# Solid-state preparation of hybrid organometallic–organic macrocyclic adducts with long chain dicarboxylic acids†

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**The supramolecular macrocyclic adducts of general formula $\{[Fe(\eta^5\text{-}C_5H_4\text{-}C_5H_4N)_2]\cdot[HOOC(CH_2)_nCOOH]\}_2$ with $n = 4$ (adipic acid), $n = 6$ (suberic acid), $n = 7$ (azelaic acid) and $n = 8$ (sebacic acid) have been obtained quantitatively by kneading powdered samples of the crystalline organometallic and organic reactants with drops of MeOH (for $n = 4$, 6 and 7) and by direct crystallization from MeOH for $n = 8$, while the adduct with $n = 5$ represents an isomeric open chain alternative to the macrocycle.**

Mechanochemistry is an established branch of the chemical sciences where solid reactants are ground together in the solid-state to obtain polycrystalline products.[1] In recent years, there has been an expansion of this chemistry into the areas of supramolecular chemistry[2] and crystal engineering,[3] fuelled by an interest in exploring solvent free synthetic procedures for the preparation of molecular aggregates as an alternative to conventional solution chemistry.[4]

The number of papers reporting the solid-state preparation of molecular co-crystals,[5] coordination networks[6] and salts[7] is increasing rapidly. The impact on the investigation of crystal polymorphs and solvates is also noteworthy.[8]

Besides the absence of solvents being advantageous, reactions between solids often lead to very pure products and require very simple equipment to be carried out. The mixing of reactants can be achieved by simple manual grinding or by mechanical milling. Sometimes the reaction is accelerated or made altogether possible by kneading (also called "solvent drop grinding"), *i.e.*, by carrying out the grinding process in the presence of a "catalytic" amount of solvent.[5,7]

The main drawback of inter-solid reactions arises from the characterization of the polycrystalline reaction products. In the case of complex supramolecular systems, such as those described herein, the lack of single crystals can forsake a detailed knowledge of the structure, and often of the nature of the reaction product. This problem can be circumvented if single crystals of the target material can be grown from solution, often by seeding.[9]

We have already used solid-state methods in the preparation of molecular co-crystals, mainly with organometallic building blocks and coordination networks.[10]

In this communication we report the solid-state preparation of a series of novel hybrid organic–organometallic macrocycles of general formula $\{[Fe(\eta^5\text{-}C_5H_4\text{-}C_5H_4N)_2]\cdot[HOOC(CH_2)_nCOOH]\}_2$ ($n = 4$, 6 and 7), while the adducts with $n = 5$ and $n = 8$ have been obtained from solution crystallization. In all cases, the organic and organometallic moieties are held together by hydrogen bonds between the carboxylic –OH groups and the pyridine nitrogen atoms. More specifically, manual grinding of the solid organometallic complex $[Fe(\eta^5\text{-}C_5H_4\text{-}C_5H_4N)_2]$‡ (**1**) with the solid dicarboxylic acids of formula $HOOC(CH_2)_nCOOH$ [where $n = 4$ (adipic), 5 (pimelic), 6 (suberic), 7 (azelaic) and 8 (sebacic)] in the presence of traces of MeOH (by kneading) yields five novel compounds, as easily ascertained by comparing the powder diffraction patterns of the starting materials with those of the products. No formation of intermediate liquid phases has been observed. The reactions are easily followed by their diagnostic change in colour; while all organic acids are white and the organometallic complex **1** is orange, the colour of the solid macrocycle varies from orange-red to purple-red. It is worth recalling that the starting organometallic complex $[Fe(\eta^5\text{-}C_5H_4\text{-}C_5H_4N)_2]$ (**1**) can also be prepared by Suzuki coupling under solvent-free conditions.[11]

Single crystals§ of **1·adipic(4)**, **1·pimelic(5)**, **1·suberic(6)**, **1·azelaic(7)** and **1·sebacic(8)** (numbers in parentheses indicate the number of $CH_2$ groups in the acid chain) were grown from MeOH solutions where direct reaction between complex **1** and the acid had occurred. In the cases of **1·adipic(4)**, **1·suberic(6)** and **1·azelaic(7)**, comparison between the X-ray diffraction patterns measured for the kneaded samples and those calculated on the basis of the single crystal structures confirmed that the same compound had been prepared both from solution and mechanochemically, whereas in the cases of **1·pimelic(5)** and **1·sebacic(8)**, the observed and calculated patterns were different (*vide infra*).

All complexes, with the exception of **1·pimelic(5)**, share a common structural feature, namely the formation of supramolecular macrocycles comprising of two organometallic and two organic units linked in large tetramolecular units by O–H···N hydrogen bonds between the –COOH groups of the dicarboxylic acids and the N-atoms of the ferrocenyl complex. Fig. 1 shows the structures of **1·adipic(4)**, **1·suberic(6)**, **1·azelaic(7)** and **1·sebacic(8)**. It can be appreciated how the even/odd alternation of the carbon atoms in the organic spacers is accommodated by the twist of the cyclopentadienyl-pyridyl groups and by the eclipsed or staggered juxtaposition of the organic moieties.

The comparison between observed and calculated X-ray powder diffraction patterns in the case of **1·suberic(6)**, taken as an example, is shown in Fig. 2.¶

As mentioned above, in the case of **1·pimelic(5)**, crystallization from solution yields an adduct with the same stoichiometric composition as the macrocycles **1·adipic(4)**, **1·suberic(6)** and

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† Electronic supplementary information (ESI) available: Crystal data and XRPD patterns for all compounds. See DOI: 10.1039/b608691h

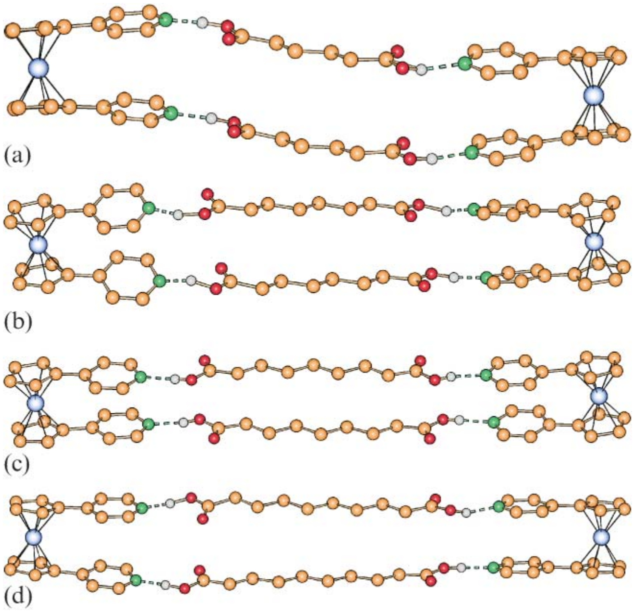

**Fig. 1** The supramolecular structures of the macrocycles (a) **1·adipic(4)**, (b) **1·suberic(6)**, (c) **1·azelaic(7)** and (d) **1·sebacic(8)** showing the hydrogen bond links between the two outer organometallic molecules and the inner organic spacers.

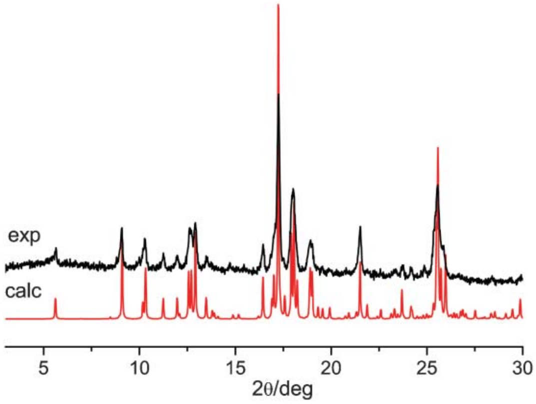

**Fig. 2** Comparison between the experimental (top) and calculated (bottom) X-ray powder patterns for **1·suberic(6)**.

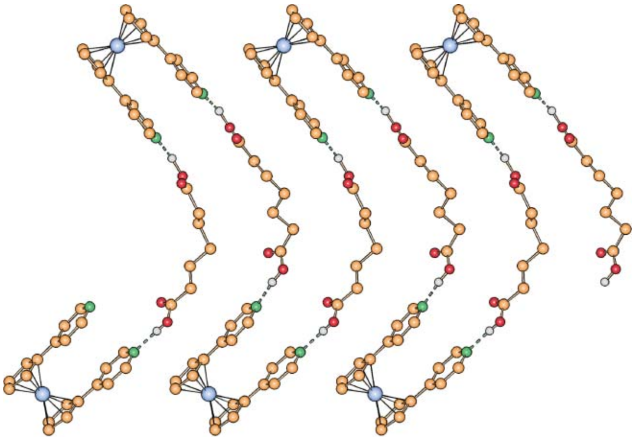

**Fig. 3** The zig-zag chain found in **1·pimelic(5)**. This structure suggests the existence of supramolecular isomers of the macrocycles shown in Fig. 1.

**1·azelaic(7)**, but with acid and base moieties organized in a zig-zag chain instead of as a macrocycle, and linked *via* $O–H_{COOH}\cdots N$ hydrogen bonds, as shown in Fig. 3. This structure does not yield the same powder diffraction pattern as that obtained by grinding. It is therefore interesting to speculate on the possibility of structural isomerism between closed (macrocycles) and open (zig-zag or other chain structures) arrangements, and also on their possible interconversion, which may also depend on the choice of solvent.[12] A similar, though inverse, situation is observed in the case of **1·sebacic(8)**; crystallization from solution yields the macrocycle, while grinding experiments produce a different

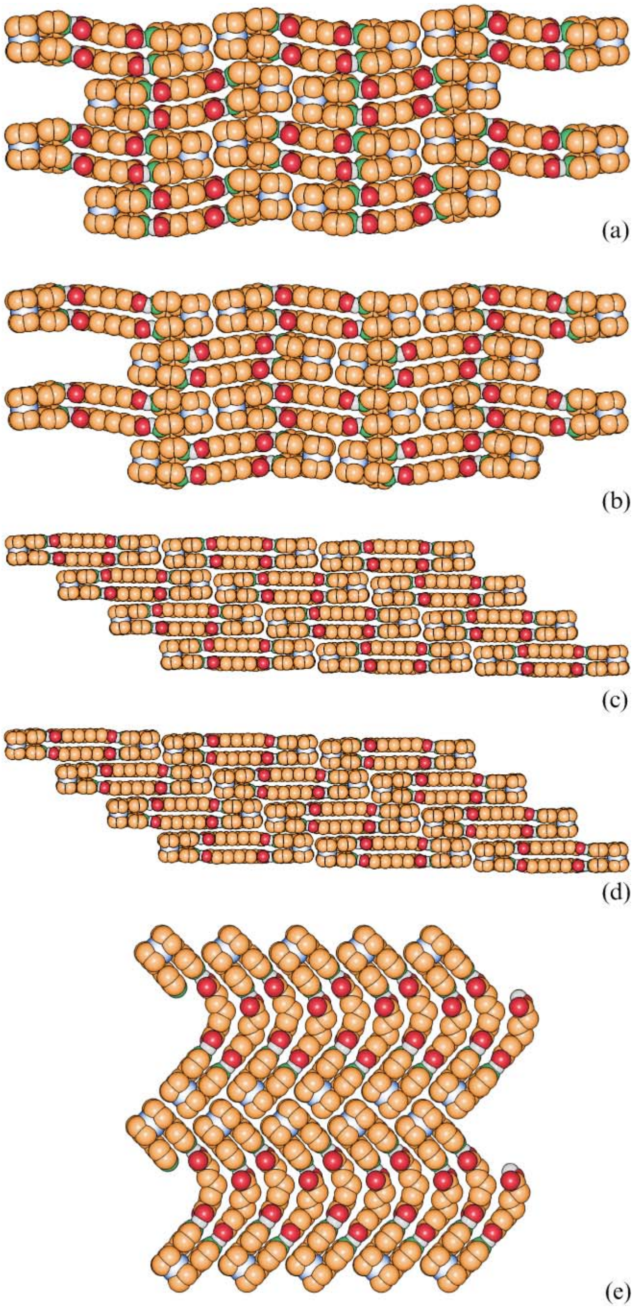

**Fig. 4** Strong structural analogy in the supramolecular organization of the layers in (a) **1·adipic(4)**, (b) **1·suberic(6)**, (c) **1·azelaic(7)** and (d) **1·sebacic(8)**. Note also the structural relationship with the ribbons in (e) **1·pimelic(5)**.

substance, which has not yet been characterized. Further studies are needed to address the problem of supramolecular isomerism in this class of compounds.

It is worth noting that, even though the quality of the X-ray data does not allow the drawing of confident conclusions, no proton transfer from acid to base appears to take place. Therefore, all adducts are made of neutral components. However, a solid-state NMR investigation[10a] is under way. The supramolecular metallamacrocycles also share some remarkable packing features in the solid-state, with all compounds forming layered structures, as shown in Fig. 4. The macrocycles are very anisotropic in shape, being characterized by two smaller dimensions (corresponding approximately to the size of the ferrocenyl moiety, which is constant) and one longer dimension, which varies with the dicarboxylic acid chain length, and form a "LEGO"® type of construct. These macrocycles are then placed next to each other in layers that can be wavy (**1·adipic(4)** and **1·suberic(6)**) or planar (**1·azelaic(7)** and **1·sebacic(8)**).

It is interesting to speculate on the fact that the formation of these complex packings implies the existence of molecular diffusion, significant molecular motion and bond breaking/forming, in agreement with Kaupp's model of molecular motion, phase reconstruction and extrusion as the solid-state reaction proceeds.[13]

Reactions between crystalline solids of the type used to prepare these macrocycles can be regarded as supramolecular reactions between solid, periodic supermolecules. In reactions between molecular solid reactants to form a new molecular solid product, the covalent bonding is not affected, while non-covalent van der Waals or hydrogen bonding interactions are broken and formed. In summary, we have provided further evidence that the kneading of organometallic and organic crystals can be exploited to prepare new supramolecular hybrid organic–organometallic macrocycles and networks.

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## Notes and references

‡ All reagents were purchased from Sigma-Aldrich and used without further purification. Reagent grade solvents were used. $Fe[\eta^5\text{-}C_5H_4\text{-}1\text{-}(4\text{-}C_5H_4N)]_2$ was synthesized as previously reported.[11] All crystallization solutions and mixtures for grinding reactions were initially prepared with an excess of the acid with respect to $[Fe(\eta^5\text{-}Cp\text{-}C_5H_4N)_2]_2$. After characterization, preparations were repeated with a 1 : 1 stoichiometric ratio. The mixtures of $[Fe(\eta^5\text{-}Cp\text{-}C_5H_4N)_2]_2$ and $COOH(CH_2)_nCOOH$ ($n = 4, 5, 6, 7$ and 8) were manually ground in an agate mortar for 5 min; single crystals of **1·adipic(4)**, **1·pimelic(5)**, **1·suberic(6)**, **1·azelaic(7)** and **1·sebacic(8)** suitable for single crystal X-ray diffraction were obtained by slow evaporation of a solution obtained by dissolving equimolar quantities of $[Fe(\eta^5\text{-}Cp\text{-}C_5H_4N)_2]_2$ (50 mg, 0.147 mmol) and $COOH(CH_2)_nCOOH$ (0.147 mmol, 21, 23, 25, 27 and 30 mg for $n = 4, 5, 6, 7$ and 8, respectively) in 5 mL of 99.8% MeOH. Co-grinding of the solids in stoichiometric ratios other than 1 : 1 (*e.g.*, 1 : 2 or 2 : 1) led to the formation of solid mixtures, with diffraction peaks corresponding to the unreacted excess reagent in addition to the peaks of the 1 : 1 compounds.

§ CCDC 614138–616142. For crystallographic data in CIF or other electronic format, see DOI: 10.1039/b608691h

¶ Powder data for all samples were collected on a Philips PW-1100 automated diffractometer with Cu-Kα radiation and a graphite monochromator using quartz sample holders. 25 mg of substance was employed for the pure reagents. The program PowderCell[14] was used for the calculation of X-ray powder patterns.

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