Supplementary Information – Single-crystal X-ray Crystallography

Charge Transfer Complex (8)

Table S1: Single-crystal X-ray data for the structure of complex **8**

Temperature	100(2) K
Radiation Source	Mo K_α
Wavelength	0.71073 Å
Empirical formula	C28 H23 Cl1 F3 N5 O3
Formula Weight	569.96 g mol^{-1}
Crystal Size	0.30 x 0.03 x 0.02 mm
Crystal System	Monoclinic
Space Group	$P2_1/c$
Unit cell parameters	a = 6.6629(7) Å α = 90° b = 25.004(3) Å β = 97.810(12)° c = 14.956(2) Å γ = 90°
Volume	2468.6(5) $Å^3$
Z	4
Density (calculated)	1.534 M g m^{-3}
Absorption coefficient μ	0.221 mm^{-1}
F(000)	1176
R(int)	0.1227
R1 (obs. data)	0.0558
wR2 (all data)	0.0968
Completeness (0.8 Å)	0.996
Reflections (independent)	16521 (4509)
Largest residual density (peak and hole)	0.347 and -0.283 e $Å^{-3}$

Data Collection

Single-crystals of complex **8** were obtained by slow evaporation from a methanolic solution. The complex forms very thin, needle-like crystals that are deep-red to near-black in colour.

A single-crystal X-ray diffraction experiment was performed using an Agilent Technologies micro-focus dual-source Supernova diffractometer, equipped with and Eos Series 2 detector. Data were collected using Mo K_α radiation (λ = 0.71073 Å) to a target resolution of 0.8 Å. However, owing to the size and limited diffraction power of the sample, in practice a diffraction limit of ~ 0.9 Å was observed and the crystals appeared twinned. Subsequent experiments using Cu K_α radiation did not improve the diffraction quality sufficiently.

In light of these limitations, final values of R(int) = 0.1227 (HKLF 5) and a completeness of 0.996 (HKLF5, to 0.8 Å) were obtained from the data reduction.

Data Processing

The data were indexed and integrated using Agilent Technologies CrysAlisPro software, solved using SHELXT[1] and refined using SHELXL.[2] Crystal structure visualisation and image preparation were completed using the Cambridge Crystallographic Data Centre software Mercury.[3]

Structure solution was performed using the data in HKLF4 format. Once a sensible model had been established, final refinement stages were completed using the HKLF5 reflection file. The final refined BASF value was 0.36433. The final residual factors of R1 = 0.0558 (observed data) and wR2 = 0.0968 (all data) are reasonable and are a significant improvement on the HKLF4 refinement used for structure solution.

Crystal Structure Analysis

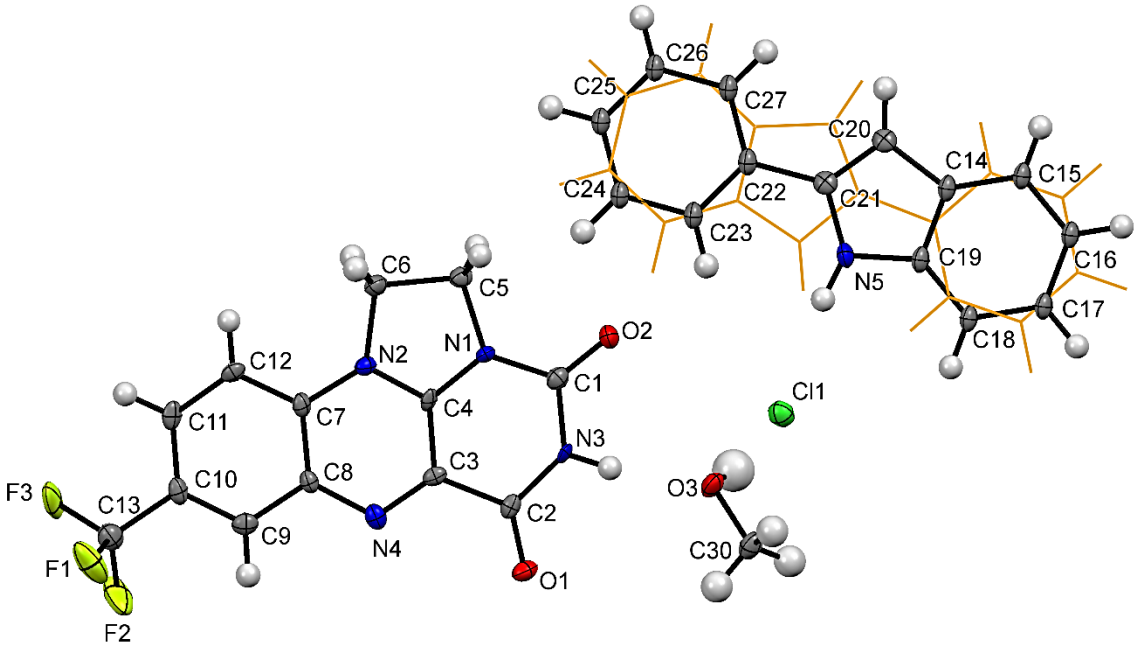

Figure S1: Single-crystal X-ray structure showing the asymmetric unit of complex **8**, non-hydrogen atoms shown at 50% probability and disorder in the indole fragment shown in wireframe for clarity

In spite of the aforementioned data limitations, a satisfactory anisotropic refinement was completed for all components, providing unambiguous structural evidence for the charge transfer complex 8.

Complex **8** crystallises in the monoclinic space group $P2_1/c$ (Group 14) with one flavin cation **5a**, one chloride anion, one molecule of indole **6a** and one methanol solvent molecule in the asymmetric unit. As indicated by the wireframe fragment in Figure S1, the indole moiety is disordered over two positions, with an approximately 50:50 occupancy ratio of these two orientations. These disordered components are allowed to refine anisotropically, using standard PART instructions, with the implementation of rigid group and EADP constraints.

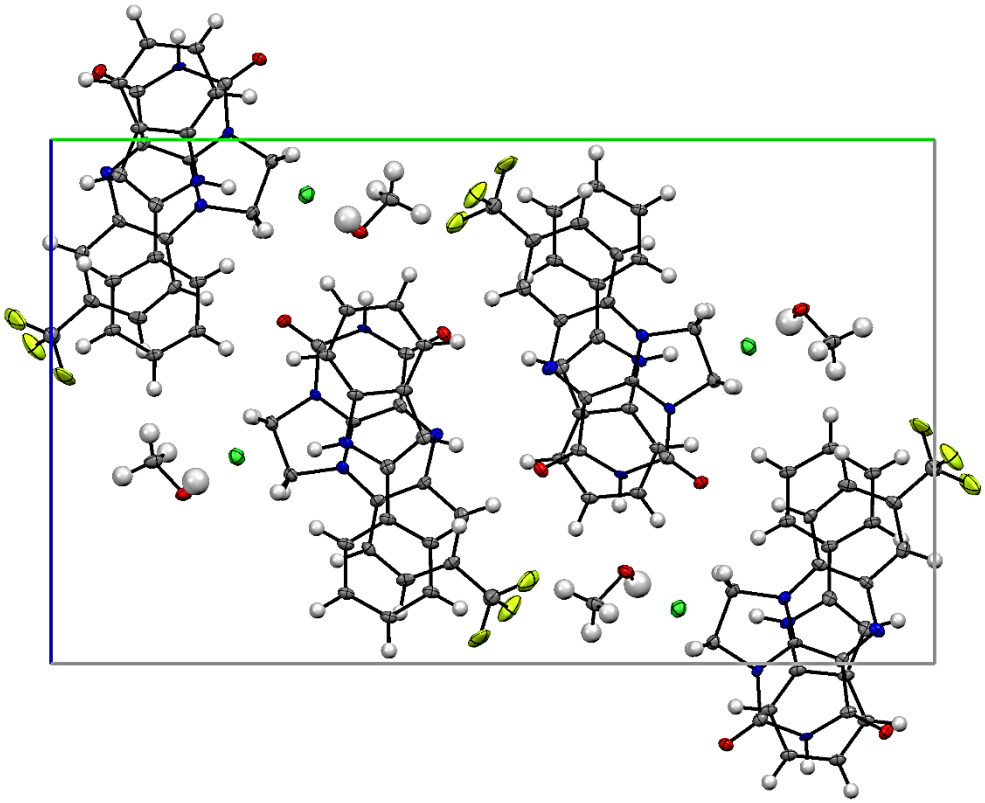

Figure S2: Packing diagram for complex **8** viewed along the crystallographic *a*-axis, *b*-axis horizontal

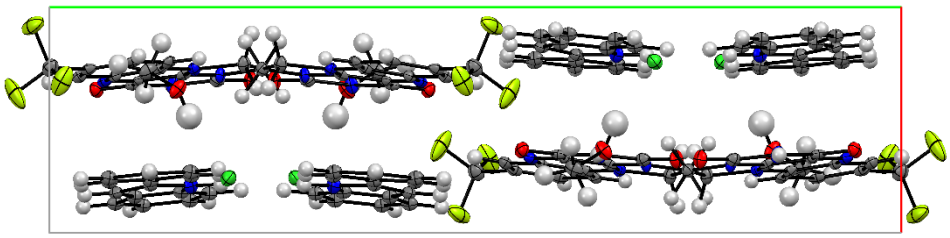

Figure S3: Packing diagram for complex **8** viewed along the crystallographic *c*-axis, *b*-axis horizontal

Figures S2 and S3 show the π-stacking between neighbouring flavin and indole moieties along the crystallographic *a*-axis (into the page in Figure 2 and up-down the page in Figure 3), supporting the assertion that a charge transfer complex is formed.

Flavin – Indole Adduct (9)

Table S2. Single crystal X-ray data for the structure of **9**

Temperature	100(2) K
Radiation Source	Mo K_α
Wavelength	0.71073 Å
Empirical formula	C69 H48 F6 N11 O5
Formula Weight	1225.18 g mol^{-1}
Crystal Size	0.2 x 0.13 x 0.11 mm
Crystal System	Monoclinic
Space Group	P -1
Unit cell parameters	a = 11.4992(8) Å α = 80.075(4)° b = 13.2277(6) Å β = 80.054(5)° c = 20.0327(10) Å γ = 76.358(5)°
Volume	2889.0(3) $Å^3$
Z	2
Density (calculated)	1.408 M g m^{-3}
Absorption coefficient μ	0.105 mm^{-1}
F(000)	1266
R(int)	0.0591
R1 (obs. data)	0.0783
wR2 (all data)	0.2479
Completeness (0.8 Å)	0.990
Reflections (independent)	14950 (10429)
Largest residual density (peak and hole)	0.609 and -0.452 e $Å^{-3}$

Data Collection

Crystals of **9** were obtained by slow evaporation from a methanolic solution of **8** containing a small quantity of distilled water. **9** forms as yellow blocks, which were cut to obtain a single-crystal shard.

A single-crystal X-ray diffraction experiment was performed using an Agilent Technologies micro-focus dual-source Supernova diffractometer, equipped with and Eos Series 2 detector. Data were collected using Mo K_α radiation (λ = 0.71073 Å) to a target resolution of 0.8 Å. However, owing to the limited diffraction power of the sample, in practice a diffraction limit of 0.97 Å was observed. Subsequent experiments using Cu K_α radiation did not improve the diffraction quality sufficiently.

Despite these limitations, final values of R(int) = 0.0591 and a completeness of 0.990 were obtained from the data reduction.

Data Processing

The data were indexed and integrated using Agilent Technologies CrysAlisPro software, solved using SHELXT[1] and refined using SHELXL.[2] Crystal structure visualisation and image preparation were completed using the Cambridge Crystallographic Data Centre software Mercury.[3]

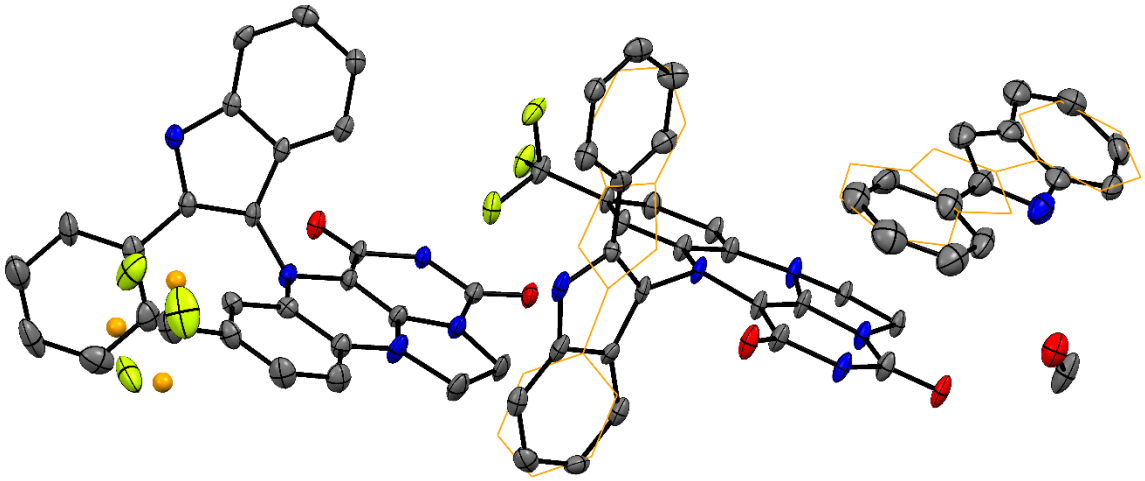

Figure S4: Single-crystal X-ray structure showing the asymmetric unit of **9**, non-hydrogen atoms for ordered and major disordered components shown as ellipsoids at 50% probability. Minor disordered components shown in wireframe and hydrogen atoms removed for clarity

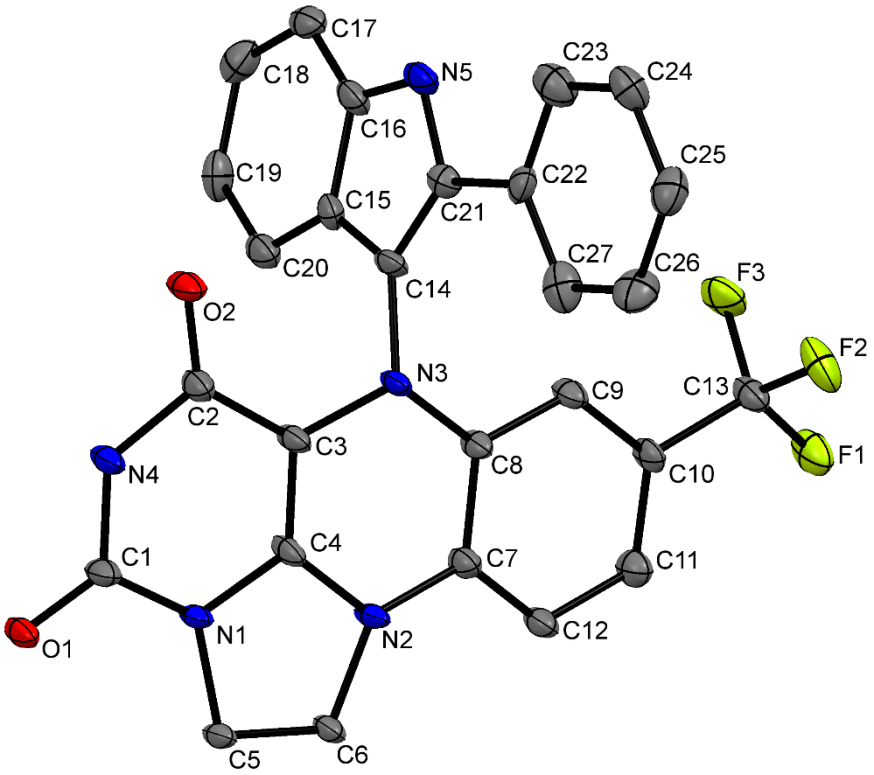

Figure S5: Single-crystal X-ray structure showing the atomic connectivity in a single molecule of **9**, non-hydrogen atoms shown at 50% probability and hydrogen atoms removed for clarity

9 crystallises in the triclinic space group *P* -1 (Group 2) with two adduct molecules, one free indole molecule and one methanol solvent molecule in the asymmetric unit (Figure S4). The structure is heavily disordered as indicated by the wireframe fragments in Figure S4, with two positions identified for both the free indole, one of the bound indole fragments and one trifluoromethyl group. These disordered components are allowed to refine freely using a standard PART instructions, with the implementation of rigid group constraints.

Figure S5 provides a clear picture and atomic numbering scheme for one molecule of the adduct **9**.

Due to the high level of disorder it was not possible to identify the hydrogen atom positions, expected for the amine groups involving N5, N5A and N105 on the bound indole fragments, in the electron density difference map. As such, these hydrogen atoms were omitted from the refinement.

The final residual factors of R1 = 0.0783 (observed data) and wR2 = 0.2479 (all data) are slightly higher than ideal values, but are believed to be a result of both the heavy disorder and limited diffraction power of the sample.

The crystal packing in **9** shows no stacking features similar to those observed for the charge transfer complex **8**, which accounts for the paler yellow colour observed for crystals of the adduct.

Crystallographic Information Files for **8** and **9** are submitted to the Cambridge Crystallographic Data Centre and are available on request.

[1] G. Sheldrick, *Acta Crystallographica Section A* **2015**, *71*, 3-8.

[2] M. Sheldrick George, *Acta Crystallographica Section A* **2008**, *64*, 112-122.

[3] C. F. Macrae, I. J. Bruno, J. A. Chisholm, P. R. Edgington, P. McCabe, E. Pidcock, L. Rodriguez-Monge, R. Taylor, J. van de Streek and P. A. Wood, *Journal of Applied Crystallography* **2008**, *41*, 466-470.