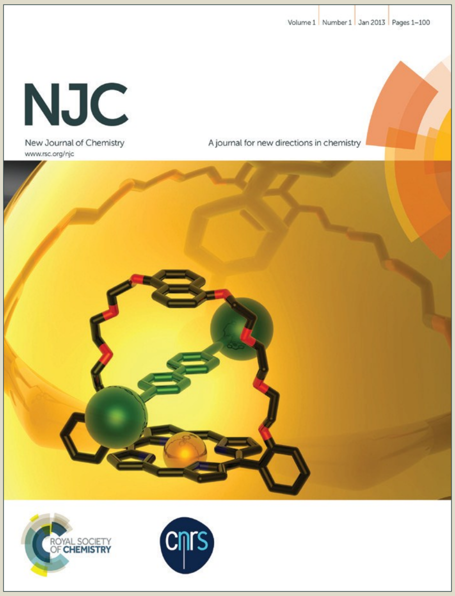

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Synthesis, Characterization and Aggregation Induced Emission Properties of Anthracene Based Conjugated Molecules

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Aggregation induced emission-active branched and linear 9,10-distyrylanthracene derivatives with different length of alkoxy chains have been designed, synthesized and systematically investigated the effect of chain length on the solid-state fluorescence properties. All the three anthracene derivatives possess a typical aggregation induced emission (AIE) property, i.e., they exhibit faint emission in their solutions, but intense emission in their aggregate states, as a result of the dominant nonradiative decay of free intramolecular torsion in the solution and also the restricted torsional motion by supramolecular interaction in the solid states. The results show that these materials exhibit not only AIE properties, but also observed the position and chain length dependent fluorescence properties. In the case of shorter the alkoxy chains, more red shifted than the longer one and also different aggregation behaviours of branched and linear molecules are observed. This work demonstrates once again the accessibility of tuning the solid-state optical properties of organic fluorophores by combining the simple alternation of molecular chemical structure and the physical change of aggregate morphology under external stimuli.

Introduction

Organic conjugated supramolecules have drawn considerable research interest in the past two decades, owing to their potential applications in fluorescence imaging,[1] chemo sensors,[2] optical power limiting materials[3] and active gain media for light-emitting devices.[4] However, most organic luminophore materials exhibits aggregation caused quenching effect (ACQ)[5] in the solid state due to strong π–π stacking interactions,[6] which is a typical problem of common organic fluorophores. To overcome these problems, Tang and co-workers[7] observed a phenomenon of aggregation induced emission (AIE) of conjugated molecules with twisted skeleton conformation have been demonstrated, which are mainly attributed to the restriction of intramolecular rotation or conformation planarization in the aggregates and also it restrict the nonradiative relaxation pathway and promote the radiative excitons.[8] Hereafter, many researchers have been developing the AIE materials and extensively investigated their properties. Recently, some of the researchers have been reported a different kinds of conjugated luminophore molecules such as tetraphenyl ethylene, 2,3,4,5-tetraphenylsiloles, 1-cyano-*trans*-1,2-bis(4'-methyl biphenyl)ethylene (CN-MBE), cis-2,5-diphenyl-1,4-distyryl benzene (DPDSB) derivatives, anthracene derivatives, conjugated polymers with AIE and piezo-fluorochromism (PFC) properties.[9] Among them, 9,10-distyrylanthracene derivatives have promising and attractive AIE and PFC molecules than the others. Because, anthracene is one of the most common fluorophore, which is having good aggregation behavior and often useful for potential optoelectronic and biological applications, due to it has unique chemical and electron-rich structure, low electronic band gap and strong blue fluorescence as emitters in blue OLEDs.[10] The large π-conjugation system of anthracene show higher electroluminescence efficiency, long lifetime, and it can be used in solution-processed devices.[11]

Very recently Wenjun Yang et al.[12] reports the aggregation-induced emission of 9,10-bis(alkoxystyryl)anthracenes with different chain lengths as well as the position of the substitution. The linking positions and length of the alkoxy chains should significantly affect the optical properties of AIE molecules. They are not only reported the AIE properties, but also to investigate the PFC behavior of these types of molecules. However, AIE with PFC behavior materials are currently carried out in the simple molecules and the dendritic types of molecules have been reported very limited. In this context, systematic molecular design and investigation of their AIE with PFC behaviour is extremely desirable.

In order to investigate the AIE and PFC phenomenon, we designed and synthesized a series of 9,10-distyrylanthracene derivatives with different length of alkyl chains (octyl and dodecyl) (Scheme 1 and scheme 2). We find that the aggregation behavior of branched anthracene derivatives is quite different with linear one and also investigate the redox behavior in all the compounds through cyclic voltammetry.

Results and Discussion

Synthesis and Characterization

The synthetic routes to the long alkyl chain containing branched and linear anthracene derivatives (**C8-ant**, **C12-ant** and **PV-C12**) are depicted in scheme 1 and scheme 2. First, the long alkyl chain substituted dendrons are synthesized by stepwise reaction. Finally synthesized dendrons are coupled with 9,10-dibromoanthracene to get final compounds. In scheme 1, the compounds 1 to 4 was prepared according to the previously reported procedure.[13] The compound 4 was Heck coupled with methyl 3,5-dibromobenzoate to give dendron ester 5. This ester 5 was reduced to corresponding alcohol 6 using lithium aluminium hydride in THF. The compound 6 oxidized with pyridinium chlorochromate in DCM to offer

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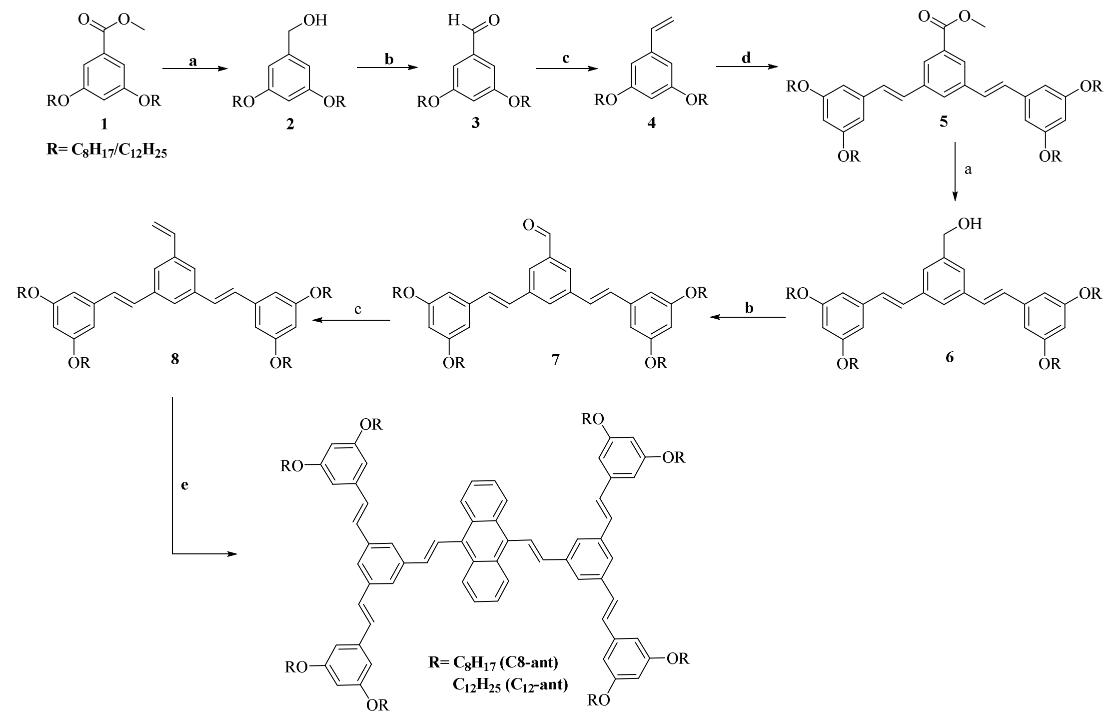
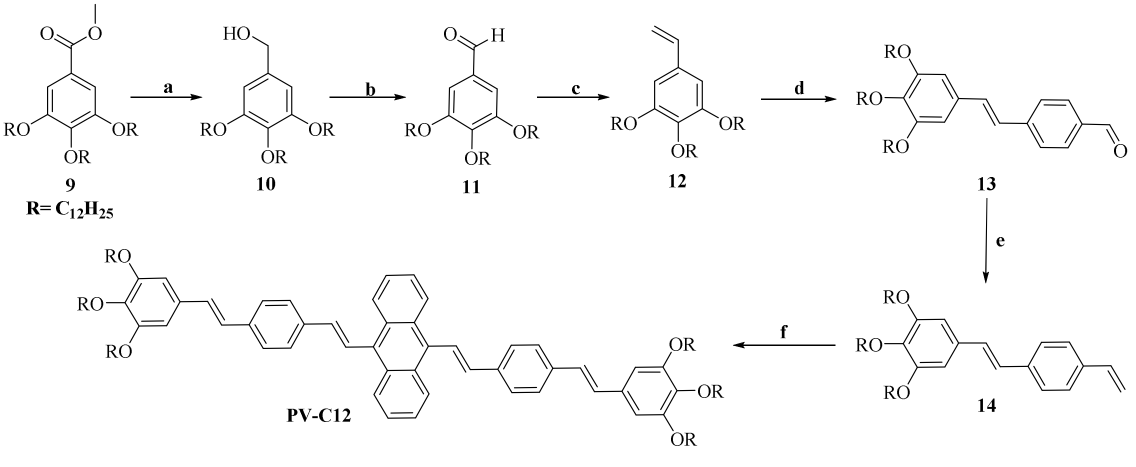


Scheme 1. Synthesis of branched anthracene dendrimers **C8-ant** and **C12-ant**.

Reagents and Conditions. a) LAH, THF, 0 ºC, 6 hrs; b) PCC, DCM, 0 ºC, 4 hrs; c) PPh_3CH_2I, DCM, RT, 8 hrs; d) methyl 3,5-dibromobenzoate, TBAB, $Pd(OAc)_2$, DMF/ toluene (1:1), Et_3N, 90 ºC, overnight; e) 9,10-dibromoanthracene, TBAB, $Pd(OAc)_2$, DMF/ toluene (1:1), Et_3N, 90 ºC, overnight.



Scheme 2. Synthesis of linear anthracene compound **PV-C12**.

Reagents and Conditions. a) LAH, THF, 0 ºC, 6 hrs; b) PCC, DCM, 0 ºC, 4 hrs; c) PPh_3CH_2I, DCM, RT, 8 hrs; d) 4-bromobenzaldehyde, TBAB, $Pd(OAc)_2$, DMF/ toluene (1:1), Et_3N, 90 ºC, overnight; e) PPh_3CH_2I, DCM, RT, 8 hrs; f) 9,10-dibromoanthracene, TBAB, $Pd(OAc)_2$, DMF/ toluene (1:1), Et_3N, 90 ºC, overnight.

compound 7 and it reacts with methyltriphenylphosphonium iodide in the presence of K^{t}OBu to provide corresponding vinylated dendron (8) with very good yield. Finally compound 8 (8a and 8b) Heck coupled with 9,10-dibromoanthracene to offered final compounds **C8-ant** and **C12-ant** respectively. The same trend of synthesis was also followed for scheme 2 to give good yields of linear anthracene compound **PV-C12**.

Photophysical properties

Fig. 1 shows the absorption and the emission spectra of all the anthracene derivatives in dilute THF solutions. In the absorption spectra (Fig. 1a), two main absorption bands are observed in all the compounds in THF solution. The first absorption band can be attributed to the absorption of the styryl segment (ranging from 312-345 nm) and the second moderately weak absorption in the range from 405-422 nm can be assigned to the characteristic vibronic patterns of π-π* transition of anthracene. The emission spectrum of the three compounds in dilute THF solutions is shown in Fig. 1b and all these compounds were recorded by exciting at its longer wavelength absorption maximum.

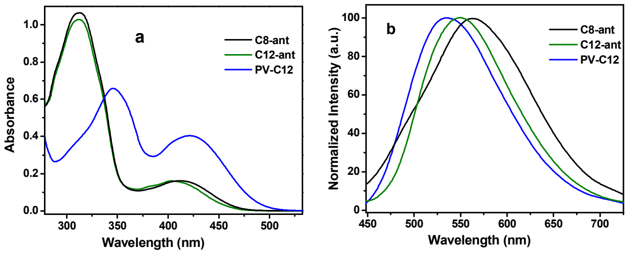


Fig. 1 Absorption (a) and normalized emission (b) spectra of **C8-ant**, **C12-ant** and **PV-C12** in THF solution.

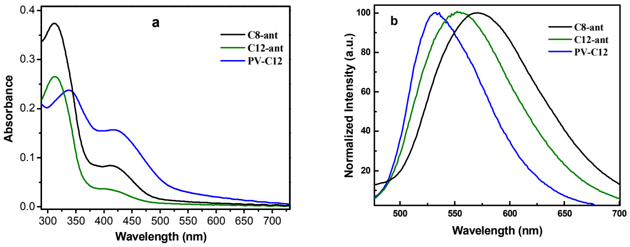


Fig. 2 Absorption (a) and normalized emission (b) spectra of **C8-ant**, **C12-ant** and **PV-C12** in thin film.

All the compounds were exhibited weak and broad emission in molecularly dissolved solutions and the spectral values are 560, 542 and 534 nm for **C8-ant**, **C12-ant** and **PV-C12** respectively. The linking positions and size of the alkoxy chains at peripheral aryl rings should significantly affect the twisted backbone conformations and intermolecular stacking structure of AIE molecules to change the optical properties. i.e., long alkyl chains (**C12-ant**) substituted compounds have more twisted conjugated backbones and weaker intermolecular interactions than the short alkyl chains containing compound (**C8-ant**) and it can emit shorter emission wavelength. The quantum yield of the three compounds in dilute THF solutions measured by using 9,10-diphenylanthracene (Φ_F=0.90) as the secondary standard. All the anthracene containing compounds show lower quantum yields (Table. 1), which means that the fluorescence of the compounds is quenched in solutions, due to the lower energy of the emitting states, which may intern to facilitate the nonradiative pathways. To investigate the photophysical properties of all the compounds in different solvents of varying polarity (Fig. S1, see supplementary material), there is no change in absorption spectrum, so that the solvatochromism in absorption is very weak or negligible. However, in emission spectra the negative solvatochromism was observed, i.e., in more polar solvents the emission was blue shifted (hypsochromic relative to its solution).

The absorption and the emission spectra of these three materials in solution and thin film are quite different as summarized in Table 1. However the emission spectra of the synthesized compounds in the solid state show significantly a different pattern (Fig. 2b). In contrast, these anthracene cored luminogens are highly emissive in the solid state. The films of **C8-ant**, **C12-ant** and **PV-C12** emit intensely, with emission maxima at 568, 549 and 530 nm respectively, suggesting that the absence of strong intermolecular interactions in thin films. In solution, the active intramolecular rotations of the molecules effectively deactivate in the excited states and gives very weak emission. The efficient emissions of thin films reveal that the anthracene derivatives possess aggregation-enhanced emission (AEE) characteristic, due to the bulky and non-coplanar groups of these compounds have effectively controlled intermolecular aggregation.

Table 1. Photphysical properties of **C8-ant**, **C12-ant** and **PV-C12**

Compounds	$\lambda_{abs, sol}$ (nm) [a]	$\lambda_{em, sol}$ (nm) [a]	$\lambda_{abs, film}$ (nm)[b]	$\lambda_{em, film}$ (nm)[b]	Stokes shift (cm^{-1})	Φ_F [c]	Φ_F film [d]
C8-ant	313, 414	560	312, 415	568	6297	0.22	0.62
C12-ant	312, 405	542	312, 405	549	6241	0.19	0.59
PV-C12	345, 422	534	338, 423	530	4907	0.08	0.33

[a] measured at 1.0×10^{-5} M for UV-Vis absorption spectra and fluorescence spectra (excited at corresponding absorption maximum); [b] measured for UV-Vis absorption spectra and fluorescence spectra in thin film; [c] fluorescence quantum yield in solution; [d] determined by a calibrated integrating sphere.

Fluorescence Lifetime

The lifetime of anthracene derivatives of **C8-ant**, **C12-ant** and **PV-C12** was measured in THF solutions monitored at 375 nm. The fluorescence transients were fitted to multiexponential functions and were convoluted with the system response function obtained from Time Correlated Single Photon Counting (TCSPC) measurement. Fig. 3 shows the fluorescence decay profiles for **C8-ant**, **C12-ant** and **PV-C12** in THF solutions, based on the obtained results all the three compounds exhibits biexponential decay curve with a lifetime of 1.37 ns (16.52%) and 3.45 ns (83.48%) for **C8-ant**, 7.58 ns (22.93%) and 3.39 ns (77.07%) for **C12-ant** and 7.72 ns (47.98%) and 2.31ns (52.02%) for **PV-C12**. All the compounds adopt twisted conformation, so that the electron distribution imparts the anthracene molecules with an intrinsic intramolecular charge transfer properties.

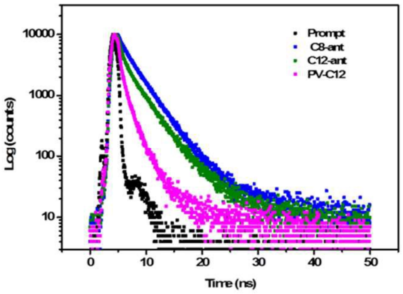


Fig. 3 The fluorescence decay profiles of anthracene derivatives recorded in THF solvent.

Aggregation Induced Emission (AIE)

All the anthracene derivatives are dissolved readily in common organic solvents such as dichloromethane, chloroform and THF, but are insoluble in water. So we find that all the compounds are AIE-active, they are practically weak fluorescence in THF solution, but the addition of water into the anthracene derivatives which can greatly affect their photoluminescence (PL) i.e., enhanced fluorescence in THF/H_2O mixtures. These weak emission behaviours in solution is caused by free intramolecular torsion motions, facilitating nonradiative relaxation pathways, but in the case of aggregation, the fluorescence emission is enhanced, because of their induced restricted intramolecular rotational motions of molecular self-aggregations, and to exhibit strongly aggregation enhanced emission. Based on this concept we inspect the aggregation behaviour in the anthracene derivatives by increasing the water fraction in THF solution and the absorption and emission spectra of **C12-ant** in THF/H_2O are shown in Fig. 4. From this absorption spectrum, the addition of water fraction up to 60% there is no considerable shift. Upon the addition of water fraction above 60% the absorption will be shifted to red shift due to precipitation of the compounds, which effectively decrease the light transmission through the solution mixture. This obvious high absorbance caused by the light-scattering (i.e., Mie effect) of the nanoparticle suspensions in the aqueous mixtures with high water contents, which is proved by the level of tails, were clearly observed in the long wavelength region of the absorption of the compounds.

Fig. 4b shows, the emission spectrum of **C12-ant** in THF solution, very weak and the broad emission band were observed, which means that the fluorescence of the compounds in solution is quenched. When increasing the water concentration up to 50% the emission intensity is blue shifted (546 to 495 nm) and also the emission intensity is reduced, due to the increasing the polarity of the solvent (i.e., solvatochromic behaviours), which is previously discussed. Further increasing the water percentage up to 90% the fluorescence emission was enhanced with red shift, giving the emission band from 495 to 534 nm. This is due to the formation of excimer[14] and also it is confirmed by the TEM analysis shown in Fig. 5c (see, for example, the photo shown in the formation of aggregation with changing water fraction in Fig. 5a). The formation of excimer is activating the excited state radiatively with restricted intramolecular rotation and excimer formation cooperatively makes the anthracene molecules highly emissive in the solid state. To demonstrate the emission intensity changes of the compounds more visually, we plotted the changes in their emission peak intensities (I/I_0) versus water content of the mixture (Fig. 4e).The Similar phenomena are also observed for **C8-ant** molecules, the PL intensity was reduced up to 40% and gradually increase the emission intensity as well as red shift for the addition of water into the THF solution (Fig. S2 see supporting information). The linear anthracene derivative (**PV-C12**), there is a different absorption and emission behaviours observed and depicted in Fig. 4(c and d). The compound **PV-C12** in the molecularly dissolved solution displays a very weak emission. Upon the addition of water from 0% to 40% the sudden jump in emission intensity was observed and the mixture becomes visually emission (Fig. 5b) and further it is confirmed by TEM analysis (Fig. 5d). Thus, it is clear that **PV-C12** has the lowest solubility, and can aggregate more easily and hence the red shift of the emission was observed, suggestive of the formation of J-aggregates[15] in the solvent mixture. Clearly, the emission of **PV-C12** is induced by the aggregate formation, or in other words, it activates the AIE effect. Further, increment of water content up to 90% the emission intensity is reduced with red shift, suggesting that the molecules are weakened the intermolecular electronic interaction and may have changed the packing structure.

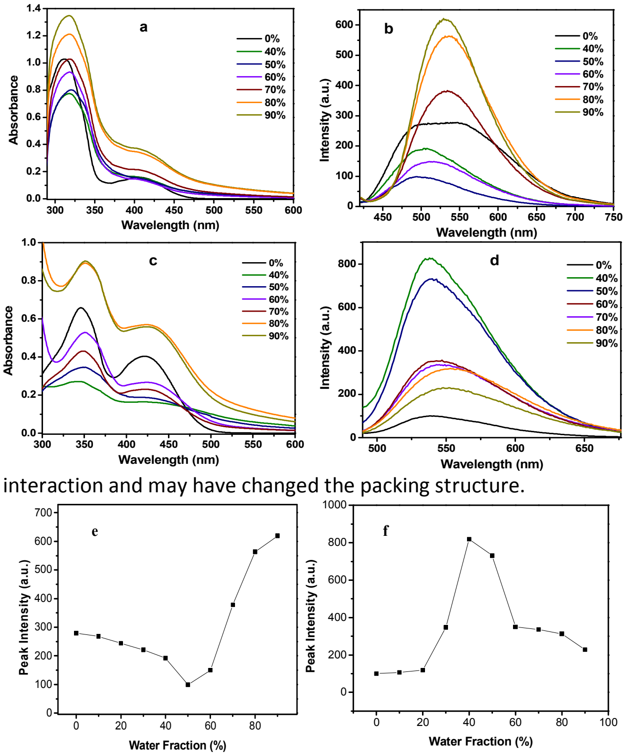


Fig. 4 Aggregation-induced absorption (a), (c), emission (b), (d) spectra and peak intensity plot (e), (f) of **C12-ant** and **PV-C12** in THF/water system respectively (excitation wavelength at 405 nm for **C12-ant** and 422 nm for **PV-C12**).

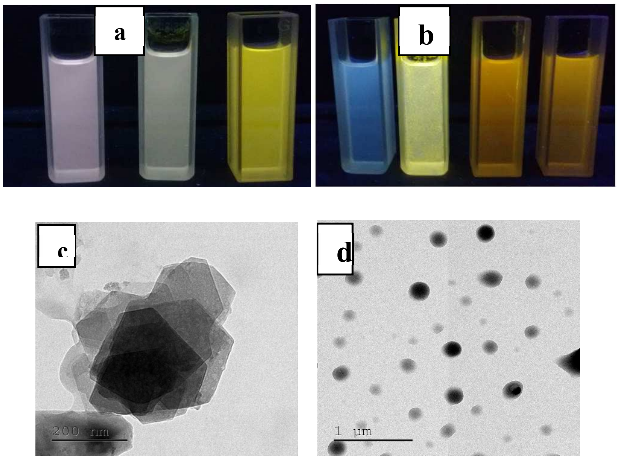


Fig. 5 Photographs of (a) **C12-ant** (0%, 40% and 80%) and (b) **PV-C12** (0%, 40%, 80% and 90%) in different THF/water fractions taken under UV illumination at 365 nm; TEM images of nanoaggregates of (c) **C12-ant** and (d) **PV-C12** formed in THF/water mixtures with 80% and 40% water fractions respectively.

Piezochromism

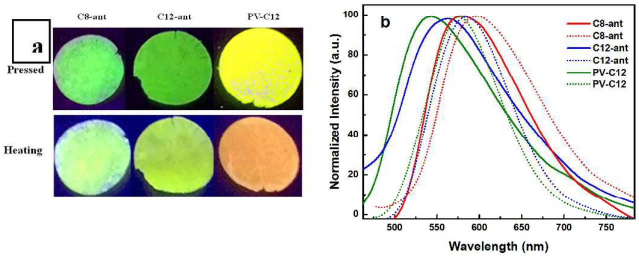


Fig. 6 (a) Fluorescence images of anthracene derivatives mixed with KBr upon pressing and heating under a 365 nm UV lamp; (b) normalized emission spectra of anthracene derivatives solids mixed with KBr upon pressing (solid line) and heating (dotted line).

Molecules with external stimuli-induce the fluorescence properties and efficiently tuning and switching the solid-state luminescence by means of external mechanical forces like pressing or thermal heating (Piezo or thermo-fluorochromism). In order to examine the Piezochromic behavior of all anthracene derivatives (mixed with KBr to minimize the amount of fluorophores) by pressing with an IR pellet press (30 seconds at 1500 psi). The emission spectra recorded on a spectrometer are well consistent with the fluorescence colors observed under a UV lamp (Fig. 6a). When the molecules are pressed the color changing with around 10-12 nm red shift was observed (578 nm, 562 nm, 541 nm for **C8-ant**, **C12-ant** and **PV-C12** respectively (Fig. 6b)). This effect reduces the distance between the molecules decreases the freedom of their molecular motion and strengthens the intramolecular rotation process. In contrast, it boosts molecular interactions and endorses the excimer formation.[16] Further, the color changes induced by thermal heating can be well restored by pressing one and the color changes can be regenerated by after cooling. This process is reversible and reproducible for all the anthracene derivatives. It is noted that the longer the alkyl chain substituted anthracene derivatives are, the more remarkable the fluorescence color change upon pressing and heating compare to that of the shorter alkyl chain (C8) one. The pressing-heating spectral shifts differences of **C8-ant**, **C12-ant** and **PV-C12** solids are 17, 23 and 35 nm, respectively (Fig. 6b). This indicates that the anthracene derivatives are chain length and position dependent and also, the substituted alkyl chains in the anthracene molecules have played a functional role in tuning the piezochromic behaviour.[17]

Electrochemical Properties

The electrochemical properties of all the anthracene derivatives were studied in DCM solution using cyclic voltammetry (CV) and tetrabutylammonium hexafluorophosphate ($TBAPF_6$) as the supporting electrolyte and ferrocene as the internal standard. As shown in Fig. 7, during the anodic scan in dichloromethane, **C8-ant**, **C12-ant** and **PV-C12** exhibits similar quasi reversible oxidation process, this can be assigned to the oxidation of electron-donating alkyl group substituted on phenyl moiety, with the onset potentials of 0.98, 0.97 and 0.85 V, respectively and there are no reduction waves were detected. The HOMO energy levels were obtained according to the following equation: HOMO = $-(E_{ox} + 4.76)$ eV, using ferrocene as an internal standard. On the basis of the onset potentials for oxidation, we estimated the HOMO energy of **C8-ant**, **C12-ant** and **PV-C12** to be -5.58, -5.57 and -5.45 eV. These results revealed that the introduction of alkyl group substituted phenyl moiety to the anthracene core can lead to the raising of HOMO levels.[14,18] Then, the LUMO energy levels were obtained from the HOMO energy and the energy band gap (E_g = HOMO - LUMO). Whereas E_g value is calculated from the onset wave length of their UV absorption. Table 2 shows that the energy levels of the compounds are very similar. Which is beneficial for hole injection and transportation in an electroluminescent device.

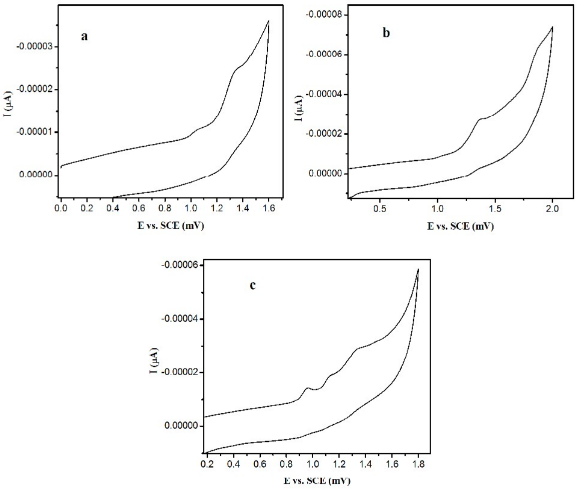


Fig. 7 Cyclic voltammogram of **C8-ant** (a), **C12-ant** (b) and **PV-C12** (c) in DCM containing tetrabutylammonium hexaflurophosphate (0.1 M) at the scan rate of 100 mV/s.

Table 2. The energy level parameters and the electrochemical properties of **C8-ant, C12-ant** and **PV-C12**

Entry	E^{onset} (V)	Ep^{1ox} (V)	Ep^{2ox} (V)	HOMO (eV)	LUMO (eV)	E_g (eV)
C8-ant	0.98	1.05	1.33	-5.58	-2.96	2.62
C12-ant	0.97	1.06	1.36	-5.57	-2.93	2.64
PV-C12	0.85	0.95, 1.13	1.33	-5.45	-2.97	2.48

Conclusions

We have successfully synthesized 9,10-bis-(alkoxystyryl)anthracene derivatives with different lengths of alkoxy chains (octyl-oxy, dodecyl-oxy) linked at the end of the phenyl rings and thoroughly characterized by various techniques. Further, we investigated the photophysical properties of anthracene derivatives in solution as well as solid phases. Furthermore, we studied the aggregation fluorescence properties and aqueous dispersion fluorescence properties were strongly dependent the chain length and position-of the anthracene derivatives. From the observed results, we concluded that the short alkyl chain-containing **OC8-ant** exhibit more red shifted than the others, which was related to their strongly conjugated backbone conformations and strong intermolecular interactions. These findings suggest that changing the nature and linking position of substituents at peripheral aryl rings of 9,10-bis (arylvinyl) anthracenes can alter the molecular backbone conformation and solid-state packing structure to afford unique and tunable solid state optical properties.

Experimental section

Materials and Methods

All the chemicals and reagents were used in this work as an analytical grade without further purification. Anthracene, tetrabutylammoniumbromide, 4-bromobenzaldehyde, tetrabutylammonium hexaflurophosphate, lithium aluminium hydride, pyridinium chlorochromate, Palladium acetate, K^tOBu, were obtained from Sigma Aldrich. THF, DMF, toluene, DCM, $CHCl_3$, methanol, DMSO were obtained from Merck and all the solvents were obtained from spectroscopy grade.

The ^1H and ^{13}C NMR spectra were recorded on a Bruker (Avance) 300 MHz NMR instrument using TMS as an internal standard, $CDCl_3$ as solvent. Standard Bruker software was used throughout. Chemical shifts are given in parts per million (δ-scale) and the coupling constants are given in Hertz. Silica gel-G plates (Merck) were used for TLC analysis with a mixture of petroleum ether and ethyl acetate as an eluent. Column chromatography was carried out in silica gel (60-120 mesh) using pet.ether and ethyl acetate as an eluent. UV-Vis absorption spectra were recorded on JASCO V630 Spectro Photometer. Photoluminescence spectra were recorded on Agilent 8000. FT-IR spectra were recorded on Nicolet 1600 FT-IR Thermo scientific company. Mass spectra were analyzed by Voyager DE PRO Biospectrometry Workstation (Applied Biosystems) Matrix-Assisted Laser Desorption Ionization Time-Of-Flight (MALDI-TOF) Mass Spectroscopy (MS) instrument. A pulsed nitrogen laser of 337 nm was used, and the TOF was operated in the delayed extraction mode.

General Procedure for Heck Coupling Reaction (A)

Methyl-3,5-dibromobenzoate (1 eq), vinylated aromatic compound (2 eq), Bu_4NBr (4 eq), $Pd(OAc)_2$ (4 mol%) were dissolved in dry DMF/ toluene (1:1) mixture. The resulting solution was purged under nitrogen for half an hour, then triethylamine (0.23 mmol) was added as a base and heated the reaction mixture to 95 °C and maintained for overnight. After completion of the reaction, the resulting mixture was passed through the celite bed and washed with ethyl acetate. The organic layer was further washed with a saturated brine solution and dried over anhydrous Na_2SO_4. The crude material was purified by column chromatography using petroleum ether / ethyl acetate (97:3) as an eluent, to afford white solid as a product.

Compound 5a. Synthesized according to the general procedure **A** using methyl-3,5-dibromobenzoate (0.13 g, 0.016 mmol) and 1,3-bis(octyloxy)-5-vinylbenzene (**4a**) (0.32 g, 0.05 mmol). Yield is 77%; ^1H NMR (300 MHz, $CDCl_3$) δ 8.07 (d, *J* = 1.5Hz, 2H), 7.76 (s, 1H), 7.12 (d, *J* = 1.5 Hz, 4H), 6.68 (d, *J* = 2.1 Hz, 4H), 6.42 (t, *J* = 1.8 Hz, 2H), 3.98 (m, 11 H, merged three protons of $COOCH_3$), 1.81 (m, 8H), 1.48 (m, 8H), 1.32 (m, 32H), 0.90 (t, *J* = 6.6 Hz, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.89, 160.62, 138.78, 138.07, 131.03, 130.41, 128.76, 127.76, 126.50, 105.33, 101.58, 68.20, 52.18, 31.83, 29.39, 29.38, 29.24, 26.10, 22.65, 14.05.

Compound 5b. Synthesized according to the general procedure **A** using methyl-3,5-dibromobenzoate (0.13 g, 0.016 mmol) and 1,3-bis(dodecyloxy)-5-vinylbenzene (**4b**) (0.32 g, 0.05 mmol). Yield is 74%,^1H NMR (300 MHz, $CDCl_3$) δ 8.07 (d, *J* = 1.5Hz, 2H), 7.75 (s, 1H), 7.12 (s, 4H), 6.68 (d, *J* = 1.8 Hz, 4H), 6.41 (d, *J* = 1.8 Hz, 2H), 3.98 (m, 11 H, merged three protons of $COOCH_3$), 1.79 (m, 8H), 1.46 (m, 8H), 1.27 (m, 64H), 0.88 (t, *J* = 6.3 Hz, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.92, 160.51, 138.68, 137.96, 130.96, 130.28, 128.81, 127.69, 126.46, 105.18, 101.32, 68.09, 52.26, 31.91, 29.66, 29.63, 29.60, 29.40, 26.06, 22.68, 14.10.

General Procedure for Reduction of Compounds (B)

The ester (1 eq) in THF was added to a suspension of lithium aluminum hydride (1.5 eq) in THF at 0 ºC. The suspension was allowed to warm at room temperature and stirred until the reaction was complete. After completion of the reaction, the mixture was quenched by 2N HCl and filtered through celite. The filtrate was extracted with ethyl acetate and washed with brine. The combined organic layers were dried over anhydrous Na_2SO_4 and purified by column chromatography using petroleum ether / ethyl acetate (4:1) as an eluent, to afford a target compound.

Compound 6a. Synthesized according to the general procedure **B** using ester **5a** (4 g, 0.8 mmol). Yield is 80%; ^1H NMR (300 MHz, $CDCl_3$) δ 7.54 (s, 1H), 7.42 (s, 2H), 7.10 (d, 4H), 6.68 (s, 4H), 6.41 (s, 2H), 4.75 (d, 2H), 3.99 (m, 8H), 1.80 (m, 8H), 1.45 (m, 8H), 1.27 (m, 32H), 0.90 (t, *J* = 6.2 Hz, 12H); ^{13}C NMR (75MHz, $CDCl_3$) δ 160.47, 141.62, 138.98, 137.91, 129.42, 128.46, 128.33, 124.27, 124.12, 105.12, 101.09, 68.09, 65.21, 31.82, 29.36, 29.28, 29.25, 26.07, 22.07, 14.08.

Compound 6b. Synthesized according to the general procedure **B** using ester **5b** (5 g, 0.71 mmol). Yield is 79%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52 (s, 1H), 7.41 (s, 2H), 7.08 (s, 4H), 6.65 (d, *J* = 1.5 Hz, 4H), 6.39 (s, 2H), 4.73 (s, 2H), 4.61 (s, 1H), 3.94 (m, 8H), 1.78 (m, 8H), 1.44 (m, 8H), 1.26 (m, 64H), 0.87 (t, *J* = 6.0 Hz, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.60, 139.10, 138.06, 137.62, 129.58, 128.56, 124.29, 124.18, 105.31, 101.33, 68.19, 65.21, 31.92, 29.66, 29.40, 26.09, 22.67, 14.06.

General Procedure for Aldehyde Synthesis (C)

PCC (1.5 eq) added to the solution of alcohol (1 eq) in CH_2Cl_2 at 0 ºC under nitrogen atmosphere. The reaction was allowed to room temperature and stirred until the reaction was complete. After completion of the reaction, the mixture was quenched by 2N HCl and filtered through celite. The filtrate was extracted with ethyl acetate and washed with brine. The combined organic layers were dried over anhydrous Na_2SO_4 and purified by column chromatography using petroleum ether/ ethyl acetate (97:3) as an eluent, to afford a target compound.

Compound 7a. Synthesized according to the general procedure **C** using alcohol **6a** (2.2 g, 0.33 mmol). Yield is 85%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.07 (s, 1H), 8.13 (d, *J* = 1.5 Hz, 2H), 7.82 (s, 1H), 7.14 (d, *J* = 1.5 Hz, 4H), 6.69 (d, *J* = 2.1 Hz, 4H), 6.42 (t, *J* = 2.1Hz, 2H), 3.99 (t, *J* = 6.6 Hz, 8H), 1.80 (m, 8H), 1.48 (m, 8H), 1.30 (m, 32H), 0.89 (t, *J* = 6.6 Hz, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.86, 160.91, 139.44, 138.64, 138.22, 129.77, 128.99, 124.55, 124.16, 105.53, 101.50, 68.50, 32.34, 30.10, 30.02, 29.84, 29.78, 26.50, 23.11, 14.54.

Compound 7b. Synthesized according to the general procedure **C** using alcohol **6b** (3.6 g, 0.76 mmol). Yield is 88%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.06 (s, 1H), 7.88 (s, 2H), 7.81 (s, 1H), 7.14 (d, *J* = 1.5 Hz, 4H), 6.69 (d, *J* = 2.1 Hz, 4H), 6.44 (s, 1H), 3.99 (t, *J* = 6.6 Hz, 8H), 1.83 (m, 8H), 1.48 (m, 8H), 1.27 (m, 64H), 0.88 (t, *J* = 6.2 Hz, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 192.02, 160.65, 138.74, 138.56, 137.32, 130.98, 130.20, 127.30, 126.31, 105.42, 101.66, 68.19, 31.92, 29.67, 29.64, 29.61, 29.41, 29.34, 26.09, 22.67,14.05.

General Procedure for the Synthesis of Vinyl Compounds (D)

Methyltriphenylphosphonium iodide (1.2 eq) and aldehyde (1 eq) was dissolved in 10 ml of DCM under a nitrogen atmosphere and then K^{t}OBu (2 eq) was added slowly. The mixture was stirred for 8 hrs. After completion of the reaction, the mixture was poured into 100 ml water. The crude product was extracted with ethyl acetate and washed with brine. The combined organic layers were dried over anhydrous Na_2SO_4. The crude material was purified by column chromatography using petroleum ether / ethyl acetate (99:1) as an eluent, to afford white solid as a product.

Compound 8a. Synthesized according to the general procedure **D** using aldehyde **7a** (2.84 g, 0.44 mmol) and methyltriphenylphosphonium iodide (2.1 g, 0.52 mmol). Yield is 73%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.53 (s, 1H), 7.44 (s, 2H), 7.09 (s, 4H), 6.75 (m, 1H), 6.68 (s, 4H), 6.40 (s, 4H), 5.84 (d, *J* = 17.4 Hz, 1H), 5.32 (d, *J* = 10.8 Hz, 1H), 4.00-3.92 (t, *J*= 6.3 Hz, 8H), 1.84-1.79 (m, 8H), 1.47-1.41 (m, 8H), 1.40-1.26 (m, 32H), 0.90-0.86 (t, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.59, 139.11, 137.90, 136.66, 129.47, 128.65, 124.16, 123.79, 105.27, 101.29, 68.17, 31.83, 29.34, 29.24, 26.10, 22.65, 14.06.

Compound 8b. Synthesized according to the general procedure **D** using aldehyde **7b** (1 g, 0.21 mmol) and methyltriphenylphosphonium iodide (0.9 g, 0.25 mmol). Yield is 75%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54 (s, 1H), 7.45 (s, 2H), 7.10 (s, 4H), 6.72 (m, 1H), 6.69 (s, 4H), 6.43 (s, 2H), 5.84 (d, *J* = 17.4 Hz, 1H), 5.32 (d, *J* = 10.8 Hz, 1H), 3.99 (t, *J* = 6.6 Hz, 8H), 1.93–1.76 (m, 8H), 1.50 (m, 8H), 1.28 (m, 64H), 0.89 (t, *J* = 6.1 Hz, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.49, 139.02, 138.22, 137.80, 136.58, 129.36, 128.57, 124.13, 123.74, 105.11, 101.08, 68.08, 31.92, 29.68, 29.64, 29.62, 29.41, 29.35, 26.08, 22.69, 14.12.

Compound C8-ant

Synthesized according to the general procedure **A** using 9,10-dibromoanthracene (31 mg, 0.92 mol) and compound **8a** (0.15 g, 1.8 mol). Green color powder, yield is 65%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.47 (m, 4H), 8.06 (d, *J* = 16.5 Hz, 2H), 7.74 (s, 4H), 7.66 (s, 2H), 7.54 (m, 4H), 7.20 (s, 8H), 7.17 (d, *J* = 10.8 Hz, 2H), 6.73 (s, 8H), 6.43 (s, 4H), 3.99 (t, *J* = 6.6 Hz, 16H), 1.93–1.79 (m, 16H), 1.46 (m, 16H), 1.26 (m, 64H), 0.89 (t, *J* = 6.1 Hz, 24H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.63, 139.08, 138.28, 137.28, 135.28, 133.99, 132.69, 129.68, 128.57, 125.39, 124.09, 105.33, 101.41, 68.19, 31.83, 29.69, 29.37, 29.24, 26.10, 22.70, 22.65, 14.05; MS (MALDI-TOF): *m/z* calculated for $C_{126}H_{174}O_8$: 1816.77; found 1816.32.

Compound C12-ant

Synthesized according to the general procedure **A** using 9,10-dibromoanthracene (26 mg, 0.8 mol) and compound **8b** (0.16 g, 1.6 mol). Green color semi solid, yield is 61%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.63 (d, *J* = 9.0 Hz, 2H), 8.47 (m, 4H), 8.03 (m, 2H), 7.72 (m, 4H), 7.65 (m, 2H), 7.55 (m, 4H), 7.19 (m, 8H), 7.09 (m, 2H), 6.95 (s, 8H), 6.43 (s, 4H), 4.00 (t, 16H), 1.81 (m, 16H), 1.45 (m, 16H), 1.27 (m, 128H), 0.88 (t, 24H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.63, 139.09, 138.28, 129.69, 128.60, 128.22, 127.05, 126.56, 125.39, 125.36, 124.09, 105.33, 101.39, 68.19, 31.92, 29.67, 29.63, 29.42, 29.34, 26.10, 22.67, 14.07; MS (MALDI-TOF): *m/z* calculated for $C_{158}H_{238}O_8$: 2265.63; found 2264.86.

Compound PV-C12

Synthesized according to the general procedure **A** using 9,10-dibromoanthracene (53 mg, 0.15 mol) and compound **14** (0.18 g, 0.3 mol). Orange color powder, yield is 72%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.42 (m, 4H), 7.99 (d, *J* = 16.5 Hz, 2H), 7.68 (d, *J* = 8.4 Hz, 4H), 7.59 (d, *J* = 8.1 Hz, 4H), 7.49 (m, 4H), 7.06 (d, *J* = 5.1 Hz, 4H), 6.93 (d, *J* = 16.5 Hz, 2H), 6.76 (s, 4H), 4.03 (m, 12H), 1.84 (m, 12H), 1.48 (m, 12H), 1.27 (m, 96H), 0.85 (t, *J* = 6.0 Hz, 18H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.29, 138.38, 137.17, 137.05, 136.35, 132.65, 132.48, 129.55, 129.01, 127.16, 126.88, 126.76, 125.22, 124.91, 105.20, 73.52, 69.16, 31.93, 29.76, 29.74, 29.71, 29.67, 29.44, 29.37, 26.14, 22.69, 14.11; MS (MALDI-TOF): *m/z* calculated for $C_{118}H_{178}O_6$: 1692.71; found 1692.33.

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Notes and references

1 (a) S. Kim, H. E. Pudavar, A. Bonoiu and P. N. Prasad, *Adv. Mater.*, 2007, **19**, 3791; (b) S. Kim, T. Y. Ohulchanskyy, H. E. Pudavar, R. K. Pandey and P. N. Prasad, *J. Am. Chem. Soc.*, 2007, **129**, 2669; (c) Y. Sagara and T. Kato, *Nat. Chem.*, 2009, **1**, 605.

2 (a) F. Qian, C. Zhang, Y. Zhang, W. He, X. Gao, P. Hu and Z. Guo, *J. Am. Chem. Soc.*, 2009, **131**, 1460; (b) M. Sauer, *Angew. Chem., Int. Ed.*, 2003, **42**, 1790; (c) Y. Suzuki and K. Yokoyama, *J. Am. Chem. Soc.*, 2005, **127**, 17799.

3 (a) Y. Jiang, Y. Wang, B. Wang, J. Yang, N. He, S. Qian and J. Hua, *Chem. Asian. J,* 2011, **6**, 157; (b) G. S. He, T. C. Lin, P. N. Prasad, C. C. Cho and L. J. Yu, *Appl. Phys. Lett.*, 2003, **82**, 4717.

4 (a) Y. Shirota, *J. Mater. Chem.*, 2005, **15**, 75; (b) K. R. Justin Thomas, J. T. Lin, Y. T. Tao and C. H. Chuen, *Chem. Mater.*, 2004, **16**, 5437; (c) S. Tao, L. Li, J. Yu, Y. Jiang, Y. Zhou, C. S. Lee, S. T. Lee, X. Zhang and O. Kwon, *Chem. Mater.*, 2009, **21**, 1284; (d) J. Huang, J. H. Su, X. Li, M. K. Lam, K. M. Fung, H. H. Fan, K. W. Cheah, C. H. Chen and H. Tian, *J. Mater. Chem.*, 2011, **21**, 2957.

5 (a) J. B. Birks, *Photophysics of Aromatic Molecules*; *Wiley:* London, U.K., 1970; (b) I. Capek, *Adv. Colloid Interface Sci.,* 2002, **97**, 91; (c) F. Mancin, P. Scrimin, P. Tecilla and U. Tonellato, *Coord. Chem. Rev.,* 2009, **253**, 2150; (d) D. Oelkrug, A. Tompert, J. Gierschner, H. J. Egelhaaf, M. Hanack, M. Hohloch and E. Steinhuber, *J. Phys. Chem. B*, 1998, **102**, 1902.

6 S. W. Thomass, G. D. Joly and T. M. Swager, *Chem. Rev.,* 2007, **107**, 1339.

7 J. Luo, Z. Xie, J. W. Y. Lam, L. Cheng, H. Chen, C. Qiu, H. S. Kwok, X. Zhan, Y. Liu, D. Zhu and B. Z. Tang, *Chem. Commun.*, 2001, 1740.

8 (a) J. Chen, C. C. W. Law, J. W. Y. Lam, Y. Dong, S. M. F. Lo, I. D. Williams, D. Zhu and B. Z. Tang, *Chem. Mater.,* 2003, **15**, 1535; (b) Z. Li, Y. Dong, B. Mi, Y. Tang, M. Haussler, H. Tong, Y. Dong, J. W. Y. Lam, Y. Ren, H. H. Y. Sun, K. S. Wong, P. Gao, I. D. Williams, H. S. Kwok and B. Z. Tang, *J. Phys. Chem. B*, 2005, **109**, 10061; (c) G. Yu, S. Yin, Y. Liu, J. Chen, X. Xu, X. Sun, D. Ma, X. Zhan, Q. Peng, Z. Shuai, B. Z. Tang, D. Zhu, W. Fang and Y. Luo, *J. Am. Chem. Soc.*, 2005, **127**, 6335; (d) N. W. Tseng, J. Liu, J. C. Y. Ng, J. W. Y. Lam, H. H. Y. Sung, I. D. Williams and B. Z. Tang, *Chem. Sci*., 2012, **3**, 493; (e) Z. Zhang, B. Xu, J. Su, L. Shen, Y. Xie and H. Tian, *Angew. Chem., Int. Ed.*, 2011, **50**, 11654; (f) Z. Zhao, J. W. Y. Lam and B. Z. Tang, *J. Mater. Chem.*, 2012, **22**, 23726.

9 (a) Y. J. Hong, W. Y. J. Lam and B. Z. Tang, *Chem. Commun*., 2009, 4332; (b) J. Liu, J. W. Y. Lam and B. Z. Tang, *Chem. Rev*., 2009, **109**, 5799.

10 (a) K. Danel, T. H. Huang, J. T. Lin, Y.T. Tao and C.H. Chuen, *Chem. Mater.*, 2002, **14**, 3860; (b) C. H. Wu, C. H. Chien, F. M. Hsu, P. I. Shih and C. F Shu, *J. Mater. Chem.*, 2009, **19**, 1464.

11 C. H. Chien, C. K. Chen, F. M. Hsu, C. F. Shu, P. T. Chou and C. H. Lai, *Adv. Funct. Mater.*, 2009, **19**, 560.

12 W. Liu, Y. Wang, M. Sun, D. Zhang, M, Zheng and W. Yang, *Chem. Commun.,* 2013, **49**, 6042.

13 R. Balasaravanan, K. Duraimurugan, J. Sivamani, V. Thiagarajan and A. Siva, *New J. Chem.,* 2015, **39**, 7472.

14 X. Zhang, Z. Chi, X. Zhou, S. Liu, Y. Zhang and J. Xu, *J. Phys. Chem. C,* 2012, **116**, 23629.

15 (a) H. Yao, K. Domoto, T. Isohashi and K. Kimura, *Langmuir.,* 2005, **21**, 1067; (b) Y. Wang, T. Liu, L. Bu, J. Li, C. Yang, X. Li, Y. Tao and W. Yang, *J. Phys. Chem. C,* 2012, **116**, 15576.

16 (a) L. He, F. Xiong, S. Li, Q. Gan, G. Zhang, Y. Li, B. Zhang, B. Chen and G. Yang, *J. Phys. Chem. B*, 2004, **108**, 7092; (b) S. Li, Q. Wang, Y. Qian, S. Wang, Y. Li and G. Yang, *J. Phys. Chem. A*, 2007, **111**, 11793.

17 (a) Y. Wang, W. Liu, L. Bu, J. Li, M. Zheng, D. Zhang, M. X. Sun, Y. Tao, S. F. Xue and W. J. Yang, *J. Mater. Chem. C*, 2013, **1**, 856; (b) L. Bu, M. X. Sun, D. Zhang, W. Liu, Y. Wang, M. Zheng, S. F. Xue and W. J. Yang, *J. Mater. Chem. C*, 2013, **1**, 2028; (c) Q. K. Sun, W. Liu, S. A. Ying, L. L. Wang, S. F. Xue and W. J. Yang, *RSC Adv*., 2015, **5**, 73046; (d) S. F. Xue, X. Qiu, Q. K. Sun and W. J. Yang, *J. Mater. Chem. C,* 2016, **4**, 1568.

18 (a) Z. Zhao, S. Chen, C. Deng, J. W. Y. Lam, C. Y. K. Chan, P. Lu, Z. Wang, B. Hu, X. Chen, P. Lu, H. S. Kwok, Y. Ma, H. Qiua and B. Z. Tang, *J. Mater. Chem.*, 2011, **21**, 10949.

Graphical Abstract

Synthesis, Characterization and Aggregation Induced Emission Properties of Anthracene Based Conjugated Molecules

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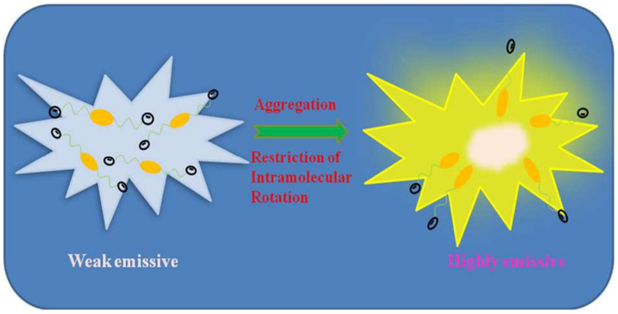

A series of long alkyl chain substituted linear and branched conjugated anthracene derivatives have aggregation-induced emission properties and also show PFC behavior, which can be useful for optoelectronic applications.