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Fluorene-Based π-Conjugated Oligomers for Efficient Three-Photon Excited Photoluminescence and Lasing

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Abstract: A novel series of diphenylamino- and 1,2,4-triazole-end-capped, fluorene-based, π-conjugated oligomers that includes extended oligofluorenes and oligothienylfluorenes has been synthesized by means of the 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 a key step. It was demonstrated that efficient two- and three-photon excited photoluminescence and lasing in the blue region are obtained by pumping near-infrared femtosecond lasers on these materials. Although the absorption and emission maxima of the highly fluorescent and extended oligofluorenes reach a saturation limit, there exists an effective conjugation length for an optimum three-photon absorption cross section in the homologous oligofluorene series. On the other hand, the multiphoton excited emission spectrum and lasing wavelength can easily be modified or tuned by an incorporation of thienyl unit(s) into the fluorene-based π-conjugated core with which exceptionally large three-photon absorption cross sections up to $3.59\times10^{-77}\,\mathrm{cm^6\,s^2}$ in the femtosecond regime have been obtained, thereby highlighting the potential of this series of photonic materials. The optimized full width at half-maximum of the cavityless three-photon upconverted blue lasing spectra are sharply narrowed to approximately 6 nm with an efficiency of up to 0.013 %.

Keywords: absorption · laser chemistry · luminescence · oligofluorenes · photochemistry

Introduction

Multiphoton absorption, mainly two-photon and three-photon absorption, has drawn considerable interest over the years due to its potential applications in various optoelectronics and photonics capacities. Owing to the use of the long-wavelength/low-energy excitation source and the characteristics of the intensity dependence of the multiphoton absorption process, multiphoton absorption offers many advantages for the technological applications of high-capacity data storage,[1] three-dimensional microfabrication,[2] biological imaging,[3] photodynamic therapy,[4] and frequency-upconverted lasing.[5] Three-photon absorption may be more advantageous than two-photon absorption because of the use of a longer excitation wavelength and the cubic dependence of the input light intensity, which give rise to a better spatial confinement of the excitation volume. In contrast to the tremendous effort spent on the investigation of two-photon-absorption properties over the past decades, there have been only a few studies on the structure–property relationships for three-photon-absorption.[6] In principle, donor–acceptor chromophores possessing a highly polarizable π-conjugated system are highly two-photon-absorption active; however, it is not guaranteed that they will exhibit an interesting and useful three-photon-absorption property and can be used for applications such as frequency-upconverted lasing. To exhibit multiphoton-absorption upconverted lasing, molecules are required to possess high-fluorescence quantum efficiency, a significant multiphoton absorption cross section, and low fluorescent reabsorption, which could affect the lasing threshold and the attainment of optical

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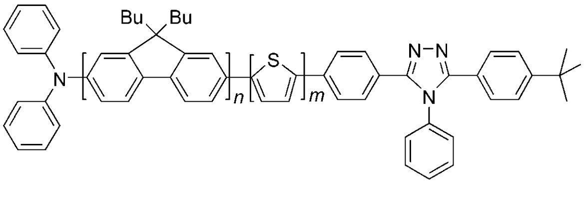
gain. As a result, only a few multiphoton-excited (and in particular, three-photon-excited) fluorescent molecules can exhibit frequency-upconverted lasing.[5]

Because of their excellent chemical, thermal, and photochemical stabilities, as well as the ease of structural tuning to adjust their electronic and morphological properties, fluorene-based functional molecules/materials constituting one of the important classes of π-conjugated molecular materials have recently drawn considerable attention for their potential applications in optoelectronic devices, particularly for blue-emitting organic light emitting diodes (OLED).[7] Electron-deficient triazole (TAZ) derivatives have been found useful as a thermally stable and efficient electron-transporting and hole-blocking material in OLEDs;[8] however, their potential use as a photonic material has been rarely explored. On account of its electron-deficient nature, the triazole moiety could play the functional role in an electron-accepting group when coupled with a strong electron donor, that is, a diphenylamino group, thereby giving rise to a donor–acceptor chromophore.

We have recently demonstrated efficient multiphoton-excited deep blue photoluminescence and lasing on a homologous series of diphenylamino- and 1,2,4-triazole-end-capped, π-conjugated oligofluorenes (OFs), *p*-Ph_2N-OF(*n*)-TAZ ($n=2$–4), in which the multiphoton-excited emission and lasing wavelengths are independent of the oligofluorenyl length. However, the three-photon absorption cross section and the lasing efficiency increase with a change in the oligofluorenyl unit from bifluorene to quarterfluorene.[9] To continue our investigation on the structure–multiphoton-absorption property correlations of functional materials including upconverted emission properties, the multiphoton absorption cross section, wavelength dependence of the three-photon-absorption cross section, and upconverted lasing properties, we report herein the synthesis and structure–multiphoton-absorption property relationships of a new series of fluorene-based π-conjugated oligomers including pentafluorene, sexifluorene (*p*-Ph_2N-OF(*n*)-TAZ, in which $n=5$ and 6, respectively), and oligothienylfluorenes, *p*-Ph_2N-OF(*n*)OT(*m*)-TAZ, asymmetrically disubstituted with diphenylamino and 1,2,4-triazole end-caps.



p-Ph_2N-OF(*n*)OT(*m*)-TAZ

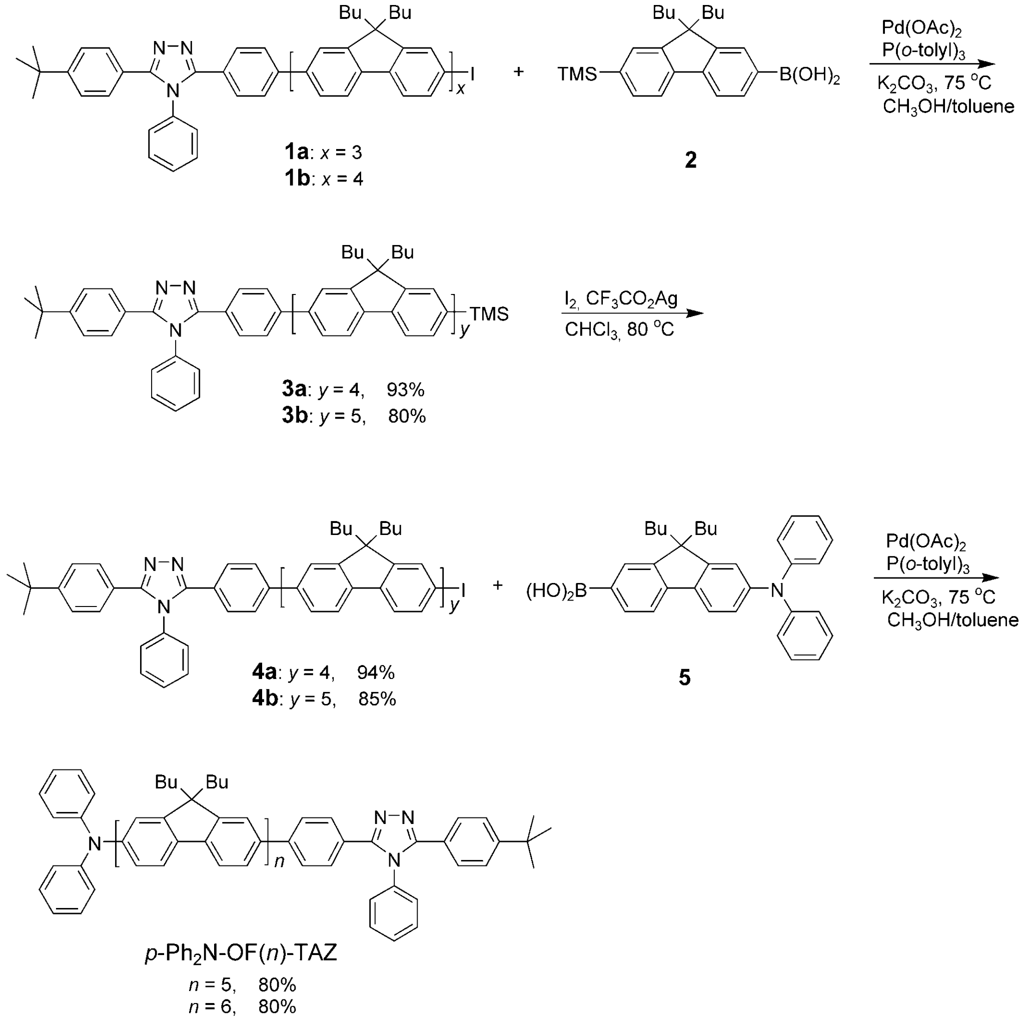
In this contribution, we have demonstrated that the multiphoton-excited emission spectrum and lasing wavelength can easily be modified or tuned by an incorporation of thienyl unit(s) into a fluorene-based, π-conjugated core with diphenylamino and 1,2,4-triazole end-caps. Importantly, thienylfluorene-derived oligomers exhibit remarkably large three-photon-absorption cross sections up to $3.59\times10^{-77}\,cm^6\,s^2$ at 1270 nm, which is the highest value measured in the femtosecond regime so far. In addition, the highest cavityless three-photon-upconverted blue-lasing efficiency of 0.013 % was achieved by using *p*-Ph_2N-OF(5)-TAZ.

Results and Discussion

Synthesis: The previously developed convergent approach[7e] was used to synthesize the highly extended, asymmetrically disubstituted diphenylamino- and 1,2,4-triazole-end-capped, fluorene-based, π-conjugated oligomers that include pentafluorene and sexifluorene (*p*-Ph_2N-OF(*n*)-TAZ, in which $n=5$ and 6, respectively), and oligothienylfluorenes (*p*-Ph_2N-OF(*n*)OT(*m*)-TAZ). The synthetic routes to these compounds are outlined in Schemes 1 and 2. Palladium-catalyzed Suzuki cross-coupling of 9,9-dibutyl-7-(diphenylamino)-2-fluorenylboronic acid (**5**) and the corresponding 1,2,4-triazole-based aryl halide was employed as a key step to synthesize the target oligomers.

Palladium-catalyzed Suzuki cross-coupling of triazole-substituted terfluorene iodide **1a** and trimethylsilylfluorenylboronic acid **2** by using $Pd(OAc)_2/2\,P(o\text{-tolyl})_3$ as a catalyst afforded triazole-substituted trimethylsilylquaterfluorene **3a** in excellent yield (93 %). Iododesilylation of **3a** was performed in the presence of silver trifluoroacetate at 80 °C, thereby giving the corresponding iodide **4a** in 94 % yield. Suzuki cross-coupling of iodide **4a** and boronic acid **5** gave the desired *p*-Ph_2N-OF(5)-TAZ in 80 % yield. Following a similar reaction sequence for the preparation of the intermediates, the higher homologue *p*-Ph_2N-OF(6)-TAZ was readily synthesized by the cross-coupling of boronic acid **5** and iodide **4b** in 80 % yield.

Palladium-catalyzed Suzuki cross-coupling of the bromide **6** and 2-thienylboronic acid **7** yielded the 1,2,4-triazole derivative **8** in 82 % yield. Bromination of **8** with *N*-bromosuccinimide (NBS) in $CHCl_3$ heated at reflux gave bromide **9** in 87 % yield. Suzuki cross-coupling bromide **9** and boronic acid **5** afforded *p*-Ph_2N-OFOT-TAZ in 82 % yield. In a similar fashion, the cross-coupling of triazole-substituted fluorene iodide **10** and boronic acid **7** gave triazole-substituted fluorenylthiophene **11** in an excellent yield. NBS bromination of **11** afforded the corresponding bromide **12** in a quantitative yield. Suzuki cross-coupling of **11** and **5** afforded *p*-Ph_2N-OFOTOF-TAZ in a moderate yield. On the other hand, palladium-catalyzed Kumada cross-coupling of bromide **12** and the freshly prepared thienylmagnesium bromide in THF afforded triazole-substituted fluorenylbithiophene **13**, which was iodinated by *N*-iodosuccinimide (NIS), thereby giving the corresponding iodide **14** in 89 % yield. Suzuki cross-coupling of **14** and **5** gave the desired *p*-Ph_2N-OFOT(2)OF-TAZ in 68 % yield. All the newly synthesized, asymmetrically disubstituted dipolar oligofluorenes were fully characterized with ^1H and ^{13}C NMR spectroscopy,



Scheme 1. Synthesis of asymmetrically disubstituted diphenylamine and 1,2,4-triazole pentafluorene (p-Ph$_2$N-OF(5)-TAZ) and sexifluorene (p-Ph$_2$N-OF(6)-TAZ).

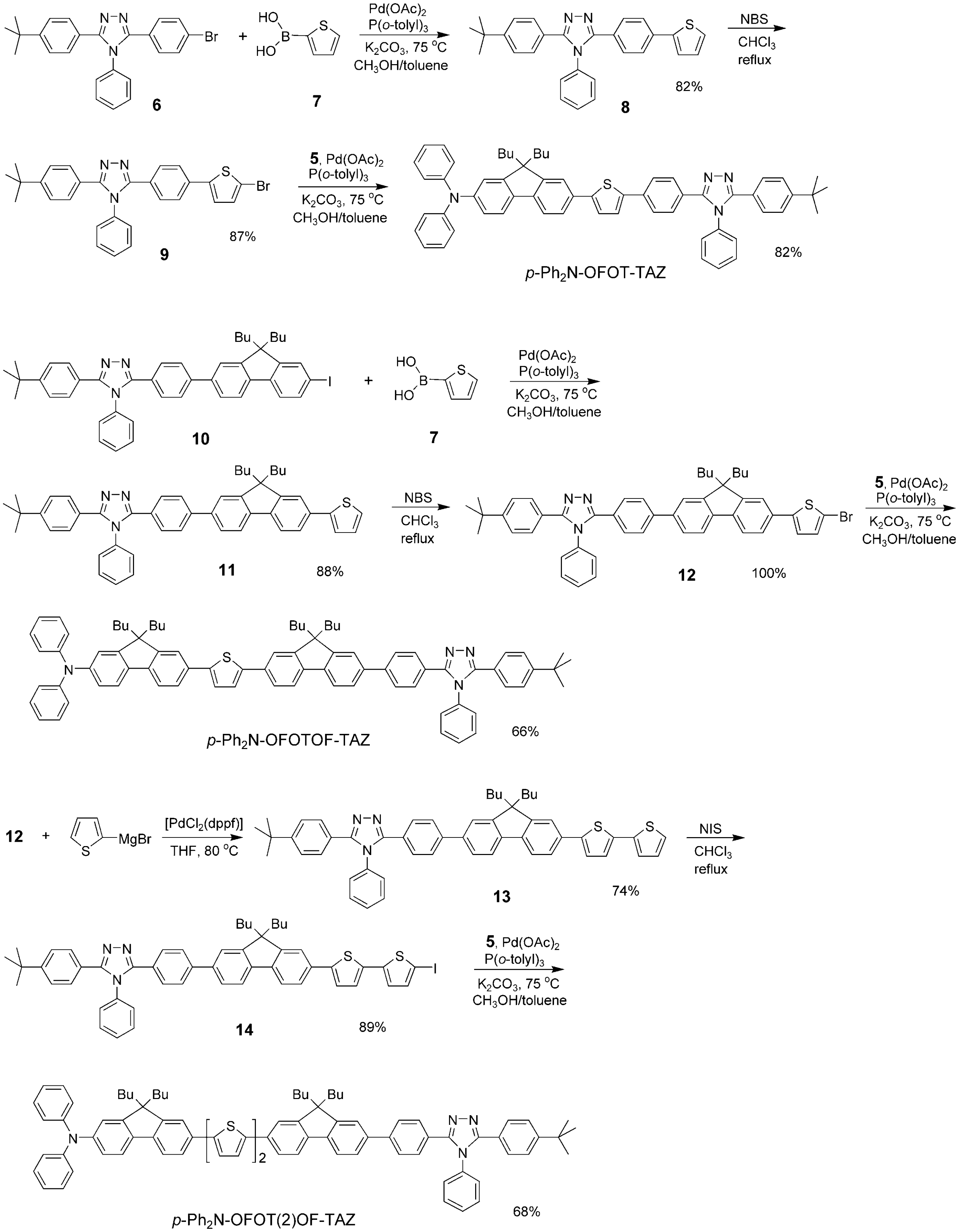
MALDI-TOF HRMS, and elemental analysis, and were found to be in good agreement with their structures. The thermal properties of the newly synthesized oligomers were examined by thermogravimetric analysis (TGA) under nitrogen. All the oligomers showed very high thermal stabilities with decomposition temperatures (T_d) greater than 450 °C, which is a prerequisite for high-energy laser pumping.

Linear optical properties: The linear and nonlinear optical properties of the newly synthesized donor–acceptor oligomers measured in toluene are summarized in Table 1. All these fluorene-based oligomers show very similar spectral features, which are composed of two major absorption bands. The weak absorption peak appears around 300–310 nm and is attributed to the n→π* transition of triarylamine moieties, and the broad absorption band spanning

Table 1. Summary of linear optical measurements of p-Ph$_2$N-OF(n)-TAZ and p-Ph$_2$N-OF(n)OT(m)-TAZ in various solvents and their thermal properties.

	$\lambda_{max}^{abs\,[a]}$ [nm] (ε [$\times10^4$ M^{-1}cm^{-1}])	$\lambda_{max}^{em\,[a]}$ [nm]	Φ_{FL}[a,b]	$\lambda_{max}^{abs\,[c]}$ [nm] (ε [$\times10^4$ M^{-1}cm^{-1}])	$\lambda_{max}^{em\,[c]}$ [nm]	Φ_{FL}[b,c]	$\lambda_{max}^{abs\,[d]}$ [nm] (ε [$\times10^4$ M^{-1}cm^{-1}])	$\lambda_{max}^{em\,[d]}$ [nm]	Φ_{FL}[b,d]	T_{dec}[e] [°C]
p-Ph$_2$N-OF(5)-TAZ	378 (18.66)	421	0.95	379 (19.30)	436	0.86	384 (20.55)	470	0.80	460
p-Ph$_2$N-OF(6)-TAZ	379 (22.02)	420	0.99	380 (23.40)	435	0.86	385 (21.92)	470	0.82	456
p-Ph$_2$N-OFOT-TAZ	397 (6.16)	452	0.61	398 (5.82)	487	0.54	397 (6.00)	538	0.63	508
p-Ph$_2$N-OFOTOF-TAZ	403 (8.43)	454	0.67	403 (8.34)	471	0.61	406 (9.08)	506	0.64	450
p-Ph$_2$N-OFOT(2)OF-TAZ	415 (6.89)	483	0.40	416 (7.79)	488	0.37	418 (7.53)	523	0.34	488

[a] Measured in toluene (≈10^{-5} M). [b] Using quinine sulfate monohydrate ($\Phi_{350}=0.58$) as a standard. [c] Measured in CHCl$_3$ (≈10^{-5} M). [d] Measured in DMF (ca. 10^{-5} M). [e] Determined by using a thermal gravimetric analyzer with a heating rate of 10 °C min^{-1} under N$_2$.



Scheme 2. Synthesis of asymmetrically disubstituted diphenylamine and 1,2,4-triazole oligothienylfluorenes, p-Ph$_2$N-OF(n)OT(m)-TAZ.

from 378–415 nm corresponds to the π→π* transition of the fluorene-based π-conjugated core (Figure 1). In general, the absorption spectra of these donor–acceptor fluorene-based oligomers do not show a significant solvatochromic effect. In contrast, the fluorescence spectra are solvent dependent, which is to say the spectra become structureless and exhibit large redshifts (40–70 nm) with an increase in solvent polarity (Figure 2). This indicates the dipolar or charge-transfer character of these oligomers in the first excited states.

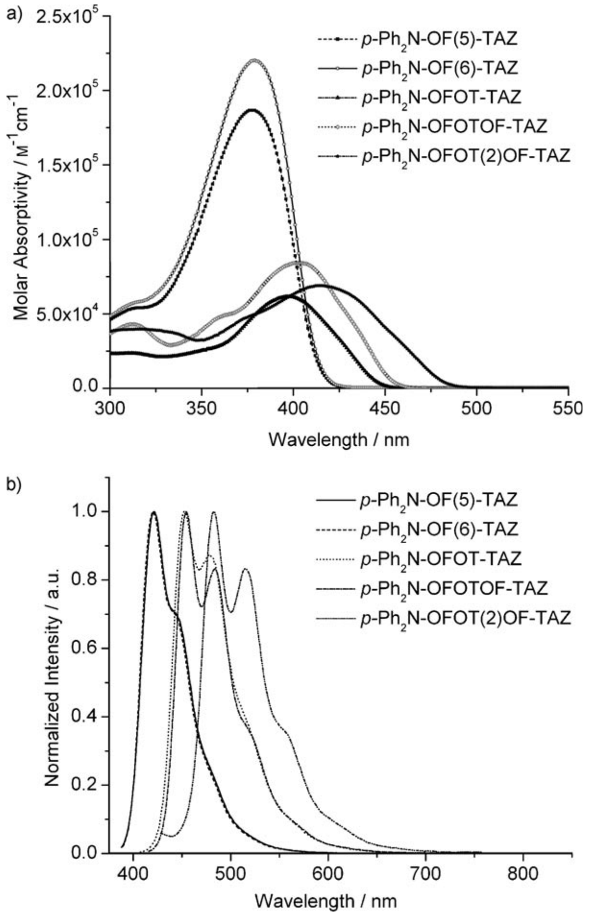


Figure 1. Absorption (a) and fluorescence (b) spectra of *p*-Ph$_2$N-OF(*n*)-TAZ and *p*-Ph$_2$N-OF(*n*)OT(*m*)-TAZ in toluene.

Furthermore, as seen from the absorption and fluorescence spectra of the homologous oligofluorene series *p*-Ph$_2$N-OF(*n*)-TAZ, in which $n=2$–6 in different solvents, the molar absorptivity continues to increase and the fluorescence quantum yield (Φ_{FL}) remains very high with an extension of the oligomeric length; however, the absorption and emission maxima show a trend of saturation for the newly synthesized pentafluorene and sexifluorene, thereby indicating that the effective conjugation length for the optical gap is reached in this end-capped oligofluorene series. On the other hand, the fluorescence quantum yields of the series generally decrease concomitantly with an increase in the solvent polarity.

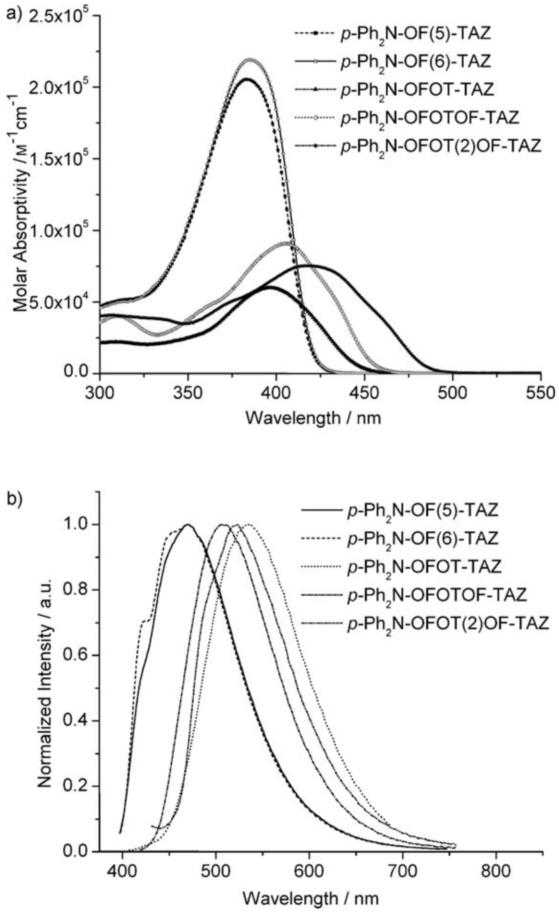


Figure 2. Absorption (a) and fluorescence (b) spectra of *p*-Ph$_2$N-OF(*n*)-TAZ and *p*-Ph$_2$N-OF(*n*)OT(*m*)-TAZ in DMF.

Upon replacing the fluorenyl with the thienyl ring(s) in the π-conjugated core, the absorption and fluorescence spectra of *p*-Ph$_2$N-OF(*n*)OT(*m*)-TAZ redshift substantially with $\Delta\lambda_{\text{max}}$ in the range of 20–65 nm relative to those of the corresponding *p*-Ph$_2$N-OF(*n*)-TAZ (e.g., *p*-Ph$_2$N-OFOT-TAZ: $\lambda_{\text{max}}^{\text{abs}}=397$ nm and $\lambda_{\text{max}}^{\text{em}}=452$ nm vs. *p*-Ph$_2$N-OF(2)-TAZ: $\lambda_{\text{max}x}^{\text{abs}}=375$ nm and $\lambda_{\text{max}}^{\text{em}}=424$ nm in toluene). Although the fluorescence quantum yields of this *p*-Ph$_2$N-OF(*n*)OT(*m*)-TAZ series are scarcely affected by various solvents, they are significantly smaller (40–67 %) than the corresponding *p*-Ph$_2$N-OF(*n*)-TAZ series (86–89 %), which is attributable to the increased nonradiative decay through intersystem crossing caused by the heavy-atom effect of sulfur.[10]

Multiphoton-absorption properties: The multiphoton-absorption photoluminescence and lasing properties were investigated by using a femtosecond pulsed laser as an excitation source. The results of the multiphoton-absorption measurements are tabulated in Table 2. The newly synthesized donor–acceptor fluorene-based, π-conjugated oligomers show not only two-photon-induced photoluminescence (PL) when excited at 800 nm but also strong three-photon-upconverted PL when excited at 1.3 μm. The two-photon- and three-photon-upconverted PL spectral characteristics are

Table 2. Summary of nonlinear optical measurements of *p*-Ph_2N-OF(*n*)-TAZ and *p*-Ph_2N-OF(*n*)OT(*m*)-TAZ.

	2PA λ_{max}^{em} [a,b] [nm]	2PA λ_{lasing} [a,b] [nm]	3PA λ_{max}^{em} [a,c] [nm]	σ_3 [a,c,d] [$cm^6 s^2$]	3PA λ_{lasing} [a,c] [nm]	3PA lasing efficiency[a,c] [%]
p-Ph_2N-OF(5)-TAZ	447	447	449	5.27×10^{-79}	445	0.013
p-Ph_2N-OF(6)-TAZ[e]	449	452	452	1.38×10^{-79}[f]	448	–
p-Ph_2N-OFOT-TAZ	488	484	488	9.66×10^{-78}	482	0.0013
p-Ph_2N-OFOTOF-TAZ	489	–	487	2.35×10^{-78}	–	–
p-Ph_2N-OFOT(2)-TAZ	520	–	520	2.03×10^{-78}	–	–

[a] Measured in toluene using 10^{-2} M. [b] Excited at 800 nm femtosecond laser pulses [c] Excited at 1.34 μm femtosecond laser pulses. [d] Determined by using an optical limiting method using femtosecond laser pulses. [e] Measured using 5×10^{-3} M. [f] Determined by a comparative method using *p*-Ph_2N-OF(5)-TAZ as a standard.

very similar to those of one-photon excited counterparts (Figure 3), thereby suggesting that their emission states should be the same. Compared with the one-photon emission spectra, the two- and three-photon excited fluorescence spectra consistently show a small redshift at high concentration likely due to the reabsorption effect. To determine the three-photon-absorption cross sections (σ_3), an optical limiting method[6d] using 1.34 μm-femtosecond laser pulses in toluene (10^{-2} M) were carried out. Interestingly, the extended oligofluorenes *p*-Ph_2N-OF(5)-TAZ and *p*-Ph_2N-OF(6)-TAZ show a progressive decrease in σ_3, with values of 5.27×10^{-79} and 1.38×10^{-79} $cm^6 s^{-2}$, respectively, relative to that of their lower homologue *p*-Ph_2N-OF(4)-TAZ (σ_3=2.48×10^{-78} $cm^6 s^{-2}$),[9] even though their absorption and emission maxima reach the convergent limit. These findings suggest that an optimal oligofluorenyl length exists for σ_3 in this series. Figure 4 (left) shows the three-photon-absorption cross-section spectra of *p*-Ph_2N-OF(*n*)OT(*m*)-TAZ measured by comparing the fluorescence intensity excited from 1100 to 1600 nm with that of the investigated molecule excited at 1.34 μm, at which σ_3 was obtained by the optical limiting method. It is important to note that upon replacing

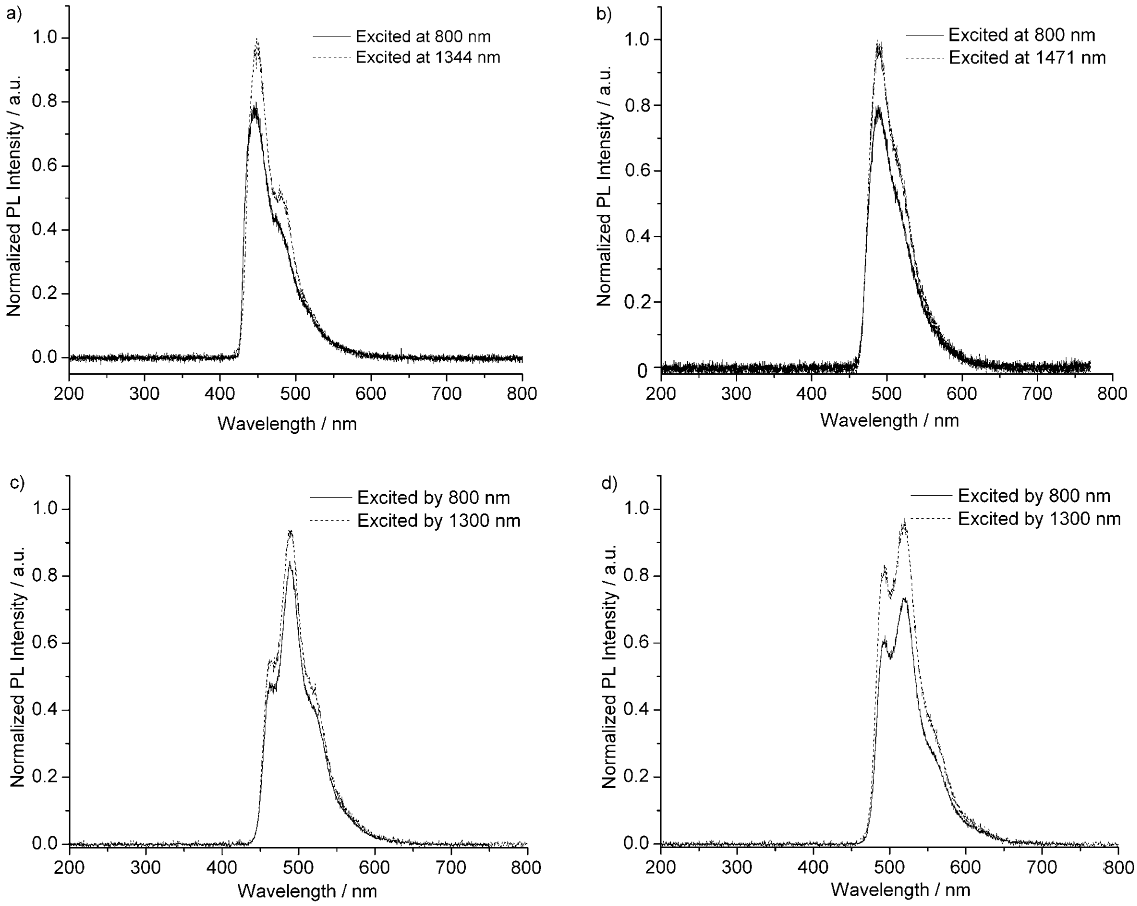


Figure 3. Comparison of photoluminescence spectra of a) *p*-Ph_2N-OF(5)-TAZ, b) *p*-Ph_2N-OFOT-TAZ, c) *p*-Ph_2N-OFOTOF-TAZ, and d) *p*-Ph_2N-OFOT(2)OF-TAZ excited by two- and three-photon excitation in toluene. One of the photoluminescence spectra is offset for clarity.

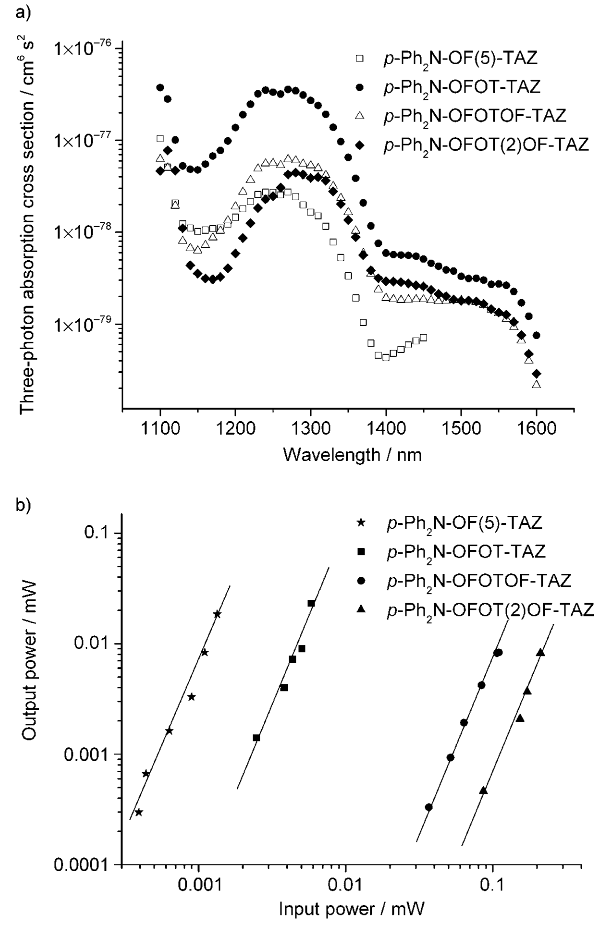


Figure 4. a) Three-photon-absorption cross-section spectra of *p*-Ph_2N-OF(5)-TAZ and *p*-Ph_2N-OF(*n*)OF(*m*)-TAZ measured by using a comparative method. b) Logarithmic plots of the power dependence of relative three-photon-induced fluorescence on pulse intensity using an infrared femtosecond laser as the exciting source for *p*-Ph_2N-OF(5)-TAZ and *p*-Ph_2N-OF(*n*)OT(*m*)-TAZ.

fluorenyl unit(s) with thienyl unit(s) into a π-conjugated core, σ_3 is substantially enhanced relative to the corresponding oligofluorene counterparts (Table 2), with σ_3 values up to $3.59\times10^{-77}\,cm^6s^2$ at 1270 nm for *p*-Ph_2N-OFOT-TAZ (Figure 4, left), which is the highest value ever measured in the femtosecond regime. These results also suggest that the thienyl moiety is a useful and effective structure unit to enhance the three-photon-absorption cross section. The increased nonlinearity is attributed to the enhanced electron delocalization and intramolecular charge transfer of an entire thiophene-incorporated π-conjugated system relative to that of the corresponding oligofluorene, which is consistent with the redshift of the absorption and emission spectra. This also provides a means to tune the three-photon-excited emission wavelengths and cross sections of the oligomers. The power-cubic dependence of three-photon-excited fluorescence for *p*-Ph_2N-OF(5)-TAZ and *p*-Ph_2N-OF(*n*)OT(*m*)-TAZ at 1.3 or 1.5 μm has a gradient in the range of 2.97–3.14, as shown in Figure 4 (right), which directly gives the experimental evidence of a three-photon excitation process.

Upon pumping femtosecond laser pulses at 800 nm, *p*-Ph_2N-OF(*n*)-TAZ ($n=5$ and 6) exhibit remarkable two-photon-upconverted blue lasing. The two-photon-excited lasing spectra of these extended oligofluorenes were very similar in which the lasing spectra are significantly narrowed (FWHM ≈ 12 nm), even though such an upconversion at 800 nm is not an optimum condition for the two-photon-excited process. Interestingly, *p*-Ph_2N-OFOT-TAZ also exhibits spectral narrowing (FWHM = 17 nm) and lasing upon pumping at 800 nm; however, the other oligothienylfluorenes, *p*-PhN-OFOTOF-TAZ and *p*-PhN-OFOT(2)OF-TAZ, only show two-photon-excited photoluminescence, which is attributed to their decreased fluorescence quantum yields.

Consistently, *p*-Ph_2N-OF(5)-TAZ, *p*-Ph_2N-OF(6)-TAZ, and *p*-Ph_2N-OFOT-TAZ also exhibit remarkable three-photon-upconverted blue lasing with peaks at 445, 449, and 482 nm, respectively, upon pumping femtosecond laser pulses at 1.34 μm. Figure 5 shows the plot of the full width at half-maximum (FWHM) of three-photon-upconverted PL and lasing spectra with various excitation wavelengths for *p*-Ph_2N-OFOT-TAZ. As shown in Figure 6, the three-photon-upconversion lasing spectra of *p*-Ph_2N-OF(5)-TAZ, *p*-Ph_2N-OF(6)-TAZ, and *p*-Ph_2N-OFOT-TAZ are sharply narrowed relative to their respective PL spectra. The optimized FWHM of the lasing spectra is 5.5 nm for *p*-Ph_2N-OF(5)-TAZ, 6.5 nm for *p*-Ph_2N-OF(6)-TAZ, and 6.2 nm for *p*-Ph_2N-OFOT-TAZ. Figure 7 shows the plot of the output versus input power relation for *p*-Ph_2N-OF(5)-TAZ, thereby clearly indicating the lasing threshold behavior. Despite the smaller three-photon-absorption cross-sections for *p*-Ph_2N-OF(5)-TAZ, its three-photon-upconverted cavityless lasing efficiency is still very high, thus making it as efficient as that of *p*-Ph_2N-OF(4)-TAZ.[9] Because of its poor solubility and photostability, the lasing efficiency of *p*-Ph_2N-OF(6)-TAZ could not be determined. On the other hand, *p*-Ph_2N-OFOT-TAZ showed rather low three-photon-upconverted

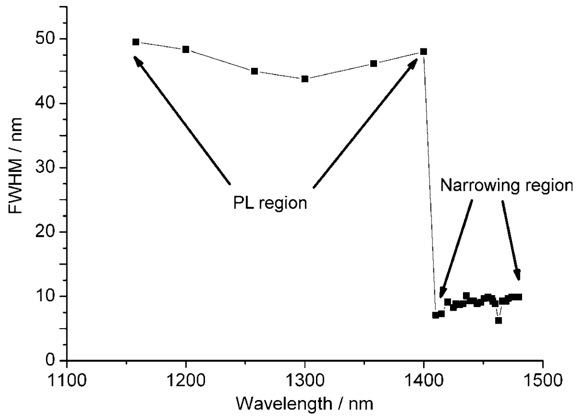


Figure 5. Plots of full width at half-maximum (FWHM) of emission spectra of *p*-Ph_2N-OFOT-TAZ versus excitation wavelength.

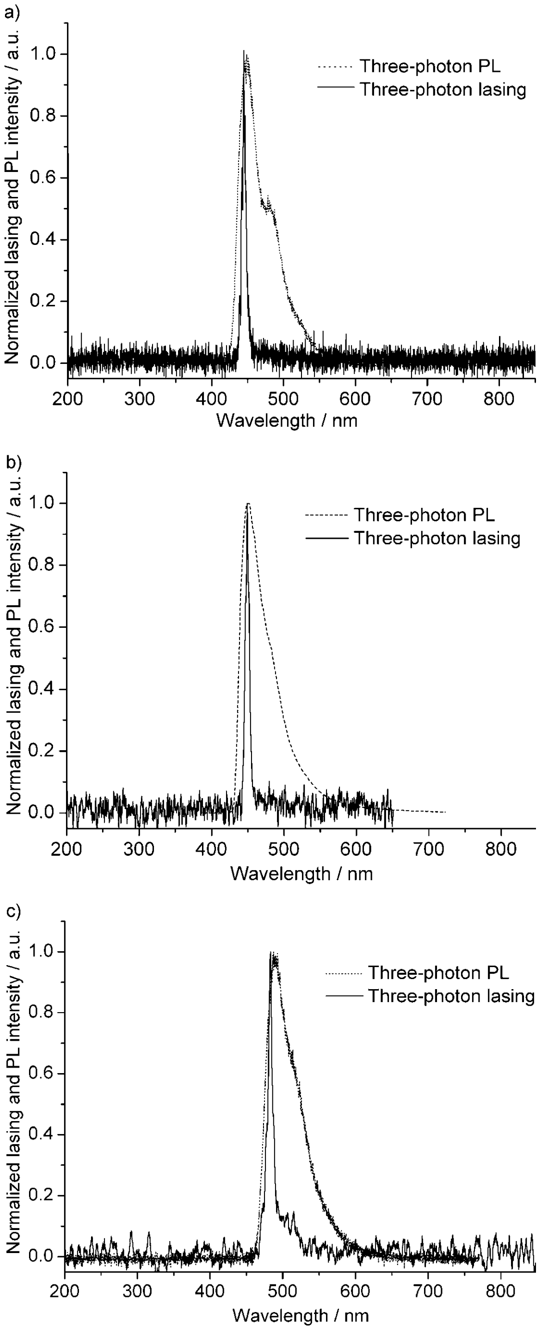


Figure 6. Three-photon-upconversion photoluminescence and lasing spectra of p-Ph$_2$N-OF(5)-TAZ (a) and p-Ph$_2$N-OF(6)-TAZ (b) pumped at 1.34 μm, and p-Ph$_2$N-OFOT-TAZ (c) pumped at 1.48 μm.

lasing efficiency, which is attributed to its reduced fluorescence quantum yield.

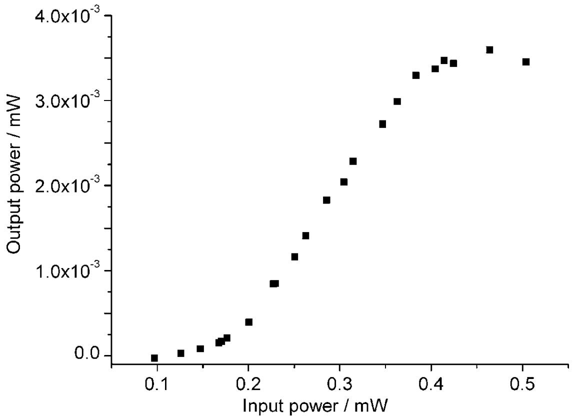


Figure 7. Plots of output power versus input pump power for the three-photon-pumped lasing process for p-Ph$_2$N-OF(5)-TAZ.

Conclusion

In summary, we have synthesized a new class of diphenylamino- and 1,2,4-triazole-end-capped, fluorene-based, π-conjugated oligomers, namely, p-Ph$_2$N-OF(n)-TAZ ($n=5$ and 6), and p-Ph$_2$N-OF(n)OT(m)-TAZ, by 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 a key step. Efficient multiphoton-excited photoluminescence and lasing were obtained by pumping with near-infrared femtosecond lasers. Despite the exhibition of the saturation behavior of absorption and emission properties/maxima in the p-Ph$_2$N-OF(n)-TAZ series, the highly fluorescent and extended oligofluorenes show a decrease in the three-photon-absorption cross section. On the other hand, the multiphoton-excited emission spectrum and lasing wavelength can easily be modified or tuned by an incorporation of thienyl unit(s) into the fluorene-based π-conjugated core. Upon the incorporation of thienyl unit(s), the three-photon-absorption cross section increases significantly up to 3.59×10^{-77} cm^{6}s^2 in the femtosecond regime, thereby highlighting the promising potential of this series. The optimized full width at half-maximum (FWHM) of the three-photon lasing spectra of these materials is sharply narrowed to approximately 6 nm. Our findings show that the thienyl moiety is a useful and effective π-conjugated unit to enhance the three-photon-absorption cross section; however, it is detrimental to upconversion lasing applications.

Experimental Section

For multiphoton-excited photoluminescence and cavityless upconversion lasing experiments, the concentration used was 1×10^{-2} M in toluene except p-Ph$_2$N-OF(6)-TAZ (5×10^{-3} M) because of its poor solubility. The pump source was an optical parametric amplifier (OPA; Topas, Coherent) that was pumped by a self-mode-locked Ti:sapphire laser with a Spitfire regenerative amplifier (Spectra Physics–Tsunami; 800 nm, pulsed width 100 fs, repetition rate 1 kHz). The laser beam passed through a polarizer and a focusing lens, and an IR filter (Hot Filter) was used to block the 800 nm light. The incident laser beam was focused on the center of the oligomer solution inside the cuvette. A second lens focused a transmitted signal into the spectrometer (Ocean Optics, USB4000). The same laser system was used for PL experiments. For both PL and lasing excitation, an 800 nm lasing line directly from the Spitfire regenerative amplifier was used, and for lasing the threshold pump power was 6 mW. For three-photon-upconversion excitation, laser lines from the OPA pumped by the Spitfire regenerative amplifier were used so that the laser wavelength could be tuned for optimum excitation.

Compound 3a: A mixture of **1a** (1.10 g, 0.84 mmol), compound **2** (0.49 g, 1.26 mmol), palladium(II) acetate (10 mg, 0.045 mmol), tri(*o*-tolyl)phosphine (28 mg, 0.092 mmol), 2 M K_2CO_3 (2 mL), toluene (25 mL), and methanol (10 mL) under a nitrogen atmosphere was heated at 75 °C overnight with good magnetic stirring. After cooling to room temperature, the reaction mixture was poured into water and extracted with ethyl acetate (30 mL) followed by dichloromethane (30 mL). The combined organic layer was dried over anhydrous Na_2SO_4, evaporated to dryness, and the residue was purified by silica gel column chromatography using 8:1 dichloromethane/ethyl acetate as eluent, thereby affording **3a** (1.20 g, 93 %) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ=7.76–7.83 (m, 7H), 7.46–7.73 (m, 24H), 7.36–7.38 (m, 2H), 7.30 (d, J=6.4 Hz, 2H), 7.25 (d, J=7.2 Hz, 2H), 2.04–2.10 (m, 16H), 1.28 (s, 9H), 1.09–1.18 (m, 16H), 0.68–0.79 (m, 40H), 0.33 ppm (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ=154.8, 154.4, 152.7, 151.7, 151.6, 150.1, 142.5, 141.3, 140.6, 140.4, 140.3, 140.0, 139.9, 139.7, 139.0, 138.7, 135.5, 131.8, 130.0, 129.6, 129.0, 128.3, 128.0, 127.5, 126.9, 126.0, 125.6, 125.3, 123.9, 121.4, 121.2, 120.0, 119.9, 118.9, 55.2, 55.0, 40.2, 39.9, 34.7, 31.1, 26.1, 26.0, 23.0, 23.0, 13.8, 13.7, −0.8 ppm; MS (FAB): *m*/*z*: 1530.2 $[M^+]$.

Compound 3b: The synthetic procedure for compound **3a** was followed using compound **1b** (158.5 mg, 0.1 mmol), compound **2** (58.3 mg, 0.15 mmol), palladium(II) acetate (1.1 mg, 0.005 mmol), tri(*o*-tolyl)phosphine (3.2 mg, 0.01 mmol), 2 M K_2CO_3 (1 mL), toluene (10 mL), and methanol (4 mL). The crude product was purified by silica gel column chromatography using 8:1 dichloromethane/ethyl acetate as an eluent, thereby affording **3b** (153 mg, 80 %) as a light yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ=7.77–7.85 (m, 8H), 7.46–7.74 (m, 29H), 7.38 (d, J=8.4 Hz, 2H), 7.32 (d, J=8.8 Hz, 2H), 7.24–7.27 (m, 2H), 2.03–2.09 (m, 20H), 1.27 (s, 9H), 1.08–1.18 (m, 20H), 0.66–0.78 (m, 50H), 0.31 ppm (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ=154.8, 154.4, 152.8, 151.7, 151.7, 151.6, 150.1, 142.5, 141.3, 140.6, 140.6, 140.4, 140.3, 140.3, 140.0, 140.0, 139.9, 139.7, 139.0, 138.7, 135.5, 131.8, 130.0, 129.6, 129.0, 128.3, 127.9, 127.5, 126.9, 126.0, 125.9, 125.6, 125.3, 123.9, 121.4, 121.2, 120.0, 119.9, 118.9, 55.2, 55.0, 40.2, 39.9, 34.7, 31.1, 26.1, 26.0, 23.0, 23.0, 23.0, 13.8, 13.7, −0.86 ppm; MS (FAB): *m*/*z*: 1806.3 $[M^+]$.

Compound 4a: A mixture of **3a** (1.09 g, 0.71 mmol), silver trifluoroacetate (0.24 g, 1.1 mmol), and iodine (0.22 g, 0.85 mmol) in chloroform (30 mL) was heated to reflux and stirred for 4 h. After cooling to room temperature, the mixture was poured into sodium sulfite solution and extracted with dichloromethane (3×30 mL). The combined organic layer was dried over anhydrous Na_2SO_4 and evaporated to dryness. The crude product was purified by short silica gel column chromatography using 8:1 dichloromethane/ethyl acetate as eluent, thereby affording the iodide **4a** as a light yellow solid (1.06 g, 94 %). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ=7.81–7.84 (m, 9H), 7.45–7.71 (m, 24H), 7.37 (d, J=8.8, 2H), 7.30 (d, J=8.8, 2H), 7.23–7.25 (m, 2H), 1.95–2.13 (m, 16H), 1.28 (s, 9H), 1.07–1.18 (m, 16H), 0.65–0.78 ppm (m, 40H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ=154.8, 154.4, 153.4, 152.8, 150.8, 142.5, 141.0, 140.6, 140.6, 140.4, 140.3, 140.3, 140.1, 140.0, 139.9, 139.9, 139.7, 139.2, 138.7, 135.8, 135.5, 132.0, 130.0, 129.6, 129.0, 128.3, 128.0, 126.9, 126.1, 126.1, 125.6, 125.3, 123.9, 121.4, 121.2, 120.0, 119.9, 92.4, 55.3, 55.2, 40.2, 40.0, 34.7, 31.1, 26.0, 26.0, 25.9, 23.0, 23.0, 13.8 ppm; MS (FAB): *m*/*z*: 1583.9 $[M^+]$.

Compound 4b: The iodo-desilylation procedure for compound **4a** was followed using compound **3b** (547 mg, 0.30 mmol), iodine (92 mg, 0.36 mmol), silver trifluoroacetate (100 mg, 0.45 mmol), and chloroform (20 mL). The crude product was purified by silica gel column chromatography using 8:1 dichloromethane/ethyl acetate as an eluent, thereby affording **4b** (530 mg, 85 %) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ=7.75–7.84 (m, 9H), 7.48–7.71 (m, 28H), 7.37 (d, J=8.4 Hz, 2H), 7.30 (d, J=8.4 Hz, 2H), 7.25 (d, J=7.6 Hz, 2H), 2.03–2.11 (m, 20H), 1.28 (s, 9H), 1.09–1.17 (m, 20H), 0.68–0.80 ppm (m, 50H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ=154.8, 154.4, 153.3, 152.7, 150.8, 142.5, 141.0, 140.6, 140.5, 140.3, 140.1, 139.9, 139.9, 139.7, 139.2, 138.7, 135.8, 135.5, 132.0, 130.0, 129.6, 129.0, 128.3, 127.9, 126.9, 126.1, 126.0, 125.6, 125.3, 123.9, 121.4, 121.2, 121.2, 120.0, 119.9, 92.4, 55.3, 55.2, 40.1, 40.0, 34.7, 31.1, 26.0, 26.0, 25.9, 23.0, 22.9, 13.8 ppm; MS (FAB): *m*/*z*: 1860.1 $[M^+]$.

***p*-Ph_2N-OF(5)-TAZ**: The synthetic procedure for compound **3** was followed using compound **4a** (158.5 mg, 0.1 mmol), compound **5** (97.9 mg, 0.2 mmol), palladium(II) acetate (1.2 mg, 0.005 mmol), tri(*o*-tolyl)phosphine (3.1 mg, 0.01 mmol), 2 M K_2CO_3 (1 mL), toluene (10 mL), and methanol (4 mL). The crude product was purified by silica gel column chromatography using 8:1 dichloromethane/ethyl acetate as an eluent, thereby affording *p*-Ph_2N-OF(5)-TAZ (153 mg, 80 %) as a light yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ=7.77–7.85 (m, 8H), 7.49–7.72 (m, 27H), 7.38 (d, J=8.4 Hz, 2H), 7.31 (d, J=8.4 Hz, 2H), 7.24–7.32 (m, 4H), 7.15 (d, J=8.0 Hz, 5H), 7.00–7.06 (m, 3H), 1.90–2.37 (m, 20H), 1.29 (s, 9H), 1.03–1.19 (m, 20H), 0.68–0.80 ppm (m, 50H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ=154.8, 154.4, 152.8, 152.3, 151.7, 151.4, 147.9, 147.1, 142.5, 140.6, 140.6, 140.4, 140.1, 140.0, 139.9, 139.8, 139.7, 139.5, 138.7, 135.9, 135.5, 130.0, 129.6, 129.1, 129.0, 128.3, 128.0, 126.9, 126.0, 125.6, 125.3, 123.9, 123.8, 123.4, 122.4, 121.4, 121.2, 121.1, 120.3, 120.0, 119.9, 119.3, 55.2, 55.0, 40.2, 39.9, 34.7, 31.1, 26.0, 23.0, 23.0, 13.8, 13.8 ppm; HRMS (MALDI-TOF): *m*/*z*: 1903.2173 $[M^++H]$; elemental analysis calcd (%) for $C_{141}H_{152}N_4$: C 89.00, H 8.05, N 2.94; found: C 88.97, H 7.76, N 2.94.

***p*-Ph_2N-OF(6)-TAZ**: The synthetic procedure for compound **3** was followed using compound **4b** (531 mg, 0.29 mmol), compound **5** (279 mg, 0.57 mmol), palladium(II) acetate (3.2 mg, 0.014 mmol), tri(*o*-tolyl)phosphine (8.7 mg, 0.029 mmol), 2 M K_2CO_3 (1.5 mL), toluene (20 mL), and methanol (8 mL). The crude product was purified by silica gel column chromatography using 8:1 dichloromethane/ethyl acetate as an eluent, thereby affording 530 mg (80 %) of a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ=7.76–7.84 (m, 10H), 7.47–7.70 (m, 33H), 7.35 (d, J=8.8 Hz, 2H), 7.29 (d, J=8.4 Hz, 2H), 7.22–7.24 (m, 2H), 2.13 (m, 6H), 6.98–7.04 (m, 4H), 2.09 (m, 24H), 1.27 (s, 9H), 1.01–1.14 (m, 24H), 0.66–0.78 ppm (m, 60H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ=154.8, 154.4, 152.8, 152.3, 151.8, 151.4, 147.9, 147.1, 142.5, 140.6, 140.4, 140.1, 140.0, 139.8, 139.7, 139.5, 138.7, 135.9, 135.5, 130.0, 129.6, 129.1, 129.0, 128.3, 128.0, 126.9, 126.1, 125.6, 125.4, 123.9, 123.8, 123.4, 122.4, 121.4, 120.3, 120.0, 119.9, 119.3, 55.2, 55.0, 40.2, 40.0, 34.7, 31.1, 26.1, 23.1, 23.0, 13.8, 13.8 ppm; HRMS (MALDI-TOF): *m*/*z*: 2179.4032 $[M^++H]$; elemental analysis calcd (%) for $C_{162}H_{176}N_4$: C 89.29, H 8.14, N 2.57; found: C 89.55, H 8.13, N 2.56.

Compound 8: The synthetic procedure for compound **3** was followed using compound **6** (609 mg, 1.41 mmol), 2-thiopheneboronic acid (**7**; 360 mg, 2.81 mmol), palladium(II) acetate (11 mg), tri(*o*-tolyl)phosphine (26 mg), toluene (15 mL), methanol (6 mL), and 2 M K_2CO_3 (2 mL). The crude product was purified by silica gel column chromatography using 8:1 dichloromethane/ethyl acetate as an eluent, thereby affording **8** (468 mg, 82 %) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ=7.05–7.50 (m, 16H), 1.28 ppm (s, 9H); ^{13}C NMR (67 MHz, $CDCl_3$, 25 °C): δ=154.6, 154.0, 143.0, 135.1, 129.8, 129.5, 128.9, 128.1, 128.0, 127.7, 125.6, 125.4, 125.2, 123.7, 123.6, 117.6, 34.7, 31.1 ppm; MS (FAB): *m*/*z*: 435.9 $[M^+]$.

Compound 9: A mixture of compound **8** (271 mg, 0.62 mmol) and NBS (133 mg, 0.75 mmol) in chloroform was heated at reflux overnight. The reaction mixture washed with brine, dried over anhydrous sodium sulfate, and evaporated in vacuum. The residue was purified by silica gel column chromatography using 8:1 dichloromethane/ethyl acetate as an eluent, thereby affording **9** (468 mg, 87 %) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ=7.02–7.49 (m, 15H), 1.28 ppm (s, 9H); ^{13}C NMR (67 MHz, $CDCl_3$, 25 °C): δ=154.6, 153.8, 152.6, 144.3, 135.1, 134.2, 130.8, 129.8, 129.5, 128.9, 128.1, 127.7, 126.0, 125.2, 125.0, 123.7, 123.6, 112.1, 34.7, 31.0 ppm; MS (FAB): *m*/*z*: 516.1 $[M^+]$.

***p*-Ph_2N-OFOT-TAZ**: The synthetic procedure for compound **3** was followed using compound **9** (400 mg, 0.78 mmol), compound **5** (571 mg, 1.17 mmol), palladium(II) acetate (20 mg), tri(*o*-tolyl)phosphine (45 mg), 2 M K_2CO_3 (3 mL), toluene (20 mL), and methanol (8 mL). The crude product was purified by silica gel column chromatography using 8:1 dichloromethane/ethyl acetate as an eluent, thereby affording *p*-Ph_2N-OFOT-TAZ (560 mg, 82 %) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ=7.34–7.61 (m, 16H), 7.23–7.27 (m, 7H), 7.11–7.14 (m, 5H), 6.99–7.03 (m, 3H), 1.85–1.92 (m, 4H), 1.29 (s, 9H), 1.03–1.18 (m, 4H), 0.66–0.72 ppm (m, 10H); ^{13}C NMR (100 MHz, CDCl$_3$, 25 °C): δ = 154.8, 154.2, 152.7, 152.2, 151.4, 147.8, 147.2, 145.3, 140.7, 135.5, 135.3, 135.2, 130.0, 129.6, 129.1, 129.0, 127.9, 125.9, 125.5, 125.3, 125.1, 124.7, 123.8, 123.6, 123.3, 122.5, 120.3, 119.6, 119.4, 119.0, 54.9, 39.9, 34.6, 31.0, 25.9, 22.9, 13.8 ppm; HRMS (MALDI-TOF): *m*/*z*: 878.4379 [M^+]; elemental analysis calcd (%) for $C_{61}H_{58}N_4S$: C 83.33, H 6.65, N 6.37; found: C 83.12, H 6.60, N 6.32.

Compound 11: The synthetic procedure for compound **3** was followed using compound **10** (1.50 g, 2.0 mmol), 2-thiopheneboronic acid (**7**; 762 mg, 6.0 mmol), palladium(II) acetate (45 mg), tri(*o*-tolyl)phosphine (63 mg), 2 M K_2CO_3 (7 mL), toluene (40 mL), and methanol (15 mL). The crude product was purified by silica gel column chromatography using 8:1 dichloromethane/ethyl acetate as an eluent, thereby affording **11** (1.24 g, 88 %) as a yellow solid. ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C): δ = 7.68–7.73 (m, 2H), 7.59–7.62 (m, 3H), 7.486–7.56 (m, 8H), 7.37–7.39 (m, 3H), 7.25–7.32 (m, 5H), 7.09–7.12 (m, 1H), 1.99–2.02 (t, J = 5.6 Hz, 4H), 1.28 (s, 9H), 1.04–1.10 (m, 4H), 0.60–0.67 ppm (m, 10H); ^{13}C NMR (100 MHz, CDCl$_3$, 25 °C): δ = 154.7, 154.3, 152.6, 151.6, 151.5, 144.9, 142.3, 140.3, 140.0, 138.7, 135.3, 133.2, 129.9, 129.5, 128.9, 128.2, 127.9, 127.8, 126.8, 125.9, 125.5, 125.2, 124.8, 124.4, 123.8, 122.8, 121.0, 120.1, 119.9, 119.9, 55.1, 40.1, 34.6, 31.0, 25.8, 22.9, 13.7 ppm; MS (FAB): *m*/*z*: 711.5 [M^+].

Compound 12: The synthetic procedure for compound **9** was followed using compound **11** (700 mg, 0.98 mmol) and NBS (210 mg, 1.18 mmol) in CHCl$_3$ (30 mL). The crude product was purified by silica gel column chromatography using 8:1 dichloromethane/ethyl acetate as an eluent, thereby affording 778 mg of a yellow solid, which was still a mixture and used for the coupling reaction without further purification. ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C): δ = 7.61–7.67 (m, 2H), 7.36–7.58 (m, 13H), 7.23–7.29 (m, 3H), 7.15–7.19 (m, 3H), 7.09 (d, J = 4, 1H), 6.96–6.98 (m, 1H), 2.00–2.03 (m, 4H), 1.25 (s, 9H), 1.03–1.09 (m, 4H), 0.61–0.65 ppm (m, 10H); ^{13}C NMR (100 MHz, CDCl$_3$, 25 °C): δ = 154.6, 154.1, 152.4, 151.5, 151.3, 143.9, 143.4, 143.0, 142.1, 140.1, 140.1, 140.0, 138.6, 138.6, 137.4, 137.1, 136.4, 136.1, 135.2, 134.8, 132.7, 132.5, 131.1, 129.8, 129.4, 128.8, 128.1, 127.7, 127.6, 126.7, 125.8, 125.4, 125.1, 124.8, 124.6, 124.4, 124.1, 123.7, 123.4, 123.1, 120.8, 120.1, 119.9, 119.4, 71.7, 55.0, 54.9, 40.0, 34.4, 30.8, 25.7, 22.8, 13.6 ppm; MS (FAB): *m*/*z*: 579.2 [M^+].

***p*-Ph$_2$N-OFOTOF-TAZ**: The synthetic procedure for compound **3** was followed using compound **12** (423 mg, 0.53 mmol), compound **5** (519 mg, 1.06 mmol), palladium(II) acetate (40 mg), tri(*o*-tolyl)phosphine (60 mg), 2 M K_2CO_3 (4 mL), toluene (30 mL), and methanol (8 mL). The crude product was purified by silica gel column chromatography using 8:1 dichloromethane/ethyl acetate as an eluent, thereby affording *p*-Ph$_2$N-OFOTOF-TAZ (403 mg, 66 %) as a yellow solid. ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C): δ = 7.59–7.63 (t, J = 8, 2H), 7.34–7.55 (m, 15H), 7.26–7.29 (m, 4H), 7.12–7.21 (m, 8H), 7.03–7.05 (d, J = 7.6, 5H), 6.89–6.94 (m, 3H), 1.75–1.97 (m, 8H), 1.29 (s, 9H), 1.06–1.16 (m, 8H), 0.67–0.76 ppm (m, 20H); ^{13}C NMR (100 MHz, CDCl$_3$, 25 °C): δ = 154.8, 154.3, 152.7, 152.2, 151.7, 151.5, 151.3, 147.8, 147.1, 144.2, 143.6, 142.3, 140.5, 140.4, 140.0, 138.7, 135.6, 135.4, 133.3, 132.2, 129.9, 129.5, 129.0, 128.9, 128.2, 127.9, 126.8, 126.0, 125.6, 125.3, 124.4, 123.8, 123.8, 123.5, 123.3, 122.5, 121.0, 120.3, 120.2, 119.9, 119.6, 119.4, 119.0, 55.1, 54.9, 40.2, 39.9, 34.6, 31.0, 25.9, 25.9, 22.9, 22.9, 13.8, 13.7 ppm; HRMS (MALDI-TOF): *m*/*z*: 1154.6238 [M^+]; elemental analysis calcd (%) for $C_{82}H_{82}N_4S$: C 85.23, H 7.15, N 4.85; found: C 84.92, H 7.05, N 4.38.

Compound 13: A piece of iodine was added to a stirred mixture of magnesium (124 mg, 5.16 mmol) and 2-bromothiophene (883 mg, 5.4 mmol) in THF. The resulting mixture was gently heated to reflux after the color faded and was stirred until magnesium was consumed completely. The reaction solution was cooled to room temperature before [PdCl$_2$(dppf)] (dppf = 1′-bis(diphenylphosphino)ferrocene; 50 mg) and compound **12** (777 mg, 0.98 mmol) were added. The reaction mixture was stirred overnight while heated at reflux. The crude product was purified by silica gel column chromatography using 8:1 dichloromethane/ethyl acetate as an eluent, thereby affording **13** (780 mg, 74 %) as a yellow solid. ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C): δ = 7.68–7.72 (m, 2H), 7.45–7.61 (m, 11H), 7.36–7.38 (d, J = 8.4, 2H), 7.29–7.31 (m, 3H), 7.21–7.25 (m, 4H), 7.16–7.17 (d, J = 3.6, 1H), 7.02–7.04 (t, J = 4.4, 1H), 2.0–2.05 (m, 4H), 1.28 (s, 9H), 1.04–1.13 (m, 4H), 0.61–0.68 ppm (m, 10H); ^{13}C NMR (100 MHz, CDCl$_3$, 25 °C): δ = 154.8, 154.3, 152.7, 151.7, 151.6, 143.7, 142.3, 140.3, 140.2, 138.8, 137.4, 136.4, 135.4, 132.9, 129.9, 129.6, 129.0, 128.2, 127.9, 127.8, 126.9, 126.0, 125.6, 125.3, 124.5, 124.3, 123.9, 123.5, 121.1, 120.2, 120.0, 119.7, 55.2, 40.2, 34.6, 31.0, 25.9, 23.0, 13.7 ppm; MS (FAB): *m*/*z*: 793.2 [M^+].

Compound 14: A mixture of compound **13** (488 mg, 0.61 mmol) and NIS (180 mg, 0.80 mmol) in CHCl$_3$ (30 mL) was heated at reflux overnight with stirring. The crude product was purified by silica gel column chromatography using 8:1 dichloromethane/ethyl acetate as an eluent, thereby affording **14** (501 mg, 89 %) as a yellow solid. ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C): δ = 7.63–7.69 (m, 2H), 7.42–7.59 (m, 11H), 7.36–7.38 (d, J = 8.4, 2H), 7.27–7.30 (m, 3H), 7.12–7.25 (m, 4H), 7.98–7.00 (m, 4H), 2.00–2.04 (m, 4H), 1.26 (s, 9H), 1.03–1.10 (m, 4H), 0.63–0.66 ppm (m, 10H); ^{13}C NMR (100 MHz, CDCl$_3$, 25 °C): δ = 154.6, 154.1, 152.4, 151.5, 151.3, 143.9, 143.0, 142.1, 140.1, 140.1, 140.0, 138.6, 138.6, 137.4, 137.1, 136.1, 135.2, 134.8, 132.7, 132.5, 129.8, 129.4, 128.8, 128.1, 127.7, 127.6, 126.8, 126.7, 125.8, 125.7, 125.5, 125.1, 124.8, 124.6, 124.6, 124.4, 124.1, 123.7, 123.6, 123.4, 123.3, 120.8, 120.1, 119.9, 119.4, 71.7, 55.0, 40.0, 34.4, 30.8, 25.7, 22.8, 13.6 ppm; MS (FAB): *m*/*z*: 919.5 [M^+].

***p*-Ph$_2$N-OFOT(2)OF-TAZ**: The synthetic procedure for compound **3** was followed using compound **14** (435 mg, 0.47 mmol), compound **5** (463 mg, 0.95 mmol), palladium(II) acetate (40 mg), tri(*o*-tolyl)phosphine (60 mg), 2 M K_2CO_3 (4 mL), toluene (30 mL), and methanol (8 mL). The crude product was purified by silica gel column chromatography using 8:1 dichloromethane/ethyl acetate as an eluent, thereby affording *p*-Ph$_2$N-OFOT(2)OF-TAZ (432 mg, 68 %) of a yellow solid. ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C): δ = 7.46–7.74 (m, 17H), 7.21–7.38 (m, 15H), 7.12–7.14 (d, J = 8.4, 2H), 6.99–7.03 (t, J = 7.6, 3H), 1.86–2.05 (m, 8H), 1.28 (s, 9H), 1.05–1.12 (m, 8H), 0.66–0.73 ppm (m, 20H); ^{13}C NMR (100 MHz, CDCl$_3$, 25 °C): δ = 155.1, 154.6, 153.0, 152.5, 152.0, 151.9, 151.7, 148.1, 147.5, 144.2, 143.8, 142.6, 140.9, 140.6, 14.05, 139.1, 136.8, 136.4, 135.8, 135.7, 133.2, 132.2, 130.2, 129.8, 129.4, 129.3, 128.5, 128.2, 127.2, 126.3, 125.9, 125.6, 124.8, 124.7, 124.6, 124.6, 124.2, 124.1, 123.9, 123.6, 122.8, 121.4, 120.6, 120.5, 120.3, 119.9, 119.8, 119.7, 119.3, 55.4, 55.3, 40.5, 40.2, 34.9, 31.3, 26.2, 26.2, 23.2, 23.2, 14.1, 14.0 ppm; HRMS (MALDI-TOF): *m*/*z*: 1237.6248 [M^++H]; elemental analysis calcd (%) for $C_{86}H_{84}N_4S_2$: C 83.45, H 6.84, N 4.53; found: C 83.18, H 6.69, N 4.38.

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