## Supporting Information

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

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#### Abstract

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VI. FT-IR spectra of compounds 1 and $2 \ldots-\ldots-\ldots-\ldots-\ldots-\ldots-\ldots$


## 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. ${ }^{\text {S1 }}$

Melting points were determined on WRS-2 melting point apparatus. ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ NMR spectra were recorded on a Bruker Avance III $400 \mathrm{MHz}\left(100 \mathrm{MHz}\right.$ for $\left.{ }^{13} \mathrm{C}\right)$ or a VARIAN INOVA 600 MHz spectrometer ( 150 MHz for ${ }^{13} \mathrm{C}$ ) spectrometer. The chemical shifts of ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ 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. ${ }^{\text {S2 }}$



The synthesis of compound $\mathbf{1 b}$ : Compound $\mathbf{1 a}(63 \mathrm{mg}, 0.1 \mathrm{mmol})$ was dissolved in the mixed solvent of $\mathrm{CH}_{2} \mathrm{Cl}_{2}(5.0 \mathrm{~mL})$ and $\mathrm{CH}_{3} \mathrm{NO}_{2}(5.0 \mathrm{~mL}) . \mathrm{FeCl}_{3}(162 \mathrm{mg}, 1.0 \mathrm{mmol})$ 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, $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ ) to afford 1b as blue powder ( 16 mg , yield, $48 \%$ ). mp: 226.4-227.9 ${ }^{\circ} \mathrm{C} .{ }^{1} \mathrm{H} \mathrm{NMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right)$ $\delta(\mathrm{ppm}) 4.40(\mathrm{t}, J=6.4 \mathrm{~Hz}, 4 \mathrm{H}), 4.21(\mathrm{t}, J=6.4 \mathrm{~Hz}, 4 \mathrm{H}), 1.92-1.85(\mathrm{~m}, 4 \mathrm{H}), 1.84-1.77$ $(\mathrm{m}, 4 \mathrm{H}), 1.67-1.53(\mathrm{~m}, 8 \mathrm{H}), 1.06(\mathrm{t}, J=5.4 \mathrm{~Hz}, 6 \mathrm{H}), 1.03(\mathrm{t}, J=5.3 \mathrm{~Hz}, 6 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta(\mathrm{ppm}) 174.70,151.49,145.51,140.32,137.96,130.78,129.75$, 128.24, 127.08, 73.24, 72.98, 32.24, 32.11, 19.21, 13.89. HRMS ( $\left.\mathrm{C}_{34} \mathrm{H}_{36} \mathrm{O}_{6} \mathrm{~S}_{3}+\mathrm{H}\right)$ : Calc. 637.1747, found 637.1758.

The synthesis of compound 2b: Compound $\mathbf{2 a}(89 \mathrm{mg}, 0.1 \mathrm{mmol})$ was dissolved in the mixed solvent of $\mathrm{CH}_{2} \mathrm{Cl}_{2}(5.0 \mathrm{~mL})$ and $\mathrm{CH}_{3} \mathrm{NO}_{2}(5.0 \mathrm{~mL}) . \mathrm{FeCl}_{3}(162 \mathrm{mg}, 1.0 \mathrm{mmol})$ 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, $\mathrm{CHCl}_{3}$ ) to afford $\mathbf{2 b}$ as blue powder ( 60 mg , yield $77 \%$ ), mp: 247.8-249.0 ${ }^{\circ} \mathrm{C} .{ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta(\mathrm{ppm}) 4.30(\mathrm{t}, J=6.3 \mathrm{~Hz}$, $4 \mathrm{H}), 4.15(\mathrm{t}, J=6.3 \mathrm{~Hz}, 4 \mathrm{H}), 1.91-1.84(\mathrm{~m}, 4 \mathrm{H}), 1.82-1.75(\mathrm{~m}, 4 \mathrm{H}), 1.09-1.02(\mathrm{~m}, 8 \mathrm{H})$, $1.06(\mathrm{t}, J=7.4 \mathrm{~Hz}, 6 \mathrm{H}) 1.03(\mathrm{t}, J=7.4 \mathrm{~Hz}, 6 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR $\left(100 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta(\mathrm{ppm})$
$175.00,152.73,147.34,142.46,136.76,131.90,130.55,128.10,127.21,72.66,71.93$, 32.37, $32.15,19.32,13.94$. HRMS $\left(\mathrm{C}_{34} \mathrm{H}_{36} \mathrm{O}_{6} \mathrm{Se}_{3}+\mathrm{H}\right)$ : Calc. 779.0088, found 779.0099.


The synthesis of compound 1: Compound $\mathbf{1 b}(32 \mathrm{mg}, 0.05 \mathrm{mmol})$ and meso-1,2-diphenylethane-1,2-diamine ( $12.7 \mathrm{mg}, 0.06 \mathrm{mmol}$ ) were dissolved in glacial acetic acid $(2 \mathrm{~mL})$. 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 $\left(\mathrm{CH}_{2} \mathrm{Cl}_{2}\right.$ : petro ether, $\left.1: 1, \mathrm{v} / \mathrm{v}\right)$ to afford $\mathbf{1}$ as red powder ( 13 mg , yield $33 \%$ ), mp: $276.8-278.0{ }^{\circ} \mathrm{C} .{ }^{1} \mathrm{H}$ NMR ( $600 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta(\mathrm{ppm}) 7.73-7.71(\mathrm{~m}, 4 \mathrm{H}), 7.45-7.38$ $(\mathrm{m}, 6 \mathrm{H}), 4.45(\mathrm{t}, J=6.5 \mathrm{~Hz}, 4 \mathrm{H}), 4.43(\mathrm{t}, J=6.5 \mathrm{~Hz}, 4 \mathrm{H}), 1.92-1.86(\mathrm{~m}, 8 \mathrm{H}), 1.69-$ $1.63(\mathrm{~m}, 8 \mathrm{H}), 1.05-1.08(\mathrm{~m}, 12 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $150 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta(\mathrm{ppm}) 149.99,139.59$, $139.14,136.30,134.52,133.72,130.37,129.82,128.73,128.14,73.18,73.10,32.33$, 19.32, 19.30, 13.97. HRMS $\left(\mathrm{C}_{48} \mathrm{H}_{46} \mathrm{~N}_{2} \mathrm{O}_{4} \mathrm{~S}_{3}+\right.$ 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 $=30 \%), \mathrm{mp}:>300{ }^{\circ} \mathrm{C} .{ }^{1} \mathrm{H}$ NMR $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta$ (ppm) 7.73-7.71 (m, 4H), 7.45-7.38 (m, 6H), 4.48 (t, $J=6.4 \mathrm{~Hz}, 4 \mathrm{H}), 4.43(\mathrm{t}, J=6.4$ $\mathrm{Hz}, 4 \mathrm{H}), 1.96-1.88(\mathrm{~m}, 8 \mathrm{H}), 1.73-1.62(\mathrm{~m}, 8 \mathrm{H}), 1.10-1.06(\mathrm{~m}, 12 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR (150 $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta(\mathrm{ppm}) 150.38,148.89,139.39,133.91,130.45,129.51,128.78,128.64$, 128.09, 72.54, 72.49, 32.43, 32.41, 19.44, 19.40, 14.03. HRMS ( $\left.\mathrm{C}_{48} \mathrm{H}_{46} \mathrm{~N}_{2} \mathrm{O}_{4} \mathrm{Se}_{3}+\mathrm{H}\right)$ : Calc. 953.1034, found 953.1031.

## III. Theoretical calculation

All calculations were performed with Gaussian 16 programs. ${ }^{53}$ The $n$-butoxyl groups were placed into methoxyl groups to simplify the calculation. Geometry optimizations were carried out using the B3LYP ${ }^{\text {S4 }}$ functional with $6-31 \mathrm{G}(\mathrm{d})$ 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 $(\mathrm{NBO})^{\mathrm{S} 5}$ 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) ${ }^{\text {S6 } 6}$ software to perform orbital composition analyses. ${ }^{\text {S7 }}$ The optimized structures and molecular orbital distributions were displayed with GaussView (version 5.0) software. ${ }^{\text {S8 }}$ 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 $\mathbf{1}$ and Molecule 2, we optimized the structure of molecule $\mathbf{1}$ with Cs symmetry; the imaginary frequency of phenyl ring rotation is inevitable, indicating the $C_{\mathrm{s}}$ symmetric conformation is not the most stable one. Therefore, we optimize the structure of Molecule $\mathbf{1}$ with $C_{1}$ symmetry. The bowl moiety of Molecule $\mathbf{2}$ is flat, considering the different orientation of MeOgroups, there are two conformations Molecule $2\left(C_{1}\right)$ and Molecule $2\left(C_{2}\right)$, respectively. The Gibbs free energies of Molecule $2\left(C_{1}\right)$ is $0.3 \mathrm{kcal} / \mathrm{mol}$ lower than that of Molecule $2\left(C_{2}\right)$, their relative ratio is Molecule $2\left(C_{1}\right)$ : Molecule $2\left(C_{2}\right)=1.66: 1$. The optimized structures, HOMO-1, HOMO, LUMO, LUMO+1 of Molecule $1\left(C_{1}\right)$, Molecule $2\left(C_{1}\right)$ and Molecule $2\left(C_{2}\right)$ are displayed in Table S1-S6.

For first singlet excited state calculation of $\mathbf{1}$ 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 $\mathbf{1}$ and $\mathbf{2}$.

Table S1. The contribution percentage of three components to LUMO+1, LUMO, HOMO, HOMO-1 of Molecule $\mathbf{1}\left(C_{1}\right)$. Molecular orbital energies are in eV .

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

Table S2. The contribution percentage of three components to LUMO+1, LUMO, HOMO, HOMO-1 of Molecule $2\left(C_{1}\right)$. Molecular orbital energies are in eV .

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

Table S3. The contribution percentage of three components to LUMO+1, LUMO, HOMO, HOMO-1 of Molecule $2\left(C_{2}\right)$. Molecular orbital energies are in eV.

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

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

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


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

Total energy: =-2990.5242 Hartrees

Table S5. Coordinates and energy of $\mathbf{2}\left(C_{1}\right)$ based DFT calculations at the level of B3LYP/6-31g(d,p).

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


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



Table S6. Coordinates and energy of $\mathbf{2}\left(C_{2}\right)$ based DFT calculations at the level of B3LYP/6-31g(d,p).

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


| 35 | H | 0.20315 | -6.69785 | 2.35964 |
| :--- | :---: | :---: | :---: | :---: |
| 36 | H | -0.98063 | -4.45782 | 6.74452 |
| 37 | H | 0.98063 | 4.45782 | 6.74452 |
| 38 | H | -0.20315 | 6.69785 | 2.35964 |
| 39 | C | -0.07377 | -0.71916 | -4.20991 |
| 40 | C | 0.07377 | 0.71916 | -4.20991 |
| 41 | N | -0.06884 | -1.39346 | -3.06821 |
| 42 | N | 0.06884 | 1.39346 | -3.06821 |
| 43 | C | -0.28627 | -1.54319 | -5.43214 |
| 44 | C | -1.14304 | -1.12961 | -6.46489 |
| 45 | C | 0.31912 | -2.807 | -5.52222 |
| 46 | C | -1.37688 | -1.95496 | -7.56355 |
| 47 | H | -1.63842 | -0.16621 | -6.40276 |
| 48 | C | 0.09524 | -3.62434 | -6.62812 |
| 49 | H | 0.96127 | -3.13845 | -4.71263 |
| 50 | C | -0.75342 | -3.20102 | -7.65336 |
| 51 | H | -2.05097 | -1.62416 | -8.34903 |
| 52 | H | 0.5806 | -4.59492 | -6.68762 |
| 53 | H | -0.93185 | -3.84002 | -8.51409 |
| 54 | C | 0.28627 | 1.54319 | -5.43214 |
| 55 | C | -0.31912 | 2.807 | -5.52222 |
| 56 | C | 1.14304 | 1.12961 | -6.46489 |
| 57 | C | -0.09524 | 3.62434 | -6.62812 |
| 58 | H | -0.96127 | 3.13845 | -4.71263 |
| 59 | C | 1.37688 | 1.95496 | -7.56355 |
| 60 | H | 1.63842 | 0.16621 | -6.40276 |
| 61 | C | 0.75342 | 3.20102 | -7.65336 |
| 62 | H | -0.5806 | 4.59492 | -6.68762 |
| 63 | H | 2.05097 | 1.62416 | -8.34903 |
| 64 | H | 0.93185 | 3.84002 | -8.51409 |
| 65 | Se | 0.00000 | 3.30821 | -0.21141 |
| 66 | 0 | 0.00000 | -3.30821 | -0.21141 |
| 67 | 0.00000 | 0.00000 | 5.54517 |  |
|  |  |  |  |  |
| 7 |  |  |  |  |



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

| n | $X$ | $Y$ | $Z$ | $X^{2}+Y^{2}+Z^{2}$ | 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 S8. Transition electric dipole moments (in atomic unit) and oscillator strengths of $\mathbf{2}$ from ground state to the nth excited states.

| n | $X$ | $Y$ | $Z$ | $X^{2}+Y^{2}+Z^{2}$ | 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. ${ }^{\text {S9 }}$ using to determine the magnitude of the excited-state absorption cross-section ( $\sigma_{\mathrm{ex}}$ ), nonlinear absorption coefficient ( $\beta_{\mathrm{eff}}$ ) 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 $v$ incident intensity of 1 in 1,1,2,2-tetrachloroethane at different energies ( $10 \mu \mathrm{~J}, 20 \mu \mathrm{~J}$, and $30 \mu \mathrm{~J}$ ) 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 $v$ incident intensity of 2 1,1,2,2-tetrachloroethane at different energies ( $10 \mu \mathrm{~J}, 20 \mu \mathrm{~J}$, and $30 \mu \mathrm{~J}$ ) 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 $v$ incident intensity of 1 in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ at different energies ( $5 \mu \mathrm{~J}, 10 \mu \mathrm{~J}, 17 \mu \mathrm{~J}$, and $27 \mu \mathrm{~J}$ ) 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 $v s$ incident intensity of $\mathbf{2}$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ at different energies ( $5 \mu \mathrm{~J}, 10 \mu \mathrm{~J}, 17 \mu \mathrm{~J}$, and $27 \mu \mathrm{~J}$ ) under 532 nm .; The linear transmittance is $70 \%$ under 532 nm .


Fig. S7 The $\beta_{\text {eff }}$ value vs input intensity curves of $\mathrm{C}_{60}, \mathbf{1}$ and $\mathbf{2}$.

Table S9 NLO coefficients of $\mathrm{C}_{60}$, $\mathbf{1}$, and $\mathbf{2}$ in dichloromethane with identical linear transmittance of $70 \%$ at 532 nm

| Samples | $I_{0}{ }^{a}[\mu \mathrm{~J}]$ | $T_{\min }{ }^{b}[\%]$ | $F_{\text {on }}{ }^{c}\left[\mathrm{~mJ} \mathrm{~cm}^{-2}\right]$ | $\beta_{\mathrm{eff}}{ }^{d}\left[\mathrm{~cm} \mathrm{GW}^{-1}\right]$ |
| :---: | :---: | :---: | :---: | :---: |
|  | 5 | 62 | 35 | 312 |
| $\mathbf{1}$ | 10 | 52 | 64 | 206 |
|  | 17 | 45 | 79 | 162 |
|  | 27 | 39 | 103 | 126 |
|  | 5 | 71 | 68 | 199 |
| $\mathbf{2}$ | 10 | 61 | 72 | 155 |
|  | 17 | 54 | 98 | 121 |
|  | 27 | 46 | 129 | 99 |

${ }^{a}$ incident intensity; ${ }^{b}$ the minimum transmittance at the position $Z=0 ;{ }^{c}$ optical energy-limiting onset fluence ( $F_{\text {on }}$ ) 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. S10 The FT-IR spectrum of $\mathbf{1}$.


Fig. S11 The FT-IR spectrum of $\mathbf{2}$.

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