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A phosphonic acid appended naphthalene diimide motif for self-assembly into tunable nanostructures through molecular recognition with arginine in water†

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A naphthalene diimide motif bearing phosphonic acid functionalities has been found to be self-assembled with L- and D-arginine through chirality induced molecular recognitions and leads to the formation of micrometre long nanobelts and spherical aggregates at pH 9 in water, respectively.

Supramolecular self-assembly and self-organisation of small molecules play an important role in nano- and biotechnology.¹ Selfassembly in a controlled fashion within pseudo 1-D to form organized nanostructures is the subject of current research.² These paradigms have been widely studied with large aromatic macrocycles, especially in the design of conducting materials.³ Among them, 1,4,5,8-naphthalene diimides (NDIs) have attracted much attention due to their tendency to form n-type rather than p-type semiconducting materials.⁴ NDIs have allowed several research groups to probe the function of this dye molecule in a molecular and supramolecular sense.⁵ NDIs appended with various motifs such as amino acids,⁶ pyridyl-metal complexes,7 quaternion ammonium salts,8 phosphonates, carboxylates9 and hydrophilic as well as hydrophobic character10 have been used for decades for the formation of various supramolecular architectures such as nanotubes,¹¹ nanobelts,¹² organogels,¹³ hydrogels,¹⁴ synthetic ion channels,¹⁵ nanoparticles,¹⁶ fluorescent chemosensors¹⁷ and artificial supramolecular photosystems.¹⁸ Amongst all, the formation of nanobelts is an important task as the large area interface of nanobelts, when deposited on electrodes, facilitates the fabrication of optoelectronic devices with electrical contact.¹⁹

During the past few years, phosphorous atoms attached to photoactive dyes have been identified as most versatile building blocks in supramolecular chemistry.²⁰ In particular, a phosphonic acid group shows remarkable selectivity towards zwitterionic amino

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acids and amongst them arginine is the most attractive, mainly due to its involvement in selective protein binding with DNA and RNA.²¹ The phosphonic acid motif, which acts as a hydrogen bonding receptor, for guanidium ion recognition, has been studied intensively.²²

Here we report the use of NDI bearing phosphonic acid (Phos) self-assembled with L- and D-arginine (L- and D-arg) through molecular recognition and leading to the formation of well-defined long nanobelts and particular aggregates in water at pH 9, respectively (Fig. 1; for detailed self-assembly, see Scheme S1 in the ESI[†]).

The absorption of Phos–NDI (1) ([1] = 0.5×10^{-5} M), in water (pH 9, pH adjusted by addition of 0.1 M NaOH) showed two wellresolved sharp absorption bands at 363 nm and 384 nm with a shoulder at 347 nm, which is characteristic of the S0–S1 transition.²³ Fig. 2a shows the absorption spectra of **1** for various ratios of L- and D-arg in water at pH 9. It can be clearly seen that upon gradual addition of L-arg (0–10 equiv.), a reduction in peak intensity along with a loss of fine structures at higher % v/v was observed. However after 2 equivalent additions, there were no further changes in the absorption spectrum thus indicating the



Fig. 1 Schematic illustration of the proposed organized structure of Phos–NDI (1) with L- and D-arginine assembled into nanobelts and spherical aggregates, respectively.

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Fig. 2 UV/Vis absorption changes of Phos–NDI **1** (0.5×10^{-5} M) upon adding 0–10 equiv. of (a) L-arg and (b) D-arg, ($c = 1 \times 10^{-2}$ M), respectively. (c) Mirror image circular dichroism spectra of premixed Phos–NDI **1** with 2 equiv. of D- and L-arg as well as CD of competitive guest binding D-arg vs. L-arg. (d) Changes in CD upon titration with L-arg (1 and 2 equiv.) in water at pH 9.

saturation point (Fig. S1, ESI†). Practically, similar behaviour was observed in the presence of D-arg (Fig. 2b).

To gain an insight into the chiral transcription ability of achiral **1** with two equivalents of L-arg and D-arg, we probed the circular dichroism (CD) study (Fig. 2c),^{7,24} which exhibited strong Cotton effects through an isodichroic point at the zero-crossing at 372 nm. CD was found to be inactive when only **1** (10^{-5} M) was employed in water at pH 9; however in the presence of L-arg (2 equiv.) it showed strong negative and positive CD bands in the region of 391 nm and 361 nm, respectively, and the characteristic of excitonically coupled chromophores.

On the other hand, Phos-NDI with D-arg showed an opposite bisignated CD signal with positive and negative maxima at 390 nm and 359 nm, respectively. The mirror image Cotton effects of 1 clearly suggest the chirality with opposite handedness in the self-assembly. The CD signal induced by L- and D-arg at ~360 nm was attributed to the π - π * transition of the NDI chromophore. Furthermore, upon varying molar ratios of L-arg to 1, the CD signal indicates gradual evolution with an increase in concentration of L-arg (Fig. 2d). To understand further in depth, we have studied competitive molecular recognition by addition of L-arg to 1/D-arg using CD spectroscopy (Fig. 2c). A solution of Phos–NDI ($c = 1 \times 10^{-5}$ M, water) with 2 equiv. D-arg was titrated with the same amount of L-arg. Interestingly, addition of 2 equiv. of L-arg to 1/D-arg resulted in assemblies with a positive bisignated CD signal which exactly matched that of 1/L-arg stacks. This clearly suggests the competitive replacement of p-arg with L-arg from the assemblies, a result similar to the results obtained for ATP over ADP.⁷

Furthermore, the emission spectroscopy of **1** indicates that upon gradual addition of L- and D-arg, enhancement of emission was observed for each addition (λ_{ext} 384 nm; Fig. S2 and S3 in ESI[†]). These results strongly suggest the formation of



Fig. 3 (a and b) SEM images and (c) TEM image of nanobelts in premixed solution (1:2 molar ratio) of **1** (1×10^{-4} M) with L-arginine (1×10^{-2} M) in water at pH 9. (d) XRD pattern of nanobelts (films prepared by evaporating premixed solution of **1** and L-arginine (1:2 molar ratio) from water on a glass slide for 2 h and plotted against the angle 2 θ at 298 K).

NDI self-assembly through π - π stacking of the central NDI core. A similar effect was observed in the case of J- and H-aggregates.^{2,3}

The mixture of **1** and L-arg (1:2 molar ratio) in water at pH 9 consists of nanobelts, as determined by means of scanning electron microscope (SEM) images (Fig. 3a and b). A droplet of the water mixture was dropped onto a carbon tape and the tape was allowed to air-dry prior to imaging. One can clearly observe the presence of highly aligned and well defined nanobelts of Phos–NDI–L-arg. These nanobelts show quite uniform widths and thicknesses. The average width is ~900 nm with a thickness of *ca.* 10–30 nm and the length is in the range of a few tens of micrometers (Fig. S4, ESI⁺), leading to an aspect ratio (length over width).

Transmission electron microscopy (TEM) also supports the formation of nanobelt nanostructures. A droplet of premixed **1** and L-arg (1:2 molar ratio) in water was dropped onto a TEM grid (a 400 mesh copper grid coated with a carbon film) followed by staining with 2% uranyl acetate and the grid was allowed to dry in air. TEM images clearly show that **1** and L-arg self-assembled into a unique nanobelt nanostructure several micrometers in length with a uniform diameter of *ca.* 600–800 nm (Fig. 3c).

Further, to examine the mode of self-organization within the nanostructures, X-ray diffraction (XRD) measurements were carried out. Low angle XRD measurement displayed the strongest peak at $2\theta = 27.5^{\circ}$ corresponding to an interlayer *d*-spacing of 11.2 Å (the 012 diffraction of layered structure) and another diffraction peak at $2\theta = 26.1^{\circ}$ with the other interlayer *d*-spacing of 7.5 Å (the 101 diffraction of layered structure). The peaks at 39.9°, 42.4°, 47.2°, 52.1° and 66.5° can be attributed to the second to the fifth order diffraction of the (012) plane respectively. The intense and sharp peak (012) indicated that the nanobelts grew preferentially along the axis.²⁵

1 with D-arg was self-assembled into particular aggregates in water at pH 9 (Fig. 4). TEM clearly showed that compound **1** with D-arg (1:2 molar ratios) self-assembled into well-defined spherical aggregates, with a mean diameter of 80–110 nm.

The formation of spherical aggregates in solution was confirmed by dynamic light scattering (DLS) study of the premixed **1** with p-arginine (1:2 ratio, 1×10^{-4} M). The average diameter of the



Fig. 4 (a) TEM micrograph of the mixture of **1** and p-arginine $(1: 2 \text{ ratio}, 1-10^{-4} \text{ M})$ deposited onto the carbon-coated copper grid, and (b) the dynamic light scattering (DLS) of the above mixture.

spherical aggregates was observed at ~110 nm with a polydispersity index of 0.11 (Fig. 4b). The hydrodynamic radius (R_h) of the spherical aggregates derived from the characteristic line width was calculated by the CONTIN analysis method.²⁶

SEM and atomic force microscopy (AFM) further support the self-assembly of **1** with 2 equiv. of *D*-arginine that aggregates into a spherical form (Fig. S5 and S6 in ESI[†]). The average diameter of the spherical aggregates observed using SEM and AFM is 50–150 nm and 11–30 nm, respectively, which was notably smaller than that observed in TEM analysis (see Fig. 4 for the TEM micrograph). This may be due to the high local force applied by the AFM tip.²⁷

Importantly and from a molecular recognition issue, Phos-NDI itself or L-/D-arg alone or even a premixed solution of 1 and L-lysine failed to give any well-defined nanostructures at any pH indicating the subtleties of the self-assembly process, which may be due to lack of H-hydrogen bonding (Fig. S7, ESI⁺). Importantly, nanostructures of Phos-NDI with L or D-arg were only observed at pH 9, as lowering the pH does not produce any nanostructures (Fig. S8, ESI⁺). Although the self-assembly is predominantly driven by π - π stacking interactions between NDI cores, electrostatic interactions and chirality play an important role in the formation of each stack at pH 9 in water (Fig. 1). We believe that self-assembly of 1 with 1-arg leads to nanobelt formation mainly due to two reasons: (i) molecular conformation of two independent L-arg molecules arranged in a head to tail manner and superimposed directly i.e. adjacent molecules are linked by two N-H···O hydrogen bonds between the guanidium tail of one molecule and the carboxylate head of the adjacent molecule²⁸ and (ii) the "arginine fork" type arrangement would help in recognising Phos⁻...arg⁺...Phos⁻ units.²⁹ On the other hand, in the case of D-arg, only Phos⁻...arg⁺ molecular interactions may occur (Fig. S10 and Scheme S1, ESI⁺).

In conclusion, we have demonstrated the self-assembly behaviour of a phosphonic acid appended naphthalene diimide with L- and D-arg, which forms well-defined nanobelts and spherical aggregates in water at pH 9, respectively, *via* chirality induced molecular recognitions. The perfect morphological features of the nanostructures of NDI-arginine complexes may make them attractive for nano- and biomaterial research. We also believe that the assembly concept reported in this communication would be a valuable tool to identify protein surface areas by distinctive sequence specific self-assembly. Sid. V. Bhosale thanks the DAE-BRNS, Mumbai, India, for financial support under the project no. 2009/37/39/BRNS.

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