Polymer and Magnetic Nanoparticle Composites with Tunable Magneto-Optical Activity: Role of Nanoparticle Dispersion for High Verdet Constant Materials

Pavlopoulos, N. G.[a,b]; Kang, K. S.[a]; Holmen, L.N.[a]; Lyons, N.P.[c]; Akhoundi, F.[c]; Carothers, K.J.[a]; Jenkins, S.L.[c]; Lee, T.[a]; Kochenderfer, T.M.[a]; Phan, A.[a]; Phan, D.[d]; Mackay, M.E.[d]; Shim, I.[e]; Char, K.[e]; Peyghambarian, N.[c]; LaComb L.[c]; Norwood, R.A[c]; Pyun, J.[a]

Department of Chemistry & Biochemistry, University of Arizona[a]; Schulich Faculty of Chemistry, Technion – Israel Institute of Technology[b]; Wyant College of Optical Sciences, University of Arizona[c]; Department of Chemical Engineering, University of Delaware[d]; Department of Nanoscale Physics, Kookmin University[e]

Email: jpyun@email.arizona.edu

Supporting Information

Table of Contents

1) Experimental

a) Materials

All chemicals were used as purchased. Cellulose acetate (M_n~50,000), cobalt acetylacetonate ($Co(acac)_2$, 97%), benzyl ether (98%), high molecular weight polystyrene (M_w~350,00), iron acetylaconetate ($Fe(acac)_3$, 97%), and oleic acid (OLAC) (90%) were purchased from Sigma Aldrich. 4-hydroxy-4-methyl-2-pentanone (diacetone alcohol) (>99%) was purchased from Acros. Activated Neutral Alumina (~60 mesh) was purchased from Alfa Aesar. Absolute ethanol was commercially available from Decon labs and used as received. Acetone, hexanes, methanol, and toluene were commercially available from Fisher Scientific. Uncoated glass slides (25.0mm x 75.0mm, 1.0 mm thick, VWR) were commercially available, and gold coated microscope slides were prepared from these using a Leica EM ACE600 vacuum sputter coater equipped with a gold target. Spin-coating was performed on a Laurell Technologies Corporation Spin Coater (Model: WS-400BZ-6NPP/LITE). An Omega temperature controller CSC32K with a K-type utility thermocouple and a Glas-Col fabric heating mantle were used for cobalt ferrite synthesis. All centrifugation was performed in 50 mL centrifuge tubes (unless otherwise stated) using a rotor with a radius of 11 cm. TEM images were obtained on a Technai G2 Spirit transmission electron microscope at 80-100 kV, using carbon coated copper grids (Cu, square, 200 mesh) purchased from Electron Microscopy Sciences. High Resolution STEM imaging was performed on a Hitachi HF-5000 High Resolution aberration-corrected TEM/STEM operated at 200 kV. Field-emission scanning electron microscopy (FE-SEM) was performed using a Hitachi S-4800 Type II/ThermoNoran NSS EDS Field Emission Scanning Electron Microscope. Thermogravimetric analysis (TGA) was performed using a Q500 TGA (TA Instruments), with measurements being made in a temperature range of 30-700 °C under a nitrogen atmosphere. Image analysis was performed using ImageJ software (Rasband, W.S., National Institutes of Health, http://rsb.info.nih.gov/ij/, 1997-2007).

b) $CoFe_2O_4$ Nanoparticles

The $CoFe_2O_4$ nanoparticles synthesized herein were prepared via a modified method of Lu et al.[1]. Details of the method used herein are included below.

i. Preparation of Hot Injection Stock Solution

To a 50 mL three necked round bottomed flask equipped with a ½ ” Teflon coated stirbar, reflux condenser, thermocouple, and rubber septa was added cobalt acetylacetonate (Co(acac)2; 0.232 g, 0.90 mmol), iron acetylacetonate (Fe(acac)3; 0.636 g, 2.40 mmol), oleic acid (5.64 mL, 5.04 g, 17.70 mmol). Subsequently, the contents of the flask were heated to 150 ºC at a rate of 20 ºC/min under vacuum, promoting the formation of metal-oleate species and facilitating the removal of acetyl acetone over the course of 2 hours. Subsequently, the contents of the flask were heated to 195 ºC under vacuum for 30 minutes before being cooled to room temperature.

ii. Synthesis of 5 nm $CoFe_2O_4$ Nanoparticles on a 200 mg scale

To a 100 mL three necked round bottomed flask equipped with a 1/2” Teflon coated stirbar, reflux condenser, thermocouple, and rubber septa was added benzyl ether (10.00 mL, 10.43 g, 52.6 mmol). Subsequently, the flask was heated to 295 ºC under argon. A heating rate of 20 ºC/min was employed, and upon reaching 295 ºC, the hot injection stock solution was rapidly injected (1.88 mL; 0.30 mmol $Co(acac)_2$, 0.60 mmol $Fe(acac)_3$). Next, the flask was allowed to react at 290-295 ºC for 75 minutes. At 75 minutes the mantle was removed at which point the solution was cooled to room temperature.

iii. Synthesis of 5 nm $CoFe_2O_4$ Nanoparticles on a 500 mg scale

To a 100 mL three necked round bottomed flask equipped with a 1” Teflon coated stirbar, reflux condenser, thermocouple, and rubber septa was added benzyl ether (25.00 mL, 26.08 g, 131.5 mmol). Subsequently, the flask was heated to 295 ºC under argon. A heating rate of 20 ºC/min was employed, and upon reaching 295 ºC, the hot injection stock solution was rapidly injected (4.70

mL; 0.75 mmol $Co(acac)_2$, 1.50 mmol $Fe(acac)_3$). Next, the flask was allowed to react at 290-295 ^oC for 75 minutes. At 75 minutes the mantle was removed at which point the solution was cooled to room temperature.

c) PS-COOH Ligand

i. Preparation of PS-COOH coated $CoFe_2O_4$ Nanoparticles and Ligand Exchange Stock Solution

The PS-COOH ligand exchange depends partially on the organic content of the purified nanoparticles, as the exchange is designed to replace the small molecule ligands with polymeric analogues. For a successful ligand exchange, it was empirically found that a 1:2 mass ratio of $CoFe_2O_4$ NPs (inorganic content) to PS-COOH ligand resulted in successful exchange. As for the exchange solvent, DCB has been chosen in the past due to its high boiling point (ligand exchange performed at 180 ^oC) and ideal polarity for nanoparticle and polymer ligand dispersion. In this ligand exchange stock, the concentration of PS-COOH is ideally targeted at 20 mg/mL, and the concentration of $CoFe_2O_4$ NPs (inorganic content) has been targeted at 10 mg/mL. These conditions have yielded products that provide superior films and will be targeted herein.

First, a stock solution of oleic acid coated $CoFe_2O_4$ NPs in DCB was prepared at a concentration of 20 mg/mL (inorganic content) by dispersing $CoFe_2O_4$ NPs (120.2 mg, 61.79 mg inorganic content) in 3.090 mL of DCB, followed by vortex mixing and sonication (< 5 minutes total to disperse). Subsequently, to a 4-dram scintillation vial, was added an appropriate volume of the CoFe2O4 nanoparticle stock to correspond to 15 mg of inorganic content (0.75 mL). Next, an equivalent volume of PS-COOH stock solution (0.75 mL), that was made at a concentration of 10mg/mL in DCB, was added to the vial. The contents of the vial were then placed on an aluminum heating mantle thermostatted at 180 ^oC for 1 hour, while vortex mixing ever 15 minutes, to commence and complete the ligand exchange process. The vial was then probe sonicated for 1 hour to assure homogenization. After the PS-COOH ligand exchange, the ligand exchange stock solution (total volume = 1.50 mL) contained PS-COOH coated $CoFe_2O_4$ NPs (15 mg inorganic content, inorganic concentration = 10 mg/mL), PS-COOH ligands (30 mg PS-COOH, PS-COOH concentration = 20 mg/mL), and OLAC ligands + remaining benzyl ether solvent (estimated OLAC+benzyl ether content = 14.18 mg, OLAC+benzyl ether concentration = 9.45 mg/mL based on TGA of parent NPs).

ii. Figure ESI.1 Pre and Post Ligand Exchange Dispersion Quality

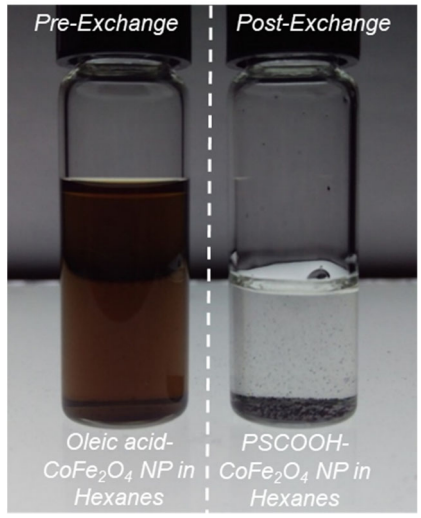

Figure ESI.1. Pre and post ligand exchange dispersion quality in hexanes

iii. Figure ESI.2 TGA of PS-COOH Coated $CoFe_2O_4$ Nanoparticles

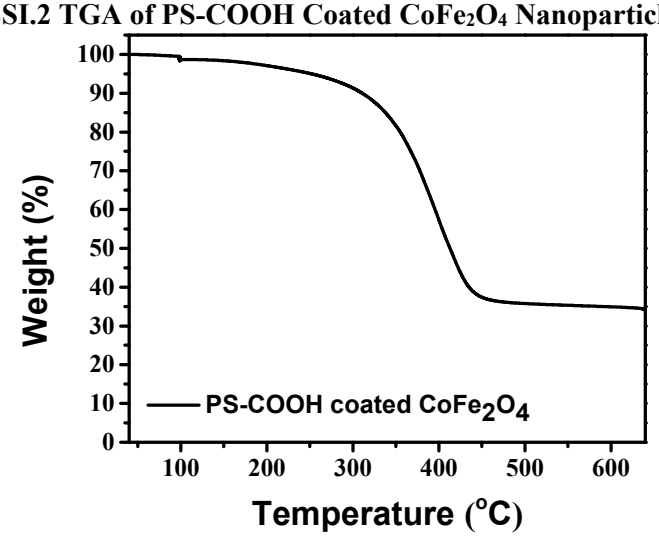

Figure ESI.2. TGA of PS-COOH Coated $CoFe_2O_4$ nanoparticles.

iv. Calculation of Apparent PS-COOH Grafting Density

The calculation of grafting density of PS-COOH ligands is based on the geometric approximation of the $CoFe_2O_4$ nanoparticles as solid spheres and the assumption that all organic content in the TGA shown in Figure ESI.2 originates from surface bound PS-COOH ligands. The evaluation was made according to the following.

The number of nanoparticles per gram of PS-COOH coated $CoFe_2O_4$ (N_{NP}) can be calculated from the nanoparticle radius (r), the bulk density of $CoFe_2O_4$ (ρ), and the inorganic fraction from the TGA data (I_{TGA}), as shown below:

$$N_{NP} = I_{TGA} * \frac{1}{\left(\frac{4}{3}\pi r^3\right)\rho} = 0.3492 \frac{1}{\left(\frac{4}{3}\pi(2.6nm)^3\right)\left(5.15x10^{-21}\frac{g}{nm^3}\right)} = 2.6_{3745}\text{x}10^{18} NP/g \quad (1)$$

The surface area per gram of PS-COOH coated $CoFe_2O_4$ NPs (S_{NP}) can then be calculated from the nanoparticle radius (r) and $N_{NP/g}$ as shown below:

$$S_{NP} = 4\pi r^2 * N_{NP} = 4\,\pi(2.6nm)^2 * 2.6_{3745}\text{x}10^{18} NP/g = 7.8_{2375} x10^{19} nm^2/g \quad (2)$$

We can then calculate the number of PS-COOH ligands per gram of PS-COOH coated $CoFe_2O_4$ (N_L) using the molecular weight of the PS-COOH ligand (MW_L), Avogadro's number (N), and the organic fraction from the TGA data (O_{TGA}):

$$N_L = MW_L * \frac{1}{N} * O_{TGA} = 12000\frac{g}{mol} * \frac{1}{N} * 0.6508 = 3.2_{6601} x10^{19} ligands/g \quad (3)$$

Finally, we can approximate the ligand grafting density (L_G) as the ratio of N_L and S_{NP} as shown below:

$$L_G = \frac{N_L}{S_{NP}} = \frac{3.2_{6601} x10^{19} ligands/g}{7.8_{2375} x10^{19} nm^2/g} = 0.42\ \frac{ligands}{nm^2} \quad (4)$$

v. Preparation of High Molecular Weight PS Stock Solution

To a 20 mL scintillation vial, high molecular weight PS (Mw: 350,000 g/mol) was dissolved in DCB at a concentration of 150 mg/mL by heating and vortex mixing to homogenize.

vi. Composite Dispersion Preparation

To prepare the composite dispersion, the high molecular weight PS stock solution was blended with the ligand exchange stock solution, followed by heating and minimal vortex mixing to homogenize. After this, the dispersions were precipitated into methanol, which OLAC and benzyl ether are highly soluble in but in which PS is completely insoluble. The collected precipitate was then dried and used to prepare the final ink from which films will be spin coated.

It is at this point that the final particle loadings in the films are set. This required a number of assumptions that needed to be made which are highlighted below:

1) considering the relevant organic content in the ligand exchange stock solution (the PS-COOH component, since this will be retained post precipitation)

2) considering the inorganic content in the ligand exchange stock solution

3) making the assumption that all of the $CoFe_2O_4$ nanoparticles in the ligand exchange stock will be incorporated into the final films

4) making the assumption that all of the PS-COOH in the ligand exchange stock will be incorporated into the final films (some losses are likely, resulting in an *underestimation* of nanoparticle loading; i.e. loadings may be *higher* than expected slightly)

5) determining the mass of high molecular weight binder required to achieve the targeted nanoparticle loading in the final films. For this, a detailed table has been prepared listing all relevant conditions.

Table 1. Representative Conditions for Composite Dispersion Preparation

Concentration of Inorganics in PS-COOH/$CoFe_2O_4$ Stock (g/mL): 0.010			Concentration of Organics in PS-COOH $CoFe_2O_4$ Stock (g/mL): 0.020		Concentration of High MW PS Binder Stock (g/mL): 0.150		
Relevant Data			**PS-COOH $CoFe_2O_4$ Stock Considerations**		**Binder Considerations**		**Solids Loadings**
Target $CoFe_2O_4$ Loading (wt%)	Target Composite Mass (g)	Target Inorganic Mass (g)	Volume of PS-COOH CoFe2O4 Stock (mL)	Organic Mass in Added Stock (g)	Target Mass of High MW PS Binder (g)	Volume of High MW PS Binder Stock Added (mL)	Total Solids Concentration Prior to Precipitation (mg/mL)
2.50%	0.20	0.005	0.5	0.010	0.185	1.23	115.38
5.00%	0.20	0.010	1.0	0.020	0.170	1.13	93.75
7.50%	0.20	0.015	1.5	0.030	0.155	1.03	78.95
10.00%	0.20	0.020	2.0	0.040	0.140	0.93	68.18
15.00%	0.20	0.030	3.0	0.060	0.110	0.73	53.57

In short, the appropriate quantities of ligand exchange stock solution and high molecular weight PS binder stock solution were added to a 4-dram vial, followed by being placed on an aluminum heating mantle thermostatted at 105 ºC for 90 minutes, while vortex mixing the vials every 15 minutes. The vials were then probe sonicated for 1 hour to assure homogenization.

After the homogeneous composite dispersion was prepared, the dispersion contained PS-COOH $CoFe_2O_4$ nanoparticles, free PS-COOH, high molecular weight polystyrene, dichlorobenzene, and the entire organic content from the initial as-prepared $CoFe_2O_4$ nanoparticles (mostly OLAC, perhaps some quantity of benzyl ether). This step is effectively a "complete" purification designed to remove OLAC/benzyl and dichlorobenzene entirely before the inks for spin coating are prepared.

After the composite dispersions had cooled to room temperature, the dispersions were precipitated with 15 mL of methanol, placed atop an AlNiCo magnet. Subsequently, the vials were vortex mixed for 5 seconds at maximum setting before carefully decanting the methanol supernatant and drying of the pellets thoroughly with an air gun. The pellets were then transferred to tarred 4-dram vials using a set of acid-cleaned metal tweezers, before being dried overnight at room temperature and ambient pressure in a dust free environment. After this, the pellets were dried at 80 ºC for 2 hours at ambient pressure, followed by being dried at 80 ºC in vacuo for 2 hours.

vii. Composite Ink Preparation

After the composites had thoroughly dried, the pellets were dispersed in an appropriate quantity of chlorobenzene for a concentration of 100 mg/mL total solids to be achieved. The pellets were then dispersed by continuous vortex mixing at maximum setting for 5 minutes. The vials were then probe sonicated for 1 hour to assure homogenization.

d) Film Preparation by Spin Coating

The method for multilayer film preparation utilized herein was inspired by previously published methods for preparing all-polymer Bragg-reflectors.[2]

i. Preparation of Cellulose Acetate Stock Solution

Cellulose acetate is added to diacetone alcohol (4 wt%) and vortex mixed to prepare the cellulose acetate stock solution that was used in the preparation of the multi-layered films.

ii. Multi-layer Film Preparation

A 1x1 cm^2 gold-coated glass slide is fixed to a spin coater, to which enough volume of cellulose acetate stock solution is deposited to cover the surface of the film. The first cellulose acetate layer is spun at 2700 rpm with an acceleration of 250 rpm/s for 1 minute. The film is then dried on a

ceramic hot plate at 100ºC for 2 minutes. Once dry, the composite ink is deposited onto the surface of the film and spun at 2000 rpm with an acceleration of 250 rpm/s for 1 minute. The film is then dried on a ceramic hot plate at 100ºC for 2 minutes. This process of alternating cellulose acetate and composite ink layers is repeated with spin speeds of 2300 rpm and 2000 rpm, respectively, until the desired number bilayers are achieved.

2) Scanning Electron Microscopy (SEM)

i. Sample Preparation

To prepare the 5 bilayer films for cross sectional imaging, the film was first scored at the edge and carefully manually detached from the substrate. Subsequently, the thin film was placed in a liquid nitrogen with both ends held by two tweezers. After 2 minutes, the films were fractured in liquid nitrogen. The cross-sections were then mounted to 90º SEM-stubs, followed by being coated with 8 nm of amorphous carbon using the Leica EM ACE600 to prepare them for SEM-measurements. This procedure was identical for the 30 bilayer sample, as well.

ii. Figure ESI.3 Delamination

Figure ESI.3. Delamination observed upon freeze fracturing of a 30-bilayer multilayer film.

iii. Imaging Conditions

Edge-on imaging of the multilayer samples was performed on a Hitachi S-4800 SEM equipped with a Field Emission tip at a sample working distance of 8 mm, an accelerating voltage of 5.0 kV, and an emission current of 11.3 μA. Whereas films that were not carbon-coated exhibited significant charging and deformation, both top-down and edge-on carbon coating was found to greatly increase sample stability without affecting contrast of alternating polymer-nanoparticle composite/cellulose acetate layers (Figure ESI.4).

iv. Figure ESI.4 Example Film Thickness Measurements

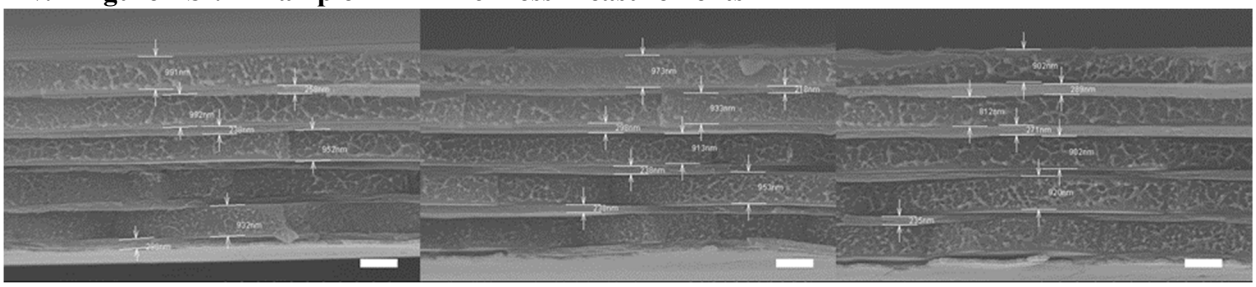

Figure ESI.4. Example film thickness measurements performed on bilayer samples. All scale bars are 1 μm.

3) Figure ESI.5 Verdet Constant as a Function of Nanoparticle Loading

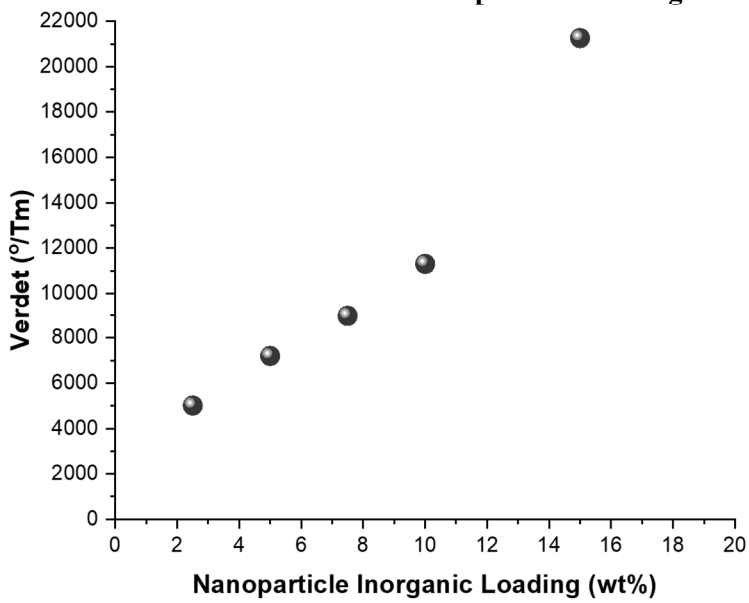

Figure ESI.5. Verdet constant as a function of nanoparticle loading.

4) Optical Measurements: Verdet Measurements

Verdet constant measurements and calculations were performed using a setup similar to that reported by Miles and coworkers.[3] The setup to measure Verdet constants consists of a 1310nm Fabry-Perot laser where the output polarization is controlled using a half wave plate in conjunction with a high extinction ratio Glan-Thompson polarizer. This light passes through a non-polarizing beamsplitter (NPBS), and then interacts with the sample placed in the solenoid. The gold backing of the multi-film stack then reflects the light through the sample again and back to the NPBS. The light that is reflected by the NPBS then passes through a Wollaston prism that breaks this light into the *s* and *p* polarized components. A lens is then used to focus these beams onto the detector components of a 2017 Nirvana auto-balanced optical receiver. The input polarization of the laser source is set to be at 45° after leaving the polarizer, so the irradiance on both sides of the detector are of equal magnitude.

A sinusoidal current at 100Hz is generated by a Stanford Research Systems SR830 lock-in amplifier. This current is amplified by a Bose PowerShare PS602 amplifier which then drives the solenoid holding the sample. The Nirvana is connected to the lock-in amplifier, such that the Stanford lock-in can pick up the AC fluctuation between the difference of the *s* and *p* polarized light beams resulting from the

change in magnetic field. As measurements are taken, the current used to drive the solenoid is increased, and the AC fluctuation signal at 100Hz and the DC signal on the differential detector were recorded by a computer program. A Lakeshore 421 gaussmeter was used to measure the magnetic field at the sample for these various driving currents to the solenoid.

For small angles, the Faraday rotation at a given magnetic field can then be expressed as:

$$\theta = \frac{180}{\pi}\frac{AC_{rms}}{8DC}\frac{1}{g}$$

where AC_{rms} is the difference in signal between the two detectors measured by the lock-in amplifier, DC is the magnitude of the signal of one of the detectors, and g is the gain of the Nirvana detector, which was set to x10 in these measurements.

A plot is then generated of Faraday rotation vs magnetic field, and linear regression is used to find the slope of the best fit line through the data points, denoted as θ/B. After thickness measurements are taken (L), the resulting Verdet constant of the nanoparticle composite is calculated using the following:

$$V = \frac{\theta}{B}\frac{1}{L}$$

5) Control Experiments

i. Composite Ink Preparation with Oleic Acid coated $CoFe_2O_4$ Nanoparticles

First, a stock solution of oleic acid coated $CoFe_2O_4$ NPs in DCB was prepared at a concentration of 50 mg/mL (inorganic content), followed by vortex mixing and sonication (< 5 minutes total to disperse). The contents of the vial were then placed on an aluminum heating mantle thermostated at 180 ºC for 1 hour, while vortex mixing every 15 minutes, to mimic the ligand exchange process. The vial was then probe sonicated for 1 hour to assure homogenization.

The appropriate quantity of oleic acid coated $CoFe_2O_4$ NP stock solution and 150 mg/mL high MW PS binder stock solution, as shown in Table 2, was added to a 4 dram vial, followed by being placed on an aluminum heating mantle thermostated at 105ºC for 90 minutes, while vortex mixing the vial every 15 minutes. The vial was then probe sonicated for 1 hour to assure homogenization.

Table 2. Conditions for Composite Dispersion Preparation Using Oleic Acid Coated $CoFe_2O_4$ NPs

Concentration of Inorganics in Oleic Acid/$CoFe_2O_4$ Stock (g/mL): 0.050					Concentration of High MW PS Binder Stock (g/mL): 0.150	
Relevant Data			**$CoFe_2O_4$ Stock Considerations**		**Binder Considerations**	**Solids Loadings**
Target $CoFe_2O_4$ Loading (wt%)	Target Composite Mass (g)	Target Inorganic Mass (g)	Volume of Oleic Acid CoFe2O4 Stock (mL)	Target Mass of High MW PS Binder (g)	Volume of High MW PS Binder Stock Added (mL)	Total Solids Concentration Prior to Precipitation (mg/mL)
2.50%	0.20	0.00500	0.10000	0.195	1.30	142.86
5.00%	0.20	0.01000	0.20000	0.190	1.27	136.36
7.50%	0.20	0.01500	0.30000	0.185	1.23	130.43
10.00%	0.20	0.02000	0.40000	0.180	1.20	125.00
15.00%	0.20	0.03000	0.60000	0.170	1.13	115.38

After the composite dispersions had cooled to room temperature, the dispersions were precipitated dropwise into 15mL of methanol each, placed atop an AlNiCo magnet. Subsequently, the vials were vortex mixed for 5 seconds at maximum setting before carefully decanting the methanol supernatant. The pellets were allowed to for 1 hour. The vials were dried overnight at 60 ºC in ambient pressure, followed by being dried at 80 ºC in vacuo for 3 hours.

After the composites had thoroughly dried, the pellets were dispersed in an appropriate quantity of chlorobenzene for a concentration of 100 mg/mL total solids to be achieved. The pellets were then dispersed by continuous vortex mixing at maximum setting for 5 minutes. The vials were then probe sonicated for 1 hour to assure homogenization.

At this point, identical steps were performed to obtain 5-bilayer films for 2.5, 5, 7.5, 10, and 15 wt% samples and carried through for Verdet constant measurements.

6) References

1. L. T. Lu, N. T. Dung, L. D. Tung, C. T. Thanh, O. K. Quy, N. V. Chuc, S. Maenosono and N. T. K. Thanh, *Nanoscale*, 2015, **7**, 19596-19610.
2. T. S. Kleine, L. Ruiz Diaz, K. M. Konopka, L. E. Anderson, N. G. Pavlopolous, N. P. Lyons, E. Tae Kim, Y. Kim, R. S. Glass, K. Char, R. A. Norwood and J. Pyun, *One Dimensional Photonic Crystals Using Ultrahigh Refractive Index Chalcogenide Hybrid Inorganic/Organic Polymers*, 2018.
3. A. Miles, Y. Gai, P. Gangopadhyay, X. Wang, R. A. Norwood and J. J. Watkins, *Optical Materials Express*, 2017, **7**, 2126-2140.