

## Constitutional Dynamic Self-Sensing in a Zinc<sup>II</sup>/Polyiminofluorenes System

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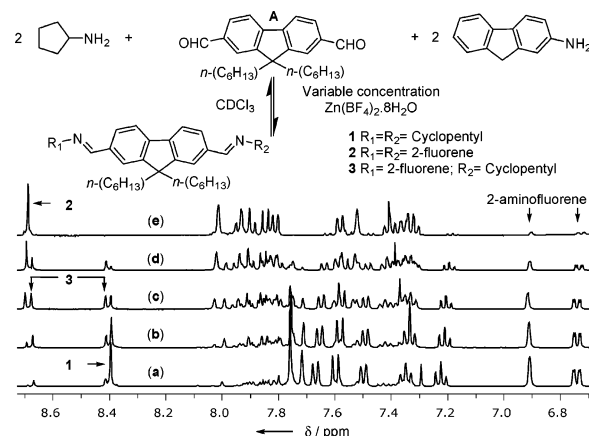
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Constitutional dynamic chemistry (CDC)<sup>1</sup> expresses adaptative behavior, as its entities are in principle capable of responding to external effectors via reorganization of their constitution through incorporation, decorporation, and reshuffling of components. This may occur on either the molecular or the supramolecular level, the components being connected through reversible covalent bonds<sup>2–4</sup> or noncovalent interactions<sup>1,5a,b</sup> (or both), respectively. The resulting constitutional plasticity generates dynamic (virtual<sup>3a</sup> or real) diversity and gives access to a range of properties that connectively static entities do not present.

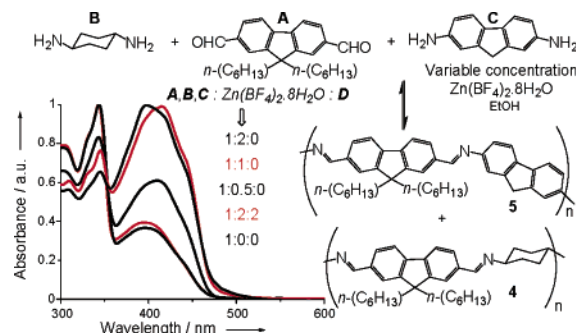
On the molecular level, CDC is implemented in dynamic combinatorial chemistry that has been applied toward drug discovery,<sup>3</sup> as well as in materials science.<sup>3a,5</sup> We have recently investigated selection processes within constitutional dynamic libraries (CDLs), induced by chemical and/or physical stimuli; indeed, proton concentration or temperature markedly rearrange the composition of equilibrating libraries of imines.<sup>6</sup> In particular, such a dynamic system may undergo constitutional reorganization in response to an external effector so as to generate a signal due to that species that is inducing the reorganization in the first place. This behavior amounts to a “self-sensing” (or self-signaling) process, whereby the effector induces the formation of that CDL constituent that allows its own detection. It appeared reasonable to expect that metal ions interacting with the library constituents could strongly affect its composition.

We demonstrate here the ability of a set of oligo- and polyimine species to undergo such a process in response to the effect of Zn<sup>II</sup> ions, whose presence is in return revealed by the appearance of a spectral signal. Zinc ions were found to promote component exchange within a set of imines as well as in polyimine dynamers,<sup>6b,7</sup> i.e., in dynamic polymers in which the monomers are connected by reversible imine bonds. Furthermore, the interaction of zinc ions with fluorescent polymers based on fluorene monomers connected through imine bonds leads to marked changes in both emissions intensity and wavelength. Finally, as a result of the two distinct effects of the metal ions (i.e., polymer selection and enhancement of fluorescence), zinc ions induce a constitutional reorganization within the CDL, leading to the selective formation of a polymeric structure whose optical properties are strongly affected by the ions themselves, so that it signals the presence of its own promoter.

A 1:2:2 mixture of 2,7-fluorenedicarboxaldehyde **A** with cyclopentylamine and 2-aminofluorene (CDL **I**) in CDCl<sub>3</sub> was found by <sup>1</sup>H NMR to contain mainly (70%) the expected diimine **1**, formed from the more nucleophilic aliphatic amine, together with the mixed species (pale yellow solution). Addition of increasing amounts of Zn(BF<sub>4</sub>)<sub>2</sub>·8H<sub>2</sub>O in CD<sub>3</sub>CN (Figure 1) led to fast and total conversion of compound **1** into the conjugated compound **2** (orange solution).<sup>8</sup> A quantitative selection of compound **2** is obtained for 2 equiv of Zn<sup>II</sup> with respect to **A**, while 1 equiv leads to a statistical mixture of **1**, **2**, and **3** in a 1/1/2 ratio. Moreover, the process can be fully reversed by trapping the Zn<sup>II</sup> ions with 1 equiv



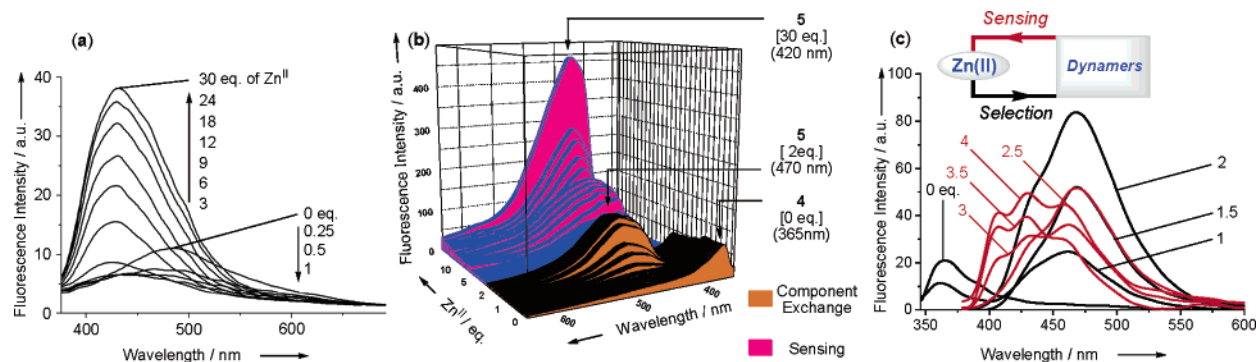
**Figure 1.** (Top) Constitutional dynamic library of iminofluorenes, CDL **I**, with Zn(BF<sub>4</sub>)<sub>2</sub>·8H<sub>2</sub>O promoted component exchange and (bottom) <sup>1</sup>H NMR spectra (400 MHz) of the CDL for different Zn(BF<sub>4</sub>)<sub>2</sub>·8H<sub>2</sub>O concentrations at 298 K in CDCl<sub>3</sub>. (a) 0 M. (b) 3.10 × 10<sup>−2</sup> M. (c) 6.20 × 10<sup>−2</sup> M. (d) 8.68 × 10<sup>−2</sup> M. (e) 1.24 × 10<sup>−1</sup> M. Initial concentration of **A**: 5.12 × 10<sup>−2</sup> M.



**Figure 2.** CDL of polymeric iminofluorenes, CDL **II**, with Zn<sup>II</sup>-promoted component exchange and (bottom left) absorption spectra of the CDL recorded at 298 K in CHCl<sub>3</sub> for various amounts of Zn(BF<sub>4</sub>)<sub>2</sub>·8H<sub>2</sub>O solubilized in CH<sub>3</sub>CN. [A] = 2.50 × 10<sup>−3</sup> M. **D** = Hexamethylhexacyclen.

of hexamethylhexacyclen, leading to quantitative regeneration of **1**. The constitutional modifications observed may be attributed to the preferential coordination of Zn<sup>II</sup> to the more basic aliphatic amine than to an aromatic amino group; as a consequence, the former is engaged in coordination, allowing the latter to participate in imine formation.<sup>9</sup>

We then examined the exchange of components in the polymers formed from a 1:1:1 mixture of **A**, *trans*-1,4-cyclohexanediamine **B**, and 2,7-diaminofluorene **C** (CDL **II**) in ethanol at room temperature (Figure 2).<sup>10a,b</sup> In principle, CDL **II** consists of the two-component polymers **4** and **5** together with all possible intermediate three-component **A/B/C** mixed species. Polymers **4** and **5** were prepared independently in the same conditions as reference compounds for <sup>1</sup>H NMR, UV–vis, and fluorescence spectral data. The composition of the polymers generated from the **A/B/C** mixture was characterized on the basis of the NMR signal of the imine



**Figure 3.** (a) Fluorescence spectra at 298 K in  $\text{CHCl}_3$  of pure fluorene polyimine **5** ( $c = 4.05 \times 10^{-6}$  M) on addition of increasing amounts of  $\text{Zn}(\text{BF}_4)_2 \cdot 8\text{H}_2\text{O}$  (equivalent with respect to initial **A** in **5**) solubilized in  $\text{CH}_3\text{CN}$ ; excitation at 350 nm. (b) Fluorescence spectra at 298 K in  $\text{CHCl}_3$  of the CDL **II** of fluorene polyimines of Figure 2, on addition of increasing amounts of  $\text{Zn}(\text{BF}_4)_2 \cdot 8\text{H}_2\text{O}$  (equivalent with respect to initial **A** in CDL **II**) solubilized in  $\text{CH}_3\text{CN}$ ; excitation at 320 nm. (c) Partial titration (0 to 4 equiv  $\text{Zn}^{\text{II}}$ ) in the same conditions as (b), illustrating the self-sensing occurring after the component exchange process (sensor formation) is completed, i.e., beyond 2 equiv of  $\text{Zn}^{\text{II}}$ .

protons of **1–3** (Figure 1) and **4** and **5**, as well as of the UV–vis electronic absorption bands (Figure 2) and the fluorescence emission (vide infra). It contained mainly (80% of the mixture with a cis/trans ratio of 25:75) the alternating fluorene/cyclohexane sequence **4**, incorporating the more nucleophilic diamine **B**, and displaying a characteristic absorption band at 345 nm. Integration of the imino-CH and the remaining aldehyde proton NMR signals gave a degree of polymerization (DP)  $n$  of about 9 ( $\text{MW} \approx 5000$ ).<sup>10b</sup> On addition of  $\text{Zn}^{\text{II}}$  to the CDL **II**, its color evolved from a pale yellow (without zinc) to a red brown suspension (2 equiv of zinc compared to **A**). The change in composition was followed by  $^1\text{H}$  NMR and UV spectroscopy in chloroform (Figure 2).<sup>10b</sup> The increase of the aromatic and the concomitant decrease of the aliphatic imine-CH proton NMR signals indicated that the polymer incorporated an increasing amount of **C** unit, up to practically pure **5**. Simultaneously, the absorption band at 345 nm decreased, and the band at 418 nm strongly increased, becoming finally similar to the bands displayed by the isolated polymer **5**. The reversibility was again shown by addition of hexamethylhexacyclen **D** (1 equiv with respect to  $\text{Zn}(\text{BF}_4)_2$ ), which led to the same pattern as was observed for the system without zinc. The fluorescence of the polyiminofluorene **5** itself in presence of various amounts of  $\text{Zn}^{\text{II}}$  (Figure 3a) displayed a shift from yellow to blue as well as an increase in emission intensity (4 times) for 30 equiv of  $\text{Zn}^{\text{II}}$ . No such changes were observed for the nonconjugated polymeric structure **4**.

Finally, the combined effects of the  $\text{Zn}^{\text{II}}$  ions, i.e., simultaneous modification of constitution and fluorescence enhancement, were examined by adding increasing amounts of metal salt, from 0 to 30 equiv, to the CDL **II** (Figure 3b).<sup>10b</sup> As indicated above, the constitution of the polymeric structure changes progressively from **4** toward genuine **5** at 2 equiv of zinc salt (orange color on the graph). For higher amounts of zinc ions, marked spectral changes occur; new emission bands appear at 400 and 430 nm and evolve toward a very intense band at 420 nm for large amounts of metal salt. These effects may be considered as resulting from the interaction of the fully aromatic polyimine **5** with the  $\text{Zn}^{\text{II}}$  ions, which manifests itself by a marked fluorescence change after more than 2 equiv of  $\text{Zn}^{\text{II}}$  have been added to the CDL **II**; they amount to an ion-induced signal generation (Figure 3c). A similar behavior is observed for pure **5** itself (Figure 3a).<sup>11,12</sup>

From a conceptual point of view, these results express a synergistic adaptative behavior: the addition of an external effector (e.g., zinc ions) drives a constitutional evolution of the dynamic mixture toward the selection and amplification of that species (compound **5**) that allows the generation of a (optical) signal indicating the presence of the very effector that promoted its

generation in the first place. It embodies a “constitutional dynamic self-sensing” process that extends the range of self-processes.<sup>13</sup> Such constitutional reorganization of a system is of special interest for the design of dynamic “smart” materials, allowing the expression and fine-tuning of a given virtual (latent) property and/or producing an adaptative response under the pressure of external conditions. Moreover, the self-sensing behavior, where an effector induces the upregulation of its own detector, amounts to a further step in the emergence, at the molecular and supramolecular levels, of dynamic systems of increasing complexity.

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- (8) The equilibrium is reached in less than 1 min after the addition of  $\text{Zn}(\text{BF}_4)_2 \cdot 8\text{H}_2\text{O}$ .
- (9)  $\text{Zn}^{\text{II}}$  coordination to cyclopentylamine is indicated by a 0.35 ppm shift of the  $\alpha$ -CH proton NMR signal toward higher ppm values.
- (10) (a) The reaction product was a pale yellow solution and precipitate ( $[\text{A}]_0 = 5.12 \times 10^{-2}$  M). (b) For spectral characterization, this product was either dissolved in chloroform (for UV–vis and fluorescence spectroscopy) or evaporated to dryness under vacuum without heating and a sample was dissolved in chloroform (for  $^1\text{H}$  NMR as well as UV–vis and fluorescence spectral determinations); when both procedures were used they gave the same results. The concentration of the solutions used for NMR spectroscopy was  $10^{-4}$  M.
- (11) The origin of the optical sensing effect is unclear; it may be due to  $\text{Zn}^{\text{II}}$  coordination to a imine nitrogen site, but that it does indeed occur suffices for the present purposes. On addition of large amounts of zinc salt (up to 50 equiv), the DP decreases to about 5; however, the emission wavelength remains practically unchanged, indicating that the effect is not due to this factor.
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