Nanometer-Scale Precision Tuning of 3D Photonic Crystals Made Possible Using Polyelectrolytes with Controlled Short Chain Length and Narrow Polydispersity

Zhuo Wang, Mauricio E. Calvo, Georgeta Masson, André C. Arsenault, Frank Peiris, Marc Mamak, Hernán Míguez,* Ian Manners,* and Geoffrey A. Ozin*

Dr. Z. Wang, G. Masson, A. C. Arsenault, Prof. F. Peiris, M. Mamak, Prof. I. Manners, Prof. G. A. Ozin
Department of Chemistry, University of Toronto, 80 St. George Street, Toronto, Ontario M5S 3H6, Canada
E-mail: gozin@chem.utoronto.ca

Dr. M. E. Calvo, Prof. H. Míguez
Instituto de Ciencias de Materiales de Sevilla (CSIC-US), Américo Vespucio 49, Isla de la Cartuja 41092, Sevilla, España
E-mail: h.miguez@csic.es

Prof. F. Peiris
Physics Department, Kenyon College, Gambier, OH 43022, United States

Prof. I. Manners
School of Chemistry, University of Bristol, Bristol BS8 1TS, United Kingdom
E-mail: Ian.Manners@bristol.ac.uk

Herein we report the development of an effective method which enables nanometer-scale precision tuning of prefabricated 3D colloidal photonic crystals (PCs). In our approach which involves the layer-by-layer (LbL) electrostatic assembly of polyelectrolytes in the photonic crystals, a key conceptual novelty lies in the development and utilization of polyelectrolytes with controlled short chain lengths and narrow polydispersity as the infiltrating materials. This allows uniform deposition of the polyelectrolytes in the PCs while circumventing the leading problem in the LbL approach − blockage of the PC interstitial openings by large polyelectrolytes during the early filling stages. As a result, nanometer-scale precision tuning of photonic stopband of 10 nm or less has been achieved, which few other

methods can attain. The method is facile and reproducible, and can be applied to photonic crystal lattices ranging from small to large dimensions.

Photonic crystals are an interesting class of photon control materials characterized by periodic array of dielectric lattices at the scale of light wave lengths.[1] These materials possess photonic band gaps or stop bands where light within a range of frequencies is prohibited from propagating along specific lattice directions in the structure. As a result, PCs have attracted significant recent attention as powerful tools for the manipulation of photons with potential applications ranging from telecommunications to optical computing.[2] Three-dimensional photonic crystals can be created by top-down methods such as holographic lithography and direct laser writing or bottom-up methods such as self-assembly of monodisperse colloidal silica or polymer spheres.[3] In both fabrication methods, the PC structures generated are of a passive nature with fixed optical properties, and any slight change in the requirement of the photonic band gaps or stop bands, such as in solar cell, light emitting diode or lasing applications, will generally need the fabrication of a new photonic crystal.

In comparison, fine tuning of existing photonic structures through controlled infiltration represents an attractive and cost-effective alternative. However, since many of these photonic structures possess an interconnected pore network, control at the nanometer regime of the infiltrated materials is a challenge for designed optical response.[4] In our efforts to develop post-fabrication strategies to tailor the optical properties of PCs, LbL assembly[5] of polyelectrolytes (PEs)[6] in preformed photonic crystal lattices[7] emerged as a promising approach. Importantly, we found that PEs which possessed controlled short chain lengths and narrow polydispersity were suitable as infiltrating materials for the fine tuning of photonic stop bands. In this communication, we report the development of the method and the precision tuning of photonic properties on the nanometer scale.

Our approach involved the alternate deposition of oppositely charged polyelectrolytes on the entire interstitial surfaces of a PC lattice **(Figure 1)**. As the resulting thin films possessed a nanometer-scale thickness which could be controlled by the number of layers deposited, it was anticipated that this approach would give rise to controlled filling of the air voids in the PC lattices, leading to precise structural and optical tuning.
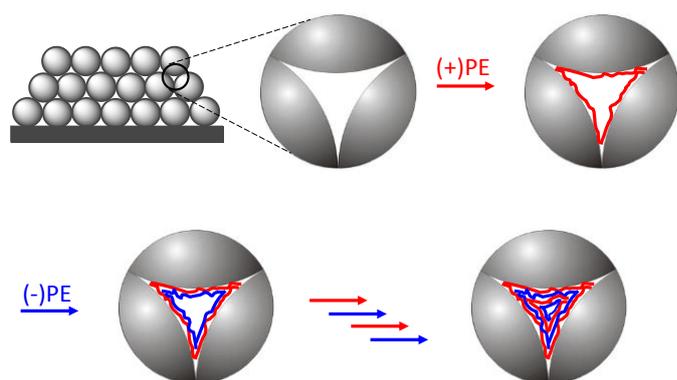

Figure 1. Schematic illustration of lay-by-layer deposition of cationic (+) and anionic (-) polyelectrolytes (PE) with controlled short chain length and narrow polydispersity in the interstitial voids of photonic crystal lattices.

A significant challenge in this method lay with the highly confined interstitial spaces where the LbL assembly took place. For a crystal lattice composed of colloidal spheres with a diameter of 275 nm, the air voids possessed narrow openings which became smaller as more polyelectrolyte layers built up.[4] The theoretical upper limit for the coating thickness of the PC was calculated as the diameter of the colloidal spheres multiplied by 0.07735 times (i.e. 21 nm), at which point the narrowest interstitial spaces were closed off.[8] This meant that if PEs with uncontrolled large molecular weights were used, they could block the narrow openings at an early stage of the LbL assembly which would ultimately result in low filling fractions as well as non-uniform tailoring of the PCs.[8]

To circumvent the problem, it was essential that the polymers possess controlled short chain lengths relative to air-void spaces within the PC. This would ensure uniform polyelectrolyte infiltration and coating throughout the photonic lattice and thus precise fine-

tuning of the optical properties. In addition, the use of polymers with controlled structures would allow fundamental studies of the LbL assembly process in highly confined spaces such as the air voids in photonic crystals as well as in micro- and nano-channels.

For this purpose, we have developed facile synthetic routes which provided access to polyferrocenylsilane (PFS) polyelectrolytes **1 – 3**[9] with controlled architectures (**Figure 2**).[10] The approach involved living photolytic anionic ring-opening polymerization (PROP) of amine-functionalized [1]silaferrocenophanes followed by functionalization of the amino groups. The metallopolyelectrolytes thus obtained (**1 – 3**) possessed short chain lengths with a degree of polymerization (DP) of ca. 10 and polydispersity index (PDI) of 1.1 – 1.3, and were ideal for the study of LbL assembly in the highly confined air voids in PCs.[11] Notably, in comparison to their organic counterparts, these metal-containing polymers[12] exhibited interesting redox, conductive and preceramic properties as well as high refractive indices which could be utilized for further active tuning of photonic crystals.[13]
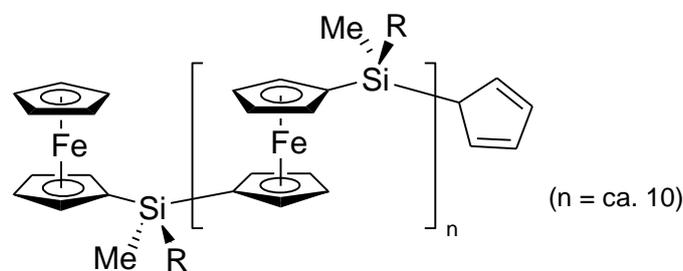

R = p-(C$_6$H$_4$)CH$_2$$\overset{+}{N}Me_3$ MeSO$_4^-$ (**1**); CCCH$_2$$\overset{+}{N}Me_3$ MeSO$_4^-$ (**2**); CCCH$_2$N[(CH$_2$)$_3$SO$_3^-$ $\overset{+}{Na}$]$_2$ (**3**).

Figure 2. Polyferrocenylsilane (PFS) polyelectrolytes used for LbL infiltration.

The cationic and anionic PFSs **1** and **3** were infiltrated, in a LbL fashion, into the PC films[14] which consisted of colloidal silica spheres (d = 275 nm) crystallized on a glass substrate and exhibiting a photonic stop band at λ = 597 nm (number of lattice planes: ~ 30). The variation of the photonic stop band frequency with the degree of LbL coating was monitored by optical transmission measurements and the spectra was recorded along the

crystal lattice [111] direction using a Perkin-Elmer Lambda 900 UV-Vis spectrophotometer. Optical properties of the PFS multilayers were determined separately by variable angle spectroscopic ellipsometry measurements.[9] The thickness of every bilayer was thus determined as 1.3 nm and refractive index (RI) as $1.68 - 1.66$ in the wavelength range of $\lambda = 600 - 650$ nm,[9] significantly different from a bilayer thickness of 4.8 nm and a RI of 1.52 nm when PFSs **1** and **3** with uncontrolled high molecular weight ($M_w \sim 10^5 - 10^6$) were used.[8]

LbL infiltration of PFSs **1** and **3** in the photonic crystals led to a gradual red shift of the photonic stop band **(Figure 3a)**. The largest stop-band shift of 10 nm was observed after the first bilayer deposition, and the increment of the red shift decreased gradually upon each additional bilayer coating **(Figure 3b)**. The shift eventually stopped at 643 nm after 9 bilayers of PFS deposition, which indicated that polyelectrolyte infiltration no longer took place in the air voids. Fine tuning of the photonic stop band at even smaller increments can be achieved through monolayer deposition.
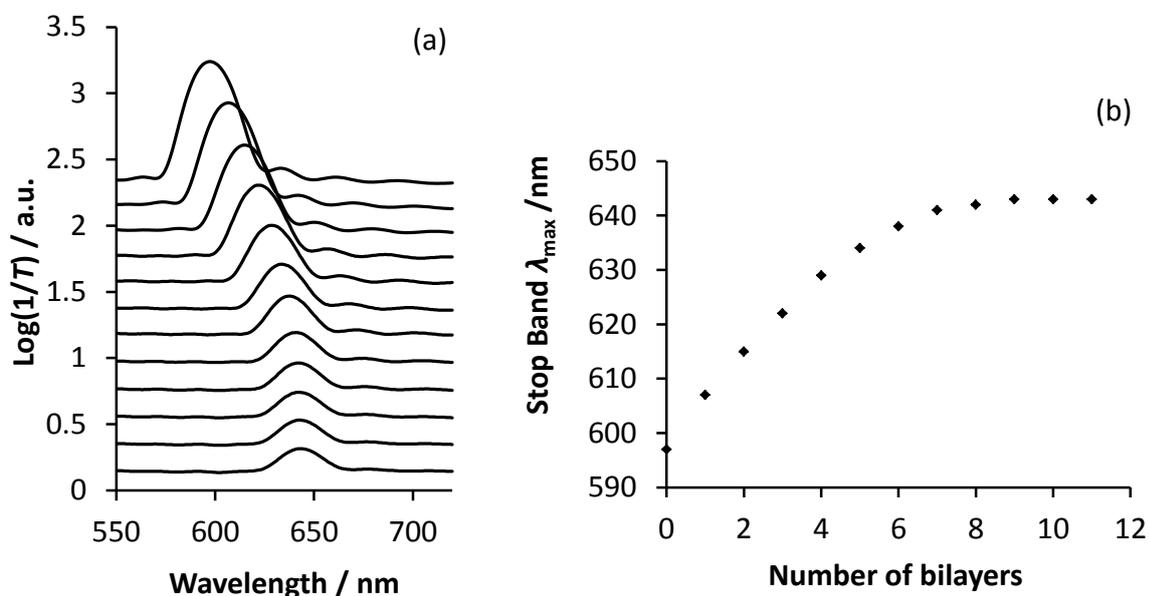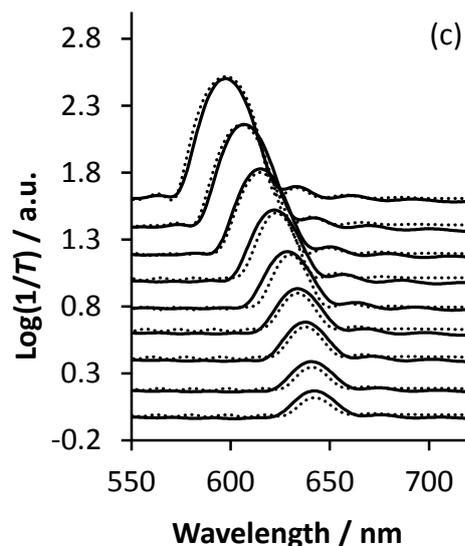
Figure 3. (a) Experimental optical spectra for a silica colloidal crystal film infiltrated by cationic and anionic PFSs **1** and **3**. The number of bilayer depositions increases from top (0 bilayer) to bottom (11 bilayers) by an increment of one bilayer between each curve, with each bilayer consisting of a cationic and an anionic PFS monolayer. (b) Plot of photonic stop band wavelength vs. the number of bilayers deposited. (c) Comparison of theoretical simulation (dotted lines) and experimental (solid lines) spectra for each bilayer deposition, from 0 (top) to 8 (bottom) bilayers.

In contrast to LbL assembly on open flat surfaces where linear and regular film growth was observed, the aforementioned results were consistent with an assembly process in which the coating surface was reduced as thin layers of polymers gradually built up in the spatially confined air voids of the colloidal crystals.

The observed PC optical spectra at $0 - 8$ bilayers of PFS deposition were simulated by using a scalar-wave approximation (SWA) model with a disorder correction **(Figure 3c)**.[15] The resulting theoretical spectra (dotted lines) demonstrated a good agreement with the experimental data (solid lines) for all considered cases. The fit of the spectra allowed us to not only calculate the filling fraction of the photonic structure (see below) but also check the spatial uniformity of the sample as the fitting parameters (sphere size, film thickness, refractive indices) have not been changed more than 10% in all cases.

The overall polyelectrolyte filling fractions in the air voids were estimated in the SWA simulation.[16] In the case of PFSs with controlled low molecular weights, the overall filling

fraction was estimated as $ff_{PFS} = 58\%$, corresponding to an average film thickness of ca. 11.5 nm.[11] While this was less than the theoretical maximum filling fraction of 86% and thickness of 21 nm at which point the smallest air-void opening in an fcc structure was closed, it was a significant increase from the 42% overall filling fraction when PFSs of uncontrolled high molecular weight ($M_w \sim 10^5 - 10^6$, PDI > 1.5) were used.[8] It should be noted that by using PFSs of controlled low molecular weights, we were able to achieve uniform LbL assembly across the entire sample areas of $0.5 - 1$ cm^2 where the stop band wavelength varied within 1 – 2 nm. In the case of PFSs with uncontrolled high M_w, however, only a rough tuning of the photonic properties and a non-uniform LbL deposition were observed.[8]

The LbL infiltration of PFSs in the colloidal crystal films was examined by using scanning electron microscopy (SEM), and images of randomly selected areas of the films indicated gradual filling of the air voids as more layers of the polyelectrolytes were deposited on the surface of the interstitial spaces **(Figure 4)**. Upon completion of the infiltration, SEM images of the top, middle, and bottom layers and the cross section of the films showed that the polyelectrolyte deposition was uniform throughout the colloidal crystals.
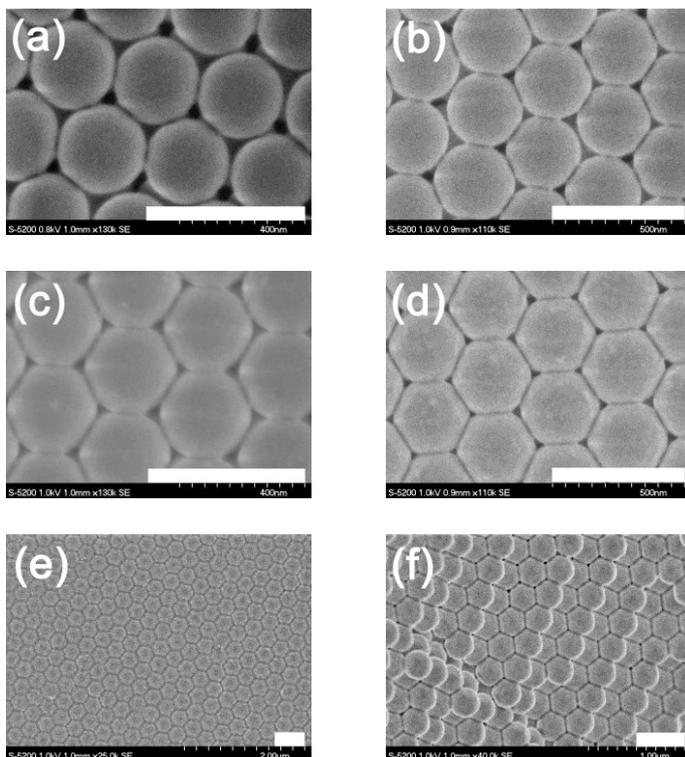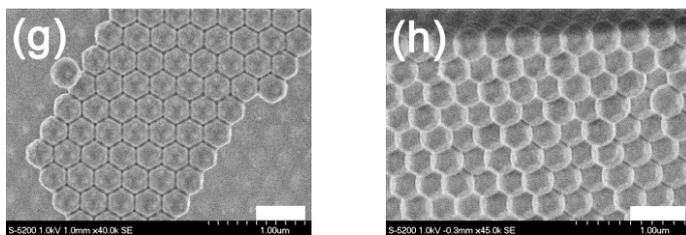
Figure 4. (a) – (d) SEM images of silica colloidal photonic crystals infiltrated by 0, 2, 4, and 6 bilayers of PFSs **2** and **3**, respectively. (e) – (h) SEM images of top layer, middle layers, bottom layer, and cross section of silica colloidal photonic crystals infiltrated by 16 PFS bilayers of PFSs **2** and **3**, respectively. The scale bars represent 500 nm.

In conclusion, tuning of prefabricated colloidal photonic crystals with nanometer-scale precision has been achieved through LbL electrostatic assembly of PFS polyelectrolytes in the interstitial spaces. Essential to the approach is using polyelectrolytes which possess controlled low molecular weights and narrow polydispersity. With their small sizes, the PFS polyelectrolytes do not block the air voids during the early stages of LbL infiltration. This ensures uniform coating across the entire photonic lattice and thus precise and reproducible optical tuning. The approach presented, herein demonstrated for 3D self-assembled opal films, is of relevance for the field of photonic nanostructures as a whole, since it can be applied to vary at will with great precision the optical response of any sort of porous structures. In this sense, not only a wide range of periodic arrays could benefit from this method,[17] but also random or amorphous photonic media[18] in which multiple or resonant scattering could be accurately modulated by controlled homogeneous deposition of a dielectric thin coating on the inner pore or cavity walls.

Experimental Section

Polyferrocenylsilane (PFS) polyelectrolytes **1** – **3** were synthesized through living photolytic ring-opening polymerization of amino-functionalized [1]silaferrocenophanes according to the literature procedure.[9] More experimental details can be found in the Supporting Information.

The photonic crystal films were prepared on the surface of glass slides by means of a vertical deposition technique previously reported in the literature[14] using silica colloidal spheres (d = 275 nm) synthesized by the Stöber process.[19]

Each polyelectrolyte solution used in the LbL infiltration process contained 10 mM PFS (based on the respective monomer repeat units) in deionized water with 0.1 M NaCl. The PC substrates were alternately placed in the PFS polyanion and polycation solutions for 15 min, with a triple rinse in deionized water for 5 min each after every exposure to the polyelectrolyte. The LbL assembly was monitored by UV-Vis spectroscopy.

The photonic stopband spectra were recorded on a Perkin-Elmer Lambda 900 spectrophotometer, using a 3 mm diameter aperture. Three positions on the PC films were designated for the recording of the spectra after each cycle of polyelectrolyte deposition to evaluate the uniformity of the LbL tuning of the PC film.

The SEM images of the colloid crystal samples were obtained on a Hitachi S-5200 field-emission high resolution scanning electron microscope. No conductive coating was deposited on the samples prior to imaging.

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and $V_{pore} = 26\%$. A correction that took account of the the disorder of the colloidal crystal was included in the calculation.

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Nanometer-scale tuning of the optical properties of prefabricated photonic crystals has been achieved via layer-by-layer assembly of polyelectrolytes in the interstitial spaces of the photonic lattice. Key to the approach is using polyelectrolytes with controlled short chain lengths. This ensures they do not block the air voids, thereby maintaining uniform coating and thus precise and reproducible optical tuning.
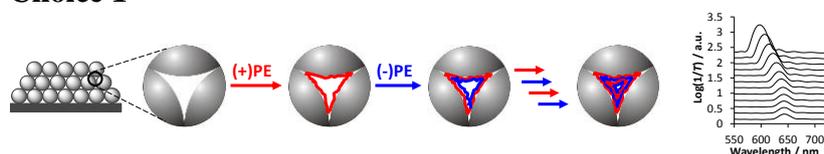
Keyword Photonic Crystals

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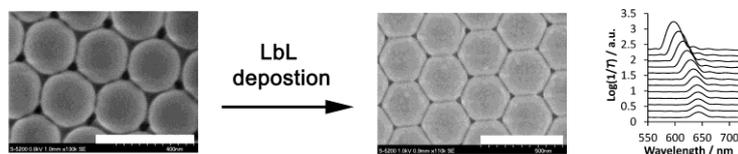
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ToC figure

Choice 1

Choice 2

Supporting Information

Nanometer-Scale Precision Tuning of 3D Photonic Crystals Made Possible Using Polyelectrolytes with Controlled Short Chain Length and Narrow Polydispersity

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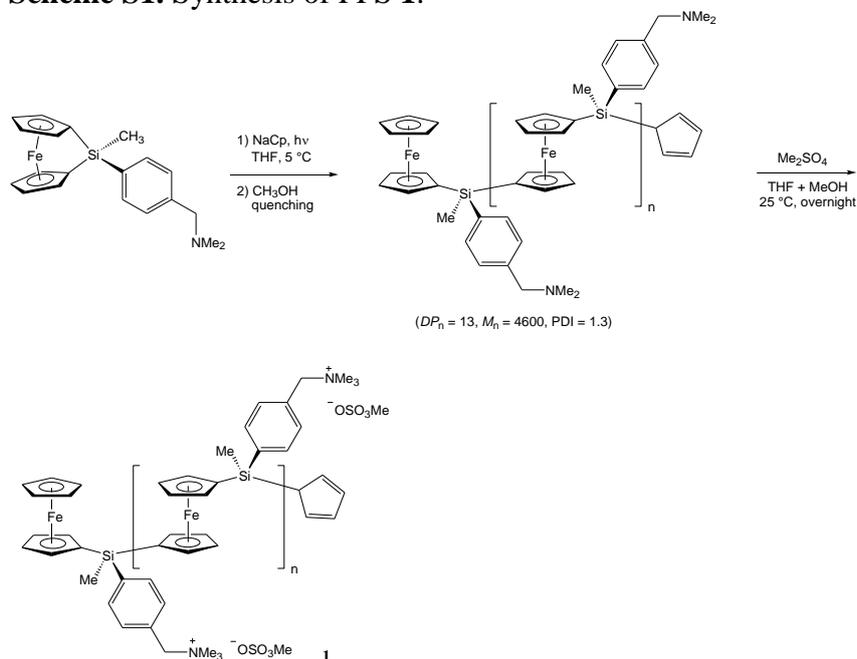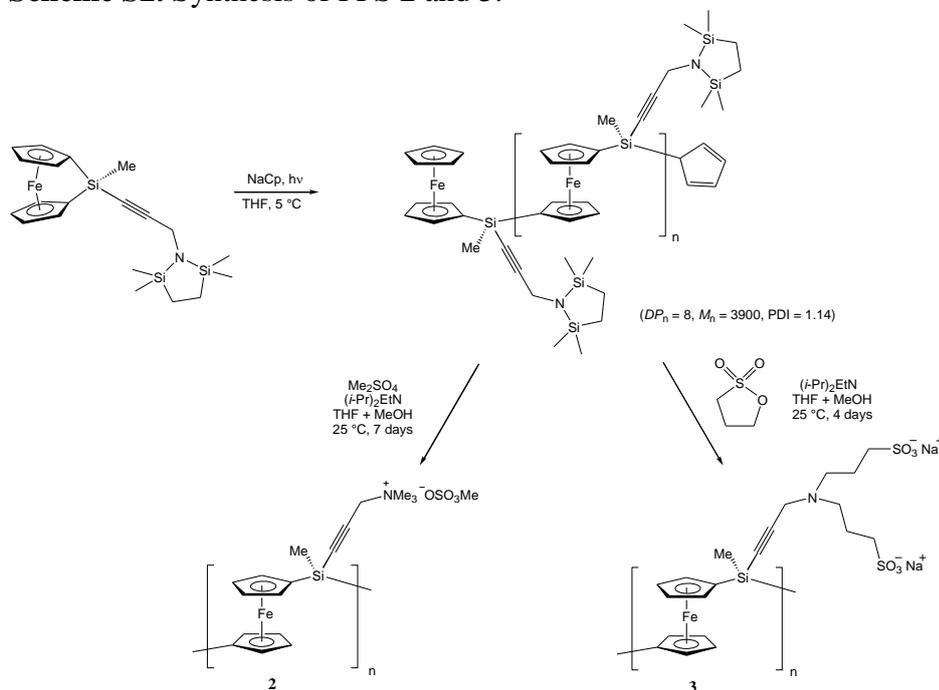
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Experimental details of polyferrocenylsilanes (PFS) 1 – 3

PFS **1** – **3** were synthesized as shown below according to literature procedures.[1]
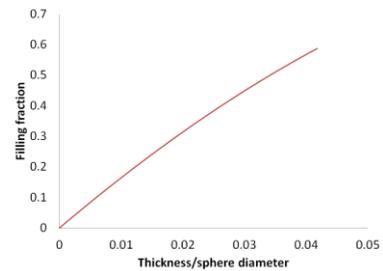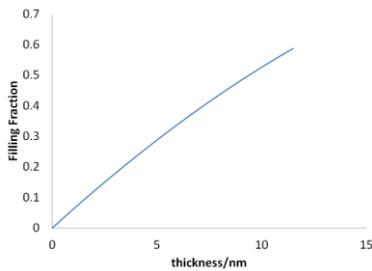
Scheme S1. Synthesis of PFS **1**.

(DP_n = 13, M_n = 4600, PDI = 1.3)

Scheme S2. Synthesis of PFS **2** and **3**.

(DP_n = 8, M_n = 3900, PDI = 1.14)

Theoretical calculation of film thickness in the interstitial spaces of PCs

The filling fraction (*ff*) was calculated as a function of film thickness (*t*):

t (nm)	*t/D*	*ff*
0.5	0.00181818	0.030899573
1.0	0.00363636	0.061342279
1.5	0.00545455	0.091324003
2.0	0.00727273	0.120840627
2.5	0.00909091	0.149888037
3.0	0.01090909	0.178462116
3.5	0.01272727	0.206558748
4.0	0.01454545	0.234173818
4.5	0.01636364	0.26130321
5.0	0.01818182	0.287942807
5.5	0.02000000	0.314088495
6.0	0.02181818	0.339736156
6.5	0.02363636	0.364881674
7.0	0.02545455	0.389520935
7.5	0.02727273	0.413649822
8.0	0.02909091	0.437264219
8.5	0.03090909	0.460360011
9.0	0.03272727	0.482933081
9.5	0.03454545	0.504979313
10.0	0.03636364	0.526494591
10.5	0.03818182	0.547474801
11.0	0.04000000	0.567915824
11.5	0.04181818	0.587813547
12.0	0.04363636	0.607163853

$t = R - R_0, \quad ff = 4 \text{ x } (V_{shell} - 12 \text{ x } V_{overlap})/V_{void}$

$V_{shell} = (4/3) \pi \text{ x } (R^3 - R_0^3), \quad V_{overlap} = \pi \text{ x } (2 \text{ x } R^3/3 - R^2 \text{ x } R_0 + R_0^3/3),$
$V_{void} = V_{cell} - 4 \text{ x } V_{sphere}, \quad V_{cell} = (2 \text{ x } 2^{1/2} \text{ x } R_0)^3, \quad V_{sphere} = (4/3) \pi \text{ x } R_0^3$

Note: t = thickness of deposit; D = diameter of silica colloidal sphere, 275 nm; ff = filling fraction; R_0 = sphere radium (137.5 nm); R = sphere radium + thickness of deposit.

Fitting parameters of the theoretical simulation spectra in Figure 3c

BL	fill factor	n polymer	number of spheres	n SiO$_2$	k (imag) SiO$_2$	sphere size /nm
0	0	1.68	27	1.425	0.0019	275
1	0.1	1.68	27	1.425	0.0016	275
2	0.205	1.68	27	1.428	0.0003	275
3	0.295	1.66	31	1.43	0	275
4	0.36	1.65	30	1.435	0	275
5	0.395	1.65	30	1.435	0	276
6	0.417	1.65	30	1.435	0	277
7	0.436	1.65	30	1.435	0	277
8	0.45	1.65	29	1.433	0	277

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