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Tris(pentafluorophenyl)corrolatoindium(III) – A Long-awaited Metallocorrole: Synthesis and Characterization

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Abstract: The first attempts at the synthesis of an indium corrole compound were synthesized in the late 80s, but it has not been possible to obtain and characterize such complex completely, and the indium part of metallocorrole's periodic table remained unfilled. In this work, an efficient insertion of indium into the 5,10,15-tris(pentafluorophenyl)corrole was achieved. The obtained 5,10,15-tris(pentafluorophenyl)corrolato indium(III) derivatives has been successfully characterized by relevant analytical techniques and some photophysical and electrochemical features were studied and investigated for the first time. As a novel research, ^{19}F-^{19}F COSY NMR technique was employed for the first time in corrole chemistry and the obtained results were further compared to the geometry-optimized molecular structure via density functional theory (DFT) calculations.

Keywords: corrole, indium, metallocorrole, NMR, ^{19}F-^{19}F COSY

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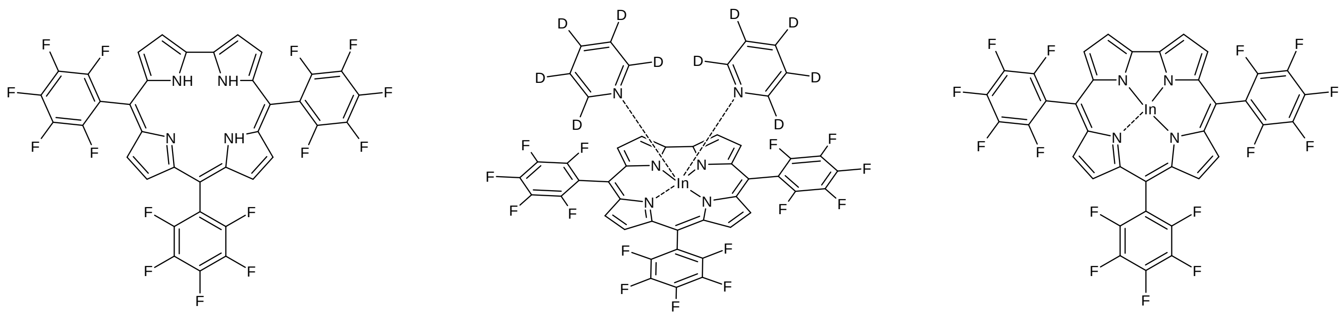

Figure S1. The basic structures of free-base corrole (***left***), indium corrole complex 1 (***middle***) and indium corrole complex 2 (***right***)

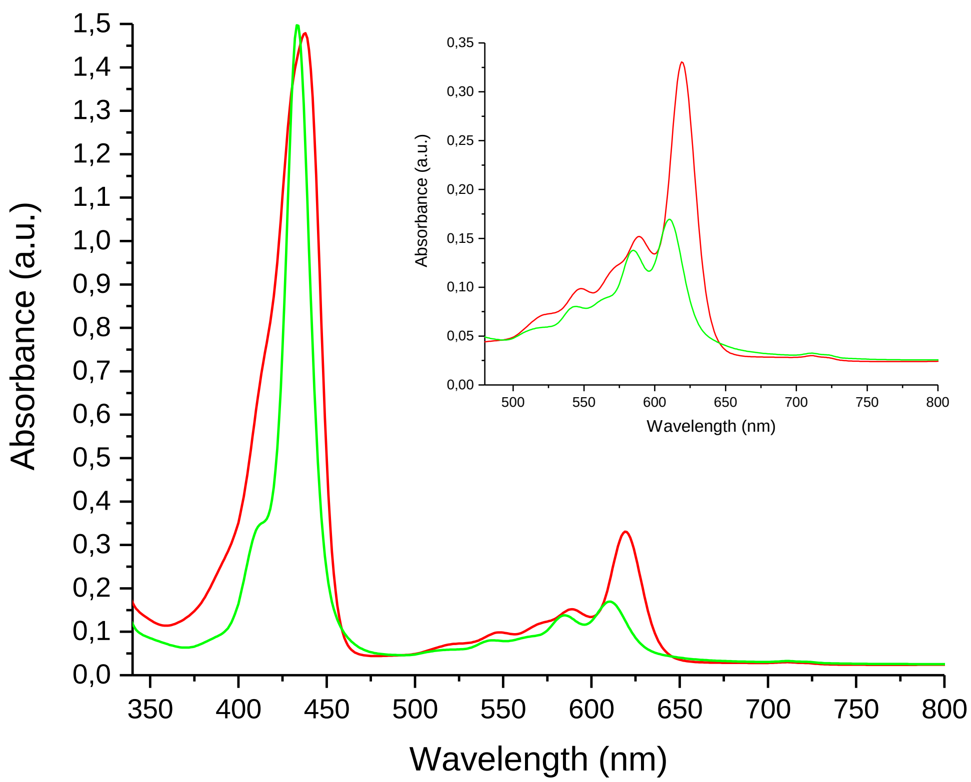

Figure S2. The UV-vis spectra of free-base corrole as corrolato (**red**), indium corrole complex 1 (**green**) in pyridine

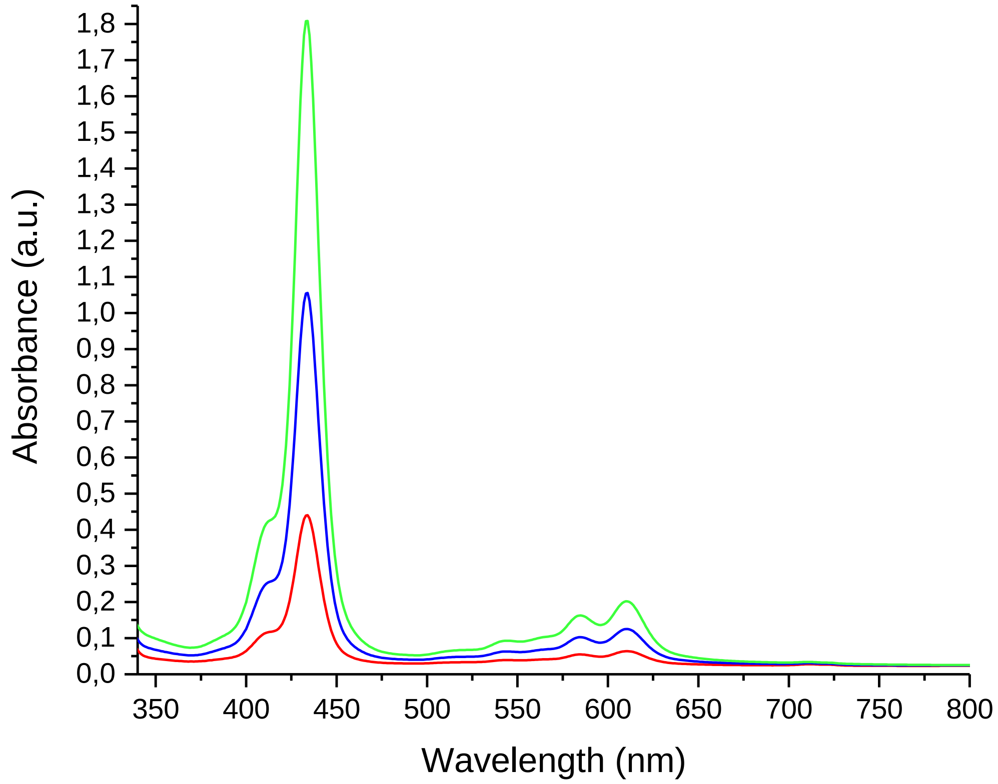

Figure S3. The UV-vis spectra indium corrole complex 1 in pyridine with different concentrations

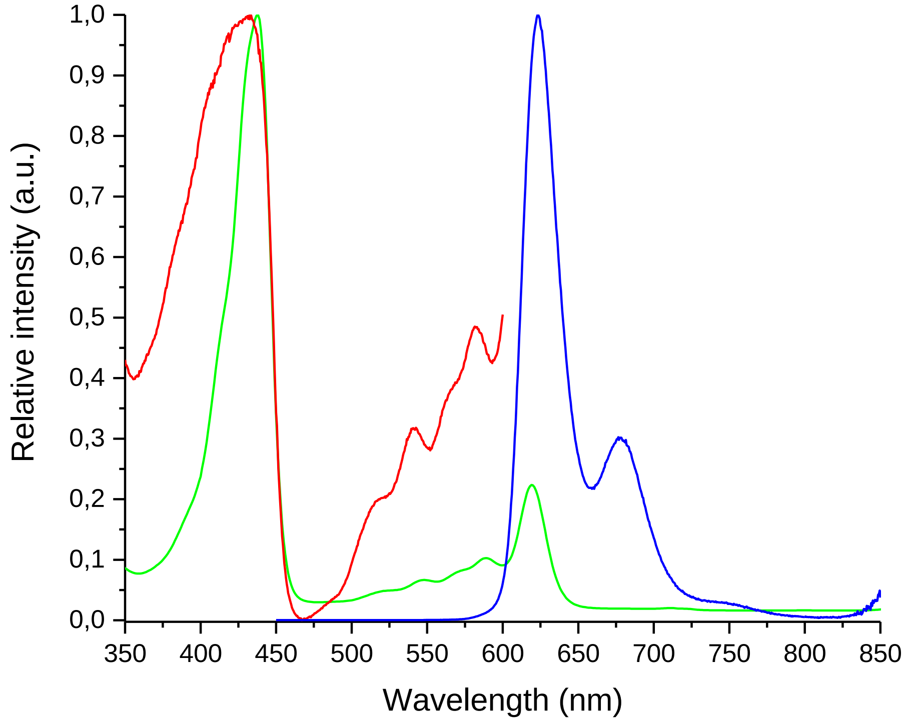

Figure S4. The absorbance (**green**), excitation (**red**) and fluorescence (**blue**) spectra of free-base corrole in d_5-pyridine

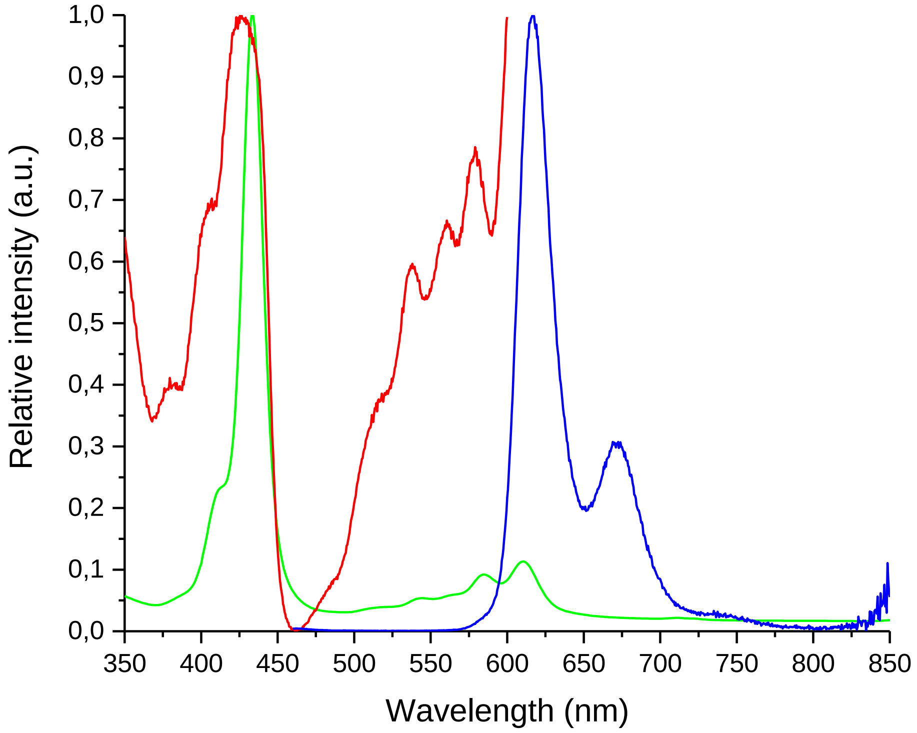

Figure S5. The absorbance (**green**), excitation (**red**) and fluorescence (**blue**) spectra of indium corrole complex 1 in d_5-pyridine

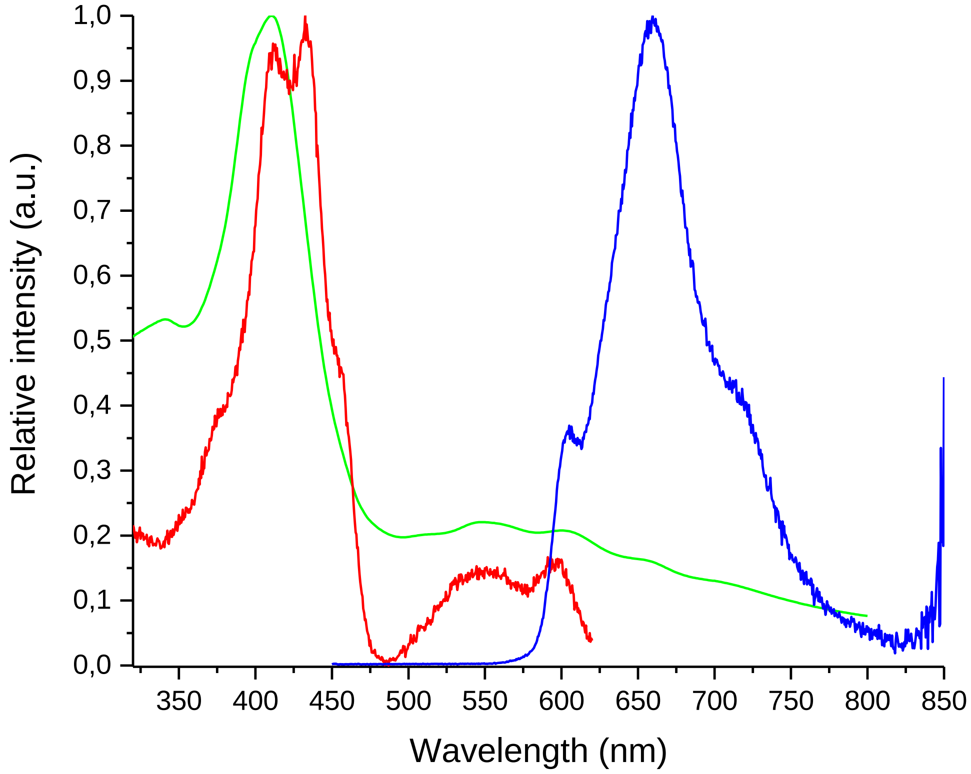

Figure S6. The absorbance (**green**), excitation (**red**) and fluorescence (**blue**) spectra of indium corrole complex 2 in d_3-acetonitrile

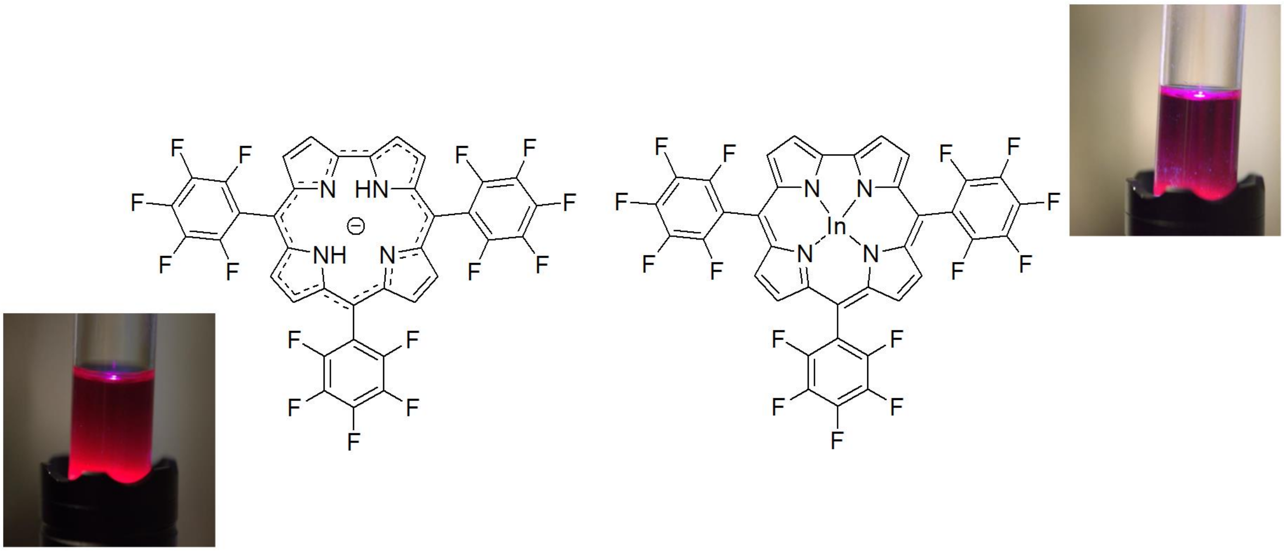

Figure S7. The fluorescence reflectances of monoanionic free-base corrole (left) and indium corrole complex 1 in d$_5$-pyridine

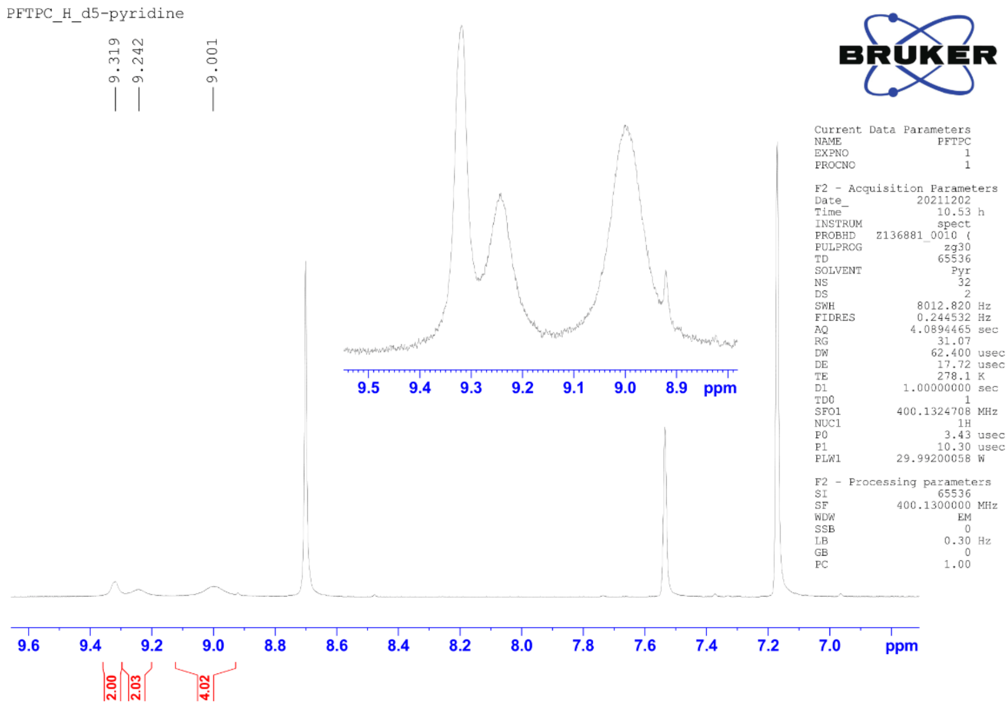

Figure S8. The ^{1}H-NMR spectrum of free-base corrole in d$_5$-pyridine

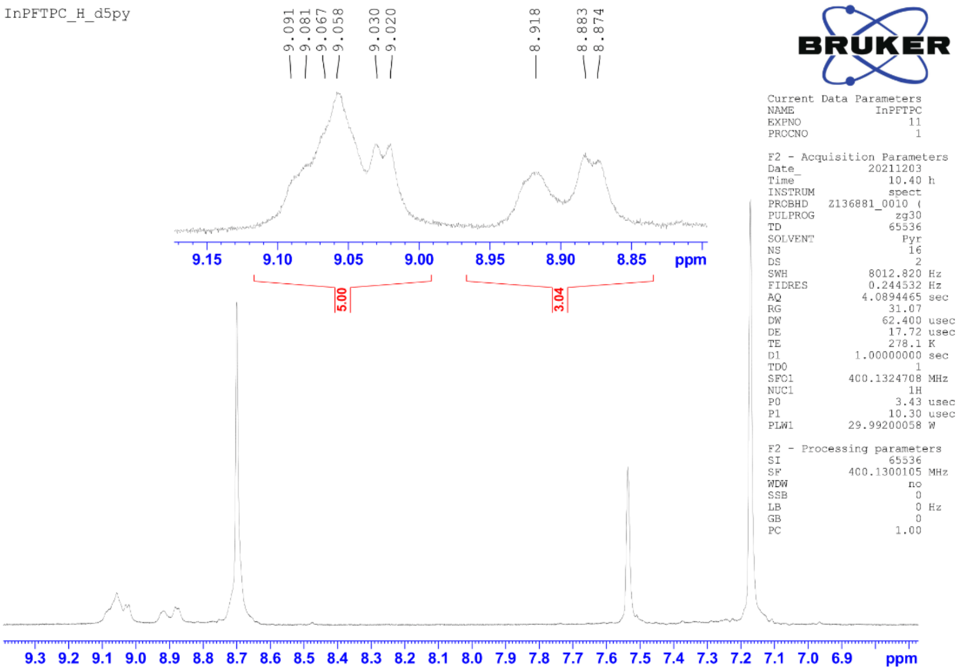

Figure S9. The ^{1}H-NMR spectrum of indium corrole complex 1 in d_5-pyridine

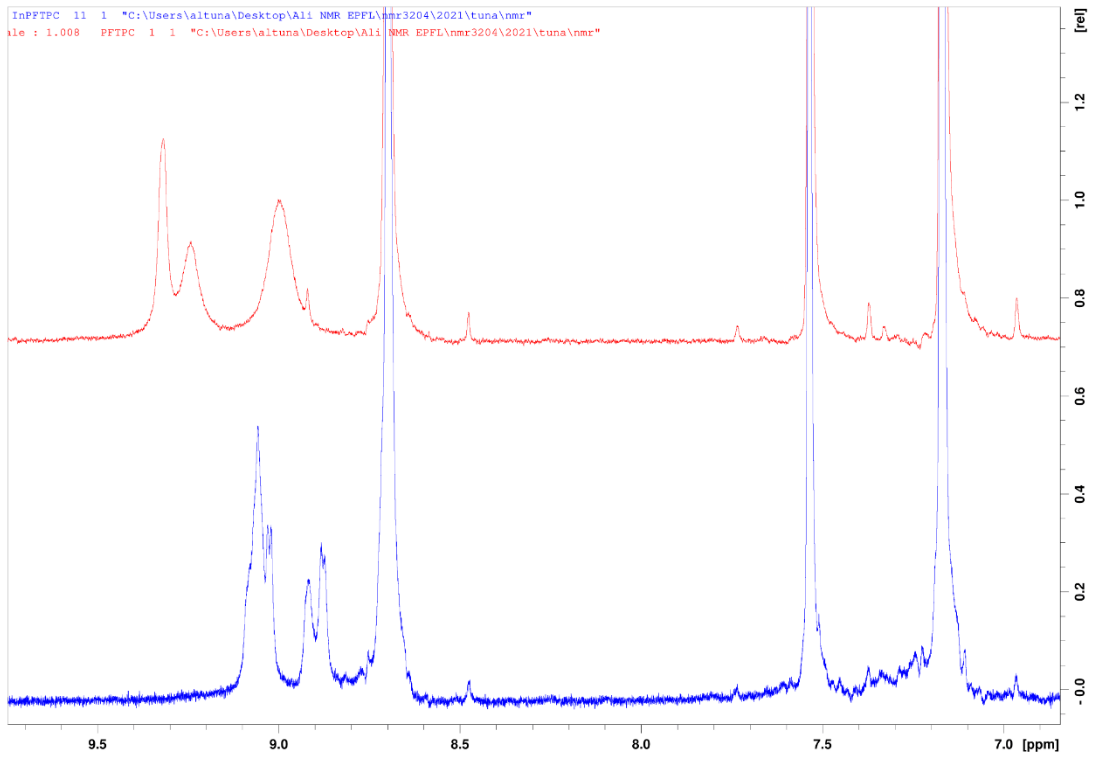

Figure S10. The ^{1}H-NMR spectra comparison of free-base corrole (**red**) and indium corrole complex 1 (**blue**) in d_5-pyridine

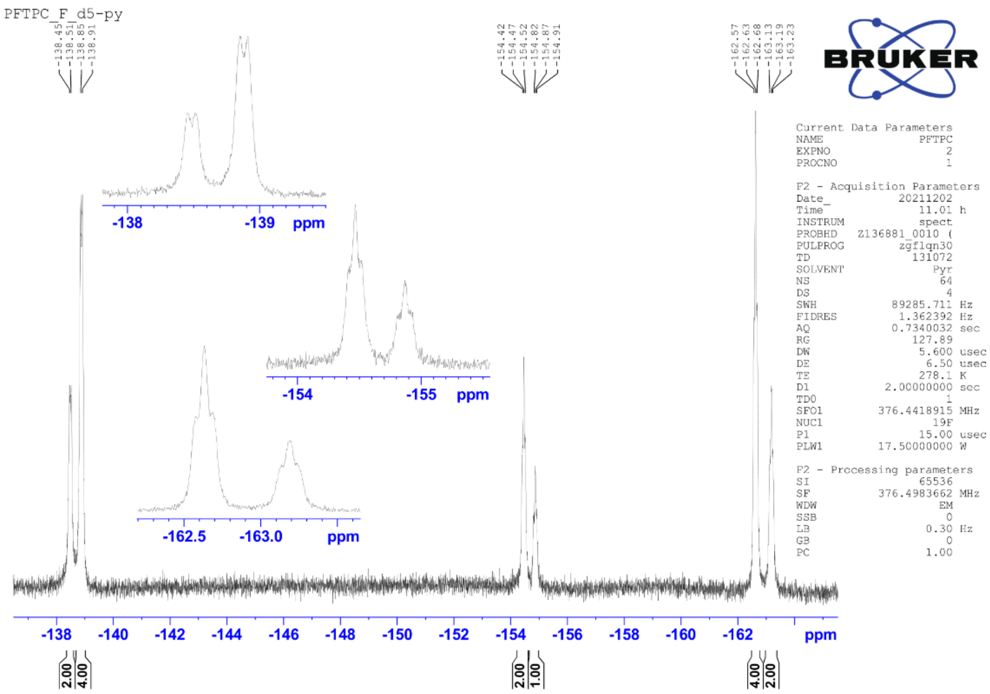

Figure S11. The ^{19}F-NMR spectrum of free-base corrole in d_5-pyridine

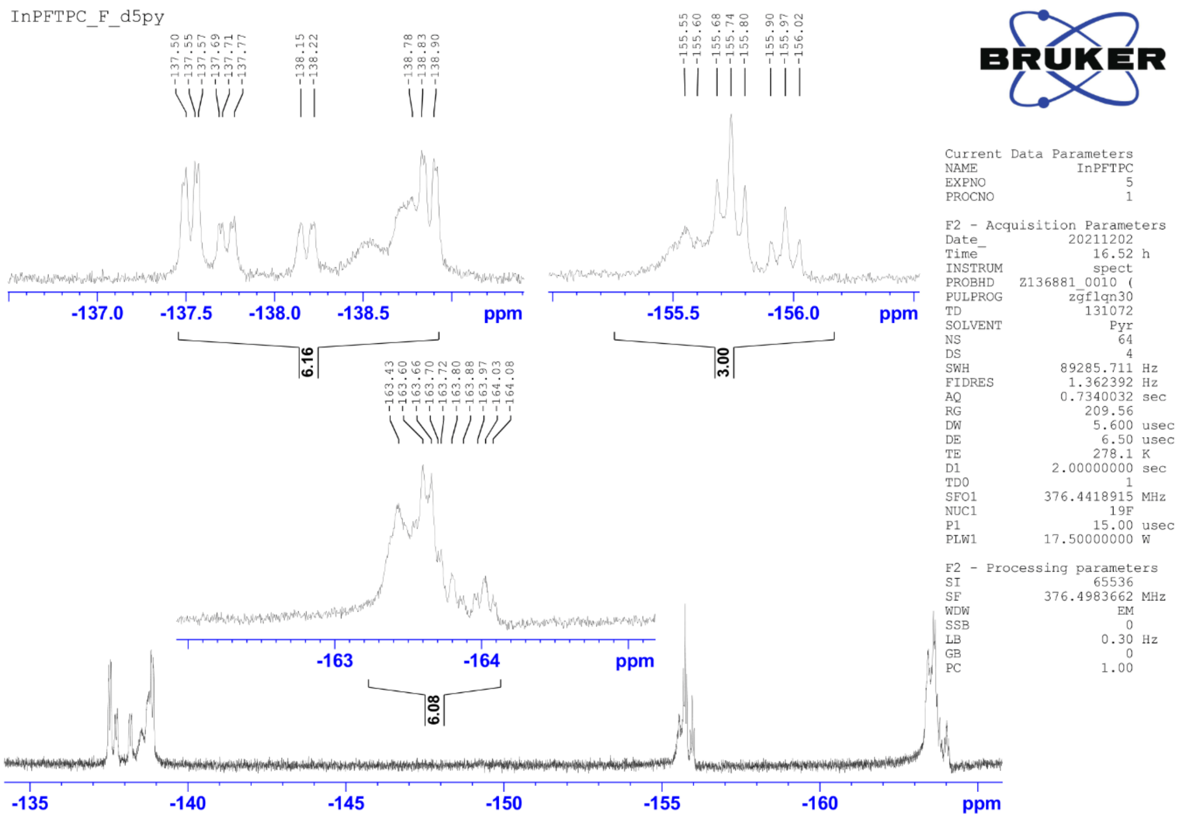

Figure S12. The ^{19}F-NMR spectrum of indium corrole complex 1 in d_5-pyridine

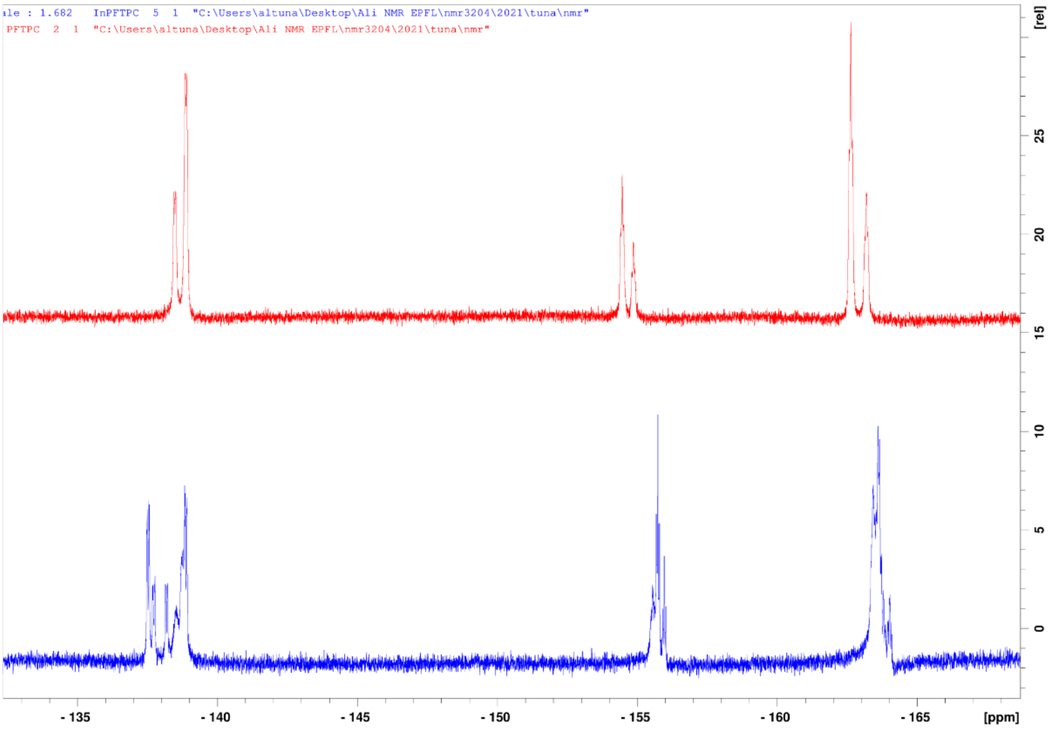

Figure S13. The ^{19}F-NMR spectra comparison of free-base corrole (**blue**) and indium corrole complex 1 (**red**) in d_5-pyridine

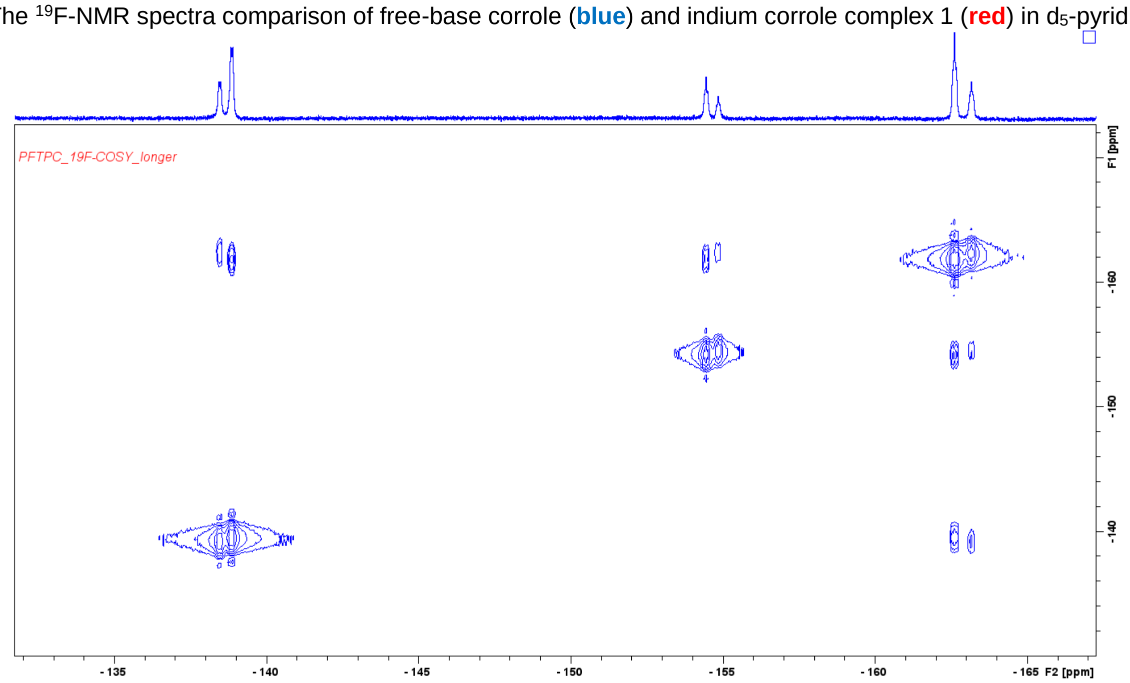

Figure S14. The ^{19}F-^{19}F COSY NMR spectrum of free-base corrole in d_5-pyridine

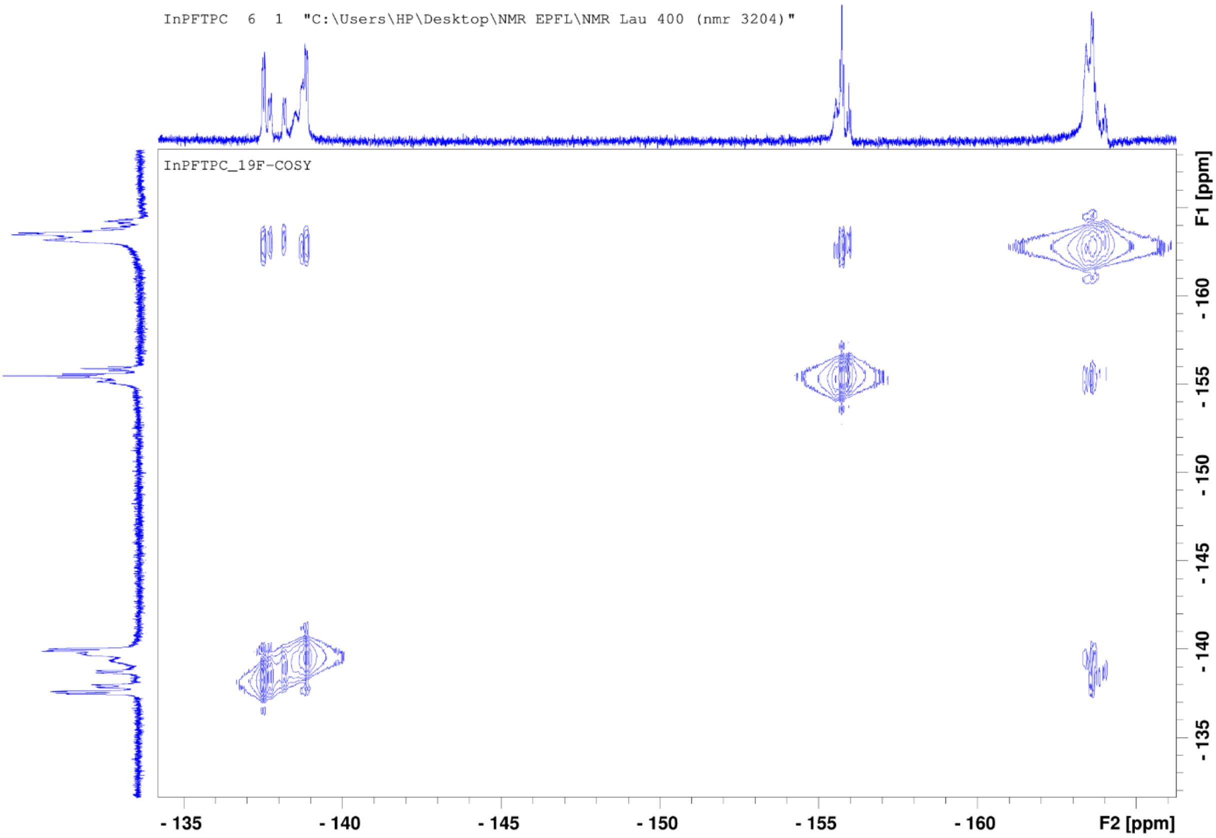

Figure S15. The ^{19}F-^{19}F COSY NMR spectrum of indium corrole complex 1 in d_5-pyridine

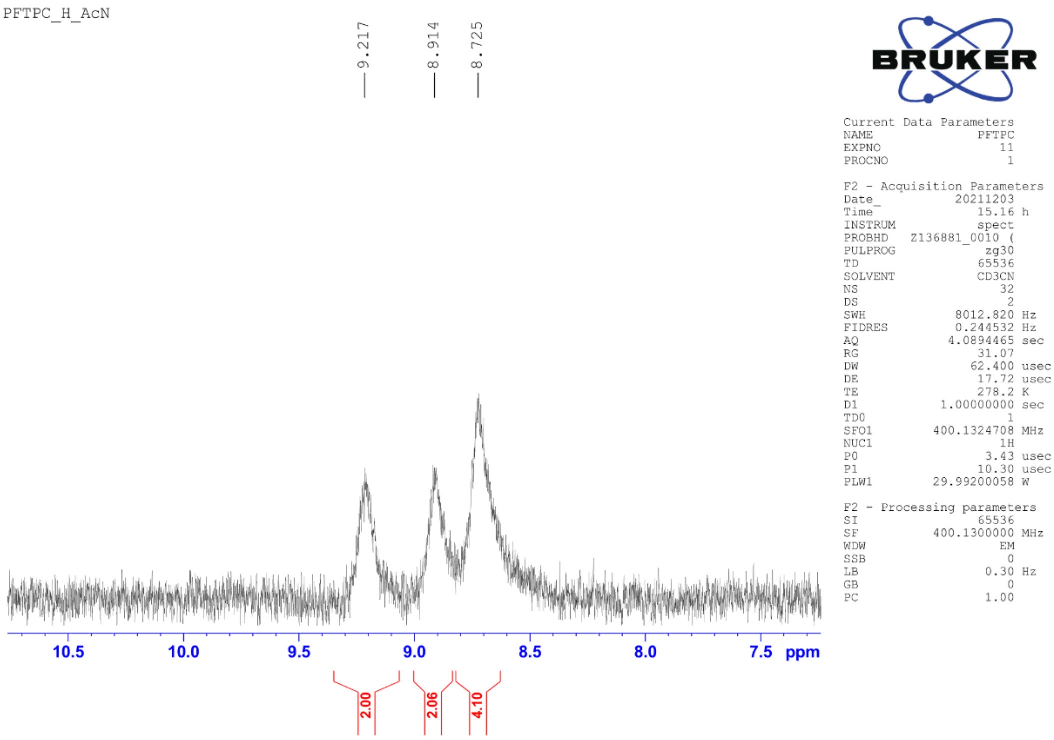

Figure S16. The ^1H-NMR spectrum of free-base corrole in d_3-acetonitrile

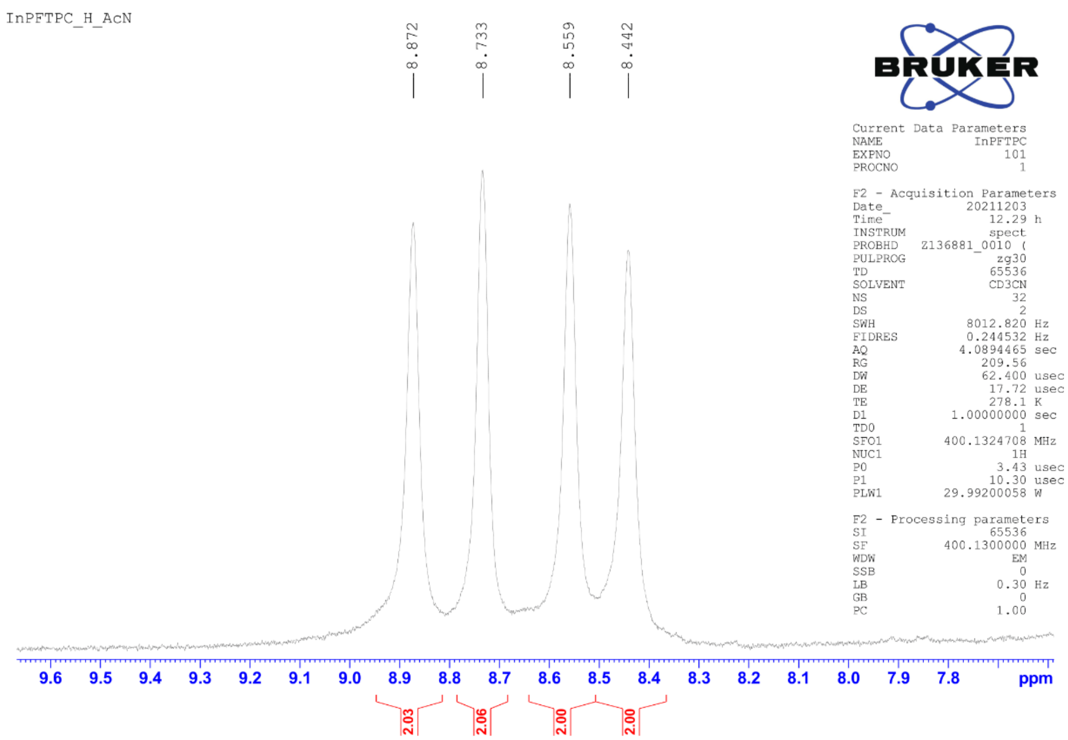

Figure S17. The ^{1}H-NMR spectrum of indium corrole complex 2 in d_3-acetonitrile

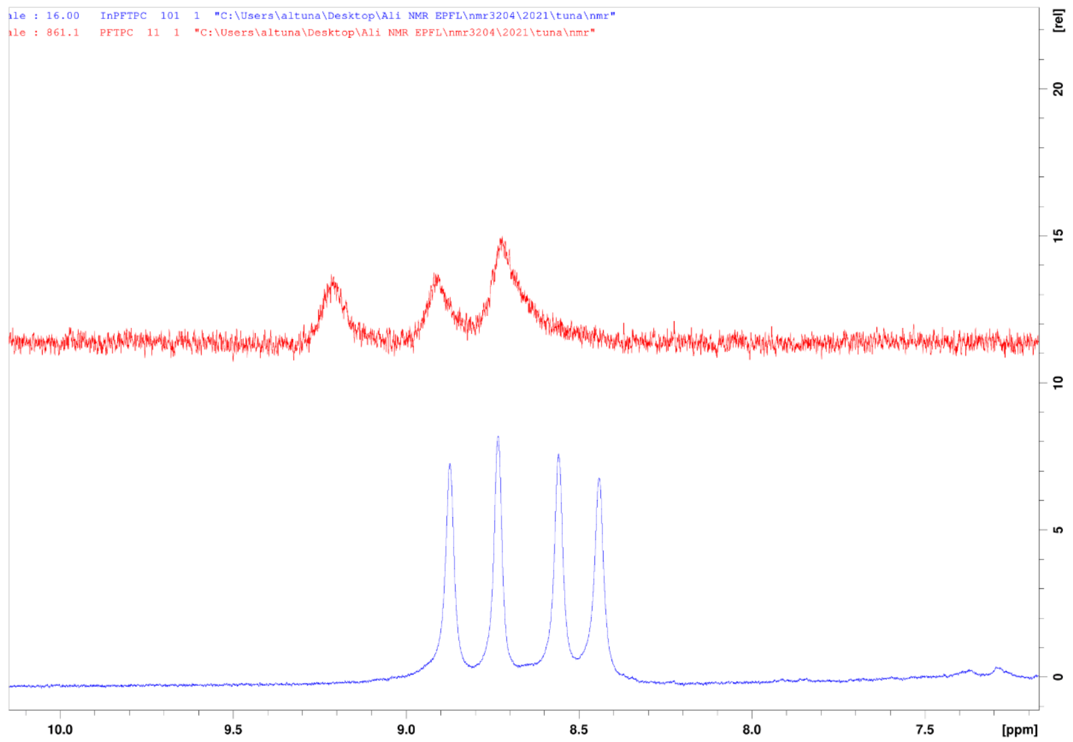

Figure S18. The ^{1}H-NMR spectra comparison of free-base corrole (**blue**) and indium corrole complex 2 (**red**) in d_3-acetonitrile

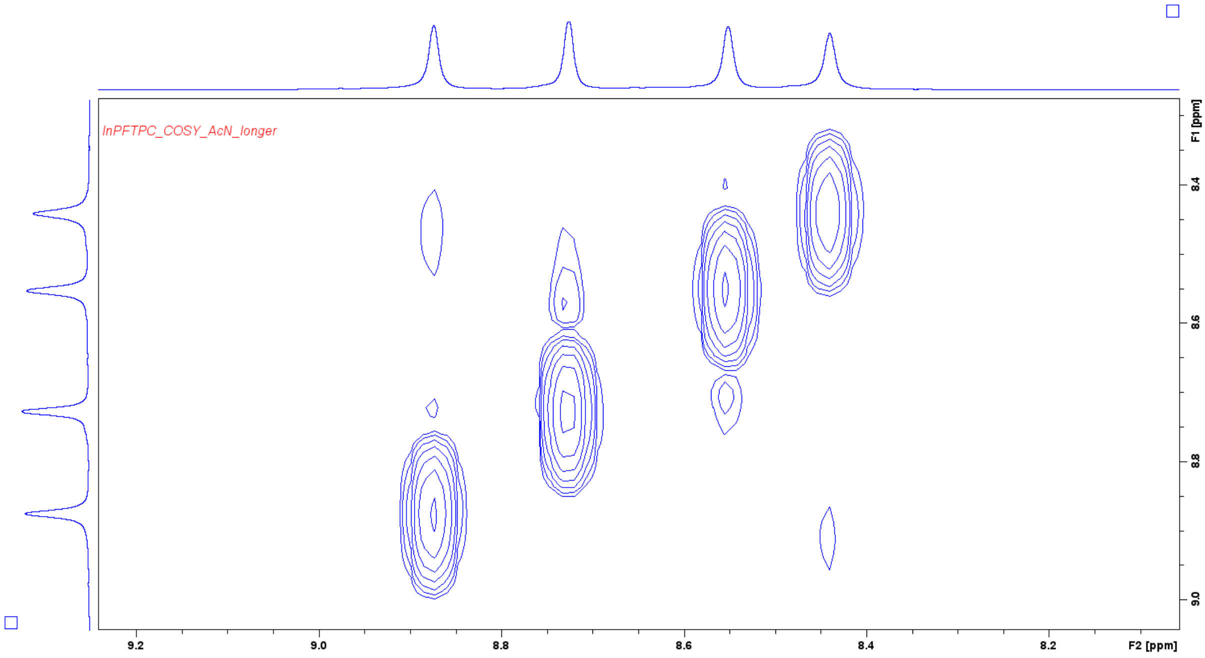

Figure S19. The ^{1}H -^{1}H COSY NMR spectrum of indium corrole complex 2 in d_3-acetonitrile

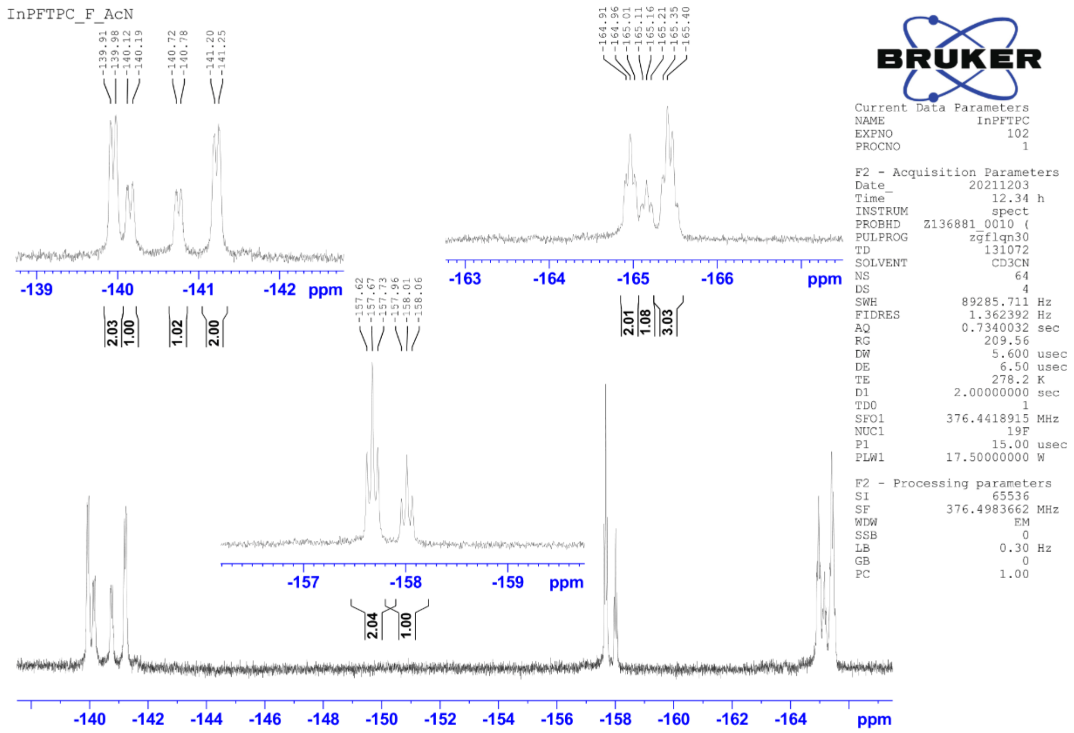

Figure S20. The ^{19}F-NMR spectrum of indium corrole complex 2 in d_3-acetonitrile

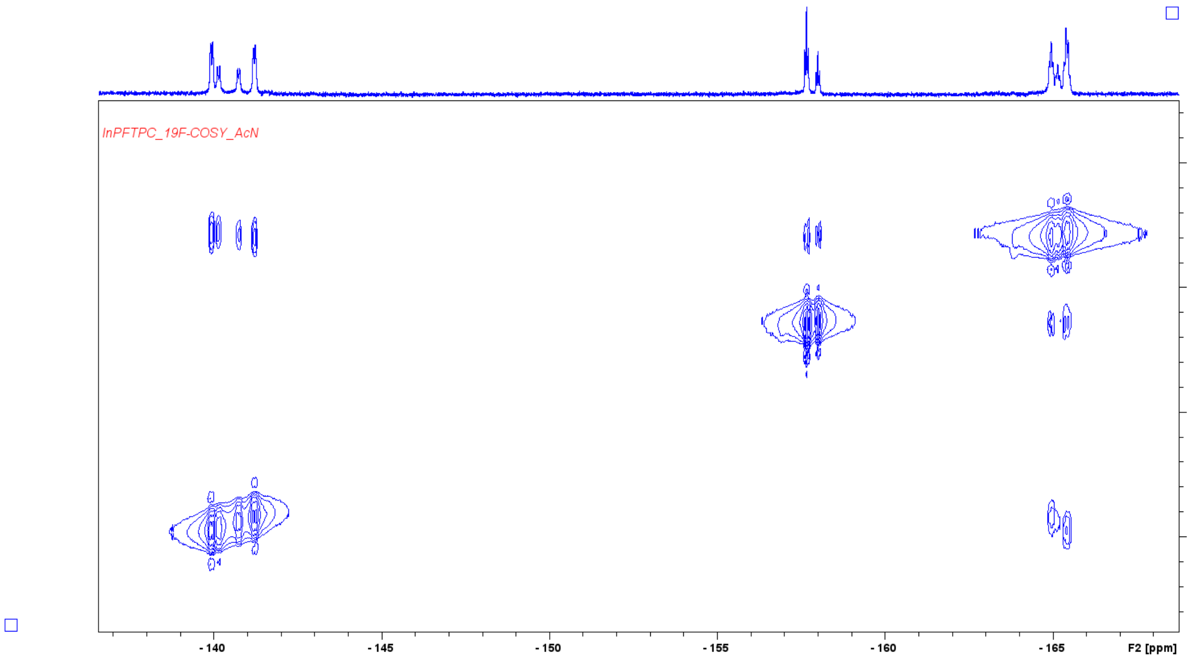

Figure S21. The ^{19}F-^{19}F COSY NMR spectrum of indium corrole complex 2 in d_3-acetonitrile

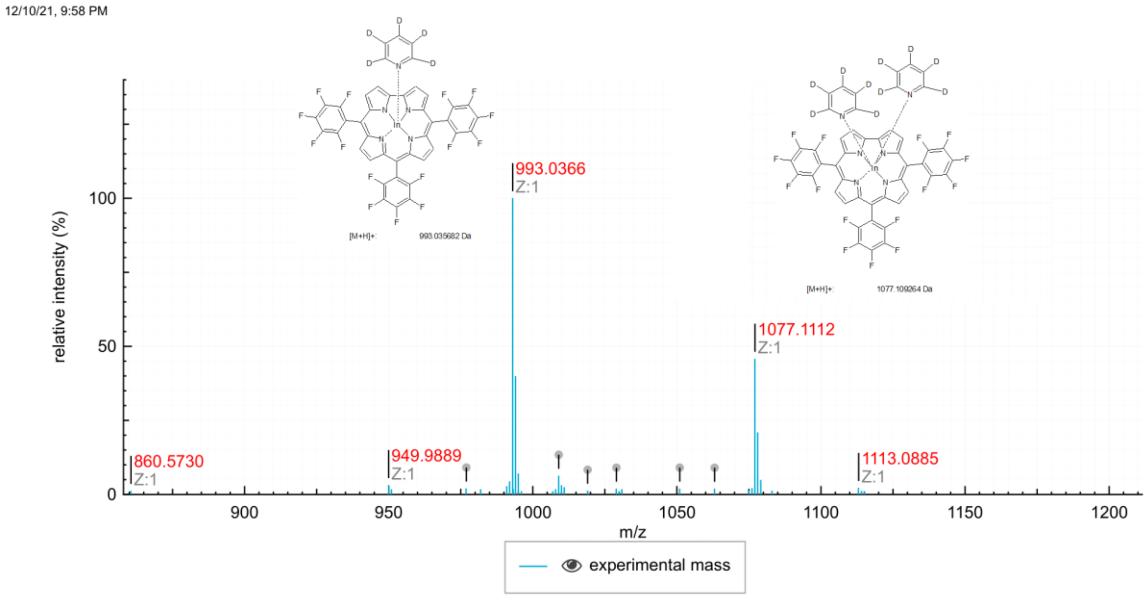

Figure S22. The experimental HR-MS spectrum of indium corrole complex 1 in d_5-pyridine/dilution with acetonitrile (visualized on EPFL's online spectra viewer/visualising program)

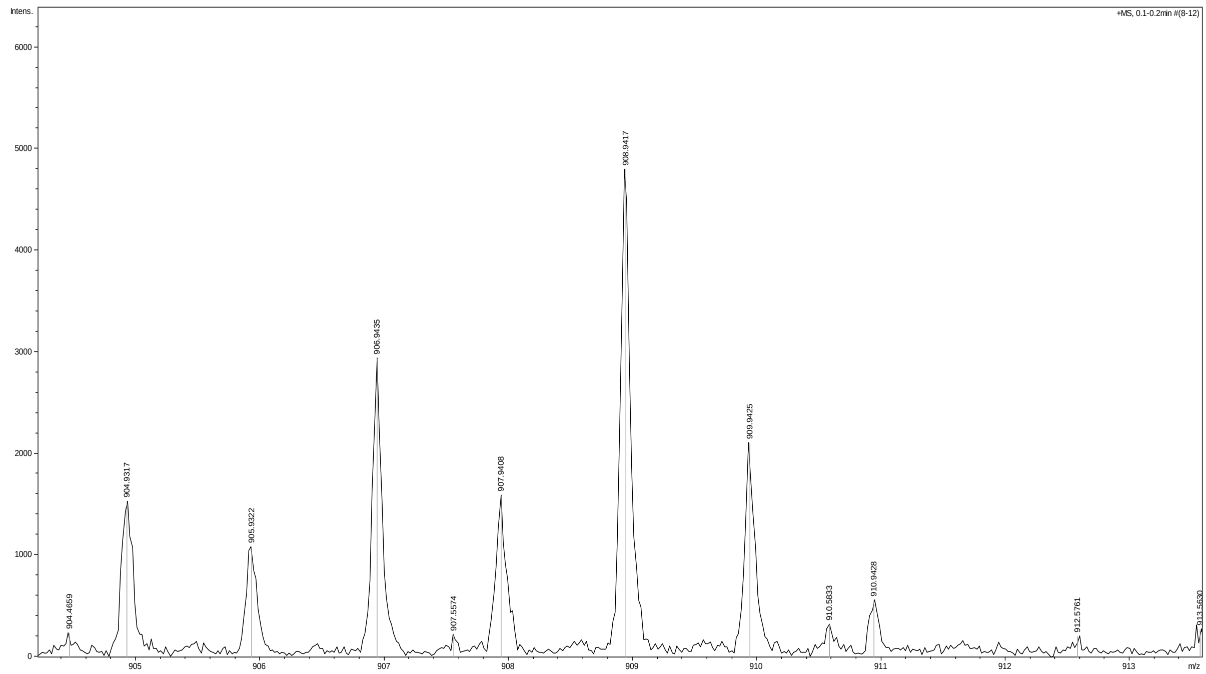

Figure S23. The HR-MS spectrum of indium corrole complex 2 in d_3-acetonitrile/dilution with acetonitrile

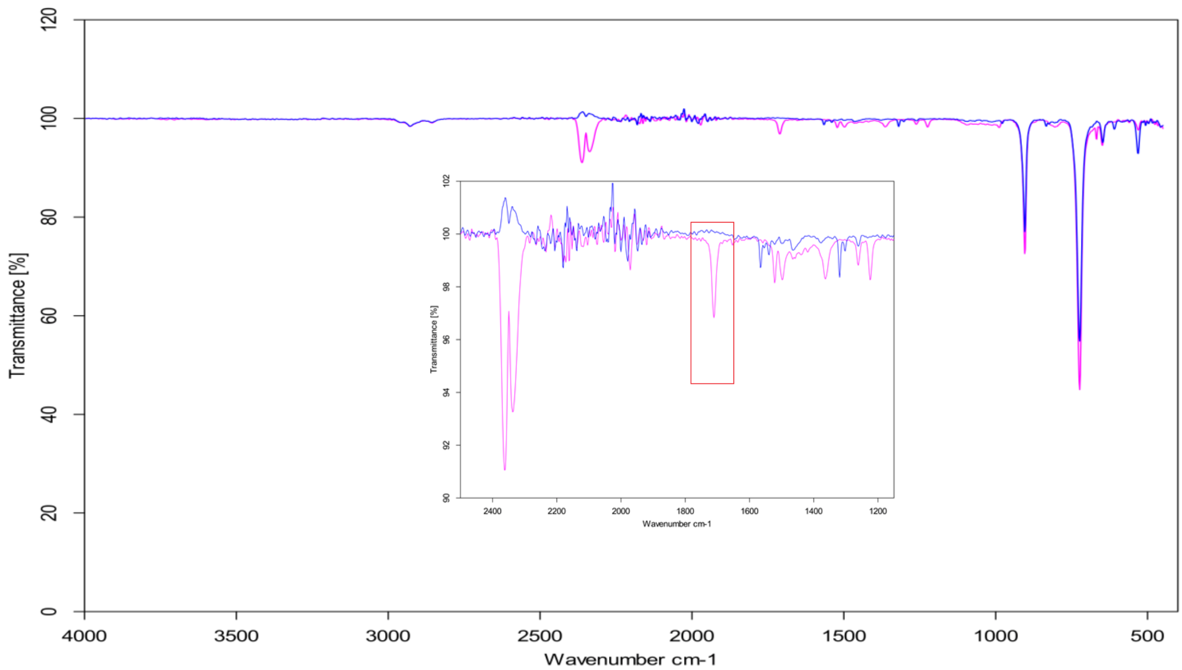

Figure S24. The ATR-FTIR spectrum of free-base corrole (**pink**) and indium corrole complex 1 (**blue**) in d_5-pyridine

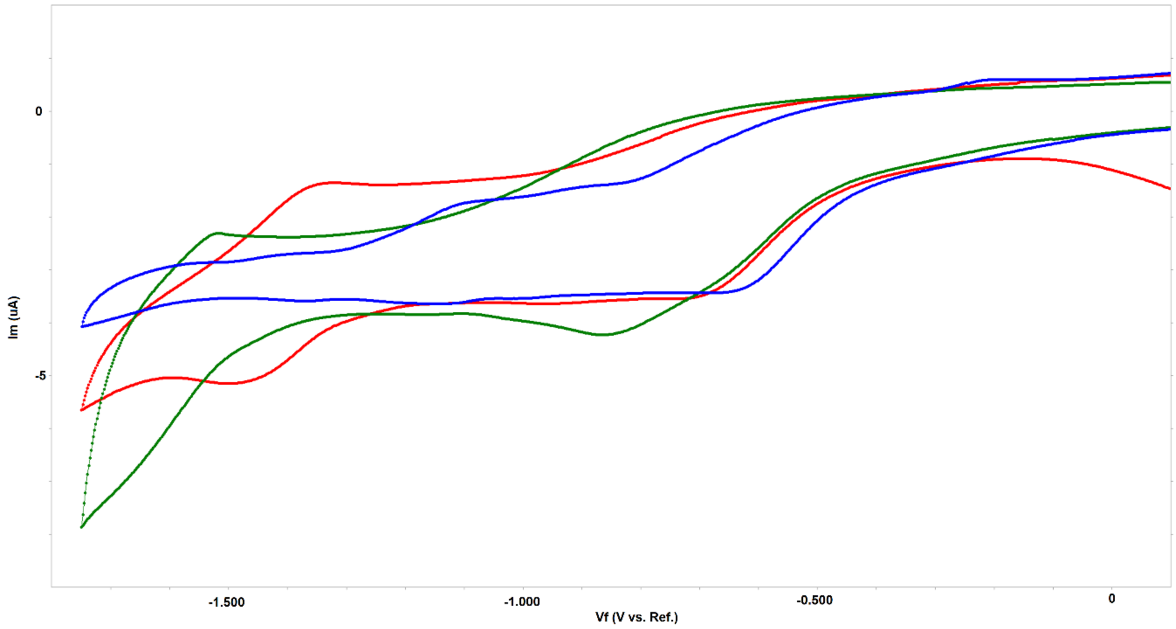

Figure S25. The cyclic voltammogram of free-base corrole (**blue**), indium corrole complex 1 (**green**) and indium corrole complex 1 after addition of ferrocene (**red**) plus 100 mM TBAP as a supporting electrolyte versus Ag/$AgNO_3$ in pyridine (scan rate: 50 mV/sec)

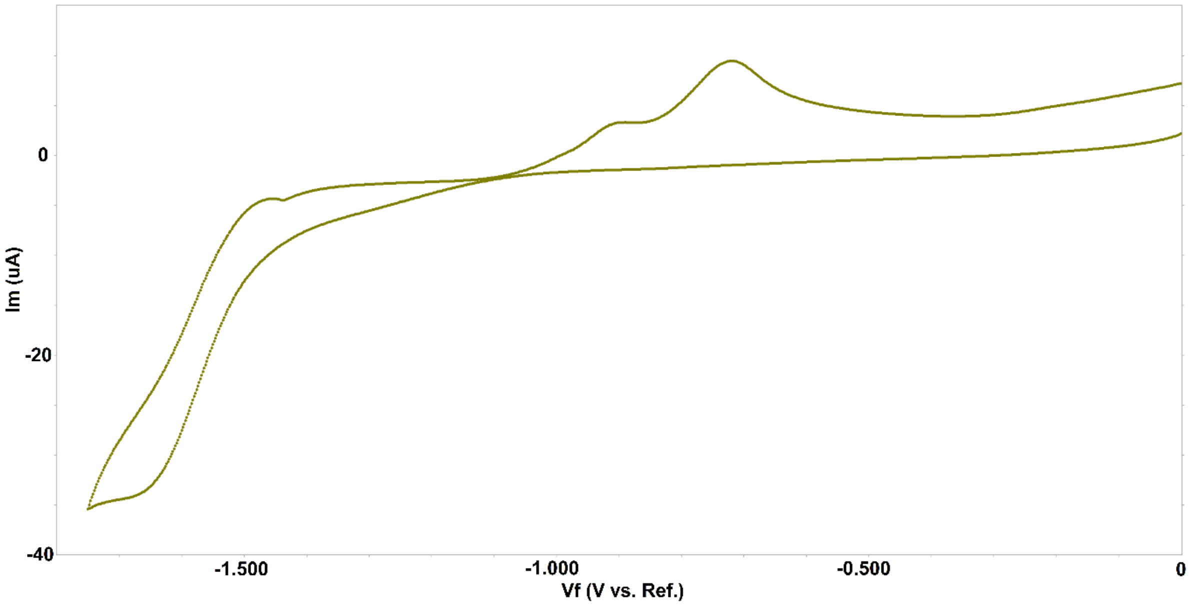

Figure S26. The cyclic voltammogram of indium corrole complex 1 plus 100 mM TBAP as a supporting electrolyte versus Ag/$AgNO_3$ in pyridine as showing reduction of indium corrole to demetallation and free indium species' formations (scan rate: 100 mV/sec)

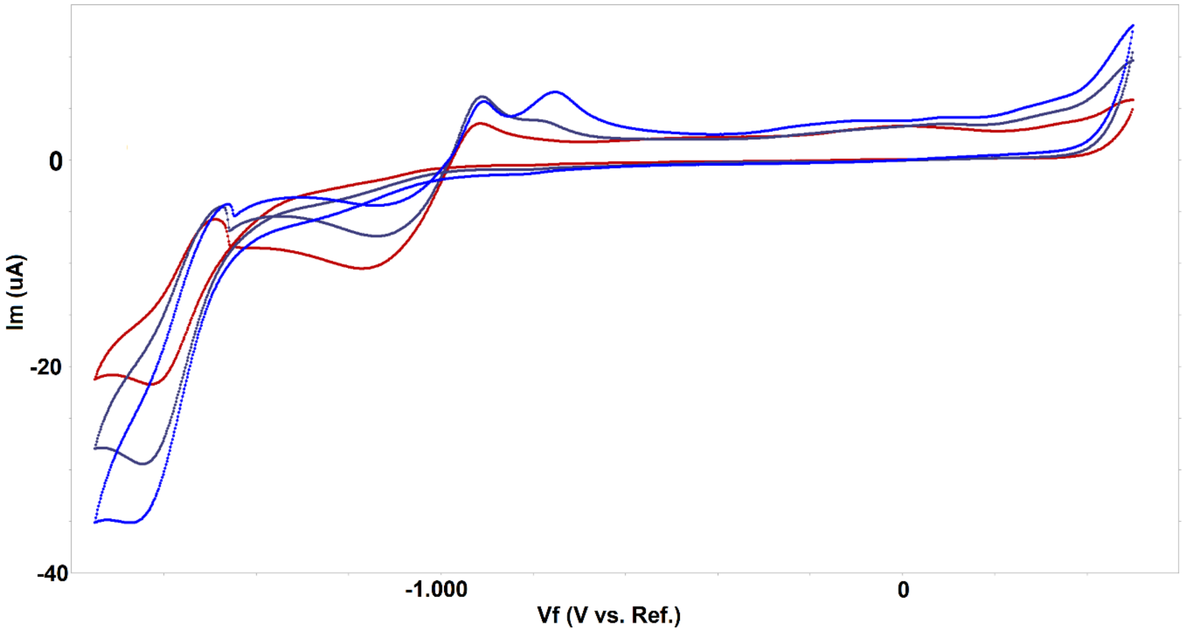

Figure S27. The cyclic voltammogram of indium corrole complex 1 plus 100 mM TBAP as a supporting electrolyte versus Ag/$AgNO_3$ in pyridine: first scan (**blue**), second scan (**black**) and third scan (**brown**) as showing demetallation and formation of In(0), In(I), In(II) and In(III) by time (scan rate: 75 mV/sec)

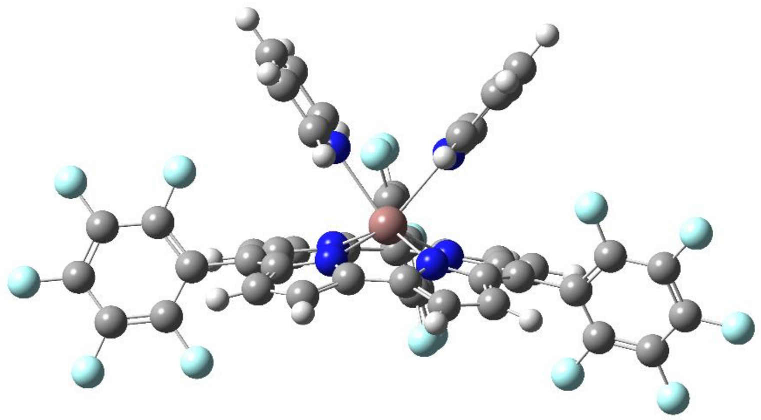

Figure S28. The DFT optimized structure of indium corrole complex 1 in pyridine

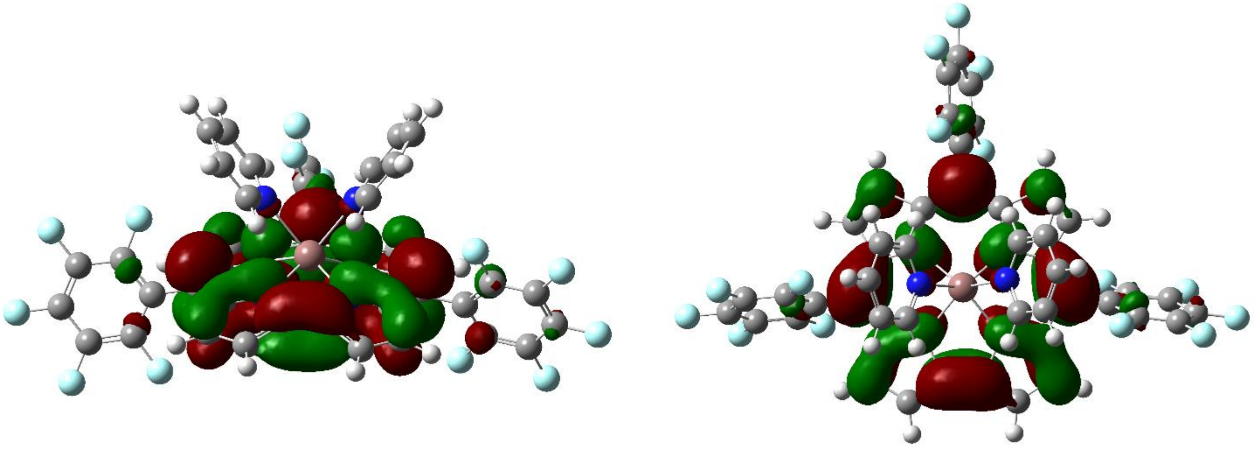

Figure S29. The DFT optimized LUMO of indium corrole complex 1 in pyridine

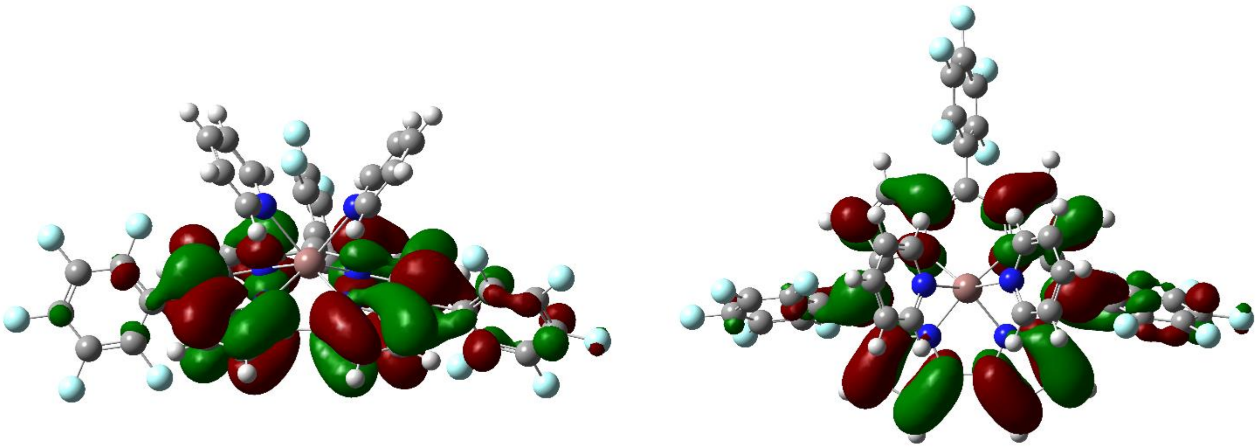

Figure S30. The DFT optimized HOMO of indium corrole complex 1 in pyridine

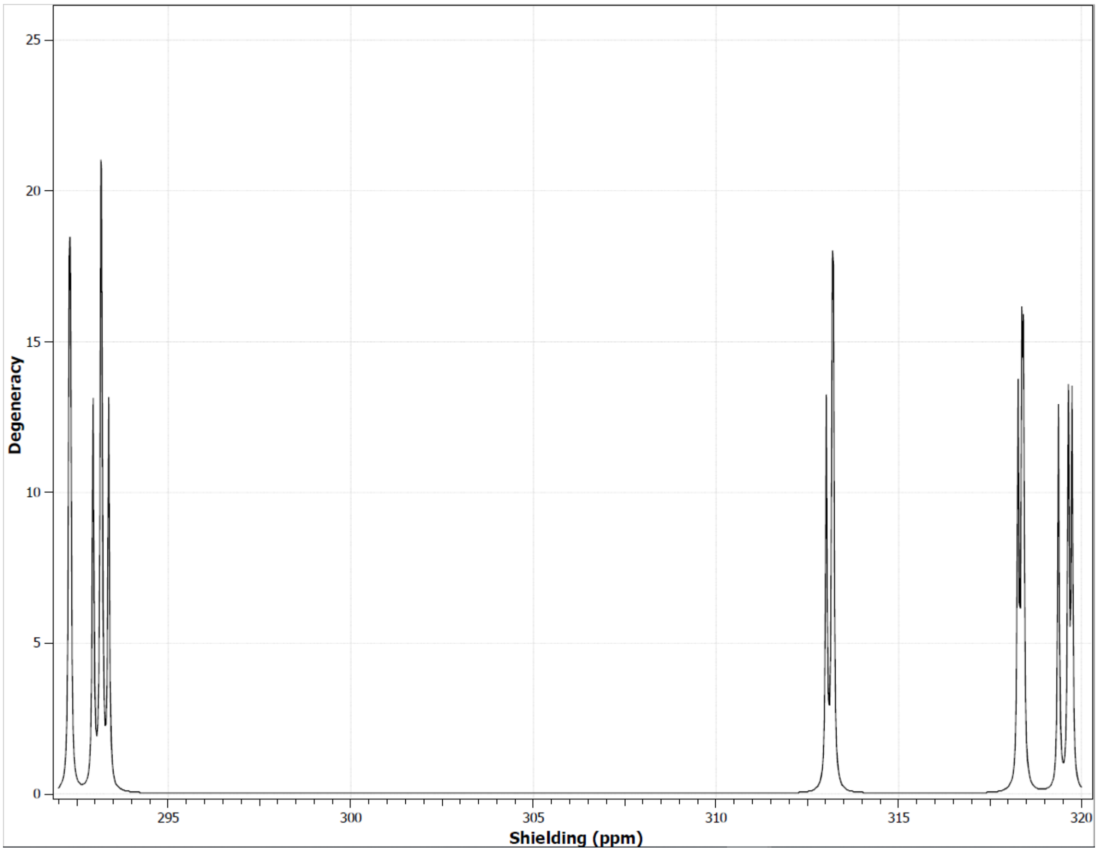

Figure S31. The DFT optimized ^{19}F-NMR spectrum of indium corrole complex 1 in pyridine (with shielding)

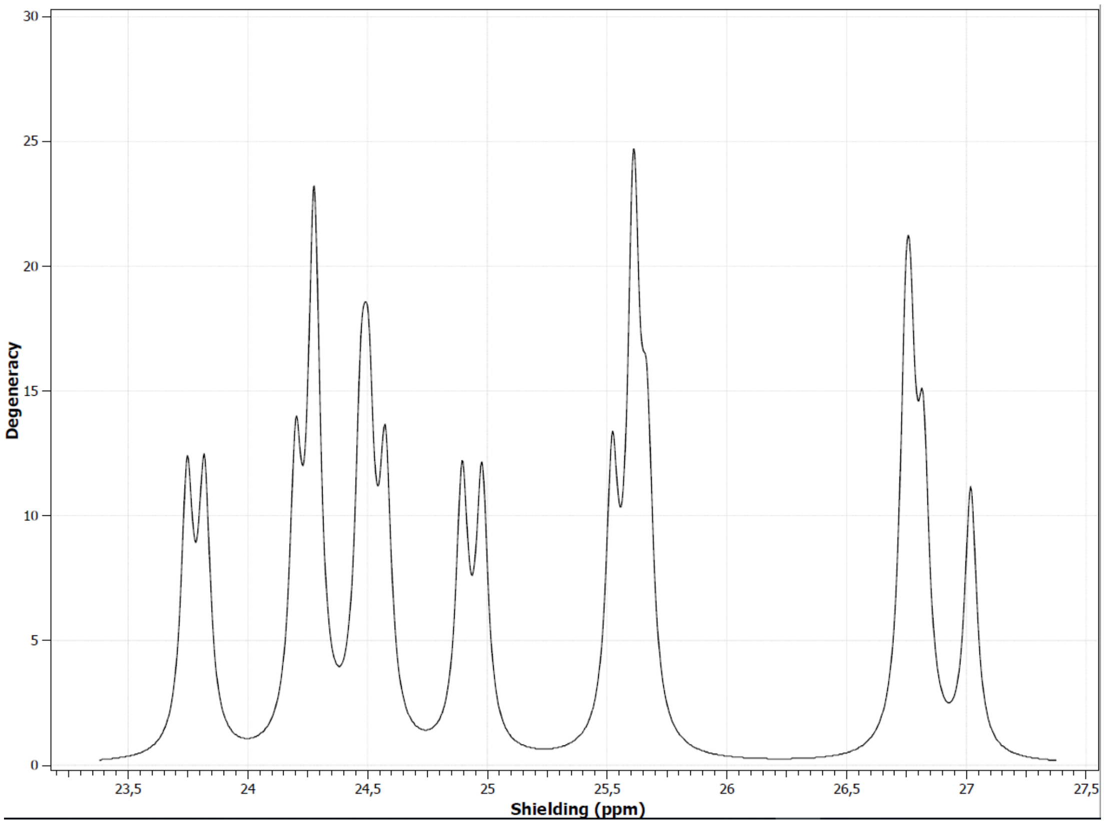

Figure S32. The DFT optimized ^{1}H-NMR spectrum of indium corrole complex 1 in pyridine (with shielding)

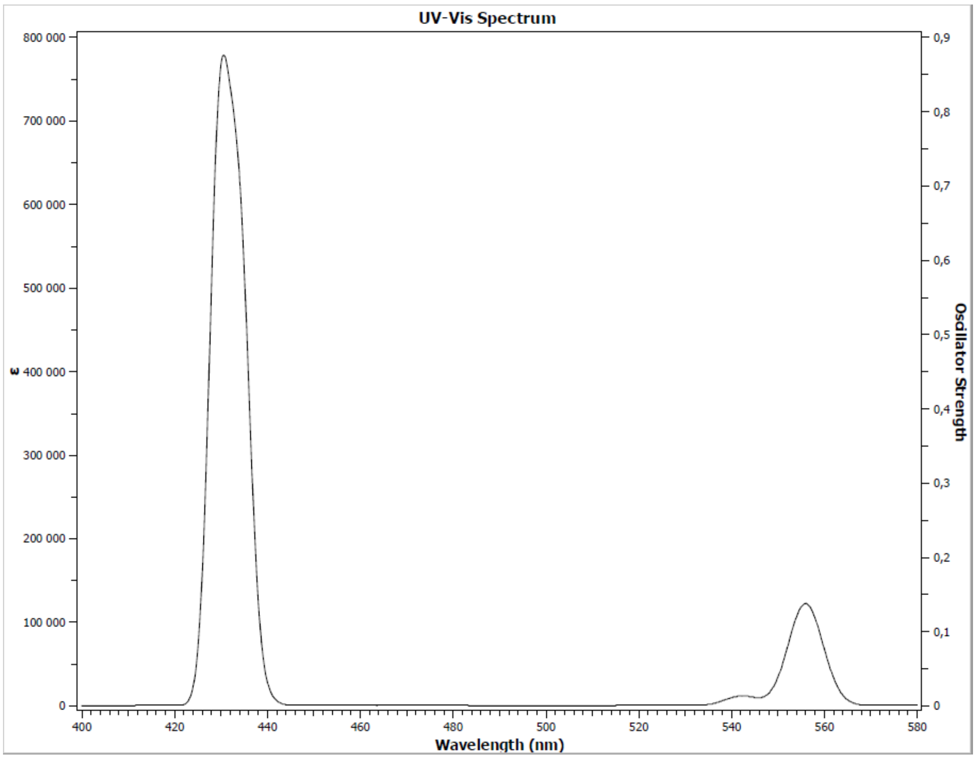

Figure S33. The DFT optimized UV-vis spectrum of indium corrole complex 1 in pyridine

Table S1. The DFT optimization parameters of indium corrole complex 1 in pyridine

InPFTPC_py_py_syn_pyridine_OPT_25092023_1025					
FOpt RB3LYP LANL2DZ					
Number of atoms I 87					
Info1-9 I N= 9					
186	185	0	0	0	110
2	18	-502			
Full Title C N= 47					
InPFTPC_py_py_syn_pyridine_OPT_25092023_1025					
Route C N= 9					
# opt b3lyp/lanl2dz scrf=(solvent=pyridine) pop=(full,nbo,savenbos) geom=connectivity scf=maxcycle=1000					
Charge I 0 Multiplicity I 1 Number of electrons I 480 Number of alpha electrons I 240 Number of beta electrons I 240 Number of basis functions I 656 Number of independent functions I 656 Number of point charges in /Mol/ I 0 Number of translation vectors I 0					
Atomic numbers I N= 87					
6	6	6	6	6	6
6	6	6	6	6	6
6	6	6	6	6	6
6	6	7	7	7	7
6	6	6	6	6	6
6	6	6	6	6	6
6	6	6	6	6	1
1	1	1	1	1	1
1	9	9	9	9	9
9	9	9	9	9	9
9	9	9	9	49	6
6	6	6	6	6	6
6	6	6	7	7	1
1	1	1	1	1	1
1	1	1			

Table S2. The current cartesian coordinates of DFT optimized indium corrole complex 1 in pyridine

2.36713853E+00	3.62148250E+00	-4.58890024E-01	-2.42528326E+00	3.55366897E+00
-5.18158572E-01	-5.27524614E+00	3.66525656E-01	-9.51912763E-01	-6.63099029E+00
2.74971836E+00	-1.14859200E+00	-4.89854653E+00	4.69277129E+00	-8.84692994E-01
5.32649699E+00	5.18666406E-01	-7.99834648E-01	6.62797473E+00	2.94052807E+00
-8.08642480E-01	4.83215047E+00	4.82965449E+00	-6.01373378E-01	6.43570499E+00
-1.90139806E+00	-1.18048517E+00	9.22538697E+00	-2.04147756E+00	-1.61243634E+00
5.06050418E+00	-4.21698339E+00	-1.40708482E+00	1.50983179E+00	-6.55970547E+00
-1.80249410E+00	5.76497145E+00	-6.61615836E+00	-2.53809511E+00	3.55208313E+00
-8.05659378E+00	-2.79494139E+00	-1.21259769E+00	-6.58668883E+00	-1.87227698E+00
-4.84279520E+00	-4.34669598E+00	-1.61956259E+00	-3.18790882E+00	-8.17627911E+00
-2.86227156E+00	-5.44989550E+00	-6.80302183E+00	-2.68599169E+00	-6.29251409E+00
-2.08215051E+00	-1.40060044E+00	-9.07356729E+00	-2.26339228E+00	-1.89467976E+00
2.72928985E+00	1.01307065E+00	-5.01721015E-01	2.51088151E+00	-4.31945155E+00
-8.89545160E-01	-2.29820062E+00	-4.34994852E+00	-1.06313960E+00	-2.72006285E+00
9.40816653E-01	-4.91733042E-01	1.08415277E+01	-3.25005645E+00	1.19085289E-01
1.34484546E+01	-3.46179234E+00	-2.57515656E-01	1.45392220E+01	-2.44247531E+00
-2.43578990E+00	1.30028926E+01	-1.23390688E+00	-4.21119361E+00	1.03999659E+01
-1.05666832E+00	-3.78566361E+00	-1.08527548E+01	-2.14078369E+00	7.43982356E-02
-1.34567589E+01	-2.33161038E+00	-3.34352393E-01	-1.43688787E+01	-2.66464640E+00
-2.79033388E+00	-1.00709145E+01	-2.59080921E+00	-4.33519315E+00	-1.26651509E+01
-2.79343441E+00	-4.80375825E+00	5.71553217E-01	9.17134439E+00	-2.33436131E+00
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1.30160197E+01	-1.98086082E-02	-1.08901896E-01	7.63419583E+00	-2.75093076E-01
-4.65647058E-02	4.81025083E+00	-3.83193960E-01	-7.29149229E+00	-7.42493909E+00
-3.32124782E+00	-2.95405337E+00	-1.00505356E+01	-3.64495252E+00	3.38970770E+00
-9.90608760E+00	-3.65128182E+00	7.63339303E+00	-7.14518611E+00	-3.18034843E+00
8.64614898E+00	3.20718879E+00	-9.87792953E-01	5.18313624E+00	6.84257209E+00
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2.94969416E+00	-1.52600329E+00	1.40637789E+01	-2.41908706E-01	-6.38725156E+00
8.95028199E+00	9.82507349E-02	-5.64287067E+00	9.85373319E+00	-4.25555076E+00
2.33424021E+00	1.49563031E+01	-4.65499889E+00	1.51731639E+00	1.71137659E+01
-2.63309871E+00	-2.83250511E+00	-1.00287008E+01	-1.84286900E+00	2.54929701E+00
-8.45378058E+00	-2.68124787E+00	-6.39921571E+00	-1.35557346E+01	-3.10649110E+00
-7.24343134E+00	-1.69369817E+01	-2.85978472E+00	-3.22404916E+00	-1.51330999E+01
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1.31117868E+00	8.06397460E+00	-4.59505635E+00	1.17874966E+00	1.32405107E+01
-4.31911781E+00	-3.72552024E-01	1.56236524E+01	1.03674040E-01	-1.75959141E+00
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3.45005074E+00	2.48654018E-01	5.60726750E+00	3.45321673E+00	-4.16452033E+00
5.25142433E+00	4.99097950E+00	1.52624135E-01	7.76207971E+00	4.99753424E+00
-4.41268350E+00	7.39151361E+00	5.77747845E+00	-2.21862939E+00	8.67726861E+00
-3.53111501E+00	-4.54766402E+00	4.96769106E+00	-3.59383292E+00	-1.64147122E-01
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4.37256542E+00	2.83712593E+00	2.04526852E+00	4.83480077E+00	2.84577130E+00
-5.81103732E+00	4.19338723E+00	5.55837546E+00	1.89379632E+00	8.68250189E+00
5.57427431E+00	-6.27774519E+00	8.01558515E+00	6.97412692E+00	-2.35176411E+00
1.03388547E+01	-7.25543843E+00	-3.07367526E+00	1.00206384E+01	-5.71771377E+00
-6.84225701E+00	7.53010532E+00	-2.86437768E+00	-6.12364154E+00	3.84049005E+00
-2.97470275E+00	1.68209072E+00	4.94320206E+00	-5.83772604E+00	1.27639435E+00
8.66454407E+00				