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### From Molecular to Macroscopic Engineering: Shaping Hydrogen-Bonded Organic Nanomaterials

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Abstract: The self-assembly and selforganization behavior of chromophoric acetylenic scaffolds bearing 2,6-bis(acetylamino)pyridine (1, 2) or uracyl-type (3-9) terminal groups has been investigated by photophysical and microscopic methods. Systematic absorption and luminescence studies show that 1 and 2, thanks to a combination of solvophilic/solvophobic forces and  $\pi - \pi$ stacking interactions, undergo self-organization in apolar solvents (i.e., cyclohexane) and form spherical nanoparticles, as evidenced by wide-field optical microscopy, TEM, and AFM analysis. For the longer molecular module, 2, a more uniform size distribution is found (80-200 nm) compared to 1 (20-1000 nm). Temperature scans in the range 283-353 K show that the self-organized nanoparticles are reversibly formed and destroyed, being stable

#### at lower temperatures. Molecular modand 2 were ules 1 then thoroughly mixed with the complementary triply hydrogen-bonding units 3-9. Depending on the specific geometrical structure of 3-9, different nanostructures are evidenced by microscopic investigations. Combination of modules 1 or 2 with 3, which bears only one terminal uracyl unit, leads to the formation of vesicular structures: instead, when 1 is combined with bis-uracyl derivative 4 or 5, a structural evolution from nanoparticles to nanowires is observed. The length of the wires obtained by mixing 1 and 4 or 1 and 5 can be controlled by addition of 3,

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#### Introduction

In the last decades, chemists have devoted a great deal of effort to the preparation of novel nanostructured materials

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wires into shorter rods. The replacement of linear system 5 with the related angular modules 6 and 7 enables formation of helical nanostructures, unambiguously evidenced by AFM. Finally, thermally induced self-assembly was studied in parallel with modules 8 and 9, in which the uracyl recognition sites are protected with tert-butyloxycarbonyl (BOC) groups. This strategy allows further control of the self-assembly/ self-organization process by temperature, since the BOC group is completely removed on heating. Microscopy studies show that the BOC-protected ditopic modules 8 self-assemble and self-organize with 1 into ordered linear nanostructures, whereas BOC-protected tritopic system 9 gives rise to extended domains of circular nano-objects in combination with 1.

which prompts transformation of the

based on the controlled assembly of molecular building blocks.<sup>[1-8]</sup> Indeed, the geometric structure of molecules can considerably influence their ability to self-organize into more complex objects<sup>[9-14]</sup> and therefore tune the structure and properties of the final material.<sup>[8,10,15,16]</sup> Functional molecular-ordered materials nowadays have potential applications in a wide range of fields, such as solar cells,<sup>[17,18]</sup> polymer-based transistors,<sup>[19-21]</sup> and the production of new semiconductors.<sup>[22-25]</sup> Various approaches including colloidal,<sup>[5,26]</sup> templated,<sup>[27,28]</sup> and self-assembly<sup>[29-31]</sup> methods have been developed to prepare materials with properties distinct from those of the single molecule or bulk phase. In this context, the supramolecular approach,<sup>[32]</sup> which exploits molecular recognition processes based on the combination of a variety of noncovalent interactions, can give access to a large number of self-assembled molecular architectures,[33-39] which may undergo further self-organization with formation of controlled macroscopic systems.<sup>[12,30,40-44]</sup> In the literature the terms self-assembly and self-organization are often used interchangeably, probably because there is no general consensus on their definitions.<sup>[45,46]</sup> Herein, the term self-assem-

bly refers to the processes of molecular recognition through hydrogen-bonding interactions between the single molecular modules, whereas the self-organization processes are considered to be those in which the macroscopic pattern emerges solely from numerous interactions among the molecular components of the system, resulting in the formation of larger submicrostructures with varying sizes and shapes.

Recognition sites based on complementary hydrogenbonding systems are versatile tools for organization and tuning of the shape of materials at the nanoscale level.<sup>[47-50]</sup> Recently, we showed that, under the control of temperature and solvent polarity, supramolecular adducts between two  $\pi$ -conjugated molecules bearing complementary hydrogenbonding groups can be formed in solution and further evolve as hollow spherical nanoparticles with a vesicular structure.<sup>[51]</sup> Most notably, we have demonstrated that the size distribution and shape of the vesicles can be tuned by means of the stoichiometric ratio of the two constituent molecular components. This behavior was interpreted to be a consequence of the specific solvophobic/solvophilic interactions established between the supramolecular adducts.

Herein we extend this strategy and report a systematic study on several combinations of suitably designed molecular modules 1-9 that undergo complementary triple hydrogen-bonding interactions. Specifically, supramolecular recognition is mediated by triple parallel hydrogen bonds established between the NH-N-NH (donor-acceptor-donor, DAD) groups of 2,6-di(acetylamino)pyridine and the CO-NH-CO (ADA) imidic groups of a uracyl derivative.[52-54] Selection of these two moieties is based on the fact that they show very high hydrogen-bonding association constants on the order of  $10^3 M^{-1}$  in polar solvents like CHCl<sub>3</sub> and  $10^4$ –  $10^5 M^{-1}$  in apolar solvents like cyclohexane (CHX) and CCl<sub>4</sub>.<sup>[51,55,56]</sup> Our aim is to investigate how the structural properties of the molecular modules affect the nanoscale morphology of the self-assembled hydrogen-bonded aggregates.

Molecular modules 1-9 can be classified into three different groups: molecules bearing 1) bis(acetylamino)pyridyl (DAD) groups (1, 2), 2) uracyl (ADA) groups (3-7), and 3) tert-butyloxycarbonyl (BOC)-protected uracyl (ADA) groups (8, 9). Compound 2, an elongated analogue of module 1, is essentially a linear conjugated phenyleneethynylene oligomer (OPE) terminated with two DAD hydrogen-bonding recognition units. Molecule 3 bears only one uracyl moiety and is terminated with an anthracenyl unit, which is used to tune the solvophobicity of the resulting supramolecular aggregate (vide infra). The other modules bearing uracyl ADA units (4-7) were conceived as angular modules in which the peripheral recognition sites occupy para, meta, or ortho positions relative to the central alkoxylated benzene ring. Finally, in modules 8 and 9, BOC-protected uracyl recognition sites provide better solubility in organic solvents and thus easier processability when nanostructured under thermal control. Combination of complementary modules 1 and 2 with 3-9 gives rise to a variety of nanostructured architectures such as nanoparticles, nanovesicles, nanofibres, and nanorods.

#### **Results and Discussion**

Self-organization of individual molecules into nanoparticles: The UV/Vis absorption and emission spectra of 1 and 2 in different solvents show that, in most cases, there is little effect of the solvent polarity, while the redshifted absorption and emission profiles observed in H<sub>2</sub>O and CHX suggest formation of aggregates (Figure 1). This could be due to a self-organization process initiated by solvophilic/solvophobic forces and  $\pi$ - $\pi$  stacking interactions.<sup>[10,57]</sup>

The self-organization behavior of these molecules in CHX was confirmed by spectroscopic investigations as a function of temperature (Figure 2). On increasing the temperature from 298 to 353 K the absorption spectra in CHX underwent a gradual hypsochromic shift (Figure 2a and c). The



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Figure 1. Absorption (left) and fluorescence (right) spectra of 3.3  $\mu$ M solutions of **1** (a, b;  $\lambda_{exc}$ =370 nm) and **2** (c, d;  $\lambda_{exc}$ =360 nm) in solvents of different polarity.



Figure 2. Absorption (left) and emission (right) spectra of 3.3  $\mu$ M solutions of **1** (a, b;  $\lambda_{exc}$ =390 nm) and **2** (c, d;  $\lambda_{exc}$ =370 nm) as a function of temperature in CHX.

spectral shape at the highest temperature is virtually identical to that in solvents in which the compounds are soluble at room temperature (Figure 1) and thus indicates disruption of the aggregates. Notably, these changes in the absorption and emission spectra are completely reversible on cooling the sample, with a gradual redshift of the absorption profile (Figures S1 and S2, Supporting Information). During the cooling cycle ( $353 \rightarrow 298$  K), in line with the absorption trends, the initial fluorescence band of **1** is progressively quenched, while a new redshifted feature appears with maximum at about 460 nm (Figure S1, Supporting Information). In extended  $\pi$ -conjugated module **2**, the growing emission feature is weaker and appears only as a shoulder of the original fluorescence band above 500 nm (Figure S2, Supporting Information). The observed redshifts at low temperatures are attributed to  $\pi$ - $\pi$  stacking, most likely in J-type aggregates.<sup>[10,58,59]</sup>

Simulated spectra for 1 and 2 (Figure 3) match their experimental counterparts well (see Figure 1). In particular, theory reproduces the redshift of the lowest energy band on enlarging the conjugated segment (exptl: from 380 to



Figure 3. Calculated absorption spectra of 1 (a) and 2 (b) with a manifold of  $50 \times 50$  states and shifted by 0.23 eV and 0.26 eV, respectively, to match the lowest-energy experimental absorption peak.

420 nm; theory: from 355 to 384 nm). Nevertheless, for **1**, the relative position of the highest energy absorption band with respect to the lowest one is not well reproduced: the excitation energy is overestimated by about 0.7 eV. Calculations on J aggregates of both **1** and **2** showed an exciton shift of about 1000 cm<sup>-1</sup>, which can explain the change of shape of the lowest energy absorption band.<sup>[60,61]</sup>

To determine the shape and size of the materials formed through self-organization, various microscopic studies such as wide-field optical microscopy (WFM), tapping mode atomic force microscopy (TM-AFM), and transmission electron microscopy (TEM) were performed (Figure 4). In all characterization experiments, the solution used was subjected to several heating and cooling cycles in order to un-



Figure 4. WFM (a, d), TM-AFM (b, e), and TEM (c, f) images of self-organized nanostructures formed from CHX solutions containing molecules 1 (a-c) or 2 (d-f).

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ambiguously probe the self-organization. The WFM images recorded from different areas indicated that both 1 (Figure 4a) and 2 (Figure 4d) form bright fluorescent particles of different sizes.

AFM and TEM images of 1 recorded from different areas of the sample indicate the presence of both nano- and microparticles with sizes typically ranging from about 20 nm to greater than 1 µm (Figure 4b and c and Figure S3, Supporting Information). In contrast, molecular module 2 alone generates nanoparticles with a much more uniform size distribution ranging from 80 to 200 nm (Figure 4e and f and Figure S4, Supporting Information). This difference in size distribution can be rationalized by taking into account the different lengths of the OPE spacing units of 1 and 2. These molecules have a central apolar phenyleneethynylene core functionalized with alkoxyl groups and terminal polar bis(acetylamino)pyridyl moieties. In an apolar solvent like CHX, molecules 1 and 2 undergo self-organization through either electrostatic or hydrogen-bonding interactions of the terminal polar groups, leading to the formation of energyminimized spherical particles (Scheme 1). Compared to 1, extended linear module 2 exhibits a larger percentage of solvophilic structure and hence can form nanoparticles with a narrower size distribution.



Figure 5. a) Absorption spectra of **1**, **3**, their 1:2 adduct  $[\mathbf{1}\cdot(\mathbf{3})_2]$  and algebraic sum of the absorption profiles of the individual compounds  $(\mathbf{1}+(\mathbf{3})_2)$ . b) Variable-temperature absorption and c) emission ( $\lambda_{exc}=347$  nm) spectral changes in CHX of adduct  $[\mathbf{1}\cdot(\mathbf{3})_2]$ . d) WFM, e) TM-AFM, and f) TEM images of nanostructures composed of  $[\mathbf{1}\cdot(\mathbf{3})_2]$ .

ure 5 a). In particular, the observed redshift of the lower energy absorption band of anthracenyl derivative 3 (not observed for 3 alone, Figure S5 in Supporting Information)



Scheme 1. Schematic representation of the combined self-assembly and self-organization processes of the linear modules **1--4**, leading to different nanostructures, namely, particles, fibers, vesicles, and rods. The use of angular modules, such as **6** or **7**, can also lead to helical nanofibres (vide infra).

**From particles to vesicles:** In a given solvent, the nature of the functional groups (i.e., solvophobic or solvophilic) plays a key role in the aggregation process,<sup>[62]</sup> and one can expect to tune structural features by combining molecules with different functional groups. First, compound 3, which has only one hydrogen-bonding site, was combined with ditopic linear unit 1. The 2:1 self-assembly of 3 with 1 in CHX results in a dramatic change of the chemical nature of peripheral functionalities from solvophobic to solvophilic, due to the presence of an anthracenyl unit in 3 (Scheme 2).

In a typical experiment, 6.6  $\mu$ M of compound **3** was combined with 3.3  $\mu$ M of **1** in CHX (2:1 ratio). The absorption spectrum of the mixture is rather different from that obtained by adding those of the separated components (Figpoints to the presence of  $\pi$ - $\pi$ stacking interactions, most likely promoted by preliminary formation of triple hydrogen bonds between complementary uracyl and 2,6-di(acetylamino)pyridyl moieties.[63] The emission spectrum at 353 K is due to a combination of the fluorescence features of both isolated 1 and 3 (see the absorption and emission profiles of 1 and 3 at 353 K in CHX, Figure S6 in the Supporting Information), since both chromophores are excited at 347 nm. Most notably, only the sample containing both 1 and 3 (1:2) exhibits a fluorescence spectrum with a broad

tail on the low-energy side (Figure 5c) at 298 K.

The simulated and experimental spectra for compounds 1 and 3 as well as for the trimeric assembly  $[1\cdot(3)_2]$  are presented in the Supporting Information (Figure S7). They confirm that the lowest-energy absorption band of the trimer comes from the spectrum of compound 3 and that, in absence of aggregation, the spectrum of the supramolecular adduct corresponds almost to the algebraic sum of the spectra of its components.

Wide-field microscopic (WFM) images (Figure 5d) indicate the presence of bright hollow, luminescent, circular shapes, which are attributable to either rings or vesicular structures; similar shapes are observable by AFM (Figure 5e and Figure S8, Supporting Information). Conclusive support

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for the formation of nanovesicles is obtained from TEM images (Figure 5 f).

The formation of nanovesicles can be rationalized by the changing nature of molecular end groups. In CHX compound **1** alone, due to the presence of polar bis(acylamino)-pyridyl groups, tends to self-organize through electrostatic or weak hydrogen-bonding interactions involving the terminal moieties and leading to spherical nanostructures (vide supra). After the establishment of complementary hydrogen-bonding interactions with molecule **3**, the nature of the end functionality of the supramolecular adduct  $[1\cdot(3)_2]$  is inverted from solvophobic (hydrogen-bonding sites) to solvophilic (anthracene units, prompting the change from filled to vesicular/hollow structures, Scheme 2).

From nanoparticles to nanowires: To probe the effect of extended linear hydrogen bonding, we then investigated the self-assembly of 1 with linear OPE derivatives of different solubility equipped with uracyl termini (4 or 5). In principle, the complementary hydrogen-bonding interaction can result, in this case, in a supramolecular linear polymer (Scheme 3). On mixing 1 and 4 in CHX in a 1:1 molar ratio, a precipitate is immediately generated, indicating the formation of an insoluble supramolecular polymer aggregate, which cannot be dissolved even at temperatures as high as 353 K. To avoid formation of this intractable material, further studies were carried out in toluene, which also exhibits low polarity but it is more likely to dissolve organic conjugated aromatic systems. The absorption and emission spectra of 4 recorded in different solvents (Figure S9, Supporting Information) show that it undergoes self-organization in H<sub>2</sub>O and CHX, whereas it dissolves well in toluene and most of the other solvents.

The absorption spectrum of a mixture of 1 and 4 in toluene at room temperature  $([1\cdot4]_n)$  is rather different from that of their algebraic sum; in particular, a new redshifted band around 430 nm is observed (Figure 6a). To understand the origin of the new band and hence to prove the reversibility, absorption and emission studies as a function of temperature were carried out. On increasing the temperature



Figure 6. a) Absorption spectra of 3.3  $\mu$ M toluene solutions of 1, 4, [1-4]<sub>n</sub>, and algebraic sum of the absorption profiles of the individual compounds (1+4). b) Absorption and c) emission ( $\lambda_{exc}$ =380 nm) spectral changes of [1-4]<sub>n</sub> in toluene as a function of temperature. The dashed line in c) is the fluorescence spectrum at 293 K normalized in intensity relative to that at 358 K. d–f) TM-AFM images of the wirelike nanostructures, organized in toluene and deposited on mica.



Scheme 2. Representation of H-bonded self-assembly between 1 and 3, adduct  $[1_{\bullet}(3)_2]$ .



Scheme 3. Molecular representation of linear hydrogen-bonded self-assembly between 1 and 4 to give adduct  $[1-4]_{n}$ .

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from 298 to 358 K, the absorption band around 430 nm gradually disappears with concomitant increase of the optical density at higher energy (Figure 6b). At 358 K, an absorption spectrum very similar to that of the algebraic sum of the absorption profiles of the individual compounds is observed. As the temperature rises, the corresponding emission spectra show a gradual increase of the band intensity at 430 nm (Figure 6c). At the highest temperature, 358 K, the detected fluorescence spectrum corresponds to that of a mixture of individual units 1 and 4, with a prevalent contribution from 1, which exhibits the highest absorbance at the excitation wavelength of 380 nm and almost unitary fluorescence quantum yield (see Figure 6a and Figure S10, Supporting Information). On cooling the system from 358 to 293 K, complete restoration of the original absorption spectrum is observed, along with a steady decrease of the emission intensity to the initial value. Normalization of the spectral profiles obtained at the highest and lowest temperatures (at peak wavelength) shows widening on the low-energy side at 293 K, and again indicates formation of aggregates at lower temperatures (vide supra). The observed spectral changes on heating are attributed to the disruption of the supramolecular aggregates, which are formed by hydrogenbonding and  $\pi$ -stacking interactions at room temperature. Indeed, AFM images of nanostructures deposited from a toluene suspension onto mica recorded at different areas of the sample indicate the presence of nanowires with lengths greater than 400 nm and widths of about 30 nm (Figure 6d and f).

A quite similar spectroscopic behavior in toluene is observed for a 1:1 mixture of **1** and **5** ([**1**•**5**]<sub>n</sub>). Typical TM-AFM images recorded for [**1**•**5**]<sub>n</sub> also show the formation of nanofibres (Figure 7). Compared to assembly [**1**•**4**]<sub>n</sub>, [**1**•**5**]<sub>n</sub> forms much longer nanofibres with lengths on the order of several micrometers and typical widths between 40 and 80 nm (Figure S11, Supporting Information). The increase in fiber length is probably attributable to the presence of the alkoxyl chains, which enhance the solubility of the supramolecular polymer. At any rate, the hydrogen-bonding interactions between **1** and either **4** or **5** cause the formation of extended linear polymeric structures that, through  $\pi$ - $\pi$ stacking interactions between the aromatic units, prompt the formation of nanowire-like architectures (Scheme 1).

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Figure 7. TM-AFM images of self-organized nanostructures of  $[1-5]_n$ , organized from toluene and deposited on mica.

From nanowires to nanorods: In an attempt to further modulate the structure of the self-organized nanomaterials, we combined three different molecular components: the anthracene derivative bearing only one uracylic unit (3) with modules 1 and 4, both with H-bonding sites at the ends. The rationale behind this choice is to control the length of the polymers on addition of a predetermined amount of molecular stopper 3, which should reduce the extent of the linear hydrogen-bonded assembly in  $[1\cdot4]_n$  (Scheme 4) and possibly lead to size-controlled nanomaterials. To test this possibility we investigated the self-organization behavior of mixtures of 1, 4, and 3 in the molar ratio 10:10:1 in toluene.

In a typical experiment, modules 1, 4, and 3 were added to toluene at 373 K, stirred for 3 min, and slowly cooled to room temperature. About 20  $\mu$ L each of this solution was drop casted onto a freshly cleaved mica surface for AFM imaging or onto a carbon-coated copper grid for TEM measurements. Both the AFM and TEM images (Figure 8) recorded from different areas of the sample clearly showed the presence of a large portion of nanorods along with some



Figure 8. a, b) TMAFM and c) TEM images of nanostructures, organized from a toluene solution of modules **1**, **4**, and **3** in molar ratio 10:10:1.



Scheme 4. Molecular representation of the anthracenyl-capped hydrogen-bonded self-assembly between 1, 4 and 3.

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spherical aggregates. The typical length and width of the rods are 80-200 and 40-60 nm, respectively; their formation is schematically depicted in Scheme 1. The absorption and luminescence properties of the mixture of 1, 4, and 3 are substantially identical to those of 1 and 4 due to the very low concentration of 3.

**Helical nanowires:** Self-assembly between a linear module (1) and molecules having angular structures (6 and 7) was also investigated (Scheme 5). Molecular modules 5-7 are similar in composition and in the number of hydrogen-bonding sites, but the latter differ in their relative position. Molecule 5 is a linear module with a twofold symmetry and the reactive sites are placed at  $180^{\circ}$  (*para*) relative to each other; in molecules 6 and 7 the hydrogen-bonding sites are located at 120 (*meta*) and  $60^{\circ}$  (*ortho*), respectively.

Compound **1** was mixed with either **6** or **7** (1:1 molar ratio) in CHX/4% tetrahydrofuran (THF).<sup>[64]</sup> This solvent composition was chosen to prevent self-organization of the individual compounds, which was evidenced in pure CHX (Figure 1 and Figure S12, Supporting Information). Similar to previous cases, on mixing the two components, redshifting of the absorption and emission features is observed. Furthermore, variable-temperature studies show reversible changes of the absorption and emission spectra, with blueshifted features at higher temperature, eventually shifted to lower emission features.



Figure 9. Absorption (left) and emission (right,  $\lambda_{exc}=380 \text{ nm}$ ) spectral changes of  $[1\cdot 6]_n$  (a, b) and  $[1\cdot 7]_n$  (c, d) as a function of temperature in CHX/THF(4%) solutions.

ergies on cooling (Figure 9). This trend can be again attributed to the formation of aggregates arising from complementary hydrogen-bonding and  $\pi$ - $\pi$  stacking interactions.

The  $[1.6]_n$  and  $[1.7]_n$  assemblies were also characterized by molecular modeling and compared with experiments



Scheme 5. Molecular representation of hydrogen-bonded self-assembly between 1 and either 6 or 7, giving adducts  $[1-6]_n$ , and  $[1-7]_n$ .

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Figure 10. Calculated absorption spectrum for the a) [1-6] and b) [1-7] dimers (manifold of  $50 \times 50$  excited states and redshifted by 0.4 eV). c) Spectral evolution ( $25n \times 25n$  manifold) for 1-6 oligomers.

(Figure 10). For the dimer [1-6], the nature of the lowest transition, with two peaks at 360 and 400 nm is well reproduced by the calculations whereas the peak around 320 nm is predicted to appear at a shorter wavelength (280 nm). Again, there is a good match between the spectrum of the dimer and the algebraic sum of the spectra of the two moieties. Thus, calculations performed on trimers [6-1-6] and [1-6-1] as well as on tetramer [6-1-6-1] show that size effects are rather small but that the stoichiometry strongly impacts on the relative intensities, since the lowest-energy band results from both molecules.

For both  $[1\cdot6]_n$  and  $[1\cdot7]_n$  assemblies, the AFM images indicate the formation of nanofibres, but a close analysis of the images revealed that they are entirely different from those formed by combining 1 with either 4 or 5 (see above). In the present case, each fiber exhibits humps and lumps suggesting the formation of helicoidally organized nanostructures (Figure 11).

Such helicoidal structures are indeed obtained from PM6 geometry optimizations, as illustrated in Figure S13 of the Supporting Information, with three- and sixfold symmetry for *ortho* and *meta* substitution, respectively. Figure S14 of the Supporting Information further shows that these helical structures display specific CD signatures, which could be revealed provided the nonracemic mixtures are obtained. Typically the lowest Cotton absorptions of the helices display



Figure 11. TMAFM images of assemblies  $[1-6]_n$  (a–c) and  $[1-7]_n$  (d, e) deposited on mica from a CHX/THF (4%) solution. f) Height cross-section profile along the delimited lines traced in e).

evident intensity enhancements as well as a shift with respect to the monomeric species.

**Thermally controlled polymerization**: To achieve better solubility and thus improved processability of our molecular modules in organic solvents (otherwise impossible for triuracyl molecule **9** without BOC groups), BOC-protected molecular modules **8** and **9** were also synthesized (Figure S15 and S16, Supporting Information). In these compounds, the uracyl recognition sites are protected with BOC groups, which prevent homomolecular self-assembly directed by double hydrogen-bonding recognition. Since a BOC group can be selectively removed by heat treatment,<sup>[65]</sup> the hydrogen-bonded assemblies could be generated in situ upon thermal treatment (Scheme 6).



Scheme 6. Schematic representation of the self-assembly process induced by thermal removal of the BOC protecting group.

To test the stability and thermal cleavage as well as to obtain quantitative data on BOC removal from modules **8** and **9**, thermogravimetric analysis (TGA) under inert atmosphere was carried out (Figure 12 and Figure S17, Supporting Information). As shown in Figure 12, a steep one-step weight loss in the temperature interval of 388-423 K (115– $150^{\circ}$ C), corresponding to about 28.4 wt% is observed for



Figure 12. Temperature-modulated (solid line) and differential (dashed line) TGA plots of **9** (0.796 mg) recorded under a  $N_2$  flow of 60 mL min<sup>-1</sup>. Insets: details of the <sup>1</sup>H NMR spectra of **9** before and after the thermal removal of the BOC moieties.

both compounds. This weight loss is attributed to the pyrolysis of the BOC moieties, since it completely matches the calculated theoretical weight loss for the removal of these groups. To further confirm selective thermal deprotection and the integrity of the deprotected synthon after thermogravimetric analysis, the organic residues were characterized by <sup>1</sup>H NMR spectroscopy in DMSO (Figure 12, insets). The NMR spectra of the compounds show total disappearance of the BOC proton resonances centered at 1.60 ppm and the onset of a broad resonance at 11.5 ppm, which is unambiguously attributed to the imidic protons of the free uracyl moieties. The other signals are maintained, which confirms that the molecular skeleton of both **8** and **9** is preserved and that only BOC groups have been efficiently removed after thermal treatment.

These results prompted a TM-AFM study of the nanostructures on mica surfaces, by combining 8 or 9 with 1, followed by a thermal treatment (Figure S18, Supporting Information). In a typical experiment, the two mixtures (8/1 and 9/1, 1:1 molar ratio) were prepared in a CH<sub>2</sub>Cl<sub>2</sub>/o-xylene (9:1) solution, drop cast on a freshly cleaved mica surface, and heated at 145 °C under Ar atmosphere for 15 min.

As intuitively expected from their molecular shape and reciprocal positioning of the recognition sites, the combination of **1** and **8** leads to the formation of linear structures resembling rods or blocks with nanoscopic dimensions (Figure 13, Scheme 7). In every image, the observed rectangular objects exhibit a flat surface with a linear shape and well-defined borders. The average dimensions of the objects range from 50 to 500 nm in length, from 40 to 200 nm in width, and from 1 to 9 nm in height. By comparison with the structures obtained by direct mixing of modules **1** and **4** (Figure 6), increased homogeneity of the nanostructures is evidenced (Figure 13). We tentatively explained it by considering that the thermally induced self-assembly of **1** and **8** occurs directly on the surface and thus in a confined environment, which has fewer degrees of freedom and reduces



Figure 13. TM-AFM height images, at different magnifications, of the self-organized nano-objects obtained after thermal removal of the BOC groups  $[\mathbf{1-8}\text{-BOC}]_n$  (a–c) and  $[\mathbf{1-9}\text{-BOC}]_n$  (d–f) assemblies on mica surface. 3D representation of the AFM topographies for  $[\mathbf{1-8}\text{-BOC}]_n$  and  $[\mathbf{1-9}\text{-BOC}]_n$  (g, h), respectively.



Scheme 7. Schematic representation of the thermally induced self-assembly process of **1** with BOC-protected linear (**8**) and trigonal (**9**) modules.

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the number of possible secondary aggregation phenomena. Moreover, in solution the aliphatic lateral chains present on both complementary modules can foster aggregation of the supramolecular system by means of secondary solvophobic interactions. At the solid/liquid interface not only may this effect be reduced, but also the interaction between the single molecules and the surface can increase the order of the system and thus favor the formation of flat, well-defined nanostructures. Remarkably, modulation of the self-organization process by the surface is strongly dependent on the concentration of the molecular modules deposited on the surface. At higher concentration (1.4 mM), for which the interaction with the surface is less extensive and thus the intermolecular interactions dominate, no ordered nanostructures are observed (Figures S18-S26, Supporting Information).

Unexpectedly, the combination of 1 and 9 (Scheme 7) leads to the formation of nano-objects with circular shapes, resembling a ring (Figure 13d and f). The average dimensions of the objects range from 680 to 860 nm and 290 to 390 nm in outer and inner diameter, respectively, and from 1 to 4 nm in height. The unique geometrical features of assembled objects can be tentatively attributed to a biphasic nature of the self-assembly/self-organization processes, which could originate from a nucleation step taking place during the thermal polymerization process. As a consequence of the two-dimensional molecular character of module 9, assembly  $[1.9-BOC]_n$  could give birth to bidimensional nanostructures that, depending on the concentration of the single modules, could cover the entire surface. At higher concentration (1.2 mM), these nanostructured objects cover the entire mica surface, and still conserve the circular structures of the nucleation process (Figures S18-S26, Supporting Information).

This example suggests how a univocal correlation between the molecular structure of the organic module and the architecture of the nano-objects is difficult to achieve. Thus, the elucidation of the mechanisms of formation of the observed nanostructures would need an inquiry into the link between molecular short-range and macromolecular long-range scales. In principle, a promising framework for this approach would be supplied by the theories of self-assembling patterns and interfaces,<sup>[66]</sup> successfully exploited and improved over the years to understand the complex energetic and geometric issues of self-organized dispersions such as micelles, vesicles, and microemulsions. Whether their present level of understanding could suffice for this aim, or will require to be somehow reformulated, is an interesting prospect left for future work on these supramolecular systems.

#### Conclusion

A library of nine chromophoric acetylenic scaffolds peripherally equipped with 2,6-bis(acetylamino)pyridine or uracyltype terminal fragments was designed to take advantage of self-assembly and self-organization processes driven by hydrogen-bonding,  $\pi$ - $\pi$  stacking, and solvophobic/solvophilic interactions. Preparation of specific nanostructures was achieved by solvent and temperature control of thoroughly mixed binary or ternary mixtures of selected compounds. Photophysical and microscopic studies allowed the formation of structures of different shapes and sizes to be evidenced and rationalized, such as nanoparticles, nanovesicles, nanofibres, and nanorods, also with helicoidal or circular variants.

The assortment of nanostructures obtained in this work represents a first step towards the design and preparation of functional macroscopic supramolecular materials with welldefined shapes that, in the future, might be engineered to express functionality at the macroscopic level. To this end, we are now conducting qualitative and quantitative theoretical simulations for understanding in detail the formation mechanisms of the observed nanostructures, merging the theories of molecular self-assembly (i.e., molecular recognition phenomena) with those of self-organizing patterns and/ or interfaces, such as micelles, vesicles, and microemulsions.

Although no specific systems for a particular application have been created yet, the systematic approach described here demonstrates that thoroughly designed libraries of novel organic modules can, under specific boundary conditions, bring closer the perspective of a truly "bottom-up" approach toward the fabrication of tailored nanomaterials potentially exploitable for practical technologies.

#### **Experimental Section**

Spectrometric characterization: The solutions for spectroscopic studies were prepared by injecting microliter amounts (10/20 µL) of 1 mM solutions in THF of each compound into 3 mL of various solvents such as cyclohexane (CHX), toluene, CCl4, THF, dichloromethane, DMSO, methanol, and water. Electronic absorption and emission measurements were carried out, respectively, on a Lambda 950 UV/VIS/NIR spectrophotometer (Perkin-Elmer) and on a Edinburgh FLS920 spectrofluorimeter (continuous 450 W Xe lamp), equipped with a Peltier-cooled Hamamatsu R928 photomultiplier tube (185-850 nm). The temperature of the solutions was varied with a Haake F3-C digital heated/refrigerated water bath (Haake Mess-Technik GmbH u. Co., Germany), which can be manually connected to a cuvette holder and controlled externally. Emission quantum yields were determined according to the approach described by Demas and  $\text{Crosby}^{[67]}$  with quinine sulfate ( $\Phi_{\text{em}} = 0.546$  in air-equilibrated acidic aqueous solution, 1 N H2SO4) as standard. All solvents were of spectrophotometric grade (Carlo Erba, 99+%) and were used as received.

Wide-field optical microscopy (WFM): The samples for WFM were prepared by spin coating about  $20 \,\mu\text{L}$  of solution onto a glass microscope slide and mounted on a inverted Olympus microscope. The samples were then irradiated through a  $100 \times$  objective lens (N.A. 1.4) with a 400 nm laser. The emission from the sample was collected through the same objective lens and filtered from excitation light by using a dichroic mirror and fed to a CCD camera.

**TEM analysis:** The samples for TEM studies were prepared by drop casting about 20  $\mu$ L of self-organized solution onto a carbon-coated nickel grid (3.00 mm, 200 mesh), air dried, and imaged on a Philips EM 208 TEM microscope (accelerating voltage of 100 kV).

**TM-AFM analysis**: Tapping-mode AFM measurements on the mica substrates were carried out in air at 298 K by using a Nanoscope IIIa (Digital Instruments Metrology Group, USA) instrument, model MMAFMLN.

**AFM study of assemblies**  $[1\cdot(3)_2]$ ,  $[1\cdot4]_n$ ,  $[3\cdot1\cdot(4\cdot1)_n\cdot3]$ ,  $[1\cdot6]_n$  and  $[1\cdot7]_n$ : The samples were prepared by drop casting about 20 µL of self-organized solution on to a freshly cleaved mica surface, air drying, and imaging under a multimode scanning probe microscope (Veeco digital instruments, Nanoscope III) using the tapping mode facility.

Assembly [1-8-BOC],, preparation of samples: Solutions of 8 and 1 (in 1:1 molar ratio) were prepared in  $CH_2Cl_2/o$ -xylene (9:1) at concentrations of 1.4 and 0.14 mM, respectively. 20  $\mu$ L of each solution was then drop cast onto a freshly cleaved mica surface and heated at 145 °C under argon atmosphere for 15 min. The samples were then dried under vacuum for 10 min to assure the complete removal of all residual solvent.

Assembly [1-9-BOC],, preparation of samples: Solutions of 9 and 1 (in 1:1 molar ratio) were prepared in  $CH_2Cl_2/o$ -xylene (9:1) at concentrations of 1.2 mM and 0.12 mM, respectively. 20  $\mu$ L of each solution was then drop cast onto a freshly cleaved mica surface and heated at 145 °C under argon atmosphere for 15 min. The samples were then dried under vacuum for 10 min to assure complete removal of the residual solvent.

**Thermogravimetric analysis (TGA):** TGA analysis of **8** (0.919 mg) and **9** (0.796 mg) were performed as follows: equilibration of the sample at 30 °C for 10 min, temperature ramp of 2.00 °C min<sup>-1</sup> up to 200 °C. All analyses were performed under a nitrogen flow of 60 mL min<sup>-1</sup>. The profiles of the compound are reported in the Supporting Information Figure S14.

**Computational modeling**: The geometry optimizations were carried out at the PM6<sup>[69]</sup> semiempirical level of approximation with the MOPAC2009 package.<sup>[70]</sup> The excited-state properties (excitation energies, oscillator strengths, and rotatory strengths) necessary to simulate the UV/Vis absorption and circular dichroism spectra were computed with the INDO/S<sup>[71]</sup> approximation in a development version of MOSF4.2 program.<sup>[72,73]</sup>

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