Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Support Information

A new scheme for significant enhancement of the second order nonlinear optical response from molecule to ordered aggregates

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The static β_0, dipole moment, and the electronic spectra of the aggregates of corannulene, sumanene and $C_{36}H_{12}$.

Major absorption peaks of buckybowl aggregates predicted by ZINDO

Table S1. Dipole moment (μ in debye), NLO Response (β in 10^{-30} cm^5 esu^{-1}), and the strongest absorption peak of electronic spectra of $(Corannulene)_{1\text{-}10}$, $(Sumanene)_{1\text{-}10}$, and $(C_{36}H_{12})_{1\text{-}5}$.

n	$(Corannulene)_n$				$(Sumanene)_n$				$(C_{36}H_{12})_n$			
	μ	β	β_{Per}	λ	μ	β	β_{Per}	λ	μ	β	β_{Per}	λ
1	−2.95	−7.98	−7.98	317.2	−3.05	−7.82	−7.82	380.5	−5.40	−36.2	−36.2	422.4
2	−5.84	−27.27	−13.64	287.2	−5.96	−28.05	−14.03	384..8	−11.89	−170.52	−85.26	450.3
3	−8.74	−57.25	−19.08	303.8	−8.89	−60.23	−20.07	386.9	−17.75	−364.76	−121.59	444.4
4	−11.64	−94.57	−23.64	293.5	−11.80	−103.99	−26.00	386.8	−23.60	−639.83	−159.96	443.2
5	−14.54	−147.64	−29.53	304.7	−14.73	−159.71	−31.94	386.3	−29.46	−955.72	−191.14	436.7
6	−17.44	−199.03	−33.17	335.2	−17.64	−218.50	−36.42	365.7				
7	−20.34	−265.29	−37.90	337.5	−20.57	−270.18	−38.60	361.4				
8	−23.24	−350.41	−43.80	319.6	−23.47	−369.15	−46.14	365.9				
9	−26.13	−436.22	−48.67	335.9	−26.41	−451.71	−50.19	361.0				
10	−29.03	−526.74	−52.60	317.8	−29.32	−563.30	−56.30	359.6				

Table S2. Major absorption peaks (absorption wavelength λ in nm, transition dipole moments μ and dipole moment change Δμ in debye) predicted by ZINDO with important contributions to β_0 of buckybowls.

Molecule	Transition	λ	μ_x	μ_y	μ_z	$\Delta\mu$
$C_{20}H_{10}$	S_1-->S_{10}	255.1	−7.80	−0.36	−0.02	1.12
	S_1-->S_{11}	254.0	0.36	−7.79	−0.00	1.12
	S_1-->S_{16}	237.3	−0.67	−0.07	2.02	1.87
$C_{30}H_{10}$	S_1-->S_9	436.1	0.00	−0.00	−1.66	1.00
	S_1-->S_{24}	284.1	8.12	1.22	0.00	0.77
	S_1-->S_{25}	284.1	1.22	−8.13	0.00	0.77
	S_1-->S_{43}	239.0	0.00	0.00	3.37	1.35
$C_{40}H_{10}$	S_1-->S_{11}	389.3	0.00	0.00	−1.32	1.66
	S_1-->S_{23}	329.9	−3.91	7.11	0.00	1.74
	S_1-->S_{24}	329.9	−7.11	−3.91	0.00	1.74
	S_1-->S_{80}	227.4	0.00	0.00	4.46	5.75
$C_{21}H_{12}$	S_1-->S_2	375.0	0.00	0.00	-0.49	0.61
	S_1-->S_6	297.6	2.56	−5.87	0.00	0.96
	S_1-->S_7	297.6	−5.87	−2.56	0.00	0.96
	S_1-->S_{29}	198.6	0.00	0.00	2.46	1.12
$C_{36}H_{12}$	S_1-->S_9	369.1	0.01	0.00	−2.13	3.93
	S_1-->S_{21}	289.4	−0.92	8.22	−0.01	1.12
	S_1-->S_{22}	289.4	−8.24	−0.94	0.01	1.12
	S_1-->S_{77}	202.6	−0.03	−0.02	4.75	4.16
$C_{39}H_{12}$	S_1-->S_8	408.0	−0.00	0.00	1.61	4.17
	S1-->S_{15}	349.6	−3.95	−1.74	0.00	1.02
	S_1-->S_{16}	349.6	−1.74	3.95	0.00	1.02
	S_1-->S_{82}	211.9	−0.01	0.02	4.59	4.74

Table S3. Major absorption peaks (absorption wavelength λ in nm, transition dipole moments μ and dipole moment change Δμ in debye) of $(Sumanene)_n$ (n=1,2,4,6,8) predicted by ZINDO with important contributions to β_0 of Sumanene aggregates. *f* is oscillator strength.

$(Sumanene)_n$	Transition	λ	*f*	μ_x	μ_y	μ_z
Monomer	S_1-->S_2 (intra-CT)	375.0	0.003	0.00	0.00	-0.49
	S_1-->S_6 (intra-CT)	297.6	0.648	2.56	−5.87	0.00
	S_1-->S_7 (intra-CT)	297.6	0.648	−5.87	−2.56	0.00
	S_1--S_{40} (intra-CT)	184.7	0.008	0.00	0.00	0.56
Dimer	S_1-->S_2 (inter-CT)	383.2	0.011	0.00	0.00	0.95
	S_1-->S_{12} (intra-CT)	294.1	0.878	−3.38	6.59	0.00
	S_1-->S_{13} (intra-CT)	294.1	0.878	−6.59	−3.37	0.00
	S_1-->S_{89} (inter-CT)	199.4	0.151	0.00	0.00	2.53
Tetramer	S_1-->S_2 (inter-CT)	386.6	0.022	0.00	0.00	1.33
	S_1-->S_{24} (intra-CT)	289.7	1.221	−6.83	5.34	0.00
	S_1-->S_{25} (intra-CT)	289.7	1.221	−5.34	−6.83	0.00
	S_1-->S_{226} (inter-CT)	199.9	0.243	0.00	0.00	3.21
Hexamer	S_1-->S_2 (inter-CT)	373.5	0.043	0.00	0.00	1.85
	S_1-->S_{118} (intra-CT)	247.9	1.699	9.30	−1.73	0.00
	S_1-->S_{119} (intra-CT)	247.9	1.699	1.73	9.30	0.00
	S_1-->S_{310} (inter-CT)	204.8	0.584	0.00	0.00	5.04
Octamer	S_1-->S_2 (inter-CT)	365.9	0.052	0.00	0.00	2.00
	S_1-->S_{161} (intra-CT)	247.0	2.313	10.52	3.27	0.00
	S_1-->S_{162} (intra-CT)	247.0	2.313	3.271	−10.52	0.00
	S_1-->S_{468} (inter-CT)	199.7	1.420	0.00	0.00	7.76

Note: inter-CT represents intermolecular charge transfer transition; intra-CT represents intramolecular charge transfer transition.