Supplementary Material (ESI) for Chemical Communications

Revised Supporting Information of B718147G

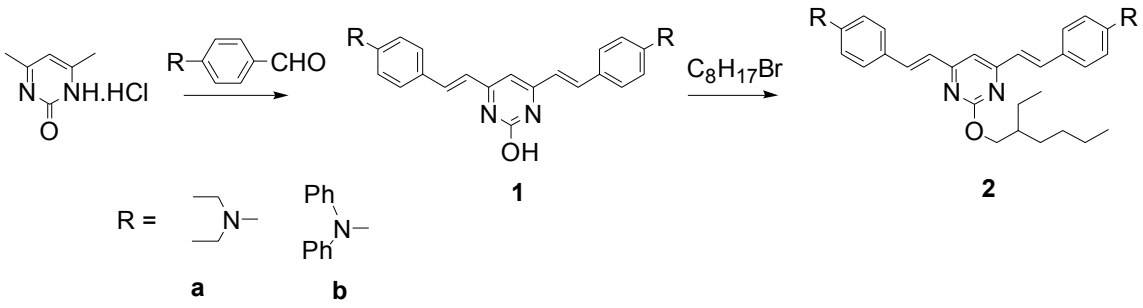
Two-photon absorption enhancement induced by aggregation due to intermolecular hydrogen bonding in V-shaped 2-hydroxypyrimidine derivatives

Zijun Liu, Pin Shao, Zhenli Huang, Bo Liu, Tao Chen and Jingui Qin

Instrumentation and Synthesis

^{1}H NMR and ^{13}C NMR spectra were recorded on Varian Mercury VX300 FT-NMR spectrometer in $CDCl_3$ (Varian, USA) operating at 298 K. Elemental analysis was performed by Vario EL III (German). Mass spectra were recorded on Finnigan Trance Mass spectrometer. High Resolution MS was operated on Finnigan-NAT 8430 in Shanghai Institute of Organic Chemistry, Chinese Academic of Sciences. UV-vis spectra were obtained using a Schimadzu 160A spectrometer. Fluorescence spectra were recorded on a Hitachi F-4500 fluorescence spectrophotometer. Two-photon absorption was measured by two-photon induced fluorescence (TPIF) technique. A mode-locked Ti: sapphire laser (Mai Tai, Spectra-Physics Inc., USA) was used as the excitation source. The average output power, pulse width and repetition rate were 0.5 W, 100 fs, and 82 MHz, respectively. After passing through a Pockel cell (350-80 LA BK, Conoptics Inc., USA) that was used to control the power of the laser, the laser was focused on the cell (polished on all sides) by a focusing lens (f = 6 cm). The excitation light was adjusted to approach to the wall as near as possible in order to reduce the re-absorption effect. The emission light was collected at one side vertical to the excited beam by an objective lens (10×, NA = 0.30, Olympus, Japan) and then was focused by another objective lens (10×, NA = 0.25, DHC Inc., China) into a fiber Spectrometer (HR2000, Ocean Optics Inc., USA), which was used to record the fluorescence spectra. In addition, a liquid barrier filter (1 cm path-length, 1 M $CuSO_4$ solution) was placed in front of the fiber optic spectrometer to exclude excitation illumination.

All beginning chemicals are commercially available and were used as received unless stated otherwise. The solvent was dried as normal procedure and the solution of samples were prepared freshly and wrapped in silver paper before measurement.



General synthetic procedure for preparation of 1 [1]

Aldehyde (2.2 equivalent) and 4, 6-dimethy-2-hydroxypyrimidine hydrochloride (1 equivalent) were dissolved in 95% ethanol. The solution was cooled to 0 □ and treated with hydrochloric acid. Then the mixture was refluxed for 24h under argon, during which time a purple color developed. After cooled to room temperature, it was neutralized with aqueous sodium carbonate solution, and then extracted with chloroform, dried with sodium sulfate, and concentrated. Purification was performed by column chromatography. Elution with methanol-ethyl acetate-chloroform (1:5:30 v/v) and evaporation of the solvent gave a red powder. The product was crystallized from ethanol/chloroform gave pure products.

4, 6-Bis-[2-(4-diethylamino-phenyl)-vinyl]-pyrimidin-2-ol (1a)

Red powder. Yield, 27 %. EI-MS: m/z, 441.6 (M-H). ^{1}H NMR (300MHz, $CDCl_3$): δ 1.21 (t, J = 7.2 Hz, 12 H, CH_3), 3.42 (q, J_1 = 6.6 Hz, J_2 = 13.8 Hz, 8H, N-CH_2), 6.53 (s, 1H, pyrimidine), 6.65 (d, J = 8.7 Hz, 4H, phenyl), 6.72 (d, J = 16.5 Hz, 2H, CH=CH), 7.52 (d, J = 8.1 Hz, 4H, phenyl), 7.76 (d, J = 15.3 Hz, 2H, CH=CH), 12.65 (b, 1H, OH). ^{13}C NMR: δ 161.45, 160.22, 149.31, 139.98, 130.38, 122.66, 111.52, 99.69, 44.71, 12.87. Elemental analysis (%): Calcd. for $C_{28}H_{34}N_4O$: C 75.98, H 7.74, N 12.66; found: C 75.77, H 7.48, N 12.37.

4, 6-Bis-[2-(4-diphenylamino-phenyl)-vinyl]-pyrimidin-2-ol (1b)

Orange powder. Yield, 21 %. EI-MS, m/z: 633.6 (M-H), ^{1}H NMR (300MHz, $CDCl_3$):

δ 6.54 (s, 1H, pyrimidine), 6.78 (d, *J* = 15.9 Hz, 2H, CH=CH), 7.02 (d, *J* = 8.4Hz, 4H, p-phenyl), 7.06-7.15 (m, 13H), 7.26-7.32 (m, 9H), 7.47 (d, *J* = 8.4 Hz, 4H, p-phenyl), 7.78 (b, 2H, CH=CH), 12.87 (b, 1H, OH). ^{13}C NMR: δ 161.65, 160.34, 149.82, 147.22, 139.51, 129.65, 129.50, 128.77, 125.52, 124.10, 122.17, 101.07. Elemental analysis (%): Calcd. for $C_{44}H_{34}N_4O$: C 83.25, H 5.40, N 8.83; found: C 83.54, H 5.23, N 8.50.

General synthetic procedure for preparation of 2.

1 (0.5 mmol) and K_2CO_3 (654 mg, 5mmol) were dissolved in DMF (15 ml). After stirred for 30 min under Argon at room temperature, the mixture was treated with 3-bromomethyl-heptane (0.2 ml, 1.1 mmol) and then heated to 80 □. The mixture was stirred for 24 h at this temperature and then poured into ice water. It was extracted with chloroform, dried with sodium sulfate, and concentrated. Purification was performed by column chromatography. Elution with petroleum / ether-ethyl acetate (4:1) and evaporation of the solvent gave product.

4, 6-Bis-[2-(4-diethylamino-phenyl)-vinyl]-2-(2-ethyl-hexyloxy)-pyrimidine (2a)

Yield, 46.2 %. ^{1}H NMR (300MHz, $CDCl_3$): δ 0.84-0.92 (m, 6H, CH_3), 1.11 (t, *J* = 6.6 Hz, 12H, CH_3), 1.29-1.54 (m, 8H, CH_2), 1.76-1.80 (m, 1H, CH), 3.31 (q, J_1 = 6.6 Hz, J_2 = 13.8 Hz, 8H, N-CH_2), 4.22-4.32 (q, J_1 = 3.0 Hz, J_2 = 6.0 Hz, 2H, O-CH_2), 6.57 (d, *J* = 8.1 Hz, 4H, phenyl), 6.71 (d, *J* = 16.2 Hz, 2H, CH=CH), 6.75 (s, 1H, pyrimidine), 7.38 (d, *J* = 8.7 Hz, 4H, phenyl), 7.71 (d, *J* = 16.2 Hz, 2H, CH=CH). ^{13}C NMR: δ 165.86, 165.57, 148.68, 136.93, 129.56, 123.32, 121.08, 111.57, 109.61, 69.74, 44.65, 39.33, 30.68, 29.40, 23.96, 23.36, 14.42, 12.87, 11.36. HR-MS, for $C_{35}H_{47}N_4O$, target: m/z = 555.4043 (M+1), search: m/z 555.40574 (M+1).

4, 6-Bis-[2-(4-diphenylamino-phenyl)-vinyl]-2-(2-ethyl-hexyloxy)-pyrimidine (2b)

Yield, 50 %. ^{1}H NMR (300MHz, $CDCl_3$): δ 0.93-1.01 (m, 6H, CH_3), 1.26-1.52 (m, 8H, CH_2), 1.82-1.89 (m, 1H, CH), 4.35-4.40 (q, J_1 = 3.0 Hz, J_2 = 6.0 Hz,2H, O-CH_2), 6.88-6.92 (m, 3H, pyrimidine and CH=CH), 7.02-7.31 (m, H), 7.44 (d, *J* = 8.7 Hz, 4H, p- phenyl), 7.82 (d, *J* = 8.7 Hz, 2H, CH=CH). ^{13}C NMR: δ165.59, 165.30, 149.08, 147.40, 136.40, 129.64, 129.34, 128.86, 125.31, 124.10, 123.86, 122.62, 110.49, 70.00, 39.31, 30.69, 29.40, 23.97, 23.35, 14.43, 11.37. HR-MS, for $C_{52}H_{50}N_4O$, target: m/z = 747.4037 (M+1), search: m/z 747.40574 (M+1).

^{1}H NMR Experiment

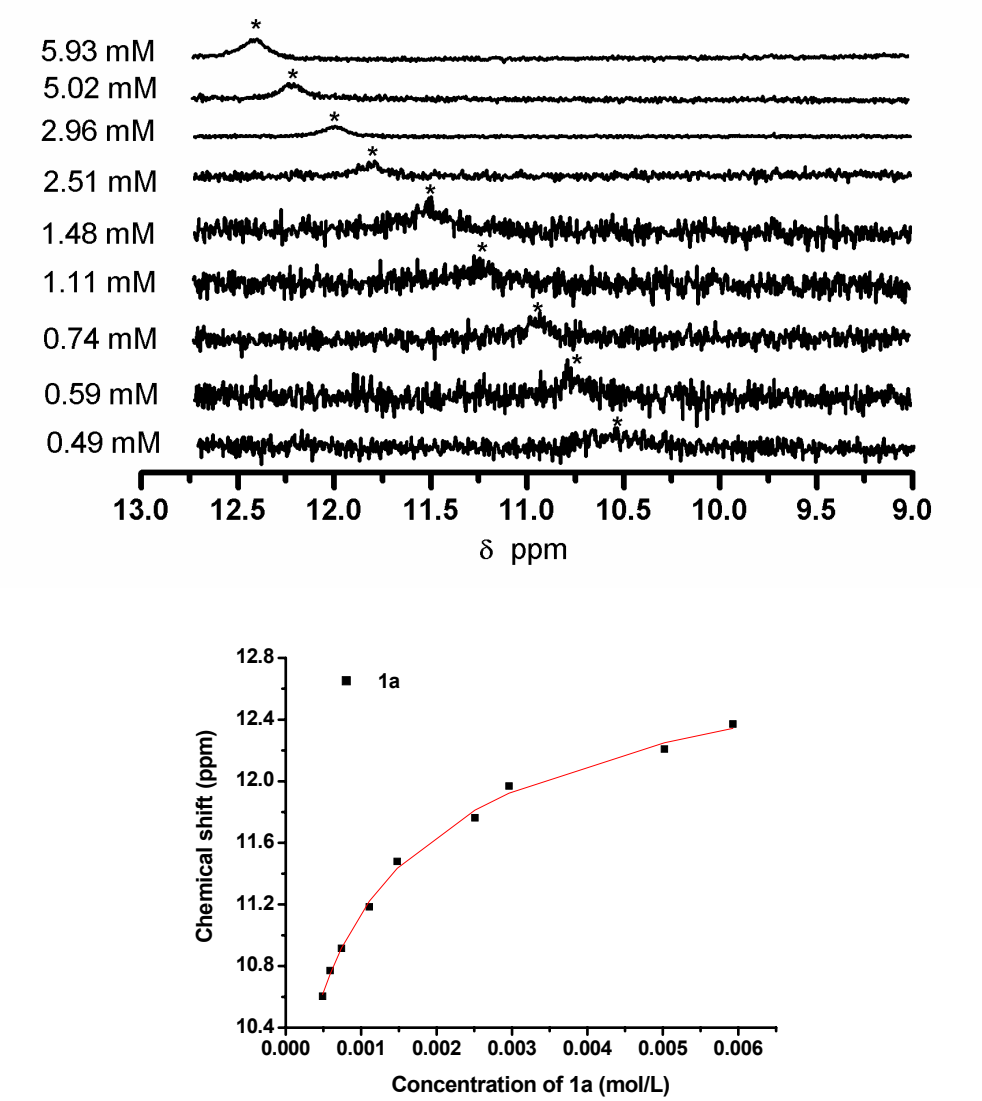


Fig. S1 The ^{1}H NMR spectrum of **1a** in $CDCl_3$ (top,* the chemical shift of OH) and chemical shift of hydroxyl on **1a** in $CDCl_3$ *vs* concentration (below)

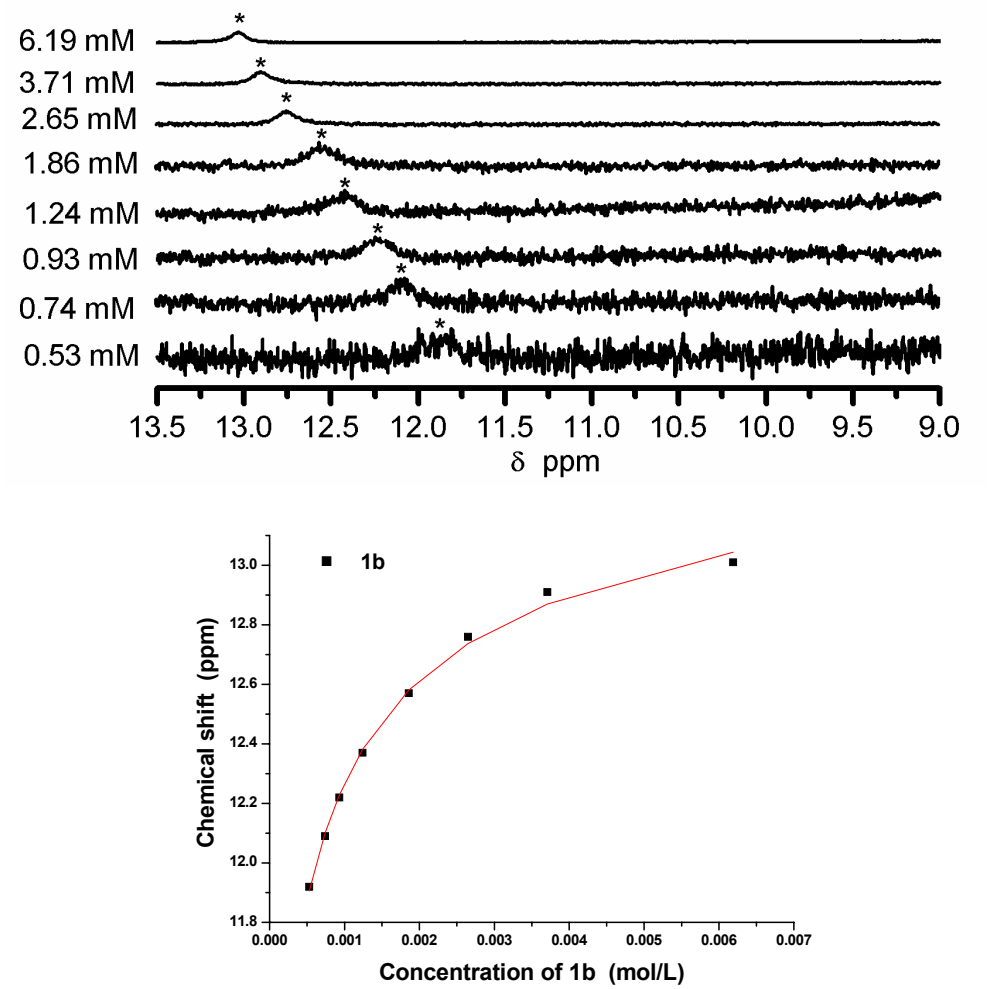


Fig. S2 The ^{1}H NMR spectrum of **1b** in $CDCl_3$ (top,* the chemical shift of OH) and chemical shift of hydroxyl on **1b** in $CDCl_3$ *vs* concentration (below)

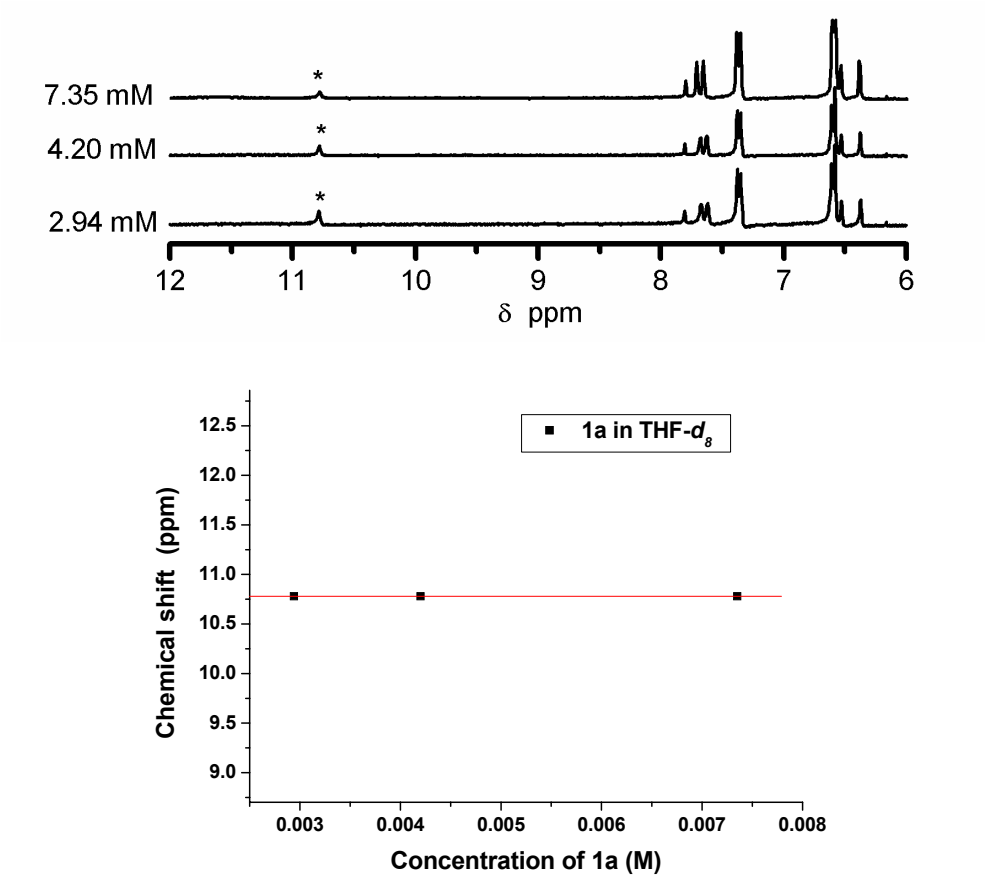


Fig. S3 The ^{1}H NMR spectrum of **1a** in THF-d_8 (top,* the chemical shift of OH) and the chemical shift of hydroxyl on **1a** in THF-d_8 *vs* concentration (below)

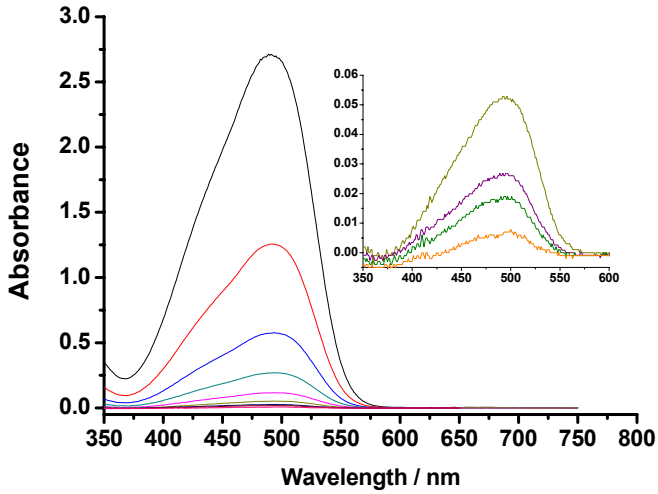


Fig. S4 The dependence of UV-vis spectra of **1a** in chloroform on the concentration (from 6.2×10^{-5} to 2.4×10^{-7} M), and the inset is the amplified figure with concentration from 1.9×10^{-5} to 2.4×10^{-7} M. The concentration decreases by 50% each time. The absorbance decreases continuously when the concentration decreases each time but the λ_{max} keeps almost the same.

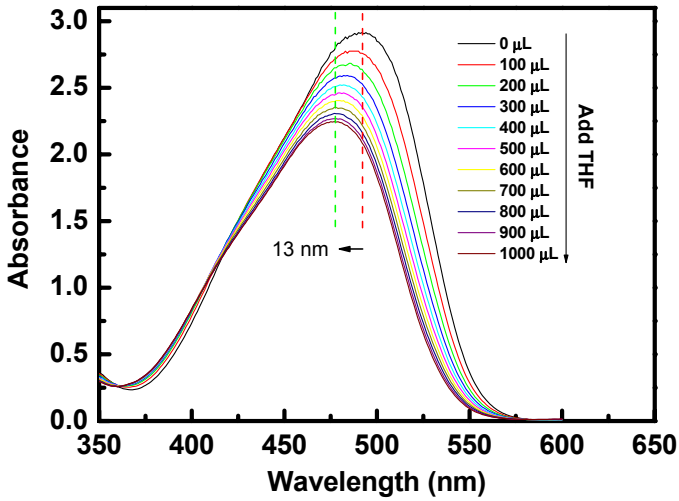


Fig. S5 The UV-vis spectra change of **1a** in $CHCl_3$ (with the beginning concentration of 6.3×10^{-5} M and volume of 3 mL) with the gradual addition of THF.

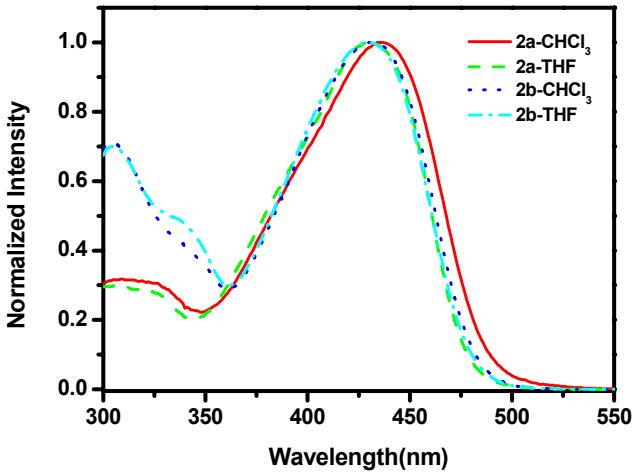


Fig. S6 The Uv-vis spectra of **2a** and **2b** in $CHCl_3$ and THF (~1.0×10^{-5} M).

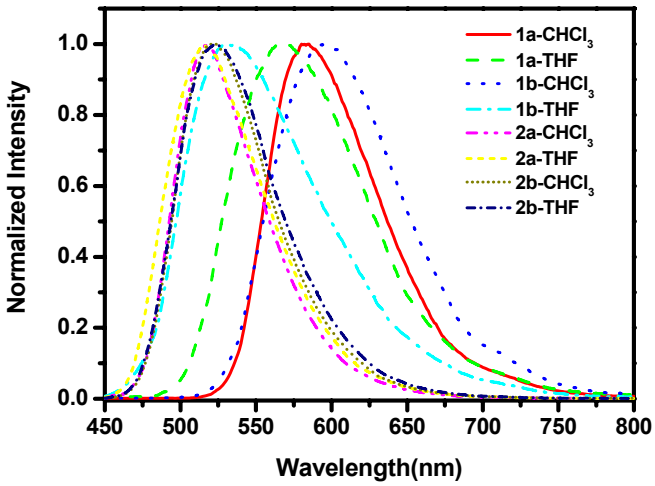


Fig. S7 The fluorescent spectra of four compounds in $CHCl_3$ and THF (~1.0×10^{-5} M).

Two-photon-induced fluorescence measurement

The two-photon cross-section σ was measured by using the two-photon-induced fluorescence measurement technique with the following equation [2].

$$\sigma_s = \sigma_r (F_s / F_r) (\Phi_r / \Phi_s) (c_r / c_s)(n_r / n_s)$$

The subscripts "s" and "r" stand for the sample and reference molecules respectively. F is the integrated fluorescence intensities measured at the same power of the excitation beam. Φ is the fluorescence quantum yield. n is refractive index. The number density of the molecules in the solution was denoted as c. σ_r is the TPA cross section of the reference molecule. In this experiment, fluorescein was selected as reference molecule (5.0×10^{-5} M in 0.1 M NaOH).

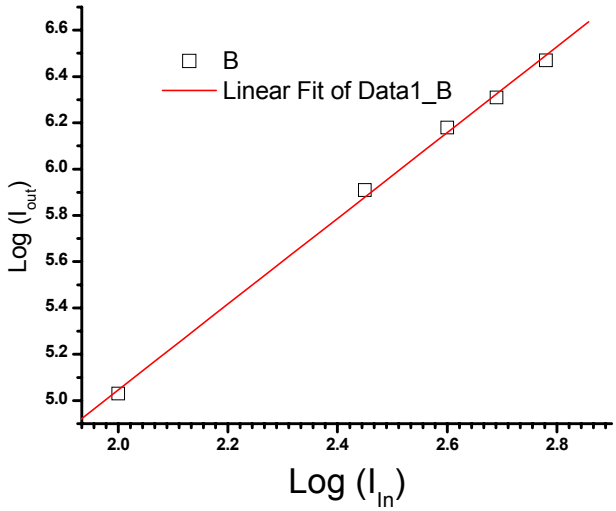


Fig. S7 The dependence of fluorescence intensity of **1a** in chloroform on the laser energy at 850 nm. (Slope = 1.85)

Reference:

[1] Brown, D. M.; Kon, G. A. R. *J. Chem. Soc.* 1948, 2147.
[2] M. A. Albota, C. Xu, W. W. Webb, *Appl. Opt.*, 1996, 13, 481.