Supporting Information

The Kröhnke synthesis of benzo[a]indolizines revisited: towards small, red light emitters

Jaqueline S. A. Badaro,[a] Beata Koszarna,[a] Manon H. E. Bousquet,[b] Erik Ouellette,[c] Denis Jacquemin,*[b] and Daniel T. Gryko,*[a]

[a]Institute of Organic Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland.

[b]CEISAM Lab—UMR 6230, CNRS, University of Nantes, Nantes, France.

[c]Department of Chemistry, University of California, Berkeley, 420 Latimer Hall, Berkeley, CA, USA.

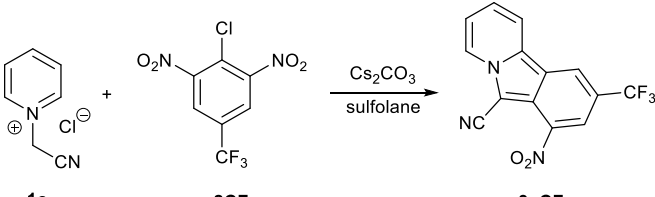[c]Chemical Sciences Division, Lawrence Berkeley National Laboratory, 1 Cyclotron Road, Berkeley, CA, USA.

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1.   Optimization studies

According to the two-step approach initially proposed by Kröhnke *et al.* two different bases were required (Scheme 1), however 5 years later the same group published an optimized one-pot protocol (Scheme 1). We considered it to be a promising starting point and we focused on a one-step procedure modifying bases and solvents (Table S1). First, Lewis bases were evaluated in DMSO, but unfortunately the yield was not satisfactory, only ca. 20% (Table 1, entries 2-3). Common Brønsted bases were then investigated, but this strategy was also not efficient enough. In fact, the best result was obtained for Cs_2CO_3 (entry 1), so we decided to increase its concentration to 4 mmol which allowed to obtain a 56% yield for the desired product **3cCF** (entry 8). Finally, different aprotic polar solvents were evaluated and sulfolane gave the most gratifying result, increasing the yield to 68% (entry 1). Additionally, we tried increasing the temperature and decreasing the reaction time; but both changes did not enhance the yield; in fact, in some cases it resulted in a yield decrease as well as many side-products, so we set on room temperature and 16 h as optimal conditions. Furthermore, the reactivity of reagents having different leaving groups at position 4 of nitroarenes was compared. The reaction was successful not only when 4-chloro-3,5-dinitrobenzotrifluoride was used (68%) but also with 4-fluoro-3,5-dinitrobenzotrifluoride, though with a slight decrease in yield (60%).

**Table S1** First optimization studies of the reaction conditions[a]

Entry	Deviation from the standard conditions	Yield (%)[a]
1	none	68
2	DBU and DMSO instead of Cs_2CO_3 and sulfolane	17
3	piperidine and DMSO instead of Cs_2CO_3 and sulfolane	20
4	K_2CO_3 and DMSO instead of Cs_2CO_3 and sulfolane	ND
5	KO*t*Bu and DMSO instead of Cs_2CO_3 and sulfolane	trace
6	cesium pivalate and DMSO instead of Cs_2CO_3 and sulfolane	18
7	Cs_2CO_3 (2 mmol) and DMSO instead of Cs_2CO_3 (4 mmol) and sulfolane	25
8	DMSO instead of sulfolane	56
9	DMPU instead of sulfolane	44
10	NMP instead of sulfolane	43

[a] Reaction was performed using 1 mmol of substrates and 4 mmol of base in sulfolane at RT and overnight. ND = not detected.

Further optimization study. As stated previously, under the previously optimized conditions, dye **3eCN** was obtained in a considerably lower yield (24%) compared to analogous benzo[*a*]indolizines (Scheme 2). First, various Brønsted bases were evaluated, but in line with the first optimization study the yield was even lower (Table S2, entry 3). At this point, our focus moved towards non-nucleophilic Lewis bases. Among those both *tert*-butylimino-tri(pyrrolidino) phosphorane (BTPP) and tetramethylguanidine (TMG) gave better yields (Table S2, entries 1, 5 and 6), BTPP being the best choice. Consistent with the former study, an increase in temperature and a variation in reaction time did not enhance reactivity.

Table S2 Second optimization studies of the reaction conditions[a]
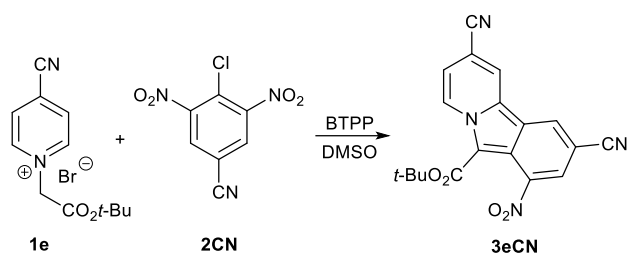
Entry	Deviation from the standard conditions	Yield (%)[a]
1	none	58
2	Cs$_2$CO$_3$ (4 mmol) instead of BTPP	24
3	KOAc instead of BTPP	15
4	piperidine (2 mmol) instead of BTPP	Trace
5	TMG (2.5 mmol) instead of BTPP	40
6	TMG (4 mmol) instead of BTPP	Trace

[a] Reaction was performed using 1 mmol of substrate and 4 mmol of P1-t-Bu-tris (tetramethylene) BTTP = P1-t-Bu-tris(tetramethylene)

2.   Crystallographic data of 3bCN

Table S1: Summary of crystal data for 3bCN

Chemical formula	C$_{18}$H$_8$N$_4$O$_2$
Molecular weight	312.28 g/mol
Crystal size	$0.08 \times 0.04 \times 0.04$ mm
Temperature	100 K
Wavelenght	0.72880 Å
Crystal system	monoclinic
Space Group	P2$_1$/n
Unit cell dimension	a/Å 10.6574(7)
	b/Å 11.6570(8)
	c/Å 10.8159(7)
	α/° 90
	β/° 98.605(3)
	γ/° 90
Volume	1328.57(15) Å^3
Z	4
Diffractometer	Bruker D8 with PHOTON-II CPAD detector
Radiation Rource	synchrotron (λ = 0.7288)
Reflections collected	3319
Independent reflections	3319 [R$_{int}$ = ?, R$_{sigma}$ = 0.0571]
Tmin, Tmax	0.630,0.746
Absorption correction	multi-scan
Refinement method	SHELXL using Least Squares minimisation
Data / Restraints / parameters	3319/0/218
Goodness-of-fit on F^2	1.074
Final R indices	R_1 0.0508 (I > 2σ(I)
	R_2 0.1401
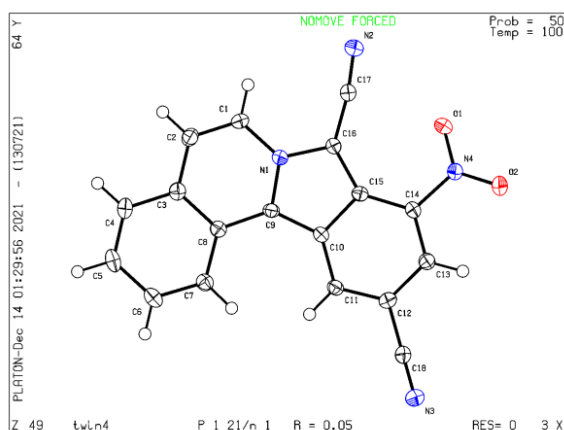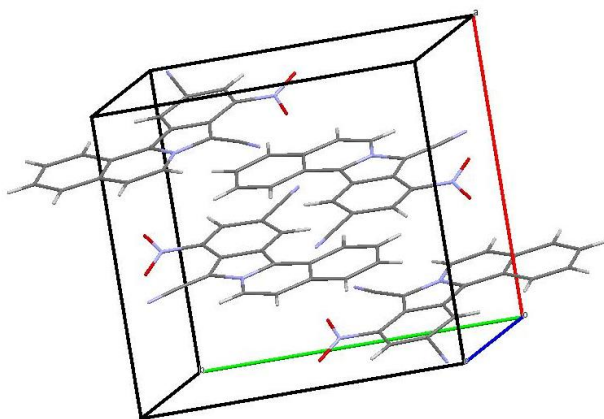
Figure S1: Packing diagram of crystals in elementary cell and thermal elipsoid plot with 50% probability level of ellipsoid contour

3.   Photophysical measurements
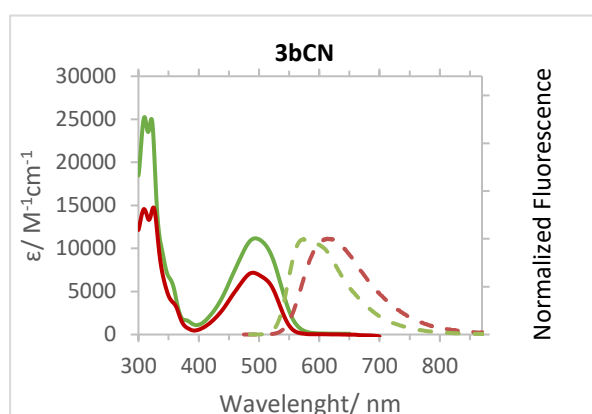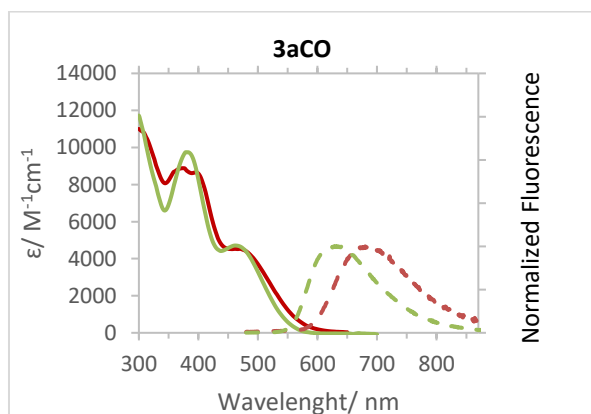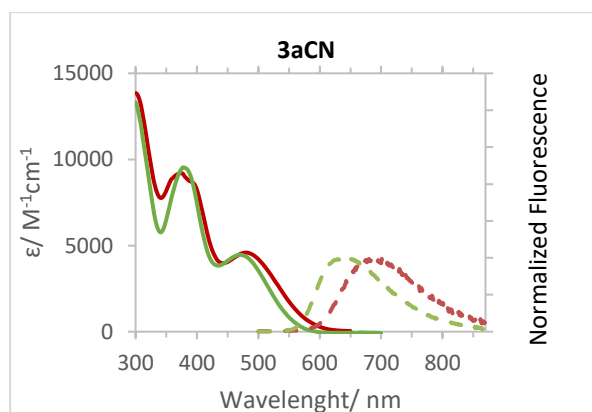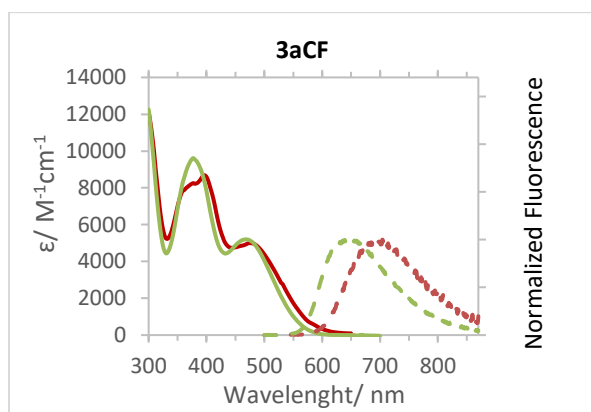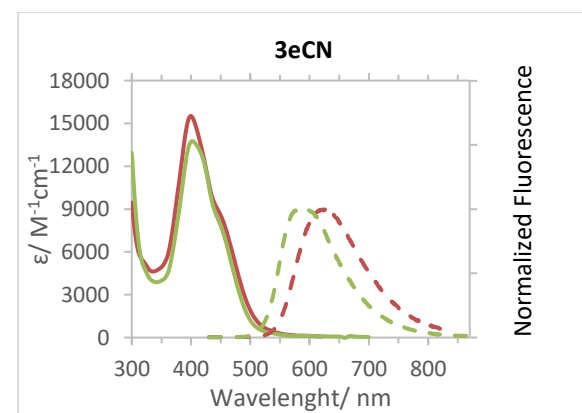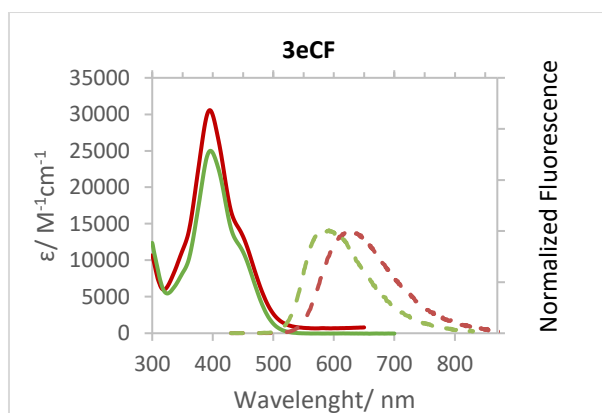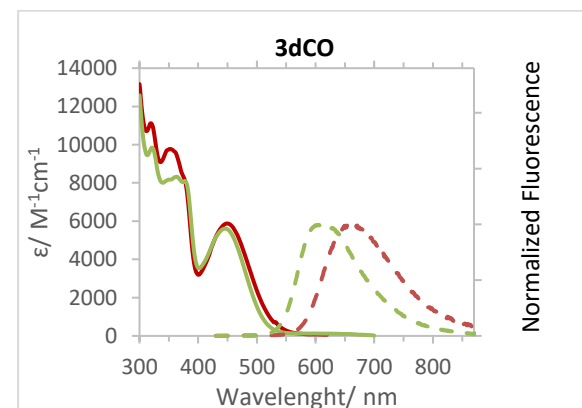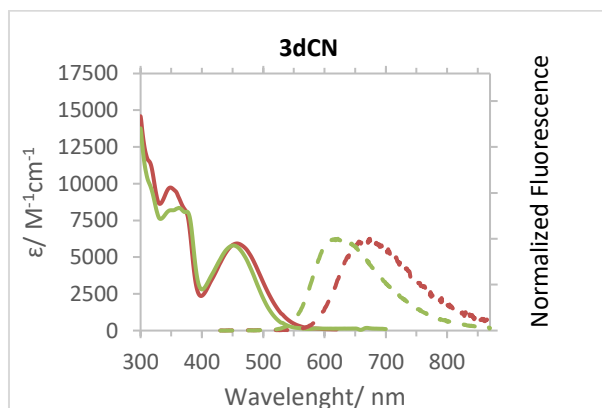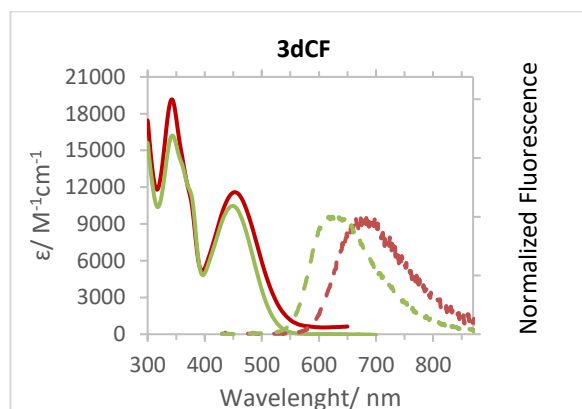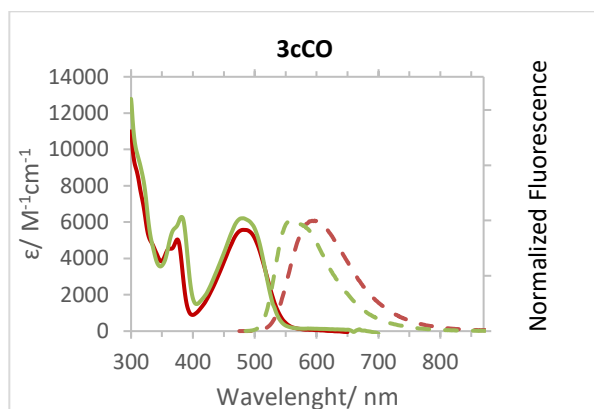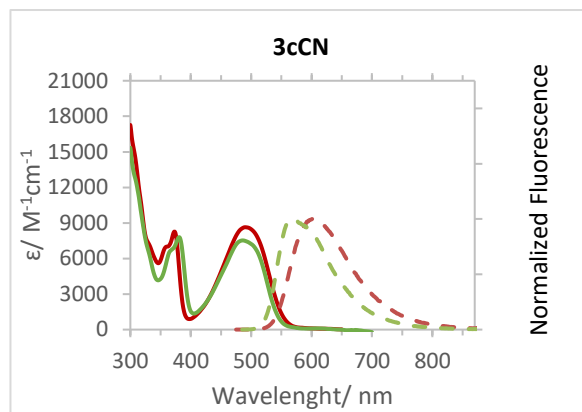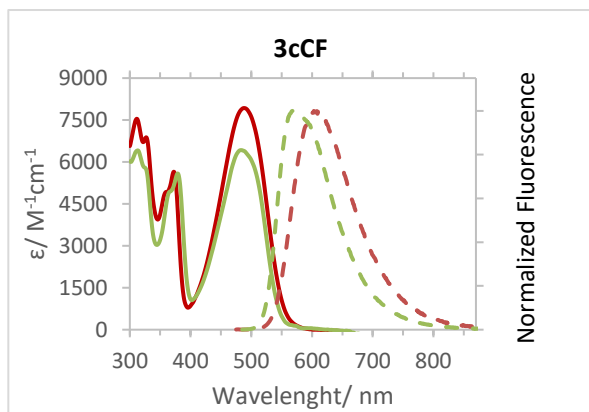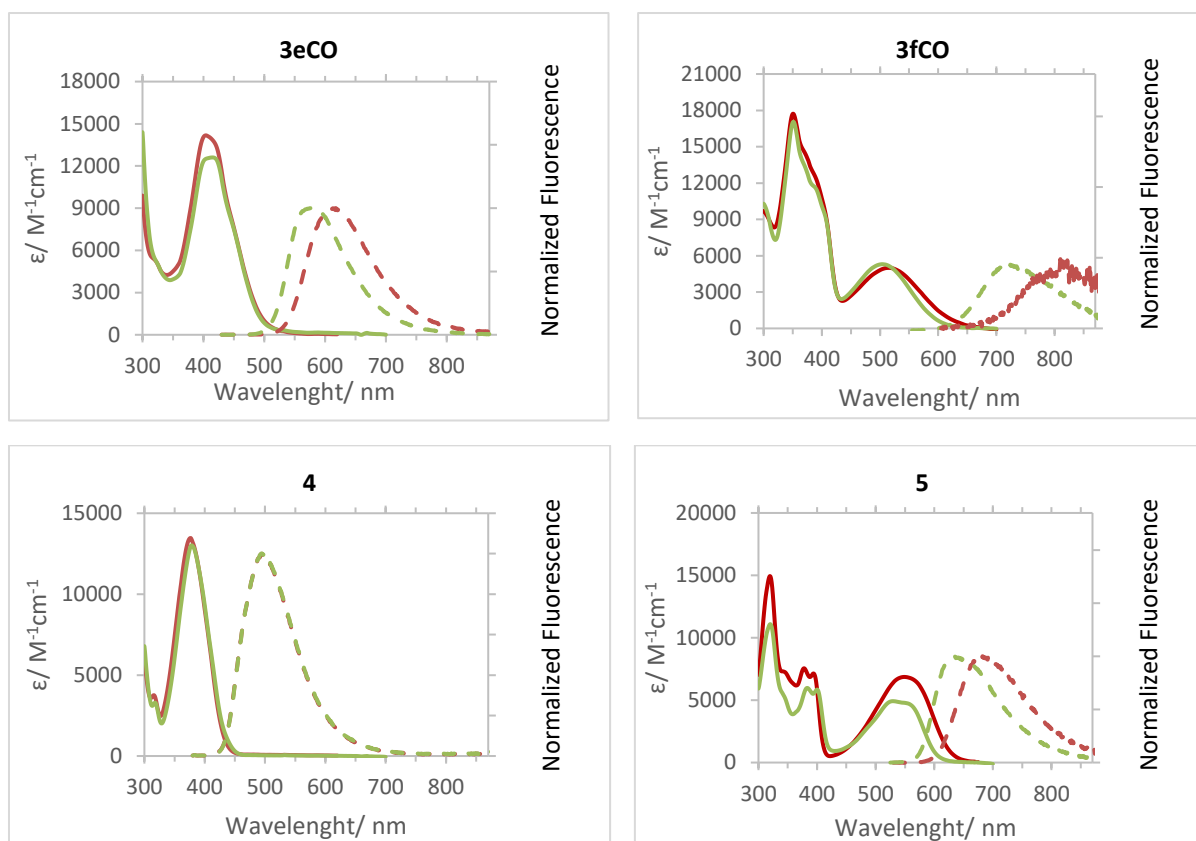
Figure S2: Absorption (solid) and Emission (dashed) of compounds in DCM (red) and Toluene (green)

4.   Computational Details
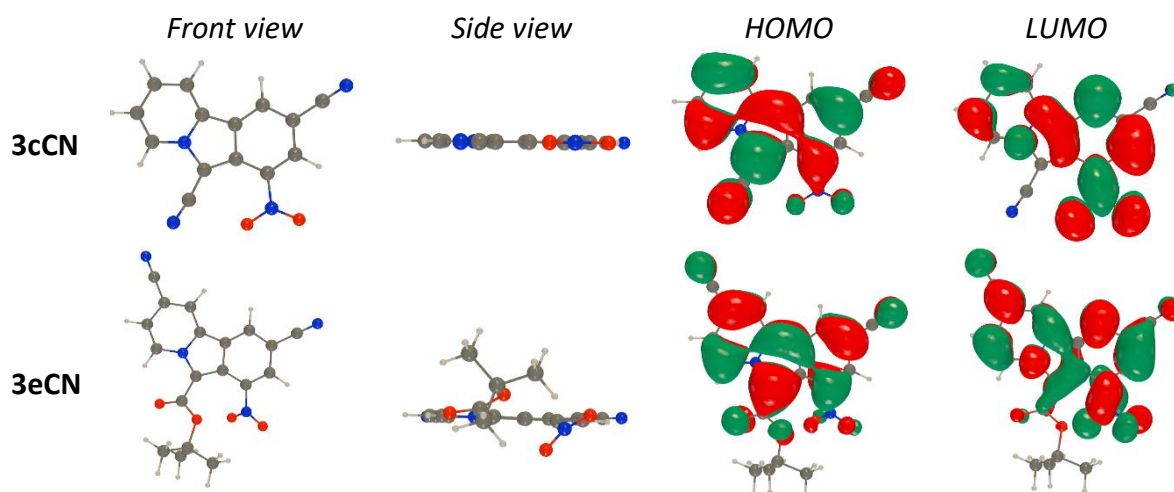
Figure S3: Representation of the optimal ground-state geometries of **3cCN** and **3eCN** in two views, together with the corresponding frontier orbitals. Note the clear twist of the groups at positions 6 and 7 due to the steric clash in **3eCN**

XYZ geometries are available as a separate SI file, in which GS indicate the (DFT) ground-state geometries and ES the (TD-DFT) excited-state geometries.

5.   Electrochemical Studies

Cyclic voltammograms of compounds (1 mg/mL) were measured at 20 °C, under argon atmosphere, in deoxygenated 0.1 M solutions of tetrabutylammonium perchlorate in anhydrous dichloromethane. A glassy carbon working electrode, a Ag/AgCl / NaCl (sat) reference electrode s, and auxiliary platinum wire were used, while the scan rate was v = 100 mV×s^{-1}. All values of E [V] are reported with respect to Fc$^+$/Fc redox potential.

3dCN
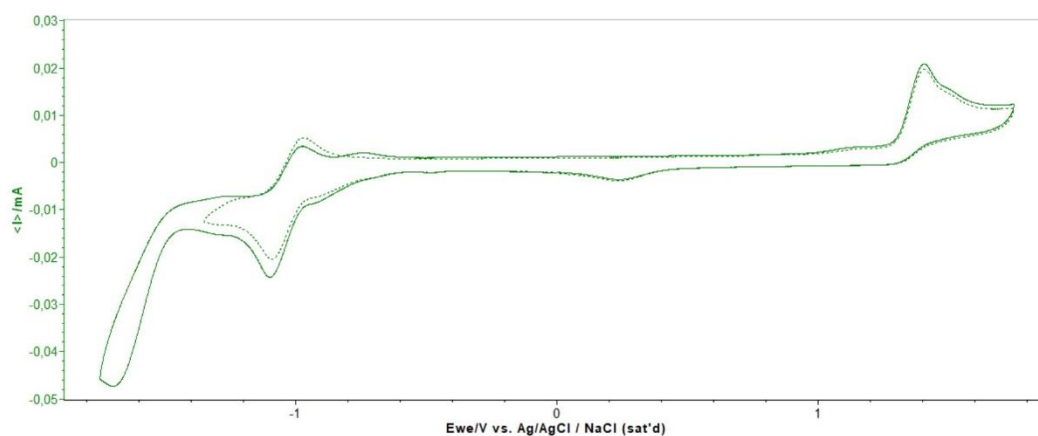
3fCO
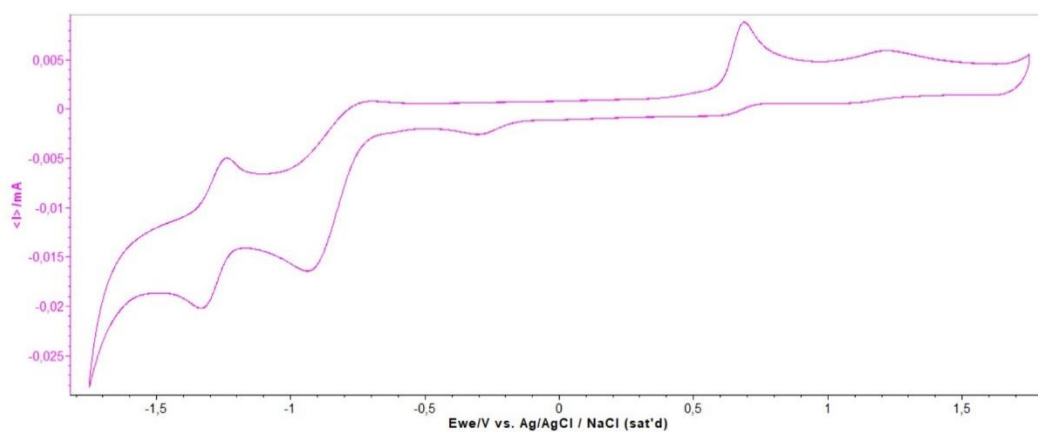
3aCF
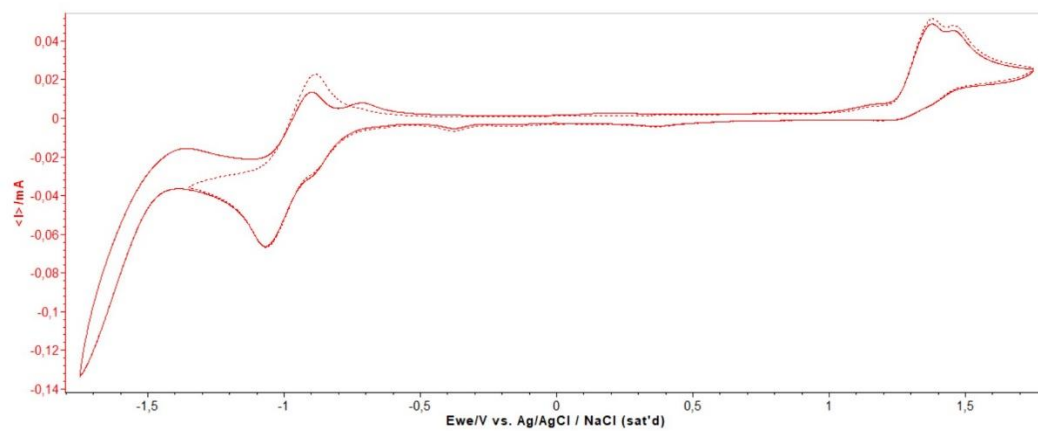
3cCN
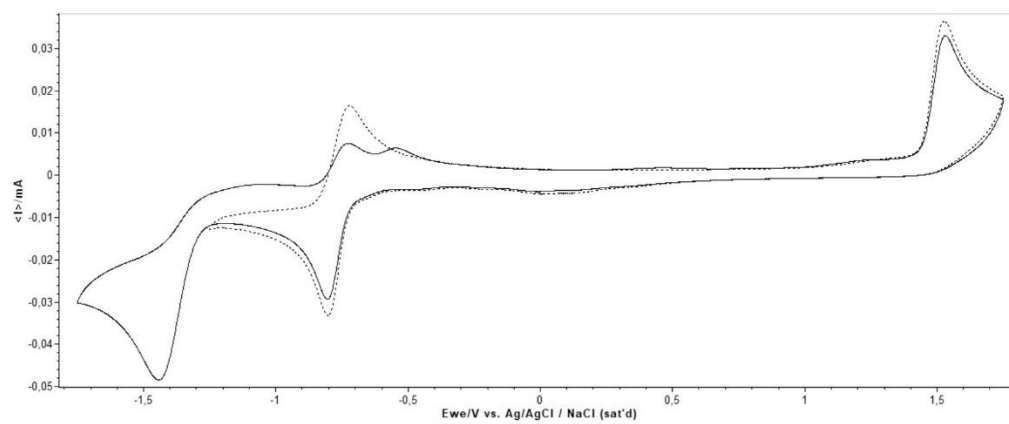
3eCN
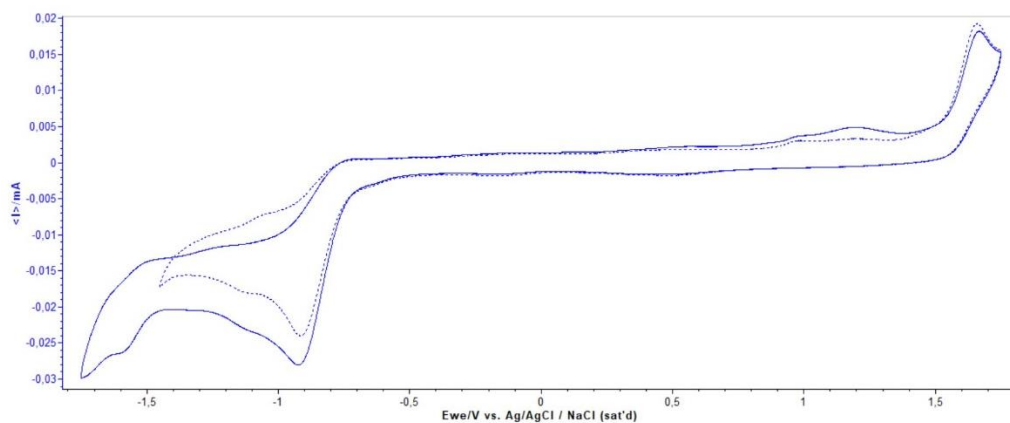
Figure S4: Cyclic voltammograms of compounds

6.   1^H NMR and ^{13}C NMR spectra of new compounds

Carbon-13 NMR spectrum, peaks at 186.64, 141.36, 140.56, 132.52, 132.39, 129.01, 127.99, 127.58, 125.56, 124.82, 123.54, 123.50, 122.32, 121.67, 120.88, 120.61, 120.30, 120.00, 118.02, 112.90, 77.00 cdcl3, 76.75 cdcl3

3aCF

Proton NMR spectrum, peaks at 9.86, 9.84, 8.78, 8.40, 8.39, 8.30, 7.73, 7.72, 7.70, 7.61, 7.60, 7.55, 7.53, 7.52, 7.44, 7.42, 7.40, 7.26 CDCL3, 1.58 H2O, 0.00

Integration values: 1.03, 0.86, 1.09, 0.73, 0.99, 1.90, 1.85, 2.18

3aCN

13C NMR spectrum with peaks labeled: 186.72, 171.13, 140.99, 140.33, 132.71, 132.31, 130.95, 129.09, 128.03, 127.75, 127.13, 126.33, 121.08, 120.49, 120.40, 118.15, 118.04, 101.00, 77.25 cdcl3, 76.74 cdcl3, -0.02

3aCN

1H NMR spectrum with peaks labeled: 9.91, 9.90, 9.18, 8.74, 8.42, 8.40, 7.67, 7.66, 7.64, 7.62, 7.61, 7.52, 7.50, 7.49, 7.48, 7.47, 7.45, 7.42, 7.40, 7.39, 7.25 CDCl3, 4.01, 1.58 H2O, -0.00

Integration values: 0.95, 0.56, 0.51, 0.96, 0.99, 1.70, 1.58, 2.09, 3.15

3aCO

13C NMR peaks (3aCO):
186.76
165.70
141.39
140.12
133.29
132.33
128.96
128.52
128.00
127.70
126.19
125.85
122.39
120.72
120.59
119.84
118.10
113.20
52.55
1.01

f1 (ppm)

3aCO

1H NMR peaks (3bCN):
10.09
9.46
9.44
8.98
8.97
8.37
8.35
8.30
8.28
8.03 DMF

3bCN

1.03
1.23
1.93
1.25
1.25

f1 (ppm)

3cCF

13C NMR spectrum peaks:
136.67, 133.63, 128.34, 127.75, 127.56, 123.14, 122.30, 122.08, 121.21, 120.42, 120.38, 119.77, 119.48, 114.13, 89.06, 40.57 dmso, 40.48 dmso, 40.40 dmso, 40.31 dmso, 40.24 dmso, 40.15 dmso, 39.98 dmso, 39.81 dmso, 39.65 dmso, 39.48 dmso, 0.55

3cCF

1H NMR spectrum peaks:
9.24, 8.95, 8.76, 8.71, 7.88, 7.80, 2.66 H2O

3cCN

13C NMR spectrum with peaks labeled:
205.18

133.55, 133.23, 132.39, 128.29, 127.99, 127.10, 121.80, 121.53, 121.04, 119.62, 117.67, 112.82, 101.39

29.38 acetone, 29.23 acetone, 29.07 acetone, 28.76 acetone, 28.61 acetone, 28.46 acetone

3cCN

f1 (ppm)

1H NMR spectrum with peaks labeled:
9.23, 9.23, 9.21, 9.20, 8.95, 8.94, 8.42, 8.41, 7.72, 7.71, 7.69, 7.61, 7.60, 7.58, 7.27 CDCl3

4.05

3cCO

Integrations: 1.78, 1.00, 1.00, 1.13, 1.09, 2.59

f1 (ppm)

165.38

129.77
127.27
126.60
126.33
121.64
120.59
120.23
118.83
113.60

77.25 cdcl3
77.00 cdcl3
76.74 cdcl3

22.78

−0.02

3cCO

10.05
10.03

8.63
8.32
8.31
8.23
7.58
7.56
7.55
7.47
7.45
7.44
7.26 CDCl3

1.64
1.54 H2O
1.53 H2O

0.00

3dCF

0.94

0.95
0.98
0.91

1.00
0.99

9.00

13C NMR spectrum with peaks labeled: 161.03, 141.69, 132.16, 128.00, 124.94, 124.22, 122.27, 121.25, 120.72, 120.49, 119.94, 119.42, 117.78, 106.39, 83.37, 77.25 CDCl3, 76.74 CDCl3, 28.41, -0.02

Structure labeled: tBuO2C, O2N, CF3, 3dCF

1H NMR spectrum with peaks labeled: 10.03, 10.02, 8.67, 8.67, 8.31, 8.29, 8.17, 8.16, 7.64, 7.64, 7.62, 7.62, 7.61, 7.60, 7.51, 7.51, 7.50, 7.49, 7.48, 7.25 CDCl3, 1.62, 1.55 H2O, -0.01, -0.02

Integrations: 0.94, 0.97, 0.98, 0.91, 1.07, 1.09, 8.89

Structure labeled: tBuO2C, O2N, CN, 3dCN

3dCO

3eCF

Top spectrum (13C NMR) peak labels:
160.19
142.44, 129.29, 127.36, 124.43, 123.84, 123.56, 123.29, 123.01, 122.92, 122.12, 122.09, 122.05, 122.02, 121.59, 121.56, 121.54, 121.51, 120.85, 120.54
116.96, 110.03, 105.15
84.94
77.25 cdcl3, 76.99 cdcl3, 76.74 cdcl3
28.22
−0.03

Structure label: 3eCF (CN, CF3, tBuO2C, O2N)

Bottom spectrum (1H NMR) peak labels:
9.98, 9.97
8.75, 8.63
8.25
7.58, 7.57, 7.56
7.26 CDCl3
1.63, 1.63
0.00, −0.00

Integrations: 0.97, 0.88, 1.32, 0.95, 0.99, 8.93

Structure label: 3ecN (CN, CN, tBuO2C, O2N)

f1 (ppm)

— 159.96

— 142.32
— 131.89
— 129.69
— 129.15
— 127.63
— 126.10
— 122.90
— 120.96
— 120.23
— 119.68
— 117.34
— 116.70
— 110.53
— 106.12
— 104.06

— 85.31

— 77.20 cdcl3
— 76.99 cdcl3
— 76.78 cdcl3

— 28.19

3ecN

— 9.94
— 9.92

— 9.14

— 8.70
— 8.65

— 7.51
— 7.50
— 7.49
— 7.49
— 7.26 CDCl3

— 4.04

— 1.88 H2O
— 1.61

— 0.00

3eCO

0.95
1.15
1.13
1.20
0.93
3.26
9.42

f1 (ppm)

13C NMR spectrum

3eCO

1H NMR spectrum

3fCO

8.61
8.60
8.14
8.13
7.83
7.37
7.37
7.36
7.36
7.35
7.34
7.32
7.32
7.31
7.31
7.26 CDCl3
6.84
6.83
4.51
1.56 H2O

4

0.96
0.99
0.95
1.13
1.11
0.96
2.26

12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

137.45
132.01
125.76
125.45
125.34
125.08
124.83
124.57
123.59
123.50
122.54
118.94
118.09
117.35
115.93
107.83
107.79
107.75
107.71
105.29
105.26
105.24
105.21
84.81
77.25 cdcl3
76.74 cdcl3

f1 (ppm)

NC
CF$_3$
H$_2$N

4

8.76
8.65
8.54
8.53
8.52
8.27
8.25
7.41
7.40
7.40
7.39
7.38
7.36
7.36
7.35
7.35
7.34
7.34
7.26 CDCl3
1.56 H2O
1.55 H2O
0.00

CN
O$_2$N

5

1.00
0.93
1.12
0.85
1.07
1.39
1.28

f1 (ppm)

13C NMR spectrum (compound 5):

136.97, 132.58, 129.62, 126.19, 125.94, 121.60, 119.99, 119.03, 118.85, 118.83, 106.71, 98.37, 77.25 cdcl3, 76.74 cdcl3

1H NMR spectrum (compound 1f):

8.25, 8.23, 7.07, 7.06, 5.10, 3.32 H2O, 3.19, 2.48 DMSO, 1.43

Integrations: 2.40, 2.44, 2.00, 5.92, 8.74

1f