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SYNTHESIS AND CHARACTERIZATION OF SOME HYBRID MATERIALS BASED ON CURCUMIN DERIVATIVES EMBEDDED IN MODIFIED PALYGORSKITE

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The paper presents obtaining of some hybrid materials by depositing of some organic diketone derivatives on inorganic support. The synthesized asymmetrical curcuminoid dyes were embedded in modified palygorskites with organosilane derivatives with amino groups. The obtained organic-inorganic hybrids were characterized by IR, UV-VIS and fluorescence spectroscopy, thermal analysis and porosity measurements of the surface. Hybrid materials have fluorescence and can be used as luminescent materials.

Keywords: β-diketone, palygorskite, hybrid materials, fluorescence.

1. Introduction

The fluorescent dyes are considered to be those which absorb light energy of a specific wavelength and re-emit light at a longer wavelength.

Due to this feature, the fluorescent dyes are applied in fields like optoelectronics [1,2,11], in biology [3,4,5,6,7] or printed textiles [8,9]. The types of compounds studied so far are of different classes of dyes, like: coumarins [1,4,8], phthalocyanines [2,3], porphyrins [2], pyrene [5], β-diketones [6] and

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have several deficiencies related primarily to photochemical resistance, thermal and mechanical resistance. Thus, in recent years many studies have been initiated to improve these properties and find new areas of application by obtaining hybrid materials in which the dye is included or deposited on an inorganic host matrix of silica [9], metal oxides [10] or clays [11].

The natural clay minerals are acknowledged to be exceptionally promising candidates as low-cost, high adsorption properties and non-toxicity. Owing to its lamellar structure, the palygorskite has remarkable properties due to its chemical stability and durability when exposed to various external factors [12]. These characteristics have determined their use as adsorbents for the removal of organic compounds from wastewater [13,14]. Another area in which the clays are used as a support or carrier matrix is that of obtaining organic-inorganic hybrid materials. Thus, the surface of the mineral clays, such as palygoskite are modified with different organic reagents [15-20] to enhance the adsorption capacity and selectivity, aimed to obtain some nanocomposites with photocatalytic [15] and biological applications [16], usually obtained by adsorption of organic dyes onto the surface of these inorganic matrices.

This study is intended to provide data on obtaining hybrid materials with luminescent properties by depositing the acetylacetone derivatives on an inorganic matrix. For improvement in the adsorption property, the surface of palygorskite was modified using an alkoxysilane derivative (3-aminopropyl triethoxysilane). Onto the modified substrate were deposited acetylacetone derivatives from alcoholic solution and obtained new organic-inorganic hybrids.

2. Experimental

2.1. Materials

All chemicals used were of laboratory reagent grade and were obtained from Merck (Germany) and Aldrich (USA). Boron trioxide (B_2O_3), acetylacetone, tri-butyl borate, aromatic aldehydes (4-hydroxy-, 3-methoxy-4-hydroxy-, 4-N,N-diethyl-benzaldehyde), dodecylamine, acetic acid, ethylacetate, methanol (MeOH), ethanol (EtOH), hydrochloric acid (0.1 N) and 3-aminopropyl triethoxysilane (APTES) were used as they were received without further purification. The Palygorskite (PAL) clay used in this study was obtained from SERVA (Germany).

2.2. Equipment

IR spectra of all the studied compounds were recorded on a Jasco FTIR 6300 spectrometer equipped with a Specac ATR Golden Gate (KRS5 lens), in the 400-4000 cm^{-1} range (32 accumulations at a resolution of 4 cm^{-1}). Total color differences in CIELAB system, using a 10-degree standard observer and illuminant D65 and diffuse reflectance spectra of powders were measured with a

JASCO V570 UV-Vis-NIR spectrophotometer equipped with a JASCO ILN-472 (150 mm) integrating sphere, using Spectralon as reference. Fluorescence spectra were recorded with a JASCO FP 6500 spectrofluorimeter, at 25^0C, using the device for solid samples at an excitation wavelength of 450 nm. In order to investigate the thermal stability of the hybrid composites, TGA was performed using a Q5000IR (TA Instruments) thermogravimetric analyzer. The samples were heated up to 800°C from the ambient temperature at a heating rate of 10°C/min under 50 mL/min Nitrogen (99.999%) atmosphere. Surface area, pore volume and size measurements of raw clay and hybrid materials were performed using Nova 2200e Quantachrome automated gas adsorption system.

2.3. The general procedure for the synthesis of asymmetric β-diketone derivatives

In this study three asymmetric derivatives of acetylacetone (C1-C3) were obtained by Van Alphen method [11]. Over the boron complex of acetylacetone formed by a mixture of boron trioxide (4 mmol), acetylacetone (8 mmol) and tri-butyl borate (3.2 mmol) were added the aromatic aldehyde (3.5 mmol) and dodecylamine (0.1mmol). After processing the reaction mass and purification, orange to dark red powders were obtained in 60-72% yields.

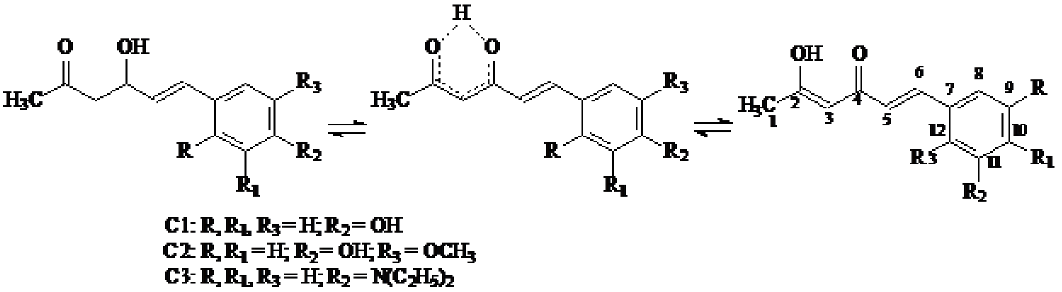

Fig.1 Structural formula of 6-aryl-5-hexene-2,4-diones

2.4. General method of depositing dyes on modified palygorskite

The palygorskite (PAL) clay used in this study was modified at thesurface with an amino-organosilicon derivative [14]. Thus, 6 g of clay initially activated in acid solutions (PalH) [11] were dispersed into 100 mL anhydrous ethanol by ultrasonication for 10 min., and 6 mL APTES were added to the mixture with vigorous stirring for 2 h at 45^0C. The product was filtered, washed with ethanol and dried at 110^0C, for 5h. Onto the modified substrate (Pal-APTES) were deposited acetylacetone asymmetric derivatives (C1-C3), obtaining hybrid materials. Thus, Pal-APTES (1 g) was suspended in 50 mL dye alcoholic solution 0.34g/L for 20 h at room temperature. The dispersion was filtered and dried at 70^0C for 4h.

3. Results and discussions

The compounds which were obtained by condensation of acetylacetone with the three aromatic aldehydes (4-hydroxybenzaldehyde, vanillin and 4-N,N-diethylaminobenzaldehyde) were structurally characterized, the results can be found in Table 1.

Table 1

The main physical and structural characteristics of C1-C3 dyes

Compound		**C1**	**C2**	**C3**
Molecular mass, [g/mol]		204.22	234.25	259.34
Color		Yellow	Orange	Dark-red
Yield, [%]		72	68	60
Melting point, [^{0}C]		119-121	165-168	93-97
Elemental analysis, [%]	**C$^{1)}$**	71.24 (70.59)	66.74 (66.67)	74.86 (74.13)
	H$^{1)}$	5.95 (5.88)	6.09 (5.98)	8.73 (8.11)
	N$^{1)}$	-	-	5.82 (5.41)
Characteristic frequencies (cm^{-1}) and intensities (vi-very intense; i-intense; m-medium; w-weak; vw-very weak)		3310w; 1627m; 1570vw; 1540w; 1507w; 1425i; 1376w; 1359w; 1302m; 1282m; 1234i; 1157i; 1105w; 1002w; 981i; 938i; 831vi; 646 m; 574m; 516i; 472i.	3470m; 3351w; 2939w; 2841w; 1627m; 1585i; 1506i; 1427i; 1359m; 1264m; 1231m; 1200m; 1153i; 1071i; 1027i; 958i; 856m; 807i; 772m; 713w; 599w; 575w; 546 m; 513w; 496w; 465i.	2970i; 2930m; 2901m; 2872m; 1626i; 1544i; 1512i; 1400i; 1357i; 1268m; 1228w; 1187m; 1153i; 1071i; 984i; 941i; 865m; 817vi; 802m; 782i; 526m; 508i; 484m.

1) Value found (calculated)

The hybrid materials (AC1-AC3) were characterized by FTIR spectra, thermogravimetric analysis, specific surface area measurement and fluorescence spectra. The DRIFT spectra (Fig.2) of the modified clay powders and the hybrid composites are characterized by the presence of more bands at 3614 and 3547 cm^{-1} assigned to hydroxyl stretching vibrations of water, or to hydroxyl bands associated with coordinated hydroxyl groups. The next two bands at 3374, 3276 cm^{-1} respective, are attributed to the hydroxyl groups involved in hydrogen bonds [19]. The FTIR spectrum of Pal-APTES revealed the absorption band at 2936 cm^{-1} corresponding to the C–H stretching vibration of CH$_2$ groups of APTES and the peaks situated at 1560 and 1492 cm^{-1} assigned to deformation modes of the amino groups [13,14]. The results confirm that the aminopropyl group was successfully anchored on the surface of palygorskite and the structure has not been modified during the dyes' deposition process.

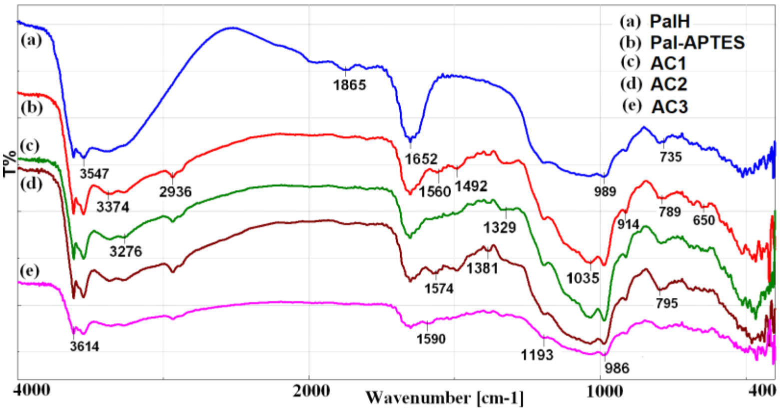

Fig.2. Diffuse reflectance Fourier-transform infrared (DRIFT) spectra of modified clay powders and the hybrid composites

The hybrid materials obtained by deposition of asymmetrical curcuminoid dyes on the modified clay, have maximum of the absorption bands in the UV-Vis spectra (Fig.3) situated at around 380-400 nm. The peaks are shifted by 18-23 nm under the maxima obtained in different solvents, due to molecular aggregation. Color parameters (lightness (L*), red–green (a*) and yellow–blue (b*) color components) are calculated using spectralon as a standard material (C0). The color differences resulted (table 2) reveal that the volume of the substitution groups in the aromatic rings leads to decreases of lightness and because the Δb value is positive, the shade is shifted toward yellow. The interactions between the dye and the clay substrate lead to changes in color parameters. Thus, in the case of AC1 and AC2 materials where are established hydrogen bonds between the dyes and the host matrix, in the case of AC3 material the presence of a more polar structure of the dye makes the color become duller and darker due to a ΔC increase.

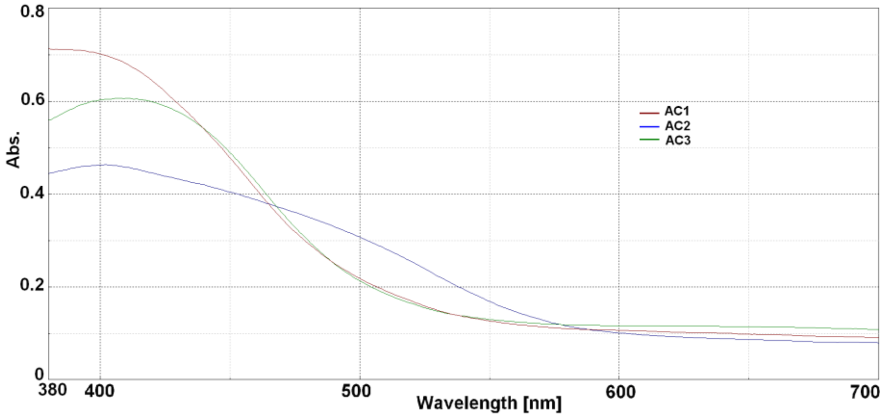

Fig.3. Absorption spectra of hybrid composites (concentration of the dye in the solution relative to the mass of the host matrix 1.7% wt.)

Table 2

Color parameters in the CIELab system and absorption maxima

Sample	Colour parameters and differences									$\lambda_{abs.}$ [nm]
	L*	a*	b*	ΔL*	Δa*	Δb*	ΔE*	ΔC*	ΔH*	
C0	93.21	-0.56	-0.57	-	-	-	-	-	-	-
Pal-APTES	89.07	0.07	4.09	-4.14	0.63	4.66	6.26	3.29	3.36	-
AC1	89.27	-4.56	25.54	-3.94	-4	26.12	26.71	25.15	8.1	383
AC2	84.9	6.76	26.29	-8.31	7.32	26.86	29.06	26.35	9	402
AC3	87.04	-5.42	35.5	-6.17	-4.86	36.07	36.92	35.11	9.59	406

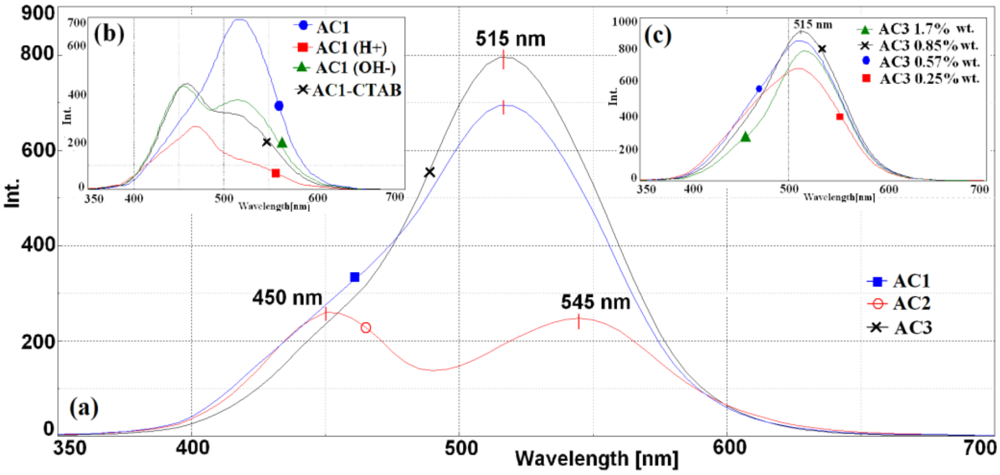

Fig.4. Fluorescence spectra of the hybrid composites (a), in different conditions of deposition (b) and at various concentrations of dye (c)

The host−guest interactions (electrostatic and ion−dipole interactions) were reported to be responsible for luminescent properties of hybrid materials. The absorption spectra of hybrid materials are characterized by a wide band, so that after the simulated 3D spectrum (emission spectra recorded at different excitation wavelengths) optimal excitation wavelength could be established in the range 400-450nm in order to maximize the fluorescence emission. The fluorescence spectra (Fig.4 (a)), which were measured on solid samples using $\lambda_{ex.}$ = 450 nm, showed the emission peak situated at 515 nm and different intensities, the highest intensities were recorded for AC3 (Stokes shift Δ ~ 109 nm) and for AC1 (Stokes shift Δ ~ 132 nm). The change of the position of the fluorescence emission peak varies between 25-30 nm and is caused by the lack of solvent and its interactions. In the case of AC2, two emission peaks at 450 and 545 nm are observed (Stokes shift Δ ~ 48 nm). These are attributable to the presence of several polar tautomeric structures, characteristic for this type of dyestuffs. In the literature are studies [21] showing that the curcumin derivatives in polar solvents are predominantly found in enolic form, which can explain the formation of intramolecular and intermolecular hydrogen bondings with the amino groups on the clay surface. It can be seen that the presence of cations leads to a decrease in fluorescence intensity, as well as the type of clay surface modification (fig.4(b)). Another factor influencing the fluorescent properties is the concentration of the dye in the solution relative to the mass of the host matrix. For compound C3 an optimal concentration of 0.85% wt. was found wherein the obtained hybrid compound presented the highest fluorescence intensity (fig.4(c)). For higher concentrations of dye, fluorescence intensity decreases as a consequence of molecular aggregates [22].

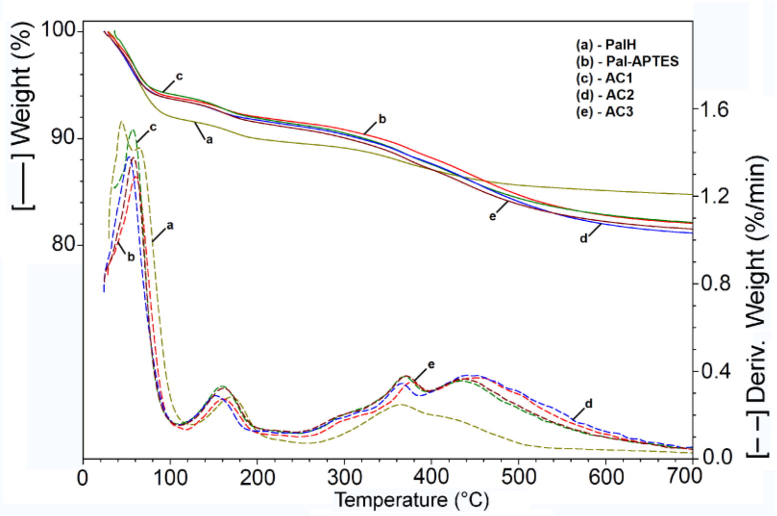

Fig.5. Thermo-gravimetric analysis of fluorescent powders

Table 3

Results of Thermo-gravimetric Analysis

Sample	Temperature range									Residue 700°C
	RT-110°C	110 - 240°C		240 - 325°C		325 - 395°C		395 - 700°C		
	Wt. loss	Wt. loss	Tmax	Wt. loss	Tmax	Wt. loss	Tmax	Wt. loss	Tmax	N_2
	%	%	°C	%	°C	%	°C	%	°C	%
PalH	8.14	2.24	169.5	0.86	297.1	1.57	365.3	2.42	432.8	84.77
Pal-APTES	6.22	2.18	162.7	1.24	297	2.00	377.9	6.28	459	82.07
AC1	5.98	2.62	159.4	1.44	295.2	2.23	368.8	5.58	434.7	82.15
AC2	6.42	2.33	152.0	1.41	289.3	2.04	365.8	6.66	441.8	81.14
AC3	6.42	2.59	161.3	1.48	291.4	2.25	370.9	5.73	436.5	81.53

All TG curves (Fig.5) show a first stage at a temperature around 110^0C, on account of the physically adsorbed water evaporation. The mass loss (table 3) was of 8.14% for activated clay and 5.98-6.42% after adsorption of diketone derivatives. In the range 240-325^0C, the curves show a mass loss of 1.24-1.48%, attributed to the degradation of the organic compounds deposited on the inorganic matrix. Over 300^0C, mass loss corresponds to the coordinated water and structural water in palygorskite. The residue for all hybrids is high and it is formed of silica from the inorganic matrix and carbonaceous char of organic moieties because of the thermal decomposition in an inert atmosphere [11,20].

Table 4

Results of textural analysis

Sample	Surface area (method BET) [m^2/g]	Pore volume (method BJH) [cm^3/g]	Pore size (method BJH) [nm]
Pal	117	0.327	3.85
PalH	266.8	0.23	3.86
Pal-APTES	86.1	0.15	3.83
AC1	84.6	0.18	3.28
AC2	74.5	0.13	3.12
AC3	72.8	0.11	3.27

The specific surface area, pore volume, and pore diameter were summarized in table 4. Adsorption and desorption experiments using N_2 were carried out at 77 K, prior to each measurement the samples were degassed at 423 K for 4h. Nitrogen adsorption–desorption isotherms for clay and amino-functionalized palygorskite resulted in type II isotherms, according to the IUPAC classification, with a hysteresis loop that indicated the presence of a large proportion of mesopores and macropores [17]. The shape of the hysteresis loops was of type H3, which is associated with plate-like particles or slit-shaped pores. After modification with the silane derivative, the surface area decreased from 266.8 to 86.1 m^2/g, which is ascribed to the formation of polymeric siloxane chains and crosslinking. The amino terminal groups of APTES and hydroxyl groups, generated during hydrolysis, strongly interact with hydroxyl groups of palygorskite. Therefore, APTES can lead to a multilayer network on the PalH surface and block of some channels. Pore diameter was, on average, greater than the 3 nm characteristic in the case of mesoporous materials.

6. Conclusions

By depositing three asymmetrical curcuminoid dyes on palygorskite modified with organosilane derivatives containing amino groups, there were obtained new hybrid materials with luminescent properties. The spectrophotometric measurements revealed that organic-inorganic hybrids preserved optical properties of the chromophores. The amount of fluorophore adsorbed on the clay surface has strongly influenced photo-physical properties of the hybrids. By using asymmetric derivatives, the interactions between auxochromic groups grafted on aromatic rings and modified inorganic matrix resulted in hybrid materials with fluorescence intensities significantly increased compared to hybrids with symmetrical diketone derivatives.

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