Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

Third-Order Nonlinear Optical Property Contrast as Self-Assembly Recognition for Nanorings⊃C_{60}

Nana Ma,*[a] Wenyue Guo,[a] Zhu Zhu[b] and Guisheng Zhang*[a]

[a]School of Chemistry and Chemical Engineering, Key Laboratory of Green Chemical Media and Reactions, Ministry of Education; NMPA Key Laboratory for Research and Evaluation of Innovative Drug, Henan Normal University, Xinxiang, Henan, 453007, China.
[b]Xiangyang Public Inspection and Testing Center, Xiangyang, Hubei, 441000, China.

Content

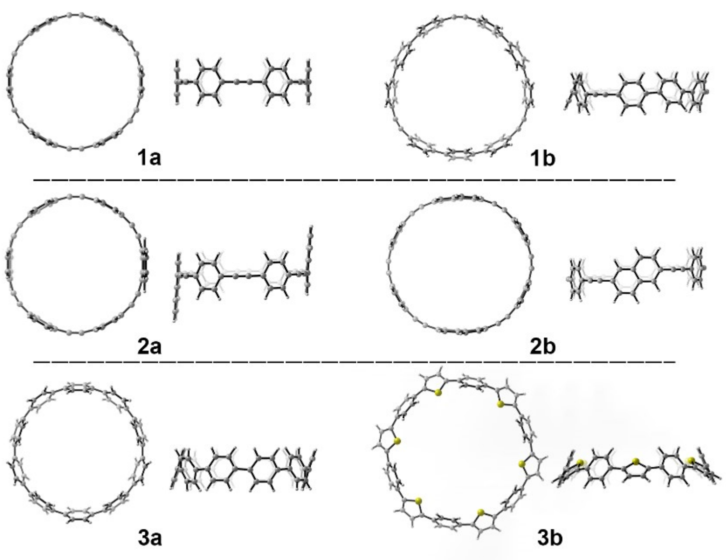


Fig. S1. The optimized structures of nanorings in top view and side view.

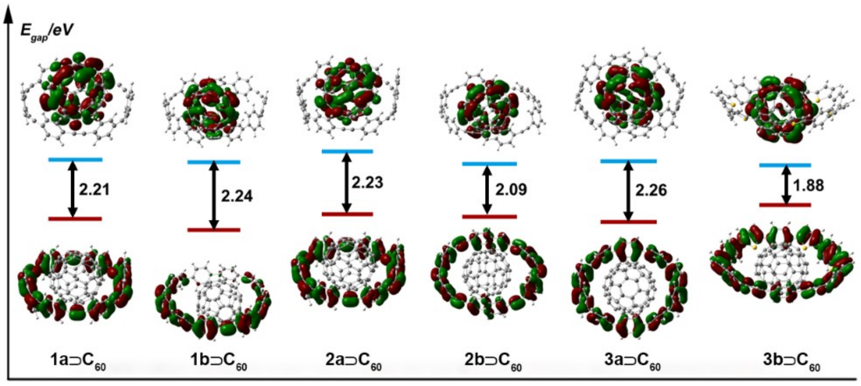
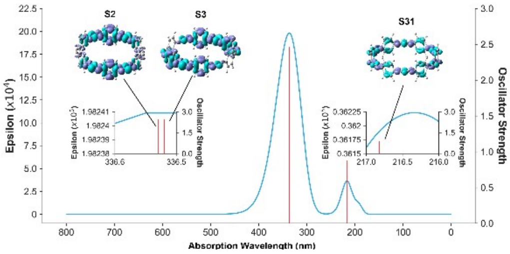


Fig. S2. The HOMO and LUMO composition and HOMO-LUMO gap ($\boldsymbol{E}_{\text{H-L}}$) of nanorings⊃$C_{60}$.



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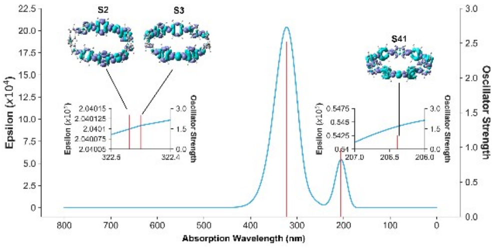

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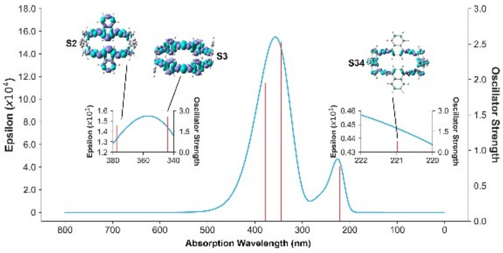

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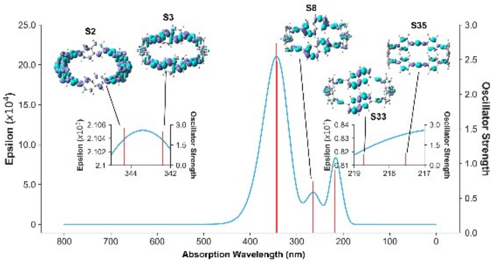

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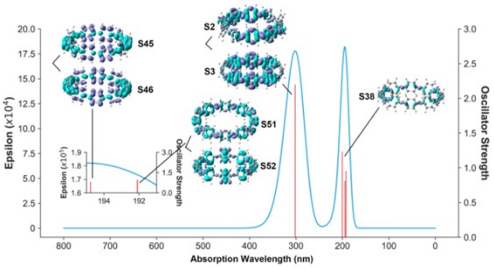

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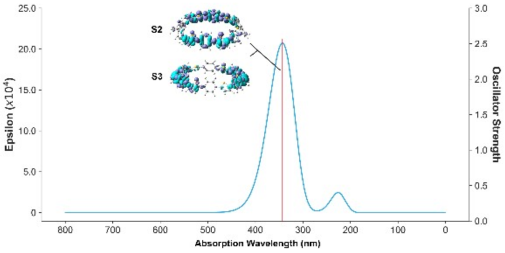

CPT-3b

Fig. S3. The electron density difference maps (EDDMs) of the ground state and the excited state of the nanorings corresponding to the primary absorption.

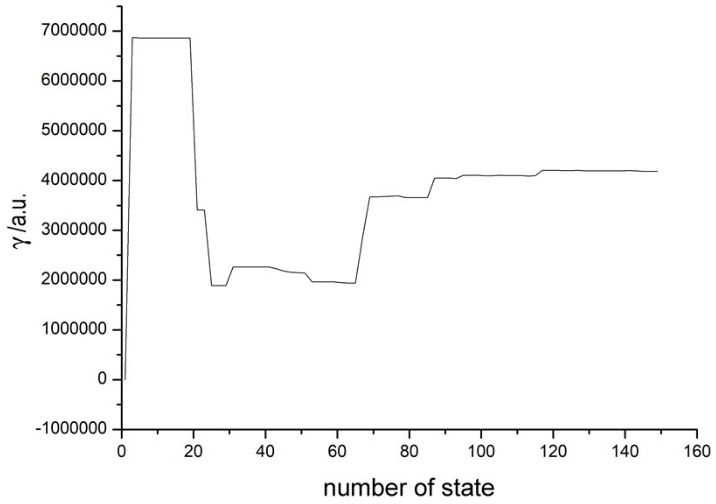

Fig. S4. The curve of γ values with the number of states by SOS method.

Table S1. The TDDFT results calculated at ωB97XD/6−31+G(d) level (absorption wavelength (λ/nm), transition energy (Δ*E*/eV), and oscillator strength (*f*) of major molecular orbital transitions) for nanorings.

nanoring	**Transition State**	**Δ*E***/eV	***λ***/nm	***f***
1a	S0-S2	3.6842	336.53	2.4387
	S0-S3	3.6843	336.52	2.4560
	S0-S31	5.7183	216.82	0.8775
1b	S0-S2	3.8449	322.47	2.5150
	S0-S3	3.8451	322.45	2.5131
	S0-S41	6.0073	206.39	0.9747
2a	S0-S2	3.2835	377.59	1.9473
	S0-S3	3.6043	343.99	2.5293
	S0-S34	5.6103	220.99	0.7706
2b	S0-S2	3.6007	344.34	2.7280
	S0-S3	3.6209	342.41	2.4717
	S0-S8	4.6695	265.52	0.7442
	S0-S33	5.6685	218.73	0.7710
	S0-S35	5.6998	217.53	0.9009
3a	S0-S2	4.1088	301.75	2.1955
	S0-S3	4.1088	301.75	2.1956
	S0-S38	6.1909	200.27	1.2291
	S0-S45	6.3658	194.77	0.8072
	S0-S46	6.3658	194.77	0.8068
	S0-S51	6.4543	192.10	0.9486
	S0-S52	6.4543	192.09	0.9487
3b	S0-S2	3.6128	343.18	2.5611
	S0-S3	3.6128	343.18	2.5610

Table S2. The first hyperpolarizabilities of nanorings and nanorings ⊃ C_{60}.

	a.u.				esu ($\times 10^{-30}$)
	β_x	β_y	β_z	β^a	β
1a	0	0	0	0	0
1b	156	-399	750	864	7
2a	10	-14	-10	20	0.2
2b	0	0	0	0	0
3a	0	0	0	0	0
3b	0	0	-9034	9034	78
C_{60}	0	0	0	0	1
1a ⊃ C_{60}	-4353	-1973	4481	6551	57
1b ⊃ C_{60}	1936	-342	-1269	2340	20
2a ⊃ C_{60}	1018	2304	-636	2598	22
2b ⊃ C_{60}	9097	4145	-1414	10096	87
3a ⊃ C_{60}	16	14	14	25	0.2
3b ⊃ C_{60}	-68	-11	3476	3476	30

[a] the β were calculated by software Multiwfn in the sum-overstates (SOS) method, the total magnitude of β can be measured by eqs.

$$\beta_{ABC}(-\omega_\sigma;\omega_1,\omega_2) = \hat{P}[A(-\omega_\sigma);B(\omega_1),C(\omega_2)]\sum_{i\neq 0}\sum_{j\neq 0}\frac{\mu^A_{0i}\overline{\mu^B_{ij}}\mu^C_{j0}}{(\Delta_i-\omega_\sigma)(\Delta_i-\omega_2)};$$

$$\mu^A_{ij} =< i|\hat{\mu}^A|j > ;\quad \overline{\mu^A_{ij}} = \mu^A_{ij} - \mu^A_{00}\delta_{ij};\quad \omega_\sigma = \sum_i \omega_i$$

Table S3. The frequency-dependent second hyperpolarizabilities $\gamma(-\omega; \omega, 0, 0)$ of nanorings and nanorings ⊃ C_{60}.

	esu (×10^{-36})		
	γ(ω=0.06 a.u., 760 nm)	γ(ω=0.07 a.u., 650 nm)	γ(ω=0.08 a.u., 570 nm)
1a	1151	1214	1280
1b	320	379	521
2a	1400	1457	1480
2b	649	662	778
3a	656	780	967
3b	350	550	919
1a ⊃ C$_{60}$	4297	4928	5853
1b ⊃ C$_{60}$	1506	1683	1906
2a ⊃ C$_{60}$	4170	5093	6677
2b ⊃ C$_{60}$	3417	3866	4473
3a ⊃ C$_{60}$	3504	3896	4408
3b ⊃ C$_{60}$	5531	6406	7720

Table S4. The third-order NLO coefficients of nanorings and nanorings ⊃ C_{60} in dichloroethane.

	a.u.				esu (×10^{-36})	R^{a}
	γ_x	γ_y	γ_z	γ	γ	
1a	-2.64	-2.57	-0.66	3.74	1886	1.92
1b	-0.83	-0.83	-0.49	1.27	638	2.20
2a	-2.66	-2.06	-1.07	3.53	1780	1.48
2b	-0.97	-2.66	-1.19	3.07	1547	2.34
3a	-1.48	-1.48	-0.81	2.25	1131	2.63
3b	-0.06	-0.10	-0.49	0.50	251	1.48
C$_{60}$	-2.57	-2.45	-2.53	4.36	2198	1.54
1a ⊃ C$_{60}$	-5.13	-4.93	-1.36	7.24	3647	1.18
1b ⊃ C$_{60}$	-2.16	-1.41	-0.67	2.66	1342	1.19
2a ⊃ C$_{60}$	-2.53	-5.06	-0.75	5.70	2871	1.07
2b ⊃ C$_{60}$	-2.67	-3.85	-0.94	4.78	2408	0.96
3a ⊃ C$_{60}$	-4.78	-4.85	-1.42	6.95	3501	1.31
3b ⊃ C$_{60}$	-5.23	-5.19	-1.96	7.62	3840	0.98

[a] the magnification of γ value in solution divided by γ value in gas phase.