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**THEORETICAL INVESTIGATION OF
MODEL-POLYMERS FOR EUMELANINS.
I: FINITE AND INFINITE POLYMERS**

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ABSTRACT

We investigate the electronic structure of ideal ordered polymers of 5,6-indolequinone, in one or other redox form. These molecules are the most abundant constituents of eumelanin, the pigment appearing in human skin. Our study is carried out through Hückel π -electron theory, which allows us to follow the trends in electronic structure from a single monomer - the isolated molecules - to finite polymers of up to 10 units, and to infinite polymers. We have chosen different polymerization directions which produce semiconducting chains. The comparison between finite and infinite polymers is very useful and leads us to propose a model that accounts for some of the known properties of eumelanins.

1. Introduction

This is the first of a series of papers directed to the study of the electronic structure of polymers of 5,6-indolequinone. This study, we believe, may help understand the behavior of human melanin - eumelanin - as a cell-protecting pigment.

The word "melanin" is coined from the Greek "black" and is used for a group of pigments of biological origin, widely spread in all phyla from fungi to man⁽¹⁾. Very little is known with certainty about melanins, roughly classified⁽²⁾ in eumelanins, black or dark-brown nitrogen-containing pigments; pheomelanins, the pigments giving color to, e.g., red hair, and which contain also sulphur; and allomelanins, occurring in plants.

In this and the following papers we will be interested in eumelanins alone. In spite of a great effort on the part of experimentalists⁽¹⁻¹⁷⁾ only a very peripheral understanding of eumelanins has been reached up to the present day. On the theoretical side virtually no work appears in the literature with the notable exception of the papers by Pullman⁽¹⁸⁾. Recently we have shown⁽¹⁹⁾ that a systematic study of polymers of 5,6-indolequinone, such as we report now, might bring insight into the problem.

We present in the next section a brief survey of relevant information on eumelanins⁽¹⁻²⁰⁾; the techniques used in this work are described in section 3; and finally we present and discuss our results in section 4. This first paper is devoted to the analysis of ideal, ordered polymers. The monomeric units are derived from either 5,6-indolequinone (IQ), or the reduced forms semiquinone (SQ), and hydroquinone, 5,6-dihydroxyindole (HQ). We start from the

isolated molecules, shown schematically in figure 1, build the dimers and successively add more units. We also study infinite polymers in the Bloch limit. Disorder effects are introduced in the subsequent papers.

2. Survey of Previous Information

It is accepted that the main protection of the skin against the biochemical devastation induced by solar exposure derives from the presence⁽⁴⁾ of melanin-containing granules (melanosomes) in the epithelial tissue. Different possible mechanisms are proposed to be responsible for cell protection⁽⁴⁾: filtering and attenuation of radiation by scattering; absorption of radiation followed by energy dissipation as heat, or by redox reactions, or even electron-transfer processes. In each case protection against radiation is focused. However, the presence of melanin in non-illuminated areas such as the substantia nigra of the brain (and its possible correlation with Parkinson's disease⁽⁵⁾) leads to the postulation⁽⁶⁻⁷⁾ of other biological functions for melanins. It is concluded, in particular, that melanin should act as deactivator of free radicals⁽⁷⁾, produced or not by ionizing radiation.

It is clear that elucidation of the properties and behavior of melanins carries more than academic interest. Unfortunately, no melanin sample has yet been fully and unambiguously characterized chemically. It is not possible, up to now, to prove that two samples are identical, even for synthetic melanin samples prepared from the known precursors^(3a) tyrosine or dopa (3,4-dihydroxyphenylalanine). Indeed, the history of melanin

research is unusual⁽¹⁾: the natural precursors and some intermediate products have been found and still the chemical identity and structure of the pigment are not known.

In spite of that, there are strong evidences⁽¹⁾ that the planar 5,6-indolequinone molecule IQ and/or the reduced forms SQ and HQ compose the major part of the active material of the pigment, believed to be a copolymerization of these molecules and both residual precursors and intermediate products. In the melanosome this active material is coupled to a proteic matrix^(1b).

Different models have also been suggested for polymerization paths. As early as 1951 an oxidative reaction was proposed⁽⁸⁾ joining site 7 of IQ (see fig.1), viewed as the monomeric unit, and site 3 or site 4 of the following unit (3x7 or 4x7 bonds). Later investigations, with synthetic and natural melanins, to determine the polymer structure and relative occurrence of bonding sites⁽⁹⁾ did not seem to indicate a preferential site among positions 2,3,4 and 7; it was concluded, however, that the majority of units were linked to other two, suggesting a linear-chain skeleton. With synthetic samples the results tend to indicate that⁽¹⁾ the polymers are highly irregular, with amorphous character and random bonding. It is not certain whether these assumptions may be carried through to natural melanins, or to what extent: some authors⁽¹⁰⁾ still defend the model of a homopolymer for natural melanins.

Summarizing the results of many years of investigations, the consensus seems to be that eumelanin is some polymer mostly constituted by IQ or one of its redox forms. Recently even the chemical analysis methods have been questioned⁽¹¹⁾.

The physical studies of eumelanins are few, and seem to corroborate the hypothesis of an amorphous material. X-ray

studies⁽¹²⁾ point to the existence of planar sections (as would be expected of IQ polymers), stacked with an interplanar separation of 3.4Å; no long range order is detected in most melanins, whatever their source or method of preparation. The effect of thresholdswitching, typical of the electrical behavior of amorphous materials, is found in experiments with synthetic melanin solid pellets⁽¹³⁾. Intensive investigations of electron paramagnetic resonance (EPR) established⁽³⁾ the existence of a stable concentration of unpaired electrons (free radicals) trapped in natural or synthetic melanins; the spin-density is highly localised over a single or at most a couple of molecular units. This result seemed to reinforce the view that the polymer had to be highly disordered⁽³⁾, to prevent extensive conjugation and spin delocalization. And finally optical absorption experiments with different samples of natural and synthetic melanins in solution^(14,15) do not show any well-resolved structure in the absorption spectra; the usual spectrum is a smooth, monotonically rising curve [α vs $h\nu$] starting from an ill-defined threshold at $h\nu \approx 1.5\text{eV}$, with sometimes a shoulder at $\approx 3.5\text{eV}$ ⁽¹⁴⁾.

The above considerations strongly point to the need of theoretical support to allow choosing among the different models.

Theoretical contributions date from 1960 when a speculative model⁽²⁰⁾ was suggested, picturing eumelanin as a linear-chain semiconducting polymer. In 1960 Pullman and Pullman studied^(18a) the electronic structure of IQ and one particular dimer (shown as dimer 1 in fig.2); the authors pointed out the bonding character of the lowest unoccupied orbital of the dimer: assuming the same property could be extrapolated to the lowest conduction band of the infinite polymer (not calculated), this would indicate an

electron-acceptor tendency and explain the trapping of free-radicals. This semiconducting polymer model was later rejected⁽³⁾ based on the EPR data, which seemed to rule out the occurrence of π -electron delocalized bands. Recently, however, we presented results⁽¹⁹⁾ that conciliate the EPR data with extensive π -electron delocalization for a particular IQ polymer. Here we extend our previous studies to other forms of IQ, SQ and HQ polymers, and lay the basis for our further investigations of disorder effects.

3. Method

We used throughout the approach of Hückel π -electron theory HT⁽²¹⁾, and are thus assuming σ - π separation is complete, i.e., the polymers are always planar. It is also assumed that the optical, electrical and magnetic properties of the systems are dominated by π -electron characteristics. As we intend to study polymers with up to ten monomeric units (110 heavy atoms), the use of ab-initio or even sophisticated semi-empirical techniques is precluded; the hypothesis that a π -electron approximation is acceptable needs, nevertheless, further inspection. We may first draw from experiment the information that the polymer certainly presents planar pieces, and argue that any non-planarity effects would be lessened by stacking. Furthermore, preliminary results with the INDO/CI technique indicate⁽²²⁾ that we are indeed justified, i.e., that the orbitals mostly involved in the above-mentioned properties of the molecules show dominant π -symmetry characteristics. We will restrict our analysis, hence, to properties amenable to this approximation: we will not be able,

for instance, to discuss relative stabilities between the different polymers, or any property depending on total energy.

All calculations were carried out within the same parametrization, already used by Pullman⁽¹⁸⁾. We introduce translational symmetry to study infinite chains still within the same parametrization. Band structure and charge density results are obtained using 1500 k-points equally spaced in the first Brillouin zone, which is sufficient to obtain a very good charge and bond order description.

Here we present results for the dimers shown schematically in fig.2, and for selected polymers. These polymers are built by successively adding more units following the particular polymerization direction dictated by the dimer seed (dimers 1 to 4 in the figure), so as to have finite ordered linear polymers of IQ, SQ or HQ (we do not mix redox forms). Finally we study the corresponding infinite polymers.

These polymers are very special in the sense that only one type of bonding between units is allowed throughout. We investigated other possible polymerizations, following a wider choice of dimerizations and dimer combinations, and learned that different polymerization directions can lead to electronic properties ranging from insulators to metals. Still, a number of binding sequences lead to semiconductor structures. We concluded that the four selected polymers are fair representatives of the semiconducting structures, and also that more complex bonding sequences in linear chains may be thought of as alloying combinations of these chains.

4. Results and Discussion

We present first the results obtained through HT for the electronic structure of the molecules IQ, SQ and HQ. In Table I we repeat from Ref.19 the relevant numbers for the one-electron eigenvalue spectra. We remark⁽¹⁹⁾ that the SQ already shows bonding character for the lowest unoccupied molecular orbital (LUMO) indicating that this redox form may present good electron-acceptor properties. This feature can be traced to the presence of oxygen in both single and double bonding situations.

From Table I we may follow the broad differences in electronic structure caused by reducing IQ. The effect is more strongly felt in the value of the eigenvalue difference between the LUMO and the HOMO (highest occupied molecular orbital): for the fully reduced HQ this value is almost three times that obtained for SQ, indicating at this stage that HQ is probably not suitable for producing electron-acceptor material.

We pass now on to the analysis of the five dimers selected. The electronic structure characteristics are summarized in Table II, and the notation follows fig.2. It is interesting to note that only for S-dimers (derived from SQ units), and for all of them, the LUMO presents bonding character. Although the results may depend to a small extent on parametrization, they leave no doubt that S structures are most probably good electron acceptors, while H forms (built from HQ units) would hardly accept electrons. On the other hand, within the same redox form there are no pronounced differences between dimers as far as the π -electronic structure is concerned. It would seem probable that the same function could be performed by more than one polymer, and that stability at growing

conditions would determine the most abundant kind of chain.

As said above, we will only consider polymers built through uniform bonding, following the paths imposed by the dimers 1 to 4. It is easily seen that the dimer obtained by 2x2 bonding (dimer 5 in fig.2), often found⁽¹⁶⁾ as residue by chemical analysis, is not suitable for forming uniform chains. This type of bonding, however, could be very effective to form polymer seeds, or at inter-chain linking. We investigated polymers formed by alternating 2x2 with 3x7 or 4x7 bonds and found that the main results do not differ significantly from the polymers presented here.

We form the trimer and so on, and continue adding units until some relevant quantities stabilize (such as the HOMO-LUMO difference, charge distribution at central cell, etc.). Results are then compared to data for the infinite polymer. This study has twofold importance: in the first place it is useful to know to what extent information obtained from small molecules may be extrapolated to infinite (extremely long) chains; secondly, it allows us to determine at what length (number of units) a finite chain is, in its central portion, equivalent to the infinite chain.

The relevant quantities for finite polymers are summarized in Table III. Results for polymer S1 were already published⁽¹⁹⁾, and are shown again for comparison. Also for the sake of comparison all quantities are for chains with 10 units, at which length all electronic properties have stabilized even for the more difficult structures (most chains show stable properties already for smaller lengths).

The first feature that can be noted is that semiquinonoid structures maintain the bonding character of the LUMO (seen for the

dimers) while the chains are finite; a new feature is that this characteristic is seen also for indole-derived polymers I3 and I4. Another interesting result is obtained for the reduced polymer H1 which presents an antibonding HOMO corresponding to electron donor behavior. It is worth mentioning that these novel characteristics are only manifest after a certain length is reached: 7 units for I3 and 6 for H1. These results show that in investigating finite polymers it is necessary to follow the electronic structure trends with increasing length of chain until stabilization is attained, otherwise results cannot be reliably extrapolated to long chains. This places a constraint on the calculation technique to be used, in that more sophisticated methods than the HT employed here can hardly handle such huge systems.

The main conclusion to be drawn from Table III is that, if for the dimers the bonding sites were of less importance than the redox form, here this trend is altered. Except for the large LUMO-HOMO difference for H polymers, the polymerization direction proves to have a strong influence over electronic properties. The effect of polymerization is strongly felt by the charge distribution of the border orbitals HOMO and LUMO, which basically control the electronic behavior of the chains. We show in fig.3 the general trends of charge localization for the HOMO (lower half of the boxes representing the 10-unit linear chains) and LUMO (upper half) for all structures. As can be noted, the tendency to concentrate the charge of the LUMO over one end (or both) of the chain is strong, except for H forms. This phenomenon proves extremely important when comparing results for finite versus infinite chains.

We included also in Table III the summary of electronic structure results for the corresponding infinite polymers, in

brackets. We observe that conclusions drawn from the 10-unit chains are roughly confirmed, if we consider valence band width, character of the LUMO (translated into lowest conduction band), etc. Important exceptions, which will be discussed below, are S1, I3 and S4.

More detailed information can be gathered from the complete π band structures shown in fig.4. A general feature is that, besides the larger gaps, the H forms (figs. 4h to k) also show very flat bands corresponding to molecular-like, confined states with little interaction between units. These forms correspond more closely to insulators than to semiconductors, even in valence band character.

At this level the polymerization direction is also extremely important, as may be observed comparing the band structures obtained for polymers #1 (fig. 4d and h) and #2 (fig. e h and i). These chains differ only by one bond (through the oxygen in #1, which does not occur in #2, see fig.2) and present strikingly different bands. This difference indeed shows that the path through the lone-pair of the oxygen atom is contributing to conduction mechanisms in #1.

The polymer showing smaller dispersion of bands is #4, (fig. 4c, g, k) with the 2x4 bond, which seems to indicate that this path is not so effective in inducing π -electron delocalization. This structure would appear to be a promising model for eumelanin, since it offers in the I form a bonding conduction band (fig.4c). Furthermore, it leaves open a number of active sites for the lateral aggregation of impurity molecules, usually found⁽¹⁶⁾ as residues in chemical analyses. However, it should be noted that the bonding path through site 2 excludes the incorporation of impurity molecules as substitutional for the monomeric unit (as

frequently suggested⁽¹²⁾), since for most of the precursor/intermediate molecules either this site is blocked, as in DHIC (5,6-dihydroxyindole-2-carboxylic acid), or the pyrrole ring does not exist, as in tyrosine or dopa.

The occurrence of bonding conduction bands also for other chains, such as S2, is worth remarking, as it fulfills the prediction of Pullman and Pullman^(18a) even if not for S1, the chain suggested by the authors. Again, the presence of oxygen atoms in different bonding situations is a requisite.

The case of S1 was already discussed in our previous work⁽¹⁹⁾ and we repeat the same argument here for I3. We may see from Table III that the LUMO-HOMO eigenvalue difference for the finite polymer is only about half the gap value of the infinite polymer for both structures. If we go back to fig.3, we note that the charge distribution of the LUMO is highly concentrated over one end of the chain for S1 (more than 95% of charge over the end cell) and also for I3 (with more than 60% of charge over two cells). These localised states are not present for infinite periodic structures, where only delocalised (itinerant) states remain. In other words, the bonding character of the LUMO for the finite chains is a typical end-effect, which disappears for the infinite periodic polymers.

The end-states are equivalent to localised deep-level defect states in normal semiconductors, as may be realized from fig.5. In part a we plot the density of states (DOS) for the unit cell of the infinite chain S1 in the first column, and I3 in the second column. These DOS may be compared to the local DOS (LDOS) at a monomer or "cell" in the central portion of the corresponding finite chains, shown in part b; the similarity between parts a and

b of the figure states that, in the central portion of the finite polymer, convergence to the infinite chain is already reached. We note, in particular, the gap between occupied and unoccupied states. The introduction of a deep defect state in the gap region becomes clear if we plot the LDOS of the end cell of the finite polymers as in fig.5c: we see a bound state at $\approx 0.0\beta$, quite in the middle of the gap. The main difference between S1 and I3 is that for this later chain the end-defect is less localised (the defect state is still seen, with very small density, at the middle cells and is seen again at the opposite end).

Results for polymer S4 are very similar, as regards the "end-type defect", to polymer S1 and the same discussion holds, even if the first conduction band itself is already partially bonding: energy will be minimized if an itinerant electron is trapped at a deep-level defect. It is interesting to note, furthermore, that this polymer presents also a very localized HOMO (see fig.3) which introduces a (donor) level in the lower half of the band gap.

Other polymers, such as I2, S3 and H1, show no deep-level states. However, highly localised states are introduced around the band edges, as illustrated in the third column of fig.5 where we focus on polymer I2. An acceptor state is placed very close to the conduction band, corresponding to the LUMO of the polymer which is extremely localised over one end cell as we may check from fig.3. These states would contribute to the creation of the localised band-tails typical of amorphous materials, and would, in the same way as the deep states discussed above, be effective in trapping unpaired electrons. "Amorphization" of the material may also be accomplished through introduction of localised states close to the

valence band top, as in polymers I3 and S3.

In this way, we could picture solid melanin as a dense packing of long but finite chains⁽¹⁹⁾ of one of the types discussed. If we discard the effect of inter-chain coupling, the band structure of the compound would be that of the infinite polymer, perturbed (around chain ends) by the introduction of localised states in the gap region. The optical and electrical characteristics would thus be roughly those of the semiconducting infinite chain, modified by the presence of defect levels. An electron injected at the surface of the pigment (by a donor molecule) could be trapped at an end-type defect state. Capture of a second electron at the same defect would not be favored: due to electron repulsion, the second-electron trapping level would be higher in energy, closer to the conduction band. This electron could then easily be ionized to the band, to be captured at an empty defect state elsewhere. Unpaired electrons would be rather uniformly distributed among defects; the spin density should be proportional to the ratio between available electrons and end-type defects and thus roughly independent of temperature⁽³⁾.

In solutions, on the other hand, the chains would behave more like individual molecules. If, in spite of the increase in electron repulsion, the second-electron level is still bonding, there will occur capture of two electrons by some molecules. In the absence of the semiconducting media, these electrons could remain trapped in pairs. A slight increase in paramagnetism⁽¹⁷⁾ is now expected as the second electron is thermally emitted, leaving an unpaired spin.

5. Summary

We studied, using the Hückel π -electron approximation, a family of polymers descending from the 5,6-indolequinone molecule. We followed the evolution of the electronic properties from the monomers, to finite polymers, to infinite periodic chains. We found that structural effects (polymerization direction) begin to emerge as the polymer length increases, although some characteristics may be traced directly to the redox form of the monomeric unit. In particular, H chains (built from 5,6-dihydroxyindole units) consistently show larger gaps, and bands with smaller dispersion; and S finite chains (built from semiquinone units) show bonding LUMO's.

Although based on these results it is not possible to suggest a possibly preferred polymerization direction, the model itself of a basically linear polymeric semiconductor for eumelanins stands strongly supported.

One main conclusion is the importance of end-type defects, which may either introduce states deep in the gap region, or contribute to create band tails. This postulation allows us to conciliate some features of the melanin puzzle, such as the behavior of paramagnetism with temperature and the structureless shape of the optical absorption curve, while still retaining the model of a semiconducting polymer with extensive π -electron delocalization.

We stress the relevance of extending the study to other defects, either chemical (introducing "impurities" such as a precursor molecule in the chain) or structural (sudden change of polymerization direction, etc.). The treatment of defects is the subject of the second paper in the series.

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- 22) D.S. Galvão and M.J. Caldas, to be published. We investigated the isolated molecules, and the dimers shown in fig.2.

Figure Captions

Fig.1 - Schematic representation of the molecules 5,6-indolequinone (IQ) semiquinone (SQ) and 5,6-dihydroxyindole or hydroquinone (HQ); the active sites are indicated in IQ.

Fig.2 - Schematic representation of the dimers studied in this work. Dimers are studied in the three redox forms, I, S or H (except for dimer #1) and as such no particular form is assumed in the diagrams. Results presented in this work are according to the polymerization directions indicated in the figure for dimers #1 to 4, and for simplicity this numbering is extended to the corresponding polymers throughout this paper.

Fig.3 - Diagram of HOMO and LUMO charge localization over the individual monomeric units of the studied finite polymers with 10-unit chain length, obtained through Hückel theory. Each rectangular box represents a particular polymer, as indicated. The lower half of the boxes pictures the charge distribution of the HOMO (highest occupied molecular orbital) according to the bar-code inserted in the figure. The upper half corresponds to the LUMO (lowest unoccupied molecular orbital). As indicated, the boxes in the first column correspond to I-polymers (built from IQ units); in the second column to S-polymers (from SQ units); and in the third column to H-polymers (from HQ units). Rows keep a particular polymerization direction 1 to 4.

Fig.4 - Energy bands obtained through Hückel theory for the infinite polymers studied in this work. Energies are in terms of the parameter β , and the zero of the scale is set at $E = \alpha$. Occupied bands in solid lines, unoccupied bands in dashed lines. As indicated, figures in the first row (a to c) correspond to I-polymers (built from IQ units); in the second row (d to g) to S-polymers (from SQ units); and the third row (h to k) to H-polymers (from HQ units). Columns keep a particular polymerization direction 1 to 4.

Fig.5 - Density of states (DOS) obtained through Hückel theory for (a) the unit cell of infinite polymers; (b) local DOS for internal cell of 10-unit finite polymers; and (c) local DOS for relevant end cell of finite polymers (check fig.3). For the finite chains the discrete spectrum was Lorentzian enveloped and weighted to reproduce the DOS localized over the specific cell or monomeric unit. First column corresponds to polymer S1 (built from SQ units polymerization direction 1), second column to polymer I3 (from IQ units in direction 3) and third column to polymer I2 (from IQ units in direction 2). Dashed lines separate occupied from unoccupied states. Arrows in (a) and (b) indicate location of the defect level seen in (c).

Tables

Table I. One-electron energies (in units of the parameter β) for the π -electronic structure of the molecules 5,6-indolequinone (IQ), semiquinone (SQ), and 5,6-dihydroxyindole (HQ): the energy of the highest occupied molecular orbital-HOMO; lowest unoccupied molecular orbital-LUMO; and the eigenvalue difference LUMO-HOMO.

	IQ	SQ	HQ
HOMO	-0.327	-0.391	-0.468
LUMO	+0.188	-0.057	+0.910
LUMO-HOMO	0.515	0.334	1.378

Table II. One-electron energies (in units of the parameter β) for the π -electronic structure of dimers of 5,6-indolequinone (I), semiquinone (S) and 5,6-dihydroxyindole (H): the energy of the highest occupied molecular orbital-HOMO; lowest unoccupied molecular orbital-LUMO; and eigenvalue difference LUMO-HOMO. Dimers are labelled according to the redox form (I, S, or H), and to the bonding structure, following Fig.2.

	I2	I3	I4	I5	
HOMO	-0.143	-0.147	-0.232	-0.281	
LUMO	+0.182	+0.087	+0.084	+0.084	
LUMO-HOMO	0.325	0.234	0.316	0.365	
	S1	S2	S3	S4	S5
HOMO	-0.271	-0.241	-0.353	-0.355	-0.295
LUMO	-0.051	-0.074	-0.079	-0.118	-0.084
LUMO-HOMO	0.220	0.167	0.274	0.137	0.211
	H1	H2	H3	H4	H5
HOMO	-0.156	-0.257	-0.288	-0.292	-0.302
LUMO	+0.834	+0.793	+0.705	+0.690	+0.690
LUMO-HOMO	0.990	1.050	0.993	0.982	0.992

Table III. One-electron energies (in units of the parameter β) for the π -electronic structure of polymers of 5,6-indolequinone (I), semiquinone (S) and 5,6-dihydroxyindole (H). Results for finite polymers with 10 monomeric units are compared to band structure results (in brackets) for infinite polymers: the energy of the highest occupied molecular orbital-HOMO-with the valence band maximum-VBM; energy of the lowest unoccupied molecular orbital-LUMO-with the conduction band minimum-CBM; eigenvalue difference HOMO-LUMO with the gap; and eigenvalue difference HOMO-LUMO (lowest occupied molecular orbital) with the valence band width-VBW. Polymers are labelled according to polymerization direction in the notation of Fig.2.

	I2	I3	I4	
HOMO (VBM)	-0.054 (-0.050)	-0.010 (-0.125)	-0.145 (-0.155)	
LUMO (CBM)	+0.181 (+0.224)	-0.006 (+0.210)	-0.005 (-0.004)	
LUMO-HOMO (gap)	0.235 (0.274)	0.004 (0.335)	0.145 (0.151)	
HOMO-LUMO (VBW)	3.256 (3.260)	3.362 (3.245)	3.163 (2.850)	
	S1	S2	S3	S4
HOMO (VBM)	-0.263 (-0.280)	-0.192 (-0.190)	-0.344 (-0.355)	-0.344 (-0.405)
LUMO (CBM)	-0.052 (+0.165)	-0.081 (-0.070)	-0.083 (-0.075)	-0.140 (-0.090)
LUMO-HOMO (gap)	0.211 (0.445)	0.111 (0.120)	0.261 (0.280)	0.204 (0.315)
HOMO-LUMO (VBW)	3.013 (3.000)	2.904 (2.905)	2.821 (2.810)	2.771 (2.710)
	H1	H2	H3	H4
HOMO (VBM)	+0.046 (+0.055)	-0.139 (-0.135)	-0.072 (-0.045)	-0.181 (-0.175)
LUMO (CBM)	+0.867 (+0.870)	+0.718 (+0.715)	+0.489 (+0.460)	+0.537 (+0.525)
LUMO-HOMO (gap)	0.821 (0.815)	0.857 (0.850)	0.561 (0.505)	0.718 (0.700)
HOMO-LUMO (VBW)	3.182 (3.120)	2.666 (2.670)	2.784 (2.810)	2.615 (2.620)





