

Supporting Information

Synthesis and Two-photon Properties of A Novel Multi-branched Chromophore with Unsymmetrically Substituted Scaffold Derived from Functionalized Quinoxalinoid Heterocycles

Tzu-Chau Lin,*^a May-Hui Li,^a Che-Yu Liu,^a Ja-Hon Lin,^b Yu-Kai Shen^b and Ying-Husan Lee,^a

^aPhotonic Materials Research Laboratory, Department of Chemistry, National Central University, Jhong-Li 32001, Taiwan. E-mail: tclin@ncu.edu.tw

^bPhotonic Technology Laboratory, Department of Electro-Optical Engineering, National Taipei University of Technology, Taipei10608, Taiwan.

◆ Representative Numbering of C and H on Various Structural Units

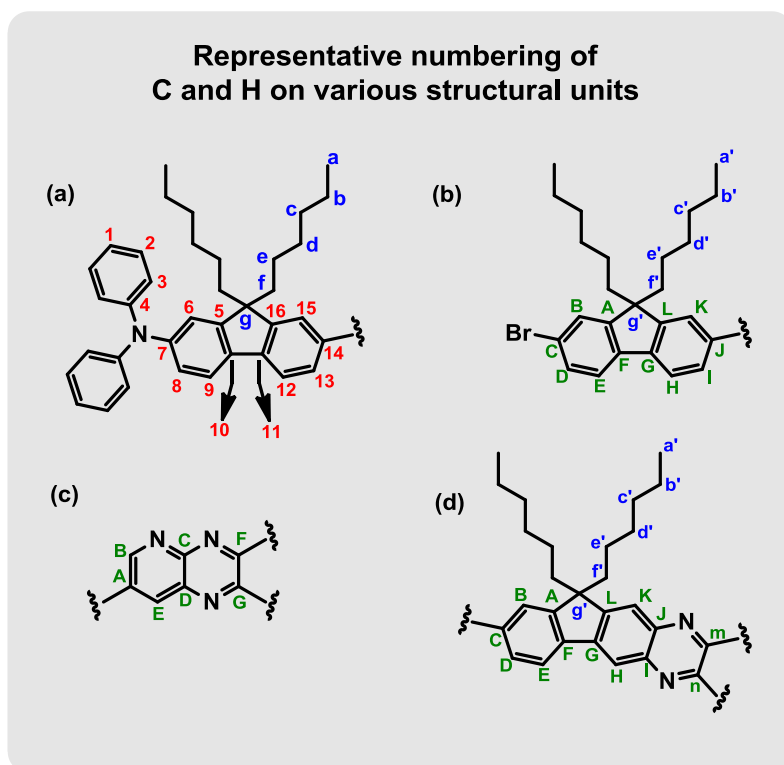


Figure S1. Representative numbering of C and H on different structural units.

◆ 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 various solvents ($1 \times 10^{-5} \text{M}$). 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 integrated sphere (Labsphere from Jobin-Yvon; diameter = 100mm) was also employed to measure the absolute fluorescence quantum yield of each model compound in solution phase ($1 \times 10^{-5} \text{M}$) at room temperature;^[1] Coumarin 153 ($\Phi_{\text{F}} = 0.38 \pm 5\%$ at $\lambda_{\text{exc}} = 423 \text{ nm}$) was used as the standard for the calibration of the integrated sphere and the instrument.^[2,3]

Two-photon-excited fluorescence (2PEF) measurements

Two-photon-excited fluorescence spectra of the studied model fluorophores in solution phase (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.^[4] The experimental setup is illustrated in Figure S1. 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 (10mm \times 10mm cuvette) and the 2PEF emissions were collected and induced by a fiber bundle into a CCD imaging spectrometer (USB-4000, Ocean Optics) for the spectra recording. This optical system was also utilized for the characterization of the quadratic dependence of the 2PA-induced up-conversion emission intensity on the pumping intensity for every data point.

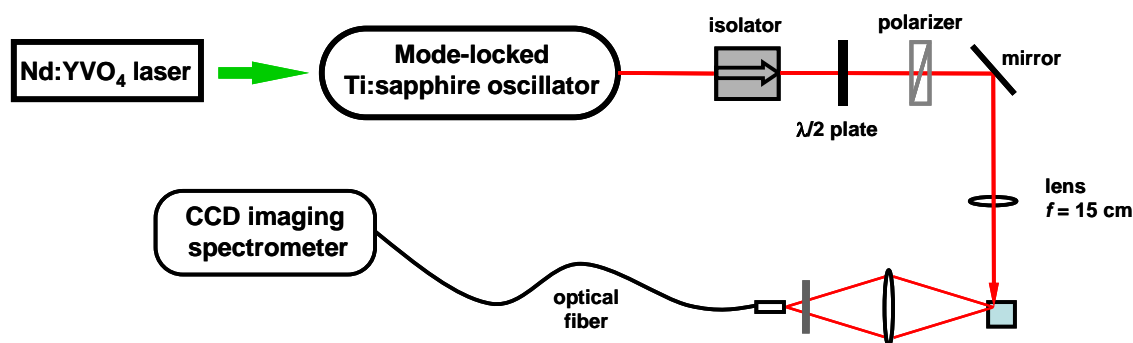


Figure S2. Optical setup for 2PEF-related experiments.

Effective optical-power limiting property studies

Effective optical-power limiting performance of compounds **1-4** in solution phase (0.02M in THF, light path-length = 1 cm) was probed at ~800nm using nanosecond laser pulses as the working tool. As shown in Figure S2, a nanosecond tunable laser system (an integrated OPO and Q-switched Nd:YAG laser: NT 342/3 from Ekspla) were employed as the excitation source to provide ~6 ns laser pulses with repetition rate of 10 Hz 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 a ND filter set. In all cases, the energy of transmitted laser beam from the sample cell was detected by an optical power (energy) meter with a large detection area of ~25 mm in diameter.

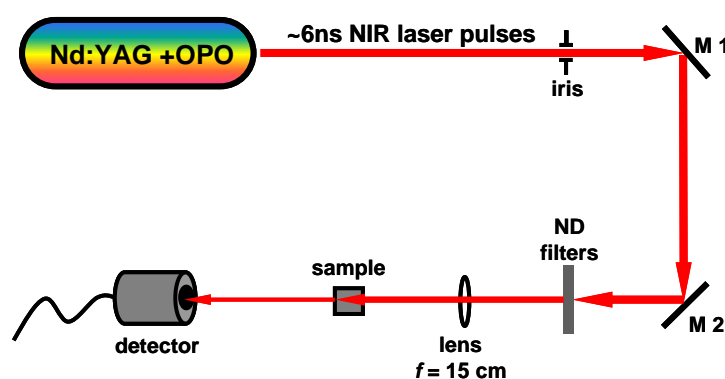


Figure S3. Experimental setup for the effective optical power limiting behavior studies.

References

- [1] L. Porres, A. Holland, L.-O. Palsson, A. P. Monkman, C. Kemp, A. Beeby, *J. Fluoresc.* **2006**, *16*, 267.
- [2] J. A. Gardecki, M. Maroncelli, *Appl. Spectrosc.* **1998**, *52*, 1179.
- [3] G. A. Reynolds, K. H. Drexhage, *Opt. Commun.* **1975**, *13*, 222.
- [4] C. Xu, W. W. Webb, *J. Opt. Soc. Am. B* **1996**, *13*, 481.