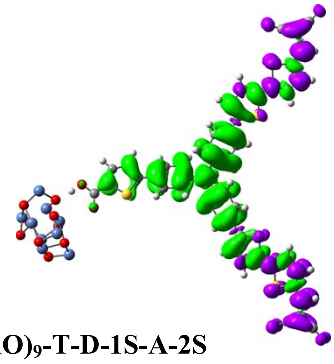
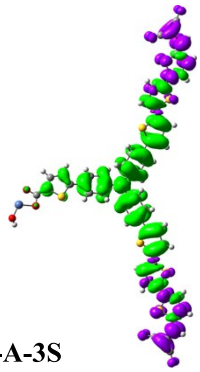
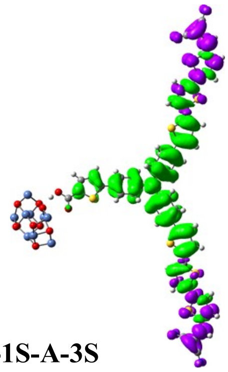
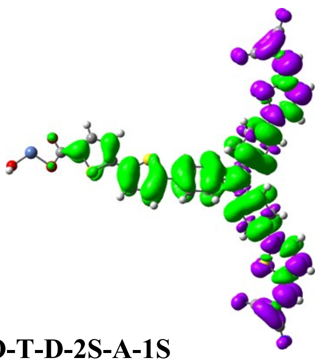
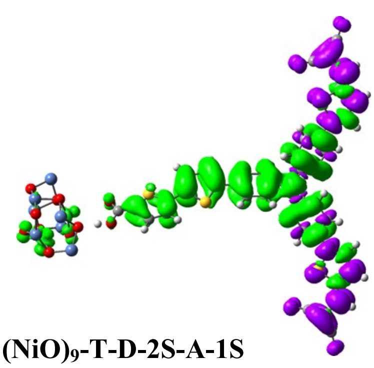
Table S3 Electronic transition data obtained at BMK/6-31G(d) level for Q band and B band of sensitizers, respectively.

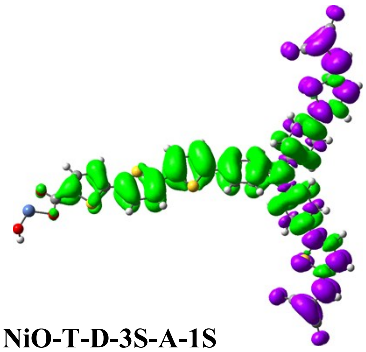
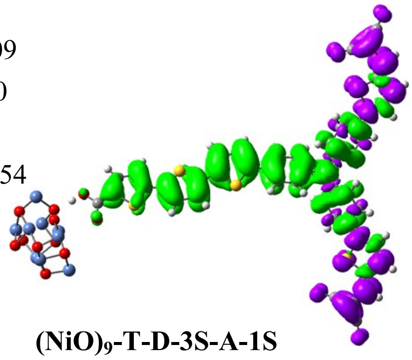
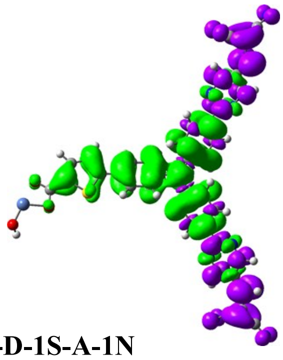
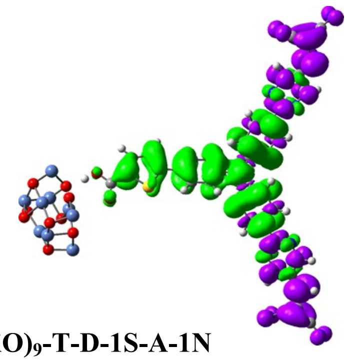
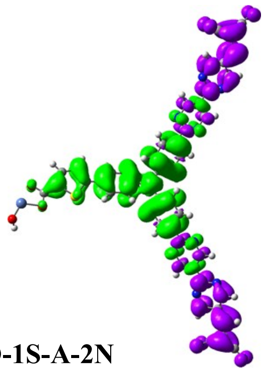
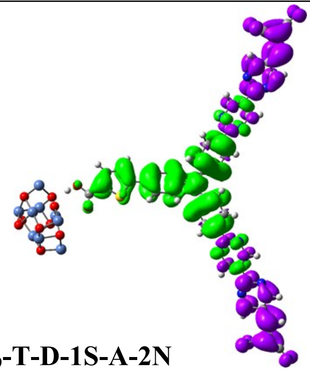
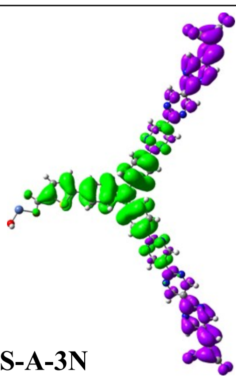
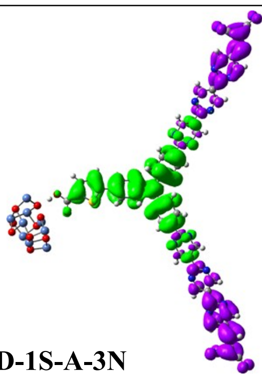
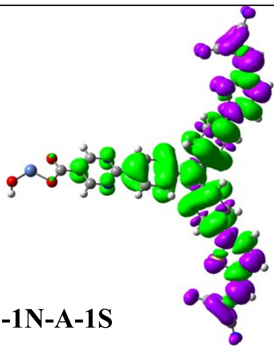
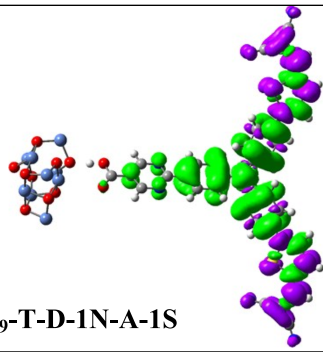
Molecules		Q band		B band	
		λ_1 (nm)	Major configuration	λ_2 (nm)	Major configuration
T-D-1S-A-1S	Dye	498	H→L (91%), H-1→L+1 (5%)	344	H-1→L+1 (53%), H-2→L (33%), H-3→L (6%), H→L (6%)
	NiO-Dye	497	H→L (91%), H-1→L+1 (5%)	344	H-1→L+1 (55%), H-2→L (31%), H-3→L (6%), H→L (6%)
	$(NiO)_9$-Dye	501	H→L (91%), H-3→L+1 (5%)	346	H-3→L+1 (50%), H-4→L (35%), H-11→L (6%), H→L (6%)
T-D-1S-A-2S	Dye	527	H→L (80%), H-1→L+1 (12%)	372	H→L+2 (84%), H-2→L+2 (6%)
	NiO-Dye	525	H→L (80%), H-1→L+1 (13%)	386	H→L+2 (84%), H-2→L+2 (7%)
	$(NiO)_9$-Dye	530	H→L (81%), H-1→L+1 (12%)	365	H→L+2 (84%), H-3→L+2 (6%)
T-D-1S-A-3S	Dye	543	H→L (65%), H-1→L+1 (22%), H-2→L (6%)	387	H→L+2 (80%), H-2→L+2 (6%)
	NiO-Dye	543	H→L (64%), H-1→L+1 (23%), H-2→L (6%)	401	H→L+2 (80%), H-2→L+2 (8%)
	$(NiO)_9$-Dye	547	H→L (66%), H-1→L+1 (21%), H-2→L (6%)	383	H→L+2 (79%), H-2→L+2 (5%)
T-D-2S-A-1S	Dye	504	H→L (88%), H-2→L+1 (5%)	385	H→L+2 (74%), H-1→L+2 (15%), H→L+1 (6%)
	NiO-Dye	504	H→L (89%), H-2→L+1 (5%)	395	H→L+2 (72%), H-1→L+2 (15%), H→L+1 (8%)
	$(NiO)_9$-Dye	508	H→L (88%), H-3→L+1 (5%), H-1→L (5%)	378	H→L+2 (73%), H-1→L+2 (15%), H→L+1 (6%)

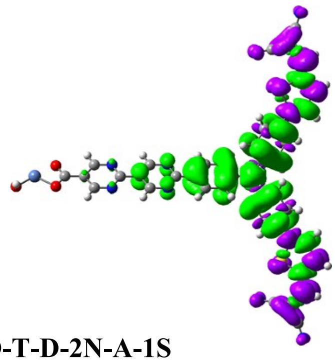
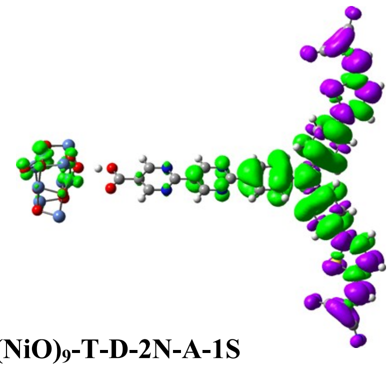
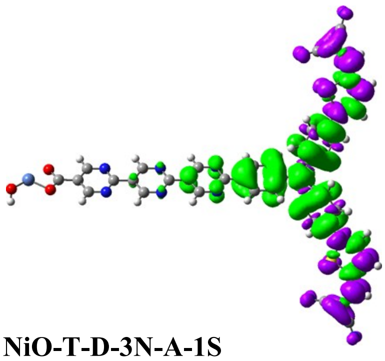
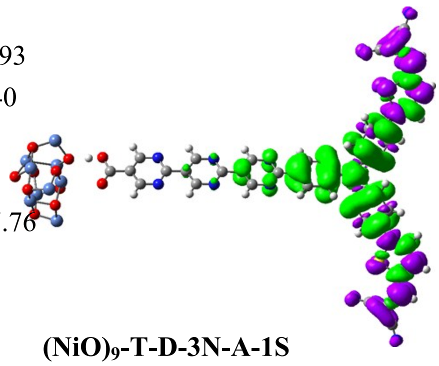
	Dye	508	H→L (81%), H-1→L (12%)	415	H→L+2 (61%), H-1→L+2 (19%), H→L+1 (11%), H-1→L+1 (5%)
T-D-3S-A-1S	NiO-Dye	509	H→L (82%), H-1→L (11%)	425	H→L+2 (56%), H-1→L+2 (18%), H→L+1 (16%), H-1→L+1 (6%)
	$(NiO)_9$-Dye	511	H→L (79%), H-1→L (13%)	413	H→L+2 (63%), H-1→L+2 (18%), H→L+1 (10%), H-1→L+1 (5%)
	Dye	497	H→L (92%)	326	H-1→L (61%), H-2→L+1 (24%), H-5→L (6%), H→L (5%)
T-D-1S-A-1N	NiO-Dye	496	H→L (93%)	324	H-1→L (55%), H-2→L+1 (28%), H-5→L (6%), H→L (5%)
	$(NiO)_9$-Dye	501	H→L (92%)	331	H-5→L (62%), H-9→L+1 (17%), H-4→L (6%), H→L (5%)
	Dye	497	H→L (89%), H→L+3 (5%)	351	H→L+3 (43%), H-2→L+1 (19%), H-1→L (13%), H→L (10%), H-3→L (6%)
T-D-1S-A-2N	NiO-Dye	496	H→L (89%), H→L+3 (5%)	350	H→L+3 (44%), H-2→L+1 (20%), H-1→L (12%), H→L (10%), H-3→L (6%)
	$(NiO)_9$-Dye	502	H→L (89%), H→L+2 (5%)	354	H→L+2 (43%), H-8→L+1 (18%), H-4→L (15%), H→L (10%), H-14→L (6%)
	Dye	482	H→L (86%), H→L+2 (8%)	379	H→L+2 (66%), H→L (13%), H-2→L+1 (5%), H→L+9 (5%)
T-D-1S-A-3N	NiO-Dye	481	H→L (86%), H→L+2 (8%)	378	H→L+2 (66%), H→L (13%), H-2→L+1 (5%), H→L+10 (5%)
	$(NiO)_9$-Dye	487	H→L (86%), H→L+2 (8%)	381	H→L+2 (67%), H→L (13%), H-8→L+1 (5%), H→L+10 (5%)
T-D-1N-A-1S	Dye	490	H→L (91%), H-1→L+1 (6%)	341	H-1→L+1 (62%), H-2→L (28%), H→L (6%)
	NiO-Dye	487	H→L (91%), H-1→L+1 (6%)	341	H-1→L+1 (62%), H-2→L (29%), H→L (6%)

	$(NiO)_9$-Dye	493	H→L (90%), H-3→L+1 (5%)	341	H-3→L+1 (62%), H-8→L (25%), H→L (6%)
T-D-2N-A-1S	Dye	493	H→L (91%), H-1→L+1 (5%)	342	H-1→L+1 (60%), H-2→L (28%), H→L (6%)
	NiO-Dye	493	H→L (91%), H-1→L+1 (5%)	342	H-1→L+1 (59%), H-2→L (28%), H→L (6%)
	$(NiO)_9$-Dye	494	H→L (91%), H-2→L+1 (5%)	342	H-2→L+1 (61%), H-6→L (18%), H-7→L (10%), H→L (6%)
T-D-3N-A-1S	Dye	494	H→L (91%), H-1→L+1 (5%)	313	H→L+3 (49%), H-2→L+1 (11%), H-2→L+2 (10%), H→L+2 (10%), H-3→L+2 (5%)
	NiO-Dye	494	H→L (91%)	320	H→L+3 (54%), H-2→L+1 (11%), H→L+1 (7%), H→L+2 (6%)
	$(NiO)_9$-Dye	494	H→L (91%), H-3→L+1 (5%)	308	H→L+3 (27%), H-6→L+1 (14%), H-6→L+2 (15%), H-1→L+5 (13%), H-11→L+2 (7%)

Table S4 Electron density difference plots of electronic transition in Q band for all the dyes binding with NiO or $(NiO)_9$, which are performed in acetonitrile solvent using BMK functional together with 6-31G(d) basis set. L is the electron transfer distance (Å), Δe is the fraction of electron exchange (|e-|), Ω is overlaps between the regions of density depletion and increment (Isovalue: 4×10^{-4} e au^{-3}), E is the energy of molecule (a.u.).

NiO-Dye	$(NiO)_9$-Dye
L= 3.238 Δe= 1.0467 Ω= 0.6404 E= -3359.66  **NiO-T-D-1S-A-1S**	L= 4.365 Δe= 1.1076 Ω= 0.5812 E= -5310.39  **$(NiO)_9$-T-D-1S-A-1S**
L= 6.229 Δe= 1.0359 Ω= 0.4790 E= -4462.82  **NiO-T-D-1S-A-2S**	L= 6.210 Δe= 1.0445 Ω= 0.3433 E= -6413.54  **$(NiO)_9$-T-D-1S-A-2S**
L= 3.816 Δe= 1.0484 Ω= 0.3686 E=-5565.98  **NiO-T-D-1S-A-3S**	L= 4.203 Δe= 1.0596 Ω= 0.6012 E= -7516.70  **$(NiO)_9$-T-D-1S-A-3S**
L= 4.351 Δe= 1.0621 Ω= 0.4377 E=-3911.24  **NiO-T-D-2S-A-1S**	L= 5.902 Δe= 1.1637 Ω= 0.3716 E= -5861.96  **$(NiO)_9$-T-D-2S-A-1S**

L= 6.942 Δe= 1.1427 Ω= 0.3000 E= -4462.83  **NiO-T-D-3S-A-1S**	L= 7.446 Δe= 1.1409 Ω= 0.2840 E= -6413.54  **$(NiO)_9$-T-D-3S-A-1S**
L= 4.618 Δe= 1.1672 Ω= 0.6107 E= -2782.46  **NiO-T-D-1S-A-1N**	L= 4.654 Δe= 1.1547 Ω= 0.3591 E= -4733.18  **$(NiO)_9$-T-D-1S-A-1N**
L= 6.253 Δe= 1.2700 Ω= 0.1859 E=-3308.43  **NiO-T-D-1S-A-2N**	L= 6.416 Δe= 1.2719 Ω= 0.2986 E= -5259.15  **$(NiO)_9$-T-D-1S-A-2N**
L= 8.511 Δe= 1.3131 Ω= 0.0573 E= -3834.40  **NiO-T-D-1S-A-3N**	L= 8.305 Δe= 1.3138 Ω= 0.3631 E= -5785.11  **$(NiO)_9$-T-D-1S-A-3N**
L= 3.036 Δe= 1.0423 Ω= 0.6568 E=-3071.07  **NiO-T-D-1N-A-1S**	L= 2.984 Δe= 1.0246 Ω= 0.3922 E= -5021.78  **$(NiO)_9$-T-D-1N-A-1S**

L= 3.047 Δe= 1.0359 Ω= 0.4141 E= -3334.05  **NiO-T-D-2N-A-1S**	L= 4.327 Δe= 1.0844 Ω= 0.3819 E= -5284.77  **$(NiO)_9$-T-D-2N-A-1S**
L= 3.163 Δe= 1.0196 Ω= 0.3800 E= -3597.04  **NiO-T-D-3N-A-1S**	L= 3.071 Δe= 1.0393 Ω= 0.4240 E= -5547.76  **$(NiO)_9$-T-D-3N-A-1S**

Electron densities move from the green area to the purple area.

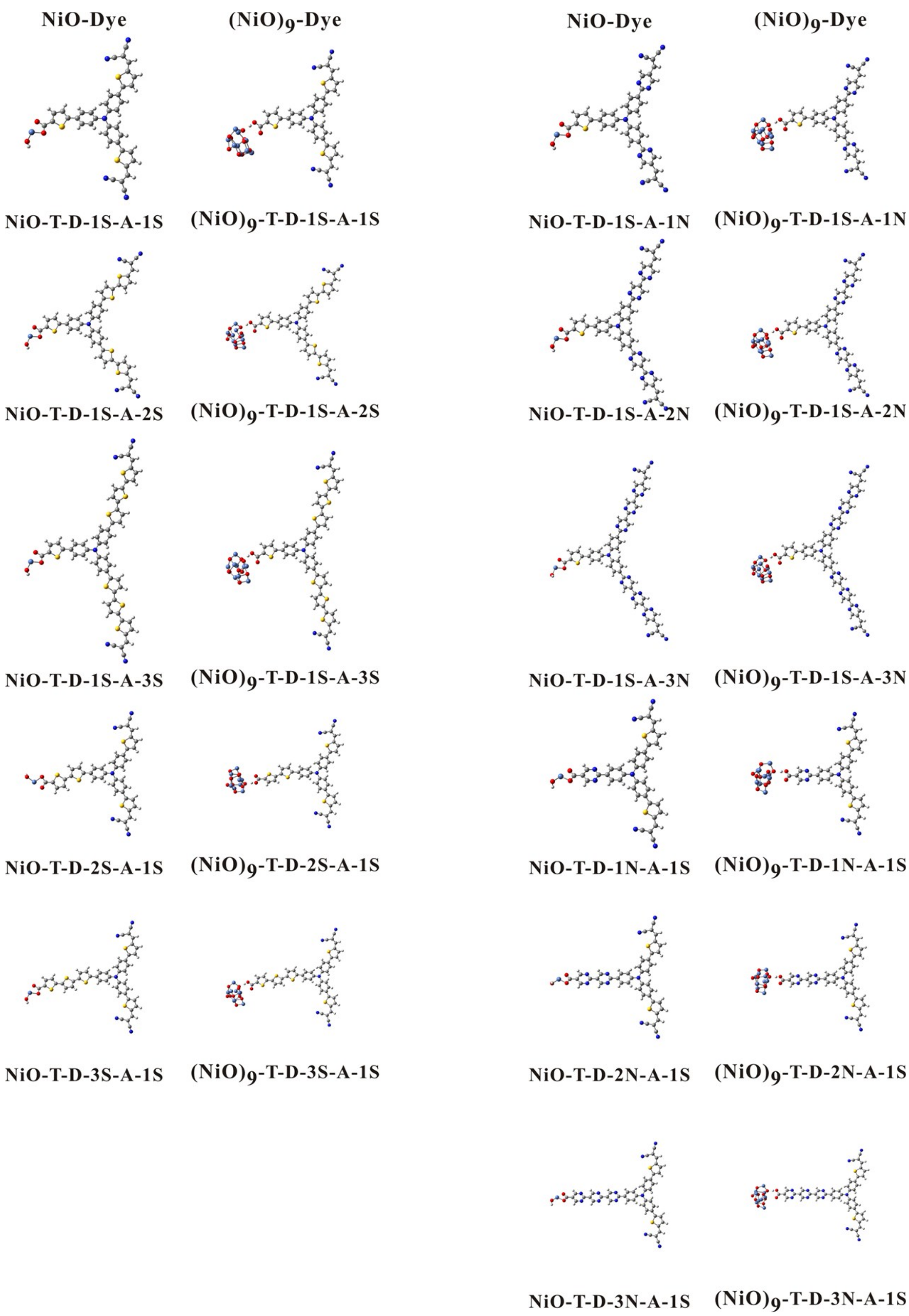


Fig. S1 Geometries of all the dyes binding with NiO or $(NiO)_9$, which are optimized at PBE0/6-31G(d) level.

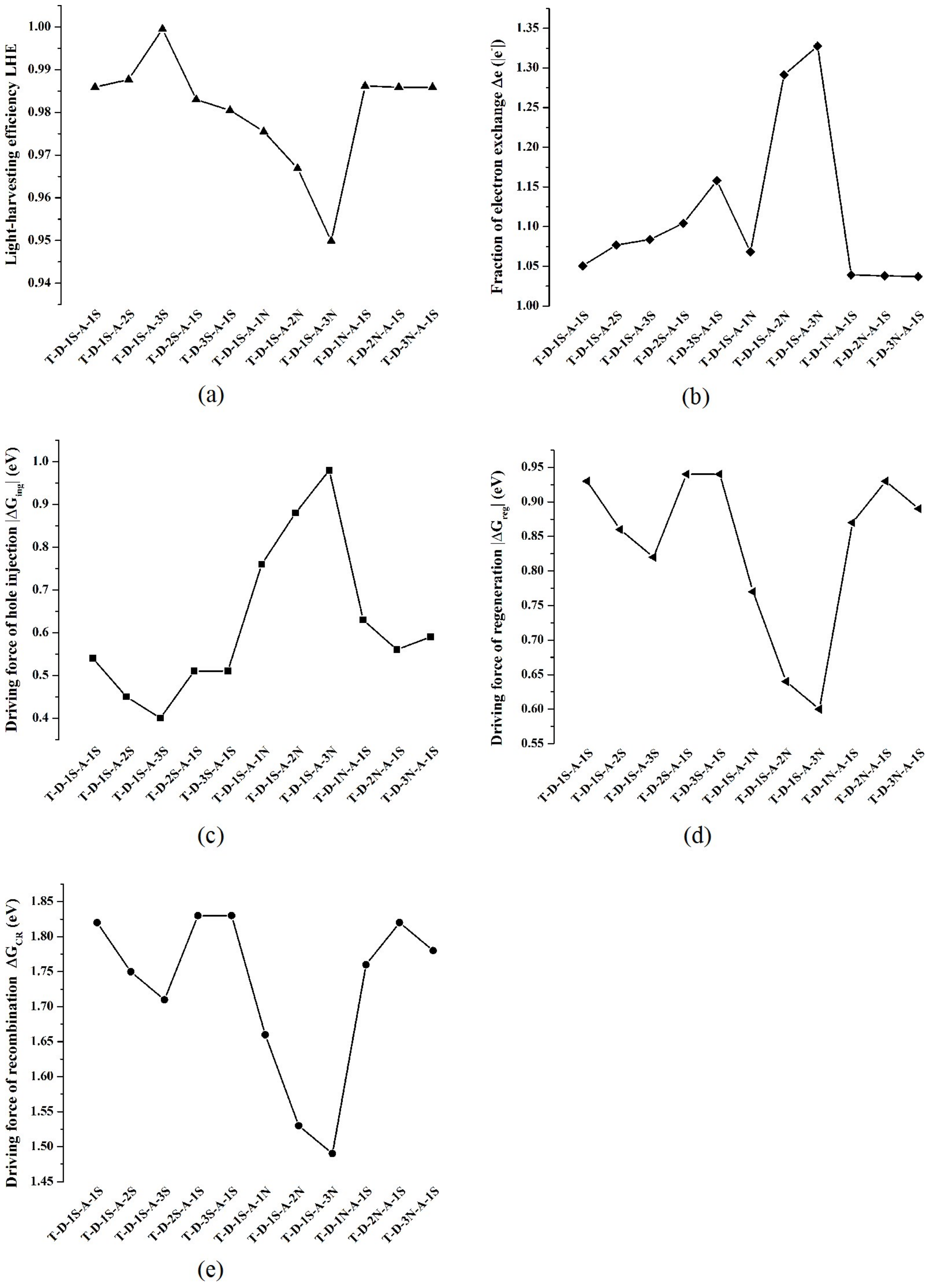


Fig. S2 The diagram of several important performance parameters for designed sensitizers. (a) The light-harvesting efficiency at maximum wavelength. (b) The fraction of electron exchange in the process of electron transfer. (c) The driving force of hole injection. (d) The driving force of regeneration. (e) The driving force of recombination.