Supplementary Material

Design of donor-π-acceptor type cyclo[18]carbon derivatives for infrared nonlinear optical materials: A theoretical perspective

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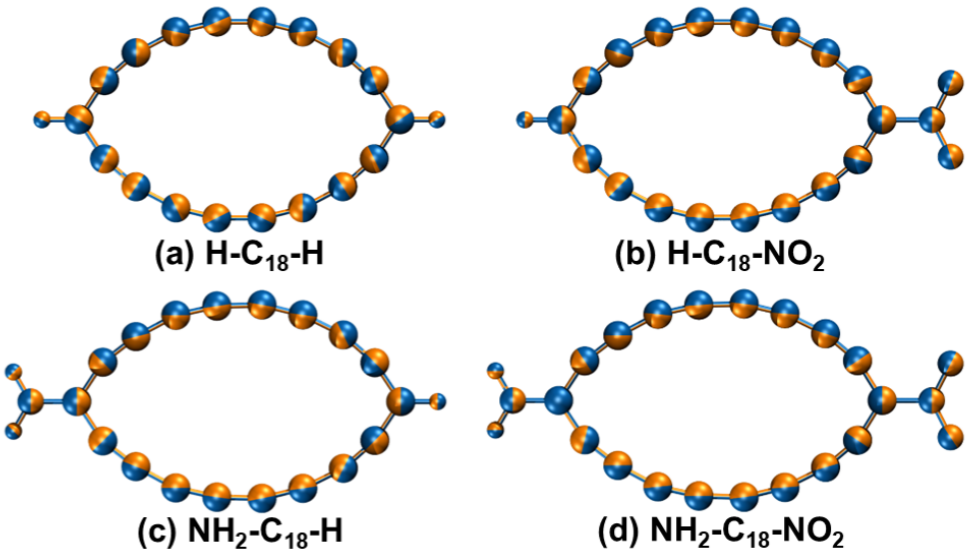

Figure S1. Conformational superposition of the structures of the studied C_{18} derivatives optimized at the ωB97XD/def2-TZVP (orange) and M06-2X/def2-TZVP (blue) levels.

Table S1. Optimized Cartesian coordinates (in Å) of H-C_{18}-H

atom	*x*	*y*	*z*
C	-0.01939934	2.87539010	0.00015892
C	-1.32922636	2.87518157	0.00041431
C	-2.53569213	2.58384646	0.00042537
C	-3.69818932	1.97586994	0.00034287
C	-4.63124546	1.16215499	0.00017011
C	-5.37608535	0.02662622	-0.00006365
C	-4.62624643	-1.12738898	-0.00010283
C	-3.70554292	-1.93939148	-0.00005871
C	-2.53123623	-2.55837665	-0.00003029
C	-1.33618955	-2.84926088	-0.00000378
C	-0.01051645	-2.84905449	0.00001172
C	1.18443280	-2.55776990	0.00003657
C	2.35852489	-1.93840890	0.00000343
C	3.27894176	-1.12608276	-0.00006831
C	4.02840180	0.02816670	-0.00022287

C	3.28318904	1.16344476	-0.00029242
C	2.34985736	1.97684760	-0.00018158
C	1.18716268	2.58444926	-0.00001903
H	-6.45880962	0.02593260	-0.00017759
H	5.11112645	0.02782392	-0.00034226

Table S2. Optimized Cartesian coordinates (in Å) of H-C_{18}-NO_2

atom	*x*	*y*	*z*
C	-0.43461463	2.85495547	0.00000000
C	-1.75264498	2.85774100	0.00000000
C	-2.95267273	2.56769852	0.00000000
C	-4.12271244	1.95737111	0.00000000
C	-5.04892384	1.14472230	0.00000000
C	-5.79467238	-0.00002024	0.00000000
C	-5.04903447	-1.14483520	0.00000000
C	-4.12290547	-1.95757828	0.00000000
C	-2.95282820	-2.56783462	0.00000000
C	-1.75270629	-2.85748857	0.00000000
C	-0.43467540	-2.85473505	0.00000000
C	0.76678934	-2.57206579	0.00000000
C	1.93464568	-1.95692323	0.00000000
C	2.87832779	-1.16724331	0.00000000
C	3.58496425	-0.00001812	0.00000000
C	2.87828364	1.16718001	0.00000000
C	1.93456787	1.95681931	0.00000000
C	0.76682306	2.57217265	0.00000000
N	5.05112208	0.00000971	0.00000000
O	5.59759963	-1.07958019	0.00000000
O	5.59755867	1.07962035	0.00000000
H	-6.87774803	0.00003218	0.00000000

Table S3. Optimized Cartesian coordinates (in Å) of NH_2-C_{18}-H

atom	*x*	*y*	*z*
C	1.09120281	2.82900416	0.00000000
C	-0.22937222	2.79303525	0.00000000
C	-1.43284668	2.52486927	0.00000000
C	-2.60181801	1.90214127	0.00000000
C	-3.57507737	1.15277480	0.00000000
C	-4.33736453	0.00000000	0.00000000
C	-3.57507737	-1.15277480	0.00000000
C	-2.60181801	-1.90214127	0.00000000
C	-1.43284668	-2.52486927	0.00000000
C	-0.22937222	-2.79303525	0.00000000
C	1.09120281	-2.82900416	0.00000000
C	2.29042829	-2.53858540	0.00000000
C	3.47644300	-1.95500812	0.00000000
C	4.40056747	-1.13983632	0.00000000
C	5.15849772	0.00000000	0.00000000
C	4.40056747	1.13983632	0.00000000
C	3.47644300	1.95500812	0.00000000
C	2.29042829	2.53858540	0.00000000
N	-5.68788870	0.00000000	0.00000000
H	-6.19394091	-0.86483452	0.00000000
H	-6.19394091	0.86483452	0.00000000
H	6.24002319	0.00000000	0.00000000

Table S4. Optimized Cartesian coordinates (in Å) of NH_2-C_{18}-NO_2

atom	*x*	*y*	*z*
C	-0.00945103	2.82317236	0.00000000
C	-1.33366756	2.78971365	0.00000000
C	-2.53462939	2.52406567	0.00000000
C	-3.70685283	1.90083937	0.00000000
C	-4.68063145	1.15622303	0.00000000
C	-5.44311417	0.00000000	0.00000000
C	-4.68063145	-1.15622303	0.00000000
C	-3.70685283	-1.90083937	0.00000000
C	-2.53462939	-2.52406567	0.00000000
C	-1.33366756	-2.78971365	0.00000000
C	-0.00945103	-2.82317236	0.00000000
C	1.18802328	-2.53974044	0.00000000
C	2.37708633	-1.95393431	0.00000000
C	3.31682040	-1.16390563	0.00000000
C	4.03989619	0.00000000	0.00000000
C	3.31682040	1.16390563	0.00000000
C	2.37708633	1.95393431	0.00000000
C	1.18802328	2.53974044	0.00000000
N	-6.78574136	0.00000000	0.00000000
H	-7.29328314	-0.86508701	0.00000000
H	-7.29328314	0.86508701	0.00000000
N	5.48905035	0.00000000	0.00000000
O	6.04274364	-1.07985101	0.00000000
O	6.04274364	1.07985101	0.00000000

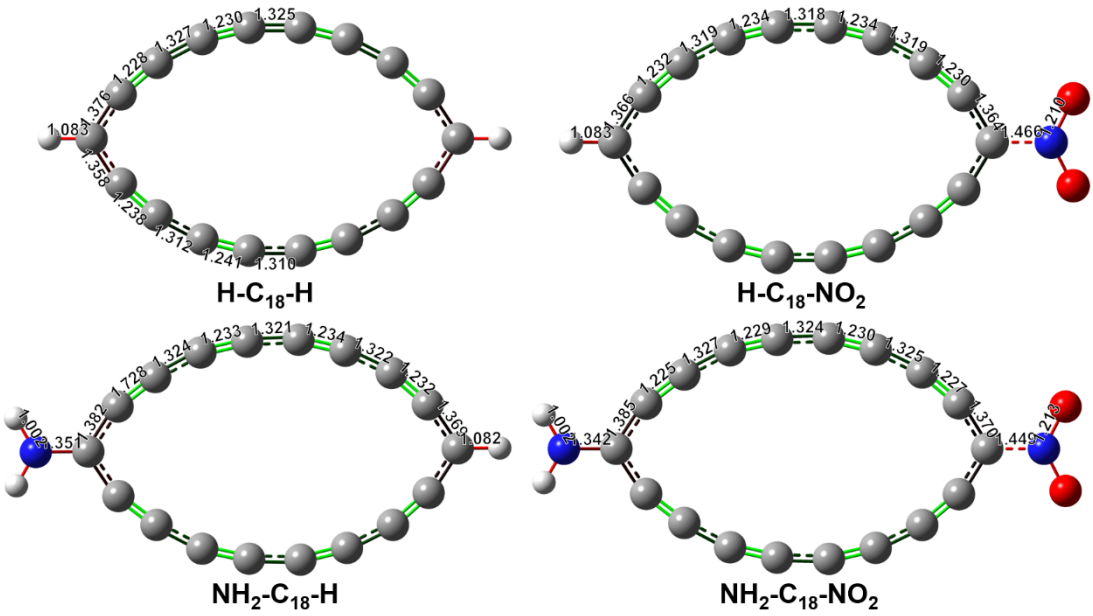

Figure S2. Bond-length colored molecular structure of the studied C_{18} derivatives. The bond lengths (in Å) are given.

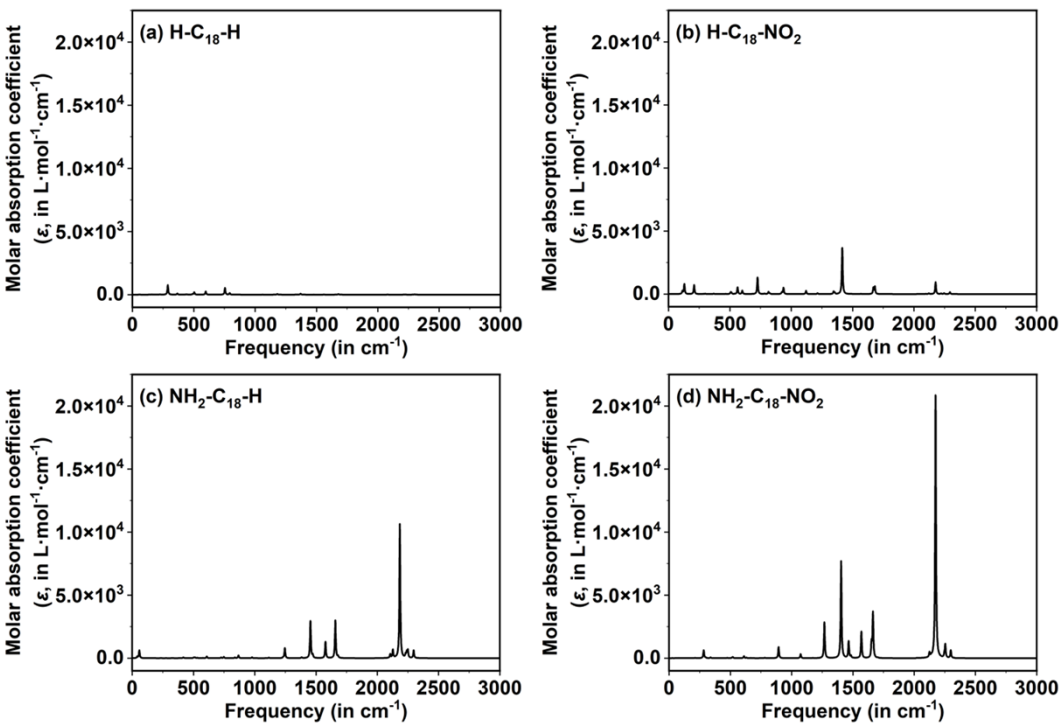

Figure S3. Simulated infrared (IR) spectrum of the studied C_{18} derivatives. Gaussian function with full width at half-maximum of 8 cm^{-1} was employed for broadening the theoretical data as spectrum curves.

Table S5. Contributions of the main transition orbitals (MTOs) of crucial excited state involved in maximum wavelength absorption

Molecules	MTOs
H-C_{18}-H	HOMO→LUMO (86.1%)
H-C_{18}-NO_2	HOMO→LUMO (89.4%)
NH_2-C_{18}-H	HOMO→LUMO (88.4%)
NH_2-C_{18}-NO_2	HOMO→LUMO (90.3%)

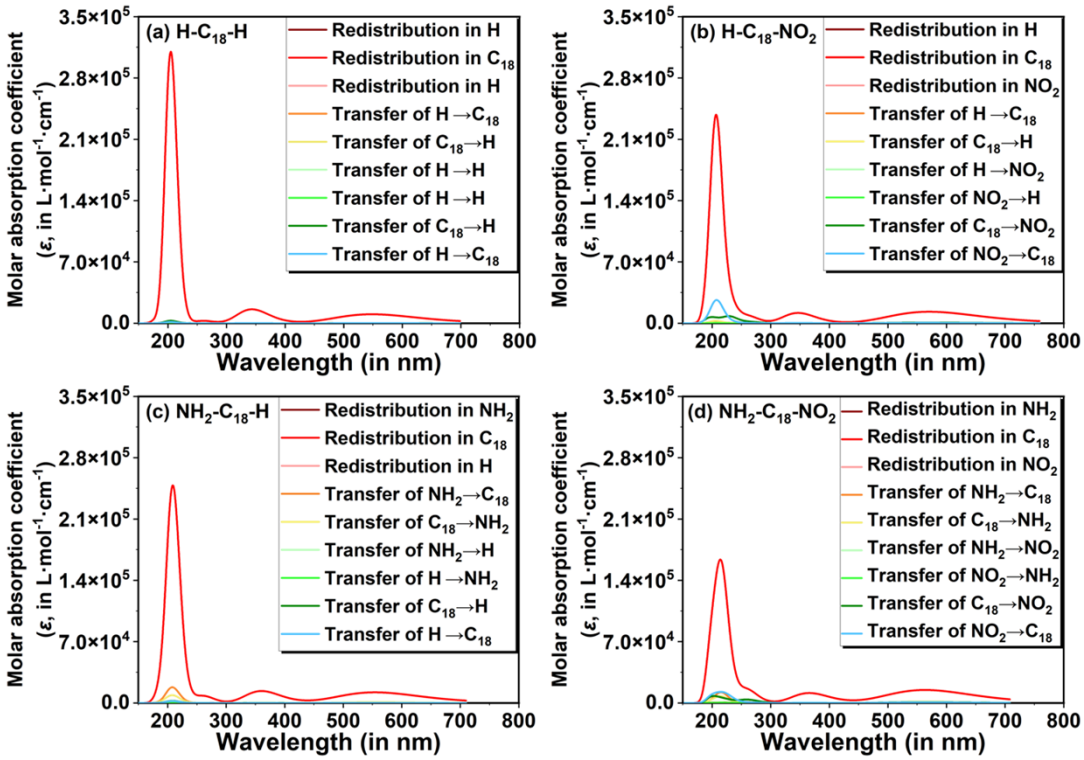

Figure S4. Simulated charge-transfer spectrum (CTS) of the studied C_{18} derivatives. The Gaussian function with full width at half-maximum of 0.333 eV was employed for broadening the theoretical data as spectrum curves.

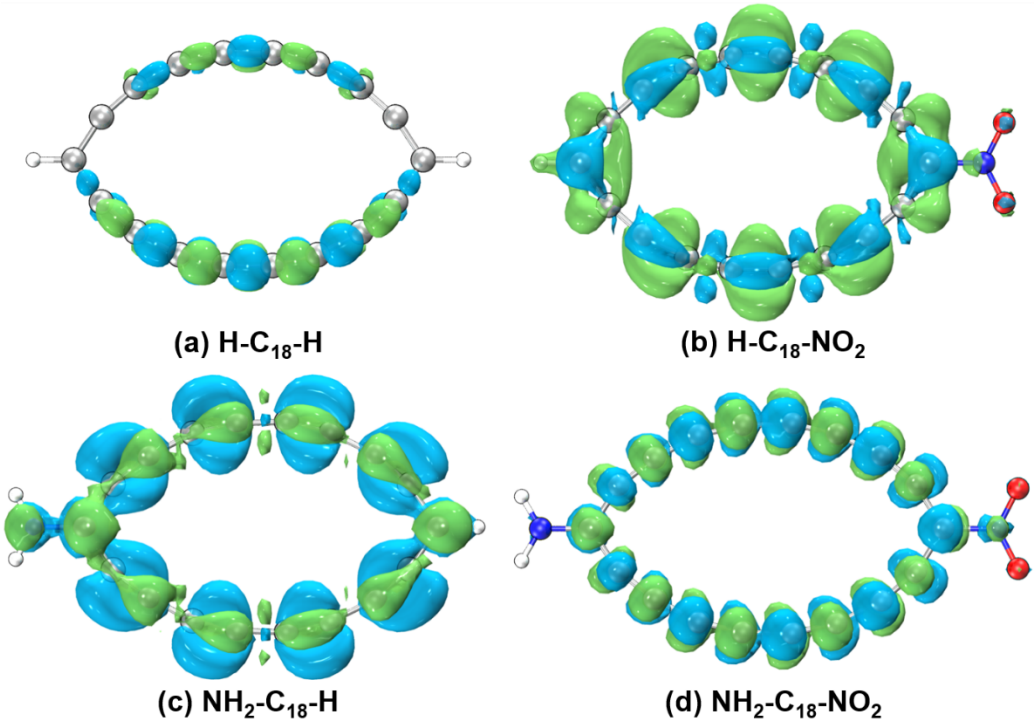

Figure S5. Isosurface maps of electron density difference (EDD) (isovalue = 0.001) of the studied C_{18} derivatives. Green and blue regions denote where electron density is increased and decreased, respectively, after electronic excitation.

Table S6. Transition energy (ΔE, in eV), oscillator strength (f_0), magnitude of the vector difference between the dipole moment of the ground state and those of the excited state ($|\Delta\mu|$, in D), and calculated first hyperpolarizability (β_0*(-2ω;ω,ω), in a.u.) derived from the two-level model for the lowest five excited states of the studied C_{18} derivatives

	S_n	ΔE	f_0	$\|\Delta\mu\|$	β_0*(-2ω;ω,ω)
H-C_{18}-H	S_1	1.88	0.000	2.49	0
	S_2	2.09	0.026	0.68	16
	S_3	2.28	0.242	0.20	33
	S_4	2.43	0.000	1.66	0
	S_5	2.54	0.001	4.15	1
NH_2-C_{18}-H	S_1	1.85	0.000	0.62	0
	S_2	2.11	0.001	0.16	0
	S_3	2.24	0.353	1.24	309
	S_4	2.2	0.000	0.44	0
	S_5	2.58	0.000	0.26	0
H-C_{18}-NO_2	S_1	1.72	0.000	1.70	0
	S_2	1.98	0.041	1.78	74
	S_3	2.19	0.332	4.38	1094
	S_4	2.39	0.000	2.80	0
	S_5	2.45	0.000	0.85	0
NH_2-C_{18}-NO_2	S_1	1.86	0.000	2.93	1
	S_2	2.10	0.000	3.71	0
	S_3	2.15	0.002	2.84	4
	S_4	2.20	0.476	6.37	2252
	S_5	2.54	0.000	1.26	0

Table S7. Total amounts of the first hyperpolarizability ($\beta_0(-2\omega;\omega,\omega)$, in a.u.), projection of the first hyperpolarizability onto the dipole vector ($\beta_{vec}(-2\omega;\omega,\omega)$, in a.u.), and Cartesian component of the first hyperpolarizability ($\beta_x(-2\omega;\omega,\omega)$, $\beta_y(-2\omega;\omega,\omega)$, and $\beta_z(-2\omega;\omega,\omega)$, in a.u.) in zero-frequency limit ($\lambda = \infty$ nm) and under frequency-dependent fields (λ = 1907 and 1460 nm) of the studied C_{18} derivatives in the gas phase (outside parenthesis) and in cyclohexane solution (inside parenthesis) calculated by analytic derivatives of the system energy (CPKS) method

	λ	$\beta_0(-2\omega;\omega,\omega)$	$\beta_{vec}(-2\omega;\omega,\omega)$	$\beta_x(-2\omega;\omega,\omega)$	$\beta_y(-2\omega;\omega,\omega)$	$\beta_z(-2\omega;\omega,\omega)$
H-C_{18}-H	∞ nm	518 (1019)	-518	0	-518	0
	1907 nm	887 (1841)	-887	0	-887	0
	1460 nm	1622 (3536)	-1622	0	-1622	0
H-C_{18}-NO_2	∞ nm	570 (294)	570	-570	0	0
	1907 nm	773 (124)	773	-773	0	0
	1460 nm	928 (1712)	928	-928	0	0
NH_2-C_{18}-H	∞ nm	2770 (8234)	-2770	2770	0	0
	1907 nm	4834 (15097)	-4834	4834	0	0
	1460 nm	8487 (28400)	-8487	8487	0	0
NH_2-C_{18}-NO_2	∞ nm	4462 (13928)	-4462	4462	0	0
	1907 nm	8107 (26063)	-8107	8107	0	0

- - - - - - - - - -	1460 nm	15072 (50661)	-15072	15072	0	0

Table S8. Tensorial component of the first hyperpolarizability (in a.u.) in the principal axis of the studied C_{18} derivatives in zero-frequency limit (λ = ∞ nm) and under frequency-dependent fields (λ = 1907 and 1460 nm) of the studied C_{18} derivatives calculated by both analytic derivatives of the system energy (CPKS, outside parenthesis) and finite field (FF, inside parenthesis) methods

	λ	$\beta_{xxy}(-2\omega;\omega,\omega)$	$\beta_{yyy}(-2\omega;\omega,\omega)$	$\beta_{yzz}(-2\omega;\omega,\omega)$
	∞ nm	-161	-357 (-352)	-1
H-C_{18}-H	1907 nm	-273	-578	-1
	1460 nm	-461	-1014	-1
	λ	$\beta_{xxx}(-2\omega;\omega,\omega)$	$\beta_{xyy}(-2\omega;\omega,\omega)$	$\beta_{xzz}(-2\omega;\omega,\omega)$
	∞ nm	-937 (-948)	282	85
H-C_{18}-NO_2	1907 nm	-1158	455	101
	1460 nm	-1268	799	126
	∞ nm	1910 (1910)	881	-21
NH_2-C_{18}-H	1907 nm	3699	1357	-31
	1460 nm	6994	2158	-49
	∞ nm	2635 (2612)	1742	84
NH_2-C_{18}-NO_2	1907 nm	5716	2659	98
	1460 nm	11884	4252	116