NJC

PAPER



Cite this: DOI: 10.1039/c7nj04503d

Received 20th November 2017, Accepted 18th March 2018

DOI: 10.1039/c7nj04503d

rsc.li/njc

Introduction

Molecular self-assembly enables the fabrication of complex nano- and micro-architecture morphologies guided by the rational design of organic molecules, and strategically utilising the non-covalent interactions.^{1,2} Such non-covalent interactions include hydrogen bonding, hydrophobic interactions, van der Waals interactions, ionic and electrostatic interactions and π - π stacking between adjacent aromatic cores. The assembly of molecules is also influenced by other chemical and physical stimuli of the molecular environment such as pH,³ temperature,⁴ and solution parameters such as concentration, solvent polarity and dielectric constant.⁵ The balance of hydrophilic/hydrophobic interactions within the molecule, and between molecules, is a determining factor in the morphology of the resulting selfassembled nanomaterials.^{5,6} This allows for the construction of a range of supramolecular nanostructures by varying the solution parameters of a single molecule.5



Sopan M. Wagalgave,^{ab} Duong DucLa,^c Rajesh S. Bhosale,^a Mohammad Al Kobaisi,^c Lathe A. Jones, ^b^c Sidhanath V. Bhosale*^a and Sheshanath V. Bhosale^b*^{cd}

A naphthalene diimide (NDI) derivative bearing four carbamate groups (coded as: **W2**) was synthesised using a multistep strategy, and utilizing solvophobic effects, the self-assembly of this molecule was studied using solvent mixtures. Self-assembly led to a variety of controllable morphologies of supramolecular structures on both the micro and nanoscale. Nanobelts, nanospheres, nano-corals, microflowers and nanograss-like morphologies were obtained in DMF, MCH, CHCl₃, THF, water and MeOH solvent mixtures. UV-vis absorption, fluorescence emission spectroscopy, FT-IR and XRD gave insight into the mode of aggregation of **W2** in various solvents. The polarity of the solvent mixtures used directed the self-organisation of **W2** by driving the π - π stacking interaction between NDI cores, and the H-bonding between the carbamate moieties. Our studies show that the solvent polarity guides the self-assembly process during solvent evaporation leading to the formation of supramolecular nano- and microstructures under ambient conditions.

Although there have been various reports where molecules are designed with chemical structures containing responsive amphiphiles to control the self-assembly process,⁷ it is still challenging to fabricate multiple nanostructures based on a single amphiphilic unit.⁸ In this context, the ability to engineer and synthesize variable molecular structures remains a crucial step towards fabrication of nano-sized technology.

To guide the self-assembly process towards a specific nanostructure, both well-engineered functionality in the molecular structure and a well-controlled environment where the selfassembly takes place are required.^{9–11} Dong and co-workers recently reported the self-assembly of dipeptide and the effect of graphene oxide on the morphology of the self-assembled peptides.^{12–15} This field of study is heading towards developing the novel concept of nanoarchitectonics by the unification of supramolecular self-assembly/self-organization with nanotechnology.^{16–18}

To this end, naphthalene diimides (NDIs) are ideal candidates due to their large planar aromatic core that gives rise to π - π stacking interactions.¹⁹ The amphiphilic derivatives of NDI were recently found to self-assemble to obtain nanotube, nanowire, nanosphere, nanorod, nanobelt, fractal, vesicle and nanoflower morphologies.²⁰ This indicates that NDIs have a strong tendency to form nanostructures of various shapes and sizes. Aggregation of NDI units may alter their photochemical and photophysical properties when compared with their solvated monomer molecules.^{19,20} This change can have a significant

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^a Polymers and Functional Materials Division, CSIR-Indian Institute of Chemical Technology, Hyderabad-500 007, Telangana, India. E-mail: bhosale@iict.res.in

^b Academy of Scientific and Innovative Research (AcSIR), CSIR-IICT,

Hyderabad-500 007, Telangana, India

^c School of Science, RMIT University, GPO Box 2476, Melbourne, VIC-3001, Australia

^d Department of Chemistry, Goa University, Taleigao Plateau, Goa-403 206, India. E-mail: svbhosale@unigo.ac.in, bsheshanath@gmail.com

[†] Electronic supplementary information (ESI) available. See DOI: 10.1039/c7nj04503d



Fig. 1 Molecular structure and different nano-architectures of W2.

influence on NDI based optoelectronic materials with n-type semiconducting properties.

Herein, we show the self-assembly of the π -conjugated aromatic NDI core functionalised with four hydrogen bond forming carbamate groups that gives a range of nano- and micro-structures (Fig. 1). The amphiphile **W2** assembles into eight fundamentally different self-organized nanostructures. It is demonstrated that by varying the solution parameters, a range of distinct nano-architectures can be generated from a single π -conjugated engineered amphiphile **W2**.

Results and discussion

The synthesis of 2,6-dibromo-1,4,5,8-naphthalene tetracarboxylicdianhydride **1** was achieved from 1,4,5,8-naphthalene tetracarboxylicdianhydride and DBH in the presence of sulphuric acid at 72 °C.²¹ The monoboc protected ethylene diimide **2** was synthesized according to a literature procedure.²² The condensation of **1** with **2** in acetic acid at 80 °C yielded the NDI derivative **3**. The NDI amphiphile **W2** was synthesized *via* the nucleophilic substitution reaction between NDI derivative **3** and boc protected ethylene diamine **2** in toluene at 70 °C (Scheme 1). The synthesized compounds were characterized and their structure was confirmed by means of FT-IR, ¹H NMR, ¹³C NMR, ESI mass and MALDI-TOF-MS spectroscopic techniques (Fig. S1–S8, ESI†). Thermogravimetric analysis of **W2** was carried out to examine the thermal properties. At 205.45 °C, a 2% weight



Scheme 1 Synthetic pathway of naphthalene diimide derivative W2.

loss was observed, suggesting that the compound **W2** is thermally stable (Fig. S9, ESI[†]). Due to its NDI core and four amide subunits, it is expected to engage in π - π stacking interactions on the NDI core, van der Waals interactions and carbamate based hydrogen bonding. These non-covalent interactions along with solvophobic control are utilized in the self-assembly of **W2** into different shapes. In this study, the self-assembly behaviour of **W2** was monitored by UV-vis absorption and fluorescence emission spectroscopy techniques, and the morphology of the formed structures was visualized by field emission scanning electron microscopy and polarized optical microscopy studies.

Absorbance spectra of **W2** are shown in Fig. 2(a–d), allowing a study of aggregation. The spectra are recorded in chloroform solution. In CHCl₃ solution, **W2** exhibits three main absorbance peaks at 346, 363, and 607 nm and a shoulder peak at 568 nm. Fig. 2a shows the UV-vis absorption changes of **W2** solution in CHCl₃ with MCH addition.

Upon incremental addition of MCH to a solution of W2, the absorption peaks at 346, 363 and 607 nm show a gradual decrease in intensity, with a disappearance of the shoulder at 568 nm. At 80% of MCH in CHCl₃, the peaks at 346 and 363 nm are broadened with a decrease in intensity of the peak at 607 nm, which is red shifted to 611 nm. It is also observed that a new band grows gradually at 673 nm. At 90% MCH, the intensity of 673 nm increases to a maximum and a second new broad band appears at 694 nm, as indicated by the arrow in Fig. 2a. The bathochromic shift and broadening of the absorbance band and the appearance of a new band at 694 nm can be assigned to J-type aggregation of W2. Fig. 2b and c displays the UV-vis absorption spectra of W2 in CHCl₃/MeOH and CHCl₃/DMF; in both solvent mixtures, a gradual decrease in peak intensity is seen for both bands at 346 nm and 363 nm, along with a blue-shift of the peak at 568 nm to 607 nm. This clearly indicates that W2 assembled into H-type aggregates in both the solvent mixtures, *i.e.* CHCl₃/MeOH and CHCl₃/DMF. Fig. 2d shows the absorption spectra of W2 in various ratios of H_2O to THF. With the incremental addition of water (0–70%), a reduction of peak intensities along with a red shift of all the bands was seen, *i.e.* the peak at 343 nm shifted to 360 nm, the peak at 559 nm shifted to 599 nm and the peak at 346 nm shifted to 364 nm, respectively. After addition of water to 80-90%, all the peaks broaden with an intense red-shifted broad band appearing at 671 nm, which indicates the formation of J-type of aggregates of W2.

These results suggest the effect of solvent polarity on the self-assembly and molecular aggregation. The formation of such aggregates in various solvent mixtures was further verified by the corresponding fluorescence emission measurements. The fluorescence emission spectra of **W2** in CHCl₃ are shown in Fig. 3a–d. Upon excitation at 550 nm, the fluorescence emission spectrum of **W2** in neat CHCl₃ shows an intense peak at 637 nm along with a shoulder peak at 695 nm. The intensity of the peaks at 637 nm and 695 nm decreased gradually, and were completely diminished eventually with the addition of MCH (0–90%). The decrease in emission peak intensity indicated strong π – π stacking of the NDI cores leading to



Fig. 2 UV-vis absorption spectra of W2 in (a) CHCl₃: MCH, (b) CHCl₃: MeOH, (c) CHCl₃: DMF and (d) THF : H₂O at room temperature

head-to-tail J-type aggregation. The differential scanning calorimetry (DSC) measurements (Fig. S10, ESI†) show the melting point of **W2** is 212.78 °C. This melting point suggests strong NDI molecular packing *via* π - π stacking interactions.

In CHCl₃/MeOH (0–90%), **W2** exhibited a decrease in fluorescence emission intensities at 637 and 695 nm (Fig. 3b). Furthermore, Fig. 3c displays the emission spectra of **W2** in various ratios of CHCl₃ to DMF (0–90%), where aggregation of the NDI molecule is evidenced by the general decrease in fluorescence intensity. As shown in Fig. 3d, fluorescence emission peaks in THF at 631 nm red shifted to 654 nm and decreased with increasing water content. As shown in Fig. 3c, up until 70% water content, the emission peak broadened with a red shift. When the water content was more than 80%, the intensity of the peak at 631 nm further decreased and diminished to the baseline. These fluorescence emission spectral changes promoted by the increasing water content may be attributed to the formation of J-type (head-to-tail conformation) aggregates of **W2**.

To further investigate the electronic structure of **W2**, time dependent density functional theory (TDDFT) calculations were carried out. The *in vacuo* TDDFT calculations using the Gaussian 16 suite of programs²³ and the B3LYP/6-31+G(d,p)//B3LYP/6-311++G(d,p) level of theory gave a HOMO–LUMO gap of 508.3 nm (2.44 eV) and HOMO \rightarrow LUMO transition at 568 nm (Fig. 4A).

The HOMO \rightarrow LUMO shows an electron transfer from the HOMO concentrated on the amine groups 2,6-substituted on the NDI to the LUMO with electron density concentrated on the core (Fig. 4B). Table S1 (ESI⁺) lists the first 25 singlet excitations of the **W2** molecule, a significant red shift of 44 nm from 568 to 612 nm in the experimental spectrum in chloroform shows the solvation effect on electron transitions, and similar red shifts were observed in other transitions in the calculated and observed spectra (Fig. 4C). The calculated CD spectrum shows evidence of chirality for **W2** *in vacuo* (Fig. 4D).

Scanning electron microscopy (SEM) was used to investigate the morphology of the W2 aggregates. Fig. 5 displays the SEM images of the self-assembled nanostructures. The samples of W2 for SEM measurements were prepared in CHCl₃:MCH (50:50, v/v) and CHCl₃:MCH (30:70, v/v) and drop cast onto a clean glass cover slip substrate, followed by sputter coating with gold for 10 s at 0.016 mA. The SEM image of W2 in CHCl₃:MCH (50:50, v/v) shows that W2 self-assembled into several micrometer long nanobelts (Fig. 5a, b and Fig. S11a, ESI†).

We observed densely interwoven nanobelts deposited on the substrate surface (see Fig. 5a). The nanobelts are approximately 150 nm in width and are cross-stacked to form an interwoven structure. We also examined the morphology of **W2** in CHCl₃: MCH (30:70, v/v) by increasing the percentage of MCH. The SEM of **W2** showed well resolved nanobelts of approximately



Fig. 3 Fluorescence emission spectra of W2 (λ_{ex} = 550 nm) in (a) CHCl₃: MCH, (b) CHCl₃: MeOH, (c) CHCl₃: DMF and (d) THF: H₂O at room temperature.



Fig. 4 The frontier molecular orbital HOMO and LUMO wave function and energy levels of W2 as calculated using TD-DFT at the B3LYP/ 6-311++G(d,p) level of theory.

 $40~\mu m$ in length and 150 nm in width, as shown in Fig. 5b and Fig. S11b (ESI†). In this case, an increase in MCH in $CHCl_3$ also

affects the nanobelt morphologies. We presume that the driving attractive force leading to such well-organized nanobelts may arise from van der Waals interactions, π - π stacking interaction of aromatic NDI cores and intermolecular carbamate hydrogen bonding.

In addition to the effect of MCH, we investigated the selfassembly of **W2** in $CHCl_3$: MeOH (50: 50, v/v) and $CHCl_3$: MeOH (30:70, v/v) (Fig. 5c and d). The formation of supramolecular nanostructures was monitored by SEM imaging of the morphology formed. These SEM images revealed that addition of 50% MeOH to a $CHCl_3$ solution of **W2** led to a supramolecular globular particle morphology, with snail-like horns (Fig. 5c and Fig. S11c, ESI†). The globular particles are heterogeneous in size with an approximate diameter of 400–500 nm. Increasing the MeOH content to 70% in $CHCl_3$ leads to a similar type of globular particle assembly (Fig. 5d and Fig. S11d, ESI†). In this case also, the globular particle aggregates are surrounded with snail-like horns. SEM images suggest that the particle size is approximately 400–500 nm. These results reveal that an increase in MeOH content does not affect the morphology of



Fig. 5 SEM images of W2 in $CHCl_3$: MCH: (a) 50:50%, (b) 30:70%; in $CHCl_3$: MeOH: (c) 50:50%, (d) 30:70%; in $CHCl_3:DMF$: (e) 50:50%, (f) 30:70%.

aggregates. We presume that the three-dimensional (3D) morphological growth mechanism of **W2** involves three types of interactions: van der Waals interactions, π - π stacking and carbamate hydrogen bonding.

Thus, the morphologies of W2 have been shown to change from nanobelt (Fig. 5a and b) to globular particles (Fig. 5c and d) by adding a solvent (MCH or MeOH) to the CHCl₃ solution, suggesting the nature of the solvent plays an important role in these non-covalent interactions to tune the morphology. We also examined the effect of DMF on the morphology of W2 in chloroform. The SEM measurements are shown in Fig. 5e and f in $CHCl_3$: DMF (50:50, v/v) and $CHCl_3$: DMF (30:70, v/v). Fig. 5e and Fig. S11e (ESI⁺) show that the self-assembly of W2 in $CHCl_3$: DMF (50: 50, v/v) leads to a coral-like morphology of several microns in size. The zoomed image of the coral reef morphology is shown in Fig. 5e. Interestingly, when the DMF content was increased to 70%, the collapse of the coral reef morphology is observed (Fig. 5f and Fig. S11f, ESI⁺), presumably due to a reduction in interfacial energy between W2 and DMF in this arrangement.¹

In addition to organic solvent driving the self-assembly of **W2**, the addition of water to organic media was achieved using THF and water aqueous mixtures with 60, 80 and 90% water contents. The SEM images of the self-assembled micro-structures of **W2** in these mixtures are shown in Fig. 6a–f and Fig. S12a–c (ESI[†]). In THF: H_2O (60%), **W2** self-assembled into



Fig. 6 SEM images of W2 in THF : H_2O : (a) 40 : 60% and (b) zoomed image in 40 : 60%; (c) 20 : 80% and (d) zoomed image in 20 : 80%; (e) 10 : 90% and zoomed image in 10 : 90%.

nanobelts several micrometers in length and 400 nm in width, as well as flower like nanostructures (Fig. 6a). It is notable that the nanobelt and flower-like morphologies coexisted in the same sample (Fig. 6a, b and Fig. S12a, ESI†). The flower like microstructure is composed of a nanofiber formation radially organized spreading out from a seed point resulting in an approximately 20 μ m diameter super structure.

Here, we speculate that the NDI unit undergoes π - π stacking and that amide hydrogen bonding leads to self-assembled micrometer long fiber formation of W2. In the THF:H₂O (60%) solvent system, the microstructures gradually changed from nanofiber structures to 3D microflowers, indicating that solvent polarity regulated the morphology of the microstructures. In THF: H₂O (80%), W2 self-assembled into microfibers several microns in length and 20-30 nm in width (Fig. 6c, d and Fig. S12b, ESI[†]). It is observed that the nanofibers of W2 stack on top of each other at intersections to lead an interwoven structure (Fig. 6d). When the THF ratio increased to 90%, the self-assembled W2 was changed to a grass-like morphology, as shown in the SEM micrograph. Magnified SEM images reveal the grass-like W2 nanostructures to be flat as well as sharp leaves (Fig. 6e, f and Fig. S12c, ESI⁺) that are vertically arranged. Furthermore, these leaf like structures have sharp edges and tips. The top of some of the leaves is flat at the bottom, suggesting W2 assembled via strong π -stacking of the NDI core in the presence of a high water content in THF. The large

surface area covered by the vertical grass like morphology may be useful for catalytic applications.

The morphologies of **W2** formed under different solvent systems were systematically examined using polarized optical microscopy (POM). The different types of morphology of **W2** were clearly observed in the POM images (Fig. S13a–f and S14a–c, ESI†). At 50% MCH in CHCl₃: MCH, intertwined nanofibril bundles could be observed (Fig. S13a, ESI†). Furthermore, in CHCl₃: MCH (70%), long nanobelt structures were observed (Fig. S13b, ESI†). In the presence of MeOH (50%) as well as 70% MeOH in CHCl₃, POM images demonstrated a nanosphere morphology (Fig. S13c and d, ESI†). On the other hand, at 50% and 70% DMF in CHCl₃, the coral reef like morphology was observed (Fig. S9e and f, ESI†).

We evaluated the morphology of **W2** in THF: water solvent systems (Fig. S14a–c, ESI†). In the presence of 60% water in THF, **W2** formed long nanobelt structures embedded with flowers (Fig. S14a, ESI†). However, in 80% water in THF, we observed a dense nanofibril morphology (Fig. S14b, ESI†). On the other hand, by increasing water content to 90% in THF, we found a grass-like morphology (Fig. S14c, ESI†). Therefore, we can conclude that an increase in the water content leads to changes in the morphology of **W2** from nanobelt to nanofibril, and finally to nanograss. Here, we presume that an increase in water affects the intermolecular NDI π – π stacking interactions. These experiments confirmed that carbamate hydrogen bonding and changes in the solvent system yield similar nanoarchitectures on different surfaces.

We presume that fabrication of such diverse nanoarchitectures from the single naphthalene diimide derivative bearing four carbamate groups is due to several factors: (i) four carbamate hydrogen bonding interactions, (ii) intermolecular π - π stacking interactions, and (iii) the balance between hydrophilic and hydrophobic interactions in mixed solvent systems, *i.e.* organic–organic and organic–aqueous.

Dynamic light scattering (DLS) experiments were performed on self-assembled solutions of W2 under various solvent conditions, such as CHCl₃:MCH, CHCl₃:MeOH, CHCl₃:DMF and THF:H₂O. The DLS analysis showed that in the size distributions of the W2 nanobelts with an average size of 63.21 nm (CHCl₃:MCH, 1:1 v/v), when the percentage of MCH in CHCl₃ was increased, a prominent peak appeared at 193.7 nm (CHCl₃: MCH, 3:7 v/v), as shown in the ESI,[†] Fig. S15. DLS results showed that the addition of methanol to a chloroform solution of W2 to increase the ratio from 50% and 70%, leads to an increase in the average hydrodynamic diameter of spheres from 63.08 nm and 561.5 nm (Fig. S16, ESI†). We presume that this was due to the increase in methanol content in chloroform, which is a driving force to form larger size aggregates. Furthermore, DLS analysis shows that the diameters of the aggregate structures in $CHCl_3$: DMF (1:1 v/v) solvent mixtures are about 2471 nm (59%) and 1.91 nm (41%) whereas in $CHCl_3$: DMF (3:7 v/v), the diameters are about 1410 nm (60.6%) and 3.38 nm (39.4%) (Fig. S17, ESI⁺). We speculate that this was due to the increased concentration of DMF in chloroform. The DLS measurements were undertaken



Fig. 7 Schematic illustration of **W2** self-assembly to give various morphologies of superstructures.

on a self-assembled solution of **W2** in THF: H_2O solvent systems (Fig. S18, ESI[†]). The DLS analysis revealed a 141.8 nm average diameter of the flower morphology in THF: H_2O (4:6 v/v). In THF: H_2O (2:8 v/v) and (1:9 v/v), the hydrodynamic diameters of aggregates were approximately 768.4 nm and 467.8 nm, respectively.

The flat four-paddle fan-like molecular conformation of **W2** indicates intermolecular π - π stacking interactions of the NDI cores, as well as H-bonding interactions between the carbamates may occur. Fig. 7 is a schematic representation of the aggregation mode of **W2** in the self-assembled state, giving a supramolecular planar sheet, twisted ribbons or tubular structures, which depends on the balance between the hydrophobic π - π interactions and H-bonding interaction, which is driven by the solvophobic effects. The carbamate subunits on the *N*-substitution moieties lead to in plane intermolecular interaction while the core 2,6-substitution helps the stacking of the molecules *via* H-bonding.

In order to investigate H-bonding involvement in the selfassembled microstructure formation of W2, we have studied the FT-IR spectra. The W2 compound containing four carbamate functional subunits forms microflowers and microfibers in THF: water, 40:60% v/v and 20:80% v/v, respectively. We presume that carbamate hydrogen bonding plays a crucial role in the formation of these microstructures. FT-IR spectra of the self-assembled structures from W2 are shown in Fig. S19 (ESI⁺). Strong vibrational bands were observed at 1695 cm⁻¹ and 1635 cm⁻¹ for W2, which were assigned to the symmetric and asymmetric stretching vibrations of the carbonyl of -NH-CO-O-, respectively. It was noticed that upon addition of 60% water in a THF solution of W2, the peak intensity at 1695 cm⁻¹ was decreased and broadened with a significant shift to 1648 cm⁻¹. Further, increasing the water ratio to 80% resulted in a decrease of the 1648 cm^{-1} peak intensity and a shift to 1643 cm⁻¹. This broadening and shifting of the -C=O peak indicates intermolecular hydrogen bonding between carbamates in the self-assembled microstructures in THF: water.

Fig. S20 (ESI \dagger) shows the X-ray diffraction pattern (XRD) of W2 as amorphous powder and as deposited from various

solvent systems. However, when it was self-assembled in THF: $H_2O(40:60\%, v/v)$ and $CHCl_3:MCH(50:50\%, v/v)$ mixtures, it became crystalline as confirmed by the presence of peaks in the XRD patterns, which is consistent with observations in SEM images (Fig. 6a and 5a). In $CHCl_3:MeOH$ and $CHCl_3:DMF$, self-assembled **W2** shows low crystallinity as evidenced by the appearance of a broad peak at around 17° ; this is also explained by the spherical shape of the **W2** nanostructures observed in the SEM images (Fig. 5c and e).

Conclusions

In summary, we have succeeded in fabricating 1D, 2D and 3D supramolecular naphthalene diimide structures based on a simple NDI derivative (**W2**) containing four carbamate hydrogen bonding subunits. The diverse nanoarchitectures obtained include nanobelts, nanoparticles, coral structures, nanobelts embedded with micro-flowers, micro-fibrils and grass-like morphologies, indicating possible self-assembly methodologies towards novel self-assembled materials. We believe that construction of such solvent responsive nanomaterials is the result of intermolecular carbamate hydrogen bonding and π - π stacking interactions. The approach we have presented here opens a new door to the fabrication of new complex supramolecular nanoarchitectures of naphthalene diimide molecules by employing different solvent systems.

Experimental section

General methods and materials

1,4,5,8 Naphthalene tetracarboxylicdianhydride, ethylene diamine, di-*tert*-butyl dicarbonate and 1,3-dibromo-5,5-dimethylhydantoin were purchased from Sigma-Aldrich Company, Bengaluru, Karnataka, India. Dichloromethane, acetic acid, toluene and conc. H_2SO_4 were purchased as reagent grade from S.D. Fine Chemicals Limited (SDFCL), India and used without further purification. Solvents were dried using a commercial solvent purification system. Dry solvents were degassed for 10–15 min with nitrogen gas. Thin layer chromatography (TLC) (Merck Co.) was performed using 0.25 mm thick plates pre-coated with silica gel (40–60 μ m, F_{254}) and visualized using UV light (254 and 365 nm).

Nuclear magnetic resonance (NMR). ¹H NMR spectra were recorded on a Bruker Avance-400 MHz and 500 MHz spectrometer, at 300°. ¹³C NMR spectra were recorded at 75 MHz, 100 MHz and 125 MHz as indicated in the experimental procedures. Chemical shift (δ) was reported in parts per million (in ppm) referenced to tetramethylsilane (TMS) as an internal standard.

MALDI-TOF spectroscopy. For MALDI-TOF measurements, a Schimadzu Biotech Axima performance spectroscopic instrument was used.

Infrared spectroscopy. IR spectra were recorded on a Thermo Nicolet Nexus 670 FR-IR spectrometer in the form of non-hygroscopic KBr pellets.

UV-visible spectroscopy (UV-vis). UV-vis spectra were recorded using a Shimadzu UV-1800 spectrophotometer at room temperature. UV-vis experiments were run in a 3 mL quartz cuvette.

Fluorescence emission spectroscopy. Fluorescence emission spectra were measured on an RF-6000 (Schimadzu, Japan) spectrofluorophotometer. All experiments were performed in a quartz cell with a 1 cm path length with 550 nm excitation wavelength.

Sample preparation for SEM and POM. A stock solution of W2 (2 mM) was prepared first in organic solvents (CHCl₃ and THF). The 100 μ M solution of W2 was prepared using different solvent compositions such as CHCl₃:MCH: (a) 50:50%, (b) 30:70%; CHCl₃:MeOH: (c) 50:50%, (d) 30:70%; CHCl₃: DMF: (e) 50:50%, (f) 30:70% and THF:H₂O: (a) 40:60%, (b) 20:80% and (c) 10:90%. 10 μ L of the prepared solution mixture was then drop cast on silicon wafers.

Scanning electron microscopy. The silicon wafer was cleaned by acetone, ethanol and then Milli Q water. SEM samples were prepared by solvent evaporation on a silicon wafer and then sputter coated with gold for 10 s at 0.016 mA Ar plasma (SPI, West Chester, USA) for SEM imaging using an FEI Nova NanoSEM (Hillsboro, USA) operating at high vacuum at the voltage of 15 keV.

Polarized optical microscopy measurements. The silicon wafer was cleaned by acetone, ethanol and then Milli Q water. POM samples were prepared by solvent evaporation on a silicon wafer. POM images were observed on a Leica Optical Microscope.

DLS measurements. DLS measurements were conducted using a Brookhaven Instrument Corp., 90Plus Particle Size equipped with a He–Ne laser (632.8 nm, 35 mW) and quartz cuvette.

Synthesis of 2,6-dibromo-1,4,5,8-naphthalene tetracarboxylicdianhydride 1

Compound 1 was prepared following a literature method with slight modification.¹¹ In a 100 mL single-necked round bottomed (RB) flask, NDA (1 g, 3.72 mmol) was slurried in concentrated sulphuric acid (15 mL); the mixture was stirred at room temperature for 15 min to obtain a black solution. DBH (1.81 g, 6.34 mmol) was added in four portions over a period of 2 h at room temperature in the reaction mixture and the RB flask was tightly stoppered to avoid the escape of bromine from the reaction mixture. The resulting brown solution was stirred at 72 °C for 16 h. The mixture was poured into crushed ice. The obtained precipitated solid was filtered, washed with water followed with methanol, and finally dried under vacuum to afford the crude product. We used it without purification in the next synthesis step.

Synthesis of N-boc-ethylenediamine 2²²

In a 1000 mL RB flask was dissolved 8.56 mL (128 mmol) of ethylene diamine in 40 mL of dry dichloromethane, which was stirred at 0 $^{\circ}$ C. Then, a solution of di-*tert*-butyl dicarbonate (7.36 mL, 32 mmol) in 450 mL of dichloromethane was added drop by drop in the reaction mixture. After completion of the

addition, the resultant reaction mixture was further stirred for 24 h at room temperature. The completion of the reaction was monitored by TLC. The solvent was removed under reduced pressure to yield a colourless viscous oil. It was redissolved in a solution of 2 M NaCO₃ (150 mL) and extracted twice with 100 mL of dichloromethane. The organic phase was dried over NaSO₄ and concentrated on a rotary evaporator to yield N-boc-ethylenediamine (4.75 g, 92%). The crude product was used directly in the next step without further purification. FT-IR (KBr, cm⁻¹): ν 3353 (NH), 2976 and 2933 (CH), 1692 (N-CO-O), 1525, 1366, 1251, 1172; ¹H NMR (500 MHz, $CDCl_3$): δ 5.243 (br, 1H, -NH-CO), 3.173 (m, 2H, -<u>CH</u>₂-NCO), 2.80-2.78 (t, J = 5.45 Hz, 2H, -CH₂-N), 1.44 (s, 9H -CH₃), 1.386 (br, 2H, -NH₂); ¹³C NMR (125 MHz, CDCl₃): δ 156.11 (N–<u>C</u>O–O), 78.87 (O–<u>C</u>–), 43.22 (NH-CH2-), 41.67 (NH2-CH2-), 28.22 (O-CH3); ES-MS (m/z%): 161 (100) $[M + H]^+$.

Synthesis of di-*tert*-butyl ((4,9-dibromo-1,3,6,8-tetraoxobenzo [*lmn*][3,8]phenanthroline -2,7(1*H*,3*H*,6*H*,8*H*)-diyl)bis(ethane-2,1-diyl)) dicarbamate 3

2,6-Dibromo-1,4,5,8-naphthalenetetracarboxylic dianhydride 1 (200 mg, 0.469 mmol) and N-boc-ethylenediamine 2 (225 mg, 1.408 mmol) were dissolved in 20 mL of glacial acetic acid and stirred at 80 $^{\circ}$ C for 6 h under a N₂ atm. The reaction was monitored by TLC. After completion of the reaction, the mixture was cooled to room temperature. The pale yellow reaction mixture was poured into crushed ice to precipitate. The precipitated solid was filtered off, washed with ice cold water and purified by column chromatography (silica gel 60-120 mesh, eluent: dichloromethane/methanol, 1:0.01 v/v), the compound was isolated as a pale yellow solid. Yield: 217 mg (65%). FT-IR (KBr, cm⁻¹): ν 3380 (NH), 2975 and 2928 (CH), 1697 (O-CO-N), 1667, 1529, 1434, 1364, 1231, 1163; ¹H NMR (300 MHz, DMSO d_6): δ 8.72 (s, 2H, H–NDI–H), 6.92 (t, J = 6.05 Hz, 2H, –NH–), 4.15 (m, 8H, CH₂-N), 1.22 (s, 18H, -CH₃); ¹³C NMR (75 MHz, DMSOd₆): δ 160.83, 160.64, 155.79, 136.86, 127.42, 126.18, 125.69, 124.07, 77.50, 40.71, 37.41 and 27.96; mass (ESI) m/z 733 $[M + Na]^+$.

Synthesis of compound W2

Di-*tert*-butyl((4,9-dibromo-1,3,6,8-tetraoxobenzo[*lmn*][3,8]phenanthroline-2,7(1*H*,3*H*,6*H*,8*H*)-diyl)bis(ethane-2,1-diyl))dicarbamate (100 mg, 0.1407 mmol) and *N*-boc-ethylenediamine (67 mg, 0.2116 mmol) were dissolved in toluene and heated at 70 °C for 4 h under a nitrogen atm. After completion of the reaction, the excess toluene was removed by rotary evaporator and the product was purified by column chromatography (silica gel 60–120 mesh, eluted with dichloromethane/methanol 1:0.05 v/v). The compound was isolated as a dark blue solid. Yield: 58 mg, 47%. FT-IR (KBr, cm⁻¹): ν 3366 (NH), 2975 and 2932 (CH), 1697 (N–CO–O), 1635, 1495, 1257, 1169; ¹H NMR (400 MHz, CDCl₃): δ 9.16 (br, 2H, NH), 7.62 (s, 2H, H–NDI–H), 5.85–5.25 (br, 4H, NH), 4.16 (m, 4H, CH), 3.53 (m, 12H, CH), 1.50–1.34 (s, 36H, CH₃); MALDI-TOF: *m/z* 868.97 [M]⁺, 869.45 [M + H]⁺, 891.42 [M + Na]⁺.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

S. V. B. (GU) acknowledges financial support and award of the Professor Position under UGC-FRP, New Delhi. S. V. B. (IICT) is grateful for financial support from the SERB (DST) SB/S1/ IC-009/2014, New Delhi, India. S. M. W. would like to thank CSIR, New Delhi for JRF. R. S. B acknowledges financial support from CSIR, New Delhi under the SRA scheme [13(8772)-A/2015-Pool]. The authors acknowledge the facilities, and the scientific and technical assistance, of the Microscopy & Microanalysis Research Facility at RMIT University (RMMF).

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