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ARTICLE TYPE

N-salicylidene aniline derivatives based on the *N′*-thiophosphorylated thiourea scaffold

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New family of *N′*-thiophosphorylated thiourea-containing *N*-salicylidene aniline derivatives (anils) of the common formula 6-{(2-OH-aryl)–CH=N}-Py-2-NHC(S)NHP(S)(O*i*Pr)$_2$ [aryl = C_6H_4 (**2**), 5-Cl-C_6H_3 (**3**), 5-Br-C_6H_3 (**4**), 3,5-Cl_2-C_6H_2 (**5**), 3,5-Br_2-C_6H_2 (**6**)] have been synthesized by the condensation of *N*-thiophosphorylated thiourea 6-NH_2-Py-2-NHC(S)NHP(S)(O*i*Pr)$_2$ (**1**) with the corresponding salicylaldehyde. Compound **2** was obtained by dissolving of **1** in pure salicylaldehyde, while anils **3–6** were synthesized in EtOH. Synthesis in EtOH with aniline led to X-ray suitable crystals of **1**, which crystal structure was challenging so far. All compounds were characterized by elemental analysis, NMR, diffuse reflectance and fluorescence spectroscopy. The crystal structures of **2–6**, elucidated by X-ray diffraction, are stabillized by two intra- and two intermolecular hydrogen bonds and a broad network of intermolecular π···π stacking interactions. Compounds **2** and **6** trapped salicylaldehyde and ethanol molecules, respectively, in their crystal structures through the formation of intermolecular hydrogen bonds. Molecules **3–6** show the presence of a mixture of enol, *cis*- and *trans*-keto forms in the solid state at room temperature. Only two former forms are observed for **2**. Compounds **2–6** are exclusively thermochromic, while no photochromism was observed regardless of the irradiation wavelength and time.

Introduction

Crystal engineering[1] is one of the most powerful tool for new materials with desirable structures and properties. Non covalent interactions seem to be the most effective driving force for molecular aggregates and assemblies.[1,2] Hydrogen bonds and π···π stacking interactions are the most efficient approaches for rational design.[3] Furthermore, (di)halogen interactions, being first recognized in the second half of 19th century,[4] are also of great importance for directing intra- and intermolecular assemblies and, thus, tuning supramolecular aggregations.[5] In this frame, the (thio)urea group is frequently used as a crystallizing building block since it contains both hydrogen donors through the NH groups and acceptor centres through the C=O or C=S groups.[6] Facile ways to modify (thio)urea, with a wide range of functional groups at the nitrogen atoms, makes these molecules very attractive.

We have extensively studied the synthesis, membrane transport, extraction, separation and complexation properties of *N*-(thio)phosphorylated thioureas RR′NC(X)NHP(Y)(O*i*Pr)$_2$ (X, Y = O, S) (**NTTU**).[7] The easiest synthetic way of **NTTU** is the reaction of primary or secondary amines with the corresponding (thio)phosphorylated isocyanates.[7a] The main advantageous of this synthetic procedure is the ability to work with molecules having one or more amine groups as a starting amine. Depending on the nature of the donor C=X and P=Y atoms, as well as on the presence of the NH fragment at the (thio)carbonyl group, a number of hydrogen bonded structures were observed in crystals of **NTTU**.[7a,f,8] The influence of the R and R′ substituents is also crucial for the formation of assemblies in crystals. Thus, investigation of **NTTU** is an outstanding and evergrowing branch of crystal engineering.

On the other hand, *N*-salicylidene aniline derivatives (anils) can be highlighted among the rare classes of molecules, that exhibit solid state thermo- and photochromic properties,[9] which arise from a proton transfer between an uncoloured enol form and a yellow *cis*-keto form and/or a red *trans*-keto form. In general, it was recognized, that the solid state thermochromism of anils is the evidence of essential planarity of single molecules with a low dihedral angle between phenolic and benzoic rings (Φ < 25°).[10] These molecules are closely packed in their crystal lattice thanks to π···π and/or CH···π interactions. Photochromism is caused by a significant rotation (Φ > 25°) and the formation of an open crystal packing, which favour the formation of the *trans*-keto form.[9b,c] However, it is currently impossible to correctly explain photo- and thermochromism of anils solely on the basis of their crystal structures. Energy differences between ground and excited states must also be taken into account,[11] together with a complete crystal structure determination. We have recently revisited optical *vs.* structural property relationships on this class of molecules based on crystal engineering concepts focusing on amino(methyl)pyridine,[12] tetrazoles,[13] phenanthroline,[14] 1,2,4-triazoles,[13,14] crown ethers,[15] polyamines,[16] sulfonate [17] and pyrene derivatives.[18]

Herein, we report five new *N′*-thiophosphorylated thiourea-

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containing *N*-salicylidene aniline derivatives (anils), containing various acceptor and donor centers (Chart 1). While the *N*′-thiophosphorylated thiourea fragment remained constant for all compounds, the *N*-salicylidene aniline function was modified by incorporation one or two halogen (Cl or Br) atoms. The crystal structures and packing of all new compounds as well as the starting *N*-thiophosphorylated thiourea 6-NH_2-Py-2-NHC(S)NHP(S)(O*i*Pr)$_2$ were elucidated by X-ray diffraction. Optical and fluorescent properties of have also been studied in detail.

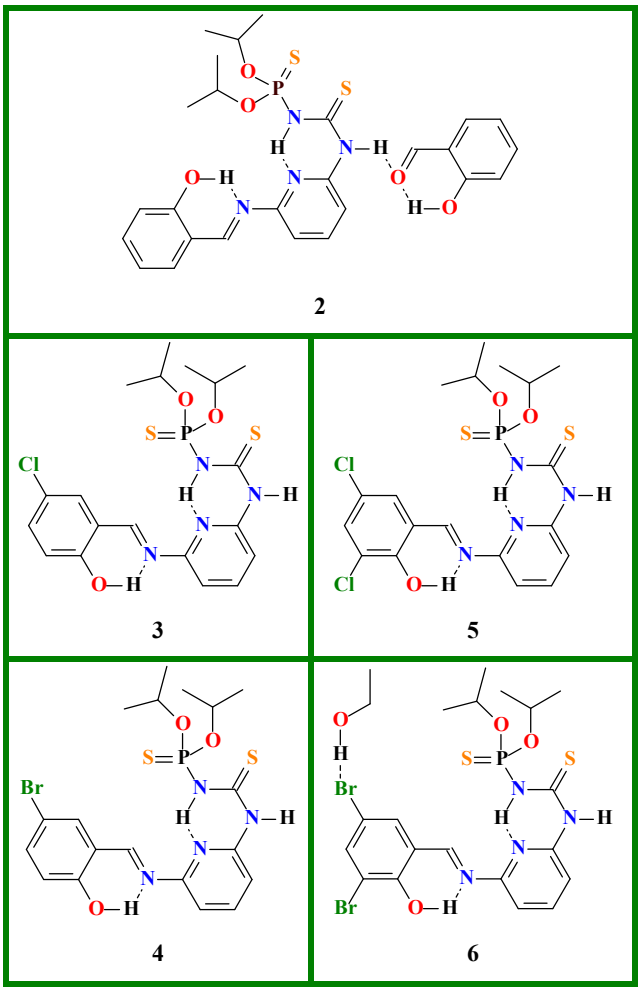
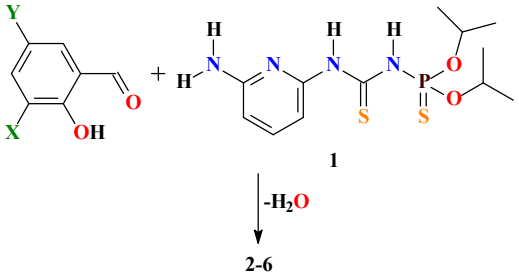


Chart 1

Results and discussion

Synthesis

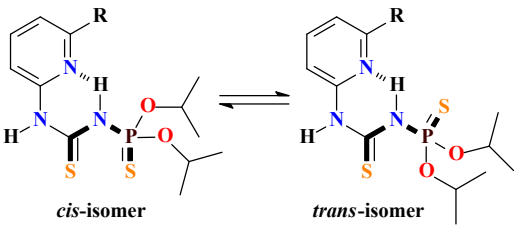
Anils **3–6** were readily synthesized with high yields by reacting *N*-thiophosphorylated thiourea 6-NH_2-Py-2-NHC(S)NHP(S)(O*i*Pr)$_2$ (**1**) with the corresponding salicylaldehyde in ethanol (Scheme 1). Using the same procedure with aniline surprisingly led to the formation of X-ray suitable crystals of **1**, which X-ray suitable crystals were challenging so far.[19] Compound **2** was however obtained by dissolving **1** in pure salicylaldehyde. These compounds are crystalline solids, which are soluble in most polar solvents and insoluble in aliphatic solvents.



X = Y = H (2);
X = H, Y = Cl (3), Br (4);
X = Y = Cl (5), Br (6)

Scheme 1 Preparation of **2–6**

$^{31}P\{^1H\}$ NMR spectra of **2** and **5** in DMSO-d_6 each contain a singlet peak at 56.7 and 57.5 ppm, respectively. The phosphorus spectra of **3**, **4** and **6** exhibit two peaks at 57.4–57.7 and 58.2–58.5 ppm. The relative integral intensity ratio changes from about 2:1 to 2.5:1 for the high- and low-field signals, respectively. These signals are in the same region as for the starting thiourea **1** and its close analogue Py-2-NHC(S)NHP(S)(O*i*Pr)$_2$,[20] and in the area characteristic for **NTTU** (X = Y = S).[7a] It is known that for **NTTU** the hindered rotation around the C–N(P) bond may significantly influence on the chemical shift of the phosphorus nuclei.[7a,21] This hindered rotation causes the formation of *cis*- and *trans*-isomers (Scheme 2). On the other hand, the zwitterion formation, due to the migration of the NH(P) proton to the pyridine nitrogen atom, can be also tentatively suggested. This might be further supported by an efficient intramolecular hydrogen bonding between the pyridine nitrogen atom and the hydrogen atom of the phosphoramide fragment. The pK_a values for pyridine (pK_a = ~0–10)[22] and **NTTU** (pK_a = 6.93–11.7)[7a] derivatives vary in a wide range, depending on both the nature of substituents and solvents. Thus, the pyridine fragment might possess basic nature, while the NH(P) group is acidic due to the electron withdrawing groups C=S and P=S. Two signals were also recently observed in the $^{31}P\{^1H\}$ NMR spectra of *N*-(thio)phosphorylated thiosemicarbazides $NH_2N(R)C(S)NHP(X)(O*i*Pr)_2$ (R = Me, Et; X = O, S) and 2-pyridine-containing **NTTU** (X = S, Y = O, S).[7g,20a,23]



Scheme 2

The ^1H NMR spectra of **3**, **4** and **6** in the same solvent also contain two sets of signals due to two different isomers, while the

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spectra of **2** and **5** each exhibit one set of peaks. The spectra reveal signals for the *i*PrO protons: peaks for the CH_3 protons at 1.24–1.41 ppm and a doublet of septets for the CHO protons in the area 4.71–4.96 ppm. The signals for the pyridine and benzene fragments were found at 5.89–8.13 ppm, while the CHN and OH protons were shown as singlet peaks at 9.20–10.16 and 13.20–14.11 ppm, respectively. The spectra also exhibit signals for the PyNH and NHP protons at 9.27–11.57 and 11.15–12.96 ppm, respectively. Furthermore, the proton spectra of **2** and **6** contain signals for the co-crystallized salicylaldehyde and ethanol molecules, respectively.

Structural Aspects

Crystals of **1** and **3–6** were obtained by slow evaporation of their ethanol solutions, while crystals of **2** were formed in the pure salicylaldehyde. It should be noted that several single crystals of each compound have been checked by X-ray diffraction identifying their identity. The molecular structures and crystal packing are shown in Figures 1–5 and 6, respectively, whereas the crystal and structure refinement data are given in the Experimental section.

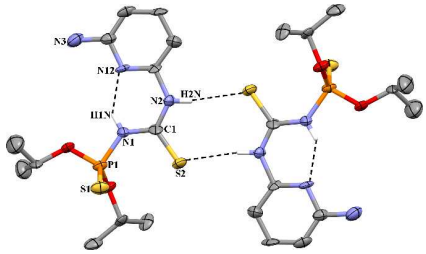

Fig. 1 Thermal ellipsoid (50%) plot of **1**. H-atoms, not involved in hydrogen bonding, were omitted for clarity.

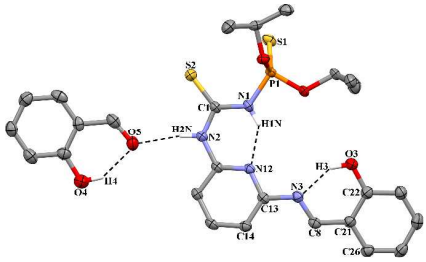

Fig. 2 Thermal ellipsoid (50%) plot of **2**. H-atoms, not involved in hydrogen bonding, were omitted for clarity. The molecule of salicylaldehyde is at equivalent position ($1-x$, $1-y$, $1-z$).

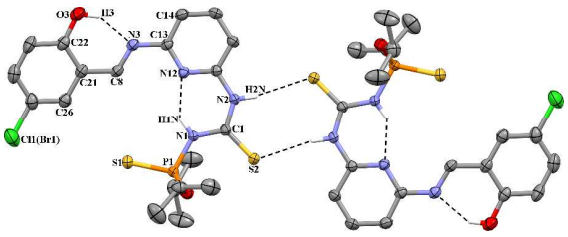

Fig. 3 Thermal ellipsoid (50%) plot of **3** and **4**. H-atoms, not involved in hydrogen bonding, were omitted for clarity.

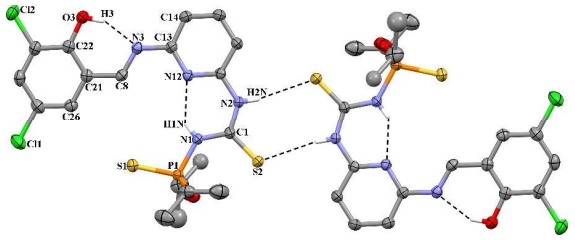

Fig. 4 Thermal ellipsoid (50%) plot of **5**. H-atoms, not involved in hydrogen bonding, were omitted for clarity.

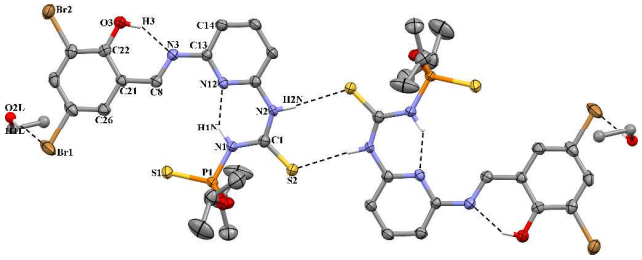

Fig. 5 Thermal ellipsoid (50%) plot of **6**. H-atoms, not involved in hydrogen bonding, were omitted for clarity.

Molecules **1** and **6** crystallize in the monoclinic space groups $P2_1/c$ and $C2/c$, respectively, while the structures of **2–5** each were refined in the triclinic $P\bar{1}$ space group. It should be noted, that **3–5** are almost isostructural. Compounds **2** and **6** trapped salicylaldehyde and ethanol molecules, respectively, in their crystal structures through the formation of intermolecular hydrogen bonds. Furthermore, the structure of **2** differs significantly from those of **3–6** thanks to the phenolic fragment of a molecule, which is rotated to a different side relative to the pyridine ring. Molecules **2–6** were found in the enolimine form (Fig. 2–6). Indeed, the bond lengths O(3)–C(22) and C(8)–C(21) indicate single bonds, whereas a double bond is confirmed for N(3)–C(8) which identifies the enol form (Tables S2–S6 in ESI†). The bond lenghts and bond angles in the benzene and pyridine fragments of all molecules are within the typical values. The dihedral angles Φ between the pyridine and benzene rings are 18.89(14), 8.24(15), 6.44(16), 7.99(12) and 11.4(3)° for **2–6**, respectively, which would call for exclusive thermochromic properties.[3] However, this is less pronounced for **2**, which exhibits a much higher dihedral angle Φ, compared to that of **3–6**. This is also supported by the two torsion angles N(12)–C(13)–N(3)–C(8) and C(14)–C(13)–N(3)–C(8) (Table S1–S5 in ESI†).

The parameters of the C=S, C–N, P–N and P=S bonds are in the typical range for **NTTU** (X = Y = S) (Tables S1–S6 in ESI†).[7,8] However, the S=C–N–P=S backbone in **1** and **2** has a *cis*-conformation (Fig. 1 and 2), while the same fragment has a *trans*-conformation in the structures of **3–6** (Fig. 3–5). The crystal structures of all compounds each stabillized by an intramolecular hydrogen bond of the type N(1)–H(1N)···N(12), formed between the hydrogen atom of the NHP group and the nitrogen atom of the pyridine fragment within the thiourea scaffold (Fig. 1–5, Table S7 in ESI†). The remaining PyNH proton and the thiocarbonyl sulfur atom in the structure of **1** and **3–6** are involved in the intermolecular hydrogen bonds of the

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type N(2)–H(2N)···S(2) formed between two neighbouring molecules (Fig. 1–5, Table S7 in ESI†). The same PyNH hydrogen in the structure of **2** forms however an intermolecular hydrogen bond with the carbonyl oxygen atom of the co-crystallized salicylaldehyde molecule (Fig. 2, Table S7 in ESI†). The latter O-atom is further involved in the intramolecular hydrogen bonding with the OH proton from the hydroxyl group (Fig. 2, Table S7 in ESI†). The crystal structures of **2–6** are additionally stabilized by an intramolecular hydrogen bond of the type O(3)–H(3)···N(3), which is formed between the hydrogen atom of the OH group and the nitrogen atom of the imine group (Fig. 2–5, Table S7 in ESI†). One of the bromine atoms in the structure of **6** forms an intermolecular hydrogen bond of the type O(2L)–H(1L)···Br(2) with the H-atom of the hydroxyl group of the ethanol molecule (Fig. 5, Table S7 in ESI†).

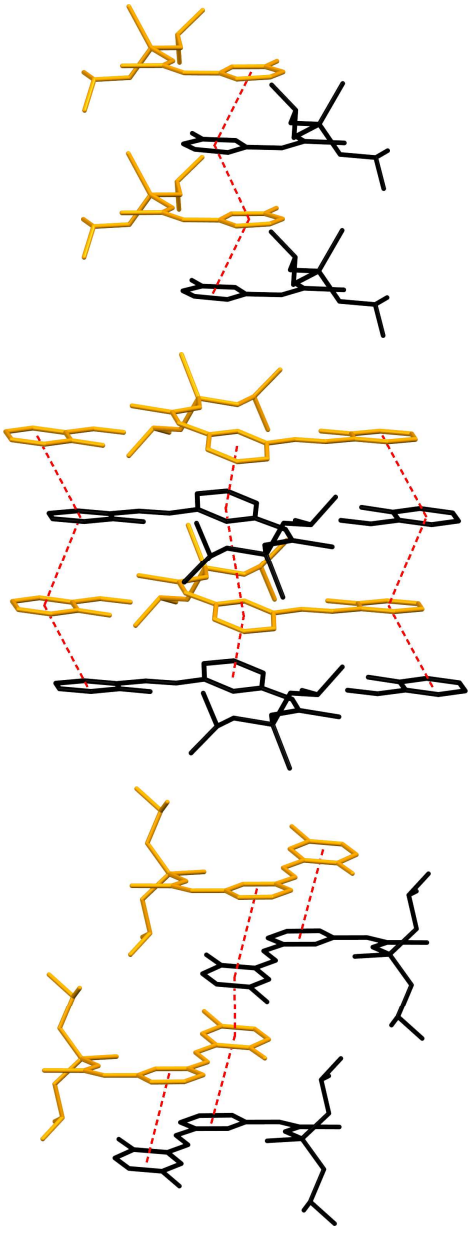

Fig. 6 Stick best views of the crystal packing of **1** (top), **2** (middle) and **3** (bottom). The crystal packing of **4–6** is similar to **3**. H-atoms were omitted for clarity.

Additionally, molecules in the crystal structures of **1–6** are stacked through π···π stacking interactions between the aromatic rings (Fig. 6, Table S8 in ESI†). While the strcuture of **1** forms 1D polymeric pillars with molecules being packed head-to-head, compound **2** exhibits 1D polymeric ribbons, where the anil molecules are stacked with each other exclusively through the pyridine functions, exhibiting a head-to-head packing, and the phenolic groups are involved in the stacking with salicylaldehyde molecules. The crystal packing of **3–6** is very similar with the formation of dimers, which are packed head-to-tail. These dimers are further stacked in a head-to-head manner.

Most interestingly, C–X···X–C (X = Cl, **3** and **5**; X = Br, **4**) dihalogen bonds were identified in **3–5**. These bonds are formed between the 5-Cl (**3** and **5**) or 5-Br (**4**) atoms of neighbouring dimers, which are formed through intermolecular N(2)–H(2N)···S(2) hydrogen bonds (Chart 2). The C–X···X angles in **3–5** are 152–155° (Tables S9 in ESI†). The R_{XX} dihalogen distances, the normalized X···X bond lengths to the van der Waals radii of the different halogen atoms, indicate that the Br···Br bond is stronger compared to that of the Cl···Cl interactions (Table S9 in ESI†). This observation is in agreement with the literature background on the halogen bonds of organic compounds.[24]

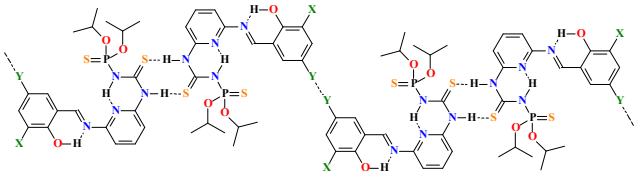

Chart 2 The simplified line diagram of dihalogen interactions in the structures of **3** (X = H, Y = Cl), **4** (X = H, Y = Br) and **5** (X = Y = Cl).

Bulk samples of **1–6** were studied by means of X-ray powder diffraction analysis (Fig. S1–S3 in ESI†). The experimental X-ray powder patterns are in full agreement with the calculated ones obtained from single crystal X-ray diffraction. This validates a single phase for the microcrystalline powders used in the optical properties sections. Other possible phases (e.g. *trans*-keto form) were not observed in the powder patterns due to concentrations below the resolution of X-ray powder diffraction.

Optical Properties

Microcrystalline powders of **3–6** change the original colour at 298 K (see the Experimental section) to yellow or pale yellow on cooling to 77 K. This colour change arises from the keto-enol tautomerisation. No thermochomism was noticed for **2**.

Diffuse Reflectance Spectroscopy

Molecules **1** and **2–6** were analysed by diffuse reflectance spectroscopy at 298 K as microcrystalline powders (Fig. 7). The spectrum of **1**, for which a Kubelka-Munk (KM) treatment was applied, contains a broad absorption band, with three maxima at 260, 300 and 345 nm, exclusively in the UV region. These absorptions correspond to intraligand n-π and/or π-π* transitions. The KM spectra of **2–6** exhibit three band regions: a broad range in the UV region, corresponding to the enol form of the *N*-

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salicylidene aniline fragment, accompanied with the band from the thiourea scaffold; a second range in the visible region from about 400 to 530 nm, originating from the *cis*-keto form; and a third range above 530 nm originating from the *trans*-keto form. However, no *trans*-keto form was observed in the KM spectrum of **2** (Fig. 7). At first sight, it could seems contradictory to observe three (or two for **2**) types of molecular structures whereas the crystal structures only reveal the enol form (Fig. 1–5). It is however known that when the keto form is present in too low concentration, it cannot be detected by X-ray diffraction.[9b,c]

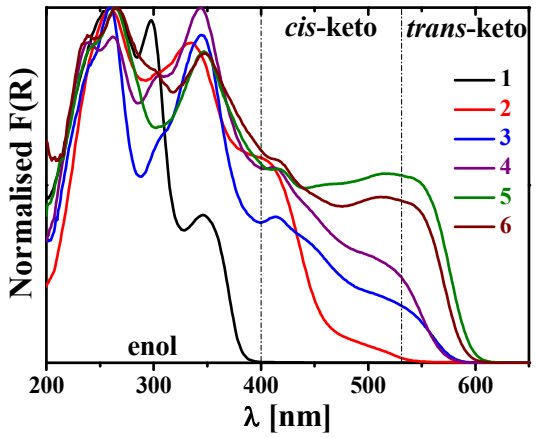

Fig. 7 Normalised Kubelka-Munk spectra of **1–6** at 298 K.

Recently, several examples revealing the presence of *trans*-keto form in the ground state have been reported.[12,13,15] This phenomenon must be considered both from the energy differences between the excited and ground states, as well as from structural aspects. As mentioned in the X-ray description part, compounds **3–6** each exhibit a close packed structure with dihedral angles Φ between aromatic rings being significantly less than 25°, which favor exclusive thermochromic properties[10] thanks to the proton transfer between both *cis*-keto and enol forms. We have recently established that both head-to-head and head-to-tail packing of molecules in the structures of benzo-15-crown-5-N=CH–(2-OH-C_6H_4)[15] and *N*-(3,5-dichlorosalicylidene)-1-aminopyrene,[18] respectively, are responsible for photochromic properties, thus being mainly driven by the nature of substituents in the *N*-salicylidene aniline scaffold and thereby the crystal packing. Compounds **3–6** feature head-to-head and head-to-tail packing for dimeric aggregates and between these dimers, respectively (Fig. 6, see X-ray description above), which might thus favor photochromism. However, presence of the bulky (iPrO)$_2$P(S)NH fragments prevents any rotation/motion and therefore no photochromism. The same holds for **2**, due to the presence of guest salicylaldehyde molecules, which, in turn, fill the interphenolic space between the equally oriented molecules (Fig. 6). Furthermore, efficient halogen interactions in the structures of **3–6** might also disadvantage photochromism.

Molecules **2–6** were also analysed by diffuse reflectance spectroscopy upon irradiation at λ = 254, 365, 450 and 546 nm in order to photo-address the enol and keto forms. No photochromism was noticed regardless of the irradiation wavelength and time.

Solid State Fluorimetry

Solid state fluorimetric studies of **2–6** were undertaken to examine energy levels responsible for the optical properties. The emission spectra of microcrystalline powders of **2–6** at λ_{exc} = 400 nm, which corresponds to the band of the *cis*-keto form in the diffuse reflectance spectrum, are given in Figure 8. Two bands of the same intensity were observed in the spectrum of **2** at 555 nm and 565 nm. One of these bands is red-shifted to 590–595 nm in the spectra of **3** and **4**, while the second band, now being significantly less intense, remained constant and was found as a shoulder of the main band (Fig. 8). The main band is further red-shifted to 620 nm in the spectra of **5** and **6**, while the high energy shoulder shows very low intensity. These bands are presumably due to the *cis*-keto* to *cis*-keto relaxation. All spectra contain a third emission band centred at about 650 nm, which is assigned to the radiative relaxation of the *trans*-keto* form (Fig. 8), which can be formed through the absorption of enol, *cis*-keto and *trans*-keto forms in their ground state. Thus, incorporation of halogen atoms, varying their number (**1** or **2**) and nature (Cl or Br), leads to the observed red-shift of the main band in the fluorescence spectra within the following trend: **5** = **6** > **3** ≈ **4** > **2**. The almost vice versa trend is observed for the intensity decrease of the high energy band, centered at about 550 nm, and low energy band, centered at about 650 nm, as a shoulder. Furthermore, the energy of the main band strongly depends on the number of halogen substituents but not on their nature.

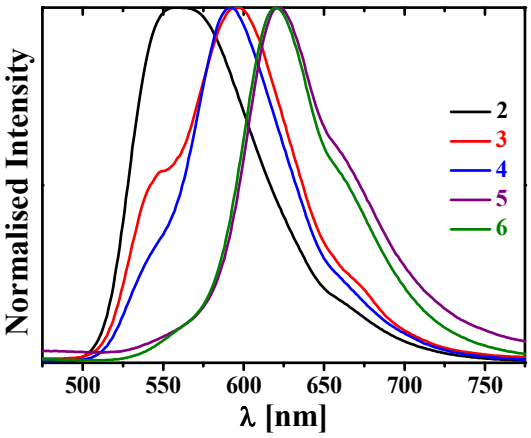

Fig. 8 Normalised solid-state emission spectra of **2–6** at 298 K (λ_{exc} = 400 nm).

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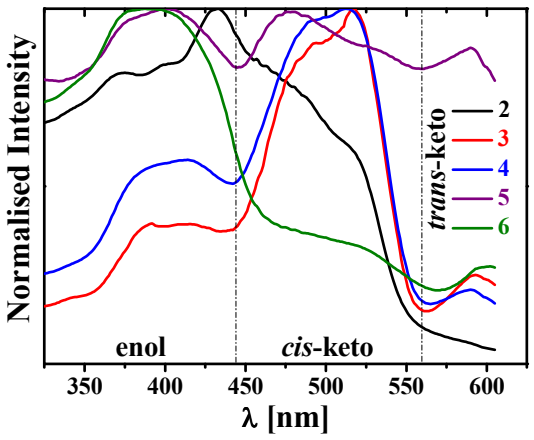

Fig. 9 Normalised solid-state excitation spectra of **2–6** at 298 K (λ_{em} = 620 nm).

Confirmation of the assignment of these bands is made after inspection of excitation spectra of **2–6** at λ_{em} = 620 nm (Fig. 9). These spectra reveal two contributions in the *cis*-keto region, which are assigned to the emission of two different conformers.[25] A third band, observed above 560 nm, but not detected for **2**, can be assigned to the *trans*-keto form by comparison with diffuse reflectance spectroscopy (Fig. 7).

Conclusions

In summary, we have synthesized five new *N*′-thiophosphorylated thiourea-containing *N*-salicylidene aniline derivatives of the common formula 6-{(2-OH-aryl)–CH=N}-Py-2-NHC(S)NHP(S)(O*i*Pr)$_2$ [aryl = C_6H_4 (**2**), 5-Cl-C_6H_3 (**3**), 5-Br-C_6H_3 (**4**), 3,5-Cl_2-C_6H_2 (**5**), 3,5-Br_2-C_6H_2 (**6**)] by condensation of *N*-thiophosphorylated thiourea 6-NH_2-Py-2-NHC(S)NHP(S)(O*i*Pr)$_2$ (**1**) with the corresponding salicylaldehyde. The reaction was performed in EtOH for compounds **3–6**, while using the same solvent and aniline leads to the exclusive formation of X-ray suitable crystals of **1**. Compound **2** was readily formed by dissolving **1** in pure salicylaldehyde. According to single crystal X-ray diffraction , **1–6** contain an intramolecular hydrogen bond of the N(1)–H(1N)···N(12) type, and are additionally stabilized by intermolecular hydrogen bonds and π···π stacking interactions. Anils **2–6** each exhibit the enol form. Furthermore, the structures of **3–6** are stabilized by intermolecular (di)halogen bonds.

Diffuse reflectance spectroscopy reveals a mixture of the dominant enol and *cis*-keto forms in the solid state at room temperature for **2–6**. Furthermore, **3–6** present a *trans*-keto form, despite the absence of phototochromism for steric reasons, thus demonstrating the impact of the substituents onto the arylOH fragment. Molecules **3–6** are exclusively thermochromic contrary to **2** which is not switchable. We have also established that the main emission properties of **2–6** are originating from the *cis*-keto* to *cis*-keto relaxation.

The anils **2–6** are attractive ligands for coordination chemistry, exhibiting features of both the thiourea and Schiff base fragments, for the preparation of hybrid materials. In particular, we have recently reported trinuclear heteroleptic Ni^{II} helical complexes of the doubly deprotonated **2–4** using the direct reaction of the [Ni{2-Py(6-NH_2)NHC(S)NP(S)(O*i*Pr$_2$}$_2$] starting precursor with the corresponding salicylaldehyde in ethanol.[19] A new range of complexes with transition metals comprising non coordinated salicylaldehyde aniline units is also expected to feature both coordination properties of thiourea thiophosphorylated thiourea ligand as well as fascinating optical properties of anils.

Experimental

General procedures

NMR spectra in DMSO-d_6 were obtained on a Bruker AC 300 MHz spectrometer at 25 °C. ^{1}H NMR spectra were recorded at 299.948 MHz. Chemical shifts are reported with reference to $SiMe_4$. Elemental analyses were performed on a Perkin Elmer 2400 CHN microanalyser. Diffuse reflectance spectra were obtained with a Varian Cary 5E spectrometer using polytetrafluoroethylene (PTFE) as a reference. Spectra were measured on pure solids to avoid matrix effects.[26] Solid-state emission spectra were obtained with a Fluorolog-3 (Jobin-Yvon-Spex Company) spectrometer. Kubelka-Munk and emission spectra were normalized to allow meaningful comparisons. Light irradiations were carried out with a LOT-ORIEL 200 W high-pressure mercury Arc lamp (LSN261).

Synthesis of 1

The *N*-thiophosphorylated thiourea **1** was prepared following a literature procedure.[20] Single crystals were obtained by reacting **1** with salicylaldehyde in ethanol following a similar synthesis for **3–6** as described below.

Synthesis of 2

1 (0.30 mmol, 0.105 g) was dissolved in pure salicylaldehyde (20 mL) and left for slow evaporation. The resulting yellow needles, which formed after about one month, were washed with ethanol (3 × 10 mL) and *n*-hexane (6 × 50 mL), and dried under vacuum. Yield: 0.148 g (86%). ^{1}H NMR: δ = 1.41 (t, $^3J_{H,H}$ = 6.2 Hz, 12H, CH_3, O*i*Pr), 4.96 (d. sept, $^3J_{POCH}$ = 10.6 Hz, $^3J_{H,H}$ = 6.2 Hz, 2H, CH, O*i*Pr), 6.66–7.18 (m, 5H, Py + C_6H_4, thiourea), 7.36–7.62 (m, 4H, C_6H_4, aldehyde), 7.70–7.86 (m, 2H, Py), 9.27 (br. s, 1H, PyNH), 9.49 (s, 1H, CHN), 9.90 (s, 1H, CHO, aldehyde), 11.01 (s, 1H, OH, aldehyde), 12.73 (br. s, 1H, NHP), 13.20 (s, 1H, OH, thiourea). ^{1}P{^{1}H} NMR: δ = 56.7 (s) ppm. *Anal.* Calc. for $C_{26}H_{31}N_4O_5PS_2$ (574.65): C 54.34, H 5.44, N 9.75. Found: C 54.25, H 5.37, N 9.82.

Synthesis of 3–6

A solution of 5-chlorosalicylaldehyde, 5-bromosalicylaldehyde, 3,5-dichlorosalicylaldehyde or 3,5-dibromosalicylaldehyde (0.33 mmol; 0.052, 0.066, 0.063 or 0.092 g) dissolved in ethanol (20 mL) was added to a suspension of **1** (0.30 mmol, 0.105 g) in the same solvent (10 mL). The resulting dark orange or dark red solution was stirred for 30 min and, afterwards, heated at reflux

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for 2 h. It was then allowed to cool to room temperature to give the product, which was filtered, washed with ethanol (10 mL) and *n*-hexane (3 × 50 mL), and dried under vacuum.

3. Orange plates. Yield: 0.137 g (94%). ^{1}H NMR: δ = 1.28 (d, $^3J_{H,H}$ = 6.2 Hz, 8.4H, CH_3, O*i*Pr), 1.33 (d, $^3J_{H,H}$ = 6.2 Hz, 3.6H, CH_3, O*i*Pr), 4.74 (d. sept, $^3J_{POCH}$ = 12.0 Hz, $^3J_{H,H}$ = 6.2 Hz, 2H, CH, O*i*Pr), 6.11 (d, $^3J_{H,H}$ = 8.3 Hz, 0.29H, Py), 6.27 (d, $^3J_{H,H}$ = 8.2 Hz, 0.28H, Py), 7.14 (d, $^3J_{H,H}$ = 8.3 Hz, 0.67H, Py), 7.23 (d, $^3J_{H,H}$ = 8.0 Hz, 0.72H, Py), 7.49 (d, $^3J_{H,H}$ = 8.3 Hz, 1H, Py), 7.69 (d. d, $^3J_{H,H}$ = 8.3 Hz, $^4J_{H,H}$ = 2.5 Hz, 0.70H, C_6H_3), 7.84 (d. d, $^3J_{H,H}$ = 8.3 Hz, $^4J_{H,H}$ = 2.4 Hz, 0.28H, C_6H_3), 7.99 (d, $^4J_{H,H}$ = 2.3 Hz, 1H, C_6H_3), 8.12 (d, $^3J_{H,H}$ = 8.3 Hz, 1H, C_6H_3), 9.28 (s, 0.69H, CHN), 10.04 (s, 0.29H, CHN), 11.04 (d, $^4J_{PNCNH}$ = 2.5 Hz, 0.24H, PyNH), 11.24 (br. s, 0.22H, NHP), 11.57 (d, $^4J_{PNCNH}$ = 2.9 Hz, 0.61H, PyNH), 12.96 (d, $^2J_{PNH}$ = 12.4 Hz, 0.68H, NHP), 13.52 (br. s, 0.24H, OH), 14.11 (s, 0.61H, OH) ppm. ^{31}P{^{1}H} NMR: δ = 57.4 (s, 0.70P), 58.5 (s, 0.30P) ppm. *Anal*. Calc. for $C_{19}H_{24}ClN_4O_3PS_2$ (486.97): C 46.86, H 4.97, N 11.51. Found: C 46.97, H 4.88, N 11.57.

4. Yellow-orange plates. Yield: 0.145 g (91%). ^{1}H NMR: δ = 1.24 (d, $^3J_{H,H}$ = 6.2 Hz, 4.3H, CH_3, O*i*Pr), 1.27 (d, $^3J_{H,H}$ = 6.2 Hz, 4.3H, CH_3, O*i*Pr), 1.31 (d, $^3J_{H,H}$ = 6.2 Hz, 3.2H, CH_3, O*i*Pr), 4.82 (d. sept, $^3J_{POCH}$ = 11.0 Hz, $^3J_{H,H}$ = 6.2 Hz, 2H, CH, O*i*Pr), 5.97 (d, $^3J_{H,H}$ = 8.2 Hz, 0.27H, Py), 6.34 (d, $^3J_{H,H}$ = 8.2 Hz, 0.27H, Py), 6.99 (d, $^3J_{H,H}$ = 8.3 Hz, 0.71H, Py), 7.12 (d, $^3J_{H,H}$ = 7.9 Hz, 0.70H, Py), 7.42 (d, $^3J_{H,H}$ = 8.2 Hz, 1H, Py), 7.61 (d. d, $^3J_{H,H}$ = 8.2 Hz, $^4J_{H,H}$ = 2.6 Hz, 0.72H, C_6H_3), 7.69 (d. d, $^3J_{H,H}$ = 8.4 Hz, $^4J_{H,H}$ = 2.3 Hz, 0.26H, C_6H_3), 7.93 (d, $^4J_{H,H}$ = 2.3 Hz, 1H, C_6H_3), 7.98 (d, $^3J_{H,H}$ = 8.3 Hz, 1H, C_6H_3), 9.20 (s, 0.73H, CHN), 10.16 (s, 0.27H, CHN), 10.92 (d, $^4J_{PNCNH}$ = 2.7 Hz, 0.26H, PyNH), 11.15 (br. s, 0.25H, NHP), 11.44 (d, $^4J_{PNCNH}$ = 3.3 Hz, 0.64H, PyNH), 12.82 (d, $^2J_{PNH}$ = 12.1 Hz, 0.71H, NHP), 13.41 (br. s, 0.25H, OH), 13.98 (s, 0.64H, OH) ppm. ^{31}P{^{1}H} NMR: δ = 57.7 (s, 0.72P), 58.2 (s, 0.28P) ppm. *Anal*. Calc. for $C_{19}H_{24}BrN_4O_3PS_2$ (531.42): C 42.94, H 4.55, N 10.54. Found: C 42.82, H 4.51, N 10.61.

5. Red blocks. Yield: 0.149 g (95%). ^{1}H NMR: δ = 1.27 (d, $^3J_{H,H}$ = 6.2 Hz, 6H, CH_3, O*i*Pr), 1.30 (d, $^3J_{H,H}$ = 6.2 Hz, 6H, CH_3, O*i*Pr), 4.83 (d. sept, $^3J_{POCH}$ = 10.6 Hz, $^3J_{H,H}$ = 6.2 Hz, 2H, CH, O*i*Pr), 7.24 (d, $^3J_{H,H}$ = 8.1 Hz, 1H, Py), 7.30 (d, $^3J_{H,H}$ = 7.7 Hz, 1H, Py), 7.77 (d, $^4J_{H,H}$ = 2.6 Hz, 1H, C_6H_2), 7.82 (d, $^4J_{H,H}$ = 2.6 Hz, 1H, C_6H_2), 8.01 (t, $^3J_{H,H}$ = 8.1 Hz, 1H, Py), 9.31 (s, 1H, CHN), 11.49 (d, $^4J_{PNCNH}$ = 3.3 Hz, 1H, PyNH), 12.70 (d, $^2J_{PNH}$ = 12.8 Hz, 1H, NHP), 13.76 (s, 1H, OH) ppm. ^{31}P{^{1}H} NMR: δ = 57.5 (s) ppm. *Anal*. Calc. for $C_{19}H_{23}Cl_2N_4O_3PS_2$ (521.42): C 43.77, H 4.45, N 10.75. Found: C 43.64, H 4.39, N 10.71.

6. Orange needles. Yield: 0.186 g (98%). ^{1}H NMR: δ = 1.21 (t, $^3J_{H,H}$ = 6.3 Hz, 1.5H, CH_3, EtOH), 1.24–1.35 (m, 12H, CH_3, O*i*Pr), 3.44 (q, $^3J_{H,H}$ = 6.3 Hz, 1H, CH_2, EtOH), 4.71–4.93 (m, 2H, CH, O*i*Pr), 5.89 (d, $^3J_{H,H}$ = 8.4 Hz, 0.30H, Py), 6.22 (d, $^3J_{H,H}$ = 8.1 Hz, 0.30H, Py), 7.24 (d, $^3J_{H,H}$ = 8.1 Hz, 0.70H, Py), 7.31 (d, $^3J_{H,H}$ = 7.7 Hz, 0.70H, Py), 7.43 (d, $^3J_{H,H}$ = 7.9 Hz, 0.30H, Py), 7.89–8.13 (m, 2.74H, Py + C_6H_2), 9.29 (s, 0.68H, CHN), 10.05 (s, 0.32H, CHN), 10.92 (d, $^4J_{PNCNH}$ = 2.6 Hz, 0.29H, PyNH), 11.28 (br. s, 0.24H, NHP), 11.49 (d, $^4J_{PNCNH}$ = 3.3 Hz, 0.67H, PyNH), 12.69 (d, $^2J_{PNH}$ = 13.6 Hz, 0.69H, NHP), 13.39 (br. s, 0.28H, OH), 13.93 (s, 0.65H, OH) ppm. ^{31}P{^{1}H} NMR: δ = 57.5 (s, 0.67P), 58.2 (s, 0.33P) ppm. *Anal*. Calc. for $C_{20}H_{26}Br_2N_4O_{3.5}PS_2$ (633.36): C 37.93, H 4.14, N 8.85. Found: C 38.05, H 4.19, N 8.91.

Powder X-ray diffraction

X-ray powder diffraction for bulk samples of **1–6** was carried out using a Rigaku Ultima IV diffractometer. The Parallel Beam mode was used to collect the data (λ = 1.541836 Å).

Single crystal X-ray diffraction

The X-ray data for **1–4** were collected on a Mar345 image plate detector using Mo-K_α radiation (Xenocs Fox3D mirror). The data were integrated with the crysAlisPro software.[27] The implemented empirical absorption correction was applied. The structures were solved by direct methods using the SHELXS-97 program[28] and refined by full-matrix least squares on $|F^2|$ using SHELXL-97.[28] Non-hydrogen atoms were anisotropically refined and the hydrogen atoms were placed on calculated positions in riding mode with temperature factors fixed at 1.2 times U_{eq} of the parent atoms. Crystals of **1** diffracted poorly and a resolution cutoff of 0.9 Å was imposed during integration. The twinrotmat analysis in Platon[29] was used to generate a hklf5 formated reflection file to account for the detected twinning. **1** was pseudo-merohedrally twinned around the reciprocal *a*-axis. No merging was performed when refining against a HKLF5 formatted reflection file, thus the reported R_{int} of 0.000. Reporting this low quality structure has to be seen in the light of previous unsuccessful attempts to crystallize this compound.

The X-ray data for **5** and **6** were collected on a STOE IPDS-II diffractometer with graphite-monochromatised Mo-K_α radiation generated by a fine-focus X-ray tube operated at 50 kV and 40 mA. The reflections of the images were indexed, integrated and scaled using the X-Area data reduction package.[29] Data were corrected for absorption using the PLATON program.[30] The structures were solved by direct methods using the SHELXS-97 program[28] and refined first isotropically and then anisotropically using SHELXL-97.[28] Hydrogen atoms were revealed from $\Delta\rho$ maps and those bonded to C were refined using appropriate riding models.

Figures were generated using the program Mercury.[31]

Crystal data for 1. $C_{12}H_{21}N_4O_2PS_2$, M_r = 348.42 g mol^{-1}, monoclinic, space group $P2_1/c$, a = 17.145(3), b = 14.7090(18), c = 7.0193(11) Å, β = 93.319(15)°, V = 1767.2(5) Å^3, T = 293(2) K, Z = 4, ρ = 1.310 g cm^{-3}, μ(Mo-Kα) = 0.400 mm^{-1}, reflections: 1396 collected, 1396 unique, R_{int} = 0.000, R_1(all) = 0.1307, wR_2(all) = 0.3384.

Crystal data for 2. $C_{19}H_{25}N_4O_3PS_2$, $C_7H_6O_2$; M_r = 574.64 g mol^{-1}, triclinic, space group P–1, a = 6.8774(5), b = 14.6409(14), c = 15.1569(12) Å, α = 70.775(8), β = 89.447(6), γ = 83.841(7)°, V = 1432.2(2) Å^3, T = 150(2) K, Z = 2, ρ = 1.333 g cm^{-3}, μ(Mo-Kα) = 0.284 mm^{-1}, reflections: 12647 collected, 4893 unique, R_{int} = 0.039 R_1(all) = 0.0520, wR_2(all) = 0.1447.

Crystal data for 3. $C_{19}H_{24}ClN_4O_3PS_2$, M_r = 486.96 g mol^{-1}, triclinic, space group P–1, a = 8.5874(7), b = 11.9114(14), c = 12.8574(15) Å, α = 98.428(10), β = 109.104(9), γ = 96.547(8)°, V = 1210.7(2) Å^3, T = 295(2) K, Z = 2, ρ = 1.336 g cm^{-3}, μ(Mo-Kα) = 0.423 mm^{-1}, reflections: 10918 collected, 4261 unique, R_{int} = 0.033, R_1(all) = 0.0463, wR_2(all) = 0.1261.

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Crystal data for 4. $C_{19}H_{24}BrN_4O_3PS_2$, M_r = 531.42 g mol^{-1}, triclinic, space group *P*–1, a = 8.5957(13), b = 11.821(2), c = 12.807(2) Å, α = 98.558(15), β = 108.643(15), γ = 97.790(15)°, V = 1195.8(4) Å^3, T = 150(2) K, Z = 2, ρ = 1.476 g cm^{-3}, μ(Mo-Kα) = 1.987 mm^{-1}, reflections: 8518 collected, 4077 unique, R_{int} = 0.044, R_1(all) = 0.0424, wR_2(all) = 0.1141.

Crystal data for 5. $C_{19}H_{23}Cl_2N_4O_3PS_2$, M_r = 521.40 g mol^{-1}, triclinic, space group *P*–1, a = 9.0052(8), b = 11.7572(10), c = 12.3225(11) Å, α = 98.558(7), β = 106.445(7), γ = 97.060(7)°, V = 1218.5(2) Å^3, T = 173(2) K, Z = 2, ρ = 1.421 g cm^{-3}, μ(Mo-Kα) = 0.532 mm^{-1}, reflections: 23183 collected, 4997 unique, R_{int} = 0.066, R_1(all) = 0.0468, wR_2(all) = 0.1118.

Crystal data for 6. $C_{19}H_{23}Br_2N_4O_3PS_2$, $CH_3O_{0.5}$; M_r = 633.36 g mol^{-1}, monoclinic, space group *C*2/*c*, a = 25.4932(13), b = 8.2482(5), c = 25.1957(14) Å, β = 101.280(4)°, V = 5195.6(5) Å^3, T = 173(2) K, Z = 8, ρ = 1.619 g cm^{-3}, μ(Mo-Kα) = 3.374 mm^{-1}, reflections: 29742 collected, 4580 unique, R_{int} = 0.105, R_1(all) = 0.0546, wR_2(all) = 0.1318.

CCDC 980848 (**1**), 980849 (**2**), 980850 (**3**), 980851 (**4**), 980852 (**5**) and 980853 (**6**) contain the supplementary crystallographic data. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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† Electronic Supplementary Information (ESI) available: Figures S1–S3 and Tables S1–S9. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b000000x.

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New family of *N′*-thiophosphorylated thiourea-containing *N*-salicylidene aniline derivatives (anils) of the common formula 6-{(2-OH-aryl)–CH=N}-Py-2-NHC(S)NHP(S)(O*i*Pr)$_2$ [aryl = C_6H_4 (**2**), 5-Cl-C_6H_3 (**3**), 5-Br-C_6H_3 (**4**), 3,5-Cl_2-C_6H_2 (**5**), 3,5-Br_2-C_6H_2 (**6**)] have been synthesized by the condensation of *N*-thiophosphorylated thiourea 6-NH_2-Py-2-NHC(S)NHP(S)(O*i*Pr)$_2$ (**1**) with the corresponding salicylaldehyde. **2–6** are exclusively thermochromic, while no photochromism was observed.