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## Supramolecular construction of vesicles based on core-substituted naphthalene diimide appended with triethyleneglycol motifs†

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The self-assembly of core-substituted naphthalene diimides bearing triethylene glycol motifs leads to the formation of stable vesicles in DMSO and CHCl<sub>3</sub>/MeOH (6:4, v/v) solvents. The vesicles were evaluated by means of UV/vis and fluorescence spectroscopy, transmission electron microscopy, atomic force microscopy and dynamic light scattering.

Non-covalent interactions play an important role in the construction of stable nanostructures with nanometre to millimetre dimensions utilising a ‘bottom-up’ or ‘bioinspired’ approach.<sup>1</sup> This approach is relevant to applications in the development of functional devices where the use of  $\pi$ - $\pi$  interactions and solvophobicity is required to produce supramolecular nanostructures.<sup>2</sup> Self-assembled, well-defined nanostructures such as nanobelts, nanowires and vesicular aggregates have been produced from larger aromatic macrocycles.<sup>3,4</sup> Amongst aromatic molecules that have found utility, especially in the design of conducting materials, the 1,4,5,8-naphthalene diimides (NDIs) have attracted much attention due to their tendency to form n-type semiconductor materials.<sup>5</sup> Core-unsubstituted naphthalene diimides have been used for decades as electron acceptors in dyads and more sophisticated architectures such as catenanes and rotaxanes.<sup>2</sup> However, their optical properties are unremarkable limiting their utility. A slight modification by core substitution by one, two or up to four electron-donating groups on the naphthalene ring introduces a new electronic transition with charge transfer character located in the visible region.<sup>6</sup> Core-substituted naphthalene diimides (c-NDIs) have opened this class to further investigation, by combining optical and structural changes to develop function as supramolecular<sup>7</sup> and molecular sensors.<sup>8,9</sup> Self-assembled nanostructures of c-NDI derivatives have not yet been extensively studied, with only a few controlled nanostructures being reported.<sup>7</sup> Recently, we have shown that

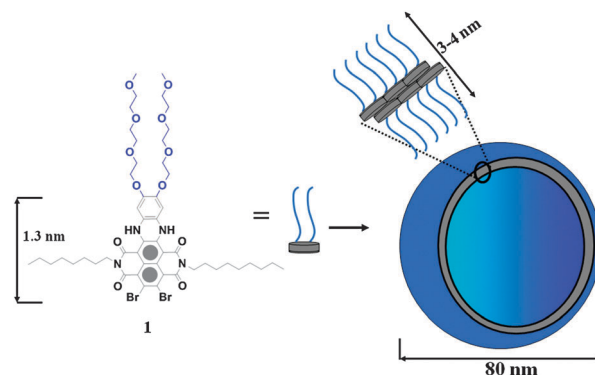


Fig. 1 Schematic illustration of the proposed organised structure of c-NDI **1** into vesicles.

alkyl-annulated c-NDIs self-assemble in a controlled process into discrete worm-like nanostructures with defined diameters from 40% v/v MeOH in CHCl<sub>3</sub>.<sup>7a</sup>

In this work, we explore on the development and use of methoxytriethylene glycol-annulated core-substituted NDIs **1** (mTEG-cNDI) for the precision-controlled assembly of vesicles formed from DMSO and CHCl<sub>3</sub>/MeOH (Fig. 1).

Naphthalene diimide **1** bears three important features: (1) the use of hydrophobic alkyl chains at the periphery through both the imide nitrogen, (2) the use of hydrophilic methoxytriethylene glycol chains (mTEG) *via* amine linkage to the core, and (3) a near planar core available for  $\pi$ -stacking, consistent with other methodologies used for studying self-assembly of this class.<sup>7</sup> The driving force for the formation of vesicles of **1** lies with the balance of  $\pi$ - $\pi$ -interactions between NDI cores with the outer and interior hydrophilic interaction of the mTEG and solvophobic interactions of the long alkane chains. We postulate, based on the evidence to be shown, that **1** self-assembles in a bilayer fashion with the hydrophilic ethoxy chains exposed both internally and externally to the polar solvent with the hydrophobic alkyl groups interacting in the middle of the bilayer.

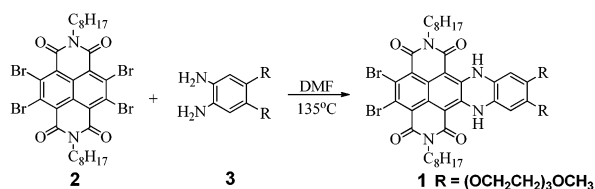
Compound **1** was prepared by reacting the tetrabromo-NDI **2**<sup>10</sup> with 4,5-bis(tetraethyleneglycol)benzene-1,2-diamine **3** in dry DMF solution at elevated temperature (Scheme 1). m-TEG-c-NDI **1** was obtained in 76% yield as a deep green crystalline solid after purification by column chromatography on silica. The fact that monoannulation results in high yield

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† Electronic supplementary information (ESI) available: Synthesis of **1**, and details of UV/vis and AFM data for all assemblies and aggregates. See DOI: 10.1039/c1cc11318f

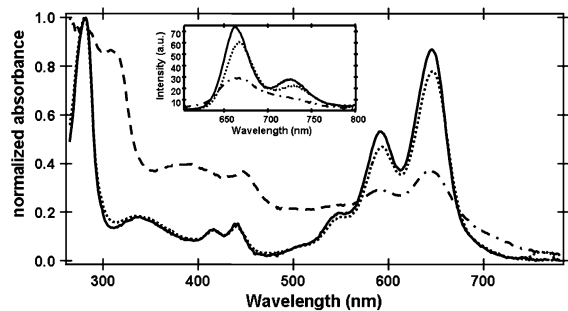


**Scheme 1** Synthesis of core-substituted NDI used in this study.

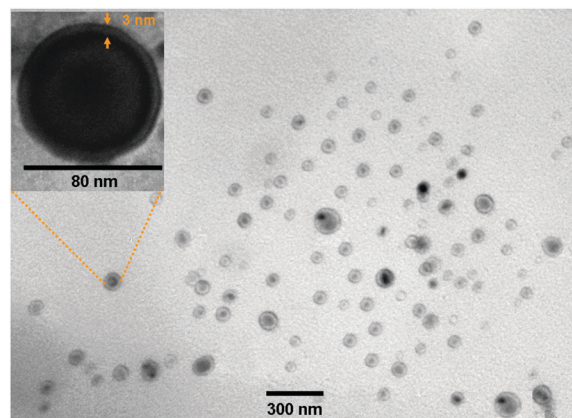
can be attributed to two factors: aniline amines such as **3** are less nucleophilic than the aliphatic amines used in examples where tetrasubstitution takes place<sup>6c</sup> and once the first addition is complete, the deactivating feature of the two donating amino groups leads to a balance of the two effects that prevents further addition.<sup>7a</sup> This result is very important as it may allow variation to the structure through the two remaining aryl bromide groups.

The UV-VIS absorption spectrum of **1** in CHCl<sub>3</sub> shows a structured band with a maximum at 646 nm, which is red-shifted compared to that of bromo-substituted NDI **2**,<sup>10</sup> and is characteristic for the S<sub>0</sub> → S<sub>1</sub> transition of the isolated NDI chromophore (Fig. 2).<sup>6</sup> In DMSO, this band shifts to 652 nm. The results demonstrate that the electron-donating 2,3-diamino substituent introduced to the naphthalene core affects the electronic structure of NDI in a similar fashion to 2,6- or 2,3,6,7-core-substitution.<sup>6,7</sup> The second absorption band (400–450 nm) is due to a π–π\* transition involving only the NDI unit. In this case the absorption bands of **1** in CHCl<sub>3</sub> and in CHCl<sub>3</sub>/MeOH mixtures coincide with a λ<sub>max</sub> of 580 nm, whereas in the DMSO solvent, we observed both a reduction in the peak intensity along with a significant red-shift of the absorption maximum, indicating the possibility of molecular aggregation. These features suggest the formation of face-to-face π-stacks of rotationally displaced NDI chromophores.<sup>11</sup> The emission spectra of NDI **1** recorded in all the three solvents upon excitation in the S<sub>0</sub> → S<sub>1</sub> absorption band at 600 nm are also shown in Fig. 2. c-NDI **1** in CHCl<sub>3</sub> shows an emission maximum at 662 nm. The emission spectrum recorded in CHCl<sub>3</sub>/MeOH (v/v 6:4) has the same shape as that in CHCl<sub>3</sub> but with red-shifted maximum at λ<sub>em</sub> = 667 nm. In DMSO the emission band peaks at λ<sub>em</sub> = 665 nm.<sup>4</sup>

These features suggest an influence of solvent polarity and perhaps the formation of larger aggregates as similar behaviour has been observed in the case of perylenediimides.<sup>11</sup>



**Fig. 2** UV-vis absorption of NDI **1** ( $1 \times 10^{-4}$  M) in CHCl<sub>3</sub> (solid line), CHCl<sub>3</sub>/MeOH (v/v, 6:4, dotted line) and in DMSO (broken line), the inset shows steady state fluorescence of **1** in the same solvents respectively.

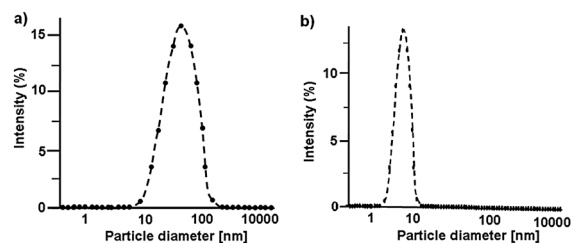


**Fig. 3** TEM image of **1** prepared from DMSO solution and stained with uranyl acetate. The inset shows high magnification of a vesicle to identify the interlamellar spacing between two adjacent layers, the scale bar represents 80 nm.

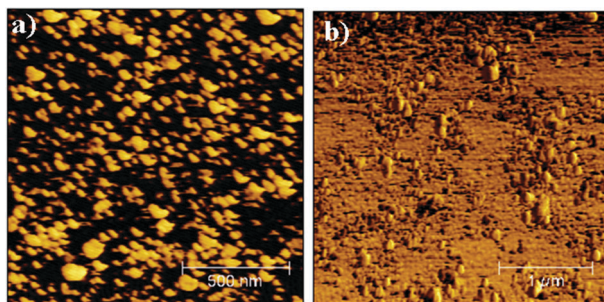
This prompted us to further investigate the products formed in solutions of **1** using transmission electron microscopy (TEM), atomic force microscopy (AFM) and dynamic light scattering (DLS).

The green solution of c-NDI **1** ( $1 \times 10^{-4}$  M) in DMSO consists of vesicles, as determined by means of negatively stained TEM images (Fig. 3). A droplet of DMSO solution was dropped onto a TEM grid (400 mesh copper grid coated with a carbon film). Immediately the non-aqueous solution was stained with 2% uranyl acetate and the grid was allowed to air-dry. One can clearly see a mass of vesicles and the bilayer structure can be identified from the enlarged micrograph (inset Fig. 3). The TEM image clearly shows that all the c-NDIs self-assemble into spherical vesicles, with a diameter of ca. 60–100 nm and an estimated membrane thickness of ca. 3–4 nm. DMSO is a strongly coordinating ligand for the hydrophilic mTEG chain, the staining agent giving rise to the even darker inner area compared to the membrane itself.

The formation of vesicles in solution was confirmed by DLS studies of **1** ( $1 \times 10^{-4}$  M) in DMSO. The average diameter of the vesicles was observed to be 90 nm with a polydispersity index of 0.11 (Fig. 4a). The diameter of the vesicles formed from CHCl<sub>3</sub>/MeOH (6:4, v/v, Fig. 4b) falls into the range 17–20 nm. From this size organization, c-NDIs **1** in DMSO form a multilamellar membrane. Moreover, the vesicles display a very narrow size distribution, and are highly stable against coagulation. The  $R_H$  of the vesicles derived from the characteristic line width were obtained by the CONTIN analysis method.<sup>12</sup>



**Fig. 4** Size distributions of vesicles of **1** ( $1 \times 10^{-4}$  M) measured by DLS from (a) DMSO and (b) CHCl<sub>3</sub>/MeOH (6:4, v/v) solutions.



**Fig. 5** AFM image of vesicles formed by NDIs **1** in DMSO: (a) height, image and (b) phase image was spin-cast on silica wafer before taking the AFM images.

AFM also supported the formation of vesicular structures. AFM imaging was performed on spin coated samples of **1** ( $1 \times 10^{-4}$  M) on silica wafers in DMSO and analyzed in the tapping mode (Fig. 5). Compound **1** produces a well defined vesicular pattern. The average diameter of the vesicles is *ca.* 40 nm, which was notably smaller than that revealed by TEM. The ratio of the diameter and height of the vesicle formed by **1** was estimated to be *ca.* 55 nm indicating important flattening upon being transferred from solution to the silicon surface (see Fig. S3, ESI<sup>†</sup>).<sup>12,13</sup> This result may be due to the high local force applied by the AFM tip.

Vesicles were also observed within the range 35%–45% *v/v* methanol in chloroform (see Fig. S4, ESI<sup>†</sup>).<sup>10</sup> AFM indicated that the apparent size of the structures determined in DMSO is larger than  $\text{CHCl}_3/\text{MeOH}$  (Fig. 5).<sup>13,14</sup> This result may be due to the fact that the scanning AFM tip drags the particles in volatile solvents.<sup>15,16</sup>

The fluorescence decay profile of *c*-NDI **1** in  $\text{CHCl}_3$  measured using the Time Correlated Single Photon Counting (TCSPC) technique is monoexponential with a 1.84 ns lifetime, whereas in DMSO the same profile is biexponential with 1.9 and 4.8 ns lifetimes (see Fig. S11 and S12, ESI<sup>†</sup>). The biexponential nature points to the existence of two emitting populations, one with a 1.9 ns lifetime like in  $\text{CHCl}_3$  and another 4.8 ns, which may be due to the emission from the aggregated dyes. Furthermore, transient absorption (TA) spectra measured with **1** in  $\text{CHCl}_3$  and in DMSO upon excitation with a 50 fs pulse at 630 nm do not exhibit significant difference (see Fig. S13 and S14, ESI<sup>†</sup>, respectively).

In conclusion, we have demonstrated that a novel non-ionic  $\pi$ -electronic amphiphile consisting of a core-substituted NDI bearing mTEG-chain self-assembles into uniformly sized multilamellar vesicles in DMSO. The perfect morphological features of the present vesicles of *c*-NDI may make them attractive in nanomaterial and biomaterial research. Further investigation of the packing structure, selective formation of a vesicle with changing internal and external environment, and use of vesicles in artificial photosynthesis are currently underway.

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