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Supporting Information

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

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Table of Contents

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

	4		
Formula	$C_{23}H_{21}N_3O_2$	D_{calc} (g/cm^3)	1.349
fw	371.43	packing coefficient (%)[a]	69.9
Cryst. System	Orthorhombic	accessible void (Å^3)[a]	0
Space group	$Pna2_1$	μ (mm^{-1})	0.088
Z	4	Measd reflns	7735
a (Å)	30.652(5)	Indep reflns	3143
b (Å)	5.3082(9)	R_1[on F_0^2, I>2σ(I)]	0.0663
c (Å)	11.243(2)	wR_2 (all data)	0.1116
α (deg)	90		
β (deg)	90		
γ (deg)	90		
V (Å^3)	1829.3(6)		

[a]Calculated with Platon; for the accessible void calculation a probe of 1.2 Å^3 was employed.

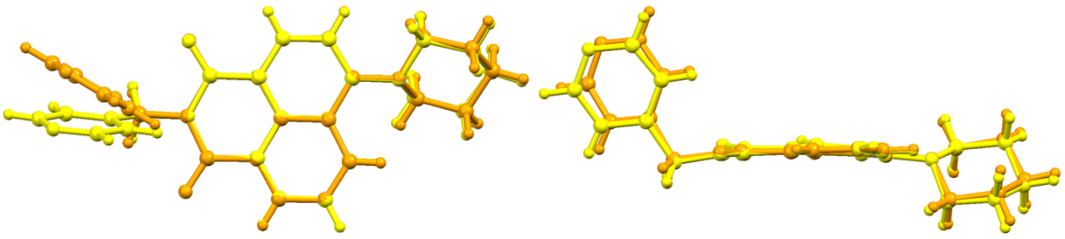

Figure S1. Top (left) and side (right) views for the superimposition of **4** (**Form I**) (orange) and **4** (**Form II**) (yellow) molecular structures for crystalline **4**, showing that the two conformations are almost exactly the same in the two polymorphs. H_{CH} are omitted for clarity.

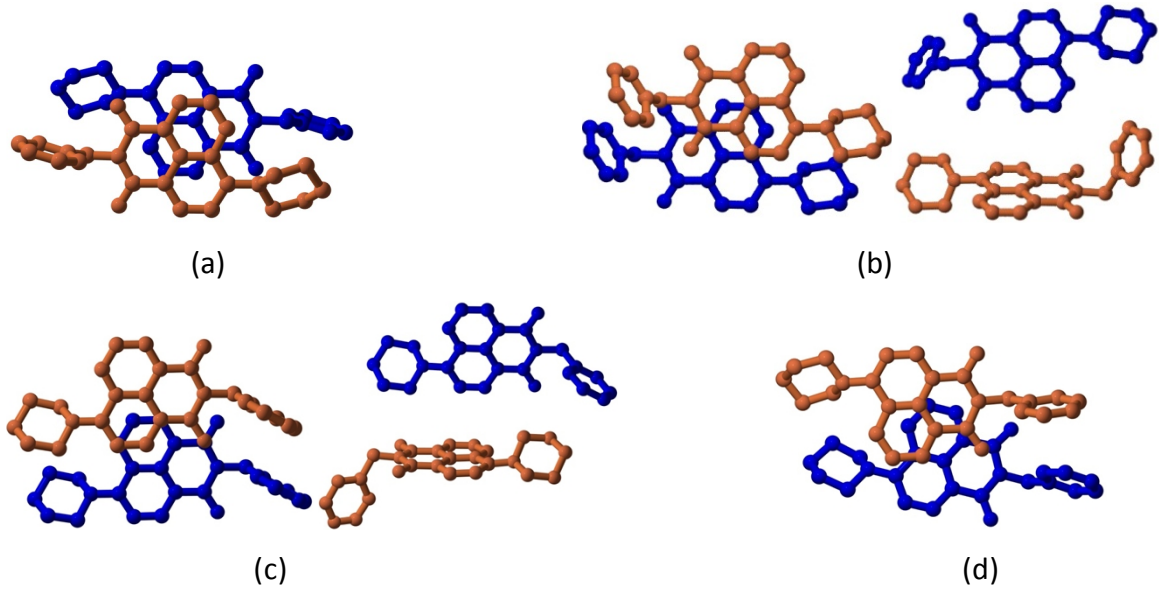

Figure S2. Types of dimers observed in crystalline **2-4**: (a) head-to-tail dimer in crystalline **2**, CD = 3.8Å, ID = 3.4Å, offset = 1.7 Å; (b) head-to-head dimer in crystalline **3**: CD = 5.3 Å, ID = 3.5 Å, offset 3.9 Å (left), and T-dimers with dC–H···π = 3.2 Å or dC···π = 4.0 Å (right); (c) head-to-head 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_{CH} omitted for clarity.

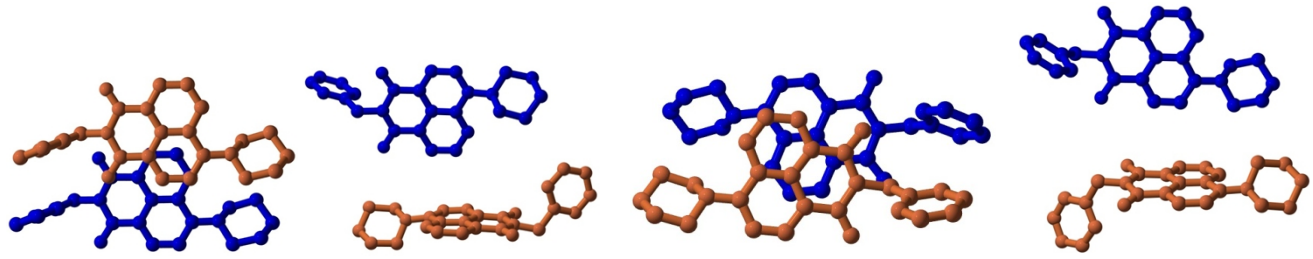

Figure S3. Types of dimers observed in **n_2·I2F4** co-crystals. (a) head-to-head dimer in crystalline **2_2·I2F4**,CD = 5.2 Å, ID = 3.3 Å, offset = 4.0Å (left), and T-dimer dC–H···π = 2.8 –3.1 Å or dC···π = 3.7 – 3.8 Å (right); (b) head-to-head dimer in crystalline **3_2·I2F4**,CD = 4.1 Å, ID = 3.5 Å, offset = 2.1Å; (c) T-dimer in crystalline**4_2·I2F4**,dC–H···π = 2.8-3.0 Å or dC···π = 3.7-3.9 Å.H_{CH} omitted for clarity.

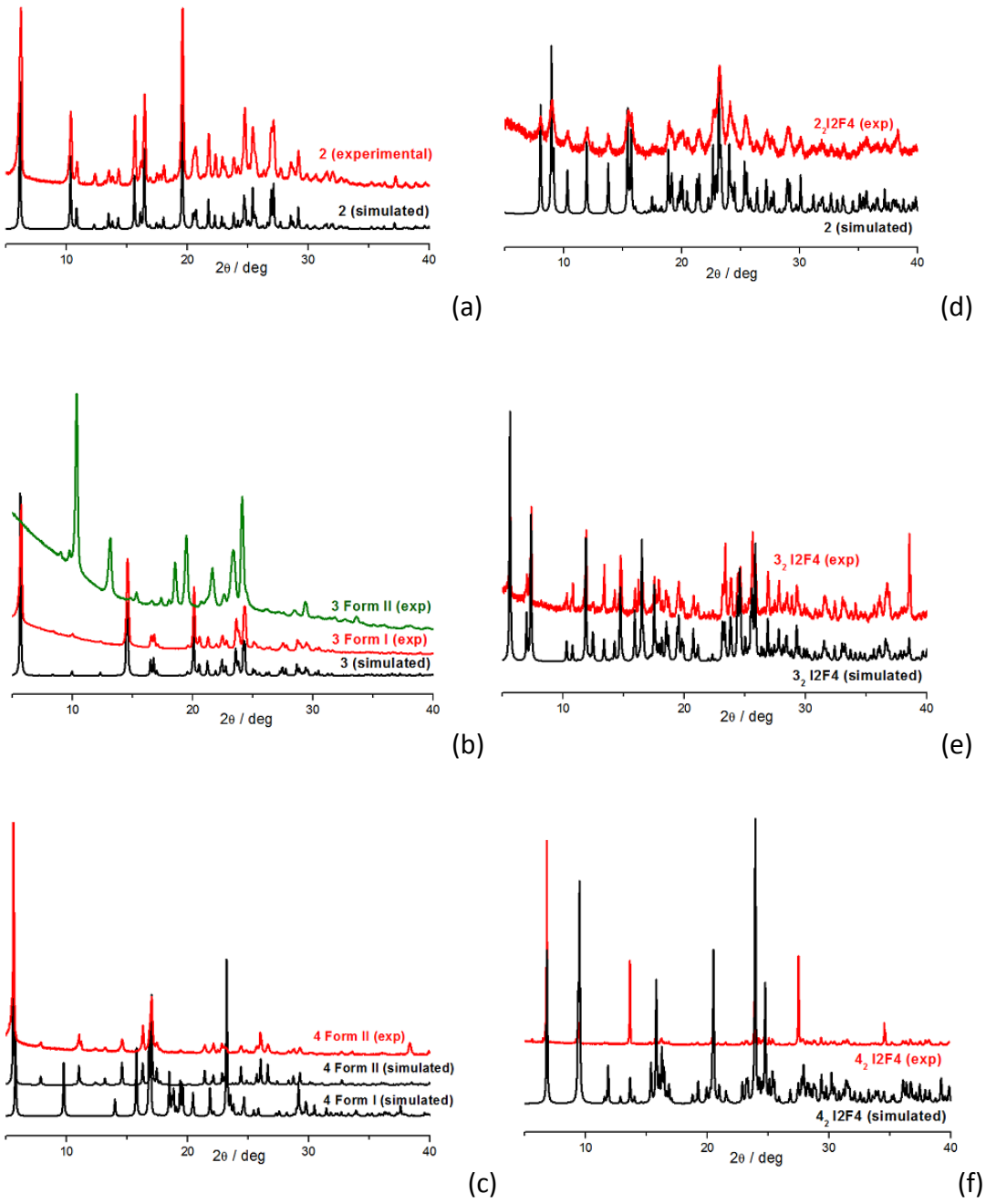

Figure S4. Experimental (red-line) and simulated (black-line) X-ray powder diffraction patterns for compounds: (a) **2**, (b) **3**, and (c) **4** of for corresponding co-crystals: (d) **2_2·I2F4**, (e) **3_2·I2F4**, and (f) **4_2·I2F4**.

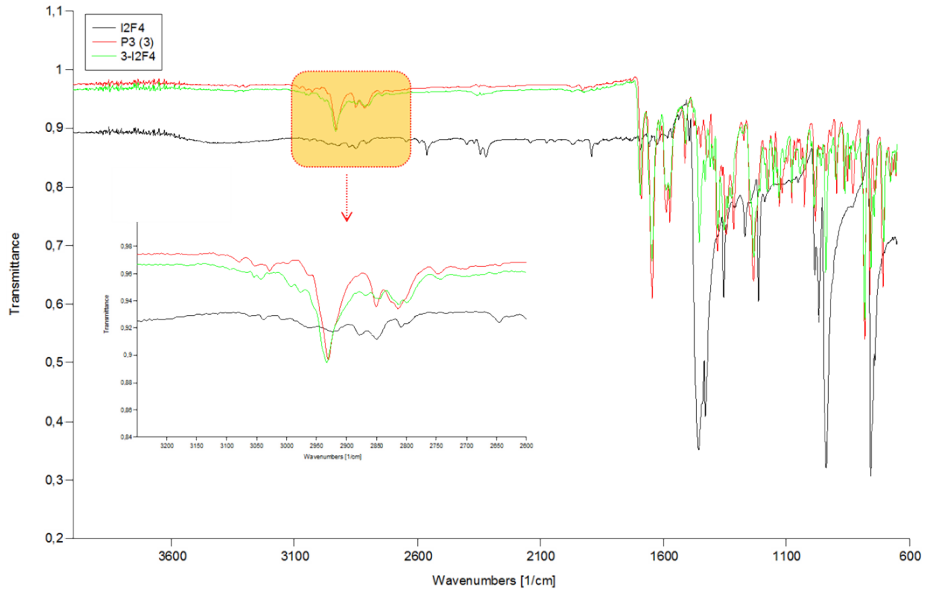

Figure S5. ATR-FTIR spectra of components I2F4 (black line), **3** (red line) and **3_2·I2F4** (green line) in the range 4000-600 cm^{-1}. The inset highlights the shifts to higher frequencies for the vC_{pyr}—H stretching (from **3**) of the pyridine involved in the halogen bond.

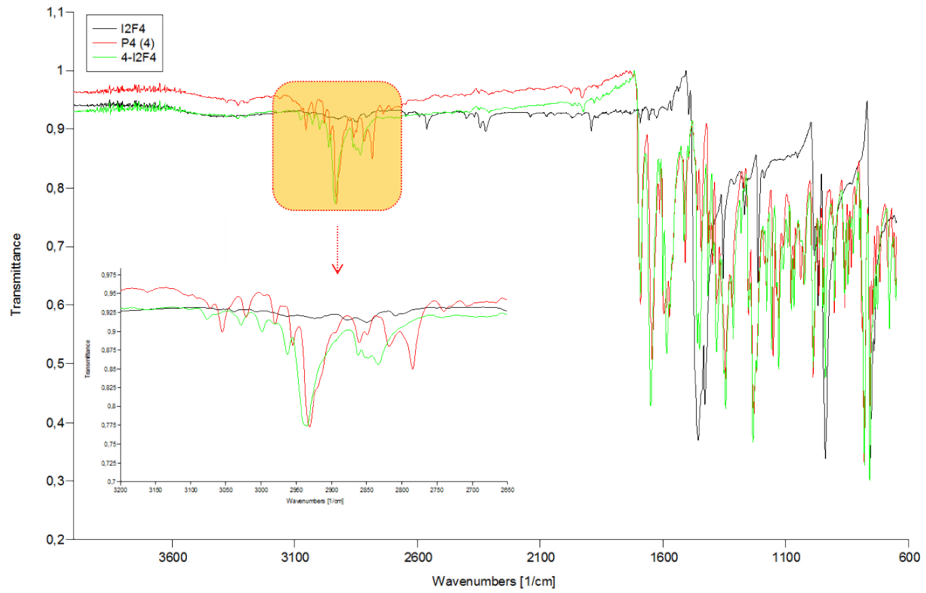

Figure S6. ATR-FTIR spectra of components I2F4 (black line), **4** (red line) and **4_2·I2F4** (green line) in the range 4000-600 cm^{-1}. The inset highlights the shifts to higher frequencies for the vC_{pyr}—H stretching (from **4**) of the pyridine involved in the halogen bond.

Thermal characterization (TGA-DSC-VTPXRD).

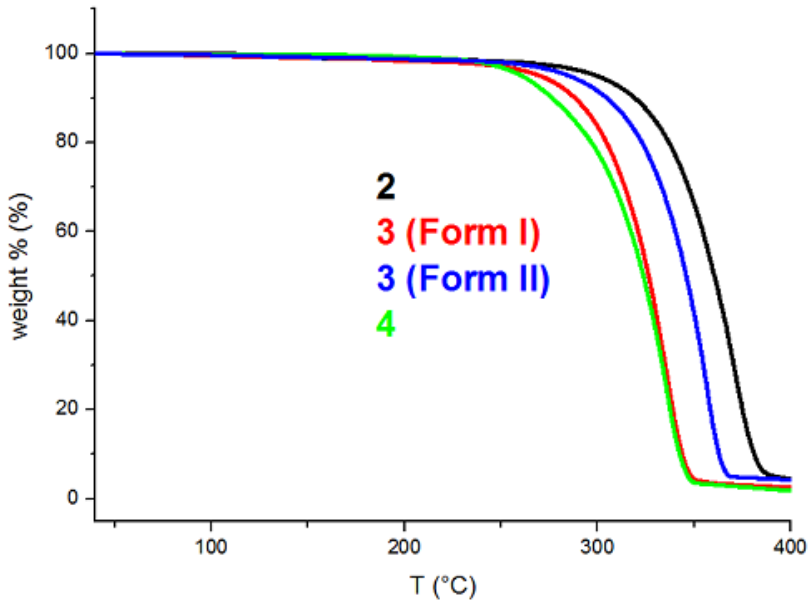

Figure S7. TGA thermograms for the compounds **2**, **3** (**Form I** and **Form II**), and **4** (**Form II**).

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, ΔH = 35.8kJ 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, ΔH = 17.8kJ mol^{-1}), followed by melting at 190 °C (peak temperature, ΔH = 35.0kJ mol^{-1}) (see SI-Fig. 8).Compound **3** (**Form I**) melts at 157 °C (peak temperature, ΔH = 28.9kJ 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, ΔH = 2.5KJ mol^{-1}). When the same measurement is performed on a sample of **3** (**Form II**) melting is now observed at 176 °C (peak temperature, ΔH = 38.9kJ 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).

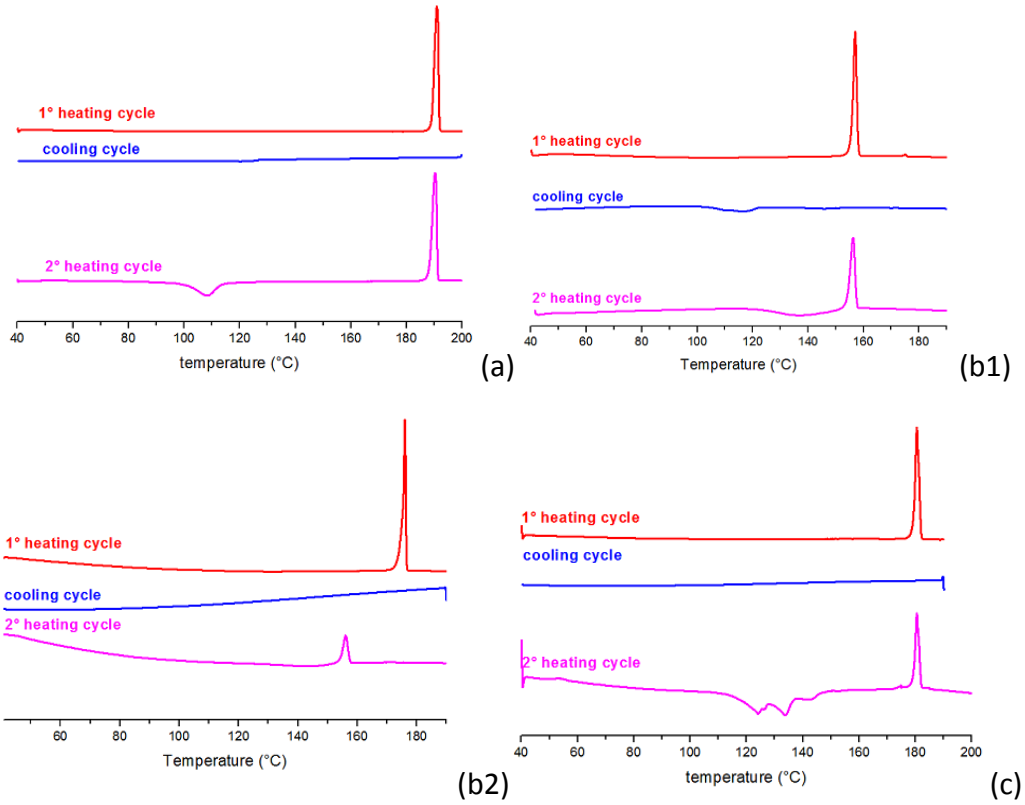

Figure S8. DSC traces for the compounds: (a) **2**, (b1) **3** (**Form I**), (b2) **3** (**Form II**), and (c) **4** (**Form II**).

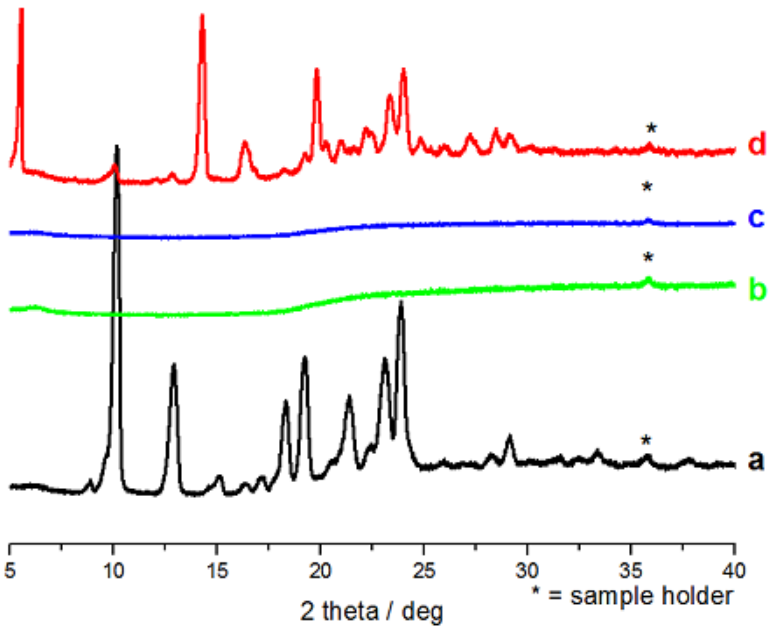

Figure S9. VT-XRPD patterns for crystalline **3** (**Form II**) at RT (a), at 180 °C (melting occurs) (b) and back at RT (the solid is amorphous); a second heating to 153 °C (d) shows recrystallization to **3** (**Form I**).

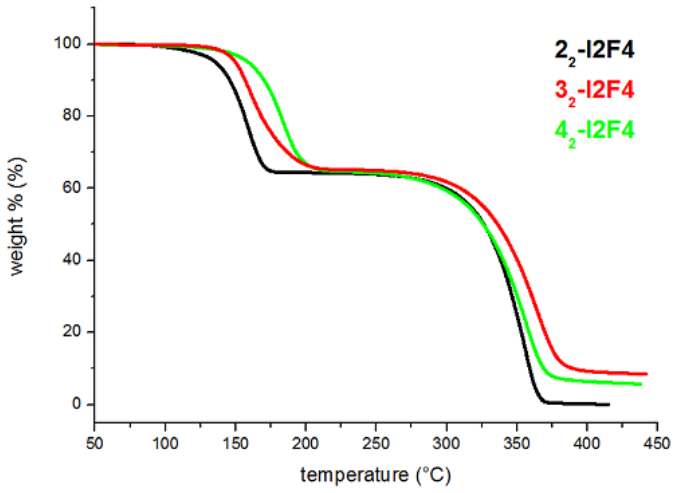

Figure S10. TGA thermograms for the co-crystals **2_2·I2F4**, **3_2·I2F4**, and **4_2·I2F4**.

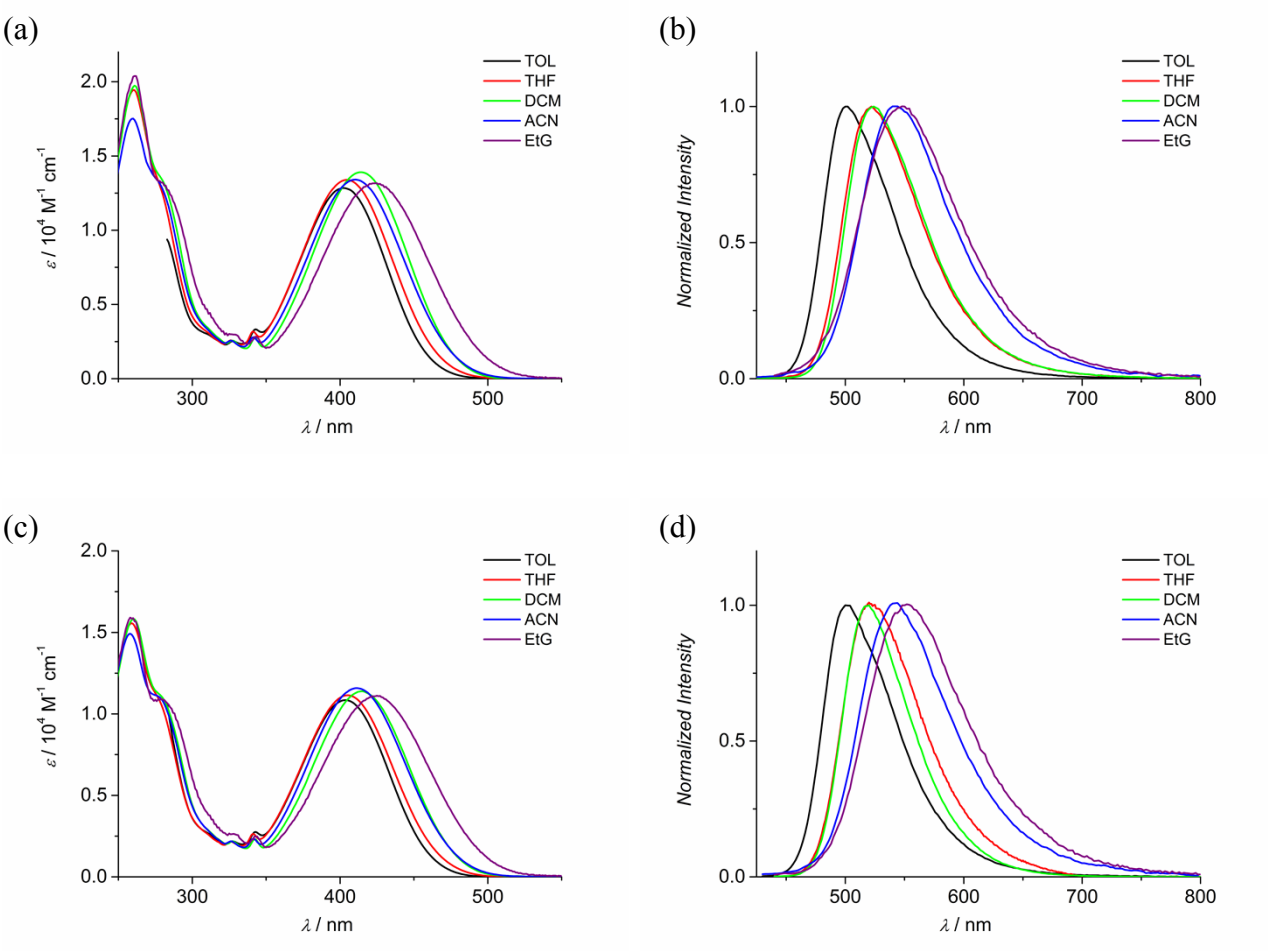

Figure S11. Absorption (a, c) and normalized emission (b, d) spectra of **3** (a, b) and **4** (c, d) in the explored solvents at room temperature.

Table S2. Luminescence data in toluene glassy matrix at 77 K.

	λ_{fl}^{max} / nm[a]	τ / ns[b]	*E* / eV
2	491	7.0	2.53
3	493	7.2	2.51
4	493	7.1	2.51

[a] From corrected spectra. [b]Fluorescence lifetimes, excitation at 373 nm.

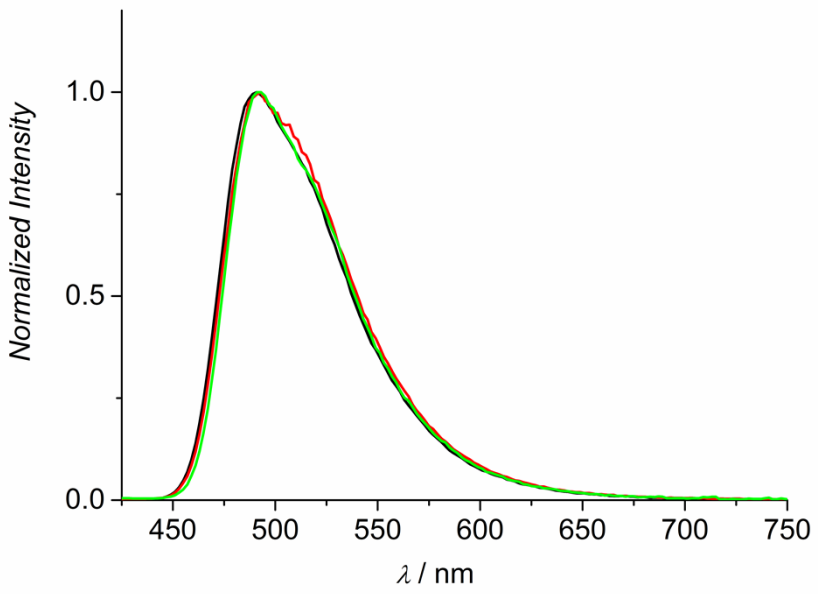

Figure S12. Normalized fluorescence spectra of **2** (black), **3** (red) and **4** (green) in toluene at 77K. Excitation at 400 nm.

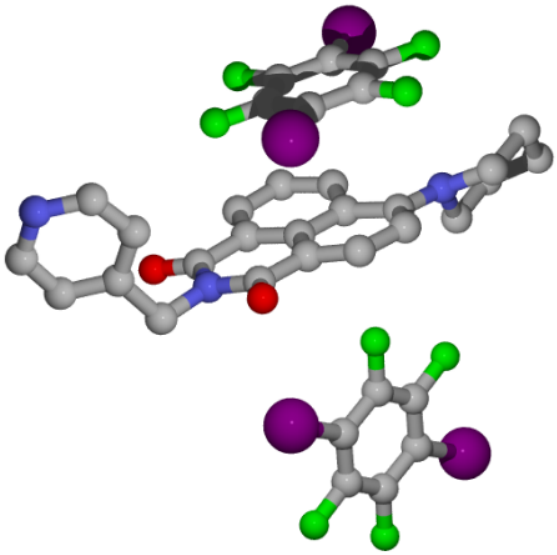

Figure S13. Structural detail that highlights how the halogenated co-formers lie above and below the naphthalimide units in crystalline **4_2·I2F4**. H_{CH} omitted for clarity.