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Exceptionally Strong Multiphoton-Excited Blue Photoluminescence and Lasing from Ladder-Type Oligo(*p*-phenylene)s

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Supporting Information

ABSTRACT: We report the synthesis and investigation of multiphoton absorption properties of a novel series of diphenylamino-end-capped ladder-type oligo(*p*-phenylene)s which exhibit greatly enhanced and efficient multiphoton (from two- to five-photon) upconverted blue photoluminescence with which the record-high intrinsic three-photon absorption cross-section of 4.56×10^{-76} cm^6 s^2 in the femtosecond regime has been obtained. Exceptionally efficient two- to five-photon-excited lasing in the blue region has also been demonstrated in which the highest two-photon-excited lasing efficiency of 0.34% has been achieved.

Multiphoton absorption is a higher order nonlinear optical process in which an atom or a molecule simultaneously absorbs two or more photons with identical or different energies to undergo an excitation. The multiphoton absorption process has a transition probability that is proportional to I^n, where I is the intensity of the input laser pulse and n is the number of photons involved. The intensity dependence of the multiphoton absorption process gives rise to a stronger spatial confinement and hence a higher spatial resolution and contrast in imaging.[1] As a result, multiphoton absorption offers many advantages for various emerging technological applications, including three-dimensional optical data storage,[2] optical limiting,[3] lithographic microfabrication,[4] fluorescence excitation microscopy and imaging,[5] photodynamic therapy,[6] and infrared frequency up-conversion lasing.[7] The use of multiphoton absorption to produce smaller and cheaper visible laser sources especially in the short wavelength region is one of intriguing applications as compared to other coherent frequency upconversion techniques, such as optical harmonic generation or sum frequency mixing. Multiphoton upconversion lasing offers capability of adopting waveguide and fiber configurations and feasibility of using semiconductor lasers as pump sources, and importantly, it does not require stringent phase-matching requirements. The short lasing wavelengths will bring in new merits and breakthroughs in various laser-based applications. Although molecules/materials with large two-photon-absorption (2PA) cross-sections have been developed in the past decades, most of them are not useful and efficient for multiphoton-induced blue lasing.

Fluorene-based π-conjugated oligomers have recently been shown to exhibit excellent multiphoton-excited blue photoluminescence and lasing properties; however, further enhancement in optical nonlinearity is limited by the non-coplanarity of the fluorenyl−fluorenyl backbone. On the other hand, the rigid and planar structure of ladder-type oligo(*p*-phenylene)s would facilitate π-electron delocalization and thus improve multiphoton absorption response. Such a structure motif would also increase photoluminescence efficiency with enhanced thermal and photochemical stability. In addition, it has been shown that 9,9-diphenyl substitution onto fluorene moiety is a very useful strategy/tool to enhance the 2PA properties with excellent nonlinearity−transparency trade-off, which is due to the participation of the non-coplanar phenyl rings in the enhancement of the electron delocalization.[8] Nevertheless, there is only limited study on exploring the ladder-type oligomers for multiphoton absorption,[3e] and no attempts have been made for multiphoton lasing applications. The potential of 9,9-diphenyl substitution onto fluorene moiety for three-photon absorption (3PA) properties still remains to be explored.

We report herein the design and synthesis of a novel series of highly extended diphenylamino-end-capped ladder-type oligo(*p*-phenylene)s which exhibits greatly enhanced two-, three-, four-, and five-photon absorption-induced blue-light photoluminescence. The 2PA and 3PA cross-sections are as high as 1045.6 GM and 45.63×10^{-77} cm^6 s^2, which is the highest intrinsic 3PA cross-section obtained so far,[7f] respectively. In addition, these oligo(*p*-phenylene)s exhibit exceptionally efficient two-, three-, and four-photon-induced up-conversion blue lasing, peaking at 460−482 nm, with record-high two-photon and three-photon lasing efficiency of 0.336% and 0.0025%, respectively. Our findings open up a new vista to develop highly efficient multiphoton-absorbing fluorophores for practical applications, particularly the blue emissive molecules for high-contrast imaging and new coherent light sources in the short wavelength region.

Novel D-π-D ladder-type oligophenylenes, composed of linear fused fluorenes, containing up to seven phenyl rings, symmetrically end-capped with diphenylamino donors, namely **(*L*)-Ph(*n*)-NPh**, where n = 3−7, have been designed, synthesized, and investigated for highly efficient multiphoton absorption and frequency-upconverted blue-lasing applications. To circumvent the solubility and processability problem for the extended ladder-type oligomers as well as to enhance the electron delocalization for large nonlinear optical response,[8] the non-coplanar 4-decylphenyl substituents are tethered at the 9-position of a fluorenyl unit in these ladder-type oligopheny-

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lenes, as shown in Figure 1. They were synthesized by means of convergent approach using palladium-catalyzed Suzuki coupling, Buchwald amination, and triflic acid-catalyzed intramolecular ring closure as key steps. The full synthetic details of the entire homologous series can be found in the Supporting Information. All the newly synthesized diphenylamino end-capped ladder-type oligo(p-phenylene)s were fully characterized with ^{1}H NMR, ^{13}C NMR, HRMS, and elemental analysis and found to be in good agreement with the proposed structures (see Supporting Information).

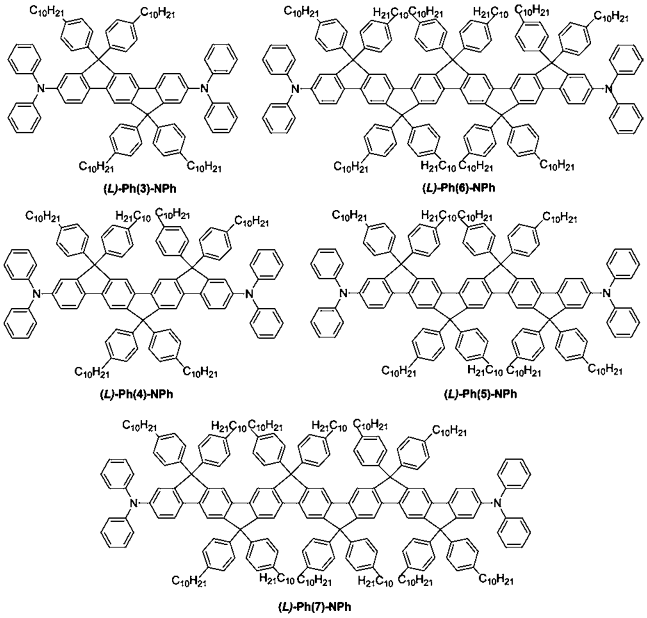

Figure 1. Molecular structures of (L)-**Ph**(n)-**NPh**, n = 3−7.

All the ladder-type oligo(p-phenylene)s are highly soluble in common organic solvents such as toluene, chloroform, and DMF. For example, the solubility of (L)-**Ph**(7)-**NPh** in toluene can be up to 10^{-1} M. The results of the linear optical properties of (L)-**Ph**(n)-**NPh** measured in toluene are summarized in Table 1 and S1. As seen in the absorption spectra shown in Figure 2a, these oligomers exhibit similar absorption characteristics, mainly composed of two absorption bands: the $n \rightarrow \pi^*$ transition of triarylamine moieties and the $\pi \rightarrow \pi^*$ transition of the oligomeric cores. In contrast to diphenylamino end-capped oligofluorenes, the absorption wavelength maximum of these ladder-type oligo(p-phenylene)s exhibits bathochromic shifts as the conjugation length increases, indicating the enhancement of electron delocalization along the π-conjugated core. These ladder-type oligophenylenes also show very large molar absorption coefficients up to 2.53×10^5 M^{-1} cm^{-1} for (L)-**Ph**(7)-**NPh**, which is attributed to the rigid planar ladder structure. Such a rigid planar system would also facilitate p-orbital overlap and electron delocalization through the entire system and thus enhance the multiphoton absorption responses.[3e] Upon excitation at the absorption maximum, these oligo(p-phenylene)s show two resolved emission bands in the range of 420−480 nm, with high fluorescence quantum yields (Φ) greater than 85%. Consistently, the emission wavelength maximum also shows bathochromic shifts with an increase in the conjugation length. On the other hand, the absorption and emission spectra show no significant red/blue shifts in different solvents, e.g., $CHCl_3$ and DMF, except merging of the two emission bands in DMF, suggesting nonpolar ground and excited states.

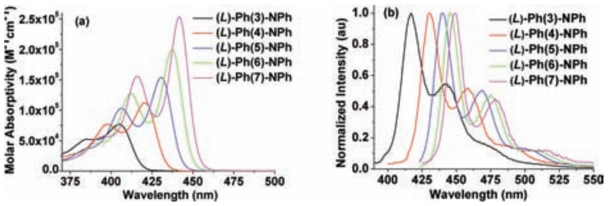

Figure 2. (a) Absorption and (b) emission spectra of (L)-**Ph**(n)-**NPh**, where n = 3−7, measured in toluene.

Interestingly, these ladder-type oligomers exhibit very strong multiphoton—including two-, three-, four-, and five-photon—upconverted photoluminescence (PL) when excited by near-infrared femtosecond laser pulses. The multiphoton-excited PL spectral characteristics are very similar to those of the corresponding one-photon-excited counterparts (Figure S1), indicating that their emission energy levels are likely to be identical. Figure 3 shows the logarithmic plots of power dependence of relative multiphoton-induced fluorescence intensity of (L)-**Ph**(5)-**NPh** on pulse intensity using a femtosecond laser as excitation source at 800, 1250, 1650, and 2000 nm. The solid lines are the best-fit straight lines with gradient n = 1.94, 3.08, 4.09, and 5.08. Hence, the square, cubic, fourth-order, and fifth-order dependence of the fluorescence intensity versus pumping power at 800, 1250, 1650, and 2000 nm, respectively, is clearly demonstrated. These corroborate that the frequency-upconverted fluorescence is due to the two-, three-, four-, and five-photon absorption, respectively.

The two-, three-, and four-photon excitation fluorescence spectra of the (L)-**Ph**(n)-**NPh**s are shown in Figures 4. The 2PA cross-section, σ_2, was measured by the two-photon-induced fluorescence method in the range of 800−950 nm using Rhodamine 6G as the reference standard.[9] The results of the maximum 2PA cross-sections for (L)-**Ph**(n)-**NPh**s are tabulated in Table 1. The 2PA enhancement is found throughout the full spectrum measured as the conjugation length increases. In addition, very large σ_2 up to 1045.6 GM at 880 nm was obtained for (L)-**Ph**(7)-**NPh**, highlighting the promise of ladder-type oligo(p-phenylene)s for 2PA applica-

Table 1. Linear and Nonlinear Optical Properties of (L)-Ph(n)-NPh (n = 3−7) Measured in Toluene

n	λ_{abs}/nm[a]	λ^{em}/nm	Φ	σ_2 (λ_{ex}/nm)[b]	σ_3 (λ_{ex}/nm)[c]	η_2 (λ_{ex}/nm)[d]	η_3 (λ_{ex}/nm)[e]
3	405	417, 443	0.85	59.6 (810)	2.02 (1230)	no lasing	no lasing
4	420	431, 459	0.86	220.9 (840)	7.23 (1250)	0.132 (830)	1.01 (1220)
5	431	440, 469	0.84	570.6 (850)	22.41 (1300)	0.163 (890)	1.33 (1250)
6	437	446, 475	0.92	782.9 (840)	34.30 (1310)	0.253 (890)	2.10 (1220)
7	442	449, 478	0.90	1045.6 (880)	45.63 (1330)	0.336 (890)	2.50 (1220)

[a]Dissolved in toluene. [b]2PA cross-section (GM). [c]3PA cross-section ($\times 10^{-77}$ cm^6 s^2). [d]2PA lasing efficiency (%). [e]3PA lasing efficiency ($\times 10^{-3}$ %).

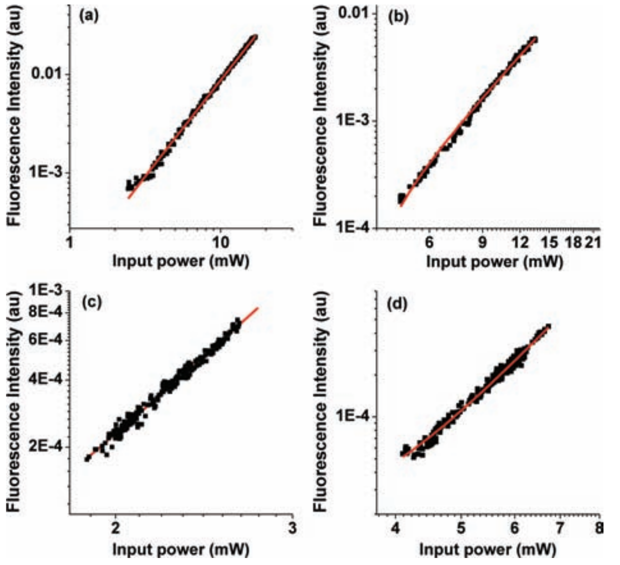

Figure 3. Logarithmic plots of the power dependence of relative multiphoton-induced fluorescence intensity of **(*L*)-Ph(5)-NPh** on pulse intensity using (a) 800, (b) 1250, (c) 1650, and (d) 2000 nm femtosecond laser as an exciting source. The solid lines are the best-fit straight lines with gradient *n* = 1.94, 3.08, 4.09, and 5.08, respectively.

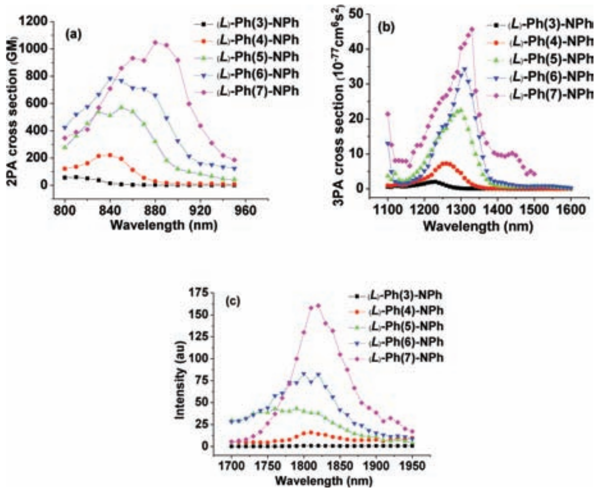

Figure 4. (a) Two-, (b) three-, and (c) four-photon-excited spectra of **(*L*)-Ph(*n*)-NPh**.

tions. The 3PA cross-sections, σ_3, were determined by comparing the fluorescence intensity with that of **PhN-OF(4)-TAZ-OF(4)-NPh** in the range of 1100−1500 nm.[7f] Consistently, the 3PA cross-sections increase with the extension of conjugation length in this series. Remarkably, the exceptionally large intrinsic σ_3 of 4.56×10^{-76} cm^6 s^2 at 1330 nm for **(*L*)-Ph(7)-NPh** in the femtosecond regime was obtained, affirming the importance of extended and planar oligo(*p*-phenylene) core as well as 9,9-diaryl-substitution onto fluorenyl moiety for large 3PA enhancement. The four-photon-excited fluorescence intensities measured in the range of 1700−1950 nm were also found to increase with extension of conjugation length, further corroborating the merit of extending the π-conjugated ladder-type system for multiphoton absorption.

Upon pumping with near-infrared femtosecond laser pulses, the longer homologues of ladder-type oligo(*p*-phenylene)s **(*L*)-Ph(*n*)-NPh**, where *n* = 4−7, exhibit exceptionally strong multiphoton-excited blue lasing. In addition, in sharp contrast to this diphenylamino end-capped series, the un-end-capped**(*L*)-Ph(*n*)** series, where *n* = 3−5, only exhibit multiphoton-excited photoluminescence but not lasing phenomenon. This signifies the importance of the extended π-conjugation and diphenylamino end-caps for multiphoton-excited lasing. Figure 5a shows the intense and highly directional stimulated blue emission from the **(*L*)-Ph(4)-NPh** solution upon pumped with laser pulses at 1200 nm. The plots of input pumped power versus two-photon-excited lasing output relationship for **(*L*)-Ph(*n*)-NPh**, *n* = 4−7, are shown in Figure 5b, unambiguously showing evidence of lasing threshold behavior. It is worth mentioning that the lasing threshold decreases with an increase in the conjugation length of these oligo(*p*-phenylene)s, demonstrating the advantage of using higher homologues for lasing. Remarkably, the two-photon-excited lasing efficiency enhances greatly with the conjugation length, increasing up to 0.34% for **(*L*)-Ph(7)-NPh**, which is the record high value achieved so far for the multiphoton-excited blue lasing efficiency. The three-photon upconversion lasing spectra of **(*L*)-Ph(*n*)-NPh**, *n* = 4−7, excited at 1.25 μm are shown in Figure 6a. The optimized full width at half-maximum (fwhm) of the three-photon lasing spectra narrowed sharply to ~4 nm with a peak in the range of 460−482 nm. In addition, the plots of input power versus output power of the three-photon pumped lasing process for **(*L*)-Ph(*n*)-NPh**, *n* = 4−7, are shown in Figure 6b. Compared to the slopes in Figure 5b, the slopes in Figure 6b appear to be gentle, which is attributed to the fact that 3PA is a much higher order nonlinear optical process resulting in smaller gain. The three-photon-excited lasing efficiency of **(*L*)-Ph(*n*)-NPh**, *n* = 4−7, also increases

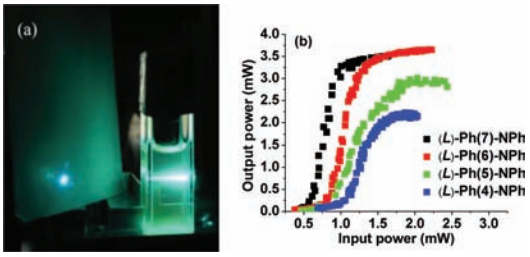

Figure 5. (a) Photo of highly directional, frequency-upconverted stimulated (blue) emission from a **(*L*)-Ph(4)-NPh** solution pumped with a focused 1.2 μm laser beam. (b) Plots of input power versus output power of two-photon-pumped lasing process for **(*L*)-Ph(*n*)-NPhs** excited at 890 nm.

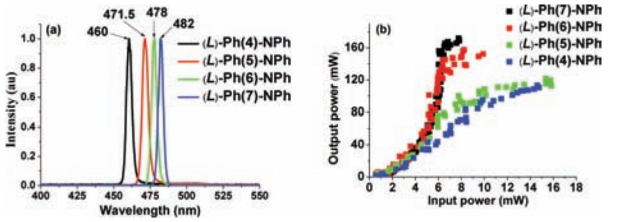

Figure 6. (a) Three-photon absorption upconverted lasing spectra of **(*L*)-Ph(*n*)-NPh** (*n* = 4−7) at the concentration of 1.2×10^{-2} M. (b) Plots of input power versus output power of three-photon pumped lasing process for **(*L*)-Ph(*n*)-NPh**, where *n* = 4−7, excited at 1300, 1300, 1250, and 1230 nm, respectively.

with the conjugation length up to 0.0025%. The upconverted lasing spectra of **(*L*)-Ph(5)-NPh** at wavelengths of 800, 1250, 1650, and 2000 nm, corresponding to two-, three-, four-, and five-photon excitation processes, respectively, are shown in Figure S2. These multiphoton upconverted lasing spectral characteristics are very similar to those of the two-photon-excited counterparts, thereby suggesting the emission comes from the same emission states. The fwhm of these spectra can also be narrowed to ∼4 nm, except that of the five-photon-excited one, which is due to the weak five-photon absorption and low lasing efficiency.

In summary, we have synthesized a novel series of quadrupolar ladder-type oligophenylenes, containing up to seven phenyl rings, symmetrically end-capped with diphenylamino donors, namely **(*L*)-Ph(*n*)-NPh**, where $n = 3-7$, using palladium-catalyzed Suzuki coupling, Buchwald amination, and triflic acid-catalyzed intramolecular ring closure as key steps. 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. Because of the rigid and planar structure and the participation of π-electron delocalization of the non-coplanar 9,9-diaryl substitution of fluorenyl moiety, these ladder-type oligo(*p*-phenylene)s exhibit exceptionally efficient multiphoton—from two- to five-photon—excited blue photoluminescence and lasing. The highest intrinsic three-photon absorption cross-section of 4.56×10^{-76} cm^6 s^2 in the femtosecond regime has been obtained from **(*L*)-Ph(7)-NPh**. Furthermore, the record-high two-photon-excited lasing efficiency of 0.34% has been achieved from **(*L*)-Ph(7)-NPh** upon pumping with infrared laser pulses, which is 3-fold higher than the previous record. As a result, these oligomers show great potential for practical use. Our results also open a new avenue to develop highly effective multiphoton absorbing fluorophores for various potential applications.

■ ASSOCIATED CONTENT

Supporting Information

Details of synthesis and characterization; multiphoton absorption measurements and results. This material is available free of charge via the Internet at http://pubs.acs.org.

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[⊥]H.H.F. and L.G. contributed equally to this work.

Notes

The authors declare no competing financial interest.

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