SUPPORTING INFORMATION FOR:

HARD-TEMPLATING OF PRUSSIAN BLUE ANALOGUES IN MESOPOROUS SILICA AND ORGANOSILICA

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Materials and Characterization

1,2-Bis(trimethoxysilyl)ethane (Aldrich, 96%), tetramethylorthosilicate (Acros, 99%), (3-iodopropyl)trimethoxysilane (Aldrich, 95%), and 4,4'-bipyridine (AKSci, 98%) were used without further purification. Cellulose nanocrystals (prepared by sulfuric acid hydrolysis of kraft pulp) were provided by CelluForce, Inc. TEM imaging of the cellulose nanocrystals gave sizes of ~195 \pm 93 nm x 15 \pm 8 nm.

 $Na_{3}[Fe(CN)_{5}NH_{3}]$ ·3H₂O was synthesized from the reaction of $Na_{2}[Fe(CN)_{5}NO]$ with concentrated NH_{3} ·H₂O solution according to the method by Kenney et al.¹

UV-Vis-NIR spectra were recorded on a Varian Cary 5000 spectrophotometer by mounting the films on a quartz slide perpendicular to the beam path. CD spectra were collected using a Jasco J-815 Circular Dichroism Spectrometer by mounting the films in the same procedure. IR spectroscopy was performed on a PerkinElmer Frontier FT-IR equipped with a diamond ATR. Powder X-ray diffraction patterns were recorded on a Bruker D8 Advance diffractometer equipped with a CuKα sealed tube X-ray source. Optical microscopy was performed on an Olympus BX41 microscope. N₂ adsorption data were collected at 77 K using a Micromeritics ASAP 2000 analyzer. All the samples were degassed at 70 °C under vacuum for 240 min before analysis. Scanning electron microscopy (SEM) experiments were conducted using a Hitachi S4700 electron microscope. Before imaging, samples were sputter-coated with 5 nm of gold or gold-palladium alloy. Energy-dispersive X-ray analysis (EDX) was performed on a Hitachi S2600N scanning electron microscope (SEM) equipped with a Quartz XOne EDS System.

Shown below are the elemental analyses of two different samples of BiPy-functionalized chiral nematic mesoporous silica:

- A. 1.77% N, 13.38% C, 1.98% H; N:C = 13.2.
- B. 1.63% N, 11.39% C, 1.87% H; N:C = 14.3.

The theoretical N:C ratio for the fully functionalized material is 17.9. We estimate that ~40-50% of the iodide groups have been substituted by BiPy according to the above. From these numbers and the surface area of the silica, we calculate a graft density of ~1.2-1.4 BiPy molecules per square nanometer – the surface is nearly covered.

(1) D. J. Kenney, T. P. Flynn, J. B. Gallini, J. Inorg. Nucl. Chem. 1961, 20, 75-81.



Figure S1. Nitrogen adsorption/desorption isotherm of organosilica films.



Figure S2. Photomicrographs taken from the cross-sections of chiral nematic organosilica, **OrgSi-BiPy**, **OSBP-FeCmp** and monolayer **OSFeFe** films (from top to bottom, scale bar = $100 \ \mu$ m).



Diagram S1. A deposition cycle of zinc PBA in a piece of **OSBP-FeCmp** or **Silica-FeCmp** film: (1) immersion in $Zn(NO_3)_2$ + KCl solution; (2-4) washing with deionized water in three separate beakers; (5) immersion in $K_4[Fe(CN)_6]$ + KCl solution; (6-8) washing with deionized water for three times again.



Figure S3. Powder X-ray diffraction (PXRD) patterns of silica (black curve), monolayer **SiFeZn** (red curve), 10 layer **SiFeZn** (green curve), **SiZnHF** (from 10 layer **SiFeZn**, blue curve), and zinc PBA prepared from solution without silica templates (purple curve).



Figure S4. Photograph of monolayer SiFeFe, SiFeCo, SiFeNi, SiFeSn and SiFeZn (left to right and top to bottom) composite films used for CD and UV-Vis measurements.



Figure S5. CD spectra of a SiBP-FeCmp film (red curve), which was immersed in CoCl₂ to give a SiFeCo film (green curve), and then treated with NaOH to remove Co-PBA (blue curve).



Figure S6. **OSFeFe** (left part) and **OSFeZn** (right part) composite films before (a, c; red curves) and after (b, d; yellow curves) etching by HF aqueous solution in the presence of $K_4[Fe(CN)_6]$ and K_2SO_4 .



Figure S7. Photographs of **SiFeFe** composite films (a) before and (b) after HF etching in the presence of $K_4[Fe(CN)_6]$ and K_2SO_4 . (c) FTIR spectra before (red curve) and after (yellow curve) etching. (d-e) SEM images after etching (Scale bar = 20 μ m).



Figure S8. Additional FTIR spectra of (a) **SiFeFe** after HF etching (red curve) in the presence of $K_4[Fe(CN)_6]$ (green curve) and K_2SO_4 (blue curve); (b) $Na_3[Fe(CN)_5NH_3]\cdot 3H_2O$ (red curve) and zinc PBA prepared from solution without hard templates (blue curve).



Figure S9. Energy dispersive X-ray analysis (EDX) of SiFeZn composite films (a) before and (b) after etching in 2 wt % HF aqueous solution for 1h.

Table S1. Elemental compositions of SiFeZn and SiZnHF determined by EDX.

Element	0	Si	к	Fe	Zn
SiFeZn (wt. %)	22.5	47.6	5.0	9.1	16.0
SiZnHF (wt. %)	0	0.7	0.3	41.7	57.4



Figure S10. Additional SEM images of Zinc PBA films prepared from SiFeZn composites through HF etching and supercritical drying.



Figure S11. Additional SEM images of SiFeZn etched by 2 wt% HF ethanol solution for 14 h.



For a chiral nematic mesoporous silica film with pigments like PBAs inside, the CD signal originated from the silica template was reshaped by the UV-Vis transmittance spectrum of the pigment. Consequently, a unique CD pattern would be measured, which can be deemed as a complex of the CD signal from the hard template and the UV-Vis transmittance spectrum of the pigment.

Here the CD signals of a chiral nematic silica template and a PBA@Silica composite film are defined as $g_1(\lambda)$ and $g_2(\lambda)$, respectively, while the UV-Vis transmittance spectra of them are defined as $f_1(\lambda)$ and $f_2(\lambda)$, respectively. In theory the UV-Vis transmittance spectra of the PBAs in the films can be calculated by $f_2(\lambda)/f_1(\lambda)$ to remove the background absorption from silica templates, but actually the pristine silica films were almost completely transparent and colorless, while PBA@Silica composite films were intensely colored. After several attempts of simulating $g_2(\lambda)$ by $g_1(\lambda) \times f_2(\lambda)/f_1(\lambda)$, we found the background absorption of silica templates could be disregarded, and the original UV-Vis transmittance spectra should be normalized between 0 and 1 by (x-Min)/(Max-Min), which can better represent the influence of the PBAs on the elliptically polarized light that passed through them. Thus we finally built a mathematical model of $g_2(\lambda) = g_1(\lambda) \times f_2(\lambda)$, in which the CD signal of the silica template $g_1(\lambda)$ and the UV-Vis transmittance of the PBA@Silica composite $f_2(\lambda)$ were normalized between 0 and 1 before calculation, and their product was also normalized in the same way before being compared with the normalized real CD spectra of PBA@Silica composites. Thus the final relationship among them is $N[g_2(\lambda)] = N\{N[g_1(\lambda)] \times N[f_2(\lambda)]\}$, where N means 0 to 1 normalization.



Figure S12. Other examples of CD signal simulation: solid curves are the normalized CD spectra of Silica-BiPy (a), SiBP-FeCmp (b), SiFeFe (c), and SiFeNi (d), dotted curves are simulated CD signals.