Electronic Supplementary Information

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Table S1. One-Photon Absorption of **HBC-CN**, **HBC-CF3**, and **HBC-NO2** by ZINDO and TD-DFT//MPW1B95/6-31G* in gas, and different solvents.

molecule	λ^{O}_{max}/nm	gas	toluene	THF	DCM
HBC-CF3	λ^{O}_{ZINDO}	394.8	395.8	395.5	395.6
	λ^{O}_{TDDFT}	405.2	413.8	412.0	412.2
	experiment		404	402	403
HBC-CN	λ^{O}_{ZINDO}	403.7	403.1	404.5	404.7
	λ^{O}_{TDDFT}	418.4	428.3	426.7	426.9
	experiment		411	408	411
HBC-NO2	λ^{O}_{ZINDO}	413.7	422.0	430.6	431.4
	λ^{O}_{TDDFT}	446.8	463.1	466.3	466.9
	experiment		431	431	442

λ^{O}_{TDDFT} and λ^{O}_{ZINDO} denote the OPA spectra by TD DFT//MPW1B95/6-31G* and ZINDO, respectively. Additionally, the experimental data are measured at the concentration of 10^{-5} M in ref 22.

Table S2. The contribution of electron density (%) for all chromophores, A (containing all π-conjugated bridges and acceptors) and D (containing all π-conjugated bridges and donors).

molecule	HOMO			LUMO		
	HBC core	A	D	HBC core	A	D
HBC-CF3	81.7	11.3	7.0	65.6	30.6	3.8
HBC-CN	81.6	11.3	7.1	54.0	43.0	3.0
HBC-NO2	82.3	10.3	7.4	25.5	73.3	1.2
N-HBC-E-CF3	18.6	1.3	80.1	64.1	25.5	10.4
N-HBC-E- CN	16.0	1.0	83.0	54.3	38.6	7.1
N-HBC-E- NO2	14.5	0.9	84.6	25.9	71.8	2.3
N-HBC-A-CF3	15.6	0.9	83.5	70.9	18.0	11.1
N-HBC-A- CN	14.0	0.7	85.3	60.5	31.6	7.9
N-HBC-A- NO2	12.6	0.6	86.8	23.9	74.1	2.0
N-HBC-C6	32.3		67.7	68.5		31.5

Table S3. The most intense TPA response for all the investigated molecules.

molecule	λ_{max}^{T}/nm	δ_{max}/GM	channel	transition nature
HBC-CF3	623.0	1377.8		
	574.5	1326.7	$S_0 \rightarrow S_5/S_6 \rightarrow S_{30}$	(HOMO-7)→(LUMO) 11%
				(HOMO-8)→(LUMO+1) 11%
			$S_0 \rightarrow S_5/S_6 \rightarrow S_{31}$	(HOMO-7)→(LUMO+1) 11%
				(HOMO-8)→(LUMO) 11%
HBC-CN	621.2	2010.8		
	577.7	2167.9	$S_0 \rightarrow S_5/S_6 \rightarrow S_{33}$	(HOMO-7)→(LUMO+1) 15%
				(HOMO-8)→(LUMO) 15%
			$S_0 \rightarrow S_5/S_6 \rightarrow S_{34}$	(HOMO-7)→(LUMO) 16%
				(HOMO-8)→(LUMO+1) 16%
HBC-NO2	725.9	1072.1		
	621.2	3850.6	$S_0 \rightarrow S_3/S_4 \rightarrow S_{25}$	(HOMO)→(LUMO+12) 13%
				(HOMO-2)→(LUMO) 11%
			$S_0 \rightarrow S_3/S_4 \rightarrow S_{26}$	(HOMO-1)→(LUMO+12) 13%
				(HOMO-2)→(LUMO+1) 11%
N-HBC-E-CF3	696.5	541.9		
	599.5	4771.0	$S_0 \rightarrow S_3/S_4 \rightarrow S_{25}$	(HOMO)→(LUMO+5) 10%
			$S_0 \rightarrow S_3/S_4 \rightarrow S_{26}$	(HOMO-1)→(LUMO+5) 10%
	706.0	350.8		
	613.8	4660.8		
N-HBC-E-CN	701.3	545.2		
	615.6	4704.3		
	594.4	4923.3	$S_0 \rightarrow S_3/S_4 \rightarrow S_{27}$	(HOMO-2)→(LUMO) 21%
			$S_0 \rightarrow S_3/S_4 \rightarrow S_{28}$	(HOMO-2)→(LUMO+1) 21%
	701.3	554.6		
	615.6	4710.1		
	594.4	4937.2		
N-HBC-E-NO2	715.8	1298.8		
	619.3	4779.7		
	577.7	9547.7	$S_0 \rightarrow S_3/S_4 \rightarrow S_{32}$	(HOMO)→(LUMO+2) 12%
			$S_0 \rightarrow S_3/S_4 \rightarrow S_{33}$	(HOMO-1)→(LUMO+2) 12%
N-HBC-A-CF3	694.2	591.6		
	599.5	5284.5	$S_0 \rightarrow S_3/S_4 \rightarrow S_{23}$	(HOMO-6)→(LUMO+1) 14%
			$S_0 \rightarrow S_3/S_4 \rightarrow S_{24}$	(HOMO-6)→(LUMO) 15%
	694.2	423.8		
	599.5	4803.7		
N-HBC-A-CN	698.9	604.2		
	601.3	5240.0	$S_0 \rightarrow S_3/S_4 \rightarrow S_{27}$	(HOMO-2)→(LUMO) 19%
	696.5	493.7		(HOMO)→(LUMO+6) 10%
	596.1	4575.6	$S_0 \rightarrow S_3/S_4 \rightarrow S_{28}$	(HOMO-2)→(LUMO+1)20%
N-HBC-A-NO2	703.7	1278.1		
	606.6	5427.3		

	571.4	8645.5	$S_0 \rightarrow S_3/S_4 \rightarrow S_{39}$	(HOMO-9)→(LUMO) 16%
			$S_0 \rightarrow S_3/S_4 \rightarrow S_{40}$	(HOMO-9)→(LUMO+1) 16%
	715.8	1673.6		
	650.5	2599.4		
	582.6	8848.9		
N-HBC-C6	594.4	7538.6	$S_0 \rightarrow S_3/S_4 \rightarrow S_{32}$	(HOMO-8)→(LUMO) 16%
				(HOMO-2)→(LUMO) 14%
				(HOMO)→(LUMO+2) 13%
			$S_0 \rightarrow S_3/S_4 \rightarrow S_{33}$	(HOMO-8)→(LUMO+1) 16%
				(HOMO-2)→(LUMO+1) 14%
				(HOMO)→(LUMO+2) 13%

The results in red are calculated in THF.

Table S4. Linear optical parameters of two-photon absorption, $X=M^2_{0k}M^2_{kn}/[(E_{0k}-E_{0n}/2)^2\Gamma]$.

molecule	M_{0k}(Debye)	M_{kn}(Debye)	E_{0k}(eV)	E_{0n}(eV)	E_{0k}-E_{0n}/2	X	δ_{max}(GM)
HBC-CF3	14.47	1.91	3.13	4.27	1.00	7680.1	1326.7
HBC-CN	12.74	4.26	3.09	4.29	0.95	32633.7	2167.9
HBC-NO2	15.59	4.63	3.00	3.99	1.01	51087.4	3850.6
N-HBC-E-CF3	19.11	5.05	3.12	4.15	1.05	84492.6	4771.0
N-HBC-E-CN	19.72	5.45	3.11	4.15	1.04	106800.0	4923.3
N-HBC-E-NO2	19.84	6.31	3.07	4.23	0.96	171690.5	9547.7
N-HBC-A-CF3	18.52	6.40	3.14	4.11	1.08	119364.5	5284.5
N-HBC-A-CN	18.97	7.00	3.13	4.16	1.05	159835.4	5240.0
N-HBC-A-NO2	19.35	6.60	3.11	4.35	0.94	184760.1	8645.5
N-HBC-C6	19.81	8.02	3.15	4.18	1.06	224545.8	7538.6

Table S5. Two-photon absorption properties of the linear quadrupolar and 2D-octupolar molecules studied.

molecule	λ_{max}^{T}/nm	δ_{max}/GM	channel	transition nature
HBC-CF3-2	526.3	791.7	$S_0 \rightarrow S_5 \rightarrow S_{34}$	(HOMO)→(LUMO+10) 25%
				(HOMO-8)→(LUMO) 22%
N-HBC-E-CF3-2	537.2	2446.0	$S_0 \rightarrow S_4 \rightarrow S_{37}$	(HOMO)→(LUMO+3) 14%
				(HOMO-2)→(LUMO+6) 18%
N-HBC-E-NO2-2	535.8	2172.2	$S_0 \rightarrow S_3 \rightarrow S_{39}$	(HOMO)→(LUMO+14) 15%
				(HOMO-2)→(LUMO+17) 12%
N-HBC-A-CF3-2	540.0	2315.9	$S_0 \rightarrow S_3 \rightarrow S_{37}$	(HOMO)→(LUMO+3) 17%
				(HOMO-2)→(LUMO+6) 17%
N-HBC-A-NO2-2	537.2	2244.4	$S_0 \rightarrow S_3 \rightarrow S_{39}$	(HOMO)→(LUMO+14) 15%
				(HOMO-2)→(LUMO+17) 12%
N-HBC-A-CF3-4	610.2	3082.3	$S_0 \rightarrow S_3 \rightarrow S_{20}$	(HOMO)→(LUMO+4) 13%
				(HOMO-6)→(LUMO) 11%

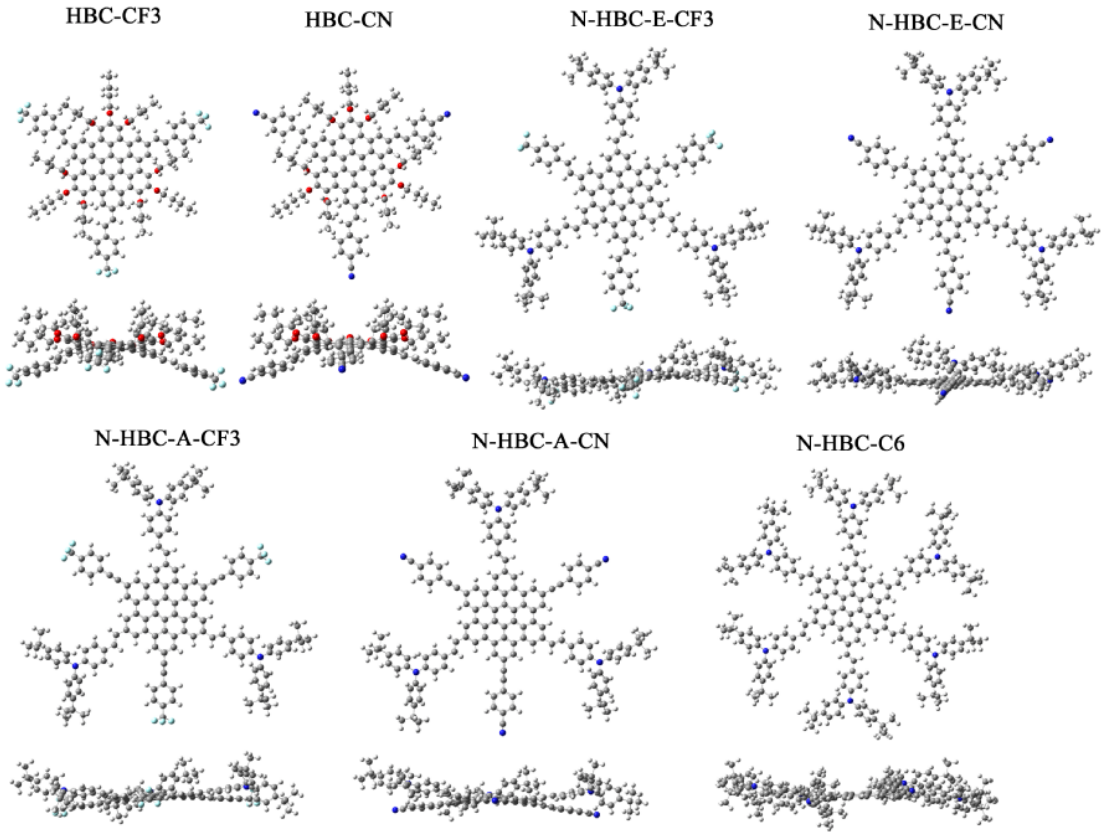


Fig. S1. The optimized ground-state geometries of the chromophores without nitro groups.

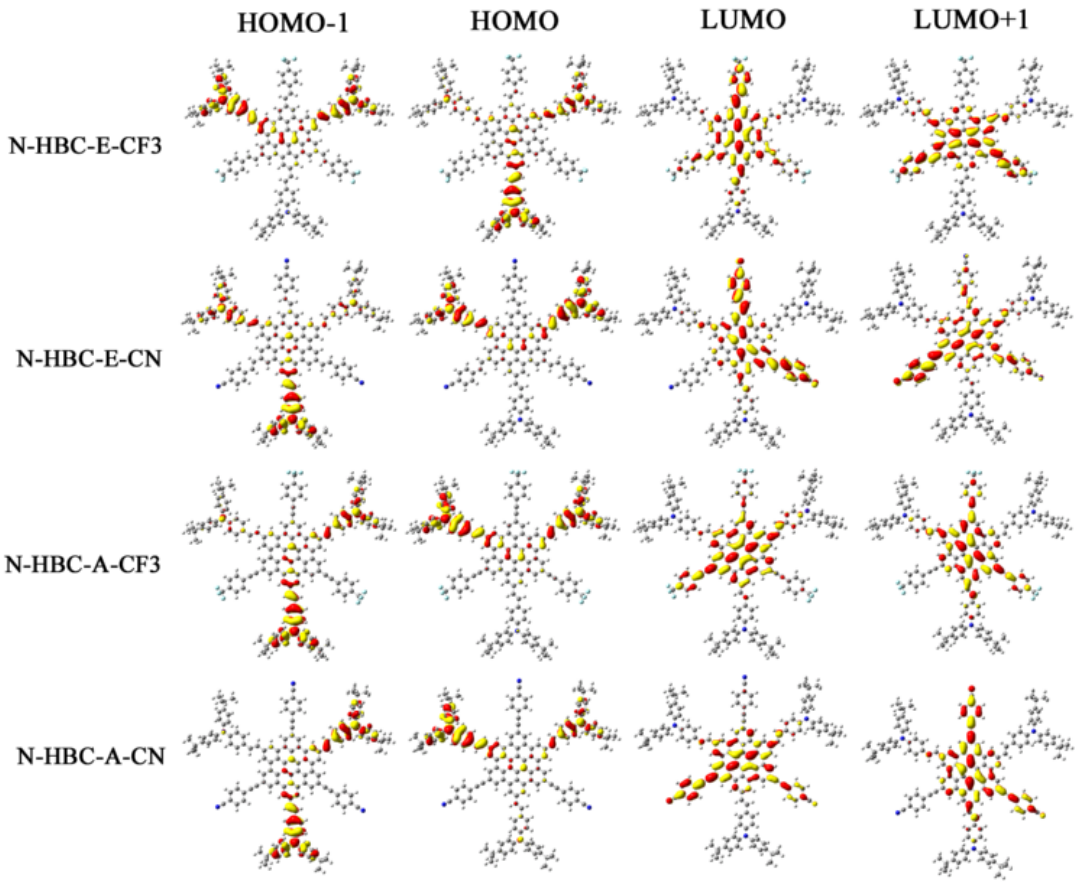
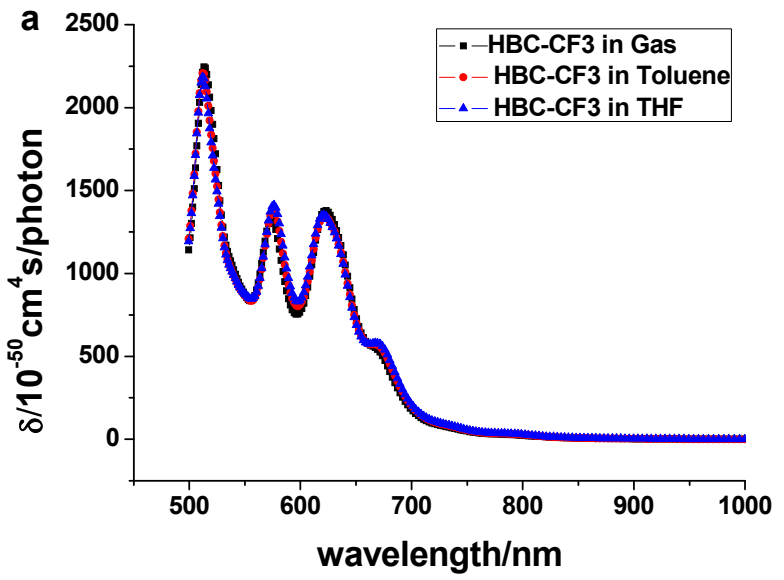
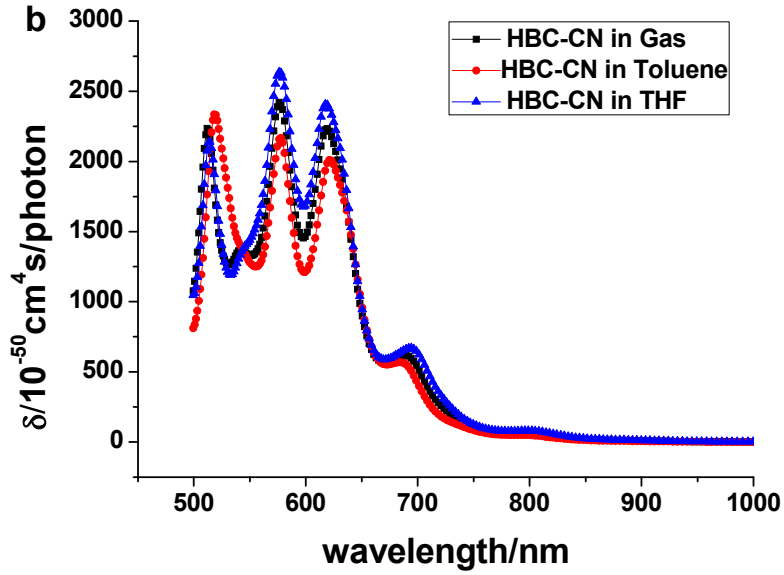
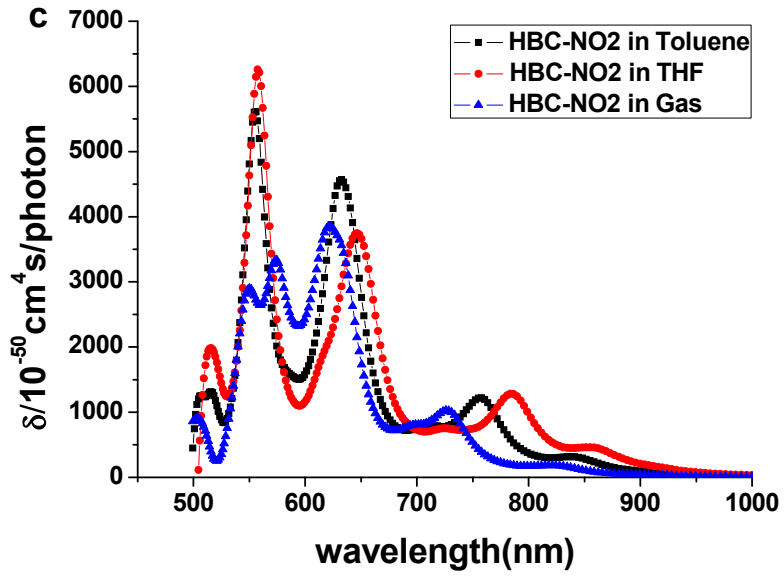


Fig. S2. Molecular orbitals of chromophores **N-HBC-E-CF3**, **N-HBC-E-CN**, **N-HBC-A-CF3**, and **N-HBC-A-CN**.







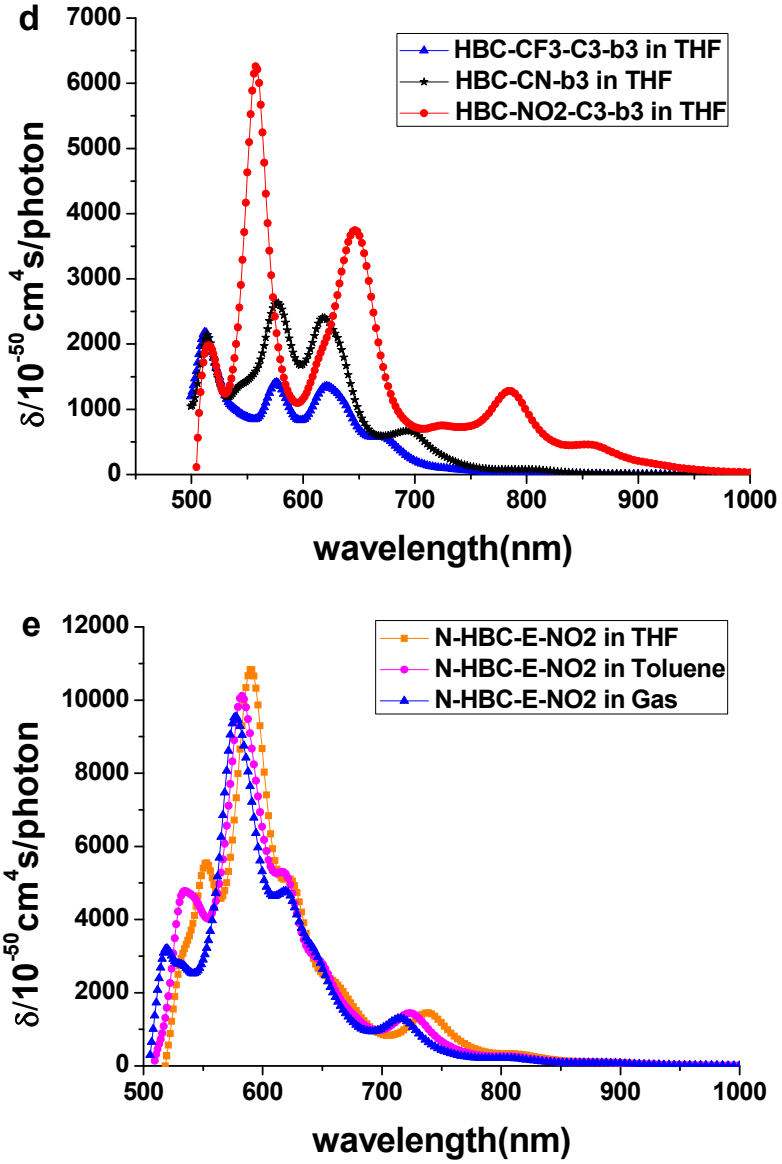


Fig. S3. Two-photon absorption spectra for molecules in gas, toluene and THF.

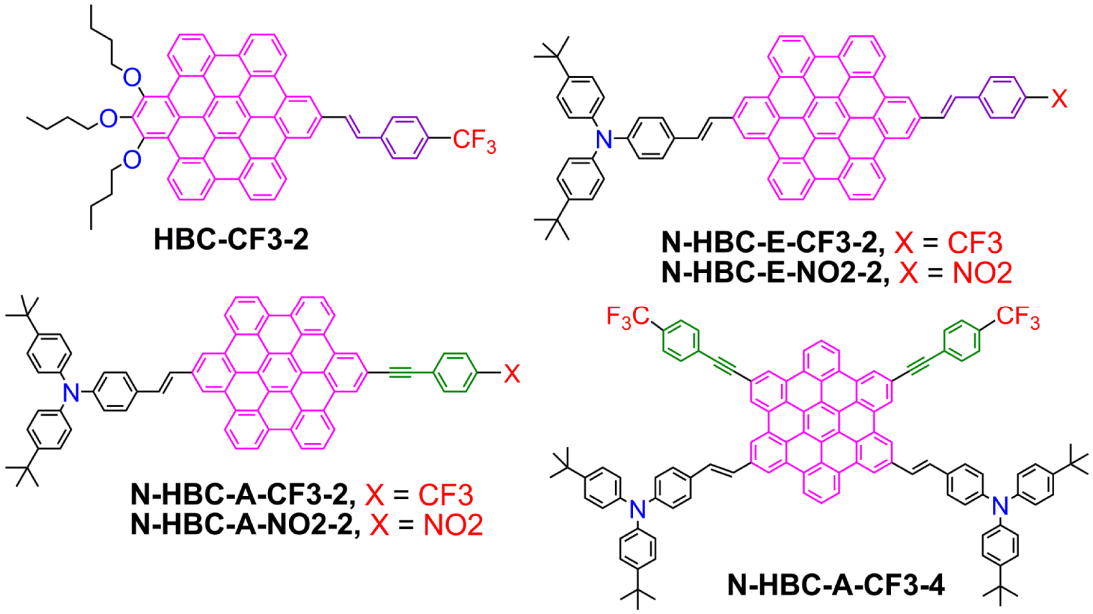


Fig. S4. Molecular structures of the linear quadrupolar and 2D-octupolar chromophores studied.

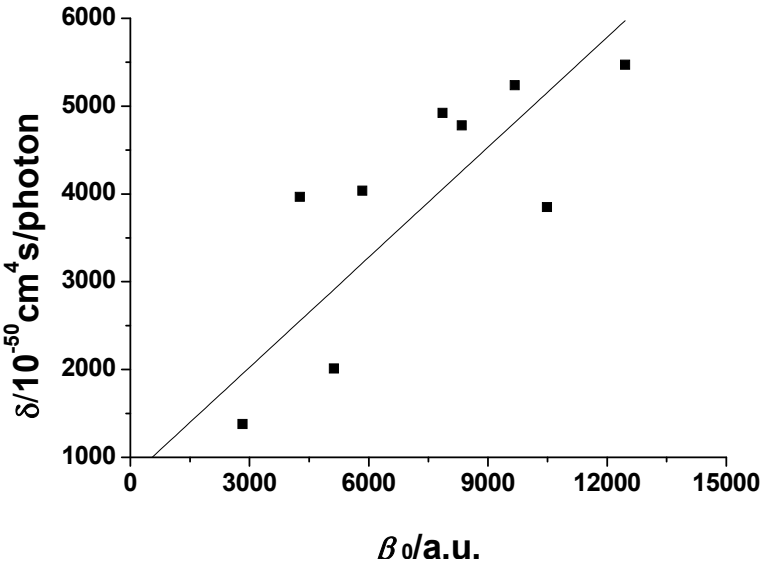


Fig. S5. The calculated δ_{max} vs β_0.