Tetrathiafulvalene-Capped Hybrid Materials for the Optical Detection of Explosives

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Ⓢ Supporting Information

ABSTRACT: Mesoporous silica microparticles capped with TTF moieties and containing a ruthenium dye in the pores were used for the turn-on optical detection of the nitro-aromatic explosives Tetryl and TNT via a selective pore uncapping and release of the entrapped dye.
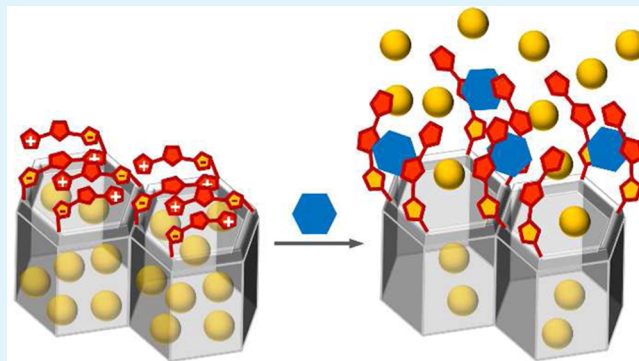
KEYWORDS: controlled release, mesoporous solids, molecular gates, nitroaromatic explosives, tetrathiafulvalene, chemosensors

Among sulfur-containing heterocycles, tetrathiafulvalene (TTF) and its derivatives have been intensively studied in materials science during the past two decades.[1−8] Moreover, the utility of TTF derivatives as building blocks in macrocyclic and supramolecular chemistry has revealed that the TTF moiety is useful beyond the field of materials chemistry and it has been incorporated into a number of exotic molecules, such as catenanes, cyclophanes, dendrimers, polymers, rotaxanes, etc.[9,10] The huge potential of TTF and its derivatives was first established by the discovery of their conductive behavior.[11,12] Since then, other properties of the TTF unit, such as its electroactive and strong π-donor nature, have proven advantageous. As a result, a number of redox responsive ligands and sensors which incorporate the TTF unit into their framework have been reported.[13]

Current international public awareness on terrorist attacks using explosives has resulted in an increasing interest in the development of quick and reliable methods to detect these chemicals.[14] Furthermore, explosives are used in landmines and large quantities of explosives have been dumped in the environment. In the midst of the different chemical explosives, nitroaromatics are perhaps among the most commonly used. Current procedures employed for the detection of nitro-aromatic explosives are in many cases based on complex instrumental analysis.[15−17] Recently, as an alternative to these classical analytical protocols, the design of optical probes has freshly emerged.[18] In these systems, the interaction of explosive molecules with the probe (alone or attached in a polymeric matrix) induced color changes or quenching of the fluorophore emission. Jeppesen and co-workers has used TTF to prepare colorimetric sensors for nitroaromatic explosives, in the shape of TTF-calix[4]pyrroles.[19−21] In these systems, the strong interaction between the electron-deficient nitroaromatics and the electron-rich TTF subunits are responsible for the observed color modulation.

Very recently, the development of nanoscopic hybrid materials equipped with "molecular gates" showing the ability of releasing target entrapped guests upon application of an external trigger has attracted great attention and has been extensively explored during the past years.[22,23] These nano-devices are composed by two subunits, namely, a suitable support and certain capping entities grafted on the surface of the scaffold.[24] The support is used as a suitable reservoir in which certain chemicals could be stored, whereas the molecules

Scheme 1. Schematic Representation (top) of the Sensing Mechanism of the Solid S1 in the Presence of Explosives, Synthesis (middle) of TTF Derivative c, and Synthesis (bottom) of the S1 Material
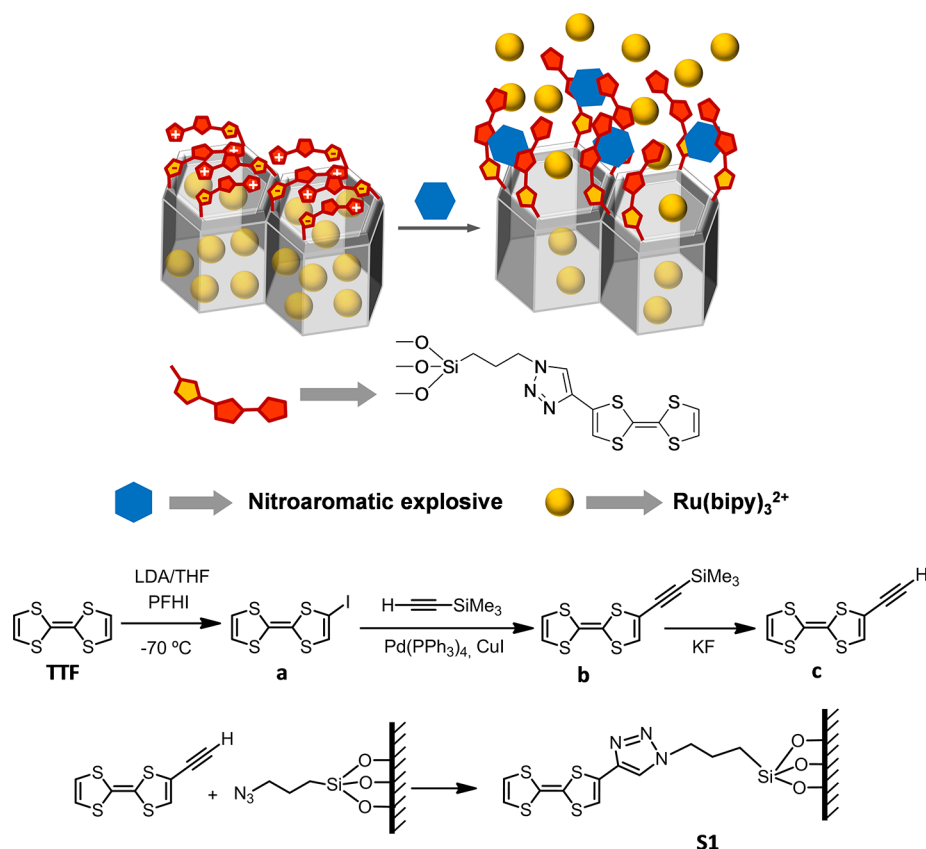
attached on the outer surface act as a "gate" and could control the release of the entrapped molecules at will. Both components have been carefully selected and arranged in order to achieve a wide range of required functionalities using diverse chemistries. These capped materials have been fundamentally used as controlled drug delivery nanoplatforms.[25−28] In contrast their use in sensing applications are less common.[29−31]

Bearing in mind these independent research fields and as a continuation of our work in the design of new explosive probes[32] and new applications using capped mesoporous materials, we report herein the synthesis and sensing behavior of a gated solid functionalized with TTF subunits for the turn-on chromo-fluorogenic detection of nitroaromatic explosives. An illustration of the signaling protocol is shown in Scheme 1. In our approach, a suitable inorganic mesoporous support has been selected and their pores loaded with a dye. Subsequently, a TTF derivative, which can act as a molecular cap, was grafted on the outer surface. The presence of a dense network of TTF units around the pores was expected to inhibit the delivery of the dye. The signaling paradigm relies on the strong electron accepting character of the nitroaromatic derivatives and the formation of TTF-nitroaromatic complexes,[34−36] which result in the rupture of TTF-TTF interactions, e.g., the gate is unlocked followed by delivery of the dye.

As inorganic support, mesoporous MCM-41 silica micro-particles were chosen on account of their unique properties such as large load capacity and well-known functionalization procedures.[36−38] The MCM-41 mesoporous scaffold was prepared by using tetraethyl orthosilicate (TEOS) as inorganic

precursor and hexadecyl-trimethylammonium bromide (CTABr) as a porogen species.[39] The surfactant was removed by calcination and the final MCM-41 support was obtained. The inorganic material was then loaded with $[Ru(bipy)_3]^{2+}$ as a suitable fluorophore and the outer surface was functionalized with 3-(azidopropyl)triethoxisylane groups. In the second step (Scheme 1), the TTF derivative c was attached to solid S1 by a copper(I)-catalyzed Huisgen azide/alkyne 1,3-dipolar cyclo-addition "click" reaction.[40] This led to the formation of a 1,2,3-triazole heterocycle and yielded the final hybrid material S1. The resulting solid was filtered, intensively washed with water and with organic solvents before being dried overnight at 36 °C. Water washings were carried out in order to eliminate possible traces of copper in the surface of S1. SEM analysis using energy-dispersive X-ray spectroscopy (EDX, 20 kV) carried out on the S1 material did not show any characteristic signal for copper indicating that residual copper is not present in the final isolated S1 material. EDX also clearly indicated the presence of sulfur atoms (due to the grafted TTF moieties) in S1.

The TTF derivative c was synthesized (Scheme 1) following a three-step procedure[41,42] from TTF (see the Supporting Information for experimental details). In the first step, 2-iodo-TTF (compound a) was prepared by lithiation of TTF with lithium diisopropylamide (LDA) in THF at −70 °C following reaction of the lithiated TTF derivative with perfluorohexyl iodide (PFHI). Subsequently, compound a was reacted with trimethylsilylacetylene in a mixture of THF and diisopropyl-amine and with catalytic amounts of CuI and Pd(PPh₃)₄ to afford 2-trimethylsilylethynyl-TTF (compound b). Finally, the
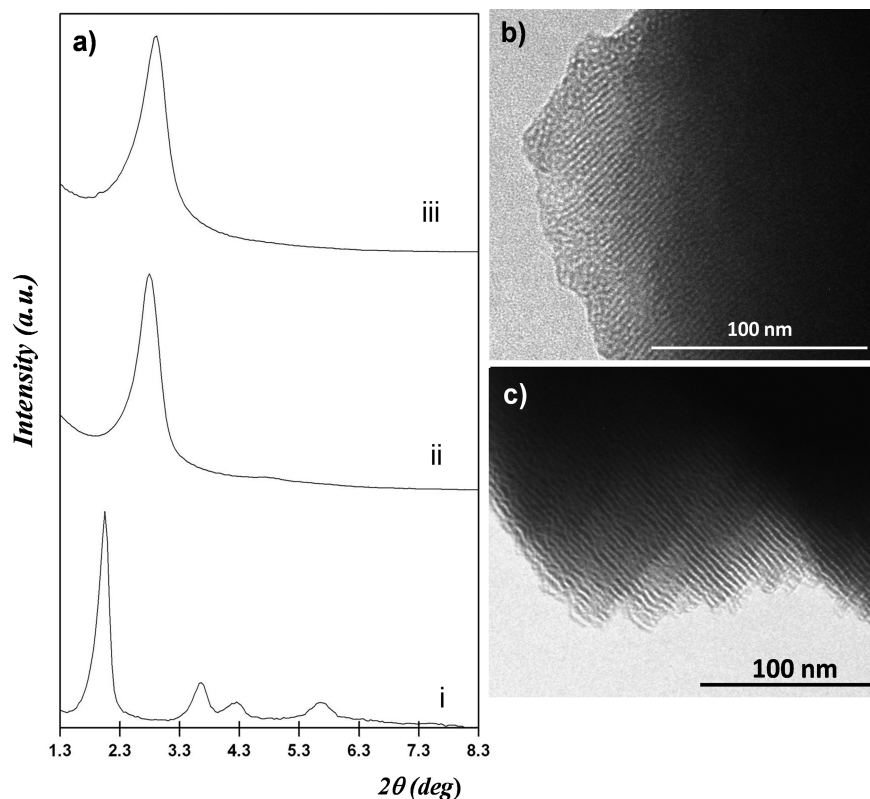
Figure 1. (a) X-ray patterns of (i) MCM-41 as-synthesized, (ii) MCM-41 calcined, and (iii) solid **S1**. (b) TEM image of MCM-41 calcined. (c) TEM image of solid **S1**.

conversion to the corresponding ethynylated-TTF derivative (compound **c**) was carried out by treatment of compound **b** with KF.[43] Moreover, to corroborate the negligible effect of the click reaction in the electrochemical features of TTF, a model compound **2** was synthesized (see the Supporting Information). Solution oxidation potentials obtained from the cyclic voltammograms (CVs) of TTF and **2** are summarized in Table S3 in the Supporting Information. CV of compound **2** and TTF showed two reversible one-electron redox waves as expected (see Figure SI-12 and Table S3 in the Supporting Information).

The starting MCM-41 materials and final sensing solid **S1** were characterized by a variety of different techniques. The presence of the MCM-41 support was confirmed (Figure 1) by X-ray diffraction (XRD) and transmission electron microscopy (TEM) techniques. Figure 1a shows the powder X-ray pattern of MCM-41 as-synthesized, MCM-41 calcined, and the **S1** material. The powder XRD of siliceous MCM-41 as-synthesized shows four low-angle peaks typical of an hexagonal-ordered array which can be indexed as (100), (110), (200), and (210) Bragg reflections. A shift of the (100) peak and a remarkable broadening of the (110) and (200) reflections in the XRD of the MCM-41 calcined sample was observed, whereas **S1** only shows the characteristic (100) reflection. The presence of this peak in **S1** indicates that the mesoporous structure was preserved throughout the filling process with the dye and the anchoring of the TTF derivative. Pictures b and c in Figure 1 show TEM images of the micrometric MCM-41 solid support and of the final hybrid material **S1**, showing the typical porosity associated with this type of inorganic support. The N_2 adsorption−desorption isotherms of calcined MCM-41 showed a typical type IV-curve with a specific surface of 1036.2 m^2 g^{-1}, and a pore volume of

0.45 cm^3 g^{-1} (see Figure SI-5 in the Supporting Information). From the XRD, porosimetry, and TEM studies, the a_0 cell parameter (3.65 nm), the pore diameter (2.25 nm) and the wall thickness (1.40 nm) were obtained. Additionally, the N_2 adsorption−desorption isotherm of **S1** was typical of mesoporous systems with partially filled mesopores,[44] and a decrease in the N_2 volume adsorbed and surface area (816.2 m^2 g^{-1}) was observed. The organic content in **S1** was determined by thermogravimetric analyses (see Figure SI-6 in the Supporting Information); **S1** contained 0.044 mmol of the ruthenium complex/g SiO_2 and 0.290 mmol of the TTF derivative/g SiO_2. ^{29}Si and ^{13}C MAS NMR studies on **S1** were also carried out confirming the functionalization of the solid with TTF groups (see Figure SI-7 and Table S2 in the Supporting Information).

To prove the proposed sensing mechanism (Scheme 1), the interaction of **S1** with nitroaromatics was studied through the delivery of the ruthenium complex. Release studies were carried out in acetonitrile where a tight pore closure was observed (vide infra) and both, the ruthenium dye and the selected nitroaromatics were soluble. In a preliminary assay, it was demonstrated that acetonitrile solutions of **S1** in the absence of nitrated explosives showed "zero release". The capping molecule is composed by an electron donating TTF subunit, and a triazole heterocycle, that have electron accepting character. Consequently, the grafted molecular gate have a permanent dipole moment of 1.78 D (estimated by molecular calculations with Hyperchem 8.0 software) and dipole−dipole interactions between gating TTF molecules in the dense network around the pore outlets seems likely to inhibit dye delivery (Scheme 1, left top). In further studies, delivery assays in the presence of nitroaromatics were carried out. In a typical

assay, 4 mg of **S1** was suspended in 10 mL of acetonitrile containing the selected explosives and after a certain time the solution was filtered. Delivery of the dye to the bulk solution was easily detected by monitoring the metal-to-ligand-charge-transfer (MLCT) transition band of the $[Ru(bipy)_3]^{2+}$ complex centered at 453 nm or its luminescence at 615 nm.[45,46]

Following this protocol, the chromo-fluorogenic response of **S1** to 2,4,6-trinitrophenylmethylnitramine (Tetryl), 2,4,6-trinitrotoluene (TNT), 1,3,5-trinitrobenzene (TNB), 2,4-dinitrotoluene (2,4-DNT), N-methylaniline (NM), 2-nitro-toluene (NT), nitrobenzene (NB), hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), and pentaerythritol tetranitrate (PETN) was studied. As could be interfed from Figure 2, dye delivery
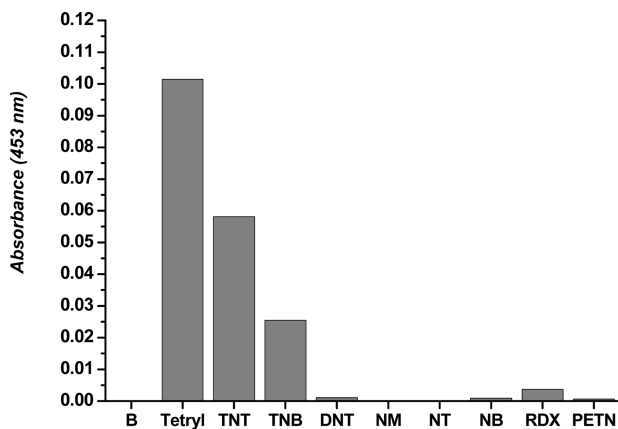

Figure 2. Absorbance intensity at 453 nm (ruthenium complex band) of acetonitrile suspensions of **S1** in the presence of different nitroaromatics (2×10^{-3} mol L^{-1}) and nonaromatic nitrated compounds after 150 min of addition.

from **S1** was only observed for Tetryl, TNT, and in a lesser extent for TNB.[47] Additionally, Figure 3 shows the kinetics of the release of the ruthenium dye from **S1** in the presence of Tetryl, TNT, and TNB. In all cases dye delivery was observed within ca. 20 min. This observation can most likely be accounted for by the formation of TTF-nitroaromatic complexes, which results in the rupture of the dipole−dipole
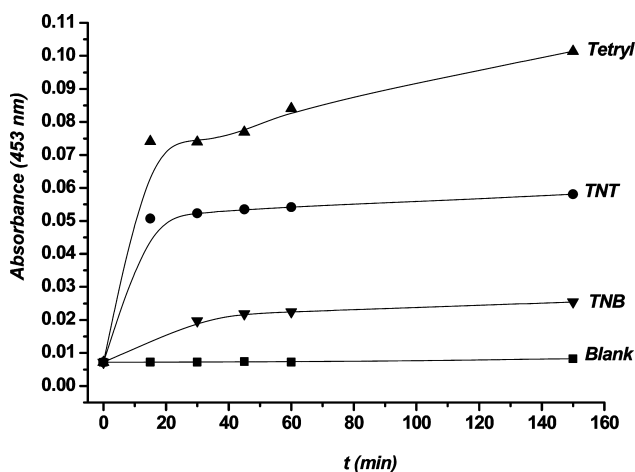

Figure 3. Kinetics of the release of the $[Ru(bipy)_3]^{2+}$ dye from the solid **S1** in the absence (blank) and the presence of the nitroaromatic explosives Tetryl, TNT, and TNB (2.0×10^{-3} mol L^{-1}) in acetonitrile obtained using the $[Ru(bipy)_3]^{2+}$ absorbance at $\lambda = 453$ nm as probe.

interactions between the grafted TTF molecules allowing the gate to open.[34−36] This hypothesis is supported by the fact that for a certain concentration, the amount of dye delivered from **S1** follow the order Tetryl > TNT > TNB, which is also the order of the electron accepting character of these nitro derivatives, an observation which strongly suggest that it is their interaction with the electron donating TTF units which are responsible for the uncapping process. In addition, ^{13}C NMR spectroscopic investigations carried out on the solid **S1** in the presence of Tetryl (see materials characterization in the Supporting Information) supported the proposed opening mechanism.

Further studies were carried out and titration curves in the presence of Tetryl and TNT were obtained (see limits of detection studies in the Supporting Information). In particular, the controlled release of $[Ru(bipy)_3]^{2+}$ from the inner of the pores of **S1** in the presence of increasing quantities of TNT and Tetryl was studied though the absorbance (at 453 nm) or emission (at 593 nm) of the complex. In these experiments, an increase in the absorbance (see Figure SI-9 for TNT in the Supporting Information) or in the intensity of the luminescence emission band (see Figure 4 for Tetryl) of the
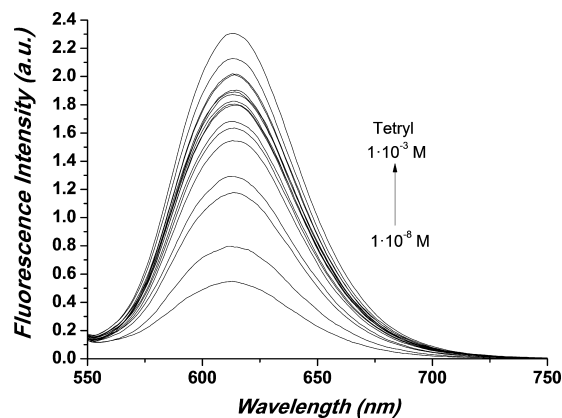

Figure 4. Changes in the emission band of the ruthenium complex released from acetonitrile suspensions of **S1** upon addition of increasing quantities of Tetryl ($\lambda_{ex} = 453$ nm) after 60 min.

$[Ru(bipy)_3]^{2+}$ dye in the solution was found to be proportional to the concentration of the explosive, which is in agreement with the above-described assisted uncapping protocol. A simple UV−visible titration (by plotting the absorbance of the released complex versus nitroaromatic explosive concentration) allowed us to calculate limits of detection (LOD) of 28 μM (8 ppm) and 66 μM (15 ppm) for Tetryl and TNT, respectively. By means of fluorescence measurements LOD of 3.5 μM (1 ppm) and 26 μM (6 ppm) were found for Tetryl and TNT, respectively (see Figure SI-8 and SI-10 in the Supporting Information). For the sake of comparison Table S4 (see the Supporting Information) list some sensing characteristics of recently reported colorimetric probes for the detection of nitroaromatic explosives using supramolecular-based concepts.

The limits of detection measured for **S1** are in the range reported for related TTF-calix[4]pyrroles (ca. 3 ppm).[21] Subtle differences in LOD and selectivity for nitroaromatic explosives of **S1**, and these reported TTF-calix[4]pyrol derivatives are most likely due to the different sensing mechanism in both systems. Whereas in the latter, the explosive interacts directly with the TTF-calix[4]pyrol cavity yielding color changes, for

S1, the nitroaromatic explosive interacts with the grafted TTF opening the pores and allowing the release of the entrapped ruthenium complex. An additional advantage of our system, when compared with others supramolecular-based probes for TNT detection, is that in our case a turn-on of the emission is observed. Besides, despite the relatively high limit of detection obtained, in the ppm range, another difference of our hybrid material is its modular character. In particular, the possible use of different fluorophores as cargo and the possible functionalization of the external surface of mesoporous materials with other gating electron-deficient groups (to tune or enhance selectivity) makes this approach versatile for the future development of materials with appropriate sensing properties.

Finally, the possible use of solid **S1** for explosive detection in soil samples was tested. In particular we used soil samples spiked with a known amount of Tetryl (97 μM, 27.81 ppm) and applied the standard addition method in order to overcome the matrix effect. The spiked soil samples were extracted with acetonitrile and then increasing volumes of a standard Tetryl solution were added (see soil extraction procedures in the Supporting Information). Figure 5 depicts the absorbance of
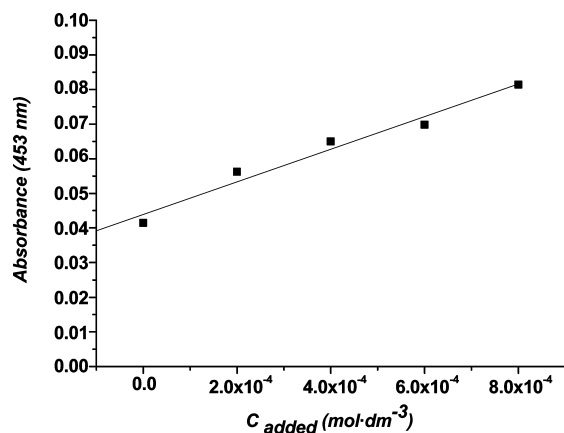

Figure 5. Absorbance measured at 453 nm (ruthenium complex band released from **S1**) in acetonitrile soil extracts in the presence of increasing quantities of Tetryl.

the ruthenium complex release as a function of Tetryl concentration. By using this curve a concentration of 88 μM (25.15 ppm) of Tetryl was measured (88% of recovery).

In summary, we have reported the synthesis of new nanoscopic silica mesoporous supports capped with an electron donating TTF derivative for the easy turn-on optical sensing of nitroaromatic explosives. The presence of Tetryl, TNT, and in a lesser extent TNB in acetonitrile suspensions of the hybrid material induced pore opening with the subsequent release of an entrapped dye. This allows the detection of Tetryl and TNT in a new protocol that uses a standard MCM-41 material functionalized with TTF π-donor units and a dye. It is advisable to note that this paradigm relies on a different poorly explored approach and therefore it displays new possibilities of modulation that cannot be obtained in simple molecular-based receptors. Moreover, the preparation of the sensing material is synthetically undemanding and allows a large number of binding (TTF-like donors) and signaling units (dyes) to be probed. By using this simple procedure, color or emission changes allows the selective detection of Tetryl and TNT at the ppm level. Finally, the hybrid material was used for the detection of Tetryl in soil samples with good results. To the

best of our knowledge, this represents one of the very few examples showing a turn-on of color or luminescence in the presence of nitroaromatic explosives,[32] and the first example using TTF as a molecular gate. Further functionalization of the external surface of mesoporous materials with other electron-donating TTF derivatives (containing different linking units and number of sulfur atoms) to enhance and tune the selectivity are currently being pursued.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Synthetic procedures, materials characterization, dye release studies, and soil extraction measurements. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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(47) Addition of benzoquinone (2.0×10^{-3} mol L^{-1}) to acetonitrile suspensions of solid **S1** (4 mg in 10 mL) induced pore opening with the subsequent release of the entrapped ruthenium complex. The release of the complex was observed by emission measurements (λ_{em} = 615 nm, λ_{exc} = 453 nm) but not by UV−visible because the yellow color of the benzoquinone solution masked the $[Ru(bipy)_3]^{2+}$ MLCT band at 453 nm. This pore opening is due to the formation of strong charge-transfer complexes between the electron donor TTF subunits and the electron acceptor benzoquinone molecules. This suggested that as it happens in other molecular-based probes planar electron-acceptor molecules (such as benzoquinone) are potential interferents.

■ NOTE ADDED AFTER ASAP PUBLICATION

This paper was published on the Web on February 25, 2013, with errors in the Supporting Information. The corrected version was reposted on February 27, 2013.