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Discovery of New Fluorescent Materials from Fast Synthesis and Screening of Conjugated Polymers

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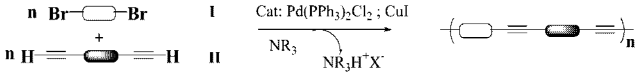
Polymeric organic light-emitting diodes OLED present a high potential for future display devices.[1] These materials combine color tuning through the change of molecular structure via variable length, substitution or degree of conjugation, and outstanding mechanical and processability properties of polymers, such as the easy preparation of flexible thin film from casting which is essential for low-cost broadly diffused material.

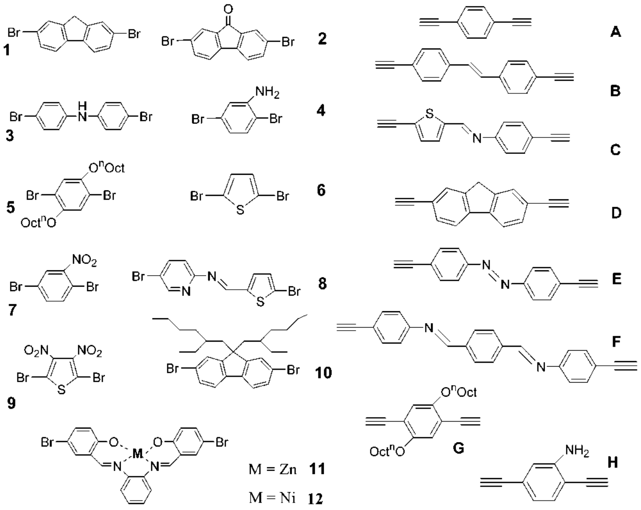
To obtain red, green, and blue colors required for full color display, fluorescent polymers with corresponding narrow emission wavelength must be prepared. During the last 10 years, several fluorescent conjugated polymers were investigated as OLED precursors.[2,3] Results clearly demonstrate that, depending on the nature of substituents of conjugated polymers, both color and light emission efficiency could be dramatically modified.[2,4] Consequently, it has become crucial in the field of optoelectronics to develop innovative approaches allowing synthesis and fast evaluation of a large diversity of polymer compositions for the detection of new generations of materials showing specifications of light-emitting diodes such as fluorescence brightness and filmogene properties. An intensive effort is currently devoted toward the development of high throughput experiments (HTE) approaches in several research areas including polymers for biomaterials and chiral recognition,[5] inorganic materials,[6,7] or catalysis.[7] Here, we report the first application of the HTE concept to the Pd-catalyzed carbon−carbon coupling reaction for (i) the rapid generation of sets of conjugated polymers and (ii) the fast qualitative detection of new fluorescent polymers (Scheme 1).

Our preliminary studies focused on polymers derived from the poly(arylene ethynylene) PAE[4] family (Scheme 1), due to their interesting photoluminescence and high quantum yield of fluorescence.[8] A diversity of conjugated polymers was prepared in a parallel way from the Pd-catalyzed carbon−carbon coupling reaction between a diversity of dihalogenated and diethynyl monomers **I** (**1**−**12**) and **II** (**A**−**H**) (Scheme 2). Phenylenevinylene, dialkoxybenzene, and fluorenone building blocks were already involved into fluorescent polymers,[2,4,8−9] but one cannot predict which combinations of the monomers **1**−**12** with the building blocks **A**−**H** respectively should give high blue, red, or green fluorescence. In a glovebox, 96 vials (1 mL), dispatched in a 12 × 8 format, were filled with 120 μL of 0.1 M solutions of monomers **I** (**1**−**12**) and **II** (**A**−**G**) in THF and 50 μL of a catalyst solution 0.025 M ($PdCl_2(PPh_3)_2$ + CuI + in THF/diisopropylamine 1/1, v/v). As a result, because each column and each row has received a specific dibromo and diethynyl derivative solution, each vial corresponds to a unique combination of monomers **I** and **II**.

Scheme 1. Pd-Catalyzed Synthesis of Poly(arylene ethynylene) PAE by Polycondensation Reaction



Scheme 2. Dibromo Monomers **I** (**1**−**12**) and Diethynyl Monomers **II** (**A**−**H**) Involved in the Synthesis of the Library



After 24 h at 60 °C, 500 μL of THF were added to each tube, and aliquots were transferred for dilution into a 96-well quartz plate. Simple irradiation of this plate with a hand-held UV lamp (365 nm) led to easily discriminate fluorescent and nonfluorescent polymers and to visualize the corresponding emission color in solution. To check different excitation wavelengths, a spectrofluorimeter able to read 96-well plates for several excitation and emission wavelength combinations was used. For instance, for an excitation wavelength at 460 nm, the fluorescence of wells was measured with filters working at 485, 508, 530, and 550 nm for the emission. For each of excitation wavelengths, raw data of emissions were transformed into 3D histograms as depicted in the Figure 1. The *x*,*y* axes gave the nature of the conjugated polymer, based on the nature of monomers, and the *z* axis indicated the relative fluorescence intensity. The analysis of all of these 3D graphs led to the fast and unpredictable detection of the new polymers showing green-emitting fluorescence **G8** and **H8** (Figure 1). The same strategy was used for the detection of new blue-emitting polymers **B3**, **B9**, and **C10** (excitation: 360 nm; emission: 460 nm).

To our knowledge and according to reviews on polymers containing ethynyl bridges,[4] these polymers were not described. The selected polymers were submitted to GPC measurements (versus polystyrene standards). The results indicated average molecular weights between 3000 and 6000 g/mol which are in accordance with values reported in the literature for PAE polymers obtained by the Pd carbon−carbon coupling.[4] The fluorescence of each corresponding monomer was individually measured to be sure

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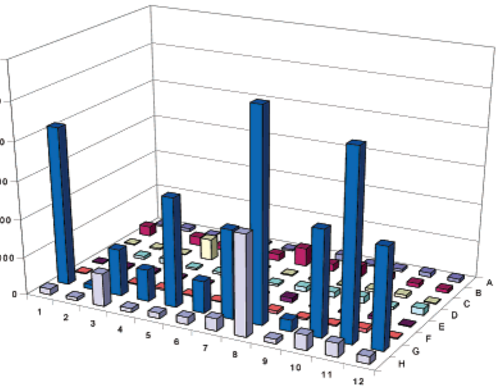

Figure 1. Solution fluorescence of the 96 polymers measured at 530 nm (excitation 460 nm).

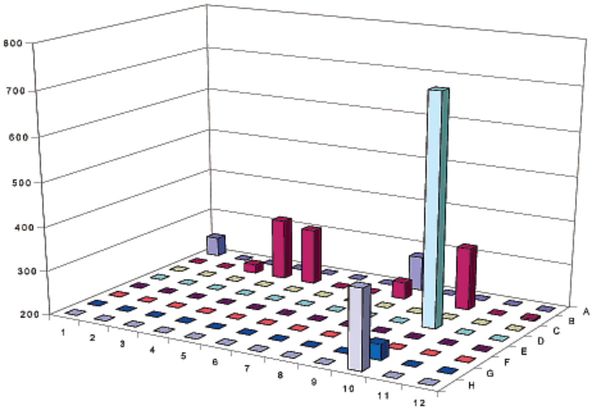

Figure 2. Solid-state fluorescence of the 96 film spots library measured at 425 nm (excitation 360 nm).

that the fluorescence of polymers was really the consequence of the carbon−carbon coupling of two monomers. To ascertain whether this HTE approach based on small volumes (200 to 400 μL) was accurate, the fast-detected polymers were prepared in large scale (5- to 10-mL solutions). The emission spectra of the new polymers **C10**, **G8**, and **H8** clearly indicated that results obtained from the HTE approach reflected the real fluorescence properties of polymers.[10] Moreover, this was confirmed with polymers already described **G6** and **G5** as the information obtained from the corresponding solutions in the 96-well plate are in good concordance with the results in the literature.[10] However, for aplication as OLED devices new solid-state fluorescent polymers are required. Due to the presence of aggregates, excimers, or both[11] the emission color of conjugated polymers in solid state could be different than the color obtained from a solution. As this effect is unpredictable, 96 film spots were prepared by the slow evaporation of 20 μL of each polymer solution. Again, a simple irradiation of this plate with a hand-held UV lamp (365 nm) led to the visualization of the color emitted by the fluorescent polymers. With a 96-well plate reader spectrofluorimeter, a large library of 3D graphs was obtained for several different excitation/emission wavelengths combinations. In this way, polymers showing a blue fluorescence in solid-sate **B4, B5**, **B10**, **H10**, and the recently reported polymer **D10**[12] were detected (Figure 2). These results were in accordance with the color seen for the different film spots after irradiation of the plate with the hand held fluorescence lamp. In addition to their unexpected blue emission, the new polymers **B4** and **H10** present a potential as fluorescent chemical sensors[13] via their reactive amino groups.

This HTE method is suitable for the fast qualitative detection of new compounds showing specifications of light-emitting diodes as the fluorescence brightness and filmogene properties can be checked simultaneously. For instance, a polymer with good fluorescence properties but with a poor solubility (synonymous with a low probability to generate OLED devices as concentrated solutions are required for film forming) will be not detected. In conclusion, we report that the HTE approach could be applied successfully to the synthesis of a large variety of conjugated polymers and to the fast discovery of potential new candidates for OLED via a simple prescreening test based on the detection of polymers showing a red, green, or blue solid-sate fluorescence. The classical one-by-one evaluation of thin-film fluorescence properties of these 96 polymers would have been very time-consuming and would necessitate significant amounts of all starting monomers. With this fast prescreening test reported here, only compounds showing the targeted solid-sate fluorescence have to be prepared in large scale and carefully investigated for OLED properties. This could be done by the classical one-by-one evaluation because the number of potential candidate is strongly reduced or again by the HTE approach.[14] The evaluation for OLED properties of new polymers and the studies of others libraries by this approach are in progress.

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Supporting Information Available: Experimental protocol for the synthesis and fluorescence screening of the library and for the synthesis of selected polymers and monomers (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(10) Emission (excitation) by HTE-conventionnal approaches: C10 430(360)−450(380); G8 530(440)−540(450); H8 510(425)−500(430); G6 510-(425)−518sh(440) see ref 4a; G5 525(425)−505sh(449) see ref 4a.
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