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Efficient Synthesis and Characterization of Dibenzo[*a*,*m*]rubicenes and Tetrabenzo[*a*,*f*,*r*,*m*]rubicenes

Hung-Hung Hseuh, Ming-Yu Hsu, Tien-Lin Wu, and Rai-Shung Liu*

Department of Chemistry, National Tsing-Hua Univeristy, Hsinchu, Taiwan, ROC

rsliu@mx.nthu.edu.tw

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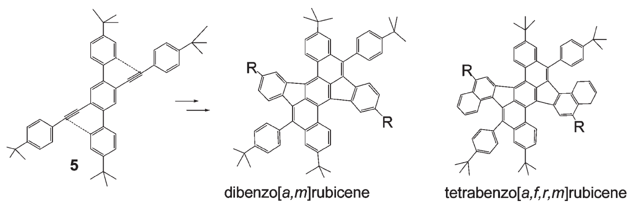
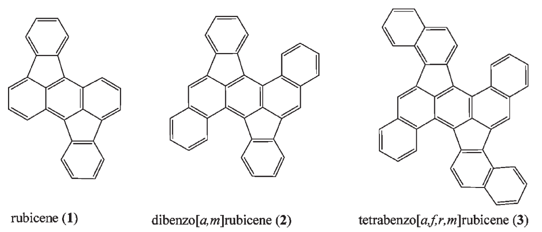


We report an efficient synthesis of dibenzo[*a*,*m*]rubicenes and tetrabenzo[*a*,*f*,*r*,*m*]rubicenes involving ICl-mediated benzannulation of 1,4-diphenyl-2,5-dialkynylbenzene **5** as the key step. Preliminary data on the photophysical properties of these new indeno-PAHs are reported.

Significant attention has been directed to the synthesis of indeno-PAHs, which are polycyclic aromatic hydrocarbons (PAHs) containing one or more five-membered carbocyclic units.[1,2] Known for a century, rubicene (**1**) is an interesting heptacyclic arene of which an efficient synthesis was achieved a decade ago.[3,4] The interesting properties and uses of rubicene include a red color, yellow fluorescence, a large rate of intersystem crossing (ISC),[5] electrochemically generated luminescene,[6] and application as a chemical sensor for metal cations.[6a] Large PAHs such as hexabenzocorenene show outstanding hole transport properties because of a strong interaction to support columnar (liquid)−crystalline mesophases.[7] To increase the ring sizes of rubicene frameworks, herein we report an efficient synthesis of dibenzo[*a*,*m*]rubicene (**2**) and tetrabenzo[*a*,*f*,*r*,*m*]rubicene (**3**) (Scheme 1); the synthesis and characterization of these compounds remains virtually unknown.[8]

SCHEME 1



Scheme 2 shows the synthetic protocol of dibenzo[*a*,*m*]rubicene **8** and **9** with ICl-mediated benzannulation[9,10] of 1,4-diphenyl-2,5-dialkynylbenzene **5** as the key step. The targeted molecules **8** and **9** bear four *tert*-butyl groups to increase solubility in commonly used solvents. Preparation of key species **5** begins with Sonogashira coupling[11] of 1,4-dibromo-2,5-diiodobenzene **3**, followed by Suzuki coupling[12] of the resulting 1,4-dibromo-2,5-diakynylbenzene **4**. Treatment of compound **5** with ICl (2.2 equiv) in CH_2Cl_2 at 23 °C induced a 6-*endo-dig* benzannulation to give 6,13-diiodobenzo[*k*]tetracene **6** in 74% yield; its subsequent Suzuki coupling with 4-substituted phenylboric acid afforded 5,6,12,13-tetraphenylbenzo[k]tetracene **7a** and **7b**, in 71% and 70% yields, respectively. In the final step, we employed $FeBr_3$[12] in excess proportion (4 equiv) to transform species **7a** and **7b** into the desired dibenzo[*a*,*m*]rubicene **8** and **9** in 59% and 68% yields, respectively; this oxidative coupling

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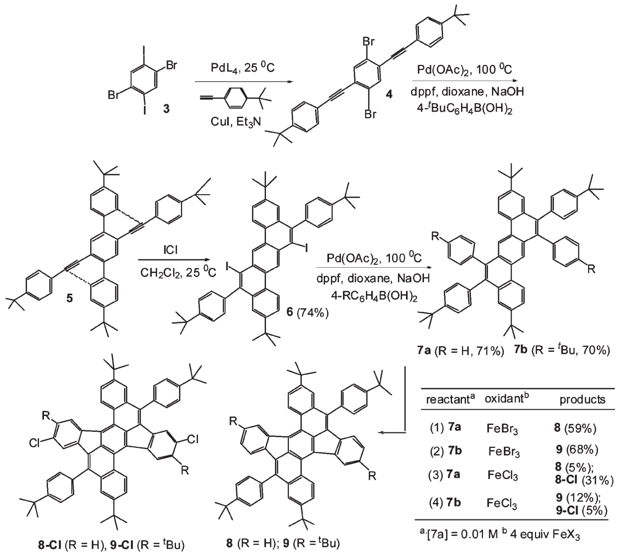
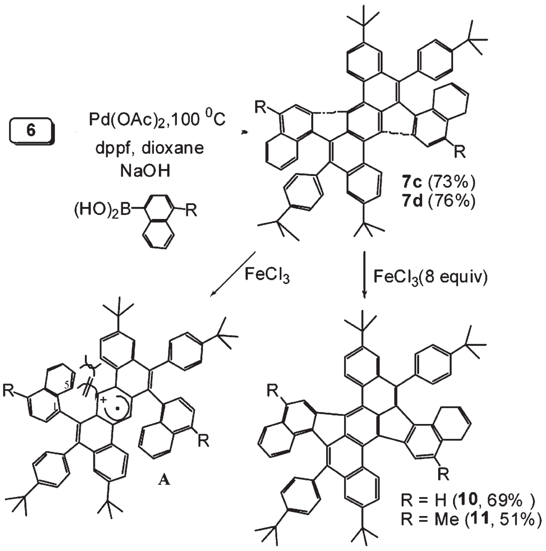
SCHEME 2



reactant[a]	oxidant[b]	products
(1) **7a**	$FeBr_3$	**8** (59%)
(2) **7b**	$FeBr_3$	**9** (68%)
(3) **7a**	$FeCl_3$	**8** (5%); **8-Cl** (31%)
(4) **7b**	$FeCl_3$	**9** (12%); **9-Cl** (5%)

[a] [7a] = 0.01 M [b] 4 equiv FeX_3

SCHEME 3



(Scholl oxidation)[13] was performed at a dilute concentration (1.0×10^{-2} M) in dry nitromethane at 23 °C for 10 min. Under the same conditions, $FeCl_3$ (4 equiv) gave poor yields (5−12%) of the desired **8** and **9** accompanied by formation of their chloro derivatives **8-Cl** and **9-Cl** in 31% and 5% yields, respectively.

Scheme 3 shows the successful extension of this approach to the synthesis of tetrabenzo[*a*,*f*,*r*,*m*]rubicenes **10** and **11**. The starting benzo[*k*]tetracenes **7c** and **7d** were prepared efficiently from the Suzuki coupling[11] of compound **6** with 4-R-1-naphthylboric acid (R = H, Me). We found that oxidation of **7c** and **7d** with $FeBr_3$ under various concentrations (0.01−0.002 M) was unsuccessful with exclusive recovery of unreacted **7c** and **7d**, but use of $FeCl_3$ (8 equiv) in dilute solution ([substrate] = 0.005 M) led to formation of tetrabenzo[*a*,*f*,*r*,*m*]rubicenes **10** and **11** in 69% and 51% yields, respectively; the two compounds were purified chromatographically under argon to avoid oxidation with air. In the presence of $FeCl_3$, we envisage that species **7c** and **7d** undergo one-electron oxidation to form a radical cation at the C(7) carbon of the central benzo[*k*]tetracene framework as represented by intermediate **A**; this reactive cationic center reacts preferably with the C(2) carbon, rather than the C(5) carbon, of the tethered naphthyl ring although the C(5) carbon has a greater effect in the HOMO orbital.[14] We envisage that steric hindrance in the C(5)-addition prohibits this benzannulation reaction.

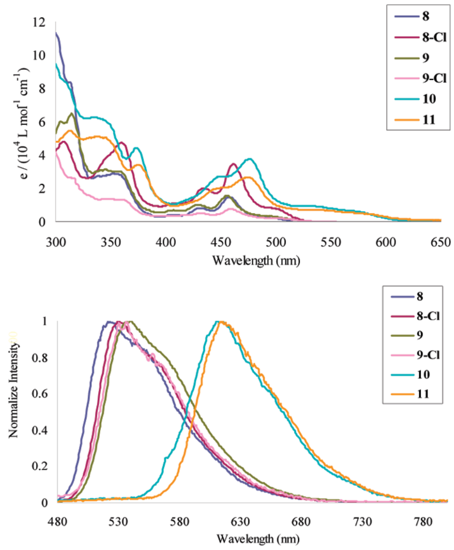


FIGURE 1. Absorption and emission spectra of compounds **8**−**11**.

Dibenzo[*a*,*m*]rubicene (**8**−**9**, **8-Cl**, and **9-Cl**) and tetrabenzo[*a*,*f*,*r*,*m*]rubicene (**10**−**11**) are orange and red solids, but the latter PAHs decomposed completely in CH_2Cl_2 within 12 h at 25 °C in the presence of air. Species **10** and **11** were stored safely in sold forms at 0 °C for 24 h under argon. We characterized these compounds with NMR, Maldi-mass, and elemental analysis. ^{1}H NMR signals of these new compounds were assigned with the ^{1}H NOE effect and sequential proton decoupling; the data appear in the Supporting Information.

Table 1 shows key data for the photopysical properties of rubicene derivatives **8**−**10** and their chloro derivatives **8-Cl** and **9-Cl**; the dichloromethane solutions were degassed carefully to avoid interference from oxygen. These indeno-PAHs are highly fluorescent with quantum yields of 4.9−10.6% despite their small energy gaps. We envisage that the attached bulky *tert*-butyl groups minimize molecular aggregation to prevent intermolecular energy transfer. Figure 1 shows their absorption spectra measured at 1×10^{-6} M in CH_2Cl_2. Parent compound **8** has four absorption bands at 3,11 357, 431, and 459 nm, and their substituented derivatives **8-Cl**, **9**, and **9-Cl** retain the same absorptions. Tetrabenzo[*a*,*f*,*r*,*m*]rubicenes **10** and **11** have five absorptions at 308, 351, 374, 448, and 476 nm, respectively, and the latter three absorptions are shifted to large wavelengths by

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TABLE 1. Photophysical Properties of Compounds 8−11

compd	abs$_{max}$^{a} (nm)	PL$_{max}$^{a} (nm)	Q.Y.^{a,b} (%)	$E_{1/2}^{ox}$ (V)	HOMO−LUMO^{c} (eV)	band gap^{d} (eV)
8	311, 354, 428, 453	522	9.1	0.86	−5.66 −3.40	2.26
8-Cl	306, 356, 425, 453	531	4.9	0.88	−5.68 −3.35	2.33
9	303, 312, 358, 431, 459	538	10.6	0.78	−5.58 −3.28	2.30
9-Cl	315, 358, 428, 456	536	5.8	0.79	−5.59 −3.35	2.24
10	311, 372, 446, 475	611	8.5	0.66	−5.46 −3.46	2.00
11	372, 441, 475	616	4.9	0.58	−5.38 −3.40	1.98

[a] In CH_2Cl_2, 1×10^{-5} M. [b] Coumarin I as a standard with a standard deviation of 3%. [c] The energy levels of HOMO are determined from CV. [d] Band gaps were calculated from uv absorption.

16−18 nm, relative to those of dibenzo[*a*,*m*]rubicene **8**. Figure 1b showed normalized photoluminescence (PL) spectra with emission maxima at 524−536 nm for the family of dibenzo[*a*,*m*]rubicenes, and at longer wavelengths of ca. 611−616 nm for tetrabenzo[*a*,*f*,*r*,*m*]rubicene species **10** and **11**.

Dibenzo[*a*,*m*]rubicenes (**8**−**9**, **8-Cl**, and **9-Cl**) and tetrabenzo[*a*,*f*,*r*,*m*]rubicenes **10** and **11** show one-electron reversible oxidation in CH_2Cl_2 according to cyclic voltammetry measurements (see the Supporting Information). We estimated their HOMO−LUMO gaps from the intersection of the absorption and fluorescence spectrum, giving 2.23−2.33 and 1.98−2.00 V for dibenzo[*a*,*m*]rubicenes (**8**, **9**, **8-Cl**, and **9-Cl**) and tetrabenzo[*a*,*f*,*r*,*m*]rubicenes **10** and **11**, respectively. We deduced the HOMO energy levels from their oxidation potentials ($E_{1/2}^{ox}$), and calculated the LUMO levels from the measured energy gaps. As shown in Table 1, the family of dibenzo[*a*,*m*]rubicene species have the HOMO and LUMO orbitals at 5.59−5.67 V and 3.25−3.40 eV, and the two tetrabenzo[*a*,*f*,*r*,*m*]rubicenes have corresponding values at 5.38−5.46 V and 3.40−3.45 eV, respectively. The observed low-lying LUMO and high-lying HOMO indicate that these new indeno-PAHs may have ambipolar properties to conduct both electrons and holes transport efficiently.

In summary, we have developed a new and efficient synthesis of dibenzo[*a*,*m*]rubicenes and tetrabenzo[*a*,*f*,*r*,*m*]rubicenes involving ICl-mediated benzannulation of 1,4-diphenyl-2,5-dialkynylbenzene **5** as the key step. These indeno-PAHs absorb light in the visible light regions, and have small energy gaps (2.33−1.99 eV) and fair quantum yields. Their HOMO−LUMO energy levels indicate ambipolar properties. Further application of these indeno-PAHs in materials application is under current investigation.

Experimental Section

Synthesis of 4,4′-(2,5-Dibromo-1,4-phenylene)bis(ethyne-2,1-diyl)bis(*tert*-butylbenzene) (4). To a Et_3N solution (20 mL) of CuI (45.8 mg, 0.24 mmol, 4 mol %) was added compound **3** (3.0 g, 6.12 mmol); the mixture was degassed with nitrogen for 15 min at 23 °C. To the resulting solution was added $Pd(PPh_3)_4$ (0.141 mg, 0.12 mmol, 2 mol %); the mixture was stirred for 15 min before addition of 1-*tert*-butyl-4-ethynylbenzene (2.43 g, 14.7 mmol). The solution was stirred at 25 °C for 3 h, filtered through a Celite bed, concentrated, and eluted through a silica column to give 4,4′-(2,5-dibromo-1,4-phenylene)bis(ethyne-2,1-diyl)bis(*tert*-butylbenzene) (**4**) (2.78 g, 5.07 mmol) in 83% yield. Spectral data for **4**: IR (neat, cm^{-1}) 3054 (m), 2918 (m), 2112 (w), 1630 (w), 1539 (w), 1365 (s), 1130 (m); ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.77 (s, 2 H), 7.52 (d, $J = 8.4$ Hz, 4 H), 7.40 (d, $J = 8.4$ Hz, 4 H), 1.34 (s, 18 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 152.5, 135.9, 131.5 (2×CH), 126.4, 125.4 (2×CH), 123.7, 119.3, 96.9, 86.4, 34.9, 31.1; HRMS calcd for $C_{30}H_{28}Br_2$ 546.0558, found 546.036.

Synthesis of 1,4-Di(*tert*-butylphenyl)-2,5-di(*tert*-butylacetylenyl)benzene (5). To a solution of dppf (282.5 mg, 0.51 mmol) in dioxane (20 mL) was added 4,4′-(2,5-dibromo-1,4-phenylene)-bis(ethyne-2,1-diyl)bis(*tert*- butylbenzene) (**4**) (2.78 g, 5.1 mmol) at room temperature, and the solution was degassed with nitrogen. To this mixture was added 4-*tert*-butylphenylboronic acid (2.17 g, 12.2 mmol), $Pd(OAc)_2$ (282.5 mg, 0.51 mmol, 10 mol %), and 5 M $NaOH_{(aq)}$ (3 mL, 15.3 mmol), and the resulting mixture was heated to 105 °C for 6 h. After completion of the reaction, the solution was cooled to room temperature; the aqueous layer was extracted with dichloromethane, washed with brine solution, dried over $MgSO_4$, and concentrated. The residues were purified by washing several times with acetone to give compound **5** as a white solid (2.42 g, 3.72 mmol, 73% yield). Spectral data for **5**: IR (neat, cm^{-1}) 3051 (m), 2921 (m), 2110 (w), 1620 (w), 1541 (w), 1362 (s), 1130 (m); ^1H NMR (400 MHz, $CDCl_3$) δ 7.68 (s, 2H), 7.70 (d, $J = 8.0$ Hz, 4H), 7.48 (d, $J = 8.0$ Hz, 4H), 7.29−7.24 (m, 8H), 1.39 (s, 18H), 1.29 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.5, 150.5, 142.0, 136.6, 130.2, 133.7(4 × CH), 131.2(4 × CH), 125.3 (2 × CH), 124.9 (4 × CH), 121.7, 120.4, 93.8, 89.0, 34.8, 34.6, 31.4, 31.2; HRMS calcd for $C_{50}H_{54}$ 654.4226, found 654.421. Anal. Calcd for $C_{50}H_{54}$: C, 91.69; H, 8.31. Found: C, 91.56; H, 8.46.

Synthesis of 3,10-Di(*tert*-butyl)-5,12-di[4-(*tert*-butyl)phenyl]-6,13-diiododibenzo[*a*,*h*]anthracene (6). To a CH_2Cl_2 solution (15 mL) of compound **5** (12.43 g, 3.72 mmol) was added ICl (1.0 M in CH_2Cl_2, 3.7 mL, 9.3 mmol) at −78 °C, and the mixture was stirred at −40 °C for 0.5 h before being quenched with sodium thiosulfate solution. The solution was extracted with CH_2Cl_2, dried over $MgSO_4$, and purified by washing several times with acetone to give compound **6** as a light yellow solid (2.49 g, 2.75 mmol) in 74% yield. Spectral data for **6**: IR (neat, cm^{-1}) 3062 (m), 2932 (m), 1628 (w), 1541 (w), 1362 (s), 1130 (m); ^1H NMR (400 MHz, $CDCl_3$) δ 9.73 (s, 2H), 8.89 (d, $J = 8.4$ Hz, 2H), 7.79 (dd, $J = 8.4$, 2.0 Hz, 2H), 7.58 (d, $J = 8.4$ Hz, 4H), 7.36 (s, 2H), 7.28 (d, $J = 6.4$ Hz, 4H), 1.45 (s, 18H), 1.24 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.1, 150.5, 141.4, 134.8, 133.9, 133.1, 129.5, 129.2, 128.0, 126.8, 125.4, 125.2 (4 × CH), 124.2, 123.3, 105.0, 34.9, 34.8, 31.5, 30.8; MALDI-MS calcd for $C_{50}H_{52}I_2$ 906.2158, found 906.262. Anal. Calcd for $C_{50}H_{52}I_2$: C, 66.23; H, 5.78. Found: C, 66.76; H, 5.56.

Synthesis of 3,10-Di(*tert*-butyl)-5,12-di[4-(*tert*-butyl)phenyl]-6,13-diphenyldibenzo[*a*,*h*]anthracene (7a). To a solution of dppf

(33.18 mg, 0.061 mmol, 10 mol %) in dioxane (20 mL) was added 3,10-di(*tert*-butyl)-5,12-di[4-(*tert*- butyl)phenyl]-6,13-diiododibenzo[*a,h*]anthracene (**6**) (0.56 g, 0.61 mmol) at room temperature, and the solution was degassed with nitrogen. To this mixture was added phenylboronic acid (0.17 g, 1.46 mmol) and Pd(OAc)$_2$ (13.6 mg, 0.061 mmol, 10 mol %) and 5 M NaOH$_{(aq)}$ (0.36 mL, 1.83 mmol), and the resulting mixture was heated to 105 °C for 6 h. After completion of the reaction, the solution was cooled to room temperature and washed with water. The aqueous layer was extracted with dichloromethane, washed with brine solution, dried over MgSO$_4$, and concentrated. The residues were purified by washing several times with acetone to give compound **7a** as a light yellow solid (2.42 g, 3.72 mmol) in 71% yield. Spectral data for **7a**: IR (neat, cm^{-1}) 3053 (m), 2916 (m), 1622 (w), 1539 (w), 1362 (s), 1130 (m); ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.90 (s, 2H), 8.31 (d, J = 8.4 Hz, 2H), 7.59 (d, J = 8.4 Hz, 2H), 7.51 (s, 2H), 7.33−7.25 (m, 12H), 7.10 (d, J = 8.4 Hz, 4H), 1.29 (s, 18H), 1.22 (s, 18H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 148.9, 148.7, 139.8, 137.4, 136.8, 136.5, 131.9, 131.2, 131.1, 130.6, 130.2, 128.2, 127.8, 126.3, 124.3, 124.2, 123.8, 122.3, 121.1, 34.5, 34.1, 31.2, 31.1; MALDI-mass calcd for C$_{62}$H$_{62}$ 806.4852, found 806.470. Anal. Calcd for C$_{62}$H$_{62}$: C, 92.26; H, 7.74. Found: C, 92.00; H, 7.66.

Synthesis of 3,12-Di(*tert*-butyl)-5,14-di[4-(*tert*-butyl)phenyl]-dibenzo[*a,m*]rubicene (8). Compound **7a** (100 mg, 0.124 mmol) was dissolved in dry CH$_2$Cl$_2$ (2 mL), and the solution was bubbled with argon for 20 min. To this solution was added dry CH$_3$NO$_2$ (0.248 mL) and FeBr$_3$ (270 mg, 1.24 mmol) dropwise at 23 °C; the reaction was quenched on adding methanol (10 mL) after 30 min. The solvent was removed under reduced pressure and purified by a silica column to give compound **8** as an orange solid (58.7 mg, 59%). IR (neat, cm^{-1}) 3023 (m), 2915 (m), 2110 (w), 1628 (w), 1539 (w), 1365 (s), 1130 (m); ^{1}H NMR (600 MHz, CD$_2$Cl$_2$) δ ppm 9.15 (d, J = 8.4 Hz, 2H), 8.60 (d, J = 7.8 Hz, 2H), 7.67 (dd, J = 8.4, 1.8 Hz, 2H), 7.64 (d, J = 7.8 Hz, 4H), 7.62 (s, 2H), 7.42 (d, J = 7.8 Hz, 4H), 7.22 (t, J = 7.2 Hz, 2H), 6.97 (t, J = 7.2 Hz, 2H), 6.69 (d, J = 7.2 Hz, 2H), 1.44 (s, 18H), 1.26 (s, 18H); ^{13}C NMR (150 MHz, CD$_2$Cl$_2$) 152.1, 151.2, 141.9, 140.1, 138.3, 136.1 (2 × CH), 135.8, 132.7, 132.5, 130.2, 130.0, 129.3, 128.9, 128.5, 128.0, 127.4, 126.6, 125.3, 125.0, 124.6, 124.5, 35.5, 35.4, 32.0, 31.7; MALDI-mass calcd for C$_{62}$H$_{58}$ 802.4539, found 802.528. Anal. Calcd for C$_{62}$H$_{58}$: C, 92.72; H, 7.28. Found: C, 92.43; H, 7.40.

Spectral data for tetrabenzo[*a,f,r,m*]rubicenes (10):. IR (neat, cm^{-1}) 3022 (m), 2914 (m), 2113 (w), 1623 (w), 1532(w), 1353 (s), 1134 (m); ^{1}H NMR (600 MHz, CD$_2$Cl$_2$) δ 9.09 (d, J = 8.4 Hz, 2H), 8.72 (d, J = 8.4 Hz, 2H), 8.14 (s, 2H), 7.80 (d, J = 8.4 Hz, 2H), 7.75−7.73 (m, 4H), 7.64 (d, J = 8.4 Hz, 4H), 7.58 (d, J = 8.4 Hz, 4H), 7.20−7.17 (m, 4H), 6.76 (t, J = 7.8 Hz, 2H), 1.50 (s, 18H), 1.40 (s, 18H); ^{13}C NMR (150 MHz, CD$_2$Cl$_2$) δ 152.8, 151.5, 142.1, 140.7, 138.8, 136.4 (6×C), 135.9, 135.0, 132.8, 132.6 (4×CH), 130.7, 130.3, 129.9, 129.3, 129.1, 127.9, 127.0 (4×CH), 126.5, 126.2, 125.5, 125.1, 125.0, 123.5, 36.2, 35.9, 32.4, 32.2; MALDI-MS calcd for C$_{70}$H$_{62}$ 902.4852, found 902.470. Anal. Calcd for C$_{70}$H$_{62}$: C, 93.08; H, 6.92. Found: C, 92.99; H, 7.05.

Spectral data for compound 11:. IR (neat, cm^{-1}) 3022 (m), 2914 (m), 2103 (w), 1623 (w), 1532 (w), 1364 (s), 1134 (m); ^{1}H NMR (400 MHz, CD$_2$Cl$_2$) δ 9.01 (d, J = 8.4 Hz, 2H), 8.61 (s, 2H), 8.14 (s, 2H), 7.90 (d, J = 8.0 Hz, 2H), 7.72 (dd, J = 8.0, 1.6 Hz, 4H), 7.62(d, J = 8.0 Hz, 4H), 7.56 (d, J = 8.0 Hz, 4H), 7.29 (d, J = 8.4 Hz, 2H), 7.23 (t, J = 8.4 Hz, 2H), 6.76 (t, J = 8.4 Hz, 2H), 2.74 (s, 6H), 1.50 (s, 18H), 1.40 (s, 18H); ^{13}C NMR (150 MHz, CD$_2$Cl$_2$/CS$_2$) δ 152.1, 151.0, 141.6, 139.5, 138.5, 136.2, 136.1, 135.8, 135.6, 134.6, 133.5, 132.6, 132.3 (2 × CH), 130.3, 130.1, 128.7, 128.0, 126.6 (4 × CH), 126.0, 125.4, 125.2, 125.0 (4 × CH), 124.6, 124.3, 124.2, 35.8, 35.5, 32.0, 31.9, 31.8, 21.1; MALDI-MS calcd for C$_{72}$H$_{66}$ 930.5165, found 930.476. Anal. Calcd for C$_{72}$H$_{66}$: C, 92.67; H, 7.33. Found: C, 92.39; H, 7.59.

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Supporting Information Available: Spectral data, NMR spectra, and Maldi-Mass and cyclic voltammetry curves of new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.