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# PAPER

# Structure engineering of naphthalene diimides for improved charge carrier mobility: self-assembly by hydrogen bonding, good or bad?<sup>†</sup>

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Two families of naphthalene diimide (NDI) derivatives were compared and contrasted for the effect of self-assembly on charge carrier transport. One series of NDI derivatives had a terminal phenyl ring attached to a hexyl spacer substituted naphthalene core either through an ester or an amide linkage (NDI-E and NDI-A, respectively), while the other series had a 3,4,5-tridodecyloxy phenyl unit (NDI-E3, NDI-A3) instead of the terminal phenyl unit. Solution processed thin films of these molecules exhibited n-type charge transport characteristics in a bottom gate top contact organic field effect transistor (OFET) geometry. The amide derivatives showed evidence of self-organization with observation of red shifted aggregate emission in solution as well as solid state. Variable temperature FTIR studies in the solid state confirmed the existence of strong hydrogen bonding which could be broken only at very high temperature. However, contrary to expectations, the NDI ester derivatives showed better device efficiency with electron mobilities in the range  $8.5 \times 10^{-3}$  to  $2 \times 10^{-2}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> and on/off ratio ~10<sup>4</sup>. The thin film crystallinity and morphology of NDI-E and NDI-A were examined through X-ray diffraction and atomic force microscopy (AFM). The correlation of crystallinity, hydrogen bonding and charge carrier mobility was studied using energy minimized structures from density functional theory (DFT). The higher electron mobility of ester linked NDI derivatives over the amide linked ones was attributed to the freedom in charge transport pathways offered by a three dimensional crystalline organization in the ester compared to the restricted directional hydrogen bonding interaction in the amide derivatives.

# Introduction

Organic n-type semiconductors with high charge-carrier mobilities have been increasingly reported in the literature in recent years.<sup>1-9</sup> A fundamental requirement in the development of new materials with improved properties is the challenging task of achieving a rigorous understanding of the relationship between molecular structure and charge transport properties. Efficient charge transport has been associated with better packing leading to strong electronic coupling between neighboring molecules.<sup>10</sup> However, attaining high charge carrier mobilities is not just a question of simple design principles. It is known that for the same organic molecule, the observed charge carrier mobilities vary depending on the mode of processing – vacuum deposited, spin coated or single crystal.<sup>11</sup> Defects are observed even using controlled growth deposition techniques of crystalline thin-films

in the form of different degrees of crystallinity, morphology at the dielectric interface, grain boundaries, twining and grain connectivity.<sup>12</sup> All these strongly affect the electrical transport property of the resultant film as multiple length scales are involved in the electrical transport in such systems. The charge motion in these films has a hopping like transport at the dielectric-semiconductor interface, which has a higher density of defect states, and band like transport is dominant in the ordered bulk of the crystalline thin films.<sup>13,14</sup> Thus, bottom-up approaches designed for enabling microscopic control over crystal engineering have been the focus of increasing attention in this area of research, where the success is often gauged by the enhancement of the microscopic mobility. However crystal engineering is still a matter of trial and error and a simple structural variation has been shown to have a huge impact on the way a molecule organizes in the solid state. A face-to-face arrangement of molecules may enhance the  $\pi$ - $\pi$  overlap, however charge transport seems to be further enhanced with slipped crystal packs since 2-D structure is preserved.<sup>15</sup> The rational design of molecules with improved optoelectronic properties should take into account their geometrical as well as electrical structures. For instance, a pentacene crystal has a herringbone structure with an angle of 52° between molecular

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planes whereas perfluoropentacene is packed nearly perpendicular along the same direction.<sup>16</sup> Perfluoropentacene has exhibited electron transport with mobilities  $\sim 0.22$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> in FET devices whereas pentacene exhibits FET hole mobilities in the range of 0.5–1 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>. In these examples, both band gap engineering of the HOMO-LUMO gap and crystal engineering of face-to-face  $\pi$ -stacking play a role in the nature as well as efficiency and stability of charge transport. Among the n-type materials other than C60 derivatives both naphthalene and perylene diimides (NDI-PDI) have been studied quite extensively.<sup>17-28</sup> In small molecules based on naphthalene diimide (NDI) or perylene diimide (PDI) also, the effect of small structural variations on the molecular packing and thin film morphology has been intensely looked into. For instance Shukla et al. described the effect of a simple structural variation like that of a cyclohexyl end group on the overall crystalline packing and charge carrier mobility.<sup>29</sup> They demonstrated a dramatic improvement in FET mobility of  $\sim 6 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  which was attributed to the propensity of the cyclohexyl terminated NDI derivatives to assemble into thin films with bulk phase crystalline packing. The possibility of using non-covalent interactions like  $\pi$ -stacking and H bonding to drive the molecule to pack in the favored arrangement for improved charge carrier transport is an interesting question to address. A few reports are available in the literature where researchers have sought answers to the above question.<sup>30-36</sup> An example of crystal engineering taking help from hydrogen bonding interactions was provided by Würthner et al., where they introduced eight chlorine substituents on the bay position of a perylene derivative having free NH imide functionalities that could be involved in H bonding.33 The combination of NH imide group induced H bonding and the contortion of the ring afforded by the bay substitution resulted in a two-dimensional  $\pi$ - $\pi$ -stacked percolation path for electron transport. The molecule exhibited excellent air-stable operation with a mobility as high as  $0.82 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  with  $I_{\text{on}}/I_{\text{off}}$  of  $10^8$ . In this example, the supramolecular ordering aided crystallization in the preferred direction. However, supramolecular organization can alter or compete with free crystallization to restrict the charge transport in all directions. Thus, the question of supramolecular ordering versus crystallinity, which is better at inducing higher charge carrier mobility, is of fundamental importance.

The aim of this work was to address the question of the effect of three-dimensional crystalline organization vs. directional selfassembly on electron transport mobility in naphthalene diimide (NDI) derivatives. Two series of molecules based on NDI were chosen for this study having identical structure except for a replacement of ester group with amide. The NDI derivatives with an ester linkage did not have the additional non-covalent interaction in the form of hydrogen bonding to direct the molecular organization, whereas the amide molecules had a directional hydrogen bonding of the amide linkage as a constraint to restrict their freedom of organization. The effect of this minor structural alteration on the self-organizing properties in solution was probed using UV-Vis absorption and fluorescence emission studies. The solid state organization was studied using wide angle X-ray diffraction (WXRD), differential scanning calorimetry (DSC) and polarized light microscopy (PLM). Hydrogen bonding in the amide molecules was traced using variable temperature FTIR studies in the solid state. The

charge transport characteristics of these NDI derivatives were compared in an organic field effect transistor (OFET) in bottom gate top contact geometry. A better understanding of the structure-device performance relationship in the NDI/PDI class of compounds is essential to be able to design better molecules as well as to extract the best device performance from them.

# **Experimental section**

### Materials

1,4,5,8-Naphthalenetetracarboxylicdianhydride (NTCDA), 1,6diaminohexane, 6-aminohexanol, N,N dimethylacetamide (DMAc), 3,4,5-trihydroxy benzoic acid and benzoyl chloride were purchased from Sigma Aldrich and used without further purification. Zinc acetate, imidazole, thionyl chloride and pyridine were purchased locally and purified using standard procedures.

#### Measurements

<sup>1</sup>H NMR spectra were recorded using a 200 MHz Brucker NMR spectrophotometer with samples dissolved in CDCl<sub>3</sub> containing small amounts of TMS as internal standard. The purity of the compounds was determined by elemental analysis, as well as MALDI-TOF. Elemental analysis was performed using a Thermofinnigan flash EA 1112 series, CHNS analyser. The matrix used for MALDI was 2,5-dihydroxy benzoic acid dissolved in CHCl<sub>3</sub> which was spotted on the MALDI target and allowed to dry before introduction into the mass spectrometer. The purity of the oligomers was further analyzed by SEC (size exclusion chromatography) in chloroform using polystyrene standards for the calibration. The flow rate of CHCl<sub>3</sub> was maintained as 1  $\mu$ l min<sup>-1</sup> throughout the experiments, and the sample solutions at concentrations of 2-3 mg ml<sup>-1</sup> were filtered and injected for recording the chromatograms at 30 °C. FTIR spectra were recorded using a Brucker  $\alpha$ -T spectrophotometer in the range of 4000 to 400 cm<sup>-1</sup>. UV-Vis spectra were recorded using a Perkin Elmer Lambda 35 UV-Vis spectrometer. The emission studies were performed by SPEX Fluorolog F112X spectrofluorimeter. The fluorescence quantum yields of the naphthalene derivatives were determined in chloroform using quinine sulfate in 0.5 M sulfuric acid ( $\phi = 0.546$ ) as the standard by exciting at 360 nm. The optical density at  $\lambda_{382}$  was maintained at  $0.1 \pm 0.05$  to avoid re-absorption artifacts. For recording solid state photophysical properties, thin films were spin coated (1000 rpm per 60 s) from chloroform as well as o-DCB (ortho-dichlorobenzene) solution on a quartz plate. Thermogravimetric analysis (TGA) was performed using a PerkinElmer STA 6000 thermogravimetric analyser. Samples were run from 40 to 800 °C with a heating rate of 10 °C min<sup>-1</sup> under nitrogen. DSC (differential scanning colorimeter) measurements were performed on a TA Q10 differential scanning calorimeter at a heating rate of 10 °C min<sup>-1</sup> under nitrogen atmosphere. Typically, 2-3 mg of sample was placed in an aluminum pan, sealed properly and scanned from -50 to 300 °C. The phase behaviors of the molecules were analyzed using a Leica DM2500P polarized optical microscope equipped with a Linkam TMS 94 heating and cooling stage connected to a Linkam TMS 600 temperature programmer. The X-ray diffraction data were recorded by using a Philips analytical diffractometer using Cu Ka emission, and the spectra were recorded in the range of  $(2\theta)$  3–50° and analyzed using X'pert software. Powder X-ray diffraction of all the samples was carried out in a PANalytical X'pert Pro dual goniometer diffractometer. An X'celerator solid-state detector was employed in wide-angle experiments. The radiation used was Cu K $\alpha$  (1.54 Å) with a Ni filter and the data collection was carried out using a flat holder in Bragg-Brentano geometry. Care was taken to avoid sample displacement effects. Variable temperature in situ XRD experiments were carried out in an Anton-Paar XRK900 reactor. AFM images were taken by a Multimode<sup>™</sup> Scanning Probe Microscope equipped with a Nanoscope IV<sup>TM</sup> controller from Veeco Instrument Inc., Santa Barbara in the tapping mode using a SiN probe, with maximum scan size  $10 \ \mu m \times 10 \ \mu m$  and with vertical range of 2.5 µm. For the AFM studies, samples were prepared by spin coating from a  $1 \times 10^{-3}$  M solution in *o*-DCB on a glass slide and allowed to dry before being subjected to AFM analysis. An FEI-Tecnai<sup>™</sup>-F30 electron microscope operating at 100 kV was used for HR-TEM sample observation, and was equipped with a Gatan digital camera for recording micrographs. The electrochemical behavior of NDI ester and amide derivatives was studied by using a BAS-Epsilon potentiostat.

## **Device fabrication**

Bottom-gate top contact structures were fabricated for field effect transistor studies as per standard procedures.<sup>41</sup> In the present case hydroxyl free divinyltetramethylsiloxanebis-benzocyclobutene (BCB) polymer dielectric was spin coated at 1000 rpm for 1 min and annealed at 290 °C under glove box (N<sub>2</sub>) atmosphere. The dielectric thin film thus formed had a capacitance per unit area ( $C_0$ ) ~2 to 4 nF cm<sup>-2</sup> measured using a Keithley 4200 semiconductor parameter analyzer for a film of thickness 0.5-0.6 µm. The surface of the dielectric was coated (1500 rpm for 30 s) with a thin monolayer of hexamethyldisilazane (HMDS) and annealed at 110 °C for 2 h. This was followed by spin coating of the solution prepared from 1,2-dichlorobenzene solution with a concentration of 25 mg ml<sup>-1</sup> at 300-400 rpm for 1 minute to obtain films with thickness  $\sim 100$  nm. The spherulite phases in NDI-E3 and NDI-A3 were obtained by thermal treatment at temperatures above the melting transition temperature (NDI-A3  $\sim$  150 °C and NDI-E3  $\sim$  100 °C) for 20–30 min and gradual cooling. In the case of the molecules NDI-A and NDI-E, where the melting transition temperature was very high, annealing of samples was done at 200 °C and 150 °C respectively to get the optimum device performance. The average and the highest mobility magnitude of each system are mentioned in the table and are based on measurements on a number of devices ( $\sim$ 10 to15 devices of each molecule).

## Synthesis of ester and amide functionalized naphthalenebisimides

*N*,*N*-Bis[6-hexylbenzester]naphthalene-1,4,5,8-tetracarboxyldiimide (NDI-E). (0.5 g, 1.07 mmol) of *N*,*N'-bis[6-hydroxyhexyl]naphthalene-1,4,5,8-tetracarboxyldiimide*, (a) in 10 ml dry pyridine was heated to 80 °C under nitrogen atmosphere to obtain a homogeneous solution. To this solution benzoyl chloride (0.33 g, 2.36 mmol) was added dropwise over a period of 15 minutes. The reaction was continued for 12 hours and then the excess solvent was removed by distillation under reduced pressure and the slurry was poured into acetone. The obtained precipitate was filtered and dried in a vacuum oven for 12 hours (0.1 mm of Hg). The crude compound was purified by column chromatography using chloroform–methanol (98 : 2 v/v) Yield: 590 mg (82%); <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>) δ ppm: 8.73 (s, 4H, Ar naphthalene), 8.02 (d, 4H, Ar benzoyl), 7.54 (m, 2H, Ar benzoyl), 7.40, (m, 4H, Ar benzoyl), 4.34 (t, 4H, ester CH<sub>2</sub>), 4.22 (t, 4H, imide CH<sub>2</sub>), 1.80–1.54 (16H, CH<sub>2</sub>). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ ppm: 166.5, 162.7, 132.7, 130.8, 130.3, 129.4, 128.2, 126.5, 64.8, 40.7, 28.5, 27.8, 26.6, 25.7. FTIR (KBr, cm<sup>-1</sup>): 2939, 2851,1725, 1660, 1586, 1453, 1371, 1340, 1272, 1245, 1106, 772, 707; Anal. Calcd for C<sub>40</sub>H<sub>38</sub>N<sub>2</sub>O<sub>8</sub>: C, 71.20; H, 5.68; N, 4.15. Found C, 70.76; H, 5.23; N, 4.15%. MALDI-TOF MS ( $M_w = 674$ ); m/z = 697.33 [M + Na]<sup>+</sup>, 713.28 [M + K]<sup>+</sup>.

*N*,*N*-**Bis**[6-hexyl-3,4,5-tridodecyloxybenzester]naphthalene-1,4,5,8tetracaroxyldiimide (NDI-E3). The same procedure as above was followed using (0.5 g, 1.07 mmol) of *N*,*N'-bis*[6-hydroxyhexyl] naphthalene-1,4,5,8-tetracarboxyldiimide, (a) and (1.85 g, 2.67 mmol) 3,4,5-tridodecyloxy benzoyl chloride. The crude compound was purified by column chromatography using chloroform–methanol (99 : 1 v/v). Yield: 1.3 g (68%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  ppm: 8.73 (S, 4H, Ar naphthalene), 7.22 (s, 4H, Ar benzoyl), 4.28 (t, 4H, ester CH<sub>2</sub>), 4.20 (t, 4H, imide CH<sub>2</sub>), 3.99 (t, 12H, OCH<sub>2</sub>), 1.8–1.24 (m, 136H, CH<sub>2</sub>), 0.86 (t, 18H, CH<sub>3</sub>). FTIR (KBr, cm<sup>-1</sup>): 2920, 2850, 1717, 1699, 1667, 1581, 1500, 1468, 1430, 1344, 1348, 1245, 1218, 1122, 993 and 770. Anal. Calcd for C<sub>112</sub>H<sub>182</sub>N<sub>2</sub>O<sub>14</sub>: C, 75.55; H, 10.30; N, 1.57. Found C, 75.51; H, 10.85; N, 1.67%. MALDI-TOF MS ( $M_w$  = 1780.65); m/z = 1888.82 [M + Ag]<sup>+</sup>.

N,N'-Bis[6-hexylbenzamide]naphthalene-1,4,5,8-tetracarboxyldiimide (NDI-A). (0.5 g, 1.86 mmol) NTCDA, (0.9 g, 4.10 mmol) N-(6-aminohexyl)benzamide (b), zinc acetate (50 mg) and (20 g) of imidazole were taken in a 100 ml two neck round bottom flask and heated to 130 °C under nitrogen atmosphere for 18 h. The reaction mixture was cooled to 90 °C and treated with 150 ml of 2 N hydrochloric acid. The crude product was filtered, washed with plenty of distilled water followed by washing with hot methanol and then dried in a vacuum oven for 12 hours (0.1 mm of Hg). The crude compound was purified by column chromatography using chloroform-methanol (98:2 v/v). Yield: 890 mg (71%); <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>) δ ppm: 8.78 (s, 4H, Ar naphthalene), 7.71-7.44 (m, 10H, Ar benzoyl), 4.22 (t, 4H, CH<sub>2</sub>), 3.50 (t, 4H, amide CH<sub>2</sub>), 1.80–1.54 (16H, CH<sub>2</sub>). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ ppm: 163.2, 159.9, 130.8, 130.2, 128.8, 128.1, 69.7, 47.4, 40.6, 31.3, 29.6, 29.5, 29.2. FTIR (KBr, cm<sup>-1</sup>): 3299 (NH), 2938, 2852, 1697 (amide CO), 1652, 1586, 1453, 1371, 1340, 1272, 1245, 1106, 772, 707; Anal. Calcd for C<sub>40</sub>H<sub>40</sub>N<sub>4</sub>O<sub>6</sub>: C, 71.41; H, 5.99; N, 8.33. Found C, 70.97; H, 5.64; N, 8.77%. MALDI-TOF MS ( $M_w = 672.29$ ); m/z = 695.36 $[M + Na]^+$ , 711.32  $[M + K]^+$ .

N,N'-Bis[6-hexyl-3,4,5-tridodecyloxybenzester]naphthalene-1,4,5,8-tetracaroxyldiimide (NDI-A3). The same procedure as above was followed using (80 mg, 0.268 mmol) of NTCDA and (455 mg, 0.589 mmol) N-(6-aminohexyl)-3,4,5-tris(dodecyloxy) benzamide (b). The crude material was purified by column chromatography using chloroform–methanol (99 : 1 v/v). Yield: 380 g (77%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  ppm: 8.67 (S, 4H, Ar naphthalene), 6.89 (s, 4H, Ar benzoyl), 6.07 (broad NH amide), 4.14 (t, 4H, imide CH<sub>2</sub>), 3.93 (t, 12H, OCH<sub>2</sub>), 4.38 (t, 4H, amide CH<sub>2</sub>), 1.8–1.24 (m, 136H, CH<sub>2</sub>), 0.86 (t, 18H, CH<sub>3</sub>). FTIR (KBr, cm<sup>-1</sup>): 3272 (amide NH) 2920, 2850, 1701 (amide CO), 1699, 1667, 1581, 1500, 1468, 1430, 1344, 1348, 1245, 1218, 1122, 993 and 770. Anal. Calcd for C<sub>112</sub>H<sub>184</sub>N<sub>4</sub>O<sub>12</sub>: C, 75.63; H, 10.43; N, 3.15. Found C, 75.82; H, 10.89; N, 3.14%. MALDI-TOF MS ( $M_w = 1778.39$ ); m/z = 1886.27 [M + Ag]<sup>+</sup>.

# **Results and discussion**

### Synthesis and characterization

The syntheses of the ester and amide functionalized naphthalene diimides (NDI) are outlined in Scheme 1 and their structures are shown in Scheme 2. Four derivatives of naphthalene diimides were synthesized by varying the type of linkage (ester or amide) and the flexible alkyl chain attached to the phenyl ring, two without any terminal alkyl chain and two with 3,4,5-tridodecyloxy substitution. The NDI ester derivatives were named NDI-E (phenyl substitution) and NDI-E3 (1,2,3-tridodecyloxy phenyl substitution). Similarly the NDI amide derivatives were named NDI-A and NDI-A3 respectively for the phenyl and 3.4,5-tridodecyloxy phenyl substitution. A core to periphery approach was adopted for the synthesis of the ester molecule in which the first step was the synthesis of a hydroxyl functionalized NDI derivative by a reaction between 1,4,5,8-naphthalene tetracarboxylicdianhydride (NTCDA) and two equivalents of 6-aminohexanol in DMAc at 160 °C using Zn(OAc)<sub>2</sub> as catalyst. It was further coupled with the corresponding acid chloride in dry pyridine to obtain the ester functionalized molecules. A periphery to core approach was adopted for the synthesis of the

 $HO_{A} = (A_{1}, A_{2}, A_{3}, A_{4}, A_{4$ 

Scheme 1 Synthetic route for naphthalene diimide ester and amide derivatives.



Scheme 2 Structures of all NDI-ester and NDI-amide molecules.

amide molecules in which the required acid chloride was first monocoupled with 1.6-diaminohexane to obtain the amine terminated derivative; two equivalents of which were coupled with NTCDA in imidazole and zinc acetate to obtain the final amide functionalized molecules. All molecules were purified by using column chromatography with chloroform and methanol as mobile phase. The compounds were fully characterized by <sup>1</sup>H, <sup>13</sup>C NMR spectroscopy, size exclusion chromatography, MALDI-TOF mass spectroscopy and elemental analysis. All NDI derivatives were soluble in common organic solvents like tetrahydrofuran (THF), chloroform (CHCl<sub>3</sub>) and toluene. The labeled <sup>1</sup>H NMR spectra of all NDI molecules are given in Fig. S1<sup>†</sup>. The SEC analysis showed a single peak for all the molecules confirming the purity. As expected, the elution time of the molecules (Fig. S2<sup>†</sup>) increased with decrease in molecular weights. The amide and the ester molecule of each series differed in mass by 2 units, which was well reflected in the SEC plots. Elemental analysis of the compounds was carried out to confirm the purity and the observed CHN values were matching with the calculated values. The samples were subsequently subjected to MALDI-TOF analysis recorded using 2,5-dihydroxybenzoic acid and titanium dioxide as the matrix and molecular ion peaks were obtained for cationic species such as  $[M + Na^+]$ ,  $[M + K^+]$ , and  $[M + Ag^+]$ . The MALDI spectra of the ester and amide series are given in Fig. S3<sup>†</sup>. Thus, the NMR, SEC, MALDI-TOF spectra and elemental analysis of the molecules confirmed the structure and high purity of the molecules.

#### Optical and electrochemical properties

The photophysical properties of the naphthalene diimide derivatives were investigated by UV-Vis absorption and fluorescence emission spectroscopy and electrochemical properties were studied using cyclic voltammetry (CV). The variation in the optical properties of the naphthalene diimide ester vs. amide derivatives was used as a tool to study their different molecular organization in chloroform. Chloroform being a good solvent for rigid  $\pi$ -systems like naphthalene diimides, all four NDI molecules were molecularly dissolved in it. The absorption spectra of all naphthalene diimides in chloroform (Fig. 1a) showed three characteristic peaks at 380 nm, 360 nm and 342 nm



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**Fig. 1** (a) UV-Vis absorption and (b) emission spectra of 0.1 OD solutions of naphthalene diimides in chloroform.

corresponding to the 0–0, 0–1 and 0–2 vibronic transitions of a  $S_0$ – $S_1$  transition with the intensity of the 0–0 transition being the maximum.<sup>37</sup> No differentiation of ester *versus* amide linkage among the molecules was observed in the absorption spectra in chloroform as solvent.

Fig. 1b shows the fluorescence emission spectra of all the naphthalene diimide molecules recorded for 0.1 OD solution in chloroform. The emission spectrum was the mirror image of the absorption spectrum with the emission maximum centered at 408 nm and other peaks at 387 nm, 432 nm *etc.*<sup>37,38</sup> The quantum

yields were calculated using quinine sulfate as the standard and the values are given in Table 1. Except for NDI-E, the intensity of emission was very much quenched for the other three molecules. which was also reflected in the quantum yield values. Quenching of fluorescence was observed due to the presence of the 3,4,5trialkoxy substitution in NDI-E3 and NDI-A3.39,40 The amide molecules NDI-A and NDI-A3 (inset) additionally exhibited a broad aggregated red shifted emission peak at  $\sim$ 550 nm, which reflected their strong tendency to form aggregates in chloroform. This red shifted aggregate emission at 550 nm was clearly absent in the two ester molecules thereby differentiating them from the amide series of molecules in terms of their self-organization behavior. The device fabrication (discussed later) of the molecules was carried out using ortho-dichlorobenzene (o-DCB) as solvent. Therefore, the self-organization characteristics of the ester and amide molecules were studied in o-DCB also (given in Fig. S4<sup> $\dagger$ </sup>). A red-shifted aggregate emission around ~550 nm was observed for NDI-A in o-DCB also. The emission of the trialkoxy substituted derivatives NDI-A3 and NDI-E3 was quenched similar to the observation in CHCl<sub>3</sub>.

The influence on self-organization induced by hydrogen bonding of the amides was more apparent in the solid state emission than in solution. Absorption (Fig. S5†) and emission spectra of naphthalene diimides were recorded in the solid state. Solid films were obtained by spin coating the solution of corresponding molecule in chloroform and the emission and excitation spectra are given in Fig. 2. The emission spectrum of **NDI-E** showed a monomeric emission peak at 455 nm and aggregate



**Fig. 2** Solid-state emission ( $\lambda_{ex} = 360 \text{ nm}$ ) and excitation ( $\lambda_{em} = 455 \text{ nm}$ ) spectra of naphthalene diimides spin coated from chloroform solution.

Table 1 Absorption and emission data of naphthalene diimides

NDI-molecule	Chloroform			Film					
	$\lambda_{\max}^{a}$ abs. (nm)	$\lambda^b$ emission (nm)	$\phi_{\mathrm{FL}}{}^c$	λ <sub>max</sub> abs. (nm)	$\lambda_{\max}^{b}$ emission (nm)	Optical band $gap^d$	$E_{\rm pc}$ (V) average	LUMO (eV)	HOMO (eV)
NDI-E	380	387, 408, 432	0.016	368	455 (530, 564)	3.0	-0.79	-3.66	-6.66
NDI-A	380	387, 408, 432 (552)	0.007	366	460 (560)	2.9	-0.76	-3.69	-6.67
NDI-E3	380	387, 408, 432	0.003	365	438 (550)	3.0	-0.77	-3.68	-6.70
NDI-A3	380	387, 408, 432 (552)	0.002	362	437 (565)	3.0	-0.76	-3.69	-6.69

<sup>*a*</sup> Values corresponds to 0–0 transition. <sup>*b*</sup> Excitation at 360 nm and values reported in bracket are for aggregate emission. <sup>*c*</sup> The fluorescence quantum yields were obtained upon excitation at 360 nm and were measured using quinine sulphate as standard. <sup>*d*</sup> Calculated from the absorption edge in the solid state.  $E_{pc}$  average: average of first and second reduction peak; ( $E_{1/2onset}$  FC = 0.35 V).

emission peaks were observed at  $\sim$ 528 nm and  $\sim$ 560 nm (a similar observation was seen with film drop cast from o-DCB also). The excitation spectra collected at 530 nm, 570 nm and at the monomer emission of 455 nm were all identical to the absorption spectra indicating that the emitting and absorbing species were identical. NDI-A showed mostly red shifted aggregate emission at  $\sim$ 565 nm with only minor contribution from monomer emission in the 400-500 nm region. A similar observation was reported for the carboxyl functionalized unsymmetrical NDI derivative, where a broad, featureless red shifted emission with large stock shift occurred at 545 nm, which was attributed to the emission from the pre-assembled hydrogen bond mediated J-aggregate.<sup>41</sup> As observed in solution, in solid state also strong quenching of fluorescence was observed for NDI-E3 and NDI-A3 (the data have been scaled by a factor of 10 for sake of comparison). The aggregate emission at  $\sim$ 565 was also observed for NDI-A3, but with less intensity.

The cyclic voltammetry studies of the NDI derivatives were done using a three electrode system in dichloromethane (DCM) solvent and tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub> 0.1 M-DCM) used as supporting electrolyte. A representative cyclic voltammogram for NDI-E3 and NDI-A3 was shown in Fig. S6<sup>†</sup> and the electrochemical data are given in Table 1. Two reversible reduction peaks corresponding to formation of radical anion and dianions were observed. The reduction potential peak values were similar for all the four molecules demonstrating that they had similar molecular electronic structures and the electronic properties were insensitive to the nature of the imide substitution. The LUMO energy levels of the all NDI derivatives were estimated based on the average onset value of the first and second reduction peaks and reference energy level of ferrocene (4.8 V below the vacuum level) according to  $E_{\rm LUMO}$  (eV) =  $-e \times (E^{\rm red} \text{ onset } + 4.8)$ below the vacuum level.<sup>42</sup> The HOMO levels were calculated based on the optical band gap obtained from the solid state absorption onset measurements. The facile reduction, along with ease of solution processability, makes these NDI derivatives promising candidates for use as n-type materials in organic field effect transistors.

### **Bulk organization**

The NDI derivatives were examined for mesogenic characteristics using DSC, PLM and variable temperature WXRD. The four NDI derivatives of the ester as well as amide series were found to be thermally stable to 400 °C using thermogravimetric analysis (TGA, Fig. S7<sup>†</sup>) and their 10% wt loss temperature is given in Table S1<sup>†</sup>. The thermal phase transition temperature observed from DSC along with the enthalpy of transition is also given in Table S1<sup>†</sup>. The amide molecules had higher melting temperatures compared to the ester molecules due to the increased rigidity afforded by the hydrogen bonding interaction. The ester and amide molecules without any terminal alkyl substitution *i.e.* NDI-E and NDI-A showed only a melting transition in their DSC thermogram (Fig. S8<sup>†</sup>). Upon introduction of the three flexible dodecyloxy units at the terminal phenyl group, multiple transitions appeared in the DSC thermogram in addition to a drastic reduction in the melting transitions for the NDI-E3 and NDI-A3 molecules. Fig. 3 shows the second heating and first cooling cycles in the DSC thermograms of NDI-E3 and NDI-A3. The PLM (polarized light microscope) images showing a spherulitic crystalline phase collected at 65 °C and 132 °C respectively for the two samples NDI-E3 and NDI-A3 are also given in Fig. 3. To understand the nature of the observed phases, variable temperature WXRD measurements were collected for both NDI-E3 and NDI-A3. Fig. 4 shows the WXRD data collected between  $2\theta = 3$  to  $35^{\circ}$  at various temperature intervals while cooling from the isotropic melt at 110 °C for NDI-E3. The small angle region from  $2\theta = 2-5^{\circ}$  was scanned in a separate experiment and the inset in the figure shows the small angle data at  $2\theta = 1.91^{\circ}$  for the sample at room temperature (25 °C). The room temperature WXRD pattern was indexed via rigorous iteration method (DICVOL43) to a monoclinic cell of dimensions a = 47.386 (27) A; b = 3.307 (2) A; c = 24.799 (15) A; and  $\beta = 104.13$  (8)°. The Bragg reflection at  $2\theta = 1.91^{\circ}$  corresponding to d-spacing of 46.06 A was indexed as (100) and hence assigned as the molecular length peak, and a peak at  $2\theta = 26.94^{\circ}$ (3.306 Å) was indexed as the (010). The molecular length obtained from the Chem draw 3D energy minimized structure was 54.06 Å. The shorter length observed by XRD indicated



Fig. 3 DSC heating and cooling curves for NDI-E3 and NDI-A3 and PLM images at 65 °C and 132 °C respectively for NDI-E3 (top) and NDI-A3 (bottom).



**Fig. 4** Variable temperature X-ray diffraction pattern of (top) **NDI-E3** and (bottom) **NDI-A3**. Inset shows the peak at low angle ( $2\theta = 0.5$  to 5°).

considerable interdigitation of the terminal alkyl chains. In the isotropic phase at 110 °C, no peaks were observed (Fig. 4), at 65 °C (Fig. 4) sharp peaks were observed both in the small angle and wide angle region indicating a crystalline phase. Fig. 4 (bottom) shows the variable temperature WXRD pattern for NDI-A3 taken from the isotropic melt at 150 °C to room temperature (25 °C). This could also be indexed to a monoclinic cell, a =48.040 (36) Å, b = 3.831 (3) Å, c = 24.846 (18) Å and  $\beta = 104.09$ (9)°. The clearly distinguishing feature between the XRD patterns of NDI-E3 and NDI-A3 was the reduced crystallinity in the latter. NDI-A3 had very few sharp peaks in the entire  $2\theta$ range of 3-35°. Another very important difference compared to **NDI-E3** was that the amide the peak around  $2\theta = 23.37^{\circ}$  (3.80 A) was very sharp and intense and matched with the unit cell length along the b axis (010), which could be assigned to the  $\pi$ - $\pi$ stacking of NDI-core.4,41,44 Moreover, annealing increased the intensity of this peak much more than for the ester (Fig. S9<sup>†</sup>). Thus, the important observations made by analyzing the PWXRD pattern of both NDI-E3 and NDI-A3 were (a) NDI-E3 was more crystalline compared to NDI-A3 and (b) the  $\pi$  stacking along the b axis was much shorter for NDI-E3 at 3.307 Å compared to 3.831 A for NDI-A3.

The powder XRD pattern of NDI-E and NDI-A showed that they were more crystalline compared to NDI-E3 and NDI-A3. Fig. 5 shows the powder X-ray diffraction pattern of NDI-E and NDI-A. NDI-A was indexed to a monoclinic cell with cell parameters a = 45.10 (4) Å; b = 7.708 (11) Å; c = 9.200 (7) Å and  $\beta = 99.48$  (5)°. NDI-A had a more layer ordered structure compared to NDI-E with the peaks indexed as (200), (400), (600) and (800) along with other higher order (*hk*1) planes. A careful observation of systematic absences in the (*h*00) and (0*k*0) planes indicated a plausible non-standard space group of  $P2_1/a$ . NDI-E



Fig. 5 Powder WXRD data for NDI-E (top) and NDI-A (bottom).

was indexed to a monoclinic cell with parameters a = 26.592 (21) Å, b = 4.687 (2) Å, c = 19.973 (9) Å and  $\beta = 94.56$  (3)°. The length of  $\sim 26$  Å along the 'a' axis of the cell was equal to the observed d-spacing at 26.20 A ( $2\theta = 3.36^{\circ}$ ) in XRD corresponding to the (100) reflection. No other peaks were observed in the low angle region  $< 2\theta = 3^\circ$ . Systematic absence evaluation pointed to a definite lack of screw axis when compared to NDI-A and the space group was tentatively assigned as P2/m since no extinction conditions could be observed. A simple model building exercise based on molecular length comparison to the unit cell length led to some interesting observations. In the case of NDI-E, the "b" axis length of  $\sim 4.68$  Å restricted any other orientation than a parallel face to face arrangement for the naphthalene rings occupying the corners of the unit cell. However, this distance is longer than the  $\pi$ - $\pi$  interstack distance in the range 3.3 to 3.5 Å reported for similar systems.<sup>4,44</sup> On the other hand, fluorescence studies in the solid state showed an absence of quenching of fluorescence for NDI-E (Fig. 2) indicating the absence of face-to-face  $\pi$  stacking interaction in these molecules. To account for these observations from WXRD as well as solid state emission, an arrangement with the end phenyl rings of two naphthalene molecules interdigitated with each other and the naphthalene rings occupying the unit cell corners was arrived at leading to an a axis length of 26.592 Å which matches with the indexed unit cell. In comparison to this structure, NDI-A exhibited an elongated a axis; however, the molecular interactions can be summarized to be more or less similar since the screw axis effects a face centering in this system reducing the distance between two naphthalene centers to  $\sim 23$  Å (this distance also matched with observed  $d_{200}$  spacing of 22.13 Å at  $2\theta = 3.99^{\circ}$  in XRD). Density Functional Theory (DFT) was used to obtain energy minimized structures for both NDI-E and NDI-A by using the turbomole suite of programs.<sup>45</sup> Geometry optimizations were performed using the B-P 86 functional.<sup>46,47</sup> Fig. 6a compares the energy minimized structures of NDI-E and NDI-A with the molecules oriented along the NDI aromatic core. The NDI core was out of plane with respect to the hexyl and phenyl planes; however, unlike NDI-E, the amide and phenyl rings of NDI-A were not totally perpendicular but it was twisted and had a dihedral angle of  $\sim 26^{\circ}$ . This twisting, which occurred to accommodate the restraining hydrogen bonding, also resulted



Fig. 6 (a) DFT energy optimized structures of NDI-E and NDI-A. (b) Schematic representation of molecular packing in NDI-E and NDI-A.

in interdigitation to a larger extent in NDI-A. This was reflected in the shorter d-spacing value of 22.13 Å for NDI-A compared to 26.20 Å for NDI-E, which is shown schematically in Fig. 6b.

To demonstrate the existence of hydrogen bonding in the solid state, variable temperature FTIR studies were carried out (Fig. 7). FTIR spectra of both NDI-E and NDI-A were recorded in the powder form (pellet made from KBr ground with sample). Fig. 7 shows the expanded NH stretching region (4000-3300  $cm^{-1}$ ) and the carbonyl stretching frequency in the range 1700-1600 cm<sup>-1</sup> at two different temperatures (at 30 °C and at 250 °C) for NDI-A and at 30 °C for NDI-E. The carbonyl group of the naphthalene imide has a stretching frequency at 1700 and 1660 cm<sup>-1</sup> whereas the carbonyl group of the amide has the amide I stretching frequency in the range 1650-1690 cm<sup>-1</sup>. At 30 °C, NDI-A showed an NH stretching vibration at 3304 cm<sup>-1</sup> and three peaks were observed at 1704, 1656 and 1634 cm<sup>-1</sup> in the carbonyl stretching region. The NDI-E molecule, which clearly did not have an amide I stretch, also had a peak at 1659 cm<sup>-1</sup> due



Fig. 7 Expanded FTIR spectra of NDI-E at 30 °C and NDI-A at 30 °C and 250 °C showing the disappearance of the hydrogen bonded carbonyl stretch  $\sim 1634$  cm<sup>-1</sup>.

to the carbonyl of the naphthalene core. However, clearly differentiating the two (ester vs. amide) was the peak at 1634  $cm^{-1}$  in the NDI-A (circled peak) which was assigned as the hydrogen bonded carbonyl stretch. At 250 °C the peak at 1634 cm<sup>-1</sup> vanished completely and the peak at 1656 cm<sup>-1</sup> also shifted to higher frequency 1667 cm<sup>-1</sup>. In the NH stretching region also, the hydrogen bonded NH stretch at 3304 cm<sup>-1</sup> reduced in intensity and shifted to 3327 cm<sup>-1</sup> and a new broad peak corresponding to a free NH stretch appeared at 3673 cm<sup>-1</sup> (circled peak). This shift was clearly reversible with the hydrogen bonded carbonyl and amide peaks shifting to their original values upon cooling.

#### **Device characteristics**

Bottom-gate top contact structures were fabricated for field effect transistor studies. The fabrication procedure adopted was as described in the Experimental section. Except NDI-A, all the other molecules were spin coated from a solution of concentration 25 mg ml<sup>-1</sup> to obtain films of  $\sim$ 80 to 100 nm thickness. In the case of NDI-A, spin coating could not be done due to poor solubility in o-DCB and the films could only be drop cast from o-DCB. This method resulted in a thicker ( $\sim 0.4 \mu m$ ) and more uniform film. The molecules NDI-E3 and NDI-A3 were heated above their melting transition temperature 100 °C and 150 °C respectively and then cooled to room temperature to retain them in the spherulitic crystalline phase. In the case of NDI-E and NDI-A, where the melting transition temperature was very high, the samples were annealed at 150 °C and 200 °C respectively and then cooled to room temperature to get the optimum device performance. Fig. 8 shows the typical OFET output and transconductance characteristics of NDI-E (a) and NDI-A (b) respectively (NDI-E3 and NDI-A3, Fig. S10<sup>†</sup>) and values of electron mobility with on/off ratio are reported in Table 2. The devices showed typical n-type characteristics with a clear transition from linear to saturation behavior. The performance parameters were extracted in the saturation regime from the transconductance characteristics curves by using the following equation.

$$I_{\rm ds} = (\mu_{\rm FET} WC/2L) (V_{\rm g} - V_{\rm th})^2$$

where  $I_{ds}$  is the drain current, W and L are, respectively, the channel width and length, C is the capacitance per unit area of the gate insulator layer, and  $V_{\rm g}$  and  $V_{\rm th}$  are the gate voltage and the threshold voltage, respectively. The  $\mu_{\text{FET}}$  values of the NDI molecules were in the order  $5.7 \times 10^{-3}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> (for NDI-A3) to  $2 \times 10^{-2}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> (for NDI-E) with the NDI-E exhibiting the most sizable performance parameters. The amide molecules exhibited relatively lower mobilities. The lower on/off ratio observed in NDI-A could be attributed to higher off currents from the residual bulk conductance of the thicker films. Table 2 also compares the mobility values of NDI-E3 and NDI-A3 films which were not heated to the isotropic phase and then cooled but only subjected to annealing at temperatures lower than their melting transitions. The mobility values were found to be one order of magnitude lower for these low temperature annealed samples which were not in the spherulitic crystalline phase. The interdigitation of the terminal alkyl chains in NDI-E3 and



Fig. 8 Typical output and transconductance curves for NDI-E (top) and NDI-A (bottom) from the transistor with  $W \sim 2 \text{ mm}$  and  $L \sim 60$  to 100 µm respectively and BCB as the dielectric with  $C_0 \sim 4 \text{ nF cm}^{-2}$ . Inset shows the schematic of the device.

<b>Table 2</b> Of ET Characteristics of the hapitthatene annua	Table 2	OFET	Characteristics	of the	naphthalene	diimide
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Molecule	$\mu_{avg} \ (cm^2 \ V^{-1} \ s^{-1})$	$\mu_{\rm max} \ ({\rm cm}^2 \ {\rm V}^{-1} \ {\rm s}^{-1})$	$I_{ m on}/I_{ m off}$	$V_{\rm th}\left({\rm V} ight)$	T <sub>annealing</sub> (°C)
NDI-E	(a) $2 \times 10^{-2}$	(a) $6 \times 10^{-2}$	>104	-5 to 15	150
NDI-A	(b) $4.3 \times 10^{-4}$ (a) $9.5 \times 10^{-3}$ (b) $2.6 \times 10^{-4}$	(b) $5 \times 10^{-4}$ (a) $1.7 \times 10^{-2}$ (b) $4.5 \times 10^{-4}$	>10 <sup>2</sup>	-20 to 20	200
NDI-E3	(b) $2.0 \times 10^{-3}$ (a) $8.5 \times 10^{-3}$ (b) $1.5 \times 10^{-4}$	(b) $4.3 \times 10^{-2}$ (a) $4 \times 10^{-2}$ (b) $5.1 \times 10^{-4}$	>104	-10 to $20$	100
NDI-A3	(b) $1.5 \times 10^{-3}$ (a) $5.7 \times 10^{-3}$ (b) $1.4 \times 10^{-4}$	(b) $5.1 \times 10^{-2}$ (a) $1 \times 10^{-2}$ (b) $4.1 \times 10^{-4}$	>10 <sup>3</sup>	-15 to 30	50-60 150

" (a) After annealing. (b) Before annealing.

**NDI-A3** resulted in a stacked columnar organization with cofacial alignment along the column,<sup>48,49</sup> as indicated by the XRD data. The quenching of fluorescence in the solid state also indicated a cofacial alignment in these 3,4,5-tridodecyloxy terminated NDI derivatives. Therefore, higher mobilities were observed in the samples annealed at higher temperature compared to that annealed at low temperatures. However, the charge carrier mobility in the spherulitic phase of **NDI-E3** and **NDI-A3** was still one order lower compared to that obtained for their non-alkyl chain terminated analogues **NDI-E** and **NDI-A**. This could be attributed to the decreased electron density and the associated defects because of the alkyl chains in the spherulite systems.<sup>10</sup>

The effects of annealing on the thin film morphology of NDI-E and NDI-A were studied using tapping mode AFM images of thin films deposited on glass. Fig. 9 (top) shows the tapping mode AFM images of thin films of **NDI-E** and **NDI-A** spin coated from *o*-DCB both at room temperature (25 °C) and after annealing to 150 °C and 200 °C respectively<sup>50</sup> and then cooled to 25 °C. Fig. 9a and b shows the height and amplitude image of **NDI-E** at 25 °C respectively. After heat treatment the sample became smoother with improved grain size (Fig. 9c and d – the height and amplitude images on the right side of Fig. 9 correspond to thin films of **NDI-A** before (a and b) and after (c and d) annealing. It was observed that annealing helped improve the overall smooth morphology of the films.

Thin film X-ray diffraction could be used as a tool to understand out of plane ordering of layered films of crystalline small molecules.<sup>12,51</sup> Fig. 9 (bottom) shows the thin film (spin coated from *o*-DCB) WXRD data of **NDI-E** and **NDI-A** annealed at 150 °C and 200 °C respectively and then cooled to 25 °C. The percentage crystallinity of a thin film of **NDI-E** was much higher compared to the powder with a very high intense (100) peak. Lamellar ordering up to 6<sup>th</sup> order could be observed, which was consistent with edge-on orientation on the substrate.<sup>18,19</sup> The thin film XRD was similar to the powder data (Fig. S11†) indicating that the crystal structure was retained in the thin film also with



**Fig. 9** AFM images of **NDI-E** and **NDI-A** (top) taken on glass slide (a) height (b) amplitude before heating and (c) height and (d) amplitude after thermal annealing and (bottom) thin film WXRD data for **NDI-E** and **NDI-A**.

the preferred orientation in the lamellar direction.<sup>29</sup> Due to the poor solubility of NDI-A, only a very thin film could be obtained by spin coating from hot o-DCB. Lamellar ordering up to three orders only could be observed due to the extremely low thickness of the film (the amorphous hump  $\sim 2\theta = 20^{\circ}$  being diffraction from glass). However, the lower  $d_{200}$  value (21.62 Å) of NDI-A compared to the molecular length of 33.91 Å (from DFT) indicated a tilted orientation on the substrate.<sup>6,23,24</sup> In most bottom gate OFET configurations the preferred orientation of  $\pi$ conjugated cores should be approximately perpendicular to the dielectric surface (edge-on arrangement) for efficient charge transport from source to drain.52,53 The tilt angle with respect to the substrate normal was given by  $\cos^{-1}(21/33.91) = 50^{\circ}$  for NDI-A, and  $\cos^{-1}(26/33.91) = 40^{\circ}$  for NDI-E.<sup>2,54</sup> The different dihedral twisting angle, obtained for the energy minimized structure from DFT, though not important in solution, becomes an important parameter while considering the orientation on the substrate surface. In the thin film, this distortion of NDI-A from planarity resulted in lower observed crystallinity and charge carrier mobility as compared to NDI-E.11 Another factor favoring the improved mobility in NDI-E compared to NDI-A was the increased flexibility of the molecule as a whole due to absence of the highly restricting directional hydrogen bonding interaction which gave it more freedom to pack in a more favored bulk crystalline packing which facilitated electron transport. NDI-E had isotropic electronic charge transport owing to its flexible ordered structure. The critical role of restrictive interactions leading to reduced dimensionality on the charge carrier mobility was shown in the case of C60 derivatives recently. The group of Dario M. Bassani et al. reported a comparative study of charge carrier mobility of C60 with that of a derivatized C60 capable of organizing into infinite hydrogen bonded tapes oriented along one of the crystal axes.30 The charge carrier mobility of the self-assembled fullerene ribbons was found to be two-orders of magnitude lower than that of C60 and this was attributed to the reduced dimensionality of the fullerene tapes as a wire-like semiconductor in contrast to C60 as a bulk semiconductor. We speculate a similar reasoning of restricted dimensionality of transport for NDI-A which could explain its lower mobility compared to NDI-E. For instance, the more soluble NDI-A3 molecule formed gels in non-polar solvents like methyl cyclohexane (MCH) in contrast to NDI-E3 which remained crystalline. Fig. 10 compares the TEM images of NDI-E3 and NDI-A3, respectively, drop cast from MCH solution. It can be seen that NDI-A3 formed a continuous network of highly



Fig. 10 TEM (transmission electron microscope) images for NDI-E3 and NDI-A3 drop casted from  $1 \times 10^{-4}$  M solution of MCH.

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entangled nanofibers. Although this morphology of **NDI-A3** in MCH cannot be directly correlated with the thin film morphology in the OFET devices, it could be used to illustrate the reduced dimensionality of the hydrogen bonded molecules **NDI-A** and **NDI-A3** compared with their non-hydrogen bonded ester analogues. Since the overall device performances of the ester derivatives were better compared to the amides, it could be concluded that hydrogen bonding in the amides proved to be more restrictive compared to the more crystalline ester molecules, which had more freedom to realign for efficient charge transport.

# Conclusions

The present work described a full account of the synthesis, characterization and molecular/thin film properties of two series of naphthalene diimide (NDI) derivatives – one series had an amide group linking a terminal phenyl or 3,4,5-tridodecyloxy phenyl unit to a hexyl spacer substituted NDI core, while in the other series the linkage was through an ester unit. The amide linked NDI derivatives formed strong hydrogen bonded aggregates with pronounced red shifted emission both in solution and solid state. All the four NDI derivatives exhibited good n-type charge transport characteristics in an OFET device in the bottom gate top contact geometry with values ranging from  $2 \times 10^{-2} \text{ cm}^2$  $V^{-1} s^{-1}$  to  $5.7 \times 10^{-3} cm^2 V^{-1} s^{-1}$ . The mobility values for the NDI ester and amide derivatives without terminal alkyl substitution were one order higher in magnitude compared to their terminal alkyl substituted counterparts. This was expected, since the alkyl chains formed an insulating barrier for efficient charge transport in the NDI-E3 and NDI-A3 derivatives although they also facilitated formation of cofacially  $\pi$  stacked columns by interdigitation. The comparison of mobility values of the ester versus amides revealed some interesting observations. Contrary to expectations, the hydrogen bonding in the amide derivatives did not facilitate better electron mobility. The ester derivatives exhibited better device performance compared to the amides. Analyzing the packing in these molecules based on DFT energy minimized structures and power XRD data, especially in the case of NDI-E and NDI-A, the NDI amide derivative showed a dihedral twist of the terminal phenyl unit with respect to the naphthyl aromatic core with a consequent shortening of the molecular length packing along the a axis. This small difference in the dihedral twist angle reduced the crystallinity and resulted in a more tilted orientation of the NDI-A molecules on the substrate surface. On the whole, the present studies with NDI derivatives thus demonstrated that the restrictive directional hydrogen bonding interaction is not so favorable for efficient charge transport compared to the freedom in charge transport pathways offered by a three dimensional crystalline organization.

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