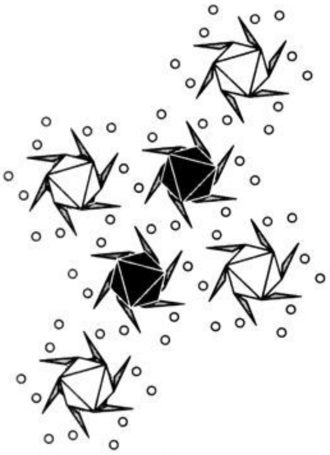
Table I. Cell Parameters for Selected Members of the Family $A_6MM'(BO_3)_6$

	a, Å	*c*, Å	*V*, Å^3
$Sr_3Sc(BO_3)_3$[a]	12.135 (1)	9.184 (1)	1171.3 (3)
$Sr_3Ho(BO_3)_3$	12.509 (1)	9.254 (1)	1254.0 (2)
$Sr_6HoSc(BO_3)_6$[a]	12.285 (3)	9.268 (2)	1211.2 (5)
$Sr_6YAl(BO_3)_6$	12.190 (2)	9.109 (5)	1172.3 (1)
$Ba_6YFe(BO_3)_6$	12.797 (1)	9.372 (2)	1329.1 (2)
$Sr_6CaZr(BO_3)_6$	12.453 (1)	9.367 (1)	1258.0 (5)
$LaSr_5YMg(BO_3)_6$	12.237 (2)	9.215 (3)	1194.9 (4)
$LaSr_2Mg(BO_3)_3$	12.318 (1)	9.254 (2)	1216.1 (2)

[a] Single-crystal data.

manner according to view **2** along the chain axis; the Sr atoms (small open circles) bridge adjacent chains by occupation of 9-coordinate sites. In each chain the octahedral sites of M and M′ are crystallographically and chemically distinct. The site M is larger and exhibits an elongation along the chain axis whereas site M′ is smaller and compressed along the same axis. This dissimilar nature of the octahedra contributes to the existence of the large number of ordered materials within the family.

1



2

The largest subgroup of the structural type forms with M and M′ as tripositive cations in conjunction with the A atom Sr. The formula with M = M′ = Sc corresponds to the material $Sr_3Sc(BO)_3$, and the formula with M = Ho and M′ = Sc corresponds to the material $Sr_6HoSc(BO_3)_6$. The ordering that occurs between the two different octahedral sites when occupied by atoms M and M′ of disparate sizes is one of the critical issues concerning the crystal chemistry of this family. A structure determination of the derivative $Sr_6HoSc(BO_3)_6$ indicates that it crystallizes in a selective manner with the Ho atom preferring the larger octahedral site and the Sc atom the smaller site.[3] The Ho–O and Sc–O distances, 2.296 (4) and 2.092 (4) Å, respectively, are consistent with values computed from crystal radii.[4] The crystal used for the structure determination was grown by melting the stoichiometric compound at 1773 K in a Pt crucible followed by cooling at 4 K/h to 1273 K and 40 K/h to 298 K. A small, light pink crystal was cleaved from the resulting transparent button and mounted for X-ray analysis.

We have found that Ba analogues crystallize in this structure type only in those instances where atoms M and M′ have dissimilar sizes; derivatives with atoms M and M′ of similar sizes form a different, unique family of layered materials.[5] For example, the compound $Ba_6TbSc(BO_3)_6$ crystallizes in the chain structure whereas the compound $Ba_6HoSc(BO_3)_6$ crystallizes in the layered structure.

The total formal charge (+6) of atoms M and M′ may be realized by the combination of charges 2 + 4 as exemplified by the compounds $Sr_6CaZr(BO_3)_6$ and $Sr_6CdSn(BO_3)_6$. Smaller dipositive cations may be incorporated in compounds of the type $LaSr_5YMg(BO_3)_6$ and $LaSr_2Mg(BO_3)_3$ where the La atom likely occupies a 9-coordinate site. In this way, a variety of derivatives containing, for example, dipositive transition-metal ions may be accessed. From consideration of current results it appears likely that all cations of formal charge +2, +3, or +4 that prefer octahedral or 9-coordinate environments can be incorporated into this structural type in significant amounts.

A full account of the crystal chemistry of these families of materials[5] as well as results on the optical and magnetic properties of selected members will be given in future articles.

Acknowledgment. This work was supported by the National Science Foundation, Solid State Chemistry Program, and by the Department of Energy (W-7405-ENG-48) under subcontracts B076260 and 2143103 administered by Lawrence Livermore National Laboratory. D.A.K. is grateful to the Alfred P. Sloan Foundation for a research fellowship, 1989–1991.

Supplementary Material Available: Listing of 115 derivatives with cell parameters and crystallographic data for the compound $Sr_6HoSc(BO_3)_6$ (8 pages); listing of observed and calculated structure factors for $Sr_6HoSc(BO_3)_6$ (5 pages). Ordering information is given on any current masthead page.

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(3) Crystal and refinement data: space group $R\bar{3}$, $a = 12.285$ (3) Å, $c = 9.268$ (2) Å, $V = 1211.2$ (5) Å^3, $Z = 6$; 693 observations with $I > 3\sigma(I)$ and 50 variables; $R = 0.027$, $R_w = 0.041$. A constrained refinement indicates a disorder of 8% between the Ho and Sc sites. Single-crystal X-ray diffraction data were collected on a Rigaku AFC6R diffractometer with graphite-monochromated Mo Kα radiation to $\sin \theta_{max}/\lambda = 1.22$ Å^{-1}.

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Quantifying Acid–Base Properties of Organic Functional Groups at a Polyethylene–Water Interface by Photoacoustic Calorimetry

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This paper describes the use of photoacoustic calorimetry (PAC)[1] to characterize acid–base equilibria involving organic chromophores covalently attached at the interphase between surface-functionalized polyethylene (PE) film[2,3] and water. We use proton transfer reactions to define the polarity and solvating capability of the interphase between organic surfaces and water.[4] Characterizing these physical–organic properties of interphases is difficult: light scattering at interfaces (especially *rough* interfaces) complicates many UV–vis absorption and fluorescence methods; infrared spectroscopy cannot be applied routinely to systems involving water; thermometric and conductometric methods are insensitive for solids having low surface areas. The measurement of the contact angle of buffered water on surfaces as a function of pH—"contact angle titration"—yields valuable information about acid–base equilibria,[3] but depends on unverified assumptions.[5]

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Table I. Experimental Values of $pK_{1/2}$ and pK_a for Organic Functional Groups in Aqueous Solution and at a Polyethylene–Water Interface[a]

	R = PE–CO[b]		R = H	
	$pK_{1/2}$	*n*	pK_a	*n*
$RNH(CH_2)_2NH$-dansyl	0.56 ± 0.11	3	3.52 ± 0.03[c]	2
$RNH(CH_2)_5NH$-dansyl	1.2 ± 0.2[c]	3	3.57 ± 0.09[c]	2
$RNHC_6H_3$-3-NO_2-6-OH	9.3 ± 0.1	3	7.00 ± 0.10[d]	2
$RNHNHCOC_6H_4$-4-OH	12.4 ± 0.2	3	8.29 ± 0.30	3

[a] Aqueous solutions of HCl and NaOH were used to vary the pH during these acid–base titrations. The addition of these trace amounts of acid or base themselves cause no change in the PAC signal other than that due to degree of protonation of the substrate. The errors listed are 1 standard deviation of the number of independent experiments indicated by *n*. [b] All films were prepared from PE-CO-Cl as described in ref 8. A fresh film was prepared for each measurement. Any acid chloride functionality that was not converted to the appropriate amide is hydrolyzed during the synthetic workup. [c] See refs 8 and 13 for previous estimates of these values. [d] The pK_a of R = $COCH_3$, as determined by PAC, is 6.02 ± 0.03 (*n* = 2).

We have used as substrates for this work surface-oxidized polyethylene films (ρ = 0.92 g/mL; 100 μm thick; pretreated to remove additives) to which were covalently attached 1-(dimethylamino)naphthalene-5-sulfonyl (dansyl) or phenolic groups (Table I).[6] These functionalized polyethylene films were suspended in water in a standard UV–vis cuvette and irradiated with a low-energy, unfocused light pulse from a nitrogen laser (337.1 nm; ca. 10 μJ/pulse; 2-mm-diameter spot).[7] The photoacoustic signal generated from each of the four films exhibited an excellent signal-to-noise ratio (Figure 1). Control experiments established that these PAC signals were due to the attached organic functionality and that each system was stable to irradiation: (i) Both unfunctionalized (PE-H) and oxidized (PE-CO_2H) polyethylene films gave weak, pH-independent PAC signals. (ii) The functionalized polyethylene films that gave strong, pH-dependent signals showed contact angle titration behavior consistent with that reported earlier.[8] (iii) The intensity of the PAC signal from a functionalized film at constant pH was linearly proportional to laser energy.[7,9] (iv) The PAC signal remained invariant over long periods of time at fixed pH, indicating that no solvolytic chemistry occurred. (v) Extended irradiation had no effect on the PAC signal, implying that no beam damage occurred. (vi) Upon removal of the films from the cuvette, no PAC signal was detected in the aqueous solution.

The changes in the PAC signal as a function of the degree of protonation are due to changes both in the heat release quantum yield, f_h, and in the extinction coefficient of the protonated/deprotonated substrates. For example, the dansyl moiety has an extinction coefficient of ~4000 M^{-1} cm^{-1} at 337.1 nm while the protonated dansyl moiety has a value of ~200 M^{-1} cm^{-1}.[10] In addition, the fluorescence quantum yields of these two species are quite different. The pH titration data generated in these PAC experiments were readily fit by a standard pK_a titration expression.[11] The similar quality of the fit for the data from the films and from solution suggests that the PAC experiment samples a single population of functional groups in the interphase.

The value of $pK_{1/2}$—the *solution* pH at which the *surface* ionization of a functional group in the interphase appeared to be half complete—differed from the value of pK_a for that group in homogeneous solution in the direction predicted if one assumes it is more difficult to create a charge in the interphase than in solution.[2,3,5] The magnitude of these shifts (2.3–4.1 pH units) is consistent with a previous characterization of a PE-dansyl–water interphase as having an effective dielectric constant $\epsilon \simeq 9$.[8] For all functionalized films examined, the fractional change in the amplitude of the PAC signal for the functionalized films on going from low- to high-pH asymptotes was consistently smaller than that for the same chromophore in solution (Figure 1). Experiments are in progress to define the cause of the changes in relative amplitudes.

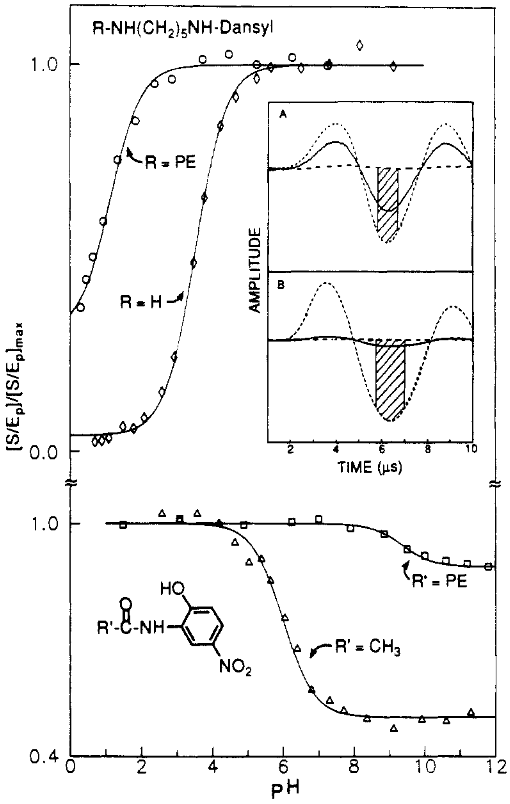

Figure 1. Acid–base titration curves for the molecules and polyethylene films indicated. The solid lines are the calculated titration curves.[11] S/E_p refers to the observed PAC signal normalized to laser energy and is based on the basic PAC equation, $S = KE_pf_h(1 - 10^{-A})$. Inset A: Photoacoustic waves at pH = 11.5 (- - -) and pH = 0.3 (—) for the dansyl film shown, and for distilled water (– –). Inset B: Photoacoustic waves at pH = 10.0 (- - -) and pH = 0.8 (—) for the dansyl derivative in homogeneous solution, and for distilled water (– –). For both insets, the hatched area indicates the "integration" performed to obtain *S*, the experimental value of the photoacoustic signal.

Our results demonstrate that PAC is a simple and sensitive method to quantify acid–base equilibria at the interface between polyethylene film and water. This photoacoustic technique has the advantages that it is insensitive to scattering of light from the interface and is easily applicable to systems in which water is the liquid phase. For PAC to be useful as a technique for characterization of interphases, the signal due to molecules at the interphase must be large compared to that arising from bulk solid or liquid phases. The chromophore used to label the interphase and to characterize the degree of ionization should therefore have a high extinction coefficient relative to that of the solid and liquid phases. The system used here—with optically transparent polyethylene and water as the two phases and strongly absorbing functional groups attached at the polyethylene–water interphase—takes advantage of one of the strengths of photoacoustic spectroscopy: the ability to detect very weak absorption against a near-zero background.[12]

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We believe that PAC has the characteristics to be a highly useful tool for studying interphases between optically transparent solid and liquid phases, provided that an appropriate reporter group with a suitable extinction coefficient can be localized in that environment.

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Supplementary Material Available: Methodology for extracting pK_a's from the data generated in the PAC studies described in the paper (2 pages). Ordering information is given on any current masthead page.

Binuclear Non-Heme Iron Oxo Transfer Analogue Reaction System: Observations and Biological Implications

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Evidence from mechanistic studies on a variety of non-heme Fe metalloproteins suggests the intimate involvement of the $[Fe^{2+}O \leftrightarrow Fe^{4+}{=}O]$ species as a source of reactive oxygen atom. This intermediate is involved in the proposed mechanisms of a wide variety of mononuclear non-heme Fe^{2+} monooxygenases such as the H_4biopterin-dependent hydroxylases,[1] the α-ketoglutarate-dependent hydroxylases,[2] isopenicillin-N synthase,[3] the bacterial iron hydroxylases,[4] and the aromatic dioxygenases.[5] More recently, a similar reactive oxygen species was postulated to play a key role in the μ-hydroxo-bridged binuclear iron center in soluble methane monooxygenase (MMO) isolated from *Methylococcus capsulatus* (Bath)[6a-h] and *Methylosinus trichosporium* OB3b.[6i-k] This enzyme is particularly interesting owing to its remarkably broad substrate specficity, catalyzing not only the conversion of methane to methanol but also the incorporation of oxygen into the C–H bonds of a variety of alkanes, alkenes, ethers, and alicyclic, aromatic, and heterocyclic compounds.

Table I. Products from the Fe^{2+} and Fe^{3+} Catalyzed Oxygen Atom Transfer Reactions of Organic Substrates (RH) by PhIO in CH_2Cl_2/1% DMF

substrate	catalyst[c]	% reacn efficiency[d]	products
cyclohexene[a]	I	35	cyclohexene epoxide (12.5%), cyclohexenol (25%), cyclohexenone (50%), cyclohexanone (12.5%)[f]
	II	NR[e]	PhI
	III	NR[e]	PhI
PhSMe[b]	I	30	PhS(O)Me (90%), $PhS(O)_2Me$ (10%)[g]
PhS(O)Me[a]	I	80	$PhS(O)_2Me$[g]

[a] Ratio of catalyst:PhIO:substrate was 1:(2×10^3):(1×10^4), [catalyst] = 0.05 mM. Reactions were followed over a 6-h time period. Reported values were obtained at 6 h. [b] Ratio of I:PhIO:PhSMe was 1:200:1000, [I] = 0.05 mM. [c] I = $[Fe^{2+}(H_2HBAB)(N\text{-MeIm})]_2$; II = $[Fe^{3+}(H_2HBAB)]_2(NO_3)_2$; III = $[Fe^{3+}(H_2HBAB)]_2O$. [d] 100% represents one substrate oxygenation per PhIO consumed in the reaction. [e] NR, less than 2% substrate reaction within 6 h. [f] Product quantization indicates a turnover number of ≈30. [g] Product quantization indicates a turnover number of 4.

Although various non-heme Fe model systems are proposed to involve iron–oxene species, the active oxygenating agents are not amenable to spectroscopic/structural characterization.[7-10] We are interested in evaluating (i) the ability of simple iron complexes to act as oxygen atom transfer catalysts and (ii) the kinetic, reactivity, and structural/electronic properties of the reactive intermediates. We disclose herein the ability of a binuclear non-heme Fe^{2+} coordination compound to catalytically decompose peracids in a heterolytic fashion and present evidence for the formation of an intermediate and its involvement in the transfer of an oxenoid equivalent to simple organic substrates.

Starting with 1,2-bis(2-hydroxybenzamido)benzene (H_4HBAB),[11] formation of the dilithium salt (LiOH, MeOH) followed by meticulous drying and reaction with an equimolar amount of *trans*-$Fe^{2+}(N\text{-MeIm})_2(Cl)_2(MeOH)_2$[12] in anhydrous MeOH under anaerobic conditions gave binuclear $[Fe^{2+}(H_2HBAB)(N\text{-MeIm})]_2$ (I) (80%) as a yellow microcrystalline product.[15a,16] The reaction of Li_2H_2HBAB with anhydrous

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