Recent advances in the study of mechanochromic transitions of organic compounds

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The article reviews a wide variety of mechanically induced colour changes in organic compounds. It considers structural and chemical transformations of the compounds that cause mechanochromism. When relevant, technical applications of the phenomenon are also highlighted.

Keywords: mechanochromism, tribolumnescence, coloration, mechanochemistry, conformational changes, structural phase transition, pressure effect

1. Introduction

This review deals with mechanically induced colour changes, or “mechanochromism”. Its aim is to describe molecular transformations, inner-crystal phenomena, and disordering, or reorientation of monolayers provoked by mechanical effects.

Mechanochromism is used to record and treat information, to study lubrication phenomena, the mechanically generated changes in molecular structures, or crystal packaging. In the present treatise, different causes of organic mechanochromism are considered and the corresponding representative examples are discussed. When relevant, technical applications of the phenomenon are also highlighted.

2. Triboluminescence

2.1. Luminescence caused by mechanical generation of crystal defects or changes in intermolecular contacts

Triboluminescence, the emission of light by solids when they are stressed or fractured, is a very common phenomenon. For a long time, it has been known that sugar shines when it is triturated in the dark. According to the literature estimates, 36 % of inorganic, 19 % of aliphatic, and 37% of aromatic compounds, 70% of alkaloids, and perhaps 50 % of all crystalline materials are triboluminescent**, (**see ref.1 and references therein).

Although it remains an obscure phenomenon, the effect is generally explained in terms of excitation of the molecule by an electric discharge between the surfaces of the fractured crystals.[2] Indeed, emission of light, radio signals, electrons, and ions has been clearly demonstrated at the moment of fracture under vacuum.[3] Some materials, even molecular crystals or small molecules, do emit light without involvement of the surface, most likely by recombination of energetic defects during deformation or fracturing.[1] The discharge causes luminescence.

Triboluminescent compounds have received increasing attention due in part to a growing need for optical-pressure sensor devices and structural damage sensors.[4] These compounds are useful in the study of wear[5] and material fracture.[6] Photochemistry resulting from triboluminescence is implicated in the mechanism of explosions.[7]

Recently, a novel and potentially important application of the phenomenon has been proposed for the development of real-time damage sensors in composite materials.[8] Specifically, the idea is based on the observation that light emission occurs when a composite material containing the triboluminescent molecule is damaged. Monitoring the wavelength and measuring the amount of emission yield information on the extent of the damage. During the development of such sensors, relationships between triboluminescence and solid-state photoluminescence were carefully studied and some important features were revealed. For instance, certain pure organic crystals emit light upon fracturing but this light is significantly self-absorbed within the bulk of a damaged crystal.[9]

Further, a principal difference should be emphasised between pressure effects and the effects of fracture, shock wave, or shear. Pressure is the thrust distributed over a surface. From this definition, the difference is clear. Pressure can provoke changes in photoluminescence spectra. Thus, the crystalline chloride salts of the dioxorhenium(V) complexes containing ethylene diamine derivatives[10] or the crystalline tetrabutylammonium salts of the platinum(II) and palladium(II) complexes carrying thiocyanate or selenocyanate ligands,[11] undergo blue shifts of band maxima and enhancement of luminescent intensities under pressure up to 4 MPa. The external pressure changes the interaction between ground and excited (emitting) states of the crystalline compounds that results in the spectral effects observed.

Early experiments indicated that the triboluminescent phenomenon was commonly observed in materials with non-centrosymmetric (non-centric) crystal structures, and which therefore were piezoelectric. For metal complexes with organic ligands, this feature is discussed in the literature as Zink’s rule.[12]

Several examples of triboluminescent molecules should be considered here with respect to their structural features. These examples differ in their centrosymmetry, *i.e.* in order–disorder features of the molecular structures. Thus, tris (2-thienoyltrifluoroacetone)-europium(4,4'-dimethyl-2,2'-dipyridyl) [$(tta)_3{\cdot}Eu{\cdot}dmdpy$ in Scheme 1], has a non-centrosymmetric crystal structure, and disorder of the thienyl rings and the trifluoromethyl groups.[13]

On the other hand, hexakis(2,3-dimethyl-1-phenyl-pyrazolone-5) terbium triiodide [$(dmpp{=}O)_6TbI_3$ in Scheme 1] is clearly centrosymmetric without any disorder.[14] Centrosymmetry has been also proven for a μ_2-(pyridine *N*-oxide) bridged binuclear europium(III) complex [$(tta)_6{\cdot}Eu{\cdot}Eu{\cdot}(py\text{-}O)_2$ in Scheme 1].[15]

All the metallocomplexes in Scheme 1 are brilliantly triboluminescent. Sparks are displayed when their crystals are cut or crushed in the dark and even with room illumination. For the non-centrosymmetrical europium mononuclear complex, the observed triboluminescent activity is ascribed to charge separation caused by piezoelectricity which occurs when the non-symmetric crystal is deformed or fractured. For the centrosymmetric terbium complex, the authors assume that impurities create piezoelectric charge separation. For the other centrosymmetrical species, $(tta){\cdot}Eu{\cdot}Eu{\cdot}(py\text{-}O)_2$, the authors experimentally excluded impurities by careful crystallisation, and in their opinion, impurities are not responsible for the triboluminescence observed. The complex is not ionic and could not gain the local piezoelectricity essential to its triboluminescent activity. However, there is disorder of all of the six thienyl rings and the trifluoromethyl

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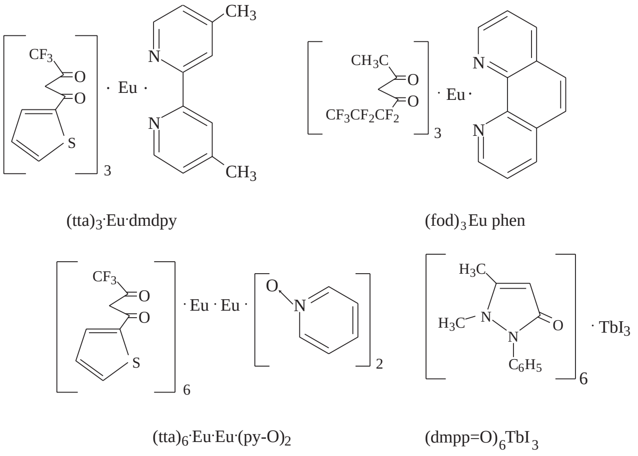


Scheme 1

groups. This disorder may provide a structural basis for charge separation by creating randomly distributed sites of slightly different ionisation potentials and electron affinities at the faces of developing cracks. Some authors consider disorder as the essential condition for triboluminescent activity even in cases of the centrosymmetric ionic crystals; for example, see ref. 16. Such disorder may provide the local dissymmetry needed to support charge separation.

The mechanoluminescence of the tris(6,6,7,7,8,8,8-heptafluoro-3,5-octanedione-2,2-dimethyl) europium phenathroline complex [$(fod)_3$·Eu·phen in Scheme 1] was also observed and studied with respect to the role of the two constituents – $(fod)_3$·Eu and phen.[17] When it is crushed separately, the phenathroline (phen) crystal emits luminescence which is distinct from that of the $(fod)_3$·Eu·phen complex, whereas the disintegration of $(fod)_3$·Eu crystals is not accompanied by any luminescence. However, luminescence analogous to that from the $(fod)_3$·Eu·phen complex does take place on grinding a mixture of phen with $(fod)_3$·Eu. The inference is that the chromic effect observed is due to the sensitisation of phen triboluminescence by the $(fod)_3$·Eu part of the $(fod)_3$·Eu·phen complex.

The complexes (piperidinium)[Eu(benzylacetyl methide)$_4$] and Tb(antipyrine)$_4$I$_3$ provide additional examples of exceptions to Zink's rule. Careful X-ray studies show that they are centrosymmetric, but when they are ground, they display luminescence visible to the naked eye.[18]

One special case of mechanochromism is provided by the complex bis[gold(1+) trifluoroacetate] containing uracilate (or methyluracilate) and bis(diphenylphosphino)methane as ligands, which forms crystals of helical geometry, and in which there are weak gold-gold intermolecular contacts. When it is gently crushed under a spatula, the complex exhibits bright blue photoluminescence; the complex eliminates trifluoroacetic acid and becomes more linear, and this markedly enforces the gold–gold contacts.[19]

2.2. Luminescence induced by shock waves

Shock waves also generate triboluminescence in crystalline organic compounds such as *N*-isopropylcarbazole.[20] In this work, a novel technique was elaborated to generate a shock wave by means of laser irradiation onto a glass plate whose side (frontal to the laser beam) was coated with a black pigment film. The film did not transmit light irradiation but propagated an intense pulsed-acoustic wave (*i.e.*, shock wave) through it, which was sufficient to cause some fracture in crystalline *N*-isopropylcarbazole.[20] Piezoelectrisation of the fresh crystal surface was followed by an electrical discharge which produced luminescence.

Of course, shock waves can sometimes induce destruction of organic compounds, resulting in the formation of high-energy radicals which emit luminescence. The phenomenon was demonstrated for perfluoroalkanes, perfluoroalkyl amines, and pertfluorotoluene.[21]

2.3. Colouration as a result of radical-ion generation upon milling

Mechanical processing (*e.g.*, abrasion) of metallic surfaces causes the emission of electrons; this is known as Kramer effect.[22] The effect has been shown by the measurement of self-generated voltages between two metallic surfaces under boundary lubrication.[23,24] Since the exoelectrons have a kinetic energy of about 1–4 eV,[25] they may initiate some chemical reactions. For instance, if the metal (whose surface has been worked) is placed in an aqueous solution of acrylonitrile, the latter forms an abundant amount of insoluble polymer, and this accumulates after four *days* of contact. The same solution of acrylonitrile contains no polymer even after four *months* of contact with a piece of *non-worked* metal. The following sequence of the reaction steps was proposed to explain the formation of polymer:[26]

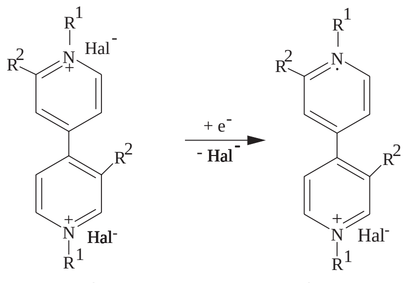
$$H_2O + e^- \rightarrow H\bullet + OH^-;\ H\bullet + O_2 \rightarrow HO_2\bullet;\ HO_2\bullet + H_2O \rightarrow H_2O_2 + HO\bullet$$

$$HO\bullet + CH_2{=}CHCN \rightarrow HOCH_2\bullet CHCN$$

$$HOCH_2\bullet CHCN + CH_2{=}CHCN \rightarrow HOCH_2CH(CN)CH_2\bullet CHCN,\ \textit{etc.}$$

When mechanical vibration of dipyridinium dications (see Scheme 2) was conducted with a stainless steel ball in a stainless steel blender at room temperature under strictly anaerobic conditions, the powdery white surface of the dication salts turned a deep blue-purple.[27] Nearly isotropic broad single-line ESR spectra were recorded in the resulting powder. No ESR spectra were observed in any of the dipyridinium salts when mechanical vibration was conducted with a Teflon ball in a Teflon blender under otherwise identical conditions. When observed, the ESR signals were quickly quenched on exposure to air and the starting dications were recovered. Each of the resulting powders was dissolved in air-free acetonitrile, and the ESR spectra of the solutions were recorded after the material had been milled under anaerobic conditions. Analysis of the hyperfine structure confirmed the formation of the corresponding radical cations according to Scheme 2.

An unpaired electron in the molecular orbital of the radical cation increases the molecule's polarisability and facilitates its excitation by light. This enhances the intensity of light



R^1 = Me, R^2 = CN, Hal = Br; R^1 = Ph, R^2 = H, Hal = Cl;

R^1 = Me, R^2 = H, Hal = Cl

Scheme 2

absorption and shifts it to the region of higher wavelength. The electrochromism is thus caused by the emission of exoelectrons from a metal abraded surface.

3. Bond-breaking mechanochromism

Mechanically induced bond breaking and skeletal isomerisation can result in formation of coloured forms of organic molecules. Several examples below illustrate the origins of the phenomenon.

Spiropyrans contain a weak bond between the nodal carbon atom and the ethereal oxygen, and this bond is easily disrupted upon photoirradiation, selective (polar) solvation, or thermal action. The isomerisation is accompanied with a change of the initial yellow colour to blue, Scheme 3.

The same colour changes are also observed upon grinding of the spiropyran,[28] and the mechanically induced colouration is reversible. Oxidation or other chemical reactions in air do not cause the colouration. The sample warms by not more than 6 K during grinding, and, as the melting point of the compound is 170 °C, this temperature increase cannot lead to global melting of the sample and isomerisation. Moreover, at liquid nitrogen temperature, the mechanochromic effect is enhanced. According to quantum mechanical calculation,[29] almost simultaneous intramolecular electron transfer and bond disruption can occur upon mechanical stress.

In this case**,** mechanochromism is conditioned by the formation of defects in the rigid matrix. The spiropyran molecules are excited in the surroundings of the defects and undergo ring opening to give the quinoid (coloured) molecule which is trapped in the crystal by lattice forces.

It would be interesting to check the possibility of generating the coloured form during grinding, not of the pure spiropyran depicted on Scheme 3, but of the spiropyran included in a cyclodextrin cavity; such inclusion has been shown to prevent the ring-opening isomerisation of the spiropyran under thermal conditions.[30]

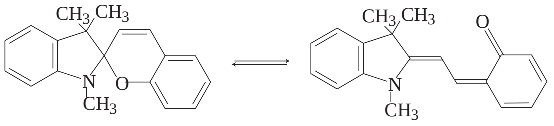
In other cases, bond breaking gives radicals that cause oscillating colouration. Scheme 4 represents mechanochemically induced formation of two radicals from 2,2'-bis[4-(dimethylamino)phenyl]-1,3-indandiones.[31]

In the radicals, an unpaired electron is distributed between the two carbonyls and aromatic rings, resulting in coloration. In the solid phase, the radicals can recombine, and the mechanochemical reaction is reversible. Onium substituents (trimethylammonium or 2,4,6-triphenylpyridinium) increase the thermodynamic stability of the radicals, shift the equilibrium to the coloured products, and intensify the mechanochromic effect.

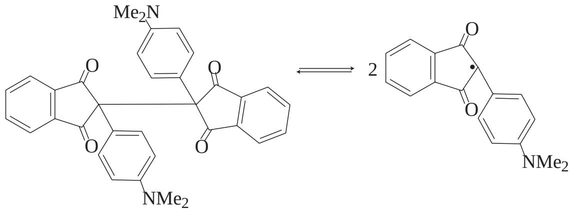
Studies of di(benzofuranone)s revealed structural effects on mechanochromism. The skeleton difference between the beta–beta' and alpha–alpha' isomers is depicted in Scheme 5.[32]

The beta–beta' isomer was reported to exhibit piezochromism when the solid was rubbed or pressed.[33] Reversible homolytic rupture of the beta–beta' bond gives blue-coloured radicals, which recombine to give the colourless dimer.[34]

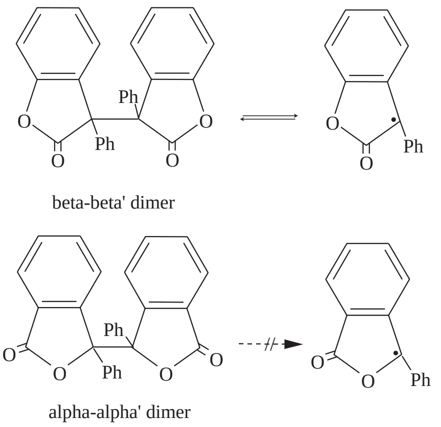
On the other hand, the alpha–alpha' isomer does not undergo homolysis under the same conditions.[32] The crystal structure of the beta–beta' isomer and conformational analysis of both isomers, show that the beta–beta' isomer experiences strong internal strain and restriction of rotation around the exocyclic bond, whereas such restriction is absent in the alpha–alpha' isomer. The former is less stable and much more sensitive to rubbing and pressing, resulting in mechanochromism.



Scheme 3



Scheme 4



Scheme 5

One interesting (but not completely explained) case of colouring resulting from bond scission was observed upon grinding polymeric oxovanadium(IV) complexes carrying Schiff-base ligands.[35-37] For instance, the orange vanadyl complex with *N*,*N*'-disalicylidene-(*R*,*R*')-1,2-diphenyl-1,2-ethanediamine turns green during grinding. The compound has a linear polymeric structure containing an infinite chain of ···V=O···V=O··· bonds, and these are cleaved to yield monomer species. The green product obtained by grinding reverts to orange when moistened with small amounts of acetonitrile or acetone, or by exposure to the acetonitrile vapour, which suggests a reformation of the thermodynamically stable polymeric structure. This colour change can be repeated. It is clear that the mechanochromic rearrangement starts at the lattice defect sites; formation of solvatocomplexes may also play an important role in crystal packing.

Grinding or milling of poly(methylmethacrylate) in steel apparatus causes mechanical destruction of the polymer, which is accompanied by luminescence.[38] The elastic energy of the broken chain transforms into electron excitation, which is centered on the carbonyl chromophore of the polymer fragments. A short-term emission induced at the instant of the mechanical fracture was detected. Kinetically, mechanolumnescence develops through two phases: the first stage is related to the propagation of the main crack at a subsonic velocity, whereas the second stage is related to the cracking of a freshly formed fracture surface upon its rapid cooling and a concomitant glass transition. Processes of mechanoluminescence emission and crack initiation/propagation are synchronous. The rupture of polymer chains causes this behaviour, exclusively. The phenomenon can be used for measuring the initiation and growth of brittle cracks in polymers.

4. Spectral changes as a result of mechanically induced reorganization of crystal packing

One novel thioindigoid, 11-(3'-oxodihydrobenzothiophen-2'-ylidene)cyclopenta-[1,2-*b*:4,3-*b*']dibenzothiophene, was found to undergo a colour change from red to black when the powders were ground in a mortar with a pestle.[39] Interestingly, the colour is recovered when the powder (after grinding) is heated at about 280 °C for 2 h or immersed in an organic solvent. Based on data from X-ray diffraction, electron spectroscopy, and molecular orbital calculations, the authors picture the following sequence of events, leading to the colour change: Mechanical stress initiates partial slipping of the thioindigoid molecules along the stacking axis in the crystal. This shortens an interplanar distance along the molecular stack. This is accompanied by the appearance of an additional (new) band around 750 nm to make the colour black. The new band has been interpreted as arising from excitonic interactions between transition dipoles based on the reorganized molecular arrangement during mechanical shearing.[39]

The recovery of the colour from black to red is explained by the disturbed lattice, corresponding to a metastable state, relaxing and returning to a stable state. Upon heating, the metastable-stable phase transition happens due to the lattice vibration. Immersion in organic solvents loosens the crystal lattice, thus allowing the molecules to slide and/or rotate to find an energetically more stable site in the initial state.

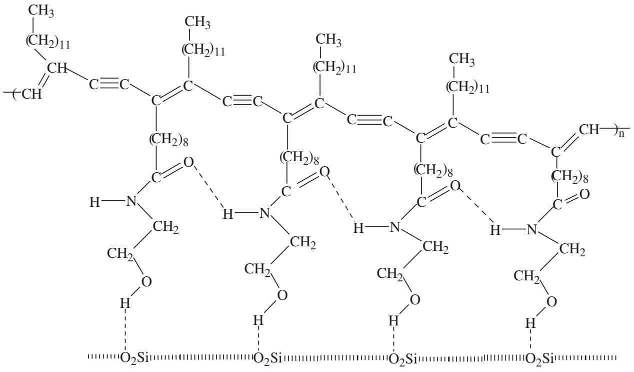
This picture describes a new route to mechanochromic transition at the expense of reorganization in crystal packing.

5. Spectral changes as a result of mechanically induced structural phase transition

Changes in optical thickness of self-assembled polymeric photonic crystals are manifestations of mechanochromism resulting from structural phase transition. Mechanochromic films, which respond to deformation by colour alteration, are examples.

Thus, co-extruded AB elastomer multilayers reflect light from the visible to infrared regions. A recent review[40] cites spectrochemical results of biaxial compression on multilayers fabricated by casting polystyrene and polyvinyl alcohol. At an applied pressure of 18 MPa, a shift of 65 nm in the peak reflectivity was found. Mao *et al.* described applications of such self-assembled block polymeric materials to optical switches.[41]

The shear-forced-nanoscale mechanochromism of polydiacetylene monolayers was studied on atomically flat silicon oxide support.[42-45] The mechanochromism was observed as irreversible transformation of the initial long-wave absorbed form into the short-wave absorbed conformation, corresponding to a change from blue to red. This blue-to-red transition is dependent on the shear forces exerted on the pendant side chains. The transformation is also facilitated by defects in the support lattice. Structurally, the side chains are being pushed towards the surface, Scheme 6.



Scheme 6

The initial (blue) form contains the polymer backbone in the planar all-*trans* geometry, where the side chains are in the same plane as the backbone. This geometry permits extended, continuous conjugation between the double and triple bonds of the backbone, that runs parallel with the support surface.

Shear action leads to rotation around the C–C bonds of the polymer backbone, thus changing the backbone planarity. The out-of-plane conformation of the side chains is achieved and the conjugation in the backbone is disrupted. This shortens the conjugation length and evokes the hypsochromic shift in the absorption spectrum of the film. The same phenomenon was observed when mica[46] and gold[47] were used as the supports for Langmuir-deposited monolayer films.

The packing of the alkyl side chain, and hydrogen bonding of the head groups, jointly restrict the torsional mobility of the polymer backbone. The irreversibility of the transition observed indicates the greater stability of the "red" phase as compared to the "blue" one. Importantly, the friction in the red (bent) transformed regions increases up to 100 % with respect to the blue regions, and appears to correlate directly with the compression or re-orientation of the side chains towards the surface.

This mechanochromism can be used for elucidation of disordering, film defects, or shear forces, operating in coated parts of technical devices.

Let us consider now mechanochromism of liquid crystalline linear polyacetylenes. One structure of this type is $H\text{-}(CH_2)_m\text{-}C{\equiv}C\text{-}C{\equiv}C\text{-}(CH_2)_8\text{-}[p\text{-}C(O)O\text{-}C_6H_4\text{-}C_6H_4OC(O)\text{-}p']\text{-}(CH_2)_8\text{-}C{\equiv}C\text{-}C{\equiv}C\text{-}(CH_2)_m\text{-}H$. Such liquid crystals can serve as strain and pressure sensors.[48]

Mechanical action changes the liquid-crystal orientation and second-harmonic optical generation takes place. This kind of mechanochromism is observed if an electric field is applied to the mechanically stressed samples. Liquid crystals are oriented in the external electric field and this ordering is disturbed when the field is eliminated. The long-axial molecules relax towards their equilibrium orientational order. The decay with time of the mechanically induced second-harmonic signal after the electric field has been switched off is a direct measure of the in-plane order rupture.[49]

In the absence of an electric field, stretching or rubbing leads to the blue-to-red change of the polyacetylene films placed on the top of the quartz slide, and optical micrographs of the polymer coated on glass fibres show different morphology of the blue and red phases. The mechanochromic changes correspond to the structural phase transition from the original crystalline (blue) phase to the liquid crystalline (red) phase. This mechanochromic transition is a partially irreversible process because of residual strain, and the chemical structure factors such as an alkyl spacer length play an important role in controlling the optical properties.

6. Conclusion

As seen from the materials reviewed, mechanochromism is a growing part of organic chemistry and the chemistry of materials. Our consideration has been made on the molecular level, and this review illustrates the conversion of mechanical energy into chemical energy. Knowledge of the molecular transformations that cause mechanochromism provides access to new molecular systems that can be interesting both for academy and technology.

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