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15. We also prepared a randomly oriented sample with a separating layer by transferring a PM-LB monolayer film on an electrode modified with a hapten phospholipid and a BS antibody. The response obtained from this sample decreased by 30% as compared with an LB film directly attached to a substrate.
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Excimers and Exciplexes of Conjugated Polymers

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Observations of intermolecular excimers in several π-conjugated polymers and exciplexes of these polymers with tris(*p*-tolyl)amine are reported. It is shown that the luminescence of conjugated polymer thin films originates from excimer emission and that the generally low quantum yield is the result of self-quenching. Thus, in sufficiently dilute solution, the "single-chain" emission has a quantum yield of unity. Exciplex luminescence and exciplex-mediated charge photogeneration have much higher quantum yields than the excimer-mediated photophysical processes. These results provide a basis for understanding and controlling the photophysics of conjugated polymers in terms of supramolecular structure and morphology.

Conjugated polymers have attracted much research interest in science and technology in the past two decades (*1–5*). Conducting polymers (*1–5*), which are ground-state, charge-transfer complexes of conjugated polymers, are of wide interest as semiconductors and electroactive materials for diverse applications ranging from biosensors, batteries, and loudspeakers to molecular electronic devices (*3–5*). In their pristine form, π-conjugated polymers are of wide interest as third-order nonlinear optical materials for photonic switching devices (*4, 6, 7*) and as optoelectronic materials for light-emitting diodes (*8, 9*), solar cells (*10*), and xerographic photoreceptors (*11*). Exciplexes, which are charge-transfer complexes that are stable only in the excited state, are important materials that have only recently begun to be explored in conjugated polymers (*12, 13*). Although much theoretical and experimental work has been done on the photophysics of conjugated polymers (*14–18*), including the nature of the excited states, the origin of luminescence, and the nature of charge photogeneration, these photophysical processes in conjugated polymers remain poorly understood and controversial (*14–18*).

One common way in which excimers (*19–27*) are formed is by interaction of an excited chromophore $^1A^*$ with an unexcited chromophore ^1A: $^1A^* + {}^1A \rightleftharpoons {}^1(AA)^*$. Such an excited-state complex is stable as a result of resonance contributions from exciton and charge-transfer configurations: $^1(A^*A) \leftrightarrow {}^1(AA^*) \leftrightarrow {}^1(A^-A^+) \leftrightarrow {}^1(A^+A^-)$. The corresponding excimer wave function is (*21, 23*).

$$\Psi_{\text{excimer}} = c_1[\Psi(A^*A) + \Psi(AA^*)] + c_2[\Psi(A^-A^+) + \Psi(A^+A^-)]$$

The ratio c_1/c_2 and hence the relative contributions from exciton and charge transfer may vary for different materials. Singlet exciplexes are formed similarly but from two distinct chromophores A (acceptor) and D (donor) [either A or D is excited, that is, $^1A^* + {}^1D$ or $^1A + {}^1D^* \rightarrow {}^1(A^{\cdot-}D^{\cdot+})$], and are similarly stabilized (*21, 24*) [$^1(A^*D) \leftrightarrow {}^1(AD^*) \leftrightarrow {}^1(A^{\cdot-}D^{\cdot+})$].

Studies (*19–27*) of excimers and exciplexes in small molecules have shown that their basic supramolecular structures are cofacial sandwich-type configurations with interplanar distances of 3 to 4 Å. Interestingly, π-conjugated polymers are generally stiff chain molecules with relatively planar geometries and very strong intermolecular interactions, leading to cofacial chain packing in the solid state (*2, 3, 28, 29*). Intermolecular distances of 3.3 to 3.6 Å in sandwich-type cofacial packing have been determined by x-ray diffraction and by computational modeling of the supramolecular structure and morphology of many π-conjugated polymers (*28, 29*). It is therefore reasonable to expect that excimers might efficiently form in excited π-conjugated polymers because the materials are already configured into potential excimer-forming sandwich-type supramolecular structures.

We report the formation of intermolecular excimers by a series of π-conjugated polybenzobisthiazoles (**1**), polybenzobisoxazole (**2a**), and poly(benzimidazobenzophenanthroline ladder) (**3**) (Fig. 1). We also report the formation of intermolecular exciplexes between these polymers and tris(*p*-tolyl) amine (**4**). The formation and properties of excimers $^1(AA)^*$ and exciplexes $^1(A^{\cdot-}D^{\cdot+})^*$, where A is a conjugated polymer chromophore and D is **4**, were investigated by steady-state and time-resolved fluorescence spectroscopy, picosecond transient absorption spectroscopy, and charge photogeneration in xerographic photoinduced discharge experiments. Dilute and concentrated fluid and solid solutions as well as thin films of these rigid chain polymers were investigated (*30*).

All photophysical measurements were done at room temperature. Optical absorption and excitation spectra of 10^{-7} to 10^{-3} M fluid solutions in methanesulfonic acid (MSA) and 10^{-3} to 12 M solid solutions in poly(benzobisthiazole decamethylene) were obtained (*30*). Steady-state photoluminescence (PL) measurements were made on the same fluid and solid solutions as well as on thin films of the polymers. We measured the PL quantum yield Φ_f by comparing the integration of the emission spectrum of a sample to that of a standard of known Φ_f under identical optical conditions (*25, 31, 32*). A 10^{-6} M quinine sulfate solution (0.1 N in H_2SO_4, Φ_f = 55%) (*31*) and a thin film of ~10^{-3} M 9,10-diphenylanthracene in poly(methyl methacrylate) (Φ_f = 83%) (*32*) were used as fluorophore standards for fluid solutions and thin films, respectively. We made picosecond time-resolved PL decay measurements using the time-correlated

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single-photon counting technique and laser system described elsewhere (*12*). The picosecond transient absorption spectroscopy is a typical pump and probe experiment described in (*33*). Field-dependent quantum yield $\phi(E)$ for charge photogeneration was measured in the applied electric field range of 7×10^3 to 10^6 V/cm as described elsewhere (*11*).

The π-conjugated polymers in Fig. 1 have very rigid chain structures (*28, 29*) similar to the structures found in highly fluorescent dye molecules (*32*). However, the measured fluorescence quantum yield Φ_f for thin films varied from 0.001% for **3** to 10% for **2a**. These low quantum yields are very similar to those reported in other classes of conjugated polymers (*3, 8, 9*). To clarify the PL quenching in these polymers, we measured the concentration dependence of Φ_f for fluid and solid solutions. Typical results for fluid solutions (Fig. 2) of **1a** and **1d** showed an increase of PL quantum efficiency with decreasing concentration. The quantum yield in dilute solution ($\leq 10^{-6}$ M) is 100%, sharply decreasing to ~50% at 10^{-5} M and to only 10 to 13% at 10^{-4} M. Approximately similar variation of quantum yield with concentration was observed in solid solutions of **1a** and **1d**. In thin films, the limiting Φ_f values of **1a** and **1d** were 6 and 5%, respectively.

These results suggest that the rather low PL quantum yield of thin films of these polymers is caused by concentration or self-quenching. Furthermore, the observed high quantum yield in dilute solutions of all the polymers rules out intrachain interactions, torsional vibrations, defects along the chains, or impurities as important channels for nonradiative deactivation of the excited state. Therefore, we propose excimer formation as the intermolecular mechanism of concentration quenching, and we use "excimer" here as the central concept, even though the possibility that more than two chromophores are involved cannot be ruled out.

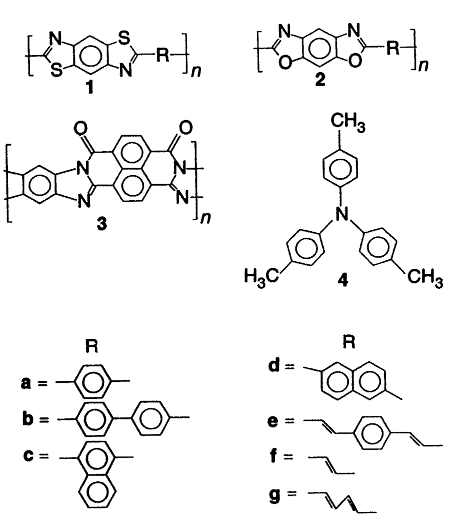

Fig. 1. Structures of π-conjugated polymers (**1**, **2**, and **3**) and donor molecule (**4**) investigated.

The ground-state absorption and excitation spectra of fluid and solid solutions of the polymers in a wide concentration range (10^{-7} to 10^{-3} M) were similar to the thin-film spectra. The absorption spectra of **1a** at selected solution concentrations and in the solid state are shown in Fig. 3A. In contrast to the line shape and peak of the absorption spectra, which were similar at different concentrations, the line shape and peak of the emission spectra changed dramatically with concentration. In dilute solution, the emission spectra showed well-resolved vibronic structure (Fig. 3, B and C). The thin-film emission spectra were generally broad, structureless, and red-shifted from the dilute solution spectra as exemplified for **1a** in Fig. 3, B and C. The progressive evolution of the broad and structureless emission of thin films from the highly structured emission spectra in dilute solutions was seen with increasing concentration in fluid or solid solutions. In dilute solid solution of **1a**, a mirror image relation between the excitation and emission spectra is seen, as often observed in small molecules (*32*). We interpret the dilute solution emission spectra of these polymers as those attributable to the singlet excited state of the "single chain" or "isolated chromophore" $^1A^*$. The emission from $^1A^*$ is not observed in the thin films; thus, we interpret the observed thin-film emission of the conjugated polymers as originating from mainly singlet excimers, $^1(AA)^*$.

The time-resolved PL decay dynamics of dilute solutions of all the polymers exhibited a single exponential decay (Fig. 4A), indicating a single fluorescent species $^1A^*$. The measured lifetime of $^1A^*$ varied from 0.2 ns for **3** to 0.6 ns for **1a** and **1c**. The corresponding PL decay dynamics of thin films of the same polymers was found to be nonexponential (Fig. 4B), requiring two or three exponentials to fit the data. For example, the PL decay dynamics of **1a** thin film was best described by a biexponential with lifetimes of ~50 and ~500 ps. Multiexponential decay dynamics of thin films may be a result of complex kinetics that include distinct species of $^1(AA)^*$, $^1A^*$, and even different types of excimers and aggregated complexes.

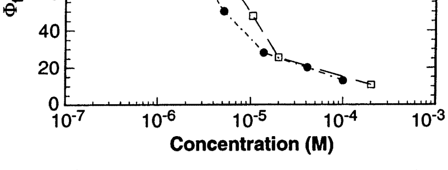

Fig. 2. Concentration dependence of the photoluminescence quantum yield Φ_f of **1a** (dark circles) and **1d** (open squares) in fluid solution.

The stabilization energy E_λ of the excimers in these polymers, which is the spectroscopic energy difference between the "single chain" $^1A^*$ (0–0 line) and excimer $^1(AA)^*$ emission maxima (*21, 23*), varied from 0.3 and 0.45 eV for **1b** and **1a**, respectively, to 0.5 eV for **3**. These E_λ values provide an explanation for the apparently large Stokes shift (~0.5 to 0.7 eV)

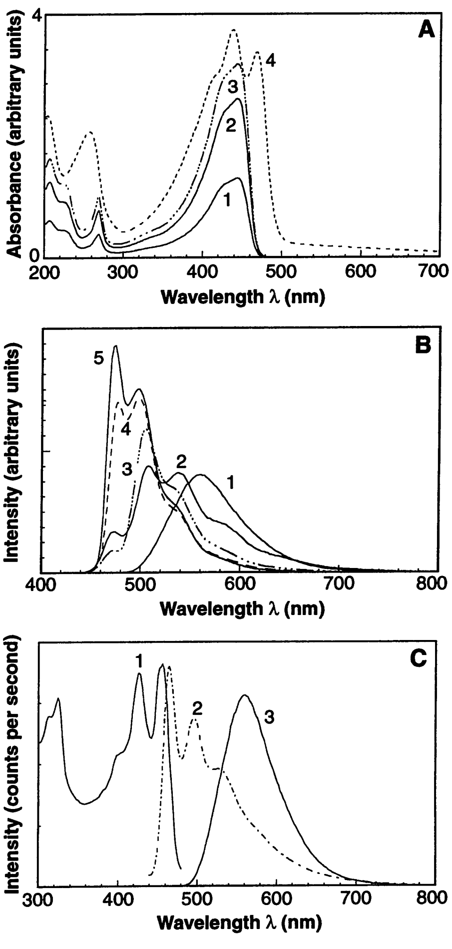

Fig. 3. (**A**) Optical absorption spectra of **1a** in fluid solution in MSA (curves 1 through 3) and thin film (curve 4): 1 = 1.5×10^{-6} M; 2 = 2.5×10^{-5} M; 3 = 1.0×10^{-4} M. (**B**) Photoluminescence spectra of **1a** thin film (curve 1) and in fluid solution in MSA (curves 2 through 5): 2 = 5×10^{-3}; 3 = 1×10^{-4} M; 4 = 1.4×10^{-5} M; 5 = 3.6×10^{-6} M. All solution PL spectra correspond to excitation at 420 nm, and the thin-film spectrum is for 438-nm excitation. (**C**) Excitation (curve 1) and photoluminescence (curve 2) spectra of 2×10^{-3} M **1a** in solid solution in poly(benzobisthiazole decamethylene) compared to emission of **1a** thin films (curve 3). The excitation wavelengths for the PL spectra are 430 nm (curve 2) and 438 nm (curve 3).

of thin-film emission spectra in that, once E_λ is subtracted to account for excimer emission, the true Stokes shift between the "single chain" emission (0–0 line) and absorption becomes small (for example, 0.05 eV for **1a**) and comparable to values normally found in small molecules (*25, 32*) (Fig. 3C).

The triarylamine **4**[$E_D^{ox} = 0.74$ V versus the saturated calomel electrode (SCE)], which is known to form exciplexes with many conjugated aromatic molecules (*34*), was used as a probe donor molecule to investigate exciplex formation by the series of π-conjugated polymers. Bilayer D/A thin-film assemblies were found to have absorption and excitation spectra that are composed of only the component spectra. The absence of the $\mathbf{4}^{+\cdot}$ radical cation, which absorbs strongly at ~680 nm, proved the absence of ground-state interaction. Photoexcitation of the D/A bilayer thin films, at 355 nm, produced a strong transient absorption band at 680 nm attributable to $\mathbf{4}^{+\cdot}$ in about 125 ps, suggesting the formation of excited-state, charge-transfer complexes. PL spectra showed that D/A bilayer thin films exhibited strong luminescence that was relatively broad and structureless (*12*), similar to the excimer emission of the pristine thin films. However, the emission from the D/A bilayers has two distinct features relative to the emission of the polymer thin film: (i) a blue shift and (ii) a large enhancement of PL quantum yield by a factor of 3 to 4. In the case of **2a**, for example, this means that the PL quantum yield has been increased from 10 to 40% by the formation of excited-state, charge-transfer complexes with **4**.

The measured PL decay dynamics of the D/A bilayers was not monoexponential, similar to the observation on the pristine polymer thin films. However, the lifetimes of the D/A emitting states were significantly longer than those of the polymer thin films. This fact along with the steady-state PL results suggested that the emitting state in these bilayers is the singlet exciplex $^1(\mathrm{A}^{\cdot-}\mathrm{D}^{\cdot+})^*$. The blue shift (~0.16 to 0.28 eV) of the exciplex luminescence relative to the emission from the pristine polymer thin films is explained in terms of the smaller stabilization energy of an exciplex compared to an excimer. The $^1(\mathrm{A}^{\cdot-}\mathrm{D}^{\cdot+})^*$ exciplex emission is still red-shifted from the "single chain" $^1\mathrm{A}^*$ emission in accord with the well-known behavior of molecular exciplexes and what should be expected from energetic considerations (*20–25*).

In the absence of knowledge that the emission of the conjugated polymer thin films originates from excimers, the blue shift of the exciplex emission would be difficult to explain with the current models of the photophysics of π-conjugated polymers (*14–18*). Our explanation of the enhanced PL quantum yield of exciplex luminescence is that the quantum yield of radiative decay of $^1(\mathrm{A}^{\cdot-}\mathrm{D}^{\cdot+})^*$ is significantly larger than that of $^1(\mathrm{AA})^*$ and that exciplex formation efficiently competes for $^1\mathrm{A}^*$ with excimer formation and self-quenching.

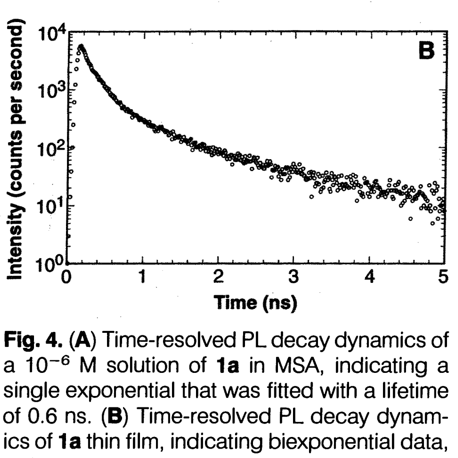

Fig. 4. (**A**) Time-resolved PL decay dynamics of a 10^{-6} M solution of **1a** in MSA, indicating a single exponential that was fitted with a lifetime of 0.6 ns. (**B**) Time-resolved PL decay dynamics of **1a** thin film, indicating biexponential data, which were fitted with lifetimes of 50 and 500 ps.

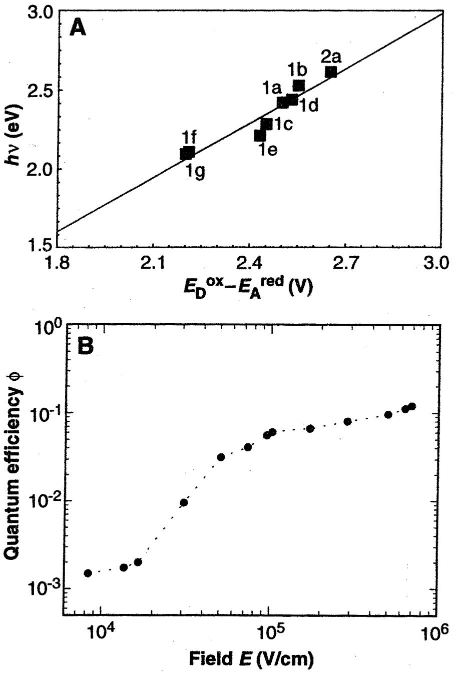

Fig. 5. (**A**) Exciplex luminescence peak as a function of the difference between donor (**4**) oxidation potential and acceptor (π-conjugated polymer) reduction potential. The line is a least square fit to the data. (**B**) Field-dependent quantum efficiency $\phi(E)$ for charge photogeneration in a **4**/**1b** bilayer photoexcited at the absorption band of **1b** (430 nm).

In the exciplex emission process, $^1(\mathrm{A}^{\cdot-}\mathrm{D}^{\cdot+})^* \rightarrow (\mathrm{AD}) + h\nu$, it has been shown in molecular exciplexes that a linear relation holds between the exciplex emission maximum $h\nu$ and the redox properties (E_D^{ox}, E_A^{red}) of the components (*21–24*). Figure 5A shows that such a linear relation holds approximately in exciplexes of conjugated polymers. This approach to tuning emission color has been successfully applied to the problem of achieving efficient blue luminescence in conjugated polymers for light-emitting diode applications (*12*). With regard to electroluminescence in π-conjugated polymers (*8, 9*), we point out that excimers and exciplexes discussed here can also be electrically generated through recombination of injected positive and negative charges (*21, 23, 34*): $^2\mathrm{A}^- + {}^2\mathrm{A}^+ \rightarrow {}^{1,3}(\mathrm{AA})^*$ and $^2\mathrm{A}^- + {}^2\mathrm{D}^+ \rightarrow {}^1(\mathrm{A}^{\cdot-}\mathrm{D}^{\cdot+})^*$.

Photocarrier generation in the conjugated polymers in the forms of thin films of the pristine materials and D/A bilayers was measured by the xerographic photodischarge technique (*11*). The field-dependent quantum efficiency $\phi(E)$ for photogeneration of charge carriers was too small to be measurable in thin films of the pristine materials but was readily measured and was found to be large in D/A bilayers of the polymers. For example, $\phi(E)$ varied from ~0.15% at low fields ($<10^4$ V/cm) to ~14% at 7×10^5 V/cm for **4**/**1b** bilayers photoexcited at 430 nm (Fig. 5B). This strong dependence of photogeneration efficiency on applied electric field, wherein $\phi(E)$ varied by two to three orders of magnitude between ~10^4 to 10^6 V/cm, was generally observed. The highest $\phi(E)$ values were on the order of 30 to 50% at 10^6 V/cm, for instance, in **4**/**1a** bilayers (*11*). These results suggest that excimers are the key photogenerated species in the pristine materials and that exciplexes are the key photogenerated species in the D/A bilayers. Field-assisted dissociation of the excimers, $^1(\mathrm{AA})^* \rightarrow \mathrm{A}^{\cdot-} + \mathrm{A}^{\cdot+}$, proves to be an inefficient process. In contrast, field-assisted dissociation of the exciplexes, $^1(\mathrm{A}^{\cdot-}\mathrm{D}^{\cdot+})^* \rightarrow \mathrm{A}^{\cdot-} + \mathrm{D}^{\cdot+}$, is intrinsically more efficient owing to the greater charge transfer in exciplexes and their dipole moments.

The observation of excimers and exciplexes in π-conjugated polymers opens up new vistas for theoretical and experimental understanding of the materials and for developing them for applications. The preliminary picture of the photophysics of conjugated polymers that is emerging from our observations suggests that excitons are produced on photoexcitation but they rapidly form excimers. Poor quantum yields of luminescence and photocarrier generation are consequences of excimer formation. Exciplex formation enhances quantum yields of the photophysical processes. Our results also suggest that the fundamental approach to efficient photophysical processes in conjugated polymers is through control of the supramolecular structure and morphology of the materials. For example, copolymerization and side-group substitutions can be used to control interchain packing distances and the degree of intermolecular excimer formation (*35*).

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30. The synthesis and characterization of the molecular and supramolecular structures of the conjugated polymers have been reported (*28, 29*). These polymers are soluble in MSA and nitromethane-$AlCl_3$ in which they form liquid crystalline phases at high solution concentrations (>~5 to 10% by weight) as a result of their rigid rodlike conformations (*29*). Polymer thin films were prepared by spin casting from ~0.5 to 1.0% by weight solutions in nitromethane-$AlCl_3$ as described in (*28*). Thin films of solid solutions of a conjugated polymer in poly(benzobisthiazole decamethylene) were similarly prepared through solutions in nitromethane-$AlCl_3$. We prepared the D/A bilayer thin films by first spin-casting the conjugated polymer layer (A, 15 to 40 nm thick) and then the D layer as described in (*11*).
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The Molecular Fossil Record of Oleanane and Its Relation to Angiosperms

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Frederick J. Fago,† Leo J. Hickey, Torren M. Peakman,
David Winship Taylor

Oleanane has been reported in Upper Cretaceous and Tertiary source rocks and their related oils and has been suggested as a marker for flowering plants. Correspondence of oleanane concentrations relative to the ubiquitous microbial marker 17α-hopane with angiosperm diversification (Neocomian to Miocene) suggests that oleanane concentrations in migrated petroleum can be used to identify the maximum age of unknown or unavailable source rock. Rare occurrences of pre-Cretaceous oleanane suggest either that a separate lineage leads to the angiosperms well before the Early Cretaceous or that other plant groups have the rarely expressed ability to synthesize oleanane precursors.

Oleananes are diagenetic alteration products of oleanane and taraxerene precursors (*1*), which in modern plants, except for a lichen (*2*) and a few related fern species (like *Polypodium* and *Marsilea*) (*3, 4*), are concentrated among the angiosperms (flowering plants) (*5*). Oleananes in rock extracts and petroleum are also thought to derive from angiosperms (*6*) and have been reported in numerous sources worldwide (*7–11*).

Undoubted angiosperm fossils are unknown earlier than the Early Cretaceous (*12, 13*). However, some fossil remains and cladistic analyses imply that angiosperms originated in the Triassic (*14, 15*), and studies with chloroplast DNA sequences and angiosperm DNA nucleotide sequences set angiosperm evolution to 200 million years ago (*16*) to more than 300 million years ago (*17, 18*), respectively. In any case, angiosperms were sparse in Early Cretaceous floras and begin dominating floras by the beginning of the Late Cretaceous (*19, 20*). Early Cretaceous angiosperm fossils have an extremely narrow range of variation (*12, 21*) and are scarce, a condition that may reflect a sparse population and herbaceous habit with relatively weak construction compared with their shrubby or arborescent descendants (*22*). Other studies yield a similar pattern (*23, 24*) with low occurrence of angiosperms during the Early Cretaceous but a major increase during the Late Cretaceous and early Tertiary.

The problematic evolutionary history of angiosperms and their probable connection with oleananes prompted us to study the occurrence of oleananes in rock extracts. Two components were necessary to implement this study: (i) a rapid quantitative analytical method providing firm oleanane determinations at low concentrations and (ii) a large, diverse sample suite of biostratigraphically well-defined, organic-rich, fine-grained sedimentary rocks.

Commonly used techniques for oleanane

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