



ABOUT THE ELECTROCHEMICAL DETERMINATION OF ENERGY GAP IN PHTHALOCYANINES

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ABSTRACT Redox potentials of substituted phthalocyanines have been measured in various solvents. Experimentally, the difference $\Delta E_{\text{redox}} (= E_{\text{ox1}}^0 - E_{\text{red1}}^0)$ between the potentials of first oxidation and first reduction is constant and independent of the polarity of the solvent used. The solvation energies of neutral molecules (H_2Pc , MgPc) and ions (MgPc^+ , MgPc^-) in solvents with varied dielectric constants (CH_2Cl_2 and DMF) have been evaluated by quantum mechanical calculations. They confirm that for large aromatic molecules, the redox potentials are practically insensitive to the polarity of the medium in which they are determined. It is shown that ΔE_{redox} determined for molecules in solution gives an estimation of the energy gap of the corresponding molecular materials.

KEYWORDS Electrochemical potential, Molecular materials, Phthalocyanine, Energy gap, Solvation energy

RESUME Les potentiels redox de phthalocyanines substituées ont été mesurés dans divers solvants. Expérimentalement, la différence entre les potentiels de première oxydation et de première réduction, $\Delta E_{\text{redox}} (= E_{\text{ox1}}^0 - E_{\text{red1}}^0)$, est constante et indépendante de la polarité du solvant utilisé. Les énergies de solvation des molécules neutres (PcH_2 , PcMg) et des ions (PcMg^+ , PcMg^-) dans les solvants de constantes diélectriques variées (CH_2Cl_2 et DMF), évaluées par des calculs de mécanique quantique confirment que, pour des molécules aromatiques de suffisamment grandes tailles, les potentiels redox sont peu sensibles à la polarité du milieu dans lequel ils sont déterminés. On montre que la valeur de ΔE_{redox} , déterminée pour des molécules en solution, donne une évaluation du gap d'énergie des matériaux moléculaires correspondants.

MOTS-CLES Potentiel électrochimique, Matériaux moléculaires, Phthalocyanine, Energie de solvation

1. INTRODUCTION

During the last decades molecular materials have been the object of intensive researches due to their electrical properties.^[1-4] A number of potential applications are considered. For example, phthalocyanines have been used in field-effect transistors,^[5-9] sensors^[10-16] and various junctions and diodes.^[17-20]

Among the electrical properties of molecular materials, the energy gap (E_g) is one of the fundamental characteristics of the charge carrier generation and transport processes.^[2,3,21,22] According to the Marcus model electron transfer,^[23-25] the electrical conductivity of a material depends on the ratio $(E_g)/\lambda$, where λ is the reorganization energy of a molecule at adding/removing an electron.^[22,26] For example, monophthalocyanines of divalent metals, $\text{M}^{\text{II}}\text{Pc}$, are insulators while radical phthalocyanines LiPc and LuPc_2 and their derivatives are intrinsic semiconductors.^[27]

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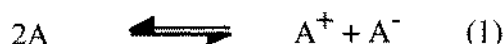


Experimentally, E_g can be determined by different methods, i) the thermal activation energy (E_{act}) of the dark conductivity,^[27] ii) the energy (E_{opt}) of the charge transfer band, obtained by optical absorption measurements,^[27] iii) the threshold energy (E_{th}) of the photoconduction,^[28,29] iv) Ultraviolet Photoelectron Spectroscopy (UPS)^[30,31] and Inverse Photoemission Photoelectron Spectroscopy (IEPS),^[32,33] v) the difference between the redox potentials $\Delta E_{redox} (= E_{ox}^0 - E_{red}^0)$,^[28,29] obtained in cyclic voltammetry experiments.

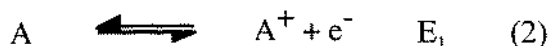
In this paper a relation of the energy gap E_g to the redox potentials is reviewed and a method for determination of E_g in solids from the redox potentials, measured in solutions, is discussed. This is illustrated for phthalocyanines and supported by quantum-chemical and molecular dynamics calculations of solvation energies of neutral and charged species.

2. REDOX POTENTIALS AND ENERGY GAP VALUES

In the case of weak intermolecular interactions, the electric conduction of a material proceeds by electron jumps between two molecular units.^[34] It can be described by a disproportionation reaction:



where A represents a neutral molecule, and A^+ and A^- its cationic and anionic forms. The process in eq.(1) corresponds to the oxidation of one molecule and the reduction of another one. It depends on the electrochemical potentials E_1 and E_2 of the pairs A^+/A and A/A^- , respectively:



E_1 and E_2 can be obtained from the Nernst law:

$$E_1 = E_{ox}^0 + \frac{RT}{F} \ln \frac{[A^+]}{[A]} \quad (4)$$

$$E_2 = E_{red}^0 + \frac{RT}{F} \ln \frac{[A]}{[A^-]} \quad (5)$$

where R is the ideal gas constant, F is the Faraday's constant, E_{red}^0 and E_{ox}^0 are the standard electrochemical potentials of oxidation and reduction of a molecule A . An assumption used here is that concentrations approximate the chemical activities. At equilibrium $E_1 = E_2 = \frac{E_{ox}^0 + E_{red}^0}{2}$ and it is analogous to the Fermi level E_f for inorganic materials.

In the solid state, the intrinsic density n of the charge carriers in molecular materials is given by:

$$n = [A^+] = [A^-] = [A] \exp\left(\frac{E_{red}^0 - E_{ox}^0}{2kT}\right) \quad (6)$$

where $[A]$ is the concentration in molecular units. In the case of inorganic semiconductors $[A]$ is equivalent to $\sqrt{N_c N_v}$ where N_c and N_v are the densities of states in the conduction band and the valence band, respectively; kT is the thermal energy.

At reduction, molecule A accepts an electron in its Lowest Unoccupied Molecular Orbital (LUMO). At oxidation an electron is removed from its Highest Occupied Molecular Orbital (HOMO). HOMO and LUMO correspond to the filled and empty states in inorganic semiconductors.



The electric conductivity can be calculated from:

$$\sigma = \sigma_0 \exp\left(\frac{E_{\text{red}}^0 - E_{\text{ox}}^0}{2kT}\right) \quad (7)$$

where $\sigma_0 = [A] e \mu$, e is the charge of an electron and μ the mobility of charge carriers.

For most of molecular materials under normal conditions, $[A]$ calculated from the volumic mass, is approximately 10^{21} cm^{-3} and μ is in the range $10^{-3} - 1 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$. In the case of intrinsic dark conductivity in the ohmic domain, $e(E_{\text{ox}}^0 - E_{\text{red}}^0)$ corresponds to the thermal activation energy E_{act} . Redox potentials E_{ox}^0 and E_{red}^0 can be determined for molecules in solution whereas conductivity in the context of this paper is related to the solid state. Charge carriers in molecular materials jump from one molecule to another and then polarize the host molecules and their neighbors. Thus the term "molecular polaron" has been introduced to describe charged species accompanied by local deformations.^[21,34] Stabilization of the neutral and charged species in embedding media depends on the dielectric constant of the latter, that is generally larger for solvents than for molecular solids.^[1]

Measurements of redox potentials in solid state are rarely reliable because of the difficulty for ions to penetrate the solid and to ensure the electroneutrality of films, except in the case of crown ether-substituted phthalocyanines.^[35] At reduction, a cation M^+ has to enter the film (or an anion has to exit from the film) as it has been demonstrated by the mirage effect.^[36-38] Thus, in general, redox potential differences ΔE_{redox} are unknown in solid state and the reliable values of E_{red}^0 and E_{ox}^0 are those determined in organic solvents. Gutmann and Lyons^[1,39] proposed a method to calculate the activation energy E_{act} in organic solids, single crystals and thin films. It uses the redox potentials and the differences between the electronic polarization energies of charge carriers, in solution and solid phase. The authors used a simplified model of a charge carrier in continuum of dielectric constant ϵ . According to the model, the electronic polarization energy is given by:

$$P = e^2 (1-1/\epsilon)/2a \quad (8)$$

where a is the radius of a spherical ion.

For evaluation of the activation energy in solid state, the following equation has been proposed.^[1,39]

$$E_{\text{act}} = \Delta E_{\text{redox}} + (S^+ + S^-) \left(1 - \frac{1-1/\epsilon_2}{1-1/\epsilon_1}\right) \quad (9)$$

where S^+ and S^- are the differences between the solvation energies of A^+ and A^- and the corresponding neutral form A ; ϵ_1 and ϵ_2 are the dielectric constants of solution and solid phase, respectively.

A slightly different equation, taking into account the ionization potential I_g and the electron affinity A_g of molecules in the gas phase has been proposed.^[40]

$$e \Delta E_{\text{redox}} = (I_g - A_g) + E_{\text{solv}}^+ + E_{\text{solv}}^- \quad (10)$$

where E_{solv}^+ and E_{solv}^- are the solvation energy terms. E_{solv}^+ (respectively E_{solv}^-) describes the free energy change ΔF^+ (resp. ΔF^-) resulting from the transfer of a radical cation MPC^+ (resp. radical anion MPC^-) from vacuum to a condensed medium.

Since S generally is in the range 1-1.5 eV, correction introduced by the solvation energy (the second term in eq.(9)) is about 0.4-0.5 eV. However, experimental results showed that the correction factor can not be applied in all cases. For example, in the case of the lutetium bisphthalocyanine LuPc_2 , the thermal activation energy E_{act} for thin films (0.5 eV)^[41] is about the same as ΔE_{redox} in solution (0.48



V).^[42,43] This particular case is not an exception, as demonstrated by experiments on phthalocyanines.^[44]

For large aromatic molecules the redox potentials are rather insensitive to the embedding media^[44] and the following interpretation of this effect has been given by one of the authors.^[29]

The chemical potentials of a molecular species i in solvents s_1 and s_2 at temperature T are given by:

$${}^{s_1}\bar{\mu}_i = {}^{s_1}\bar{\mu}_i^\circ + RT \ln [A_i] + RT \ln {}^{s_1}\gamma_i \quad (11)$$

$${}^{s_2}\bar{\mu}_i = {}^{s_2}\bar{\mu}_i^\circ + RT \ln [A_i] + RT \ln {}^{s_2}\gamma_i \quad (12)$$

On transfer from an arbitrary chosen reference solvent, s_1 , to another solvent s_2 , the difference of the chemical potentials ${}^{s_2}\bar{\mu}_i^\circ - {}^{s_1}\bar{\mu}_i^\circ$ of a molecular species i , hypothetically infinitely diluted, can be calculated:^[40]

$${}^{s_2}\bar{\mu}_i^\circ - {}^{s_1}\bar{\mu}_i^\circ = RT \ln {}^{s_1}\gamma_i^{s_2} \quad (13)$$

where ${}^{s_1}\gamma_i^{s_2} = \frac{{}^{s_1}\gamma_i}{{}^{s_2}\gamma_i}$ is a parameter characterizing the chemical potential change.

For species i and j of sufficiently large size, in the Parker's hypothesis, ${}^{s_1}\gamma_i^{s_2}$ is independent of their chemical structure and charge:

$${}^{s_1}\gamma_i^{s_2} = {}^{s_1}\gamma_j^{s_2} \quad (14)$$

Thus, according to eq.(14):

$${}^{s_1}\gamma_{A^+}^{s_2} = {}^{s_1}\gamma_{A^+}^{s_2} = {}^{s_1}\gamma_{A^-}^{s_2} \quad (15)$$

From eq. (13) it follows:

$${}^{s_2}\bar{\mu}_{A^+}^\circ - {}^{s_1}\bar{\mu}_{A^+}^\circ = {}^{s_2}\bar{\mu}_{A^+}^\circ - {}^{s_1}\bar{\mu}_{A^+}^\circ = {}^{s_2}\bar{\mu}_{A^-}^\circ - {}^{s_1}\bar{\mu}_{A^-}^\circ \quad (16)$$

It shows that the difference of chemical potentials in different solvents remains the same for A^+ , A^- and also for A .

The eq.(16) can be rewritten as:

$${}^{s_1}\bar{\mu}_{A^+}^\circ - {}^{s_1}\bar{\mu}_A^\circ = {}^{s_2}\bar{\mu}_{A^+}^\circ - {}^{s_2}\bar{\mu}_A^\circ \quad (17)$$

for A and A^+ ; and similarly for A and A^- :

$${}^{s_1}\bar{\mu}_{A^-}^\circ - {}^{s_1}\bar{\mu}_A^\circ = {}^{s_2}\bar{\mu}_{A^-}^\circ - {}^{s_2}\bar{\mu}_A^\circ \quad (18)$$

These relations have important consequences in the process of creation of charge carriers (see eq.(1)). According to the definition of the free energy variation $\overline{\Delta G}^\circ$ at equilibrium:

$$\overline{\Delta G}^\circ = \bar{\mu}_{A^+}^\circ + \bar{\mu}_{A^-}^\circ - 2 \bar{\mu}_A^\circ \quad (19)$$

for a molecule in two different solvents we obtain:

$${}^{s_2}\overline{\Delta G}^\circ - {}^{s_1}\overline{\Delta G}^\circ = {}^{s_2}(\bar{\mu}_{A^+}^\circ + \bar{\mu}_{A^-}^\circ - 2 \bar{\mu}_A^\circ) - {}^{s_1}(\bar{\mu}_{A^+}^\circ + \bar{\mu}_{A^-}^\circ - 2 \bar{\mu}_A^\circ) \quad (20)$$

From eq. (17) it follows:

$$\Delta(\overline{\Delta G}^\circ) = {}^{s_2}\overline{\Delta G}^\circ - {}^{s_1}\overline{\Delta G}^\circ = 0 \quad (21)$$



The standard free energy variation $\overline{\Delta G}^\circ$ for the process given in eq. (1) is related to the redox potential:

$$\overline{\Delta G}^\circ = -RT \ln \frac{[A^+][A^-]}{[A]^2} \quad (22)$$

$$\text{and } \overline{\Delta G}^\circ = F (E_{\text{ox}}^\circ - E_{\text{red}}^\circ) \quad (23)$$

Thus, in the framework of the Parker's hypothesis, for large molecules,^[44] the energy needed for the disproportionation reaction should not depend significantly on the properties of solvents 1 and 2. It does not mean that the individual processes of oxidation and reduction of species A are solvent independent, but only that the total effect is the same. This phenomenological rule has been confirmed by measurements in solvents with different dielectric constants of the redox potentials of two large aromatic molecules, LuPc₂^[41,43] and 2,3-NcLuPc.^[45] Of course, other parameters, such as the donor number, the acceptor number^[46,47] or the Brönstedt and Lewis acidities, could affect the redox potential values. So, dielectric constant is not the only parameter that varies, but it is the only one that we can consider in the solid state since it is well known that intermolecular interactions are weak, and no specific interaction occurs. The experimental results (Table I) show that $E_{\text{act}} = \Delta E_{\text{redox}}$. Due to their poor solubility, only few experimental data are available, in different solvents, for monophthalocyanines.^[48]

Among metallophthalocyanines (MPcs), copper and zinc phthalocyanines CuPc and ZnPc were chosen because they do not lead to coordinated species such as LMPc and L₂MPc with donor solvents which can act as ligands (L). Indeed Cu²⁺ and Zn²⁺ are metallic ions that prefer a coordination number of four rather than six.^[48] But, due to this lower affinity for coordinating solvents, CuPc and ZnPc are much less soluble than Fe(II)Pc or Co(II)Pc for example. It is the reason why we studied substituted phthalocyanines.

Table I. Differences between the first oxidation and the first reduction potentials of two lutetium complexes in different solvents, compared to the thermal activation energies of the dark conductivity of thin films.

	solvent	ϵ	ΔE_{redox} (V)	E_{act} (eV)
LuPc ₂ ^[41,43]	CH ₂ Cl ₂	9.1	0.48	0.52
	DMF	36.7	0.48	
2,3-NcLuPc ^[45]	DMF / THF 5/5	36.7 / 7.4	0.47	0.48
	CH ₂ Cl ₂ / THF 3/7	9.1 / 7.4	0.48	

3. EXPERIMENTAL

3.1. Electrochemical measurements

Octa(ethyl-2-hexyloxy)copper phthalocyanine Cu[(ethyl-2-hexyloxy)₈Pc] (**1**) was obtained as a by-product during synthesis of 4,5-di(ethyl-2-hexyloxy)phthalonitrile and purified by classical methods.^[49] Tetra tertibutyl copper phthalocyanine Cu[(t-Bu)₄Pc] (**2**) was purchased from Aldrich (Fig. 1).



Electrochemical measurements were performed in three-electrode cell at laboratory temperature (22 ± 2 °C), using a Radiometer potentiostat / galvanostat. The working electrode was a platinum disc ($\phi = 2$ mm) or graphite (C_{gr}) with diameter $\phi = 2$ mm. The counter electrode was a platinum wire. A AgCl/Ag electrode in a compartment separated by a porous glass was used as a reference. Solutions, containing tetrabutylammonium tetrafluoroborate (TBABF₄) as supporting electrolyte at concentration of 0.1 M, were outgassed with N₂ for at least 20 min before each cyclic voltammetry measurement. For some experiments, another platinum wire was used as a quasireference. In that case ferrocene (Fluka) was added at the end of experiments and the ferricinium/ferrocene couple was used as a reference. N₂ flow was maintained above solutions during the experiment. Dichloromethane (CH₂Cl₂, SDS), dimethylacetamide (DMA, SDS) and dimethylsulfoxide (DMSO, SDS) of analytical grade were used as received.

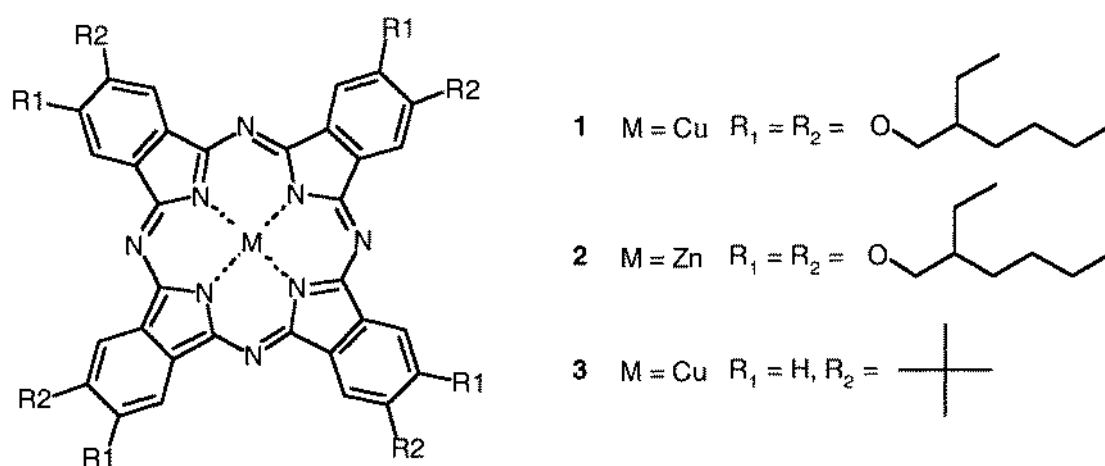
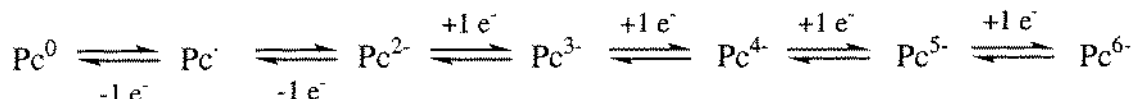


Figure 1. Schematic view of the substituted monophthalocyanines 1, 2 and 3.

4. RESULTS AND DISCUSSION

4.1. Cyclic Voltammetry

The redox activity in phthalocyanines is associated with successive removal of two electrons from the HOMO ($1a_{1u}$) at oxidation, and addition of up to four electrons to the degenerated LUMO ($1e_{1g}$) at reduction (Scheme 1).^[48] For the main group phthalocyanines the first oxidation potential E_{ox} of the macrocycle is separated from the first reduction potential E_{red} by approximately 1.5 V. It roughly corresponds to the energy difference between the HOMO and LUMO.



Scheme 1

Examples of cyclic voltammograms for **1** in CH₂Cl₂ and mixture CH₂Cl₂/DMA 30% are shown in Figure 2. Two well-defined reduction reoxidation peaks appear in the potential range -1.0 to -1.6 V vs AgCl/Ag with anodic and cathodic currents i_a^p and i_c^p of equal magnitude. By increasing the scan rate ν , i_a^p and i_c^p both increase proportionally to $\nu^{1/2}$. Separation between the anodic and cathodic peaks, ΔE^p , is independent of the scan rate and is often slightly higher than 60 mV. The first two reduction - reoxidation waves and oxidation - rereduction peaks, observed in the range 0.25 to 1.0 V

vs AgCl/Ag, are monoelectronic and reversible processes. The redox potentials can be deduced from the anodic and cathodic peak potentials E_a^p and E_c^p :

$$E_{\text{ox/red}} = \frac{E_a^p + E_c^p}{2} \quad (22)$$

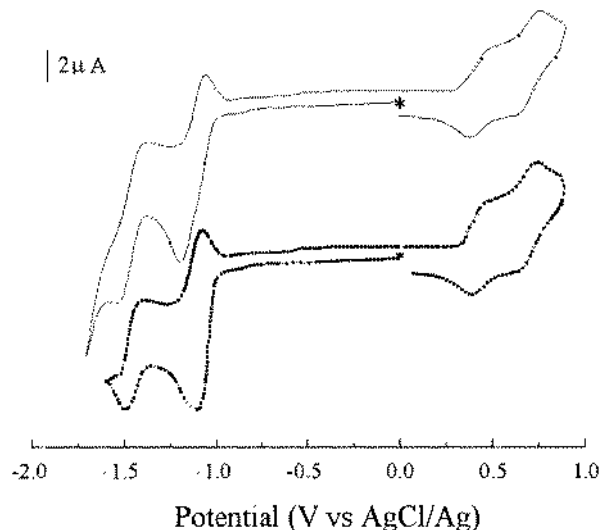


Figure 2. Examples of cyclic voltammograms for **1** in CH_2Cl_2 (above) and in a mixture $\text{CH}_2\text{Cl}_2/\text{DMA}$ (70/30) (below), on C_{gr} . * denotes the initial potential.

The following parameters were measured: $E_{\text{red1}} - E_{\text{red2}}$, $E_{\text{ox2}} - E_{\text{ox1}}$, and $E_{\text{ox1}} - E_{\text{red1}}$. The dielectric constants of the solvent used are 9.1 for CH_2Cl_2 , 37.8 for DMA and 46.7 for DMSO. CH_2Cl_2 is known as a non-donor solvent whereas DMA and DMSO are commonly used donor and potentially coordinating solvents. Here, we will discuss the effect of the dielectric constant, even though parameters such as basicity and donor-acceptor number could have been also considered.^[48]

Table II. Redox potentials (V) of **1** in different conditions, vs AgCl/Ag or Pt (*).

Solvent (working electrode)	Reduction		Oxidation		$E_{\text{ox1}} - E_{\text{red1}}$	$E_{\text{red1}} - E_{\text{red2}}$	$E_{\text{ox2}} - E_{\text{ox1}}$
	2nd	1st	1st	2nd			
CH_2Cl_2 (Pt)	-1.34	-1.01	0.54	0.80	1.55	0.33	0.26
CH_2Cl_2 (C_{gr})	-1.47	-1.14	0.42	0.69	1.56	0.33	0.27
$\text{CH}_2\text{Cl}_2/\text{DMA}$ 70/30 (C_{gr})	-1.50	-1.11	0.49	0.80	1.60	0.39	0.31
$\text{CH}_2\text{Cl}_2/\text{DMA}$ 20/80 (C_{gr})	/	-1.00	0.61	/	1.61	/	/
$\text{CH}_2\text{Cl}_2/\text{DMA}$ 75/25 (Pt)	-1.44*	-1.02*	0.46*	0.78*	1.48	0.32	0.32

Phthalocyanine **1** is reduced on Pt, in CH_2Cl_2 , at -1.01 and -1.34 V vs AgCl/Ag and oxidized at +0.54 and +0.80 V. On C_{gr} , the redox waves are shifted by 0.11-0.13 V towards negative potentials. In $\text{CH}_2\text{Cl}_2/\text{DMA}$ (20/80), on C_{gr} , only the first reduction and oxidation potentials are seen at -1.00 and +0.61 V vs AgCl/Ag, respectively. Slight differences (≤ 0.1 V) appear between measurements in pure CH_2Cl_2 and in $\text{CH}_2\text{Cl}_2/\text{DMA}$ (70/30) mixture (Table II). Compound **3** is reduced in CH_2Cl_2 ,



on Pt, at -0.96 and -1.33 V vs AgCl/Ag and oxidized at +0.42 and +0.81 V. On C_{gr} , the redox waves appears at the same potentials (Table III). For species **2**, reduction occurs at -1.04 and -1.43 vs Pt and oxidation at 0.21 and 0.83 V, in CH_2Cl_2 (Table IV).

For **1**, the ΔE_{redox} value measured on Pt, in CH_2Cl_2 , is 1.55 V. In the same conditions, for species **2** and **3**, ΔE_{redox} values are smaller, 1.25 and 1.38 V, respectively.

Table III. Redox potentials (V) of **3** in different conditions, vs AgCl/Ag or ferricinium/ferrocene (*).

Solvent (working electrode)	Reduction		Oxidation		$E_{ox1} - E_{red1}$	$E_{red1} - E_{red2}$	$E_{ox2} - E_{ox1}$
	2nd	1st	1st	2nd			
CH_2Cl_2 (Pt)	-1.33	-0.96	0.42	0.81	1.38	0.37	0.39
DMA (Pt)	-1.33	-0.85	0.42	/	1.27	0.48	/
DMSO (Pt)	-1.09*	-0.82*	0.53*	/	1.35	0.27	/
CH_2Cl_2 /DMA 75/25 (Pt)	-1.44	-1.02	0.46	0.78	1.48	0.42	0.32
CH_2Cl_2 (Cgr)	-1.36	-0.96	0.42	0.81	1.38	0.40	0.39
CH_2Cl_2 /DMA 65/35 (Cgr)	-1.31	-0.90	0.53	0.83	1.38	0.41	0.30
CH_2Cl_2 /DMA 30/70 (Cgr)	-1.34	-0.90	0.58	0.83	1.48	0.44	0.25

Table IV. Redox potentials (V) of **2** in different conditions, versus ferricinium/ferrocene, or versus Pt (*).

Solvent (working electrode)	Reduction		Oxidation		$E_{ox1} - E_{red1}$	$E_{red1} - E_{red2}$	$E_{ox2} - E_{ox1}$
	2nd	1st	1st	2nd			
CH_2Cl_2 (Pt)	-1.43*	-1.04*	0.21*	0.83*	1.25	0.39	0.62
CH_2Cl_2 /DMA 80/20 (Pt)	-1.43*	-1.04*	0.16*	0.83*	1.20	0.39	0.67
CH_2Cl_2 (Cgr)	-1.76	-1.35	0.04	0.41	1.39	0.41	0.37
CH_2Cl_2 /DMA 75/25 (Cgr)	-1.75	-1.31	0.00	0.35	1.31	0.44	0.35
CH_2Cl_2 /DMA 25/75 (Cgr)	-1.92	-1.19	0.00	0.35	1.19	0.73	0.35

ΔE_{redox} varies, for species **1**, from 1.55 V in pure CH_2Cl_2 to 1.61 V in CH_2Cl_2 /DMA (20/80) mixture. This value slightly decreases to 1.48 V for the experiment carried out in a CH_2Cl_2 /DMA mixture containing 25% of DMA (Table II). For **3**, on a C_{gr} electrode, ΔE_{redox} varies from 1.38 to 1.48 V from pure CH_2Cl_2 to a CH_2Cl_2 /DMA (30/70) mixture. On Pt, ΔE_{redox} varies from 1.27 in pure DMA to 1.38 in pure CH_2Cl_2 and 1.48 V is found in the mixture CH_2Cl_2 /DMA (75/25) (Table III). So a variation of 0.2 V is found for ΔE_{redox} depending on the nature of the solvent and on the nature of the working electrode. For species **2**, differences between the redox potentials in various solvents are in the same order of magnitude than for species **3**. For example, E_{red1} , measured on C_{gr} , varies from -1.35 V in CH_2Cl_2 to -1.19 V in CH_2Cl_2 /DMA (25/75), whereas in the same time E_{ox1} is shifted only by 0.04 V, vs Fc^+/Fc^0 (Table IV). Thus, ΔE_{redox} varies from 1.39 V in CH_2Cl_2 to 1.19 V in CH_2Cl_2 /DMA (25/75). In CH_2Cl_2 /DMA (75/25) mixture ΔE_{redox} is 1.31 V.

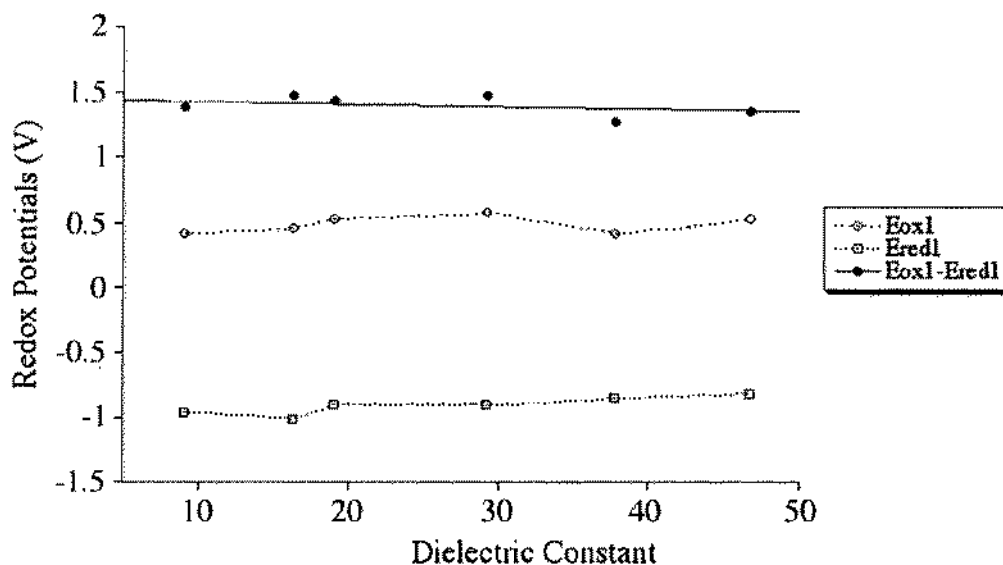


Figure 3. Variation of E_{ox1} , E_{red1} and $E_{ox1} - E_{red1}$ for **3** measured on Pt or C_{gr} as indicated in Table III, as a function of the dielectric constant of the solvents used. The solid line corresponds to a linear fit. For solvent mixtures, the arithmetic average of the dielectric constants of pure solvent are considered. All the values are given versus AgCl/Ag except for DMSO (abscissa = 46.7) vs ferricinium/ferrocene.

We observed that the chemical structure of solvent and electrodes noticeably affects the values of redox potentials. Figure 3 shows the variation of redox potentials E_{red1} and E_{ox1} for phthalocyanine **3** as a function of the dielectric constant of the solvent in which they are determined. In any cases their difference, ΔE_{redox} , does not exceed 0.2 V. For mixtures, the arithmetic average of the dielectric constant of pure solvents, was considered.

For all three molecular species and for the solvents used in this study, ΔE_{redox} does not vary by more than 0.2 V. Such a variation was observed (0.16 V), for $Zn[(neopentoxy)_4Pc]$, from *o*-dichlorobenzene ($\epsilon = 9.1$) to DMF ($\epsilon = 36.7$).^[50] For species **1**, variations observed for $E_{ox2} - E_{ox1}$ and for $E_{red1} - E_{red2}$ are less than 0.1 V. Only species **2** (Table IV) shows variations of $E_{ox2} - E_{ox1}$ and $E_{red1} - E_{red2}$ higher than 0.2 V, up to 0.35 V, that is to say higher than for $E_{ox1} - E_{red1}$. These results may be related to stronger interactions of solvents with doubly charged species than with single charged species, affecting potentials E_{ox2} and E_{red2} .

4.2. Calculation of Solvation Energies

The interaction energy E_s^{int} between metal-free phthalocyanine (H_2Pc) and its first solvation shell was estimated using the atom - atom potential and coulombic interaction approach.^[51] 18 CH_2Cl_2 molecules (or 14 DMF molecules) were stucked one by one to a H_2Pc molecule. In order to avoid local minima on the potential energy curve, positions of the solvent molecules were optimized using the simulated annealing method.^[29,51] The charge distributions and dipole moments of H_2Pc , CH_2Cl_2 and DMF (dimethylformamide) molecules were calculated using MNDO-AMI^[52-56] optimized geometries and CNDO method with the Boyd-Whitehead parametrization.^[57,58] The correction factor E_s^{solv} , accounting for reorganization of the solvent molecules in the cavity of the guest molecule upon its removal was obtained by removing the H_2Pc molecule from the cluster and allowing the solvation shell to relax. This term describes the energy needed to create the cavity for the guest molecule in the solvent (cf the Archimedes principle)^[59] (Fig. 4).

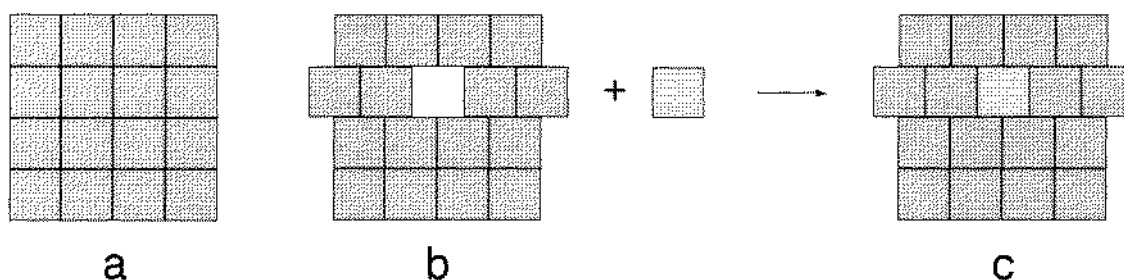


Figure 4. The two-step process of the solvation of molecular units: a) starting medium, b) creation of a proper cavity and c) incorporation of the molecular unit.

Thus, the solvation energy E_S of a H_2Pc molecule was approximated as

$$E_S = E_S^{tot} - E_S^{solvent} \quad (23)$$

For solvents of various polarities, different E_S^{tot} and $E_S^{solvent}$ are expected. For H_2Pc , used as a model of a large molecule, E_S was calculated in two solvents, CH_2Cl_2 with $\epsilon = 9.1$ and dimethylformamide (DMF) with $\epsilon = 36.7$. Table V shows that terms E_S^{tot} and $E_S^{solvent}$ depend rather strongly on polarity of the solvent. However, the solvation energy E_S is about the same, 34.0 kcal/mol in CH_2Cl_2 and 35.4 kcal/mol in DMF.

Table V. Solvation energies of the H_2Pc molecule in CH_2Cl_2 and DMF solvents.

Solvent	ϵ	μ_g (D)	n	E_S^{tot} (kcal mol ⁻¹)	$E_S^{solvent}$ (kcal mol ⁻¹)	E_S (kcal mol ⁻¹)
CH_2Cl_2	9.1	1.50	18	240.1	206.1	34.0
DMF	36.7	3.55	14	155.5	120.1	35.4

ϵ : dielectric constant; μ_g : calculated electric dipole moment; n: number of solvent molecules in the solvation shell.

Another set of calculations was carried out for $MgPc$, and its corresponding anionic and cationic forms $MgPc^-$ and $MgPc^+$. Molecular mechanics force field together with constant point-charge electrostatic interaction term were used in the framework of molecular dynamic simulation approach. Charge distribution for $MgPc$ and its ionic forms, CH_2Cl_2 and DMF molecules was calculated using semiempirical ZINDO/1 method.^[60,61] Two solvation shells of CH_2Cl_2 and DMF solutions were formed from 100 and 60 molecules, respectively. Slightly larger differences in E_S were obtained, 4.2% for the neutral species, 8.0% for the cation and 16.5 % for the anion. In the elementary oxidation and reduction processes, the effect of solvent is proportional to the difference of solvation energy between the neutral and ionized species:

$$\Delta E_{S^+}^{1,2} = (E_S^2(A^+) - E_S^2(A)) - (E_S^1(A^+) - E_S^1(A)) \quad (24)$$

$$\Delta E_{S^-}^{1,2} = (E_S^2(A^-) - E_S^2(A)) - (E_S^1(A^-) - E_S^1(A)) \quad (25)$$

For $MgPc$ and both aforementioned solvents, these differences are 0.6 eV and 0.8 eV for $MgPc^+$ and $MgPc^-$, respectively. Obviously the correction factors in eq.(24-25) are not negligible, but at least remain of the same order of magnitude. It means that the redox potentials can be affected by nature of the medium in which they are measured. The energy gap E_g , defined as $e \Delta E_{redox}$ should be



corrected by $\Delta(\Delta E^{1,2}) = \Delta E_{S^+}^{1,2} - \Delta E_{S^-}^{1,2}$ ie, about 0.2 eV. This value is comparable to variation of the redox potentials measured for monophthalocyanines in different solvents.

Since $e \Delta E_{\text{redox}}$ is approximately 1.5 eV for non-radical mono-phthalocyanines, the correction factor is not very important. Even smaller difference is expected for larger molecules. For lutetium bisphthalocyanine and lutetium naphthalophthalocyanine the same ΔE_{redox} was observed in different solvents (Table I). In both cases, $e \Delta E_{\text{redox}}$ gives a very good estimation of the thermal activation energy of the dark conductivity.

It is worth noting that in the polyacene series, by increasing the size of the molecule, the difference between the activation energy of the dark conductivity and $e \Delta E_{\text{redox}}$ decreases.^[29] For example, for pentacene this difference is about 0.25 eV whereas for anthracene it is 0.8 eV.

Thus, the redox potentials, determined in solutions, can be used to determine the energy gap value of the dark conductivity and measurements of redox potentials in the solid state can be avoided.

CONCLUSION

We showed that for sufficiently large molecules like phthalocyanines and pentacene the thermal activation energy is directly related to the difference between the potentials of the first oxidation and the first reduction of a molecular unit. Correction factor, describing the solvation energies of molecules in solution, can be neglected. ΔE_{redox} , measured for different substituted monophthalocyanines in solvents of different dielectric constants varies by less than 0.2 V. Calculations of solvation energies upon changing the solvent from CH_2Cl_2 to DMF support these electrochemical studies. Both electrochemical studies and calculations indicate that the energy of creation of the charge carriers should not be affected by more than 0.2 eV when going from low dielectric constant medium to high dielectric constant medium.

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