Electronic Supplementary Material (ESI) for RSC Advances.

Two-Photon Absorption and Two-Photon Circular Dichroism of Hexahelicene Derivatives: A Study of the Effect of the Nature of Intramolecular Charge Transfer.

Carlos Díaz,[1] Yuly Vesga,[1] Lorenzo Echevarria,[1,2] Irena G. Stará,[3] Ivo Starỳ,[3] Emmanuel Anger,[4] Chengshuo Shen,[4] Mehdi El Sayed Moussa,[4] Nicolas Vanthuyne,[5] Jeanne Crassous,[4] Antonio Rizzo,[6] Florencio E. Hernández [1,7,*]

[1] Department of Chemistry, University of Central Florida, P. O. Box 162366, Orlando, Florida 32816-2366, USA

[2] Departamento de Química, Universidad Simón Bolívar, Caracas 1020A, Venezuela

[3] Institute of Organic Chemistry and Biochemistry ASCR, Flemingovo nám. 2, CZ-166 10 Prague 6, Czech Republic

[4] Sciences Chimiques de Rennes UMR 6226 CNRS, Universitè de Rennes 1, 35042 Rennes Cedex, France

[5] Aix Marseille Université, Centrale Marseille, CNRS, iSm2 UMR 7313, 13397, Marseille, France

[6] CNR - Consiglio Nazionale delle Ricerche, Istituto per i Processi Chimico Fisici (IPCF-CNR), UOS di Pisa, Area della Ricerca, Via G. Moruzzi 1, I-56124 Pisa, Italy

[7]The College of Optics and Photonics, CREOL, University of Central Florida, P. O. Box 162366, Orlando, Florida 32816-2366, USA

* *Corresponding Authors:* florencio.hernandez@ucf.edu

Supporting Information

I. Theoretical and computational approaches

OPA spectra were calculated from f_{0f}, and reported in molar absorptivity (ε), [1, 2]

$$\varepsilon^{OPA}(\omega) = \frac{4\pi^2 \omega N_A}{3\times 1000 \times Ln(10)(4\pi\epsilon_0)\hbar c_0} \times \frac{3}{2\hbar}\sum_f g(\omega, \omega_{0f}, \Gamma)\frac{f_{0f}}{\omega_{0f}}, \quad (1)$$

$$\varepsilon^{OPA}(\omega) \approx 1.05495\times 10^3 \times \omega \sum_f g(\omega, \omega_{0f}, \Gamma)\frac{f_{0f}}{\omega_{0f}}, \quad (2)$$

where, $\omega = 2\pi c_0/\lambda$ is the circular frequency of the incident light (c_0 being the speed of light in *vacuo*) and $f_{0f} = \frac{2\mathrm{m}_e \omega_{0f}\left|\mu_{0f}\right|^2}{3\hbar \mathrm{e}^2}$.

ECD spectra were computed from R_{0f}^{ECD}, and reported in molar absorptivity difference ($\Delta\varepsilon$), [1-3]

$$\Delta\varepsilon^{ECD}(\omega) = \frac{64\pi^2 N_A \omega}{9\times 1000\times \ln(10)(4\pi\varepsilon_0)\hbar c_0^2}\sum_f g(\omega, \omega_{0f}, \Gamma)\cdot R_{0f}^{ECD}, \quad (3)$$

$$\Delta\varepsilon^{ECD}(\omega) \approx 2.73719\times 10^1 \times \omega \sum_f g(\omega, \omega_{0f}, \Gamma)\cdot R_{0f}^{ECD}, \quad (4)$$

where $R_{0f}^{ECD} = \frac{3}{4}\Im(\boldsymbol{\mu}_{ij}\cdot\mathbf{m}_{ij})$.

OPA and ECD spectra have units of $mol^{-1}cm^{-1}l$, as long as all the elements in Equations (2) and (4) are introduced in atomic units.

TPA spectra were obtained from [2, 4]

$$\delta^{TPA}(\omega) = \frac{1}{30}\frac{(2\pi)^3\omega^2}{c_0^2(4\pi\varepsilon_0)^2}\times\sum_f g(2\omega, \omega_{0f}, \Gamma)\cdot\bar{\delta}_{0f}^{TPA}(\omega_{0f}), \quad (5)$$

$$\delta^{TPA}(\omega) \approx 8.35150\times 10^{-4}\times\omega^2\sum_f g(2\omega, \omega_{0f}, \Gamma)\cdot\bar{\delta}_{0f}^{TPA}(\omega_{0f}), \quad (6)$$

where $\bar{\delta}_{0f}^{TPA}\left(\omega_{0f}\right)$ is the orientationally averaged two-photon probability for the degenerate case and is defined in terms of the molecular parameters A_1 and A_2,

$$\bar{\delta}_{0f}^{TPA}(\omega_{0f}) = F \times \mathcal{A}_1(\omega_{0f}) + \left(G + H\right) \times \mathcal{A}_2(\omega_{0f}), \tag{7}$$

$$\mathcal{A}_1(\omega_{0f}) = \sum_{\rho\sigma} \mathcal{S}_{\rho\rho}^{0f}(\omega_{0f}) \mathcal{S}_{\sigma\sigma}^{0f,*}(\omega_{0f}), \tag{8}$$

$$\mathcal{A}_2(\omega_{0f}) = \sum_{\rho\sigma} \mathcal{S}_{\rho\sigma}^{0f}(\omega_{0f}) \mathcal{S}_{\rho\sigma}^{0f,*}(\omega_{0f}), \tag{9}$$

here $\mathcal{S}_{ii}^{0f}$ refers to the two-photon transition matrix elements and F, G and H are scalars that define the polarization of the excitation. For linearly polarized light $F = G = H = 2$.

TPCD spectra were simulated according to, [2, 5, 6]

$$\Delta\delta^{TPCD}\left(\omega\right) = \frac{4}{15} \frac{(2\pi)^3 \omega^2}{c_0^3 (4\pi\varepsilon_0)^2} \times \sum_f g\left(2\omega, \omega_{0f}, \Gamma\right) \cdot R_{0f}^{TPCD}\left(\omega_{0f}\right), \tag{10}$$

$$\Delta\delta^{TPCD}\left(\omega\right) \approx 4.87555x10^{-5} \times \omega^2 \sum_f g\left(2\omega, \omega_{0f}, \Gamma\right) \cdot R_{0f}^{TPCD}\left(\omega_{0f}\right), \tag{11}$$

where $R_{0f}^{TPCD}\left(\omega_{0f}\right)$ was obtained from,

$$R_{0f}^{TPCD}\left(\omega_{0f}\right) = -b_1 \mathcal{B}_1(\omega_{0f}) - b_2 \mathcal{B}_2(\omega_{0f}) - b_3 \mathcal{B}_3(\omega_{0f}) \tag{12}$$

here b_1, b_2 and b_3 are scalars that depend on the experiment. In the double L-scan setup[7] two co-linear right or left circularly polarized photons traveling in the same direction are employed, for such conditions $b_1 = 6$ and $b_2 = -b_3 = 2$. The molecular parameters $\mathcal{B}_i(\omega_{0f})$ were obtained from,

$$\mathcal{B}_1^{TI}(\omega_{0f}) = \frac{8}{\omega_{0f}^3}\sum_{\rho\sigma}\mathcal{M}_{\rho\sigma}^{p,0f}(\omega_{0f})\mathcal{P}_{\rho\sigma}^{p*,0f}(\omega_{0f}) \quad (13)$$

,

$$\mathcal{B}_2^{TI}(\omega_{0f}) = \frac{4}{\omega_{0f}^3}\sum_{\rho\sigma}\mathcal{T}_{\rho\sigma}^{+,0f}(\omega_{0f})\mathcal{P}_{\rho\sigma}^{p*,0f}(\omega_{0f}) \quad (14)$$

,

$$\mathcal{B}_3^{TI}(\omega_{0f}) = \frac{8}{\omega_{0f}^3}\sum_{\rho\sigma}\mathcal{M}_{\rho\rho}^{p,0f}(\omega_{0f})\mathcal{P}_{\sigma\sigma}^{p*,0f}(\omega_{0f}) \quad (15)$$

,

where $\mathcal{P}_{ii}^{p*,0f}$ and $\mathcal{T}_{ii}^{+,0f}$ are the electric transition dipole and quadrupole matrix elements in the velocity formulation, respectively, and $\mathcal{M}_{ii}^{p,0f}$ is the magnetic transition dipole matrix element. TPA and TPCD spectra obtained from Equations (6) and (11) are given in Göppert-Mayer units (GM), i.e., 10^{-50} cm^4·s·molecule^{-1}·photon^{-1}, as long as all the equation elements are introduced in atomic units.

In order to obtain the corresponding theoretical linear and nonlinear spectra of all the helicene derivatives we used normalized Lorentzian lineshape functions $g\left(\omega,\omega_{0f},\Gamma\right)$, $g\left(2\omega,\omega_{0f},\Gamma\right)$ for the one- and two-photon cases respectively, centered on the computed excitation circular frequency ω_{0f} for a $0\rightarrow f$ transition. All the OPA and ECD spectra were obtained using a linewidth (Γ) of 0.5 eV (FWHM). For the TPA and TPCD spectra a value of Γ = 0.15 eV (FWHM) was used.

II. OPA, ECD, TPA and TPCD spectra of A6 and CN6 calculated with B3LYP

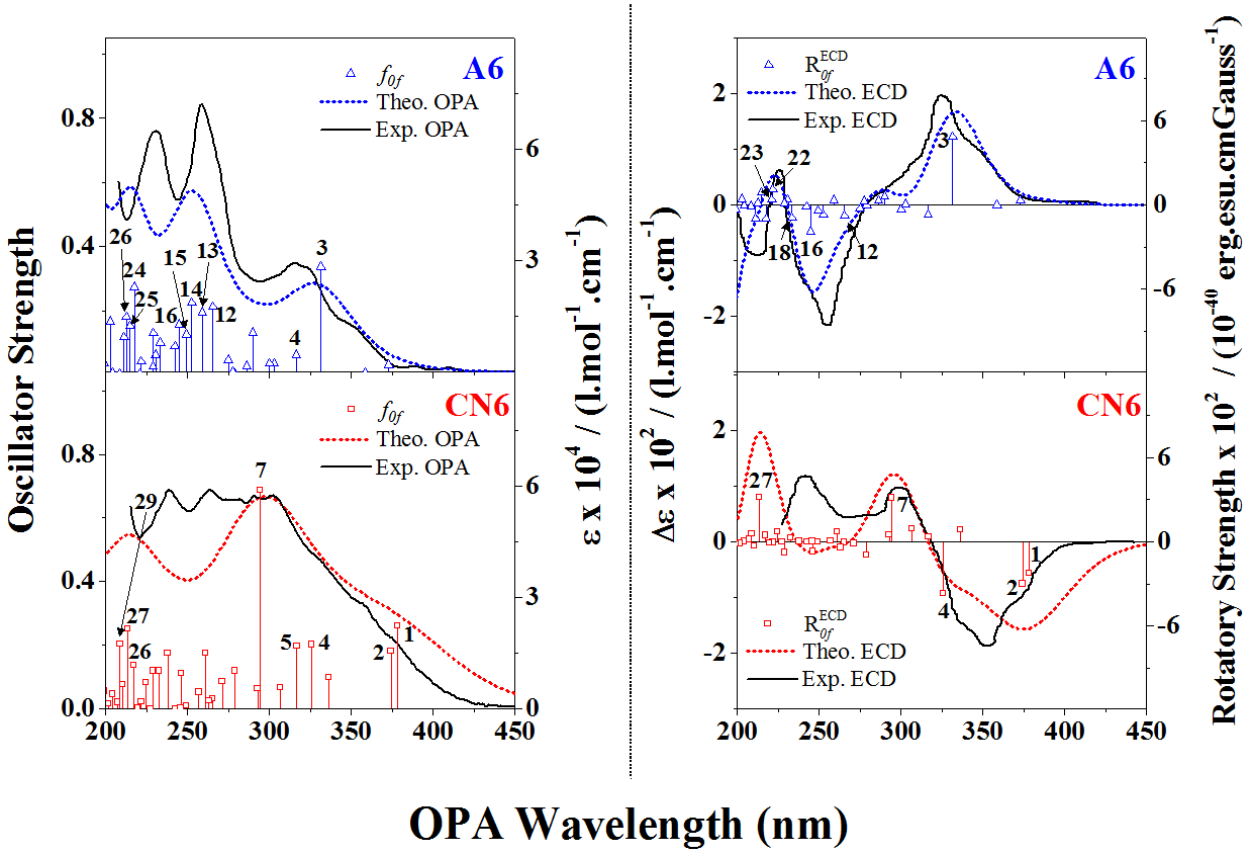

Figure SI-1. Experimental (black solid line) and theoretical (colored dotted lines) UV-*vis* (left column) and ECD (right column) spectra of A6 and CN6. Colored empty symbols display the oscillator strengths for each molecule. OPA for the lowest 60 electronic excited states were computed at the B3LYP/6-31G(d) level of theory using Gaussian 09 in THF using PCM. The theoretical spectra are only shown within the measurable spectral range (200 nm through 450 nm) with spectral shifts: A6 (-11 nm) and CN6 (-35 nm). Γ = 0.5 eV (FWHM) was used for all the spectra. Excited states contributing to 20 % or more of the total intensity of prominent spectral features observed in the theory and the experiment are highlighted. All the experimental spectra were taken in THF solutions.

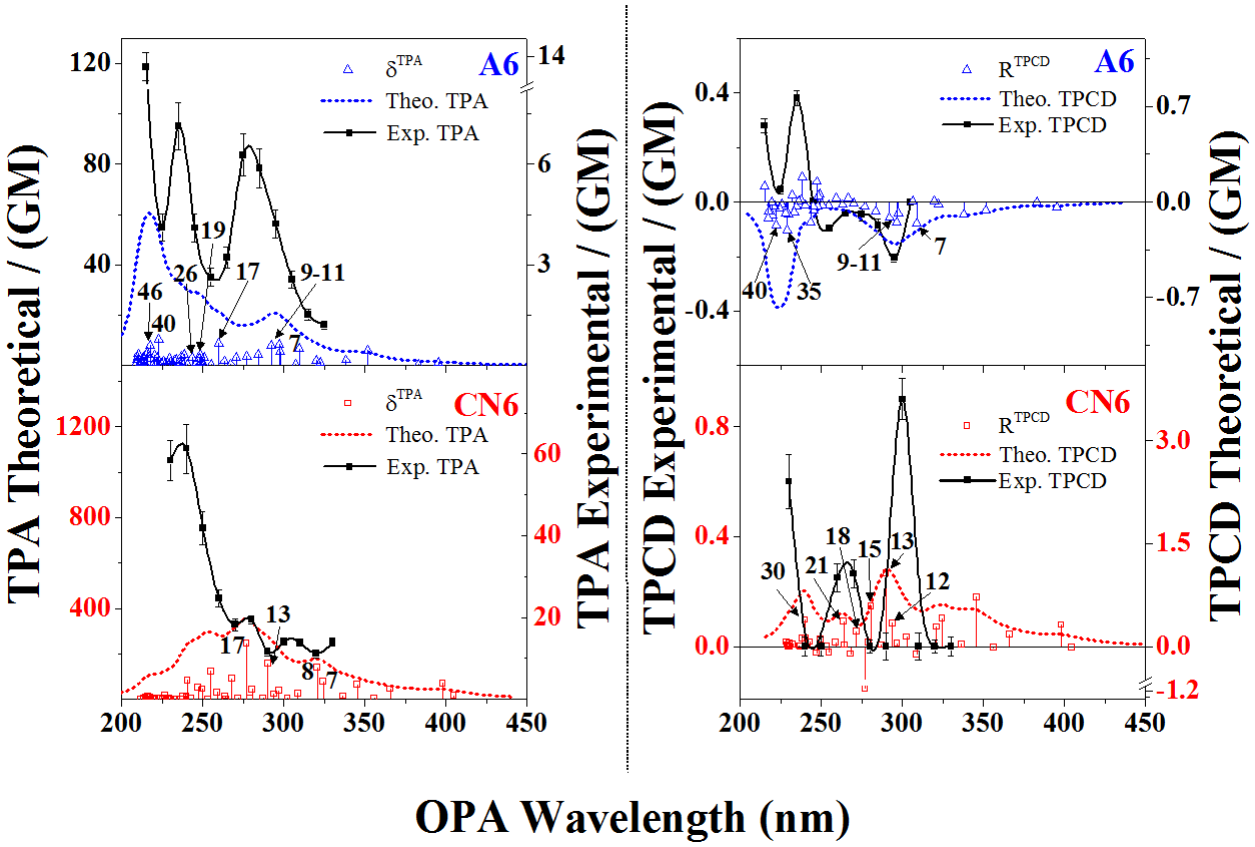

Figure SI-2. Experimental (black scattered squares) and theoretical TPA (left column) and TPCD (right column) spectra of A6 and CN6 calculated *in vacuo* using Dalton 2011. TPA was computed for the first 60 electronic excited states (colored scattered symbols) for both molecules. TPCD was computed for the first 48 and 40 electronic excited states (colored scattered symbols) for A6 and CN6, respectively. The Lorentzian convolution (colored dotted lines) was obtained using a linewidth $\Gamma = 0.15$ eV (FWHM). The theoretical spectra were calculated with B3LYP/ aug-cc-pVDZ for A6, and B3LYP/ 6-311++G(d,p) for CN6.. The theoretical spectral shifts are: A6 (0 nm) and CN6 (-10 nm). Excited states contributing to 20 % or more of the total intensity of prominent spectral features observed in the theory and the experiment are highlighted. All the experimental spectra were taken in THF solutions.

III. ASSIGNMENT OF THEORETICAL TRANSITIONS TO EXPERIMENTAL BANDS

Tables 1.a and 1.b. Assignment of theoretical (B3LYP and CAM-B3LYP) excited states (E.S.) to experimental (Exp.) bands. Only E.S. contributing to 20 % or more of the total intensity of the corresponding bands are shown. Tables for A6 and CN6 are labeled 1.a and 1.b, respectively. Each table contains data for the OPA, ECD, TPA and TPCD spectra of the corresponding helicenes. The theoretical OPA wavelengths are shown with the corresponding spectral shift (see figure captions of the corresponding spectra for the exact value of the spectral shifts) ($\boldsymbol{\lambda^{MAX}}$ = OPA wavelength of the corresponding band for its maximum amplitude, ***E.S*** = Excited State Number, $\boldsymbol{\varepsilon}$ = molar absorptivity in $l.mol^{-1}.cm^{-1}$, $\boldsymbol{\Delta\varepsilon}$ = difference in molar absorptivity in $l.mol^{-1}.cm^{-1}$, $\boldsymbol{f}$ = oscillator strength, $\boldsymbol{R^{ECD}}$ = rotatory strength in 10^{-40} erg.esu.cm.Gauss^{-1}, ***TPA*** = two-photon absorption cross-section in GM, ***TPCD*** = two-photon circular dichroism in GM, $\boldsymbol{\delta^{TPA}}$ = two-photon probability in GM, $\boldsymbol{R^{TPCD}}$ = two-photon circular dichroism rotatory strength in GM)

1.a (A6)	**Exp.**	**B3LYP**		**CAM-B3LYP**	
	λ^{MAX} (ε)	λ^{MAX} (ε)	*E.S. (f)*	λ^{MAX} (ε)	*E.S. (f)*
OPA Bands	321 (28,310)	328 (23,870)	3 (0.34) 4 (0.06)	310 (32,040)	3 (0.50) 5 (0.25) 6 (0.13)
	259 (72,160)	252 (48,860)	12 (0.21) 13 (0.20) 14 (0.23) 15 (0.13) 16 (0.16)	257 (87,390)	9 (0.23) 11 (0.24) 13 (0.19) 14 (0.48) 15 (0.32) 16 (0.26)
	230 (64,780)	215 (49,940)	24 (0.27) 25 (0.15) 26 (0.18)	220 (40,160)	22 (0.25) 25 (0.18)

	Exp.	**B3LYP**		**CAM-B3LYP**	
	λ^{MAX} ($\Delta\varepsilon$)	λ^{MAX} ($\Delta\varepsilon$)	*E.S.* (R^{ECD})	λ^{MAX} ($\Delta\varepsilon$)	*E.S.* (R^{ECD})
ECD (+) Bands	325 (207)	334 (168)	3 (4.87)	328 (188)	3 (7.35)
	225 (70)	223 (53)	22 (1.10) 23 (0.89)	227 (52)	19 (1.88) 21 (1.22)
ECD (-) Bands	256 (-225)	246 (-155)	12 (-0.77) 16 (-1.91) 18 (-0.94)	247 (-144)	8 (-1.07) 9 (-1.03) 15 (-1.95) 16 (-2.60)

	Exp.	**B3LYP**		**CAM-B3LYP**	
	λ^{MAX} (*TPA*)	λ^{MAX} (*TPA*)	*E.S.* (δ^{TPA})	λ^{MAX} (*TPA*)	*E.S.* (δ^{TPA})
TPA Bands	280 (6.50)	295 (21.0)	7 (6.66) 9 (5.51) 10 (8.36) 11 (8.14)	292 (42.6)	9 (16.16) 12 (9.17) 13 (10.46) 14 (9.13)
	235 (7.13)	247 (29.2)	17 (8.76) 19 (3.17) 21 (4.46) 23 (2.81) 26 (3.15)	234 (93.2)	26 (3.97) 28 (6.04) 29 (5.44) 35 (4.43) 45 (14.03) 55 (10.02)
	215 (13.4)	216 (60.6)	40 (10.44) 46 (8.04)	-	-

	Exp.	**B3LYP**		**CAM-B3LYP**	
	λ^{MAX} (*TPCD*)	λ^{MAX} (*TPCD*)	*E.S.* (R^{TPCD})	λ^{MAX} (*TPCD*)	*E.S.* (R^{TPCD})
TPCD (+) Bands	235 (0.76)	-	-	237 (0.13)	44 (0.07) 48 (0.03)
TPCD (-) Bands	295 (-0.41)	295 (-0.15)	7 (-0.08) 9 (-0.04) 10 (-0.08) 11 (-0.06)	293 (-0.43)	9 (-0.18) 12 (-0.12) 13 (-0.11)
	250 (-0.20)	225 (-0.38)	35 (-0.10) 40 (-0.09)	249 (-0.10)	33 (-0.06) 34 (-0.08)

1.b (CN6)	Exp.	B3LYP		CAM-B3LYP	
	λ^{MAX} (ε)	λ^{MAX} (ε)	E.S. (*f*)	λ^{MAX} (ε)	E.S. (*f*)
OPA Bands	333 (39,127)	376 (25,962)	1 (0.26) 2 (0.18)	345 (40,810)	1 (0.25) 2 (0.42)
	280 (56,205)	297 (57,230)	4 (0.20) 5 (0.20) 7 (0.69)	297 (67,290)	3 (0.23) 4 (0.80) 5 (0.23) 6 (0.19) 7 (0.28)
	210 (76,345)	215 (46,940)	26 (0.14) 27 (0.25) 29 (0.20)	222 (55,016)	20 (0.21) 21 (0.25) 22 (0.33)

	Exp.	B3LYP		CAM-B3LYP	
	λ^{MAX} (Δε)	λ^{MAX} (Δε)	E.S. (R^{ECD})	λ^{MAX} (Δε)	E.S. (R^{ECD})
ECD (+) Bands	305 (103)	295 (121)	7 (3.13)	296 (206)	4 (4.94) 5 (1.65)
	246 (130)	214 (197)	27 (3.18)	220 (148)	21 (1.23) 22 (3.59)
ECD (-) Bands	353 (-180)	376 (-157)	1 (-2.24) 2 (-3.00) 4 (-3.66)	345 (-254)	1 (-3.13) 2 (-4.73) 3 (-2.47)

	Exp.	B3LYP		CAM-B3LYP	
	λ^{MAX} (TPA)	λ^{MAX} (TPA)	E.S. (δ^{TPA})	λ^{MAX} (TPA)	E.S. (δ^{TPA})
TPA Bands	306 (14.9)	320 (178.8)	7 (77.79) 8 (139.1)	298 (196.8)	8 (155.34)
	280 (20.5)	278 (354.0)	13 (157.8) 17 (245.5)	-	-
	237 (62.5)	-	-	256 (1208.8)	19 (699.0)

	Exp.	B3LYP		CAM-B3LYP	
	λ^{MAX} (TPCD)	λ^{MAX} (TPCD)	E.S. (R^{TPCD})	λ^{MAX} (TPCD)	E.S. (R^{TPCD})
TPCD (+) Bands	300 (1.80)	290 (1.12)	12 (0.34) 13 (1.06) 15 (0.58)	297 (1.35)	8 (1.13)
	265 (0.70)	262 (0.48)	18 (0.22) 21 (0.36)	257 (3.51)	18 (1.80) 20 (1.20) 21 (1.08)
	230 (1.20)	238 (0.82)	30 (0.39)	237 (2.62)	32 (0.55) 33 (0.97)

IV. RAW THEORETICAL DATA

Tables A6-1, A6-2, CN6-1 and CN6-2. Raw data for the B3LYP and CAM-B3LYP calculations for OPA, ECD, TPA and TPCD for A6 and CN6. The tables labeled as X-1 contain the oscillator strength (*f*) and the rotatory strength (R^{ECD}) for all the calculated excited states of the helicene "X". The tables labeled as X-2 contain the two-photon probability (δ^{TPA}) and the two-photon circular dichroism rotatory strength (R^{TPCD}) for all the calculated excited states of the helicene "X". The OPA wavelength (λ) is used for excited states in all the X-1 and X-2 tables. The units used are shown in the corresponding header of each column except for the case of R^{ECD} were the units are10^{-40} erg.esu.cm.Gauss^{-1}. Calculations of the values in tables X-1 were performed in Gaussian 09 while those in tables X-2 were performed in Dalton 2011.

A6-1	**B3LYP/6-31G(d)**			**CAM-B3LYP/6-31G(d)**		
Excited State	**λ (nm)**	***f***	R^{ECD}	**λ (nm)**	***f***	R^{ECD}
1	383.8493	0.0299	31.9944	362.4670	0.0201	21.1000
2	369.6361	0.0049	-2.0448	344.0547	0.0138	11.8000
3	342.4481	0.3370	486.5820	324.4329	0.5044	735.0000
4	327.5303	0.0615	-71.6155	305.2487	0.0253	4.5325
5	313.9852	0.0358	6.2104	298.0082	0.2504	-317.8760
6	311.0080	0.0347	-33.2799	294.5789	0.1289	-56.0258
7	300.8720	0.1321	61.1488	288.0257	0.0651	96.1980
8	297.1440	0.0276	28.8598	271.9679	0.0999	-107.1200
9	290.1213	0.0018	-0.4479	264.6685	0.2278	-103.1310
10	288.6018	0.0104	26.2499	262.8047	0.1319	7.4937
11	285.9658	0.0459	-27.0694	261.2315	0.2399	-24.3476
12	276.5140	0.2120	-76.5799	259.7527	0.0329	2.5996
13	270.1751	0.1952	34.7556	256.7857	0.1923	-50.7176
14	263.5476	0.2252	-71.8864	255.8129	0.4874	109.0203
15	260.3543	0.1257	-41.6449	247.5717	0.3210	-195.0000
16	255.9577	0.1564	-190.6840	242.3518	0.2604	-258.9580
17	253.1512	0.0897	-11.3075	235.7095	0.0367	25.1375
18	244.3070	0.1006	-93.6114	231.6334	0.0108	7.3625
19	241.5228	0.0617	38.5629	228.3228	0.0904	187.7094
20	240.1149	0.1302	14.7367	226.5666	0.0498	6.6348
21	239.8362	0.0254	13.3179	225.1482	0.1098	121.6693
22	232.6753	0.0421	109.9029	221.0595	0.2485	-28.2072
23	232.0048	0.0043	36.1537	219.2853	0.0166	10.3000
24	228.5660	0.2731	-98.3775	216.5961	0.0186	10.9512
25	225.7896	0.1516	89.3951	216.2631	0.1753	-203.2640
26	223.5747	0.1810	12.1399	213.4580	0.0633	-48.2560
27	222.1287	0.1179	-100.3100	212.5297	0.0953	-81.8469
28	219.4007	0.0042	-10.3609	210.5179	0.0255	-18.9000
29	215.2563	0.0070	-4.7123	207.7170	0.0082	18.6838
30	213.8197	0.1656	42.1417	206.0411	0.0225	3.4196

A6-1 (cont.)	B3LYP/6-31G(d)			CAM-B3LYP/6-31G(d)		
Excited State	**λ (nm)**	***f***	R^{ECD}	**λ (nm)**	***f***	R^{ECD}
31	210.0736	0.0371	-34.8616	203.2013	0.0171	30.3746
32	208.6629	0.1100	-105.9810	201.1219	0.0365	4.3316
33	206.1819	0.2459	-161.5840	200.0435	0.0850	79.8726
34	205.1821	0.0582	-46.1860	199.1278	0.1317	17.2864
35	204.7247	0.0619	5.6543	198.0091	0.1569	-79.4301
36	203.4982	0.0433	-0.8139	197.8023	0.0857	13.2392
37	201.9931	0.0095	46.4539	196.5968	0.0726	34.6459
38	201.5563	0.0070	-19.2163	195.8853	0.0147	25.7737
39	200.2897	0.0289	21.7335	194.8757	0.0180	-14.8585
40	199.7540	0.0213	-21.4638	194.5998	0.0734	2.1300
41	198.4781	0.0624	-16.4580	193.5635	0.0534	15.4218
42	197.2812	0.0443	4.0291	192.8858	0.0255	-10.3269
43	196.4528	0.0971	-14.0167	191.9030	0.0288	14.6782
44	194.9056	0.0775	-19.9429	190.8819	0.0392	2.2263
45	194.1760	0.0168	3.8906	189.5522	0.0017	-8.7754
46	193.4097	0.0268	25.2834	188.3321	0.0337	-5.6122
47	192.1716	0.0047	12.5531	188.2430	0.1312	42.7722
48	190.4360	0.0239	-15.6655	187.0394	0.0299	-14.9016
49	189.7830	0.0306	31.8045	186.5592	0.0523	2.0942
50	188.2071	0.0300	29.6835	185.3045	0.0498	-28.8560
51	187.1051	0.0868	10.3974	185.1482	0.0096	5.3992
52	184.8428	0.0389	31.4701	182.9901	0.0487	24.6249
53	183.9980	0.0308	-11.9482	182.8360	0.0190	9.8560
54	182.5728	0.1364	35.8981	182.4967	0.0546	16.1728
55	181.8097	0.0019	4.1482	180.9609	0.0190	6.0398
56	181.2225	0.0590	130.7983	180.7126	0.1324	-55.4119
57	180.3027	0.0635	37.7378	179.4395	0.0290	13.7060
58	179.8841	0.0211	29.9612	178.5019	0.0431	22.6407
59	178.6581	0.0540	-33.2511	176.8496	0.0568	-7.8536
60	178.3702	0.0574	10.4427	175.7893	0.0406	-12.9415

A6-2	B3LYP/aug-ccpVDZ			CAM-B3LYP/aug-cc-pVDZ		
Excited State	λ (nm)	δ^{TPA} (GM)	R^{TPCD} (GM)	λ (nm)	δ^{TPA} (GM)	R^{TPCD} (GM)
1	394.8543	1.27000	-0.01929	351.2301	0.14782	-0.00270
2	382.6674	0.55496	-0.00102	334.1893	0.39210	-0.00030
3	351.2301	5.93794	-0.03153	310.7374	1.85404	-0.00907
4	337.8317	2.20480	-0.04397	293.1070	0.69526	-0.00797
5	322.0370	1.21139	-0.00863	286.3377	0.32696	0.00007
6	319.5470	2.05448	0.00281	282.4242	0.50485	-0.00793
7	309.1876	6.66452	-0.07773	276.1342	0.08506	-0.00366
8	306.8917	0.47980	0.00180	259.9250	5.01092	-0.04873
9	297.3243	5.51201	-0.04130	252.0005	16.16021	-0.18182
10	296.6130	8.35570	-0.07505	249.4653	3.41995	-0.05208
11	291.7276	8.14274	-0.05743	248.4654	0.51988	-0.01182
12	283.7168	4.53000	-0.03320	247.4735	9.16998	-0.12015
13	276.7505	3.54522	-0.01721	243.5840	10.46029	-0.10813
14	270.1182	3.34479	-0.00426	241.2145	9.13240	-0.04457
15	266.6328	0.62261	0.01411	233.4920	4.72279	0.01242
16	262.6785	1.77888	-0.01046	228.7532	1.40306	-0.01530
17	259.3813	8.75658	0.01282	227.9122	1.01346	-0.03824
18	254.5878	0.45975	-0.01210	223.7983	1.00344	-0.01116
19	250.4732	3.16941	-0.01231	222.1940	2.41777	0.00905
20	248.9643	1.60349	0.02837	221.4004	0.48731	0.00459
21	247.9685	4.45972	0.02239	217.8985	7.64165	-0.01487
22	247.9685	1.02473	-0.01556	216.7557	0.58502	0.00143
23	247.4735	2.81864	0.07415	216.0004	4.19664	0.02102
24	245.5133	1.12620	-0.03143	215.6248	1.34042	-0.01469
25	245.0281	0.53116	-0.01577	213.7659	0.52615	-0.00122
26	243.1064	3.15688	-0.07519	212.3018	3.97115	0.01664
27	240.2795	0.47478	-0.01202	210.4996	0.34701	0.02074
28	237.9736	4.52235	0.09125	209.4328	6.03816	-0.00151
29	237.5177	0.38960	0.00708	209.0797	5.43685	-0.03276
30	236.1605	3.80830	0.00249	206.6404	1.55338	0.00835
31	234.8186	1.09113	-0.01735	206.2966	0.34575	0.01981
32	233.0531	2.56000	-0.03841	205.6123	0.63513	0.01016
33	232.1802	1.89162	0.02551	204.9326	1.60349	-0.05550
34	229.6004	1.39053	-0.04503	202.9202	1.19510	-0.07543
35	229.1760	2.68084	-0.10427	202.5886	4.43466	-0.02056
36	227.9122	0.90447	-0.04254	201.2731	2.76853	0.04818
37	226.6622	0.76792	-0.01408	199.9746	1.74129	-0.01044
38	225.4259	1.71624	-0.00904	199.3316	0.64891	0.00664
39	224.2030	0.87065	-0.02497	198.6927	0.36454	0.03203
40	222.1940	10.43523	-0.08556	197.7420	0.67021	-0.00776

A6-2 (cont.)	B3LYP/aug-ccpVDZ			CAM-B3LYP/aug-cc-pVDZ		
Excited State	**λ (nm)**	**δ^{TPA} (GM)**	**R^{TPCD} (GM)**	**λ (nm)**	**δ^{TPA} (GM)**	**R^{TPCD} (GM)**
41	221.4004	3.34479	-0.01526	197.4271	2.14217	0.00976
42	220.6125	0.94080	-0.01627	195.8677	0.68274	0.00567
43	219.8302	4.20917	-0.04847	194.6377	3.58281	-0.03247
44	219.4411	1.20763	0.00057	193.4232	3.73313	0.07446
45	217.5162	2.79359	-0.03416	193.1219	14.03057	-0.00135
46	217.1353	8.04252	-0.02958	191.3337	2.10459	0.01111
47	215.2504	5.22388	-0.05972	191.0389	1.65360	0.00315
48	214.8774	4.37203	0.05850	190.4520	4.15906	0.03409
49	214.1351	0.82805		189.8687	3.47006	
50	213.0313	1.39053		189.2889	2.40524	
51	212.6659	3.36000		188.4259	5.73750	
52	211.9389	1.55338		188.1400	2.95644	
53	211.9389	1.18000		187.5707	1.65360	
54	211.5772	1.08987		186.7233	6.85243	
55	210.4996	0.65392		186.1625	10.02183	
56	210.1428	0.26057		185.6052	0.40338	
57	209.7872	4.59752		185.3277	0.68900	
58	209.4328	3.38237		184.7753	3.38237	
59	209.0797	2.19228		183.9529	3.84588	
60	208.3769	0.95207		183.6804	3.95862	

CN6-1	B3LYP/6-31G(d)			CAM-B3LYP/6-31G(d)		
Excited State	λ (nm)	*f*	R^{ECD}	λ (nm)	*f*	R^{ECD}
1	413.0850	0.2605	-224.3103	351.6360	0.2496	-312.7565
2	409.1859	0.1810	-299.9886	344.9155	0.4168	-473.1605
3	371.1743	0.0971	85.7189	322.0681	0.2257	-246.6560
4	360.8783	0.2014	-366.2307	300.6531	0.7991	493.8419
5	351.7457	0.1961	36.5134	297.9581	0.2256	165.2079
6	341.7402	0.0654	94.7993	284.6200	0.1934	73.0071
7	329.4188	0.6885	313.0046	277.1630	0.2828	-12.1014
8	327.7208	0.0625	49.0672	267.5168	0.0530	-31.1877
9	313.9852	0.1182	-92.8447	263.3293	0.2926	14.8910
10	306.1922	0.0860	-12.0795	257.1788	0.0150	-31.2452
11	300.1945	0.0314	-2.4993	254.8947	0.2557	64.4046
12	297.9939	0.0246	-40.2860	254.0798	0.0048	0.0757
13	295.8818	0.1746	70.3055	251.5232	0.0094	-0.4300
14	291.8148	0.0515	8.4334	247.1806	0.1085	15.4467
15	284.3655	0.0084	-2.0336	242.2165	0.1551	-0.5010
16	281.2306	0.1099	-67.8264	239.2669	0.1247	-31.3011
17	280.7403	0.0015	3.7972	234.7236	0.1096	46.8440
18	277.4732	0.0002	-0.1544	231.3165	0.1365	127.5695
19	272.8326	0.1737	4.2144	226.5902	0.0597	-6.2689
20	267.5976	0.1181	27.9440	223.8370	0.2096	-181.0844
21	263.7719	0.1192	-76.3986	222.6193	0.2537	122.6683
22	262.2598	0.0001	0.0116	218.1883	0.3364	359.3828
23	259.4228	0.0822	73.3694	217.5223	0.0267	-75.6681
24	256.6837	0.0211	-3.2626	213.6060	0.0481	59.9085
25	254.6434	0.0028	-5.8270	208.9407	0.1847	-7.0017
26	251.9526	0.1362	46.0876	206.6217	0.0348	-26.3946
27	248.5084	0.2505	317.5084	206.3431	0.0022	-8.5636
28	245.4095	0.0755	-28.9192	204.7924	0.0521	-49.7379
29	243.6588	0.2041	55.8883	204.3434	0.0752	40.4847
30	242.1597	0.0198	17.9935	201.8352	0.0158	-30.6210
31	239.3131	0.0449	2.7475	199.1444	0.0062	-3.9081
32	236.5011	0.0154	-11.7069	198.2750	0.0275	-4.1987
33	233.8999	0.0553	-14.5338	197.3786	0.1346	-26.9690
34	233.5651	0.0599	7.3640	196.6023	0.0078	13.1800
35	232.0786	0.0127	4.4386	194.4898	0.0247	22.8200
36	230.7268	0.0001	0.0342	193.0032	0.0734	118.3548
37	230.4694	0.0084	2.4079	192.4072	0.0592	22.4782
38	228.2714	0.0099	-41.8456	191.1170	0.0016	-1.2014
39	226.8680	0.0022	0.6319	189.8702	0.0260	23.4941
40	226.4784	0.0787	-22.9982	188.7860	0.0050	1.7189

CN6-1 (cont.)	B3LYP/6-31G(d)			CAM-B3LYP/6-31G(d)		
Excited State	λ (nm)	*f*	R^{ECD}	λ (nm)	*f*	R^{ECD}
41	224.9988	0.0016	-1.4341	188.2500	0.0662	60.1178
42	223.1481	0.0709	-84.4783	187.6091	0.0002	-4.5005
43	222.6952	0.0156	-5.6236	187.2549	0.0256	29.8030
44	221.9100	0.1414	146.3171	185.6121	0.0752	-68.5416
45	220.6031	0.0790	-23.8800	185.5816	0.0413	60.1034
46	219.7273	0.1024	109.6089	182.9310	0.0353	21.4315
47	219.4862	0.0006	0.7182	182.1650	0.0165	-63.8994
48	217.8395	0.0092	-5.1052	181.9912	0.0082	-7.7402
49	215.6645	0.0767	27.3114	181.3921	0.0026	5.6976
50	215.1405	0.0568	55.8714	180.8102	0.1811	-81.3842
51	213.8307	0.0764	-38.3731	180.7206	0.0176	-20.7916
52	212.0098	0.0318	125.1603	179.8867	0.3512	-184.0033
53	211.4349	0.0515	9.9544	179.2055	0.0385	-47.4507
54	211.1685	0.0537	-34.1161	178.1651	0.2542	199.2258
55	209.4101	0.0094	-3.5030	178.0347	0.3509	-139.9201
56	207.8514	0.0131	-4.8020	177.7208	0.0093	-9.4533
57	206.5528	0.0002	-1.7731	176.9623	0.0104	-5.5484
58	205.3248	0.0312	-1.3186	176.2679	0.0395	55.2400
59	205.0091	0.0353	19.0356	175.6088	0.0175	-0.1892
60	204.8228	0.0004	1.5980	174.1706	0.0388	-5.6931

CN6-2	B3LYP/6-311++G(d,p)			CAM-B3LYP/6-311++G(d,p)		
Excited State	λ (nm)	δ^{TPA} (GM)	R^{TPCD} (GM)	λ (nm)	δ^{TPA} (GM)	R^{TPCD} (GM)
1	414.6630	16.6613	-0.0098	357.3033	2.9063	0.0010
2	407.8429	70.9045	0.3175	348.2703	18.7909	0.0539
3	375.7098	44.9730	0.1763	328.0006	10.0093	-0.0077
4	365.7352	6.5643	-0.0139	305.3799	4.3595	0.0895
5	355.2557	65.1419	0.7197	301.6648	10.3977	0.0575
6	346.3247	14.6569	0.0312	289.6828	3.3949	0.0172
7	334.1893	77.7945	0.4078	282.4242	10.2849	-0.0282
8	330.6246	139.0530	0.2877	273.0930	155.3384	1.1258
9	318.7256	27.1842	-0.1110	267.2074	21.1711	0.1822
10	312.3029	6.5017	0.1422	263.7963	9.2326	0.0752
11	306.8917	37.8324	0.0421	259.9250	16.4108	0.2643
12	303.8829	23.9271	0.3410	257.7635	1.4908	0.0045
13	300.2040	157.8439	1.0630	254.5878	0.0410	0.0097
14	297.3243	4.4347	0.0247	253.0291	17.6635	0.3448
15	290.3612	44.0961	0.5835	247.4735	1.6787	0.0621
16	289.0076	3.0942	0.0582	245.5134	33.5731	0.4448
17	287.0006	245.5349	-0.9255	240.2795	5.9505	-0.0429
18	281.7824	4.4973	0.2175	236.6112	129.0311	1.7996
19	277.9916	91.4492	-0.1073	231.7462	699.0229	0.2074
20	274.3014	0.4635	0.0231	228.7532	88.0669	1.2002
21	273.6959	15.0328	0.3622	226.6622	136.5475	1.0764
22	268.9463	31.4435	0.0600	224.6091	9.5458	-0.0078
23	264.9236	123.1433	-0.0806	223.7983	75.4143	-0.4924
24	263.2362	0.4598	-0.0006	222.9932	61.1332	-0.3568
25	259.9250	44.8477	0.1011	221.7965	41.0895	0.2599
26	257.2287	53.3663	-0.0940	219.4411	16.1602	-0.0405
27	253.0291	3.7206	0.0678	217.5162	0.3332	-0.0177
28	250.4732	83.6823	0.0106	216.7557	0.7191	0.1054
29	249.9682	6.9151	0.1205	216.3774	3.0191	-0.0445
30	249.9682	13.7800	0.3907	213.0313	10.2599	0.0531
31	247.9685	12.9031	0.1225	211.9389	34.0742	0.2216
32	247.4735	2.2173	0.0024	211.5772	276.8532	0.5505
33	246.4895	0.1791	0.0075	209.4328	49.8586	0.9684
34	242.1567	1.5409	0.0355	209.0797	17.6635	0.0220
35	240.7461	0.0271	0.0001	207.3315	21.9228	-0.3651
36	240.2795	1.3404	0.0514	206.9854	52.8652	0.2605
37	239.8148	0.7266	-0.0011	205.9539	6.2135	-0.0224
38	239.3518	2.2674	0.0103	205.2719	25.5557	-0.1060
39	239.3518	2.8813	0.0236	204.9326	3.0817	0.0712
40	238.4312	2.7184	0.0689	204.2574	6.4265	0.0104

CN6-2 (cont.)	B3LYP/6-311++G(d,p)			CAM-B3LYP/6-311++G(d,p)		
Excited State	λ (nm)	δ^{TPA} (GM)	R^{TPCD} (GM)	λ (nm)	δ^{TPA} (GM)	R^{TPCD} (GM)
41	236.6111	0.3658		202.9202	5.5245	
42	236.6111	16.6613		201.9287	40.2126	
43	235.2642	1.7664		201.6004	4.3470	
44	234.3747	3.6830		201.6004	5.5371	
45	231.7462	4.2342		200.6218	1.9417	
46	230.4540	0.5424		199.9746	18.6657	
47	230.0264	0.3683		199.3316	40.0873	
48	229.6004	1.4532		198.6927	5.2114	
49	229.1760	6.3889		197.7420	0.5988	
50	227.4940	9.8339		196.8004	18.9162	
51	227.0774	0.1992		196.1776	1.1625	
52	226.6622	0.4660		195.5587	9.7838	
53	226.2486	14.0306		195.2508	3.5828	
54	225.4259	0.4735		194.6377	4.4472	
55	225.4259	1.9292		194.3327	43.8455	
56	224.6091	1.3530		193.7254	1.6411	
57	224.6091	7.6291		192.8215	13.2789	
58	223.7983	0.5963		192.5221	5.9630	
59	223.3950	5.5245		191.3337	1.2653	
60	221.7965	0.7729		191.0389	4.2342	

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