

- [11] The molar composition of this mixture prepared from silicic acid, TPAOH, and NaOH: $(\text{TPA}_2\text{O})(\text{SiO}_2)_4(\text{Na}_2\text{O})_{0.33}(\text{H}_2\text{O})_{47}$.
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- [13] The molar composition of this mixture prepared from silicic acid and TPAOH: $(\text{TPA}_2\text{O})(\text{SiO}_2)_4(\text{H}_2\text{O})_{47}$; the suspension was gently heated to 50 °C to initiate reaction.
- [14] The molar composition of the TEOS system: $(\text{TPA}_2\text{O})(\text{SiO}_2)_{3.75}(\text{H}_2\text{O})_{30}(\text{EtOH})_{15}$; in the silicic acid system, the sample was the final product from the preparation of ref. [11].
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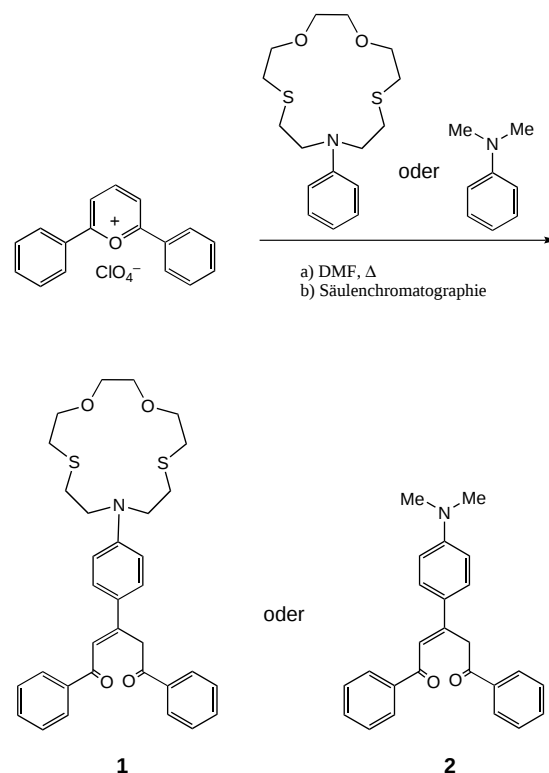
A Colorimetric ATP Sensor Based on 1,3,5-Triaryl-2-en-1,5-diones**

Félix Sancenón, Ana B. Descalzo, Ramón Martínez-Máñez,* Miguel A. Miranda, and Juan Soto

The development of systems that are capable of sensing or recognizing and are based on supramolecular concepts is an area of current interest.^[1] One of the most appealing approaches involves the construction of chromoionophores. Although such systems have been widely used for the analysis of metal cations,^[2] chromogenic sensors for the “naked-eye” sensing of anions are not common;^[3] this is especially the case in aqueous environments.^[4]

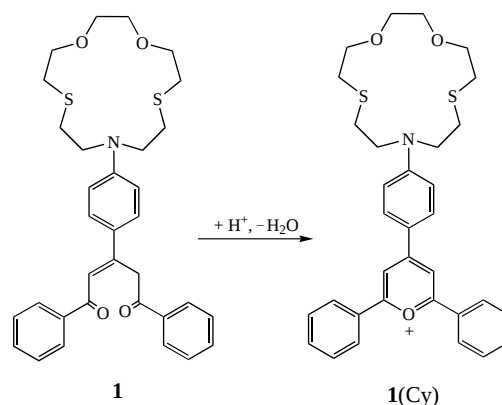
We report here the synthesis of 1,3,5-triaryl-2-en-1,5-dione derivatives and demonstrate their ability to act as colorimetric anion sensors. The new family of chromogenic reagents is easily obtained by condensation of the 2,6-diphenylpyrylium cation with N-functionalized anilines. For instance, the reaction of N-phenyl-1-aza-7,10-dioxo-4,13-dithiacyclopentadecane with 2,6-diphenylpyrylium gave the

1,3,5-triaryl-1,5-pentanedione derivative **1** after column chromatography (Scheme 1). The NMR (¹H, ¹³C) and mass spectra of **1** are consistent with the proposed formulation. The UV/Vis spectrum of **1** shows bands in the range of 200–300 nm along with a band centered at 380 nm, which is responsible for the pale yellow color of the receptor.



Scheme 1. Synthesis of the 1,3,5-triaryl-1,5-pentanedione derivatives **1** and **2**. The reaction is carried out in refluxing dimethylformamide (DMF) for 3 h, and subsequent column chromatography on alumina with $\text{CH}_2\text{Cl}_2/\text{MeOH}$ (50/1 v/v) as eluent provides **1** (35 % yield) or **2** (50 % yield).

The 1,5-pentanedione system of **1** can be readily transformed into the corresponding pyrylium ion (Scheme 2):^[5] Addition of nitric acid to solutions of **1** in 1,4-dioxane/water (70/30 v/v) caused a dramatic change in color from yellow to magenta. This change was accompanied by a new intense



Scheme 2. Transformation of the 1,5-pentanedione **1** into the pyrylium cation **1(Cy)**.

[*] Dr. R. Martínez-Máñez, F. Sancenón, A. B. Descalzo, Prof. M. A. Miranda, Dr. J. Soto
Departamento de Química
Universidad Politécnica de Valencia
Camino de Vera s/n, 46071 Valencia (Spain)
Fax: (+34) 9-6-387-7349
E-mail: rmaez@qim.upv.es

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band centered at 550 nm in the UV/Vis spectrum. We ascribe this new band to the highly delocalized pyrylium cation formed upon cyclization. This cation was isolated as the perchlorate salt, and the spectroscopic characterization fully supported the proposed formulation.

The changes in the absorption spectrum of **1** at neutral pH values upon addition of anions such as chloride, bromide, sulfate, and phosphate (as tetrabutylammonium salts) as well as ATP, ADP, and GMP (as sodium salts) have also been studied. The photograph in Figure 1 shows the color changes



Figure 1. Color changes induced on **1** (1.0×10^{-4} M) at pH 6 in the presence of the following anions in dioxane/water (70/30 v/v): from left to right: no anion, bromide, chloride, phosphate, sulfate, GMP, ADP, and ATP.

after addition of equimolar amounts of these anions to **1** in dioxane/water at pH 6. At this pH value, **1** forms a yellow solution, either alone or in the presence of bromide, chloride, phosphate, GMP, or ADP. Upon addition of sulfate, the solution turns pale red. However, the most remarkable effect is observed in the presence of ATP, whereby a bright magenta color is fully developed.

The analytical determination of anions, for instance in water or in biological systems, is commonly carried out in the presence of alkali and alkali earth cations. Therefore, we also studied the effect that the metal ions Li^+ , Na^+ , K^+ , Ca^{2+} , and Mg^{2+} (as their nitrate or perchlorate salts) have on solutions of **1** at pH 6. We found that there is no analytical interference, as the presence of these cations does not induce any significant color change.

A more detailed study has been carried out using basic solutions of **1** containing equimolar amounts of the corresponding anions, which were placed in dioxane/water (70/30 v/v) and subsequently acidified. The absorbance at 550 nm was then monitored at different pH values; the results are shown in Figure 2a. The pH values where the transformation of the diketonic form (yellow) to the pyrylium form (magenta) takes place are in the range 2–5. Cyclization and color development are thus a function of the pH value of the medium. Enhancement of the absorbance at 550 nm is ascribed to ring closure, as stated above. In general there is no remarkable effect in the presence of the anions, except for ATP, which is able to shift selectively the pH at which the magenta color is observed towards higher values. At acidic pH the situation is more complex, and in general all the anions studied modify the pH value at which the solution changes

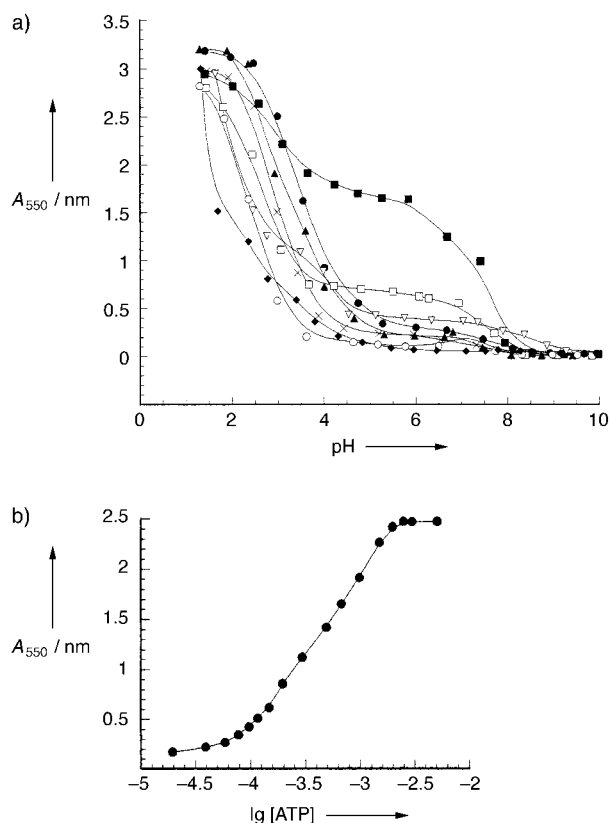


Figure 2. a) Plot of the absorbance at 550 nm (A_{550}) as a function of the pH value for **1** (●) and **1** in the presence of the anions chloride (×), bromide (▲), sulfate (□), phosphate (○), ATP (■), ADP (▽), and GMP (◆) in dioxane/water (70/30 v/v). b) Absorbance at 550 nm of **1** (1.0×10^{-4} M) versus the logarithm of the ATP concentration at pH 6 in dioxane/water (70/30 v/v).

from yellow to magenta. However, in the range pH 2–4 there is no selective pattern.

It can be concluded that there is a remarkable selective ATP colorimetric detection. Hence, **1** is a selective chromogenic reagent for the sensing of ATP.^[6] It is important to note that the color change in **1** from yellow to magenta observed upon addition of ATP is a very simple and easy “naked-eye” method. Additionally the pyrylium cation formed from **1**, responsible for the color change, has a molar absorptivity as high as $30\,600 \text{ L mol}^{-1} \text{ cm}^{-1}$; this allows sensitive spectrophotometric detection of the anion ATP. Figure 2b shows the color response as a function of the ATP concentration at pH 6 ($[\text{1}] = 9.5 \times 10^{-5} \text{ M}$). Under these conditions, a linear response range from 40 to 1100 ppm of ATP was found (higher ATP concentrations result in the formation of a precipitate).

For the sake of comparison compound **2** was also synthesized by reaction of *N,N*-dimethylaniline and 2,6-diphenylpyrylium (Scheme 1). Figure 3 shows a photograph of the color changes observed for **2** in dioxane/water (70/30 v/v) at pH 6 in the presence of certain anions. There is a remarkable switch from yellow to magenta in the presence of sulfate, ADP, and ATP, whereas bromide, chloride, phosphate, and GMP do not change the color of the **2** solution. The addition of Li^+ , Na^+ , K^+ , Ca^{2+} , or Mg^{2+} had no effect. In the absence of ATP and ADP, **2** can be considered as a selective chromogenic reagent for sulfate.

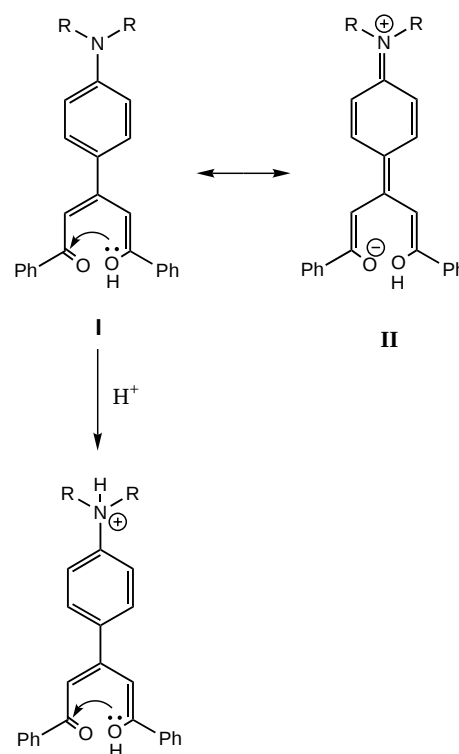


Figure 3. Color changes induced on **2** (1.0×10^{-4} M) at pH 6 in the presence of the following anions in dioxane/water (70/30 v/v): from left to right: no anion, bromide, chloride, phosphate, sulfate, GMP, ADP, and ATP.

Although further studies need to be carried out to correlate selectivity and molecular architecture, some preliminary considerations concerning the origin of the color change can be advanced. First of all, the occurrence of ring closure as a function of the pH value can be ascribed to the well-known chemistry of the pyrylium cation. It has been reported that nucleophilic attack of hydroxide anions or related nucleophiles over C2 results in ring opening, with the formation of 1,5-diketones (see form **1** in Scheme 2).^[7] In a similar manner, under certain circumstances, **1** is able to undergo intramolecular cyclization to restore structure **1**(Cy). As stated above, for **1** and **2** the color change is observed in the pH range of about 2–5. In this pH range protonation of the aniline nitrogen atom is expected to take place. Consequently, there is an apparent correspondence between protonation of the amine and transformation of the diketone to the pyrylium. To explain this observation, it should be considered that cyclization must result from nucleophilic attack of the hydroxyl group of the enol tautomer at C1 of the carbonyl group (see structure **I** in Scheme 3). When the amine is not protonated the electron density at C1 is too high; in other words, the resonance structure **II** makes a significant contribution and, hence, nucleophilic attack is disfavored. Upon protonation, the nitrogen lone pair is engaged, and structure **II** does not play a role. As a consequence, one would expect C1 to be more electrophilic and thus subject to attack by the enol.

To explain the color change observed in the presence of certain anions, one should consider that structure **1** contains functional groups such as amine, enol, and carbonyl that are capable of coordinating anions through electrostatic forces or hydrogen bonding. By such coordination it could be possible to modulate the nucleophilic character of the hydroxyl oxygen atom of the enol tautomer or the electrophilic character of the C1 carbonyl carbon atom. A possible explanation might involve coordination between the receptor **1** and ATP in such a way that the pK_a value of the amine increases, therefore favoring cyclization at higher pH values.

In conclusion we have synthesized a new family of easy-to-prepare chromogenic reagents and have found a highly selective color response against ATP in an aqueous–organic environment. Remarkably, ATP is capable of changing the absorption spectrum of **1** in the pH range 4–8, whereas inorganic anions (with the exception of sulfate), other anions



Scheme 3. Proposed resonance structures involved in the ring closure of 1,5-pentanediones **1** and **2** to the corresponding pyrylium cations.

of biological importance, and cations do not induce any color change. In this sense, **1** is a chromogenic reagent for ATP sensing. In the absence of biological anions, **2** can be considered a selective chromogenic reagent for sulfate.

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High-Pressure Synthesis of γ -P₃N₅ at 11 GPa and 1500 °C in a Multianvil Assembly: A Binary Phosphorus(v) Nitride with a Three-Dimensional Network Structure from PN₄ Tetrahedra and Tetragonal PN₅ Pyramids**

Kai Landskron, Hubert Huppertz, Jürgen Senker, and Wolfgang Schnick*

Phosphorus(v) nitride, P₃N₅, has structural similarities to the polymeric nonmetal nitrides α - and β -Si₃N₄ as well as to cubic boron nitride (*c*-BN). These compounds are built up from three-dimensional networks of linked TN₄ tetrahedra (T = B, Si, P). In cubic boron nitride as well as in α - and β -silicon nitride corner-sharing tetrahedra exclusively occur, whereas in α -P₃N₅ corner- and edge-sharing PN₄ units exist.^[1, 2] Recently the synthesis of cubic γ -Si₃N₄ was reported. This high-pressure modification, which crystallizes in the spinel structure type, consists of SiN₄ tetrahedra and SiN₆ octahedra.^[3]

With respect to its material properties phosphorus(v) nitride differs significantly from BN and Si₃N₄: P₃N₅ is

thermally stable only up to 850 °C, whereas boron nitride and silicon nitride decompose at much higher temperatures.^[1] The thermal lability of phosphorus(v) nitrides is an important reason why the synthesis of highly condensed crystalline nitridophosphates (molar ratio P:N > 1:2) is difficult. The irreversible elimination of N₂, which is the main process during the thermal decomposition of phosphorus(v) nitrides, can be suppressed by using high-pressure conditions. Recently, the synthesis of highly condensed nitridophosphates by reaction of the respective metal azides with P₃N₅ was successfully carried out at about 4 GPa and 1300 °C. We obtained the alkali and alkaline earth nitridophosphates (e.g. M^IPN₂, M^IP₄N₇, M^IP₆N₁₁, M^IP₂N₄)^[4] without thermal decomposition of P₃N₅ or the reaction products.

By increasing the pressure further we have now been able to synthesize the high-pressure phase γ -P₃N₅. The reaction was carried out at 1500 °C and 11 GPa with partially crystalline P₃N₅ as starting material. The reaction was performed by using a boron nitride capsule in a multianvil assembly, which allowed the synthesis of about 50 mg γ -P₃N₅ (see Experimental Section).

The crystal structure of γ -P₃N₅ (Table 1) was determined by direct methods from powder X-ray diffraction data and refined using the Rietveld method (Figure 1).^[5] The novel high-pressure modification consists of a polymeric three-dimensional network structure of linked PN₄ tetrahedra and tetragonal-pyramidal PN₅ units. In accord with the nomen-

Table 1. Atomic parameters and isotropic thermal displacement factors [pm²] of γ -P₃N₅.^[a]

Atom	Wyckoff position	x	y	z	U _{iso}
P1	2a	0	0	0.3114(10)	274(14)
P2	4c	0.8191(2)	1/2	−0.0420(9)	360(10)
N1	2b	0	1/2	0.5159(15)	62(29)
N2	4c	0.8953(4)	0	0.0768(9)	214(19)
N3	4c	0.7265(6)	1/2	0.2196(12)	263(25)

[a] The temperature factor is defined by $\exp(-8\pi^2 U_{\text{iso}} \sin^2 \theta / \lambda^2)$, space group *Imm2*, *a* = 1287.20(5), *b* = 261.312(6), *c* = 440.04(2) pm, *Z* = 2.

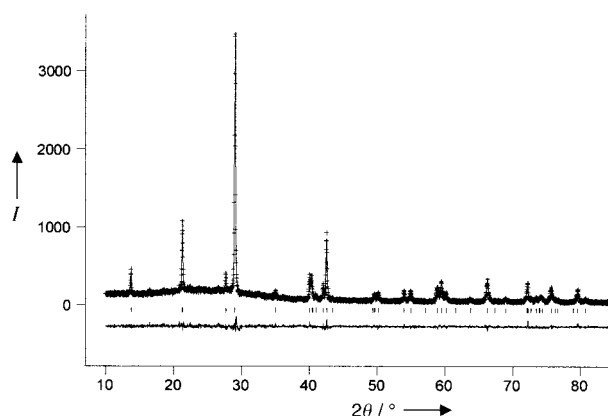


Figure 1. Observed (crosses) and calculated (line) X-ray powder diffraction pattern as well as difference profile (bottom line) of the Rietveld refinement of γ -P₃N₅. Positions of Bragg reflections are marked by vertical lines. The diffraction pattern was obtained with a conventional STOE-Stadi-P powder diffractometer (CuK α , λ = 154.05 pm).

[*] Prof. Dr. W. Schnick, Dipl.-Chem. K. Landskron, Dr. H. Huppertz, Dr. J. Senker
Department Chemie der Ludwig-Maximilians-Universität
81377 München (Germany)
Fax: (+49)89-2180-7440
E-mail: wsc@cup.uni-muenchen.de

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