

Mesophase Transformation in Amphiphilic Hyperbranched Polymers Induced by Transition Metal Ion Complexation. Creating Well-Defined Metallo-Supramolecular Assemblies from “Ill-Defined” Building Blocks

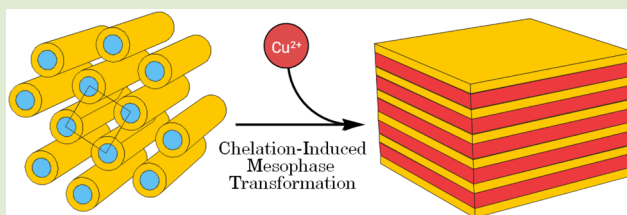
Agustín S. Picco,[†] Wolfgang Knoll,[‡] Marcelo Ceolín,^{*,†} and Omar Azzaroni^{*,†}

[†]Instituto de Investigaciones Físicoquímicas Teóricas y Aplicadas (INIFTA), Universidad Nacional de La Plata, CONICET, CC 16 – Suc. 4, 1900 La Plata, Argentina

[‡]Austrian Institute of Technology (AIT), Donau-City-Strasse 1, 1220 Vienna, Austria

S Supporting Information

ABSTRACT: Self-organized metallo-supramolecular heterostructures have potential applications that include molecular electronics, photovoltaics, and magnetic devices, among other examples. The main challenge that scientists typically face when designing advanced supramolecular materials is to achieve structurally defined assemblies by resolving conflicting demands on the topological and/or chemical features of the constituting building blocks. Accordingly, the formation of well-defined metallo-supramolecular arrays using ill-defined, highly polydisperse, self-assemblable starting compounds marks a profound departure from traditional supramolecular paradigms. The present work describes the first observation of spontaneous mesophase transformation of well-defined metallo-supramolecular assemblies in solution as a result of the complexation of transition metal ions into the ionophilic domains of highly branched unimolecular micelles constituted of *N*-acylated hyperbranched polyethylenimine. Experimental results based on a combination of different synchrotron-based techniques provide unprecedented experimental evidence revealing that ion-induced self-assembly of amphiphilic hyperbranched polymers can be used to achieve highly ordered metallo-supramolecular structures not only in solution but also on solid surfaces. We believe that this emerging conceptual framework can open extremely interesting new synthetic and technological opportunities in the area of self-assembly of well-defined metallo-supramolecular architectures obtained from building blocks with poor structural regularity but easily provided in large quantities by simple and inexpensive preparative chemistries.



One of the hallmarks of contemporary materials science is the use of molecular building blocks capable of forming self-assembled structures. Self-assembly has given access to a range of supramolecular entities of impressive architectural complexity, thereby making full use of noncovalent interactions for holding specific building blocks in predefined spatial configurations. Learning new ways to induce and direct such self-assembly processes is of the utmost importance to improve and develop methodologies for assembling active molecular modules in suitable device architectures, such as thin films. In this context, amphiphilic self-assembly represents a simple yet flexible strategy¹ to create supramolecular materials that provides extensive control of the structure and function over different length scales. Among the traditional building blocks for preparing self-assembled architectures, amphiphilic dendrimers and dendrons emerged as very attractive structural units to form supramolecular materials with molecular precision.² In particular, the modification of peripheral groups of dendrimers with hydrophobic tails led to the creation of molecularly defined systems with inverse micelle properties. Indeed, inspiring works of Percec,³ Meijer,⁴ Kato,⁵ and Mezzenga,⁶ among others, provided the framework for

designing an unprecedented number of superstructural assemblies from precisely engineered dendrons and dendrimers. To that end, it has been considered for many years that precise matching of directional interactions and topological complementarities were absolutely necessary to attain well-defined self-assembled supramolecular objects. In other words, for many years, investigations in supramolecular materials were almost exclusively based on the use of building blocks with well-defined molecular weight and topological features.^{7,8} However, this vision changed after Tsukruk and co-workers demonstrated that self-assembly of irregular, high polydispersity amphiphilic hyperbranched polymers can also lead to the formation of well-ordered supramolecular structures in the solid state.⁹ Taking into account these concepts and being aware of the promising features of self-organization exhibited by amphiphilic hyperbranched polymers we took this new paradigm one step further by integrating transition metal ions into the hydrophilic cores of these “ill-defined” amphiphilic

Received: October 28, 2014

Accepted: December 30, 2014

Published: December 31, 2014



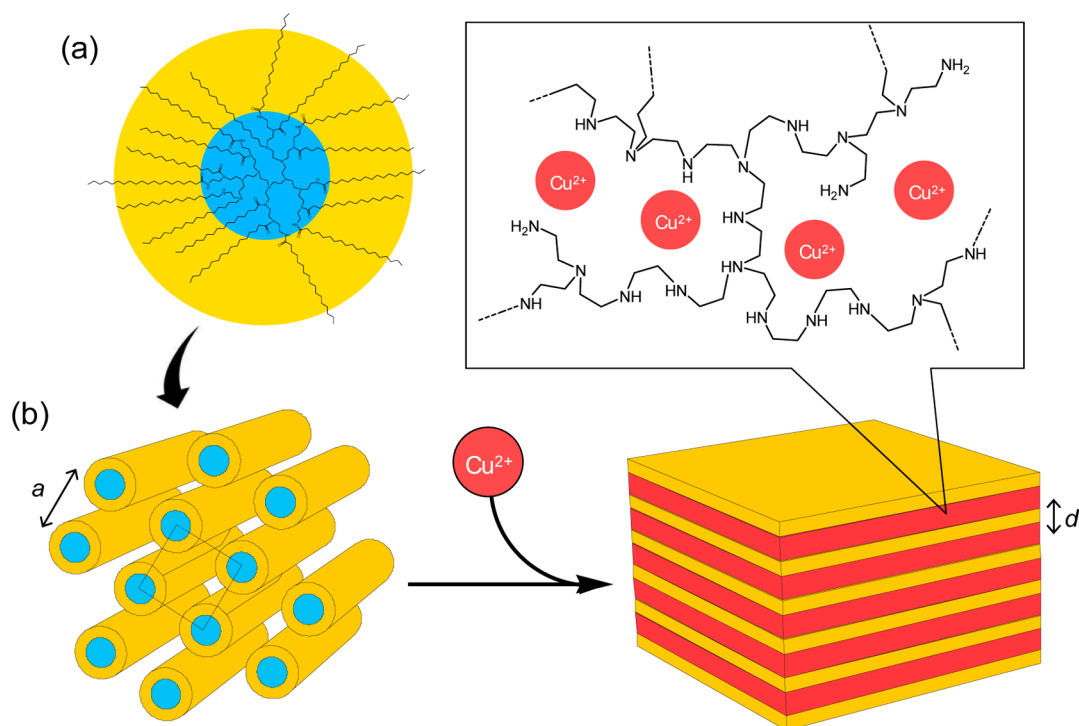


Figure 1. (a) Simplified cartoon depicting the core–shell architecture of the unimolecular micelle. (b) Scheme describing the mesophase transformation induced by the complexation of Cu^{2+} ions.

nanoobjects in order to create well-defined metallo-supramolecular assemblies. Metal ions embedded in a specific ligand field offer diverse chemical and physical properties that make these systems promising candidates for active components in functional materials. In relation to this field, the combination of coordination chemistry with amphiphilic self-assembly of irregular building blocks can thus be considered as a promising starting point for applying the versatility of supramolecular ideas to the design of new functional mesostructured architectures. With these ideas in mind, we report here the first observation of spontaneous, self-organized formation of well-defined metallo-supramolecular assemblies as a result of the complexation of transition metal ions into the hydrophilic domains of unimolecular micelles constituted of *N*-acylated hyperbranched polyethylenimine. Our results provide unprecedented experimental evidence revealing outstanding superstructural features of unimolecular micelles loaded with transition metal ions that include the formation of well-defined long-range supramolecular organization in solution and thin-film configurations and the square columnar-to-lamellar mesophase transformation induced by the complexation of the transition metal ion host.

The unimolecular micelles¹⁰ were constituted of hyperbranched polyethylenimine (hydrophilic core) covalently modified with a hydrophobic shell of palmitoyl chains (HPEI–C16) (Mn: 39 kDa). These building blocks were synthesized according to the protocol described by Stiriba and co-workers.¹¹ The synchrotron-based small-angle X-ray scattering (SAXS)-derived electron density spatial profile corroborated that amphiphilic HPEI–C16 unimolecular micelles exhibit a core–shell structure (Figure 1) and present a radius of gyration (R_g) equal to 1.59 ± 0.01 nm (see Supporting Information (SI) for further information).

Figure 2 gives the synchrotron-based SAXS profiles for HPEI–C16 assemblies in toluenic solution. These supra-

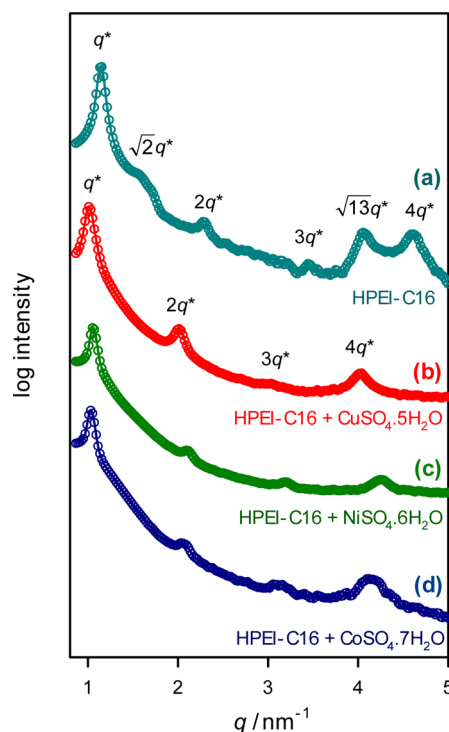


Figure 2. Synchrotron-based SAXS profiles obtained in toluenic solutions (10 mg/mL) at 298 K for: (a) HPEI–C16, (b) HPEI–C16 + $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, (c) HPEI–C16 + $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, and (d) HPEI–C16 + $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$.

macromolecular assemblies are characterized by the presence of multiple peaks, suggesting the presence of ordered structures. The SAXS pattern shows six reflections with q -spacing ratios of $1:\sqrt{2}:2:3:\sqrt{13}:4$, consistent with a square

columnar mesophase¹² (shown schematically in Figure 1). The intercolumnar distance (a) was estimated to be 5.52 ± 0.02 nm.

The experimental evidence indicates that the enthalpic gain of the long alkyl chains arranged as in a typical liquid crystalline mesophase dominates over the entropic tendency of the irregular branched polymeric core to adopt a globular conformation.¹³ The intrinsic flexibility of the HPEI core allows the amphiphilic macromolecule to adopt a microphase-separated conformation which gives rise to the square columnar supramolecular structure (Col_{sq}). As thoroughly described by Tschierske,¹⁴ mesogeneity can be driven by nanosegregation of incompatible molecular parts, thus leading to the formation of well-organized different nanodomains. The nanosegregation depends on the size of the incompatible segments and on the degree of incompatibility between them.¹⁵ In our case the mesoorganization should be ascribed to nanosegregation of the polar hyperbranched cores from the peripheral lipophilic long alkyl chains.

Our structural observations on the HPEI–C16 system are in close agreement with previous results reported by Tschierske and co-workers on the supramolecular organization of diaminobutane poly(propyleneimine) (DAB) dendrimers bearing amphiphilic carboxylic acids.¹⁶ Both systems are described by square columnar mesophases resulting from the stacking of the amphiphilic molecules driven by microphase separation between the incompatible segments of the macromolecule. For instance, it has been shown that preorganization of the lipophilic chains around the central polar region favors the formation of columnar aggregates.¹⁷

At this point, it is interesting to note that even though HPEI refers to “ill-defined”, high polydisperse macromolecular units they can form mesophases in close resemblance to those obtained with molecularly defined PAMAM dendrimers. This intriguing aspect can be explained considering previous research done by Serrano and co-workers on the self-assembly of poly(propyleneimine) dendrimers. These authors found that upon increasing the dendrimer generation the diameter of the columns varied irregularly between 5.3 and 6.7 nm, despite the fact that the molecular weight of the dendrimers was increased from 2.6 up to 48.5 kDa.¹⁸ This might indicate that during the self-assembly process the dendritic cores suffer strong deformations, and at the same time the mesogenic units adopt a radial arrangement to ensure efficient lateral interactions within and between columnar slices. The main conclusion from these studies is that the fundamental dimensions of mesophases constituted of molecularly defined amphiphilic dendrimers do not depend on the size of the dendrimer itself. In terms of our amphiphilic hyperbranched polymers these results reinforce the idea that the polydispersity of the branched polyethylenimine core is not a limiting factor to attain well-defined mesophases.

So far, we have shown that amphiphilic hyperbranched polymers exhibit mesostructural features fully comparable with well-defined dendrimer analogues. Now, we will study the meso-organization of hyperbranched unimicelles in a scenario where polyethylenimine cores are complexed with Cu^{2+} ions.

Plot b in Figure 2 shows that the incorporation of the Cu^{2+} ion in the inner environment of amphiphilic polyethylenimine leads to sharp changes in the SAXS profile. Amphiphilic complexes with Cu^{2+} show four reflections whose q positions follow the ratios 1:2:3:4, which are indicative of well-ordered lamellar phases. The interlamellar distance (d) estimated from SAXS data was 6.19 ± 0.04 nm. This experimental observation

clearly indicates that Cu^{2+} complexation triggers a square columnar-to-lamellar mesophase transformation of the amphiphilic HPEI assemblies. Ion-induced mesophase transformation has been already observed in a variety of supramolecular systems composed of well-matched, interacting counterparts, namely, block copolymers or dendrons.^{19,20} For instance, seminal works of Percec and collaborators²¹ elegantly demonstrated how the incorporation of metal ions can influence the self-assembly of well-defined amphiphilic building blocks. More recently, Choi et al.²² showed that the presence of lithium ions can induce the mesostructural transformation of discotic block codendrimers from hexagonal columnar to bicontinuous cubic mesophases.

However, to the best of our knowledge, this is the first observation of ion-induced mesophase transformation in *irregular, highly branched, and polydisperse molecules*. It is evident that this structural change stems from the binding of Cu^{2+} ions to the amino groups in the polar core of the unimolecular micelle. Spectroscopic characterization combining UV–visible, X-ray absorption near-edge structure (XANES), extended X-ray absorption fine structure (EXAFS), X-ray photoelectron, and infrared (FT-IR) spectroscopies provided insightful information about the chelation of Cu^{2+} in the polymeric cores. The UV–vis spectrum of HPEI–C16 unimicelles hosting Cu^{2+} ions (Figure 3a) shows a broad band located at 696 nm deriving from d–d transitions.²³ Typically, HPEI and ethylenediamine Cu(II) complexes exhibit d–d bands at shorter wavelengths arising from CuN_xO_y distorted octahedra or square planar configurations.²⁴ On the other hand, pentacoordinated complexes of Cu^{2+} ions with nitrogen ligands usually present bands around 700 nm.²⁵ In our case, the broad band in the UV–vis spectrum of the HPEI–C16– Cu^{2+} complex was satisfactorily fitted with two Gaussian components located at 673 and 825 nm, which is in good agreement with the transitions observed for pentaamine–Cu(II) complexes displaying square pyramidal coordination geometry.²⁶ Figure 3b shows the FT-IR spectra of HPEI–C16 and HPEI–C16– Cu^{2+} complexes. The region between 1500 and 1700 cm^{-1} is dominated by the amide I (1650 cm^{-1}) and amide II (1550 cm^{-1}) bands,²⁷ which remain almost unaffected after the complexation process. This observation supports the idea that amide groups play no role in the stabilization of the metal centers, and amine groups are the only chelating entities responsible for complexing the Cu^{2+} species. These results are in line with a previous report by Ottaviani et al. on the binding abilities of nitrogen donors to metal ions, amines > amides, in PAMAM dendrimers.²⁸ Concomitantly, the X-ray absorption near-edge structure (XANES) spectra of HPEI–C16– Cu^{2+} exhibited its edge at 8986 eV, a characteristic feature of the copper(II) ions. Moreover, the position of the first broad resonance above the energy threshold (8996 eV) is characteristic of Cu(II) ions coordinated with nitrogen ligands (Figure 3c).²⁹ The absence of resonances at energies lower than the absorption edge is a clear indication of low-symmetry environments for the Cu(II) absorbing centers, thus reinforcing the idea of a 5-coordinated pyramidal model (a more detailed description of XANES spectra is included in the SI file). In addition, EXAFS spectroscopy was employed as an excellent tool for studying the local environment of Cu^{2+} ions in the hyperbranched core at the molecular level.

This enabled us to determine average coordination numbers and interatomic distances for the metal centers. Supported on the analysis of the XANES region of the absorption spectrum,

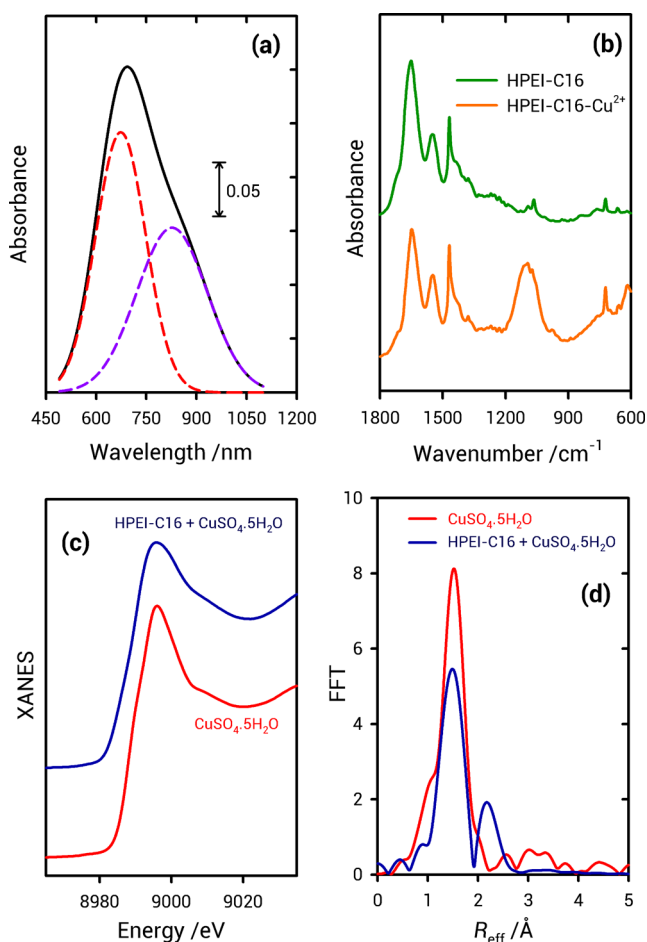


Figure 3. (a) UV-vis spectrum of the HPEI-C16-Cu²⁺ system measured in toluenic solution (10 mg/mL). The spectrum was fitted with two Gaussian components located at 673 and 825 nm suggesting a square pyramidal geometry around the metal centers. (b) FT-IR spectra of HPEI-C16 prior to and after complexation with Cu²⁺ ions. (c) XANES spectra at the copper *K* edge for HPEI-C16 assemblies after complexation with Cu²⁺ ions (blue trace) in comparison with the spectrum of CuSO₄·5H₂O reference (red trace). (d) Fourier transforms of EXAFS data corresponding to HPEI-C16-Cu²⁺ (blue trace) and CuSO₄·5H₂O (red trace).

EXAFS data of HPEI-C16-Cu²⁺ complexes were successfully fitted by a pentacoordinated structure containing four nitrogens at 2.0 ± 0.2 Å and another ligand located at 2.1 ± 0.2 Å from the copper center. These values are in full agreement with typical coordination distances found in Cu(II)-N₅ complexes with square pyramidal coordination geometry.³⁰ In addition to this first shell, four carbon atoms are adjusted at 2.8–2.9 Å, in concordance with the distances present in N-C-C-N rings,³¹ presumably bonded to the equatorial nitrogens (see SI). Similar values have been reported for copper-containing poly(propyleneimine) (PPI) dendrimers.³²

Finally, XPS provided precise information on the chemical nature and stoichiometry of the core environment (Figure 4). Besides Cu²⁺, XPS detected the presence of sulfur species which were assigned to sulfate ions. The Cu²⁺:SO₄²⁻ ratio was 0.9:1 which indicates that each Cu²⁺ ion retains its counterion in the polyethylenimine core after the complexation. XPS characterization also indicated that the Cu:N ratio was 1:9.

Referring back to the SAXS patterns, it is well-known that HPEI also forms stable complexes with other transition metal

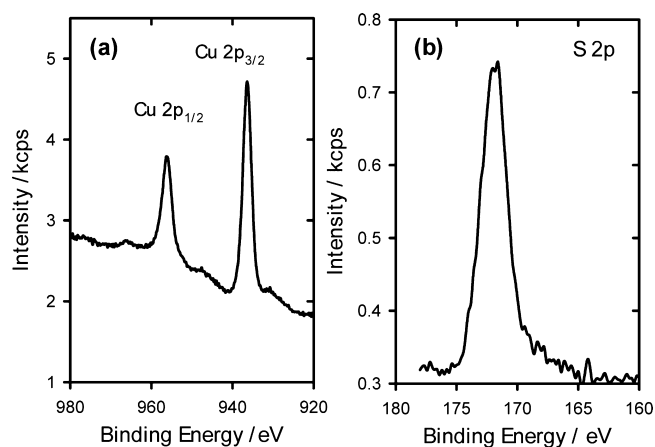


Figure 4. High-resolution synchrotron-based XP spectra for: (a) Cu 2p and (b) S 2p.

ions, like Co²⁺ or Ni²⁺.^{33,34} Hence, we hypothesized that this mesophase reorganization could also take place in the presence of other transition metals. Plots c and d in Figure 2 show SAXS patterns of HPEI-C16-Ni²⁺ and HPEI-C16-Co²⁺ measured at room temperature in toluenic solution. SAXS characterization unequivocally demonstrates that chelation of Co²⁺ and Ni²⁺ also leads to a COL_{squ}-to-LAM mesophase transformation, as previously observed in the presence of Cu²⁺, with *d* values equal to 6.07 ± 0.08 nm and 5.94 ± 0.08 nm, respectively. This mesophase transformation induced by the complexation process can be interpreted in terms of the nanosegregation that takes place within the assembly as the main driving force guiding the formation of the lamellar phases. In principle, the accumulation of functional groups with polar character gives rise to a polar domain in the center of the amphiphilic polymers. These polar regions of different hyperbranched molecules interact preferably with each other and thus segregate from the aliphatic chains into separate domains. However, the mesophase stability is greatly governed by the hydrophilic-hydrophobic balance within the amphiphilic molecules. Hence, changes in the intramolecular polarity contrast can lead to significant changes in the original mesophase organization.³⁵ In our case, the deliberate introduction of ionic (polar) interactions effected by the complexation of transition metal ions by the amino groups and the concomitant incorporation of the corresponding sulfate counterions significantly increased the polarity contrast between the polyethylenimine core and the peripheral aliphatic chains. As a consequence, the complexation processes enabled nanosegregation to occur with formation of well-defined lamellar supramolecular assemblies. To understand the formation of these lamellar mesophases we need to consider the shape of the interfaces resulting during the complexation process. As is well-known the increase of the curvature of internal interfaces leads to a change of the phase type in the order lamellar-bicontinuous cubic-columnar.³⁶ It is clear that metal ion complexation not only increases the hydrophilic part of the molecules but also reduces the curvature of the interface between hydrophilic and hydrophobic regions. This observation is in full agreement with previous results reported by Cook et al.¹⁶ in which the protonation of nitrogen atoms in ionic self-assemblies of DAB dendrimers and mesogenic acids gives rise to an enhanced amphiphilicity with the subsequent formation of new mesophase structures. Typically, long side chains give a

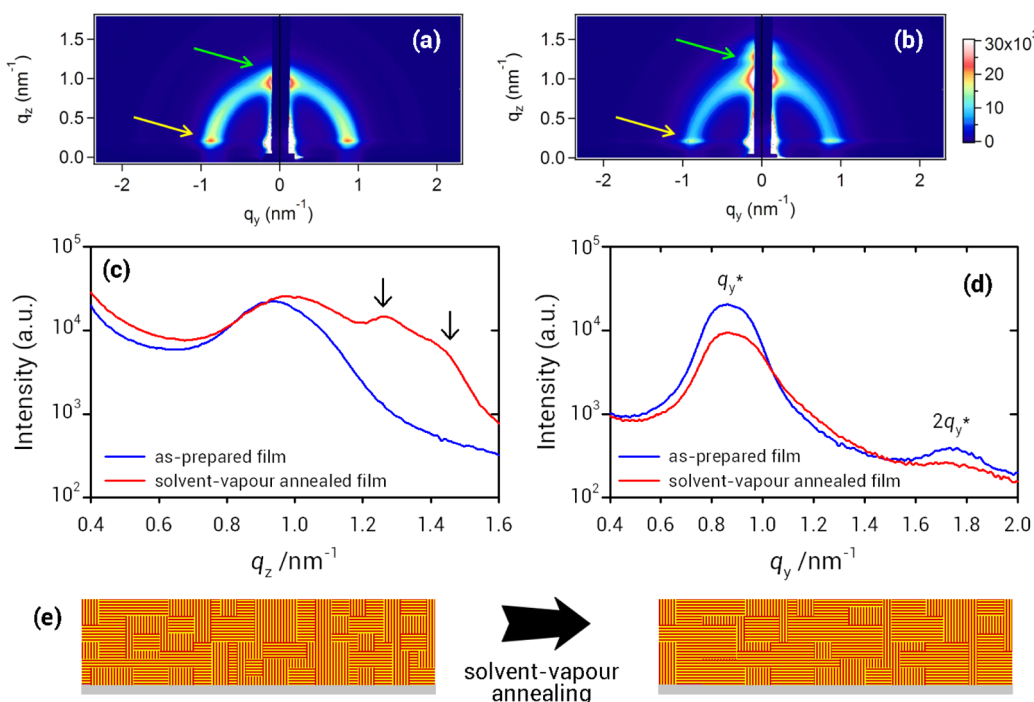


Figure 5. 2D-GISAXS data for (a) as-prepared and (b) solvent-vapor annealed thin films constituted of lamellar HPEI–C16–Cu²⁺ metallo-assemblies. (c) Semilogarithmic representation of the intensity profiles along q_z (at $q_y = 0.16 \text{ nm}^{-1}$) for as-prepared (blue trace) and solvent-vapor annealed (red trace) HPEI–C16–Cu²⁺ films. (d) Semilogarithmic representation of the intensity profiles along q_y (at $q_z = 0.22 \text{ nm}^{-1}$) for as-prepared (blue trace) and solvent-vapor annealed (red trace) HPEI–C16–Cu²⁺ films. (e) Simplified representation describing the reorganization of lamellae after the solvent-vapor annealing treatment of HPEI–C16–Cu²⁺ films.

strong curvature of the interface and lead to columnar mesomorphism, whereas in large hydrophilic domains coupled to short hydrophobic chains the curvature is reduced and only lamellar phases are observed.³⁷

On the other hand, construction of self-assembled metallo-supramolecular systems into thin-film formats on suitable surfaces is often required for implementation of practical devices that address specific applications. Such interfacial architectures require strict control over the organization at the nanometer scale, and therefore it is essential to study and develop methods for the controlled assembly of multi-component nanostructures on surfaces. To this end, once we demonstrated the ion-induced mesophase transformation we attempted to extrapolate these results to the formation of mesostructured metallo-supramolecular films from hyper-branched building blocks.

Metallo-supramolecular thin-film assemblies were prepared by casting a toluenic solution of HPEI–C16–Cu²⁺ (10 mg/mL) onto silicon substrates. Solvent evaporation took place during a few hours, resulting in the formation of a homogeneous thin film. These samples were characterized by grazing-incidence small-angle X-ray scattering (GISAXS) with an incident angle of 0.22° to elucidate the orientation of the lamellar domains with respect to the substrate. The GISAXS pattern for the HPEI–C16–Cu²⁺ system shows the presence of a very faint circular halo and very intense bright regions in the q_z and q_y directions for $q_y \rightarrow 0$ and $q_z \rightarrow 0$, respectively. The presence of the faint circular halo is attributed to the presence of a randomly oriented lamellae (Figure 5a,b). In this case, rings of relatively low intensity (diffuse Debye–Scherrer rings) around the direct beam and around the reflected beam are expected. However, the intensity distribution along the ring is indicative of the distribution of lamellar orientations. Our 2D

GISAXS maps indicate that lamellar structures of HPEI–C16–Cu²⁺ metallo-assemblies transferred from the solution to the substrate by solvent casting are predominantly oriented in directions parallel (\parallel) or perpendicular (\perp) to the substrate. Lamellar spacing of horizontally (d^{\parallel}) and vertically (d^{\perp}) oriented lamellae estimated from horizontal and vertical cuts of 2D-GISAXS patterns (Figure 5c,d) corresponded to $6.80 \pm 0.20 \text{ nm}$ and $6.85 \pm 0.20 \text{ nm}$, respectively.

Thereafter, postprocessing by solvent-vapor annealing (SVA) in an atmosphere saturated with toluene vapors was explored as a method to further manipulate the meso-organization and orientation of the lamellar domains on the substrate. In SVA, the solvent partially dissolves the deposited layer leading to reorganization and the concomitant evolution toward thermodynamically stable morphologies.^{38,39} The results obtained for solvent-vapor annealed samples showed interesting changes (Figure 5c,d). GISAXS characterization revealed a decrease in the population of lamellar domains oriented perpendicular to the substrate as indicated by the decrease in the intensity of the bright spots in the q_y direction without noticeable modification of the interlamellar spacing (yellow arrows in Figures 5b and red trace in Figure 5d). Concomitantly, scattering in the q_z direction indicated the appearance of several strong scattering spots (green arrows in Figure 5b and red trace in Figure 5c), thus revealing the presence of a layered structure stacked normal to the film plane that could be interpreted as extended lamellar metallo-supramolecular domains oriented parallel to the substrate surface (Figure 5e). According to GISAXS data the lamellar spacing of the vertically stacked heterostructures is $6.50 \pm 0.20 \text{ nm}$.

GISAXS results of this film led us to the conclusion that lamellae which are parallel to the substrate surface prevail and play a dominant role in defining the film meso-organization

during the solvent-vapor annealing, even though a fraction of the sample consists of perpendicular lamellae, giving rise to weak spots in the q_y direction.

In conclusion, our findings show that irregular, polydisperse, highly branched amphiphilic polymers can be assembled in solution to form well-defined square columnar mesophases. More importantly, we demonstrate that the complexation of the polymeric cores with transition metal ions triggers a mesophase transformation leading to the creation of well-defined metallo-supramolecular assemblies displaying lamellar structures. We hypothesize that the complexation of the metal ions alters the intramolecular polarity contrast and the interface curvature of the hydrophilic–hydrophobic domains, and consequently the nanosegregation leads to the formation of well-defined lamellar assemblies. A combination of spectroscopic techniques revealed molecular features indicating that the coordination chemistry of metal ions hosted in the hyperbranched polyethylenimine cores resembles that encountered in pentacoordinated complexes with square pyramidal coordination geometry.

Some examples of induction of liquid crystalline phases by integration of ions in ionophilic parts of amphiphilic entities have already been demonstrated using well-defined discotic block codendrimers or Janus dendrimers. However, the self-assembling concept elaborated in this work is different from previously reported ones since it generates well-defined metallo-supramolecular assemblies arising from the ion-induced mesophase reorganization of ill-defined, polydisperse constructs. To the best of our knowledge, this is the first example in which well-defined metallo-supramolecular assemblies in solution are created from highly irregular building blocks. The results presented here leap forward by breaking new conceptual ground and provide a new design paradigm for developing structurally configurable, mesoscale organized, metallo-supramolecular materials employing ill-defined, robust constituents readily available in large quantities.

Furthermore, we demonstrate that ion-induced self-assembly of amphiphilic hyperbranched polymers can be used to achieve highly ordered metallo-supramolecular structures not only in solution but also at solid surfaces. GISAXS experiments provided details on the internal ordering within the films and revealed that stacked heterostructures can be transferred onto solid surfaces via drop-casting from dilute solutions containing the metallo-supramolecular lamellar modules. Likewise, we show that complementing the deposition process with solvent-vapor annealing offers additional control over the formation of extended lamellar domains oriented parallel to the substrate surface. This combination of assembly and post-treatment strategies might thus constitute an important tool to achieve directed bottom-up construction and controlled manipulation of functional, surface-confined metallo-supramolecular arrays.

We believe that these results may have significant implications in areas where the formation of self-organized heterosupramolecular assemblies plays a decisive role, such as optical, electronic, or magnetic devices, for which the present extended, well-defined lamellar metallo-supramolecular assemblies may shed new light on advanced supramacromolecular designs.

■ ASSOCIATED CONTENT

■ Supporting Information

Experimental procedures including: amphiphilic polymer synthesis, preparation of metal-loaded hyperbranched polymers,

and characterization by XPS, SAXS, GISAXS, EXAFS, and XANES. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Authors

*(O.A.) azzaroni@inifta.unlp.edu.ar.

*(M.C.) mceolin@inifta.unlp.edu.ar. Web: <http://softmatter.quimica.unlp.edu.ar>.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

A.S.P. gratefully acknowledges CONICET for a scholarship. O.A. and M.C. are staff researchers of CONICET. This work was supported by CONICET, ANPCyT (PICT-163/08, PICT-2010-2554, PICT-2013-0905), the Austrian Institute of Technology GmbH (AIT–CONICET Partner Group: “Exploratory Research for Advanced Technologies in Supramolecular Materials Science” – Exp. 4947/11, Res. No. 3911, 28-12-2011), and Laboratório Nacional de Luz Síncrotron (LNLS) (SAXS1-8575/9108/9868, XRD2-14358/13391, XAFS1-9237, and SXS-11642).

■ REFERENCES

- (1) Kurth, G. D. *Sci. Technol. Adv. Mater.* **2008**, *9*, 014103.
- (2) Rosen, B. M.; Wilson, C. J.; Wilson, D. A.; Peterca, M.; Imam, M. R.; Percec, V. *Chem. Rev.* **2009**, *109*, 6275–6540.
- (3) (a) Hudson, S. D.; Jung, H.-T.; Percec, V.; Cho, W.-D.; Johansson, G.; Ungar, G.; Balagurusamy, V. S. K. *Science* **1997**, *278*, 449–452. (b) Zeng, X.; Ungar, G.; Liu, Y.; Percec, V.; Dulcey, A.; Hobbs, J. K. *Nature* **2004**, *428*, 157–160.
- (4) van Hest, C. M.; Delnoye, D. A. P.; Baars, M. W. P. L.; van Genderen, M. H. P.; Meijer, E. W. *Science* **1995**, *268*, 1592–1595.
- (5) (a) Baranoff, E. D.; Voignier, J.; Yasuda, T.; Heitz, V.; Sauvage, J.-P.; Kato, T. *Angew. Chem., Int. Ed.* **2007**, *46*, 4680–4683. (b) Ichikawa, T.; Yoshio, M.; Hamasaki, A.; Mukai, T.; Ohno, H.; Kato, T. *J. Am. Chem. Soc.* **2007**, *129*, 10662–10663.
- (6) (a) Canilho, N.; Kasëmi, E.; Mezzenga, R.; Schlüter, A. D. *J. Am. Chem. Soc.* **2006**, *128*, 13998–13999. (b) Li, C.; Schlüter, A. D.; Zhang, A.; Mezzenga, R. *Adv. Mater.* **2008**, *20*, 4530–4534.
- (7) Yoo, Y.-S.; Choi, J.-H.; Song, J.-H.; Oh, N.-K.; Zin, W.-C.; Park, S.; Chang, T.; Lee, M. *J. Am. Chem. Soc.* **2004**, *126*, 6294–6300.
- (8) Cho, B.-K.; Jain, A.; Gruner, S. M.; Wiesner, U. *Science* **2004**, *305*, 1598–1601.
- (9) (a) Ornatska, M.; Peleshanko, S.; Genson, K. L.; Rybak, B.; Bergman, K. N.; Tsukruk, V. V. *J. Am. Chem. Soc.* **2004**, *126*, 9675–9684. (b) Ornatska, M.; Bergman, K. N.; Rybak, B.; Peleshanko, S.; Tsukruk, V. V. *Angew. Chem., Int. Ed.* **2004**, *43*, 5246–5249.
- (10) (a) Stiriba, S.-E.; Kautz, H.; Frey, H. *J. Am. Chem. Soc.* **2002**, *124*, 9698–9699. (b) Sunder, A.; Krämer, M.; Hanselmann, R.; Mülhaupt, R.; Frey, H. *Angew. Chem., Int. Ed.* **1999**, *38*, 3552–3555. (c) Mecking, S.; Thomann, R.; Frey, H.; Sunder, A. *Macromolecules* **2000**, *33*, 3958–3960.
- (11) Liu, H.; Chen, Y.; Zhu, D.; Shen, Z.; Stiriba, S.-E. *React. Funct. Polym.* **2007**, *67*, 383–396.
- (12) Foster, S.; Timmann, A.; Konrad, M.; Schellbach, C.; Meyer, A.; Funari, S.; Mulvaney, P.; Knott, R. *J. Phys. Chem. B* **2005**, *109*, 1347–1360.
- (13) Barberá, J.; Donnio, B.; Gehringer, L.; Guillon, D.; Marcos, M.; Omenat, A.; Serrano, J. L. *J. Mater. Chem.* **2005**, *15*, 4093–4105.
- (14) Tschierske, C. *Prog. Polym. Sci.* **1996**, *21*, 775–852.
- (15) Marcos, M.; Giménez, R.; Serrano, J. L.; Donnio, B.; Heinrich, B.; Guillon, D. *Chem.—Eur. J.* **2001**, *7*, 1006–1013.
- (16) Cook, A. G.; Baumeister, U.; Tschierske, C. *J. Mater. Chem.* **2005**, *15*, 1708–1721.

- (17) Pegenau, A.; Hegmann, T.; Tschierske, C.; Diele, S. *Chem.—Eur. J.* **1999**, *5*, 1643–1660.
- (18) Donnio, B.; Barberá, J.; Gimenez, R.; Guillón, D.; Marcos, M.; Serrano, J. L. *Macromolecules* **2002**, *35*, 370–381.
- (19) (a) Huang, J.; Tong, Z.-Z.; Zhou, B.; Xu, J.-T.; Fan, Z.-Q. *Polymer* **2013**, *54*, 3098–3106. (b) Cho, B.-K.; Kim, S.-H.; Lee, E. J. *Polym. Sci., Part A: Polym. Chem.* **2010**, *48*, 2372–2376. (c) Ioannou, E. F.; Mountrichas, G.; Pispas, S.; Kamitsos, E. I.; Floudas, G. *Macromolecules* **2008**, *41*, 6183–6190.
- (20) Kamikawa, Y.; Nishii, M.; Kato, T. *Chem.—Eur. J.* **2004**, *10*, 5942–5951.
- (21) (a) Percec, V.; Johansson, G.; Ungar, G.; Zhou, J. *J. Am. Chem. Soc.* **1996**, *118*, 9855–9866. (b) Percec, V.; Johansson, G.; Heck, J.; Ungar, G.; Batty, S. V. *J. Chem. Soc., Perkin Trans.* **1993**, *1*, 1411–1420.
- (22) Choi, J.-W.; Ryu, M.-H.; Lee, E.; Cho, B.-K. *Chem.—Eur. J.* **2010**, *16*, 9006–9009.
- (23) Cotton, F. A.; Wilkinson, G.; Murillo, C.; Bochmann, M. *Advanced Inorganic Chemistry*, 6th ed.; Wiley-Interscience: New York, 1999.
- (24) Kislenco, V. N.; Oliynyk, L. P. *Polymer* **2002**, 914–922.
- (25) Hathaway, B. J.; Billing, D. E. *Coord. Chem. Rev.* **1970**, *5*, 143–207.
- (26) Hathaway, B. J.; Tomlinson, A. G. *Coord. Chem. Rev.* **1970**, *5*, 1–43.
- (27) Stuart, B. *Infrared Spectroscopy: Fundamentals and applications*; John Wiley & Sons Ltd.: Chichester, 2004.
- (28) Ottaviani, M. F.; Montalti, F.; Turro, N. J.; Tomalia, D. A. *J. Phys. Chem. B* **1997**, *101*, 158–166.
- (29) (a) Choy, J.-H.; Yoon, J.-B.; Jung, H. *J. Phys. Chem. B* **2002**, *106*, 11120–11126. (b) Chaboy, J.; Muñoz-Páez, A.; Carrera, F.; Merklng, P.; Marcos, E. S. *Phys. Rev. B* **2005**, *74*, 134208.
- (30) Frank, P.; Benfatto, M.; Hedman, B.; Hodgson, K. O. *Inorg. Chem.* **2008**, *47*, 4126–4139.
- (31) Carrera, F.; Marcos, E. S.; Merklng, P. J.; Chaboy, J.; Muñoz-Páez, A. *Inorg. Chem.* **2004**, *43*, 6674–6683.
- (32) Floriano, P. N.; Noble, C. O.; Schoonmaker, J. M.; Poliakoff, E. D.; Mccarley, R. L. *J. Am. Chem. Soc.* **2001**, *123*, 10545–10553.
- (33) Rivas, B.; Seguel, G.; Geckeler, K. *Angew. Makromol. Chem.* **1996**, *238*, 1–10.
- (34) Zelewsky, A. Von; Barbosa, L.; Schlapfer, C. W. *Coord. Chem. Rev.* **1993**, *123*, 229–246.
- (35) Tschierske, C. *J. Mater. Chem.* **1998**, *8*, 1485–1508.
- (36) Tschierske, C. *Angew. Chem., Int. Ed.* **2013**, *52*, 8828–8878.
- (37) Tschierske, C. *Chem. Soc. Rev.* **2007**, *36*, 1930–1970.
- (38) Balakrishnan, K.; Datar, A.; Oitker, R.; Chen, H.; Zuo, J. M.; Zang, L. *J. Am. Chem. Soc.* **2005**, *127*, 10496–10497.
- (39) De Luca, G.; Liscio, A.; Maccagnani, P.; Nolde, F.; Palermo, V.; Müllen, K.; Samori, P. *Adv. Funct. Mater.* **2007**, *17*, 3791–3798.