Supporting Information

Spin engineering of triangulenes and application for nano nonlinear optical materials design

Cui-Cui Yang,[a] Xue-Lian Zheng,[a] Jiu Chen,[a] Wei Quan Tian,*[a] Wei-Qi Li,*[bcd] Ling Yang,*[e]

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Supporting Information list:

Fig. S10 The transition nature of the electron excitations with major contributions to the <β_0> of TG7-BNB-ba.

Fig. S11 The structure of TG7-BNB-ba with Cartesian coordinate, in which the solid line arrow indicates parallel to the paper surface and the dotted arrow indicates outward.

Fig. S12 The two-dimensional second order nonlinear optical spectra (in 10^{-30} esu) of (a) TG7-B-ba, (b) TG7-N-ba, (c) TG7-NBN-ba, and (d) TG7-BNB-ba scanned up to 7.00 eV with a step size of 0.05 eV.

Fig. S13 Two-dimensional second order NLO spectra of (a) and (b) TG7-B-ba, (c) and (d) TG7-N-ba, (e) TG7-NBN-ba, and (f) TG7-BNB-ba with step size of 0.005 eV [(a) ω_1 scanned from 2.50 eV to 3.50 eV and ω_2 scanned from –1.50 eV to –0.50 eV; (b) ω_1 scanned from 1.50 eV to 2.50 eV and ω_2 scanned from 0.50 eV to 1.50 eV; (c) ω_1 scanned from 1.50 eV to 2.50 eV and ω_2 scanned from 0.50 eV to 1.50 eV; (d) ω_1 scanned from 2.50 eV to 3.50 eV and ω_2 scanned from –2.50 eV to –1.50 eV; (e) ω_1 scanned from 1.30 eV to 2.30 eV and ω_2 scanned from –0.50 eV to 0.50 eV; (f) ω_1 scanned from 1.00 eV to 2.00 eV and ω_2 scanned from –0.50 eV to 0.50 eV].

Table S1 The relative electronic energy differences of TGn (n=2 to 7) predicted with (U)PBE0/6-31G(d,p). The doublet in TG2, triplet in TG3, quartet in TG4, quintet in TG5, sextet in TG6, and septet in TG7 are taken as reference, respectively.

Table S2 The electronic properties including energy gap (E_{gap}, in eV) between the highest occupied molecular orbital (E_H) and the lowest unoccupied molecular orbital (E_L), the lowest vibrational frequency (LVF, in cm^{-1}) and the dipole moment of ground state (D_g, in Debye), and the static first hyperpolarizability (<β_0>, in 10^{-30} esu), the <β_0> per heavy atom (<β_0>/N) of TGn (n=2 to 6) series of molecules in closed-shell singlet predicted with PBE0/6-31G(d,p) and TD-CAM-B3LYP/6-31++G(d,p)-SOS, respectively. The relative electronic energy differences (ΔE_{OS-CS} and ΔE_{T-CS}, in Kcal/mol) between open-shell singlet (OS) or triplet (T) and closed-shell singlet (CS) (CS is taken as reference), and spin contamination of open-shell singlet (<S^2>) obtained at the UPBE0/6-31G(d,p) level.

Table S3 Major electronic spectra absorption peaks with transition nature in TG7 series of molecules (*f* is the oscillator strength in arbitrary unit, E is the transition energy in eV unit, λ is the wavelength in nm unit, TNMC to <β_0> is the transition nature of electron excitation with major contribution to <β_0>, <β_0>$_{Con}$ is contribution value to <β_0> in 10^{-30} esu unit).

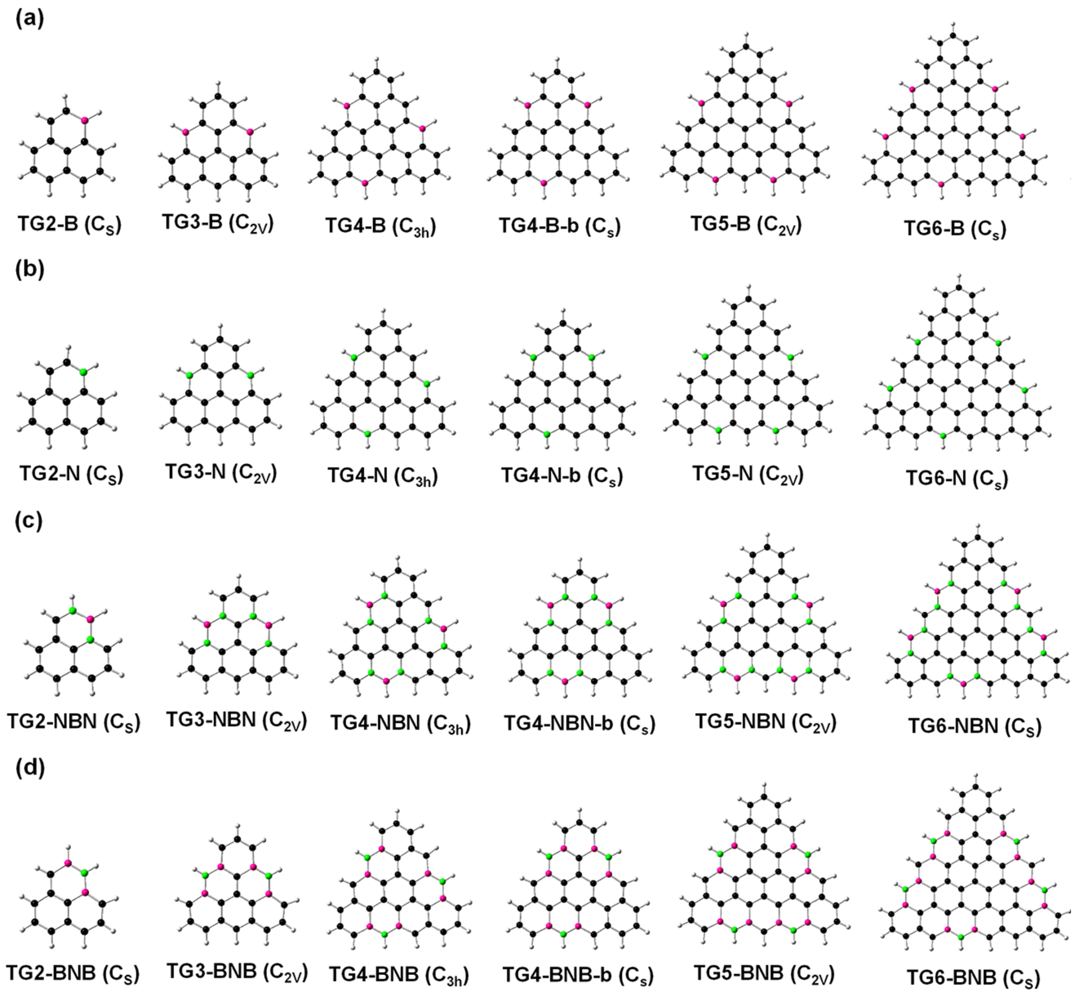


Fig. S1 The structures of (a) B, (b) N, (c) NBN and (d) BNB doped TGn (n=2 to 6). The white, deeppink, black and green denote the hydrogen, boron, carbon and nitrogen atoms, respectively.

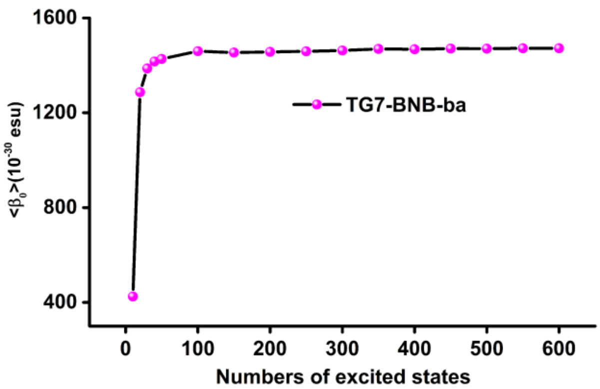


Fig. S2 Evolution of the static first hyperpolarizability (<β_0>) with the numbers of excited states in TG7-BNB-ba.

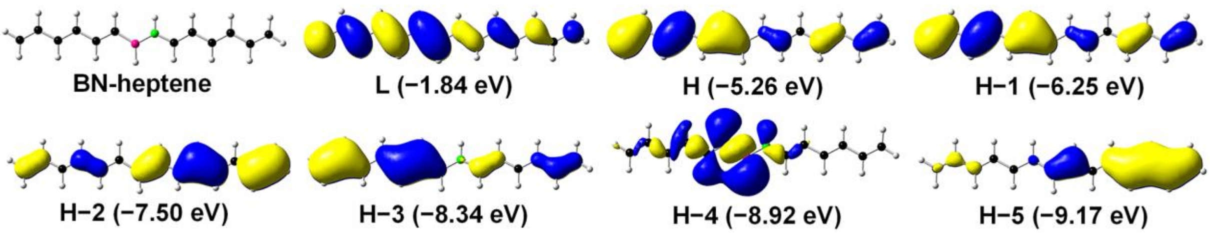


Fig. S3 The frontier molecular orbitals of BN doped heptene. The molecular orbitals are predicted with PBE0/6-31G(d,p).

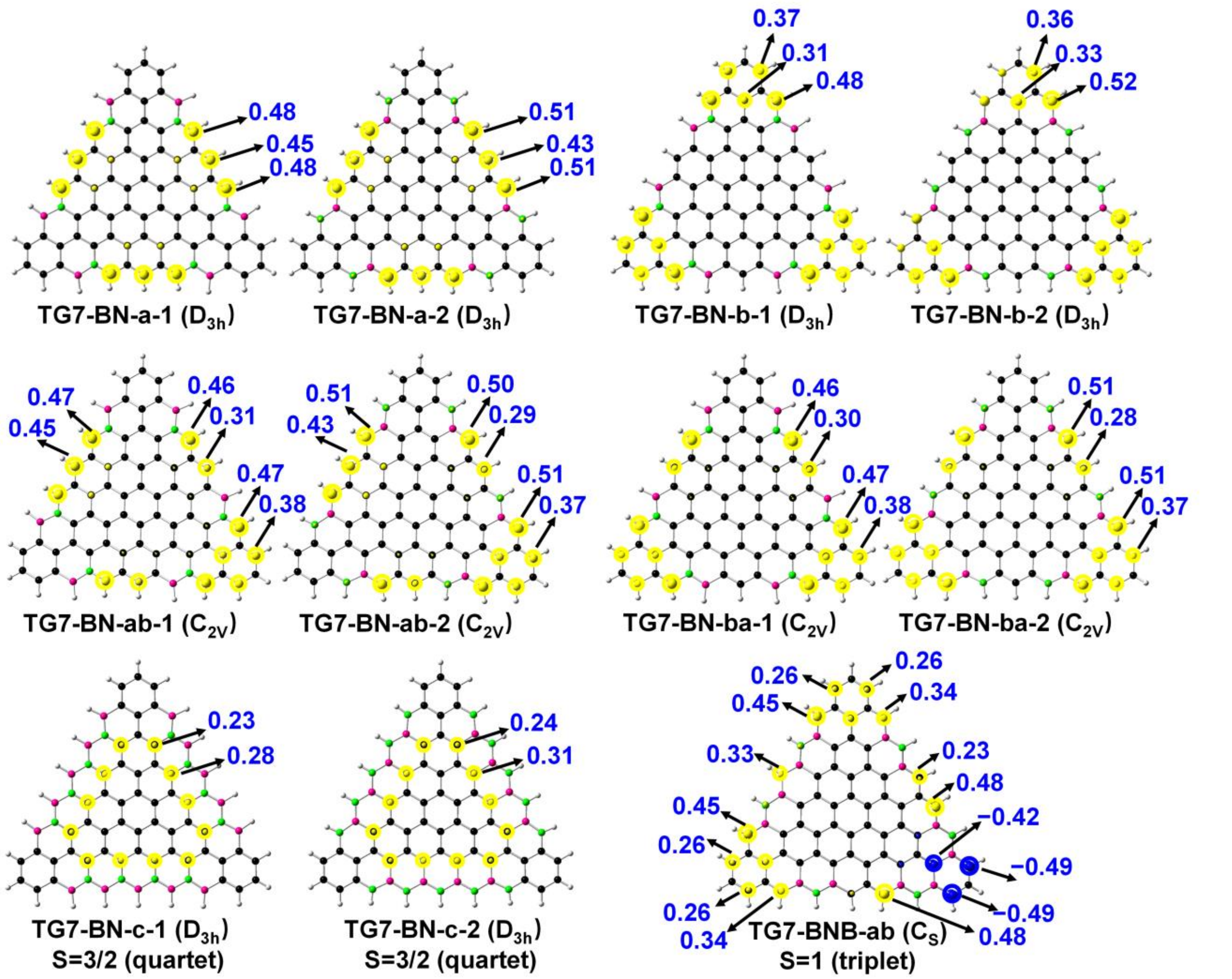


Fig. S4 The natural atomic spin density distributions (spin up: yellow circle, spin down: blue circle) of BN-doped TG7-a/b/ab/ba/c series of molecules and TG7-BNB-ab. Numbers in blue are spin density.

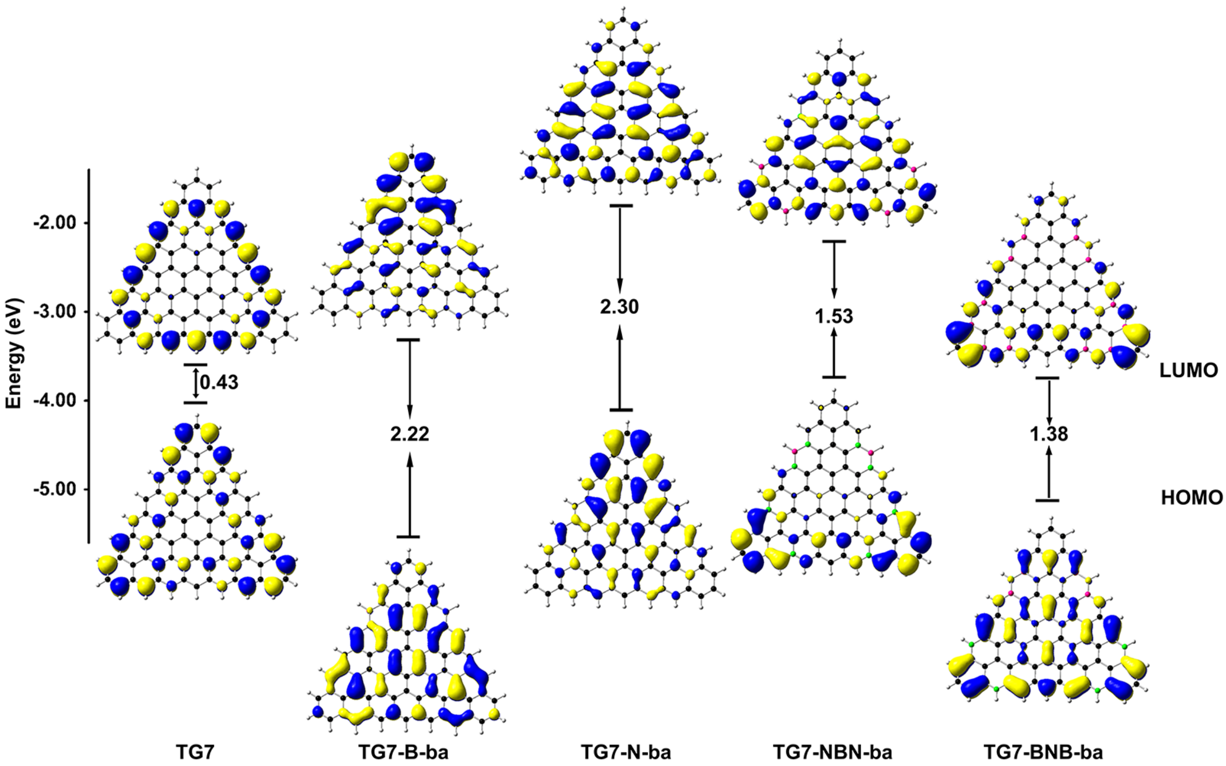


Fig. S5 The frontier molecular orbitals (plotted with isosurface value of 0.02 a.u.) of TG7 and TG7-ba series of molecules. The molecular orbitals are predicted with PBE0/6-31G(d,p).

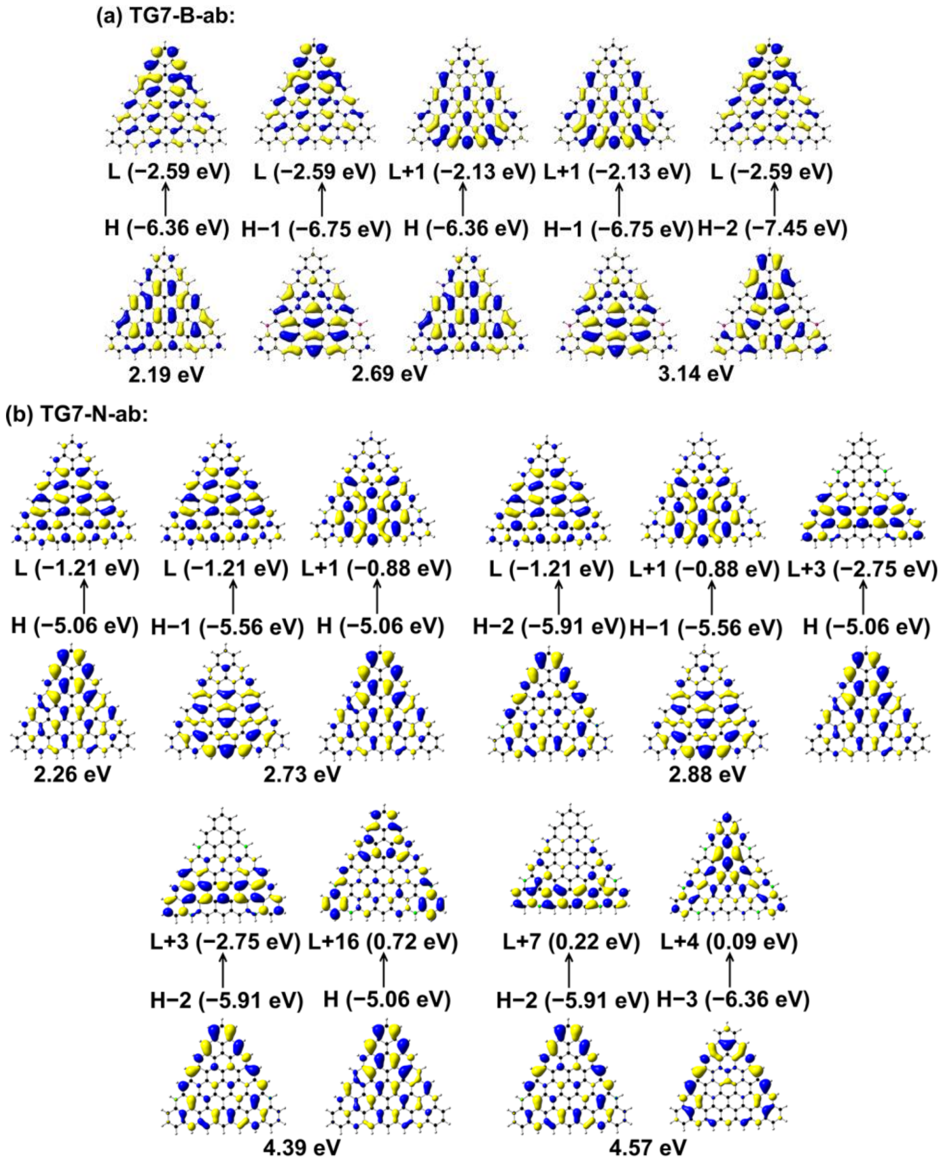


Fig. S6 The transition nature of the electron excitations with major contributions to the <β$_0$> of (a) TG7-B-ba and (b) TG7-N-ba. Molecular orbitals (with isosurface value of 0.02 a.u.) associated with the major electron excitations of these molecules predicted with CAM-B3LYP/6-31++G(d,p).

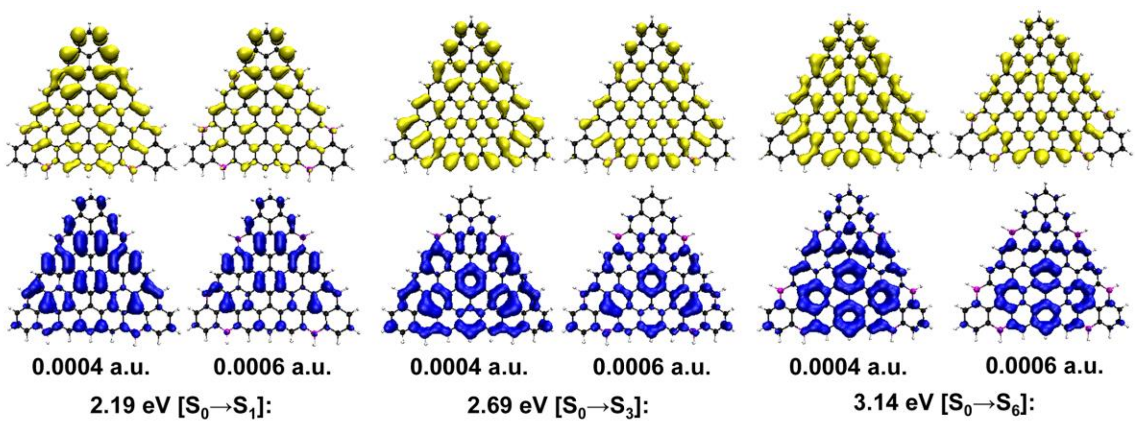


Fig. S7 Hole (blue opaque) and electron (yellow opaque) distributions for TG7-B-ba with isosurfaces of 0.0004 and 0.0006 a.u., respectively.

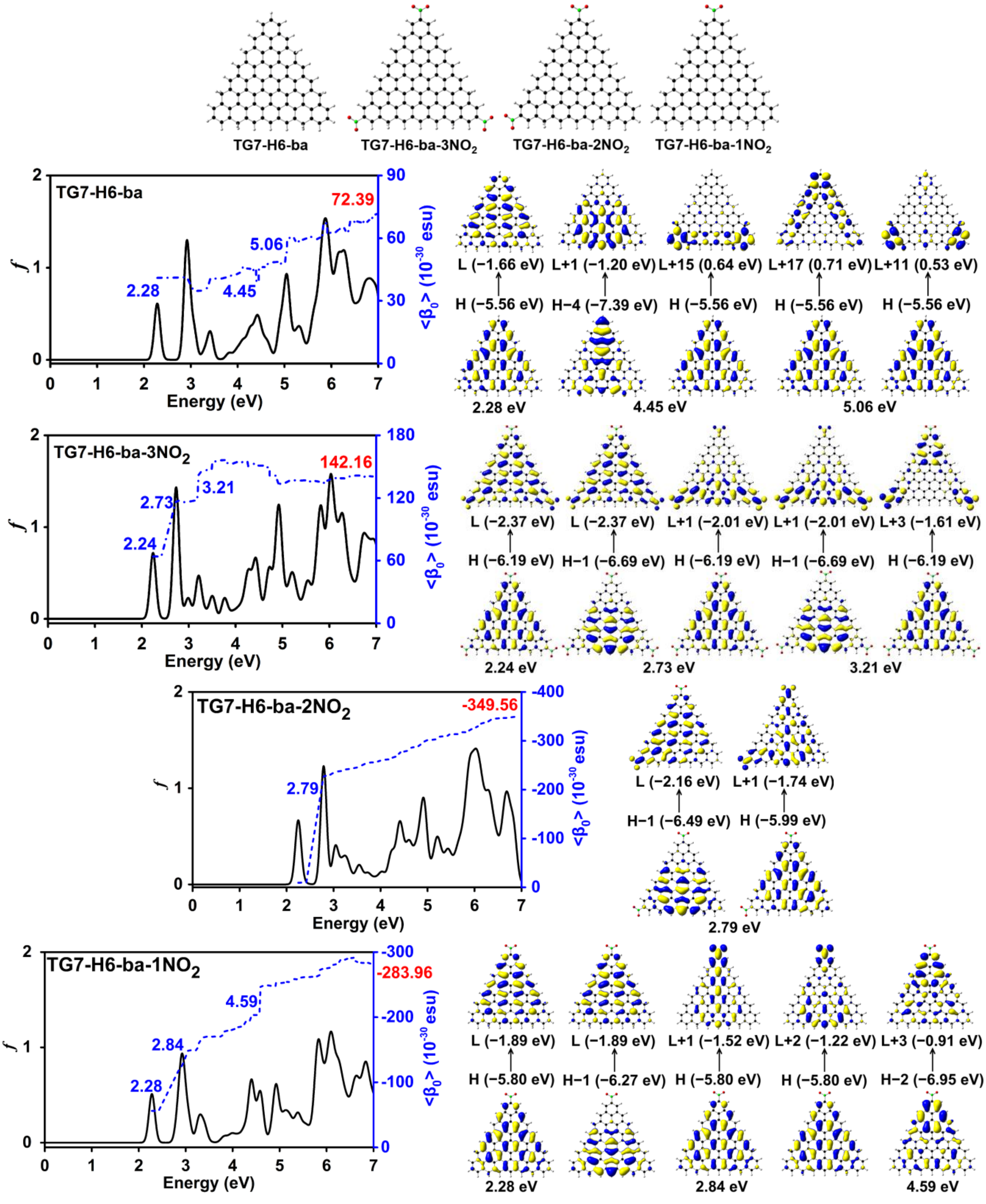


Fig. S8 Evolution of the <β0> with the electron excitations and the transition nature of the electron excitations with major contributions to the <β0> of TG7-H6-ba, TG7-H6-ba-3NO2, TG7-H6-ba-2NO2, and TG7-H6-ba-1NO2. Hereafter, molecular orbitals (with isosurface value of 0.02 a.u.) associated with the major electron excitations of these molecules predicted with CAM-B3LYP/6-31++G(d,p). *f* is the oscillator strength (in a.u.).

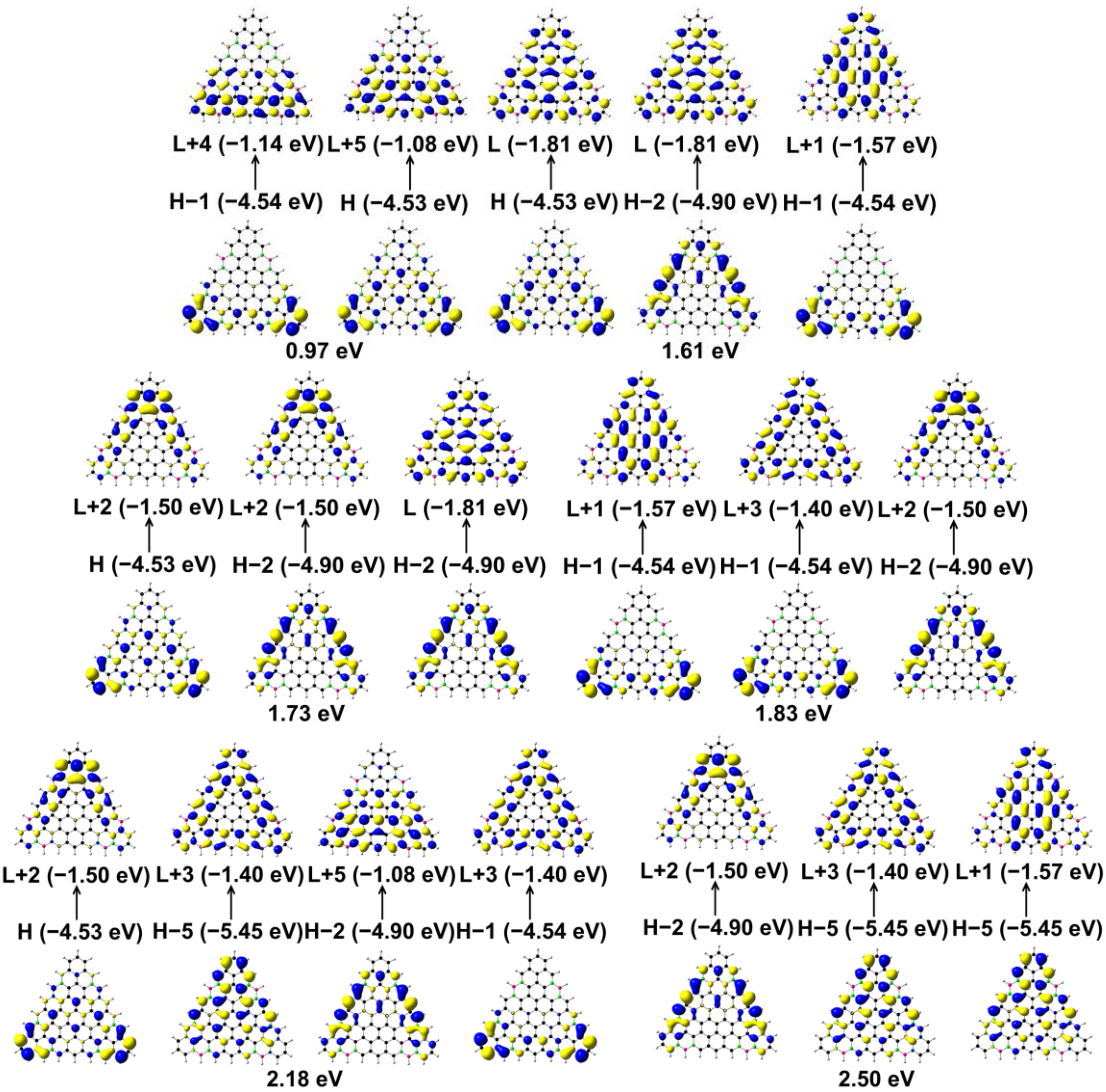
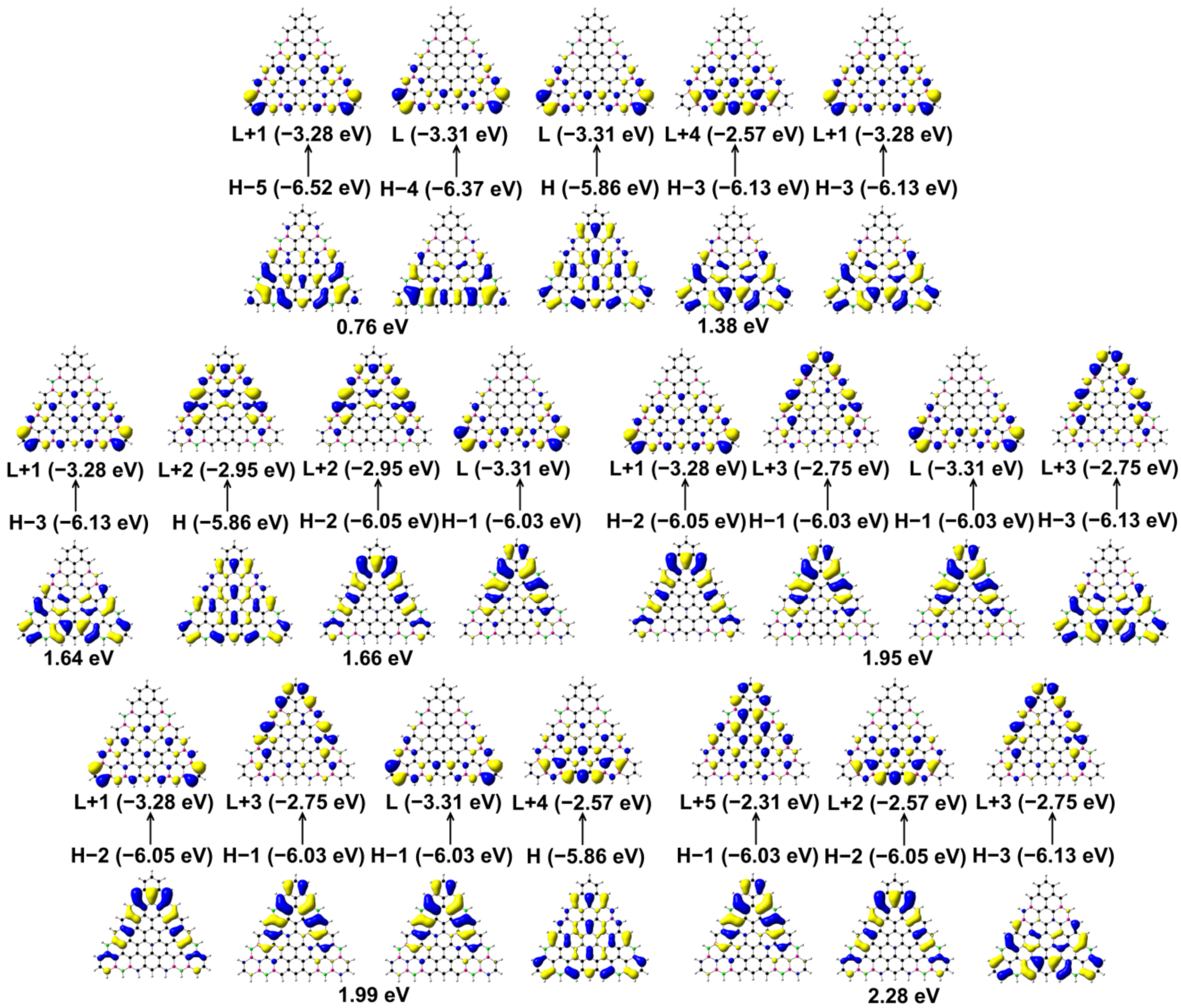


Fig. S9 The transition nature of the electron excitations with major contributions to the <β_0> of TG7-NBN-ba.



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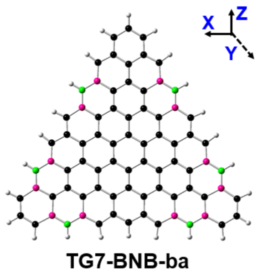

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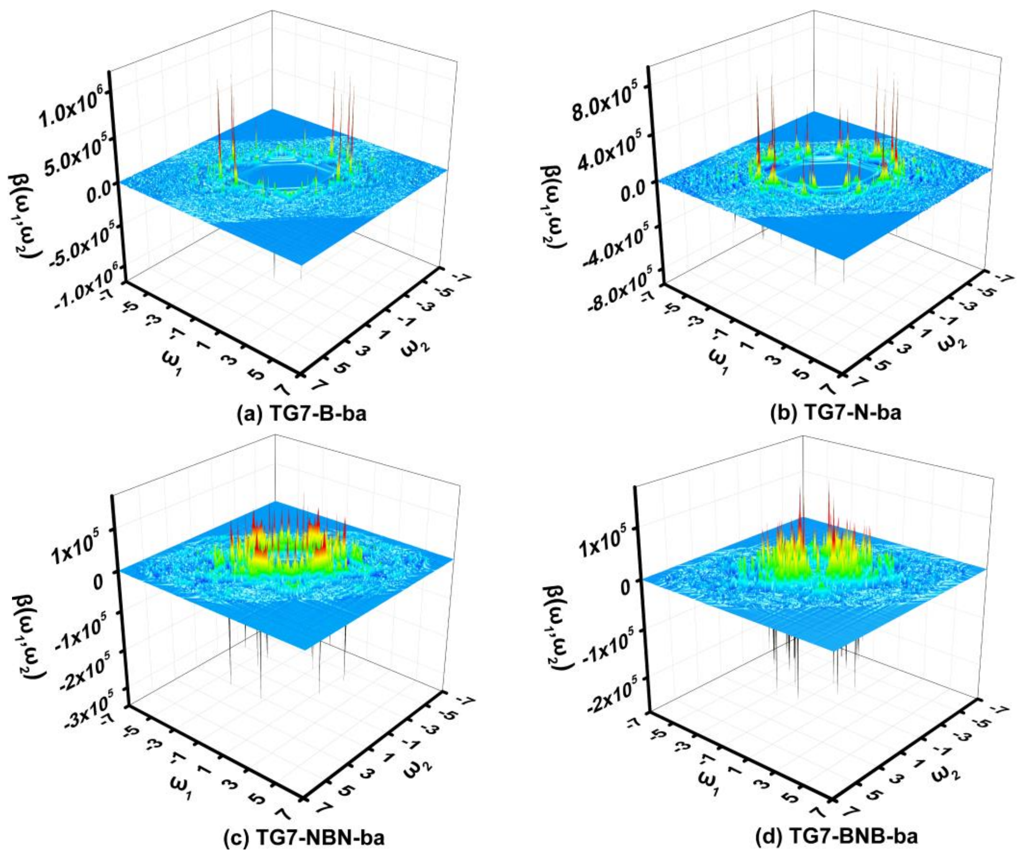

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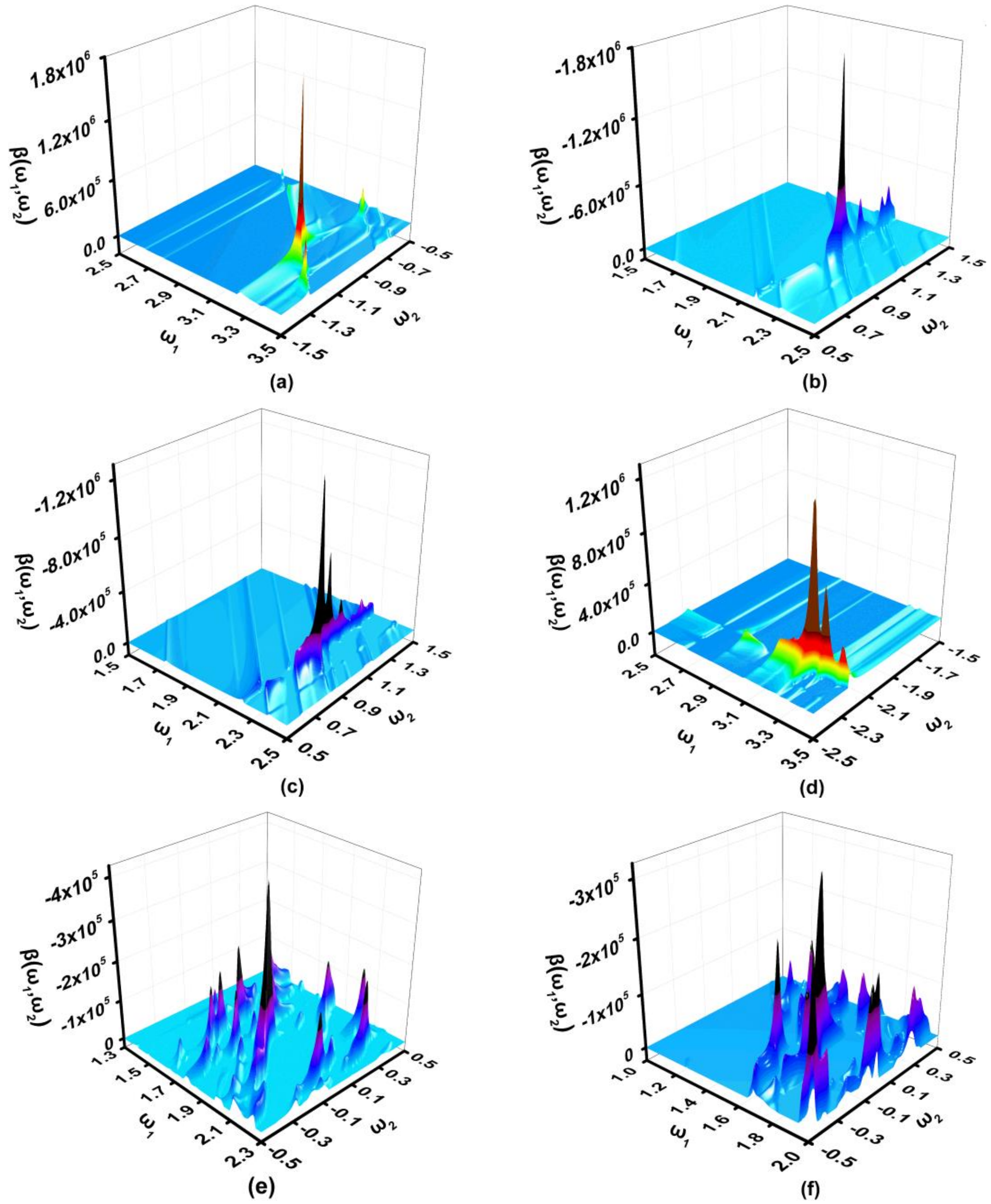

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	TG2	**TG4**	**TG6**	**TG7-BN-c-1**	**TG7-BN-c-2**
doublet	0.00	18.42	19.05	13.75	5.80
quartet	108.01	0.00	21.08	0.00	0.00
sextet	163.18	80.89	0.00	78.41	67.89
octet	242.47	162.65	79.69	136.18	142.74
	TG3	**TG5**	**TG7**	**TG7-BNB-ab**	
open-shell singlet	6.78	20.36	28.22	7.57	
closed-shell singlet	26.13	46.41	67.77	8.80	
triplet	0.00	9.56	21.21	0.00	
quintet	82.04	0.00	9.47	4.46	
septet	162.24	77.68	0.00	3.97	
nonet	242.05	154.00	72.99	14.79	

Table S2 The electronic properties including energy gap (E_{gap}, in eV) between the highest occupied molecular orbital (E_H) and the lowest unoccupied molecular orbital (E_L), the lowest vibrational frequency (LVF, in cm^{-1}) and the dipole moment of ground state (D_g, in Debye), and the static first hyperpolarizability ($\langle\beta_0\rangle$, in 10^{-30} esu), the $\langle\beta_0\rangle$ per heavy atom ($\langle\beta_0\rangle/N$) of TGn (n=2 to 6) series of molecules in closed-shell singlet predicted with PBE0/6-31G(d,p) and TD-CAM-B3LYP/6-31++G(d,p)-SOS, respectively. The relative electronic energy differences (ΔE_{OS-CS} and ΔE_{T-CS}, in Kcal/mol) between open-shell singlet (OS) or triplet (T) and closed-shell singlet (CS) (CS is taken as reference), and spin contamination of open-shell singlet ($\langle S^2\rangle$) obtained at the UPBE0/6-31G(d,p) level.

Compound	**ΔE_{OS-CS}**	**ΔE_{T-CS}**	**$\langle S^2\rangle$**	**LVF**	**E_g**	**E_L**	**E_H**	**E_{gap}**	**$\langle\beta_0\rangle$**	**$\langle\beta_0\rangle/N$**
TG2-B	0.00	44.48	0.00	141.74	2.49	−2.33	−6.40	4.07	−4.68	−0.36
TG3-B	0.00	33.17	0.00	71.26	2.85	−2.68	−5.90	3.22	20.34	0.93
TG4-B	0.00	50.56	0.00	44.25	0.00	−2.33	−6.13	3.80	12.85	0.39
TG4-B-b	0.00	34.10	0.00	42.97	2.36	−2.75	−5.81	3.06	68.21	2.07
TG5-B	0.00	32.08	0.00	24.16	4.10	−2.87	−5.67	2.80	92.57	1.52
TG6-B	0.00	33.11	0.00	22.23	1.30	−3.02	−5.64	2.62	23.55	0.37
TG2-N	0.00	46.23	0.00	146.55	2.81	−0.39	−4.62	4.23	−0.83	−0.08
TG3-N	0.00	34.76	0.00	89.70	3.14	−1.06	−4.39	3.33	20.48	0.93
TG4-N	0.00	52.03	0.00	62.65	0.00	−0.98	−4.90	3.92	3.04	0.09
TG4-N-b	0.00	36.17	0.00	62.06	2.85	−1.27	−4.42	3.15	78.03	2.36
TG5-N	0.00	35.04	0.00	42.38	4.65	−1.41	−4.35	2.94	79.87	1.74
TG6-N	0.00	36.11	0.00	30.72	1.49	−1.53	−4.28	2.75	49.99	0.82
TG2-NBN	0.00	5.51	0.00	139.82	2.74	−1.35	−3.65	2.30	22.03	1.69
TG3-NBN	0.00	4.64	0.00	75.19	0.03	−1.59	−3.54	1.95	81.72	3.71
TG4-NBN	0.00	13.19	0.00	53.97	0.00	−1.62	−3.80	2.18	40.33	1.22
TG4-NBN-b	0.00	3.09	0.00	52.98	0.69	−1.84	−3.64	1.80	14.67	0.44
TG5-NBN	0.00	5.04	0.00	39.98	1.98	−1.96	−3.72	1.75	−200.85	4.37
TG6-NBN	0.00	3.71	0.00	29.73	0.19	−2.05	−3.67	1.62	126.48	2.07
TG2-BNB	−4.05	−1.35	0.14	144.00	2.84	−3.37	−5.32	1.95	—	—
TG3-BNB	−8.96	−5.73	2.94	80.54	0.06	−3.58	−5.21	1.63	—	—
TG4-BNB	−1.86	7.36	1.14	48.79	0.00	−3.43	−5.25	1.82	—	—
TG4-BNB-b	−9.87	−7.71	5.70	47.99	0.46	−3.54	−5.10	1.56	—	—
TG5-BNB	−4.47	−5.32	4.26	27.73	1.90	−3.52	−5.01	1.49	—	—
TG6-BNB	−10.43	−10.97	10.29	9.36	0.53	−3.62	−5.03	1.41	—	—

Table S3 Major electronic spectra absorption peaks with transition nature in TG7 series of molecules (*f* is the oscillator strength in arbitrary unit, E is the transition energy in eV unit, λ is the wavelength in nm unit, TNMC to $<\beta_0>$ is the transition nature of electron excitation with major contribution to $<\beta_0>$, $<\beta_0>_{Con}$ is contribution value to $<\beta_0>$ in 10^{-30} esu unit).

Compounds	*f*	E	λ	Transition	TNMC to $<\beta_0>$	$<\beta_0>_{Con}$
TG7-B-ba ($C_{72}H_{24}B_6$)	0.4972	2.19	566.3	$S_0 \rightarrow S_1$	H→L (87.29%)	236.31
	1.1611	2.69	460.7	$S_0 \rightarrow S_3$	H→L+1 (45.27%) H−1→L (42.57%)	60.43
	0.4314	3.14	395.4	$S_0 \rightarrow S_6$	H−1→L+1 (51.66%) H−2→L (22.79%)	21.80
TG7-N-ba ($C_{72}H_{24}N_6$)	0.4388	2.26	549.5	$S_0 \rightarrow S_1$	H→L (84.25%)	199.88
	0.9443	2.73	454.4	$S_0 \rightarrow S_3$	H−1→L (52.06%) H→L+1 (31.10%)	41.19
	0.2178	2.88	430.0	$S_0 \rightarrow S_4$	H−2→L (35.62%) H−1→L+1 (24.70%) H→L+3 (24.39%)	28.10
	0.1539	3.09	400.9	$S_0 \rightarrow S_6$	H−1→L+1 (36.81%) H→L+3 (36.56%)	15.90
	0.6377	3.30	375.7	$S_0 \rightarrow S_9$	H−2→L (33.43%) H−1→L+1 (22.59%) H−1→L+2 (15.90%) H→L+3 (9.94%)	10.49
	0.1831	3.36	368.6	$S_0 \rightarrow S_{10}$	H−2→L (15.93%) H−1→L+2 (25.52%) H→L+8 (24.58%) H→L+3 (9.74%)	11.73
	0.4538	3.56	348.0	$S_0 \rightarrow S_{14}$	H−2→L+1 (26.40%) H→L+10 (14.80%)	17.93
	0.5665	4.39	282.7	$S_0 \rightarrow S_{41}$	H−2→L+3 (20.66%) H→L+16 (25.84%)	30.18
	0.4901	4.57	271.1	$S_0 \rightarrow S_{51}$	H−2→L+7 (16.00%) H−3→L+4 (12.80%)	28.30
TG7-NBN-ba ($C_{60}H_{24}B_6N_{12}$)	0.0223	0.97	1273.7	$S_0 \rightarrow S_2$	H−1→L+4 (48.57%) H→L+5 (29.25%)	61.41
	0.4582	1.61	770.8	$S_0 \rightarrow S_7$	H→L (29.69%) H−2→L (22.03%) H−1→L+1 (13.81%)	135.91
	0.0534	1.73	718.3	$S_0 \rightarrow S_9$	H→L+2 (38.01%) H−2→L+2 (20.90%) H−2→L (13.48%)	67.66
	0.1181	1.83	677.6	$S_0 \rightarrow S_{12}$	H−1→L+1 (32.52%) H−1→L+3 (21.95%) H−2→L+2 (15.23%)	239.36
	0.1341	2.18	569.6	$S_0 \rightarrow S_{21}$	H→L+2 (18.56%) H−5→L+3 (14.76%) H−1→L+3 (14.58%) H−2→L+5 (12.96%)	108.98
	0.6694	2.50	496.6	$S_0 \rightarrow S_{31}$	H−2→L+2 (22.53%) H−5→L+3 (17.62%) H−5→L+1 (14.38%)	251.02
TG7-BNB-ba ($C_{60}H_{24}B_{12}N_6$)	0.0291	0.76	1622.7	$S_0 \rightarrow S_2$	H−4→L (49.68%) H−5→L+1 (29.26%)	195.65
	0.3271	1.38	895.7	$S_0 \rightarrow S_6$	H→L (61.28%) H−3→L+4 (11.50%) H−3→L+1 (11.49%)	126.27

	0.4427	1.64	757.7	$S_0 \rightarrow S_{10}$	H−3→L+1 (47.76%) H−2→L+2 (28.02%)	112.59
	0.2097	1.66	747.8	$S_0 \rightarrow S_{11}$	H−1→L (26.26%) H→L+2 (22.38%)	407.69
	0.3322	1.95	635.1	$S_0 \rightarrow S_{17}$	H−2→L+1 (31.39%) H−1→L+3 (22.38%) H−1→L (13.07%) H−3→L+3 (11.90%)	211.36
	0.0716	1.99	624.4	$S_0 \rightarrow S_{18}$	H−1→L+3 (18.85%) H−2→L+1 (18.71%) H→L+4 (15.01%) H−1→L (14.52%)	78.97
	0.3265	2.28	544.2	$S_0 \rightarrow S_{27}$	H−1→L+5 (35.05%) H−2→L+4 (11.91%) H−3→L+3 (11.40%)	52.69
TG7-H6-ba ($C_{78}H_{30}$)	0.7353	2.28	542.8	$S_0 \rightarrow S_1$	H→L (90.26%)	41.05
	0.1713	4.45	278.4	$S_0 \rightarrow S_{29}$	H−4→L+1 (17.84%) H→L+15 (15.58%)	6.80
	0.1090	5.06	245.3	$S_0 \rightarrow S_{57}$	H→L+17 (18.97%) H→L+11 (12.82%)	6.88
TG7-H6-ba-3NO2 ($C_{78}H_{27}N_3O_6$)	0.7906	2.24	553.5	$S_0 \rightarrow S_1$	H→L (88.09%)	63.95
	1.5789	2.73	453.9	$S_0 \rightarrow S_3$	H−1→L (38.42%) H→L+1 (45.66%)	54.09
	0.4268	3.21	385.7	$S_0 \rightarrow S_7$	H−1→L+1 (30.96%) H→L+3 (25.92%)	25.73
TG7-H6-ba-2NO2 ($C_{78}H_{28}N_2O_4$)	1.4120	2.79	444.6	$S_0 \rightarrow S_3$	H−1→L (39.21%) H→L+1 (44.44%)	−218.40
TG7-H6-ba-1NO2 ($C_{78}H_{29}NO_2$)	0.7508	2.28	543.7	$S_0 \rightarrow S_1$	H→L (90.13%)	−56.18
	0.3907	2.84	436.2	$S_0 \rightarrow S_3$	H−1→L (21.21%) H→L+1 (28.79%) H→L+2 (22.82%)	−61.10
	0.6445	4.59	269.9	$S_0 \rightarrow S_{39}$	H−2→L+3 (13.34%)	−41.80