Supporting information for the paper:  
**Guiding Structure in Cocrystals of Perylene with TCNQFx by Stoichiometry and Polymorphism**

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![Diagram](image)

(a) TCNQ  
(b) TCNQ-F2  
(c) TCNQ-F4
Figure S1. Crystal structures of (a) TCNQ, (b) TCNQ-F2 (from CCDC BERZON02), and (c) TCNQ-F4.

Figure S2. Upper panel: IR absorption spectrum of TCNQ. Lower panel: IR reflectivity spectra of K:TCNQ single crystal. Red dashed line corresponds to light polarized parallel to the TCNQ stacks, while black line refers to the perpendicular direction.
Figure S3. Extended polarized IR spectra (a) perylene:TCNQ-F$_2$ 1:1 and (b) perylene:TCNQ-F$_2$ 3:2.
Figure S4. IR absorption spectra of TCNQ-F$_2$ (upper panel) and K:TCNQ-F$_2$ (lower panel).

Figure S5. IR and Raman spectra of perylene:TCNQ-F$_2$ 3:2. The vibronic features which are present in both IR and Raman spectra are indicated with dashed vertical lines.
Figure S6. Crystal structure of perylene:TCNQ-F$_4$:Toluene 1:1:1. Projections on the $bc$ and $ac$ planes.
Figure S7. Extended polarized IR spectra (a) perylene:TCNQ-F4 1:1 and (b) perylene:TCNQ-F4 3:2 (b). The onset of the CT exciton bands is clearly observable in both systems.
Figure S8. IR absorption spectra of TCNQ-F$_4$ (upper panel) and KTCNQ-F$_4$ (lower panel).
**Figure S9.** Extended polarized IR spectra of the solvated crystal perylene:TCNQ-F4:Toluene 1:1

**Table S1.** Structural parameters for all the investigated mixed compounds.
<table>
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<tr>
<th>Compound</th>
<th>Space Group</th>
<th>Z</th>
<th>a [Å]</th>
<th>b [Å]</th>
<th>c [Å]</th>
<th>α [°]</th>
<th>β [°]</th>
<th>γ [°]</th>
<th>Cell volume [Å³]</th>
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<tr>
<td>TCNQ</td>
<td>C2/c</td>
<td>4</td>
<td>8.8746(4)</td>
<td>6.9335(3)</td>
<td>16.4071(6)</td>
<td>90</td>
<td>98.315(4)</td>
<td>90</td>
<td>998.95</td>
</tr>
<tr>
<td>TCNQ-F₄</td>
<td>Pcab</td>
<td>4</td>
<td>8.0828(2)</td>
<td>9.2231(2)</td>
<td>14.5974(4)</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>1088.21</td>
</tr>
</tbody>
</table>

**Table S2.** Structural parameters for the pure TCNQ and TCNQ-F₄.