

Luminescence properties of a Fibonacci photonic quasicrystal

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Abstract: An active one-dimensional Fibonacci photonic quasi-crystal is realized via spin coating. Luminescence properties of an organic dye embedded in the quasi-crystal are studied experimentally and compared to theoretical simulations. The luminescence occurs via the pseudo-bandedge mode and follows the dispersion properties of the Fibonacci crystal. Time resolved luminescence measurement of the active structure shows faster spontaneous emission rate, indicating the effect of the large photon densities available at the bandedge due to the presence of critically localized states. The experimental results are in good agreement with the theoretical calculations for steady-state luminescence spectra.

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Characteristics of light propagating in a dielectric medium can be significantly altered by means of spatial modulation of the dielectric constant of the medium. If the spatial profile is periodic the respective structures are called photonic crystals (PC) emphasizing similarities between properties of light in these structures and those of electrons in semiconductors. Photonic bandgaps that form in PCs modify many of fundamental properties of light providing new opportunities for fundamental research and applications that have been explored widely. One of the important examples is the realization of ultralow threshold lasers using active photonic crystals consisting of either quantum wells or quantum dots embedded in them [1]. This breakthrough achievement became possible due to the development of high quality factor cavities with small mode volumes permitting the modification of spontaneous emission.

A great deal of attention was also paid to structures with random spatial distribution of the refractive index, which demonstrated a plethora of novel effects such as Anderson localization, coherent back scattering, optical Hall Effect, among others. At the same time, very little is known about propagation of light in media with deterministic and yet non-periodic spatial profile of refractive index [2]. Such structures, called quasicrystals, may exist in one-, two-, or three-dimensional realizations and exhibit properties intermediate between periodic and completely disordered systems. Among one-dimensional quasicrystals the most studied are structures based on the Fibonacci sequence. Both classical (light) and quantum (electrons) waves in these structures have been shown to have a self-similar energy spectrum [3], a pseudo-bandgap corresponding to regions of forbidden frequencies [4], and critically localized states whose wave functions are characterized by power law asymptotes and self-similarity [5]. All these properties are typical for quasi-periodic structures so that Fibonacci superlattices are considered as archetype structures to study the fundamental aspects of wave propagation in quasicrystals [6].

The first experimental study of Fibonacci structures was concerned with electron transport in semiconductor heterostructures [7] and was followed by numerous other experimental and theoretical works dealing with electron propagation in such systems [8-13]. Studies of various aspects of light propagation in Fibonacci quasicrystals carried out in Refs. [14-18] have considerably improved our understanding of light transport in passive Fibonacci quasicrystals. However, with exception of recent work on exciton polaritons in quantum well based

Fibonacci lattices [19, 20] and enhanced light extraction from aperiodic structures [21], there have been so far no studies of active structures, in which optically active elements are arranged in the form of a Fibonacci quasicrystal. In particular, effects of pseudo-bandedge critically localized modes on emission properties of such structures have yet to be studied either theoretically or experimentally.

In this work we report the realization and study of photoluminescence (PL) of an active one dimensional Fibonacci photonic quasi-crystal based on polymer layers containing embedded organic dye molecules.

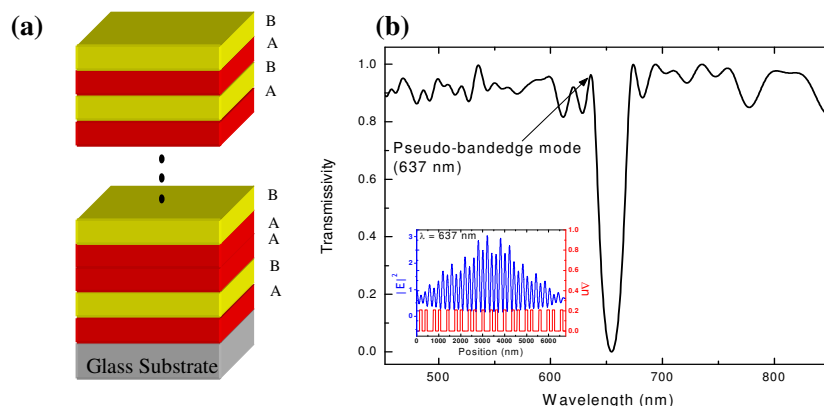


Fig. 1. (a) Schematic drawing of the spin-coated one-dimensional Fibonacci photonic quasicrystal and (b) its calculated transmissivity. The inset in 1(b) shows the calculated spatial distribution of the intensity of the electric field at the pseudo-bandedge indicating a localized mode.

The one-dimensional photonic crystal was built by stacking two different materials A and B and was designed using the following deterministic generation scheme: $S_{j+1} = \{S_{j-1}, S_j\}$ for $j \geq 1$, where $S_0 = \{B\}$ and $S_1 = \{A\}$, where S_j is a structure obtained after j iterations of the generation rule. In place of materials A and B we used Cellulose Acetate (CA) and Poly Vinyl Carbazole (PVK) respectively. The choice of the two polymers was dictated by their refractive index contrast and their solubility. The refractive indices of CA and PVK at 600 nm are 1.475 and 1.683, respectively. CA is soluble in polar solvents such as diacetone alcohol and PVK is soluble in non-polar solvent such as chlorobenzene. Similar approach using alternating layers of spin coated polymers has been previously used to realize Bragg mirrors for bandedge lasing, electro optical switching, enhanced spontaneous emission and microcavity lasing [22-25]. A schematic drawing of the active one-dimensional Fibonacci photonic crystal is shown in Fig. 1. Also shown in Fig. 1 is the simulated transmissivity of the structure calculated using transfer matrix method. A pseudo photonic bandgap is observed in the 640-700 nm wavelength range. In the present work we focused on the bandedge state that lies on the high frequency side of this pseudogap. The electromagnetic field distribution in the structure at the bandedge, shown in the inset of Fig. 1b, clearly indicates a localized state.

The Fibonacci structure corresponding to $j=9$ iterations was realized on a glass substrate using the polymers PVK with concentration of 0.5g in 20 ml of chlorobenzene and CA with concentration of 0.30g in 10 ml of diacetone alcohol. The {AA} layer was realized using a CA solution having twice the concentration. The CA polymer solutions were then infiltrated with *sulforhodamine* dye, with an emission wavelength of 618 nm. The concentration of the dye in the CA solution was 1 mg in 10 ml of diacetone alcohol. The fabrication methodology involved spin coating process for every layer of polymer added onto the structure, which was subsequently heated on a hot plate for 15 minutes to remove the solvent. Cellulose acetate layers were heated at 120°C, while PVK layers were heated at 80°C. The desired thickness of the CA and PVK layers to yield a pseudo-bandgap around 600 nm were 132 nm and 109 nm and were realized by spin coating the layers at 1800 rpm and 2200 rpm, respectively. The {AA} layer was realized by spin coating the CA solution with double the concentration at

3000 rpm. The layer thicknesses were separately calibrated using reflectivity and surface profiling. Experiments revealed that the emission wavelength of the dye in CA was 594 nm, instead of bare dye's emission wavelength (618 nm). This change introduced smaller overlap between the emission spectra and the bandedge state. Despite this detrimental effect, optical characterization of the system revealed interesting results which are discussed below.

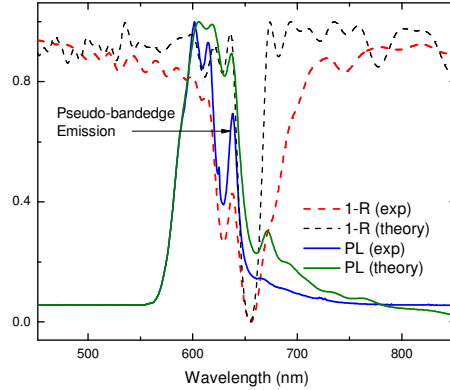


Fig. 2. Room temperature transmissivity and PL observed from the active Fibonacci photonic quasicrystal in the direction normal to the surface of the sample. Also shown in the figure are the theoretically simulated transmission and PL spectra

The Fibonacci photonic crystal was characterized using reflectivity and PL measurements. All optical measurements reported here were carried out at room temperature. Angular resolved reflectivity measurements were carried out using a fiber coupled Tungsten-Halogen lamp as the white light excitation source. Light from the excitation source was focused to spot size of approximately 1mm in diameter, thus averaging out spatial inhomogeneities arising from spin coating. The reflected light was collected by a fiber coupled spectrometer.

Continuous wave PL measurements were carried out using the 488 nm line of an argon ion laser for optical excitation and excitation spot diameter of 1mm. An emission peak is observed at the wavelength corresponding to the higher frequency bandedge state. Figure 2 shows the experimental reflectivity at normal incidence along with the theoretical simulation of such a structure. Also shown in the same figure are the experimentally observed steady state PL spectra and the simulated PL spectra. The pseudo-bandedge emission from the dye is also indicated in Fig. 2.

Theoretical simulation of the PL spectra was based on the transfer matrix approach developed in Ref. [26]. In this method we describe luminescence by solving Maxwell equations with a random polarization term imitating incoherent nature of spontaneous emission. Using, for instance, the density matrix formalism, one can show that this polarization can be described by equation

$$\left(\omega^2 - \omega_{em}^2 + 2i\gamma\omega\right)P_{nc}(z, \omega) = \Gamma \omega_{em} \Sigma(z, \omega, k), \quad (1)$$

where, ω is the frequency of the emitted wave, ω_{em} corresponds to maximum of the emission spectrum of dye in CA, γ characterizes the width of the emission line, and Γ is proportional to the oscillator strength of the transition responsible for the luminescence. The term $\Sigma(z, \omega, k)$ is the incoherent source of the polarization present due to population of optically active levels due to incoherent relaxation processes following initial excitation of the molecules in PL experiments. We model properties of this source by a random function, which is delta-correlated both in time and space.

Propagation of the emitted light depends on spatially modulated dielectric constant $\varepsilon(\omega, z)$, When z falls inside a passive PVK layer $\varepsilon(\omega, z) = \varepsilon_b = 2.832$, for values of z inside CA layers embedded with dye the value of the dielectric constant is

$$\varepsilon(\omega, z) = \varepsilon_A + \frac{A}{\omega^2 - \omega_{abs}^2 + 2i\gamma\omega}, \quad (2)$$

where the second term takes into account the contribution of optical transitions induced in dye molecules into the dielectric constant of the layer A . Frequency ω_{abs} corresponds to the maximum of the absorption of dye molecules dissolved in CA polymer layers. One should notice that we introduced two different resonance frequencies ω_{em} and ω_{abs} to describe emission and absorption properties of the dye molecules, which, is done to reflect a large experimentally observed Stokes shift between the emission and absorption spectra.

We solve respective Maxwell equations following the approach of Ref. [24], in which the amplitude of the emitted light is expressed in terms of transfer-matrices describing transport of light across the structure:

$$E_-^{(m)} = t \langle - | T_R T(N, m+1) | V^{(m)} \rangle, \quad (3)$$

where $E_-^{(m)}$ is the amplitude of the light emitted to the right of the structure, t is its transmission coefficients, and two by two transfer matrices T_R , and $T(N, m+1)$ describe propagation of light across the interface between the last layer of the structure and vacuum, and between the m^{th} and the last layer, respectively. Two dimensional bra and ket vectors appearing in Eq. (3) are given as $|- \rangle = (0 \ 1)$, $|V^{(m)} \rangle = (V_1^{(m)} \ V_2^{(m)})$, where

$$V_{1,2}^{(m)} = \zeta_{1,2} \frac{\Gamma \omega_{em}}{\omega^2 - \omega_{em}^2 + 2i\gamma\omega} \frac{e^{\pm iq_{\pm}^{(m)} z_{\pm}^{(m)}}}{2q} \int_{z_{\pm}^{(m)}}^{z_{\pm}^{(m)}} e^{-iqz} \Sigma(z) dz; \zeta_1 = -i, \zeta_2 = 1 \quad (4)$$

and $z_{\pm}^{(m)}$ are right and left coordinates of m^{th} active layer respectively. Total non-coherent emitted intensity is given as $I \propto \sum_m \langle |E_-^{(m)}|^2 \rangle$, where brackets indicate averaging over

random function Σ . Comparison between theoretical and experimental data was carried out by fitting theoretical reflection curves to the experiment adjusting layer thicknesses, and then using the obtained parameters to calculate the luminescence spectra without any additional fitting. In the light of this procedure we can conclude that we obtained an extremely good agreement between theory and experiment in terms of shape and position of the main luminescent peak in the vicinity of the bandedge. This agreement is not a trivial fact because the position of this peak is determined by interplay between luminescence spectra of dye molecules as measured outside of the photonic structure, and the band structure of the quasicrystal. At the same time, our calculations failed to reproduce fine details of the experimental spectra such as appearance of the secondary peaks. This discrepancy can be explained by several factors such as inhomogeneous broadening of the dye spectra, or fluctuations in the widths of the constituting layers. Both these effects were ignored in our initial calculations. Allowing for fluctuations of the layers' thickness in our transfer-matrix calculations we did not find any significant changes in the luminescence spectra. Inhomogeneous broadening, on the other hand, turned out to be more important. We took this effect into account in the effective medium approximation, which entails replacing the dye susceptibility defined in Eq. (1) with a quantity averaged over a distribution of the emission frequencies. We assumed that these frequencies are random Gaussian variables with distribution function centered at the nominal exciton frequency ω_{em} and characterized by the second moment Δ . Neglecting the homogeneous broadening contribution to the susceptibility we assumed that the most of the width of the luminescence spectrum of pure dye is due to inhomogeneous broadening, thus we postulated that $\Delta = \gamma$. Our calculations showed that indeed, the inhomogeneous broadening

results in appearance of the second peak in the spectra. Taking this into account results in a better agreement with experiment of not only the main feature, but also of the finer details of the spectra.

Under weak coupling between the emitter and the bandedge mode, the emission follows the bandedge mode dispersion and the emission spectrum takes on the linewidth of the bandedge state as seen in our case. In addition, the radiative decay rate is expected to be altered when the emitter couples to the bandedge mode. In planar microcavities with no lateral confinement one expects approximately one-third reduction in the radiative lifetime [27]. In the quasi-periodic structure investigated here, we do not expect similar reduction due to the lower Q factor the bandedge mode. Time resolved luminescence measurements were carried out on the active Fibonacci photonic quasicrystals. The structure was pumped using a 469 nm diode laser with 50 ps pulse width and the emission was detected by a high speed photomultiplier tube via a monochromator. Measurements were carried out with the emission monochromator on and off resonance with respect to the pseudo-bandedge mode. All the measurements were carried out with the same concentration of the dye in CA. The results of the time resolved PL measurements are shown in Fig. 3. A control sample consisting of the dye in CA with the same concentration as that used in the Fibonacci structure was used for comparison. The *sulforhodamine* dye in CA showed PL lifetime of 4.57 ns independent of the wavelength. The dye showed decay time of 4.4 ns when observed off resonance from the bandedge state, while on resonance we observed noticeable reduction in the PL lifetime of 3.9 ns. This reduction in PL lifetime is attributed to the increased photon density of states available at the bandedge due to the presence of critically localized states.

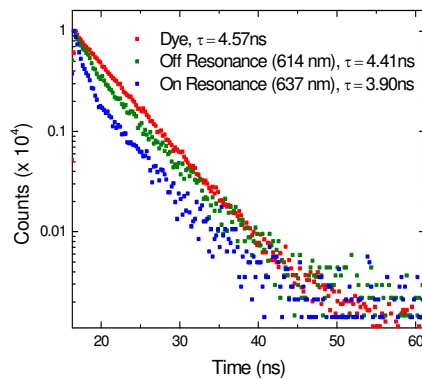


Fig. 3 Time resolved PL spectra of the *sulforhodamine* dye embedded in the Fibonacci photonic quasicrystal on resonance (blue) and off resonance (green) with the pseudo bandedge mode. Also shown is the time resolved PL observed from the bare dye (red).

In summary, we have successfully demonstrated the fabrication of an active Fibonacci photonic crystal structure with an organic dye embedded in it and demonstrated the modification of luminescence properties. Theoretical modeling based on the transfer-matrix approach confirmed the origin of the main luminescence peak as a result of coupling between dye transitions and the pseudogap state of the photonic structure. The entire structure was fabricated using spin coating. The emission from the dye followed the dispersion of the bandedge state and demonstrated spectral narrowing. Time resolved PL measurements on the structure indicate faster radiative decay rate due to the large photon density of states available at the edge of the pseudo-bandgap due to the presence of critically localized states. Through better overlap between the bandedge states and the gain maximum of the active medium, mirrorless lasing and low threshold nonlinear optical mirrors may be achievable in these structures.

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