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Star-shaped ladder-type *ter*(*p*-phenylene)s for efficient multiphoton absorption†

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Star-shaped ladder-type *ter*(*p*-phenylene)s exhibit remarkably efficient multiphoton absorption properties with 2PA cross-section up to 2579 GM at 700 nm and 3PA cross-section up to 3.35 × 10^{-76} cm^6 s^2 in the femtosecond regime for a blue-emissive molecule despite having such a short π-conjugated framework.

The development of organic materials that exhibit large multiphoton absorption (MPA) properties has drawn considerable interest in the past decades because of the utilization of the long-wavelength/low-energy excitation source and the unique characteristics of the intensity-dependent multiphoton absorption process, which offers many advantages for various technological applications including three-dimensional optical data storage,[1] two-photon optical power limiting,[2] two-photon excited fluorescence (TPEF) microscopy,[3] photodynamic therapy,[4] two-photon microfabrication,[5] and frequency-upconversion lasing.[6] To be useful and efficient for MPA applications, molecules/materials exhibiting large MPA cross-sections such as two-photon absorption (2PA) cross-sections (σ_2) or three-photon absorption (3PA) cross-sections (σ_3) are essential. Besides, other desirable physical and chemical properties of a molecule or material such as a high fluorescence quantum yield, good solubility and processibility, as well as high photochemical and thermal stability would play a crucial role in the realization of practical MPA applications.

The strategies for the design of one-dimensional π-conjugated chromophores that exhibit strong two-photon absorption (2PA) responses have been successfully developed and established in the past decade.[7] Most of these structure modifications/guidelines often cause a red shift of the 2PA spectrum due to the enhanced intramolecular charge transfer. Thus, blue-emissive molecules with large 2PA cross-sections are relatively limited although they are potentially useful for 2PA induced fluorescence microscopy and low-cost high-energy coherent light sources. Nevertheless, the introduction of multi-dimensional π-conjugated systems provides an alternative means to increase the 2PA cross-sections due to the excitonic coupling among the π-conjugated moieties.[8] On the other hand, the structure–property relationships for three-photon absorption properties and the effect of the multi-dimensional structure on the 3PA cross-sections are far less studied. It has recently been shown that besides enhanced photoluminescence efficiency and improved photochemical stability, the rigid and planar ladder-type oligophenylene backbone is superior to oligofluorene counterparts in enhancing multiphoton absorption properties of a linear π-conjugated system.[9]

To continue our ongoing effort on investigating the structure–property relationships for efficient multiphoton absorption responses and exploring structural factors that can achieve excellent nonlinearity–transparency trade-off for multiphoton absorption, we report herein synthesis and an investigation of multiphoton absorption properties of novel star-shaped ladder-type *ter*(*p*-phenylene)s, composed of an amine-based central core, three fused ladder-type *ter*(*p*-phenylene) arms decorated with non-coplanar alkylphenyl rings and electron-donating diarylamine-based or electron-accepting triazole-based endcaps. Despite such a short π-conjugated length being employed, these multi-branched ladder-type oligomers have been found to exhibit remarkably large MPA properties with 3PA cross-section (σ_3) up to 3.35 × 10^{-76} cm^6 s^2 in the femtosecond regime as well as excellent nonlinearity–transparency trade-off with 2PA cross-section (σ_2) up to 2579 GM emitting at 445 nm which is the highest σ_2 reported so far for a blue emissive molecule.[10]

The molecular structures of star-shaped ladder-type oligomers built onto the framework of triarylamine endcapped with various electron-donating or withdrawing groups, namely **N(*TL*)-Ph(3)-TAZ**, **N(*TL*)-Ph(3)-CBZ**, and **N(*TL*)-Ph(3)-NPh** are shown in Fig. 1. By adapting the convergent approach, novel star-shaped ladder-type *ter*(*p*-phenylene)s bearing either amine-based or triazole-based endcaps have been successfully synthesized *via* palladium catalyzed Suzuki-cross coupling, Buchwald amination, and acid catalyzed intramolecular ring-closure as key steps. The synthetic routes for the star-shaped ladder-type

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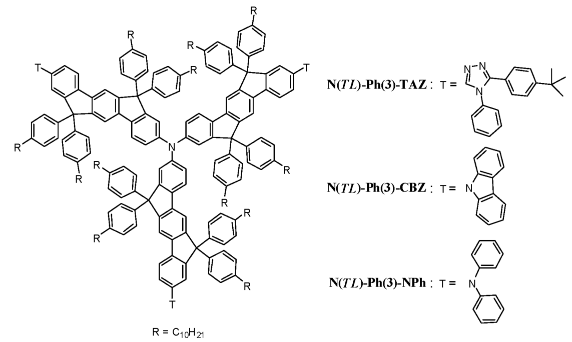

Fig. 1 Molecular structures of star-shaped ladder-type *ter*(*p*-phenylene)s **N(*TL*)-Ph(3)-TAZ**, **N(*TL*)-Ph(3)-CBZ**, and **N(*TL*)-Ph(3)-NPh**, respectively.

ter(*p*-phenylene)s are outlined in Scheme S1 (see ESI†). All the newly synthesized star-shaped ladder-type *ter*(*p*-phenylene)s were fully characterized using ^{1}H NMR, ^{13}C NMR, HRMS, and elemental analysis and found to be in good agreement with their structures (see ESI†). With the use of fused aromatics such as π-conjugated backbones, all the star-shaped ladder-type oligomers are highly thermally stable with thermal decomposition temperatures of over 400 °C (see Table S1, ESI†).

All the star-shaped ladder-type *ter*(*p*-phenylene)s are highly soluble in most of the common organic solvents but poorly soluble in highly polar DMF. The summary of the linear and nonlinear optical properties is provided in Table 1 and the linear optical spectra in toluene are shown in Fig. 2. These star-shaped oligomers exhibit mainly two absorption bands. The strong absorption band spanning from 380 to 440 nm with overlapped vibronic structures corresponds to the π → π* transition of the rigid π-conjugated *ter*(*p*-phenylene) backbones. The weaker absorption at around 300 to 325 nm is due to the n → π* transition of the triarylamino moiety. Upon excitation of these oligomers at around 400 nm, a very strong blue-light emission with a fluorescence quantum yield over 84% peaking at 443–450 nm is observed. In contrast to the absorption spectra, these star-shaped oligomers show a notable solvatochromic effect in the emission spectra in which the emission peaks exhibit a red shift in polar solvents particularly for **N(*TL*)-Ph(3)-TAZ** ($\Delta\lambda_{em}$ = 43 nm in DMF), suggesting dipolar or charge-transfer character in the excited state (Table S1, ESI†). As compared with the linear quadrupolar counterparts, **(*L*)-Ph(3)-NPh**,[9] the star-shaped **N(*TL*)-Ph(3)-NPh** shows much enhanced absorption properties including the red-shift and broadening of spectra as well as increased molar absorptivity, which is attributed to the strong coupling of the proximate, rigid, ladder-type *ter*(*p*-phenylene) backbones leading to the enhanced electron delocalization throughout the entire system. This also results in ~26–33 nm red-shift of the emission maxima for these star-shaped oligomers as compared to that of the linear *ter*(*p*-phenylene)s.

Table 1 Summary of photophysical properties of star-shaped ladder-type *ter*(*p*-phenylene)s, **N(*TL*)-Ph(3)-NPh** (I), **N(*TL*)-Ph(3)-TAZ** (II) and **N(*TL*)-Ph(3)-CBZ** (III)

	$\lambda_{max}{}^a$/ nm (ε)	$\lambda_{em}{}^{a,b}$/ nm	$\Phi_{FL}{}^a$	2PA $\lambda_{max}{}^e$/nm	$\sigma_2{}^e$	$\sigma_{2,M}{}^f$	3PA $\lambda_{max}{}^g$/nm	$\sigma_3{}^g$	$\sigma_{3,M}{}^h$
(I)	429 (1.74)	443	0.86^c	445	2579	0.66	444	2.45	6.3
(II)	429 (1.34)	450	0.84^c	453	1620	0.39	450	3.35	8.0
(III)	423 (1.33)	443	0.96^d	443	1887	0.49	442	2.23	5.8

[a] Measured in toluene, ε × 10^5 M^{-1} cm^{-1}. [b] Excited at ~400 nm. [c] Average of two independent measurements using Norharman ($\Phi_{330\text{–}390}$ = 0.58) as a standard. [d] Average of two independent measurements using Coumarin 6 (Φ_{420} = 0.78) as a standard. [e] 2PA cross-section (GM) determined by a two-photon-induced fluorescence method using 700 nm femtosecond laser pulses in toluene at a concentration of ~10^{-5} M. [f] $\sigma_{2,M}$ = 2PA cross-section scaled by molecular weight (GM/g). [g] 3PA cross-section (× 10^{-76} cm^6 s^2) determined by comparing the fluorescence intensity with that of **PhNOF(4)-TAZ-OF(4)-NPh** using 1270 nm femtosecond laser pulses in toluene at a concentration of ~10^{-5} M. [h] $\sigma_{3,M}$ = 3PA cross-section scaled by molecular weight (× 10^{-80} cm^6 s^2 g^{-1}).

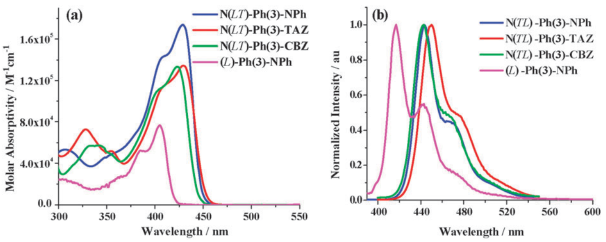

Fig. 2 (a) UV-Vis absorption and (b) fluorescence spectra of star-shaped oligomers in toluene with a linear counterpart, **(*L*)-Ph(3)-NPh**, for comparison.

To gain an insight into the influence of the star-shaped structure motif on nonlinear optical responses, the MPA properties of the newly synthesized star-shaped *ter*(*p*-phenylene)s were investigated by using a femtosecond pulsed laser as an excitation source. These star-shaped oligomers exhibit extremely strong multiphoton induced blue photoluminescence (PL) upon excitation at 700, 1270, and 1800 nm corresponding to the two-, three-, and four-photon absorption, respectively. The MPA excited PL spectral characteristics were almost identical to those of the corresponding one-photon excited one in Fig. S3 (ESI†) suggesting that their emission states are the same.

Fig. 3 shows the logarithmic plots of power dependence of upconversion fluorescence intensity of the star-shaped oligomers

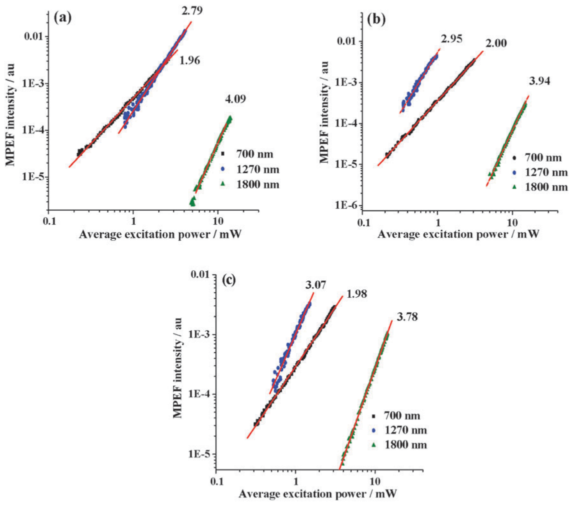

Fig. 3 The logarithmic plots of the power dependence of relative multiphoton induced fluorescence intensity of the star-shaped oligomers, (a) **N(*TL*)-Ph(3)-NPh**, (b) **N(*TL*)-Ph(3)-CBZ**, and (c) **N(*TL*)-Ph(3)-TAZ**, as a function of pump power at an excitation wavelength of 700 nm, 1270 nm and 1800 nm, respectively. The red solid lines are the best-fit straight lines with a gradient, *n* indicates the two-photon, three-photon or four-photon nature of the absorptions.

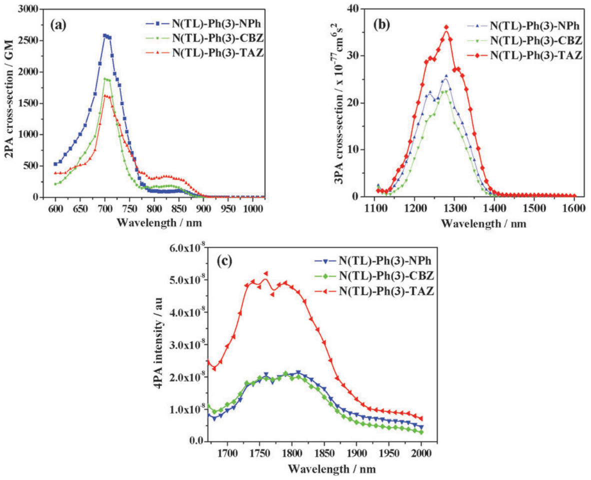

Fig. 4 (a) 2PA, (b) 3PA, and (c) 4PA excited spectra of the star-shaped ladder-type *ter*(*p*-phenylene)s measured in toluene by femtosecond laser pulses.

as a function of the input pump pulse power using a femtosecond laser as the excitation source at 700, 1270, and 1800 nm. The solid lines are the best fitting straight lines with gradients n = 1.96, 2.79, and 4.09 for **N(*TL*)-Ph(3)-NPh**; 2.00, 2.95, and 3.94 for **N(*TL*)-Ph(3)-CBZ**; and 1.98, 3.07, and 3.78 for **N(*TL*)-Ph(3)-TAZ**, respectively. Therefore, the square, cubic, and fourth-order dependence of the fluorescence intensity against input pump power is experimentally shown providing direct evidence of the MPA excitation process for the upconversion fluorescence.

The conventional two-photon induced fluorescence method was used to determine the TPA cross-sections and two-photon excited spectra of these ladder-type oligomers in the range of 600–1000 nm using a femtosecond pulsed laser. Fig. 4a shows the 2PA excited spectra of the star-shaped ladder-type *ter*(*p*-phenylene)s by comparing with rhodamine 6G, in which their maximum 2PA cross-section ($\sigma_{\max}$) appears at around 700 nm with $\sigma_{\max}$ up to 2579 GM for **N(*TL*)-Ph(3)-NPh**, which is the highest value reported so far for a blue-light emissive molecule. Furthermore, the 2PA cross-sections of these star-shaped oligomers are more than one order of magnitude higher than that of their linear counterparts, **(*L*)-Ph(3)-NPh** ($\sigma_{\max}$ = 127 GM at 700 nm), highlighting the advantage of using the multi-dimensional structure motif together with the rigid, planar ladder-type *ter*(*p*-phenylene) backbone to enhance the 2PA properties without significantly red-shifting the absorption/emission spectra.

The 3PA cross-sections (σ_3) were determined in the range of 1100–1600 nm by comparing the fluorescence intensity with that of **PhNOF(4)-TAZ-OF(4)-NPh** at 1270 nm with $\sigma_3 = 2.72 \times 10^{-77}$ cm^6 s^2.[11] As shown in Fig. 4b, the remarkably large 3PA cross-sections ($\sigma_{\max}$) in the range of 2.23×10^{-76}–3.35×10^{-76} cm^6 s^2 at 1270 nm were obtained in spite of a relatively short π-conjugation length of these ladder-type *ter*(*p*-phenylene)s, which is more than one-order of magnitude higher than that of the linear counterparts ($\sigma_{\max}$ of **(*L*)-Ph(3)-NPh** = 2.02×10^{-77} cm^6 s^2).[9] These 3PA cross-sections are comparable to the highest intrinsic σ_3 values reported previously, which further highlights the efficient electron delocalization of the ladder-type *ter*(*p*-phenylene) backbone and the importance of the star-shaped structure motif to induce the strong intra-chromophoric coupling for the large 3PA enhancement. The four-photon excited fluorescence intensities were also measured in the range of 1650–2000 nm. Similar to 3PA responses, the triazole-endcapped **N(*TL*)-Ph(3)-TAZ** shows the strongest four-photon absorption among the star-shaped ladder-type *ter*(*p*-phenylene)s.

In conclusion, we have synthesized a novel series of triarylamine-based star-shaped ladder-type *ter*(*p*-phenylene)s with various electron-donating or electron-withdrawing endcaps, which exhibit a high fluorescence quantum yield and remarkably large multiphoton absorption properties. Although these star-shaped oligomers only consist of short π-conjugated *ter*(*p*-phenylene) units, they have been found to show extremely large 3PA cross-section ($\sigma_{\max}$) up to 3.35×10^{-76} cm^6 s^2 from **N(*TL*)-Ph(3)-TAZ** which is comparable to the highest intrinsic σ_3 values reported previously. In addition, **N(*TL*)-Ph(3)-NPh** exhibits excellent nonlinearity–transparency trade-off with a 2PA cross-section (σ_2) of 2579 GM emitting at 445 nm which is the highest σ_2 for a blue emissive molecule reported so far. Our findings demonstrate that the star-shaped structural motif combined with the rigid, planar ladder-type oligophenylene backbone is highly efficient in enhancing multiphoton absorption, in particular 3PA properties offering an excellent nonlinearity–transparency trade-off.

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