Supporting Information

Fluorescent crystals and co-crystals of 1,8-naphthalimide derivatives: synthesis, structure determination and photophysical characterization

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**Table S1.** Crystallographic data and details of measurements for crystalline 4 Form I.

<table>
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<tr>
<td>Formula</td>
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<td>b (Å)</td>
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<tr>
<td>β (deg)</td>
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<tr>
<td>γ (deg)</td>
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</tr>
<tr>
<td>V (Å\textsuperscript{3})</td>
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\textsuperscript{a}Calculated with Platon; for the accessible void calculation a probe of 1.2 Å\textsuperscript{3} was employed.

**Figure S1.** Top (left) and side (right) views for the superimposition of 4 (Form I) (orange) and 4 (Form II) (yellow) molecular structures for crystalline 4, showing that the two conformations are almost exactly the same in the two polymorphs. H\textsubscript{CH} are omitted for clarity.
Figure S2. Types of dimers observed in crystalline 2-4: (a) head-to-tail dimer in crystalline 2, CD = 3.8 Å, ID = 3.4 Å, offset = 1.7 Å; (b) head-to-head dimer in crystalline 3: CD = 5.3 Å, ID = 3.5 Å, offset 3.9 Å (left), and T-dimers with dC–H···π = 3.2 Å or dC···π = 4.0 Å (right); (c) head-to-head dimer in crystalline 4 (Form I): CD = 5.3 Å, ID = 3.5 Å, offset 3.9 Å (left), and T-dimers dC–H···π = 2.7 – 2.9 Å or dC···π = 3.6 Å (right), and (d) head-to-head dimer in crystalline 4 (Form II): CD = 4.6 Å, ID = 3.3 Å, offset 3.2 Å. H\textsubscript{CH} omitted for clarity.

Figure S3. Types of dimers observed in n\textsubscript{2}·I\textsubscript{2}F\textsubscript{4} co-crystals. (a) head-to-head dimer in crystalline 2\textsubscript{2}·I\textsubscript{2}F\textsubscript{4}, CD = 5.2 Å, ID = 3.3 Å, offset = 4.0 Å (left), and T-dimer dC–H···π = 2.8 – 3.1 Å or dC···π = 3.7 – 3.8 Å (right); (b) head-to-head dimer in crystalline 3\textsubscript{2}·I\textsubscript{2}F\textsubscript{4}, CD = 4.1 Å, ID = 3.5 Å, offset = 2.1 Å; (c) T-dimer in crystalline 4\textsubscript{2}·I\textsubscript{2}F\textsubscript{4}, dC–H···π = 2.8 – 3.0 Å or dC···π = 3.7–3.9 Å. H\textsubscript{CH} omitted for clarity.
Figure S4. Experimental (red-line) and simulated (black-line) X-ray powder diffraction patterns for compounds: (a) 2, (b) 3, and (c) 4 of for corresponding co-crystals: (d) $2\cdot$I2F4, (e) $3\cdot$I2F4, and (f) $4\cdot$I2F4.
Figure S5. ATR-FTIR spectra of components I2F4 (black line), 3 (red line) and 3₂-I2F4 (green line) in the range 4000-600 cm⁻¹. The inset highlights the shifts to higher frequencies for the $\nu_{C_{pyr}-H}$ stretching (from 3) of the pyridine involved in the halogen bond.

Figure S6. ATR-FTIR spectra of components I2F4 (black line), 4 (red line) and 4₂-I2F4 (green line) in the range 4000-600 cm⁻¹. The inset highlights the shifts to higher frequencies for the $\nu_{C_{pyr}-H}$ stretching (from 4) of the pyridine involved in the halogen bond.
Thermal characterization (TGA-DSC-VTPXRD).

Figure S7. TGA thermograms for the compounds 2, 3 (Form I and Form II), and 4 (Form II).

Differential scanning calorimetry (DSC) measurements below the decomposition temperature were also performed, and are shown in SI-Figure 8. For compound 2 the DSC trace shows that melting occurs at ca 190 °C (peak temperature, $\Delta H = 35.8$kJ mol$^{-1}$) in the first heating cycle; recrystallization to the same crystalline form is observed in a second heating cycle (exothermic peak at 108 °C, peak temperature, $\Delta H = 17.8$kJ mol$^{-1}$), followed by melting at 190 °C (peak temperature, $\Delta H = 35.0$kJ mol$^{-1}$) (see SI-Fig. 8). Compound 3 (Form I) melts at 157 °C (peak temperature, $\Delta H = 28.9$kJ mol$^{-1}$) but a second, small peak is observed at ca. 175 °C. Recrystallization occurs during the cooling process and in a second heating cycle, in which melting is observed at 156 °C (peak temperature, $\Delta H = 2.5$KJ mol$^{-1}$). When the same measurement is performed on a sample of 3 (Form II) melting is now observed at 176 °C (peak temperature, $\Delta H = 38.9$kJ mol$^{-1}$), and recrystallization occurs on a second heating cycle to 3
(Form I), which melts at 156 °C (peak temperature, ΔH = 5.1 kJ mol⁻¹). The small peak observed at 175 °C in the DSC trace of Form I is likely due to traces of Form II.

The DSC trace of compound 4 (Form II) shows an endothermic peak at 181 °C (peak temperature, ΔH = 35.9 kJ mol⁻¹), due to melting. A second heating cycle shows the compound melts at the same temperature, i.e. Form II recrystallizes from the melt.

The thermal behavior of 3 (Form II) has also been investigated via variable temperature X-ray powder diffraction (see SI-Figure 8).

![DSC traces for the compounds](image)

**Figure S8.** DSC traces for the compounds: (a) 2, (b1) 3 (Form I), (b2) 3 (Form II), and (c) 4 (Form II).
Figure S9. VT-XRPD patterns for crystalline 3 (Form II) at RT (a), at 180 °C (melting occurs) (b) and back at RT (the solid is amorphous); a second heating to 153 °C (d) shows recrystallization to 3 (Form I).

Figure S10. TGA thermograms for the co-crystals $2_2$-I$2F_4$, $3_2$-I$2F_4$, and $4_2$-I$2F_4$. 
Figure S11. Absorption (a, c) and normalized emission (b, d) spectra of 3 (a, b) and 4 (c, d) in the explored solvents at room temperature.
Table S2. Luminescence data in toluene glassy matrix at 77 K.

<table>
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<th>( \lambda_{\text{fl}}^{\text{max}} / \text{nm}^a )</th>
<th>( \tau / \text{ns}^b )</th>
<th>( E / \text{eV} )</th>
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<td>4</td>
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\( ^a \) From corrected spectra. \( ^b \) Fluorescence lifetimes, excitation at 373 nm.

Figure S12. Normalized fluorescence spectra of 2 (black), 3 (red) and 4 (green) in toluene at 77K. Excitation at 400 nm.
**Figure S13.** Structural detail that highlights how the halogenated co-formers lie above and below the naphthalimide units in crystalline $4_2\cdot\text{I}_2\text{F}_4$. H$_\text{CH}$ omitted for clarity.