Assisted π-stacking: a strong synergy between weak interactions

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I. Materials and methods:

Reagents were received from Sigma Aldrich Chemical Co. and used without further purification. Solvents were purchased from commercial sources and purified following reported protocol [1]. Spectroscopic grade solvents were used for physical studies.

NMR Spectroscopy: ^1H and ^{13}C NMR spectra were measured on AVANCE III 500 BRUKER spectrometer and the data were calibrated against TMS.

Optical absorption spectroscopy: Optical absorption spectroscopy was performed on a Perkin-Elmer Lambda 35 spectrometer.

Mass spectrometry: Mass spectra were recorded using an electron spray ionization (ESI) technique on a MASSLYNX 4.0 (WATER Micromass Q-Tof-micro TM (+ve) mode mass spectrometer (Micro mass). Matrix assisted laser desorption ionization time-of-flight (MALDI-ToF) mass spectrometry was performed on a Bruker Daltonics Flex-PC. Mass spectrum was recorded in positive reflectron mode, using dithranol (DT) as the matrix and sodium trifluoroacetate (NaTFA) as the cationizing salt.

Cyclic voltammetry: Dichloromethane (CH_2Cl_2) was pre-dried by using $CaCl_2$, then distilled under inert atmosphere, and stored overnight over molecular sieves. Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) experiments were carried out in dry CH_2Cl_2 solution at room temperature (298 K) in CH Instruments electrochemical Analyzer Model no. CHI620E, using a glassy carbon working electrode. The electrode surface was routinely polished with 0.05 μm alumina water slurry on a felt surface immediately before use. A Pt wire served as an auxiliary electrode, and a saturated calomel electrode (SCE) was used as the reference electrode. Concentrations of the redox active samples were kept at 10 μM, and that of the supporting electrolyte, tetrabutylammonium hexafluorophosphate (TBAPF$_6$) was 1 mM. Before every experiment, the solution was purged with dry Ar gas.

Quantum Chemical calculations: The ground state geometry for **Py-2NDI** was optimized using Gaussian 09 software with ωB97XD/6-311G (d, p) level of theory.[10] The terminal n-dodecyl groups at the two imide Ns were truncated to n-pentyl groups. The effect of chloroform solvent in geometry optimization was implemented implicitly through Polarizable Continuum Model (PCM) model in Gaussian 09. The Natural Bond Orbital (NBO) analysis was performed using NBO program available in Gaussian 09 software.[11]

II. Syntheses and characterization
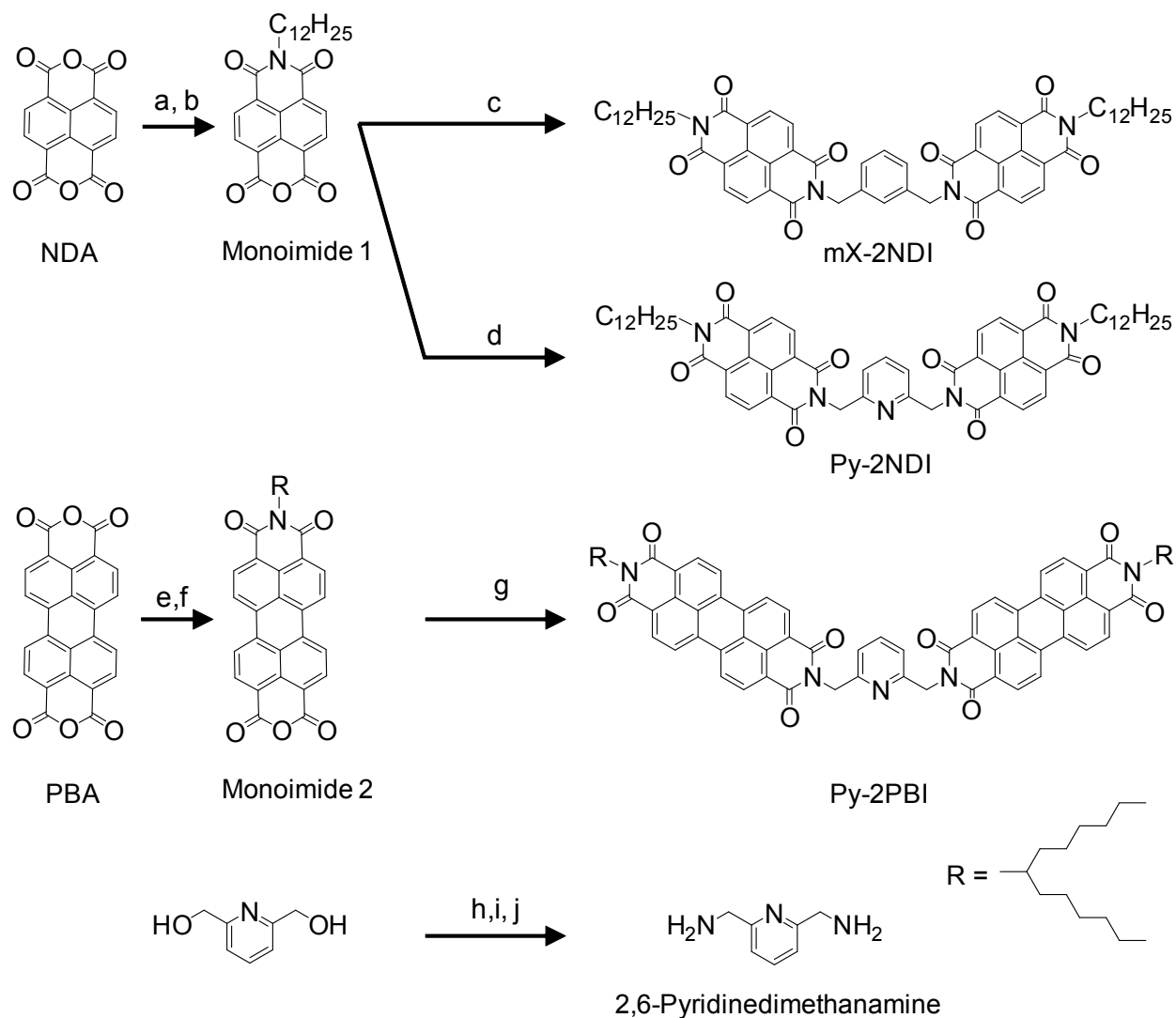
Scheme 1. .(a) $C_{12}H_{25}NH_2$, 1:1 $^iPrOH/H_2O$, 343 K, Ar (b) Glacial AcOH, reflux (c) m-xylenediamine, DMF, 393 K, 12h (d) 2-Picolylamine, DMF, 393 K, 12 h (e) Trideca-7-amine, imidazole, 403 K, Ar, 3 h (f) KOH, ^tBuOH, 383 K, 2 h (g) 2, 6 pyridinedimethanamine , imidazole/DMF (5:1 w/w), 403 K, Ar, 6 h. (h) PBr$_3$, diethyl ether, N$_2$ flow, 273 K, 3 h (i) NaN$_3$, DMF/H_2O, 300 K, 8 h. (j) Pd/C, H$_2$, dry MeOH, 12 h.

Monoimide 1 and mX-2NDI

Monoimide 1 and **mX-2NDI** were prepared and characterized according to the previously reported method.[12]

2, 6-Pyridinedimethanamine

The synthesis was carried out using a reported procedure,[13] after necessary modifications. PBr$_3$ (0.6 ml, 6.3mmol) was added drop wise to a suspension of 2,6-Bishydroxymethylpyridine (2.7 g, 16.1 mmol) in 8 ml of dry diethyl

ether in a 25 ml flask under N_2 atmosphere at 273 K . After 3 h, the reaction mixture was poured in to 30 ml of 1:1 (v/v) ice cold water and dichloromethane mixture. To this mixture, a saturated aqueous sodium carbonate solution was added drop wise until the solution turned clear. The resultant mixture was washed twice with 50 ml water, dried over Na_2SO_4, filtered, and concentrated to afford a pink liquid that solidifies in open. The resultant 2, 6-Bisbromomethyl pyridine (200 mg, 0.75 mmol) was mixed with sodium azide (400 mg, 6.13 mmol) and added to a mixture of 0.3 ml N, N- dimethyl formamide (DMF) and 0.5 ml water. The mixture was stirred for 8 h at room temperature, after the organic fraction was extracted in 20 mL of dichloromethane. The organic fraction was dried over Na_2SO_4 and concentrated to get the azide derivative as light yellow oil. The yellow oil was taken in 5 ml dry methanol and stirred under H_2 atmosphere in presence of 250 mg of 5% Pd/Charcoal. After 12 h the reaction mixture was filtered through celite bed in Ar atmosphere to obtain 2, 6-pyridinedimethanamine, which was used in next step without any purification.

Py-2NDI

Monoimide (2 mmol, 0.871 g) was taken in a 100 ml flask with DMF (20 ml) and stirred under Ar atmosphere at 328 K for 30 mins. until the suspension turned into a clear solution. To this solution 2, 6-pyridinedimethanamine (1 mmol, 0.136 g) was slowly added with stirring. The reaction mixture was refluxed under Argon flow at 393 K for 18 h. The progress of the reaction was monitored using TLC. The reaction mixture was subsequently refrigerated overnight to obtain a brown precipitate that was washed with cold methanol and hexane. As synthesized **Py-2NDI** was purified using column chromatography (Silica gel, 100-200 mesh). Yield: 74 mg (3.1%). ^{1}H NMR (500 MHz, CDCl$_3$) δ/ppm 8.39-8.20 (8 H, m), 7.71 (1 H, t), 7.24 (2 H, d), 5.31 (4 H, s), 4.22 (4 H, t), 1.74 (4 H, m), 1.23 (36 H, m), 0.85 (6H, t); ^{13}C NMR (125 MHz, CDCl$_3$) δ/ppm 162.29, 153.99, 137.23, 130.22, 125.845, 119.862, 44.578, 41.183, 31.90, 29.634, 27.998, 27.170, 22.669, 14.096. ESI-MS (MeOH, 0.1% DMSO) calcd. for $C_{59}H_{65}N_5O_8$ 971.4833, found 971.4830. Anal. Calc. for $C_{59}H_{65}N_5O_8$: C, 72.89; H, 6.74; N, 7.20% found C, 72.92; H; 6.81; N, 7.11%. Melting point >250 °C.

Monoimide 2 and mX-2PBI

Monoimide 2 and mX-2PBI were prepared and characterized according to a previously reported method.[14]
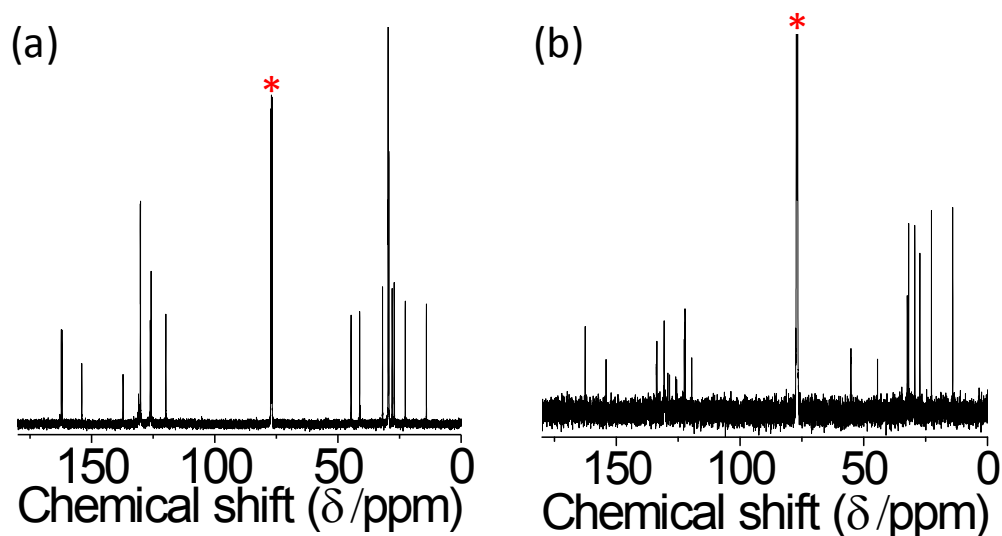
Py-2PBI

Monoimide 2 (2 mmol, 0.966 g) was taken in a 100 ml flask with 5 g imidazole and stirred under Ar atmosphere at 383 K for 30 mins until the suspension turned into a clear solution. To this solution 2, 6 pyridinedimethanamine (1 mmol, 0.136 g) in 1 ml DMF was slowly added with stirring. The reaction mixture was refluxed under Ar flow at 403 K for 6 h. The reaction mixture was cooled to room temperature, 30 ml EtOH and 50 ml HCl solution was added to it and stirred for 12 h. The reaction mixture was filtered to obtain a red precipitate which was washed with cold methanol, water followed by acetone, and further purified using column chromatography (Silica gel, 100-200 mesh) to obtain **Py-2PBI**. Yield: 49 mg (5.7%). ^{1}H NMR (500 MHz, CDCl₃) δ/ppm 8.48-7.9 (16 H, m), 7.71 (1 H, t),

7.24-7.28 (2 H, d), 5.36 (4 H, s), 5.12 (2 H, m), 2 (16 H, m), 1.39-1.20 (24 H, m), 0.85 (12H, t); ^{13}C NMR (125 MHz, CDCl$_3$) δ/ppm 163.06, 154.63, 131.17, 128.36, 122.71, 120.0, 55.68, 44.94, 32.90, 29.88, 27.83, 23.15, 14.56. MS (MALDI-TOF): calc. for [C$_{81}$H$_{77}$N$_5$O$_8$]$^+$, 1247.577, found 1247.571. Anal. Calc. for C$_{81}$H$_{77}$N$_5$O$_8$: C, 77.92; H, 6.22; N, 5.61%; found C, 78.03; H, 6.28; N, 5.54%. Melting point >250 °C.
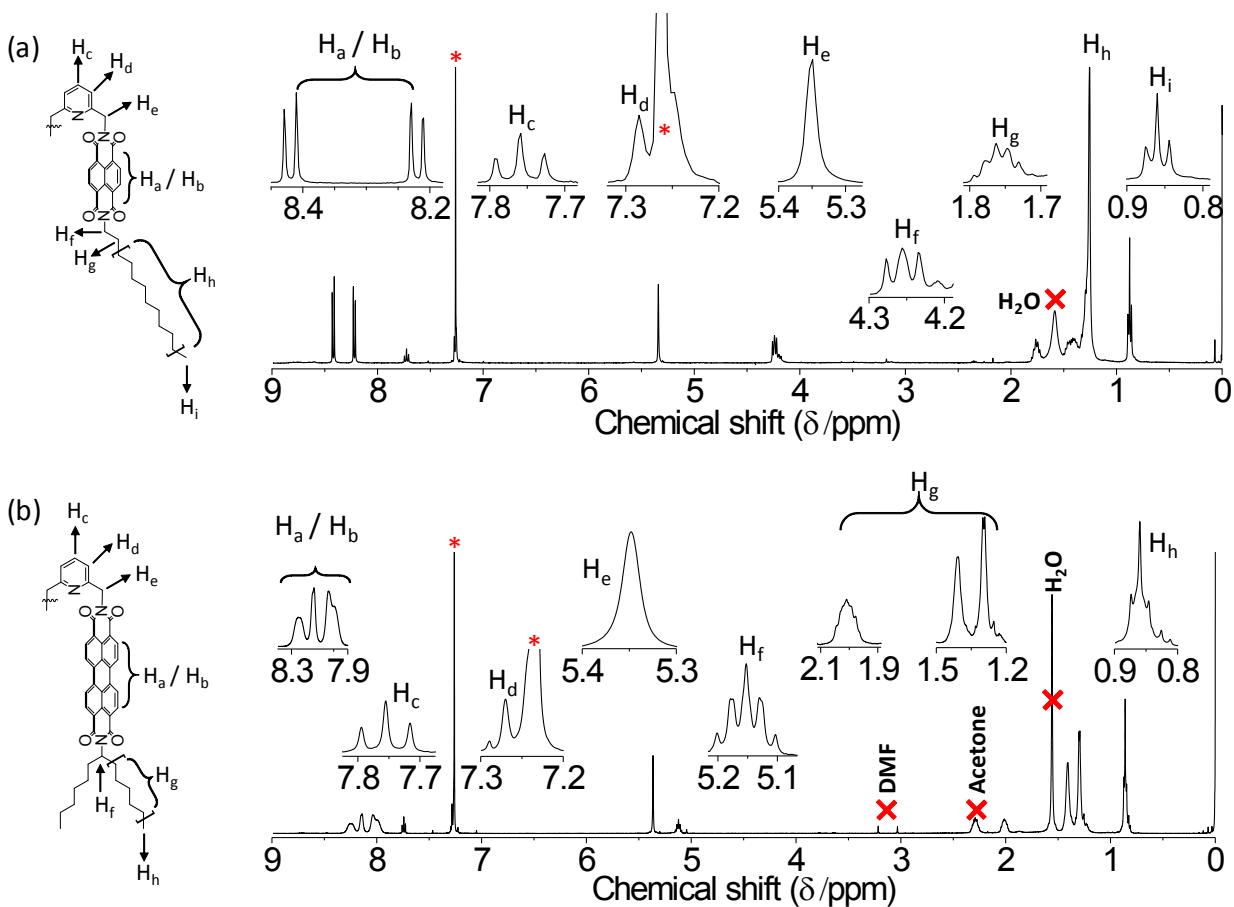
Figure S1. ^{1}H NMR (500 MHz, CDCl$_3$, 298K) spectrum of (a) **Py-2NDI** and (b) **Py-2PBI**. Red asterisk marks the signal of residual CHCl$_3$.
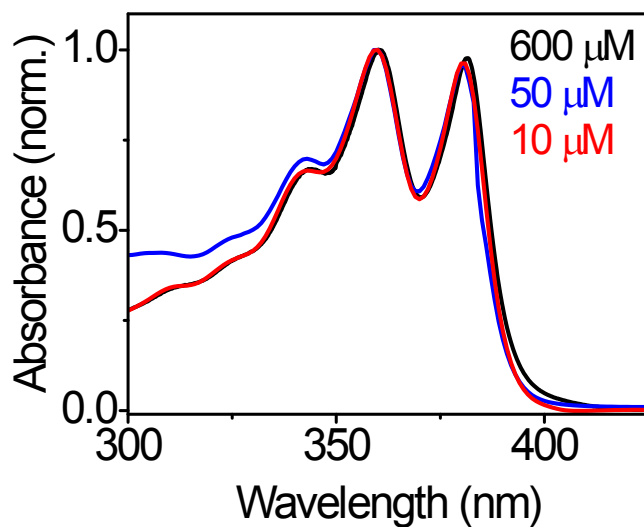
Figure S2. ^{13}C NMR (125 MHz, CDCl$_3$, 298 K) spectrum of (a) **Py-2NDI** and (b) **Py-2PBI**. Red asterisk mark the signal of CDCl$_3$.
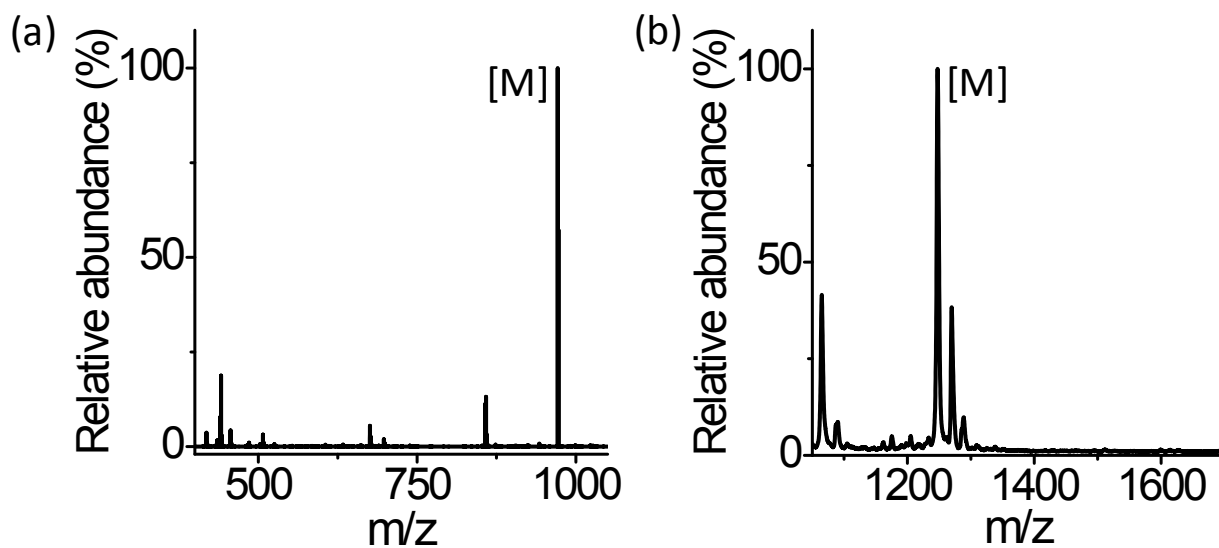

Figure S3. ESI Mass spectra of (a) **Py-2NDI**, and (b) MALDI-TOF mass spectrum of **Py-2PBI**. Molecular ion peak is marked as [M].

III. Additional results

Figure S4. Normalized optical absorption spectra of **Py-2NDI** in CHCl$_3$ at 600, 50 and 10 µM concentrations. Identical $A_{0\text{-}0}/A_{0\text{-}1}$ ratio and spectral shape confirms that the observed H-type excitonic coupling is fully intramolecular in nature, resulting from dimer folding. Absence of any intermolecular self-assembly even at 600 µM proves that regular NDI pi-stacking is not possible in non-aggregating CHCl$_3$.
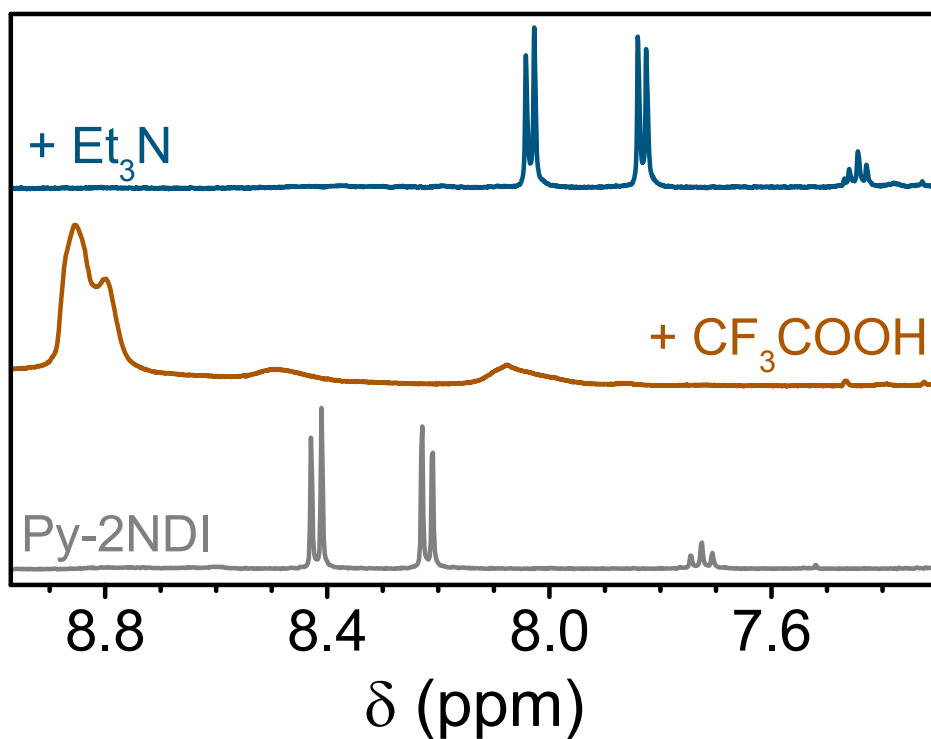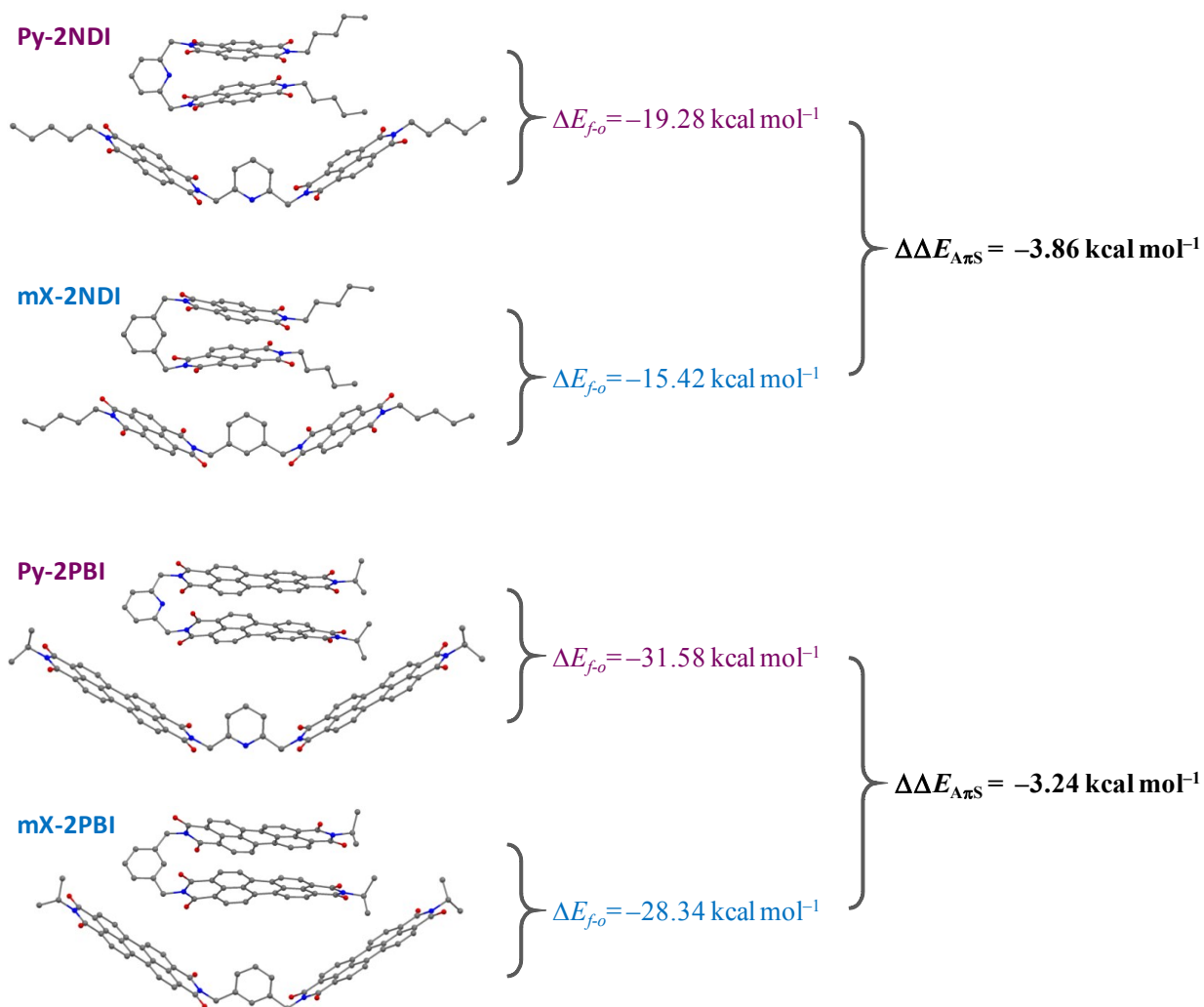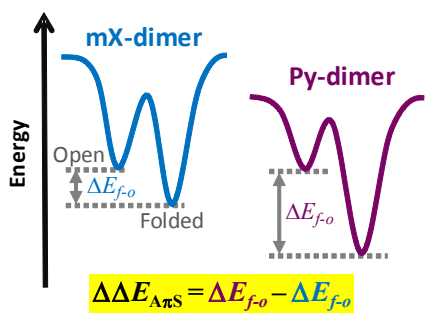

Figure S5. Effect of protonation/deprotonation on the ^{1}H-NMR spectra of **Py-2NDI** in CHCl$_3$, protonation is carried out using a weaker acid, CF$_3$COOH.
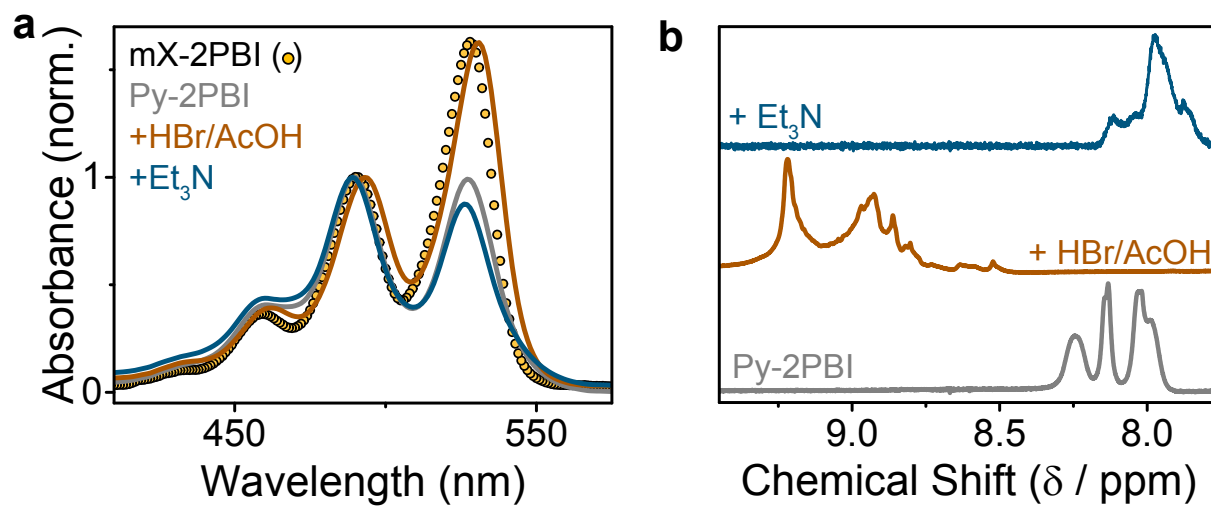
Figure S6. (a) Normalized optical absorption and (c) ^{1}H-NMR spectra in CHCl$_3$ confirm the intramolecularly H-aggregated folded state of **Py-2PBI**, and the effect of protonation/deprotonation on dimer folding.

Figure S7. A comparison of assisted pi-stacking (AπS) interaction with regular pi-stacking. The energy difference between geometry-optimized folded and open conformers of pyridyl dimers vis-à-vis that of m-xylylene dimers allows us to estimate the additional stabilization gained through assisted pi-stacking, $\Delta\Delta E_{A\pi S} \cong$ 3–4 kcal/mol. Despite being a stronger pi-stacking motif, assisted pi-stacking interaction is comparatively weaker in **Py-2PBI**. H-atoms are hidden for clarity.

(a)	(b)	(c)	(d)
Py-2NDI	**Py-2PBI**	**mX-2NDI**	**mX-2PBI**
$3.13\,\text{Å} \geq d_{\text{N-C}} \geq 3.3\,\text{Å}$	$3.1\,\text{Å} \geq d_{\text{N-C}} \geq 3.34\,\text{Å}$	$3.0\,\text{Å} \geq d_{\text{O-H}} \geq 3.51\,\text{Å}$	$3.12\,\text{Å} \geq d_{\text{O-H}} \geq 3.41\,\text{Å}$
$3.29\,\text{Å} \geq d_{\text{C-C}} \geq 3.45\,\text{Å}$	$3.3\,\text{Å} \geq d_{\text{C-C}} \geq 3.48\,\text{Å}$	$3.27\,\text{Å} \geq d_{\text{C-C}} \geq 3.47\,\text{Å}$	$3.32\,\text{Å} \geq d_{\text{C-C}} \geq 3.48\,\text{Å}$
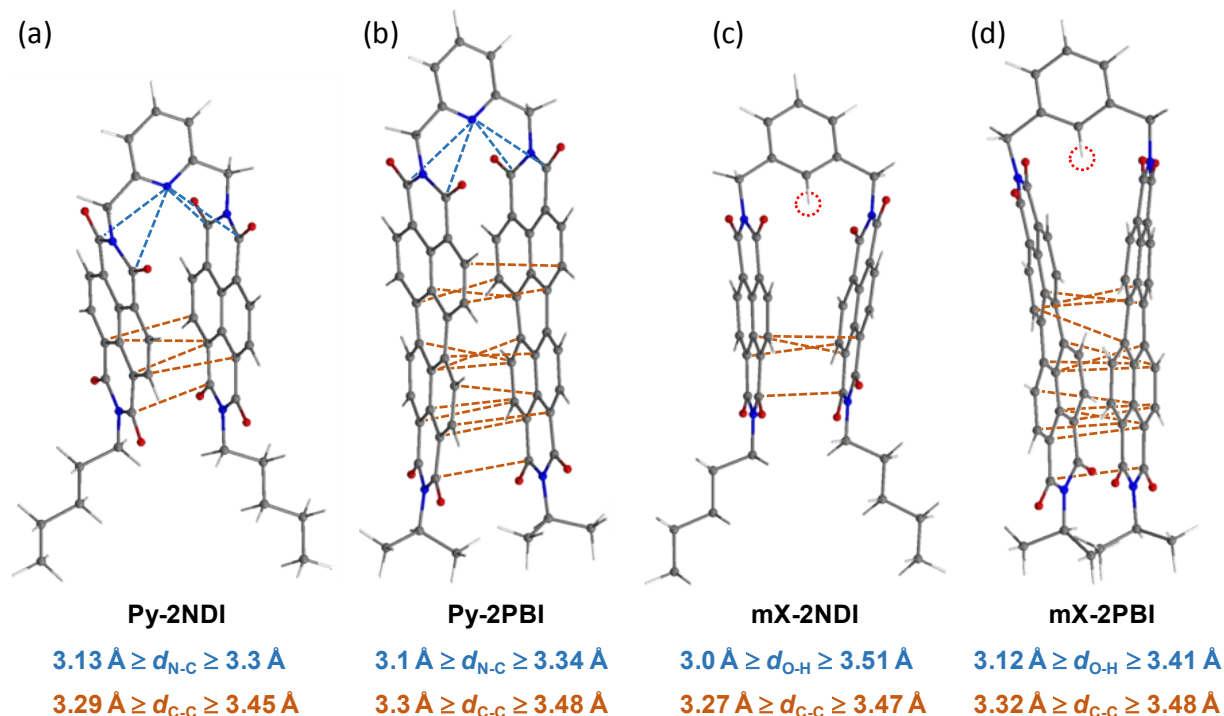
Figure S8. Geometry optimized structures of the folded conformers of (a) **Py-2NDI**, (b) **Py-2PBI**, (c) **mX-2NDI**, and (d) **mX-2PBI**. In (a) and (b), the folded conformers are stabilized through a synergy of $n{\rightarrow}\pi^*$ (blue) and pi-stacking (orange) interactions, while in case of (c) and (d) regular pi-stacking is the only interaction. The dashed lines indicate short contacts, where the interaction distance shorter than the sum of van der Waal's radii of the atoms involved. The interaction distances are also provided in respective colors. In (c) and (d), the distance between benzene ring hydrogen (circled in red dotted line) and the closest vicinal carbonyl O atom ($d_{\text{O-H}}$) is greater than 2.72 Å, the sum of O and H van der Waal radii, downplaying the role of any steric interaction in m-xylylene dimers.

Interaction	Donor (n)	Acceptor (π^*)	Occupancy of N_{95} before and after deletion of C=O NBOs	Change in occupancy
$n_{\text{N}}{\rightarrow}\pi^*_{\text{C=O}}$	N_{95}	Not deleted $C_{40}{=}O_{56}$ $C_{36}{=}O_{57}$ $C_5{=}O_{21}$ $C_1{=}O_{22}$	1.91572	0.0018
	N_{95}	Deleted $C_{40}{=}O_{56}$ $C_{36}{=}O_{57}$ $C_5{=}O_{21}$ $C_1{=}O_{22}$	1.91752	

Table S1. NBO deletion analysis of **Py-2NDI**. Occupancy of the donor pyridyl nitrogen (N95) lone pair orbital increases upon deletion of $n_{\text{N}}{\rightarrow}\pi^*_{\text{C=O}}$ interactions.
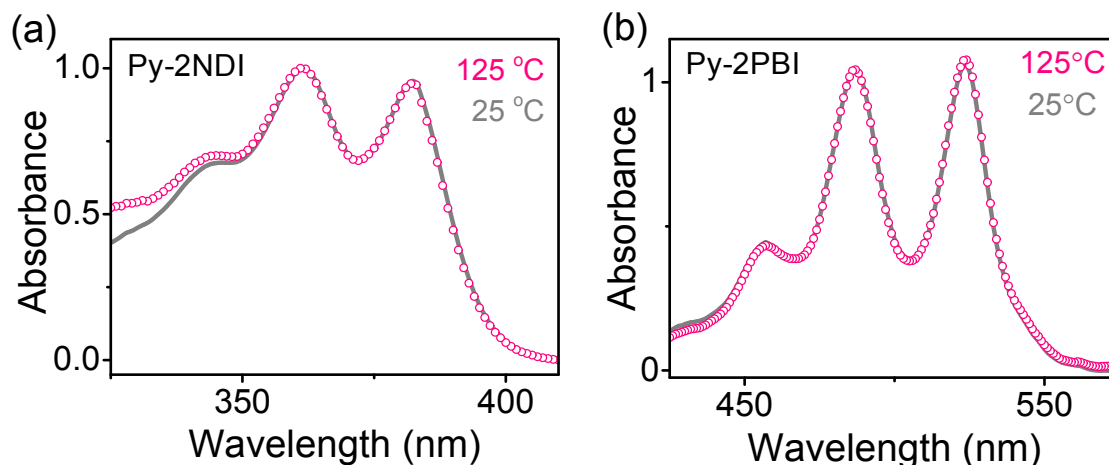
Figure S9. Normalized absorption spectra of (a) **Py-2NDI** and (b) **Py-2BI** in chlorobenzene (10 µM) at 25 and 125 **°**C highlight the thermal stability of the folded H-aggregated conformers.

IV. References

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