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Low Molecular Weight Fluorescent Organogel for Fluoride Ion Detection

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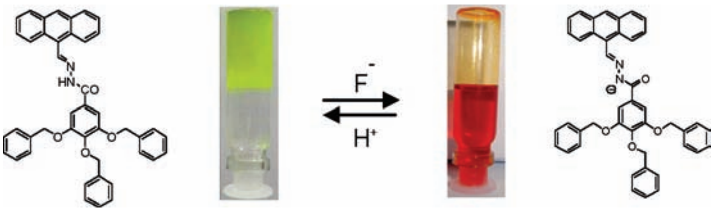
ABSTRACT



The design, synthesis, and the photophysical properties of a Low Molecular Weight Gel (LMWG) based on AB_3 and AB_2 type poly(aryl ether) dendrons with an anthracene chromophore attached through an acylhydrazone linkage are described. The gel is utilized for an efficient 'naked eye' detection of fluoride ions (as low as 0.1 equiv with respect to the gelator concentration), through a reversible gel–sol transition, which is associated with a color change from deep yellow to bright red.

During the past few years, intensive research has been focused on the development of functional soft materials (micelles, liposomes, colloidal particles, gels, liquid crystals, etc.) through molecular self-assembly.[1] Among these self-assembling systems, Low Molecular Weight Gelators (LMWGs) have gained increased attention due to their propensity to form a stable three-dimensional (3D) network through weak intermolecular interactions such as H-bonding, $\pi-\pi$ stacking, and van der Waals forces.[2] Organic gels are soft materials with many applications in material science.[3] Numerous efforts have been devoted to the development of stimuli responsive gels, where the properties of the system can be either switched on–off or tuned in the presence of an external or internal chemical or physical stimulus. Such responsive gel systems are highly desirable for the development of sensor devices.[4]

Also, considerable interest exists in the design and synthesis of gels with light emitting properties. Light emitting gel systems based on oligo(*p*-phenylenevinylene), 1-cyano-trans-1,2-bis-(3′,5′-bis-trifluoromethylbiphenyl) ethylene, perylene diimide, porphyrins, phthalocynanines, triphenylene, amphiphiles imidazoles, and stilbene have been reported in the presence of conventional gelation motifs.[5] These gels are potential candidates for optoelectronic devices and light harvesting materials.[6]

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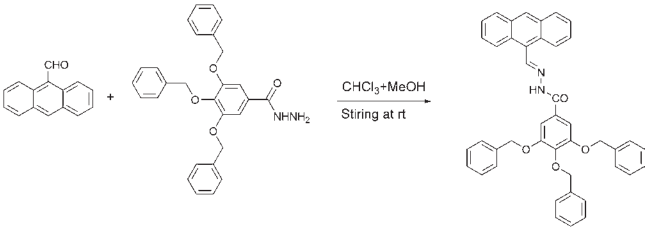
Dendrimers and dendrons represent an important class of molecules which act as gel precursors since their self-replicating structure provides a suitable structural scaffold for multiple intermolecular interactions, leading to effective gelation and efficient sensing.[7] However, most of the reported cases of dendrimer based gel systems involves the presence of conventional gelation motifs such as long alkyl chains, steriodal groups, and a large number of amide groups for facilitating the intermolecular interactions.[8] Low molecular weight, nonconventional dendritic gelators with light emitting properties are rarely reported in literature.[9]

Here, we have shown that poly(aryl ether) dendrons with an anthracene moiety attached to the core through a acylhydrazone linkage can form an '*instant gel*' in the absence of the above-mentioned conventional gelation motifs. Most importantly, the resulting gel undergoes a gel-to-sol transition, accompanied by a color change from deep yellow to bright red, in the presence of fluoride ions. The onset of the color change was noticed at a fluoride ion concentration as low as 0.1 equiv with respect to the gelator concentration. This provides an opportunity for the 'naked eye' detection of fluoride ions, which is one of the targeted anions due to its important role in biological systems. While a few anion-sensing organogels are reported,[10] herein we demonstrate the first example of a dendrimer based fluorescent LMWG which undergoes a reversible sol–gel transition in the presence of fluoride ions at very low concentrations of the analyte.

We have synthesized the first and second generations (G1 and G2, respectively) of AB$_2$ and AB$_3$ type poly(aryl ether) dendrons according to a reported procedure,[9d] and anthracene was attached to the dendron through a acylhydrazone spacer unit (Scheme 1) (synthetic procedure is given in the Supporting Information (SI)). The structures of the poly(aryl ether) dendron derivatives utilized in the present study are shown in Figure 1.

Scheme 1. Reaction between Anthraldehyde and Hydrazide of First Generation AB$_3$ Type Poly(aryl ether) Dendron



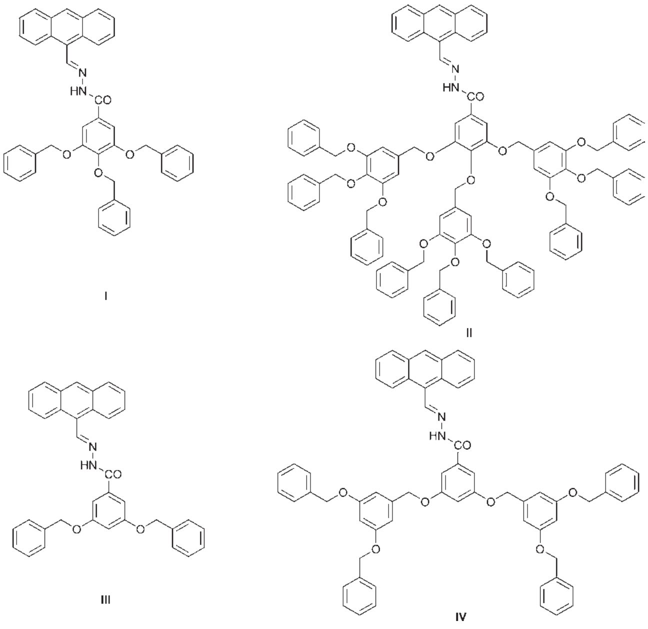


Figure 1. Structure of the anthracene cored AB$_3$ and AB$_2$ type poly(aryl ether) dendrons examined in the present study.

A mixture of the poly(aryl ether) dendron derivative and anthraldehyde (1:1 equiv) was stirred in a chloroform–methanol mixture (1:1% v/v) for 1 h at room temperature to yield a robust gel in the reaction flask. The product was then characterized by NMR, mass, and FT-IR spectroscopic techniques (SI Figures S1 to S8), and the analysis suggests that the reactants were completely transformed to the acylhydrazone derivative.

The gelation propensity of the dendrons in other dielectric media was examined in a wide range of solvents and solvent mixtures. The 'instant gel' from the chloroform–methanol mixture was dried under vacuum and then dissolved in a selected solvent or solvent mixtures by heating. The homogeneous solution is then sonicated and cooled to room temperature to obtain the gel. The critical gel concentration (CGC) of the compounds was determined in various solvents as well as solvent mixtures, and the values are given in Table S1. AB$_3$ type poly(aryl ether) dendrons form gel in the presence of several organic solvents at a very low CGC (0.4 wt %). For example, 4 mg

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of compound **I** can gel in 1 mL of $CHCl_3$, suggesting that 1895 $CHCl_3$ molecules are immobilized per molecule of compound **I**. In a similar way, 5005 toluene molecules are immobilized per molecule of compound **II**, in the gel. Compound **III** forms gel only at a relatively higher concentration compared to the other dendron derivatives. This is presumably due to the lesser number of aryl groups present in the dendrons, which play an important role in invoking the gelation through $\pi-\pi$ interactions.

The morphology of the xerogels (air-dried gels) of the dendron derivatives was examined by scanning electron microscopy (SEM). Figure 2a depicts the electron micrograph of the xerogel obtained from compound **I** deposited on a silicon wafer. All the dendron derivatives shown in Figure 1 self-assembled into a network of fibers, leading to similar SEM images (SI Figure S9). The xerogel of compound **I** appeared to have a 3D network of interlocked thin fibers 120–140 nm in diameter, extending over several micrometers in length. However, the relatively decreased length and increased thickness of the fibers for compound **III** suggest that a higher number of individual units are involved in the gel formation, which is substantiated by the corresponding higher CGC values in Table S1. Atomic force microscopy (AFM), in the noncontact mode, was utilized to examine the gel systems. The images depict the diameter of the bundled fibers as approximately 130 nm in width and 55 nm in height (Figure 2b, SI Figure S10).

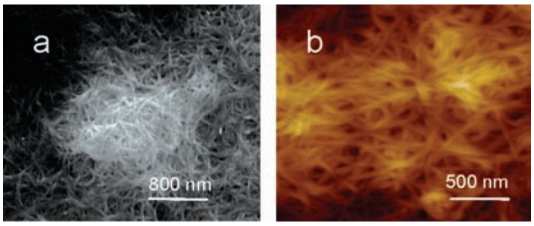

Figure 2. (a) SEM and (b) AFM images of **I**.

The role of H-bonding in the formation of the observed fibers was investigated by infrared spectroscopy. The FT-IR spectrum of compound **I** shows a single amide band at 1645 cm^{-1} and an intense NH stretching vibration at 3205 cm^{-1} (SI Figure S11). These spectroscopic data are an unambiguous signature of a network of hydrogen-bonded amides. In the powder XRD pattern of the compounds, a prominent reflection peak characteristic of a typical $\pi-\pi$ stacking distance was observed in the wide-angle region at 3.5 Å (SI Figure S12). Most likely, gelation in G1 and G2 dendrons occurs through a two step hierarchical supramolecular mechanism. First, the molecules are assembled through H-bonding and $\pi-\pi$ interactions into one-dimensional extended assemblies, followed by the intertwining of the chains together to form the resulting fiber with a mean diameter of ~130 nm. The low molecular weight organogels were found to be completely thermoreversible in organic solvents and solvent mixtures. The gel–sol phase transition temperature (T_{gel}) was estimated according to a reported procedure,[11] and the values fall in between 60 and 70 °C in a THF/water mixture (0.2–1.2 wt %). Interestingly, the gel transition temperature increases as the concentration of the gel increases (SI Figure S13). Also, compound **II** forms a transparent gel in toluene, presumably due to the controlled agglomeration of the sterically encumbered individual dendron units. The photograph of the transparent gel is shown in Figure S14.

While poly(aryl ether) dendron derivatives shown in Figure 1 were almost nonfluorescent in solution, a significant enhancement in emission intensity was observed as a result of the gelation. Figure 3a shows the photographs of compound **I** in solution (1×10^{-3} M) and gel phase, under visible and UV light illumination. As evident from the photograph, there is no emission from the solution phase under UV and visible light irradiation. Conversely, the gel system emits bright green luminescence under UV irradiation. The remarkable fluorescence enhancement from the gel systems can be explained by gel-induced enhanced emission (GIEE).[12] Molecules in Figure 1 exhibited 590-fold enhancement in the emission intensity in the gel compared to that in solution (Figure 3b, SI Figure S15). Laser Scanning Confocal Microscopy (LSCM) was utilized to obtain the images of the fluorescing gels through drop casting on a microscope coverslip. The confocal microscopic image of compound **I** is given in Figure 3b, which reveals a dense 3D network of greenish fluorescent fibers.

The excited state luminescence lifetime of the gels were measured. The fluorescence decays were best fit for a double exponential curve with 7.03 ns (88.77%) and 1.23 ns (11.23%). The excited state lifetime studies of the corresponding solutions were not carried out because of the very weak fluorescence from the solution. The structureless luiminescence emission from the gel systems (λ_{max} = 490 to 505 nm) suggests the formation of an anthracene excimer, upon photoexcitation (SI Figure S16).

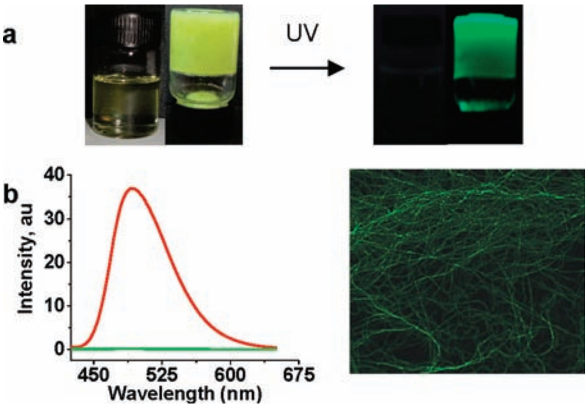

Figure 3. (a) Photograph of **I** in chloroform (1×10^{-3} M) and gel; under visible light illumination (left) and UV light illumination (right). (b) Emission spectrum of **I** in chloroform (1×10^{-3} M) (green) and gel phase (red) (λ_{exc} = 440 nm (left); LSCM image of **I** (right)).

Next, the anion binding properties of the gel systems toward a number of selected anions (F^-, Cl^-, Br^-, I^-, ClO_4^-, CH_3COO^-, $H_2PO_4^-$, and HSO_4^-) as Bu_4N^+ salts were examined in THF. The gels show intense variation in their electronic absorption spectra *only* upon the addition of tetrabutylammoniumfluoride (TBAF) (0.1 equiv) at room temperature. The presence of F^- not only changes the color of the system but also disrupts the preformed gel to a solution through slow diffusion of the anion. The photographs of the gel-to-sol conversion of compound **I** in the presence of fluoride ions is shown in Figure 4.

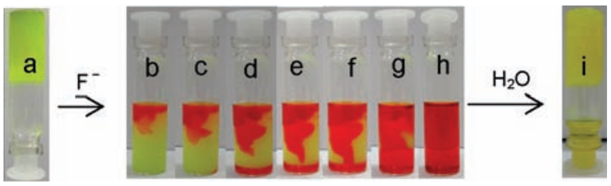

Figure 4. (a) Organogel formed from **I** in THF (4 mg/mL); (b) immediately after addition of TBAF (1 equiv); after (c) 1 min; (d) 3 min; (e) 5 min; (f) 7 min; (g) 9 min; (h) 10 min; and (i) after addition of 0.2 mL of water.

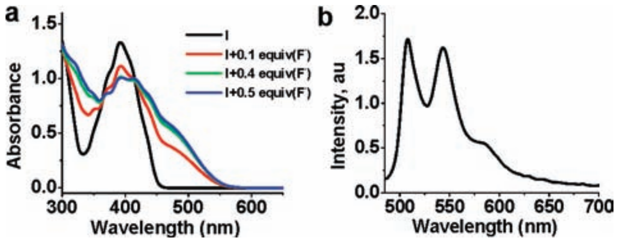

Figure 5. (a) UV–vis absorption spectra of **I** (1×10^{-4} M) in the presence of F^- in THF at room temperature. (b) Emission spectrum of **I** + 1 equiv of F^- in DMSO (1×10^{-3} M) (λ_{exc} = 470 nm).

The drastic color change of the gels accompanied by the addition of fluoride ions suggests changes in the electronic structure of the system. The UV–vis absorption spectra of compound **I** in THF (1×10^{-4} M) in the presence of 1 equiv of various anions were taken at room temperature (SI Figure S17). As it is clear from the figure, the absorption band of compound **I** is shifted to a longer wavelength *only* in the presence of fluoride ions. The UV–vis spectra of compound **I** in THF (1×10^{-4} M) in the presence of an increasing amount of fluoride ions are given in Figure 5a, which shows an isosbestic point, indicating that the addition of fluoride ions generates a species with increased conjugation. This could be, presumably, through proton abstraction from the gel by the fluoride ion. Subsequently, the H-bonding in the gel is weakened, leading to the gel–sol conversion (Figure 4). The Job plot analysis suggested the formation of a complex with a 1:1 stoichiometric ratio between the gelator and anion (SI Figure S19), with an association constant value of 2.9×10^4 M^{-1} (SI Figures S20 and S21).

The increased conjugation was further corroborated by the observation of the structured vibronic emission from the anthracene unit of compound **I**, which appeared at a much red-shifted wavelength in the presence of fluoride ions (Figure 5b). Additional evidence for the reaction mechanism was obtained from ^1H NMR experiments (SI Figure S18) in DMSO-d_6. Before the addition of F^- ions, the ^1H NMR chemical shift values of $-CH{=}N-$ and $-NH$ protons in the compounds were at 9.65 and 12.05 ppm, respectively. After addition of 1 equiv of F^- ions, the NH signal disappeared which suggested that the NH groups perhaps underwent a deprotonation reaction.

In summary, we have developed a low molecular weight fluorescent organogel system based on poly(aryl ether) dendron derivatives containing an anthracene unit attached through an acylhydrazone linkage, in a variety of solvents and solvent mixtures, which can act as an efficient 'naked eye' detecting system for F^- ions at very low concentrations of the analyte. The 590-fold enhancement in the excimer emission of anthracene during gelation indicates that a gelation induced emission enhancement (GIEE) mechanism controls the emission properties in the system, which is of paramount importance in device fabrications for field effect transistors and organic light emitting devices.

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Supporting Information Available. Complete experimental section including preparation and characterization of the synthetic precursors and characterization of the gel sysetms. This material is available free of charge via the Internet at http://pubs.acs.org.

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