Supporting Information

Multi-Photon Properties of Branched Chromophores Derived from Indenoquinoxaline and oxadiazole Heterocyclic Units

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Photophysical Methods

Linear absorption and emission spectra measurements

Linear absorption spectra were recorded on a Shimadzu 3150 PC spectrophotometer with freshly prepared sample solutions. The same sample solutions were also used for the measurement of one-photon-induced fluorescence emission spectra and life-time by utilizing a Jobin-Yvon FluoroMax-4 spectrometer equipped with TCSPC accessories (FluoroHub-B + NanoLED from Jobin-Yvon). The aforementioned fluorospectrometer equipped with an integrating sphere (Labsphere from Jobin-Yvon; diameter = 100 mm) was also employed to measure the absolute fluorescence quantum yield of each model compound in solution phase at room temperature;[1] Coumarin 153 ($\Phi_F = 0.38 \pm 5\%$ at $\lambda_{exc} = 423$ nm) was used as the standard for the calibration of the integrating sphere and the instrument.[2,3]

Multi-photon-excited fluorescence (MPEF) measurements

Multi-photon-excited fluorescence technique was employed to determine the power dependence of the fluorescence intensity on the incident intensity at a selected wavelength. If such power dependence experiment is continuously performed within a certain spectral range, a spectrum that represents the dispersion of the order of absorption process (i.e. OAP-spectrum) can then be delineated. The experimental setup is illustrated in Figure S1. In brief, the excitation light source was an integrated mode-locked Ti:Sapphire laser and OPO system (Chameleon Ultra II and Compact OPO, Coherent Inc.) which delivers ~140 fs pulses with the repetition rate of 80 MHz and the beam diameter of 2 mm. The wavelength range utilized for these MPEF-related experiments was 680-1500 nm and the intensity level of the excitation beam was carefully controlled by the combination of a $\lambda/2$ wave plate and a polarizer in order to avoid the occurrence of either saturation of absorption or photodegradation within the tested sample during the measurements. To minimize the effects of re-absorption, the excitation beam was focused as close as possible to the wall of the quartz cell (10 mm×10 mm cuvette) and the MPEF emissions were collected and induced by an optical fiber into a CCD imaging spectrometer (QE-Pro, Ocean Optics) for the spectra recording.



Figure S1. Optical setup for MPEF-related experiments.

The same optical system was also utilized for the characterization of 2PA and 3PA-spectra of the studied model fluorophores in solution phase using Fluorescein (0.1 N NaOH solution) and BDPAS (in deuterated dichloromethane) as the corresponding standards,[4-6] respectively. The measured OAP-spectrum for compound **1** is as follows:



Figure S2. OAP-spectrum for compound 1.

• 2PA- and 3PA-based optical power-limiting

The 2PA- and 3PA-based optical-power limiting performance of the compound **2** in solution phase (0.01M in toluene or deuterated toluene, light path-length = 1 cm) was probed at ~750 and ~1280 nm using femtosecond laser pulses as the working tool. An integrated regenerative amplifier and OPA system (Spitfire Ace and TOPAS Prime, Spectra-Physics) was employed as

the excitation source to provide \sim 30 fs laser pulses with repetition rate of 5 KHz for this study. The laser beam was slightly focused onto the center of the sample solution in order to obtain a nearly uniform laser beam radius within the whole cell path-length. The local intensity within the sample solution was tuned by adjusting the incident laser power level with the aid of the combination of a half-wave plate and a polarizing beam splitter. In all cases, the incident and transmitted laser power were simultaneously acquired and recorded by a data acquisition card (myDAQ, National Instruments) and a computer. Besides, we did not meet any difficulties to prepare the high concentration solutions of these two compounds for three-photon-related experiments (*vide supra*). In fact, neither distortion of their fluorescence spectra nor the generation of extra fluorescence bands possibly caused by the aggregation at high sample concentration was observed in our case.



Figure S3. Experimental setup for the 2PA- and 3PA-based power-limiting behavior studies.

References

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• Numbering of C and H of the precursors and final chromophores for NMR assignment











$\blacklozenge \Box^{1}H$ and ^{13}C NMR spectra of the precursors and final compounds

¹³C NMR spectrum of compound 4 (solvent: CDCl₃)







¹³C NMR spectrum of compound 7 (solvent: CDCl₃)







¹³C NMR spectrum of compound **8** (solvent: CDCl₃)



¹³C NMR spectrum of compound **9** (solvent: CDCl₃)



¹³C NMR spectrum of compound **11** (solvent: CDCl₃)



¹³C NMR spectrum of compound **12** (solvent: CDCl₃)



¹³C NMR spectrum of compound **13** (solvent: CDCl₃)



¹H NMR spectrum of compound **14** (solvent: CDCl₃)



¹³C NMR spectrum of compound **14** (solvent: CDCl₃)



¹H NMR spectrum of compound **15** (solvent: CDCl₃)



¹³C NMR spectrum of compound **15** (solvent: CDCl₃)



¹H NMR spectrum of compound **16** (solvent: CDCl₃)



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 1 H NMR spectrum of compound **1** (solvent: CDCl₃)



¹³C NMR spectrum of compound **1** (solvent: CDCl₃)



¹H NMR spectrum of compound **2** (solvent: CDCl₃)

