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Selective photodetection of nitro compounds *via* cophotolysis with cymantrene

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A specific color reaction of cymantrene with nitro containing compounds (C–NO_2) that produces dark blue coloring after a short time exposure to UV irradiation at room temperature was studied.

Fast identification of nitro compounds and especially certain explosives is now emerging as a promising detection tool for the environmental and forensic science. However, in spite of the spectacular progress in real-time detection of explosives made lately, the issue still remains one of the challenging tasks.[1] Modern detection techniques and commercially available sensors can be used for both gas and surface analysis. They are primarily based on ionization, GC/MS, pyrolysis, Raman spectroscopy, X-ray diffraction, and immunochemical reactions between explosive compounds and their specific antibodies, *etc*.[2,3] Their sensitivity is high, but most of them are rather expensive and require skilled technicians to perform the analysis.

At present, there is no simple, common method of nitro group detection available. IR spectroscopy is usually considered the most universal indicator of the presence of a nitro group.[4] However, the reliability of detection of trace explosives in heavily contaminated environmental samples by this method seems dubious. In this respect, detection of explosives with chemicals by readily identifiable specific color or fluorescent reaction might be a good alternative. Progress in this field is associated with new fluorophore chemosensors for molecular recognition[1,5] and ions including nitro ions.[6–8] Indeed, different spray kits commercially available at present are able to detect a variety of explosive contaminants on surfaces through colorful chemical reactions.[1] Surprisingly, certain organometallic compounds that are excellent ion-selective receptors[9,10] have never been used for this purpose.[1,11–13] The only exception to this is the recent report on a novel sensing technique/material for detection of trace amounts of explosives on different objects by a specific color reaction with cyclopentadienylmanganese tricarbonyl (cymantrene).[14] The reaction was performed within a designed thin film polymer with embedded cymantrene. The resulting color could be easily seen after a short time exposure to UV irradiation.

The reaction between cymantrene **1a** (Scheme 1) and a nitro compound results in a rapid formation of a distinct blue color at room temperature after a short exposure to UV light. The cophotolysis reaction is seen both in solutions and on surfaces (*e.g.*, TLC plates, filter paper, *etc*.). The blue coloring (λ_{max} = = 670–700 nm)[†] is typical of only C–NO_2 groups and the presence of other functional groups usually does not interfere with the reaction. The color fades with time but may be restored, if UV irradiation is repeated. Other nitrogen-containing functional groups also show characteristic colors upon interaction with cymantrene and subsequent UV irradiation: nitrile groups yield yellow to red complexes, depending on the structure of the nitrile; cyclic imines form yellow to purple complexes (see Online Supplementary Materials).

It is known that photolysis of **1a** in a methane matrix at –200 °C or in a polymeric bonding leads to an unstable dicarbonyl complex of manganese **2a** (Scheme 1) with two characteristic IR carbonyl bands at 1950 and 1980 cm^{-1}.[15,16] This complex may be stabilized by THF, pyridine, acetonitrile, *etc*., due to the interaction with their π electrons.[17] The reaction is used to obtain stable triphenylphosphine complexes (ν_{CO} 1931, 1863 cm^{-1}).[†]

Photolyzed cymantrene **2a** is a strong reducing agent that is evidenced by the discoloration of iodine and quinones. Since the nitro group is not an electron donor, it was never regarded as a potential ligand to replace the carbonyl. However, IR spectra of blue photocomplexes of cymantrene with *para*-replaced nitrobenzenes yield two carbonyl absorption bands with equal intensities that are shifted to lower frequencies compared to **1a** and are characteristic of the presence of two carbonyl groups.[16] Furthermore, nitroaryls can easily replace THF in the complex $C_5H_5Mn(CO)_2{\cdot}THF$ with generation of the same dark blue complexes as above. High frequencies of carbonyl groups, 1947 ($\nu_{as\,CO}$) and 1912 cm^{-1} ($\nu_{s\,CO}$) in a complex of **1a** with *p*-nitrotoluene (Figure 1) indicate the strong electron acceptor influence of NO_2 group in a complex **3**, and suggest the formation of a covalent binding between the nitrogen and manganese atoms (Scheme 1).

Indeed, the reaction at the nitro group, upon formation of the complex, can be considered aprotonic one-electron reduction. Though, as evidenced by EPR spectroscopy, the dark blue complexes of nitro compounds (**3a**, R = H, R^1 = Ph, MeC_6H_4)[‡] do not have uncoupled electrons, they may still be regarded as

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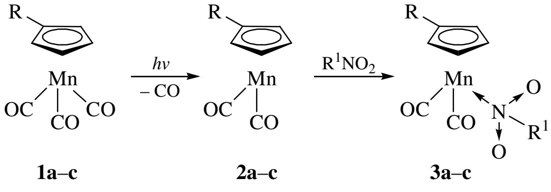
[†] IR spectra were measured on a Bruker Tensor-27 spectrometer with the sanction of 4 cm^{-1} (0.1 M solutions in toluene and hexane, thin ditches KBr). UV spectra were measured on a Shimadzu UV-2501PC spectrophotometer in toluene. ^1H NMR spectra were recorded on a Bruker AM300 (300 MHz) spectrometer (C_6D_6 was used as an internal standard). TLC was carried out on Silufol UV-254 plates, for UV irradiations a Spectroline* Q-Series UV Magnifier Lamp (intensity at 15.2 cm: 650/750 μw cm^{-2}) was used.

anion-radical nitro compounds complexed to and stabilized by cymantrenyl fragments. The likely formation of a covalent bond between nitrogen and manganese in the complex (**3a**, R = H, R^1 = Ar) is also suggested by the results of TLC: the mobility of the complex is almost identical to the initial nitroaryl.

By varying the time of UV irradiation and the concentration of a nitro compound in an excess of cymantrene, it is possible to follow the formation of photocomplexes by IR spectroscopy (Figure 1 for ethylcymantrene **1b**). The absorption of free NO_2 group at 1530 and 1360 cm^{-1} decreases as the concentration of the complex increases; symbathically, the absorption at considerably lower frequencies of 1213 and 1071 cm^{-1} increases (Figure 1). All substituted nitrobenzenes photolyzed with cymantrene show the increased absorption in this area, which is rather characteristic of *N*-oxides[4] (for example, pyridine *N*-oxides absorb at 1220 cm^{-1}) than for organic nitrates and nitrites. The latter exhibit much higher N=O bond frequencies,[4] compared to those observed in our case. Thus, these results are consistent with the $C_5H_5(CO)_2Mn–NO_2R$ binding (complex **3a**, Scheme 1), rather than with the possible alternative binding of the nitro group through an oxygen atom [*e.g.*, $C_5H_5(CO)_2Mn–ON(O)R$, **4a**]. Furthermore, we did not observe the formation of colored complexes of photolyzed cymantrene with the carbonyl compounds $R_2C=O$, RC=O(OEt) and RCH=O, that would not have been the case had the formation of complex **4a** formed. Since basicity of carbonyls in C=O groups is not higher than that of oxygen in RNO_2 the above reaction could have taken place had the binding occurred through the oxygen atom.

There are additional data that may support the formation of $Mn–NO_2R$ bond. The nitro group that binds to the $C_5H_5Mn(CO)_2$ fragment in the dark blue complex is a weak electron acceptor with regard to arenes. It follows from the changes of the NMR spectrum of cymantrene and *m*-nitrocarboethoxybenzene in C_6D_6: singlet from ^1H at 8.78 ppm is shifted up the field to 8.35 ppm after irradiation of the solution and the appearance of dark blue color.[†] This indicates a decrease in electron acceptor properties of the NO_2 group after complex formation. So, it seems likely that during the photolysis of **1** with liberation of complex **2** (a reducing agent), the initial products are stabilized in the presence of a nitro compound by the formation of a new complex **3**. Among other compounds with electron-acceptor groups, capable of binding complex **2**, are nitriles, quinones with high oxidizing potentials and pyridines (see Online Supplementary Materials). In contrast, carbonyl groups, such as those of ketones and esters, as well as sulfones, do not have this capability.

Compounds with $O–NO_2$, O–NO or $N–NO_2$ groups do not yield dark blue color in the presence of cymantrene. Simultaneous presence of $C–NO_2$ and $RNH–NO_2$ groups during photolysis with cymantrene leads to the production of brown-red color. Photolysis of **1a** and compounds with several $O–NO_2$ groups leads to cymantrene decomposition with formation of light brown inorganic products.



1a–c **2a–c** **3a–c**

a R = H
b R = Et
c R = Ac

R^1 = Alk, C_6H_4X
X = H, Me, OMe, CO_2Me, Cl, CN, NO_2

Scheme 1

The sensitivity of detection of nitro compounds with cymantrene **1a** depends on the extent of overlap between the absorbance of a nitro compound and the area of photosensitivity of cymantrene (λ_{max} = 330 nm). In hexane, the dark blue color is observed at nitro compound concentrations of 10^{-6}–10^{-7} mol dm^{-3}. About 10^{-5} g of a nitro compound in a mix with cymantrene can be detected on a filter paper. As suggested by the results of the experiments with substituted nitrobenzene, the more electrophilic the substitute group is the higher the sensitivity of detection and the more stable the dark blue coloring (half-life of distaining). Sensitivity increases with the increasing number of nitro groups. The stability of a blue color formation also depends on the structure of a nitro compound. For instance, in a row of nitroanisoles, the color of *m*-isomer is the most stable, and that of *p*-isomer is the least (see Online Supplementary Materials). In contrast, nitrobenzonitrile–cymantrene complexes exhibit the reverse stability: *meta* < *para* < *ortho*. During the photolysis with cymantrene nitrobenzonitrile isomers react with both their nitro and nitrile groups. The latter complexes are more mobile on TLC and differ in color from dark blue nitro complexes: light yellow for *o*-isomers, orange for *m*-, and violet for *p*-isomers.

Selectivity of nitro compound detection and identification is primarily determined by the differences in stability and TLC mobility of formed complexes. Aliphatic, as well as aromatic, nitro compounds, in a solution, on a TLC plate or a chromatographic paper yield dark blue unstable coloring (λ_{max} = 600 nm), which may persist for tens of seconds. Different cymantrene derivatives have been tested for their ability to provide the formation of stable colored complexes with nitro compounds. For instance, complexes of acetylcymantrene **1c** with aliphatic

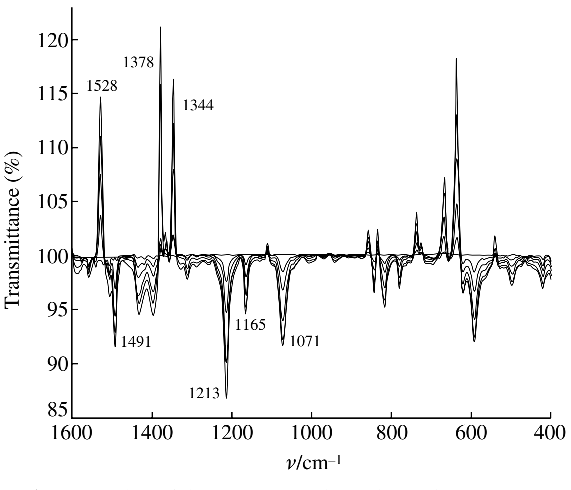


Figure 1 Attenuation of the NO_2 group absorption (1528 and 1344 cm^{-1}) and strengthening of bands at 1213 and 1071 cm^{-1} after UV irradiation of a solution of ethylcymantrene **1b** and *meta*-nitrochlorobenzene in hexane (at 10^{-1} mol dm^{-3}).

[‡] *Rapid detection of nitro compounds.* There are several easy ways to do this. (1) A drop of a nitro compound solution is applied onto a piece of a filter paper, dried, and probed with cymantrene solution; subsequent illumination of the spot with UV light produces dark blue color; about 50 μg of a nitro compound per zone may be detected in this way. (2) A sample of a nitro compound is rendered visible on a Silufol plate and then eluted with a solution of cymantrene (1–3%) in hexane (toluene, ethyl acetate, *etc.*); after elution the plate is dried and illuminated with UV light (mercury lamp or daylight); complexes of nitro compounds with cymantrene appear as zones of dark blue color; the sensitivity is about the same as above. (3) A strip of a filter paper (after removal of solvent) impregnated with diluted cymantrene is placed onto TLC plate with separated nitro compounds and heated (*e.g.*, with a lamp). Cymantrene diffuses into the surface of a plate forming a mixture with nitro compound (in 5–10 s) that upon illumination produces dark blue colour (see Online Supplementary Materials).

nitro compounds yielded more stable crimson color in contrast to the usual dark blue coloring with aromatic ones. In rapid TLC[‡] detection of nitro compounds, cymantrene in quantities of 1–3% is added to eluent and the chromatogram is visualized after short time low-power UV irradiation (UV lamp or sun light). Rapid detection of vapors in the air may be done with the use of chromatographic or blotting paper containing cymantrene **1a** or ethylcymantrene **1b** that absorb vapours and produce color upon subsequent UV irradiation.

In conclusion, the mechanisms of an operationally simple sensing technique for detection of certain nitro group containing compounds based on coordination with organometallic sensors (cymantrenes) were investigated. It was shown that the blue coloring was typical only of C–NO_2 groups and the presence of other functional groups usually did not interfere with the reaction. Based on the results obtained, the formation of a covalent bond between cymantrene Mn and N atom of a nitro group in cymantrene–nitro compound complex is suggested.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2007.05.012.

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