Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Photophysical property and optical nonlinearity of cyclo[18]carbon (C_{18}) precursors, C_{18}-$(CO)_n$ (n = 2, 4, and 6): Focusing on the effect of carbonyl (-CO) groups

Xia Wang[a], Zeyu Liu[*a], Xiufen Yan[a], Tian Lu[*b], Haowei Wang[a], Weiwei Xiong[*a] and Mengdi Zhao[c]

[a]*School of Environmental and Chemical Engineering, Jiangsu University of Science and Technology, Zhenjiang 212100, People's Republic of China*

[b]*Beijing Kein Research Center for Natural Sciences, Beijing 100022, People's Republic of China*

[c]*Department of Materials Science and Engineering, Suzhou University of Science and Technology, Suzhou 215009, People's Republic of China*

[*]Corresponding author. E-mail: liuzy@just.edu.cn (Zeyu Liu); sobereva@sina.com (Tian Lu); xiongweiwei@just.edu.cn (Weiwei Xiong)

Contents:

Table S1. Polarizabilities and second hyperpolarizabilities of C_{18}-$(CO)_n$ (n = 2, 4, and 6) in zero-frequency limit ($\lambda = \infty$ nm) and under frequency-dependent fields (λ = 1907, 1460, 1340, 1180, and 1064 nm) calculated at ωB97XD/aug-cc-pVTZ(-f,-d) level with default quality grid

	field frequency (λ, in nm)	polarizability (in au)				second hyperpolarizability (in au)			
		$\alpha_{iso}(\lambda)$	$\alpha_{xx}(\lambda)$	$\alpha_{yy}(\lambda)$	$\alpha_{zz}(\lambda)$	$\gamma_{\|\|}(\lambda)$	$\gamma_{xxxx}(\lambda)$	$\gamma_{yyyy}(\lambda)$	$\gamma_{zzzz}(\lambda)$
C_{18}-$(CO)_2$	∞	334.99	561.88	333.69	109.42	211749.30	632254.00	148371.00	13856.00
	1907	338.35	568.32	337.12	109.61	243190.10	732984.00	168596.00	14274.90
	1460	340.78	572.98	339.62	109.74	271380.90	823193.00	186629.00	14583.20
	1340	341.90	575.13	340.78	109.81	286434.40	871185.00	196240.00	14726.20
	1180	343.99	579.12	342.94	109.92	319421.90	975416.00	217363.00	14995.70
	1064	346.18	583.29	345.21	110.04	364545.20	1113170.00	246867.00	15282.70
C_{18}-$(CO)_4$	∞	374.83	411.52	591.72	121.23	269172.50	265595.00	740194.00	13725.40
	1907	378.89	416.00	599.25	121.43	314102.70	308259.00	869272.00	14118.20
	1460	381.86	419.28	604.74	121.57	355095.20	347485.00	987204.00	14406.60
	1340	383.23	420.79	607.27	121.64	377163.40	368721.00	1050760.00	14540.30
	1180	385.80	423.63	612.02	121.75	425623.60	415579.00	1190530.00	14791.50

	1064	388.49	426.61	617.00	121.88	490946.80	478521.00	1378470.00	15058.20
C_{18}-$(CO)_6$	∞	417.16	559.19	559.18	133.12	347641.00	634862.00	634839.00	13551.50
	1907	422.08	566.46	566.45	133.32	412991.60	756526.00	756500.00	13917.70
	1460	425.69	571.80	571.79	133.46	473740.30	869741.00	869713.00	14185.80
	1340	427.36	574.28	574.27	133.53	506759.10	931311.00	931282.00	14309.80
	1180	430.50	578.93	578.92	133.65	579657.50	1067310.00	1067280.00	14542.20
	1064	433.81	583.83	583.83	133.77	677074.80	1249140.00	1249120.00	14786.70

Table S2. First hyperpolarizabilities of C_{18}-$(CO)_n$ (n = 2, 4, and 6) in zero-frequency limit ($\lambda = \infty$ nm) and under frequency-dependent fields (λ = 1907, 1460, 1340, 1180, and 1064 nm) calculated at ωB97XD/aug-cc-pVTZ(-f,-d) level with default quality grid

	field frequency (λ, in nm)	first hyperpolarizability (in au)			
		$\beta_{vec}(\lambda)$	$\beta_{xxx}(\lambda)$	$\beta_{yyy}(\lambda)$	$\beta_{zzz}(\lambda)$
C_{18}-$(CO)_2$	∞	885.31	910.06	0.00	0.00
	1907	1177.99	1156.28	0.00	0.00
	1460	1459.05	1389.12	0.00	0.00
	1340	1615.67	1517.35	0.00	0.00
	1180	1972.81	1805.24	0.00	0.00
	1064	2483.23	2202.73	0.00	0.00
C_{18}-$(CO)_4$	∞	939.86	445.54	0.00	0.00
	1907	1231.20	629.12	0.00	0.00
	1460	1504.40	805.48	0.00	0.00
	1340	1653.08	903.06	0.00	0.00
	1180	1980.11	1121.73	0.00	0.00
	1064	2409.57	1418.93	0.00	0.00
C_{18}-$(CO)_6$	∞	N/A[a]	469.86	0.00	0.00
	1907	N/A[a]	523.48	0.00	0.00
	1460	N/A[a]	568.23	0.00	0.00
	1340	N/A[a]	590.79	0.00	0.00
	1180	N/A[a]	636.79	0.00	0.00
	1064	N/A[a]	691.44	0.00	0.00

[a]Not available, because C_{18}-$(CO)_6$ has vanished dipole moment.

Table S3. Polarizabilities and second hyperpolarizabilities of C_{18}-$(CO)_n$ (n = 2, 4, and 6) in zero-frequency limit ($\lambda = \infty$ nm) and under frequency-dependent fields (λ = 1907, 1460, 1340, 1180, and 1064 nm) calculated at ωB97XD/aug-cc-pVTZ(-f,-d) level with higher quality grid (using *int=superfine* and *CPHF=grid=fine* keywords) than default

	field frequency (λ, in nm)	polarizability (in au)				second hyperpolarizability (in au)			
		$\alpha_{iso}(\lambda)$	$\alpha_{xx}(\lambda)$	$\alpha_{yy}(\lambda)$	$\alpha_{zz}(\lambda)$	$\gamma_{\|\|}(\lambda)$	$\gamma_{xxxx}(\lambda)$	$\gamma_{yyyy}(\lambda)$	$\gamma_{zzzz}(\lambda)$
C_{18}-$(CO)_2$	∞	334.99	561.88	333.69	109.41	211749.30	632254.00	148371.00	13856.00
	1907	338.35	568.32	337.12	109.61	243189.90	732984.00	168597.00	14274.90
	1460	340.78	572.98	339.62	109.74	271380.20	823192.00	186629.00	14583.20
	1340	341.90	575.12	340.78	109.81	286433.70	871184.00	196240.00	14726.20
	1180	343.99	579.12	342.94	109.92	319420.60	975414.00	217363.00	14995.70
	1064	346.18	583.29	345.21	110.04	364541.90	1113160.00	246867.00	15282.70
C_{18}-$(CO)_4$	∞	374.83	411.52	591.72	121.23	269173.60	265592.00	740205.00	13725.30
	1907	378.89	416.00	599.25	121.43	314104.50	308256.00	869288.00	14118.10
	1460	381.86	419.28	604.74	121.57	355098.20	347483.00	987225.00	14406.50
	1340	383.23	420.79	607.28	121.64	377168.10	368719.00	1050790.00	14540.10

	1180	385.80	423.63	612.02	121.75	425628.70	415578.00	1190560.00	14791.40
	1064	388.49	426.61	617.00	121.88	490956.30	478523.00	1378520.00	15058.00
C_{18}-$(CO)_6$	∞	417.16	559.19	559.18	133.12	347639.60	634858.00	634834.00	13551.30
	1907	422.08	566.46	566.45	133.32	412988.80	756520.00	756492.00	13917.40
	1460	425.69	571.80	571.79	133.46	473736.60	869733.00	869703.00	14185.50
	1340	427.36	574.27	574.27	133.53	506754.90	931302.00	931271.00	14309.50
	1180	430.50	578.93	578.92	133.65	579649.00	1067290.00	1067260.00	14541.90
	1064	433.81	583.83	583.83	133.77	677066.10	1249120.00	1249100.00	14786.50

Table S4. First hyperpolarizabilities of C_{18}-$(CO)_n$ (n = 2, 4, and 6) in zero-frequency limit ($\lambda = \infty$ nm) and under frequency-dependent fields (λ = 1907, 1460, 1340, 1180, and 1064 nm) calculated at ωB97XD/aug-cc-pVTZ(-f,-d) level with higher quality grid (using *int=superfine* and *CPHF=grid=fine* keywords) than default

	field frequency (λ, in nm)	first hyperpolarizability (in au)			
		$\beta_{vec}(\lambda)$	$\beta_{xxx}(\lambda)$	$\beta_{yyy}(\lambda)$	$\beta_{zzz}(\lambda)$
C_{18}-$(CO)_2$	∞	885.26	910.01	0.00	0.00
	1907	1177.93	1156.23	0.00	0.00
	1460	1458.97	1389.06	0.00	0.00
	1340	1615.59	1517.28	0.00	0.00
	1180	1972.71	1805.16	0.00	0.00
	1064	2483.11	2202.63	0.00	0.00
C_{18}-$(CO)_4$	∞	939.99	445.63	0.00	0.00
	1907	1231.36	629.22	0.00	0.00
	1460	1504.59	805.61	0.00	0.00
	1340	1653.29	903.20	0.00	0.00
	1180	1980.35	1121.88	0.00	0.00
	1064	2409.86	1419.12	0.00	0.00
C_{18}-$(CO)_6$	∞	N/A[a]	469.80	0.00	0.00
	1907	N/A[a]	523.41	0.00	0.00
	1460	N/A[a]	568.15	0.00	0.00
	1340	N/A[a]	590.70	0.00	0.00
	1180	N/A[a]	636.70	0.00	0.00
	1064	N/A[a]	691.33	0.00	0.00

[a]Not available, because C_{18}-$(CO)_6$ has vanished dipole moment.

Table S5. Polarizabilities and second hyperpolarizabilities of C_{18}-$(CO)_n$ (n = 2, 4, and 6) in zero-frequency limit ($\lambda = \infty$ nm) and under frequency-dependent fields (λ = 1907, 1460, 1340, 1180, and 1064 nm) calculated at CAM-B3LYP/aug-cc-pVTZ(-f,-d) level with higher quality grid (using *int=superfine* and *CPHF=grid=fine* keywords) than default

	field frequency (λ, in nm)	polarizability (in au)				second hyperpolarizability (in au)			
		$\alpha_{iso}(\lambda)$	$\alpha_{xx}(\lambda)$	$\alpha_{yy}(\lambda)$	$\alpha_{zz}(\lambda)$	$\gamma_{\|\|}(\lambda)$	$\gamma_{xxxx}(\lambda)$	$\gamma_{yyyy}(\lambda)$	$\gamma_{zzzz}(\lambda)$
C_{18}-$(CO)_2$	∞	336.17	565.14	334.43	108.93	220260.90	673118.00	149033.00	12626.90
	1907	339.61	571.78	337.94	109.12	255737.50	789907.00	170644.00	13019.00
	1460	342.12	576.59	340.50	109.26	288183.50	896923.00	190161.00	13308.00
	1340	343.27	578.81	341.68	109.32	305766.90	954864.00	200659.00	13442.30
	1180	345.42	582.94	343.89	109.43	344951.80	1083330.00	223969.00	13695.60
	1064	347.67	578.25	346.21	109.55	399971.40	1259200.00	257099.00	13966.30
C_{18}-$(CO)_4$	∞	376.19	412.73	595.16	120.69	283410.00	271930.00	788982.00	12478.70
	1907	380.39	417.33	602.94	120.89	334579.20	318593.00	937611.00	12842.80
	1460	383.45	420.70	608.63	121.03	382243.10	362373.00	1076190.00	13110.40
	1340	384.87	422.25	611.26	121.09	408306.70	386454.00	1151990.00	13234.50

	1180	387.52	425.17	616.18	121.21	466572.90	440607.00	1321460.00	13468.00
	1064	390.31	428.24	621.35	121.33	547269.40	515746.00	1555240.00	13715.90
C_{18}-$(CO)_6$	∞	418.83	562.00	562.00	132.50	370142.70	678033.00	678069.00	12259.40
	1907	423.92	569.53	569.53	132.70	445218.10	817928.00	817975.00	12594.50
	1460	427.66	575.07	575.07	132.84	516504.00	950892.00	950950.00	12840.10
	1340	429.40	577.65	577.65	132.91	555865.30	1024350.00	1024410.00	12953.80
	1180	432.66	582.48	582.48	133.03	644321.90	1189500.00	1189580.00	13167.00
	1064	436.11	587.59	587.59	133.15	765956.90	1416710.00	1416820.00	13391.40

Table S6. First hyperpolarizabilities of C_{18}-$(CO)_n$ (n = 2, 4, and 6) in zero-frequency limit ($\lambda = \infty$ nm) and under frequency-dependent fields (λ = 1907, 1460, 1340, 1180, and 1064 nm) calculated at CAM-B3LYP/aug-cc-pVTZ(-f,-d) level with higher quality grid (using *int=superfine* and *CPHF=grid=fine* keywords) than default

	field frequency (λ, in nm)	first hyperpolarizability (in au)			
		$\beta_{\text{vec}}(\lambda)$	$\beta_{xxx}(\lambda)$	$\beta_{yyy}(\lambda)$	$\beta_{zzz}(\lambda)$
C_{18}-$(CO)_2$	∞	1023.85	1037.76	0.00	0.00
	1907	1359.33	1323.68	0.00	0.00
	1460	1686.67	1599.22	0.00	0.00
	1340	1871.28	1753.18	0.00	0.00
	1180	2297.98	2104.76	0.00	0.00
	1064	2920.64	2603.99	0.00	0.00
C_{18}-$(CO)_4$	∞	1077.67	496.81	0.00	0.00
	1907	1408.60	698.29	0.00	0.00
	1460	1724.03	894.79	0.00	0.00
	1340	1897.96	1004.79	0.00	0.00
	1180	2286.66	1254.62	0.00	0.00
	1064	2811.87	1601.85	0.00	0.00
C_{18}-$(CO)_6$	∞	N/A[a]	540.18	0.00	0.00
	1907	N/A[a]	608.96	0.00	0.00
	1460	N/A[a]	667.70	0.00	0.00
	1340	N/A[a]	697.80	0.00	0.00
	1180	N/A[a]	760.26	0.00	0.00
	1064	N/A[a]	836.47	0.00	0.00

[a]Not available, because C_{18}-$(CO)_6$ has vanished dipole moment.

Table S7. Axial tensorial components of the (hyper)polarizabilities of C_{18}-$(CO)_n$ (n = 2, 4, and 6) obtained by FF method in static electric field

		polarizability (in au)			first hyperpolarizability (in au)			second hyperpolarizability (in au)		
		$\alpha_{xx}(\lambda=\infty)$	$\alpha_{yy}(\lambda=\infty)$	$\alpha_{zz}(\lambda=\infty)$	$\beta_{xxx}(\lambda=\infty)$	$\beta_{yyy}(\lambda=\infty)$	$\beta_{zzz}(\lambda=\infty)$	$\gamma_{xxxx}(\lambda=\infty)$	$\gamma_{yyyy}(\lambda=\infty)$	$\gamma_{zzzz}(\lambda=\infty)$
C_{18}-$(CO)_2$	-C_{18}	370.42	297.43	93.29	-420.90	1.04	0.35	379896.20	149597.40	12446.14
	-$(CO)_n$	191.97	36.26	16.08	1336.44	-0.02	0.03	252796.30	-1280.00	1087.29
	total	562.39	333.69	109.37	915.54	1.02	0.38	632692.50	148317.40	13533.43
C_{18}-$(CO)_4$	-C_{18}	279.78	247.53	89.25	-51.27	-0.09	0.31	204489.50	320261.60	11296.16
	-$(CO)_n$	131.71	345.03	31.94	502.25	0.79	0.06	60091.06	421705.30	2124.12
	total	411.49	592.56	121.19	450.99	0.70	0.37	264580.50	741967.00	13420.28
C_{18}-$(CO)_6$	-C_{18}	174.95	175.07	85.41	-621.41	-0.61	0.25	239010.50	238158.50	9597.75
	-$(CO)_n$	385.33	385.50	47.67	1085.08	-1.29	0.09	396974.20	397856.40	2817.42
	total	560.28	560.57	133.08	463.68	-1.90	0.35	635984.70	636014.90	12415.17

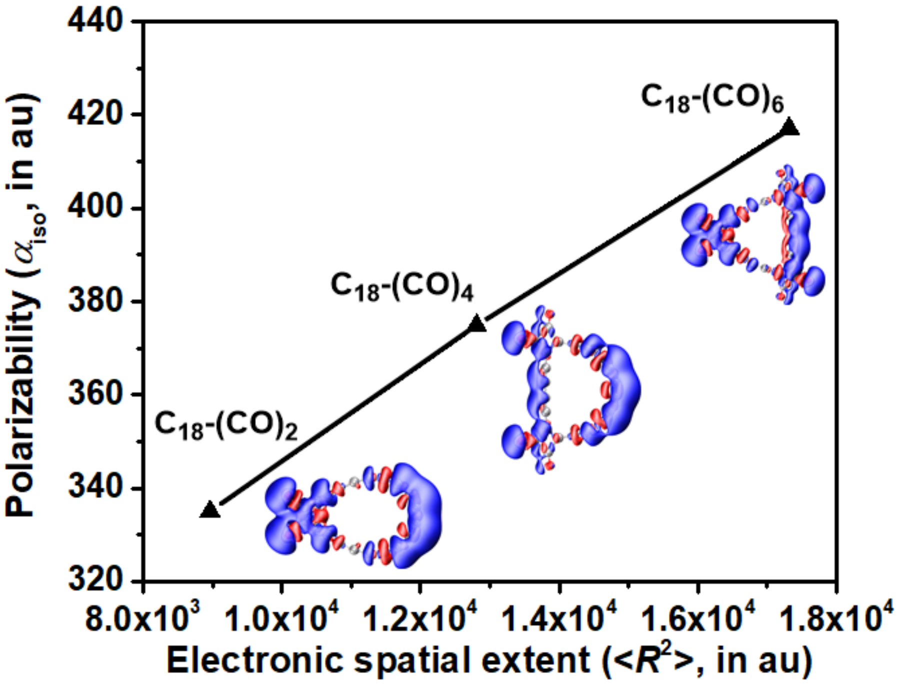


Figure S1. Relationship between the polarizabilities and the corresponding electronic spatial extents values of C_{18}-$(CO)_n$ (n = 2, 4, and 6).

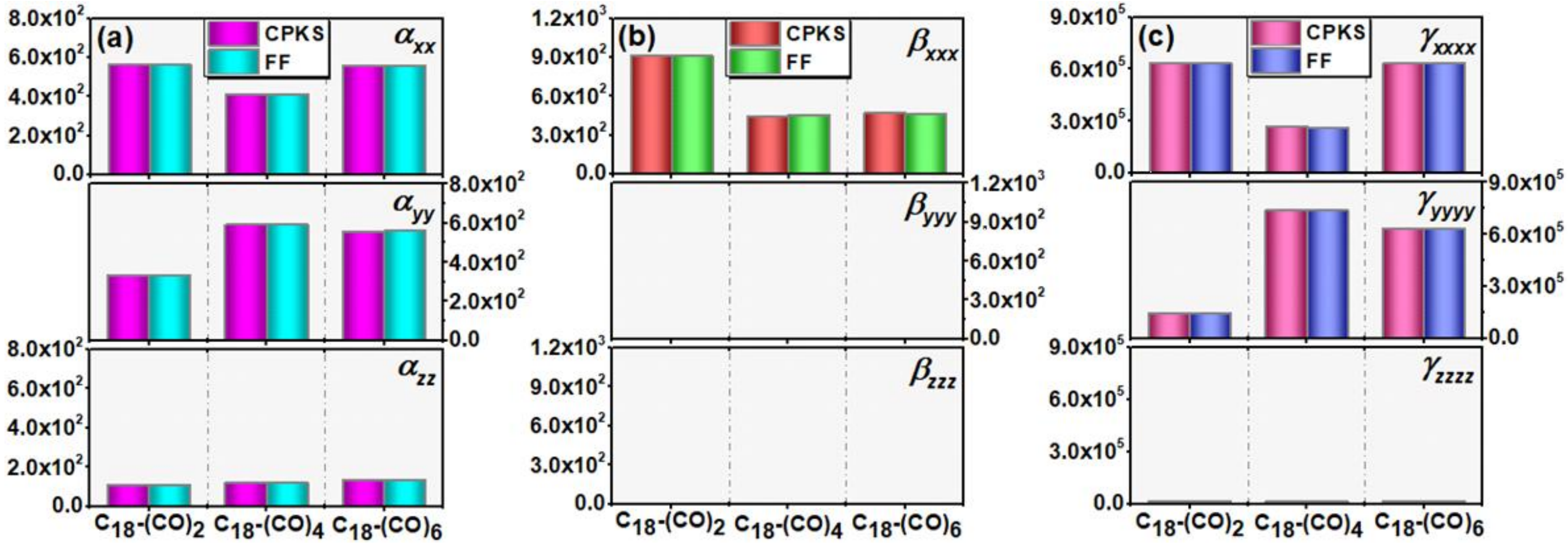


Figure S2. Tensorial components of the (hyper)polarizability for C_{18}-$(CO)_n$ (n = 2, 4, and 6) calculated by coupled-perturbed Kohn-Sham (CPKS) and finite field (FF, with step size of 0.0001 au) methods. The values of (hyper)polarizabilities are given in au.

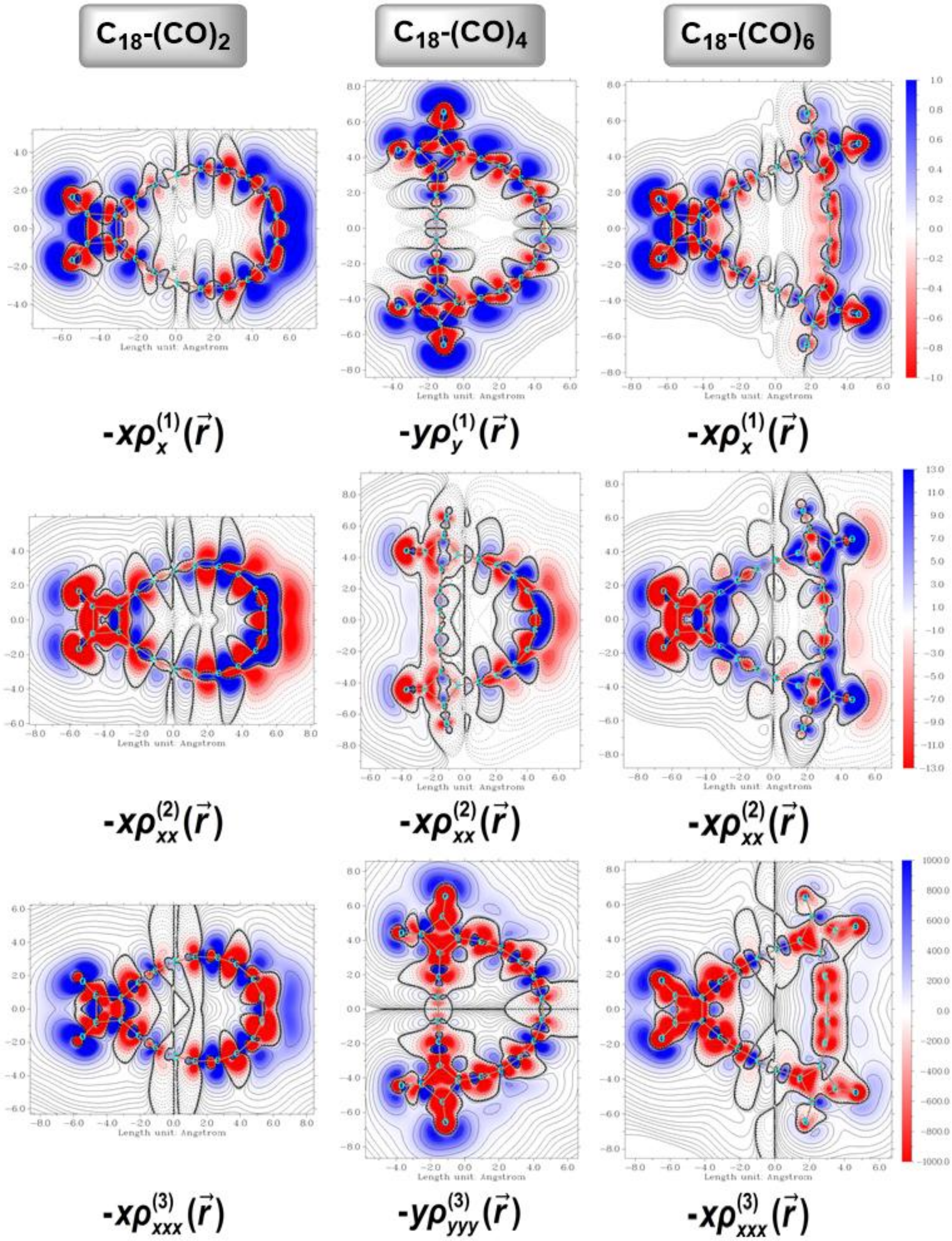


Figure S3. Color-filled contour maps on molecular plane (XY-plane) of the local contribution maps of (hyper)polarizabilities of C_{18}-$(CO)_n$ (n = 2, 4, and 6) in direction with their largest tensorial component in static electric field.

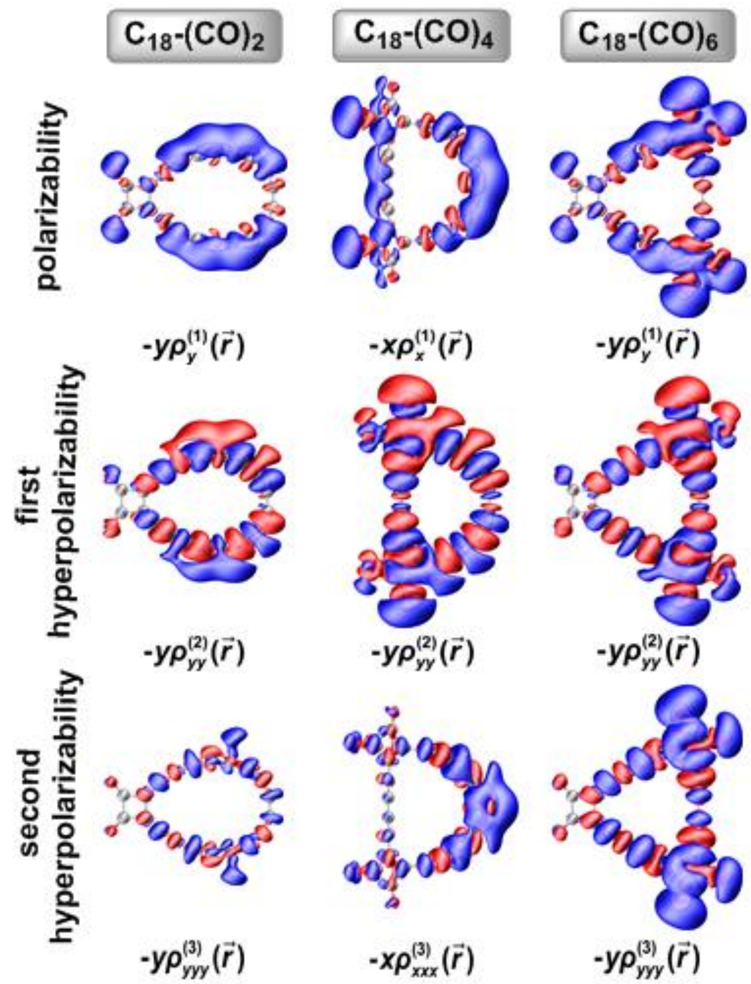


Figure S4. Local contribution maps of (hyper)polarizabilities of C_{18}-$(CO)_n$ (n = 2, 4, and 6) except the direction with their largest tensorial component on the molecular plane in static electric field. Blue and red isosurfaces represent positive and negative electron contributions, respectively. The isovalues of polarizabilities, first hyperpolarizabilities, and second hyperpolarizabilities are set to be 0.2, 2.5, and 200.0 au, respectively.

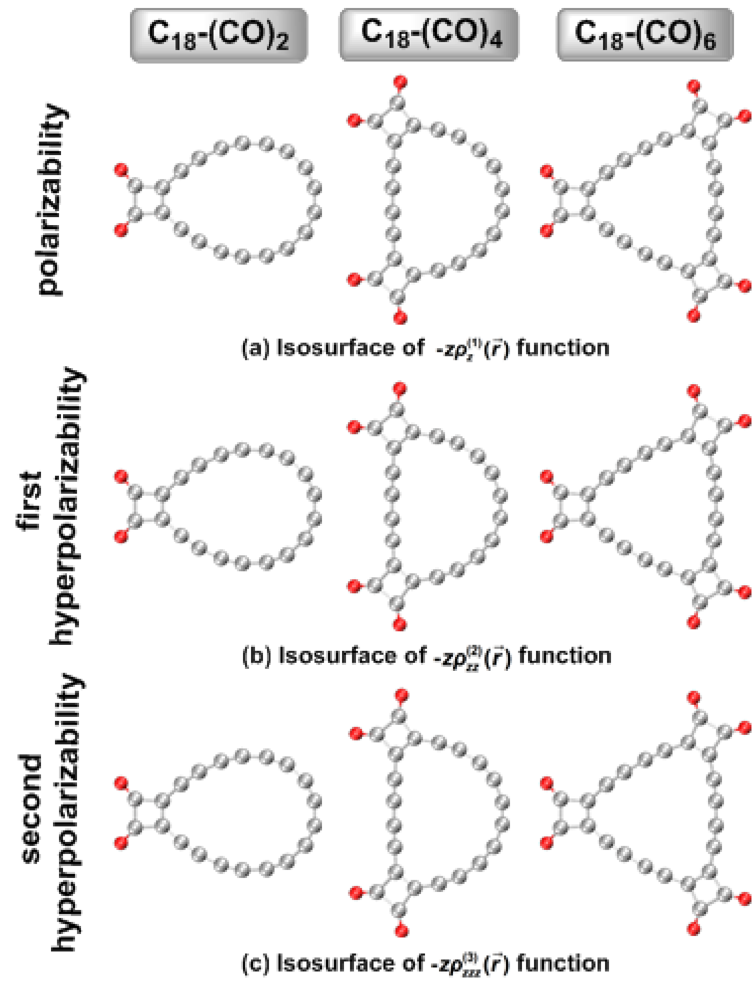
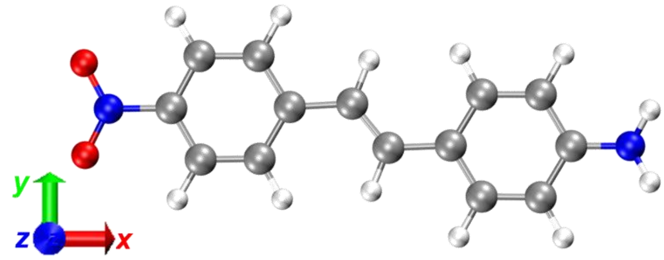


Figure S5. Local contribution maps of (hyper)polarizabilities of C_{18}-$(CO)_n$ (n = 2, 4, and 6) along Z-axis direction in static electric field. Blue and red isosurfaces represent positive and negative electron contributions, respectively. The isovalues of polarizabilities, first hyperpolarizabilities, and second hyperpolarizabilities are set to be 0.2, 2.5, and 200.0 au, respectively.

Table S8. Optimized geometric structure and Cartesian coordinates for *trans*-4-nitro-4'-aminostilbene ($C_{14}H_{12}N_2O_2$) at ωB97XD/def2-TZVP level. The values are given in Å



trans-4-nitro-4'-aminostilbene ($C_{14}H_{12}N_2O_2$)

charge = 0, spin multiplicity = 1			
atom	*x*	*y*	*z*
C	1.21697331	-0.42274085	-0.00261185
C	0.27169576	0.52163394	-0.00337193
C	-1.17431787	0.30071852	-0.00202494
C	-2.02176918	1.41293613	-0.00203153
C	-1.76219318	-0.96990915	-0.00062853
C	-3.39621998	1.27658280	-0.00044583
H	-1.58982652	2.40613252	-0.00335878
C	-3.13216306	-1.12372396	0.00096541
H	-1.14377119	-1.85703345	-0.00090190
C	-3.93656561	0.00433457	0.00114034
H	-4.04896257	2.13705611	-0.00044535
H	-3.58772346	-2.10308391	0.00202469
C	2.66334126	-0.22612363	-0.00370715
C	3.50121408	-1.34196375	-0.00425249
C	3.27631859	1.03029147	-0.00346940
C	4.87681825	-1.22315757	-0.00432648
H	3.06082491	-2.33269393	-0.00398502
C	4.64714525	1.16310226	-0.00395777
H	2.67286594	1.92913783	-0.00248673
C	5.47653526	0.03625182	-0.00295375
H	5.49599173	-2.11254845	-0.00888214
H	5.09162106	2.15164683	-0.00854657
N	-5.39411886	-0.15595596	0.00307888
N	6.85097701	0.17128956	-0.05248352
H	7.39017179	-0.62119360	0.24905142
H	7.22630285	1.05078142	0.25621163

O	-6.07294527	0.84963080	0.00332374
O	-5.83771228	-1.28533369	0.00464890
H	0.91233514	-1.46523356	-0.00123923
H	0.56654684	1.56592456	-0.00533536

Table S9. Polarizabilities and second hyperpolarizabilities of *trans*-4-nitro-4'-aminostilbene ($C_{14}H_{12}N_2O_2$) in zero-frequency limit ($\lambda = \infty$ nm) and under frequency-dependent fields (λ = 1907, 1460, 1340, 1180, and 1064 nm) calculated at ωB97XD/aug-cc-pVTZ(-f,-d) level with default quality grid

field frequency (λ, in nm)	polarizability (in au)				second hyperpolarizability (in au)			
	$\alpha_{\text{iso}}(\lambda)$	$\alpha_{xx}(\lambda)$	$\alpha_{yy}(\lambda)$	$\alpha_{zz}(\lambda)$	$\gamma_{\|\|}(\lambda)$	$\gamma_{xxxx}(\lambda)$	$\gamma_{yyyy}(\lambda)$	$\gamma_{zzzz}(\lambda)$
∞	235.48	418.88	184.77	102.80	378977.30	1818210.00	22075.40	19467.40
1907	238.21	426.18	185.45	103.00	481037.20	2327330.00	23047.90	20262.30
1460	240.22	431.60	185.93	103.14	580959.80	2826630.00	23791.30	20855.60
1340	241.16	434.13	186.15	103.20	636980.30	3106810.00	24145.10	21133.20
1180	242.93	438.90	186.56	103.32	764196.70	3743550.00	24827.60	21659.20
1064	244.80	443.97	186.98	103.44	940304.10	4625770.00	25576.10	22220.50

Table S10. First hyperpolarizabilities of *trans*-4-nitro-4'-aminostilbene ($C_{14}H_{12}N_2O_2$) in zero-frequency limit ($\lambda = \infty$ nm) and under frequency-dependent fields (λ = 1907, 1460, 1340, 1180, and 1064 nm) calculated at ωB97XD/aug-cc-pVTZ(-f,-d) level with default quality grid

field frequency (λ, in nm)	first hyperpolarizability (in au)			
	$\beta_{\mathrm{vec}}(\lambda)$	$\beta_{xxx}(\lambda)$	$\beta_{yyy}(\lambda)$	$\beta_{zzz}(\lambda)$
∞	8459.58	8778.72	-3.03	-3.24
1907	10369.87	10723.60	-1.39	-3.48
1460	12141.45	12525.40	0.02	-3.66
1340	13098.49	13498.20	0.73	-3.75
1180	15189.08	15622.10	2.20	-3.92
1064	17922.63	18397.40	3.94	-4.10