Side Substituent Dependence of Photophysical Properties of 9-Arylanthracene-Based π-Conjugates

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Three new 9-arylanthracene-based π-conjugated derivatives with different side substituent (methyl, methoxy, and hexyloxy) were synthesized using Heck coupling/Horner–Emmons reaction in good yields (72–78%) and their photophysical properties investigated. The dependence of the photophysical properties on the side substituent methyl, methoxy, and hexyloxy has been discussed. The absorption maxima of the synthesized compounds in the solution possess similar absorption bands located at 420–423 nm. They are shown to be thermally stable and emit light in sky blue region (ca. 490 nm) in solution. Photoluminescence measurements show a 25–28 nm red shift between solution and powdered states indicated some aggregation in the solid state. The results of cyclic voltammetry measurements of the compounds show good reversibility, indicating that the compounds have good electrochemical stability.

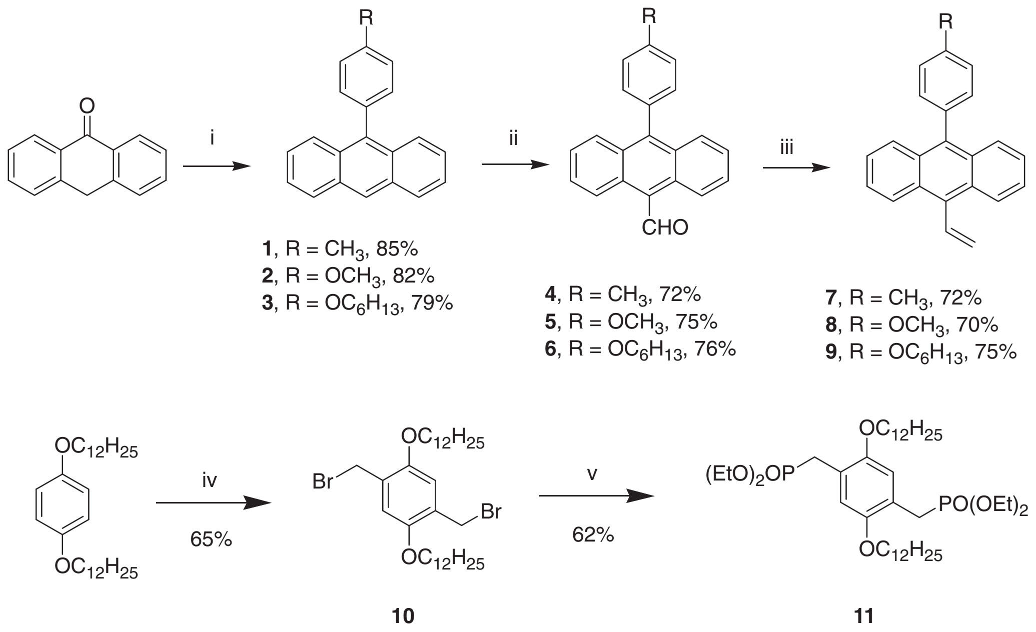
Anthracene-based π-conjugates have received considerable interest in both academic research and industrial applications due to their good electrochemical properties, thermal properties, and ease of modification at its 9- and 10-positions. Recently, Yoshizawa and co-workers[1] reviewed anthracene-based assemblies and their intrinsic photophysical, photochemical, and chemical properties. These materials are potential candidates as active materials for blue OLED,[2] fluorescent biosensors,[3] chem-sensors,[4] OFET devices,[5] solar cell,[6] liquid crystals,[7] and supramolecular chemistry.[8] The planar structure of anthracene moiety quenched the fluorescence efficiency in the solid state due to intermolecular π–π stacking interaction, which hampers its application in OLEDs. To mitigate these problems, several deep-blue anthracene derivatives have been synthesized by introducing aryl groups at the 9- and 10-positions. For example, Kim and co-workers[9] reported the synthesis of 9,10-diphenylanthracne-based blue-emitting materials. Kobayashi and co-workers[10] prepared alkylene-strapped diphenylanthracene-based oligomers used as solid-state blue-emitting material. Kwon and co-workers[11] fabricated deep-blue OLEDs using anthracene derivatives bearing multi-phenyl-based bulky substituent in 9,10-positions as emitters.

The nonplanar structure of 9,10-aryl-substituted anthracene can prevent excimer or exciplex formation resulting in high fluorescence quantum efficiency in dilute solution.[12] Particularly, in 9-, and 10-aryl-substituted anthracene, the benzene ring is rotated out of the plane of the anthracene moiety because of the steric interactions between the 1,8-hydrogens of the anthracene and the 2,6-hydrogens of the aryl group.[13] The nonplanar configuration of 9-, and 10-aryl-substituted anthracene unit decreases conjugation resulting in a low lying highest occupied molecular orbital (HOMO).[14] Therefore, it is necessary to improve electron-donating ability of blue-emitting materials for display or lighting applications. In our recent papers, the synthesis and optical properties of a few blue-emitting materials were reported.[15] This manuscript focuses on the synthesis of 9-aryl-substituted anthracene-based π-conjugated derivatives and also their optical and electrochemical properties.

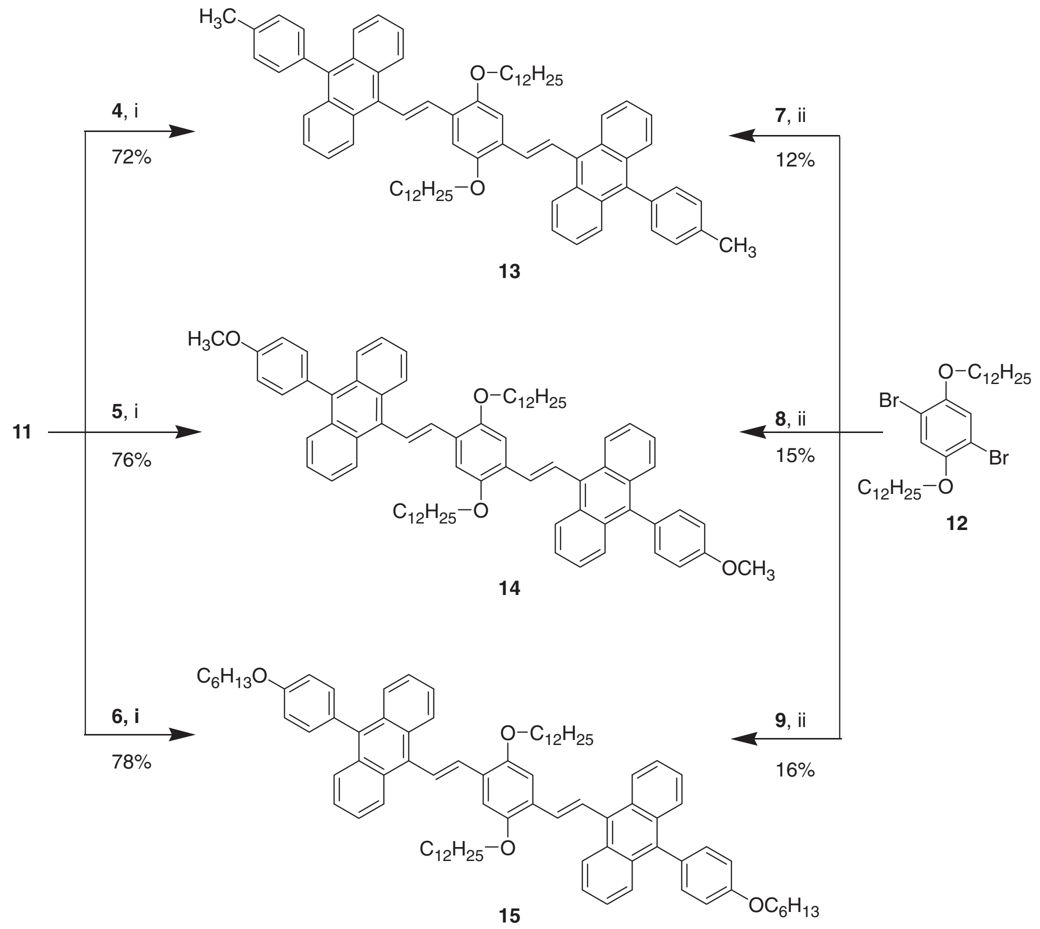
Results and Discussion

Synthesis. The synthetic procedures for the preparation of arylanthracene derivatives **7–9** and the core, diethyl [4-(diethoxyphosphorylmethyl)-2,5-bis(dodecyloxy)benzyl]phosphonate (**11**) used in this study are depicted in Scheme 1. Arylanthracene derivatives **1–3** were obtained in 79–85% yield from the reaction of anthrone with arylmagnesium bromide under refluxing conditions followed by removal of a water molecule from the resulting tertiary alcohol with formic acid. Formylation of **1–3** with phosphorus oxychloride and dimethylformamide at 90 °C gave aldehyde derivatives **4–6** in good yield. Wittig reaction of aldehydes **4–6** with methyltriphenylphosphonium bromide and *n*-BuLi at −20 °C afforded vinylarylanthracene derivatives **7–9** in 70–75% yield. Diphosphonate **11** can be readily prepared from hydroquinone in a three-step procedure. Reaction of hydroquinone with 1-bromododecane in DMSO in the presence of KOH resulted in 1,4-bis(dodecyloxy)benzene, which on treatment with concentrated HBr (48% aq.) and paraformaldehyde to give a benzyl bromide derivative **10**. Reaction of **10** with $P(OEt)_3$ afforded diphosphonate **11** in good yield.

The synthetic strategy employed for the synthesis of compounds **13–15** was based on the Horner–Wadsworth–Emmons reaction (HWE)/Heck coupling as outlined in Scheme 2. Conjugated derivatives **13–15** can be readily synthesized from 1,4-dibromo-2,5-bis(dodecyloxy)benzene (**12**)[16] using double-fold palladium-catalyzed Heck cross-coupling with vinylarylanthracene derivatives **7–9**. However, the double-fold Heck coupling strategy seemed to be unsuitable for the synthesis of **13–15** because the reaction yield is very poor (12–16%) due to



Scheme 1. *Reagents and conditions*: (i) ArMgBr, THF, reflux, 1 h; then HCO_2H, reflux, 15 min.; (ii) $POCl_3$, DMF, 90 °C, 4 h; (iii) $Ph_3P^+CH_3Br^-$, *n*-BuLi, THF, −20 °C to rt, 6 h; (iv) 48% (aqueous) HBr, HOAc, $(CH_2O)_n$, reflux; (v) $P(OEt)_3$, reflux.



Scheme 2. Synthesis of 9-arylanthracene-based conjugated compounds **13**–**15**. *Reagents and conditions*: (i) ^{t}BuOK, THF, rt, 12 h; then catalytic I_2, toluene, reflux, 48 h; (ii) $Pd(OAc)_2$, $P(o\text{-tol})_3$, $n\text{-}Bu_4NBr$, KOAc, DMF, 100 °C, 16 h.

the insolubility of mono-fold coupled intermediates, which were observed to precipitate from solution during early reaction times. The yield of desired conjugates was improved to 70% with the HWE reaction, in which **11** is treated with aldehyde derivatives **4**, **5**, and **6** afforded a mixture of *cis*- and *trans*-isomers of **13**, **14**, and **15**. In order to get all *trans* product, a catalytic isomerization of the mixtures was performed in the presence of iodide in toluene. The newly synthesized 9-arylanthracene-based conjugates **13–15** were characterized with ^{1}H NMR, MALDI-MS, elemental analysis and found to be in good agreement with their structures. The dodecyloxy side chain is attached to the 2- and 5-positions of the central benzene ring to enhance the solubility in organic solvents as well as the electron-donating ability of the compounds.

Optical Properties. The UV–vis absorption spectra of the new conjugated 9-arylanthracene compounds **13–15** in THF are shown in Figure 1 and the data are collected in Table 1. The absorption band at a shorter wavelength (ca. 292 nm) is attributed to the localized π–π^* transition of the 9-arylanthracene chromophore. The broad absorption band appears at 420–424 nm and possesses a high extinction coefficient (5.37×10^4 $M^{-1}\,cm^{-1}$ for **13**, $5.61 \times 10^4\,M^{-1}\,cm^{-1}$ for **14**, and 4.64×10^4 $M^{-1}\,cm^{-1}$ for **15**) is due to the more delocalized π–π^* transition originating from 1,4-bis(dodecyloxy)benzenevinylene-bridged 9-arylanthracene unit. The PL spectra for **13–15** in tetrahydrofuran are shown in Figure 2a and the data are summarized in Table 1. All compounds in this study are fluorescent active. The color of fluorescence of **13–15** ranges from blue to sky blue. The PL spectra of **13–15** (excited at 420 nm) show a sharp emission band at ca. 450 nm and a shoulder broad emission band at ca. 490 nm. The broad emission is attributed to the aggregation formation in the excited state due to the presence of planar π-conjugated anthracene backbone. The fluorescence quantum yields (Φ_{fl}) of **13**, **14**, and **15** are 40, 25, and 24% respectively in tetrahydrofuran. Low fluorescent quantum yield indicates significant aggregation in the excited state. It has been observed that onset PL emission slightly red shifted from **13** to **15** indicates minor change in conjugation effect in the molecular framework. Compound **15** has lower Φ_{fl} value and red-shifted emission, which implies hexyloxy side chain restricted the rotation of phenyl group resulting in more

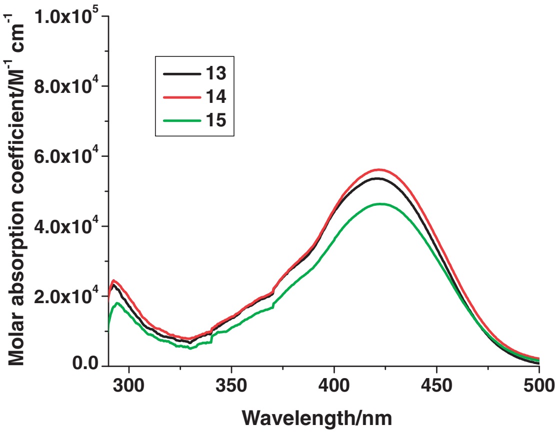
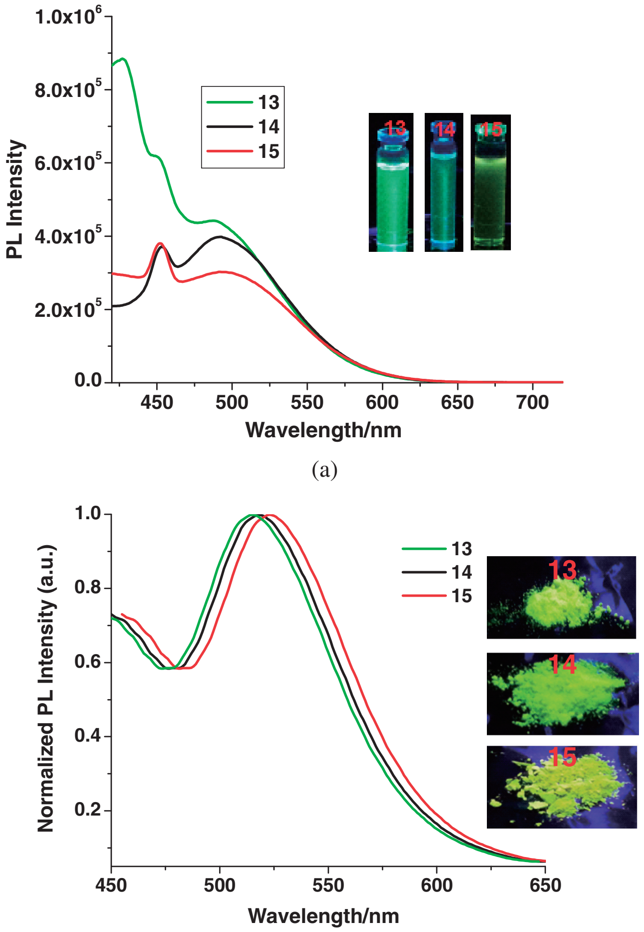


Figure 1. Absorption spectra of compounds **13–15** in tetrahydrofuran ($C = 1.0 \times 10^{-6}$ M).



(a)

(b)

Figure 2. (a) Photoluminescence spectra of compounds **13–15** ($\lambda_{ex} = 420$ nm) in tetrahydrofuran ($C = 1.0 \times 10^{-6}$ M) and (b) normalized photoluminescence spectra of compounds **13–15** ($\lambda_{ex} = 420$ nm) in powdered state.

Table 1. Photophysical Properties of Compounds **13–15**

Compd	UV–vis /nm	PL/nm THF/powder[a]	Φ%[b]	E_{ox}(onset) /eV	HOMO[c] /eV	LUMO[c] /eV	ΔE[d] /eV	T_d[e] /°C
13	292, 420	489/515	40	0.80	−5.46	−2.51	2.95	335
14	292, 422	492/518	25	0.68	−5.34	−2.41	2.93	365
15	294, 423	495/523	24	0.49	−5.15	−2.22	2.93	320

a) Measured in powdered state. b) Fluorescence quantum yields (Φ), measured in dichloromethane solution using pyrene ($\Phi_{fl} = 0.32$, in CH_2Cl_2) as standard, excited at 275 nm. c) HOMO $= -[E_{ox}(\text{onset}) + 4.66\,\text{eV}]$; LUMO $=$ HOMO $+ \Delta E$. d) $\Delta E =$ HOMO–LUMO gap; Estimated from the onset of the absorption spectra: $1240/\lambda_{onset}$. e) Decomposition temperature (T_d, 5% weight loss) obtained from thermogravimetric analysis (TGA).

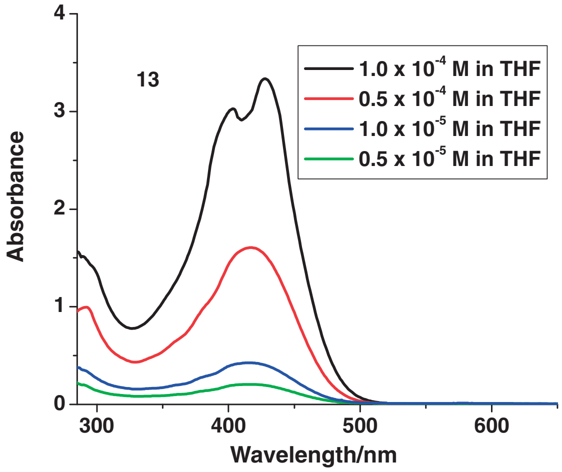
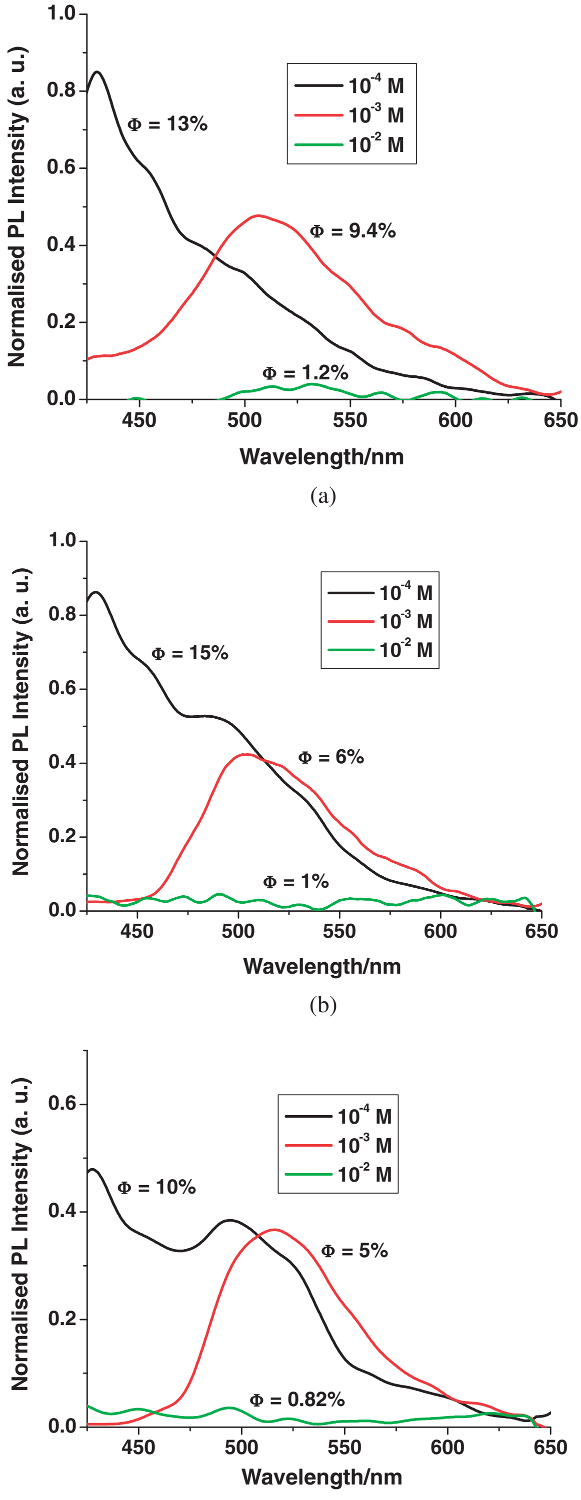


Figure 3. Absorption spectra of compound **13** in tetrahydrofuran with different concentration.

planar architecture than **14** (methoxy side chain) and **13** (methyl side chain). The planarity of compounds **13**–**15** have been attenuated due to the presence of side chain methyl, methoxy, and hexyloxy group on the 9-arylanthracene moiety. The more planar structure of **15** induces more aggregation in excited state. As a result, the $\Phi_{\rm fl}$ values are arranged in the order of **13** > **14** > **15**. The emission spectra are also measured in the powdered state of the compounds. The peak values are presented in Table 1 and displayed in Figure 2b. Compounds **13**, **14**, and **15** exhibited red-shifted (ca. 30 nm) emission in the powdered state compared to those observed in THF solutions. Moreover, these derivatives show a red shifted broad peak in the powdered state at around 520 nm indicating molecular aggregation or excimer formation in the solid state.[17] For understanding the aggregation behavior in the ground state, the absorption property of compound **13** was studied in tetrahydrofuran at different concentrations (0.5×10^{-5} to 1×10^{-4} M) as shown in Figure 3. The spectra show that the absorbance increases with concentration. When the concentration increased from 0.5×10^{-5} to 1×10^{-4} M, the UV absorption maximum wavelength of **13** red-shifted from 420 to 428 nm (an 8-nm red shift), indicating the formation of J-aggregates.[18] This result indicates that the compound **13** has a tendency to form aggregates at higher concentration solution. We also examined the aggregation behavior of **13**–**15** in excited state, the PL of their concentrated solutions (10^{-4}–10^{-2} M) was studied as shown in Figures 4a–4c. When the concentration was increased from 10^{-4} to 10^{-2} M, the PL intensity and also quantum yield ($\Phi_{\rm fl}$) of oligomers were decreased. For oligomer **13**, the $\Phi_{\rm fl}$ decreases (13% to 1.2%) with increasing concentration (10^{-4} to 10^{-2} M) and the maximum emission bands showed red shifts from 489 to 507 nm (an 18-nm red shift). The PL emission spectra of oligomers **14** and **15** also showed red shifts in higher concentrated (10^{-4} to 10^{-2} M) solution from 492 to 506 nm (a 14-nm red shift) and 495 to 516 nm (a 21 nm shift) with decrease $\Phi_{\rm fl}$ value (15% to 1% for **14**; 10% to 0.82% for **15**) respectively.



(a)

(b)

(c)

Figure 4. Normalized photoluminescence spectra of (a) compound **13** ($\lambda_{\rm ex} = 420$ nm), (b) **14** ($\lambda_{\rm ex} = 420$ nm), and (c) **15** ($\lambda_{\rm ex} = 420$ nm) in tetrahydrofuran with different concentration.

Thermal Stabilities. The thermal properties of the 9-arylanthracene derivatives **13**–**15** were studied by thermogravimetric analysis (TGA) and presented in Table 1. The thermal decomposition ($T_{\rm d}$) temperatures (5% weight loss in nitrogen atmosphere) were observed in the range of 320 to 365 °C. These compounds exhibit moderate thermal stabilities. The decomposition temperatures with 5% weight loss under N_2

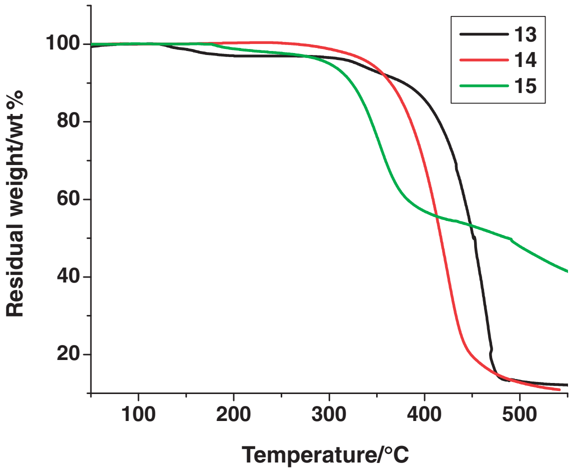


Figure 5. TGA curves for compounds **13–15** in nitrogen at a heating rate of 10 °C min^{-1}.

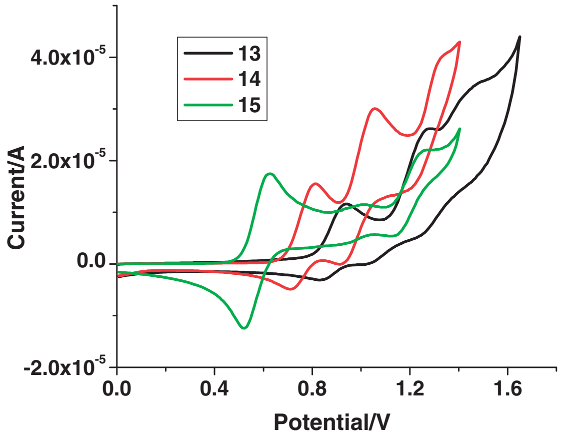


Figure 6. Cyclic voltammetry of compounds **13–15** (ca. 1 mM) measured in 0.1 M n-Bu_4NPF_6–CH_2Cl_2, scan rate 100 mV s^{-1}.

atmosphere (T_d) for **13**, **14**, and **15** were 335, 365, and 320 °C, respectively (Figure 5). The T_d value of **15** exhibited lower decomposition temperature attributed to the fragile hexyloxy chains in the compound.

Cyclic Voltammetric Studies. The electrochemical behavior of compounds **13–15** was investigated by cyclic voltammetric measurements using a three-electrode cell. The working electrode was a glassy carbon, the auxiliary electrode was a Pt wire, and Ag/Ag^+ was used as reference electrode. Tetrabutylammonium hexafluorophosphate (0.1 M) was used as the supporting electrolyte in dry dichloromethane. The redox potentials were calibrated by using ferrocene as an internal standard. The cyclic voltammograms measured for the compounds **13–15** are presented in Figure 6 and the data are listed in Table 1. Compounds **13**, **14**, and **15** exhibit three successive quasi-reversible anodic oxidations (0.94, 1.27, and 1.49 V for **13**; 0.80, 1.05, and 1.34 V for **14**; 0.62, 1.01, and 1.25 V for **15**). The first redox wave may be attributed to the oxidation of the central 1,4-bis(dodecyloxy)benzene segment, while the second and third redox waves most likely stem from the oxidation of the peripheral 9-arylanthracene-conjugated segment. The onset oxidation potential of the compounds **13–15** is located at 0.80, 0.68, and 0.49 V respectively. The HOMO levels were calculated by using the known equation HOMO $= -(E_{ox}(\text{onset}) + 4.66\,\text{eV})$.[19] The calculated HOMO values are in the range of −5.46 to −5.15 eV. Calculating the HOMO–LUMO gap (measured from the absorption maxima), the LUMO levels are found to be ca. 2.22–2.51 eV. The HOMO–LUMO gaps (E_g) of **13–15** are 2.95, 2.93, and 2.93 eV, respectively. From this observation, it is clear that the aryl substituent at 9-position of anthracene moiety have significantly impact on HOMO and LUMO energy level, but little influence on HOMO–LUMO gaps. 9-Aryl-substituted anthracene is partially conjugated because of sterically unfavorable nonplanar conformation between the aryl ring and the anthracene skeleton. The electron-donating ability (HOMO energy level) of **14** and **15** is significantly increased compared to **13** suggesting that the 9-*p*-tolyl group in **13** significantly rotated with respect to the anthracene moiety. Interestingly, it was found that the HOMO value for **15** (OC_6H_{13}) is higher than that of **14** (OCH_3) demonstrating that the cation is more stabilized by the delocalized π-system in **15** (hexyloxy side chain) than **14** (methoxy side chain). This can be explained by the fact that the aryl substituent at the 9-position of anthracene moiety does not favor electronic communication probably due to the greater distortion from planarity in **14** than in **15**. The results of CV measurements of synthesized conjugates show good reversibility, indicating that compounds have good electrochemical stability. The HOMO levels (5.46–5.15 eV) lying between those of tris(8-hydroxyquinoline)aluminum (Alq_3) (5.80 eV) and indium tin oxide (ITO) (4.80 eV), suggests these compounds may act as a hole-transporting materials (HTL).

Experimental

General. All melting points are uncorrected. Unless otherwise noted, all reactions were carried out under an inert atmosphere in flame dried flasks. Solvents obtained from Spectrochem were dried and purified by distillation before use as follows: tetrahydrofuran and toluene from sodium benzophenone ketyl; dichloromethane from P_2O_5; DMF from CaH_2; triethylamine from solid KOH. After drying, organic extracts were evaporated under reduced pressure and the residue was column chromatographed on silica gel (Spectrochem, particle size 100–200 mesh), using an ethyl acetate–petroleum ether (60–80 °C) mixture as eluent unless specified otherwise. Hydroquinone, anthrone, 4-bromotoluene, 4-bromoanisole, methcyltriphenylphosphonium bromide, palladium(II) acetate [$Pd(OAc)_2$] were purchased from Aldrich and used as received.

9-*p*-Tolylanthracene (1).[13] To a stirred solution of anthrone (1.0 g, 5.15 mmol) in THF (12 mL) was added dropwise a solution of *p*-tolylmagnesium bromide in THF [prepared from 4-bromotoluene (1.40 g, 8.2 mmol) and magnesium (210 mg, 8.7 mmol) in 6 mL THF] at room temperature. The reaction mixture was stirred at 60–70 °C for 2 h. After cooling to room temperature, the reaction mixture was quenched with 10% aqueous sulfuric acid solution (5 mL); the organic layer was extracted with dichloromethane (2 × 15 mL). The combined organic layer was washed with brine (10 mL) and dried over anhydrous Na_2SO_4. The solvent was removed in a rotary evaporator. The crude alcohol was treated with formic acid (5 mL) and the mixture was refluxed for 15 min to complete the dehydration. After cooling to room temperature, water (15 mL) was added and extracted with diethyl ether (2 × 10 mL). The ether solution was washed with water (10 mL) and dried over anhydrous Na_2SO_4. Solvent was removed in a rotary evaporator. Purification by column chromatography using hexane as eluent afforded compound **1** (1.17 g, 85%) as white solids.

9-(4-Methoxyphenyl)anthracene (2). The synthetic procedure used was similar to that described for **1**. Starting from anthrone (1.0 g, 5.15 mmol), 1-bromo-4-methoxybenzene (1.53 g, 8.2 mmol) and magnesium (210 mg, 8.7 mmol) compound **2** (1.19 g, 82%) was obtained as a white solid.

Mp 126–128 °C; IR (KBr, cm^{-1}): 3058, 2998, 2964, 1600; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.44 (s, 1H), 8.00 (d, 2H, $J = 8.4$ Hz), 7.77–7.67 (m, 2H), 7.42 (t, 2H, $J = 8.1$ Hz), 7.40–7.28 (m, 4H), 7.13–7.03 (m, 2H), 3.90 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.0, 136.8, 132.3, 131.4, 130.8, 130.5, 128.3, 126.9, 126.4, 125.2, 125.0, 113.8, 55.3; Anal. Calcd for $C_{21}H_{16}O$: C, 88.70; H, 5.67%. Found: C, 88.68; H, 5.68%.

9-(4-Hexyloxyphenyl)anthracene (3). The synthetic procedure used was similar to that described for **1**. Starting from anthrone (1.0 g, 5.15 mmol), 1-bromo-4-hexyloxybenzene (2.10 g, 8.2 mmol) and magnesium (210 mg, 8.7 mmol), compound **3** (1.44 g, 79%) was obtained as a white solid.

Mp 53–55 °C; IR (KBr, cm^{-1}): 3042, 2934, 1608; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.44 (s, 1H), 8.01 (d, 2H, $J = 8.4$ Hz), 7.72 (d, 2H, $J = 8.4$ Hz), 7.48–7.28 (m, 6H), 7.08 (d, 2H, $J = 7.2$ Hz), 4.06 (t, 2H, $J = 6.6$ Hz), 1.95–1.80 (m, 2H), 1.55–1.48 (m, 2H), 1.47–1.30 (m, 4H), 0.95 (t, 3H, $J = 6.6$ Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 158.5, 136.9, 132.3, 132.2, 131.3, 130.5, 128.2, 126.9, 126.2, 125.1, 125.0, 114.3, 68.0, 31.6, 29.3, 25.8, 22.6, 14.0; Anal. Calcd for $C_{26}H_{26}O$: C, 88.09; H, 7.39%. Found: C, 88.08; H, 7.41%.

10-*p*-Tolylanthracene-9-carbaldehyde (4). $POCl_3$ (1.6 mL, 16.3 mmol) was added slowly to dry DMF (20 mL) at 0 °C with intensive stirring under argon atmosphere. After stirring for 15 min, the reaction mixture was allowed to come to room temperature. 9-*p*-Tolylanthracene (**1**) (2.18 g, 8.15 mmol) was added slowly and the reaction mixture was stirred at 90–100 °C for 3 h. After cooling to room temperature, the mixture was poured into a mixture of water (100 mL) and ice (50 g), then neutralized with a 20% aqueous solution of sodium carbonate. A pale yellow precipitate was collected by filtration, washed with cold water and 20% aqueous ethanol. The crude product was purified by column chromatography on silica gel (petroleum ether/EtOAC:4/1) to afford **4** (1.73 g, 72%) as a light yellow solid.

Mp 138 °C; IR (KBr, cm^{-1}): 2914, 2861, 1679, 1612; ^{1}H NMR (300 MHz, $CDCl_3$): δ 11.58 (s, 1H), 9.00 (d, 2H, $J = 9.0$ Hz), 7.74 (d, 2H, $J = 9.0$ Hz), 7.65 (ddd, 2H, $J = 9.0$, 6.6, 1.3 Hz), 7.44–7.36 (m, 4H), 7.29–7.24 (m, 2H), 2.53 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 193.3, 145.8, 137.7, 135.1, 131.7, 130.5, 130.0, 129.1, 128.6, 128.1, 125.4, 124.8, 123.4, 21.4; Anal. Calcd for $C_{22}H_{16}O$: C, 89.16; H, 5.44%. Found: C, 89.13; H, 5.47%.

10-(4-Methoxyphenyl)anthracene-9-carbaldehyde (5). The synthetic procedure used was similar to that described for **4**. Starting from 9-(4-methoxyphenyl)anthracene (**2**) (2.31 g, 8.15 mmol), $POCl_3$ (1.6 mL, 16.3 mmol), and DMF (20 mL), compound **5** (1.90 g, 75%) was obtained as a yellow solid.

Mp 128 °C; IR (KBr, cm^{-1}): 2956, 2934, 1675, 1604; ^{1}H NMR (300 MHz, $CDCl_3$): δ 11.54 (s, 1H), 8.99 (d, 2H, $J = 9.0$ Hz), 7.75 (d, 2H, $J = 8.7$ Hz), 7.64 (ddd, 2H, $J = 9.0$, 6.6, 1.2 Hz), 7.45–7.35 (m, 2H), 7.29 (d, 2H, $J = 8.7$ Hz), 7.12 (d, 2H, $J = 8.7$ Hz), 3.94 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 193.2, 159.3, 145.4, 131.7, 131.6, 130.1, 130.0, 128.5, 128.0, 125.3, 124.7, 123.3, 113.8, 55.3; Anal. Calcd for $C_{22}H_{16}O_2$: C, 84.59; H, 5.16%. Found: C, 84.58; H, 5.18%.

10-(4-Hexyloxyphenyl)anthracene-9-carbaldehyde (6). The synthetic procedure used was similar to that described for **4**. Starting from 9-(4-hexyloxyphenyl)anthracene (**3**) (2.88 g, 8.15 mmol), $POCl_3$ (1.6 mL, 16.3 mmol), and DMF (20 mL), compound **6** (2.36 g, 76%) was obtained as a yellow solid.

Mp 85 °C; IR (KBr, cm^{-1}): 2926, 2858, 1668, 1604; ^{1}H NMR (300 MHz, $CDCl_3$): δ 11.57 (s, 1H), 9.01 (d, 2H, $J = 9.0$ Hz), 7.78 (d, 2H, $J = 9.0$ Hz), 7.65 (t, 2H, $J = 7.5$ Hz), 7.41 (t, 2H, $J = 7.5$ Hz), 7.32–7.20 (m, 2H), 7.12 (d, 2H, $J = 8.4$ Hz), 4.10 (t, 2H, $J = 6.6$ Hz), 1.89 (quin, 2H, $J = 6.6$ Hz), 1.55–1.50 (m, 2H), 1.49–1.30 (m, 4H), 0.94 (t, 3H, $J = 6.6$ Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 193.3 (d), 159.0 (s), 145.6 (s), 131.7 (d), 130.2 (s), 129.8 (s), 128.5 (d), 128.1 (d), 125.3 (d), 124.7 (s), 123.4 (d), 114.4 (d), 68.1 (t), 31.6 (t), 29.3 (t), 25.8 (t), 22.6 (t), 14.0 (q); Anal. Calcd for $C_{27}H_{26}O_2$: C, 84.78; H, 6.85%. Found: C, 84.75; H, 6.87%.

9-*p*-Tolyl-10-vinylanthracene (7). To a stirred solution of methyltriphenylphosphonium bromide (3.9 g, 10.9 mmol) in THF (20 mL) was added *n*-BuLi (1.6 M in hexane) (5 mL, 10 mmol) at −20 °C. The reaction mixture was stirred for 0.5 h at this temperature. A solution of 10-*p*-tolylanthracene-9-carbaldehyde (**4**) (2.16 g, 7.32 mol) in THF (15 mL) was added dropwise. The reaction mixture was allowed to come to room temperature within 6 h. The mixture was quenched with saturated NH_4Cl solution (5 mL). The reaction mixture was extracted with dichloromethane (50 mL) and dried over anhydrous Na_2SO_4. The solvent was removed and purified by column chromatography on silica gel (petroleum ether). Compound **7** (1.54 g, 72%) was obtained as a white solid.

Mp 73–74 °C; IR (KBr, cm^{-1}): 3061, 2993, 2914, 2858, 1623; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.37 (d, 2H, $J = 8.7$ Hz), 7.68 (d, 2H, $J = 8.7$ Hz), 7.52 (dd, 1H, $J = 17.7$, 11.4 Hz), 7.48–7.30 (m, 8H), 6.04 (dd, 1H, $J = 11.4$, 1.8 Hz), 5.65 (dd, 1H, $J = 17.7$, 1.8 Hz), 2.52 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 136.9 (s), 135.9 (s), 133.8 (d), 133.5 (s), 131.1 (d), 130.0 (s), 129.0 (d), 128.8 (s), 127.2 (d), 126.0 (d), 125.0 (d), 124.9 (d), 122.9 (t), 21.3 (q); Anal. Calcd for $C_{23}H_{18}$: C, 93.84; H, 6.16%. Found: C, 93.83; H, 6.17%.

9-(4-Methoxyphenyl)-10-vinylanthracene (8). The synthetic procedure used was similar to that described for the preparation of **7**. Starting from 10-(4-methoxyphenyl)anthracene-9-carbaldehyde (**5**) (1.0 g, 3.20 mmol), vinyl compound **8** was obtained as a white solid (695 mg, 70%).

Mp 102 °C; IR (KBr, cm^{-1}): 3065, 3001, 2952, 2835, 1608; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.03 (d, 2H, $J = 8.7$ Hz), 7.62 (d, 2H, $J = 8.7$ Hz), 7.48 (dd, 1H, $J = 17.6$, 11.4 Hz), 7.48–7.41 (m, 2H), 7.37–7.30 (m, 4H), 7.14–7.08 (m, 2H), 6.04 (dd, 1H, $J = 11.4$, 2.1 Hz), 5.67 (dd, 1H, $J = 17.6$, 2.1 Hz), 3.94 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.0 (s), 136.7 (s), 133.9 (d), 133.6 (s), 132.4 (d), 131.1 (s), 130.3 (s), 129.0 (s), 127.3 (d), 126.1 (d), 125.1 (d), 125.0 (d), 123.1 (t), 113.9 (d), 55.4 (q); Anal. Calcd for $C_{23}H_{18}O$: C, 89.00; H, 5.85%. Found: C, 88.97; H, 5.87%.

9-(4-Hexyloxyphenyl)-10-vinylanthracene (9). The synthetic procedure used was similar to that described for the preparation of **7**. Starting from 10-(4-hexyloxyphenyl)anthracene-9-carbaldehyde (**6**) (1.0 g, 2.61 mmol), vinyl compound **9** was obtained as a white solid (745 mg, 75%).

Mp 76 °C; IR (KBr, cm^{-1}): 3073, 2922, 2855, 1608; ^1H NMR (300 MHz, $CDCl_3$): δ 8.37 (d, 2H, $J = 8.7$ Hz), 7.71 (d, 2H, $J = 8.7$ Hz), 7.52 (dd, 1H, $J = 17.7$, 11.4 Hz), 7.48–7.27 (m, 6H), 7.10 (d, 2H, $J = 8.7$ Hz), 6.05 (dd, 1H, $J = 11.4$, 1.8 Hz), 5.66 (dd, 1H, $J = 17.7$, 1.8 Hz), 4.09 (t, 2H, $J = 6.6$ Hz), 1.88 (quin, 2H, $J = 6.6$ Hz), 1.60–1.50 (m, 2H), 1.48–1.32 (m, 4H), 0.94 (t, 3H, $J = 6.9$ Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 158.5 (s), 136.7 (s), 133.9 (d), 133.5 (s), 132.3 (d), 130.8 (s), 130.2 (s), 128.9 (s), 127.3 (d), 126.0 (d), 124.9 (d), 124.8 (d), 122.9 (t), 114.3 (d), 68.1 (t), 31.6 (t), 29.3 (t), 25.8 (t), 22.6 (t), 14.0 (q); Anal. Calcd for $C_{28}H_{28}O$: C, 88.38; H, 7.42%. Found: C, 88.36; H, 7.43%.

1,4-Bis(bromomethyl)-2,5-bis(dodecyloxy)benzene (10).[13] A mixture of 1,4-bis(dodecyloxy)benzene (1.0 g, 2.23 mmol), paraformaldehyde (200 mg, 6.71 mmol), HOAc (6 mL), and HBr (48% aqueous, 4 mL) was refluxed for 24 h; after cooling, the precipitate was collected and washed with water. The compound **10** was obtained as a white solid (917 mg, 65%) and it was used for the next step without further purification.

Mp 65–67 °C; IR (KBr, cm^{-1}): 2918, 2851, 1509, 1472; ^1H NMR (300 MHz, $CDCl_3$): δ 6.85 (s, 2H), 4.52 (s, 4H), 3.98 (t, 4H, $J = 6.3$ Hz), 1.88–1.74 (m, 4H), 1.56–1.20 (m, 36H), 0.88 (t, 6H, $J = 6.3$ Hz).

Diethyl [4-(Diethoxyphosphorylmethyl)-2,5-bis(dodecyloxy)benzyl]phosphonate (11). A mixture of compound **10** (1.0 g, 1.58 mmol) and triethyl phosphite (786 mg, 4.74 mmol) was refluxed for 12 h, and then the excess triethyl phosphite and volatile materials were removed by high vacuum pump. The residue diphosphonate **11** (731 mg, 62%) was obtained as a white solid and it was used directly without further purification.

Mp 43–45 °C; IR (KBr, cm^{-1}): 2914, 2847, 1521, 1476, 1393, 1272; ^1H NMR (300 MHz, $CDCl_3$): δ 6.91 (s, 2H), 4.03 (q, 4H, $J = 7.2$ Hz), 4.00 (q, 4H, $J = 7.2$ Hz), 3.91 (t, 4H, $J = 6.6$ Hz), 3.22 (d, 4H, $J = 20.0$ Hz), 1.85–1.69 (m, 4H), 1.45–1.20 (m, 48H), 0.87 (t, 6H, $J = 6.9$ Hz); HRMS (ESI): Calcd for $C_{40}H_{80}NO_8P_2$ $[M + NH_4]^+$: 764.5359, found: 764.5352.

Compound 13. Route I: A mixture of dried KOAc (56 mg, 0.576 mmol) and n-Bu_4NBr (185 mg, 0.576 mmol) in DMF (6 mL) was stirred for 15 min in a double necked round-bottomed flask in argon atmosphere at room temperature. To this reaction mixture, 1,4-dibromo-2,5-bis(dodecyloxy)benzene (**12**)[13] (120 mg, 0.198 mmol), P(o-tol)$_3$ (17 mg, 0.057 mmol), and 9-p-tolyl-10-vinylanthracene (**7**) (141 mg, 0.48 mmol) were added simultaneously and stirred for another 15 min. Catalytic amount of $Pd(OAc)_2$ (10 mg) was added and heated for 48 h at 100 °C. The mixture was cooled to room temperature and extracted with dichloromethane (30 mL). The organic layer was washed with water (3 × 5 mL), brine (5 mL), and dried over anhydrous Na_2SO_4. Solvent was removed in a rotary evaporator and the crude product was purified using column chromatography (silica gel/ethyl acetate:petroleum ether: 5/95) to yield compound **12** (24 mg, 12%) as pale yellow solids.

Route II: To a stirred solution of **11** (100 mg, 0.133 mmol) in THF (12 mL) under argon atmosphere at 0 °C, ^{t}BuOK (45 mg, 0.401 mmol) was added at 0 °C. The reaction mixture was stirred for 0.5 h at this temperature. A solution of 10-p-tolylanthracene-9-carbaldehyde (**4**) (86 mg, 0.292 mmol) in THF (15 mL) was added dropwise. The reaction mixture was stirred at room temperature for 12 h. The mixture was poured into water (50 mL) and extracted with dichloromethane (50 ml). Solvent was removed and purified by column chromatography on silica gel (petroleum ether) to afford yellow solid compound **13** (106 mg, 78%) as a mixture of *cis*- and *trans*-isomers.

To a solution of the compound **13** (100 mg, 0.096 mmol) in toluene (5 mL) catalytic amount I_2 (5 mg) was added and then the mixture was refluxed for 72 h. After completion, the mixture was extracted with dichloromethane (5 mL) and the organic extracts were washed with sodium thiosulfate solution (5%, 5 mL), water (5 mL), brine (10 mL), and dried over anhydrous sodium sulfate. Solvent was removed and the crude product was purified by column chromatography (petroleum ether) affording *trans*-isomer of **13** (92 mg, 92%) as a yellow solid.

Mp 132–134 °C; IR (KBr, cm^{-1}): 2922, 2847, 1604; ^1H NMR (300 MHz, $CDCl_3$): δ 8.52 (d, 4H, $J = 8.7$ Hz), 8.08 (d, 2H, $J = 16.5$ Hz), 7.73 (d, 4H, $J = 8.7$ Hz), 7.55–7.30 (m, 20H), 4.16 (t, 4H, $J = 6.6$ Hz), 2.54 (s, 6H), 1.84 (quin, 4H, $J = 6.6$ Hz), 1.55–1.42 (m, 4H), 1.40–1.12 (m, 32H), 0.84 (t, 6H, $J = 6.6$ Hz); ^{13}C NMR spectral data was not recorded due to poor solubility; MALDI-TOF MS: m/z 1030.3 (M^+, 100%). Anal. Calcd for $C_{76}H_{86}O_2$: C, 88.49; H, 8.40%. Found: C, 88.38; H, 8.41%.

Compound 14. The synthetic procedure used was similar to that described for the preparation of **13**.

For route I: Starting from 1,4-dibromo-2,5-bis(dodecyloxy)benzene (**12**) (120 mg, 0.198 mmol) and 9-(4-methoxyphenyl)-10-vinylanthracene (**8**) (153 mg, 0.495 mmol), compound **14** was obtained as a yellow solid (32 mg, 15%).

For route II: Starting from **11** (100 mg, 0.133 mmol) and 10-(4-methoxyphenyl)anthracene-9-carbaldehyde (**5**) (103 mg, 0.332 mmol), and then isomerization in the presence of iodine, compound **14** was obtained as a yellow solid (114 mg, 76%).

Mp 152–154 °C; IR (KBr, cm^{-1}): 3065, 2993, 2851, 1608; ^1H NMR (300 MHz, $CDCl_3$): δ 8.46 (d, 4H, $J = 8.7$ Hz), 8.02 (d, 2H, $J = 16.8$ Hz), 7.69 (d, 4H, $J = 8.7$ Hz), 7.43 (t, 4H, $J = 7.2$ Hz), 7.39 (s, 2H), 7.38–7.24 (m, 10H), 7.09 (d, 4H, $J = 8.7$ Hz), 4.11 (t, 4H, $J = 6.3$ Hz), 3.91 (s, 6H), 1.78 (quin, 4H, $J = 6.3$ Hz), 1.52–1.36 (m, 4H), 1.32–1.05 (m, 32H), 0.79 (t, 6H, $J = 6.9$ Hz); ^{13}C NMR spectral data was not recorded due to poor solubility; MALDI-TOF MS: m/z 1062.2 (M^+, 100%); Anal. Calcd for $C_{76}H_{86}O_4$: C, 85.83; H, 8.15%. Found: C, 85.62; H, 8.17%.

Compound 15. The synthetic procedure used was similar to that described for the preparation of **13**.

For route I: Starting from 1,4-dibromo-2,5-bis(dodecyloxy)benzene (**12**) (120 mg, 0.198 mmol) and 9-(4-hexyloxyphenyl)-10-vinylanthracene (**9**) (188 mg, 0.495 mmol), compound **15** was obtained as a yellow solid (38 mg, 16%).

For route II: Starting from **11** (100 mg, 0.133 mmol) and 10-(4-hexyloxyphenyl)anthracene-9-carbaldehyde (**6**) (126 mg, 0.332 mmol), and then isomerization in the presence of iodine, compound **15** was obtained as a yellow solid (134 mg, 78%).

Mp 134–135 °C; IR (KBr, cm^{-1}): 3055, 2991, 2885, 1602; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.52 (d, 4H, $J = 8.7$ Hz), 8.30 (d, 2H, $J = 16.8$ Hz), 7.76 (d, 4H, $J = 8.7$ Hz), 7.49 (t, 4H, $J = 7.4$ Hz), 7.42 (s, 2H), 7.44–7.32 (m, 10H), 7.13 (d, 4H, $J = 8.4$ Hz), 4.16 (t, 4H, $J = 6.6$ Hz), 4.11 (t, 4H, $J = 6.6$ Hz), 1.98–1.81 (m, 8H), 1.55–1.32 (m, 8H), 1.30–1.12 (m, 40H), 0.95 (t, 6H, $J = 6.9$ Hz), 0.84 (t, 6H, $J = 6.9$ Hz); ^{13}C NMR spectral data was not recorded due to poor solubility; MALDI-TOF MS: m/z 1202.3 (M^+, 100%); Anal. Calcd for $C_{86}H_{106}O_4$: C, 85.81; H, 8.88%. Found: C, 85.73; H, 8.89%.

Conclusion

In conclusion, we have reported the synthesis and photophysical properties of three new 9-arylanthracene-based π-conjugates. Heck coupling and HWE olefination reaction are two key steps in constructing the π-conjugated materials. However, HWE olefination in the final step has been proven more effective than the Heck coupling reaction. All materials emit light in the blue to sky blue region. These compounds were found to exhibit interesting photophysical properties which dependent on the nature of the side substituent. Hence, the long chain (hexyloxy)-substituted derivative **15** displayed slightly red-shifted emissions and high HOMO values compared to the methoxy- and methyl-substituted compound. The comparatively low Φ_{fl} value of **15** attributed to the greater aggregation–excimer formation in the excited state. Compounds displayed red-shifted (ca. 30 nm) emission in the powdered state compared to those observed in THF solutions due to molecular aggregation or excimer formation in the solid state. The HOMO levels of compounds lying between ITO (4.80 eV) and Alq_3 (5.80 eV) suggest that they can be used as a hole-transporting material (HTL). All compounds enjoy moderate thermal stability. Further studies addressing the electroluminescence of new 9-arylanthracene-based π-conjugated compounds are currently underway in our laboratory.

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Supporting Information

^{1}H NMR spectra of new compounds **2–9**, **11**, **13–15** and ^{13}C NMR spectra of **2–9**. This material is available electronically on J-STAGE.

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