



Fluorophores Hot Paper



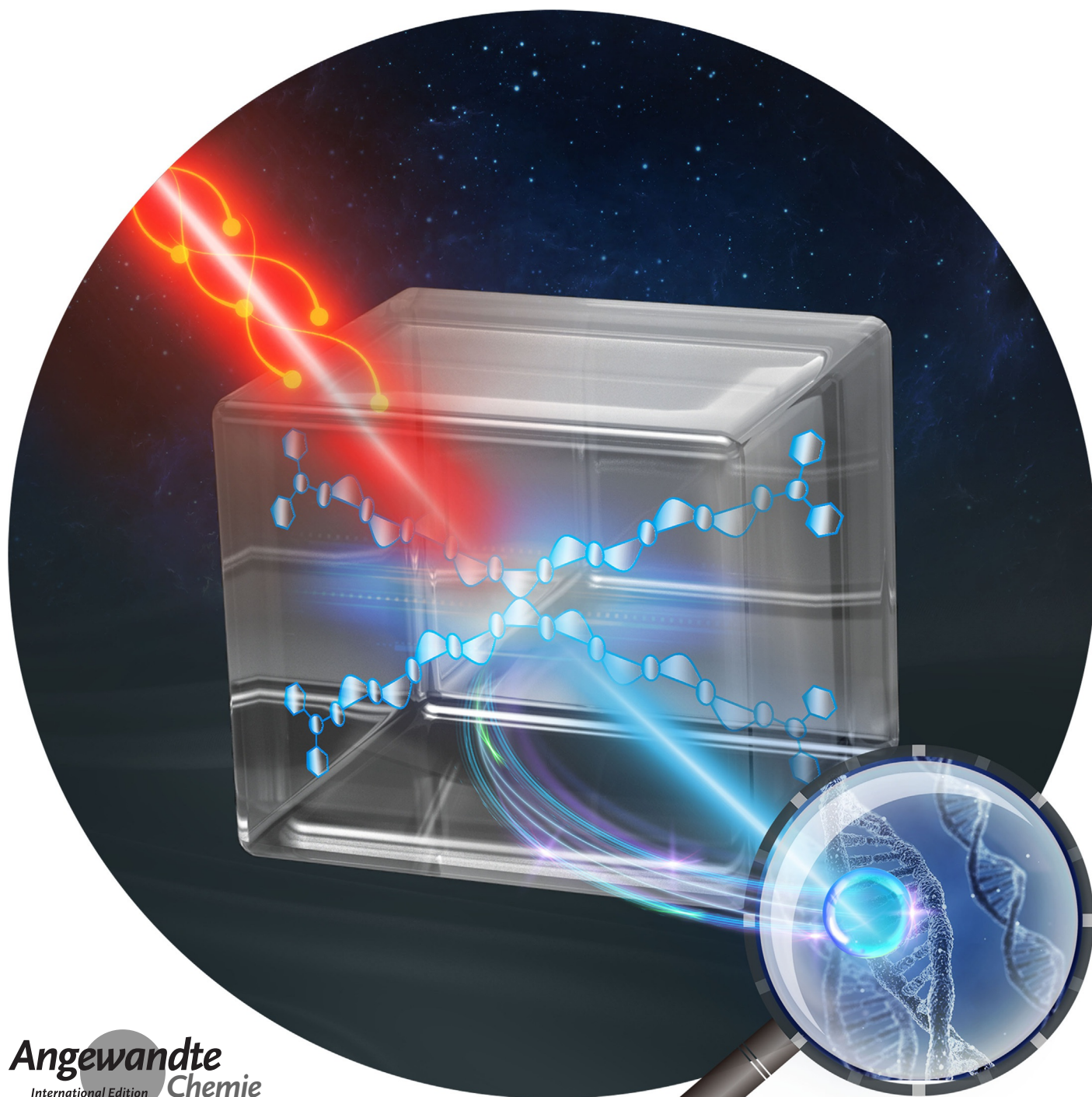
Frequency-Upconverted Stimulated Emission by Up to Six-Photon Excitation from Highly Extended Spiro-Fused Ladder-Type Oligo(*p*-phenylene)s

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How to cite: *Angew. Chem. Int. Ed.* **2021**, 60, 10007–10015

International Edition: doi.org/10.1002/anie.202100542

German Edition: doi.org/10.1002/ange.202100542



Angewandte
International Edition
Chemie

Angew. Chem. Int. Ed. **2021**, 60, 10007–10015

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Abstract: Frequency-upconverted fluorescence and stimulated emission induced by multiphoton absorption (MPA) have attracted much interest. As compared with low-order MPA processes, the construction of high-order MPA processes is highly desirable and rather attractive, yet remains a formidable challenge due to its inherent low transition probability. We report the observation of the first experimental frequency-upconverted fluorescence and stimulated emission by simultaneous six-photon excitation in an organic molecular system. The well-designed organic conjugated system based on cross-shaped spiro-fused ladder-type oligo(*p*-phenylene)s (SpL-*z*, *z* = 1–3) manifests reasonably high MPA cross-sections and brilliant luminescence emission simultaneously. The six-photon absorption cross-section of SpL-3 with an extended π -conjugation was evaluated as $8.67 \times 10^{-169} \text{ cm}^2 \text{ s}^5 \text{ photon}^{-5}$. Exceptionally efficient 2- to 6-photon excited stimulated emission was achieved under near-infrared laser excitation.

Introduction

Optical materials play important roles in promoting the advances of basic science and modern technology.^[1] With the mature of ultrashort laser technology, non-linear optical materials have got remarkable advances, in the fields of high-order frequency,^[2] stimulated Raman scattering and Raman lasers,^[3] multiphoton pumped (MPP) fluorescence,^[4] four-wave mixing,^[5] and attosecond ultrashort lasers,^[6] etc. The exploration of optical materials with high-order nonlinearity has been an exciting research topic.^[7] Thereinto, the frequency-upconverted fluorescence and stimulated emission induced by multiphoton absorption (MPA) have attracted much recent interest because of various fascinating merits, including high spatial resolution, no phase-matching requirement, large penetration depth, less Rayleigh scattering, as well as little photodamage and photobleaching.^[8] Moreover, MPA can be induced with excitation wavelengths in near-infrared (NIR) or red region. These distinct properties enable MPA for a large variety of improved and novel technologies, such as, three-dimensional optical data storage, infrared sensors, optical communication, microfabrication, and biomedical imaging.^[8b,9]

MPA, as the name implies, is a nonlinear process in which a molecule can absorb multiple photons simultaneously to achieve its excitation from ground states to excited states. Efficient MPA essentially requires a strong light-matter

coupling, consistent with a high oscillator strength in a molecule.^[4b,c,e] Fluorescence and stimulated emission induced by two-/three-photon absorption (2/3PA) have been demonstrated in diverse inorganic structures,^[8b,10] organic materials,^[4,11] and organic/inorganic hybrid perovskites^[12] with high 2/3PA cross-sections. Compared with 2/3PA, the construction of MPA process in higher order is of great significance to promote the advances of basic science and modern technology applications. The highly localized beam spot from high-order MPP fluorescence, amplification, or lasing enables the formation of fine structures and corresponding microscopic imaging beyond the diffraction limit of light.^[8a,9c] The enhanced dependence on incident light intensity of high-order MPA process also provides improved spatial selectivity and resolution in imaging.^[4d,13] Predictably, high-order MPA leads to novel technologies in high-resolution imaging and precise pattern fabrication with nanometer feature size, which are not accessible for 2PA and 3PA. However, owing to the inherent low transition feasibility of high-order MPA process, MPP fluorescence with simultaneously absorbed photon number more than 4 is notoriously challenging. Especially considering the huge frequency-upconverted photons and sufficient optical gain needed for population inversion,^[14] it is actually much more difficult to realize high-order MPP amplification (or lasing), which requires the unification of high MPA cross-section, brilliant luminescence emission, and excellent optical gain properties. Till now, only two experimental examples on five-photon pumped (5PP) fluorescence or stimulated emission have been reported based on organic dye system.^[4d,15] To the best of our knowledge, the observation of over six-photon pumped (6PP) fluorescence or stimulated emission from organic material system remains yet to be demonstrated. Nevertheless, organic materials manifest the merits of low toxicity, facile synthesis, ease of chemical and spectral tuning, which render them intrinsically attractive for MPP fluorescence and stimulated emission applications.

In this contribution, we report the first demonstration of fluorescence and amplification by simultaneous six-photon excitation in organic molecular system. A well designed organic conjugated system based on cross-shaped spiro-fused ladder-type oligo(*p*-phenylene)s, SpL-*z* (*z* = 1–3) (Scheme 1), has been explored. The effects of molecular-structure motif and conjugation length on MPA characteristics have been investigated in comparison with their linear

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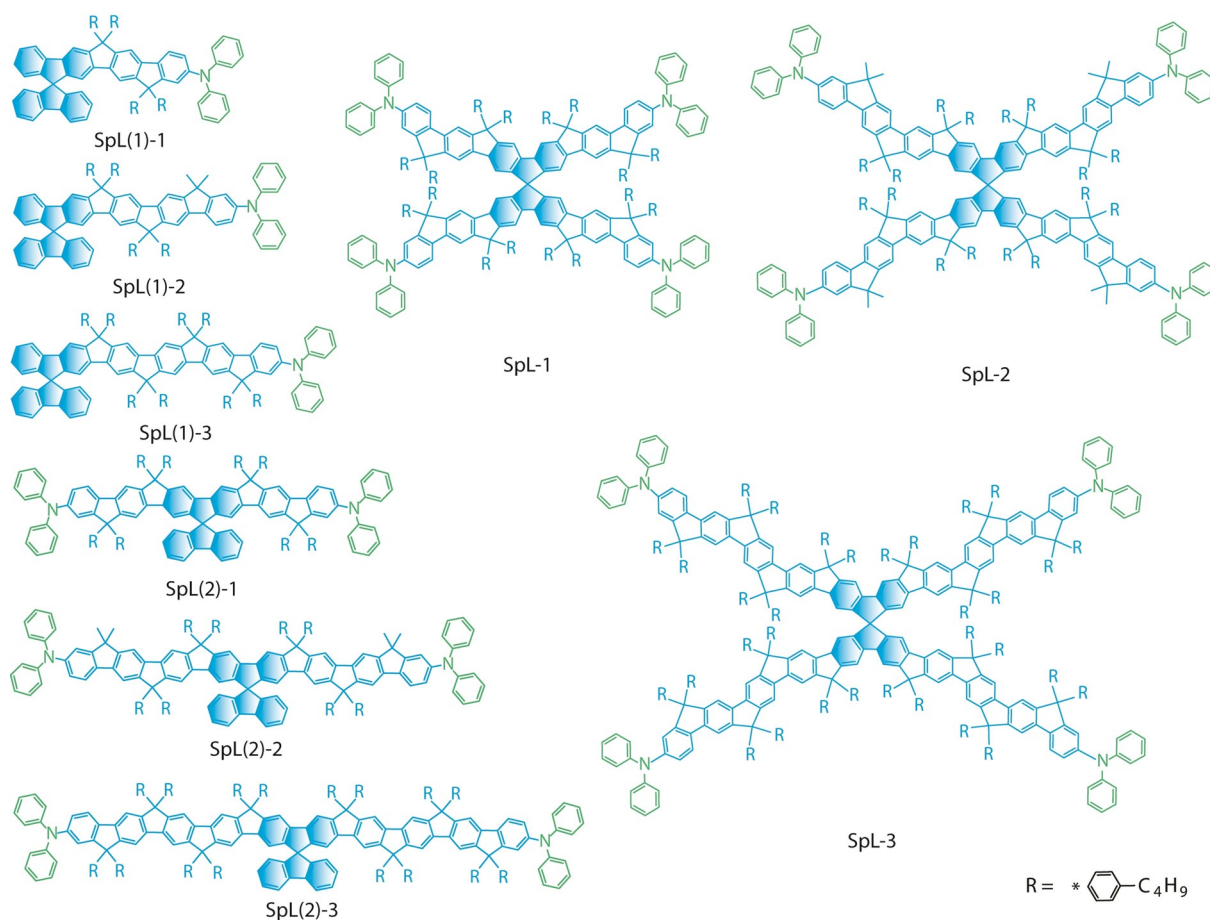
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Supporting information and the ORCID identification number(s) for
the author(s) of this article can be found under:
<https://doi.org/10.1002/anie.202100542>.



Scheme 1. Representation of the chemical structures of spiro-fused ladder-type oligo(*p*-phenylene)s (SpL(1)–*x*, SpL(2)–*y*, and SpL–*z*, *x*, *y*, *z* = 1–3).

counterparts, SpL(1)–*x* and SpL(2)–*y* (*x*, *y* = 1–3; Scheme 1). Ladder-type oligo(*p*-phenylene)s, comprising of rigid and fused fluorene skeleton, are selected as the main backbone structures because of their interesting potentials in the development of MPP fluorescence, stimulated emission and lasing.^[11a–d,15,16] The extended ladder-type molecular skeletons not only facilitate the π -electron delocalization but also aid to improve the MPA responses and emissive properties. Diphenylamine units are attached onto the ladder-type skeleton backbone as end-cappers to induce strong electron-donating properties and enhance optical stability.^[17] Spirobifluorene, with two π -conjugated fluorene systems cross-connected through a sp^3 -hybridized carbon atom, is selected as the core structure to fully fuse the ladder-type molecular configurations, due to its facile functionalization and steric configuration that would finely modulate the intermolecular interactions with depressing the molecular aggregation.^[18] The resulting ladder-type oligo(*p*-phenylene)s manifest slightly redshifted absorption and emission with increasing the number of phenylene rings, unlike those based on oligo(*p*-phenylenevinylene)s^[9a,19] and carbon-bridged oligo(*p*-phenylenevinylene)s.^[20] The photoluminescence (PL) excitation (PLE) spectra covering the whole excitation wavelength region (630–2200 nm) in the MPA process were recorded. Compared with 2PA-induced fluorescence, the emission

intensity with several orders (≤ 8) of magnitudes lower has been detected in their MPP fluorescence. The power dependence measurement suggested that the partition of different excitation wavelength regions for two- to six-photon absorption (2- to 6-PA) processes was achieved. The 6PA cross-section was evaluated as $8.67 \times 10^{-169} \text{ cm}^2 \text{ s}^5 \text{ photon}^{-5}$ in SpL-3 with a cross-shaped molecular configuration and an extended π -conjugation by non-linear transmission measurement. Significantly, exceptional efficient two- to six-photon pumped (2- to 6-PP) stimulated emission have been successfully demonstrated. An amplified spontaneous emission (ASE) threshold of 12.1 μJ (1.28 TW cm^{-2}) was achieved in 6PP amplification process with excitation wavelength of 1820 nm.

Results and Discussion

Synthesis and structure characterization. The schematic illustration of spiro-fused ladder-type oligo(*p*-phenylene)s chemical structures, SpL(1)–*x*, SpL(2)–*y* and SpL–*z* (*x*, *y*, *z* = 1–3), are depicted in Scheme 1. The synthetic routes to the ladder-type precursors are outlined in Scheme S1 (Supporting Information), using similar procedures as we previously reported.^[21] Due to the facile functionalization of spirobi-

fluorene unit, spiro-fused ladder-type oligo(*p*-phenylene)s were formulated by stepwise synthetic strategies. The synthetic strategies and detailed procedures for SpL(1)–*x*, SpL(2)–*y* and SpL–*z* (*x*, *y*, *z* = 1–3) are shown in Schemes S2–S4. By using the synthetic methods, including palladium catalyzed Suzuki-cross coupling, Friedel–Crafts acylation/alkylation reaction, and organic acid catalyzed intramolecular ring-closure alkylation, the spiro-fused ladder-type backbones have been constructed efficiently, attached with alkyl side chains and electron-donating end-cappers.

The chemical purities and well-defined structures of the spiro-fused ladder-type oligo(*p*-phenylene)s were adequately verified by ^1H NMR, ^{13}C NMR, matrix assisted laser desorption/ionization time of flight (MALDI-TOF) mass spectrometry. All MALDI-TOF mass spectra exhibit single intense signals, as illustrated in Figure S1 (Supporting Information), with an expanded view. At a higher magnification, most of the assigned peaks are isotopically resolved, which are corresponding well with their calculated theoretical distributions. Except for SpL-3, it shows only one single peak, probably due to its quite large molecular weight.^[22] The well-matched molecular ion masses of spiro-fused ladder-type oligo(*p*-phenylene)s provide direct evidence for the efficient construction of fully spiro-fused ladder-type scaffolds with no obvious chemical defects.

One-photon excited and MPP fluorescence emission. The linear optical properties of SpL(1)–*x*, SpL(2)–*y* and SpL–*z* (*x*, *y*, *z* = 1–3) measured in toluene are depicted in Figure S2. The absorption spectra of all samples present well-defined vibronic structures with two main absorption bands (the $\pi \rightarrow \pi^*$ transition and $n \rightarrow \pi^*$ transition from the ladder-type

skeleton and triarylamine moieties, respectively). There are systematic, albeit modest, bathochromic shifts in the absorption peaks with increasing the number of phenylene rings in SpL(1)–*x*, SpL(2)–*y*, and SpL–*z* (*x*, *y*, *z* = 1–3) series, which are consistent with the responses of their fluorescence spectra. Unlike SpL(1)–*x* (*x* = 1–3), the absorption and fluorescence spectra of SpL(2)–*y* and SpL–*z* (*y*, *z* = 1–3) series show perfect mirror symmetry, mainly due to their rigid and extended π -conjugated molecular skeletons. The large π -conjugated and rigid molecular systems lead to very large molar absorptivities up to $4.49 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$ for SpL-3, which can improve the MPA response by thus enhancing the transition oscillation strength from ground state to excited state.^[4c] Upon excitation, the resulting spiro-fused ladder-type oligo(*p*-phenylene)s show fluorescence from blue to sky-blue, with PL quantum yields (PLQYs) higher than 86 % (Supporting Information, Figure S3, Table S1).

The 2PA spectra of SpL(1)–*x*, SpL(2)–*y*, and SpL–*z* (*x*, *y*, *z* = 1–3) solution samples are shown in Figure 1a (Figure S4). The 2PA cross-sections, σ_2 , were determined by comparing the 2PA induced upconverted fluorescence with that of Rhodamine 6G as the reference standard in the wavelength range of 630–900 nm.^[23] As illustrated in Figure 1a, the 2PA spectra of SpL–*z* (*z* = 1–3) could be clearly divided into two parts, i.e., a major 2PA band between 600 nm and 800 nm, and a small 2PA band (the wavelength region of 800–900 nm), that is, close to twice the one-photon PLE maximum of these octupolar molecules. The excited state of the small 2PA band from 800 nm to 900 nm is consistent with the one-photon absorption band, indicating that it belongs to the first excited state of these molecules. For comparison, the excited state of

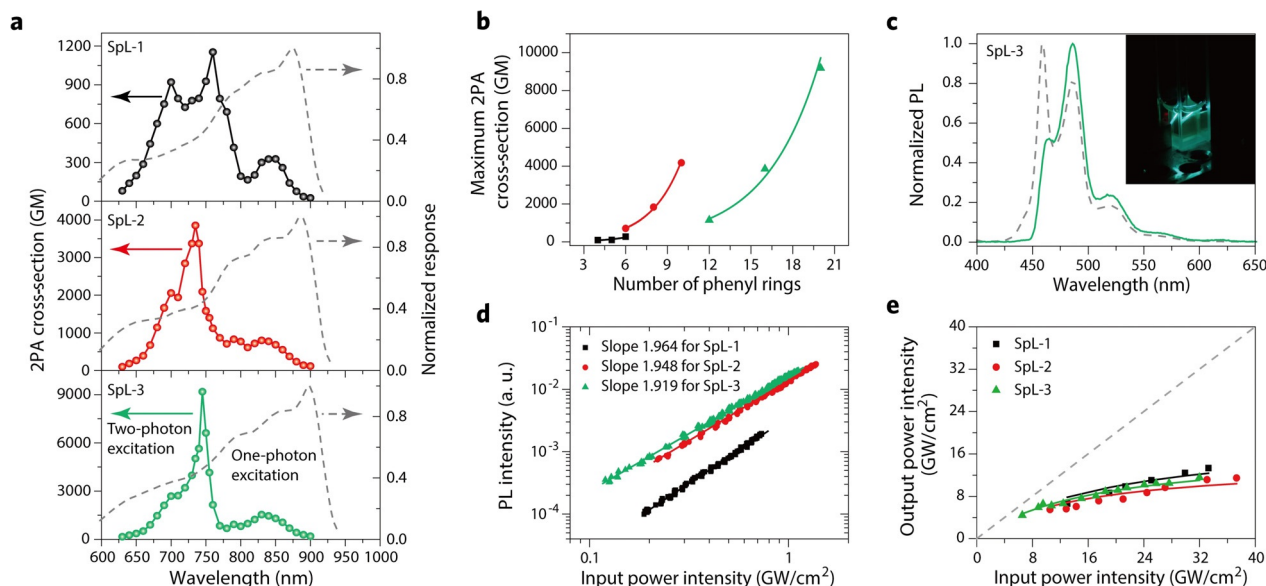


Figure 1. 2PA characteristics. a) 2PA cross-section spectra of SpL–*z* (*z* = 1–3) in the wavelength range of 630–900 nm. The one-photon PLE spectra are also shown with excitation wavelength multiplied by 2 for comparison. b) Plots of maximum 2PA cross-section as a function of the conjugation length in SpL(1)–*x* (black squares and line), SpL(2)–*y* (red circles and line), and SpL–*z* (green triangles and line), where *x*, *y*, and *z* = 1–3. c) 2PP PL spectrum of SpL-3 solution (green line) excited at 800 nm. The PL spectrum under one-photon excitation (gray dashed line) is also shown as a reference. Inset: 2PP fluorescence image of SpL-3 solution. d) The logarithmic power-dependent plots of relative 2PP fluorescence intensity of SpL–*z* (*z* = 1–3) solution samples as a function of input power intensity excited at 800 nm. e) The nonlinear transmitted intensity versus input power intensity of 800 nm laser pulses based on SpL–*z* (*z* = 1–3) solution samples. The lines represent the best fitting curves with the represented 2PA processes. The dashed line represents the characteristic of a linear medium with $\beta = 0$ (β is the 2PA coefficient).

the major 2PA band is higher than its one-photon excited state, which is related with the excited virtual state in the 2PA process, and is consistent with the 2PA selection rule for the octupolar (and quadrupolar) molecule.^[4b,c,24] Like their one-photon absorption spectra, the sharp peaks were observed in their 2PA spectra with extending the rigid π -conjugated molecular skeletons, especially for SpL-3. It means that the transition dipole moments (in the transitions from the ground state to the intermediate state and from the intermediate state to the excited state) are significantly enhanced at some specific energy levels of the cross-shaped spiro-fused ladder-type materials with highly extended and rigid π -conjugated molecular skeletons.^[4c,25] The similar phenomena were also observed in SpL(2)- y ($y=1-3$) quadrupolar molecules (Figure S4). For comparison, the distributions of 2PA at the first excited state of SpL(1)- x ($x=1-3$) dipolar molecules are relatively high. Again, with increasing the π -conjugated lengths of ladder-type skeletons, the 2PA distribution at the higher excited state has increased in SpL(1)- x ($x=1-3$). Note that due to the selection rules, the pathways of resonance enhancements and molecular transitions for one-photon and multiphoton processes are generally different.^[4b] The phenomenon of a higher excited state is more obvious in the high-order MPA process.

As illustrated in Figure 1b and Table S1, the maximum σ_2 of all samples, which were extracted throughout the 2PA spectra, are significantly enhanced as increasing the π -conjugated lengths of the ladder-type skeletons in spiro-fused molecules. A recorded large σ_2 of 9188 GM was obtained in SpL-3, which has a cross-shaped molecular configuration with an extended π -conjugation. The 2PP PL spectra exhibit the same peaks, and more likely low energy band emission (0–1 and 0–2 emission bands) in comparison with the one-photon-excited fluorescence (Figure 1c; Figure S5). Compared with their linear counterparts, SpL(1)- x and SpL(2)- y ($x, y=1-3$), the unification of an extremely high σ_2 (up to ca. 9.2×10^3 GM) and brilliant luminescence emission (PLQY: $\geq 86\%$) in SpL- z ($z=1-3$) make them ideal candidates as high-order MPP upconversion emitters.

The logarithmic power-dependent plots of the relative 2PP fluorescence intensity of SpL(1)- x , SpL(2)- y , and SpL- z ($x, y, z=1-3$) solution samples as a function of input power intensity excited at 800 nm afford straight line relationships with slopes in the range of 1.829–2.109, 2.045–2.150, and 1.919–1.964, respectively (Figure 1d; Figure S6), demonstrating a strong quadratic dependence of excited fluorescence on input power intensity, and thus corroborating the 2PA-induced frequency-upconverted fluorescence. Meanwhile, the nonlinear transmission of input power density exists in the 2PA process. Figure 1e and Figure S7 show that the transmitted intensities of 800 nm laser pulses follow the expected behaviors in solution samples of SpL(1)- x , SpL(2)- y , and SpL- z ($x, y, z=1-3$), further verifying the 2PA processes. The nonlinear 2PA coefficients (β) extracted from the fitting curves for SpL-1, SpL-2, and SpL-3 are calculated as 0.051, 0.070, and 0.059 cm/GW, respectively, when excited at 800 nm femtosecond pulses.

Due to their larger 2PA cross-sections as compared with SpL(1)- x ($x=1-3$), SpL(2)- y and SpL- z ($y, z=1-3$) series

were further investigated on their high-order MPP fluorescence properties. The strong high-order MPP fluorescence responses and characteristics were studied with excitation wavelengths varying from 900 nm to 2200 nm. For comparison, we finely modulate the laser beam area and pump energy intensity to avoid the possible presence of third-harmonic generation (THG) from laser beam, which impact the MPA-induced fluorescence intensity and data analysis, especially for the power dependence measurement.^[26] The PLE spectra covering the whole excitation wavelength region of SpL(2)- y and SpL- z ($y, z=1-3$) solutions are summarized in Figure 2a (Figure S8). The MPA-induced fluorescence emission intensity of SpL-3 solution is in fact several orders (≤ 8) of magnitudes lower than that of 2PP, and no MPP PL signal was detected when the excitation wavelength exceeds 2200 nm. Figure 2b depicts the slopes from power dependence measurement as a function of excitation wavelength of SpL-3 solution; the 2PA processes could be clearly observed with slopes changing from 1.844 to 1.905 with the wavelength range of 600–900 nm. The cubic dependence of fluorescence on input power intensity is observed in the wavelength region of 900 nm to 1100 nm. Here the wavelength of one-photon absorption band is shorter than a half of the excitation wavelength (larger than 950 nm). Therefore, the 3PA processes could be confirmed in this excitation wavelength region. When the excitation wavelengths exceed 1100 nm, it is difficult to ascertain whether the frequency-upconverted fluorescence is a pure high-order MPA process, since the individual excitation mechanism from 3- to 6-PA cannot be established from the power dependence measurement. Detailed information is available in Figure S9 (Figure 2c). We can approximately divide the excitation wavelength regions for 3- to 6-PA processes into 900–1400 nm, 1100–1520 nm, 1520–1760 nm, and 1720–2200 nm, respectively. In the overlapped wavelength regions, the large variation in power-dependent index indicates the manifold excitation contribution to the MPA process, consistent with our previous report.^[16c] The manifold excitation contribution to the MPA process is attributed to the overlap of energy levels in different MPA processes. Figure 2c shows the log-log plots of fluorescence emission intensity versus input power intensity of SpL-3 solution at the selected excitation wavelengths (990 nm, 1440 nm, 1540 nm, and 1820 nm, respectively), with slope gradients of 3.198, 4.384, 5.185, and 5.882, corresponding to the typical 3- to 6-PA processes.

The 3PA cross-sections, σ_3 , were measured in the range of 900–1400 nm with (L)-Ph(4)-NPh as a reference standard (Figure 2d; Figure S10).^[15] The 3PA processes of SpL(2)- y and SpL- z ($y=1-3, z=1, 2$) were also confirmed by the power dependence and nonlinear transmission measurements at 990 nm (Figures S11 and S12). Consistently, the maximum σ_3 increase with extending the conjugation length in these series (Figure 2e). A record-high intrinsic σ_3 of 2.39×10^{-74} cm⁶s² photon⁻² at 940 nm for SpL-3 was obtained.^[4d,27] From the fitted curves of non-linear transmission, the 3- to 6-PA processes of SpL-3 could be further confirmed at the selected wavelengths of 990 nm, 1440 nm, 1540 nm, and 1820 nm, respectively (Figure 2f). The 3-, 4-, 5-, and 6-PA coefficients (γ, δ, φ , and ω) of SpL-3 were evaluated as

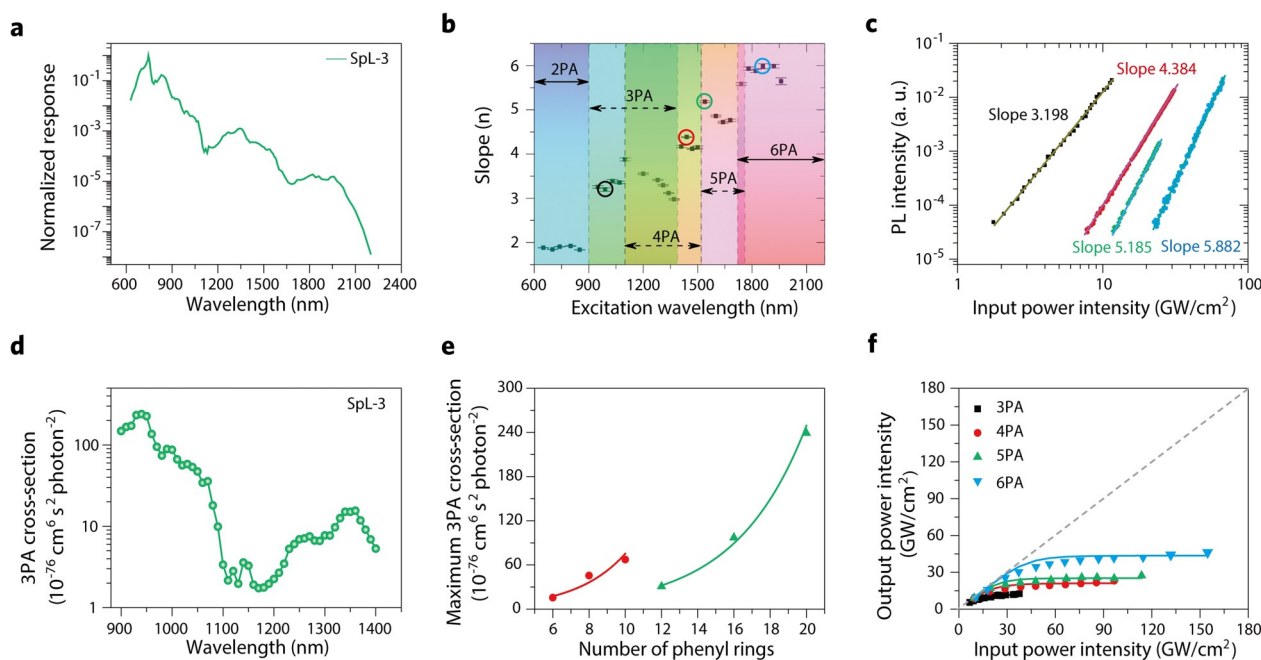


Figure 2. MPA characteristics. a) Normalized multiphoton PLE spectrum of SpL-3 solution in the wavelength region of 630 nm to 2200 nm. The PL intensities were detected at the maximum emission peak. b) Dependence of slope (n) on laser excitation wavelength of SpL-3 solution; n is defined as the power-dependent index of the logarithmic power dependence of MPP PL signal as a function of input power intensity. The fluorescence from 2- to 6-PA processes are broadly divided into five zones for ease of discussion. The circles highlight the selected excitation wavelengths for the typical 3- to 6-PA processes, respectively. c) The logarithmic power-dependent plots of relative 3- to 6-photon excited fluorescence intensity of SpL-3 solution, as a function of input power intensity excited at 990 nm (black square and dark-yellow line), 1440 nm (red circles and magenta line), 1540 nm (green diamonds and cyan line), and 1820 nm (blue hexagons and dark cyan line), respectively. d) 3PA cross-section spectrum of SpL-3 in the wavelength range of 900–1400 nm. e) Plots of maximum 3PA cross-section as a function of the conjugation length in SpL(2)– y (red circles and line), and SpL– z (green triangles and line), where y and $z = 1–3$. f) The nonlinear transmitted intensity versus input power intensity of 990 nm, 1440 nm, 1540 nm, and 1820 nm laser pulses based on SpL-3 solution. The lines represent the best fitting curves with the represented 3- to 6-PA processes. The dashed line represents the characteristic of a linear medium with γ, δ, φ , and $\omega = 0$ ($\gamma, \delta, \varphi, \omega$ are the 3–6 PA coefficients, respectively).

$3.08 \times 10^{-3} \text{ cm}^3/\text{GW}^2$, $3.51 \times 10^{-5} \text{ cm}^5/\text{GW}^3$, $6.08 \times 10^{-7} \text{ cm}^7/\text{GW}^4$, and $1.01 \times 10^{-10} \text{ cm}^9/\text{GW}^5$, at the selected excitation wavelengths. Furthermore, the 4-, 5-, and 6-PA cross-sections (σ_4 , σ_5 , and σ_6) for SpL-3 were determined to be $5.10 \times 10^{-107} \text{ cm}^8 \text{ s}^3 \text{ photon}^{-3}$, $9.32 \times 10^{-137} \text{ cm}^{10} \text{ s}^4 \text{ photon}^{-4}$, $8.67 \times 10^{-169} \text{ cm}^{12} \text{ s}^5 \text{ photon}^{-5}$ at the excitation wavelengths of 1440 nm, 1540 nm, and 1820 nm, respectively.

MPA-induced stimulated emission. We further investigate the MPA-induced stimulated emission properties of the spiro-fused ladder-type materials. Moderate concentrations of the gain media (0.01 mol L^{-1} for SpL(1)– x and SpL(2)– y , $x, y = 1–3$; $3 \times 10^{-3} \text{ mol L}^{-1}$ for SpL– z , $z = 1–3$) were used in the ASE measurement to provide enough photons for population inversion while depressing aggregation-caused quenching. Upon pumping at the optimized excitation wavelengths for all samples with the maximum 2PA cross-sections, strong 2PP ASE phenomena were observed for most samples. Detailed 2PP ASE properties of all ladder-type solution samples are depicted in Figure 3a,b, and Figures S13 and S14. As an example, the 2PP ASE image of SpL-3 solution is shown in Figure 3a. A very low 2PP ASE threshold of 80 nJ (17.0 GW cm^{-2}) was recorded in SpL-3 solution. At an input energy of 1.28 μJ (input power intensity: 23.7 GW cm^{-2}), the output energy is ca. 24 nJ (Figure 3b). Figure 3c summarizes

the ASE thresholds and slope efficiencies of the samples. No gain narrowing was observed in SpL(1)–1 solution sample, even at an high excitation energy condition ($> 10 \mu\text{J}$; full width at half maximum (FWHM): @ 18.6 nm; Figure S14). The ASE thresholds are gently decreased with increasing the length of the π -conjugated ladder-type skeletons. Remarkably, a very high ASE slope efficiency of 8.7% was achieved in SpL-2 solution.

3PP upconversion amplification of SpL(2)– y and SpL– z ($y, z = 1–3$) solution samples were excited at 990 nm. By modulating the molecular configurations and increasing the π -conjugated lengths, the 3PP ASE thresholds significantly decreased from 0.88 μJ to 0.37 μJ (Figure 3d). The lowest 3PP ASE threshold was observed in SpL-3 solution (Figure 3b). When the input energy achieved 1.3 μJ (input power intensity: 139.9 GW cm^{-2}), an output energy of 2.3 nJ was obtained for SpL-3 solution. The ASE slope efficiencies were determined to be between 0.11% and 0.45% for the resulting spiro-fused ladder-type solution samples. Detailed 3PP ASE properties of SpL(2)– y and SpL– z ($y = 1–3, z = 1–2$) solution samples are depicted in Figures S15 and S16. It should be noted that 2PP (or 3PP) ASE thresholds and slope efficiencies were evaluated by only considering the contributed pumped energy for stimulated emission, and the transmitted excitation

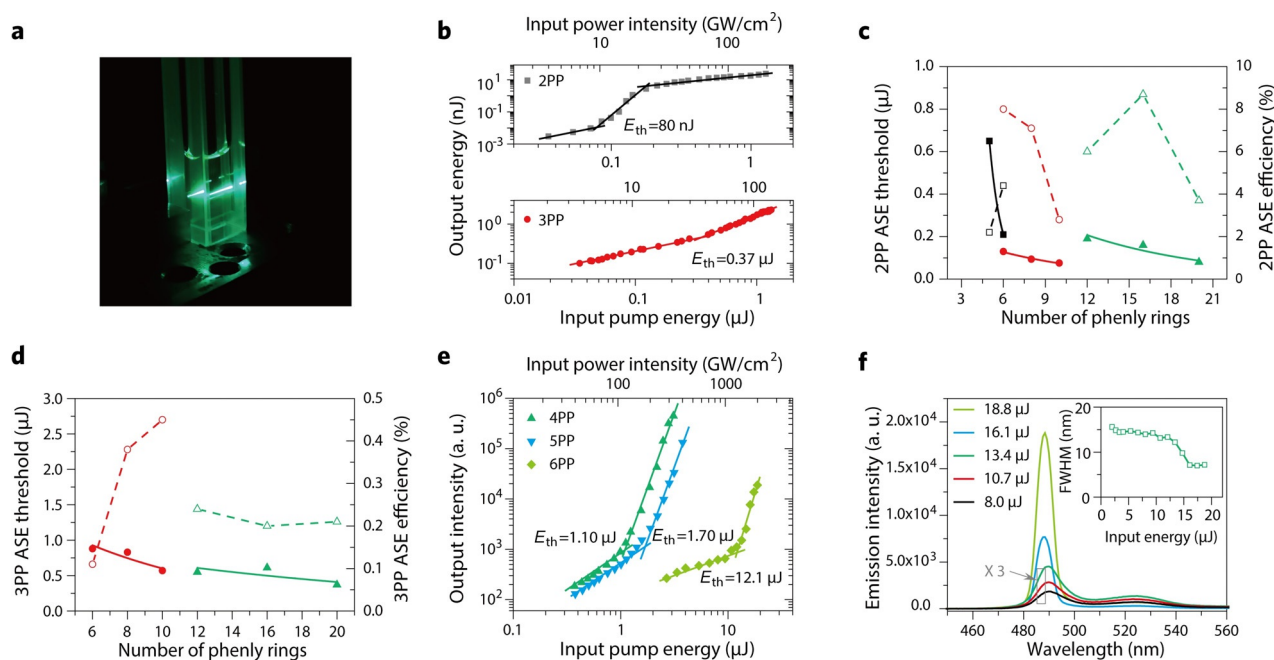


Figure 3. MPP stimulated emission properties. a) 2PP ASE image of SpL-3 solution. b) Output energy versus input energy (and input power intensity) for SpL-3 solution excited at 745 nm and 990 nm, representing the 2PP and 3PP ASE processes. c) Plots of 2PP ASE threshold (left ordinate; solid dot and solid line) and efficiency (right ordinate; hollow dot and dashed line) as a function of the conjugation length in SpL(1)– x (black squares and line), SpL(2)– y (red circles and line), and SpL– z (green triangles and line) solution samples, where $x = 2, 3, y, z = 1-3$. The excitation wavelengths were selected at the wavelengths of samples with the maximum 2PA cross-sections. d) Plots of 3PP ASE threshold (left ordinate; solid dot and solid line) and efficiency (right ordinate; hollow dot and dashed line) as a function of the conjugation length in SpL(2)– y (red circles and line), and SpL– z (green triangles and line) solution samples, where $y, z = 1-3$. The excitation wavelength was selected at 990 nm. e) Dependence of the output intensity on input energy (and input power intensity) for SpL-3 solution excited at 1440 nm, 1540 nm, and 1820 nm, respectively, corresponding with the 4- to 6-PP ASE processes. f) 6PP emission spectra of SpL-3 solution at different input energies. Inset: dependence of FWHM on input energy in SpL-3 solution.

energy was excluded. Furthermore, high-order (from 4 to 6) MPP amplification characteristics were evaluated by using SpL-3 as gain medium pumping at 1440 nm, 1540 nm, and 1820 nm, respectively. Figure 3e shows plots of the output intensity versus input energy (and input power intensity) for 4- to 6-PP stimulated emission of SpL-3 solution. The ASE thresholds induced by 4- to 6-PP processes of SpL-3 solution were recorded as 1.1 μJ (116.7 GW cm^{-2}), 1.7 μJ (180.4 GW cm^{-2}), 12.1 μJ (1.28 TW cm^{-2}), respectively. The upconverted 4PP and 5PP ASE spectra of SpL-3 solution are depicted in Figure S17. Figure 3f shows the emission spectra of SpL-3 solution at different input energies excited at 1820 nm. At low input energy, the 6PP PL shows analogous optical properties in comparison with 2PA-induced emission, i.e., the almost forbidden 0-0 emission band and a small FWHM of @ 15 nm. When the input energy above the 6PP ASE threshold, the emission intensity significantly increased and emission spectrum collapsed into a single narrow peak (at 489 nm). Meanwhile, the FWHM of the emission spectrum decreased sharply to only 7 nm, which is also very similar with the FWHM results in 2- to 5-PP stimulated emission procedures (@ 7 nm; Figures S14, S16, and S17). Overall, the results demonstrate that the resulting spiro-fused ladder-type materials, especially for the cross-shaped spiro-fused ladder-type molecules, are promising candidates for high-performance MPA-induced amplification/lasing.

Conclusion

In summary, efficient frequency-upconverted fluorescence and stimulated emission have been demonstrated in spiro-fused ladder-type oligo(*p*-phenylene)s through MPA with an absorbed photon number up to six. The cross-shaped ladder-type molecules (SpL– z , $z = 1-3$) exhibit superior MPA responses and MPA-induced stimulated emission characteristics due to their unification of high MPA cross-sections and high PLQYs. Promising intrinsic MPA cross-sections (3–6 photons) of $2.39 \times 10^{-74} \text{ cm}^6 \text{ s}^2 \text{ photon}^{-2}$, $5.10 \times 10^{-107} \text{ cm}^8 \text{ s}^3 \text{ photon}^{-3}$, $9.32 \times 10^{-137} \text{ cm}^{10} \text{ s}^4 \text{ photon}^{-4}$, and $8.67 \times 10^{-169} \text{ cm}^{12} \text{ s}^5 \text{ photon}^{-5}$, are recorded for SpL-3 with a cross-shaped molecular configuration and an extended π -conjugation, which are the largest values ever reported by far for organic molecules. Moreover, efficient 2- to 6-PPA-induced amplification has been demonstrated in the resulting spiro-fused ladder-type solution samples with low thresholds (only 12.1 μJ in 6PPA process) and high-energy output efficiencies (up to 8.4% in 2PA process) under near-infrared laser excitation. This work represents an important breakthrough in achieving 6-photon stimulated upconversion emission from organic conjugated systems. The results demonstrate an effective molecular design strategy in exploring highly efficient MPA fluorophores for multiphoton optical applications.

Acknowledgements

The authors acknowledge financial support from the National Natural Science Foundation of China (21835003, 91833304, 21422402, 21674050), the National Key Basic Research Program of China (2017YFB0404501, 2014CB648300), the Natural Science Foundation of Jiangsu Province (BE2019120), Program for Jiangsu Specially-Appointed Professor (RK030STP15001), the Six Talent Peaks Project of Jiangsu Province (TD-XCL-009), the 333 Project of Jiangsu Province (BRA2017402), the NUPT "1311 Project" and Scientific Foundation (NY218164, NY217169), the Leading Talent of Technological Innovation of National Ten-Thousands Talents Program of China, the Excellent Scientific and Technological Innovative Teams of Jiangsu Higher Education Institutions (TJ217038), the Synergetic Innovation Center for Organic Electronics and Information Displays, and the Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD, YX030003).

Conflict of interest

The authors declare no conflict of interest.

Keywords: frequency-upconverted stimulated emission · MPA cross-section · multiphoton absorption (MPA) · oligo(*p*-phenylene)s · spiro-fused molecules

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Manuscript received: January 13, 2021

Accepted manuscript online: January 21, 2021

Version of record online: April 1, 2021