Irradiation (<400 nm) of dimer **8** also gives **9**. This surprising transformation uses only one quantum of light and does not involve intermediates. Isosbestic points at 324 and 363 nm are clearly observed (Figure 3).

The thermal chemistry of 7-phenoxy-3,4-benzotropone (**9**) clarifies the formation of dimer **5**. Dimer **6** appears to be a primary product under certain conditions[17] but can also be formed from the triplet state of dimer **5**. Energy transfer from triplet 2-phenoxy-4,5-benzotropone to **5** has been shown to produce **6**. Oxygen quenches the formation of **6** and **8**. Dimer **7** is formed on direct irradiation of **6** and is clearly not a primary product.[6]

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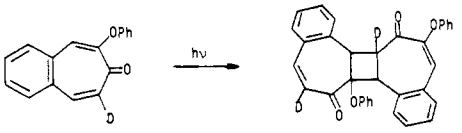
(8) Dimer **8** on heating to 210 °C gives **4** in quantitative yield. The mass spectrum of **8** shows a parent ion at *m/e* 496 and the base peak at *m/e* 248. The infrared spectrum of **8** shows an intense band at 1670 cm^{-1} (ν_{CO}), and the ultraviolet spectrum has λ_{max}^{EtOH} 208 (48 000), 234 (24 000), 266 (sh, 9600), 276 (9600), and 305 nm (15 000). The ^1H NMR spectrum ($CHCl_3$, δ) shows a broad multiplet at 6.96–7.47 (13 H aromatic plus 1 H olefinic), a multiplet at 6.84 (2 H, phenolic meta protons), a multiplet at 6.76 (1 H, phenolic para proton), a multiplet at 6.22 (2 H, phenolic ortho protons), an AX pattern at 7.31 and 6.54 (J_{AX} = 12.6 Hz), and an AMX pattern at 4.59, 4.37, and 3.97 (J_{AX} = 11.0, J_{MX} = 9.5, $J_{AM} \simeq$ 0 Hz). The low-field portion of the AX system was observed directly by difference decoupling techniques. When 7-deuterio-2-phenoxy-3,4-benzotropone (i) is irradiated, dideuterio dimer **8** (ii) is formed. The NMR spectrum of ii has, in addition



i ii

to the aromatic protons and the low-field olefinic protons, only two singlets at δ 4.59 and 4.37. The stereochemistry of dimer **8** has not been determined.
(9) The reason that the intermediate **9** was not observed in previous studies is the much greater quantum yield for the reverse process and the visible light absorption by **9**.
(10) The molar extinction coefficient of **9** at 458 nm in ethanol was calculated from the optical density and molar extinction coefficient (43 400) at 273 nm of **4** formed from irradiation with λ >420 nm of **9** which had been formed from very high photoconversion of **8** (see Figure 3).
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Investigation of the System CO_2–HCO_3^- in the Presence of Copper(II) Bovine Carbonic Anhydrase B

Sir:

The hydration of CO_2 and dehydration of HCO_3^- are catalyzed by carbonic anhydrase isoenzymes and by the cobalt-substituted derivatives at a rate which can be very high.[1-6] One of the major problems in understanding the catalytic mechanism is to identify the binding sites of both HCO_3^- and CO_2 within the active site cavity.[2,7,8] ^{13}C NMR studies on the native enzyme–substrate and cobalt derivative–substrate systems have been performed. The high activity forms (bovine and human C) are capable of causing coalescence of the two signals of the CO_2 and HCO_3^- species.[9] If added in limited amounts the enzyme causes line broadening of the two signals, whose analysis may provide useful kinetic information.[10,11] In the case of the cobalt-substituted low-activity human carbonic anhydrase B the $CO_2 \rightleftharpoons HCO_3^-$ interconversion frequency is lower than the difference in chemical shift, whereas it is higher than the experimental T_1^{-1} values.[12] Therefore two separate signals were observed for CO_2 and HCO_3^-, but the T_1^{-1} values were the same for the two signals. The T_1^{-1} values, however, were substantially independent of pH, thus indicating that the average C–Co distance is constant, and typical of short-range interactions. Therefore the possibility that CO_2 is directly bound at the metal was taken into consideration.[12] On the other hand coordination of CO_2 to metals in inorganic models is quite rare. So far, CO_2 as such has been found to bind transition metals only through carbon,[13] or through both carbon and oxygen.[14] To better characterize the type of interactions between the two interconverting species, CO_2 and HCO_3^-, with metals in carbonic anhydrase derivatives, the copper-substituted bovine carbonic anhydrase B (CuBCAB) has been investigated. The choice of this metal ion is based on its high relaxing capability compared to cobalt[15-17] and on the very low catalytic activity of its enzyme derivative.[18] The latter property allows longer independent life of the two substrate species, whereas, owing to shorter ^{13}C relaxation times, a shorter lifetime is enough to provide information on the interaction of a single substrate species with the surroundings. Therefore the NMR parameters of the ^{13}C nuclei will result from independent interaction of each single species with the paramagnetic center rather than by the average due to the interconversion. Furthermore copper(II) has a large affinity for ligands[19] and, indeed, copper carbonic anhydrase shows a larger affinity for inhibitors than any other metallo-substituted carbonic anhydrase.[20]

Bovine carbonic anhydrase B obtained through chromatography[21] of the commercial enzyme (Sigma) was carefully demetallized[6] to a zinc content of <5% as monitored by esterase activity[22] and then reacted with copper sulfate.[16] Since relatively low concentrations of native enzyme could considerably shorten the lifetimes of the CO_2 and HCO_3^- species, thus averaging their relaxation rates, 10% of acetazolamide with respect to the total amount of enzyme was always added to the copper carbonic anhydrase solutions. The affinity constant of the above inhibitor for the zinc enzyme ($\sim 10^7\ M^{-1}$)

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Table I. Longitudinal and Transverse Relaxation Rates of $H^{13}CO_3^-$ and $^{13}CO_2$ in the Presence of Bovine Carbonic Anhydrase B. T_{1p}^{-1} Values Are the Paramagnetic Contributions to the Experimental Values and f Is the Ligand/Enzyme Molar Ratio. The Sample Temperature Was 12 °C Unless Otherwise Specified

pH	enzyme	substrate	T_1^{-1} (s^{-1})	T_2^{-1} (s^{-1})	T_{1p}^{-1} (s^{-1})	T_{2p}^{-1} (s^{-1})	fT_{1p}^{-1} (s^{-1})
6.9	apoBCAB ($1.3 \times 10^{-}$ 10^{-3} M	HCO_3^- (7.7×10^{-2} M)	0.71	*a*			
	+ acetazolamide (1.0×10^{-4} M)	CO_2 (2.5×10^{-2} M)	0.25	3.3			
6.6	CuBCAB (1.1×10^{-3} M)	HCO_3^- (7.0×10^{-2} M)	77	77	77	77	5.0×10^3
	+ acetazolamide (9×10^{-5} M)	CO_2 (4.5×10^{-2} M)	1.7	5.0	1.4	1.7	62
7.0	CuBCAB (1.1×10^{-3} M)	HCO_3^- (7.2×10^{-2} M)	9.1	20	8.3	20	
	+ acetazolamide (9×10^{-5} M)	CO_2 (1.5×10^{-2} M)	0.30	3.8			
	+ NaN_3 (1.3×10^{-3} M)						
8.3	CuBCAB (1.1×10^{-3} M)	HCO_3^- (7.0×10^{-2} M)	77	77	(12 °C)		
	+ acetazolamide (9×10^{-5} M)		140	140	(26 °C)		

[a] Line width smaller that 1 Hz.

is more than two orders of magnitude higher than that for the copper enzyme[18] and therefore addition of acetazolamide almost completely inhibits any residual native enzyme present. NMR samples were prepared by mixing aliquots of the above solutions with D_2O solutions of 90% ^{13}C-enriched sodium bicarbonate (Prochem B.O.C.). Buffers were not used; lower pH values were obtained by addition of solid CO_2 directly in the NMR tube, modified to minimize the air volume above the sample and to bear a moderate buildup of pressure. The pH of the samples was measured from the relative integrated intensities of the two signals. The physical measurements were obtained with the apparatus and techniques described elsewhere.[16,23]

^{13}C NMR spectra (20 MHz) of solutions containing the system CO_2–HCO_3^- at various pH in presence of CuBCAB show two signals whose intensities depend on the relative amounts of the two species. The line width of the two signals is also quite different: in particular the line of HCO_3^- is broader than that of CO_2. This means that the interconversion rate between the two forms is slow on the NMR time scale both from the points of view of the chemical shift and of the transversal relaxation times. The T_1^{-1} values were also determined and their enhancements relative to the blank with the apoenzyme (T_{1p}^{-1}) were found to be different for the two signals (Table I). In particular the T_{1p}^{-1} values of HCO_3^- at different enzyme–substrate ratios are consistent with the idea that all of the present CuBCAB is bound in a 1:1 ratio; indeed, the affinity constant of HCO_3^- for CuBCAB had been evaluated to be $\sim 3.5 \times 10^3$ M^{-1}.[20]

T_1 and T_2 of the HCO_3^- signal are the same and decrease with increasing temperature (Table I), indicating that the exchange time is not fast on the NMR time scale. Since in this case T_{1p}^{-1} yields a lower limit to the paramagnetic relaxation enhancement, and neglecting contact and pseudocontact contributions, a distance Cu–C $\leq$ 320 pm is consistent with the above enhancement and with τ_c values in the range of those previously reported for CuBCAB, i.e., $\simeq 10^{-9}$ s. Such a distance is typical of inner-sphere coordination. The HCO_3^- ion appears, therefore, directly bound to the metal in copper carbonic anhydrase, as it is in the case of the cobalt derivative.[9,12] The product fT_{1p}^{-1}, where f is the molar ratio between the ligand and the enzyme, is equal to 5×10^3 s^{-1} for the HCO_3^- ion; it represents a measure of the dissociation rate of the above anion from the coordination sphere, and therefore it sets an upper limit to the turnover rate. The decrease in the dissociation rate of HCO_3^- from the Zn^{24} to the Cu enzyme may account by itself for the difference in activity of the two derivatives.

T_1 and T_2 measurements on the $^{13}CO_2$ signal could not be performed at increasing temperatures owing to the decrease in CO_2 solubility; however, the relaxation rate of $^{13}CO_2$ is 60 s^{-1}, and it seems unlikely that the exchange rate is as small as this value. If this were the case, CO_2 could be bound to the metal without showing dramatic relaxation enhancements. However, a check of the electronic spectra up to pH 9.3 seems to definitely rule out this possibility, since the electronic spectra do not change with pH and it is hard to believe that the amount of CO_2 present at pH 9.3 is still capable of saturating a metal binding site.

Table II. ESR Parameters[a] and Electronic Absorption Maxima of Copper(II) Bovine Carbonic Anhydrase B and of Its Adduct with HCO_3^- at pH 9.2

derivative	$g_\parallel$	$g_\perp$	$A_\parallel$, $cm^{-1} \times 10^4$	d-d transition, $cm^{-1} \times 10^{-3}$ [b]
CuBCAB	2.31	2.06	131	13.3 (125)
CuBCAB–HCO_3^-	2.30	2.04	138	13.6 (170)

[a] ESR spectra were recorded at liquid-nitrogen temperature. [b] Molar absorption coefficients (M^{-1} cm^{-1}) are given in parentheses.

Therefore, either CO_2 feels the paramagnetic center within the cavity at a large distance (Cu–C $\simeq$ 600 pm, or even more in the case of more than one molecule being present within the cavity) or the effect is due to an incompletely quenched effect of the $CO_2 \rightleftharpoons HCO_3^-$ interconversion. Addition of N_3^- in a 1:1 molar ratio with respect to the copper enzyme reduces to 10% the T_{1p}^{-1} values of HCO_3^-, in accordance with the relative affinity constants of N_3^- and HCO_3^- for the metalloenzyme.[20] The T_{1p}^{-1} values of CO_2 are also reduced by the same amount. Thus, either the bound N_3^- hinders the binding site of CO_2, wherever it is, within the cavity, or the T_1^{-1} enhancement of CO_2 is due to the effect of the residual interconversion rate, which is slowed by addition of N_3^-. Even the latter case would require the presence of CO_2 within the cavity because the interconversion rate within the cavity itself is orders of magnitude larger than outside, and larger than that of the mercury derivative.[18] Concluding, all the evidence suggests the presence of a binding site of CO_2 within the cavity at a distance beyond any direct chemical bonding to the metal. Of course this site may not be determinant in the catalytic pathway of active enzyme derivatives; however, if there is a binding interaction of CO_2 with the protein part of the cavity in the copper enzyme, presumably the same is true for the active enzymes.

The donor atoms of copper in carbonic anhydrase were suggested to be three histidine nitrogens and a water oxygen.[20] The possibility of a fifth donor at a larger distance was also taken into consideration.[16] The monoanionic inhibitors of the native enzyme investigated (I^-, CH_3COO^-, CN^-, N_3^-, etc) were found to bind to the metal of CuBCAB at a fifth coordination site since the ^1H T_1^{-1} values of the water solutions containing the metalloenzyme do not change by addition of

inhibitors.[16] Addition of HCO_3^- until the electronic spectrum of the derivative is fully developed causes the ^1H T_1^{-1} to drop to ~20% of the original value. This peculiar behavior can be interpreted as due to the substitution of H_2O by HCO_3^-. The electronic absorption maxima and ESR parameters of the adduct are shown in Table II and might be consistent with this suggestion. Addition of I^- restores the proton relaxivity values typical of the iodo derivative, indicating that HCO_3^- is removed from coordination by I^-; therefore, although the HCO_3^- and I^- binding sites are different, there is overlap between them. The binding of HCO_3^- at a different site with respect to the other monoanionic inhibitors and in particular the binding at the site of water may tentatively be ascribed to the presence of a proton which can give rise to hydrogen bonds.

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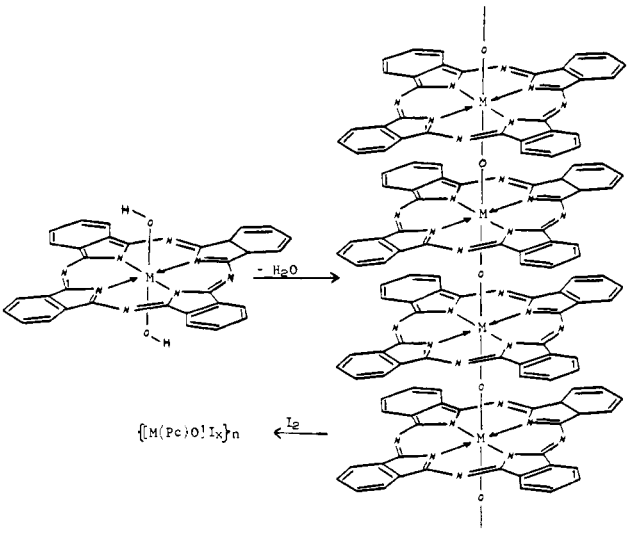
Conductive Polymers Consisting of Partially Oxidized, Face-to-Face Linked Metallomacrocycles

Sir:

Halogen doping of planar, conjugated metallomacrocycles has been shown to be an effective strategy for the synthesis of electrically conductive, low-dimensional mixed-valence materials consisting of partially oxidized molecular stacks.[1-4] This strategy suffers, however, as do all analogous ones based upon molecular stacking, from the weakness that solid-state properties are completely dependent on the unpredictable and as yet largely uncontrollable intermolecular forces that dictate whether or not stacks form, whether stacks are integrated or segregated, the relative orientation of donors with respect to acceptors, the relative orientation of units within a stack (D_{nh} or canted stacks), and the stacking repeat distance.[5] It would clearly be desirable to devise methods for better control of the above parameters, both from the standpoint of providing information on how these factors are related to collective properties such as charge transport and metal-insulator transitions, as well as for learning how to manipulate these characteristics rationally through modification of stack and lattice architecture. In this communication we report on one approach to controlling molecular stacking, partial oxidation of oligomers in which metallomacrocycles have been covalently linked in a "face-to-face" orientation, and some of the interesting properties of these new materials. Although we illustrate this approach with one particular class of halogen-doped, linked metallomacrocycle (phthalocyanine), we wish to emphasize that this strategy has obvious generality.

Scheme I



Using the methodology originally developed by Kenney[6,7] or a simpler "one-pot" procedure,[8] dichlorosilicon, germanium, and tin phthalocyanines ($M(Pc)Cl_2$) were prepared and then hydrolyzed in pyridine[7] to produce the corresponding dihydroxides ($M(Pc)(OH)_2$). Polymerization under high vacuum[6,9] at 300–400 °C (Scheme I) produced the corresponding phthalocyaninato polysiloxanes, polygermyloxanes, and polystannyloxanes in high yield and purity. In regard to charge

Table I. Electrical Conductivity Data for Polycrystalline Samples of Halogen-Doped $[M(Pc)O]_n$ Materials[a]

compd	σ $(\Omega\ cm)^{-1}$ [b]	activation energy, eV
$[Si(Pc)O]_n$	3×10^{-8}	
$\{[Si(Pc)O]I_{0.50}\}_n$	2×10^{-2}	
$\{[Si(PC)O]I_{1.40}\}_n$	2×10^{-1}	0.04 ± 0.001
$\{[Si(Pc)O]I_{4.60}\}_n$	1×10^{-2}	
$\{[Si(Pc)O]Br_{1.00}\}_n$	6×10^{-2}	
$[Ge(Pc)O]_n$	$<10^{-8}$	
$\{[Ge(Pc)O]I_{1.80}\}_n$	3×10^{-2}	0.08 ± 0.006
$\{[Ge(Pc)O]I_{1.90}\}_n$	5×10^{-2}	0.06 ± 0.003
$\{[Ge(Pc)O]I_{1.94}\}_n$	6×10^{-2}	0.05 ± 0.007
$\{[Ge(Pc)O]I_{2.0}\}_n$	1×10^{-1}	
$[Sn(Pc)O]_n$	$<10^{-8}$	
$\{[Sn(Pc)O]I_{1.2}\}_n$	1×10^{-6}	
$\{[Sn(Pc)O]I_{5.5}\}_n$	2×10^{-4}	0.68 ± 0.01

[a] Four-probe van der Pauw techniques. [b] At 300 K.

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