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Keywords: SAXS, structures of metalloorganic complexes, nanotechnology

P08.14.136

Drastic modulation of solid-state luminescence derived from molecular arrangement of organic salts

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Polycyclic p-conjugated molecules, such as anthracene and pyrene, are employed in many systems owing to their electro- and photophysical properties. Their properties in solid state depend not only on the molecular structure but on the molecular arrangements. As for the photoluminescent properties, there are several reports on the relationships with molecular arrangements. However, the relationships have not been elucidated exactly and therefore further study is necessary for the application to the development of sophisticated organic devices. Here, we present drastic modulation of luminescent color triggered by change of the anthracene arrangement of ammonium anthracene-1,8-disulfonate. The organic salts gave seven kinds of anthracene arrangements depending on the amine of the salts. Alkyl chain of n-butylamine surround anthracene moieties, resulting in blue luminescence attributed to monomer emission. Whereas, s-butylamine afforded formation of dimer pairs and contact of the pairs, resulting in orange luminescence attributed to excimer emission. Up to 150 nm of red shift depending on anthracene arrangements was achieved.

Keywords: organic crystals, luminescence, properties and structure relationships

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Electronic structures of heme a of cytochrome c oxidase in the redox states

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The electronic structures of heme a of cytochrome c oxidase in the redox states have been investigated by using the UB3LYP method. Heme a is involved in not only electron transfer process but also in proton translocation process, which has recently been proposed by using X-ray structures at high resolution. We found that the most stable electronic configurations of the d electrons of the Fe ion were determined by the orbital interactions with the p orbitals of the porphyrin ring and the His residues. The redox reaction of the Fe ion influences the charge density on the peripheral parts of heme a, such as formyl and propionate groups, through the pi conjugation of the porphyrin ring and the orbital interaction with the sigma* orbital

of the C-C bond of the propionate group. The point charge model implies that electric field generated by surrounding protein enhances the charge transfer from Fe ion to the propionate group. The atomic charge differences of these groups are insensitive to distortion of the porphyrin ring, implying that heme a could be a "flexible electron mediator". The present results show why heme is ubiquitous in the biological systems.
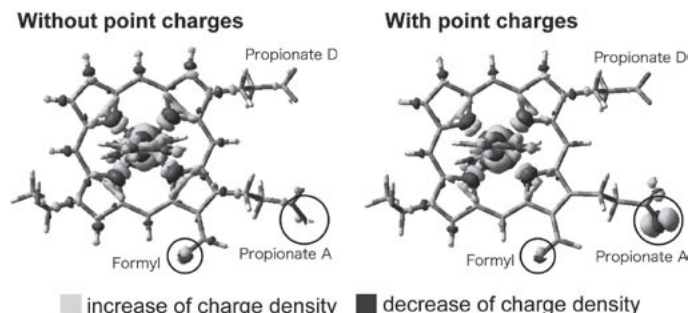
Keywords: heme proteins, density functional theory, cytochrome oxidase

P08.14.138

Functional annotation by sequence-weighted structural alignments

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A method to functionally annotate "hypothetical" proteins, based on a novel structural alignment scoring function, is introduced. In the proposed method, position specific scoring matrices are used to weight structurally aligned residue pairs, highlighting evolutionarily conserved motifs. The functional form of the score is first optimized for discriminating domains belonging to the same Pfam family from domains belonging to different families but the same CATH or SCOP superfamily. The alignment method is next applied to the task of functionally annotating 230 query proteins released to the public as part of the Protein 3000 structural genomics project in Japan. Of these queries, 49 were found to match distantly related templates (seq ID < 30%). Within this group, the template predicted by our method to be the closest functional relative was often not the most structurally similar. Nevertheless, in a number of cases, the scoring function was able to identify key residues in the query that are likely to be involved in biochemical function. Several such nontrivial cases are discussed in detail.

Keywords: structural genomics, position-specific scoring matrix, maximum substitution probability

P08.14.139

Formation of ε -martensite (ε -Fe) in stainless steels

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ε-martensite (ε-Fe) [1] is one of four forms of crystalline iron besides

bcc α-ferrite (α-Fe) [2], α'-martensite (α'-Fe) and fcc γ-austenite (γ-Fe) [2]. α-Fe and γ-Fe form under thermo-dynamically stable condition while α'-Fe and ε-Fe are kinetically stable phase. However, ε-martensite (ε-Fe) has hexagonal crystal structure with parameters of a=2.45 Å and c=3.93 Å. Formation of needle-like ε-Fe (Fig.1a) was found to have contributed to the high strength of non-magnetic Mn-containing austenitic stainless steel . Electron diffraction in Fig.1b reveals the composite pattern from zone axes of $<0001>_\varepsilon$//$<111>_\alpha$. The formation of・ ε-Fe in this case is due to Mn concentration and hence, lowers SFE.The formation of Zigzag chips was attributed to the formation of ε-Fe during high speed cutting of 304 and 316, as shown in Fig.2.

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2. P. Villars and L. D. Calvert, Pearson's Handbook of Crystallographic Data for Intermetallic Phases, Vol3, ASM, Metals Park, 1985, 2162.
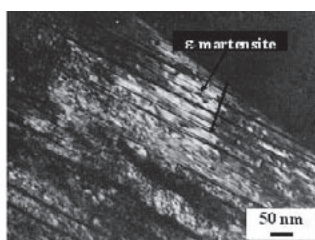3. H. Holmberg, J.-O. Nilsson and P. Liu, ISIJ Intern. 1990, 30, 594-599.

Fig.1a. Formation of needle-like ε-Fe in a non-magnetic Mn-containing austenitic stainless steel
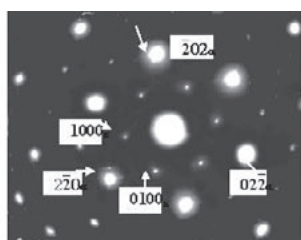
Fig.1b. Composite electron diffraction from the $<0001>_\varepsilon$//$<111>_\gamma$.
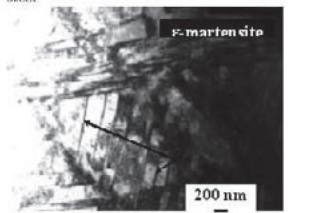
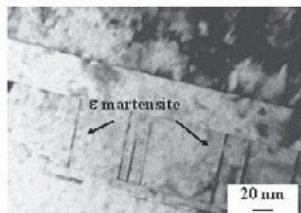Fig 2a. Formation of ε-Fe in 304 stainless steel during high steed cutting.

Fig 2b. Formation of ε-Fe in 316 stainless steel during high steed cutting.

Keywords: martensites, stainless steels, TEM

P08.14.140

Structure of homologous series $Zn_k(In,Ga)_2O_{k+3}$ of as thermoelectric materials

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Homologous compounds $Zn_kIn_2O_{k+3}$ are ones of candidates for good thermoelectric and transparent conducting materials and the performances are being improved by partial substitution of Zn or In, and so on. The homologous compounds are reported to be stable when k in $Zn_kIn_2O_{k+3}$ is 3 or over, and the electrical conductivity increases as k decreases, as a result of increased carrier concentration. The trend in electrical conductivity tells that the lower k member would show the higher electrical conductivity when the member could be prepared. According to our previous work, substitution of In by Ga stabilized the structure of homologous compounds even for k=1 and 2. In this presentation, the results of crystal structural analysis for $Zn_k(In,Ga)_2O_{k+3}$ (k=1, 3, 5) by X-ray Rietveld analysis are shown and the relationships between the structure and the physical properties are discussed. The basic structure of the compounds consists of InO_2^- and $(In,Ga)Zn_kO_{k+1}^+$ layers alternately stacked along the c-axis to have a space group of R-3m. Edge-shared InO_6 octahedra form the continuous InO_2^- layer on the c-plane. The results of structural analysis indicated that the longer In-O length in the InO_2^- layer is attributable to the higher electrical conductivity. Band structure of $Zn_3In_2O_6$ are also evaluated by first-principle calculation (CASTEP), using the structural data obtained from the Rietveld analysis. Considering the electronic structure and the formation enthalpy, $Zn_3In_2O_6(4)$ in which In^{3+} in the $InZn_3O_4^+$ layer occupies the tetrahedral site preferentially, is likely to be the favored structure.

Keywords: Rietveld analysis, relation between structure and thermoelectricity, band calculation

P08.14.141

X-ray crystallography and NMR spectroscopy in unrevealing the catalytic mechanism of a peroxiredoxin

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The protozoan parasite Trypanosoma cruzi is the causative agent of Chagas' disease. In Latin America, 16-18 million people are infected by the parasite creating a major health problem. The disease is fatal in 15-30% of those infected while others are inflicted by serious disabilities. Drugs currently used in the treatment of Chagas' disease often have toxic side effects and fail to clear parasitaemia and their mode of action is unknown. One of these drugs, nifurtimox, undergoes redox cycling with the parasite. Reactive oxygen species (ROS), such as hydroperoxides, are the unwanted by-products of aerobic metabolism. To protect cells against their potentially lethal effects a series of pathways have evolved that are collectively called the oxidative defence system. Uniquely, trypanosmatidae contain several enzyme-mediated pathways for the removal of hydroperoxides that are centred upon the unusual thiol trypanothione and are potential therapeutic targets. We have investigated one of the key terminal peroxiredoxins from this system, glutathione peroxidase I (TcGPXI). By using X-ray crystallography, NMR spectroscopy, site-directed mutagenesis and enzymatic assays we were able to unravel the catalytic mechanism of this enzyme. Crucially, we have shown that despite significant sequence homology to the glutathione-dependent peroxidases the catalysis, in contrast, involves atypical 2-Cys peroxiredoxin mechanism. The mechanism relies on a significant conformational change including unravelling of an alpha helices and formation of a disulphide bridge. We have identified the role of the specific Cys residues in the structure and investigated TcGPX in oxidized and the fully reduced form in the presence and absence of a substrate.

Keywords: catalytic mechanisms, dynamic properties, conformational change

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