Non-coplanar 9,9-diphenyl-substituted oligofluorenes with large two-photon absorption enhancement†

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The non-coplanar substituted phenyl rings at the 9-position of a fluorenyl unit can be involved in π-electron delocalization in which the resulting oligofluorenes exhibit a very large enhancement of two-photon absorption cross sections up to 2559 GM at 710 nm.

Molecular materials that show a large multi-photon absorption response have drawn increasing attention due to their potential applications in various emerging technologies such as 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 up-converted lasing.[6] A highly polarizable π-conjugated molecule often exhibits strong two-photon absorption (TPA) activity. The TPA cross-section of a molecule can generally be enhanced by increasing the donor/acceptor strength, extending the π-conjugated length/dimension and improving the planarity of the π-conjugated system.[7] Nevertheless, such structural modifications often lead to a red shift of the TPA spectrum because of the enhanced intramolecular charge transfer. Hence, structural motifs that can enhance the TPA cross-section (σ) of a molecule without causing a red shift of the two-photon excitation wavelength are particularly important and useful as they can be used to optimize σ at a specific wavelength, such as at 800 nm for TPEF microscopy. However, such structural guidelines for TPA cross-section enhancement are rather limited. It has been shown that increasing the non-conjugated chromophore density within a molecule, or increasing the structural dimensions of the conjugated moieties, could provide a useful means to enhance TPA cross-section at a specific wavelength.[8] In addition to a large TPA cross-section, other useful physical and chemical properties of a molecule, such as a high fluorescence quantum yield, good solubility and processibility, as well as high photochemical and thermal stabilities, play a crucial role for the realization of practical TPA applications.[9]

Monodisperse oligofluorenes, which constitute an important class of π-conjugated organic materials due to their excellent chemical, thermal and photochemical stabilities, as well as the ease of structural tuning to adjust their electronic and morphological properties, have recently drawn considerable attention for their potential applications in optoelectronic devices, particularly for blue-emitting organic light emitting diodes.[10] In addition, fluorene-based derivatives have been explored for two-photon absorbing materials.[7e,8h,11] It has been widely shown that the morphological properties, processibility and stability of a fluorene-based material can be easily modified by various substituents incorporated at the 9-position of a fluorenyl unit. In this contribution, we have demonstrated for the first time that the nature of the substituent at the 9-position of a fluorenyl unit has a tremendous effect on the nonlinear optical properties of an oligofluorene in which the two-photon absorption cross-section can be dramatically enhanced with diphenyl substituents when compared to their dibutyl-substituted counterparts, despite the subtle difference in their linear optical properties. We report, herein, the synthesis and investigation of the influence of 9,9-substitution on the optical and two-photon absorption properties of a series of diphenylamino-endcapped oligofluorenes (Fig. 1).

The molecular structures of two series of diphenylamino-endcapped oligofluorenes, namely ***(Bu)*-OF(*n*)-NPh**, which bears 9,9-dibutyl substituent, and ***(Ph)*-OF(*n*)-NPh**, which contains 9,9-diphenyl substituent on the fluorenyl units, where n = 2–5, are shown in Fig. 1. By adapting the convergent approach used previously,[10e] homologous series of diphenylamino-endcapped oligofluorenes bearing different substituents at the 9-position of the fluorenyl rings have been synthesized by palladium-catalyzed Suzuki cross-coupling of 7-diphenylamino-fluorenyl-2-boronic acid and the corresponding aryl bromide as a key step. All the newly synthesized oligofluorenes were fully characterized by ^{1}H NMR, ^{13}C NMR, MALDI-TOF MS and elemental analysis, and found to be in good agreement with their structures (see the ESI†).

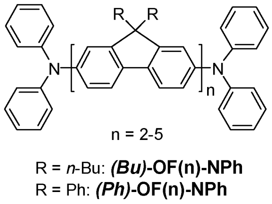

Fig. 1 Molecular structure of the oligofluorenes.

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Table 1 Summaries of physical measurements of ***(Bu)*-OF(*n*)-NPh** and ***(Ph)*-OF(*n*)-NPh** series

	$\lambda_{\max}^{\text{abs}}$/nm ($\varepsilon_{\max}$ 10^4/$M^{-1}cm^{-1}$)^a	$\lambda_{\max}^{\text{em}}$/nm^{ab}	Φ_{FL}^{a}	TPA $\lambda_{\max}^{\text{em}}$/nm	σ_{800}/GM^{ae}	σ_{710}/GM^{af}	T_g/°C^g	T_{dec}/°C^h
(Bu)-OF(2)-NPh	384 (7.1)	425	0.67^c	440	55		91	452
(Bu)-OF(3)-NPh	386 (8.5)	432	0.93^c	446	61		99	461
(Bu)-OF(4)-NPh	387 (14.2)	432	0.94^c	440	117	213	117	464
(Bu)-OF(5)-NPh	387 (18.9)	433	0.93^c	446	118	221	120	447
(Ph)-OF(2)-NPh	389 (9.2)	428	0.85^d	438	129		164	563
(Ph)-OF(3)-NPh	389 (14.7)	435	0.86^d	443	230		195	585
(Ph)-OF(4)-NPh	390 (18.9)	439	0.86^d	446	550	996	217	606
(Ph)-OF(5)-NPh	390 (21.8)	439	0.80^d	446	1390	2559	226	587

[a] As measured in $CHCl_3$. [b] Excited at the absorption maxima [c] Using 9,10-diphenylanthrancene (Φ_{360} = 0.9) as a standard. [d] Average of two independent measurements using quinine sulfate in 0.1 M H_2SO_4 (Φ_{350} = 0.58) as a standard. [e] Determined by two-photon-induced fluorescence method using 800 nm femtosecond laser pulses with rhodamine 6G as a standard (σ_{800} = 134 GM). [f] Determined by two-photon-induced fluorescence method using 710 nm femtosecond laser pulses with rhodamine 6G as a standard. [g] Determined by differential scanning calorimetry with a heating rate of 10 °C min^{-1} under N_2. [h] Determined by thermal gravimetric analysis with a heating rate of 10 °C min^{-1} under N_2.

The glass transition (T_g) and the decomposition temperatures (T_{dec}) as measured by a differential scanning calorimeter and thermal gravimetric analyser, respectively (Table 1), are greatly increased with the use of diphenyl substituents at the 9-position of the fluorenyl unit, indicating the enhanced morphological and thermal stability of this series.

As shown in Fig. 2, the two series of oligofluorenes show very similar absorption features that are mainly composed of two structureless absorption bands. The absorption peak around 310 nm is due to the n → π* transition of triarylamine moieties and the absorption contributed from the oligofluorene core spanning from 384–390 nm corresponds to the π → π* transition of oligofluorene core. Upon excitation of the oligomers at the absorption maximum, a very strong blue-light emission at around 425–439 nm results. Upon extension of the conjugation length, the absorption and emission maxima of these two oligofluorene series converge to a limited value of 387 nm and 390 nm for ***(Bu)*-OF(*n*)-NPh** and ***(Ph)*-OF(*n*)-NPh**, respectively. Despite similar absorption and emission features of these two series, there is a small red shift (Δ 3–6 nm) in both of the optical spectra of ***(Ph)*-OF(*n*)-NPh**s as compared to those of ***(Bu)*-OF(*n*)-NPh**s. In addition, there is a minor decrease in the fluorescence quantum efficiency upon replacing the 9,9-dibutyl with 9,9-diphenyl substituents of diphenylamino-endcapped oligofluorenes.

The two-photon absorption cross-sections (δ) of the diphenylamino-endcapped oligofluorenes were determined by the two-photon induced fluorescence method using a femtosecond (fs) pulsed laser as an excitation source in $CHCl_3$.[8h] The results of two-photon absorption cross-sections measured at 800 nm are tabulated in Table 1. Compared with the one-photon emission spectra, the two-photon excited fluorescence (TPEF) spectra consistently show a small red shift, which is presumably due to a reabsorption effect, suggesting that they have very similar emissive states (Table 1). There is a nonlinear increase in the two-photon absorption cross-sections (σ_{800}) as the oligomeric chain length increases with σ_{800} of ***(Bu)*-OF(5)-NPh** up to 118 GM and of ***(Ph)*-OF(5)-NPh** up to 1390 GM at 800 nm. This is in agreement with the nonlinear optical theory that the two-photon absorption property is parabolically proportional to the polarization, which can be enhanced by extending the conjugation path.[7g] Remarkably, 9,9-diphenyl-substituted oligofluorenes ***(Ph)*-OF(*n*)-NPh** exhibit much larger TPA cross-sections than their corresponding 9,9-dibutyl-substituted counterparts ***(Bu)*-OF(*n*)-NPh** (Table 1). Fig. 3a shows TPA spectra of ***(Ph)*-OF(*n*)-NPh** and ***(Bu)*-OF(*n*)-NPh**, where *n* = 4 and 5, in which the maximum of the TPA cross-sections falls at around 710 nm, with $\sigma_{\max}$ reaching 2559 GM for ***(Ph)*-OF(5)-NPh** and 221 GM for ***(Bu)*-OF(5)-NPh**, respectively. Consistently, the TPA cross-section enhancement for ***(Ph)*-OF(n)-NPh** series occurs in the full TPA spectra measured as compared to those of ***(Bu)*-OF(*n*)-NPh**s. These results underline the importance of 9,9-diphenyl substitution onto a fluorenyl unit in enhancing the nonlinear optical properties. Fig. 4 shows that the allowed two-photon excited states of ***(Bu)*-OF(4)-NPh** and ***(Ph)*-OF(4)-NPh** are higher than their one-photon excited states, which is consistent with the TPA selection rule for the quadrupolar molecule.[12] The power-squared dependence of two-photon excited fluorescence for ***(Ph)*-OF(5)-NPh** and ***(Bu)*-OF(5)-NPh** were also investigated. In both cases, the power-squared dependence of TPEF as shown in Fig. 3b was followed with the slope in the range of

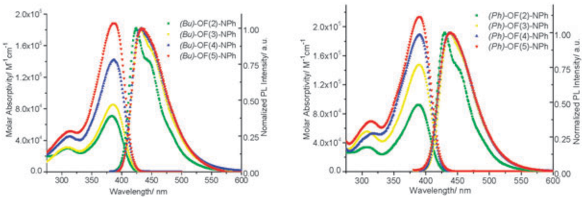

Fig. 2 Absorption and emission spectra of ***(Bu)*-OF(*n*)-NPh** and ***(Ph)*-OF(*n*)-NPh**, *n* = 2–5 in $CHCl_3$.

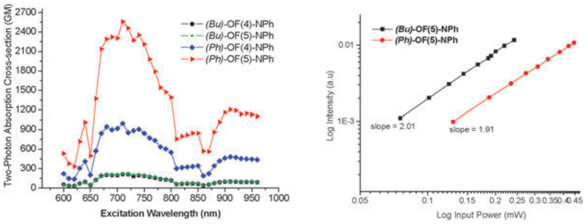

Fig. 3 (a) TPA spectra of ***(Bu)*-OF(*n*)-NPh** and ***(Ph)*-OF(*n*)-NPh**, *n* = 4 and 5 in $CHCl_3$ from 600–960 nm. (b) Logarithmic plots of the power dependence of relative two-photon induced fluorescence on pulse intensity using an 800 nm femtosecond laser as an excitation source for ***(Ph)*-OF(5)-NPh** and ***(Bu)*-OF(5)-NPh**.

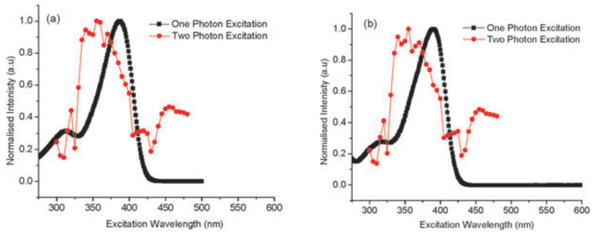

Fig. 4 Normalized one- and two-photon excitation spectra of (a) **_(Bu)_-OF(4)-NPh** and (b) **_(Ph)_-OF(4)-NPh**. The two-photon excited wavelengths are divided by 2 for easy comparison.

1.91–2.01, which directly gives the experimental evidence of a two-photon excitation process.

To gain an insight into molecular property differences in these two series, the quantum chemical calculations were also performed. The geometries of **_(Ph)_-OF(3)-NPh** and **_(Bu)_-OF(3)-NPh** were optimized by *ab inito* calculations using Gaussian 03 on the B3LYP 6-31G* level (see the ESI†). The optimized geometry of **_(Ph)_-OF(3)-NPh** showed that the two phenyl rings substituted at the 9-position of the fluorenyl units are far from coplanar with the terfluorenyl backbone. It is important to note that the frontier molecular orbitals such as the HOMO (−4.77 eV) and LUMO (−1.42 eV) of **_(Ph)_-OF(3)-NPh** are more stabilized than those of **_(Bu)_-OF(3)-NPh** (HOMO = −4.74 eV and LUMO = −1.34 eV), which is due to the more extended electron delocalization in **_(Ph)_-OF(3)-NPh** arising from participation of the non-coplanar diphenyl moieties at the 9,9-position of a repeating fluorenyl unit. Such participation can be reflected from the contributions of the atomic orbitals of 9,9-diphenyl moieties to the overall molecular orbitals, which are involved to a much greater extent than those of 9,9-dibutyl groups. This has resulted in a slight reduction of the HOMO–LUMO energy gap of **_(Ph)_-OF(3)-NPh** (E_g = 3.35 eV) relative to **_(Bu)_-OF(3)-NPh** (E_g = 3.40 eV), which explains the observed small red-shift of absorption and emission. It also explains that the TPA enhancement in **_(Ph)_-OF(_n_)-NPh** series also originates from the more extended electron delocalization or increased conjugated path[13] over the non-coplanar diphenyl rings at the 9,9-position of the fluorenyl units.

In summary, we have synthesized homologous series of diphenylamino-endcapped oligofluorenes bearing different substituents at the 9-position of fluorenyl rings, which exhibit a high fluorescence quantum yield and a large two-photon absorption cross section of up to 2559 GM at a 710 nm fs laser pulse. Although the absorption and emission remain fairly constant with an extension of the oligomeric chain length, the two-photon absorption cross-sections increase nonlinearly. It is remarkably found that oligo-9,9-diphenylfluorenes exhibit much larger TPA cross-sections than the corresponding 9,9-dibutyl-substituted counterparts despite only a slight red-shift in absorption and emission. The participation of the non-coplanar diphenyl moieties at the 9,9-position of the fluorenyl units in enhancing electron delocalization and conjugated path is theoretically shown, which is attributed to the origin of the red shift of optical spectra and the TPA enhancement. Our findings show that the 9,9-diphenylfluorene structural unit is a very useful building block to construct highly efficient TPA materials with an excellent nonlinearity-transparency trade-off.

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