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ARTICLE TYPE

Crystal growth and characterization of solvated organic charge-transfer complexes built on TTF and 9-dicyanomethylenefluorene derivatives

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A series of 1:1 organic complexes has been synthesized by reaction between TTF (tetrathiafulvalene) and three 9-dicyanomethylenefluorene derivatives: 9-dicyanomethylene-2,7-dinitrofluorene (DDF), 9-dicyanomethylene-2,4,7-trinitrofluorene (DTF) and 9-dicyanomethylene-4,5,7-trinitrofluorene-2-carboxylic acid (DC2TF). The following formulas were determined by X-ray diffraction and elemental analysis for these complexes: (TTF-DDF).CH_3CN (1), (TTF-DDF).0.5PhCl (2), (TTF-DTF).CH_3CN (3), (TTF-DTF).0.5Me_2CO (4) and (TTF-DC2TF).H_2O (5). A sixth solvated compound was also obtained, with a different stoichiometry, $(TTF)_3(DC2TF)_2.2CH_3CN$ (6). The degree of charge transfer in 1-5 was estimated by IR and Raman spectroscopy. Lattice solvent, acetonitrile, chlorobenzene, or acetone, is slowly released from crystals of complexes 1-4, inducing a significant decrease of the charge transfer over time. These crystals converge over months towards materials close to the neutral state. Hydrate 5 is air-stable, and displays a degree of charge transfer, $\boldsymbol{\delta = 0.48\ e^-}$, close to the range of semi-conducting or metallic organic complexes. Finally, compound 6 is an ionic crystal, and is thus expected to be an insulating material.

Introduction

Functionalization of the aromatic polycyclic core of 9-dicyanomethylenefluorene with electron withdrawing groups makes this molecule less nucleophilic. This enhanced π-acid character has been used for a long time, for the synthesis of electron acceptor molecules (*A* hereafter), which are useful building blocks for the preparation of organic radical ion salts, known as charge-transfer complexes (CTC). The combination of these acceptors with electron donor molecules behaving as π-bases (*D* hereafter), like tetrathiafulvalene (TTF), results in complexes where partial reduction and oxidation of both moieties allows electron transport in a more or less anisotropic way.[1] Such CTC systems are synthesized with the hope to obtain interesting materials having metallic properties, despite they do not include metals. Most of them are insulating or semiconducting materials, but some strategies are known to orient the material toward a metallic behaviour, characterized by a significant conductivity ($\sigma > 10\ \mathrm{S.cm^{-1}}$ at 300 K), or even superconductivity, as in Bechgaard salts.[2]

Of particular importance is the mode of stacking of donors and acceptors in the crystal: segregated stacks of the *D* and *A* components lead to quasi-1D electronic systems. The metallic conduction is then affordable, providing that the charge transfer in the complex $D^{\delta+}A^{\delta-}$ falls within the window $0.5 < \delta < 0.75$, at least in the case of 1:1 complexes.[1a] However, many other criteria must be considered when screening candidates for organic metals, for instance the difference between redox potentials of *A* and *D*, which should be enough to promote oxidation and reduction of both entities, but not too high, otherwise both molecules remain essentially neutral.[3] Ionic complexes, characterized by integral charges ($\delta = 1, 2, \cdots$), are also undesirable in this context, since they lead to insulating materials.

Although the accumulated literature gives a number of useful guidelines for the design of such materials,[4] no gold rules have been established regarding electrical properties. Surprising results are reported from time to time, like the complex between 1,6-diaminopyrene and *p*-bromanil, for which some polymorphs are fairly conductive ($\sigma \approx 10^{-1}\ \mathrm{S.cm^{-1}}$ at 300 K), although their crystal structures feature mixed stacks of neutral components.[5] Also surprising was the discovery of molecular metals composed of single-component molecules, in which $\delta = 0$ by nature.[6]

On the other hand, some aspects of the synthesis may result difficult to control, for example the contamination of the product by unreacted starting materials, the variability of the stoichiometric ratio between *D* and *A*,[1a] or the unexpected crystallization of polymorphic phases.[7] In any case, as accurate as possible evaluation of δ is essential in the preliminary study of an organic CTC. The semi-empirical method devised by Chappell *et al*. in 1981 remains very popular, because it is based on common vibrational spectroscopy, IR and Raman, without the need for crystallized samples.[8] The primary drawback to this technique is that neutral and ion radical states of the component used as a probe must be available. This point is never a trouble for the neutral molecule, since it is a starting material for the synthesis of the CTC. In contrast, authentic ionic salts like $\mathrm{Na^+}A^-$ or $D^+\mathrm{Cl^-}$ in which $\delta = 1$ are sometimes impossible to stabilize. Hopefully, δ can be computed through:

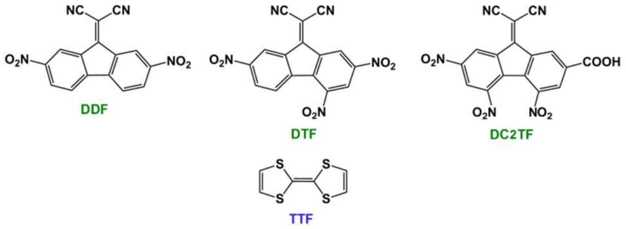
$$\delta = \frac{2(\Delta\nu/\nu_0)}{1-(\nu_1/\nu_0)^2}$$

where ν_0 and ν_1 are the vibrational frequencies for neutral ($\delta = 0$) and ionized ($\delta = 1$) component, respectively, and $\Delta\nu =$

$\nu_{\mathrm{CTC}} - \nu_0$ is the shift observed for the same vibrational mode in the CTC with respect to the neutral component used as a probe.

We have been interested in assessing the accuracy of this method in difficult cases, for instance when comparing polymorphic phases,[9] complexes close to the neutral state,[10] or complexes with stoichiometry other than 1:1, for which some components may not participate to the charge transfer.[11]

During these studies,[12] we obtained a set of solvated complexes, using TTF and three 9-dicyanomethylenefluorene derivatives (see Scheme 1) as *D* and *A* components. We realized that the role of lattice solvent is frequently overlooked in such compounds, despite that solvent can be pro-active in the mechanism of charge transfer. It seems that this issue was addressed at the beginning of the TTF-TCNQ saga,[13] but was then gradually discarded, because researchers focussed on the preparation of unsolvated species, which are crystallized in a more controllable way. A recent review compiles 9-dicyanomethylenefluorene derivatives and their complexes characterized by X-ray diffraction up to 2009.[14] For 23 compounds retrieved from the literature, five solvated complexes are listed with the following solvents: chlorobenzene,[15] 1,4-dioxane,[16] dichloromethane,[17] and acetonitrile.[18]



Scheme 1 Acceptor and donor molecules used in this work

The present work addresses the following question: within the series of complexes we obtained, is the presence of lattice solvent a factor favouring the charge transfer?

Experimental

TTF was purchased from Sigma and purified by recrystallization from hexane, until constant mp (120-121 °C). Acetonitrile (Merck or Baker, HPLC grade), chlorobenzene (Baker) and acetone (Baker) were used as received. 2,7-Dinitro-9-fluorenone (Aldrich, 97%), was purified twice by chromatography over silicagel, and then recrystallized, first from benzene and then from ethyl acetate, until constant mp (290 °C). 2,4,7-Trinitro-9-fluorenone (Matheson) was used as received. 4,5,7-Trinitro-9-fluorenone-2-carboxylic acid was prepared by nitration of 9-fluorenone-2-carboxylic acid with HNO_3/H_2SO_4,[19] recrystallized from a mixture of acetonitrile, chloroform and hexane, and finally heated at 95-100 °C under reduced pressure (3 mm Hg), until constant mp (274-280 °C; lit.,[19] 267-275 °C). Malononitrile (Eastman Kodak) was purified by distillation under reduced pressure or recrystallization from chloroform. Elemental analyses were performed by Desert Analytics, Tucson (AZ, USA).

Synthesis of acceptors

Acceptors DDF, DTF and DC2TF were prepared starting from the corresponding 9-fluorenone derivatives, using a Knoevenagel condensation with malononitrile, in refluxing methanol. Yields above 95% are obtained with an excess of malononitrile.

DDF: synthesized from 2,7-dinitro-9-fluorenone (25 mg) and malononitrile (18.6 mg) in refluxing methanol for 9 h. and recrystallized from acetonitrile. Yield: 98%. Bright yellow needles, mp 306-308 °C (Lit.,[20] 298-299 °C). Found: C, 60.14; H, 2.05; N, 17.49. Calc. for $C_{16}H_6N_4O_4$: C, 60.39; H, 1.90; N, 17.61%.

DTF: synthesized from 2,4,7-trinitro-9-fluorenone (25.3 mg) and malononitrile (8.0 mg) in refluxing methanol for 2.5 h. and recrystallized from methanol. Yield: 98%. Yellow solid, mp 266 °C (Lit.,[21] 266-268 °C). Found: C, 52.56; H, 1.41; N, 19.18. Calc. for $C_{16}H_5N_5O_6$: C, 52.91; H, 1.39; N, 19.28%.

DC2TF: synthesized from 4,5,7-trinitro-9-fluorenone-2-carboxylic acid (25 mg) and malononitrile (13.7 mg) in refluxing methanol for 0.75 h. and recrystallized from acetonitrile or methanol. Yield: 96%. Bright yellow solid, mp 314-316 °C (Lit.,[19] 307-310 °C). Found: C, 50.16; H, 1.07; N, 17.07. Calc. for $C_{17}H_5N_5O_8$: C, 50.14; H, 1.24; N, 17.20%. For samples recrystallized from MeOH, elemental analysis fits better for the hydrated acceptor, DC2TF.H_2O: C, 48.51; H, 1.81; N, 16.48. Calc. for $C_{17}H_7N_5O_9$: C, 48.01; H, 1.66; N, 16.47%.

Synthesis of complexes 1-6

*(TTF-DDF).CH$_3$CN (**1**)*. Hot acetonitrile solutions of DDF (5.4 mg, 17 μmol in 2.5 mL) and TTF (3.5 mg, 17 μmol in 1 mL) were combined. After reduction of the volume to *ca*. 1 mL, the solution turned yellowish green. The solution was then cooled to room temp., affording dark-brown needles (6.6 mg, 69%), mp 174-176 °C. Found: C, 51.20; H, 2.09; N, 12.11; S, 22.42. Calc. for $C_{24}H_{13}N_5O_4S_4$: C, 51.14; H, 2.32; N, 12.43; S, 22.75%. Single crystals suitable for X-ray diffraction were obtained by evaporation over 3 d. of an acetonitrile solution (4 mL) of the raw material.

*(TTF-DDF).0.5PhCl (**2**)*. The previous synthesis was repeated, with chlorobenzene solutions of DDF (10.3 mg, 32 μmol in 3 mL) and TTF (20.1 mg, 98 μmol in 1 mL), affording irregular dark-brown needles (14.9 mg, 80%). mp 172 °C. Found: C, 52.02; H, 2.22; N, 9.78; S, 22.11. Calc. for $C_{25}H_{12.5}Cl_{0.5}N_4O_4S_4$: C, 51.87; H, 2.18; N, 9.68; S, 22.15%.

(TTF-DTF).CH$_3$CN (3). Hot acetonitrile solutions of DTF (6.2 mg, 17 μmol in 2 mL) and TTF (3.5 mg, 17 μmol in 1.5 mL) were combined and the resulting solution instantaneously turned green. The solution was then cooled to room temp., and evaporated, affording dark-brown plates (9 mg, 90%), mp 224 °C. A typical elemental analysis gives a solvent content corresponding to a 1:1:0.5 complex, due to acetonitrile loss over time; found: C, 46.80; H, 1.70; N, 13.03; S, 21.32. Calc. for $C_{23}H_{10.5}N_{5.5}O_6S_4$: C, 46.97; H, 1.80; N, 13.10; S, 21.81%.

(TTF-DTF).0.5Me$_2$CO (4). The same procedure as for **3** was repeated, with acetone in place of acetonitrile, affording dark-brown plates (9.6 mg, 99%), mp 226 °C. A typical elemental analysis corresponds to the unsolvated complex; found: C, 46.68; H, 1.59; N, 12.22; S, 22.40. Calc. for $C_{22}H_9N_5O_6S_4$: C, 46.56; H, 1.60; N, 12.34; S, 22.59%. Single crystals suitable for X-ray diffraction were obtained by evaporation over 4 d. of an acetone solution (4 mL) of the raw material.

(TTF-DC2TF).H$_2$O (5). Acetonitrile solutions of DC2TF previously recrystallized from methanol (10 mg, 25 μmol in 1.9

mL) and TTF (10 mg, 49 µmol in 2.4 mL) were combined at room temp., and the resulting solution instantaneously turned dark green. The solution was slowly evaporated, over 3-4 d., affording brown needles (yield < 50%), mp 236-237 °C (dec.). Found: C, 44.73; H, 1.53; N, 10.87. Calc. for $C_{23}H_{11}N_5O_9S_4$: C, 43.88; H, 1.76; N, 11.12%.

*(TTF)$_3$(DC2TF)$_2$.2CH$_3$CN (**6**)*. Acetonitrile was dried over P_2O_5, and a solution of TTF was prepared (3.5 mg, 17 µmol in 2 mL). DC2TF was recrystallized from methanol, dried at 100 °C for 8 h. and dissolved in hot acetonitrile (7 mg, 17 µmol in 3.7 mL). Both solutions were mixed in a small Büchner flask equipped with a $CaCl_2$ trap, and air was evacuated with argon. After 2 d. all solvent had evaporated, affording brown crystals (yield < 50%), mp 234-240 °C (dec.). No elemental analysis was carried out, and the formula was assigned from the X-ray refinement.

Synthesis of alkaline ionic crystals

Alkaline salts of acceptors DDF, DTF and DC2TF were obtained by reaction between the acceptor and an excess of LiI, NaI or KI, in refluxing acetonitrile. After cooling to room temperature, unreacted acceptor was eliminated by filtration and the solution concentrated *in vacuo*. In the case of DDF, impure $\mathrm{Li^+DDF^-}$ and $\mathrm{Na^+DDF^-}$ were obtained after long reactions times, 29 h. and 72 h. respectively. With DTF, Li^+ and Na^+ salts were obtained after 2, and 6 h. of reaction. Finally, with DC2TF, shorter reaction times, *ca*. 30 min., allowed to isolate quite pure samples of $\mathrm{Li^+DC2TF^-}$, $\mathrm{Na^+DC2TF^-}$ and $\mathrm{K^+DC2TF^-}$.

Characterization of complexes

Single crystals were diffracted as soon as crystallized, in order to minimize the impact of solvent loss. Data were measured on a Bruker P4 diffractometer (Table 1) using the Mo-K_α radiation,[22] and structures refined on the basis of absorption-corrected data,[23] with the SHELX package released by G. Sheldrick in 2014.[24] Treatment of disordered parts in **2**, **3**, **4** and **5** is detailed in the ESI, and CIF files, along with structure factors, have been deposited with the CCDC. FT-IR spectra were recorded on a Nicolet Magna 750 spectrometer in the $3500-350\ \mathrm{cm^{-1}}$ range, with a resolution of $4\ \mathrm{cm^{-1}}$. Samples were diluted in KBr (1/65 *w*/*w*) to form 3 mm-diameter pellets. We took special care to follow the same protocol for all spectra, for example by systematically using only one single crystal for each spectrum. Some attempts to obtain spectra using a bulk crystal with no previous dilution were unsuccessful, since no transmittance over the sample thickness, *ca*. 100 µm, was detectable. Full spectra may be consulted in the ESI. FT-Raman spectra were measured on raw crystalline materials packed in glass capillary, with a Nicolet 800 spectrophotometer equipped with a Nd:YAG laser ($\lambda \approx 1000$ nm) operated in the 50-100 mW range.

Table 1 Crystallographic data

	1	**2**	**3**	**4**	**5**	**6**
Chemical formula	$C_{24}H_{13}N_5O_4S_4$	$C_{25}H_{12.5}Cl_{0.5}N_4O_4S_4$	$C_{24}H_{12}N_6O_6S_4$	$C_{23.5}H_{12}N_5O_{6.5}S_4$	$C_{23}H_{11}N_5O_9S_4$	$C_{56}H_{28}N_{12}O_{16}S_{12}$
Formula mass	563.63	578.85	608.64	596.62	629.61	1509.62
Space group	$P2_1/c$	$P\bar{1}$	*Pbca*	*Pbca*	$C2/c$	$P\bar{1}$
a/Å	7.141(2)	7.3769(11)	7.1635(16)	7.1682(15)	15.9432(14)	10.0608(10)
b/Å	17.151(4)	9.3811(9)	19.881(4)	19.902(6)	12.1351(9)	10.3528(11)
c/Å	20.891(5)	18.9293(19)	37.705(8)	37.805(9)	13.5738(11)	15.612(2)
α/°	90	81.218(7)	90	90	90	107.535(8)
β/°	99.18(3)	88.805(10)	90	90	104.572(7)	100.525(9)
γ/°	90	75.958(10)	90	90	90	90.877(8)
V/Å^3, Z	2525.6(12), 4	1255.8(3), 2	5370(2), 8	5393(2), 8	2541.7(4), 4	1520.2(3), 1
T/K	298(2)	298(2)	298(2)	298(2)	298(2)	298(2)
$2\theta_{max}$/°, complete/%	48, 99.8	50, 99.7	50, 100	45, 99.9	50.5, 99.9	50, 96.9
No. ref meas. (R_{int})	5355 (0.066)	6313 (0.024)	6049 (0.027)	8389 (0.105)	6560 (0.026)	6125 (0.047)
Data/param./restr.	3950/336/0	4400/370/86	4730/417/111	3545/399/53	2918/227/14	5172/437/1
R_1 [I>2σ(I)]	0.0664	0.0408	0.0570	0.0621	0.0547	0.0569
wR_2 [all data]	0.1773	0.1098	0.1647	0.1848	0.1511	0.1567

Results and discussion

(TTF-DDF).CH$_3$CN (1) and (TTF-DDF).0.5PhCl (2)

With acceptor 9-dicyanomethylene-2,7-dinitrofluorene (DDF), two complexes were successfully crystallized, which contain acetonitrile (**1**, Fig. 1) or chlorobenzene (**2**, Fig. 2) as lattice solvent. The crystal structure of neutral free DDF is known,[25] showing that the C_2 molecular symmetry is retained in the solid state. This molecule is essentially aromatic, having the dicyanomethylene group coplanar with the fluorene core, and the nitro groups twisted by *ca*. 18° from this plane. A conformation close to that of neutral DDF is observed in complexes **1** and **2**. The only significant modification is a slight twist of the C(CN)$_2$ group from the fluorene plane, of 5.3(3)° in **1** and 5.0(2)° in **2**. In both compounds, DDF is stacked with TTF molecules, forming 1:1 complexes. Mixed stacks along [100] are similar to arrangements observed in all fluorene-derivatives CTC's obtained so far with TTF as donor, and the geometry of the stacks is favourable for a significant charge transfer: in **1**, molecules are separated by 3.509 and 3.788 Å and their mean planes are almost parallel, making a dihedral angle of 1.34(8)° (Fig. 1).[26] Corresponding figures in **2** are 3.908 and 3.942 Å for DDF…TTF separations and 2.12(4)° for the tilt angle (Fig. 2). The relative orientation of DDF and TTF seems also to facilitate the charge transfer, with the central π bond of the TTF placed above the centre of gravity of the aromatic core of DDF (Fig. 1, inset), or close to this centre (Fig. 2, inset).

The unexpected feature is the presence of solvent, intercalated between TTF-DDF stacks. Compound **1** is a 1:1:1 complex TTF:DDF:CH_3CN, with the solvent molecules placed in general positions, and poorly interacting with the DDF-TTF stacks in the crystal. The shortest intermolecular contact involving acetonitrile is characterized by the separation N…S_{TTF} of 3.238 Å (van der Waals radii sum: $R_{\mathrm{N}} + R_S = 3.35$ Å). Acetonitrile solvates of complexes built with TTF derivatives are rather common and have been X-ray characterized, for mixed-stacks[27] as well as for segregated-stacks systems.[28] However, insertion of acetonitrile is generally unintentional, and arises merely from the fact that acetonitrile is a solvent of choice for the crystallization or electrocrystallization of these compounds.

Less common are complexes crystallized as chlorobenzene solvates. With TTF, only two structures have been reported.[15] For compound **2**, the hemisolvate is formed, TTF-DDF.0.5C_6H_5Cl, with the solvent molecule disordered by symmetry across inversion centres. As in **1**, solvent fills the voids between mixed DDF-TTF columns, without forming strong interactions with them. However, crystal symmetry is modified, from $P2_1/c$ (**1**) to $P\bar{1}$ (**2**), possibly because steric volume and shape are different for chlorobenzene and acetonitrile.

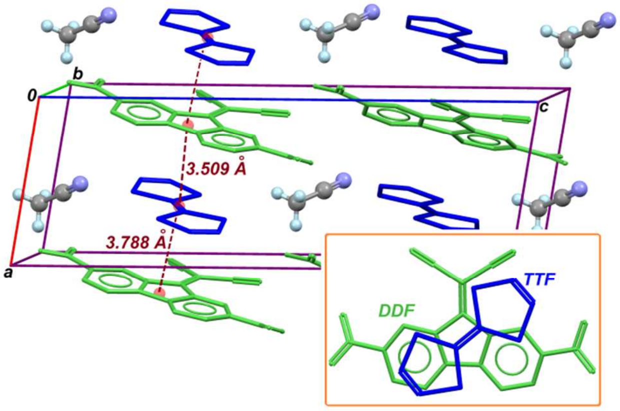


Fig. 1 Crystal structure of **1**, showing *DA* stacks along [100]. The inset displays one stack down stacking axis.

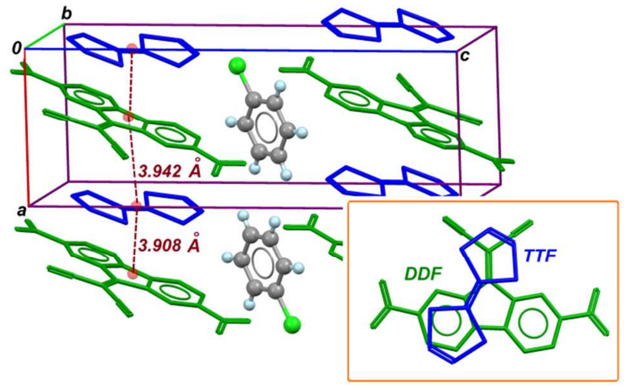


Fig. 2 Crystal structure of **2**, showing *DA* stacks along [100]. A single orientation for the disordered chlorobenzene molecule is retained. The inset displays one stack down stacking axis.

With 9-dicyanomethylene derivatives of fluorene, the b_{2u} stretching mode of the cyano groups is active in IR, and this sharp band falls in a frequency range uncontaminated by other vibrations of the fluorene moiety or TTF. It is thus a probe of choice for estimating δ using IR spectroscopy. Neutral DDF gives a symmetrical vibration at $\nu_0 = 2236\,\mathrm{cm}^{-1}$ (Fig. 3), consistent with the C_2 molecular symmetry, which makes both cyano groups equivalent. Frequency ν_1 was estimated with spectra of radical ionic salts $\mathrm{Li^+DDF^-}$ and $\mathrm{Na^+DDF^-}$. These salts, obtained by reacting DDF with LiI or NaI, are difficult to obtain in pure form, and all attempts we have done resulted in sample with residual $\mathrm{DDF^0}$ precursor, detected by a small band around $2236\,\mathrm{cm}^{-1}$. However, the main vibration for $\mathrm{DDF^-}$ appears at 2196 and $2194\,\mathrm{cm}^{-1}$, for $\mathrm{Li^+}$ and $\mathrm{Na^+}$ salts, respectively. We retained $\nu_1 = 2195\,\mathrm{cm}^{-1}$ for computations.

Complex **1**, as analyzed just after crystallization, shows the vibration for the cyano group of DDF at $\nu = 2221\,\mathrm{cm}^{-1}$ (Fig. 3, left panel). The frequency shift with respect to neutral DDF is thus $\Delta\nu = 15\,\mathrm{cm}^{-1}$, which allows to estimate the charge transfer using the Chappell's formula: $\delta_{\mathbf{1}} = 0.37\,e^-$. A less intense cyano vibration, at $2254\,\mathrm{cm}^{-1}$, accounts for the presence of acetonitrile as lattice solvent, since pure acetonitrile presents an intense vibration at this position.[29] However, as time runs away, the spectrum is modified. The measured $\Delta\nu$ shift slowly decreases, and stabilizes around $\Delta\nu = 10\,\mathrm{cm}^{-1}$ after three months. At this point, the charge transfer dropped to $\delta'_{\mathbf{1}} = 0.25\,e^-$. The simultaneous disappearance of the vibration assigned to acetonitrile, which has vanished three months after exposure of crystals to air, shows that solvent is slowly released from the solid. This degradation does not favour the charge transfer. However, with these data in our hands, it cannot be determined whether the degradation of the charge-transfer results from an actual topochemical reaction with partial re-oxidation of DDF and structural rearrangement in the solid state for DDF and TTF, or results from the crystal lattice collapse induced by solvent loss. Anyhow, the crystals are not stable in air over months: although their shape and aspect seem unaltered, the crystals do no longer diffract X-ray after this time.

The same behaviour is observed in complex **2** (Fig. 3, right panel). Freshly crystallized complex displays the cyano stretching band of DDF at $2220\,\mathrm{cm}^{-1}$, giving a shift $\Delta\nu = 16\,\mathrm{cm}^{-1}$, corresponding to $\delta_{\mathbf{2}} = 0.39\,e^-$. After some months, the charge transfer converges to $\delta'_{\mathbf{2}} = 0.25\,e^-$. We assume that almost all solvent has then been extruded from the crystal, yielding, as for **1**, the stable unsolvated compound TTF-DDF.

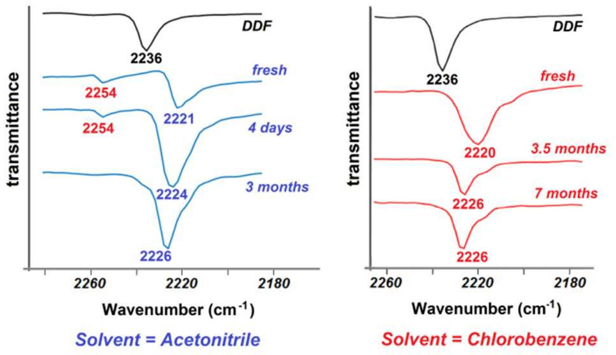


Fig. 3 Evolution of the cyano vibrations in the IR spectra for complexes **1** (left) and **2** (right). The upper spectra (black lines) are for the neutral DDF acceptor molecule.

(TTF-DTF).CH$_3$CN (3) and (TTF-DTF).0.5Me$_2$CO (4)

In order to check if crystal instability over long times was a characteristic feature for solvates of CTC complexes in this series, we repeated the work using an acceptor molecule with a slightly higher electron affinity, namely 9-dicyanomethylene-2,4,7-trinitrofluorene (DTF). Two solvates were successfully crystallized with acetonitrile and acetone, for which formulas were determined by X-ray analysis: the 1:1:1 complex (TTF-DTF).CH$_3$CN (**3**), and the 1:1:0.5 complex (TTF-DTF).0.5C$_3$H$_6$O (**4**).

Unlike previous compounds **1** and **2**, both complexes are isomorphous, and crystallize in space group *Pbca*. Mixed stacks TTF-DTF run in the [100] direction, with *D*…*A* separations and relative orientation compatible with charge-transfer (See Figs. 4 and 5). For instance, the most important criterion for overlap between π orbitals of DTF and TTF is well fitted: mean planes of both components are nearly parallel, with tilt angles of 2.17(5) and 1.60(8)° in **3** and **4**, respectively. The nitro group at C4 in DTF is unequally disordered over two sites, bonded to C4 and C5, with occupancies 0.317(6)/0.683(6) in the case of **3**, and 0.365(10)/0.635(10) in **4**. A similar disorder has been described for neutral DTF in a low resolution study,[30] and in other related CTC's with derivatives of TTF[31] or porphyrin.[32] It thus seems that DTF attempts to approximate the C_2 local symmetry while crystallizing.

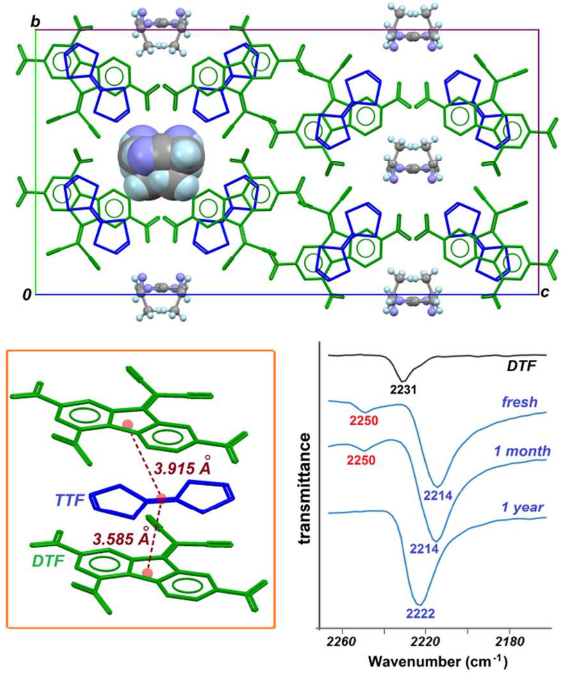


Fig. 4 Crystal structure of acetonitrile solvate **3** and evolution of the IR cyano vibrations for this complex. For the sake of clarity, a single site for disordered NO$_2$ groups in DTF and CH$_3$CN molecules are represented. One column of solvent is represented using spacefill model. The upper spectrum (black line) is for the neutral DTF acceptor molecule.

Once TTF-DTF stacks are in place, *ca*. 15% of the crystal volume is still empty, forming channels parallel to the short *a* axis. These voids are filled with guest solvent, which, as in **1** and **2**, poorly interact with the TTF-DTF host. As a consequence, acetonitrile in **3** is disordered over a number of orientations, and we limited the model to two sites, with the sum of occupancies constrained to unity, 0.248(8) and 0.752(8). In complex **4**, acetone is also almost certainly disordered, but the crystal structure was refined with a single position and a strongly restrained geometry for acetone. Acetone content was estimated by refinement of the occupancy. Compounds **3** and **4** were expected to release solvent, and this behaviour indeed hindered elemental analysis. For **4**, analysis match a formula with no solvent at all, while for **3**, acetonitrile content is less than that expected from X-ray analysis (see experimental section).

These features are fully consistent with IR data. Acetonitrile is present in the crystal **3** just after crystallization, as reflected by the vibration at $2250\ \mathrm{cm}^{-1}$. This vibration survives after one month, but disappears after one year elapsed. The vibration of the cyano groups in DTF is initially found at $2214\ \mathrm{cm}^{-1}$, shifted by $17\ \mathrm{cm}^{-1}$ with respect to neutral DTF.[33] On the other hand, parameter ν_1 for fully oxidized DTF was extracted from IR spectra of $\mathrm{Li}^{+}\mathrm{DTF}^{-}$ and $\mathrm{Na}^{+}\mathrm{DTF}^{-}$, affording $\nu_1 = 2184\ \mathrm{cm}^{-1}$. The calculated charge transfer in freshly crystallized complex **3** is then $\boldsymbol{\delta_3} = 0.37\ e^{-}$, very close to that observed in **1** and **2**. After one year, vibration of free acetonitrile is no longer detected, and charge-transfer has been halved to $\boldsymbol{\delta'_3} = 0.19\ e^{-}$ (Fig. 4). For **4**, lattice acetone being a low boiling solvent, bp = 56 °C, we assume that solvent release starts as soon as crystals are exposed to air, precluding measurements on a 1:1:1 complex. A fresh crystallized sample, with a stoichiometry close to 1:1:0.5 as observed in the X-ray analysis, shows the characteristic vibration of the carbonyl group for acetone, at $1712\ \mathrm{cm}^{-1}$.[34] After five days in air, the intensity of this band decreases, and finally vanishes after ten months. Over the same period, charge transfer experiments a drop from $\boldsymbol{\delta_4} = 0.37$ to $\boldsymbol{\delta'_4} = 0.19\ e^{-}$ (Fig. 5), as observed in complex **3**.

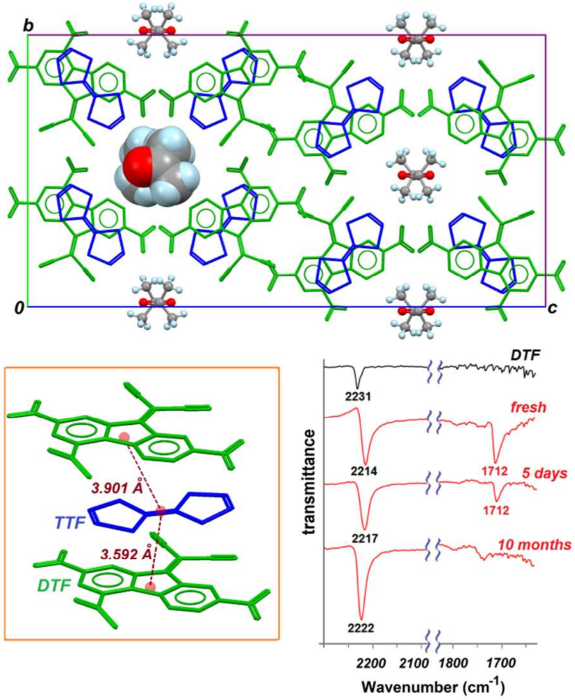


Fig. 5 Crystal structure of acetone solvate **4** and evolution of the IR cyano and carbonyl vibrations for this complex. The upper spectrum (black line) is for the neutral DTF acceptor molecule.

(TTF-DC2TF).H_2O (5) and $(TTF)_3(DC2TF)_2.2CH_3CN$ (6)

We finally attempted the crystallization of solvate complexes based on a tetra-substituted dicyanomethylenefluorene acceptor, namely 9-dicyanomethylene-4,5,7-trinitrofluorene-2-carboxylic acid (DC2TF). First attempts of reaction between TTF and DC2TF afforded **5**, an unexpected 1:1:1 hydrate (Fig. 6). Although the source of water is unclear, the formation of this hydrate has been confirmed by two single-crystal refinements from independent batch, and the presence of a broad band centred at $3500\ \mathrm{cm}^{-1}$ in IR spectra, which is not observed in other complexes (see ESI, Fig. S15).

Complex (TTF-DC2TF).H_2O crystallizes in space group *C*2/*c*, with the DC2TF molecule lying on the crystallographic twofold axis. As a consequence, carboxylic and nitro groups substituting the fluorene core at C2 and C7 are disordered by symmetry. The TTF moiety, whose site symmetry is -1, is stacked along [001] with the acceptor at a rather short and constant distance, 3.752 Å, and the tilt angle between TTF and DC2TF mean planes is 4.06(4)° (Fig. 6). The stack arrangement allows alignment of the centres of exocyclic double bonds of TTF with atoms C9 in acceptors, along the stacking direction. Finally, water molecules, with occupancy factor of ½, are disordered over inversion centres, and are involved in hydrogen bonding with carboxylic groups and nitro groups of DC2TF (Fig. 6, lower panel; ESI, Table S30). Lattice solvent is thus, as in previous complexes, filling voids between stacks, but hydrogen bonds and high boiling point of water in comparison with acetone or acetonitrile has two important consequences: the crystals are stable in air, and the crystal structure is not based on an actual 1D framework, a feature which should favour charge-transfer. This point is confirmed by IR spectroscopy.

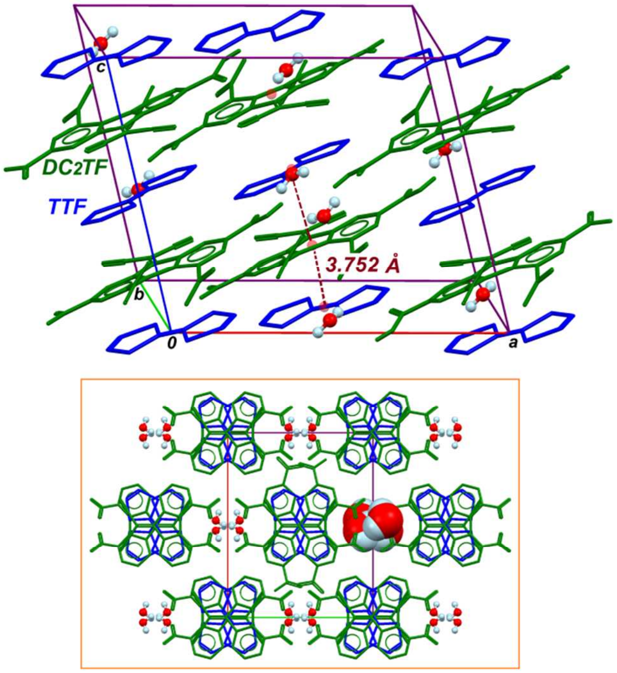


Fig. 6 Crystal structure of hydrate **5**, omitting the disorder in DC2TF. The inset is a part of the packing structure, as viewed down the stacking axis [001]. One column of water molecules, each one with site occupancy of ½, is represented with a spacefill style.

For neutral DC2TF, the b_{2u}-cyano vibration is found at $\nu_0 = 2234\ \mathrm{cm}^{-1}$, while the same vibration for ionic salts $\mathrm{Li}^{+}\mathrm{DC2TF}^{-}$ and $\mathrm{Na}^{+}\mathrm{DC2TF}^{-}$ is shifted to $\nu_1 = 2188\ \mathrm{cm}^{-1}$. The vibration observed in the complex, at $2212\ \mathrm{cm}^{-1}$, corresponds to the charge-transfer $\delta_5 = 0.48\ e^{-}$, which makes hydrate **5** a prospective candidate for a semi-conducting or metallic-like material.

In order to assess if lattice water had an actual influence on the charge-transfer in **5**, we attempted the crystallization of the anhydrous complex TTF-DC2TF, avoiding as much as possible the presence of moisture during synthesis and crystallization steps. However, preparation of TTF-DC2TF resulted very challenging, and in spite of considerable efforts, we only obtained an acetonitrile solvate, with different stoichiometry. Complex **6**, $(TTF)_3(DC2TF)_2.2CH_3CN$, was also characterized by X-ray diffraction (Fig. 7), revealing an arrangement essentially different from those observed in **1**-**5**. In the asymmetric unit, one TTF and one DC2TF molecules are in general positions, and their mean planes are separated by 3.690 Å. The asymmetric unit is completed by a half TTF, close to an inversion centre. This TTF is eclipsed with respect to the first one, and located further from the acceptor, at 3.920 Å (Fig. 7, inset). The central bond lengths of TTF components also reflect different oxidation states. The molecule placed on an inversion centre presents a short bond length of 1.330(9) Å, which fits for a neutral TTF molecule (1.345 Å),[35] while the TTF interacting with the acceptor has an exocyclic bond length of 1.369(6) Å. The lengthening accounts for oxidation of this TTF. Compound **6** is thus best described as an ionic crystal, $(\mathrm{TTF}^{+})_2(\mathrm{DC2TF}^{-})_2(\mathrm{TTF}).2\mathrm{CH}_3\mathrm{CN}$, and is not an actual CTC. This description is confirmed by IR spectroscopy. The cyano vibration of the acceptor in **6** is observed at $2185\ \mathrm{cm}^{-1}$, close to the vibration of pure ionic salts $\mathrm{Li}^{+}\mathrm{DC2TF}^{-}$ and $\mathrm{Na}^{+}\mathrm{DC2TF}^{-}$, at $2188\ \mathrm{cm}^{-1}$. As a consequence, compound **6** is expected to be an insulating material, with $\delta_6 \approx 1\ e^{-}$.

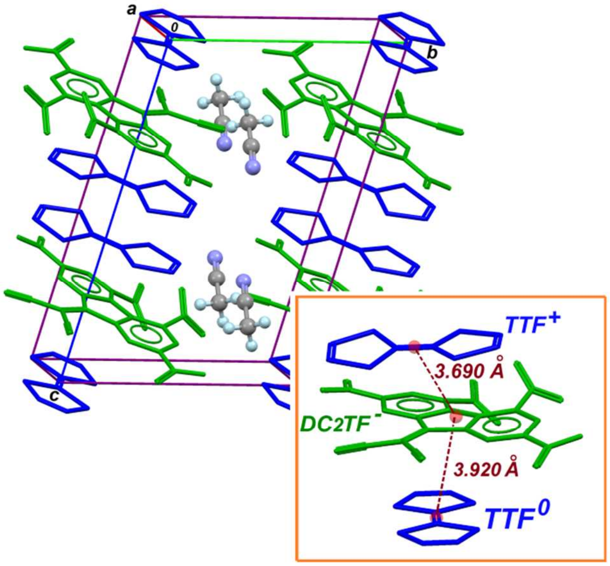


Fig. 7 Crystal structure of ionic compound **6**. The inset gives charge assignation in the symmetric unit.

Raman spectroscopy

Previous estimations for δ in complexes **1**-**6** were based on IR spectroscopy, but this characterization may be completed by Raman data. The most used charge sensitive vibration is the A_g symmetric stretching ν_3 mode for the central double bond in TTF, which we detected at $1513\ \mathrm{cm}^{-1}$.[36] The standard material used as reference for the ionic state of the donor is $\mathrm{TTF_2(FeCl_4)}$, for which the same stretching mode gives a Raman shift of $1416\ \mathrm{cm}^{-1}$.[37] As an example, Fig. 8 shows Raman spectra of complex **1**, (TTF-DDF).CH_3CN and its neutral components.

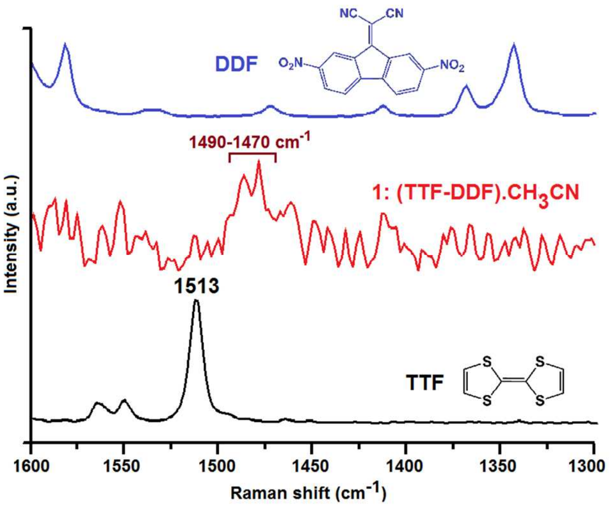


Fig. 8 Raman spectra for TTF, DDF and complex (TTF-DDF).CH_3CN

The spectrum of **1** is poorly resolved, as a consequence of an experimental issue common to all complexes reported here: raw crystals packed out in a glass capillary are damaged under laser irradiation, and this requires to measure Raman shifts with as low as possible laser power. The ν_3 vibration of TTF is nevertheless located in the range 1490-1470 cm^{-1}, corresponding to a charge transfer in the range $\delta_1 = 0.24 \cdots 0.46\ e^-$. Although this broad band is not very useful for an accurate estimation of the charge transfer, Raman data, based on the donor, are in agreement with IR data, based on the acceptor. Since Raman spectrum of **1** was measured on crystals few days after crystallization, some crystals should still be unaltered solvates with a formula close to (TTF-DDF).CH_3CN, while partial desolvation could affect other crystals. From IR spectroscopy, the degree of charge transfer would thus be between 0.29 and 0.37 e^- (Fig. 3, IR absorptions at 2224 and 2221 cm^{-1}, respectively), a range within that determined by Raman spectroscopy.

Conclusions

For non air-stable solvated complexes **1**-**4**, a similar behaviour has been established, regardless of the nature of lattice solvent. A gradual loss of solvent, occurring over few months, is correlated to a decrease of the degree of charge-transfer. Such a correlation is an evidence of the involvement of the solvent in the charge transfer. These solvates converge slowly towards unsolvated 1:1 complexes, which are close to the neutral state. Interestingly, preliminary results regarding the possibility of reversible solvation-desolvation of these *DA* crystals appear to be positive, at least for some solvents. In contrast, we obtained by chance a hydrate, **5**, which is an air-stable compound presenting a charge transfer, $\delta_5 = 0.48\ e^-$, on the boundary of CTC's exhibiting metallic conductivity.[1a] We assume that hydrogen bonding plays a role both in the stability and higher δ parameter for this compound. This is in line with other studies, pointing out that conducting properties of some organic complexes are closely related with interaction between *D* and *A* layers, involving hydrogen bonds.[38]

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Notes and references

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† Electronic Supplementary Information (ESI) available: IR spectra of acceptor molecules DDF, DTF, and DC2TF and their alkaline salts; IR spectra of complexes **1**-**6**; details of crystal structure refinements of complexes **1**-**6**. CCDC deposition numbers for structures **1**-**6**: 1055659-1055664. See DOI: 10.1039/b000000x/

1 (*a*) K. P. Goetz, D. Vermeulen, M. E. Payne, C. Kloc, L. E. McNeil and O. D. Jurchescu, *J. Mater. Chem. C*, 2014, **2**, 3065-3076. (*b*) F. Wudl, *Acc. Chem. Res*., 1984, **17**, 227-232.

2 (*a*) K. Bechgaard, K. Carneiro, F. B. Rasmussen, M. Olsen, G. Rindorf, C. S. Jacobsen, H. J. Pedersen and J. C. Scott, *J. Am. Chem. Soc*., 1981, **103**, 2440-2442; (*b*) J.-P. Pouget, *Crystals*, 2012, **2**, 466-520.

3 (*a*) R. C. Wheland and J. L. Gillson, *J. Am. Chem. Soc*., 1976, **98**, 3916-3925; (*b*) R. C. Wheland, *J. Am. Chem. Soc*., 1976, **98**, 3926-3930.

4 (*a*) M. Bendikov, F. Wudl, and D. F. Perepichka, *Chem. Rev*., 2004, **104**, 4891-4945; (*b*) J.-i. Yamada, H. Akutsu, H. Nishikawa and K. Kikuchi, *Chem. Rev*., 2004, **104**, 5057-5083.

5 (*a*) T. Fujinawa, H. Goto and T. Inabe, *Synth. Met*., 1997, **86**, 1865-1866; (*b*) T. Fujinawa, H. Goto, T. Naito, T. Inabe, T. Akutagawa and T. Nakamura, *Bull. Chem. Soc. Japan*, 1999, **72**, 21-26.

6 (*a*) H. Tanaka, Y. Okano, H. Kobayashi, W. Suzuki and A. Kobayashi, *Science*, 2001, **291**, 285-287; (*b*) A. Kobayashi, E. Fujiwara and H. Kobayashi, *Chem. Rev*., 2004, **104**, 5243-5264.

7 J.-P. Legros and L. Valade, *Solid State Commun*., 1988, **68**, 599-604.

8 J. S. Chappell, A. N. Bloch, W. A. Bryden, M. Maxfield, T. O. Poehler and D. O. Cowan, *J. Am. Chem. Soc*., 1981, **103**, 2442-2443.

9 A. Salmerón-Valverde, S. Bernès and J. G. Robles-Martínez, *Acta Cryst. B*, 2003, **59**, 505-511.

10 A. Salmerón-Valverde and S. Bernès, *Crystals*, 2015, **5**, 283-293.

11 A. Salmerón-Valverde and S. Bernès, *C. R. Chimie*, 2005, **8**, 1017-1023 (in French).

12 A. Salmerón-Valverde, Ph.D. Thesis, Universidad Autónoma de Puebla, 2008.

13 (*a*) M. Ohmasa, M. Kinoshita and H. Akamatu, *Bull. Chem. Soc. Japan*, 1971, **44**, 391-395; (*b*) M. Ohmasa, M. Kinoshita and H. Akamatu, *Bull. Chem. Soc. Japan*, 1971, **44**, 395-400; (*c*). N. Takahashi, K. Yakushi, K. Ishii and H. Kuroda, *Bull. Chem. Soc.*

Japan, 1976, **49**, 182-187; (*d*) T. Kemény, Z. Pokó, G. Mihály, K. Holczer and G. Grüner, *Mol. Cryst. Liq. Cryst*., 1978, **48**, 201-207.
14 L. A. Chetkina and V. K. Belsky, *Crystal. Rep*., 2013, **58**, 26-48.
15 (*a*) I. F. Perepichka, L. G. Kuz'mina, D. F. Perepichka, M. R. Bryce, L. M. Goldenberg, A. F. Popov and J. A. K. Howard, *J. Org. Chem*. 1998, **63**, 6484-6493; (*b*) I. F. Perepichka, A. F. Popov, T. V. Orekhova, M. R. Bryce, A. M. Andrievskii, A. S. Batsanov, J. A. K. Howard and N. I. Sokolov, *J. Org. Chem*., 2000, **65**, 3053-3063.
16 A. S. Batsanov, M. R. Bryce, A. Chesney, J. A. K. Howard, D. E. John, A. J. Moore, C. L. Wood, H. Gershtenman, J. Y. Becker, V. Y. Khodorkovsky, A. Ellern, J. Bernstein, I. F. Perepichka, V. Rotello, M. Gray and A. O. Cuello, *J. Mater. Chem*., 2001, **11**, 2181-2191.
17 (*a*) F. Diederich, D. Philp and P. Seiler, *J. Chem. Soc. Chem. Commun*., 1994, 205-208; (*b*) D. Philp, V. Gramlich, P. Seiler and F. Diederich, *J. Chem. Soc. Perkin Trans. II*, 1995, 875-886.
18 A. V. Bulatov, R. M. Lobkovskaya, M. L. Khidekel', A. N. Chekhlov and R. P Shibaeva, *Izv. Akad. Nauk SSSR, Ser. Khim*., 1980, 1203 (in Russian): *Chem. Abstr*., 1980, **93**, 186032k.
19 T. Sulzberg and R. J. Cotter, *J. Org. Chem*., 1970, **35**, 2762-2768.
20 T. K. Mukherjee, *J. Phys. Chem*., 1966, **70**, 3848-3852.
21 T. K. Mukherjee and L. A. Levasseur, *J. Org. Chem*., 1965, **30**, 644-646.
22 J. Fait, XSCAnS, version 2.31, Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, 1996.
23 A. C. T. North, D. C. Phillips and F. S. Mathews, *Acta Cryst. A*, 1968, **24**, 351-359.
24 G. M. Sheldrick, *Acta Cryst. C*, 2015, **71**, 3-8.
25 (*a*) J. Silverman, A. P. Krukonis and N. F.Yannoni, *Acta Cryst. B*, 1968, **24**, 1481-1488; (*b*) A. Salmeron and S. Bernes, 2009, Private communication to the CCDC (715820; Refcode: CMDNFL01).
26 Throughout this report, mean planes and centroids for *D* and *A* molecules are calculated using all 10 non-H atoms of *D* (TTF) and 13 C atoms of the fluorene core of *A*.
27 (*a*) G. Saito, H. Ikegami, Y. Yoshida, O. O. Drozdova, K. Nishimura, S. Horiuchi, H. Yamochi, A. Otsuka, T. Hiramatsu, M. Maesato, T. Nakamura, T. Akutagawa and T.Yumoto, *Bull. Chem. Soc. Jpn*., 2010, **83**, 1462-1480; (*b*) T. Murata, Y. Morita, Y. Yakiyama, K. Fukui, H. Yamochi, G. Saito and K. Nakasuji, *J. Am. Chem. Soc*., 2007, **129**, 10837-10846.
28 (*a*) J. Lieffrig, O. Jeannin, K.-S. Shin, P. Auban-Senzier and M. Fourmigué, *Crystals*, 2012, **2**, 327-337; (*b*) S. C. Lee, A. Ueda, A. Nakao, R. Kumai, H. Nakao, Y. Murakami and H. Mori, *Chem.-Eur. J*., 2014, **20**, 1909-1917.
29 Spectral Database for Organic Compounds, SDBS N° 1218. IR vibration of the cyano group of acetonitrile is reported at 2254 cm^{-1}.
30 J. Silverman, A. P. Krukonis and N. F. Yannoni, *Acta Cryst*., 1967, **23**, 1057-1063.
31 A. J. Moore, M. R. Bryce, A. S. Batsanov, J. N. Heaton, C. W. Lehmann, J. A. K. Howard, N. Robertson, A. E. Underhill and I. F. Perepichka, *J. Mater. Chem*., 1998, **8**, 1541-1550.
32 M. M. Olmstead, A. de Bettencourt-Dias, H. M. Lee, D. Pham and A. L. Balch, *Dalton Trans*., 2003, 3227-3232.
33 DTF is reported in the Spectral Database for Organic Compounds, (SDBS N° 5835). The cyano vibration is reported at 2231 cm^{-1}, and we measured the same frequency on our samples.
34 Spectral Database for Organic Compounds, SDBS N° 319. IR vibration of the carbonyl group of acetone is reported at 1715 cm^{-1}.
35 (*a*) A. S. Batsanov, *Acta Cryst C*, 2006, **62**, o501-o504. (*b*) A. Ellern, J. Bernstein, J. Y. Becker, Sh. Zamir, L. Shahal and S. Cohen, *Chem. Mater*., 1994, **6**, 1378-1385.
36 (*a*) J. E. Eldridge, H. H. Wang, A. M. Kini and J. A. Schlueter, *Spectrochim. Acta A Mol. Biomol. Spectrosc*., 2002, **58**, 2237-2243. (*b*) R. Bozio, A. Girlando and D. Pecile, *Chem. Phys. Lett*., 1977, **52**, 503-508.
37 R. P. Van Duyne, T. W. Cape, M. R. Suchanski and A. R. Siedle, *J. Phys. Chem*., 1986, **90**, 739-743.
38 (*a*) M. Fourmigué and P. Batail, *Chem. Rev*., 2004, **104**, 5379-5418. (*b*) Y. Morita, T. Murata and K. Nakasuji, *Bull. Chem. Soc. Jpn*., 2013, **86**, 183-197.

A series of solvated donor-acceptor organic complexes was shown to slowly release lattice solvent, while the degree of charge transfer decreases steadily. This behavior is not observed in the case of a hydrate.