

Supramolecular Dendritic π -Conjugated Systems: Enhancement of Fluorescence in Amorphous Dendritic Blue Emitting Thin Film

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Glycylurea functionalized π -conjugated diphenylanthracene guests (DPA guests) that bind to adamantyl urea modified dendritic hosts were synthesized and fully characterized optical measurements. The resulting supramolecular assemblies have been investigated with respect to their photophysical properties. DPA guests molecules were able to click into urea functionalized N,N-bis[(3-adamantyl ureido) propyl] methyl amine host as a result of acid-base (between COOH of the guest and amines of the host) and hydrogen bonding interactions (between the urea linkages of dendrimer and the guest). Size exclusion chromatography showed that 32 of the DPA guests strongly bind to the fifth generation adamantyl functionalized dendritic host. In the case of the supramolecular dendritic host/guest system smooth homogeneous thin films could be obtained by spin coating. The thin film of host-guest complexes shows brilliant blue fluorescence while in the case of the guest itself the fluorescence is quenched. The π -conjugated oligomers are less aggregated in the supramolecular assemblies presumably because of a shielding effect of the bulky adamantyl units present in the hosts.

Key words: dendrimers, supramolecular assemblies, host, guest, "click-in" concept, enhancement of fluorescence, quenching of fluorescence, shielding effect

Dendrimers are generally roughly spherical molecules with very well defined size and shape [1]. This physical characteristic, combined with their multivalency (a large number of active chemical groups located at the surface of the dendrimer) makes them especially suitable for use as hosts for small molecules [2]. Dendrimers have also been used as templates to obtain larger structures with particular characteristics. It has been suggested that these molecules could be used in a number of applications including those related to the controlled release of pharmaceuticals [3]. Several host - guest systems have already been developed, for example, dendritic hosts with unimolecular (inverted) micellar structures [4], the "dendritic box" [5], crown ether dendrimers [6], and cyclophane dendrimers [7].

It is well known the fact that when secondary interactions are introduced into the dendritic system (for example those based on the affinity of the end groups for a particular surface or hydrophobic interactions that can lead to self-assembly) dendrimers have the ability to completely change their conformations to form layers or even self-assembled structures.

Some of the most interesting applications for dendrimers are in the area of LED's. The high density of chromophore in the branched architecture of the dendrimer makes lots of transition dipoles available for the capture of light and to enhance optical properties. It is possible to create dendrimers which can improve the device efficiency and lifetime and can control the color of material. The efficiency of using dendrimers is a result of three-dimensional architecture which permits a spatial control of the active components and thus the electroluminescent properties of materials. For example high quality amorphous thin films can be prepared by conventional spincoating from dendrimers [8]. Moreover, dendrimers modified with π -conjugated oligomers can be used as hosts for dye

molecules [9] showing efficient energy transfer from the π -conjugated units to the encapsulated dye.

One of the most interesting characteristic of the dendrimers is that they can be designed so that the core defines the color of the light emission, whereas the branching units act as charge transporting units and the end (or surface) groups control the processing properties of the material [10]. An important feature of incorporating chromophores as cores is that it supplies the chromophores in a solution processible form, and this way the aggregation is reduced [11]. Moreover, site-isolation of the chromophores and light harvesting is achieved [12].

Recently, we have been interested to functionalize diphenylanthracene in such a way that it can be easily incorporated in dendrimers and attached to self-organizing molecules. By incorporation in dendrimers the stacking of π -conjugated materials (especially H-type aggregates) can be overcome.

Lately, we published a supramolecular strategy for modifying the periphery of the adamantyl urea modified dendritic poly(propylene imine) hosts with glycylurea functionalized π -conjugated oligo(*p*-phenylene vinylene) guests [13]. Glycine-urea functionalized guests were bound at the periphery of dendritic hosts using hydrogen bonds (between the urea linkages of dendrimer and the guest) and acid-base interactions (between COOH of the guest and amines of the host). We have demonstrated that the conjugated guests show improved emission upon binding. In the solid state this enhancement is ten times higher than the guest itself. The π -conjugated oligomers are most likely less aggregated in the supramolecular assemblies because of shielding effect of the bulky adamantyl units present in the host. In the case of the dendrimer system smooth homogeneous thin films could be obtained by spin coating. It shows that the dendritic host/guest complexes are the most promising ones in applying this supramolecular concept in LEDs.

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that bind to adamantyl urea modified dendritic hosts. Adamantyl dendrimers are known to adopt a persistent globular conformation, similar to the dendritic box, due to the three-dimensional dendritic scaffold, resulting in the formation of the amorphous films. The resulting supramolecular assemblies are investigated with respect to their photophysical properties.

Experimental part

UV-vis spectra and fluorescence spectra were recorded on a Perkin-Elmer Lambda 40 Spectrometer and a Perkin-Elmer luminescence spectrometer LS 50 B instrument. Spin-coated thin films were prepared by spin-coating from THF solutions using a Headway Research Spin-coat apparatus.

Results and Discussion

The synthesis and full characterisation of the guest molecules DPAGR (10-{4-[(tris 3,4,5-tri(R-oxy)benzamide] phenyl}-9-(4-ureido acetic acid phenyl)-anthracene) (DPAGALK=10-{4-[(tris 3,4,5-tri(dodecyl-oxy)benzamide] phenyl}-9-(4-ureido acetic acid phenyl)-anthracene and DPAGEG=10-{4-[(tris 3,4,5-tri(tetraethylen-oxy) benzamide] phenyl}-9-(4-ureido acetic acid phenyl)-anthracene), have been published recently [19, 20]. In that article, have been described the synthesized and fully characterized by NMR spectroscopy ($^1\text{H-NMR}$, $^{13}\text{C-NMR}$) and MALDI-TOF-MS of two new guest molecules (DPAGALK and DPAGEG), which are able to click into urea functionalized dendritic hosts as a result of acid-base and hydrogen bonding interactions. The binding properties of diphenylanthracene guests were first tested with *N,N*-bis[(3-adamantylureido) propyl]methylamine (*Pincer*) and then further investigated with the fifth generation

adamantyl functionalized propylene dendrimer *Dendr*. The urea NH resonances of *Pincer* as well as for the guests and dendritic scaffold show a downfield shift for both guests, indicating binding at the periphery of the host.

In the case of *Pincer* · DPAGEG and *Pincer* · DPAGALK the guest molecules were bound as 1:1 inclusion complexes while in the case of *Dendr* · (DPAGEG)₃₂ and *Dendr* · (DPAGALK)₃₂, a maximum of 30 ± 2 guests were bound and this stoichiometry is preserved after repeated preparative size exclusion chromatography.

In this article, we study the optical properties of guests DPAGEG, DPAGALK, and the host-guest complexes *Pincer* · DPAGEG, *Pincer* · DPAGALK, *Dendr* · (DPAGEG)₃₂ and *Dendr* · (DPAGALK)₃₂ (fig. 1a and 1b) by UV-Vis and fluorescence spectroscopy.

The absorption maximum of DPAGEG and DPAGALK were readily detected by UV-Vis spectroscopy in solution in the spectral range 350–410 nm by three bands characteristic of anthracenic core at 357, 378 and 397 nm. The UV-Vis spectrum of *Pincer* · DPAGEG and *Pincer* · DPAGALK shows a typical curve of the molecularly dissolved DPA derivative with an absorption maximum characteristic of anthracenic core at 361, 379 and 397 nm while the dendritic complexes show an absorption maximum at $\lambda_{\text{max}} = 358, 378, 397$ nm and 361, 377 and 397 nm respectively. Fluorescence measurements show an emission maximum at $\lambda_{\text{max,em}} = 428\text{--}432$ nm for DPAGEG, *Pincer* · DPAGEG and *Dendr* · (DPAGEG)₃₂ and $\lambda_{\text{max,em}} = 427\text{--}439$ nm for DPAGALK, *Pincer* · DPAGALK and *Dendr* · (DPAGALK)₃₂ typical for DPA derivatives in molecularly dissolved form. Interestingly, an increase in the intensity for the bound guest was observed: 1.6 times for *Pincer* · DPAGEG and 2 times for *Pincer* · DPAGALK (figs. 2–4).

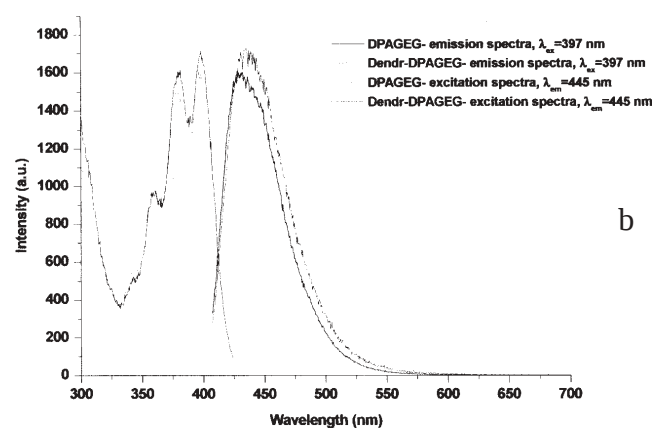
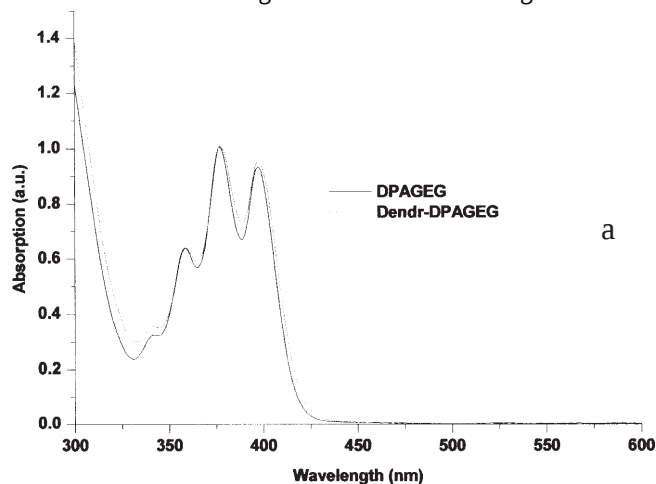


Fig. 2. UV-Vis (a) and fluorescence (b) of DPAGEG and *Dendr*-(DPAGEG)₃₂ in solution

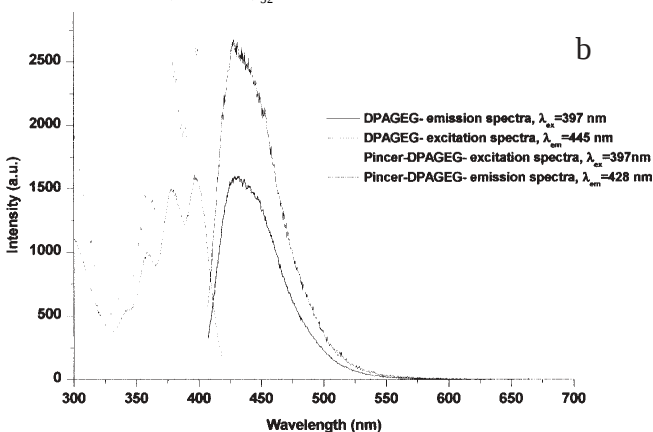
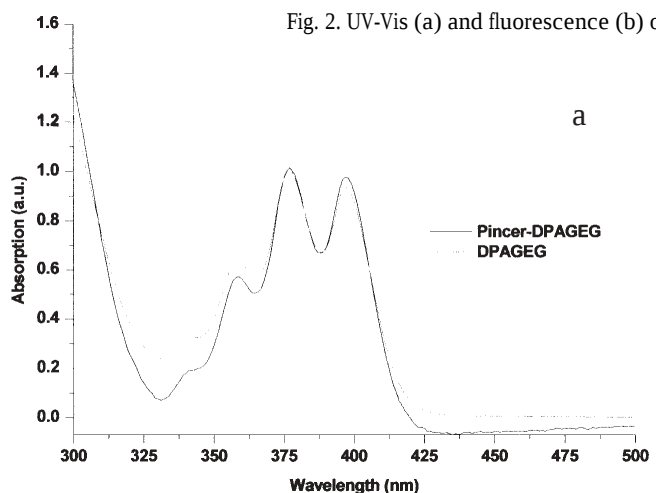


Fig. 3. UV-Vis (a) and fluorescence (b) of DPAGEG and *Pincer*-DPAGEG in solution

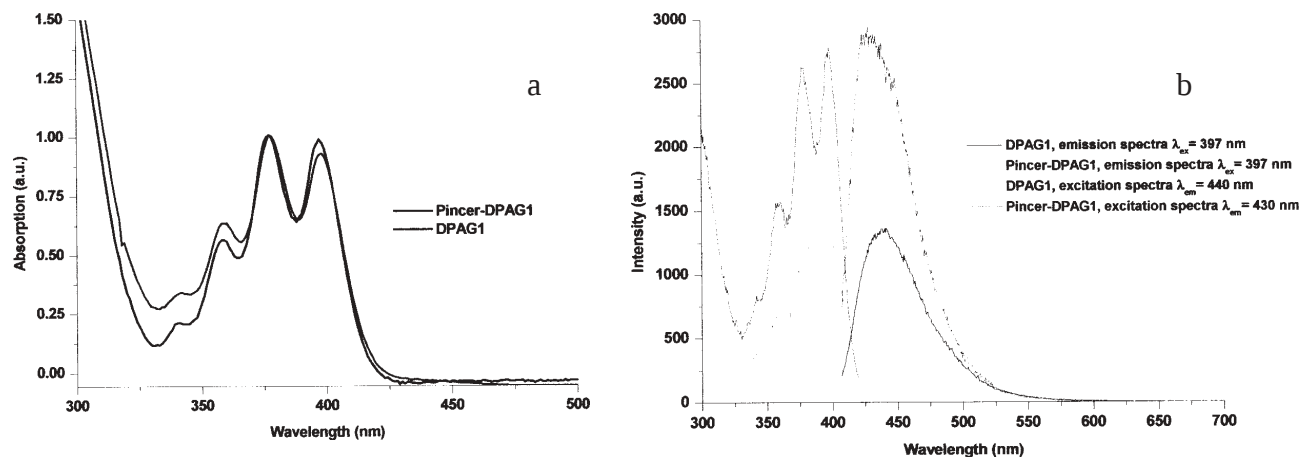


Fig. 4. UV-Vis (a) and fluorescence (b) in DPAGALK and *Pincer*-DPAGEG in solution

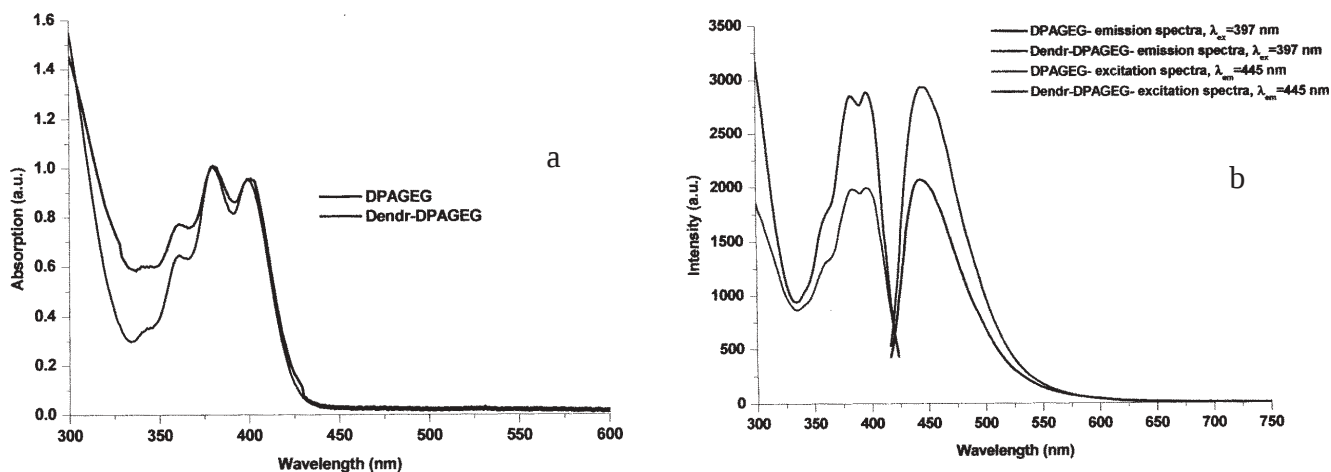


Fig. 5. UV-Vis (a) and fluorescence (b) of DPAGEG and *Dendr*-(DPAGEG)₃₂ in thin film

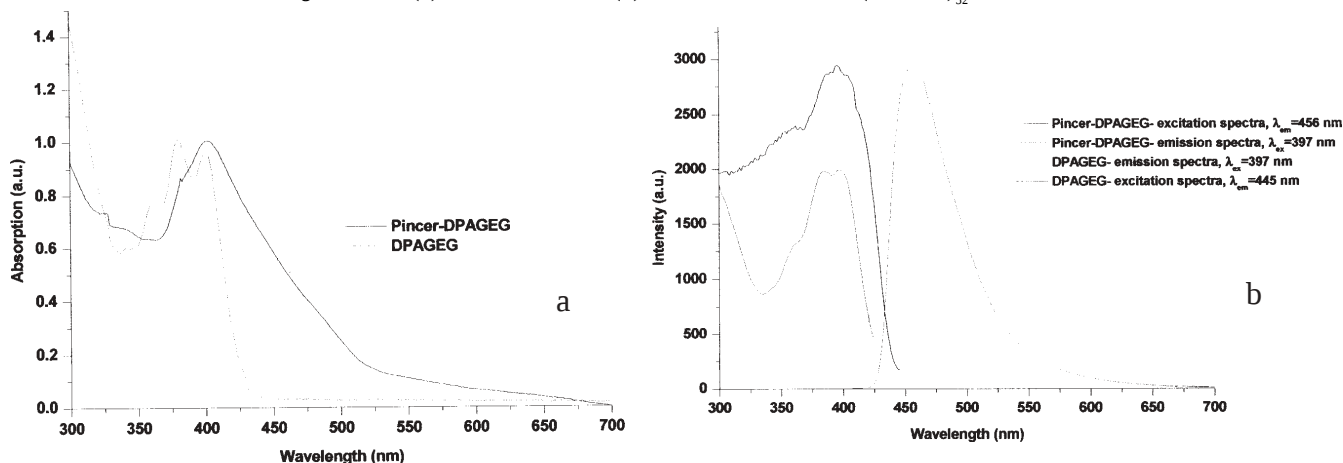


Fig. 6. UV-Vis (a) and fluorescence (b) of DPAGEG and *Pincer*-DPAGEG in thin film

This behaviour indicates that the guest molecules are not completely molecularly dissolved in solution. When no host is present weak interactions between the p-conjugated oligomers are presumably present and therefore the fluorescence is slightly quenched. In the supramolecular complexes no such interactions exist due to the bulky adamantyl groups.

In the case of the dendritic host-guest complexes [*Dendr* · (DPAGEG)₃₂ and *Dendr* · (DPAGALK)₃₂] we obtained good quality thin films by spin coating from a chloroform solution. The supramolecular systems based on pincer as host (*Pincer* · DPAGEG and *Pincer* · DPAGALK) showed spots indicating domain formation. In the case of the guest poor quality films were obtained.

Fluorescence spectra of these films show an emission at $\lambda_{\text{max,em}} = 443$ nm for the DPAGEG and $\lambda_{\text{max,em}} = 451$ nm for DPAGALK. The films show a bathochromic shift of the emission maximum when comparing with the emission in solution (for example DPAGEG: $\Delta\lambda_{\text{max}} = 29$ nm, *Pincer* · DPAGEG: $\Delta\lambda_{\text{max}} = 14$ nm, *Dendr* · (DPAGEG)₃₂: $\Delta\lambda_{\text{max}} = 14$ nm, DPAGALK: $\Delta\lambda_{\text{max}} = 26$ nm, *Pincer* · DPAGALK: $\Delta\lambda_{\text{max}} = 14$ nm, *Dendr* · (DPAGALK)₃₂: $\Delta\lambda_{\text{max}} = 12$ nm) indicating aggregation of the π -systems (figs. 5-7).

This red shift is larger in the free guest than in the case of the host-guest systems. Presumably the bulky and rigid adamantyl units avoid the chromophore from interdigitation and in this way prevent interchromophore

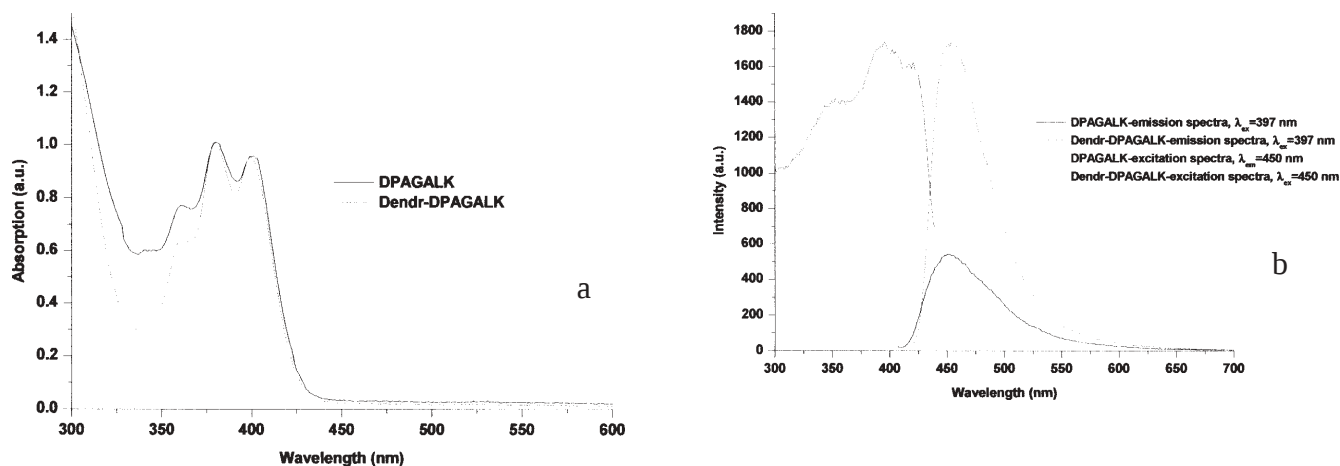


Fig. 7. UV-Vis (a) and fluorescence (b) in DPAGALK and *Dendr*-(DPAGEG)₃₂ in thin film

contacts leading to an enhancement of fluorescence. The terminal adamantyl substituents of the dendritic scaffold avoid effectively close contacts along the long axis of the chromophore. Each chromophore is thus insulated from its partner and behaves independently. The thin film of host-guest complexes shows brilliant blue fluorescence while in the case of the guest itself the fluorescence is quenched. Presumably the high emission is the result of the bulky adamantyl unit sealing the chromophores from aggregation.

Conclusions

In conclusion, we have studied the optical properties of glycinyurea functionalized π -conjugated guests diphenylanthracene guests to *N,N*-bis[(3-adamantyl ureido)propyl]methylamine, and to a adamantyl urea modified fifth generation poly(propylene imine) dendritic hosts that contain 32 of these binding sites. Furthermore, we have demonstrated that the conjugated guests show improved emission upon binding. In the solid state this enhancement is higher than the guest itself. The π -conjugated oligomers are most likely less aggregated in the supramolecular assemblies because of shielding effect of the bulky adamantyl units present in the host. In the case of the dendrimer system, smooth homogeneous thin films with brilliant blue fluorescence could be obtained by spin coating. External quantum efficiencies of the thin films should be measured and work along this line is in progress. The supramolecular approach shows clearly that chromophores can be isolated in the solid state and behave independently, while dendritic hosts give rise to films of good quality.

It is of interest to develop materials with improved efficiency, stability and that combine the advantages of small-molecule and polymer-emitters. And in this regard dendritic macromolecules offer a special opportunity.

The supramolecular approach that uses non-covalent interactions opens the way toward dynamic multi-component assemblies that are of interest for electron and energy transfer reactions. Work is currently in progress in this direction.

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Manuscript received: 26.10.2006

