SUPPLEMENTARY MATERIAL

for

Halogen Bonding – A Key Step in Charge Recombination of the Dye-Sensitized Solar Cell

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EXPERIMENTAL

The N3 dye was obtained from Solaronix, iodine was obtained from Merck and methanol from J. T. Baker. All chemicals were used as received without further purification. The crystals were obtained by dissolving the dye (3.5 mg, 4.7mmol) and I_2 (2.5 mg, 9.8mmol) separately in 2ml of methanol . The solutions were mixed in a small vial and left to evaporate in the laboratory. Black crystals were obtained after two days. A good quality crystal was selected for diffraction experiments. The experiment was repeated by adding two equivalents of KI with respect to I_2 to the mixture. The crystals structures obtained from I_2 and I^-/I_2 solutions turned out to be identical.

CRYSTALLOGRAPHY

The crystals of 1 were immersed in cryo-oil, mounted in a Nylon loop, and measured at a temperature of 100 K. The X-ray diffraction data were collected on a Bruker Smart Apex II diffractometer. The *APEX2 software suite* was used for cell refinements and data reductions. The structures were solved by direct methods using the *SHELXS-97* programs with the *WinGX* graphical user interface. A semi-empirical absorption correction was applied to all data. Structural refinements were carried out using *SHELXL-97*. All OH hydrogen atoms could be located from the difference Fourier map. The positions of these hydrogens were idealized with O-H = 0.84 Å, and C-O-H 109.47°. The OH hydrogen atoms were constrained to ride on their parent oxygen atoms, with U_{iso} = 1.5 U_{eq}(parent atom). Other hydrogen atoms were positioned geometrically and were also constrained to ride on their parent atoms, with C-H = 0.95-0.98 Å, and U_{iso} = 1.2-1.5 U_{eq}(parent atom). The highest peak is located 0.83 Å from atom I4 and the deepest hole is located 0.59 Å from atom I1. The crystallographic details are summarized in Table S1. H-bonds and halogen bonds are shown in tables S2 and S3.

Table S1. Crystal data and structure refinement for $Ru(dcbpy)_2(SCN)_2]\cdot 2(I_2)\cdot 4(CH_3OH)$

Identification code	$Ru(dcbpy)_2(SCN)_2]\cdot 2(I_2)\cdot 4(CH_3OH)$	
Empirical formula	$C_{30}H_{32}I_4N_6O_{12}RuS_2$	
Formula weight	1341.41	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	$P\ \bar{1}$	
Unit cell dimensions	a = 9.4272(6) Å	α= 89.605(3)°.
	b = 10.9639(7) Å	β= 81.177(3)°.
	c = 21.8249(13) Å	γ = 72.800(3)°.
Volume	2127.6(2) $Å^3$	
Z	2	
Density (calculated)	2.094 Mg/m^3	
Absorption coefficient	3.431 mm^{-1}	
F(000)	1276	
Crystal size	0.15 x 0.10 x 0.08 mm^3	
Theta range for data collection	1.89 to 25.50°.	
Index ranges	-11<=h<=10, -13<=k<=13, -24<=l<=26	
Reflections collected	10500	
Independent reflections	7906 [R(int) = 0.0244]	
Completeness to theta = 25.50°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7685 and 0.6271	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7906 / 0 / 507	
Goodness-of-fit on F^2	1.045	
Final R indices [I>2sigma(I)]	R1 = 0.0496, wR2 = 0.1281	
R indices (all data)	R1 = 0.0742, wR2 = 0.1402	
Largest diff. peak and hole	2.393 and -2.084 $e.Å^{-3}$	

Table S2. Hydrogen bonds for $Ru(dcbpy)_2(SCN)_2]\cdot 2(I_2)\cdot 4(CH_3OH)$ [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(2)-H(2A)...O(11)#1	0.84	1.77	2.592(8)	164.3
O(3)-H(3A)...O(10)#2	0.84	1.70	2.521(9)	165.1
O(5)-H(5A)...O(12)	0.84	1.72	2.536(9)	164.9
O(8)-H(8A)...O(6)#3	0.84	1.85	2.665(8)	162.9
O(10)-H(10A)...O(4)#4	0.84	1.87	2.682(9)	161.7
O(11)-H(11)...O(1)#5	0.84	2.02	2.789(9)	152.6
O(12)-H(12)...O(13)#6	0.84	1.89	2.716(10)	170.0
O(13)-H(13A)...S(2)	0.84	2.58	3.346(8)	151.3

Symmetry transformations used to generate equivalent atoms:

#1 x+1,y,z #2 x,y+1,z #3 -x+1,-y+2,-z+2 #4 -x,-y+2,-z+1

#5 -x+1,-y+2,-z+1 #6 -x+1,-y+1,-z+2

Table S3. Halogen bonds (Å) for $Ru(dcbpy)_2(SCN)_2]\cdot 2(I_2)\cdot 4(CH_3OH)$.

S(1)-I(1)	2.836(3)
S(2)-I(3)	2.954(3)
I(1)-I(2)	2.7770(10)
I(3)-I(4)	2.7669(9)
S(1)-I(4)#1	3.531(2)Å

Symmetry transformations used to generate equivalent atoms: x+1, y+1, z

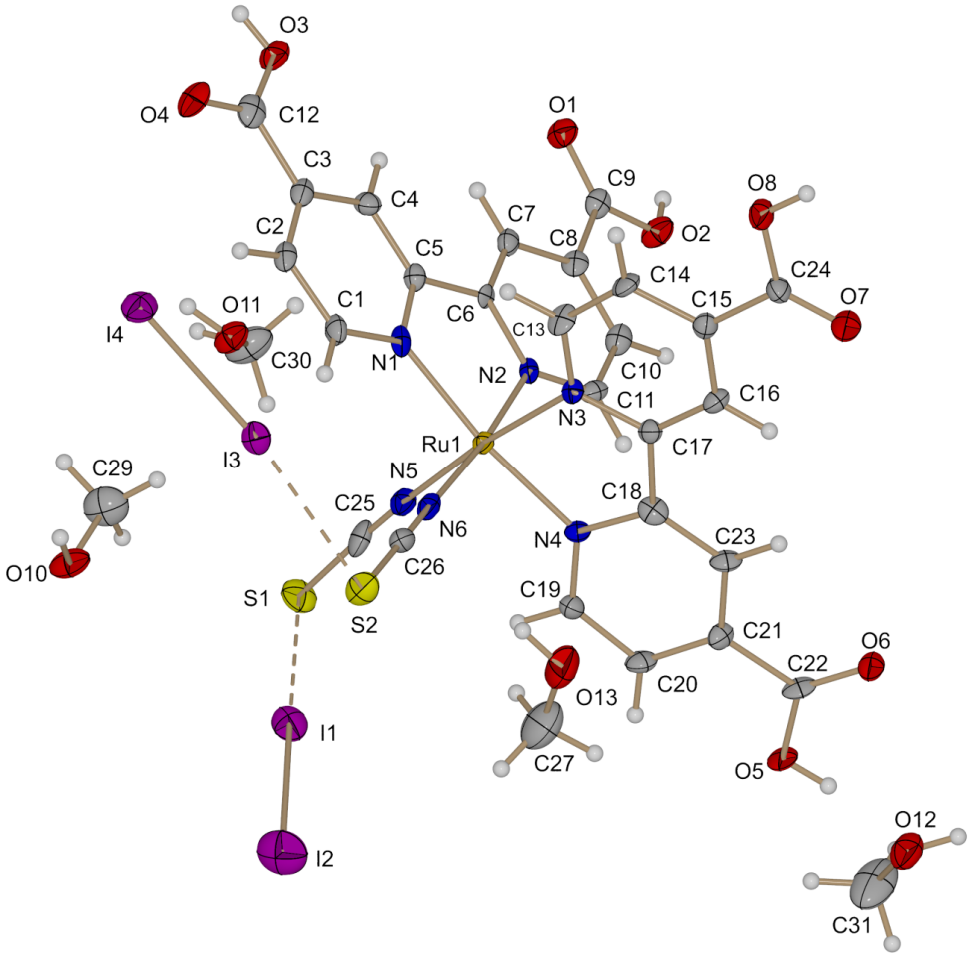

Figure S1. The asymmetric unit of $[Ru(dcbpy)_2(SCN)_2]\cdot 2(I_2)\cdot 4(CH_3OH)$. The thermal ellipsoids are drawn at 50 % probability.

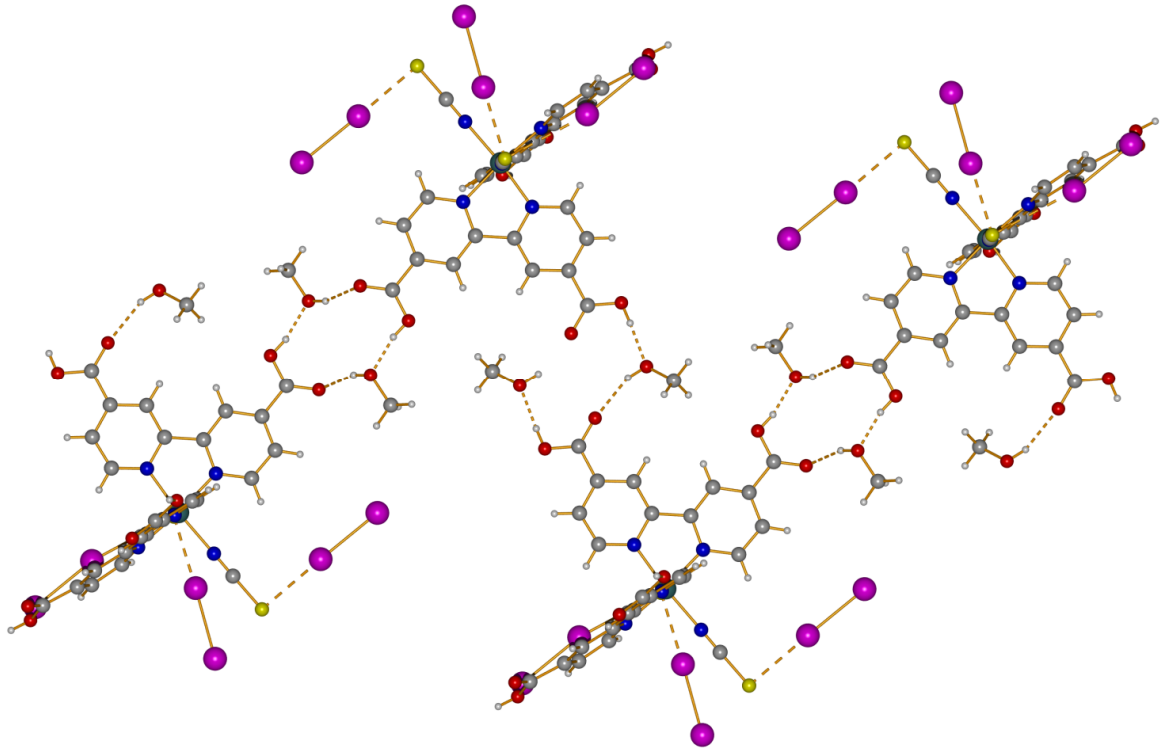

Figure S2. Hydrogen bonding network in $[Ru(dcbpy)_2(SCN)_2]\cdot 2(I_2)\cdot 4(CH_3OH)$.

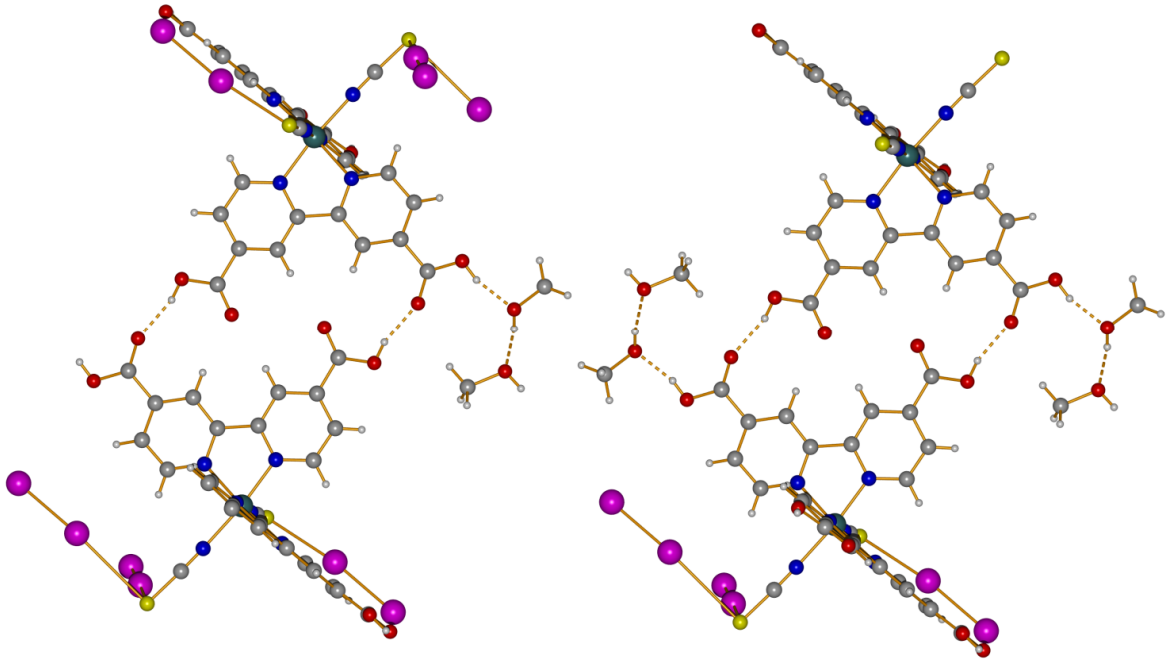

Figure S3. Hydrogen bonded "dimers" in $[Ru(dcbpy)_2(SCN)_2]\cdot 2(I_2)\cdot 4(CH_3OH)$.

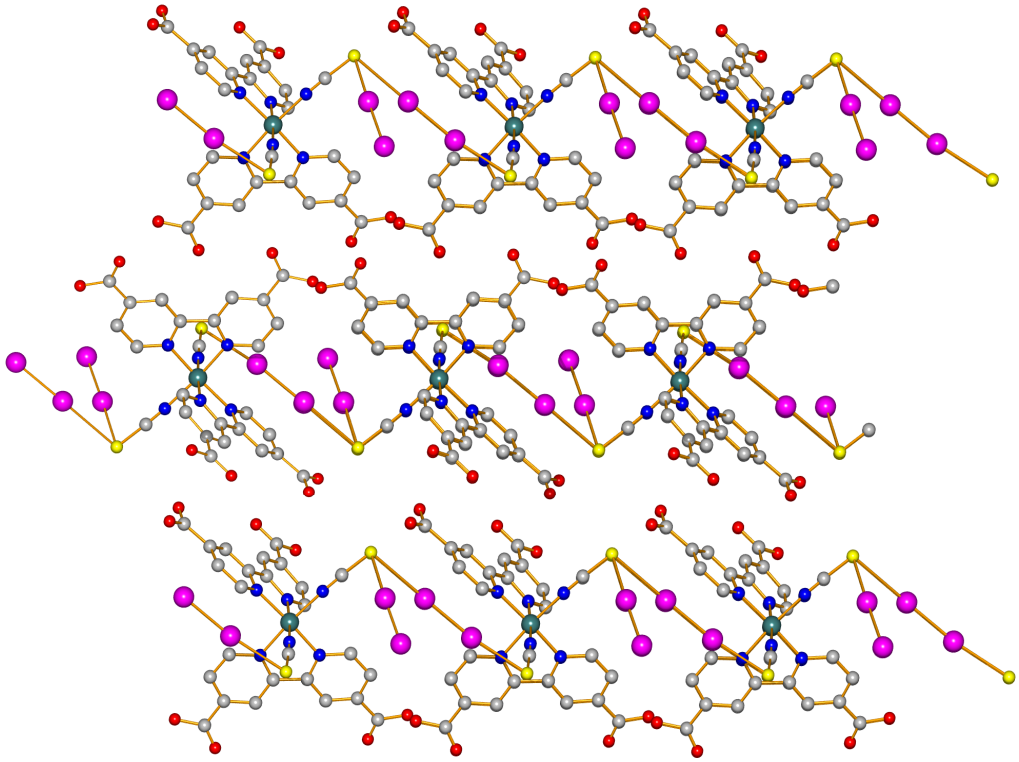

Figure S4. Halogen bonded chains in $[Ru(dcbpy)_2(SCN)_2]\cdot 2(I_2)\cdot 4(CH_3OH)$. Hydrogens and methanol molecules are omitted for clarity.

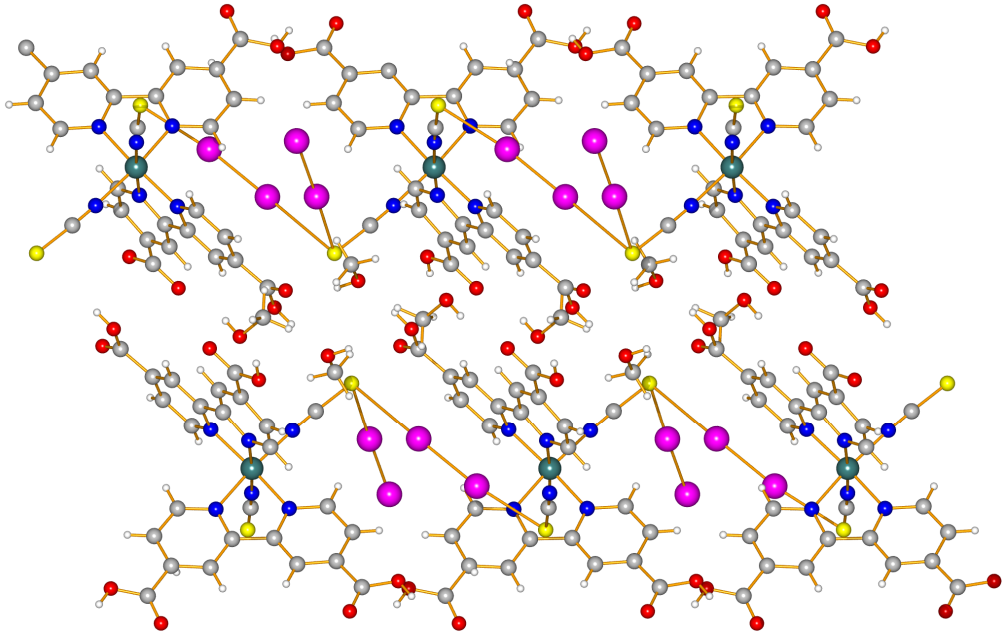

Figure S5. Packing view of $Ru(dcbpy)_2(SCN)_2]\cdot 2(I_2)\cdot 4(CH_3OH)$ along the a-axis showing the channels of halogen bonded I_2.