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## COMMUNICATION

## Influence of ionic liquids on the crystalline structure of nanocolloids

Shu Chen,<sup>ab</sup> Mark J. Muldoon,<sup>c</sup> Kris Anderson<sup>c</sup> and Pascal André<sup>\*a</sup>

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**This communication demonstrates that ionic liquids can alter the crystallinity and chemical ordering of nanocolloids synthesized in solution.**

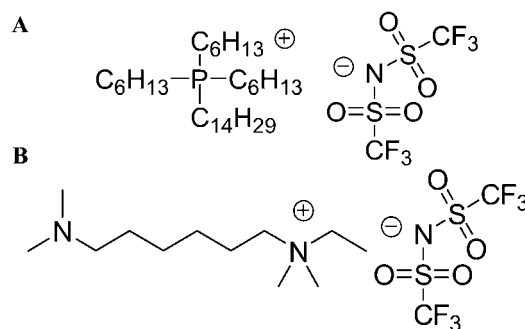
Ionic liquids (ILs) are attractive materials for a wide range of industrial applications, ranging from solvents for catalysis to electrolytes in batteries.<sup>1</sup> ILs are organic salts with low melting points, with many possessing melting points below room temperature. A well-known property of ILs is that they generally have a very low vapour pressure,<sup>2,3</sup> which for many applications offers advantages over volatile organic solvents. ILs can be prepared from a wide array of potential cations and anions and the choice of ions determines their thermophysical and physicochemical properties. The ability to design ILs with the desired properties by judicious choice of ions makes them attractive for creating new synthetic opportunities in materials science,<sup>4,6</sup> including nanomaterials.<sup>6–13</sup> Herein we demonstrate for the first time that ILs can be used to control the crystallinity of colloidal nanostructures synthesized in solution.

While likely to be valid for other systems, in this preliminary study we have focussed on the formation of chemically ordered face-centered-tetragonal (*ftc*) iron platinum (FePt) nanocolloids utilizing a direct synthesis and without any post-treatments. FePt belongs to a promising class of magnetic materials with its *ftc* crystalline phase having a high Curie temperature and magneto-crystalline anisotropy.<sup>14,15</sup> Additionally its superparamagnetic fluctuations could also be overcome at room-temperature for nanoparticles with a diameter as small as 2.5 nm.<sup>14</sup> The combination of these properties makes FePt nanocolloids a highly desirable constituent of future solution processable ultra-high density magnetic recording media of >1 T bit per inch,<sup>2</sup> as well as for various biomedical applications.<sup>15–20</sup> Over the past 10 years, several chemical pathways have been developed to synthesize FePt nanocolloids,<sup>21–28</sup> controlling both composition and shape.<sup>24,29–33</sup> Nevertheless, direct synthesis of the *ftc* structure remains one of the main challenges associated with this class of material. A post-synthetic annealing step above 550 °C can be used to convert the face-centred-cubic (*fcc*) into *ftc* crystalline structure, however this can

also lead to sintering. This side-effect can be partially overcome at the cost of further processing steps, for example, using SiO<sub>2</sub> or MgO shells, ball-milled salt powder or metal doping techniques.<sup>34–41</sup> While there have been efforts aimed at developing direct synthetic pathways for *ftc*-FePt, these have been met with limited success.<sup>42–45</sup> Among the few promising approaches, the use of polyol based solutions using ethylene glycol derivatives stands out. FePt nPs stabilised by poly(*N*-vinyl-2-pyrrolidone) were for instance synthesized with precursors including iron and platinum acetylacetonate. This allowed partial *ftc* phase formation at temperatures as low as 260 °C.<sup>43</sup> While the thermal decomposition approach normally requires higher temperatures, usually above 350 °C, there is evidence of direct formation of partial *ftc* crystalline phase when, for instance when alkyl amines are used as coordinating solvents.<sup>46</sup> Despite these achievements, it is noticeable that the exact impact of the stabilising molecules on the chemical ordering of the as-synthesized nanocolloids still remains unclear. To date the synthesis of FePt nPs has relied on a narrow range of precursors, ligands, and solvents, which have almost become standards.<sup>45</sup> Therefore we believe that to gain further understanding and to develop successful methods for direct formation of *ftc*-FePt nanomaterials, it is necessary to explore less conventional pathways.

This communication points towards an exciting new alternative based on the use of ILs and presents the direct formation of *ftc*-FePt nanocolloids *via* a simple solution method with no post-treatment necessary. It was found that ILs can be used to alter both crystallinity and chemical ordering of colloidal nanostructures, which is likely to be valid for other systems and should have a broader impact in materials science.

Fig. 1A presents the chemical structure of the first IL used in this work.



**Fig. 1** Chemical structures of ionic liquids: [P<sub>6,6,6,14</sub>][NTf<sub>2</sub>] (A) and [N<sub>1,1</sub>(CH<sub>2</sub>)<sub>6</sub>N<sub>1,2</sub>][NTf<sub>2</sub>] (B).<sup>47,48</sup>

<sup>a</sup>School of Physics and Astronomy (SUPA), University of St Andrews, St Andrews, KY16 9SS, UK. E-mail: Pascal.Andre@st-andrews.ac.uk; Tel: +44 (0)1334 463036

<sup>b</sup>School of Chemistry (EaStChem), University of St Andrews, St Andrews, KY16 9ST, UK

<sup>c</sup>School of Chemistry and Chemical Engineering and Queens University Ionic Liquids Laboratories (QUILL), Queen's University Belfast, David Keir Building, Belfast, BT9 5AG, UK

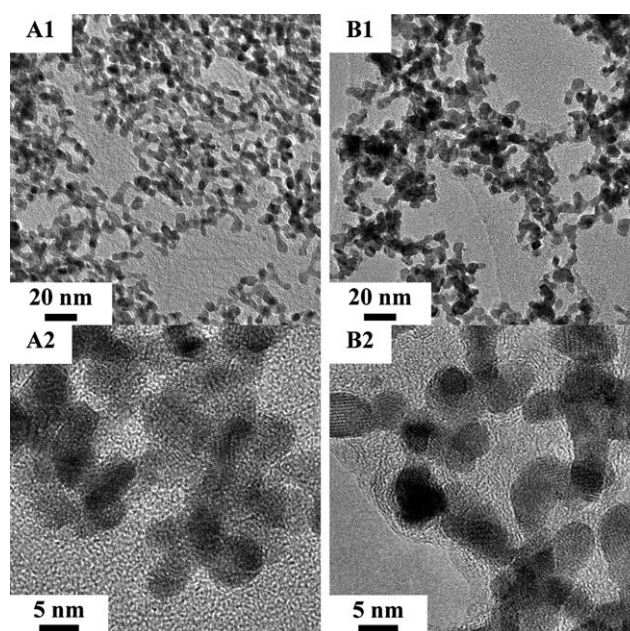
Trihexyl(tetradecyl)phosphonium bis(trifluoromethylsulfonyl) amide ( $[P_{6,6,6,14}][NTf_2]$ ) was prepared by mixing trihexyl(tetradecyl) phosphonium chloride ( $[P_{6,6,6,14}][Cl]$ ) supplied by Cytec with a 5 mol% excess of  $Li[NTf_2]$  dissolved in de-ionized water. After stirring for 3 hours the hydrophobic  $[P_{6,6,6,14}][NTf_2]$  was washed with portions of de-ionized water to remove  $LiCl$  and excess  $Li[NTf_2]$ . After the aqueous washings were found to be chloride free by testing with silver nitrate ( $AgNO_3$ ), the IL was washed a further two times. The resulting IL was then dried under vacuum at 70 °C. The water content of the dried IL was found to be less than 400 ppm. The structure was confirmed by  $^1H$  NMR and  $^{13}C$  NMR.

The second IL used in this study was 1-(6-dimethylamino)hexyl dimethylethylammonium bis(trifluoromethylsulfonyl)amide ( $[N_{1,1}(CH_2)_6N_{1,1,2}][NTf_2]$ ) whose structure is shown in Fig. 1B. This IL was prepared as previously published:<sup>48</sup>  $N,N,N',N'$ -tetramethyl-1,6-hexanediamine was dissolved in diethyl ether, then an equimolar amount of iodoethane was added drop wise and stirred for 48 h in the dark. The mono-quaternised product precipitated from the solution and was collected by filtration. It was then suspended in chloroform and filtered to remove small quantities of the di-quaternised product. After drying under vacuum the (dimethylamino)hexyl dimethylethylammonium iodide (a white solid) was dissolved in dichloromethane and the metathesis reaction was carried out in a similar manner as described above using an aqueous solution of  $Li[NTf_2]$ . After drying under high vacuum, the structure was confirmed by  $^1H$  NMR,  $^{13}C$  NMR and mass spectrometry.

The syntheses of the inorganic FePt nanocolloids were all completed in a glove-box and under a nitrogen atmosphere. In a typical reaction, the Collman's reagent  $Na_2Fe(CO)_4$  (0.2 mmol) was dissolved in 2 mL of  $[P_{6,6,6,14}][NTf_2]$ .  $Pt(acac)_2$  (0.2 mmol), oleylamine (1.6 mmol) and oleic acid (0.8 mmol) were dissolved separately in another 2 mL of  $[P_{6,6,6,14}][NTf_2]$ . After both these solutions had stirred at 100 °C for 1 h, they were mixed together and heated to 150 °C for 1 h to form complexes preventing Pt precursor self-reduction and hence favoring the formation of a stoichiometric Fe : Pt alloy.<sup>21,28,39</sup> To initiate the reaction, the temperature of the solution was further increased to 340 °C with a heating rate of 15 °C  $min^{-1}$ . After 3 h, the solution was cooled down to room temperature, thus stopping the reaction. The nanocolloids were then precipitated by addition of ethanol and centrifugation. The supernatant was discarded, the sediment was redispersed in hexane, mixed with ethanol and precipitated one more time by centrifugation. In the second approach, the oleylamine was simply replaced by the  $[N_{1,1}(CH_2)_6N_{1,1,2}][NTf_2]$  IL.

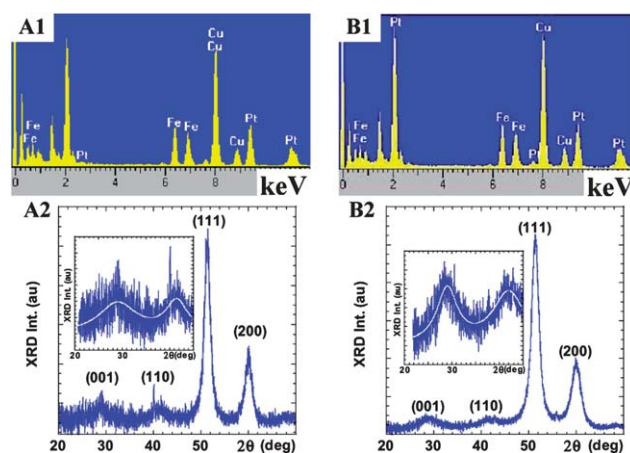
Transmission electron microscopy (TEM) characterization of the FePt nanocolloids synthesized using  $[P_{6,6,6,14}][NTf_2]$  as a solvent is presented in Fig. 2A1 and A2. At low magnification (Fig. 2A1), the TEM image shows homogeneous nanocolloids forming a 2-dimensional network which appears crystalline and interconnected at higher magnification (Fig. 2A2). When the synthesis was carried out with  $[N_{1,1}(CH_2)_6N_{1,1,2}][NTf_2]$ , nano-colloids with very similar morphology were formed, as illustrated by TEM in Fig. 2B.

Typical energy-dispersive X-ray (EDX) spectra of the FePt nanostructure are shown in Fig. 3A1 and B1 and indicate close to equimolar composition regardless of the IL-based synthesis.  $[P_{6,6,6,14}][NTf_2]$ -oleylamine synthesis led to an average chemical composition of the nanocolloids of Fe (0.56) : Pt (0.44). While the  $[P_{6,6,6,14}][NTf_2]$ - $[N_{1,1}(CH_2)_6N_{1,1,2}][NTf_2]$  synthesis displayed an Fe content  $x$  of  $\sim 0.57$  (Table 1). Noticeably the nanocolloid stoichiometry is within



**Fig. 2** TEM of FePt nanocolloids synthesized using  $[P_{6,6,6,14}][NTf_2]$  as a solvent and the following ligands: oleic acid and oleylamine (A), oleic acid and  $[N_{1,1}(CH_2)_6N_{1,1,2}][NTf_2]$  (B).

the required *fcc* to *fcc* phase transition composition range of  $0.4 < x < 0.6$ .<sup>28,39</sup> The wide-angle powder X-ray diffraction (XRD) data presented in Fig. 3A2 and B2 were collected with a  $Fe_{K\alpha 1}$  source,  $\lambda = 1.936$  Å. After the instrumental line broadening was subtracted from the spectra, the crystalline grain size,  $D_{XRD}$ , was calculated with the Scherrer's formula.<sup>49</sup> Based on the (111) XRD peak, the average crystalline size of the nanocolloids synthesised with  $[P_{6,6,6,14}][NTf_2]$  was calculated and found to be  $\sim 5.8$  nm (Fig. 2A2). The altered synthetic pathway using both  $[P_{6,6,6,14}][NTf_2]$  and  $[N_{1,1}(CH_2)_6N_{1,1,2}][NTf_2]$  led to a slightly larger crystal size of  $\sim 6.7$  nm (Fig. 2B2). This could be attributed to the amine functionalized cation inducing a slower nucleation rate of the nanocolloids.



**Fig. 3** FePt nanocolloids synthesized using  $[P_{6,6,6,14}][NTf_2]$ -oleic acid-oleylamine (A) and  $[P_{6,6,6,14}][NTf_2]$ -oleic acid- $[N_{1,1}(CH_2)_6N_{1,1,2}][NTf_2]$  (B): EDX spectra (1), background extracted and normalized XRD patterns (2).

**Table 1** Characterisation of FePt nanocolloids: peak position ( $2\theta$ ),  $d$ -spacing ( $d$ ), crystalline grain size ( $D_{\text{XRD}}$ ), iron content ( $x$ ) in  $\text{Fe}_x\text{Pt}_{1-x}$ , crystalline order parameter ( $S$ ), blocking temperature ( $T_b$ ), coercivity ( $H_c$ ), magnetization at saturation ( $M_s$ ), remanent magnetization ( $M_r$ ) and their ratio ( $M_s/M_r$ )

Sample	$[\text{P}_{6,6,6,14}][\text{NTf}_2]$	$[\text{N}_{1,1}(\text{CH}_2)_6\text{N}_{1,1,2}][\text{NTf}_2]$
$2\theta/\text{deg}$ [(111)/(110)]	51.6/41.7	51.4/41.4
$d/\text{\AA}$ [(111)/(110)]	2.23/2.72	2.23/2.74
$D_{\text{XRD}}/\text{nm}$ [(111)/(110)]	$5.8/1.6 \pm 0.1$	$6.7/2.0 \pm 0.1$
$x$	0.56	0.57
$S$	0.54	0.42
$T_b/\text{K}$	195	195
$H_c/\text{kOe}$	1.5	1.4
$M_s/\text{emu g}^{-1}$	30.0	25.1
$M_r/\text{emu g}^{-1}$	12.7	14.2
$M_r/M_s$	0.42	0.57

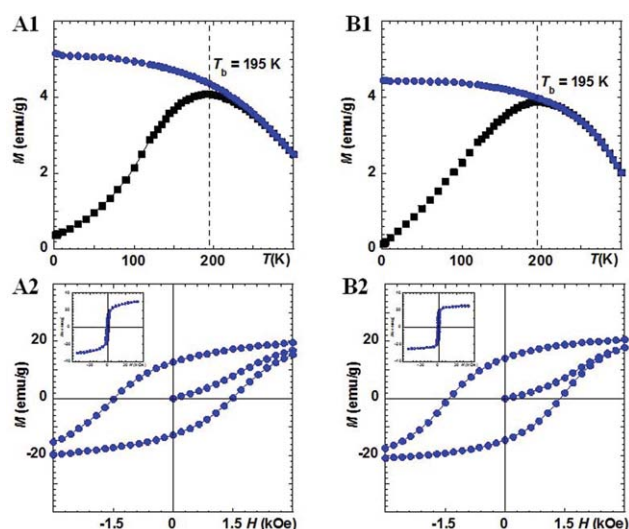
The key-element of the XRD nanocolloids characterization is however the presence of the *fcc*-FePt crystalline phase as revealed by the (001) and (110) XRD peaks (Fig. 3A2 and B2) in the product of both synthetic pathways. The ordering parameter ( $S$ ) is widely used to quantify the chemical ordering, *i.e.* the fraction of *fcc*-crystalline phase ( $S_{\text{fcc}} = 0.0$  to  $S_{\text{fcc}} = 1.0$ ) and was quantified based on standard calculations relying on the intensity ratio of the (110) and (111) XRD peaks.<sup>50</sup>  $S$  was found to be  $\sim 0.54$  and  $\sim 0.42$ , depending upon whether the FePt nanocolloids were formed with the 1<sup>st</sup> or the 2<sup>nd</sup> synthetic pathway, respectively (Table 1); while the presence of *fcc*-crystalline phase in the product of the two syntheses highlights the consistency of the results.

The nanocolloids were then dispersed in a polyvinylpyrrolidone matrix (PVP) with a polymer to nanocolloid ratio equal to 20 to reduce the interactions between the nPs. The resulting sample was loaded into a low background gelatin capsule and the nanocolloid's magnetic properties characterised with a Superconducting Quantum Interference Device (SQUID). Zero-field cooled and field cooled (ZFC/FC) measurements with a magnetic field of 100 Oe were completed between 2 K and 275 K (Fig. 4, row 1). Hysteresis measurements were completed at temperatures of 2 K (Fig. 4A2 and B2). The magnetization of the gelatine capsules and the PVP matrix was subsequently subtracted. The presence and hence the formation of the *fcc* crystalline phase were then further confirmed by the high blocking temperature  $T_b \sim 195$  K (Fig. 4A1 and B1) and a high coercivity of  $\sim 1.4$  to  $1.5$  kOe (Fig. 4A2 and B2) as characterized with a SQUID magnetometer. The nanocolloids obtained with both IL based synthetic pathways displayed similar magnetic properties. Still,  $T_b$  was found to be lower than room temperature which could be attributed to the following contributions:

(i) Surface effects induced by the IL and the ligands lead to the formation of a non-magnetic shell by electron transfer.<sup>51–54</sup>

(ii)  $S < 1$  indicates that the nanocolloids contain both *fcc* and *fcc* crystalline phases. Consequently, the crystalline size of the *fcc* phase in the nanocolloids could be too small to provide large enough magnetoanisotropy to compensate for the thermal agitation at ambient conditions. The crystalline grain size of the *fcc* phase obtained with  $[\text{P}_{6,6,6,14}][\text{NTf}_2]$  as a solvent is about 1.6 nm. This is deduced from the full width at half maximum of both (001) and (110) diffraction peaks (Table 1).

(iii) Finally, the apparent poly-crystalline and multi-domain structure of the nanocolloids (Fig. 2) could favor inter-granular



**Fig. 4** FePt nanocolloids synthesized using  $[\text{P}_{66614}][\text{NTf}_2]$  as a solvent and both oleic acid and oleylamine as ligands (A) and  $[\text{P}_{66614}][\text{NTf}_2]$  as a solvent and both oleic acid and  $[\text{N}_{1,1}(\text{CH}_2)_6\text{N}_{1,1,2}][\text{NTf}_2]$  as ligands (B): FC–ZFC magnetization curves completed under a 100 Oe magnetic field (1) and hysteresis loops at 2 K (2).

exchange coupling, which is known to decrease the magneto-crystalline anisotropy and to reduce the coercivity.<sup>55</sup>

The present results demonstrate then that ILs can have a significant impact on the crystalline phase of as-synthesized nanocolloids, as evidenced by the direct *fcc* formation. In comparison, CoPt nanorods synthesized at  $\sim 350$  °C were reported in the literature, combining the IL 1-butyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl)amide ( $[\text{BMIM}][\text{NTf}_2]$ ) with cetyltrimethylammonium bromide.<sup>7</sup> No *fcc*-CoPt was obtained despite running the syntheses at a higher temperature. This might be explained by the use of ionic surfactants and their interactions with both precursors and ILs. FePt nP preparations have also been reported using 1-ethyl-3-methyl-imidazolium tetrafluoroborate ( $[\text{EMI}][\text{BF}_4]$ ) and 1-butyl-1-methyl-pyrrolidinium trifluoromethanesulfonate ( $[\text{BMP}][\text{TF}_3\text{S}^-]$ ).<sup>8</sup> The synthetic conditions utilised a lower temperature, an Fe(0) iron precursor ( $\text{Fe}(\text{CO})_5$ ) and a 1,2-hexadecanediol *i.e.* a polyol type of solvent. The significant differences in these reaction parameters may explain why their synthetic method did not produce any *fcc* phase.

In summary, while ionic liquids are well known in the context of “green” chemistry and are expected to offer new synthetic opportunities in materials science, to the best of our knowledge, we have herein demonstrated for the first time that ILs can be used successfully to alter the crystallinity and the chemical ordering of inorganic nanomaterials. Identifying more appropriate ligands should also allow the synthesis of well dispersed individual nanocolloids, and the ILs molecular structure and properties could be advantageously tuned to deliver such an outcome. While premature at that stage, the control of the mechanisms involved in the *fcc*-phase formation will require a large combination of experimental and computational work to fully understand the interplay between the Fe/Pt precursors, the stabilizers and the components of the ILs.

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