

Cite this: *Soft Matter*, 2011, **7**, 3565

www.rsc.org/softmatter

PAPER

Promoted formation of coordination polyelectrolytes by layer-by-layer assembly†

Yuru Lan,^a Limin Xu,^a Yun Yan,^{*ab} Jianbin Huang,^{*a} Arie de Keizer,^b Nicolaas A. M. Besseling^c and Martien A. Cohen Stuart^b

Received 14th November 2010, Accepted 10th January 2011

DOI: 10.1039/c0sm01316a

Metal mediated coordination polymers offer the opportunity to fabricate devices and materials that are equally important for fundamental research and new technologies. Most coordination polymers were synthesized at the desired stoichiometry. We demonstrate that coordination polyelectrolytes can form in layer-by-layer (LBL) assembled films regardless of the initial metal to bisligand ratio in solution. Upon dipping a substrate alternately into a covalent polyelectrolyte solution and then into the mixed solution of Fe³⁺ and bisligands, the Fe³⁺ to ligand ratio in the LBL film tends to be 1 : 1 and forms polymeric structures even if the ratios in the bulk solution strongly deviate from unity. Our results suggest that layer-by-layer assembly promotes the formation of coordination polyelectrolytes.

Introduction

In recent years, self-assembly has become an active area of investigation in chemistry and materials science since it allows for the preparation of elegant molecular devices from relatively simple starting materials.^{1–7} The fabrication of metal-mediated coordination polymers is a fine example of this.^{1,2,5} In this strategy, versatile polymeric structures can be prepared with relative ease using coordination-driven self-assembly between electron-poor transition metal ions and various multitopic ligands which are electron-rich donors.^{1,2,5} Owing to the presence of metal ions in these coordination systems, the resultant supramolecular structures often behave like polyelectrolytes, and hence were named as metallopolyelectrolytes (MEPE) by Kurth *et al.*^{2,5} These authors have demonstrated that MEPEs, like conventional covalent polyelectrolytes, can be fabricated into thin films *via* the layer-by-layer (LBL) method,^{2,5} which opens new avenues to functional materials with potential applications in electronics, photonics, and catalysis.

Most of the reported metal mediated coordination polyelectrolytes were synthesized at the desired stoichiometry under reflux, including the MEPEs used by Kurth *et al.*^{1,2,5,8} The degree of polymerisation of the coordination polyelectrolytes so obtained is

extremely sensitive to the coordination stoichiometry because excess multitopic ligands or metal ions form additional chain ends or chain stoppers. Deviations from the stoichiometry of greater than 20% lead to only small clusters. Therefore, the mixing ratio between the metal ions and the ligands must always be accurately controlled when preparing coordination polymers.^{1,2,8}

However, here we show an example of formation of polymeric structures at metal to ligand ratios unexpectedly far away from the coordination stoichiometry, in the LBL assembled thin films. We found that coordination polymers can always be formed in the LBL films even when the metal to ligand ratios in the aqueous solutions range from 1 : 16 to 16 : 1.

Experimental

Materials

Polyethyleneimine (PEI) (Aldrich, $M_w = 25\,000$) and FeCl₃·6H₂O (Beijing Chemicals Company, AR) were used as received. L₂EO₄ was synthesized according to literature procedures.⁹ The substrates for the UV/Vis spectroscopic investigations were quartz glass. For the XPS measurements, polished (100) silicon wafers were employed. FT-IR measurements were made on a CaF₂ substrate.

Methods

LBL film fabrication: the LBL films were prepared on substrates of quartz glass, silicon wafers or CaF₂ plates. The quartz substrates were used for UV-vis, the silicon wafers for XPS measurements and the CaF₂ substrates for FT-IR measurements. The quartz glass and silicon wafers were cleaned in a mixture of H₂SO₄ : H₂O₂ (7 : 3) at 80 °C for 1 h, and washed with Milli-Q-water. The substrates were further purified by the RCA cleaning

^aBeijing National Laboratory for Molecular Science (State Key Laboratory for Structural Chemistry of Unstable and Stable Species), College of Chemistry and Molecular Engineering, Peking University, Beijing, 100871, China. E-mail: Yunyan@pku.edu.cn; jbhuan@pku.edu.cn

^bLaboratory of Physical Chemistry and Colloid Science, Wageningen University, Dreijenplein 6, 6703 HB Wageningen, The Netherlands

^cDepartment of Chemical Engineering, section Nanostructured Materials, Technical University of Delft, Julianalaan, 126 Delft, The Netherlands

† Electronic supplementary information (ESI) available: Additional spectra and XPS data. See DOI: 10.1039/c0sm01316a

procedure in a $\text{H}_2\text{O} : \text{H}_2\text{O}_2 : \text{NH}_3(5 : 1 : 1)$ mixture, washed with Milli-Q-water and after drying with air were immersed in a 10 mM polyethyleneimine (PEI) aqueous solution for 1 h. The CaF_2 wafers were rinsed with chloroform, methanol, and water and then immersed in 10 mM PEI solution for 2 h. After being washed with Milli-Q-water three times (1 min each) and dried with air, the surfaces with a PEI monolayer were obtained. The LBL films were fabricated by alternating immersion of the modified substrates in PEI (10 mM) for 1 min and a mixed solution of Fe^{3+} (1 mM, 2 mM, 4 mM) and L_2EO_4 (2 mM) for 15 min, followed by rinsing with Milli-Q-water three times (1 min each) and dried with air.

Ultraviolet-visible (UV-vis) spectra: UV spectra for all the samples were collected on a Pgeneral TU-1810 UV-vis spectrophotometer.

Fourier transform infrared (FT-IR) spectra: FT-IR spectra were recorded on a Bio-Rad FTS-65A/896 instrument at a resolution of 8 cm^{-1} .

X-Ray photoelectron spectroscopy (XPS): XPS was carried out on an AXIS-Ultra instrument from Kratos Analytical using monochromatic $\text{Al K}\alpha$ radiation (225 W, 15 mA, 15 kV) and low-energy electron flooding for charge compensation. To compensate for surface charge effects, binding energies were calibrated using the C 1s hydrocarbon peak at 284.80 eV. The data were converted into VAMAS file format and imported into the hCasaXPS software package for manipulation and curve-fitting.

Results and discussion

The coordination polyelectrolytes used in our study were prepared simply by mixing an aqueous solution of Fe^{3+} and a bisligand compound based on pyridine-2,6-dicarboxylic acid groups (Fig. 1a).⁹ Coordination of Fe^{3+} and L_2EO_4 occurs immediately as detected by changes in the UV spectra. Fig. 2 demonstrates that with the Fe^{3+} to L_2EO_4 ratio approaching 1,

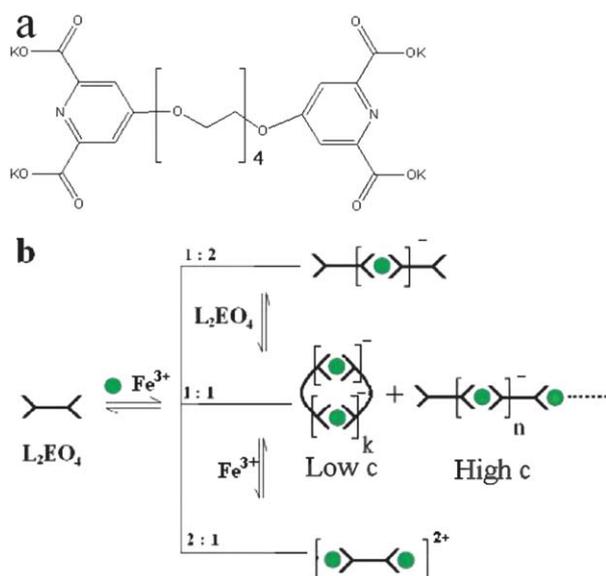


Fig. 1 a: Structure of L_2EO_4 . b: Schematic illustration of the dominant Fe^{3+} - L_2EO_4 coordination species with different $\text{Fe}^{3+} : \text{L}_2\text{EO}_4$ molar ratios.

the wavelength of the maximum absorption remains constant, suggesting the presence of only one coordination species, namely Fe^{3+} fully coordinated with L_2EO_4 . As the ratio goes beyond 1, partially coordinated Fe^{3+} appears, which leads to a blue shift of the absorption maximum from 371 to 341 nm. As expected, the coexistence of two coordinating Fe^{3+} species also introduces an isosbestic point at 311 nm. The variation of the coordination species with the Fe^{3+} -to- L_2EO_4 ratio is schematically illustrated in Fig. 1b.

It is clear that in a homogeneous system significant polymerisation is only possible at Fe^{3+} to ligand ratio of 1 : 1 which allows chain extension. However, at very low concentrations long chains do not exist in the 1 : 1 system, since this family of coordination polymers features weak, reversible bonds, which renders the chain length highly concentration dependent.¹⁰ It has been shown both in experiments and theoretical calculations that small coordination rings dominate in dilute systems whereas chains dominate at higher concentrations.¹⁰ Excess of either component results in additional chain ends, reducing the degree of polymerisation, as illustrated in Fig. 1b. Assuming that each metal ion or bisligand molecule yields an additional chain end, it is predicted that the average degree of polymerisation is limited at $1/|1 - y|$, where y is the molar ratio of Fe^{3+} and bisligand.

The degree of polymerisation at different Fe^{3+} to L_2EO_4 ratios can be reflected in the polyion complex (PIC) micellization experiments. It is well-known that the formation of PIC micelles is dependent on the relative chain length of a pair oppositely charged polyelectrolyte blocks.¹¹ Well-defined micelles can only be formed when the number of charges in each block is very close.¹¹ As demonstrated in Fig. 3, a strong scattering intensity was observed in the mixed system of a very dilute 1 : 1 Fe^{3+} - L_2EO_4 solution and that of an oppositely charged-*b*-neutral block copolymer P2MVP₄₁-PEO₂₀₅ (poly-*N*-methyl-2-pyridinium iodide-*b*-poly ethylene oxide), indicating formation of well-defined micelles.¹² In contrast, the scattering intensity is greatly lowered when 1 : 2 or 2 : 1 Fe^{3+} - L_2EO_4 complexes were used under the same conditions. (Fig. 3) This result strongly indicated that polymeric structures are formed in the 1 : 1 mixed Fe^{3+} - L_2EO_4 system which enables charge matching with the

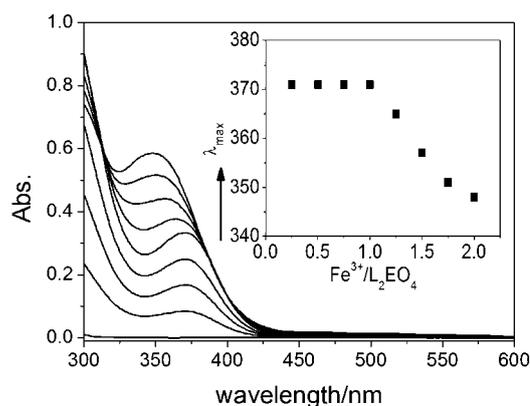


Fig. 2 UV-vis spectra evolution with variation of the ratio of Fe^{3+} / L_2EO_4 . The concentration of L_2EO_4 is fixed at 1 mM, whereas that of Fe^{3+} varies from 0 to 2 mM in steps of 0.25 mM (from bottom to top). (inset: variation of the wavelength where maximum absorption occurs for different ratios of $\text{Fe}^{3+} : \text{L}_2\text{EO}_4$).

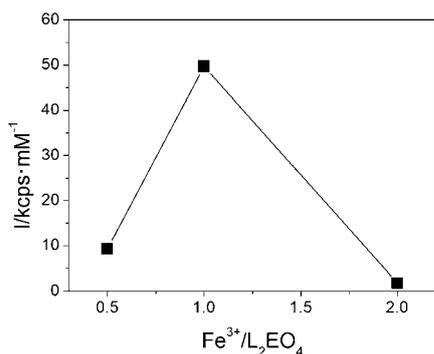


Fig. 3 Scattered intensity for mixed systems of 0.4 mM P2MVP₄₁-PEO₂₀₅ and coordination complexes of Fe³⁺-L₂EO₄ with different Fe³⁺ to L₂EO₄ ratios.

P2MVP₄₁ block; whereas only small coordination clusters are formed in the 1 : 2 and 2 : 1 systems.

It should be born in mind that under our experimental condition, no polymeric structures, except for small rings, exist even in the 1 : 1 mixed Fe³⁺-L₂EO₄ aqueous system due to the low concentrations used. As pointed out in the previous text, polymeric structures can exist only at high enough concentrations. However, in the presence of an oppositely charged polyelectrolyte block, the coordination rings in the 1 : 1 system may transform into long chains owing to the enhancement of their local concentrations.^{13,14} In turn, this allows the formation of a complex coacervate that constitutes the core of the micelle. In contrast, the 1 : 2 and 2 : 1 mixed systems do not allow chain growth under the same conditions, since the excess components, either L₂EO₄ or Fe³⁺, behave as chain stoppers. Therefore, we expected to fabricate LBL films using the dilute 1 : 1 coordination complexes to introduce Fe³⁺ ions into thin films. We supposed that the coordination rings would also automatically transform into polymeric structures on the surface of the oppositely charged polyelectrolytes as a result of the enhancement of their local concentration.

Since the metallopolyelectrolytes in the 1 : 1 Fe³⁺-L₂EO₄ system are negatively charged, as illustrated in Fig. 1b, the polycation polyethyleneimine (PEI) is used as the oppositely charged polyelectrolyte in LBL experiments. Indeed, upon dipping a quartz plate (or Si or CaF₂) into the PEI solution and into the 1 : 1 Fe³⁺-L₂EO₄ mixture alternately, a multilayer was found to build up as revealed by the linear increase of UV absorbance with the number of dipping cycles (Fig. 4). To verify whether the success of this LBL assembly was facilitated by chain extension of the 1 : 1 Fe³⁺-L₂EO₄ coordination complexes on the surface of PEI, we performed two control experiments, namely replacing the 1 : 1 coordination complexes with (a) 2 : 1 and (b) 1 : 2 complexes, respectively, as we did in the micellar system. We expected no LBL assembly to occur since the presence of many chain ends formed by the excess components would preclude polymerization.

Surprisingly, formation of LBL films occurred successfully in both off-stoichiometric systems (See ESI Fig. S1 and S2a-b†). As demonstrated in Fig. 5, a linear increase of the UV absorbance is observed for both the 1 : 2 and 2 : 1 mixed systems. In contrast, the increase of the UV absorbance is almost negligible when

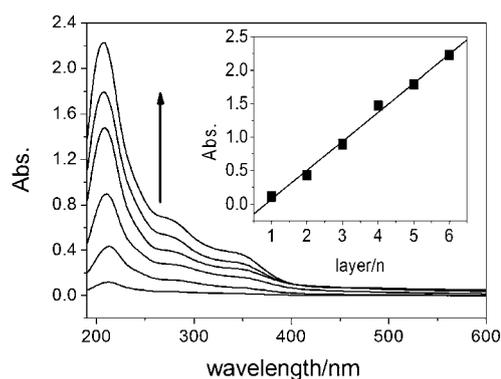


Fig. 4 UV-vis spectra of a (PEI/Fe³⁺-L₂EO₄)_n multilayers with $n = 1-6$ on a PEI modified quartz substrate (inset: absorption of individual band maxima at 206 nm as a function of the number of adsorbed layers).

negatively charged L₂EO₄ alone is used instead of any coordinating system. This means that L₂EO₄ alone, as a small molecule, cannot be used to fabricate LBL thin films even though it carries charges opposite to PEI. Only in the presence of Fe³⁺ ions, is formation of LBL films remarkably successful.

It is worth noting that the UV absorbance for the 2 : 1 system is virtually the same as that for the 1 : 1 system. Note that the 2 : 1 mixture of Fe³⁺ and L₂EO₄ on their own would give overall positively charged coordination complexes, as illustrated in Fig. 1b, which cannot participate in electrostatic attraction-driven LBL assembly with like-charged PEI. Hence, the success of the LBL assembly in the 2 : 1 ratio must imply that negatively charged coordination polymers were formed in the LBL films even when the assembling was started from the 2 : 1 system. This indicates that although the mixing ratios between Fe³⁺ and L₂EO₄ greatly deviate from 1 : 1, polymeric structures of overall negative charge were very likely formed in the LBL films. In order to check this hypothesis, we determined the Fe³⁺ to L₂EO₄ ratio in the films by XPS experiments on the films made from 2 : 1, 1 : 1, and 1 : 2 coordination systems.

As listed in Table 1, the Fe³⁺/L₂EO₄ values for Fe³⁺/L₂EO₄ = 0.5, 1 and 2 are 1.15, 1.22, and 1.39, respectively. Obviously, the Fe³⁺/L₂EO₄ values in the 0.5 and 2 system are very close to that for the Fe³⁺/L₂EO₄ = 1 system. It seems that the thin films of

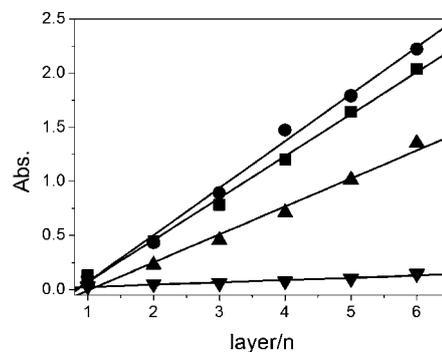


Fig. 5 Linear increase of UV-vis absorption of individual band maxima at 206 nm as a function of the number of adsorbed layers, for (PEI/Fe³⁺-L₂EO₄)_n multilayers at different Fe³⁺/L₂EO₄ molar ratios (concentration of L₂EO₄ is 2 mM, Fe³⁺/L₂EO₄ molar ratio: ▲ 0.5, ● 1, ■ 2, ▼ 0).

Table 1 $\text{Fe}^{3+}/\text{L}_2\text{EO}_4$ molar ratios determined by XPS in multilayers prepared at different $\text{Fe}^{3+}/\text{L}_2\text{EO}_4$ in bulk solutions

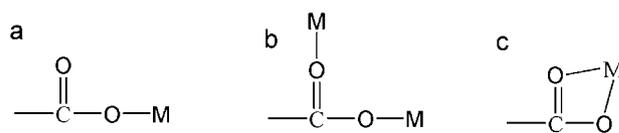
$\text{Fe}^{3+}/\text{L}_2\text{EO}_4(\text{solution})$	$\text{Fe}^{3+}/\text{L}_2\text{EO}_4$ (multilayer)
2	1.39
1	1.22
0.5	1.15

LBL have a leveling effect on the ratios between Fe^{3+} and L_2EO_4 , which implies that formation of coordination polyelectrolytes is significantly promoted.

It is noted that in all cases, metal ions are slightly in excess in the XPS results. This is probably caused by the binding of extra iron with those remaining chelating groups, such as the N of PEI, and the O of the COO^- groups. It has been reported that the N in PEI binds with many metal ions. However, the maximum capacity of PEI for Fe^{3+} is less than 1 mM Fe^{3+}/g polymer, namely less than 0.01 mM/1 mM polymer.^{15,16} In addition, the N 1s energy of PEI in the XPS results didn't change (See ESI Fig. S3†), suggesting that no specific interaction occurs between PEI and Fe^{3+} .¹⁷ Besides, we found that if the iron was replaced by europium ions, excess bisligands will be present in the films (data not shown). This means that the metal to bisligand ratio in the LBL films is dependent on the nature of the coordinating system, suggesting that binding of the metal with PEI is not the main reason for the excess of iron in the LBL films.

Next, we are to verify the possibility of binding of Fe^{3+} with the O of the COO^- groups in the ligand. This can be reflected in the FT-IR spectra. Therefore, FT-IR spectroscopy was used to diagnose the coordination mode of the carboxylate ligands. It is well-known in literature that the wave number separation between the asymmetric and symmetric stretching vibration of COO^- groups corresponds to different coordinating states. $\Delta\nu_{\text{as}} \gg 200 \text{ cm}^{-1}$ suggesting unidentate binding, as illustrated in Scheme 1a; $\Delta\nu_{\text{as}} \approx 200 \text{ cm}^{-1}$ for bridging binding (Scheme 1b); and $\Delta\nu_{\text{as}} \ll 200 \text{ cm}^{-1}$ bidentate binding (Scheme 1c).^{18–20}

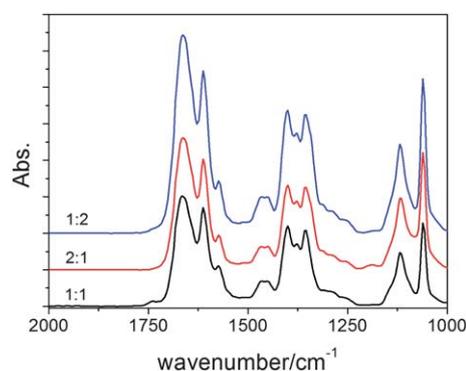
First of all, we found similar spectroscopic features for multilayers made at different Fe^{3+} to ligand molar ratios (Fig. 6), which confirms that Fe^{3+} and L_2EO_4 in the multilayers adapt almost the same coordination mode regardless their original mixing ratios. Secondly, it is noticeable that the strong characteristic bands of carboxyl groups appear at 1666, 1613 cm^{-1} for the asymmetric and 1402, 1356 cm^{-1} for the symmetric vibrations. This allows separations of 310 (1666 – 1356) and 211 (1613 – 1402) cm^{-1} , suggesting the coexistence of unidentate and bridging modes of the coordination complexes. The occurrence of unidentate coordination is as expected since it is accompanied by the coordination polymer formation as illustrated in Scheme 2a. However, the presence of the bridging mode of coordination indicates that some Fe^{3+} is coordinated by another oxygen of the COO^- groups, which probably exists as the mode illustrated in Scheme 2b. Of course, there might be other possibilities of binding of the extra Fe^{3+} in the coordination networks. We will not focus too much on this point. The coexistence of unidentate and bridging coordination modes clearly suggests that some extra Fe^{3+} is involved in the coordinated structures, which

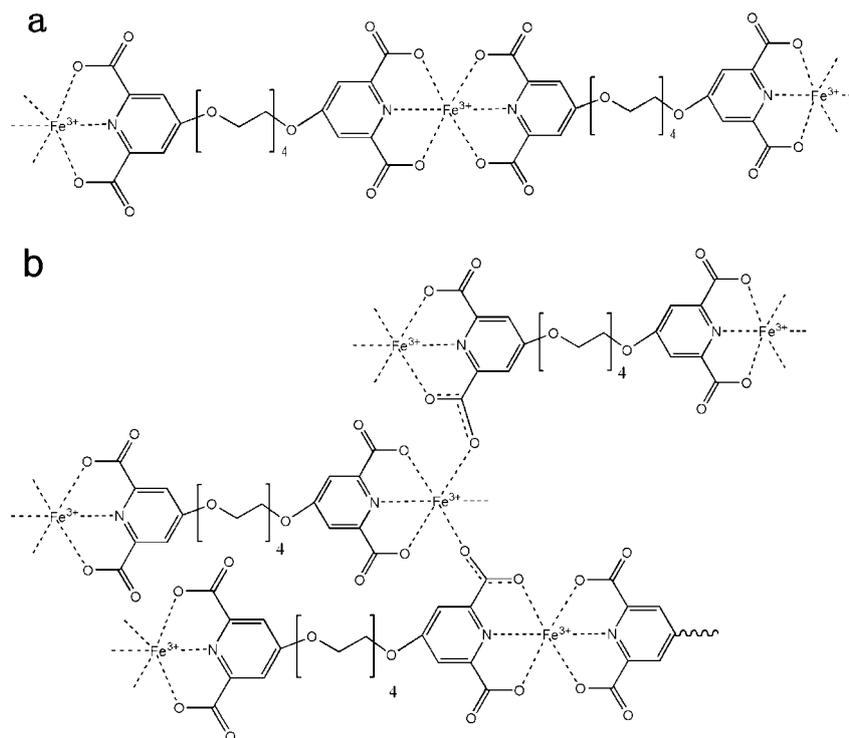
**Scheme 1** Different binding modes between carbonate group and metal ions. a) unidentate; b) bridging; c) bidentate.

explains why an excess of Fe^{3+} was found for all the three films in the XPS results.

Conclusion

In summary, layer-by-layer enhanced chain extension of a coordination polyelectrolyte was found to occur at metal/ligand ratios which would be disproportionate in homogeneous systems. Hence, it seems that the phase-separation drives the necessary composition shift, which is similar to that in the hydrogen bonding supramolecular system investigated by Zweistra *et al.*²¹ They showed that some reversible supramolecular polymers phase separate into a dense and a dilute phase under suitable conditions. The concentrated phase tends to expel species that act like chain stoppers. One may wonder why in micellar systems, which also involve (micro-) phase separation, this effect had not been observed; most likely, the reason is that during LBL fabrication cycles the film ingredients are always supplied in very large excess, allowing composition shifts to occur more easily. Actually, as the mixing ratios shift further from 1 : 1, say as Fe^{3+} to L_2EO_4 becomes 1 : 16 and 16 : 1, respectively, the corresponding ratios in the LBL films are found to be 1.31 and 1.87. (See ESI Fig. S2 c–f†). This means that polymeric structures can always be formed in the LBL films even when the initial metal to bisligand ratio deviates considerably from unity. It is likely that some coordination clusters were enriched on the oppositely charged PEI surface which enables rearrangement of the coordination between Fe^{3+} and L_2EO_4 owing to the reversible nature of the coordination complexes. This allows forming 'poly anions' which may interact effectively with the PEI polycations, releasing small counter-ions and

**Fig. 6** FT-IR spectra of the films prepared at different $\text{Fe}^{3+}/\text{L}_2\text{EO}_4$ ratios in solution. The ratios between Fe^{3+} and ligand are 1 : 1 (black), 2 : 1 (red), and 1 : 2 (blue). The number of the $(\text{PEI}/\text{Fe}^{3+}\text{-L}_2\text{EO}_4)_n$ layers are 6, 6, and 10, respectively.



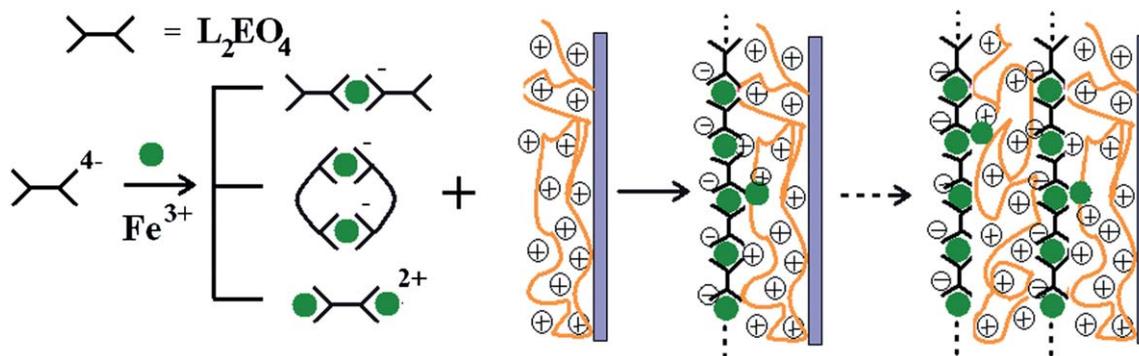
Scheme 2 Schematic illustration of the structure of $\text{Fe}^{3+}\text{-L}_2\text{EO}_4$ coordination polymer with different coordination mode, a: the unidentate coordination, b: the bridging coordination.

thereby increasing the entropy. This process is briefly illustrated in Scheme 3. Our results indicate that metallic LBL assemblies can be easily prepared without strict control of the metal to ligand ratio and/or careful preparation of the coordination polymers in advance. This greatly simplifies procedures to obtain coordination polyelectrolytes (namely without having to maintain strict mixing ratio control) and paves the way for facile and extensive fabrication of metal ion-containing LBLs with potential applications in electronics, photonics, and catalysis. As an example, the $(\text{PEI}/\text{Fe}^{3+}\text{-L}_2\text{EO}_4)_n$ films can be used as redox active materials for uptake and controlled release, which will be presented in our later work. Furthermore, by replacing Fe^{3+} with other metal ions, such as Eu^{3+} or other rare earth metals, fluorescent supermolecular thin films with desired colors that don't

depend on nanoparticles or quantum dots can be easily fabricated. Hence, this approach is relevant for the construction and exploitation of metallopolyelectrolytes functional films. This will also be reported in our forthcoming work.

Acknowledgements

This research was supported by the National Natural Science Foundation of China (20903005, 20873001, 20633010 and 50821061), the Scientific Research Foundation for the Returned Overseas Chinese Scholars, State Education Ministry (SRF for ROCS, SEM) and New Century Training Programme Foundation for the Talents by the State Education Commission.



Scheme 3 Transition of coordination complexes made at different metal to ligand ratios into polymers in the LBL assembly. For clearance, the negative charges on L_2EO_4 , the coordination complexes and the coordination polymers are not shown. The excess iron ions in the metallopolyelectrolytes layer illustrate the bridge binding mode.

References

- 1 M. Chipper, M. A. R. Meier, J. M. Kranenburg and U. S. Schubert, *Macromol. Chem. Phys.*, 2007, **208**, 679.
- 2 D. G. Kurth, J. P. Lopez and W. F. Dong, *Chem. Commun.*, 2005, 2119.
- 3 G. A. Ozin and A. C. Arsenault, *Nanochemistry*, RSC Publishing, Cambridge, 2005.
- 4 R. Savić, L. B. Luo, A. Eisenberg and D. Maysinger, *Science*, 2003, **300**, 615.
- 5 M. Schüttele, D. G. Kurth, M. R. Linford, H. Colfen and H. Mohwald, *Angew. Chem., Int. Ed.*, 1998, **37**, 2891.
- 6 J. Simon and P. Bassoul, *Design of Molecular Materials: Supramolecular Engineering*, Wiley, New York, 2000.
- 7 B. H. Sohn, J. M. Choi, S. I. Yoo, S. H. Yun, W. C. Zin, J. C. Jung, M. Kanehara, T. Hirata and T. Teranishi, *J. Am. Chem. Soc.*, 2003, **125**, 6368.
- 8 G. Schwarz, Y. Bodenthin, T. Geue, J. Koetz and D. G. Kurth, *Macromolecules*, 2010, **43**, 494.
- 9 T. Vermonden, J. van der Gucht, P. de Waard, A. T. M. Marcelis, N. A. M. Besseling, E. J. R. Sudholter, G. J. Fleer and M. A. C. Stuart, *Macromolecules*, 2003, **36**, 7035.
- 10 T. Vermonden, M. J. van Steenberghe, N. A. M. Besseling, A. T. M. Marcelis, W. E. Hennink, E. J. R. Sudholter and M. A. C. Stuart, *J. Am. Chem. Soc.*, 2004, **126**, 15802.
- 11 A. Harada and K. Kataoka, *Science*, 1999, **283**, 65.
- 12 Y. Yan, Y. R. Lan, A. de Keizer, M. Drechsler, H. Van As, M. A. C. Stuart and N. A. M. Besseling, *Soft Matter*, 2010, **6**, 3244.
- 13 Y. Yan, A. A. Martens, N. A. M. Besseling, F. A. de Wolf, A. de Keizer, M. Drechsler and M. A. C. Stuart, *Angew. Chem., Int. Ed.*, 2008, **47**, 4192.
- 14 Y. Yan, N. A. M. Besseling, A. de Keizer, A. T. M. Marcelis, M. Drechsler and M. A. C. Stuart, *Angew. Chem., Int. Ed.*, 2007, **46**, 1807.
- 15 B. L. Rivas, E. D. Pereira and I. Moreno-Villoslada, *Prog. Polym. Sci.*, 2003, **28**, 173.
- 16 B. L. Rivas and K. E. Geckeler, *Adv. Polym. Sci.*, 1992, **102**, 171.
- 17 J. F. Moulder, W. F. Stickle, P. E. Sobol and K. D. Bomben, *Handbook of X-ray Photoelectron Spectroscopy*, Perkin-Elmer Corporation Physical Electronics Division, Eden Prairie, Minnesota, 1992.
- 18 G. B. Deacon and R. J. Phillips, *Coord. Chem. Rev.*, 1980, **33**, 227.
- 19 H. L. Gao, B. Ding, L. Yi, P. Cheng, D. Z. Liao, S. P. Yan and Z. H. Jiang, *Inorg. Chem. Commun.*, 2005, **8**, 151.
- 20 X. Hu, J. X. Guo, Y. J. Wang and C. Liu, *Spectrochim. Acta, Part A*, 2009, **74**, 48.
- 21 H. J. A. Zweistra, N. A. M. Besseling and M. A. C. Stuart, *J. Phys. Chem. B*, 2006, **110**, 18629.