Theoretical Study on Photophysical Properties of Triphenylamine-Cored Molecules with Naphthalimide Arms and Different π-Conjugated Bridges as Organic Solar Cells Materials

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Table S4: Calculated the longest wavelength of absorption λ_{max} and corresponding oscillator strength *f* of TPA–DHT–DCN by various methods with 6-31G(d,p) basis set, along with available experimental data.

Methods	λ_{max}	*f*
TD-B3LYP/6-31G(d,p)	588	1.11
TD-PBE0/6-31G(d,p)	548	1.36
TD-CAM-B3LYP/6-31G(d,p)	434	2.69
TD-BLYP/6-31G(d,p)	838	0.56
TD-OLYP/6-31G(d,p)	825	0.57
TD-BHandH/6-31G(d,p)	439	2.64
TD-BHandHLYP/6-31G(d,p)	439	2.66
TD-MPWB95/6-31G(d,p)	848	0.56
TD-SVWN/6-31G(d,p)	842	0.58
Exp[a]	580	

[a] Experimental data for TPA–DHT–DCN in film state were taken from ref. [22]

Table S2: The HOMOs and LUMOs contributions of individual fragments (in %) to the FMOs of the investigated molecules.

	HOMO			LUMO		
Species	NI[a]	CB[b]	TPA[c]	NI[a]	CB[b]	TPA[c]
1a	19.9	15.9	64.2	77.9	9.3	12.8
1b	23.1	15.6	61.2	76.6	9.6	13.7
1c	20.8	16.0	63.2	77.0	9.6	13.5
1d	19.8	15.8	64.4	78.4	9.2	12.3
2a	11.9	24.8	63.3	84.2	11.1	4.6
2b	6.6	25.0	68.5	85.9	10.2	3.9
2c	19.6	23.8	56.6	83.4	11.6	5.0
2d	6.3	24.8	68.9	87.0	9.6	3.4
3a	3.8	18.1	78.1	17.9	75.8	6.3
3b	4.3	18.3	77.4	13.7	79.8	6.5
3c	4.1	18.2	77.7	14.8	78.8	6.4
3d	3.7	18.0	78.3	20.6	73.2	6.3
4a	7.2	28.8	63.9	86.0	10.4	3.6
4b	7.4	29.2	63.4	85.0	10.8	4.2
4c	7.3	29.1	63.5	85.3	10.7	4.0
4d	7.3	28.7	64.0	86.2	10.2	3.6

[a] NI: 1,8-naphthalimide moieties; [b] CB: conjugate bridge moieties; [c] TPA: triphenylamino moieties.

Table S3: The natural population analysis (NPA) for **1a**–**1d** in the S_0 and S_1 at the B3LYP/6-31G(d,p) and TD-B3LYP/6-31G(d,p) levels, respectively.

	q (S_0)			q (S_1)			Δq[d]		
Species	NI[c]	CB[b]	TPA[a]	NI	CB	TPA	NI	CB	TPA
1a	-0.130	0.063	0.067	-0.140	0.065	0.075	-0.010	0.002	0.008
1b	-0.113	0.057	0.056	-0.125	0.063	0.062	-0.012	0.006	0.006
1c	-0.118	0.059	0.059	-0.129	0.062	0.067	-0.011	0.003	0.008
1d	-0.137	0.065	0.072	-0.148	0.068	0.080	-0.011	0.003	0.008

[a]NI: 1,8-naphthalimide moieties; [b] CB: conjugate bridge moieties; [c] TPA: triphenylamino moieties; [d] $\Delta q = q\ (S_1) - q\ (S_0)$.

Table S4: Calculated E_{HOMO}, E_{LUMO}, and E_g (all in eV) of **NI** and **TPA** at the TD-B3LYP/6-31G(d,p) level.

species	E_{HOMO}	E_{LUMO}	E_g
TPA	-4.96	-0.32	4.64
NI	-6.57	-2.49	4.08

Table S5: The absorption wavelengths λ_{abs} and corresponding *f* (in parenthesis) of the first fifteen excited states for **1a**–**1d** and **2a**–**2d** obtained by the TD-B3LYP/6-31G(d,p) level.

species	**1a**	**1b**	**1c**	**1d**	**2a**	**2b**	**2c**	**2d**
S_1	521(0.96)	519(0.25)	517(1.04)	527(0.98)	546(0.55)	516(0.58)	538(0.62)	542(0.54)
S_2	520(0.90)	519(0.26)	515(1.14)	526(1.07)	532(0.29)	515(0.45)	524(0.39)	540(0.41)
S_3	477(0.00)	517(0.06)	471(0.00)	481(0.00)	459(0.75)	498(0.02)	461(0.77)	522(0.02)
S_4	396(0.69)	513(0.79)	452(0.00)	398(0.75)	438(0.22)	490(0.00)	461(0.40)	412(1.17)
S_5	395(0.57)	512(0.81)	448(0.00)	398(0.70)	431(0.00)	488(0.00)	454(0.01)	411(0.82)
S_6	390(0.01)	469(0.00)	448(0.00)	392(0.00)	405(0.73)	486(0.00)	430(0.00)	406(0.07)
S_7	387(0.00)	464(0.00)	407(0.01)	390(0.00)	404(0.27)	432(0.00)	428(0.00)	397(0.15)
S_8	376(0.13)	462(0.00)	406(0.01)	378(0.15)	399(0.06)	431(0.00)	419(0.06)	395(0.19)
S_9	375(0.14)	462(0.00)	403(0.02)	378(0.14)	393(0.12)	429(0.00)	406(1.00)	390(0.00)
S_{10}	358(0.22)	447(0.00)	396(0.72)	361(0.25)	375(0.27)	427(0.00)	401(0.18)	388(0.02)
S_{11}	358(0.24)	445(0.00)	395(0.69)	361(0.25)	374(0.04)	427(0.00)	392(0.09)	386(0.00)
S_{12}	354(0.00)	445(0.00)	394(0.01)	355(0.00)	370(0.02)	423(0.00)	387(0.01)	351(0.13)
S_{13}	354(0.00)	395(0.79)	393(0.00)	355(0.00)	346(0.00)	402(1.34)	385(0.00)	351(0.02)
S_{14}	354(0.00)	394(0.67)	390(0.00)	355(0.00)	346(0.00)	401(0.96)	380(0.00)	350(0.05)
S_{15}	345(0.00)	388(0.00)	388(0.02)	350(0.00)	345(0.08)	394(0.04)	379(0.00)	347(0.02)

Table S6: The absorption wavelengths λ_{abs} and corresponding *f* (in parenthesis) of the first fifteen excited states for **3a**–**3d** and **4a**–**4d** obtained by the TD-B3LYP/6-31G(d,p) level.

species	**3a**	**3b**	**3c**	**3d**	**4a**	**4b**	**4c**	**4d**
S_1	592(0.46)	588(0.50)	589(0.50)	594(0.51)	578(0.53)	564(0.67)	569(0.66)	589(0.61)
S_2	587(0.51)	584(0.54)	585(0.54)	591(0.54)	574(0.38)	561(0.42)	566(0.41)	585(0.39)
S_3	552(0.00)	549(0.00)	550(0.00)	554(0.00)	553(0.04)	539(0.04)	544(0.03)	562(0.04)
S_4	473(0.01)	524(0.00)	463(0.02)	479(0.01)	437(0.70)	477(0.00)	434(0.87)	443(0.81)
S_5	471(0.01)	524(0.00)	461(0.02)	477(0.01)	436(0.32)	476(0.00)	432(0.40)	441(0.34)
S_6	469(0.01)	524(0.00)	459(0.01)	475(0.01)	433(0.12)	474(0.00)	430(0.13)	439(0.14)
S_7	423(0.33)	495(0.00)	450(0.00)	422(0.45)	418(0.02)	431(0.89)	419(0.02)	422(0.03)
S_8	422(0.23)	492(0.00)	450(0.00)	422(0.29)	415(0.02)	429(0.39)	418(0.02)	420(0.01)
S_9	421(0.19)	488(0.00)	499(0.00)	420(0.17)	412(0.29)	427(0.15)	416(0.01)	416(0.24)
S_{10}	401(0.00)	482(0.00)	427(0.33)	400(0.00)	409(0.39)	426(0.03)	413(0.12)	413(0.30)
S_{11}	395(0.00)	480(0.00)	427(0.28)	394(0.00)	408(0.24)	422(0.00)	412(0.22)	412(0.42)
S_{12}	392(0.00)	477(0.00)	426(0.05)	393(0.00)	376(0.02)	419(0.00)	411(0.17)	380(0.02)
S_{13}	384(0.02)	460(0.01)	425(0.11)	383(0.03)	375(0.02)	418(0.00)	408(0.33)	379(0.02)
S_{14}	382(0.03)	458(0.01)	424(0.00)	382(0.04)	374(0.02)	415(0.00)	405(0.02)	378(0.02)
S_{15}	375(0.00)	458(0.00)	421(0.00)	376(0.00)	360(0.06)	414(0.00)	377(0.00)	367(0.01)

Table S7: Calculated lattice constants of **1a** in different space groups.

Space groups	total energy	*a* (Å)	*b* (Å)	*c* (Å)	*α* (°)	*β* (°)	*γ* (°)
C2	175.7068	36.02	34.87	10.97	90.0	78.1	90.0
C2/c	185.0624	42.38	30.44	29.34	90.0	93.2	90.0
Cc	182.9068	31.60	31.32	24.89	90.0	145.8	90.0
$P2_1$	164.9213	31.26	33.41	5.58	90.0	89.7	90.0
$P2_1/c$	164.3638	9.46	36.42	35.19	90.0	118.6	90.0
$P2_12_12_1$	172.3915	15.68	27.95	24.05	90.0	90.0	90.0
$P\bar{1}$	173.1959	9.29	21.15	33.13	78.6	73.3	75.4
Pbca	182.5234	41.48	40.03	17.09	90.0	90.0	90.0
Pbcn	181.2880	19.33	27.30	66.35	90.0	90.0	90.0
$Pna2_1$	166.8797	23.93	35.92	10.76	90.0	90.0	90.0

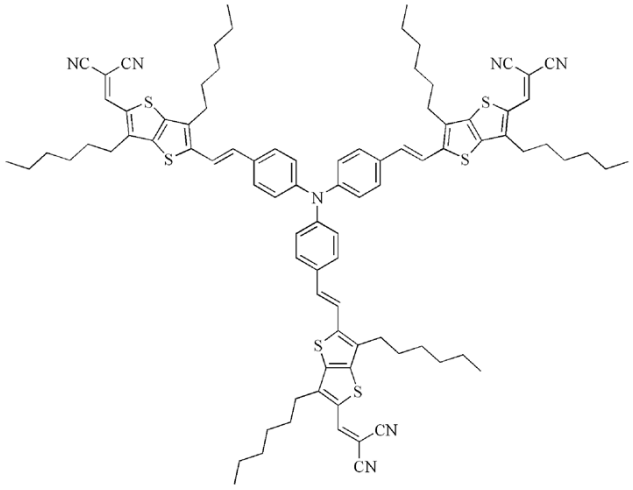

Fig. S2 The sketch map of the structure of TPA–DHT–DCN.

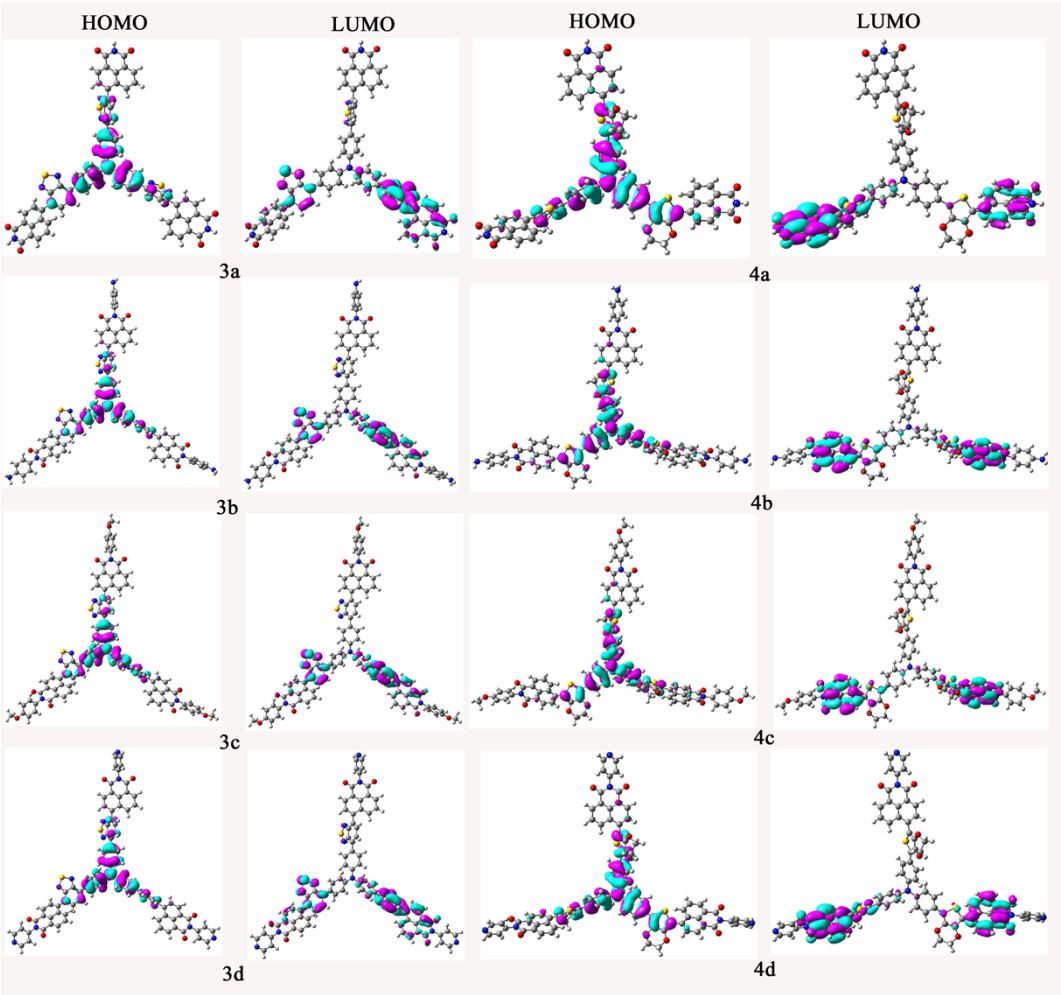

Fig. S1 Electronic density contours of the frontier molecular orbitals for **3a**–**3d** and **4a**–**4d**.