Supramolecular Assembly

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Stimuli-Responsive Self-Assembly of a Naphthalene Diimide by Orthogonal Hydrogen Bonding and Its Coassembly with a Pyrene Derivative by a Pseudo-Intramolecular Charge-Transfer Interaction**

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Abstract: *A naphthalene diimide (NDI) building block containing hydrazide (H1) and hydroxy (H2) groups self-assembled into a reverse-vesicular structure in methylcyclohexane by orthogonal H-bonding and π-stacking. At an elevated temperature (LCST = 43 °C), destruction of the assembled structure owing to selective dissociation of H2–H2 H bonding led to macroscopic precipitation. Further heating resulted in homogeneous redispersion of the sample at 70 °C (UCST) and the formation of a reverse-micellar structure. In the presence of a pyridine (H3)-functionalized pyrene (PY) donor, a supramolecular dyad (NDI–PY) was formed by H2–H3 H-bonding. Slow transformation into an alternate NDI–PY stack occurred by a folding process due to the charge-transfer interaction between NDI and PY. The mixed NDI–PY assembly exhibited a morphology transition from a reverse micelle (with a NDI–PY mixed-stack core) below the LCST to another reverse micelle (with a NDI core) above the UCST via a "denatured" intermediate.*

Ongoing interest in the area of supramolecular chemistry originates from the ambition to emulate the incredible elegance and precision that exists in biological systems owing to the assembly of small building blocks. This interest has led to the creation of diverse self-organized materials from abiotic units.[1] The ability to design the self-assembly of π-conjugated chromophores[2] (organic semiconductors, liquid-crystalline mesogens, dipolar and ambipolar systems) to obtain desired photophysical properties, dimensionality, and morphology is intimately related to the goal of arriving at efficient organic molecular electronics.[3] Naphthalenediimide (NDI),[4] a promising n-type semiconductor,[5] has been used to build a range of organized structures in solution.[6] In the recent past, we have been engaged in studying the supramolecular assembly of NDI derivatives by H-bonding[7] that operates along the direction of π-stacking, a strategy that has been utilized by many research groups for the assembly of other π-systems.[8] A slightly different design involves H-bonding and π-stacking that operate in perpendicular directions.[9]

We envisioned that the integration of dissimilar and self-complementary H-bonding groups of an orthogonal nature[10] in a single building block might provide new opportunities to influence the dimensionality of self-organized π-systems by the concurrence of different H-bonding interactions parallel as well as perpendicular to the direction of π-stacking. With this aim, we synthesized **1** (Figure 1), which contains an electron-deficient NDI chromophore and two different H-bonding groups, a hydrazide (H1) and a hydroxy (H2) group.

Herein, we describe the self-assembly of **1** in organic solvents and highlight the distinct role of orthogonal H-bonding (H1–H1 and H2–H2) and its unique dual thermo-responsive phase transitions, namely, at the lower critical solution temperature (LCST)[11] and the upper critical solution temperature (UCST).[12] Furthermore, we show the coassembly of **1** and **2** (Figure 1) by complementary H-bonding between H2 and a pyridine nitrogen atom (H3)[13] to produce a transient supramolecular donor (D)–acceptor (A) complex, which by back folding is transformed into an alternate D–A stack (Figure 1)[6g–o,14] owing to a NDI–pyrene charge-transfer (CT) interaction.[15]

The UV/Vis spectrum of **1** (2.0 mM) in methylcyclohexane (MCH; Figure 2a) showed redshifted absorption bands with a reversal of intensity for the S_0–S_1 and S_0–S_2 transitions as compared to the spectrum of the monomer in $CHCl_3$, thus suggesting offset NDI stacking.[6a–c,7] Interestingly, in presence of a trace amount (ca. 4%) of the protic solvent MeOH, the absorption spectrum in MCH appeared similar to that in $CHCl_3$ (Figure 2a), thus indicating disassembly. This result confirms that the assembly of **1** is primarily driven by H-bonding, as was also ascertained from the FTIR spectrum of **1** in MCH, which was almost identical to that of the solid sample (see Figure S1 in the Supporting Information). The FTIR spectrum of **1** showed sharp peaks at 1667 and 1582 cm^{-1} for the H-bonded amides of the H1 group, and a broad peak at 3400 cm^{-1} due to coincidentally overlapped NH and OH stretching of H-bonded H1 and H2. Notably, dilute solutions of **1** (1.0 mM or less) showed macroscopic precipitation (see Figure S2), thus indicating that **1** remains dispersed in MCH only in the assembled form, which occurs beyond a certain concentration, as the assembly depends on intermolecular H-bonding.

Transmission electron microscopy (TEM) images (Figure 2b; see also Figure S3) showed unilamellar reverse vesicles as spherical hollow objects (diameter ≈ 100–120 nm) with a very thin wall.[16] The hydrodynamic diameter (D_h) found by dynamic light scattering (DLS) was 150 nm (Fig-

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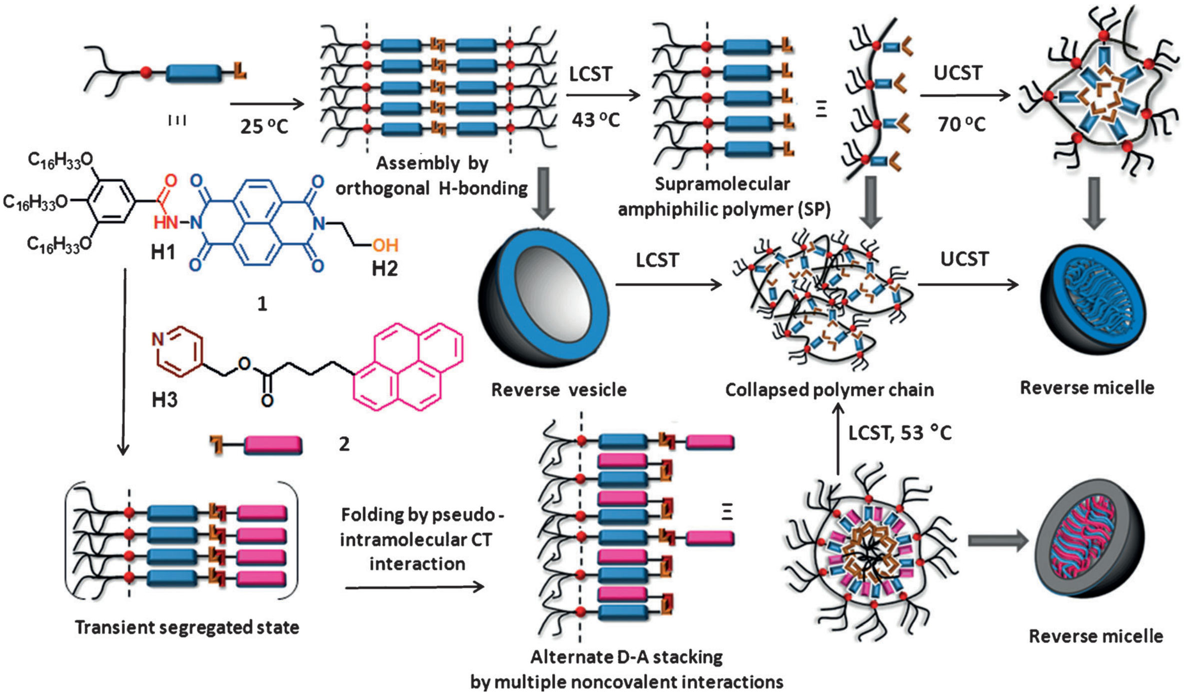

Figure 1. Schematic representation of the self-assembly of **1** and its coassembly with **2**.

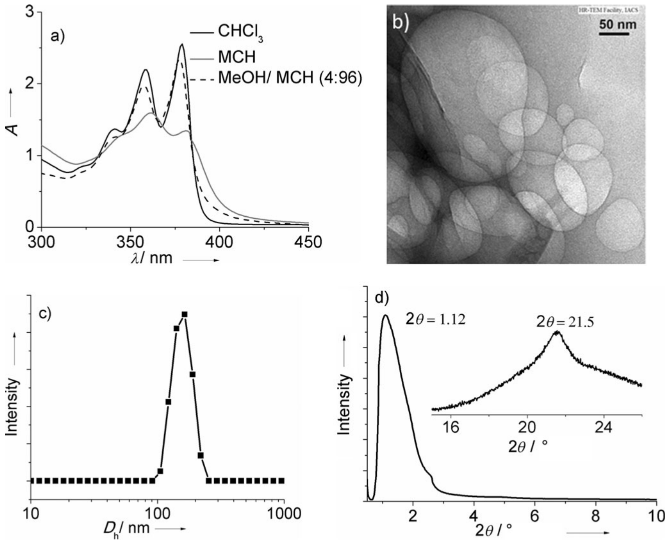

Figure 2. a) Solvent-dependent UV/Vis spectra, b) TEM image, c) DLS (in MCH), and d) powder XRD spectrum of **1** (c = 2.0 mM in all experiments).

ure 2c), which is slightly greater than the size obtained by TEM, presumably owing to compression of the hollow objects in the dry state.[17] Molecular packing in the membrane could be elucidated by powder XRD (Figure 2d), which showed a sharp reflection at $2\theta = 1.1°$ corresponding to $d = 78$ Å, which closely matches the estimated length of dimer of **1** (see Figure S4) and thus supports the proposed assembly (Figure 1).

Variable-temperature UV/Vis spectra of **1** in MCH (Figure 3a) exhibited several interesting features: 1) With increasing temperature, the baseline intensity showed a sharp increase at $T1 \approx 40$ °C, followed by an equally sharp decrease at $T2 \approx 70$ °C (Figure 3b). 2) However, the spectral nature suggests intact NDI–NDI stacking in the entire range of temperature variation. 3) A blueshift observed at higher temperature indicates a change in the spatial organization of the stacked chromophores. The optically clear solution at room temperature became a macroscopic dispersion beyond T1 and regained homogeneity above $T2$, thus confirming two different phase transitions (Figure 3c). An increase in the baseline intensity at $T1$ may be related to the scattering arising from macroscopic precipitation and thus can be assigned as the lower critical solution temperature (LCST) of **1**,[18] whereas $T2$ is the upper critical solution temperature (UCST). TEM images (Figure 3d; see also Figure S5) revealed lumps of particles above the LCST, in contrast to highly organized reverse vesicles below $T1$ (Figure 2b), thus confirming denaturation. The structural change can be attributed to the thermal dissociation of the H2–H2 linkage and the resulting disassembly of the bilayer membrane to expose the polar hydroxy groups, which then face unfavorable interactions with MCH, thus leading to macroscopic precipitation of the supramolecular polymer (SP; Figure 1). In variable-temperature ^{1}H NMR spectroscopic experiments, signals for the methylene groups adjacent to the hydroxy unit became detectable at only about 50 °C (just above LCST; see Figure S6), thus reflecting their increased mobility due to dissociation of H2–H2 bonding. This result indirectly supports the model for the observed LCST. However, the hydrogen atoms on the NDI aromatic ring were not visible by ^{1}H NMR spectroscopy immediately above $T1$ (see Figure S6), and even at very high temperature the signals for these atoms remained broad and shifted significantly upfield, thus suggesting intact

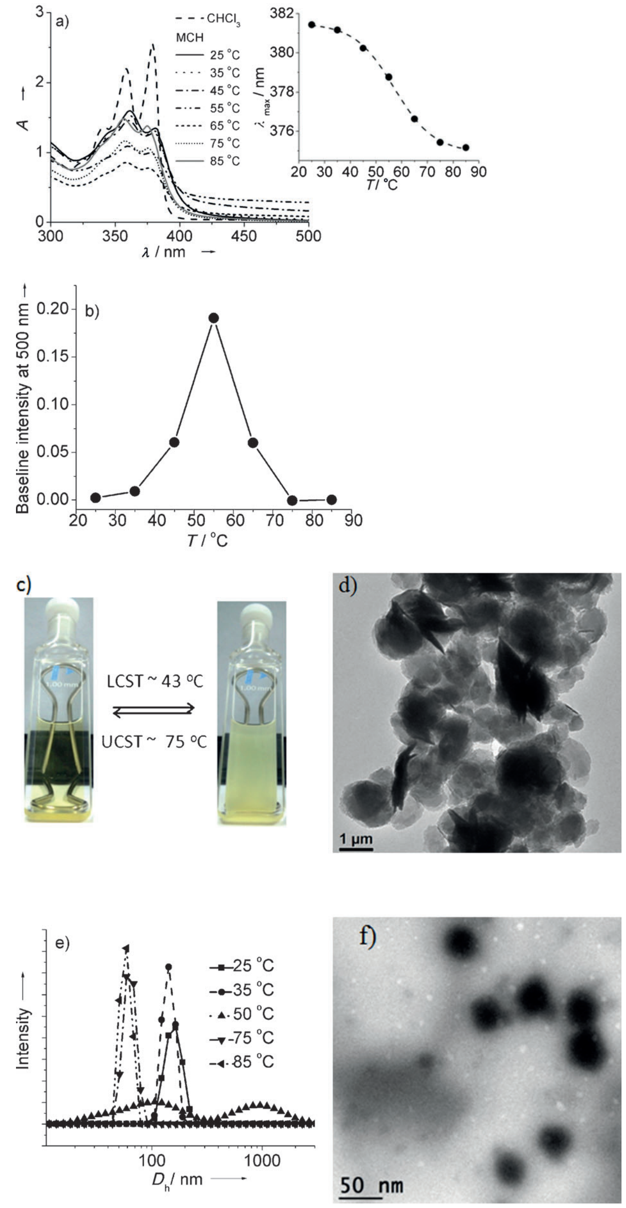

Figure 3. a) Variable-temperature UV/Vis spectra of **1** ($c = 2.0$ mM) in MCH (inset: λ_{max} (S_0–S_1) versus temperature). b) Plot of the absorption of **1** at 500 nm versus temperature. c) Photographs of the cuvette containing **1** in MCH below (left) and above the LCST (right). The image on the left also resembles the appearance of **1** in the cuvette above the UCST. d) TEM image of **1** above the LCST. e) Variable-temperature DLS of **1**. f) TEM image of **1** above the UCST.

π-stacking. FTIR spectroscopy further supported unaltered H1–H1 H-bonding below the LCST and above the UCST (see Figure S7).

Interestingly, the precipitated SP redissolved in the medium above the UCST owing to the availability of more thermal energy. To examine whether the SP remained a "unimer" or aggregated above the UCST, we carried out variable-temperature DLS experiments. Understandably, irregular scattering data were observed in the window between *T*1 and *T*2 (Figure 3e) owing to macroscopic precipitation; however, a single peak appeared above the UCST with an average D_h value of 60 nm. TEM images showed spherical particles with an average diameter of approximately 40 nm (Figure 3 f). Thus, the SP existed neither as the original reverse-vesicular structure, nor as a unimer. Rather, it adopted a reverse-micellar assembly (Figure 1) to conceal the polar hydroxy groups from the bulk solvent, as reported earlier for covalent amphiphilic homopolymers.[19] Notably, the UV/Vis spectrum of **1** at 85 °C (above the UCST) was blueshifted by about 6 nm (inset in Figure 3a) relative to the spectrum at room temperature, thus indicating more face-to-face π-stacking, which is possibly related to the geometrical demand associated with the formation of reverse micelles, which have a smaller radius of curvature than vesicles.

We further explored the utility of the pendent hydroxy groups of the SP for the noncovalent anchoring of a pyridine (H3)-functionalized pyrene (PY) donor **2** through H2–H3 H-bonding (Figure 1).[20] As PY forms an effective CT complex with NDI,[21] such a system offers a design challenge to control either segregated or alternate stacking.[22] An equimolar mixture of **1** and **2** formed a deep-red solution in MCH (Figure 4a), thus indicating CT-complex formation by alternate NDI–PY stacking, which was also confirmed by the presence of a new CT band with $\lambda_{max} \approx 530$ nm (Figure 4b). Interestingly, the red color did not appear in the relatively polar solvent $CHCl_3$, and even in MCH it spontaneously disappeared upon the addition of MeOH (only ca. 5%; Figure 4a), thus confirming that the CT complex is an auxiliary to H-bonding. Furthermore, the failure of PY without the attached pyridine group to produce any CT color (see Figure S8) established the essential role of the H2–H3 interaction for donor–acceptor (D–A) stacking. Concentration-dependent UV/Vis spectroscopic studies showed that supramolecular D–A complexation mediated by intermolecular H-bonding occurred only above a critical concentration (1.75 mM; see Figure S9). Variable-temperature UV/Vis spectroscopic experiments showed negligible change in the CT band up to a certain temperature (Figure 4c), beyond which the baseline intensity sharply increased; at an even higher temperature, the baseline intensity returned to zero and resembled that observed for **1** alone. A plot of the scattering intensity at 750 nm versus temperature (Figure 4d) revealed the LCST and UCST to be approximately 50 and 70 °C. Notably, the LCST is about 10 °C higher than that of **1** alone, possibly owing to additional stability of the D–A mixed assembly as a result of the CT interaction. However, the UCST was similar in both cases because it is related to the dissolution of the same SP.

On the basis of these observations, it is postulated that the SP brings the PY donors into proximity of the backbone by H2–H3 H-bonding, and that the electron-deficient NDI stack then engulfs the electron-rich PY by back folding of the flexible linker. This process can be monitored by UV/Vis spectroscopy (Figure 5a), which showed a CT band that reached a maximum and its saturation point only after 8–10 h (Figure 5b). Identical C=O stretching frequencies for the hydrazide group in the FTIR spectra of **1** and **1**+**2** (see Figure S10) confirmed intact H1–H1 H-bonding even after PY insertion.[7c,23] The association constant (*K*) of the CT

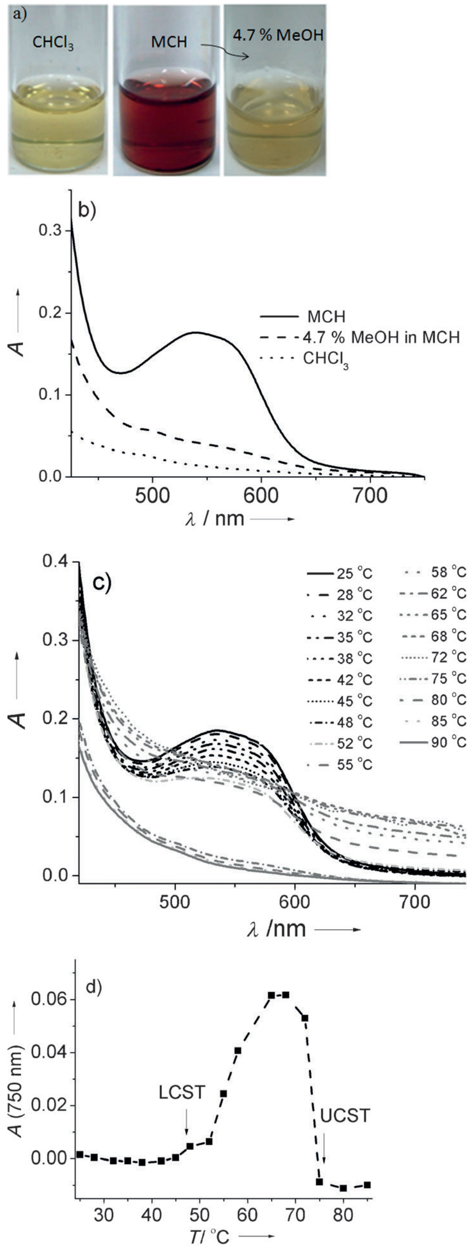

Figure 4. a) Photographs and b) UV/Vis spectra of an equimolar mixture of **1** and **2** in different solvents. c) Variable-temperature UV/Vis spectra of **1**+**2** in MCH. d) Plot of the absorbance of an equimolar mixture of **1** and **2** at 750 nm against temperature. In all experiments, $c=4.0$ mм.

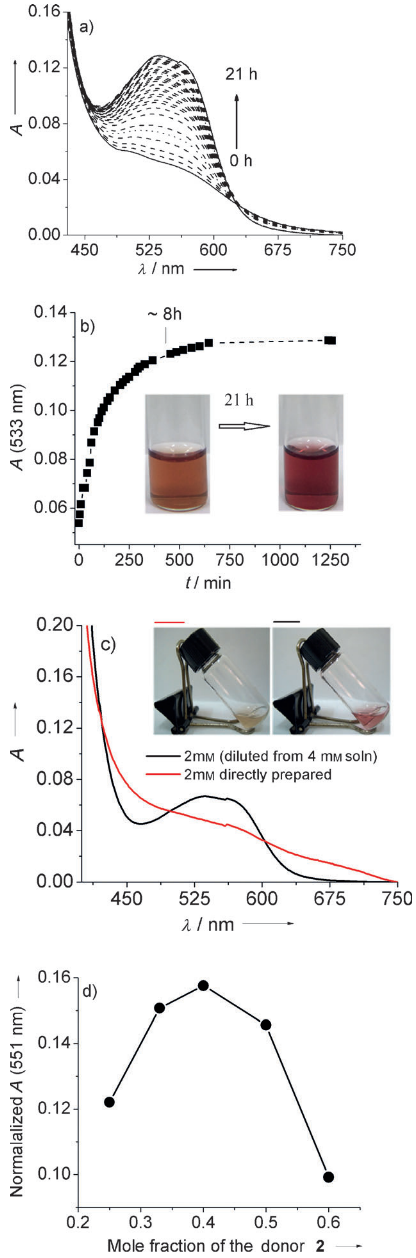

Figure 5. a) CT band as a function of time for **1**+**2** in MCH. b) Plot of the CT-band intensity as a function of time (inset shows a photograph of the solution as prepared and after 21 h). c) Comparison of the CT band and the appearance of 2 mм solutions of **1**+**2** either prepared directly at this concentration or prepared by dilution from a concentrated solution. d) CT-band intensity (normalized with respect to the concentration of the limiting component) as a function of a varying ratio of **1** and **2.** In all experiments, $c=4.0$ mм.

complex was estimated to be $0.6\times10^{4}\,\mathrm{M}^{-1}$ by concentration-dependent UV/Vis spectroscopic experiments (see Figure S11).[24] Such a high value has rarely been reported for intermolecular D–A complexes[25] and can be attributed to the synergistic assistance of multiple H-bonding interactions (Figure 1) in stabilizing the CT state. Interestingly, equimolar **1**+**2** ($c=2$ mм) prepared by half-dilution of a concentrated mixture was significantly more red in color than the mixture prepared directly at 2 mм (Figure 5c). This result suggests that at a lower concentration, intermolecular H2–H3 H-bonding does not exist, owing to the inherently weak binding affinity of this interaction, and that consequently, the CT state is not formed because of the absence of a pseudo-intramolecular PY–NDI adduct. In contrast, at a higher concentration, once the folded state is established, it does not disassemble even upon dilution owing to the additional stability due to the CT interaction and H1–H1 H-bonding.

The ΔH and ΔS values of the assembly process were roughly estimated[26] to be -31.3 and -0.087 kcal$\,\mathrm{M}^{-1}$, respectively (see Figures S11 and S12 in the Supporting Information for details), and thus indicated that the self-engulfing process becomes thermodynamically feasible ($\Delta G = -5.19$ kcal$\,\text{M}^{-1}$ at $T = 25\,°\text{C}$) because of favorable enthalpy. To examine the stoichiometry of the D–A complex, we constructed a Job plot by monitoring the CT band[14b,27] (Figure 5 d; see also Figure S13) and found a 3:2 NDI/PY ratio, which indicates that approximately 66 % of PY is engulfed by the NDI stack. In a statistical distribution, at this ratio all the NDI acceptors will have either one or two adjacent PY partners, and thus more donor intercalation may not substantially lower the enthalpy of the system to compensate the entropy loss associated with folding.

TEM images of this mixed D–A assembly (Figure 6 a; see also Figure S14) show the presence of spherical particles with an average diameter of 30–40 nm, in good agreement with DLS (Figure 6 b), which indicated an average D_h value of 50 nm. The significantly smaller size of the particles as compared to the reverse vesicles formed by **1** alone at room temperature and also the contrasting morphology are indicative of reverse-micellar assembly that is driven by the solvophobic repulsion of the polar H-bonded pyridine–hydroxy complex.

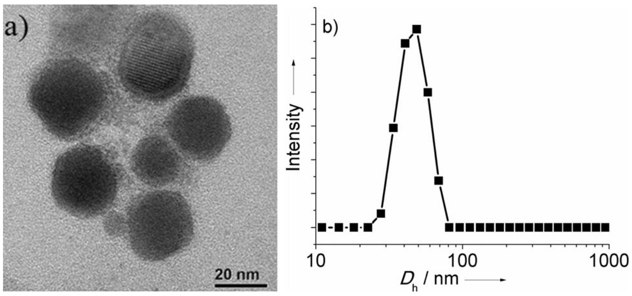

Figure 6. a) TEM image and b) DLS of an equimolar mixture of **1**+**2** in MCH ($c = 4.0$ mM).

In summary, we have shown 1) the reverse-vesicular assembly of an electron-deficient NDI by orthogonal H-bonding, and the thermally induced phase transitions of the assembly to a denatured followed by a recaptured (reverse-micelle) state at the LCST and UCST, respectively, and 2) the coassembly of the same NDI building block with a pyridine-functionalized pyrene building block by a different mode of H-bonding to produce a transient segregated D–A complex, which was gradually transformed into an alternate D–A stack as a result of an enthalpy-driven pseudo-intramolecular CT interaction. This is the first reported system to exhibit both a LCST and an UCST in an organic solvent owing to solute–solute interactions and thus provides a new and generalized guideline for the construction of stimuli-responsive supramolecular materials of biological relevance.[28] Furthermore, CT complexes have received immense attention in the recent past owing to excellent performance in organic electronic devices.[29] Thus, a remarkably high (ca. $10^4\,\text{M}^{-1}$) association constant for the D–A stacking in the present system should be of great interest for the application of such complexes as organic materials.

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