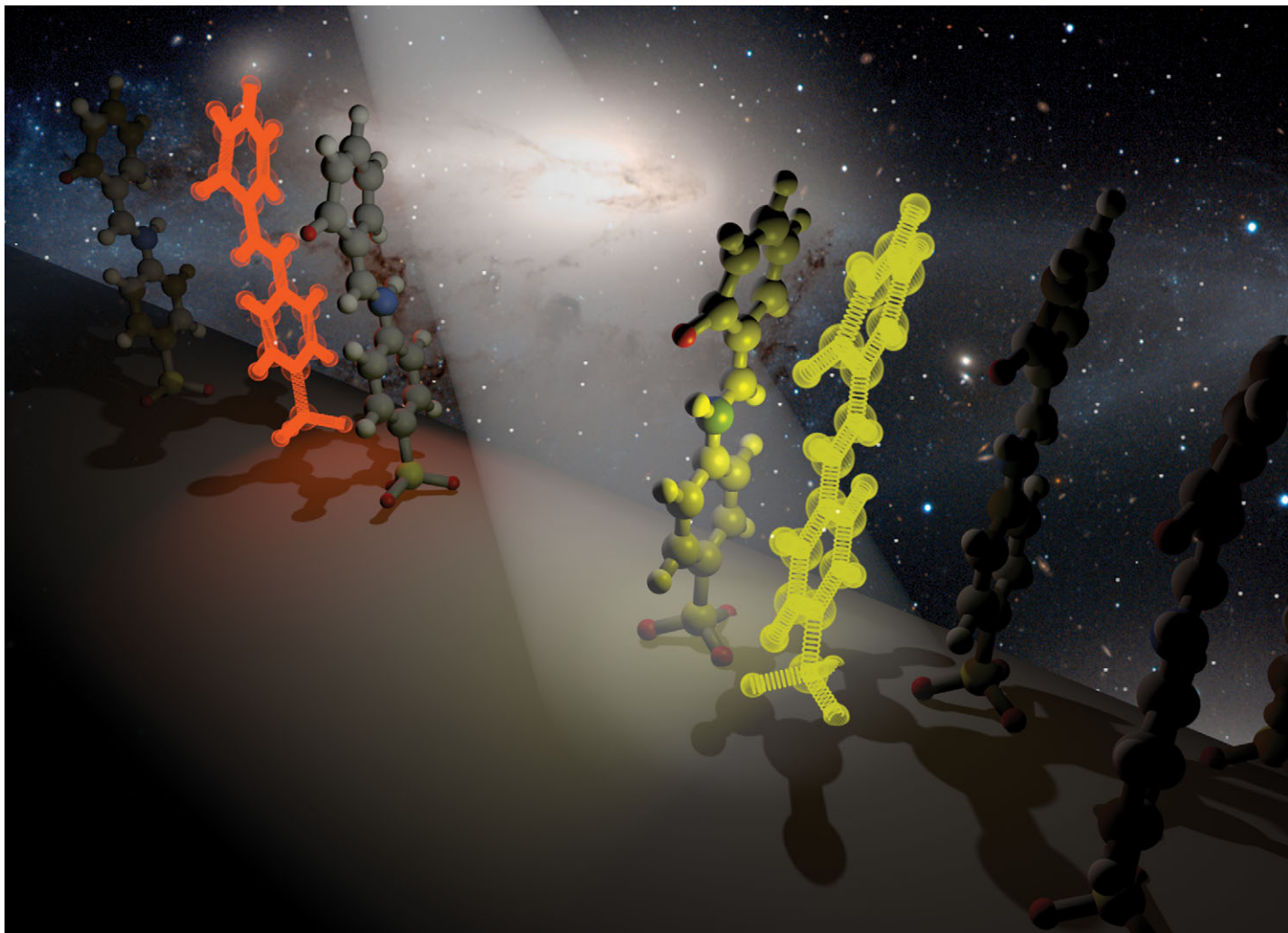


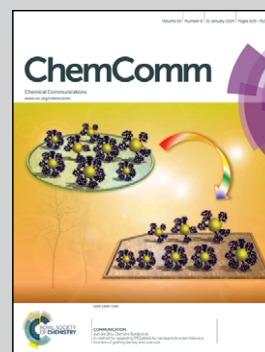


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#### Reversible photochromism of an *N*-salicylidene aniline anion

An *N*-salicylidene aniline anion shows reversible photochromism at room temperature. This opens up the possibility to insert this guest charged molecule into various matrixes (polymers, molecular conductors, spin crossover switches and molecular magnets, coordination polymers and metal–organic frameworks...) in a controlled manner to prepare functional hybrids.

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# Reversible photochromism of an *N*-salicylidene aniline anion†

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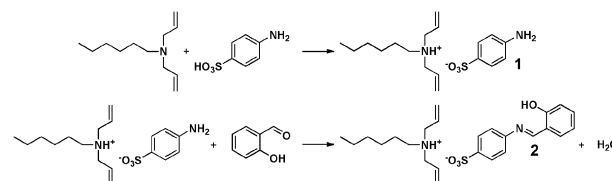
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The first *N*-salicylidene aniline anion showing reversible solid state thermochromic and photochromic properties is described. The photo-isomerization involves a *trans*-keto form which is stabilized thanks to the local anion surrounding. This photochromic anion can be used as a guest for the preparation of hybrid materials by insertion into a cationic host matrix.

Photochromic molecules are of current interest, since they can find applications in optical data storage and displays.<sup>1</sup> In particular, *N*-salicylidene aniline derivatives (anils) are considered as an important class for the preparation of hybrid materials since they can present both solid state thermo- and photochromism.<sup>2–4</sup> Such materials were prepared by insertion of neutral anil derivatives inside host matrices such as clathrates,<sup>4,5</sup> zeolites,<sup>6,7</sup> mesoporous silicas,<sup>8–10</sup> polymers,<sup>11</sup> or cyclodextrins.<sup>12</sup> While these methods do not allow precise control of the amount of guest anils, the use of molecular capsules,<sup>13</sup> and the functionalization of these molecules as ligands, was reported. Unfortunately, the impact of coordination on the energy levels of anils is too important and the photochromic ability is lost after insertion.<sup>14–16</sup> Anionic derivatives as counter-ions constitute an attractive alternative for the controlled incorporation into coordination complexes.<sup>17,18</sup> To avoid Schiff base coordination competition, a sulfonate group was selected because of its permanent charge. *N*-Salicylidene *m*-aminobenzene sulfonate presents a tautomeric equilibrium after insertion into [M(phen)<sub>3</sub>]<sup>2+</sup> (M = Cu, Ni) complexes.<sup>17</sup> The keto–enol equilibrium was preserved too for a Fe<sup>II</sup> 1,2,4-triazole spin crossover complex with *N*-salicylidene *p*-aminobenzenesulfonate.<sup>18</sup> The incorporation of a photo-isomerizable counteranion into coordination complexes could favour an Anion Driven-Light Induced Spin Change (-LISC) effect.<sup>17</sup>

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† Electronic supplementary information (ESI) available: Synthesis and crystal data of **2** and instrumentation. CCDC 947429 (**2**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3cc45080e



Scheme 1 Synthesis of diallyl hexyl ammonium-*N*-salicylidene *p*-aminobenzenesulfonate.

In this work, *N*-salicylidene *p*-aminobenzenesulfonate was crystallized, for the first time, in two steps using diallyl hexyl ammonium (**2** in Scheme 1). In contrast to previous observations with alkaline earth metals or alkaline metals,<sup>19</sup> a photochromic salt with an important stabilization of the *trans*-keto form was obtained meaning that the photochromic ability of anilinesulfonate derivatives is mainly driven by structural properties. This discovery is a milestone in the use of *N*-salicylidene aniline sulfonate as a counter-ion in multifunctional materials, taking into account their high thermal stability.<sup>17</sup>

The colours of *N*-salicylidene *p*-aminobenzenesulfonate diallyl hexyl ammonium (**2**) shown in Fig. 1 are meaningful. At 298 K, the yellow colour stems from the presence of the *cis*-keto form whereas the orange colour stems from traces of the *trans*-keto form (Fig. 1a). Upon cooling to 77 K, the *cis*-keto form converts to the white enol form, as shown by the light-orange colour (Fig. 1a).

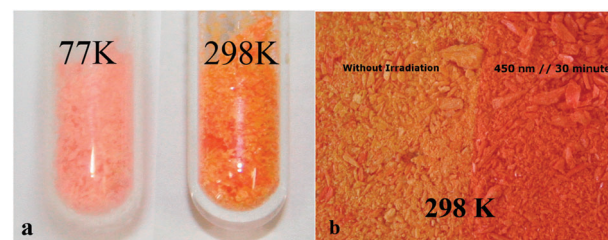
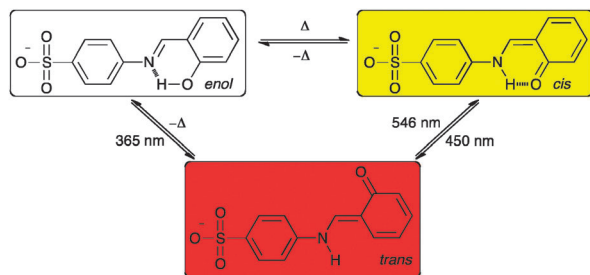


Fig. 1 (a) Solid state thermochromism of **2**: at 77 K (left); at 298 K (right); (b) solid state photochromism of **2** before (left) and after (right) irradiation at  $\lambda = 450$  nm for 30 min.



Scheme 2 Thermo- and photochromism of *N*-salicylidene aniline *p*-aminobenzenesulfonate. Dashed lines indicate H-bonds.

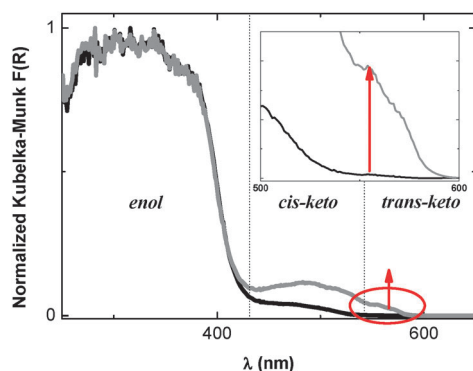


Fig. 2 Diffuse reflectance spectra of **2**: before (black) and after (grey) irradiation at  $\lambda = 450$  nm for 20 min.

The *trans*-keto form remains at 77 K since no intramolecular H transfer is possible between amine and keto groups (Scheme 2).

Solid state photochromism is observed by switching the colour from yellow-orange (*cis*-keto) to dark orange (*trans*-keto) after irradiation of **2** at  $\lambda = 450$  nm for 30 min (Fig. 1b). This observation is confirmed by diffuse reflectance spectroscopy (Fig. 2).

The microcrystalline powder of **2** at 298 K shows three bands corresponding to the enol and keto forms of *N*-salicylidene *p*-aminobenzenesulfonate diallyl hexyl ammonium (Fig. 2). The band below 425 nm corresponds to the enol form whereas a contribution of the *cis*-keto form is observed between 425 and 550 nm. Above 550 nm, a third band appears after irradiation at  $\lambda = 450$  nm for 20 min, which is attributed to the *trans*-keto form.<sup>2,3,15,16</sup>

Time-dependent experiments were performed in order to investigate the reversibility of the photochromism (Fig. 3). Thermal relaxation analysis shows interesting *trans*-keto stability after light irradiation (Fig. 3a). Indeed, a weak relaxation of the *trans*-keto form is noticed at 10 000 min (about 13% of *trans*-keto form are isomerized back into the *cis*-keto form).<sup>20</sup> This exceptional behaviour was earlier observed only for two examples.<sup>15,21</sup>

Diffuse reflectance spectra were also recorded with irradiation cycles at  $\lambda = 450$  nm for 30 min to initiate the *cis*–*trans* isomerization and at  $\lambda = 546$  nm for 30 min for the reverse photoreaction (Fig. 3b). These experiments highlight the photo-reversible *cis*–*trans* isomerization as well as the stability of the *trans*-keto form.

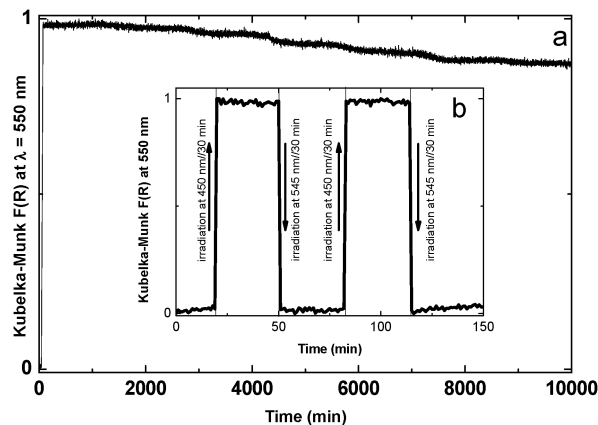


Fig. 3 Time dependence of the Kubelka–Munk function  $F(R)$  of **2** at 550 nm showing: (a) thermal relaxation after irradiation at  $\lambda = 450$  nm for 20 min. (b) Reversibility of the *cis*–*trans* isomerization with an irradiation cycle at  $\lambda = 450$  nm and 545 nm.

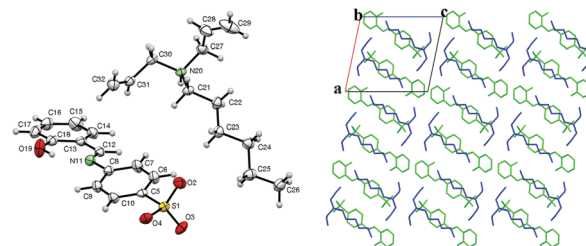
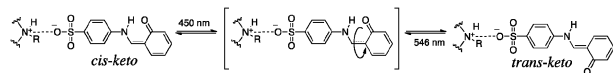


Fig. 4 Left: ORTEP view of the asymmetric part of the unit cell of **2**, showing 50% probability displacement ellipsoids; right: projection of the crystal packing of **2** along the *b* axis.

The crystal structure of **2** was measured at 150(2) K. **2** is solved in the monoclinic  $P2_1$  space group. The asymmetric unit presents one *N*-salicylidene *p*-aminobenzenesulfonate anion and one diallyl hexyl ammonium cation (Fig. 4). The bond lengths C18–O19 (1.347(3) Å) and C12–C13 (1.444(3) Å) correspond to single bonds and N11–C12 (1.285(3) Å) is typical of a double bond (Table S1 in ESI<sup>†</sup>), which indicate that the major form observed in the crystal is the enol form. With its dihedral angle of 18(1)°, *N*-salicylidene *p*-aminobenzenesulfonate can be considered as nearly planar. The planarity of the molecule is also observed through the three torsion angles  $\Gamma_1$ ,  $\Gamma_2$  and  $\Gamma_3$  (17(1)°, 179(1)° and –1(1)° respectively) (Table S1 in ESI<sup>†</sup>), which calls for thermochromic properties.<sup>2</sup>

The intramolecular hydrogen bond, observed between imine and enol functions (O19–H19...N11) with a bond length of 1.89(1) Å, allows the tautomeric equilibrium between enol and *cis*-keto forms. Two intermolecular hydrogen bonds at 1.98(1) and 2.51(1) Å (Table S2 in ESI<sup>†</sup>) and various closed contacts are observed in the crystal packing (Fig. 4). With respect to the average intermolecular distance (the distance between centroids of molecules of 4.6 Å), the packing can be however considered as ‘open’,<sup>2</sup> which allows the *cis*–*trans* isomerization upon light irradiation at 450 nm to proceed. Since the sulfonate anchors the anil switch to the diallylammonium, the rotation of the ketone bearing ring allows the photoisomerization with minimal





Scheme 3 Possible pathway for the *cis*–*trans* photoisomerization of **2**.

packing restraint (Scheme 3), compared to the usual photoisomerization process in *N*-salicylidene derivatives.<sup>15</sup> The presence of flexible neighbouring alkyl chains around the anil switch may favour this situation. On the other hand, the presence of intermolecular H-bonds in addition to van der Waals interactions may allow better stabilization of the *trans*-keto form (Table S2 in ESI†).

In conclusion, we have crystallized the first *N*-salicylidene anilinesulfonate derivative, which shows solid state photochromism at room temperature, and thermochromism upon cooling. Taking advantage of its structural properties, the isomerization leads to the stabilization of the *trans*-keto form. This achievement is encouraging for the use of anionic *N*-salicylidene aniline derivatives in hybrid multifunctional materials, especially in Fe<sup>II</sup> spin crossover compounds. Irradiating the anion should favour a photo-induced spin state change through a modification of the anion geometry,<sup>22</sup> thanks to the AD-LISC effect. We anticipate that photochromic anions of this class shall be inserted into a wide range of functional cationic molecules (polymers, conductors, spin crossover switches and molecular magnets, coordination polymers and metal–organic frameworks, ...).

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