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Synthesis and characterization of polybrominated fluorenes and their conversion to polyphenylated fluorenes and cyclopenta[*def*]triphenylene

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ABSTRACT

We report the synthesis and characterization of polyphenylated fluorene derivatives and a ring cyclized product containing cyclopenta[*def*]triphenylene core. Polybromination on fluorene was achieved either by solid state reaction with bromine or utilizing $Br_2/KBrO_3$ in $AcOH/H_2SO_4$ mixture. The bromofluorenes were converted to the corresponding polyphenylated fluorenes by Suzuki coupling protocol. A hexabromofluorene underwent a multifold Suzuki coupling followed by C–H activation to produce a cyclopenta[*def*]triphenylene derivative. Fluorene ring showed a severe distortion from planarity beyond *tetra*-substitution which manifested in the optical properties.

Organic semiconducting materials derived from polyaromatic hydrocarbons such as fluorene,[1,2] anthracene,[3] triphenylene,[4] fluoranthene,[5] perylene,[6] pyrene,[7] and acenes[8] have attracted immense attraction in recent years due to their display of novel properties such as charge transport, tunable luminescence, and non-linear optical properties such as two-photon absorption and hyperpolarizability. They are widely used as emitters in organic light-emitting diodes (OLED), semiconducting layers in thin-film transistors (TFT), reporters in fluorescent sensors, and π-conjugating linkers in nonlinear optical materials and organic sensitizers suitable for dye-sensitized solar cells (DSSC). As a result of their extended conjugation and rigidity, they display strong emission with relatively low Stokes shifts. Also, due to their planar structure they exhibit long-range solid state electronic communications facilitated by intermolecular π-interactions which enhance the charge transporting properties usually beneficial for their application in electronic devices such as TFT, OLED, and bulk heterojunction solar cells.

Fluorene-based small molecules[1] and polymers[2] have been demonstrated as promising emitters for electroluminescent devices and light-harvesting chromophores in photovoltaic devices. Their emission properties can be effectively tuned by chemical modifications. Generally, functionalization of fluorene at 2-, 4-, 7-, and 9-positions has been easily accomplished by the established electrophilic substitution procedures followed by metal-catalyzed coupling reactions.[9] But, introduction of chromophores on several other positions on fluorene required synthetic methodologies generating fluorene framework from acyclic building blocks.[10] Notable methods are the intramolecular dehydrogenative cyclization of 1-amino-1,1-diarylalkanes[11] or triarylmethanols[12] catalyzed by Rh(III) or Ir(III) catalysts. Access to 3,6-disubstituted fluorene derivatives from phenanthrene-9,10-dione involving conventional synthetic strategies have also been reported.[13] Though, these methods allow the precise positioning of the substituents on the fluorene nucleus, they suffer from limited options available for substituents. Alternatively, variety of synthetic explorations can be used to generate polysubstituted fluorenes, if polyhalogenated fluorenes can be obtained from the commercial fluorene. To the best of our knowledge, polyhalogenations have not been demonstrated for fluorene.[14] This is partially due to the deactivating influence of the bromo substituents. In this Letter, we report tri-, tetra-, penta- and hexabromination of fluorene and the use of the resulting polybromides in the generation of polyphenylated fluorenes by palladium-catalyzed cross-coupling reactions. Polyphenylated arenes,[15] commonly termed as '*Müllen dendrons*' are attractive due to their wide use in electro-optical devices[16] and as precursors for nanosized graphene molecules possessing one atom thick planar sheet structures.[17]

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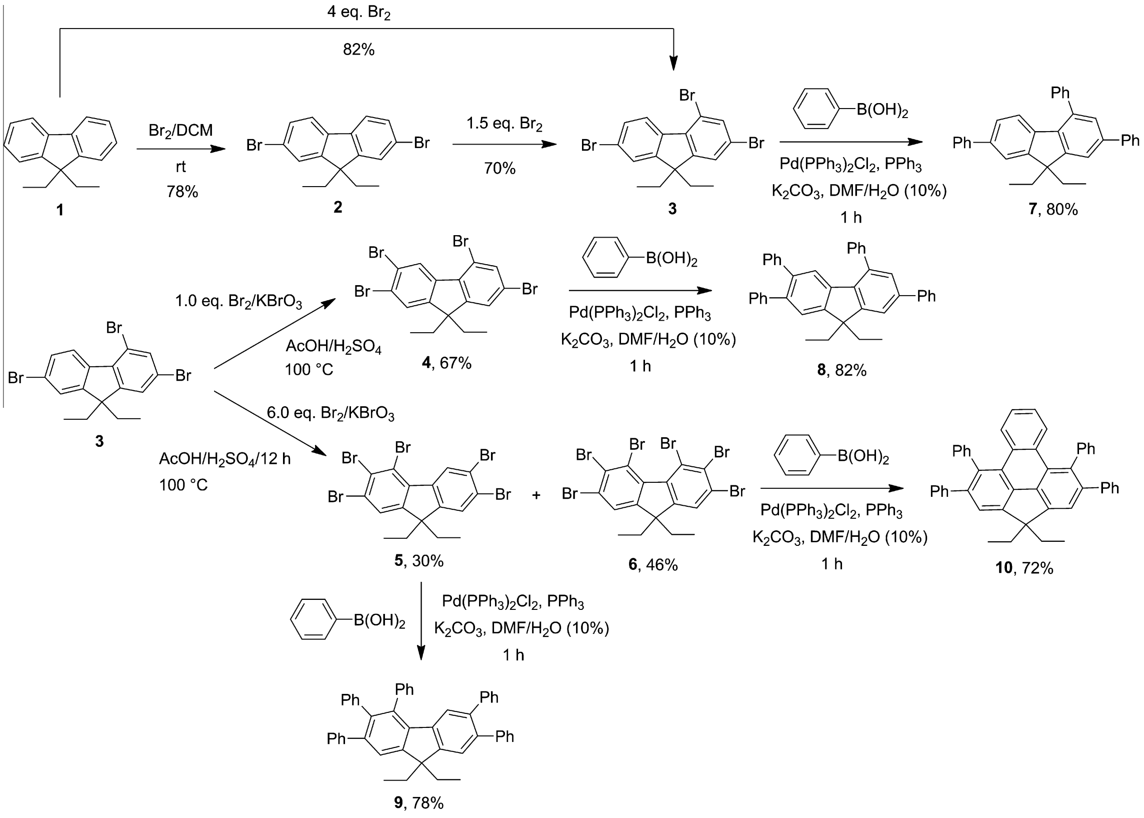
Mono- and dibromination of fluorene is conveniently achieved by treating with bromine in dichloromethane.[18] By controlling the stoichiometry, either 2-bromo- or 2,7-dibromofluorene can be obtained with reasonable purity. Our initial attempts to obtain tribromo- or tetrabromo-derivatives under similar conditions, but using excess bromine, failed. However, in the initial experiments, we observed the formation of 2,4,7-tribromo-9,9-diethyl-9*H*-fluorene (**3**) and other higher substitution products when 9,9-diethyl-9*H*-fluorene (**1**) was reacted with bromine in neat. Optimization experiments revealed the formation of **3** in major amount when 1.5 equiv of bromine were used.[19] Attempts to obtain highly brominated fluorenes in pure form under these conditions did not yield the desired results. Use of excess bromine under neat conditions produced inseparable mixture of polybrominated products. So, we turned our attention to other available brominating methods. Bromination using $Br_2/KBrO_3$[20] reagent system in acetic acid/sulfuric acid mixture was found to be tenable. The tri-substituted derivative, **3** on reaction with 1.0 equiv of $Br_2/KBrO_3$ reagents produced 2,3,5,7-tetrabromo-9,9-diethyl-9*H*-fluorene (**4**) exclusively.[21] Use of the same reagent system, *albeit* under extreme harsh conditions, produced 2,3,4,6,7-pentabromo-9,9-diethyl-9*H*-fluorene (**5**) and 2,3,4,5,6,7-hexabromo-9,9-diethyl-9*H*-fluorene (**6**) in reasonable yields (Scheme 1).

To check the utility of the polybrominated fluorenes, we have first chosen the Suzuki coupling reactions with phenylboronic acid as the coupling partner. Initial attempts employing the conventional catalyst system, $Pd(OAc)_2/K_2CO_3$/toluene:H_2O were not successful in replacing all the bromines in **5** and **6**. However, the use of reaction conditions involving $Pd(PPh_3)_2Cl_2$ and PPh_3, K_2CO_3 and DMF:H_2O (45/5) gave desired results.[22] Interestingly, with **6**, instead of the expected hexaphenyl derivative, a cyclized product, 1,2,6,7-tetrasubstituted cyclopenta[*def*]-triphenylene (**10**), was formed.[23] The formation of **10** probably involves C–H activation after a pentafold Suzuki coupling reaction. Suzuki-Heck-type coupling cascade reactions producing fused polycycles have been previously demonstrated for other substrates, particularly peri-dihalo-polyaromatic hydrocarbons.[24] It has been found that for sterically less demanding substrates, addition of bulky phosphines as additive was required to force the annulation. In the present case, the exclusive formation of cyclized product without additives is probably driven by a steric release on annulation.

The structures of two bromo-derivatives (**4** and **6**) and the cyclopenta[*def*]-triphenylene derivative (**10**) (Fig. 1) have been established by single crystal X-ray diffraction measurements. The fluorene unit is planar in the tetra-substituted derivative (**4**). But the hexa-bromo derivative (**6**) and the cyclopenta[*def*]-triphenylene derivative (**10**) exhibited significant deviation from the planarity for the central cores. The benzene rings were tilted (8.54°, 8.26°) from the central cyclopentadiene ring in **6** owing to the substitution at the bridgehead positions. Though the compound **10**, showed good planarity for the fluorene moiety the appended benzene ring was titled (12.15°) from the fluorene segment considerably.

Absorption and emission spectra of the compounds **7**–**10** recorded in dichloromethane are presented in Figure 2 and relevant data listed in Table 1. All the fluorene derivatives (**7**–**9**) displayed a moderate π–π^* absorption band in the 300–350 nm range. Though the absorption pattern of the present compounds is not significantly different from 9,9-dioctyl-2,7-diphenyl-9*H*-fluorene (λ_{abs} = 327 nm; ε_{max} = 76,100 M^{-1} cm^{-1} in $CHCl_3$)[25] reported earlier, their molar extinction coefficients are drastically reduced. This points that, introduction of phenyl groups on additional fluorene nuclear sites do not extend the chromophore conjugation but diminishes the transition probability mainly due to the twisting in the fluorene segment. The absorption spectrum of **10** is significantly blue shifted (>45 nm) with a concomitant increase in the



Scheme 1. Synthesis of polyphenylated fluorenes and cyclopenta[*def*]triphenylene.

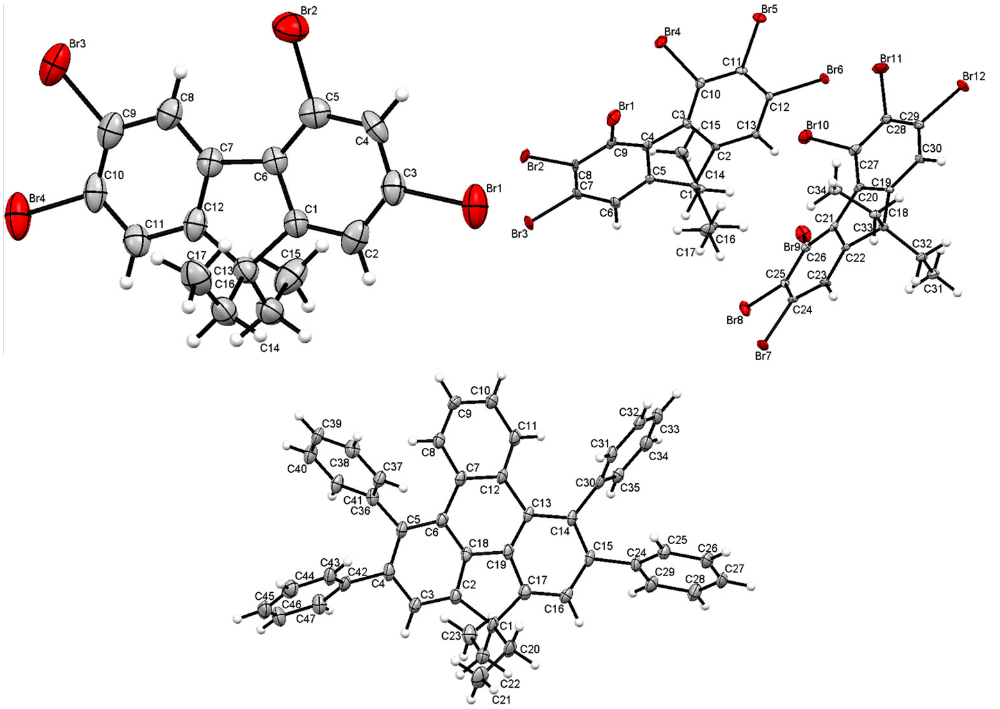


Figure 1. ORTEP plots of the compounds **4** (top-left), **6** (top-right), and **10** (bottom).

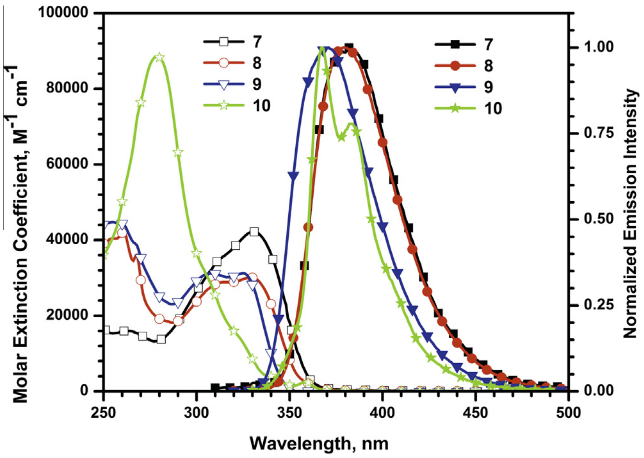


Figure 2. Absorption (unfilled symbols) and emission (solid symbols) spectra of the compounds recorded in CH_2Cl_2.

molar extinction coefficient due to the change in the nature of the absorbing chromophore. All the compounds showed violet-blue fluorescence (Fig. 2) with high quantum efficiency. The Stokes shifts observed for the fluorene derivatives (**7**–**9**) were significantly larger than that observed for **10**. It suggests that compound **10** resists structural reorganization in the excited state.

All the derivatives underwent an irreversible oxidation at moderate redox potentials (1.26–1.33 V) with reference to internal ferrocene, attesting the reasonable electron-richness of the core structure. Additionally, they have also exhibited decent decomposition temperatures in the range 383–431 °C. Interestingly, the annulated derivative, **10** showed the highest thermal decomposition temperature in the series which probably originates from its rigid structure.

In summary, we have devised high yield methods for the synthesis of polybrominated fluorene derivatives by the use of simple reagents. These bromides can be used to construct polyarylated fluorene derivatives as demonstrated in this work by the multifold Suzuki coupling reactions with phenylboronic acid. A reaction cascade involving pentafold Suzuki coupling reaction and a final Heck type C–H activation with the hexabromide leading to a unique pentacyclic product is demonstrated. The synthetic pathway presented in this Letter may be extended further to obtain fluorene containing polymers and oligomers with additional functional chromophores on the peripheral sites of the fluorene nucleus. Work to extend this strategy to obtain functional materials displaying pure blue emission and suitable for solution processed organic light-emitting diodes are under progress in our lab.

Table 1
Optical data for the compounds

Compound	$\lambda_{abs.}$[a], nm ($\varepsilon \times 10^3$, $M^{-1}cm^{-1}$)	λ_{em}/nm[a]	Φ_F[b]	Stokes shift, cm^{-1}	λ_{em}/nm[c]
7	331 (41.9), 264 (16.0)	382	0.78	4033	392
8	330 (30.3), 261 (41.9)	379	0.74	3918	432
9	325 (31.4), 258 (45.3)	371	0.82	3815	404
10	279 (88.5)	367, 383	0.68	607	409, 386

[a] Measured for CH_2Cl_2 solution.
[b] Obtained with reference to 2-aminopyridine (Φ_F = 60%) in 0.1 N H_2SO_4.
[c] Measured for spin-cast film.

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Supplementary data

Supplementary data (synthetic procedures, characterization details and spectra for new compounds) associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2014.02.002. Crystallographic data for the compounds **4**, **6**, and **10** (CCDC 936751, 936752 and 937481) can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or e-mail:deposit@ccdc.cam.ac.uk.)

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19. *Preparation of **3**:* Bromine (1.0 mL, 20.0 mmol) was added drop wise to 9,9-diethyl-9*H*-fluorene (**1**) (1.10 g, 5.0 mmol) with constant mixing using a glass rod. After 30 min, the brown reaction mass was poured into aqueous solution of sodium metabisulfite and extracted with dichloromethane. On removal of volatiles a colorless solid was formed. It was crystallized from methanol to obtain the analytically pure title compound. Yield: 1.88 g (82%). mp = 75 °C. ^{1}H NMR (CDCl$_3$, 500.13 MHz): δ 0.29 (t, J = 7.5 Hz, 6H), 1.94–2.04 (m, 4H), 7.38 (d, J = 2.0 Hz, 1H), 7.44 (d, J = 2.0 Hz, 1H), 7.50 (dd, J = 8.0 Hz, 2.0 Hz, 1H), 7.66 (d, J = 2.0 Hz, 1H), 8.36 (d, J = 8.0 Hz, 1H). ^{13}C NMR (CDCl$_3$, 125.77 MHz): δ 8.3, 33.0, 56.8, 117.2, 121.2, 122.5, 124.5, 125.1, 125.9, 130.1, 134.3, 138.0, 139.0, 152.1, 154.1. MALDI-TOF MS: calcd for $C_{17}H_{15}Br_3$ 455.87 (M$^+$), found 455.86. Anal. Calcd for $C_{17}H_{15}Br_3$: C, 44.48; H, 3.29. Found: C, 44.54; H, 3.23.
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21. *Preparation of **4** and data for **5** and **6**:* A suspension of 2,4,7-tribromo-9,9-diethyl-9*H*-fluorene (**3**) (2.30 g, 5.0 mmol) in acetic acid (25 mL) and 20% H_2SO_4 (2.4 mL) was treated with potassium bromate (0.50 g, 3.0 mmol) and bromine (0.30 mL, 6.0 mmol) and heated at 100 °C for 24 h. On completion of the reaction, excess bromine was quenched by the addition of sodium metabisulfite and reaction mixture extracted with dichloromethane. After evaporation of the volatiles, the residue was purified by crystallization from hexane to obtain the compound as colorless solid. Yield: 1.80 g (67%). mp = 80 °C. ^{1}H NMR (CDCl$_3$, 500.13 MHz): δ 0.30 (t, J = 7.5 Hz, 6H), 1.98 (q, J = 7.5 Hz, 4H), 7.38 (d, J = 1.5 Hz, 1H), 7.55 (s, 1H), 7.67 (d, J = 1.5 Hz, 1H), 8.74 (s, 1H). ^{13}C NMR (CDCl$_3$, 125.77 MHz): δ 8.4, 32.9, 56.7, 117.5, 122.0, 123.1, 124.4, 125.2, 127.6, 127.8, 134.5, 136.9, 140.8, 150.6, 154.3. MALDI-TOF MS: calcd for $C_{17}H_{14}Br_4$ 537.78 (M$^+$+4), found 537.76. Anal. Calcd for $C_{17}H_{14}Br_4$: C, 37.96; H, 2.62. Found: C, 38.07; H, 2.56. **5**: Yield: 0.93 g (30%). mp 150–152 °C; ^{1}H NMR (CDCl$_3$, 500.13 MHz) δ 0.30 (t, J = 7.5 Hz, 6H), 1.96–2.01 (m, 4H), 7.54 (s, 1H), 7.56 (s, 1H), 8.84 (s, 1H); ^{13}C NMR (CDCl$_3$, 125.77 MHz) δ 8.3, 32.8, 56.3, 120.7, 123.1, 125.0, 125.1, 126.8, 127.7, 128.3, 139.3, 140.8, 150.8, 152.2. MALDI-TOF MS: calcd for $C_{17}H_{13}Br_5$ 615.69 (M$^+$+4), found 615.65. Anal. Calcd for $C_{17}H_{13}Br_5$: C, 33.10; H, 2.12. Found: C, 33.02; H, 2.04. Compound **6**: Yield: 1.60 g (46%). mp = 160 °C. ^{1}H NMR (CDCl$_3$, 500.13 MHz): δ 0.32 (t, J = 7.5 Hz, 6H), 2.00 (q, J = 7.5 Hz, 4H), 7.54 (s, 2H). ^{13}C NMR (CDCl$_3$, 125.77 MHz): δ 8.4, 33.1, 57.2, 119.5, 125.6, 126.2, 128.8, 141.9, 152.4. MALDI-TOF MS: calcd for $C_{17}H_{12}Br_6$ 695.60 (M$^+$+6), found 695.58. Anal. Calcd for $C_{17}H_{12}Br_6$: C, 29.35; H, 1.74. Found: C, 29.21; H, 1.68.
22. *Compound **7**:* A mixture of 2,4,7-tribromo-9,9-diethyl-9*H*-fluorene (**3**) (2.30 g, 5.0 mmol), phenyl boronic acid (16.0 mmol), potassium carbonate (6.9 g, 50.0 mmol), $Pd(PPh_3)_2Cl_2$ (120 mg), PPh_3 (80 mg), DMF, (45 mL) and water (5 mL) were heated at 110 °C under inert atmosphere for 2 h. The residue obtained on evaporation of the volatiles was purified by column chromatography using dichloromethane/hexanes (1:5) to obtain the title compound as colorless powder. Yield: 1.80 g (80%). mp = 135–137 °C. ^{1}H NMR (CDCl$_3$, 500.13 MHz): δ 0.46 (t, J = 7.5 Hz, 6H), 2.14 (q, J = 7.5 Hz, 4H), 6.98 (d, J = 8.0 Hz, 1H), 6.94 (dd, J = 8.0, 1.5 Hz, 1H), 7.33–7.36 (m, 2H), 7.42–7.48 (m, 6H), 7.51–7.54 (m, 3H), 7.57–7.58 (m, 3H), 7.61–7.63 (m, 2H), 7.71–7.72 (m, 2H). ^{13}C NMR (CDCl$_3$, 125.77 MHz): δ 8.7, 33.2, 55.7, 120.3, 121.3, 122.8, 125.6, 127.1, 127.2, 127.3, 127.6, 128.0, 128.5, 128.8, 129.3, 137.5, 137.8, 139.5, 139.7, 140.4, 141.2, 141.3, 141.5, 151.3. ESI HRMS: calcd for $C_{35}H_{30}$+Na 473.2240 (M$^+$+Na), found 473.2257. Anal. Calcd for $C_{35}H_{30}$: C, 93.29; H, 6.71. Found: C, 93.37; H, 6.64. Compound **8**: Yield: 2.16 g (82%). mp = 105–107 °C. ^{1}H NMR (CDCl$_3$, 500.13 MHz): δ 0.56–0.59 (m, 6H), 2.17–2.21 (m, 4H), 7.02 (s, 2H), 7.07 (s, 1H), 7.15 (s, 3H), 7.20–7.25 (m, 4H), 7.37–7.41 (m, 3H), 7.49–7.54 (m, 6H),

7.64–7.65 (m, 3H), 7.76–7.77 (m, 2H). ^{13}C NMR ($CDCl_3$, 125.77 MHz): δ 8.8, 33.0, 55.6, 120.3, 124.8, 124.9, 126.0, 126.3, 127.2, 127.6, 127.8, 128.4, 128.8, 129.2, 129.9, 130.0, 132.0, 133.6, 133.8, 137.4, 137.8, 138.5, 139.1, 139.6, 140.4, 141.0, 141.2, 141.7, 142.3, 149.8, 151.9. ESI HRMS calcd for $C_{41}H_{34}$+Na 549.2553 (M^++Na), found 549.2567. Anal. Calcd for $C_{41}H_{34}$: C, 93.49; H, 6.51. Found: C, 93.21; H, 6.59. Compound **9**: Yield: 2.35 g (78%). mp = 210–213 °C. ^{1}H NMR ($CDCl_3$, 500.13 MHz): δ 0.59–0.62 (m, 6H), 2.11–2.15 (m, 4H), 6.31 (s, 1H), 6.86–6.87 (m, 2H), 6.93–6.94 (m, 5H), 7.06–7.07 (m, 3H), 7.15–7.25 (m, 15H), 7.34 (s, 1H), 7.43 (s, 1H). ^{13}C NMR ($CDCl_3$, 125.77 MHz): δ 9.0, 32.8, 55.4, 123.8, 123.9, 124.9, 125.1, 125.5, 125.9, 126.0, 126.2, 126.6, 126.8, 127.4, 127.5, 127.6, 127.8, 128.0, 130.0, 130.1, 130.3, 131.7, 136.8, 138.3, 138.4, 138.6, 138.8, 139.6, 139.9, 140.2, 140.9, 141.6, 142.4, 142.6, 149.8. ESI HRMS calcd for $C_{47}H_{38}$+Na 625.2866 (M^++Na), found 625.2881. Anal. Calcd for $C_{47}H_{38}$: C, 93.65; H, 6.35. Found: C, 93.72; H, 6.23.

23. Compound **10**: Yield: 2.16 g (72%). mp = 235–238 °C. ^{1}H NMR ($CDCl_3$, 500.13 MHz): δ 0.67 (t, *J* = 7.5 Hz, 6H), 2.25 (q, *J* = 7.5 Hz, 4H), 6.94–6.96 (m, 2H), 7.16–7.19 (m, 10H), 7.25 (s, 2H), 7.27–7.29 (m, 8H), 7.56–7.58 (m, 4H). ^{13}C NMR ($CDCl_3$, 125.77 MHz): δ 9.3, 31.9, 58.0, 123.3, 125.0, 125.8, 126.7, 127.2, 128.4, 128.5, 130.4, 131.1, 133.2, 135.4, 136.7, 141.8, 142.3, 143.5, 147.8. ESI HRMS calcd for $C_{47}H_{36}$+Na^+ 600.2817 (M^++Na), found 600.2816. Anal. Calcd for $C_{47}H_{36}$: C, 93.96; H, 6.04. Found: C, 94.08; H, 6.02.
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