# Multi-functional supramolecular polymer networks as next generation consolidants for archaeological wood conservation

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**The preservation of our cultural heritage is of great importance to future generations. Despite this, significant problems have arisen with the conservation of waterlogged wooden artefacts. Three major issues facing conservators are structural instability upon drying, biological degradation and chemical degradation on account of $Fe^{3+}$ catalysed production of sulfuric and oxalic acid in the waterlogged timbers. Currently, no conservation treatment exists that effectively addresses all three issues simultaneously. A new conservation treatment is reported here based on a supramolecular polymer network constructed from natural polymers with dynamic crosslinking formed by a combination of both host-guest complexation and a strong siderophore pendant from a polymer backbone. Consequently, the proposed consolidant has the ability to chelate and trap iron while enhancing structural stability. The incorporation of anti-bacterial moieties through a dynamic covalent linkages into the network provides the material with improved biological resistance. Exploiting an environmentally compatible natural material with completely reversible chemistries is a safer, greener alternative to current strategies and may extend the lifetime of many culturally relevant waterlogged artefacts around the world.**

supramolecular polymers | conservation | waterlogged archaeological wood | Mary Rose

Abbreviations: CB[8], cucurbit[8]uril; MV, methyl viologen; BA, boronic acid

## Significance statement

The preservation of cultural heritage is of widespread importance all over the world. Yet the lack of development in the field of conservation treatments means the fate of some of the most culturally important artefacts in the world remain in jeopardy. In the preservation of waterlogged wooden artefacts, conservators rely almost exclusively on poly(ethylene glycol) doped with a broad-spectrum biocide. The concept of a chemotactic consolidant, one which can adapt to the artefact it is treating, as described in this manuscript has never before been described for an archaeological/conservation treatment. Additionally, the crosslinks holding the consolidant together are entirely reversible, resulting in a material which is a greener, safer, sustainable alternative to current conservation strategies.

## Introduction

The $16^{th}$ century *Mary Rose* was a marvel of her time, a world-class warship with state-of-the-art weaponry. She sank in battle in 1545 and lay submerged for over 400 years until she was raised in 1982.[1, 2] Centuries underwater have caused many complications in her preservation as the cellulosic components of the wood cells have been severely damaged from water-logging and biological action by marine organisms.[3, 4] The production of acid within the timbers [5, 6] from localised $Fe^{3+}$ deposits is a third contributor to the loss of cellulose, but has yet to be adequately addressed by conservation technologies.[7, 8]

For the last 20 years, the ship's timbers have been sprayed continuously with increasing concentrations of aq. poly(ethylene glycol) (PEG, max. 50 vol.%) containing a broad spectrum biocide.This treatment aims to support the cell walls, preventing collapse, while the biocide hinders biological growth. While PEG is easily applied, non-toxic and cheap, a number of significant disadvantages exist for the conservation process. The need for lengthy treatment makes PEG application costly; [9] additionally, PEG acts as a solid-state ion transporter [10] enabling the movement of acidic salts and iron through the timbers, creating more widespread chemical degradation issues. Finally, the action of bacteria, $Fe^{3+}$, natural acids, temperature and humidity on PEG can cause its degradation to acidic by-products over time.[9] It is clear from examination of PEG consolidants that another conservation strategy is necessary.[11]

Recently, alternative consolidants have appeared in literature with the focus moving towards oligoamides and natural polymers such as chitosan, guar and 2-hydroxyethyl cellulose.[11, 12, 13, 14] These represent renewable and environmentally friendly alternatives to PEG with no acidic degradation products, enhanced timber compatibility and a significantly reduced cost as they are often sourced as waste products from industrial processes. Despite such benefits, these materials alone do not offer a method of reducing or trapping $Fe^{3+}$.

Through a straightforward chemical functionalisation of chitosan and guar and addition of a macrocyclic host molecule,

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cucurbit[8]uril (CB[8]), a new supramolecular polymer network was developed for the conservation of water-logged wooden artefacts that simultaneously addresses the three major issues facing conservators (Fig. 1). Chitosan was selected on account of its native antibacterial properties, ability to form a gel network and readily accessible amine groups for functionalisation.[30] Guar shares the gelling ability of chitosan and is amenable to dynamic functionalisation through the diol unit. Neither polymer forms acidic by-products upon degradation.[11]

The ability to link polymers through dynamic and reversible interactions has received much attention recently.[15, 16, 17, 18] The functional consolidants developed here exploit the unique host-guest chemistry of CB[8] to link polymer chains and form dynamic networks in equilibrium.[17, 19] On account of its ability to bind two guests in its cavity simultaneously, CB[8] has gained much interest as a supramolecular physical crosslink.[20, 21, 31] This supramolecular 'handcuff' is particularly effective in joining together polymer chains to form 3D networks.[21, 22] Aqueous solutions of chitosan and guar, two naturally-sourced polymers, have been shown to provide enhanced structural support and stability at reduced concentrations.[11] Functionalising these polymers created a material tailored towards hindering biological activity and chelating catalytically active $Fe^{3+}$.

Electron poor ($1^{st}$ guest) and electron-rich ($2^{nd}$ guest) moieties pendant from the polymer chains facilitated physical crosslinking through CB[8] ternary complexation to create the dynamic network. The functionalisation of chitosan with both naphthol (Nap, CB[8] complexation) and catechol (Cat, siderophore) second guests was carried out using amidation/esterification chemistry. Appending a methyl viologen (MV, $1^{st}$ guest) proved more problematic on account of the chitosan's reducing environment. The use of a boronic acid (BA) functionalised viologen derivative (MV-BA) enabled attachment to guar through a boronic acid-diol dynamic covalent interaction. Coupled with the natural anti-bacterial properties of chitosan, MV-BA significantly enhanced the biocidal activity of the entire network.

Upon addition of CB[8] to the functionalised polymers, both chitosan polymers could be crosslinked with the MV-BA guar. The reversibility of the ternary complex formation and, therefore of the assembly of the polymer network, is of particular interest to this application. Formation and disassembly of the ternary complex can be mediated by heat and modulating the water content. As is described later, the CB[8] linkage provides the structural component for the consolidant. Thus, by manipulating the ternary complex with, most likely water content in this application due to the heat sensitivity of the archaeological timbers, the viscosity of the structural element can be controlled. This suggests that the material could be made to flow out of the conserved timbers at some later point after consolidant if required, a feature that is currently under investigation.

The catechol functionalised polymer binds more strongly to $Fe^{3+}$ than the CB[8] ternary complex; therefore, in the presence of $Fe^{3+}$ these metal-ligand interactions create an additional set of crosslinks further strengthening the system. On account of this difference in affinity, the naphthol functionalised chitosan is essential to preserve the network formed by CB[8] crosslinks. By using a combination of all three functional polymers, biological degradation (MV-BA, chitosan), iron saturation (catechol) and structural stability (guar, chitosan, CB[8] crosslinks) were all addressed in a single treatment (Fig. 1). Natural polymers provide the additional benefit of removing the plasticising effect of consolidants on the timbers.[11, 23] While none of the constituent materials of the polymer are themselves extraordinary or novel, the interaction of the various units and their assembly to form a multifunctional chemotactic consolidant material is completely innovative, to both this field and supramolecular chemistry in general, and results in a consolidant material which addresses the three most pressing issues facing conservators of waterlogged archaeological timbers.

## Results and Discussion

Confirmation of iron and sulfur deposits in the ship's hull (*Quercus rober*) were shown by SEM-EDX (See SI Appendix, Fig. S3-4). Formation of acid (oxalic, sulfuric, formic) can be attributed to both chemical and biological factors related to $Fe^{3+}$ saturation.[24] Chemical degradation relies on the catalytic activity of $Fe^{3+}$, present in high concentrations from corrosion of bolts used in the ship's construction 500 years ago. The $Fe^{3+}$ is capable of mediating the conversion of elemental sulfur in the wood (mainly from anaerobically reduced seawater sulfates) to sulfuric acid.[8] Naturally occurring oxalates in oak can be converted to oxalic acid through Fenton-type processes.[6, 25] Biological degradation occurs through an anaerobic sulfur-reducing bacteria (genus *Desulfovibrio* and *Desulfomaculatum*) present in the timbers, which also generates sulfuric acid.[24, 26] Both chemical and biological routes lead to damage of the cellulosic materials. Saturation of the timber with $Fe^{3+}$ may be addressed by washing small artefacts with solutions of iron chelators;[7] although promising in the laboratory, such techniques are impractical for artefacts the size of the *Mary Rose*. Unlike previous conservation treatments, the functional supramolecular polymer network presented here could trap $Fe^{3+}$ preventing its catalytic activity.

Three four-component polymer systems were examined, in all cases the 1st guest polymer was MV-BA guar, while the $2^{nd}$ guest polymer is either catechol (PolyCat), naphthol (PolyNap)or a 50:50 mixture of catechol and naphthol functionalised chitosan (PolyCatNap). The ability of PolyCat, PolyNap and PolyCatNap to chelate and trap $Fe^{3+}$ was first determined visually by addition of $Fe_2(SO_4)_3$ ($Fe^{3+}$) or $FeSO_4$ ($Fe^{2+}$) to each polymer solution (9 mM in water). Upon addition of $Fe^{3+}$, PolyCat and PolyCatNap changed from orange-brown to green-brown, while PolyNap became more intensely orange. The green hue indicated the formation of a catechol-$Fe^{3+}$ complex while the intense orange colour was likely due to an interaction between the free amines of the chitosan and $Fe^{3+}$. A similar orange colour was observed in all samples upon addition of $Fe^{2+}$, as amines preferentially bind to $Fe^{2+}$ while catechol has no interaction.

Introducing $Fe^{3+}$ to the PolyCatNap sample yielded an additional structuring effect to the polymer network by providing more crosslinks between the polymer chains through metal-ligand interactions. This enhanced crosslinking was illustrated by a simple inverted vial test (see SI Appendix, section S6) and confirmed by small angle X-ray scattering (SAXS), Fig. 2A. Such an effect was not observed in the PolyCat or PolyNap systems, as the formation of any metal-ligand interactions would in turn reduce the number of crosslinks from CB[8] ternary complexation in the PolyCat and cannot occur in PolyNap. Comparison of PolyCatNap by SAXS before and after addition of $Fe^{3+}$ indicates that PolyCatNap behaves as a micro-particulate gel with large particles solubilised in a polymer matrix (see SI Appendix, section S6) in the absence of $Fe^{3+}$.[32, 33, 34, 35, 36] At pH 6.5, the gel particles are likely due to H-bonding between chitosan chains, which would not be expected of guar below pH 9, leaving guar

as the solubilising matrix. When $Fe^{3+}$ was added, the particulate nature of PolyCatNap diminished and an enhanced polymer network formed.

Ordering was achieved by a combination of metal-ligand and ternary complex crosslinks through the host-guest system. Visual inspection of the samples coupled with SAXS data confirmed that PolyCatNap readily and selectively binds $Fe^{3+}$, one of the three development criteria for a new consolidant.

Rheological studies were carried out on PolyCat, PolyNap, PolyCatNap and their constituent materials. Data obtained was compared with currently-used consolidants, PEG200 and PEG2000.[11] At standard concentrations, there was little difference in the viscosity of unfunctionalised guar, chitosan and PEG solutions. The PolyCat, PolyNap and PolyCatNap materials, however, have a significantly enhanced solution viscosity and shear strength. On addition of $Fe^{3+}$, PolyCatNap (Fig. 2B) and PolyCat (See SI Appendix, Fig. S8) transition from 'gel-like' materials to gels, with G'$\geq$G" over almost the entire shear range (3 decades). This response is ideal as wood cells in the vicinity of $Fe^{3+}$ deposits will likely be the most damaged on account of a high local acid concentration. In contrast, all three polymer networks displayed a decrease in viscosity upon addition of $Fe^{2+}$ (Fig. 2B). Such a chemotactic phenomenon is critical for the use of these materials as consolidants; when $Fe^{3+}$ is absent the material flows readily (through the timbers), secondary crosslinks form only when $Fe^{3+}$ is encountered with concommitant *in situ* strengthening of the material.

Rheology and SAXS indicated that the PolyCatNap system showed the best structural enhancement with iron chelation and was subjected to biological resistance tests. To determine the effect of PolyCatNap on bacterial growth, three species were cultured in the presence of PolyCatNap and suitable controls in Mueller-Hinton broth (10% v/v, Fig. 3). The bacterial species tested were Gram-negative *Pseudomonas aeruginosa* [27] and *Escherichia coli* and Gram-positive *Staphylococcus aureus*, all detected in the timbers of the *Mary Rose*. Growth was monitored every 2 h according to a previously described method [28] (See SI Appendix, section S9).

Growth of all three species was inhibited in the presence of both PolyCatNap and chitosan over an 8 h period. Intriguingly, growth was enhanced by unfuctionalised guar relative to the negative control. It is noteworthy that while PolyCatNap does contain guar, bacterial growth is still completely inhibited, likely due to the presence of the MV-BA moiety. Although growth was moderately reduced by PEG200 compared to the negative control, complete inhibition was only observed in the presence of chitosan, a known anti-bacterial agent [29], and PolyCatNap. The mode of action of PolyCatNap is unknown, yet it could potentially be exhibiting a dual antibacterial effect by; 1) the strong chelation of iron, which is essential for bacterial metabolism and survival, and 2) the presence of the antibacterial MV in the polymer backbone. Biological studies combined with rheological and SAXS data confirmed that PolyCatNap fulfils all three idealised criteria for a new consolidant material and has the potential to be a significant improvement on the state-of-the-art PEG treatments.

Understanding the long-term ageing behaviour of this new consolidant material is extremely important to its future use. Performing accelerated ageing experiments is a convenient method of obtaining information on he degradation behaviour of the material in a reduced amount of time.[9] On account of the sensitivity of the CB[8] complex to temperatures in excess of 60°C (reversibility of the handcuff effect at elevated temperatures), it was not possible to conduct a standard ageing experiment with this material, such as described by Mortensen *et al.*[9] We have, however, recently studied the degradation behaviour of unfunctionalised natural polymers and found no negative effects of the accelerated ageing compared to PEG.[11] In order to understand long-term behaviour of these materials, particularly the effect of the natural degradation of the wood on the material, more than 10 pieces of previously untreated waterlogged oak from the *Mary Rose* in 1 cm x 1 cm x 0.25 cm dimensions were treated with the new conservation materials. These pieces will be observed regularly over the coming months and years for changes in the appearance of the timber to provide more information on the long-term behaviour of these new consolidants.

Consolidant infiltration of timbers is also a long-term process, requiring months to years to extract meaningful results. Shorter-term experiments can, however, be useful to determine whether PolyCatNap might realistically replace PEG in the treatment of water-logged archaeological timbers. Both high resolution FT-IR imaging and surface treatment experiments were carried out on sections of an oak (*Quercus rober)* supporting beam and an oak chisel handle (raised with the *Mary Rose*), respectively.

Analysis with the IRENI beamline of 10$\mu$m thick untreated and PolyCatNap treated samples showed that similarities exist in the characteristic cellulose (1347–1400 $cm^{-1}$) and lignin (1486–1529 $cm^{-1}$) regions as expected, however, the samples exhibited distinctly different intensities in the N–H region (1630–1690 $cm^{-1}$).[37, 38, 39, 40] As the chitosan polymers have a high N–H content, it is deduced that this increase in intensity signified the presence of chitosan polymers in the wood cells. Interestingly, hotspots appeared in the characteristic cellulose region in the PolyCatNap treated sample, which are not present prior to treatment. These hotspots are likely due to the presence of the boronic ester (MV-BA) whose characteristic signals occur in the same region as cellulose. The IR data confirmed that the PolyCatNap infiltrated the damaged timbers where it acted as a three-pronged consolidant, conferring structural stability and bacterial protection to the wood while acting as an $Fe^{3+}$ scavenger. Additionally, analysis of the treated sample exhibited only a 30% shrinkage in the PolyCatNap treated sample (See SI Appendix, Fig. S9) compared to over 50% without any treatment.Even after such a short treatment noticeable improvements are observed in the artefact, a promising outcome of these preliminary tests.

Finally, the PolyCatNap system also showed great promise as a surface treatment on artefacts with significant surface iron deposits. Solutions of PolyCatNap and unfunctionalised chitosan (4% w/v) were applied to visible iron deposits on an oak chisel handle (Fig. 4B). Within a week of drying the PolyCatNap had incorporated a significant amount of the surface iron into the functional network and began delaminating from the artefact surface. In fact, it was possible to manually remove the surface salt layer through the self-assembled network material without damaging the artefact or leaving behind any visible residue; moreover, after 22 months of visual observation, no surface salts have reappeared. Chitosan alone did not provide sufficient surface treatment confirming the need for the multi-component PolyCatNap system.

## Conclusion

The combination of SAXS, IR imaging, rheology and biological testing along with evaluation of surface treatment clearly shows the designed functional supramolecular polymer network can simultaneously address the three major issues facing conservators of waterlogged wooden artefacts. While long-

term studies to elucidate the diffusion of these materials in larger artefacts are necessary, the PolyCatNap system already represents a real and quantifiable advantage over current PEG treatments. With the relative ease of polymer functionalisation, tailoring the dynamic network to address other issues in conservation science such as Fe/Cu inclusions in wood, leather and bone and degradation of iron-gall inks in precious manuscripts is imminently possible. Additionally, with similar chemical functionalities, aqueous-based multi-functional orthogonal supramolecular polymer systems such as PolyCatNap have the potential to expand beyond conservation into the treatment of metal-based blood disorders (haemochromatosis and thalassaemias). Thus, the system can be readily tuned and the true power of supramolecular self assembly realised and appreciated by the general public.

## Materials and Methods

**Synthesis of 1-(4-boronobenzyl)-1'-methyl-[4,4'-bipyridine]-1,1'-diium (MV-BA).** 1-methyl-4,4'-bipyridinium was first synthesised from 4,4'-bipyridine from a standard literature method. Following this, (4-(bromomethyl)phenyl)boronic acid (100 mg, 0.47 mmol) and 1-methyl-4,4'-bipyridinium (120 mg, 0.40 mmol) were dissolved in acetonitrile (4 ml) and the solution heated to reflux overnight. The resulting red solid was isolated by filtration and recrystallised from ethanol, containing a few drops of water, to yield a red solid (132.2 mg, 0.28 mmol, 70%). Further details of all syntheses are given in the **SI Materials and Methods**.

**Preparation of biopolymers.** Guar (20 g) was stirred in water (2 L, 50○C) overnight. The resulting suspension was centrifuged at 3500 RPM for 2 min, the supernatant precipitated from ethanol, isolated by filtration, dried under vacuum and ground to yield a white powder. For each functionalisation experiment chitosan was prepared fresh using the general procedure that 3 wt.% chitosan (approx. 720 mg) was stirred in 1 vol.% acetic acid (approx. 20 ml) at pH 6 until all of the chitosan was dissolved and a viscous yellow liquid was obtained. This liquid was then added into the reaction vials to be functionalised with pendant guest molecules.

**Functionalisation of chitosan with 3,4-dihydroxyphenylacetic acid (PolyCat)or 2-naphthylacetic acid (PolyNap).** Either 3,4-dihydroxyphenylacetic acid (HPAA) or 2-naphthylacetic acid (NPAA) was stirred for 24 h with 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC) in an equimolar ratio, in order to aminate the carboxylic acid of the HPAA or NPAA. After 24 h a 3 wt.% solution of chitosan in 1 vol.% acetic acid was added to the guest solution in a molar ratio of 0.2:1 (functional group:chitosan) and stirred for a further 72 h to attach the aminated guest molecule to the free amine on the chitosan backbone. After 72 h the polymer was precipitated from solution using a 10 wt.% solution of NaOH, which was then filtered and washed with copious amounts of water (approx. 3 L) to return the pH to neutral. The material was then collected and frozen in dry ice and then lyophilised for 72 h before use.

**Formation of the gel-like consolidant materials.** Gels were prepared by weighing 10 mg of guar, 1 mg of MV-BA, 30 mg of the HPAA-CS or NPAA-CS (or a 1:1 mixture of the two polymers) and 4 mg of cucurbit[8]uril into a clean vial and solvating in 4 ml of a 1 vol.% solution of acetic acid by stirring overnight on a magnetic stirring plate. Once prepared the HPAA containing gels appeared brown/orange in colour, while the NPAA containing gels are white, combination gels were an opaque, beige colour.

**Preparation of samples for analysis on IR beamline.** Samples were prepared by placing a 1 cm x 1 cm x 0.25 cm piece of supporting beam in the PolyCatNap solution for 1 week, followed by storage in a sealed environment for 1 week and finally freeze-dried to remove water. 10 $\mu$m slices of these samples were cut with a microtome and laid flat on standard glass microscope slides for analysis.

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1. Bell LS, Thorp JAL, Elkerton A (2009) The sinking of the Mary Rose: A medieval mystery solved? J Arch Sci 36:166-173.
2. Millard AR, Schroeder H (2010) 'True British Sailors': A comment on the origin of the men of the Mary Rose. J Arch Sci 37:680-682.
3. Bjurhager I, et al. (2012) State of degradation in archaeological oak from the $17^{th}$ century Vasa ship: Substantial strength loss correlates with reduction in holo(cellulose) molecular weight. Biomacromolecules 13:2521.
4. Bjordal CG, Nilsson T, Daniel G (1999) Microbial decay of waterlogged archaeological wood found in Sweden applicable to archaeology and conservation. Int Biodeterior Biodegrad 43:63-73.
5. Almkvist G, Persson I (2008) Degradation of polyethylene glycol and hemicellulose in the Vasa. Holzforschung 62:64-70.
6. Almkvist G, Persson I (2008) Fenton-induced degradation of polyethylene glycol and oak holocellulose. A model experiment in comparison to changes observed in conserved waterlogged wood. Holzforschung 62:704-708.
7. Fors Y, Sandström M (2006) Sulfur and iron in shipwrecks cause conservation concerns. Chem Soc Rev 35:399-415.
8. Sandström M, et al. (2002) Deterioration of the seventeenth-century warship Vasa by internal formation of sulphuric acid. Nature 415:893-897.
9. Mortensen MN, Egsgaard H, Hvilsted S, Shashoua Y, Glastrup J (2007) Characterisation of the polyethylene glycol impregnation of the swedish warship Vasa and one of the Danish Skuldev Viking ships. J Arch Sci 34:1211-1218.
10. Gray FM (1997) Polymer Electrolytes, RSC Materials Monographs, Royal Society of Chemistry
11. Walsh Z, Janeček E-R, Jones M, Scherman OA (2014) Natural polymers as alternative consolidants for the preservation of waterlogged archaeological wood. Stud Conservat accepted.
12. Cipriani G, Salvini A, Baglioni P, Bucciarelli E (2010) Cellulose as a renewable resource for the synthesis of wood consolidants. J Appl Polym Sci 118:2939-2950.
13. Cipriani G, Salvini A, Fioravanti M, diGiulio G, Malavolti M (2013) Synthesis of hydroxylated oligoamides for their use in wood conservation. J Appl Polym Sci 127:420-431.
14. Christensen M, Kutzke H, Hansen FK (2012) New materials used for the consolidation of archaeological wood – past attempts, present struggles, and future requirements. J Cult Her 13:S183-S190.
15. Lehn J-M (2002) Toward self-organization and complex matter. Science 295:2400-2403.
16. deGreef TFA, Meijer EW (2008) Supramolecular polymers. Nature 453:171-173.
17. Zhang J, et al. (2012) One-step fabrication of supramolecular microcapsules from microfluidic droplets. Science 335:690-694.
18. Service RF (2005) How far can we push chemical self-assembly? Science 309:95.
19. del Barrio J, et al. (2013) Photocontrol over cucurbit[8]uril complexes: Stoichiometry and supramolecular polymers. J Am Chem Soc 135:11760-11763.
20. Kim HJ, et al. (2001) Selective inclusion of a hetero-guest pair in a molecular host: Formation of stable charge-transfer complexes in cucurbit[8]uril. Angew Chem, Int Ed 40:1526-1529.
21. Appel EA, et al. (2010) Supramolecular cross-linked networks via host-guest complexation with cucurbit[8]uril. J Am Chem Soc 132:14251-14260.
22. Rauwald U, Scherman OA (2008) Supramolecular block copolymers with cucurbit[8]uril in water. Angew Chem, Int Ed 47:3950-3953.
23. Bardet M, Gerbaud G, Tran QK, Hediger S (2007) Study of interaction between polyethylene glycol and archaeological wood components by C-13 high-resolution solid-state CP-MAS NMR. J Arch Sci 34:1670-1676.
24. May E, Jones M (2008) Molecular Bacterial Diversity in the Timbers of the Tudor Warship the Mary Rose. Heritage Microbiology and Science: Microbes, Monuments and Maritime Materials, Royal Society of Chemistry pp. 204-218.
25. Almkvist G, Persson I (2008) Analysis of acids and degradation products related to iron and sulfur in the Swedish warship Vasa. Holzforschung 62:694-703.
26. Berko A, et al. (2009) XAS studies of the effectiveness of iron chelating treatments of Mary Rose timbers. J Phys: Conf Ser 190:012147.
27. Sun H-Y, Fukitani S, Quintiliani R, Yu VL (2011) Pneumonia due to pseudomonas aeruginosa: Part ii: Antimicrobial resistance, pharmacodynamic concepts, and antibiotic therapy. Chest 139:1172-1185.
28. Tokura S, Ueno K, Miyazaki S, Nishi N (1997) Molecular weight dependent antimicrobial activity by chitosan. Macromol Symp 120:1-9.
29. Raafat D, von Bargen K, Haas A, Sahl H-G (2008) Insights into the mode of action of chitosan as an antibacterial compound. Appl Environ Microbiol 74:3764-3773.
30. Chenite A, Buschmann M, Wang D, Chaput C, Kandani N (2001) Rheological characterisation of thermogelling chitosan/glycerol-phosphate solutions. Carbohydr Polym 46:39-47.
31. Rauwald U, Biedermann F, Deroo S, Robinson CV, Scherman OA (2010) Correlating solution binding and ESI-MS stabilities by incorporating solvation effects in a confined cucurbit[8]uril system. J Phys Chem B 114:8606-8615.
32. Horkay F, Hecht A-M, Mallam S, Geissler E, Rennie AR (1991) Macroscopic and microscopic thermodynamic observations in swollen poly(vinyl acetate) networks. Macromolecules 24:2896-2902.

33. Pezron I, Djabourov M, Leblond J (1991) Conformation of gelatin chains in aqueous solutions: 1. A light and small-angle neutron scattering study. Polymer 32:3201-3210.
34. Debye P, Bueche A (1949) Scattering by an inhomogeneous solid. J Appl Phys 20:518-525.
35. Koberstein JT, Picot C, Benoit H (1985) Light and neutron scattering studies of excess low-angle scattering in moderately concentrated polystyrene solutions. Polymer 26:673-681.
36. Mallam S, Horkay F, Hecht A-M, Geissler E (1989) Scattering and swelling properties of inhomogeneous polyacrylamide gels. Macromolecules 22:3356-3361.
37. Nasse MJ, et al. (2011) High-resolution Fourier-transform infrared chemical imaging with multiple synchrotron beams. Nature Meth 8:413-416.
38. Nasse MJ, et al. (2011) Multi-beam synchrotron infrared chemical imaging with high spatial resolution: Beam line realization and first reports on image restoration. Nucl Instr Meth A 649:172-176.
39. Hirschmugl CJ, Gough KM (2012) Fourier transform infrared spectrochemical imaging: Review of design and applications with a focal plane array and multiple beam synchrotron radiation source. Appl Spectrosc 66:475-490.
40. Kastyak-Ibrahim MZ, et al. (2012) Biochemical label-free tissue imaging with subcellular-resolution synchrotron FTIR with focal plane array detector. NeuroImage 60:376-383.

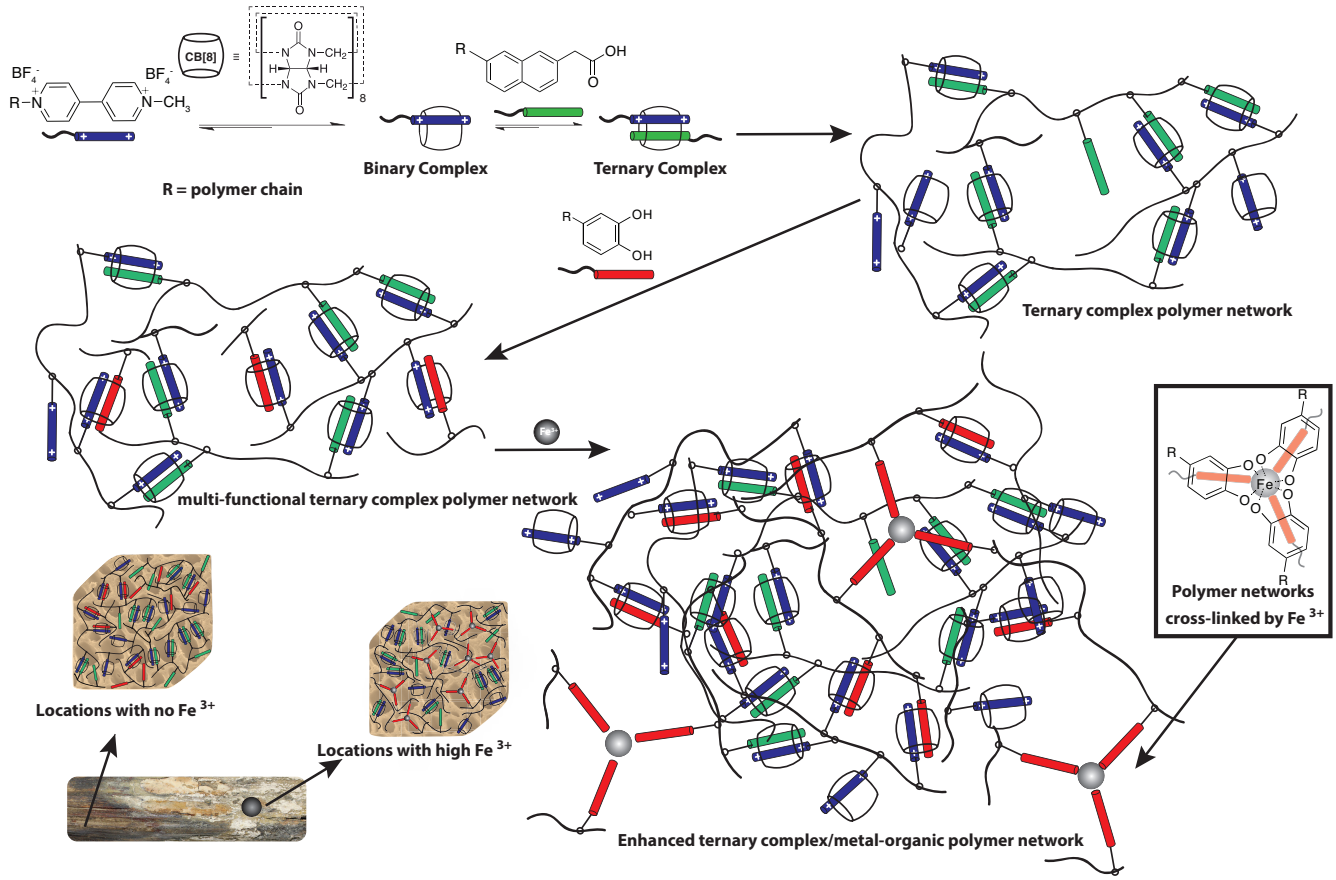


**Fig. 1.** Supramolecular consolidants: Schematic representation of the formation of the functional supramolecular polymer network and its suggested differing behaviours within timbers which have a low or high iron concentration, showing the dynamic behaviour of the material.

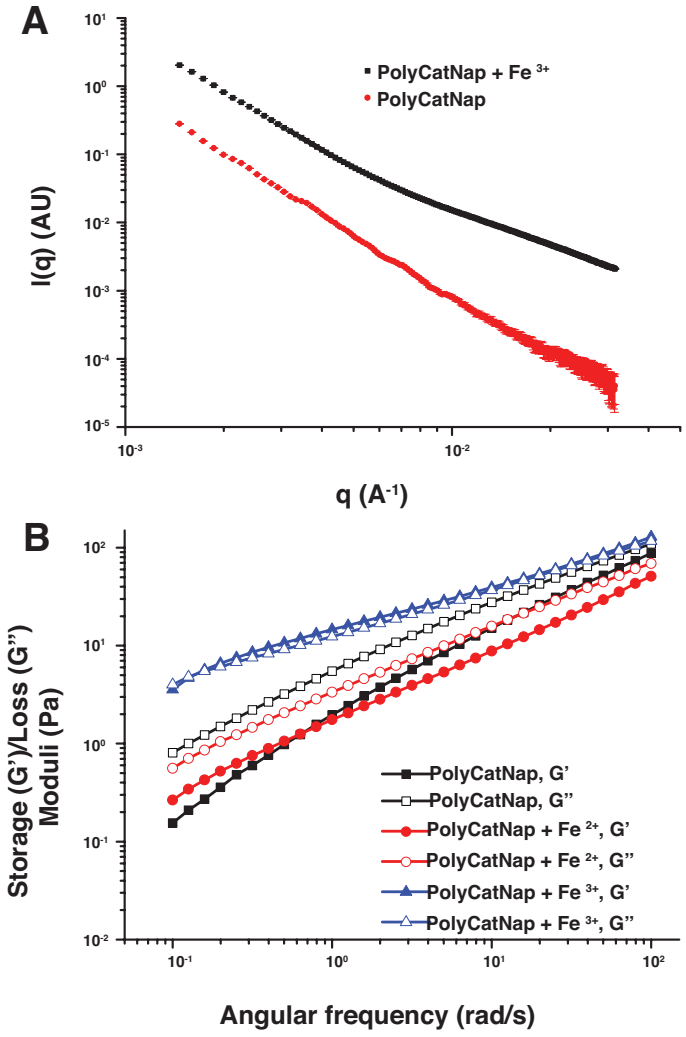


**Fig. 2.** Effect of iron on the polymer network: (A) Inverted vial test showing PolyCatNap (top) and the effect of the addition of $Fe^{2+}$ (bottom left) and $Fe^{3+}$ (bottom right) to the system, (B) SAXS data showing the change in the structure of the networks in the presence (black line) and absence (red line) of $Fe^{3+}$, (C) angular frequency (rad $s^{-1}$) *vs.* storage (G')/loss (G") moduli for PolyCatNap (black), PolyCatNap with $Fe^{3+}$ (red), PolyCatNap with $Fe^{2+}$ (blue) and (D) angular frequency (rad $s^{-1}$) *vs.* complex viscosity (Pa.s) for PolyCatNap (black), PolyCatNap with $Fe^{3+}$ (red), PolyCatNap with $Fe^{2+}$ (blue).

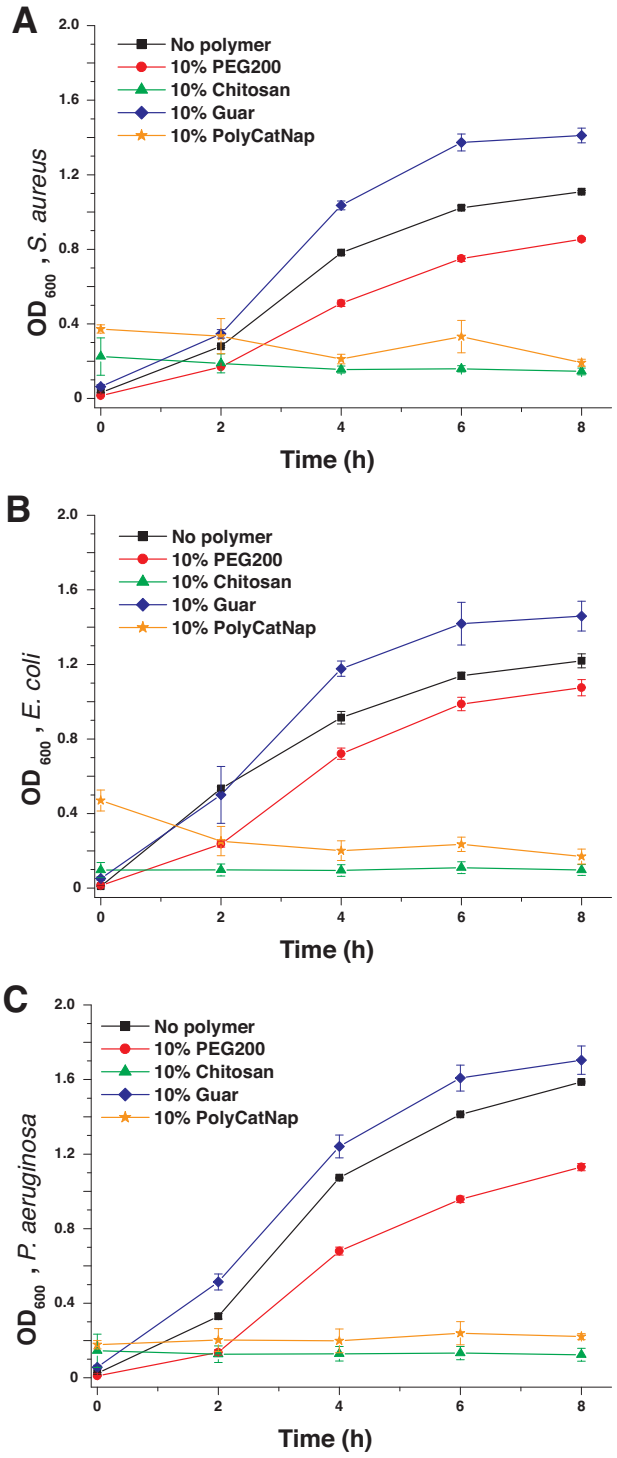


**Fig. 3.** Biological resistance of the polymer network: Activity of the negative control (black), PEG200 (red), chitosan (green), guar (blue) and PolyCatNap (orange), all at 10% v/v, against bacterial growth are shown in plots of time (h) *vs.* $OD_{600nm}$ for (A) *Staphylococcus aureus*, (B) *Escherichia coli* and (C) *Pseudemonas aeruginosa*.

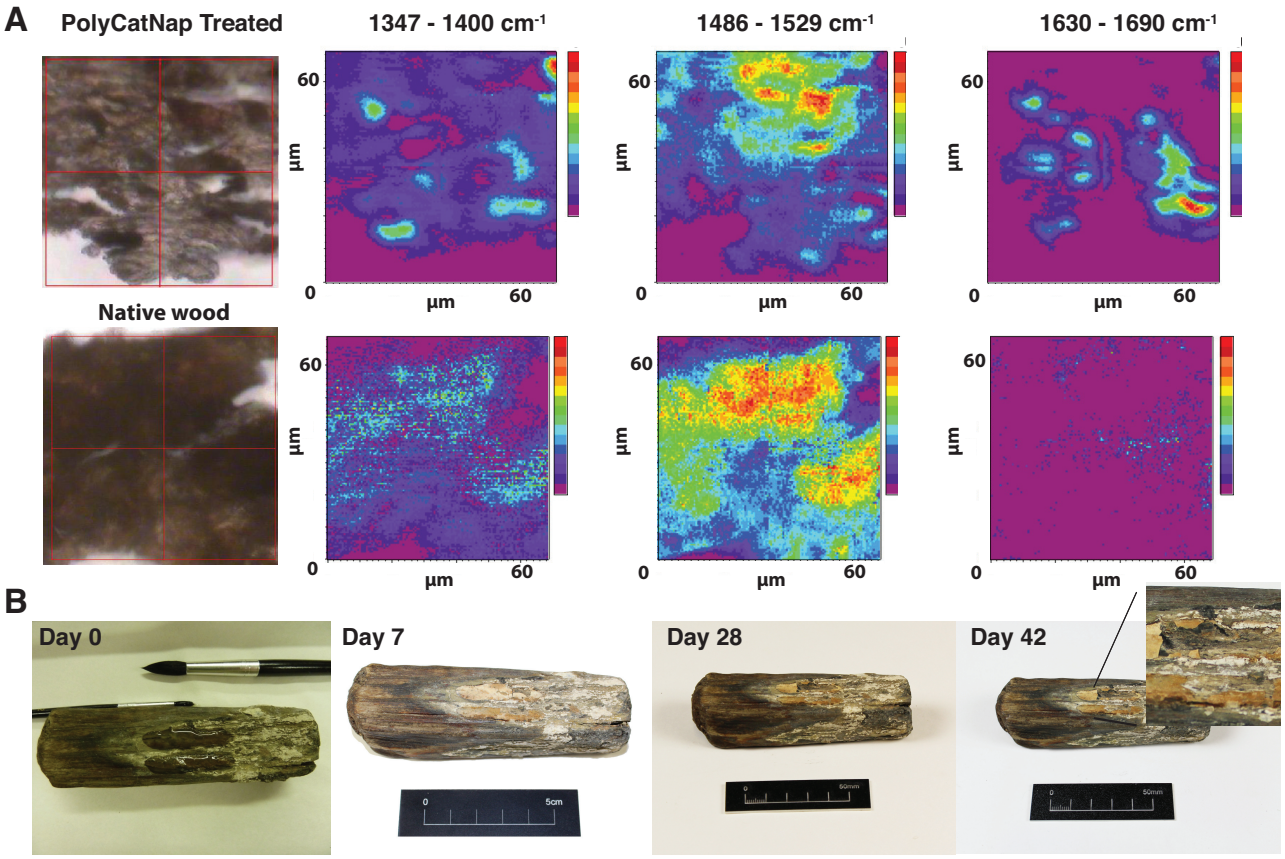


**Fig. 4.** Treatment of *Mary Rose* timbers: (A) Optical microscope (left) and images of integration over specific spectral regions (right) from high-resolution FT-IR imaging which shows the characteristic signals of cellulose (1347–1400 $cm^{-1}$) and lignin (1486–1529 $cm^{-1}$) in both treated and untreated wood and those of chitosan (1630–1690 $cm^{-1}$) in the PolyCatNap treated sample, on a high-low absorbance scale where violet is 'low' and red is 'high'. (B) photographic images of the treatment with PolyCatNap (1) and pure chitosan (2) of a chisel handle found on board the *Mary Rose* with significant surface iron deposits over a period of 6 weeks, (inset) with removal of the treatment to leave a cleaned artefact surface