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Fluorescent polystyrene photonic crystals self-assembled with water-soluble conjugated polyrotaxanes

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We demonstrate control of the photoluminescence spectra and decay rates of water-soluble green-emitting conjugated polyrotaxanes by incorporating them in polystyrene opals with a stop-band spectrally tuned on the rotaxane emission (405–650 nm). We observe a suppression of the luminescence within the photonic stop-band and a corresponding enhancement of the high-energy edge (405–447 nm). Time-resolved measurements reveal a wavelength-dependent modification of the emission lifetime, which is shortened at the high-energy edge (by ~11%, in the range 405–447 nm), but elongated within the stop-band (by ~13%, in the range 448–482 nm). We assign both effects to the modification of the density of photonic states induced by the photonic crystal band structure. We propose the growth of fluorescent composite photonic crystals from blends of “solvent-compatible” non-covalently bonded nanosphere-polymer systems as a general method for achieving a uniform distribution of polymeric dopants in three-dimensional self-assembling photonic structures. © 2013 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution 3.0 Unported License. [<http://dx.doi.org/10.1063/1.4826544>]

Photonic crystals (PhCs)^{1,2} have been widely investigated over the last two decades and are now proposed in applications such as light-emitting diodes (LEDs),³ solar cells,^{4,5} and lasers.^{6,7} Among them, self-assembled PhCs have been studied in detail due to their low cost of fabrication and ease of preparation, with artificial opals^{1,2,8,9} being especially popular. Synthetic opals provide versatile systems that can be infiltrated by vapour phases,¹⁰ or solutions,¹¹ thereby enabling the investigation of a variety of photonic effects and especially the fine-tuning of the optical properties.¹² These include the modification of the emission spectra and of the radiative rates,^{13,14} optical switching,¹⁵ and Fano resonances.⁹ Different active materials such as metal nanoparticles,¹⁵ semiconductor nanocrystals,¹⁶ or conjugated molecules¹⁷ can be incorporated into the opals via infiltration, although achieving homogeneity of infiltration through a pre-formed opal remains somewhat challenging. This problem is particularly severe when infiltrating macromolecular systems, and, to overcome this issue, different techniques have been proposed, such as monomer infiltration followed by *in situ* polymerization¹⁸ or layer-by-layer (LBL) polymer deposition on the sphere surface.¹⁹ These are not completely satisfactory as *in situ* polymerisation restricts the number of synthetic approaches and

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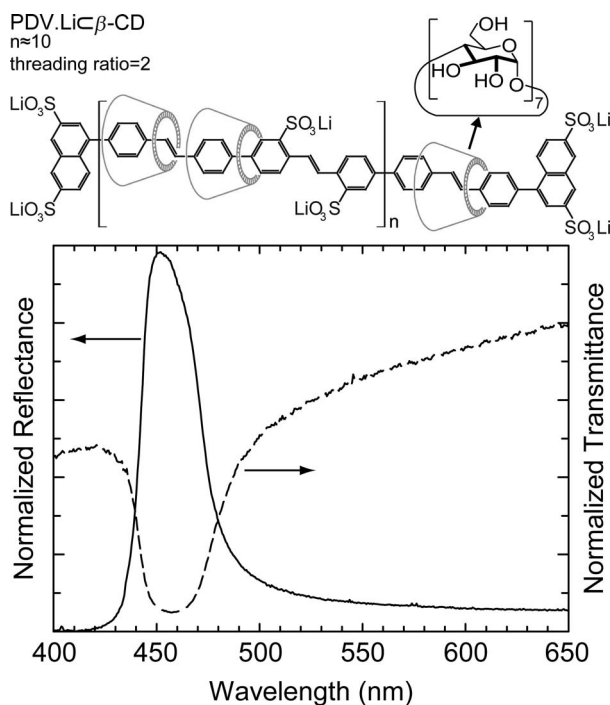


FIG. 1. (Top) Chemical structure of PDV.LiC β -CD, threading ratio = 2, with an average number of repeat units $n = 10$. (Bottom) Reflectance (R, solid line) and transmittance (T, dashed line) spectra of a polystyrene opal film co-grown with PDV.LiC β -CD (sphere diameter $a = 200$ nm, refractive index, $n_{ps} = 1.59$). The full-width-half-maximum of the PBG is not affected by the incorporation process.

precursors, whereas LBL is both time-consuming and requiring a significant level of complexity. Processability of the active materials is obviously crucial to their incorporation into organic PhC, and, interestingly, water-soluble conjugated polymers with high photoluminescence (PL) efficiency provide an intriguing opportunity for use in combination with plastic PhC templates, but only a few attempts have been reported so far.^{19–22}

Conjugated polyelectrolytic rotaxanes²³ (Fig. 1) offer a very interesting class of materials to incorporate into PhCs since they benefit from a supramolecular architecture in which conjugated backbones such as poly(4,4'-diphenylene vinylene) (PDV) are threaded through cyclodextrin rings (β -CD), that sterically impose increased intermolecular distances. Such structures lead to higher PL efficiency and reduced polaron formation compared to unthreaded materials, even at relatively high concentration regimes,²⁴ thereby allowing their use for optically pumped lasing,²⁵ optical amplification,²⁶ white-emitting organic light-emitting diodes,^{27,28} and polarized-light-emitting films.²⁹ For all these properties, and especially for the processability in polar solvents, conjugated rotaxanes constitute a particularly well-suited class of materials for incorporation into plastic PhCs such as opals without the need of covalently binding the polymer to the microspheres.

In this work, we study the modification of the luminescence of highly efficient conjugated polyrotaxanes²³ upon their incorporation in polystyrene opals to obtain PL enhancement effects. This is superior to both infiltration of the precursor followed by post-polymerisation, which restricts both synthetic versatility and the further polymer purification and characterisation, and to LBL assembly, which requires a much higher level of sophistication, and is therefore not “technologically robust” both in terms of production cost and tolerance to environmental parameters.

For opal films preparation we used commercially available aqueous suspensions of monodisperse polystyrene nanospheres³⁰ (Duke Scientific, 10% in volume, diameter $a = 200, 222,$ and 260 nm; standard deviation $<5\%$; refractive index, $n_{ps} = 1.59$) and, as luminescent semiconductor we used β -CD-threaded PDV, a polyelectrolytic derivative of poly-*para*-phenylene vinylene (PPV) where sulfonate sidegroups balanced by Li^+ ions afford solubility in polar solvents (PDV.LiC β -

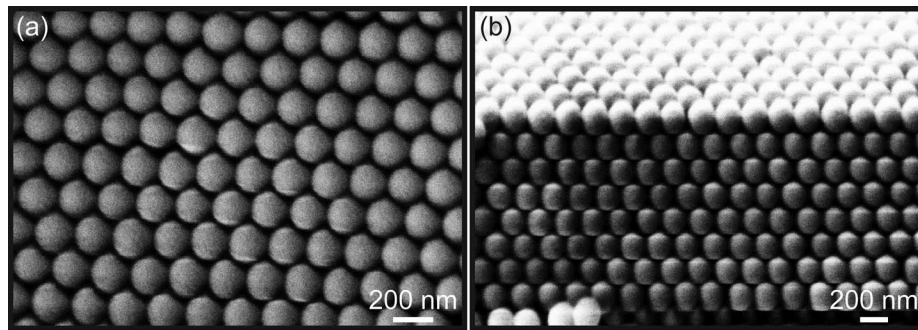


FIG. 2. Scanning electron microscope (SEM) micrographs of an opal film incorporating PDV.LiC β -CD: (a) cryo-cleaved wall surface showing the internal structure of the opal, (b) film cross-section. Strong contrast between the sphere and the interstices is observed, confirming that the latter are not filled up by the conjugated polyelectrolytes (the density of the conjugated moiety and of the spheres being comparable). Images were collected using the SEM mode of a dual beam Carl Zeiss XB1540 “Cross-Beam” focussed-ion-beam microscope and the cross section was obtained via cryo-cleaving an opal film.

CD, threading ratio = 2,²⁴ molecular structure in Fig. 1). The polystyrene nanospheres suspensions were diluted in de-ionized water as necessary to obtain the desired film thickness ($d \sim 5 \mu\text{m}$) upon complete water evaporation.^{6,17} PDV.LiC β -CD incorporation was obtained by adding an 8×10^{-3} mg/ml polyrotaxanes water solution to the nanospheres suspension before proceeding with the PhC growth process inside a BF53 Binder incubator. The growth process was carried out at $45 \text{ }^\circ\text{C} \pm 1 \text{ }^\circ\text{C}$ on soda-lime glass slides using the meniscus technique,^{17,30,31} which yields a face-centered cubic lattice of nanospheres with the [111] direction perpendicular to the substrate.

The obtained co-grown PhCs had an area of $\sim 7 \times 7 \text{ mm}^2$ and normal incidence reflectance spectra collected in different areas of the film reveal only minor changes in reflectance peak position and shape,³² thus demonstrating good uniformity of the PhCs. We also note that preservation of the opal structure and optical properties upon polyrotaxane incorporation is also demonstrated by the presence in the reflectance spectra (at wavelengths near and below 300 nm) of van Hove-like structures.³² These features are due to diffraction along directions different from the incident one^{32,33} and are known to depend strongly on the order of the system,³²⁻³⁴ the microsphere quality,³⁴ and the degree of incorporation of the luminescent material.^{10,12,13,15,17,35} Indeed, they disappear when the structure is not regular enough, or when strongly absorbing materials are embedded. In our case, van Hove-like structures can still be observed for co-grown opals both in the reflectance and transmittance spectra.³² Furthermore, such structures show a dispersion opposite to that of the stop-band³² as predicted for bare opals. All these features, and the additional effect of the stop band on the PL spectra, can only be compatible with a minor incorporation of the rotaxinated polymer within the opals, such that the opal optical properties are essentially undisturbed.

The main results discussed here concern spheres with a diameter $a = 200 \text{ nm}$ since these ensure an optimal spectral overlap of the polyrotaxane PL spectrum and of the opal stop-band. To ensure that the presence of the polyrotaxane does not hinder or negatively affects the growth of the PhC, we investigated concentrations for the polyrotaxane water solutions ranging from 0.5 mg/ml to 1×10^{-3} mg/ml and we found that a PDV.LiC β -CD concentration of 8×10^{-3} mg/ml yielded undistorted, homogenous opals without deposition of an excess polymer layer on their surface (which would result in a concomitant lack of photonic confinement for such a layer), while preserving strong PL properties of the system.

Remarkably, lack of spectral shifts and changes in the width of the stop-band of the co-grown PhCs (Fig. 1), compared to the neat PhCs, suggests that incorporation of the conjugated polymer occurs spontaneously on the sphere surface and does not lead to complete filling of the interstitial voids. Scanning electron microscope (SEM) micrographs of the co-grown PhCs further confirm the interpretation of the reflectance spectra. In fact, Figs. 2(a) and 2(b) show no presence of lattice distortion induced by the incorporation of polyrotaxanes, nor an excess polymer layer on the opal surface for co-grown PhCs with 8×10^{-3} mg/ml PDV.LiC β -CD solution and, more importantly,

that the interstices between nanospheres are empty, thereby preserving a desirable higher dielectric contrast within the structure than otherwise possible in case of substantial filling of the interstices.

Steady-state PL spectra at different incidence angles of the exciting beam were carried out by using a pulsed laser diode ($\lambda_{\text{ex}} = 371$ nm, pulse width ~ 40 ps), a spectrometer (Andor Shamrock 163i) coupled to a CCD camera (Andor Newton CCD, cooled at -50°C), and a rotating stage (M-060.DG, Physik Instrumente, resolution $<0.1^\circ$). Time-resolved PL measurements were carried out with a time-correlated single-photon-counting unit (Edinburgh instruments, F900, time response ~ 150 ps) and the previous pulsed laser diode as the excitation source. All transmittance (T) and normal incidence reflectance (R) spectra were collected with a setup previously described.^{6,17}

Figure 1 shows R and T spectra of a typical synthetic opal made with polystyrene beads with diameter $a = 200$ nm. As expected, the peak of reflectance at 455 nm ($E_B = 2.74$ eV) corresponds to a minimum in the transmittance spectrum. Importantly, we do not observe any significant change in the optical properties of the stop-band of the PhC, upon incorporation of the rotaxanes, namely, the spectral position of the stop-band and its full width at half-maximum ($\Delta E_B = 0.16$ eV), are unchanged compared to a bare opal,^{6,17} thus proving, as mentioned above, that the growth of the opal from a nanosphere dispersion containing the luminophores does not lead to a structure in which the interstices between the spheres are significantly filled with the luminescent moiety.^{15,35,36} Furthermore, the quality of the opal structure is preserved upon the rotaxane incorporation as demonstrated by the presence in the reflectance spectra of van Hove-like structures, which exhibit a dispersion opposite to that of the pseudo-stopband.³² Such features, due to diffraction along directions different from the incident one,³³ are known to depend strongly on the order of the system and on the microsphere quality.³⁴

As a reference sample to study PL modifications induced by the PhC, we have used the very same opal but thermally annealed at 75°C for 5 min. Thermal annealing at 75°C is enough to partially melt the polystyrene spheres, and thus destroy any photonic property of the structure³⁷ (as also proven by the PL spectrum in Fig. 3), but without changing the PL properties of the conjugated polyrotaxane, due to the higher thermal stability of this class of supramolecular systems.³⁸

To be able to compare the different properties, both measurements were carried out in the same area of the sample before and after the thermal process and the PL spectra were normalized at $\lambda = 550$ nm, far away from the photonic stop-band. Such a PL normalization is well-established in the literature.^{13,14,17}

In Figure 3 we report the PL spectra as a function of the angle of incidence of the excitation beam, for the PhCs incorporating PDV.LiC β -CD and the reference sample. First, we notice a 50 nm blue-shift of the PL peak and a small increase of the PL quantum yield (Φ_{PL}) to $38 \pm 3\%$ (for the melted-opal “reference” samples) compared to a neat spin-coated film of PDV.LiC β -CD ($\Phi_{\text{PL}} \sim 18 \pm 2\%$).^{23,39} We assign such a blue-shift and variation of the Φ_{PL} to electrostatic interactions of the Li cations with the negatively charged surface of the polystyrene nanospheres thus changing the polymer structure and then the electronic structure of semiconducting chains close to the surface. Furthermore, we note that the opal growth is mainly driven by capillary forces³⁰ that would also act on the polyrotaxanes and impose additional structural constraints, with a concomitant modification of the PL dynamics of the polyrotaxane compared to that observed in a neat-polymer film or solution.²⁴ Additional support for this interpretation comes from solutions of poly(phenylene-ethynylene) polyelectrolytes neat and grafted to silica microspheres, for which a spectral blue-shift has also been observed in agreement with our data.

Most importantly, the PL spectrum of PDV.LiC β -CD (Fig. 3(a), solid line) is strongly modified by the photonic band gap (PBG): in particular, the PBG partially suppresses light propagation between 448 nm and 482 nm (at 0° incidence). Remarkably, the presence of the photonic structure also induces a decrease (increase) of the PL intensity in the PBG spectral region (short-wavelength edge of the PBG) by up to 33%. As expected, both the enhancement and the suppression depend on the detection angle^{14,17} according to the dispersion of the photonic band structure at the PBG, thus inducing a directionality to the observed effect.

The enhancement/suppression effects caused by the PhC with respect to the “melted reference” can be made more obvious by plotting the ratio between the two PL spectra, as in Fig. 3(b). Here we note that within the PBG the ratio is <1 , but >1 at the short-wavelength edge of the PBG.^{14,16,17,40}

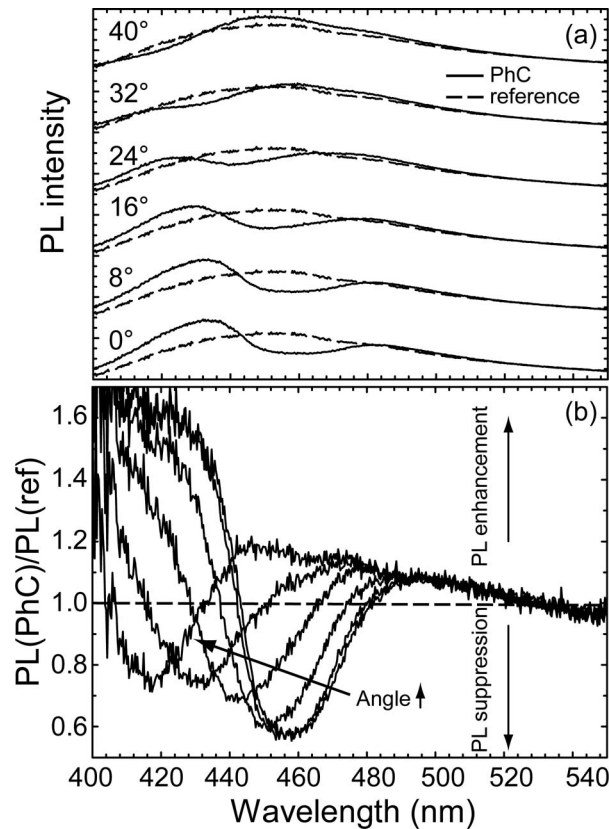


FIG. 3. (a) PL spectra of an opal film co-grown with PDV.LiC β -CD before (solid line) and after (dashed line) the thermal treatment at 75 °C at different incidence angle of the exciting beam,⁴⁴ (b) ratio between the two PL spectra before and after the thermal process. All spectra were collected in air and at room temperature. A pulsed laser diode ($\lambda_{\text{exc}} = 371$ nm, pulse width ~ 40 ps) was used as the excitation source for the PL spectra. In both panels the detection angle has been increased up to 40° with steps of 8°.

To gain further insight into the underlying photophysics of these photonic structures we have also carried out time-resolved PL measurements at the relevant wavelengths, i.e., at 437 nm, where we observe an enhancement of the PL spectrum, and at 460 nm within the photonic stop-band, where the emission is suppressed (Fig. 4). In previous studies, the PL decay dynamics of polyrotaxane films have been fitted with a double exponential expression and assigned to the *intramolecular* singlet exciton and *inter-molecular* aggregate states.²⁴ Surprisingly, for our photonic structure we had to use a triple exponential expression: $I(t) = I_0 + I_1 e^{-\left(\frac{t}{\tau_1}\right)} + I_2 e^{-\left(\frac{t}{\tau_2}\right)} + I_3 e^{-\left(\frac{t}{\tau_3}\right)}$, whose parameters are reported in Table I. Whereas the longer decay times (τ_2 and τ_3) can be readily assigned to those previously identified ($\tau_{\text{exciton}} \sim 850$ ps, $\tau_{\text{aggregate states}} \sim 2600$ ps),²⁴ we assign the (fast) additional decay channel to a new emissive species arising from the previously discussed interaction of the polyrotaxane with the nanospheres surfaces. This hypothesis is further supported by the observation of a three-exponential decay also in the annealed reference sample, suggesting that such a de-excitation pathway is observed only in the presence of polyrotaxane/colloid interaction. Furthermore, the weight of the different decay channels is essentially the same at 437 nm and 460 nm for the PhC and the melted “reference,” thus corroborating the interpretation above.

We also notice that τ_3 is comparable in the opal, in the melted “reference” (2650 ps at 437 nm and 2750 ps at 460 nm) and in neat spin-coated films. At the short-wavelength edge of the stop-band (437 nm) the decay for the co-grown opal is shorter than for the reference (by $\sim -11\%$, as estimated from the weighted mean of τ_1 and τ_2), whereas within the stop-band (460 nm) the reverse situation occurs ($\sim +13\%$, Table I). Expectedly, both these effects are smaller than those observed for PhCs

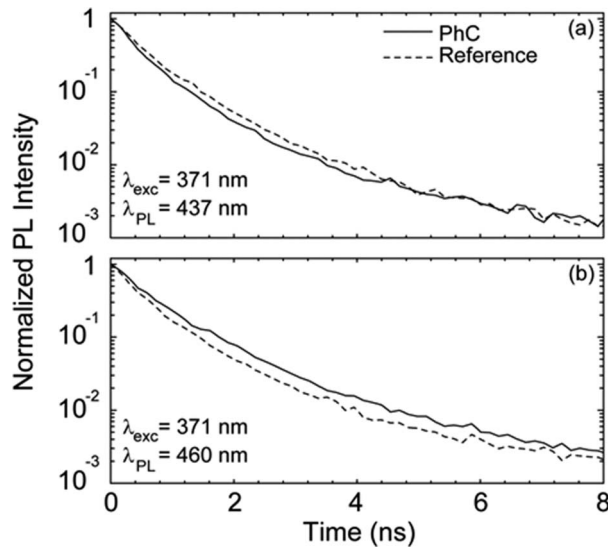


FIG. 4. Temporal evolution of the PDV.LiC- β -CD PL measured at the short-wavelength edge ((a) 437 nm) and inside ((b) 460 nm) the PBG before (solid line) and after (dashed line) the thermal treatment at 75 °C for 5 min. All measurements were carried out in air and at room temperature.

TABLE I. Lifetime values (τ_1 , τ_2 , τ_3) used in the fit-curves the temporal evolution of the PL (the relative contribute of each time constant is included in parentheses). We estimated an error of 5% on the measured value.

	τ_1 (ps) (I_1)	τ_2 (ps) (I_2)	τ_3 (ps) (I_3)
437 nm (high energy PBG edge)			
PhC	300 ± 15 (0.33)	790 ± 40 (0.56)	2720 ± 140 (0.11)
Reference	370 ± 20 (0.33)	860 ± 43 (0.57)	2650 ± 130 (0.10)
460 nm (PBG)			
PhC	430 ± 20 (0.32)	950 ± 50 (0.55)	2850 ± 140 (0.13)
Reference	365 ± 20 (0.34)	860 ± 40 (0.53)	2750 ± 140 (0.13)

with higher dielectric contrast,¹⁶ but it is remarkable that we are able to observe such modifications at such a low-dielectric contrast as that achieved with the polystyrene opals investigated here.^{14,40}

Indeed, a sizable effect on the radiative lifetime (Purcell effect)⁴¹ can only be observed in photonic crystals for which the photonic density of states is strongly modified in the whole of the k -space. In our case the PBG is present only along the [111] (Γ L) crystallographic direction and it is spectrally narrow (447–482 nm) when compared to the width of the PL spectrum (405–650 nm), thus reducing the observable effect.¹⁴ Furthermore, Φ_{PL} of PDV.LiC- β -CD in the reference sample is $\sim 38\% \pm 4\%$, meaning that the radiative rate (K_R) is smaller than the non-radiative rate (K_{NR}) so that any modification caused by a redistribution of the photonic density of states will have a small effect on the PL lifetime.

Interestingly, the PL lifetime modification that we observe is wavelength-dependent with a precise overlap with the PBG spectrum. According to this observation and previously reported experiments^{14,17} we can assign this effect to the modification of the density of photonic states along the Γ L direction.

As a first order approximation, we can consider the modification of the PL lifetime as only induced by the redistribution of the photonic density of states and estimate the variation of K_R . If we consider Φ_{PL} as the sum of contributions of the 3 emissive species, we obtain

$$\Phi_{PL} = I_1 \Phi_{PL1} + I_2 \Phi_{PL2} + I_3 \Phi_{PL3}, \quad (1)$$

where I_x is the relative contribution to the total PL intensity (as obtained from the PL-decays) of all emissive species. As previously discussed, τ_2 and τ_3 are similar to previously measured values; we

TABLE II. Radiative (K_R) and non-radiative (K_{NR}) rates for PDV.Li $\subset\beta$ -CD incorporated inside the PhC and in the reference sample. All rates were calculated using the model proposed in the text. We include an error of 10% on the calculated value.

	Decay channel 1 (τ_1)	Intrachain exciton (τ_2)	Aggregate states (τ_3)
437 nm (high energy PBG edge)			
$K_{R(\text{PhC})}$ (s^{-1}) ($\times 10^8$)	19.8 ± 2	5.1 ± 0.5	0.10 ± 0.01
$K_{R(\text{Reference})}$ (s^{-1}) ($\times 10^8$)	13.5 ± 2	4.1 ± 0.4	0.10 ± 0.01
460 nm (PBG)			
$K_{R(\text{PhC})}$ (s^{-1}) ($\times 10^8$)	9.5 ± 0.9	3.0 ± 0.3	0.10 ± 0.01
$K_{R(\text{Reference})}$ (s^{-1}) ($\times 10^8$)	13.6 ± 2	4.1 ± 0.4	0.10 ± 0.01
K_{NR} (s^{-1}) ($\times 10^8$)	13.7 ± 2	7.5 ± 0.7	3.5 ± 0.3

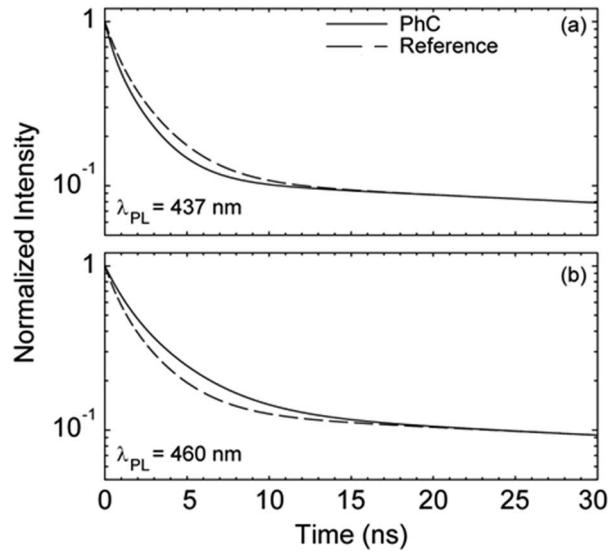


FIG. 5. Radiative decay for PDV.Li $\subset\beta$ -CD incorporated into the PhC (solid line) and in the reference sample (dashed line) at 437 nm (a) high energy PBG edge) and at 460 nm (b) inside the PBG).

can assume that τ_2 corresponds to a Φ_{PL2} of $\sim 35\%$, the relevant PL-lifetime being similar to the one measured in diluted PDV.Li $\subset\beta$ -CD water solutions (for which emission is mainly due to the intrachain exciton).²⁴ Instead, we can assume τ_3 to correspond to a Φ_{PL3} of $\sim 3\%$ since the related PL-lifetime is similar to the one measured for PDV.Li films (for which the emission is mainly due to aggregate states).⁴² From these two considerations, we can calculate a Φ_{PL1} for the decay channel 1 (τ_1) of $\sim 52\% \pm 5\%$.

From Φ_{PL} and τ we can calculate K_R and K_{NR} for all three decay channels, by using the following set of equations (for $x = 1, 2, 3$):

$$\Phi_{PLx} = \frac{K_{Rx}}{K_{Rx} + K_{NRx}}; \frac{1}{K_{Rx}} = \frac{\tau_x}{\Phi_{PLx}}. \quad (2)$$

Since we do not know Φ_{PL} for PDV.Li $\subset\beta$ -CD after the photons redistribution takes place in the PhC, we can only calculate K_R and K_{NR} for the reference sample. Nevertheless, we propose that the variation of the photonic density of states only affects K_R , leaving K_{NR} unchanged (according to Fermi's golden rule, $K_R(\omega) \propto \frac{2\pi}{\hbar} \rho(\mathbf{r}, \omega)$,⁴³ in which ρ is the photonic density of states). Therefore, knowing K_{NR} from the reference sample we can calculate K_R from $\tau = \frac{1}{K_R + K_{NR}}$.

Although this is a relatively simple model, it enables us to estimate an increase of K_R of 46% and 24% at the high-energy PBG edge (437 nm), and a decrease of 31% and 27% inside the PBG (460 nm) for τ_1 and τ_2 , respectively (Table II). τ_3 appears to be completely unaffected by the

redistribution of the photonic density of states; a likely explanation of this finding is once again the large K_{NR} (for decay channel “3”) that is not modified by the presence of the PhC leaving the modification of K_R too small to be estimated or measured.

A plot of the radiative decay $I(t) = I_0 + I_1 e^{-K_{R1}t} + I_2 e^{-K_{R2}t} + I_3 e^{-K_{R3}t}$ (Fig. 5) clearly reveals the modification in dynamics between PDV.LiC- β -CD incorporated into the PhC and in the reference sample. We note, in particular, the measurable effect of the PhC on the radiative lifetime of PDV.LiC- β -CD.

In conclusion, we have investigated an all-plastic water-solution processable photonic crystal functionalized with a class of supramolecular conjugated polymer grown in a single-step process. The photoluminescent PhC exhibits both directional enhancement and suppression (both 33%) of the steady-state PL intensity of the embedded polyrotaxane. Furthermore, a wavelength dependent modification of the PL lifetime is observed correspondent to the enhancement/suppression spectral regions. Using a simple model to analyse the various rates we observed an increase in the radiative rate of 46% and 24% at the high-energy PBG edge (437 nm), and a decrease of 31% and 27% inside the PBG (460 nm) for τ_1 and τ_2 , respectively. All effects are assigned to a modification of the photonic density of states occurring at the PBG and at its short-wavelength edge, which in turn modify the radiative rate of the incorporated luminescent polymer.

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