Highly Efficient Multiphoton-Absorbing Quadrupolar Oligomers for Frequency Upconversion

Xin Jiang Feng,^[a] Po Lam Wu,^[b] King Fai Li,^[b] Man Shing Wong,^{*[a]} and Kok Wai Cheah^{*[b]}

Abstract: Two series of quadrupolar diphenylamino-endcapped oligofluorenes, **PhN-OF**(*n*)-**NPh** (n=2-5) and **PhN-OF**(*n*)-**TAZ-OF**(*n*)-**NPh** (n=1-4), which have an electron-withdrawing 1,2,4-triazole (TAZ) moiety as central core, with D– π –A– π –D structural motif (D=donor, A=acceptor), have been synthesized by palladium-catalyzed Suzuki cross-coupling of 9,9-dibutyl-7-(diphenylamino)-2-fluorenylboronic acid and the corresponding (1,2,4-

triazole-based) aryl halide as key step. On pumping with infrared femtosecond lasers, these oligomers showed very strong multiphoton-excited blue photoluminescence. These D– π –D and D– π – A– π –D quadrupolar oligofluorenes exhibit superior three-photon absorption properties compared to the respective D– π –A counterparts with a highest three-photon absorption cross-section (σ_3) of up to 2.72×10⁻⁷⁷ cm⁶ s². Despite the comparable linear and multiphoton absorption properties of the two types of quadrupolar oligomers **PhN-OF**(n)-

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PhN-OF(n)-TAZ-OF(n)-NPh and NPh, only the former exhibit remarkably intense and highly efficient multiphoton-excited frequency-upconverted deep blue lasing, which gives rise to record high lasing efficiency of 0.097 % and very narrow of full width at halfmaximum of the lasing spectra. Our findings suggest that quadrupolar-type molecules/oligomers are superior for multiphoton excited frequency upconverted lasing to their dipolar counterparts and also provide important guidelines to design highly efficient threephoton absorption molecules for photoluminescence and lasing applications.

Introduction

Nonlinear optical materials that exhibit efficient multiphoton absorption (MPA) have drawn tremendous attention in the past decades, as they show great potential in various emerging technological applications, which include twophoton excited fluorescence (TPEF) imaging and microscopy,^[1] two-photon optical power limiting, three-dimensional optical data storage,^[2] two-photon photodynamic therapy,^[3] and two-photon microfabrication.^[4] Another attractive application of multiphoton absorption is fabricating low-cost high-energy coherent light sources in the short-wavelength region, such as deep blue and ultraviolet, by means of multi-

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be easily achieved in liquids, films, or optical fibers without stringent phase-matching requirements. The short lasing wavelengths will offer new advantages and breakthroughs in various laser-based applications. In addition, multiphotonexcited lasing in dye-based systems provides the advantage of tunable lasing wavelength, which is guaranteed by a relatively broad spectral range of fluorescence emission of dye materials.^[6] To exhibit MPA upconverted lasing, molecules are required to have high fluorescence quantum efficiency, a large

photon-excited frequency-upconverted lasing,^[5] which can

quired to have high fluorescence quantum efficiency, a large MPA cross section, a large Stokes shift, which could affect the lasing threshold and the attainment of optical gain, as well as high photochemical and thermal stability. Hence, it is not guaranteed that the best MPA material can be used for multiphoton pumped lasing. As a result, there are only a few reported MPA molecules that can be used for multiphoton pumped lasing, and there are still no molecular-structural guidelines that can assist to judge the MPA lasing capability of a fluorophore. The common features of most reported MPA-pumped lasing dyes are derived from donor–acceptor π -conjugated chromophores such as stilbazolium salts.^[7]

In the past decade, there was remarkable success in developing highly active two-photon-absorption chromophores; however, there were far fewer studies on the structure–property relationships for three-photon absorption.^[8] We recently demonstrated efficient multiphoton-excited frequency-upconverted photoluminescence and lasing in a series of

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donor–acceptor oligomers endcapped with diphenylamino and 1,2,4-triazole groups, in which the multiphoton-excited emission properties and upconversion lasing properties can easily be modified/tuned by using various fluorene-based π conjugated cores.^[9]

To continue investigating the structural factors that can enhance multiphoton-absorption responses, particularly three-photon absorption, and exploring their potential for applications, we report herein our systematic investigation on multiphoton absorption properties of two series of quadrupolar-type oligofluorenes with D- π -D and D- π -A- π -D structural motifs, which have been shown to exhibit superior multiphoton-excited photoluminescence and blue lasing properties compared to the respective $D-\pi-A$ type dipolar oligofluorenes. In contrast to two-photon absorption properties, incorporation of a 1,2,4-triazole electron-accepting central core into the D- π -D type oligofluorenes does not enhance the three-photon absorption properties. Despite the comparable linear and three-photon absorption properties of the two quadrupolar series PhN-OF(n)-NPh and PhN-OF(n)-TAZ-OF(n)-NPh, only PhN-OF(n)-NPh exhibit remarkably strong MPA-excited frequency upconverted lasing with record high blue lasing efficiency of 0.097 %.



PhN-OF(n)-TAZ-OF(n)-NPh

Results and Discussion

Synthesis of the symmetrically diphenylamino disubstituted oligofluorenes containing 1,2,4-triazole as central core, namely, **PhN-OF**(*n*)-**TAZ-OF**(*n*)-**NPh**, is outlined in Scheme 1. Double palladium-catalyzed Suzuki cross-coupling of 9,9-dibutyl-7-(diphenylamino)-2-fluorenylboronic acid^[10] and 1,2,4,-triazole-based diaryl dibromides was used

as a key step to synthesize the backbone of the oligofluorenes. 4-Bromobenzoyl chloride, freshly prepared from 4-bromobenzoic acid (1) was treated with anhydrous hydrazine in the presence of triethylamine in THF at room temperature to afford disubstituted hydrazine 2 in 68% yield. Condensation of 2 with aniline in the presence of POCl₃ at 200°C afforded 1,2,4-triazole derivative 3 in 73% vield. Double palladiumcatalyzed Suzuki cross-coupling of dibromide 3 and 9,9-dibutyl7-(diphenylamino)-2-fluorenylboronic acid (4) with Pd-(OAc)₂/2P(o-tolyl)₃ as catalyst afforded PhN-OF(1)-TAZ-OF(1)-NPh in good yield. On the other hand, Suzuki crosscoupling of dibromide 3 and 7-(trimethylsilyl)-2-fluorenylboronic acid (5) afforded difluorene-substituted 1,2,4-triazole derivative 6 in 74% yield. Iododesilylation of 6 was carried out in the presence of silver trifluoroacetate at 80 °C affording the corresponding diiodide 7 in excellent yield. Double Suzuki cross-coupling of diiodide 7 and boronic acid 4 gave the desired PhN-OF(2)-TAZ-OF(2)-NPh in 81% yield. The same reaction sequence was applied to further extend the oligofluorenyl units: cross-coupling with 7-(trimethylsilyl)-2-fluorenylboronic acid, iododesilylation, and cross-coupling with 9,9-dibutyl-7-(diphenylamino)-2-fluorenylboronic acid gave the higher homologues PhN-OF(3)-TAZ-OF(3)-NPh and PhN-OF(4)-TAZ-OF(4)-NPh in good yield (Scheme 1). The corresponding series of diphenylamino-endcapped oligofluorenes, PhN-OF(n)-NPh, was synthesized according to the previously published procedures. The new oligofluorenes were fully characterized by ¹H and ¹³C NMR spectroscopy, MALDI-TOF MS, and elemental analysis, which were found to be in good agreement with their proposed structures. All oligofluorenes are highly solu-



PhN-OF(n)-NPh

ble in common organic solvents; **PhN-OF**(*n*)-**TAZ-OF**(*n*)-**NPh** show high thermal stabilities with decomposition temperatures greater than 448 °C.

As shown by the absorption spectra, these two series exhibit similar absorption characteristics, mainly composed of two absorption bands: the $n \rightarrow \pi^*$ transition of triaryl amine moi-

eties and the $\pi \rightarrow \pi^*$ transition of the oligomeric cores. Incorporation of a 1,2,4-triazole (TAZ) electron-withdrawing group into the π -conjugated framework of **PhN-OF**(*n*)-**NPh** as central core enhances the molar absorptivity but slightly shifts (ca. 8 nm) the absorption spectra to shorter wavelengths. (Figure 1 and Table 1) On the other hand, both series show almost identical blue photoluminescence spectra

Table 1.	Summary	of lines	ar optical,	three	photon	absorption	and	thermal	properties	of PhN-C)F(n)-NPh	and
PhN-OI	F(n)-TAZ-	OF(n)-N	NPh.									

	$\lambda_{\max}^{[a]} [nm] \ (\varepsilon [10^4 \mathrm{m}^{-1} \mathrm{cm}^{-1}])$	$\lambda_{\max}^{em [a, b]}$ [nm]	$arPhi^{[c]}$	3PA PL peak ^[d] [nm]	$\sigma_{3,\max}^{[f]}$ [cm ⁶ s ²]	T _{decomp} ^[g] [⁰C]
PhN-OF(2)-NPh	382 (8.04)	417	0.95	443	1.50×10^{-77}	
PhN-OF(3)-NPh	385 (11.75)	423	0.99	451	1.20×10^{-77}	
PhN-OF(4)-NPh	385 (14.29)	422	0.97	452	2.35×10^{-77}	
PhN-OF(5)-NPh	385 (18.19)	420	0.94	454	2.21×10^{-77}	
PhN-OF(1)-TAZ-OF(1)-NPh	377 (10.72)	421	0.88	450	1.01×10^{-77}	485
PhN-OF(2)-TAZ-OF(2)-NPh	378 (16.67)	423	0.87	448	2.28×10^{-77}	451
PhN-OF(3)-TAZ-OF(3)-NPh	377 (24.10)	422	0.88	451	2.61×10^{-77}	451
PhN-OF(4)-TAZ-OF(4)-NPh	376 (28.03)	421	0.91	439 ^[e]	2.72×10^{-77}	448

[a] Measured in toluene. [b] Excited at the absorption maximum. [c] With quinine sulfate monohydrate ($\Phi_{350} = 0.58$) as standard. [d] Measured in 0.02 M toluene solution. [e] Measured in 0.002 M toluene solution. [f] Determined by the relative method. [g] Determined by thermal gravimetric analysis with a heating rate of 20 °C min⁻¹ under N₂.

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1

Br

3

Bu









87%

11 Scheme 1. Synthesis of PhN-OF(n)-TAZ-OF(n)-NPh (n = 1-4).

peaking at about 422 nm upon excitation at the absorption maximum (Figure 2) and very large fluorescence quantum yields in toluene in the range of 87-91% for the PhN- OF(n)-TAZ-OF(n)-NPh series and 94–99% for the PhN-OF(n)-NPh series. In contrast to PhN-OF(n)-NPh, PhN-OF(n)-TAZ-OF(n)-NPh show a strong solvatochromic

PhN-OF(4)-TAZ-OF(4)-NPh



Figure 1. Absorption spectra of a) **PhN-OF**(*n*)-**TAZ-OF**(*n*)-**NPh** and b) **PhN-OF**(*n*)-**NPh** in toluene.

effect in the emission spectra in which the emission peak exhibits a large redshift (67 nm) in polar solvents, suggesting a dipolar or charge-transfer character in the excited state (Figure 3).

The multiphoton absorption photoluminescence and lasing properties were investigated by using a femtosecond pulsed laser as an excitation source (Table 1). In spite of the moderate two-photon absorption properties,^[11] PhN-OF(n)-NPh show strong three-photon excited photoluminescence with a small redshift of the emission spectra due to a re-absorption effect. Remarkably, these oligomers exhibit large three-photon absorption (3PA) cross sections in the range of 8.31×10^{-78} to 1.51×10^{-77} cm⁶s², as measured by the openaperture Z-scan technique at $1.3 \,\mu\text{m}$, which are much larger than those of dipolar diphenylamino- and 1,2,4-triazole-endcapped oligofluorenes.^[9] On the other hand, the incorporation of a TAZ moiety into the PhN-OF(n)-NPh system as a central electron-withdrawing core, giving a D-n-A-n-D structural motif, does not significantly affect/modify the 3PA cross section of the resulting oligomers PhN-OF(n)-TAZ-**OF**(*n*)-**NPh**, for which 3PA cross sections are in the range of 5.44×10^{-78} to 1.93×10^{-77} cm⁶s² at 1.3 µm. This finding is in



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Figure 2. Emission spectra of a) **PhN-OF**(*n*)-**TAZ-OF**(*n*)-**NPh** and b) **PhN-OF**(*n*)-**NPh** in toluene

sharp contrast to the typical trend often found in the twophoton absorption properties. For both the series, the 3PA cross sections initially increase with increasing chain length and then show a tendency for saturation up to four fluorenyl units. The cubic power dependence of 3PA fluorescence for PhN-OF(n)-NPh (Figure 4) and PhN-OF(n)-TAZ-OF(n)-**NPh** at 1.3 µm has a gradient in the range of 2.91–3.22, providing direct experimental evidence of a three-photon excitation process. Figure 5 shows the three-photon-excitation spectra of PhN-OF(n)-NPh and PhN-OF(n)-TAZ-OF(n)-NPh measured by comparing the fluorescence intensity excited from 1100 to 1600 nm with that of the respective molecule excited at 1.3 µm. As seen from the excitation spectra, the maximum 3PA cross section occurs at about 1270 nm for all oligometrs and gives rise to the highest σ_3 of 2.72× 10^{-77} cm⁶s² for **PhN-OF(4)-TAZ-OF(4)-NPh**.

Upon pumping with femtosecond laser pulses at 800 nm, all **PhN-OF**(*n*)-**NPh** exhibit intense two-photon upconverted deep blue lasing peaking at 445–449 nm. The two-photonexcited lasing spectra of all these homologous oligofluorenes are almost identical, and the full width at half-maximum (FWHM) of the lasing spectra are sharply narrowed relative to the corresponding PL spectra (Figure 6). Figure 7 shows a



Figure 3. Solvent effect of a) PhN-OF(1)-TAZ-OF(1)-NPh and b) PhN-OF(2)-NPh.

plot of output versus input power for **PhN-OF**(*n*)-**NPh** (n = 2-5), which unambiguously shows evidence of lasing threshold behavior. The decreasing lasing threshold with increasing conjugation length of these oligofluorenes demonstrates the merits of using higher homologues. Remarkably, the lasing efficiency is also greatly enhanced with increasing conjugation length, up to 0.097 %, which is the highest value for multiphoton-excited deep blue lasing reported so far even though the excitation at the most easily accessible 800 nm is not optimized for the two-photon absorption process in this series^[11] (Table 2).

Consistently, all **PhN-OF**(*n*)-**NPh** exhibit prominent three-photon upconverted deep blue lasing upon pumping

with femtosecond laser pulses at 1.34 µm (Figure 8). The three-photon-excited lasing spectra are nearly identical to those of two-photon-excited lasing spectra with very narrow FWHM and peak at around 447 nm indicating that the same emissive state is involved. A plot of output versus input power for PhN-OF(3)-NPh and PhN-OF(4)-NPh (Figure 9) clearly indicates lasing threshold behavior. Compared to the slopes in Figure 7, the slopes in Figure 9 appear to be gentle, which is attributed to the intrinsically smaller 3PA cross section, which results in weaker induced fluorescence and hence smaller gain. The three-photon-excited lasing efficiency also increases initially with increasing conjugation length, up to 0.063% for PhN-OF(4)-NPh, and then decreases for higher homologues. However, despite comparable linear and nonlinear optical responses, PhN-OF(n)-TAZ-OF(n)-**NPh** show no lasing behavior under the same experimental conditions.

Conclusion

We have synthesized two series of quadrupolar diphenylamino-endcapped oligofluorenes, **PhN-OF**(n)-**NPh** (n=2-5) and PhN-OF(n)-TAZ-OF(n)-NPh (n=1-4), which have an electron-withdrawing 1,2,4-triazole moiety as central core, with D-n-A-n-D structural motif, using palladium-catalyzed Suzuki cross-coupling of 9,9-dibutyl-7-(diphenylamino)-2-fluorenylboronic acid and the corresponding (1,2,4,triazole-based) aryl halide as key step. Despite exhibiting saturation behavior of absorption and emission properties/ maxima, both series of oligofluorenes show an increase in three-photon absorption cross-sections with increasing chain length and reach a saturation limit at four fluorenyl units. These D- π -D and D- π -A- π -D quadrupolar oligofluorenes exhibit superior three-photon absorption properties compared to the respective $D-\pi-A$ counterparts, with a highest three-photon absorption cross section (σ_3) of up to 2.72× 10^{-77} cm⁶s². In contrast to two-photon absorption properties, incorporation of a 1,2,4-triazole electron-accepting central core into the $D-\pi-D$ type oligofluorenes does not enhance the 3PA properties. Despite the comparable linear and multiphoton absorption properties of PhN-OF(n)-NPh and PhN-OF(n)-TAZ-OF(n)-NPh quadrupolar oligomers, only **PhN-OF**(*n*)-**NPh**s exhibit remarkably strong MPA excited frequency upconverted lasing, which also achieves a record blue lasing efficiency of 0.097%. Our findings suggest for the first time that quadrupolar-type molecules/oligomers are

Table 2. Summary of two- and three-photon-excited lasing properties of PhN-OF(n)-NPh in toluene.

	2PA lasing peak [nm]	FWHM [nm]	Lasing efficiency ^[a] [%]	3PA lasing peak [nm]	FWHM [nm]	Lasing efficiency ^[b] [%]
PhN-OF(2)-NPh	445	5.8	0.0245	447	5.3	0.0295
PhN-OF(3)-NPh	449	6.1	0.0619	446	3.9	0.0624
PhN-OF(4)-NPh PhN-OF(5)-NPh	445 449	6.3 6.0	0.0856 0.0967	448 448	6.3 5.3	0.0627

superior for multiphoton-excited frequency-upconverted lasing compared to their dipolar counterparts and also provide important guidelines to design highly efficient 3PA molecules for photoluminescence and lasing.

[a] Pumped at 800 nm. [b] Pumped at 1.34 µm.

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Figure 4. Logarithmic plots of the power dependence of relative three-photon-induced fluorescence on pulse intensity with a femtosecond infrared laser as an exciting source at 1.3 μ m for **PhN-OF**(*n*)-**TAZ-OF**(*n*)-**NPh** (*n*=1-4). The solid line represents the best-fit straight line of all the data points.

Experimental Section

Photoluminescence (PL) and cavityless upconversion lasing experiments were performed on 2×10^{-2} M solutions of oligofluorenes in toluene in quartz cuvettes. In the cavityless upconversion lasing experiment, the pump source was an Optical Parametric Amplifier (Topas, Coherent) pumped by self-mode-locked Ti:sapphire laser with Spitfire Regenerative Amplifier (Spectra Physics-Tsunami; 800 nm, pulse width 100 fs, repetition rate 1 kHz). The laser passed through a polarizer, focusing lens (focal distance 100 mm), and IR filter (Hot Filter), used to block 800 nm light. The incident laser was focused at the center of oligofluorene solution in the cuvette (1 cm in length). A second lens focused the transmitted signal into the spectrometer (Ocean Optics, USB4000). The laser powers at each wavelength were calibrated and monitored throughout the measurements. The beam size of the incident laser was about 1 mm. The focal length of the lens was 100 mm. The minimum spot size of the pump laser was 0.166 mm, and its Rayleigh length was calculated to be 2.48 cm. So the maximum peak power at spot area was less than 232 GW cm⁻². The same laser system was used for PL experiments. For both PL and lasing excitation, the 800 nm laser line directly from the Spitfire Regenerative Amplifier was used, and for lasing the threshold pumping power was 6 mW. For three-photon upconversion excitation, laser lines from an optical parametric amplifier pumped by the Spitfire Regenerative Amplifier were used so that the laser wavelength could be tuned for optimum excitation.

N,*N*'-Bis(4-bromobenzyl)hydrazide (2): A solution of 4-bromobenzoic acid (1, 1.37 g, 6.9 mmol) and thionyl chloride (2.49 mL, 34.3 mmol) in

chloroform was heated to reflux and stirred for 4 h. The solvent and excess reagents were removed under vacuum. Dry toluene (20 mL) was added and then evaporated under vacuum. The light yellow oil was dissolved in dry THF and the solution added dropwise to a solution of hydrazine (0.16 mL, 3.4 mmol) and triethylamine (2.10 g, 20.8 mmol) in THF cooled in an ice/water bath. The reaction mixture was allowed to warm to room temperature and stirred overnight. Potassium carbonate solution was added to the reaction mixture. The resulting suspension was stirred for 2 h and then filtered. The collected solid was washed with water and dried under vacuum, affording 1.36 g of **2** as a white solid in 68% yield. ¹H NMR (400 MHz, [D₆]DMSO): δ =10.64 (s, 2H), 7.85 (d, *J*=8.0 Hz, 4H), 7.75 ppm (d, *J*=8.0 Hz, 4H); ¹³C NMR (100 MHz, [D₆]DMSO): δ =165.0, 131.7, 131.5, 129.6, 125.8 ppm; MS (FAB): *m/z*: 396.1 [*M*⁺].

4-Phenyl-3,5-bis(4-bromophenyl)-1,2,4-triazole (3): POCl₃ (4.3 mL, 46.3 mmol) was added slowly to a solution of aniline (12.94 g, 139 mmol) in 120 mL of 1,2-dichlorobenzene with cooling in an ice/water bath. After complete addition, the resulting mixture was allowed to warm to room temperature and then **2** was added (9.22 g, 23.2 mmol). After refluxing under nitrogen for 5 h, the reaction mixture was cooled to room temperature and washed with water. The organic layer was dried over anhydrous Na₂SO₄ and purified by silica-gel column chromatography with 8:1 dichloromethane:ethyl acetate as eluent affording 7.69 g (73%) of a white solid. ¹H NMR (400 MHz, CDCl₃): δ =7.51–7.40 (m, 7H), 7.26 (d, *J*= 8.0 Hz, 4H), 7.13 ppm (d, *J*=8.4 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃): δ =154.0, 134.7, 131.7, 130.3, 130.1, 130.0, 127.6, 125.6, 124.0 ppm; MS (FAB): *m/z*: 453.3 [*M*⁺].



Figure 5. Three-photon excitation spectra of a) **PhN-OF**(*n*)-**TAZ-OF**(*n*)-**NPh** and b) **PhN-OF**(*n*)-**NPh** measured in toluene from 1100 to 1600 nm.

4-N-Phenyl-3,5-bis{4-[9',9'-di-n-butyl-7'-(diphenylamino)-2'-fluorenyl]phenyl]-1,2,4-triazole (PhN-OF(1)-TAZ-OF(1)-NPh): A mixture of 3 $(228 \text{ mg}, 0.50 \text{ mmol}), 4 (979 \text{ mg}, 2.00 \text{ mmol}), Pd(OAc)_2 (10 \text{ mg}, 10 \text{ mg})$ 0.04 mmol), P(o-tolyl)₃ (27 mg, 0.09 mmol), 2 м K₂CO₃ (3 mL), toluene (25 mL), and methanol (10 mL) under nitrogen atmosphere was heated at 75°C overnight with magnetic stirring. After cooling to room temperature, the reaction mixture was poured into water and extracted with ethyl acetate (35 mL), followed by dichloromethane (40 mL). The combined organic layers were dried over anhydrous Na2SO4, evaporated to dryness, and the residue was purified by silica-gel column chromatography with 20:1 dichloromethane:ethyl acetate as eluent affording 288 mg (74%) of a light yellow solid. ¹H NMR (400 MHz, CDCl₃): $\delta = 7.64-7.48$ (m, 19H), 7.21-7.28 (m, 10H), 7.12 (m, 10H), 7.03-6.98 (m, 6H), 1.92-1.83 (m, 8H), 1.09–1.01 (m, 8H), 0.60–0.70 ppm (m, 20H); $^{13}\mathrm{C}\,\mathrm{NMR}$ (100 MHz, $CDCl_3$): $\delta = 154.6$, 152.3, 151.3, 147.8, 147.3, 142.6, 140.8, 137.8, 135.5, 135.4, 130.1, 129.7, 129.1, 129.0, 127.9, 126.9, 125.9, 125.3, 123.8, 123.3, 122.5, 120.9, 120.4, 119.3, 119.1, 55.0, 40.0, 25.9, 22.9, 13.8 ppm; HRMS (MALDI-TOF): m/z: 1183.6450 [M⁺]; elemental analysis (%) calcd for C86H81N5: C 87.20, H 6.89, N 5.91; found: C 87.16, H 6.82, N 5.81.

4-N-Phenyl-3,5-bis[**4-**[**9**',**9**'-di-*n*-butyl-**7**'-trimethylsilyl-**2**'-fluorenyl]phenyl]-**1**,**2**,**4**-triazole (6): The synthetic procedure for **PhN-OF(1)-TAZ-OF(1)-NPh** was followed using **3** (178 mg, 0.39 mmol), 9,9-di-*n*-butyl-7-(trimethylsilyl)-2-fluorenylboronic acid (**4**, 456 mg, 1.17 mmol), Pd(OAc)₂ (8.6 mg, 0.04 mmol), P(*o*-tolyl)₃ (24 mg, 0.08 mmol), $2 \le K_2CO_3$ (3 mL), toluene (20 mL), and methanol (8 mL). The residue was purified by silica-gel column chromatography with 20:1 dichloromethane:ethyl acetate as eluent affording 389 mg (74%) of **6** as a white solid. ¹H NMR (400 MHz, CDCl₃): δ =7.73 (d, *J*=8.0 Hz, 2H), 7.67 (d, *J*=7.6 Hz, 2H),



Figure 6. Two-photon upconversion photoluminescence and lasing spectra of **PhN-OF**(n)-**NPh**(n=4, 5) pumped at 800 nm.



Figure 7. Plot of output power versus input power of the two-photon pumped lasing process for **PhN-OF**(n)-**NP** (n=2–5).

7.60 (d, J=8.4 Hz, 4H), 7.45–7.54 (m, 15H), 7.27 (dd, J=8.0 Hz, 1.2 Hz, 2H), 2.02–1.93 (m, 8H), 1.08–1.01 (m, 8H), 0.67–0.58 (m, 20H), 0.30 ppm (s, 18H); ¹³C NMR (100 MHz, CDCl₃): δ =154.6, 151.6, 150.0, 142.6, 141.1, 140.9, 139.3, 138.7, 135.4, 131.8, 130.1, 129.7, 129.0, 127.9, 127.5, 126.9, 125.8, 125.4, 121.2, 120.0, 119.0, 54.9, 39.9, 25.9, 22.9, 13.7, -0.9 ppm; MS (FAB): m/z: 993.7 [M^+].

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4-N-Phenyl-3,5-bis{4-[9',9'-di-*n*-butyl-7'-iodo-2'-fluorenyl]phenyl}-1,2,4-

triazole (7): A mixture of 6 (1.88 g, 1.89 mmol), silver trifluoroacetate (1.25 g, 5.67 mmol), and iodine (1.15 g, 4.53 mmol) in chloroform (50 mL) was heated to reflux with stirring for 4 h. After cooling to RT, the reaction mixture was filtered through Celite and the filtrate was poured into sodium sulfite solution. The aqueous layer was extracted with dichloromethane (3×40 mL). The combined organic layer was dried over anhydrous Na2SO4 and evaporated to dryness. The crude product was purified by chromatography on a short silica-gel column with 20:1 dichloromethane:ethyl acetate as eluent followed by recrystallization from dichloromethane and MeOH to afford iodide 7 as a white solid in 97% yield (2.01 g). ¹H NMR (400 MHz, CDCl₃): $\delta = 7.68$ (d, J = 8.0 Hz, 2H), 7.64 (d, J=7.6 Hz, 4H), 7.58 (d, J=8.4 Hz, 4H), 7.47-7.53 (m, 11H), 7.43 (d, J=8.0 Hz, 2 H), 7.26 (d, J=6.8 Hz, 2 H), 1.98–1.90 (m, 8 H), 1.09–1.01 (m, 8H), 0.67–0.53 ppm (m, 20H); 13 C NMR (100 MHz, CDCl₃): $\delta =$ 154.5, 153.2, 150.8, 142.4, 140.1, 139.9, 139.3, 135.8, 135.3, 131.9, 130.1, 129.7, 129.0, 127.9, 127.0, 126.1, 125.5, 121.5, 121.0, 92.7, 55.3, 40.0, 25.8, 22.9, 13.7 ppm; MS (FAB): m/z: 1101.27 [M+].

4-*N*-Phenyl-3,5-bis[4-[9',9',9'',9'',ettra-*n*-butyl-7''-diphenylamino-2',7'-bifluorenyl]phenyl]-1,2,4-triazole (PhN-OF(2)-TAZ-OF(2)-NPh): The synthetic procedure for PhN-OF(1)-TAZ-OF(1)-NPh was followed using 7 (500 mg, 0.45 mmol), 4 (888 mg, 1.81 mmol), Pd(OAc)₂ (10 mg, 0.05 mmol), P(o-tolyl)₃ (31 mg, 0.10 mmol), 2M K₂CO₃ (3 mL), toluene (25 mL), and methanol (8 mL). The crude product was purified by silicagel column chromatography with 20:1 dichloromethane:ethyl acetate as eluent affording 639 mg (81%) of PhN-OF(2)-TAZ-OF(2)-NPh as a light yellow solid. ¹H NMR (400 MHz, CDCl₃): δ =7.79 (d, J=8.0 Hz, 2H), 7.77 (d, J=8.0 Hz, 4H), 7.69 (d, J=8.0 Hz, 2H), 7.67–7.52 (m,



Figure 9. Plot of output power versus input power of the three-photon pumped lasing process for **PhN-OF(3)-NPh** (a) and **PhN-OF(4)-NPh** (b).

25 H), 7.32–7.23 (m, 10 H), 7.15–7.13 (m, 10 H), 7.06–6.99 (m, 6 H), 2.08–1.89 (m, 16 H), 1.16–1.06 (m, 16 H), 0.77–0.68 ppm (m, 40 H); ¹³C NMR (100 MHz, CDCl₃): δ =154.6, 152.3, 151.7, 151.7, 151.4, 147.9, 147.1, 142.7, 140.7, 140.6, 140.2, 139.6, 139.4, 138.6, 135.8, 135.4, 130.1, 129.7, 129.1, 129.0, 128.0, 127.0, 126.0, 126.0, 125.4, 123.8, 123.4, 122.4, 121.2, 121.1, 120.3, 120.0, 119.3, 55.2, 55.0, 40.2, 39.9, 26.0, 26.0, 23.0, 23.0, 13.8, 13.8 ppm; HRMS (MALDI-TOF): *m*/*z*: 1737.0271 [*M*⁺]; elemental analysis (%) calcd for C₁₂₈H₁₂₉N₅: C 88.49, H 7.48, N 4.03; found: C 88.35, H 7.33, N 3.91.

4-N-Phenyl-3,5-bis{4-[9',9',9",9"-tetra-n-butyl-7"-trimethylsilyl-2',7'-bi-

fluorenyl]phenyl]-1,2,4-triazole (8): The synthetic procedure for PhN-OF(1)-TAZ-OF(1)-NPh was followed using 7 (0.94 mg, 0.85 mmol), 9,9di-*n*-butyl-7-(trimethylsilyl)-2-fluorenyl boronic acid (5; 0.99 g, 2.55 mmol), Pd(OAc)₂ (21 mg, 0.09 mmol), $P(o-tolyl)_3$ (55 mg, 0.18 mmol), 2M K₂CO₃ (4 mL), toluene (50 mL), and methanol (15 mL). The crude product was purified by silica-gel column chromatography with 20:1 dichloromethane:ethyl acetate as eluent affording 1.31 g (81%) of **8** as a white solid. ¹H NMR (400 MHz, CDCl₃): $\delta = 7.79-7.76$ (m, 5H), 7.71 (d, J=7.6 Hz, 2 H), 7.66–7.62 (m, 11 H), 7.58–7.48 (m, 15 H), 7.30 (m, 4H), 2.06-2.00 (m, 16H), 1.13-1.05 (m, 16H), 0.73-0.66 (m, 40H), 0.31 ppm (s, 18H); 13 C NMR (100 MHz, CDCl₃): $\delta = 154.6$, 151.7, 151.7, 150.1, 142.6, 141.3, 140.7, 140.3, 139.7, 138.6, 131.8, 130.1, 129.1, 128.0, 127.5, 127.0, 126.0, 125.9, 125.5, 121.4, 121.2, 120.0, 120.0, 118.9, 55.2, 55.0, 40.2, 39.9, 26.0, 23.0, 23.0, 13.8, 13.7, -0.85 ppm; MS (FAB): m/z: 1545.8 [M⁺].

4-N-phenyl-3,5-bis{4-[9',9',9",9"-tetra-*n*-butyl-7"-iodo-2',7'-bifluorenyl]-

phenyl]-1,2,4-triazole (9). The synthetic procedure for compound 7 was followed using 8 (580 mg, 0.37 mmol), silver trifluoroacetate (231 mg, 0.91 mmol), iodine (252 mg, 1.14 mmol), and chloroform (20 mL). The

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crude product was purified by chromatography on a short silica-gel column with 20:1 dichloromethane:ethyl acetate as eluent followed by recrystallization from dichloromethane and MeOH to afford iodide **9** as a brown solid in 90% yield (570 mg). ¹H NMR (400 MHz, CDCl₃): $\delta = 7.79-7.72$ (m, 6H), 7.67–7.45 (m, 29H), 7.29 (d, J = 8.0 Hz, 2H), 2.05–1.93 (m, 16H), 1.12–1.07 (m, 16H), 0.70–0.63 ppm (m, 40H); ¹³C NMR (100 MHz, CDCl₃): $\delta = 153.3$, 151.7, 151.7, 150.9, 142.6, 140.9, 140.6, 140.3, 139.9, 139.3, 138.7, 135.8, 135.4, 132.0, 130.1, 129.7, 129.1, 127.9, 127.0, 126.1, 126.1, 126.0, 125.9, 125.5, 121.4,121.3, 121.2, 120.1, 120.0, 92.4, 55.3, 55.2, 40.2, 40.0, 26.0, 25.9, 23.0, 23.0, 13.8, 13.7 ppm; MS (FAB): m/z: 1653.9 [M+].

4-N-Phenyl-3,5-bis{4-[9',9',9'',9'',9''',9'''-hexa-*n*-butyl-7'''-diphenylamino-

2',7',2"-terfluorenyl]phenyl}-1,2,4-triazole (PhN-OF(3)-TAZ-OF(3)-NPh): The synthetic procedure for PhN-OF(1)-TAZ-OF(1)-NPh was followed using 9 (520 mg, 0.31 mmol), 4 (615 mg, 1.26 mmol), Pd(OAc)₂ (7 mg, 0.03 mmol), P(o-tolyl)₃ (18 mg, 0.06 mmol), 2м K₂CO₃ (3 mL), toluene (25 mL), and methanol (8 mL). The residue was purified by silica-gel column chromatography with 20:1 dichloromethane:ethyl acetate as eluent affording 554 mg (77%) of PhN-OF(3)-TAZ-OF(3)-NPh as a light yellow solid. ¹H NMR (400 MHz, CDCl₃): $\delta = 7.82-7.77$ (m, 8H), 7.70– 7.52 (m, 34H), 7.31–7.23 (m, 12H), 7.14 (d, J=7.2 Hz, 9H), 7.05–6.99 (m, 6H), 2.09-1.91 (m, 24H), 1.17-1.08 (m, 24H), 0.77-0.68 ppm (m, 60H); ¹³C NMR (100 MHz, CDCl₃): $\delta = 154.6$, 152.3, 151.8, 151.7, 151.4, 151.3, 150.9, 147.9, 147.1, 142.6, 140.7, 140.6, 140.4, 140.2, 140.1, 140.1, 139.8, 139.7, 139.5, 138.6, 135.9, 135.4, 130.1, 129.7, 129.1, 129.1, 128.0, 127.0, 126.7, 126.1, 126.0, 126.0, 125.5, 123.8, 123.4, 122.9, 122.4, 121.3, 121.2, 121.2, 121.1, 120.3, 120.0, 119.9, 54.2, 54.2, 54.0, 39.2, 38.9, 28.6, 25.0, 25.0, 22.0, 22.0, 12.8, 12.8 ppm; HRMS (MALDI-TOF): *m/z*: 2289.4063 [*M*⁺]; elemental analysis (%) calcd for $C_{170}H_{177}N_5;\ C$ 89.15, H 7.79, N 3.06; found: C 88.78, H 7.75, N 2.88.

4-N-Phenyl-3,5-di-{4-[9',9',9'',9''',9'''-hexa-*n*-butyl-7'''-trimethylsilyl-

2',7',2"-terfluorenyl]phenyl]-1,2,4-triazole (10): The synthetic procedure for **PhN-OF(1)-TAZ-OF(1)-NPh** was followed using **8** (1.07 g, 0.65 mmol), 9,9-di-*n*-butyl-7-(trimethylsilyl)-2-fluorenylboronic acid (**5**, 0.75 g, 1.94 mmol), Pd(OAc)₂ (15 mg, 0.07 mmol), P(*o*-tolyl)₃ (40 mg, 0.13 mmol), $2 \le CO_3$ (4 mL), toluene (50 mL), and methanol (12 mL). The residue was purified by silica-gel column chromatography with 20:1 dichloromethane:ethyl acetate as eluent affording 1.06 g (78%) of **10** as a white solid. ¹H NMR (400 MHz, CDCl₃): δ = 7.81–7.77 (m, 10H), 7.71–7.62 (m, 21H), 7.59–7.48 (m, 16H), 7.31–7.28 (dd, *J*=8.0 Hz, 1.6 Hz, 2H), 2.11–2.00 (m, 24H), 1.16–1.06 (m, 24H), 0.77–0.67 (m, 60H), 0.31 ppm (s, 18H); ¹³C NMR (100 MHz, CDCl₃): δ = 154.6, 151.7, 151.7, 151.6, 150.1, 142.6, 141.3, 140.6, 140.6, 140.4, 140.3, 140.2, 139.9, 139.7, 139.0, 138.6, 135.4, 131.8, 130.1, 129.7, 129.1, 127.9, 127.5, 127.0, 126.0, 125.9,125.5, 121.4,121.2, 120.1, 119.9, 118.9, 55.2, 55.2, 55.0, 40.2, 39.9, 26.0, 23.0, 23.0, 13.8, 13.7 ppm; MS (FAB): *m*/z: 2098.7 [*M*⁺].

4-N-Phenyl-3,5-bis[**4-**[**9**',**9**'',**9**'',**9**'',**9**''',**e**'''-hexa-*n*-butyl-7'''-iodo-2',7',2''-terfluorenyl]phenyl]-1,2,4-triazole (11): The synthetic procedure for **8** was followed using **10** (1.00 mg, 0.48 mmol), silver trifluoroacetate (0.32 mg, 1.43 mmol), iodine (0.29 mg, 1.14 mmol), and chloroform (40 mL). The crude product was purified by chromatography on a short silica-gel column with 20:1 dichloromethane:ethyl acetate as eluent followed by recrystallization from CH₂Cl₂ and MeOH affording iodide **11** as a brown solid in 96% yield (1.01 g). ¹H NMR (400 MHz, CDCl₃): δ =7.82–7.74 (m, 10H), 7.68–7.52 (m, 36H), 7.53 (d, *J*=7.6 Hz, 2H), 2.09–2.00 (m, 24H), 1.18–1.09 (m, 24H), 0.79–0.65 ppm (m, 60H); ¹³C NMR (100 MHz, CDCl₃): δ =153.6, 152.3, 150.7, 150.7, 149.8, 141.6, 140.0, 139.6, 139.5, 139.3, 139.1, 138.1, 138.9, 138.7, 138.2, 137.7, 134.8, 134.4, 131.0, 129.1, 128.7, 128.1, 126.9,126.0, 125.1, 125.0, 124.5, 120.4, 120.2, 120.2, 119.0, 119.0, 119.0, 91.4, 54.3, 54.2, 54.2, 39.2, 39.1, 39.0, 25.0, 25.0, 24.9, 22.0, 22.0, 12.8, 12.8 ppm; MS (FAB): *m/z*: 2206.7 [*M*⁺].

4-*N*-Phenyl-5-(4-*tert*-butylphenyl)-3-{4-[9',9',9'',9''',9''',9''',9''',9'''',9'''',9''''-octa*n*-butyl-7''''-diphenylamino-2',7',2'',7''',2'''-quaterfluorenyl]phenyl}-1,2,4-triazole (PhN-OF(4)-TAZ-OF(4)-NPh): The synthetic procedure for PhN-OF(1)-TAZ-OF(1)-NPh was followed using 11 (500 mg, 0.23 mmol), 4 (333 mg, 0.68 mmol), Pd(OAc)₂ (5 mg, 0.02 mmol), P(o-tolyl)₃ (14 mg, 0.05 mmol), 2M K₂CO₃ (3 mL), toluene (30 mL), and methanol (8 mL). The residue was purified by silica-gel column chromatography with 20:1 dichloromethane:ethyl acetate as eluent affording 560 mg (87%) of **PhN-OF(4)-TAZ-OF(4)-NPh** as a light yellow solid. ¹H NMR (400 MHz, CDCl₃): δ = 7.84–7.78 (m, 12 H), 7.71–7.53 (m, 42 H), 7.32–7.24 (m, 11 H), 7.15–7.14 (m, 10 H), 7.06–6.99 (m, 6H), 2.11–1.90 (m, 32 H), 1.19–1.08 (m, 32 H), 0.79–0.69 ppm (m, 80 H); ¹³C NMR (100 MHz, CDCl₃): δ = 154.7, 152.3, 151.8, 151.7, 151.4, 151.4, 150.9,147.9,147.1, 142.6, 140.7, 140.7, 140.6, 140.4, 140.3, 140.3, 140.1, 140.0, 139.9, 139.8, 139.7, 139.5, 138.7, 135.9, 135.5, 130.1, 129.8, 129.1, 129.1, 128.0, 127.0, 126.1, 126.0, 125.5, 123.8, 123.4, 122.9, 122.5, 121.4, 121.3, 121.2, 121.1, 120.3, 120.1, 129.9, 129.9, 129.7, 129.3, 55.2, 55.2, 55.0, 40.2, 40.0, 26.1, 26.0, 23.0, 23.0, 13.9, 13.8 ppm; HRMS (MALDI-TOF): *m/z* 2842.7779 [*M*⁺]; elemental analysis (%) calcd for C₂₁₂H₂₂₅N₅: C 89.56, H 7.98, N 2.46; found: C 89.67, H 7.93, N 2.44.

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