

Silica Mineralization of DNA-Inspired 1D and 2D Supramolecular Polymers

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The preparation of hybrid materials from supramolecular polymers through the sol-gel process is presented. Supramolecular polymers are assembled from phosphodiester-linked pyrene oligomers and act as water-soluble one- or two-dimensional templates for silicification. The fibrillary and planar morphologies of the assemblies, as well as the excitonic interactions between the chromophores, remain unaffected by the silicification process.

The mineralization of organic matter is an essential natural process that serves as a source of inspiration for the development of hybrid systems in materials science.^[1,2] A special place in the realm of hybrid systems belongs to silicates prepared through the sol-gel process.^[3,4] These functional materials find widespread applications in many fields, including biocompatible delivery and visualization, surface patterning, adsorption, separation, and sensing techniques.^[5–7] The key step in the synthesis of such materials is the polycondensation of silica precursors. Self-assembled organic molecules can serve as templates for the synthesis of mesoporous silicates.^[8–11] The structural design of organic templates enables the imprinting of sophisticated morphological features into 3D shapes through silicification.^[12,13]

The usage of nucleic acids as templates for the synthesis of hybrid materials has received considerable attention over recent years.^[14] DNA possesses several properties that are beneficial for this purpose, such as a long-range order in chiral helices or the possibility to form liquid-crystalline phases.^[15] Che^[16,17] and Shinkai^[18] pioneered the field of silicification of nucleic acids. Introducing co-interacting reagents was a major breakthrough, which led to the various applications, including

chiral optical materials.^[19–21] Recently, Grass and co-workers showed that silica is a perfect environment to preserve nucleic acids for the information storage and biomedical purposes.^[22–24] Mirkin and co-workers used silicification to generate stable nanoparticle superlattices,^[25] which were further converted into catalytically active materials.^[26]

The availability of water-soluble bio-inspired materials^[27,28] would be a considerable extension for the design of silicified hybrid materials. In our previous studies, we developed several systems capable of mimicking various aspects of nucleic acids.^[29–32] For this purpose, we took advantage of the supramolecular polymerization of short aromatic oligophosphates.^[28,30,33] These self-assembled structures appear as one- or two-dimensional objects sharing common structural features—a hydrophobic core of aromatic chromophores shielded from the aqueous environment by a network of negatively charged phosphates.^[34–36] Here, we propose a strategy to access fibrillar and planar hybrid materials from polyanionic supramolecular polymers.

The synthesis of free-standing nanoscale silica fibers and sheets remains challenging and highly desirable.^[37–40] We demonstrate, herein, two kinds of supramolecular polymers acting as 1D or 2D templates for the controlled growth of a silica coating (Figure 1). The supramolecular polymers are accessible

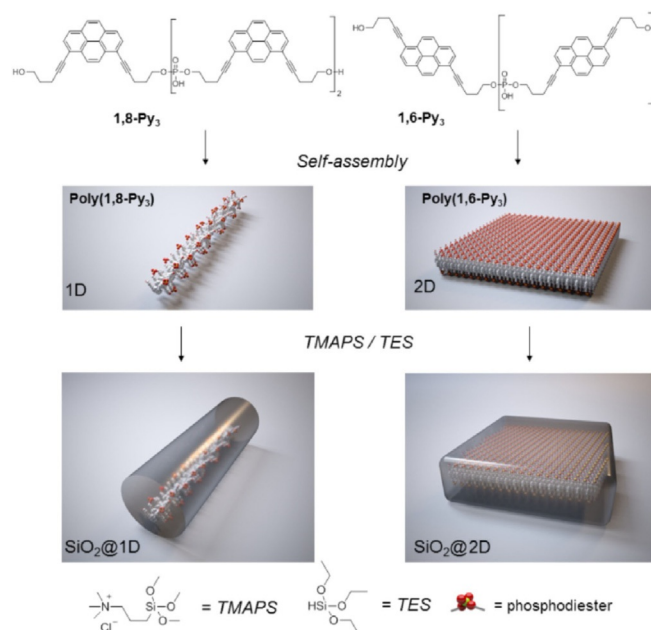


Figure 1. Illustration of the self-assembly of 1,8-Py₃ and 1,6-Py₃ into morphologically defined supramolecular polymers and subsequent silicification of the self-assembled structures.

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via the self-assembly of trimers of two types of phosphodiester-linked, disubstituted pyrenes, **1,8-Py₃** and **1,6-Py₃**. Both oligomers are prepared through solid-phase synthesis by using phosphoramidite chemistry and finally purified using reversed-phase (RP) HPLC (see the Supporting Information).^[41] The trimers self-assemble into morphologically defined structures, that is, **1,8-Py₃** forms micrometer-long fibers and **1,6-Py₃** yields nanometer thin sheets.

Self-assembly of the aromatic oligophosphates is conveniently followed spectroscopically. The supramolecular polymerization process occurs during slow cooling of a micromolar solution of the trimer in a buffered aqueous medium from 90 °C to room temperature. The self-assembly process is largely driven by hydrophobic and aromatic stacking interactions between alkynyl-substituted pyrenes. At 20 °C, both **1,8-Py₃** and **1,6-Py₃** exist in the assembled state. In the UV/Vis spectrum of **1,8-Py₃**, the bands assigned to the first electronic transition are red-shifted in the aggregated form and appear with maxima at 372 and 398 nm (Figure 2A). The fluorescence spectrum at 20 °C is dominated by a pyrene excimer signal with a maximum at 516 nm (Figure S1A). As described before,^[34] the self-assembly of **1,6-Py₃** is manifested by the emergence of J ($\lambda_{\text{max}} = 305$ nm) and H bands ($\lambda_{\text{max}} = 335$ nm) as a result of exciton interactions between pyrenes in 2D confinement (Figure 2B). In the fluorescence spectrum, both monomer and excimer emission signals are present (Figure S1B).

A two-step protocol is used to grow a silica shell on the supramolecular polymers. First, an ion-pair forming reagent, tri-

methyl[3-(trimethoxysilyl)propyl]ammonium chloride (TMAPS), binds to the negatively charged phosphates along the supramolecular polymers, thus creating nucleation centers for the following silanization.^[15] Second, addition of triethoxysilane (TES) as a condensation agent^[24] leads to the growth of a silica shell on the 1D and 2D templates, resulting in the formation of **SiO₂@1,8-Py₃** and **SiO₂@1,6-Py₃**, respectively (Figure 1). The silanized products are purified through repetitive centrifugation–washing cycles. Importantly, UV/Vis data show that the excitonic interactions between pyrene units remain largely undisturbed during and after the silanization process. This proves that the supramolecular polymers retain their native structures after encapsulation within the silicate matrix. For the 1D supramolecular polymers, the spectrum of **1,8-Py₃** in the aqueous solution resembles the one of **SiO₂@1,8-Py₃**; the spectra exhibit coinciding absorption maxima (Figure 2C). Also, for the 2D supramolecular polymers, the characteristic bands of **1,6-Py₃** at 305 and 335 nm remain at the same positions in the silanized state. TEM measurements further confirmed that the silica growth occurs on the supramolecular templates to yield morphologically defined shapes. Figure 3 highlights the difference between pristine (Figures 3A and 3B) and silanized fibers (Figures 3C and 3D). Pristine fibers of **1,8-Py₃** appear as thin objects with a width below 10 nm. Silanized **SiO₂@1,8-Py₃** fibers, in turn, exhibit a larger width (15–20 nm), owing to the presence of the silica shell. Typical TEM images of the silanized 2D supramolecular polymers are shown in Figure 4. Once encapsulated in the silica matrix, the 2D assemblies have lost their flexible nature and their folded texture trapped.

In conclusion, we have presented a new approach toward the synthesis of hybrid materials through the silicification of 1D and 2D supramolecular templates. Both templates, fibers and sheets, consist of a self-assembled core of stacked pyr-

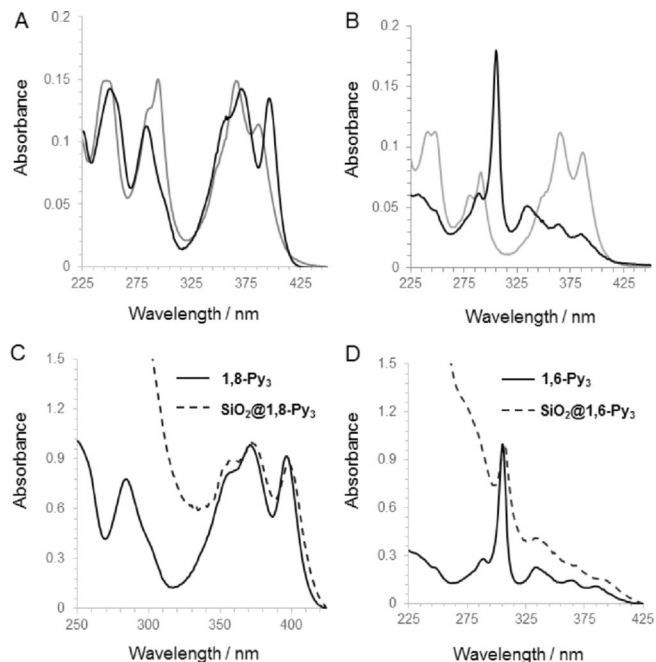


Figure 2. UV/Vis spectra. A) 2 μM **1,8-Py₃** at 20 °C (black) and 90 °C (grey); B) 2 μM **1,6-Py₃** at 20 °C (black) and 80 °C (grey); C) normalized at 368 nm absorption for **1,8-Py₃** and **SiO₂@1,8-Py₃** at 20 °C; D) normalized at 305 nm absorption for **1,6-Py₃** and **SiO₂@1,6-Py₃** at 20 °C. Conditions for (A) and (C): 10 mM sodium chloride, 10 mM phosphate buffer pH 7.0. Conditions for (B) and (D): 10 mM sodium chloride, 10 mM phosphate buffer pH 7.0, ethanol 15% vol.

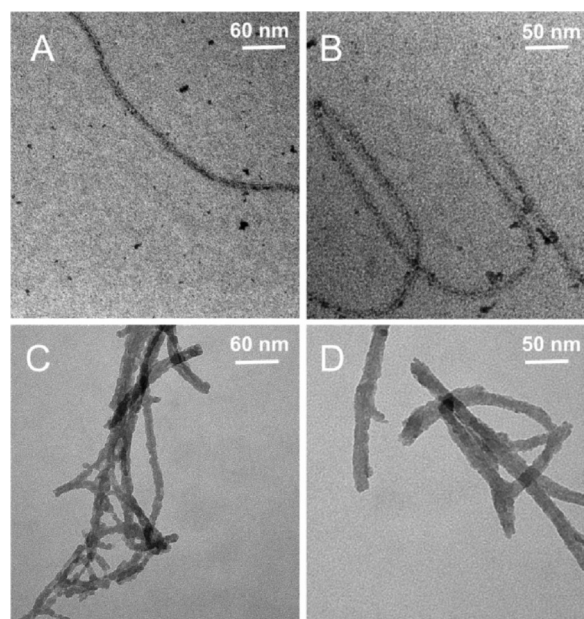


Figure 3. TEM images of self-assembled **1,8-Py₃** without silica shell (A, B) and **SiO₂@1,8-Py₃** (C, D).

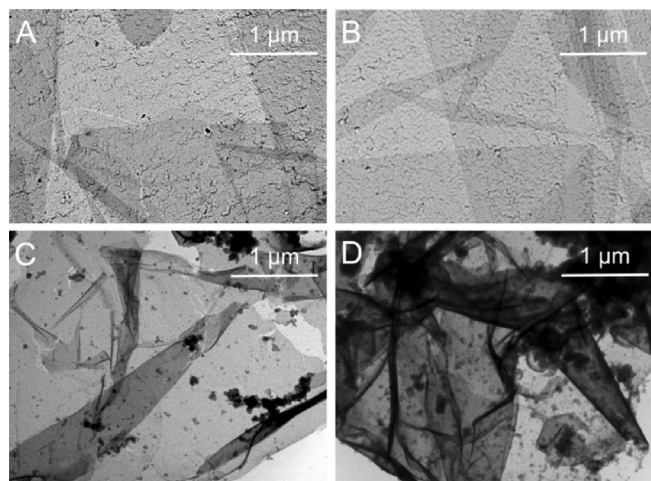


Figure 4. TEM images of self-assembled 1,6-Py₃ without silica shell (A, B) and SiO₂@1,6-Py₃ (C, D).

enes, which is covered on the outside by a network of phosphates mimicking some of the structural aspects of DNA. The morphological and optical properties of the mineralized polymers remain unaffected by the silicification process. As the structural and electronic properties of the oligophosphates are readily tailored by the chemical structure of the aromatic moieties, such supramolecular polymers may help to extend the range of architectures and potential applications of hybrid materials.

Experimental Section

Oligophosphate Synthesis

Oligomers 1,8-Py₃ and 1,6-Py₃ were prepared on an ABI 394 DNA synthesizer by using the respective phosphoramidite building blocks (0.1 M in DCM) on 1 μmol of Universal Support III PS (Glen Research).^[34] The oligomers (DMT-off) were cleaved from the solid support by treatment with 2 M ammonia in methanol (0.9 mL) for 16 h at 55 °C in microcentrifuge tubes tightly sealed with a screw cap. Supernatants were collected, treated with 0.9 mL of 28% aqueous ammonia for 30 min at 20 °C, and lyophilized. The lyophilized samples were purified by using RP HPLC (see the Supporting Information).

Self-Assembly of Supramolecular Polymers

A solution of the 1,8-Py₃ (50 μM) in water containing 10 mM sodium chloride and 10 mM phosphate buffer at pH 7.0 was slowly heated to 90 °C (0.5 °C min⁻¹) in a heating block. After reaching 90 °C, the solution was cooled (0.1 °C min⁻¹) to room temperature. The self-assembly of 1,6-Py₃ followed the same procedure except for using water containing 15% of ethanol (v/v).

Silicification

To a solution of the self-assembled 1,8-Py₃ in or 1,6-Py₃, TMAPS (TCI, 100 equivalents relative to phosphates) was added. The obtained solution was gently shaken (600 rpm) for 15 min at 20 °C. Growth of the silica shell was triggered by the addition of TES (Al-

drich, 1000 equiv relative to phosphates). The suspension was left under gentle shaking (600 rpm) for 4 days at 20 °C. The samples were purified by three rounds of centrifugation and resuspension in water.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: polyphosphates • pyrenes • self-assembly • silicification • supramolecular polymers

- [1] E. Dujardin, S. Mann, *Adv.Eng.Mater.* **2002**, *4*, 461–474.
- [2] G. T. Zan, Q. S. Wu, *Adv.Mater.* **2016**, *28*, 2099–2147.
- [3] D. Avnir, T. Coradin, O. Lev, J. Livage, *J. Mater.Chem.* **2006**, *16*, 1013–1030.
- [4] T. Coradin, J. Livage, *Acc.Chem.Res.* **2007**, *40*, 819–826.
- [5] C. Sanchez, P. Belleville, M. Popall, L. Nicole, *Chem. Soc. Rev.* **2011**, *40*, 696–753.
- [6] R. Ciriminna, A. Fidalgo, V. Pandarus, F. Béland, L. M. Ilharco, M. Pagliaro, *Chem. Rev.* **2013**, *113*, 6592–6620.
- [7] F. Sancenón, L. Pascual, M. Oroval, E. Aznar, R. Martinez-Manez, *ChemistryOpen* **2015**, *4*, 418–437.
- [8] K. Ariga, A. Vinu, Y. Yamauchi, Q. Ji, J. P. Hill, *Bull. Chem. Soc. Jpn.* **2011**, *85*, 1–32.
- [9] V. Malgras, Q. Ji, Y. Kamachi, T. Mori, F. K. Shieh, K. C. W. Wu, K. Ariga, Y. Yamauchi, *Bull. Chem. Soc. Jap.* **2015**, *88*, 1171–1200.
- [10] Y. Wan, D. Zhao, *Chem. Rev.* **2007**, *107*, 2821–2860.
- [11] Y. Qiao, F. Polzer, H. Kirmse, S. Kirstein, J. P. Rabe, *Chem. Commun.* **2015**, *51*, 11980–11982.
- [12] Y. Okazaki, J. Cheng, D. Dedovets, G. Kemper, M. H. Delville, M. C. Durrieu, H. Ihara, M. Takafuji, E. Pouget, R. Oda, *ACS Nano* **2014**, *8*, 6863–6872.
- [13] E. Pouget, E. Dujardin, A. Cavalier, A. Moreac, C. Valery, V. Marchi-Artzner, T. Weiss, A. Renault, M. Paternostre, F. Artzner, *Nat.Mater.* **2007**, *6*, 434–439.
- [14] B. Liu, Y. Cao, Z. Huang, Y. Duan, S. Che, *Adv.Mater.* **2015**, *27*, 479–497.
- [15] M. Nakata, G. Zanchetta, B. D. Chapman, C. D. Jones, J. O. Cross, R. Pindak, T. Bellini, N. A. Clark, *Science* **2007**, *318*, 1276–1279.
- [16] C. Jin, H. Qiu, L. Han, M. Shu, S. Che, *Chem. Commun.* **2009**, 3407–3409.
- [17] C. Jin, L. Han, S. Che, *Angew. Chem. Int. Ed.* **2009**, *48*, 9268–9272; *Angew. Chem.* **2009**, *121*, 9432–9436.
- [18] M. Numata, K. Sugiyasu, T. Hasegawa, S. Shinkai, *Angew. Chem. Int. Ed.* **2004**, *43*, 3279–3283; *Angew. Chem.* **2004**, *116*, 3341–3345.
- [19] Y. Cao, K. Kao, C. Mou, L. Han, S. Che, *Angew. Chem. Int. Ed.* **2016**, *55*, 2037–2041; *Angew. Chem.* **2016**, *128*, 2077–2081.
- [20] Y. Cao, S. Che, *Chem. Mater.* **2015**, *27*, 7844–7851.
- [21] B. Liu, Y. Yao, S. Che, *Angew. Chem. Int. Ed.* **2013**, *52*, 14186–14190; *Angew. Chem.* **2013**, *125*, 14436–14440.
- [22] R. N. Grass, R. Heckel, M. Puddu, D. Paunescu, W. J. Stark, *Angew. Chem. Int. Ed.* **2015**, *54*, 2552–2555; *Angew. Chem.* **2015**, *127*, 2582–2586.
- [23] M. Puddu, W. J. Stark, R. N. Grass, *Adv. Healthc. Mater.* **2015**, *4*, 1332–1338.
- [24] D. Paunescu, M. Puddu, J. O. B. Soellner, P. R. Stoessel, R. N. Grass, *Nat. Protocols* **2013**, *8*, 2440–2448.
- [25] E. Auyeung, R. J. Macfarlane, C. H. Choi, J. I. Cutler, C. A. Mirkin, *Adv. Mater.* **2012**, *24*, 5181–5186.

- [26] E. Auyeung, W. Morris, J. E. Mondloch, J. T. Hupp, O. K. Farha, C. A. Mirkin, *J. Am. Chem. Soc.* **2015**, *137*, 1658–1662.
- [27] E. Krieg, M. M. C. Bastings, P. Besenius, B. Rybtchinski, *Chem. Rev.* **2016**, *116*, 2414–2477.
- [28] T. Steinbach, F. R. Wurm, *Angew. Chem. Int. Ed.* **2015**, *54*, 6098–6108; *Angew. Chem.* **2015**, *127*, 6196–6207.
- [29] R. Häner, F. Garo, D. Wenger, V. L. Malinovskii, *J. Am. Chem. Soc.* **2010**, *132*, 7466–7471.
- [30] A. L. Nussbaumer, D. Studer, V. L. Malinovskii, R. Häner, *Angew. Chem. Int. Ed.* **2011**, *50*, 5490–5494; *Angew. Chem.* **2011**, *123*, 5604–5608.
- [31] Y. Vyborna, M. Vybornyi, A. V. Rudnev, R. Häner, *Angew. Chem. Int. Ed.* **2015**, *54*, 7934–7938; *Angew. Chem.* **2015**, *127*, 8045–8049.
- [32] Y. Vyborna, M. Vybornyi, R. Häner, *J. Am. Chem. Soc.* **2015**, *137*, 14051–14054.
- [33] A. Al Ouahabi, L. Charles, J.-F. Lutz, *J. Am. Chem. Soc.* **2015**, *137*, 5629–5635.
- [34] M. Vybornyi, A. V. Rudnev, S. M. Langenegger, T. Wandlowski, G. Calzaferri, R. Häner, *Angew. Chem. Int. Ed.* **2013**, *52*, 11488–11493.
- [35] M. Vybornyi, Y. B.-C. Hechevarria, M. Glauser, A. V. Rudnev, R. Häner, *Chem. Commun.* **2015**, *51*, 16191–16193.
- [36] C. D. Bösch, S. M. Langenegger, R. Häner, *Angew. Chem. Int. Ed.* **2016**, *55*, 9961–9964.
- [37] H. Lutz, V. Jaeger, R. Berger, M. Bonn, J. Pfaendtner, T. Weidner, *Adv. Mater. Interfaces* **2015**, *2*, 1500282.
- [38] H. Yang, N. Coombs, I. Sokolov, G. A. Ozin, *Nature* **1996**, *381*, 589–592.
- [39] N. Hao, L. Li, F. Tang, *Biomater. Sci.* **2016**, *4*, 575–591.
- [40] T. Kimura, K. Kuroda, *Adv. Funct. Mater.* **2009**, *19*, 511–527.
- [41] M. Vybornyi, A. Rudnev, R. Häner, *Chem. Mater.* **2015**, *27*, 1426–1431.

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