Supporting information:

Fused Perylenebisimide-Carbazole: New Ladder Chromophores with Enhanced Third-Order Nonlinear Optical Activities

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1 Reagents, instruments and methods

Compound 1(1'), 2 and 2' was synthesized by literature method. ^{S1-3}All other reactants were purchased from commercial sources. NMR spectra were measured with a 400MHz Bruker spectrometer using TMS as reference for ¹H and ¹³C NMR. Accurate mass correction is measured with MALDI Tof Mass Spectrometer (MALDI micro MX). Cyclic voltammetry (CV) was performed in 0.05M solution in CH₂Cl₂ with a standard commercial electrochemical analyzer in a three electrode single-component cell under argon with a scan rate of 100 mV/s. Working electrode: glassy carbon; reference electrode: Ag/AgCl; auxiliary electrode: Pt disk; internal standard: ferrocene (Fc). The energy of Fc/Fc⁺ is 5.08 eV relative to vacuum.^{S4} UV-vis absorption spectrum is measured with UV-vis Spectrophotometer (HP 8453). Fluorescence spectrum is measured with Fluorescence Lifetime Spectrometer (PTI-700). Atomic structures of all compounds were optimized with density functional theory (DFT) calculations using the B3LYP hybrid functional with the basis set 6-31G. The quantum-chemical calculations were performed with the Gaussian 09 package. We employed a femtosecond laser system (Spitfire, Spectra Physics, made in USA) to study the nonlinear optical properties of the five compounds. The system consists of a mode-locked Ti: sapphire oscillator and a regenerative amplifier.

2 Synthesis of intermediates and target compounds



Scheme S1. Synthetic step I: Pd(PPh₃)₄, K₂CO₃, DMF, H₂O, 80°C, 3h.

Synthesis of compound 3 and 4

A mixture of 1 and 1[/] (500 mg, 0.62 mmol), 2 (420 mg, 1.57 mmol), Pd (PPh₃) 4 (36 mg, 5%), K₂CO₃ (440 mg, 3.2 mmol), 25ml DMF, 3ml H₂O was heated to 80°C under an argon atmosphere for 3 hours. The mixture was extracted with dichloromethane, washed with water, dried with MgSO₄ and filtrate. The filtrate was evaporated and the crude product was purified by silica gel column chromatography with dichloromethane as eluent. Compound 3 (418 mg, 62%) and 4 (124 mg, 18%) was obtained as red solid. **Compound 3.** M.p. 250-255 °C. ¹H NMR (400 MHz, CDCl₃): δ = 0.85-1.05 (m, 18H), 1.35-1.52 (m, 12H), 1.65-1.82 (m, 8H), 1.88 (m, 4H)4.25 (t, 4H), 4.34 (m, 8H), 7.26 (t, 2H), 7.33-7.57 (m, 10H), 7.61 (d, 2H), 8.15 (d, 2H), 8.23 (s, 2H), 8.36 ppm (s, 2H). ¹³C NMR (100 MHz, CDCl₃): $\delta = 13.8$, 19.3, 20.7, 30.6, 31.2, 43.1, 65.3, 109.0, 110.1, 119.2, 120.8, 121.1, 122.9, 124.1, 126.1, 127.0, 127.7, 128.6, 128.7, 129.2, 129.4, 131.3, 132.3, 133.5, 133.7, 135.2, 139.6, 140.1, 140.9, 168.8 ppm. MALDI-TOF-MS: Calcd for C₇₂H₇₄N₂O₈ 1094.5445, found: 1094.5393(M⁺). Compound 4. M.p. 104.4-114.4 °C. ¹H NMR (400 MHz, CDCl₃): $\delta =$ 0.85-1.05 (m, 18H), 1.32-1.52 (m, 12H), 1.68 (m, 4H), 1.79 (m, 4H), 1.91(m, 4H), 4.22 (t, 4H), 4.37 (m, 8H), 7.10-7.30 (m,4H), 7.30-7.43 (m, 5H), 7.50 (m, 4H), 7.60 (d, 2H), 8.00-8.20 (b, 2H), 8.26(s, 2H), 8.30-8.40 ppm (b, 1H). ¹³C NMR (100 MHz, CDCl₃): $\delta = 13.8$, 19.3, 20.7, 30.6, 31.2, 43.1, 65.3, 109.0, 110.1, 119.2, 120.7, 120.9, 122.9, 124.0, 126.0, 126.1, 127.4, 127.9, 128.7, 129.2, 131.3, 132.0, 132.3, 133.2, 134.0, 135.1, 140.0, 140.8, 168.7 ppm. MALDI-TOF-MS: Calcd for C₇, H₇₄N₂O₈ 1094.5445, found: 1094.5358(M⁺).



Scheme S2. Synthetic step II : Toluene, I_2 , sunlight, O_2 , rt, 3 h.

Synthesis of compound 5

A mixture of 3 (100 mg, 0.091 mmol), 100 mL toluene, and I_2 (20 mg, 0.079 mmol) was illuminated by sunlight for 3 hours at room temperature. The crude product was purified through silica gel column chromatography with a mixture of CH₂Cl₂ and ethyl acetate as eluent and compound 5 was obtained as a yellow solid (88 mg, 88%). **Compound 5.** M.p. >300°C. ¹H NMR (400 MHz, CDCl₃): δ = 0.85 (t, 6H), 0.97 (t, 6H), 1.23 (q, 9H), 1.35 (m, 4H), 1.46(m, 4H), 1.80 (m, 8H), 1.90 (m, 4H), 2.14(m, 4H), 4.28 (t, 4H), 4.44 (t, 4H), 4.74 (t, 4H), 7.22-7.28 (m, 2H), 7.33 (m, 4H), 8.00 (d, 2H), 9.04 (d, 2H), 9.26 (d, 2H), 10.04 (s, 2H), 10.44 ppm (s, 2H). ¹³C NMR (100 MHz, CDCl₃): δ = 13.9, 14.1, 14.3, 19.5, 19.8, 29.9, 31.0, 31.2, 31.7, 43.1, 65.7, 65.9, 109.1, 111.6, 116.8, 119.4, 122.0, 122.2, 123.5, 123.7, 124.0, 125.7, 126.2, 126.4, 127.2, 127.8, 129.3, 129.9, 140.2, 169.2, 169.9 ppm. MALDI-TOF-MS: Calcd for C₇₂H₇₀N₂O₈ 1090.5132, found: 1090.5073(M⁺).

Synthesis of compound 6

Compound 4 (100 mg, 0.091 mmol), 100 mL toluene, and I₂ (20 mg, 0.079 mmol) was illuminated by sunlight at room temperature for 3 hours. compound 6 was obtained as a yellow solid (79 mg, 79%), whose polarity is smaller than compound 5. **Compound 6.** M.p. 200-212°C. ¹H NMR (400 MHz, CDCl₃): $\delta = 0.98$ (m, 12H), 1.10 (t, 6H), 1.48 (m, 8H), 1.65 (m, 4H), 1.91(m, 8H), 2.02 (m, 4H), 4.33 (t, 4H), 4.52 (t, 4H), 4.67 (t, 4H), 7.34-7.47 (m, 6H), 8.02 (d, 2H), 9.11 (d, 2H), 9.29 (d, 2H), 10.03 (s, 2H), 10.58 ppm (s, 2H). ¹³C NMR (100 MHz, CDCl₃): $\delta = 14.0$, 19.6, 20.7, 31.1, 31.6, 43.0, 65.7, 65.9, 109.0, 111.5, 116.9, 119.5, 121.9, 123.7, 124.0, 124.2, 124.7, 125.5, 125.6, 126.0, 126.8, 127.4, 128.0, 129.4, 130.3, 140.2, 140.3, 169.2, 170.0 ppm. MALDI-TOF-MS: Calcd for $C_{72}H_{70}N_2O_8$ 1090.5132, found: 1090.5059(M⁺).



Scheme S3. Synthetic step III: 4-methylbenzenesulfonic acid, 110 °C, 3 h.

Synthesis of compound 7

A mixture of compound 5(100 mg, 0.092 mmol) and 1.4g 4-methylbenzenesulfonic acid were heated to 110 °C for 3h, The mixture was washed with water to remove the 4-methylbenzenesulfonic acid and filtrate. The crude product was dealed with Soxhlet extractor to remove the soluble impurity and lead to black solid compound 7 (80 mg, 100%). mp: >300 °C. Due to the extremely poor solubility, compound **7** was not characterized and it was directly used for next reaction.

Synthesis of compound 8

Compound 6(90 mg, 0.082 mmol) and 1.26g 4-methylbenzenesulfonic acid were heated to 110 $^{\circ}$ C for 3h and lead to black solid compound 8 (60mg, 88%). mp: >300 $^{\circ}$ C. Due to the extremely poor solubility, compound 8 was not characterized and it was directly used for next reaction.



Scheme S4. Synthetic step IV: C₁₂H₂₅NH₂, Imidazole, 200°C, 4 h.

Synthesis of Y1

Compound 7 (140 mg, 0.17 mmol), 12- alkyl amine (77.9 mg, 0.42 mmol) and imidazole (2.6 g) were heated to 200°C under an argon atmosphere for 4 hours. The reaction mixture was cooled to room

temperature and 5% HCl was added. The mixture was extracted with dichloromethane, washed with water, dried with MgSO₄ and filtrate. The filtrate was evaporated and the crude product was purified by silica gel column chromatography with dichloromethane and n-hexane as eluent. Compound Y1 was yielded as a purplish red solid (126 mg, 64.3%). **Compound Y1.** M.p. 218.4-230.8°C. ¹H NMR (400 MHz, CDCl₃): δ = 0.89 (t, 6H), 0.99 (t, 6H), 1.21-1.38 (m, 45H), 1.48 (s, 7H), 1.79(s, 3H), 3.80 (s, 4H), 3.91 (s, 4H), 7.16 (s, 2H), 7.34 (s, 2H), 7.47 (d, 2H), 7.52 (d, 2H), 8.01 (s, 2H), 8.35 (s, 2H), 8.52 (s, 2H), 9.93 ppm (s, 2H). ¹ NMR (100 MHz, CDCl₃): δ = 13.9, 14.3, 20.6, 22.9, 27.6, 29.5, 29.6, 29.9, 30.0, 31.2, 32.1, 40.6, 42.3, 109.0, 110.5, 115.7, 117.9, 118.7, 118.9, 119.6, 120.9, 122.1, 123.9, 125.1, 125.2, 126.2, 128.0, 138.9, 139.5, 162.8 ppm. MALDI-TOF-MS: Calcd for C₈₀H₈₄N₄O₄ 1164.6493, found: 1164.6431 (M⁺).

Synthesis of Y2

Compound 8 (50 mg, 0.06 mmol), 12- alkyl amine (28 mg, 0.15 mmol) and imidazole (1 g) were heated to 200°C under an argon atmosphere for 3 hours. Compound Y2 was yielded as a purplish red solid (42mg, 60%), whose polarity is smaller than Y1. Compound Y2. M.p. 250.5-263.1°C. ¹H NMR (400 MHz, CDCl₃): δ = 0.84-0.98 (m, 12H), 1.28-1.42 (m, 38H), 1.44-1.54 (m, 3H), 1.56-1.76 (m, 7H), 3.56(s, 2H), 3.71 (s, 2H), 3.93 (s, 4H), 6.96(s, 2H), 7.20 (t, 2H), 7.33(d, 2H), 7.40 (t, 2H), 7.54 (s, 2H), 8.24 (s, 2H), 8.40 (s, 2H), 9.65 ppm (s, 2H). ¹³C NMR (100 MHz, CDCl₃): δ = 13.9, 14.3, 20.6, 22.9, 27.7, 27.9, 28.1, 29.7, 29.9, 30.0, 31.2, 32.2, 40.7, 42.8, 108.9, 110.4, 116.8, 115.9, 118.2, 119.0, 119.2, 119.5, 119.7, 120.7, 1216.4, 122.2, 122.5, 122.7, 123.0, 123.3, 124.4, 125.9, 126.0, 126.6, 128.7, 139.6, 139.8, 163.1 ppm. MALDI-TOF-MS: Calcd for C₈₀H₈₄N₄O₄ 1164.6493, found: 1164.6548 (M⁺).



Scheme S5. Synthetic step VII: (1) 3-pentanamine, Imidazole, 160°C, 3 h. (2) Br₂, K₂CO₃, CHCl₃, reflux, 4h.

Synthesis of PBI-1

PBI-1 was synthesized according to literature methods.^{55,56} perylene-3,4:9,10-tetracarboxydianhydride (563 mg, 1.44 mmol), 3-pentanamine(300 mg, 3.45 mmol) and imidazole (4 g) were heated to 160°C under an argon atmosphere for 3 hours. The reaction mixture was cooled to room temperature and 5% HCl was added. The mixture was extracted with dichloromethane, washed with water, dried with MgSO₄ and filtrate. The filtrate was evaporated and the crude product was purified by silica gel column chromatography with dichloromethane as eluent. Compound PBI-1 was yielded as a red solid (699 mg, 92%).

Synthesis of compound 9 and 12, 12^{\prime}

A mixture of PBI (3.5 g, 6.6 mmol), K₂CO₃ (3.5g, 25.4 mmol), 70mL CHCl₃ and 17mL Br₂ was stirred at reflux for 4h. The excess bromine was removed by adding aqueous Na₂SO₃. Then, the crude product was purified by silica gel column chromatography with dichloromethane as eluent. Compound 9 (1.63 g, 41%) and 12 ,12'(1.9 g, 42%) were obtained as red solid. Compound 9. M.p. >300°C. ¹H NMR (400 MHz, $CDCl_3$): $\delta = 0.93$ (m, 12H), 1.94 (m, 4H), 2.27 (m, 4H), 5.06 (m, 2H), 8.60(d, 1H), 8.62 (d, 1H), 8.68(d, 3H), 8.91 (s, 1H), 9.77 ppm (d, 1H). ¹³C NMR (100 MHz, CDCl₃): δ =11.5, 25.1, 58.1, 121.0, 123.0, 123.4, 123.8, 127.0, 128.1, 128.2, 128.7, 129.0, 130.6, 131.1, 133.5, 133.9, 139.2, 163.9 ppm. MALDI-TOF-MS: Calcd for $C_{34}H_{28}N_2O_4Br_2$ 686.0416, found: 686.0414(M⁺). Compound 12 and 12′. M.p. >300°C. ¹H NMR (400 MHz, CDCl₃): $\delta = 0.92$ (t, 12H), 1.94 (m, 4H), 2.25 (m, 4H), 5.05 (m, 2H), 8.69(d, 2H), 8.92 (s, 2H), 9.50 ppm (d, 2H). ¹³C NMR (100 MHz, CDCl₃): δ =11.4, 25.1, 58.1, 120.9, 121.7, 123.2, 123.6, 126.5, 127.4, 128.2, 128.6, 129.4, 130.2, 130.5, 132.5, 132.9, 133.0, 133.3, 138.2, 163.6 ppm. MALDI-TOF-MS: Calcd for C₃₄H₂₉N₂O₄Br 608.1311, found: 608.1323(M⁺).



Scheme S6. Synthetic step V: Pd(PPh₃)₄, K₂CO₃, DMF, H₂O, 80°C, 3h.

Synthesis of compound 10

A mixture of compound 9 (500 mg, 0.82 mmol), compound 2' (128 mg, 0.41 mmol), Pd (PPh₃) 4 (50 mg, 5%), K₂CO₃ (235 mg, 1.7 mmol), 25 ml DMF, 2 ml H₂O was heated to 80°C under an argon atmosphere for 3 hours. The mixture was extracted with dichloromethane, washed with water, dried with MgSO₄ and filtrate. The filtrate was evaporated and the crude product was purified by silica gel column chromatography with dichloromethane and ethyl acetate as eluent. Compound 10(460 mg, 87.6%) was obtained as purplish red solid. **Compound 10.** M.p. >300°C. ¹H NMR (400 MHz, CDCl₃): $\delta = 0.93$ (m, 24H), 1.08 (m, 3H), 1.56 (m, 2H), 1.90 (m, 8H), 2.02(m, 2H), 2.20 (m, 8H), 4.46 (m, 2H), 5.03 (m, 4H), 7.35-7.65(m, 4H), 7.8-8.25 (m, 5H), 8.45-8.8 ppm (m, 11H). ¹³C NMR (100 MHz, CDCl₃): $\delta = 11.3$, 14.0, 20.7, 25.0, 31.2, 43.5, 57.5, 110.8, 111.1, 120.8, 121.1, 122.4, 123.4, 124.5, 124.7, 126.9, 127.6, 128.1, 128.3, 129.2, 129.7, 130.6, 132.4, 133.8, 134.4, 134.7, 135.1, 140.8, 142.5, 164.2 ppm. MALDI-TOF-MS: Calcd for C₈₄H₇₃N₅O₈ 1279.5459, found: 1279.5455(M⁺).

Synthesis of compound 11

A mixture of compound 9 (500 mg, 0.82 mmol), compound 2 (328 mg, 1.23 mmol), Pd (PPh₃) $_{4}(47 \text{ mg}, 5\%)$, K₂CO₃ (339 mg, 2.46 mmol), 25 ml DMF, 2.6 ml H₂O was heated to 80°C under an argon atmosphere for 3 hours. Compound 11(620 mg, 100%) was obtained as wine solid. **Compound 11.** M.p. 171-176.3°C. ¹H NMR (400 MHz, CDCl₃): $\delta = 0.87(t, 6H)$, 0.93 (t, 6H), 1.02 (t, 3H), 1.50 (m, 2H), 1.92 (m, 6H), 2.25 (m, 4H), 4.38 (t, 2H), 5.01 (m, 1H), 5.08 (m, 1H), 7.28 (d, 1H), 7.3-7.56 (m, 4H), 7.92 (d, 1H), 7.98 (d, 1H), 8.10 (d, 1H), 8.33 (s, 1H), 8.60-8.70(m, 4H), 8.74 ppm (s, 1H). ¹³C NMR (100 MHz, CDCl₃): $\delta = 11.3$, 13.9, 20.6, 25.0, 29.7, 31.2, 43.2, 57.5, 57.7, 109.2, 110.5, 119.4, 120.5, 120.6, 122.4, 122.8, 123.5, 124.6, 126.1, 126.4, 127.7, 128.2, 128.4, 129.2, 129.7, 132.4, 133.0, 134.6, 134.8, 135.3, 140.4, 141.0, 143.0, 164.3 ppm. MALDI-TOF-MS: Calcd for C₅₀H₄₅N₃O₄ 751.3410, found: 751.3467(M⁺).



Scheme S7. Synthetic step VI: I₂, Toluene, Sunlight, O₂, 5 h.

Synthesis of Y3

A mixture of Compound 10 (100 mg, 0.078 mmol), 100 mL toluene, and I_2 (20 mg, 0.079 mmol) was illuminated by sunlight for 5 hours at reflux. The crude product was purified through silica gel column chromatography with a mixture of CH₂Cl₂ and ethyl acetate as eluent and Y3 was obtained as red solid (75 mg, 75%). **Compound Y3.** M.p. >300°C. ¹H NMR (400 MHz, CDCl₃): δ =0-0.5(m, 8H), 0.80-1.40(m, 24H), 1.60 (s, 3H), 1.76 (m, 2H), 2.09 (m, 4H), 2.40(m, 6H), 3.60-4.10 (m, 2H), 5.11 (t, 2H), 5.25 (m, 2H), 8.56(t, 4H), 8.95 (t, 4H), 9.06 (t, 4H), 9.55 (d, 2H), 10.38 ppm (s, 2H). ¹³C NMR (100 MHz, CDCl₃): δ =10.9, 11.5, 14.0, 20.9, 25.2, 29.7, 32.3, 44.2, 56.6, 58.0, 112.6, 116.8, 118.5, 120.9, 122.3, 122.9, 123.1, 123.2, 123.3, 123.4, 124.4, 124.9, 126.3, 126.8, 128.9, 129.9, 133.1, 133.4, 133.5, 165.0 ppm. MALDI-TOF-MS: Calcd for C₈₄H₆₉N₅O₈Na 1298.5044, found: 1298.5125(M+Na⁺).

Synthesis of Y4

A mixture of Compound 11 (150 mg, 0.2 mmol), 150 mL toluene, and I_2 (30 mg, 0.12 mmol) was illuminated by sunlight for 5 hours at room temperature. Y4 was obtained as red solid (93 mg, 62%). **Compound Y4.** M.p. >300°C. ¹H NMR (400 MHz, CDCl₃): $\delta = 1.04$ (m, 15H), 1.53 (m, 2H), 1.92-2.14 (m, 6H), 2.30(m, 4H), 4.38 (t, 2H), 5.13(m, 2H), 7.21 (m, 1H), 7.47 (m, 2H), 7.77 (d, 1H), 8.44 (d, 1H), 78.53 (d, 1H), 8.62 (d, 4H), 9.53 (s, 1H), 10.25 ppm (s, 1H). ¹³C NMR (100 MHz, CDCl₃): $\delta = 11.8$, 14.1, 20.8, 22.9, 25.2, 25.3, 29.9, 31.5, 43.2, 57.8, 58.0, 109.7, 112.2, 116.2, 120.0, 121.2, 121.6, 122.1, 122.3, 122.6, 123.2, 123.6, 126.3, 126.9, 127.0, 128.3, 128.7, 132.5, 132.9, 140.1, 140.2, 164.6 ppm. MALDI-TOF-MS: Calcd for C₅₀H₄₃N₃O₄ 749.3254, found: 749.3293(M⁺).

(S1) Yuan, Z. Y.; Xiao, Y.; Li, Z.; Qian, X. Org. Lett. 2009, 11, 2808-2811.

(S2) Tavasli, M.; Bettington, S.; Bryce, M. R.; Batsanov, A. S.; Monkman, A. P. Synthesis-Stuttgart 2005, 1619-1624.

(S3) Li, Y.; Ding, J.; Day, M.; Tao, Y.; Lu, J.; D'Iorio, M. Chem.Mater. 2004, 16, 2165-2173.
(S4) Thompson, B. C.; Kim, Y.-G.; McCarley, T. D.; Reynolds, J. R. J. Org. Chem. 2006, 128, 12714-12725.

- (S5) Demmig, S.; Langhals, H. *Chem. Ber.* **1988**, *121*, 225-230.
- (S6) Tauber, M. J.; Kelley, R. F.; Giaimo, J. M.; Rybtchinski, B.; Wasielewski, M. R. J. Am. Chem. Soc. 2006, 128, 1782-1783.

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3 Absorption and emission spectra of Y4 and PBI-1



Figure S1. Absorption spectra of Y4.



Figure S2. Absorption spectra of PBI-1.





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Figure S3. Emission spectra of Y4.

Figure S4. Emission spectra of PBI-1.

Table S1. Flu	e S1. Fluorescence quantum yields of Y4 in different solvents (with PBI-1 as standard, $\Phi = 1$).				
	DMC	Acetic ether	DMF	Toluene	
Φ	0.062	0.053	0.007	0.092	

4 electrochemical properties of Y1, Y2, Y3, Y4 and PBI-1







Figure S5. Cyclovoltammograms of Y1, Y2, Y3, Y4 and PBI-1 in dichloromethane.

5 HOMO and LUMO electron density of Y1, Y2, Y3, Y4 and PBI-1



Table S2. HOMO and LUMO electron density of Y1, Y2, Y3, Y4 and PBI-1.



Table S3. Theoretical HOMO and LUMO energy level of Y1, Y2, Y3, Y4 and PBI-1.

	Theoretical	Theoretical
	LUMO (eV)	HOMO (eV)
¥1	2.88	5.26
¥2	2.88	5.28
¥3	3.26	5.58
¥4	3.11	5.45
PBI-1	3.42	5.95

6 Z-scan curve of open/close aperture

The third-order NLO properties of all compounds were determined by open/close aperture Z-scan measurements, which were performed at 800 nm with a pulse duration of 140 fs and a repetition rate of 1kHz from a Ti-sapphire femtosenond laser system, the laser beam with approximately 0.3μ J pulse energy was focused on the solution in 1 mm cell by a lens of 10 cm focal length and the transmitted light after the sample was collected by a photodiode detector connected with a lock in amplifier.

sample was collected by a photodiode detector connected with a lock in amplifier. The real and imaginary parts of the third-order nonlinear susceptibility $\chi_R^{(3)}$, $\chi_I^{(3)}$ and the third-order nonlinear susceptibility $\chi_R^{(3)}$, $\chi_I^{(3)}$, χ_I Electronic Supplementary Material (ESI) for Chemical Communications This journal is © The Royal Society of Chemistry 2011

$$\chi_{\alpha}^{(3)} = \chi_{R}^{(3)} + i\chi_{I}^{(3)}$$
(1)

$$\chi_{\rm R}^{(3)}(\rm esu) = cn_0^2 n_2 / 120\pi^2$$
(2)

$$\chi_{\rm I}^{(3)} (\rm{esu}) = c^2 n_0^2 \beta / 240 \pi^2 \omega$$
 (3)

Where n_0 is the linear refractive index of the dichloromethane. ω is the angular frequency of the light field.

The two-photon absorption (TPA) cross section can be calculated by using the equation of $\sigma=h\nu\beta/N_0$, where $N_0=N_AC$ is the number density of the absorption center, N_A is the Avogadro constant, and C represents the solute molar concentration.





Figure S6. Z-scan curves of open/close aperture (0.01 M).

7 Copy of NMR spectrum

¹ H NMR (400 MHz) spectrum of 3 in CDCl₃



 ^{13}C NMR (100 MHz) spectrum of 3 in CDCl₃



¹ H NMR (400 MHz) spectrum of 4 in CDCl₃

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¹³C NMR (100 MHz) spectrum of 4 in CDCl₃



H NMR (400 MHZ) spectrum of 5 III CDCI3



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¹³C NMR (100 MHz) spectrum of 5 in CDCl₃





¹ H NMR (400 MHz) spectrum of 6 in CDCl₃



¹³C NMR (100 MHz) spectrum of 6 in CDCl₃



^{170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 (} ppm (f1)

¹H NMR (400 MHz) spectrum of Y1 in CDCl₃



 ^{13}C NMR (100 MHz) spectrum of Y1 in CDCl_3





¹H NMR (400 MHz) spectrum of Y2 in CDCl₃



 ^{13}C NMR (100 MHz) spectrum of Y2 in CDCl_3



160 150 140 130 120 110 100 90 80 70 60 50 40 30 2C 1C C ppm (f1)

¹ H NMR (400 MHz) spectrum of 9 in CDCl₃



¹³C NMR (100 MHz) spectrum of 9 in CDCl₃



 $^1\,\text{H}$ NMR (400 MHz) spectrum of 12 and 12' in CDCl_3



 ^{13}C NMR (100 MHz) spectrum of 12 and 12' in CDCl_3



¹H NMR (400 MHz) spectrum of 10 in CDCl₃



¹³C NMR (100 MHz) spectrum of 10 in CDCl₃



¹H NMR (400 MHz) spectrum of 11 in CDCl₃





¹³C NMR (100 MHz) spectrum of Y3 in CDCl₃



ppm (f1) ' | C

¹H NMR (400 MHz) spectrum of Y4 in CDCl₃



¹³C NMR (100 MHz) spectrum of Y4 in CDCl₃

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