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Hybrid systems based on organic dyes and clay minerals: Fundamentals and potential applications[#]

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ABSTRACT: This review summarizes several aspects of the interactions between organic dyes and clay minerals, and presents some interesting properties of hybrid materials based on these components. It explains the basic phenomena and photophysical properties of dye/clay mineral hybrid systems (DCHS) while examining the role of clay minerals in them. A brief history of using dyes as tools for clay research and on traditional materials based on DCHS is presented. Metachromasy, the phenomenon of colour change related to the formation of dye molecular aggregates is described in detail and analysed from various perspectives. The properties of DCHS, including photoactivity, luminescence, photocatalytic properties, optical anisotropy and non-linear optical properties are analysed in detail. Clay minerals often play a significant role in the occurrence of specific photophysical phenomena such as resonance energy transfer and luminescence quenching and may influence various reactions, such as conformational changes in dye molecules, photochromism, photoisomerization, photosensitization and other photochemical processes. Routes to synthesize various types of hybrid materials are also described here. The relevance of DCHS for clay research, chemistry and materials science is summarized briefly.

KEYWORDS: dye/clay mineral hybrid systems, photoactivity, luminescence, photocatalytic properties, optical anisotropy, organic dyes.

INTRODUCTION

Basic research and industrial applications of systems based on clay minerals and organic dyes have always been closely related. Possibly inspired by discoveries in clinical biology and related fields, dyes have been used for staining rocks, minerals and sediments in order to identify clay minerals, to detect admixtures or to characterize sample composition (Yariv, 2002). Some of the tests were based on redox reactions of aromatic amines or other aromatic dyestuffs, which formed variably coloured compounds depending on the mineral's properties (Hambleton & Dodd, 1953; Ramachandran *et al.*, 1961). Acid/base indicators have been used for estimating the acid/base properties of clay-mineral surfaces (Bailey & Karickhoff, 1973). These techniques flourished in the 1960s and were later replaced by modern and more efficient methods, such as X-ray diffraction (XRD), electron microscopy, infrared (IR) spectroscopy, *etc.* Methylene blue (MB) is a cationic organic dye, which has been used most frequently for the characterization of clay minerals. It is still used by industries and laboratories for the quantification of smectite content in bentonites, sediments and soils (Yukselen & Kaya, 2008). This method is based on the irreversible adsorption of the dye onto the smectite surface in large amounts, with

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negligible retention by other minerals occurring as admixtures in bentonites. The adsorption of MB proceeds *via* ion exchange, which is thought to be controlled by cation exchange capacity (CEC). The MB test provides approximate values of the smectite content. Besides this, this dye was also tested for the determination of the specific surface area of clay-mineral particles (Hang & Brindley, 1970). However, the relevance of this method was not considered widely (Hähner *et al.*, 1996) or established. The role of MB in later studies related to clay research will be mentioned below.

HISTORY AND PRESENCE OF HYBRID MATERIALS BASED ON DYES AND CLAY MINERALS

Hybrid materials based on organic compounds and clay minerals are of interest to various modern scientific fields. In particular, complexes of clay minerals with organic dyes fascinate scientists because of the variability of the materials, their interesting optical properties, fascinating phenomena and potential industrial applications. Some hybrids of this type were also used historically, however. Dye-inorganic mixtures, including coloured clays, have been used as paints for a long time. It is difficult to recall when the first true hybrid material based on clay minerals and organic dyes was reported in the scientific literature. It is easier to determine, however, which true hybrid materials of this type were compounded and used for the first time by humans. It was probably Maya blue, a pigment material consisting of the natural dye indigo and palygorskite crystals (Van Olphen, 1966; José-Yacamán *et al.*, 1996). Maya blue paintings exhibit excellent resistance to heat, chemical and microbial corrosion, and remain in good condition, maintaining their bright colours for centuries, up to the present day. The clay mineral component has been proven to play a significant role in stabilizing the dye molecules in the Maya blue pigment. The results of archaeological exploration and materials research indicate that further similar materials based on clays could have been developed in ancient times (Doménech *et al.*, 2011). In the modern era, scientists investigate these pigments for inspiration in the development of useful new materials. There have only been a few attempts by modern science to prepare hybrid materials based on clay minerals and dyes extracted from plants or other natural resources. For example, purple anthocyanins isolated from the fruits of the Amazonian palm exhibited better stability against heat in the intercalation compound with the clay mineral, and their properties as radical scavengers were preserved (Teixeira-Neto *et al.*, 2012). Most of the research has been focused on hybrid systems based on synthetic dyes, which are also used in other branches of research or industrial fields.

TABLE 1. List of the most relevant literature related to the interaction of organic dyes with various materials.

Type of materials	References
Polymers	(Dawydoff *et al.*, 1991; Kugel, 1993)
Biopolymers, biological systems	(Tuite & Kelly, 1993)
Sol-gel materials	(Gvishi *et al.*, 1997; Lebeau & Sanchez, 1999; Sanchez *et al.*, 2003; Shibata *et al.*, 2008)
Layered compounds	(Li & Li, 2003a; Bujdák, 2006; Takagi *et al.*, 2006; Latterini *et al.*, 2007; Liu & Zhang, 2007)
Glasses	(Sanchez *et al.*, 2003)
Porous inorganics	(Schulz-Ekloff *et al.*, 2002)
Minerals	(Schulz-Ekloff *et al.*, 2002; Li & Li, 2003a; Bujdák, 2006)
Clay minerals	(Schulz-Ekloff *et al.*, 2002; Bujdák, 2006; Takagi *et al.*, 2006; Zhou *et al.*, 2011)
Nanomaterials	Takagi *et al.*, 2006

A BRIEF OVERVIEW OF HYBRID SYSTEMS BASED ON DYES AND CLAY MINERALS AND RELATED MATERIALS

Understanding the properties of organic dyes in hybrid systems with clay minerals requires extensive knowledge of the structure, chemistry and physical properties of both the components. Furthermore, one has to understand the fundamentals of the interactions between the dyes and clay minerals. Some misinterpretations of the phenomena in dye/clay mineral systems may occur purely because of neglect of knowledge from other, related scientific fields. Phenomena occurring upon the reaction between dyes and clay-mineral particles are, in principle, the same as those taking place for similar materials. However, phenomena that are sometimes, at first glance, identical can occur *via* very different reaction systems. For example, the interaction of ionic dyes with polyelectrolytes leads, in principle, to the same changes in the optical properties of dyes as are often observed for the hybrid systems with clay-mineral colloids. Very useful information can be obtained from the literature related to the reactions of organic dyes in porous or mesoporous materials, layered inorganic compounds (layered double hydroxides, titanates, niobates, phosphates, *etc.*), oxide surfaces and glasses, amorphous materials, nanomaterials, in monomolecular layers, Langmuir-Blodgett films, layer-by-layer assemblies, *etc.* Several valuable reviews have been published summarizing the most relevant aspects of such interactions. These papers are essential for obtaining fundamental information about the properties and interactions of organic dyes in hybrid systems and at interfaces. Some of the most relevant examples of such reviews are summarized in Table 1.

DYE ADSORPTION

The functionality of organo-inorganic hybrid materials often requires the homogeneous, well defined and strong adsorption of organic molecules onto the matrix of an inorganic host material. In particular the optical homogeneity resulting from the homogeneous distribution of the guest dye molecules can be very important for the functionality of the material. Irreversible adsorption/intercalation guarantees the stability of the material. Homogenous adsorption is optimally achievable on completely delaminated layered particles in dilute and stable colloidal dispersions, with the surface fully accessible by dye molecules. Smectites consisting of small (<100 nm) particles saturated with Na^+ or Li^+ cations exhibit the optimal properties for this purpose. This irreversible adsorption can, in principle, be achieved in several ways, which are depicted schematically in Fig. 1. The most common procedure is based on an ion-exchange reaction. Cationic dyes are adsorbed strongly on smectite particles bearing a permanent negative charge which is located on the basal oxygen atoms near the sites of non-equivalent isomorphic substitutions (Fig. 1a). The basal siloxane surface exhibits the properties of weak soft bases with a preference for association with large, easily polarizable organic cations. Therefore, chemical equilibrium is generally shifted in favour of dye cation adsorption replacing inorganic cations. The binding coefficients of organic cations are, in general, several orders of magnitude greater than those of the hydrated inorganic cations (Rytwo *et al.*, 1995). Therefore, natural clays are very efficient adsorbents for cationic dyes (Liu & Zhang, 2007) and excellent materials for the straightforward synthesis of organoclays. Moreover, the molecular aggregation of large organic cations with the contribution of van der Waals forces can further contribute to the irreversible adsorption of the dye. The occurrence of dye molecular aggregation was observed by spectroscopy methods (Bergmann & O'Konski, 1963; Bujdák, 2006) and is analysed in detail below. The role of molecular aggregation in reaction enthalpy was proven by thermometric titration (Demoz & Mikula, 2011). The adsorption of neutral and anionic dyes is weak, and therefore, their application in hybrids with clay minerals is rather problematic. Neutral dye molecules at low concentrations cannot compete for the adsorption sites with solvent molecules. The adsorption of non-polar dye molecules was studied experimentally using a neutral dye – pyrene (Labbé & Reverdy, 1988). According to the spectral response of the pyrene probe, the adsorption site was assigned to the hydrophobic siloxane planes of clay-mineral particles. Some neutral organic dyes, especially those with larger molecules, are insoluble in water. Using an aqueous colloid of clay minerals, the solubilization of insoluble phthalocyanines was achieved, ending with the successful adsorption of dye molecules (Staniford *et al.*, 2015). Dye anions are repelled from surfaces with negative charge, but are adsorbed efficiently by compounds with positively charged particles, such as layered double hydroxides. The modification of clay minerals with cationic surfactants of a quaternary alkylammonium type leads to the formation of materials which might also be suitable for the adsorption of neutral, hydrophobic or anionic dye molecules (Fig. 1d) (Wang *et al.*, 2004). The superior adsorption properties of cationic surfactant-based organoclays are due to their surface activation. The large amount of surfactant cations in organoclays may partially reverse the surface charge to positive values. Another way to enhance the adsorption of neutral dye molecules would be to incorporate organic surfactants or modifiers with functional groups, which would be designed to selectively associate with a specific type of dye molecules (Fig. 1e). Such materials are still relatively rare, but may become more commonplace in the future (Liu & Zhang, 2007). The incorporation of anionic dyes into hosts with negative charge can be also realized *via* modification with positively charged polyelectrolytes (Hata *et al.*, 2007). Another type of strategy to incorporate irreversibly dye molecules on the surface of clay-mineral particles is based on chemisorption (Fig. 1b,c). Covalent bonding can be achieved by grafting the particles of the clay mineral

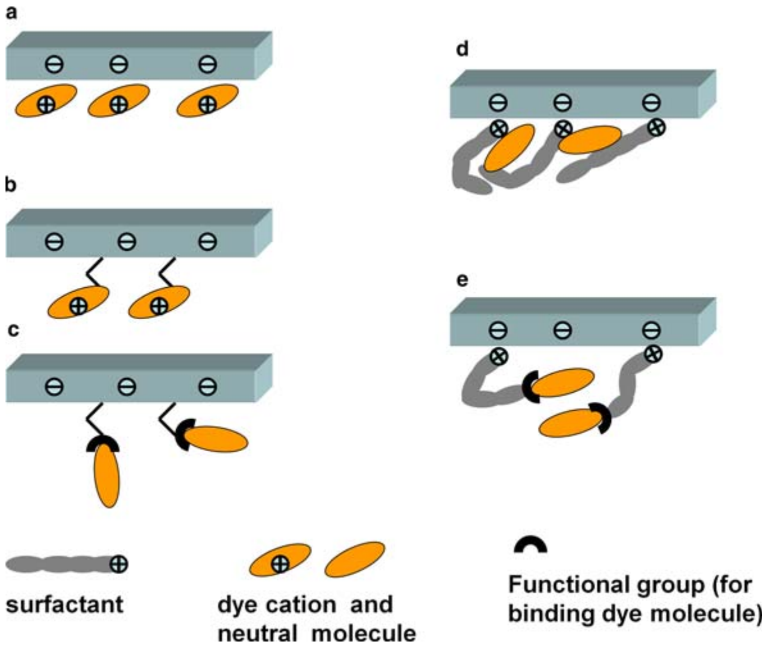

FIGURE 1. Schematic illustration of various types of organic dyes bonding to clay-mineral particles: (a) ion exchange; (b) covalent bonding; (c) surface modification with moieties with appropriate functional groups; (d) organoclays with surfactant cations; and (e) organoclays with surfactants with appropriate functional groups.

with reactive dyes (Bujdák *et al.*, 2012; de Carvalho *et al.*, 2014), or incorporating chromophore moieties directly during the synthesis of the organo-silicate (Kuroda *et al.* 2010; Fujii *et al.*, 2008). More about such hybrid materials is given below. Other strategies would be based on grafting of the particles with functional modifiers to create new functional groups (Zhou *et al.*, 2011; de Carvalho *et al.*, 2014) to change the surface properties of clay-mineral particles, or to covalently attach chromophoric units to cationic or polar polymers, which are adsorbed irreversibly onto the clay-mineral surface.

INTRODUCTION TO DYE MOLECULAR AGGREGATION

Dye molecular aggregation often plays a key role in the properties of dye/clay mineral hybrid systems. The phenomenon known as metachromasy, related to dye molecular aggregation, was observed for the first time about a century ago (Pappenheim, 1910; Holmes, 1926), although it was not fully understood for several decades after its discovery (Michaelis & Granick, 1945). Dye molecular aggregation is accompanied by a colour change representing significant shifts of spectral absorption bands reaching the ranges of thousands of cm^{-1}. For example, methylene blue in the form of dilute solutions absorbs red light (maximal absorption at 665 nm), but in its aggregated form the absorption band shifts to lower wavelengths related to the absorption of green and yellow light (550–600 nm). In some cases the protonized form or J-aggregates of MB also absorb at significantly longer wavelengths in the near-IR region (770 nm). Biologists observed this phenomenon for the first time when staining cells and biological tissues for optical microscopy (Holmes, 1926). The molecular aggregation of MB in montmorillonite colloids was reported ~50 y ago (Bergmann & O'Konski, 1963), when exciton theory had already been established and the role of molecular aggregation on spectral changes was well understood (Kasha, 1963).

Thermodynamics and reaction mechanism

The simplest case of dye molecular aggregation is a dimerization reaction:

$$2\text{M} \leftrightarrows \text{D}$$

Dimer (D) formation from two monomer (M) molecules is controlled by the thermodynamic equilibrium constant. At low dye concentrations, the thermodynamic equilibrium (K_D) can be expressed by the equation:

$$K_D = \frac{c_D}{c_M^2}$$

where c_D is the dimer concentration and c_M is the monomer concentation. The hydrophobic effect is a driving force for the formation of dye molecular aggregates, which is, in principle, similar to micelle formation from surfactant molecules. The hydrophobic effect is the tendency of non-polar molecules to form assemblies in an aqueous solution. Upon the formation of dye molecular aggregates, a fraction of the water molecules originally surrounding the monomers are released to the bulk water phase. The hydration structures of the monomers and their changes upon aggregation play the most significant role in this phenomenon. The water molecules released have lower energy due to their strong H-bonding in the bulk water and gain entropy due to freedom of mobility. There are some similarities and distinct differences between the molecular association of surfactants and dye molecules. In particular, ionic dyes are more polar compounds compared to surfactants with long, non-polar hydrophobic chains. The polar character of the dyes mainly affects the enthalpy of the association. The standard free-energy change of the dimerization is related directly to the equilibrium constant, and can be expressed by standard enthalpy (ΔH_D°) and entropy changes of dimerization (ΔS_D°).

$$\Delta G_D^\circ = \Delta H_D^\circ - T\Delta S_D^\circ$$

Both ΔH_D° and ΔS_D° depend on the molecular structure of the dyes. There is roughly a linear growth relationship between these two parameters, if they are collected for a large number of organic compounds (Fig. 2) (Murakami, 2002). Depending on the dye structure, molecular aggregation can be driven by entropy or enthalpy change (enthalpy–entropy compensation relationship). For non-polar and large molecules, a large entropy change is expected due to the release of a large number of water molecules upon dimerization. On the other hand, a positive enthalpy change results from the low dispersion forces between associated dye molecules resulting from low van der Waals intermolecular forces. The association of small and highly polar dye molecules is characterized by a small to negative change in the standard entropy and negative enthalpy, which promotes the dimerization reaction. If the effect of entropy is zero, there is still some enthalpy effect ($\Delta H_D^\circ < 0$) to contribute to the dye association. The contributions of both ΔH_D° and ΔS_D° are important to predict dye association under various conditions, especially the influence of temperature, or to estimate the effects of solvent properties. Increasing ionic strength contributes to the tendency of the dyes to form aggregates, which can play a crucial role in their aggregation on clay-mineral surfaces (Bujdák & Komadel, 1997).

The simplest mechanism of dye molecular aggregation can be described by at least two consecutive steps (Murakami, 2002):

$$2M \leftrightarrows M \cdot M \leftrightarrows D$$

where the first step represents a diffusion-controlled reaction of the formation of the M·M complex (reaction rate constant is on the order of $\sim 10^9$ mol s^{-1}). The second reaction step can be significantly slower, especially for non-polar molecules, or ions with non-polar alkyl groups. In this case, the dimerization is driven entropically because of a positive change of the activation enthalpy. The enthalpy–entropy compensation relationship also applies for the activation parameters, thus affecting reaction kinetics, which is a similar trend to the thermodynamics of molecular aggregation. With dye aggregation in clay-mineral colloids, the first step includes dye cation adsorption. In dilute and completely delaminated clay-mineral particles, dye adsorption is very fast. The second step including the dye aggregate rearrangement is much slower, taking several hours to reach spectral equilibrium.

Spectral properties of molecular aggregates

Molecular aggregation is a phenomenon which is quite common for almost any organic compounds, including non-polar molecules, surfactants, polymers, *etc.* The molecular aggregation brings about unique changes, however, especially for organic dyes with planar molecules. The molecular planarity enables very short distances and strong electrostatic interactions between the neighboring molecules forming an aggregate. The changes in the electronic structure of the aggregated molecules are often visually observable as a change in colour, and can be characterized precisely by molecular spectroscopy methods. The strong interaction between the transition moments of the interacting chromophores mainly affects the energies of their excited states. The 'exciton theory'

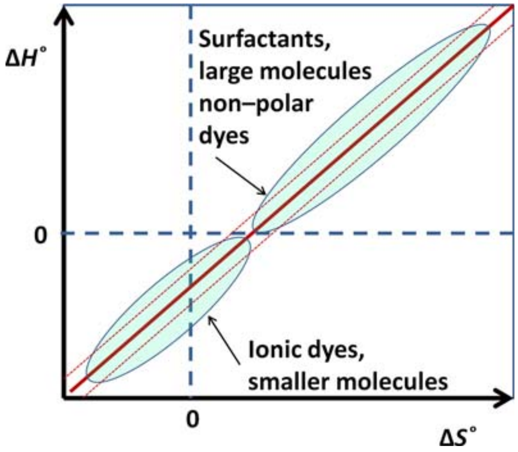

FIGURE 2. Relationship between thermodynamic parameters of dimerization. The trends were adopted from the review by Murakami (2002). The compounds can be divided into two types according to the following parameters: (a) compounds with a purely entropically driven dimerization (upper-right, $\Delta S^\circ_D > 0$, $\Delta H^\circ_D > 0$); and (b) compounds with negative enthalpy of dimerization (lower-left, $\Delta H^\circ_D < 0$).

explains successfully these changes with a model of exciton electrostatic coupling. The electronic excited states are so-called 'excitons', which are described as a bound state of an electron and an electron hole. Exciton coupling (the interaction of at least two excitons, *i.e.* two excited molecules) leads to the splitting of the excited state energy. This leads to the appearance of strong spectral shifts or band splitting, which may reach the order of several hundreds or thousands of cm^{-1}. All of the spectral changes are extremely sensitive to the structure of the molecular aggregates. Depending on the particular structure and arrangement of the molecules in the aggregate, different changes in the energies and spectral transitions can occur. The variability of the changes can be assigned to the sensitivity of the electrostatic interaction to the orientation of the interacting dipoles. The most relevant types of dye dimers are shown schematically in Fig. 3.

Dye molecular aggregation in clay-mineral colloids

Methylene blue is the organic dye used most often in clay research (Hang & Brindley, 1970; Yukselen & Kaya, 2008) and has therefore also attracted significant attention in terms of its metachromatic properties. When MB solution is mixed with a colloidal dispersion of smectite, a change in colour can be observed. The changes to absorption spectra in the visible region due to the formation of MB molecular aggregates are illustrated in Fig. 4. Since the first pioneering work on MB aggregation in a montmorillonite colloid (Bergmann & O'Konski, 1963), several papers have reported various aspects of this phenomenon (Schoonheydt & Heughebaert, 1992; Breen & Loughlin, 1994; Breen & Rock, 1994; Bujdák & Komadel, 1997; Bujdák *et al.*, 1998; Jacobs & Schoonheydt, 1999, 2001; Bujdák *et al.*, 2002b).

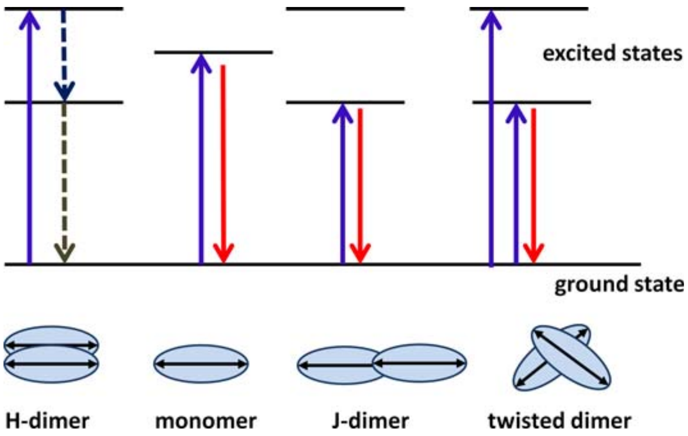

FIGURE 3. Splitting of electronic excitation energy levels in terms of their dependence on the structure of the dimers. Up arrows – light absorption (excitation); down arrows – deactivation (light emission); dashed line (non-radiative deactivation).

The MB colour change is sometimes highly unpredictable, and therefore for a long time there was no universal theory which could explain the large metachromatic variability of MB in colloidal dispersions of clay minerals. Fascinating properties of MB were noted by researchers, who referred to the dye as a "fingerprint molecule" for probing the surface properties of clays (Cenens & Schoonheydt, 1988). The role of exchangeable cations was often interpreted in terms of the effect on the stability and properties of smectite colloidal dispersions, particle flocculation and the variation of external *vs.* internal surface area (Schoonheydt & Heughebaert, 1992; Cione *et al.*, 2000; Czímerová *et al.*, 2004). A large variation in the MB molecular aggregation in the dispersions of macroscopically swelling Na^+- or Li^+-saturated smectites still existed, however. At the same time, the metachromasy of other cationic dyes was being investigated extensively (see review by Shichi & Takagi, 2000), but also failed to yield definitive answers to the question of which clay mineral parameter(s) affected dye molecular aggregation most significantly and led to the large variation in this phenomenon.

The older models for the adsorption of dye cations onto clay-mineral surfaces considered a purely parallel orientation of flat dye cations with respect to the plane of basal surfaces of clay-mineral particles (Garfinkel-Shweky & Yariv, 1997). Such an orientation would ensure an interaction with a maximal overlapping area between the dye cations and clay-mineral particle surface. The sorption capacity of smectites for MB cations often correlates well with the area covered by the flat orientation of adsorbed MB cations (Hang & Brindley, 1970). The parallel orientation would not enable the formation of large molecular aggregates of dye cations adsorbed on the clay-mineral surface, however. The first report, which raised the issue of the MB orientation on clay-mineral surfaces was about MB/mica systems (Hähner *et al.*, 1996), providing clear evidence of an inclined, almost perpendicular orientation of the dye cations. Some similar examples were reviewed later (Bujdák, 2006). H-aggregates consisting of MB cations in oriented smectite films were analysed by polarized spectroscopy in the visible region, and a perpendicular orientation with respect to the clay-mineral surface was proven in several cases (Bujdák *et al.*, 2003c; Kaneko *et al.*, 2003; Bujdák *et al.*, 2008). Similar conclusions were made for the H-aggregates of other types of dyes embedded onto clay-mineral surfaces (Chen *et al.*, 2002; Iyi *et al.*, 2002; Bujdák & Iyi, 2005, 2006b; Bujdák *et al.*, 2007).

Layer-charge effect on dye metachromasy

The hypothesis about the influence of the layer charge of smectites on dye molecular aggregation came relatively late (Bujdák & Komadel, 1997). The effect of the distribution of negatively-charged groups was first hypothesized for dye metachromasy in the solutions of polyelectrolytes (Stone & Bradley, 1967). Electrostatic forces control the association between the ionic groups in polyelectrolyte chains with ionic dyes of an opposite charge. Later, similar studies confirmed the trends in polyelectrolyte solutions (Bhattacharyya & Bhattacharya, 1996; Nandini & Vishalakshi, 2009, 2010). If there is a high density of the charged groups in the polymer chain, the molecular aggregation of oppositely charged dye ions would be promoted (Fig. 5). The effect of the layer charge of clay minerals was unknown, and had not been studied systematically for several decades since the work of Bergman and O'Konski (1963) was published. As mentioned above, metachromasy was believed to be influenced predominantly by the properties of clay-mineral colloids (Cenens & Schoonheydt, 1988; Neumann *et al.*, 1996). To eliminate such effects, Na^+- or Li^+-saturated smectites were tested to achieve maximal swelling and high stability of the colloidal dispersions. The first report on the layer-charge effect was based on a study using reduced-charge montmorillonites (RCMs) prepared by Li^+ fixation upon heating (Bujdák & Komadel, 1997). The series of RCMs represented a suitable model for this study. The mild charge reduction in Li^+-treated samples does not change the swelling properties or other parameters of the mineral significantly. Particle-size distribution, mineral content and the presence of admixtures remain unchanged upon mild Li^+ thermal treatment. Similar to the influence of the ionic groups in the chains of polyelectrolytes, the effect of the layer charge of smectites was found to be significant. The highest-charge smectites promote the formation of H-aggregates. The charge reduction is reflected in the destabilization of the H-aggregates, in favour of dye monomers, H-dimers and J-type assemblies. With MB, relatively large amounts of the H-aggregates were also formed in the colloids of RCMs of moderate layer-charge densities (Bujdák & Komadel, 1997; Bujdák *et al.*, 1998, 2001). They were relatively unstable, however, and often decomposed with time. The relation of dye molecular aggregation to the layer-charge density can be explained using a simplified scheme shown in Fig. 5. The effect of the distribution of charged sites is shown for both the layered particles

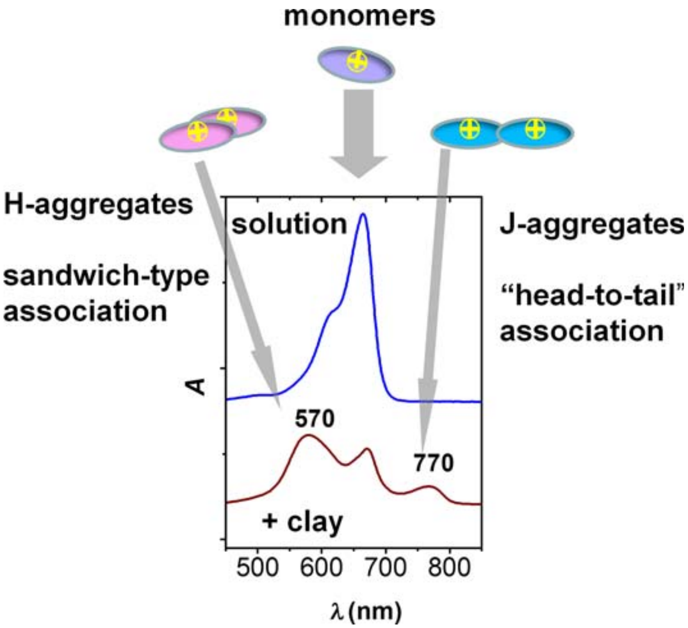

FIGURE 4. Absorption spectra of methylene blue in the visible region: aqueous solution; in colloid with montmorillonite; and assignments of bands to H- and J-aggregates.

and polyelectrolyte chains. Besides the distribution of charged sites, there are also other parameters which secondarily affect dye molecular aggregation, but some of them relate directly to the layer charge, such as the ionic force of the electrolyte in the vicinity of the particle surface, the electric double layer surrounding colloidal particles, *etc.* Consequently, the physical interpretation of the charge effect can be very complex. Although the layer-charge effect was discovered using RCMs, it was also verified later in studies using a series of smectites, based on minerals of various types, different not just in terms of the layer charge but also in terms of other properties (Bujdák *et al.*, 1998; Czímerová *et al.*, 2006). The origin and the structural types of smectites were found to be irrelevant with respect to the dye molecular aggregation. The layer-charge density, which mainly affects dye molecular aggregation, does not principally relate to the structural type of smectite. There are smectite specimens with a broad range of layer-charge densities regardless of the

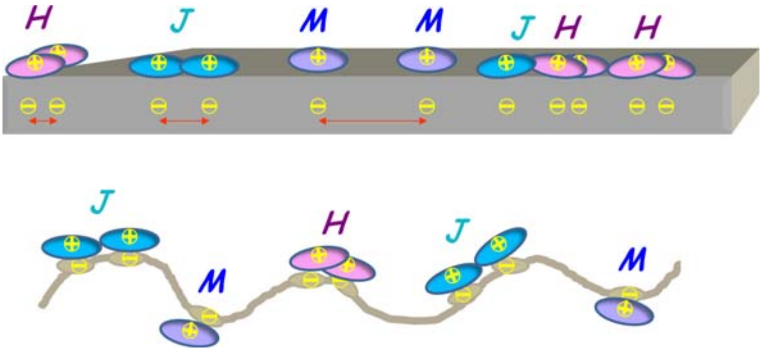

FIGURE 5. Schematic image of the effect of the distribution of charged sites in layers of smectites, and in the chain of cationic polyelectrolytes on the molecular aggregation of cationic dyes.

type, the origin and charge location in octahedral or tetrahedral sheets. Moreover, the effect of the charge distribution was proven to be a general phenomenon, potentially occurring for systems with any cationic dyes exhibiting metachromatic properties (Bujdák, 2006). It is interesting to note that the effect of the layer-charge distribution was also observed for the aggregation of anionic dyes adsorbed on layered double hydroxides (Bujdák & Iyi, 2008). The close relationship between the dye molecular aggregation and the layer-charge distribution was also indicated by results obtained with other inorganic layered materials. For example, cationic phthalocyanines were oriented parallel to hectorite layers with low charge densities, but analogous anionic dyes formed aggregates that were inclined perpendicular to the surface of the layered double hydroxide layers. The difference in aggregation as well as orientation of the molecules were assigned to the hosts' layer-charge densities (Carrado *et al.*, 1993).

The principal relationship between the distributions of dye cations and the layer charge was used in the design of hybrid materials to control the molecular aggregation of chromophoric units. The presence of molecular aggregation is essential due to its effects on photochemical and photophysical properties. For example, hybrid luminescent materials exhibit mostly optimal properties if the dye cations are in a non-aggregated state. To get an organic fluorophore sufficiently concentrated in the matrix of hybrid material, and at the same time avoid undesired molecular aggregation, is not a simple task. Using low-charge smectites is one of the ways to at least partially avoid this problem (Bujdák *et al.*, 2007; Klika *et al.*, 2009).

Evolution of dye aggregation with time

As mentioned above, dye molecular aggregation is a relatively complex reaction, proceeding with at least two main steps. Dye cation adsorption on the clay-mineral surface is a nearly instantaneous process, limited purely by the rate of diffusion of the molecules and the accessibility of the clay-mineral surface. The adsorption is very fast in dilute colloidal dispersions of Na^+-saturated smectites (Gemeay, 2002; Lofaj *et al.*, 2013) and the rate of formation of dye molecular aggregates is comparable to that in homogenous systems. The second step of the reaction is the transformation of the initially formed aggregates into stable dye species. This process can be followed efficiently by molecular spectroscopy as it is rather slow. The direction of this reaction can be very different for various types of dyes. For example, MB forms H-aggregates instantaneously at the surfaces of smectites with moderate or high charge densities (Bujdák & Komadel, 1997; Bujdák *et al.*, 2001, 2002b). At surfaces with moderate charge, H-aggregates decompose over time, forming monomers and J-type assemblies as stable species. With Rhodamine dyes, which typically have a more complex molecular structure, the trend is quite the opposite (Bujdák *et al.*, 2004; Bujdák & Iyi, 2006a): J-type assemblies or adsorbed monomers are initially detected and H-aggregates are formed over time. A new, interesting phenomenon was described for Rhodamine 6G. The layer charge influenced not only the reaction kinetics or extent of dye molecular aggregation, but also affected the reaction pathways of the dye assemblies' reorganization (Bujdák *et al.*, 2004). In other words, it influenced which types of dye spectral species were initially formed as metastable forms, and which were produced over time.

Metachromasy for probing clay-mineral properties and smectite detection

Dye molecular aggregation can be used for the sensitive probing of layer charge. Therefore, it has been applied often when changes in the layer charge were expected. One group of experiments was Li^+ fixation in montmorillonites with the charge located in octahedral sheets (Bujdák & Komadel, 1997; Bujdák *et al.*, 2001). Methylene blue aggregation helped to detect sensitively layer-charge changes in Li^+-treated smectites which carry only a small fraction of the octahedral charge, such as nontronites and beidellites (Bujdák *et al.*, 2001). The decrease in layer charge was proven repeatedly for acid-treated smectites (Bujdák *et al.*, 1998). H^+ cations attack the sites at both the octahedral and tetrahedral sheets located near non-equivalent isomorphous substitutions. The reaction of H^+ cations with the structural -OH groups may lead to the formation of water molecules, up to the release of ions from the structure. The sensitivity of the method was challenged in the characterization of heated NH_4^+-montmorillonites (Jankovič, unpublished results). The heated NH_4^+-montmorillonites exhibited slightly lower CEC values than the original, untreated sample. The mechanism was probably related to the decomposition of NH_4^+ cations yielding H^+ cations at elevated temperatures. The reaction of released protons with layers led to a charge reduction similar to acid treatment proceeding in strong acid solutions.

Besides charge reduction upon chemical treatment, there are several papers related to the characterization of various natural and synthetic clay minerals using dye aggregation. Most of the studies looked at smectites, but there were some attempts to characterize more complicated specimens, such as mixed-layered minerals (Šucha *et al.*, 2009). An idea to use dye molecular aggregation in the sensitive detection and quantification of smectites in aqueous colloidal dispersions was published recently (Lofaj & Bujdák, 2012). The smectites can be detected in aqueous systems below ppm concentrations. The sensitivity was achieved by using spectrophotometric titrations, enabling the resolution of dye molecular aggregates adsorbed on the clay-mineral surface from free molecules remaining in solution in a non-adsorbed state. The detection of dye molecules at concentrations of ~10^{-6} mol dm^{-3} is achievable using a common UV-Vis spectrophotometer. The detection limit can be further improved by applying fluorescence spectroscopy and chemometric methods. An example of the identification of the equivalence point from the spectrophotometric titration data, evaluated using principal component analysis (PCA) is shown in Fig. 6. The colloidal dispersion of Kunipia montmorillonite in water (5 ppm) was titrated with MB. The results of PCA detect sensitively the relationship between the spectral components evolved during the titration. The first eight points, which related to MB addition up to 0.8 mmol g^{-1}, represent the formation of pure H-aggregates. At points 9–11 (0.9–1.1 mmol g^{-1}), partial aggregation occurred, leading to equilibrium between H aggregates and monomers. After point 11, only monomers were accommodated as the titration progressed. The equivalence point near 1.0–1.1 mmol g^{-1} reflects closely the CEC value at such a low concentration.

These methods based on both surface characterization and smectite detection can be applied in environmental sciences, mineralogy and geology. Their application in other sciences related to other nanomaterials bearing a negative charge can also be considered. Understanding the mechanisms of dye metachromatic behaviour is very important to interpret correctly phenomena observed in other research fields, such as nanotechnology, polymer sciences, cell biology or histology. Metachromasy may be essential in the development of new histochemical methods based on staining with metachromatic dyes for the characterization of biological tissues (Stockert *et al.*, 2011). Due to the capacity of some smectites to promote the molecular aggregation of various dyes, clay minerals can be used as affordable and relatively simple model substrates to study aspects of dye metachromatic reactions in detail. Thus, models based on clay minerals can help to understand dye metachromasy in more complex systems, including substrates of biological origin (Stockert *et al.*, 2011).

PHENOMENA AND PROPERTIES RELATED TO HYBRID MATERIALS BASED ON DYES AND CLAY MINERALS

Photoactivity

Molecular aggregation leads to substantial changes in the optical properties of dyes. Preserving the photoactivity of dye molecules embedded in solid matrixes is often very difficult. The loss of photoactivity can be observed as a decrease in luminescence, but also affects other photophysical and photochemical properties. In particular, H-aggregates are molecular assemblies that exhibit low photoactivity. The excited dye molecules forming H-aggregates relax in a non-radiative pathway, transforming a majority of the excitation energy into heat. Moreover, the H-aggregates can be very efficient quenchers of the molecules of coexistent active forms, such as monomers or J-aggregates. The quenching proceeds *via* the mechanism of Förster resonance energy transfer, which is based on electrostatic interactions and is efficient up to distances of a few nanometers. As a result, a relatively low fraction of the dye molecules forming H-aggregates can lead to a substantial loss of photoactivity. Several attempts have been made to minimize the formation of H-aggregates in hybrid systems with clay minerals. Significant elimination of dye aggregation can be achieved by appropriate selection of the clay mineral. As was mentioned above, smectites with low layer charge, mostly synthetic Laponites or saponites, exhibit excellent properties to form stable colloids and adsorb dye cations mainly in a non-aggregated form. Nevertheless, in most cases dye aggregation cannot be fully suppressed purely by the proper choice of smectite component. Molecular aggregation can be reduced significantly for dyes of a specific structure. Some dye molecules with shape which is not perfectly flat exhibit the formation of dye assemblies with lower effects on spectral properties. Using dyes that form J-aggregates preferentially, which represent a photoactive type of assemblies, is another strategy. Applying low-charge smectites helps to preserve the photoactivity of the dyes carrying more than one cationic group in

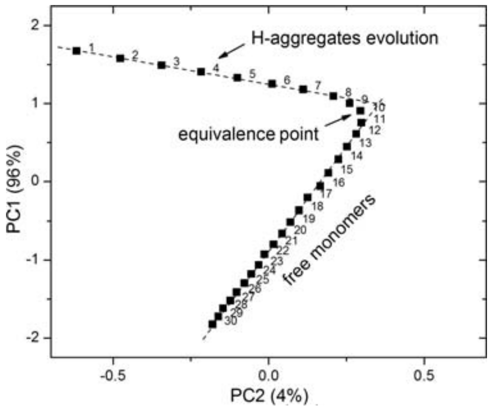

FIGURE 6. Equivalence point estimated from spectrophotometric titration data (Lofaj *et al.*, 2012) using principal component analysis. Kunipia montmorillonite (5 ppm dispersion) was titrated with Methylene blue solution.

their molecules. The reduced mobility of the polyvalent cations prevents their aggregation efficiently (Takagi *et al.*, 2001; Shiragami *et al.*, 2006). The procedure for the synthesis of photoactive hybrid materials with densely packed porphyrin cations was developed based on this strategy (Ishida *et al.*, 2012; Fujimura *et al.*, 2013; Takagi *et al.*, 2013). The so-called 'size-matching rule' was adopted for finding optimal conditions matching the charge distribution at both the clay-mineral surface and on the dye molecule. Under such conditions a maximal coverage of the surface with dye cations can be achieved, avoiding dye molecular aggregation and a significant loss of photoactivity. Tetracationic porphyrins exhibit much lower aggregation than other types of dyes, even at surfaces with a relatively large layer charge.

A substantial reduction in dye aggregation can also be achieved by appropriate conditions. Dye aggregation is promoted in aqueous colloids, but can be minimized efficiently in non-aqueous environments (Bujdák & Iyi, 2012). Minimizing the dye/clay mineral ratio is also often reflected in the reduction of dye molecular aggregates. Several studies have reported the successful enhancement of dye photoactivity by using chemically modified smectites. Alkylammonium-treated specimens with small amounts of adsorbed dyes were very photoactive materials (Sasai *et al.*, 2009). The optical properties of these materials often depend on humidity, which could be used for sensing applications. The other approaches included further components, such as polyelectrolytes (Czimerová *et al.*, 2013) or molecular cavitands (Ishida *et al.*, 2014; Matejdes *et al.*, 2015) to avoid dye aggregation and improve photoactivity.

Conformational changes in dye molecules upon adsorption

Before the exciton theory was well established, metachromasy was considered to be related to structural changes in dye molecules. Indeed, the spectral properties of organic dyes are primarily dependent on the structure of conjugated, aromatic or heteroaromatic chromophores, and furthermore on the presence of functional groups. In some cases, dye adsorption on the clay-mineral surface leads to structural changes affecting the dye's spectral properties. Conformational changes are minor structural changes which do not include the decomposition or formation of new covalent bonds. They lead to changes in the shape of molecules which are, in principle, achieved by rotation around single bonds. However, they may lead to remarkable changes in spectral properties. The most significant were observed for porphyrin dye cations, such as those with p-methylpyridinium groups in the four corners of the porphyrin molecule (Takagi *et al.*, 2006; Eguchi *et al.*, 2007; Čeklovský *et al.*, 2011). The pyridinium cationic groups of free porphyrin molecules are slightly tilted with respect to the plane of the porphyrin ring. In such a conformation, the nitrogen atoms in the cationic pyridinium groups could not effectively interact with negatively charged sites on the clay-mineral surface upon adsorption. When these cations are adsorbed on the surface of clay-mineral particles, a slight rotation around the bond between pyridinium groups and the porphyrin ring takes place, which leads to a more planar conformation of the molecules (Takagi *et al.*, 2001). Flattening the porphyrin cation leads to a more efficient delocalization of π electrons, which was observed experimentally in UV-vis spectra and confirmed by theoretical calculations (Chernia & Gill, 1999). Interestingly, the rotation depends on the type of system (colloid, film), pre-treatment of the clay mineral, as well as on the type of porphyrin itself (Čeklovský *et al.*, 2009, 2011). The investigation of the dyes with different isomerism of their methyl-pyridinium moiety (ortho-, metha- or para-) proved the importance of electrostatic forces in the changes in molecular conformation. Structural changes led to shifts in both the absorption and emission bands to significantly lower energies, achieving shifts of up to 2000 cm^{-1}. Improved molecular planarity achieved after adsorption/intercalation may be suitable for enhancing the non-linear optical properties of the chromophores (Suzuki *et al.*, 2012).

Optical anisotropy of hybrid materials

Anisotropy is a property which is directionally dependent. It is opposite to isotropy, which implies identical properties in all directions. Solids exhibiting optical anisotropy are defined as birefringent materials, having optical characteristics dependent on light polarization and the propagation direction of the electromagnetic wave. Optical anisotropy was observed for intercalated dye molecules in thin solid films of clay minerals (Iyi *et al.*, 2002; Bujdák *et al.*, 2003b,c, 2011). Optical anisotropy can also be achieved under certain conditions with colloidal dispersions (Yamaoka *et al.*, 2000). The property of optical anisotropy has been applied for the determination of the molecular orientation of dye molecules on a clay-mineral surface (Bujdák *et al.*, 2003b, c; Kaneko *et al.*, 2003; Bujdák & Iyi, 2005; Martinez *et al.*, 2005). Several methods have been developed applying both absorption (Bujdák *et al.*, 2003b,c; Kaneko *et al.*, 2003; Bujdák & Iyi, 2005) and fluorescence spectroscopy (Martinez *et al.*, 2005; López Arbeloa & Martínez Martínez, 2006a,b), conducted using linearly polarized light. Only rarely were other spectroscopy methods used (Hähner *et al.*, 1996; Fischer *et al.*, 1998; Ras *et al.*, 2003a, 2004a, 2007). The basic principle of the methods is very simple and is based on the close relationship between the probability of an electronic transition of the molecule to the orientation between the transition dipole moment and electric vector of the electromagnetic wave. If both the vectors are parallel, there is a maximal probability of light absorption. If they are perpendicular, no light absorption occurs. When a film with preferentially oriented particles of the clay mineral parallel to the substrate contains intercalated dye molecules oriented perpendicular to the clay-mineral surface, they are not visible if the light propagation direction is perpendicular to the surface of the film. They start to absorb light when the film is tilted with respect to the light beam. It is possible to calculate the most probable orientation of the transition moment with respect to the clay-mineral surface from linearly polarized spectra. The parameter of the transition moment, its relationship to the molecular structure, is either known or can be calculated by quantum chemistry methods. For monomers and J-aggregates, an almost parallel orientation with respect to the film surface was observed for the most part (20–30°). On the other hand, H-aggregates are often built from molecules with an almost perpendicular orientation (40–70°). Hence, the orientation of chromophores is important for the optical properties of materials. Birefringence plays an important, sometimes key, role in non-linear optical materials, displays, sensors, polarizers, filters, light modulators, *etc*.

Resonance energy transfer in hybrid materials

Förster resonance energy transfer (FRET) plays a key role in photosynthetic cells in the delivery of light energy from molecular antennas absorbing photons to the sites where the energy is converted into chemical bonds. Light energy transfer in plants is very efficient. Future solar cells working at a molecular level will probably utilize FRET in the same way. FRET can be described in the simplest terms as the phenomenon occurring between two different chromophores interacting *via* an electrostatic coupling. An energy donor (ED) selectively excited by the absorption of a photon of a certain energy may transfer its excitation energy to the second chromophore, an energy acceptor (EA). The transfer is through electrostatic coupling between the dipoles of the interacting molecules, as a resonance which is a radiationless process. The FRET efficiency is inversely proportional to the sixth power of the distance between the ED and EA, and therefore the phenomenon is limited to distances of a few nanometers. Furthermore, there must be a strong spectral overlap between the ED emission and the EA absorption spectra for the resonance to occur, which can be achieved with an appropriate selection of the interacting dyes. The orientation of the interacting chromophores is another important parameter for FRET to occur. Hybrids based on clay minerals in which dye molecules are embedded have properties which meet a resonance condition, are ideal for FRET to occur in high yields (Schoonheydt, 2002; Czimerová *et al.*, 2008; Bujdák *et al.*, 2010; Hussain *et al.*, 2010; Bujdák *et al.*, 2011; Dey *et al.*, 2013; Bujdák, 2014). The concentration of the dyes, which are adsorbed on the surface of colloidal particles or are intercalated in solid matrix, is mostly sufficiently high. The close intermolecular distances between ED and EA molecules support an efficient FRET (Takagi *et al.*, 2007). Multistep FRET has been observed in ternary or more complex systems based on clay minerals and three types of interacting dyes (Bujdák *et al.*, 2011; Belušáková *et al.*, 2015). In some cases, one EA molecule is able to efficiently quench several molecules of EDs (Bujdák *et al.*, 2010). The phenomenon in dilute colloids of smectites is limited to two-dimensional

FRET (on the surface of a particle) and does not exhibit the efficiency occurring in solid hybrid materials with similar dye concentrations. FRET through smectite layers has been proved in layer-by-layer (LbL) assemblies and Langmuir-Blodgett films based on smectites with adsorbed dye cations and cationic polyelectrolyte molecules (Place *et al.*, 2003; Ras *et al.*, 2003b). Attempts have also been made to promote FRET ending with the charge transfer reaction, thus more accurately mimicking photosynthetic systems or solar cells. Interestingly, the FRET phenomenon can potentially be used for measuring the distances and possibly also spatial orientations of interacting molecules adsorbed on clay-mineral surfaces. It could help to characterize the dynamic processes involved in dye/clay mineral systems. FRET has built up an excellent reputation as a diagnostic tool in molecular biology, protein chemistry, nucleic acid analysis, in nanosciences, *etc.*, and its use in clay research in the future is awaited.

Non-linear optical properties

Non-linear optical (NLO) materials are important for their application in optical devices. NLO properties describe the behaviour when dielectric polarization responds non-linearly to a light electric field. They are only observable at very high light intensities. The best known NLO phenomena include second harmonic generation (SHG), when two photons combine creating a single photon with double energy and sum-frequency generation when the resulting frequency is the sum of the frequencies of the combined photons. NLO properties were observed for some organic dyes with specific structure and properties. It is interesting that molecular aggregation induced at the surface of clay minerals can significantly enhance the NLO properties of some dyes (Boutton *et al.*, 1997; Wang *et al.*, 2000). Hybrid materials composed of clay minerals and organic dyes with non-linear optical properties have been studied by several research groups (Jehnichen *et al.*, 2008; Kawamata *et al.*, 2010; Suzuki *et al.*, 2012; Epelde-Elezcano *et al.*, 2014). Those authors used clay-mineral carriers for the restricted confinement of dye molecules to achieve a suitable molecular alignment and orientation for the optimization of NLO materials (Kawamata & Hasegawa, 2006; Suzuki *et al.*, 2011). Another problem to be solved to fabricate composites that exhibit the properties of a real applicable optical material is perfect light transparency, low light scattering and homogeneity (Kawamata *et al.*, 2010). These parameters are achieved using synthetic clay minerals with small particle dimensions, below the wavelength of visible light. More complex materials, such as nanocomposites with polymers or LbL assemblies bearing NLO dyes were also reported (Laschewsky *et al.*, 1997; Dudkina *et al.*, 2005; Chao *et al.*, 2008). NLO materials based on kaolinite intercalates with nitroaniline dyes have also been reported (Takenawa *et al.*, 2001).

Photochromism

Photochromism is the phenomenon of reversible transformation of photochromic molecules between two isomeric forms. The isomerization is induced by the absorption of light, and the two isomers exhibit different absorption spectra and physical properties. The structural changes are often accompanied by a reversible visible change in the substance's colour. There are several types of photochromic organic compounds, and some of them were also studied in the hybrids with clay minerals (Ogawa *et al.*, 2001; Li & Li, 2003a). Among the simplest examples are colloidal dispersions and solid films of the hybrids of cationic azobenzene dyes (Ogawa, 1996; Ogawa *et al.*, 1999). Azobenzene changes its structure upon irradiation with UV light from a more stable *trans*-form to a *cis*-isomer. This change is reversible and upon irradiation with visible light returns to the *trans*-isomer. A monocationic derivative of azobenzene also exhibited similar properties when adsorbed on the surface of clay-mineral particles. The adsorption of an azobenzene dication led to the loss of dye photochromicity, occurring with both the colloidal dispersion and thin solid films (Bujdák *et al.*, 2003a; Umemoto *et al.*, 2014). This phenomenon was interpreted in terms of ionic interaction (Fig. 7). Photochromism was also observed for clay mineral-diarylethene (Sasai *et al.*, 2000), spirooxazine (Nishikiori *et al.*, 2006) and spiropyran (Bae *et al.*, 2004) hybrid materials. The efficiency of the diarylethene molecules' response to alternating UV and visible irradiation decreased when the cycles were repeated. The reversibility of photochromism was improved when diarylethene molecules were co-adsorbed with surfactant molecules (Sasai *et al.*, 2000). In another instance, the photochromism and materials properties were improved by electrostatic self-assembly with polyelectrolyte molecules (Li & Li, 2003b). In some cases, photochromism also changed other properties of the material significantly. The azobenzene photochromism-induced intercalation/deintercalation of phenol molecules was studied and found to be an alternative way to control the reversible retention/release of dangerous chemical pollutants (Okada *et al.*, 2008).

Photochemical processes and photosensitization

Photochemical processes are chemical reactions following the absorption of electromagnetic radiation. Light provides the energy for a reactant activation, which can be transferred directly to the molecule participating in the reaction or *via* a photosensitizer. The photochemistry provides some advantages to thermally activated reactions, such as alternative mechanisms and pathways, selective activation, faster reaction rates, *etc.* Photochemistry is important for various scientific and industrial subfields. Among the most important challenges of photochemistry are artificial photosynthetic systems, aimed at the conversion of light energy to chemical energy or to electricity. Only rare attempts have been made to incorporate clay minerals directly in the materials implemented for dye-sensitized solar cells (Scully *et al.*, 2004). A detailed review of the photochemistry of inorganic oxides, zeolites, including clay mineral systems, has been published (Kerry Thomas, 1993). The adsorption of a photoactive molecule onto the particles of clay minerals introduces new aspects to their photochemistry, affecting the photochemical and photophysical properties of the reactants, as well as altering the reaction conditions (Thomas, 1988). Molecular aggregation can play a significant role, but the resulting photochemical properties can also be crucially dependent on the geometry of molecular aggregates. In general, the formation of the molecular aggregates can eliminate, or in other cases promote photochemical reactions (Thomas, 1988). The degradation of Rhodamine B in clay-mineral colloids upon their irradiation took various pathways, including the decomposition of the chromophore or dealkylation reaction, depending on the type of mineral present. Differences were attributed to the stability of reactive oxygen species at the systems of different clay minerals (Wang *et al.*, 2014). Some examples of the decomposition processes were reported for cyanine-type dye cations (Bujdák *et al.*, 2002a,c). Interestingly, the decomposition was influenced by the layer charge of the clay mineral. The decomposition reactions were probably thermally activated, and the photochemical pathways have not been confirmed or investigated in detail yet. On the other hand, the photochemical decomposition of methylene blue clearly depends on the formation of molecular aggregates (Samuels *et al.*, 2013). The dye was stabilized at the surfaces of clay minerals which induced the formation of H-aggregates.

Some organic dyes have the properties of photosensitizers, which are a type of mediator activating the processes which would not be possible *via* the direct irradiation of the reactants. A large group of photosensitizers are dyes activating molecular oxygen. The interaction results in the formation of reactive oxygen species (ROS) including radicals and singlet oxygen. In these cases important redox processes can be catalyzed by various photosensitizers. An example of such a process is photochemical water splitting for the generation of hydrogen (Detellier & Villemure, 1984). Eosin-sensitized attapulgite was efficient in the catalytic decomposition of water to generate hydrogen under visible light irradiation. It is likely that structural iron played a significant role in this process (Zhang & Liu, 2014). The action of evolved hydrogen, or other reduction mechanism, could also play a role in the photoreduction of Cr(VI) in colloidal dispersions of montmorillonite under visible light (Liu *et al.*, 2014). Iron probably played a role in this reaction also.

The formation of organic radicals is another example of photochemical redox processes which are mediated in dye/clay mineral hybrid systems. The photoreduction of methyl viologen in smectite intercalation compounds was investigated in several studies. Methyl viologen intercalated in synthetic saponite and Laponite were photoionized by UV irradiation (Kakegawa *et al.*, 2003). When viologen di-cations intercalated into montmorillonite were co-intercalated with poly(vinyl pyrrolidone), the colour of the intercalation compounds changed to blue, demonstrating the formation of the radical cations (Miyata *et al.*, 1987). The photo-ionization of pyrene on Laponites dramatically increased the yield of pyrene cation radicals (Liu *et al.*, 1992). Similar compounds, such as perylene, anthracene and phenylenediamine formed cation radicals *via* photolysis in a Laponite colloid (Iu *et al.*, 1991). The reaction products were stable for hours under vacuum. Oxygenated samples exposed to UV radiation produced cation radicals and unknown coloured substances, probably the products of reactive radical species (Iu *et al.*, 1991). The photooxidation of the polycyclic aromatic hydrocarbon chrysene was significantly enhanced in aqueous Laponite suspensions compared to photolysis in an aqueous solution (Kong & Ferry, 2003). The role of the singlet oxygen was proved in some photosensitization experiments: the photooxidation of electron-rich substrates such as quinol, 1-naphthol and anthracene by

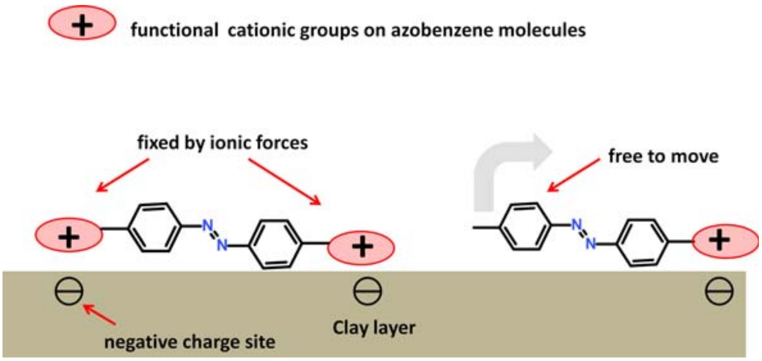

FIGURE 7. Schematic image illustrating the stabilization of dicationic azobenzene dye on a clay-mineral surface *via* ionic bonds.

clay mineral-bound methylene blue/Bengal rose was studied under an oxygen atmosphere (Epelde-Elezcano *et al.*, 2014). The photochemical formation of reactive organic radicals has an almost unlimited range of applications, especially in organic synthesis. Photochemical radical initiation for the preparation of clay mineral/polymer composites was also investigated (Paczkowska *et al.*, 2004).

SYNTHESIS OF DYE/CLAY MINERAL HYBRID MATERIALS

A recently published paper summarized promising applications of various types of hybrid systems based on organic compounds and clay minerals (Schoonheydt, 2014). Various studies have reported a large variety of dye/clay mineral hybrid materials and advances in the preparation of specialized and functional materials. Clay minerals of the smectite type and their synthetic analogues such as montmorillonites, saponites and Laponites have been used most frequently as components in hybrid materials with cationic organic dyes. The simplest way to prepare these hybrids is by mixing the components in colloid form. Optically transparent films are more difficult to prepare, but are still one of the common forms of hybrid materials based on clay minerals. Transparency and optical homogeneity, in particular, are key factors for optical materials. Numerous studies on transparent film formation have been published and reviewed (Zhou *et al.*, 2011); the simplest procedures included colloid casting or spin-coating. A novel procedure is based on the vacuum filtration of a dilute colloidal dispersion of smectite particles with an adsorbed organic dye (Kawamata *et al.*, 2010). The effects of various parameters for the synthesis of thin hybrid films were investigated. These include the type of clay mineral, its surface properties, layer charge, the type of exchangeable cations, solvent, pH, temperature, organic components or modifiers, *etc.* The best way to prepare transparent optical films is by using a smectite-type clay mineral with a very small particle size (below visible light wavelength) to reduce light scattering. The best results were with some synthetic, commercially available trioctahedral smectites. The stability of the colloids, as a starting material for the film preparation, and homogeneous dispersion of the particles can be accomplished by using smectites in their Na^+ or Li^+ forms.

Besides aqueous colloids or simple thin hybrid films, there are some less frequent types of hybrid materials or more complex procedures which are worth mentioning. Phthalocyanines were incorporated into hectorite *via in situ* crystallization. Intercalation compounds of hectorite and cationic phthalocyanines were prepared directly by refluxing oxide/hydroxide solution and the organic dye (Carrado *et al.*, 1993). The combination of organoclays with adsorbed Rhodamine dye led to the formation of materials with large fluorescence yields (Bujdák & Iyi, 2012). The colloids and gels of these materials in xylene exhibited not only high luminescence but also perfect transparency because of the match between the refractive indices of the material and the solvent. Both the colloids and gels of this type are new types of materials with interesting optical properties, which might be applied in paints or lacquers, or in other related applications. Colloidal dispersions of hectorite particles attached covalently to sub-micrometer monodispersed spherical silica particles were synthesized (Okada *et al.*, 2012). Ion exchange with MB did not lead to the flocculation of the colloidal dispersion. The colloids remained stable even after the charge of the hectorite particles was fully compensated by MB cations. The unique properties of such materials can lead to various applications, such as building blocks for photonic crystals, a chromatography stationary phase, and drug support for controlled release, *etc.* (Okada *et al.*, 2012).

Worthy of attention is a special type of thin film, the structure, composition and functionality of which can be controlled at the molecular or nanometer-scale level. The most frequent approaches for the preparation of such films were LbL assembly and the Langmuir-Blodgett (LB) techniques. These synthesis procedures led to the formation of films with variable properties, such as film thickness, surface morphology, structure ordering, *etc.* These parameters then secondarily affected other properties, such as optical properties, reactivity and stability of the films, transparency, hydrophobicity *vs*. hydrophylicity, *etc.* Langmuir–Blodgett films represent a relatively old type of material. They contain one or several monolayers of organic molecules, which are deposited on a substrate from the liquid phase as a film formed between the air/solution interface. The monolayers are formed predominantly from surfactant or other amphiphilic molecules driven by the hydrophobic effect and self-assembly. In recent decades, Langmuir–Blodgett films including clay-mineral particles were also prepared (Ras *et al.*, 2004b,c). Thin films represent another type of LbL assemblies and these are formed most frequently from monolayers of oppositely charged particles and macromolecules. LbL assemblies are formed in a step-by-step procedure, depositing one layer at each step, alternating the charge of the outer layer in each step. Clay minerals are useful materials for creating layers bearing a net negative charge which can alternate with positively charged polyelectrolyte molecules. Using this approach, optical LbL films bearing two types of dyes and smectite particles were built, and each step was characterized by molecular spectroscopy methods (Bujdák, 2014).

Clay minerals grafted with covalently attached dye molecules are a very interesting and promising group of hybrid materials. The immobilization of the molecules may lead to a substantial reduction in molecular aggregation. Besides this, dye molecules can be stabilized against thermal or chemical treatment and are more difficult to release from the solid matrix. There have been two main approaches to constructing such materials: (1) attaching dye molecules onto clay-mineral particles; and (2) forming the clay mineral and the hybrid with covalently attached molecules *via in situ* synthesis. Clay-mineral particles were modified with reactive luminescent dyes forming covalent bonds *via* reaction with their hydroxyl groups. The efficient modification of particle edges of smectites led to luminescent materials with large fluorescence yields (Bujdák *et al.*, 2012). Due to the location of the dye molecules at particle edges, the optical homogeneity depended on the smectite particle size. A similar approach was used for the preparation of the hybrid with kaolinite. The mineral pre-expanded with DMSO was modified with active silane carrying a fluorophore group, which reacted with the surface OH-groups of the mineral surface (Sas *et al.*, 2015). Significant luminescence was also achieved in this case. A direct synthesis with coumarin attached covalently to the clay-mineral layer was performed from the reaction of organoalkoxysilane, silica sol, and inorganic salts (Fujii *et al.*, 2008, 2009). The hybrid material obtained *via* hydrothermal synthesis exhibited significant luminescence and was further modified with Rhodamine cations. The resulting materials carried two fluorophores: one was covalently bound coumarin moieties; the other, electrostatically bound Rhodamine cations. FRET between the two dyes was also investigated (Fujii *et al.*, 2008, 2009).

More complex, ternary systems have also been explored, also incorporating other components or modifiers besides dyes and clay minerals, such as functional polymers, transition-metal complexes, protein or nucleic acid molecules or their combinations. Such highly complex materials have potential applications in many areas such as photocatalysts, optoelectronic devices, solid luminescent materials, photosensitizers, *etc.* One example is nanolatexes with azo dye moieties and montmorillonite particles (Ianchis *et al.*, 2009). The clay-mineral component in the nanocomposite did not interfere with the dye's spectral properties. The attachment of dye molecules to the clay mineral can also be useful in other ways. If the hybrid is used as a filler in a polymer, the dye attached to the filler particles can probe the composite structure. Confocal fluorescence microscopy then provides very valuable information on the size and distribution of the filler inside the polymer.

SUMMARY

Hybrid materials based on organic dyes embedded in clay minerals seem to offer great potential for a variety of different functions. In the current era of nanomaterials, in particular, clay minerals offer control of the distribution of dye molecules at a molecular scale, by separating the components with layers or controlling the distribution of the chromophores *via* ionic or other interactions. There are several aspects and potential applications which deserve further study in the future. For example, the analysis and selective optical detection of analytes with suitable indicator chromophores can be improved using the hybrid system and dye probes embedded in a solid matrix of clay minerals. Preferential molecular orientation and anisotropy of the hybrid systems makes these materials respond specifically to polarized light. There are many possibilities for the development of photocatalysts based on dye/clay-mineral hybrids, where the catalytic properties of both the components combine with other advantages compared to homogeneous catalytic systems. Some hybrids with dyes-photosensitizers have the same properties as antimicrobial and self-disinfecting materials and could be used for bioactive surfaces or as components and fillers for industrial polymers, paints, medicines, drug delivery systems, medical supplies and equipment, disinfection agents, *etc.* Not much is known about the limits for the synthesis of materials with photoactivated species, such as stabilized radicals and reactive intermediates. NLO materials and systems exhibiting resonance energy transfer occurring at a molecular level could be used as optical materials or components in optoelectronic devices and solar cells. A dye combined with clay-mineral particles enable the miniaturization of devices based on these materials. Furthermore, there are already some well established procedures that enable the components in the hybrids to be organized at a molecular level, such as deposition based on layer-by-layer assemblies, intercalates of specific structure, hybrids with dye molecules of preferential orientation, dye molecules incorporated into the silicate layer skeleton during hydrothermal synthesis, *etc.* Clay minerals could be used for stabilizing organic dyes, or in other cases for the photocatalytic decomposition of environmentally dangerous pollutants. Dye/clay-mineral hybrid systems have a broad variety of promising applications, offering various directions for further research and, therefore, deserve a great deal of attention from scientists.

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