Synthesis of Pyrene-Based Ester Dendrimers for Applications in Dye-Sensitized Solar Cells

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Synthesis of dendrimers with pyrene at the surface and benzenetricarboxylic acid and phloroglucinol at the core and with ester functionality as branching points has been described. When such dendrimers are used as an additive in DSSC, power conversion efficiency of 6.78% is observed.

Dye-sensitized solar cells (DSSCs) have attracted world wide attention for its low production cost, easy handling, and relatively high electrical power conversion efficiency. The first efficient DSSC was reported by Grätzel in 1991.[1] DSSCs are composed of nanocrystalline mesoporous photoanodes[2] coated with a suitable dye molecule,[3] electrolyte containing a redox couple,[4] and counter electrode.[5] The electrolyte is the charge-transfer media between photoanode and counter electrode. The most efficient and widely used redox couple used in DSSCs is I^-/I_3^-. Solar cell performance has been remarkably enhanced by the addition of various additives to the electrolytic solution.[6,7]

Dendrimers, being regularly branched and three-dimensional macromolecules, have attracted scientific attention exceptionally, because of their size, shape, dimension, flexibility, and functionality, which can be controlled at molecular level.[8–12] Pyrene derivatives due to their richness in photophysical properties, find application in microenvironment sensors,[13] liquid crystals,[14] and organic light-emitting diodes.[15] The pyrene units, attached to the dendrimer skeleton through imine bonds play a pivotal role in enhancing the aggregation propensity of the PAMAM dendrimers.[16] Crooks et al.[17] have synthesized four generations of PPI dendrimers fully substituted with pyrene and the fluorescence spectroscopy reveals that with the increase in dendrimer generation, the excimer to monomer ratio for pyrene emission also increases. The pyrene-containing eight-arm star-shaped dendrimer-like copolymer[18] exhibited unique thermal properties and crystalline morphologies, distinct from that of the linear polymer. Dendrimeric compounds bearing pyrene units were synthesized by Cicchi et al.[19] to afford light-harvesting antennae based on the formation of intramolecular excimers. Dendrimers with ester linkage[20,21] provides easy access, facile branching, versatility, solubility, applicability, and processability from inexpensive raw materials.

Addition of additives possessing N-containing heterocycles and ester groups could enhance the efficiency of DSSCs due to valence effect.[22] Fascinated by the applications of ester groups in improving solar cell performance, we report herein the synthesis of pyrene-based dendrimers **1**–**6** (Chart 1) having ester functionalization as branching point, benzenetricarboxylic acid and phloroglucinol as the core unit and a study of their photophysical properties as well as solar cell performance when used as an additive in the redox couple of DSSCs is also described.

Results and Discussion

Syntheses. The pyrene-based ester dendrimers **1**, **2**, and **3** were synthesized by convergent approach (Scheme 1). Tris(pyren-1-ylmethyl) benzene-1,3,5-tricarboxylate (**1**) was obtained in 88% yield by the condensation of one equiv of pyren-1-ylmethanol (**7**) with 0.3 equiv of benzene-1,3,5-tricarboxylic acid (**8**) in dry dichloromethane (DCM) in the presence of diisopropylcarbodiimide (DIPC) and 4-(*N*,*N*-dimethylamino)pyridinium toluene-4-sulfonate (DPTS) respectively. DPTS[23] in turn was prepared by stirring *N*,*N*-dimethyl-4-aminopyridine (DMAP) and *p*-toluenesulfonic acid monohydrate in THF. The ^{1}H NMR spectrum of **1** displayed a singlet at δ 5.99 for *O*-methylene protons integrating for six protons, in addition to the thirty aromatic protons ranging from δ 7.93 to 8.79. In the ^{13}C NMR spectrum, **1** showed the *O*-methylene and carbonyl carbons at δ 63.6 and 163.9 respectively, in addition to the signals for eighteen aromatic carbons. In IR, the ester carbonyl group appeared at 1720.6 cm^{-1}. Further FAB-MS and elemental analysis also confirmed the structure of **1**.

Pyren-1-ylmethyl 4-formylbenzoate (**10**) was obtained in 92% yield by the coupling of one equiv of 4-formylbenzoic acid (**9**) with one equiv of **7** in dry DCM using DIPC and DPTS. The reduction of **10** with sodium borohydride at 0 °C in a 1:1 mixture of THF and ethanol gave pyren-1-ylmethyl 4-hydroxymethylbenzoate (**11**) in 89% yield. One equiv of **11** underwent DIPC coupling with 0.3 equiv of **8** to give tris[4-(pyren-1-ylmethoxycarbonyl)phenylmethyl] benzene-1,3,5-tricarboxylate (**2**) in 85% yield. The ^{1}H NMR spectrum of **2** displayed two singlets at δ 5.32 and 6.01 for *O*-methylene protons integrating for six protons each, a doublet at δ 7.66–7.69 ($J =$ 8.1 Hz) integrating for six protons, in addition to the aromatic

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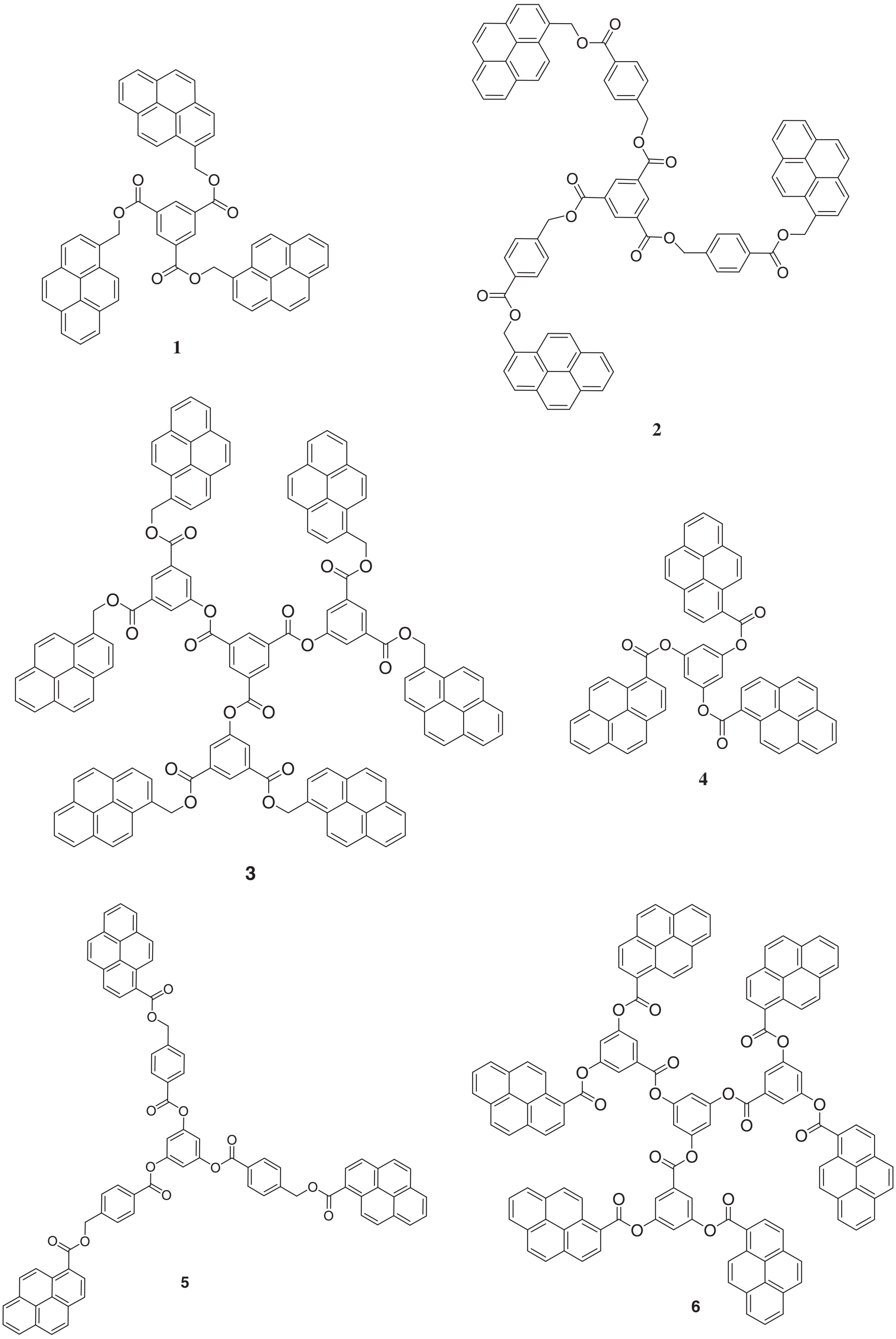
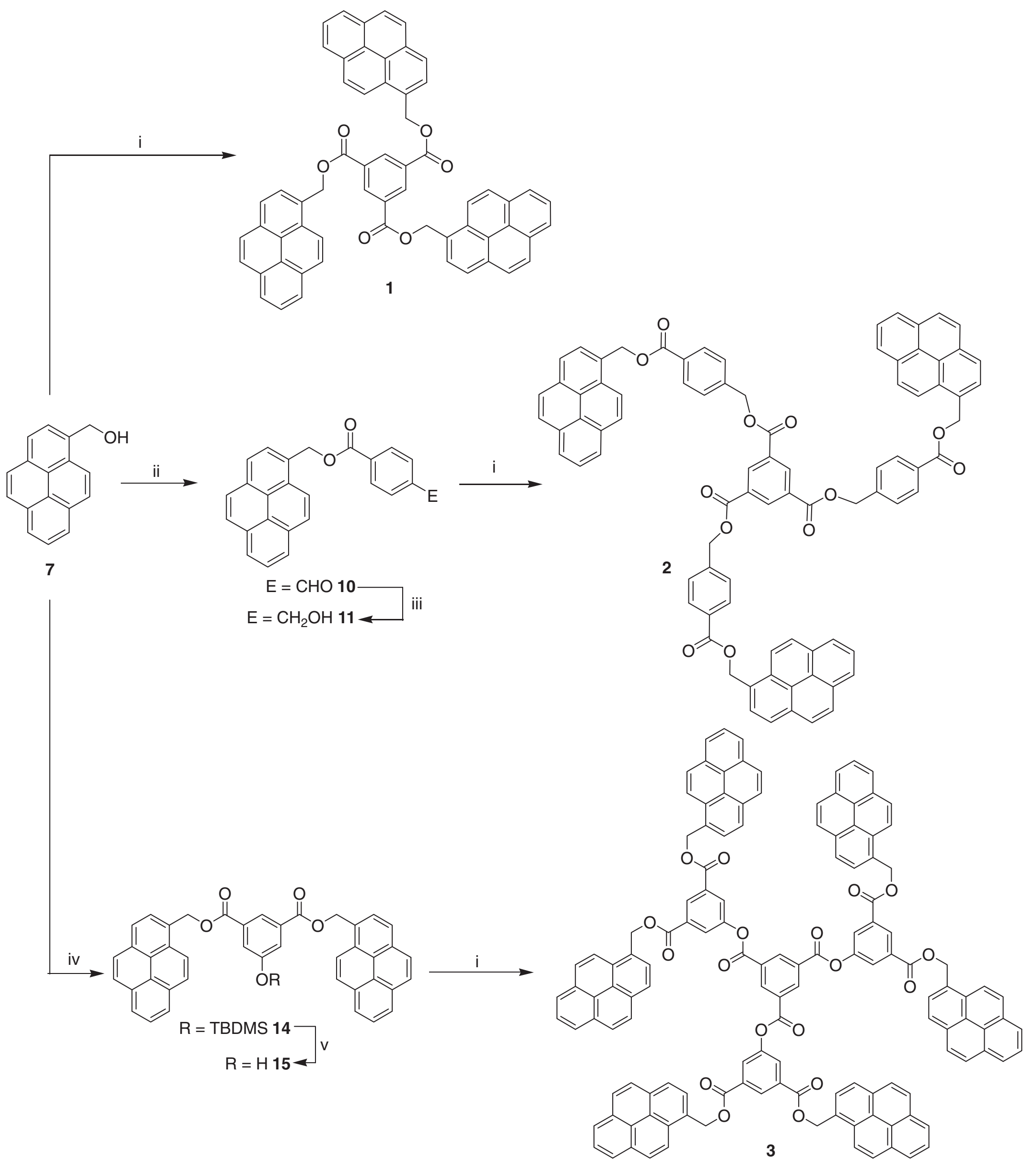


1 **2** **3** **4** **5** **6**

Chart 1.

protons. In the ^{13}C NMR of **2** showed the *O*-methylene carbons at δ 65.5 and 66.6 and the carbonyl carbons at δ 166.1 and 170.1 along with the signals for nineteen aromatic carbons which confirmed the structure of **2**. The structure of **2** was further confirmed from FAB-MS and elemental analysis also.

The bis(pyren-1-ylmethyl) 5-(*tert*-butyldimethylsiloxy)isophthalate (**14**) was obtained in 87% yield by the treatment of 0.5 equiv of 5-(*tert*-butyldimethylsiloxy)isophthalic acid (**13**)[24] with one equiv of **7** using DIPC and DPTS. The reaction of **14** with 1 M HCl in acetone yielded the bis(pyren-1-ylmethyl) 5-

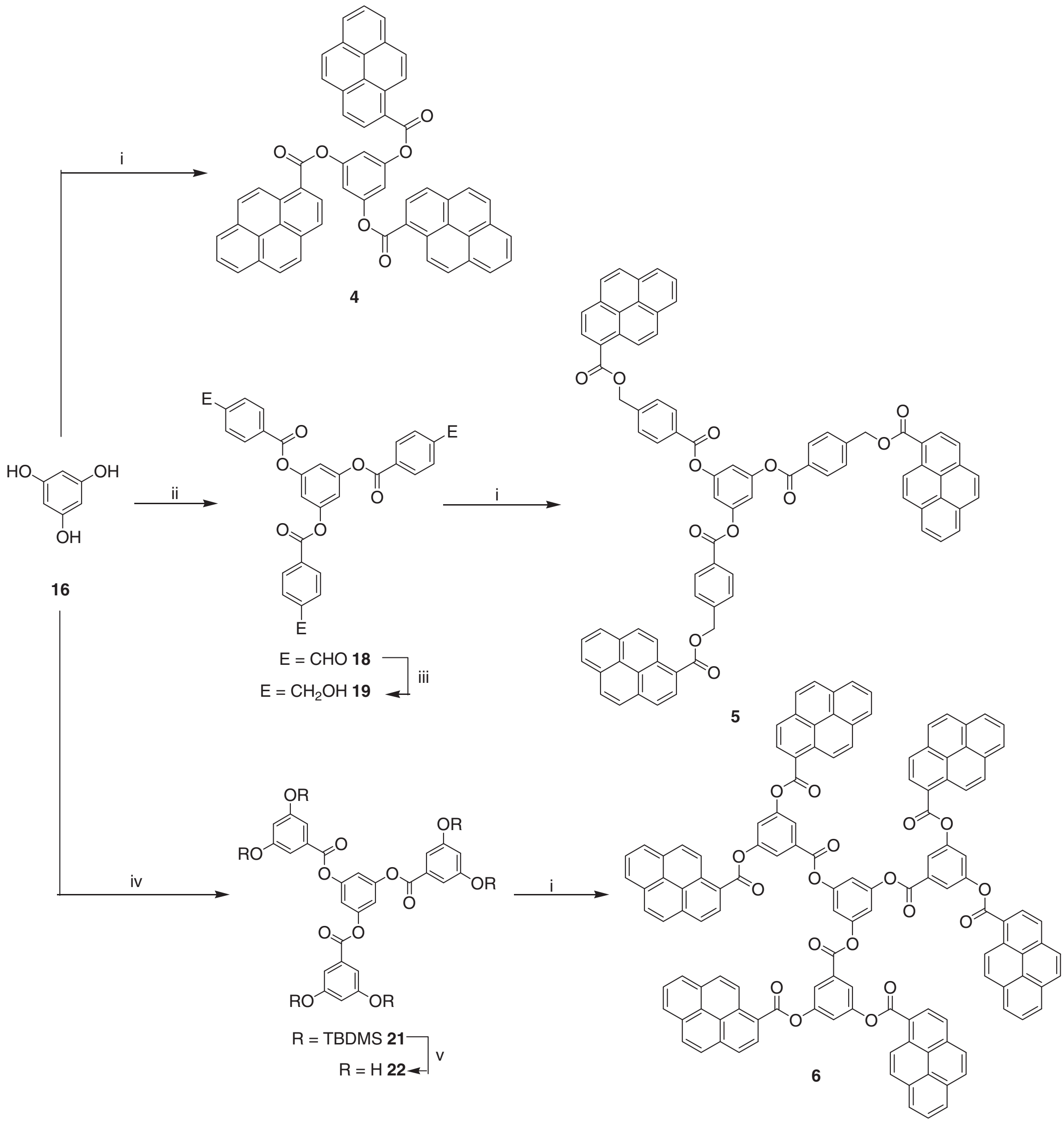


Scheme 1. Synthesis of pyrene-based ester dendrimers **1**–**3**. *Reagents and conditions*: (i) 0.3 equiv of benzene-1,3,5-tricarboxylic acid (**8**), DIPC, DPTS, dry CH_2Cl_2, 24 h, **1** (88%), **2** (85%), **3** (84%); (ii) 1 equiv of 4-formylbenzoic acid (**9**), DIPC, DPTS, dry CH_2Cl_2, 24 h, **10** (95%); (iii) THF/EtOH (1:1), $NaBH_4$, 0 °C, 3 h, **11** (89%); (iv) 0.5 equiv of 5-(*tert*-butyldimethylsiloxy)isophthalic acid (**13**), DIPC, DPTS, dry CH_2Cl_2, 24 h, **14** (87%); (v) acetone/1 M HCl, 12 h, **15** (85%).

hydroxyisophthalate (**15**) in 85% yield. DIPC coupling of one equiv of **15** with 0.3 equiv of benzene-1,3,5-tricarboxylic acid (**8**) in dry DCM in the presence of DPTS gave nonaester **3** having six pyrene units. The ^{1}H NMR spectrum of nonaester **3** displayed a singlet at δ 5.30 for *O*-methylene protons integrating for twelve protons, a doublet at δ 8.29–8.32 ($J =$ 9.3 Hz) integrating for six pyrenyl protons, in addition to the aromatic protons. In the ^{13}C NMR spectrum, nonaester **3** showed the *O*-methylene carbon at δ 67.1 and the carbonyl carbons at δ 160.9 and 166.8 along with the signals for twenty aromatic carbons. Two sharp bands appeared for the nonaester **3** at 1733.3 and 1719.0 cm^{-1} in IR indicating the presence of ester carbonyl group. FAB-MS and elemental analysis are also in accordance with the proposed structure **3**.

Pyrene-1-carboxylic acid (**17**) was obtained by the oxidation of pyrene-1-carbaldehyde using potassium permanganate, pyridine and water at 100 °C for 12 h. The pyrene-based ester dendrimers **4**, **5**, and **6** were synthesized by divergent approach (Scheme 2).

The triester **4** having three pyrene units was obtained in 91% yield by the DIPC coupling of one equiv of benzene-1,3,5-triol (**16**) with three equiv of **17** (Scheme 2). The ^{1}H NMR spectrum of triester **4** displayed a singlet at δ 7.53 for the central phloroglucinol core integrating for three protons and two doublets at δ 8.96–8.99 ($J =$ 8.1 Hz) and 9.45–9.48 ($J =$ 9.3 Hz) integrating for three protons each, in addition to the aromatic protons. In the ^{13}C NMR spectrum, triester **4** showed the carbonyl carbon at δ 162.4 along with the signals for



Scheme 2. Synthesis of pyrene-based ester dendrimers **4**–**6**. *Reagents and conditions*: (i) 3/3/6 equiv of pyrene-1-carboxylic acid (**17**), DIPC, DPTS, dry CH_2Cl_2, 24 h, **4** (91%), **5** (71%), **6** (78%); (ii) 3 equiv of 4-formylbenzoic acid (**9**), DIPC, DPTS, dry CH_2Cl_2, 24 h, **18** (81%); (iii) THF/EtOH (1:1), $NaBH_4$, 0 °C, 3 h, **19** (68%); (iv) 3 equiv of 3,5-di(*tert*-butyldimethylsiloxy)benzoic acid (**20**), DIPC, DPTS, dry CH_2Cl_2, 24 h, **21** (79%); (iv) acetone, 1 M HCl, 12 h, **22** (74%).

eighteen aromatic carbons. In IR, the ester carbonyl group appeared at 1673.5 cm^{-1}. The structure of the triester **4** was also confirmed from FAB-MS and elemental analysis.

The trialdehyde **18** was obtained by the coupling of three equiv of 4-formylbenzoic acid (**9**) with one equiv of **16** in dry DCM using DIPC and DPTS. The reduction of trialdehyde **18** with sodium borohydride at 0 °C in a 1:1 mixture of THF and ethanol gave the triol **19** in 68% yield. One equiv of the triol **19** underwent DIPC coupling with three equiv of **17** to give hexaester **5** having three pyrene units. The ^{1}H NMR spectrum of hexaester **5** displayed two singlets at δ 4.76 and 7.36 for the *O*-methylene and the phloroglucinol protons respectively, integrating for six and three protons each, two doublets at δ 8.69–8.72 ($J = 8.1$ Hz) and 9.35–9.38 ($J = 9.3$ Hz) integrating for three protons each, in addition to the aromatic protons. In the ^{13}C NMR spectrum, hexaester **5** showed the *O*-methylene carbon at δ 66.1 and the carbonyl carbons at δ 157.5 and 170.2 along with the signals for sixteen aromatic carbons. Two sharp bands appeared for the hexaester **5** at 1618.3 and 1659.8 cm^{-1} in IR indicating the presence of ester carbonyl group. FAB-MS and elemental analysis are also in accordance with the proposed structure.

The hexasilyloxy triester **21**[25] was obtained in 79% yield by the treatment of three equiv of 3,5-di(*tert*-butyldimethylsiloxy)benzoic acid (**20**)[26] with one equiv of **16** as mentioned earlier. The reaction of hexasilyloxy triester **21** with 1 M HCl in acetone yielded the triester **22**[25] in 84% yield. DIPC coupling of six equiv of **17** with one equiv of triester **22** in dry DCM in

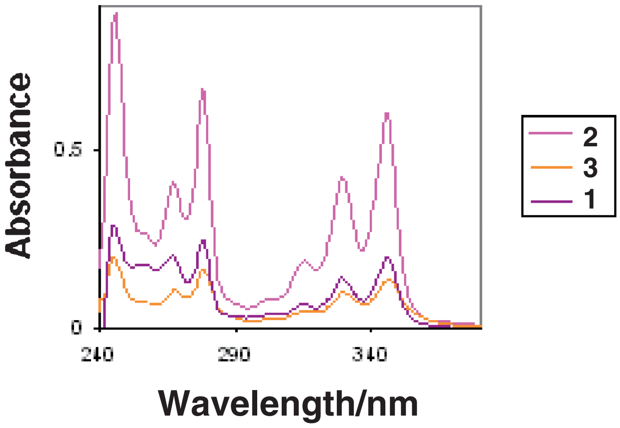


Figure 1. UV–visible absorption spectra of **1** in DMSO; **2** and **3** in $CHCl_3$.

Table 1. Photophysical Data for the Dendrimers **1**, **4**, **5**, and **6** in DMSO and **2** and **3** in $CHCl_3$

Dendrimers	UV λ_{max}/nm	Emission λ_{max}/nm
1	245.3, 266.8, 278.0, 329.1, 345.7	487
2	245.8, 267.2, 278.0, 315.2, 329.1, 345.4	490
3	241.1, 245.3, 267.7, 278.3, 329.5, 346.3	492
4	245.9, 284.0, 357.5, 390.1	402, 420
5	246.0, 283.2, 354.6, 389.0	410, 421
6	259.0, 285.1, 357.2, 389.0	411, 422

the presence of DPTS gave the nonaester **6** with six pyrene units showing complete conjugation. The ^{1}H NMR spectrum of nonaester **6** displayed a singlet at δ 7.53 for the aromatic protons of the central core integrating for three protons, three doublets at δ 7.04–7.05 ($J = 2.4$ Hz), 8.96–8.99 ($J = 8.1$ Hz), and 9.34–9.37 ($J = 9.3$ Hz) integrating for six protons each and a triplet at δ 6.47–6.48 ($J = 1.8$ Hz) integrating for three protons, in addition to the aromatic protons. Two sharp bands appeared for the nonaester **6** at 1685.2 and 1615.0 cm^{-1} in IR indicating the presence of ester carbonyl group. The mass spectrum (FAB-MS) of nonaester **6** showed a molecular ion peak at m/z 1902. The structure of the nonaester **6** was further confirmed by elemental analysis.

Photophysical Properties of Ester-Linked Dendrimers Having Pyrene Surface. Benzenetricarboxylic Acid as the Core Unit: The electronic absorption spectra of the pyrene-based ester dendrimers **1** (in DMSO), **2**, and **3** (in $CHCl_3$) shows five sharp characteristic transitions of the pyrene unit with maxima between 241 and 346 nm (Figure 1 and Table 1). The excimer emission (Figure 2) of the pyrene-based ester dendrimers **1** (in DMSO), **2**, and **3** (in $CHCl_3$) was observed at 487, 490, and 492 nm respectively. Pyrene-containing compounds can form excited-state dimers (excimers) by stacking interaction between excited-state and ground-state monomers. Excimer formation requires close proximity between the pyrene moeities.[27] The pyrene-based ester dendrimers **1**, **2**, and **3** show excimer emission owing to the flexibility caused by the *O*-methylene carbons which could result in close proximity of the pyrenyl units. Further the conjugation between the pyrene unit and carbonyl group is absent in dendrimers **1**, **2**, and **3** due to the presence of intervening methylene groups.

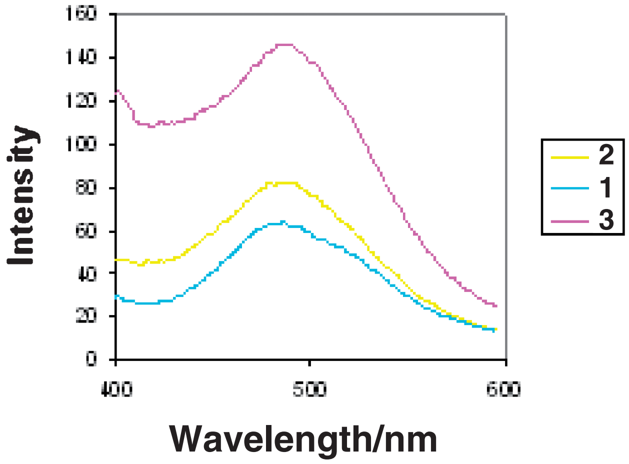


Figure 2. Fluorescence spectra of **1** in DMSO; **2** and **3** in $CHCl_3$.

Phloroglucinol as the Core Unit: Ester dendrimers **4**, **5**, and **6** show two absorption bands and two shoulders which are attributed to the π–π^* transitions of the pyrene moiety and the values are listed in Table 1. The dendrimers **4**, **5**, and **6** show monomeric pyrene emission around 420–422 nm (Table 1) purely because the pyrenyl units do not have flexibility due to the absence of an intervening methylene group and hence they are not in close proximation as that of the dendrimers **1**, **2**, and **3**. Further more, the absorption of **4**, **5**, and **6** show red shift of about 45 nm when compared with the dendrimers **1**, **2**, and **3** due to the presence of carbonyl group conjugated to the pyrene pendant.

DSSC Studies of Ester-Linked Dendrimers Having Pyrene Surface. The current–voltage characteristics was measured under AM 1.5 illumination (100 mW cm^{-2}) using a BAS100A Electrochemical Analyzer. A 150-W tungsten halogen lamp (OSRAM, Germany) served as the light source. The values are derived from the equation $\eta = (V_{oc} \times J_{sc} \times ff)/P^s$, where V_{oc} is open circuit potential (V), J_{sc} is short circuit current density (mA cm^{-2}), ff is the fill factor, and P^s is the power of the incident (solar) light.

In general organic nitrogenous compounds[6a,28] are introduced as additives in the redox couple of DSSC, however introduction of dendrimers containing oxygen atoms and pyrene units resulted in good performance. Both V_{oc} and J_{sc} increased in the doped electrolyte systems when compared to the undoped redox counterparts. The increase in V_{oc} is due to the effective formation of charge-transfer complex of the n and π electrons present in the dendrimer with iodine in the redox couple. Iodide is regenerated in turn by the reduction of triiodide at the counter electrode. The circuit is completed via electron migration as given in the following equation.

$$I^- + I_2 \rightleftharpoons I_3^- \quad (1)$$

$$3I^- + 2\mathrm{dye}^+ \rightarrow I_3^- + 2\mathrm{dye}\ (\mathrm{TiO_2\ electrode}) \quad (2)$$

$$I_3^- + 2e^- \rightleftharpoons 3I^-\ (\mathrm{counter\ electrode}) \quad (3)$$

To investigate the effects of pyrene-based ester dendrimers **1–6** as an additive in the redox couple, UV–visible absorption of

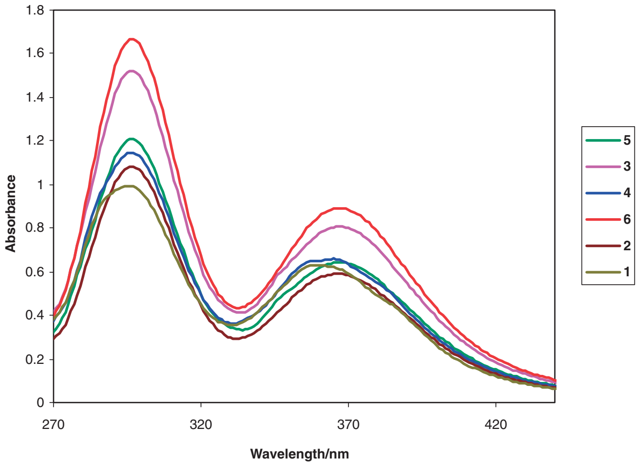


Figure 3. UV–visible absorption spectra of KI and I_2 with additives **1**–**6**.

the prepared electrolytes was measured. The peaks around 290 and 360 nm indicate the presence of I_3^-.[29] The intensity and the width of the absorption peaks at 296 and 364 nm in the spectra (Figure 3) increased with the addition of dendrimers **1**–**6**, implying an increase in I_3^- concentration. With an increase in iodide ion concentration due to the addition of additives in the redox couple, the regeneration of oxidized dye may be accelerated and the accumulated electrons in TiO_2 via charge injection from the excited dye molecule increase, resulting in high V_{oc}. The pyrene dendrimers work as a hole transporter to shuttle a hole from the oxidized dye to the counter electrode by forming complex with iodine. The pyrene-based ester dendrimers **1**–**6** act as an additive in the redox couple and efficiently convert light into electrical current. 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.[30]

Charge-transfer complex formation of the additives with iodine prevents the facile sublimation of iodine thus enhancing the stability of the electrolyte. In addition to this, the additive interacting with iodine in the redox couple may shift the semiconductor band edge toward negative potential by adsorption on to the TiO_2 surface in DSSC and enhance the efficiency.[31] The concentrations of I^-, I_2, and the additives used (3.2×10^{-3} M of KI, 4.1×10^{-4} M of I_2, and the pyrene-based ester dendrimers of 6.4×10^{-6} M) resulted in better performance in DSSC.

Benzenetricarboxylic Acid as the Core Unit: Table 2 shows the photovoltaic performance of DSSCs based on the incorporation of pyrene-based ester dendrimers **1**, **2**, and **3** in the redox couple.

From the results it is clear that with the increase in the number of pyrene unit, η value, open circuit voltage (V_{oc}), and short circuit current density (J_{sc}) of the DSSCs increases. Figure 4 shows the current versus voltage curve of a DSSC using pyrene-based ester dendrimers **1**, **2**, and **3** as an additive along with the I^-/I_3^- redox couple.

Table 2. Performance of the Cells Fabricated with and without the Additives in the Redox Couple

Electrolyte systems	J_{sc}/mA cm^{-2}	V_{oc}/mV	*ff*	η/%
1 + I^-/I_3^- redox couple	4.10	600	0.51	3.14
2 + I^-/I_3^- redox couple	4.50	630	0.52	3.69
3 + I^-/I_3^- redox couple	6.10	710	0.51	5.52
I^-/I_3^- redox couple Without additive	1.60	430	0.45	0.95

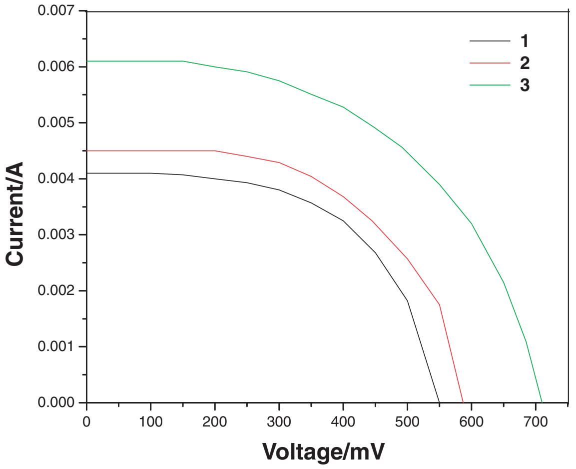


Figure 4. *I*–*V* curve for **1**, **2**, and **3** as an additive in the redox couple.

Table 3. Performance of the Cells Fabricated with and without the Additives in the Redox Couple

Electrolyte systems	J_{sc}/mA cm^{-2}	V_{oc}/mV	*ff*	η/%
4 + I^-/I_3^- redox couple	5.10	655	0.48	4.01
5 + I^-/I_3^- redox couple	5.30	685	0.48	4.30
6 + I^-/I_3^- redox couple	6.60	790	0.52	6.78
I^-/I_3^- redox couple Without additive	1.60	430	0.45	0.95

Phloroglucinol as the Core Unit: The photovoltaic performance of the DSSC is evaluated based on three parameters. These include the open circuit photovoltage (V_{oc}), the short circuit photocurrent (J_{sc}), and the overall efficiency (η). The first two parameters, V_{oc} and J_{sc}, are readily obtained from the current–voltage characteristic (*I*–*V*) of the DSSC. Table 3 shows the photovoltaic performance of DSSCs based on the incorporation of pyrene-based ester dendrimers **4**, **5**, and **6** in the redox couple.

The comparison of DSSCs using pyrene-based ester dendrimers **4**, **5**, and **6** as additives along with I^-/I_3^- redox couple and without additives (Figure 5) reveals that dendrimer **6** shows higher efficiency than that of the dendrimers **1**–**5** because of the increase in number of pyrene pendants with carbonyl substitution. However, all the pyrene-based ester dendrimers **1**–**6** gives high efficiency when compared to the undoped redox couple. The cell fabricated without the additive in the redox couple shows the efficiency of 0.95%. The dendrimer **3** in I^-/I_3^- redox couple shows the second highest efficiency among the six dendrimers which has been screened. This is due to the presence of six pyrene pendants which are not directly linked with carbonyl function and hence results

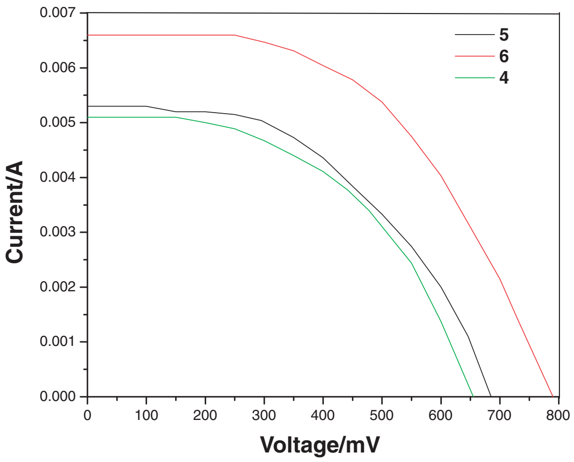


Figure 5. *I–V* curve for **4**, **5**, and **6** as an additive in the redox couple.

in breakdown of conjugation between pyrene and carbonyl group. The dendrimer **5** used as an additive in the redox couple shows the third highest efficiency among all the compounds that are screened due to the presence of three pyrene units. The dendrimer **4** in I^-/I_3^- redox couple shows the fourth highest efficiency among all the tested compounds due to the presence of three pyrene pendants with carbonyl substitution. Finally the dendrimers **1** and **2** having three pyrene units show moderate efficiency since there is a breakdown in conjugation between pyrene pendants and carbonyl group.

Conclusion

In conclusion, we have synthesized pyrene-based dendrimers with ester branching points which shows the power conversion efficiency was sensitive to the effect of the number of pyrene pendants and its conjugation with carbonyl group. Efficient power conversion will be possible through the structural modifications on conjugated pyrene units. Further our results suggests that π-conjugated systems might show better light harvesting ability and hence better performance in the solar cells than other types of molecular systems.

Experimental

General Considerations. All melting points were uncorrected. The ^{1}H and ^{13}C NMR spectra were recorded on Bruker 300 spectrometers. The chemical shifts are reported in ppm (δ) with TMS as internal standard and coupling constant (J) are expressed in Hz. MALDI-TOF mass spectra were recorded on a Voyager-DE PRO mass spectrometer using α-cyano-4-hydroxycinnamic acid (α-CHCA) as matrix and EI-MS spectra on a JEOL DX-303 mass spectrometer. The FAB-MS spectra were recorded on a JEOL SX 102/DA-6000 mass spectrometer using *p*-nitrobenzyl alcohol (NBA) 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. Glass plates coated with silica gel-G (ACME) of about 0.25 mm thickness were used for TLC and visualized with iodine. Column chromatography was carried out with silica gel (ACME, 100–200 mesh). All solvents used were purified as per standard procedure.[32]

General Procedure for Esterification Reactions (Procedure A). To a solution of alcohol (2.2/1.8/2.6/6.5/0.2 mmol) in dry dichloromethane (150 mL) was added the carboxylic acid (0.7/1.8/1.2/1.6/1.2 mmol), followed by 4-(*N*,*N*-dimethylamino)pyridinum toluene-4-sulfonate (DPTS) (2.2/1.8/2.5/1.5/0.5 mmol). The mixture was stirred at room temperature under nitrogen for 15 min. Diisopropylcarbodiimide (DIPC) (2.2/2.1/2.6/1.6/1.3 mmol) was then added and stirring continued at room temperature until the completion of the reaction. The reaction mixture was diluted with CH_2Cl_2 (2 × 50 mL) and washed with water (50 mL). The organic layer was separated, dried over $MgSO_4$, and solvent was removed by rotary evaporation. The residue, thus obtained after evaporation of the solvent was purified by column chromatography using suitable eluent as mentioned for each compound to give the corresponding ester.

General Procedure for Sodium Borohydride Reduction (Procedure B). To a solution of aldehyde (0.7 mmol) in a mixture of THF and ethanol (1:1, 20 mL) was added in portions $NaBH_4$ (1.4 mmol) at 0 °C. The reaction mixture was then stirred at room temperature for 3 h, after which concd HCl (3–5 drops) was added. The inorganic residue obtained was filtered off. Evaporation of the solvent from the reaction mixture in vacuo gave a residue, which was purified by column chromatography using suitable eluent as mentioned for each compound to give the corresponding alcohol.

General Procedure for TBDMS Deprotection of an Alcohol (Procedure C). The silyl-protected alcohol (1.2 g) was heated at 50 °C with acetone (100 mL) and 1 M HCl (30 mL) for 12 h. The solvent was removed under reduced pressure. The residue was diluted with $CHCl_3$ (100 mL), washed with water (3 × 50 mL) and brine (50 mL). The organic layer was separated, dried over $MgSO_4$, and the solvent was removed by rotary evaporation. The residue, thus obtained after evaporation of the solvent was purified by column chromatography using suitable eluent to give the corresponding alcohol.

Tris(pyren-1-ylmethyl) Benzene-1,3,5-tricarboxylate (1). Following the general procedure A, tris(pyren-1-ylmethyl) benzene-1,3,5-tricarboxylate (**1**) was obtained as a colorless solid from benzene-1,3,5-tricarboxylic acid (**8**) (0.15 g, 0.7 mmol) and pyren-1-ylmethanol (**7**) (0.5 g, 2.2 mmol). The ester was chromotographed over SiO_2 using hexane/ethyl acetate (4:1) as an eluent. Yield: 88%; mp: 240–242 °C. IR (KBr, cm^{-1}): 1720.6 (C=O); ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.99 (s, 6H), 7.93–8.25 (m, 27H), 8.79 (s, 3H). ^{13}C NMR (75 MHz, DMSO-d_6): δ 63.6, 121.6, 121.9, 122.1, 122.3, 122.7, 122.9, 130.3, 130.5, 130.9, 132.1, 132.3, 132.7, 132.8, 133.4, 133.5, 133.6, 133.9, 134.0, 163.9. Mass spectrum (FAB-MS): *m*/*z* 852 (M+). Elemental Anal. calculated for $C_{60}H_{36}O_6$: C, 84.49; H, 4.25%. Found: C, 84.59; H, 4.17%.

Pyren-1-ylmethyl 4-Formylbenzoate (10). Following the general procedure A, pyren-1-ylmethyl 4-formylbenzoate (**10**) was obtained as a colorless solid from pyren-1-ylmethanol (**7**) (0.48 g, 2.1 mmol) and 4-formylbenzoic acid (**9**) (0.26 g, 1.7 mmol). The ester **10** was chromatographed using hexane/$CHCl_3$ (3:2) as an eluent. Yield: 95%; mp: 136–138 °C. IR (KBr, cm^{-1}): 1721.2, 1704.6 (C=O). ^{1}H NMR (300 MHz,

$CDCl_3$): δ 5.93 (s, 2H), 7.66–7.69 (d, 2H, $J = 8.1$ Hz), 7.85–8.07 (m, 10H), 8.16–8.19 (d, 1H, $J = 9.0$ Hz), 9.85 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 64.8, 121.6, 123.4, 123.5, 123.9, 124.5, 124.6, 125.1, 126.2, 126.8, 126.9, 127.2, 127.3, 128.3, 128.6, 129.1, 129.5, 130.1, 130.8, 133.9, 138.0, 164.4, 190.4. Mass spectrum (EI, 70 eV): *m*/*z* 364 (M+). Elemental Anal. calculated for $C_{25}H_{16}O_3$: C, 82.40; H, 4.43%. Found: C, 82.34; H, 4.50%.

Pyren-1-ylmethyl 4-Hydroxymethylbenzoate (11). Following the general procedure B, pyren-1-ylmethyl 4-hydroxymethylbenzoate (**11**) was obtained as a colorless solid from pyren-1-ylmethyl 4-formylbenzoate (**10**) (0.26 g, 0.7 mmol) and $NaBH_4$ (0.06 g, 1.5 mmol). The alcohol **11** was purified by column chromatography using hexane/$CHCl_3$ (2:3) as an eluent. Yield: 89%; mp: 114–116 °C. IR (KBr, cm^{-1}): 1715.3 (C=O). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.08 (bs, 1H), 4.77 (s, 2H), 6.06 (s, 2H), 7.25–7.34 (d, 2H, $J = 8.1$ Hz), 7.98–8.20 (m, 10H), 8.33–8.36 (d, 1H, $J = 9.3$ Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 64.6, 65.3, 122.9, 124.6, 124.9, 125.5, 125.6, 126.1, 126.5, 127.4, 127.8, 127.9, 128.3, 129.2, 129.7, 130.0, 130.7, 131.2, 131.8, 146.2, 166.4. Mass spectrum (EI, 70 eV): *m*/*z* 366 (M+). Elemental Anal. calculated for $C_{25}H_{18}O_3$: C, 81.95; H, 4.95%. Found: C, 82.01; H, 4.88%.

Tris[4-(pyren-1-ylmethoxycarbonyl)phenylmethyl] Benzene-1,3,5-tricarboxylate (2). Following the general procedure A, tris[4-(pyren-1-ylmethoxycarbonyl)phenylmethyl] benzene-1,3,5-tricarboxylate (**2**) was obtained as a colorless solid from benzene-1,3,5-tricarboxylic acid (**8**) (0.05 g, 0.21 mmol) and pyren-1-ylmethyl 4-hydroxymethylbenzoate (**11**) (0.23 g, 0.63 mmol). The ester **2** was chromotographed using hexane/ethyl acetate (4:1) as an eluent. Yield: 85%; mp: 188–190 °C. IR (KBr, cm^{-1}): 1677.0, 1718.0 (C=O). ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.32 (s, 6H), 6.01 (s, 6H), 7.36–7.39 (d, 6H, $J = 8.1$ Hz), 7.94–8.31 (m, 36H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 65.5, 66.6, 122.9, 124.6, 125.5, 125.6, 126.1, 127.4, 127.8, 128.0, 128.3, 128.8, 130.2, 130.7, 131.0, 131.2, 131.8, 140.4, 153.4, 156.4, 164.4, 166.1, 170.1. Mass spectrum (FAB-MS): *m*/*z* 1255 (M+). Elemental Anal. calculated for $C_{84}H_{54}O_{12}$: C, 80.37; H, 4.34%. Found: C, 80.29; H, 4.44%.

Bis(pyren-1-ylmethyl) 5-(*tert*-Butyldimethylsiloxy)isophthalate (14). Following the general procedure A, bis(pyren-1-ylmethyl) 5-(*tert*-butyldimethylsiloxy)isophthalate (**14**) was obtained as a colorless liquid from 5 (*tert*-butyldimethylsiloxy)isophthalic acid (**13**) (0.5 g, 1.7 mmol) and pyren-1-ylmethanol (**7**) (0.78 g, 3.4 mmol). The ester **14** was chromotographed using hexane/DCM (1:1) as an eluent. Yield: 87%; IR (KBr, cm^{-1}): 1727.2 (C=O). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.19 (s, 6H), 0.96 (s, 9H), 5.67 (s, 4H), 7.83–8.09 (m, 19H), 8.14–8.17 (d, 2H, $J = 9.3$ Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ −4.0, 16.3, 20.9, 64.2, 121.9, 122.2, 122.4, 122.6, 123.6, 123.9, 124.0, 124.2, 125.7, 126.1, 126.7, 126.8, 127.0, 127.6, 130.1, 130.4, 130.7, 130.9, 132.3, 168.0. Mass spectrum (FAB-MS): *m*/*z* 724 (M+). Elemental Anal. calculated for $C_{48}H_{40}O_5Si$: C, 79.53; H, 5.56%. Found: C, 79.44; H, 5.62%.

Bis(pyren-1-ylmethyl) 5-Hydroxyisophthalate (15). Following the general procedure C, bis(pyren-1-ylmethyl) 5-hydroxyisophthalate (**15**) was obtained as a colorless solid from bis(pyren-1-ylmethyl) 5-(*tert*-butyldimethylsiloxy)isophthalate (**14**) (2.0 g), acetone (100 mL), and 1 M HCl (13 mL). The alcohol **15** was chromotographed using hexane/$CHCl_3$ (3:1) as an eluent. Yield: 85%; mp: 136–138 °C. IR (KBr, cm^{-1}): 1735.4 (C=O). ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.34 (s, 4H), 5.82 (s, 1H), 7.96–8.05 (m, 11H), 8.13–8.18 (m, 8H), 8.33–8.36 (d, 2H, $J = 9.3$ Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 64.7, 122.9, 123.6, 124.5, 124.6, 125.2, 125.5, 126.0, 127.3, 127.5, 127.6, 127.7, 127.8, 128.2, 129.5, 129.6, 130.6, 130.9, 131.3, 131.4, 131.8, 171.0. Mass spectrum (EI, 70 eV): *m*/*z* 610 (M+). Elemental Anal. calculated for $C_{42}H_{26}O_5$: C, 82.61; H, 4.29%. Found: C, 82.66; H, 4.21%.

Nonaester 3. Following the general procedure A, nonaester **3** was obtained as a colorless solid from bis(pyren-1-ylmethyl) 5-hydroxyisophthalate (**15**) (0.53 g, 0.73 mmol) and benzene-1,3,5-tricarboxylic acid (**8**) (0.05 g, 0.24 mmol). The nonaester **3** was recrystallized from $CHCl_3$. Yield: 84%; mp: 168 °C; IR (KBr, cm^{-1}): 1733.3, 1719.0 (C=O). ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.30 (s, 12H), 7.91–8.01 (m, 38H), 8.08–8.13 (m, 22H), 8.29–8.32 (d, 6H, $J = 9.3$ Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 67.1, 113.1, 122.6, 123.5, 124.2, 124.9, 126.3, 126.4, 126.5, 126.7, 126.8, 127.3, 127.8, 127.9, 128.6, 128.7, 129.9, 130.2, 130.3, 130.4, 138.3, 160.9, 166.8. Mass spectrum (FAB-MS): *m*/*z* 1986 (M+). Elemental Anal. calculated for $C_{135}H_{78}O_{18}$: C, 81.56; H, 3.95%. Found: C, 81.48; H, 4.03%.

Pyrene-1-carboxylic Acid (17). A 100 mL RB flask charged with pyrene-1-carbaldehyde (1 g, 4.37 mmol), water (16 mL), and pyridine (16 mL) was heated at 100 °C. A solution of potassium permanganate (1 g, 6.45 mmol) in water (10 mL) was added dropwise and the reaction mixture was heated at 100 °C for 12 h. The solvent was removed with a rotary evaporator and then added water (100 mL) to the residue and was heated on a water bath for 15 min and filtered. The filtrate was acidified with concentrated HCl and the pyrene-1-carboxylic acid (**17**) precipitated out was filtered, washed with water and dried. Yield: 85%; mp: 270 °C (lit.[33] 268–269 °C).

Triester 4. Following the general procedure A, triester **4** was obtained as a pale yellow solid from benzene-1,3,5-triol (**16**) (0.063 g, 0.65 mmol) and pyrene-1-carboxylic acid (**17**) (0.4 g, 1.6 mmol). The ester **4** was chromotographed using hexane/$CHCl_3$ (3:2) as an eluent. Yield: 91%; mp: 180–182 °C. IR (KBr, cm^{-1}): 1673.5 (C=O). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.53 (s, 3H), 8.08–8.34 (m, 21H), 8.96–8.99 (d, 3H, $J = 8.1$ Hz), 9.45–9.48 (d, 3H, $J = 9.3$ Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 119.0, 122.6, 123.7, 124.2, 126.4, 126.6, 126.7, 126.9, 127.1, 129.0, 129.3, 129.5, 130.3, 130.5, 131.1, 131.9, 133.1, 156.9, 162.4. Mass spectrum (FAB-MS): *m*/*z* 810 (M+). Elemental Anal. calculated for $C_{57}H_{30}O_6$: C, 84.43; H, 3.73%. Found: C, 84.55; H, 3.64%.

Trialdehyde 18. Following the general procedure A, trialdehyde **18** was obtained as a colorless solid from benzene-1,3,5-triol (**16**) (0.5 g, 4.0 mmol) and 4-formylbenzoic acid (**9**) (1.86 g, 12.4 mmol). The trialdehyde **18** was chromotographed using hexane/$CHCl_3$ (1:4) as an eluent. Yield: 81%; mp: 182–184 °C. IR (KBr, cm^{-1}): 1618.4, 1676.6 (C=O). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.25 (s, 3H), 8.03–8.06 (d, 6H, $J = 7.8$ Hz), 8.35–8.38 (d, 6H, $J = 7.8$ Hz), 10.16 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 113.3, 130.8, 133.7, 139.8, 151.3, 157.0, 163.4, 191.4. Mass spectrum (EI, 70 eV): *m*/*z* 522 (M+). Elemental Anal. calculated for $C_{30}H_{18}O_9$: C, 68.97; H, 3.47%. Found: C, 68.90; H, 3.52%.

Triol 19. Following the general procedure B, triol **19** was obtained as a colorless solid from trialdehyde **18** (0.52 g, 1.0 mmol) and $NaBH_4$ (0.23 g, 6.0 mmol). The triol **19** was purified by column chromatography using hexane/$CHCl_3$ (2:3) as an eluent. Yield: 68%; mp: 184–186 °C. IR (KBr, cm^{-1}): 1615.3 (C=O). ^1H NMR (300 MHz, $CDCl_3$): δ 3.62 (bs, 3H), 4.78 (s, 6H), 7.27 (s, 3H), 7.43–7.46 (d, 6H, $J = 8.7$ Hz), 8.02–8.05 (d, 6H, $J = 8.1$ Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 64.9, 126.4, 126.6, 128.5, 129.7, 130.1, 140.3, 157.5. Mass spectrum (EI, 70 eV): m/z 528 (M+). Elemental Anal. calculated for $C_{30}H_{24}O_9$: C, 68.18; H, 4.58%. Found: C, 68.09; H, 4.66%.

Hexaester 5. Following the general procedure A, hexaester **5** was obtained as a pale yellow solid from triol **19** (0.10 g, 0.2 mmol) and pyrene-1-carboxylic acid (**17**) (0.15 g, 0.6 mmol). The hexaester **5** was chromatographed using hexane/$CHCl_3$ (3:2) as an eluent. Yield: 71%; mp: 180–182 °C; IR (KBr, cm^{-1}): 1618.3, 1659.8 (C=O). ^1H NMR (300 MHz, $CDCl_3$): δ 4.76 (s, 6H), 7.36 (s, 3H), 8.03–8.11 (m, 11H), 8.17–8.20 (m, 11H), 8.24–8.28 (m, 11H), 8.69–8.72 (d, 3H, $J =$ 8.1 Hz), 9.35–9.38 (d, 3H, $J = 9.3$ Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 66.1, 124.1, 124.2, 124.4, 124.8, 125.2, 126.0, 126.1, 126.2, 127.2, 128.8, 129.0, 129.4, 130.3, 130.9, 131.0, 134.1, 157.5, 170.2. Mass spectrum (MALDI-TOF): m/z 1212 (M+). Elemental Anal. calculated for $C_{81}H_{48}O_{12}$: C, 80.19; H, 3.99%. Found: C, 80.25; H, 3.88%.

Hexasilyloxy Triester 21. Following the general procedure A, hexasilyloxy triester **21** was obtained as a colorless liquid from 3,5-di(*tert*-butyldimethylsiloxy)benzoic acid (**20**)[26] (8.14 g, 21.3 mmol) and benzene-1,3,5-triol (**16**) (0.89 g, 7.1 mmol). The ester **21**[25] was chromatographed using hexane/DCM (1:1) as an eluent. Yield: 79%.

Triester 22. Following the general procedure C, triester **22** was obtained as a pale yellow solid from hexasilyloxy triester **21** (7.5 g), acetone (150 mL), and 1 M HCl (275 mL). The triester **22** was chromotographed using hexane/EtOAc (3:2) as an eluent. Yield: 84%; mp: 226–228 °C (lit.[25] 225 °C).

Nonaester 6. Following the general procedure A, nonaester **6** was obtained as a brown solid from triester **22** (1.0 g, 1.9 mmol) and benzene-1,3,5-triol (**16**) (2.8 g, 11.4 mmol). The nonaester **6** was chromatographed using hexane/EtOAc (7:3) as an eluent. Yield: 78%; mp: 158 °C. IR (KBr, cm^{-1}): 1685.2, 1615.0 (C=O). ^1H NMR (300 MHz, DMSO-d_6): δ 6.47–6.48 (t, 3H, $J = 1.8$ Hz), 7.04–7.05 (d, 6H, $J = 2.4$ Hz), 7.53 (s, 3H), 7.80–8.86 (m, 42H), 8.96–8.99 (d, 6H, $J = 8.1$ Hz), 9.34–9.37 (d, 6H, $J = 9.3$ Hz). Mass spectrum (FAB-MS): m/z 1902 (M+). Elemental Anal. calculated for $C_{129}H_{66}O_{18}$: C, 81.38; H, 3.49%. Found: C, 81.45; H, 3.37%.

General Procedure for Dye-Sensitized Solar Cell Studies. The TiO_2 photoelectrode was prepared as reported in the literature.[34] The N3 dye was adsorbed on the TiO_2 surface by soaking the TiO_2 photoelectrode in a 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 acted as a counter electrode. The electrolyte solution was injected into the space between 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 pyrene based ester dendrimers of 6.4×10^{-6} M as additives in DMF (10 mL). The solar to electric energy conversion efficiency was measured under simulated 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).

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