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Fluoride-Induced Cyclization of Pentacenequinone to Higher Quinones

Vandana Bhalla,* Ankush Gupta, Roopa, Hardev Singh, and Manoj Kumar

Department of Chemistry, UGC Sponsored-Centre for Advance Studies-I, Guru Nanak Dev University, Amritsar-143005, Punjab, India

Supporting Information

ABSTRACT: Novel pentacenequinone derivatives **3**, **7**, and **10** have been synthesized via Suzuki−Miyaura coupling. Derivatives **3** and **7** having OTBS groups undergo irreversible fluoride-induced cyclization to substituted higher quinones in the presence of TBAF in dry THF using one-pot, two-step strategies in moderate yields. These functionalized higher quinone derivatives are freely soluble in THF and DMSO and can be used as precursors for the synthesis of higher acene derivatives.

INTRODUCTION

Acenes have attracted attention because of their applications for electronic devices such as organic field-effect transistors (OFETs), organic light-emitting diodes (OLEDs), and film-making characteristics.[1,2] However, higher acenes (ring number $n \geq 5$) are less known due to their low stability under ambient conditions and low solubility in organic solvents. Anthony et al.[3,4] synthesized stable and solution-processable acene derivatives from pentacenequinone, dithienoacenequinone, hexacenequinone, and heptacenequinone by nucleophilic addition of an organometallic reagent to the corresponding acenequinones. Miller et al.[5] reported synthesis of stable and soluble acenes ($n = 7, 9$) from their corresponding acenequinones. Synthesis of higher acenes could be convenient from stable and solution-processable precursors. In this context, convenient synthesis of higher quinones having good solubility in common organic solvents is an area of great interest.

Our research work on the molecular recognition and sensing is focused on the development of novel artificial receptors for the selective sensing of soft metal ions[6] and inorganic anions[7] and evaluation of their logic behaviors for the construction of molecular switches and molecular level devices.[8] Recently, we reported a facile cyclization of terphenyl derivatives having dimethyl-*tert*-butylsilyloxy groups (OTBS) groups to symmetrically and unsymmetrically substituted triphenylenes through oxidative dehydrogenation in the presence of tetrabutylammonium fluoride (TBAF).[9] Taking into consideration the electron-rich nature of terphenyls, we planned to investigate the effect of electronic nature of the core moiety in the case of fluoride-induced cyclization. In this context, we were interested in studying fluoride-induced desilylation reactions in electron-deficient pentacenequinone derivatives as convenient cyclization of these derivatives could give a facile synthetic route for the synthesis of higher quinones, precursors for higher acenes. To our delight, the electron-deficient pentacenequinone derivatives underwent fluoride-mediated cyclization smoothly, and we were successful in developing a convenient synthetic route for preparation of solution-processable functionalized heptaquinone and hexaquinone derivatives. These higher quinones are freely soluble in THF and DMSO.

To the best of our knowledge, this is the first report of the synthesis of solution-processable higher quinone derivatives from a pentacenequinone derivative in a single step in moderate yields.

RESULTS AND DISCUSSION

Pentacenequinone derivative **3** was synthesized by Suzuki−Miyaura coupling of boronic ester **2** with tetrabromopentacenequinone[10] **1** in 40% yield as shown in Scheme 1. The structure of compound **3** is characterized by spectroscopic and analytical data. The ^{1}H NMR spectrum of **3** showed four singlets (24H, 24H, 36H, 36H) for the protons of dimethyl-*tert*-butylsilyloxy groups and one multiplet and two singlets (4H, 16H) for the aromatic protons.

In the next step, we planned to carry out deprotection of the dimethyl-*tert*-butylsilyloxy groups using tetrabutylammonium fluoride (TBAF) in dry THF. The reaction was accompanied by significant color change, and after usual workup, the crude product was used as such for the next reaction with propargyl bromide and triflic anhydride, respectively, as shown in Scheme 2. However, in both reactions after usual workup an insoluble solid was obtained that could not be characterized.

To overcome this problem, we then adopted a two-step, one-pot strategy wherein deprotection using tetrabutylammonium fluoride (TBAF) in dry THF and subsequent reaction with triflic anhydride was carried out in one pot under nitrogen atmosphere to furnish compound **4** in 50% yield as shown in Scheme 2. The ^{1}H NMR spectrum of **4** showed four singlets (4H, 4H, 4H, 4H) for aromatic protons.

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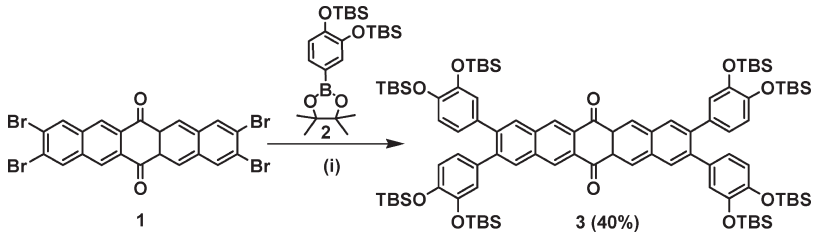
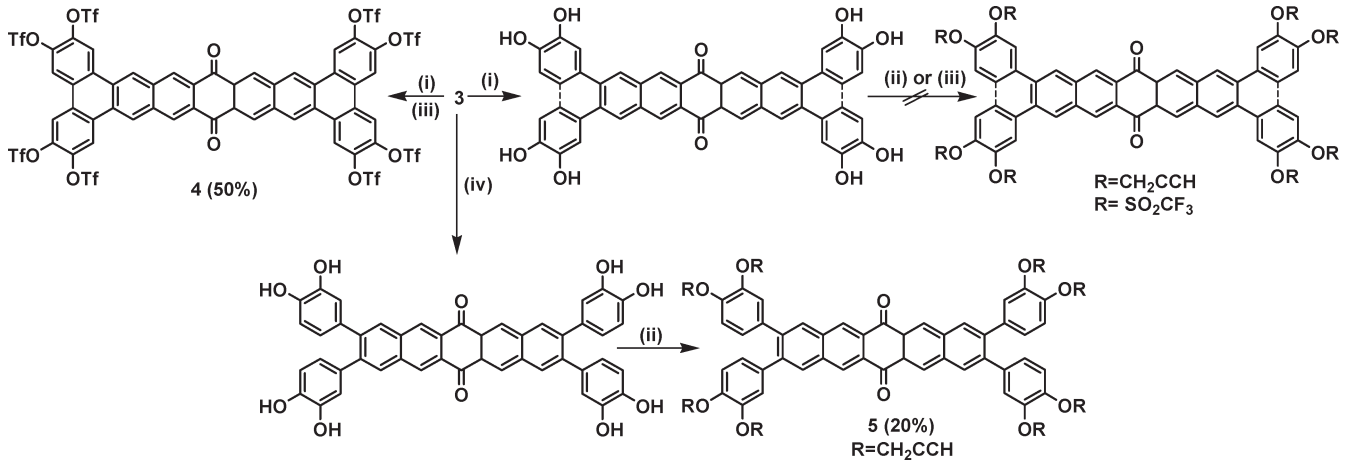
Scheme 1[a]



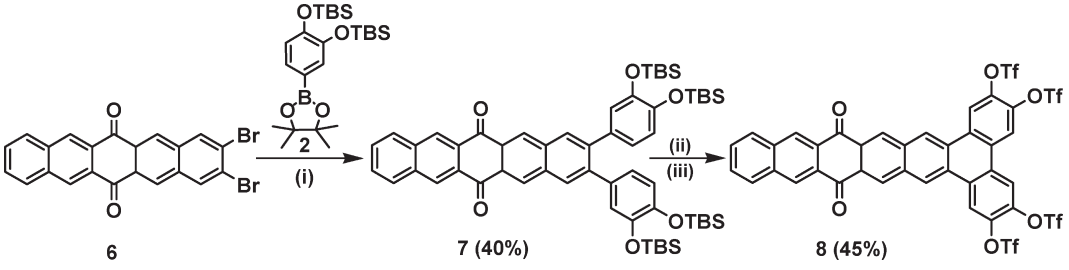
[a] Key: (i) $Pd(PPh_3)_4$, 2 M K_2CO_3, toluene, 90−100 °C TBS = $-Si(CH_3)_2C(CH_3)_3$.

Scheme 2[a]



[a] Key: (i) TBAF, THF(dry), 2 h; (ii) $BrCH_2CCH$, K_2CO_3, DMF(dry), 80 −90 °C; (iii)Tf_2O, pyridine, 0 °C,Tf = SO_2CF_3; (iv) TBAF, THF/H_2O (9:1), 2 h.

Scheme 3[a]



[a] Key: (i) $Pd(PPh_3)_4$, 2 M K_2CO_3, toluene, 90−100 °C; (ii)TBAF, THF(dry); (iii)Tf_2O, pyridine, 0 °C.

These results show that fluoride-promoted cyclization is observed when deprotection reaction is carried out in dry THF with TBAF using a two-step, one-pot strategy. We also carried out the deprotection reaction in a mixture of THF/H_2O (9:1). The crude product was used as such for the next reaction with propargyl bromide, and pentacenequinone derivative **5** was obtained in 20% yield as shown in Scheme 2. Along with derivative **5**, a black solid was also obtained which could not be characterized because of its insolubility in organic solvents. Formation of pentacenequinone derivative **5** shows obstruction to fluoride-induced cyclization in the presence of aqueous THF. This may be attributed to a lack of optimum electron density on phenolate oxygens required for cyclization due to spontaneous protonation of phenolate oxygens after fluoride-induced desilylation.

To gain deeper insight into the reaction, we also prepared compounds **7** and **10** using Suzuki−Miyaura coupling between dibromopentacenequinone **6** and tetrabromopentacenequinone **1** with respective boronic esters **2** and **9** as shown in Schemes 3 and 4. Deprotection of compound **7** using TBAF and its subsequent reaction with triflic anhydride yielded hexaquinone derivative **8** in 45% yield. The structure of derivative **8** is characterized from its spectroscopic data (see the Supporting Information).

However, no aryl−aryl bond formation was observed in the case of deprotection reaction of compound **10** with boron tribromide

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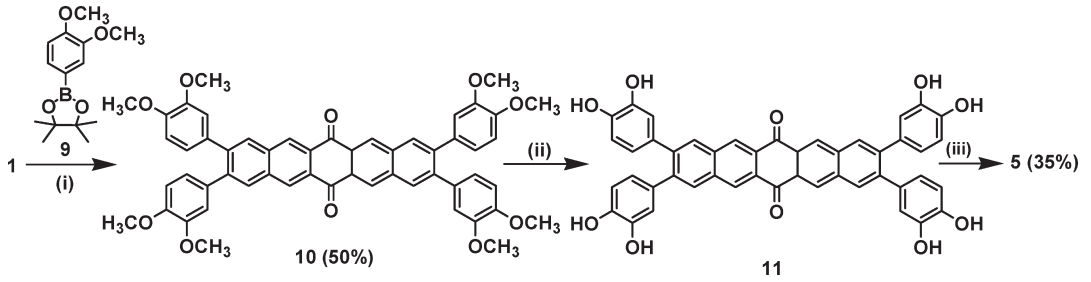
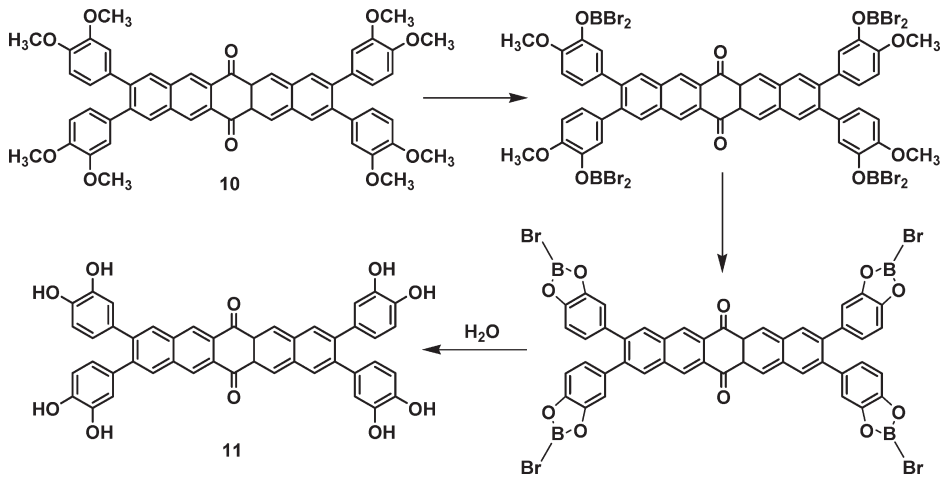
Scheme 4[a]

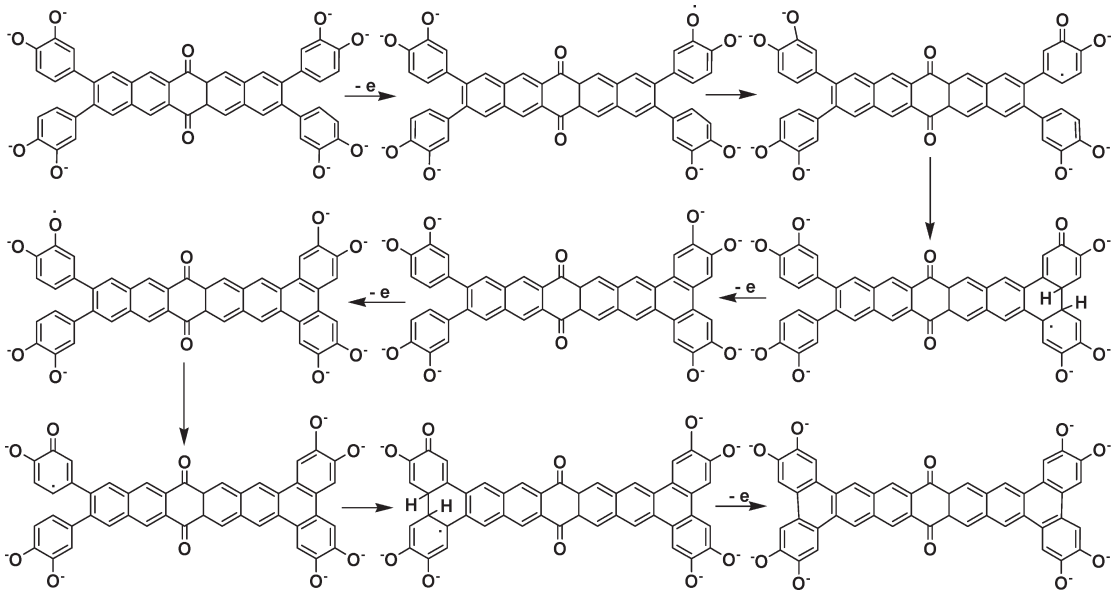


[a] Key: (i) $Pd(PPh_3)_4$, 2 M K_2CO_3, toluene, 90−100 °C; (ii) BBr_3, DCM(dry), −78 °C; (iii) $BrCH_2CCH$, K_2CO_3, DMF (dry), 80−90 °C.

Scheme 5. Proposed Mechanism for the Deprotection of Methoxy Groups in the Presence of BBr_3



Scheme 6. Proposed Mechanism for Cyclization in the Presence of TBAF



(BBr_3). The deprotection reaction with BBr_3 was not accompanied by any color change, and after usual workup, a green solid was obtained which was used without further purification in the subsequent reaction with propargyl bromide to furnish pentacenequinone derivative **5** in 35% yield. The structure of derivative **5** is characterized from its spectroscopic data. The ^1H NMR

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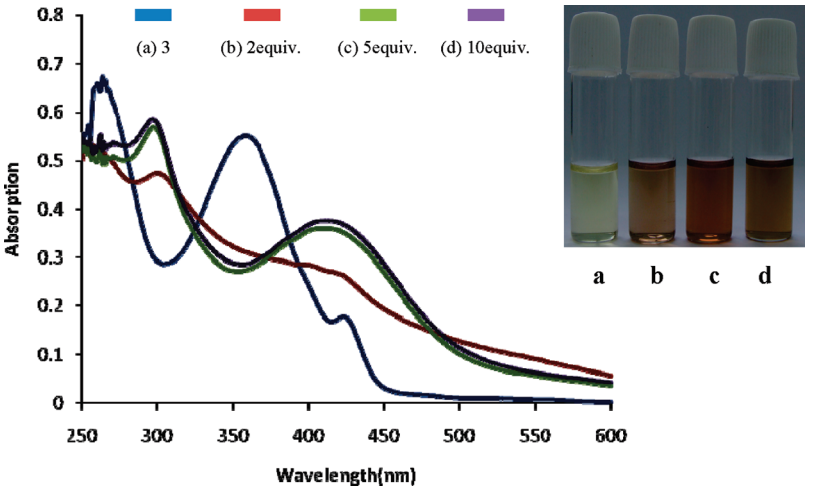

Figure 1. UV−vis spectra of **3** (5×10^{-5} M) in the presence of (a) free ligand, (b) 2 equiv, (c) 5 equiv, and (d) 10 equiv of TBAF in THF.

spectrum of **5** showed three singlets (4H, 4H, 4H) and one multiplet (8H) for aromatic protons and four singlets (4H, 4H, 8H, 8H) for aliphatic protons (see the Supporting Information).

We assume that the deprotection reaction with boron tribromide proceeds stepwise, and in the first step a complex between reagent and the ethereal oxygen atom is formed which leads to the formation of cyclic borate as shown in Scheme 5. Thus, formation of cyclic borates prevented the oxidative cyclization of pentacenequinone to heptaquinone derivative during deprotection reaction with BBr_3.

Based on these results, we may conclude that increased negative charge on four phenolate oxygens after deprotection of OTBS groups in pentacenequinones **3** and **7** provides an optimal amount of directing ability and electron density to complete cyclization to the hexaquinone and heptaquinone derivatives, respectively. The proposed mechanism for the cyclization is as shown in Scheme 6.

Since the deprotection reaction of compound **3** with TBAF was accompanied by significant color change, this prompted us to examine the deprotection reaction of compound **3** with TBAF using UV−vis and fluorescence spectroscopy. The UV−vis titration experiments were carried out in THF at 5×10^{-5} M concentration of derivative **3** upon incremental amounts of 3 μM of tetrabutylammonium fluoride (TBAF); the spectrum is shown in Figure 1. Compound **3** shows two absorption bands at λ_{max} 357 nm ($\varepsilon = 5.51 \times 10^4$ M^{-1} cm^{-1}) and 263 nm ($\varepsilon = 6.72 \times 10^4$ M^{-1} cm^{-1}). Upon the addition of 2 equiv of F^-, the absorption band at 357 nm disappeared completely and two new bands appeared at 400 nm ($\varepsilon = 2.86 \times 10^4$ M^{-1} cm^{-1}) and 299 nm ($\varepsilon = 4.75 \times 10^4$ M^{-1} cm^{-1}) with two isosbestic points at 392 and 326 nm. The band at 263 nm was shifted to 260 nm ($\varepsilon = 5.29 \times 10^4$ M^{-1} cm^{-1}). On further addition of 3 equiv of fluoride ion, absorption bands at 400 and 299 nm reached their limiting value and the band at 400 nm was red-shifted to 411 nm ($\varepsilon = 3.61 \times 10^4$ M^{-1} cm^{-1}), whereas bands at 299 nm were blue-shifted to 296 nm ($\varepsilon = 5.69 \times 10^4$ M^{-1} cm^{-1}) (Figure 1). These changes are accompanied by a gradual change of color from yellow to brown, visible to the naked eye. The spectral behavior revealed that fluoride-induced desilylation leads to enhanced negative charge on phenolate oxygen which is responsible for the red shift in the absorbance spectra because of extended conjugation.

Compound **3** is fluorescent with maximum emission at 551 nm when excited at λ_{max} 358 nm. Upon addition of 10 equiv of fluoride ion, fluorescence was exclusively and efficiently quenched (Figure 2).

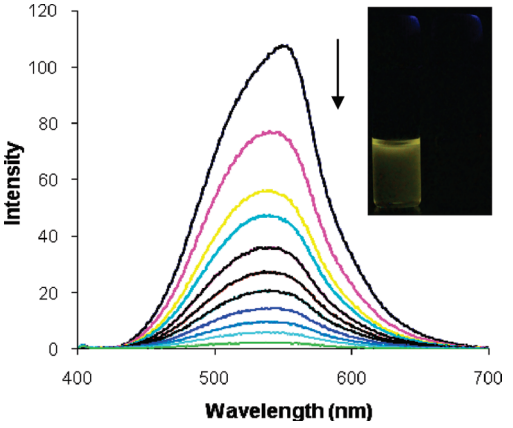

Figure 2. Fluorescence spectra of **3** (1×10^{-5} M) upon addition of TBAF (100 μM) in THF.

The complete fluorescence quenching may be ascribed to an electron transfer from phenolate oxygen to quinone moiety.[11] Thus, the presence of fluoride ions results in cleavage of the Si−O bond, which increases negative charge on the phenolate oxygen, and this increased electron density on phenolate oxygens is responsible for the change in absorption and emission spectra of the compound **3**.

CONCLUSION

We have prepared pentacenequinone derivatives **3** and **7** having OTBS groups. During the deprotection reaction of OTBS groups using TBAF, these derivatives undergo fluoride-induced irreversible cyclization to form heptaquinone and hexaquinone derivatives, respectively. Both of the higher quinones are freely soluble in THF and DMSO. The studies on the synthesis of stable and solution-processable acenes from these solution-processable precursor compounds are under investigation in our laboratory.

EXPERIMENTAL SECTION

General Experimental Methods. All reagents were purchased from commercial suppliers. THF (AR grade) was used to perform analytical

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studies. Reactions that require anhydrous conditions were carried out under nitrogen in oven-dried glassware. Tetrahydrofuran was distilled from sodium/benzophenone. Melting points were determined with a capillary melting point apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on a 300 MHz spectrophotometer using $CDCl_3$ as solvent and TMS as internal standards. Data are reported as follows: chemical shifts in ppm (δ), multiplicity (s = singlet, d = doublet, br = broad singlet, m = multiplet), coupling constants (Hz), integration, and interpretation. Silica gel 60 (60−120 mesh) was used for column chromatography.

2,3,9,10-Tetrakis(1,2-di-*tert*-butyldimethylsiloxyphenyl)-6,13-pentacenequinone (3). To a mixture of **1** (270 mg, 0.43 mmol) and tetrakis(triphenylphosphine)palladium(0) in toluene (20 mL) was added a suspension of **2** (1 g, 2.15 mmol) in ethanol (5.2 mL) and 2 M aqueous solution of K_2CO_3 (475 mg, 3.44 mmol). The mixture was degassed and purged with N_2 for 15 min. The mixture was refluxed overnight. After completion of the reaction (TLC), the flask was allowed to cool to room temperature. The mixture was extracted with CH_2Cl_2, and the organic layer was washed with brine, dried over $MgSO_4$, and filtered. The filtrate was evaporated to dryness under reduced pressure. Flash chromatography over silica gel (90:10 hexane/ethyl acetate) provided the coupled product **3** in 40% yield: mp 165−170 °C; ^{1}H NMR δ 0.13 (s, 24H), 0.22 (s, 24H), 0.96 (s, 36H), 1.00 (s, 36H), 6.69−6.74 (m, 8H), 6.79 (s, 4H), 8.06 (s, 4H), 8.95 (s, 4H); ^{13}C NMR δ (75.45 MHz, $CDCl_3$) −4.1, −4.0, 18.4, 18.5, 25.9, 120.5, 122.4, 122.9, 129.5, 130.7, 131.2, 133.8, 134.3, 142.8, 146.5, 146.6; MS (FAB) *m*/*z* 1655. Anal. Calcd for $C_{94}H_{142}O_{10}Si_8$: C, 68.14; H, 8.64. Found: C, 68.12; H, 8.55.

Heptaquinone (4). To a stirred solution of **3** (150 mg, 0.09 mmol) in dry THF (2 mL) was added a solution of 1 M tetrabutylammonium fluoride (TBAF) (237 mg, 0.90 mmol) under nitrogen atmosphere which was accompanied by an immediate color change to dark violet. The mixture was stirred at room temperature for 2 h. After completion of the reaction (TLC), dry pyridine (231 μL, 2.88 mmol) and trifluoromethanesulfonic anhydride (304 μL, 1.81 mmol) was slowly added to the reaction mixture in situ at −20 °C. The flask was allowed to warm to room temperature, and the mixture was stirred overnight. The reaction was quenched by adding 2 N HCl solution. The aqueous layer was extracted with tetrahydrofuran (THF). The organic layer was separated, dried over $MgSO_4$, and evaporated under reduced pressure to obtain a solid residue, which was purified by recrystallization from methanol and dichloromethane to give the pure product in 50% yield: mp >250 °C; ^{1}H NMR δ (300 MHz, DMSO-d_6) 7.63 (s, 4H), 8.20 (s, 4H), 9.08 (s, 4H), 9.28 (s, 4H); ^{13}C NMR (75.45 MHz, DMSO-d_6) 25.5, 57.7, 67.4, 108.6, 110.7, 121.5, 123.9, 124.4, 129.8, 131.1, 132.2, 146.2, 148.2, 182.2; MS (MALDI) *m*/*z* 1790. Anal. Calcd for $C_{54}H_{18}F_{24}O_{26}S_8$: C, 36.13; H, 1.01. Found: C, 36.01; H, 0.98.

2,3,9,10-Tetrakis(1,2-diprop-2-ynyloxyphenyl)-6,13-pentacenequinone (5). K_2CO_3 (335 mg, 2.43 mmol) was added to a solution of **11** (150 mg, 0.20 mmol) in dry DMF. The reaction mixture was stirred for 5 min, and then propargyl bromide (217 μL, 2.43 mmol) was added dropwise. The mixture was stirred overnight at 70−80 °C. After completion of the reaction (TLC), the flask was allowed to cool to room temperature, and thereafter, water was added to the reaction mixture. A solid compound precipitated after addition of water to the reaction mixture. The solid compound was filtered and washed with methanol, and the solid was recrystallized from dichloromethane to give compound **5** in 40% yield: mp 140−150 °C; ^{1}H NMR δ (300 MHz, $CDCl_3$) 2.46 (s, 4H), 2.56 (s, 4H), 4.52 (s, 8H), 4.79(s, 8H), 6.89 (s, 4H), 6.98−7.07 (m, 8H), 8.15 (s, 4H), 8.97 (s, 4H); MS (FAB) *m*/*z* 1047. Anal. Calcd for $C_{70}H_{46}O_{10}$: C, 80.29; H, 4.43. Found: C, 80.10; H, 4.30.

2,3-Bis(1,2-di-*tert*-butyldimethylsiloxyphenyl)-6,13-pentacenequinone (7). To a mixture of **6** (435 mg, 0.93 mmol) and tetrakis(triphenylphosphine)palladium(0) in toluene (20 mL) was added a suspension of **2** (1 g, 2.15 mmol) in ethanol (5.2 mL) and 2 M aqueous solution of K_2CO_3 (475 mg, 3.45 mmol). The mixture was degassed and purged with N_2 for 15 min. The mixture was refluxed overnight. After completion of the reaction (TLC), the flask was allowed to cool to room temperature. The mixture was extracted with CH_2Cl_2, and the organic layer was washed with brine, dried over $MgSO_4$, and filtered. The filtrate was evaporated to dryness under reduced pressure. Flash chromatography over silica gel (97:3 hexane/ethyl acetate) provided the coupled product **7** in 40% yield: mp >250 °C; ^{1}H NMR δ (300 MHz, $CDCl_3$) 0.12 (s, 12H), 0.22 (s, 12H), 0.96 (s, 18H), 1.00 (s, 18H), 6.66−6.74 (m, 4H), 6.79 (s, 2H), 7.69−7.72 (m, 2H), 8.04 (s, 2H), 8.11−8.14 (m, 2H), 8.94 (s, 2H) 8.95 (s, 2H); ^{13}C NMR δ (75.45 MHz, $CDCl_3$) −4.1, −4.0, 18.4, 18.5, 25.91, 25.94, 120.6, 122.4, 122.9, 129.4, 129.5, 129.7, 130.1, 130.6, 130.7, 131.2, 133.8, 134.3, 135.2, 142.8, 146.5, 146.6, 182.9; MS (MALDI) *m*/*z* 981. Anal. Calcd for $C_{58}H_{78}O_6Si_4$: C, 70.83; H, 7.99. Found: C, 70.80; H, 7.90.

Hexaquinone (8). To a stirred solution of **7** (155 mg, 0.16 mmol) in dry THF (2 mL) was added a solution of 1 M tetrabutylammonium fluoride (TBAF) (206 mg, 0.79 mmol) under nitrogen atmosphere. The mixture was stirred at room temperature for 2 h. After completion of the reaction (TLC), dry pyridine (196 μL, 2.44 mmol) and trifluoromethanesulfonic anhydride (257 μL, 1.53 mmol) were slowly added to the reaction mixture in situ at −20 °C. The flask was allowed to warm to room temperature, and the mixture was stirred overnight. The reaction was quenched by adding 2 N HCl solution. The aqueous layer was extracted with tetrahydrofuran (THF). The organic layer was separated, dried over $MgSO_4$, and filtered. The filtrate was evaporated under reduced pressure to get the crude which was purified by recrystallization from methanol and dichloromethane to give the product in 45% yield: mp >250 °C; ^{1}H NMR δ (300 MHz, DMSO-d_6) 7.52 (s, 2H), 7.64 (s, 2H), 8.65 (s,2H), 8.90 (s, 2H), 9.10 (s, 2H), 9.41 (s, 2H), 9.84 (s, 2H); ^{13}C NMR (75.45 MHz, DMSO-d_6) 60, 95.4, 98.5, 101.8, 108.0, 110.0, 120.9, 123.2, 123.9, 128.7, 129.4, 129.9, 130.5, 131.4, 134.2, 145.6, 147.6, 168, 181.4; ESI MS *m*/*z* 1051. Anal. Calcd for $C_{38}H_{16}F_{12}O_{14}S_4$: C, 43.35; H, 1.53. Found: C, 43.30; H, 1.45.

2,3,9,10-Tetrakis(1,2-dimethoxyphenyl)-6,13-pentacenequinone (10). To a mixture of **1** (575 mg, 0.92 mmol) and tetrakis(triphenylphosphine)palladium(0) in toluene (20 mL) was added a suspension of **9** (1 g, 3.77 mmol) in ethanol (5.2 mL) and 2 M aqueous solution of K_2CO_3 (1.01 mg, 7.37 mmol). The mixture was degassed and purged with N_2 for 15 min. The mixture was refluxed overnight. After completion of the reaction (TLC), the flask was allowed to cool to room temperature. The mixture was extracted with CH_2Cl_2 ,and the organic layer was washed with brine, dried over $MgSO_4$, and filtered. The filtrate was evaporated to dryness under reduced pressure. Flash chromatography over silica gel (85:15 hexane/ethyl acetate) provided the coupled product **10** in 50% yield: mp 170−180 °C; ^{1}H NMR δ (300 MHz, $CDCl_3$) 3.65 (s, 12H), 3.91 (s, 12H), 6.70 (s, 4H), 6.84−6.94 (m, 8H), 8.16 (s, 4H), 8.98 (s, 4H); ^{13}C NMR δ (75.45 MHz, $CDCl_3$) 15.7, 50.3, 55.7, 58.6, 110.9, 113.2, 122.0, 126.2, 129.5, 130.9, 133.1, 134.4, 142.6, 148.0, 148.4, 173.6; MS (FAB) *m*/*z* 853. Anal. Calcd for $C_{54}H_{46}O_{10}$: C, 75.86; H, 5.42. Found: C, 75.80; H, 5.35.

2,3,9,10-Tetrakis(1,2-dihydroxyphenyl)-6,13-pentacenequinone (11). BBr_3 (2.87 mL, 2.87 mmol, 1 M in dichloromethane) was added to a solution of **10** (200 mg, 0.23 mmol) in dry dichlorolomethane (5 mL) at −78 °C, and the mixture was stirred for 30 min. The flask was allowed to warm to room temperature, and the mixture was stirred overnight. The reaction was quenched with water. A solid compound precipitated after addition of water to the reaction mixture. The solid compound was filtered and used for further reaction without purification.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Characterization data including melting point and ^{1}H, ^{13}C, and mass spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author
*E-mail:vanmanan@yahoo.co.in.

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