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**Definitions contributed to the “Electrochemical dictionary” (edited by Allen J. Bard, György Inzelt, and Fritz Scholz).**

**Roger J. Mortimer**

**Electrochromism, electrochromic devices** Electrochromism is the phenomenon whereby a reversible color change takes place upon  $\rightarrow$  *reduction* or  $\rightarrow$  *oxidation*, on passage of electrical current after the application of an appropriate  $\rightarrow$  *electrode potential* [i], [ii]. Where the switching of redox states generates new or different visible region bands, the material is said to be electrochromic. Color changes in an object give visual signals that can be used to convey useful information to an observer. Furthermore, by selective absorption or transmission of light by a material, the light energy impinging upon an observer can be modulated.

Many chemical species can be switched between  $\rightarrow$  *redox states* that have distinct electronic absorption spectra [i], [ii], [iii], [iv]. Such spectra arise from either a moderate-energy internal electronic excitation or an intervalence optical charge transfer where the chemical species has two centers of differing valence or oxidation state. While materials are considered to be electrochromic when marked visible color changes are shown under illumination, recent interest in electrochromic devices for multispectral energy modulation by reflectance and absorbance has extended the definition. Chemical species are now being studied for modulation of radiation in the near infra-red (NIR), thermal infra-red, and microwave regions, and “color” can mean response of detectors to these electromagnetic regions, not just the human eye [v].

Electrochromic materials are of three basic types [i]. In a given  $\rightarrow$  *electrolyte* solution, “type I” materials are soluble in both the reduced and oxidized (redox) states, an example being 1,1'-di-methyl-4,4'-bipyridylium (“methyl viologen”), which, on reduction, switches from the colorless di-cation to the blue radical cation. “Type II” materials are soluble in one redox state, but form a solid film on the surface of an electrode following electron transfer. An example here is 1,1'-di-heptyl-4,4'-bipyridylium (“heptyl viologen”). In “type III” materials, such as  $\rightarrow$  *tungsten oxide*,  $\rightarrow$  *Prussian blue*, and electroactive conjugated polymers, both or all redox states are solids, and such systems are generally studied as thin films on electrode surfaces. For types II and III, once the  $\rightarrow$  *redox state* has been switched, no further charge injection is needed to retain the new electrochromic state and such systems are said to have “optical memory”. For type I electrochromic materials,  $\rightarrow$  *diffusion* of the soluble electrochemically-generated product material away from the electrode occurs and it is necessary to keep current flowing until the whole solution has been electrolyzed. Where more than two  $\rightarrow$  *redox states* are electrochemically accessible in a given  $\rightarrow$  *electrolyte* solution, the electrochromic material may exhibit several colors and be termed polyelectrochromic, a frequent property of thin films of electroactive conjugated polymers.

Commercial applications of electrochromic materials in devices include anti-glare car rear-view mirrors [vi], [vii], electrochromic strips as battery state-of-charge indicators and electrochromic sunglasses. Proposed applications include “smart windows” (based on modulation of either the transmitted or reflected solar radiation) for use in cars and in buildings [vi], re-usable price labels, protective eyewear, controllable aircraft canopies, glare-reduction systems for offices, devices for frozen-food monitoring, camouflage materials, spacecraft thermal control, and controllable light-reflective or light-transmissive display devices for optical information and storage.

There is a vast number of chemical species that show electrochromic properties [i], including both metal coordination complexes in solution and as polymer films [iv], metal

oxide films (especially → *tungsten oxide*) [i], [ii], viologens (4,4'-bipyridylum salts; in solution and as polymer films) [viii] and electroactive conjugated polymers [iii], such as → *polypyrrole*, → *polythiophene* and → *polyaniline*, as thin films. Other classes of electrochromic material include Y, La and Y/La alloys [vi], which switch from a reflecting-mirror metallic state to a transparent semi-conducting phase on hydride formation, and metal deposition/stripping systems [i]. See → *electrodeposition*. It is important, however, to realize that while many types of chemical species exhibit electrochromism, only those with favorable electrochromic performance parameters [i] are potentially useful in commercial applications. Thus most applications require electrochromic materials with high contrast ratio, coloration efficiency, cycle life, and write-erase efficiency. Some performance parameters are application dependent; displays need low response times, whereas “smart windows” can tolerate response times of up to several minutes.

*Refs.:* [i] Monk PMS, Mortimer RJ, Rosseinsky DR (1995) *Electrochromism: fundamentals and applications*. VCH, Weinheim; [ii] Granqvist CG (1995) *Handbook of inorganic electrochromic materials*. Elsevier, Amsterdam; [iii] Mortimer RJ, Dyer AL, Reynolds JR (2006) *Displays* 27: 2; [iv] Mortimer RJ, Rowley NM (2004) *Metal complexes as dyes for optical data storage and electrochromic materials*. In: McCleverty JA, Meyer TJ, Ward MD (eds) *Comprehensive coordination chemistry II: from biology to nanotechnology* 9.2 Elsevier, Oxford, pp 581-619; [v] Rauh RD (1999) *Electrochim Acta* 44: 3165; [vi] Mortimer RJ, Rosseinsky DR (2001) *Adv Mater* 13: 783; [vii] Green M (1996) *Chem Ind* 641; [viii] Monk PMS (1998) *The viologens: Physicochemical properties, synthesis and applications of the salts of 4,4'-bipyridine*. J Wiley & Sons, Chichester.

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***Indium tin oxide (ITO) optically transparent electrode*** An indium tin oxide (ITO) optically transparent electrode consists of a thin film of semi-conducting tin-doped indium oxide ((In<sub>2</sub>O<sub>3</sub>)<sub>x</sub>(SnO<sub>2</sub>)<sub>1-x</sub>) coated onto a glass, quartz or plastic substrate [i], [ii]. Such an “optically transparent electrode” (OTE) is a prerequisite for spectroelectrochemical transmission measurements in the UV/visible region [iii], [iv]. See → *spectroelectrochemistry*. In addition to fundamental spectroelectrochemical studies, indium tin oxide (ITO) optically transparent electrodes see applications in liquid crystal displays, electrochromic devices, organic light emitting diodes (OLED) and in the development of photovoltaic devices. ITO is a “controlled band-gap material”, an increase of the Sn(IV) content having several important effects [i]: the semiconductor band gap is shifted towards the ultraviolet, the luminous transmittance remains high, the infrared reflectance increases to a high value beyond a certain wavelength which shifts towards the visible, phonon-induced infrared absorption bands vanish, the microwave reflectance goes up, and the DC resistivity drops. A resistivity of  $\sim 1 \times 10^{-4} \Omega \text{ cm}$  is often quoted as a number characteristic of an optimized ITO film [ii].

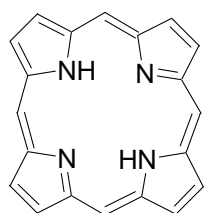
*Ref.:* [i] Hamberg I, Granqvist CG (1986) *J Appl Phys* 60: R123; [ii] Granqvist CG, Hultåker A (2002) *Thin Solid Films* 411: 1; [iii] Mortimer RJ (1999) *Electronic spectroscopy: Spectroelectrochemistry, methods and instrumentation*. In: Lindon JC, Tranter GE, Holmes JL (eds), *Encyclopedia of spectroscopy and spectrometry*. Academic Press, London, pp 2174-2181; [iv] Bard AJ, Faulkner LR (2001) *Electrochemical methods: Fundamentals and applications*. Second Edition, Wiley, New York, chapter 17.

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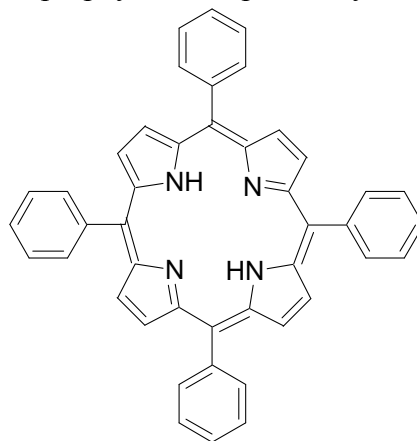
**Porphyrin** The porphyrins are a group of highly colored, naturally occurring pigments containing a porphine nucleus (figure) with substituents at the eight  $\beta$ -positions (2,3,7,8,12,13,17,18) of the pyrroles, and/or the four meso-positions (5,10,15,20) between the pyrrole rings [i]. The natural pigments are metal chelate complexes of the porphyrins. Electrochemical studies of porphyrins reveal characteristic reversible multi-step redox chemistry, with two reversible successive ligand-centered one-electron transitions on both oxidation and reduction [ii]. The electrochemical behavior and  $\rightarrow$  *redox potentials* for a given metalloporphyrin will depend on the solution and experimental factors, as well as upon the type and oxidation state of the metal ion, the type and planarity of the macrocycle and the specific set of axial ligands [iii].

Porphyrins are an important class of  $\rightarrow$  *electron-transfer* ligands. Photosynthesis is primarily driven by chromophores (light-harvesting antenna and reaction centres) which consist of special assemblies of porphyrins. See  $\rightarrow$  *electron transfer in photosynthesis*. Porphyrins are intensively studied for their possible applications, including their use as photonic materials, catalysts, photosensitizers for photodynamic therapy, receptor models in molecular recognition, and components of  $\rightarrow$  *electrochemical sensors* [v].

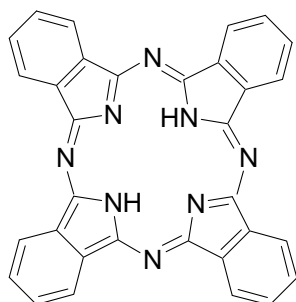
Figure: Structures of a selection of porphyrins and phthalocyanines



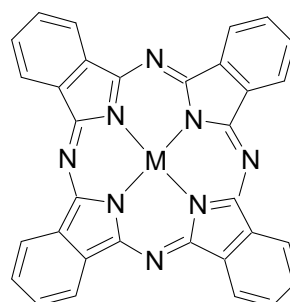
21H, 23H-porphyrin



Tetraphenyl porphyrin (TPP)



29H, 31H-phthalocyanine



A 1:1 metallo-phthalocyanine complex

Phthalocyanines (figure) are tetraazatetrabenzo derivatives of porphyrins with highly delocalised  $\pi$ -electron systems. The metal ion in metallophthalocyanines lies either at the center of a single phthalocyanine ligand (Pc = dianion of phthalocyanine) (figure), or between two rings in a sandwich-type complex. Phthalocyanine complexes of transition metals usually contain only a single Pc ring while lanthanide-containing species usually form

bis(phthalocyanines), where the  $\pi$ -systems interact strongly with each other. See  $\rightarrow$  *phthalocyanines*.

Ref.: [i] Mashiko T, Dolphin D (1987) *Porphyryns, hydroporphyrins, azaporphyrins, phthalocyanines, corroles, corrins and related macrocycles*. In: Wilkinson G, Gillard RD, McCleverty JA (eds) *Comprehensive coordination chemistry 2*, Pergamon, Oxford, chapter 21.1; [ii] Zanello P (2003) *Inorganic chemistry: Theory, practice and application*, The Royal Society of Chemistry, Cambridge, pp 363-371; [iii] Kadish KM, Royal G, van Caemelbecke E, Gueletti L (2000) 59. *Metalloporphyrins in nonaqueous media: Database of redox potentials*. In: Kadish KM, Smith KM, Guillard R (eds), *The porphyrin handbook*, Academic Press, New York, Volume 9; *Database of redox potentials and binding constants*; [iv] Leznoff CC, Lever ABP (eds) *Phthalocyanines: properties and applications 1*, Wiley & Sons, New York, Vol 1 (1989); Vol 2 (1993); Vol 3 (1993); Vol 4 (1996); [v] Kadish KM, Smith KM, Guillard R (eds), (2000) *The porphyrin handbook*, Academic Press, New York, Vol 6, *Applications: Past, present and future*.

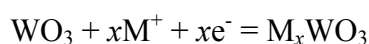
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**Tetraalkylammonium salts** Tetraalkylammonium perchlorates ( $R_4NClO_4$ ), especially tetraethylammonium perchlorate ( $Et_4NClO_4$ ) and tetra-*n*-butylammonium perchlorate ( $n-Bu_4NClO_4$ ) were traditionally used as  $\rightarrow$  *supporting electrolytes* in  $\rightarrow$  *nonaqueous solutions* [i]; however, they have the disadvantage that they may explode if they are heated or shocked [ii]. Tetraalkylammonium tetrafluoroborates ( $R_4NBf_4$ ), tetraalkylammonium hexafluorophosphates ( $R_4NPF_6$ ) and tetraalkylammonium trifluoromethanesulfonates ( $R_4NCF_3SO_3$ ) are now more widely used. Solubilities, electrical resistivities and potential windows of  $R_4NClO_4$ ,  $R_4NBf_4$ , and  $R_4NCF_3SO_3$  in several  $\rightarrow$  *aprotic solvents* are available in the literature [ii], [iii], [iv], [v]. Where not commercially available, methods for preparing and purifying tetraalkylammonium salts for use as supporting electrolytes are likewise available [i], [ii], [iii], [iv], [v]. With mercury electrodes, these ammonium salts may form Zintl-salts at very negative electrode potentials (see  $\rightarrow$  "Ammonia" amalgam).

Ref.: [i] Mann CK (1969) *Nonaqueous solvents for electrochemical use*. In: Bard AJ (ed) *Electroanalytical chemistry: A series of advances*, vol 3. Marcel Dekker, New York, pp 57-134; [ii] Izutsu K (2002), *Electrochemistry in nonaqueous solutions*, Wiley-VCH, Weinheim, ch 11; [iii] Sawyer DT, Sobkowiak A, Roberts JL, Jr (1995) *Electrochemistry for chemists*, second edition, Wiley & Sons, New York; [iv] House HO, Feng E, Peet NP (1971) *J Org Chem* 36: 2371; [v] Rousseau K, Farrington GC, Dolphin D (1972) *J Org Chem* 37: 3968.

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**Tungsten oxides** Tungsten oxide,  $WO_3$ , films have been intensely studied for possible electrochromic applications [i]. See  $\rightarrow$  *electrochromism, electrochromic devices* Tungsten oxide thin films may be prepared by numerous methods, including evaporation or sputtering of oxide, sol-gel deposition, spin-coating, dipping or spraying, chemical vapor deposition (CVD), and tungsten anodization [i], [ii], [iii], [iv]. Tungsten oxide, with all tungsten sites in oxidation state  $W^{VI}$ , is transparent as a thin film. On electrochemical reduction,  $W^V$  sites are generated to give the electrochromic effect, in the following electrochemical reaction:



Although there is still controversy about the detailed coloration mechanism, it is generally accepted that the injection and extraction of electrons and metal cations ( $M^+ = H^+, Li^+, Na^+, \text{ or } K^+$ ) play a key role. The stated  $WO_3$  stoichiometry is a simplification, thin films of practical interest being hydrous, and containing hydroxyl groups and incorporated water molecules [ii]. At low  $x$  the films have an intense blue color caused by intervalence charge transfer between adjacent  $W^V$  and  $W^{VI}$  sites. At higher  $x$ , insertion occurs irreversibly yielding a metallic “bronze” which is red or golden in color.

*Ref.: [i] Granqvist CG (1995) Handbook of inorganic electrochromic materials. Elsevier, Amsterdam; [ii] Granqvist CG (2000) Sol Energy Mater Solar Cells, 60: 201; [iii] Granqvist CG, Avendaño E, Azens A (2003) Thin Solid Films 442: 201; [iv] Avendaño E, Berggren L, Niklasson GA, Granqvist CG (2006) Thin Solid Films 496: 30.*

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