Entrapment of Organic Molecules within Metals: Dyes in Silver

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We proved the feasibility of entrapment of organic molecules within a metal. Specifically, Congo red, Safranin-O, and thionine were entrapped in metallic silver, obtained through the aqueous reduction of silver cations with sodium hypophosphite. Not only were these water-soluble molecules entrapped, but so was the hydrophobic Sudan III by solubilizing it with sodium dodecyl sulfate. It was proven that the molecules remain intact by the entrapment procedure and that the entrapment is within cages and narrow pores formed by Ag crystallites which aggregate into bulk powder of low porosity. Furthermore, it was proven that a population of nonleachable entrapped molecules is accessible to reaction with external reagents which diffuse inside through the metal pore network.

1. Introduction: From the Doping of Sol−Gel Materials to the Doping of Metals

Merging organic chemistry and the chemistry of ceramics and glasses has proven to be very fruitful in forming new functional materials.[1] A major branch that has evolved in this domain has been the entrapment of organic molecules within inorganic oxide sol−gel materials through the sol−gel methodology: this methodology found useful applications practically all across modern chemistry and biochemistry.[2,3] The next "Everest" awaiting to be climbed from a similar point of approach has been the doping of *metals* with organic molecules. Here we prove the feasibility of the idea. We do it by entrapping several dye molecules within silver, showing that the entrapment leaves the molecules intact and showing that, as in the case of doped sol−gel materials, the entrapped molecules are accessible to chemical interaction with an external reagent. We have not encountered earlier reports on directed efforts to incorporate small organic molecules within a metal by its intentional physical entrapment. Studies which border it are some propositions that metal preparation in organic media may result in organic impurities[4a−c] and Warshawsky's et al. studies of the surface metallization of polymer microbeads with added or tethered dyes.[4d] Of course, adsorption onto metal surfaces[5] and doping of various matrixes with metals[6] are very well studied, but our goal has been different: incorporating an organic molecule within a metallic matrix.

Doping Approach. Classical inorganic chemistry served that purpose. The molecules to be entrapped were dissolved in the following Ag^+-reducing aqueous solution:

$$2AgNO_3 + NaH_2PO_2 + H_2O \rightarrow 2Ag + NaH_2PO_3 + 2HNO_3 \quad (1)$$

Sodium hypophosphite was selected as a reducing agent[4d,7] because it is easy to remove the unreacted reagent as well as its products, because its reducing power is such that it did not react with the selected dyes for entrapment while still being active on Ag^+, because the resulting metal has the classical shine of silver (Figure 1, part 1), because the metal-formation procedure can be carried out at room temperature, and because no added catalyst, acid, or base is needed—just half of a water molecule is consumed per one Ag^+ cation (see eq 1). As an example for a reducing agent which was tested but rejected, we mention $NaBH_4$, which produces metallic black Ag and which, as reported elsewhere, probably contains some boron.[8]

The selected dyes were (Chart 1) as follows: Congo red (CR), an anionic dye and a counterion to Ag^+; Safranin-O (SaO), a cationic dye and a redox reagent;[9]

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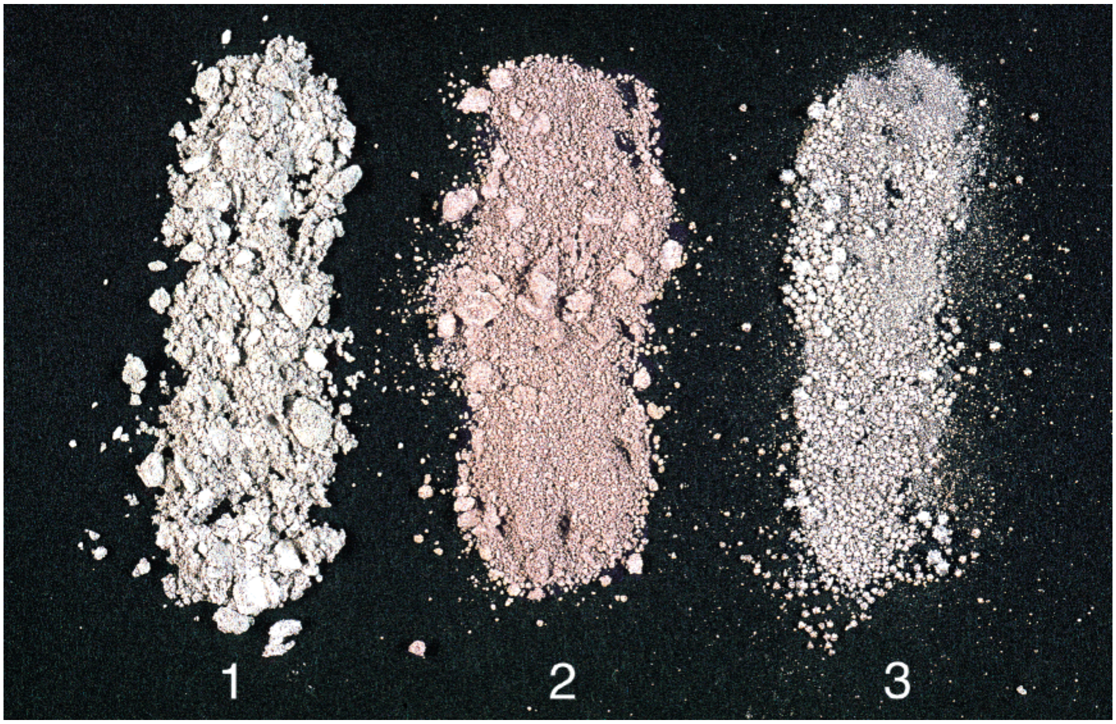
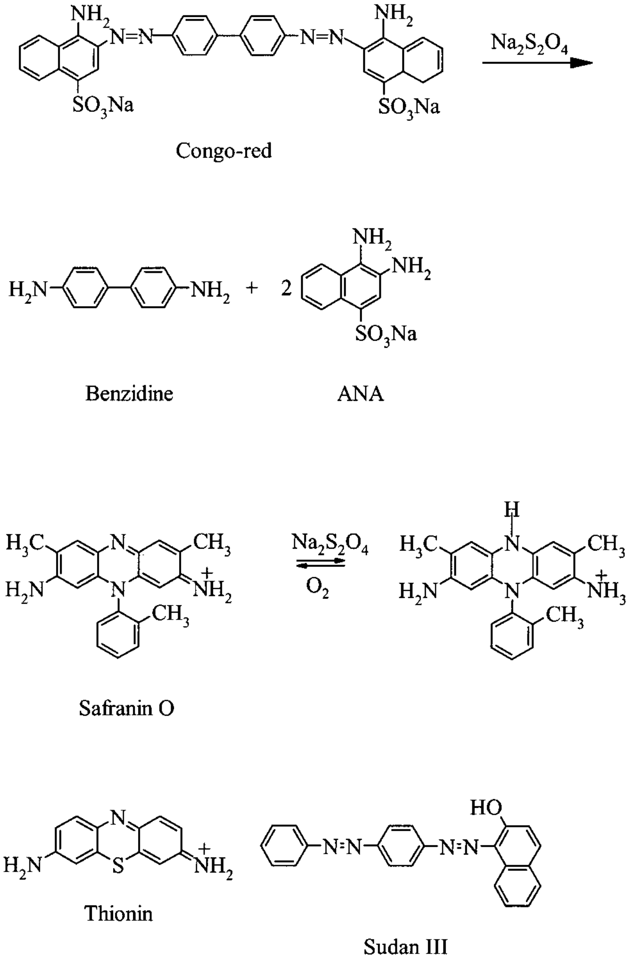


Figure 1. (1) Silver powder prepared according to eq 1. (2) Silver doped with S-III. (3) Silver doped with SaO.

Chart 1



thionine (Th), a molecule which possesses a cyclic R−S−R metal-ligating group (which proved later to be an unnecessary condition for good entrapment); the *hydrophobic* dye Sudan III (S-III), with which we demonstrated that entrapped molecules need not be water soluble and that surfactants can be used for that purpose. The stability of all dyes to the reducing environment during trapping was checked in solution, and indeed it was found that the mild reductant used does not affect the dyes (see below).

Many future applications can be envisaged of using the *reactivity* of metal-entrapped molecules. The accessibility of the entrapped dyes to an external reagent, diffusing in and interacting with it, was shown for CR and SaO. We used for this purpose one of the most typical reactions of these dyes, namely, their bleaching with $Na_2S_2O_4$ (which is converted mainly to SO_4^{2-} and HSO_3^{-} [7b]). This well-studied reaction is used, for instance, in industrial and environmental applications.[10] The bleaching reactions, irreversible for CR (forming benzidine and 1,2-diamino-4-naphthalenesulfonic acid (ANA)), and reversible under air for SaO, are shown in Chart 1.

2. Experimental Details and Results

Chemicals. *Dyes.* CR, SaO, and Th were from Aldrich. S-III was from Sigma.

Reagents. $AgNO_3$, $Na_2S_2O_4$ (85%), and $NaH_2PO_2{\cdot}xH_2O$ were from Aldrich (based on data provided from the producer, x in the phosphite is approximately 0.2). The surfactant sodium dodecyl sulfate (SDS) was from BDH. Ag powder (5−8 μm) was from Aldrich (No. 48,405-9). Ag_2O was from Riedel de Haen.

Instrumentation. UV−vis absorption spectroscopy was carried out with a Hewlett-Packard 8452A diode array UV−vis spectrophotometer, Fourier transform infrared (FTIR) spectroscopy with a Bruker Vector 22 FTIR instrument, and X-ray diffraction (XRD) measurements with a Philips automated powder diffractometer (with a PW1830 generator, a

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Table 1. Rates of Dye Extraction

	H_2O		acetone		DMSO	
dye	initial rate (mol s^{-1} g^{-1})	$t_{1/2}$	initial rate (mol s^{-1} g^{-1})	$t_{1/2}$	initial rate (mol s^{-1} g^{-1})	$t_{1/2}$
CR	1.06×10^{-12}	343 days	8.32×10^{-12}	43 days	7.5×10^{-10}	0.5 days
SaO	6.30×10^{-10}	20 h	4.64×10^{-9}	3 h	1.09×10^{-8}	1 h

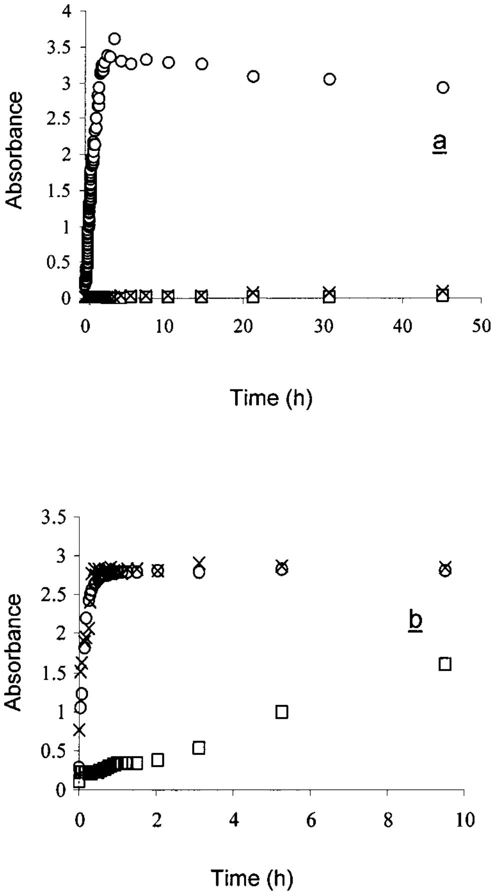

Figure 2. Dye extraction rates with water (□), acetone (×), and DMSO (○): (a) CR; (b) SaO.

PW1710 control unit, a PW1820 vertical goniometer, 40 kV, 35 mA, and Cu Kα (1.5405 Å)). Scanning electron microscopy (SEM) was carried out with a JEOL JXA SEM 8600 instrument with an energy-dispersive analysis of X-rays (EDAX) attachment. Nitrogen Brunauer–Emmett–Teller (BET) surface area and porosity were determined from adsorption/desorption isotherms on a Micromeritics ASAP-2000 physisorption instrument. Density was measured with a Quantachrome multipycnometer 4AC232 instrument using helium as a displacing gas; all samples were pretreated with a flow of helium for 15 min. The density was also measured by weighing 0.1 mL samples.

Entrapment Procedure. We select to give as a typical procedure for entrapment the case of SaO because it needs more attention in preparation; all other dyes were entrapped better and easier (see below). A 125 mL water solution of 3.03 g (0.018 mol) of $AgNO_3$, 1.5 g (0.017 mol) of sodium hypophosphite, and 0.06 g (0.17 mmol) of SaO were mechanically stirred (200 rpm on a Heidolph RZR 2021 stirrer, here and below) at room temperature for 4 days. The precipitate was filtered, washed with one portion of 100 mL of distilled water, dried for 2 days at 30 °C (this is an important step in the procedure; without it more dye is washed out at later stages), and washed again with 10 × 10 mL portions, until dye extraction becomes negligible. The total of the washed dye is about 40% of the initial dye used in the reaction mixture, leaving as entrapped SaO 60% of that initial amount. The dye-doped metal, SaO@Ag—we shall use the notation "dopant@metal" (as used for doped fullerenes)—was dried and finally stored under a nitrogen atmosphere.

Table 2. Dye Extraction Results from the Final Doped Silver Materials

dye	H_2O (%)[a]	solvent (%)[a]		DMSO (%)[a]
CR	0	acetone	40	52
SaO	4	acetone	10	16
Th	6	acetone	60	100
S-III	0	ethanol	14	100
		THF	39	
		toluene	60	

[a] Percentage of the dye which remained entrapped after the washing.

Table 3. Adsorption of Dyes on Silver Powders

dye	self-made Ag (%)[a]	commercial Ag (%)[a]
SaO[b]	10	7
CR	1	1
Th	19	21

[a] Percentage of the initial concentration. [b] Water washing of adsorbed SaO on self-made Ag: 1st, 1.31%; 2nd, 0.22%; 3rd, 0.26%. SaO with commercial Ag: 1st, 0.67%; 2nd, 0.10%; 3rd, 0.10%.

All other dyes were entrapped following a similar procedure (except that 0.05 g of the dye was taken). For the entrapment of the hydrophobic S-III, 0.3 g (1.0 mmol) of SDS was added to the mixture. CR and S-III were very well entrapped, and only one cycle of washing was enough; even this one did not show any leaching for both dyes. Th was likewise fairly well entrapped with a total of about 9% of the initial dye used, which was washed out.

Experiments in Dye Extraction. Useful information on the various populations of the entrapped molecules was obtained by following the rates of dye extraction with three solvents: dimethyl sulfoxide (DMSO), acetone, and water. These tests were performed with SaO@Ag and with CR@Ag at an intermediate stage of the preparation, namely, after the 30 °C drying step and before the washing with water portions. As explained in the previous section, at this stage CR is already tightly held and nonextractable by water. The extraction experiments (to be analyzed in section 3) were carried out by suspending 0.03 g of CR@Ag or 0.01 g of SaO@Ag in 3.0 mL of solvent, following spectroscopically the released dye through its wavelength of maximum absorption (which varied slightly for each solvent). With CR@Ag, readings were taken every 35 s for 2 h and then at increased time intervals (a 50% increase for each successive reading) for a total of 45 h (Figure 2a). With SaO@Ag, readings were taken every 60 s for 1 h and then at increased time intervals (a 100% increase for each successive reading) for a total of 10 h (Figure 2b). Because the accumulated amount extracted is linear in time (until the plateau is reached), initial rates and half-life values based on these initial rates were calculated, taking the first 20 min for SaO and the first 30 min for CR, and these are collected in Table 1. Extraction experiments were carried also on all final dye@Ag materials by stirring 0.1 g of the doped metal with 30 mL of solvent for 24 h, and the results are collected in Table 2 .[11]

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(11) Release of the entrapped dyes was also affected under harsher conditions in order to identify the limits of the matrix strength (for the various experiments carried out). These conditions included mechanical flattening of SaO@Ag and treating CR@Ag with a 0.01 M NaOH solution for 1 h.

Table 4. XRD Patterns of Doped and Undoped Ag

	lit. data[a] for Ag		prepared Ag		SaO@Ag		CR@Ag		S-III@Ag	
plane (*hkl*)	2*θ*	Int	2*θ*	Int	2*θ*	Int	2*θ*	Int	2*θ*	Int
111	100	38.160	100	38.010	100	38.080	100	38.125	100	38.115
200	39.3	44.355	42.2	44.185	27.3	44.270	38.3	44.205	40	44.276
220	19.6	64.505	44.6	63.870	21.2	64.430	21.6	64.415	25	64.423
311	17.3	77.435			18.9	77.330			26	77.469

[a] JCPDS. *X-rays Powders Diffraction Patterns of Silver 4-783* (1953).

Experiments in Dye Adsorption/Desorption. For comparing entrapment to adsorption, the following experiments were carried out: Metallic silver was prepared as described above but without an entrapped dye. Then, 12.5 mg (0.036 mmol) of SaO or 10.0 mg of CR (0.014 mmol) or Th (0.035 mmol) and 380 mg (3.5 mmol) of silver were stirred in 30 mL for 24 h. The amount adsorbed was determined spectroscopically from the supernatant solution. For comparison of the "homemade" silver to commercial silver, the experiment was repeated with Aldrich micronized Ag. Results are collected in Table 3. Although small, the amount adsorbed is held tight for water washings. Results for adsorbed SaO (the Ag was filtered, stirred with 30 mL of water, and filtered again, the filtrate was checked, and the procedure was repeated three times) are collected in the footnote of Table 3.

Reactions with the Metal-Doped Molecules. *(a) Blank Reactions in Solution*. Bleaching of CR and of SaO was carried out by dissolving 0.003 g (4.3×10^{-6} mol of CR and 8.6×10^{-6} mol of SaO) of dye and 0.1 g (0.49 mmol) of $Na_2S_2O_4$ in 5.0 mL of water. The bleaching from deep red to slightly yellowish (for both dyes) was immediate. While the reaction with CR is irreversible (because of cleavage of the azo bonds[12] (Chart 1), the reduced form of SaO is spontaneously back-oxidized by air−oxygen (Chart 1). This can be avoided if air is excluded by purging with argon.

(b) Reactions with the Doped Molecules. A total of 0.09 g of powdered silver doped with SaO as described above was stirred in a solution of 0.1 g (0.049 mmol) of $Na_2S_2O_4$ in 5.0 mL of water for 2 h under argon. The solids were then filtered and washed with 10 mL of argon-purged H_2O. The content of the doped metal after reaction was extracted with 5.0 mL of DMSO, and the amount of extractable unreacted dye was determined spectroscopically and compared to unreacted doped silver, which was extracted similarly. It was found that 33% of the entrapped SaO has reacted. A higher yield, 78% (out of the DMSO-extractable dye; Table 2), was obtained with CR@Ag because of the much better stability of this material, which allowed the reaction to be carried out for 48 h. The probable contribution to the reaction from leached dye was tested and found to be negligible for SaO@Ag and practically zero for CR@Ag.

3. Results and Interpretations

Material Properties. Figure 1 shows Ag-doped (and undoped) materials; the metallic appearance is clear, and slight coloration is clearly evident (pointing to yet another possible application of this technology). XRD measurements confirm that the metal is crystalline Ag (Table 4), and the addition of the dopant to the Ag-forming solution does not alter the positions of the typical diffraction lines [JCPDS]. No peaks of silver salts or silver oxide were seen. A typical SEM picture, that of SaO@Ag, is shown in Figure 3, revealing the crystallite aggregated nature of the material (with apparent particle sizes on the order of 100 μm). EDAX analysis of the surface resulted in 99.28% Ag with some Si and Al impurities but no C or O.

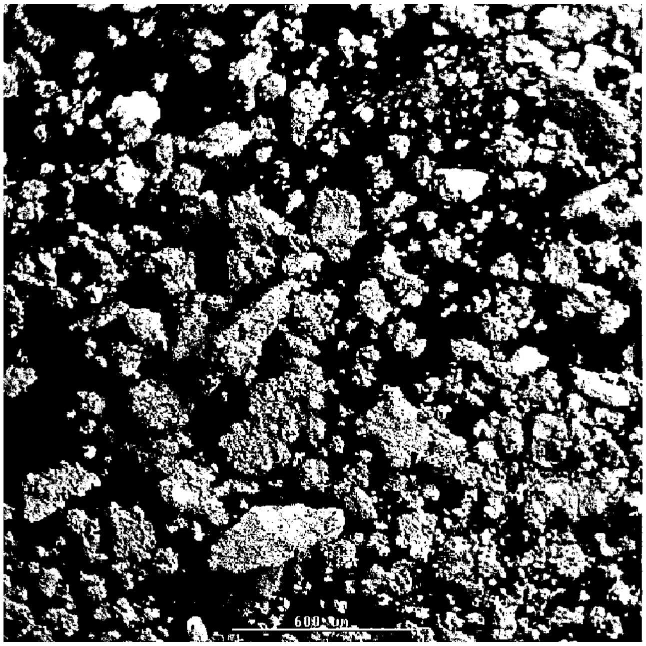

Figure 3. SEM micrograph of SaO@Ag.

Table 5. Some Typical Surface Area and Porosity Values

	surface area (m^2/g)	pore volume (mL/g)	pore size (Å)	BET constant
self-made Ag	5.65	0.021	149	78
SaO@Ag	3.75	0.010	110	41
S-III@Ag	3.40	0.002	21	24
Ag_2O	0.039	0.025		close to zero

Table 6. Some Typical Material Densities

	density[a] (g/mL)
bulk Ag[b]	10.5
commercial Ag (powder)	3.1
self-made Ag	3.6
CR@Ag	2.3 (2.7)[c]
S-III@Ag	1.5 (1.4)[c]

[a] By volume−weight determination. [b] CRC. [c] Measured with a pycnometer.

N_2 surface area, porosity, BET *C* constants, and density values for some typical samples are collected in Tables 5 and 6. Nitrogen adsorption on silver prepared without dopant shows a typical macroporous adsorption/desorption isotherm (Figure 4a) which obeys nicely the BET equation (Figure 4b; correlation coefficient = 0.9998). The surface area of 5.6 m^2/g, the nominal BET-derived average pore size of ~150 Å, and the small pore volume of 0.02 mL/g are all indicative of an aggregated microcrystallite system and interstitial porosity. With SaO@Ag the shape of the isotherm and the compliance with the BET equation remain similar (Figure 4c,d), but the characteristic values are smaller (Table 5), i.e., 3.8 m^2/g, ~110 Å and 0.01 mL/g. This decline in values seems to indicate that much of the dopant resides in closed interstitial pores formed by the Ag crystallite aggregation. The significantly low densi-

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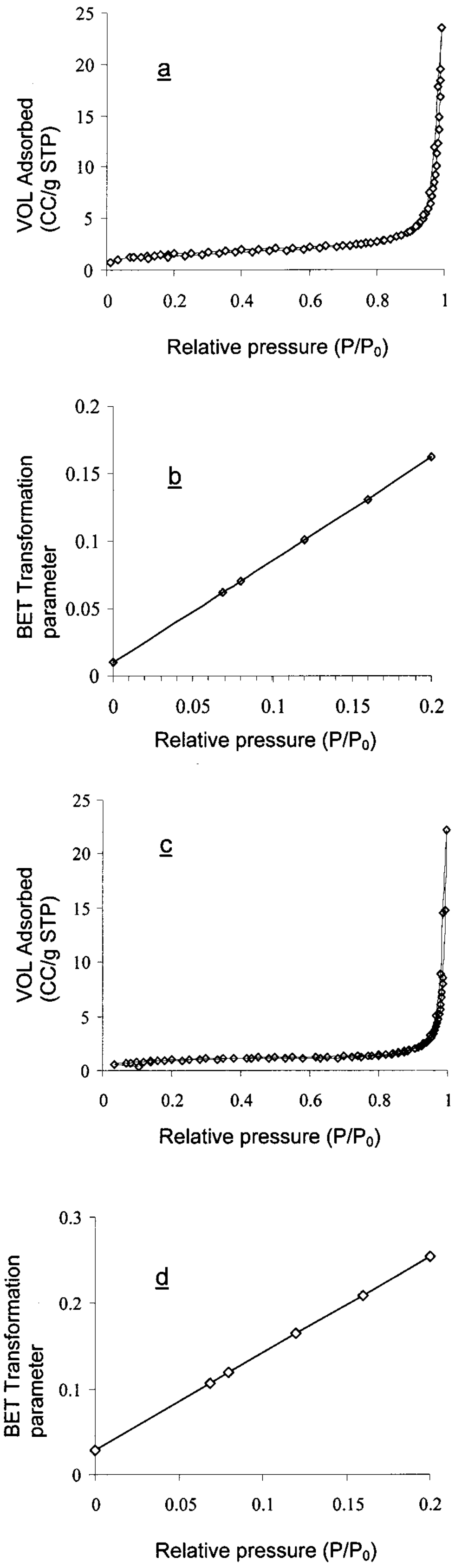

Figure 4. Adsorption/desorption isotherms and compliance to the BET equation of undoped (a and b) and SaO-doped (c and d) silver.

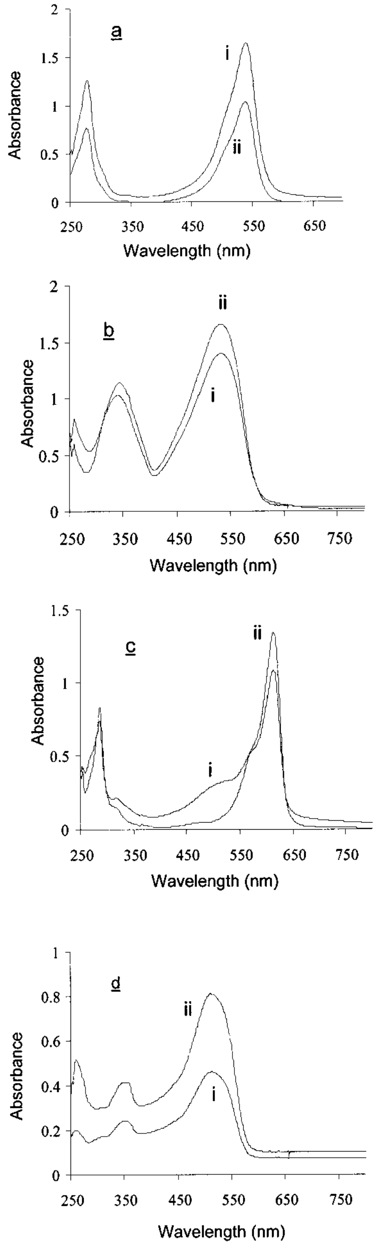

Figure 5. Entrapment in the metal leaving the dyes intact. Shown are absorption spectra in (i) DMSO blanks and (ii) in DMSO after extraction of the dye@Ag: (a) SaO; (b) CR; (c) Th; (d) S-III.

ties, compared to monolithic Ag crystal (Table 6), are further confirmation to intercrystallite porosity. The BET *C* constants, which drop from a value of 78 in the undoped Ag to 41 in the doped sample, indicate that the entrapped molecules reside on the crystallite surface, and the fact that they are completely different from the *C* value obtained for Ag_2O corroborates once again that the interface is not oxidized.

Entrapment. Spectral analyses of the DMSO-extracted dyes proved that all dyes were kept intact during the reductive entrapment process (Figure 5). It is an important observation, because it shows that this entrapment procedure may be general enough for other dopant molecules as well. The successful entrapment of hydrophobic S-III (Figure 5d) adds to the generality of the procedure.

The entrapment of CR was particularly successful: On the one hand, it was tightly entrapped and, on the other hand, much of it remained accessible for reaction. Thus, when the silver was washed with water after the

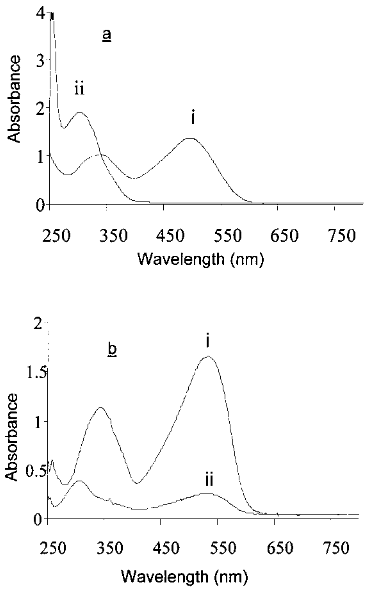

Figure 6. CR before (i) and after (ii) reaction with $Na_2S_2O_4$ (a) in a blank solution and (b) in the DMSO-extracted CR@Ag.

entrapment procedure, no dye leached out, and so 100% of the dye used is entrapped. The distinction between entrapment and adsorption is particularly evident from the adsorption experiment: only 1% of the CR was adsorbed either on Ag made by us or on commercial Ag (Table 3), whereas *all* of the CR (with the same CR/Ag ratio) was entrapped (Table 2). It should be noted that the behavior of the commercial and the prepared Ag as adsorbents is quite similar (as seen also for SaO; Table 3), corroborating not only that the Ag^+ reduction reaction indeed produces the desired Ag (see also the XRD results above) but also that it is apparently aggregated in a way similar to that of the commercial Ag particles. DMSO, which proved powerful for the extraction of Th and S-III, was able to extract here 52% of the CR. The strength of the entrapment of CR was evident also from the intial rates of extraction (Figure 2a) and from the half-lives, which for water is about 1 year (Table 1).

As explained above, the reduction reaction of entrapped CR (Chart 1) was performed in water, and then DMSO was used for extraction of the unreacted CR (and the reaction products). Comparative spectra are shown in parts a (blank-solutions) and b (before and after reaction within silver) of Figure 6. Confirmation of the N=N reduction reaction was also obtained with FTIR (Figure 7; see the figure caption for details of peak assignment). Although the entrapping system is quite different from sol–gel entrapment,[2,3] the basic observation is similar: Entrapment provides a population of molecules which are water nonextractable and yet available for reaction with a water-soluble reagent.

Each dye@metal represents a set of different populations with different strengths of interactions. Thus, SaO@Ag is quite different from CR@Ag. Although SaO is better adsorbed on the surface of silver compared to CR (10% compared to 1% for CR), part of the entrapped dye molecules are less strongly held within the metallic matrix, compared to CR. After the 30 °C drying stage, an additional 30–40 mol % is washed out by water (compared to 0% for CR), but DMSO extracts only an additional 16% of entrapped SaO. We see then that simple adsorptive arguments cannot explain the nature of the entrapment. Indeed, that entrapment is a distinctly different process compared to adsorption is also evident from the Th@Ag data. Of the three water-soluble dyes, this one is best adsorbed (20% adsorption), probably because of the existence of the sulfur in its structure; and yet this dye is somewhat less well entrapped compared to CR (although it is better entrapped than SaO): 6% of this water-soluble entrapped dye was leached out with water (compared to 0% for CR), and all of it (100%) was extracted DMSO (and 60% with acetone; see Table 2 for comparison). Not only that, but even water solubilization with a surfactant is no limitation for efficient nonleachable entrapment. This was evident for S-III/SDS@Ag. Although the solubilization with SDS is very effective, leaching of the entrapped dye in water was 0% (and for other solvents, see Table 2).

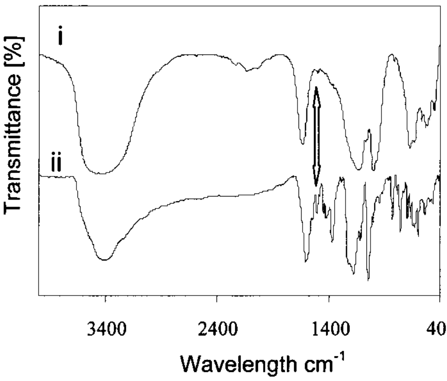

Figure 7. FTIR confirmation of the typical $Na_2S_2O_4$ bleaching reaction of entrapped CR: the 1430 cm^{-1} trans-azo band (ii); disappeared (i).

Overall Picture of the Entrapment. The picture that emerges then from all of the experimental observations is of an entrapment which is due to physical caging inside partially closed pores, the walls of which are the faces of small Ag crystals. In fact, as we have seen, there are several types of populations of molecules that are obtained from the entrapment process: those which are easily washed away in the cleaning procedure of the doped silver, those which are extractable by prolonged treatment with various solvents, those which are well entrapped and yet accessible to reaction (very much like sol–gel materials), and those which are entrapped and not accessible for reaction. The efficiency of the entrapment is remarkable considering the fact that water-soluble species remain unextractable by water and that much less is adsorbed than entrapped, in controlled experiments.

The aim of this preliminary report has been to prove the feasibility of the idea that molecules can be entrapped by metals. Having the feasibility proof at hand, the scope of this methodology, its improvement, and its potential applications are next to be explored; this is currently being carried out in our laboratory.

Acknowledgment. See ref 13.

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(13) This project was made possible mainly by using the existing infrastructure, because funding agencies traditionally do not support projects which have a flavor of "I have an idea which apparently has not been tested before and, furthermore, I do not know if it will work, but anyway please provide me with the means to check it". This situation is quite familiar, we believe, with many of our readers.