J. Phys. Chem. A **2005,** *109,* 7677−7681

Photophysical Properties of Anthanthrene-Based Tunable Blue Emitters

Bipin K. Shah* and Douglas C. Neckers*

Center for Photochemical Sciences,[1] Bowling Green State University, Bowling Green, Ohio 43403

Jianmin Shi,* Eric W. Forsythe, and David Morton

U.S. Army Research Laboratory, AMSRD-SE-EO, 2800 Power Mill Road, Adelphi, Maryland 20783

Received: May 5, 2005; In Final Form: July 12, 2005

Anthanthrene (**1**) derivatives substituted at the 4,10 and 6,12 positions (**2**−**6**) were synthesized as promising candidates for organic light emitting diodes (OLEDs). The emission of these compounds can be manipulated in the blue region ($\lambda_{\max} = 437-467$ nm) through structural modifications. Photophysical and electrochemical properties ($\phi_F = 0.20-0.47$; $\tau_F = 2.97-6.06$ ns; HOMO−LUMO energy gap = 2.25−2.56 eV) as well as geometry optimized structures of **1**−**6** are reported.

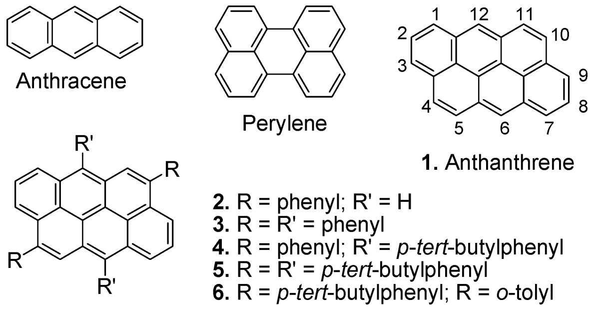
Introduction

Since the initial work by Tang and VanSlyke,[2] interest in organic light-emitting diodes (OLEDs) has been steadily growing. Their performance now approaches a commercially viable level for applications such as low-cost, flat-panel displays. Nevertheless, considerable advances are still to be made, especially toward full-color displays,[3] which require three primary colors, i.e., blue, green, and red emitting materials. The actively pursued areas of research are improvements in the efficiency and the stability (lifetime) of such devices and the tuning of color using different emitting materials.[4] The design and synthesis of blue emitting materials suitable for the fabrication of stable OLEDs remains one major obstacle. Enormous effort has focused on the achievement of higher efficiency and longer operational stability in blue electroluminescent (EL) devices.[5]

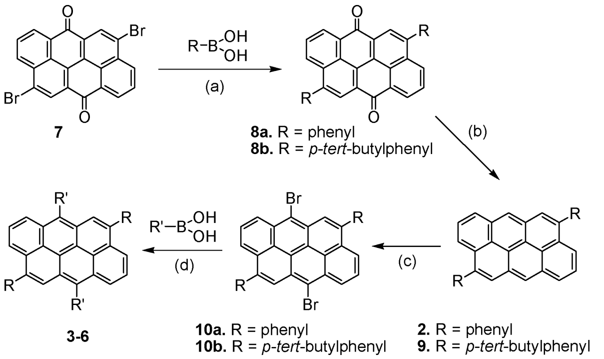
Anthracene exhibits violet luminescence in the solid state and in solution and is one of the earliest reported luminescent materials. Its derivatives such as 9,10-di-2-naphthylanthracene and 2-*tert*-butyl-9,10-di-2-naphthylanthracene doped with aggregation-resistant 2,5,8,11-tetra-*tert*-butylperylene have been successfully used in commercial OLED products.[6] On the basis of the reported efficiency and stability of anthracene derivatives, we have designed and synthesized a new class of anthanthrene-based blue emitters.[7] These compounds are structurally related to anthracene and perylene (Chart 1). Anthanthrene (**1**) emits blue in solution and shows a higher reactivity at its 4,10 and 6,12 positions, similar to the reactivity at the 9,10 positions of anthracene.[8] Therefore, 4,10-diphenyl substituted (**2**) and 4,6,-10,12-tetrasubstituted anthanthrene derivatives (**3**−**6**) were selected for this study. The synthesis, photophysical, and electrochemical properties as well as geometry optimized structures of this new class of blue emitting materials are reported. We show that their emission can be manipulated in the blue region by modifying structure.

Results and Discussion

CHART 1: Chemical Structures of Anthracene, Perylene, Anthanthrene, and Substituted Anthanthrenes



SCHEME 1[a]



[a] (a) Pd(PPh$_3$)$_4$, 18-Crown-6, 2N K$_2$CO$_3$, Toluene/EtOH, reflux overnight. (b) 1 M BH$_3$.THF complex, THF, 70 °C, 3 h. (c) Br$_2$, CH$_2$Cl$_2$, room temperature to 50 °C, 2−3 h. (d) Pd(PP$_3$)$_4$, 2N K$_2$CO$_3$ or 3 eq. wt. of NaOH, Toluene/EtOH, reflux overnight.

The synthesis of **2**−**6** involves a Suzuki coupling of 4,9-dibromoanthanthrone (**7**) with phenylboronic acid or 4-*tert*-butylpenylboronic acid to yield the corresponding diarylanthanthrone (**8a**,**b**) (Scheme 1). These were reduced with BH$_3$·THF to the corresponding 4,10-diarylanthanthrenes. Bromination of the latter followed by a second Suzuki coupling with a suitable arylboronic acid gave the desired anthanthrene derivatives (**2**−**6**), which were purified by train sublimation.

The absorption spectra of **1**−**6** (10^{-5} to 10^{-7} M) indicated no ground-state charge-transfer complex formation. The absorption spectra of some representative examples recorded in CH$_2$Cl$_2$ are presented in Figure 1. Dilute solutions of **1**−**6** showed

---

* Corresponding authors. E-mail: B.K.S., bipin@bgnet.bgsu.edu; D.C.N., neckers@photo.bgsu.edu; J.S., jshi@arl.army.mil.

10.1021/jp052337z CCC: $30.25

TABLE 1: Photophysical Properties of 1−6 Measured in CH_2Cl_2[a]

compound	A_{max} (nm)/logϵ (L mol^{-1} cm^{-1})	λ_{max} (nm)	ϕ_F	τ_F (ns) a	τ_F (ns) b	$10^{-7}k_R{}^0$ (s^{-1})	$10^{-8}k_{NR}{}^0$ (s^{-1})
1	234/4.95, 308/4.94, 433/4.80	437	0.24 ± 0.01	2.85	3.06	7.84	2.48
2	246/4.93, 317/4.99, 439/4.68	442	0.33 ±0.01	3.83	4.21	7.84	1.59
3	251/4.87, 322/4.95, 454/4.70	462	0.26 ± 0.02	2.87	2.97	8.75	2.49
4	251/5.10, 322/5.18, 454/4.87	465	0.26 ± 0.02	2.91	2.98	8.72	2.48
5	252/5.00, 324/5.06, 456/4.80	467	0.27 ± 0.01	2.90	3.01	8.97	2.43
6	250/5.03, 321/5.05, 447/4.68	455	0.28 ± 0.01	3.03	3.39	8.26	2.12

[a] Excitation wavelength = 330 nm for measuring ϕ_F and τ_F; decay was monitored at the corresponding λ_{max} for τ_F. (a) τ_F values measured from air saturated solutions. (b) τ_F values measured from argon saturated solutions. The ϕ_F values are relative to that of 9,10-diphenylanthracene (0.90 in cyclohexane). The radiative ($k_R{}^0$) and nonradiative ($k_{NR}{}^0$) rate constants were calculated using τ_F values measured from argon saturated solutions.

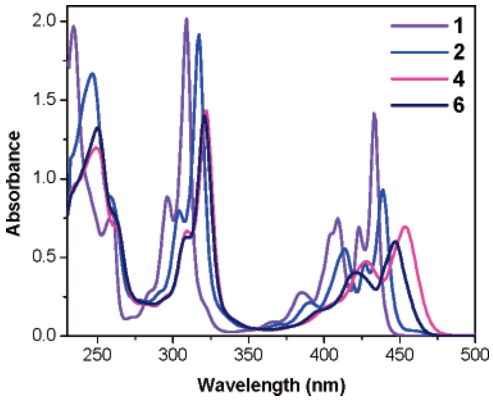


Figure 1. Absorption spectra of **1** (2.23×10^{-5} M), **2** (1.96×10^{-5} M), **4** (1.16×10^{-5} M), and **6** (1.25×10^{-5} M) recorded in CH_2Cl_2.

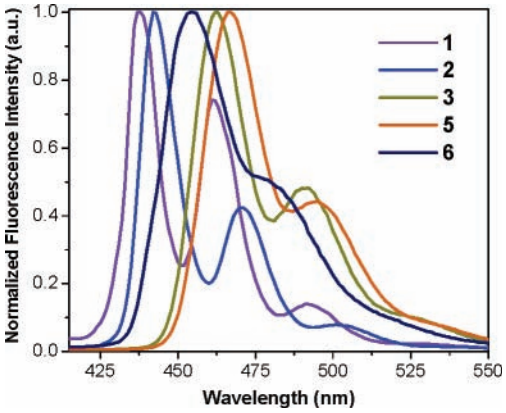


Figure 2. Normalized fluorescence spectra of **1**−**3**, **5**, and **6** recorded in CH_2Cl_2.

blue fluorescence in several solvents; the fluorescence spectra of **1**−**6** recorded in CH_2Cl_2 are presented in Figure 2. The absorption maxima (A_{max}), emission maxima (λ_{max}), fluorescence quantum yields (ϕ_F), and lifetimes of fluorescence (τ_F) of **1**−**6** measured in CH_2Cl_2 are reported in Table 1. Substitution at the 4,10 and 6,12 positions of **1** causes a red shift in the A_{max} and λ_{max}. The red shift is systematic in a similar series of compounds. For example, the λ_{max} value increases gradually with increasing phenyl substitution in **1** (437 nm), **2** (442 nm), and **3** (462 nm). The increase in the emission maxima of 5 nm from **1** to **2** is interestingly lower than that from **2** to **3** (20 nm).

The red shifts in emission maxima seem related to an effective increase in the delocalization of π electrons in the molecules due to aryl substitution. To estimate the effect of structure on the photophysical properties, we optimized the geometries of the ground state of the molecules by the density functional theory (DFT) method using B3LYP/6-31G* level of basis sets. The structures of **1**, **3**, and **5** are depicted in Figure 3. The phenyl groups are expectedly out of the plane of the anthanthrene core. However, they are not completely orthogonal, allowing some degree of conjugation between the anthanthrene core and the phenyl substitutions. Replacement of the phenyl groups with the *o*-tolyl groups at the 6,12 positions allowed a slight increase in the orthogonality of the *o*-tolyl groups and the anthanthrene core. This is also verified by the experimentally observed blue shift in the λ_{max} value of **6** (455 nm) compared to that of **5** (467 nm).

Fluorescence decay of **1**−**6** (see Figure 1, for example) could be satisfactorily fitted with monoexponential functions, indicating emission from a single excited state (S_1 state) in each case. The τ_F values were found to be ∼3 ns for each of the compounds except for **2**, which showed a relatively larger fluorescence lifetime (4.24 ns). The τ_F values obtained from nondegassed solutions of each were lower than those obtained from argon-degassed solutions (Table 1).

The ϕ_F values of the anthnathrene and its derivatives (**1**−**6**) measured in CH_2Cl_2 fall between those of anthracene and perylene. Relative to the ϕ_F of 9,10-diphenylanthracene (0.90 in cyclohexane),[8] the ϕ_F values of **1**−**6** were obtained in the range 0.24−0.33 in CH_2Cl_2 under 330 nm excitation.[9] The ϕ_F values of these molecules were found to be much lower than those of perylene and 2,5,8,11-tetra-*tert*-butylperylene (TBP) (0.93 and 0.85, respectively, in CH_2Cl_2 obtained under 380 nm excitation). Surprisingly, our preliminary reports on the electroluminescent (EL) emission of **2** and **5** showed them to be as good as TBP.[10] It is also noted that the ϕ_F of **1** was 2.4 times that of anthracene. The ϕ_F of the later was measured 0.10 ± 0.02 in CH_2Cl_2 under similar experimental conditions, which is lower than the value obtained in ethanol (0.27)[11,12] or benzene (0.27),[11,12] but close to the value determined in $CHCl_3$ (0.13)[13] against quinine hydrogen sulfate in 0.05 M H_2SO_4 as reference.

Substitution of the 9,10 positions of anthracene by several groups, e.g., methyl, phenyl, or cyano, usually enhances the ϕ_F to ∼0.8−0.9.[12] However, a similar effect was not observed when **1** was substituted at the 4,10 or 6,12 positions. The ϕ_F values of the derivatives of anthanthrene included in this study were found to be similar or only slightly higher than that of **1**.

No phosphorescence was observed from any of the compounds, indicating that about 70−75% ($\sim 1.0 - \phi_F$) of excited molecules decay without radiation in solution. The radiative (fluorescence) rate constants ($k_R{}^0$) of deactivation of the singlet states (ϕ_F/τ_F) of **1**−**6** were found to be $\sim 8 \times 10^7$ s^{-1} in CH_2Cl_2, about 3 times lower than the corresponding nonradiative rate constants ($k_{NR}{}^0 \sim 2.5 \times 10^8$ s^{-1}). The latter are the sum of the rate constants of all nonradiative pathways that the singlet state may follow to deactivate. It is known that the rate of $S_1 \rightarrow T_1$ intersystem crossing (ISC) for rigid aromatic molecules falls in the range of $\sim 10^6$ to 10^8 s^{-1} and that internal conversion from the S_1 surface cannot compete with $S_1 \rightarrow T_1$ ISC.[14] Thus, the nonradiative rate constants observed for **1**−**6** probably represent the rate constants of $S_1 \rightarrow T_1$ ISC.[15]

TABLE 2: Photophysical Properties of 1 and 5 Measured in Different Solvents[a]

	1					**5**				
solvent	λ_{max} (nm)	ϕ_F	τ_F (ns)	k_R^0 (s^{-1})	$10^{-8}k_{NR}^0$ (s^{-1})	λ_{max} (nm)	ϕ_F	τ_F (ns)	k_R^0 (s^{-1})	$10^{-8}k_{NR}^0$ (s^{-1})
cyclohexane	436	0.31 ± 0.01	5.02	6.17×10^7	1.37	463	0.23 ± 0.01	3.13	7.35×10^7	2.46
toluene	436	0.47 ± 0.01	3.48	1.35×10^8	1.52	467	0.41 ± 0.03	3.02	1.36×10^8	1.95
dichloromethane	437	0.24 ± 0.03	3.06	7.84×10^7	2.48	467	0.27 ± 0.02	3.01	8.97×10^7	2.42
methanol	436	0.38 ± 0.04	6.06	6.27×10^7	1.02	462	0.21 ± 0.02	3.49	6.02×10^7	2.26
acetonitrile	436	0.32 ± 0.01	5.49	5.83×10^7	1.24	464	0.20 ± 0.01	3.56	5.62×10^7	2.25

[a] Excitation wavelength = 330 nm for measuring ϕ_F and τ_F; decay was monitored at the corresponding λ_{max} for τ_F. The ϕ_F values are relative to that of 9,10-diphenylanthracene (0.90 in cyclohexane).

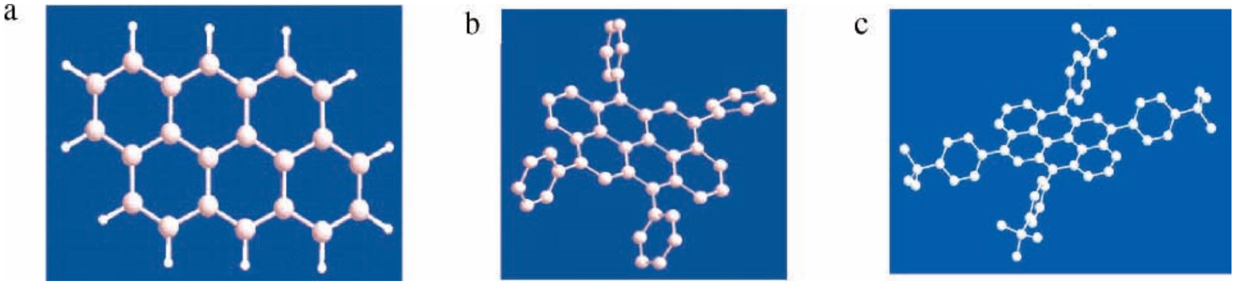


Figure 3. Structure of (a) **1**, (b) **3**, and (c) **5** optimized by the density functional theory (DFT) method at the B3LYP/6-31G* level. H-atoms removed structures of **3** and **5** are shown for clarity.

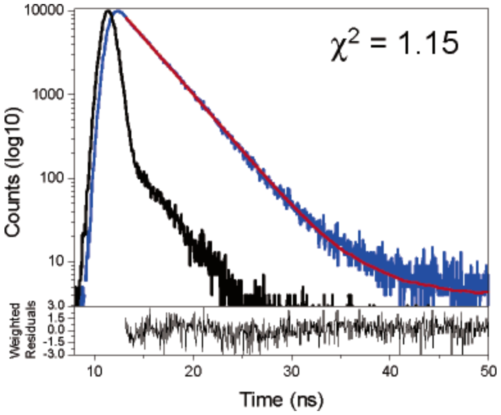


Figure 4. Fluorescence decay of **1** monitored at λ_{max} = 437 nm in CH_2Cl_2; excitation wavelength = 330 nm.

TABLE 3: Electrochemical Properties and HOMO−LUMO Energy Gaps (E_{H-L}) of 1 and 3−5

compound	oxidation potential (V)[a]	reduction potential (V)[a]	E_{H-L}[a] (eV)	E_{H-L}[b] (eV)	dipole[b] (D)
1	+1.04	−1.52	2.56	2.88	0.0
3	+0.76, +1.28	−1.52	2.28	2.78	0.072
4	+0.79, +1.36	−1.56	2.35	2.79	0.035
5	+0.71, +1.27	−1.54	2.25	2.77	0.093

[a] Determined from cyclic voltammetry (solvent, CH_2Cl_2). [b] Calculated using density functional theory method [B3LYP/6-31G(d)].

The similar λ_{max} values (within 5 nm range) of emissions of **1** and **5** in different solvents indicate a negligible solvatochromic effect on their emission (Table 2). The polarity of solvent has no systematic effect on their ϕ_F and τ_F values. The ϕ_F of **1** (0.47) and **5** (0.41) are the highest in toluene among the solvents employed. The ϕ_F of **1** in toluene (0.47) was found to be lower than the absolute quantum yield of fluorescence reported for **1** in benzene (0.62).[11] It is generally believed that the excited singlet state of polyaromatic hydrocarbons is more polar than the ground state. Although the τ_F values of each of **1** and **5** decrease going from cyclohexane to dichloromethane, they were found to be higher in polar solvents such as methanol and acetonitrile than those in cyclohexane or toluene.

The nonradiative rate constants of **1** ($k_{NR}^0 \sim (1-2) \times 10^8$ s^{-1}) were found to be 2−3 times higher than the respective radiative rate constants ($k_R^0 \sim (6-8) \times 10^7$ s^{-1}) in almost all solvents employed, except for toluene (Table 2). The observation was similar for **5**. The trend is also similar to that observed for anthracene. The nonradiative rate constants of the later ($\sim(1-2) \times 10^8$ s^{-1}) are 2−3 times higher than the radiative rate constants ($\sim(5-6) \times 10^7$ s^{-1}) in various solvents such as cyclohexane and ethanol.[16] It is, however, interesting to note that the radiative and nonradiative rates of deactivation of the singlet states of both **1** and **5** are comparable in toluene. Thus, fluorescence becomes more competitive to $S_1 \rightarrow T_1$ ISC in toluene than in any other solvent employed for **1** and **5**.

Cyclic voltammetry (CV) was employed to investigate the electrochemical properties of **1** and **3**−**5**. The CV graphs were obtained with a positive scan from 0 to 1.7 V and a negative scan from 0 to −2 V with the compounds in 0.1 M tetrabutylammonium perchlorate in anhydrous CH_2Cl_2. CV revealed oxidation and reduction potential peaks of **1** at +1.04 V and −1.52 V, respectively (Table 3). The oxidation potential of **1** is in good agreement with the reported value (+0.99 V).[17] Reduction potentials of **3**−**5** were similar to that of **1**. Nevertheless, two oxidation potentials were recorded for **3**−**5**. This again demonstrates the structural proximity of anthanthrene and anthracene. The latter shows a single one-electron oxidation, while 9,10-disubstituted anthracene, e.g., 9,10-dipenylanthracene shows two well-defined one-electron oxidations at +1.22 and +1.6 V.[18] Interestingly, the relative HOMO−LUMO energy gaps estimated[19] from the oxidation and reduction potentials of **1**, **3**, **4**, and **5** show a similar trend to that obtained from DFT calculations. For example, the HOMO−LUMO gap either measured from CV or obtained by calculation is the highest for **1** and the lowest for **5**.

Experimental Section

Solvents and reagents were used as received from commercial suppliers. $Pd(PPh_3)_4$ and anthanthrene (**1**) were purchased from Strem Chemicals and AccuStandard, respectively. Standard grade silica gel (60 Å, 32−63 μm) and silica gel plates (200 μm) were purchased from Sorbent Technologies. Reactions that required anhydrous conditions were carried out under argon in oven-dried glassware. Tetrahydrofuran (THF) and CH_2Cl_2 were distilled under argon from K−Na alloy and CaH_2, respectively.

Mass spectra were recorded on Shimadzu GCMS-QP5050A instrument equipped with a direct probe (ionization 70 eV). Matrix assisted laser desorption ionization (MALDI) spectra were obtained using Bruker Daltonic Omniflex instrument (N_2 laser, 337 nm). A Bruker spectrometer (working frequency 300.0 MHz for ^{1}H) was used to record the NMR spectra. $CDCl_3$ was the solvent for NMR and chemical shifts relative to TMS at 0.00 ppm are reported in parts per million (ppm) on the δ scale. Elemental analyses were performed at Atlantic Microlab, Inc., Atlanta, GA. Absorption and fluorescence spectra were recorded on a Shimadzu UV-2401 spectrophotometer and a Fluorolog-3 spectrometer, respectively. All measurements were carried out at room temperature.

General Synthetic Procedure. The synthesis of **5** is described as a representative example; **2**−**6** were synthesized using similar procedures. 4,9-dibromoanthanthrone (**7**, 5 mmol, 2.30 g) and 4-*tert*-butylphenylboronic acid (12 mmol, 2.15 g) were mixed in a 250 mL flask containing 150 mL of toluene. Ethanol (15 mL) and 2 N K_2CO_3 solution in water (25 mL) were added. After bubbling the mixture with nitrogen for ~15 min, $Pd(PPh_3)_4$ (0.01 g) and 18-crown-6 (0.01 g) were added to it. The mixture was refluxed overnight keeping it under nitrogen. After reaction was complete, the mixture was cooled and washed with water four times (150 mL × 4) in a separatory funnel. The toluene layer was collected, filtered, and washed with acetone. The residue (di-*p*-*tert*-butylphenylanthanthrone, **8b**, 2.2 g, yield ~80%) was oven-dried overnight and used in the next step without further purification.

8b (3.5 mmol, 2 g) was placed in a dry and nitrogen-filled flask containing 300 mL of dry THF. BH_3·THF (1 M, 10 mmol, 10 mL) was slowly added to the above stirring suspension while the temperature increased gradually to 70 °C. The reaction mixture was stirred at 70 °C under nitrogen for 3 h during which time it turned into a blue fluorescing solution. To ensure the complete reduction, 3 mmol of BH_3·THF was added again and the reaction mixture was stirred for one more hour. The solution was cooled and the excess of BH_3·THF was quenched with methanol. The mixture was filtered and the solvent evaporated in vaccuo to produce a yellowish solid. The blue fluorescing compound (4,10-di-*p*-*tert*-butylphenylanthanthrene, **9**, 0.55 g, yield ~30%) was separated by column chromatography using hexanes:CH_2Cl_2 (4:1) as the eluent.

9 (1 mmol, 0.55 g) was dissolved in 150 mL of dry CH_2Cl_2, and a 5 mL solution of 2 mmol (0.32 g) of Br_2 in CH_2Cl_2 was added to it. The mixture was stirred at room temperature for 30 min. A 5 mL solution of 1 mmol (0.16 g) of Br_2 in CH_2Cl_2 was added again, and the solution was refluxed for 30 min. Disappearance of the blue fluorescence on a thin layer chromatogram (hexanes:CH_2Cl_2 2:1) indicated completion of the reaction. The reaction mixture was cooled and evaporated, from which a dark red solid was obtained. It was washed with hexanes twice. For the subsequent Suzuki coupling the reddish solid was dissolved in 150 mL of toluene. 4-*tert*-butylphenylboronic acid (2.5 mmol, 0.45 g), ethanol (10 mL) and 2 N K_2CO_3 solution in water (20 mL) were added to it. The mixture was degassed (bubbling N_2) for 15 min. After adding 0.007 g of $Pd(PPh_3)_4$, the mixture was refluxed for overnight under nitrogen. The reaction mixture was cooled, washed with water (100 mL × 3), and evaporated. The solid obtained was subjected to a flash column chromatography using toluene as the eluent. The fluorescent products were collected and separated by another column chromatography (hexanes:CH_2Cl_2, 12:1) as the eluent, yielding **5** (0.16 gm, 20%). Yields of **2**−**6** were in the range 15−30%. Each compound (**2**−**6**) was further purified by train sublimation. In the preparation of **6**, NaOH (3 equiv wt) was used instead of K_2CO_3 during the second Suzuki coupling of **10b** with *o*-tolylboronic acid.

4,10-Diphenylanthanthrene (2). ^{1}H NMR (300 M Hz, $CDCl_3$), δ: 7.55 (m, 2H), 7.61 (m, 4H), 7.80 (m, 4H), 8.10 (dd, 2H), 8.15 (s, 2H), 8.24 (d, 2H), 8.58 (d, 2H), 8.87 (s, 2H). MS (MALDI): calcd for $C_{34}H_{20}$, 428.2; found, 428.3 ([M]$^+$, 100%). MS (DIP): m/z 428 (100) [M]$^+$, 350 (11), 212 (50). Anal. Calcd for $C_{34}H_{20}$ (428.2): C, 95.30; H, 4.70. Found: C, 95.16; H, 4.52.

4,6,10,12-Tetraphenylanthanthrene (3). ^{1}H NMR (300 M Hz, $CDCl_3$), δ: 7.45−7.64 (m, 20H), 7.87 (s, 2H), 7.96 (m, 2H), 8.18 (m, 4H). MS (MALDI): calcd for $C_{46}H_{28}$, 580.2; found, 580.7 ([M]$^+$, 100%). Anal. Calcd for $C_{46}H_{28}$ (580.2): C, 95.14; H, 4.86. Found: C, 94.91; H, 4.50.

4,10-Diphenyl-6,12-di-*p*-*tert*-butylphenylanthanthrene (4). ^{1}H NMR (300 M Hz, $CDCl_3$), δ: 1.48 (s, 18H), 7.52−7.69 (m, 10H), 7.78 (m, 2H), 7.95 (m, 4H), 8.10 (m, 2H), 8.19 (m, 8H). MS (MALDI): calcd for $C_{54}H_{44}$, 692.4; found, 692.9 ([M]$^+$, 100%). Anal. Calcd for $C_{54}H_{44}$ (692.4): C, 93.60; H, 6.40. Found: C, 93.34; H, 6.37.

4,6,10,12-Tetra-*p*-*tert*-butylphenylanthanthrene (5). ^{1}H NMR (300 M Hz, $CDCl_3$), δ: 1.43 (s, 18H), 1.50 (s, 18H), 7.55−7.67 (m, 16H), 7.95 (m, 2H), 7.98 (s, 2H), 8.18 (m, 4H). MS (MALDI): calcd for $C_{62}H_{60}$, 804.5; found, 804.3 ([M]$^+$, 100%). Anal. Calcd for $C_{62}H_{60}$ (804.5): C, 92.49; H, 7.51. Found: C, 92.24; H, 7.33.

4,10-Di-*p*-*tert*-butylphenyl-6,12-*o*-tolylanthanthrene (6). ^{1}H NMR (300 M Hz, $CDCl_3$), δ: 1.43 (s, 9H), 1.48 (s, 9H), 2.02 (s, 3H), 2.04 (s, 3H), 7.45−7.76 (m, 16H), 7.99−8.03 (m, 6H), 8.58 (d, 2H). MS (MALDI): calcd for $C_{56}H_{48}$, 720.4; found, 720.6 ([M]$^+$, 100%). Anal. Calcd for $C_{56}H_{48}$ (720.4): C, 93.29; H, 6.71. Found: C, 93.10; H, 6.43.

Fluorescence Quantum Yields (ϕ_F). Fluorescence quantum yields were measured following a general method using 9,10-diphenylanthracene ($\phi_F = 0.9$ in cyclohexane) as the standard.[8] Diluted solutions of **1**−**6** (10^{-5} −10^{-7} M) in appropriate solvents were used for recording the fluorescence spectra. Sample solutions were taken in quartz cuvettes and degassed for 15 min. The degassed solution had an absorbance of 0.04−0.06 at the excitation wavelength (330 nm). The fluorescence spectra of each of the sample solutions were recorded three times and an average value of integrated areas of fluorescence was used for the calculation of ϕ_F. The refractive indices (n) of solvents at sodium D line were used.

Fluorescence Lifetime (τ_F) Measurement. Solutions of **1**−**6** (10^{-4} to 10^{-6} M) in appropriate solvents showing absorbance 0.07−0.1 at 330 nm were taken in quartz cuvettes. Fluorescence decay profiles of nondegassed and argon-degassed (~15 min) solutions were recorded using a single photon counting spectrofluorometer from Edinburgh Analytical Instruments (FL/FS 900). Decays were monitored at the emission maximum of the corresponding compounds. In-built software allowed the fitting of the decay spectra ($\chi^2 = 1.1−1.5$) and yielded the fluorescence lifetimes.

Electrochemical Measurements and Estimation of HOMO and LUMO Energies. Cyclic voltammetry measurements were carried out with an Electrochemical Workstation using a three-electrode cell assembly (platinum working electrode) at room temperature. The CH_2Cl_2 solutions of the samples containing 0.1 M of the recrystallized supporting electrolyte tetrabutylammonium perchlorate (TBAP) were used. All potentials are referred against Ag/AgNO$_3$ as the reference electrode, which was calibrated against the ferrocene/ferrocenium (Fc) redox system. The Fc couple potential was determined to be $+0.161$ vs Ag/Ag$^+$. The HOMO and LUMO energies were estimated following a literature procedure.[19] The energy level of the ferrocene/ferrocenium (Fc) redox system is estimated to be 4.8 eV below the vacuum level, determined from -4.6 eV for the standard electrode potential (E) of normal hydrogen electrode (NHE) on the zero vacuum level scale and a value of 0.2 V for Fc vs NHE. Given that the energy level of the Fc system is -4.8 eV, the HOMO and LUMO levels of 1 must be located at ca. -5.84 and -3.28 eV, respectively, below the vacuum. Thus, the HOMO$-$LUMO gap is 2.56 eV. The electrochemical HOMO$-$LUMO gaps of **3**$-$**5** were estimated similarly.

Geometry Optimization. The Gaussian 98 program package[20] was used for density functional theory (DFT) calculations to optimize the geometries and calculate the HOMO and LUMO energies as well as the dipole moments of the molecules.

Conclusions

4,10-Disubstituted and 4,6,10,12-tetrasubstituted anthanthrenes were synthesized through a simple synthetic route. They constitute a new class of emitting materials for which the emission can be manipulated in the blue region ($\lambda_{max} = 437-467$ nm). They show average ϕ_F values in solution (0.20$-$0.47), depending upon solvents. They are amorphous and stable at room temperature and have good solubility in various solvents, e.g., CH$_2$Cl$_2$ and toluene. Preliminary work indicates these materials to be highly efficient EL materials. Thus, they are promising candidates for OLED applications. The study of several other derivatives of anthanthrene and their performance in devices is underway.

Acknowledgment. We thank Dr. C. W. Tang for helpful discussions. We are pleased to acknowledge the support of the Army Research Laboratory (contract no. DAAD19-03-2-0032).

Supporting Information Available: Absorption and fluorescence spectra of **1** recorded in different solvents, absorption spectra of **3** and **5** and fluorescence spectrum of **4** recorded in CH$_2$Cl$_2$, geometry optimized structures of **4** and **6**, fluorescence decay profiles, and cyclic voltammetry graphs. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Contribution number 557 from the Center for Photochemical Sciences.

(2) Tang, C. W.; VanSlyke, S. A. *Appl. Phys. Lett.* **1987**, *51*, 913.

(3) (a) Fave, C.; Cho, T. Y.; Hissler, M.; Chen, C. W.; Luh, T. T.; Wu, C. C.; Reau, R. *J. Am. Chem. Soc.* **2003**, *125*, 9254. (b) Li, B.; Li, J.; Fu, Y.; Bo, Z. *J. Am. Chem. Soc.* **2004**, *126*, 3430 and references therein.

(4) (a) Tao, Y. T.; Balasubramaniam, E.; Danel A.; Jarosz, B.; Tomasik, P. *Chem. Mater.* **2001**, *13*, 1207. (b) Thomas, K. R. J.; Lin, J. T.; Tao, Y. T.; Chuen, C. H. *Chem. Mater.* **2002**, *14*, 2796. (c) Pohl, R.; Anzenbacher, P., Jr. *Org. Lett.* **2003**, *5*, 2769. (d) Wolak, M. A.; Jang, B. B.; Palilis, L. C.; Kafafi, Z. H. *J. Phys. Chem. B* **2004**, *108*, 5492. (e) Liu, X. M.; He, C.; Huang, J.; Xu, J. *Chem. Mater.* **2005**, *17*, 434.

(5) (a) Zheng, S.; Shi, J.; Mateu, R. *Chem. Mater.* **2000**, *12*, 1814. (b) Lee, S. H.; Nakamura, T.; Tsutsui, T. *Org. Lett.* **2001**, *3*, 2005. (c) Zheng, S.; Shi, J. *Chem. Mater.* **2001**, *13*, 4405. (d) Holmes, R. J.; D'Andrade, B. W.; Forrest, S. R.; Ren, X.; Li, J.; Thompson, M. E. *J. Appl. Phys.* **2003**, *83*, 3818. (e) Li, J.; Djurovich, P. I.; Alleyne, B. D.; Tsyba, I.; Ho, N. N.; Bau, R.; Thompson, M. E. *Polyhedron* **2004**, *23*, 419. (f) Hosokawa, C.; Fukuoka, K.; Kawamura, H.; Sakai, T.; Kubota, M.; Funahashi, M.; Moriwaki, F.; Ikeda, H. *SID04 Digest*; Vol XXXV, Society for Information Display: San Jose, CA, 2004; p 780.

(6) (a) Shi, J.; Tang, C. W.; Chen, C. U.S. Patent 6,720,090, 2004. (b) Shi, J.; Tang, C. W. *Appl. Phys. Lett.* **2002**, *80*, 3201.

(7) (a) Shi, J.; Forsythe, E. W.; Morton, D. C. U.S. Patent Appl. 10/807,099, 2004. (b) Shi, J.; Forsythe, E. W.; Morton, D. C. U.S. Patent Appl. 10/807,103, 2004.

(8) Eaton, D. F. In *Handbook of Organic Photochemistry*; Scaiano, J. C., Ed.; CRC Press: Boca Raton, FL, 1989; Vol. I.

(9) The absorption of many of the materials included in this study and the standard (9,10-diphenylanthracene) overlap only in the 330 nm region, necessitate the use of 330 nm as the excitation wavelength.

(10) Detailed electroluminescence and solid-state photoluminescence results will be reported elsewhere.

(11) Dawson, W. R.; Windsor, M. W. *J. Phys. Chem.* **1968**, *72*, 3251.

(12) Murov, S. L.; Carmichael, I.; Hug, G. L. *Handbook of Photochemistry*; Marcel Dekker: New York, 1993; p 8.

(13) Quesada, E.; Ardhammar, M.; Nordén, B.; Miesch, M.; Duportail, G.; Bonzi-Coulibaly, Y.; Nakatani, Y.; Ourisson, G. *Helv. Chim. Acta* **2000**, *83*, 2464.

(14) Turro, N. J. *Modern Molecular Photochemistry*; University Science Books: Mill Valley, CA, 1991; p 186.

(15) It can be safely assumed that photoreaction from the S$_1$ surface of these compounds is negligible, especially in an oxygen free environment, because the most probable photoreaction they undergo is photooxidation.

(16) Birks, J. B. *Photophysics of Aromatic Molecules*; Wiley-Interscience: New York, 1970; p 178.

(17) Cremonesi, P.; Hietbrink, B.; Rogan, E.; Cavalieri, E. L. *J. Org. Chem.* **1992**, *57*, 3309.

(18) Visco, R. E.; Chandross, E. A. *J. Am. Chem. Soc.* **1964**, *86*, 5350.

(19) Pommerehne, J.; Vestweber, H.; Guss, W.; Mahrt, R. F.; Bassler, H.; Porsch, M.; Daub, J. *Adv. Mater.* **1995**, *7*, 551.

(20) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.9; Gaussian, Inc.: Pittsburgh, PA, 1998.