X-ray PDF investigations of complex metal-organic materials.

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Introduction

PDF investigation of luminescent gold thiolate glasses

PEDOT conducting polymer confined in mesoporous MOFs

Crystal Structure of the spin transition polymeric compound [Fe(Htrz)2(trz)](BF_4)

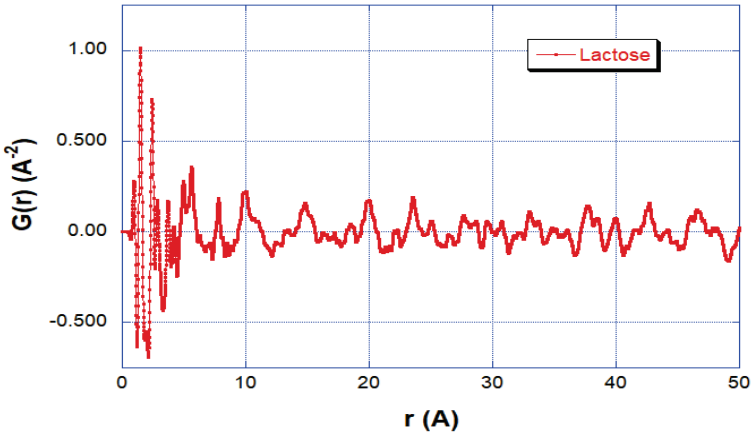
Conclusion

Many organic/organo metallic materials exist in disordered state (on purpose or not).
PDF analysis would be a tool of choice for the structural chracterization of such materials

But treating the PDF for organic/organometallic materials has specific difficulties

- low symmetry implies many parameters
  => possibility to handle large number of atoms

- necessity to limit the correlations between parameters+ presence of species with very different scattering powers
  => chemical contraints/restraints or rigid blocks



- different types of bonds and bond strengths (ionic, covalent, hydrogen, van derWaals)
  => different PDF peak widths depending on bond type, not distance

So, relatively few PDF studies of MOFs, even less with attempts to refine the structure

The Chemistry of Nucleation:InSitu Pair DistributionFunction AnalysisofSecondary Building Units During UiO-66 MOF Formation,
Xu et al. Chem. Eur.J. 2019, 25, 2051
Early stage structural development of prototypicalzeolitic imidazolate framework (ZIF) in solution, ,
Terban et al., Nanoscale,2018,10,4291
Pair distribution function-derived mechanism of a single-crystal to disorderedto single-crystal transformation in a hemilabile metal–organic framework ,
Allan et al. Chem. Sci., 2012,3, 2559

First successful refinements of organic compounds in **DiffPy-CMI** using rigid blocks and combining PDFs with different a.d.p.'s

DiffPy-CMI: Complex modeling: a strategy and softwareprogram for combining multiple informationsources to solve ill posed structure andnanostructure inverse problems, *Juhas et al., ActaCryst.2015. A71, 562*
Modelling pair distribution functions (PDFs) oforganic compounds: describing both intra- andintermolecular correlation Functions in calculated PDFs *Prill et al. J. Appl. Cryst.(2015).48, 171*

Here we use a different approach: applying distance/angle restrainsts and different a.d.p.'s for selected bonds, developped in **MolPDF**

MolPDF, Juan Rodriguez-Carvajal and Aleksei Bytchkov, ILL and ESRF, November 2016

In MolpDF, **distance and angle restraints** are input into the minimized cost function. The « strength » of the ith restraint depends on the value of $\sigma(i)$.

$$\chi^2 = \sum_r \left[\frac{G_{obs}(r) - G_{calc}(r, \boldsymbol{\beta})}{\sigma(r)} \right]^2 + \sum_{i=1}^{N_{rest}} \left[\frac{V_{obs}(i) - V_{calc}(i, \boldsymbol{\alpha})}{\sigma(i)} \right]^2$$

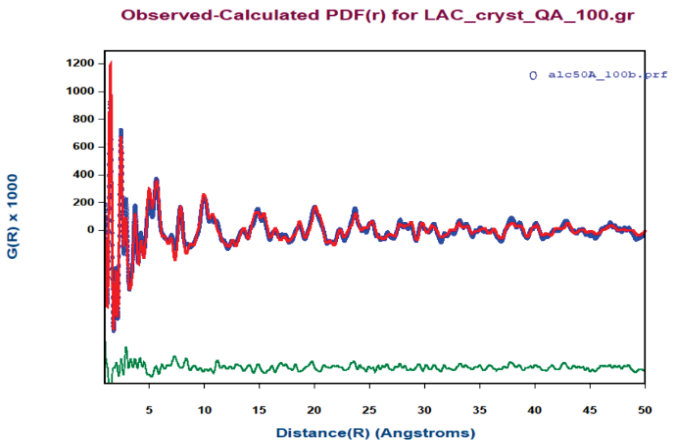
V_{obs}: prescribed value of the ith restrained variable (distance or angle)
V_{calc}: corresponding calculated value

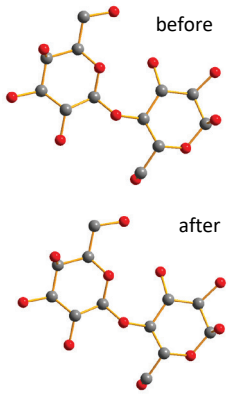
The PDF peak width due to thermal motion is described as in PDFGui plus the $\boldsymbol{s_{mol}}$ **sharpening** factor, $0<s_{mol}<=1$, applied to selected atomic pairs (e.g. differentiate between intra- and intermolecular distances)

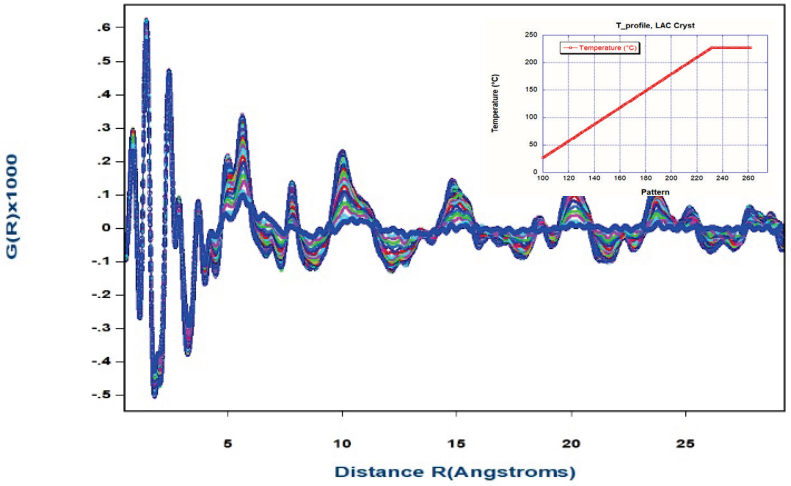
$$\sigma_{ij} = s_{mol}\sigma'_{ij}\sqrt{1 - \frac{\delta_1}{r_{ij}} - \frac{\delta_2}{r_{ij}^2} + Q_B^2 r_{ij}^2}$$

eg: structure refinement of *α-lactose* vs temperature up to melting,

XPD-2, NSLSII, E=67keV, Perkin-Elmer 2D detector

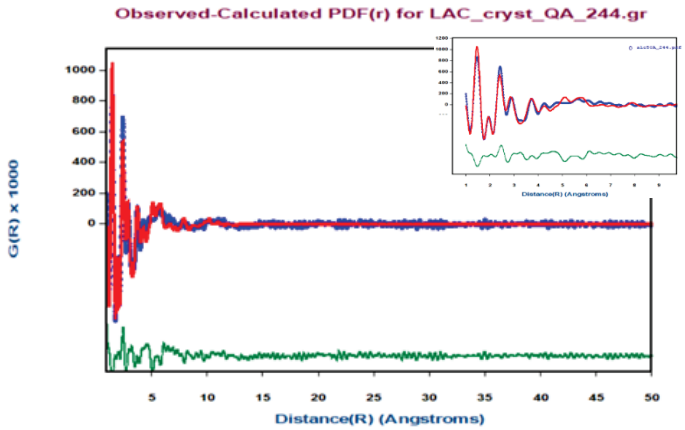


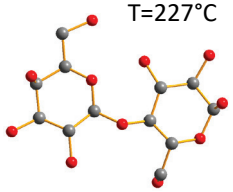


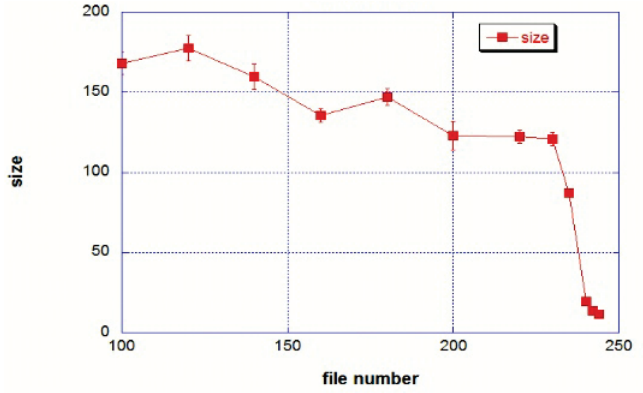


Refined: scale, δ1, cell, atom positions, size, s_{mol}, $B_{overall}$

Restraints on distances and angles within each molecule cycle







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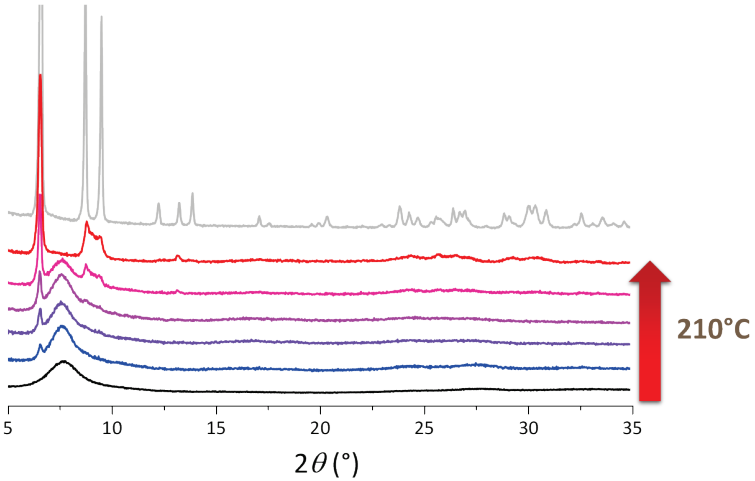
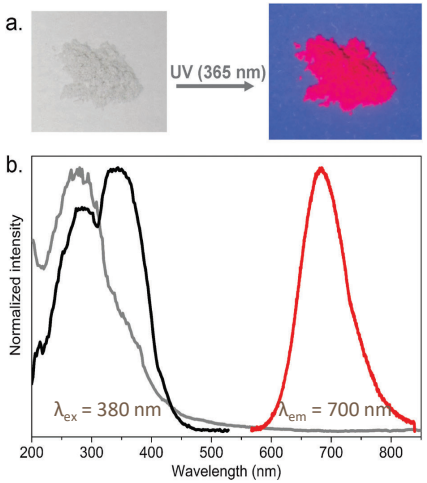
Coordination polymers glasses combine unique mechanical/shaping properties with interesting physical propoerties: porosity, conductivity, magnetism, luminescence

-**Gold–thiophenolate CP, $[Au(SPh)]_n$,**
-hydrothermal synthesis at RT => amorphous. recrystallizes on heating up to 200°C
-hydrothermal synthesis at 120°C => crystalline



Lavenn et al. J. Mater. Chem. C, 2015, 3, 4115



(a) Photographs of 1b under ambient (left) and UV (right) lights.(b) Absorption (grey), excitation (black), emission (red) spectra of crystalline [Au(SPh)]n at room temperature

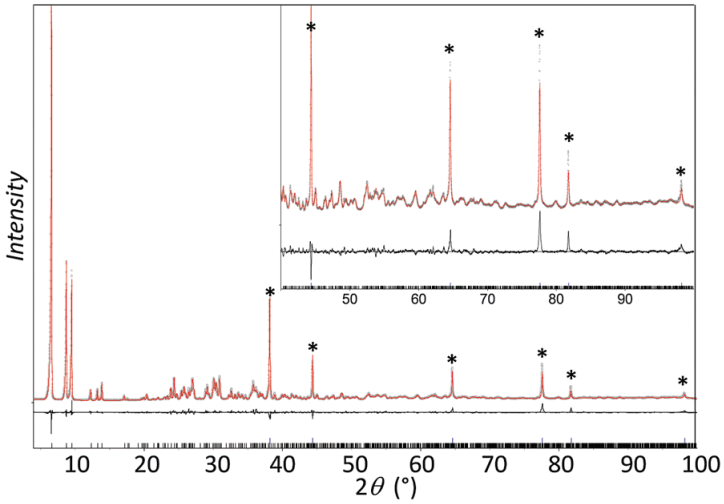
-The **crystalline** phase is red luminescent under UV light, the **amorphous** phase is not.
Closely dependent on aurophilic interactions*, d(Au-Au).*

What is the local structure of the amorphous phase ?

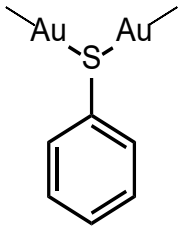
The structure of the crystalline phase was solved / refined by PXRD

$[Au(SPh)]_n$

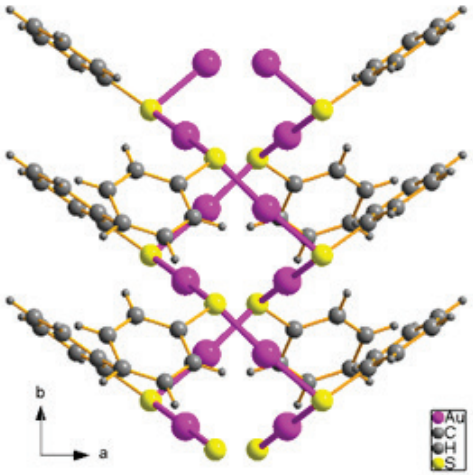
Au2 C12 H10 S2
Space group C2/c
a = 27.5009(7) Å
b = 4.5327(1) Å
C = 20.8032(3) Å
β = 104.935(2)°
V = 2505.6(1) Å^3
Z 8



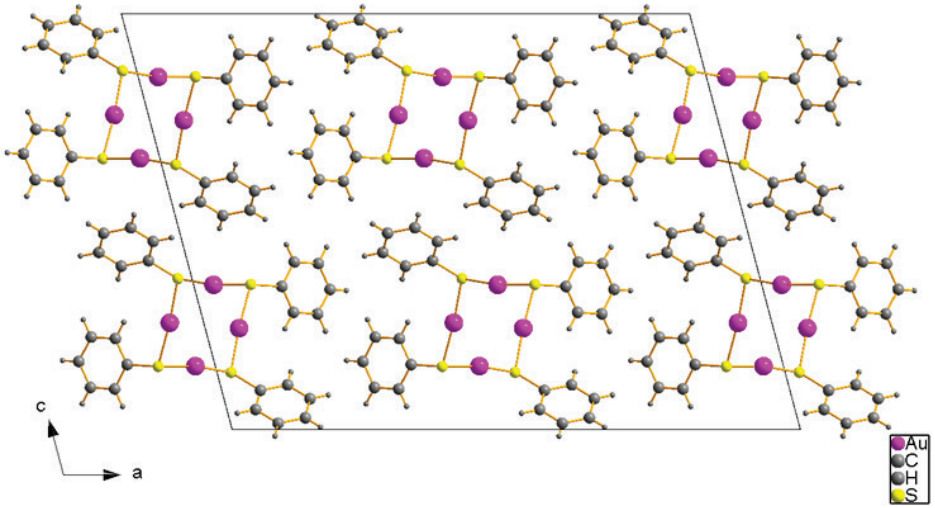
« monomer »



-S-Au-S- double helix chain

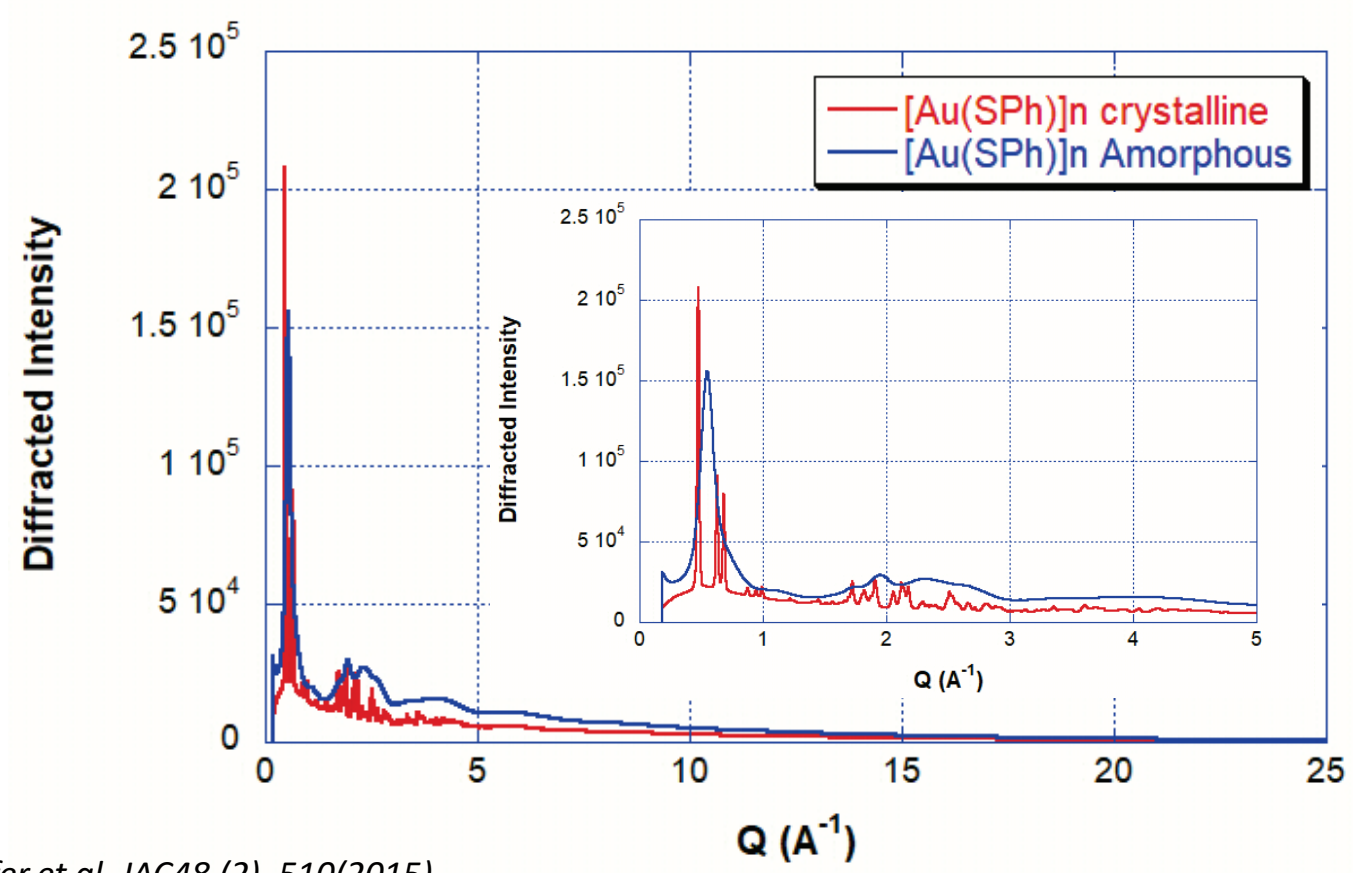


Chain packing in the crystalline phase



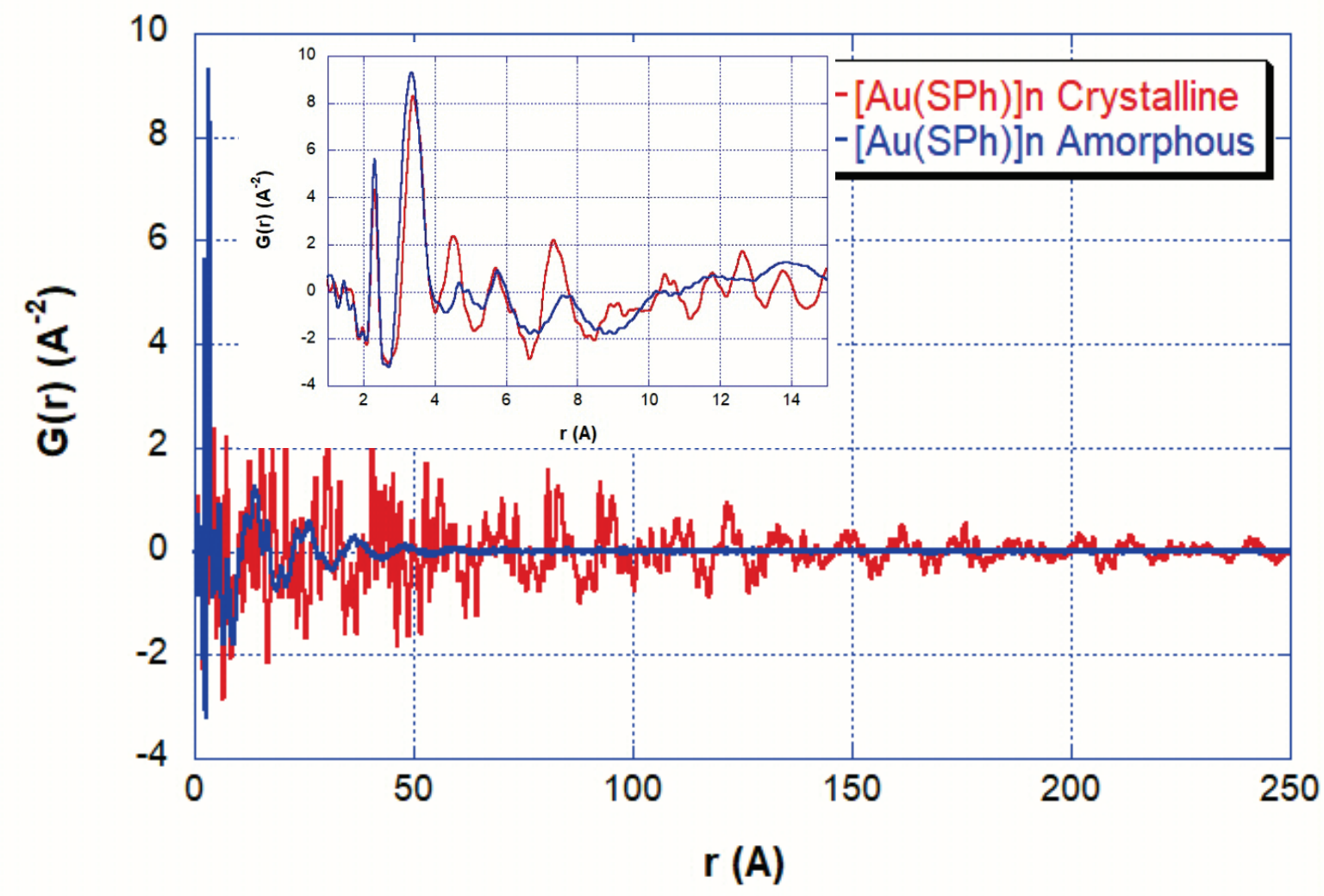
Total scattering measurement

at **ID 22-ESRF**, λ = 0.2068 Å (60 keV) , 0.7mm boro glass capillary
Perkin-Elmer flat panel detector at 38.5 cm from the sample => Qmax=24Å^{-1}.
Image integration with ***PyFAI.*** Calibration using Ni and LaB_6



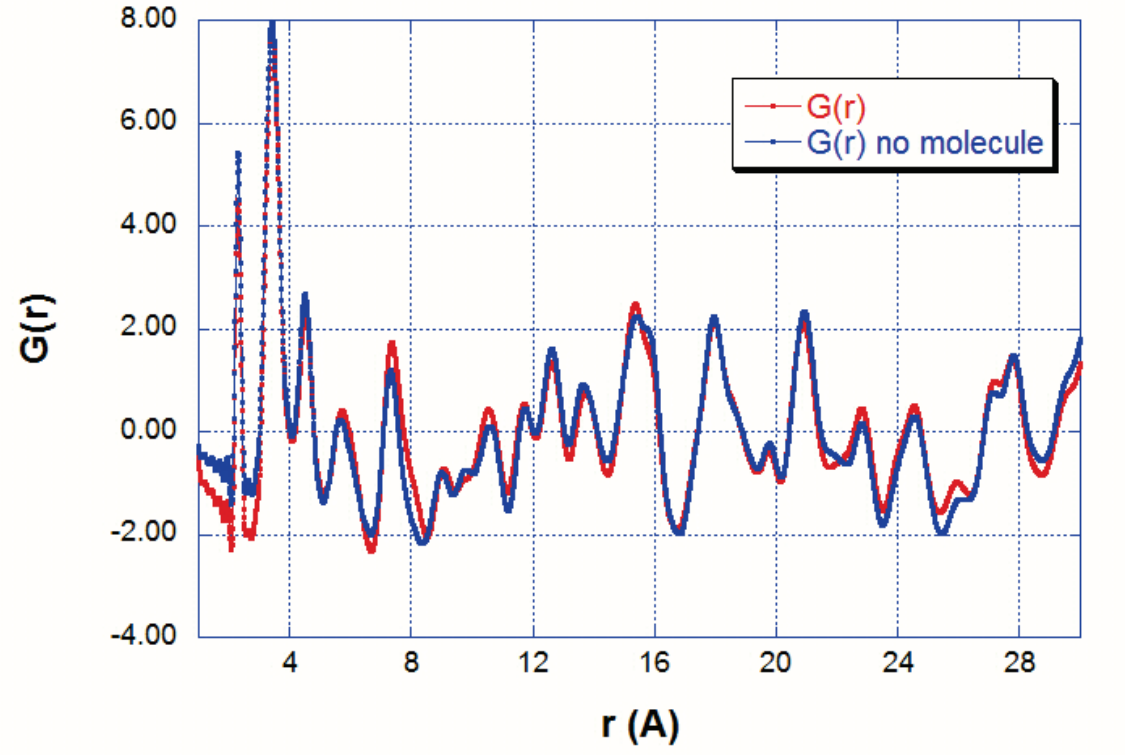
PyFAI: *J. Kieffer et al. JAC48 (2), 510(2015)*

The PDFs are obtained using PDFGetX3



*Farrow et al., J. Phys.: Condens. Matter **19** (2007) 335219*

The contribution of the molecules to the PDF is very small,
⇒ impossible to refine the carbon atom positions without applying rigid group or strong distance/angle restraints



PDF refinement of the crystalline phase using MolPDF

All atomic position parameters are free

With strong restraints on C-C molecule distances (14) and angles (16)

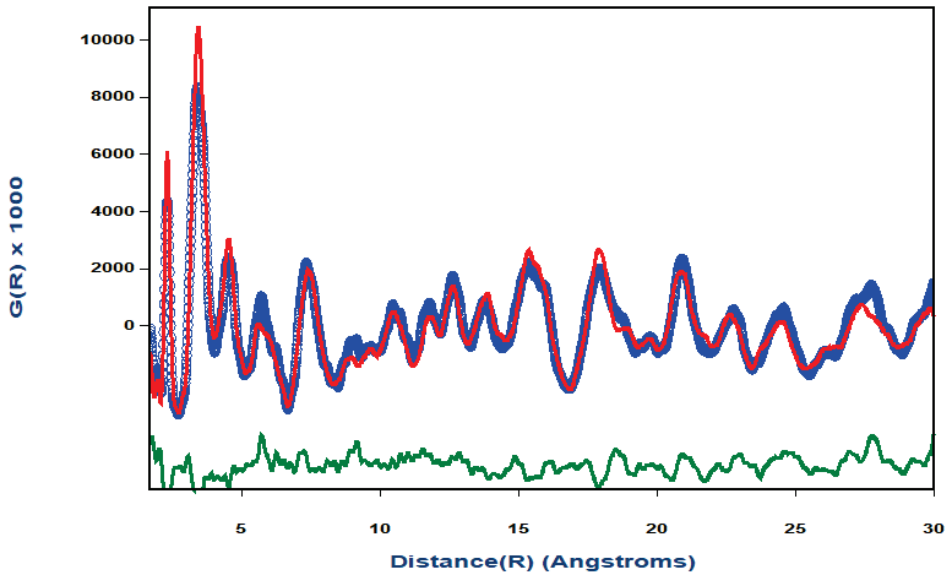
Using *C2/c* space group constraints

59 refined parameters

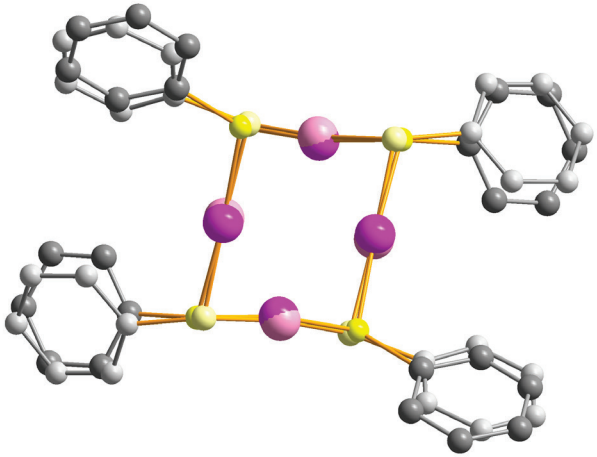
Scale factor, unit cell, δ1, diameter, U sharpening factor

xyz of Au & S atoms, Uiso-overall

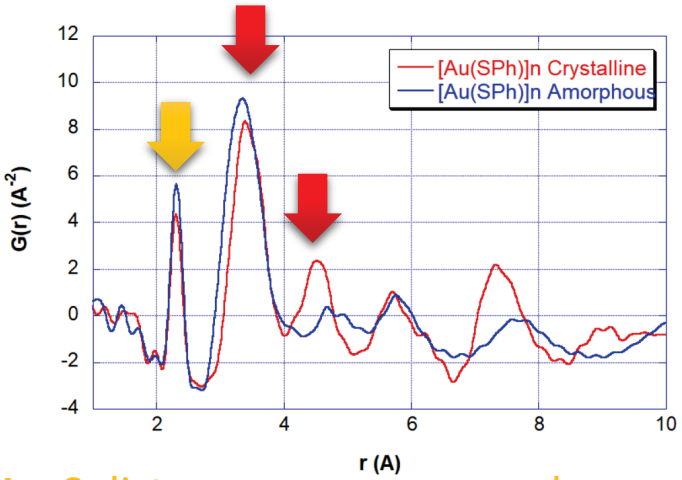
R_F(Sum(|Gobs-Gcal|)/Sum|Gobs|): 26.1, Chi2: 5.6051



Refined vs original structure

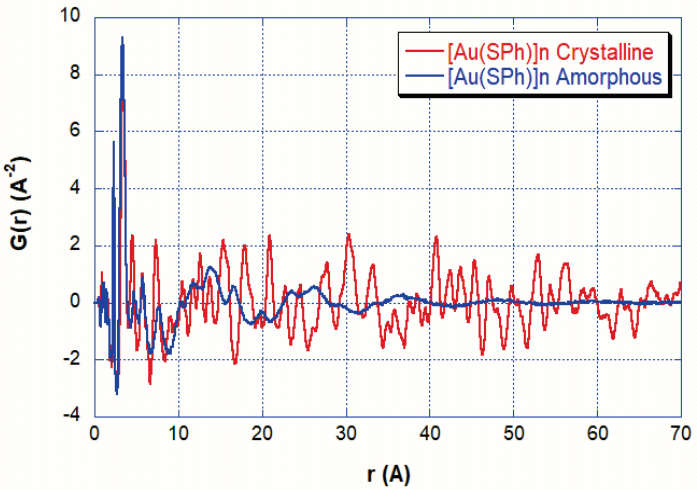


Local structure of the amorphous phase

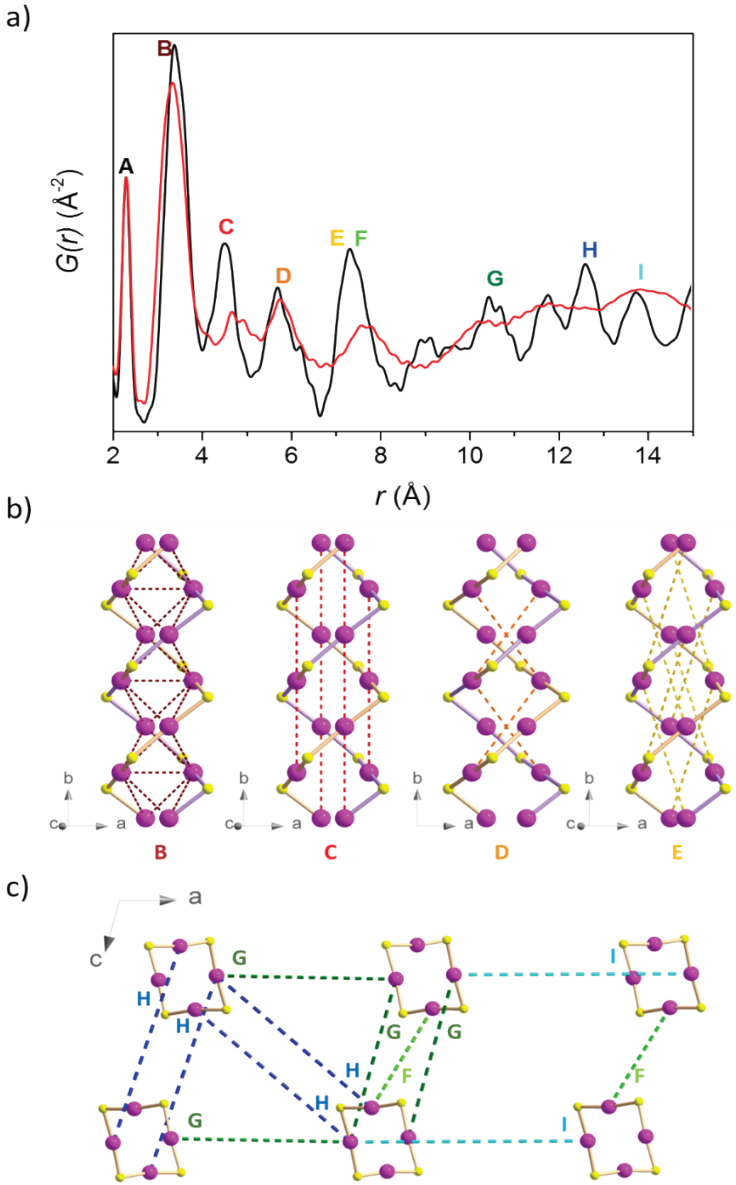


Au-S distances are conserved

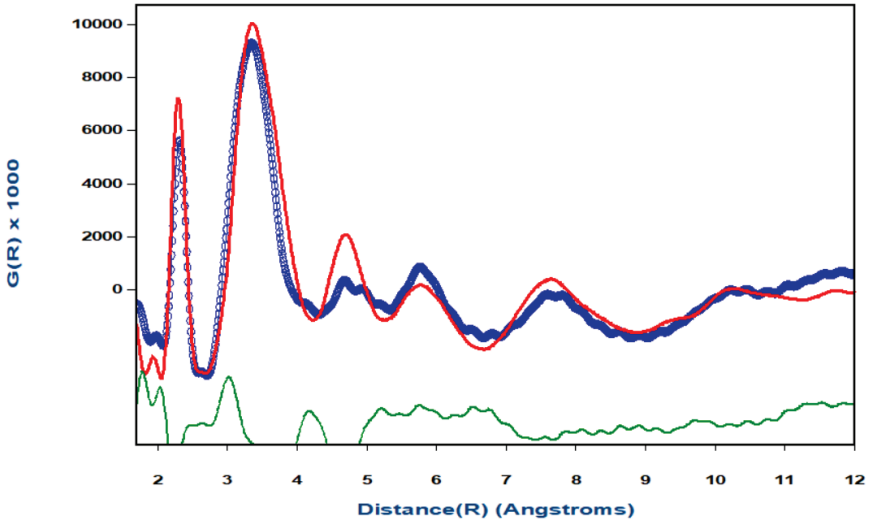
Au-Au distances are modified with a larger distribution

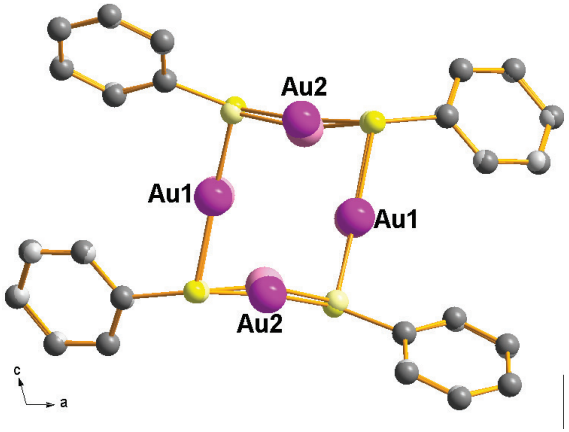


Broad oscillations of the PDF correspond to interchain correlations, up to ~50 Å.



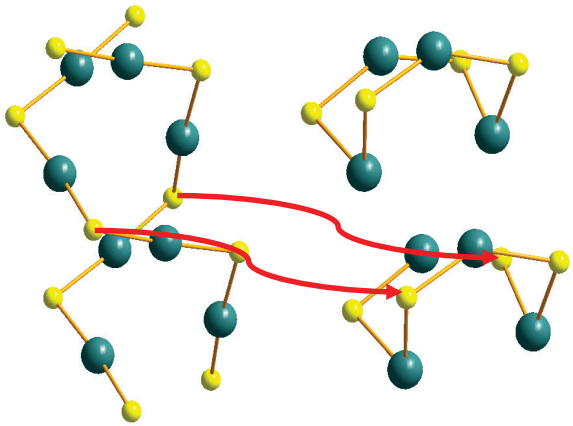
Refinement using MolPDF (molecules are restrained). Still based on same *C2/c* model.
R_F(Sum(|Gobs-Gcal|)/Sum|Gobs|)= 40.186 Chi2= 30





Crystalline (heavy) vs amorphous (light)

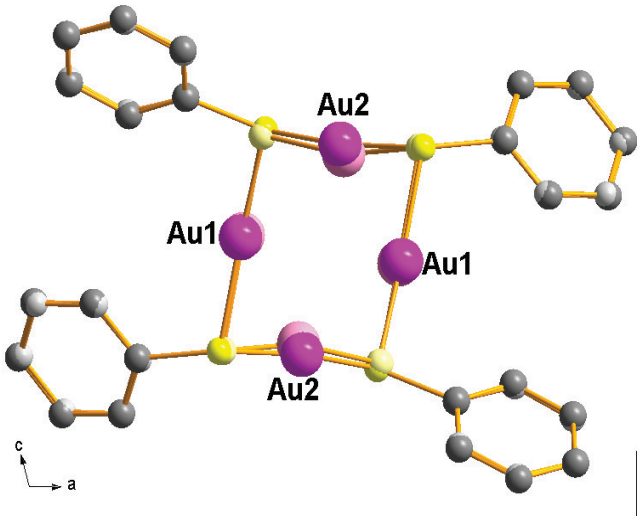
Several other cluster models from literature checked, with much poorer agreement.
Including a known tetramer block model.



⇒ **Double helix chain model preserved**
⇒ **Short coherence length along the chains (~10Å): defects**
⇒ **~50Å coherence length between chains: precursor of the crystal arrangement**

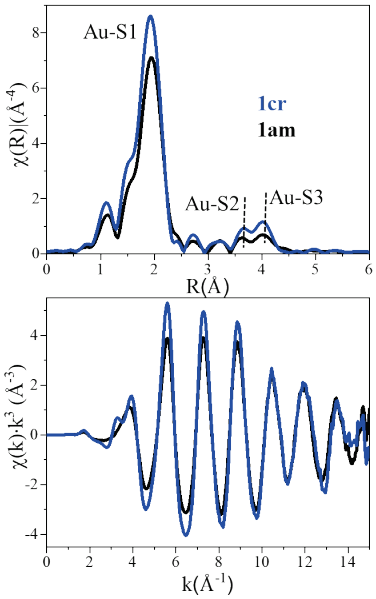
Simpson et al. Inorg. Chem.2010,49, 10858

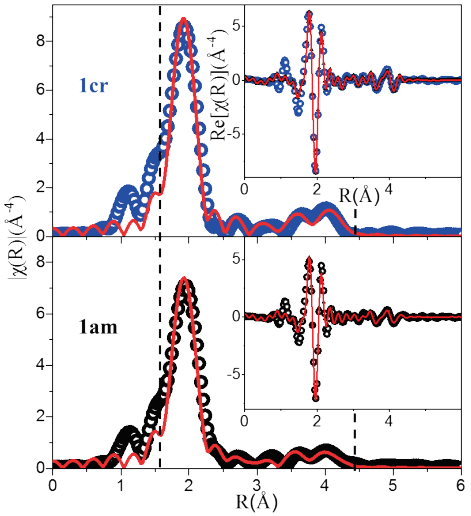
The Au-Au distances are shorter in the amorphous phase,
and the helices are more square



	Au1-Au1	Au2_Au2
crystalline	3.36	4.15
amorphous	3.27	3.81

The obtained model was used successfully to fit **Au-L_3 EXAFS** data
Coll. M. Diaz-Lopez





The change of photoluminescent properties may be related to the change of aurophilic interactions, which strongly influence the electronic structure.

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Electrochromic polymers compared to TMO, PB analogues:

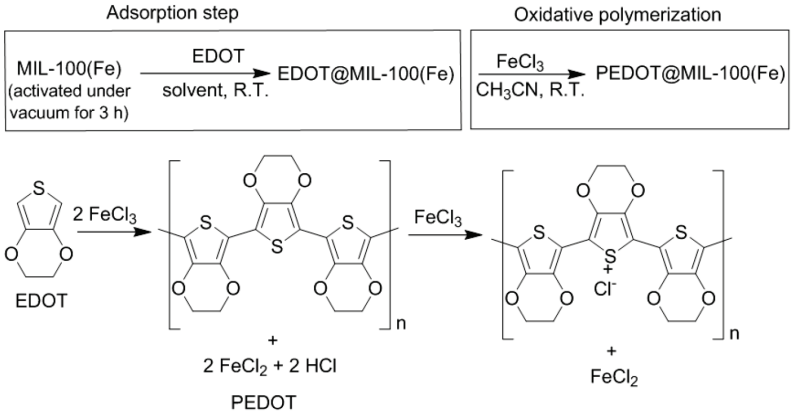
- higher color intensity
- larger variability in the choice of the color range
- faster stimulus response
- easy chemical tuneability
- low-cost
- facile processability

But ***low stability*** => poor cyclability
Try to stabilize by ***encapsulation in a matrix*** (zeolites, MOFs)

Here, we investigate the confinement of the electrochromic PEDOT polymer in the highly porous and stable MIL100Fe MOF

PEDOT encapsulation in MIL100Fe using a two-stage process:

EDOT monomer is adsorbed by suspending the previously dehydrated MOF in a concentrated EDOT solution.
Subsequently, encapsulated EDOT is submitted to *in situ* oxidative polymerization within the MOF pores using an acetonitrile solution of anhydrous $FeCl_3$



The amount of encapsulated EDOT and PEDOT. Sample 2 will be used.

Table 1. Textural properties, PEDOT content and ζ-potential values of PEDOT, MIL-100(Fe) and PEDOT@MIL-100(Fe) composites.

	S_{BET} ($m^2\ g^{-1}$)	Pore volume ($cm^3\ g^{-1}$)	EDOT: MIL100(Fe) (wt ratio)	PEDOT loading (wt %)	ζ-potential (mV)
MIL-100(Fe)	1210	0.54	-	-	-24 ±14
PEDOT@MIL-100(Fe)-1	800	0.35	0.45	40 ± 6	-1 ±13
PEDOT@MIL-100(Fe)-2	630	0.28	0.90	60 ± 9	35 ±15
PEDOT@MIL-100(Fe)-3	155	0.20	1.80	80 ± 12	37 ±12

Physical Properties

Electrical conductivity

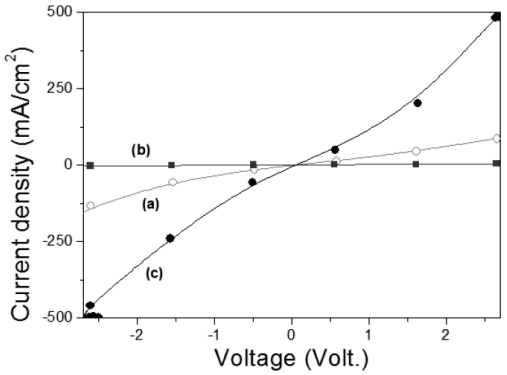
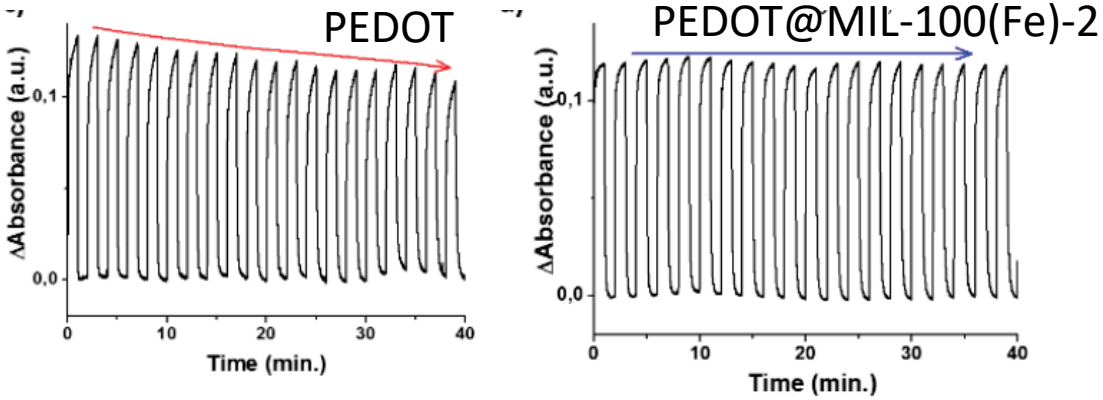


Figure 3. J-V plot corresponding to PEDOT (a), MIL-100(Fe) (b) and PEDOT@MIL-100(Fe)-2 (c).

Table 2. Electrical conductivity data of the materials	
Sample	**Conductivity (S·cm^{-1})***
PEDOT	508
MIL-100(Fe)	53
PEDOT@MIL-100(Fe)-1	1983
PEDOT@MIL-100(Fe)-2	4883
PEDOT@MIL-100(Fe)-3	1266
PEDOT:PSS	4600[39]
*All calculations were carried out at 2 Volt. Potential	

Electrochromic switching properties



Electrochromic switching monitoring the optical absorbance changes at 600 nm of PEDOT (c) and PEDOT@MIL-100(Fe)-2 (d) acquired by repeated potential steps between -1 V (reduced) and 1 V (oxidized) in 0.1 M LiClO4 and acetonitrile.

MIL100Fe

$Fe^{III}_3O(H_2O)_2F.\{C_6H_3(CO_2)_3\}_2.nH_2O$, n~14

Space-group ***Fd-3m*** (227)

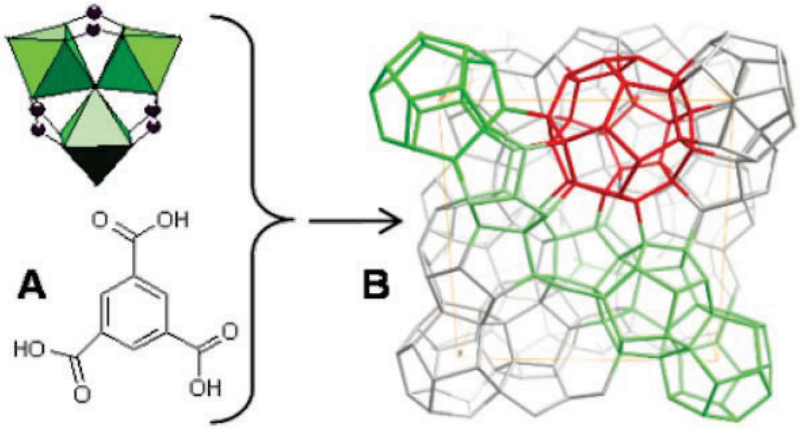
Cell a=73.34 Å

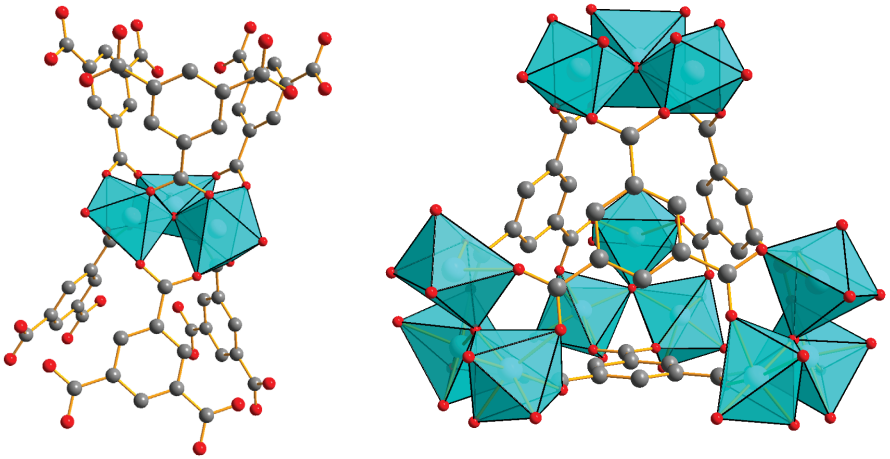
V= 394 480 Å^3

Independent positions:

7 Fe, 28 O, 33 C, 30 O water

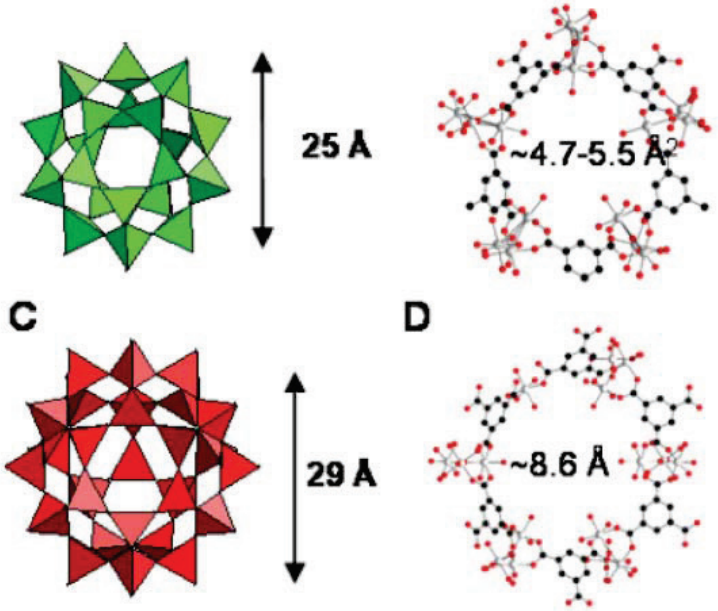
10 064 atoms in unit cell (excluding water)





$Fe(O,F)_6$ octahedra

benzene-1,3,5-tricarboxylate molecules

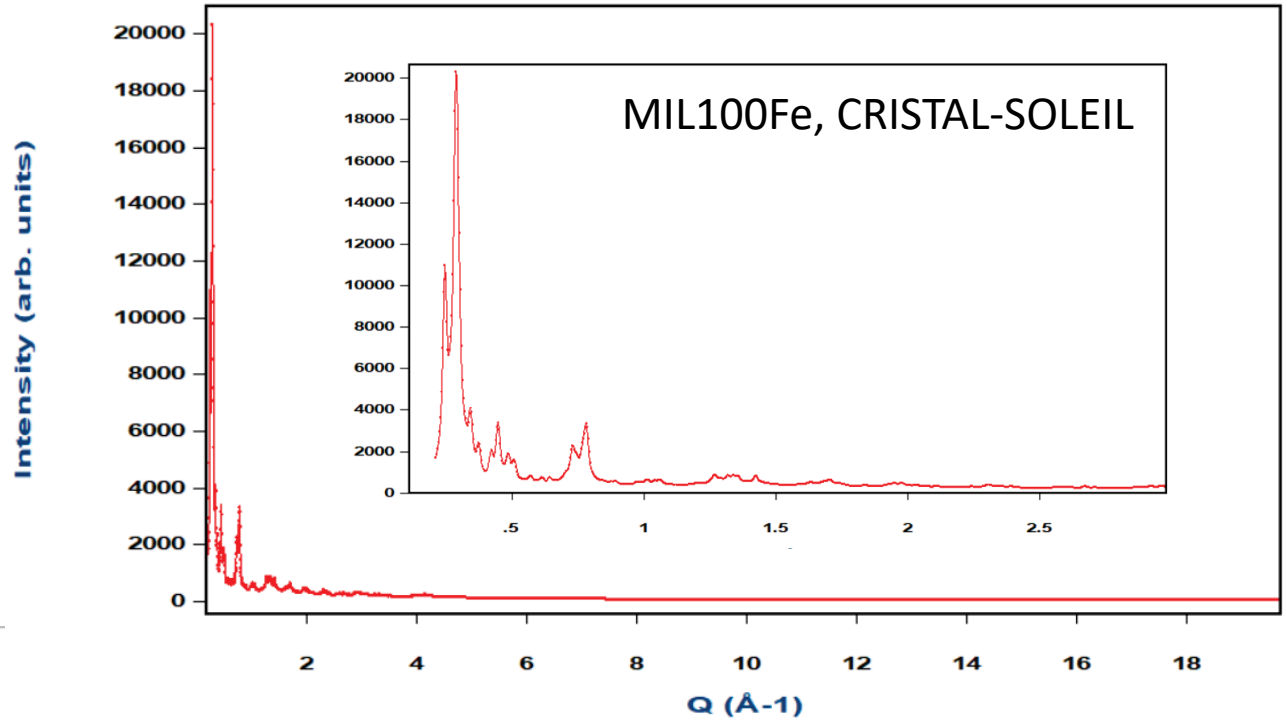


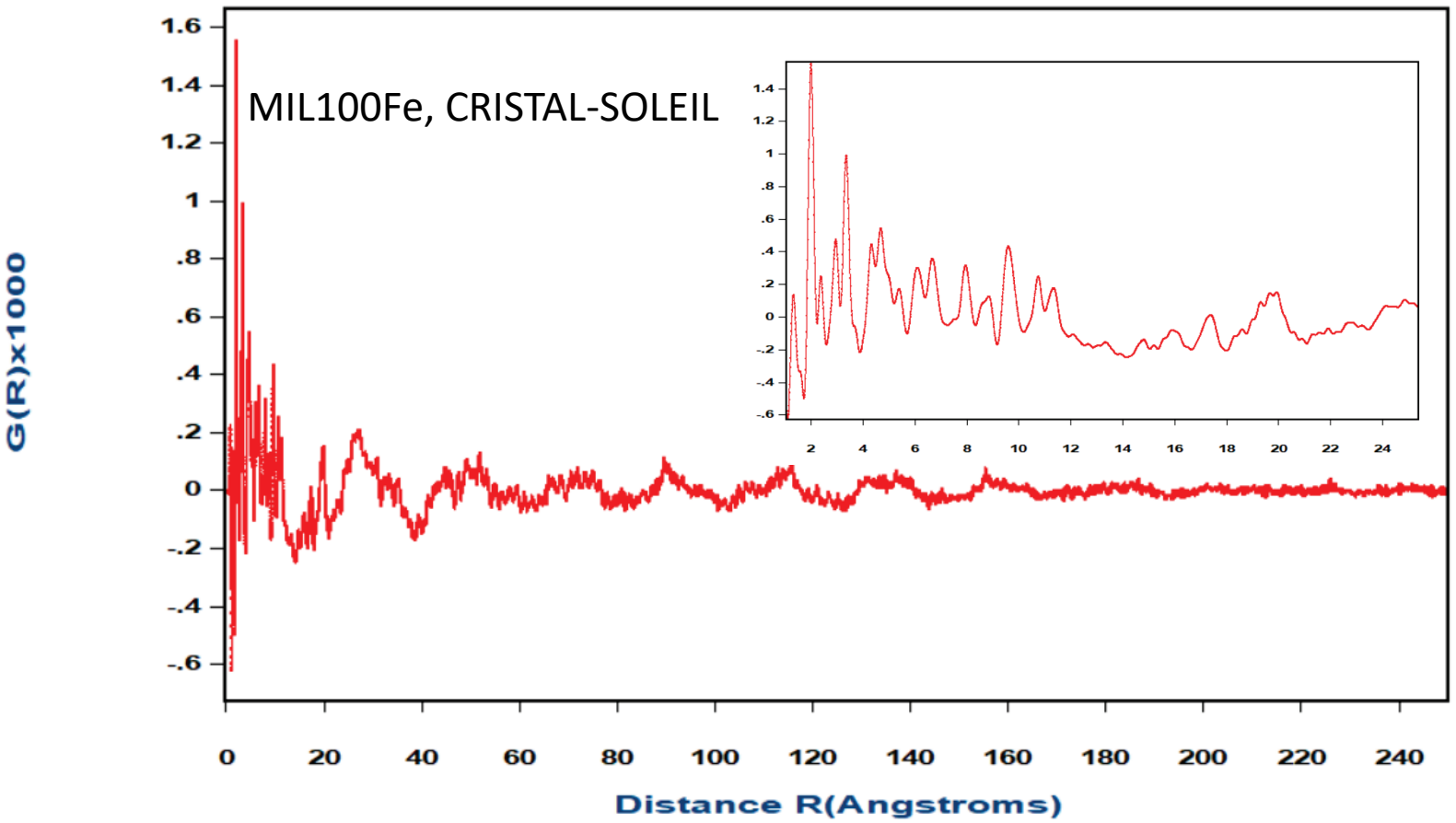
Horcajada et al. Chem. Commun., 2007, 2820–2822

Two total scattering synchrotron experiments:

at **ID 22-ESRF**, λ = 0.2068 Å (60 keV) , 0.7mm boro glass capillary
Perkin-Elmer flat panel detector at 38.5 cm from the sample => Qmax=24Å^{-1}.
Image integration with ***PyFAI.*** Calibration using Ni and LaB_6

at **CRISTAL-SOLEIL**, λ = 0. 51368 Å (24.1 keV) , 0.7mm boro glass capillary
XPAD3.2 hybrid pixel 2D detector at ~450mm,
image every deg up to 120°, 80s / image, => Qmax=20Å^{-1}.
Image integration using ***ImageReducerCristal*** developed at SOLEIL.





The coherent domain size is ~200 Å, i.e. < 3 unit cells.

PDF refinement attempt using MolPDF up to 20 Å

Initial position from Rietveld refinement of the same data using rigid blocks (N. Guillou)

For the PDF,

all positions are varied, except water O

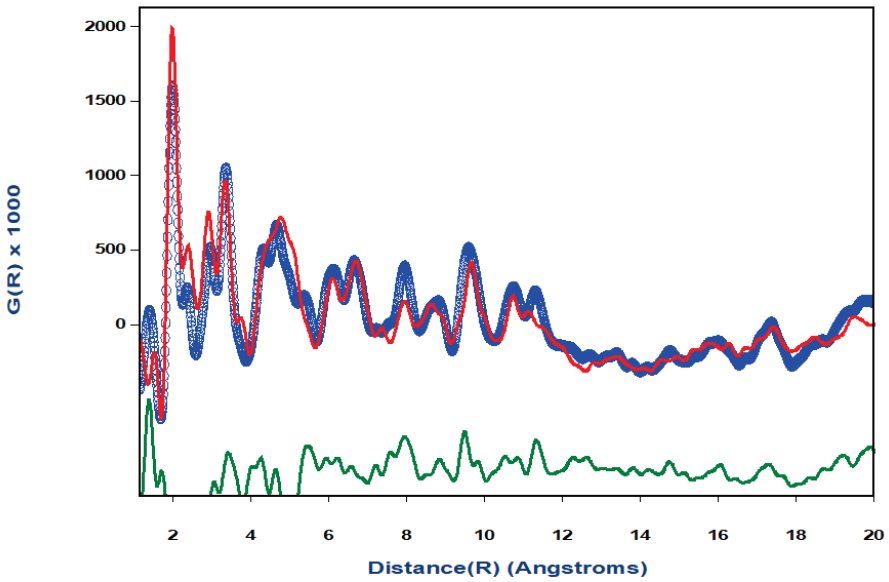
constrained Uiso for Fe, O&C, water.

392 restraints on distances up to 5 Å : molecule atoms, σ=0.0001, Fe-O, σ =0.01

68 restrainsts on angles only for molecule atoms, , σ=0.0001

R_F(Sum(|Gobs-Gcal|)/Sum|Gobs|)= 40.635, Chi2= 12.27, 167 refined parameters

About 1 min CPU time per iteration on a standard laptop



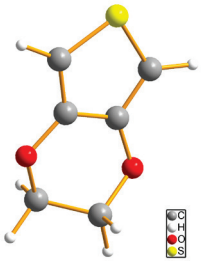
Average dist. to initial=0.09 Å

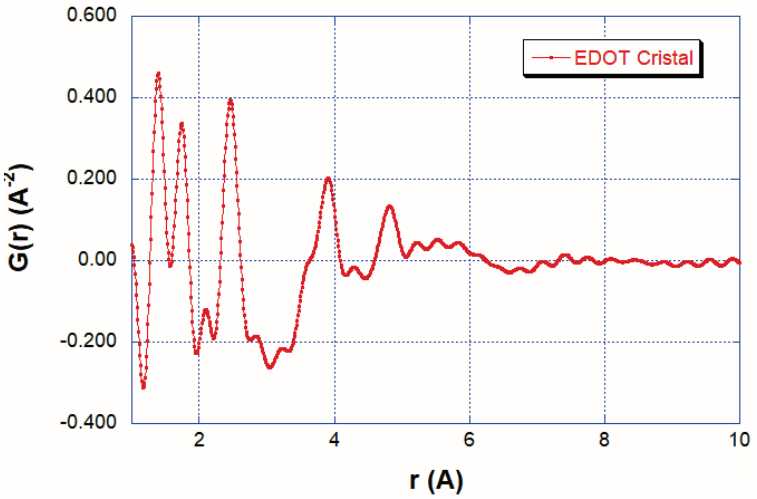
Maximum dist. to initial=1.3 Å

It would not be possible to directly obtain info about inserted PEDOT from such refinement.

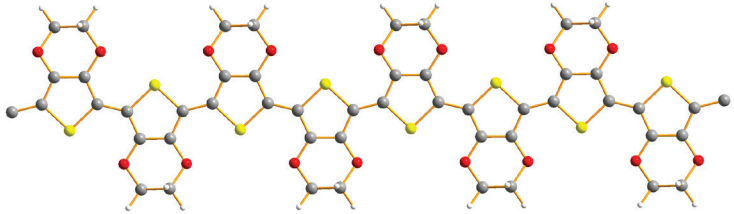
=> ***Qualitative inspection of the PDF from the encapsulated polymer***.

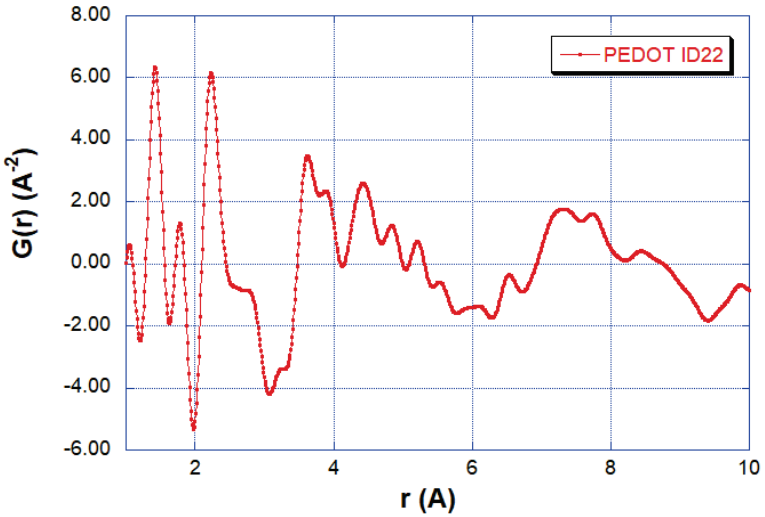
The EDOT monomer

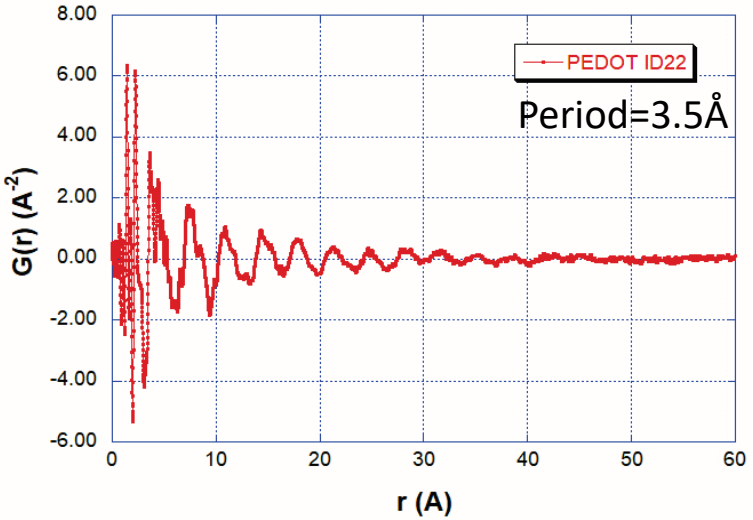




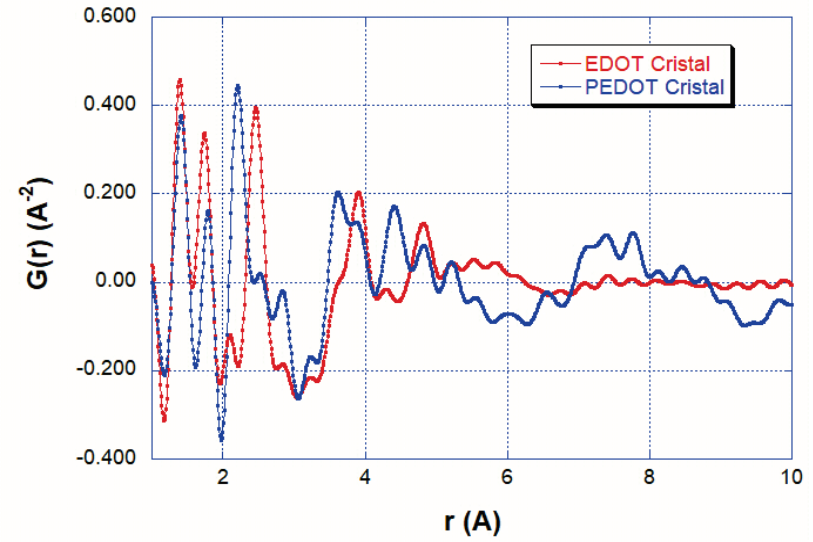
The PEDOT polymer



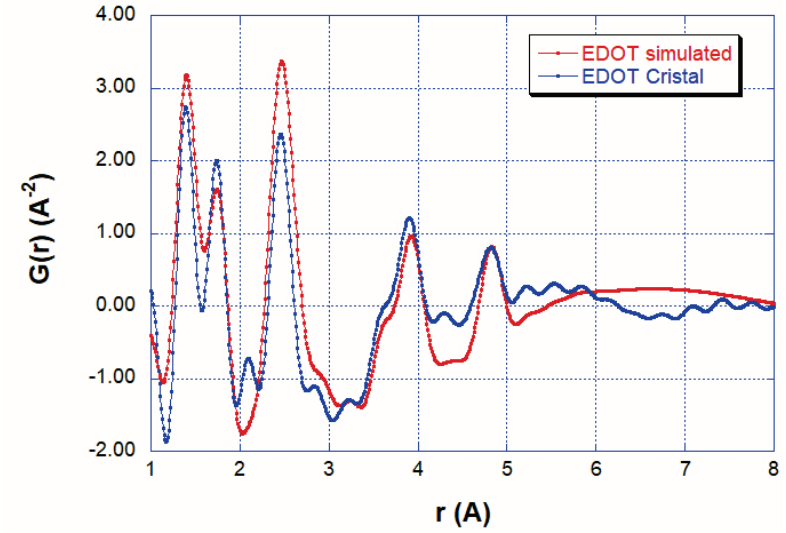


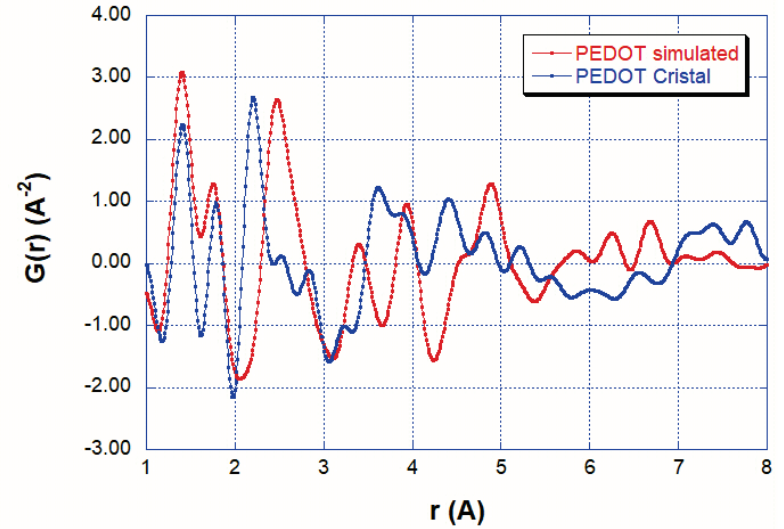


Compare the experimental PDFs of EDOT and PEDOT



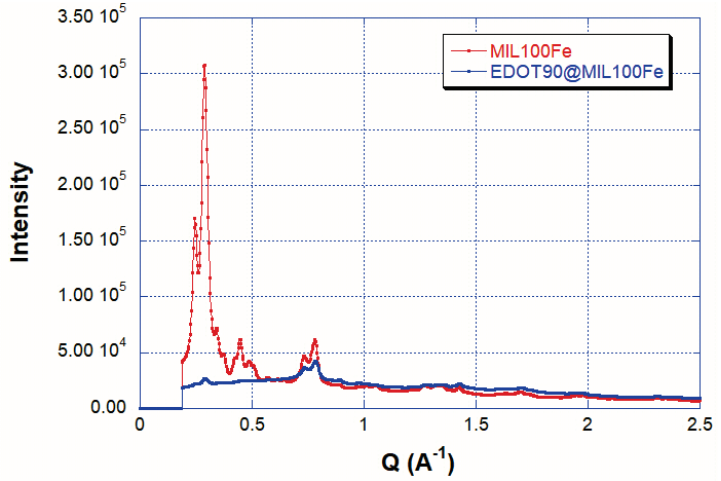
Compare the PDFs from experiment and DFT calculations

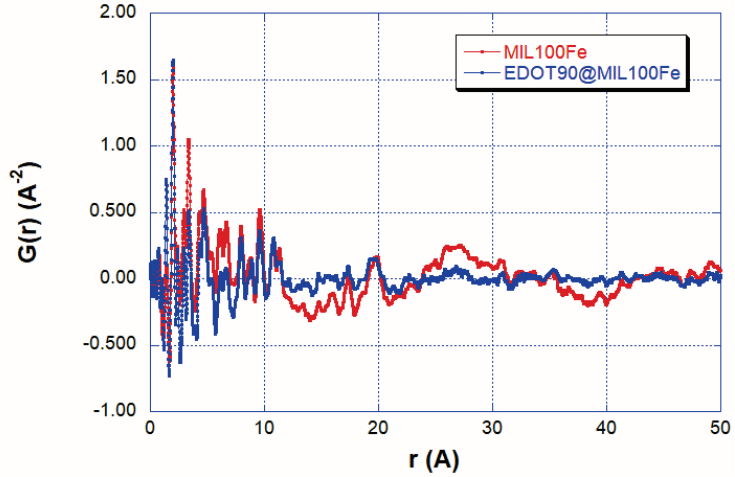




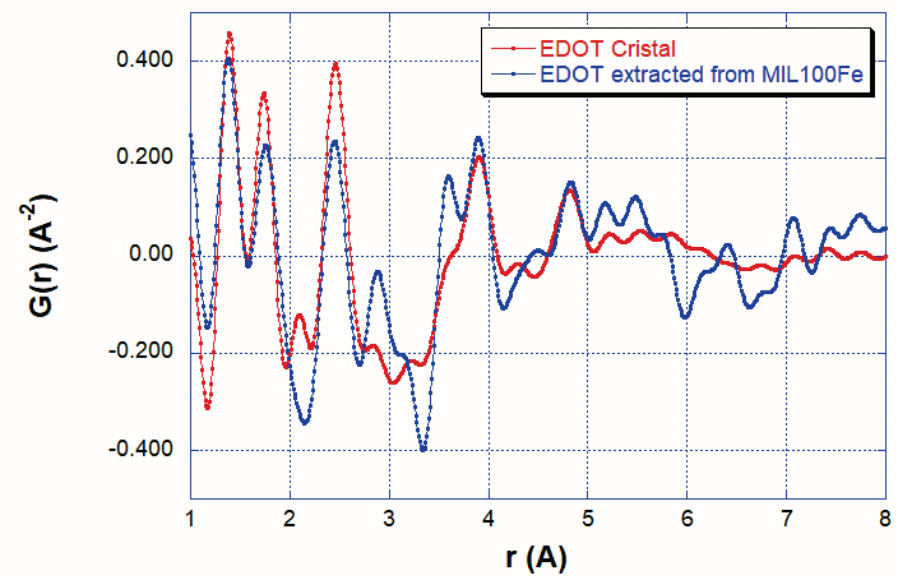
DFT simulations cannot reproduce correctly the PDF from PEDOT !

Extract the PDFs of EDOT encapsulated in MIL100Fe



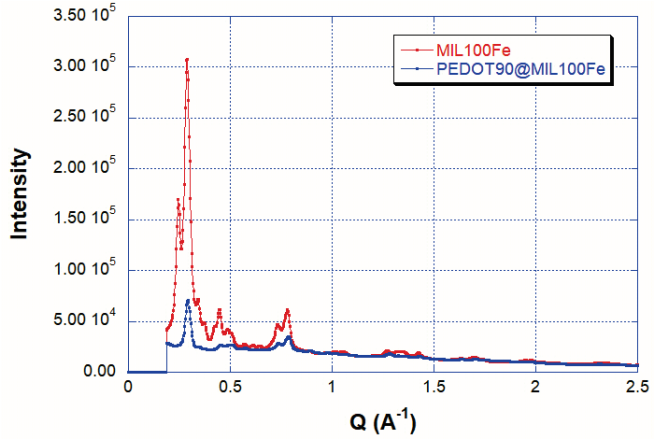


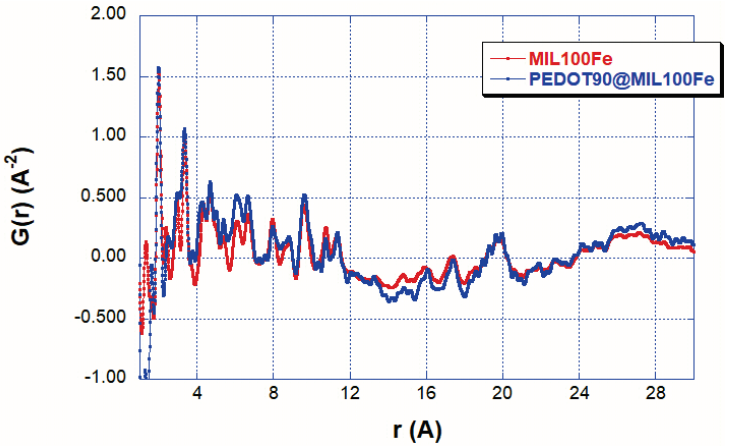
Before making the difference PDF, correct for different correlation lengths and scale



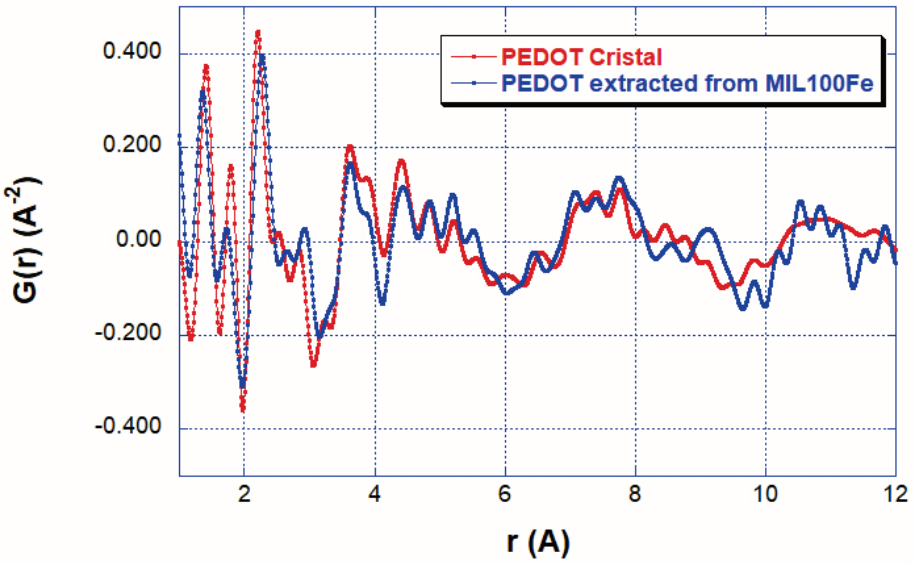
Encapsulated EDOT is similar to free EDOT

Extract the PDFs of PEDOT encapsulated in MIL100Fe





Encapsulated PEDOT is similar to free PEDOT, even longer range oscillations



Oxidative polymerization takes place into the MIL100Fe pores.
The local structure of the polymer is preserved.
Conductivity may be increased due to alignment of polymer molecules in the pores.
Cyclability is enhanced due to protection and stabilization by the MOF framework.

Introduction

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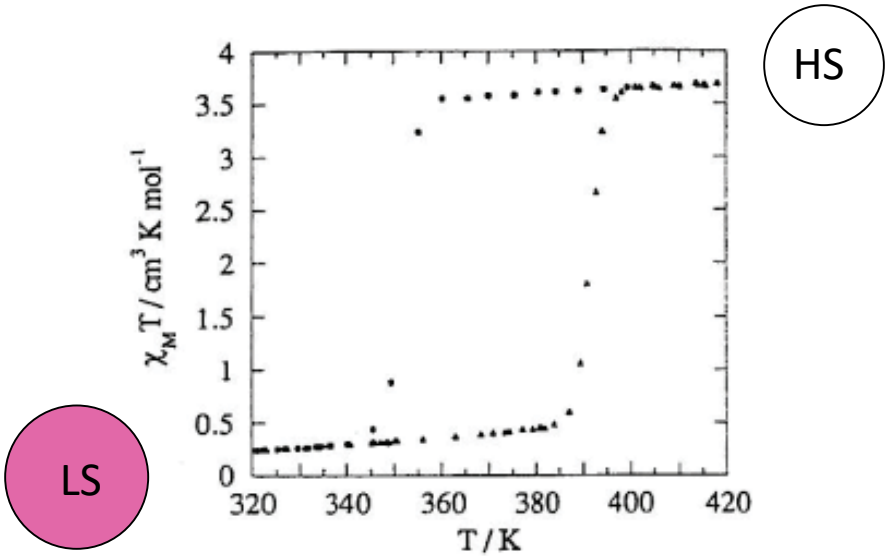
Crystal Structure of the spin transition polymeric compound [Fe(Htrz)2(trz)](BF_4)

Conclusion

Crystal Structure of the spin transition polymeric compound $[Fe(Htrz)_2(trz)](BF_4)$

Polymeric compound based on Fe II complex, spin transition close to RT.



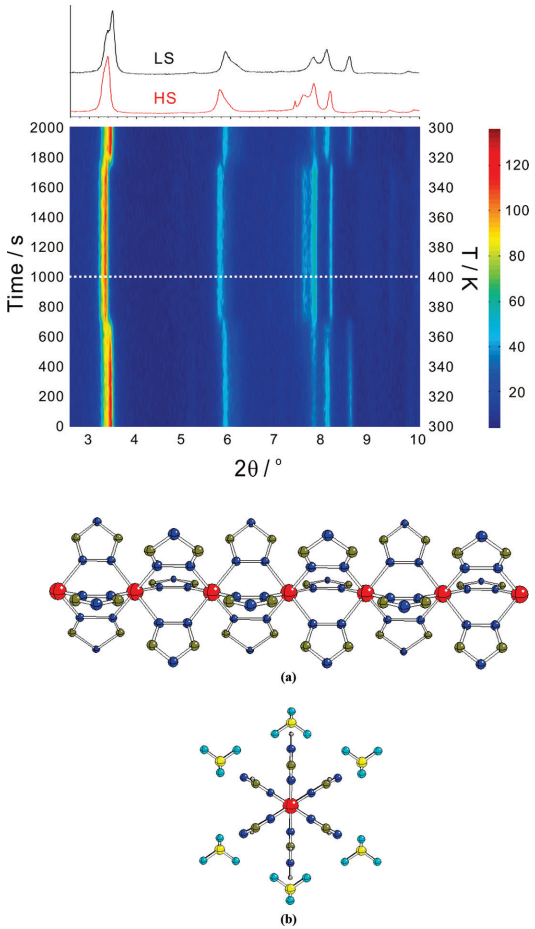
O. Kahn, J. Kröber, C. Jay, *Adv. Mat.* **1992**, *4*, 718

No crystals, badly crystalline powder=> uncertain structure (2 models proposed)

Grosjean et al., Eur. J. Inorg. Chem. **2013**, 796

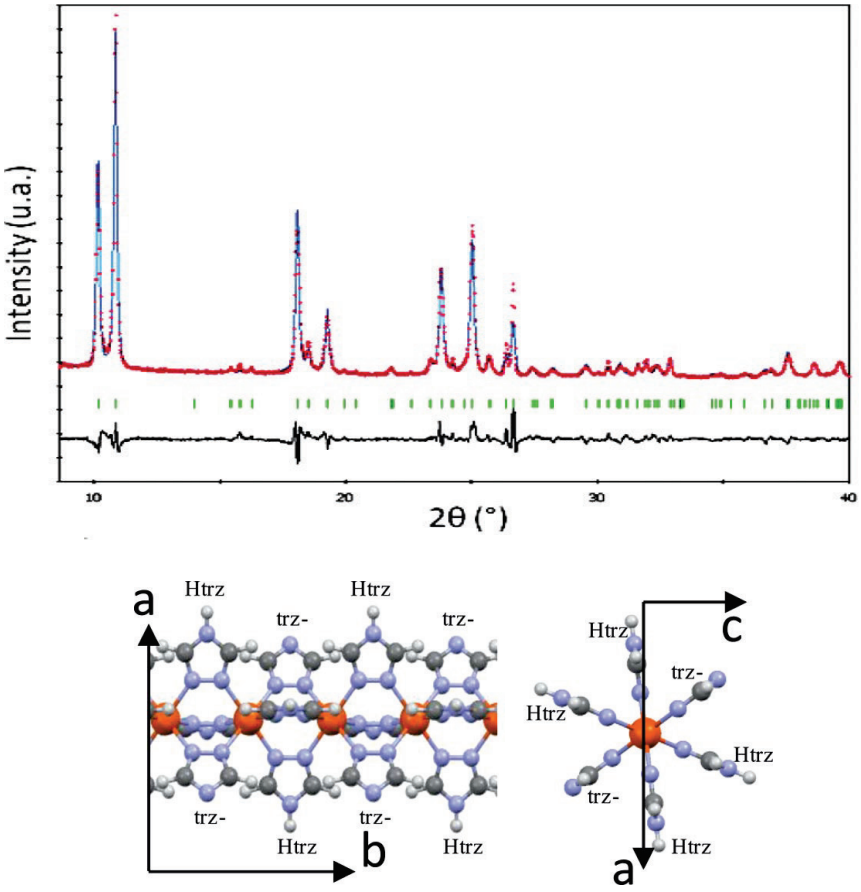
Urakawa et al. *J. Phys. Chem. C* **2011,** *115,* 1323

Cmcm



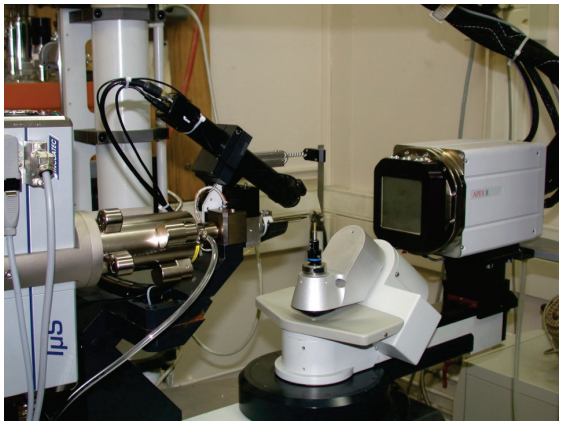
Grosjean et al. *Eur. J. Inorg. Chem.* **2013**, 796

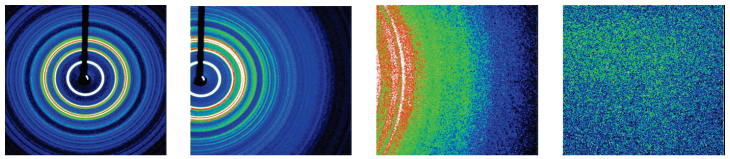
Pnma

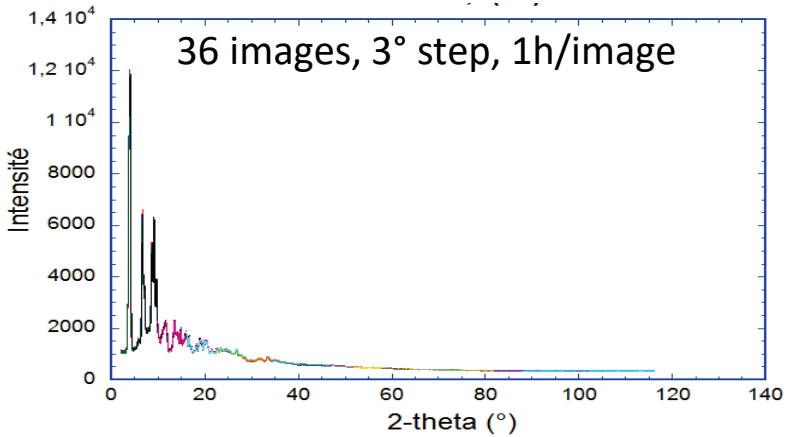


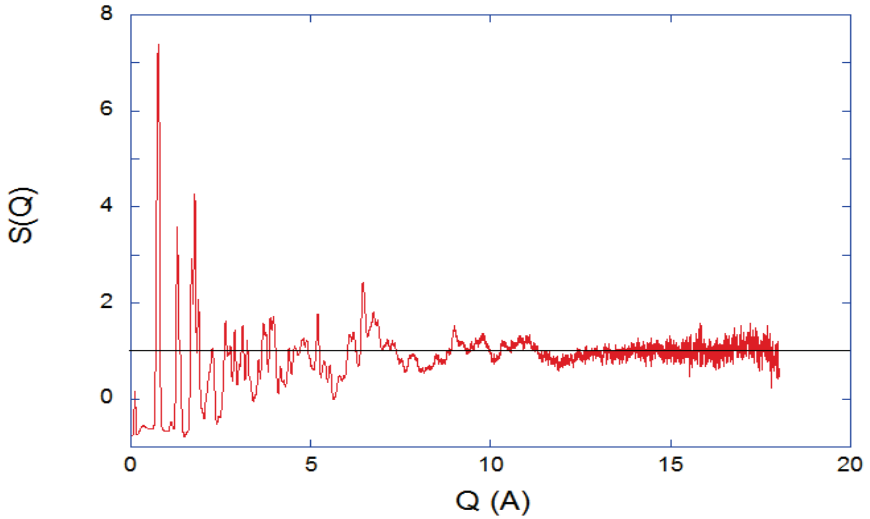
Can we use PDF analysis to decide which one is the right structure ?

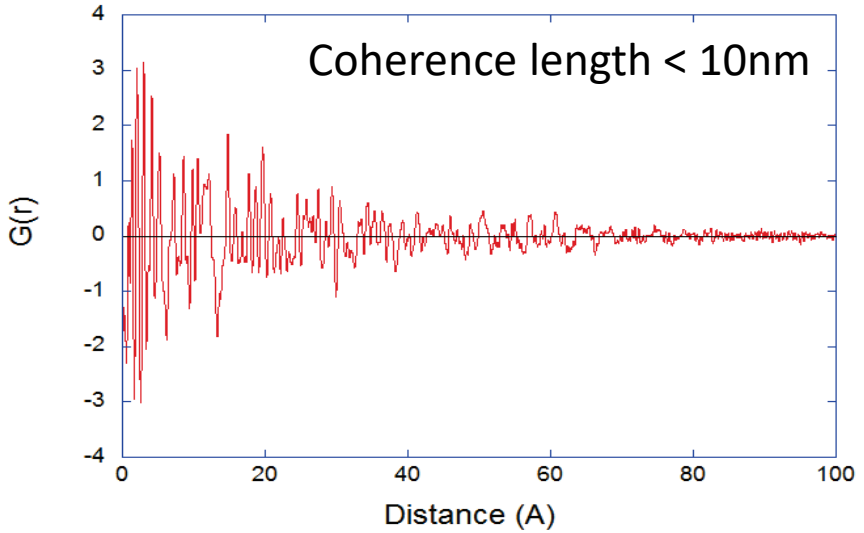
Total scattering data measured with a AgKα microsource + CCD camera



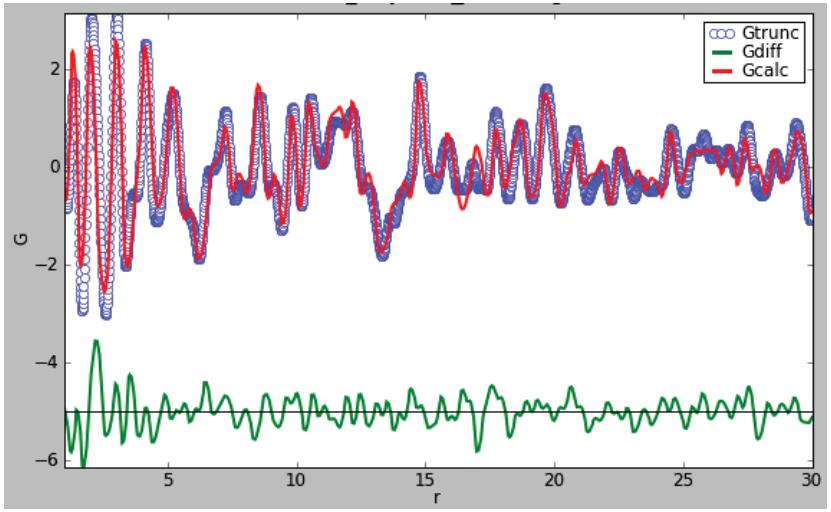




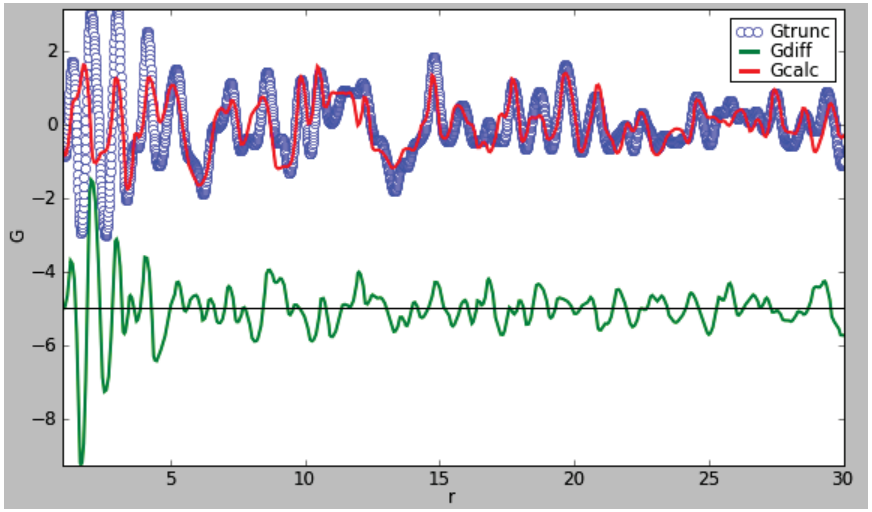




Pnma



Cmcm

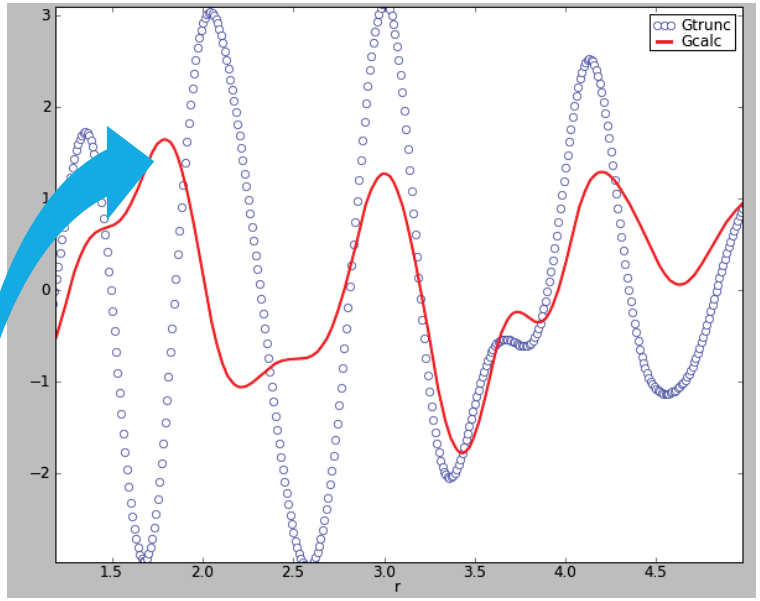


All positional parameters fixed from cif files

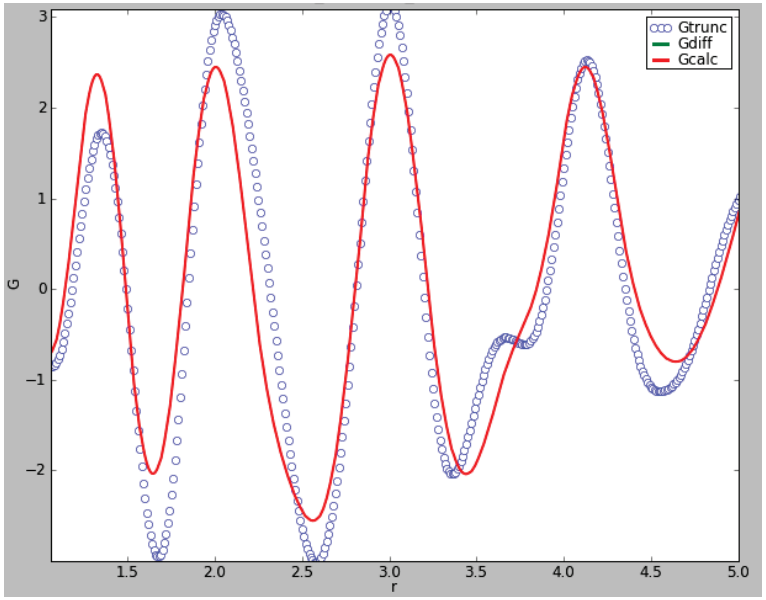
refined : scale factor
δ1 (correlations)
d nanoparticles ~7 nm
a, b, c
Uiso (Fe; C,N,H; B,F)

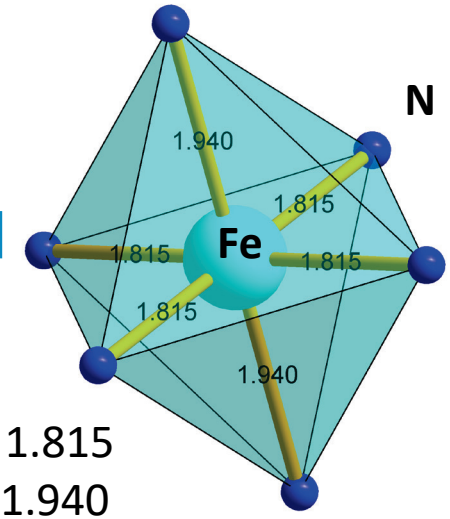
Large differences at short distances

Cmcm

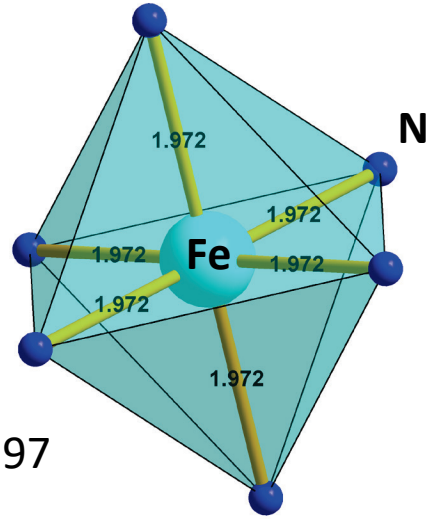


Pnma





Fe-N : 4 x 1.815
2 x 1.940

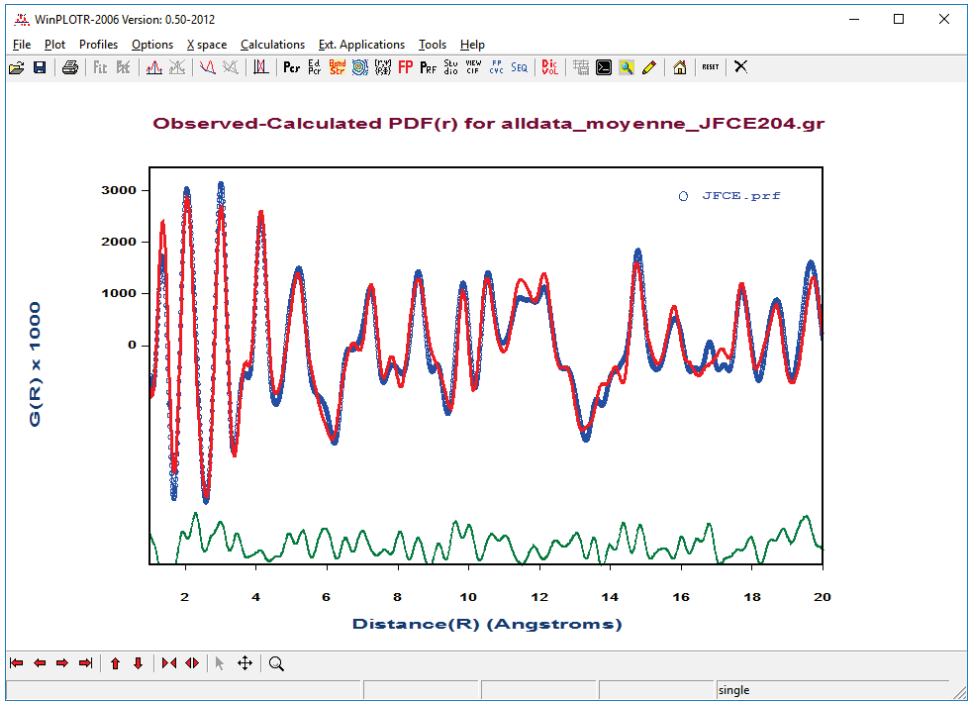


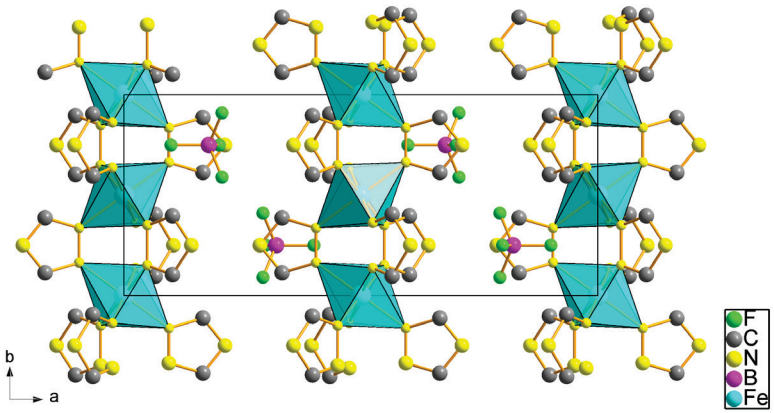
Fe-N : 6 x 1.97

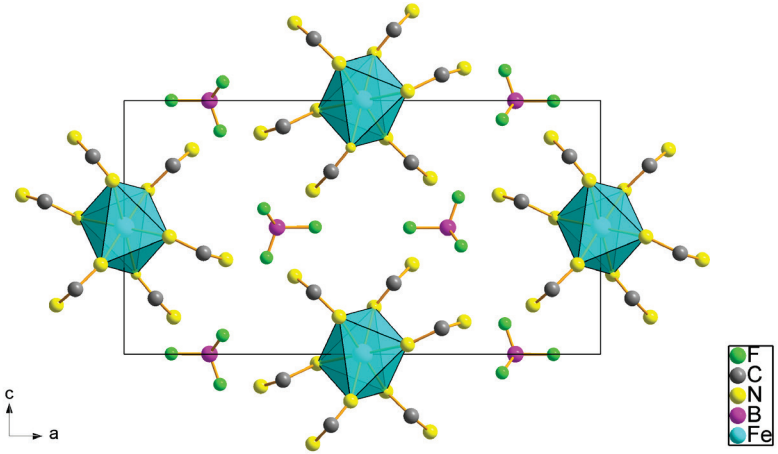
Refinement using MolPDF

Retraints on distances and angles:
C-N pentagonal rings,
B-F tetrahedra

δ1=1.16(1)
D=67(2)Å
R_F(Sum(|Gobs-Gcal|)/Sum|Gobs|)= 22.9







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Special thanks to :

Gold thiolates

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PEDOT into MIL100Fe

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Spin transition polymer

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ANR

… and you !