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## Multi-Functional Materials through Self-Assembly of N-Alkyl Phenothiazine Linked Poly(Aryl Ether) Dendrons

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**Multi-functional self-assembled systems are developed from first and second generation poly aryl ether dendrons, which are covalently attached to N-alkyl phenothiazine unit through an acylhydrazone linkage. For the first time, dendron based systems have been utilized for efficient oil spill recovery. Further, the hydrophobic nature of the compound has been exploited to make self-cleaning surfaces with anti-wetting properties. More importantly, the visco-elastic property of the gel enables us to develop a gel based ink from the compound, which can be read under UV-light.**

Multi-stimuli responsive behaviour and self-healing properties of dendron based low molecular weight gelators (LMWGs) provide opportunities to engineer these molecules towards various applications.<sup>[1]</sup> In particular, lower generations of poly(aryl ether) dendrons (Fréchet type) with acylhydrazone linker units have been emerged as fascinating LMWGs owing to their optimum flexibility, extensive  $\pi$ - $\pi$  interaction, and the feasibility of peripheral modification with various functional groups for enhanced intermolecular interactions.<sup>[2]</sup> Despite the indisputable progress in the field of low molecular weight gelators (LMWGs) based on poly(aryl ether) dendrons during the last decade, attempts to develop multi-functional materials using these compounds hardly found success. In this context, a new derivative of poly(aryl ether) dendron based LMWGs has been synthesized, with multi-functional properties such as phase selective gelation (PSG), formation of a hydrophobic surface with anti-wetting property, and formation of an 'invisible ink'.

Phase selective gelation is an efficient method of oil spill recovery from a biphasic mixture of oil–water.<sup>[3,4,5]</sup> The existing materials for oil spill recovery are classified into three major categories, such as dispersants,

sorbents, and solidifiers.<sup>[6]</sup> Dispersants emulsify the oil, sorbents absorb the oil, and solidifiers, which are usually polymeric materials, gelate the oil layer.<sup>[7]</sup> However, they all have some limitations in (i) recovery of the spilled oil and (ii) reusability of the material. To address these issues, we have developed poly(aryl ether) based PSGs (Chart 1). Although, phase selective gelators have been used for oil spill recovery, PSGs based on low molecular dendrons have not been reported for this purpose, to date.

We have synthesized two dendron based phase selective gelators (DPSGs) (D1 and D2) from first and second generation poly(aryl ether) dendrons containing a phenothiazine derivative as the core unit. The phenothiazine unit is attached to the dendron *via* acylhydrazone linkage as shown in Chart 1.

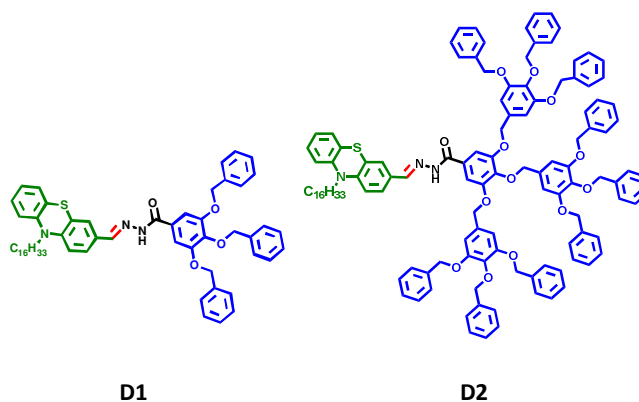


Chart 1. Structure of dendron based phase selective gelators DPSGs D1 and D2

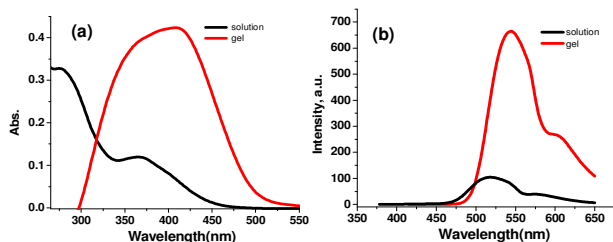
The organogelators **D1** and **D2** were synthesized by aldimine coupling between 10-hexadecyl-10*H*-phenothiazine-3-carbaldehyde **1** and the corresponding acylhydrazide **2a** or **2b** (Scheme S1 and S2) and characterized by spectroscopic techniques (Figures S1–S6). We have investigated the propensity of gel formation by the compounds in pure solvents (polar and nonpolar) as well as mixtures of solvents (Table S1). Compounds **D1** and **D2**

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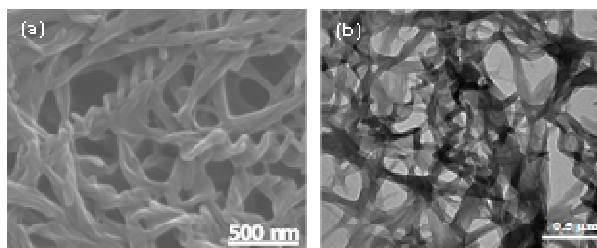
form yellow colored gels in non-polar solvents, aromatic solvents and solvent mixtures. The critical gel concentration values are given in Table S1. The gels in closed vials are stable for more than six months without phase separation. The FT-IR analysis of the gelator **D2** reveals that stretching vibrations of amide carbonyl bond and –NH bond appear at  $1642\text{ cm}^{-1}$  and  $3438\text{ cm}^{-1}$ , respectively. Upon gelation, the two bands are shifted to  $1601\text{ cm}^{-1}$  and  $3258\text{ cm}^{-1}$ , respectively, owing to their extensive intermolecular hydrogen bonding in the system through acyl hydrazone linkage (Figure S7). In the UV-vis spectrum of **D2**, the absorption at 265 and 365 nm are assigned to  $\pi$ - $\pi^*$  transitions in the benzene units of Fréchet type dendron and phenothiazine unit, respectively. As a result of gelation, the absorption band is broadened and red-shifted indicating prominent  $\pi$ - $\pi$  interactions in the gel phase (Figure 1a). The gels from both the DPSGs emit green luminescence under UV light irradiation. Even though, the DPSG **D2** was emissive in solution phase ( $\lambda_{em}=518\text{ nm}$ ), a remarkable enhancement in emission intensity was observed in gel phase, along with a red shift in the peak ( $\lambda_{em}=544\text{ nm}$ ). This is due to the well-known gel-induced enhanced emission (GIEE) effect<sup>[2c,j,8]</sup> (Figure 1b). The UV-Visible and emission spectra of the compound **D1** in solution and gel phase are shown in Figure S8. The excited state lifetime values of the compounds **D1** ( $\tau_1(\text{solution})=6.97\text{ ns}$  and  $\tau_2(\text{gel})=8.44\text{ ns}$ ) and **D2** ( $\tau_1(\text{solution})=6.79\text{ ns}$  and  $\tau_2(\text{gel})=7.05\text{ ns}$ ) did not exhibit drastic difference in solution and gel phase, indicating that the aggregated structure is similar in both phases (Figure S9).



**Figure 1.** (a) UV-visible spectra of compound **D2** in solution and gel phase, and (b) Emission spectra of compound **D2** in solution ( $\lambda_{ex} = 365\text{ nm}$ ) and gel phase ( $\lambda_{ex} = 405\text{ nm}$ ).

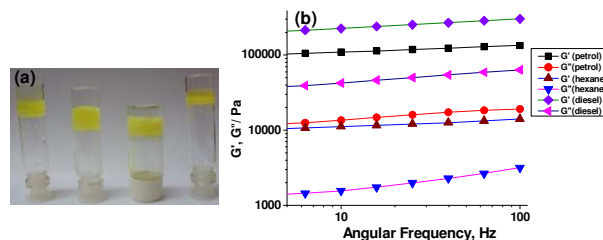
In order to verify the morphology of the self assembled systems, scanning electron microscopy (SEM) analysis has been carried out and the images show helical fibrous self-organization for both the gelators in hexane. Transmission electron microscopy (TEM) images show morphologies which are consistent with the SEM images (Figure 2a, 2b, S10). Conversely, fractal type morphology has been exhibited by the gelators in solvent mixtures, which are more polar than hexane (Figure S11). The results suggest that solvent plays a key role in deciding the morphology of the self-assembly by regulating the solute-solute and solute-solvent interactions. The observed morphologies are typical for poly(aryl ether) dendron derivatives and the mechanistic aspects of the self-assembly has been discussed elsewhere.<sup>[2f]</sup> Powder XRD analysis of both the compounds have shown lamellar packing

arrangement, similar to other poly(aryl ether) dendron derivatives. The data also indicates that the distance of  $\pi$ - $\pi$  stacking interactions is  $3.58\text{ \AA}$  and  $3.66\text{ \AA}$  for the compounds **D1** and **D2**, respectively (Figures S12, S13).

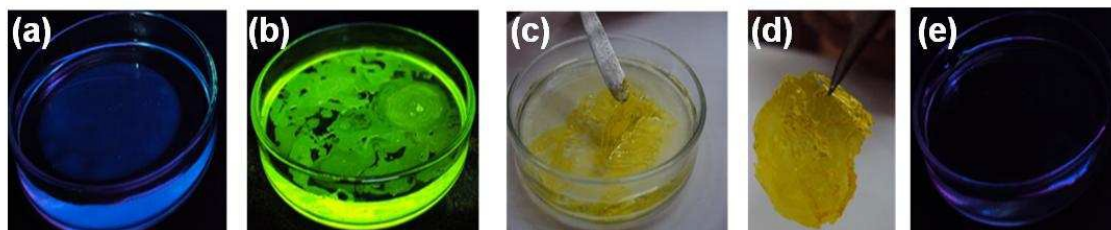


**Figure 2.** (a) SEM and (b) TEM image of xerogel from **D2** ( $7\text{ mg mL}^{-1}$ ) in hexane

Since the free flow of the solvents is arrested by the entangled fibres, the poly(aryl ether) dendron derivatives can form robust gel systems in non-polar solvents and oils, which might lead to phase selective gelation. We then attempted selective gelation of oil (hexane, petrol, diesel, silicone oil, pump oil and sunflower oil) using the DPSGs in a biphasic mixture of oil and water in a closed vial. A warm solution of the DPSGs dissolved in oil was added from the top of the vial which contains 1:1 mixture of identical oil and water. Gratifyingly, the new DPSGs entrapped the oil layer selectively and form a gel, which was confirmed by inversion tube method (Figure 3a, S11a). The CGCs (critical gel concentration) is lower for gelator **D2** ( $7\text{--}10\text{ mg mL}^{-1}$ ) than gelator **D1** ( $10\text{--}15\text{ mg mL}^{-1}$ ) (Table S1). This observation suggests that increased number of  $\pi$ -aromatic rings enhances the gelation process in oil phase. To our delight, these gelators congeal the oil layer selectively and effectively even in the presence of sea water,  $\text{KMnO}_4$ , acidic and basic media, with identical CGCs. The mechanical strength of the gels formed in various oils was studied using rheology. The results show higher  $G'$  (storage moduli) values for second generation DPSG **D2** compared to the first generation DPSG **D1**, which clearly indicates the robustness and high gelation propensity of gelator **D2** in oils. The diesel gel from compound **D2** is stronger ( $G' = 208752\text{ Pa}$ ) than all the other oil gels formed from both **D1** and **D2** (Figure 3b and Figure S14b). The  $\Delta G$  values ( $G' - G''$ ) for **D2** in diesel, petrol and hexane are  $171152\text{ Pa}$ ,  $88218\text{ Pa}$  and  $8632\text{ Pa}$ , respectively. The  $\Delta G$  values indicate the viscoelastic nature of the gel and the above values indicate that the gels formed from **D2** are highly visco-elastic in oil phase.



**Figure 3.** (a) Phase selective gelation from compound **D2** in 1:1 mixture of oil and water; (from left) diesel, hexane, sunflower oil and petrol ( $8\text{ mg mL}^{-1}$ ), and (b)  $G'$  and  $G''$  of gels from compound **D2** in petrol, hexane and diesel



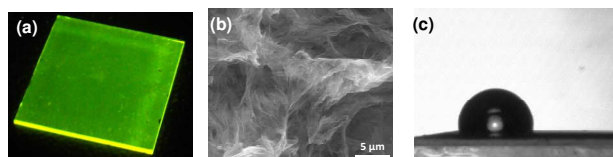
**Figure 4.** (a) Oil spill (petrol) in sea water under UV illumination (b) Formation of thin layer of oil upon spraying **D2** under UV light, (c) Removal of oil flakes, (d) thin film of oil gel and (e) Sea water under UV illumination after removal of thin film of oil gel

In phase selective gelation, recovery of the oil from the gel and reusability of the gelator are important aspects. The scooped diesel gel was subjected to vacuum distillation. The gel becomes disrupted on heating and the diesel was distilled off leaving the gelator intact. The diesel was recovered almost quantitatively (93% by volume). The recovered gelator was characterized by thin layer chromatography and the  $R_f$  values were compared with that of the original compound. The identical  $R_f$  values for the original and the recovered gelators indicate that there was no decomposition or melting during the distillation process. The reusability of the material was further confirmed by gelation of fresh oil using the recovered gelator (Figure S15). The recovered material has been used five to six times with comparable efficiency. The overall dendron recovery was found to be 87%. The stability of the self-assembly of the system was further analysed by taking the SEM image of **D2** after 5<sup>th</sup> distillation cycle, which show similar morphology to that of the original gel (Figure S 15c). The dendron based low molecular weight gelators, **D1** and **D2**, satisfied the following requirements for desirable phase selective gelation: (i) selective, efficient and instant gelation of the oil phase in the presence of water at room temperature, (ii) facile recovery of the oil from the gel, and (iii) reusability of the gelator.<sup>[4a, 9]</sup> We next set out an oil spill by aerial spraying petrol in sea water taken in a petri dish. Upon aerial spray of **D2**, a thin layer of petrol gel was formed, which was floated on the sea water. The thin film of gel can be easily removed from water with a spatula. Photographic images depicting the above description are given in Figure 4 and Figure S16. Next, we have dipped the thin film of compound **D2** in oil and water media separately. While the material was settled down in oil, it was floating on water medium. This suggests that, under the circumstances of an oil spill, the oil gel flakes will likely to float on water and can be easily picked up manually or mechanically (Video S1, S2 in supporting information).

In light of these results, we wondered whether we could extend the applicability of these DPSGs in fabrication of hydrophobic thin films. The hydrophobic surfaces offer practical benefits such as anti-icing, self-cleaning, anti-corrosive coating, frictional force reduction, and micro/macro fluidic channels owing to their water-repellent and self-cleaning properties.<sup>[10]</sup> The thin films have a wide array of applications in smart membranes, optical devices, microelectronics, catalytic coating, and chemical sensors.<sup>[11]</sup> We

then focused our attention to make a thin film over a glass substrate by spin-coating technique using gelators solution in THF/hexane. The solvent used was evaporated soon and an uniform transparent green emitting thin film was obtained. We have measured the thickness of the film by non-contact mode of AFM. The thickness of the film from the compounds **D1** and **D2** are 833 nm and 102 nm, respectively. The AFM images of the surface and the line profile of the films are given in the supporting information (Figure S 17, S18).

On the successful fabrication of thin films from the gelators, we measured the contact angle of water on the thin films. We have observed that the contact angle of water on both the thin films from the DPSGs **D1** ( $97.4 \pm 2^\circ$ ) and **D2** ( $98.5 \pm 2^\circ$ ) are greater than  $90^\circ$  using a goniometer (Figure 5 and Figure S14). This may be attributed to the hydrophobic nature of the gelators and their rough surface morphologies as evidenced by SEM images (Figure 5 and Figure S19). The materials, which form contact angle with water greater than  $90^\circ$  are termed as hydrophobic materials. Motivated by the favourable hydrophobization of glass substrate, these gelators were used with a view to exploit their potential use to prepare anti-wetting and self-cleaning materials. Upon spraying water repeatedly, the film from **D2** was not wetted even at a single place. The film from **D1** also showed the similar behavior but with slightly less efficiency (Video S3, S4 in supporting information). This behavior shows that the thin films are enough hydrophobic to show anti-wetting and self-cleaning properties.



**Figure 5.** (a) Formation of thin film on glass substrate from compound **D2** in THF/hexane under UV illumination, (b) SEM image of thin film and (c) Contact angle ( $98.5 \pm 2^\circ$ ) photograph of thin film with deionized water.

The rheology studies suggested that the gel is having high visco-elastic property. Hence, we consider whether the gelators can form gel based ink,

which will be water proof due to its high hydrophobic nature. To probe this idea, we systematically studied the ink formation by loading the dilute gelators solution in acetone/hexane with various concentrations into an injector. The results indicate that they can be written on various surfaces like plain sheet, chart paper, glass substrate and plastics (Figure 6, S20). As soon as the ink touches the surface, it was immediately dried before spreading over the surface due to the easily evaporable solvents. It is worth noting that these compounds can be used as gel based ink due to the optimum visco-elastic properties of the gel, which allows the gel to have a controlled flow through the re-filler of a ball-headed pen. The gel based ink can be used to write messages on dark surfaces which are invisible under normal light illumination and can be clearly seen only under UV light illumination (Figure 6). This is due to the presence of UV active phenothiazine which fluoresces in the green region of the visible spectrum. The ink is permanent and cannot be washed off from the surface as a result of water repellency. The invisible secure inks have a plethora of applications as follows: (1) to make security codes, (2) to mark personal belongings invisibly, (3) to sign documents to avoid fraud and forgery and (4) to prepare secret code which can only be seen under UV lamp by police/defense departments.<sup>[12]</sup>



**Figure 6.** (a) The word INK (from compound D2) written by an injector (a & c) under visible light illumination, (b & d) under UV light illumination.

The results revealed that these gelators can have multi-functional properties such as phase selective gelation, oil spill recovery, hydrophobic thin film and invisible ink formation which make them promising candidates for developing multi-functional materials.

In summary, the first dendron based phase selective gelators (DPSGs) have been successfully achieved which selectively and instantaneously gelate the oil phase from a 1:1 mixture of oil and water at room temperature. It is noteworthy to mention that the gelators and oil can be recovered by using vacuum distillation without affecting the structure of the gelators. Also, the gelators can be reused several times. In addition to phase selective gelation and oil spill recovery, anti-wetting, self-cleaning properties and invisible ink formation have been achieved from the same system. The DPSGs reported in the present study represent an emerging class of novel multifunctional smart materials.

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