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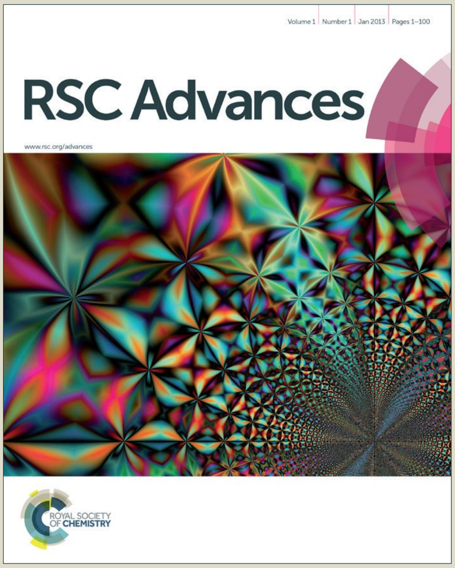

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Synthesis of Highly Emissive 1,8-diaryl Anthracene Derivatives and Fabrication of their Micro/nanostructures

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Abstract

We report a new route for the synthesis of 1,8 Diaryl-anthracene derivatives (**1-6**) starting form anthroquinone. The reduction of 1,8 dichoroanthraquinone followed by aryl-aryl coupling using modified Suzuki-Miyuara reaction conditions furnished 1,8 diaryl anthracene derivatives in the good yields. Detailed photophysical and electrochemical studies show that these anthracene derivatives emit in the blue region with a narrow FWHM and provide a high quantum yield (upto 75%). The HOMO and LUMO energy levels of these compounds are in the range of -5.62 to 5.71 and 2.68 to 2.79 eV, respectively. Furthermore, anthracene derivative **5** was used for the surfactant assisted self assembling process to obtain the micro/nano structures. Compound **5** showed microplates in the polyvinylpyrrolidone (PVP) and nonowires with an average diameter of ~290 nm in the cetyl trimethylammonium bromide (CTAB). Absorption and emission properties of micro/nano assemblies of compound **5** showed red shift of about 12 nm. It was also noticed that the emission intensity of **5** has been retained even in the nano assemblies and is found to be comparable with the solution of **5** in organic solvents. The DFT calculations suggest that multiple hydrogen bonding

interactions are possible between two interacting monomers of **5**. We reckon that the possibility of H-bonding interactions in **5** is one of the factors which may helps in the formation of micro/nano-assemblies. The blue emitting properties, compatible HOMO and LUMO energy levels, highly blue emitting micro/nano assemblies of these compounds makes them suitable material for the organic light emitting devices (OLED).

Introduction

Anthracene derivatives have attracted a great deal of attention in the recent times owing to their various chemical, photophysical and medical applications.[1-3] For instances, they have been frequently used as fluorescence probes, singlet oxygen acceptors, as well as in optoelectronic devices including organic thin-film transistors, solar cells, upconversion of energy using triplet-triplet annihilation process etc.[4-9] Moreover, anthracene derivatives possessing a high fluorescence quantum yield and good chemical photo stability have found applications in the organic light emitting devices (OLEDs).[10] Recently, it has been shown that triplet–triplet annihilation (or triplet fusion) and thermally-activated delayed fluorescence in the anthracene based OLEDs led to a very high external quantum efficiency (16.5%).[11,12] However, unsubstituted anthracene has a very low fluorescence quantum yield and it readily crystallizes in thin film which limits their application in the solid state devices. Consequently, several attempts were made to improve the emission and thin film properties of anthracene derivatives. In particular, phenyl substitution at the 9 and 10 positions of anthracene is found to be a successful protocol towards improving photophysical properties of the anthracene.[13,14] Phenyl rings of diphenyl anthracene (DPA) are found to be out of the plane on the anthracene core which causes a marginal bathochromic shift and also prevents crystallization of DPA in the thin film.[14] It was demonstrated that film forming properties of DPA can be improved by introducing the bulky aryl-based substituents at the -9,10 positions or other positions (2,6 position) of anthracene.[15] While substitution at the 9,10-positions of anthracene is well reported and studied in the literature, substitution at other positions of anthracene are rarely explored. Recently, 2,6-diphenyl anthracene was reported using 2,6-dihydroxy anthracene as a starting material which was obtained by the reduction of 2,6-dihydroxy anthraquinone (Scheme 1a).[16] Similarly, 1,8 diphenyl anthracene has been reported using reaction of phenyl magnesium bromide with 1,8-dichloroanthracene which was obtained by the reduction of 1,8-dichloroanthraquinione.[17] However, this method employs Grignard reagents which are not easy to prepare and requires perfect anhydrous reaction conditions (Scheme 1b) and hence, make it less practical. It is worthwhile to mention that the preparation of Grignard reagent has limitation towards several organic functional groups. Alternatively, to synthesize aryl substituted anthracene, the convenient approach is the aryl-aryl bond formation using Suzuki-Miyaura, Stille or Negishi coupling reactions.[18] Such coupling reactions requires 1,8-haloanthracene derivatives which are difficult to synthesize, since 9,10 positions of anthracene are more active towards halogenations. In this work, we have synthesized 1,8-dichlroanthracene from readily available strating material 1,8-dichloroanthraquinone. 1,8-Dichlroanthracene is further subjected to the Suziki-Miyaura coupling using 1,3-Bis(2,6-Diisopropylphenyl)imidazol-2-ylidene](3-chloropyridyl)palladium(II) dichloride (PEPPSI-*i*Pr)[18h,i] to obtain six different 1,8-aryl substituted anthracene derivatives (**1**-**6**). The substituents such as methoxy (**3**), acetyl (**4**) fluro (**5**) and trifluromethyl (**6**) on phenyl group are expected to facilitate intermolecular hydrogen bonding interactions. Moreover, the substitution at various positions of polycyclic aromatic systems helps in aggregates or micro/nano assemblies formation which in turn, improves the optical properties of the material.[19] Lee et al. reported the self-assembled nano-ribbons and nano-rods by varying the solubility of DPA molecules in the solution.[20] More recently, surfactant assisted nanowires and microrods of DPA molecules were synthesized and used in OLEDs and it was also noticed that the nanowire is the best shape for the heterojunction light emitting devices.[20] Hence, the surfactant assisted micro/ nano-sized self assemblies formations of new anthracene derivatives (**1-6)** are also attempted and successful attempts for **5** are reported in this article.

Scheme 1.

Results and discussions

Typically, the Suzuki-Miyaura coupling reactions employs the reaction of bromo or iodo-subtituted aryl substrate with the aryl boronic acid in the presence of Pd^0 and base to produce diaryl derivatives.[18a] However, Suzuki-Miyaura coupling reaction is not efficient with the chloro-substituted aryl substrate in the presence of conventional catalyst $Pd(PPh_3)_4$. To overcome this problem, we have taken the advantage of recently reported Suzuki-Miyaura coupling reaction with chloro aryl substrate in the presence of new catalyst, Pd-PEPPSI-*i*Pr. Using this strategy, we have synthesized 1,8-diaryl anthracene derivatives (**1-6**) from compound **7** as shown in Scheme 2. Compound **7** is obtained by reduction of commercially available 1,8-dichloro anthraquinone.[17d] Compound **7** is then, reacted with substituted aryl boronic acid, Na_2CO_3, toluene, THF and water in the presence of catalytic amount of Pd-PEPPSI-*i*Pr (5-7 mole %) at 85^0C for 16-18 h. Usual reaction work up and purification by column chromatography afforded the 1,8- diaryl anthracene derivatives **1-6** as white or off white solids (except **3,4** which are slightly yellow) in 52-77 % yields.

Scheme 2.

All these compounds were identified using several spectroscopic techniques such as ^{1}H-NMR, ^{13}C-NMR, mass spectrometry etc. and their characterization data have been summarized in the experimental section. Representative ^{1}H-NMR of 1,8-di(4-fluorophenyl)-anthracene, **5** is shown in Figure 1. Singlet at 8.57 and 8.50 ppm were assigned for protons at 9- and 10-positions. Proton at 9-position of substituted anthracene is downfield shifted as compared to unsubstituted anthracene may be because of the presence of electron withdrawing nature of aryl group in the neighborhood. Doublet for two protons at 8.07 ppm and triplet for two protons at 7.54 ppm were assigned for the protons at 4- and 3- positions respectively. Protons at the 2-positions were appeared as doublet at 7.40 ppm. 4-Fluorophenyl protons showed two different doublets for four protons each at 7.46 and 7.15 ppm. It can be noticed from Figure 1 that the signals for protons are slight broader presumably because of H-bonding (*vide infra*). Signals related to molecular mass ion is observed in MALDI for compounds **1-6** (see supplimentary information) which further confirm the formation of **1-6**. All these compounds are fairly soluble in common organic solvents. Melting points of these compounds are high.

Figure 1:

The UV-visible absorption spectroscopic studies of **1-6** were carried out in toluene (Figure 2) and in drop casted film (see supplimentary information). Toluene solution of **1** shows absorption maxima (λ_{max}) at 395 nm and other high energy absorption peaks at 354 and 375 nm (π-π^* transition). Compounds **2-6** also showed the similar pattern in absorption spectra with a marginal blue or red shift of 4-5 nm depending on the substituents. Drop casted thin film absorption spectra showed slight broad peaks and a bathochromic shift of about 2-3 nm except in **5**. Compound **3** and **5** showed a large bathochromic shift of 17 nm and 11 nm respectively, which shows inter molecular interaction in the thin films. Similar trend was observed in the emission spectra having fluorescence maxima at 432 nm for **1** and 432 to 440 nm for compounds **2-6** (Figure 2). Fluorescence quantum yields of these anthracene derivatives were calculated in the toluene using 9, 10-diphenyl anthracene (0.95 in ethanol) [13] as standard and have been summarized in table 1. Fluorescence life time data of these compounds (1-6) recorded using TCSPC technique are provided in Table 1. Single exponential fit was observed and spectra are given in the supplementary information.

Figure 2:

Table 1:

Compounds **1-6** were studied by cyclic voltammetry to get the insight on their oxidation potentials which together with photophysical studies give information on their HOMO and LUMO energy levels. Cyclic voltammetry and differential pulse voltammetry were recorded in CH_3CN at a scan rate of 100 mV/s using tetrabutylammoniumhexafluorophosphate (TBAHP) as supporting electrolyte. In these experimental conditions only oxidation waves were observed for **1-6** (except **3**) and reduction of these couldn't be seen. A comparison of first oxidation wave of compounds **1-6** except **3** is shown in Figure 3 and the data for them are presented in Table 2. The 1,8-diaryl substituted anthracene are relatively difficult to oxidize compared to 9,10-diphenylanthracene (E_{ox} of DPA is lesser by 0.1 eV) which is clearly evident from the data presented in Table 2.[21] E_{HOMO} of new anthracene derivatives were calculated using oxidation peak potentials and using the internal standard Fc/Fc^+ value at 4.8 eV versus vacuum. E_{LUMO} were calculated using the E_{HOMO} and optical band gap for the respective compounds obtained from onset of absorption spectra in drop casted film. E_{HOMO} and E_{LUMO} of **1-6** were found ~ -5.6 eV and -2.7 eV. The HOMO and LUMO energy levels of (**1-6)** suggest that these compounds can be used in OLEDs as blue emitter.

Figure 3:

Table 2:

Next, the surfactant assisted micro/nano self assemblies formations of **1-6** were studied. Out of these anthracene derivatives, only **5** have provided well-organized nano-sized assemblies. Figure 4 shows the SEM images of the **5** micro/nano structures with different morphologies, which were obtained by the surfactant-assisted precipitation method. Different surfactants such as PVP and CTAB were used in this procedure (details are given in the experimental section). As shown in Figure 4 (A), discontinuous rectangular plates were observed when **5** (in THF) added to the aqueous solution of PVP with a vigorous stirring. The inset in Fig 4(A) shows magnified image of rectangular plates with the smooth surface of different sizes. Variation in surfactants led to changes in the morphologies of **5**. The CTAB assisted assembly formation of **5** in THF gave nanowires as shown in Figure 4(B). It can be noticed that nanowires of **5** (inset Figure 4(B)) have virtually uniform diameter and shows continuous structures. The average length and diameter of nanowires is found to be around 100 μm and 290 nm, respectively. We believe that the inter-molecular H-bonding interactions in **5** facilitated by the presence of terminal fluorine group on phenyl may be the reason for the nono-sized assemblies formations in **5**.

Figure 4.

Micro/ nanostructures of **5** were studied with UV-visible and emission spectroscopies. UV-vis absorption showed red-shifted spectrum with a broad tail absorption in a longer wavelength region as shown in Figure 5. Absorption spectra of **5** in PVP and CTAB showed 18 nm red shift as compare to compound **5** in THF. Long tail absorption is assigned due to scattering effect caused by micro/nano particles. The emission spectra of **5** and its assemblies in PVP and CTAB showed similar trend as observed in UV-vis absorption. A bathochromic shift of 10 nm and broad tail was observed in the emission spectra as well. These findings in absorption and emission spectra further prove the formation of surfactant assisted micro/nano sized assemblies.

Figure 5:

In order to identify the nature of non bonding interactions in the substituted anthracenes, we performed computational investigations on the **1** and **5** using density functional theory (DFT) methods. All calculations were performed using Gaussian 09 suite of programmes.[22] Several chemically intuitive guess structures of the dimer of **1** and **5** were considered for the geometry optimization at the B3LYP/6-311G** level of theory [23] and optimized structures were further identified as minima using harmonic force constant analysis at the same level of theory. Only the lowest-energy structures are reported in this paper. Calculated interaction energies between two interacting monomers were corrected by the counterpoise (CP) method.[24]

Substitution of fluoro on the phenyl substituted anthracene allows the possibility of H-bonding interactions between two monomers. Consequently, the two monomers of **5** are found to be closely placed in the optimized structures than the two monomers of **1**. The shortest inter-atomic distance between two monomers of **5** is 2.45Ǻ (average) whereas, in the case of **1**, two monomers are separated by 3.63 Ǻ (Figure 6). Such H-bonding interactions also lead to the strong interactions between two monomers in **5**. The calculated interaction energies between two interacting monomers in **5** and **1** are -1.86 and -0.12 kcal/mol, respectively. Furthermore, to assign H-bonding interactions in more than two units of **5**, the tetramer structure of **5** was optimized at the B3LYP/6-311G** level of theory. The optimized structure of tetramer of **5** delineating multiple hydrogen bonding interactions between interacting monomers is shown in figure 6. Our calculations evidently suggest that multiple hydrogen bonding interactions are possible in **5** which may help in forming nano-sized self assemblies in the surfactant assisted precipitation method.[25]

Figure 6.

Conclusions

We have synthesized six anthracene derivatives having different aryl groups at the 1,8 positions of anthracene by applying Suzuki-Miyaura coupling reaction conditions on the 1,8-dichlroanthrace. Substitutions such as methoxy, acetyl, fluoro, trifluoromethyl on the phenyl groups were expected to facilitate intermolecular hydrogen bonding interactions. Photophysical characterizations of these derivatives show that absorption and emission maxima of these derivatives are slightly bathochromically shifted with reference to the DPA. Overall, these anthracene derivatives emits in the blue region and show high extinction coefficients and fluorescence quantum yields. Furthermore, the surfactant assisted micro/nano-sized assemblies formations of these anthracene derivatives were attempted. The nano-sized assemblies were successfully obtained only in the case of anthracene derivative **5** which have fluoro substituent on the phenyl groups. We have noticed that anthracene derivative **5** provides nanostructures with the different shapes in different surfactants. In PVP/THF solution, rectangular microplates of **5** were obtained whereas in CTAB/THF solution, nanowires with uniform diameter were observed. Theoretical investigations on the anthracene derivative **5** have established the different possibilities for the intermolecular H-bonding interactions in **5**. Such H-bonding interactions may favor the formation of micro/nanosized orderly structured as it is observed in the case of **5**. In all, we believe that the photophysical and electrochemical parameters of the anthracene derivatives (**1-6**) can be exploited in the organic light emitting devices. Currently, we are in the process of establishing the facility to explore the possible applications of these compounds in OLEDs.

Experimental:

Chemicals

All general chemicals and solvents were procured from S D. Fine Chemicals, India and Sigma-Aldrich. Column chromatography was performed using silica gel obtained from Sisco Research Laboratories, India. Tetrabutylammoniumhexafluorophosphate was purchased from Aldrich and used without further purifications.

Instrumentation

The ^{1}H and ^{13}C-NMR (δ in parts per million) spectra were recorded using a Bruker 500 MHz spectrometer. Tetramethylsilane (TMS) was used as an internal reference for recording ^{1}H-NMR spectra (residual proton; $\delta = 7.26$ ppm) in $CDCl_3$. The MS spectra were recorded on Bruker MALDI-TOF. UV–vis spectra were acquired at room temperature on Shimadzu 1800. Fluorescence emission measurements were carried out at room temperature using Horiba Fluoromax 4. For emission, compounds **1-6** were excited at 380 nm. Cyclic voltammetry measurements were carried out using the electrochemical analyzer (620D, CH Instruments Co.) at room temperature by utilizing the three-electrode configuration consisting of Pt disc (working electrode), platinum wire (auxiliary electrode), and standard calomel (reference electrode) electrodes. The experiments were done in dry acetonitrile with 0.1 M tetrabutylammoniumhexafluoro phosphate as the supporting electrolyte. The sizes and shapes of the micro/nanostructures were observed on a SEM (Quanta-200 ESEM, FEI) at an accelerating voltage of 5 kV.

Characterization.

1,8-Dichloro anthracene, 7: M.P.: 155 °C (lit.[20] 156-157 °C) ^{1}H-NMR (δ in ppm): 9.29 (s, 1H), 8.50 (s, 1H), 7.98 (d, 2H, *J* = 8.5 Hz), 7.66 (d, 2H, *J* = 7.1 Hz), 7.44 (t, 2H, J = 8.0 Hz).

General Procedure for the synthesis of anthracene derivatives 1–6:

A two necked round bottom flask was charged with compound **7** (1 eqv.), Na_2CO_3 (4-6 eqv.) and respective aryl boronic acid (2.4 eqv.) under Ar atmosphere. Mixture of toluene, THF and water in equal volume ratio was added and temperature was raised to 60 °C. Pd-PEPPSI-iPr (5-7 mol%) was added and reaction was refluxed at 85 °C. After 12 h a fresh 2 mol % of catalyst was added, if required based on TLC analysis. Reaction mixture was further stirred at 85 °C for total 16-18 h. Reaction mixture was cooled and extracted with dichloromethane, organic layers were washed with brine and water. Solvents were removed on rotary evaporator under vacuum; crude product obtained was purified by column chromatography using hexane and ethyl acetate to afford the compounds **1-6** (~ 50-70%) as white or off white solids.

1,8-Diphenyl anthracene, 1: Mixture of **7** (0.12 g, 0.5 mmol), phenylboronic acid (0.15 g, 1.2 mmol) and Na_2CO_3 (0.40 g, 4 mmol) in water/THF/toluene (1:1:1) 15 mL were stirred under argon for 5 min and IPr-PEPPSI (0.05 g, 0.07 mmol) was added. Reaction mixture was refluxed at 85 °C for 18 h. Silica gel column chromatography of crude compound afforded compound **1** as white solid. Yield: (0.11 g, 69%). M.P.: 190

°C. FTIR (KBr, cm-^{1}): ν 3029, 2922, 1545, 1490, 1444, 1323, 1167, 1072, 879, 745, 695, 603, 549. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.65 (s, 1H), 8.57 (s, 1H), 8.07 (d, 2H, *J* = 8.5 Hz), 7.55 (t, 2H, *J* = 6.9 Hz), 7.52 (d, 4H, *J* = 7.3 Hz), 7.43 (m, 6H), 7.39 (d, 2H, *J* = 7.3 Hz) ppm. ^{13}C NMR (500 MHz, $CDCl_3$) δ 140.5, 140.4, 131.8, 129.9, 128.0, 127.6, 127.1, 126.7, 126.1, 125.2, 123.9 ppm. MALDI-TOF mass calcd. for $C_{26}H_{18}$ $(M)^+$: 330.14; found: 330.55 (M+).

1,8-Dinaphthyl anthracene, 2: Mixture of **7** (0.12 g, 0.5 mmol), naphthylboronic acid (0.21 g, 1.2 mmol) and Na_2CO_3 (0.40 g, 4 mmol) in water/THF/toluene (1:1:1) 15 mL were stirred under argon for 5 min and IPr-PEPPSI (0.05 g, 0.07 mmol) was added. Reaction mixture was refluxed at 85 °C for 18 h. Silica gel column chromatography of crude compound afforded compound **2** as white solid. Yield: (0.11 g, 52%). M.P.: 208 °C. FTIR (KBr, cm-^{1}): ν 3031, 2660, 1550, 1494, 1442, 1326, 1160. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.63 (d, 1H, *J* = 8.7 Hz), 8.14 (t, 2H, *J* = 8.5 Hz), 7.85 (d, 1H, *J* = 8.1 Hz), 7.65 (t, 4H, *J* = 7.6 Hz), 7.56-7.57 (m, 2H), 7.41-7.46 (m, 4H), 7.30 (t, 1H, *J* = 8.0 Hz), 7.23-7.29 (m, 3H), 6.87 (t, 1H, *J* = 7.5Hz), 7.04-7.09 (m, 2H), 7.20 (t, 1H, *J* = 7.5 Hz) ppm. ^{13}C NMR (500 MHz, $CDCl_3$): δ = 140.5, 131.8, 129.9, 128.1, 127.6, 127.1, 126.7, 126.1, 125.2, 123.9 ppm. MALDI-TOF mass calcd. for $C_{34}H_{22}$ $(M)^+$: 430.17; found: 429.95 (M+).

1,8-Di (4-methoxyphenyl) anthracene, 3: Mixture of **7** (0.12 g, 0.5 mmol), 4-methoxy phenylboronic acid (0.18 g, 1.2 mmol) and Na_2CO_3 (0.40 g, 4 mmol) in water/THF/toluene (1:1:1) 15 mL were stirred under argon for 5 min and IPr-PEPPSI (0.05 g, 0.07 mmol) was added. Reaction mixture was refluxed at 85 °C for 18 h. Silica gel column chromatography of crude compound afforded compound **3** as slightly yellow solid (0.11 g, 58%). M.P.: above 220 °C. FTIR (KBr, cm-^{1}): ν 3036, 2923, 1609, 1534, 1508, 1439, 1317, 1287, 1243, 1173, 1098, 1030, 885, 872, 828, 735, 555. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.67 (s, 1H), 8.54 (s, 1H), 8.03 (d, 2H, *J* = 8.5 Hz), 7.54 (t, 2H, *J* = 6.9 Hz), 7.46 (d, 4H, *J* = 8.5 Hz), 7.41 (d, 2H, *J* = 6.6 Hz), 7.00 (d, 4H, *J* = 8.6 Hz), 3.90 (s, 6H, OCH_3) ppm. MALDI-TOF mass calcd. for $C_{28}H_{22}O_2$ $(M)^+$: 390.16; found: 389.84 (M+).

1,8-Di (4-actyl phenyl) anthracene, 4: Mixture of **7** (0.12 g, 0.5 mmol), 4-acetyl phenylboronic acid (0.196 g, 1.2 mmol) and Na_2CO_3 (0.40 g, 4 mmol) in water/THF/toluene (1:1:1) 15 mL were stirred under argon for 5 min and IPr-PEPPSI (0.05 g, 0.07 mmol) was added. Reaction mixture was refluxed at 85 °C for 18 h. Silica gel column chromatography of crude compound afforded compound **4** as off-white (yellowish) solid. (77 %, 0.16 g). M.P.: 175 °C. FTIR (KBr, cm-^{1}): ν 3038, 2916, 1670 (CO), 1552, 1455, 1424, 1400, 1312, 1356, 1262, 1167, 1091, 1016, 957, 828, 794, 732, 671, 593, 472. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.60 (s, 1H), 8.42 (s, 1H), 8.09 (d, 2H, *J* = 8.55 Hz), 8.03 (d, 2H, J = 8.1 Hz), 7.56-7.61 (m, 6H), 7.52 (m, 2H), 7.47 (d, 2H, *J* = 6.7 Hz), 2.67 (s, 6H, $COCH_3$) ppm. HRMS mass calcd. for $C_{30}H_{22}O_2$ $(M+H)^+$: 414.16; found: 384.42 ($M-2CH_3$), 414.90 (M+).

1,8-Di (4-fluoro phenyl) anthracene, 5: Mixture of **7** (0.12 g, 0.5 mmol), 4-fluoro phenylboronic acid (0.17 g, 1.2 mmol) and Na_2CO_3 (0.40 g, 4 mmol) in water/THF/toluene (1:1:1) 15 mL were stirred under argon for 5 min and IPr-PEPPSI (0.05 g, 0.07 mmol) was added. Reaction mixture was refluxed at 85 °C for 18 h. Silica gel column chromatography of crude compound afforded compound **5** as off-white solid. (0.12 g, 67%). M.P.: 204 °C. FTIR (KBr, cm-^{1}): ν 3037, 2917, 1598, 1503, 1443, 1462, 1326, 1218, 1157, 1093, 1015, 940, 906, 834, 791, 564, 525. ^{1}H NMR (500 MHz, CDCl$_3$): δ 8.57 (s, 1H), 8.50 (s, 1H), 8.07 (d, 2H, *J* = 8.2 Hz), 7.54 (t, 2H, *J* = 7.2 Hz), 7.39-7.45 (m, 6H), 7.13 (t, 4H, *J* = 8.3 Hz) ppm. ^{13}C NMR (500 MHz, CDCl$_3$): δ = 163.18, 161.22, 139.32, 136.29, 131.75, 131.40, 130.09, 127.75, 126.88, 126.26, 125.22, 123.35, 116.15, 115.97, 115.07, 107.46 ppm. MALDI-TOF mass calcd. for $C_{26}H_{16}F_2$ $(M)^+$: 366.12; found: 365.71 (M+).

1,8-Di (4-trifluoromethoxy phenyl) anthracene, 6: Mixture of **7** (0.12 g, 0.5 mmol), 4- (trifluoromethoxy) phenyl boronic acid (0.23 g, 1.2 mmol) and Na_2CO_3 (0.40 g, 4 mmol) in water/THF/toluene (1:1:1) 15 mL were stirred under argon for 5 min and IPr-PEPPSI (0.05 g, 0.07 mmol) was added. Reaction mixture was refluxed at 85 °C for 18 h. Silica gel column chromatography of crude compound afforded compound **6** as white solid. (0.17 g, 75%). M. P. 218 °C. FTIR (KBr, cm-^{1}): ν 2925, 1612, 1549, 1405, 1322, 1184, 1102, 1064, 978, 948, 839, 792, 743, 705, 631, 614, 603, 542. ^{1}H NMR (500 MHz, CDCl$_3$): δ 8.60 (s, 1H), 8.30 (s, 1H), 8.12 (d, 2H, *J* = 8.2 Hz), 7.67-7.75 (m, 5H), 7.56-7.60 (m, 5H), 7.45 (d, 2H, *J* = 6.3 Hz) ppm. ^{13}C NMR (500 MHz, CDCl$_3$): δ 143.82, 138.92, 131.69, 130.17, 129.84, 128.32, 127.56, 126.97, 126.16, 125.88, 124.96, 123.02 ppm. MALDI-TOF mass calcd. for $C_{28}H_{16}F_6$ $(M+H)^+$: 466.11; found: 465.97 (M+).

Methods for micro/nano assemblies formation: The plate shape **5** microcrystals were prepared by adding 0.5 mL of 0.5 mM **5**/THF solution into 4 mL water containing PVP (0.5 mg/mL) with a strong stirring. After stirring for 10 min, the solution was kept undisturbed overnight at room temperature before characterization. When PVP was replaced by CTAB and other conditions kept same, nanowires rather than microplates were produced. The preparation of SEM samples: An aliquot (20μL) of the solution was put on a silica wafer and dried over 24 h.

Supporting Information

NMR, mass spectra, absorption and emission spectra and differential pulse voltammograms of compounds **1-6**.

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Legends

Scheme 1: Literature methods used to synthesize aryl substituted anthracene

Scheme 2: Synthesis of anthracene derivatives **1-6**

Table 1. Photophysical data for compounds **1-6**.

Table 2. Electrochemical data for compounds **1-6**.

Figure 1: ^{1}H NMR of 1,8-(4-fluorophenyl) anthracene, **5** in $CDCl_3$.

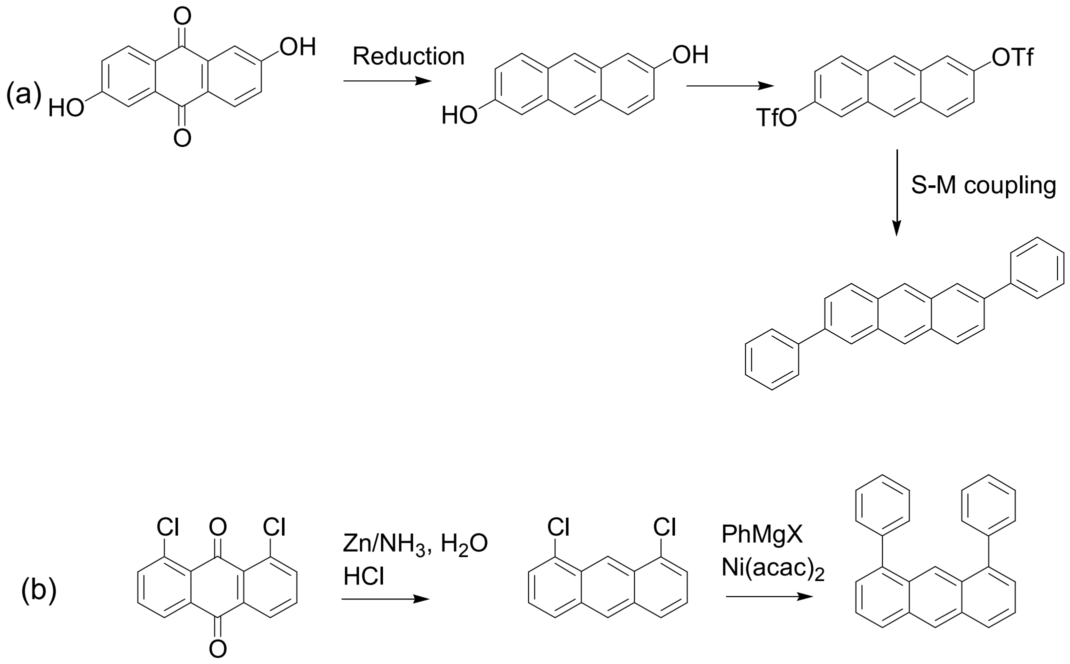
Figure 2: Absorption (above) and emission (below) spectra of compounds **1-6** recorded in toluene.

Figure 3: Cyclic voltammograms of **1-6** (except for **3**) with ferrocene in CH_3CN.

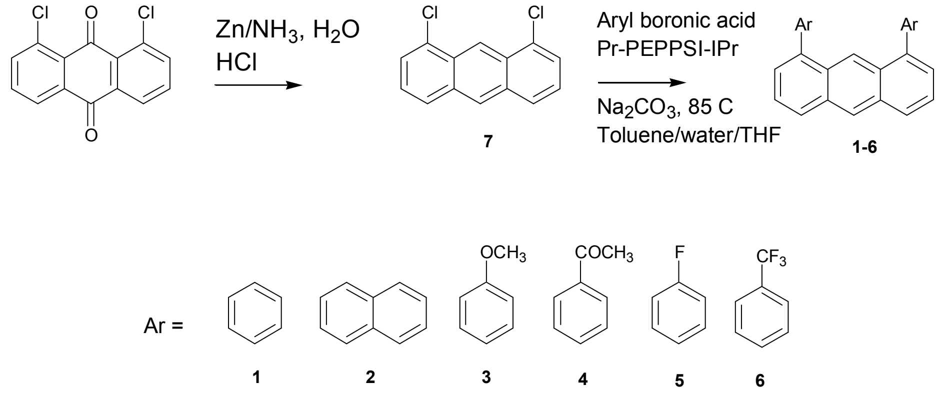
Figure 4: SEM images of different morphologies of **5** dissolved in THF/surfactant/water. A) Rectangular plate like shape for **5** in PVP as surfactant, inset is a magnified area. B) nanowires for **5** in CTAB as surfactants, inset is a magnified area.

Figure 5: Absorption and emission spectra of micro/nano assemblies of **5** in PVP, CTAB and THF surfactants.

Figure 6: Optimized geometries of dimers of **1** (**A**) and **5** (B) and tetramer of **5** (**C**).


(a)
HO
O
OH
O
Reduction
HO
OH
TfO
OTf
S-M coupling
(b)
Cl
O
Cl
O
Zn/NH$_3$, H$_2$O
HCl
Cl
Cl
PhMgX
Ni(acac)$_2$

Scheme 1:


Cl
O
Cl
O
Zn/NH3, H2O
HCl
Cl
Cl
7
Aryl boronic acid
Pr-PEPPSI-IPr
Na2CO3, 85 C
Toluene/water/THF
Ar
Ar
1-6
Ar =
OCH3
COCH3
F
CF3
1
2
3
4
5
6

Scheme 2

Table 1

Comp	λ_{abs} **(nm)**[a]	λ_{abs} **(nm)**[b]	λ_{em} **(nm)**[a]	Φ[c]	τ **(ns)**[a]
DPA	371, 392	-	404, 425	0.95	0.93
1	375, 396	381, 401	416, 432	0.75	3.54
2	371, 390	373, 393	410, 432	0.71	3.60
3	379, 399	391, 416	419, 440	0.65	
4	369, 387	378, 400	431	0.45	2.58
5	374, 394	382, 405	409, 431	0.72	3.79
6	374, 394	376, 397	410, 432	0.67	3.75

[a] In toluene; [b]in drop casted thin film; [c]Relative quantum yields were calculated using 9,10-DPA as reference (Ethanol, ϕ = 0.95);

Table 2

Comp	**E^{ox} (V)**	**$^{a}E_g$ (eV)**	**$^{b}E_{HOMO}$ (eV)**	**$^{c}E_{LUMO}$ (eV)**
DPA	1.22	-	-	-
1	1.32	-2.92	-5.63	-2.71
2	1.26	-2.94	-5.62	-2.68
3	nd	-2.83	-	-
4	1.34	-2.86	-5.71	-2.85
5	1.30	-2.92	-5.66	-2.74
6	1.32	-2.93	-5.68	-2.75

[a]Optical band gap, calculated from absorption spectrum recorded in drop-casted films; [b]E_{HOMO} calculated from oxidation potentials (vs ferrocene) i.e. E_{HOMO} = - (Δox w.r.t. Fc/Fc^{+} + 4.8 eV); [c]E_{LUMO} = E_{HOMO} - E_g; nd = not detected

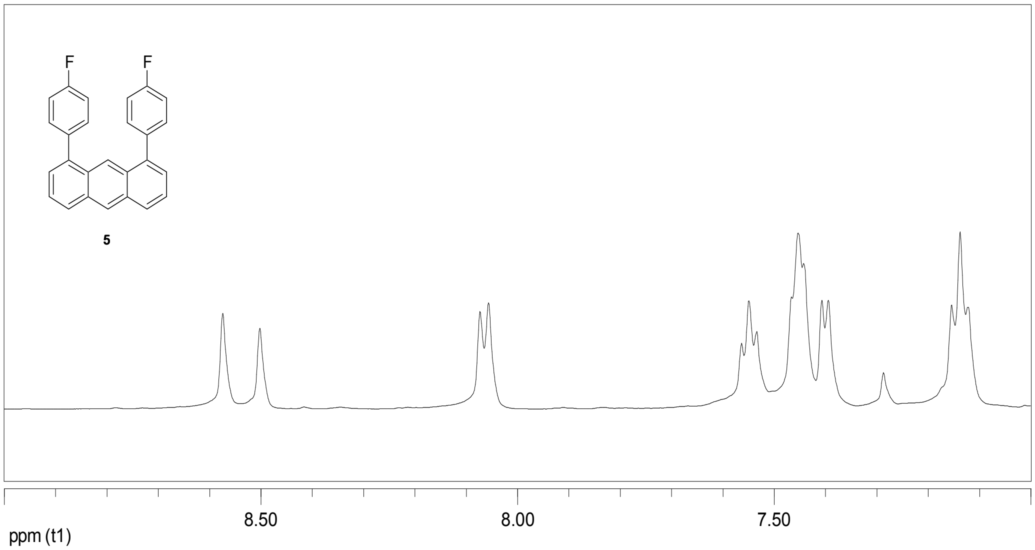
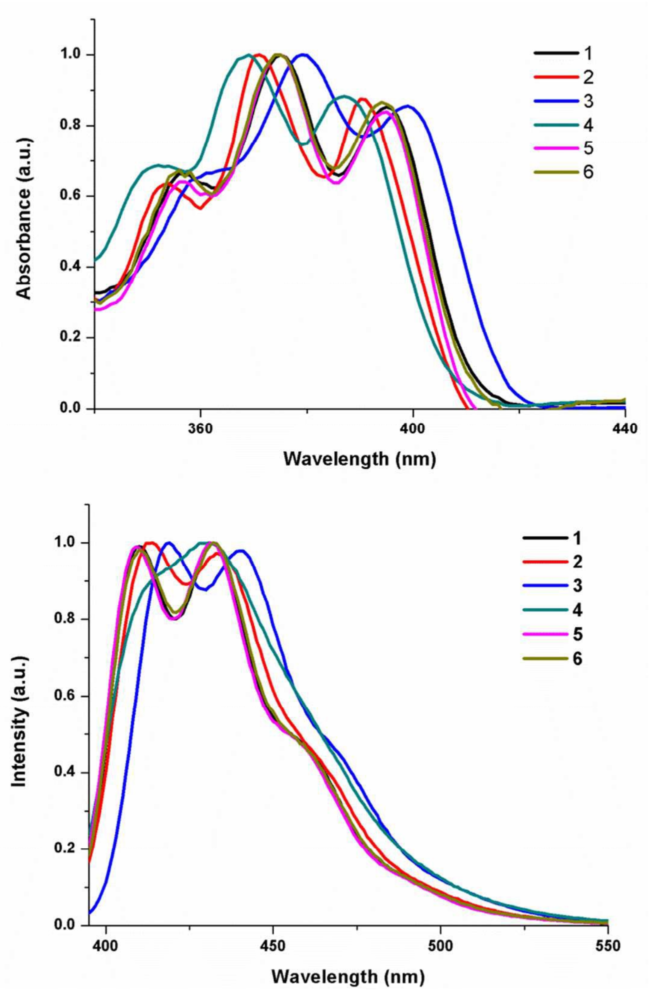


Figure 1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0.4
0.2
0.0
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400
440
Wavelength (nm)
1
2
3
4
5
6
Intensity (a.u.)
1.0
0.8
0.6
0.4
0.2
0.0
400
450
500
550
Wavelength (nm)
1
2
3
4
5
6

Figure 2

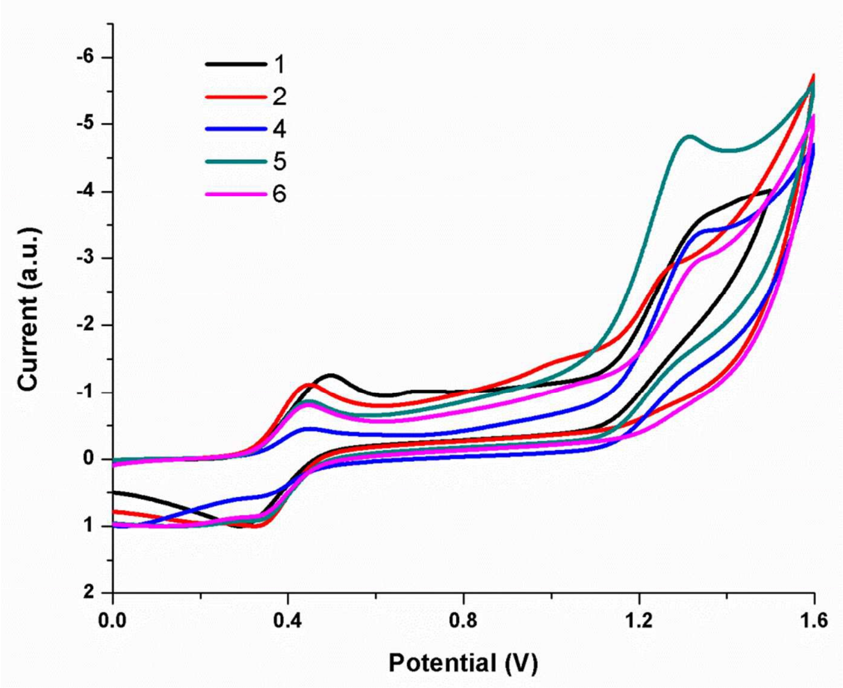
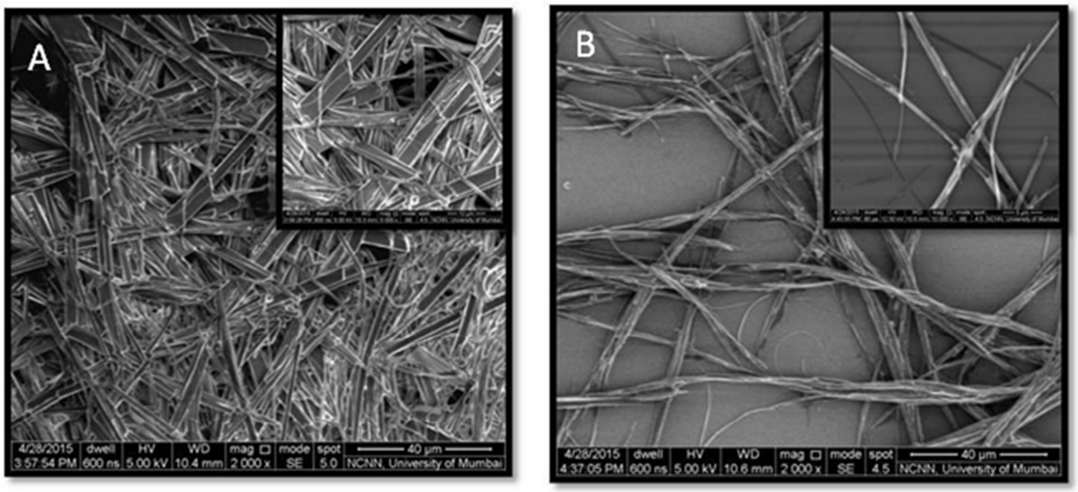


Figure 3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HV 5.00 kV
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mag 2 000 x
mode SE
spot 5.0
40 µm
NCNN, University of Mumbai
B
4/28/2015 4:37:05 PM
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mode SE
spot 4.5
40 µm
NCNN, University of Mumbai

Figure 4

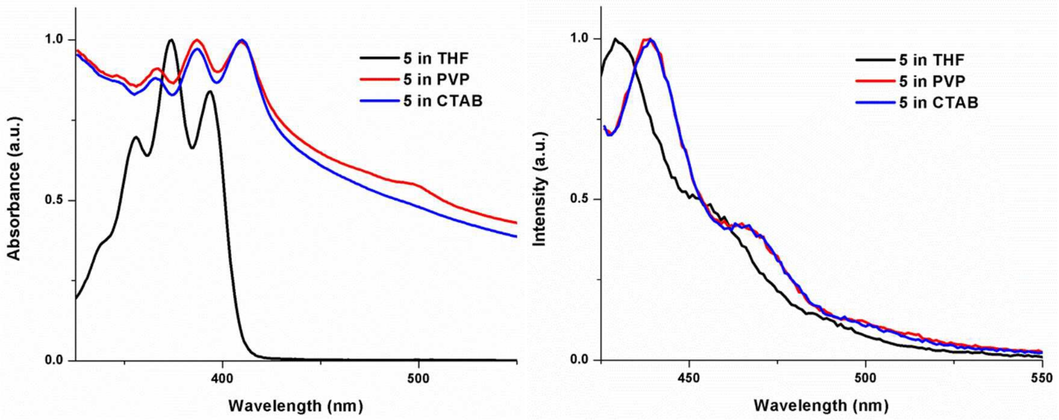
1.0
0.5
0.0
Absorbance (a.u.)
400
500
Wavelength (nm)
5 in THF
5 in PVP
5 in CTAB
1.0
0.5
0.0
Intensity (a.u.)
450
500
550
Wavelength (nm)
5 in THF
5 in PVP
5 in CTAB

Figure 5

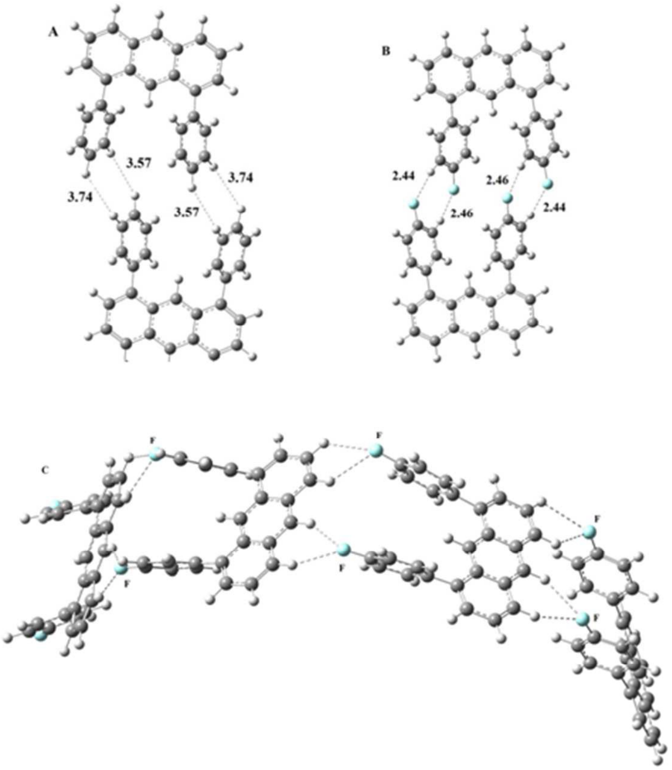

Figure 6