

Supporting Information

Two-photon absorption and optical power limiting properties in femtosecond regime of novel multi-branched chromophores based on tri-substituted olefinic scaffolds

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◆ Synthetic Procedures

General

All commercially available reagents for the preparation of the intermediates and targeted chromophores including triphenylamine, tetrabutylammonium tribromide (TBABr₃), 1-bromohexane, 2,7-dibromofluorene, *N,N*-diphenylamine, sodium hydroxide, sodium *tert*-butoxide, bis(tri-*t*-butylphosphine)palladium(0) (Pd[P(*t*Bu)₃]₂), diisopropylamine (*i*-Pr₂NH), vinylboronate pinacol ester were obtained from Aldrich Chemical Co. and were used as received, unless stated otherwise. THF was distilled from sodium benzophenone ketyl. Benzyltrimethylammonium tribromide (BTMABr₃) was synthesized by following reported procedure.¹ ¹H-NMR and ¹³C-NMR spectra were recorded either at 200 or 300 MHz spectrometers and referenced to TMS or residual CHCl₃. High-resolution mass spectroscopy (HRMS) was conducted by using a Waters LCT ESI-TOF mass spectrometer. MALDI-TOF MS spectrum was obtained on a Voyager DE-PRO mass spectrometer (Applied Biosystem, Houston, USA). Elemental analysis was performed utilizing a Perkin Elmer series II CHNS/O Analyzer 2400.

Synthesis

In Scheme 1, compounds **3**, **5**, and **6** were synthesized by following the established literature processes^{1,2} and obtained with yields of ~56 % for compound **3**, ~70 % for compound **5**, and ~98 % for compound **6**. Both model compounds **1** and **2** were synthesized according to the established one-pot catalytic coupling methodology developed by K. Itami and J.-i. Yoshida and co-workers³ and the synthesis of model compound **1** has been reported by us previously.⁴ The experimental details for the syntheses of these compounds are presented as the following:

Compound 5

A mixture of 2,7-dibromo-9*H*-fluorene (10g; 0.03 mol), potassium iodide (0.1g; <0.1 mol), and sodium hydroxide (10.19g; 0.15 mol) in DMSO was pre-heated at reflux for 30 minutes and then cooled down to the room temperature. To this reaction mixture was added 1-bromohexane (10ml; 0.07 mol) and the resultant solution was stirred at reflux for another 24 hours. After cooling to the room temperature, the reaction mixture was extracted with ethyl acetate. The organic phase was collected and then dried over MgSO_{4(s)}. After removing the solvent, the crude product was purified

through column chromatography on silica gel using hexane as the eluent to obtain the final purified product as white powder with yield of ~70% (10.63g). $^1\text{H-NMR}$ (200 MHz, CDCl_3): δ 7.55~7.50(dd, 2H), 7.47~7.45(dd, 2H), 7.46~7.42(dd, 2H), 1.96~1.88(m, 4H), 1.18~1.06(m, 12H), 0.81~0.75(m, 4H), 0.63~0.60(m, 6H).

Compound 3

A mixture of compound **5** (10g; 0.02 mol), diphenylamine (4.12g; 0.02 mol), $\text{Pd}_2(\text{dba})_3$ (0.19g; 0.2 mmol), *rac*-2,2-bis(diphenylphosphino)-1,1-biphenyl (0.38g; 0.6 mmol), and sodium *tert*-butoxide (2.73g; 0.02 mol) in toluene was stirred at 80°C for 24 hours. After cooling to the room temperature, the reaction mixture was extracted with ethyl acetate and then dried over $\text{MgSO}_{4(\text{s})}$. After removing the solvent, the crude product was purified through column chromatography on silica gel using hexane as the eluent to give the final purified product as colorless oil with yield of 56% (6.60g). $^1\text{H-NMR}$ (200 MHz, CDCl_3): δ 7.54~7.50(m, 1H), 7.50~7.44(dd, 1H), 7.45~7.40(dd, 2H), 7.30~7.22(m, 4H), 7.14~7.09(dd, 2H), 7.14~7.09(m, 2H), 7.05~6.98(m, 4H), 1.87~1.79(m, 4H), 1.17~0.99(m, 12H), 0.81(t, $J = 7.04$ Hz, 6H), 0.64(m, 4H). HRMS-FAB(m/z): M^+ calcd for $\text{C}_{37}\text{H}_{42}\text{BrN}$, 579.2501, found, 579.2507.

Compound 6

To a solution of triphenylamine (5.0g; 0.02 mol) in CH_2Cl_2 (50ml) was added TBABr_3 (29.4g; 0.06 mol) and methanol (20ml) was stirred at room temperature for 24 hours. After filtration, the crude product was collected and subjected to vacuum drying oven for the removal of solvent. The product was obtained as white powder with yield of 98% (8.84g). $^1\text{H-NMR}$ (200MHz, CDCl_3): δ 7.38~7.31(m, 6H), 6.95~6.88 (m, 6H). HRMS-FAB(m/z): M^+ calcd for $\text{C}_{18}\text{H}_{12}\text{Br}_3\text{N}$, 323.1674; found, 323.1669.

Compound 1

A mixture of compound **3** (0.945g; 1.65 mmol), vinylboronate pinacol ester (0.125g; 0.81 mmole), $\text{Pd}[\text{P}(t\text{Bu})_3]_2$ (0.021g; 0.04 mmol), and *i*- Pr_2NH (0.33g; 3.25 mmol) in dry toluene was stirred at 90°C for 24 hours under nitrogen. To this reaction mixture were added compound **5** (0.20g; 0.405 mmol), NaOH (0.325g; 8 mmol), and H_2O (0.5ml; 0.03 mole) and the resultant mixture was further stirred at reflux for another 24 hours and then gradually cooled to room the temperature. After removing the solvent, the crude product was purified through column chromatography on silica gel using hexane-ethyl acetate(200:1) as the eluent to afford 0.7g yellow powder with ~73% overall yield. $^1\text{H-NMR}$ (300MHz, CDCl_3): δ 7.57~7.52(d, 4H), 7.52~7.48(d, 8H), 7.48~7.43(d, 4H), 7.25~7.15(m, 44H), 7.04~7.00 (m, 12H), 1.88(br, 24H), 1.09(br, 72H), 0.83-0.80(m, 60H) ; $^{13}\text{C-NMR}$ (75 MHz, CDCl_3): δ 152.45, 151.21, 150.77, 148.05, 140.65, 136.18, 135.88, 129.20, 128.37, 125.70, 123.83, 122.51, 121.71, 120.40, 119.41, 118.68. HRMS-FAB(m/z): M^+ calcd for $\text{C}_{177}\text{H}_{202}\text{N}_4$, 2385.5246; found, 2385.5250. Anal calcd for $\text{C}_{177}\text{H}_{202}\text{N}_4$: C, 89.12; H, 8.53; N, 2.35; found: C, 89.15; H, 8.45; N, 2.40.

◆ Photophysical Methods

Linear absorption and emission spectra measurements

Linear absorption spectra were recorded on a Shimadzu 3150 PC spectrophotometer with freshly prepared sample solutions in THF ($1 \times 10^{-5} \text{M}$). One-photon-induced fluorescence emission spectra were measured by using a Jobin-Yvon FluoroMax-3 spectrometer with the same sample solutions in THF ($1 \times 10^{-5} \text{M}$). Fluorescence quantum yield were measured on degassed samples at room temperature by following the protocol suggested in the literature⁵; Coumarin 153 ($\Phi_F = 0.38$ at $\lambda_{\text{exc}} = 423 \text{ nm}$) was used as the standard and refractive index correction was also performed.^{5,6} The linear absorption and emission spectra of the reference compound (**R**) are shown in Figure S1.

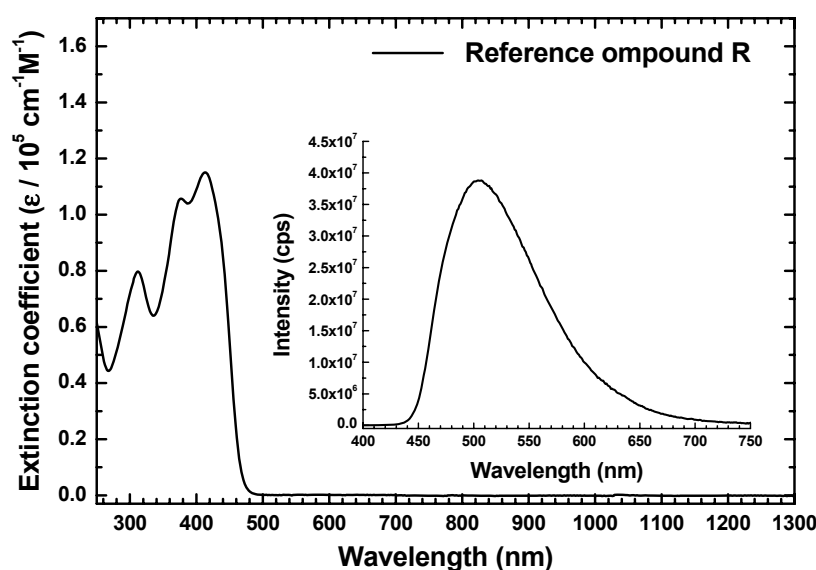


Figure S1. Linear absorption and emission spectra of the reference compound (**R**).

Two-photon-excited fluorescence (2PEF) measurements

Two-photon-excited fluorescence spectra of the studied model fluorophores in THF (concentration: $1 \times 10^{-4} \text{M}$) were measured according to the protocol established by Xu and Webb using Fluorescein (0.1N NaOH solution) as the standard.⁷ The experimental setup is illustrated in Figure S2. In brief, the excitation light source was a mode-locked Ti:Sapphire laser (Tsunami pumped with a Millennia 10W, Spectra-Physics) which delivers $\sim 80 \text{fs}$ pulses with the repetition rate of 80MHz and the beam diameter of 2mm. The intensity level of the excitation beam was carefully controlled by a $\lambda/2$ wave plate in order to avoid the saturation of absorption and photodegradation. To minimize the effects of re-absorption, the excitation beam was focused as close as possible to the wall of the quartz cell (5mm \times 5mm cuvette) and the 2PEF emissions were collected and induced by a fiber bundle into a Jobin-Yvon FluoroMax-3 spectrometer for the spectra recording. This optical system was also utilized for the characterization of the quadratic dependence of the 2PA-induced upconversion emission intensity on the pumping intensity for every data point.

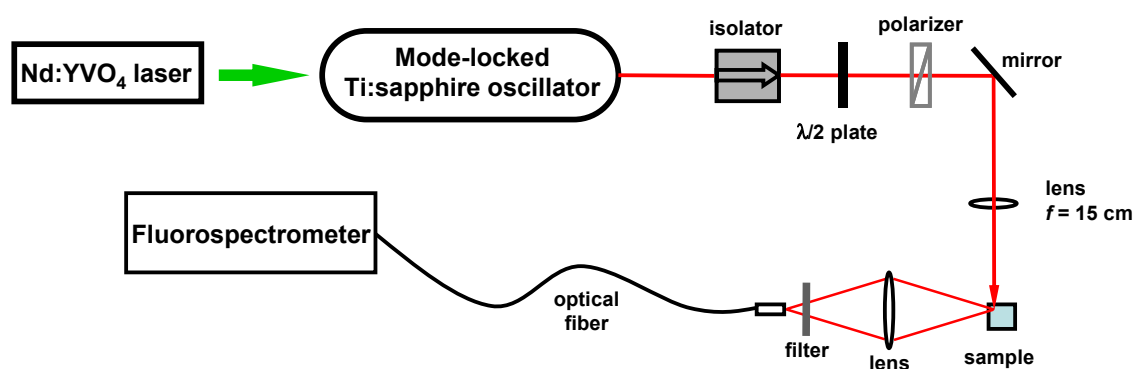


Figure S2. Optical setup for 2PEF-related experiments.

The 1PA- and 2PA-induced fluorescence lifetime of the same sample solutions were measured by a Hamamatsu C5680-22 high-speed streak camera. The optical setup for this experiment was very similar with the one shown in Figure S1, only differs in the pumping source and the detection system. The excitation light source for this measurement was a Ti: sapphire laser oscillator/amplifier system (CPA-2010 from Clark-MXR) producing ~ 160 fs duration of Gaussian shape, ~ 775 nm wavelength, and ~ 8 nm spectral width laser output with a repetition rate of 1 KHz. This laser beam can be used directly for the 2PA-induced fluorescence life-time measurements or it can be used to pump a BBO crystal in order to generate frequency-doubled laser pulses (at ~ 388 nm) for 1PA-induced fluorescence life-time studies of the investigated samples. Figure S3 illustrates the measured 2PEF spectrum and the quadratic dependence of the 2PA-induced fluorescence intensity on the pumping intensity for the reference compound (**R**). Also, the measured 1PA- and 2PA-induced fluorescence decay curves and the degenerate 2PA spectrum of this reference compound are depicted in Figures S4 and S5, respectively.

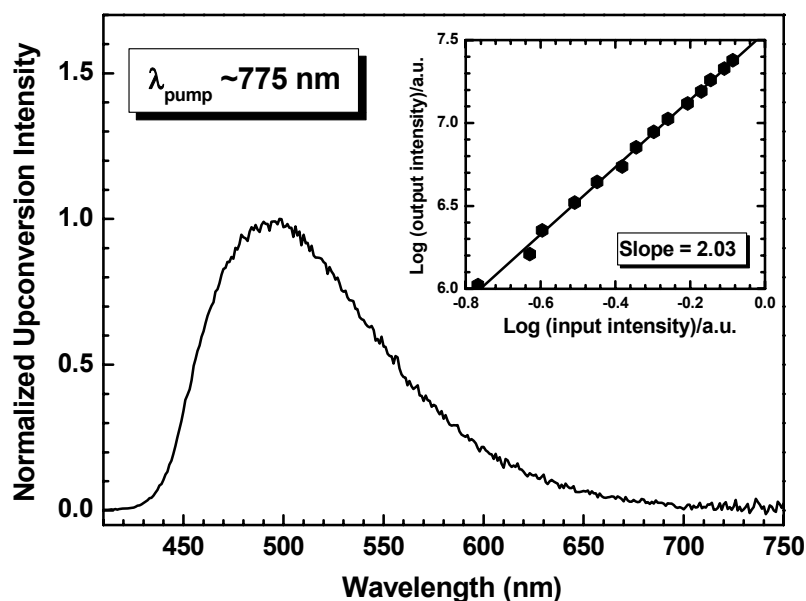


Figure S3. Normalized two-photon excited upconversion spectra of fluorophore **R** in THF at $5 \times 10^{-3} \text{M}$. Inset, power dependence of the 2PA-excited upconversion intensity on the input intensity.

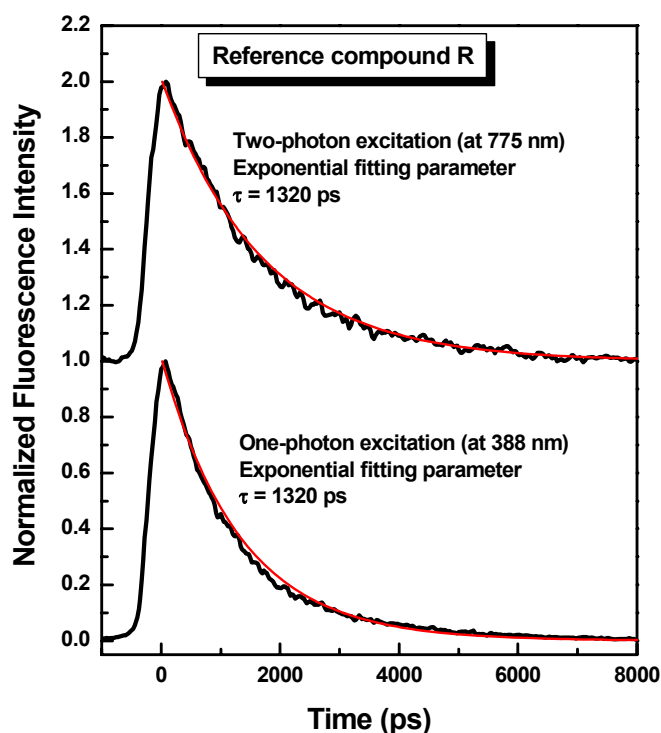


Figure S4. Normalized fluorescence decay curves of the reference compound (**R**) in solution phase excited by one-photon absorption (at 388 nm) and two-photon absorption (at 775 nm).

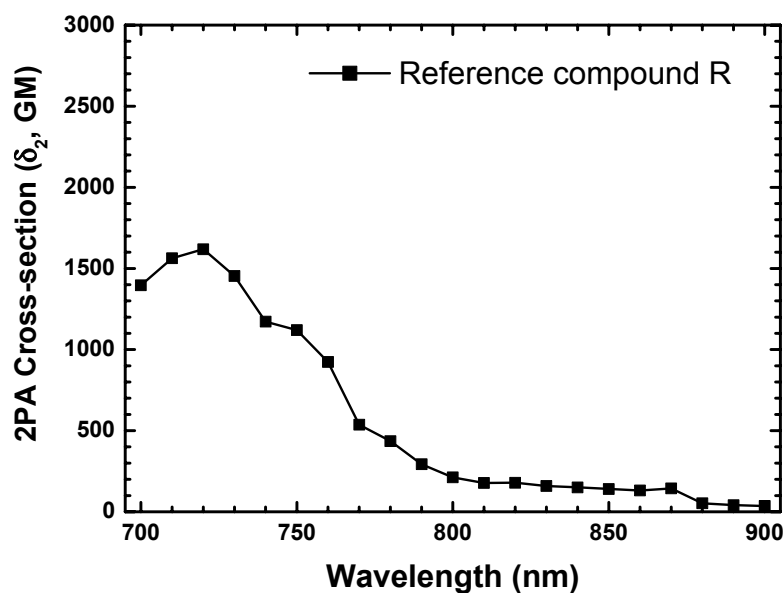


Figure S5. Degenerate two-photon absorption spectrum of the reference compound (**R**) by 2PEF method in THF solution at 1×10^{-4} M (with experimental error $\sim \pm 15\%$).

2PA-based optical-power limiting property studies

The two-photon absorption induced optical power limiting properties of model compounds **1** and **2** were determined by using the nonlinear transmission method.⁸ The same laser oscillator/amplifier system (CPA-2010 from Clark-MXR) as utilized in the temporal behavior analyses was employed for this experiment. The optical setup for this measurement is illustrated in Figure S2. In this study, a 775 nm laser beam of 2.5 mm size was focused by an $f=15$ cm lens onto the center of a 1 cm quartz cell filled with model compound solution (0.005 M in THF). By tuning the intensity of the input laser beam and measuring the intensity of the transmitted laser beam, the 2PA-induced nonlinear transmissivity at various pumping level can be deduced. These experimental data can also be presented by the measured output pulse energy as a function of input pulse energy as illustrated Fig. 6.

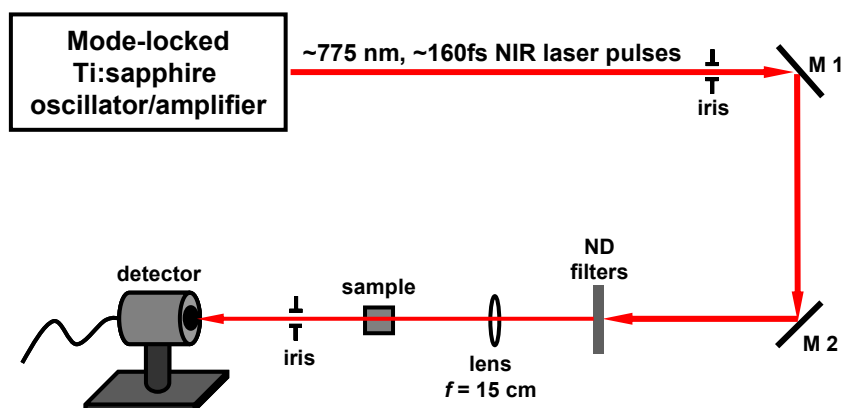


Figure S6. Experimental setup for the 2PA-based optical power limiting behavior studies.

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