Supporting Information

Remarkable Nonlinear Optical Response of Pyrazine-fused Trichalcogenasumanenes and Their Application for Optical Power Limiting

Jibin Sun,*^a Yantao Sun,^b Chaoxian Yan,^b Dongxu Lin,^b Zheng Xie,^a Shuyun Zhou,^a Chengshan Yuan,*^b Hao-Li Zhang^b and Xiangfeng Shao*^b

^a Key Laboratory of Photochemical Conversion and Optoelectronic Materials, Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing 100190, P. R. China; ^b State Key Laboratory of Applied Organic Chemistry, Lanzhou University, Lanzhou 730000, P. R. China.

E-mails: sunjibin@mail.ipc.ac.cn, shaoxf@lzu.edu.cn, yuancs@lzu.edu.cn

Contents

I.	Characterization techniques	S2
II.	Synthetic procedures	S3
III.	DFT calculation	S5
IV.	Open-aperture Z-scan measurement	515
V.	Nanosecond pump-probe measurement	519
VI.	FT-IR spectra of compounds 1 and 2	520
VII	. References	521

I. Characterization techniques

Chemicals were purchased from Alfa-Aesar, J&K and Sigma-Aldrich, and used without further purification unless otherwise stated. The trichalcogenasumanenes (**1a** and **2a**) were synthesized according to our previous report.^{S1}

Melting points were determined on WRS-2 melting point apparatus. ¹H and ¹³C NMR spectra were recorded on a Bruker Avance III 400MHz (100 MHz for ¹³C) or a VARIAN INOVA 600MHz spectrometer (150 MHz for ¹³C) spectrometer. The chemical shifts of ¹H and ¹³C NMR were recorded using TMS as internal standard. High-resolution mass spectral analysis (HRMS) was carried out on a maXis 4G mass spectrometer (Bruker Daltonic Inc.). The Fourier transportation infrared spectra (FTIR) of were obtained from an Excalibur 3100 by KBr parallel method.

II. Synthetic procedures.^{S2}



The synthesis of compound 1b: Compound 1a (63 mg, 0.1 mmol) was dissolved in the mixed solvent of CH₂Cl₂ (5.0 mL) and CH₃NO₂ (5.0 mL). FeCl₃ (162 mg, 1.0 mmol) was added in one portion. The resulting mixture was stirred at room temperature (RT) for 2 h. The reaction was quenched by adding anhydrous methanol (30 mL). The precipitate was filtered and washed with anhydrous methanol. The crude product was further purified by column chromatography on silica-gel (eluent, CH₂Cl₂) to afford 1b as blue powder (16 mg, yield, 48%). mp: 226.4–227.9 °C. ¹H NMR (400 MHz, CDCl₃) δ (ppm) 4.40 (t, *J* = 6.4 Hz, 4H), 4.21 (t, *J* = 6.4 Hz, 4H), 1.92–1.85 (m, 4H), 1.84–1.77 (m, 4H), 1.67–1.53 (m, 8H), 1.06 (t, *J* = 5.4 Hz, 6H), 1.03 (t, *J* = 5.3 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 174.70, 151.49, 145.51, 140.32, 137.96, 130.78, 129.75, 128.24, 127.08, 73.24, 72.98, 32.24, 32.11, 19.21, 13.89. HRMS (C₃₄H₃₆O₆S₃ + H): Calc. 637.1747, found 637.1758.

The synthesis of compound 2b: Compound 2a (89 mg, 0.1 mmol) was dissolved in the mixed solvent of CH₂Cl₂ (5.0 mL) and CH₃NO₂ (5.0 mL). FeCl₃ (162 mg, 1.0 mmol) was added in one portion. The resulting mixture was stirred at RT for 2 h. The reaction was quenched by adding anhydrous methanol (50 mL). The precipitate was filtered and washed with anhydrous methanol. The crude product was further purified by column chromatography on silica-gel (eluent, CHCl₃) to afford **2b** as blue powder (60 mg, yield 77%), mp: 247.8–249.0 °C. ¹H NMR (400 MHz, CDCl₃) δ (ppm) 4.30 (t, *J* = 6.3 Hz, 4H), 4.15 (t, *J* = 6.3 Hz, 4H), 1.91–1.84 (m, 4H), 1.82–1.75 (m, 4H), 1.09–1.02 (m, 8H), 1.06 (t, *J* = 7.4 Hz, 6H) 1.03 (t, *J* = 7.4 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 175.00, 152.73, 147.34, 142.46, 136.76, 131.90, 130.55, 128.10, 127.21, 72.66, 71.93, 32.37, 32.15, 19.32, 13.94. HRMS (C₃₄H₃₆O₆Se₃ + H): Calc. 779.0088, found 779.0099.



The synthesis of compound 1: Compound 1b (32 mg, 0.05 mmol) and meso-1,2diphenylethane-1,2-diamine (12.7 mg, 0.06 mmol) were dissolved in glacial acetic acid (2 mL). The resulting mixture was refluxed for 12 h under the inert atmosphere. After cooled down to RT, the solvent was removed by evaporation under reduced pressure. The crude product was further purified by column chromatography on silica-gel (CH₂Cl₂: petro ether, 1 : 1, v/v) to afford **1** as red powder (13 mg, yield 33%), mp: 276.8–278.0 °C. ¹H NMR (600 MHz, CDCl₃) δ (ppm) 7.73–7.71 (m, 4H), 7.45–7.38 (m, 6H), 4.45 (t, *J* = 6.5 Hz, 4H), 4.43 (t, *J* = 6.5 Hz, 4H), 1.92–1.86 (m, 8H), 1.69– 1.63 (m, 8H), 1.05–1.08 (m, 12H). ¹³C NMR (150 MHz, CDCl₃) δ (ppm) 149.99, 139.59, 139.14, 136.30, 134.52, 133.72, 130.37, 129.82, 128.73, 128.14, 73.18, 73.10, 32.33, 19.32, 19.30, 13.97. HRMS (C48H46N2O4S₃ + H): Calc. 811.2692, found 811.2684.

The synthesis of compound 2: The synthesis procedure was same as the synthesis of compound 1. Red powder (Yield = 30%), mp: > 300 °C. ¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.73–7.71 (m, 4H), 7.45–7.38 (m, 6H), 4.48 (t, J = 6.4 Hz, 4H), 4.43 (t, J = 6.4 Hz, 4H), 1.96–1.88 (m, 8H), 1.73–1.62 (m, 8H), 1.10–1.06 (m, 12H). ¹³C NMR (150 MHz, CDCl₃) δ (ppm) 150.38, 148.89, 139.39, 133.91, 130.45, 129.51, 128.78, 128.64, 128.09, 72.54, 72.49, 32.43, 32.41, 19.44, 19.40, 14.03. HRMS (C₄₈H₄₆N₂O₄Se₃ + H): Calc. 953.1034, found 953.1031.

III. Theoretical calculation

All calculations were performed with Gaussian 16 programs.^{S3} The *n*-butoxyl groups were placed into methoxyl groups to simplify the calculation. Geometry optimizations were carried out using the B3LYP^{S4} functional with 6-31G(d) basis set. Vibrational frequency calculations were carried out at the same level to ensure that the optimized structures are energy minima without imaginary frequencies. Single point energy calculations and natural bond orbital (NBO)^{S5} analyses of all the optimized structures were performed at the B3LYP/6-311+G(d,p) level of theory to obtain accurate energies of molecular orbitals and natural atomic orbitals(NAOs).

We further used Multiwfn (version 3.5)^{S6} software to perform orbital composition analyses.^{S7} The optimized structures and molecular orbital distributions were displayed with GaussView (version 5.0) software.^{S8} Each structure was divided into three moieties: bowl moiety, pyrazine moiety and phenyl rings moiety (Fig. S1). The contribution percentage of one moiety to a certain frontier molecular orbital is defined as the contribution percentage of all NAOs to the certain frontier molecular orbital in the moiety. Rydberg composition is defined as 100% - (bowl)% - (pyrazine)% - (phenyl rings)%, which is not investigated in this article. In Molecule 1 and Molecule 2, we optimized the structure of molecule 1 with C_s symmetry; the imaginary frequency of phenyl ring rotation is inevitable, indicating the C_s symmetric conformation is not the most stable one. Therefore, we optimize the structure of Molecule 1 with C_1 symmetry. The bowl moiety of Molecule 2 is flat, considering the different orientation of MeOgroups, there are two conformations Molecule $2(C_1)$ and Molecule $2(C_2)$, respectively. The Gibbs free energies of Molecule $2(C_1)$ is 0.3 kcal/mol lower than that of Molecule 2 (C₂), their relative ratio is Molecule 2 (C₁): Molecule 2 (C₂) = 1.66:1. The optimized structures, HOMO-1, HOMO, LUMO, LUMO+1 of Molecule 1 (C1), Molecule 2 (C1) and Molecule $2(C_2)$ are displayed in Table S1-S6.

For first singlet excited state calculation of **1** and **2**, geometry optimization was carried out at B3LYP/6-31G(d) (nstates=4, root=1) level of theory. Transition electric dipole moment calculation was further carried out at B3LYP/Def2-TZVP/IEFPCM

(dichloromethane) (nstates=6, root=1) level of theory using optimized structures, the results was collected in Table S7 and S8.



Fig. S1. The demonstration of bowl moiety, pyrazine moiety and phenyl rings moiety in molecules 1 and 2.

Table S1. The contribution percentage of three components to LUMO+1, LUMO, HOMO, HOMO-1 of Molecule 1 (C_1). Molecular orbital energies are in eV.

Molecular Orbitals	Molecular Orbital Energy/eV	bowl	pyrazine	phenyl rings	Rydberg composition
LUMO+1	-1.89	32.41%	38.93%	25.33%	3.33%
LUMO	-2.50	39.48%	49.68%	7.92%	2.92%
НОМО	-5.32	91.69%	6.34%	0.93%	1.04%
HOMO-1	-5.81	77.57%	13.57%	7.87%	0.99%

Molecular Orbitals	Molecular Orbital Energy/eV	bowl	pyrazine	phenyl rings	Rydberg composition
LUMO+1	-1.85	32.17%	38.31%	26.57%	2.95%
LUMO	-2.50	38.74%	50.18%	8.16%	2.92%
НОМО	-5.26	91.76%	6.37%	0.91%	0.96%
HOMO-1	-5.73	82.42%	11.07%	5.66%	0.85%

Table S2. The contribution percentage of three components to LUMO+1, LUMO, HOMO, HOMO-1 of Molecule $2(C_1)$. Molecular orbital energies are in eV.

Table S3. The contribution percentage of three components to LUMO+1, LUMO, HOMO, HOMO-1 of Molecule 2 (C_2). Molecular orbital energies are in eV.

Molecular Orbitals	Molecular Orbital Energy/eV	bowl	pyrazine	phenyl rings	Rydberg composition
LUMO+1	-1.85	32.24%	38.30%	26.51%	2.95%
LUMO	-2.50	38.74%	50.21%	8.16%	2.89%
НОМО	-5.26	91.78%	6.35%	0.90%	0.97%
HOMO-1	-5.73	82.39%	11.09%	5.67%	0.85%

Labels	Atoms	X	Y	Z
1	С	0.32499	1.43165	-0.6034
2	С	-0.81413	0.67873	-0.77954
3	С	-0.8101	-0.72863	-0.72876
4	С	0.33288	-1.46325	-0.50879
5	С	1.56696	-0.74159	-0.42255
6	С	1.55999	0.7234	-0.45087
7	С	-2.03327	1.3889	-0.66177
8	С	-3.21683	0.68272	-0.49953
9	С	-3.21291	-0.73007	-0.45527
10	С	-2.02498	-1.43757	-0.57057
11	С	-1.91135	2.74843	-0.37202
12	С	-3.10609	3.41141	0.01786
13	С	-4.33209	2.67221	0.18943
14	С	-4.37492	1.28223	-0.0251
15	С	-4.36794	-1.30643	0.05396
16	С	-4.31753	-2.68103	0.35106
17	С	-3.08777	-3.42279	0.2232
18	С	-1.89612	-2.77721	-0.20324
19	Ο	-3.19875	-4.724	0.61117
20	С	-2.12494	-5.61973	0.34502
21	Ο	-5.41327	-3.29164	0.90124
22	С	-6.12197	-4.1897	0.03988
23	Ο	-5.43106	3.30846	0.70286
24	С	-6.14321	4.15159	-0.20963
25	О	-3.22449	4.73206	0.33004
26	С	-2.14677	5.61388	0.035
27	Н	-1.82347	-5.57944	-0.70844
28	Н	-1.26053	-5.41384	0.98622
29	Н	-6.46059	-3.67386	-0.86773
30	Н	-5.50156	-5.04926	-0.23175
31	Н	-5.52586	4.99564	-0.53192
32	Н	-6.48041	3.58184	-1.08497
33	Н	-1.29163	5.44014	0.69766

Table S4. Coordinates and energy of 1 based DFT calculations at the level of B3LYP/6-31g(d,p).

34	Н	-1.83085	5.52166	-1.01097
35	Н	-2.50702	-6.61594	0.57618
36	Н	-6.98931	-4.52911	0.61007
37	Н	-7.01152	4.52106	0.34003
38	Н	-2.53198	6.62008	0.21106
39	С	3.87111	-0.71102	-0.16669
40	С	3.84441	0.72751	-0.05147
41	Ν	2.74062	-1.39351	-0.30023
42	Ν	2.70997	1.3923	-0.23243
43	S	-0.11558	-3.1656	-0.16026
44	S	-5.56724	-0.00311	0.41524
45	S	-0.13277	3.14727	-0.34621
46	С	5.114	-1.53072	-0.19262
47	С	6.25081	-1.12827	-0.91176
48	С	5.12758	-2.77922	0.44991
49	С	7.37527	-1.94965	-0.97535
50	Н	6.25107	-0.17647	-1.43299
51	С	6.25795	-3.59202	0.39725
52	Н	4.24072	-3.10249	0.98524
53	С	7.38617	-3.18011	-0.31557
54	Н	8.24308	-1.62791	-1.54473
55	Н	6.25651	-4.55041	0.90968
56	Н	8.26637	-3.81591	-0.36066
57	С	5.01916	1.56485	0.3178
58	С	5.18652	2.82004	-0.28913
59	С	5.92255	1.17243	1.3186
60	С	6.24467	3.64964	0.07609
61	Н	4.4742	3.13541	-1.04461
62	С	6.97204	2.01014	1.69239
63	Н	5.79677	0.21611	1.81565
64	С	7.14166	3.24748	1.06813
65	Н	6.36636	4.61341	-0.41121
66	Н	7.65614	1.69595	2.47603
67	Н	7.96448	3.8962	1.35656

Total energy: = -2990.5242 Hartrees

Labels	Atoms	X	Y	Ζ
1	С	0.66098	-1.44294	-0.01716
2	С	-0.50178	-0.70618	-0.05969
3	С	-0.50222	0.70223	-0.10021
4	С	0.65991	1.44115	-0.09061
5	С	1.89312	0.73033	-0.03826
6	С	1.89406	-0.72992	-0.01929
7	С	-1.72763	-1.41791	-0.0624
8	С	-2.92067	-0.71057	-0.09893
9	С	-2.92118	0.70289	-0.13509
10	С	-1.72865	1.41206	-0.13639
11	С	-1.67675	-2.8125	-0.02268
12	С	-2.91945	-3.48693	-0.01861
13	С	-4.15462	-2.74773	-0.04885
14	С	-4.15316	-1.3488	-0.0883
15	С	-4.15415	1.33997	-0.15457
16	С	-4.15672	2.73914	-0.18238
17	С	-2.92218	3.47995	-0.18641
18	С	-1.67892	2.80707	-0.15993
19	Ο	-3.10146	4.83168	-0.2136
20	С	-1.96709	5.67271	-0.37985
21	Ο	-5.34678	3.4154	-0.26041
22	С	-5.78622	4.01619	0.96368
23	Ο	-5.34424	-3.42755	-0.09608
24	С	-5.78289	-3.97458	1.1532
25	Ο	-3.0974	-4.83872	0.01543
26	С	-1.96328	-5.68518	-0.12292
27	Н	-1.29553	5.61989	0.48643
28	Н	-1.41286	5.42176	-1.29187
29	Н	-5.91428	3.2548	1.7438
30	Н	-5.08226	4.78242	1.30334
31	Н	-5.07932	-4.72608	1.52495
32	Н	-5.9096	-3.18012	1.89983
33	Н	-1.41571	-5.47296	-1.04865

Table S5. Coordinates and energy of $2(C_1)$ based DFT calculations at the level of B3LYP/6-31g(d,p).

34	Н	-1.28573	-5.59491	0.73559
35	Н	-2.36147	6.68703	-0.46441
36	Н	-6.75149	4.47699	0.74296
37	Н	-6.74876	-4.44363	0.95344
38	Н	-2.35709	-6.70252	-0.16127
39	С	4.20773	0.72299	0.08034
40	С	4.21159	-0.71831	-0.03492
41	Ν	3.06613	1.39594	0.03508
42	Ν	3.07038	-1.39338	-0.0396
43	С	5.42448	1.55267	0.30227
44	С	6.43871	1.15828	1.18968
45	С	5.5266	2.80389	-0.32692
46	С	7.53128	1.98975	1.43025
47	Н	6.36675	0.20522	1.70341
48	С	6.62654	3.62724	-0.09584
49	Н	4.73097	3.12089	-0.99334
50	С	7.63347	3.22289	0.78344
51	Н	8.30224	1.67392	2.12789
52	Н	6.69571	4.58766	-0.59975
53	Н	8.48954	3.86659	0.96731
54	С	5.43858	-1.5458	-0.20146
55	С	5.51549	-2.79551	0.43428
56	С	6.49012	-1.15092	-1.04408
57	С	6.62623	-3.61699	0.25366
58	Н	4.69186	-3.11296	1.06556
59	С	7.59383	-1.98064	-1.23463
60	Н	6.43891	-0.19891	-1.56223
61	С	7.66996	-3.21229	-0.58142
62	Н	6.67511	-4.57625	0.76215
63	Н	8.39409	-1.66464	-1.89837
64	Н	8.53455	-3.85455	-0.7263
65	Se	0.21315	-3.30849	0.02114
66	Se	0.21043	3.30625	-0.12959
67	Se	-5.54396	-0.00541	-0.14142

Total energy: = -9000.5405 Hartrees

Tabels	Atoms	X	Y	Z
1	С	-0.00369	1.4425	-0.65985
2	С	-0.00431	0.70449	0.50291
3	С	0.00431	-0.70449	0.50291
4	С	0.00369	-1.4425	-0.65985
5	С	-0.00712	-0.73016	-1.89327
6	С	0.00712	0.73016	-1.89327
7	С	-0.00649	1.41556	1.72917
8	С	-0.00371	0.70694	2.92201
9	С	0.00371	-0.70694	2.92201
10	С	0.00649	-1.41556	1.72917
11	С	-0.0084	2.81078	1.67875
12	С	-0.00873	3.48452	2.92189
13	С	-0.00602	2.74415	4.1567
14	С	-0.00322	1.34477	4.15473
15	С	0.00322	-1.34477	4.15473
16	С	0.00602	-2.74415	4.1567
17	С	0.00873	-3.48452	2.92189
18	С	0.0084	-2.81078	1.67875
19	О	0.00964	-4.83644	3.10131
20	С	0.15163	-5.68091	1.96629
21	Ο	0.06014	-3.42302	5.34663
22	С	-1.18244	-3.99155	5.77775
23	Ο	-0.06014	3.42302	5.34663
24	С	1.18244	3.99155	5.77775
25	О	-0.00964	4.83644	3.10131
26	С	-0.15163	5.68091	1.96629
27	Н	-0.71089	-5.59964	1.2928
28	Н	1.07259	-5.45869	1.41449
29	Н	-1.94324	-3.21004	5.90012
30	Н	-1.53683	-4.74887	5.07134
31	Н	1.94324	3.21004	5.90012
32	Н	1.53683	4.74887	5.07134
33	Н	0.71089	5.59964	1.2928
34	Н	-1.07259	5.45869	1.41449

Table S6. Coordinates and energy of $2(C_2)$ based DFT calculations at the level of B3LYP/6-31g(d,p).

35	Н	0.20315	-6.69785	2.35964
36	Н	-0.98063	-4.45782	6.74452
37	Н	0.98063	4.45782	6.74452
38	Н	-0.20315	6.69785	2.35964
39	С	-0.07377	-0.71916	-4.20991
40	С	0.07377	0.71916	-4.20991
41	Ν	-0.06884	-1.39346	-3.06821
42	Ν	0.06884	1.39346	-3.06821
43	С	-0.28627	-1.54319	-5.43214
44	С	-1.14304	-1.12961	-6.46489
45	С	0.31912	-2.807	-5.52222
46	С	-1.37688	-1.95496	-7.56355
47	Н	-1.63842	-0.16621	-6.40276
48	С	0.09524	-3.62434	-6.62812
49	Н	0.96127	-3.13845	-4.71263
50	С	-0.75342	-3.20102	-7.65336
51	Н	-2.05097	-1.62416	-8.34903
52	Н	0.5806	-4.59492	-6.68762
53	Н	-0.93185	-3.84002	-8.51409
54	С	0.28627	1.54319	-5.43214
55	С	-0.31912	2.807	-5.52222
56	С	1.14304	1.12961	-6.46489
57	С	-0.09524	3.62434	-6.62812
58	Н	-0.96127	3.13845	-4.71263
59	С	1.37688	1.95496	-7.56355
60	Н	1.63842	0.16621	-6.40276
61	С	0.75342	3.20102	-7.65336
62	Н	-0.5806	4.59492	-6.68762
63	Н	2.05097	1.62416	-8.34903
64	Н	0.93185	3.84002	-8.51409
65	Se	0.00000	3.30821	-0.21141
66	Se	0.00000	-3.30821	-0.21141
67	Se	0.00000	0.00000	5.54517

Total energy: = -9000.5404 Hartrees

n	Х	Y	Ζ	$X^2 + Y^2 + Z^2$	oscillator strength
1	0.0636	0.8531	-0.0421	0.7336	0.0346
2	-1.1633	0.0054	-0.0610	1.3569	0.0867
3	3.7081	-0.0322	0.0186	13.751	0.9706
4	0.9814	-0.0061	0.1627	0.9897	0.0798
5	0.2456	-0.1655	-0.0308	0.0887	0.0074
6	-0.9294	-0.0544	-0.0931	0.8755	0.0731

Table S7. Transition electric dipole moments (in atomic unit) and oscillator strengths of **1** from ground state to the nth excited states.

Table S8. Transition electric dipole moments (in atomic unit) and oscillator strengths of **2** from ground state to the nth excited states.

n	Х	Y	Ζ	$X^2 + Y^2 + Z^2$	oscillator strength
1	-0.0233	0.9831	0.0000	0.9670	0.0457
2	0.0000	0.0000	-1.4462	2.0916	0.1332
3	0.0000	0.0000	3.4490	11.8956	0.8421
4	0.0000	0.0000	1.3698	1.8765	0.1500
5	0.0000	0.0000	1.4460	2.0908	0.1698
6	-0.0045	0.0516	0.0000	0.0027	0.0002

IV. Open-aperture Z-scan measurement



Fig. S2 The typical double-beams experimental arrangement of Z-scan measurement

The detail description of Z-scan measurement: The Z-scan method was introduced in 1989 by Sheik-Bahae *et al.*^{S9} using to determine the magnitude of the excited-state absorption cross-section (σ_{ex}), nonlinear absorption coefficient (β_{eff}) and the sign and magnitude of the nonlinear refractive index (n_2). In this work, the optical performances are collected using Z-scan technology with FWHM of 8 ns laser pulses with a repetition frequency of 10 Hz from a Nd:YAG laser under wavelength of 532 nm. The spatial and temporal profiles of the laser pulses presented an approximately Gaussian distribution. As shown in Fig. S2, the laser beam has been divided into two beams: one laser beam is collected directly by reference detector to monitor energy fluctuations. Meanwhile, another beam is focused with lens on samples to detect the transmittance as the sample is scanned through the Z-direction to tune the intensities on it.

Herein, the Z-scan curves, which are the normalized transmittance as a function of the sample position (Z), were measured with an open-aperture. The samples were placed in quartz cell with thickness of 1 mm with identical linear transmittance 70% at 532 nm and fixed on a stepper motor which was controlled by a computer to move along the Z axis reference to the focal point. In this measurement, normalized transmittance of 1.0 indicates that the material exhibits no NLO behavior. When the sample exhibits saturable absorption, normalized transmittance above 1.0 will be observed. In contrast, the normalized transmittance below 1.0 indicates that the sample exhibits reverse saturable absorption.



Fig. S3 (a) Typical open-aperture Z-scan data and theoretically fitted curves (solid curves) and (b) corresponding plots of normalized transmittance *vs* incident intensity of **1** in 1,1,2,2-tetrachloroethane at different energies (10 μ J, 20 μ J, and 30 μ J) under 532 nm.



Fig. S4 (a) Typical open-aperture Z-scan data and theoretically fitted curves (solid curves) and (b) corresponding plots of normalized transmittance *vs* incident intensity of **2** 1,1,2,2-tetrachloroethane at different energies (10 μ J, 20 μ J, and 30 μ J) under 532 nm.



Fig. S5 (a) Typical open-aperture Z-scan data and theoretically fitted curves (solid curves) and (b) corresponding plots of normalized transmittance *vs* incident intensity of **1** in CH₂Cl₂ at different energies (5 μ J, 10 μ J, 17 μ J, and 27 μ J) under 532 nm; The linear transmittance is 70% under 532 nm.



Fig. S6 (a) Typical open-aperture Z-scan data and theoretically fitted curves (solid curves) and (b) corresponding plots of normalized transmittance *vs* incident intensity of **2** in CH₂Cl₂ at different energies (5 μ J, 10 μ J, 17 μ J, and 27 μ J) under 532 nm. ; The linear transmittance is 70% under 532 nm.



Fig. S7 The β_{eff} value vs input intensity curves of C₆₀, **1** and **2**.

Samples	<i>I</i> ₀ <i>a</i> [μJ]	$T_{\min} b [\%]$	$F_{\rm on} ^c [{\rm mJ} {\rm cm}^{-2}]$	$\beta_{\rm eff} d [{ m cm} { m GW}^{-1}]$
1	5	62	35	312
	10	52	64	206
	17	45	79	162
	27	39	103	126
2	5	71	68	199
	10	61	72	155
	17	54	98	121
	27	46	129	99

Table S9NLO coefficients of C_{60} , 1, and 2 in dichloromethane with identical lineartransmittance of 70% at 532 nm

^{*a*} incident intensity; ^{*b*} the minimum transmittance at the position Z = 0; ^{*c*} optical energy-limiting onset fluence (*F*_{on}) at normalized T = 95%; ^{*d*} nonlinear extinction coefficient.

V. Nanosecond pump-probe measurement



Fig. S8 Schematic diagram of the time-resolved transient absorption experimental arrangement.



Fig. S9 Representative pump–probe results for compounds **1** (a) and **2** (b) under different probe wavelengths. The pump wavelength is 450 nm.

VI. FT-IR spectra of compounds 1 and 2.



Fig. S11 The FT-IR spectrum of **2**.

VII. References

- S1 X. Li, Y. Zhu, J. Shao, B. Wang, S. Zhang, Y. Shao, X. Jin, X. Yao, R. Fang and X. Shao, *Angew. Chem.*, *Int. Ed*, 2014, **53**, 535.
- S2 Y. Sun, X. Li, C. Sun, H. Shen, X. Hou, D. Lin, H. L. Zhang, C. A. Di, D. Zhu and X. Shao, *Angew. Chem.*, *Int. Ed*, 2017, 56, 13470.
- S3 Gaussian 16, Revision A.03, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.
- S4 (a) A. D. Becke, J. Chem. Phys., 1993, 98, 5648-5652. (b) C. Lee, W. Yang, R. G.
 Parr, Phys. Rev. B, 1988, 37, 785.
- S5 A. E. Reed, L. A. Curtiss, F. Weinhold, *Chem. Rev.*, 1988, 88, 899. (b) A. E. Reed,
 R. B. Weinstock, F. Weinhold, *J. Chem. Phys.*, 1985, 83, 735.
- S6 Tian Lu, Feiwu Chen, J. Comput. Chem., 2012, 33, 580.
- S7 Tian Lu, Feiwu Chen, Acta Chim. Sinica, 2011, 69, 2393.
- S8 R. Dennington, T. Keith, J. Millam, GaussView, version 5; Semichem Inc.: Shawnee Mission, KS, 2009.