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PAPER

Luminescent micro and nanogel formation from AB₃ type poly(aryl ether) dendron derivatives *without* conventional multi-interactive gelation motifs†

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We report the synthesis, gelation and photophysical properties of luminescent AB₃ type poly(aryl ether) dendron derivatives in the absence of conventional multi-interactive gelation motifs. The gelation process is controlled through employing partial polar solvent milieu, which significantly enhances the propensity of π - π interaction between the aryl units present in the system. The self-assembly leads to unprecedented gelation through entrapping solvent molecules in the fibrillar arrangement of poly(aryl ether) units. The strategy was further utilized to prepare an excimer based photoluminescent gel through incorporating anthracene units in the dendrons. The close proximity between the anthracene units in the gel renders the formation of anthracene excimers at room temperature, resulting in the emission of bright green light from the gel, upon UV excitation. The study suggests that the size and packing of the self-assembled fibre can be controlled by the generation and functional groups present in the dendron. Furthermore, the strategy envisages an easy approach to generate fluorescent Low Molecular-mass Organic Gelator (LMOG) through incorporating poly cyclic aromatic hydrocarbon units to the poly(aryl ether) dendrons, since the self-assembly is largely guided by π - π interactions.

Introduction

Study of self-assembly by organic molecules has gained increasing attention due to the potential applications of such molecular systems in developing functional soft materials.^{1–6} For example, the remarkable self-assembling property of tetrathiafulvalene,^{7,8} oligothiophene,^{9,10} and diacetylene^{11–13} in a fibrillar fashion can potentially lead to the formation of molecular wires and field-effect transistors. In general, multiple non-covalent interactions such as hydrogen bonding, π - π interactions, and/or ionic interactions have been utilized for the self-assembly of molecules to generate functional soft materials.^{14–19} In this context, dendrimers and dendrons deserve special attention since the feasibility of multiple interactions is very high in such systems due to their well-known fractal geometry. Self-assembly in dendrimers has been intensively investigated due to their potential candidacy in soft matter chemistry and numerous structural patterns have already been recognized in this regard.^{20–28} Recently, organogelators based on dendrimers and/or dendrons have also gained much interest because of the unique nature of multiple

non-covalent interactions among the dendrons, which can ‘immobilize’ the solvent milieu, thereby generate gel systems with tunable properties.^{29–31}

In the reported cases of dendritic gelators, presence of large number of amide functional groups, long alkyl chains and/or peripheral functional groups for specific ‘head’-to-‘tail’ interaction were essential for effective gel formation.^{32–37} A recent report from Zhang and Fan describes the self-assembly of tetraphenylethene, perylenediimide, and spiropyran functionalized poly(aryl ether) dendron derivative to a photoresponsive organogel.^{38a,b} However, the design of organogelators, particularly dendritic gelators, with no conventional gelation motifs such as peptide, long alkyl chains, steroidal groups *etc.* remains as a great challenge to date,^{38c,d} even though such gelators have better potential applications in optoelectronic systems.³⁷

Herein, we report the unprecedented gel formation through the self-assembly of AB₃ type (also known as Percec type) poly(aryl ether) dendrons containing *no* long alkyl chains or bulky substituents. While Percec type dendrons have been known for their self-assembly and gelation properties,^{39,40} most of the reported cases utilized multiple non-covalent interactions for the gel stability. In the present study, a series of poly(aryl ether) dendron derivatives were selected (Chart 1) and the self-assembly is invoked through π - π interactions, which was controlled by the polarity of the medium. The results from the present study suggest that π - π interactions

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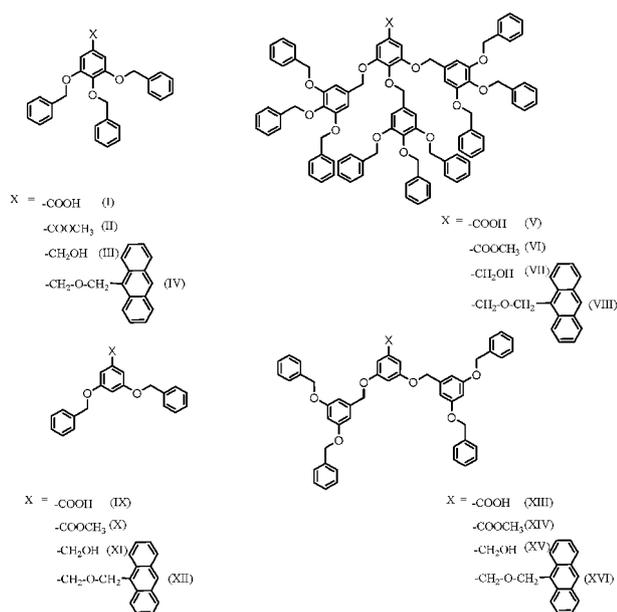


Chart 1 Structure of AB₃ and AB₂ type poly(aryl ether) dendron derivatives utilized in the present study.

predominate when partial polar medium is employed through proper solvent mixtures, which leads to a remarkable columnar type self-assembly in poly(aryl ether) dendron derivatives without conventional gelation motifs. The close packing of the poly(aryl ether) units enhances the feasibility of the excimer formation upon photo-excitation of the gel.⁴¹ To the best of our knowledge, this is the first example of excimer based fluorescent low-molecular-mass organogelators (LMOG) by poly(aryl ether) dendrons, in the absence of usual gelating motifs. Most importantly, the present study demonstrates the importance of π - π interactions, which *alone* can be successfully utilized for a columnar gel formation in the case of poly(aryl ether) dendron derivatives. Extensive investigation based on scanning electron microscopy (SEM), atomic force microscopy (AFM) and X-ray diffraction (XRD) studies have been carried out to understand the morphology and molecular arrangement in the gel structure. The fluorescence properties of the gels were investigated using steady state fluorescence measurement techniques.

Table 1 Gelation properties and critical gel concentrations (CGCs) of the poly(aryl ether) dendrons in various organic solvents and solvent mixtures at 25 °C. The solvent ratio is specified in parentheses. S = solution, G = gel, PG = partial gel

Solvent	I	II	III	V	VI	VII
CH ₂ Cl ₂ :hexane	G (8.5 mg mL ⁻¹) (2:1)	S	G(18 mg mL ⁻¹) (1:3)	G(2 mg mL ⁻¹) (1:3)	G(5 mg mL ⁻¹) (1:5)	PG
CHCl ₃ :hexane	G(10 mg mL ⁻¹) (2:1)	S	G(17 mg mL ⁻¹) (1:3)	G(2.5 mg mL ⁻¹) (1:3)	G(4 mg mL ⁻¹) (1:5)	PG
CHCl ₃ :CCl ₄	G(3 mg mL ⁻¹) (1:8)	S	S	G(4 mg mL ⁻¹) (1:8)	S	PG
Ethyl acetate:hexane	G(5.7 mg mL ⁻¹) (3:2)	G(50 mg mL ⁻¹) (1:3)	G(25 mg mL ⁻¹) (1:3)	G(4 mg mL ⁻¹) (1:1)	G(3.5 mg mL ⁻¹) (1:5)	PG
THF:hexane	G(10 mg mL ⁻¹) (3:1)	S	G(20 mg mL ⁻¹) (1:3)	G(4 mg mL ⁻¹) (1:1)	G(6 mg mL ⁻¹) (1:4)	PG
Dioxane:hexane	G(10.5 mg mL ⁻¹) (3:1)	S	G(22 mg mL ⁻¹) (1:3)	G(4.5 mg mL ⁻¹) (1:1)	G(8 mg mL ⁻¹) (1:5)	PG

Results and discussion

Chart 1 contains the structure of the poly(aryl ether) dendron derivatives ((AB)₃-G1, (AB)₃-G2, (AB)₂-G1, and (AB)₂-G2 series, where G represents the generation of the dendrimer utilized in the present study.

All the sixteen poly(aryl ether) dendron derivatives were synthesized according to a reported procedure⁴² with slight modifications. The characterization was carried out using ¹H NMR, ¹³C NMR and mass spectrometry (the synthetic procedure and spectral data are given in the Experimental section as well as in the ESI[†]).

Gel formation by the dendrons

The gelation behavior of the molecules in Chart 1 was evaluated in a series of organic solvents and solvent mixtures. The experimental results suggest that for the compound in the AB₃ series (both G1 and G2), the compounds prefer to form a gel in solvent mixtures, rather than in pure solvents. For example, compound V is completely soluble in dichloromethane and practically insoluble in hexane at identical concentration. However, V readily forms a gel in a dichloromethane:hexane mixture (1:3% v/v), above the critical gel concentration (CGC), which was 2 mg mL⁻¹.⁴³ Similar observations were made for other AB₃ compounds in Chart 1, suggesting that polarity of the medium plays a pivotal role in enhancing the gelation process in poly(aryl ether) derivatives. The solubility data along with the critical gel concentration (CGC) of the compounds are given in Table 1. The lowest value of CGC obtained was 2 mg mL⁻¹ for compound V in the dichloromethane:hexane mixture (1:3% v/v).

A careful examination of the data in Table 1 indicates that the propensity to form gel is greatly enhanced in the second generation (G2) poly(aryl ether) dendrons, compared to that in the first generation (G1). It is also clear from the table that the presence of an alcoholic group does not favor the gelation in the second generation (G2) AB₃ dendron series (compounds V, VI and VII). In order to explore the effect of functional groups on the gelation process in G2 AB₃ series, we have compared the physical properties of V with VI and VII, where the carboxylic acid functional group is replaced by methyl ester and alcohol, respectively. Differential scanning calorimetry (DSC) experiments indicate that the melting point follows the order VII < VI < V (63 °C, 87 °C and 150 °C,

respectively). Parallel to this observation, we have noted that **VII** forms partial gels in all the solvent mixtures examined and **VI** forms gel only through sonication. This indicates that the two point hydrogen bonding interaction enhances the propensity of the self-assembly and gel formation in **V**, compared to the dipole–dipole interaction in **VI** and relatively less strong hydrogen bonding in **VII**. The importance of the hydrogen bonding in the gel formation was evident in the first generation (**G1**) AB_3 series also. Quite contrary, the first and second generation of AB_2 type poly(aryl ether) dendrons ($(AB)_2$ -**G1** and $(AB)_2$ -**G2** series) bearing carboxylic acid functional groups (**IX** and **XIII**, Chart 1) exhibited little gelation properties in any of the solvent mixtures utilized in the study, even at relatively higher concentrations. This suggests that the cooperative effect originated from the hydrogen bonding and π – π interactions leads to the gelation in the present study. It has been recognized that relatively weak π – π interactions can stabilize supramolecular aggregates due to their presence in sheer large numbers.^{44–46}

NMR study to probe the π – π interactions

Since the preliminary results indicate that π – π interactions in the poly(aryl ether) dendron derivatives might be crucial, the presence of π – π interaction in **V** was closely examined by ¹H-NMR spectroscopy. The compound was dissolved in $CDCl_3$ in the presence of increasing concentrations of hexane (from 10 to 80% v/v). The NMR spectra for compound **V** in the presence of increasing amount of hexane is given in Fig. 1. As anticipated, the aromatic as well as benzyl protons in **V** were shifted up-field due to the enhanced self-assembly through π – π interactions in the increased non-polar environment (Fig. 1).³⁶ The peaks at 7.2, which correspond to the benzyl ring proton were shifted up field by 0.12 δ . Also, peaks at 4.9 and 6.7 were also up field shifted in the presence of hexane. The shifts for the entire peak were monitored using TMS signal as the reference. Also, above 70% v/v of hexane, NMR experiments could not be performed due to the sudden gel formation by the system in the NMR tube.

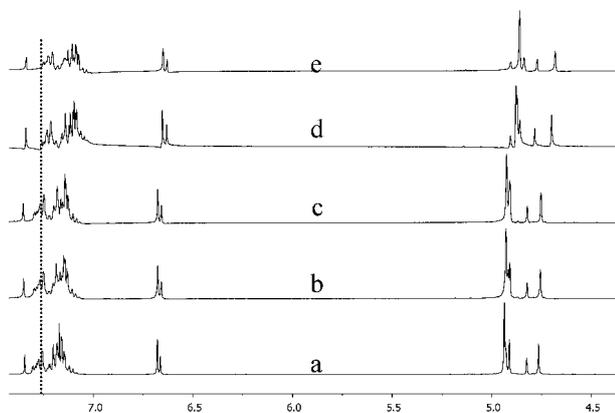


Fig. 1 NMR spectra of **V** (concentration: 4 mg mL⁻¹) in $CDCl_3$ in the presence of increasing amount of hexane. From a to e, the mol% of hexane increases from 10%, 20%, 30%, 50% and 60%, respectively.

SEM and AFM imaging study

The unprecedented solvent induced self-assembly by tri-substituted poly(aryl ether) dendron derivatives without conventional gelation motifs was further examined through scanning electron microscopy (SEM) and the images clearly show intensely packed nano-fibrils of the self-assembled poly(aryl ether) dendron derivatives. Fig. 2 shows the SEM images of compounds **I–III** and **V**. As clear from the figure, all compounds show amazingly well defined fibrillar type self-assembly. The self-assembly confined to a definite shape has direct impact on the gelation properties of the system. For example, the SEM images of compound **VI** does not indicate fibrillar type assembly, even though undefined self-assembly was evident from the SEM images (Fig. S1, ESI[†]). Corollary to this, no gelation was observed in the case of **VI** until the system is sonicated. This observation was identical for anthracene substituted second generation AB_3 type poly(aryl ether) dendrons as well (*vide infra*), suggesting that the self-assembly of poly(aryl ether) dendrons in the fibrillar fashion enables them to easily contain the solvent molecules inside the entangled fiber-like segments.

Furthermore, a parallel AFM analysis also revealed the formation of well-defined fibrils by the poly(aryl ether) dendron derivatives, which are entangled to each other, upon gel formation. Fig. 3 contains the AFM images of all compounds exhibiting gelation. The images show fibers with two distinct heights: one set with 150–200 nm and another with 50–80 nm. The AFM images clearly illustrate a correlation between the fiber thickness of the self-assembled poly(aryl ether) dendron derivatives and the dendron generation. For example, while the compound in the **G1** series forms fibers with approximately 1 μ m width, the fiber width from compounds in the **G2** series is only a few nanometres (110 nm). This could be presumably due to the closely packed molecular arrangement in **G2** dendrons as a result of the enhanced π – π interactions between the relatively large numbers of aryl units present, compared to that in the **G1** dendron.

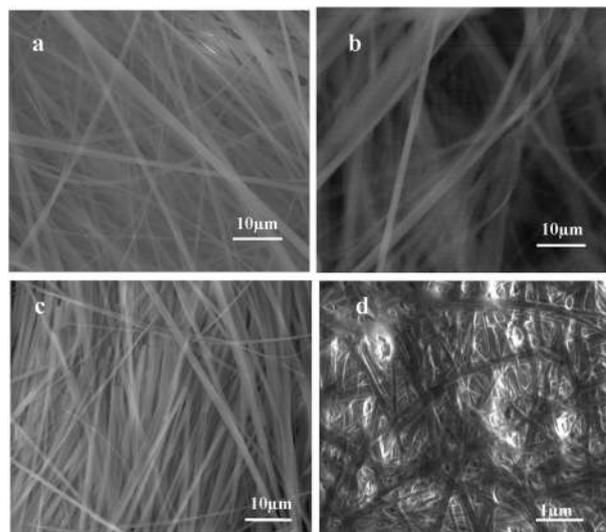


Fig. 2 SEM images of compounds (a) **I**, (b) **II**, (c) **III**, (d) **V**.

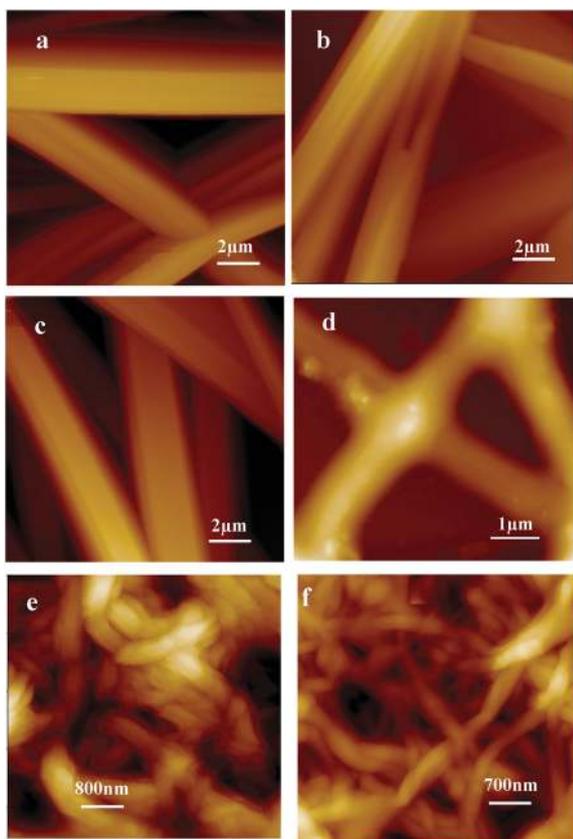


Fig. 3 AFM images of compounds (a) **I**, (b) **II**, (c) **III**, (d) **IV**, (e) **V** and (f) **VI**.

The results from SEM and AFM taken together suggest that poly(aryl ether) dendron derivatives in the AB₃ series (both first and second generations) self-assemble in suitable solvent mixtures into well-defined fibrillar type arrangement. Since solvent molecules can be contained well inside the entangled fibrillar assembly, gelation was a natural outcome of the self-assembly. Fig. S1 (ESI[†]) shows the photographs of compound **V** in dichloromethane : hexane mixture (1 : 3% v/v), below and above the critical gel concentration (*a* and *b* respectively).

XRD analysis of the gel

In order to understand the molecular packing pattern of the self-assembly, X-ray diffraction pattern of the compounds shown in Chart 1 was analyzed. A peak in the wide angle region characteristic of a typical π - π stacking distance of 3.6 Å was observed in all the X-ray diffraction patterns (Fig. 4, Fig. S2 to S3, ESI[†]).³⁶ Fig. 4 shows the XRD pattern of **V**, which follows the scattering vector ratio of 1 : $\sqrt{3}$: $\sqrt{4}$: $\sqrt{7}$ in the low angle region, indicating a columnar hexagonal lattice with $a = b = 30.46$ Å, where *a* and *b* are the lattice parameters.⁴⁷ It can be envisaged that the molecules self-organize in a columnar hexagonal (Col_h) fashion through stacking the dimer of **V**, where the hydrogen bonded carboxyl groups are located in the middle of the column. The hexagonal columnar phase with a column diameter of 30.46 Å was consistent with the results obtained from geometry optimization, which was performed using DFT at the B3LYP 3-21G level of theory with the Gaussian 03 suite of programs.

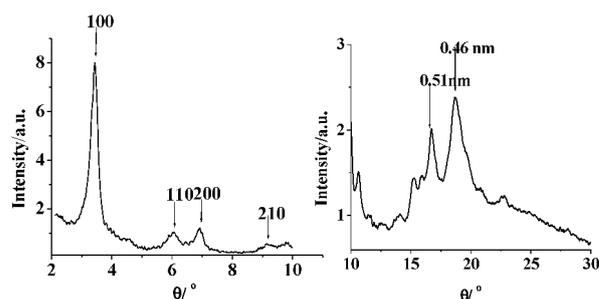


Fig. 4 Powder XRD pattern of compound **V** taken at (a) lower angle and (b) wide angle.

Table 2 Powder X-ray diffraction (XRD) data for compounds **I** to **VI**

Compound	Phase	Lattice parameter	$d_{\text{obs}}/\text{Å}$	<i>hkl</i>
I	Col _h	$a = b = 25.48$	22.12	100
			11.88	110
			10.84	200
			9.54	210
II	Cub	$a = 28.74$	14.47	200
			12.42	210
			9.33	310
			7.09	400
			6.47	420
III	Col _h	$a = b = 26.18$	22.65	100
			12.76	110
			11.32	200
			8.45	210
IV	Col _h	$a = b = 27.35$	23.69	100
			13.41	110
			11.76	200
			9.05	210
V	Col _h	$a = b = 30.46$	26.38	100
			15.25	110
			13.16	200
			9.99	210
			8.85	210
VI	Cub	$a = 44.48$	22.22	200
			18.55	211
			13.89	310
			11.08	400
			8.85	500

The wide angle region reflection peaks at $2\theta = 16.7^\circ$ (*d*-spacing of 5.1 Å) and $2\theta = 18.7^\circ$ (*d*-spacing of 4.6 Å) are seemingly due to the crystal packing of rod like segments in the aromatic units in the gel, consistent with the SEM and AFM results (Table 2).⁴⁷ The hexagonal columnar packing of the poly(aryl ether) dendrons has been slightly altered to cubic columnar when the functional group was changed from acid to ester (Fig. S3, ESI[†]).

Anthracene substituted poly(aryl ether) dendrons

In order to verify the hypothesis that only π - π interactions play the leading role in governing the self-assembly and gelation in AB₃ type poly(aryl ether) dendron derivatives, anthracene substituted poly(aryl ether) dendrons **IV** and **VIII** were synthesized and the gelation properties were examined in various solvent mixtures. The compounds **IV** and **VIII** were designed to investigate whether π - π interactions alone can drive the self-assembly in poly(aryl ether) derivatives at appropriate polarity of the medium, as there are no potential hydrogen bonding sites available in these compounds.

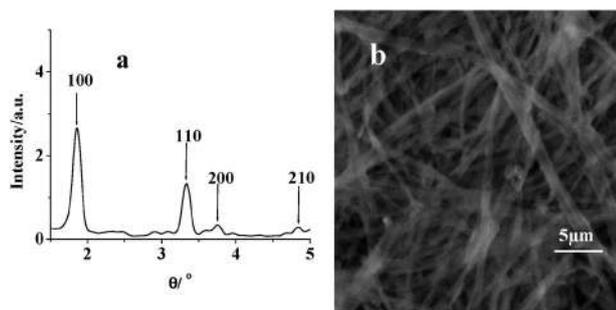


Fig. 5 Powder XRD pattern (a) and SEM image (b) of compound **IV**.

Corroborating our hypothesis, compound **IV** readily self-assembled in the chloroform–methanol mixture (1:3% v/v) to hexagonal columnar arrangement, as evident from the XRD of the sample (Fig. 5). The AFM and SEM images of compound **IV** exhibited entangled nano-fibrils as shown in Fig. 3 and 5, respectively. The SEM images of compound **IV** are similar to other poly(aryl ether) dendron derivatives utilized in the present study.

In the case of compounds **I**, **II**, **III**, **V**, **VI** and **VII**, the self-assembly is also assisted by the hydrogen bonding or dipolar interaction at the core of the dendron, which drives two such units together, placing the whole assembly one on the top of the other. However, in the case of compounds **IV** and **VIII**, the self-assembly should be purely driven by π – π interactions. As the steric repulsion is less in the case of compound **IV**, the propensity of self-assembly as well as gel formation is high in the case of compound **IV**. For compound **IV**, two such molecules could come on top of one another and form the fibrillar assembly. The XRD studies of compound **IV** provide direct evidence for a hexagonal columnar arrangement in the system, similar to that observed in other poly(aryl ether) dendron derivatives utilized in this study.

The experimental data taken together indicate that the pattern of self-assembly (*i.e.*, columnar) remains unchanged in all the poly(aryl ether) dendron derivatives examined in this study. Experimental results indicate that π – π interactions between the aromatic units can be invoked at appropriate polarity of the medium, which can result in such unusual self-assembly in the absence of any conventional, multi-interactive gelation motifs. It is interesting to note that while the poly(aryl ether) dendron is not planar, especially in the G2 case, the self-assembly is not affected by the non-planarity of the benzene rings. A cartoon representation of the self-assembly of AB₃ type poly(aryl ether) dendrons in the presence of a suitable solvent mixture is given below (Chart 2).

Fluorescence properties of the gel

Since unprecedented aggregation driven by the solvent might result in the close packing of aromatic units in the poly(aryl ether) dendrons, it is quite likely that they can form aggregation induced fluorescence emission.⁴⁸ In order to verify this hypothesis, we have carried out the fluorescence studies of the compounds shown in Chart 1. Photoexcitation of **V** by UV light readily provides an intense blue emission around 350 nm. Fig. 6 contains the emission spectra of **V** in the gel form. The blue luminescence with λ_{max} 343 nm is attributed to the

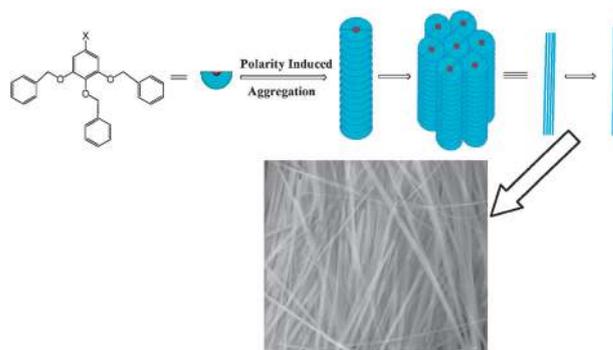


Chart 2 Cartoon representation of the self-assembly of poly(aryl ether) dendrons utilized in the present study.

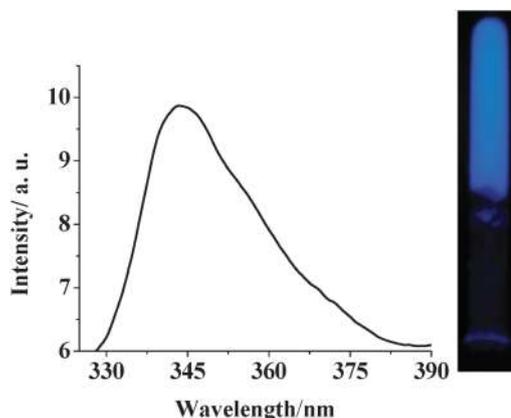


Fig. 6 Steady state emission spectrum (left) ($\lambda_{\text{exc.}}$ = 310 nm), and UV-illuminated photo (right) of compound **V**.

emission from the aggregation of benzene units in **V** as a result of the columnar arrangement of the system.⁴⁸ More interestingly, photoexcitation of **IV** by UV light readily provided anthracene excimer emission around 505 and 530 nm.⁴⁹ Fig. 7 contains the emission spectra of **IV** in the solution phase

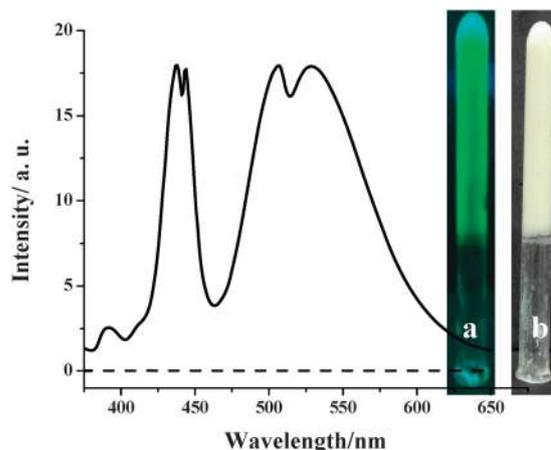


Fig. 7 Steady state emission spectra from compound **IV** in solution (dash) (solvent used is CHCl₃) and in the gel phase (solid) {CHCl₃: CH₃OH (1:3% v/v)} ($\lambda_{\text{exc.}}$ = 360 nm). Right: photographs of compound **IV**, (a) in the presence and (b) in the absence of UV illumination.

(chloroform, 4 mg mL⁻¹) and in gel form (chloroform : methanol mixture CGC is 4 mg mL⁻¹), along with the photographs of the gel in the presence and absence of UV light. Compound **IV** exhibited negligibly small emission intensity in chloroform. On the other hand, clear anthracene excimer emission was observed at 505 nm and 530 nm, upon photo-excitation of the gel. The intensity of emission from the gel was 1118 folds higher than that observed in the solution, confirming the aggregation induced emission (AIE) in the system examined.

It has been reported in the literature that anthracene can form mainly two types of excimers based on the geometry of each individual anthracene units adopted in the excited state.⁵⁰ The first one is relatively stable and two anthracene units overlap at an angle of 55° to each other and has an emission maximum close to 470 nm. The second one forms sandwich type excimer where the two anthracene units are symmetrically π -stacked with emission maxima at 560 nm. A recent report suggests the emission from a third type of anthracene excimer (T-shaped excimer) at 510 nm.⁵¹ The different emission maxima observed in the emission spectrum of compound **IV** in the gel form suggest the presence of a fraction of anthracene monomer and more than one type of anthracene excimers in the excited state.

The emission maxima at 505 and 530 nm in the present case indicate that 'partial' and 'sandwich' type overlap between the anthracene units occur in the self-assembled gel system, upon photoexcitation.⁴⁹ As evident from Fig. 7, the anthracene based gel system exhibits bright green color upon shining UV light, suggesting that excimer emission is quite intense ($\lambda_{\text{exc.}} = 505 \text{ nm}$ and 530 nm) in the system. The gel systems based on the simple poly(aryl ether) dendron derivatives were found to be highly stable under normal laboratory conditions for more than six months. It is clear from the data that solvent induced aggregation in simple poly(aryl ether) dendron derivatives can easily result in the excimer formation as a result of the closely packed chromophoric groups in a columnar fashion. This strategy can be useful to generate fluorescent gel systems in the presence of poly aromatic hydrocarbons, without any conventional multi-interactive gelation motifs in the system.

Conclusion

In summary, we have shown the first example of the formation of fluorescent gel utilizing low molecular weight simple AB₃ type poly(aryl ether) dendron derivatives through selecting solvent mixtures which render partial polar environment, enabling self assembly. The results suggest that the gelation properties of the dendrons, in the absence of conventional gelation motifs, are largely guided by π - π interactions and strongly dependent on the dendron generation. It might be possible to utilize these LMOGs, especially those composed by first generation AB₃ type poly(aryl ether) dendrons, in various optoelectronic applications since remarkable columnar type self-assembly is achieved utilizing these compounds.⁵²⁻⁵⁵ Further studies to explore the possibility of incorporating other polycyclic aromatic hydrocarbons to the poly(aryl ether) dendrons to generate gel systems with tunable light emitting properties are in progress in our laboratory and the results will be published in due course.

Experimental section

Materials

The poly(aryl ether) dendron derivatives were synthesized according to a reported procedure⁴² with slight modifications. All the starting materials were obtained from Aldrich or SD fine-chemicals Pvt. Ltd. India and used as received unless otherwise mentioned. The organic solvents used were dried according to standard procedures.

Instruments

¹H and ¹³C NMR data were collected on a Bruker 400 MHz spectrometer (¹H: 400 MHz; ¹³C: 100 MHz). Mass spectra were recorded using a Micromass Q-TOF mass spectrometer. Luminescence experiments were carried out on a Horiba Jobin Yvon Fluoromax-4 fluorescence spectrophotometer. The scanning electron microscopic studies were carried out using a FEI-Quanta Microscope. AFM samples were prepared by a spin-coating method on a silicon wafer and images were recorded using a Park-system XE-100 in the non-contact mode regime. Powder-XRD patterns were recorded on a Bruker D8 Advance X-ray diffractometer using Cu-K α radiation ($\lambda = 1.54178 \text{ \AA}$). Melting points were recorded using Q200 MDSC from TA Instruments under a dry nitrogen atmosphere with a heating rate of 5 °C min⁻¹.

Synthetic procedures

1 Synthesis of (AB)₃ G₁-COOCH₃(ii)

Methyl-3,4,5-trihydroxybenzoate (9 g, 0.045 moles) and potassium carbonate (24.84 g, 0.18 moles) in 130 mL of 1,4-dioxane were taken in a 250 mL round bottom flask. Benzyl chloride (33 mL, 0.135 moles) was added followed by the addition of a catalytic amount of tertiary butyl ammonium iodide (1.4 g, 0.0045 moles). The solution was heated to reflux with stirring for 24 hours. The solvent was removed under reduced pressure using a rotary evaporator to afford an oil that turned into a solid upon standing. The solid was recrystallized from methanol. The yield of (AB)₃ G₁-COOCH₃ was 18.5 g (90.5%). Spectral characterization: ¹H NMR (400 MHz, CDCl₃) δ : 3.8 (s, COOCH₃, 3H), 4.9 (s, ArCH₂O, 2H), 5.01 (s, ArCH₂O, 4H), 7.1–7.3 (m, ArH and PhH, 17H). ¹³C NMR (100 MHz, CDCl₃) δ : 52.25, 71.27, 75.15, 109.13, 125.26, 127.57, 127.96, 128.04, 128.21, 128.56, 136.69, 137.48, 142.46, 152.59, 166.66. MS: *m/z* calcd for C₂₉H₂₆O₅: 454, found: 455 [M + H]⁺.

2 Synthesis of (AB)₃G₁-CH₂OH(iii)

Lithium aluminium hydride (0.809 g, 0.0213 moles) was suspended in 40 mL of freshly distilled THF in a dry three-neck round-bottom flask under a nitrogen atmosphere. (AB)₃ G₁-COOCH₃ (9 g, 0.0198 moles) was dissolved in 50 mL of freshly distilled THF and added dropwise to the lithium aluminium hydride solution. The reaction mixture was refluxed with stirring for 2 h. The THF solution was cooled to room temperature and transferred to a beaker. Water was added very slowly dropwise to the vigorously stirred THF solution until the gray color of the lithium aluminium hydride

disappeared and a white solid was formed which was filtered and washed with THF. Excess solvent was removed under reduced pressure and the crude product was recrystallized from 95% methanol/water mixture to get the alcohol ((AB)₃G₁-CH₂OH) with 90% yield (7.6 g). Spectral characterization: ¹H NMR (400 MHz, CDCl₃) δ: 4.6 (s, CH₂OH, 2H), 5.09 (s, ArCH₂O, 2H), 5.15 (s, ArCH₂O, 4H), 6.72 (s, ArH, 2H), 7.30–7.48 (m, PhH, 15H). ¹³C NMR (100 MHz, CDCl₃) δ: 65.42, 71.22, 75.26, 106.46, 127.45, 127.83, 127.90, 128.18, 128.52, 128.62, 136.66, 137.13, 137.81, 137.87, 153.02. MS: *m/z* calcd for C₂₈H₂₆O₄: 426, found: 449 [M + Na]⁺.

3 Synthesis of (AB)₃G₁-COOH(1)

A solution of KOH (5 mL, 10 N) was added to compound 1 (5 g, 0.0110 moles) in 95 mL ethanol. The mixture was refluxed for three hours and was acidified with concentrated HCl. After refluxing the acidified reaction mixture for 15 minutes the precipitate was filtered and washed with water several times to get the product (AB)₃G₁-COOH with a yield of 4.4 g (90.9%). ¹H NMR (400 MHz, CDCl₃) δ: 5.20 (s, ArCH₂O, 6H), 7.30–7.49 (m, ArH and PhH, 17H). ¹³C NMR (100 MHz, CDCl₃) δ: 71.29, 75.19, 109.72, 124.12, 127.58, 128.01, 128.23, 128.53, 128.59, 136.58, 137.40, 142.42, 152.62, 170.02. MS: *m/z* calcd for C₂₈H₂₅O₅: 440, found: 441 [M + H]⁺.

4 Synthesis of An-G₁(AB)₃(iv)

(AB)₃G₁-CH₂-OH (0.9 g, 0.002 moles) was dissolved in 10 ml freshly distilled THF in a dry 100 mL two neck flask under nitrogen and temperature was maintained around 0 °C. To this solution NaH (100 mg, 0.004 moles) was added under a nitrogen atmosphere and stirred for 5 minutes followed by the addition of 9-chloromethyl-anthracene (0.5 g, 0.0022 moles). The reaction mixture was kept at room temperature with stirring for 2 hours. After completion of the reaction excess NaH was quenched by methanol followed by the addition of water to get a yellow precipitate which was filtered and washed with methanol to give the product G₁TAN in 89.4% yield (1.1 g). Spectral characterization: ¹H NMR (400 MHz, CDCl₃) δ: 4.63 (s, ArCH₂O, 2H), 5.07–5.10 (s, ArCH₂O, 6H), 5.51 (s, AnCH₂O, 2H), 6.71 (s, ArH, 2H), 7.31–8.36 (m, AnH and PhH, 24H). ¹³C NMR (100 MHz, CDCl₃) δ: 63.85, 71.14, 72.23, 75.23, 107.50, 124.45, 125.01, 126.17, 127.48, 127.85, 128.17, 128.28, 128.63, 129.03, 131.12, 131.51, 134.15, 137.15, 137.95, 152.89. MS: *m/z* calcd for C₄₃H₃₆O₄: 616, found: 634 [M + NH₄]⁺.

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