

# Communications

## Conduction Type of Substituted Tetraazaporphyrins and Perylene Tetracarboxylic Acid Diimides As Detected by Thermoelectric Power Measurements

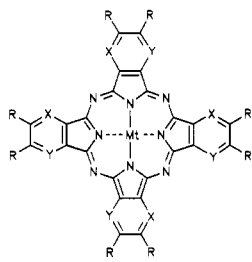
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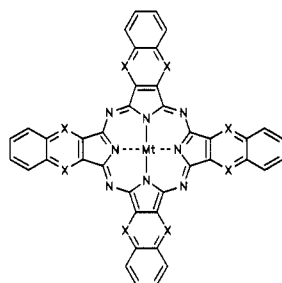
Received July 19, 1993

Revised Manuscript Received October 29, 1993

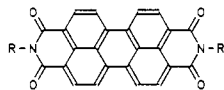
Organic pigments such as phthalocyanines (I), naphthalocyanines (II), and diimides of perylene-tetracarboxylic acid (III) are of basic as well as application-related interest



I



II



III

due to their electrical and photoelectrical properties. Presently there is great interest in photovoltaic as well as photoelectrochemical devices in which the materials behave like classical semiconductors.<sup>1-12</sup> Quite a number of derivatives of the mentioned classes of materials could

be synthesized, showing strongly differing junction properties. Derived from these experiments, different conduction types based on the nomenclature of classical semiconductors have been assigned to the materials. n-type behavior is typical for III, and p-type behavior for unsubstituted I4 and II1. By appropriate chemical substitution of I4, however, n-type photoelectrochemical behavior could be obtained.<sup>13</sup> These assignments need independent proof because not only the conduction type but also the position of frontier energy levels of each material have an influence on the overall junction properties. Furthermore, most results have been obtained at illuminated interfaces in which various relaxation phenomena of the excited state have to be considered. Independent results about different conduction types in organic pigments can serve as a valuable basis for the ongoing discussion of how n- and p-type properties of not only these materials but also molecular semiconductors in general have to be looked at and in which model they can be rationalized.<sup>6,14-20</sup> Measurements of the thermoelectric power<sup>21-23</sup> (in the dark) have been shown earlier to yield the desired insight into the conduction type of organic materials.<sup>24-28</sup>

In this study thermoelectric power measurements were performed at annealed tetraazaporphyrins IIa-I7c and II1a, II2a as well as 3,4,9,10-perylenebis(dicarboximides) III1-III3. The samples were chosen to investigate the influence of different central metals as well as the influence of different substituents in I and II which change the electron density of the inner ring  $\pi$ -system. The materials were obtained and purified as follows: 2,3,9,10,16,17,23,24-octabutoxyphthalocyaninatozinc (IIa) as described in ref 29; 2,3,9,10,16,17,23,24-octamethoxyphthalocyaninatozinc (IIa) as described in ref 30; 2,3,9,10,16,17,23,24-octamethylphthalocyaninatozinc (IIa) as described in ref 31; unsubstituted phthalocyanines (I4a-d) obtained from

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Table I. Thermoelectric Power at Substituted Phthalocyanine and Perylene Imide Pigments

no.	formula	voltage (mV) between electrodes of				results <sup>a</sup> from illuminated junctions
		Al	Fe	Au	Pt	
I1a	I (X, Y = C; R = OC <sub>4</sub> H <sub>9</sub> ; Mt = Zn)		+35			
I2a	I (X, Y = C; R = OCH <sub>3</sub> ; Mt = Zn)		+43			
I3a	I (X, Y = C; R = CH <sub>3</sub> ; Mt = Zn)		+46			
I4a	I (X, Y = C; R = H; Mt = Zn)	+1	+1	+1	+2	p-type <sup>1,2,5,7,10,34</sup>
I4b	I (X, Y = C; R = H; Mt = Cu)		+36			p-type <sup>1,2,5,7,10,34</sup>
I4c	I (X, Y = C; R = H; Mt = Co)	+3	+6	+5	+7	p-type <sup>1,2,5,7,10,34</sup>
I4d	I (X, Y = C; R = H; Mt = Fe)		+38			p-type <sup>1,2,5,7,10,34</sup>
I5a	I (X, Y = C; R = CN; Mt = Zn)	-35	-33	-58	-36	n-type <sup>13</sup>
I5b	I (X, Y = C; R = CN; Mt = Cu)	-9	-9	-7		
I5c	I (X, Y = C; R = CN; Mt = Co)	+2	+6	+4	+6	
I5d	I (X, Y = C; R = CN; Mt = Fe)	+55	+41			
I5e	I (X, Y = C; R = CN; Mt = 2H)	-41	-40	-39		
I6a	I (X = C; Y = N; R = H; Mt = Zn)		-1			n-type <sup>13</sup>
I6b	I (X = C; Y = N; R = H; Mt = 2H)		-46			
I7a	I (X, Y = N; R = H; Mt = Zn)		-45			n-type <sup>13</sup>
I7b	I (X, Y = N; R = H; Mt = Cu)		-50			
I7c	I (X, Y = N; R = H; Mt = Co)		+11			
II1a	II (X = C; Mt = Zn)		+43			p-type <sup>4*</sup>
II2a	II (X = N; Mt = Zn)		-1			n-type <sup>4*</sup>
III1	III (R = CH <sub>3</sub> )	-19	-22	-13	-13	n-type <sup>8-11</sup>
III2	III (R = C <sub>6</sub> H <sub>5</sub> )		-5			n-type <sup>8-11</sup>
III3	III (R = C <sub>6</sub> H <sub>4</sub> OCH <sub>3</sub> )		-37			n-type <sup>8-11</sup>

<sup>a</sup> Superscripts indicate references.

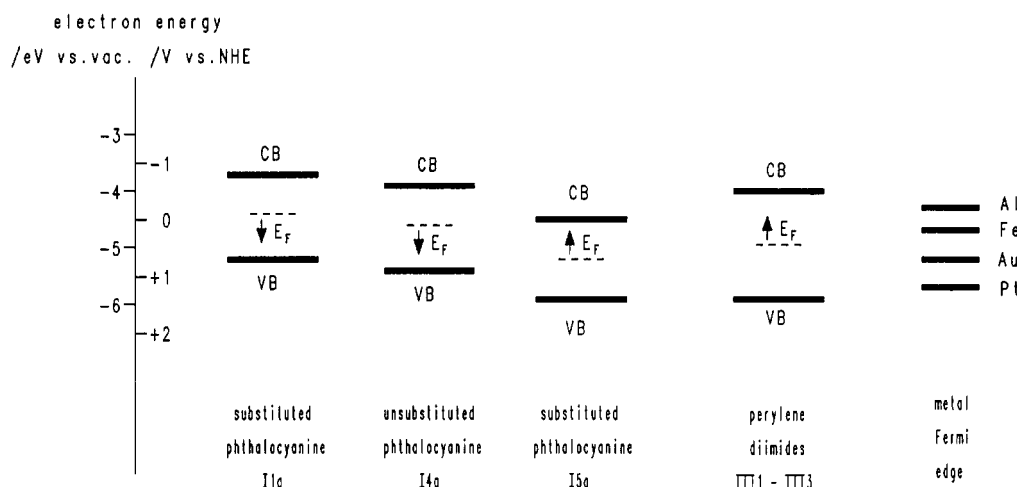


Figure 1. Energy-level diagram of representative tetraazaporphyrin Zn complexes as compared to the perylene imides and the employed metal electrodes. Arrows indicate deviations in the position of the Fermi energy from the intrinsic position. Electron energies are plotted upward.

Aldrich and purified by zone sublimation; 2,3,9,10,16-, 17,23,24-octacyanophthalocyanine complexes (I5a-e) as described in ref 32; tetra-2,3-pyridoporphyrazines (I5a,b) as described in ref 33; tetra-2,3-pyrazinoporphyrazines (I7a-c) as described in ref 34; naphthalocyaninatozinc (II1a) as described in ref 35; tetra-2,3-quinoxalinoporphyrazinatozinc (II2a) as described in ref 36; *N,N'*-dimethyl-3,4,9,10-perylenebiscarboximide (III1) obtained from Hoechst AG, Germany, and purified by zone sublimation; *N,N'*-diphenyl-3,4,9,10-perylenebiscarboximide (III2) and *N,N'*-bis(4-methoxyphenyl)-3,4,9,10-perylene-

biscarboximide (III3) as described in ref 37. Measurements were performed at pellets of compressed (6.4 kN cm<sup>-2</sup>) powders between metal blocks. Each block was in electrical and thermal contact with one side of a vacuum chamber (5 × 10<sup>-6</sup> Torr). The two parts of the chamber were pressed together by use of a Perkin-Elmer hydraulic press and were thermally and electrically insulated against each other by a flexible Teflon bellow. One part of the chamber was electrically floating and air ventilated; the other part was grounded to earth and heated by a thermostated liquid. The resulting temperatures of the metal blocks can be approximately taken as the temperatures of the two parts of the chamber which were 301 and 382 K. The thickness of the samples was measured to be 300–500 μm. This method is of general interest for comparative investigations of molecular semiconductors as it provides results under the same defined conditions for each sample. This is especially useful if not all of the

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studied materials can be vapor-deposited or coated from solution to obtain thin films.

The obtained voltages of the electrode of lower temperature (301 K) are listed in Table I. From a comparison with the results from junction studies under illumination, it is seen that the applied temperature gradient across the sample results in a polarization direction that confirms the conduction type in each case. To make sure that a property of the bulk materials and not contact phenomena such as temperature-dependent charge injection from the metal electrodes is measured, the work functions of the metal electrodes were varied in the highest accessible range from 4.3 eV at Al (Fe, 4.7 eV; Au, 5.1 eV) to 5.7 eV at Pt.<sup>38</sup> In Figure 1 the metal work functions are compared to the positions of the frontier energy levels (HOMO/VB, LUMO/CB) of the organic semiconductors. The position of those is calculated (0 V vs NHE = 4.5 eV vs vacuum)<sup>39</sup> from redox potentials of the first oxidation and the first reduction<sup>29,34,40-43</sup> (in volts vs NHE:  $E^\circ(\text{I1}^+/\text{I1}) = +0.72$ ,  $E^\circ(\text{I1}/\text{I1}^-) = -0.84$ ;  $E^\circ(\text{I4}^+/\text{I4}) = +0.93$ ,  $E^\circ(\text{I4}/\text{I4}^-) = -0.64$ ;  $E^\circ(\text{I5}^+/\text{I5}) = +1.4$ ,  $E^\circ(\text{I5}/\text{I5}^-) = +0.07$ ;  $E^\circ(\text{I7}/\text{I7}^-) = +0.28$ ;  $E^\circ(\text{III}^+/\text{III}) = +0.82$ ;  $E^\circ(\text{III}/\text{III}^-) = -0.7$ ;  $E^\circ(\text{III}^+/\text{III}) = +1.44$ ;  $E^\circ(\text{III}/\text{III}^-) = -0.49$ ). The shift of the redox potentials and therefore the positions of VB and CB is a result of the influence of substituents on the intramolecular electron density distribution. Electron-withdrawing groups in phthalocyanines cause both the occupied and unoccupied levels to shift to lower energy, whereas the symmetries of the orbitals and the frontier orbital gap remain constant.<sup>44</sup> The same general trend has been derived from He I photoelectron spectra of the materials.<sup>45</sup>

The influence of a changed metal work function was investigated at samples of octacyanophthalocyanines (I5a-I5e), unsubstituted phthalocyanines (I4a, I4c), and a perylene imide (III1). As can be seen from Table I the results obtained at Fe were reproduced using electrodes of the other metals. Not only is the polarization direction confirmed, but even the absolute values are very close. From these comparisons it is concluded that the measured voltage arises from properties of the bulk material in all cases. A junction with the metal electrode is excluded to have a significant influence on the obtained voltage as its influence should be opposite if Al is exchanged against Pt.

When the results obtained at different zinc complexes I are compared (Table I), it is seen that the influence of a substituent on the electronic density distribution within the molecule directly controls not only the position of the energy levels of the frontier orbitals, as confirmed by appropriate shifts in the redox potentials<sup>29,34,42</sup> (Figure 1), but also the conduction type of the materials. The zinc complexes I5a, I6a, and I7a with electron-withdrawing substituents yield a negatively polarized thermovoltage characterizing electrons to be the majority charge carrier in the materials (n-type). The unsubstituted complex I4a

and compounds with electron-donating substituents (I1a, I2a, I3a) show the opposite effect of a positive thermovoltage indicating defect electrons (holes) to be the majority charge carrier (p-type material). Electron-donating substituents favor the interaction of the materials with electron-accepting molecules such as oxygen or impurities due to a higher position of the energy levels. This reaction leads to defect electrons in the solid and has a strong influence on the electrical properties of unsubstituted phthalocyanines I4.<sup>1</sup> At those materials with electron-withdrawing substituents the position of the energy levels is lower, and the reaction with molecular oxygen is suppressed.<sup>13</sup> Instead the materials in these cases obviously interact with electron-donating molecules such as water or with impurities leading to excess electrons in the material (n-type).

It is known that such interactions with dopant molecules and impurities occur not only on the surface but also in the bulk of the crystals.<sup>1</sup> Therefore the materials have to be discussed as extrinsic molecular semiconductors. Charge transfer toward the dopant molecules leads to additional levels within the frontier orbital gap which are known to also act as an efficient trap for the generated charge carrier. Although many properties of the materials can be explained by use of a band model approach,<sup>1</sup> the rather low  $\pi$ - $\pi$  overlap of adjacent molecules in the crystal as derived from electronic spectra and MO calculations<sup>46,47</sup> indicates that contributions from a hopping transport have to be considered, based on trapping and thermal detrapping of the charges in localized levels energetically close to the HOMO (VB) in the case of hole conduction and close to the LUMO (CB) in the case of electron-conduction.

The effect of these interactions is indicated in Figure 1 as the corresponding shift of the Fermi level away from the intrinsic position in the middle of the bandgap toward the valence band (p-type, I1a-I4a) or toward the conduction band (n-type, I5a, I6a, I7a). In a semiquantitative approach even the absolute values reflect the trend which was observed in photoelectrochemical experiments;<sup>13</sup> the zinc complexes could be listed I1a, I2a, I3a < I4a < I6a < I5a, I7a in ascending n-type and descending p-type characteristics. More quantitative results based on a study of temperature-dependent measurements at thin films<sup>48</sup> will be reported in a subsequent article.

The same influence of a substituent as in the case of I is observed in the investigation of the zinc complexes of naphthylcyanines II1a vs II2a. The unsubstituted complex II1a clearly shows its p-type by the positive voltage. The size of the conjugated ligand system leads to no change in the conduction type as can be seen from a comparison with the corresponding phthalocyanine I4a. This fact is in reasonable agreement with the observation of a very similar potential for the first reduction<sup>41</sup> and a higher HOMO position of II1a compared to I4a.<sup>46</sup> The electron-withdrawing nitrogen atoms in the quinoxalino ligand of II2a, however, lead to a negative voltage (n-type). This is the same trend as that in the pyrido and pyrazino ligands of I6a and I7a when compared to I4a. It is explained by the same arguments and has recently been seen also in photoelectrochemical experiments.<sup>49</sup>

The influence of a change in the central metal atom can be most clearly observed in complexes of octacyanophthalocyanines I5a-I5e (Table I). Whereas the metal-free material and the Cu complex show the above-mentioned n-type characteristics of the Zn complex, the complexes of Co and Fe exhibit p-type behavior. The same trend

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can be seen in the comparison of I7a,b with I7c. Fe and Co in the molecules favor a p-type behavior of the crystals. These central metals are known to have a pronounced tendency to axially bind molecular oxygen in phthalocyanines.<sup>1</sup> Localized ionized states are formed in the solid. Transfer of electron density to dioxygen results in an enhanced hole concentration. It is concluded that Co and Fe as central atoms allow the binding of oxygen even to those molecules, whose energies of the ring frontier orbitals would not favor such an interaction. Support for this conclusion can also be drawn from the comparison of phthalocyanine redox potentials<sup>1</sup> and from molecular orbital calculations.<sup>1,46,47</sup> Fe and Co as central metal atoms lead to occupied d orbitals in I4 which are positioned within the  $\pi$ - $\pi^*$  frontier orbital gap. The relative position of those metal d orbitals in I5 and I7 would be even higher due to the lower position of the  $\pi$  systems. The absolute position when compared to I4 will be lower due to interaction with the  $\pi$  system. As that interaction is small, however, the position of Fe and Co d orbitals would still

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be high enough to facilitate electron transfer toward O<sub>2</sub>. The bound oxygen leads to the observed p-type characteristics whereas n-type behavior is seen in the metal-free systems or the complexes of other metals which do not provide these occupied orbitals leading to axial binding of O<sub>2</sub>.<sup>1</sup>

In conclusion, it should be noted that differences in the conduction type of molecular semiconductors could be established without the possible influence of relaxation phenomena from optically excited states. The electron-withdrawing or -donating capabilities of the ligand in its interaction with the inner ring  $\pi$ -system as well as the tendency of the central atom toward additional donative axial binding turned out to be critical for the observed conduction type. This opens the way toward tailored molecular semiconductors which could be of interest in xerographic and solar cell applications.<sup>10,50</sup>

**Acknowledgment.** The authors are grateful to N. R. Armstrong (University of Arizona, Tucson, AZ), N. I. Jaeger, and J. P. Meyer (University of Bremen) for fruitful discussions as well as to the University of Bremen's special Research Project "Harvesting the Energy of Visible Light" (FNK NFSP2/90) and to the Deutsche Forschungsgemeinschaft (Schl 340/1-1) for financial support.

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