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A Supramolecular Miktoarm Star Polymer Based on Porphyrin Metal Complexation in water

Received 00th January 20xx, Accepted 00th January 20xx

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DOI: 10.1039/x0xx00000x

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A novel supramolecular miktoarm star polymer was successfully constructed in water from a pyridine end-decorated polymer (Py-PmDEGA) and a metalloporphyrin based star polymer (ZnTPP-(PEG)₄) via metal-ligand coordination. The Py-PmDEGA moiety was prepared via a combination of reversible addition-fragmentation chain transfer polymerization (RAFT) and subsequent aminolysis and Michael addition reaction to introduce the pyridine endgroup. The ZnTPP(PEG)₄ star-polymer was synthesized by reaction between tetrakis (p-hydroxyphenyl)porphyrin and toluenesulfonyl-PEG, and followed by insertion of a zinc ion into the porphyrin core. The formation of a well-defined supramolecular AB₄-type miktoarm star polymer was unambiguously demonstrated via UV-Vis spectroscopic titration, isothermal titration calorimetry (ITC) and diffusion ordered NMR spectroscopy (DOSY).

Polymer properties are mainly influenced by the chemical composition and topology of the constituting macromolecules. A broad range of applications have been proposed for different polymer architectures, e.g. stabilization of polymer blends with block copolymers,¹ drug delivery *via* amphiphilic block copolymers² or drug-delivery with star polymers.³ Therefore, the design of complex macromolecular architectures constitutes an important field in modern polymer chemistry and provides the opportunity to generate a broad range of materials with tunable properties.⁴ Star polymers are an important class of polymers that have attracted significant attention in the last few years.⁵ They are typically synthesized via one of three common methodologies, i.e. core-first, arm-first and coupling-onto.⁶ Various combinations of these three approaches can be employed to make even more complex miktoarm star block copolymers,

unavoidably involving a significant number of synthetic steps. Miktoarm star polymers, also called asymmetric or mixed-arm star polymer, whose arms vary in chemical structure and/or molecular weight. They exhibit unique and unusual phase separation behaviour in bulk and selected solvents, which tremendously increased the variety of morphological structures. Thus, miktoarm star polymers are promising materials with many potential applications in fields of nanoscience and nanotechnology such as electronic and optical nanodevices. nanomaterials for lithography. nanoreactors carrying metal catalysts and enzymes, nanoscale microfilters and complex self-assembly.

The advent of supramolecular chemistry, which utilizes noncovalent, reversible bonds for the assembly of materials, has had a tremendous influence on the synthesis and applications of macromolecular architectures.⁸ It has introduced the possibility of using noncovalent interactions for the creation of polymers, featuring a degree of flexibility, tunability and dynamics that was impossible using covalent chemistry.9 Hence, supramolecular polymers have received growing interest in recent years due to their unique dynamic properties making them applicable to a broad range of fields in chemistry, biology and physics.^{8, 10} To date, various supramolecular polymers with different architectures, such as linear,¹¹⁻¹³ branched, star-shaped,^{14, 15, 16} and dendronized,¹⁷ have been prepared based on hydrogen bonding, $^{13,\ 15,\ 17}$ $\pi\text{-}\pi$ interaction,¹⁸ metal-ligand binding,^{16, 19} and host-guest interaction.¹⁴ Among the non-covalent interactions, metalligand coordination is particularly interesting for the synthesis of supramolecular polymers. Indeed, in addition of being highly directional, metal-ligand coordination can be prepared from a wide range of easily functionalized ligands and metal ions, thereby allowing a large panoply of tunable metal-ligand complexes to be prepared both in organic and aqueous media.¹¹ Moreover, the presence of a metal complex in the polymer structure can impart further properties of interest including electrochemical, photophysical, catalytic and magnetic properties.

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[†] Electronic Supplementary Information (ESI) available. See DOI: 10.1039/x0xx00000x

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Porphyrins and their metal derivatives have attracted interest of chemists and biologists due to their importance and applications in biological fields. In particular, they represent a key-component of haemoglobin as well as for the inhibition of protease-resistant prion protein formation or for thermotherapy due to their strong affinity towards cancer cells.²⁰ Also, owing their ability of forming π - π interaction or metal-ligand coordination, they constitute an important class of supramolecular building blocks,²¹ which has been widely employed in supramolecular chemistry.²² However, to the best of our knowledge, there has been no report on the use of metalloporphyrin for the construction of supramolecular block copolymers, star polymers or other even more complex polymer structures based on this interaction.

In this report, we present a straightforward strategy allowing the formation of an AB₄-type miktoarm star polymer in water, governed by the complexation of a pyridine unit and a metalloporphyrin moiety, from a zinc-porphyrin based star polymers ((ZnTPP(PEG)₄) and a pyridine end-functionalized PmDEGA (Py-PmDEGA) (Figure 1). These two building blocks were synthesized and characterized by proton nuclear magnetic resonance (¹H NMR) spectroscopy, size exclusion chromatography (SEC) and MALDI-TOF mass spectrometry. Finally, in aqueous solution, the effective formation of the supramolecular star polymer was proven *via* diffusion ordered NMR spectroscopy (DOSY), isothermal titration calorimetry (ITC) and UV-Visible spectroscopy (UV-Vis).

The molecular design of the supramolecular miktoarm starblock copolymer is based on the metal-ligand interaction between a zinc-porphyrin and pyridine, as they can form noncovalent interactions with high association constants up to 10^5 M^{-1} in water.²³ the synthetic strategy towards these two building blocks is illustrated in Scheme 1 and Scheme S1.

The coupling of four PEG chains to the porphyrin core was performed by the reaction between tetrakis(*p*-hydroxyphenyl) porphyrin and *p*-toluenesulfonyl-PEG followed by the subsequent insertion of the zinc(II) ion into the porphyrin core (Scheme 1a). The metal-free porphyrin star polymer was purified *via* precipitation (diethyl ether / dichloromethane=4:45) followed by column chromatography and then analyzed *via* ¹H NMR spectroscopy, SEC and MALDI-TOF MS. The ¹H NMR



Figure 1: Graphical representation of the formation of a supramolecular miktoarm star polymer in water by complexation of a zinc-porphyrin with four PEG chains and a pyridine end-functionalized poly(methoxydiethyleneglycol acrylate). (Gray framework with blue bend line: Porphyrin and pyridine; Light blue sphere: Zinc ion; Black curve: PEG chain; Orange curve: PmDEGA chain)



Scheme 1. Synthetic routes of building blocks: a) Star polymer with zinc-porphyrin (ZnTPP(PEG)₄); b) Pyridine end-functionalized PmDEGA (Py-PmDEGA).

Spectrum of the metal-free porphyrin star polymer indicated that all four PEG chains were successfully attached based on the integration ratio of the peaks from the porphyrin (8.78, 8.05 and -2.83 ppm) and the PEG (4.37 and 3.99 ppm) protons (Figure S1). In addition, the star polymer was determined by SEC and MALDI-TOF MS (Figure S2 and Figure S3), confirming the formation of a four-arm star architecture. Furthermore, the MALDI-TOF MS spectrum revealed two distributions, both corresponding to the four-arm star polymer ionized with a sodium or a potassium ion, respectively.

After insertion of the zinc(II) ion by Zn metalation, the peak of the N-H pyrrole protons in the ¹H NMR spectrum disappeared, revealing that the pyrrole protons were successfully replaced by the zinc(II) ion (Figure S4). Furthermore, UV-Vis spectroscopy was performed evidencing the successful metalation based on the red-shift of the Soret band of the porphyrin unit to 428 nm and the disappearance of main Q-band (520 nm) (Figure S5).

The second part required for the supramolecular miktoarm star complex is a pyridine end-decorated poly(methoxydiethyleneglycol acrylate) (PmDEGA). The PmDEGA polymer was synthesized by RAFT polymerization using methyl-2-(nbutyltrithiocarbonyl)propanoate as chain transfer agent (CTA) and azobutyronitrile as radical initiator, at 70 °C in toluene.²⁴ After determination of the polymerization kinetics (Figure S6), a well-defined polymer was prepared with a degree of polymerization of 56. The polymer was purified by precipitation in diethyl ether (four times) and analyzed by ${}^{1}H$ NMR spectroscopy and SEC. The acquired polymer was subjected to an aminolysis reaction to convert the CTA endgroup into a thiol group followed by introducing N-(pyridine-4ylmethyl) acrylamide by thiol-ene Michael addition (Scheme 1b).²⁵ The polymers obtained before and after end group modification were characterized by SEC with refractive index (RI) detection, which revealed a minor change in the Mn and dispersity (D) giving a first indication of successful end group modification (Figure S7). Furthermore, no additional shoulder was present in the SEC trace of the polymer after end group transformation indicating the absence of disulfide formation after aminolysis, which could only be achieved when working in oxygen free conditions. The transformation was also

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assessed by UV-Vis spectroscopy using the characteristic absorbance of the trithiocarbonate group around 310 nm (Figure S8). The original polymer exhibits a strong absorption at this wavelength while no absorption can be detected for the resulting pyridine end-decorated polymer.

Next, the formation of the supramolecular miktoarm star block copolymer *via* metal-ligand coordination—between the ZnTPP(PEG)₄ and Py-PmDEGA was assessed (Scheme 1). The assembly process of the two building blocks can be efficiently followed by the characteristic changes in the absorption intensity of the porphyrin *via* UV-Visible spectroscopy.

Detailed information regarding the stoichiometry of the self-assembly is very important for the study of the supramolecular system, as it directly affects the arm number of the miktoarm star polymer. Herein, we determined the stoichiometry by the continuous variation approach (job plot) based on the change of the absorption intensity of the zinc-porphyrin upon complexation with Py-PmDEGA in water. The total concentration of the two building blocks was kept constant at 5.05 μ M, while the concentration ratio was changed between 0:1 and 1:0. The anticipated 1:1 stoichiometry between the two blocks was indeed confirmed by the Job plot diagram (Figure S9a) by the minimum absorption intensity at the ratio 1:1 of the two blocks at 25 °C. The stoichiometry was also determined by fluorescence spectroscopy to supporting the UV-Vis results (Figure S9b).

After confirming the stoichiometry of the two building blocks, we focused our attention on the strength of the supramolecular assembly characterized by the thermodynamic association constant, K_a, of the Py-PmDEGA@ZnTPP(PEG)₄ complex. A UV-Vis spectrophotometric titration was employed to determine the binding constant in which a concentrated aqueous solution of Py-PmDEGA was added to a dilute aqueous solution of ZnTPP(PEG)₄. As shown in Figure 2a, the addition of Py-PmDEGA resulted in a small red shift and a hyperchromicity of the Soret maximum in accordance with literature reports.^{26, 27} The binding isotherm shown in Figure 2b was used for fitting with a 1:1 binding model, as confirmed by the Job plot, revealing a K_a of (2.9 ± 0.2) x 10⁴ M⁻¹ for this supramolecular system. This value is similar to that reported for small molecule analogues indicating that the polymer chains do not significantly affect the supramolecular interaction strength.²⁶ Furthermore, the ITC binding isotherm resulting from addition of a concentrated aqueous solution of Py-PmDEGA (14.28 mM) to a dilute aqueous solution of Zn-TPP(PEG)₄ (1.49 mM) showed exothermic responses (Figure S10), indicating the binding events. Fitting of the ITC curve was, however, not straightforward due to the strong exothermic dilution of Py-PmDEGA in water. Nonetheless, the ITC confirms exothermic binding of Py-PmDEGA to ZnTPP(PEG)₄ with a K_a in the range of $10^3 - 10^4$ M⁻¹. For comparison, the binding affinity of ZnTPP(PEG)₄ with pyridine was also determined revealing a K_a of (1.92+0.1) x 10⁴ M⁻¹, which is close to the K_a of ZnTPP(PEG)₄ with Py-PmDEGA indicating that the polymer does not strongly influence the supramolecular association (Figure S11). Furthermore, the association constant was investigated at different temperatures indicating that there



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Figure 2. a: UV-Vis titration of Py-PmDEGA to a 5 μ M ZnTPP(PEG)₄ solution in Milli-Q water at 25 °C; b: absorbance changes of ZnTPP(PEG)₄ at 429.5 nm upon the addition of Py-PmDEGA; the red solid line is the binding isotherm obtained by the least-squares fit to the experimental data (R² = 0.99856).

was no significant effect of temperature at 10 $^{\circ}$ C, 25 $^{\circ}$ C and 40 $^{\circ}$ C, which are all below the cloud point transition temperature, on the association constant (Figure S12). At last, the effect of the pH of the solution (pH=1.68, 7.00 and 10.01) on the binding affinity was studied, also demonstrating roughly similar association constants (Figure S13).

Two-dimensional diffusion-ordered ¹H NMR spectroscopy (DOSY) is a simple and fast technique to determine diffusion coefficients of species in solution. The diffusion coefficient of the formed supramolecular miktoarm star block copolymer (one diffusion coefficient for the complex if fully associated) will differ from the free precursors and, therefore, can be used to further prove the formation of the supramolecular star polymer. Figure 3 shows the diffusion coefficients of the ZnTPP(PEG)₄, the Py-PmDEGA and the formed complex revealing that the diffusion coefficient for the complex is in between the two components. The lowest diffusion coefficient of the ZnTPP(PEG)₄ is rather surprising and indicates association of this component in water. The intermediate diffusion coefficient of the mixture of the two components demonstrates the existence of the uniform miktoarm star block copolymer and, apparently, the suppression of the ZnTPP(PEG)₄ agglomerates. Moreover, no signals for the free blocks were detected, which suggest the highly efficient association between the two blocks ZnTPP(PEG)₄ and Py-PmDGEA, at least at this concentration. The reversibility of the metal-ligand complexation can also be assessed by DOSY spectroscopy. The addition of a large excess amount of the competitive low molecular weight pyridine ligand induced the disassembly process of the complexation, observed from the diffusion coefficient value transition of Pv-PmDEGA. Hence. based on the



Figure 3. Diffusion coefficients, D, as function of the chemical shifts of the resonances associated with the initial polymer blocks (ZnTPP(PEG)₄ and Py-PmDEGA), the supramolecular AB₄ complex and the complex in the present of large excess amount of pyridine. The DOSY experiments were carried out at 2.02 mM in D₂O solution.

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DOSY measurements, it is evident that the supramolecular copolymer is capable of undergoing a reversible transition triggered by the addition of competitive ligand.

Apart from the investigation of the supramolecular interaction between the two building blocks, we also studied the effect of the complexation on the thermoresponsive behaviors of Py-PmDEGA. The phase transitions were determined by turbidimetry for Py-PmDEGA and the complex Py-PmDEGA@ZnTPP(PEG)₄ (Figure S14). The results indicated that the cloud point temperature of Py-PmDEGA did not significantly change after complexation. However, the hysteresis diminished after complexation, which may indicate that the hysteresis of PmDEGA could result from (de)protonation of the pyridine group upon phase transition and that this is no longer the case upon complexation.

In summary, a novel strategy is demonstrated for the preparation of supramolecular AB₄ miktoarm star block copolymers by association of a four-armed star-polymer with a Zn-porphyrin core and a pyridine end-functionalized polymer. The metalloporphyrin based star polymer was prepared by reaction between tetrakis (p-hydroxyphenyl)porphyrin and ptoluenesulfonyl-PEG followed by insertion of the metal ion into the porphyrin core. The synthesis of pyridine end-functionalized linear polymer was carried out via RAFT polymerization and subsequent aminolysis and Michael addition reaction. The building blocks were characterized by SEC, MALDI-TOF MS and ¹H NMR spectroscopy. The formation of the supramolecular miktoarm star polymer was investigated in H_2O or D_2O at 25 $^{\circ}C$ and successful formation was confirmed via a combination of UV-Vis spectrophotometric titration, ITC and DOSY NMR spectroscopy, while the stoichiometry was determined by Job plot analysis.

We propose that other even more complex dynamic macromolecular architectures can be constructed *via* metalloporphyrin-pyridine interaction. Taking into account that the supramolecular interaction and thermoresponsive polymer based architecture may be reversibly disassembled by applying various stimuli (temperature and the addition of competitive metal ion), this approach may open the way for the creation of a new family of responsive materials which expand the application areas of the conventional miktoarm star polymers.

Z. Hou thanks China Scholarship Council (NO. 20140765003) and Ghent University (BOF 01SC0415) for PhD scholarship. RH is grateful to BELSPO (IAP VII/5 Functional Supramolecular Systems FS2), FWO and UGent (BOF) for financial support.

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A novel strategy is reported for preparing a supramolecular miktostar polymer based on complexation of a metalloporphyrin based four-arm star polymer and a pyridine functionalized polymer

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