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# Frequency-upconverted stimulated emission by simultaneous five-photon absorption

Qingdong Zheng*, Haomiao Zhu, Shan-Ci Chen, Changquan Tang, En Ma and Xueyuan Chen*

**Since the invention of the laser in 1960, multiphoton effects have become useful in techniques for real applications as well as conceptual predictions. Here, we report the first experimental observation of frequency-upconverted stimulated emission from a novel fluorophore through simultaneous five-photon absorption. Compared to lower-order nonlinear absorption, the fifth-order dependence on input light intensity of the five-photon absorption process will provide much stronger spatial confinement, allowing the achievement of a much higher contrast in imaging. Stimulated emission has also been achieved by the absorption of two to four photons under near-infrared laser excitation, making this gain medium a promising multiphoton imaging probe with attractive features, including the absence of autofluorescence from biological samples, large penetration depth, and improved sensitivity and resolution.**

Although, being a third-order process, two-photon absorption (2PA) is several orders of magnitude weaker than linear absorption, in the past two decades the use of lasers has led to significant progress in various two-photon-related applications. These applications include biological imaging, three-dimensional optical data storage, three-dimensional microfabrication, frequency-upconverted lasing, optical power limiting, photodynamic therapy, among others[1–12]. The availability of intense ultrashort laser pulses has made the study of higher-order nonlinearity possible. He *et al.* first observed highly directional and frequency-upconverted stimulated emission produced by strong simultaneous three-photon absorption (3PA) at 1,300 nm in an organic chromophore (4-[*N*-(2-hydroxyethyl)-*N*-(methyl)amino]-4′-(6-hydroxyhexyl sulphonyl)stilbene, APSS) solution[3]. They achieved a net lasing conversion efficiency of 2.1% from the absorbed pump energy to the output energy. Three-photon pumped (3PP) stimulated emission from some oligofluorene derivatives has also been reported[13]. These achievements suggest exciting opportunities for a 3PA process in frequency-upconverted lasing, short-pulse optical communications, and the newly emerging field of biophotonics[3]. Five-photon absorption (5PA) is a nonlinear process in which a molecule can be excited from its ground state to its excited state by absorbing five photons simultaneously. It is notoriously difficult to observe the 5PA-related phenomenon because of the low transition probability of the 5PA process for a molecule[14–17]. Accordingly, five-photon absorbing materials have rarely been investigated in the literature[18]. Furthermore, the realization of five-photon pumped (5PP) stimulated emission will be even more difficult because it requires the 5PA to be large enough to create population inversion in the gain medium. To the best of our knowledge, the phenomenon of 5PP stimulated emission has never been observed, nor has it been fully analysed theoretically.

In general, there are two major mechanisms responsible for the phenomenon of frequency upconversion. One is based on sequential stepwise multiphoton excitation in materials such as rare-earth doped crystals, nanoparticles and so on[19–22]. The other is based on simultaneous multiphoton absorption (MPA) in organic or inorganic materials; this requires large MPA cross-sections if the potential applications are to be fully exploited. Nonetheless, materials for multiphoton excited lasing (or stimulated emission) should not only have large MPA cross-sections—they should also have small non-radiative decay rates. Over the past decade, several molecular design strategies have been developed for π-conjugated molecules with large nonlinear absorptivity. Among these, the donor–π-acceptor molecular architecture is one of the best choices for materials with enhanced MPA[1,2,23]. However, most materials with large MPA generally have an extended π-conjugation length, which leads to redshifted absorption and emission. To obtain molecules with short-wavelength emission, a new molecular design is required. Previously, Zheng *et al.* have reported a series of donor–acceptor structures with a pyridinium inner salt as electron acceptor and a dialkylaminobenzene moiety as electron donor. They found that the introduction of the pyridinium inner salt led to an enhancement in two-photon pumped lasing efficiency[24]. It is anticipated that the replacement of the dialkylaminobenzene moiety with an electron-rich heteroaromatic moiety will result in blueshifted absorption and emission. An alkyl group can also be introduced into the heteroaromatic moiety to increase the rigidity of the whole structure, which would be beneficial for enhanced emission. In this context, a novel molecular architecture based on a new heteroaromatic system has been proposed to obtain a material with large nonlinear absorptivity, blueshifted emission and high lasing efficiency.

In this Article, the gain medium for multiphoton pumped stimulated emission is (*E*)-3-(4-(2-(1-hexyl-4-methyl-1*H*-imidazol-5-yl)vinyl)pyridinium-1-yl)propyl sulphate (IPPS), which was synthesized via a Knoevenagel condensation reaction between 1-hexyl-4-methyl-1*H*-imidazole-5-carbaldehyde and 4-methyl-*N*-(3-sulphooxypropyl)-pyridinium inner salt. The molecular structure of IPPS is shown in the right of Fig. 1c and was characterized by high-resolution mass spectroscopy (HRMS), $^1$H NMR and elemental analysis. Figure 1a presents the linear absorption and emission spectra of IPPS in dimethyl sulphoxide (DMSO). As shown in the figure, the absorption spectrum of IPPS is centred at ~403 nm and its emission spectrum at 503 nm with a full-width at half-maximum (FWHM) of 65 nm. Because of the relatively weaker electron-donating ability of the 1-hexyl-4-methyl-1*H*-imidazole group, IPPS shows hypsochromically shifted linear absorption and emission compared to its analogue chromophores[24]. The

State Key Laboratory of Structural Chemistry and Key Laboratory of Optoelectronic Materials Chemistry and Physics, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, China. *e-mail: qingdongzheng@fjirsm.ac.cn; xchen@fjirsm.ac.cn

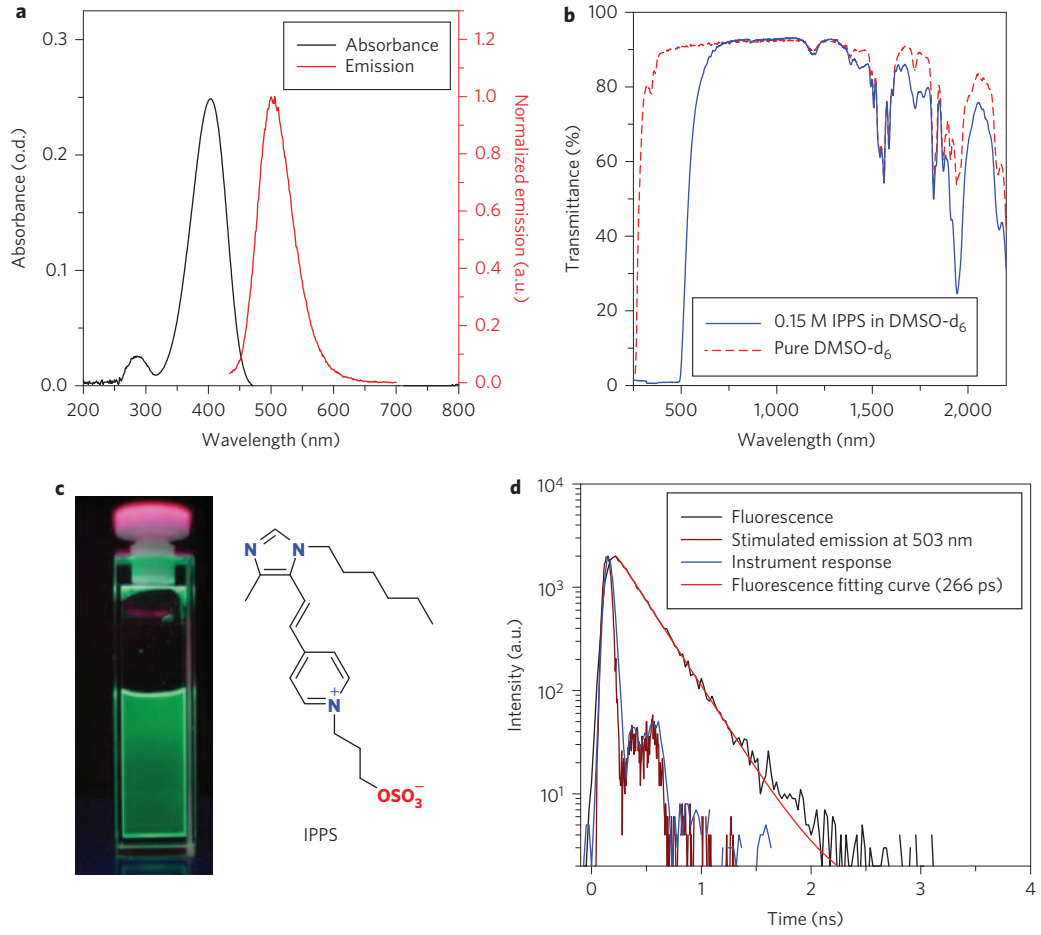


**Figure 1 | Absorption, transmission and emission. a**, Linear absorption and emission spectra of IPPS in DMSO. **b**, Transmission spectra of IPPS solution (0.15 M in DMSO-$d_6$) and pure DMSO-$d_6$. **c**, Photograph showing one-photon induced fluorescence (left) and the molecular structure of IPPS (right). **d**, Fluorescence decay profile (black) of IPPS in DMSO-$d_6$, the fitting curve with monoexponential decay (red) and 3PP stimulated emission at 503 nm (dark red) as well as the instrument response curve (blue). Q10

relatively large Stokes shift of ~4,940 $cm^{-1}$ is due to the strong solute–solvent (DMSO) interactions, which decrease the energy of the solute molecules in their excited states. IPPS is quite fluorescent in DMSO, and upon excitation at 365 nm, green emission can be observed, as shown in the left of Fig. 1c. The fluorescence quantum yield of IPPS in DMSO was determined to be ~4.4%, with Coumarin 152 as a reference[25]. The emission decay curve shown in Fig. 1d for IPPS in deuterated DMSO (DMSO-$d_6$), was measured by laser excitation at 397 nm. The black line shows a monoexponential decay curve fitted with a decay constant of 266 ps, indicative of only one existing species for IPPS in its exited state. As is known, MPA takes place at wavelengths where there is no or negligible linear absorption. DMSO-$d_6$ was therefore chosen as the solvent for the multiphoton experiment so as to reduce the linear absorption of the solvent in the near-infrared (near-IR) or mid-infrared (mid-IR) region. Figure 1b shows the transmission spectra for pure DMSO-$d_6$ and IPPS in DMSO-$d_6$ (0.15 M) with a pass length of 1 cm. As shown in Fig. 1b, pure DMSO-$d_6$ has negligible or relatively low linear absorption in the optical windows of 670–1,485 nm, 1,600–1,825 nm and 1,995–2,115 nm. As a result, these wavelength regions were chosen for the multiphoton excitation experiment described in this work.

In the present experiment, the gain medium (0.15 M IPPS in DMSO-$d_6$) was placed in a quartz cuvette with a pass length of 1 cm. A femtosecond laser at 1,197 nm was focused in the centre of the cuvette by a lens with a focal length of 5 cm. This laser beam was directed from a femtosecond optical parametric oscillator (OPO). The measured forward 3PP stimulated emission and fluorescence spectra are compared in Fig. 2a. The stimulated emission peak is very close to the central position of the corresponding fluorescence band because the population inversion can be easily built at the wavelength where there is maximum gain. For comparison purposes, the spectral profile of the third-harmonic generation (THG) of the pump beam passing through a 1 mm quartz plate is also plotted in Fig. 2a. Comparing the spectral profiles of THG, the fluorescence spectrum and 3PP stimulated emission of IPPS, we can see that the 3PP stimulated emission bandwidth (FWHM, ~18 nm) is ~2.6 times narrower than the corresponding fluorescence spectrum (FWHM, ~65 nm, Fig. 1a), and it is determined mainly by the spectral gain property of the fluorophore solution rather than the pump spectral bandwidth (~8 nm). It should be noted that the fluorescence spectrum induced by one-photon absorption has the same spectral pattern as that induced by MPA (2PA and beyond) because all the emissions originate from the same excited state[24]. The visible stimulated emission wavelength (503 nm) is shorter than half, and longer than one-third, of the pumped wavelength (1,197 nm). As illustrated in Fig. 2b, the sum energy of two photons at 1,197 nm is not large enough to overcome the bandgap between the ground state ($S_0$) and excited state ($S_1$) of IPPS. The stimulated emission of IPPS is therefore induced by the simultaneous absorption of three near-IR photons. Furthermore, as shown in Fig. 1d, the temporal profile of the 3PP stimulated emission with ultrashort pulse excitation is very similar to the instrument response, indicating a pulse duration shorter than the time

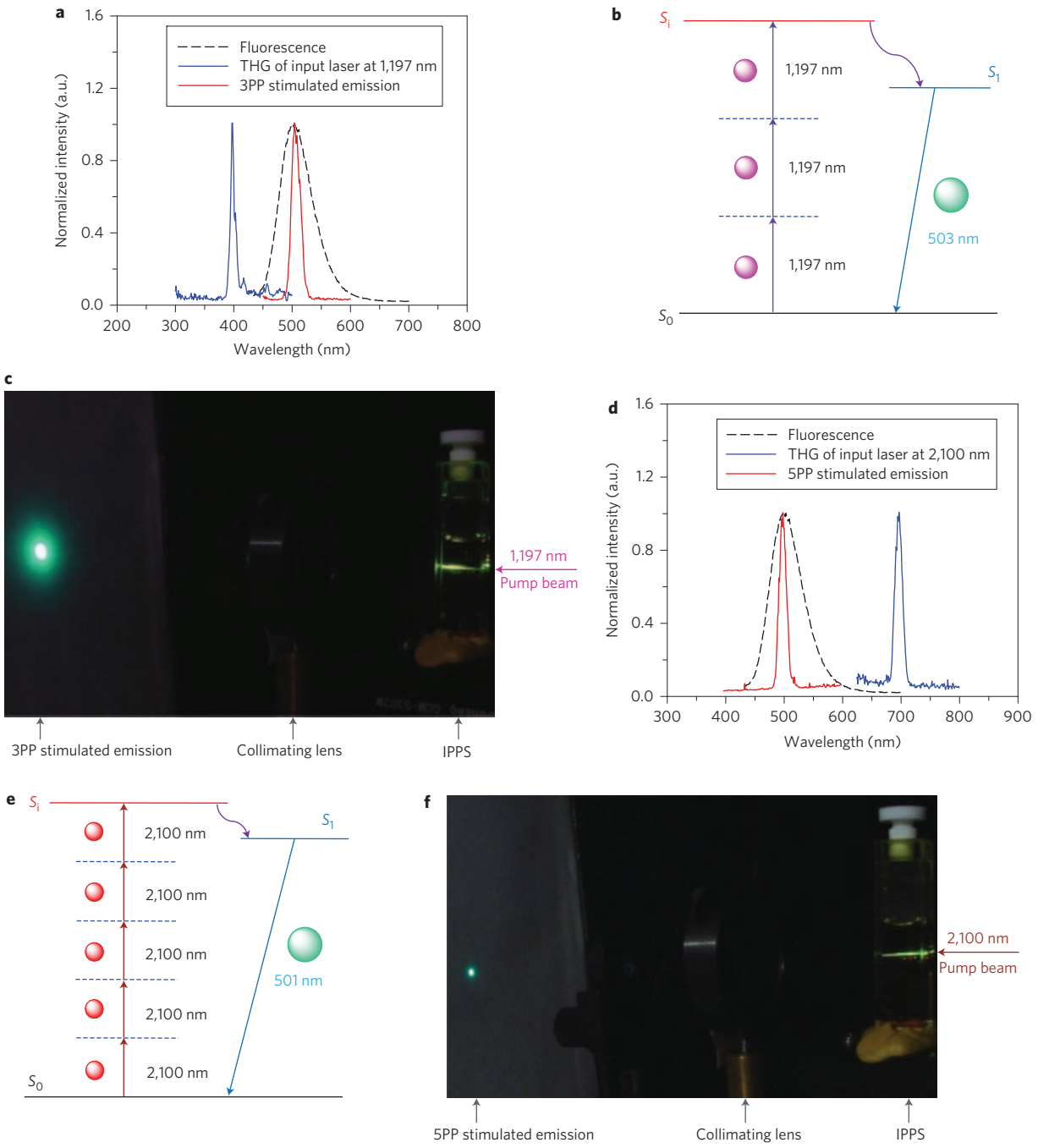


**Figure 2 | Emission spectra, energy diagrams and photographs. a**, Spectra of 3PP stimulated emission, fluorescence and THG of the pump beam. **b**, Energy diagram showing the proposed mechanism for 3PP stimulated emission. $S_i$, a higher singlet state; $S_1$, the lowest radiative singlet state; $S_0$, the ground electronic singlet state. **c**, Photograph showing 3PP stimulated emission. **d**, Spectra of 5PP stimulated emission, fluorescence and THG of the pump beam. **e**, Energy diagram showing the proposed mechanism for 5PP stimulated emission. **f**, Photograph showing 5PP stimulated emission. A pinhole was placed behind the collimating lens.

resolution limit of the instrument (~20 ps). The pulse duration of this 3PP stimulated emission (<20 ps) is much shorter than the corresponding fluorescence decay time of 266 ps (Fig. 1d), consistent with the previously reported stimulated emission under ultrashort pulse excitation[26]. Such temporal narrowing can be attributed to the threshold requirement for generating lasing and depletion in the population inversion of the gain medium with photon-stimulated amplification. The experimental set-up and 3PP stimulated emission image are shown in Fig. 2c. Surprisingly, when the pumped wavelength was shifted from 1,197 nm to 2,100 nm, a visible directional emission was also observed provided that the pump energy was higher than a certain threshold value (11.3 μJ). This blue-green emission also has a narrow bandwidth (FWHM, ~15 nm), similar to that induced by 3PA. This narrowed FWHM of 15 nm is also comparable to other stimulated emissions induced by linear absorption or 2PA[24,27]. The 5PP stimulated emission spectrum is shown in Fig. 2d, where the THG of the pumped beam is shown to reconfirm the wavelength of the input laser beam from the femtosecond OPO system. Here the emission wavelength is shorter than one-quarter, and longer than one-fifth, of the pumped wavelength (2,100 nm). Furthermore, one can find from Fig. 2e that the total energy of four photons at 2,100 nm is

**Table 1 | Threshold energy of the stimulated emission induced by 2PA, 3PA, 4PA or 5PA.**

| Multiphoton excitation* | Two-photon | Three-photon | Four-photon | Five-photon |
|---|---|---|---|---|
| Excitation wavelength (nm) | 800 | 1,197 | 1,600 | 2,100 |
| Threshold energy (μJ) | 2.0 | 0.72 | 2.0 | 11.3 |

*Measured with the same experimental set-up: lens with focal length of 5.0 cm and working distance of 6.0 cm.

smaller than the bandgap between the ground ($S_0$) and excited ($S_1$) states of IPPS. However, the total energy of five photons is large enough to excite the molecules from their ground state to the excited state (Fig. 2e). As a result, the observed stimulated emission of IPPS is induced by the simultaneous absorption of five mid-IR photons. The experimental set-up and 5PP stimulated emission image are shown in Fig. 2f. As shown in the figure, a highly directional blue-green emission can be observed upon excitation by a mid-IR laser at 2,100 nm. It should be noted that the intensity of the stimulated emission induced by 5PA was much weaker than that induced by 3PA (Fig. 2c), despite the higher input energy used for the five-photon excitation. This is reasonable, because 5PA belongs to the ninth-order nonlinear process, whereas 3PA belongs to the fifth-order nonlinear process. The above results, featuring spectral and temporal narrowing, high directionality and lasing threshold for IPPS pumped by a laser beam at 1,197 nm or 2,100 nm, show unambiguously that the coherent visible emission we observed is a single-pass stimulated emission in the form of amplified spontaneous emission arising from the population inversion of the excited IPPS molecules through 3PA or 5PA.

We should stress that, by using the same gain medium, 2PP and 4PP stimulated emission can also be achieved. The threshold energies of stimulated emission induced by 2PA, 3PA, 4PA and 5PA are listed in Table 1. The specific wavelengths are chosen according to the following two criteria: large MPA and low linear absorption of the solvent itself at the selected wavelengths. In fact, 2PA and 3PA peaks are generally located at one-half and one-third the frequency of the linear absorption peak[1]. In going from 3PA to 4PA or 5PA, there is an increase in threshold energy, which is in agreement with the prediction that the transition probability of a nonlinear phenomenon decreases with increasing nonlinearity order. However, the threshold energy for two-photon excitation is abnormally higher than that for three-photon excitation, which can be attributed to the self-focusing effect[28] and the spatial soliton[29] formed at longer wavelengths for 3PA and beyond. To the best of our knowledge, our system is the first to achieve frequency-upconverted stimulated emissions through simultaneous 2PA, 3PA, 4PA and 5PA from the same gain medium (shown in Table 1). It has come to our attention that a related work regarding multiphoton stimulated emission (lasing) from another group of chromophores was reported three months after we submitted our work[18]. However, only partial spectral narrowing (~33% narrower than its fluorescence spectrum) via five-photon excitation was demonstrated. It should be noted that lasing has several typical features, including (i) significant spectral narrowing, (ii) threshold characteristics, (iii) directionality, (iv) cavity and (v) input–output power characteristics.

We also observed that the emission spectrum of the fluorophore was independent of the excitation mechanism (from 2PA to 5PA), because, after being excited to higher excited states, the molecules relax non-radiatively to the same excited state ($S_1$) via vibrational mechanisms before the stimulated emission. Furthermore, 5PA is not a process limited only to the molecule discussed in the present Article. In fact, other blue-colour emitting (or lasing) chromophores could be designed and synthesized to be five-photon active in the spectral range ~1,400–1,600 nm, where water has high transmittance. Multiphoton excited fluorescence can also be obtained using regular mode-locked (femtosecond or picosecond) Ti:sapphire lasers without amplifiers (Supplementary Figs S1–S3). As shown in Supplementary Fig. S1, frequency-upconverted fluorescence was observed even with an unfocused femtosecond laser beam, which suggests the applicability of multiphoton probes in biological imaging.

Figure 3a shows the measured lasing output energy as a function of input energy for IPPS. At an input energy of 23 μJ, the output energy is ~0.98 μJ. The overall lasing efficiency is therefore $\eta \approx 0.98/23 \approx 4.26\%$. At the same pump level, the measured nonlinear attenuation (due to 3PA) ratio of the input energy, after passing through the 1 cm, 0.15 M IPPS solution, was measured to be ~0.409. Therefore, the net lasing efficiency is $\eta' \approx \eta/0.409 \approx 10.4\%$. It should be noted that this efficiency was calculated only by considering the contribution from the forward stimulated emission. If backward stimulated emission is also considered, the overall net efficiency will be even higher. No effort was made to achieve a higher lasing efficiency by increasing the dye concentration or by optimizing the experimental set-up. Figure 3b shows the far-field intensity distribution of the 3PP

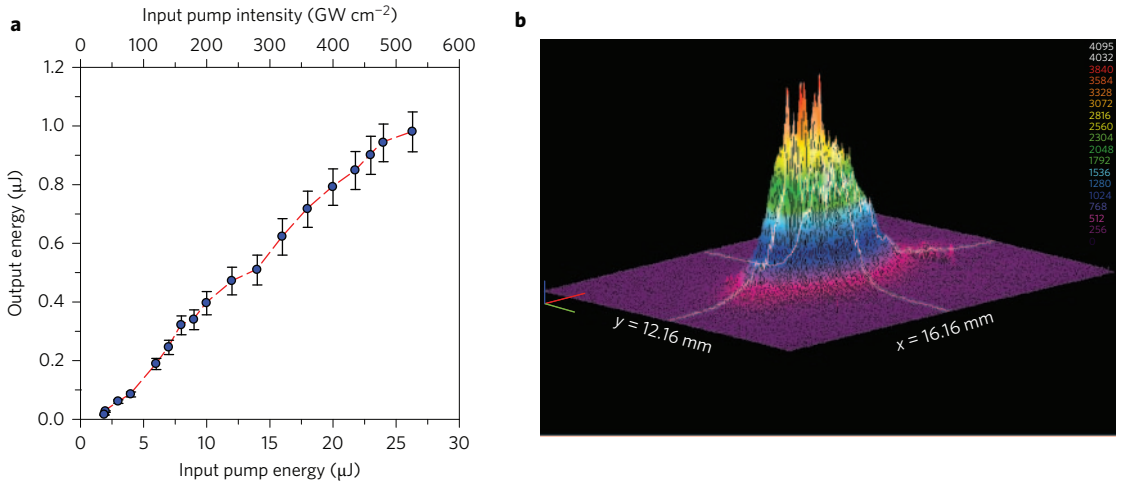


**Figure 3 | Output/input power characteristics and far-field distributions of 3PP pumped stimulated emission. a**, Output/input power characteristics for 3PP stimulated emission from IPPS solution (0.15 M in DMSO-$d_6$). **b**, Far-field distributions of the 3PP stimulated emission beam. Error bars indicate experimental uncertainty of ±10%.

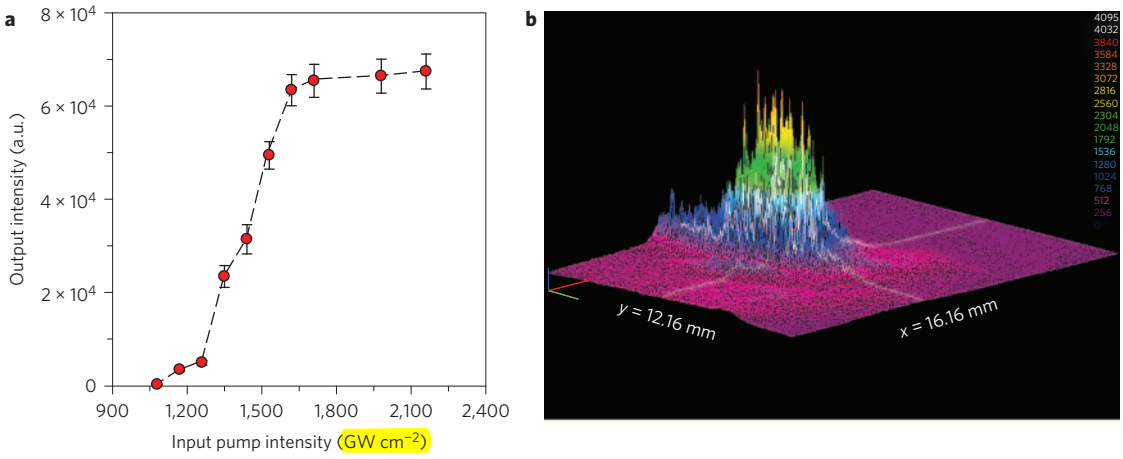


**Figure 4 | Output/input power characteristics and far-field distributions of 5PP stimulated emission. a**, Output/input power characteristics for 5PP stimulated emission from IPPS solution (0.15 M in DMSO-$d_6$). **b**, Far-field distributions of the 5PP stimulated emission beam. Error bars indicate experimental uncertainty of ±10%.

stimulated emission (which exhibits good beam quality). The divergence angle of the output beam was determined to be 3.0 mrad, which is essentially the same as that of the input beam.

Figure 4a shows the measured output/input power curve for the 5PP stimulated emission of IPPS. This output/input power curve can be separated into three regions. At a pump energy slightly larger than the threshold energy (1,170 GW cm$^{-2}$), the output energy increases slowly. When the input energy is larger than 1,250 GW cm$^{-2}$, a higher slope efficiency is observed. When the energy is greater than 1,600 GW cm$^{-2}$, the output intensity starts to saturate, which could be due to the existence of other nonlinear effects such as continuum generation. Because of the relatively low intensity of the output emission beam, we were unable to measure the exact output energy with the power meter (minimum detectable power of 1 μW). Instead, the relative output intensity was measured with a customized UV to mid-IR steady-state and phosphorescence lifetime spectrometer. This meant that the conversion efficiency of the 5PP stimulated emission was not calculated. Figure 4b shows the far-field intensity distribution of the 5PP stimulated emission. The output emission beam was found to have a divergence angle of ~3.0 mrad, nearly the same as that of the input pumped beam.

The observed stimulated emission induced by MPA indicates that the solution sample has a measurable MPA at 1,197 nm or 2,100 nm. Nonlinear optical measurements were therefore carried out to determine the 3PA and 5PA cross-sections at 1,197 nm and 2,100 nm, respectively. Theoretically, the multiphoton processes can be described by the following phenomenological expression[14–17]:

$$\frac{dI(z)}{dz} = -\alpha I(z) - \beta I^2(z) - \gamma I^3(z) - \delta I^4(z) - \varphi I^5(z) - \cdots \quad (1)$$

where $I(z)$ is the local intensity of the incident light beam propagating along the $z$-axis, $\alpha$, $\beta$, $\gamma$, $\delta$ and $\varphi$ are one-, two-, three-, four- and five-photon nonlinear absorption coefficients for a given medium. Suppose, at a certain photon frequency $\nu$, only 3PA satisfying equation (1) is available, then we have

$$\frac{dI(z)}{dz} = -\gamma I^3(z) \quad (2)$$

When $z = l_0$, the nonlinear transmissivity $T$ of a three-photon absorbing medium can be expressed as

$$T = \frac{I(l_0)}{I_0} = \frac{1}{\sqrt{1 + 2\gamma l_0 I_0^2}} \quad (3)$$

Here $l_0$ is the optical path length of the sample and $I_0$ is the intensity of the incident light. From equation (3), the $\gamma$-value of a given medium can be determined experimentally by measuring the transmission at a given pump energy. In our case, at an input energy of 68 GW cm$^{-2}$, the $\gamma$-value is determined to be $(1.2 \pm 0.18) \times 10^{-4}$ cm$^3$ GW$^{-2}$, which is more than onefold larger than the value reported for the 3PA medium (APSS in DMSO) used in 3PP stimulated emission[3]. Thus, the enhanced 3PA for IPPS gives an increased 3PP lasing efficiency over that reported previously for APSS. Furthermore, the 3PA cross-section $\sigma_3$ (in units of cm$^6$ S$^2$ photon$^{-2}$) was determined to be $3.67 \times 10^{-80}$ cm$^6$ S$^2$ photon$^{-2}$ according to the following equation:

$$\sigma_3 = \frac{(h\nu)^2 \gamma}{N_A d_0 \times 10^{-3}} \quad (4)$$

Here, $h\nu$ is the photon energy of the input light, $N_A$ is Avogadro's number and $d_0$ is the molar concentration of the gain medium (in units of mol l$^{-1}$).

Similarly, suppose at a certain photon frequency $\nu$ only 5PA satisfying equation (1) is available, then we have

$$\frac{dI(z)}{dz} = -\varphi I^5(z) \quad (5)$$

and its solution is

$$I(z) = \frac{I_0}{[1 + 4\varphi z I_0^4]^{1/4}} \quad (6)$$

When $z = l_0$, equation (6) can be rewritten as

$$T = \frac{I(l_0)}{I_0} = \frac{1}{[1 + 4\varphi l_0 I_0^4]^{1/4}} \quad (7)$$

The 5PA cross-section $\sigma_5$ (in units of cm$^{10}$ S$^4$ photon$^{-4}$) can be expressed as

$$\sigma_5 = \frac{(h\nu)^4 \varphi}{N_A d_0 \times 10^{-3}} \quad (8)$$

Therefore, according to equation (7), $\varphi$ can be determined experimentally by measuring the value of $T$ at a given level of $I_0$. In this experiment, at a pump energy level of 480 GW cm$^{-2}$, the $\varphi$ value

was calculated to be $(2.16 \pm 0.32) \times 10^{-11}$ cm$^7$ GW$^{-4}$ for IPPS solution (0.15 M in DMSO-$d_6$). Accordingly, the 5PA cross-section for IPPS was estimated to be $1.92 \times 10^{-143}$ cm$^{10}$ S$^4$ photon$^{-4}$ according to equation (8).

In summary, we have demonstrated an efficient frequency-upconverted stimulated emission from the mid-IR (or near-IR) to the visible region in a novel multiphoton absorbing medium (IPPS) that can simultaneously absorb as many as five photons and produce population inversion. By direct 3PA, the IPPS system exhibited a high net conversion efficiency of 10.4%, thereby enabling the realization of novel frequency-upconverted lasing in practical device applications. Furthermore, the observed frequency-upconverted stimulated emission induced by 2PA, 3PA, 4PA or 5PA shows unique advantages such as being free of autofluorescence, improved sensitivity and resolution in bio-imaging, and reduced cellular damage, and may therefore have great potential in applications as diverse as photonics, information storage, biology and medical theranostics.

## Methods

**Materials.** DMSO-$d_6$ was purchased from Cambridge Isotope Laboratories. IPPS was synthesized according to our previously reported procedures[24]. $^1$H NMR (400 MHz, DMSO-$d_6$), δ 8.76 (d, $J$ = 6.8 Hz, 2H), 8.18 (d, $J$ = 6.8 Hz, 2H), 7.97 (d, $J$ = 15.6 Hz, 1H), 7.75 (s, 1H), 7.18 (d, $J$ = 15.6 Hz, 1H), 4.50 (t, $J$ = 6.8 Hz, 2H), 3.92 (t, $J$ = 7.6 Hz, 2H), 3.75 (t, $J$ = 6.0 Hz, 2H), 2.40 (s, 3H), 2.17–2.14 (m, 2H), 1.68–1.65 (m, 2H), 1.27–1.25 (m, 6H), 0.86 (t, $J$ = 6.8 Hz, 3H). HRMS ($m/z$): $[M + H]^+$ calc. for $C_{20}H_{30}N_3O_4S$, 408.19515; found, 408.19453; elemental analysis (calc., found for $C_{20}H_{29}N_3O_4S$): C (58.94, 58.77), H (7.17, 7.25), N (10.31, 9.93).

**Optical measurements.** Absorption and fluorescence spectra were acquired using a spectrophotometer (Lambda 900 UV/vis) and a Cary spectrofluorometer, respectively. The downconverted steady-state fluorescence spectra and transient decays were recorded using a picosecond lifetime spectrometer (LifeSpec-ps, Edinburgh Instruments) equipped with a multichannel plate detector (R3809U-50, Hamamatsu) and time-correlated single-photon counting electronics. The excitation source was a 397 nm pulsed diode laser with a pulse width of ~50 ps. The maximum repetition rate was 40 MHz, which could be divided by a factor of 2, 4, 8 or 16.

For frequency-upconverted experiments, the excitation pulse (1 kHz, 240–2,600 nm, pulse width <120 fs) was generated by an optical parametric amplifier (TOPAS-F-UV2, Spectra-Physics) pumped by a regeneratively amplified femtosecond Ti:sapphire laser system (800 nm, 1 kHz, pulse energy 4 mJ, pulse width <120 fs, Spitfire Pro-F1KXP, Spectra-Physics), which was seeded by a femtosecond Ti-sapphire oscillator (80 MHz, pulse width <70 fs, 710–920 nm, Maitai XF-1, Spectra-Physics). The steady-state spectra of the stimulated emission and THG of the excitation pulse were recorded with a customized UV to mid-IR steady-state and phosphorescence lifetime spectrometer (FSP920-C, Edinburgh Instruments) equipped with a photomultiplier tube detector (R928, Hamamatsu).

The decay curves of the upconverted emissions were measured on the same LifeSpec-ps spectrometer. To measure the decay of the upconverted fluorescence, the pump laser was directed at the sample without focusing to ensure that no stimulated emissions were generated. To measure the decay of the stimulated emission, the pump laser was tightly focused on the sample so that strong stimulated emission could be achieved.

The laser power was measured with a power meter (Detector 818P-001-12, meter 1918-C, Newport). The far-field intensity distributions of the stimulated emissions were recorded using a charge-coupled device detector (LBA-USB-SP620U, Spiricon). The images for 3PP and 5PP stimulated emission were taken by a regular digital camera, and the output beams were collimated by a lens.

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## Author contributions

Q.Z. conceived the experiments. Q.Z. and H.Z. were primarily responsible for the experiments. H.Z., E.M., X.C. and Q.Z. carried out stimulated emission experiments and the time-decay measurements. S.C. and C.T. carried out linear optical property measurements and characterizations of the multiphoton absorbing material. All authors discussed the results and the manuscript.

## Additional information

Supplementary information is available in the online version of the paper. Reprints and permission information is available online at http://www.nature.com/reprints. Correspondence and requests for materials should be addressed to Q.Z. and X.C.

## Competing financial interests

The authors declare no competing financial interests.

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