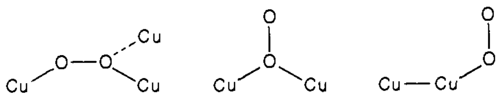
a useful technique in the structural characterization of metastable synthetic dioxygen adducts, and we plan further studies within this family of compounds.[10]



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Supplementary Material Available: A figure showing raw experimental EXAFS data and Fourier transforms for compounds I-III (2 pages). Ordering information is given on any current masthead page.

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(26) Model-building studies indicate that equatorial-axial coordination of peroxide to individual copper centers of the dinuclear pair is possible provided that one copper adopts trigonal-bipyramidal geometry while the other adopts the square-pyramidal geometry found in compound I. Examples of dinuclear complexes exhibiting just such mixed coordination polyhedra are known: (a) Sorrell, T. N.; Malachowski, M. R.; Jameson, D. L. *Inorg. Chem.* **1982**, *21*, 3250-3252. (b) Berends, H. P.; Stephan, D. W. *Inorg. Chim. Acta* **1985**, *99*, L53-L56.

Langmuir-Blodgett Ultrathin Membranes of Fumarate Polymers

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The authors wish to demonstrate the noble ultrathin LB membranes of poly(dialkyl fumarate) (PDF)[2-6] with bulky ester groups such as isopropyl (PDPF), *tert*-butyl (PDBF), and cyclohexyl (PDHF) of $\overline{M}_n = 60\text{-}(4 \times 10^4)$, which are highly soluble in common organic solvents such as chloroform, THF, benzene, etc. They are known to have a rigid rodlike structure, a high glass transition temperature ($T_g > 200$ °C dec),[2-6] and high thermal stability. In Figure 1 are illustrated the surface pressure-area (FA) isotherms of these polymers on a pure water subphase at 21 °C. The steep inclining part corresponding to the solid membrane formation and the high surface pressure of the membrane collapsing point indicate the versatility of these polymers in the fabrication of LB membranes. The limiting molecular area for the fumarate residue is ca. 32, 34, and 38 Å^2 for PDPF, PDBF, and PDHF, respectively. These Langmuir membranes could be transferred to solid substrate surfaces either by the vertical dipping (VD) or horizontal lifting (HL) method at the surface pressure of 20 ± 5 dyn/cm. The transfer ratio was essentially unity within the limit of error. The VD method was utilizable when the critical surface tension of the substrate plate was smaller than 30 dyn/cm. When the HL method was used, the LB membranes were easily prepared, regardless of the kind of substrate plate. The addition of inorganic neutral salt, acid, or base in a water subphase did not affect the transfer ratio. As a reflection of the high T_g of these polymers, the profile of FA isotherms and the ease of LB membrane preparation were unchanged even at elevated subphase temperatures, such as 50 °C.

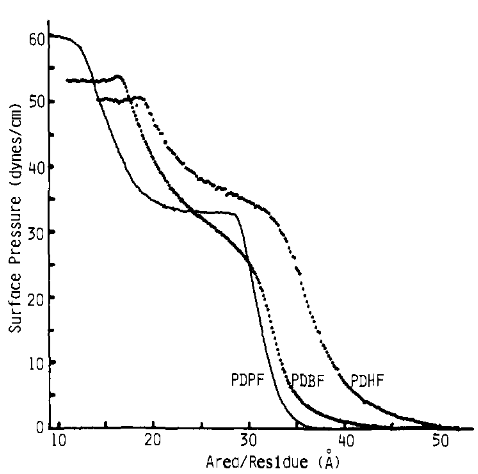

Figure 1. FA isotherms of PDF at 21 °C. Casting solvent: chloroform, $\overline{M}_n = 60 \times 10^4$ (PDPF), 4×10^4 (PDBF), and 16×10^4 (PDHF).

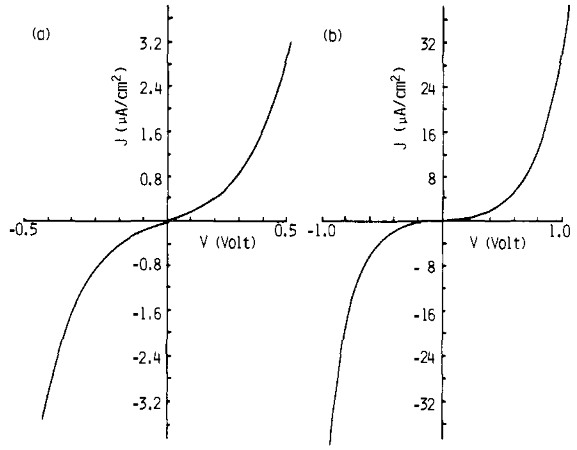

Figure 2. *J-V* Curve of [ITO/PDPF monolayer/Al] cell of (a) ±0.5 V and (b) ±1 V range measured by continuous potential scan at 5.0 mV/s. The area of Al electrode is 1.5 × 3 mm. The PDPF monolayer was prepared by the VD method at the surface pressure, initial compression speed, and substrate up-down speed of 20 dyn/cm and 1.0 and 6.0 mm/min, respectively, at 21 °C on an ITO plate of geometric area 2.5 × 4.0 cm.

It was possible to prepare more than 200 monolayers on an ITO (indium-tin oxide Nesa glass, 10 Ω/sq) substrate. In observations of multilayered LB-membranes of these polymers by a differential interference contrast optical microscopy under the polarized light, no defects larger than 0.01 μm were found. Unfortunately, because these PDF LB membranes were almost transparent to X-rays, no diffraction patterns were detected. The monolayer thicknesses calculated from the results of surface profilometry of the multilayered LB membranes were 8.5 ± 1.5, 10 ± 1.0, and 12 ± 1.5 Å for PDPF, PDBF, and PDHF, respectively, which coincided with those expected for the monolayer LB membrane composed of horizontal assemblies of rodlike PDF macromolecules. The observation by ellipsometry gave the same monolayer thicknesses described above.

Figure 2 is the current density-voltage (*J-V*) curve, characteristic of the tunneling barrier MIM (metal/insulator/metal) cell of [ITO/monolayer LB of PDPF by VD method/Al (ca. 200 Å)]. Exactly the same *J-V* curve was reproduced many times by using LB membranes obtained by VD and HL methods under the ordinary LB conditions (see captions of Figure 2), and in our experience only a few out of 100 were unsuccessful. The conductivity of PDF membranes estimated either from the tangent

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(2) Toyoda, N.; Ohtsu, T. *J. Macromol. Sci.-Chem.* **1983**, *A19*, 1011.

(3) Yamada, K.; Takayanagi, M.; Murata, Y. *Rep. Polym. Phys. Jpn.* **1984**, *27*, 321.

(4) Hiroshima, K.; Yamada, K.; Takayanagi, T.; Murata, Y. *Rep. Polym. Phys. Jpn.* **1984**, *27*, 325.

(5) Ohtsu, T.; Shiraishi, K.; Matsumoto, A.; Yasuhara, T.; Amaya, N.; Mori, S. *Polym. Commun.* **1985**, *26*, 367.

(6) Ohtsu, T.; Minai, H.; Toyoda, N.; Yashuhara, T. *Makromol. Chem. Suppl.* **1985**, *12*, 133.

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of J–V curves of Figure 2 at 0 V or from the ohmic J–V curves of thicker LB membranes was found to be less than 10^{-14} S/cm. The breakdown voltage of the MIM cell of monolayer PDPF was ca. 8 V, i.e., 10^{10} V/m. Compared with the similar MIM device of [Al/fatty acid monolayer/Hg] by Kuhn et al.,[7] our PDF systems gave much better results. Note that, in the fatty acid system, (1) the oxide insulator layer on the substrate surface played an important role[8] in preventing short circuit (the fatty acid monolayer membrane was an imperfect tunneling barrier unless the metallic substrate plates covered with insulating oxides, such as Al–Al_2O_3, Si–SiO_2, and so on, were used), and (2) liquid mercury was used as the counter electrode in order to minimize the damage to the LB membrane.[7] It was found that our polymer LB membrane could be prepared even on Nesa glass, semiconductors, derivative semiconductors, organic semiconductors, or fresh metal surfaces including Pt, Au, etc. Furthermore, due to the thermally stable properties of the PDF LB membranes, it was possible to use vacuum-deposited counter electrodes. In the example shown in Figure 2, the aluminum layer was vacuum-deposited within 5 s, during which the temperature of the LB membrane surface was elevated to ca. 100 °C. Such high stability of PDF LB membranes may have wide applications to MIM or MIS (metal/insulator/semiconductor) devices.

Registry No. PDPF, 39050-69-6; PDBF, 41700-07-6; PDHF, 101490-50-0.

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(7) Mann, G.; Kuhn, H. *J. Appl. Phys.* **1971**, *42*, 4398.
(8) Mann, G.; Kuhn, H.; Szentpaly, L. V. *Chem. Phys. Lett.* **1971**, *8*, 82.

Why Does Nature Not Use the Porphyrin Ligand in Vitamin B_{12}?

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It is now widely recognized that coenzyme B_{12}-dependent rearrangements are initiated by homolytic dissociation of the Co–C bond to generate a 5′-deoxyadenosyl radical.[1,2] It has been suggested that this dissociation is triggered by a steric perturbation involving an enzyme-induced conformational distortion of the corrin ring toward the 5′-deoxyadenosyl group, thereby weakening the cobalt–carbon bond.[1,3-6] Indeed, the X-ray analysis of coenzyme B_{12} reveals a crowded structure with several close contacts between atoms of the 5′-deoxyadenosyl group and atoms in the corrin ring and its substituents.[3] Furthermore, structural studies of different corrinoid complexes reveal highly puckered and variable conformations of the corrin ring attesting to its flexibility.[3]

Previously, we have cited parallels between the roles of hemes as reversible O_2 carriers and the role of coenzyme B_{12} as a reversible "free radical carrier".[1] Indeed, many aspects of the chemistry of organocobalt porphyrin complexes, including the range of Co–C bond dissociation energies (BDE's) reported below, closely parallel those of coenzyme B_{12} and related cobalamins. Why, then, does nature use the corrin ligand specifically in vitamin B_{12} and its coenzymes, rather than the porphyrin ligand which is used in so many other biological contexts? In this paper we report results of studies that bear on this theme.

Table I. Summary of Kinetic Data

chelate	PR_3	T, °C	10^4k_1, s^{-1}	$\Delta H_1^\ddagger$, kcal/mol	$\Delta S_1^\ddagger$, cal/(mol K)	D_{Co-R}, kcal/mol
$(DH)_2$	PMe_2Ph	66.0	0.20	32.4	15	30.4
		71.8	0.43			
		82.0	2.2			
		91.0	6.2			
		100.0	14			
	P-n-Bu_3	62.0	0.58	30.9	13	28.9
		73.6	2.8			
		87.0	20			
		92.0	22			
		100	69			
	$PEtPh_2$	49.6	0.26	28.8	10	26.8
		66.2	2.4			
		71.8	5.1			
		82.3	18			
	PPh_3	47.0	0.16	27.8	6	25.8
		57.0	0.69			
		67.0	2.5			
		75.0	5.8			
	$P(c\text{-}C_6H_{11})_3$	10.0	0.07	24.8	6	22.8
		15.0	0.12			
		23.2	0.55			
		28.4	1.0			
		35.0	3.7			
		45.6	10			
OEP	PMe_2Ph	55.0	0.096	29.1	7	27.1
		65.0	0.31			
		71.5	0.60			
		89.0	6.6			
		90.4	7.7			
	P-n-Bu_3	65.0	0.031	31.3	7	29.3
		75.0	0.088			
		85.0	0.40			
		90.4	0.80			
		100	2.4			
	$PEtPh_2$	55.0	0.20	28.1	6	26.1
		72.8	2.0			
		85.0	8.2			
		90.4	15			
	PPh_3	50.4	0.46	25.8	2	23.8
		55.4	0.92			
		60.4	1.6			
		70.4	5.2			
	$P(c\text{-}C_6H_{11})_3$	72.8	0.018	31.6	6	29.6
		82.8	0.069			
		85.0	0.088			
		91.2	0.194			

One possible rationale that occurred to us is that porphyrins might be unsuitable ligands for coenzyme B_{12} because they are insufficiently flexible, compared with corrins, to sterically modulate the Co–C BDE. Unfortunately, it is not possible to make direct comparisons of the steric and electronic influences of axial ligand variation for organocobalt porphyrin complexes with the corresponding corrin complexes because of the limited tendency of the latter to bind axial ligands. Accordingly, we have compared the influence on the Co–C BDE of varying the electronic and steric properties of the axial ligand (L) in a series of benzylcobalt octaethylporphyrin complexes [$PhCH_2$–Co(OEP)L] and in a corresponding series of benzylcobalt complexes of another flexible equatorial ligand, dimethylglyoxime (DH_2). For the latter family of complexes, [R–Co$(DH)_2$L], it has been shown that increasing the size of the axial ligand L does induce, in a manner analogous to that proposed for coenzyme B_{12}, Co–C bond lengthening and weakening due to conformational distortion of the equatorial $(DH)_2$ ligand away from L and toward the R group.[7]

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(1) Halpern, J. *Science (Washington, D.C.)* **1985**, *227*, 869 and references therein.
(2) (a) Babior, B. M. *Acc. Chem. Res.* **1975**, *8*, 376. (b) Abeles, R. H. In *Vitamin B_{12}*; Zagalak, B., Friedrich, W., Eds.; de Gruyter: Berlin, 1979; p 373. (c) Golding, B. T. In *B_{12}*; Dolphin, D., Ed.; Wiley: New York, 1982; Vol. 2, p 543.
(3) Glusker, J. In *B_{12}*; Dolphin, D., Ed.; Wiley: New York, 1982; Vol. 1, p 23 and references therein.
(4) Chemaly, S. M.; Pratt, J. J. *J. Chem. Soc., Dalton Trans.* **1980**, 2259, 2267, 2274.
(5) Marzilli, L. G.; Toscano, P. J.; Randaccio, L.; Bresciani-Pahor, N.; Calligaris, M. *J. Am. Chem. Soc.* **1979**, *101*, 6754.
(6) (a) Babior, B. M. In *B_{12}*; Dolphin, D., Ed.; Wiley: New York, 1982; Vol. 2, p 263. (b) Babior, B M. In *Vitamin B_{12}*; Zagalak, B., Friedrich, W., Eds.; de Gruyter: Berlin, 1979; p 461.
(7) (a) Randaccio, L.; Bresciani-Pahor, N.; Toscano, P. J.; Marzilli, L. G. *J. Am. Chem. Soc.* **1981**, *103*, 6347. (b) Bresciani-Pahor, N.; Calligaris, M.; Nardin, G.; Randaccio, L. *J. Chem. Soc., Dalton Trans.* **1982**, 2549. (c) Summers, M. F.; Toscano, P. J.; Bresciani-Pahor, N.; Nardin, G.; Randaccio, L.; Marzilli, L. G. *J. Am. Chem. Soc.* **1983**, *105*, 6250 and references therein.

0002-7863/87/1509-1238$01.50/0