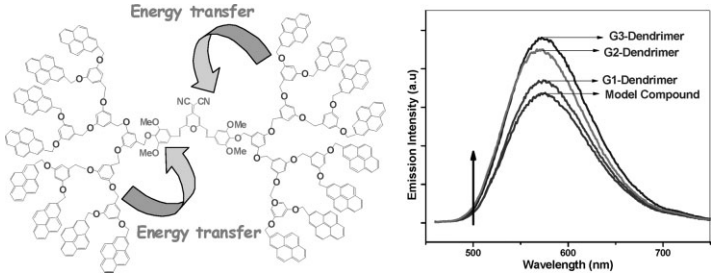
Macromolecular Journals

Macromolecular Chemistry and Physics

Synthesis, Characterization and Photophysical Properties of DCM-Based Light-Harvesting Dendrimers

Mahalingam Vanjinathan, Hong-Cheu Lin, A. Sultan Nasar*

A series of highly soluble light-harvesting dendrimers up to third generation were synthesized using a DCM-based core and Frechet-type benzyl ether dendrons containing pyrene end groups. All dendrimers and intermediates were characterized by FTIR, ^{1}H NMR, MALDI-TOF MS, UV-Vis, and PL spectra and EA, GPC, and TGA techniques. The dendrimers emit strong red PL around 570 nm. The excitation of the terminal chromophores results in core emission alone, as the donor emission is seriously quenched due to FRET to the core. The dendrimers showed enhanced luminescence properties of the core, and its efficiency was dependent on the generation number of the dendrimers. The above results reveal that these dendrimers are suitable candidates for red emissive materials in OLEDs.



Introduction

Light-emitting dendrimers are macromolecules with a well-defined structure and are composed of a core, dendrons and surface groups. The appropriate selection of each of these components provides a good and independent control of the electronic and solution processing properties. This makes them convenient model systems to study the organic semiconductor physics.[1–3] In contrast to linear polymers, the beauty of dendrimers is their size and architecture that can be specifically controlled during the synthesis.[4] A characteristic of dendritic macromolecules is the presence of a single core surrounded by numerous peripheral chain ends. The globular shape of dendrimers provides a large surface area that can be decorated with chromophores, resulting in a large absorption cross-section and enabling effective capture of photons.[5] In a dendritic antenna, the peripheral donor units collect photons and transfer the excitation energy through space to the core or focal point acceptor chromophores, i.e., dendrons acts as the "molecular lens".[6] For an efficient energy transfer from the outer to the inner dye arrays, a pair of chromophores is required which should be capable of exhibiting high fluorescence quantum yields, and should have a good spectral overlap of the absorption spectrum of the energy acceptor dye with the fluorescence band of the energy donor dye. In addition to these two criteria, individual excitation of specific absorption band in the dyes should also be considered for an efficient energy transfer. The first two properties are prerequisite for an efficient space-through resonance energy transfer (Förster mechanism)[7] and the latter condition is important for an easy evaluation of the energy transfer efficiency.

If we consider a dendrimer containing pyrene units as surface groups, that groups can act as energy donors (light antenna) for core acceptor chromophores. The fluorescence

M. Vanjinathan, H.-C. Lin
Department of Materials Science and Engineering, National Chiao Tung University, Hsinchu, Taiwan
A. S. Nasar
Department of Polymer Science, University of Madras, Guindy Campus, Chennai-600025, India
E-mail: drasultannasar@yahoo.co.in

DOI: 10.1002/macp.201000674

properties of pyrene are well known and characterized by long excited-state lifetimes[8] and distinct solvatochromic shifts.[9] Furthermore, pyrene exhibits characteristic excimer formation in concentrated solutions and in the solid state, due to self-association of the polyaromatic hydrocarbon moieties. However, this leads to a dramatic decrease in fluorescence and also to less defined, broadened fluorescence spectra. Therefore, excimer formation of pyrene can be used to study aggregation phenomena.[8b,10] Moreover, monolayers and thin films containing pyrene derivatives turned out to be promising candidates for several applications such as organic light-emitting diodes (OLEDs);[11] light-emitting materials have been reviewed very recently by Li and Bo.[12] Thayumanavan and co-workers studied the photo physics of a series of non-conjugated systems consisting of a benzthiadiazole core and benzyl ether arms terminated with aminopyrene chromophores, which function as both energy and electron donors.[13]

2,6-Dimethyl-4*H*-pyran-4-ylidene)malononitrile (DCM) is a fluorescent material with good chemical stability and its derivatives are known to be used as promising low-molecular-weight red-emitting materials.[14–18] All DCM-class red dyes contain the 2-pyran-4-ylidenemalononitrile (PM) moiety as electron acceptor. The synthesis and characterization of numerous DCM-type molecules and their applications in electroluminescent devices were reviewed by Chen.[19] New derivatives of DCM for device applications were published by Jung et al.[20] Jin and co-workers reported the synthesis and luminescent properties of fluorene copolymers bearing DCM pendants.[21] Recently, Choi and co-workers reported the red-emitting phenothiazine dendrimers encapsulated with DCM derivatives.[22]

So far, light harvesting molecule of pyrene/DCM combination has not been reported. In the present work, for the first time, we report the synthesis and photophysical properties of dendrimers up to third generation consisting of pyrene as energy donor, DCM as red-emitting and energy acceptor core and non-conjugated benzyl ether branches. We found that the electron-rich pyrene molecules are excellent light-harvesting molecular wedges whose photoluminescence (PL) emission was well suited to excite the red-emitting core.

Experimental Part

Chemicals

4-Dicyanomethylene-2,6-dimethyl-4*H*-pyran (**8**) was synthesized from 2,6-dimethyl-4-pyrone as described by Woods.[23] Pyrene-1-carboxaldehye (Lancaster), 3,5-dihydroxybenzoic acid (Lancaster), *N,N*-diisopropylazido dicarboxylate (DIAD, TCI Chemicals Co.), triphenylphosphine (PPh_3, Lancaster), $LiAlH_4$ (Lancaster), piperidine (Across Chemicals Co.), malononitrile (Lancaster), acetic anhydride (Lancaster), 4-hydroxy-3,5-dimethoxybenzaldehyde (Lancaster), and trichloroethane (Merck) were used without further purification. Tetrahydrofuran (THF) was distilled to keep anhydrous before use. Other solvents were purified by standard procedures.

Measurements

Fourier-transform infrared (FTIR) spectra of samples (dispersed in KBr discs) were recorded on a Perkin-Elmer Spectrum 100 Series instrument. ^{1}H NMR spectra were recorded on a Varian Unity 300 MHz spectrometer using $CDCl_3$ and DMSO-d_6 as solvents. The electron impact (EI) mass spectra were recorded using a JEOL DX-303 spectrometer. Elemental analyses were performed on a HERAEUS CHN-OS RAPID elemental analyzer. Thermogravimetric analyses (TGA) were carried out on a TA Instruments Q500 thermogravimetric analyzer at a heating rate of 20 °C · min^{-1} under nitrogen. Gel permeation chromatography (GPC) measurements were made on a Waters liquid chromatograph equipped with a 410 differential refractometer (refractive-index detector). THF containing 0.01% lithium bromide was used as an eluent at a flow rate of 1 mL · min^{-1}. Styragel columns of pore size 10^3, 10^4, 10^5 and 10^6 Å were used. The molecular weight calibrations were carried out using polystyrene standards having molecular weight ($\overline{M}_w$) in the range of 2.9×10^3 to 1.7×10^5 g · mol^{-1}. Matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF MS) was performed on a Micromass Tof Spec 2E instrument using a nitrogen 337 nm laser (4 ns pulse) and 2,5-dihydroxybenzoic acid as a matrix. UV-Vis absorption spectra and PL spectra were recorded on an HP G1103A spectrophotometer, and Hitachi F-4500 spectrophotometer, respectively, in dilute THF solutions (10^{-6} M).

Synthesis of Pyrene-2ylmethanol (1)

5.0 g (21.7 mmol) of pyrene-1-carboxaldehye was dissolved in 150 mL of dry methanol and the solution was cooled under ice. Under vigorous stirring, 4.2 g (108.66 mmol) of $NaBH_4$ was added portionwise. After completion of the addition, the temperature was increased to room temperature and maintained for 3 h. Excess reducing agent was cautiously destroyed by drop wise addition of 15 mL of dilute HCl at 0 °C. Then, the solvents were removed under vacuum, and the residue was extracted three times with 300 mL of CH_2Cl_2. The solvent was removed under vacuum after drying with Na_2SO_4. Purification of the crude product by column chromatography on silica gel using 4:1 mixture of hexane and dichloromethane gave a light green coloured compound. Yield 4.83 g (96%).

IR (KBr): $\nu = 3\,562$, 3 065, 3 035, 2 929, 2 870, 1 590, 1 458, 1 376, 1 169, 1 067 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 7.99$–8.39 (m, 9H, pyrene H), 5.41 (s, 2H, pyrene-CH_2). MS (70 eV, EI): $m/z = 232.1$ [M^+]. $C_{17}H_{12}O$: Calcd. C 87.90, H 5.21, O 6.89; Found C 87.68, H 5.19.

Synthesis of 2-(2,6-Bis[2-{(4-hydroxy-3,5-dimethoxy)phenyl}vinyl]-4H-pyran-4-ylidene)malononitrile (9)

1.72 g of compound **8** (9.99 mmol), 4.0 g of 4-hydroxy-3,5-dimethoxybenzaldehyde (22 mmol) and five drops of piperidine were dissolved in 150 mL of dry acetonitrile at 90 °C and stirred for overnight under reflux temperature. The reaction mixture was cooled; the solution was filtered through a D3 glass frit to isolate the product. After washing the product twice with 20 mL of methanol,

thin-layer chromatogram confirmed absence of impurities in the product. The product was dried in vacuo. Recrystallization of this product in methylene chloride gave the product (**9**) as light yellow crystalline solid. Yield 4.30 g (86%).

IR (KBr): $\nu = 3\,510, 3\,068, 2\,932, 2\,223, 1\,654, 945\ cm^{-1}$. ^1H NMR (DMSO-d_6, 300 MHz): $\delta = 3.83$ (s, 12H), 6.71 (s, 2H), 7.14 (s, 4H), 7.29 (d, 2H), 7.69 (d, 2H), 9.10 (br, 2H, phenolic −OH). MS (70 eV, EI): $m/z = 500.1$ [M^+]. $C_{28}H_{24}N_2O_7$: Calcd. C 67.19, H 4.83, O 22.38, N 5.60; Found C 66.89, H 4.67, N 5.45.

General Procedure for Synthesis of Dendrons (2), (4), (6), Model Compound (13) and G1, G2, G3 Dendrimers Using Mitsunobu Conditions

A mixture of appropriate pyrene-substituted benzyl alcohol (2.2 equiv.), 3,5-dihydroxymethyl benzoate (1.0 equiv.), triphenylphosphine (2.2 equiv.) and DIAD (2.2 equiv.) in 100 mL dry THF was kept under sonication for 2.0 h at room temperature followed by stirring at room temperature under nitrogen atmosphere for 24 h. The reaction mixture was evaporated to dryness, and portioned between CH_2Cl_2 and water. The aqueous layer was extracted with CH_2Cl_2 (3 × 100 mL), the combined organic layers were dried and evaporated to dryness. The crude product was purified as outlined in the following.

Synthesis of Pyrene G1-COOMe Dendron (2)

The dendron (**2**) was prepared from pyrene-2yl-methanol (**1**) and 3,5-dihydroxymethyl benzoate. Purification of the crude compound by column chromatography on silica gel (CH_2Cl_2/Et_2O) = 50:1) gave (**2**) as a white solid. Yield 73%.

IR (KBr): $\nu = 3\,089, 3\,062, 3\,031, 2\,930, 2\,873, 1\,720, 1\,595, 1\,448, 1\,372, 1\,156, 1\,046\ cm^{-1}$. ^1H NMR ($CDCl_3$, 300 MHz): $\delta = 3.88$ (s, 3H), 5.30 (s, 4H), 7.00 (t, 1H), 7.49 (d, 2H), 8.00–8.26 (m, 18H, pyrene H). MS (70 ev, EI): $m/z = 596$ [M^+]. $C_{42}H_{28}O_4$: Calcd. C 84.54, H 4.73, O 11.53; Found C 84.23, H 4.45.

Synthesis of Pyrene G2-COOMe Dendron (4)

The dendron (**4**) was prepared from pyrene G1-CH_2OH (**3**) and 3,5-dihydroxymethyl benzoate. Purification of the crude compound by column chromatography eluting with CH_2Cl_2/hexane = 70:30 gave (**4**) as a light yellow solid. Yield 68%.

IR (KBr): $\nu = 3\,075, 3\,058, 3\,028, 2\,938, 2\,865, 1\,728, 1\,586, 1\,459, 1\,364, 1\,165, 1\,058\ cm^{-1}$. ^1H NMR (DMSO-d_6, 300 MHz): $\delta = 3.78$ (s, 3H), 5.00 (s, 8H), 5.52 (s, 4H), 6.05 (t, 1H), 6.17 (d, 4H), 6.45 (t, 2H), 6.82 (d, 2H), 8.03–8.40 (m, 36H, pyrene H). MALDI-TOF MS $m/z = 1\,268$ [M^+]. $C_{90}H_{60}O_8$: Calcd. C 85.15, H 4.76, O 10.08; Found C 84.98, H 4.64.

Synthesis of Pyrene G3-COOMe Dendron (6)

The dendron (**6**) was prepared from pyrene G1-CH_2OH (**5**) and 3,5-dihydroxymethyl benzoate. Purification of the crude compound by column chromatography eluting with CH_2Cl_2/hexane/THF = 80:10:1 gave (**6**) as a white solid. Yield 59%.

IR (KBr): $\nu = 3\,068, 3\,055, 3\,020, 2\,935, 2\,869, 1\,720, 1\,575, 1\,465, 1\,356, 1\,159, 1\,063\ cm^{-1}$. ^1H NMR (DMSO-d_6, 300 MHz): $\delta = 3.70$ (s, 3H), 4.31 (s, 8H), 5.00 (s, 4H), 5.58 (s, 16H), 6.07 (t, 6H), 6.19 (d, 12H), 6.48 (t, 1H), 6.89 (d, 2H), 8.01–8.38 (m, 72H, pyrene H). MALDI-TOF MS $m/z = 2\,612$ [M^+]. $C_{186}H_{124}O_6$: Calcd. C 85.43, H 4.78, O 9.79; Found C 85.20, H 4.56.

Synthesis of G1 Dendrimer (10)

This was prepared from pyrene-**G1**-CH_2OH (**3**) and compound (**9**). Purification of the crude compound by column chromatography eluting with CH_2Cl_2/hexane/THF = 60:35:5 gave G1-dendrimer (**10**) as a light brown coloured solid. Yield 57%.

IR (KBr): $\nu = 3\,068, 2\,933, 2\,265, 1\,676, 1\,467, 1\,365, 1\,160, 1\,067, 976\ cm^{-1}$. ^1H NMR (DMSO-d_6, 300 MHz): $\delta = 3.81$ (s, 12H), 4.30 (s, 2H), 5.01 (s, 8H), 6.06 (t, 2H), 6.18 (d, 4H), 6.72 (s, 2H), 7.15 (s, 4H), 7.26 (d, 2H), 7.68 (d, 2H), 8.09–8.38 (m, 36H, pyrene H). MALDI-TOF MS $m/z = 1\,602$ [$M^+ + 1$]. $C_{110}H_{76}N_2O_{11}$: Calcd. C 82.48, H 4.79, N 1.75; Found C 82.00, H 4.56, N 1.68.

Synthesis of G2 Dendrimer (11)

This was prepared from pyrene-**G2**-CH_2OH (**5**) and compound (**9**). Purification of the crude compound by column chromatography eluting with CH_2Cl_2/hexane/THF = 75:15:10 gave G2-dendrimer (**11**) as a light brown coloured solid. Yield 56%.

IR (KBr): $\nu = 3\,064, 2\,932, 2\,230, 1\,654, 1\,478, 1\,365, 1\,167, 1\,055, 956\ cm^{-1}$. ^1H NMR (DMSO-d_6, 300 MHz): $\delta = 3.86$ (s, 12H), 4.35 (s, 8H), 5.09 (s, 4H), 5.25 (s, 16H), 6.11 (s, 2H), 6.16 (s, 4H), 6.22 (s, 4H), 6.33 (s, 8H), 6.65 (s, 2H), 7.15 (s, 4H), 7.21 (d, 2H), 7.65 (d, 2H), 8.01–8.37 (m, 72H, pyrene H). MALDI-TOF MS $m/z = 2\,949$ [$M^+ + 2$]. $C_{206}H_{140}N_2O_{19}$: Calcd. C 83.95, H 4.79, N 0.95; Found C 83.45, H 4.57, N 0.91.

Synthesis of G3 Dendrimer (12)

This was prepared from pyrene-**G3**-CH_2OH (**7**) and compound (**9**). Purification of the crude compound by column chromatography eluting with CH_2Cl_2/hexane/THF = 50:30:20 gave **G3**-dendrimer (**12**) as a light brown coloured solid. Yield 51%.

IR (KBr): $\nu = 3\,058, 2\,928, 2\,230, 1\,658, 1\,472, 1\,354, 1\,166, 1\,062, 958\ cm^{-1}$. ^1H NMR (DMSO-d_6, 300 MHz): $\delta = 3.86$ (s, 12H), 4.33 (s, 4H), 5.06 (s, 8H), 5.23 (s, 16H), 5.56 (s, 32H), 6.09–6.60 (m, 42H), 6.67 (s, 2H), 7.18 (s, 4H), 7.23 (d, 2H), 7.66 (d, 2H), 8.03–8.35 (m, 144 H, pyrene H). MALDI-TOF MS $m/z = 5\,639$ [$M^+ + 2$]. $C_{398}H_{268}N_2O_{35}$: Calcd. C 84.78, H 4.79, N 0.50; Found C 84.19, H 4.67, N 0.48.

Synthesis of Model Compound (13)

This was prepared from pyrene-2yl-methanol (**1**) and compound (**9**). Purification of the crude compound by column chromatography eluting with CH_2Cl_2/hexane = 50:10 gave model compound (**13**) as a light brown coloured solid. Yield 62%.

IR (KBr): $\nu = 3\,054, 2\,932, 2\,226, 1\,654, 1\,476, 1\,359, 1\,170, 1\,058, 954\ cm^{-1}$. ^1H NMR (DMSO-d_6, 300 MHz): $\delta = 3.81$ (s, 12H), 5.23 (s, 4H), 6.71 (s, 2H), 7.14 (s, 4H), 7.26 (d, 2H), 7.67 (d, 2H), 7.62–8.37 (m, 18H, pyrene H). MALDI-TOF MS $m/z = 929$ [M^+]. $C_{62}H_{44}N_2O_7$: Calcd. C 80.16, H 4.77, N 3.02; Found C 80.02, H 4.68, N 2.90.

General Procedure for the Synthesis of Dendrons (3), (5) and (7)

A 250 mL three-necked round-bottomed flask equipped with a magnetic stir bar, reflux condenser, thermometer and addition funnel containing dry THF was flushed with nitrogen and charged with 50 mL of dry THF, and $LiAlH_4$ (2.0 equiv.) whereupon a vigorous gas evolution was observed. Then, a solution of appropriate pyrene-substituted methyl benzoate (1.0 equiv.) in 150 mL of THF was added drop wise for 1.0 h at 0 °C. After the addition was over, the flask was heated to reflux temperature overnight. Excess reducing agent was cautiously destroyed by drop wise addition of 15 mL of dilute HCl at 0 °C. Then, the solvents were removed under vacuum, and the residue was extracted three times with 300 mL of CH_2Cl_2. After drying with Na_2SO_4, the extract was evaporated to dryness. The crude product was purified as outlined in the following text.

Synthesis of Pyrene G1-CH_2OH (3)

This was prepared by the reduction of pyrene-**G1**-COOMe (**2**) using $LiAlH_4$, purified by column chromatography eluting with CH_2Cl_2/hexane/THF = 60:40:1.Yield 89%.

IR (KBr): $\nu = 3\,568, 3\,086, 3\,059, 3\,043, 2\,928, 2\,878, 1\,587, 1\,456, 1\,367, 1\,167, 1\,054\ cm^{-1}$. ^1H NMR (DMSO-d_6, 300 MHz): $\delta = 4.30$ (d, 2H), 4.99 (b, −OH), 5.23 (s, 4H), 6.96 (t, 1H), 7.18 (d, 2H), 8.02–8.38 (m, 18H, pyrene H). MS (70 eV, EI): $m/z = 568$ [M^+]. $C_{41}H_{28}O_3$: Calcd. C 86.60, H 4.96, O 8.44; Found C 86.43, H 4.75.

Synthesis of Pyrene G2-CH_2OH (5)

This was prepared by reducing pyrene-**G2**-COOMe (**4**) using $LiAlH_4$, purified by column chromatography eluting with CH_2Cl_2/hexane/THF = 65:20:5. Yield 78%.

IR (KBr): $\nu = 3\,569, 3\,078, 3\,067, 3\,038, 2\,934, 2\,876, 1\,578, 1\,465, 1\,370, 1\,159, 1\,049\ cm^{-1}$. ^1H NMR (DMSO-d_6, 300 MHz): $\delta = 4.31$ (s, 2H), 5.51 (s, 8H), 5.56 (s, 4H), 6.08 (s, 3H), 6.18 (s, 6H), 8.02–8.38 (m, 36H, pyrene H). MALDI-TOF MS $m/z = 1\,240$ [M^+]. $C_{89}H_{60}O_7$: Calcd. C 86.11, H 4.87, O 9.02; Found C 85.81, H 4.74.

Synthesis of Pyrene G3-CH_2OH (7)

This was prepared by reducing the pyrene-**G3**-COOMe (**6**) using $LiAlH_4$, purified by column chromatography eluting with CH_2Cl_2/hexane/THF = 50:10:10 to give pyrene **G3**-CH_2OH (**7**) Yield 70%.

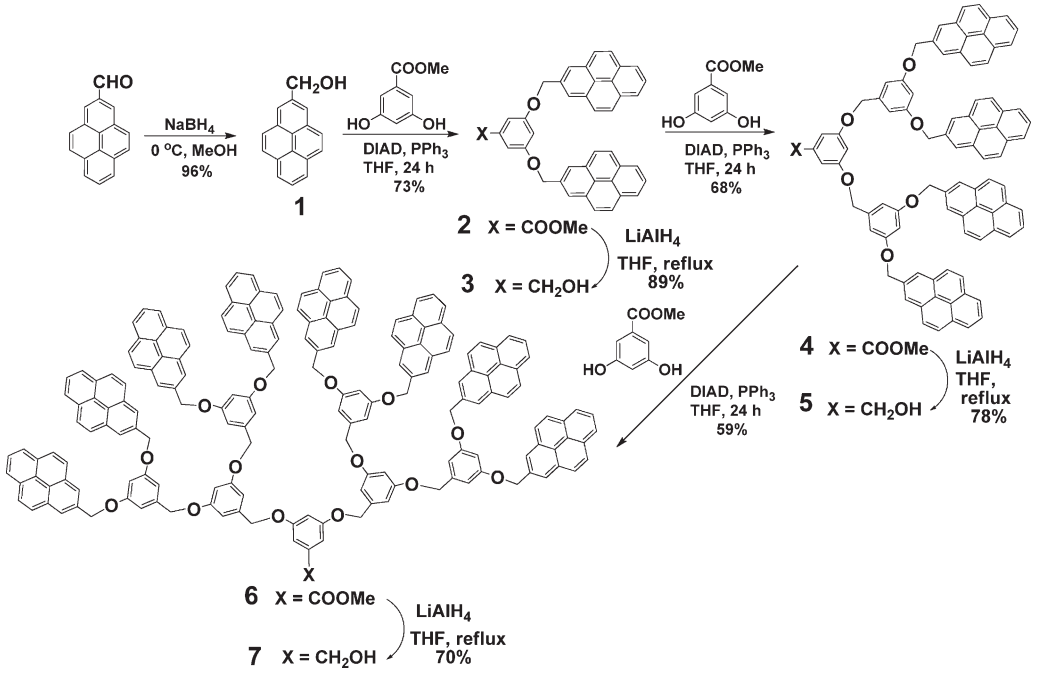
IR (KBr): $\nu = 3\,578, 3\,076, 3\,067, 3\,028, 2\,930, 2\,870, 1\,576, 1\,467, 1\,372, 1\,165, 1\,054\ cm^{-1}$. ^1H NMR (DMSO-d_6, 300 MHz): $\delta = 4.33$ (s, 2H), 5.02 (s, 2H), 5.23 (d, 16H), 5.48 (s, 8H), 6.07–6.20 (m, 21H), 8.02–8.38 (m, 72H, pyrene H). MALDI-TOF MS $m/z = 2\,584$ [M^+]. $C_{185}H_{124}O_{15}$: Calcd. C 85.89, H 4.83, O 9.28; Found C 85.67, H 4.76.

Results and Discussion

Synthesis of Dendrons, Core and Dendrimers

The dendrimers reported in this paper consist of pyrene moieties as the energy donor at the periphery, 3,5-dihydroxybenzyl alcohol units as the non-conjugated repeat unit and DCM-based chromophore units as the core. Synthesis of these dendrimers was approached in a modular fashion using the convergent approach. Thus, the pyrene containing dendrons and the DCM-based core chromophore containing two phenolic functionalities were synthesized separately and then assembled in the last step.

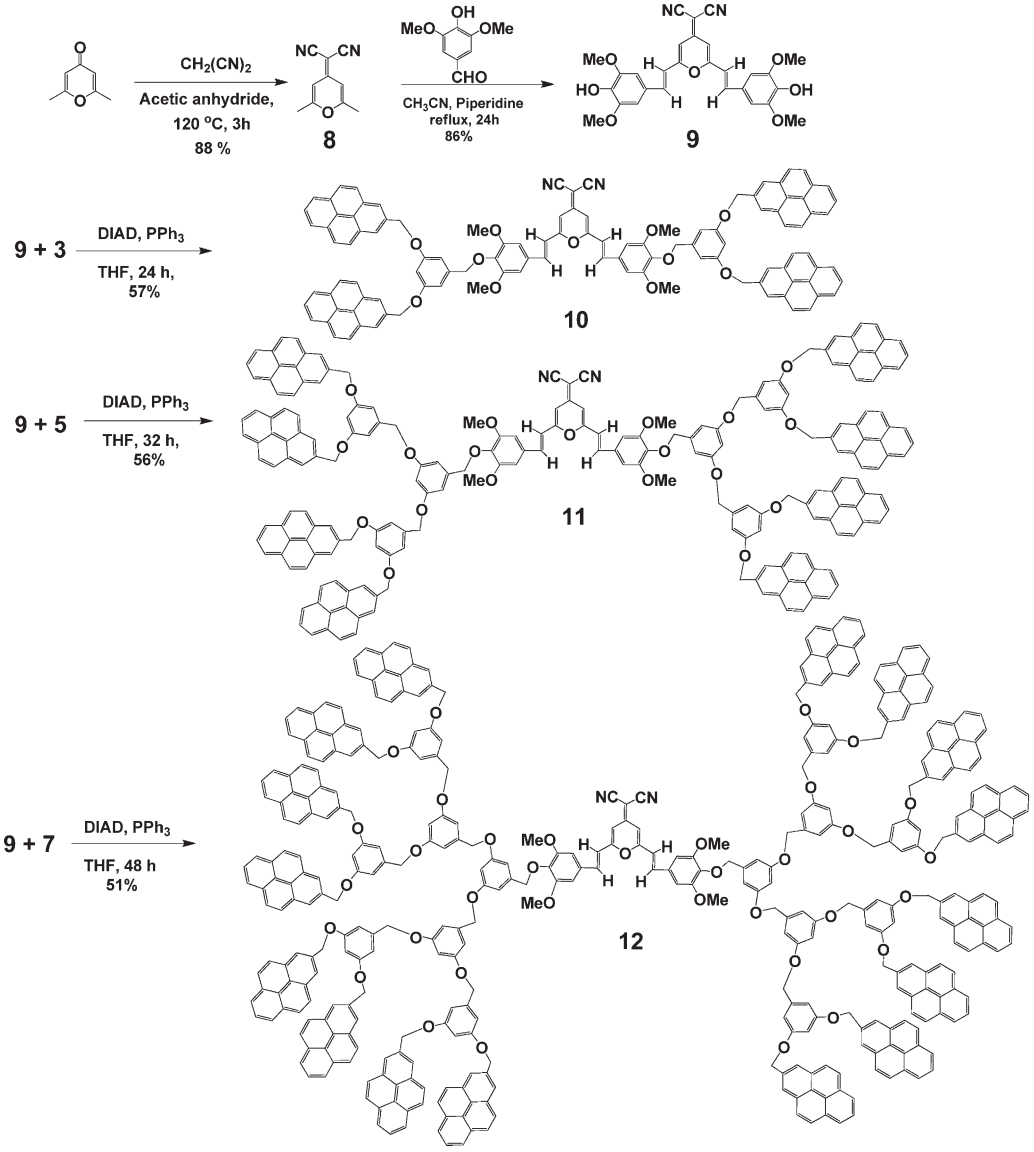
Scheme 1 describes the synthesis of **G1** (**3**), **G2** (**5**) and **G3**-dendrons (**7**), which are building components for the



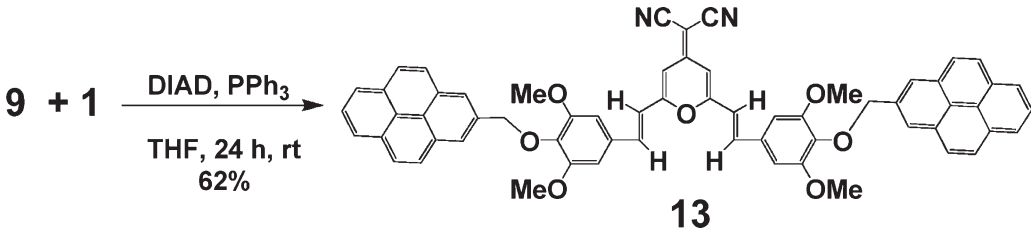
Scheme 1. Synthesis of first, second and third generation benzyl ether dendrons with pyrene end group.

construction of **G1** (**10**), **G2** (**11**) and **G3** dendrimers (**12**), respectively. Synthesis of peripheral unit (**1**) was achieved by the reduction of pyrene 1-carboxaldehyde using $NaBH_4$. This compound was then used in combination with 3,5-dihydroxymethyl benzoate for the further elaboration in to the dendrons. Since Mitsunobu etherification reaction and other functional group transformations involved in the synthesis of **G2** and **G3** dendrons were similar to that involved in the synthesis of **G1** dendron, the experimental procedures adopted for the latter case were replicated for the former cases.

Scheme 2 describes the synthesis of core molecule and bidendron dendrimers up to third generation. 2-(2,6-bis{2-[(4-hydroxy-3,5-dimethoxy)phenyl]vinyl}-4H-pyran-4-ylidene)malononitrile (**9**) was chosen as a symmetrical bifunctional core molecule, because it can form benzyl ether spacer group when condensing with dendrons. Synthesis of core (**9**) was achieved by two step procedures. In the first step, pyrone and malononitrile were condensed in acetic anhydride under reflux condition and this reaction afforded (2,6-dimethyl-4*H*-pyran-4-ylidine)propanedinitrile (**8**) in 68% yield. The second step involved Knoevenagel condensation of 3,5-dimethoxy-4-hydroxybenzaldehyde with (2,6-dimethyl-4*H*-pyran-4-ylidine)propanedinitrile (**8**), using piperidine as catalyst and CH_3CN as solvent resulted the phenolic chromophore core (**9**) in 86% yield. Finally the benzyl alcohol functionalized **G1** (**3**), **G2** (**5**) and **G3** dendrons (**7**) were treated with core (**9**) applying identical experimental conditions to obtain **G1** (**10**), **G2** (**11**) and **G3** (**12**) dendrimers, respectively. The time required



Scheme 2. Synthesis of core molecule, first, second, third generation benzyl ether dendrimers with pyrene end group.



Scheme 3. Synthesis of model compound.

for the completion of the reaction was increased with increasing the generation number of dendron used. For instance, the formation of model compound (**13**) (Scheme 3) and **G1** dendrimer needed 24 h, while **G2** and **G3** dendrimers were obtained over 32 and 48 h respectively. In the case of **G3**-dendrimer, even if the reaction time was prolonged to 48 h, a small quantity of core chromophore (**9**) and **G3** dendron (**7**) precursors were still remained. All the dendrimers were purified by simple column chromatographic technique.

Characterization

The structures of the **G1**, **G2**, **G3**-pyrene-CH_2OH dendrons (**3**, **5**, **7**), their precursors **G1**, **G2**, **G3**-pyrene-COOMe (**2**, **4**, **6**), **G1**, **G2**, **G3** dendrimers (**10**, **11**, **12**), and model compound (**13**), were confirmed by FTIR, ^{1}H NMR, MALDI-TOF MS spectra and elemental analyses. Figure 1 shows the representative FTIR spectrum of benzyl ether dendrimer with pyrene end groups. The absorption peak at around 2 918 cm^{-1} corresponds to C–H stretching vibration of saturated hydrocarbon, the absorption peak at around 2 208 cm^{-1} corresponds to C≡N stretching vibration and weak absorption peaks at around 3 061 cm^{-1} and relatively strong absorption at around 943 cm^{-1} corresponds to C–H stretching and out of plane bending motions of *trans*-vinylene, respectively.[24,25] The ^{1}H NMR spectra show well separated and clearly assignable signals for all types of protons including aromatic pyrene protons as well as benzylic and methoxy protons in the dendrons and core moieties, respectively. All the dendrons and dendrimers show characteristic benzylic protons between $\delta = 4.34$ and 5.57. **G1** dendron (**3**), **G2** dendron (**5**) and **G3** dendron (**7**) exhibited a peak around $\delta = 5.41$ which is characteristic of the benzylic proton of the benzyl alcohol group present at the focal point. The resonances of the DCM protons, vinylic protons, methoxy protons present in the core molecule of **G1**–**G3** dendrimers were observed distinctly as a singlet at $\delta = 6.75$, two doublets at $\delta = 7.29$ and 7.69 and a singlet at $\delta = 3.83$, respectively (Figure 2a–c), they were absent in the dendrons. For higher generation dendrimers, all aromatic signals could not be distinguished due to strong signal overlap, but the intensity ratios between aromatic and aliphatic signals were well matched to the expected value.

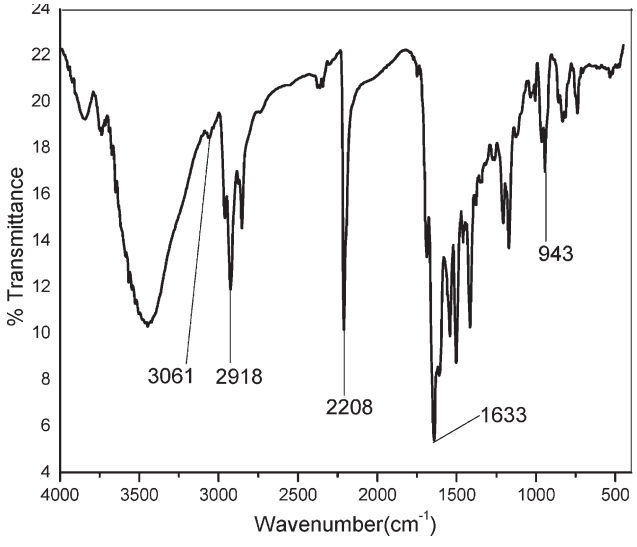


Figure 1. FTIR spectrum of **G3** dendrimer.

The monodispersity of the described dendrimers could easily be verified by MALDI-TOF mass spectrometry. The calculated and experimentally determined *m/z* values were in good agreement for all the dendrimers, even for third generation dendrimer with a molecular weight of 5 638 $g \cdot mol^{-1}$. All the dendrimers exhibited the expected molecular ion peak as $[M^+]$ or $[M^+ + H^+]$ or $[M^+ + 2H^+]$ (Figure 3a–c) and peaks arising from incomplete substitution reactions were not detected. The purity of dendrimers was also confirmed by GPC using THF as eluent. As shown in Figure 4, the retention time decreases gradually with the increasing molecular weight from **G1** to **G3** dendrimer, and all the peaks were symmetrical and monomodal with a polydispersity index of 1.1–1.2.

The thermal stability of the dendrimers was studied by TGA and the thermograms are given in Figure 5. It was observed that on increasing the generation from **G1** to **G3**, the thermal stability was also found to increase. The **G2** and **G3** dendrimers exhibit good thermal stability with an onset of degradation temperature at around 400 °C. The amount of char yield was found to be increased from **G1** to **G3** dendrimer and this observation indicates that there will not be any bond cleavage in dendron portion, but C–O bond of core molecule may be cleaved at degradation temperature

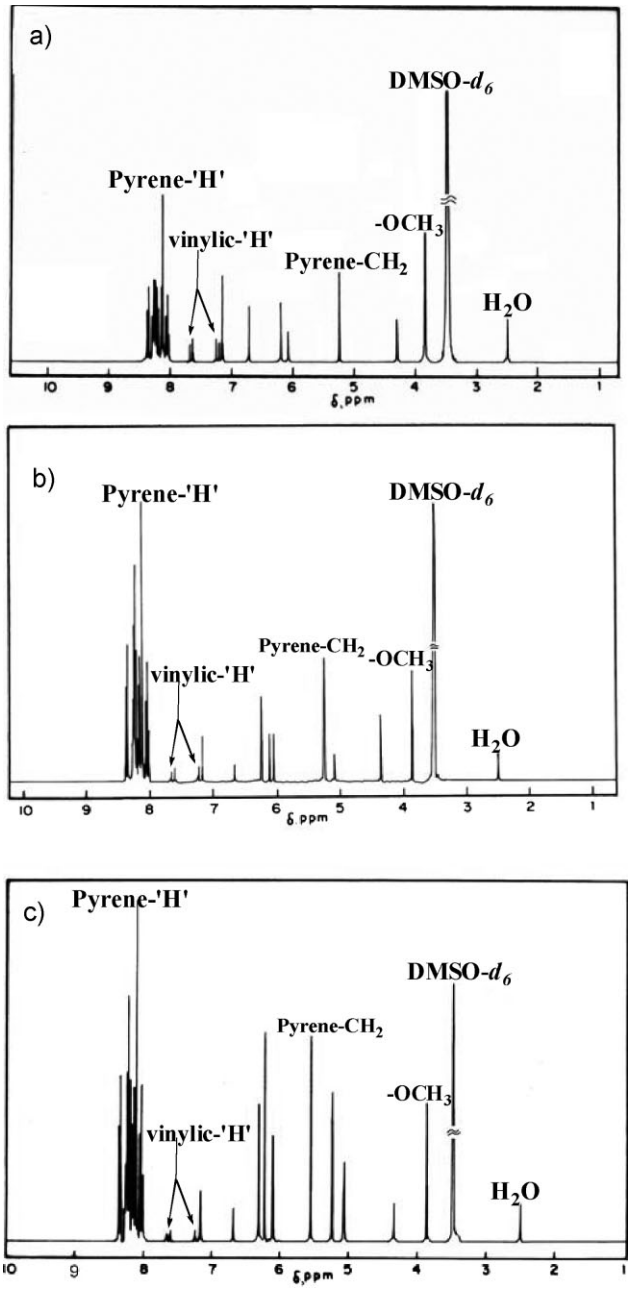


Figure 2. ^{1}H NMR spectrum of (a) **G1**, (b) **G2**, and (c) **G3** dendrimer in DMSO-d_6.

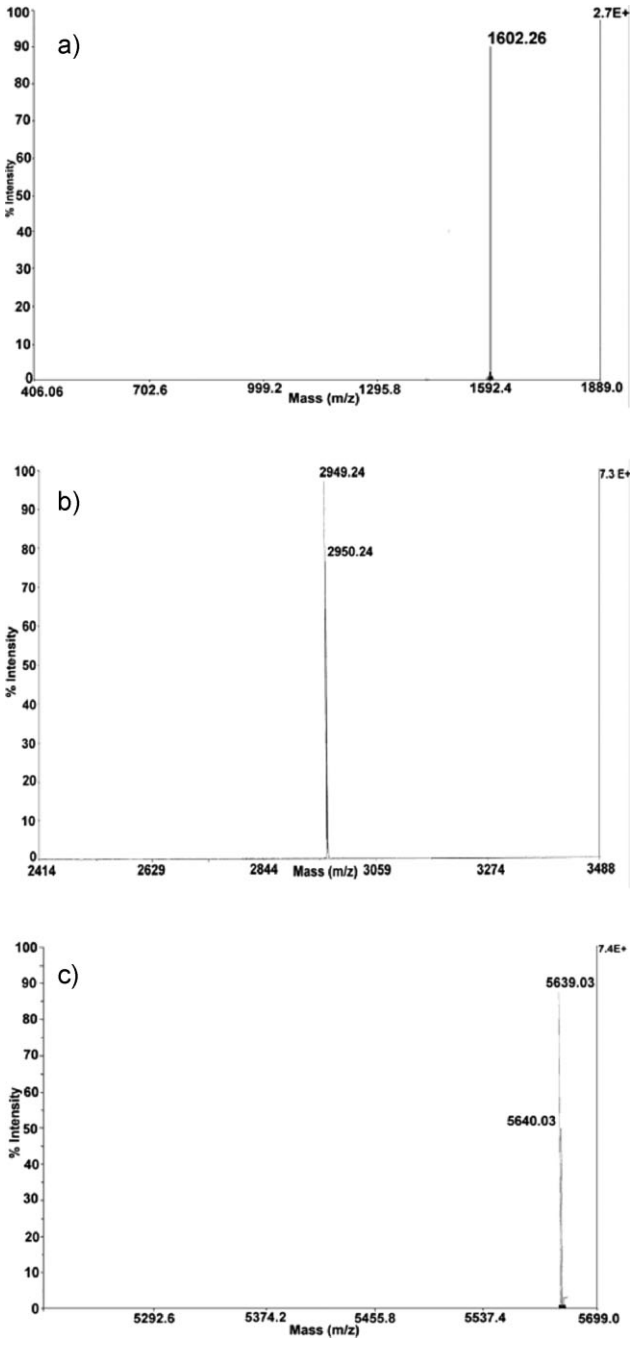


Figure 3. MALDI-TOF MS spectrum of (a) **G1**-dendrimer (b) **G2**-dendrimer and (c) **G3**-dendrimer.

range. Good thermal stability is an important requirement for the application of the dendrimers in flat panel displays.

Notably, the dendrimers synthesized with pyrene bear no alkyl groups, but they were soluble in common organic solvents such as THF, CH_3CN, dimethylformamide (DMF), dimethylacetamide (DMAc), *N*-methylpyrrolidone (NMP) and dimethyl sulfoxide (DMSO). This can be attributed to the presence of methoxy groups and ether functionality in the core and the backbone of the dendrons, respectively.

Photophysical Properties

We used both absorption and emission spectroscopy for the photophysical characterization of the dendrons, dendrimers, model compound and core, and the results like $\lambda_{max(abs)}$, $\lambda_{max(flu)}$, molar extinction coefficient (ε) and fluorescence quantum yield (Φ_{flu}) measured at two different temperatures are summarized in Table 1. Absorp-

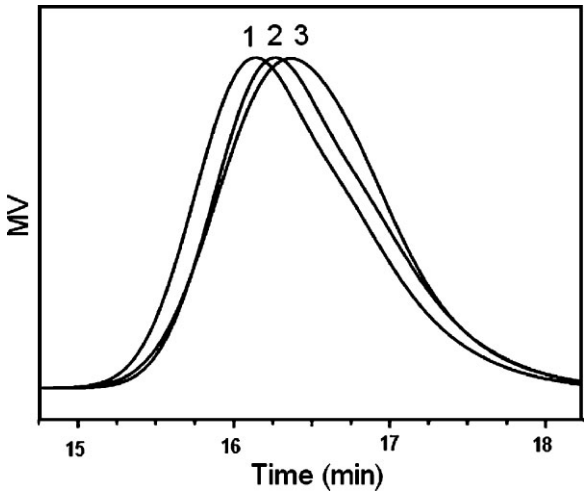


Figure 4. GPC traces of (1) **G3**, (2) **G2**, and (3) **G1** dendrimer.

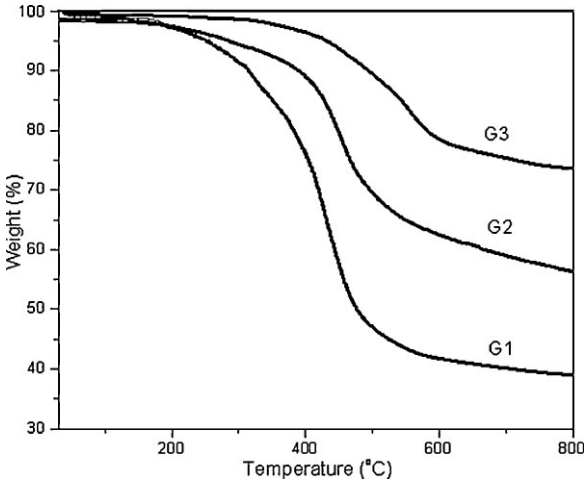


Figure 5. TGA thermograms of **G1**, **G2** and **G3** dendrimers.

tion spectra of compounds **1** (pyrene), **9** (DCM core) and **13** (model compound) are shown in fFigure 6. The spectrum of model compound **13** shows three bands at 314, 328, 344 nm and a broad band at 449 nm due to the presence of pyrene and DCM moieties respectively in the structure (Table 1); this spectrum is very well approximated by a weighted sum of compounds **1** and **9**. Similar pattern was also observed for **G1**–**G3** dendrimers (Figure 7). This provides an evidence for the lack of direct electronic communications between the pyrene periphery and DCM core in the ground electronic state.

When comparing the absorption spectra of **1** (pyrene) and **G1** through **G3** dendron, it was found that the absorbance of these compounds increased steadily with increasing generation number (figure not given). This is attributed to the increasing number of pyrene units with generation. The absorption spectrum of **G3** dendron (**7**) [ε (343 nm) = 140 000 $L \cdot mol^{-1} \cdot cm^{-1}$] was virtually identical in both shape and intensity to that of compound **1** (pyrene) [ε (343 nm) = 30 000 $L \cdot mol^{-1} \cdot cm^{-1}$]; the multiplying factor for the compound **1** was 4.66. This observation indicates that there is no significant difference in ground state interactions among the pyrenyl chromophores in compound **1**/**G1**/**G2**/**G3** dendrons.

Emission spectra of compounds **1** (pyrene) and **G1**/**G2**/**G3** dendrons are given in Figure 8 along with absorption spectrum of compound **9** (core); all these spectra were recorded at 10^{-6} M concentration. The emission spectra

Table 1. Optical properties of dendrons, dendrimers and model compounds.

Compound	$\lambda_{max\ (abs)}$ [a]	$\lambda_{max\ (flu)}$	ε [b]	Φ_{flu} [c]	
	nm	nm	$L \cdot mol^{-1} \cdot cm^{-1}$	25 °C	50 °C
G1 dendron	312, 326, 344	377, 396[d]	74 200	15.5[e]	–
G2 dendron	312, 329, 343	377, 396[d]	118 000	18.8[e]	–
G3 dendron	312, 328, 344	377, 396[d]	140 000	19.0[e]	–
core	448	570[f]	80 000	21.3[g]	–
G1 dendrimer	313, 328, 343, 449	570[f]	199 000	14.0[g]	18.6
G2 dendrimer	312, 328, 344, 448	570[f]	224 000	15.6[g]	19.5
G3 dendrimer	313, 327, 345, 448	571[f]	245 000	13.0	18.3
model compound	314, 328, 344, 449	570[f]	156 900	27.0[g]	–

[a]All spectra were recorded in THF at a concentration of 10^{-6} M; [b]In THF; [c]The quantum yields of the compounds in THF were determined using a solution of quinine sulfate (10^{-5} M in 0.1 M H_2SO_4 solution, having a quantum yield of 0.55) as a standard; [d]Spectra were recorded in THF at a concentration of 10^{-6} M by excitation with 344 nm light; [e]λ_{ex} = 344 nm; [f]Spectra were recorded in THF at a concentration of 10^{-6} M by excitation with 444 nm light; [g]λ_{ex} = 444 nm.

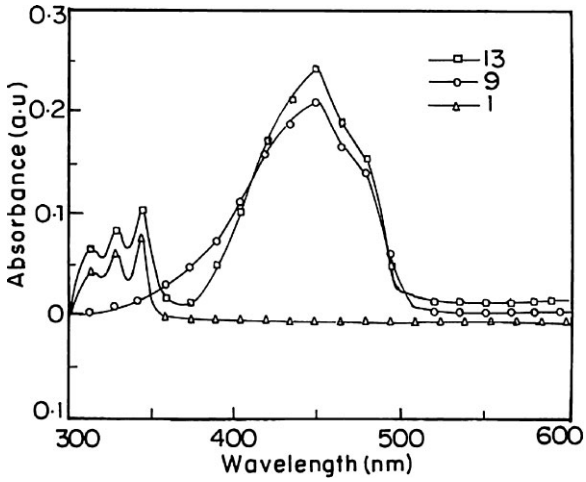


Figure 6. Absorption spectra of compounds **1**, **9** and **13**. All the spectra were recorded in THF at a concentration of 10^{-6} M.

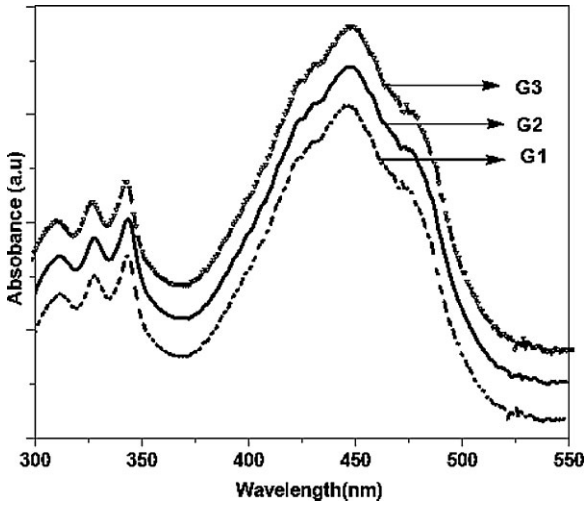


Figure 7. Absorption spectra of **G1**, **G2** and **G3** dendrimers. All the spectra were recorded in THF at a concentration of 10^{-6} M.

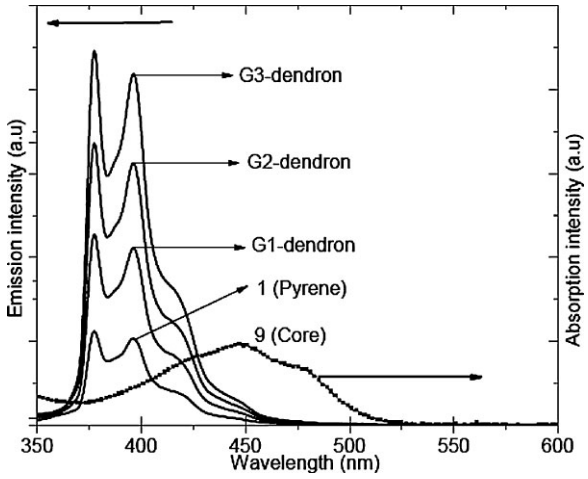


Figure 8. Emission and absorption spectra of compounds **1**, **G1**–**G3** dendrons and **9**, respectively. Note the overlap between the emission spectra of **1**, **G1**–**G3** dendrons with the absorption spectrum of **9**. All the spectra were recorded in THF at a concentration of 10^{-6} M.

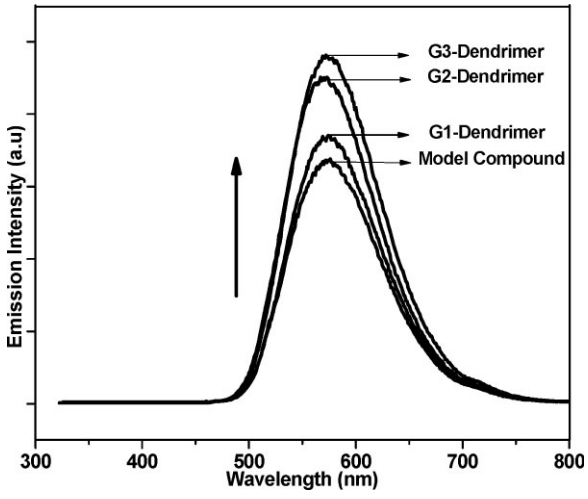


Figure 9. Emission spectra of dendrimers and model compound **13**. All spectra were recorded in THF at a concentration of 10^{-6} M by excitation with 444 nm light.

given in this figure does not show any characteristic peak for excimer formation in dendrons.[26] The overlap between the emission and absorption spectra indicates that Forster energy transfer is possible from pyrene to the DCM core. To study the energy transfer in compounds **13** (model compound), **10**, **11** and **12** (**G1**–**G3** dendrimers), emission spectra of these compounds were recorded [excitation wavelength used was 444 nm which corresponds to $\lambda_{max\ (abs)}$ of the core] and compared with the respective absorption spectra. It was observed that the emission intensity at 573 nm increased from model compound (**13**) through **G3** dendrimer (Figure 9). Increase in fluorescence intensity from **G1** to **G2** dendrimer is high compared to that of **G2** to **G3** dendrimer. The low increase in the fluorescence intensity of later molecule is due to the large distance between core and end group of **G3** dendrimer.[27] Emission from pyrene at about 377 or 396 nm was not found which implied that the emission of pyrene was almost quenched in these dendrimers. This can be attributed to the fact that there is an efficient energy transfer from the pyrene molecules present at the periphery of the dendrimers which acts as donor components to the DCM molecule present in the core which acts as the acceptor components. It is worthy to mention here that the emission spectra obtained for model compound and dendrimers when exciting these molecules at 344 nm [$\lambda_{max\ (abs)}$ of pyrene] and 444 nm (for core) were virtually identical to that of given in Figure 9.

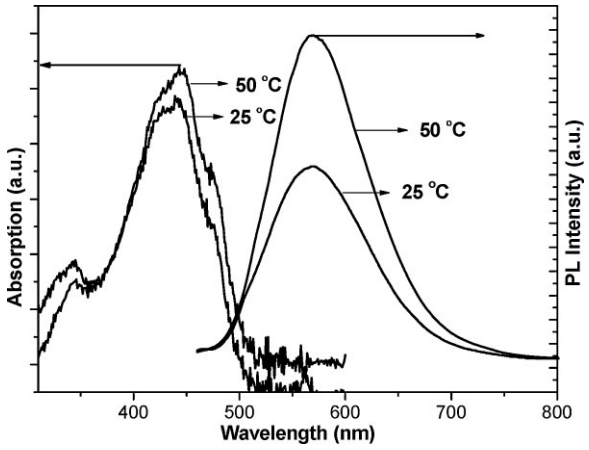


Figure 10. Absorption and emission spectra of **G3** dendrimer (10^{-6} M in trichloroethane) at 25 and 50 °C. Emission spectra were recorded by excitation with 444 nm light.

The fluorescence quantum yield (Φ_{flu}) of all the compounds were found to be ranged from 13 to 27% in THF. No significant correlation between quantum yield and generation number can be deduced from these values. The low quantum yield of dendrimers compared to that of model compound may be due to more efficient self quenching by non-radiative pathway.

Fluorescence spectroscopy is a well-established method for detecting aggregated molecules at various temperatures. It has been reported that the absorption and emission spectrum will be changed when micellization occurs.[28] In order to study the effect of temperature on aggregate formation in pyrene based dendrimers, we measured the absorption and emission spectra of these dendrimers at two different temperatures viz. 25 and 50 °C at a concentration of 10^{-6} M in trichloroethane (Figure 10). Careful analysis and comparison of these spectra with a relevant reported work[26] gave a conclusion that there was no aggregation in the dendrimers at the concentration studied. The quantum yield measured at 50 °C for **G1**–**G3** dendrimers are also included in the Table 1 and found that the values are high as expected due to more number of molecules undergo excitation upon heating.

Conclusion

In the present study, a novel class of dendrimers containing a 2-pyran-4-ylidene-malononitrile (DCM) moiety as the centre chromophore and pyrene as the peripheral chromophore were designed and synthesized through the Mitsunobu coupling reaction in high yield up to third generation. These dendrimers shown excellent thermal stability and good red emission properties. It was found that the energy transfer takes place from donor chromophore (i.e., pyrene molecules) present at the periphery to the acceptor chromophore (i.e., DCM moiety) present at the centre of the dendrimers. The emission intensity corresponding to DCM moiety was found to be increased with increasing the generation number of the dendron attached to it.

Acknowledgements: M. V. thanks the *National Science Council (NSC) of Taiwan* for financial support.

Received: October 28, 2010; Revised: January 7, 2011; Published online: February 21, 2011; DOI: 10.1002/macp.201000674

Keywords: dendrimers; fluorescence; FRET; light harvesting; star polymers

[1] J. M. Lupton, I. D. W. Samuel, R. Beavington, P. L. Burn, H. Bässler, *Adv. Mater.* **2001**, *13*, 258.
[2] P. L. Burn, S. C. Lo, I. D. W. Samuel, *Adv. Mater.* **2007**, *19*, 1675.
[3] M. E. Köse, W. J. Mitchell, N. Kopidakis, C. H. Chang, S. E. Shaheen, K. Kim, G. Rumbles, *J. Am. Chem. Soc.* **2007**, *129*, 14257.
[4] [4a] S. Hecht, J. M. J. Frechet, *Angew. Chem., Int. Ed.* **2001**, *40*, 74; [4b] G. R. Newkome, E. F. He, C. N. Moorefield, *Chem. Rev.* **1999**, *99*, 1689; [4c] D. Astruc, F. Chardac, *Chem. Rev.* **2001**, *101*, 2991.
[5] [5a] J. P. J. Markham, S. C. Lo, S. W. Magenis, P. L. Burn, I. D. W. Samuel, *Appl. Phys. Lett.* **2002**, *80*, 2646; [5b] T. D. Anthopoulous, J. P. J. Markham, B. Namdas, J. R. Lawrence, I. D. W. Samuel, S. C. Lo, P. L. Burn, *Org. Electron.* **2003**, *4*, 71.
[6] P. Furuta, J. M. J. Frechet, *J. Am. Chem. Soc.* **2003**, *125*, 13173.
[7] [7a] T. Förster, *Discuss. Faraday Soc.* **1959**, *27*, 7; [7b] N. J. Turro, *Modern Molecular Photochemistry*, University Science Books, Sausalito 1991.
[8] [8a] I. Carmichael, G. L. Hug, *Handbook of Photochemistry*, 2nd edition, Marcel Dekker, New York 1993; [8b] J. B. Birks, *Photophysics of Aromatic Molecules*, Wiley Interscience, London 1970.
[9] [9a] E. M. S. Castanheira, J. M. G. Martinho, *Chem. Phys. Lett.* **1991**, *185*, 319; [9b] D. C. Dong, M. A. Winnik, *Can. J. Chem.* **1984**, *62*, 2560.
[10] A. Thomas, S. Polarz, M. Antonietti, *J. Phys. Chem. B* **2003**, *107*, 5081.
[11] For OLEDs in general see, for example: [11a] A. P. Kulkarni, C. J. Tonzola, A. Babel, S. A. Jenekhe, *Chem. Mater.* **2004**, *16*, 4556; [11b] L. S. Hung, C. H. Chen, *Mater. Sci. Eng., R* **2002**, *39*, 143; [11c] M. T. Bernius, M. Inbasekaran, J. O'Brien, W. S. Wu, *Adv. Mater.* **2000**, *12*, 1737; [11d] Y. Cao, I. D. Parker, G. Yu, C. Zhang, A. J. Heeger, *Nature* **1999**, *397*, 414; For pyrene containing devices, see: [11e] W. L. Jia, T. McCormick, Q. D. Liu, H. Fukutani, M. Motala, R. Y. Wang, Y. Tao, S. N. Wang, *J. Mater. Chem.* **2004**, *14*, 3344; [11f] R. V. Cimrov, D. Výprachticky, *Appl. Phys. Lett.* **2003**, *82*, 642; [11g] Y. Aso, T. Okai, Y. Kawaguchi, T. Otsubo, *Chem. Lett.* **2001**, 420.
[12] C. Li, Z. Bo, *Polymer* **2010**, *51*, 4273.
[13] T.-S. Ahn, A. Nantalaksakul, R. R. Dasari, R. O. Al-Kaysi, A. M. Muller, S. Thayumanavan, C. J. Bardeen, *J. Phys. Chem. B* **2006**, *110*, 24331.

[14] Q. Peng, Z. Y. Lu, Y. Huang, M. G. Xie, S. H. Han, J. B. Peng, Y. Cao, *Macromolecules* **2004**, *34*, 260.
[15] M. Berggren, O. Inganäs, G. Gustaffusson, J. Rasmusson, M. R. Andersson, T. Hjertberg, O. Wennerström, *Nature* **1994**, *372*, 444.
[16] M. R. Andersson, M. Berggren, O. Inganäs, G. Gustaffusson, J. C. Gustafsson-Carberg, D. Selec, T. Hjertberg, O. Wennerström, *Macromolecules* **1995**, *28*, 7525.
[17] US 5908581 (1999), invs.: C. H. Chen, K. P. Klubek, J. Shi.
[18] US 5935720 (1999), invs.: C. H. Chen, K. P. Klubek, J. Shi.
[19] C. T. Chen, *Chem. Mater.* **2004**, *16*, 4389.
[20] B.-J. Jung, J.-I. Lee, H. Y. Chu, L.-M. Do, J. Lee, H. K. Shim, *J. Mater. Chem.* **2005**, *15*, 2470.
[21] C. H. Cheon, S. H. Joo, K. Kim, J.-I. Jin, H. W. Shin, Y. R. Kim, *Macromolecules* **2005**, *38*, 6336.
[22] G. W. Kim, M. J. Cho, Y. J. Yu, Z. H. Kim, J. Jin, D. Y. Kim, D. H. Choi, *Chem. Mater.* **2007**, *19*, 42.
[23] L. L. Woods, *J. Am. Chem. Soc.* **1958**, *80*, 1440.
[24] D. R. Gagnon, J. D. Capistran, F. E. Karasz, R. W. Lenz, S. Aatoun, *Polymer* **1987**, *8*, 567.
[25] Z. Bao, Y. Chen, R. Cai, L. Yu, *Macromolecules* **1993**, *26*, 5281.
[26] M. Kastler, V. Enteelmann, M. Baumgarlen, K. Mullen, *Chem. Eur. J.* **2006**, *12*, 6117.
[27] A. Adronov, J. M. J. Frechet, *Chem. Commun.* **2000**, 1701.
[28] A. Ajayaghosh, C. Vijayakumar, C. K. Praveen, S. Santhosh Babu, R. Varghese, *J. Am. Chem. Soc.* **2006**, *128*, 7174.