# Unexpected C−F activation during redox transmetallation with silver N,N′-bis(2,6-difluorophenyl)formamidinate

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*Dedicated to our good old friend and colleague, Professor Cameron Jones on the occasion of his much celebrated 60th birthday, we made it!*

The trivalent lanthanoid formamidinates, [Yb₂(DFForm)₄F₂(py)₂]·CH₃CN (**1**) (DFForm = N,N′-bis(2,6-difluorophenyl)formamidinate), and [La₆(DFForm)₈F₈O-(CH₃CN)₂]·6CH₃CN (**2**) have been prepared from redox trans-metallation (RT) reactions employing lanthanoid metals and silver formamidinate (AgDFForm) in CH₃CN. C−F activation was observed in both reactions. The structure of **1** is a fluorine bridged dimer with two seven-coordinate ytterbium metal ions.

Surprisingly the lanthanum complex is a trivalent cage with an unexpected central oxygen atom. [La₆(DFForm)₈F₈O-(CH₃CN)₂]·6CH₃CN (**2**) formed a 15 membered ring cage of six La atoms, eight F and one O at the centre. There are three different La³⁺ ions in **2** with two different coordination numbers. All the La atoms are coordinated by four bridging fluorides and the central oxygen.

## Introduction

Highly reactive lanthanoid complexes have been successfully prepared by redox transmetallation protolysis (RTP) reactions using mercury compounds, silver compounds, and bismuth compounds (Scheme 1 Equation 1).[1–5] Pentafluorophenylsilver $AgC_6F_5$ showed excellent oxidising abilities in the synthesis of lanthanoid pyrazolates (Scheme 1 Equation 2),[3,4] while this reagent was unsuccessful for the bulkier formamidinate ligands.[5]

Silver(I) complexes AgL (L = $C_6F_5$, N-heterocyclic carbenes, etc.) have been widely used in redox transmetallation (RT) reactions to transfer the L groups to metal compounds, especially for transition metal, alkaline earth metal, and rare earth metal complexes (Scheme 1 Equation 3),[6–7] consistent with the favourable $Ag^+/Ag^0$ reduction potential.[8] Recently we have reported a rapid efficient synthesis of silver formamidinates by treating silver(I) oxide with the corresponding

formamidines either in pyridine or acetonitrile (Scheme 1 Equation 4).[9]

Owing to the problematic nature of RTP reactions with pentafluorophenylsilver and formamidines, the reactivity of silver N,N′-bis(2,6-difluorophenyl)formamidinate ([Ag₂(DFForm)₂(py)₂]) was investigated in redox transmetallation (RT) reactions with two electropositive lanthanoid metals (Ln = La, Yb) as a new synthetic approach. Interestingly, C−F activation was observed in both reactions, and the only source of F is from AgDFForm. This a surprise, as DFFormH has been used in a wide range of lanthanoid free metal/DFFormH reactions without C−F activation being observed. These include direct reactions of Eu or Hg-activated Yb with DFFormH in acetonitrile,[10] and redox transmetallation/protolysis reactions between Yb, Hg($C_6F_5$)₂ and DFFormH in thf,[10] a range of Ln metals with Bi($C_6F_5$)₃ and DFFormH in thf,[5] $I_2$ activated Ln metals with $AgC_6F_5$ and DFFormH in thf,[5] and Eu with $AgC_6F_5$ and DFFormH in pyridine[4] and direct reactions of Ln metals with iodine and DFFormH giving LnI$_n$(DFForm)$_{3-n}$ complexes.[11] C−F activation has attracted much interest over four decades and is of major current interest in rare earth chemistry.[4,12–14] Unlike the RTP reactions,[5] the Ln metals react cleanly with AgDFForm in CH₃CN without the need for activation of the metal with iodine.

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## Results and discussion

### Synthesis and Characterisation

Lanthanoid formamidinates, [Yb₂(DFForm)₄F₂(py)₂]·CH₃CN (**1**) and [La₆(DFForm)₈F₈O(CH₃CN)₂]·6CH₃CN (**2**) were isolated following redox-transmetallation (RT) reactions in acetonitrile (CH₃CN) between silver N,N′-bis(2,6-difluorophenyl)formamidinate ([Ag₂(DFForm)₂(py)₂]) and an ex-

$$m \, Ln + n \, MR_m + mn \, LH \longrightarrow m \, Ln(L)_n + n \, M + mn \, RH \quad (1)$$
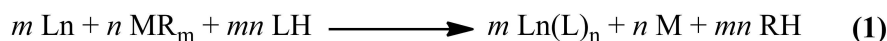
m = 1-3, n = 2, 3;
M = Ag, Hg, Bi; R = Ph, C$_6$F$_5$, PhCC;
L = OAr, NR$_2$, pz, Form, Cp, etc

$$Ln + n \, AgC_6F_5 + n \, LH \longrightarrow Ln(L)_n + n \, Ag + n \, C_6F_5H \quad (2)$$

$$Ln + n \, AgL \longrightarrow Ln(L)_n + nAg \quad (3)$$

$$Ag_2O + 2 \, LH \longrightarrow 2 \, AgL + H_2O \quad (4)$$

LH = pzH, FormH

**Scheme 1.** (Eq. 1) General redox transmetallation/protolysis reactions involving Ag, Hg and Bi reagents; (Eq. 2) Redox transmetallation/protolysis reaction involving AgC$_6$F$_5$; (Eq. 3) Redox transmetallation reaction involving silver complexes; (Eq. 4) Formation of silver complexes.

cess of lanthanoid metal (Scheme 2). [Ag$_2$(DFForm)$_2$(py)$_2$] was synthesised from Ag$_2$O and DFFormH in pyridine,[9] and provides the pyridine ligands coordinated in **1**. The RT reaction mixtures were ultrasonicated for 3 days. The reaction mixture giving **1** was also monitored by $^{19}$F NMR spectroscopy until no further change was observed. Completion of the reactions was demonstrated by qualitative testing of an aliquot of the reaction mixture with HCl, when no AgCl precipitated, thereby indicating complete consumption of AgDFForm. A silver mirror was also formed, as expected for redox transmetallation (Scheme 2). The reaction mixture giving [Yb$_2$(DFForm)$_4$F$_2$(py)$_2$]·CH$_3$CN (**1**) showed broad signals at *ca.* −116.48 and −125.74 ppm (intensity 8:1) for DFForm and

partly defluorinated DFForm, respectively. The solid formed from warming crystals of [La$_6$(DFForm)$_8$F$_8$O(CH$_3$CN)$_2$]·6CH$_3$CN (**2**) to room temperature showed broad signals at *ca.* −121.36, −124.40, and −124.90 ppm in an approximate 1:15:4 ratio, attributable to DFForm and partly defluorinated DFForm ligands. The possibility of assignment of the additional fluorine resonances to the bridging fluoride ligands was considered, especially as the *approximate* integrations could be interpreted as consistent. However, there is very little chemical shift data for F attached to Ln atoms. Yb−F was observed at −81.82 ppm in the $^{19}$F NMR spectrum of the divalent complex [Yb(C$_5$Ph$_4$H)(μ-F)(thf)$_2$]$_2$,[15] a $^{19}$F NMR resonance at +150.2 ppm was assigned to La−F of the trivalent [La(DippForm)$_2$F(thf)] (DippFormH =
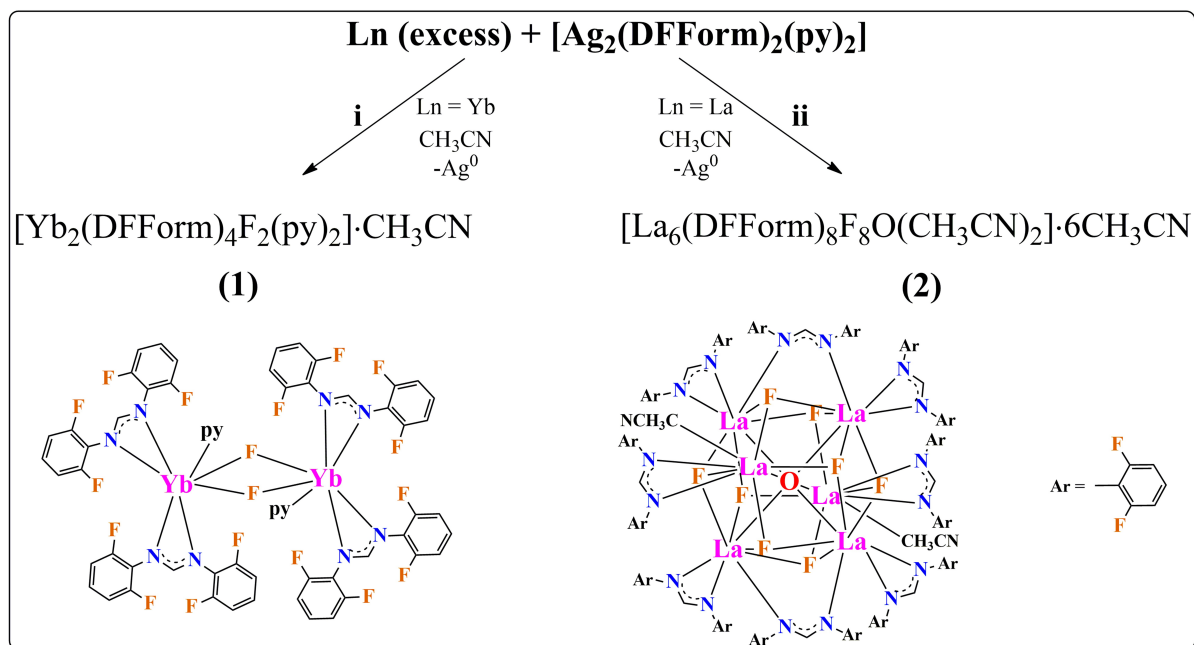


**Scheme 2.** Synthetic approaches to the formation of C-F activated products (**1**) and (**2**).
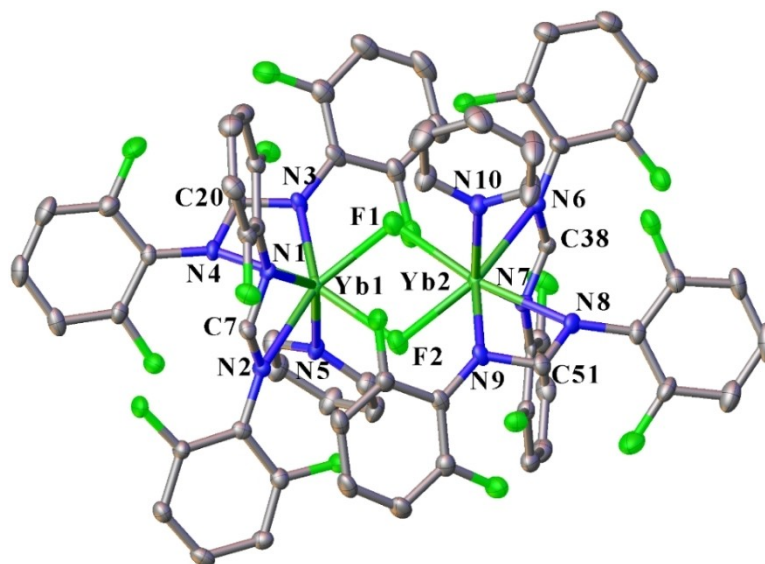
**Figure 1.** Molecular diagram of [**Yb₂(DFForm)₄F₂(py)₂**]·**CH₃CN (1)** represented by 50% thermal ellipsoids. The lattice CH₃CN and hydrogen molecules have been omitted for clarity.

*N,N′*-bis(2,6-di-*iso*propylphenyl)formamidine) complex,[16a,b] and paramagnetic [Sm(DippForm)₂F(thf)] has a Sm—F resonance at −24.8 ppm,[16c] but in many cases these resonances cannot be detected (e.g.[16b,d]). Given that the extra resonances fall in a similar region to those of DFForm, it is therefore likely that they are attributable to partially defluorinated DFForm ligands, as DFForm is the source of the fluoride found in these compounds.

Crystals of complex **1** were isolated after storing the filtered reaction mixture at −20 °C overnight, and those of complex **2** were obtained after adding Et₂O to the filtrate and storing at −20 °C for one week, which caused acquisition of an atom of oxygen. This may come from either Et₂O or more likely a trace of O₂ or water. Satisfactory microanalyses could not be obtained due to extreme air/ moisture and thermal sensitivity of the complexes. Infrared spectra of both complexes showed no absorption for ν(CN), hence CH₃CN is lost rapidly at room temperature, including coordinated CH₃CN of complex **2**, which only showed trace of an ¹H NMR resonance (0.6 ppm) for CH₃CN. The RTP reactions were not successful in tetrahydrofuran. The superiority of acetonitrile over thf has previously been observed in other syntheses utilising free Ln metals.[10]

The DFForm ligands are the sole source of fluoride in the reaction mixtures. Their C—F activation may be understood if there are Ag⁰-Ybᴵ(DFForm) or Ag⁰-Laᴵᴵ(DFForm)₂ intermediates, analogous to (C₆F₅)Hgᴵ-Ybᴵ(C₆F₅) intermediates indicated by theoretical studies for Yb metal/Hg(C₆F₅)₂ RT reactions.[17] The highly reactive unusual Ybᴵ and Laᴵᴵ are then able to promote C—F activation assisted by the thermodynamic stability of Ln—F bonds.
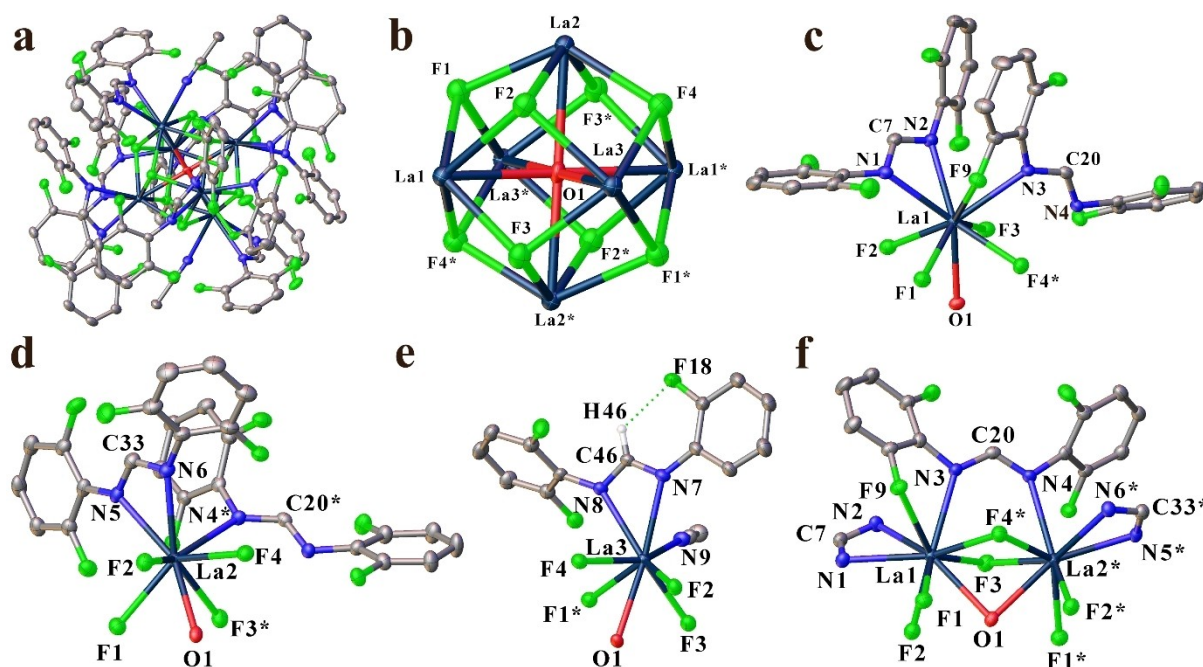
## Molecular structures

The X-ray structure of [Yb₂(DFForm)₄F₂(py)₂]·CH₃CN (**1**) (Figure 1) is a fluoride-bridged dimer, which crystallizes in the triclinic space group *P*-1, together with one lattice solvent molecule of CH₃CN. The ytterbium atom is coordinated by two terminal chelating κ(N,N′) DFForm ligands, a py ligand and two bridging fluoride ligands, giving the ytterbium metal a coordination number of seven, with the pyridine ligands on Yb1 and Yb2 on opposite sides of the Yb1—Yb2 axis. The average Yb—N (DFForm ligand) (Table 1) bond lengths of Yb1 and Yb2 are 2.416 Å and 2.410 Å respectively. The Yb—N (py) bond lengths are 2.466(8) and 2.485(8) Å. The coordination geometry of Yb in **1** is distorted trigonal prismatic with F—Yb—F angles of approximately 70°.[18] The Yb—F bond lengths [2.192(6)–2.200(6) Å] are similar to those in a number of fluoride-bridged complexes,[19] for example six coordinate [Yb(EtForm)₂F]₂,[18] in which the Yb—F bond lengths are between 2.160(2) and 2.179(2) Å.

**Table 1.** Selected bond angles (°) and lengths (Å) of **1**.

| Bond lengths | | | |
|---|---|---|---|
| Yb(1)—N(1) | 2.384(7) | Yb(2)—N(6) | 2.444(8) |
| Yb(1)—N(2) | 2.453(7) | Yb(2)—N(7) | 2.389(8) |
| Yb(1)—N(3) | 2.365(8) | Yb(2)—N(8) | 2.456(8) |
| Yb(1)—N(4) | 2.461(8) | Yb(2)—N(9) | 2.351(8) |
| Yb(1)—N(5) | 2.466(8) | Yb(2)—N(10) | 2.485(8) |
| Yb(1)—F(1) | 2.200(6) | Yb(2)—F(1) | 2.197(7) |
| Yb(1)—F(2) | 2.192(7) | Yb(2)—F(2) | 2.192(6) |
| Bond angles | | | |
| C(7)—Yb(1)—C(20) | 108.1(3) | C(38)—Yb(1)—C(51) | 110.9(3) |
| Yb(1)—F(1)—Yb(2) | 109.4(3) | Yb(1)—F(2)—Yb(2) | 109.8(3) |
| F(1)—Yb(1)—F(2) | 70.4(3) | F(1)—Yb(2)—F(2) | 70.4(3) |

[La$_6$(DFForm)$_8$F$_8$O(CH$_3$CN)$_2$]·6CH$_3$CN (**2**) (Figure 2a) crystallizes in the triclinic space group *P*-1, together with six lattice CH$_3$CN molecules. Atoms La$_6$F$_8$O form one 15-member cage frame with the O in the centre (Figure 2b). La1 is nine-coordinate with one terminal κ(N1, N2) DFForm ligand, a chelating κ(F9, N3) group of a bridging (F9, N3, N4) DFForm ligand, four bridging fluorides (F1, F2, F3, F4*) and the central oxygen (O1) (Figure 2c). La2 is eight-coordinate with one terminal κ(N5, N6) DFForm, κ(N4*) of a bridging (N4*, N3*, F9*) DFForm ligand, four bridging fluorine atoms (F1, F2, F3*, F4) and the central oxygen (O1) (Figure 2d). La3 is eight-coordinate with one terminal κ(N7, N8) DFForm, one terminal CH$_3$CN (N9), four bridging fluorine atoms (F1*, F2, F3, F4) and the central oxygen (O1) (Figure 2e). There is a fluorine-hydrogen interaction between F18 and H46 (2.156(7) Å). The bridging DFForm (F9, N3, N4) coordination is highly unusual, and has only once been reported, namely in [Yb(DFForm)$_2$(CH$_3$CN)$_2$].[10] N3 and N4 are bound to La1 and La2* respectively (Figure 2f). The bridging arrangement may be related to twisting of the ligand between

the metals owing to the La(1)–F(9) bond of 2.717(5) Å, This bond length (Table 2) is similar to the La–F bond length (2.765(4) Å) of [La(ρ-HC$_6$F$_4$N(CH$_2$)$_2$NEt$_2$)$_3$]·C$_7$H$_8$, in which an *o*-F from the ligand is coordinated to La.[20] However it is longer than the bond lengths of La–F (bridging), which range from 2.430(6) to 2.545(6) Å. It is noteworthy that La1-N3 and La2*-N4 have longer La–N bond lengths [2.715(7) and 2.722(7) Å] than the other La–N (DFForm) [from 2.631(8) to 2.672(8) Å] bond lengths in this structure, owing to this bridging. The La3–N9 (CH$_3$CN) [2.721(8)] bond length is longer than La–N (DFForm), except the bridging DFForm ligand values, consistent with the ligand charges. An oxygen bonded by six La ions is reported for the first time here, and the bond lengths between 2.6390(13) and 2.7218(7) Å, are similar to those of an oxygen bonded by five La ions (2.617–2.850 Å).[21]



**Figure 2.** Molecular diagram of **[La$_6$(DFForm)$_8$F$_8$O(CH$_3$CN)$_2$]·6CH$_3$CN (2)** represented by 50% thermal ellipsoids. The lattice CH$_3$CN molecules and hydrogen atoms have been omitted for clarity. **a** Structure of complex **2**; **b** The F–O cage framework cage without DFForm ligands; **c–e** The coordination environment of La1, La2 and La3 respectively; **f** The binding model of bridging ligand N3, N4.

**Table 2.** Selected bond lengths (Å) of **2**.

| | | | | | |
|---|---|---|---|---|---|
| La(1)–N(1) | 2.651(8) | La(2)–N(4)* | 2.722(7) | La(3)–N(7) | 2.642(7) |
| La(1)–N(2) | 2.643(7) | La(2)–N(5) | 2.631(8) | La(3)–N(8) | 2.664(7) |
| La(1)–N(3) | 2.715(7) | La(2)–N(6) | 2.672(8) | La(3)–N(9) | 2.721(8) |
| La(1)–F(1) | 2.486(6) | La(2)–F(1) | 2.545(6) | La(3)–F(1)* | 2.494(6) |
| La(1)–F(2) | 2.513(6) | La(2)–F(2) | 2.485(5) | La(3)–F(2) | 2.491(6) |
| La(1)–F(3) | 2.462(6) | La(2)–F(3)* | 2.482(6) | La(3)–F(3) | 2.458(6) |
| La(1)–F(4)* | 2.512(6) | La(2)–F(4) | 2.465(6) | La(3)–F(4) | 2.430(6) |
| La(1)–F(9) | 2.717(5) | La(2)–O(1) | 2.6569(9) | La(3)–O(1) | 2.7218(7) |
| La(1)–O (1) | 2.6390(13) | | | F(18)–H(46) | 2.156(7) |

## Conclusions

Silver formamidinate AgDFForm, with 2,6-F substituents, a potential RT reagent, provides a new synthetic route for metal-based reactions in rare earth chemistry. $[Yb_2(DFForm)_4F_2(py)_2] \cdot CH_3CN$ (**1**) and $[La_6(DFForm)_8F_8O(CH_3CN)_2] \cdot 6CH_3CN$ (**2**) are coordinated by bridging fluoride ligands, which must come from C–F activation of DFForm as the only source of fluorine. $[La_6(DFForm)_8F_8O(CH_3CN)_2] \cdot 6CH_3CN$ (**2**) is an interesting structure with a cage formed by six La, eight F and one O. The bridging oxygen coordinated to six lanthanum atoms is reported for the first time. Considering the importance of replacing mercury compounds in RT reactions by greener alternatives, the reactivity of silver formamidinates in RT reactions and their easy preparation offer a promising beginning. This method needs to be examined with other pro-ligand (weak acid) classes and other lanthanoid metals to determine if it can be extended into a general preparative route.

## Experimental

### General

The compounds described here were prepared and handled using vacuum-nitrogen line techniques and a dry box under an atmosphere of purified nitrogen. AgDFForm was prepared by the literature method.[9] Lanthanoid metals were from Santoku/Molycorp/Eutectix. Large chunks were filed in the drybox before use. $CH_3CN$ was distilled over calcium hydride, degassed and stored over dried 3 Å molecular sieves. Pyridine was distilled over potassium hydroxide, degassed and stored over dried 4 Å molecular sieves. IR spectra were recorded as Nujol mulls between NaCl plates using an ATIR instrument within the range 4000–600 cm$^{-1}$. Proton decoupled $^{19}$F NMR and $^1$H NMR spectra were recorded on a Bruker DPX 300 MHz spectrometer. Chemical shifts were referenced to the residual $^1$H resonances of the deuterated solvents ($^1$H) or external $CCl_3F$ ($^{19}$F). Melting points were determined in sealed glass capillaries under nitrogen and are uncalibrated. Crystals were measured on the MX1 beamline at the Australian Synchrotron. Crystal data and refinement details are given in Table S1 in Supporting Information. CCDC 2177388 (compound **1**) and 2177389 (compound **2**), contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

### $[Yb_2(DFForm)_4F_2(py)_2] \cdot CH_3CN$ 1

AgDFForm (0.188 g, 0.5 mmol), ytterbium powder (0.173 g, 1 mmol) and dry $CH_3CN$ (10 ml) were ultrasonicated for 3 days. The red solution was filtered. $^{19}$F NMR (THF, ext. CFCl$_3$, ppm): −116.48 (*ca.*16F), −125.74 (*ca.* 2F), DFForm and partly defluorinated DFForm. The reaction filtrate was evaporated to half volume under vacuum. Yellow crystals ((0.163 g, M.p. 138–140 °C) were obtained after storing at −20 °C overnight. IR (Nujol): 1668w, 1617m, 1570m, 1315vs, 1266m, 1218vs, 1156w, 1064m, 1040m, 1006vs, 946w, 918w, 796s, 760s, 715vs, 697m cm$^{-1}$. There was no IR band of $CH_3CN$ near 2100 cm$^{-1}$.

### $[La_6(DFForm)_8F_8O(CH_3CN)_2] \cdot 6CH_3CN$ 2

AgDFForm (0.188 g, 0.5 mmol), lanthanum powder (0.139 g, 1 mmol) and dry $CH_3CN$ (10 ml) were ultrasonicated for 3 days. The red solution was filtered. The reaction filtrate was evaporated to half volume under vacuum, colourless crystals (0.192 g, M.p. 120–122 °C) were obtained after adding Et$_2$O to the filtrate and storing at −20 °C for one week. IR (Nujol): 1669s, 1615m, 1592m, 1312s, 1269s, 1243m, 1220s, 1205vs, 1152m, 1060m, 993vs, 952m, 915m, 892w, 832m, 776s, 738m, 724s, 686m cm$^{-1}$. $^{19}$F{H} NMR (C$_6$D$_6$, 300 MHz, ppm): −121.36 (*ca.*2F), −124.40 (*ca.*30F), −124.90 (*ca.*8F), DFForm and partly defluorinated DFForm. $^1$H NMR (C$_6$D$_6$, 300 MHz, ppm): 8.03 (s, 8H, NCHN), 6.48(m, 32H, H (3, 5)), 6.33(m, 16H, H (4)), 0.60 (s, 2H, CH$_3$CN). CH$_3$CN could not be detected in IR (near 2100 cm$^{-1}$) and only a trace of CH$_3$CN (1/12) was found in the $^1$H NMR spectrum.

## Conflict of Interest

The authors declare no conflict of interest.

## Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

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