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Synthesis and Dye-sensitized Solar Cell Application of Polyolefinic Aromatic Molecules with Pyrene as Surface Group

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Synthesis of polyolefinic aromatic molecules with pyrene as the surface group, and their role as an additive in the redox couple of dye-sensitized solar cells, is described. The studies yield a promising power conversion efficiency of 5.27% with a short circuit current density of 6.50 mA cm^{-2}, an open circuit voltage of 0.60 V, and a fill factor of 0.54 under 40 mW cm^{-2} simulated air mass (A.M.) 1.5 illumination. Most importantly, the photocurrent responsivity increases with an increase in the number of pyrene units on the surface.

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Introduction

Dye-sensitized solar cells (DSSC) have attracted much attention during recent years because of their low-cost processing, simple packaging, and compatibility with flexible substrates.[1–3] Grätzel[4] and his co-workers developed a solar cell with energy conversion efficiency of 7% in 1991. The dye-sensitized solar cell consists of nanostructured TiO_2 film photoelectrodes covered with a photosensitizing dye such as [*cis*-dithiocyanato-*N*,*N*-bis(2,2-bipyridyl-4,4-dicarboxylic acid) ruthenium(II)] (N3 dye), a redox electrolyte solution (I^-/I_3^-), and a Pt counter-electrode on fluorinated tin oxide (FTO)-coated conducting glass. Under illumination, the dye absorbs light and injects photo-excited electrons into the conduction band of TiO_2. The resulting dye cations are reduced by I^-, and the generated I_3^- diffuses to a platinum counter electrode where the I_3^- is reduced back to I^-. The high efficiency of DSSC is due to the fast reduction of dye cations by I^-, and slow recombination kinetics between the injected electrons and I_3^-.[5–8]

Pyrene, a flat aromatic molecule, exhibits excellent fluorescent properties,[9] and its derivatives are promising candidates for applications in material sciences such as components in OLEDs.[10,11] Though pyrene-based solar cells have been reported,[12] polyolefinic aromatic molecules containing pyrene, and with higher orders of extensive conjugation as additive in solar cells, is not known to the best of our knowledge. The unique layered architecture of polyolefinic aromatic molecules with pyrene as surface group can be regarded as zeroth generation dendrimers. Such dendrimers have a globular shape, radially controlled chemical make-up, multivalent periphery, variable inner volume, and controlled intramolecular dynamics leading to a breadth of potential applications.

We report herein the synthesis of polyolefinic aromatic molecules **1**, **2**, **2a**, and **3** with pyrene surface group, that show enhanced energy conversion efficiency of 5.27% (Fig. 1).

Results and Discussion

Pyrene-1-carbaldehyde[13] underwent Wittig reaction with methyl triphenylphosphonium iodide in the presence of potassium *tert*-butoxide in THF to give 1-vinylpyrene in 59% yield (Scheme 1). The ^{1}H NMR spectrum of 1-vinylpyrene displayed two doublets at δ 5.50 ($J = 11.1$ Hz) and δ 5.87 ($J = 17.4$ Hz) for H_a and H_b protons, respectively, and a doublet of doublets at δ 7.63 ($J = 11.1$, 10.8 Hz) for H_c proton, in addition to the aromatic protons. In the ^{13}C NMR spectrum of 1-vinylpyrene, the vinylic carbons appeared at δ 117.2 and 134.3, in addition to 15 signals for the aromatic carbons, and in the DEPT–135 spectrum the methylene carbon appeared at δ 117.2.

Heck coupling of symmetrical tribromobenzene with 1-vinylpyrene using $Pd(OAc)_2$ in the presence of K_2CO_3 and tetrabutylammonium bromide resulted in the formation of 1,3,5-tris((*E*)-2-(pyren-1-yl)vinyl)benzene (**2**) in 73% yield. The ^{1}H NMR spectrum of 1,3,5-tris((*E*)-2-(pyren-1-yl)vinyl) benzene (**2**) displayed two doublets at δ 7.16 ($J = 16.2$ Hz) and 8.45 ($J = 9.3$ Hz) corresponding to the vinyl and pyrenyl protons, respectively, and a singlet at δ 7.59 for three protons in the benzene unit, in addition to the aromatic protons. In the ^{13}C NMR spectrum, 19 signals appeared for the aromatic and vinyl carbons between δ 122.7 and 141.3.

Similarly, Heck coupling of 1-vinylpyrene with 1,4-dibromobenzene, 2,4,6-tribromomesitylene, and hexabromobenzene afforded the polyolefinic aromatic molecules **1**, **2a**,

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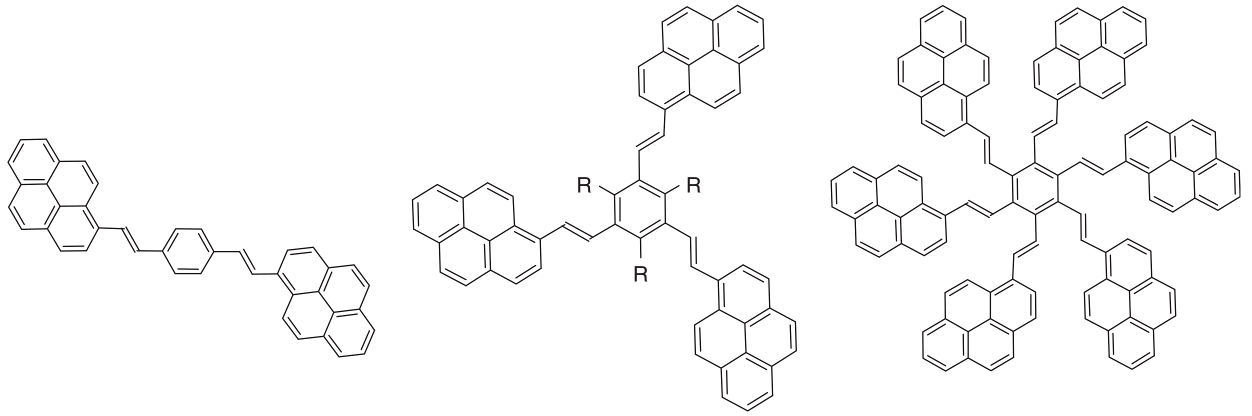
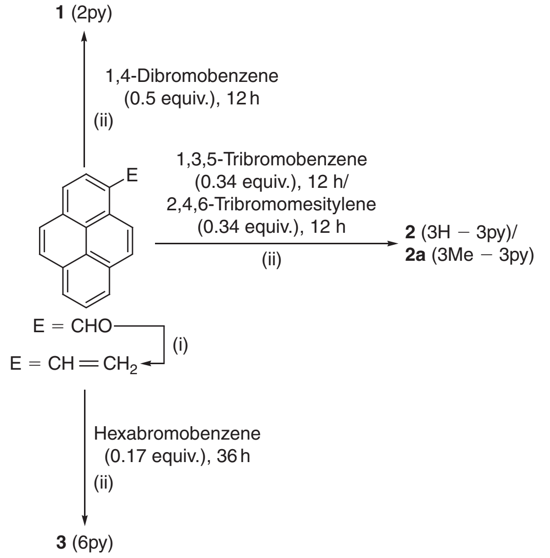


1 (2py)

R = H, **2** (3H − 3py)
R = Me, **2a** (Me − 3py)

3 (6py)

Fig. 1. Structures of polyolefinic aromatic molecules with pyrene surface group.



Reagents and conditions: (i) 1.0 equiv. methyltriphenylphosphonium iodide, KO^{t}Bu, THF, 12 h, 59%. (ii) Pd(OAc)$_2$, TBAB, K$_2$CO$_3$, DMF, 90°C, **1** (76%), **2** (73%), **2a** (75%), **3** (69%).

Scheme 1. Synthesis of polyolefinic aromatic molecules with pyrene surface group.

and **3** in 76, 75, and 69% yields, respectively (Scheme 1). The structures of the polyolefinic aromatic molecules **1**, **2a**, and **3** were confirmed from spectral and analytical data. ^{13}C NMR of polyolefinic aromatic molecules **2a** and **3** could not be obtained due to poor solubility.

Photophysical Properties

The fluorescence quantum yield (Φ_F), fluorescence lifetime (τ_F), and its relative amplitude of the polyolefinic aromatic molecules **1**, **2**, **2a**, and **3** were recorded in benzene and are presented in Table 1, along with their absorption and emission maxima.

The polyolefinic aromatic molecules **1**, **2**, **2a**, and **3** exhibit absorption maxima between 339 and 414 nm. The λ_{max} observed for the conjugated pyrene molecules **1**, **2**, **2a**, and **3** could be ascribed to π-π^* transitions of the molecular backbone (Fig. 2). A hypsochromic shift (blue shift) was observed on increasing the number of pyrene units. Though, extended conjugation usually shows a red shift in polar solvents due to the stabilization of the excited state, benzene being a non-polar solvent, stabilizes the ground state further and destabilizes the excited state. Hence a greater widening of the energy gap between π-π^* orbitals of the conjugated system resulted, on going from **1** to **3**. The insolubility of **2a** and **3** in common solvents like CHCl$_3$ and CH$_2$Cl$_2$ necessitated the use of benzene for recording UV and fluoresence spectra.

All the polyolefinic aromatic molecules exhibit intense fluorescence emission in the region 393 to 512 nm (excited at 350 nm) (Fig. 3). The emission spectra also indicate a shift towards shorter wavelength on going from dendrimer **1** to **3**, again due to destabilization of the excited state of the conjugated pyrene molecule by use of the non-polar solvent benzene. The fluorescence quantum yield (Φ_F), fluorescence lifetime (τ_F), and fluorescence amplitude were also measured for all the polyolefinic aromatic molecules **1** to **3**. The Φ_F values of the polyolefinic aromatic molecules were found to be in the range of 0.14 to 0.54 relative to that of quinine sulfate[14] (0.54 in benzene). The quantum yield decreases with increasing number of pyrene units. Fluorescence decays of polyolefinic aromatic molecules **1** and **2** are biexponential, whereas that of **2a** and **3** are triexponential.

Electrochemical Behaviour

Cyclic voltammetric studies were carried out to understand the electrochemical properties of the synthesized polyolefinic aromatic molecules. Cyclic voltammetric studies were carried out on a glassy carbon working electrode, Pt wire counter electrode, and Ag/AgNO$_3$ reference electrode from solutions of the substrates (1 mM) in benzene using tetrabutylammonium hexafluorophosphate (0.1 M) as supporting electrolyte in the potential range of −0.2 to 1.4 V. Electrochemically, all polyolefinic aromatic molecules exhibit irreversible single electron oxidation within the observable potential window (Fig. 4).

Dye-sensitized Solar Cell Studies

Dye-sensitized solar cells appear to be highly promising alternatives to more expensive solar cell technologies. The pyrene-based polyolefinic aromatic molecules **1**, **2**, **2a**, and **3** were used as additives for DSSCs, along with an I^-/I_3^- redox couple. The

Table 1. Photophysical studies of polyolefinic aromatic molecules in benzene

Polyolefinic aromatic molecule	λ_{max} absorption [nm]	λ_{max} emission [nm]	Quantum yield	Life time [ns]			Amplitudes [%]		
				τ_1	τ_2	τ_3	A_1	A_2	A_3
1	350, 370, 414	480, 512	0.54	0.63	1.67	–	36.16	63.84	–
2	370, 382	437, 457	0.47	0.45	2.09	–	4.67	95.33	–
2a	351, 363	393, 427, 441	0.45	0.33	1.46	13.91	14.93	77.33	7.73
3	320, 339	393, 414, 440	0.14	0.24	2.19	13.31	8.89	15.59	75.51

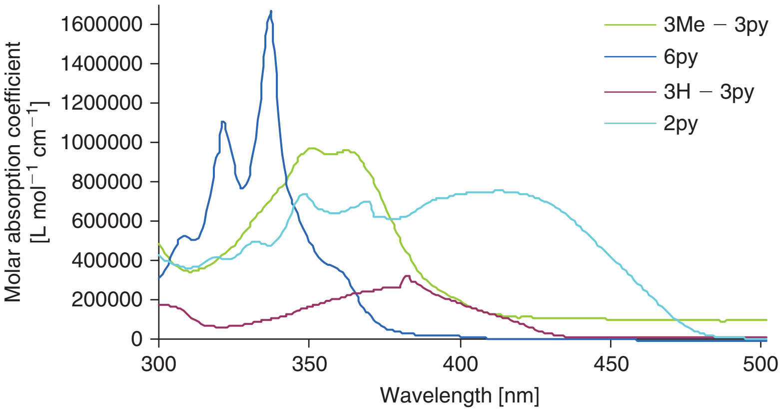


Fig. 2. UV–Visible absorption spectra in benzene.

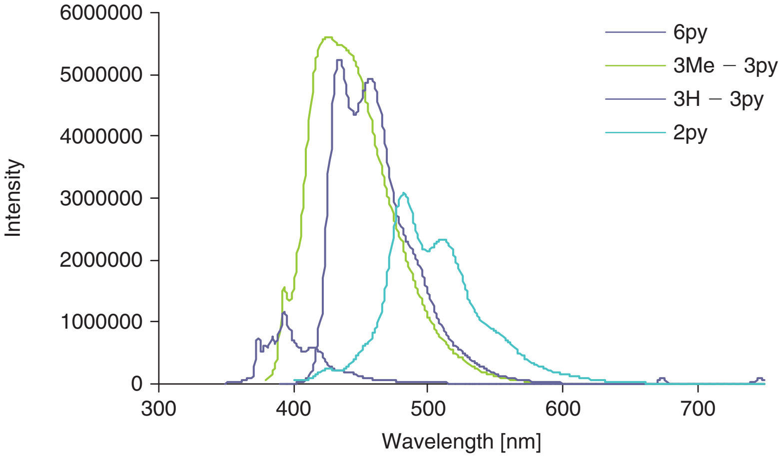


Fig. 3. Fluorescence spectra in benzene.

polyolefinic aromatic molecule was incorporated into the electrolyte to coordinate with I_2 and form an interactive bond, which would prevent the sublimation of I_2 and enhance the lifetime of the electrolyte, as well as increase the efficiency of the DSSC. Moreover the polyolefinic aromatic molecule (additive) interacting with the iodine may shift the TiO_2 conduction band edge, and result in an increased electron life time.[15] A high photocurrent is obtained with the increase in the number of pyrene units, since the pyrene is a potent photoreductant and the pyrene radical cation is a strong oxidant that is expected to oxidize iodide rapidly.[16] Table 2 shows the photovoltaic performance of DSSCs based on the incorporation of pyrene-based polyolefinic aromatic molecules **1**, **2**, **2a**, and **3** in the redox couple. Due to the poor solubility of the compounds **2a** and **3** in the routinely used solvent acetonitrile, DMF was used for all the compounds.

The comparison of DSSCs using pyrene-based polyolefinic aromatic molecules **1**, **2**, **2a**, and **3** as additives, along with an I^-/I_3^- redox couple without additives (Fig. 5), reveals that compound **3** with six pyrene units has higher efficiency compared with other three compounds. All three polyolefinic aromatic molecules **1**, **2**, and **2a** give high efficiency compared to an undoped redox couple.

Table 2 shows the influence of the polyolefinic aromatic molecules **1**, **2**, **2a**, and **3** as additives in the electrolyte on the V_{oc} of the cell. The V_{oc} values for cells containing polyolefinic aromatic molecules were greater than the cell without an additive. Among the tested additives, the highest V_{oc}, 600 mV,

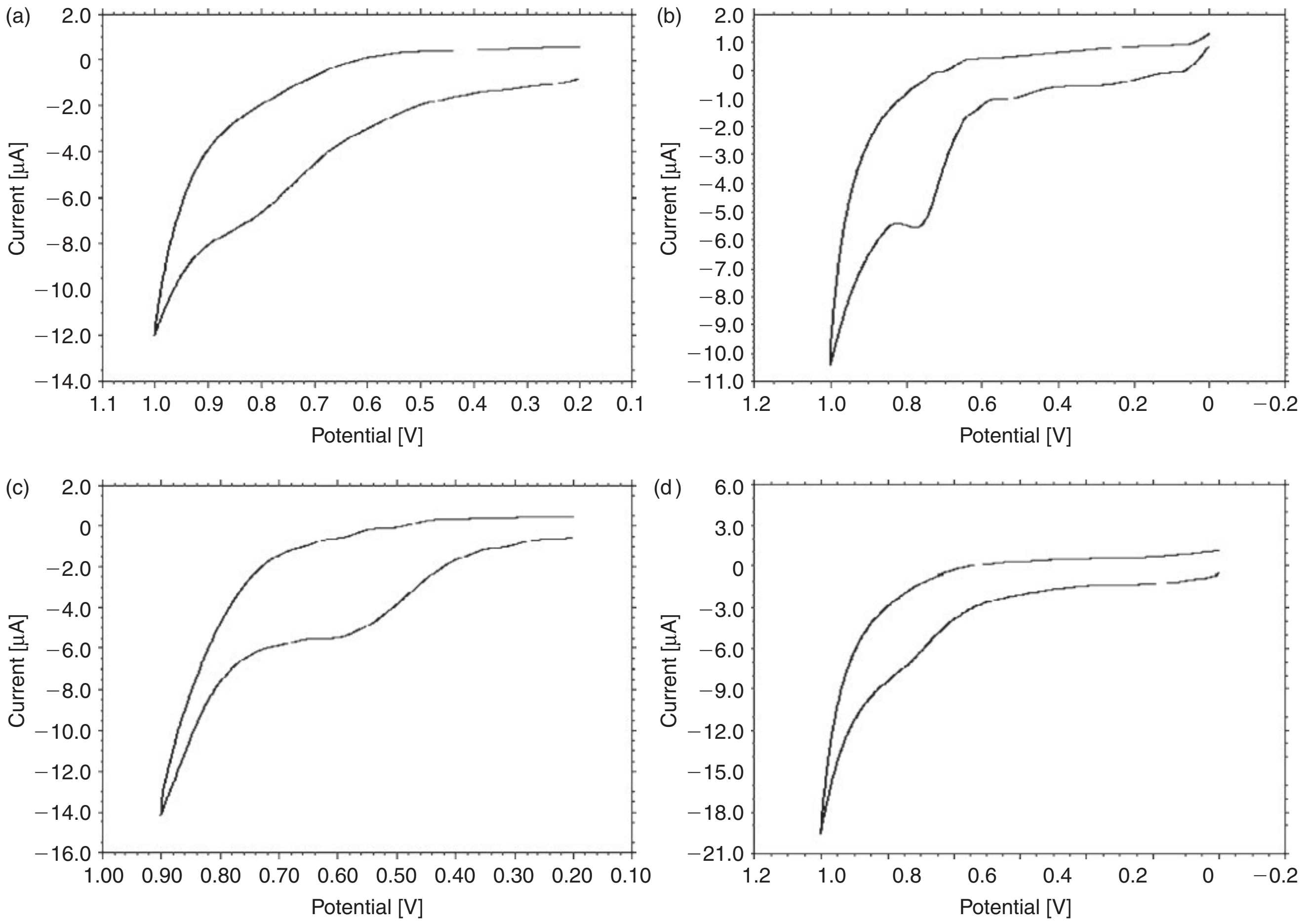


Fig. 4. Typical cyclic voltammograms of (a) **1**, (b) **2**, (c) **2a**, and (d) **3** in benzene on a glassy carbon electrode containing 0.1 M Bu_4NPF_6; scan rate 0.05 V s^{-1}.

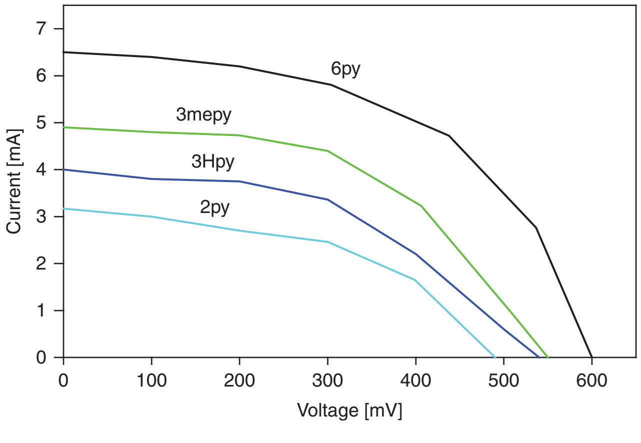


Fig. 5. *I–V* curve for polyolefinic aromatic molecules **1**, **2**, **2a**, and **3** as additives.

was observed when compound **3** with six pyrene units was added to the electrolyte.

The values are derived from the equation $\eta = (V_{oc} \times J_{sc} \times \mathrm{FF})/P^s$, where V_{oc} is the open circuit potential [mV], J_{sc} is the short circuit current density [mA cm^{-2}], FF is the fill factor, and P^s is the power of the incident (solar) light (Table 2). From the results it is clear as the number of pyrene units increases, η value, open circuit voltage (V_{oc}), and short circuit current density (J_{sc}) of the DSSCs increase.

Conclusions

In conclusion, we have successfully synthesized polyolefinic aromatic molecules with pyrene surface groups, which demonstrate the effect of the pyrene group and conjugation on controlling optical and photovoltaic properties. It should be noted that the power conversion efficiency reaches 5.27%, which is the highest value among pyrene-based additives in the redox couple. Further, synthesis of higher generations of conjugated dendrimers, and their application as additives in the redox couple in DSSCs are under way.

Experimental

General Procedure for Dye-sensitized Solar Cell Studies

The TiO_2 photoelectrode was prepared as reported in the literature.[17] The N3 dye was adsorbed on the TiO_2 surface by soaking the TiO_2 photoelectrode in an ethanol solution of the N3 dye (5×10^{-5} M concentration) for 24 h at room temperature. The photoelectrode was washed, dried, and immediately used for the measurement of solar cell performance. A sandwich-type photoelectrochemical cell was composed of a dye-coated TiO_2 photoanode. Platinum coated flourinated tin oxide (FTO) conducting glass was the counter electrode. The electrolyte solution was injected into the space between the two electrodes. The electrolyte solution was composed of 3.2×10^{-3} M of KI, 4.1×10^{-4} M of I_2, and the polyolefinic aromatic molecules of 6.4×10^{-6} M as additives in DMF (10 mL). The solar to electric energy conversion efficiency was measured under simulated

Table 2. Performance of cells fabricated with and without additives

Electrolyte systems	J_{sc} [mA cm^{-2}]	V_{oc} [mV]	FF	η [%]
1 + I^-/I_3^- redox couple	3.17	490	0.46	1.78
2 + I^-/I_3^- redox couple	4.00	540	0.47	2.54
2a + I^-/I_3^- redox couple	4.90	550	0.50	3.38
3 + I^-/I_3^- redox couple	6.50	600	0.54	5.27
Without additive + I^-/I_3^- redox couple	2.00	480	0.56	1.34

solar light at 40 mW cm^{-2}. The photocurrent-photovoltage was measured using a BAS 100A electrochemical analyzer. The apparent cell area of TiO_2 photoelectrode was 1 cm^2 (1 cm × 1 cm).

General Procedure for Cyclic Voltammetric Measurements

Cyclic voltammetric measurements of all the polyolefinic aromatic molecules were performed on a CHI model 1100A series electrochemical analyzer (CH Instrument, USA). A three compartmental cell, containing glassy carbon as a working electrode, silver/silver nitrate as the reference electrode, and Pt wire as a counter electrode was used. Cyclic voltammetric studies were carried out from solutions of the substrates (1 mM) in benzene using tetrabutylammonium hexafluorophosphate (0.1 M) as supporting electrolyte in the potential range of −0.2 to 1.4 V at 50 mV s^{-1}. All electrochemical experiments were performed at room temperature (25 ± 1°C).

Synthesis and Spectroscopy

Reactions were carried out under nitrogen. Melting points are uncorrected and solvents were purified by standard procedures.[18] Thin-layer chromatography (TLC) was carried out on glass plates coated with functionalized silica gel-G (Acme) of ~0.25 mM thickness, and were visualized with iodine. Column chromatography was carried out with silica gel (Acme, 100–200 mesh). ^1H and ^{13}C NMR spectra were recorded on a Bruker (300 MHz for ^1H and 75 MHz for ^{13}C) spectrometer in $CDCl_3$ and [d6]benzene, chemical shifts were noted in δ [ppm], and coupling constants (J) are expressed in hertz. Electron impact mass spectrometry (EI-MS) spectra were recorded on a JEOL DX-303 mass spectrometer at 70 eV. The Fast Atom Bombardment (FAB)-MS spectra were recorded on a JEOL SX 102/DA-6000 mass spectrometer using *p*-nitrobenzyl alcohol as matrix. Elemental analyses were performed on a Perkin–Elmer 240B elemental analyzer. The UV-Vis spectra were recorded on a Shimadzu 260 spectrophotometer. The emission spectra were recorded on a Perkin–Elmer LS-5B spectrophotometer.

Synthesis of 1-Vinylpyrene

To a suspension of methyl triphenylphosphoniumiodide (2.0 g, 4.9 mmol) in dry THF (100 mL), under nitrogen atmosphere at room temperature, was added potassium *tert*-butoxide (3.3 g, 29.4 mmol). The solution was stirred for 1 h and then a solution of pyrene-1-carbaldehyde (1.13 g, 4.9 mmol) in dry THF (25 mL) was added slowly. The mixture was stirred at room temperature for 12 h, and then evaporated to dryness. Unreacted potassium *tert*-butoxide was quenched with saturated aqueous NH_4Cl solution (10 mL) and then extracted with $CHCl_3$ (2 × 100 mL). The combined organic layers were washed with water (2 × 200 mL), brine (100 mL), and dried over anhydrous Na_2SO_4. Evaporation of the organic layer gave a residue which was purified by column chromatography, using hexane as eluant, to give 1-vinylpyrene (59%) as a yellow solid, mp 88°C (lit.[19] 87–89°C). δ_H (300 MHz, $CDCl_3$) 8.19–7.82 (m, 9H), 7.63 (dd, J 11.1, 10.8, 1H, H_c), 5.87 (d, J 17.4, 1H, H_b), 5.50 (d, J 11.1, 1H, H_a). δ_C (75 MHz, $CDCl_3$) 134.3, 132.4, 131.5, 131.2, 131.0, 130.9, 128.1, 127.6, 127.5, 127.3, 126.0, 125.3, 125.0, 124.9, 123.7, 123.0, 117.2. *m/z* (EI) 228 (M^+). Anal. Calc. for $C_{18}H_{12}$: C 94.70, H 5.30. Found: C 94.63, H 5.38%.

Synthesis of Polyolefinic Aromatic Molecules **1**, **2**, **2a**, and **3**

Compounds **1**, **2**, **2a**, and **3** were prepared by Heck coupling of 1,4-dibromobenzene, 1,3,5-tribromobenzene, 1,3,5-tribromo-2,4,6-trimethylbenzene, or hexabromobenzene with 1-vinylpyrene.

General Procedure for Heck Coupling

A stirred mixture of 1,4-dibromobenzene/1,3,5-tribromobenzene/1,3,5-tribromo-2,4,6-trimethylbenzene/hexabromobenzene (0.6/0.4/0.4/0.3 mmol), $Pd(OAc)_2$ (0.18/0.12/0.12/0.09 mmol) in dry DMF (25 mL) under nitrogen was successively treated with K_2CO_3 (3.5/2/2/1.5 mmol) and tetrabutylammonium bromide (0.18/0.12/0.12/0.09 mmol), and then heated at reflux for 30 min. 1-vinylpyrene (1.2/1.4/1.4/1.8 mmol) was added to the reaction mixture and heated at reflux for 12/12/12/36 h, cooled, and then filtered. The filtrate was evaporated to dryness under vacuum. The residue was extracted with $CHCl_3$ (3 × 100 mL), washed with water (3 × 100 mL) and dried over anhydrous Na_2SO_4. Evaporation of the organic layer gave a residue, which was purified by column chromatography using hexane as eluant to give the corresponding conjugated pyrene derivatives.

1,4-Bis[(E)-2-(pyren-1-yl)vinyl]benzene (**1**)

Following the general procedure for Heck coupling, 1,4-bis[(*E*)-2-(pyren-1-yl)vinyl]benzene (**1**, 76%) was obtained as a yellow solid from 1,4-dibromobenzene (0.14 g, 0.6 mmol) and 1-vinyl pyrene (0.27 g, 1.2 mmol), mp 182°C. δ_H (300 MHz, $CDCl_3$) 8.26 (d, J 9.3, 2H), 8.12–8.06 (m, 10H), 8.01 (d, J 15.3, 2H), 7.97–7.87 (m, 12H). δ_C (75 MHz, $CDCl_3$) 138.2, 134.7, 131.5, 131.1, 130.8, 130.5, 128.8, 128.5, 128.1, 127.8, 127.4, 126.2, 126.1, 125.6, 125.4, 125.1, 125.0, 124.8, 123.7, 122.7. *m/z* (EI) 530 (M^+). Anal. Calc. for $C_{42}H_{26}$: C 95.06, H 4.94. Found: C 95.11, H 5.01%.

1,3,5-Tris[(E)-2-(pyren-1-yl)vinyl]benzene (**2**)

Following the general procedure for Heck coupling, 1,3,5-tris[(*E*)-2-(pyren-1-yl)vinyl]benzene (**2**, 73%) was obtained as a yellow solid from 1,3,5-tribromobenzene (0.13 g, 0.4 mmol) and 1-vinyl pyrene (0.31 g, 1.4 mmol), mp 234°C. δ_H (300 MHz, $CDCl_3$) 8.45 (d, J 9.3, 3H), 8.27–7.72 (m, 27H), 7.59 (s, 3H), 7.16 (d, J 16.2, 3H). δ_C (75 MHz, $CDCl_3$) 141.3, 132.7, 131.4, 130.8, 130.6, 128.7, 128.6, 128.2, 128.0, 127.7, 127.4, 126.1, 125.6, 125.3, 125.1, 124.8, 123.7, 123.3, 122.7. *m/z* (FAB-MS)

756 (M^+). Anal. Calc. for $C_{60}H_{36}$: C 95.21, H 4.79. Found: C 95.15, H 4.72%.

*1-(2,4,6-Trimethyl-3,5-bis[(E)-2-(pyren-1-yl)vinyl]styryl) pyrene (**2a**)*

Following the general procedure for Heck coupling, 1-(2,4,6-trimethyl-3,5-bis[(*E*)-2-(pyren-1-yl)vinyl]styryl)pyrene (**2a**, 75%) was obtained as a colourless solid from 1,3,5-tribromo-2,4,6-trimethylbenzene (0.16 g, 0.4 mmol) and 1-vinyl pyrene (0.31 g, 1.4 mmol), mp >280°C. δ_H (300 MHz, [d6]benzene) 8.47 (d, *J* 9.3, 3H), 8.24–7.85 (m, 24H), 7.34 (d, *J* 16.2, 3H), 6.63 (d, *J* 16.2, 3H), 2.85 (s, 9H). *m/z* (FAB-MS) 798 (M^+). Anal. Calc. for $C_{63}H_{42}$: C 94.70, H 5.30. Found: C 94.77, H 5.23%.

*1,2,3,4,5,6-Hexakis[(E)-2-(pyren-1-yl)vinyl]benzene (**3**)*

Following the general procedure for Heck coupling, 1,2,3,4,5,6-hexakis[(*E*)-2-(pyren-1-yl)vinyl]benzene (**3**, 69%) was obtained as a yellow solid from hexabromobenzene (0.17 g, 0.3 mmol) and 1-vinyl pyrene (0.40 g, 1.8 mmol), mp 195–197°C. δ_H (300 MHz, [d6]benzene) 8.24 (d, *J* 9.3, 6H), 8.20 (d, *J* 8.1, 6H), 8.10–7.88 (m, 42H), 7.37 (d, *J* 16.5, 6H), 7.02 (d, *J* 16.2, 6H). *m/z* (FAB-MS) 1434 (M^+). Anal. Calc. for $C_{114}H_{66}$: C 95.37, H 4.63. Found: C 95.45, H 4.55%.

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