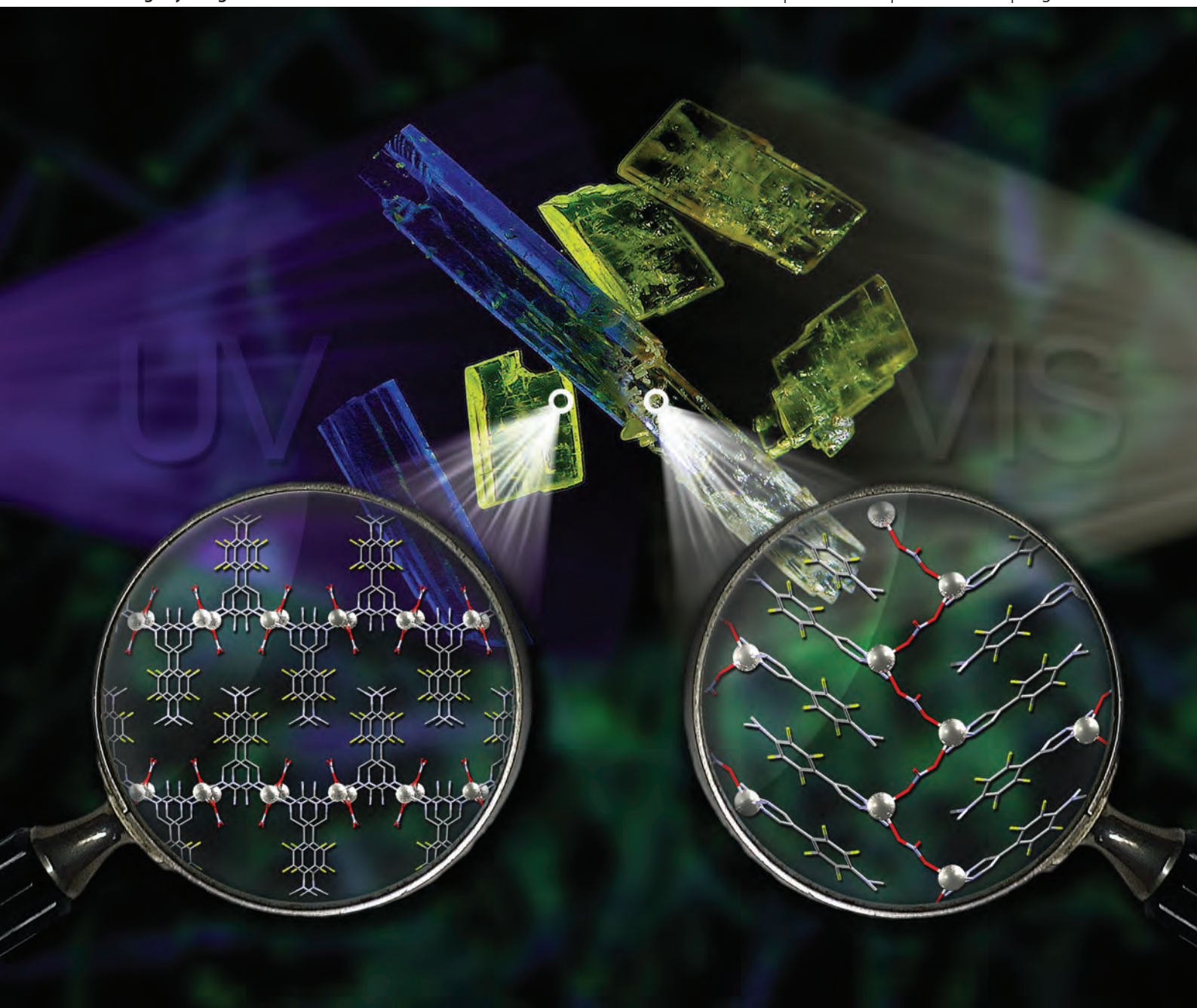


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PAPER

Structural variety of 5-fluoroarene-2-aminopyrimidine in comparison to 2-aminopyrimidine silver(I) coordination polymers: progress report and overview†

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A variety of fluoroarene-2-aminopyrimidine (FAP) silver(I) coordination polymers (CPs) has been synthesized based on newly synthesized FAP derivatives, namely 5-(*p*-methoxytetrafluorophenyl)-2-aminopyrimidine (OFAP) and 5-(*p*-dimethylaminotetrafluorophenyl)-2-aminopyrimidine (NFAP), and different counterions (OTf[−], TFA[−], ClO₄[−], NO₃[−]). Their solid-state assembly as well as optical properties in terms of luminescence and infrared (IR) spectroscopy were investigated. Out of the several structures described herein, we obtained isomorphous CPs to previous studies (**5**, **9**), a CP architecture with a short Ag–Ag distance (**8**, 3.049 Å), but also polymorphic crystals of [Ag(nfap)NO₃]_{*n*} (**11a**, **11b**) and the latter showed differences in color and luminescence emission. Polymorphism gives an unparalleled possibility to investigate the origin of such phenomena since luminescence emission is quite often observed for these silver-hybrid solid-state materials and in several cases Ag⋯Ag interactions are attributed for this phenomenon. We show that this explanation does not necessarily have to be the only one. Therefore we focus also on structural relationships and differences in a comprehensive comparison of our own and other known systems to start a more systematic description of the rich coordination capabilities of FAP and congeneric 2-aminopyrimidine (2-AP) based silver(I) coordination polymers and networks. Density functional theory (DFT) calculations with periodic boundary conditions based on a plane wave basis are used to better understand the electronic structure of these crystalline materials. To complete the picture, steady-state spectroscopy studies (UV-Vis, fluorescence, IR) on all ligands and 2-AP itself were conducted as well as re-examination of the first reported CP of 2-AP and Ag^I under the above aspects.

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Introduction

2-Aminopyrimidine (2-AP)‡ has long been known to possess the ability to form discrete molecular architectures through

self assembly by hydrogen bonding or by co-crystallization,^{1–3} especially with the aid of dicarboxylic acids for enhanced hydrogen bonding motifs or by aid of aromatic compounds for $\pi\cdots\pi$ -stacking. The latter crystal design strategy was used to build extended frameworks^{4,5} and supramolecular structures, e.g. capsules with resorcin[4]arenes.⁶

More than 40 years ago, Weiss *et al.* noticed that 2-AP and transition metal ions can form coordination complexes.⁷ Large coordination compounds with often complex structures can be built combining metal ion coordination and the above mentioned crystal design principles. In particular, both metal coordination of AP (and perturbation by anions) and strong hydrogen bonding of AP to itself and/or carboxylic acids influence the overall architecture as reported by Navarro and Lippert and others.⁸ As there are numerous references on AP metal ion coordination compounds, for obvious reasons, we focus on silver-based coordination compounds herein. The general theme of coordination polymers (CPs) of Ag^I and heterocyclic N-donor ligands was reviewed by Khlobystov *et al.* in 2001.⁹

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† Electronic supplementary information (ESI) available: Details to materials and methods, synthesis of ligands **1–3** including NMR comparison, packing diagrams of the CPs **4–11**, optical, fluorescence and powder diffraction data of the ligands, infrared spectroscopic data of all compounds, calculated atom coordinates of **1–3**, and histograms of data from Table 4 as well as photographs of **11**. CCDC 880745–880754. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2ce26388b

‡ This abbreviation is also used for aminopyridines. However, it is also common for aminopyrimidines to be abbreviated to “apym”.

To the best of our knowledge, Smith *et al.* did the first systematic studies on carboxylic acids and nitrogen heterocycles as ligands for Cu^{II} and Ag^I to form various coordination compounds over 20 years ago.¹⁰ The group also reported a CP structure motif of AP with Ag^I and *p*-toluenesulfonate ([Ag(ap)(pts)]_n) in 1998 which would eventually fall under the huge category of metal organic frameworks (MOFs) nowadays.^{10a,11} CPs and MOFs based on 2-AP and Ag^I salts have recently received attention due to easily accessible organic building blocks and the variety of crystal structures that are obtained using different stoichiometries, solvents and Ag^I counterions.^{16,14a,15q} To illustrate, one-dimensional polymeric chain structures and also 2-D molecular sheets and 3-D supramolecular frameworks were found by Su *et al.*,¹² Zhu *et al.*,¹³ Chen *et al.*,¹⁴ as well as Huang *et al.* who investigated numerous 2-AP systems and related ligands (*e.g.* guanamines, triazines) recently.¹⁵ The strong impact of counterions has also been reported for other silver(I) coordination compounds.^{17,15a}

Another important tool to tune the morphology in these coordination polymers is the introduction of additional functional groups to the AP ring. For example, Chen *et al.* substituted hydrogen for an iodine atom in the 5-position to induce additional Ag⁺⋯I and I⋯I interactions.^{14b}

Our research started with the observation of arene–arene and arene–perfluoroarene interactions of 5-arene-functionalized 2-AP in hexafluorobenzene co-crystals or by employing Ag^I salts for additional coordination possibilities.⁵ However, the overall crystal architecture was built by discrete dimeric Ag^I coordination compounds similar to the prototype AP–Ag^I dimer published by Zhu,¹⁸ while the dimer-to-dimer interaction was still controlled by the hydrogen bonding of 2-AP.

Switching to fluorinated arene residues, with hope to extend and utilize the observed arene–fluoroarene to fluoroarene–fluoroarene interactions, was the key to success.¹⁹

This provided us with access to a great variety of Ag^I hybrid-organic polymer coordination architectures with interesting properties.¹⁶ Huang *et al.* published simultaneously to our report a “series of Ag^I coordination complexes derived from aminopyrimidyl ligands and dicarboxylates”, continuing what Smith *et al.* had started.¹⁰ Recently solid-state luminescence has been reported for these and related systems. However, the description is most often phenomenological.^{15,16,20}

The investigation and focusing on luminescence of MOFs is a relatively young field. This property of a MOF can be caused by altered linker properties within the framework environment (*e.g.* increased rigidity decreases the non-radiative decay rate) while sensitizer pathways are often observed for lanthanide ions (“antenna effect”), and – the most prominent example – charge transfer phenomena (*e.g.* LMCT, MLCT, MMCT) are also possible origins of luminescence emission.²¹ For Ag^I-related systems Allendorf states that “excitation by charge transfer from the metal centers to the linker is commonly observed”, which might be modified by Ag⁺⋯Ag-interactions.²¹ The contribution of d¹⁰M⋯d¹⁰M-states and/or metal-centered (MC) transitions was reviewed on polynuclear Ag^I-clusters amongst others over ten years ago,^{22–24} including the most

striking example by Zink *et al.* that argentophilic interactions lead to luminescence.²⁵ This was also found for several other dinuclear complexes as well as unusual ligand susceptible luminescence for tetranuclear complexes in the past.^{26,27}

The scope of this work is to provide a systematic description of fluoroarene-2-aminopyrimidine and congeneric 2-AP silver(I) CP systems and to summarize the current approach to rationalize the presence of luminescence in *catena*-compounds.

The work is structured as follows: In the first sections we focus on the FAP ligands 1–3 and the parent molecule 2-AP. We describe briefly the structure of ligand 3 in the solid state and compare to DFT calculated data. Finally, we point out interesting dual emission observations of the FAP ligands and of the parent 2-AP in solid state, which are of importance for the CP-field.

In the middle sections of this report we turn to the X-ray structure description of our CP series based on Ag^I, fluoroarene-2-aminopyrimidines ligands, and different counterions (OTf[−], TFA[−], ClO₄[−], NO₃[−]). The structural motifs found in the series are compared to earlier findings¹⁶ and selected examples of 2-AP-based systems. The influence of different counterions is discussed (see for example Chen *et al.*).^{14a} DFT calculations are used to illustrate the electronic structure of these materials (*i.e.* band structures, density of states (DoS)).

In the last section, we summarize the current state of luminescence for MOF-like silver-based coordination compounds and incorporate our findings.

Experimental

Synthesis of the ligands FAP, OFAP, and NFAP, commercial sources for chemicals and solvents as well as manufacturer and model of used instruments are given in the ESI.†

Details of crystallization

X-ray suitable crystals of the NFAP ligand could be grown from a filtered concentrated trifluoroethanol solution (approx. 6 mg mL^{−1}) by slow evaporation over days in a round-bottom flask. Unfortunately this method was not transferable to the FAP and OFAP ligands, which gave only very fine needles not suitable for X-ray crystal structure elucidation.

Crystals of macroscopic size of the coordinations polymers formed by slow evaporation (days) at room temperature in the dark. If, during the first hours, some amorphous cloudy precipitate was formed the solution was filtered. This diminishes the preparative yield but better crystals were obtained by this procedure. However, it was noticed that the crystals also grew slowly from the precipitate (this was also described by Smith for [Ag(ap)(pts)]_n).^{10a}

For the formation of polymorph **11b** it was noticed that charging both components in one round-bottom flask first and addition of solvent and sonication afterwards seemed necessary. Sometimes conversion of the yellow form **11b** to the colorless form **11a** was noticed while other samples remained

stable (even at diffuse ambient light). To this point the factors for inducing/preventing the conversation are unclear.

Safety remark: **Caution!** Heavy metal perchlorate salts (and to a lesser extent nitrates) in the presence of organic ligands are potentially explosive and heating has to be avoided (several CPs have decomposition points with gas release). Only small amounts should be prepared.

Melting points of compounds **4–11** are summarized in Table 5. IR data of all compounds can be found in the ESI†

[Ag(ap)SO₃C₆H₄CH₃]_n. Prepared as described by Smith *et al.*^{10a} 303–306 °C (dec.). Elem. anal. found: C 35.27, H 3.10, N 11.10, S 8.58%; C₁₁H₁₂AgN₃O₃S requires C 35.31, H 3.23, N 11.23, S 8.57%.

[Ag(fap)CO₂CF₃]_n (4). A round-bottom flask was charged with AgCO₂CF₃ (40 mg, 0.18 mmol) and 10 mL of warm EtOH and the material was dissolved by aid of ultrasound sonication to form a homogenous solution. A solution of ligand **2** (34 mg, 0.12 mmol) in 15 mL hot EtOH was added at once and the mixture was cooled and filtered. The filtrate was allowed to evaporate slowly in darkness for several days. The obtained colorless crystals (16 mg, 0.032 mmol) were isolated by suction filtration and dried in air. Yield: 27% (based on ligand). Elem. anal. found: C 31.54, H 1.42, N 8.49%; C₁₃H₇AgF₇N₃O₃ requires C 31.60, H 1.43, N 8.50%.

[Ag(fap)SO₃CF₃·EtOH]_n (5). As described above but using AgSO₃CF₃ (95 mg, 0.37 mmol) in 20 mL EtOH and **2** (90 mg, 0.33 mmol) in 40 mL EtOH to yield colorless crystals (11%, 28 mg, 0.038 mmol). Elem. anal. found: C 29.39, H 2.20, N 7.27%; C₁₄H₁₃AgF₇N₃O₅ requires C 29.18, H 2.27, N 7.29%.

[Ag(fap)ClO₄]_n (6). Similar to above but using AgClO₄ (45 mg, 0.21 mmol) in 10 mL EtOH and **2** (52 mg, 0.19 mmol) in 25 mL EtOH to yield colorless crystals (35%, 32 mg, 0.066 mmol). Elem. anal. found: C 27.63, H 1.47, N 8.59%; C₁₁H₇AgClF₄N₃O₅ requires C 27.50, H 1.47, N 8.74%.

[Ag(fap)NO₃]_n (7). Obtained from AgNO₃ (30 mg, 0.17 mmol) in 15 mL EtOH and **2** (40 mg, 0.14 mmol) in 20 mL EtOH to yield colorless crystals (30%, 18 mg, 0.042 mmol). Elem. anal. found: C 29.92, H 1.54, N 12.41%; C₁₁H₇AgF₄N₄O₄ requires C 29.82, H 1.59, N 12.65%.

[Ag(nfap)CO₂CF₃]_n (8). From AgCO₂CF₃ (180 mg, 0.814 mmol) in 50 mL EtOH and **3** (90 mg, 0.314 mmol) in 40 mL EtOH to yield colorless crystals (60%, 97 mg, 0.191 mmol). Elem. anal. found: C 33.25, H 2.04, N 10.94%; C₁₄H₁₀AgF₇N₄O₂ requires C 33.16, H 1.99, N 11.05%.

[Ag(nfap)SO₃CF₃·EtOH]_n (9). From AgSO₃CF₃ (170 mg, 0.663 mmol) in 40 mL EtOH and **3** (100 mg, 0.349 mmol) in 40 mL EtOH to yield colorless crystals (70%, 144 mg, 0.244 mmol). Elem. anal. found: C 30.73, H 2.77, N 9.77%; C₁₅H₁₆AgF₇N₄O₄ requires C 30.58, H 2.74, N 9.51%.

[Ag(nfap)ClO₄]_n (10). From AgClO₄ (35 mg, 0.16 mmol) in 10 mL EtOH and **3** (46 mg, 0.16 mmol) in 20 mL EtOH to yield colorless crystals (62%, 53 mg, 0.10 mmol). Elem. anal. found: C 29.29, H 2.08, N 11.19%; C₁₂H₁₀AgClF₄N₄O₄ requires C 29.20, H 2.04, N 11.35%.

[Ag(nfap)NO₃]_n (11a). From AgNO₃ (161 mg, 0.947 mmol) in 60 mL EtOH and **3** (253 mg, 0.883 mmol) in 80 mL EtOH to yield colorless crystals (48%, 197 mg, 0.431 mmol). Elem. anal.

found: C 31.61, H 2.17, N 15.40%; C₁₂H₁₀AgF₄N₅O₃ requires C 31.60, H 2.21, N 15.35%.

[Ag(nfap)NO₃]_n (11b). Best results for formation of **11b** were obtained from mixing AgNO₃ (170 mg, 1.00 mmol) and **3** (250 mg, 0.873 mmol) under prolonged ultrasound sonication in 90 mL hot EtOH without filtration afterwards to yield yellow crystals (18%, 74 mg, 0.162 mmol). Elem. anal. found: C 31.69, H 2.25, N 15.08%; C₁₂H₁₀AgF₄N₅O₃ requires C 31.60, H 2.21, N 15.35%. The crystals are easily recognizable by the green fluorescence under a handheld 366 nm UV lamp (see ESI†).

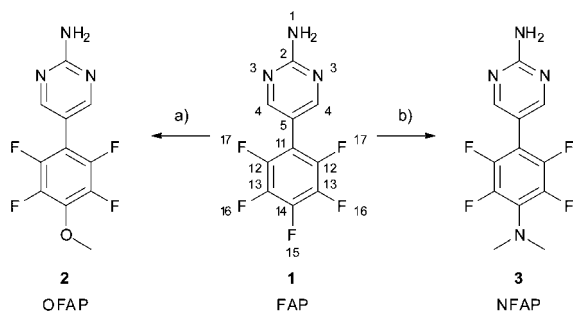
X-ray crystallography

Single crystal X-ray analyses were carried out with a Nonius Kappa CCD diffractometer by using Mo K α radiation (λ = 0.71073 Å). Temperature was usually set to 100 K but exceptions are given in Table 3 (e.g. polymorph **11b** (220 K), which shattered on further cooling). All non-hydrogen atoms were refined anisotropically on F^2 by the full-matrix least-squares technique using the SHELXL-97 crystallographic software package.²⁸ All hydrogen atoms were refined at calculated positions using a riding model. Basic crystal parameters and structure refinement data are summarized in Table 3.

X-ray powder diffraction (XRPD) measurements were performed on a Philips PW 1050/37 diffractometer using Cu K α radiation ($\lambda_{\text{CuK}\alpha} = 1.5418$ Å). A diffraction angle range between 5° and 60° was chosen using a 2 s per 0.05° step scan mode for routine measurements and a 45 s per 0.05° step for overnight measurements. Samples were either used as they were, if suitably microcrystalline, ground in an agate mortar, or sublimed as a film on standard glass substrates. The exported XRPD patterns were plotted using Origin Pro 8.5. Simulation of XRPD was done with the built-in feature of CCDC Mercury (v 2.4 Build RC5).

DFT calculations

Calculations for crystalline materials were performed using periodic boundary conditions as implemented in the plane-wave based Vienna *ab-initio* Simulation Package (VASP)²⁹ of density-functional theory (DFT). Thereby the electron exchange and correlation is treated using the generalized gradient approximation (GGA), specifically the PW91 functional.³⁰ The electron-ion interaction is described by the projector augmented-wave (PAW)^{31,32} method and we expand the valence wave functions into plane waves up to an energy cutoff of 400 eV. While calculations for single ligands are performed by fully relaxing the structural degrees of freedom, the calculations of the crystalline structures were performed on the basis of the experimental X-ray coordinates. Calculations for single gas-phase molecules were performed using Gaussian 09® with a B3LYP hybrid functional and a 6-31+G(d) basis set. All frequencies in harmonic approximation for the calculated minimum energy geometries were positive and atomic coordinates are given in the ESI.†³³



Scheme 1 Synthesis of the ligands OFAP (2) and NFAP (3), respectively, from 5-pentafluorophenyl-2-aminopyrimidine (FAP) 1. (a) NaOCH₃, CH₃OH, reflux; (b) HN(CH₃)₂, H₂O–DMSO 3 : 1, 120 °C. Numbering scheme is not according to IUPAC recommendations but adopted for symmetry reasons and is used in Table 1.

Results and discussion

Synthesis of ligands

The 5-pentafluorophenyl-2-aminopyrimidine (FAP) 1 was prepared according to the procedure published in our previous work.¹⁶ By a nucleophilic substitution the derivatives 2 and 3 are easily accessible in good yields (Scheme 1). This general procedure permits the access to further 2-aminopyrimidines with different sterical requirements and electron densities on the fluorinated arene. After work up the compounds 1–3 precipitate in a microcrystalline state from solution. Recrystallization or sublimation can be used to achieve further purification. The sublimation technique gave us the possibility to record optical spectra of better quality and compare sublimed thin films and bulk materials as XRPD spectra. Additionally, crystals suitable for X-ray single crystal analysis could be grown for the NFAP ligand, which is discussed below.

Description of the crystal structure of ligand 3

The X-ray diffraction patterns (XRPD) of the compounds 1–3 as powder and sublimed films are given in the ESI† (Fig. S29–S31). All compounds sublime unchanged (by NMR, UV, IR). As expected, sublimed samples show preferred growth/orientation effects as some reflections are entirely missing or have a relatively low intensity in comparison. Conclusively, the relative UV absorbance intensities in the solid-state spectra are not representative. However, with the preparation method used before, namely sweeping microcrystalline crystals on a optical quartz plate to obtain a thin layer of low optical density, gave similar spectra. Of course the issue of anisotropic measurement still persists, as has been long known for XRPD sample preparation.

It was observed that powder samples of the NFAP ligand (3), regardless of the synthetic batch, show more reflections than the predicted spectrum based on single crystal X-ray diffraction (Fig. 1, bottom). This indicates that a second polymorph exists. Furthermore, the XRPD pattern of sublimed NFAP (3) exhibits no sharp peaks and a high amorphous background, which indicates a rather small crystallite size and/or low apparent order. In contrast, no change in XRPD patterns is observed for compounds 1 and 2 upon sublimation. We

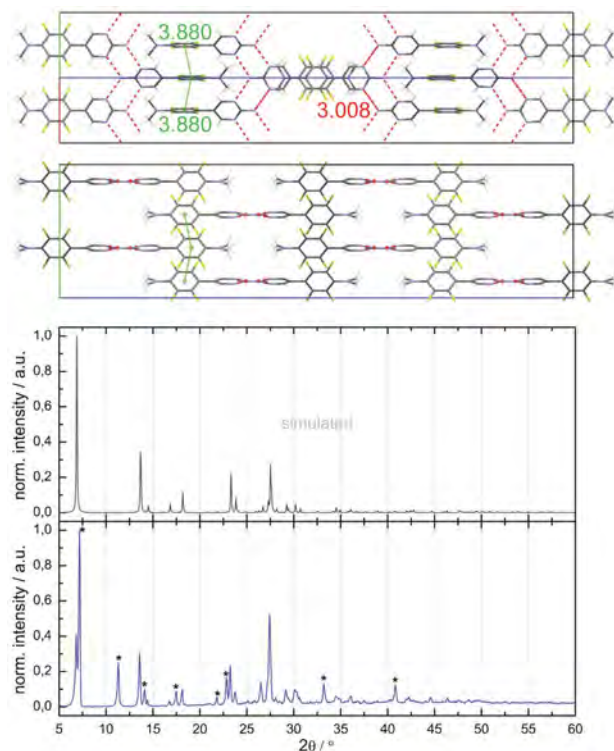


Fig. 1 Crystal packing of 3. Projection along *b*-axis + 29.3° (top, view on *hkl* 110 plane) and along *a*-axis (below) to emphasize the head-to-tail layering, fluoroarene–fluoroarene interactions (bright green) and hydrogen bonding (red, *d*(D⋯A)). Measured and simulated XRPD pattern of 3 are shown below. Unindexed peaks are labeled with an asterisk.

conclude that we were only successful in crystallization of 3 for X-ray structure elucidation in one polymorphic form.

The obtained crystals show that NFAP crystallizes in the orthorhombic centrosymmetric *Fddd* space group and crystallographic data is summarized in Table 3. It was noted that the habit as column reflects the cell parameters well, while usually fine needles are observed for FAP and OFAP or unsuccessful growth attempts on NFAP. The crystal packing consists of layers of dimeric NFAP molecules whereby the amino-groups of AP (referred to as the head) are pointing towards each other. The fluoroarene moiety (in general this is referred to as the tail) shows clear fluoroarene–fluoroarene stacking (π_F – π_F , Fig. 1) towards the upper and lower layer. The plane-to-plane distance between fluoroarene units was measured to be 3.501 Å while the centroid–centroid distance is 3.880 Å (25.5° relative displacement). This can be described as the typical parallel-displaced π – π -stacking of (fluoro)arenes.¹⁹

A second driving force for crystal formation is the well-known hydrogen bonding ability of AP mentioned in the introduction.² The usual hydrogen bonding pattern of AP can be described as a double $R_2^2(8)$ in graph set notation.³⁴ This $R_2^2(8)$ set is also observed here by the head-to-head positioned NFAP molecules between the layers. The donor to acceptor distance *d*(D⋯A) is 3.008(6) Å (Fig. 1). This value matches well with the observed values for our 5-phenyl-2-aminopyrimidine (HAP) and related naphthyl-systems (*d*(D⋯A) 2.952(2) to

Table 1 Bond lengths (in Å) and angles (°) calculated for FAP, OFAP, and NFAP on different levels of theory (DFT-PW91-GGA and DFT-B3LYP 6-31+G(d)). The atomic labels refer to Fig. 1. The comparison to X-ray data of NFAP, HAP^a, and AP (ref. 1) is shown together with calculated data (MP2 cc-pVTZ) for AP from ref. 35

Labels	FAP		OFAP		NFAP			HAP ^a Average X-ray	AP	
	PW91	B3LYP	PW91	B3LYP	PW91	B3LYP	X-ray		MP2	X-ray
<i>d</i> (1–2)	1.355	1.356	1.356	1.361	1.360	1.363	1.338(4)	1.349(8) ± 0.003(4)	1.369	1.342(2)
<i>d</i> (2–3)	1.352	1.350	1.352	1.349	1.351	1.349	1.349(2)	1.353(3) ± 0.002(9)	1.343	1.349(2)
<i>d</i> (3–4)	1.329	1.329	1.330	1.330	1.330	1.330	1.328(2)	1.327(8) ± 0.002(6)	1.334	1.331(2)
<i>d</i> (4–5)	1.406	1.405	1.405	1.405	1.405	1.405	1.385(2)	1.391(4) ± 0.008(9)	1.389	1.374(2)
<i>d</i> (5–11)	1.474	1.479	1.473	1.479	1.472	1.478	1.482(4)	1.477(3) ± 0.000(3)	—	—
<i>d</i> (11–12)	1.405	1.403	1.402	1.401	1.402	1.400	1.388(2)	1.394(4) ± 0.003(2)	—	—
<i>d</i> (12–17)	1.354	1.347	1.356	1.350	1.357	1.352	1.346(2)	—	—	—
<i>d</i> (14–15)	1.344	1.338	1.355	1.352	1.389	1.397	1.379(4)	—	—	—
∠(1,2,3)	116.91 ± 0.11	117.01	116.87 ± 0.03	117.00	116.87 ± 0.16	117.00	117.60(12)	117.8(7) ± 0.3(4)	n.a.	117.3(6)
∠(2,3,4)	116.02 ± 0.02	116.20	115.95 ± 0.06	116.21	115.97 ± 0.01	116.22	116.29(17)	116.2(2) ± 0.1(0)	n.a.	115.9(6)
∠(4,5,11)	122.53 ± 0.14	122.55	122.51 ± 0.68	122.61	122.55 ± 0.38	122.66	122.76(12)	123.1(7) ± 0.1(4) ^b	—	—
∠(5,11,12)	122.18 ± 0.09	122.11	122.46 ± 0.22	122.47	122.74 ± 0.03	122.79	122.77(12)	121.1(2) ± 0.4(9) ^b	—	—
∠(11,12,13)	122.80 ± 0.01	122.69	122.91 ± 0.05	122.92	123.01 ± 0.11	123.00	122.87(19)	121.0(7) ± 0.5(4) ^b	—	—
φ(F-Aryl-AP)	44.4	47.2	46.5	46.7	46.5	45.6	41.0(7)	31.1(7) & 41.0(5)	—	—

^a HAP = hydrogen atom derivative of FAP, namely 5-phenyl-2-aminopyrimidine.⁵ First value is HAP alone, second value is from data with hexafluorobenzene as co-crystal. ^b Note that larger deviation in angles are to be expected in the non-fluorinated ring.

3.074(2) Å, avg. 3.018 Å).⁵ Interestingly the AP ring and the *para*-dimethylamino group on the fluoroarene moiety are almost perfectly in plane in the crystal (dihedral angle 1.00°), which can be compared to the coordination compounds later, but might be interpreted as packing effect rather than electronic conjugation in comparison to what molecular modeling predicts (see next section).

Ligand structure calculations

For all ligands we calculated the structure in the gas phase on different levels of theory (Table 1) to compare and cross-check the values to the X-ray data of the NFAP ligand, to HAP ligand data of our previous work and furthermore to data of the parent 2-AP (MP2 calculation and X-ray).^{5,35} The purpose was to gain insight in the preferred dihedral angle between the dimethylamino group and the AP moiety as mentioned above (calculated to 89.0°, exp. 1.00°) and moreover the dihedral twist angle ϕ between the two arene rings (if applicable calculated to 45.6°) as it was noticed that these varied in the coordination compounds (Table 4). A plot of relative energy vs. dihedral twist angle is given in the ESI†

In general the calculations approximate the structural parameters of the ligands quite well. Next to the presumably environment sensitive N1 to C2 distance the bond length of aminopyrimidine C4 to C5 is systematical overrated by about 0.020 Å for both density functionals. This effect is also visible to a similar extent in the 2-AP comparison on a higher level of theory (Table 1). In terms of the fluoroarene part the bond lengths of C11 to C12 are slightly overrated. For NFAP the distance of the *para*-C on the fluoroarene (C14) to the dimethylamino group (N15) seems also to be overrated in both calculations (1.389 Å and 1.397 Å vs. 1.379 Å from X-ray). In contrast this bond length is underrated in calculations for OFAP (2) where an oxygen atom is introduced at position 15. For a methoxy substituent a distance of 1.370 ± 0.006 Å rather than 1.353 ± 0.002 Å is to be expected by comparison with X-ray data of perfluorarylalkylethers.³⁶ However, the overall

trend (F < OMe < NMe₂) is correctly estimated by the calculations as bond elongation is to be expected by substitution with an electron donating group.³⁷ The angles are also in very good agreement with a minor exception for the angle of the 2-amino group relative to the pyrimidine ring (atom label 1–2–3) which is always underestimated by 0.60°. All other values agree within 0.006 Å and 0.13°.

Spectroscopic properties of the ligands 1–3

UV-Vis data. In our previous work we have already shown that the optical properties of **1** in solution is only slightly affected by the solvent polarity.¹⁶ Therefore we limit our measurements in solution to ethanol as a common spectroscopic solvent. Especially the solution absorption spectra of FAP (**1**) and OFAP (**2**) are very similar. They both display an intense maximum at short wavelength (263 nm and 264 nm, respectively) and a weak absorption shoulder at longer wavelength (approx. 296 nm) with similar molar absorption coefficients (Table 2) but about twice as much as reported for 2-AP in alcoholic solvents.³⁸ By comparison with hexafluorobenzene (λ = 260 nm, ESI†) and 2-AP (λ = 296 nm, ESI†) the short wavelength absorption is ascribed to the perfluorinated arene and the long wavelength absorption to the aminopyrimidine moiety.^{38–43} It is noteworthy here that in the case of 2-AP the assignment of the 296 nm transition varies from $n \rightarrow \pi^*$,^{38,41,42} to $n \rightarrow \pi^*$ with a $\pi \rightarrow \pi^*$ transition underneath (¹L_b in Platt notation),^{40,44} or even to be pure $\pi \rightarrow \pi^*$ in nature.³⁹

The solution absorption spectra of NFAP (**3**) is significantly distinguishable from compounds **1** and **2**. A weak absorption is found at around 255 nm but the most intense absorption band is located at 289 nm. This is reflected by the molar extinction coefficients which differ also in comparison to **1** and **2** (Table 2).

As described, careful examination of UV-Vis data provides the possibility to identify the ligands in solution. In contrast, compounds **1–3** are indistinguishable in solid-state optical spectra (see ESI†). The solid-state absorption spectra display

Table 2 Optical and thermodynamical parameters of the parent ligands 1–3

Compound	$\lambda_{\text{abs.}} (\text{EtOH})/\text{nm}$ ($\epsilon/\text{L mol}^{-1} \text{ cm}^{-1}$)	$\lambda_{\text{abs.}} \text{ solid}/\text{nm}$ (fine structure/shoulders)	$\lambda_{\text{em.}} (\text{EtOH})^a/\text{nm}$ (quantum yield Φ)	$\lambda_{\text{em.}} \text{ solid}^b/\text{nm}$	$T_{\text{m}}/T_{\text{nuc.}}/T_{\text{dec.}}^d/^\circ\text{C}$
FAP (1)	263 (21 700) 296 (5300)	277 330 (300, 320, 341)	361 (0.013) ^c	387	250/n.a./250
OFAP (2)	264 (27 900) 296 (6300)	273 330 (301, 320, 341)	368 (0.029) ^c	376	261/n.a./270
NFAP (3)	221 (9200) 255 (11 400) 289 (26 700)	291 333 (324, 343)	455 (0.001) ^c Deconv. 390, 464	395	259/239/n.a.

^a Solution spectra are recorded in ethanol solution (with O.D. ≤ 0.07 for FAP, OFAP; ≤ 0.15 for NFAP in luminescence measurements). ^b Solid-state spectra are recorded from polycrystalline samples or thin sublimed films of low O.D. on optical quartz plates. ^c The quantum yield (Φ) was determined independently on two different instruments (see ESI) and by different standards *viz.* relative to 9,10-diphenylanthracene (using the common value of $\Phi = 0.95$ in ethanol⁴⁶) and anthracene ($\Phi = 0.27$ in ethanol^{46b}). For FAP and NFAP also different synthetic batches were used. We therefore estimate the relative error on Φ -value to be $\leq 10\%$. ^d T_{m} : melting temperature, $T_{\text{dec.}}$: temperature of decomposition, $T_{\text{nuc.}}$: nucleation temperature; n.a. = not available.

two maxima at wavelengths above 270 nm. The more intense transition is located at approx. 330 nm for all ligands accompanied by a slight fine structure splitting (Table 2). The short wavelength absorption is shifted bathochromic within 10 nm (1500 cm^{-1}) in contrast to the solution spectra. Therefore, the change in the optical properties are due to condensing into solid-state and presumably self-assembly as found for NFAP 3 in X-ray elucidation.

Ligand luminescence. Compounds 1 and 2 show both a weak emission in the UV-region in solution (361 and 368 nm, $\Phi < 3\%$) independently of the excitation wavelength (Fig. 2). The solid-state luminescence of these ligands is slightly bathochromic shifted (376 and 387 nm). Surprisingly the energy shift is larger for the FAP ligand 1 (1861 cm^{-1} vs. 652 cm^{-1} for 2), while compound 3 shows an odd behaviour in having a broad but very weak emission (455 nm, $\Phi \approx 0.1\%$) in solution, which is considerably red-shifted (3338 cm^{-1}) to the solid-state emission (395 nm). Gaussian deconvolution gave two bands at wavelengths of 464 nm and 390 nm, where the latter corresponds well with the observed solid-state emission band (except the 5 nm blue-shift) and also to the solid-state emission of all other ligands. This dual emission behaviour can be correlated to the change of states observed in UV-Vis spectroscopy and this can be underlined by quantum chemical calculation. HOMO and LUMO of the ligands 1–3 were calculated by us before (on DFT-PW91-GGA level) and show partial intra-ligand charge transfer (ILCT) character. The LUMO is located on the AP unit while the HOMO is spread across the entire ligand. However, with increasing donor ability of the *para*-substituent ($\text{F} < \text{OMe} \ll \text{NMe}_2$) the magnitude of this contribution changes from the AP-head to localization on the fluoroarene tail (see also HOMO in Fig. 9).⁴⁵

We examined also the luminescence of 2-AP in solid-state (and solution) for comparison (Fig. 2) and further discussion of the CPs later. 2-AP shows a dual emission in solid-state and the luminescence maximum of the main band is located at 357 nm in close accordance with published values of Huang *et al.* for the solid-state (353 to 359 nm for solid 2-AP,^{15l,k} 351 nm for 4-Me-AP,^{15f,h} and 340 to 342 nm for 4,6-DiMe-AP^{15l,p,f,h}).

The same value (357 nm) is found for the luminescence of 2-AP in ethanolic solution (Fig. 2) also matching the reported values (355 nm to 363 nm) in different polar and nonpolar solvents, which let us conclude that this emission is not sensitive to the environment.^{39,41,47,48} However, to the best of our knowledge, the dual emission of 2-AP in solid-state (Fig. 2) is described for the first time as this is contradictory to reports by Huang *et al.* citing that “free AP and 4,6-dimethyl-AP ligands do not emit any photoluminescence in the range 400–800 nm”.^{15k} Low temperature spectra reveals a structured band shape and otherwise only the expected minor temperature dependent blue shift (5 nm). A closer look at the FAP ligands in the solid-state show a broadening of the emission band at the long-wavelength end. The solution spectra of 2-AP also shows this weak vibronic-structured emission band, although we noted that the excitation wavelength choice seems to be crucial for 2-AP in solution. Excitation in each of the two main bands results in much stronger luminescence emission intensity of the Gaussian type band shape, covering the weak second emission. This also proves that two species are involved and impurities could be ruled out. § Phosphorescence spectra of 2-AP were reported by several authors, which show a Gaussian shape emission band peaking at about 390–400 nm.^{41,42,47,49} Such an emission can be excluded for the ligands although NFAP (3) matches this value by coincidence.

Detailed studies to fluorescence and phosphorescence to yield a state diagram of 2-AP were conducted by several groups, the most recent report is given by Testa *et al.* in 1992.^{42,49} They cite the quantum yield to be $\Phi = 1.7\%$ in ethanol, which matches well with the values we obtained for our FAP systems (Table 2).

An explanation for the above described behaviour of dual emission (or band shifting and broadening resp.) is given in detail by Fujimoto *et al.* in 2005 and by Lenci and Neubacher *et al.* in 1974.^{39,47} Fujimoto *et al.* studied the interaction of 2-AP with acetic acid in isooctane solution. Changes in the

§ We initially chose 260 nm as excitation wavelength in accordance with the FAP series ligands. Recrystallized (CHCl_3) and subsequently sublimed 2-AP of different suppliers was used.

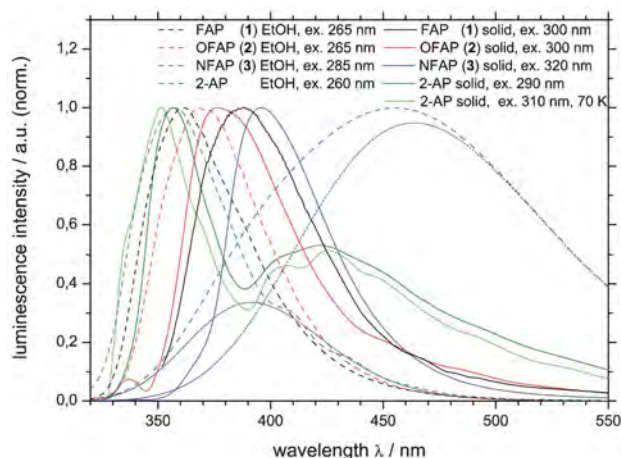


Fig. 2 Luminescence spectra of the ligands **1** (black), **2** (red), **3** (blue) in solution (dashed line) and solid-state (solid line) as well as the luminescence spectra of 2-AP (dark green) in solid-state and at low temperature (bright green).

UV-Vis spectra (e.g. shift from 285 nm to 295 nm) and luminescence spectra were apparent: the emission intensity of the maximum at 355 nm decreases with appearance of a second band at 460 nm (ex. 270 nm). A 1 : 1 hydrogen bonded complex was proposed and the new vibronic structured long wavelength emission was assigned to an amino-imino tautomerization of 2-AP by acetic acid in an excited state double proton-transfer reaction. The simple explanation of protonated 2-AP could be excluded as origin of the emission.³⁹ Lenci and Neubacher *et al.* studied the self-assembling of 2-AP in concentrated ethanol and water solutions. They observed a concentration- and also mildly excitation-sensitive broadening of the 360 nm band due to a shoulder at 425 nm, which was deconvoluted by subtraction and assigned to a 2-AP excited state complex.⁴⁷ Such double proton transfer phenomena have been studied, for example, in great detail on the DNA base-pair analogue 2-pyridone-2-hydroxypyridine and moreover on 2-aminopyridine (where the same red-shifted, structured emission is found) in recent years.^{50,51}

In our case the long wavelength shoulder shows a local maximum at 425 nm. In the study of Fujimoto *et al.* acetic acid acts as hydrogen bond partner, but as pointed out in the introduction, 2-AP forms strong hydrogen bond pattern with all kind of matching acceptor/donor molecules. It is reasonable to assume that in the solid-state similar emission behaviour must be observed where the hydrogen bonding of 2-AP to itself,¹ or, for instance, other carboxylic acids, is well documented by X-ray diffraction. We noticed that by excitation at lower energies (>340 nm) this emission can be pronounced, showing that two different species contribute. Therefore, it might be applicable to account these findings for solid 2-AP to the same excited state tautomerization. This does not disagree with previous studies of 2-AP by steady-state infrared (IR) spectroscopy stating that only the amino form is observed in solid-state. The quite low N-H stretching frequencies were explained by intermolecular hydrogen bonding, as known from the X-ray structure.^{1,52}

In summary the luminescence of the parent ligands, especially 2-AP, seems to be a delicate topic due to excited states photophysics. To the best of our knowledge this has not received attention in the crystal-based literature yet but is kept in mind for future work in this field, especially for MOF-like materials consisting of 2-AP-based ligands and (poly)carboxylate co-ligands where hydrogen bonds might exist. For the hydrogen bonded anions in this work this type of proton-transfer reaction can be excluded by the simple fact that the pK_a of the corresponding acids is too low. It is also shown that the solid state emission is slightly red-shifted in comparison to fluid solution (EtOH) and substitution influences the luminescence and (in case of NFAP) the UV-Vis characteristics.

Ligand infrared spectroscopy. In a similar manner, IR spectroscopy is not entirely suitable to distinguish between the ligands although some infrared spectroscopy studies of 2-AP and some of its metal complexes are reported.^{38,52–55} A detailed discussion of the changes in IR spectra due to coordination and present anions for the CPs **4–11** is given in the ESI†. Comparable discrete Ag^I 2-aminopyridine complexes were investigated in detail by Beauchamp *et al.*⁵⁶

The amino group stretching vibrations are found as two very broad bands at approx. 3300 and 3150 cm^{-1} . The first band shows also a high energy shoulder at 3350 cm^{-1} . Values of 3350 and 3170 cm^{-1} (all $\pm 10\text{ cm}^{-1}$) are reported for 2-AP in the solid-state (see also 2-AP IR spectra in ESI†).^{38,52,57} It is noteworthy that Beauchamp *et al.* assigned the 3300 cm^{-1} band to an overtone of the amino deformation vibration.

Upon deuterium isotopic enrichment of the amino group hydrogen atoms (preparation described in the ESI†), done for FAP (**1**) as an example, these bands shift to 2500 , 2400 and 2329 cm^{-1} (Fig. S31, ESI†). An overtone can be excluded by intensity comparison. Only NFAP **3** shows distinctive C-H and CH_3 stretching vibrations in the 3000 to 2800 cm^{-1} region.⁵⁸ A weak band at 2735 cm^{-1} is observed for all ligands but the origin remains unknown.

In the lower wavenumber region FAP (**1**), OFAP (**2**), and NFAP (**3**) show a strong broad absorption at around 1690 cm^{-1} with a more or less prominent shoulder peaking at 1652 cm^{-1} . 2-AP shows a strong absorption band at around 1650 cm^{-1} which is attributed the amino group scissor deformation mode.^{38,52,54} This could be confirmed by DFT calculations for 2-AP in the gas-phase but a value of 1663 cm^{-1} is obtained for this mode (see comparison in the ESI†). The same type of DFT calculations for the ligands **1–3** show the peak of the amino-group scissor deformation at 1665 cm^{-1} with the strongest oscillator strength of all calculated modes. After deuteration this band shifts to 1634 cm^{-1} , clearly showing an amino group participation. Furthermore a strong absorption for an amino group scissor mode coupled with a symmetric quadrant ring stretching mode of the substituted fluoroarene is predicted at 1678 cm^{-1} by the DFT calculations. Fluoroarenes are known to absorb medium strongly in this region,^{57,59,60} for instance the 1659 cm^{-1} band of pentafluorotoluene was assigned to two fundamental modes by Bailey and Hasson.^{59,60}

In similar manner the very weak absorption at 1748 cm^{-1} (and the 1725 cm^{-1} shoulder) observed for **1** and **2** seems to have its origin in the fluoroarene tail although this band is not predicted by DFT calculations. Laposa and Montgomery assign

similar frequencies ($1721, 1755\text{ cm}^{-1}$) on solid hexafluorobenzene to combined modes of C–F stretching vibrations.⁶¹ It is a valid assumption that in the case of the NFAP ligand (3) these bands cannot be observed because of coupling with vibrations of the dimethylamino group (*vide infra*).

The second prominent band of the ligands' experimental IR spectra peaks at around 1608 cm^{-1} . This band is observed for all compounds and seems to originate in the 2-AP part of the molecule. The 2-AP ring stretch is usually found at 1580 cm^{-1} and 1570 cm^{-1} .^{38,52,54} For all ligands ring stretch modes of the 2-AP part are predicted at 1581 cm^{-1} by DFT calculations. However, at low temperature the intense 1580 cm^{-1} band of 2-AP shifts to higher energy (1606 cm^{-1}) as observed by McCarthy *et al.*,⁵³ which let us assign this to the ring stretch mode. Additionally a coupled mode of the 2-AP ring stretch with the fluoroarene ring stretch is predicted for NFAP at 1600 cm^{-1} .

The experimental spectra of the ligands are dominated by a very strong and broad absorption at 1480 cm^{-1} (down to 1440 cm^{-1}). Several bands lie in this region: for example 1475 cm^{-1} is reported to be another ring stretch mode of 2-AP with a subset around 1450 cm^{-1} (ESI†).^{38,52,54,57} Furthermore fluoroarenes absorb also in this region at about 1484 and 1440 cm^{-1} .^{57,59,60} The medium intense band at 1429 cm^{-1} is only visible in the case of OFAP and NFAP and can possibly be attributed to a CH_3 bending vibration although 1427 cm^{-1} was calculated as a 4,6-C–H in-plane rocking vibration for all ligands. In contrast the double band at 1392 and 1377 cm^{-1} is visible in all spectra. 1392 cm^{-1} was also calculated for the 2-AP 4,6-C–H in-plane scissor vibration, while the same vibrations is predicted at $1354 \pm 2\text{ cm}^{-1}$ for the ligands 1–3. A band at 1356 cm^{-1} was also observed for 2-AP experimentally making a clear assignment for these two bands difficult.^{53,54}

The most prominent band in the 1300 cm^{-1} to 1100 cm^{-1} region is the medium strong band at about $1220 \pm 7\text{ cm}^{-1}$. This was assigned to a C–H deformation by Contreras but as a C– NH_2 vibration by Akyuz, although originally assigned as C–H bending mode by Spinner.^{52,54,55} Our calculations show a strong 4,6-C–H–AP scissor deformation vibration at 1235 cm^{-1} for FAP, two $-\text{OCH}_3$ coupled modes for OFAP at 1245 and 1211 cm^{-1} , and one mode at 1206 cm^{-1} for NFAP. The low value for 3 corresponds well with the broad band located at 1211 cm^{-1} in the experimental spectra of 3. We therefore neither follow fully the assignment of Contreras nor Akyuz, especially as a mode involving C–N stretching in the AP part and NH_2 rocking vibrations was calculated to $1280 \pm 3\text{ cm}^{-1}$ for 2-AP and all ligands but not matching the experimental data. Furthermore Kovala-Demertzi *et al.* do not assign a mode in this region although their assignments are based on comparison with the deuterium substituted compound.³⁸ Upon deuteration of the FAP amino group a new band at 1293 cm^{-1} appears, indicating that the above mentioned modes are usually coupled. The 1184 cm^{-1} band is only visible for OFAP (2) and NFAP (3) while for the perfluorinated FAP (1) a weak band at 1140 cm^{-1} is characteristic, which falls into a typical region for F–aryl vibrations.⁵⁸

All ligands show a medium weak band at 1034 cm^{-1} , which is near the value of 1042 cm^{-1} attributed to the amino twist vibration of 2-AP by Akyuz and Contreras *et al.*^{52,54} but to a ring

breath mode by Kovala-Demertzi *et al.*³⁸ Indeed DFT calculation on 2-AP gave 1046 cm^{-1} as value for the amino twist vibration. The $-\text{NH}_2$ twist vibration was calculated to 1056 cm^{-1} for FAP, 1060 cm^{-1} for OFAP and 1063 cm^{-1} for NFAP, which renders an unambiguous assignment difficult because of the nearly equal spacing to the next observed band at higher frequency: the broad 1085 cm^{-1} band of FAP and 1095 cm^{-1} band of OFAP with a lower energy shoulder at approx. 1075 cm^{-1} . Only for NFAP a sharp peak is experimentally observed at the calculated value. However, bands in this region (1075 cm^{-1} for 2-AP) were assigned to a ring breathing mode by other authors.^{38,54} The fluoroarene coupled ring breathing modes of the AP part for 1–3 on the other hand were calculated to 1044 cm^{-1} (FAP), 1048 cm^{-1} (NFAP), and 1054 cm^{-1} (OFAP) and might be therefore reversed here.

In the fingerprint region of the spectra the nearby bands at 980 and 949 cm^{-1} ($\pm 5\text{ cm}^{-1}$) are prominent features. Only OFAP shows a third band at 935 cm^{-1} which can serve as a further marker band to distinguish the ligands from each other. Weak transition at $991, 979$ and 954 cm^{-1} were also reported in the literature.^{53,54} Our calculation gave a mode at 996 cm^{-1} and a second stronger transition at 968 cm^{-1} that was weakly coupled with the fluoroarene part in all ligands.

A transition at 870 cm^{-1} is reported for 2-AP and assigned as the C–H deformation vibration,^{52–54} but only observed for FAP and OFAP, while for NFAP a band at 898 cm^{-1} is observed. The calculations gave a well matching transition at 896 cm^{-1} for the ring stretching mode of the AP part in all ligands. Also particularly well described by the calculations is a coupled symmetric ring breathing of both arene parts found at 854 cm^{-1} for 1, 845 cm^{-1} for 2 and 825 cm^{-1} for 3 (same values calculated). These bands can therefore serve as clear markers for the determination of the ligands.

A strongly absorbing band is reported for 2-AP at about 800 cm^{-1} and also found experimentally for all ligands.^{53,54} The closest value calculated for 2-AP as well as 1–3 (816 cm^{-1}) describes a sextant out-of-plane ring bending mode and seems to be a reasonable assignment.

All ligands show a very broad and slightly variable band at about $550 \pm 20\text{ cm}^{-1}$ which can be assigned to NH_2 deformation vibration by comparison with the deuterium enriched FAP sample. 2-AP usually shows two broad peaks at about 550 cm^{-1} ($\pm 10\text{ cm}^{-1}$) and 521 cm^{-1} . This band was not clearly assigned by literature but calculations show several group frequencies in this region *e.g.* the 4,6-C–H out-of-plane deformation at 530 (2-AP), 541 (FAP), and 544 cm^{-1} (NFAP, OFAP) as well as the $-\text{NH}_2$ twist bending at 512 (2-AP), 527 (NFAP), 532 (OFAP), and 542 cm^{-1} (FAP). The calculated values of the twist bending agree well with values calculated by McCarthy *et al.* on SCF-6-311G** level (537 cm^{-1}).⁵³

In summary identification of many bands of the ligands IR spectra is possible by literature comparison to 2-AP or computational inexpensive DFT 6-31+G(d) calculations. Some bands can serve as markers for specific ligands *e.g.* 1140 and 854 cm^{-1} for 1, 845 cm^{-1} for 2, and 825 cm^{-1} for 3, while $1748, 1429$ and 1184 cm^{-1} exclude 1.

Solid-state assembly in Ag^I CPs of the ligands 2 and 3

In general *catena*-coordination compounds **4–11b** have only a few structural features in common, making a detailed description necessary which is given in the next paragraphs. We will discuss the OFAP series **4–7** first and then switch to the NFAP series **8–11b**. The coordination polymers **4–11** are displayed in Fig. 3 and 4 and the crystal lattices are presented in the ESI.† As found for the coordination polymers of FAP earlier,¹⁶ the CPs of **2** and **3** form one-dimensional strands or anion-bridged two-dimensional layers. Basic crystal parameters like crystal system, cell size and occupancy are summarized in Table 3.

Crystal structure of [Ag(ofap)TFA]_n (**4**)

The coordination environment for the Ag^I-TFA-OFAP coordination compound **4** (Fig. 3 top left) can be described as an one-dimensional zigzag chain of OFAP ligands **2** whereby the

fluoroarene tail is pointing in the same direction to give parallel alignment of the ligands. The dihedral angle ϕ (F-aryl-AP) is the largest (53.1(4)°) measured for all compounds in the series (Table 4). The more positive ϕ -value between the two aromatic units seems to be a result of the F_{TFA}- π_F -interaction overcoming pure packing effect ($d(\text{F} \cdots \text{F-arene})$ 2.956 Å, deviation to ctr. 0.203 Å).¹⁹ The Ag^I ion shows distorted tetrahedral coordination by two ligands and two TFA anions. The N1-Ag-N3-angle is 122.3(1)° while the bond lengths are of normal length scale (Table 4). Both oxygen atoms of one TFA anion coordinate to two Ag atoms of different polymer strands in a typical acetate bridging fashion (*viz.* $\mu_2\text{-}\kappa^2(\text{O},\text{O}')$). A second TFA anion completes the distorted tetrahedral environment in same manner giving a 2D superstructure with a O2_(TFA)-Ag-O3_(TFA') angle of 130.1(8)°. The N-Ag-O angles are 92.0(4)° and 98.5(7)° (N3 to O2 and O3 resp.) and 129.5(2)° and 83.7(0)° (N1). To simplify the discussion of the Ag-coordination

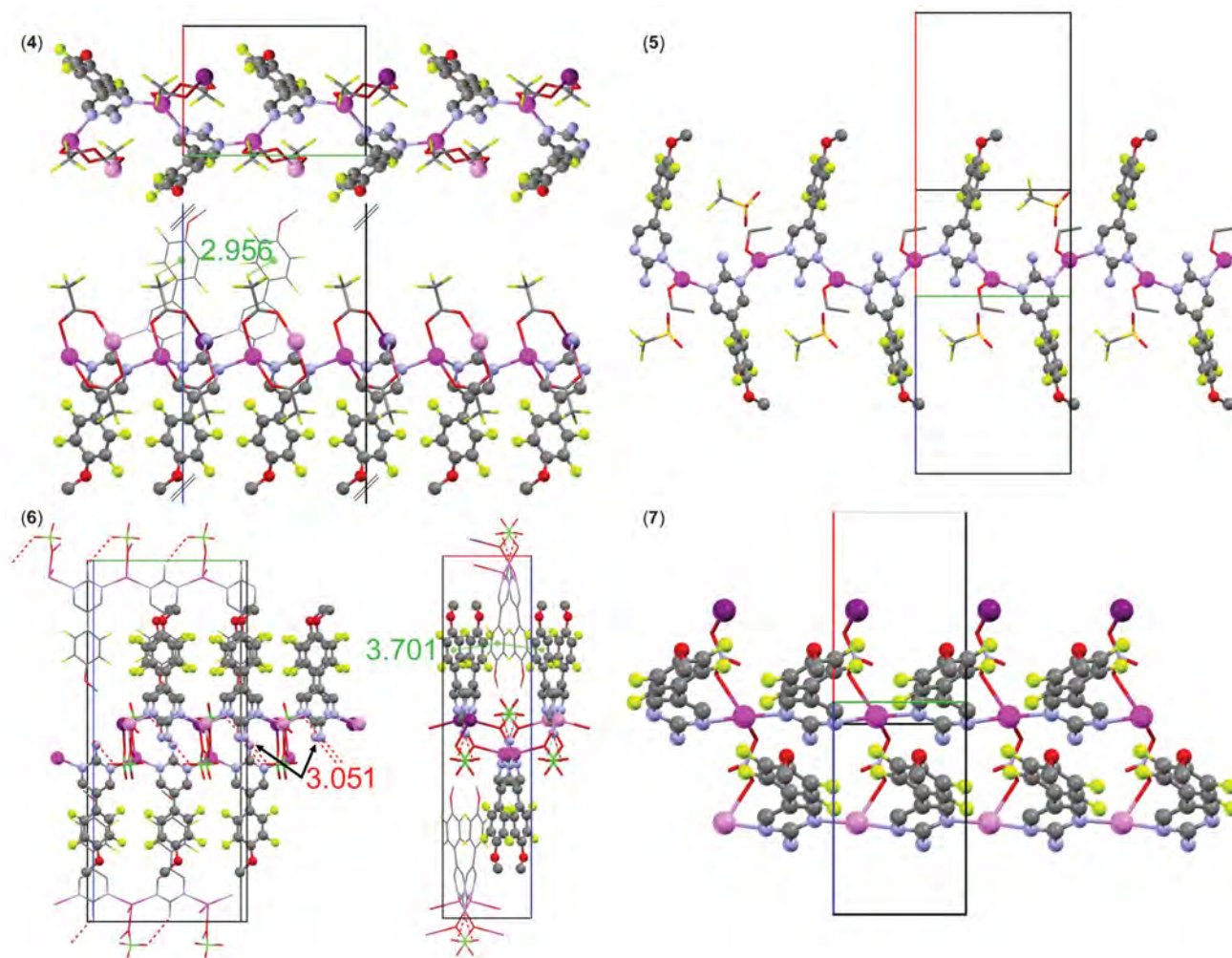


Fig. 3 Coordination polymers (CPs) **4–7** of different Ag^I salts and the OFAP ligand **2**. View along crystallographic *c*- and *a*-axis (two NFAP molecules in the cell are shown as wireframe model) for **4** (F_{TFA}⋯F-aryl contacts are marked in bright green); at *a*-axis + 50° for **5**; at *a*-axis + 4° (for visibility of all strands; next top/bottom strands are indicated as wireframe models) and *b*-axis for **6** (with π_F - π_F and D⋯A distances indicated); at *a*-axis + 30° for **7**. Anions (and coordinating solvent in case of **5**) are shown as capped-stick models, while the ligand atoms are rendered as ball-and-stick models. Silver atoms are shown in shades of magenta for indication of the nearest silver atoms of the next polymer layer. Carbon atoms are shown in grey, oxygen in red, nitrogen in blue, sulfur in yellow, chlorine in green and fluorine atoms in bright yellowish green. Hydrogen atoms are omitted for clarity. Disordered groups (if applicable) are shown in major site occupation only.

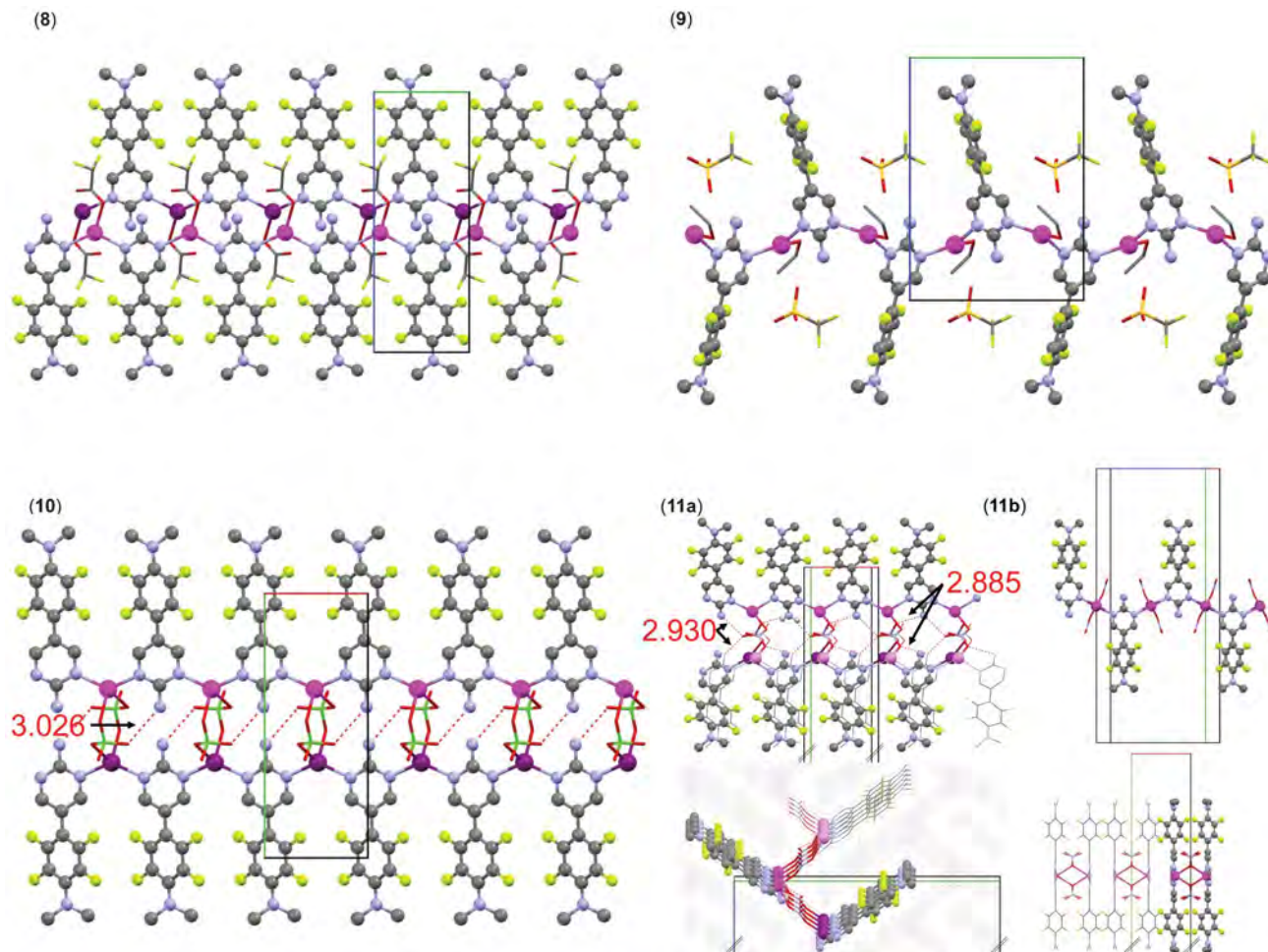


Fig. 4 Coordination polymers **8–11** of different silver(I) salts and the NFAP ligand **3**. View along crystallographic *a*-axis for **8** and **9**; view along *c*-axis for **10**. Polymorphic structure **11** is shown in two scaled views each: along *c*-axis shifted +4° (to emphasize perspective view) and along *a*-axis +4° for **11a** (surrounding packing drawn as faded wireframe model); at reciprocal *a*-axis (*i.e.* on *hkl* 100 plane) and along *c*-axis for **11b**.

geometry we wish to discuss this with help of the angular structural parameter τ_4 introduced for tetragonal geometries by Houser (*e.g.* here a T_d geometry has $\tau_4 = 1$ while D_{4h} gives $\tau_4 = 0$).⁶³ This parameter was also used by Huang and co-workers for some of their AP-systems^{15*k,h*} and in our case a comparable τ_4 -value of 0.71 is found for **4**. The TFA bridge brings the two Ag^{I} ions in close proximity of 3.357(2) Å which is a little closer than the doubled van der Waals (vdW) radius of silver.⁶²

Crystal structure of $[\text{Ag}(\text{ofap})\text{OTf}\cdot\text{EtOH}]_n$ (**5**)

The trifluoromethanesulfonate (OTf) compound **5** (Fig. 3, top right) also possesses a one-dimensional zigzag chain but with a head-to-tail arrangement of the ligand **2** within the strand. The next CP strand is well separated. The Ag^{I} atom holds a coordination number (CN) of 3, composed of two OFAP ligands and ethanol as the third ligand. The N–Ag–O(EtOH) angle shows a fractional difference (112.4(5)° and 119.0(4)°). However, the Ag atom is just marginally (0.078 Å) out of the plane defined by the coordinating ligand atoms (N1, N3, O5). In overall, the coordination appears to be distorted trigonal and the triflate ion can be considered as a nearly innocent anion:

hydrogen bonding of triflate oxygen atoms O3 and O4 to the amino group of the AP-head on different strands is detected ($d(\text{D}\cdots\text{A})$ 3.013(6) Å and 2.932(9) Å) resulting in a $R_4^4(12)$ graph set quite commonly observed,⁶⁴ while O2 has a short contact to the OH-group of the ethanol molecule (O5, $d(\text{D}\cdots\text{A})$ 2.823(2) Å). Otherwise the triflate oxygen atoms have only minor contacts to Ag^{I} ions ($>2.739(2)$ Å). The shortest oxygen contact is from solvent (Table 4). No obvious F– π_{F} -interactions are found compared to **9**. The dihedral twist angle φ is in a normal range (40.6(7)°).

Crystal structure of $[\text{Ag}(\text{ofap})\text{ClO}_4]_n$ (**6**)

The crystal structure of silver(I) perchlorate OFAP compound **6** (Fig. 3, bottom left) shows a two dimensional network. Individual head-to-head CP strands are connected by the perchlorate ion in $\mu\text{-}\kappa^1$ -fashion (O2). By this the Ag^{I} ion is in a flattened tetragonal coordination environment ($\angle(\text{N1}, \text{N3})$ 134.6(5)°, $\angle(\text{O2}, \text{O2}')$ 102.3(6)°) resulting in a corresponding τ_4 -value of 0.78. Weak fluoroarene–fluoroarene contacts are found between the tails of the layers ($d(\text{ctr}\cdots\text{ctr})$ 3.701 Å, displaced by 30.0°) indicating π – π -interactions.^{19*e*} The

Table 3 Crystal data and structure refinements of **4–11b** and NFAP (**3**)

	4	5	6	7	NFAP
Composition	[Ag(ofap)CO ₂ CF ₃] _n	[Ag(ofap)SO ₃ CF ₃ ·EtOH] _n	[Ag(ofap)ClO ₄] _n	[Ag(ofap)NO ₃] _n	v. s.
Formula	C ₁₃ H ₇ AgF ₇ N ₃ O ₃	C ₁₄ H ₁₃ AgF ₇ N ₃ O ₅ S	C ₁₁ H ₇ AgClF ₄ N ₃ O ₅	C ₁₁ H ₇ AgF ₄ N ₄ O ₄	C ₁₂ H ₁₀ F ₄ N ₄
F.w./g mol ^{−1}	494.09	576.20	480.52	443.08	286.24
Temperature/K	100	200	100	100	296
Abs. coeff./mm ^{−1}	1.439	1.239	1.715	1.607	0.134
Crystal system	Orthorhombic	Monoclinic	Orthorhombic	Monoclinic	Orthorhombic
Space group	<i>Pbca</i>	<i>C2/c</i>	<i>Pbca</i>	<i>P2₁/c</i>	<i>Fddd</i>
<i>Z</i>	8	8	8	4	16
<i>a</i> /Å	8.22210(10)	25.2591(8)	7.31770(10)	18.417(7)	7.4891(19)
<i>b</i> /Å	11.5994(2)	10.5671(3)	12.76150(10)	6.3990(8)	13.333(2)
<i>c</i> /Å	31.6633(4)	15.0340(5)	29.9513(4)	11.262(4)	51.316(8)
β /°	90	103.5966(18)	90	95.79(3)	90
Volume/Å ³	3019.77(7)	3900.3(2)	2797.00(6)	1320.4(7)	5124.1(18)
Reflections coll.	44 790	34 321	48 584	29 741	15 596
Indp. reflns	4395	4467	3208	3036	1127
Reflns. <i>I</i> > 2σ(<i>I</i>)	3356	3619	2976	2714	847
GoF on <i>F</i> ²	1.064	1.055	1.094	1.047	1.109
<i>R</i> ₁ (final)	0.0285	0.0340	0.0187	0.0233	0.0416
<i>wR</i> ₂	0.0687	0.0864	0.0457	0.0567	0.0968
<i>R</i> ₁ (all data)	0.0443	0.0452	0.0209	0.0285	0.0617
<i>wR</i> ₂	0.0738	0.0945	0.0466	0.0597	0.1067
Disordered parts	—	C atom of −OCH ₃ on two positions (56 : 44)	—	—	—
	8	9	10	11a	11b
Composition	[Ag(nfap)CO ₂ CF ₃] _n	[Ag(nfap)SO ₃ CF ₃ ·EtOH] _n	[Ag(nfap)ClO ₄] _n	[Ag(nfap)NO ₃] _n	[Ag(nfap)NO ₃] _n
Formula	C ₁₄ H ₁₀ AgF ₇ N ₄ O ₂	C ₁₅ H ₁₆ AgF ₇ N ₄ O ₄ S	C ₁₂ H ₁₀ AgClF ₄ N ₄ O ₄	C ₁₂ H ₁₀ AgF ₄ N ₅ O ₃	C ₁₂ H ₁₀ AgF ₄ N ₅ O ₃
F.w./g mol ^{−1}	507.13	589.25	493.56	456.12	456.12
Temperature/K	100	100	100	100	220
Abs. coeff./mm ^{−1}	1.324	1.172	1.601	1.486	1.387
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	<i>C2/c</i>	<i>P2₁/c</i>	<i>P2₁/c</i>	<i>P2₁/c</i>	<i>C2/c</i>
<i>Z</i>	8	4	4	4	8
<i>a</i> /Å	28.875(8)	13.6509(5)	6.42220(10)	6.32870(10)	7.8308(3)
<i>b</i> /Å	6.4421(2)	10.3996(3)	16.1283(3)	25.1946(8)	31.6394(14)
<i>c</i> /Å	20.640(4)	15.5497(6)	14.7568(3)	9.1130(3)	12.6258(5)
β /°	121.264(12)	110.8880(19)	101.4489(13)	100.5912(17)	102.043(3)
Volume/Å ³	3281.8(11)	2062.42(12)	1498.08(5)	1428.30(7)	3059.3(2)
Reflections coll.	34 803	27 663	32 418	17 026	34 698
Indp. reflns	3775	4727	4358	4132	3478
Reflns. <i>I</i> > 2σ(<i>I</i>)	2926	3637	3330	3371	2347
GoF on <i>F</i> ²	1.030	1.013	1.018	1.086	0.992
<i>R</i> ₁ (final)	0.0384	0.0317	0.0315	0.0267	0.0336
<i>wR</i> ₂	0.0792	0.0715	0.0667	0.0564	0.0792
<i>R</i> ₁ (all data)	0.0612	0.0501	0.0505	0.0389	0.0613
<i>wR</i> ₂	0.0901	0.0774	0.0718	0.0597	0.0876
Disordered parts	−CF ₃ group on two positions (85 : 15)	—	—	—	—

structure is stabilized by hydrogen bonding of the AP amino group to one of the perchlorate ion oxygens (O5, *d*(D⋯A) 3.051(3) Å). The direction of this hydrogen bond is unidirectional along the polymer strand. Perchlorate oxygen atoms O3 and O4 show weak secondary contacts to the coordinated Ag^I ion (*d*(O(ClO₄)–Ag) 2.970(2) Å and 3.075(5) Å). The dihedral angle ϕ is again unremarkable.

Crystal structure of [Ag(ofap)NO₃]_n (**7**)

Compound **7** (Fig. 3, bottom right) crystallizes in an anion-bridged 2D network. The structure is assembled by strands of OFAP ligands in head-to-head alignment and bridging κ²(O2,O4) nitrate anions. The third oxygen of NO₃[−] (O3) participates in hydrogen bonding to the amino group of AP (*d*(D⋯A) 3.026(4) Å). A similar H-bond distance is found for

coordinating O4 (*d*(D⋯A) 3.013(3) Å) giving a symmetrically repeating hydrogen bond pattern (C(6)C(6) graph set). Elongated unequal N–Ag bond lengths are found while the N1–Ag–N3 angle is slightly flattened (Table 4). The N–Ag–O angles are correspondingly enlarged ($\angle$ (N1,O4) 127.2(9)°, $\angle$ (N3,O2) 122.5(8)°) providing the two largest angles of the FAP series. The τ_4 -value calculates nevertheless to 0.78. The angle deviations are explainable by secondary contacts of the non-coordinating O3 atom to the Ag^I ion (*d*(O3–Ag) 2.814(1) Å and 2.911(1) Å). The ϕ -value is the second lowest encountered and the lowest of the OFAP series (35.9(8)°), indicating packing effects presumably by the layer structure build from the 2D–AgNO₃–OFAP network.

Table 4 Important internuclear angles and distances of the FAP, OFAP, and NFAP series as well as comparable systems from literature

Composition ^a (compound)	CN(Ag)	$\phi(\text{F-aryl/AP})^\circ$	$d(\text{N-Ag})/\text{\AA}$	$\angle(\text{N-Ag-N})^\circ$	$d(\text{Ag-Ag})/\text{\AA}$	$d(\text{Ag-O})^b/\text{\AA}$	Ref.
NFAP (3)	—	41.0(7)	—	—	—	—	This work
[Ag(ofap)TFA] _n (4)	4	53.1(4)	2.282(2), 2.350(2)	122.31(6)	3.357(3)	2.331(1), 2.534(1) ⁱ	"
[Ag(ofap)OTf·EtOH] _n (5)	3	40.6(7)	2.261(2), 2.257(2)	128.16(8)	None close	2.339(2), 2.739(2) ⁱⁱ	"
[Ag(ofap)ClO ₄] _n (6)	4	43.5(6)	2.229(1), 2.251(1)	134.65(5)	4.670(2)	2.449(1), 2.628(1) ⁱⁱⁱ	"
[Ag(ofap)NO ₃] _n (7)	4	35.9(8)	2.312(2), 2.380(2)	120.24(7)	4.620(1)	2.428(2), 2.553(2) ^{iv}	"
[Ag(nfap)TFA] _n (8)	3	34.0(9)	2.249(3), 2.319(3)	128.4(2)	3.049(5)	2.336(3), 2.812(3)	"
[Ag(nfap)OTf·EtOH] _n (9)	3	39.6(5)	2.236(2), 2.266(2)	126.31(7)	None close	2.338(2), 2.803(2) ⁱⁱ	"
[Ag(nfap)ClO ₄] _n (10)	4	35.4(3)	2.228(2), 2.253(2)	131.51(7)	5.079(6)	2.443(2), 2.502(2) ⁱ	"
[Ag(nfap)NO ₃] _n (11a)	4	36.4(8)	2.213(1), 2.411(1)	120.77(6)	None close	2.382(1), 2.399(1) ^{iv}	"
[Ag(nfap)NO ₃] _n (11b)	4	44.6(6)	2.204(2), 2.206(2)	168.85(9)	4.053(2), 4.008(1) ^v	2.512(3), 2.516(3) ^{vi}	"
[Ag(fap)TFA] _n	3	37.6(5)	2.241(2), 2.301(2)	127.73(5)	3.484(1)	2.338(2), 3.007(1)	16
[Ag(fap)OTf·EtOH] _n	3	41.0(9)	2.276(2), 2.291(2)	126.28(4)	None close	2.357(2), 2.631(2) ⁱⁱ	16
[Ag(fap)NO ₃] _n	4	44.4(5)	2.241(2), 2.249(2)	156.91(8)	None close	2.584(2), 2.684(2)	16
Other systems sorted by counterion type, starting with (poly)carboxylates (incl. TFA)							
[Ag(4,6-diOMe-ap)TFA] _n	3	n.a.	2.257, 2.319	131.4	3.890	2.392, 3.250	15o
[Ag(4,6-diMe-ap)TFA] _n	4	n.a.	2.166, 2.172	158.3	3.847	2.333, 2.382	15q
[Ag(4-Me-ap)(suc) _{0.5} ·0.5H ₂ O] _n	2 & 4	n.a.	2.167, 2.453 ^{vii}	111.2 & 170.5	3.065	2.240, 3.208	15h
[Ag ₂ (4-Me-ap) ₂ (glu) ₃ ·1.5H ₂ O] _n	3 & 4	n.a.	2.207, 2.356 ^{vii}	120.1 & 152.3	3.128	2.299, 2.378	15h
[Ag ₂ (4-Me-ap) ₂ (ipa)·2H ₂ O] _n	2 & 4	n.a.	2.184, 2.388 ^{vii}	90.7 & 172.0	3.705	2.273, 2.385	15h
[Ag ₂ (4-Me-ap) ₂ (tpa)·H ₂ O] _n	4	n.a.	2.297, 2.333 ^{vii}	113.6 & 137.9	3.630	2.482, 2.537	15h
[Ag(4,6-diMe-ap)(bbdc) _{0.5} ·0.5H ₂ O] _n	2 & 4	n.a.	2.199, 2.454 ^{vii}	97.3 & 160.1	3.137	2.313, 3.393	15h
[Ag(ap)C ₇ H ₃ N ₂ O ₆] _n	4	n.a.	2.215, 2.363	121.5	3.725	2.274, 3.283	12
[Ag(ap)C ₇ H ₅ O ₂] _n	3	n.a.	2.237, 2.345	125.4	3.455	2.313, 3.099	13
[Ag ₃ (ap) ₃ (mal)NO ₃] _n	4 & 5	n.a.	2.264, 2.293 ^{vii}	111.2 & 155.8	3.563	2.264, 2.587	15k
[Ag _{1.5} (ap)(nta) _{0.5}] _n	3	n.a.	2.189, 2.327	127.5	None close	2.242, 2.572	15f
[Ag ₄ (ap) ₄ (C ₈ Cl ₄ O ₄) ₂] _n	4	n.a.	2.204, 2.205	150.8	None close	2.456, 2.564	15g
Sulfonates (incl. OTf)							
[Ag(ap)(pts) _n] _n	3	n.a.	2.251, 2.294	133.6	4.191	2.417, 3.103	10a
[Ag(ap)(nds) _{0.5}] _n	3	n.a.	2.174, 2.176	149.5	None close	2.481, 2.911	15l
[Ag(4,6-diMe-ap)(nds) _{0.5}] _n	3	n.a.	2.280, 2.234	131.6	None close	2.387, 2.738	15l
[Ag(4,6-diMe-ap)OTf·H ₂ O] _n	4	n.a.	2.225, 2.235	150.2	None close	2.521, 2.691 ⁱⁱ	15q
[{Ag(4-OMe-6-Me-ap) ₂ }-[Ag(4-OMe-6-Me-ap)(OTf) ₂] _n]	2 & 4	n.a.	2.165, 2.260 ^{vii}	143.9 & 163.2	None close	2.506, 2.594	15o
Perchlorates							
[Ag(4,6-diMe-ap)ClO ₄ ·H ₂ O] _n	2(3)	n.a.	2.176, 2.179	156.8	None close	(2.623) ⁱⁱ	14a
[Ag(4-OMe-6-Me-ap)ClO ₄] _n	4	n.a.	2.213, 2.257	141.6	None close	2.627, 2.639	15q
[Ag(4,6-OMe-ap)ClO ₄] _n	2	n.a.	2.172, 2.183	167.1	3.376	3.561	15q
[Ag(5-iodo-ap)ClO ₄] _n	2 & 4	n.a.	2.183, 2.215	144.8 & 178.9	None close	2.676, 2.910	14b
Nitrates							
[Ag(ap)NO ₃] _n	4	n.a.	2.276, 2.281	136.6	None close	2.580, 2.680	15p
[Ag(4,6-diMe-ap)NO ₃] _n	3 & 5	n.a.	2.185, 2.278 ^{vii}	127.3 & 156.3	4.440	2.590, 2.665	14a
[Ag(4-OMe-6-Me-ap)NO ₃] _n	5	n.a.	2.275, 2.287	149.8	4.559	2.597, 2.657	15p
[Ag(4,6-OMe-ap)NO ₃] _n	3	n.a.	2.249, 2.256	147.2	4.054	2.459, 2.650	15p
[Ag ₃ (4,6-OMe-ap) ₃ (NO ₃) ₃] _n	3 & 4	n.a.	2.213–2.265	146.2–152.2	4.300	2.540, 2.618	15p
Other							
[Ag(5-iodo-ap)PF ₆] _n	2	n.a.	2.178, 2.192	174.4	None close	—	14b
Dimeric complexes							
[Ag(ap) ₂ OTf·0.5H ₂ O]	2	n.a.	2.130, 2.140	177.8	—	2.880, 3.062	18
[Ag(hap) ₂]BF ₄ ·1.5H ₂ O	2	32.6	2.182	180.0	—	—	5
[Ag(1-naphthyl-ap) ₂]BF ₄	2	58.6	2.166, 2.172	175.7	—	—	5
[Ag(2-naphthyl-ap) ₂]BF ₄	2	28.5	2.103, 2.133	169.5	—	—	5
Statistics^c							
Avg. FAP series	—	40.5 ± 10.7	2.271 ± 0.105	129.3 ± 10.1 ^d	—	—	
Avg. all (excl. dimers)	—	40.4 ± 15.6	2.251 ± 0.133	134.0 ± 33.0 ^d	—	—	

^a In this manuscript we do not follow the IUPAC recommendation and instead name the neutral AP-ligand first to allow easier comparison; note also the following abbreviations: 4,6-diMe-ap = 4,6-dimethyl-2-aminopyrimidine, 4,6-diOMe-ap = 4,6-dimethoxy-2-aminopyrimidine, 4-OMe-6-Me-ap = 4-methoxy-6-methyl-2-aminopyrimidine, bbdc = 4,4-benzenedicarboxylate (more common name: 4,4-biphenyldicarboxylate), glu = glutarate, hap = 5-phenyl-2-aminopyrimidine, ipa = isophthalate, nds = 1,5-naphthyldisulfonate, nta = nitrilotriacetate, mal = malonate, pts = *para*-toluenesulfonate, suc = succinate, tpa = terephthalate, the remaining shortened names are generated by the IUPAC substituent name and position on the AP-ring. ^b Given are the two shortest Ag–O distances; as binding motifs are plenty note the following remarks: ⁱ two anions bridge two Ag atoms of different polymer strands as di(μ-κ²O,O'); ⁱⁱ shortest distance is to solvent molecule; ⁱⁱⁱ bridged as μ-κO; ^{iv} bridged as μ-κ²O,O'; ^v lower value is inter-strand distance; ^{vi} two anions bridge as di(μ-κ); ^{vii} given here is the average length of the N–Ag bond as two unequal AP–Ag–AP subunits exist. ^c A histogram for data of all N–Ag bond lengths and N–Ag–N angles is given in the ESI; standard deviation of values given = 2σ, sample size $N_{(\text{FAP series})} = 12$ (or 24 for bonds), and $N_{(\text{all})} = 39$ (78 bonds). ^d N–Ag–N angles ≥ 160° thus approaching 180° (e.g. polymorph 11b) were excluded, sample size N is therefore smaller by this number.

Crystal structure of [Ag(nfap)TFA]_n (8)

Compound **8** (Fig. 4, top left) consists of a head-to-head assembled polymer strand of NFAP ligand and TFA anions and possesses a distorted trigonal binding mode for the Ag^I ion. The N1–Ag–N3 and the N1–Ag–O1_(TFA) angles are almost akin (128.4(2)°, 128.3(2)°) while the third angle is correspondingly lower (∠(N3,O1) 97.4(1)°). The Ag^I ion is placed 0.316 Å out of the coordination plane (N1,N3,O1). A short Ag–Ag inter-CP distance is found (3.049(5) Å), which is the shortest distance measured overall (Table 4). The TFA anion shows hydrogen bonds from NH2B to O2 (*d*(D⋯A) 2.867(3) Å) and from NH2A to the already silver-coordinating O1 (2.878(2) Å) resulting in a C(6)C(6) graph set along the strand. The Ag–N and Ag–O bond lengths fall into the usual range (Table 4). The dihedral twist angle ϕ is the lowest encountered in the series (34.0(9)°) and although the NFAP ligands are highly linear arranged no π – π or π_F interaction are found.

Crystal structure of [Ag(nfap)OTf·EtOH]_n (9)

The silver(I) triflate NFAP coordination compound **9** (Fig. 4, top right) resembles closely the structure of **5** (Fig. 3, top right). The distorted trigonal coordination geometry for the Ag^I ion in **9** is more unbalanced (∠(N1/3,O4) 103.2(2)° and 128.8(9)°) and a larger displacement out of the coordination plane (N1,N3,O4) is found (0.163 Å vs. 0.078 Å for **5**). The triflate anion shows hydrogen bonding with all three oxygen atoms. While O1 and O2 extend to the amino group of AP (*d*(D⋯A) 2.979(1) Å and 2.957(2) Å) forming an R₄⁴(12) pattern within the strand, O3 has a short contact to the OH-group of the ethanol molecule (*d*(D⋯A) 2.777(1) Å vs. 2.823(2) Å for **5**). In addition and in contrast to **5** the triflate ion shows an F– π_F -contact similar to **4** but the distance is larger (3.167 Å, 0.455 Å deviation to ctr.) indicating a packing effect. This assumption is supported by the fact that the dihedral twist angle ϕ does not vary much and compares well to triflate compound **5**. In contrast the twist angle between the 2-AP ring and the dimethylamino group is strongly deviant (87.3°) in comparison to the NFAP series compounds but close to the DFT-calculated value (89.0°) for NFAP in the gas-phase.

Crystal structure of [Ag(nfap)ClO₄]_n (10)

Perchlorate compound **10** (Fig. 4, bottom left) crystallizes in another unique structure of individual head-to-head directed polymer strands μ -bridged by the perchlorate anion (Fig. 4, bottom left) in a κ (O1,O2)-fashion. In an overall view, a one-dimensional double-strand with a symmetric binding mode (inversion center between the di- μ -ClO₄[–]-bridge) is formed. The non-bridging oxygen atom (O3) of ClO₄[–] shows hydrogen bonding to the amino hydrogen atoms (*d*(D⋯A) 3.025(7) Å). A unidirectional hydrogen bond pattern is established along the individual polymer strand, as seen for **6**. The τ_4 calculates again to 0.78 although the angle for O1–Ag–O2 falls just below 100° (99.1(9)°).⁶³ The Ag–Ag distance is large (≥ 5.000 Å and only included as an exception in Table 4). The AP–F-aryl dihedral angle ϕ is in the lower (35.4(3)°) but typical region. The AP ring and the –NMe₂ group are almost in plane (dihedral angle: 5.40°).

Crystal structure of [Ag(nfap)NO₃]_n polymorph (11a)

Compound **11a** (Fig. 4, bottom right) crystallizes in a similar κ^2 (O1,O2) nitrate-bridged 2D coordination architecture to **7**, but the structure differs in some details. The most prominent difference is the herringbone geometry of the NFAP molecules as seen in the view from the *a*-axis. Compound **3** assembles in a head-to-head ordered polymer strand. The N1–Ag–N3 angle is almost equal to that of **7** but the N–Ag bond lengths are more unequally spread (Table 4). There is a rather obvious hydrogen bond of the non-coordinating third oxygen atom of NO₃[–] (O3) to the AP amino group (*d*(D⋯A) 2.931(1) Å) and an unobtrusive one of O2 to the amino group (*d*(D⋯A) 2.885(1) Å) to be described as C(8)C(8) in graph set notation. The nitrate ions coordinate in the same vectorial alignment for an individual AgNO₃ NFAP layer. This results in two small angles (∠(N3,O1) 82.3(8)°, ∠(N3,O2) 89.0(9)°) and in summary the Ag^I-coordination can be described as distorted seesaw geometry ($\tau_4 = 0.67$, ideal $\tau_4 = 0.64$).⁶³ Weak secondary contacts, but less pronounced than in **7**, are observed between O3 and the Ag^I ion on one side (3.032(5) Å). The unremarkable value of the dihedral angle ϕ suggests no particular interaction and the 2-AP moiety and the –NMe₂ group are also almost in plane (11.6°).

Crystal structure of [Ag(nfap)NO₃]_n polymorph (11b)

Compound **11b** (Fig. 4, bottom right) is the most symmetric *catena*-coordination compound encountered in the series. The NFAP ligand coordinates the Ag^I ion in head-to-tail fashion within the strand, while two strands are held in close proximity by two μ - κ (O)-bridging nitrate ions in a symmetrical mode (inversion center) to give a double strand. The strand proceeds in a linear way parallel to the *hkl* 100 plane. The Ag^I coordination environment (CN = 4) is slightly less disturbed by NO₃[–]-coordination than in all other compounds encountered here and – with a few exceptions – in the literature. Almost equal and short bond lengths are observed (Table 4). τ_4 was calculated to 0.67, which in terms of value and geometry can be described as a narrowed seesaw-type as one angle approaches 180° (*viz.* N–Ag–N' 168.8(5)°) but the second falls below 90° (∠(O1,O1') 72.5(5)).⁶³ Interestingly the Ag–Ag distance between to double strands (referred to as inter-strand dist.) is even lower (4.008(1) Å) than the NO₃-bridged Ag–Ag distance (4.053(2) Å). The non-coordinating oxygen atoms (O2,O3) of the nitrate ion show a quadrilateral hydrogen bonding pattern to the AP-head (*d*(D⋯A) 3.024(1) Å, 3.054(1) Å) forming a repeating R₄⁴(12) graph set. The 2-AP ring and the –NMe₂ group are not remarkably twisted out of plane (11.5° vs. 11.6° for **11a**). In contrast the dihedral angle ϕ between the two arene rings is close to the calculated value (similar to **6**) and the second largest in the series (exceeded only by **4** because of F– π_F interactions). By this the fluoroarene tails show no interaction within a double strand (*d*(ctr.–ctr.) 4.431 Å), but inter-strand π_F – π_F interaction might be attributed (*d*(ctr.–ctr.) 3.570 Å, 19.9° offset angle).^{19e}

Structural comparison

General remarks. While direct comparison of CP structures assembled by OFAP (**2**) and NFAP (**3**) ligands in terms of

coordination environment (CN, angles, *etc.*) is mostly given at the appropriate points above, we want to focus on reports on *catena*-AP compounds and comparison between the structural related systems sorted by counterion in the following paragraphs. This is necessary as most of the observed architectures are hardly comparable with each other (even for polymorphs **11**) as described above if focused on the ligand (with the exception of compounds **5** and **9**).

Chen and co-workers already identified and summarized several structural motifs as well as different coordination modes for AP in 2006.^{14a} All of our compounds belong to the type **IV**-bonding mode, namely metal ion coordination through both nitrogen atoms of the pyrimidine ring. However, many 2-AP-related coordination network show what would we like to denote as a common coordination motif: a head-to-tail arrangement of 2-AP units, a distorted trigonal or tetrahedral coordination around the Ag^I center composed of one or two anion contacts (often to oxygen atoms), and a twist angle > 0° of the 2-AP units relative to each other. The last designator affects the out-of-the-plane bending in terms of spatial direction along the proceeding coordination axis to give an overall structural motif to what is to be described as twisted, wavy or zigzag 1D polymer chain by other authors.

Trifluoroacetate and related (poly)carboxylate coordination networks. By far the largest group for comparison is composed by (poly)carboxylate-related AP coordination architectures. As indicated in the general remarks it is not hard to imagine that the coordination saturation of Ag^I centers to form tetrahedral coordination environments can be provided by a carboxylate ligand in μ -bridging (as found for **4**) or κ^2 (O,O') fashion. In particular, polycarboxylates are prominent examples to extend the dimensionality, which cannot be discussed in extended detail as most of them also belong to MOF-like higher-order structures rather than CPs.

CP **8** ([Ag(nfap)TFA]_n) is in general comparable to the previous published FAP *catena*-compound ([Ag(fap)TFA]_n). Both possess the same anti-parallel alignment of two polymer strands in close proximity but the displacement of the Ag^I ion from each strand against each other is larger for the latter. As mentioned in the crystal structure description this results in a short Ag–Ag contact (3.049 Å, sum of vdW radii of silver:⁶² 3.44 Å, doubled covalent radius:⁶⁵ 2.90 Å) between the strands for **8**, while the FAP pendant shows no contact (3.483 Å).

Other bond lengths and angle values are nearly the same (see Table 4). The dihedral angle $\phi_{(\text{F-aryl-AP})}$ differs only marginally by 3.6°. The TFA anion is slightly bent inwards to the next polymer strand for the FAP CP (37.6° vs. 32.0° for **8**), measured as N1–O1–N3-plane vs. C–O1–O2-plane, giving an indication to the transition to structure **4**, where two TFA anions bridge two Ag(I) ions of different polymer strands (also indicated by a shorter Ag–O2 distance of 2.534 Å). In the case of OFAP based compound **4** the bridging μ_2 -TFA motif holds all polymer layers close together ($d(\text{Ag–Ag})$ 3.357 Å). The individual strands in **4** assemble as a tail-spread zigzag chain, while for FAP and NFAP TFA-CPs the strands are linear and in plane. This arrangement is not mediated by the TFA ligand. In contrast CP **4** is the only structure with clear F $\cdots$ fluoroarene interactions.

Focusing first on reports with TFA included as ligand CPs consisting of 4,6-diMe-AP or 4,6-diOMe-AP as second ligand are evident for comparison (Table 4).^{15g,o} The [Ag(4,6-diMe-ap)TFA]_n shares the common coordination of AP-CPs described in the general remarks with a CN = 4 and a τ_4 value of 0.72 but one TFA acting in μ - κ^1 (O) bridging fashion and the other in the more common μ - κ (O,O') binding mode to interconnect the individual CP strands. The latter is also found in **4** and besides the μ - κ^1 (O) mode the structure is likewise double bridged. The AP units in these strands are, in contrast to our compounds, nearly orthogonally twisted (86°) relative to each other along the coordination axis. The N–Ag–N angle is larger (158.3°) than for our compounds (avg. 126.1°) and the bond lengths are shorter (see Table 4).

The second CP [Ag(4,6-diOMe-ap)TFA]_n has a similar coordination environment to that found for **8** and the FAP CP, namely similar bond lengths and angles as well as a CN of 3 with TFA binding only by one oxygen atom. However, as found for many AP CPs the individual 4,6-diOMe-AP ligands form a zigzag chain along the polymer axis. Luminescence was in both cases only briefly examined and described to be of ligand type.

A very comparable structure to **8** and to the FAP–TFA CP is the [Ag(ap)(benzoate)]_n CP reported by Zhu *et al.*¹³ (Table 4). The same linear head-to-head alignment of the 2-AP units is found along the CP strand and in a similar way two strands are close in a head-to-head-fashion but unsupported by any ligands or anions. The binding mode of the acid anion is the same (κ -O), giving a CN of 3 and nearly equal angle and bond length values. Related to our FAP CP, but in contrast to **8**, the offset between individual CPs strands gives an Ag–Ag distance that is marginally above the doubled van der Waals (vdW) radii of a silver atom (3.455 Å) as in the FAP–TFA CP case. Luminescence was not examined for this compound.

A partly comparable structure to **8** in terms of Ag–Ag contacts is the [Ag_{1.5}(ap)(nta)_{0.5}]_n structure reported by Huang *et al.*,^{15f} which consists also of head-to-head polymer strands with short, non-supported Ag–Ag interactions (3.020 Å) and results in a head-to-head arranged double strand. The nitrilotriacetic acid (NTA) ligand coordinates one Ag^I ion without any AP participation but serves also as a connection between the double strands (*viz.* total coordination to three Ag^I centers) in the orthogonal spatial direction. The Ag–Ag distance found in **8** (3.049 Å) is comparable to the value reported by Huang *et al.*

Very similar in terms of coordination environment and Ag $\cdots$ Ag interactions is the two-dimensional coordination network built with 4,4'-biphenyldicarboxylic acid as the co-ligand ([Ag(4,6-diMe-ap)(bbdc)_{0.5}·0.5H₂O]_n), also reported by Huang *et al.*^{15h} It consists of Ag^I centers in linear and in distorted tetrahedral geometries, but is nevertheless described as the “least distorted” coordination environment (τ_4 = 0.79; BBDC coordinates in κ (O)-fashion twice) of the compounds investigated by them (Table 4). The typical head-to-tail 2-AP zigzag chains “interconnect with each other to form a double-chain *via* Ag $\cdots$ Ag interactions” (3.128 Å).^{15h}

Another good example is a 3D framework composed of 2-AP and 1,3,5-benzenetricarboxylic acid (BTC) also reported by Huang *et al.*¹⁵ⁿ The BTC^{3−} anion acts as linker for several “1D

wavy pattern chains" of head-to-head oriented 2-AP Ag^I units binding to five Ag^I centers. In this example unsupported as well as μ_2 -BTC mediated interactions are found to give rise to different short Ag–Ag distances (2.786 and 2.809, 3.176 and 3.253 Å). The luminescence properties comparison is given in the section below.

Another example is provided by Bosch *et al.*,⁶⁶ who reported a 1,3,5-triazine-based ligand system which self-assembles with short Ag^I–Ag interactions (2.884 to 2.973 Å) mediated by a TFA bridge as in **4**. They refer to a typical range for the distance between to metal centers of bridging TFA from 2.910 to 3.153 Å.⁶⁷ This leads to the conclusion that the TFA bridge in **4** is slightly stretched. Luminescence was regrettably not examined for this interesting system.

Finally, another CP composed by 2-AP and tetrachlorophthalate as co-ligand for Ag^I shows again the typical zigzag pattern, but also a double acetate bridging mode for three of the four independent Ag^I centers which results in a similar inter-strand connection as in **4** but no direct Ag–Ag contacts.^{15g} This CP shows shifted emission behaviour which is discussed later.

Triflate and related sulfonate coordination networks. The structural diversity of CPs built of AP-ligands and sulfonate anions seems to be limited in comparison with the mentioned prototype CP [Ag(ap)(pts)]_n of Smith and co-workers.¹⁰ The solid-state structures are made of one-dimensional strands of alternating Ag^I and 2-aminopyrimidine units. These strands form a three-dimensional lattice. All compounds encountered resemble more or less this architecture with the exception of a unique AP-coordination compound composed by cationic and anionic polymer strands of silver triflate and 4-methoxy-6-methyl-aminopyrimidine (4-OMe-6-Me-AP) published by Huang *et al.*^{15o}

Commonly found are three-coordinated (N,N',O) Ag^I centers, where the oxygen atom originates either from the sulfate counterion or from the solvent as seen for most triflate compounds. In our case the oxygen atom is from an alcoholic solvent, but Ag–O bond lengths are generally similar, ranging from 2.337 Å to 2.481 Å. N–Ag–N angles are often close to 130 ± 6°. An exception is a 1,5-naphthyldisulfonate (nds) bridged coordination network presented by Huang *et al.*,^{15l} which has shorter and nearly symmetric N–Ag bonds while otherwise unequal lengths in range of 2.234 Å to 2.294 Å are found (Table 4).

Also common are hydrogen bonding patterns of the anion to the AP head. The donor–acceptor distances (*d*(D⋯A)) range from 2.919(5) Å for nds-coordination networks to 2.95(2) Å for [Ag(ap)(pts)]_n, but for our triflate compounds and for the prototype dimer [Ag(ap)₂OTf] they range between 2.902(2) to 2.991(7) Å.^{16,18} An exception is the 4,6-dimethylaminopyrimidine *catena*-compound where the triflate anion is still close to the Ag^I ion (2.691 Å), next to coordinating solvent molecules, resulting in a formal CN of 4 and hydrogen bonds are exclusively established to solvent molecules. In this structure every second head-to-tail arranged 4,6-diMe-AP ligand is severely bent out of the plane (100°) defined by the proceeding coordination axis of the CP and the ring-plane of the remaining APs. This bending results in avoidance of the typical zigzag chain pattern, while the τ_4 -value definable in this case for once is unremarkable (0.72).^{15q}

In the same manner it is noteworthy for [Ag(ap)(nds)_{0.5}]_n that the AP-ligands are alternately bent (89°) to maximize interaction with the π -system of the naphthyl-ring (*viz.* π – π stacking). This shows the influence of secondary interactions on crystal design even for simple APs without a tail group.^{15l} In contrast the APs in the prototype CP of Smith have no secondary contacts (except hydrogen bonds) and are consecutively all in plane along the polymer strand, while in our case a zigzag chain results for **5** and **9** by a combination of packing effects and hydrogen bonding. The assumption of secondary interactions as a driving force for the spatial arrangement of AP can be underlined by structures [Ag(5-iodo-AP)X]_n with X = PF₆[–] or ClO₄[–] as counterion (the latter will be discussed in the ClO₄[–] section) where a small angle deviation per repeating unit is visible, which results in unique helical structures.^{14b} Luminescence – if examined for the referred systems – is of ligand $\pi^* \rightarrow \pi$ -type while the Smith system was subsequent examined by us and details are given in the luminescence section.

In context of our work, the inter-atomic parameters of the triflate coordination polymer of **2** and **3** (*viz.* CPs **5** and **9**) are akin. All of them have a CN = 3 with one molecule ethanol as ligand and similar angles, bond lengths and ϕ -values (see Table 4) but the solid-state structures differ in the location of the CP strands in the crystal lattice with respect to each other, while the length of the repetition unit is approximately 7.5 Å (Fig. 5). An analogous relationship was found in our previous work.¹⁶ Compounds **5** and **9** are isomorphous to the AgOTf CP of **1** crystallized from ethanol or isopropanol. This is discussed in greater detail in the DFT section at the end of this work.

Perchlorate coordination networks. Not many silver(I) perchlorate coordination compounds of AP are known and the few published by Chen and Huang include the usual methoxy- and methyl-substitution patterns, with the above mentioned exception of [Ag(5-iodo-ap)ClO₄]_n. This helical CP is composed by two independent Ag centers, where one has CN = 4 (τ_4 = 0.90) and the other one an almost perfect linear Ag^I ion coordination mode. Luminescence was not examined for this CP.^{14b}

For compounds **6** and **10** equal τ_4 values of 0.78 are obtained. However, the spatial arrangement strongly differs (2D network for **6** *vs.* μ -ClO₄-bridged double strand for **10**) The structure of **10** is on first glance comparable to TFA structure **8** but there is no bridging established by the anions (*e.g.* as in **6** or TFA case **4**).

For the 4,6-dimethyl-AP in combination with silver(I) perchlorate a *catena*-compound is reported when water molecules are present.^{14a} This CP shows again a slight zigzag chain pattern caused by weak coordination of the water molecule as the third ligand (2.623 Å) and reminds us of the sulfonate CPs **5** and **9**. Referring to the angle range, the 4,6-dimethyl-AP ClO₄[–] combination is still close to CN = 3 (see Table 4). Each second AP-ligand is bent out of the plane (74°) along the proceeding polymer axis. If water is not present, either a discrete dinuclear μ -AP₂- κ^2 (N1,N3)-AP₂- κ^1 (N1) structure or a 2D sheet structure with three trigonal coordinating dimethyl-APs are obtained but ClO₄[–] participates only in hydrogen bonding in the latter structure.^{15q,14a} Photoluminescence was not examined for these compounds.

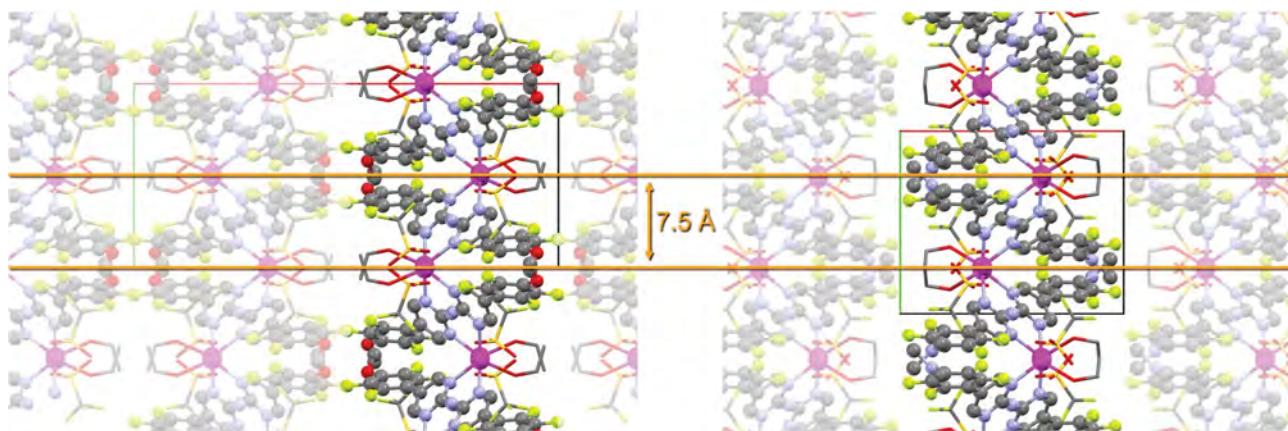


Fig. 5 Crystal lattices of **5** (left) and **9** (right). View along the *c*-axis with one strand highlighted while the surrounding packing is shown faded. The coordination polymers (CPs) are proceeding vertically along the *b*-axis. For compound **9** no displacement of the coordination polymers along one spatial direction is found. For compound **5** the coordination polymers are displaced by half of the repetition unit along the *b*-axis.

In contrast a similar structure to ours is obtained when 4-dimethoxy-6-methyl-AP is used as ligand as reported by Huang and co-workers.^{15q} The structure also consists of a 2D network assembled by head-to-head silver-coordinating AP units in a slight zigzag chain and $\mu\text{-}\kappa^2(\text{O},\text{O}')$ -bridging perchlorate ions. By this, the latter shows a single hydrogen bond to the AP-head. However, this does not prevent the usual out-of-plane bending of every second AP moiety (65°) to minimize distortion as indicated by a commonly observed τ_4 -value of 0.77.

In view of the spatial direction of the ligands the CP built of 4,6-dimethoxy-AP is most comparable.^{15q} The AP units are arranged in a head-to-tail fashion and are in-plane along the coordination axis as observed in our compounds but also parallel to the *hkl* 100 plane. However, the coordination environment of the Ag^{I} ion is almost linear. Only a weak contact (3.561 Å) of the ClO_4^- ion to Ag^{I} is observed, while our structures are commonly bridged by perchlorate as described above. In contrast the perchlorate ion connects two APs of different CP strands by hydrogen bonding. Certainly this supports the in-plane arrangement of all APs in the polymer. Furthermore this leads to short Ag–Ag inter-strand distances, which were attributed to unsupported $\text{Ag}\cdots\text{Ag}$ interactions by the authors.^{15q} Overall, the architecture is very similar to our NFAP– Ag^{I} TFA structure **8** except for different coordination numbers (2 vs. 3) while the Ag–Ag inter-strand distance is even shorter in our case. Luminescence emission for the methoxy-AP compounds was attributed to ligand-type transitions.^{15q}

Nitrate coordination networks. Similar to perchlorates CPs only a few silver nitrate coordination compounds of AP are known in literature.^{15p,14a,b} Among these the prototype structure $[\text{Ag}(\text{ap})\text{NO}_3]_n$ was also published by Huang and co-workers in 2008.^{15p} The structure is not comparable to any of our nitrate-CPs as it consists of a twisted head-to-tail zigzag chain which is in overall view (cell size *etc.*) more comparable to our triflate structures. The nitrate ion coordinates in this CP in a $\kappa(\text{O},\text{O}')$ mode, resulting in a τ_4 -value (0.91) close to the ideal tetrahedral geometry. Methyl- and methoxy-derivatives of AP were also investigated, which show different coordination

architectures related to the prototype AP structure and to our FAP systems. For instance the CPs consisting of 4-methoxy-6-methyl-aminopyrimidine ($[\text{Ag}(4\text{-OMe-6-Me-ap})\text{NO}_3]_n$) has a comparable parallel head-to-head arrangement as in **7** but the individual APs in a strand are tilted along the coordination axis, which is never seen for our compounds, most probably because of the steric demand and favorable secondary interactions of the tail group in our CPs as pointed out before. The nitrate ions bridge two CP strands in $\mu\text{-}\kappa(\text{O},\text{O}'),\kappa(\text{O}')$ mode giving a CN of 5. A similar binding motif is found for the 4,6-dimethylaminopyrimidine CPs of Chen and co-workers,^{14a} but two independent Ag centers are found. One is composed of two AP units in head-to-head mode and a $\kappa(\text{O})$ -coordinating nitrate ion (CN = 3) while the other Ag center has also the above mentioned CN = 5 motif. Then again the 4,6-dimethoxy-AP derivative was found to crystallize in two different structures: one has independent Ag^{I} centers but with an alternating $\mu\text{-}\kappa(\text{O})$ and $\mu\text{-}\kappa(\text{O}),\kappa^2(\text{O},\text{O}')$ -bridging mode between strands, while the simpler $[\text{Ag}(4,6\text{-OMe-ap})\text{NO}_3]_n$ is comparable to perchlorate **10** in structure. The local silver coordination environment is relatively similar ($\tau_4 = 0.82$) and two anions bridge neighboring strands in $\mu\text{-}\kappa(\text{O},\text{O}')$ -fashion. The AP ligands lie parallel to the *hkl* 100 plane (while parallel to *hkl* 001 for **7**) but, as tail-groups are missing, the APs in a strand prefer a head-to-tail arrangement and are tilted to maximize hydrogen bonding here, resulting in an alternating pattern where several strands are inter-connected to build up a 2D architecture. Also noteworthy in this context are the $\text{I}\cdots\text{I}$ secondary interactions found by Chen *et al.* for 5-iodo-AP to form a 3D porous structure.^{14b} Huang and co-workers also examined the luminescence of their CPs, which was in all cases concluded to be of ligand-type.

Compound **7** and **11a** have, apart from different spatial direction of the ligand tail along the CP strands (layer vs. herringbone), the same anion-mediated inter-strand connection by $\mu\text{-}\kappa(\text{O},\text{O}')$ nitrate (see packing diagrams in ESI†: view along the *b*-axis for **7** and along the *a*-axis for **11b**, the latter is also shown in Fig. 4). The same connection scheme was found for the previously investigated AgNO_3 -FAP CP but here the

typical head-to-tail arrangement of the AP ligand to form a proceeding zigzag chain was observed. The nitrate-bridge ($\text{Ag}-\mu\text{-NO}_3-\text{Ag}$) is the shortest in the AgNO_3 -FAP CP (5.532 Å), comparable to 7 (5.711 Å), but elongated in **11a** (6.285 Å). No noteworthy Ag-Ag contacts are found. This is different from the more symmetrical coordination compound **11b**, where anion-mediated but also inter-strand Ag-Ag distances in the 4.0 Å region are found.

Luminescence properties

All synthesized coordination polymers **4–11b** and ligands show solid-state luminescence (Fig. 6). In all cases except for polymorph **11b** the recorded luminescence maximum is below 500 nm and one or two unstructured emission band are observed (Table 5). In many cases one emission band is near the former ligand emission maximum which is usually found in the region of 385 ± 10 nm (Table 5). This holds also for the previously investigated FAP ligand (387 nm).¹⁶

Current status on luminescence explanations. If the luminescence emission maximum is not much altered often a intra-ligand emission (IL) is proposed. Several examples are provided by Allendorf.²¹ This phenomena is quite often found, as it was also observed for many well investigated 2-AP based polycarboxylate and some sulfonate coordination compounds in various dimensionality, which show ligand luminescence at around 327 nm to 359 nm. This is commonly attributed to the $\pi^* \rightarrow \pi$ transition and the luminescence enhancement is generally reasoned due to increased rigidity of the system in the crystal.¹⁵ Occasionally Ag $\cdots$ Ag interactions are also introduced at this stage to account for the fact that emission (at similar wavelength) is observable at all,⁶⁸ which is arguable (read below).

While the former mentioned case is the most straight forward class of emission, we also would like to point out that π - π -interactions and exciplex formation have been made accountable for altered luminescence in CP-like materials.^{69,70} Here we allow one more time to relegate on the photophysics

of 2-AP mentioned in the ligands section of this work, which leads to the case of luminescence where the emission maximum is significantly shifted (up to 100 nm): often an Ag^I-perturbed intra-ligand transition, sometimes modified by Ag $\cdots$ Ag interaction or tentative LMCT (or MLCT) character is proposed. The problems arising in identification of MC[ds/dp] or CT transitions and the possible influence of the excited state geometry are reported by Sun for Cu^I and some Ag^I examples.⁷¹

Summarized by Allendorf,²¹ examples are also known where both ligand-based and LMCT luminescence occur, which leads to dual emission of different magnitude. It seems that only copper(I) alkynyl-clusters are well understood by the work of Yam and others but they are triplet emitters.²⁴ It is stated “that an emission origin of ³MLCT character is not favored due to the large difference (1.19 eV) between the ionization energies of Cu^I_g and Ag^I_g. Instead, the emission has been attributed to originate from a LMCT state, probably mixed with a MC[ds/dp] state. In case of copper a large MC[ds/dp] character that is modified by Cu $\cdots$ Cu interactions is proposed.”²⁴ This assignment is nevertheless often used in other reports of d¹⁰-metal hybrid-material luminescence emission.

Luminescence at about 500 nm is often attributed to charge transfer phenomena in the case of Ag^I, sometimes also modified by MC[ds/dp] states having Ag $\cdots$ Ag interactions.²¹ The assignment of Ag $\cdots$ Ag interaction as a possible cause for altered luminescence phenomena is very popular although rarely proven by other methods than X-ray structure elucidation. The Ag $\cdots$ Ag interaction (argentophilicity) is now a widely accepted concept,⁷² but the use for reasoning the luminescence has to be judged in the future. In the following paragraphs we will list some selected examples: first we rely back to the tetrameric Ag^I-cluster example reported by Zink *et al.*,²⁵ who found the Ag $\cdots$ Ag interaction model cannot predict the correct emission. The chair-type cluster has shorter Ag-Ag distances (3.09 Å) but higher-energy emission (418 nm), while the cube isomer (3.12 Å) emits at 455 nm.

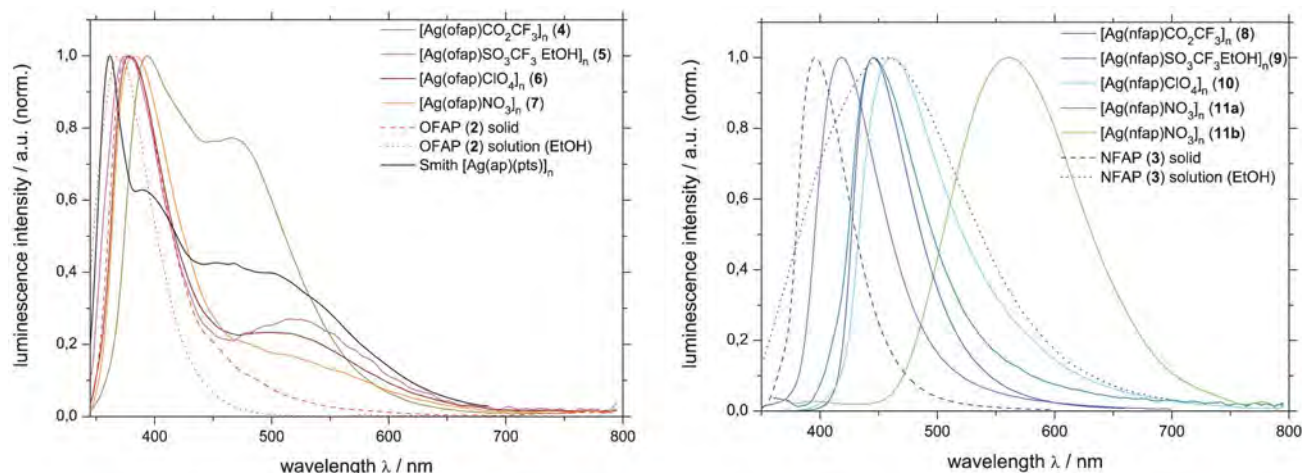


Fig. 6 Solid-state luminescence spectra of OFAP coordination compounds (left, solid lines in red and yellow shades) and $[\text{Ag}(\text{ap})(\text{pts})]_n$ (black solid line). For comparison the ligand itself in solution (EtOH, pointed line) and solid-state (dashed line) are shown again (see Fig. 2). The same indication is used for the NFAP series (right, blue and green shades). The excitation wavelength was 300 nm in all CP experiments.

Table 5 Optical and thermodynamical parameters of the silver(I) coordination polymers of **2** and **3**.

Compound	Composition	$\lambda_{\text{em.}}^{a,b}$ max./nm	$T_{\text{m}}/T_{\text{nuc.}}/T_{\text{dec.}}/T_{\text{solv.ex.}}/^{\circ}\text{C}$
4	$[\text{Ag}(\text{ofap})\text{CO}_2\text{CF}_3]_n$	393 (main), 469	238 ^c /n.a./252 ^c /—
5	$[\text{Ag}(\text{ofap})\text{SO}_3\text{CF}_3 \cdot \text{EtOH}]_n$	376 (main), 520 (weak)	244 ^c /n.a./267 ^c /113 ^c
6	$[\text{Ag}(\text{ofap})\text{ClO}_4]_n$	378, ~515 (sh.)	—/n.a./239/—
7	$[\text{Ag}(\text{ofap})\text{NO}_3]_n$	383, ~510 (sh.)	148 ^c /n.a./214 ^c /—
8	$[\text{Ag}(\text{nfap})\text{CO}_2\text{CF}_3]_n$	445	240 ^c /n.a./252 ^c /—
9	$[\text{Ag}(\text{nfap})\text{SO}_3\text{CF}_3 \cdot \text{EtOH}]_n$	418	233 ^d /n.a./n.a./n.a.
10	$[\text{Ag}(\text{nfap})\text{ClO}_4]_n$	461	—/n.a./250 ^d /—
11a	$[\text{Ag}(\text{nfap})\text{NO}_3]_n$	445	—/n.a./218 ^c /—
11b	$[\text{Ag}(\text{nfap})\text{NO}_3]_n$	560	—/n.a./210 ^d /—

^a Crystal measurements were always made from samples freshly removed from their mother liquid, washed with a minimal amount of abs. EtOH on lint-free wipes and dried on the quartz holder by a very gentle N₂ stream or simple evaporation. ^b Excited at 300 nm (also checked with 360 nm) with U340 emission and WG335 detector filter respectively. ^c Measured with a DSC instrument (see ESI). ^d Measured with a heating block instrument (see ESI). sh. = band that appears as a shoulder.

Eisenberg *et al.* reported an interesting example that demonstrates the influence of inter- vs. intramolecular separations of d¹⁰-metal ions on the photophysical properties. They obtained an emitting orange and a non-emitting colorless linear chain dimeric Au^I thiocarbamate complex, which differs in included solvent molecules. X-ray crystal structure analysis revealed similar intramolecular Au...Au separation (2.76 to 2.79 Å) but a different intermolecular separation (2.76 vs. 8.13 Å).⁷³

Also, a dinuclear aromatic formamidinato complex of Ag^I was shown to be fluorescent (446 nm) in the solid-state at room temperature.⁷⁴ The nature of luminescence could not be unambiguously resolved, but calculations show that Ag–Ag states, and more important here, contributions of the bridging ligand play a predominate role.

To complicate the picture, several examples exist where the observed metal ion interaction is not accountable for the luminescence. This is shown by a binuclear Ag^I complex where the often attributed argentophilicity was directly observed but the luminescence (420 nm in the solid-state, no possible fluorescent heterocyclic ligand present) cannot be attributed to inter-metal transitions. It was noted “that changes in metal coordination, in both ground and excited states, can dramatically alter the emissions of related systems”.²⁶

A detailed study has been carried out on a similar linear chain of a dinuclear Ag^I complex ($d(\text{Ag}–\text{Ag})$ 2.78 Å) composed of 4,5-diazospirobifluorenes and ClO₄[−] ions as ligands. No intermolecular Ag^I contacts were found ($d(\text{Ag}–\text{Ag})$ 4.58 Å) as ClO₄[−] acts as bridging ligand ($\mu\text{-}\kappa^1(\text{O})$). As a result of polarization experiments, the origin of the observed 490 nm luminescence could be shown not to originate from any Ag...Ag contact but is ascribed as “MLCT mixed, in part, with the $\pi^*(\text{ligand}) \rightarrow n(\text{ClO}_4^-)$ transition”.⁷⁵ This example shows that anion bridges, found for almost all compounds here in various geometries, are also important. Furthermore it was also noticed that the π – π stacking interaction between the adjacent chains may also play an important contribution to the luminescence phenomena, which fits in the picture drawn above about π – π interactions. Unfortunately, a definitive assignment was not possible as mixed triplet character and emission could not be ruled out.⁷⁵

A similar finding was later proposed by Guo *et al.* for a row of Ag^I complexes of 2,2-bipyridine or tetramethylammonium salts and cyanide or thiocyanate anions.⁷⁶ Emissions at ~650 nm were attributed to be MLCT type, whereby the observed 510 nm emission of one complex was attributed to be MLCT coupled with MC transitions further modified by argentophilic interactions.

Similar in spatial arrangement, but also not related in viewpoint of ligands, is a 1,8-diisocyno-*p*-menthane (dmb) CP with various silver and copper salts reported by Harvey *et al.*⁷⁷ The Ag^I CPs emit at around 500 nm at 77 K (and weakly at room temperature). The emissions were difficult to interpret as they showed polyexponential decay behaviour and a loss of polarization but are presumably MLCT in character.

Finally, an elaborated study of *N,N*-di(3-pyridyl)adipoamide as ligand for Ag^I and various anions (including pts) in terms of structural comparison is forwarded by Chen *et al.*⁷² They observe Ag...Ag as well as π – π interactions but interestingly all compounds which show luminescence near 500 nm have no Ag–Ag contacts. As usual, IL transitions are assigned tentatively for compounds which emit near the ligand emission. The origin of the shifted luminescence is described as CT character by them, “probably due to the formation of the silver(I) polymeric complexes”.⁷² It was also noted that some correlation with hydrogen bonds for the long-wavelength emission exist. One example shows both emission bands and it could be shown that a reversible transformation between these forms can be archived by extrusion/reincorporation of solvent molecules. This reminds us strongly of the example of Eisenberg *et al.* although the cause seems to be different.

In summary of the remarks and examples, it is evident that a unifying theory for the luminescence phenomena of d¹⁰-metal ion coordination polymers and networks is missing. While in certain cases comparisons to well-defined Werner-type metal ion complexes seems to be a valid choice and in other cases without much doubt only ligand-based fluorescence is observed, the above examples shows a lack of data in this field as well as a theoretical description. Seldom were quantum chemical calculations performed on this type of materials and in all cases they were, to the best of our

knowledge, restricted to model compounds and not to the ensemble of the crystal structure (e.g. ref. 77).

Discussion of 2-AP systems. For the relatively large dataset on 2-AP related systems it is appealing to search for structural reasons for the observed emission. Several dicarboxylate based CPs are given in a report by Huang *et al.*, which do not show the ligand-type emission but luminescence above 500 nm.^{15h} A closer look shows that some of these compounds inherit Ag...Ag interactions while other do not. Furthermore several different coordination environments (nearly linear and distorted tetragonal) are found for the Ag^I center in all structures (see Table 4). The luminescence emission was attributed to the usual explanation of LMCT mixed with MC transitions by the authors based on the review by Yam.²⁴

It is tempting to correlate the emission with the occurrence of linear or nearly linear coordinated Ag^I as this would fit to CP **11b** but there is also strong evidence against this hypothesis, i.e. our previously published AgNO₃-FAP CP,¹⁶ some of the *N,N*-di(3-pyridyl)adipoamide compounds of Chen *et al.*⁷² and in same manner the [Ag(4,6-diMe-ap)(bbdc)_{0.5}·0.5H₂O]_n mentioned in the report above.^{15h}

That Ag...Ag interactions can be excluded is shown by the NTA example, where one compound with a τ_5 value of 0.46 and short ligand-unsupported Ag...Ag interactions (3.020 Å) shows emission at 376 nm, while another example, a 2D sheet with τ_4 values of 0.52 and 0.78, emits at 470 nm (both exc. at 300 nm).^{15f}

Contradictorily, it was found for a related example of Huang *et al.* of a CP assembled by 2-AP and 1,2,3,4-butanetetracarboxylate as co-ligand that, next to a compound falling in the IL category, a considerably shifted variant ($\lambda_{\text{max}} = 487$ nm, exc. 330 nm) also exists. The origin of this luminescence emission was attributed to be of Ag...Ag (3.168 Å) modified LMCT type.^{15m} The same observation holds for the above mentioned BTC example which shows luminescence at 464 nm (exc. 383 nm) and two type of short Ag...Ag interactions were tentatively made responsible for this.¹⁵ⁿ

The emission wavelength values of the examples above or bathochromic shifts of the emission band fit well to most of our compounds but in summary it could be shown that the picture is inconsistent.

Description and discussion of [Ag(ap)(pts)]_n. We therefore thought the re-examination of the structural related and first reported 2-AP silver(I) CP ([Ag(ap)(pts)]_n) would clarify this issue. This system was not only interesting for historic reasons to check if CP emission had been overlooked by Smith *et al.* but also a good comparison as the arrangement of 2-AP is not twisted but linear along the CP strand, which is also found in many of our systems. Moreover no apparent structural differences in bond lengths and angles as well as the same CN at least for OTf and TFA compounds of us are found (Table 4). To our surprise [Ag(ap)(pts)]_n shows three distinctive luminescence bands, whereby the first emission (361 nm) corresponds well to the one of the ligand (357 nm), while the other two underlying emission bands (390, ~467 nm) cannot be assigned unambiguously. For instance the value of the 390 nm emission matches well with the reported phosphorescence emission of 2-AP, but this could be a coincidence. The slightly structured third band fits well with the value reported

by Fujimoto for emission of a hydrogen bonded AP-complex.³⁹ Therefore the question arises if the hydrogen bonded acid anion can be protonated by 2-AP in the excited state. However, such an explanation, as described in the ligand luminescence section, works well only for this compound due to the *p*-toluenesulfonate (pts) but scarcely for **5** and **9** because of the OTf anion.

A group of polymeric coordination compounds of silver sulfonates and N-donor ligands were also investigated by Ma and co-workers in 2005.⁷⁸ The most comparable compound consist of pyrazine and pts to give a linear double chain CP. This compound shows an emission at 493 nm (exc. 330 nm), while others only show ligand-related luminescence. However, the cause of the luminescence is only phenomenologically described by the authors.

Description and discussion for the FAP series. We already excluded Ag...Ag interactions for our CPs incorporating **1** as ligand earlier because no short Ag-Ag distances are found (Table 4).¹⁶ Although in this study the TFA CPs **4** and **8** show different structures with close, ligand supported, Ag...Ag contacts below the vdW threshold, no correlation is apparent in luminescence spectroscopy.

π - π interaction can be ruled out for both structures and the dihedral angle ϕ is most different in value here (53.1(4)° for **4** vs. 34.0(9)° for **8**) and can therefore not be held responsible. In summary, the origin of the emission peak at 469 nm is unclear for the OFAP-based CP **4**. The only noticeable difference is the F_{TFA}- π_F interaction in **4**.

Otherwise, the OFAP series corresponds well to our previously investigated FAP system but the long-wavelength emission is less pronounced and often only visible as a shoulder. As shown before, the ratio of the different emissions depends in part on the excitation wavelength, which proves that both are independent states. The overall spectra is dominated by the OFAP ligand emission (376 nm) at 300 nm excitation. The ligand band of CP **4** shows a marginal red-shift (17 nm, 1150 cm⁻¹) of the main band but a more pronounced and red-shifted shoulder at 469 nm, which is unique (Fig. 6).

In contrast, all NFAP CPs **8-11a** show a moderate shifted emission band, often slightly broadened. The shift of **8**, **10** and **11a** (avg. 55 nm, 3900 cm⁻¹) corresponds well to the second deconvolved emission band (464 nm) of the solution spectra of **3** alone (Fig. 2). CP **9** shows only a moderate shift (23 nm, 1390 cm⁻¹) and peaks between the pure ligand solid-state emission at 395 nm and the second deconvolved emission band. Furthermore the differences between the emission properties of compounds **5** and **9** are noticeable. From the crystal structure comparison with the AgOTf CPs of the FAP ligand **1** in our previous work one would conclude that CP **9** need not be luminescent.¹⁶ The observed emission can be attributed to the change in optical properties (and presumably electronic states) of the NFAP ligand and therefore to the overall electronic nature in the crystal as seen in the band gap calculation (Fig. 5).

In the case of the yellow crystals of **11b** one clear maximum at 560 nm is observed (Fig. 2), which in comparison to **11a** gives rise to the question of how this difference can be explained. It is emphasized again here that **11b** has no apparent Ag...Ag interactions but is highly ordered as intra-

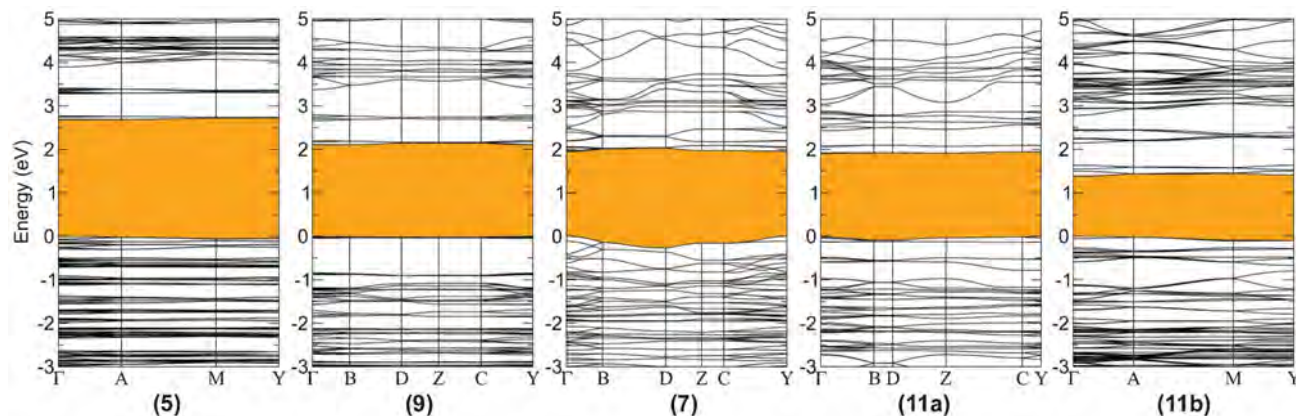


Fig. 7 Electronic band structure for AgOTf compounds **5** and **9**, and the AgNO₃ series **7**, **11a**, and **11b** of the OFAP (**2**) and NFAP (**3**) ligand respectively as calculated by DFT-GGA. Different to ref. 45, the notation of the high symmetry *k*-points is related to the unique *b*-axis.

and inter-strand Ag–Ag distances are almost equal (Table 4). Compound **11a** on the other hand shows the same emission as other NFAP compounds and can serve as a representative example.

DFT calculations for periodic structures

Due to the size of the supercells to be modeled, and the large number of atoms (*cf.* Table 3), we restrict our plane-wave DFT calculations to the most interesting configurations in terms of isomorphism and polymorphism. Compounds **5** and **9** are interesting to consider because of the structural similarities to CPs of the parent FAP ligand (**1**) of our previous work. The AgOTf CP of **1** crystallized from ethanol is a crystallographic isomorph of compound **5**. The CP of **1** crystallized from 2-propanol in a crystallographic isomorph of compound **9**. The unit cell dimensions are almost the same (**5** 3900 Å³ vs. FAP-EtOH 3682 Å³; **9** 2062 Å³ vs. FAP-iPrOH 2008 Å³) and the space group of the isomorphous CP pair is identical (*C2/c* vs. *P2₁/c*, for further data see Table 4). The electronic ground state for the AgOTf compounds **5** and **9** was obtained using a Brillouin zone sampling of 1 × 2 × 2 and 2 × 2 × 1 *Γ*-centered *k*-points sets, respectively, while for the AgNO₃ series 1 × 3 × 2 (**7**), 3 × 1 × 2 (**11a**), and 3 × 1 × 2 (**11b**) sets were used. Studying these systems can be helpful to clarify the influence of the different ligands. For the calculated band structure of AgNO₃–FAP CP see our previous study.⁴⁵

The bands at the valence and conduction band edge of compounds **5** and **9** show very little dispersion (Fig. 7, left). The OFAP-based AgOTf CP has a similar fundamental gap as observed for the corresponding FAP CP earlier (about 2.7 eV). Turning to the NFAP ligand the electronic states change: the band gap of **9** is about 0.5 eV smaller, and a small band splitting of the lowest unoccupied states occurs around the *Γ* and *Y* point. The energetically higher lying states show a stronger dispersion. Although this value does not fit the emission behaviour it clearly demonstrates the influence of the ligand.

For the AgNO₃-systems of OFAP and NFAP, including the polymorphic compounds **11**, a different picture emerges. As described in the crystal section, compounds **7** and **11a** share

the same NO₃[−] mediated inter-strand connection but along different crystal axes. The previously investigated AgNO₃–FAP CP had again a different ligand and anion arrangement (zigzag) but the same μ - κ (O,O′) anion-bridge. The band gap was calculated to about 2.3 eV. The difference between OFAP (**2**) and NFAP ligand (**3**) for **7** and **11a** diminishes (band gap shortly below 2 eV, Fig. 7, right) while some cell parameters *e.g.* crystal system, space group and volume are again comparable (Table 3). The exact structure of the state levels along the high symmetry points seems to be dictated by the coordination details as it differs again from the FAP AgNO₃ system investigated earlier. The FAP CP shows some dispersion at the band edges and a (comparatively small) band splitting at the *Γ* point for many states.

With the change in coordination geometry of ligand and anion in **11b** and the corresponding change in crystal parameters a remarkable difference results: the band gap is calculated to be further reduced by 0.5 eV and is dispersed towards the *Γ* point although still shallow in level. This is, to some extent, verified by the simple observation that the crystals of **11b** are yellow in color, although one has to be cautious about the absolute value of the band gap or any prediction of luminescence. As we have shown in our previous study,⁴⁵ the well-known DFT band gap problem leads to drastically underestimated (by more than one eV) excitation energies for the systems considered here. Still, the qualitative trends turn out to be quite reliably described in DFT-GGA when comparing different systems as well as the calculated band dispersions.

To gain deeper insight into the role of the different CP parts in the electronic properties of the crystalline materials as described by the band structure we calculated the density of states (DoS) for compounds **10**, **11a**, and **11b** within DFT-GGA deconvolved for the different functionalities (Fig. 8). Here, we chose AgClO₄ compound **10** as the best comparable example to **11a** in terms of crystal parameters (Table 3) but in favor also comparable to **11b** in terms of connectivity because it consists of individual double strands bridged in a symmetrical fashion. The difference is a μ - κ ²(O,O′) ClO₄-bridge for a double strand

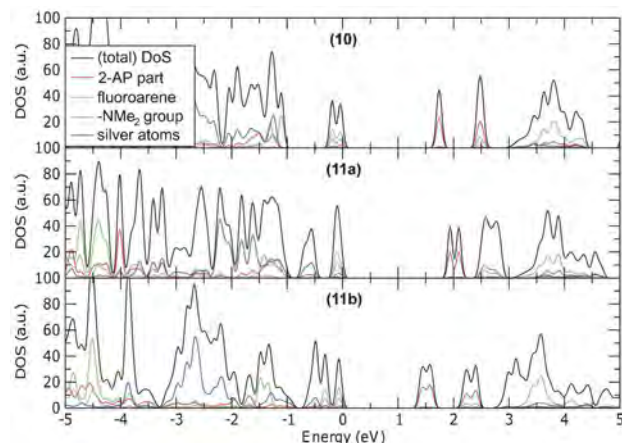


Fig. 8 Density of states (DoS) for **10**, **11a**, and **11b** from DFT-GGA. Contributions to the DoS from different molecule parts of the CP in the crystal ensemble are shown in color.

in the case of **10** while **11b** is connected by a $\mu\text{-}\kappa^1(\text{O})$ NO_3^- bridge.

For all compounds these calculations show that the HOMO states at the band edge are composed of contributions of the dimethylamino group and the fluoroarene itself and marginally also of the 2-AP part but not of any Ag^{I} -centered states. Therefore, MLCT transitions can be excluded. Larger contributions of the Ag^{I} ion but no contribution of the tail-group are visible in the next lowest states for the nitrate-CPs **11a** and **11b**. These populated states are entirely missing for **10** but the pattern becomes then similar below -1 eV for all compounds (Fig. 8).

The LUMO and to a large extent also the next higher states are almost pure 2-AP associated states. However, a very small contribution of the Ag^{I} ion is visible in the DoS projection, which theoretically enables state mixing and LMCT pathways. Nevertheless the main contributions are resembled by the isodensity orbital plots (Fig. 9) where at first glance the contribution of the tail group on the HOMO is visible (white), while the LUMO is located on the 2-AP part (red). No

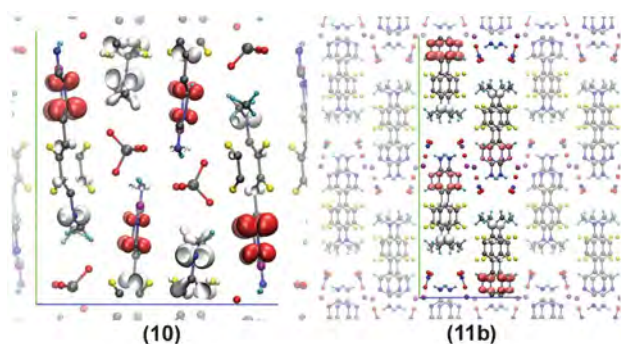


Fig. 9 Isodensity plots of HOMO (white) and LUMO (red) for the best comparable systems **10** and **11b** as calculated by DFT-GGA. Atoms outside of the unit cell are faded. The color scheme is identical to Fig. 3 but hydrogen atoms are drawn in light blue.

significant electron density was found on the bridging anions. It is important again to note that $\text{Ag}\cdots\text{Ag}$ interaction can be ruled out for **11b** (see $\text{Ag}\text{--}\text{Ag}$ distances) as an explanation for the 165 nm shift observed. However, due to the high order, the inter-strand $\pi_{\text{F}}\text{--}\pi_{\text{F}}$ interaction might be important for delocalization as overlap of the orbital clouds is given in view of the spatial arrangement of the HOMO and LUMO. CP **11b** is the only compound that shows clear $\pi_{\text{F}}\text{--}\pi_{\text{F}}$ interaction in the whole CP series, which can, in converse argumentation, not be attributed by modeling of the repetition unit or a dimeric model-compound alone and make a more complete theoretical description of the crystal lattice, as described above, imperatively necessary. In summary these DoS calculations show that no simple picture can be drawn for correlation of electronic effects in CP materials but ligand effects due to special spatial arrangement might be underestimated as an explanation of odd luminescence emission behaviour

Conclusions

In summary, it could be shown that the previous published FAP ligand (**1**) can be easily modified by $\text{S}_{\text{N}}\text{Ar}$ reaction in the *para*-position giving derivatives with different electronic and steric properties to assemble coordination compounds. In optical spectroscopy this substitution has a visible effect for the NFAP ligand (**3**), which infers that a different order of electronic states exists. For the latter structure, parameters could also be obtained by single crystal X-ray analysis, while for the other ligands **1** and **2** molecular structure data could only be generated by DFT calculations. A tentative IR assignment for the ligands and their changes upon incorporation in CPs† is given by comparison with 2-AP, literature reports, and our DFT calculations. Only subtle changes are observed, which can act as markers for distinction of the ligands and ligand coordination.

Synthesis and structure elucidation of low-dimensional CPs **4–11** have been accomplished with a range of silver salts and the ligands **2** and **3**, allowing comparison to previous studies: a comprehensive comparison of structural parameters with literature systems is given and summarized in Table 4.

Most of the presented CPs show new coordination architectures that differ from the usual 2-AP zigzag chain pattern due to the introduction of fluoroarene tail-groups. Often, the typical out-of-plane bending of AP is diminished and nearly (**6**) or highly linear (**7**, **8**, **10**, **11a**, **11b**) arrangements are found. An exception are the AgOTf CPs (**5**, **9**) where a coordinating solvent replaces the anion and isomorphous compounds to previous studies are obtained with a similar chain repetition length (7.5 Å).¹⁶

The crystal packing is influenced by anion-mediated contacts to form double strands (**10**, **11b**) or 2D networks (**4**, **6**, **7**, **11a**), but also by involvement of secondary interactions. In particular, hydrogen bond patterns seem to govern the packing for $\text{CN} = 3$ compounds (**5**, **9**; both $\text{R}_4^4(12)$) but exceptions exist (**8**; $\text{C}(6)\text{C}(6)$). In other cases hydrogen bonds additionally stabilize the structures (by chain patterns *vs.*

R_4^{12}) as seen for NO_3^- CPs (**7**, **11a**, **11b**) or unidirectional motifs in ClO_4^- CPs (**6**, **10**). Furthermore, we identify F- π_F interactions which overcome pure packing effects (**4**), π_F - π_F stacking effects (**11b**), and Ag-Ag distances clearly below the vdW threshold (**8**, less **4**).

Despite the large differences in their structures (except for **5** and **9**), some statements about structure-property relationships can be established for the luminescence spectroscopy as a probing technique. Most striking is the comparison between the polymorphic forms of **11**; with the transition from colorless to yellow crystals and a concomitant shift of cyan-colored emission to green luminescence.

It is tempting to correlate the observed spectral shift with the coordination environment of Ag^I within the CP strand. However, by reviewing the literature, this hypothesis cannot be held (see Luminescence section). Although **11b** appears to be more linear, the τ_4 value of both polymorphs are identical (0.67), but below the predominant values of the series (0.71 and 0.78).

Again, except for **11b**, these CPs are unremarkable in terms of luminescence and within the emission range of the ligand alone. Any influence of the emission by electronic conjugation of the -NMe₂ group (measured by the twist angle) can be ruled out as the values are akin for **11a** and **11b** and even lower (**10**). The largest coefficient of the HOMO is located on this part as seen from DFT-GGA calculation but even for CPs with values close to the gas-phase (**9**, 87.3° vs. 89.0° (calc. for **3**)) no drastic changes in luminescence are observed.

In the same manner, there is no evidence for correlation between the dihedral twist angle ϕ between the two arene units and observed emission. To illustrate, the AgTFA CPs **4** and **8** have the most deviant dihedral angle ϕ in the series but their emission spectra are dominated by ligand contributions.

This is especially interesting as these two CPs also show different extents of Ag...Ag interactions. Various examples of d¹⁰M...d¹⁰M interactions and the impact on luminescence are given in the appropriate section. CP **8** possesses the lowest value (3.049(5) Å) encountered for all 2-AP systems to date (Table 4) but the emission is almost identical to CPs without such interactions (**10**, **11a**).

One noticeable difference for **4** is the F_{TFA}- π_F interaction. A pronounced shoulder (a second emission band) is found on the low energy tail of the luminescence spectra. Similarly, π_F - π_F interactions are found for **11b** due to the highly parallel alignment and this is the most obvious difference to **11a**. Therefore we attribute the shifted emission to these interactions in the crystal lattice. Unfortunately, no such interactions are found in **8** for direct comparison due to slight displacement of the individual strands. Within DFT-GGA a smaller band gap is found for **11b** but no apparent effects in the correlation of different molecular parts on the density of states are visible to explain the differences (Fig. 8)

In conclusion, it is still impossible to correlate structure with the observed emission or predict the outcome. Furthermore, the excited state photochemistry of 2-AP and

fluorescence alteration should be kept in mind if suitable hydrogen bond patterns are present.

More detailed photophysical studies in this field of MOF-like coordination compounds are necessary to clarify which structural mechanisms are responsible for the luminescence.

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