

Immobilization of Thienyl-Containing Azo Pigments on Silica Gel Surface

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Abstract—Reactions of chlorinated silica gel with thienyllithium and its derivatives gave silica gels modified by organic fragments. By successive chemical transformations of the latter immobilized thienyl-containing azo pigments were obtained. Azo pigments can also be immobilized on silica gel surface through reactions with 2,4,6-trichloro-1,3,5-triazine. Silica gels with grafted azo pigments are characterized by high resistance to light and washing.

The number of organic compounds immobilized on inorganic and organic matrices continuously grows, and performance requirements to them and demands also continuously increase. Polymeric materials modified by organic fragments are widely used in various chromatographic techniques, including high-performance liquid chromatography, and in the synthesis of heterogeneous catalysts of new generation, immobilized enzymes and other biological polymers, modified electrodes and sensors, hydrophobic construction and finishing materials, etc. [1–3].

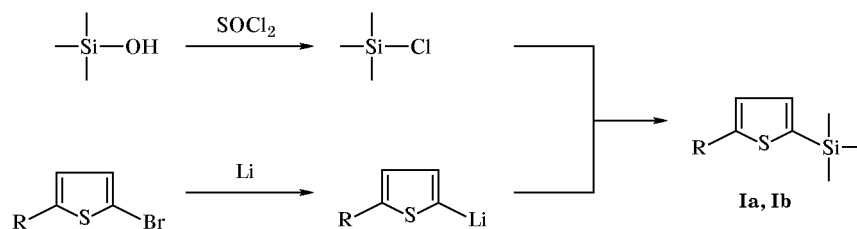
We previously reported [4, 5] on immobilization on silica gel and asbestos surface of various organic fragments, in particular phenyl, naphthyl, phenanthryl, anthryl, pyranyl, fluorenyl, etc. groups which were then converted through a series of successive chemical reactions into azo dyes and azo pigments. In the present study we made an attempt to develop procedures for immobilization on silica gel surface of thiophene and substituted thiophenes with the goal of further synthesis of various dyes on the basis of grafted heterocyclic nuclei. The nature of the bonds

between the inorganic matrix and thienyl-containing dye can be judged from the resistance of the resulting material to light, γ radiation, and washing. In addition, comparison of the properties of immobilized and model dyes could reveal the effect of silicon atoms on the organic molecule.

It was also interesting to study immobilization on inorganic matrix of both 2,4,6-trichloro-1,3,5-triazine itself and active dyes derived therefrom. In the first case, it would be possible to add any organic fragment having activated hydrogen atoms to inorganic matrix through the triazine ring, and in the second, pigments could be grafted in one step without preliminary activation of inorganic matrix. 1,3,5-Triazine is linked to inorganic matrix through an oxygen bridge which determines the strength of the bond between the matrix and organic fragment.

Immobilization of thiophene and 2-nitrothiophene was accomplished through the reaction of the corresponding lithium derivatives with preliminarily chlorinated silica gel (Scheme 1). Modified silica gel **Ib** was then used to synthesize immobilized pigments

Scheme 1.



I, R = H (a), R = NO_2 (b).

Electron absorption and IR spectra of immobilized thienyl-containing azo pigments **IVa–IVe**, **VIIa–VIIe**, and **VIII** and their resistance to light and washing

Comp. no.	Color	λ_{\max} , nm	$\nu(\text{N}=\text{N})$, cm^{-1}	Resistance ^a					
				light	H ₂ O	5% HCl	5% NaOH	EtOH	Me ₂ CO
IVa	Orange	510	1430	6	5	5	5	5	5
IVb	Violet	550	1435	5	5	4–5	4–5	5	5
IVc	Yellow	440	1435	6	5	4	4	4	4
IVd	Orange	460, 540	1440	5	5	4	5	5	5
IVe	Red	500	1430	6	5	5	5	5	5
VIIa	Purple	540	1430	5	5	4	4	5	5
VIIb	Brown	580	1440	6	5	5	4	4	4
VIIc	Orange	490	1440	6	5	5	4	4	4
VII d	Purple	530	1440	6	5	4	5	5	5
VIIe	Purple	480, 540	1430	6	5	5	5	4	4
VIII	Violet	485	1430	5	5	4	4	4	4

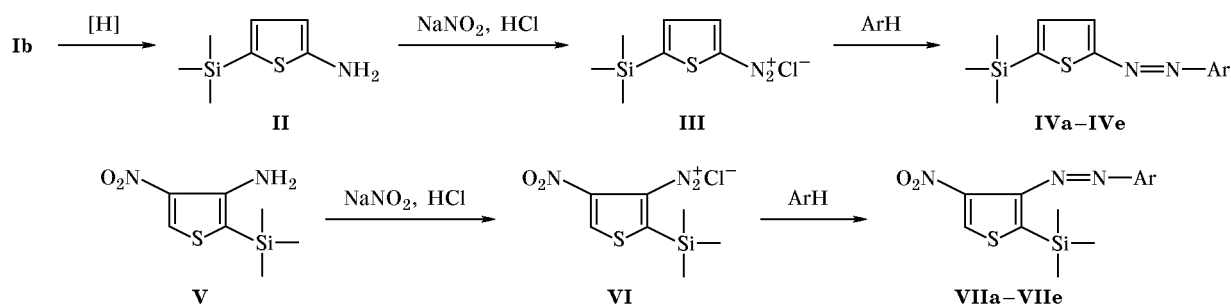
^a In arbitrary units according to GOST 9733.0-83 and GOST 9733.27-83.

through a series of chemical transformations shown in Scheme 2. Amine **II** was converted into diazo compound **III** which was brought into azo coupling with 2-naphthol, H-acid, *N,N*-dimethylaniline, R-acid, and indole. We thus obtained azo pigments **IVa–IVe** (see table). Likewise, from immobilized 3-amino-4-nitrothiophene (**V**) we obtained diazo component **VI** which was converted into azo pigments **VIIa–VIIe**. Silica gel **Ia** was used as azo component in the

reaction with diazotized *p*-nitroaniline. As a result, pigment **VIII** was obtained (Scheme 3; see table).

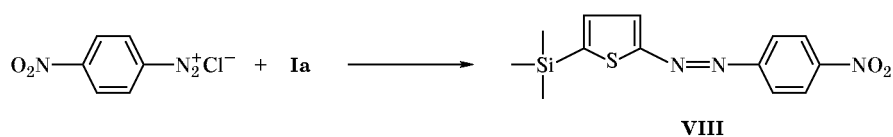
By azo coupling of 2-thiophenediazonium chloride and 4-nitro-3-thiophenediazonium chloride with the above listed azo components (according to improved procedures [6, 7] we obtained model azo dyes **IXa–IXe** and **Xa–Xe** with the goal of comparing their properties with those of immobilized analogs **IVa–IVe** and **VIIa–VIIe**.

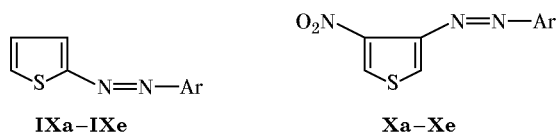
Scheme 2.



IV, **VII**, Ar = 2-HO-1-C₁₀H₆ (**a**), 8-NH₂-1-HO-3,6-(SO₃H)₂-2-C₁₀H₃ (**b**), 4-Me₂NC₆H₄ (**c**), 2-HO-3,6-(SO₃H)₂-1-C₁₀H₄ (**d**), 3-indolyl (**e**).

Scheme 3.



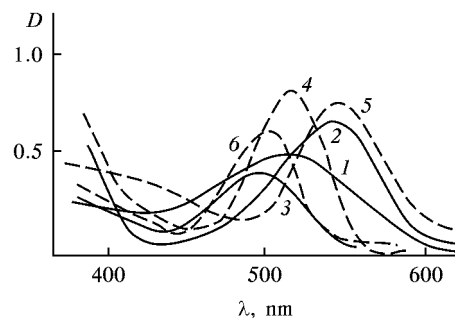


IX, X, Ar = 2-HO-1-C₁₀H₆ (**a**), 8-NH₂-1-HO-3,6-(SO₃H)₂-2-C₁₀H₃ (**b**), 4-Me₂NC₆H₄ (**c**), 2-HO-3,6-(SO₃H)₂-1-C₁₀H₄ (**d**), 3-indolyl (**e**).

Immobilization of 2,4,6-trichloro-1,3,5-triazine (**XI**) and active thienyl-containing dyes **XII** was effected by reaction of their alkaline solutions with thoroughly washed and dried silica gel on cooling to 0–5°C and under vigorous stirring; the reaction time was 5–6 h (Scheme 4). Colored silica gels were also obtained by reaction of **XI** with azo dyes **IXb**, **IXd**, **Xb**, and **Xd** on heating to 20–25°C for 3–4 h.

Figure shows the electron absorption spectra of immobilized azo dyes **IVa**, **IVb**, and **IVe** and the corresponding model compounds **IXa**, **IXb** and **IXe**. In all cases glycerol was used as solvent; it ensured clearly defined spectra of both model and grafted dyes [8]. Compounds **IVa**, **IVb**, and **IVe** showed only a slight blue shift (5–10 nm) of the absorption maximum, as compared to model compounds **IXa**, **IXb** and **IXe**. This indicates the absence of considerable effect of inorganic matrix on the properties of dyes. It is known that 1 nm² of the silica gel surface contains 4.6 hydroxy groups [9], whereas the number of immobilized organic molecules (calculated from the experimental data) does not exceed 0.40–0.45/nm². Thus bulky organic radicals replace no more than 10% of hydroxy groups on the silica gel surface.

The colors and main parameters (resistance to light and washing) of immobilized azo dyes **IVa–IVe**,



Electron absorption spectra of immobilized and model azo dyes: (1) **IVa**, (2) **IVb**, (3) **IVe**, (4) **IXa**, (5) **IXb**, (6) **IXe**.

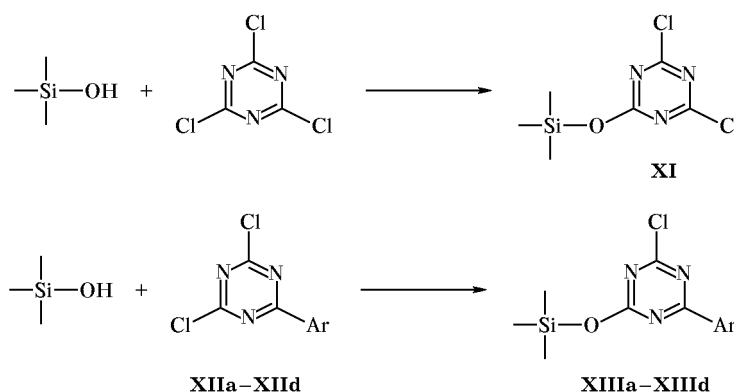
VIIa–VIIe, and **VIII** are given in table. The new colored silica gels are used as finishing and construction materials.

EXPERIMENTAL

The electron absorption spectra were measured on an SF-26 spectrophotometer. The IR spectra were recorded on a UR-10 spectrometer. The progress of reactions was monitored by TLC on Silufol-254 plates. The amount of immobilized fragments per unit surface of silica gel was calculated on the basis of elemental analyses, following the procedure reported in [10]. Silica gel L 100/250 μm was used (pore diameter 80 Å, pore volume 0.6–0.75 cm³/g, specific surface 600–750 m²/g); it was preliminarily washed with hydrochloric acid and water to pH 6.5–6.7 of the washings and was dried at 110–130°C (26.5 kPa) or at 60°C (2.7 kPa) to a constant weight (1–1.5 h); the number of surface hydroxy groups was 4.6/nm².

Thienylated silica gel (Ia). A solution of 48 ml of 2-bromothiophene in 250 ml of anhydrous THF

Scheme 4.



XII, XIII, Ar = 8-amino-1-hydroxy-2-(2-thienylazo)-3,6-disulfo-4-naphthyl (disodium salt) (**a**), 3-(2-thienylazo)-2-indolyl (**b**), 8-amino-1-hydroxy-2-(4-nitro-3-thienylazo)-3,6-disulfo-4-naphthyl (disodium salt) (**c**), 3-(4-nitro-3-thienylazo)-2-indolyl (**d**).

was added dropwise under nitrogen to 7.35 g of lithium on cooling to 0–3°C. The mixture was stirred for 1.5–2 h at a bath temperature of 100°C until lithium dissolved completely. It was then filtered and cooled to 0°C, and 20 g of chlorinated silica gel [prepared by reaction of silica gel with a solution of SOCl_2 in benzene (1:3) while stirring for 3 h at a bath temperature of 100°C] was added dropwise. The resulting mixture was heated for 1 h at 60–65°C under vigorous stirring. The product was filtered off, thoroughly washed with ethanol, acetone, and water, and dried for 1 h at 60°C (2.7 kPa). The amount of immobilized organic species was 0.698 $\mu\text{mol}/\text{m}^2$, and the number of 2-thienyl groups was 0.42/nm². IR spectrum, ν , cm^{-1} : 1420, 1120 (Si–C). Compound **Ib** was synthesized in a similar way.

Silica gel-immobilized 2-aminothiophene (II). A mixture of 10 g of immobilized 5-nitro-2-thienyl derivative **Ib**, 15 ml of a 1 M solution of tin(II) chloride in hydrochloric acid ($d = 1.19 \text{ g}/\text{cm}^3$), and 25 ml of ethanol was heated under reflux for 20 min with stirring. Hydrogen sulfide was passed through the mixture, the mixture was cooled, and the product was filtered off, washed with water until neutral washings and with acetone, and dried for 1 h at 50°C under reduced pressure (9.7 kPa). The amount of grafted organic fragments was 0.703 $\mu\text{mol}/\text{m}^2$, and the number of 5-amino-2-thienyl groups was 0.40/nm². IR spectrum, ν , cm^{-1} : 3460, 3380 (NH_2); 1420, 1120, 910 (Si–C).

Silica gel-immobilized azo pigment (IVa). A 2 N solution of sodium nitrite, 25 ml, was added on cooling to a suspension of 10 g of silica gel **II** in 125 ml of 2 N hydrochloric acid at such a rate that the temperature did not exceed 5–10°C, and the mixture was stirred for 20–30 min at that temperature. The end of the diazotization process was determined by the starch–iodine test. Excess nitrous acid was removed by adding sodium acetate (to pH 5) and urea. A 0.1 M alkaline solution of 2-naphthol (prepared preliminarily) was added to the immobilized diazo compound, and colored silica gel **IVa** was thoroughly washed with water, a 5% solution of alkali, ethanol, and pyridine. Compounds **IVb–IVe** and **VIIa–VIIe** were synthesized in a similar way.

Silica gel-immobilized 2,4,6-trichloro-1,3,5-triazine (XI). Preliminarily washed and dried silica gel, 10 g, was placed in 150 ml of a 5% solution of sodium carbonate or in 100 ml of pyridine (in both cases the results were similar). The mixture was cooled to 0–5°C, stirred for 2 h, and 5 g of 2,4,6-trichloro-1,3,5-triazine was added, maintaining pH at 6–7 (for the aqueous solution). The suspension was cooled and stirred for 3–4 h until pH 6–7 established,

and the activated silica gel was filtered off, washed with water and ethanol, and dried for 1 h at 60°C under reduced pressure (2.7 kPa). The amount of grafted species was 0.734 $\mu\text{mol}/\text{m}^2$, and the number of 4,6-dichloro-1,3,5-triazin-2-yl groups, 0.44/nm². IR spectrum, ν , cm^{-1} : 1520 (C=N); 1125, 1090, 930 (Si–O–C); 760 (C–Cl).

Silica gel-immobilized thienyl-containing azo dye XIIIa. To a suspension (10 g/l) of washed silica gel in an aqueous solution of NaHCO_3 (pH < 10) we added under vigorous stirring 2–3 wt % of silica gel and 10 ml of a 5×10^{-3} M solution of active dye **XIIIa**. The mixture was stirred for 1–2 h at 20–25°C and was then heated for 1 h at 60°C. The colored product was filtered off, washed with cold water, warm (60–70°C) water, a hot solution of OP-10 detergent (3 g/l) for 10–15 min, tap water, ethanol, acetone, diethyl ether, and pyridine, and dried for 2 h at 60°C under reduced pressure (2.7 kPa).

Colored silica gels **XIIIb–XIII d** were obtained in a similar way.

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