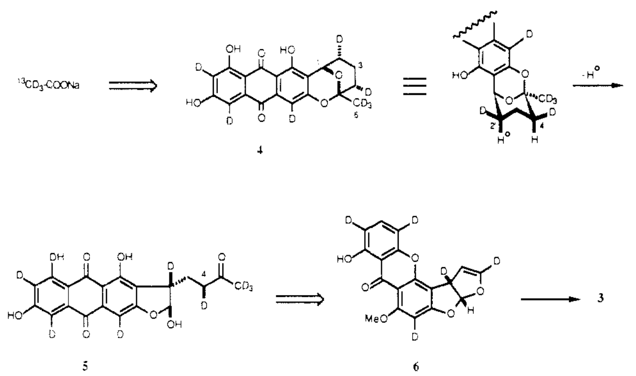
Scheme II



of *Aspergillus parasiticus* we demonstrate that this pattern is maintained not only in oleic acid but also in the six-carbon side chain of averufin.

[2-$^2H_3$, ^{13}C]Sodium acetate (35 mg) was administered to each of three 48-hour-old standing cultures of the averufin-accumulating mutant of *A. parasiticus* (ATCC 24551) grown in a low salts medium[11] (50 mL/250 mL Erlenmeyer flask). Similar additions were made every 24 h to a cumulative dose of 140 mg/flask. After the sixth day, the mycelial mats were collected, and the averufin produced was extracted and purified as previously described.[1,2] The rigid bicyclic ketal of averufin **4** provides an excellent system to apply the ^2H decoupled ^1H, ^{13}C chemical shift correlation method of Vederas[9] to determine the relative orientations of deuterium from labeled acetate. The H-2′, -3′, and -4′ methylene hydrogens give rise to resonances separated by >0.1 ppm from their geminal partners. These signals have been unambiguously assigned.[12] The result of the correlation experiments is shown in Figure 1 where the spectrum at the left shows CH_2-4′ in which the upfield correlation from CHD-4′ indicates that the methylene hydrogen is axial. Similarly, in the spectrum at the right correlations for C-6′ and C-2′ overlap somewhat in the carbon domain but are well-separated in the proton domain. Once again, hydrogen orientation at CHD-2′ is axial. Therefore, the deuterium orientation at both C-2′ and C-4′ is equatorial. Knowing further the absolute configuration of averufin as 1′*S*,[13] the absolute configuration of deuterium label at C-2′ and C-4′ may be assigned *R* in the growing fatty acid/polyketide chain. In parallel experiments oleic acid from the mutant grown in the presence of [2-$^2H_3$, ^{13}C]acetate was isolated, degraded, and analyzed essentially as described in the accompanying communication.[14] In keeping with fatty acids derived from other fungal sources,[10] the locus of deuteriation was found to be *R* in the growing chain.

Several conclusions may be drawn from these experiments. First, that a common stereochemical course is observed in the reductive formation of the six-carbon side chain of averufin and oleic acid isolated from the same organism is consistent with but does not absolutely require a hexanoylCoA primer in the aflatoxin pathway. Second, the collected findings of the preceding paper[14] are that the corresponding reductions in metabolites of clear polyketide origin take place with the opposite stereochemical course to their co-occurring fatty acids. While the present sample is admittedly small and subject to stereochemical exception in the future, it lends empirical support to the proposed role of a hexanoyl starter and may prove general for (some) species of *Fungi imperfecti*. Third, the first oxidative step in the conversion of the averufin side chain to the dihydrobisfuran characteristic of the aflatoxin pathway involves an apparently direct oxidative rearrangement of the former to 1′-hydroxyversicolorone (**5**).[15] The two deuteria present[16] at C-2′and C-4′ in **4** are known to appear in the bisfuran, as established for sterigmatocystin (**6**).[17] Therefore, in the rearrangement of **4** to **5**, it is the axial hydrogen at C-2′ (H°) in averufin that is lost in this process, trans diaxial to the migrating aryl ring, in accord with stereoelectronic considerations (Scheme II).[1,18]

Acknowledgment. We are pleased to acknowledge the support of this work by the National Institutes of Health (ES 01670) and the Camille and Henry Dreyfus Foundation. NMR and mass spectrometers used in this work were acquired with major funding from the NIH (RR 01934 and RR 02318) and the NSF (PCM 83-03176).

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$Tl_2Pt(CN)_4$: A Noncolumnar, Luminescent Form of $Pt(CN)_4^{2-}$ Containing Pt–Tl Bonds

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The ability of $Pt(CN)_4^{2-}$ to form columnar structures with varying Pt–Pt interactions in both simple salts[1] and in the partially oxidized, one-dimensional conducting materials is well known.[2] For simple salts, with metal cations, the observed Pt–Pt separations in 20 crystallographically studied examples cover a wide range, 3.09–3.75 Å,[1] while in the partially oxidized materials the corresponding separations are shorter and fall into a narrower range, 2.8–3.0 Å.[2] Only with large organic cations, the radical cation of *N,N,N′,N′*-tetramethylbenzenediamine[3] and 1,1′-dimethyl-4,4′-bipyridinium,[4] do $Pt(CN)_4^{2-}$ units exist as well-separated, square-planar ions. We report here on the novel structure of $Tl_2Pt(CN)_4$ which does not possess the usual columnar structure, but which exhibits covalent Pt–Tl bonding.

Slow diffusion of an aqueous solution of $TlNO_3$ into an aqueous solution of $K_2[Pt(CN)_4]\cdot 3H_2O$ at 23 °C produces colorless crystals of $Tl_2Pt(CN)_4$.[5-10] These crystals show an intense blue luminescence at 22 500 cm^{-1} (width at half height, 2860 cm^{-1}) at 298 K when irradiated in the near ultraviolet. The emission spectrum is shown in trace A at the top of Figure 1 while the excitation spectrum is shown in trace B. The excitation band correlates well with the absorption spectrum obtained from a

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(5) These crystals appear to be the same substance as mentioned in several earlier reports[6-8] but are different from the pale yellow-white, orthorhombic crystals with cell dimensions a = 11.84, b = 10.03, and c = 7.37 Å reported by Williams and co-workers from a different method of preparation.[9] They are also distinct from the red $Tl_4[Pt(CN)_4](CO_3)$ which has a columnar structure with a 3.245-Å Pt–Pt separation.[10]

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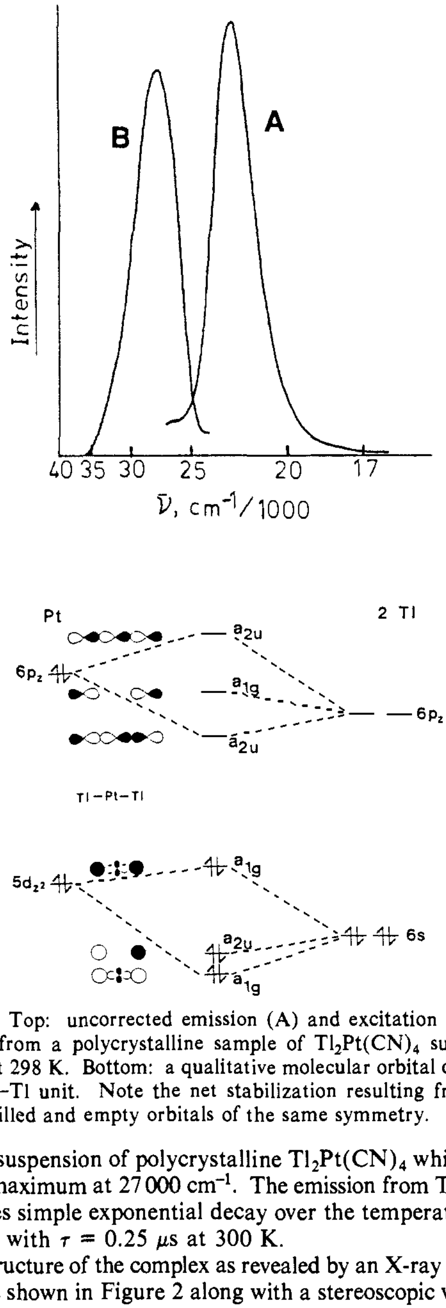

Figure 1. Top: uncorrected emission (A) and excitation spectra (B) obtained from a polycrystalline sample of $Tl_2Pt(CN)_4$ suspended in glycerol at 298 K. Bottom: a qualitative molecular orbital diagram for the Tl–Pt–Tl unit. Note the net stabilization resulting from mixing between filled and empty orbitals of the same symmetry.

glycerol suspension of polycrystalline $Tl_2Pt(CN)_4$ which reveals a single maximum at 27 000 cm^{-1}. The emission from $Tl_2Pt(CN)_4$ undergoes simple exponential decay over the temperature range 2–300 K with $\tau = 0.25$ μs at 300 K.

The structure of the complex as revealed by an X-ray diffraction study[11] is shown in Figure 2 along with a stereoscopic view of the unit cell that indicates the lack of significant interactions between adjacent $Tl_2Pt(CN)_4$ units. The usual columnar structure is not present. Instead, thallium atoms sit above and below each $Pt(CN)_4$ unit. The Pt–Tl distance is 3.140 (1) Å. This is close to the sum (3.08 Å) of the metallic radii for these two metals and shorter than most of the Pt–Pt separations seen in salts of $Pt(CN)_4^{2-}$ with columnar structures.[1]

The thallium is bound only to the adjacent platinum. The closest Tl···N distance (2.80 Å) is well beyond a covalent bonding interaction. Moreover, as seen in Figure 2, no PtCN unit points directly toward any thallium. The shortest Tl···Tl contact is 4.038 (1) Å, about twice the van der Waals radius for Tl(I).[12]

Thallium(I) to transition metal bonding is rare. Solid $Tl[Co(CO)_4]$ has an ionic structure with no direct Tl–Co bonding.[13] $[Ir_2Tl(CO)_2Cl_2\{\mu\text{-}(Ph_2PCH_2)_2AsPh\}_2]NO_3$ contains a bent Ir–Tl–Ir unit with Tl–Ir distances of 2.958 (1) and 2.979 (1) Å.[14] $[\{Ru_6C(CO)_{16}\}_2Tl]^+$ contains four-coordinate, distorted tetrahedral thallium with Tl–Ru distances of 2.775 (3), 2.785 (3), 2.853 (2), and 2.875 (2) Å.[15] $Tl[Au(CN)_2]$ shows evidence of weak, secondary Tl···Au interactions with long 3.45-Å separations.[16]

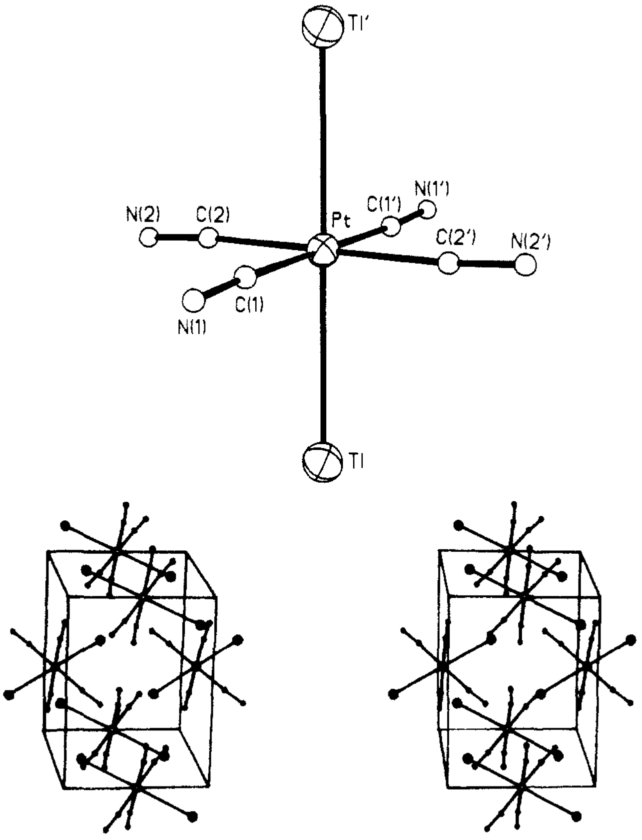

Figure 2. Top: perspective view of $Tl_2Pt(CN)_4$; anisotropic thermal ellipsoids for Pt and Tl are shown at the 50% probability level. The Pt–Tl distance is 3.140 (1) Å, and the Pt–C distances are 2.00 (2) and 2.01 (2) Å. The C–Pt–C angle is 90.8 (9). The Tl–Pt–C angles are 88.6 (6) and 89.6 (7). Bottom: a stereoscopic view showing the unit cell for $Tl_2Pt(CN)_4$ and the lack of interactions between these units. The shortest Tl···Tl contact is 4.038 (1) Å.

The optical properties of $Tl_2Pt(CN)_4$ appear to be dominated by the Tl–Pt–Tl interaction. The absorption spectra of individual $Pt(CN)_4^{2-}$ [1,17] and Tl(I)[18-20] ions occur at higher energies than the 27 000 cm^{-1} observed for $Tl_2Pt(CN)_4$. While Tl(I) in solution and in alkali halides is luminescent, the emission and particularly the excitation also occur at higher energies than those shown in Figure 1.[18-20] Hence we ascribe these to the $Tl_2Pt(CN)_4$ unit. A molecular orbital diagram (D_{4h} symmetry) illustrating the σ bonding within the Tl–Pt–Tl unit is shown in the lower part of Figure 1.[21] Stabilization of the Tl–Pt bonding arises from mixing of orbitals of the same symmetry in the lower filled set with those

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(11) White $Tl_2Pt(CN)_4$ crystallizes in the monoclinic space group $P2_1/n$ (a nonstandard setting of $P2_1/c$, no. 14) with a = 6.325 (2) Å, b = 7.386 (2) Å, c = 9.581 (3) Å, β = 104.92 (2)°, Z = 2 at 293 K, R = 0.063, and R_w = 0.063 for 689 reflections with $I > 2\sigma(I)$ and 32 parameters.

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of the upper empty set. Note the close correspondence between this picture and that used to describe the bonding in $\mathrm{Rh_3(CNR)_{12}}^{3+}$[22] and stacked trimer units of $(\mathrm{Pt(CN)_4}^{2-})_3$[23] with the filled 6s orbital of thallium(I) having similar characteristics to the filled d_{z^2} orbital in planar d^8 complexes. The strong 27 000-cm^{-1} absorption is assigned to a spin and symmetry allowed $a_{1g} \rightarrow a_{2u}$ transition. The molecular orbital diagram accounts for the occurrence of this feature at lower energies than the s → p transition in Tl(I) or the $d_{z^2} \rightarrow p,\pi$ transition in $\mathrm{Pt(CN)_4}^{2-}$. On the basis of its long lifetime, the luminescence is assigned to the spin forbidden $a_{2u} \rightarrow a_{1g}$ process (phosphorescence).

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Supplementary Material Available: Tables of atomic positional parameters, bond distances, bond angles, anisotropic thermal parameters, and data collection parameters for $\mathrm{Tl_2Pt(CN)_4}$ (3 pages); tables of observed and calculated structure factors for $\mathrm{Tl_2Pt(CN)_4}$ (4 pages). Ordering information is given on any current masthead page.

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Photoinitiated Charge Separation in a Carotenoid–Porphyrin–Diquinone Tetrad: Enhanced Quantum Yields via Multistep Electron Transfers

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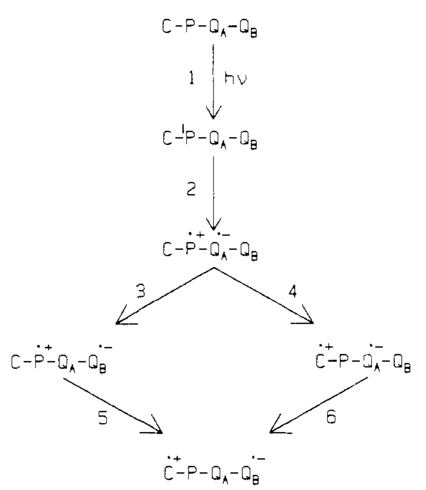
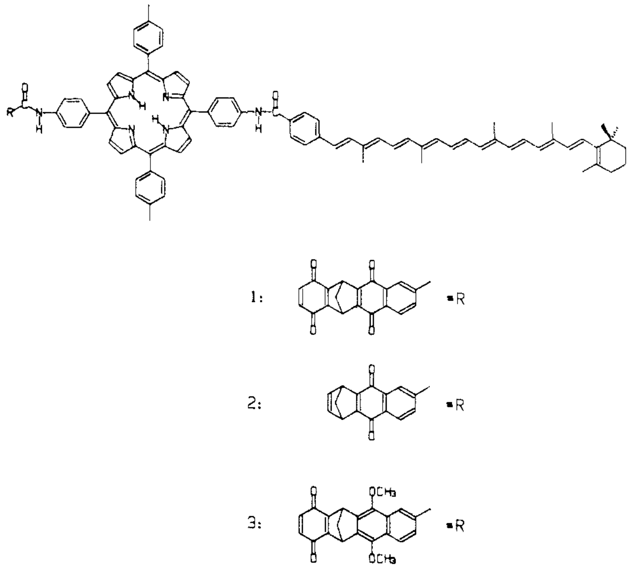
Photosynthesis converts light to chemical potential energy in the form of long-lived charge separation across a bilayer membrane. Recombination of the charge-separated state is prevented by the large distance between the final electron donor and acceptor. Because the quantum yield of a single long-range electron transfer across the bilayer would be vanishingly small, reaction centers employ a series of electron-transfer steps, each of which occurs over a short distance with high yield. Synthetic carotenoid–porphyrin–quinone triad molecules[1–8] and other molecular systems[9–12] which begin to model this approach have recently been reported. In photosynthetic bacteria, the charge separation sequence includes electron donation from a bacteriopheophytin to a quinone which then transfers an electron to a second quinone. An elegant molecule that models such electron transfer has been prepared,[12] although it did not reproduce the long-lived charge separation characteristic of the natural system. We now report the synthesis of a tetrachromophoric molecule **1** consisting of a porphyrin (P) covalently linked to both a carotenoid polyene (C) and a rigid diquinone moiety ($\mathrm{Q_A}$–$\mathrm{Q_B}$), excitation of which pro-

Scheme I





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