

Dibenzotetraphenylperiflanthene: Synthesis, Photophysical Properties, and Electrogenerated Chemiluminescence

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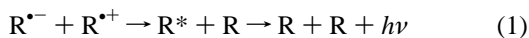
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Abstract: Fissure coupling of the fluoranthene adduct (7,12-diphenyl)benzo[*k*]fluoranthene (**3**) using AlCl₃/NaCl, CoF₃/TFA, or Ti(OCOCF₃) gave the new polyaromatic hydrocarbon dibenzo{[*f,f'*]-4,4',7,7'-tetraphenyl}diindeno[1,2,3-*cd*:1',2',3'-*lm*]perylene (**4**). Crystal data for **4**: triclinic space group *P* $\bar{1}$, *a* = 10.569(2) Å, *b* = 11.565(4) Å, *c* = 13.001(3) Å, α = 95.05(2)°, β = 111.24(1)°, γ = 100.53(1)°, *Z* = 1, *R*_F = 0.075%. Compounds **3** and **4** are both highly fluorescent in solution and display relative fluorescence quantum yields of ϕ_F = 1.0 and 0.85, respectively. The electrochemistry and electrogenerated chemiluminescence (ECL) of each compound has been investigated. The cyclic voltammogram of **3** in benzene–acetonitrile (9:1) shows that the compound undergoes a reversible reduction and an irreversible oxidation, whereas the cyclic voltammogram of **4** displays the reversible formation of both singly and doubly charged cations and anions. Compounds **3** and **4** undergo ECL to yield blue and orange-red light, respectively, with an ECL efficiency of ~2% for **4**. Emission from **4** is observed in the ECL of unstirred solutions of **3**. This indicates that **4** is produced at the electrode during the ECL experiment, presumably via an electrochemical oxidative coupling process during the anodic potential steps.

Introduction

The discovery of the fullerenes has spurred a renaissance of interest in the synthesis of polycyclic aromatic hydrocarbons (PAHs).¹ Investigations in this area are stimulated not only by the synthetic challenges involved in producing larger, more complex molecules but also by the interesting and potentially useful properties that PAHs display as a whole.

One of the most useful properties of PAHs is their intense fluorescence emissions, a characteristic that has been applied to their qualitative and quantitative analysis.² In 1964, it was shown that the emitting states of PAHs could also be produced by electron-transfer reactions,³ and this discovery sparked interest in what became known as electrogenerated chemiluminescence (ECL). ECL is initiated by the generation at an electrode of ions capable of undergoing energetic electron-transfer reactions. The simplest scheme involves production of radical anions and radical cations of a compound at an electrode surface, with subsequent ion-annihilation reactions generating excited states that are capable of luminescence (eq 1).



Other methods of producing ECL include the use of coreactants or other electrogenerated species capable of reacting with either the anion or cation alone to produce the desired excited state. Many PAH systems have been shown to undergo ECL, with

rubrene and diphenylanthracene being the most studied by far.⁴ Potential applications of ECL include uses such as in display devices,⁵ in the analytical determination of PAHs in minute concentrations,⁶ and as labels in immunoassay.⁷

Here we report the unique synthesis of the soluble, nonalternant PAH, dibenzo{[*f,f'*]-4,4',7,7'-tetraphenyl}diindeno[1,2,3-*cd*:1',2',3'-*lm*]perylene (**4**), via the oxidative coupling of (7,12-diphenyl)benzo[*k*]fluoranthene (**3**) (see Scheme 1). The electrochemistry and photophysical properties of the starting material and product compounds are also presented, along with an investigation of their electrogenerated chemiluminescence.

Experimental Section

Tetra-*n*-butyl ammonium hexafluorophosphate (TBAPF₆) (SACHEM, Inc.) was recrystallized from EtOH/H₂O (4:1) three times and dried at 100 °C before use. Rubrene (Aldrich) was used as received. Diphenylanthracene (Aldrich) was recrystallized from absolute ethanol before use. *N,N,N',N'*-Tetramethyl-*p*-phenylenediamine (TMPD, Eastman Kodak) was sublimed before use. Benzene (Aldrich, ACS grade), cyclohexane (Sigma spectrophotometric grade), and CH₃CN (Burdick and Jackson, UV grade) were used as received after being transported unopened into an inert atmosphere drybox (Vacuum Atmospheres Corp.). All UV, fluorescence, electrochemical, and ECL solutions were prepared in a drybox and were sealed in air-tight vessels for measurements.

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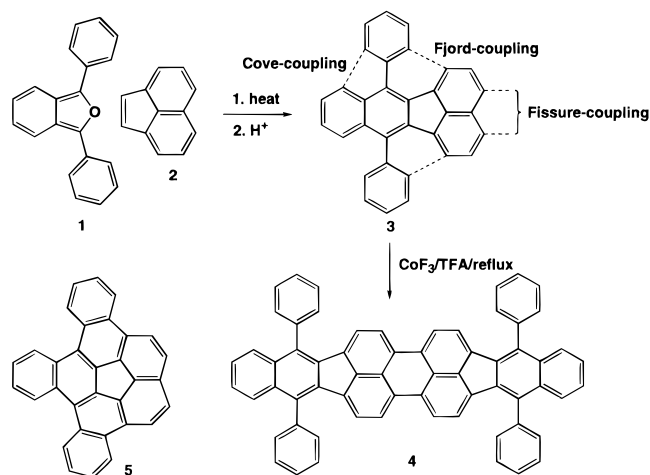
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Scheme 1



¹H-NMR spectra were recorded on a General Electric QE-300 (300 MHz) spectrometer as solutions in deuteriochloroform (CDCl₃). Chemical shifts are expressed in parts per million (ppm, δ) downfield from tetramethylsilane (TMS) and are referenced to CDCl₃ (7.24 ppm) as internal standard. ¹³C-NMR spectra were recorded on a General Electric QE-300 (75 MHz) instrument as solutions in CDCl₃ unless otherwise indicated. Exact mass determinations were obtained on a VG analytical ZAB2-E instrument.

The relative fluorescence efficiency of **3** was measured⁸ in cyclohexane using diphenylanthracene as a standard ($\lambda_{\text{ex}} = 380$ nm, $\phi_{\text{DPA}} = 0.90$ in cyclohexane⁸), and that of **4** was measured in benzene relative to rubrene ($\lambda_{\text{ex}} = 500$ nm, $\phi_{\text{Rubrene}} = 0.98$ in benzene⁹). Fluorescence spectra were recorded on an SLM Aminco SPF-500 spectrofluorometer, and UV spectra were recorded on a Milton Roy Spectronic 3000 array spectrophotometer (5 μ M solutions). Electrochemical measurements were performed on a Bioanalytical Systems 100A electrochemical analyzer or a Princeton Applied Research Model 173/175 potentiostat/universal programmer and Omnigraphic 2000 X-Y recorder (Bausch and Lomb). The working electrode for cyclic voltammetric measurements consisted of an inlaid platinum disk (1.5-mm diameter) that was polished on a felt pad with 0.05- μ m alumina (Buehler, Ltd.) prior to each experiment. A platinum wire served as a counter electrode and a silver wire was utilized as a quasi-reference electrode. All potentials are reported versus SCE and were calibrated by the addition of ferrocene as an internal standard using $E^{\circ}(\text{Fc}/\text{Fc}^+) = 0.424$ V vs SCE. Potentials are reported as half-wave values unless otherwise indicated.

Chronoamperometric data were recorded on the BAS 100A system using a platinum microelectrode (25- μ m diameter), and the data were analyzed as previously described.¹⁰ The ECL efficiency of **4** was measured in benzene-acetonitrile (9:1) solution, using Ru(bpy)₃(ClO₄)₂ in the same solvent mixture as a standard and assuming $\phi_{\text{ECL}}(\text{Ru}(\text{bpy})_3^{2+}) = 0.050$.¹¹ Apparatus and methodologies for the measurement of ECL spectra and ECL efficiencies have been previously reported.¹²

Synthesis of Dibenzotetraphenylperiflanthene (4). A mixture of (7,12-diphenyl)benzo[k]fluoranthene (**3**, 500 mg, 1.24 mmol) and cobalt trifluoride (758 mg, 6.53 mmol) in anhydrous trifluoroacetic acid (20 mL) was heated at reflux for 36 h. Upon cooling, the solution was diluted with water and extracted with dichloromethane (3 \times 100 mL). After washing the dichloromethane extracts with water and saturated brine solution, the extracts were dried (MgSO₄) and evaporated in vacuo to give a black solid. The solid was purified by chromatography over neutral alumina eluting with 10% dichloromethane/hexanes

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Table 1. Crystallographic Data for Compound **4**·3C₇H₈^a

formula	C ₈₅ H ₆₀	ρ_{calc} , g/cm ³	1.25
fw	1081.34	no. of reflns measd	12553
<i>a</i> , Å	10.569(2)	no. of unique reflns	8339
<i>b</i> , Å	11.565(4)	decay correction	0.997–1.02
<i>c</i> , Å	13.001(3)	R_{int} (F ²)	0.041
α , deg	95.05(2)	μ , cm ⁻¹	0.71
β , deg	111.24(1)	crystal size, mm	0.13 \times 0.24 \times 1.4
γ , deg	100.53(1)	R_w (F ²) ^b	0.211
<i>V</i> , Å ³	1435.5(7)	R (F) ^c	0.075
<i>Z</i>	1	goodness of fit, S^d	1.027
<i>F</i> (000)	1140	parameters	401
crystal system	triclinic	Max $ \Delta/\sigma $	<1.9 (U_{ij} 's of some atoms of the disordered toluene)
space group	$P\bar{1}$		
<i>T</i> , °C	-100		
2θ range (deg)	4–60	Min, max peaks (e ⁻ /Å ³)	-0.3, 0.4

^a Data were collected at -100 °C on a Siemens P4 diffractometer equipped with a Nicolet LT-2 low-temperature device and using monochromatized Mo K α radiation ($\lambda = 0.71073$ Å). Data were collected using ω scans with a 1° scan range in ω . Lattice parameters were obtained from the least-squares refinement of 20 reflections with $23.0 < 2\theta < 24.7^\circ$. ^b $R_w = \{\sum w(|F_o|^2 - |F_c|^2)^2 / \sum w(|F_o|^4)\}^{1/2}$, where the weight, w , is defined as follows: $w = 1/[\sigma^2(|F_o|^2) + (a^*P)^2 + b^*P]$; $P = [1/3(\text{maximum of } (0 \text{ or } |F_o|^2) + 2/3|F_c|^2)]$. The parameters a and b were suggested during refinement and are 0.0918 and 0.3572, respectively. ^c The conventional R index based on F where the 4418 observed reflections have $F_o > 4\sigma(F_o)$. ^d $S = [\sum w(|F_o|^2 - |F_c|^2)^2 / (n - p)]^{1/2}$, where n is the number of reflections and p is the number of refined parameters.

to remove nonpolar impurities followed by dichloromethane to give **4** (277 mg, 56%) as a purple-black crystalline solid. Mp ca. 550 °C (differential scanning calorimetry). ¹H NMR (300 MHz, CDCl₃) δ 6.51 (4H, d, $J = 7.7$ Hz), 7.36–7.39 (4H, m), 7.46–7.48 (8H, m), 7.59–7.62 (4H, m), 7.62–7.64 (12H, m), 7.74 (4H, d, $J = 7.7$ Hz). ¹³C NMR (75.2 MHz, CDCl₃) δ 121.5 (CH), 122.9 (CH), 125.3 (C), 125.8 (CH), 126.8 (CH), 127.9 (CH), 129.2 (2CH), 129.9 (C), 130.0 (2CH), 132.8 (C), 134.6 (C), 135.0 (C), 136.0 (C), 136.2 (C), 138.4 (C). HRMS (CI) calcd for C₆₄H₃₇ (M⁺ + 1) 805.2895. Found 805.2898.

X-ray Experimental for C₆₄H₃₆·3C₇H₈. Crystals grew as long, thin red needles from toluene. The data crystal was a needle of approximate dimensions 0.13 \times 0.24 \times 1.4 mm. The data were collected at 173 K on a Siemens P4 diffractometer, equipped with a Nicolet LT-2 low-temperature device and using a graphite monochromator with Mo K α radiation ($\lambda = 0.71073$ Å). Details of crystal data, data collection, and structure refinement are listed in Table 1. Three reflections (0,2,2; 2,5,-4; 4,-2,0) were remeasured every 97 reflections to monitor instrument and crystal stability. A smoothed curve of the intensities of these check reflections was used to scale the data. The scaling factor ranged from 0.997 to 1.02. The data were corrected for Lp effects but not absorption. Data reduction and decay correction were performed using the SHELXTL/PC software package.¹³ The structure was solved by direct methods and refined by full-matrix least-squares¹³ on F¹⁴ with anisotropic thermal parameters for the non-H atoms. The hydrogen atoms were calculated in idealized positions (C–H 0.96 Å) with isotropic temperature factors set to $1.2 \times U_{\text{eq}}$ of the attached atom. The polyaromatic molecule lies around an inversion center and crystallizes with 3 molecules of toluene solvate in the unit cell. One molecule of toluene lies in disorder about an inversion center. The geometry for this molecule, C1b–C7b, was idealized with C–C bond lengths fixed at 1.395 Å. The function, $\sum w(|F_o|^2 - |F_c|^2)^2$, was minimized, where $w = 1/[(\sigma(F_o))^2 + (0.0918^*P)^2 + (0.3572P)]$ and $P = (|F_o|^2 + 2|F_c|^2)/3$. The data were corrected for secondary extinction effects. The correction takes the following form: $F_{\text{corr}} = kF_o/[1 + [8(2) \times 10^{-6}F_c^2\lambda^3/\sin(2\theta)]^{0.25}]$, where k is the overall scale factor. Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the *International Tables for X-ray Crystallography* (1990).¹⁵ Other computer programs used in this work

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are listed elsewhere.¹⁶ All figures were generated using SHELXTL/PC.¹³ Tables of positional and thermal parameters, bond lengths, angles, and torsion angles and figures are located in the supporting information.

Results and Discussion

Synthesis and Solid-State Structure of 4. The known (7,12-diphenyl)benzo[*k*]fluoranthene (**3**) was synthesized by the route outlined in Scheme 1 in a yield greater than 90%.¹⁷ Remarkably, no investigations into the dehydrogenative coupling chemistry of this compound have been reported. We considered that the strategy shown in Scheme 1 would offer a very short and flexible route to a variety of non-benzenoid aromatics capable of dehydrogenation to more highly fused systems via core, fjord, or fissure couplings. The intramolecular fjord coupling would be particularly interesting as it would afford tribenzo[*a,d,g*]corannulene **5**.¹⁸ Upon treatment of **3** with either AlCl₃/NaCl (Scholl reaction),¹⁹ Ti(OCOCF₃)₃,²⁰ or CoF₃/TFA,²⁰ a purple-black crystalline compound was formed whose structure was shown to be the fissure-coupling dimer **4** (56%).²¹ In benzene solution, this compound exhibits a deep red fluorescent color. The results of an X-ray crystallographic analysis of **4** are recorded in Table 1. Bond lengths and angles are listed in Table 2, and Figure 1 contains an ORTEP drawing of the compound and the numbering scheme.

Absorption and Emission. The absorption and emission spectra for compounds **3** and **4** are shown in Figure 2. (7,12-Diphenyl)benzo[*k*]fluoranthene (**3**) exhibits a blue fluorescence, with emission maxima of 418 and 444 nm. The relative fluorescence quantum yield for the compound is $\phi_F = 1.0$, which was measured in cyclohexane with diphenylanthracene as a standard.⁸

Solutions of **4** are also highly fluorescent, exhibiting a bright orange-red fluorescence under ultraviolet irradiation and even a pronounced fluorescence under ambient room lighting. The absorption and emission spectra for the compound are shown in Figure 2b. Absorption bands in the visible region account for the compound's deep red color and also explain its ability to fluoresce under room lighting. The fluorescence spectrum displays two maxima at 596 and 646 nm and mirrors the absorption spectrum with a small Stokes shift of 7 nm. The structured emission observed for both compounds is typical of

Table 2. Bond Lengths (Å) and Angles (deg) for the Non-Hydrogen Atoms of **4**

atom 1	atom 2	atom 3	atom 1–2	atom 1–2–3
C2	C1	C19	1.398(2)	118.1(2)
C19	C1		1.427(3)	
C3	C2	C1	1.406(3)	123.0(2)
C4	C3	C2	1.381(4)	119.4(2)
C5	C4	C20	1.474(4)	106.1(2)
C5	C4	C3		135.9(2)
C20	C4	C3	1.416(3)	117.9(2)
C6	C5	C14	1.376(3)	121.3(2)
C6	C5	C4		130.3(2)
C14	C5	C4	1.446(3)	108.3(2)
C7	C6	C21	1.425(4)	121.5(2)
C7	C6	C5		118.6(2)
C21	C6	C5	1.491(3)	119.9(2)
C8	C7	C12	1.423(3)	119.0(2)
C8	C7	C6		120.8(2)
C12	C7	C6	1.429(3)	120.2(2)
C9	C8	C7	1.348(4)	121.3(2)
C10	C9	C8	1.406(4)	120.4(2)
C11	C10	C9	1.372(3)	120.1(3)
C12	C11	C10	1.418(4)	121.5(2)
C13	C12	C7	1.444(3)	120.3(2)
C13	C12	C11		122.1(2)
C7	C12	C11		117.6(2)
C14	C13	C27	1.377(4)	120.6(2)
C14	C13	C12		117.9(2)
C27	C13	C12	1.491(3)	121.4(2)
C15	C14	C5	1.482(3)	106.9(2)
C15	C14	C13		132.0(2)
C5	C14	C13		121.1(2)
C16	C15	C20	1.385(3)	117.3(2)
C16	C15	C14		136.0(2)
C20	C15	C14	1.414(4)	106.6(2)
C17	C16	C15	1.410(3)	119.4(2)
C18	C17	C16	1.394(4)	123.4(2)
C19	C18	C17	1.430(3)	117.8(2)
C20	C19	C1	1.394(3)	117.7(2)
C20	C19	C18		117.6(2)
C1	C19	C18		124.7(2)
C4	C20	C15		111.8(2)
C4	C20	C19		123.7(2)
C15	C20	C19		124.5(2)
C22	C21	C26	1.396(4)	118.9(2)
C22	C21	C6		119.8(2)
C26	C21	C6	1.395(4)	121.2(2)
C23	C22	C21	1.384(4)	120.4(3)
C24	C23	C22	1.382(4)	120.3(3)

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(21) The systematic name for **4** is dibenzo[*[f,f']*-4,4',7,7'-tetraphenyl]-diindeno[1,2,3-*cd*:1',2',3'-*lm*]perylene. The name of the diindeno core structure has been abbreviated to perflanthene. Perflanthene **1**, was first described in 1937, Braun, J.; Manz, G., *Ber.* **1937**, *70*, 1603. Zinke, A., *Mh. Chem.-Zh.* **1962**, *95*, 1117. λ_{\max} (ε) 540 (4.8), 503 (4.63), 471 (4.25) and 440 (3.76) nm, in 1,2,4-trichlorobenzene.

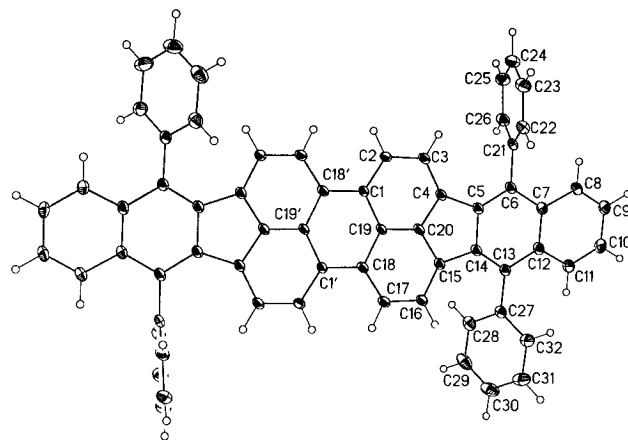
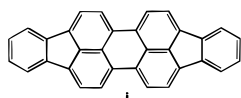


Figure 1. View of compound **4** showing the atom labeling scheme. Thermal ellipsoids are scaled to the 30% probability level. Hydrogen atoms are drawn to an arbitrary scale. The molecule lies around a crystallographic inversion center. Atoms marked by a prime are related by $2 - x, 1 - y, 1 - z$.

planar, ridged PAHs.²² A relative fluorescence quantum yield of $\phi_F = 0.85$ was measured for compound **4** in benzene using

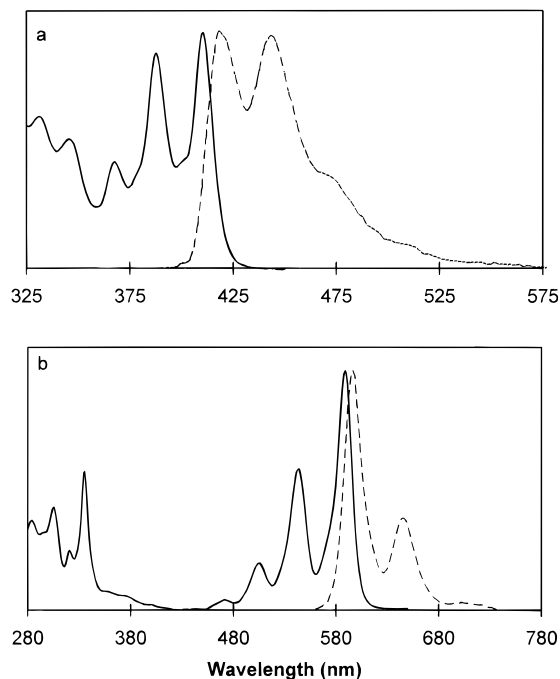


Figure 2. Absorption and emission spectra of (a) **3** ($\lambda_{\text{ex}} = 380$ nm) and (b) **4** ($\lambda_{\text{ex}} = 500$ nm) in benzene.

rubrene as a standard.^{8,9} Note the difference in emission properties of this compound and that of its parent core molecule. Periflanthene²¹ is reported to possess a very low luminescence quantum yield ($\phi_{\text{F}} = 0.015$), and its highest energy emission is at 540 nm.²³ Thus, the addition of terminal benzo groups and phenyl ligands has the expected effect of lowering the energy of the transition, but also increases the compound's fluorescence efficiency dramatically.

Electrochemistry. The redox behavior of compounds **3** and **4** was probed by solution electrochemistry, and the resulting cyclic voltammograms are shown in Figure 3. Both species display limited solubility in acetonitrile, and thus a solvent mixture of benzene and acetonitrile (9:1) was employed. Solutions of up to approximately 5 mM of **3** and 0.4 mM of **4** were prepared in this solvent combination and proved adequate for electrochemical and ECL measurements. Compound **3** displays a reversible reduction at -1.90 V vs SCE to form the radical anion and an irreversible oxidation at $E_{\text{pa}} \sim 1.6$ V vs SCE (Figure 3a), with the peak current for the oxidation being noticeably larger than that for the reduction. The unstable radical cation of **3** reacts to form products that are themselves oxidized at this potential, and thus an increase in the peak current is observed due to the transfer of more than one electron for each molecule of **3** oxidized at the electrode (vide infra).

As can be seen in the cyclic voltammogram of **4** (Figure 3b), two oxidation and two reduction features are observed for the compound within the solvent electrochemical window. **4** undergoes reduction at -1.20 V and again at -1.45 V vs SCE to generate radical anions and dianions, respectively. Oxidation of the neutral compound to the radical cation and dication occurs at potentials of 0.946 and 1.29 V vs SCE. All peak separations compare reasonably well to that of added ferrocene under the same conditions,²⁴ and chronoamperometric measurements confirm that all four waves correspond to one-electron pro-

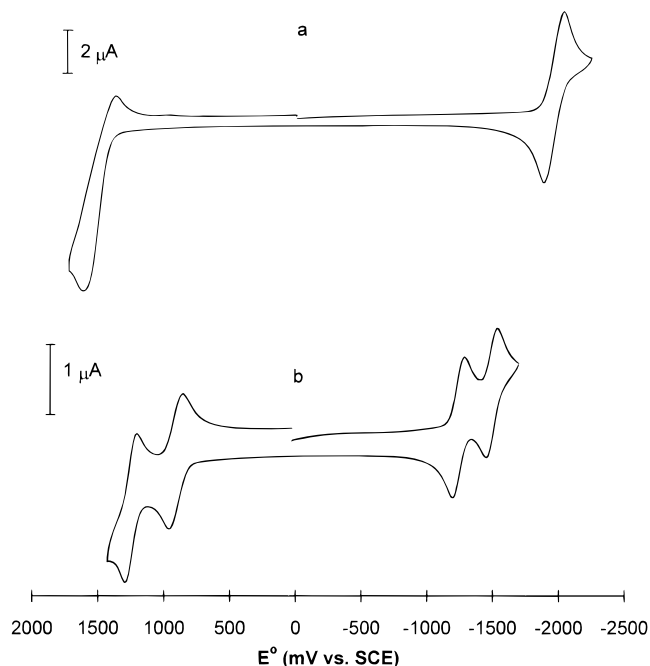


Figure 3. Cyclic voltammogram of (a) 1.5 mM **3** and (b) 0.31 mM **4** in benzene-acetonitrile (9:1), scan rate 100 mV/s. Supporting electrolyte 0.1 M TBAPF₆.

cesses.²⁵ As judged by the symmetry of the voltammetric waves, the redox processes appear reversible and indicate that all of the charged species are quite stable under the experimental conditions employed.

Studies of the redox behavior of many PAHs have been reported;²⁶ however, such investigations on the larger members of this class of molecules are rare, likely due to their low solubility in common electrochemical solvents. Typically, stable anions and dianions of PAH's can be generated in aprotic solvents,^{26c} with more stable ions being formed for the compounds with larger, more extended π systems. For example, the cyclic voltammogram in DMF of periflanthene,²¹ the parent core structure of **4**, indicates reversible formation of the radical anion and dianion,^{26b} and both charged species have been synthesized chemically by alkali metal reduction.²⁷ Radical cations of PAHs tend to be much less stable than their anions. Those that have been produced electrochemically usually display an increase in reversibility at higher scan rates,^{26d} with reactions such as deprotonation and polymerization occurring at slower scan rates. Reports of stable dications of PAHs are scarce. An example is rubrene, which exhibits a reversible first and second oxidation in benzonitrile at a reasonably slow scan rate of 100

(24) Immediately after recording the cyclic voltammogram in Figure 2, ferrocene was added and another voltammogram recorded. Peak separations in this voltammogram were 81 mV for the $4^{2+}/4^{1+}$ couple, 105 mV for $4/4^{1+}$, 81 mV for Fc/Fc^{1+} , 91 mV for $4/4^{1-}$, and 83 mV for $4^{1-}/4^{2-}$.

(25) Solutions used for chronoamperometry were similar to those used for cyclic voltammetry, and measurements were accomplished as described in ref 10. Diffusion coefficients and n values measured for the various redox processes are as follows: $4/4^{1+}$, $D = 4.5 \times 10^{-6}$ cm²/s, $n = 1.4$; $4^{1+}/4^{2+}$, $D = 1.1 \times 10^{-5}$ cm²/s, $n = 1.1$; $4/4^{1-}$, $D = 5.9 \times 10^{-6}$ cm²/s, $n = 1.1$; $4^{1-}/4^{2-}$, $D = 1.4 \times 10^{-5}$ cm²/s, $n = 0.9$.

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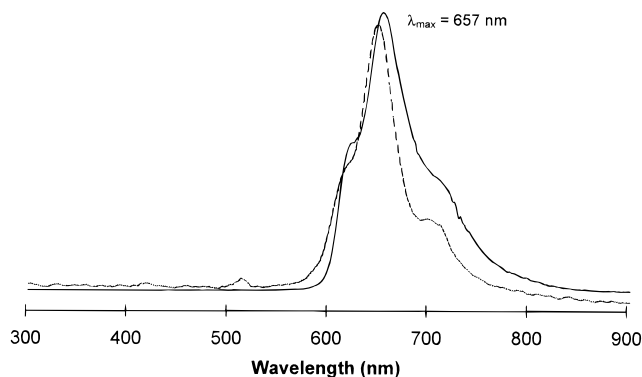


Figure 4. ECL spectra in benzene-acetonitrile (9:1) and 0.1 M TBAPF₆ of (—) 0.2 mM **4** ($4^+/4^-$ reaction) and (---) 0.2 mM **4** and 0.2 mM TMPD (TMPD⁺/4⁻ reaction).

mV/s.²⁸ The extended π system of compound **4** presumably stabilizes both the cation and dication toward further decomposition reactions. In fact, the oxidation of **4** to its dication is reversible at scan rates as slow as 10 mV/s.

Electrogenerated Chemiluminescence. Compound **4** is a prime candidate for electrogenerated chemiluminescence because it possesses stable ions and a high fluorescence efficiency. Indeed, light is produced at an electrode surface in solutions of **4** if the electrode potential is pulsed between the first reduction potential and the first oxidation potential of the compound. For these ECL experiments, solutions similar to those used for the electrochemical experiments mentioned above were utilized. This ECL is a result of annihilation reactions between the electrogenerated anions and cations, which leave molecules of **4** in excited states (eq 1). These molecules then relax from the excited singlet state by photon emission or by other non-radiative pathways.

The efficiency of the ECL process for **4** has been determined by comparing the photons of light produced per coulomb passed with a standard whose ECL efficiency is known. Using Ru(bpy)₃²⁺ as a standard, we obtained an efficiency of $\phi_{\text{ECL}} = 0.021$ for complex **4**. That is, for each 100 anions or cations formed by reduction or oxidation at the working electrode, approximately 2 photons are produced by subsequent reactions. This efficiency is about half that of Ru(bpy)₃²⁺ ($\phi_{\text{ECL}} = 0.050$).¹¹ The light produced from a 0.2 mM solution of **4** is easily visible in a darkened room and appears orange-red. The ECL spectrum as measured with a spectrometer coupled to a CCD camera is shown in Figure 4. The emission is centered around 660 nm. Typically, such spectra are identical in energy to the fluorescence spectrum of the compound, since the same singlet state is responsible for the emission in each instance. The ECL spectrum in Figure 4 does not display the structure exhibited by the fluorescence spectrum (Figure 2b), due to the lower resolution of the spectrometer used to measure the former. However, the spectrum does overlap the fluorescence emission as expected, and the slight red shift and change in relative peak heights of the ECL spectrum can be explained by self absorption of the higher energy wavelengths (an inner filter effect), as solutions used for ECL measurements were much more concentrated than those employed for fluorescence measurements.

By pulsing the working electrode between the second oxidation and reduction potentials, higher currents and a much brighter ECL are observed than are produced by pulsing between the first oxidation and reduction potentials. This emission can clearly be seen in a lighted room, and its spectrum is identical to that shown in Figure 4.

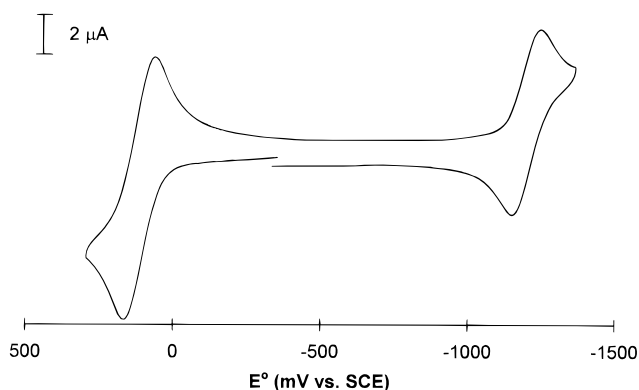


Figure 5. Cyclic voltammogram of 0.40 mM TMPD and 0.40 mM **4** in benzene-acetonitrile (9:1) (0.1 M TBAPF₆). The peak in the positive region is due to TMPD oxidation, while the peak in the negative region is due to the reduction of **4**.

Since the ECL spectrum is of similar energy to the fluorescence emission, the singlet is likely the emitting state in each case. The total free energy available in the $4^+/4^-$ annihilation reaction, ΔG_{ann} , is 2.15 eV based on the difference between the half-wave potentials of the first oxidation and first reduction peaks in the cyclic voltammogram. The energy (ΔH_s) needed to populate the singlet state, as calculated from the lowest energy absorption peak of 596 nm, is 2.10 eV. The equation governing the relation between reaction energetics and singlet energy for a reaction that produces a singlet (an S-route system) is^{4a}

$$\Delta G_{\text{ann}} \geq \Delta H_s - T\Delta S \approx \Delta H_s + \sim 0.1 \text{ eV} \quad (2)$$

i.e., the free energy available from the electron transfer must be larger than that needed to produce the excited singlet state. Thus the energy available from our ion-annihilation reaction is close to that required for direct population of the singlet state. Alternatively, the singlet can be produced via the T-route, where the annihilation reaction (eq 1) produces a triplet, with the luminescent singlet state being formed via triplet-triplet annihilation (TTA). Rubrene, for example, undergoes ECL via both S- and T-routes.^{28,29}

To determine whether the TTA mechanism was operative in this system, the annihilation reaction between the radical anion of **4** and the radical cation of a donor molecule whose oxidation potential was much lower than that of **4** was carried out. Since the free energy of the electron-transfer reaction in this case is not sufficient to populate the singlet state of **4** but presumably able to produce triplet states, any singlet emission observed would be a result of triplet-triplet annihilations.^{4b}

The cyclic voltammogram of an equimolar solution of **4** and the donor molecule TMPD is shown in Figure 5. The energy available in the TMPD⁺/4⁻ annihilation reaction ($\Delta G_{\text{ann}} = 1.31$ eV) is not enough to directly populate the singlet state of **4**. However, ECL is observed from this system by alternately generating these two ions at an electrode surface, and the emission is similar to that produced via the $4^+/4^-$ annihilation (Figure 4). The electron transfer between TMPD radical cations and the radical anions of **4** thus presumably populates the triplet state of **4**, which then undergo triplet-triplet annihilation reactions to form singlet states. The relatively low ECL efficiency of **4** compared to its fluorescence quantum yield is in part due to the involvement of this inefficient TTA mechanism.

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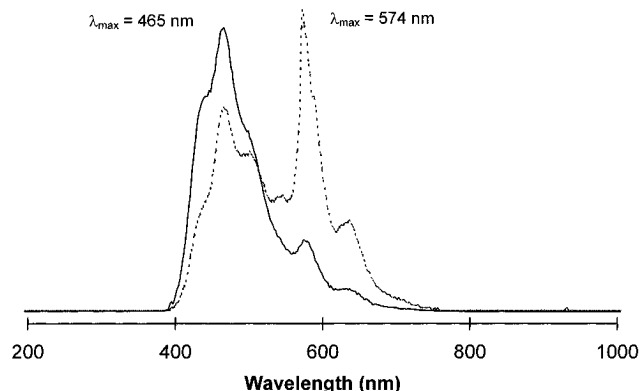


Figure 6. ECL spectrum of **3** in stirred (—) and unstirred (---) benzene–acetonitrile (9:1) solutions (0.1 M TBAPF₆).

Compound **3** also produces ECL, despite the fact that the radical cation is unstable.³⁰ Light is produced at the electrode when the potential is pulsed between the oxidation and reduction potentials of the compound; however, the spectrum of the emitted light depends upon the experimental conditions employed. Figure 6 illustrates this point by showing the ECL spectral emission from stirred and unstirred solutions of **3**. The energy of the light emitted from the electrode immersed in the stirred solution matches that of the fluorescence spectrum for the compound, as would be expected from the arguments above. This blue light is quite bright and can be easily observed in a lighted room. The ECL spectrum of the unstirred solution is more complicated, however. We believe this is due to the oxidative coupling of **3** to form **4** at the electrode surface during the anodic pulse. Thus, the spectrum contains features attributable to the ECL of **3** and **4**, since the potentials employed are sufficient to form anions and cations of both compounds. Stirring the solution prevents the buildup of the red-emitting **4** at the electrode, thereby lowering the intensity of its emission with respect to that in the unstirred solution. It is interesting to observe the electrode during the unstirred ECL experiment. The outer edges of the planar electrode glow bright blue, while the central portion emits a red glow due to the ECL of **4** that builds up in this area. Further experiments to investigate the mechanism and kinetics of this coupling reaction are under way.

Conclusions

The nonalternant hydrocarbon dibenzotetraphenylperiflanthene (**4**) has been synthesized by the oxidative coupling of (7,12-diphenyl)benzo[*k*]fluoranthene (**3**). The reaction is high-yielding and represents a simple route to large polyaromatic

(30) This has been observed in other ECL reaction studies^{4a} and is based on the very rapid reaction between R^{•-} and R^{•+} competing with that of the decomposition of R^{•+}.

systems. This coupling probably also occurs during electrochemical oxidation of **3**, as suggested by the ECL experiments discussed above.

The electrochemistry of both starting material and product has been investigated. Complex **3** displays a reversible reduction; however, its oxidation is irreversible due to the reaction of its radical cations, probably to eventually yield **4**. This coupling has been demonstrated by the observed emission from **4** during ion-annihilation ECL of its precursor, **3**, under certain experimental conditions. Compound **4** displays well-behaved electrochemistry. The **4**²⁺, **4**¹⁺, **4**¹⁻, and **4**²⁻ ions are all accessible in a benzene–acetonitrile solvent system, and all appear stable under the experimental conditions. The neutral compound is an efficient fluorescer, with a relative fluorescence quantum yield of 0.85. The electrogenerated chemiluminescence of **4** produced via an ion-annihilation route is similar in energy to that of its fluorescence. However, the ECL efficiency is relatively low given the high fluorescence efficiency and is a result of indirect population of the singlet state during the electron-transfer reaction (TTA mechanism).

Further synthetic studies are in progress to fabricate other large PAH systems using this versatile oxidative coupling reaction. In addition, attempts to synthesize derivatives of the fluoranthene complex, **3**, that favor fjord coupling to yield corranulene-like products (like **5**, Scheme 1) are planned. The photophysical and electrochemical properties of these new species will be investigated in light of the unique characteristics of the compounds discussed here. The effect of molecular structure on ECL performance and potential applications of such systems will also be considered.

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Supporting Information Available: Tables of fractional coordinates, equivalent isotropic and anisotropic thermal parameters, bond lengths, bond angles, torsion angles, and side-on and unit cell packing ORTEP views for compound **4** (11 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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