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Synthesis and Electrophoretic Properties of Novel Nanoparticles for Colored Electronic Ink and e-Paper Applications

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Abstract: A new approach based on non-pigmented, stable colored nanoparticles able to migrate upon application of an electrical field (10–60 V) has been developed for the improvement of the color brightness of e-displays. The scientific challenges comprised the development of efficient syntheses of tri- and bifunctional dendrimers including branching points for further extension and individual decoration with dye (yellow, magenta, cyan). The covalent attachment of these scaffolds to silica nanoparticles was performed *via* hydrosilylation and final *in situ* charging generated attractive silica shells for the substractive CMY color space model.

Keywords: Dendrons · Dyes · Electrophoretic displays · Silica nanocore

Introduction

New display technologies have recently gained a large increase of interest with e-reader devices such as the Amazon Kindle, iRex iLlad or SONY PRS. E-paper displays mimic the appearance of printed ink on paper and do not require backlighting. However, the mostly grey-scale electrophoretic displays available on the market are limited in their applications to written books and newspapers. The few color displays available on the market lack in color brilliance, contrast and showed insufficient stability.

A new approach based on stable colored nanoparticles exhibiting electrophoretic mobility was developed in collaboration with BASF research center and CSEM. In preliminary work,[1,2] it was established that commercially available silica nanocages were preferable to sol-gel nanoparticles in order to gain enhanced brightness of the colors. The color brightness was further amplified by the introduction of dendrimer structures of two or three branches. This approach required the preparation of different dendrimers of first generation based on tailored-made dendrons (Fig. 1) linked to the three dyes: cyan, magenta and yellow (Fig. 2). The elaboration of a model of second-generation dendrimer was established in a former Bachelor thesis work[3] and afforded the attachment of the magenta dye. The novel hybrid nanoparticles consisted of a lipophilic silica core (100 nm) covalently attached to preassembled dendrimer structures carrying a charge and decorated with a dye (Fig. 3). The sequence order for construction of the complete assembly was adapted for each color, the introduction of the silica nanoparticles was fully compatible with precise analysis and well-resolved ^{1}H NMR spectra. The introduction of the charge was performed as the last step and the mobility tests were carried out individually with the charged and non-charged nanoparticles.

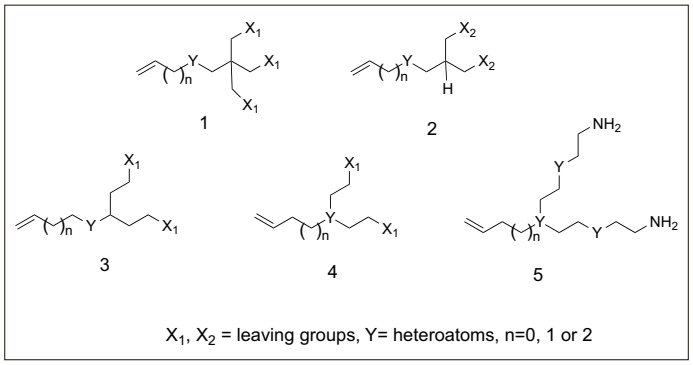

Fig. 1. Dendron structures.

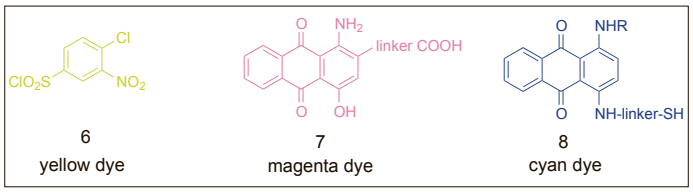

Fig. 2. Functionalized dyes prepared in this investigation.

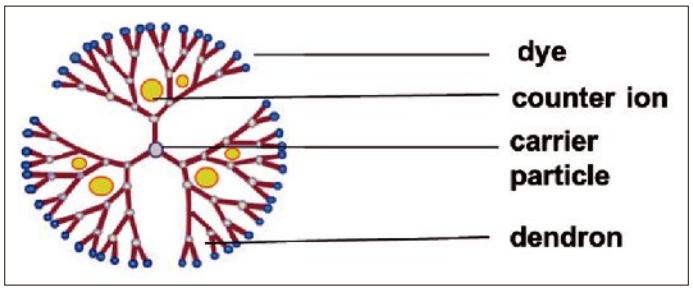

Fig. 3. Final assembly charged comprising the dye, organic dendron, and silica nanoparticles.

Linkage of the Dendrons and Dyes

Several attempts for the synthesis of a versatile three-branched dendron **1** which could be used for the linkage to the three dyes and conveniently attached to the silica nanocore were unsuccessful. Despite a few publications describing the preparation of similar dendrimers of thioether type,[4,5] the reduced reactivity due to the neopentyl effect resulted predominantly in a mono- or bifunctionalized dendron **1**.

Dendron **2** was synthesized in seven steps from a nitrotriol described in the literature.[6] After optimization of the procedure, a pure triol was isolated by simple filtration on silica gel in 77% yield. Further synthetic steps did not require any purification, the sequence was successful on a 20 g scale with a yield range of 54–92%. A short spacer bearing a sulfide moiety was then readily introduced and the linkage of the yellow dye *via* a sulfonamide was conducted under standard conditions. The yellow dye **6** was selected for its stability to UV light.

In a four-step sequence, dendron **3** could be prepared in gram scale in satisfying yield. The introduction of an unsaturated chain on the glutarate precursor required the formation of a trichloroacetimidate precursor and activation with an adequate Lewis acid. Purifications requiring column chromatography were limited to the first and last step.

Dendron **4** was designed for an efficient (three-step) synthesis of the blue dye–dendron construct. The introduction of the alkenyl group required an optimization of the reaction conditions and a careful purification of crude product. Unfortunately, all the attempts to attach the blue dye thiol **8** were fruitless, the nucleophilic character of this thiol could not be verified and possible disulfide formation was considered the main difficulty.

The planned synthetic routes for the final assemblies in the case of the magenta and blue dyes had to be adjusted owing to the limited reactivity of the different three branched dendrons prepared and the low nucleophilicity of the thiol observed for the fully functionalized dyes. Therefore a last dendron **5** was synthesized by extension of dendron **4** with a short linker for the elaboration of the final blue dye assembly. The coupling of the linker **3** and the magenta dye **7** was based on a method traditionally used for peptide coupling (PyBop coupling reagent). The final construct of the blue dye resulted from a palladium-catalyzed Buchwald-Hartwig amination.

Attachment to the Silica Nanocore

The yellow dye–dendron **2** assembly was readily linked to the silica nanoparticles by hydrosilylation. The $Q_8M_8^H$ commercially available nanocages (octakis(dimethylsiloxy)-T8-silsesquioxane) afforded a covalent modular linkage of one to eight dendrons enabling a considerable increase in color brightness. Unfortunately, the yellow dye–dendron–nanoparticle assembly required a further step for final functionalization (hydrophilic chain introduction and *in situ* charging) which could not be achieved in sufficiently mild conditions.

Similarly, dendron **3** after reaction with a short spacer including a sulfide moiety was attached to the silica nanocore quantitatively. The resulting dendron–nanocore assembly was linked to the magenta dye **7** after activation with PyBOP under standard conditions. The purification of the red-colored nanoparticles was possible by column chromatography, the complexity of the magenta dye generated side compounds and additionally an *in situ* rearrangement occurred due to the use of moderate to strong bases. The final functionalization to increase the lipophilicity and the *in situ* charging of the nanoparticles was achieved with 50% of the linkers due to severe steric hindrance. The six step sequence developed from dendron **3** required only one purification step by chromatography. The final construct was characterized by ^{1}H NMR and the expected electrophoretic mobility was observed in different electric fields.

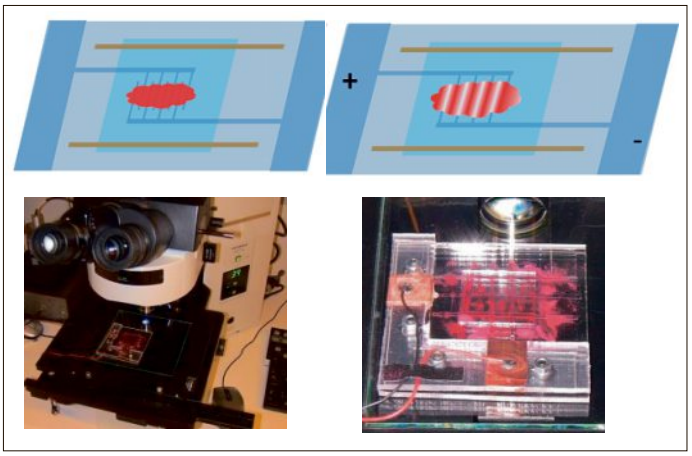

Fig. 4. a) Charged nanoparticles in an electric field of 10–60 V of variable polarization. b) Device investigated at CSEM for the test of mobility of charged nanoparticles (ITO electrode).

The extended dendron **5** reacted with a precursor of the blue dye prepared in two steps from chloroanthraquinone[7] in a limited yield (15%). The latter was attached by hydrosilylation to the silica nanoparticles and then partly positively charged (50%) by reaction with a compatibilizer. A screening of base/catalyst/ligand should be investigated for the palladium-catalyzed amination to afford a fully promising three-step synthesis of the blue dye–dendron–silica nanocore assembly which showed the requested electrophoretic properties.

Tests for Mobility

The final charged nanoparticles prepared with the magenta and blue dyes were tested by applying a voltage of 10–60 V of different polarization. The expected results were obtained: the particles were mobile when submitted to the electric field. Unfortunately, the dendrimer–dyes–silica nanoparticles showed some agglomerates in the test media applied. More material is currently needed to study in more detail the electrophoretic properties. The principle of the test in the electric field is explained in Fig. 4a. Short films were recorded at CSEM with the equipment showed in Fig. 4b; it was demonstrated that the velocity of the particles was influenced by the intensity of the voltage. Fig. 5 shows the resulting distribution of the silica nanocore after application of a +/–30 V voltage.

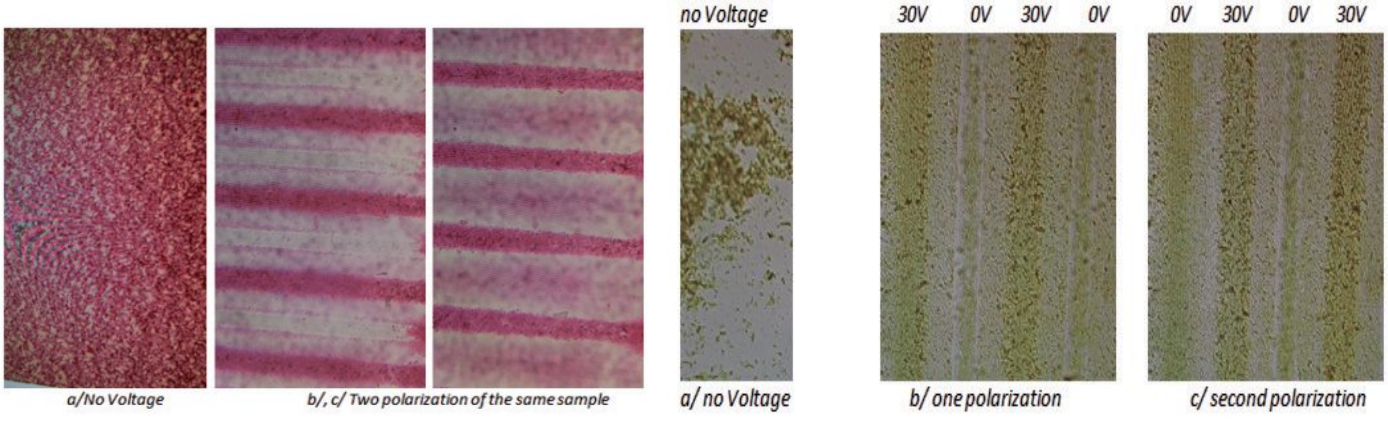

Fig 5. Mobility tests performed with the model nanoparticles (current applied +/–30 V).

Conclusion

Silica nanoparticles covalently linked to a UV-stable yellow dye *via* a two-branched dendrimer were prepared in nine steps in good overall yield and limited efforts for purification. However, the introduction of a linker on the construct enabling particle mobility by electrophoresis is not yet fully established.

The attachment of the magenta dye to nanoparticles linked to a two-branched dendron has been optimized and led to a fully functionalized and charged assembly in six steps. The mobility of the charged particles was demonstrated at CSEM.

A two-branched dendron was prepared for the linkage to a red anthaquinone dye used as precursor of the blue dye. The palladium coupling resulting in color change to blue provided unfortunately only a limited amount of dendron–blue dye construct. The properties of the final charged assemblies prepared with the magenta and blue dyes showed the expected mobility in a modular electric field of 10–60 V although some agglomerates were formed. Further tests would require the preparation of the final assemblies in gram scale.

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