Electronic Supplementary Material (ESI) for RSC Advances.

A greener procedure for the synthesis of $[Bu_4N]_2$*cis*-[Ru(4-carboxy-4'-carboxylate-2,2'-bipyridine)$_2$(NCS)$_2$] (N719), a benchmark dye for DSSC applications

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Electronic Supplementary Information

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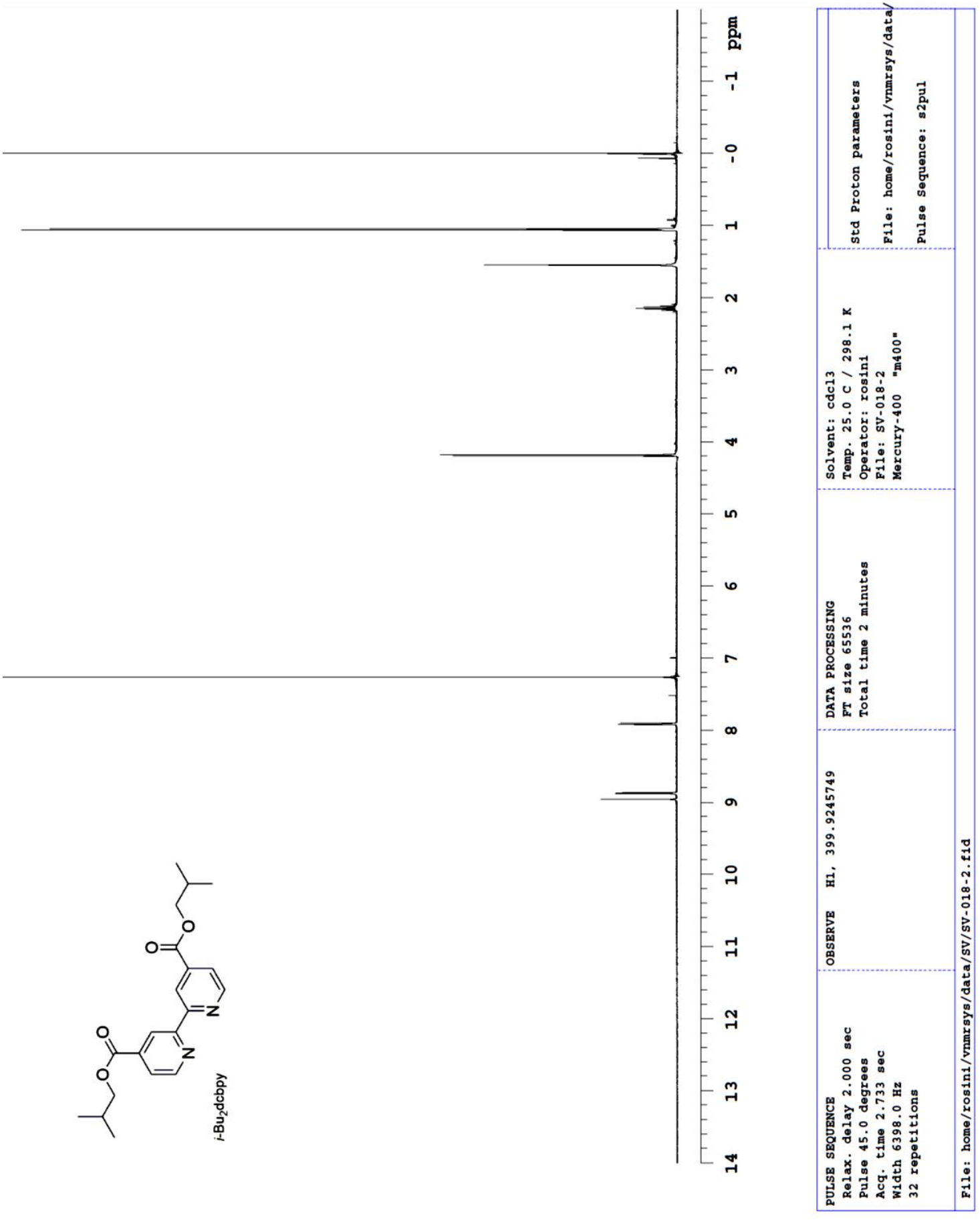
^{1}H NMR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i-Bu2dcbpy
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Relax. delay 2.000 sec
Pulse 45.0 degrees
Acq. time 2.733 sec
Width 6398.0 Hz
32 repetitions
OBSERVE H1, 399.9245749
DATA PROCESSING
FT size 65536
Total time 2 minutes
Solvent: cdcl3
Temp. 25.0 C / 298.1 K
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Mercury-400 "m400"
Std Proton parameters
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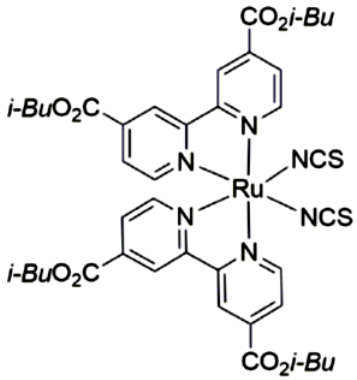

[Ru(*i*-Bu$_2$dcbpy)$_2$(NCS)$_2$]

PULSE SEQUENCE Relax. delay 1.000 sec Pulse 45.0 degrees Acq. time 2.733 sec Width 6398.0 Hz 32 repetitions	OBSERVE H1, 399.9264739	DATA PROCESSING FT size 65536 Total time 2 minutes	Solvent: dmso Temp. 25.0 C / 298.1 K Operator: rosini File: SV-001-PU-24 Mercury-400 "m400"	SAMPLE: VS-002-PU-24 Std Proton parameters Sample: VS-002-PU-24 File: home/rosini/vnmrsys/data Pulse Sequence: s2pul

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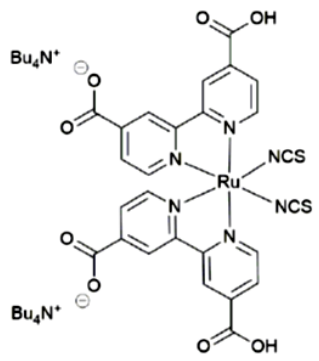


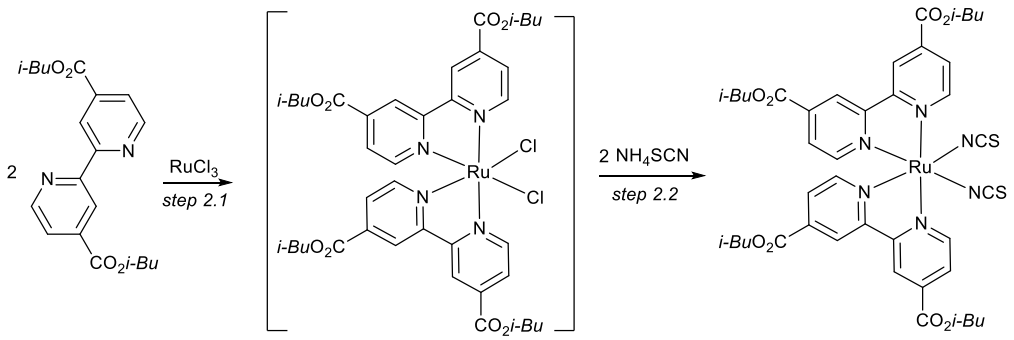
N719

$[Bu_4N]_2$cis [Ru(4-carboxy-4'-carboxylate-2,2'-bipyridine)$_2$(NCS)$_2$]

PULSE SEQUENCE Relax. delay 5.000 sec Pulse 45.0 degrees Acq. time 2.995 sec Width 9595.8 Hz 64 repetitions	OBSERVE H1, 599.7300036	DATA PROCESSING FT size 65536 Total time 8 minutes	Solvent: cd3od Temp. 25.0 C / 298.1 K Operator: rosini File: SV-033-N719-settembre INOVA-600 "i600"	i600 std parameters File: home/rosini/vnmrsys/data Pulse Sequence: s2pul

File: home/rosini/vnmrsys/data/SV/SV-033-N719-settembre.fid

HPLC monitoring of step 2



HPLC monitoring of step 2 was performed at 30 min intervals using the following analytical conditions: column Alltech Alltima 5µm C18 (250 x 4.6 mm) thermostated at 25 °C, UV 254 nm, A = 60 acetonitrile + 40 water, B = acetonitrile; isocratic A: 77 %, B: 23 %.

Step 2.1 - solvent EtOH

Initially, the reaction was run in EtOH as described in the literature and was carefully monitored. At the start of the reflux (t = 0 min) HPLC shows only the presence of the peak (rt 16.0 min) corresponding to the *i*-Bu_2dcbpy free ligand (**L**). This peak nearly disappears just after 30 min of reflux time after which time a new peak (rt 14.1 min) which possibly corresponds to the dichloro complex (**M**). Prolonging step 2.1 reflux time to 3.5 h as described in the literature, does not bring about any visible change, apart for a slight increase of the two small peaks at rt 7.6 and 8.7 (**N**) which possibly correspond to the two stereoisomeric mono ethyl transesters of the dichloro complex.

Step 2.2 – solvent EtOH

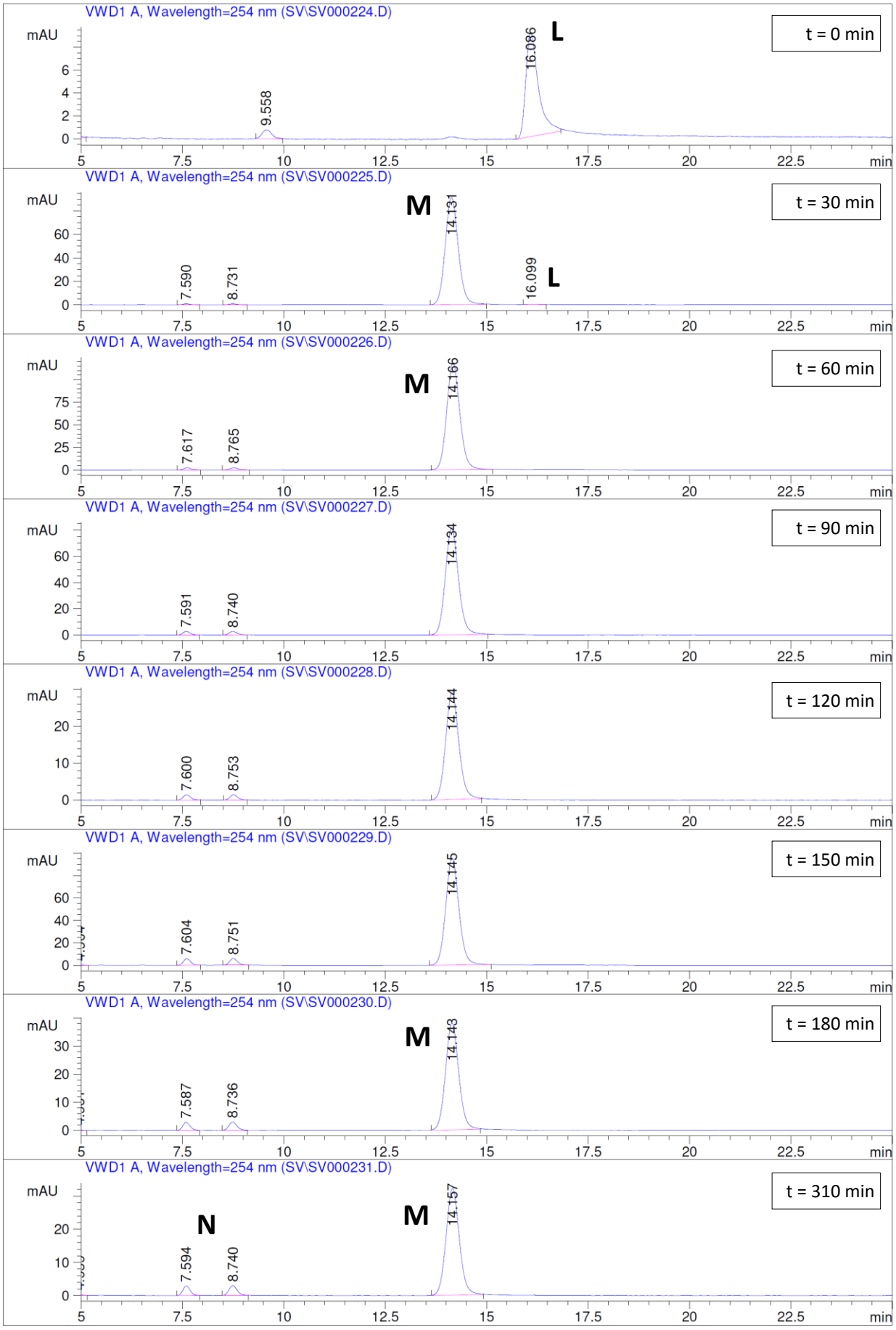
At the end of step 2.1, ammonium thiocyanate is added to the hot mixture and reflux continued for an additional 2.5 h. Just after 30 min from the addition of thiocyanate, HPLC analysis of the reaction mixture shows a complex chromatogram with many peaks. This complex mixture is due to the kinetic substitution of the thiocyanate that affords all the possible mono- and di- *S*-bound and *N*-bound isomers and has been observed previously by NMR in a similar complex.[1] This complex mixture of peaks, progressively converts over the time to final crude mixture of products which is composed of the desired product (rt 23.9 min, **A**), two peaks at 13.4 and 14.7 min (**B**) later identified as the two stereoisomeric mono ethyl transesters of the desired product, and the “S-isomer” of the desired product (rt 19.9 min, **C**)

Step 2 – solvent *i*-BuOH

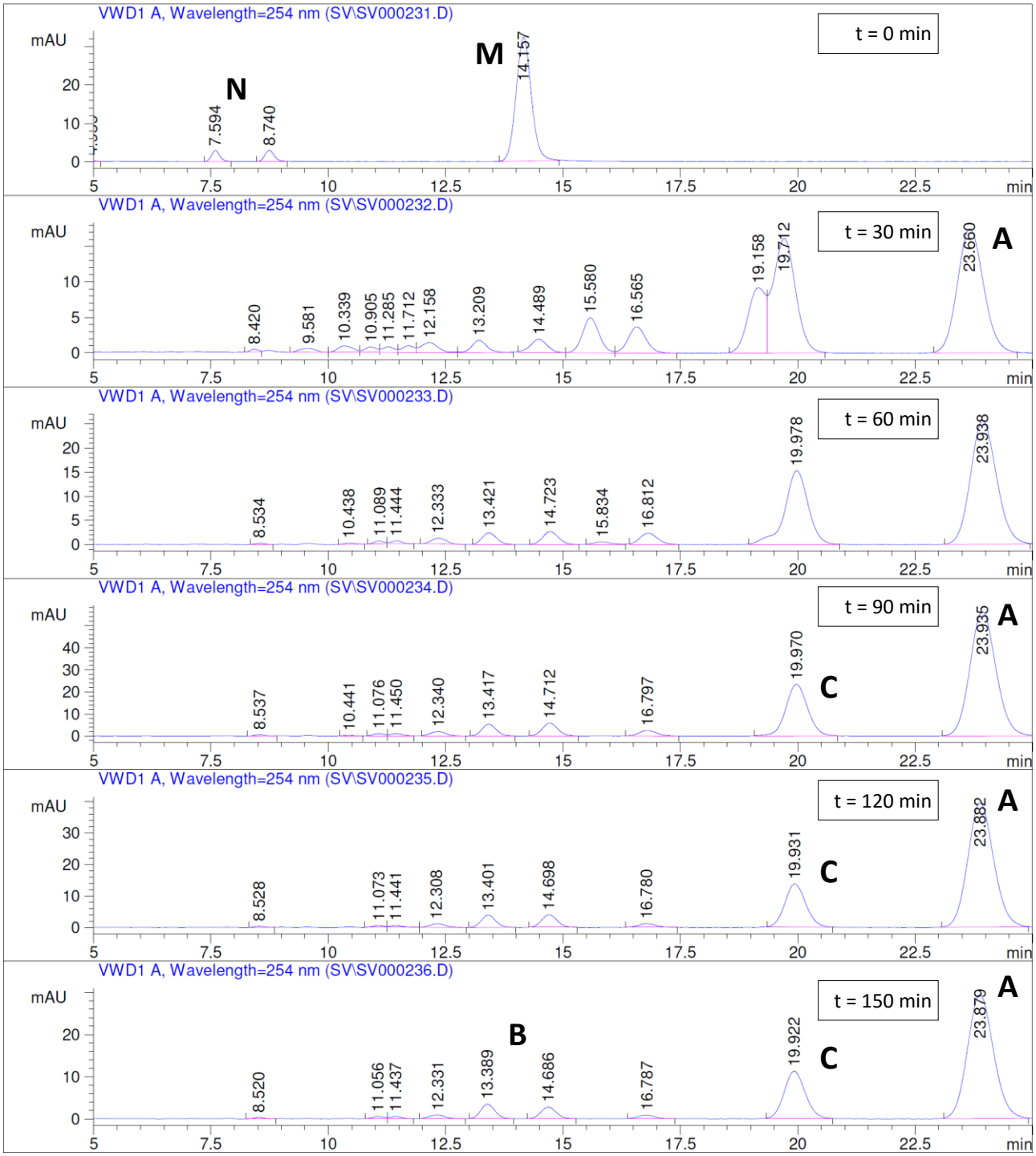
Switching the solvent of this step from EtOH to *i*-BuOH has two main beneficial effects on step 2: (a) transesters products are not formed and reaction time of step 2.2 is greatly reduced. Ammonium thiocyanate is added after the first 30 min and after that the reaction completes in another 60 min of reflux time

[1] O. Kohle, S. Ruile, M. Grätzel, *Inorg. Chem.*, **1996**, 38, 4787.

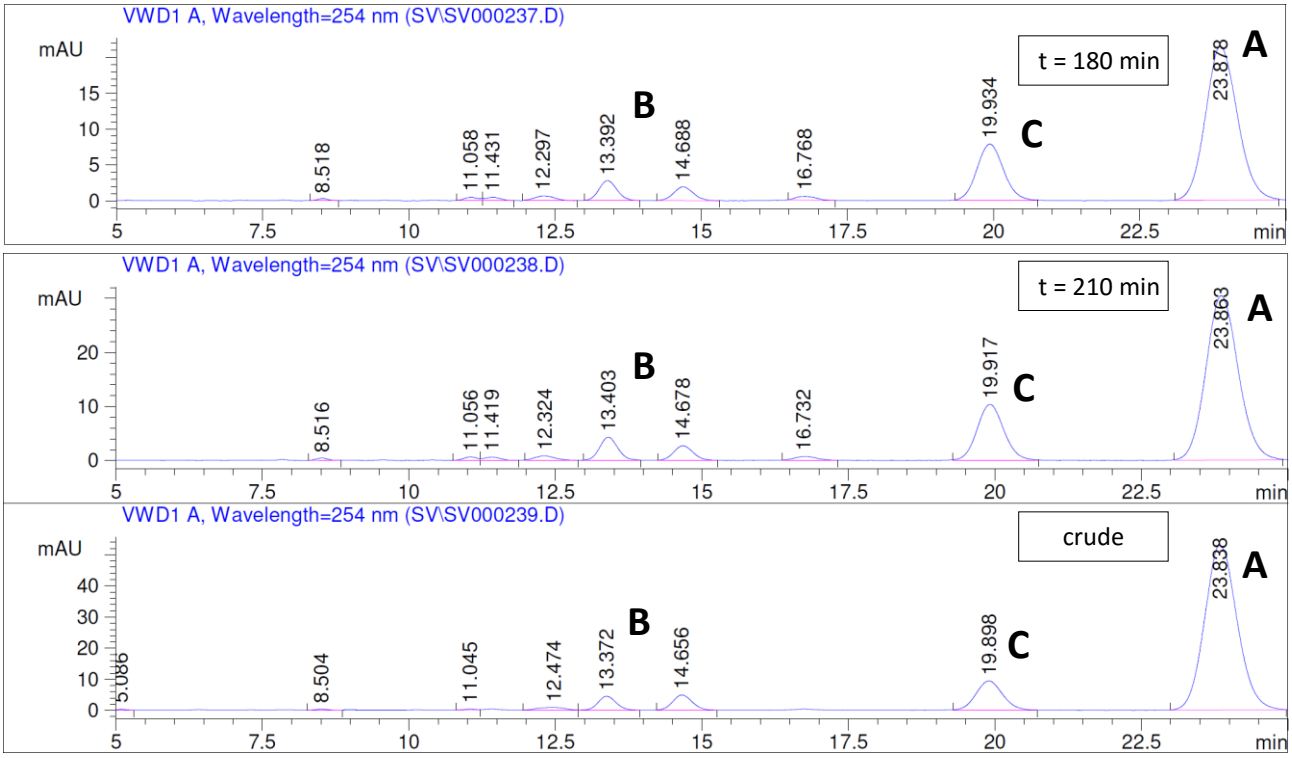
Step 2.1 - solvent EtOH



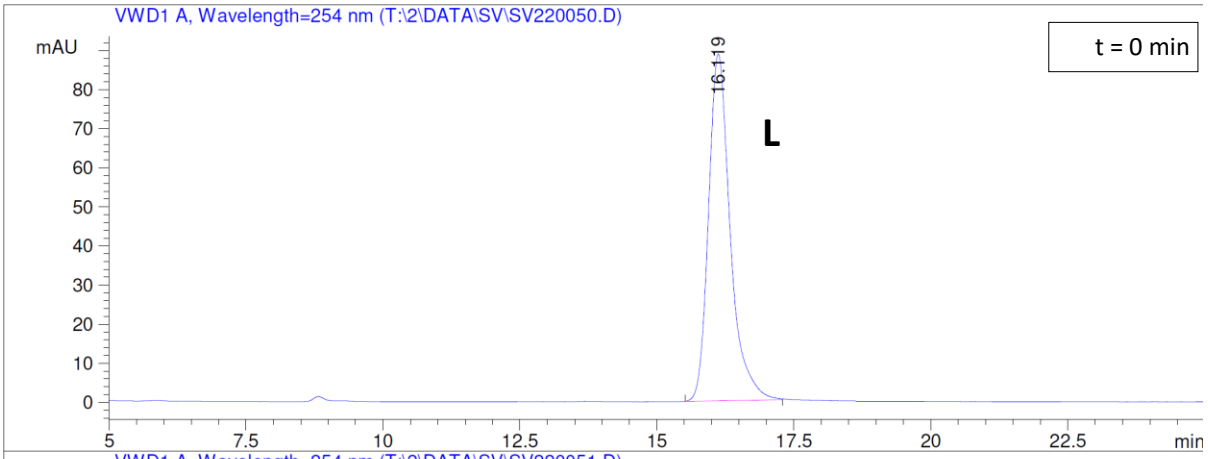
Step 2.2 - solvent EtOH

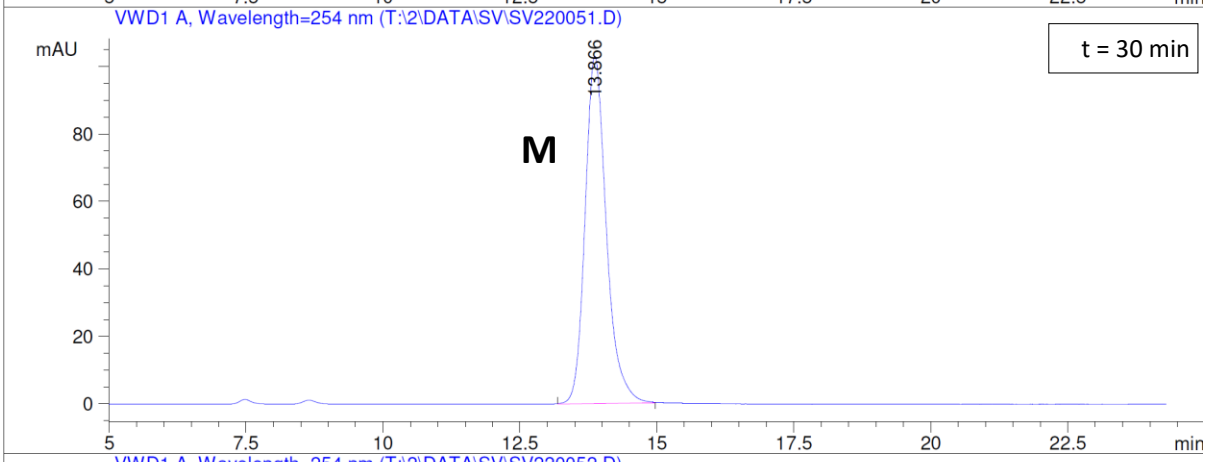


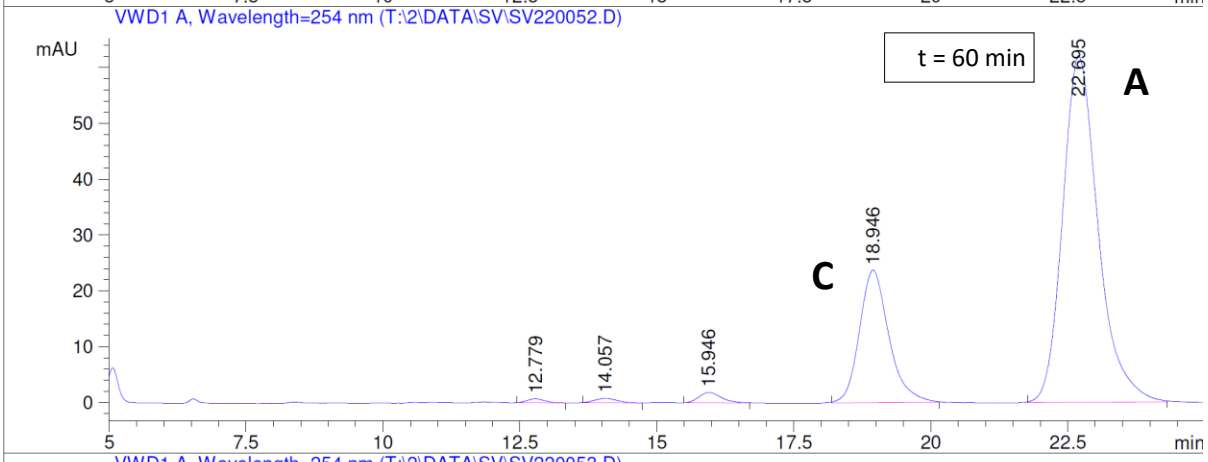
Step 2.2 - solvent EtOH (continued)

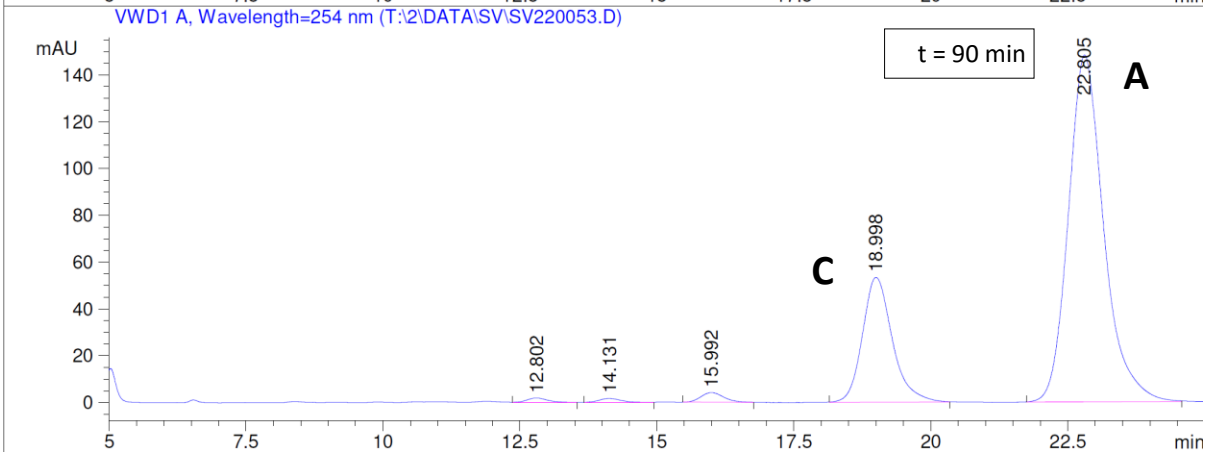


Step 2 - solvent *i*-BuOH





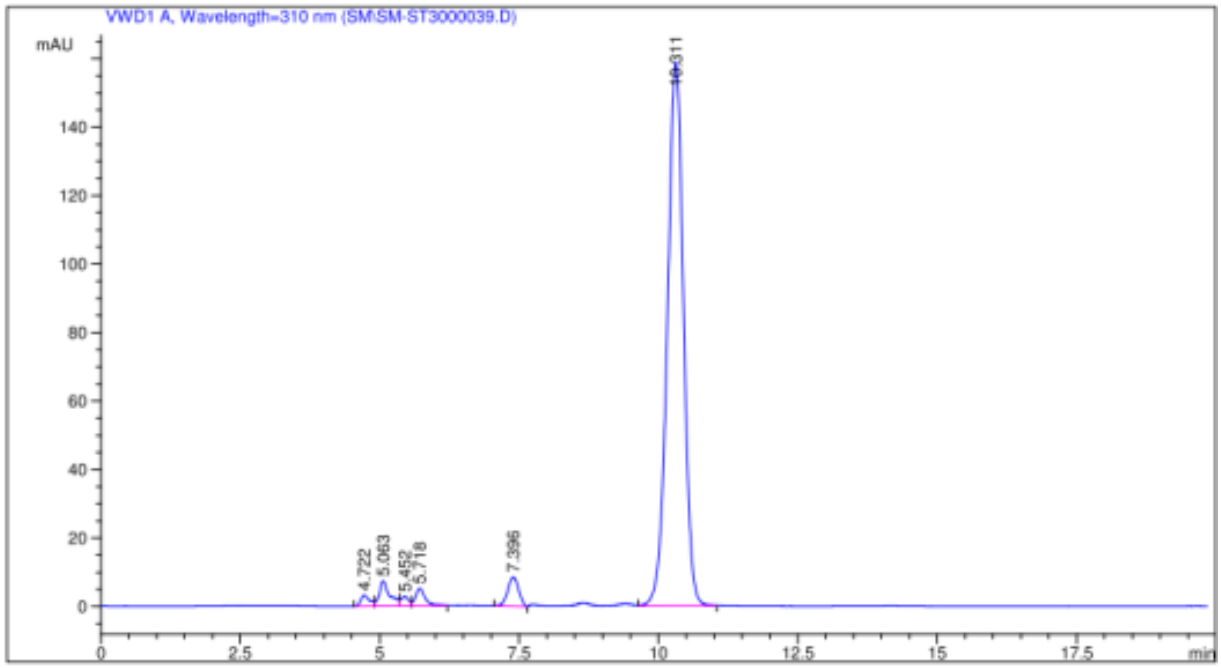


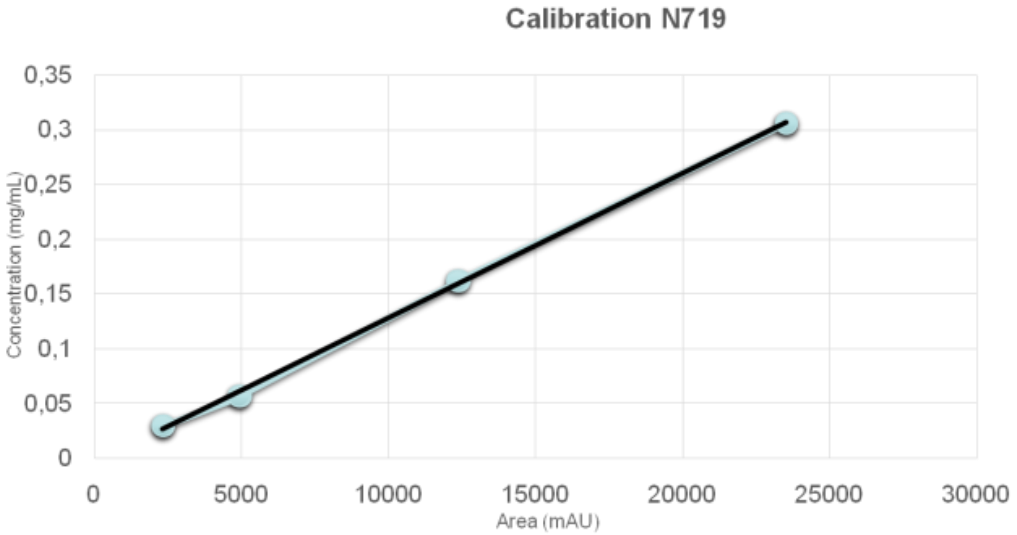


N719 HPLC – calibration line

To obtain quantitative information it was necessary to set up a calibration line (figure 13) with the Sigma Aldrich commercial dye as a standard.

Four solutions of the standard at known concentration were prepared, samples were solubilized and injected to HPLC and the value of peak area corresponding to N719 was plotted in the graph. The value of R^2 is very close to 1, it was therefore possible to analyse our synthetic dyes and compare them with the Sigma Aldrich standard.





Calibration line: conc (mg/mL) = 1.319 10^{-5} Area (mAU) – 3.487 10^{-3} R^2 = 9.994 10^{-1}

Thermo-analyses

Instrument: TA SDT Q600 DSC-TGA
Ramp: 25-650°@10°C/min
Atmosphere: air 100mL/min
Pan: alumina
Sample N719 commercial: 4,522 mg
Sample N719 Homemade: 7,264 mg

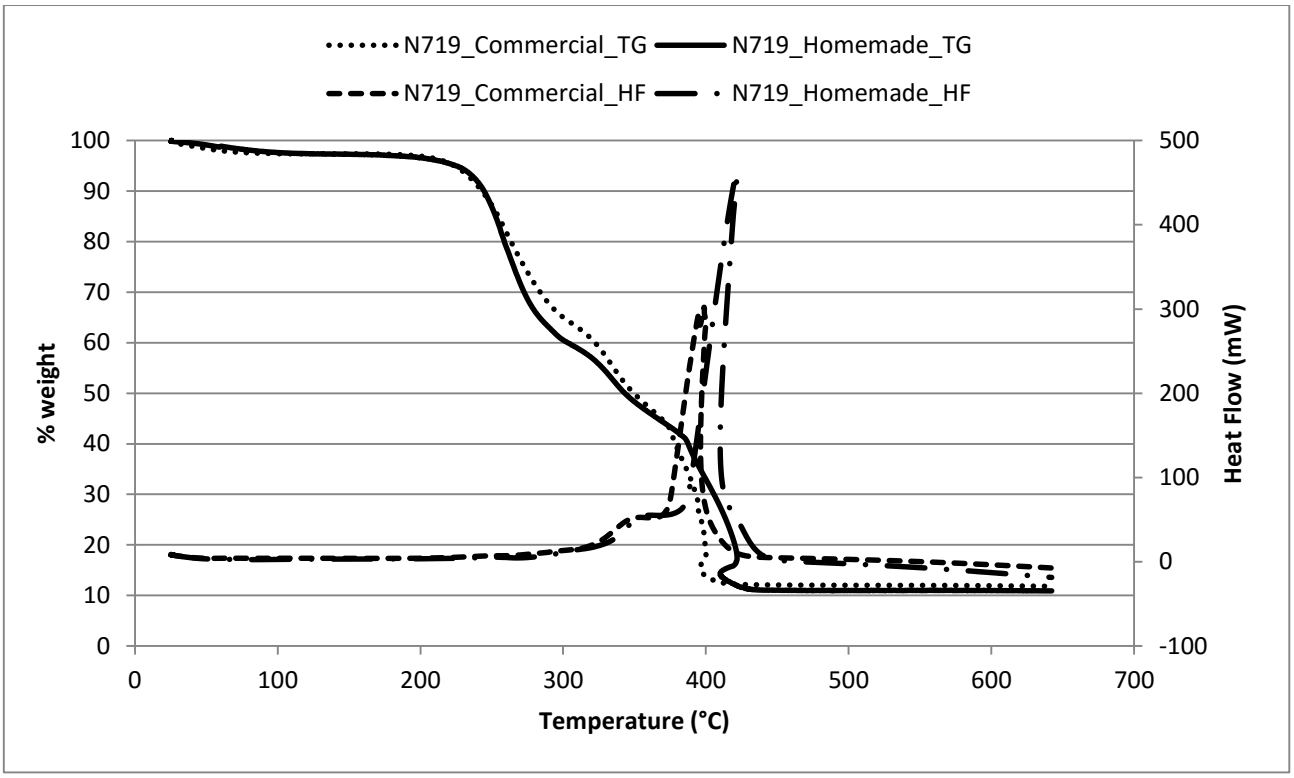


Figure 1 - TG/DSC analysis on dyes powder.

Instrument: TA SDT Q600 DSC-TGA
Isotherm @100° for 120 min
Atmosphere: air 100mL/min
Pan: alumina
Sample N719 Commercial: 1,829mg
Sample N719 Homemade: 5,770mg

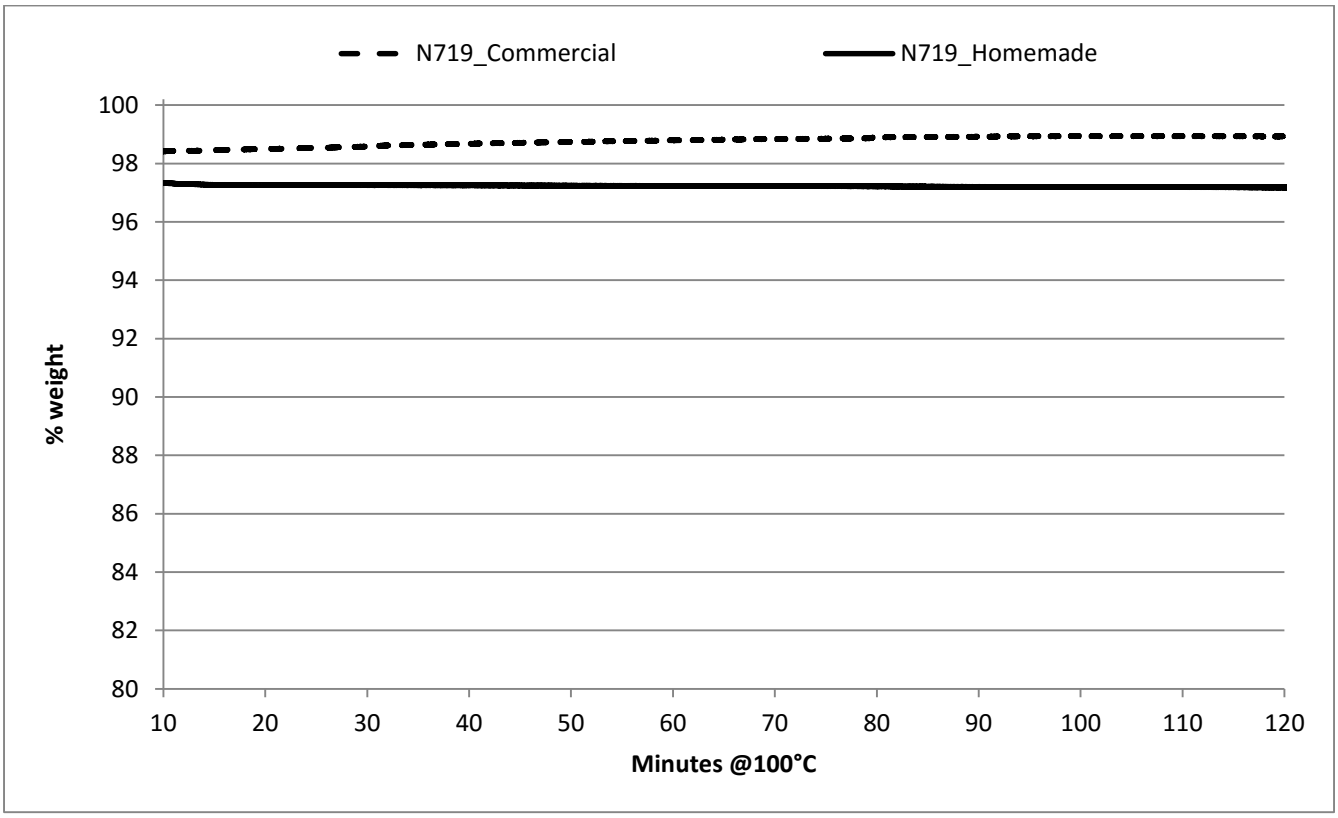


Figure 2: Mass weight @100°C of dyes powder.

UV-Vis spectra

Instrument: UV-Vis Agilent Cary 60

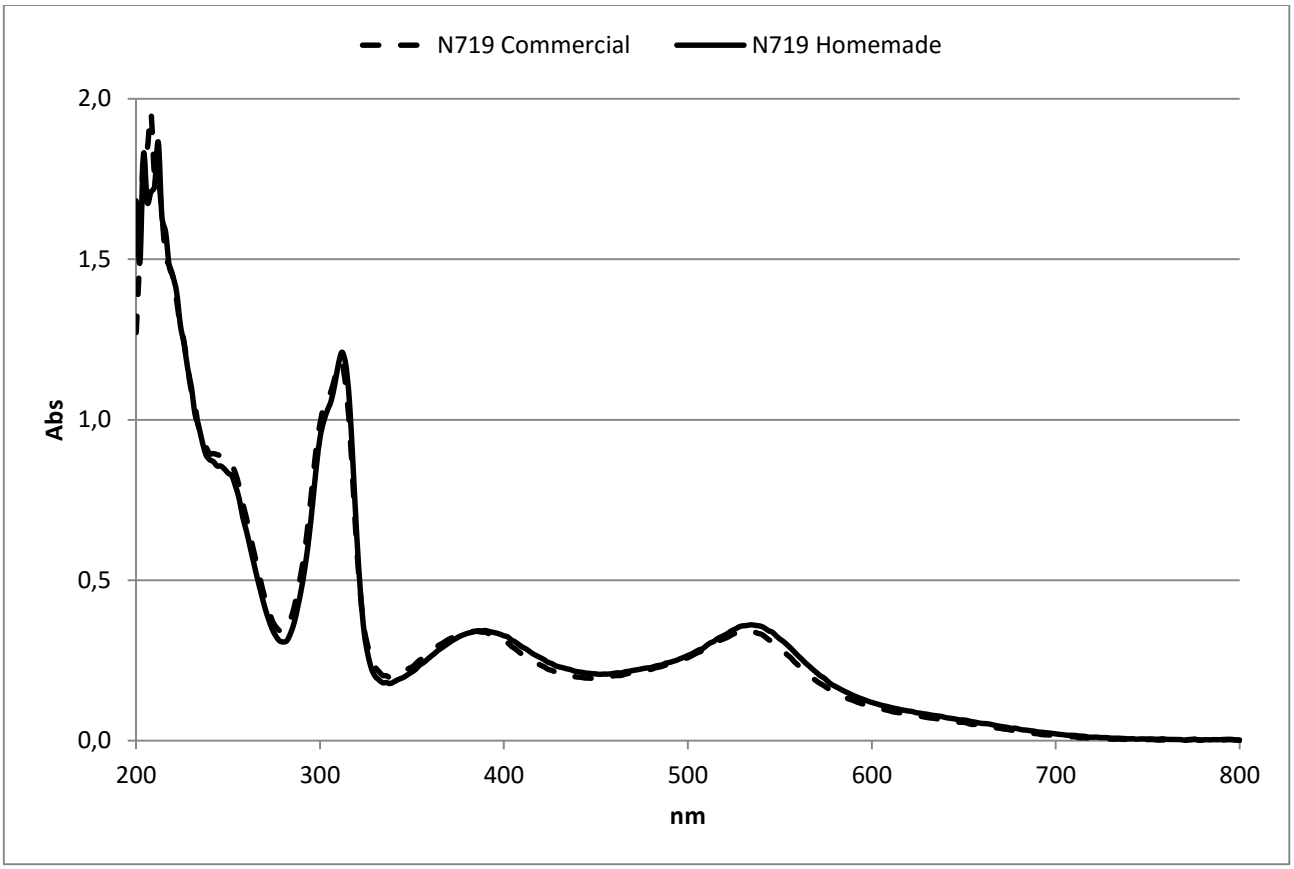


Figure 3: UV-Vis comparison of N719 dyes 0,30 mM in Ethanol.

DSSC performance charaterization

The efficiency, η, is the percentage of the solar energy to which the cell is exposed that is converted into electrical energy, this is calculated by the formula

$$\eta = Efficiency = \frac{Voc(V) * Isc(A) * FF(\%)}{P(W)}$$

Where the Voc is the open circuit voltage, Isc is the short circuit current, FF is the fill factor and their product is the power output at maximum power point while P is the product of the active area of the photovoltaic cell and the input light.

Aging test (1000 hours are equivalent at 20 years)
Climatic chamber Vötsch VCL 4006
Temperature 85°C / Relative humidity 15%
Open Circuit in dark conditions

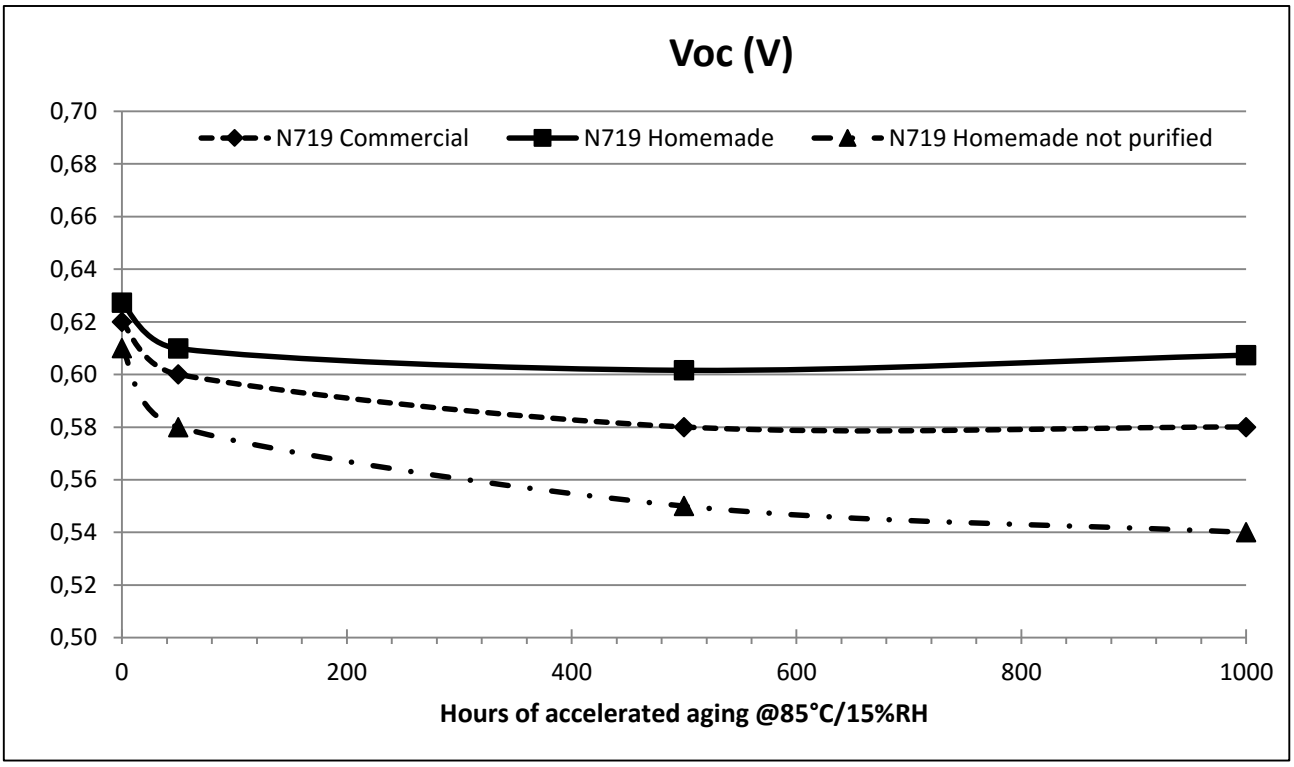


Figure 4: Average potential comparison in aging test.

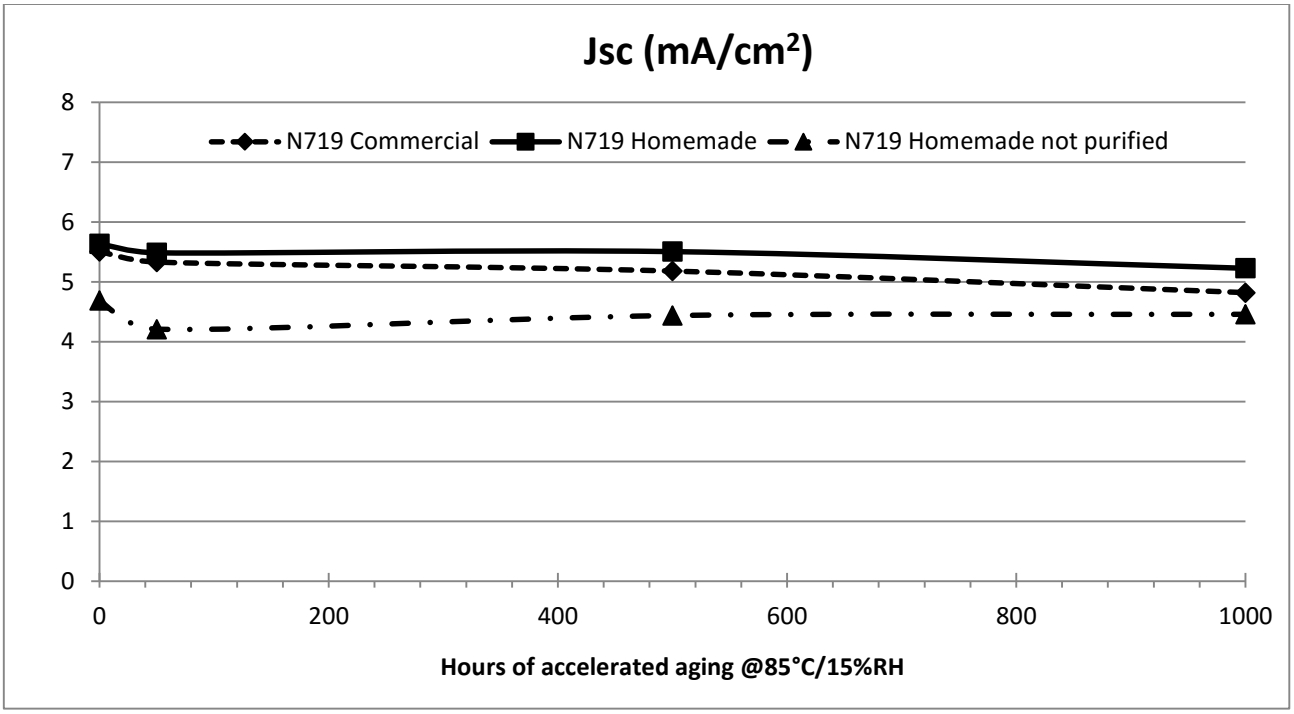


Figure 5: Average current comparison in aging test.

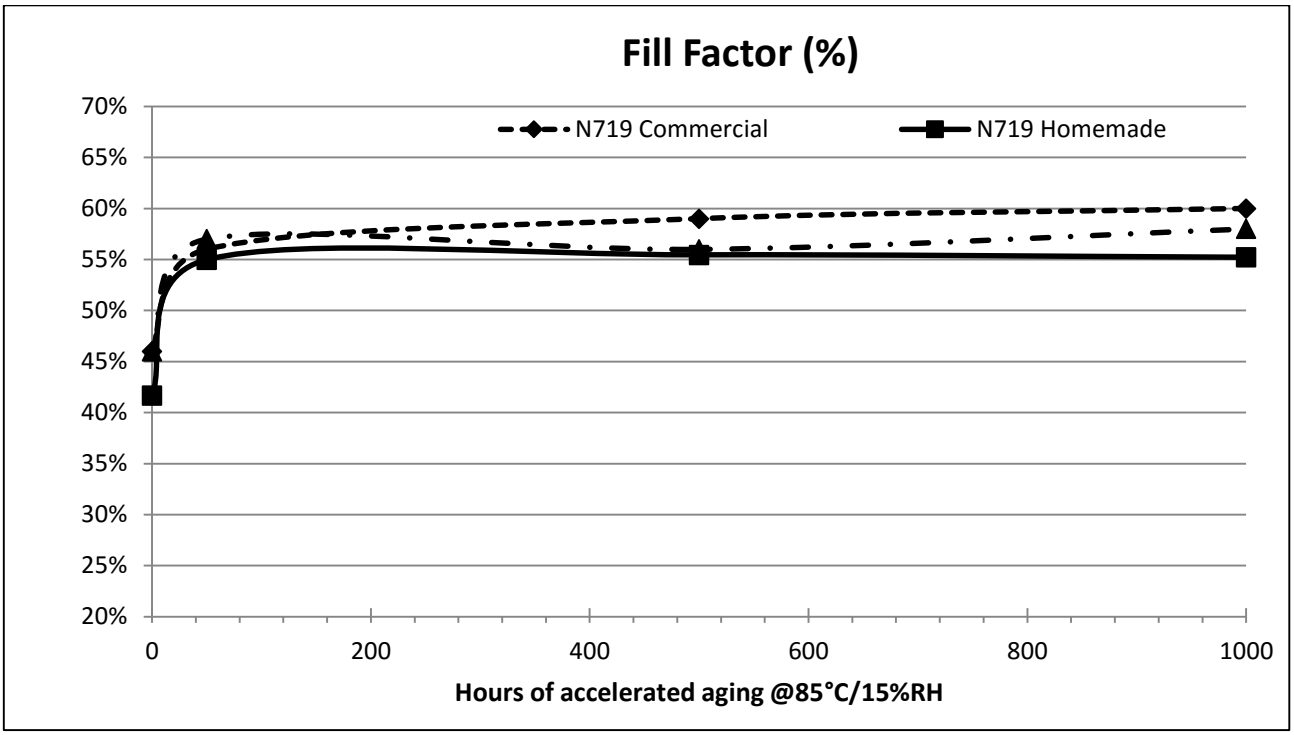
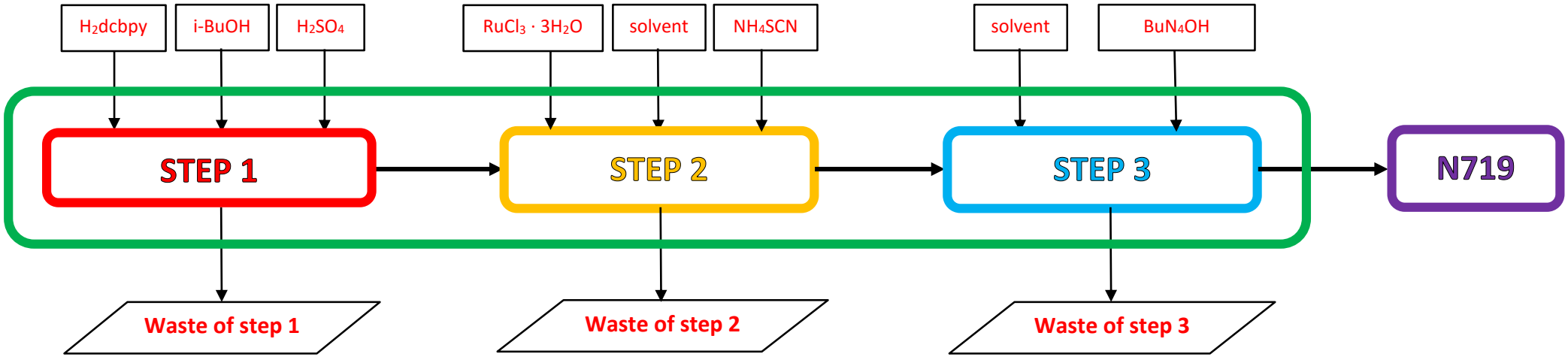


Figure 6: Average Fill Factor comparison in aging test.

E factor calculations

Schematic flow diagram representation of the N719 preparation



Notes:

a) In the diagram above, the green box represents the entire process. Arrows entering this box represents input materials of the process. Arrows exiting the green box are outputs of the process

b) Water is generally excluded from the calculation of the E factor.

c) For the comparison of the two processes, the two calculations are normalized to the same mass unit amount (1 g) of final N719

d) For any of the three steps (red, orange and blue boxes) the waste is calculated as the difference between the sum of the masses of all input materials and the mass of the desired product of that particular step

e) The E factor of the entire process is calculated as the ratio between the sum of the wastes and the mass of final N719

f) It was not possible to include in this comparison the amount of HNO_3 0.1 M used in step 3 because its amount is not reported. Anyway, we do not expect its impact on the E factor to be much different between the two processes, since both calculations are normalized to the same mass amount of N719 and HNO_3 is the last input material used in the process.

g) It was not possible to include in this comparison the materials used for work-ups, since amounts of those materials are never reported in journal articles. Anyway, for both processes the work up most impacting the waste is of course the chromatographic separation performed after step 2. We do not expect a big difference between the two processes in this regard. Actually, we assume that the change of solvent we introduced in step 2 - from EtOH to isobutanol, which eliminates transesterification products - might ease a little bit this chromatographic purification.

h) We expect our optimized process to be less energy intensive than the process reported in the literature. The most energy intensive operations of the process are the reflux conditions under which are run steps 1 and 2 and the solvent evaporations performed at the end of steps 2 and 3. The high reduction of the solvent volumes we achieved in all the three steps and the reduction of the reflux time of step 2 should have a great impact on the energy requirements of the process.

E factor calculations for the present optimized procedure

Step 1

Yield (%)	Input material	reference	FW	published amount	unit	density (g / mL)	charge mass (g)	molar amount (mmol)	mass equiv. (g / mmol of reference)	normalized molar amount (mmol / g of N719)	normalized mass amount (g / g of N719)
92	H_2dcbpy	YES	244.12	1.80	g		1.80	7.37		3.111	0.759
	i-BuOH			18	mL	0.803	14.45		1.960		6.098
	conc. H_2SO_4			0.30	mL	1.84	0.55		0.075		0.233
										Sum of step 1 input materials	7.090
	i-Bu$_2$dcbpy		*356.42*	*2.41*	*g*		*to step 2*	*6.76*		*2.862*	*1.020*
										Waste of step 1	**6.070**

Step 2

Yield (%)	Input material	reference	FW	published amount	unit	density (g / mL)	charge mass (g)	molar amount (mmol)	mass equiv. (g / mmol of reference)	normalized molar amount (mmol / g of N719)	normalized mass amount (g / g of N719)
60	*i-Bu$_2$dcbpy*	*YES*	*356.42*	*2.05*	*g*		*2.05*	*5.75*		*2.862*	*1.020*
	$RuCl_3 \cdot 3H_2O$		261.47	0.752	g		0.752	2.87	0.131		0.374
	i-BuOH			122	mL	0.803	97.97		17.042		48.744
	NH_4NCS		76,12	0.89	g		0.89	11.48	0.153		0.443
										Sum of step 2 input materials	50.581
	[Ru(i-Bu$_2$dcbpy)$_2$(NCS)$_2$]		*930.07*	*1.61*	*g*		*to step 3*	*1.731*		*0.859*	*0.799*
										Waste of step 2	**49.782**

Step 3

Yield (%)	Input material	reference	FW	published amount	unit	density (g / mL)	charge mass (g)	molar amount (mmol)	mass equiv. (g / mmol of reference)	normalized molar amount (mmol / g of N719)	normalized mass amount (g / g of N719)
98	*[Ru(i-Bu$_2$dcbpy)$_2$(NCS)$_2$]*	*YES*	*930.07*	*1.0*	*g*		*1.0*	*1.07*		*0.859*	*0.799*
	i-BuOH			56	mL	0.803	44.016		41.136		35.317
	Bu_4NOH (40%)			9.95	mL	1.00	9.95		9.299		7.984
										Sum of step 3 input materials	44.099
	N719		**1188.55**	**1.255**	**g**			**1.05**		**0.841**	**1.000**
										Waste of step 3	**43.099**

Overall process	E factor (sum of normalized masses of waste)	98.951

Yield: molar yield of the step as reported in the publication; **Input material**: Chemical name of the material; **reference**: indicates the material which was used as the reference for the step calculations; **FW**: Formula weight; **published amount and unit**: amount of the material as reported in the publication; **density**: taken from Sigma Aldrich web site; **charge mass:** amount of material expressed as mass; **molar amount**: published amount of the reference material expressed in mmol; **mass equiv.**: mass of any step material *i* relative to each mmol of the reference material (= mass charge of *i*/molar amount of *ref*); **normalized molar amount**: molar amount (mmol) of the reference material needed to obtain 1 g of final N719. Considers steps' yield; **normalized mass amount**: mass amount (g) of any material *i* needed to obtain 1 g of final N719 (= normalized molar amount of reference x mass equiv. of material *i*)

E factor calculations for the published procedure (T. Rawling *et al. Aust. J. Chem.*, **2008**, 61, 405)

Step 1

Yield (%)	Input material	limiting	FW	published amount	unit	density (g / mL)	charge mass (g)	molar amount (mmol)	mass equiv. (g / mmol of limiting)	normalized molar amount (mmol / g of N719)	normalized mass amount (g / g of N719)
92	H_2dcbpy	YES	244.12	1.50	g		1.50	6.15		4.014	0.980
	i-BuOH			60	mL	0.803	48.18		7.834		31.444
	conc. H_2SO_4			1	mL	1.84	1.84		0.299		1.201
										Sum of step 1 input materials	33.625
	i-Bu$_2$dcbpy		*356.42*	*2.01*	*g*		*to step 2*	*5.639*		*3.693*	*1.316*
										Waste of step 1	**32.309**

Step 2

Yield (%)	Input material	limiting	FW	published amount	unit	density (g / mL)	charge mass (g)	molar amount (mmol)	mass equiv. (g / mmol of limiting)	normalized molar amount (mmol / g of N719)	normalized mass amount (g / g of N719)
49	*i-Bu$_2$dcbpy*	*YES*	*356.42*	*0.400*	*g*		*0.400*	*1.12*		*3.693*	*1.316*
	$RuCl_3 \cdot 3H_2O$		261.47	0.147	g		0.147		0.131		0.485
	EtOH			120	mL	0.789	94.680		84.536		312.157
	NH_4NCS		76,12	1.712	g		1.712		1.529		5.644
										Sum of step 2 input materials	319.602
	[Ru(i-Bu$_2$dcbpy)$_2$(NCS)$_2$]		*930.07*		*g*		*to step 3*			*0.905*	*0.842*
										Waste of step 2	**318.760**

Step 3

Yield (%)	Input material	limiting	FW	published amount	unit	density (g / mL)	charge mass (g)	molar amount (mmol)	mass equiv. (g / mmol of limiting)	normalized molar amount (mmol / g of N719)	normalized mass amount (g / g of N719)
93	*[Ru(i-Bu$_2$dcbpy)$_2$(NCS)$_2$]*	*YES*	*930.07*	*0.260*	*g*		*0.260*	*0.280*		*0.905*	*0.842*
	Acetonitrile			60	mL	0.786	47.16		168.429		152.376
	Bu_4NOH (1M)			2.80	mL	1.00	2.800		10.000		9.047
										Sum of step 3 input materials	162.265
	N719		**1188.55**		**g**					**0.841**	**1.000**
										Waste of step 3	**161.265**

Overall process	E factor (sum of normalized masses of waste)	512.334

Yield: molar yield of the step as reported in the publication; **Input material**: Chemical name of the material; **reference**: indicates the material which was used as the reference for the step calculations; **FW**: Formula weight; **published amount and unit**: amount of the material as reported in the publication; **density**: taken from Sigma Aldrich web site; **charge mass:** amount of material expressed as mass; **molar amount**: published amount of the reference material expressed in mmol; **mass equiv.**: mass of any step material *i* relative to each mmol of the reference material (= mass charge of *i*/molar amount of *ref*); **normalized molar amount**: molar amount (mmol) of the reference material needed to obtain 1 g of final N719. Considers steps' yield; **normalized mass amount**: mass amount (g) of any material *i* needed to obtain 1 g of final N719 (= normalized molar amount of reference x mass equiv. of material *i*