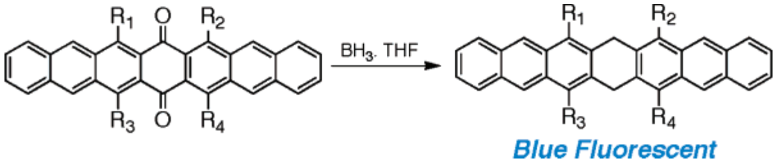
Synthesis and Photophysical Properties of Dihydroheptacenes: New Blue-Emitting Materials

Rajib Mondal, Bipin K. Shah, and Douglas C. Neckers*

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

neckers@photo.bgsu.edu

Received January 20, 2006



7,16-Dihydroheptacenes (**1**−**3**) substituted at the 6, 8, 15, and 17 positions are synthesized as blue emitters potentially useful in organic light emitting diodes (OLEDs). The photophysical properties of **1**−**3** (λ_{max} = 424−428 nm, Φ_F = 0.15−0.21, τ_F = 2.35−2.67 ns in CH_2Cl_2) are discussed. They are shown to be stable and efficient blue emitters in the solid state (Φ_F = 0.37−0.44). The X-ray crystal structure of **1** is reported.

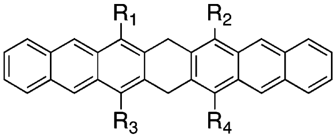
Introduction

Getting rid of the "light bulb" is the dream of every homeowner. In addition to incredible inefficiencies, incandescent bulbs are, seemingly, always "burned out". Fluorescent bulbs are not much better in that they are less than 70% energy efficient. The world awaits the white light organic light emitting diode (OLED). The development of stable, efficient, and bright emitting materials for OLEDs has impressively started to invade display technology.[2−6] Among the three primary colors required to achieve full color, the stability and efficiency of materials emitting green and red have reached commercial levels,[7] whereas the stability and efficiency of blue light emitting materials remains a challenge.[8]

Anthracene is one of the earliest luminescent materials reported and emits violet both in the solid state and in solution. 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 (TBP) have been used successfully as blue emitters in commercial OLED products.[9]

On the basis of the efficiency reported and stability of anthracene derivatives, a new class of blue emitters [7,16-dihydro-6,8,15,17-tetraphenylheptacene (**1**), 7,16-dihydro-6,15-bis(*p*-*tert*-butylphenyl)-8,17-diphenylheptacene (**2**), and 7,16-dihydro-6,8,15,17-tetrakis(*p*-*tert*-butylphenyl)heptacene (**3**)] has been synthesized and studied (Chart 1). They are dihydroheptacene derivatives in which two anthracene moieties are attached to one another via two methylene bridges. We report the synthesis of **1**−**3** herein, and their photophysical properties have been measured in different solvents. Fluorescence efficiencies in solution and in a poly(methyl methacrylate) (PMMA) matrix are compared. The effect of aging and annealing on the solid-state emission of **1**−**3** is evaluated.

CHART 1. **Structures of 7,16-Dihydroheptacene Derivatives 1−3**



1. R_1, R_2, R_3, R_4 = phenyl
2. R_1, R_4 = phenyl;
R_2, R_3 = *p*-*tert*-butylphenyl
3. R_1, R_2, R_3, R_4 = *p*-*tert*-butylphenyl

Results and Discussion

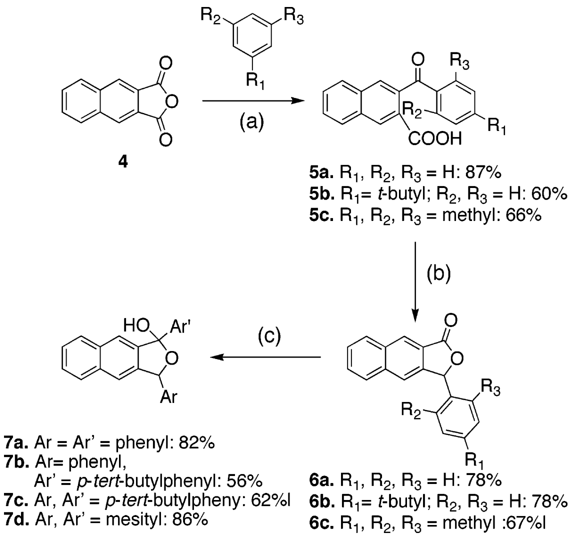
Synthesis. Cava's synthetic procedure[10] was used to synthesize lactols **7a**−**d** from 2,3-naphthalic anhydride **4** (Scheme 1). These lactols easily undergo dehydration under acidic conditions

---

[1] Contribution no. 576 from the Center for Photochemical Sciences.
[2] Mitschke, U.; Bäuerle, P. *J. Mater. Chem.* **2002**, *10*, 1471.
[3] Friend, R. H.; Gymer, R. W.; Holmes, A. B.; Burroughes, J. H.; Marks, R. N.; Taliani, C.; Bradley, D. D. C.; Dos Santos, D. A.; Brédas, J. L.; Lögdlund, M.; Salaneck, W. R. *Nature* **1999**, *397*, 121.
[4] Segura, J. L.; Martin, N. *J. Mater. Chem.* **2000**, *10*, 2403.
[5] Li, Z. H.; Wong, M. S.; Tao, Y.; Lu, J. *Chem. Eur. J.* **2005**, *11*, 3285.
[6] Zheng, S.; Shi, J. *Chem. Mater.* **2001**, *13*, 4405.
[7] Service, R. F. *Science* **2005**, *310*, 1762.
[8] Kim, D. Y.; Cho, H. M.; Kim, C. Y. *Prog. Polym. Sci.* **2000**, *25*, 1089.
[9] Shi, J.; Tang, C. W. *Appl. Phys. Lett.* **2002**, *80*, 3201.

10.1021/jo0601314 CCC: \$33.50

SCHEME 1 [a]



[a] Reagents and conditions: (a) $AlCl_3$, 90−95 °C, 15 h; (b) $NaBH_4$, aq NaOH, rt, 5 days; (c) Mg, Ar′Br, ether, THF, I_2 (catalyst), 0 °C, 5 h.

to yield 1,3-diarylnaphtho[2,3-*c*]furans. However, alkyl-substituted furans such as 1,3-di-*tert*-butylnaphtho[2,3-*c*]furan are unstable and hard to prepare via this route. Thus, **8** was synthesized by dehydration of **7a** in glacial acetic acid (Scheme 2) and was isolated in the form of a red solid by direct recrystallization from the reaction mixture. The Diels−Alder reaction of **8** with *p*-benzoquinone followed by acid-catalyzed dehydration of **9** yielded **10a**.[11,12]

Compounds **7b** and **7c** produced the corresponding furan (analogous to **8**, not shown in the scheme) in glacial acetic acid as indicated by appearance of the bright red colored solution. However, isolation of these products via recrystallization was unsuccessful because of their higher solubility in the solvent employed (glacial acetic acid). Thus, **10b** and **10c** were directly produced under optimized acidic conditions involving in situ Diels−Alder cycloaddition and dehydration steps (route d in Scheme 2). Reduction of **10a**−**c** with an excess of the borane−tetrahydrofuran ($BH_3{\cdot}THF$) complex yielded **1**−**3**.

During this synthetic scheme, the two molecules of furan produced in situ from **7b** underwent cycloaddition with *p*-benzoquinone. Two regioisomers of **10b** were produced due to the nonselective Diels−Alder reaction. One isomer had both phenyl groups on one side of the anthracene moieties, while the other had one phenyl group and one *p*-*tert*-butylphenyl group on one side of the anthracenes. These isomers were directly subjected to reduction (step e), yielding an inseparable mixture of two isomers of **2**. ^1H NMR of **2** shows two peaks for the methylene bridge protons at 3.9 and 4.1 ppm, suggesting the presence of two regioisomers. The relative sizes of the two peaks indicated their approximate ratio to be 5:1.

7d, which has two mesityl groups, failed to produce the corresponding furan in acidic solution. This may be because the resulting furan would be sufficiently sterically crowded so that its formation was prevented. Instead, **7d** underwent acid-catalyzed ring opening and, following oxidation by *p*-benzoquinone, produced diketone **11** (Scheme 3). A similar oxidative product of furan **8** was afforded when **7a** was oxidized with chromium trioxide in pyridine.[10]

Crystal Structure. Compounds **1**−**3** normally exist in amorphous form at room temperature. However, slow, deliberate recrystallization from hexane/dichloromethane yielded blocklike crystals of **1** suited for single-crystal X-ray diffraction study (Figure 1). Crystals of **1** are monoclinic, space group *P*2(1). The structure of **1** is bent with anthracene moieties forming two different planes. The four phenyl groups are almost orthogonal to the planes of anthracene moieties. The angles between the phenyl groups and the anthracene planes are observed to be 78.01°, 69.52°, 86.85°, and 67.66°. No close π-stacking was observed in the crystal structure of **1**. The presence of almost orthogonal aryl substituents may be the reason for the absence of a significant π-interaction in these molecules.

Photoluminescence in Solution. Absorption spectra of **1**−**3** were similar in shape showing a $\pi-\pi^*$ band at 372 nm ($\epsilon_{372} = 1.3 \times 10^4$ M^{-1} cm^{-1} for **1** in CH_2Cl_2). Dilute solutions of these compounds showed blue emission in several solvents such as hexane, dichloromethane, acetonitrile, toluene, and methanol. The fluorescence spectra of **1**−**3** recorded in CH_2Cl_2 are shown in Figure 2. The absorption maxima (A_{max}), emission maxima (λ_{max}), quantum yields (Φ_F), and lifetimes (τ_F) of fluorescence of **1**−**3** measured in dichloromethane are presented in Table 1. The λ_{max} of **2** (426 nm) and **3** (428 nm) are red shifted only slightly from that of **1** (424 nm), indicating almost no difference in delocalization of π electrons in these compounds. This indicates that be it the phenyl group or the substituted phenyl group, e.g., *p*-*tert*-butylphenyl, they lie almost orthogonally to the anthracene planes and there is no change in the geometry of the molecules.

The Φ_F of **1**−**3** were measured by exciting the molecules at 372 nm. These were in the range of 0.15−0.21 in CH_2Cl_2 relative to the Φ_F of 9,10-diphenylanthracene (0.90 in cyclohexane).[13] Fluorescence decays of **1**−**3** were fitted with monoexponential functions, indicating emission from the singlet excited state (S_1) in each case (Figure 3). The τ_F values were found to be ∼2.5 ns in CH_2Cl_2 (argon degassed solution).

No phosphorescence was observed for **1** even in a frozen matrix of 20% (v/v) methanol in ethanol at 77 K. This indicates ∼80% of the excited molecules decay without radiation in solution. Rate constants of the radiative (k^0_R) and nonradiative (k^0_{NR}) decay of the fluorescence of **1**−**3** were calculated from the Φ_F and τ_F values measured from CH_2Cl_2 solutions. The k^0_R of deactivation of the S_1 state (Φ_F/τ_F) were in the range of $6-8 \times 10^7$ s^{-1}. The nonradiative pathway of deactivation of the S_1 state was observed to be 4−6 times faster ($k^0_{NR} \sim (3-3.6) \times 10^8$ s^{-1}) than the radiative pathway. The observation is similar to the case of anthracene ($k^0_R \sim 2 \times 10^8$ s^{-1} and $k^0_{NR} \sim 6 \times 10^8$ s^{-1})[14] and anthanthrene ($k^0_R \sim 8 \times 10^7$ s^{-1} and $k^0_{NR} \sim 2.5 \times 10^8$ s^{-1}).[15] Furthermore, the calculated k^0_{NR} values of **1**−**3** may represent the rate of $S_1 \rightarrow T_1$ intersystem crossing (ISC) because the rate of $S_1 \rightarrow T_1$ ISC for rigid aromatic molecules is shown to be in the same range ($\sim 10^6-10^8$ s^{-1}) and internal conversion from S_1 cannot compete.[15,16]

The polarity of the solvent showed no systematic effect on its fluorescence quantum yield (Figure 4) or lifetime (Table 2)

---

[10] Cava, M. P.; VanMeter, J. P. *J. Org. Chem.* **1969**, *34*, 538−545.

[11] Miller, G. P.; Briggs, J. *Tetrahedron Lett.* **2004**, *45*, 477−481.

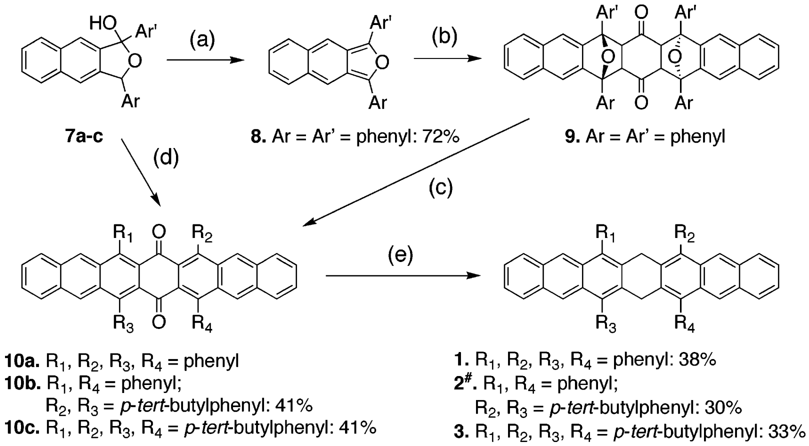
[12] Miller, G. P.; Briggs, J. *Org. Lett.* **2003**, *5*, 4203−4206.

[13] Sciano, J. C. *Handbook of Organic Photochemistry*; CRC Press: Boca Raton, Florida, 1989; Vol. 1, p 231.

[14] Birks, J. B. *Photophysics of Aromatic Molecules*; Wiley Interscience: New York, 1970; p 178.

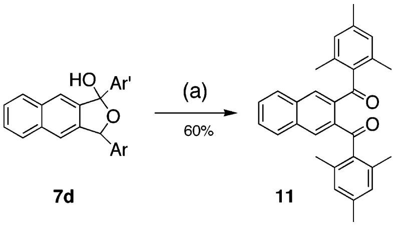
[15] Shah, B. K.; Neckers, D. C.; Shi, J.; Forsythe, E. W.; Morton, D. *J. Phys. Chem. A* **2005**, *109*, 7677.

SCHEME 2 ^{a}



^{a} Reagents and conditions: (a) glacial AcOH, 50 °C, 15 min; (b) *p*-benzoquinone, benzene, reflux, overnight; (c) *p*-toluenesulfonic acid, benzene, reflux, overnight; (d) *p*-benzoquinone, *p*-toluenesulfonic acid, benzene, reflux, overnight; (e) BH$_3$·THF, THF, 50−60 °C, 2 days; $^{\#}$**2** was obtained as a mixture of two regiosiomers; the structure of only one isomer is shown in the scheme; see the text for details.

SCHEME 3 ^{a}



^{a} Reagents and conditions: (a) *p*-benzoquinone, *p*-toluenesulfonic acid, benzene, reflux, overnight.

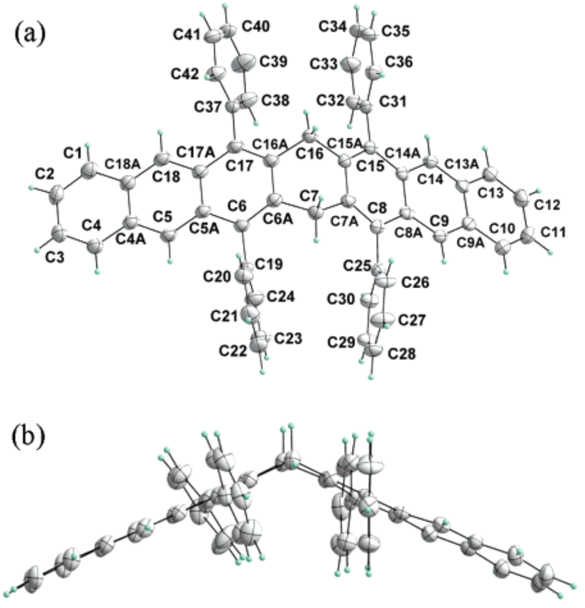


FIGURE 1. X-ray crystal structure of **1**: (a) with a labeling scheme of atoms and (b) a view showing the angle between the two anthracene planes.

of **1**. The Φ_F of **1** in toluene (0.41) was the highest among the solvents employed and is close to the absolute quantum yield value ($\Phi_F = 0.44$) measured in the solid state (vide infra). It is also noted that the τ_F of **1** was found to be much higher in acetonitrile (6.87 ns) than in other solvents.

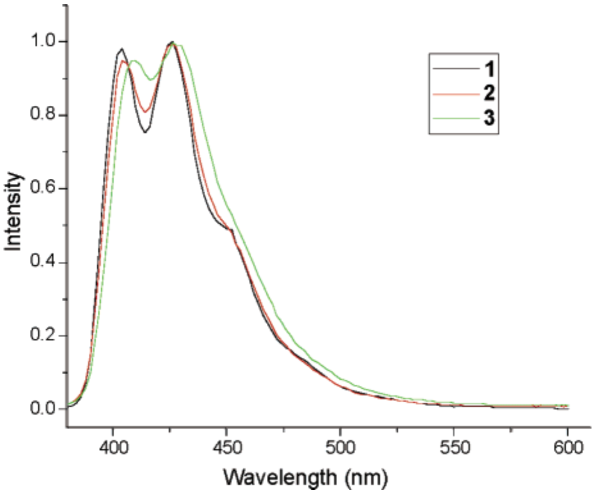


FIGURE 2. Normalized fluorescence spectra of **1**−**3** in CH$_2$Cl$_2$.

Photoluminescence in the Solid State. The solid-state emission spectra of **1**−**3** were recorded in thin films of PMMA (Figure 5), and the quantum yields were measured using an integrating sphere (Table 3).[17] The solid-state emission of these compounds ($\lambda_{max} = 420-426$ nm) is similar to those recorded in CH$_2$Cl$_2$ solution.[18] However, it appears that solid-state emission ($\Phi_F = 0.37-0.44$) is more efficient than the solution emission in each case. Anthanthrene and its derivatives show a similar trend.[19] This observation can be explained on the basis of the involvement of a T$_2$ state in the relaxation pathway similar to the case of anthracene and anthanthrene.[19] There is a larger energy gap between the S$_1$ (3.1 eV) and T$_1$ (1.8 eV) states of

---

[16] Turro, N. J. *Modern Molecular Photochemistry;* University Science Books: Sausalito, CA, 1991; pp 186−187.

[17] de Mello, J. C.; Wittmann, H. F.; Friend, R. H. *Adv. Mater.* **1997**, *9*, 230.

[18] The solid-state emission was recorded by dispersing a very low amount of emitters in thin PMMA films. This may be the reason there were no differences in the solid state and solution emissions of **1**−**3**. We did not record the solid-state emission from films composed of only the emitters. Nevertheless, given that there was no significant π-stacking observed in the crystal structure, it is unlikely that solid-state emission of **1**−**3** would differ from what was observed in the PMMA matrix.

[19] Shah, B. K.; Neckers, D. C.; Shi, J.; Forsythe, E. W.; Morton, D. *Chem. Mater.* **2006**, *18*, 603.

TABLE 1. Photophysical Properties of 1−3[a] in CH_2Cl_2

compd	A_{max} (nm)	λ_{max} (nm)	Φ_F	τ_F (ns)	χ^2	k^0_R (s^{-1})	k^0_{NR} (s^{-1})
1	354, 372, 392	402, 424	0.21 ± 0.01	2.58	1.02	8.1×10^7	3.1×10^8
2	354, 372, 392	404, 426	0.16 ± 0.01	2.67	1.30	6×10^7	3.14×10^8
3	353, 373, 393	409, 428	0.15 ± 0.01	2.35	1.27	6.4×10^7	3.61×10^8

[a] Excitation wavelength = 372 nm for Φ_F and τ_F. Φ_F values are relative to that of 9,10-diphenylanthracene (0.90 in cyclohexane). τ_F values are measured from argon-saturated solutions, and decay was monitored at the corresponding λ_{max}.

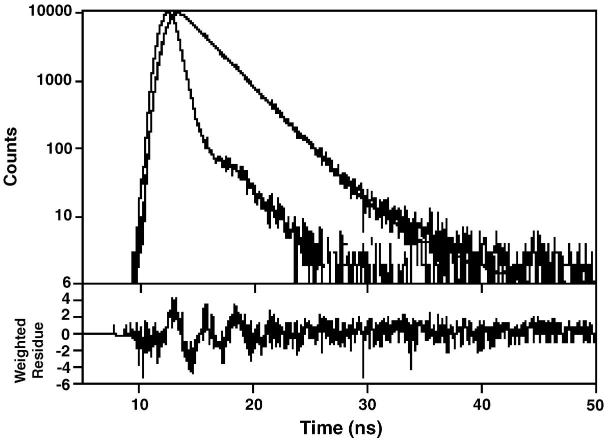


FIGURE 3. Fluorescence decay of **3** monitored at λ_{max} = 424 nm in CH_2Cl_2; excitation wavelength = 372 nm.

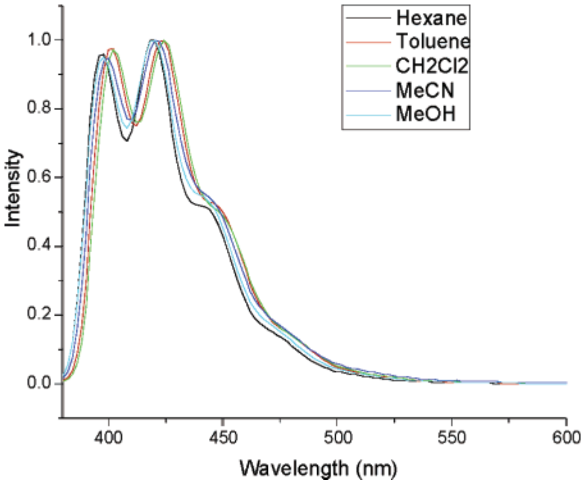


FIGURE 4. Normalized fluorescence spectra of **1** in different solvents.

TABLE 2. Photophysical Properties of 1 in Different Solvents

solvent	A_{max} (nm)	λ_{max} (nm)	τ_F (ns)	Φ_F
hexane	350, 368, 388	396, 420	3.80	0.28 ± 0.01
toluene	353, 371, 391	402, 424	3.24	0.41± 0.01
dichloromethane	354, 372, 392	402, 424	2.58	0.21 ± 0.01
methanol	351, 368, 388	398, 420	3.68	0.30 ± 0.01
acetonitrile	351, 369, 389	400, 421	6.87	0.27 ± 0.01

[a] Excitation wavelength = 372 nm for Φ_F and τ_F. Φ_F values are relative to that of 9,10-diphenylanthracene (0.90 in cyclohexane). τ_F values are measured from argon-saturated solutions, and decay was monitored at the corresponding λ_{max}.

anthracene.[20] It has been suggested that the presence of the T_2 state which is almost isoenergetic with the S_1 state provides a facile pathway for intersystem crossing for anthracene in solution, causing the molecule to lose the majority of its excited-state energy in dark processes via the T_2 and T_1 states.[16] A similar situation may pertain with the 7,16-dihydroheptacene derivatives in solution. However, in the solid state the configuration of the excited states of these molecules may be such that the T_2 state is slightly higher in energy than the S_1 state minimizing the S_1−T_2 intersystem crossing process. In such a case, energy transfer from the S_1 state to the T_1 state would not be efficient due to the reasonably high energy difference. This would cause enhanced fluorescence in the solid state as is observed experimentally.

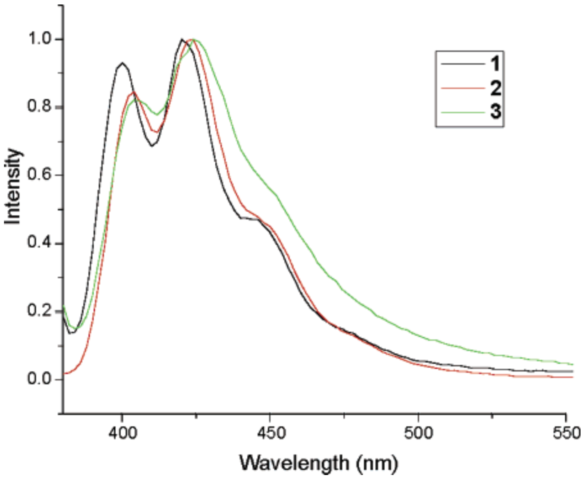


FIGURE 5. Normalized solid-state fluorescence spectra of **1**−**3** recorded in thin films of PMMA.

TABLE 3. Photophysical Properties of 1−3 Measured in the Solid State[a]

compd	λ_{max} (nm)	Φ_F
1	400, 420	0.44
2	404, 424	0.39
3	404, 426	0.37

[a] Thin films of PMMA were used as matrix; excitation wavelength = 372 nm; the Φ_F were measured using an integrating sphere (errors within 15%).

No long wavelength emission was found for **1**−**3** at concentrations as high as 10^{-3} M in CH_2Cl_2 or in the solid state suggesting there is no aggregation. The effects of aging and annealing on the solid-state emission spectra of **1**−**3** were evaluated from thin films of PMMA containing the compounds. Thin films were exposed to ambient light for 7 days and the emission recorded. Similarly, emissions were also recorded following heating the thin films to 110 °C for 24 h and subsequent cooling to room temperature. The emission spectra of **1**−**3** remained unchanged after aging or annealing (shown for **1** in Figure 6), indicating a higher stability of these compounds in the solid state in comparison to several other blue emitters such as fluorene and its derivatives.[21,22]

---

(20) Schwob, H. P.; Williams, D. F. *J. Chem. Phys.* **1973**, *58*, 1542.

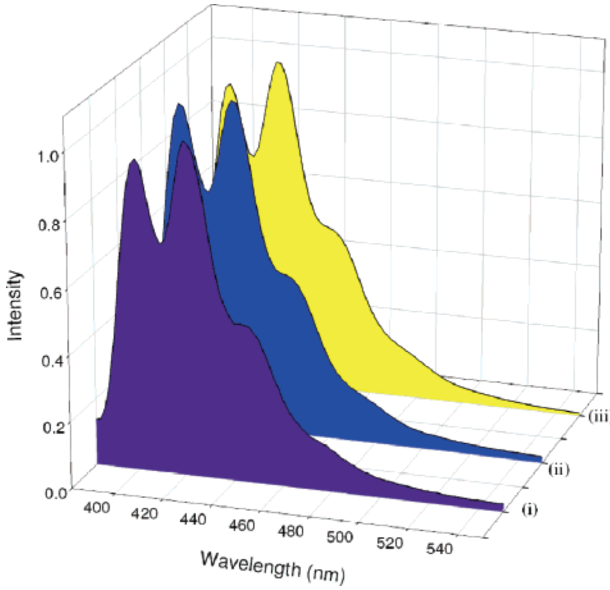


FIGURE 6. Normalized solid-state fluorescence spectra recorded from thin films of PMMA containing **1**: (i) pristine, (ii) after exposing the film for 7 days at ambient condition, and (iii) after heating the film at 110 °C for 24 h and cooling it down to room temperature.

Conclusions

Substituted dihydroheptacenes (**1**−**3**) were synthesized. Each emits in the 420−428 nm region in several solvents (Φ_F = 0.15−0.21 in CH_2Cl_2) and in the solid state (Φ_F = 0.37−0.44). These compounds have good solubility in common organic solvents, are reasonably stable, and retain color purity even after annealing for 24 h at 110 °C. Thus, they are promising candidates as an active blue emitting layer of OLED devices. Their performance in devices is underway.

Experimental Section

Synthesis. 2,3-Naphthalic anhydride (4) was synthesized following a literature procedure reported for the synthesis of 2,3-naphthalenedicarboxylic acid, except the hydrolysis step was not carried out.[23] The starting materials were α,α,α′,α′-tetrabromo-*o*-xylene and maleic anhydride. The unhydrolyzed product mostly contained the desired anhydride (**4**).

Ketoacids (5a−c). The general procedure followed to prepare ketoacids (**5a**−**c**) follows: a suspension of **4** (2.0 g, 10 mmol) was made in 25 mL of benzene (for **5a**), *tert*-butylbenzene (for **5b**), or mesitylene (for **5c**). Aluminum chloride (2.77 g, 20 mmol) was added at room temperature and the mixture stirred overnight (15 h) at 85−90 °C. An excess of 6 M aq HCl was added to the tarry reaction mixture. Excess ethyl acetate was also added. Additional aq HCl and ethyl acetate were added until the solid dissolved. The organic layer was next separated, washed with water, and extracted thoroughly with saturated sodium bicarbonate solution. Acidification of the bicarbonate solution with concentrated HCl produced a white precipitate which was filtered and then recrystallized from methanol/hexane mixture.

3-Benzoyl-2-naphthoic acid (5a): yield = 87%; mp 208−209 °C (lit.[10] mp 209.5 °C); IR (Neat) 1467, 1678, 2500−3100 (broad) cm^{-1}; ^{1}H NMR (300 MHz, MeOD) δ 7.45 (t, 2 H, *J* = 7.5 Hz), 7.55 (t, 1 H, *J* = 7.5 Hz), 7.65 (m, 2 H), 7.72 (d, 2 H, *J* = 7.2 Hz), 7.9 (s, 1 H), 8.0 (s, 1 H), 8.1 (m, 1 H), 8.62 (s, 1 H); ^{13}C NMR (300 MHz, MeOD) δ 129.04, 129.21, 129.41, 129.65, 130.24, 130.32, 130.60, 132.65, 134.22, 135.63, 139, 169, 199; mass spectrum (GC−MS) *m/e* M$^+$ 232 (100), 155 (100), 127 (80), 105 (50), 77(95).

3-(*p*-*tert*-Butylphenyl)-2-naphthoic acid (5b): yield = 60%; mp 239−240 °C; IR (neat) 1452, 1678, 2500−3100 (broad) cm^{-1}; ^{1}H NMR (300 MHz, MeOD) δ 1.35 (S, 9 H), 7.5 (d, 2 H), 7.65 (m, 4 H), 7.85 (s, 1 H), 7.95 (m, 1 H), 8.1 (m, 1 H), 8.65 (s, 1 H); ^{13}C NMR (300 MHz, MeOD) δ 31.84, 36.36, 126.88, 129.30, 129.38, 129.49, 129.73, 130.54, 130.60, 131.04, 133.09, 134.53, 135.96, 136.77, 139.72, 158.56, 169.59; mass spectrum (DIP-MS) *m/e* M$^+$ 332 (12), 317 (10), 299 (15), 273 (10), 231 (45), 216 (35), 198 (45), 172 (50), 161 (40), 155 (80), 126 (100).

3-Mesitoyl-2-naphthoic acid (5c): yield = 66%; mp 221−222 °C; IR (neat) 1658, 1692, 2400−3300 (broad) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.22 (s, 6 H), 2.36 (s, 3 H), 6.94 (s, 2 H), 7.6 (m, 2 H), 7.8 (d, 1 H, *J* = 8.2 Hz), 7.87 (s, 1 H), 7.97 (d, 1 H, *J* = 8.2 Hz), 8.42 (s. 1 H); mass spectrum (DIP) *m/e* M$^+$ 318 (55), 299 (80), 285 (70), 273 (80), 258 (50), 229 (30), 215 (25), 199 (55), 147 (54), 133 (50), 115 (100).

Lactones 6a−c were synthesized by two general procedures as described below. Route a[10] produced a higher yield of **6a** and **6b** and only a small quantity of **6c**. An alternative route (b)[24] was employed to obtain a higher yield of **6c**.

Route a (Synthesis of 6a and 6b). Compound **5a** or **5b** (7 mmol) was suspended in 40 mL of water. Sodium hydroxide (2 M) was added to enhance the solubility of the acid (**5a** or **5b**). Sodium borohydride (1.29 g, 34 mmol) was added, and the solution was stirred for 70 h at room temperature. The reaction mixture was subsequently neutralized (pH ∼7.5) with 3 M HCl. Additional sodium borohydride (0.26 g, 6.8 mmol) was added, and the mixture was stirred for another 46 h. Finally, the solution was acidified with 6 M HCl and extracted with dichloromethane. The organic extract was washed with dilute HCl and water. After the solvent was evaporated, a solid residue was obtained. Compound **6a** was purified by recrystallization from benzene, while **6b** was purified through a filter column (silica gel) using dichloromethane as the eluent.

1,3-Dihydro-3-phenylnaphtho[2,3-*c*]furan-1-one (6a): yield = 78%; mp 153−154 °C (lit.[10] 153−155 °C); IR (Neat) 1750 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.6 (s, 1 H), 7.4 (m, 5 H), 7.6 (m, 2 H0, 7.75 (s, 1 H), 7.9 (m, 1 H), 8.1 (m, 1 H), 8.55 (s, 1 H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 83, 122, 123.5, 127.05, 127.1, 127.14, 128.34, 129.01, 129.04, 129.30, 129.95, 133.34, 136.45, 137.33, 143.53, 170; mass spectrum (GC−MS) *m/e* M$^+$ 260 (80), 231 (10), 215 (40), 155 (100).

1,3-Dihydro-3-*tert*-butylphenylnaphtho[2,3-*c*]furan-1-one (6b): yield = 78%; mp 235−236 °C; IR (neat) 1755 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.36 (s, 9 H), 6.55 (s, 1 H), 7.25 (m, 4H, $CDCl_3$), 7.4 (d, 2 H, *J* = 8.4 Hz), 7.6 (m, 2 H), 7.75 (s, 1 H), 7.9 (m, 1 H), 8.1 (m, 1 H), 8.54 (s, 1 H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 31.28, 34.73, 82.76, 122, 123.77, 125.94, 126.95, 127.07, 128.35, 128.96, 129.95, 133.34, 134.24, 136.44, 143.62, 152.52, 170.35; mass spectrum *m/e* M$^+$ 316 (32), 301(48), 259 (100), 215 (42), 183 (30), 161 (50), 155 (75).

Route b (Synthesis of 1,3-Dihydro-3-mesitoyl[2,3-*c*]furan-1-one, 6c). Compound **5c** (2.35 g, 7.4 mmol), zinc dust (3.42 g, 52 mmol), water (7 mL), and glacial acetic acid (25 mL) were taken into a round-bottom flask fitted with a condenser. The reaction mixture was refluxed for 2 h and then allowed to cool to room temperature. Dilution with water yielded a white precipitate which was filtered and subjected to filter column (silica gel, dichloromethane) to obtain **6c** (1.5 gm, yield 67%): mp 144−145 °C;

---

[21] List, E. J. W.; Guentner, R.; de Freitas, P. S.; Scherf, U. *Adv. Mater.* **2002**, *14*, 374.

[22] Chan, K. L.; McKiernan, M. J.; Towns, C. R.; Holmes, A. B. *J. Am. Chem. Soc.* **2005**, *127*, 7662.

[23] Carlson, R. G.; Srinivasachar, K.; Givens, R. S.; Matuszewski, B. K. *J. Org. Chem.* **1986**, *51*, 3978.

[24] Hauser, C. R.; Tetenbaum, M. T.; Hoffenberg, D. S. *J. Org. Chem.* **1958**, *23*, 861.

^{1}H NMR (300 MHz, CDCl$_3$) δ 1.7 (s, broad, 3 H), 2.25 (s, 3 H), 2.65 (s, broad, 3 H), 6.75 (s, broad, 1 H), 7.0 (s, 2 H), 7.6 (m, 3 H), 7.8 (m, 1 H), 8.05 (s, 1 H), 8.55 (s, 1 H); ^{13}C NMR (300 MHz, CDCl$_3$) δ 20.9, 79.9, 120.7, 124.7, 126.8, 126.9, 128.2, 129.0, 129.1, 130.0, 133.1, 136.4, 139.0, 143.4, 170.8; mass spectrum (GC−MS) *m/e* M$^+$ 302 (35), 281 (10), 257 (10), 243 (20), 228 (20), 207 (50), 147 (100).

Lactols 7a−d. Dry THF (25 mL) was added to a round-bottom flask containing **6a** (7.3 mmol) under argon. The container was placed in an ice bath (−5−0 °C) and stirred for few minutes. A solution of the phenylmagnesium bromide in ether (29.1 mmol) was added dropwise over 20 min. Stirring was continued for another 0.5 h at 0 °C. The reaction mixture was poured onto a saturated solution of ammonium chloride. The organic layer was extracted with ether. The resulting solution was dried over sodium sulfate and evaporated to get an oily product (crude **7a**). Crude **7b−d** were synthesized similarly by allowing **6b−d** to react with the corresponding Grignard reagents. The Grignard reagents were freshly prepared following a general procedure. Since bromomesitylene reacts slowly with magnesium in ethyl ether, a modified procedure was employed to synthesize the mesityl Grignard reagent.[25]

Crude **7a** was purified by washing with hexanes. Crude **7b−d** were passed through a pad of alumina with dichloromethane. Evaporating the solvent produced solid white products.

1,3-Dihydro-1,3-diphenylnaphtho[2,3-*c*]furan-1-ol (7a): yield = 82%; mp 158−160 °C (lit.[10] mp 155−160 °C); mass spectrum (DIP-MS) *m/e* M$^+$ 338 (70), 320 (100).

1,3-Dihydro-1-(*p-tert*-butylphenyl)-3-phenylnaphtho[2,3-*c*]-furan-1-ol (7b): yield = 56%; mass spectrum (DIP-MS) *m/e* M$^+$ 259 (70), 289 (15), 319 (15), 337 (100), 361 (35), 376 (25), 394 (13).

1,3-Dihydro-1,3-bis(*p-tert*-butylphenyl)naphtho[2,3-*c*]furan-1-ol (7c): yield = 62%; mass spectrum (DIP-MS) *m/e* M$^+$ 450 (5), 432 (100), 417 (60), 393 (15). 377 (20).

1,3-Dihydro-1,3-dimesitoylnaphtho[2,3-*c*]furan-1-ol (7d): yield = 86%; mass spectrum (DIP-MS) *m/e* M$^+$ 422 (25), 404 (15), 389 (5), 301 (25), 287 (100), 273 (10), 256 (30).

1,3-Diphenylnaphtho[2,3-*c*]furan (8). A mixture of **7a** (2.43 g, 7.1 mmol) and glacial acetic acid (25 mL) was heated on a hot plate to a moderate temperature (∼60 °C) and stirred with a glass rod until all of the white lactol was converted to the red furan. The reaction mixture was then cooled to ∼10 °C in an ice−water bath. This, upon filtration and washing with petroleum ether, produced 1.66 g of **8** (72%): mp 146−147 °C (lit.[10] mp 148−154 °C); mass spectrum (DIP-MS) *m/e* M$^+$ 320 (100), 289 (30), 259(40).

6,8,15,17-Tetraaryl-7,16-quinone (10a−c). Compound **10a** was synthesized according to a literature procedure starting from **8**.[11] Compounds **10b** and **10c**, however, were prepared by a modified direct method during which both the Diels−Alder reaction and the subsequent dehydration steps were carried out in situ.

p-Toluenesulfonic acid (1.52 g, 8 mmol) and *p*-benzoquinone (0.108 g, 1 mmol) were added to a suspension of **7b** or **7c** (2 mmol) in 35 mL of dry benzene, and the reaction mixture was refluxed for 15 h on an oil bath. Subsequently, the mixture was allowed to cool to room temperature and was diluted with benzene. The organic extract was washed with saturated sodium bicarbonate and brine solution. Finally, the organic layer was concentrated on a rotary evaporator and subjected to column chromatography (silica gel). Elution was begun with 20% (vol.) of dichloromethane in hexane and finished with 50% (vol.) of dichloromethane in hexane. Yellowish-brown product was obtained after evaporation of the solvent.

6,15-Bis(*p-tert*-butylphenyl)-8,17-diphenyl-7,16-quinone (10b): yield = 41%; ^{1}H NMR (300 MHz, CDCl$_3$) δ 1.45 (s, 18 H), 7.3−7.5 (m, 22 H), 7.7−7.9 (m, 4 H), 8.15 (s, 2 H), 8.25 (s, 2 H); mass spectrum (MALDI) *m/e* M$^+$ 827.42, 826.43, 825.43, 824.41, 823.42; HRMS (FAB) *m/z* = 825.3736 (M + H$^+$), calcd *m/z* = 825.373256.

6,8,15,17-Tetrakis-(*p-tert*-butylphenyl)-7,16-quinone (10c): yield = 40%; ^{1}H NMR (300 MHz, CDCl$_3$) δ 1.464 (s, 36 H), 7.29 (d, 8 H, J = 8 Hz), 7.4 (dd, 4 H, J = 6.4, 6.4 Hz), 7.47 (d, 8 H, J = 8.4 Hz), 7.8 (dd, 4 H, J = 6.4, 6.4 Hz), 8.018 (s, 4 H); mass spectrum (MALDI) *m/e* M$^+$ 936.77; HRMS (FAB) *m/z* = 937.4988 (M + H$^+$), calcd *m/z* = 937.498457.

2,3-Dimesitoylnaphthalene (11). Compound **7d** leads to **11** under the same conditions as used for the synthesis of **10b** or **10c** from **7b** or **7c**, respectively: yield = 60%; ^{1}H NMR (300 MHz, CDCl$_3$) δ 2.0 (s, 6 H), 2.05 (s, 3 H), 2.22 (s, 3 H), 2.32 (s, 3 H), 2.7 (s, 3 H), 6.85 (s, 2 H), 6.97 (s, 1 H), 7.1 (s, 1 H), 7.5−7.7 (m, 2 H), 7.8−8.0 (m, 4 H); mass spectrum (DIP) *m/e* M$^+$ 420 (70), 405 (60), 389 (80), 299 (75), 285 (55), 273 (100); HRMS (FAB) *m/z* = 421.2166 (M + H$^+$), calcd *m/z* = 421.216755.

7,16-Dihydro-6,8,15,17-tetraphenylheptacene (1). To a suspension of **10a** (0.22 g, 0.3 mmol) in 10 mL of THF cooled to 0 °C was added dropwise a 1 M solution of borane·THF (0.9 mL, 0.9 mmol) under an argon atmosphere. The mixture was allowed to stir for 1 h at room temperature. The temperature was increased very slowly to 50 °C and the mixture stirred for another 12 h. The reaction mixture was allowed to cool to room temperature, and an additional quantity of 1 M BH$_3$·THF solution in THF (0.9 mL, 0.9 mmol) was added. The temperature was slowly increased again to 50 °C, and stirring was continued for 12 h. After being cooled to room temperature, the reaction mixture was quenched with methanol. The product concentrated on a rotary evaporator and subjected to column chromatography (silica gel). Elution was begun with 5% (vol) of dichloromethane in hexane and finished with 20% (vol) of dichloromethane in hexane. Evaporation of the solvent produced pure **1** in the form of a yellowish white solid (0.08 gm, yield 38%): ^{1}H NMR (300 MHz, CDCl$_3$) δ 3.9 (s, 4 H), 7.24−7.32 (m, 18 H, CDCl$_3$), 7.40 (m, 12 H), 7.74 (dd, 4 H, J = 6, 6 Hz), 7.96 (s, 4 H); ^{13}C NMR (300 MHz, CDCl3) δ 32, 124.97, 125.31, 126.97, 128.19, 128.32, 130.49, 130.75, 131, 133.5, 135.8, 139; mass spectrum (DIP-MS) *m/z* M$^+$ 685 (60), 684 (100), 607 (50), 530 (30); mass spectrum (MALDI) *m/e* M$^+$ 684.51, 685.51, 686.51; HRMS (FAB) *m/z* = 685.2899 (M + H$^+$), calcd *m/z* = 685.289526.

7,16-Dihydro-6,15-bis(*p-tert*-butylphenyl)-8,17-diphenylheptacene (2). Compound **2** was obtained from **10b** (yield −30%), using the same procedure described for the synthesis of **1**: ^{1}H NMR (300 MHz, CDCl$_3$) δ 1.4 (s, 3 H), 1.45 (s, 15 H), 3.9 (s, 3 H), 4.1 (s, 1 H) 7.15 (m, 3 H), 7.3 (m, 8 H), 7.42 (m, 10 H), 7.75 (m, 5 H), 7.95 (s, 2 H), 8 (s, 2 H); ^{13}C NMR (300 MHz, CDCl$_3$) δ 31.8, 33.7, 35, 125, 125.3, 128.2, 130.2, 130.9, 131.1, 134, 135.5., 136, 139.7; mass spectrum (MALDI) *m/e* M$^+$ 797.68, 796.68; HRMS (FAB) *m/z* = 797.4148 (M + H$^+$), calcd *m/z* = 797.414727.

7,16-Dihydro-6,8,15,17-tetrakis(*p-tert*-butylphenyl)heptacene (3). Compound **3** was obtained from **10c** (yield 33%) using the same procedure described for the synthesis of **1** (instead of 50 °C, the temperature was raised to 60 °C in this case): ^{1}H NMR (300 MHz, CDCl$_3$) δ 1.45 (s, 36 H), 4.1 (s, 4 H), 7.3 (m, 12 H), 7.45 (d, 8 H, J = 8 Hz), 7.7 (dd, 4 H, J = 6, 6 Hz), 7.8 (s, 4 H); ^{13}C NMR (300 MHz, CDCl$_3$) δ 32, 34, 35, 124.6, 125, 125.2, 128.2, 130, 130.5, 131.5, 133.5, 135.8, 136.2; mass spectrum (MALDI), *m/e* M$^+$ 908.66; HRMS (FAB) *m/z* = 909.5402 (M + H$^+$), calcd *m/z* = 909.539928.

X-ray Crystallography. Data collection was performed at 150 K with Mo Kα.[26] Intensity data were collected using three different ϕ settings and 0.3° increment ω scans, $2\theta < 56.58°$, which corresponds to more than a hemisphere of data. The SAINT[26] program was used for data integration, and corrections for absorp-

---

(25) Hawkins, R. T.; Lennarz, W. J.; Snyder, H. R. *J. Am. Chem. Soc.* **1960**, *82*, 3053.

(26) Bruker *SMART* (Ver. 5.05) and *SAINT-Plus* (Ver. 7.08); Bruker AXS Inc.: Madison, WI, 1999.

tion and decay were carried out using the SADBS program.[27] The X-ray structures was determined by direct methods,[28] and refinement was done by full-matrix least-squares[27] on F^2 using all 7698 unique data. The refinement included anisotropic thermal parameters for all hydrogen atoms. The final refinement converged to wR_2 = 0.1541 (for F^2, all data) and R_1 = 0.0737 [F, 1608 reflections with $I > 2\sigma(I)$].

Fluorescence Quantum Yields (Φ_F). Fluorescence quantum yields in solution were measured following a general method using 9,10-diphenylanthracene ($\phi_F = 0.9$ in cyclohexane) as the standard. Diluted solutions of **1**−**3** (10^{-5}−10^{-7} M) in appropriate solvents were used for recording the fluorescence spectra. Sample solutions were added to quartz cuvettes and degassed for ∼15 min. The degassed solution had an absorbance of 0.06−0.09 at 372 nm. The fluorescence spectra of each of the sample solutions were recorded 3−4 times and an average value of integrated areas of fluorescence used for the calculation of Φ_F. The refractive indices of solvents at the sodium D line were used.

Values of Φ_F in the solid state were measured following a literature method.[17] A CH_2Cl_2 solution of sample was mixed with a concentrated solution of PMMA in acetonitrile in such a way that the overall concentration of the sample was ∼10^{-4} M. The resulting solution was cast as thin films on quartz plates and then dried in an oven at ∼ 100 °C for about 1 h. The plate was inserted into an integrating sphere and the required spectra recorded. For **1**−**3**, λ_{ex} = 372 nm. It is well-known that for compounds showing an overlap of the absorption and the emission spectra (a small Stokes shift), the use of an integrating sphere results in a substantial loss of emission due to reabsorption of the emitted light. A method employed earlier was used to minimize the impact of this on the calculation of the Φ_F.[19]

Fluorescence Lifetime (τ_F) Measurement. Solutions of **1**−**3** (10^{-4}−10^{-6} M in CH_2Cl_2) showing absorbance 0.07−0.1 at 372 nm were placed in quartz cuvettes. Fluorescence decay profiles of argon-degassed (∼15 min) solutions were recorded using a single photon counting spectrofluorimeter. Decays were monitored at the emission maximum of the corresponding compounds. In-built software allowed the fitting of the decay spectra (χ^2 = 1−1.5) and yielded the fluorescence lifetimes.

Acknowledgment. We thank Dr. K. Kirschbaum from University of Toledo for analyzing the X-ray crystal structure. R.M. is thankful to the McMaster Endowment for providing a fellowship. This work has been supported by the Navy Office of Research (Grant No. N00014-5-1-0372).

Supporting Information Available: Fluorescence decay profiles of **1** and **2**, spectra showing the effect of annealing and aging on the solid-state emission of **2** and **3**, details of the X-ray crystal structure of **1**, and ^{1}H NMR of **1**−**3**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO0601314

---

[27] Sheldrick, G. M. *SADABS, Program for the Empirical Absorption Correction of Area Detector Data*; University of Göttingen: Göttingen, Germany, 1996.

[28] Sheldrick, G. M. *SHELXTL* (ver. 6.12); Bruker AXS, Inc.: Madison, WI, 2000.