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Impact of the Long-Range Electronic Effect of a Fluorous Ponytail on Metal Coordination during Solvent Extraction

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With the need for a precise description of the long-range electronic effects of a perfloroalkyl chain (F-ponytail) grafted onto metal chelators, we studied in detail the effect of a spacer inserted between the polar complexing head and the F-ponytail, in relation to the metal coordination ability of the resulting molecules. The prepared molecules were then applied for the extraction of various metals from an aqueous phase into an organic phase, and the optimum spacer length could be estimated to be between three and four methylene units, according to the extraction conditions. The study also revealed the difficulty of modeling and anticipating the tiny energy differences involved in the extraction process and the importance in peculiar cases to go beyond only these studied inductive effects to understand better the factors that govern the stabilization of a metallic cation in a complex fluorous phase.

1. Introduction

Since the work of Horváth and Ràbai on perfluorinated phosphines in catalysis,[1] over a thousand papers, in a large set of domains, have been published and report the use of perfluorinated molecules.[2] Long perfluoroalkyl chains (also referred to as fluorous groups, F-tags or F-ponytails; over 400 papers were found with the keywords “fluorous” and “tag”) are regularly employed to bring fluorophilic character to a molecule.[3] Fluorophilicity endows molecules with the propensity to segregate into a specific phase from either the aqueous or the organic phase.[4] This property has been exploited, for example, for the easy separation of organic compounds,[5] for the preparation of superhydrophobic surfaces,[6] to increase solubility in supercritical CO_2,[7] in the preparation of original ionic liquids,[8] or for original materials synthesis.[9] The major application to date remains the stabilization of metal coordination complexes with perfluorinated ligands into a distinct fluorous phase, which enables straightforward catalyst recovery during homogeneous catalysis processes[10] and new catalyst activation strategies.[11] The need to attenuate the strong electron-withdrawing character of the F-ponytail to maintain the reactivity of the system was quickly observed, and the beneficial insulation effect of a spacer located between the reactive site and the F-ponytail of the molecule was reported as early as 1996.[12] This article reported that the presence of a spacer of two methylene units had a strong impact on the physicochemical properties of both the ligand and the resulting metal complex, and also on reaction mechanisms.

A more precise assessment of the spacer effect through the study of fluorous tertiary amines with the general formula $N[(CH_2)\,m\,(C_8F_{17})]_3$ was then published.[13] Both basicity and partition coefficients between perfluoromethylcyclohexane and toluene were evaluated. The partition coefficient of the amines varied only slightly as m was changed from 3 to 5 (the total number of methylene units went from 9 to 15 and the H/F ratio from 0.375 to 0.625). For $m=5$, more than a quarter of the molecule was hydrogenated, but the fluorophilic character of the molecule was maintained. The relative basicity of the three amines was also measured by examining the proton exchange between two amines in the presence of one equivalent of trifluoroacetic acid. As expected, the longer the spacer, the higher the basicity of the molecule. Going from $m=4$ to $m=5$ still increased the basicity of the molecule and no asymptotic limit of basicity was observed. Later, the reduction in the inductive effect of the F-ponytail by the spacer was studied for phosphines employed as ligands in Ir and Rh complexes.[14] With these phosphines, with the general formula $P[(CH_2)\,m(C_8F_{17})]_3$ ($m=2$–5), long-range electronic effects were surprisingly observed because differences in experimental properties (vertical ionization potential and protonation enthalpy) were still easily detected on going from a spacer of four methylene units to one of five methylene units. Furthermore, a computational study of the electronic properties of the fluorous phosphines led to an asymptotic limit reached with a spacer of at least seven to eight methylene units, depending on the property considered. These theoretical results are fully consistent with IR studies performed on analogues of Vaska’s complex, which demonstrated that the νCO band of the complexes is still sensitive to the electron-withdrawing character of the ligand even when a spacer of five methylene units is employed.[15] To our knowledge, such studies on the effect of the spacer between the F-ponytail and the head of the molecule have not been pursued, and generally two or three methylene

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units, or also a phenylene unit,[16] are the spacers commonly encountered. This is presumably related to the large occurrence of commercially available fluorinated building blocks, such as $C_nF_{2n+1}CH_2CH_2I$ or $C_nF_{2n+1}CH_2CH_2OH$, that are directly employable in usual syntheses.

Recently, we demonstrated that the stabilization of a metal into a fluorous phase can have direct applications in the field of metal recovery from complex mixtures by solvent extraction.[17] Nowadays the recycling of valuable metals appears to be a solution of growing interest for sustainable supply strategies, so new solvent-extraction strategies are needed, particularly in the field of e-waste recycling.[18] We demonstrated that rare-earth elements (REEs) can be efficiently extracted from aqueous nitrate media into a fluorous phase.[17] The extraction solvent was based on a fluorous molecule with a classical two-methylene-unit spacer between the polar complexing head and the F-ponytail of the molecule, and the performance of the fluorous system reached that of the hydrocarbon parent only after careful control of the aqueous layer composition. With the need for a robust and general design of fluorous extractants inspired by corresponding hydrocarbon extractants, we devised questions about the design of the extractant and the choice of the best spacer. Because the major driving force of solvent extraction is metal coordination by the extracting molecule,[19] we decided to study systematically the long-range electronic effect of a F-ponytail on an extracting molecule, and to see whether it would be possible to reach efficiencies similar to hydrocarbon systems, although the above-mentioned literature precedents suggest that it would be hardly achievable with a spacer of “reasonable” size. Herein, we performed the synthesis of perfluorinated analogues of malonamides, neutral extractants with the general formula $(R''R'NCO)_2CHR$, which were developed and scaled-up for the field of nuclear fuel reprocessing and precious metals recovery,[20] and related their metal-extraction abilities to their physicochemical properties. Either a classical tetradecyl hydrocarbon chain or a F-ponytail that encompassed a C_8F_{17} perfluoroalkyl chain (denoted F8) and an alkylidene spacer of variable length (denoted H*x*) were grafted on the central methylene of malonamides (Figure 1). The long-range electronic effects of the fluorinated chain was studied for two series of compounds with different amide moieties (R = *n*Bu or Me, Figure 1).

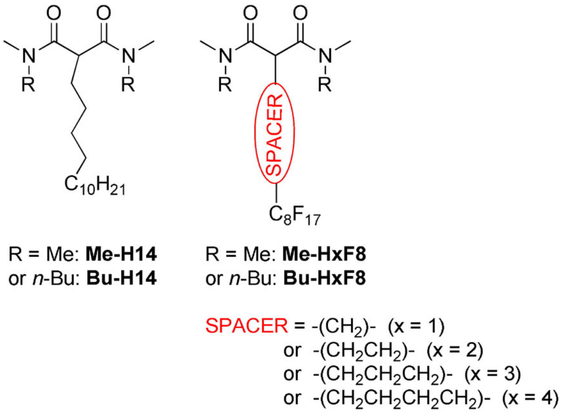
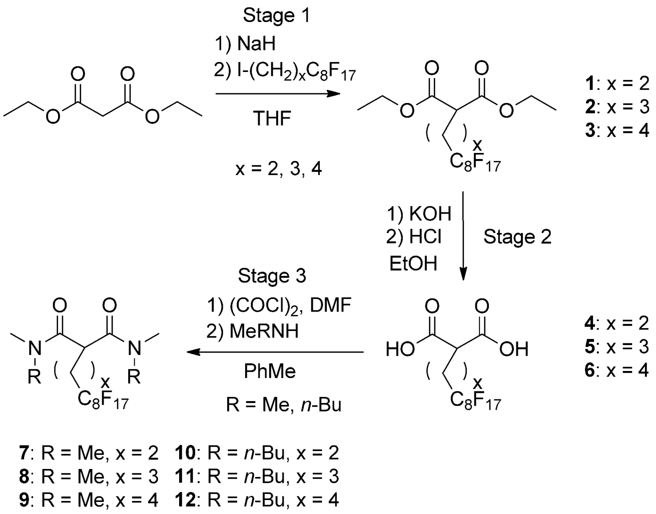


Figure 1. Structure of the F-tagged molecules employed in this study.

2. Results and Discussion

Most of the required fluorous malonamides, Me-H*x*F8 and Bu-H*x*F8 (*x* = 2, 3, 4), were synthesized by following a previously reported synthetic pathway,[17] with attention given to improvement of the synthesis protocols to obtain better yields and a shorter synthesis route (Scheme 1, Table 1).



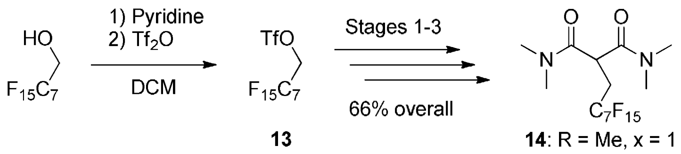
Scheme 1. Synthesis of F-tagged molecules, *x* = 2–4. Yields are reported in Table 1.

Table 1. Compounds and synthesis yields obtained according to Scheme 1.

	Abbreviation	Stage 1 yield [%]	Stage 2 yield [%]	Stage 3 yield [%]	Overall yield [%]
7	Me-H2F8	86	88	75	57
10	Bu-H2F8			46	35
8	Me-H3F8	92	94	99	86
11	Bu-H3F8			72	62
9	Me-H4F8	90	84	93	70
12	Bu-H4F8			80	60

The synthesis was performed on a multigram scale, with purification of the intermediate malonic esters **1**–**3** by distillation after stage 1 and crystallization of malonic acids **4**–**6** after stage 2. Intermediate distillation was not necessary because crystallization after stage 2 led to excellent purity. Final products **7**–**12** were purified by using column chromatography on silica gel, which was made easy owing to the generally excellent yields obtained in stage 3. Only products **7** and **10**, with the shorter spacer (*x* = 2), were obtained in moderate yields, probably because of the diminution of the electrophilic character of the carbonyl moieties of malonic acid **4**; the activation with oxalyl chloride was less effective in chloroform and required careful monitoring in toluene. Yields reported in Table 1 were obtained on a two-gram scale. Me-series compounds were white/yellow solids whereas Bu-series compounds were viscous yellow oils.

To expand the knowledge on short spacers, a malonamide with a single CH_2 unit spacer was also prepared. Because the perfluoroalkyl iodide was not available in this case, introduction of the F-ponytail was performed by starting from the corresponding alcohol. For availability reasons, we had to use 1*H*,1*H*-perfluorooctanol with a C_7F_{15} perfluoroalkyl chain instead of a C_8F_{17} chain. However, no inductive effect difference resulting from the shortening of the perfluoroalkyl chain by one CF_2 moiety is expected. The synthesis sequence requires activation of the alcohol into corresponding trifluoromethanesulfonic ester (triflate) **13** and its subsequent use in the alkylation stage (Scheme 2). Further saponification and amide formation were conducted as before with satisfactory yields and without intermediate purification because triflate **13** was moderately stable. Only derivative **14** with R = Me was prepared in this case.



Scheme 2. Synthesis of F-tagged molecule with $x=1$.

^1H and ^{13}C NMR chemical shifts (δ) and IR frequencies (ν) can provide useful information on the electronic features of the malonamide complexing head. The analysis of significant ^1H and ^{13}C chemical shift differences between the F-tagged molecules Me-HxF7–8 or Bu-HxF8 and their hydrocarbon counterparts Me-H14 or Bu-H14 is summarized in Figure 2. In both the Me- and Bu-series, the variation in the chemical shift of the proton on the central CH (between both carbonyl groups) with respect to the hydrocarbon compound became negligible with a spacer of three methylene units or more (Figure 2a). Conversely, variations in the chemical shift of the carbonyl moieties could still be observed even between -H4F8 and -H14 in both series (Figure 2b). It is known that electron-withdrawing substituents increase the stretching frequency of the carbonyl group. However, there were no noticeable differences between the νCO values for both Me- and Bu-series compounds for two-unit spacers. The only marked difference occurred for the Me-H1F7 compound: two CO stretching bands were observed at 1640 and 1662 cm^{-1}, whereas for Me-H14 the corresponding CO bands were observed at 1633 and 1651 cm^{-1}. For other compounds of the Me-series and compounds of the Bu-series ($x=2$ to 4), the νCO differences all lie within a 3 cm^{-1} range (see Table 3).

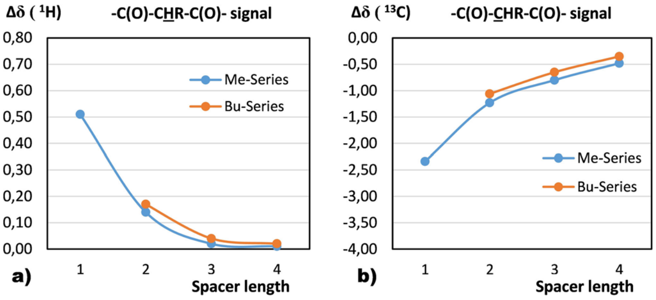


Figure 2. Evolution of significant ^1H and ^{13}C chemical shift differences between F-tagged compounds and the corresponding hydrocarbon derivatives.

The prepared malonamides were employed in the solvent extraction of eight metals representative of important metals contained in electronic waste: these include base metals (Cu, Fe, Al, Zn, Ni) present in the structure of the apparatus and valuable metals (Au, Pd, Nd) employed for specific electronic components and printed circuits.[21] Extraction and separation of these metals from plastic components and glass fibers is usually performed after total dissolution in an acidic solution by using classical hydrometallurgical routes.[22] In the first approach, we worked with a model aqueous solution that contained these metals at concentrations of approximately 100 mg L^{-1} in nitric acid of variable concentration (1–5 M). To ensure that no competition between metals occurred during the extraction process, the concentration of malonamides was kept at least twenty times higher than the total sum of the molar concentration of metals. Based on our previous results, the contact time between the aqueous and organic phases was set to 1 h, then the composition of each phase was determined. The metal content of the organic phase was determined after counter extraction by using a 0.1 M thiourea stripping solution. No issue regarding back-extraction of all metals was encountered and the error on the final mass balance was in most cases below 5 %. The reproducibility and repeatability of the results were satisfactory, and experiments were run at least twice. Extraction yields and distribution coefficients were calculated according to Equations (1) and (2).

$$\%\,\text{extraction} = \frac{[M]_{\text{Org}}}{[M]_{\text{Aq}} + [M]_{\text{Org}}} \tag{1}$$

$$D = \frac{[M]_{\text{Org}}}{[M]_{\text{Aq}}} \tag{2}$$

First, to minimize possible solvent effects, all malonamides were evaluated in 1,2-dichlorethane (DCE), a chlorinated solvent usually employed for solvent extraction in which both fluorinated and hydrocarbon compounds are soluble. Several acid concentrations and malonamide concentrations were considered and, as expected from previous studies on malonamides in heptane and toluene,[19b,20] an increase in ligand and/or acid concentration both led to higher extraction yields. A first extraction test in DCE with Bu-H14 (*N*,*N*′-dimethyl-*N*,*N*′-dibutyltetradecylmalonamide, also often referred to as DMDBTDMA), which we previously evaluated for the extraction of valuable metals,[20] was performed (Table S1 in the Supporting Information). As observed previously in heptane and toluene, precious metals (Au, Pd) are also well extracted by malonamide in DCE regardless of the conditions employed. Nd, as a representative rare-earth element, could be successfully extracted when high concentrations of ligand in the organic phase and nitric acid in the aqueous phase were employed. Of the base metals mostly present in electronic waste, Fe is sometimes largely extracted, in contrast with Cu (less than 5% extraction yield) and Al, Zn, and Ni (extraction always below the quantification limit). Therefore, Au, Pd, Nd, and Fe were selected for the comparison of extraction with fluorinated and nonfluorinated malonamides in DCE. A 3 M nitric acid concentration was chosen for the aqueous phase and two extractant concentrations were evaluated (0.25 and 0.4 M), so that extraction of Pd, Nd, and Fe with Me-H14 lay between 10 and 90% to avoid a levelling effect (this was not possible with Au, which was always completely extracted, see Table 2). All results of extraction with the fluorinated derivatives are given with respect to the extraction yield obtained with the corresponding hydrocarbon compound, according to Equation (3). The reference extraction yields with hydrocarbon compounds for these metals are given in Table 2.

Table 2. Extraction yields of Au, Pd, Nd, and Fe from a 3 M HNO_3 aqueous phase by using Me-H14 and Bu-H14 under conditions employed to evaluate the long-range electronic effect of the F-ponytail in 1,2-DCE.

Entry	Extractant	Concentration [M]	Au [%]	Pd [%]	Nd [%]	Fe [%]
1	Me-H14	0.25	99	78	23	15
2		0.4	99	86	46	35
3	Bu-H14	0.25	99	89	23	9
4		0.4	99	94	48	20

$$\text{Relative performance}(x) = \frac{\%\,\text{Ext}(-\text{H}x\text{F8})}{\%\,\text{Ext}(-\text{H14})} \tag{3}$$

The relative extraction performance of fluorinated malonamides in DCE at two different concentrations (0.25 M and 0.4 M) with the Me-series are given for the four selected metals in Figure 3. During this study, gold was always completely extracted from the aqueous phase regardless of the spacer length between the malonamide head and the F-ponytail. Even with Me-H1F7, for which a strong electron-withdrawing effect is expected, gold was quantitatively extracted from the aqueous phase (Figure 3a). This result is not surprising given the ease of extraction of Au^{III}; the industrial solvents used, such as dibutyl carbitol, are only weakly coordinating ethers.[23]

Palladium extraction highlights the strong influence of the spacer: with the classical two-unit spacer, extraction performance is on average only 40% of that of the nonfluorinated malonamide. A longer spacer leads to an attenuation of the electron-withdrawing effect of the F-ponytail. With three methylene units, 80% of the performance of the nonfluorinated system was reached, and with four units the difference lay within the error margin of the extraction yield determination (Figure 3b). The driving force for the extraction of the palladium by malonamide has been described to rely mostly on coordination of the metallic center by the amide moieties.[19b] Thus, the decrease in extraction yield with Me-HxF7-8 compared with nonfluorinated Me-H14 as x was decreased can be attributed to the electron-withdrawing effect of the F-ponytail transmitted through the spacer to the amide moieties. The same trend was also observed in the Bu-series, with the sole difference being the slightly higher extraction yields of the Bu-series compared with the Me-series (see Table S2). This can be attributed to the higher electron-donating propensity of the butyl chain compared with the methyl group. However, this effect remains low because the replacement of methyl amide by butyl amide does not compensate the addition of one methylene unit in the spacer.

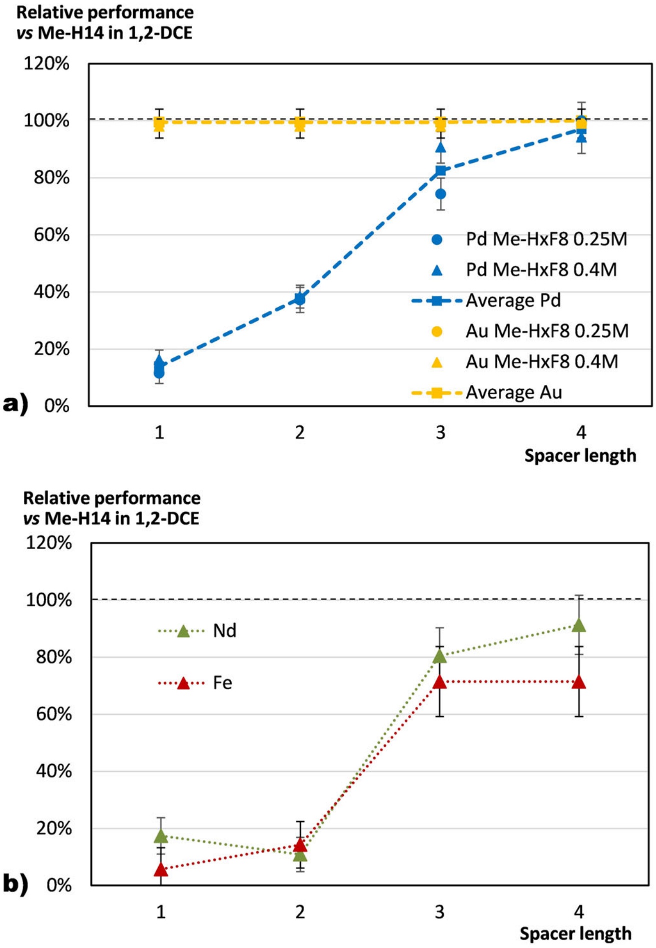


Figure 3. Relative performance for the extraction of metals from an aqueous HNO_3 (3 M) phase by using Me-series malonamides according to spacer length (x); a) Au and Pd, b) Nd and Fe.

The extraction of Nd and Fe with Me-series compounds is lower than that of Au and Pd under the chosen conditions (maximum 48% with a 3 M nitric acid aqueous layer). However, a trend similar to that of Pd can be observed, albeit with a higher error on the points, so only yields with an extractant concentration of 0.4 M in the organic phase were used (Figure 3b). For these metals, there is much more difference between the two-unit spacer and the three-unit spacer than between the three-unit and the four-unit spacers. Attempts to increase the extraction yields by using a more acidic aqueous layer led to the formation of a third phase with Me-H3F8 or Me-H4F8 as a precipitate between both layers, as already noted before with malonamides under similar conditions.[20] However, the trends remain similar to those reported in Figure 3b (complete data available in Table S2).

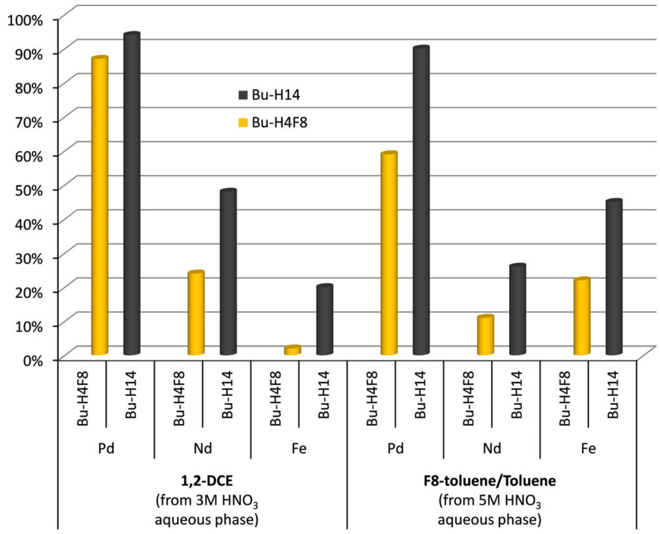


Figure 4. Comparison of the extraction yields of Pd, Nd, and Fe by Bu-H4F8 and Bu-H14 in DCE and in F8-toluene/toluene.

In contrast to Pd (and Au), for which no difference was observed between the Me- and Bu-series, the extraction of Nd and, in particular, Fe was sluggish with the Bu-series, even when a four-unit spacer was used (Figure 4). In a preceding study, we reported that fluorinated malonamides can have very peculiar behavior in dichloromethane, with a different organization of the organic phase between hydrogenated and fluorinated systems.[24] Thus, we attributed the lower yields obtained with the Bu-series compounds to a similar deactivation through unsuitable organization in the organic phase, which resulted from the Bu-series having a less hydrophilic head than the Me-series. We did not investigate this case further because the main effect revealed in this study remains the inductive effect. Altogether, it appears that the two-unit spacer does not properly shield the electron-withdrawing effect of the F-ponytail, that the addition of another methylene unit has a strong impact on the extraction outcome, and that the contribution from a fourth methylene unit becomes smaller. Also, these results indicate that a four-unit spacer can be considered a sufficient insulating group because both fluorinated and nonfluorinated molecules present the same behavior in the solvent extraction of several metals. Furthermore, a three-unit spacer appears to be a good compromise because more than 80% of the activity of the H-system is obtained under most conditions. These results do not take in consideration the change of solvent and the full transposition in fluorinated media. Therefore, in a subsequent step, the fluorinated system was compared with the hydrocarbon system in two different solvents, perfluorotoluene (F8-toluene) for fluorinated malonamides and toluene for hydrocarbon malonamides.

Molecules with a F-ponytail tend to be soluble neither in water nor in classical organic media, and to segregate into a fluorous phase. With the final goal being to develop a high-performance metal-extracting fluorous phase, we searched for a perfluorinated solvent in which to assess the spacer effect on the extraction properties of our prepared malonamides. The solubility of the Me-series compounds in perfluorinated alkanes (hexanes, decaline, methylcyclohexane) was limited, and concentrations above 0.1 M were reached with difficulty. The solubility in fluorous ethers was low in the case of HFE-7500 (3-ethoxy-2-trifluoromethylperfluorohexane) but high in the case of HFE-7100 (a mixture of perfluorobutylmethyl ether isomers). Finally, the solubility of the Me-series compounds was also total in partially or totally fluorinated aromatic solvents (perfluorohexylbenzene and F8-toluene). A first extraction experiment of the four previously examined metals from 3 M aqueous HNO_3 was performed by using Me-H2F8 (0.4 M) in HFE-7100, perfluorohexylbenzene, or F8-toluene. The use of HFE-7100 and perfluorohexylbenzene both led to the formation of a gel, which was not suitable for liquid/liquid (L/L) extraction, although phase separation could be achieved after a short centrifugation. The formation of these gels is probably related to the precipitates we observed with the Me-series in DCE (see above). In contrast, F8-toluene exhibited the behavior expected for successful L/L extraction processes, that is, no third phase or precipitate formation, clean phase separation without emulsion, and no noticeable increase in viscosity or gel formation. F8-Toluene was thus selected to perform a complete comparison of hydrocarbon versus fluorinated systems. However, it must be mentioned that F8-toluene is also miscible with most regular organic solvents. All the fluorinated compounds of both the Me- and Bu-series were fully soluble in F8-toluene, regardless of spacer length, but they were not soluble in toluene.

A comparison of extractions with fluorinated malonamides in F8-toluene (F-systems) or with hydrocarbon malonamides in toluene (H-systems) was performed under various conditions (HNO_3 concentration in the aqueous phase and malonamide concentration in the organic phase). The most significant results are presented in Figure 4 by using the same presentation as in DCE. All extraction yields are available in Table S3. In the F-systems, slightly less gold appeared to be extracted relative to the results obtained in DCE, particularly for Me-H1F7 (0.25 M) in F8-toluene (Figure 5a). The extraction yield of Au was always above 90% with a longer spacer and/or a higher extractant concentration (see Table S3). However, this result is already indicative of the lower efficacy of F-systems compared with H-systems. As for extraction in DCE, the extraction yield of palladium increased with the length of the spacer in the Me-series (Figure 5a). The performances reached by the Me-H4F8 extractant in F8-toluene are equivalent to those of Me-H14 in toluene, which shows that both F- and H-systems behave in a similar manner in terms of complexation with an extractant with a four-unit spacer. However, the use of a shorter spacer has a more marked deleterious effect in the F-sys-

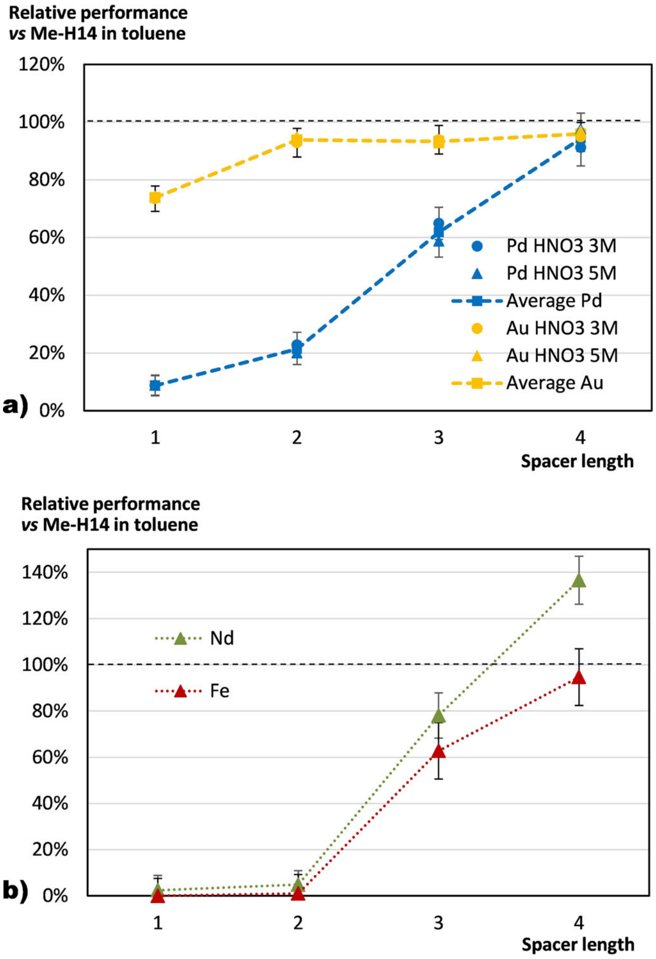


Figure 5. Relative performance for the extraction of metals from an aqueous phase by using Me-series malonamides (0.25 м) in F8-toluene according to spacer length (*x*); a) Au and Pd (3 м and 5 м HNO_3), b) Nd and Fe (5 м HNO_3).

tems, that is, the decrease in efficacy is more marked than in DCE.

For Nd and Fe, the previously observed trend regarding the spacer effect is again observed (Figure 5b). Interestingly, however, more Nd was extracted by Me-H4F8 in F8-toluene than by Me-H14 in toluene. This different behavior was observed under all the extraction conditions used (see Table S3). In DCE, we never observed a better result with a fluorinated malonamide than with the corresponding hydrocarbon malonamide. The F-systems do not outperform the H-systems in Fe extraction and, as with Nd, a severe drop in efficacy was observed on going from a three-unit spacer to a two-unit spacer (Figure 5b).

The spacer effect was also observed for the Bu-series, that is, the extraction efficiency increased as *x* increased. However, the extraction yields were in general lower than with the Me-series, particularly in the case of Nd and Fe; these metals were not extracted from 3 м aqueous HNO_3 by using Bu-H14 in toluene (compared with Me-H14), and only poorly from 5 м HNO_3 solutions. The extraction yields with fluorinated molecules Bu-HxF8 were systematically lower and the relative performance of Bu-H4F8 in F8-toluene barely reached half of that obtained with Bu-H14 in toluene, regardless of the conditions employed (Figure 4; see also Table S3). These observations suggest that the contribution of the butyl chain is not limited solely to electronic effects and must be investigated further. Therefore, we analyzed in more detail the long-range electronic effect in the Me-series compounds.

Metal extraction is driven by different interactions and the major contribution arises from coordination by the extractant in the organic phase.[19] The differences observed in the extraction outcome can result from a weaker coordination of metal by the fluorinated malonamides than by the hydrocarbon malonamides. Therefore, we aimed to characterize the coordination complexes involved in metallic cation extraction experimentally, along with a theoretical rationalization of the results. We focused on the peculiar case of Pd^{II}, which is diamagnetic and does not require time-consuming computational approaches. The coordination complexes could be characterized by using NMR and IR spectroscopies. Because the organic phase after extraction contained a much larger amount of free extractant than extractant coordinated to the metallic cation, more concentrated solutions of complexes were prepared by dissolution of a known mass of metal salt and the appropriate quantity of ligand in F8-toluene. If $Pd(NO_3)_2$ and Me-H2F8 were in a 1:1 ratio, only a minute fraction of free ligand was present and a new set of peaks could be observed in the ^1H NMR spectrum ($\delta = 4.6$, 3.87, 3.00, 2.60, and 2.11 ppm, Figure 6). If this ratio was increased to 1:2, both the complex and the free ligand were clearly identifiable. The temperature was increased up to 333 K but no peak coalescence was observed, which suggested that free and bound ligands exchange slowly on the characteristic ^1H NMR timescale at this temperature (Figure 6). Thus, the behavior of Me-H2F8 in the presence of Pd^{II} is completely identical to that of Me-H14 as observed and described previously; the possible coordination differences cannot be observed by using ^1H NMR spectroscopy.

Analysis of the IR spectra gave valuable information, that is, the νCO difference between free and bound malonamide varied according to the nature of malonamide (Table 3). As stated previously, the νCO differences for the free malona-

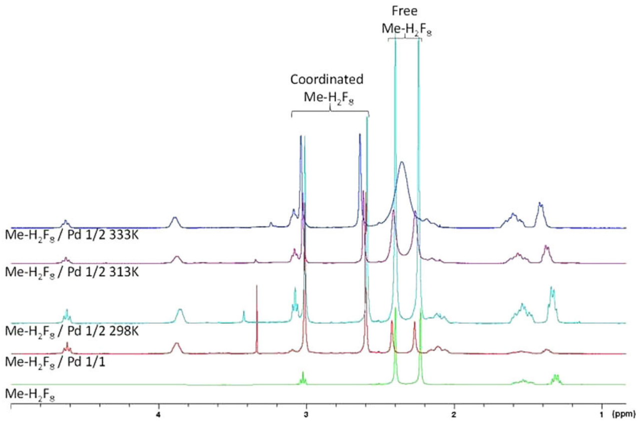


Figure 6. NMR spectra of Pd^{II}/Me-H2F8 complexes.

Table 3. Variation in the frequency of the stretching CO band between free and coordinated malonamides along the Me-series.

	νCO (free malonamide) [cm^{-1}]	νCO (malonamide–Pd^{II} complex) [cm^{-1}]	$\Delta\nu$CO [cm^{-1}]
Me-H2F8	1634	1615	19
Me-H3F8	1633	1614	19
Me-H4F8	1630	1611	19
Me-H14	1632	1606	26

mides in the Me-series are not significant as soon as the spacer has at least two methylene units. A regular shift in the position of the CO band was observed towards lower wavenumbers as the spacer length was increased, but the Me-H14 CO band lies in the middle of the Me-HxF8 bands. The same tendency is observed for the Pd^{II} complexes, albeit with a significant shift observed in the case of the Pd^{II}/Me-H14 complex. As a result, the difference between the νCO values for free and bound amide moieties ($\Delta\nu$CO) is higher in the case of Me-H14 than in the case of Me-HxF8 compounds. We did not observe any particular effect of the spacer on the CO band position, and Me-H2F8 and Me-H3F8 systems presented no difference. The higher $\Delta\nu$CO value observed for Me-H14 can be regarded as a higher covalence of the amide–Pd bond in this case. This does not preclude any energy difference, but suggests that the electron-donating ability of the amide moiety was altered by the F-ponytail, regardless of the spacer. Also, it must be mentioned that the two carbonyl moieties of the malonamide group in the free ligand do not lie in the same plane, so νCO evolution may also result from a change in the dihedral angle between both CO groups imposed by Pd^{II} coordination.

To obtain complementary data, DFT calculations were performed on the malonamides and the corresponding Pd^{II} complexes in the Me-series. The geometries of the molecules were determined coarsely in the first step by using the B3LYP hybrid functional and the 6,31-G and LANL2DZ basis sets for C, H, O, N, F, and Pd. The obtained structures were refined and the energies were computed by using the 6,31-G(d,p)** and the LANL2DZ-ECP basis sets in vacuum or in 1,2-DCE for the species present in organic phase, with 1,2-DCE modeled as a continuum ($\varepsilon_r = 10.4$). The computed structures of the organic complexes [Pd(NO$_3$)$_2$Me-HxF7-8] were oriented to be in line with the previously described Pd^{II}-malonamide complexes, that is, with two monodentate nitrato ligands and one bidentate malonamide ligand.[19b] The alkyl chain of the hydrocarbon compound was set to a linear shape in a zig-zag conformation to avoid folding and artefacts due to intramolecular hydrogen bonds with nitrato ligands. The computed physicochemical features of the free malonamides and the corresponding Pd^{II} complexes were examined in detail. The interatomic distances were not influenced by the F-ponytail regardless of the spacer; the C=O and C–N bonds of the amide moieties remained unchanged and all lay within the error margin of average C=O and C–N bonds in all the malonamides reported in the Cambridge Structural Database (1.22 Å ($\sigma = 0.014$) for C=O bonds and 1.37 Å ($\sigma = 0.023$) for C–N bonds). The O–Pd bonds in the complexes were all similar at about 2.10 Å with the Pd^{II} in a square-planar configuration. Regarding the O and N atoms charges, Mülliken charge analysis of the free amides revealed an important difference between the one-unit and two-unit spacers, but then no significant differences were found with a further increase in methylene units. The sole significant variation was found for the C atom located between the two carbonyl groups, with a trend that followed that observed for the NMR chemical shifts (Figure 2), albeit without validity for the one-unit-spacer compound. Because no molecular feature seems to correlate with the extraction results, we turned to an analysis of the Gibbs free energy of Pd complexation, which is representative of the expected molecular mechanism of extraction [Eq. (4)].

$$[\mathrm{Pd(NO_3)_2(H_2O)_2}] + \overline{\mathrm{L}} \rightarrow \overline{[\mathrm{Pd(NO_3)_2L}]} + 2\,\mathrm{H_2O} \qquad (4)$$

A precise description of the thermodynamic features of extraction reactions has been proposed by Markus and is still accepted.[25] The major contributions are the hydration energies of the charged species and the association energy of cations with counterions. As long as a unique metallic cation is considered and the aqueous phase remains unchanged, these energies should remain identical for coordination complexes with different ligands. Therefore, we studied the energy difference between Pd^{II} extraction with hydrocarbon Me-H14 taken as a reference [L = MeH14 in Eq. (4)] and with fluorinated Me-HxF7–8 [L = Me-H1–5F8 in Eq. (4)]. This approach revealed only the differences in coordination energy related to the ligand modification. The model employed does not take into account the likely modifications of the solvent–molecule/complex interactions that occur during the extraction process. These contributions are weak and thus require long computation times. Given that the compared malonamides of the Me-HxF7–8 series did not vary significantly in terms of solvation energy along the series, the analysis of energy differences enabled the elimination of these unknown solvent contributions and delivered a reliable relative positioning of the binding energies of the different ligands. To keep the first coordination sphere of square-planar Pd^{II} full, two water molecules were supposed to be bound to the Pd(NO$_3$)$_2$ salt in the aqueous phase, which thus led to the release of two free water molecules (in the aqueous phase) after Pd extraction into the organic phase. The malonamide and the formed Pd^{II} complex, denoted by the horizontal line over them in Equation (4), were taken in DCE. The computed differences in Gibbs free energy of the considered extraction reactions are presented in Figure 7. The results are in good agreement with the experimental data. The experimental tendency observed with the increase in the number of the methylene units in the spacer is reflected by the corresponding computed tendency. The average gain in coordination energy per methylene unit is approximately 1 kCal mol^{-1}, which corresponds to an approximately fivefold increase in the corresponding reaction constant and, consequently, the distri-

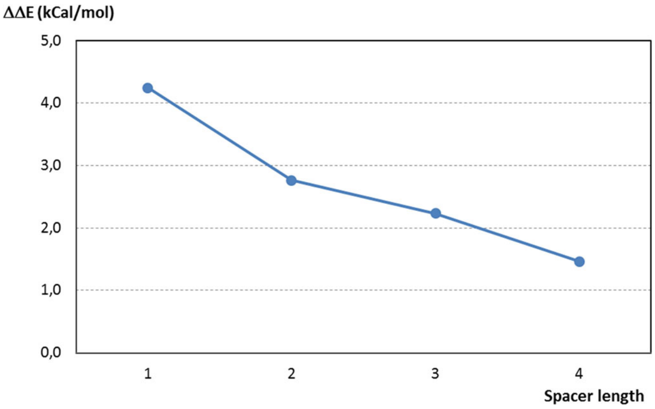


Figure 7. Differences in free energy of extraction with Me-HxF7–8 compounds computed in aqueous and organic phases according to Equation (4); extraction with Me-H14 was taken as the reference state.

bution ratio. In terms of extraction efficiency, this corresponds to an extraction yield that rose from 20 to 50%, or 50 to 80%. This is in very good agreement with the experimental results obtained for the extraction of Pd from a 3 M aqueous phase (Figure 3a). However, the theoretical values do not reveal an asymptotic tendency starting from three to four methylene units, as was observed in the experimental case. Furthermore, the four-unit spacer did not lead to the same energy as with the Me-H14 compound. This is in agreement with the previously reported computational studies,[11,13] in which a four-unit spacer appeared to screen only half of the inductive effect of the F-chain. This energy difference between Me-H4F8 and Me-H14 could also result from a non-negligible difference in solvent effect between the F-chain and the H-chain. This seems reasonable because the solvent–chain interactions are expected to vary significantly between alkyl and perfluoroalkyl groups. Consequently, the solvation energies should be different, even though the molecular volume of the H14 chain lies between those of the H2F8 and H3F8 chains. The difficulty in producing an accurate model of the observed experimental tendencies arises from the small energy differences responsible for a strong modification of the metal extraction outcome.

3. Conclusions

We synthetized and evaluated two families of fluorinated malonamides with various spacer lengths between the F-ponytail and the malonamide moiety. Both experimental and theoretical results bring consistency to the expected long-range electronic effect of the F-ponytail. In metal extraction, the present study led us to conclude that four methylene units between the polar complexing head and the F-ponytail allow complete shielding of the electronic effect. Extraction of a selection of metals showed that, in general, the extraction behavior of fluorinated malonamides with four methylene units is equivalent to analogue nonfluorinated malonamides under various conditions. Furthermore, the net gain on going from a three-unit spacer to a four-unit spacer is mostly moderate in all cases, whereas there is a marked difference between two-unit and three-unit spacers. The latter difference is highlighted by variations in some physicochemical properties, such as NMR chemical shifts, and is accompanied by a severe drop in extraction yields. However, the energy differences involved are low and there are still difficulties to find an accurate marker of the long-range electronic effect. It was possible to model the experimental trend from differences in the free energy of extraction related to metal chelation by the malonamides, albeit still with a gap between the four-unit spacer and the hydrocarbon compound. From a practical point of view, a three-unit spacer seems the best compromise for metal-stabilization purposes. The synthesis yields were also higher in this case and there was no issue of solubility in fluorous solvents. However, lower extraction yields observed in fluorinated media with Bu-series compounds suggest that supramolecular features and solvent effects need to be better taken into account. The stabilization of a metallic cation in a complex fluorinated organic phase not only depends on the attenuation of the electron-withdrawing effect of the F-ponytail, but also requires a precise description of those complex fluids by taking into account the interactions beyond first neighbors.

Experimental Section

Instrumentation and Methods

Bu-H14 (*N*,*N*′-dimethyl-*N*,*N*′-dibutyltetradecylmalonamide or DMDBTDMA) was kindly provided by the CEA, France (DEN/MAR/DRCP). Palladium(II) nitrate hydrate and gold(III) chloride trihydrate were purchased from Strem. Neodymium(III) nitrate hexahydrate, iron(III) nitrate nonahydrate, aluminum(III) nitrate nonahydrate, nickel(II) nitrate hexahydrate, copper(II) nitrate hemipentahydrate, and zinc(II) nitrate hydrate were purchased from Sigma–Aldrich and were used as received. Solvents (*n*-heptane, toluene, ethyl acetate, diethyl ether, ethanol, THF), concentrated nitric acid, and HCl were purchased from Carlo Erba Reagents. Other chemical reagents were purchased from Sigma–Aldrich. Fluorinated molecules were purchased from Abcr or Fluorochem and were used as received.

Aqueous stock solutions of palladium(II) (2000 mg L^{-1}) and gold(III) (2000 mg L^{-1}) were prepared by dissolving the required amount of metal salt in HNO_3 (10 mL, 5 M). Both solutions proved stable over 4 months, but aliquots were checked regularly by using inductively coupled plasma atomic emission spectroscopy (ICP-AES) to monitor metal precipitation. Multimetal zinc/aluminum/nickel and neodymium/iron/copper stock solutions (4000 mg L^{-1}) in HNO_3 (6 M) were also prepared by following the same protocol and proved to be stable for over a year.

Extractions were performed in 2 mL vials with equal volumes of an organic phase that contained the ligand and aqueous HNO_3 that contained a known amount of metal(s). Aqueous phases were prepared by dilution of the corresponding stock solution into aqueous HNO_3 (5 M), and the concentration was adjusted with deionized water. Aqueous concentrations were set at 100 mg L^{-1} for all metals in the study. Organic phases were prepared by dissolving the desired ligand in the appropriate solvent and were used as-synthesized. The two phases were vigorously shaken at 1500 rpm by using an IKA-Vibrax VXR basic shaker in a 20 °C (±1 °C) environment for 1 h. The tubes were removed and centrifuged for 5 min, or until complete phase separation, and the phases were separated. The organic phases were back-extracted with thiourea (1 mL, 0.1 м) in water at 20 °C (± 1 °C) for 1 h. The total concentrations of metal(s) in each phase (extraction phase and stripping phase) were determined by using ICP-AES (SpectroArcos spectrometer). NMR spectroscopy studies were performed by using a Bruker Ultrashield 400 plus engine.

Example Synthesis of Substituted Diethyl Malonates 1–3: $F(CF_2)_8(CH_2)_2CH(COOEt)_2$ (1)

NaH (60 % in oil; 1.05 g; 34 mmol; 1.5 equiv.) was washed with *n*-heptane (2×10 mL) in an oven-dried round-bottom flask (volume = 100 mL) with a magnetic stirrer. The grey powder turned white, then excess heptane was removed by using a Pasteur pipette. Dry THF (10 mL) was added, the temperature was reduced to 0 °C, and the flask was placed under a nitrogen atmosphere prior to dropwise addition of diethylmalonate (5.3 mL, 34 mmol, 2 equiv.). Gas release was observed and the suspension turned clear over 15 min. After a further 15 min at 0 °C, $F(CF_2)_8(CH_2)_2I$ (10 g, 17 mmol, 1 equiv.) in dry THF (10 mL) was added dropwise by syringe, then dry THF (10 mL; [R–I] = 0.5 м) was used to rinse the glassware and the solution was heated at reflux overnight. A white powder (NaI) precipitated after 45 min. The reaction mixture was filtered and the white deposit was washed with Et_2O. The mixture was concentrated under vacuum to afford an oil, then the residue was partitioned between EtOAc and brine. The organic phase was washed with brine then dried over $MgSO_4$, filtered, and concentrated to afford a mixture of excess diethyl malonate and substituted product, which was used directly in the subsequent step. The excess malonate could be removed by using bulb-to-bulb distillation at 110 °C (10 mmHg)$^{-1}$ to afford title compound **1** (*m* = 8.86 g yield 84 %). Compounds **1**, **2**, and **3** were obtained as colorless oils.

Diethyl 2-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)malonate (1)

$M_r(C_{17}H_{15}F_{17}O_4) = 606.27\ g\,mol^{-1}$; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 4.21$ (m, 4 H), 3.41 (t, $J = 6.8$ Hz, 1 H), 2.20 (m, 4 H), 1.27 ppm (t, $J = 7.1$ Hz, 6 H); ^{13}C NMR (101 MHz, $CDCl_3$): $\delta = 168.4$ (*C*O), 120.6–108.2 (CF_2), 61.7 (CH_2), 50.7 (*C*H), 28.5 (CH_2), 19.7 (CH_2), 13.9 ppm (CH_3); ^{19}F NMR (376 MHz, $CDCl_3$): $\delta = -81.02$, −114.64, −121.84, −122.06, −122.86, −123.55, −126.28 ppm; IR (ATR): $\tilde{\nu} = 2984$, 1735, 1200, 1145, 1029, 704, 653 cm^{-1}; HRMS-ES$^+$: *m/z* calcd for $C_{17}H_{16}F_{17}O_4$ $[MH]^+$: 607.0777; found: 607.0779.

Diethyl 2-(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecyl)malonate (2)

$M_r(C_{18}H_{17}F_{17}O_4) = 620.30\ g\,mol^{-1}$; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 4.14$ (q, $J = 7.1$ Hz, 4 H), 3.28 (t, $J = 7.4$ Hz, 1 H), 2.03 (tt, $J = 26.1$, 9.1 Hz, 2 H), 1.92 (q, $J = 7.8$ Hz, 2 H), 1.60 (m, 2 H), 1.20 ppm (t, $J = 7.1$ Hz, 6 H); ^{13}C NMR (101 MHz, $CDCl_3$):$\delta = 168.9$ (*C*O), 121.4–105.5 (CF_2), 61.5 (CH_2), 51.6 (*C*H), 30.6 (CH_2), 28.0 (CH_2), 18.2 (CH_2), 13.9 ppm (CH_3); ^{19}F NMR (376 MHz, $CDCl_3$): $\delta = -81.11$, −114.53, −121.90, −122.11, −122.92, −123.70, −126.36 ppm; IR (ATR): $\tilde{\nu} = 2993$, 1734, 1200, 1145, 1022, 705, 656 cm^{-1}; HRMS-ES$^+$: *m/z* calcd for $C_{18}H_{18}F_{17}O_4$ $[MH]^+$: 621.0934; found: 621.0938.

Diethyl 2-(5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-heptadecafluorododecyl)malonate (3)

$M_r(C_{19}H_{19}F_{17}O_4) = 634.32\ g\,mol^{-1}$; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 4.13$ (dq, $J = 7.1$, 1.4 Hz, 4 H), 3.25 (t, $J = 7.4$ Hz, 1 H), 2.00 (tt, $J = 18.1$, 8.8 Hz 2 H), 1.86 (q, $J = 7.8$ Hz, 2 H), 1.58 (m, 2 H), 1.37 (m, 2 H), 1.20 ppm (t, $J = 7.1$ Hz, 6 H); ^{13}C NMR (101 MHz, $CDCl_3$): $\delta = 169.2$ (*C*O), 120.8–108.3 (CF_2), 61.4 (CH_2), 51.7 (*C*H), 30.6 (CH_2), 28.3 (CH_2), 26.8 (CH_2), 19.9 (CH_2), 14.0 ppm (CH_3); ^{19}F NMR (376 MHz, $CDCl_3$): $\delta = -80.82$, −114.40, −121.74, −121.94, −122.73, −123.52, −126.12 ppm; IR (ATR): $\tilde{\nu} = 2989$, 1733, 1200, 1145, 1039, 704, 656 cm^{-1}; HRMS-ES$^+$: *m/z* calcd for $C_{19}H_{20}F_{17}O_4$ $[MH]^+$: 635.1090; found: 635.1094.

Example Synthesis of substituted Malonic Acids (4–6): $F(CF_2)_8(CH_2)_2CH(COOH)_2$ (4)

The reaction could be performed with either the crude mixture from the first step or with a diethyl malonate. $F(CF_2)_8(CH_2)_2CH(COOEt)_2$ (**1**; 6.85 g, 11.3 mmol 1 equiv.) was dissolved in ethanol (23 mL, [**1**] = 0.5 м) in a round-bottom flask (volume = 100 mL) equipped with a magnetic stirrer. KOH (50 % w/w) in water (2.5 mL, 33.9 mmol, 3 equiv.) was added and the mixture was stirred at reflux overnight, during which a solid precipitated. The suspension was diluted with water (20 mL, pH > 10) and washed with Et_2O (3×20 mL). The aqueous phase was cooled to 0 °C and acidified by using aqueous HCl (37 %) until pH < 2. The aqueous phase was then extracted with Et_2O (3×20 mL). The organic phase was dried over $MgSO_4$, filtered, and concentrated under vacuum. Recrystallization from ethanol afforded title compound **4** (*m* = 5.45 g, yield = 87 %). Compounds **4**, **5**, and **6** were obtained as light-yellow powders.

2-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluorodecyl)-malonic acid (4)

$M_r(C_{13}H_7F_{17}O_4) = 550.17\ g\,mol^{-1}$; m.p. 131 °C; ^1H NMR (400 MHz, MeOD): $\delta = 3.49$ (t, $J = 7.1$ Hz, 1 H), 2.32 (m, 2 H), 2.14 ppm (m, 2 H); ^{13}C NMR (101 MHz, MeOD): $\delta = 170.7$ (*C*O), 120.9–108.3 (CF_2), 50.2 (*C*H), 28.1 (CH_2), 19.4 ppm (CH_2); ^{19}F NMR (376 MHz, MeOD): $\delta = -82.37$, −115.69, −122.71, −122.89, −123.72, −124.52, −127.26 ppm; IR (ATR): $\tilde{\nu} = 2950$ (broad), 1692, 1198, 1146, 653, 559, 511 cm^{-1}; HRMS-ES$^-$: *m/z* calcd for $C_{13}H_6F_{17}O_4$ $[M]^-$: 548.9995; found: 549.0002.

2-(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-Heptadecafluoroundecyl)malonic acid (5)

$M_r(C_{14}H_9F_{17}O_4) = 564.20\ g\,mol^{-1}$; m.p. 148 °C; ^1H NMR (400 MHz, MeOD): $\delta = 3.39$ (t, $J = 7.4$ Hz, 1 H), 2.23 (tt, $J = 19.0$, 8.0 Hz, 2 H), 1.97 (t, $J = 7.9$ Hz, 2 H), 1.69 ppm (m, 2 H); ^{13}C NMR (101 MHz, MeOD): $\delta = 171.3$ (*C*O), 121.4–105.9 (CF_2), 51.2 (*C*H), 30.1 (CH_2), 27.7 (CH_2), 17.9 ppm (CH_2); ^{19}F NMR (376 MHz, MeOD): $\delta = -82.42$, −115.39, −122.75, −122.93, −123.76, −124.50, −127.28 ppm; IR (ATR): $\tilde{\nu} = 2952$ (broad), 1690, 1198, 1146, 655, 559, 529 cm^{-1}; HRMS-ES$^-$: *m/z* calcd for $C_{14}H_8F_{17}O_4$ $[M]^-$: 563.0151; found: 5563.0156.

2-(5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-Heptadecafluorododecyl)malonic acid (6)

M$_r$($C_{15}H_{11}F_{17}O_4$) = 578.22 g mol^{-1}; m.p. 113 °C; ^{1}H NMR (400 MHz, MeOD): δ = 3.35 (m, 1H), 2.18 (tt, *J* = 19.1, 8.0 Hz, 2H), 1.91 (m, 2H), 1.67 (m, 2H), 1.49 ppm (m, 2H); ^{13}C NMR (101 MHz, MeOD): δ = 171.6 (*C*O), 121.2–108.1 (*C*F$_2$), 51.4 (*C*H), 30.1 (*C*H$_2$), 28.2 (*C*H$_2$), 26.5 (*C*H$_2$), 19.7 ppm (*C*H$_2$); ^{19}F NMR (376 MHz, MeOD): δ = −82.37, −115.38, −122.73, −122.90, −123.72, −124.47, −127.26 ppm; IR (ATR): $\tilde{\nu}$ = 2963, 1700, 1195, 1145, 655, 559, 528 cm^{-1}; HRMS-ES$^+$: *m/z* calcd for $C_{15}H_{12}F_{17}O_4$ [*M*H]$^+$: 579.0464; found: 579.0469.

Example Synthesis of Substituted Malonamides (7–12): $F(CF_2)_8(CH_2)_2CH(CONMe_2)_2$ (7)

$F(CF_2)_8(CH_2)_2CH(COOH)_2$ (**4**; 2 g, 3.63 mmol, 1 equiv.) was ground to a fine powder and then suspended in toluene (60 mL; [**4**] = 0.06 M) and DMF (40 µL, 0.55 mmol, 0.15 equiv.) in an oven-dried round-bottom flask (volume = 100 mL) with a magnetic stirrer. The temperature was reduced to 0 °C and the flask was placed under a nitrogen atmosphere prior to dropwise addition of oxalyl chloride (0.78 mL, 9.10 mmol, 2.5 equiv.). The stirring speed was adapted to ensure good mixing and control of the resulting foam formation. After 20 min, the temperature was allowed to rise to RT and after 45 min the reaction mixture turned clear and the solution was transferred by syringe into a solution of $HNMe_2$ (2 M) in THF (18 mL, 36 mmol, 10 equiv.) diluted with toluene (20 mL) at 0 °C. The glassware was rinsed with toluene (10 mL) and the final solution was stirred overnight at RT. K_2CO_3 (1 g) was added to the solution and after 1 h the suspension was filtered and the solid was washed with DCM. The filtrate was concentrated under vacuum and the residue was partitioned between EtOAc and brine. The organic phase was washed twice with brine, then dried over $MgSO_4$, filtered, and concentrated under vacuum. The crude product was purified by using column chromatography (eluent: pure cyclohexane to pure EtOAc) to afford title compound **7** (*m* = 1.65 g, yield = 75 %). Compounds **7**, **8**, and **9** were obtained as white/light-yellow solids. Compounds **10**, **11**, and **12** were obtained as light-yellow oils.

2-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluorodecyl)-N^1,N^1,N^3,N^3-tetramethylmalonamide (7)

M$_r$($C_{17}H_{17}F_{17}N_2O_2$) = 604.30 g mol^{-1}; *R*$_f$ = 0.20 (EtOAc); m.p. 67 °C; ^{1}H NMR (400 MHz, CDCl$_3$): δ = 3.67 (t, *J* = 6.6 Hz, 1H), 2.95 (s, 6H), 2.92 (s, 6H), 2.24 (m, 2H), 2.12 ppm (m, 2H); ^{13}C NMR (101 MHz, CDCl$_3$): δ = 168.6 (*C*O), 121.3–108.1 (*C*F$_2$), 48.0 (*C*H), 37.0 (*C*H$_3$), 36.0 (*C*H$_3$), 28.9 (*C*H$_2$), 20.0 ppm (*C*H$_2$); ^{19}F NMR (376 MHz, CDCl$_3$): δ = −80.76, −114.15, −121.64, −121.89, −122.68, −123.30, −126.09 ppm; IR (ATR): $\tilde{\nu}$ = 2954, 1651, 1634, 1196, 1144, 656, 560, 497 cm^{-1}; HRMS-ES$^+$: *m/z* calcd for $C_{17}H_{18}F_{17}N_2O_2$ [*M*H]$^+$: 605.1097; found: 605.1100.

2-(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-Heptadecafluoroundecyl)-N^1,N^1,N^3,N^3-tetramethyl Malonamide (8)

M$_r$($C_{18}H_{19}F_{17}N_2O_2$) = 618.33 g mol^{-1}; *R*$_f$ = 0.22 (EtOAc); m.p. 84 °C; ^{1}H NMR (400 MHz, CDCl$_3$): δ = 3.56 (t, *J* = 6.7 Hz, 1H), 2.95 (s, 6H), 2.91 (s, 6H), 2.05 (tt, *J* = 19.0, 8.0 Hz, 2H), 1.91 (m, 2H), 1.62 ppm (m, 2H); ^{13}C NMR (101 MHz, CDCl$_3$): δ = 169.0 (*C*O), 121.4–105.5 (*C*F$_2$), 49.5 (*C*H), 37.0 (*C*H$_3$), 36.1 (*C*H$_3$), 30.8 (*C*H$_2$), 28.5 (*C*H$_2$), 19.2 ppm (*C*H$_2$); ^{19}F NMR (376 MHz, CDCl$_3$): δ = −80.84, −114.17, −121.74, −121.95, −122.75, −123.54, −126.14 ppm; IR (ATR): $\tilde{\nu}$ = 2948, 1651, 1633, 1199, 1143, 655, 559 cm^{-1}; HRMS-ES$^+$: *m/z* calcd for $C_{18}H_{20}F_{17}N_2O_2$ [*M*H]$^+$: 619.1253; found: 619.1257.

2-(5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-Heptadecafluorododecyl)-N^1,N^1,N^3,N^3-tetramethyl Malonamide (9)

M$_r$($C_{19}H_{21}F_{17}N_2O_2$) = 632.36 g mol^{-1}; *R*$_f$ = 0.25 (EtOAc); m.p. 75 °C; ^{1}H NMR (400 MHz, CDCl$_3$): δ = 3.54 (t, *J* = 6.7 Hz, 1H), 2.94 (s, 6H), 2.91 (s, 6H), 2.01 (tt, *J* = 19.0, 8.0 Hz, 2H), 1.86 (q, *J* = 7.5 Hz, 2H), 1.58 (p, *J* = 7.8 Hz, 2H), 1.40 ppm (p, *J* = 7.7 Hz, 2H); ^{13}C NMR (101 MHz, CDCl$_3$): δ = 169.3 (*C*O), 120.9–108.1 (*C*F$_2$), 49.5 (*C*H), 37.0 (*C*H$_3$), 36.1 (*C*H$_3$), 30.6 (*C*H$_2$), 28.7 (*C*H$_2$), 27.7 (*C*H$_2$), 20.2 ppm (*C*H$_2$); ^{19}F NMR (376 MHz, CDCl$_3$): δ = −80.74, −114.36, −121.70, −121.89, −122.67, −123.49, −126.07 ppm; IR (ATR): $\tilde{\nu}$ = 2951, 1660, 1630, 1199, 1144, 655, 560, 530 cm^{-1}; HRMS-ES$^+$: *m/z* calcd for $C_{19}H_{22}F_{17}N_2O_2$ [*M*H]$^+$: 633.1410; found: 633.1415.

N^1,N^3-Dibutyl-2-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)-N^1,N^3-dimethyl Malonamide (10)

M$_r$($C_{23}H_{29}F_{17}N_2O_2$) = 688.46 g mol^{-1}; *R*$_f$ = 0.20 (cyclohexane/EtOAc 1:1); ^{1}H NMR (400 MHz, CDCl$_3$): δ = 3.63 (m, 1H), 3.25 (m, 4H), 2.89 (m, 6H), 2.23 (m, 2H), 2.09 (m, 2H), 1.45 (m, 4H), 1.24 (m, 4H), 0.87 ppm (m, 6H); ^{13}C NMR (101 MHz, CDCl$_3$): δ = 167.3 (*C*O), 120.3–108.4 (*C*F$_2$), 48.4 (*C*H), 47.2 (*C*H$_2$), 34.1 (*C*H$_3$), 32.5 (*C*H$_2$), 29.4 (*C*H$_2$), 28.1 (*C*H$_2$), 19.0 (*C*H$_2$), 12.8 ppm (*C*H$_3$); ^{19}F NMR (376 MHz, CDCl$_3$): δ = −80.75, −114.16, −121.65, −121.89, −122.68, −123.36, −126.08 ppm; IR (ATR): $\tilde{\nu}$ = 2962, 2935, 1638, 1200, 1142, 654 cm^{-1}; HRMS-ES$^+$: *m/z* calcd for $C_{23}H_{30}F_{17}N_2O_2$ [*M*H]$^+$: 689.2036; found: 689.2037.

N^1,N^3-Dibutyl-2-(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecyl)-N^1,N^3-dimethyl Malonamide (11)

M$_r$($C_{24}H_{31}F_{17}N_2O_2$) = 702.49 g mol^{-1}; *R*$_f$ = 0.20 (cyclohexane/EtOAc 1:1); ^{1}H NMR (400 MHz, CDCl$_3$): δ = 3.52 (m, 1H), 3.23 (m, 4H), 2.88 (m, 6H), 2.05 (tt, *J* = 19.2, 7.8 Hz, 2H), 1.90 (m, 2H), 1.62 (m, 2H), 1.44 (m, 4H), 1.24 (m, 4H), 0.87 ppm (m, 6H); ^{13}C NMR (101 MHz, CDCl$_3$): δ = 168.7 (*C*O), 120.8–108.2 (*C*F$_2$), 50.3 (*C*H$_2$), 50.0 (*C*H$_2$), 49.3 (*C*H), 48.3 (*C*H$_2$), 35.1 (*C*H$_3$), 33.6 (*C*H$_2$), 30.5 (*C*H$_2$), 29.1 (*C*H$_2$), 28.6 (*C*H$_2$), 20.0 (*C*H$_2$), 19.2 (*C*H$_2$), 13.8 ppm (*C*H$_3$); ^{19}F NMR (376 MHz, CDCl$_3$): δ = −80.76, −114.13, −121.70, −121.90, −122.69, −123.49, −126.07 ppm; IR (ATR): $\tilde{\nu}$ = 2964, 2938, 1636, 1201, 1145, 655 cm^{-1}; HRMS-ES$^+$: *m/z* calcd for $C_{24}H_{32}F_{17}N_2O_2$ [*M*H]$^+$: 703.2192; found: 703.2189.

N^1,N^3-Dibutyl-2-(5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-heptadecafluorododecyl)-N^1,N^3-dimethyl Malonamide (12)

M$_r$($C_{25}H_{33}F_{17}N_2O_2$) = 716.51 g mol^{-1}; *R*$_f$ = 0.24 (cyclohexane/EtOAc 1;1); ^{1}H NMR (400 MHz, CDCl$_3$): δ = 3.56 (m, 1H), 3.32 (m, 4H), 2.96 (m, 6H), 2.09 (m, 2H), 1.92 (m, 2H), 1.66 (m, 2H), 1.52 (m, 6H), 1.32 (m, 4H), 0.95 ppm (m, 6H); ^{13}C NMR (101 MHz, CDCl$_3$): δ = 169.1, 169.04, 169.02, 165.1, 164.9 (*C*O), 120.8–108.2 (*C*F$_2$), 50.0, 49.9, 49.8, 49.3, 48.3, 48.2, 45.93, 45.90, 35.12, 35.10, 34.8, 33.64, 33.61, 31.3, 30.8, 30.6, 30.54, 30.52, 30.4, 30.1, 29.2, 29.1, 28.9, 28.8, 28.5, 27.8, 20.2, 20.0, 19.8, 13.8, 13.7 ppm (multiple rotamers); ^{19}F NMR (376 MHz, CDCl$_3$): δ = −80.80, −114.45, −121.79, −121.99, −122.77, −123.57, −126.16 ppm; IR (ATR): $\tilde{\nu}$ = 2961, 2935, 1637, 1201, 1145, 654 cm^{-1}; HRMS-ES$^+$: *m/z* calcd for $C_{25}H_{34}F_{17}N_2O_2$ [*M*H]$^+$: 717.2349; found: 717.2352.

Synthesis of the Triflic Ester ($C_7F_{15}CH_2OTf$, 13)

$C_7F_{15}CH_2OH$ (2 g, 5 mmol, 1 equiv.), pyridine (0.480 mL, 6 mmol, 1.2 equiv.), and dry DCM (10 mL, [ROH] = 0.5 M) were mixed in an oven-dried flask (volume = 25 mL) equipped with a magnetic stirrer for 10 min under argon, then cooled to 0 °C in an ice bath. $(CF_3SO_2)_2O$ (1 mL, 6 mmol, 1.2 equiv.) was introduced dropwise by syringe. The mixture was stirred at RT overnight to give a white suspension. The solvent was removed under vacuum and the residue was partitioned between Et_2O and ice-cold water. The organic phase was washed twice with a minimum of water, then dried over $MgSO_4$, filtered, and concentrated under vacuum to afford a slightly yellow oil. The crude product could be used without purification in the alkylation step; the purified product was revealed to be moisture sensitive and fairly unstable (purification by bulb-to-bulb distillation at 55 °C (10 mm Hg)$^{-1}$ with an ice/salt trap).

2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-Pentadecafluorooctyltrifluoromethane Sulfonate (13)

$M_r(C_9H_2F_{18}O_3S) = 532.15\ g\,mol^{-1}$; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 4.85$ ppm (t, $J = 12.30$ Hz, 2 H); ^{19}F NMR (376 MHz, $CDCl_3$): $\delta = -74.05, -80.87, -119.76, -121.94, -122.86, -126.21$ ppm.

Synthesis of Substituted Malonamide (Me-H1F7, 14)

NaH (60 % in oil; 152 mg; 3.8 mmol; 2.0 equiv.) was washed with *n*-heptane (2 × 10 mL) in an oven-dried round-bottom flask (volume = 50 mL) with a magnetic stirrer. The grey powder turned white, then excess heptane was removed by using a Pasteur pipette. Dry THF (3 mL) was added, the temperature was reduced to 0 °C, and the flask was placed under a nitrogen atmosphere prior to dropwise addition of diethyl malonate (0.59 mL, 3.8 mmol, 2.0 equiv.). Gas release was observed and the suspension turned clear over 15 min. After a further 15 min at 0 °C, $C_7F_{15}CH_2OTf$ (**13**; 1 g, 1.9 mmol, 1.0 equiv.) was added dropwise by syringe, then dry THF (1 mL) was used to rinse the glassware ([R–OTf] = 0.5 M). The solution was heated at reflux overnight. The reaction mixture was cooled to RT and filtered, then the white deposit was washed with Et_2O. The mixture was concentrated under vacuum to afford an oil, then the residue was partitioned between EtOAc and brine. The organic phase was washed with brine then dried over $MgSO_4$, filtered, and concentrated under vacuum. The crude product was placed in a round-bottom flask (volume = 50 mL) equipped with a magnetic stirrer and dissolved in ethanol (10 mL; [malonate] = 0.4 M). A solution of KOH (50 % w/w) in water (0.84 mL, 11.4 mmol, 3.0 equiv.) was added and the resulting solution was heated at reflux overnight. During that time, a solid precipitate appeared. The suspension was cooled to RT and diluted with 3 mL of water (pH > 10). The ethanol was removed under vacuum and the resulting solution was washed with Et_2O. The aqueous solution was cooled to 0 °C prior to acidification with HCl (12 M) until pH < 2, then the aqueous phase was extracted with Et_2O (3 × 20 mL). The combined organic phases were dried over $MgSO_4$, filtered, and concentrated under vacuum to afford a white powder. The final stage (stage 3) was performed according to the same protocol described above for compound **7** to afford **14** as a white solid ($m = 0.66$ g, overall yield 66 %).

N^1,N^1,N^3,N^3-Tetramethyl-2-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctyl)malonamide (14)

$M_r(C_{15}H_{15}F_{15}N_2O_2) = 540.27\ g\,mol^{-1}$; $R_f = 0.30$ (EtOAc); m.p. 84 °C; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 4.13$ (t, $J = 5.4$ Hz, 1 H), 3.08 (s, 6 H), 3.03 (s, 6 H), 2.89 ppm (td, $J = 29.8$, 4.9 Hz, 2 H); ^{13}C NMR (101 MHz, $CDCl_3$): $\delta = 167.5$ (*C*O), 121.4–108.2 (*C*F), 40.3 (*C*H), 37.0 (*C*H3), 36.4 (*C*H3), 30.7 ppm (*C*H2); ^{19}F NMR (376 MHz, $CDCl_3$): $\delta = -80.77, -113.48, -121.56, -122.05, -122.72, -123.37, -126.11$ ppm; IR (ATR): $\tilde{\nu} = 2937, 1662, 1194, 1140, 1095, 883, 714\ cm^{-1}$; HRMS-ES$^+$: *m/z* calcd for $C_{15}H_{16}F_{15}N_2O_2$ $[MH]^+$: 541.0972; found: 541.0975.

^1H, ^{13}C, and ^{19}F NMR spectra of all new compounds are provided in the Supporting Information.

Computational Details

Full geometry optimizations and frequency computations were performed by applying the DFT method with Becke's three-parameter hybrid functional[26] and Lee–Yang–Parr's gradient-corrected correlation functional[27] (B3LYP). 6,31-G(d,p)** and LANL2DZ-ECP basis sets[28] were used for ligands and complexes (Pd, C, H, N, O, and F) by assuming the singlet state for the ground state in all calculations. The structures of Me-H1–4F8 were fully optimized by using the 6,31-G basis set and the data were then used as the input for the optimization of the corresponding Pd^{II} complexes. The energies were computed by using the 6,31-G(d,p)** and the LANL2DZ-ECP basis sets in vacuum or in 1,2-DCE, and the solvent effect was considered by using the polarizable continuum model[29] (PCM, $\varepsilon_r = 10.4$ for DCE). All computations were performed by using the Gaussian 09 quantum-chemistry program package.[30]

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Conflict of interest

The authors declare no conflict of interest.

Keywords: electronic effects · fluorinated ligands · fluorine · metal extraction · palladium

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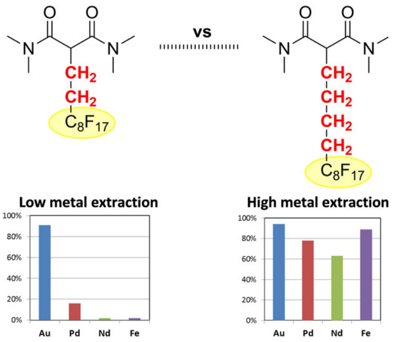

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Impact of the Long-Range Electronic Effect of a Fluorous Ponytail on Metal Coordination during Solvent Extraction