Multiphoton Absorption

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Highly Efficient Multiphoton-Pumped Frequency-Upconversion Stimulated Blue Emission with Ultralow Threshold from Highly Extended Ladder-Type Oligo(*p*-phenylene)s

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Dedicated to Professor Wing-Hong Chan

Abstract: *A series of highly extended π-conjugated ladder-type oligo(p-phenylene)s containing up to 10 phenyl rings with (L)-Ph(n)-NPh (n = 7–10) or without diphenylamino endcaps (L)-Ph(n) (n = 7 and 8) were synthesized and investigated for their multiphoton absorption properties for frequency upconverted blue ASE/lasing. Extremely large two-photon absorption (2PA) cross-sections and highly efficient 2PA ASE/lasing with ultralow threshold were achieved. (L)-Ph(10)-NPh exhibits the highest intrinsic 2PA cross-section of 3643 GM for a blue emissive organic fluorophore reported so far. The record-high 2PA pumped ASE/lasing efficiency of 2.06 % was obtained by un-endcapped oligomer, (L)-Ph(8) rather than that with larger* σ_2*, suggesting that a molecule with larger* σ_2 *is not guaranteed to exhibit higher* η_2*. All of these oligomers exhibit exceptionally ultralow 2PA pumped ASE/lasing thresholds, among which the lowest 2PA pumped threshold of circa 0.26 μJ was achieved by (L)-Ph(10)-NPh.*

Recent intense activity in exploiting efficient multiphoton absorbing organic materials have led to diverse emerging technological multiphoton absorption (MPA) applications,[1] such as MPA induced fluorescence bioimaging[2] and multiphoton-pumped (MPP) amplified spontaneous emission (ASE)/lasing[3] in search for the new fabrication of coherent light sources,[4] which is particularly attractive because none of stringent phase-matching requirement is necessary in the MPP lasing generation in sharp contrast to other conventional nonlinear techniques, such as second harmonic generation[5] and sum frequency mixing.[6] Thus, it offers great flexibility of resonator design in gain medium. Meanwhile, the MPP generation of high-energy light sources, especially in the blue region, could provide novel breakthrough in wide-range of laser-based applications.[7] However, only few contributions in designing superior MPP inorganic materials with strong ASE/lasing in the blue region have been reported to date.[8] On the other hand, it is fundamentally challenging to obtain highly efficient multiphoton-pumped ASE/lasing from organic compounds.[3a,b,9] One of the major hurdles is due to the limited or inefficient π-electron delocalization within a chromophore leading to relatively weak MPA responses particularly for those blue-emissive fluorophores.[3d] As a result, it is still of great interest to design and develop highly extended and active MPA blue-emissive fluorophores without causing significant bathochromic shift in excitation and emission wavelengths. Furthermore, other nonlinear optical (NLO) properties, including MPA pumped ASE threshold and lasing efficiency, would play a crucial role in determining its potential as an efficient and useful frequency-upconverted light-emitter. Desirable physical properties of a chromophore, such as good solubility, ease of processability, and high photochemical and thermal stability, are also important for the realization of practical MPA applications

Ladder-type oligo(*p*-phenylene)s, composed of rigid planar and linearly fused fluorene units, have captured tremendous attention on the development of NLO and organic optoelectronic materials as they can serve as a superior π-conjugated core between different functional moieties. The rigid and coplanar framework not only greatly facilitates the π-electron delocalization and thus enhancing MPA properties but also improve luminescence efficiency, carrier mobility, and thermal stability.[10] The incorporation of diphenylamino end-caps and the grafting of non-coplanar alkylphenyl substituents laterally onto this π-conjugated backbone were found to be a very useful strategy to enhance the MPA properties of ladder-type oligo(*p*-phenylene)s, affording an excellent nonlinearity–transparency trade-off.[3b,11] Nevertheless, the potential of the highly extended ladder-type oligo(*p*-phenylene)s for MPA properties has not been fully explored, particularly regarding the aspects of MPA-pumped ASE and lasing responses. There are also limited studies on exploring ultralow-threshold ASE organic materials under efficient 2PA pumping with highly stable blue emission, which can be useful in various applications.

Herein, we report the synthesis of highly extended π-conjugated ladder-type oligo(*p*-phenylene)s with or without diphenylamino end-caps, namely (*L*)-Ph(*n*)-NPh ($n = 8, 9, 10$) and (*L*)-Ph(*n*) ($n = 7$ or 8), respectively (Figure 1 a) and

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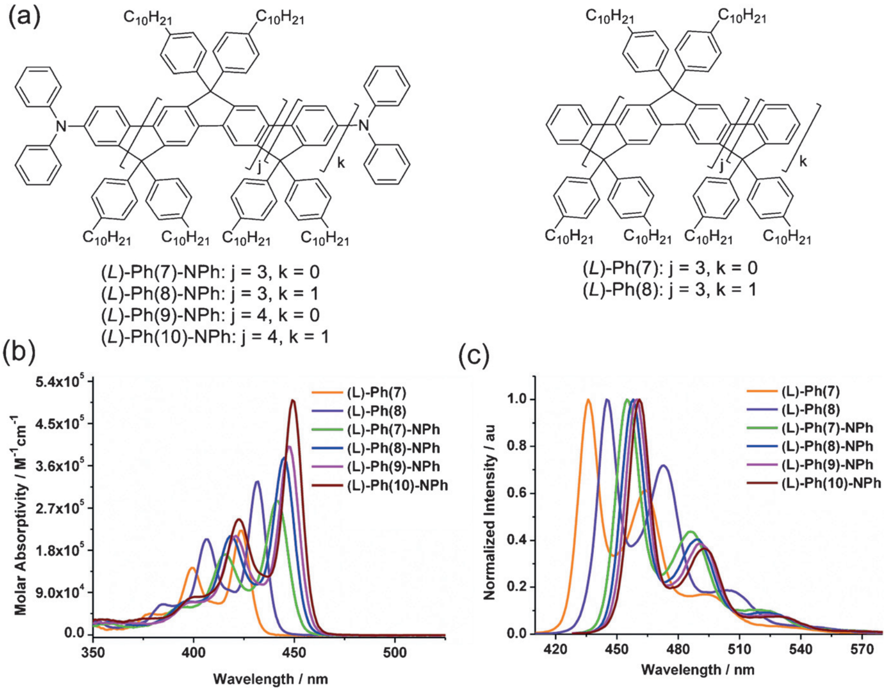

Figure 1. a) Molecular structure of linear ladder-type oligo(*p*-phenylene)s, (*L*)-Ph(*n*)-NPh ($n=7$–10) and (*L*)-Ph(*n*) ($n=7$ or 8). b) UV/Vis absorption and c) photoluminescence spectra of (*L*)-Ph(*n*)-NPh ($n=7$–10) and (*L*)-Ph(*n*) ($n=7$ or 8) in toluene.

investigation of their multiphoton absorption properties, particularly the frequency upconversion ASE/lasing properties. Remarkably, these highly extended ladder-type oligomers exhibit ultralow-threshold 2PA pumped stimulated blue emission in solution with exceptionally large 2PA cross-sections and 2PA pumped ASE efficiency. The 2PA cross-section of (*L*)-Ph(10)-NPh excited at 740 nm has reached 3643 GM ($1\,\mathrm{GM}=10^{-50}\,\mathrm{cm^4\,s\,photon^{-1}\,molecule^{-1}}$) which is six times higher than that excited at 870 nm. Furthermore, the 2PA pumped ASE threshold of (*L*)-Ph(10)-NPh is extremely low down to 0.26 μJ, which is much lower than materials reported so far. Interestingly, the uncapped ladder-type oligo(*p*-phenylene), (*L*)-Ph(8) shows exceptionally efficient 2PA pumped frequency upconversion ASE peaked at 474 nm with a record-high efficiency reaching 2.06%, which is much superior to that of the end-capped analogue, (*L*)-Ph(8)-NPh. Such extraordinary ASE response has never been observed for the low end-capped homologues that is, (*L*)-Ph(*n*), where $n=3$ to 5, highlighting the importance of the extended effective π-conjugated length for MPP ASE efficiency.

The previous synthetic strategy using convergent approach was adopted for the synthesis of the highly extended ladder-type oligo(*p*-phenylene)s, (*L*)-Ph(*n*)-NPh ($n=8$, 9, 10) and (*L*)-Ph(*n*) ($n=7$ or 8), via the key steps of palladium-catalyzed Suzuki-cross coupling and acid-catalyzed intramolecular ring-closure alkylation (Supporting Information, Scheme S2). Syntheses of key intermediates 1, 8, 9, and 11 are outlined in Scheme S1, while the previously known intermediates 3, 5, and 6 were prepared according to previous reports.[3b,11b,12] The full synthesis and details for all the newly developed ladder-type oligo(*p*-phenylene)s can be found in the Supporting Information; they were fully characterized by ^{1}H NMR, ^{13}C NMR spectroscopy, MALDI-TOF MS, and elemental analyses and found to be in good agreement with their proposed structures. Because of the linearly fused π-conjugated backbone, all of these ladder-type oligo(*p*-phenylene)s are highly thermally stable with decomposition temperatures well above 400 °C (Supporting Information, Figure S4).

All of these highly extended ladder-type oligo(*p*-phenylene)s have good solubility in most common organic solvents, including toluene, chloroform, and THF, but hardly dissolve in highly polar DMF owing to the hydrophobicity of laterally grafted alkyphenyl groups. The results of the linear and NLO properties of (*L*)-Ph(*n*)-NPh and (*L*)-Ph(*n*) measured in toluene are summarized in Table 1. As seen in the one-photon

Table 1: Summary of linear and nonlinear optical properties of (*L*)-Ph(*n*) ($n=7$ or 8) and (*L*)-Ph(*n*)-NPh ($n=7$–10) measured in toluene.

	λ_{abs} [nm] (ε)[a]	λ_{em} [nm][a]	Φ[b]	σ_2 [GM] (λ_{ex} [nm])[e]	$\sigma_{2,N}{}^2$ [GM][f]	η_2 [%] (λ_{ex} [nm])[g]	λ^{2PP}_{em} [nm] (mW)[h]	Threshold [μJ][i]	FWHM [nm][j]
(*L*)-Ph(7)	378, 399, 423 (2.21)	436, 464, 493	0.84[c]	567 (675), 487 (700)	0.32	0.74 (710)	464 (5.0)	1.12	3.8
(*L*)-Ph(8)	384, 407, 432 (2.25)	445, 473, 504	0.80[d]	1200 (685), 1120 (715)	0.52	2.06 (720)	474 (3.0)	0.70	3.5
(*L*)-Ph(7)-NPh	393, 416, 442 (2.85)	455, 486, 515	0.90[d]	1351 (720)	0.76	0.86 (720)	485 (3.0)	0.54	4.3
(*L*)-Ph(8)-NPh	397, 419, 445 (3.76)	458, 489, 523	0.94[d]	2243 (730)	0.97	1.36 (740)	489 (2.0)	0.41	4.2
(*L*)-Ph(9)-NPh	400, 421, 447 (4.00)	460, 490, 524	0.87[d]	3053 (735)	1.05	1.66 (740)	492 (1.5)	0.36	3.9
(*L*)-Ph(10)-NPh	402, 423, 449 (5.00)	461, 492, 528	0.88[d]	3643 (740)	1.01	1.51 (750)	493 (1.5)	0.26	3.7

[a] Absorption and emission peaks under an average of two independent measurements in toluene with a concentration of 10^{-6} M; The unit of the molar absorptivity is $1\times10^5\,\mathrm{M^{-1}\,cm^{-1}}$. [b] Fluorescent quantum yield. [c] Using Norharman ($\Phi_{330-390}=0.58$) as a standard. [d] Using Coumarin 6 ($\Phi_{420}=0.78$) as a standard. [e] Maximum 2PA cross-section ($1\,\mathrm{GM}=10^{-50}\,\mathrm{cm^4\,s\,photon^{-1}\,molecule^{-1}}$) at an excitation wavelength of λ_{ex} with a relative error of less than ±15%. [f] $\sigma_{2,N}{}^2=$ Maximum 2PA cross-section scaled by the square of the effective number of electrons.[14b,c] [g] Two-photon excited ASE efficiency [%] pumped by optimized excitation wavelength. [h] The 2PP upconverted ASE peaks of (*L*)-Ph(*n*) ($n=7$ or 8) and (*L*)-Ph(*n*)-NPh ($n=7$–10) pumped by optimized input power, respectively. [i] Threshold energy of the two-photon pumped ASE. [j] FWHM is the optimized full-width at half-maximum of the 2PP upconverted ASE spectrum pumped by optimized input power.

absorption (1PA) and photoluminescence spectra shown in Figure 1 b,c, these two homologous series of extended oligomers exhibit very similar absorption characteristics, distinctly composed of three overlapped absorption bands with the longest absorption peak ranging from 423 to 449 nm corresponding to the $\pi\rightarrow\pi^*$ transition of such a highly coplanar π-conjugated skeleton. In contrast to oligofluorenes, the absorption and emission wavelength/maxima of these ladder-type oligo(*p*-phenylene)s can easily be tuned by the conjugation length.[11a] Furthermore, these linear oligomers exhibit a progressive enhancement of molar absorptivity concomitant with a red-shift upon an increase in the conjugation length. The molar absorption coefficient of (*L*)-Ph(10)-NPh is as high as $5.0\times10^{5}\,\text{M}^{-1}\,\text{cm}^{-1}$, which is more than twice than that of the corresponding diphenylamino-endcapped oligofluorene, (*Ph*)-OF(5)-NPh having the same aryl units,[11a] manifesting a superior π-electron delocalization of this ladder-type π-conjugated system. Besides, the incorporation of the electron-rich diphenylamino endcaps not only gives rise to a significant bathochromic shift but also an enhancement of absorptivity. Upon excitation at its absorption maximum, these oligo(*p*-phenylene)s show a mirror-image emission spectra peaking at 436–530 nm with high fluorescence quantum yields (Φ) greater than 80 %.

To understand the structure–MPA property relationships, the MPA excited emission, wavelength-dependent 2PA cross-sections, and MPP frequency upconversion ASE/lasing properties of these newly synthesized ladder-type oligo(*p*-phenylene)s were investigated. Upon excitation at 700 and 800 nm using femtosecond laser pulses, the two-photon excited photoluminescence (PL) spectral features are very similar to those obtained by one-photon excitation indicating almost identical two-photon and one-photon excited emission states (Supporting Information, Figure S1a,b). The logarithmic plots of power dependence of the relative two-photon-induced fluorescence intensity of (*L*)-Ph(*n*)-NPh ($n=7$–10) and (*L*)-Ph(*n*) ($n=7$ or 8) on pulse intensity excited at 700 and 800 nm afforded a straight line relationship with a slope in the range of 2.17–2.20 (Figure 2 a) and 2.06–2.29 (Supporting Information, Figure S1c), respectively, demonstrating a strong quadratic dependence of excited fluorescence against the incident intensity and thus corroborating the frequency upconversion fluorescence originated from the two-photon absorption. Figure 2 b shows the two-photon excited spectra of these ladder-type oligo(*p*-phenylene)s measured in toluene $(1\times10^{-5}\,\text{M})$ by the two-photon-induced fluorescence method in the range of 620–1000 nm. The maximum 2PA cross-section, σ_2, of these oligomers was found at a wavelength less than twice their 1PA maximum, ranging from 675 to 740 nm indicating that the allowed two-photon excited states are higher than their corresponding one-photon excited one consistent to the 2PA selection rules for the quadrupolar molecules.[13] All of the measured 2PA cross-section values for (*L*)-Ph(*n*)-NPhs and (*L*)-Ph(*n*)s have been referenced and corrected to those of Rhodamine 6G reported by Rebane and co-workers (Supporting Information, Figure S1b).[14a]

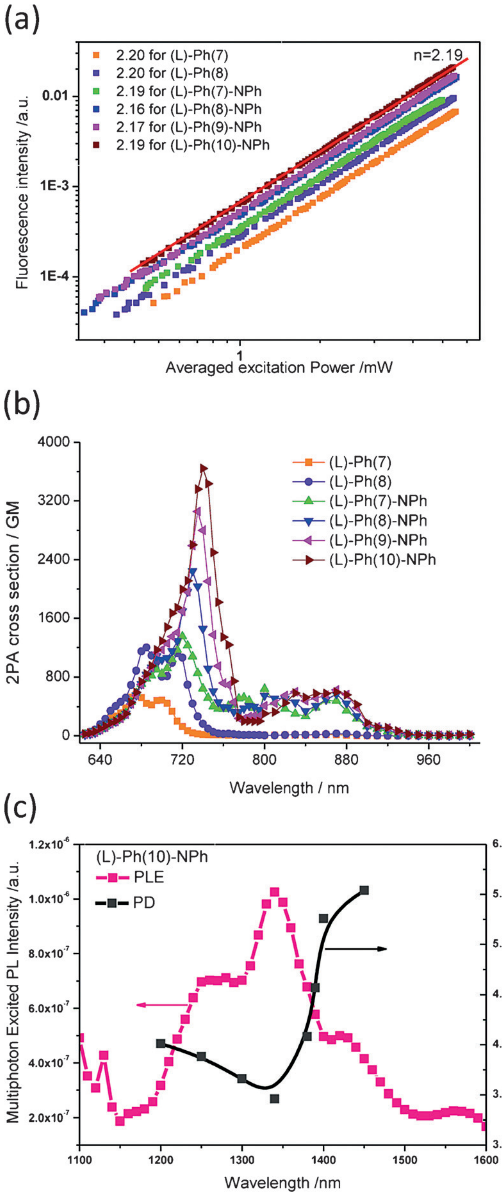

Figure 2. a) Logarithmic plots of the power dependence of relative two-photon excited fluorescence intensity of (*L*)-Ph(*n*) ($n=7$ and 8) and (*L*)-Ph(*n*)-NPh ($n=7$–10) in toluene, as a function of pump power at an excitation wavelength of 700 nm with a gradient of 2.17–2.20. An example of the solid line is the best-fit straight line for (*L*)-Ph(10)-NPh with gradient, $n=2.19$. b) 2PA excited spectra of the linear ladder-type oligo(*p*-phenylene)s measured in toluene (10^{-5} M) by femtosecond laser pulses. c) Plots of MPA excited fluorescence intensity and the relative power dependence index of (*L*)-Ph(10)-NPh measured in the excitation wavelengths ranging from 1200 to 1500 nm by femtosecond laser pulses.

A summary of maximum σ_2 for all the ladder-type oligo(*p*-phenylene)s is tabulated in Table 1, which clearly shows that there is a progressive enhancement of maximum 2PA cross-section upon an increase in the π-conjugation length resulting in more π electrons contributing effectively to 2PA merit, $\sigma_{2,\text{N}}^{2}$, maximum σ_2 scaled by the square of the effective number of electrons.[14b,c] Furthermore, the strong electron-donating diphenylamino endcaps greatly increase σ_2 of these ladder-type oligo(*p*-phenylene)s as compared to the corresponding un-endcapped counterparts attributed to the enhanced π-electron delocalization in the entire π-conjugated system. Remarkably, the highly extended (*L*)-Ph(10)-NPh exhibits exceptionally large 2PA cross-sections with a maximum σ_2 of 3643 GM at 740 nm, further affirming the significance of lateral substitution of alkylphenyl moieties[11a] and highly extended effective conjugation length[15] for a large enhancement of MPA responses, offering an effective strategy to achieve an excellent nonlinearity-transparency trade-off. Not only such a record high intrinsic σ_2 but also the scaled 2PA merit are much greater than those of (*Ph*)-OF(5)-NPh (2559 GM and 0.62 GM),[11a] 4FL (2357 GM and 0.61 GM)[10a] and the tailored truxene oligomer T6 (2183 GM and 0.038 GM)[16] and comparable to that of high molecular weight linear conjugated polymer film (ca. 4000 GM estimated from the nonlinear absorption coefficient),[15] highlighting the promise of this class of oligomers to function as a gain material for 2PP ASE/lasing applications.

For the first time, the strong higher-order MPA responses and characteristics, including 3PA, 4PA, and 5PA, were observed in such a low concentration solution of 1×10^{-5} M. The higher-order MPA properties were also studied by the MPA-induced fluorescence method using femtosecond laser pulses as an excitation source in the wavelength range of 1100 to 2000 nm. Consistently, there is substantial enhancement of multiphoton induced fluorescence intensities measured in the range of 1100–1600 nm with the extension of the π-conjugation length in both series (Supporting Information, Figure S2a). However, such frequency upconversion emission could not be verified as the pure and merely 3PA process at these measured excitation wavelengths since the cubic power dependence of multiphoton excited fluorescence measured was not well established (that is, slope = 3.46–3.63) for all the cases shown in the Supporting Information, Figure S2b and Table S1, indicating complex contributions of manifold excitations at these wavelengths. Furthermore, Figure 2c shows the results of relative MPA excited fluorescence intensity of (*L*)-Ph(10)-NPh measured between 1200 and 1600 nm as well as the plot of the power-dependent index of (*L*)-Ph(10)-NPh at different excitation wavelengths (see also the Supporting Information, Figure S3a). The inconsistent variation of power-dependent index within these excitation wavelengths further corroborate the manifold excitation contributions to the MPA processes. Interestingly, strong multiphoton excited fluorescence were also observed when excited by fs laser pulses in the range of 1650–2000 nm for the (*L*)-Ph(*n*)-NPh series (Supporting Information, Figure S3d). Upon excitation at 1780 nm, the fifth power dependence of multiphoton excited fluorescence measured was followed as illustrated in the Supporting Information, Figure S3b,c, suggesting that the origin of this excitation is due to the 5PA process.

Upon pumping at the optimized excitation wavelength of these ladder-type oligo(*p*-phenylene)s in toluene at a concentration of 0.01 M (Figure 3), an exceptionally strong two-photon pumped (2PP) amplified spontaneous emission (ASE)/lasing phenomenon was observed for all the oligomers when the pump energy was above the ASE threshold. The plots of input pumped energy versus integrated emission intensity are shown in Figure 4a, which unambiguously demonstrated the evidence of lasing threshold behavior. Such a threshold of two-photon pumped ASE/lasing decreased with an increase in the π-conjugation length of these oligomers which were reproducibly determined to be as low as about 0.70 μJ for (*L*)-Ph(8) and about 0.26 μJ for (*L*)-Ph(10)-NPh, respectively. To the best of our knowledge, the frequency upconversion ASE/lasing thresholds of the ladder-type oligo(*p*-phenylene)s achieved in this work are the lowest among the thresholds reported so far including IPPS (ca. 12 μJ)[9a] and 2-acetyl-6-(dimethylamino)naphthalene (ca. 2.0 μJ) in DMSO,[3c] PhN-OF(5)-NPh (ca. 1.5 μJ) in toluene,[17] tailored truxene oligomer (T6) (ca. 267 μJ) in solid state,[16] and even better than that of colloidal nanoplatelets (ca. 1.2 μJ) in solution.[4b] The optimized full-width half-maximum (FWHM) of the ASE spectra narrowed sharply to about 4.0 nm with the stimulated emission peak lying on the second emission band of the corresponding one-photon emission spectrum, as shown in Table 1. This finding suggested that such stable stimulated emission arises from the radiative relaxation from the first excited state (S_1) to a higher vibronic level of the ground state (S_0).

To evaluate the efficiency of the frequency upconversion ASE/lasing of these ladder-type oligo(*p*-phenylene)s, the ratio of the output power of forward ASE emission directly obtained from the output power detector to the input pumped power was determined as shown in Figure 4b, illustrating that a relatively high slope efficiency is observed after ASE/lasing thresholds. The output power intensity starts to get saturated at a higher input power due to the existence of other nonlinear effects such as continuum generation.[3c] It is worth mentioning that the forward 2PP ASE/lasing efficiency, η_2 increases progressively with an extension of π-conjugation length, increasing up to 1.66 % for (*L*)-Ph(9)-NPh and then becoming level-off for (*L*)-Ph(10)-NPh. Despite comparatively moderate σ_2 for un-endcapped (*L*)-Ph(n) series, the 2PP ASE/lasing efficiency of (*L*)-Ph(8) has reached up to 2.06 %, which is comparable to the highest values reported so

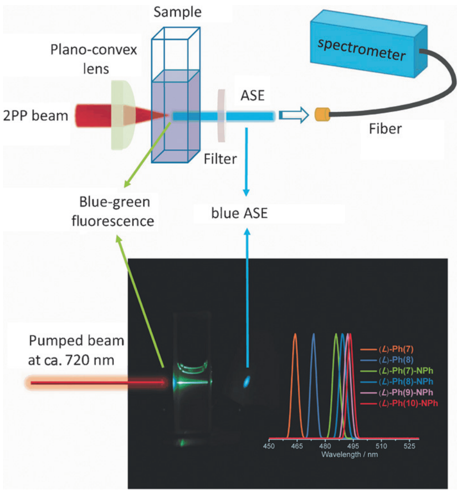

Figure 3. The 2PP ASE/lasing experimental setup for the measurement of the solution samples (top). Photo of highly directional, frequency-upconverted stimulated blue emission from a solution of (*L*)-Ph(8)-NPh pumped at 720 nm fs laser beam (bottom). Inset: 2PP upconverted ASE spectra of (*L*)-Ph(*n*) (*n* = 7, 8) and (*L*)-Ph(*n*)-NPh (*n* = 7–10).

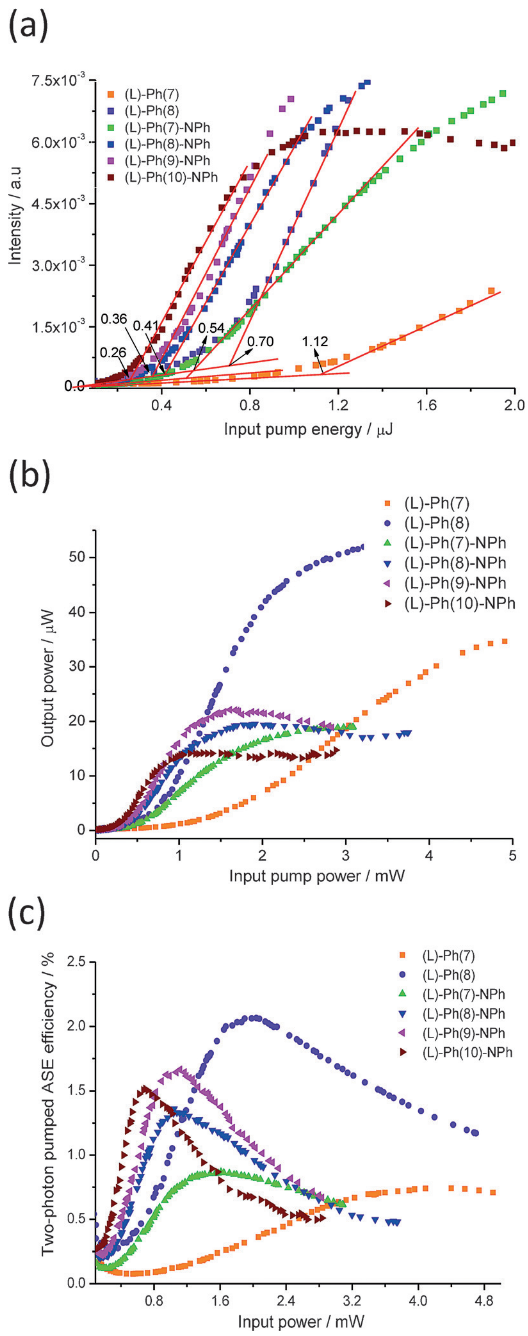

Figure 4. a) Plots of input pumped energy vs. integrated emission intensity for (*L*)-Ph(*n*) ($n=7$ or 8) and (*L*)-Ph(*n*)-NPh, ($n=7$–10). b) Plots of input power versus output power of 2PP ASE/lasing process for (*L*)-Ph(*n*) ($n=7$ or 8) and (*L*)-Ph(*n*)-NPh ($n=7$–10) excited at 710, 720, 720, 740, 740, and 750 nm, respectively. c) Plots of the 2PP ASE/lasing efficiency versus the input pumped intensity at the optimized excitation wavelength.

far for blue light source despite only considering the direct forward efficiency (see the Supporting Information, Table S2 for comparison). Furthermore, the lower homologues of this series, such as (*L*)-Ph(5), would never exhibit 2PP ASE/lasing response, further highlighting the fundamental significance of long effective π-conjugation length for amplified stimulated emission.

In summary, series of novel, blue-emissive ladder-type oligo(*p*-phenylene)s, containing up to 10 phenyl rings with or without diphenylamino endcaps, namely (*L*)-Ph(*n*)-NPh ($n=7$–10) and (*L*)-Ph(*n*) ($n=7$ and 8), respectively, have been designed and successfully synthesized. They have extremely large 2PA cross-sections and highly efficient amplified spontaneous emission/lasing with ultra-low threshold have been demonstrated. In contrast to linear π-conjugated oligofluorenes, the absorption and emission wavelength/maxima of these ladder-type oligomers can easily be tuned by extension of its π-conjugation length, which also provides a means to substantially enhance the nonlinear optical properties. Because of rigid, coplanar, and highly extended π-conjugation, all these oligomers exhibit remarkably efficient multiphoton (from two- to five-photon) excited blue photoluminescence and two-photon pumped ASE/lasing. Furthermore, the participation of laterally substituted alkylphenyl moieties in π-electron delocalization gives rise to exceptionally large 2PA cross-sections resulting in an excellent nonlinearity-transparency trade-off. Most importantly, (*L*)-Ph(10)-NPh exhibits the highest intrinsic 2PA cross-section of 3643 GM for a blue emissive organic fluorophore reported so far. The record-high 2PP blue ASE/lasing efficiency of 2.06% has been achieved by un-endcapped oligomer, (*L*)-Ph(8), rather than (*L*)-Ph(10)-NPh having larger σ_2. Thus, molecule with larger σ_2 does not fully guarantee that it can exhibit higher η_2. Furthermore, these highly extended oligomers exhibit exceptionally ultralow ASE/lasing threshold, among which the lowest 2PA pumped ASE/lasing threshold of about 0.26 μJ was achieved by (*L*)-Ph(10)-NPh. Therefore, these series of ladder-type oligo(*p*-phenylene)s show great promise for practical application of generating new blue coherent light sources by MPA process. Our findings unambiguously demonstrate that highly extended, rigid and coplanar structure is essential to achieve highly efficient multiphoton-pumped frequency upconversion ASE/lasing fluorophores with ultralow threshold, which opens up a new avenue to further development of high-performance MPA materials.

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Keywords: amplified spontaneous emission · blue lasing · ladder oligomers · multiphoton absorption · oligophenylenes

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