A Two-Photon Pumped Supramolecular Upconversion Microresonator


Abstract: A two-photon pumped non-linear optical (NLO) Fabry-Pérot (F-P) type organic micro-crystal resonator useful for a myriad of upconversion-based light technologies is presented. The resonator is parallelepiped-shaped and composed of a self-assembled donor-acceptor-donor type molecule namely, 9,9,9″,9″-tetramethyl-9H,9″H-[2,2′,7,2″-terfluoren]-9′-one (TTO). X-ray crystal structure of an orange-yellow TTO micro-crystal reveals C–H···O type weak intermolecular hydrogen bond between the oxygen atom of the fluorenone unit andfluorinehydrogen atom. For one- and two-photon excitation the micro-crystals exhibit F-P type modes in their photoluminescence signal. The fundamental frequency-dependent NLO intensity shows a continuous increase as the fundamental wavelength is decreasing down to 770 nm. The two-photon luminescence signals from these micro-resonators are several orders of magnitude higher than the thin films of similar thickness.

Infra-red laser pumped miniature organic non-linear optical (NLO) resonators are important for the amplification of inherently weak up-converted signals.[1-6] Two-photon luminescence (TPL) is one of the essential NLO up-conversion processes which arises as a result of the absorption of two photons by the NLO materials.[7] TPL is imperative for various applications such as resonators and lasers.[8-13] In this context, recently, we reported the first example of whispering-gallery-mode organic TPL resonator composed of NLO charge-transfer type dye namely, DCM.[12] Though two-photon pumped Fabry-Pérot (F-P) resonators had been realized in organic nano-wires,[11] fabrication of structurally novel organic NLO resonators still remains a challenge.

Generally, organic π-conjugated molecules with strong electron donor-acceptor groups are known to possess large two-photon absorption (TPA) cross-section due to their charge-transfer characteristics.[6,14] Further, these NLO active molecules can be aggregated into micro-crystals of well-defined shape in order to test their potentials for the up-conversion-based F-P resonator applications. Among optoelectronic molecular materials, 2,7-substituted-9-fluorenone is a well-known electron-deficient molecule. Due to the electron withdrawing tendency of keto-group, the reduction potential is lowered providing fluorone the n-type conducting ability.[15] The other advantage of fluorone is its ability to form hydrogen-bonded supramolecular aggregates in the solid state.[15] This aggregation accumulates the individual dipole of the molecules and thereby enhance the NLO susceptibility. Further, the motivation for the novel molecular design with NLO property came from 2,6-disubstituted-(9,9-diaklyfluorene), a well-known molecule used in light emitting diodes as light emitting polymers.[15,16] Therefore we envisioned synthesis of an electron push-pull system namely, 9,9″,9″-tetramethyl-9H,9″H-[2,2′,7,2″-terfluoren]-9′-one (TTO) by coupling 4,4,5,5-tetramethyl-2-(9-(propane-2-ylidene)-9H-fluoren-2-yl)-1,3,2-dioxaborolane units on both sides of 2,7-diido-9H-fluoren-9-one[18] so that a donor-acceptor-donor (D-A-D) type NLO molecule could be achieved.

In this work, we present the realization of two-photon pumped F-P resonators from TTO micro-crystals (Scheme 1A). Our studies show that these parallelepiped-shaped micro-crystals also performed as F-P resonators with a high Q-factor upon optical pumping in a single- and two-photon regimes. The TPL intensity dependency on the fundamental excitation wavelengths shows NLO signal maxima in the range of 760–770 nm. Finite difference time domain (FDTD) numerical simulations were also implemented to understand the electric-field distribution within the micro-crystals.

TTO molecule was successfully prepared via Suzuki cross-coupling reaction as an orange-yellow solid in a decent 75% yield. Further, it was subsequently crystallized in acetonitrile and chloroform (1:1) mixture, to produce orange-yellow...
parallelepiped crystalline blocks. The molecular structure of TTO was unambiguously confirmed by the single crystal X-ray diffraction studies. TTO crystallized in a triclinic system with P-1 space group. In TTO molecule both electron D-fluorine moieties (left and right segments) are twisted with respect to the central fluorenone plane with torsional angles of $\theta = 30^\circ$ and $\theta = -39^\circ$, respectively (Scheme 1B). These twists provided the asymmetric or non-centrosymmetric arrangement to the TTO molecule. The solid-state structure further revealed an intermolecular hydrogen-bond interaction between the oxygen atom of the fluorenone unit and fluorene hydrogen atom ($\text{C}(43)-\text{H} \cdots \text{O} = 2.622 \text{Å}$). Although in the crystalline state all the TTO molecules are orientated in one direction (Scheme 1C), the opposite alignment of the keto groups (nearly perpendicular to the crystallographic a-axis) points towards the non-polar interaction of TTO. D) Packing of TTO along the molecular axis view.

Solution and solid-state UV-vis absorbance and emission properties were studied in order to comprehend the molecular electronic behavior due to aggregation. In chloroform, TTO exhibited three broad absorption maxima at 310, 349 and 620 nm in solution- and solid-states, respectively (Figure 1A). TTO exhibited broad emission bands centered at 609 and 611 nm in solution- and solid-states, respectively (Figure 1A). This result corroborated well with J-type aggregation of TTO seen in the solid-state. The average FL life-time of the TTO crystals is in the range of 5.4 ns (Figure 1B).

To self-assemble TTO molecules into crystalline micro-structures, we have dissolved them in a mixture of CHCl₃/ACN (1:1) solution (1 mg/mL) and sonicated for 20 s. The solution was kept undisturbed for 10 min to allow the micro-particle growth. Then two to three drops of the solution were casted on a clean glass cover-slip and kept under slow solvent evaporation condition at ambient temperature. Confocal optical microscopy investigation of the cover-slip with the sample exhibited the formation of rod-like micro-structures of varying sizes. To further confirm the definite geometry of the rods, field emission scanning electron microscopy (FESEM) and atomic-force microscopy examinations were implemented. The top-down view of the optical and electron micrographs confirmed the parallelepiped shape of the micro-structures (Figure 1C,D). A close-up view of various rods like structures reveals that their height ($H$), width ($W$), and length ($L$) differ from crystal to crystal. A selected for FESEM micro-crystal revealed $H$, $W$, & $L$ values of $-5.5$, $6.4$, and $21.9 \mu$m, respectively (Figure 1D) whereas the microcrystal in the AFM image has the following values of $H$, $W$, & $L$: $1.9$, $3.6$ and $24.6 \mu$m (Figure 1E, F). It also can be seen from the AFM image that the micro-crystal cross-section perpendicular to the substrate has a trapezium-shaped form with the base angles of $-60^\circ$ (Figure 1E).

It is expected that the parallelepiped shape of the micro-crystals should support F-P type resonance modes due to mirror-like reflecting surfaces. To investigate this, we carried out single-particle micro-spectroscopy studies of a micro-crystal...
of $H$ hence its role in the resonator action cannot be overlooked. The estimated Q-factor also increased with increasing length of the micro-crystal to the value of nearly 600 (Figure 2H).

Furthermore, to probe the TPA property, a bunch of TTO micro-crystals was excited with Ti: Sapphire 800 nm fs pulse laser (pulse width 100 fs, repetition rate 1 KHz) having a spot size of about 100 $\mu$m. This experiment showed production of TPL from the microcrystals with the emission range (~570 nm) nearly matching with one-photon pumped PL confirming the NLO characteristics of TTO micro-crystals (Figure 1B). Motivated by this result, to create two-photon pumped FP resonators; we excited each of the TTO micro-crysal in a two-photon microscopy using a femtosecond (760 nm, repetition rate 80 MHz, pulse width 60 fs) pulse laser with the high NA (0.7) objective giving the focus spot size of 1 $\mu$m. The results are presented in Figure 3. The acquired spectrum exhibited several periodic modes along with a broad TPL background (Figure 3B, black line). The background extracted TPL spectrum evidently showed FP type optical modes generated by TTO microcrystals (Figure 3B red lines) with the maximum Q-factor of about 330. This experiment confirmed the potential of the TTO micro-crystals as frequency up-conversion resonators driven by IR pulse laser. The intensity distribution of the optical modes within the micro-crystals was mapped by using the NLO microscopy. The resultant TPL intensity map revealed produc-

Figure 2. A) Optical micrograph of a single of TTO micro-crystals. B and C) PL image of micro-crystal excited at the tip and center-edge with 405 nm CW laser. D) Optical micro-graph of a single of TTO micro-crystal used for 2D PL map. E and F) Single-particle spectra of the micro-crystal shown in D, displaying a variation of FP mode along the crystal cross-section (a-c) and no variation along the crystal length (d-g). G) Plot of FSR versus 1/L. H) The plot of $Q$-factor versus $L$.

PL at the opposite tip (Figure 2B). On the other hand, excitation of the edge of the micro-crystal center exhibited PL propagation to the opposite edge and towards both tips (Figure 2C). These preliminary experiments confirmed the active type optical waveguiding tendency of TTO micro-crystals. The resultant FL spectra showed a series of sharp peaks (optical modes) with a broad background PL. To study the excitation position-dependent modes (if any), we recorded the emission spectra along (i) the cross-section of the crystal (points: a-c) and (ii) its long axis (points: d-g) in a reflection geometry (Figure 2D). The former set of spectra showed a slight variation of the mode positions (Figure 2E), whereas the latter did not show any change in the position of the modes (Figure 2F). This confirms that the facets along the cross-section act as mirror-like surfaces. To verify the cavity type, the free spectral range (FSR) or the separation between two modes ($\Delta \lambda_m = \lambda_m - \lambda_{m-1}$) at a particular wavelength range of about 15 rods as a function of the cavity length $L$ was plotted. The fit showed a nearly linear relationship as per FSR = $\lambda/2 L \ n_{ef}$ within the experimental error, where $\lambda$ is the wavelength maximum of the mode, $L$ is the resonator length and $n_{ef}$ is the effective refractive index (Figure 2G and Figure S3). This result indicated that the TTO micro-crystals are possibly operated as FP-mode resonator along the cavity length. Though $W$ and $L$ could be estimated using the confocal images, we could not determine the value...
fundamental beam power unambiguously confirmed the role of maximum NLO intensity near the micro-crystal tip ends (Figure 3A, see also typical TPL images Figure S5). In other words, the high TPL intensity indicates the localization of high outgoing optical fields at the ends, relative to other areas.

To understand the optical field localization within the micro-crystal, FDTD numerical simulation (using Numerical FDTD Solutions software) was performed for a close to the micro-crystals geometry dielectric medium (Figure 3C,D). For the simulation, geometrical parameters of real micro-crystals were chosen and the refractive index was taken to be 5. The simulations (Figure 3C,D) showed that the crystals support excitation of F-P-like resonator modes (of λ = 566 nm and 591 nm) with complex patterns of the electromagnetic field. The modes can be excited both in the direction parallel and perpendicular to the substrate. A certain direction of the modes circulation depends on geometrical parameters ratio. Also it can be seen that in case of trapezium-shaped micro-crystal modes can be easily detected on the side planes of the micro-crystal that can explain high TPL signal on the edges of the structure.

The wavelength dependency of the TPL intensity gives a qualitative estimation of the TPA cross-section. For this, a millimeter-sized TTO crystal was pumped with a range of fundamental wavelengths from 760–860 nm and the corresponding TPL intensity is given in Figure 4A. This experiment clearly displayed an increase of the TPL intensity when the excitation of F-P-like resonator modes (of λ = 566 nm and 591 nm) with complex patterns of the electromagnetic field. The modes can be excited both in the direction parallel and perpendicular to the substrate. A certain direction of the modes circulation depends on geometrical parameters ratio. Also it can be seen that in case of trapezium-shaped micro-crystal modes can be easily detected on the side planes of the micro-crystal that can explain high TPL signal on the edges of the structure.

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In summary, we prepared arrays of parallelepiped-shaped microcrystals from 9,9',9''-tetramethyl-9H,9'H-[2,2':7,2''-terfluoren]-9'-one (TTO) molecule. These high-quality micro-sized crystals demonstrate an intense single- and two-photon excited photoluminescence that is several orders of magnitude stronger as compared to homogeneous films of the same composition and thickness. This enhancement is due to a strong localization of the electromagnetic field within the crystals associated with the Fabry-Pérot modes excitation. The existence of the resonant modes with the Q-factor up to several hundred is confirmed by direct linear and nonlinear optical microscopy studies and numerical calculations for individual microcrystals. Observed propagation of the resonant modes along the elongated crystals opens a way for IR laser pumped micro-sized organic photonic devices with frequency up-conversion technology.

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Conflict of Interest
The authors declare no conflict of interest.

Figure 4. A) TPL intensity map of a millimeter-sized TTO crystal as a function of fundamental wavelengths (760–860 nm). B) Plot of TPL intensity versus incident pump power.

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