

Tetrathiafulvalene and 7,7,8,8-tetracyano-*p*-quinodimethane in zeolite Y†

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Tetrathiafulvalene (TTF) and 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ) are included in the pores of the zeolite Y framework structure (NaY), each species individually and both together as charge-transfer complexes by absorption from the liquid phase. The positions of these guest molecules are determined by powder diffraction, difference Fourier methods and subsequent structure refinement. The TCNQ is located in the centre of the 12-ring windows of NaY, while TTF is adsorbed in front of the 6-ring windows in the supercage. Identical positions are found for the guest molecules when both molecules are adsorbed. The effect of coordination on the guest within the zeolite was studied by UV–VIS and diffuse reflectance infrared Fourier transform (DRIFT) spectroscopies. DRIFT measurements show a shift of the CN-valence vibration absorption band of TCNQ in NaY to higher wavenumbers due to a change in the triple bond character. UV–VIS spectra display a bathochromic shift (to lower wavelength) of the absorption bands of TTF after incorporation. On the other hand the shift of the charge transfer band is hypsochromic.

Introduction

Zeolites are widely and traditionally used in heterogeneous catalysis in the petrol industry, for gas separation and ion exchange. In recent years, however, host–guest systems in combination with zeolites and other mesoporous materials have been studied extensively. Incorporated dyes for example show laser activity¹ and potential applications for gas sensors were reported.² Additional investigations concentrated on nano-sized metal clusters or charge-transfer complexes in zeolites.^{3,4} Our specific interest is focussed on the influence of the framework on the guest molecules. The system chosen is TTF and TCNQ in zeolite NaY (structure type FAU, $Fd\bar{3}m$, $a = 24.69 \text{ \AA}$), both separately and together (Fig. 1). TTF and TCNQ form charge-transfer complexes, well-known in the literature with interesting properties such as one of the highest anisotropic conductivities for organic materials.^{5–7} This complex constitutes a model substance to investigate host–guest interactions and potential modifications to enhance given properties.⁸ The charge-transfer absorption band in the UV–VIS spectrum is another observable by which to examine such interactions,^{9,10} which are related to the structure of these compounds. In order to interpret the spectroscopic data a precise knowledge of the position of adsorption of the guest molecule in the host lattice and its possible co-ordination is necessary.

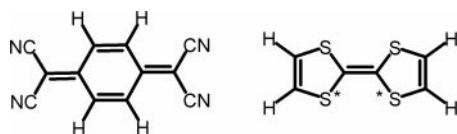


Fig. 1 Stick diagram of TCNQ and TTF.

Experimental

Zeolite NaY with the stoichiometry $\text{Na}_{52}\text{Al}_{52}\text{Si}_{140}\text{O}_{384}$ and a resulting Si/Al ratio of 2.7 is used.¹¹ The unloaded host was dried at 350°C for 2 days under high vacuum, down to a value of 6×10^{-5} mbar. The guest molecule was incorporated into the zeolite by adsorption from the liquid phase of a saturated solution of the guest in chloroform. This suspension was stirred for 2 days and filtered. The remaining solvent was removed from the sample by heating for a period of 5 days under high vacuum. TTF in NaY was dried at 120°C , TCNQ in NaY and TCNQ–TTF in NaY were dried 70°C . The TCNQ incorporated is desorbed at higher temperatures. The purity of the samples was checked by mass spectrometry: no chlorine was detected. The loading is 1.5 molecules per supercage for either TCNQ or TTF in NaY. In contrast for both TTF and TCNQ together in NaY the loading is only one charge-transfer complex per supercage.

Diffraction experiments were carried out at the beamline B2/HASYLAB in Hamburg, Germany, using synchrotron radiation. For TTF in NaY additional neutron diffraction experiments were performed at D1A/Institute Laue-Langevin, Grenoble, France. In order to minimise incoherent scattering of hydrogen, TTF was deuterated by the method of Dolphin *et al.*¹² before loading into the host. All diffraction experiments were carried out below 10 K to reduce thermal motion of the guests. The specific conditions for these experiments are given in Table 1.

The influence of the host on the guest molecules was observed by spectroscopic methods. DRIFT measurements reveal a shift of the CN-valence vibration absorption band, due to the host–guest interactions. These measurements were performed on a BIO-RAD FTS 175 C under argon atmosphere in a home-made sample chamber. UV–VIS spectroscopy shows the effect of the host on the electronic structure of the guests. This research was carried out on a Carl Zeiss Jena MCS 400 in diffuse reflexion on a powder sample and in transmission mode in a suspension of the substance in nujol.

† Electronic Supplementary Information available. See <http://www.rsc.org/suppdata/cp/b0/b005719n/>

Table 1 Conditions for the diffraction experiments

Radiation	TCNQ in NaY Sync.	TTF (deuterated) in NaY		TCNQ/TTF in NaY Sync.
		Sync.	Neutron	
Wavelength/Å	1.1608	1.2073	1.911	1.2073
2θ-range/degrees	2–70	2–78	5–154	2–80
Step size	0.01	0.01	0.05	0.01
Temperature/K	10	10	5	10

All spectroscopic investigations were carried out at room temperature.

Results and discussion

The location of the guests is determined from powder diffraction data. The host structure itself remains unchanged, but in comparison with the powder diffraction pattern of the dried and unloaded host, a change in the relative intensities of some reflections due to the loading is observed. Using the unloaded host as a starting model the non-framework scattering density can be extracted by Fourier analysis. A starting model for the following Rietveld refinement was deduced. During the refinement the conformation of the guest molecule, *i.e.* bond lengths and angles, is fixed and the molecule is treated as a rigid body. With this rigid body method the number of refined parameters increases only by 8: 3 translational and 3 rotational parameters for the rigid body orientation in the zeolite framework as well as 1 site occupation parameter and 1 temperature factor due to restraints.^{13,14} Fixed background points have been used in all refinements.

Fig. 2 displays the view through a 12-ring window into the supercage. Each supercage is connected by a 12-ring window to 4 other supercages. The contour in the middle of the 12-ring window is the residual scattering density of TCNQ in NaY, extracted by difference Fourier analysis from the change in intensities of reflexions in the diffraction pattern. Fig. 3 displays the 2D Fourier map at this position. This residual scattering density reveals the adsorption site of the guest molecule. This density in Fig. 3 is interpreted as the six-membered ring of TCNQ with its centre at (0.5 0.5 0.5) and refined by the Rietveld method (Fig. 4), which confirms this assumption. The four CN-groups of TCNQ point into the two

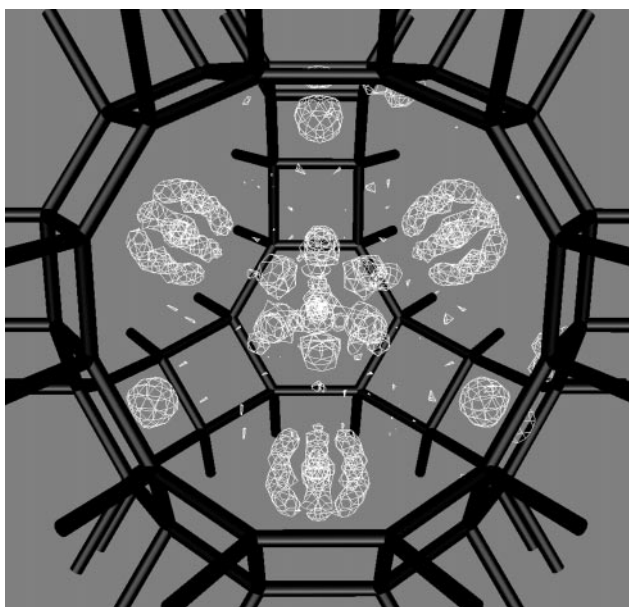


Fig. 2 Non-framework scattering density of TCNQ in NaY.

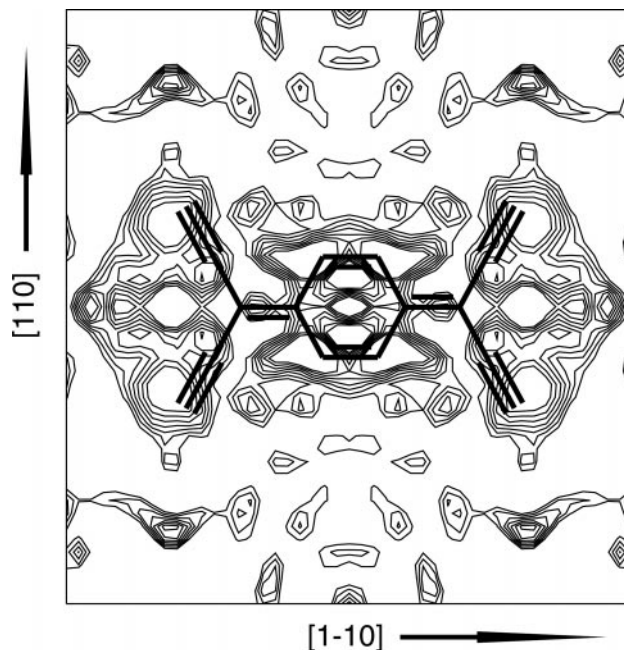


Fig. 3 Non-framework scattering density of TCNQ in NaY at 0.5 0.5 0.5.

supercages, which are connected by this window, and interact with the sodium cation at position II in the supercage in front of the 6-ring window of the sodalite cage (Fig. 5). This sodium cation is attracted along the crystallographic [1 1 1] axis towards the guest molecules by 0.34 Å. The distance between nitrogen and sodium is 2.2–2.9 Å, the TCNQ molecule and the four sodium cations in position II are almost in the same plane. Due to the 3-fold rotation axis perpendicular to the 12-ring window, these are three equivalent TCNQ positions per window. Each window can of course only be occupied by one molecule but every sodium cation in position II can be bound to 3 CN-groups of the TCNQ molecules, as this position is close to three 12-ring windows, the average however is 1.5. The refinement endorses the proposed loading of 1.5 molecules per supercage. The crystallographic details are summarized in Table 2. Bond distances and bond angles are given as Electronic Supplementary Information.†

In the system TTF in NaY no precise position of the guest was determined from the Fourier map. The structure refinement of TTF in NaY (Fig. 6) shows good agreement with the neutron ($wRp = 3.64\%$ and $Rp = 2.87\%$) and the synchrotron diffraction pattern ($wRp = 5.30\%$ and $Rp = 3.79\%$). As the profile fit of the (111) reflection is unsatisfactory due to the pronounced asymmetry, because of the umbrella effect and axial beam divergence, this reflection has been excluded from the final refinements. The position obtained for the guest molecule is not unique. Several slightly different positions of TTF in NaY lead to comparable good results in the refinement. Therefore, a statistical distribution of the guest molecules on different sites is proposed. All possible sites have some characteristics in common: The distance between the centre of mass of TTF and the cation at position II varies between 3.5 and 4.4 Å. Two sulfur atoms marked S* in Fig. 1 point to this sodium cation. The rotation angle along the main axis of the molecule (Fig. 1) is also not well defined. Table 3 displays the results of the best fit and Fig. 7 shows those arrangements of TTF in NaY which fulfil the characteristics mentioned above. These arrangements are not distinguishable in the crystal structure refinement.

For the structure refinement of the guest sites in the mixed loading of TCNQ and TTF in NaY, the previously described results for only one species were combined as a starting model, because the difference Fourier map displays their char-

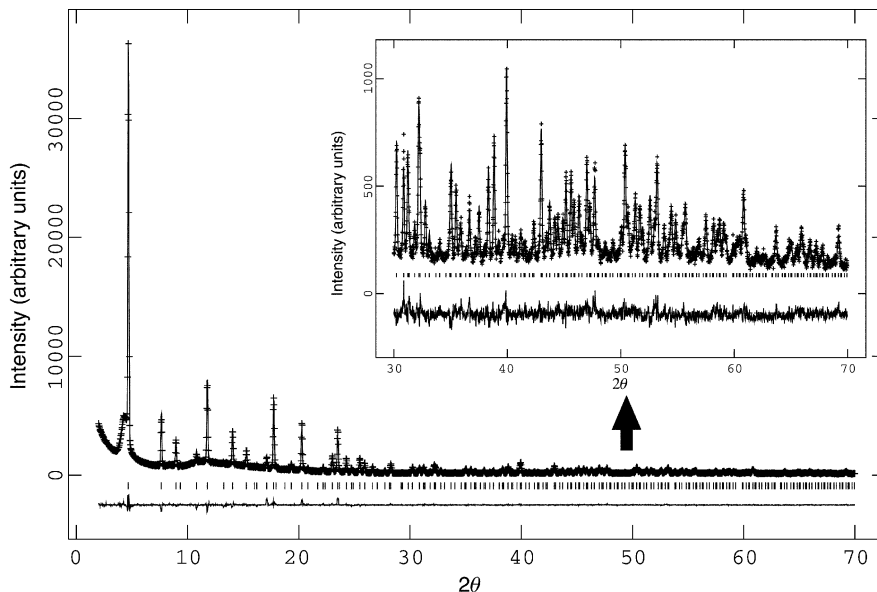


Fig. 4 Result of the Rietveld refinement for TCNQ in NaY.

acteristics mentioned above. The result of the Rietveld refinement is shown in Fig. 8 (Table 4) and confirms an identical arrangement of each of the molecules in the zeolite as in the case of TTF or TCNQ adsorbed individually. Bond distances and bond angles are given in the ESI.†

DRIFT measurements show the influence of the host on the guest molecule. Fig. 9 displays the absorption band of the CN-valence vibration. This band shifts to higher wavenumbers, *i.e.* energies, if TCNQ is incorporated in NaY. Therefore this vibration is affected by the co-ordination to the sodium

cation due to a polarisation of the CN triple bond. The ionic character increases and strengthens the bonding. This effect explains the shift to higher energies.¹⁵ Fig. 10 shows the UV–VIS spectra of pure TTF and of TTF incorporated in NaY. The spectrum of pure TTF, recorded in transmission mode in a suspension with mineral oil, is in good agreement with the data of Coffen *et al.*¹⁶ given in Table 5. If TTF is incorporated in NaY a bathochromic shift of the whole spectrum of about 59 nm is observed. This can be compared with the shift of absorption bands to lower energies in UV–VIS

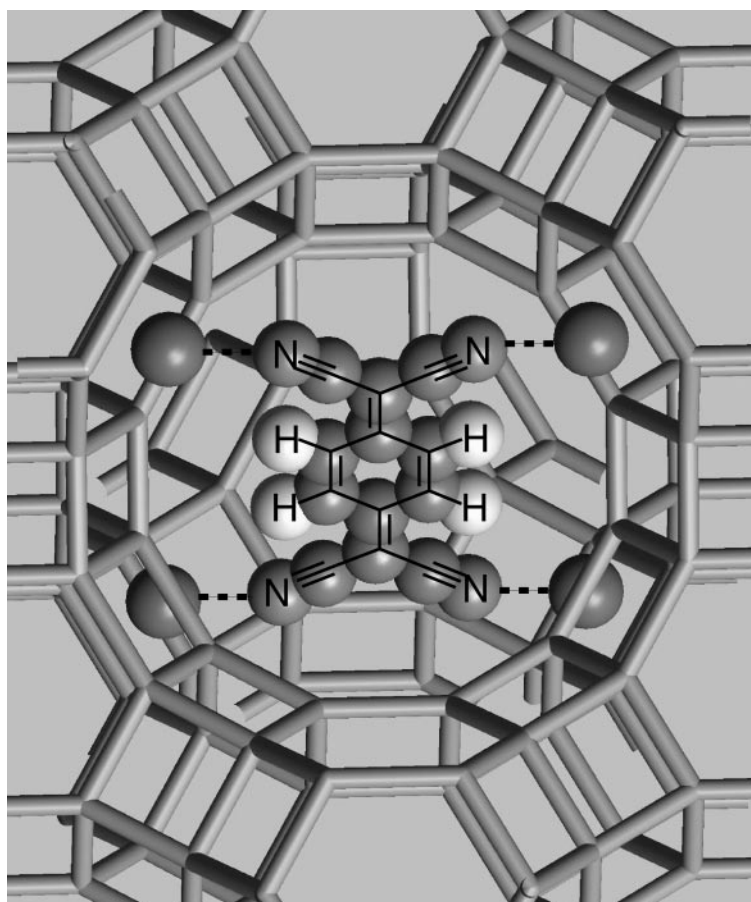


Fig. 5 Arrangement of TCNQ in NaY. The distance between the nitrogen and the sodium cation at position II in the two supercages before and behind the shown 12-ring window is 2.55 ± 0.35 Å.

Table 2 Results of the Rietveld refinement of TCNQ in NaY (wRp = 6.98% and Rp = 4.74%); $a = 24.709\ 08(16)\ \text{\AA}$

Atom	x	y	z	Frac. occupancy	U_{iso}
Si	0.124 47(10)	0.946 38(8)	0.036 64(8)	0.7 ^b	0.0122(5)
Al ^a	0.124 47(10)	0.946 38(8)	0.036 64(8)	0.3 ^b	0.0122(5)
O	0.173 53(17)	0.173 53(17)	0.971 88(28)	1.0 ^b	0.0160(22)
O	0.177 35(18)	0.177 35(18)	0.320 84(23)	1.0 ^b	0.0160(24)
O	0.249 74(16)	0.249 74(16)	0.144 85(24)	1.0 ^b	0.0179(23)
O	0.106 29(16)	0.893 70(16)	0.0	1.0 ^b	0.0134(23)
Na	0.063 78(21)	0.063 78(21)	0.063 78(21)	0.746(11)	0.031(4)
Na	0.0	0.0	0.0	0.053(17)	0.02(7)
Na	0.241 10(15)	0.241 10(15)	0.241 10(15)	0.956(13)	0.0186(29)
C ^c	0.505 76(13)	0.462 33(23)	0.457 06(21)	0.0718(5)	0.047(6)
C ^c	0.494 24(13)	0.537 67(23)	0.542 94(21)	0.0718(5)	0.047(6)
C ^c	0.4929(5)	0.517 47(35)	0.447 12(9)	0.0718(5)	0.047(6)
C ^c	0.5126(5)	0.446 60(15)	0.511 92(29)	0.0718(5)	0.047(6)
C ^c	0.4874(5)	0.553 40(15)	0.488 08(29)	0.0718(5)	0.047(6)
C ^c	0.5071(5)	0.482 53(35)	0.552 88(9)	0.0718(5)	0.047(6)
H ^c	0.4924(6)	0.5092(6)	0.407 93(6)	0.0718(5)	0.047(6)
H ^c	0.5201(8)	0.409 36(15)	0.4992(5)	0.0718(5)	0.047(6)
H ^c	0.4799(8)	0.590 64(15)	0.5008(5)	0.0718(5)	0.047(6)
H ^c	0.5076(6)	0.4908(6)	0.592 07(6)	0.0718(5)	0.047(6)
C ^c	0.511 50(26)	0.4248(5)	0.4143(4)	0.0718(5)	0.047(6)
C ^c	0.5047(5)	0.4405(8)	0.359 56(33)	0.0718(5)	0.047(6)
C ^c	0.5243(7)	0.3698(4)	0.4242(7)	0.0718(5)	0.047(6)
C ^c	0.488 50(26)	0.5752(5)	0.5857(4)	0.0718(5)	0.047(6)
C ^c	0.4953(5)	0.5595(8)	0.640 44(33)	0.0718(5)	0.047(6)
C ^c	0.4757(7)	0.6302(4)	0.5758(7)	0.0718(5)	0.047(6)
N ^c	0.4989(8)	0.4548(11)	0.315 81(26)	0.0718(5)	0.047(6)
N ^c	0.5347(11)	0.325 66(32)	0.4339(9)	0.0718(5)	0.047(6)
N ^c	0.5011(8)	0.5452(11)	0.684 19(26)	0.0718(5)	0.047(6)
N ^c	0.4653(11)	0.674 35(32)	0.5661(9)	0.0718(5)	0.047(6)

^a x, y, z, U_{iso} constrained with the corresponding Si parameter, fractional occupancy fixed. ^b Parameter fixed. ^c Bond length and angles constrained by rigid bodies, only one fractional occupancy parameter and one U_{iso} parameter were refined.

Table 3 Results of the Rietveld refinement of TTF in NaY; $a_{\text{sync}} = 24.684\ 83(21)\ \text{\AA}$, $a_{\text{neutron}} = 24.6956(7)\ \text{\AA}$

Atom	Result of the B2 experiment					Result of the D1A experiment				
	x	y	z	Frac. occupancy	U_{iso}	x	y	z	Frac. occupancy	U_{iso}
Si	0.123 73(8)	0.945 66(6)	0.035 67(7)	0.6999 ^b	0.003 23(24)	0.124 11(16)	0.946 51(14)	0.035 44(18)	0.6999 ^b	0.0118(9)
Al ^a	0.123 73(8)	0.945 66(6)	0.03567(7)	0.3001 ^b	0.003 23(24)	0.124 11(16)	0.946 51(14)	0.035 44(18)	0.3001 ^b	0.0118(9)
O	0.251 65(14)	0.251 65(14)	0.144 89(18)	1.0 ^b	0.0083(5) ^c	0.252 56(11)	0.252 56(11)	0.143 34(16)	0.991(20)	0.0192(17)
O	0.179 08(12)	0.179 08(12)	0.966 18(20)	1.0 ^b	0.0083(5) ^c	0.179 21(10)	0.179 21(10)	0.965 37(16)	1.015(20)	0.0196(14)
O	0.175 80(14)	0.175 80(14)	0.319 40(20)	1.0 ^b	0.0083(5) ^c	0.175 55(14)	0.175 55(14)	0.320 23(20)	0.972(17)	0.0219(16)
O	0.108 08(12)	0.891 93(12)	0.0	1.0 ^b	0.0083(5) ^c	0.108 25(10)	0.891 76(10)	0.0	0.946(14)	0.0135(17)
Na	0.0	0.0	0.0	0.503(13) ^d	0.005(5)	0.0	0.0	0.0	0.503(13) ^d	0.009(7)
Na	0.236 41(13)	0.236 41(13)	0.236 41(13)	0.974(11) ^d	0.0287(23)	0.236 69(29)	0.236 69(29)	0.236 69(29)	0.974(11) ^d	0.0472(35)
Na	0.059 30(22)	0.059 30(22)	0.059 30(22)	0.521(12) ^d	0.040(5)	0.057 15(22)	0.057 15(22)	0.057 15(22)	0.521(12) ^d	0.075(10)
C ^e	0.3842(4)	0.3071(4)	0.265 08(34)	0.0640(7)	0.025	0.3868(5)	0.2984(5)	0.2856(4)	0.0640(7)	0.05
C ^e	0.3727(5)	0.3600(4)	0.254 77(32)	0.0640(7)	0.025	0.3736(5)	0.3502(5)	0.2722(4)	0.0640(7)	0.05
S ^e	0.3430(5)	0.2658(6)	0.3070(5)	0.0640(7)	0.025	0.3499(6)	0.2604(6)	0.3341(6)	0.0640(7)	0.05
S ^e	0.4417(5)	0.2738(5)	0.2377(6)	0.0640(7)	0.025	0.4421(7)	0.2634(5)	0.2561(7)	0.0640(7)	0.05
S ^e	0.4139(7)	0.4013(5)	0.2129(6)	0.0640(7)	0.025	0.4104(7)	0.3882(5)	0.2237(6)	0.0640(7)	0.05
S ^e	0.3152(6)	0.3932(6)	0.2821(5)	0.0640(7)	0.025	0.3183(6)	0.3851(6)	0.3017(6)	0.0640(7)	0.05
C ^e	0.3835(7)	0.2082(6)	0.2994(8)	0.0640(7)	0.025	0.3904(6)	0.2027(6)	0.3277(6)	0.0640(7)	0.05
C ^e	0.4274(6)	0.2118(6)	0.2686(8)	0.0640(7)	0.025	0.4313(6)	0.2040(6)	0.2930(7)	0.0640(7)	0.05
C ^e	0.3734(8)	0.4589(5)	0.2205(8)	0.0640(7)	0.025	0.3700(6)	0.4459(6)	0.2301(5)	0.0640(7)	0.05
C ^e	0.3295(8)	0.4553(6)	0.2513(8)	0.0640(7)	0.025	0.3290(5)	0.4446(6)	0.2648(5)	0.0640(7)	0.05
D ^e	0.3666(8)	0.1806(7)	0.3202(10)	0.0640(7)	0.025	0.3758(7)	0.1768(7)	0.3520(7)	0.0640(7)	0.05
D ^e	0.4555(7)	0.1879(6)	0.2579(10)	0.0640(7)	0.025	0.4587(8)	0.1795(6)	0.2818(9)	0.0640(7)	0.05
D ^e	0.3903(10)	0.4865(6)	0.1997(10)	0.0640(7)	0.025	0.3846(8)	0.4718(6)	0.2058(6)	0.0640(7)	0.05
D ^e	0.3014(9)	0.4792(7)	0.2620(9)	0.0640(7)	0.025	0.3017(6)	0.4691(7)	0.2760(7)	0.0640(7)	0.05

^a x, y, z, U_{iso} constrained with the corresponding Si parameter, frac. occupancy fixed. ^b Parameter fixed. ^c Parameter constrained and refined as one. ^d Parameter constrained in both refinements and refined as one. ^e TTF molecule: bond length and angles constrained by rigid bodies, orientation of the rigid bodies was refined in both Rietveld refinements separately, only one frac. occupancy parameter was refined in both analyses and U_{iso} was fixed.

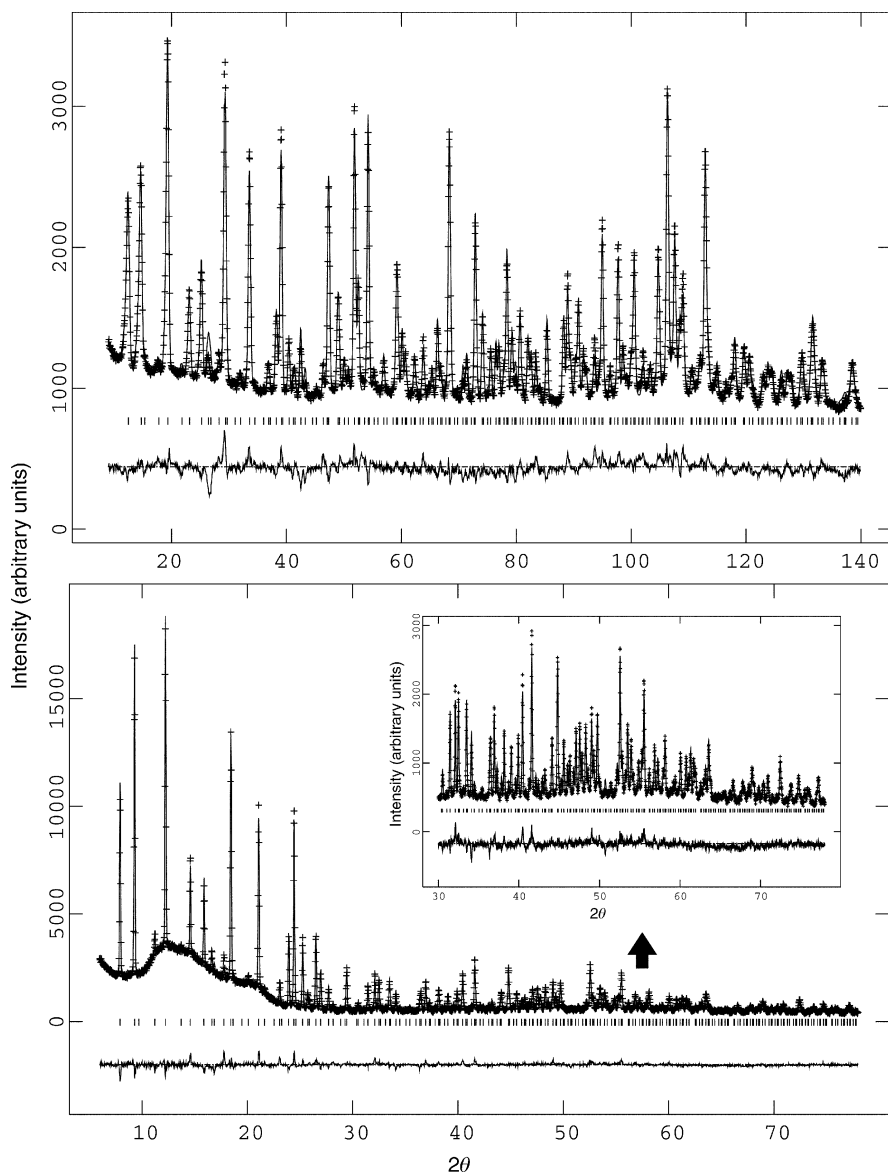


Fig. 6 Result of the Rietveld refinement for TTF in NaY.

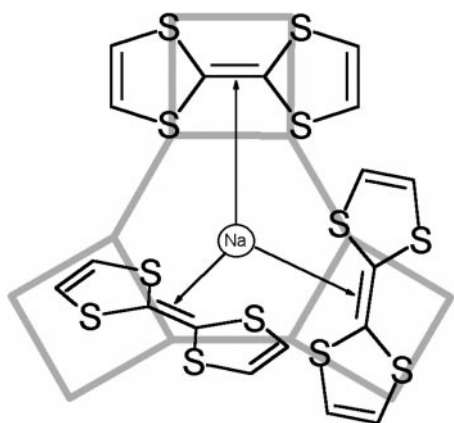


Fig. 7 Representative arrangements of TTF in NaY. All three shown positions have some characteristics in common: The distance between sodium and the centre of mass of the guest is between 3.5 and 4.4 Å. The ends of the molecule point to the neighbouring 12-ring windows, partially shown at the top on the left- and right-hand-side and at the bottom in the middle, respectively.

spectra measured in solutions with increasing solvent polarity. The polar solvent stabilizes the excited state of the molecule, which is neutral in the ground state. The bands of the radical ions shift to higher energies when TTF and TCNQ are both present in NaY. Such an anomalous effect is found when strong charge-transfer complexes are dissolved in a polar or protic solvent.^{17,18}

Until now the four fold co-ordination of TCNQ to the zeolite framework of NaY has not been reported in the literature. It clearly demonstrates the important role of the symmetry of the guest for the host-guest interactions. The zeolite NaY has a crystal structure with a very high symmetry. The point symmetry of TCNQ is mmm , therefore it is highly symmetric. The adsorption position at (0.5 0.5 0.5) exhibits a local symmetry of $\bar{3}m$. Both, TCNQ and the local symmetry at the adsorption site, have the symmetry elements $2/m$ in common, see Fig. 3 and 5. The symmetry of TCNQ fits easily into this local symmetry of the zeolite framework. In particular the sodium cations are in the ideal position to be co-ordinated to the functional groups of TCNQ. The zeolite framework reacts

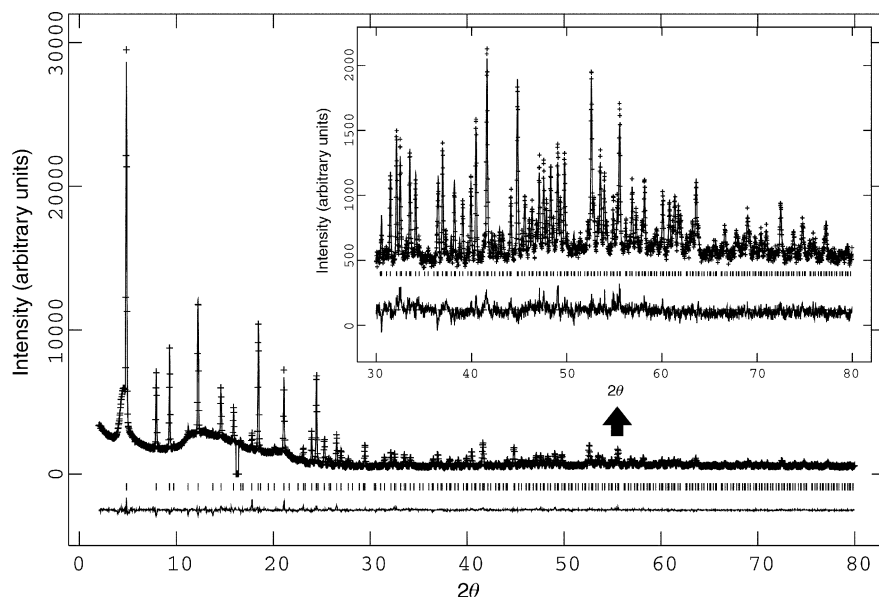


Fig. 8 Result of the Rietveld refinement for TCNQ and TTF in NaY; unidentified reflection is observed at $2\theta = 17^\circ$.

Table 4 Results of the Rietveld refinement of TCNQ and TTF in NaY, $a = 24.674\ 40(12)\ \text{\AA}$

Atom	x	y	z	Frac. occupancy	U_{iso}	Atom	x	y	z	Frac. occupancy	U_{iso}
Si	0.124 63(10)	0.946 14(7)	0.036 05(8)	0.6999 ^b	0.003 44(29)	C ^d	0.3752(6)	0.3147(6)	0.2491(5)	0.0523(10)	0.02
Al ^a	0.124 63(10)	0.946 14(7)	0.036 05(8)	0.3001 ^b	0.003 44(29)	C ^d	0.3645(6)	0.3683(6)	0.2480(5)	0.0523(10)	0.02
O	0.252 98(15)	0.252 98(15)	0.144 35(20)	1.0 ^b	0.0037(6) ^c	C ^d	0.3398(7)	0.2692(8)	0.2909(6)	0.0523(10)	0.02
O	0.179 53(14)	0.179 53(14)	0.967 58(24)	1.0 ^b	0.0037(6) ^c	N ^d	0.4256(7)	0.2846(7)	0.2088(6)	0.0523(10)	0.02
O	0.176 03(16)	0.176 03(16)	0.319 07(21)	1.0 ^b	0.0037(6) ^c	N ^d	0.3999(8)	0.4137(6)	0.2061(8)	0.0523(10)	0.02
O	0.107 74(15)	0.892 26(15)	0.0	1.0 ^b	0.0037(6) ^c	N ^d	0.3141(7)	0.3983(8)	0.2882(6)	0.0523(10)	0.02
Na	0.0	0.0	0.0	0.362(16)	0.004(9)	N ^d	0.3757(8)	0.2129(7)	0.2693(9)	0.0523(10)	0.02
Na	0.236 59(17)	0.236 59(17)	0.236 59(17)	0.956(15)	0.0460(35)	C ^e	0.4138(8)	0.2198(6)	0.2329(9)	0.0523(10)	0.02
Na	0.061 78(31)	0.061 78(31)	0.061 78(31)	0.511(11)	0.055(6)	C ^e	0.3640(9)	0.4700(6)	0.2277(11)	0.0523(10)	0.02
H ^d	0.5728(4)	0.4745(5)	0.5577(5)	0.0412(9)	0.02	S ^e	0.3259(9)	0.4631(7)	0.2642(10)	0.0523(10)	0.02
H ^d	0.4333(5)	0.5631(5)	0.5293(6)	0.0412(9)	0.02	S ^e	0.3613(9)	0.1833(7)	0.2886(11)	0.0523(10)	0.02
H ^d	0.4272(4)	0.5255(5)	0.4423(5)	0.0412(9)	0.02	S ^e	0.4386(9)	0.1972(7)	0.2147(10)	0.0523(10)	0.02
H ^d	0.5667(5)	0.4369(5)	0.4707(6)	0.0412(9)	0.02	S ^e	0.3784(11)	0.4996(6)	0.2085(13)	0.0523(10)	0.02
C ^d	0.542 63(26)	0.484 90(30)	0.533 46(30)	0.0412(9)	0.02	C ^e	0.3011(10)	0.4857(8)	0.2823(11)	0.0523(10)	0.02
C ^d	0.503 68(31)	0.522 67(20)	0.552 48(8)	0.0412(9)	0.02	C ^e	0.3752(6)	0.3147(6)	0.2491(5)	0.0523(10)	0.02
C ^d	0.460 89(27)	0.536 79(32)	0.516 78(34)	0.0412(9)	0.02	C ^e	0.3645(6)	0.3683(6)	0.2480(5)	0.0523(10)	0.02
C ^d	0.457 37(26)	0.515 10(30)	0.466 54(30)	0.0412(9)	0.02	C ^e	0.3398(7)	0.2692(8)	0.2909(6)	0.0523(10)	0.02
C ^d	0.496 32(31)	0.477 33(20)	0.447 52(8)	0.0412(9)	0.02	H ^e	0.4256(7)	0.2846(7)	0.2088(6)	0.0523(10)	0.02
C ^d	0.539 11(27)	0.463 21(32)	0.483 22(34)	0.0412(9)	0.02	H ^e	0.3999(8)	0.4137(6)	0.2061(8)	0.0523(10)	0.02
C ^d	0.5074(6)	0.5453(4)	0.604 98(16)	0.0412(9)	0.02	H ^e	0.3141(7)	0.3983(8)	0.2882(6)	0.0523(10)	0.02
C ^d	0.5500(8)	0.5314(6)	0.640 76(27)	0.0412(9)	0.02	H ^e	0.3757(8)	0.2129(7)	0.2693(9)	0.0523(10)	0.02
C ^d	0.4686(8)	0.5830(6)	0.6241(5)	0.0412(9)	0.02						

^a x, y, z, U_{iso} constrained with the corresponding Si parameter, frac. occupancy fixed. ^b Parameter fixed. ^c Parameter constrained and refined as one. ^d TCNQ molecule: bond length and angles constrained by rigid bodies, only one frac. occupancy parameter was refined and U_{iso} was fixed. ^e TTF molecule: bond length and angles constrained by rigid bodies, only one frac. occupancy parameter was refined and U_{iso} was fixed.

Table 5 Absorption bands of TTF

TTF dissolved in cyclohexane		TTF suspension in nujol	TTF in NaY suspension in nujol	Shift/nm
λ/nm	$\epsilon^a/\text{cm}^{-1}\ \text{mol}^{-1}$	λ/nm	λ/nm	
303	13.000	310	368	58
317	12.500	319	375	56
368	1.900	372	427	55
450	270	437	506	69

^a Ref. 16.

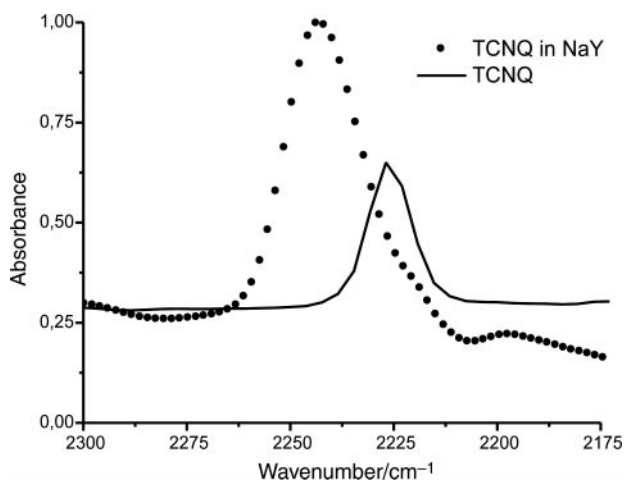


Fig. 9 DRIFT spectra of TCNQ.

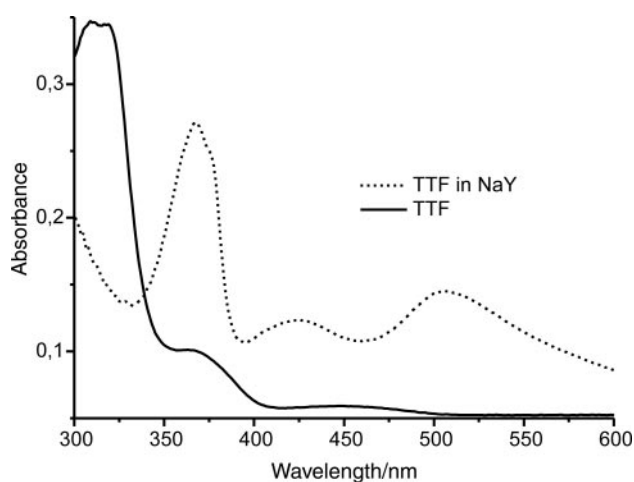


Fig. 10 UV-VIS spectra of TTF.

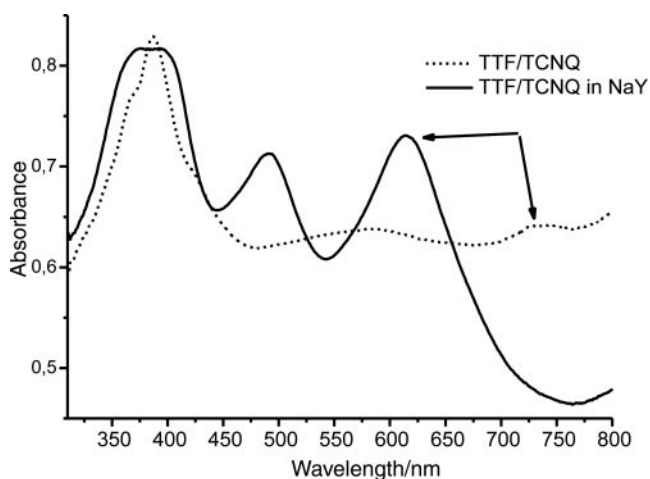


Fig. 11 UV-VIS spectra of TTF and TCNQ.

to the loading with guest molecules only by shifting cations very slightly. Through knowledge of the arrangement of the guest in the zeolite, the spectroscopic experimental results are understood.

It has been demonstrated that guest molecules with functional groups can be anchored into the pores of the zeolite framework. These guests are influenced by the co-ordination. Further investigations will show whether these effects may be systematically varied by different zeolite structures, different Si/Al ratios or ion exchanged hosts.

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