Enhanced emission from fcc fluorescent photonic crystals

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Received 24 April 2008; published 30 June 2008

We fabricated a high quality fcc photonic crystal composed of ruthenium tris-bipyridine [Ru(bpy)3]2+(PF6)2. Solid-angle-resolved spectroscopy was performed over 76% of 2π sr, with ~2° resolution. Anisotropic emission patterns are explained with an analytic model of two plane waves coupled by diffraction from a Bragg plane. Two distinct types of emissive enhancements are observed, one due to modes coupling confined directions into leaky directions and the other due to maxima in the optical mode density adjacent to partial photonic band gaps.

DOI: 10.1103/PhysRevB.77.233106 PACS number(s): 42.70.Qs

Photonic crystals,1,2 structures with periodicity on the order of the wavelength of light, can be particularly useful for light emitting diode (LED) structures. Most of the emission in ordinary LEDs is trapped by internal reflection but photonic crystals can direct more light out of the structure. Previous work has concentrated on using two-dimensional photonic crystals to scavenge photons from LEDs (Refs. 3 and 4) but three-dimensional crystals have the potential to more significantly control electromagnetic emission and propagation. In this work, we have fabricated an fcc fluorescent photonic crystal (FPC), composed primarily of ruthenium tris-bipyridine [Ru(bpy)3]2+(PF6)2, (RuBpy), a molecular semiconductor which can serve as the active emitter in LEDs.3 There are many promising reports6–11 of emitters introduced into three-dimensional photonic crystals, but the characterization and modeling of subsequent results predominately focuses on a limited set of the possible directions in which light exits the structure. We have performed angle-resolved spectroscopy encompassing 76% of 2π sr on one side of the FPC and have observed highly anisotropic emission that is attributed to the FPC optical modes and dispersion. These phenomena have not been previously reported and are explained in the context of an analytic model incorporating two plane waves coupled by diffraction from a single Bragg plane. Our results identify emissive enhancements arising from two distinct phenomena within the photonic crystal. The magnitudes of these effects relative to each other and to the background bulklike emission are clearly demonstrated over 76% of 2π sr.

Fabrication of our FPC proceeds with polystyrene colloids grown into an fcc colloidal crystal via vertical deposition12 on a glass substrate. Atomic layer deposition of 10 nm alumina improves structural stability while negligibly affecting the photonic band structure.13 RuBpy, dissolved in acetonitrile, is wicked into the interstitial pores. The solvent evaporates to form a solid RuBpy matrix. Reactive ion etching exposes the polystyrene colloids lying beneath the RuBpy layer. Finally, polystyrene is removed with toluene. Scanning electron microscopy shows excellent structural order on the polystyrene template surface [Fig. 1(a)] and in the ion-milled FPC cross-section [Fig. 1(b)]. The lattice constant a = 577 ± 9 nm, measured by surface diffraction with a 351 nm laser, gives an effective hard-sphere diameter of 408 ± 6 nm, consistent with the nominal 420 nm colloid diameter. Normal incidence reflectance [Fig. 1(c)] peaks of the template and FPC occur at the expected positions and are consistent with other works.6–11 The 50% FPC normal incidence reflectance and clear Fabry-Pérot fringes (150 μm spot size), are indicative of a high degree of order. The ~20 layer thick FPC is transparent to the eye with ~75% transmission at 532 nm, corresponding to a mean-free path of 20 μm.

Solid-angle-resolved spectroscopy is used to measure the FPC emission patterns. The crystal-air surface is irradiated with a normal-incident 532 nm continuous-wave laser beam at 30 μW focused to a 50 μm spot with 0.02 numerical aperture. A detector assembly collects fluorescent emission from the substrate side, within a 2.5° apex-angle cone. Collected emission is filtered to pass vacuum wavelengths λ > 534 nm and then focused into an optical fiber (randomiz-

FIG. 1. SEM micrographs of (a) polystyrene colloidal template and (b) FPC cross-section. (c) Normalized emission spectra, integrated over 76% of 2π sr, from FPC, RuBpy film, and their ratio. Also in (c), normal-incidence reflectance from FPC and template.
ing the polarization) coupled to a spectrometer. The detector is positioned 15 cm from the sample and is mounted on two perpendicular motorized rotary-stages with rotation axes passing through the excitation volume. The θ stage sets the detector angle relative to the FPC surface normal and the φ stage sets the azimuth angle. Measurement proceeds by sweeping θ from −75° to +75°, in 2° steps, for each φ from 0° to 180°, also in 2° steps. Photobleaching reduces fluorescent intensity ~50% during the 6 h of data collection. A correction is applied by normalizing each θ sweep to the intensity collected at θ= ±1° (normal incidence). This corrected data is further normalized by making the θ–φ-integrated intensity equal for each λ, facilitating comparison of emission patterns at different λ. A reference data set is similarly collected from a nondiffracting unstructured RuBpy film. Presented in Fig. 1(c) are the FPC and reference spectra, integrated over 76% of 2π sr and normalized in frequency space. These spectra show only minor deviations. This is consistent with the notion that a periodic dielectric structure serves to redistribute the electromagnetic modes present in free space, shifting them from forbidden energy ranges or directions and placing them in nearby allowed ranges.

Very anisotropic FPC emission patterns are presented, for five representative λ, in Figs. 2(a)(i)–2(e)(i). The threefold fcc symmetry is evident in the two sets of three bright arcs in Fig. 2(e)(i). Such detailed and dramatic emission patterns from three-dimensional photonic crystals incorporating fluorescent species have not been previously reported. We compared our results with a model16 for FPC emission. Figure 2(a)(ii) is generated by inserting our FPC parameters into the model and is directly comparable with Fig. 2(a)(i). Agreement is found for the reduced intensity ring with a minimum at θ=27°. This feature will be shown to be caused by the stopgap from the (111) planes parallel to the FPC surface. Stark disagreement occurs for the threefold symmetric reductions in the model. Instead, slight intensity enhancements are observed which we refer to as mode enhancements. We will show that these are due to the nature of the FPC optical modes. The model16 does not explain our data because it is based on photon diffusion theory17 which requires a transport distance longer than the mean-free path. However, our mean-free path is three times the FPC thickness.

Diffraction effects are predicted whenever the Bragg condition k–k′=G is nearly satisfied.18 An incident plane wave vector k is related to a diffracted wave vector k′ by a reciprocal-lattice vector Ghkl=(2π/a)(hkl) for Miller indices h, k, and l all even or all odd. The magnitude ||k||=||k′||/2 where ε000 is the average FPC dielectric constant, calculated by assuming air spheres in a RuBpy matrix. Plane waves inside the FPC are related to those in air by conservation of the parallel component of momentum across the FPC surface. Plots depicting the satisfaction of Bragg’s Law are presented in Figs. 2(b)(ii)–2(e)(ii), where the angles are directly comparable with data in Figs. 2(b)(i)–2(e)(i). FPC emission features are unmistakably correlated with Bragg diffraction. As λ decreases in the series, Figs. 2(a)(i)–2(e)(i), the (111) stopgap expands to larger θ while the mode enhancements correlated with (111), (111), (111), and (200).

FIG. 2. Parts (a)–(e) each have subparts (i), (ii), (iii). FPC emission at (a) 712 (b) 690 (c) 650 (d) 617 and (e) 560 nm. (a)(i)–(e)(i) Normalized intensity vs θ and φ, (a)(ii) Comparison with model16. (b)(ii)–(e)(ii) Satisfaction of Bragg condition (white) comparable to (b)(i)–(e)(i) but plotted at half-scale; Bragg planes labeled with Miller index; high-symmetry points U, K, and W identified. (a)(iii)–(e)(iii) φ-averaged intensity vs θ (black, with vertical bars depicting min. and max.), normalized to theoretical BLB (gray); over-bars depict theoretical width of TE (upper bar) and TM (lower bar) stopgaps. Tables point to the stopgap, mode enhancements (ME), and mode density enhancements (DE) where obscured features were extrapolated and reported in parentheses. ME111 points to vertices of bright arcs nominally at φ=90, 210, and 330°; ME200 vertices at φ=30, 150, and 270°. 

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diffraction move to smaller $\theta$, resulting in a prominent hexagon-like pattern in Fig. 2(d)(i). The FPC stopgap positions for $\lambda=560$ to 712 nm are best matched with $\varepsilon_{000}$ =1.46 to 1.42 but the theoretical $\varepsilon_{000}=1.50$ to 1.45. This discrepancy may be attributed to a reduced effective density of ~93% for RuBpy within the FPC, reasonable, since the colloidal template likely frustrates densification upon solvent evaporation.

Assuming a position and dipole orientation independence for RuBpy absorption and subsequent isotropic fluorescence, the emission pattern for a nonstructured bulk slab of RuBpy is expected to be proportional to cos $\theta$. When structured into a FPC, the dielectric contrast is small, thus bulklike behavior (BLB) dominates for $k$ far from Bragg planes and photonic crystal effects dominate for $k$ near Bragg planes.\(^1\)\(^2\)

The variations of the $\varphi$-averaged intensity versus $\theta$, relative to the BLB, are presented in Figs. 2(a)(iii)–2(e)(iii). The experimental curve was normalized to the expected BLB by first equating the total $\varphi$-integrated intensity, then dividing by the FPC to reference spectra ratio [Fig. 1(c)] at each $\lambda$, and scaling by 0.85 to overlap the large $\theta$ and long-$\lambda$ portion of the data, beyond the diffraction cutoff where the FPC acts like a bulk slab. Clear examples of BLB are seen for small and large $\theta$ in Figs. 2(b)(iii)–2(d)(iii) with other features superimposed at midrange $\theta$.

The final feature observed will be attributed to maxima in the electromagnetic mode density. These enhancements border both sides of the stopgap, have narrow $5'$ width and intensity $\sim15\%$ above the BLB. Mode density enhancements are most clearly seen in Fig. 2(b)(i) at $\theta=19^\circ$, on the stopgap inner edge, and in both Fig. 2(a)(i) at $\theta=46^\circ$ and Fig. 2(d)(i) at $\theta=61^\circ$, on the stopgap outer edge.

An analytical solution for the FPC emission is derived following an approach similar to the dynamical diffraction theory of x rays,\(^2\) but complicated by the non-negligible dielectric contrast. We assume two electric-field plane waves $E_p e^{i\mathbf{p} \cdot \mathbf{r}}$ and $E_q e^{i\mathbf{q} \cdot \mathbf{r}}$ with wave vectors $\mathbf{p}$ and $\mathbf{q}=\mathbf{p}-G_{\text{skl}}$ diffracted by a single Bragg plane defined by $G_{\text{skl}}$. Solutions are obtained from Maxwell’s equations which are linear combinations, $E=E_p e^{i\mathbf{p} \cdot \mathbf{r}}+E_q e^{i\mathbf{q} \cdot \mathbf{r}}$. This satisfies Bloch’s theorem requiring the solution be a product of a plane wave $e^{i\mathbf{p} \cdot \mathbf{r}}$ and an amplitude $E_p+E_q e^{-i\mathbf{G} \cdot \mathbf{r}}$ periodic with the FPC. We have the following two-vector system:\(^2\)\(^0\)

\[
(k^2\varepsilon_{000}-\mathbf{p} \cdot \mathbf{p})E_p + k^2\varepsilon_{skl}E_q + (\mathbf{p} \cdot \mathbf{E}_p)\mathbf{p} = 0
\]

\[
(k^2\varepsilon_{000}-\mathbf{q} \cdot \mathbf{q})E_q + k^2\varepsilon_{skl}E_p + (\mathbf{q} \cdot \mathbf{E}_q)\mathbf{q} = 0.
\]

The photon energy and magnitude of the free-space momentum are defined by $k=2\pi/\lambda$. $\varepsilon_{000}$ and $\varepsilon_{skl}$ are, respectively, the average and the $G_{\text{skl}}$-fluctuating components of the Fourier series expansion of the dielectric constant. For fcc air spheres in RuBpy, $\varepsilon_{000}=1.428$ and $\varepsilon_{111}=0.158$ at $\lambda=690$ nm. Nontrivial solutions require the matrix of coefficients to be singular. We obtain the dispersion relation $F_{\text{TE}}F_{\text{TM}}=0$ where

\[
F_{\text{TE}} = (k^2\varepsilon_{000}-\mathbf{p} \cdot \mathbf{p})(k^2\varepsilon_{000}-\mathbf{q} \cdot \mathbf{q}) - k^4\varepsilon_{skl}^2
\]

\[
F_{\text{TM}} = F_{\text{TE}} + [\varepsilon_{skl}^2/(\varepsilon_{000}^2-\varepsilon_{skl}^2)](\mathbf{p} \cdot \mathbf{q})(\mathbf{p} \times \mathbf{q}) \cdot (\mathbf{p} \times \mathbf{q}).
\]

This dispersion is a convenient product of the transverse-electric (TE) $F_{\text{TE}}(\mathbf{E} \perp \mathbf{p}, \mathbf{q}$ and $G_{skl})$ and the transverse-magnetic (TM) $F_{\text{TM}}$ contributions. It is straightforward to obtain the dispersion surface, giving $\mathbf{p}$ and $\mathbf{q}$, for a particular $\lambda$, and then back solve for a mode’s $E_p$ and $E_q$. The solution is limited to small dielectric contrast, estimated as $e_{111}<5/36\varepsilon_{000}=0.2$ derived for a stopgap centered at $1/2$; the distance between the center and the edge of a {111} Brillouin-zone face and requiring the stopgap not reach past $1/2$ that distance. This allows neighborhoods of $k$ where diffraction is only significant from no more than one Bragg plane. Also, $\mathbf{k}$ must be sufficiently distant from any intersections of multiple Bragg planes [intersections of lines in Figs. 2(a)(ii)–2(e)(ii)]. The solution will then apply to any single feature (stopgap, mode or mode density enhancements) observed at these $k$. Such features are identified in the inset tables of Fig. 2.

Figure 3 describes the FPC optical modes where diffraction is only significant from $G_{111}$ and $\lambda=690$ nm, corresponding to Fig. 2(b). Both the TE and TM dispersion surfaces have radial symmetry around $G_{111}$ and mirror symmetry in the Bragg plane. The magnitude and direction of $\mathbf{p}$ and $\mathbf{q}$ are obtained by starting from the origin and $G_{111}$, respectively, and drawing vectors to a single point (representing one FPC mode) on the dispersion surface. The $k\varepsilon_{000}^{1/2}$ radius circles centered at the origin and $G_{111}$ depict an effective $\varepsilon_{000}$ media with the Bragg condition occurring at the circle’s intersections.

The FPC optical modes describe light propagation and RuBpy fluorescence emission within the FPC. Modes are related to the data because they must decompose into the plane waves that ultimately impinge on the detector. Conversions from internal FPC propagation directions to those in free space are obtained by conserving momentum parallel to the FPC surface. Momentum conservation is applied individually to both the plane waves that comprise one FPC mode, giving $||\mathbf{p}||\sin \theta_p = k \sin \theta_{p,\text{air}}$ and $||\mathbf{q}||\sin \theta_q = k \sin \theta_{q,\text{air}}$.\(^{233106-3}\)
$=k \sin \theta_{\text{air}}$. To avoid total internal reflection at the FPC surface, we must have $|\mathbf{p}| \sin \theta_p < k$ and $|\mathbf{q}| \sin \theta_q < k$.

Both the TE and TM dispersions (Fig. 3) have ranges of parallel momentum for which no modes exist, and thus no fluorescence emission should occur. These gaps in the $G_{111}$ dispersion surface give rise to the stopgap feature. The theoretical TE and TM stopgap angular widths in free-space are plotted as horizontal over bars in Figs. 2(a)(iii)–2(e)(iii), showing good agreement with the data.

The mode density versus parallel momentum, normalized to that of $k e_{120}^b$ plane waves, is plotted in Fig. 3. Adjacent to the vanishing mode density in the stopgaps are pronounced enhancements, adjacent to the stopgap and $\sim 15\%$ higher intensity than the BLB.

Consider the (111) Bragg plane, from the {111} family but not parallel to the FPC surface. The $G_{111}$ dispersion for $\lambda = 690$ nm [Fig. 3 (inset)] is identical to the $G_{111}$ dispersion but tilted by $70.5^\circ = \arccos \frac{1}{3}$ from the FPC surface. A forbidden range of momentum parallel to (111) occurs, but contrary to the $G_{111}$ case. modes exist for all values of momentum parallel to the FPC surface less than $\sim k e_{120}^b$. This is demonstrated by the inability to draw a line perpendicular to the FPC surface which does not intersect the $G_{111}$ dispersion. This explains why strong intensity suppressions only occur for the {111} diffraction. Diffraction from the remaining {111} and the {200} planes are instead associated with mode enhancements which are clearly seen in Fig. 2(e)(i). Mode enhancements arise because the $E_p$ and $E_q$ plane waves comprising one mode may differ significantly in how strongly they are confined to the FPC. Plane waves incident on the FPC at small angles to the normal are weakly confined relative to those at large angles where strong Fresnel reflections or total internal reflection may occur. For Bragg planes not normal to $\{111\}$, $\mathbf{p}$ and $\mathbf{q}$ for a single mode may make quite different angles [Fig. 3 (inset)] with the FPC surface, resulting in $E_p$ and $E_q$ having significantly different energy flux across the surface. Since a mode’s $E_p$ and $E_q$ are coupled, the amplitude of the leaky plane wave is compensated from the more confined plane wave and should result in increased intensity in the leaky direction. This is observed as mode enhancements, where intensity is up to $\sim 50\%$ above the BLB. The effect should be stronger when $E_p$ and $E_q$ are strongly coupled, which occurs when they have comparable amplitudes. Figure 3 plots the amplitude fraction of the smaller magnitude plane wave, as a measure of coupling, versus momentum parallel to the $\{111\}$ Bragg plane. Coupling is strongest near the Bragg condition, where the largest mode enhancements are observed but enhancements are absent for diffraction from $G_{111}$ because here $|\mathbf{p}| \sin \theta_p = |\mathbf{q}| \sin \theta_q$, so both plane waves are similarly confined. Finally, we observed that BLB occurs at data points far from any Bragg planes. Here, the DOM is practically that of $k e_{120}^b$ plane waves and coupling is weak. Consequently, these modes are very much like a plane wave, giving rise to the BLB in the data.

In summary, solid-angle resolved spectroscopy captured highly anisotropic emission patterns that are explained by our approximate analytical solution. The distinct mode enhancements and mode density enhancements are separately identified, and direct geometrical insights are provided, which are not easily extracted from numerical solution methods. These insights may enable LED designs with more efficient or customized emission patterns.

This work is supported by the U.S. Army Research Office under Contract/Grant No. DAAD19-03-1-0227. Some experiments were performed in the Center for Microanalysis of Materials at UIUC, which is partially supported by the U.S. DOE under Grants No. DE-FG02-07ER46453 and No. DE-FG02-07ER46471.