

Two-dimensional second order nonlinear optical spectra: landscape of second order nonlinear optics

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1. Gaussian09 full citation

Gaussian 09, Revision **D.01**, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.

2. The 2D 2nd NLO spectra of polymethine and oligo-thiophene chromophores(in $\times 10^5 \times 10^{-30}$ esu).

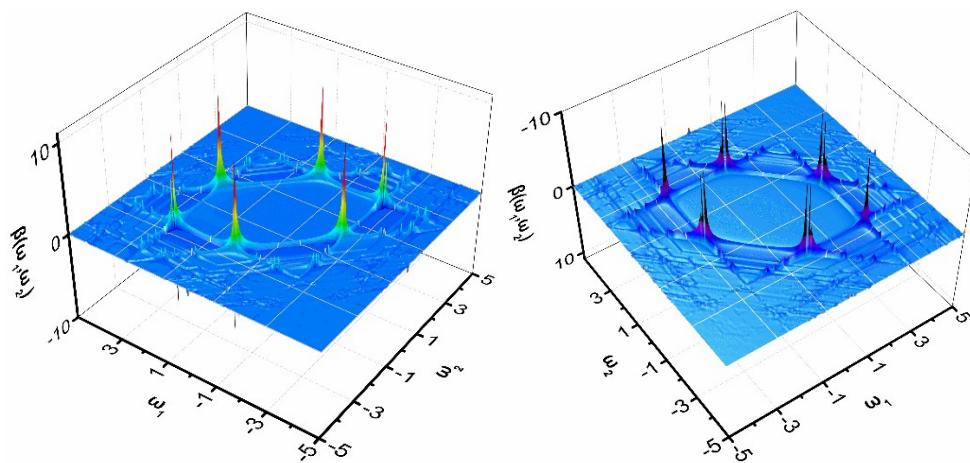
The external fields (ω_1, ω_2) range from -5.0 eV to 5.0eV. The 2D 2nd NLO spectra were plotted in

two directions along the z axis [$\beta(\omega_1, \omega_2)$] for each structure and scanned with step size of 0.05eV.

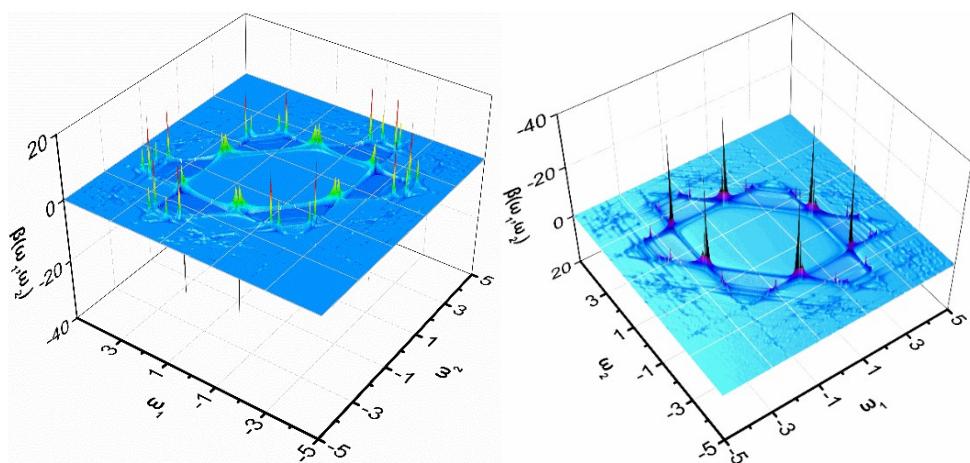
Only the 2D 2nd NLO spectra of ploymethine and cis-oligo-thiophene chromophores were predicted.

Polymethine chromophores

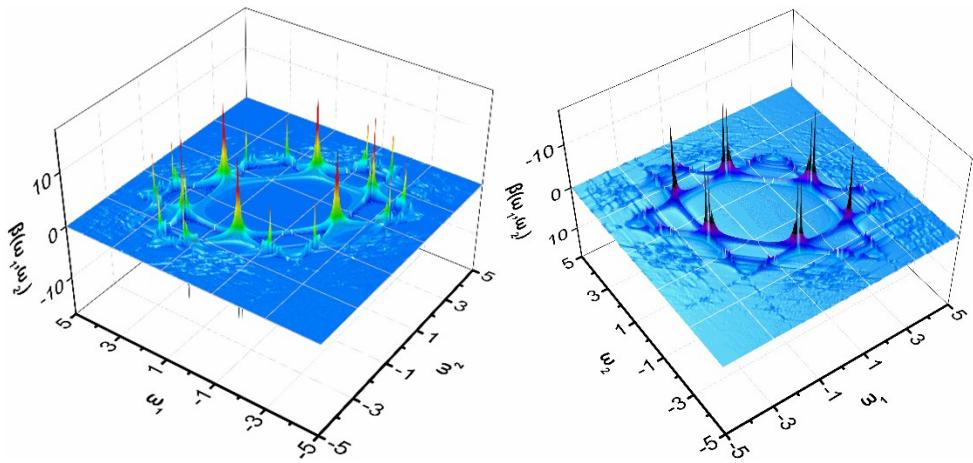
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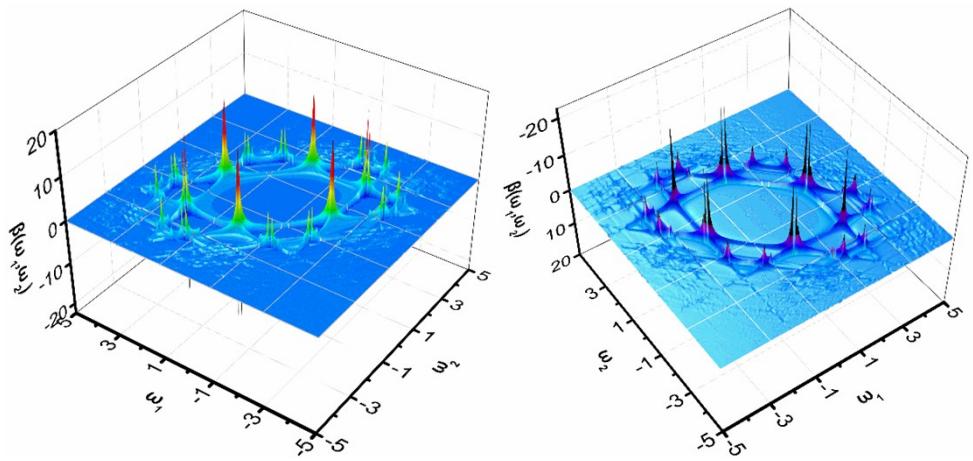
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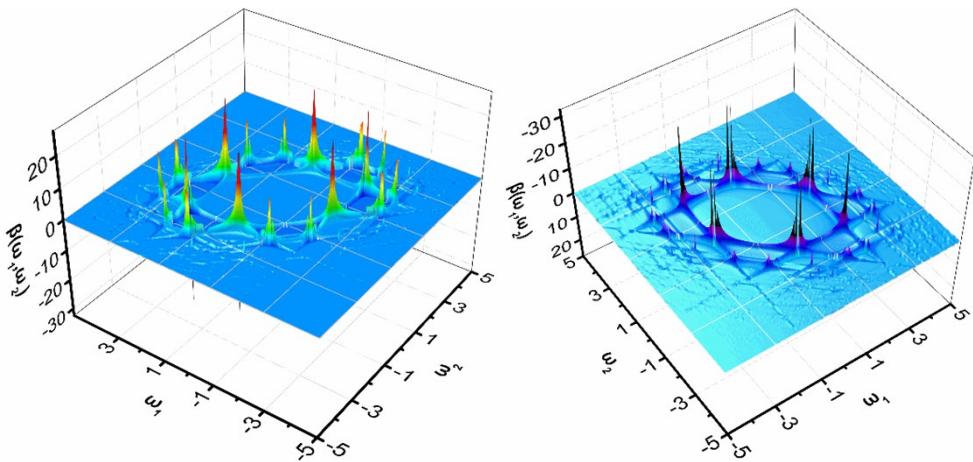
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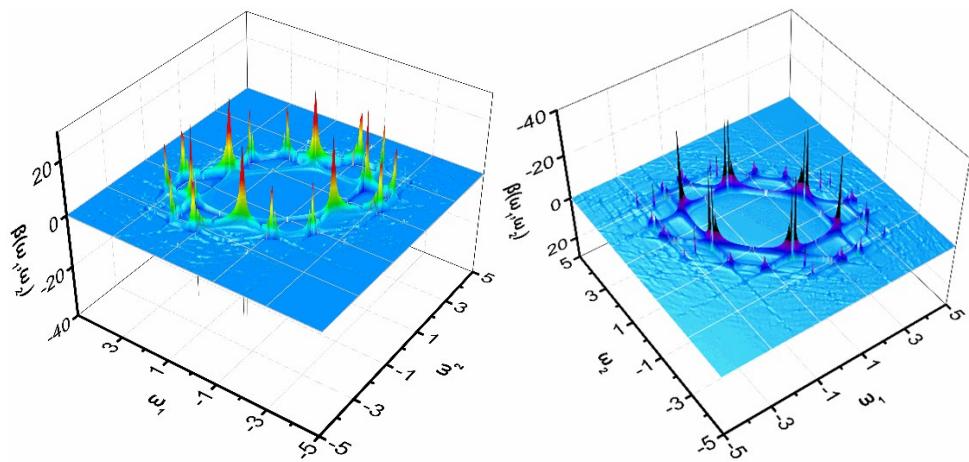
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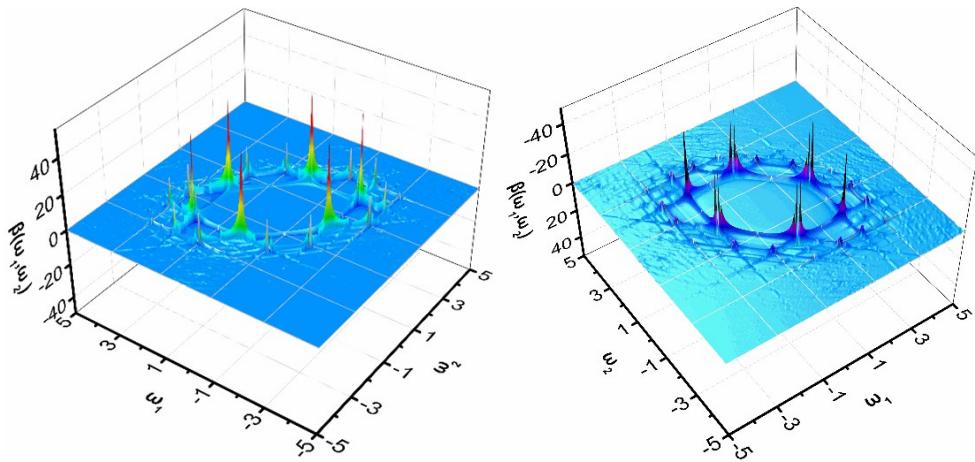
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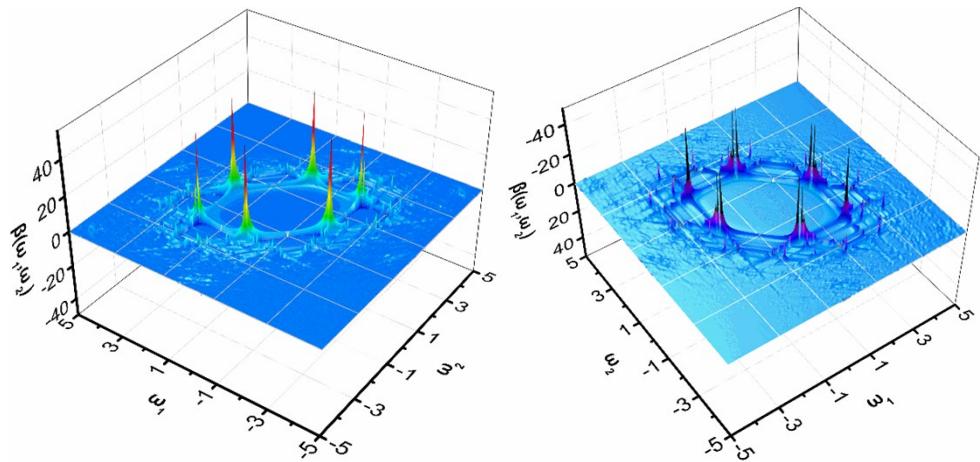
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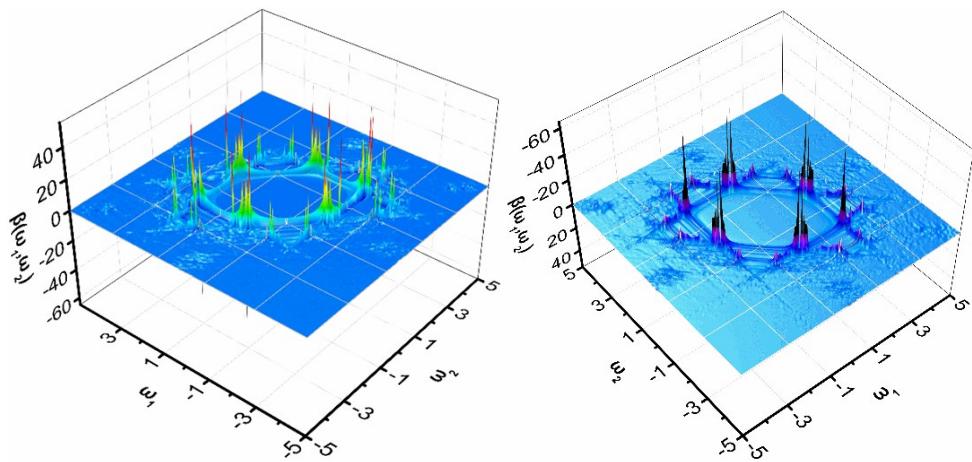
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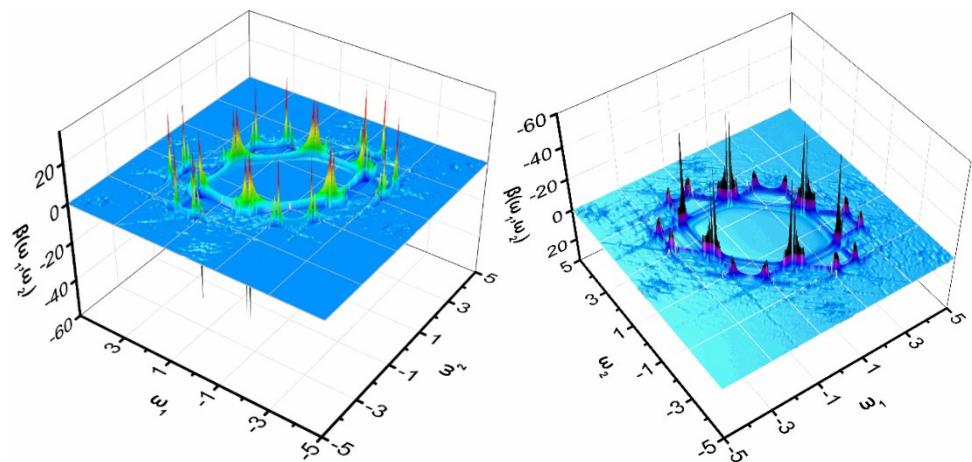
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n=24

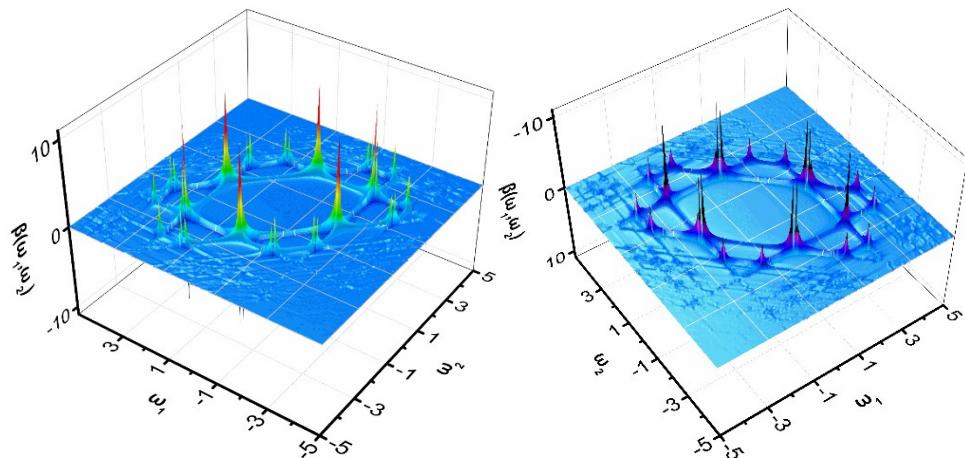


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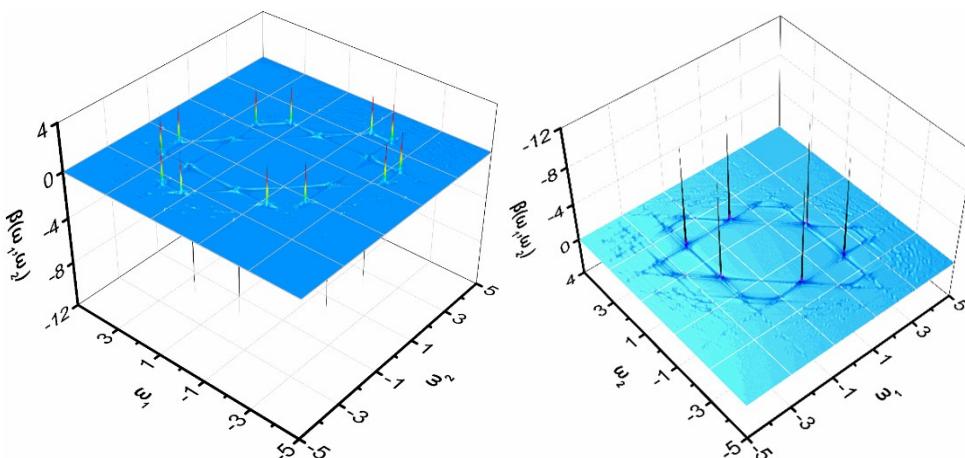


Cis-polythiophene chromophores

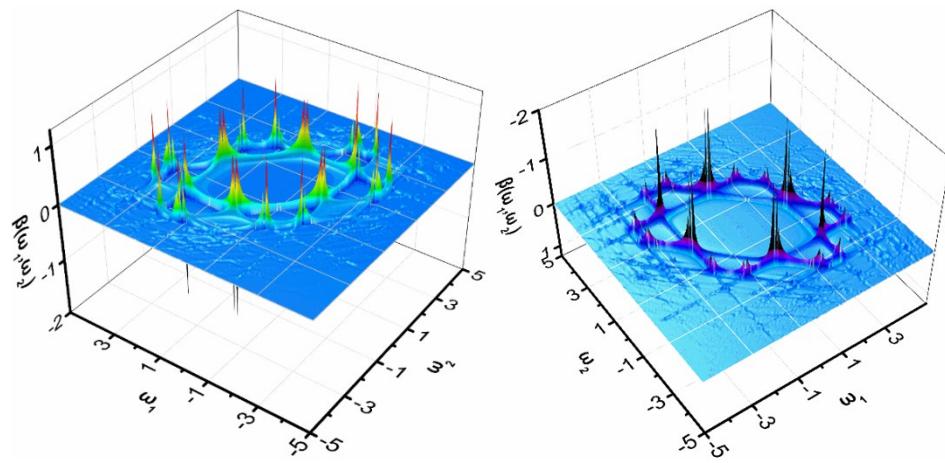
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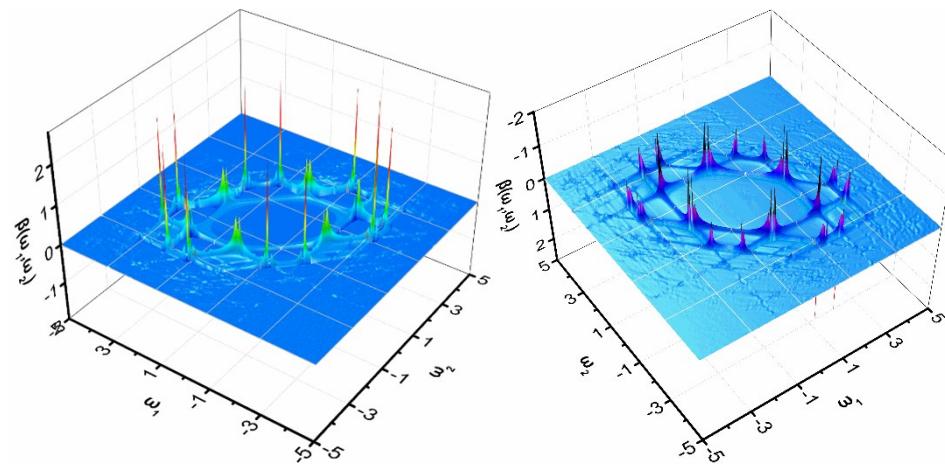
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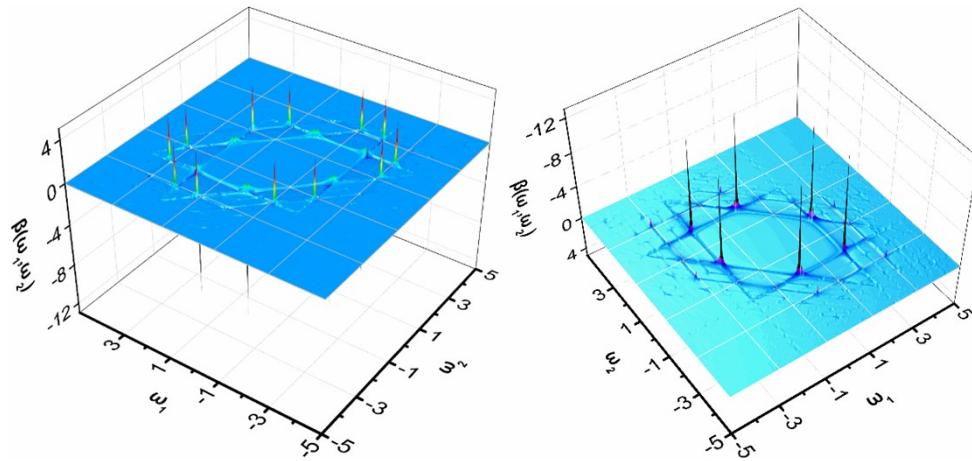
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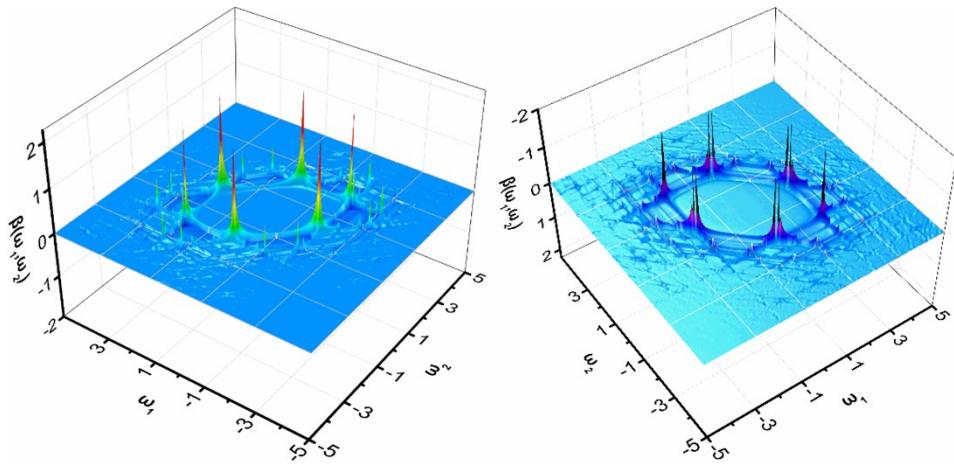
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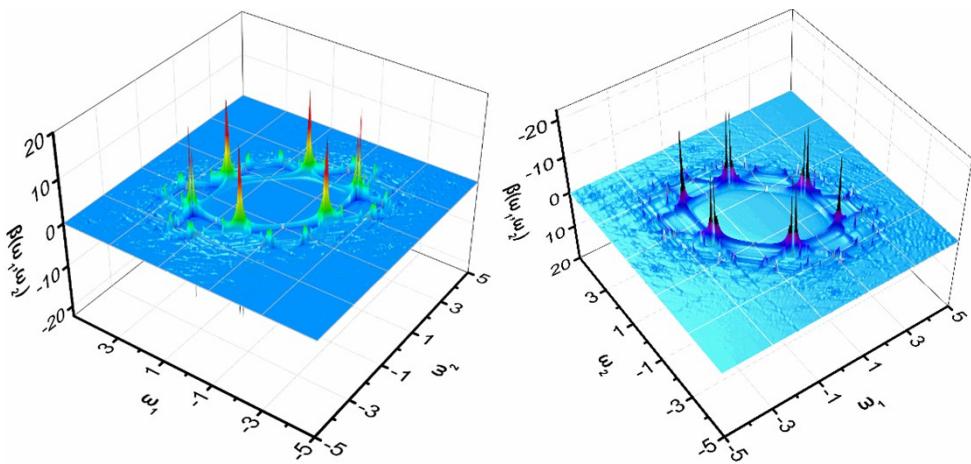
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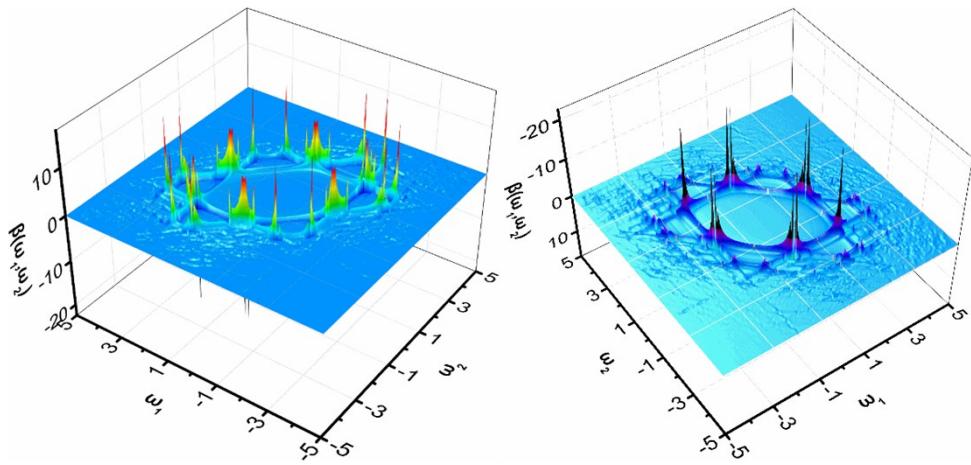
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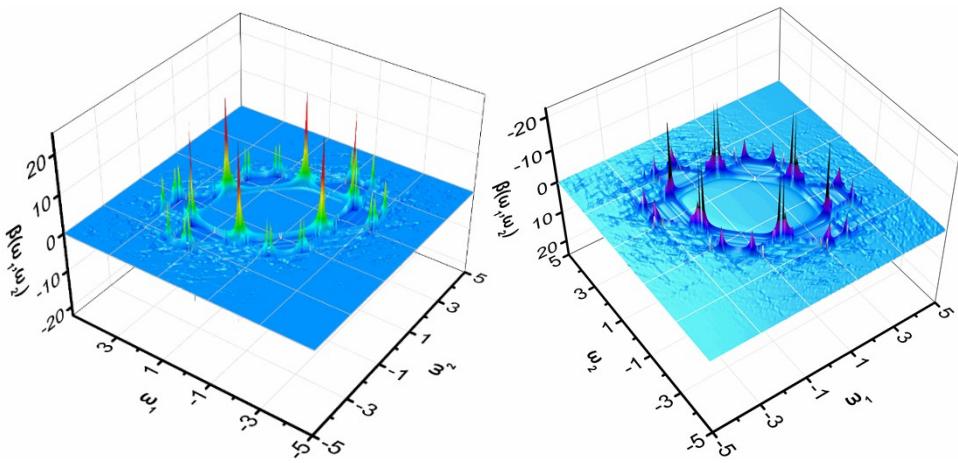
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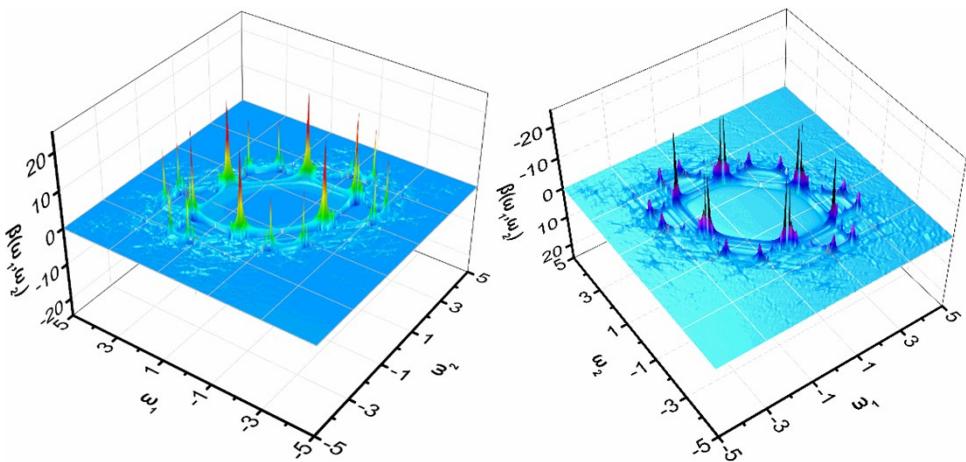
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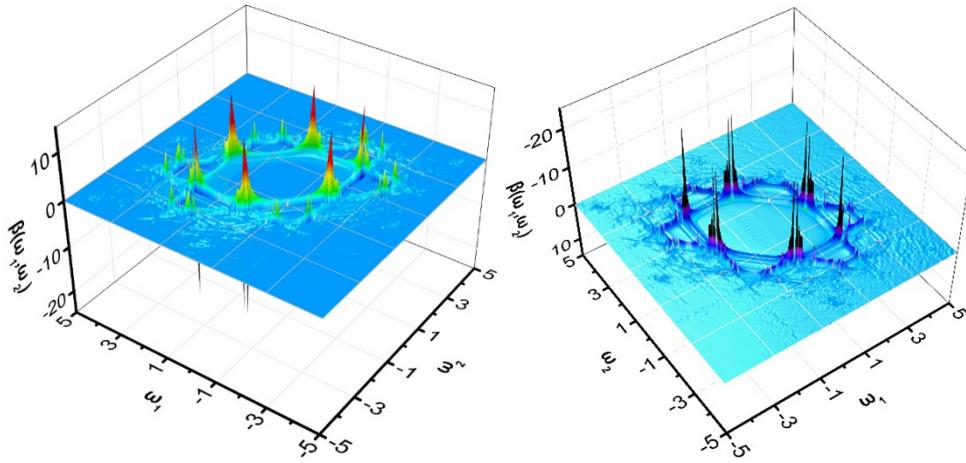
n=10



n=12



n=14



n=16

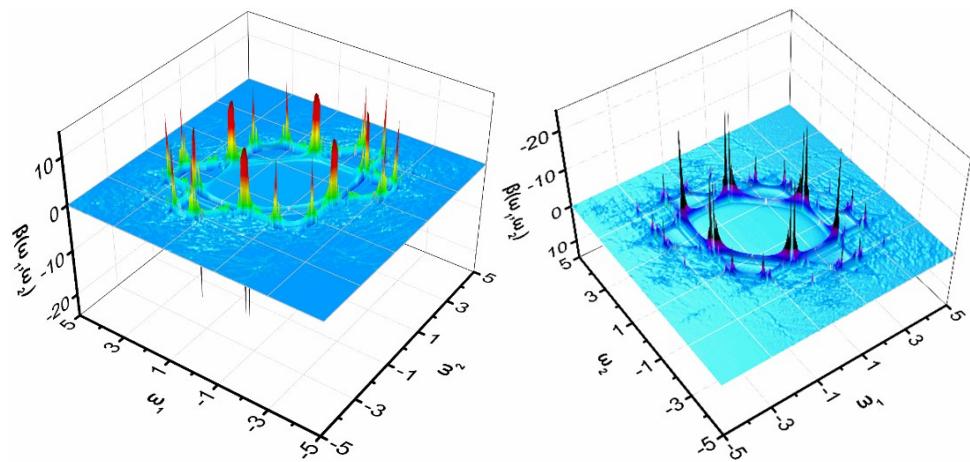
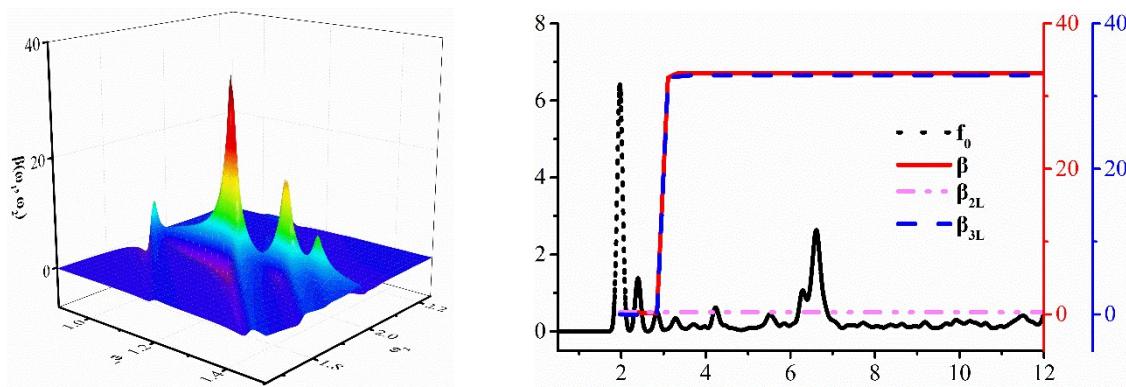


Figure S1 The 2D 2nd NLO spectra of polymethine and cis-oligo-thiophene chromophores(in $\times 10^5 \times 10^{-30}$ esu)

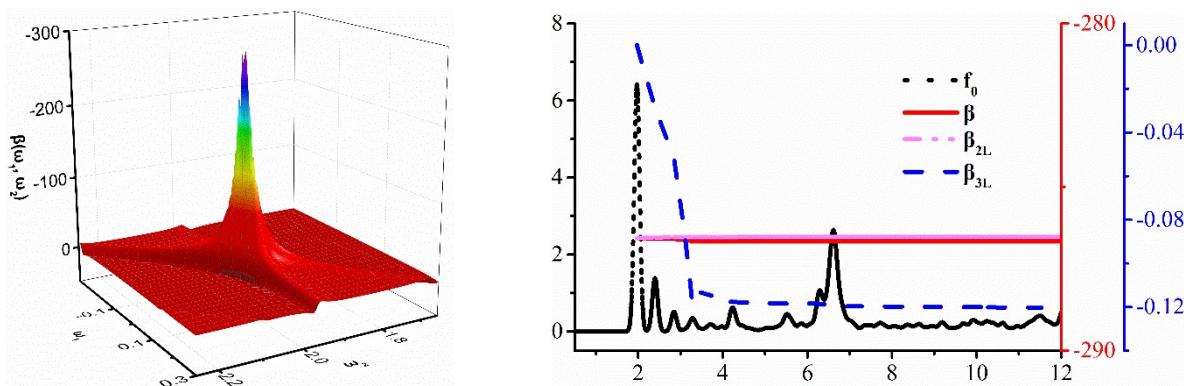
3. The analysis of resonances in 2D 2nd NLO of polymethine ($n=18$) and cis-oligo-thiophene ($n=10$) chromophores(in $10^5 \times 10^{-30}$ esu, unless specified). The external fields (ω_1, ω_2) are scanned in a step size of 0.005 eV.

Polymethine chromophore ($n=18$)

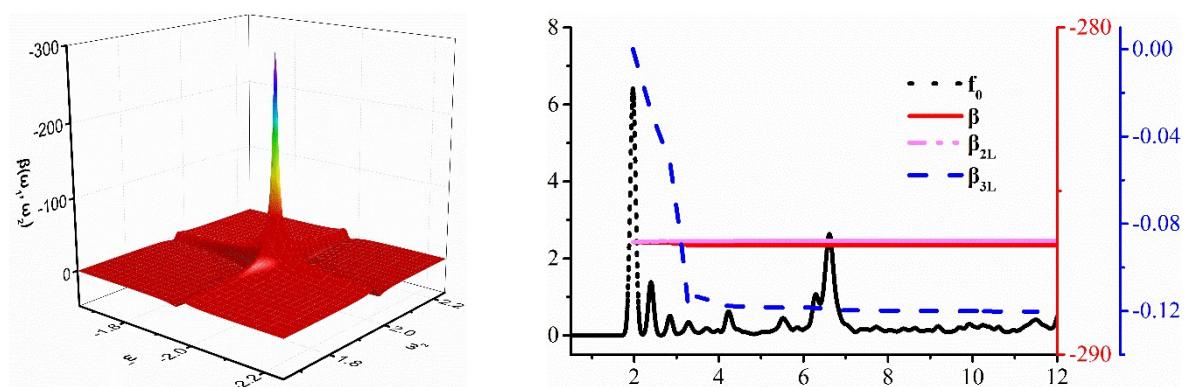
resonance at (1.970eV, 1.135eV)



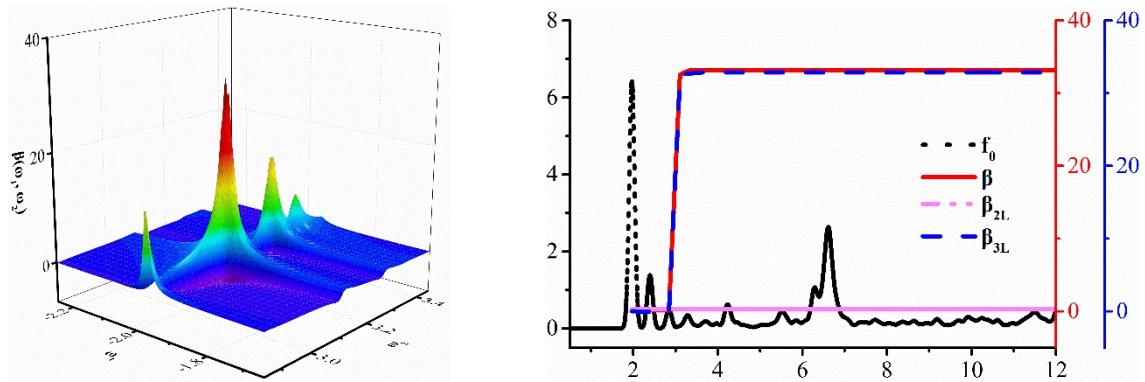
resonance at (1.965eV, 0.005eV)



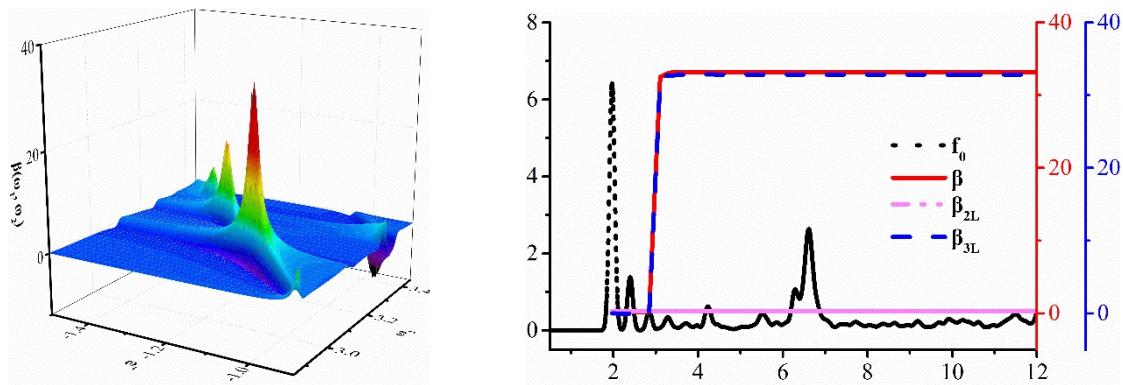
resonance at (1.970eV, -1.965eV)



resonance of (3.105eV, -1.970eV)

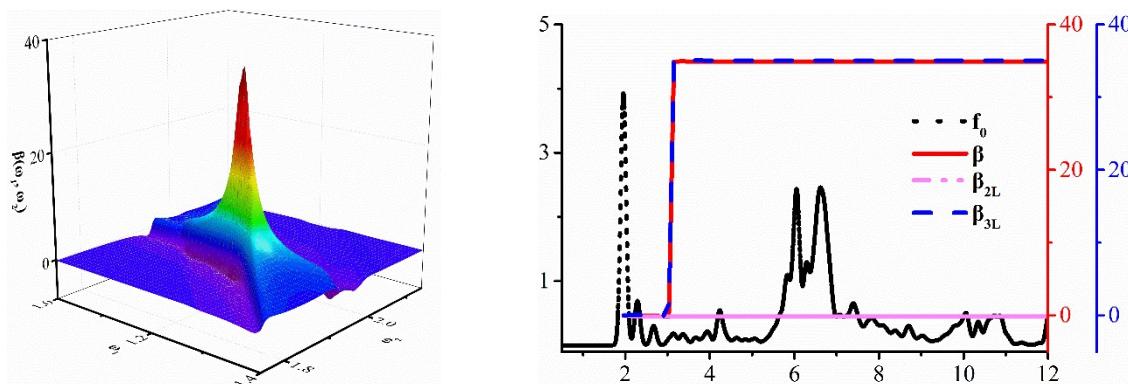


resonance of (3.105eV, -1.135eV)

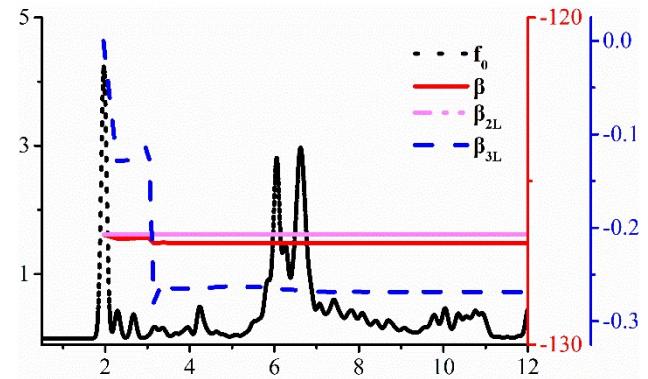
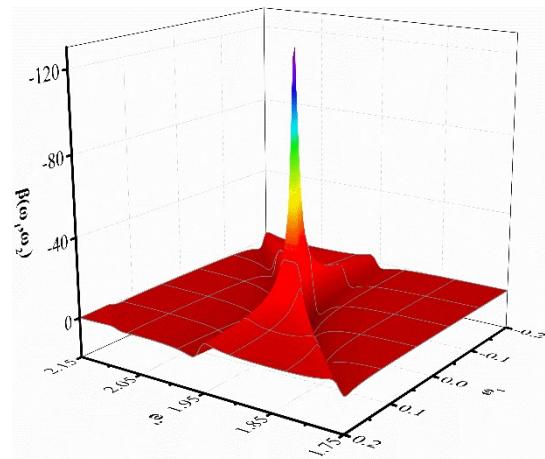


cis-oligo-thiophene chromophore (n=10)

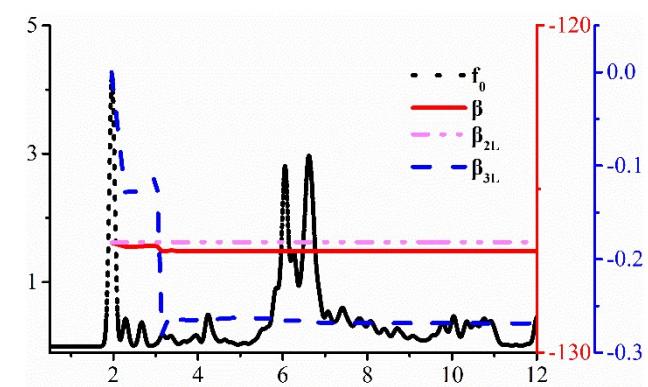
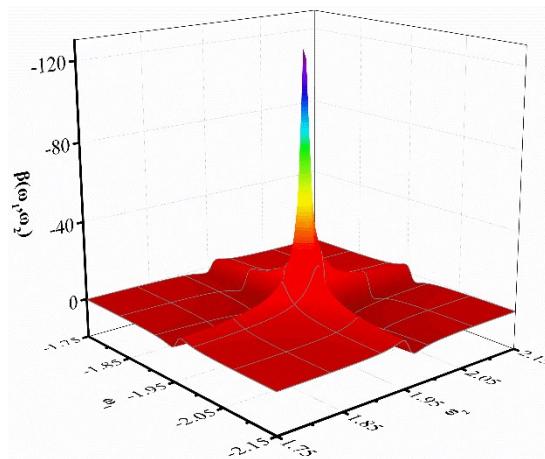
resonance of (1.955eV, 1.200eV)



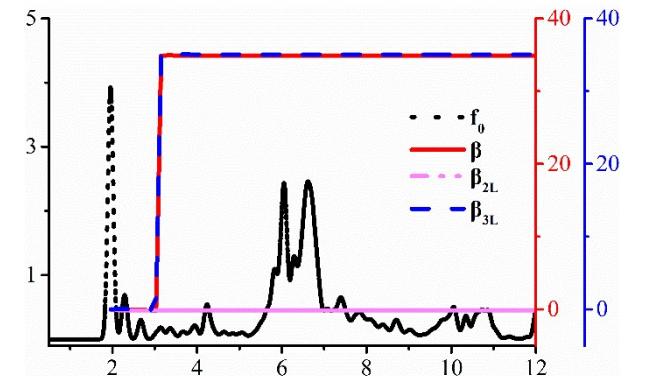
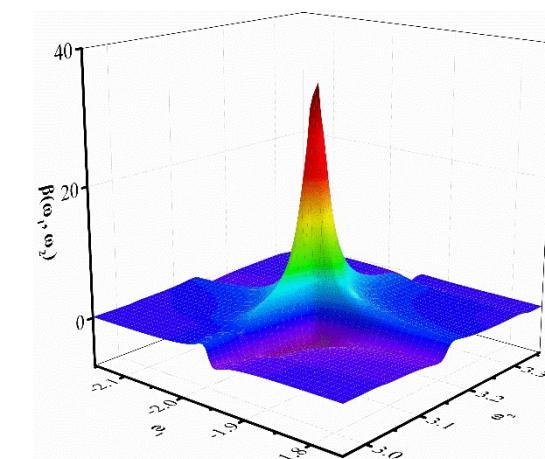
resonance of (1.955eV, 0.000eV)



resonance of (1.955eV, -1.955eV)



resonance of (3.155eV, -1.955eV)



resonance of (3.155eV, -1.200eV)

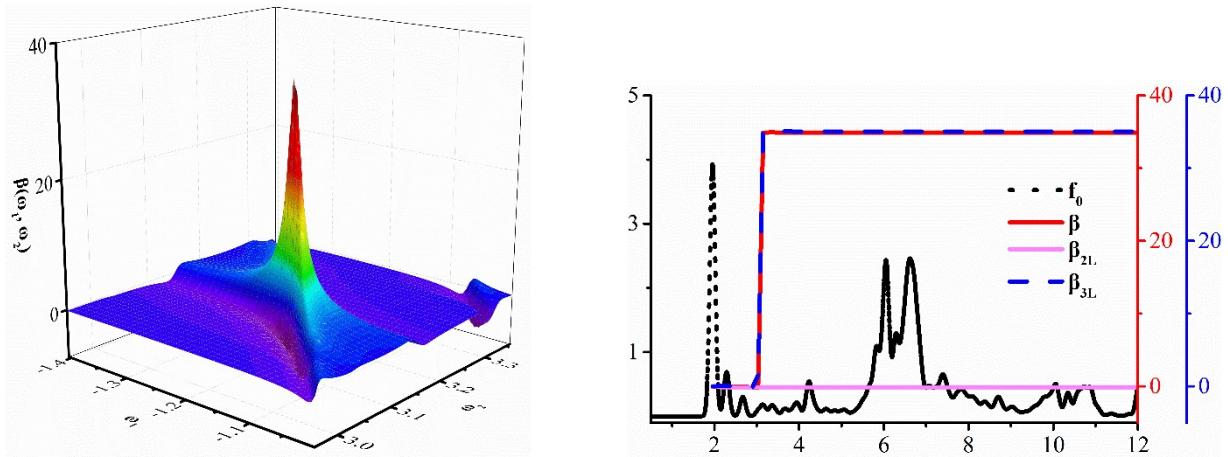
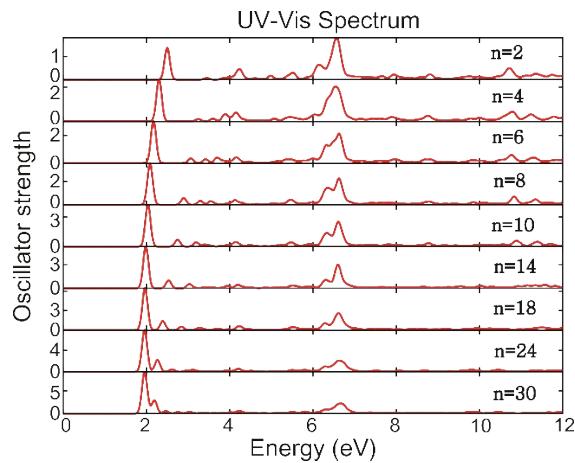


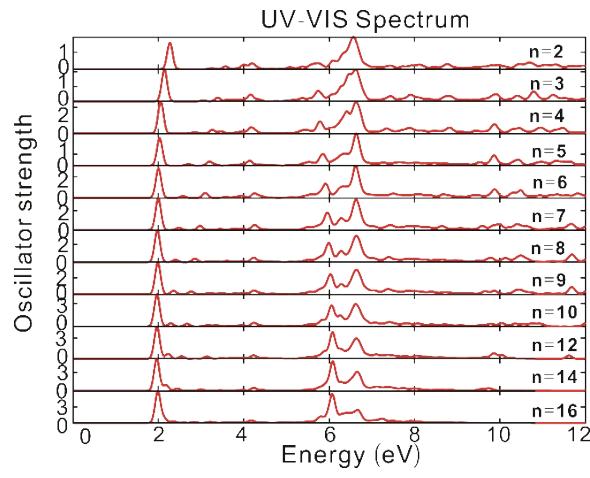
Figure S2 The location of resonances in 2D 2nd NLO of polymethine ($n=18$) and cis-oligo-thiophene ($n=10$) chromophores(in $10^5 \times 10^{-30}$ esu). The external fields (ω_1, ω_2) are scanned in a step size of 0.005 eV

4. The predicted electronic spectra of polymethine and oligo-thiophene chromophores

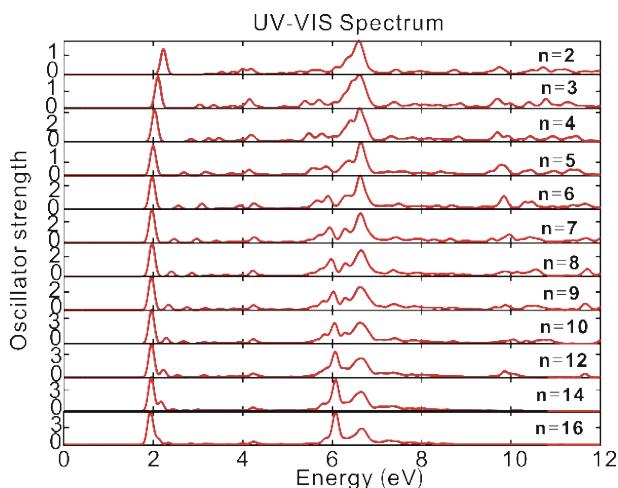
polymethine chromophores



oligo-thiophene chromophores



trans



cis

Figure S3 The electronic spectra of polymethine and oligo-thiophene chromophores, n is the number of methine pairs or the number of thiophenes.

5. The electronic properties and first hyperpolarizabilities of polymethine (Table S1) and oligothiophene chromophores (Tables S2 and S3)

Table S1. The electronic properties and first hyperpolarizabilities ($\times 10^{-30}$ esu) of polymethine chromophores

n_{meth}	β_0	β_{\max} ($\times 10^6$)	Dip(B3)	$\Delta E_{\text{H-L}}$ (ΔE_{B3LYP})	ΔD	$E_{\text{ex-l}}$	f_0	e_D	e_π	e_A
2	327.80	1.05 (EOPE)	16.88 (21.59)	5.15 (2.10)	13.75	2.50	1.81	0.256	-0.037	-0.293
4	627.55	3.83 (EOPE)	19.06 (25.72)	4.82 (1.81)	16.57	2.31	2.42	0.210	0.091	-0.301
6	952.75	2.06 (DFG)	19.80 (28.48)	4.59 (1.61)	19.01	2.17	3.00	0.183	0.124	-0.307
8	1274.48	3.12 (SFG)	20.38 (31.03)	4.43 (1.46)	21.19	2.09	3.58	0.154	0.156	-0.310
10	1505.07	3.72 (DFG)	19.72 (32.33)	4.30 (1.34)	23.21	2.04	4.19	0.151	0.159	-0.310
14	1830.04	5.03 (OR)	20.13 (35.84)	4.14 (1.16)	26.56	1.99	5.33	0.133	0.178	-0.311
18	1978.46	5.24 (EOPE)	20.28 (38.23)	4.04 (1.04)	29.30	1.97	6.42	0.122	0.189	-0.311
24	2030.69	5.73 (DFG)	20.01 (39.72)	3.98 (0.93)	32.39	1.96	7.80	0.110	0.201	-0.311
30	2049.42	6.40 (DFG)	20.30 (41.18)	3.93 (0.83)	35.27	1.96	9.25	0.108	0.200	-0.308

n_{meth} : number of methine pairs, β_{\max} : the largest NLO response; ΔD : the transition dipole of $E_{\text{ex-l}}$, Dip(B3): dipole moment from ZINDO(B3LYP), $\Delta E_{\text{H-L}}(\Delta E_{\text{B3LYP}})$: HOMO-LUMO gap from ZINDO(B3LYP), $E_{\text{ex-l}}$: lowest excitation, f_0 : oscillator strength of $E_{\text{ex-l}}$, $e_D(e_\pi, e_A)$: charge of donor(bridge, acceptor)

Table S2. The electronic properties and first hyperpolarizabilities ($\times 10^{-30}$ esu) of oligo-thiophene chromophores

cis-thiophene chromophores

n_{thio}	β_0	β_{\max} ($\times 10^6$)	Dipole- (zindo) -(DFT)	$\Delta E_{\text{H-L}}$	ΔD	$E_{\text{ex-l}}$	f_0	e_D	e_π	e_A
2	416	0.86 (SFG)	17.27 (19.95)	4.86 (1.84)	14.39	2.22	1.75	0.198	0.023	0.221
3	534	1.16 (EOPE)	19.43 (21.33)	4.67 (1.64)	15.87	2.01	2.01	0.170	0.046	0.216
4	758	1.38 (DFG)	18.13 (20.81)	4.53 (1.51)	17.23	2.03	2.29	0.154	0.056	0.210
5	785	2.65 (DFG)	19.46 (21.97)	4.43 (1.41)	18.41	1.99	2.56	0.143	0.065	0.207
6	908	1.66 (DFG)	18.56 (21.48)	4.36 (1.35)	19.54	1.97	2.86	0.137	0.068	0.205
7	862	2.14 (OR)	19.70 (22.9)	4.30 (1.28)	20.56	1.97	3.16	0.133	0.065	0.203
8	952	1.83 (DFG)	18.52 (21.67)	4.27 (1.25)	21.19	1.97	3.36	0.126	0.075	0.201
9	840	3.55 (EOPE)	21.16 (22.80)	4.23 (1.22)	22.11	1.96	3.65	0.125	0.076	0.201
10	950	4.05 (EOPE)	19.29 (22.45)	4.20 (1.20)	22.99	1.96	3.93	0.125	0.075	0.200
12	990	4.73 (EOPE)	19.06 (21.87)	4.16 (1.17)	24.20	1.96	4.35	0.125	0.075	0.200
14	977	14.41 (OR)	19.92 (22.23)	4.13 (1.15)	25.39	1.95	4.77	0.122	0.077	0.199
16	988	2.03 (SFG)	18.39 (21.92)	4.09 (1.14)	28.07	1.93	5.77	0.124	0.075	0.199

trans-thiophene chromophores

n_{thio}	β_0	β_{\max} ($\times 10^6$)	$\Delta E_{\text{H-L}}$							
			Dip(B3)	$(\Delta E_{\text{B3LYP}})$	$E_{\text{ex-l}}$	ΔD	f_0	e_D	e_π	e_A
2	443	1.08 (OR)	17.48 (20.96)	4.91 (1.83)	2.27	14.73	1.87	0.195	0.023	-0.218
3	654	1.73 (EOPE)	18.39 (22.54)	4.71 (1.64)	2.14	16.30	2.16	0.168	0.044	-0.212
4	794	1.89 (DFG)	19.37 (22.92)	4.57 (1.51)	2.06	17.68	2.44	0.152	0.057	-0.209
5	907	1.79 (DFG)	19.13 (23.37)	4.47 (1.40)	2.03	18.81	2.73	0.143	0.061	-0.204
6	954	12.20 (EOPE)	19.61 (23.35)	4.39 (1.34)	2.00	19.95	3.03	0.137	0.065	-0.202
7	987	12.4 (OR)	19.65 (23.59)	4.34 (1.28)	2.00	20.97	3.34	0.133	0.067	-0.200
8	1023	2.09 (DFG)	19.88 (23.62)	4.28 (1.24)	1.98	22.02	3.64	0.130	0.069	-0.199
9	1014	2.15 (DFG)	19.88 (23.57)	4.27 (1.21)	1.99	22.64	3.87	0.125	0.072	-0.198
10	1036	2.47 (EOPE)	20.29 (23.82)	4.21 (1.18)	1.97	23.80	4.24	0.127	0.070	-0.198
12	1012	2.36 (EOPE)	21.14 (24.14)	4.18 (1.15)	1.97	25.07	4.70	0.123	0.074	-0.197
14	1047	2.35 (DFG)	21.21 (24.15)	4.15 (1.13)	1.96	26.35	5.18	0.123	0.074	-0.197
16	1015	2.44 (DFG)	19.25 (23.40)	4.11 (1.12)	1.94	28.82	6.13	0.124	0.073	-0.197

n_{thio} : number of thiophene pairs, β_{\max} : the largest NLO response; ΔD : the transition dipole of $E_{\text{ex-l}}$, Dip(B3):

dipole moment from ZINDO(B3LYP), $\Delta E_{\text{H-L}}(\Delta E_{\text{B3LYP}})$: HOMO-LUMO gap from ZINDO(B3LYP), $E_{\text{ex-l}}$:

lowest excitation, f_0 : oscillator strength of $E_{\text{ex-l}}$, $e_D(e_\pi, e_A)$: charge of donor(bridge, acceptor).

Table S3 The β_x component, total dipole moment (debye) r_{total} , and $x(r_x)$, $y(r_y)$, $z(r_z)$ components of cis-oligo-thiophene and trans-oligo-thiophene chromophores

cis (n)	β_x	r_{total}	r_x	r_y	r_z	$\beta_x \times r_x$
2	-507.407	17.268663	-14.6113	9.1390	1.0924	7413.876
3	-717.825	19.427690	-13.8212	-9.3182	-9.9790	9921.203
4	-891.011	18.126899	-15.6472	9.1084	0.8858	13941.83
5	-1001.92	19.455870	-14.8648	-10.0714	-7.4923	14893.34
6	-1069.41	18.564751	-15.8857	9.6067	-0.0770	16988.33
7	-1094.39	19.703598	-15.0542	-9.9746	-7.8811	16475.17
8	-1081.85	18.519662	-16.2678	8.6667	1.7957	17599.32
9	-1125.97	21.158739	-15.0286	-5.7082	-13.7568	16921.75
10	-1126.11	19.292169	-16.0179	10.6602	-1.4059	18037.92
12	-1117.69	19.061179	-16.4530	-5.5780	-7.8431	18389.35
14	-1140.97	19.916236	-16.0099	-8.9846	-7.7213	18266.82
16	-1208.97	18.394451	-15.1188	10.4260	1.0372	18278.18

trans(n)	β_x	r_{total}	r_x	r_y	r_z	$\beta_x \times r_x$
2	471.849	17.482773	-16.0530	-6.2557	-2.9688	7574.592
3	-669.356	18.392116	-17.9596	3.7340	-1.3337	12021.37
4	849.358	19.371923	-17.6303	-4.6644	-6.5336	14974.44
5	-934.335	19.134644	-18.4857	4.2827	-2.4643	17271.84
6	1012.20	19.605097	-18.1487	-4.5783	-5.8331	18370.11
7	-1029.01	19.648543	-18.6211	4.8253	-4.0045	19161.3
8	1088.22	19.883410	-18.4278	-4.2856	-6.1154	20053.5
9	-1049.68	19.875800	-18.7513	5.5273	-3.5895	19682.86
10	-1108.76	20.292735	-18.5941	-3.9806	-7.0858	20616.39
12	-1097.42	21.144973	-18.7792	-2.8407	9.2942	20608.67
14	1112.73	21.213629	-19.1953	-4.7821	7.6610	21359.19
16	1081.63	19.245099	-18.2185	-4.9051	-3.7950	-19705.7

The odd-even fluctuation of β_0 with π bridge length n in oligo-thiophene chromophores is caused by the symmetry of the thiophene chains [Adv. Funct. Mater. 2011, 21, 897–910]. The β_x has dominant contribution to the average β in the donor- π -acceptor chromophores. The β_x related data were listed in Table S3. Thiophene-chains with even numbers have local C_{2h} symmetry and those with odd numbers have local C_{2v} symmetry. Those chain with different symmetries have different dipole moments (with odd-even fluctuation pattern) [Adv. Funct. Mater. 2011, 21, 897–910] as shown in Table S3. The relative position of acceptor to donor also has odd-even pattern with increase of thiophene chain. According to the calculation of average β (Eq. 4), the β_x has fluctuation pattern with dipole moment, thus the β_0 has the similar odd-even fluctuation pattern. However, as the chain elongates, the effect of symmetry gets weaker and such pattern eventually is negligible.

6. The evolution of $[\beta_0(n) - \beta_0(2)]/(n-2)$ (in $10^2 \times 10^{-30}$ esu) with the π bridge length n, the increase of β_0 chromophores per bridge unit reaches maximum with n=8 for polymethine chromophores and n=4 for oligo-thiophene chromophores.

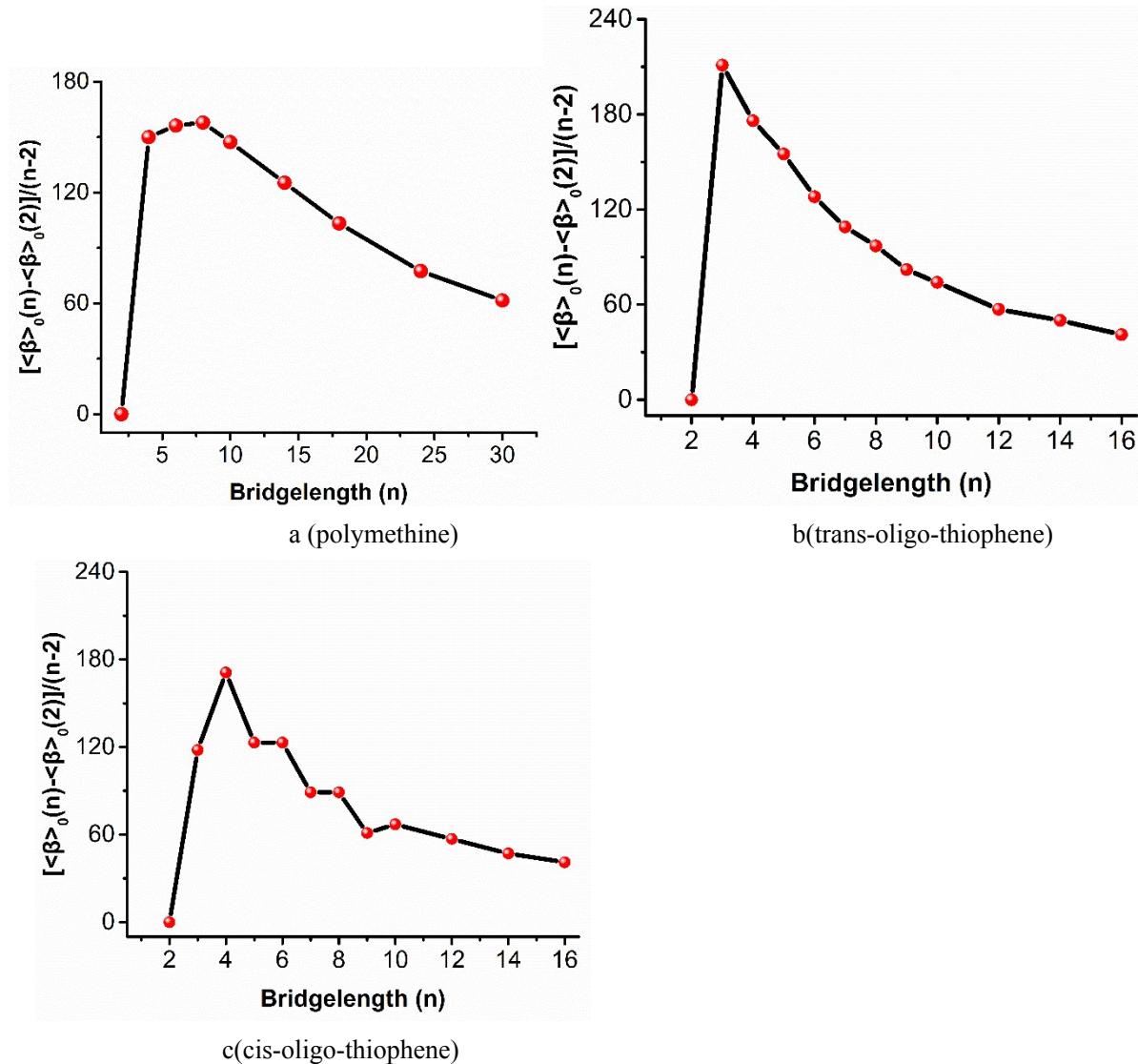
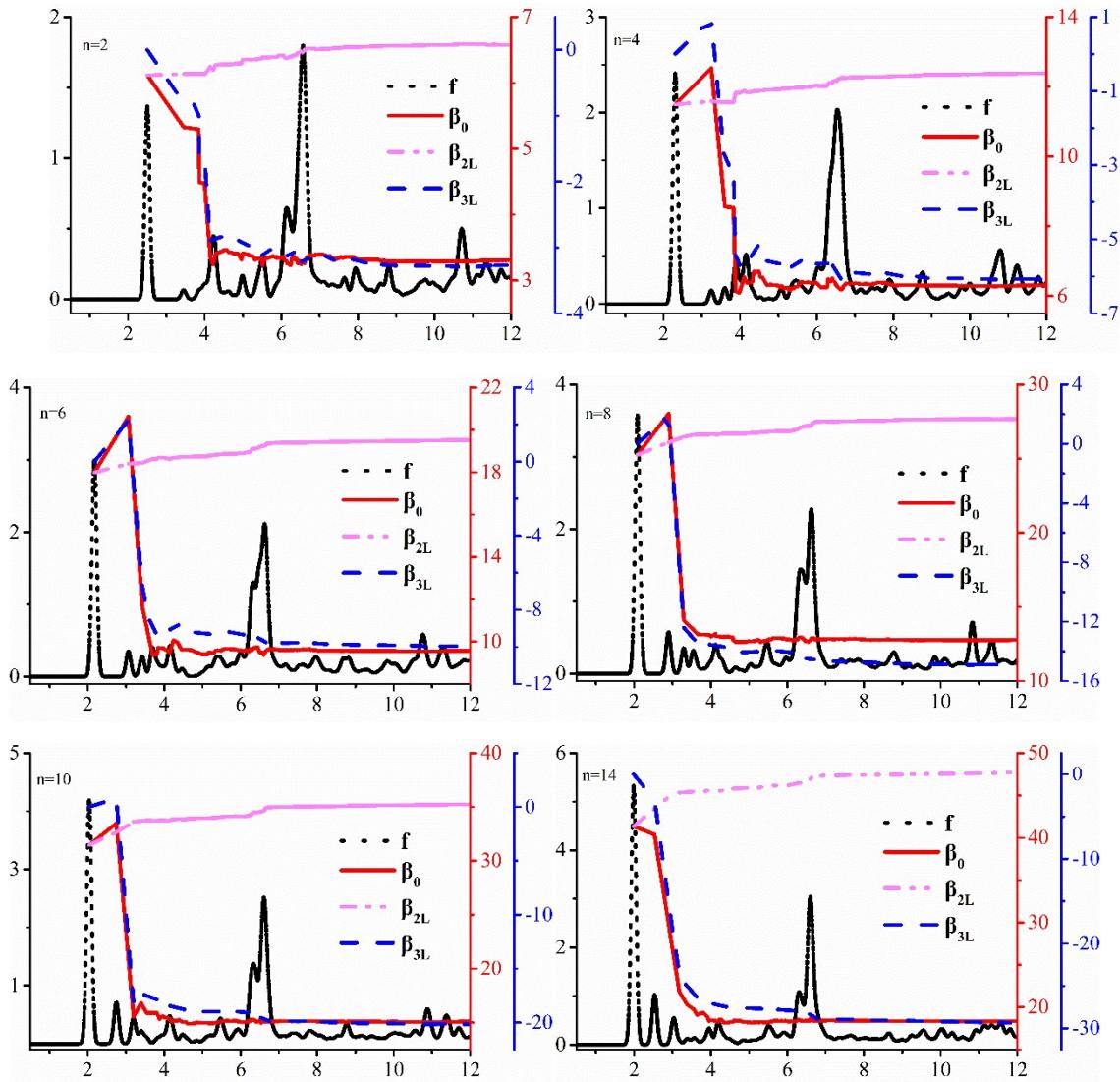
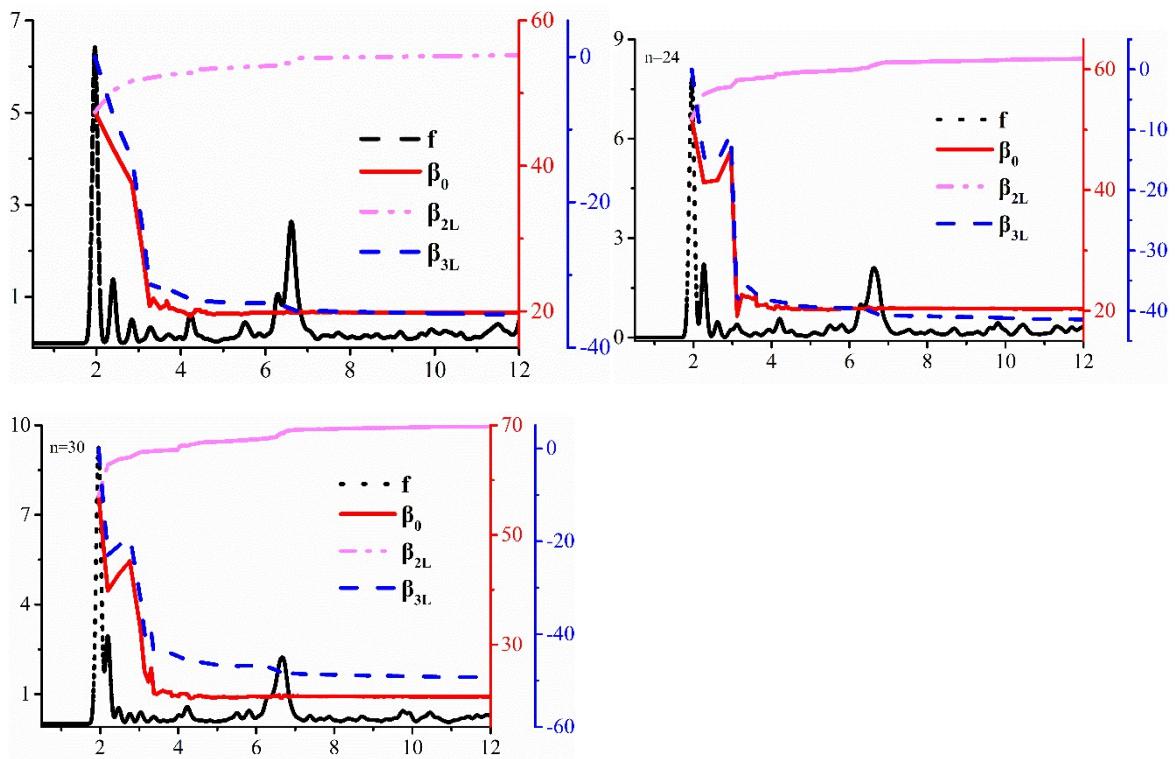


Figure S4. The evolution of $[\beta_0(n) - \beta_0(2)]/(n-2)$ (in $10^2 \times 10^{-30}$ esu) with the π bridge length n, n is the number of methine pairs or thiophenes. (a) polymethine, (b) trans-thiophenes, (c) cis-thiophenes

7. The evolution of β_0 (in $10^2 \times 10^{-30}$ esu) with electron excitation of polymethine and oligo-thiophene chromophores. The red line (β_0) is the total static first-hyperpolarizability. The purple broken dash line (β_{2L}) is the two-level model contribution to the static first-hyperpolarizability. The blue broken line (β_{3L}) is the three-level model contribution to the static first-hyperpolarizability (as described in Eq. 2). β_0 and β_{2L} share the same red axis.

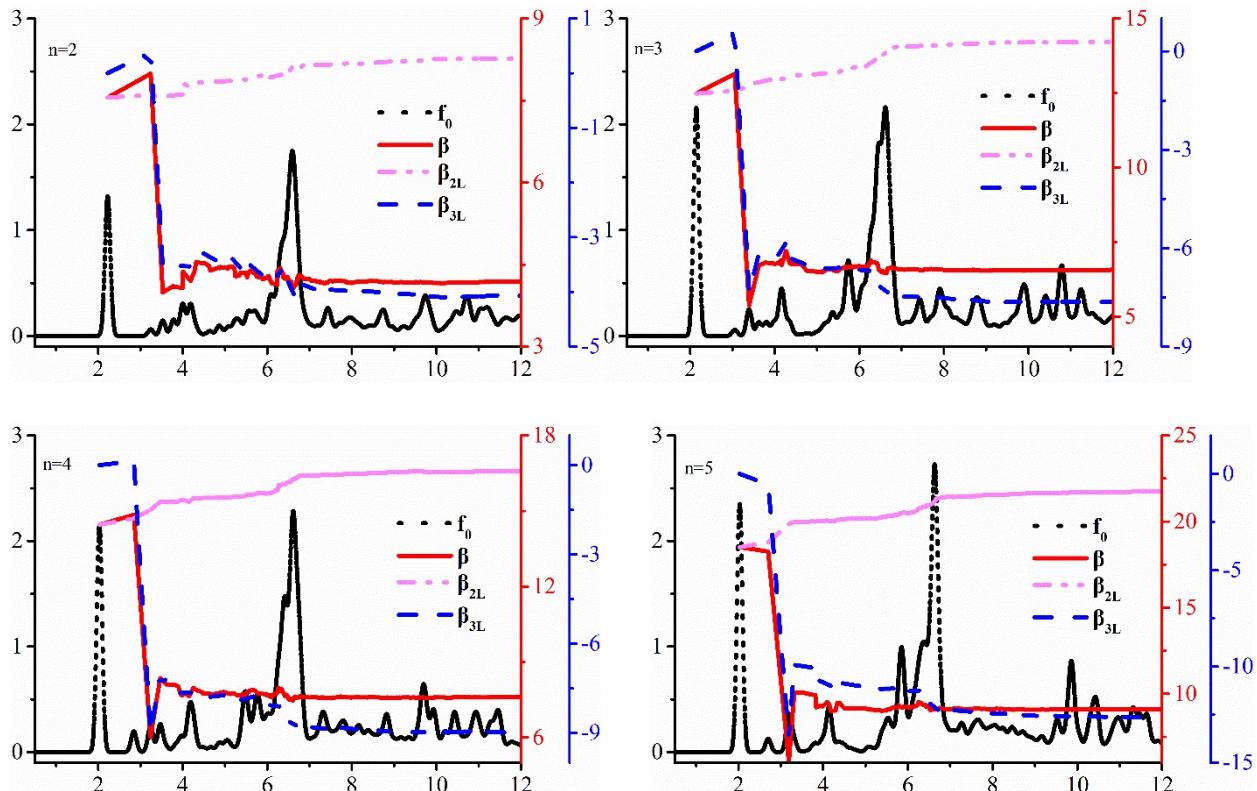
polymethine chromophores

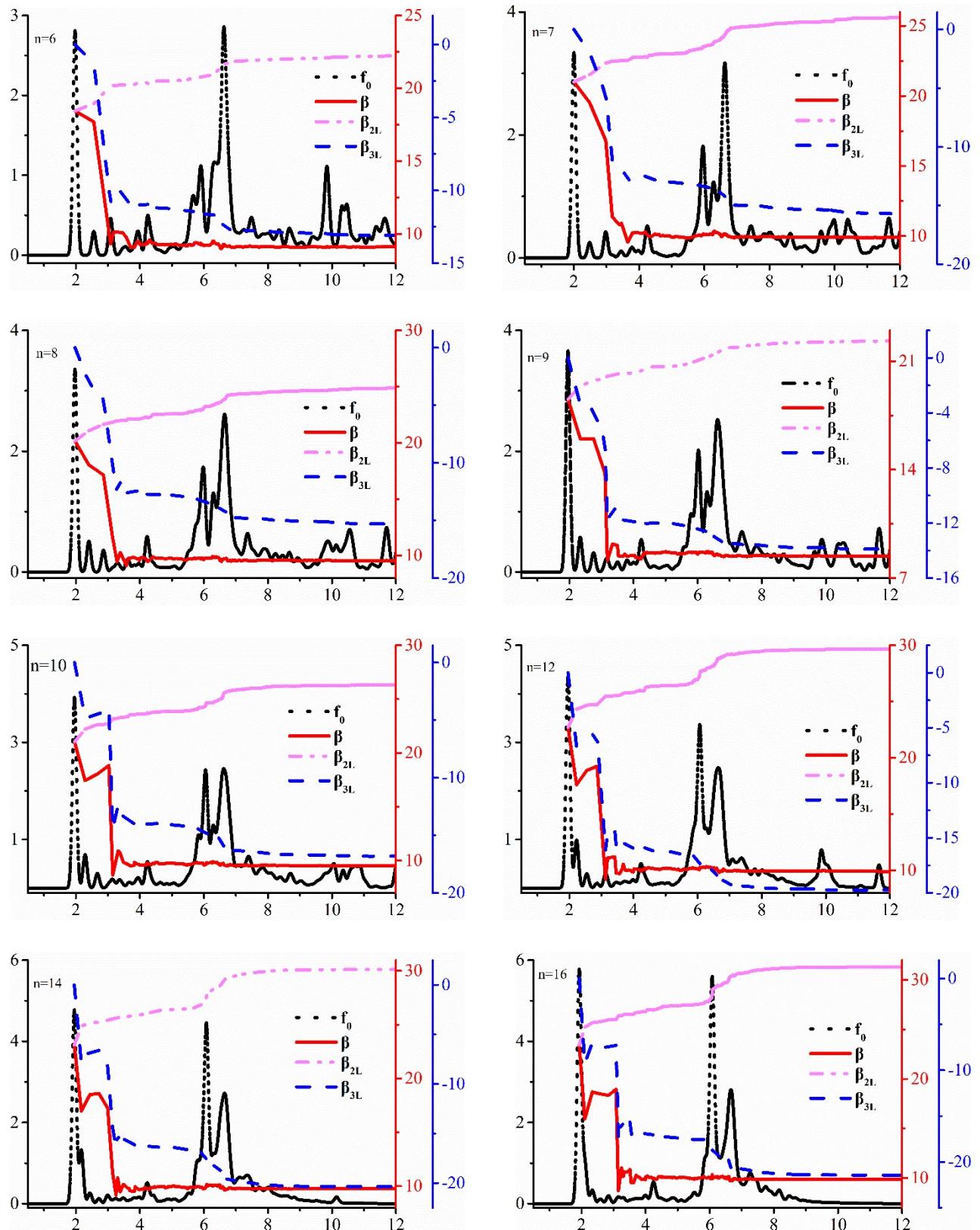




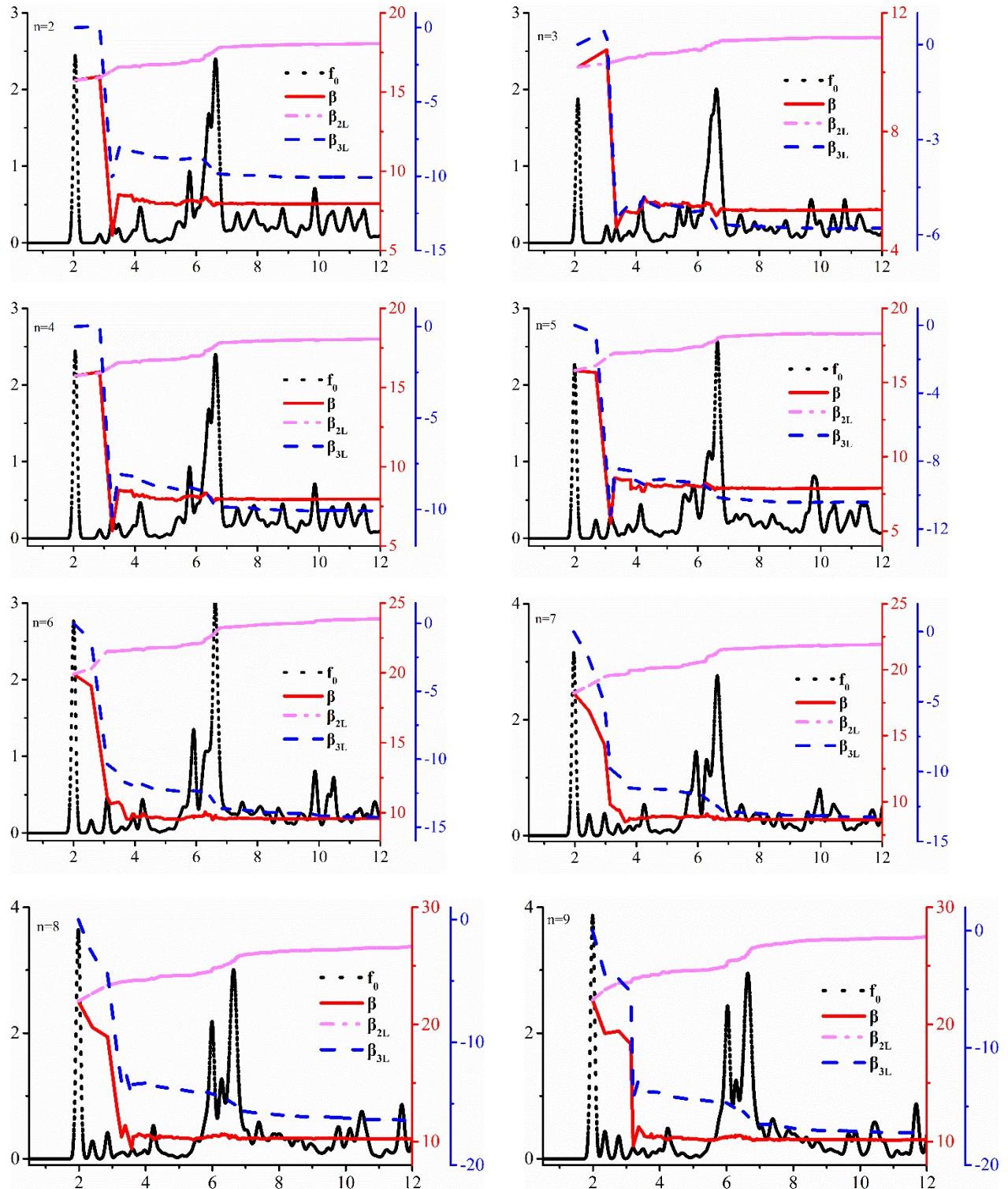
Oligo-thiophene chromophores

1. cis





2. trans



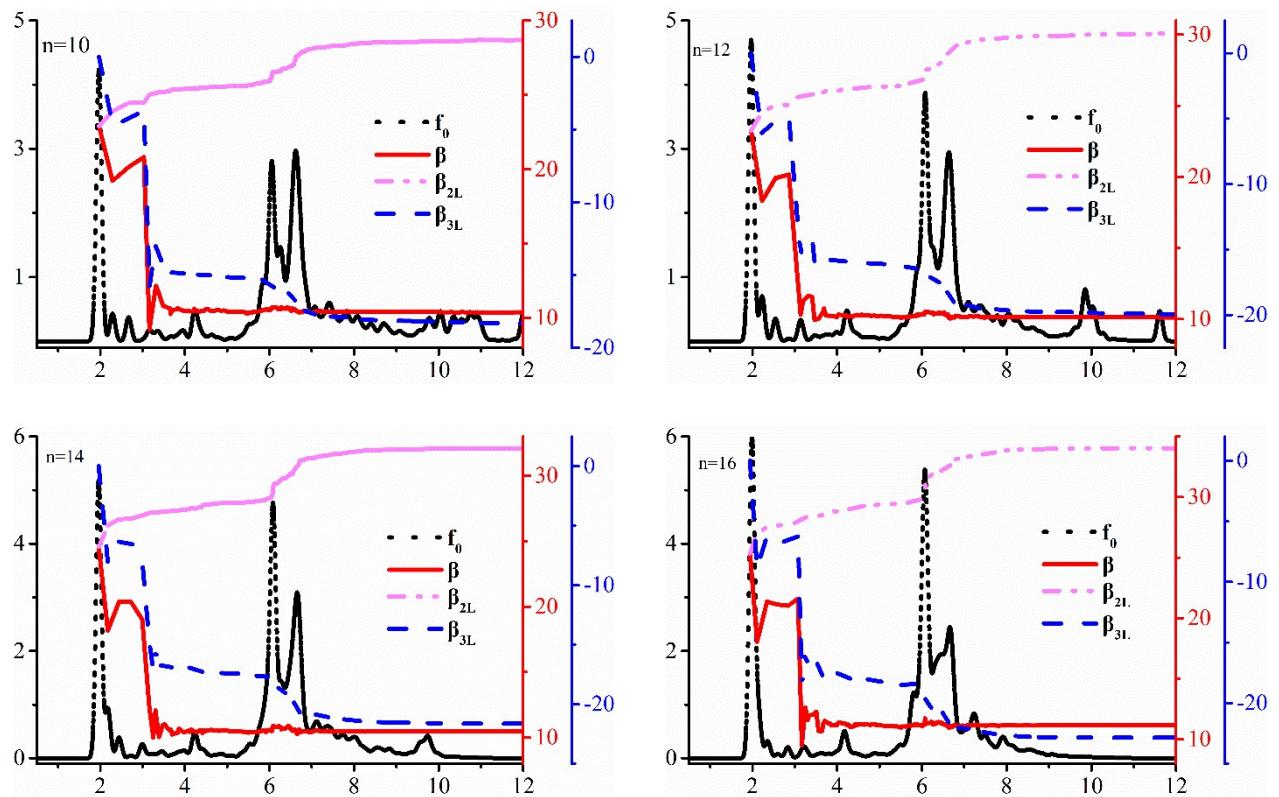


Figure S5. The evolution of β_0 (in $10^2 \times 10^{-30}$ esu) with electron excitation of polymethine and oligo-thiophene chromophores.

8. The analysis of the nature of the major contributions of electron excitations to the $\beta_0 (\times 10^{-30} \text{ esu})$ of polymethine ($n=18$) and cis-oligo-thiophene ($n=10$) chromophores

Polymethine chromophore ($n=18$)

The decomposition of static β_{xxx} into contributions from individual process calculated using equation,

$$\beta_{ijk}(\omega_\sigma; \omega_1, \omega_2)_{m,n} = \hbar^{-2} \sum P_{ijk} \sum_{\substack{m,n \\ (\neq g)}} \frac{r_{gm}^i r_{mn}^{-k} r_{ng}^j}{(\omega_{mg} + \omega_\sigma - i\Gamma_m)(\omega_{ng} - \omega_l - i\Gamma_n)}$$

r_m^n : transition moment from state m to state n.

$\beta_{xxx} (S_0 \rightarrow S_1)$ ($E_1 = 1.97 \text{ eV}$),

$S_0 \rightarrow S_1 \rightarrow S_0$

$$\frac{r_0^1(r_1^1 - r_0^0)r_1^0}{E_1^2} = 5601.1$$

$\beta_{xxx} (S_0 \rightarrow S_2)$ ($E_2 = 2.40 \text{ eV}$)

$S_0 \rightarrow S_2 \rightarrow S_0; S_0 \rightarrow S_1 \rightarrow S_2 \rightarrow S_0$

$$\frac{r_0^2(r_2^2 - r_0^0)r_2^0}{E_2^2} + \frac{r_0^1r_1^2r_2^0}{E_1 E_2} = 386.0 - 1005.1 = -619.1$$

$\beta_{xxx} (S_0 \rightarrow S_3)$ ($E_3 = 2.84 \text{ eV}$)

$S_0 \rightarrow S_3 \rightarrow S_0; S_0 \rightarrow S_1 \rightarrow S_3 \rightarrow S_0; S_0 \rightarrow S_2 \rightarrow S_3 \rightarrow S_0$

$$\frac{r_0^3(r_3^3 - r_0^0)r_3^0}{E_3^2} + \frac{r_0^1r_1^3r_3^0}{E_1 E_3} + \frac{r_0^2r_2^3r_3^0}{E_2 E_3} = 130.0 - 615.0 - 79.2 = -564.2$$

$\beta_{xxx} (S_0 \rightarrow S_4)$ ($E_4 = 3.11 \text{ eV}$)

$S_0 \rightarrow S_4 \rightarrow S_0; S_0 \rightarrow S_1 \rightarrow S_4 \rightarrow S_0; S_0 \rightarrow S_2 \rightarrow S_4 \rightarrow S_0; S_0 \rightarrow S_3 \rightarrow S_4 \rightarrow S_0$

$$\frac{r_0^4(r_4^4 - r_0^0)r_4^0}{E_4^2} + \frac{r_0^1r_1^4r_4^0}{E_1 E_4} + \frac{r_0^2r_2^4r_4^0}{E_2 E_4} + \frac{r_0^3r_3^4r_4^0}{E_3 E_4} = 20.3 - 1210.0 - 38.3 + 74.1 = -1153.9$$

$\beta_{xxx} (S_0 \rightarrow S_5)$ ($E_5 = 3.26 \text{ eV}$)

$S_0 \rightarrow S_5 \rightarrow S_0; S_0 \rightarrow S_1 \rightarrow S_5 \rightarrow S_0; S_0 \rightarrow S_2 \rightarrow S_5 \rightarrow S_0; S_0 \rightarrow S_3 \rightarrow S_5 \rightarrow S_0; S_0 \rightarrow S_4 \rightarrow S_5 \rightarrow S_0;$

$$\frac{r_0^5(r_5^5 - r_0^0)r_5^0}{E_5^2} + \frac{r_0^1r_1^5r_5^0}{E_1E_5} + \frac{r_0^2r_2^5r_5^0}{E_2E_5} + \frac{r_0^3r_3^5r_5^0}{E_3E_5} + \frac{r_0^4r_4^5r_5^0}{E_4E_5} = 56.0 - 681.7 - 377.0 + 63.4 + 6.0 = -933.3$$

β_{xxx} ($S_0 \rightarrow S_6$) ($E_6 = 3.35\text{eV}$)

$S_0 \rightarrow S_6 \rightarrow S_0; S_0 \rightarrow S_1 \rightarrow S_6 \rightarrow S_0; S_0 \rightarrow S_2 \rightarrow S_6 \rightarrow S_0; S_0 \rightarrow S_3 \rightarrow S_6 \rightarrow S_0; S_0 \rightarrow S_4 \rightarrow S_6 \rightarrow S_0; S_0 \rightarrow S_5 \rightarrow S_6 \rightarrow S_0$

$$\frac{r_0^6(r_6^6 - r_0^0)r_6^0}{E_6^2} + \frac{r_0^1r_1^6r_6^0}{E_1E_6} + \frac{r_0^2r_2^6r_6^0}{E_2E_6} + \frac{r_0^3r_3^6r_6^0}{E_3E_6} + \frac{r_0^4r_4^6r_6^0}{E_4E_6} + \frac{r_0^5r_5^6r_6^0}{E_5E_6}$$

$$= 1.8 - 208.0 + 403.0 - 7.6 + 0.8 + 7.7 = 197.7$$

β_{xxx} ($S_0 \rightarrow S_7$) ($E_7 = 3051\text{eV}$)

$S_0 \rightarrow S_7 \rightarrow S_0; S_0 \rightarrow S_1 \rightarrow S_7 \rightarrow S_0; S_0 \rightarrow S_2 \rightarrow S_7 \rightarrow S_0; S_0 \rightarrow S_3 \rightarrow S_7 \rightarrow S_0; S_0 \rightarrow S_4 \rightarrow S_7 \rightarrow S_0; S_0 \rightarrow S_5 \rightarrow S_7 \rightarrow S_0; S_0 \rightarrow S_6 \rightarrow S_7 \rightarrow S_0$

$$\frac{r_0^7(r_7^7 - r_0^0)r_7^0}{E_7^2} + \frac{r_0^1r_1^7r_7^0}{E_1E_7} + \frac{r_0^2r_2^7r_7^0}{E_2E_7} + \frac{r_0^3r_3^7r_7^0}{E_3E_7} + \frac{r_0^4r_4^7r_7^0}{E_4E_7} + \frac{r_0^5r_5^7r_7^0}{E_5E_7} + \frac{r_0^6r_6^7r_7^0}{E_6E_7}$$

$$= 0.3 - 22.7 - 19.0 - 26.8 - 5.1 + 1.0 + 2.2 = -70.1$$

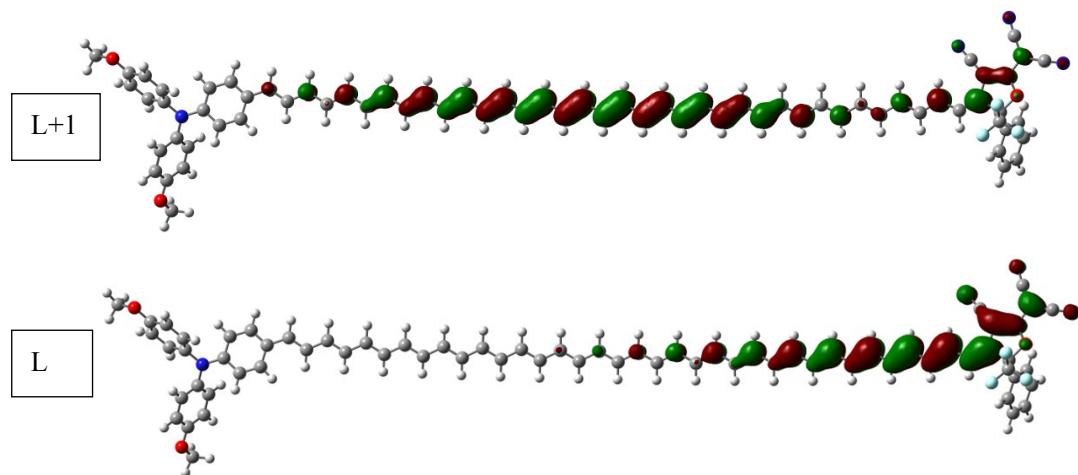
9. The single electron transition from ground state involved in the low-lying excited states of polymethine chromophore ($n=18$) and cis-oligo-thiophene chromophore ($n=10$)

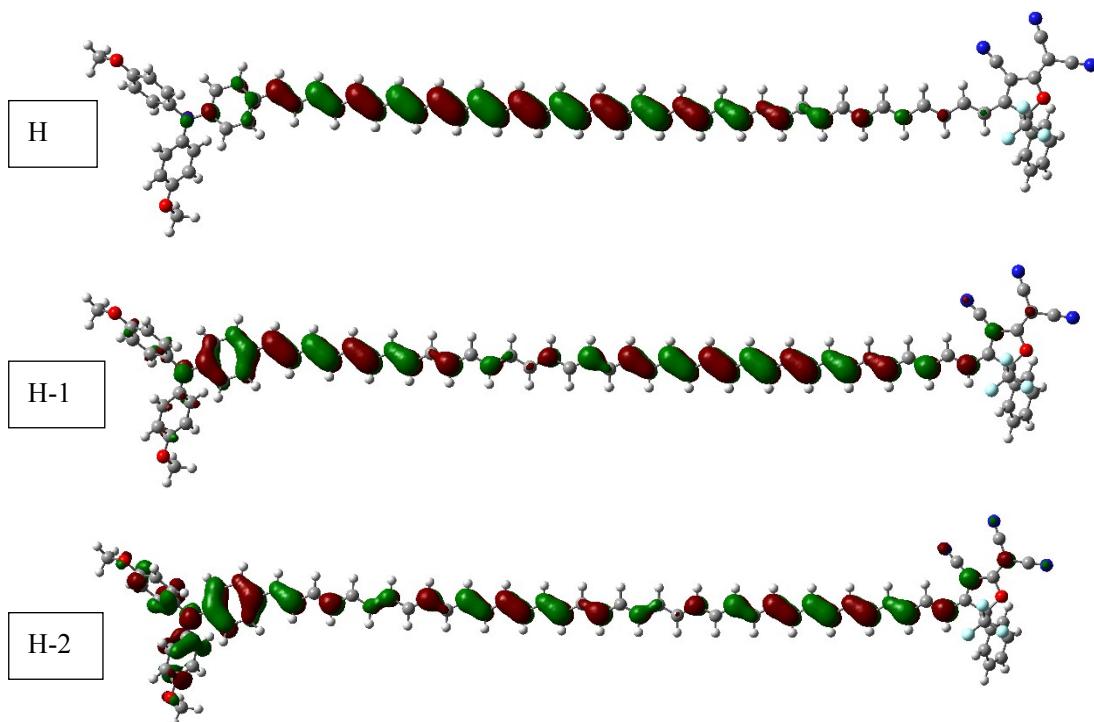
L: LUMO; H: HOMO.

polymethine chromophore ($n=18$)

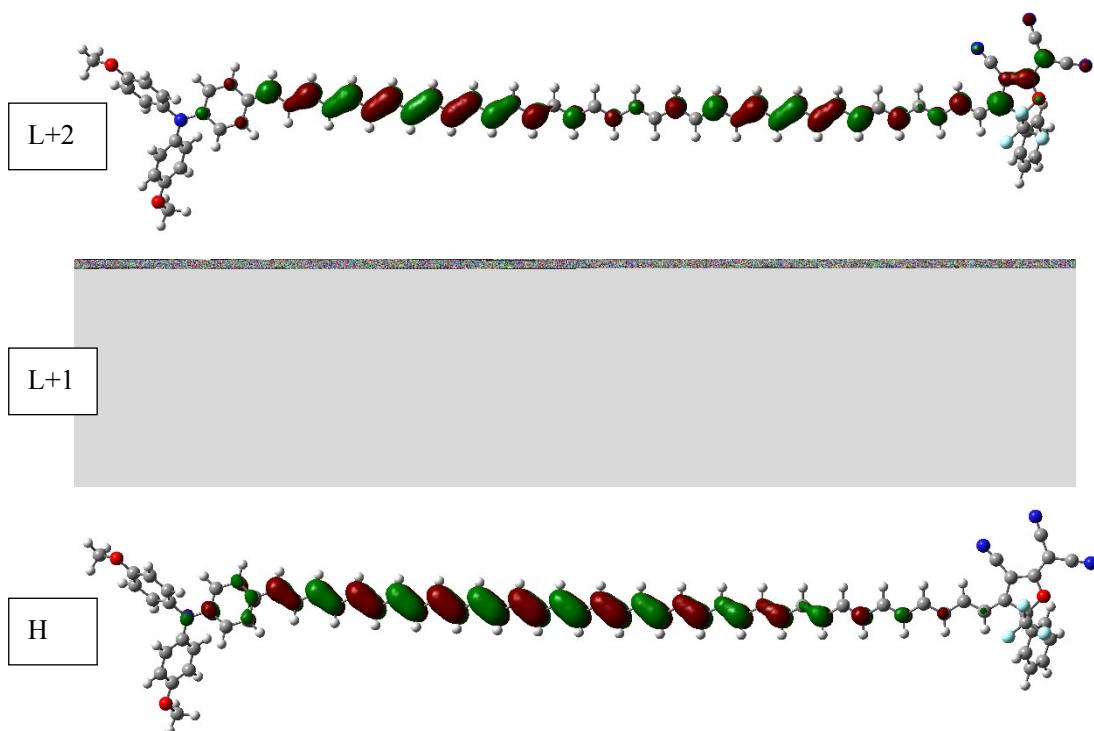
S_0 (ground state)

S_1 : H-2 \rightarrow L (13.65%); H-1 \rightarrow L (27.15%); H \rightarrow L (21.65%); H \rightarrow L+1 (14.56%)

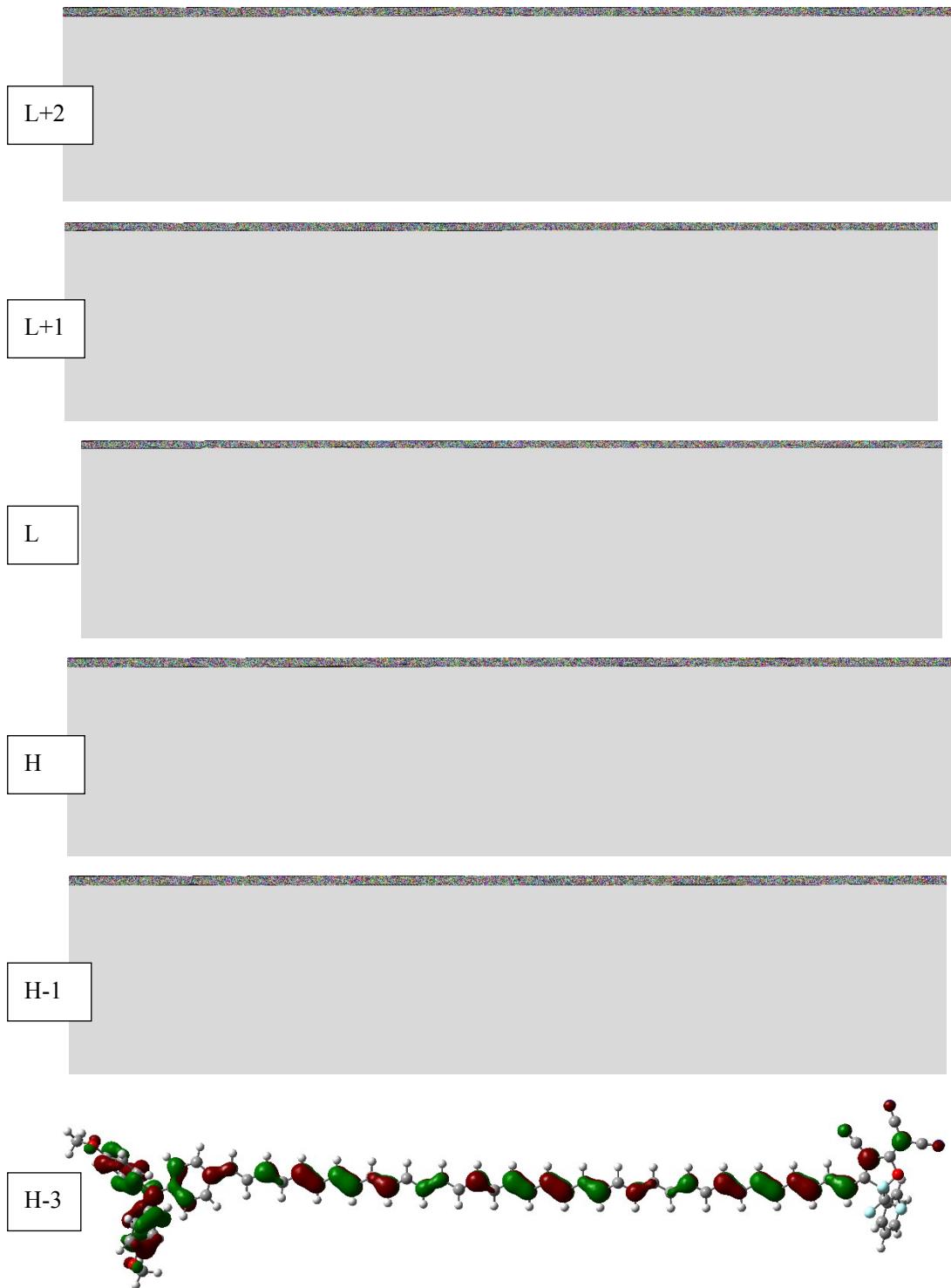




S₂: H→L+1 (41.58%); H→L+2 (12.16%)



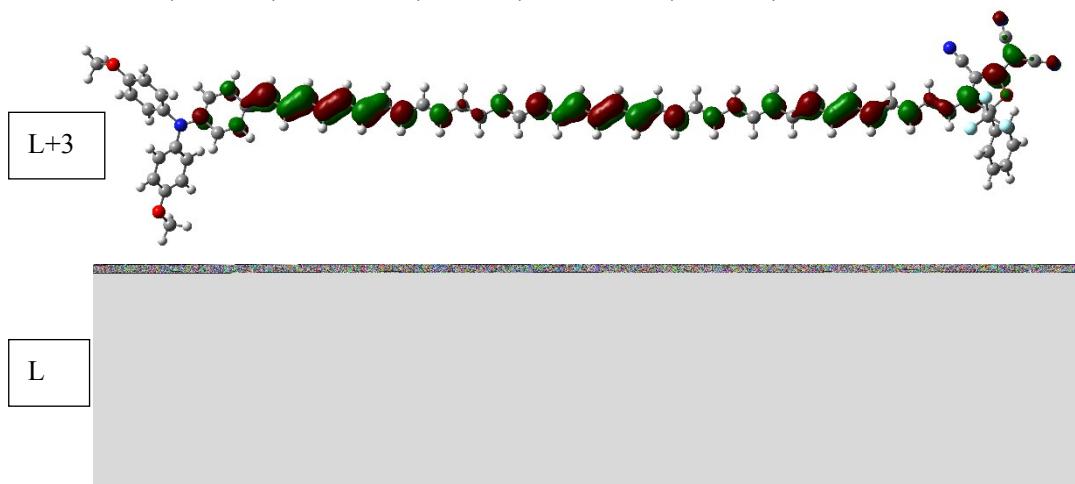
S₃: H-3→L (10.71%); H-1→L+1 (18.43%); H→L+2 (27.74%)

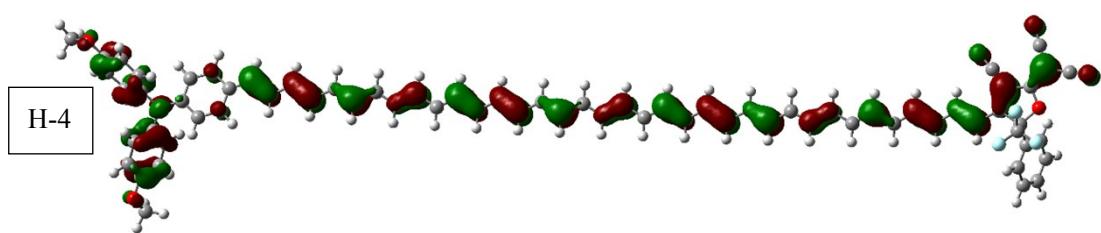


S₄: H-1→L+1 (21.21%); H→L (19.81%)



S₅: H-4→L (11.27%); H-2→L (14.02%); H→L+3 (15.65%)

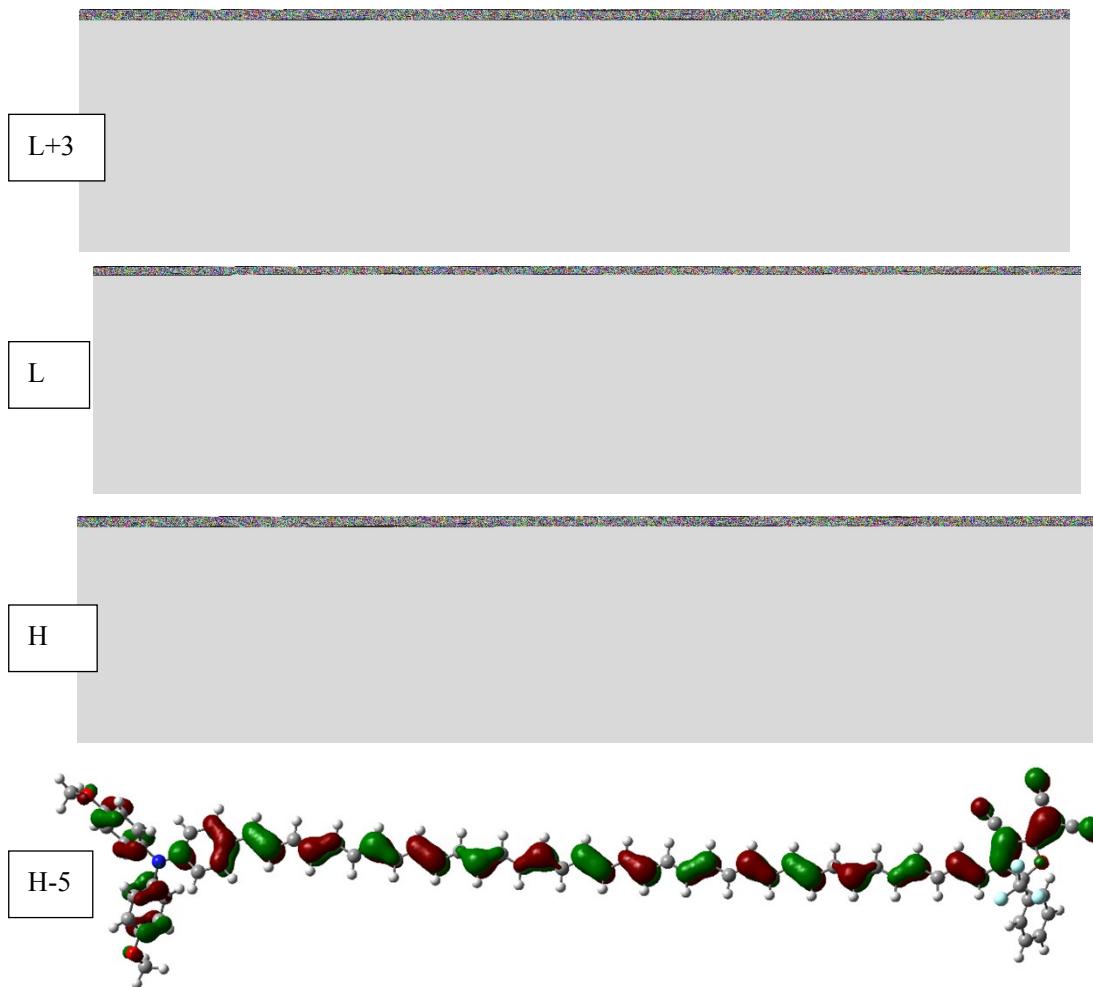




S₆: H-1→L+2 (25.70%); H→L+2 (14.98%)



S₇: H-5→L (19.39%); H→L+3 (14.08%)



Oligo-thiophene chromophore (n=10)

The decomposition of static β_{xxx} into contributions from individual process calculated using equation,

$$\beta_{ijk}(\omega_\sigma; \omega_1, \omega_2)_{m,n} = \hbar^{-2} \sum P_{ijk} \sum_{\substack{m,n \\ (\neq g)}} \frac{r_{gm}^i r_{mn}^{-k} r_{ng}^j}{(\omega_{mg} + \omega_\sigma - i\Gamma_m)(\omega_{ng} - \omega_l - i\Gamma_n)}$$

r_m^n : transition moment from state m to state n.

β_{xxx} ($S_0 \rightarrow S_1$) ($E_1 = 1.96\text{eV}$)

$S_0 \rightarrow S_1 \rightarrow S_0$

$$\frac{r_0^1(r_1^1 - r_0^0)r_1^0}{E_1^2} = 2395.0$$

β_{xxx} ($S_0 \rightarrow S_2$) ($E_2 = 2.29\text{eV}$)

$S_0 \rightarrow S_2 \rightarrow S_0; \quad S_0 \rightarrow S_1 \rightarrow S_2 \rightarrow S_0$

$$\frac{r_0^2(r_2^2 - r_0^0)r_2^0}{E_2^2} + \frac{r_0^1r_1^2r_2^0}{E_1E_2} = 155.3 + 509.5 = -443.5$$

β_{xxx} ($S_0 \rightarrow S_3$) ($E_3 = 2.67\text{eV}$)

$S_0 \rightarrow S_3 \rightarrow S_0; S_0 \rightarrow S_1 \rightarrow S_3 \rightarrow S_0; S_0 \rightarrow S_2 \rightarrow S_3 \rightarrow S_0$

$$\frac{r_0^3(r_3^3 - r_0^0)r_3^0}{E_3^2} + \frac{r_0^1r_1^3r_3^0}{E_1E_3} + \frac{r_0^2r_2^3r_3^0}{E_2E_3} = 46.6 + 66.3 - 53.1 = 59.8$$

β_{xxx} ($S_0 \rightarrow S_4$) ($E_4 = 3.03\text{eV}$)

$S_0 \rightarrow S_4 \rightarrow S_0; S_0 \rightarrow S_1 \rightarrow S_4 \rightarrow S_0; S_0 \rightarrow S_2 \rightarrow S_4 \rightarrow S_0; S_0 \rightarrow S_3 \rightarrow S_4 \rightarrow S_0$

$$\frac{r_0^4(r_4^4 - r_0^0)r_4^0}{E_4^2} + \frac{r_0^1r_1^4r_4^0}{E_1E_4} + \frac{r_0^2r_2^4r_4^0}{E_2E_4} + \frac{r_0^3r_3^4r_4^0}{E_3E_4} = 5.4 + 146 - 1.9 - 13.9 = 135.6$$

β_{xxx} ($S_0 \rightarrow S_5$) ($E_5 = 3.15\text{eV}$)

$S_0 \rightarrow S_5 \rightarrow S_0; S_0 \rightarrow S_1 \rightarrow S_5 \rightarrow S_0; S_0 \rightarrow S_2 \rightarrow S_5 \rightarrow S_0; S_0 \rightarrow S_3 \rightarrow S_5 \rightarrow S_0; S_0 \rightarrow S_4 \rightarrow S_5 \rightarrow S_0$

$$\frac{r_0^5(r_5^5 - r_0^0)r_5^0}{E_5^2} + \frac{r_0^1r_1^5r_5^0}{E_1E_5} + \frac{r_0^2r_2^5r_5^0}{E_2E_5} + \frac{r_0^3r_3^5r_5^0}{E_3E_5} + \frac{r_0^4r_4^5r_5^0}{E_4E_5} = 52.5 - 1250.5 + 32.1 + 52.7 - 18.8 = -1132.0$$

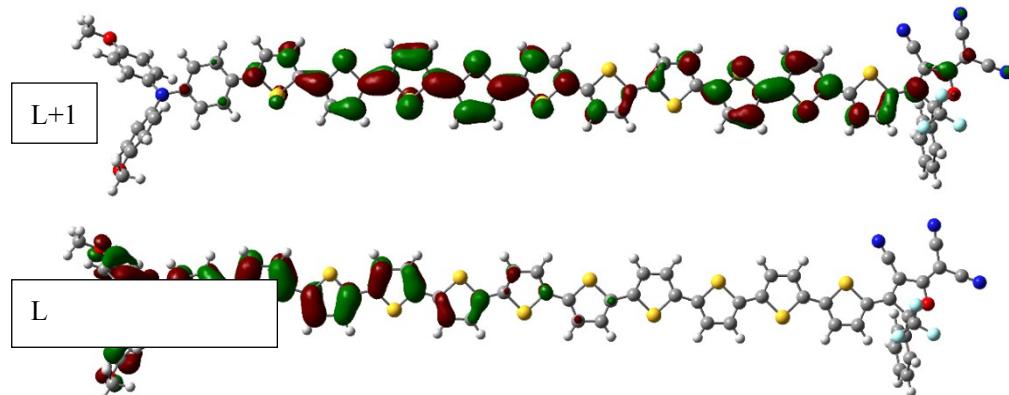
β_{xxx} ($S_0 \rightarrow S_6$) ($E_6 = 3.32\text{eV}$)

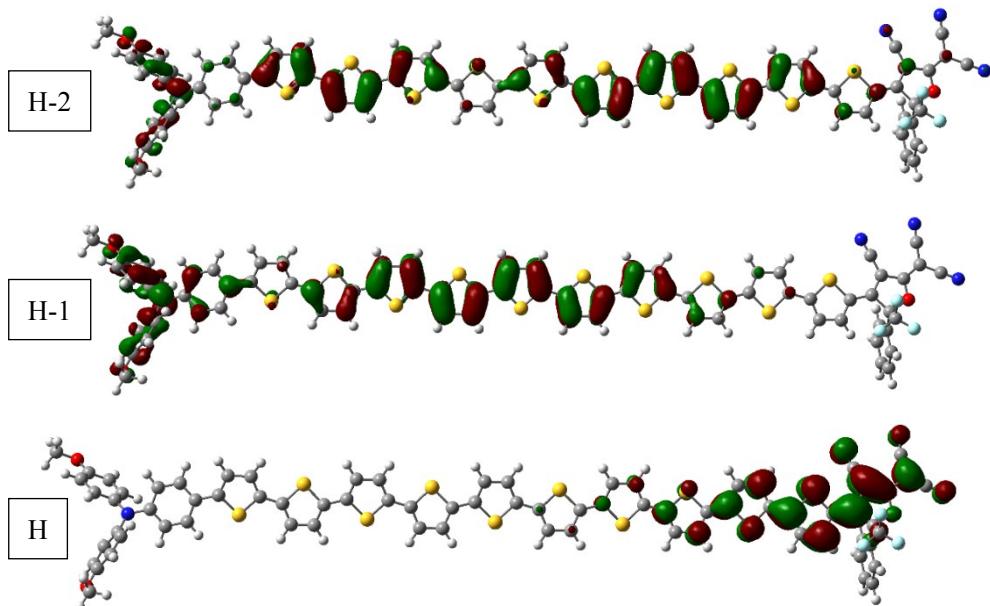
$S_0 \rightarrow S_6 \rightarrow S_0; S_0 \rightarrow S_1 \rightarrow S_6 \rightarrow S_0; S_0 \rightarrow S_2 \rightarrow S_6 \rightarrow S_0; S_0 \rightarrow S_3 \rightarrow S_6 \rightarrow S_0; S_0 \rightarrow S_4 \rightarrow S_6 \rightarrow S_0; S_0 \rightarrow S_5 \rightarrow S_6 \rightarrow S_0$

$$\frac{r_0^6(r_6^6 - r_0^0)r_6^0}{E_6^2} + \frac{r_0^1r_1^6r_6^0}{E_1E_6} + \frac{r_0^2r_2^6r_6^0}{E_2E_6} + \frac{r_0^3r_3^6r_6^0}{E_3E_6} + \frac{r_0^4r_4^6r_6^0}{E_4E_6} + \frac{r_0^5r_5^6r_6^0}{E_5E_6} = 4.8 + 123.1 + 153.0 - 19.6 - 5.0 - 10.1 = 246.2$$

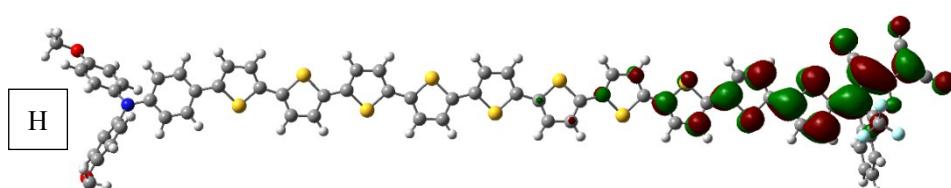
S_0 (ground state)

S1: H-2 → L (16.8%); H-1 → L (23.9%); H → L+1 (14.8%)

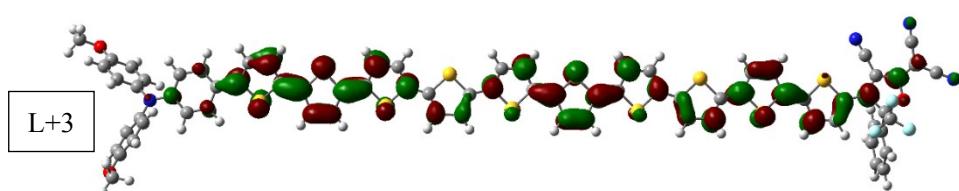


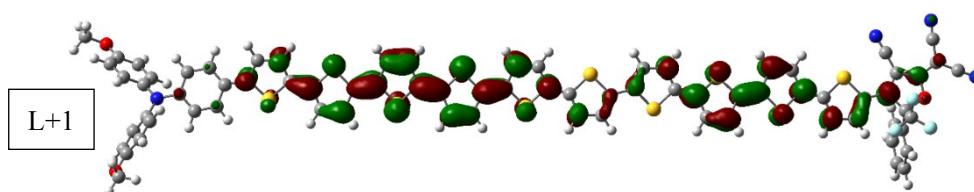


S2: $H \rightarrow L+1$ (30.9%); $H \rightarrow L+2$ (21.8%)

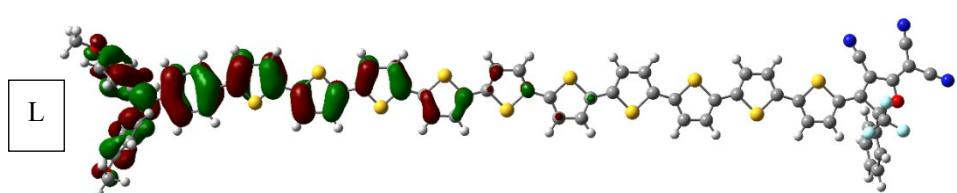
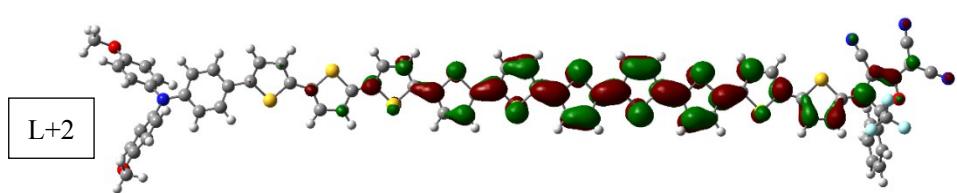
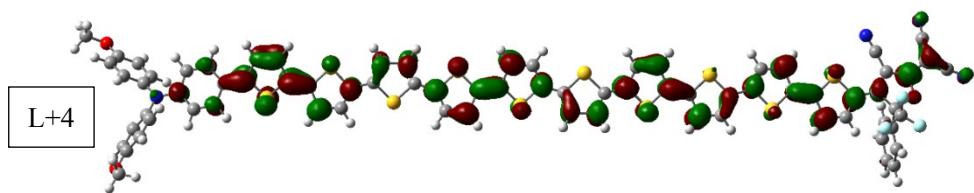


S3: $H-1 \rightarrow L+1$ (23.9%); $H \rightarrow L+2$ (20.7%); $H \rightarrow L+3$ (13.7%)





S4: H-4→L (10.4%); H-1→L+2 (19.3%); H→L+3 (17.4%); H→L+4 (10.1%)





S5: $H-2 \rightarrow L+1$ (15.9%); $H \rightarrow L$ (17.7%)



S6: $H-1 \rightarrow L+2$ (12.3%)

