Supporting Information for

Anion–π Interactions of Highly π-Acidic Dipyridinium-Naphthalene Diimide Salts

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1. Experimental Section

1.1. General

All reagents were purchased from Sigma Aldrich other than 2,6-dibromo-N,N'-bis(2-ethylhexyl)-1,8:4,5-naphthalene tetracarboxdiimide (TCI). $^1$H and $^{13}$C{$^1$H} NMR were performed on JEOL 500MHz NMR system with chemical shifts referenced to the deuterated solvent. The $^{19}$F, $^{35}$Cl, $^{81}$Br and $^{127}$I NMR spectra were recorded on a JEOL 500MHz NMR operating at 470.39, 49.94, 134.89 and 99.94 MHz for $^{19}$F, $^{35}$Cl, $^{81}$Br and $^{127}$I respectively. The $^{19}$F, $^{35}$Cl, $^{81}$Br and $^{127}$I NMR spectra were externally referenced to 1.0 M aqueous (D$_2$O) solutions of KF, NaCl, NaBr and NaI respectively, at 0 ppm. Variable-temperature $^1$H NMR was performed on Bruker DPX 400 MHz spectrometer. Matrix assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra were obtained on a Bruker Daltonics Autoflex II TOF/TOF system. Elemental analysis was carried out using CHNS FlashEA 1112 Elemental Analyzer from Thermo Fisher Scientific. UV-Vis-NIR absorption spectra were recorded on a Shimadzu UV-3101PC UV-VIS-NIR Spectrophotometer. Cyclic voltammetry (CV) experiments were performed using Autolab potentiostat (model PGSTAT30) by Echochimie. All CV measurements were recorded in dry acetonitrile with 0.1 M tetra-n-butylammonium hexafluorophosphate as supporting electrolyte (scan rate of 100 mV•s$^{-1}$), glassy carbon disk as working electrode, gold disk as counter electrode and Ag/AgCl as reference electrode. Ferrocene was used as external standard (HOMO = oxidation onset = –4.80 eV). LUMO values of the compounds were calculated using the formula: –4.80 – (reduction onset of compound). Continuous wave X-band ESR spectra were obtained with a JEOL (FA200) spectrometer at room temperature using dry dichloromethane as solvent and DPPH as standard. XPS spectra were measured on powder samples using VG Thermo Escalab 220i -XL X-ray photoelectron spectroscopy system. XPS data is analyzed using Thermo Avantage v4.12. Single crystals were submitted to X-ray Diffraction Laboratory in National University of Singapore for single crystal structure. ESI-MS measurements were performed on Shimadzu LCMS-IT-TOF, isotope distribution patterns were used as a composition proof in addition to m/z signal.
1.2. Synthetic procedures and characterization data

Py$_2$-NDI•2Br. 500 mg of 2,6-dibromo-$N,N'$-bis(2-ethylhexyl)-1,8:4,5-naphthalene tetracarboxdiimide (Br$_2$-NDI, 0.77 mmol), 50 mL of THF and 1.24 mL of pyridine (15.33 mmol) was added into a two-necked round-bottom flask with a condenser attached. The reaction setup was purged with nitrogen and refluxed for 24 hours. At the end of the reaction, the reaction mixture was filtered and washed with THF. The solids were re-dissolved in methanol, filtered and the filtrate was concentrated. The concentrated methanol solution precipitated in toluene, filtered, washed with toluene and dried under vacuum. Yield: 466 mg (75%). Orange solids. Single crystals were obtained by layering diethyl ether on a concentrated solution of Py$_2$-NDI•2Br in ethanol. $^1$H NMR (500 MHz, DMSO-$d_6$) δ 9.41 (dd, $J = 6.5$, 1.2 Hz, 4H), 9.22 (s, 2H), 8.98 (tt, $J = 7.9$, 1.3 Hz, 2H), 8.49 – 8.45 (m, 4H), 3.92 – 3.83 (m, 4H), 1.76 – 1.68 (m, 2H), 1.32 – 1.18 (m, 16H), 0.85 – 0.80 (m, 12H). $^{13}$C($^1$H) NMR (125 MHz, DMSO-$d_6$) δ 161.13, 160.59, 148.31, 145.85, 142.79, 131.55, 127.89, 127.42, 127.27, 121.47, 43.96, 37.02, 29.71, 27.70, 23.11, 22.42, 13.94, 10.23. Anal. Calcd for C$_{40}$H$_{46}$Br$_2$N$_4$O$_4$: C, 59.56; H, 5.75; Br, 19.81; N, 6.95; O, 7.93. Found: C, 59.68; H, 5.71; N, 6.88. MALDI-TOF-MS $m/z$: 646.38 (M$^+$-2Br); calcd. for C$_{40}$H$_{46}$N$_4$O$_4$ (M$^+$-2Br) = 646.35.
Py$_2$-NDI•2PF$_6$. 100 mg of Py$_2$-NDI•2Br were dissolved in 4 mL of saturated methanolic ammonium hexafluorophosphate solution. The solution was mixed well and precipitated in 100 mL of DI water. The precipitate was filtered, washed with DI water followed by minimum methanol and dried under vacuum. Yield: 82 mg (70%). White solids. Single crystals were obtained by layering diethyl ether on a concentrated solution of Py$_2$-NDI•2PF$_6$ in acetonitrile. $^1$H NMR (500 MHz, DMSO-$d_6$) $\delta$ 9.38 (dd, $J = 6.2$, 1.0 Hz, 4H), 9.22 (s, 2H), 8.98 – 8.45 (m, 4H), 3.93 – 3.84 (m, 4H), 1.74 – 1.69 (m, 2H), 1.32 – 1.15 (m, 16H), 0.85 – 0.80 (m, 12H). $^{13}$C{$^1$H} NMR (125 MHz, DMSO-$d_6$) $\delta$ 161.10, 160.57, 148.36, 145.84, 142.92, 131.60, 127.91, 127.40, 127.22, 121.41, 43.93, 37.06, 29.70, 27.69, 23.09, 22.42, 13.93, 10.22. Anal. Calcd for C$_{40}$H$_{46}$F$_{12}$N$_4$O$_4$P$_2$: C, 51.29; H, 4.95; F, 24.34; N, 5.98; O, 6.83; P, 6.61. Found: C, 51.48; H, 5.11; N, 6.23. MALDI-TOF-MS m/z: 645.86 (M$^+$-2PF$_6$); calcd. for C$_{40}$H$_{46}$N$_4$O$_4$ (M$^+$-2PF$_6$) = 646.35.

Py$_2$-NDI•2Cl. 80.6 mg of Py$_2$-NDI•2Br (0.1 mmol) was dissolved in 2 mL of methanol. 40 mg of silver chloride (0.4 mmol) was added and the suspension was sonicated in the dark for 30 mins. The suspension was allowed to stir overnight under light illumination. The reaction was filtered through 0.45 $\mu$m PTFE filter and solvent was removed using rotary evaporation. The solids were washed with toluene and dried under vacuum. Single crystals were obtained by layering diethyl ether on a concentrated solution of Py$_2$-NDI•2Cl in ethanol. Yield: 59 mg (82%). Yellow solids. $^1$H NMR (500 MHz, DMSO-$d_6$) $\delta$ 9.45 (dd, $J = 6.6$, 1.0 Hz, 4H), 9.22 (s, 2H), 8.98 (tt, $J = 7.9$, 1.3 Hz, 2H), 8.49 – 8.45 (m, 4H), 3.92 – 3.83 (m, 4H), 1.74 – 1.69 (m, 2H), 1.32 – 1.18 (m, 16H), 0.84 – 0.79 (m, 12H). $^{13}$C{$^1$H}
NMR (125 MHz, DMSO-\textit{d}_6) \delta 161.13, 160.59, 148.31, 145.89, 142.84, 131.56, 127.90, 127.42, 127.26, 121.47, 43.95, 37.04, 29.72, 27.70, 23.11, 22.43, 13.95, 10.23. Anal. Calcd for C_{40}H_{46}Cl_2N_4O_4: C, 66.94; H, 6.46; Cl, 9.88; N, 7.81; O, 8.92. Found: C, 66.68; H, 6.19; N, 7.63. MALDI-TOF-MS \textit{m/z}: 645.96 (M^+-2Cl); calcd. for C_{40}H_{46}N_4O_4 (M^+-2Cl) = 646.35.

Py2-NDI\textbullet{}2I. 100 mg of Py2-NDI\textbullet{}2Br were dissolved in 2 mL of saturated methanolic sodium iodide solution. The solution was stirred for 2 mins and precipitated in 100 mL of DI water. The precipitate was filtered, washed with DI water and dried under vacuum. Yield: 85 mg (76%). Violet solids. Single crystals were obtained by layering diethyl ether on a concentrated solution of Py2-NDI\textbullet{}2I in ethanol. $^1$H NMR (500 MHz, DMSO-\textit{d}_6) \delta 9.40 (d, $J = 5.8$ Hz, 4H), 9.22 (s, 2H), 8.98 (t, $J = 7.9$ Hz, 2H), 8.49 – 8.45 (m, 4H), 3.92 – 3.83 (m, 4H), 1.74 – 1.69 (m, 2H), 1.34 – 1.16 (m, 16H), 0.84 – 0.79 (m, 12H). $^{13}$C\{$^1$H\} NMR (125 MHz, DMSO-\textit{d}_6) \delta 148.34, 145.85, 127.94, 43.96, 37.02, 29.70, 27.68, 23.10, 22.42, 13.93, 10.22. Anal. Calcd for C_{40}H_{46}I_2N_4O_4: C, 53.34; H, 5.15; I, 28.18; N, 6.22; O, 7.11. Found: C, 53.58; H, 5.21; N, 6.33. MALDI-TOF-MS \textit{m/z}: 646.16 (M^+-2I); calcd. for C_{40}H_{46}N_4O_4 (M^+-2I) = 646.35.

Py2-NDI\textbullet{}2OH. 115 mg of Py2-NDI\textbullet{}2Br (0.14 mmol) and 66 mg of Ag_2O (0.28 mmol) were suspended in 50 mL of THF and 10 mL of DI water. The reaction was stirred for two hours and filtered through celite. Solvent was removed from the filtrate and the residue was washed with DI water. The compound was purified using column chromatography (100% dichloromethane \rightarrow 98% dichloromethane + 2% methanol). Yield: 69 mg (71%). Dark blue solids. $^1$H NMR (500 MHz, CD_2Cl_2) \delta 11.98 (d, $J = 12.2$ Hz, 2H), 9.54 (d, $J = 9.6$ Hz, 2H),
8.56 (s, 2H), 7.69 (t, J = 12.6 Hz, 2H), 7.30 (t, J = 13.6 Hz, 2H), 6.34 (t, J = 12.7 Hz, 2H), 6.13 (dd, J = 15.4, 8.4 Hz, 2H), 4.20 – 4.06 (m, 4H), 1.97 – 1.86 (m, 2H), 1.47 – 1.23 (m, 16H), 0.94 (t, J = 6.0 Hz, 6H), 0.92 – 0.86 (m, 6H). \(^{13}\)C\{\(^1\)H\} NMR (125 MHz, CD\(_2\)Cl\(_2\)) \(\delta\) 193.20, 166.95, 162.89, 151.48, 143.59, 136.00, 128.66, 126.89, 123.43, 119.71, 112.00, 105.20, 44.95, 38.50, 31.28, 29.23, 24.60, 23.63, 14.43, 10.97. Anal. Calcd for C\(_{40}\)H\(_{48}\)N\(_4\)O\(_6\): C, 70.56; H, 7.11; N, 8.23; O, 14.10. Found: C, 70.33; H, 7.00; N, 8.23. MALDI-TOF-MS \(m/z\): 680.96 (M\(^+\)); calcd. for C\(_{40}\)H\(_{48}\)N\(_4\)O\(_6\) = 680.36.
2. Proposed decomposition pathway of Py$_2$-NDI•2F

![Diagram of the proposed decomposition pathway of Py$_2$-NDI•2F](image)

**Py$_2$-NDI•2Br**

R = 2-ethylhexyl

Py$_2$-NDI•2Br decomposes via nucleophilic aromatic substitution to form I-F and II. However, in the presence of atmospheric moisture, III-F and IV are also formed.

**Figure S1.** Proposed decomposition pathway of Py$_2$-NDI•2F. Py$_2$-NDI•2F decomposes via nucleophilic aromatic substitution to form I-F and II. However, in the presence of atmospheric moisture, III-F and IV are also formed.
**Figure S2.** MALDI-TOF mass spectrum of crude reaction mixture as shown in Figure S1.
Top: positive mode, bottom: negative mode.
Figure S3. Top: $^1$H NMR of crude reaction mixture as shown in Figure S1. Bottom: $^1$H NMR of crude reaction mixture as shown in Figure S1 after removal of pyridine. Inset: $^{19}$F NMR of crude reaction mixture as shown in Figure S1. Red star: peaks corresponding to IV, blue star: peaks corresponding to II, black star: unknown impurity. Py$_2$-NDI•2F, I•F and III•F are NMR silent.
3. X-ray crystallographic structures, selected crystal data, data collection, and refinement parameters

**Figure S4.** X-ray crystallographic structure of Py$_2$-NDI•2PF$_6$ showing PF$_6^-$ above and below the NDI core. Alkyl groups are omitted for clarity. [C–H•••F] short contact distances: 2.435 and 2.538 Å, [C•••F] short contact distances: 3.069, 3.031, 3.044, 3.055, 2.997 and 2.846 Å.

**Figure S5.** X-ray crystallographic structure of Py$_2$-NDI•2Cl showing Cl$^-$ above and below the NDI core. Alkyl groups are omitted for clarity. [C–H•••Cl$^-$] short contact distances: 2.585 Å, [C•••Cl$^-$] short contact distances: 3.420 and 3.427 Å.
**Figure S6.** X-ray crystallographic structure of Py$_2$-NDI•2Br showing Br$^-$ above and below the NDI core. Alkyl groups are omitted for clarity. [C–H⋯Br$^-$] short contact distance: 2.650 Å, [C⋯Br$^-$] short contact distance: 3.541 Å.

**Figure S7.** X-ray crystallographic structure of Py$_2$-NDI•2I showing I$^-$ above and below the NDI core. Alkyl groups are omitted for clarity. [C–H⋯I$^-$] short contact distance: 3.075 Å. [C⋯I$^-$] short contact distances: 3.580 and 3.653 Å.
<table>
<thead>
<tr>
<th></th>
<th>Py2-NDI•2Cl</th>
<th>Py2-NDI•2Br</th>
<th>Py2-NDI•2I</th>
<th>Py2-NDI•2PF6</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Empirical formula</strong></td>
<td>C₄₄H₅₈Cl₂N₄O₆</td>
<td>C₄₄H₅₈Br₂N₄O₆</td>
<td>C₄₄H₅₈I₂N₄O₆</td>
<td>C₄₆H₅₃F₁₂N₇O₃P₂</td>
</tr>
<tr>
<td><strong>Formula weight</strong></td>
<td>809.84</td>
<td>898.76</td>
<td>992.74</td>
<td>1059.91</td>
</tr>
<tr>
<td><strong>Temperature of data collection</strong></td>
<td>100(2) K</td>
<td>100(2) K</td>
<td>100(2) K</td>
<td>100(2) K</td>
</tr>
<tr>
<td><strong>Wavelength</strong></td>
<td>1.54178 Å</td>
<td>0.71073 Å</td>
<td>1.54178 Å</td>
<td>1.54178 Å</td>
</tr>
<tr>
<td><strong>Crystal size</strong></td>
<td>0.286 x 0.175 x 0.072 mm³</td>
<td>0.60 x 0.46 x 0.12 mm³</td>
<td>0.070 x 0.092 x 0.118 mm³</td>
<td>0.318 x 0.211 x 0.060 mm³</td>
</tr>
<tr>
<td><strong>Crystal system</strong></td>
<td>Triclinic</td>
<td>Monoclinic</td>
<td>Triclinic</td>
<td>Monoclinic</td>
</tr>
<tr>
<td><strong>Space group</strong></td>
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<td>P2₁/c</td>
<td>P-1</td>
<td>P2₁/c</td>
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<td><strong>Unit cell dimensions</strong></td>
<td>a = 7.9255(5) Å, α = 96.993(2)°</td>
<td>a = 8.3030(10) Å, α = 90°</td>
<td>a = 9.0399(6) Å, α = 84.915(4)°</td>
<td>a = 12.6980(5) Å, α = 90°</td>
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<tr>
<td></td>
<td>b = 9.2590(6) Å, β = 98.728(2)°</td>
<td>b = 28.106(4) Å, β = 104.697(2)°</td>
<td>b = 10.7529(7) Å, β = 70.321(4)°</td>
<td>b = 17.0155(8) Å, β = 96.201(2)°</td>
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<td>c = 15.1784(9) Å, γ = 98.758(2)°</td>
<td>c = 9.5912(12) Å, γ = 90°</td>
<td>c = 12.1907(8) Å, γ = 80.746(4)°</td>
<td>c = 23.0412(10) Å, γ = 90°</td>
</tr>
<tr>
<td><strong>Volume</strong></td>
<td>1076.06(12) Å³</td>
<td>2165.0(5) Å³</td>
<td>1100.51(13) Å³</td>
<td>4949.2(4) Å³</td>
</tr>
<tr>
<td><strong>Z</strong></td>
<td>1</td>
<td>2</td>
<td>2</td>
<td>4</td>
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<tr>
<td><strong>Density (calculated)</strong></td>
<td>1.250 g/cm³</td>
<td>1.379 g/cm³</td>
<td>1.498 g/cm³</td>
<td>1.418 g/cm³</td>
</tr>
<tr>
<td><strong>F(000)</strong></td>
<td>432</td>
<td>936</td>
<td>504</td>
<td>2188</td>
</tr>
<tr>
<td><strong>Theta range for data collection</strong></td>
<td>4.887 to 70.365°</td>
<td>1.449 to 27.497°</td>
<td>3.85 to 65.47°</td>
<td>3.501 to 66.573°</td>
</tr>
<tr>
<td><strong>Reflections collected</strong></td>
<td>14083</td>
<td>35480</td>
<td>8928</td>
<td>39546</td>
</tr>
<tr>
<td><strong>Independent reflections</strong></td>
<td>4071 [R(int) = 0.0389]</td>
<td>4982 [R(int) = 0.0473]</td>
<td>3571 [R(int) = 0.0476]</td>
<td>8710 [R(int) = 0.0554]</td>
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<tr>
<td><strong>Goodness-of-fit on F²</strong></td>
<td>1.093</td>
<td>1.047</td>
<td>1.082</td>
<td>1.022</td>
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<td><strong>Final R indices [I&gt;2sigma(I)]</strong></td>
<td>R1 = 0.0630, wR2 = 0.1710</td>
<td>R1 = 0.0317, wR2 = 0.0776</td>
<td>R1 = 0.0496, wR2 = 0.1050</td>
<td>R1 = 0.0901, wR2 = 0.2703</td>
</tr>
<tr>
<td><strong>R indices (all data)</strong></td>
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<td>R1 = 0.0358, wR2 = 0.0795</td>
<td>R1 = 0.0652, wR2 = 0.1139</td>
<td>R1 = 0.1010, wR2 = 0.2855</td>
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<td><strong>Largest diff. peak and hole</strong></td>
<td>1.360 and -0.858 e.Å⁻³</td>
<td>0.563 and -0.320 e.Å⁻³</td>
<td>1.114 and -1.173 e.Å⁻³</td>
<td>1.220 and -0.768 e.Å⁻³</td>
</tr>
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</table>

**Table S1.** Selected crystal data, data collection, and refinement parameters for Py2-NDI•2Cl, Py2-NDI•2Br, Py2-NDI•2I and Py2-NDI•2PF6.
4. Characterization data of Py$_2$-NDI•2X salts

![Graphs showing XPS spectra of various elements: F 1s, Cl 2p1/2 2p3/2, Br 3d3/2 3d5/2, I 3d3/2 3d5/2.](image)

**Figure S8.** XPS of a) Py$_2$-NDI•PF$_6$, b) Py$_2$-NDI•2Cl, c) Py$_2$-NDI•Br and d) Py$_2$-NDI•2I.
Figure S9. Solution UV-Vis absorption spectra in a) CHCl₃ and b) CH₃OH. c) Solution cyclic voltammograms in CH₃CN.
Figure S10. Solution cyclic voltammograms of tetra-\textit{n}-butylammonium halides in acetonitrile.

Figure S11. Variable temperature electron paramagnetic resonance spectra of Py\textsubscript{2}-NDI\textcdot2I in CH\textsubscript{2}Cl\textsubscript{2}.
DFT calculation was carried out using the Gaussian 09 program suite. Geometry optimization in the gas phase was performed to obtain the monoradical monocation. Subsequent single-point energy calculation was carried out on the gas phase optimized structure using solvation model. Level of theory: DFT UB3LYP 6-31G (d,p). Solvation model: IEF-PCM (acetonitrile).

**Figure S12.** Electron transfer from iodide to Py$_2$-NDI$^{2+}$ will generate Py$_2$-NDI$^{+}$ with spin density mainly located on the NDI core. Low spin density was found on the pyridinium carbons, especially C3.

<table>
<thead>
<tr>
<th></th>
<th>Temp (°C)</th>
<th>Chemical Shift of Py$_2$-NDI•2X (ppm)</th>
<th>LW$_{1/2}$ (Hz)</th>
<th>Chemical Shift of TBA•X (ppm)</th>
<th>LW$_{1/2}$ (Hz)</th>
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<td>PF$_6^-$ ($^{19}$F)</td>
<td>25</td>
<td>$-$72.29, $-$73.80</td>
<td>2</td>
<td>$-$72.29, $-$73.80</td>
<td>2</td>
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<tr>
<td></td>
<td>70</td>
<td>$-$70.87, $-$72.38</td>
<td>2</td>
<td>$-$70.88, $-$72.39</td>
<td>2</td>
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<tr>
<td>Cl$^-$ ($^{35}$Cl)</td>
<td>25</td>
<td>72.79</td>
<td>90</td>
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<tr>
<td></td>
<td>70</td>
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<td>Br$^-$ ($^{81}$Br)</td>
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<tr>
<td>I$^-$ ($^{127}$I)</td>
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<td>$-$ [a]</td>
<td>$-$ [a]</td>
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<td></td>
<td>70</td>
<td>$-$ [a]</td>
<td>$-$ [a]</td>
<td>195.39</td>
<td>700</td>
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</table>

**Table S2.** $^{19}$F, $^{35}$Cl, $^{81}$Br, and $^{127}$I NMR chemical shifts and LW$_{1/2}$ of TBA•X and Py$_2$-NDI•2X where X = PF$_6$, Cl, Br and I at 25 °C and 70 °C. All halogen NMR were performed in DMSO-$d_6$. LW$_{1/2}$: line width at half height. $^{[a]}$ $^{127}$I NMR signal not observed, likely due to the I$^-$ being bounded to the Py$_2$-NDI$^{2+}$, resulting severe peak broadening, or partial electron being transferred from I$^-$ to Py$_2$-NDI$^{2+}$, resulting in a radical I$^+$ species invisible to NMR.
5. $^1$H, $^{13}$C$^\text{[1]H}$ NMR, MALDI-TOF and ESI mass spectra of synthesized compounds

Figure S13. $^1$H NMR spectrum (500 MHz) of Py$_2$-NDI•2Br in DMSO-$d_6$. 
Figure S14. $^{13}$C{$^1$H} NMR spectrum (500 MHz) of Py$_2$-NDI•2Br in DMSO-$d_6$. 
Figure S15. MALDI-TOF mass spectrum of Py2-NDI•2Br. The M⁺ corresponds to the Py2-NDI²⁺.
Figure S16. $^1$H NMR spectrum (500 MHz) of Py$_2$-NDI•2PF$_6$ in DMSO-$d_6$. 
Figure S17. $^{13}$C{¹H} NMR spectrum (500 MHz) of Py2-NDI•2PF₆ in DMSO-$d_6$. 
Figure S18. MALDI-TOF mass spectrum of Py$_2$-NDI•2PF$_6$. The M$^+$ corresponds to the Py$_2$-NDI$^{2+}$. 
Figure S19. $^1$H NMR spectrum (500 MHz) of Py2-NDI•2Cl in DMSO-$d_6$. 
Figure S20. $^{13}$C{$^{1}$H} NMR spectrum (500 MHz) of Py$_2$-NDI•2Cl in DMSO-$d_6$. 
Figure S21. MALDI-TOF mass spectrum of Py$_2$-NDI•2Cl. The M$^+$ corresponds to the Py$_2$-NDI$^{2+}$. 
Figure S22. $^1$H NMR spectrum (500 MHz) of Py2-NDI•2I in DMSO-$d_6$. 
Figure S23. $^{13}$C{$^{1}$H] NMR spectrum (500 MHz) of Py$_2$-NDI•2I in DMSO-$d_6$. 
Figure S24. MALDI-TOF mass spectrum of Py₂-NDI•2I. The M⁺ corresponds to the Py₂-NDI²⁺.
Figure S25. $^1$H NMR spectrum (500 MHz) of Py2-NDI•2OH in CD$_2$Cl$_2$. 
Figure S26. $^{13}$C($^1$H) NMR spectrum (500 MHz) of Py$_2$-NDI•2OH in CD$_2$Cl$_2$. 
Figure S27. MALDI-TOF mass spectrum of Py$_2$-NDI•2OH.
Figure S28. $^1$H-$^{13}$C heteronuclear single quantum correlation (HSQC) of Py$_2$-NDI•2Br in DMSO-$d_6$
Figure S29. Variable-temperature $^1$H NMR (400 MHz) spectra of a & d) Py$_2$-NDI•2Cl, b & e) Py$_2$-NDI•2Br and c & f) Py$_2$-NDI•2I. Left – in methanol-d$_4$, –60 °C to 55 °C. Right – in DMSO-d$_6$, 25 °C to 100 °C. Degradation was observed at 100 °C for Py$_2$-NDI•2Cl, and above 100 °C for Py$_2$-NDI•2PF$_6$, Py$_2$-NDI•2Br and Py$_2$-NDI•2I (see Figure S29 – S33).
Figure S30. Variable temperature NMR (400 MHz) of Py2-NDI•2Cl in methanol-\textit{d}_4.
Figure S31. Variable temperature NMR (400 MHz) of Py2-NDI•2Br in methanol-\textit{d}_4.
Figure S32. Variable temperature NMR (400 MHz) of Py2-NDI•2I in methanol-$d_4$. 
Figure S33. Variable temperature NMR (400 MHz) of Py2-NDI•2PF6 in DMSO-$d_6$. 
Figure S34. Aromatic proton region of the variable temperature NMR (400 MHz) of Py$_2$-NDI•2PF$_6$ in DMSO-$d_6$. 
Figure S35. Variable temperature NMR (400 MHz) of Py$_2$-NDI-2Cl in DMSO-$d_6$. 
Figure S36. Variable temperature NMR (400 MHz) of Py2-NDI•2Br in DMSO-\textit{d}_6.
Figure S37. Variable temperature NMR (400 MHz) of Py2-NDI•2I in DMSO-d$_6$. 
Figure S38. Proposed energy diagram of anion shuttling for the Py$_2$-NDI$^{2+}$ salts. The blue and red regions indicate the region where the anions are likely to be found.
**Figure S39.** (a) ESI-MS (positive mode) of experimental isotopic distribution pattern of [Py2-NDI•PF6]+. (b) Predicted isotopic distribution for [Py2-NDI•PF6]+. (c) ESI-MS (negative mode) of experimental isotopic distribution pattern of [Py2-NDI•2Cl]−. (d) Predicted isotopic distribution for [Py2-NDI•2Cl]−. (e) ESI-MS (negative mode) of experimental isotopic distribution pattern of [Py2-NDI•2Br]−. (f) Predicted isotopic distribution for [Py2-NDI•2Br]−.
Figure S40. (a) ESI-MS (positive mode) of experimental isotopic distribution pattern of Py$_2$-NDI•2I which shows [Py$_2$-NDI]$^{2+}$ at 323.50 and [Py$_2$-NDI]$^+$ at 646.20. (b) ESI-MS (negative) of experimental isotopic distribution pattern of Py$_2$-NDI•2I which shows mostly I$_3^-$ at 380.63 with a small amount of I$^-$ at 126.88.
AC & DC Resistance Measurements

The Py$_2$-NDI$^{2+}$ salts were pressed into pellets (diameter 6mm) with aluminium foil as the electrodes. AC resistance measurements were carried out using Autolab potentiostat (model PGSTAT30) by Echochimie at a 50 mV RMS. DC resistance measurements were carried out using Fluke 289 True RMS Multimeter.

Figure S41. AC impedance measurement of Py$_2$-NDI.2Cl (left), Py$_2$-NDI.2Br (middle) and Py$_2$-NDI.2PF$_6$ (right).

Figure S42. A summary of the nature of anion-π interactions of the Py$_2$-NDI$^{2+}$ salts in terms of the HOMO value of the anion. HOMO value of Py$_2$-NDI$^{2+}$ estimated from LUMO value and optical bandgap of Py$_2$-NDI•2PF$_6$. Upon exposure to water,
which is a source of \( \text{OH}^- \) ions, \( \text{HOMO} = -4.58 \text{ eV} \), n-type organic semiconductors with low LUMO energy levels, e.g. PCBM (-4.2 eV) and C\(_{60}\) (-4.5 eV), will likely degrade via HOMO-LUMO interactions to form hydroxyl-containing Meisenheimer complexes.
6. References: