
Novel fluorophore based on multi-substituted olefin skeleton with enhanced three-photon absorption in femtosecond regime

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Materials

All commercially available reagents for the preparation of the intermediates and targeted chromophores including triphenylamine, tetrabutylammonium tribromide (TBABr₃), phosphorus oxychloride (POCl₃), iodomethane, triphenylphosphine (P(C₆H₅)₃), 1-bromohexane, 2,7-dibromofluorene, *N,N*-diphenylamine, sodium hydroxide, sodium *tert*-butoxide, sodium hydride (NaH, 60% dispersion in mineral oil), palladium(II) acetate (Pd(OAc)₂), tri-*o*-tolylphosphine (P(*o*-tolyl)₃), triethylamine (NEt₃), and acetonitrile, toluene, 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.

Chemical property characterizations

¹H-NMR spectra were recorded at 200MHz and ¹³C-NMR spectra were recorded at 50MHz via a Bruker DRX-200 spectrometer in CDCl₃. 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**, **4**, **6** were synthesized by following the established literature processes^[1-3] and obtained with the overall yields of ~65 % for compound **3**, ~50 % for compound **4**, and ~90 % for compound **3**. For the synthesis of reference compound **1**, the well-known Heck coupling reaction^[4] have been adopted and this compound was obtained with the yields of 75%. On the other hand, for the synthesis of model compound **2**, a catalytic reaction condition has been followed.^[5] The experimental details for the preparation and characterization of compounds **1** and **2** are presented as the following:

Compound 1^[4]

Compound **3** (2.07g; 3.57 mmol), compound **4** (0.35g; 1.08 mmol), Pd(OAc)₂ (0.015g; 0.065 mmol), P(*o*-totyl)₃ (0.118g; 0.4 mmol), triethylamine (~5mL) and acetonitrile (~15mL) was added to a heavy-wall pressure tube equipped with a magnetic stirrer and a rigid Teflon cap. The reaction mixture was then heated up to 110 °C under nitrogen atmosphere and kept at this temperature by means of a heating mantle for 36 hours. After cooling, the reaction mixture was poured into methanol. The crude product was filtered off and purified by column chromatography on silica gel using ethyl acetate-hexane (1:8) as the eluent to afford the title compound as bright yellow powder in ~75% yield (1.46g). ¹H-NMR (200 MHz; CDCl₃): δ:7.53(m, 12H), 7.30~7.22 (m, 24H), 7.15~7.02(m, 30H), 1.85(br, 12H), 1.08(br, 36H), 0.81~0.73(m, 30H). ¹³C-NMR (50 MHz, CDCl₃): δ152.39, 151.17, 150.64, 147.99, 147.04, 136.10, 135.77, 129.13, 123.77, 122.44, 121.59, 120.34, 119.39, 118.65, 54.96, 54.79, 40.29, 31.59, 31.51, 29.63, 23.54, 22.54, 14.08. HRMS (EI): calcd for M⁺: 1821.1391; found: 1821.1343. Anal calcd for C₁₃₅H₁₄₄N₄: C, 88.96; H, 7.96; N, 3.07; found: C, 88.72; H, 8.32; N, 2.96.

Compound 2^[5]

A mixture of compound **3** (3.78g; 6.5 mmol; 2.0 equiv.), vinylboronate pinacol ester (**5**; 0.5g; 3.25 mmol, 1.0 equiv.), Pd[P(*t*Bu)₃] (0.084g; 0.05 equiv.), and *i*-Pr₂NH (1.32g; 4.0 equiv.) in dry toluene was stirred at 90°C for 24h under nitrogen. To this reaction mixture were added compound **6** (0.4g; 0.25 equiv.), NaOH (1.4g; 10.0 equiv.), and H₂O (0.5 ml; 8.0 equiv.) and the resultant mixture was further stirred at reflux for another 24h and then gradually cooled to room temperature. The reaction mixture was extracted with CH₂Cl₂ and the combined organic phase was washed with brine (30mL×3), H₂O (30mL×2) and then dried over MgSO_{4(s)}. The crude product was then purified through column chromatography on silica gel by using ethyl acetate-hexane (1:20) as the eluent to afford 1.24g yellow powder with ~45% overall yield. ¹H-NMR (200MHz, CDCl₃): δ7.63~7.42(m, 18H), 7.30~7.33(m, 39H), 7.15~7.01(m, 54H), 1.92~1.85(m, 24H), 1.08(br, 72H), 0.84~0.72(m, 60H). ¹³C-NMR (50 MHz, CDCl₃): δ152.64, 152.49, 152.41, 151.25, 148.09, 147.15, 142.01, 140.40, 136.35, 136.19, 135.90, 130.57, 129.25, 127.38, 124.41, 123.87, 122.55, 120.48, 119.48, 118.79, 55.24, 55.06, 40.43, 31.70, 31.62, 29.62, 23.91, 22.65, 14.20. MALDI-TOF MS calcd for M⁺: 3321.80; found, 3321.81. Anal calcd for C₂₄₆H₂₆₇N₇: C, 88.95; H, 8.10; N, 2.95; found: C, 88.85; H, 8.20; N, 2.96.

Nonlinear optical property characterizations

The three-photon absorption cross sections σ^{3PA} of compounds **1** and **2** were determined by using the nonlinear transmission method.^[6] A Ti:sapphire regenerative amplifier (CPA-2010, Clark MRX), was used to generate 150-fs duration pulses with 1-kHz repetition rate. These pulses were parametrically down-converted using an optical parametric generator (OPG), which yielded pulses in the wavelength range from 1100 nm to 1500 nm, and the energy range from 2.0 μ J to 10.0 μ J. The output laser energy from the OPG is kept at ~ 1.0 μ J by using neutral density filters. This beam was focused by an $f=15$ cm lens onto the center of the tested sample solution in quartz cuvette (light path-length = 1 cm). The experimental uncertainty for these measurements is $\sim \pm 15$ %. The samples were prepared as chloroform solutions at the concentration of $\sim 5 \times 10^{-3}$ M for 3PA measurements.

For a given excitation wavelength of input laser pulses, the 3PA coefficient γ and cross-section σ^{3PA} can be experimentally determined by simply measuring the nonlinear transmission behavior of a given sample medium. Assuming that the linear absorption is negligible at the excitation wavelength, and 3PA is the major mechanism for the observed nonlinear absorption, the nonlinear transmissivity of the tested material can be described by

$$T = \frac{I(l)}{I(0)} = \frac{1}{\sqrt{1 + 2\gamma I^2(0)}}, \quad (1)$$

Here, $I(0)$ and $I(l)$ are the input and output laser intensity, respectively; l is the optical path-length of the three-photon absorbing medium. In this case, once we know the value of the input intensity $I(0)$ and the value of the corresponding nonlinear transmissivity T , the γ value of the material can be directly determined. Furthermore, if the molar concentration of the absorbing molecules is known, the value of 3PA cross-section σ^{3PA} can be determined by

$$\sigma^{3PA} = \frac{\gamma}{N_A d_0 \times 10^{-3}}, \quad (2)$$

where N_A is Avogadro number, d_0 is the molar concentration of the absorbing molecules.

The three-photon excited fluorescence was obtained by excitation with a 1300 nm laser beam, which was focused by an $f = 15$ cm lens onto the center of the sample. The upconverted emission of the sample was collected from the sample surface in order to minimize the re-absorption effect. The fluorescence spectra were recorded by using a HoloSpec CCD-array spectrometer in conjunction with a fiber coupler head.

In the 3PA-based optical power limiting behavior study, a 1300 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 compound **2** in solution (0.04 M in chloroform). By tuning the intensity of the input laser beam and measuring the intensity of the transmitted laser beam, the 3PA-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. 4.

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