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COMMUNICATION K. Yoosaf, Abdelhalim Belbakra, Nicola Armaroli, Anna Llanes-Pallas and Davide Bonifazi Engineering spherical nanostructures through hydrogen bonds FEATURE ARTICLES Andrei Ghicov and Patrik Schmuki Self-ordering electrochemistry Massimo Cametti and Kari Rissanen Recognition and sensing of fluoride anion



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Engineering spherical nanostructures through hydrogen bonds†

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Chromophoric acetylenic scaffolds bearing complementary uracyl and 2,6-di(acetylamino)pyridyl moieties undergo supramolecular recognition and generate uniform nanoparticles, as observed by UV-Vis, AFM and TEM measurements.

Self-assembly of organic π -conjugated molecules into nanostructured materials is gaining attention as a potentially facile and effective route towards the development of functional materials for electronic and biological applications.¹ The optical and electronic properties of organic-based materials are highly dependent on their size and shape.² Hence for any applications, for instance in optoelectronic devices, fine control of the structural characteristics by varying the molecular constituents and functionalities is essential.³ In this context, due to their directionality and spatial arrangement, complementary multiple H-bonding interactions are attractive candidates for engineering well-defined supramolecular structures,⁴ which might undergo further self-organisation promoting the formation of controlled organic nanoparticles.⁵ To this end, we have designed chromophores 1 and 2, which are equipped with complementary uracyl and 2,6-di(acetylamino)pyridyl H-bonding moieties (Fig. 1). Under temperature and solvent-polarity control, we show that supramolecular adducts between 1 and 2 are formed in solution and further evolve as spherical nanostructures, such as vesicles (Fig. 1). Most notably, the nanoparticle size distribution and shape can be tuned by the stoichiometry ratio of the two molecular components. This behaviour is interpreted as a consequence of the



Fig. 1 Schematic representation of the self-organisation process.

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[†] Electronic supplementary information (ESI) available: Details for the experimental procedures, spectroscopic and microscopic characterisation. See DOI: 10.1039/b820462d specific solvophobic/solvophilic interactions that are established in binary or ternary supramolecular adducts.

Molecule 1 consists of a *para*-disubstituted central benzenic ring that is connected at both sides to two 2,6-di(acetylamino)-pyridyl terminal groups through ethynyl spacers, while module 2 bears only one uracyl unit equipped with an anthracenyl tailing group. These molecular units are known to undergo self-assembly through triple H-bonding with very high association constants in apolar solvents, *i.e.* of the order of 10^4-10^5 M⁻¹.⁶

Linear ditopic module **1** was prepared *via* a three-step synthesis starting from commercial 1,4-dihydroquinone (Scheme 1). Alkylation of 1,4-dihydroquinone in 1-bromodo-decane afforded molecule **4**, which was subsequently reacted with I_2 in the presence of Hg(OAc)₂ as catalyst to yield bis-iodo derivative **5**.⁷ Finally, molecule **5** was reacted *via* a Pd-catalysed Sonogashira cross-coupling reaction with a small excess (2.5 eq.) of 2,6-di(acetylamino)-4-ethynylpyridine to obtain the linear ditopic molecule **1**. Monotopic module **2** and 2,6-di(acetylamino)-4-ethynylpyridine were synthesised following the experimental protocols recently developed by us.⁸ Reference compound **3** displaying the same structure as module **1** but incapable of establishing H-bonding interactions, was obtained upon methylation of the amidic functionalities of **1** by reacting it with MeI in the presence of NaH.



Scheme 1 (a) 1-Bromododecane, K_2CO_3 , DMF, 60 °C, 12 h; (b) Hg(OAc)₂, I₂, CH₂Cl₂, rt, 12 h; (c) 2,6-di(acetylamino)-4-ethynylpyridine, [Pd(PPh₃)₄], CuI, Et₃N, THF, 85 °C, 12 h; (d) THF, NaH, MeI, rt, 12 h.

Molecules 1 and 2 exhibit intense absorption bands in the UV region and are strong luminophores in cyclohexane (CHX) solution (Fig. 2a and S1, ESI[†]); fluorescence quantum yields are 9 and 63%, respectively. The absorption and fluorescence bands of 1 in CHX exhibit fully reversible temperature-dependent profiles in the range 10–80 °C (Fig. 2b). On the contrary, small or no changes are observed for anthracenyl derivative 2 under identical conditions. These findings suggest that molecule 1 undergoes self-aggregation, which might be driven by a combination of weak homomolecular H-bonding, dipolar interactions, and π - π stacking. A temperature-dependent test experiment with tetramethylated molecule 3 evidences negligible spectral changes (Fig. S2, ESI[†]) confirming that the di(acetylamino)pyridyl

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Fig. 2 (a) Absorption spectrum of 1, 2 and of their molecular adduct (1 : 2 ratio) experimental and calculated; (b) variable-temperature absorption spectra of 1 in CHX; (c) absorption and (d) emission variable-temperature spectral changes of molecular adduct of 1 and 2 in the ratio 1 : 2.

moieties are essential to promote self-aggregation of 1. We can reasonably assume that the terminal units of the linear ditopic module 1 initially foster aggregation that further induces π - π stacking.

The absorption spectrum of $[1 \cdot (2)_2]$ turns out to be rather different from that obtained with the algebraic sum of the separated components (Fig 2a). In particular, the observed red-shift of the lower energy absorption band of anthracene derivative 2 (not observed for 2 alone) points to the presence of π - π stacking interactions, most likely promoted by the preliminary formation of triple H-bonds between complementary uracyl and 2,6-di(acetylamino)pyridyl moieties.⁸ This rationale is supported by a control experiment carried out with molecules 2 and 3, where the experimental spectrum is identical to the algebraic sum of the components (Fig. S3, ESI⁺). Furthermore, only the sample containing both molecules 1 and 2(1:2) exhibits a fluorescence spectrum with a broad tail on the low energy side (Fig. 2d). This finding further supports the formation of supramolecular complexes driven by triple H-bonding, as also confirmed by a Job plot via ¹H-NMR titration studies, which leads to intermolecular π - π stacking between adducts $[1 \cdot (2)_2]$.

The novel absorption and emission features of $[1 \cdot (2)_2]$ in CHX are progressively lost upon increasing the temperature up to 80 °C and are reversibly recovered by cooling down the sample to 10 °C, also with the observation of clean isosbestic and isoemissive points (Fig. 2c–d). These observations are consistent with the reversible formation/decomposition of the supramolecular adduct.

The morphology of the self-assembled structures was characterised using TEM and AFM microscopic techniques. The samples for microscopic studies were prepared by heating CHX solutions to 80 °C to break any kind of aggregates formed and were then slowly cooled down to rt to induce the formation of the thermodynamically favoured nanostructures.

TEM and AFM images of 1 recorded for different areas of the same sample (Fig. 3a,d and S4-5, ESI⁺) showed the presence of both spherical micro- and nanoparticles with the size ranging typically from ~10 nm to over 1 μ m. Structurally, molecule 1 has a solvophilic (with respect to CHX) aromatic and aliphatic central part and solvophobic polar end groups. Hence, in CHX, molecule 1 tends to self-assemble through electrostatic or weak H-bonding interactions involving the terminal moieties, as well as π -stacking interactions concerned with the central part of its structure. The occurrence of these combined aggregation phenomena is supported by the bathochromic shift of the absorption and emission maxima in solution upon temperature lowering (Fig. 2b).⁹

Contrary to that observed for molecule 1, both TEM and AFM images of a dropcasted solution of 1 and 2 (1:2 molar ratio) showed the presence of vesicles of highly uniform size distribution, which are spherical in shape and with a narrower diameter range of 80-180 nm (Fig. 3b,e and S6-7, ESI⁺). By passing from 1 to $[1 \cdot (2)_2]$, the change of the end functionality from solvophobic to solvophilic increases the solute-solvent interaction, prompting the formation of more thermodynamically favoured nanostructures with narrow size distribution. Since the $[1\cdot(2)_2]$ adduct has both ends being solvophilic, the vesicular-like structure¹⁰ will be more favoured, which further helps to minimise the solvophobic interaction of the polar di(acetylamino)pyridyl units. Under these specific conditions, it is reasonable to assume that π -stacking of the anthracene moieties occurs in a J fashion.¹¹ This is corroborated by the marked red shift of the absorption spectrum of the anthracene moiety when self-organisation occurs (Fig. 2c). In addition, the geometrical constraints imposed by the fact that both modules 1 and 2 self-assemble in a J fashion also dramatically affect the nanoparticle morphology.

The above interpretation was further confirmed by investigating the self-assembly between 1 and 2 in CHX at the 1 : 1 stoichiometric ratio. TEM and AFM micrographs showing the morphology of self-assembled structures are presented in Fig. 3c,f and S8–9, ESI \dagger . The analysis of these images showed that the 1 : 1 complexes also forms spherical nanoparticles, but with larger size distribution compared to those formed from 1 : 2 solutions (as well as smaller if compared to those obtained with module 1 alone). Interestingly, these nanoparticles have a bigger average size, with a diameter in the range 150–500 nm. In line with the above proposed rationale, this is explained considering that, under these conditions, there is a mixture of adducts of different stoichiometry exhibiting both solvophilic and solvophobic terminals.

In order to rule out self-assembly of the anthracenyl derivative **2** alone, we have carefully checked its behaviour. Absorption and emission spectra of **2** alone in CHX as a function of temperature did not evidence any clue of aggregation/self-organisation. This was further confirmed by AFM experiments following dropcasting of **2** onto a freshly cleaved mica surface. The images recorded from different areas of the sample (Fig. S10, ESI[†]) showed the presence of particles of different shapes with sizes ranging widely from 10 nm to over 2 μ m. This is due to uncontrolled aggregation of the molecules during solvent evaporation and confirms that only the H-bonding interactions between **1** and **2** drive the formation of nanoparticles.



Fig. 3 TEM (a, b and c) and AFM (d, e and f) of the self-assembled structures of 1 (a and d), molecular adducts between 1 and 2 in the 1:2 (b and e) and 1:1 ratio (c and f).

In summary, we have shown that by tuning the solvophilicity of organic systems through the formation of complementary hydrogen bonds it is possible to promote the formation of spherical nanostructures with novel optical and morphological properties. Very importantly, the supramolecular aggregates volume and size distribution can be tuned by the stoichiometric ratio of the molecular moieties in the parent solution. The strategy proposed here can be further refined for the engineering of nanoparticles of different size and shape by selecting appropriate molecular components and by varying their composition. We are currently working along these lines.

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