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3,6,9,12-Tetrasubstituted Chrysenes: Synthesis, Photophysical Properties, and Application as Blue Fluorescent OLED

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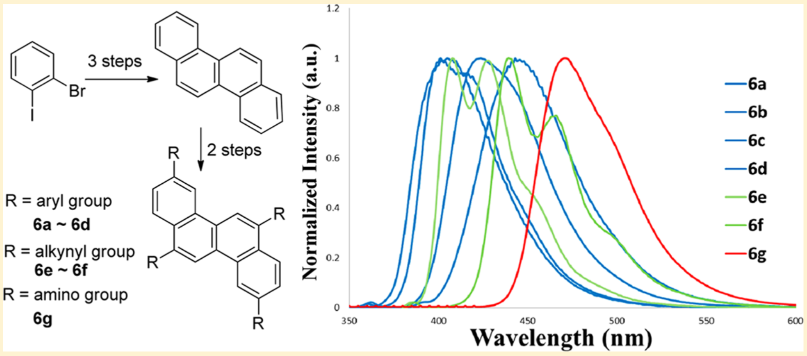
Supporting Information

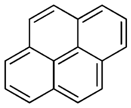


ABSTRACT: A short synthesis of unsubstituted chrysene is described to provide a cheap source of this compound. This chrysene was used to prepare 3,6,9,12-tetrabromochrysene, which was subsequently transformed into various 3,6,9,12-tetrasubstituted chrysenes bearing four aryl, alkynyl, or amino groups by means of the Suzuki, Sonogashira, or Buchwald−Hartwig coupling reaction, respectively. These substituents result in large bathochromic shifts in the chrysene absorption and emission spectra. These new chrysene derivatives show blue fluorescent emission (401−471 nm) with high quantum yields (0.44−0.87). DFT calculations on these chrysenes rationalize well the substituent effects on their HOMO and LUMO energy levels. One representative chrysene (**6g**) was used as a blue fluorescent emitter in an OLED device that showed an outstanding external quantum efficiency (η = 6.31%) with blue emission [CIE (x, y) = (0.13, 0.20)] and a low turn-on voltage (3.0 V).

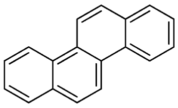
■ INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) have found widespread applications in organic light-emitting diodes (OLEDs) for decades.[1−5] Small polyaromatic hydrocarbons serve as appealing materials because of their high carrier mobility[6] and oxidation resistance.[1−6] The energy gaps (3−4 eV) of these PAHs make these compounds suitable for use as OLED active-layer materials as either host or blue dopants. Considerable interest has focused on the elaboration of anthracenes,[1] pyrenes,[2] fluorenes,[3] and perylenes[4] as OLED materials. Among these small PAHs, pyrene derivatives are particularly notable because of their outstanding OLED performance as host materials. Examples include 1-(4-(1-pyrenyl)phenyl)-pyrene (PPP), 1-(2,5-dimethoxy-4-(1-pyrenyl)phenyl)pyrene (DOPPP), and 1-(2,5-dimethyl-4-(1-pyrenyl)phenyl)pyrene (DMPPP).[2a]

Chrysene resembles pyrene in comprising a fused tetracene core; this structural comparison presages its prospective use in OLED devices.[5] However, its development has been impeded by both the lack of a convenient synthesis[7] and the costly commercial materials ($306/g, purity >97%).[8] Reported syntheses of chrysene derivatives are based mainly on naphthalene derivatives bearing special functional groups, which requires a long procedure.[7] There is only one literature report[5] on tetraphenylchrysene used in an OLED device, of which the data fail to reflect the potential of the chrysene family. For instance, the reported OLED device gave a broad blue emission with CIE (x, y) = (0.23, 0.35) in addition to a small current efficiency (1.5 cd/A). We report herein a convenient synthesis of chrysene that enables the subsequent preparation of tetrasubstituted chrysene derivatives. Notably, the introduction of suitable substituents significantly alters the photophysical properties and enhances the quantum yield. Importantly, one representative chrysene was used as a blue fluorescent emitter with outstanding OLED performance (7.2 cd/A).



Pyrene



Chrysene

■ RESULTS AND DISCUSSION

We previously reported regiocontrolled syntheses of ethylene-bridged p-phenylene oligomers based on platinum-catalyzed

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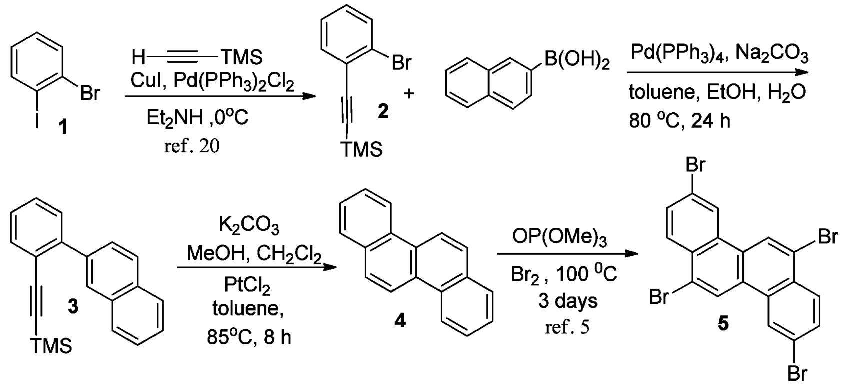
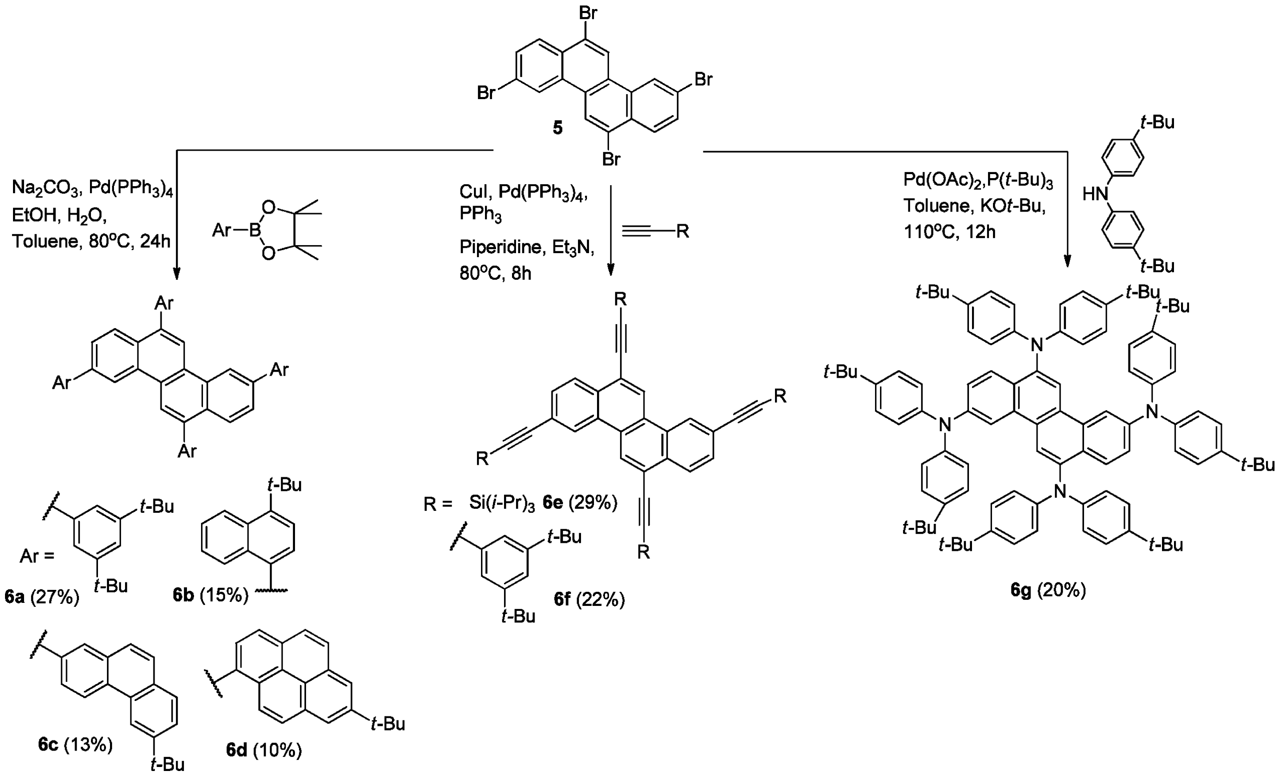
Scheme 1. Synthetic Path To Produce Chrysene (4)



Scheme 2. Synthesis of Compounds 6a−g



aromatization of 2-aryl-1-ethynylbenzenes.[9] The reported procedures for chrysene derivatives are tedious, and commercial chrysene (**4**) is costly. We employed this platinum-catalyzed aromatization to develop a short synthesis of **4**, as outlined in Scheme 1. An initial Sonogashira coupling reaction[10] of 2-bromo-1-iodobenzene with (trimethylsilyl)acetylene provided 2-alkynyl-1-bromobenzene **2** in 94% yield, of which a subsequent Suzuki coupling[11] gave the desired product **3** in 82% yield. Species **3** was then desilylated with K_2CO_3 and subsequently treated with $PtCl_2$ in hot toluene to give **4** in 85% yield with high regioselectivity (>20:1). Chrysene **4** was converted to 3,6,9,12-tetrabromochrysene (**5**) by direct bromination (Br_2, 6 equiv) in neat trimethyl phosphate at 100 °C (3 days) according to a procedure reported by Ionkin and co-workers.[5]

Among tetrasubstituted chrysenes,[5,12] there have been no reports on the systematic variation of their photophysical properties with substituents. We sought to vary the HOMO and LUMO energy levels of tetrasubstituted chrysenes with suitable aryl, alkynyl, and amino groups because these substituents can significantly alter the energy levels of an anthracene core.[1b,c] As shown in Scheme 2, treatment of tetrabromochrysene **5** with various 2-aryl-1,3,2-dioxaborolanes (6 equiv, Ar = 3,5-di-*tert*-butylphenyl, 4-*tert*-butylnaphthalen-1-yl, 6-*tert*-butylphenanthren-2-yl, and 7-*tert*-butylpyren-1-yl), Na_2CO_3 (60 equiv), and $Pd(PPh_3)_4$ (15 mmol %) in a EtOH/toluene/H_2O mixed solvent afforded the resulting Suzuki coupling products **6a**−**d** in 10−27% yield. We also employed Sonogashira coupling reactions on tetrabromide species **5** to give tetraalkynyl-substituted chrysene derivatives **6e** [R = Si(i-Pr)$_3$] and **6f** (R = 3,5-di-*tert*-butylphenyl) in 22−29% yield after purification from a silica gel column. The introduction of four diarylamino groups was achieved also with the Buchwald−Hartwig coupling reaction,[13] providing compound **6g** as a yellow solid in 20% yield. The overall yields of 10−29% in such fourfold coupling reactions are acceptable because each step corresponds to 56−72% yield. During these catalytic coupling reactions, we did not attempt to isolate the mono-, bis-, or trisubstituted products, which existed in minor proportions as monitored by TLC and NMR.

Single crystals of **6a** suitable for X-ray diffraction were grown in hexane/dichloromethane. The ORTEP drawing of **6a** (Figure 1) shows a symmetrical structure with four di-*tert*-butylphenyl substituents located on carbons C1, C20, C1′ ,and C20′. The torsion angles between chrysene and the two phenyl rings on the C1 and C1′ carbons are 49° and 54°, respectively, and the planes between chrysene and the phenyl rings on the C20 and C20′ carbons show smaller torsion angles of ca. 34°. These angles allow partial electron delocalization within four phenyl groups and the chrysene core, resulting in variability of the photophysical parameters (Table 1).

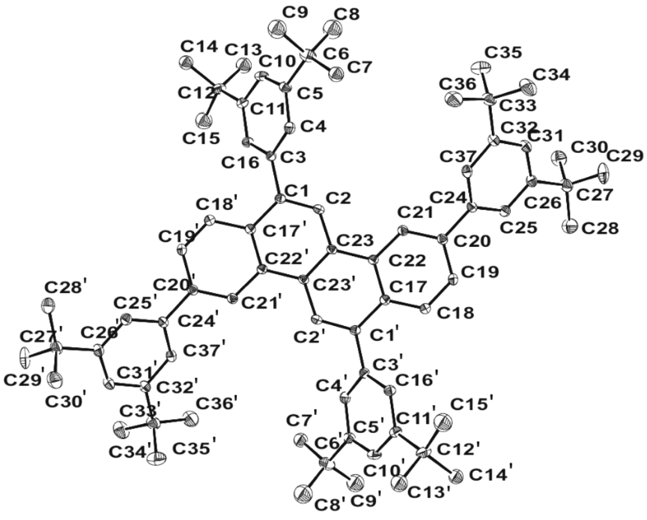


Figure 1. ORTEP drawing of species **6a**.

Figure 2 shows the UV/vis and photoluminescence (PL) spectra of chrysene derivatives **6a−g** in CH_2Cl_2 (Figure 2); their key photophysical parameters are summarized in Table 1. Relative to unsubstituted chrysene **4** (entry 1), there are large bathochromic shifts for the absorption and emission spectra of the new tetrasubstituted chrysenes **6a−6d**; their absorption maxima are observed within the range 296−433 nm, and their emission bands are within 401−470 nm. In contrast to aryl-substituted chrysenes **6a−6d**, the alkynyl- and amino-substituted analogues **6e−g** have three absorption maxima. The absorption maxima of aryl-substituted chrysenes **6a−d** increase gradually with increasing size of their aryl arrays; this phenomenon supports our postulated electron delocalization over the aryl groups and the chrysene core. Compounds **6a−g** are strongly fluorescent with high quantum yields (Φ) of 0.44−0.87), which are much greater than that of chrysene **4** itself (Φ = 0.12). The PL emission wavelength of diarylamino-substituted chrysene **6g** is somewhat affected by solvent polarity (e.g., 456 nm in hexane, 471 nm in CH_2Cl_2, and 470 nm in acetonitrile), showing a small degree of charge-transfer character in its excited states.[14] The presence of four substituents is expected to decrease intermolecular $\pi-\pi$ interactions between two chrysene cores, thus inhibiting intermolecular fluorescence quenching. The increasing quantum yields (Φ = 0.61−0.87) for chrysene derivatives **6a−d** are attributed to the increasing sizes of their aryl substituents.

Compounds **6a−d** and **6g** showed one-electron quasi-reversible oxidation in CH_2Cl_2, as revealed by cyclic voltammetry (CV) measurements;[15] compound **6g** bearing four amino groups undergoes no second oxidation to form a dicationic species.[16] We determined their HOMO energies (E_{HOMO}) from the $E_{1/2}^{\mathrm{ox}}$ potentials and the band gaps (ΔE) from the UV absorption. The LUMO energies were then obtained as $E_{\mathrm{LUMO}} = E_{\mathrm{HOMO}} + \Delta E$. Compounds **6e** and **6f** have excessively low HOMO energies that were beyond the detection limit of the CV method. Their HOMO energies were measured by photoelectron spectroscopy and found to be −6.09 and −5.84 eV, respectively [see the Supporting Information (SI)]. A summary of the HOMO and LUMO energies is provided in Figure 3. These data clearly reflect the substituent effects, which generate small band gaps for aryl-substituted chrysenes **6a−d** (ΔE = 3.08−3.30 eV, ca. 0.47−0.69 eV smaller than that of unsubstituted chrysene **4**). Electron-withdrawing alkynyl substituents, as in compounds **6e** and **6f,** lower the energies of both the HOMO and the LUMO, giving ΔE = 3.04 and 2.81 eV respectively. For compound **6g** bearing π-donating diarylamino groups, the band gap is ΔE = 2.73 eV; this small value implies that the amino groups raise the HOMO energy to a larger extent than the LUMO energy.

To understand the electronic structures of such chrysene derivatives, we performed time-dependent density functional theory (TD-DFT) calculations at the B3LYP/6-31G* level for

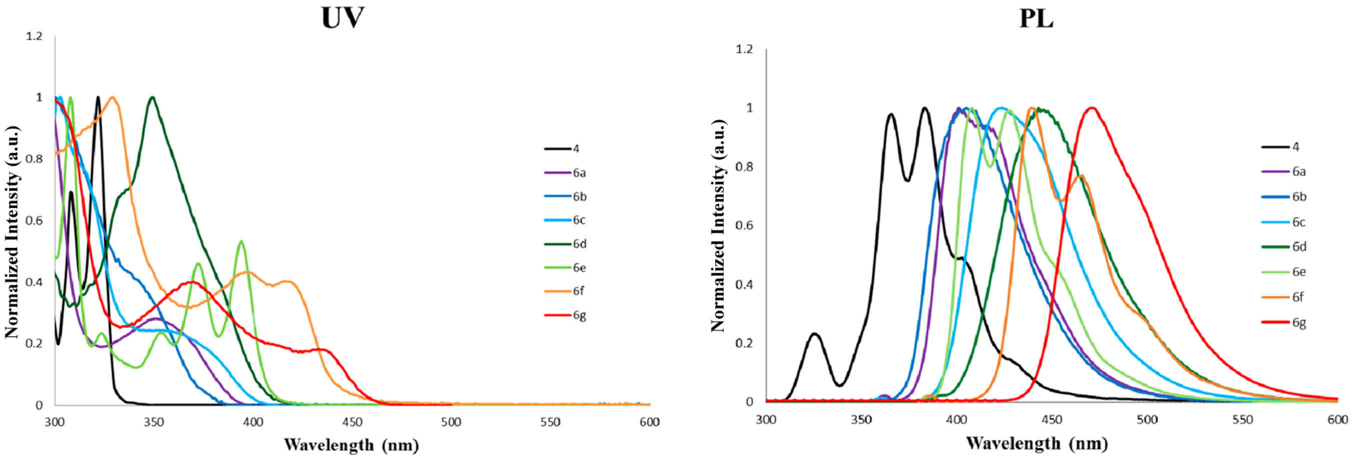


Figure 2. Absorption and emission spectra of compounds **4** and **6a−g** in CH_2Cl_2.

Table 1. Photophysical Properties of Compounds 4 and 6a−g

compound	λ_{max}^{abs} (nm)[a]	λ_{max}^{PL} (nm)[a,b]	Φ (%)[a,c]	E_{HOMO}/E_{LUMO} (eV)[d]	band gap (eV)[f]
4	309, 322	366, 383	12.2	−5.29/−1.52	3.77
6a	296, 351	401	60.9	−5.64/−2.45	3.19
6b	300	405	72.0	−5.72/−2.42	3.30
6c	303	424	78.1	−5.66/−2.58	3.08
6d	349	443	87.4	−5.63/−2.55	3.08
6e	308, 372, 394	408, 428	74.1	−6.09/−3.04[e]	3.05
6f	329, 396, 416	439, 466	62.6	−5.84/−3.03[e]	2.81
6g	299, 370, 433	471	44.0	−5.02/−2.29	2.73

[a] In CH_2Cl_2, 1.0×10^{-5} M. [b] Excitation wavelengths are shown in the Experimental Section. [c] Coumarin-1 was used as a standard. [d] E_{HOMO} values were determined by CV. [e] E_{HOMO} was determined by photoelectron spectroscopy. [f] Band gaps were calculated from UV/vis absorption.

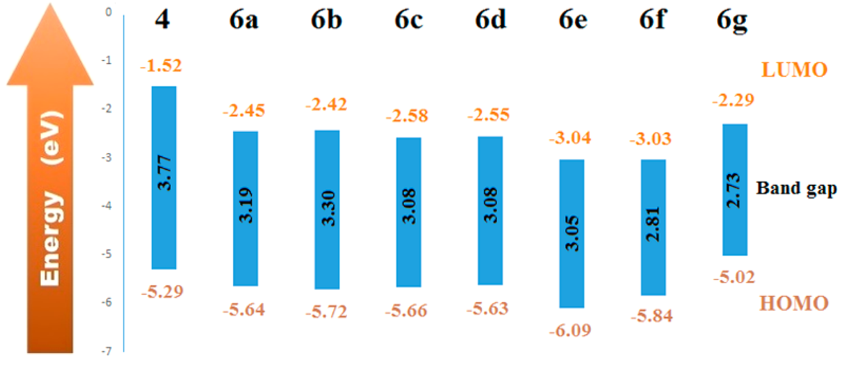


Figure 3. HOMO and LUMO energies of species **4** and **6a**−**g**.

compound **6a** using its crystallographic data (Figure 1). We found that the distributions of both the HOMO and the LUMO of compound **6a** (Figure 4) were located mainly on the central chrysene core, with minor distributions on the four phenyl rings. For both the HOMO and the LUMO, significant orbital coefficients were situated at the carbons linked to the phenyl groups (C1, C20, C1′, and C20′; see Figure 1). This feature indicates that the energies of both orbitals could be affected significantly by various electron-donating or -withdrawing substituents, consistent with our observations in Figure 3.

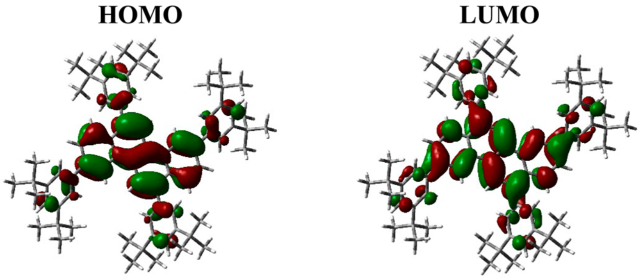


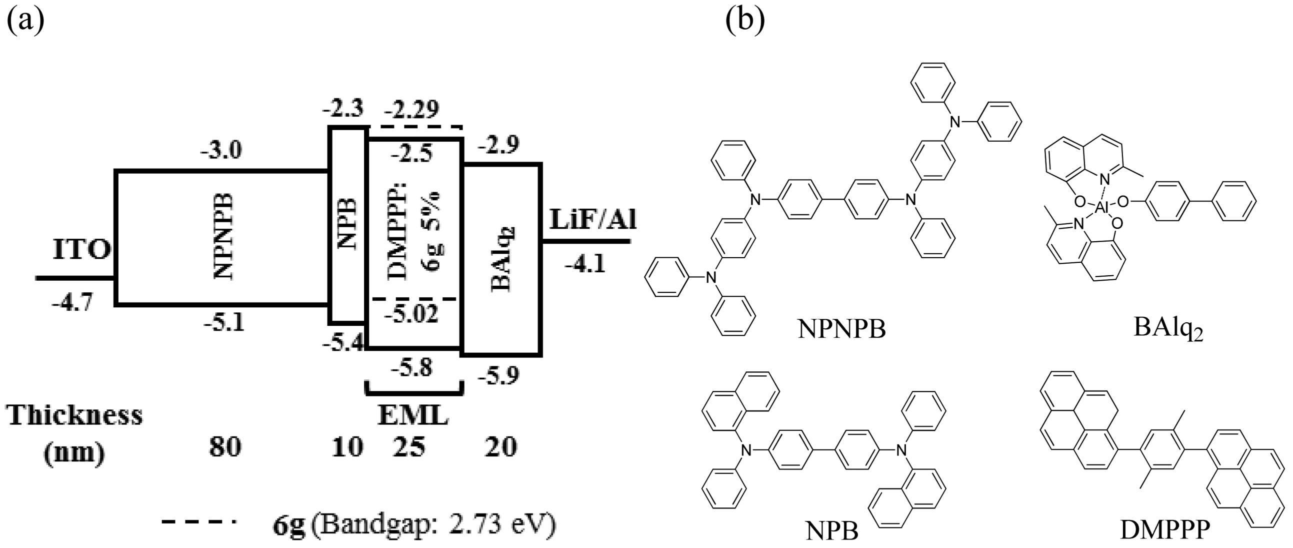
Figure 4. HOMO and LUMO of **6a** obtained from DFT calculations.

Chrysene derivative **6g** was used as a dopant to fabricate blue fluorescent OLEDs by thermal evaporation because of its suitable emission wavelength (471 nm) and satisfactory quantum yield (Φ = 0.44). Its PL is affected by solvent polarity but to only a small extent; this property does not result in undesired electroluminescence (EL) red shifts as for some monostyrylamine materials.[17] The multilayer configuration consisted of ITO/NPNPB (80 nm)/NPB (10 nm)/DMPPP:**6g** (5%) (25 nm)/$BAlq_2$ (20 nm)/LiF (1 nm)/Al (100 nm). The device components and molecular structures of *N*,*N*′-diphenyl-*N*,*N*′-bis[4-(*N*,*N*-diphenylamino)phenyl]benzidine (NPNPB), 4,4′-bis[*N*-(1-naphthyl)-*N*-phenylamino]biphenyl (NPB), 1-[2,5-dimethyl-4-(1-pyrenyl)phenyl]pyrene (DMPPP), and bis(2-methyl-8-quinolinato)(4-phenylphenolato)aluminum ($BAlq_2$) are shown in Scheme 3. The device showed a low activation voltage of 3.0 V, a large external quantum efficiency of $\eta_{ext} = 6.31\%$, a current efficiency of $\eta_c = 7.2$ cd A^{-1}, a power efficiency of $\eta_p = 3.21$ lm W^{-1}, and a maximum brightness of up to 42 325 cd/m^2. Figure 5 shows the EL spectrum with a maximum wavelength 471 nm and no shoulder at an applied voltage of 8.0 V (Figure 5); this emission pattern was unaffected by the use of a range of applied voltages (6−10 V). The CIE (*x*, *y*) coordinates of (0.13, 0.20) are indicative of a satisfactory blue color quality. A similar OLED without compound **6g** showed a distinct emission at 450 nm with $\eta_{ext} = 4.0\%$, $\eta_c = 3.4$ cd A^{-1}, and $\eta_p = 1.1$ lm W^{-1}.[18] Accordingly, the blue dopant **6g** really enhances the OLED performance with an effective energy transfer from the host material.[18] Among blue fluorescent OLEDs, distyrylamine (DSA) derivatives are the most commonly referred dopants.[19] Lee et al.[19c] reported that a light-blue EL device using *p*-bis(*p*-*N*,*N*-diphenylaminostyryl)benzene (DSA-Ph) reaches a current efficiency of 9.7 cd A^{-1} with CIE (*x*, *y*) = (0.16, 0.32). Our preliminary data reflect the prospects of chrysene derivative **6g** as a blue fluorescent material.

■ CONCLUSION

Before this work, there was no systematic study on the photophysical properties of chrysene derivatives to evaluate their prospects in OLED devices. In this work, a convenient synthesis of chrysene was developed and further utilized to prepare 3,6,9,12-tetrasubstituted chrysenes bearing various aryl, alkynyl, and diarylamino groups. Relative to unsubstituted chrysene **4**, there are large bathochromic shifts in the UV/vis

Scheme 3. (a) Structure of the 6g-Based Device and Energy Levels of the Materials; (b) Structures of NPNPB, NPB, DMPPP, and BAlq$_2$



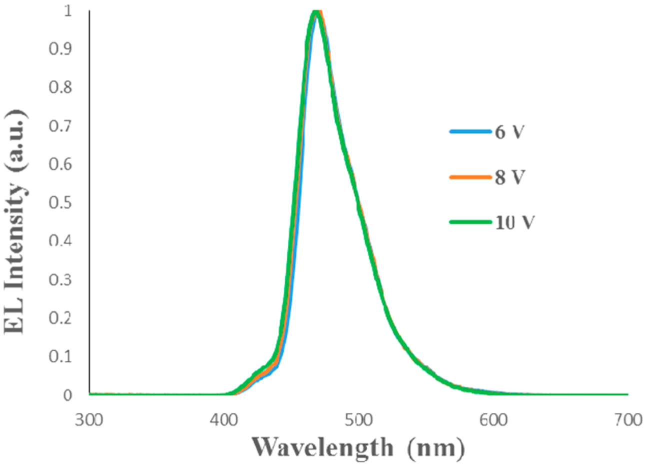


Figure 5. EL spectra of compound **6g** as a dopant at various voltages.

and PL spectra of these new chrysene derivatives, and their quantum yields are greatly enhanced. The HOMOs and LUMOs of these new chrysenes are easily affected by the presence of aryl, alkynyl, and amino substituents because significant orbital coefficients are located on the chrysene 3,6,9,12-carbons linked to these substituents. Diarylamino-substituted chrysene **6g** was tested as a blue fluorescent emitter in an OLED; this device showed an outstanding external quantum efficiency (η = 6.31%) with blue emission [CIE (x, y) = (0.13, 0.20)] and a low turn-on voltage (3.0 V).

■ EXPERIMENTAL SECTION

General Information. All of the experimental operations were performed under nitrogen; the equipment was dried in an oven at 150 °C for several hours. THF and toluene were distilled over sodium particles. CH_2Cl_2 was distilled over calcium hydride. All other specified chemicals were commercially purchased and used without further purification. ^{1}H and ^{13}C NMR spectra were determined on either a 400 or 600 MHz NMR spectrometer using $CDCl_3$ or CD_2Cl_2. HRMS was performed on double-focusing sector mass spectrometer in EI mode. MALDI mass determination was performed on a MALDI-TOF mass spectrometer. Elemental analysis was performed on an element analyzer. The single-crystal X-ray structure of **6a** was collected on an X-ray diffractometer. The compound [(2-bromophenyl)ethynyl]-trimethylsilane (**2**) was prepared from 1-bromo-2-iodobenzene according to a literature procedure.[20] 3,6,9,12-Tetrabromochrysene (**5**) was prepared from chrysene **4** according to the procedure reported by Ionkin et al.[5] Various reagents including (3,5-di-*tert*-butylphenyl)-pinacolborane,[21] (6-*tert*-butylphenanthren-2-yl)pinacolborane,[22] (7-*tert*-butylpyren-1-yl)pinacolborane,[23] 1,3-di-*tert*-butyl-5-ethynylbenzene,[24] and bis(4-*tert*-butylphenyl)amine[25] were prepared according to the cited literature.

Photophysical Properties. UV/vis absorption and PL spectra were recorded on samples in dichloromethane (1.0×10^{-5} M) using a fluorescence spectrophotometer. The quantum yield was measured with reference to coumarin-1 (Φ_f = 0.99).[26] Electrochemical measurements were undertaken with an electrochemical analyzer employing Ag/Ag$^+$ (Ag/0.01 M $AgNO_3$) as the reference electrode, a Pt wire as the counter-electrode, a glassy carbon electrode as the working electrode, and an internal ferrocene/ferrocenium (Fc/Fc$^+$) standard. Samples were prepared in dry CH_2Cl_2 (1.0×10^{-3} M) containing tetrabutylammonium hexafluorophosphate (0.1 M) as the supporting electrolyte. The energy level of Fc/Fc$^+$ was taken as 4.8 eV; the HOMO energies were determined using the equation $E_{\mathrm{HOMO}} = 4.8$ eV + $E^{\mathrm{ox}}_{1/2}$. The HOMO energies of **6e** and **6f** were measured using a photoelectron spectrometer (AC-2) in ambient air with a UV source.

OLED Device Fabrication. The EL devices with the configuration ITO/NPNPB (80 nm)/NPB (10 nm)/DMPPP:**6g** (5%) (25 nm)/BAlq$_2$ (20 nm)/LiF (1 nm)/Al (100 nm) were fabricated by sequential thermal evaporation onto clean glass precoated with a layer of indium tin oxide (ITO) having a sheet resistance of 25 Ω/square. The effective area of the emitting diode was 9.00 mm^2. Current, voltage, and light intensity were recorded simultaneously using a source meter and an optical meter equipped with a silicon photodiode. EL spectra were measured on a fluorescence spectrophotometer. All of the measurements were performed near 23 °C in air.

Synthesis of Compound 3. A mixed solution of toluene (160 mL), EtOH (40 mL), and water (40 mL) was degassed with nitrogen for 30 min; to this solution were added compound **2**[20] (1.68 g, 6.63 mmol), $Pd(PPh_3)_4$ (390 mg, 0.33 mmol), Na_2CO_3 (2.11 g, 19.89 mmol), and naphthalen-2-ylboronic acid (1.14 g, 6.63 mmol). The resulting mixture was heated at 80 °C for 24 h, and the solution was extracted with hexane and concentrated. The crude material was purified by silica gel column chromatography (hexane) to afford compound **3** (1.63 g, 5.44 mmol, 82%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (d, J = 1.3 Hz, 1H), 7.87−7.84 (m, 3H), 7.75 (dd, J = 1.8, 8.5 Hz, 1H), 7.60 (dd, J = 1.4, 7.5 Hz, 1H), 7.50−7.47 (m, 3H), 7.40 (td, J = 1.4, 7.5 Hz, 1H), 7.29 (td, J = 1.4, 7.5 Hz, 1H), 0.06

(s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.0, 137.7, 133.4, 133.4, 133.0, 132.6, 129.6, 128.7, 128.3, 128.1, 127.6, 127.5, 127.1, 126.9, 125.9, 121.6, 104.9, 97.6, −0.3. HRMS Calcd for $C_{21}H_{20}Si$: 300.1334. Found: 300.1335.

Synthesis of Compound 4. Compound **3** (1.63 g, 5.43 mmol) was dissolved in MeOH/CH_2Cl_2 (100 mL/100 mL) and then K_2CO_3 was added (75 mg, 0.54 mmol); the resulting solution was stirred for 3 h. The solution was treated with water and extracted with dichloromethane (3 × 40 mL). The combined organic phases were dried over $MgSO_4$ and evaporated to dryness. The crude product was purified on a flash silica gel column (hexane) to afford a yellow oil. This oil was treated with dry toluene (300 mL) and $PtCl_2$ (143 mg, 0.54 mmol) under an argon atmosphere at 85 °C for 8 h. The resulting solution was extracted with dichloromethane. The extract was dried over $MgSO_4$, concentrated under reduced pressure, and purified on a silica gel column (dichloromethane/hexane 1/10) to afford chrysene (**4**) (1.05 g, 4.62 mmol, 85%) as a light-yellow solid. Mp: 254−255 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.76 (d, *J* = 8.4 Hz, 2H), 8.70 (d, *J* = 9.0 Hz, 2 H), 8.01−7.97 (m, 4H), 7.71−7.67 (m, 2H), 7.64−7.60 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 132.2, 130.6, 128.5, 128.2, 127.3, 126.7, 126.4, 123.1, 121.2. HRMS Calcd for $C_{18}H_{12}$: 228.0939. Found: 228.0942. The spectral data agree satisfactorily with a literature report.[27]

Synthesis of (4-*tert*-Butylnaphthalen-1-yl)pinacolborane. To a 1,4-dioxane solution (50 mL) of Pd(dppf)Cl_2 (146 mg, 0.2 mmol) and KOAc (1.12 g, 12 mmol) were added 1-bromo-4-*tert*-butylnaphthalene (1.05 g, 4.0 mmol) and bis(pinacolato)diboron (1.29 g, 4.8 mmol); the mixture was stirred for 3 h at 80 °C. The solution was extracted with dichloromethane, and the extract was washed with water, dried over $MgSO_4$, and concentrated. The residues were purified by silica gel column chromatography (ethyl acetate/hexane 1/10) to afford the desired borane compound (1.15 g, 3.73 mmol, 93%) as a white solid. Mp: 140−146 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.82 (dd, *J* = 2.4, 7.6 Hz, 1H), 8.46 (dd, *J* = 2.0, 7.6 Hz, 1H), 7.99 (d, *J* = 7.6 Hz, 1H), 7.50−7.45 (m, 3H), 1.61 (s, 9H), 1.39 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.6, 138.4, 135.4, 131.3, 129.8, 126.9, 125.0, 124.1, 122.4, 83.5, 36.1, 31.8, 24.9. HRMS Calcd for $C_{20}H_{27}BO_2$: 310.2104. Found: 310.2109.

Synthesis of 3,6,9,12-Tetrakis(3,5-di-*tert*-butylphenyl)-chrysene (6a). Nitrogen was bubbled through a mixed solution of toluene (40 mL), EtOH (10 mL), and water (10 mL) for 30 min, and to this solution were added compound **5** (875 mg, 1.61 mmol), Pd(PPh_3)$_4$ (379 mg, 0.32 mmol), Na_2CO_3 (10.239 g, 96.60 mmol), and 3,5-di-*tert*-butylphenylpinacolborane[21] (3.055 g, 9.66 mmol). The mixture was heated at 80 °C for 24 h. The solution was extracted with hexane, concentrated, and purified by silica gel column chromatography (dichloromethane/hexane 1/10) to afford compound **8a** (427 mg, 0.43 mmol, 27%) as a white solid. Mp: >350 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.04 (d, *J* = 1.2 Hz, 2H), 8.79 (s, 2H), 8.21 (d, *J* = 8.6 Hz, 2H), 7.82 (dd, *J* = 1.6, 8.6 Hz, 2H), 7.60 (d, *J* = 1.8 Hz, 4H), 7.57 (d, *J* = 1.8 Hz, 4H), 7.55 (t, *J* = 1.8 Hz, 2H), 7.47 (t, *J* = 1.8 Hz, 2H), 1.43 (s, 36 H), 1.40 (s, 36 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.3, 150.8, 141.0, 140.5, 140.4, 139.9, 131.4, 130.2, 127.8, 127.5, 126.4, 124.8, 124.8, 122.2, 122.2, 121.6, 121.3, 35.1, 35.1, 31.7, 31.6. MALDI-TOF-MS Calcd for $C_{74}H_{92}$: 980.7199. Found: 980.523. Anal. Calcd for $C_{74}H_{92}$: C, 90.55; H, 9.45. Found: C, 90.47; H, 9.50.

Synthesis of 3,6,9,12-Tetrakis(4-*tert*-butylnaphthalen-1-yl)-chrysene (6b). Compound **6b** was prepared in a similar manner as **6a** from compound **5** (652 mg, 1.20 mmol) and (4-*tert*-butylnaphthalen-1-yl)pinacolborane (2.23 g, 7.20 mmol) and was obtained as white solid (172 mg, 0.18 mmol, 15%). Mp: >355 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.87 (s, 2H), 8.80 (s, 2H), 8.58 (d, *J* = 8.8 Hz, 2H), 8.50 (d, *J* = 8.8 Hz, 2H), 7.97 (d, *J* = 8.4 Hz, 2H), 7.71−7.43 (m, 18H), 7.35−7.29 (m, 4H), 1.72 (s, 18H), 1.64 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.2, 145.8, 139.6, 139.2, 138.1, 137.6, 134.5, 133.2, 131.7, 131.7, 131.5, 130.6, 128.9, 128.3, 127.9, 127.6, 127.5, 127.5, 127.2, 127.1, 127.1, 126.8, 124.8, 124.8, 124.4, 124.3, 123.2, 122.9, 122.8, 36.1, 36.0, 32.0, 31.9. MALDI-TOF-MS Calcd for $C_{74}H_{68}$: 956.5321. Found: 956.497. Anal. Calcd for $C_{74}H_{68}$: C, 92.84; H, 7.16. Found: C, 92.46; H, 7.20.

Synthesis of 3,6,9,12-Tetrakis(6-*tert*-butylphenanthren-2-yl)chrysene (6c). Compound **6c** was prepared in a similar manner as **6a** from compound **5** (272 mg, 0.50 mmol) and (6-*tert*-butylphenanthren-2-yl)pinacolborane[22] (1.08 g, 3.00 mmol) and was obtained as a light-yellow solid (81 mg, 0.07 mmol, 13%). Mp: >360 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.29 (s, 2H), 9.01 (s, 2H), 8.97 (d, *J* = 8.7 Hz, 2H), 8.82 (d, *J* = 8.7 Hz, 2H), 8.81 (s, 2H), 8.68 (s, 2H), 8.29−8.25 (m, 6H), 8.11 (dd, *J* = 1.8, 8.6 Hz, 2H), 8.04 (dd, *J* = 1.8, 8.4 Hz, 2H), 8.01 (dd, *J* = 1.6, 8.6 Hz, 2H), 7.91 (d, *J* = 8.4 Hz, 2H), 7.86−7.66 (m, 14H), 1.55 (s, 18H), 1.48 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.7, 149.5, 139.2, 139.2, 139.0, 132.6, 132.4, 131.4, 130.6, 130.2, 130.1, 129.9, 129.9, 129.9, 129.8, 129.8, 128.8, 128.4, 128.3, 128.1, 127.8, 127.3, 127.2, 127.1, 126.5, 126.3, 126.3, 126.3, 126.0, 125.1, 125.0, 123.4, 122.7, 122.6, 122.1, 118.4, 118.3, 35.3, 35.2, 31.6, 31.5. MALDI-TOF-MS Calcd for $C_{90}H_{76}$: 1156.5947. Found: 1156.426. Anal. Calcd for $C_{90}H_{76}$: C, 93.38; H, 6.62. Found: C, 93.29; H, 6.55.

Synthesis of 3,6,9,12-Tetrakis(7-*tert*-butylpyren-1-yl)-chrysene (6d). Compound **6d** was prepared in a similar manner as **6a** from compound **5** (290 mg, 0.52 mmol) and (7-*tert*-butylpyren-1-yl)pinacolborane[23] (1.20 g, 3.12 mmol) and was obtained as a light-yellow solid (63 mg, 0.05 mmol, 10%). Mp: >360 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.18 (s, 2H), 9.11 (s, 2H), 8.33 (dd, *J* = 2.2, 7.8 Hz, 2H), 8.25−8.19 (m, 8H), 8.16−8.06 (m, 12H), 8.01−7.91 (m, 10H), 7.73 (dd, *J* = 8.7, 12 Hz, 4H), 1.57 (s, 9H), 1.56 (s, 9H), 1.52 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.3, 149.1, 139.9, 138.4, 137.4, 135.9, 131.7, 131.3, 131.3, 131.0, 130.9, 130.9, 130.8, 130.6, 130.0, 129.5, 128.4, 128.2, 127.9, 127.9, 127.8, 127.6, 127.5, 127.3, 127.2, 125.8, 125.7, 125.3, 125.0, 124.9, 124.8, 124.5, 124.5, 123.8, 123.1, 123.0, 122.6, 122.5, 122.4, 122.4, 122.1, 35.2, 35.2, 31.9, 31.9. MALDI-TOF-MS Calcd for $C_{98}H_{76}$: 1252.5947. Found: 1252.286. Anal. Calcd for $C_{98}H_{76}$: C, 93.89; H, 6.11. Found: C, 93.55; H, 6.14.

Synthesis of 3,6,9,12-Tetrakis((triisopropylsilyl)ethynyl)-chrysene (6e). Compound **5** (300 mg, 0.55 mmol), Pd(PPh_3)$_4$ (130 mg, 0.11 mmol), CuI (42 mg, 0.22 mmol), and PPh_3 (58 mg, 0.22 mmol) were dissolved in a solution of piperidine (7.5 mL) and triethylamine (22.5 mL); the mixture was stirred for 5 min. To this mixture was added (triisopropylsilyl)acetylene (1.094 g, 6.00 mmol) dropwise under a nitrogen atmosphere; the resulting solution was heated to 80 °C for 8 h. After the solution was cooled to room temperature, the solvent was removed under reduced pressure. The residues were eluted through a long silica gel column (hexane) to give compound **6e** (151 mg, 0.16 mmol, 29%) as a white solid. Mp: >260 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.85 (s, 2H), 8.82 (s, 2H), 8.48 (d, *J* = 8.4 Hz, 2H), 7.78 (dd, *J* = 1.2, 8.4 Hz, 2H), 1.23−1.18 (m, 42H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 131.4, 130.6, 129.4, 127.5, 127.0, 127.0, 126.8, 122.5, 121.2, 107.4, 104.9, 97.7, 92.5, 18.8, 18.7, 11.5, 11.4. MALDI-TOF-MS Calcd for $C_{62}H_{92}Si_4$: 948.6276. Found: 948.547. Anal. Calcd for $C_{62}H_{92}Si_4$: C, 78.41; H, 9.76. Found: C, 78.32; H, 9.69.

Synthesis of 3,6,9,12-Tetrakis((3,5-di-*tert*-butylphenyl)-ethynyl)chrysene (6f). Compound **5** (250 mg, 0.46 mmol), Pd(PPh_3)$_4$ (107 mg, 0.09 mmol), CuI (34 mg, 0.18 mmol), and PPh_3 (47 mg, 0.18 mmol) were dissolved in a solution of piperidine (6 mL) and triethylamine (18 mL); the mixture was stirred for 5 min. To this mixture was added 1,3-di-*tert*-butyl-5-ethynylbenzene[24] (887 mg, 4.14 mmol) dropwise under a nitrogen atmosphere; the resulting solution was heated to 80 °C for 8 h. The resulting solution was cooled to room temperature, and the solvent was removed under reduced pressure. The residues were eluted through an alumina column (hexane) to give compound **6f** (108 mg, 0.10 mmol, 22%) as a yellow solid. Mp: >280 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.03 (s, 2H), 9.02 (s, 2H), 8.60 (d, *J* = 8.4 Hz, 2H), 7.89 (d, *J* = 8.4 Hz, 2H), 7.58 (d, *J* = 1.7 Hz, 4H), 7.50 (d, *J* = 1.7 Hz, 4H), 7.48 (s, 2H), 7.44 (s, 2H), 1.39 (s, 36H), 1.36 (s, 36H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.1, 151.0, 131.1, 129.9, 129.7, 127.6, 127.2, 127.0, 126.3, 126.1, 126.1, 123.3, 123.0, 122.6, 122.1, 122.0, 121.2, 96.6, 92.0, 88.7, 86.6, 34.9, 34.9, 31.4, 31.4. MALDI-TOF-MS Calcd for $C_{82}H_{92}$: 1076.7199. Found: 1076.755. Anal. Calcd for $C_{82}H_{92}$: C, 91.39; H, 8.61. Found: C, 91.51; H, 8.32.

Synthesis of 3,6,9,12-Tetrakis(bis(4-*tert*-butylphenyl)-amino)chrysene (6g). Compound **5** (212 mg, 0.39 mmol), bis(4-*tert*-butylphenyl)amine[25] (545 mg, 1.93 mmol), potassium *tert*-butoxide (263 mg, 2.34 mmol), $Pd(OAc)_2$ (2 mg, 0.004 mmol), and $P(tBu)_3$ (6 mg, 0.02 mmol) in dry toluene (15 mL) were stirred under an argon atmosphere at 100 °C for 12 h. The resulting solution was cooled to room temperature and extracted with dichloromethane. The extract was dried over $MgSO_4$, concentrated under reduced pressure, and purified on an alumina column to afford **6g** (108 mg, 0.08 mmol, 20%) as a yellow solid. Mp: >370 °C. ^1H NMR (400 MHz, CD_2Cl_2): δ 8.10 (d, J = 2.1 Hz, 2H), 7.99 (s, 2H), 7.89 (d, J = 9.0 Hz, 2H), 7.28−7.25 (m, 8H), 7.20−7.14 (m, 10H), 7.06−7.02 (m, 8H), 6.96−6.92 (m, 8H), 1.29 (s, 36H), 1.27 (s, 36H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 147.4, 146.8, 145.9, 145.2, 144.4, 142.1, 133.7, 128.2, 126.7, 126.6, 126.2, 126.1, 124.7, 123.7, 121.3, 120.9, 115.2, 34.6, 34.4, 31.6, 31.6. MALDI-TOF-MS Calcd for $C_{98}H_{112}N_4$: 1344.8887. Found: 1344.874. Anal. Calcd for $C_{98}H_{112}N_4$: C, 87.45; H, 8.39; N, 4.16. Found: C, 87.14; H, 8.41; N 4.09.

Computational Methods. Molecular geometries were optimized and electronic properties computed with the Gaussian 09 program using DFT or TD-DFT calculations in conjunction with the B3LYP hybrid exchange−correlation functional (Becke's three-parameter exchange functional combined with the Lee−Yang−Parr correlation functional) and the 6-31G* basis set. The molecular orbitals were visualized using Gaussview 4.1 software.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

NMR spectra, MALDI-TOF mass spectra, photoelectron spectra, CV measurements of new compounds, and X-ray crystallographic data for compound **6a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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