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Tunable Fluorene-Based Dynamers through Constitutional Dynamic Chemistry

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Abstract: Dynamic covalent iminofluorene-based oligomers and polymers have been generated. They undergo constitutional recomposition under the effect of two parameters, acidity and Zn^{II} metal ions. As a result, marked changes in physical properties take place. The results illustrate the response of such a dynamic system to chemical effectors (H^+ and Zn^{II}), thus demonstrating the adaptive behavior of the system under the pressure of external factors. They also point to the possibility of modulating optical properties (UV-visible absorption and fluorescence) by constitutional recomposition in response to a specific trigger. Such features allow the development of dynamic materials, the functional properties of which may respond to external stimuli.

Keywords: dynamic combinatorial chemistry · molecular diversity · polymers · stimuli-responsive systems · tunable functional materials

Introduction

Constitutional dynamic chemistry (CDC)[1] rests on the generation of plasticity in combinatorial systems whose constituents result from reversible constitutional combination of a set of basic building blocks. External stimuli may interact with the mixture of constituents, and allow for a tunable regulation of the connectivities within the library. Indeed, such molecular[2–5] or supramolecular systems,[1,6,7] linked through covalent bonds or noncovalent interactions, respectively, are able to evolve by responding to chemical or physical effectors through reorganization of their constituents. Over the last years molecular/covalent CDC has been implemented in dynamic combinatorial chemistry (DCC), particularly in the field of drug discovery.[3] Thus, the global thermodynamic equilibria between real or virtual[3a] members of a library of inhibitors are shifted by the presence of a biological target in situ, through the amplification/selection of the constituent with the highest affinity with its active site. The use of shape recognition as a driving force, able to guide thermodynamic equilibria, has also been exploited in the selective self-assembly of metallosupramolecular architectures from dynamic sets of specifically encoded ligands.[8]

Target binding is but one particular case of effect induced by external stimuli, and encompass a much broader range of triggering types; indeed, proton concentration or temperature markedly rearrange the constitutional composition of entities interconnected through coupled equilibria in libraries of imines.[9] In addition to enhancing the fundamental understanding of the intrinsically adaptative behavior present in such systems, this type of control emerges as a useful tool to tune the composition of dynamic constitutional libraries that are able to express various latent properties, which are not observed with connectively static entities. CDC is also of special interest for materials science, as it offers the possibility of designing dynamic "smart materials", allowing either the expression/nonexpression or the fine tuning of a given property under different environmental conditions through well-defined constitutional reshuffling. Access to such materials can be realized by the design and control of dynamic polymers, named "dynamers", in which monomers are connected by reversible covalent bonds or noncovalent interactions in dynamic molecular[5,10] or supramolecular[6] polymers, respectively. Functional dynamers, incorporating physically or chemically active components represent a particularly attractive type of dynamic materials.

Oligofluorenes and polyfluorenes constitute a broad and very attractive class of efficient photoactive and electroactive compounds with high charge-carrier mobility and good processability.[11] The great interest shown for these molecules over the last years reflects their special relevance for

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manufacturing organic light-emitting diodes (OLEDs)[12] and, especially, their use for display applications. Other unusual properties contribute also to this activity, such as a doped polyelectrolyte anion conductivity and thermochromism.[13]

We herein demonstrate the ability of a set of oligo- and polyiminofluorene-based dynamers to undergo tunable exchange processes through incorporation, decorporation, and exchange of their monomeric entities by means of reversible imine formation under the action of external stimuli, resulting in the generation of optical signals varying in both wavelength and intensity, according to the general pattern shown in Figure 1. In particular, fully conjugated dynamic polyfluorenes can thus be generated. The behavior of the system was investigated by ^{1}H NMR studies correlated with UV-visible and fluorescence spectroscopy under the effect of either pH or metallic ions, and the control over its constitutional dynamics has been achieved.

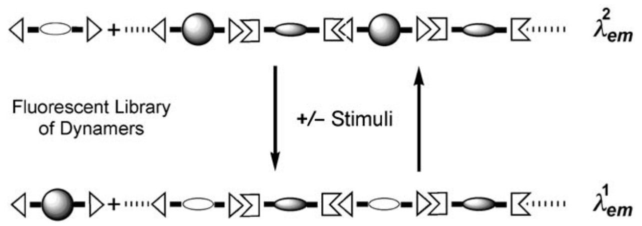


Figure 1. General representation of the tunable exchange process in a library of fluorescent dynamers. The changes in the emission properties result from the recombination of the photoactive monomeric components incorporated into the polymeric structure by using external stimuli.

In addition, these studies revealed the emergence of a more complex type of behavior whereby an effector (namely Zn^{II} ions) induces the upregulation of its own detector (reorganization process and subsequent detection of the effector); this amounts to a sort of "self-sensing" process that extends the range of self-processes towards (dynamic) systems of increasing complexity.[1,10,14]

Abstract in French: *Des oligomères et des polymères réversibles de type iminofluorènes ont été générés. Ils subissent une recomposition constitutionnelle sous l'influence des paramètres: concentration en protons et en ions zinc(II). Il en résulte des modifications prononcées des propriétées optiques. Les résultats illustrent les possibilités offertes par les changements de constitution en réponse à des stimuli chimiques (H^+ et Zn^{II}), et ils démontrent l'adaptation de tels systèmes sous la pression de paramètres environnementaux. Cette modulation de la constitution permet la modulation des propriétés optiques (absorption UV-Vis et fluorescence) en fonction des stimuli imposés. De tels systèmes présentent un intérêt particulier pour le développement de matériaux dynamiques dont les propriétés fonctionnelles se modifient en réponse à des stimulations externes.*

Finally, in addition to the selection aspect, the kinetics of the exchange processes indicate that the Zn^{II} driven evolution is catalyzed by the presence of the zinc itself by means of a transimination pathway.

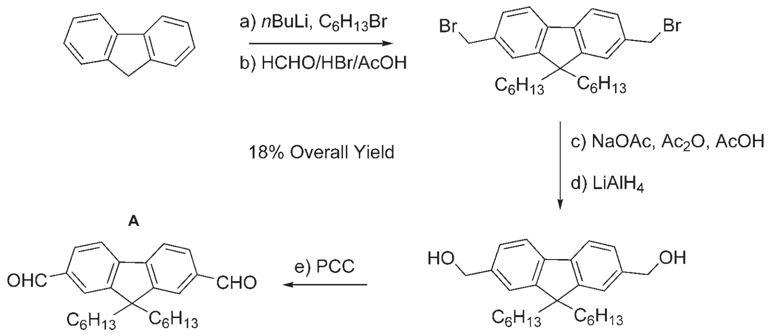
Results and Discussion

Synthesis and characterization of oligomeric and polymeric stuctures:[15] To obtain reference data for the study of the dynamic oligoimino- and polyiminofluorene entities in coupled thermodynamic equilibria, we first synthesized a series of model compounds so as to characterize their spectroscopic properties. The systems investigated are based on the use of the readily available 2,7-fluorenebiscarboxaldehyde **A** as a core building block (Scheme 1).

Compound **A** readily reacts through imine formation with aromatic and aliphatic amines in ethanol to give entities ranging from the tris-component compounds **1**–**3** (termed tris thereafter) to oligomeric **4** and **5** (when a capping agent is used) and to polymeric **6**–**9** compounds (Scheme 2). The products were isolated as white (**2** and **6**) and yellow (**1**, **3**, **4**, **5**, **7**, **8**, **9**) powders. Various analytic techniques were used for the structure determination of the conjugated and non-conjugated derivatives: MALDI-TOF mass spectrometry, ^{1}H NMR and UV-visible spectroscopy, and fluorescence optical studies.

MALDI-TOF mass spectrometry confirmed the trimeric structures of compounds **1**–**3**, as well as the oligomeric and polymeric structures of compounds **4**–**9**. For the last ones, the repetitive units were found to actually correspond to monomeric fragments bearing one amine and one aldehyde as well as some other smaller fragments (Figure 2, top). The degree of polymerization (DP) values and the corresponding masses are summed up in Table 1. In the case of oligomeric structures **4** and **5**, which were obtained by using capping agents (aniline and aminofluorene, respectively), the MALDI-TOF spectra show, as expected, shorter lengths than the polymeric ones (one third for the DP values compared to **8** and **7**, respectively) with predominant formation of the expected compounds **4** and **5** with $n=1$. The optical properties are also correlated with these observations (vide infra).

^{1}H NMR studies are particularly useful for obtaining structural information about both static and dynamic entities, for it is possible to follow the polymer length as well as its chemical composition by integration of the different imine-type and remaining aldehyde proton signals (Figure 2, bottom). Such data allow a detailed analysis of the molecular constitution during the exchange processes, as well as the interpretation of the changes in optical properties. The polymer length was estimated by ^{1}H NMR spectroscopy, using Equation (1); the different average DPs are given in Table 1.

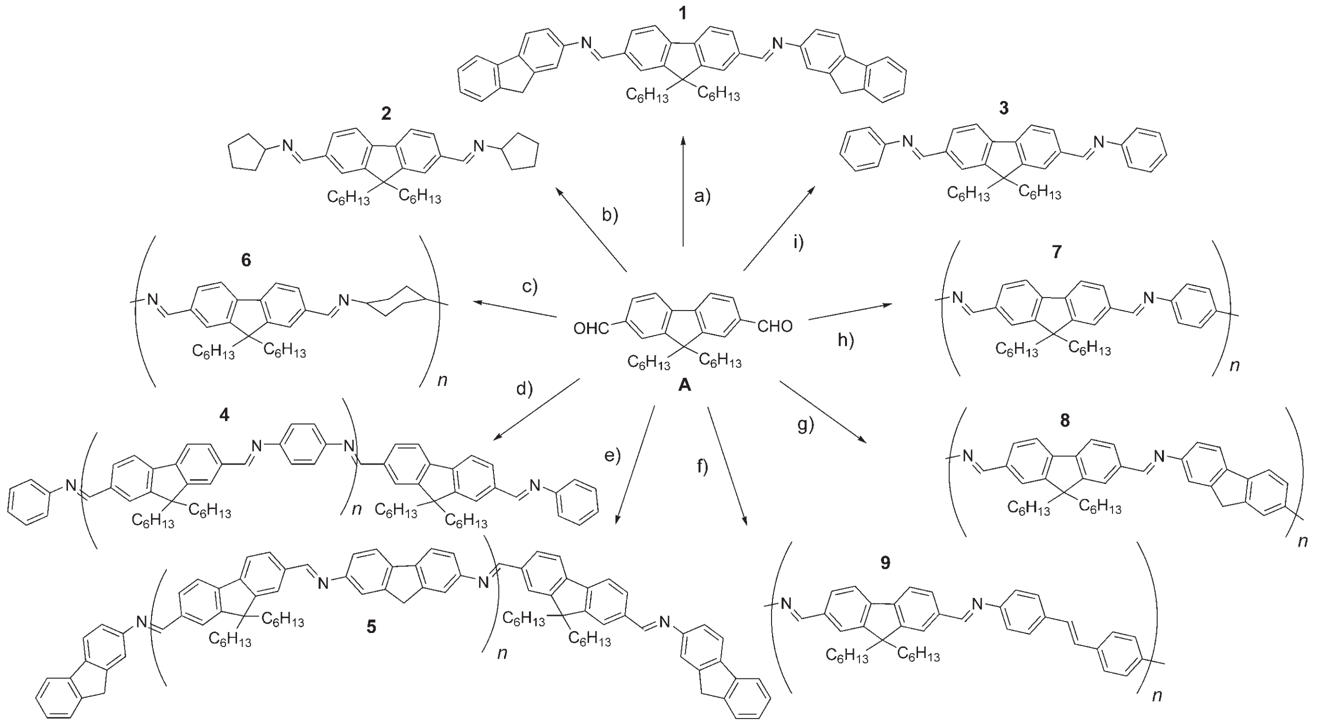


Scheme 1. Synthetic scheme for the five steps sequence leading to 2,7-fluorenebiscarboxaldehyde **A** from fluorene. a) *n*BuLi (2 equiv), slow addition (0.5 h), THF, −78 °C; then 1-bromohexane, 3 equiv, −78 °C→RT, 12 h, quantitative yield.[26] b) Paraformaldehyde (10 equiv), 0 °C; then 30 % solution of HBr in acetic acid, 65 °C, 24 h, 88 %.[26] c) Anhydrous sodium acetate (10 equiv), acetic acid anhydride (10 equiv), acetic acid, reflux, 24 h, mixture of mono and bisacetate (2:1), 30 %. d) $LiAlH_4$ (10 equiv), THF, reflux 18 h, 92 %. e) PCC (20 equiv), molecular sieves (50 mass %), silica gel (50 mass %), CH_2Cl_2, 4 h, then RT, 12 h, 75 %.

$$[\overline{\mathrm{DP}}_n] = \frac{1}{2}\left[\frac{\sum \mathrm{Imine}\,^1\mathrm{H}}{\sum \mathrm{Aldehyde}\,^1\mathrm{H}} + 1\right] \qquad (1)$$

The dialdehyde **A**, trimer **2**, and nonconjugated polymer **6** have very similar UV-visible spectra, with three absorption bands below 350 nm, and only a slight difference is observed in their purple/blue fluorescence emission spectra (416, 423, and 431 nm, respectively; Figure 3 and Table 1). As expected, the conjugated imines exhibit a bathochromic shift in their absorption spectra depending on their lengths. For example, compound **1**, which contains three conjugated fluorene moieties, absorbs at 394 nm; compound **5** with an average DP of 2 absorbs at 414 nm; and for polyfluorene **8** (average DP of 10), a plateau is reached at 418 nm. The general behavior of compounds **1**, **5**, and **8** is similar; in the fluorescence spectra emission wavelengths from blue to green at 460, 477, and 493 nm respectively, are observed. Comparable responses are obtained for compounds **4** and **7**, containing 1,4-phenylenediamine moieties, with an average DP of 2 (λ_{abs} = 408 nm; λ_{em} = 483 nm) and 16 (λ_{abs} = 420 nm; λ_{em} = 490 nm), respectively.

Based on the characteristic variations in the physical properties of the iminofluorene derivatives, as a function of constitution and length, this type of system appeared to be suitable for their implementation in constitutional dynamic experiments and for the subsequent studies of the optical signals.



Scheme 2. Synthetic scheme for the syntheses of oligomeric and polymeric structures **1**–**9** from 2,7-fluorenebiscarboxaldehyde **A**. All the reactions were set up by mixing **A** with imine derivatives in ethanol for 12 h. a) 2 equiv aminofluorene. b) 3 equiv cyclopentylamine. c) 1 equiv *trans*-1,4-cyclohexyldiamine. d) 0.5 equiv 1,4-phenylendiamine, 1 equiv aniline. e) 0.5 equiv 2,7-diaminofluorene, 1 equiv 2-aminofluorene. f) 1 equiv 4,4′-diaminostilbene. g) 1 equiv 2,7-diaminofluorene. h) 1 equiv 1,4-phenylenediamine.

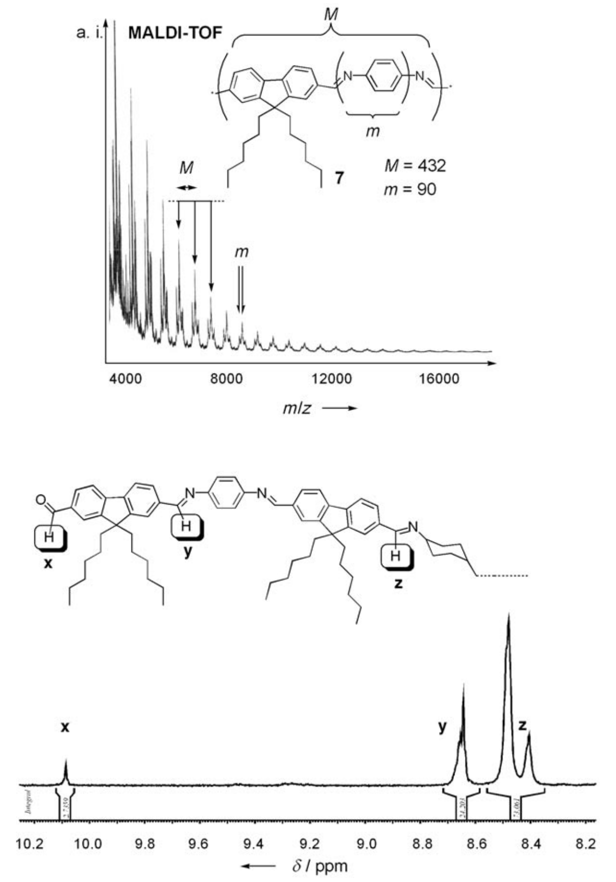


Figure 2. Top: MALDI-TOF spectroscopy in a ditranol matrix of compound **7** bearing repetitive monomeric units (with their corresponding mass fragments *M* and *m*) up to a degree of polymerization (DP) of 34 (MW≈15000). Bottom: ^{1}H NMR spectrum of a mixed polymeric structure incorporating both 1,4-phenylenediamine and *trans*-1,4-cyclohexanediamine (1:1) in chloroform ($c = 10^{-4}$ M) at RT with labeled characteristic signals of: remaining aldehyde (*x*), aromatic imine (*y*), and (*cis* + *trans*) aliphatic imine (*z*).

Protonic modulation of the constitutional dynamic libraries: Our first experiments on the control of constitutional reorganization of the iminofluorene dynamers were based on previous work, namely the use of protons as a triggering effector.[9] They involved the analysis by ^{1}H NMR spectroscopy of the effect of acid on the constitutional dynamic behavior of the library (CDL **I**) obtained from a 1:2:2 mixture of 2,7-fluorenebiscarboxaldehyde **A**, cyclopentylamine and 2-aminofluorene in $CDCl_3$ (Figure 4).

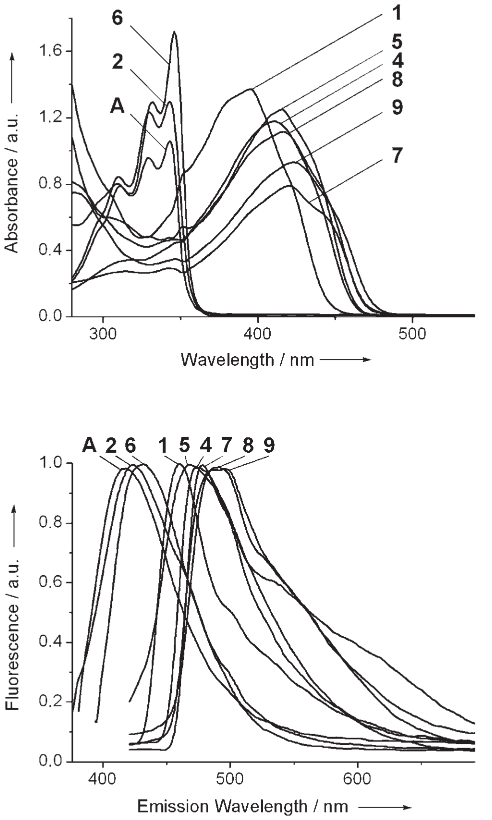


Figure 3. Top: UV-visible absorption spectra of structures **A** and **1**–**9** depicted in Scheme 2, recorded at 298 K in chloroform (see Table 1 for absorption values). Bottom: Normalized fluorescence spectra of structures **A** and **1**–**9** depicted in Scheme 2 recorded at 298 K in chloroform (see Table 1 for absorption values).

The mixture was analyzed for a range of CF_3CO_2D concentrations between 0 and 1 M. The various solutions were light yellow for $[CF_3CO_2D] = 10^{-2}$ M, then turned to orange on increasing the acid concentration to 10^{-1} M, and finally it evolved to a deep red for $[CF_3CO_2D] =$ 1 M. These observations were correlated with a dramatic evolution of the library constitution as can be followed by ^{1}H NMR spectroscopy (Figure 4, bottom).[16] For $0 < [CF_3CO_2D] = 10^{-3}$ M, the system,

Table 1. Degree of polymerization, molecular weight, and optical properties obtained from MALDI-TOF, ^{1}H NMR, UV-visible absorption, and fluorescence emission spectroscopy for compounds **A** and **1**–**9** depicted in Scheme 2.

	DP$_n$[a]	DP$_{max}$[b]	MW[c] [g mol^{-1}]	c [mol L^{-1}]	Abs. max. [nm]	ε [L mol^{-1} cm^{-1}]	Em. max. [nm]
A	–	–	390.5	5.05×10^{-5}	343, 329, 311	2.09×10^{4}	416
1	–	–	716.4	1.50×10^{-5}	394	9.15×10^{4}	460
2	–	–	524.4	7.62×10^{-5}	342, 329, 310	1.69×10^{4}	423
4	2	8	1464	5.42×10^{-6}	408	2.18×10^{5}	483
5	2	6	1816	5.36×10^{-6}	414	2.08×10^{5}	477
6	9	14	4216	6.68×10^{-5}	345, 331, 309	2.12×10^{4}	431[d]
7	16	32	7400	1.56×10^{-5}	420	8.00×10^{5}	490
8	10	18	5500	1.16×10^{-5}	418	6.80×10^{5}	493
9	13	25	7332	1.15×10^{-5}	422	8.09×10^{5}	496

[a] The DP average is given in chloroform (10^{-4} M) and was determined by ^{1}H NMR spectroscopy by using Equation (1), except for compounds **4** and **5** for which the DP average was taken directly from MALDI-TOF spectroscopy. [b] The DP maximum was taken from MALDI-TOF spectroscopy. [c] Calculated from the DP average. [d] This value is given for an excitation wavelength at 380 nm. The excitation at 320 nm leads to an emission at 370 nm.

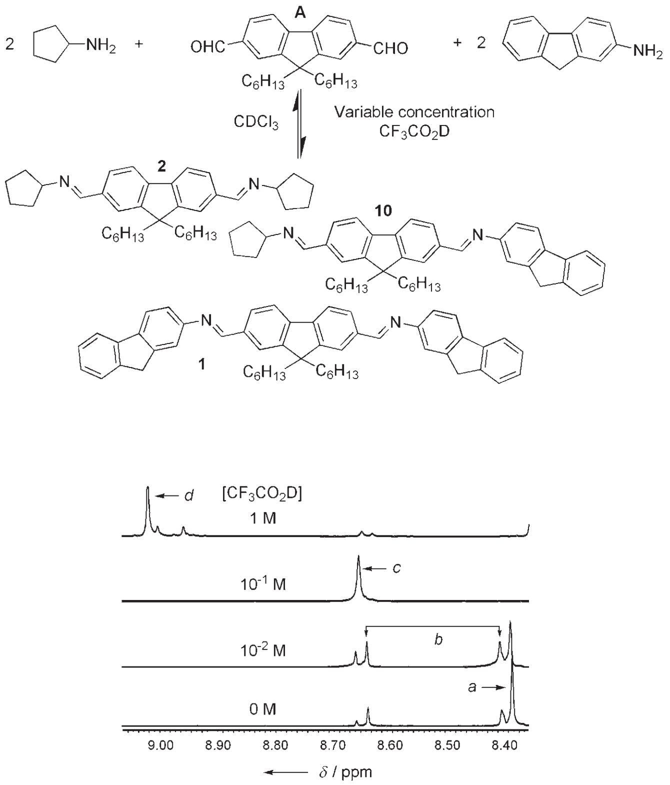


Figure 4. Top: Constitutional dynamic library of iminofluorenes (CDL **I**) with CF_3CO_2D promoted component exchange in deuterated chloroform leading to a mixture of trimeric species **1**, **2** and **10**. Bottom: Selected ^1H NMR spectra (400 MHz) of CDL **I** (5.12×10^{-2} M in $CDCl_3$) for various CF_3CO_2D concentrations at 298 K. a) signal of aliphatic imine **2**; b) imine signals of mixed compound **10**; c) signal of aromatic imine **1**; d) signal of protonated imine **1**.

as expected, expresses mainly the bis-aliphatic imine **2** with a ratio of 7:2.5:0.5 with respect to the mixed compound **10** and bis-aromatic derivative **1** respectively.[17,18] For higher H^+ concentrations, the system starts expressing more and more of bis-aromatic adduct **1** and a total selectivity in favor of **1** is obtained for $[H^+]=10^{-1}$ M (resonance imine signal at $\delta=8.65$ ppm), although a lower global conversion is also reached at this point.[19] Above this value, the aromatic imine signal is shifted toward higher ppm values ($\Delta\delta=0.45$ ppm), characteristic of protonated compound **1**, with a 90% conversion. Increasing further the amount of acid leads to a decomposition of the system into protonated free amine and aldehyde. The selectivity and dissociation of the system by hydrolysis are governed by the relative and absolute pK_a values of the two amines involved. As a consequence, the most basic cyclopentylamine is protonated first and taken out of the trimeric species **2**, allowing for its substitution by the less basic 2-aminofluorene, until the latter also undergoes protonation ($[H^+]>1$ M).

It has previously been shown that temperature variations can markedly change the distribution inside a dynamic set of imines.[9] A study of the present system between 298 K and 348 K in 5 K increments gave, unfortunately, no improvement of the selectivity.[19] These results are consistent with the fact that the large difference in the bacicities of the amines in the present system (about 6 pK_a units), leads to a predominant effect of the CF_3CO_2D concentration that cannot be significantly affected within such a range of temperature variations.

The optical absorption and emission variations due to the acidity-induced reshuffling (Figure 5) are fully correlated with the NMR studies. Thus, after equilibration at 298 K and for $[CF_3CO_2D]=0$ M, CDL **I** displays the characteristic UV-visible absorption pattern of compound **2** (trace b), superimposable to that of the reference spectrum of the isolated imine (trace a) with, in addition, a small shoulder corresponding to residual mixed compound **10** and imine **1**. For $[CF_3CO_2D]=10^{-1}$ M (trace c), the maximum of absorption fits with the λ_{max} of bis-aromatic imine **1** and finally, the absortion at 490 nm for a $[CF_3CO_2D]=1$ M corresponds to protonated imine **1** (trace d). Also consistent with NMR data, the photoluminescence properties of CDL **I** shows a dramatic shift from 420 nm (blue) to 610 nm (red) over the same range of CF_3CO_2D concentrations (traces f to i).

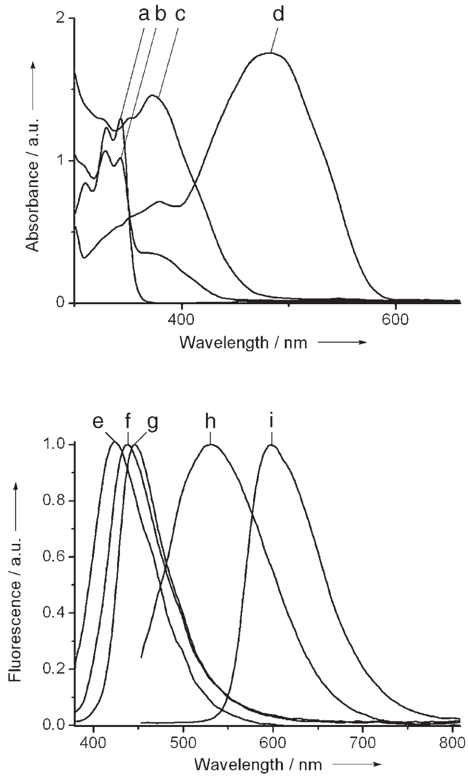


Figure 5. Top: UV-visible absorption spectra of CDL **I** in chloroform for various concentrations in CF_3CO_2D (a: reference **2**; b: CDL **I**, 0 M; c: CDL **I**, 10^{-1} M; d: CDL **I**, 1 M). Bottom: Normalized fluorescence spectra of CDL **I** in chloroform for various concentrations in CF_3CO_2D (e: reference **2**; f: CDL **I**, 0 M; g: CDL **I**, 10^{-4} M; h: CDL **I**, 10^{-1} M; i: CDL **I**, 1 M). For both experiments, the proton concentration values are given for a solution of initial concentration 5.12×10^{-2} M in dialdehyde **A**; the spectra were recorded after equilibration and subsequent dilution to reach the values of $[\mathbf{A}]=2.6\times10^{-5}$ M (top) and $[\mathbf{A}]=2.6\times10^{-6}$ M (bottom). Dilution is not expected to change the equilibria; as the measurements are conducted in chloroform, the protonation state should not be significantly affected; furthermore, no change in spectra over time has been observed.

Finally, the reversibility of the overall system has been evaluated by using triethylamine for neutralizing the reaction mixture and returning to its original constitution. The reversibility ($\mathbf{2} \rightleftarrows \mathbf{1}$) was confirmed by ^{1}H NMR experiments three times in a row, and the fluorescence behavior also illustrates the good monitoring of the system (Figure 6 top). The non-normalized fluorescence spectra (bottom) emphasize the two effects brought by the proton trigger: constitutional recombination (f$\rightleftarrows$h) and subsequent appearance of an optical signal by interaction of the protons in excess with the trimer, which had been previously formed under their influence (h$\rightleftarrows$i).

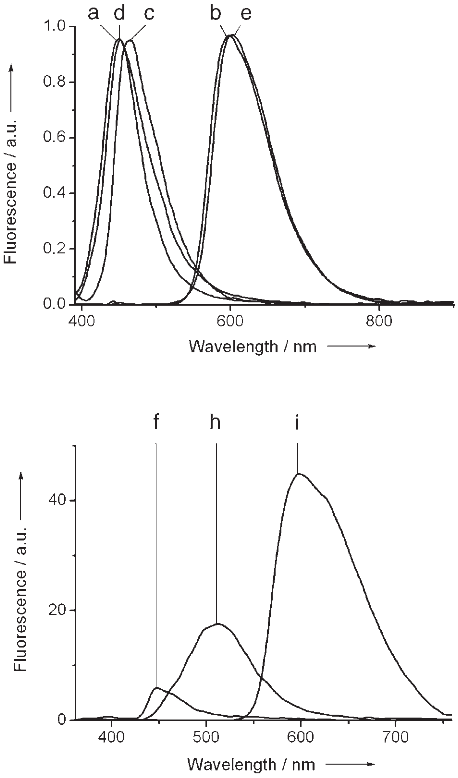


Figure 6. Top: Normalized fluorescence spectra of CDL **I** in chloroform for various concentrations in CF_3CO_2D and Et_3N (a: $[CF_3CO_2D]=0$ M; b: $[CF_3CO_2D]=1$ M; c: b then neutralization to 0 M in acid (2 min); d: b then neutralization to 0 M in acid (20 minutes); e: d then acidification to $[CF_3CO_2D]=1$ M. Bottom: Non-normalized fluorescence spectra of CDL **I** in chloroform for various concentrations in CF_3CO_2D and for a same excitation wavelength (400 nm) (f: $[CF_3CO_2D]=0$ M; h: $CF_3CO_2D]=10^{-1}$ M; i: $CF_3CO_2D]=1$ M). For both experiments, the proton concentration values are given for a solution of initial concentration 5.12×10^{-2} M in dialdehyde **A**; the spectra were recorded after equilibration and subsequent dilution to reach the values of $[\mathbf{A}]=2.6\times10^{-6}$ M (see also caption to Figure 5).

On the basis of the results obtained for the "tris" system CDL **I**, the possibility to inteconvert polyimines **6** and **8** (CDL **II**) was investigated. Again, the system appeared to be coherent with expectation based on the ^{1}H NMR studies, but the lower conversion to imine for $[CF_3CO_2D]=10^{-1}$ M did not allow the preservation of the polymeric structures. Indeed, even if CDL **II** preferentially expresses nonconjugated polyimine **6** (80 % by ^{1}H NMR spectroscopy) and if the exchange effectively occurs towards formation of **8** when the $[CF_3CO_2D]$ is increased, the system decomposes quickly (a few minutes timescale) into short size oligomeric structures, above 10^{-1} M acid, as shown by the various spectroscopic analyses. This dissociation of the polymers by acid precluded the induction of the "doping effect" as it had been done in CDL **I** (Figure 6, bottom) in order to extend the exploitable optical domain.

Modulation of the constitutional dynamic by metal ions

Interaction with metal ions: As a consequence of the difficulties encountered with protonation, we extensively looked for a suitable trigger capable of reorganizing polymeric systems, while preventing their dissociation by hydrolysis. The fluorescence shift/enhancement caused by protons with compound **1** prompted us to explore the interaction of such polyiminofluorene structures with various Lewis acid metal ions.

Interactions between C=N bonds and protons or metallic ions are well known in the literature: imines may undergo changes in optical properties upon metal-ion coordination,[20] and a few sensors were previously designed using this chemical bond.[21]

Considering that optical changes would be a sign for the interaction of given metal ions with the imine compounds, we explored the optical responses of isolated polyimines **7** and **8** upon the addition of a broad range of metal ions and a selection of some of the patterns thus obtained is represented in Figure 7, which shows the spectra obtained by addition of silver(II), cadmium(II), copper(II), and zinc(II) salts to polymer **7**. It is seen that the increase of the fluorescence emission as well as its shift from the original position depends on both the metal ion and the polymer structure. For example, the behavior of **7** upon addition of silver triflate (Figure 7, top left) results in the enhancement of the polymer emission by a factor of ten, together with a bathochromic shift of 125 nm to the yellow part of the spectrum ($\lambda_{max}=575$ nm). Addition of copper(II) triflate to **7** leads to a narrower band at the same wavelength and with a very strong increase in intensity by a factor of 40 (Figure 7, middle left). $CdCl_2$ does not cause a shift in λ_{max}, but a small positive emission response (Figure 7, top right).

The crucial role played by the nature of the backbone and its length is illustrated in the last three graphs representing the responses of polymers **7** (middle right), **8** (bottom left) and tris **1** (bottom right) upon addition of $Zn(BF_4)_2{\cdot}8H_2O$. The differences between these spectra are striking: while compounds **1** and **7** display bathochromic shifts (15 and 100 nm, respectively), compound **8** shows a hypsochromic shift of 50 nm.

Metal-ion-induced CDL reorganization: Taking the above results as an indication for which metal ions may interact with the studied dynamers, we investigated the possible re-

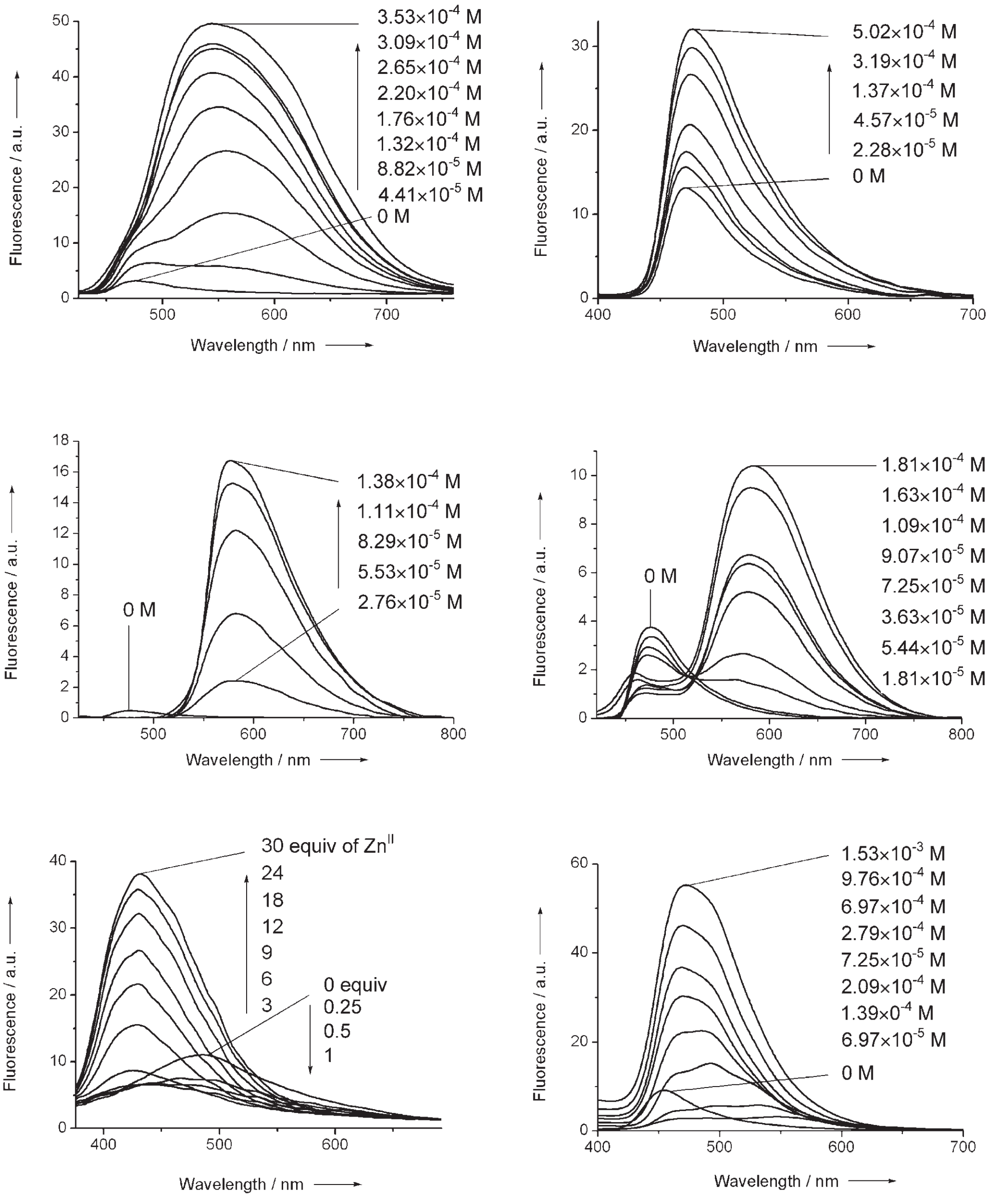


Figure 7. Top left: Fluorescence spectra at 298 K in $CHCl_3$ of compound **7** ($c=4\times10^{-6}$ M) when adding increasing amounts of Ag(OTf) solubilized in $MeNO_2$. Excitation wavelength 390 nm for all the series. Top right: Fluorescence spectra at 298 K in $CHCl_3$ of compound **7** ($c=4\times10^{-6}$ M) when adding increasing amounts of $CdCl_2$ solubilized in $CHCl_3$. Excitation wavelength 333 nm for all the series. Middle left: Fluorescence spectra at 298 K in $CHCl_3$ of compound **7** ($c=4\times10^{-6}$ M) when adding increasing amounts of $Cu(OTf)_2$ solubilized in CH_3CN; excitation wavelength 350 nm for all the series. Middle right: Fluorescence spectra at 298 K in $CHCl_3$ of fluorene polyimine **8** ($c=4\times10^{-6}$ M) when adding increasing amounts of $Cu(OTf)_2$ (equivalent with respect to initial **A** in **8**) solubilized in CH_3CN; excitation at 350 nm for all the series. Bottom left: Fluorescence spectra at 298 K in $CHCl_3$ of fluorene polyimine **8** ($c=4.05\times10^{-6}$ M) when adding increasing amounts of $Zn(BF_4)_2{\cdot}8H_2O$ solubilized in CH_3CN; excitation at 390 nm for all the series. Bottom right: Fluorescence spectra at 298 K in $CHCl_3$ of fluorene diimine **1** ($c=4.05\times10^{-5}$ M) when adding increasing amounts of $Zn(BF_4)_2{\cdot}8H_2O$ solubilized in CH_3CN; excitation at 333 nm for all the series.

organization of libraries of iminofluorenes upon metal-driven exchange. A wide set of metal salts were investigated and, although most of them led to a recombination, only $Zn(BF_4)_2{\cdot}8H_2O$ appeared to selectively realize a full exchange between cylopentylamine and 2-aminofluorene in the model system CDL **I** (Figure 8). The ^{1}H NMR titration shows that the completion of the exchange is obtained for two equivalents of zinc(II) tetafluoroborate, while one equivalent leads to a ratio of 1:1:2 in **1**, **2**, and **10** respectively: these statistical values indicate that one aliphatic amine is trapped by one Zn^{II} ion. This observation is also consistent with the shift of the signal of the proton on the α-carbon of cyclopentylamine compared to its resonance in the free amine ($\delta=3.75$ and 3.40 ppm, respectively). Zinc(II) apparently displays both the Lewis acidity and the proper interaction selectivity for catalyzing the exchange and for discriminating between aromatic and aliphatic amines, in contrast to the other tested metal salts.[22] Moreover, the system

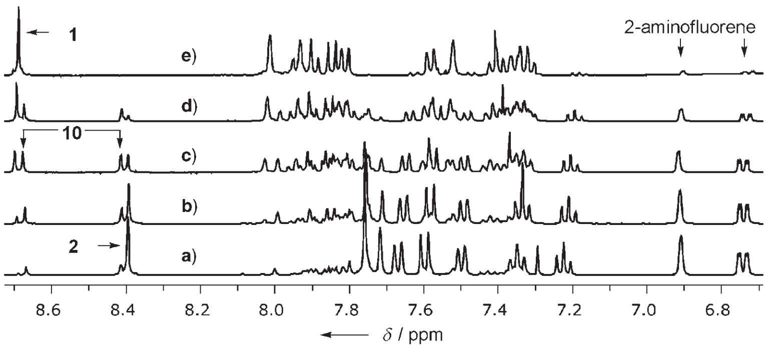


Figure 8. Constitutional dynamic library of iminofluorenes, CDL **I**, with $Zn(BF_4)_2{\cdot}8H_2O$-promoted component exchange (see Figure 4, top): ^1H NMR spectra (400 MHz) of CDL **I** for different $Zn(BF_4)_2{\cdot}8H_2O$ concentrations at 298 K in $CDCl_3$ (a = 0 M; b = 3.10×10^{-2} M; c = 6.20×10^{-2} M; d = 8.68×10^{-2} M; e = 1.24×10^{-1} M); initial concentration of **A**: 5.12×10^{-2} M (see also Figure 1 in reference [10]).

retains high conversion to imines in presence of Zn^{II} that enables an extension of its use to polymeric structures. The Zn^{II} ions can be seen as a "soft proton" capable of trapping an aliphatic amine efficiently and thus allowing its exchange for an aromatic one.

We then turned to the exchange of components in the polymers formed from a 1:1:1 mixture of **A**, *trans*-1,4-cyclohexanediamine and 2,7-diaminofluorene (CDL **II**) in ethanol at room temperature.[23] Selected ^1H NMR measurements associated with the corresponding UV-visible spectra of polymeric CDL **II** under $Zn(BF_4)_2{\cdot}8H_2O$-promoted component exchange are shown in Figure 9. CDL **II** consists in principle of the two-component polymers **6** and **8** together with a mixture of intermediate three-component **A**/cyclohexyldiamine/diaminofluorene mixed species. Polymers **6** and **8** were prepared independently in the same conditions as the reference compounds for ^1H NMR, UV-visible, and fluorescence spectroscopic studies. The composition of the polymer mixture generated from the **A**/cyclohexyldiamine/diaminofluorene mixture was characterized on the basis of the NMR signal of the imine protons of **6** and **8**, as well as of the UV-visible electronic absorption bands and the fluorescence emission (vide infra) of the isolated compounds. It contained mainly (80 % of the mixture with a *cis*/*trans* ratio of 25:75) alternating fluorene/cyclohexane sequence **6**, incorporating the more nucleophilic cyclohexane diamine and displaying a characteristic absorption band at 345 nm. Integration of the imino–CH and of the remaining aldehyde proton NMR signals gave [Eq. (1) above] a DP of about 9 (MW ~ 5000). By adding Zn^{II} to CDL **II**, its color evolved from a pale yellow (without zinc) to a red brown suspension (two equivalents of zinc with respect to **A**). The change in composition was followed by ^1H NMR and UV spectroscopy in chloroform (Figure 9).[23] 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 the diaminofluoene component, up to practically pure **8**.

Simultaneously, the absorption band at 345 nm decreased and the band at 418 nm strongly increased, finally becoming similar to the bands displayed by the isolated polymer **8**. The reversibility was shown by addition of hexamethylhexacyclen **B** (one equivalent with respect to $Zn(BF_4)_2$), which led to the same pattern as was observed for the system without zinc.[24]

Dynamic constitutional self-sensing:[10] As seen above, the fluorescence of polyiminofluorene **8** itself in the presence of various amounts of Zn^{II} (Figure 7, bottom left) dis-

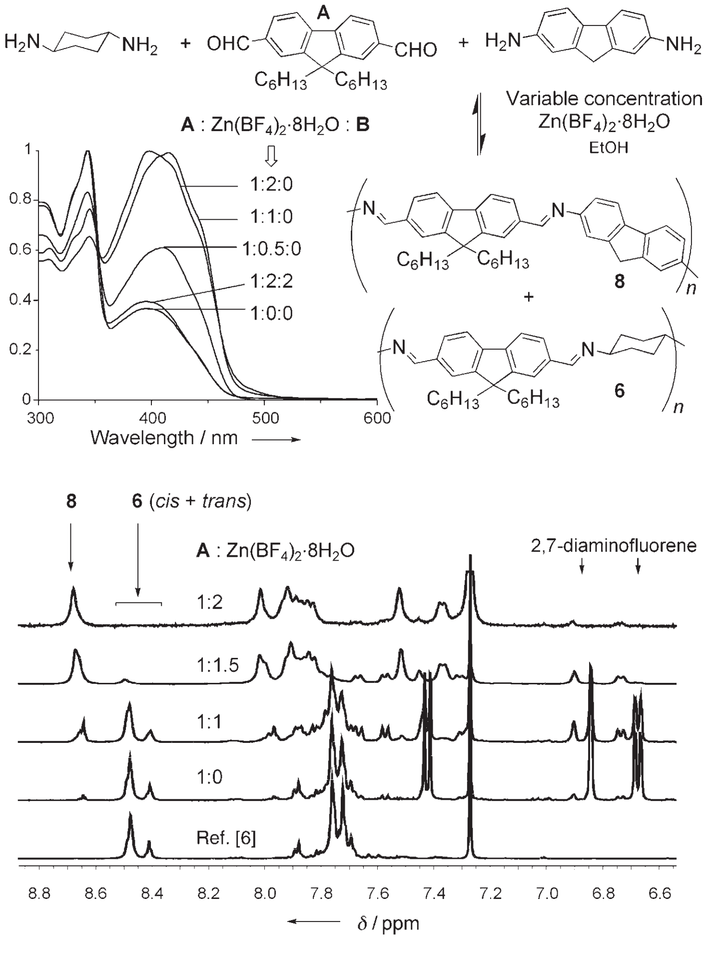


Figure 9. Top: Constitutional dynamic library of polymeric iminofluorenes, CDL **II** (**A**/cyclohexanediamine/diaminofluorene 1:1:1), with Zn^{II}-promoted component exchange and absorption spectra of the CDL recorded at 298 K in $CDCl_3$ for various amounts of $Zn(BF_4)_2{\cdot}8H_2O$ solubilized in CD_3CN. **B** = Hexamethylhexacyclen. Bottom: Selected ^1H NMR spectra (400 MHz) of CDL **II** for different **A**/$Zn(BF_4)_2{\cdot}8H_2O$ ratios at 298 K in $CDCl_3$ with [**A**] = 10^{-4} M. For both experiments, the initial concentration in dialdehyde **A** was 5.12×10^{-2} M. The spectra were recorded after equilibration and subsequent dilution to reach the values of [**A**] = 2.5×10^{-5} M (UV-visible spectroscopy) and [**A**] = 10^{-4} M (^1H NMR spectroscopy).

played a shift from yellow to blue as well as an increase in emission intensity (four times) in presence of large excess (30 equivalents) of Zn^{II}. No such changes were observed for nonconjugated polymeric structure **6**.

The combined effects of the Zn^{II} ions, that is, simultaneous modification of constitution and fluorescence enhancement, were examined by adding increasing amounts of metal salt, from 0 to 30 equivalents, to CDL **II** (Figure 10, top; see also the preliminary report, reference [10]). As indicated above, the constitution of the polymeric structure changes progressively from **6** towards genuine **8** at two equivalents of zinc salt, accompanied by pronounced spectral modifications. For higher amounts of zinc ions, new emission bands appear at 400 and 430 nm and evolve towards a very intense band at 420 nm for large amounts of metal salt. These last effects may be considered as resulting from the interaction of the fully aromatic polyimine **8** with the Zn^{II} ions; this interaction manifests itself by a marked fluorescence change after more than two equivalents of Zn^{II} have been added to CDL **II**. It amounts to an ion-induced signal generation (Figure 10, bottom). On a conceptual level, 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 towards the selection and amplification of that species (compound **8**) which allows the generation of a (optical) signal indicating the presence of the very effector that promoted its generation in the first place. This embodies a "constitutional dynamic self-sensing" process that extends the range of self-processes.[14] A similar effect is found when the acid is used for the reorganization of CDL **I**, resulting in a red shift and a large increase in intensity after the exchange, as shown in Figure 6 (bottom). The effect of both Zn^{II} and H^+ may result from a sort of doping by a positively charged entity.

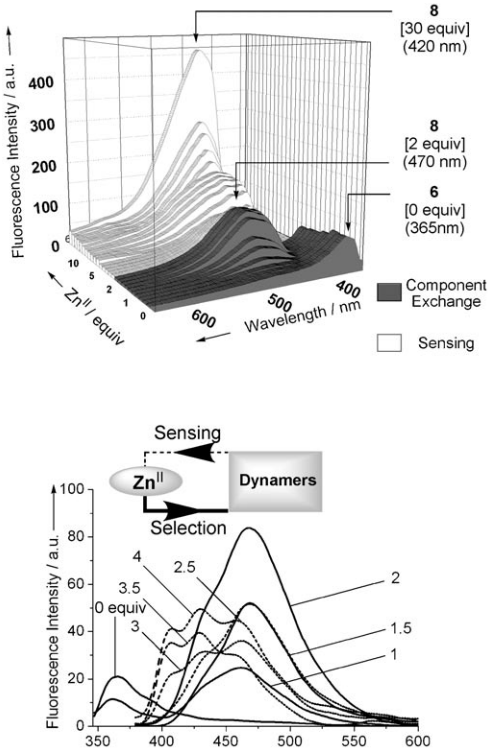
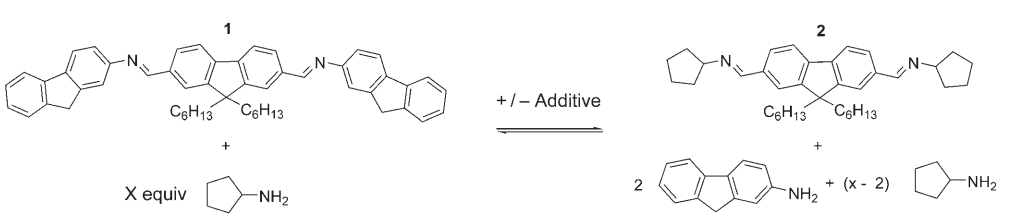


Figure 10. Top: Fluorescence spectra at 298 K in $CHCl_3$ of the CDL **II** of fluorene polyimines of Figure 9, on addition of increasing amounts of $Zn(BF_4)_2 \cdot 8H_2O$ (equivalent with respect to initial **A** in CDL **II**) solubilized in CH_3CN; excitation at 320 nm. Bottom: Partial titration (0 to 4 equiv Zn^{II}) in the same conditions as the spectra shown in the top part of the figure, illustrating the self-sensing occurring after the component exchange process (sensor formation) is completed, that is, beyond 2 equiv of Zn^{II} (see also Figure 3 in reference [10]).

Zinc plays two distinct roles: it is a selection trigger and fluorescence-enhancing agent, as it interacts selectively with the amines and imines in the system. In the following part of the discussion, we highlight that Zn^{II} ions furthermore act as catalyst for the recombination process.

Kinetic and mechanistic aspects of the constitutional dynamic processes: In the course of our investigations, we observed some interesting kinetic aspects of the effect of both protons and zinc ions on the constitutional dynamic libraries discussed above. Whereas the time required to form **2** at equilibrium from aldehyde **A** and free amines in the formation of CDL **I** was about 24 h (Figures 4 and 8), the exchange process for going from **2** to **1**, in presence of Zn^{II} ions, took less than one minute (the equilibration was even too fast to be followed by ^1H NMR spectroscopy). On the other hand, the backward reaction (regeneration of compound **2** from **1**, Scheme 3) using hexamethylhexacyclene as a zinc trapping agent,[24] takes 30 minutes to reach the equilibrium ($t_{1/2} = 3.5$ min) (entry 8, Table 2).

These observations pointed to a possible activation of the exchange process by the Zn^{II} ions. The half-life of the formation of the aliphatic bis-imine **2** starting from compound **1** (as formed in situ from its components) in presence of two



Scheme 3. Constitutional reorganization CDL **I** where the reaction is set up from the compound **1** formed in situ. The results obtained by variations of the two parameters (relative quantity of cyclopentylamine and relative quantity of zinc) are reported in Table 2.

Table 2. Thermodynamic and kinetic data for the equilibration of the reaction starting from different ratios of mixture **1**/cyclopentylamine and leading to **2** and free aminofluorene (Scheme 3) in the presence of additives.

Entry	*X* equiv	Equiv of additive	% of **2** at the equilibrium[a]	$t_{1/2}$ [min][b]
1	2	–	100	15
2	5	–	100	7.5
3	1	2 Zn	0	–
4	2	2 Zn	0	–
5	3	2 Zn	5	<1
6	4	2 Zn	25[c]	<1
7	5	2 Zn	100	<1

[a] The relative percentage is given compared to a reference which is defined from the equilibrium of CDL **I** in initial conditions (formation from free aldehyde **A** and amines). [b] Based on the formation of **2**. [c] Products **1**, **2**, **10** are expressed in a ratio equal to 1:1:2.

and five equivalents of cyclopentylamine in chloroform without metal ions (entries 1 and 2, Table 2) was found to be 15 and 7.5 minutes, respectively, by NMR measurements. This indicates that the exchange leading to **2** is faster than its formation from aldehyde **A**; it probably occurs by means of a transimination pathway rather than a hydrolysis/condensation one. As each Zn^{II} ions traps a cyclopentylamine molecule, there is no effect of the metal cation on the rate of this conversion of **1** to **2** with one or two equivalents of amine (Table 2, entries 3 and 4). In presence of an excess (3–5 equivalents) of amine, equilibration occurs in less than one minute, full conversion being reached for five equivalents (Table 2, entries 5–7). The fast rates observed reveal a catalytic effect of Zn^{II} ions as the reaction is faster than for the two control experiments (Table 2, entries 1 and 2). That this effect is due predominantly to the metal cations and not to protons, which might be formed by hydrolysis of the $Zn(BF_4)_2 \cdot 8H_2O$ salt, was indicated by the fact that, within CDL **I** (Scheme 3), 1) the rate of the **2**→**1** conversion remained very slow on addition of two equivalents of CF_3CO_2D in absence of salt, and 2) the rate of the **1**→**2** conversion remained fast on addition of triethylamine as proton trap.

Furthermore, in the course of the conversion of CDL **I** from predominantly **2** to **1** on addition of acid and back to **1** on addition of triethylamine as proton scavenger, the formation of a significant amount (up to 32%) of monoaldehyde was observed by NMR spectroscopy. In contrast, only traces (less than 5%) of monoaldehyde were detected when the same conversions were performed in presence of Zn^{II} ions (Figure 11).

Taken together, the results obtained point to two mechanistic pathways: on one hand, a hydrolysis/condensation one when H^+ is used, and on the other hand, a transimination-type exchange when zinc(II) is present. This conclusion agrees with and is supported by an extensive investigation of the catalysis of similar transimination reactions by scandium(III) ions as Lewis acid.[8b,25]

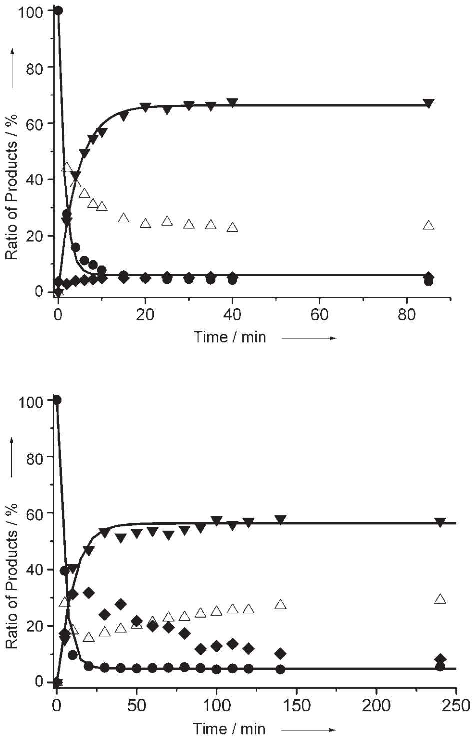


Figure 11. Top: Evolution with time of the exchange process inside CDL **I** when Zn^{II} ions are trapped with hexamethylhexacyclene **B**; plotted from ^1H NMR data and labeled as follows: black triangles (**2**); dots (**1**); open triangles (**10**, mixed imine); diamonds (aromatic monoaldehyde). Bottom: Evolution with time of the exchange process inside CDL **I** when H^+ ions are neutralized with triethylamine; plotted from ^1H NMR data and labeled as described in the top scheme.

Conclusion

The constitutional composition of a dynamic molecular material based on fluorenylimines, generated from a set of components connected by reversible covalent bonds, has been modulated by external effectors. Highly selective component exchange has been obtained by using protons or Zn^{II} ions as effectors. $Zn(BF_4)_2 \cdot 8H_2O$ was found to be the most efficient trigger for controlled rearrangement of the polyimine structures, without the drawback of hydrolysis as occurs in the presence of H^+. The data obtained indicate that the exchange takes place mainly through a zinc(II)-catalyzed transimination mechanism. In view of the important role played by fluorene-derived polymers as materials for light-emitting devices (LEDs),[12] the present polyiminofluorenes[15] constitute a dynamic analogue, which may display intriguing potential as dynamic LEDs (Dyna-LEDs), capable of responding to external solicitations by physical or chemical triggers.

In addition to inducing selection, Zn^{II} ions also lead to a fluorescence shift/enhancement. On a conceptual level, both features brought together express a synergistic adaptative behavior: the addition of an external effector (e.g., zinc ions) drives a constitutional evolution of the dynamic mixture towards the selection and amplification of the species (compound **8**) that in return allows the generation of a (optical) signal indicating the presence of the very effector that promoted its generation in the first place. This embodies a "constitutional dynamic self-sensing" process, which extends the range of self-processes. Such constitutional reorganization of a system, particularly a dynamer library, is of special interest for the design of dynamic "smart" materials, allowing the expression/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 (whereby an effector induces the upregulation of its own detector) represents a further step in the emergence, at both the molecular and supramolecular levels, of dynamic systems of increasing complexity.

Experimental Section

General aspects: All reagents and solvents were purchased at the highest commercial quality and were used without further purification unless otherwise noted. Yields refer to purified (^{1}H NMR spectroscopy) homogeneous materials. ^{1}H NMR spectra were recorded on a Bruker Avance 400 and Bruker 250 spectrometers. The spectra were internally referenced to the residual proton solvent signal. In the ^{1}H NMR assignments, the chemical shifts are given in ppm. The coupling constants J are listed in Hz. The following notation is used for the ^{1}H NMR spectral splitting patterns: singlet (s), doublet (d), triplet (t), multiplet (m), broad (br). The temperatures that are given for the kinetic and thermodynamic data were directly measured and regulated in the NMR probe by using a thermocouple. Electrospray (ESI and ESI-TOF) studies were performed on a Bruker Micro TOF mass spectrometer (sample solutions were introduced into the mass spectrometer source with a syringe pump with a flow rate of 160 μL min^{-1}). MALDI-MS was carried out on a Bruker Autoflex or on a Perspective Biosystems Voyager Pro DE with dithranol as matrix. Melting Points (m.p.) were recorded on a Kofler Heizblock and on a Büchi Melting Point B-540 apparatus and are uncorrected. Microanalyses were performed by the Service de Microanalyse, Institut de Chimie, Université Louis Pasteur.

General procedures for the synthesis of isolated imines and polyimines: Equimolar amounts of amine and aldehydes were solubilized or suspended in ethanol at a concentration of 0.1 M and the reaction mixtures were refluxed overnight under vigorous stirring. The solutions were then either evaporated to dryness and the crude residues were purified by flash chromatography or, after cooling of the solutions to 0 °C, the precipitates formed from the reaction mixture were filtered and washed with cold ethanol and the compounds crystallized or precipitated from AcOEt/hexane mixtures.

General procedure for crossover experiments in CDL I and determinations of thermodynamic and kinetic data: A typical protocol was realized by the preparation of a fresh solution of the compounds to exchange in $CDCl_3$ (0.6 mL, 5.12×10^{-2} M in **A**) in a NMR tube. To avoid the catalysis of the transimination reaction, the traces of acid in the deuterated chloroform were removed by flash chromatogaphy through neutral alumina, immediately prior to use. The NMR tubes were topped with teflon caps in order to keep a constant concentration and avoid water evaporation upon heating. The mixtures were equilibrated for 24 h at room temperature and ^{1}H NMR spectra were recorded upon addition of increasing amounts of CF_3CO_2D (direct addition using a teflon coated microsyringe) or $Zn(BF_4)_2{\cdot}8H_20$ dissolved in CD_3CN (5–50 mL, 0.2–8.0 vol% of CD_3CN in $CDCl_3$), at the same temperature.

General procedure for crossover experiments in CDL II and determinations of thermodynamic and kinetic data: A typical protocol was realized by the preparation of a fresh solution of the compounds to exchange in EtOH (3 mL, 5.12×10^{-2} M in **A**) in a 10 mL flask. The mixtures were equilibrated for 24 h at room temperature and the exchange reactions were performed upon addition of increasing amounts of CF_3CO_2D (direct addition using a teflon coated microsyringe) or $Zn(BF_4)_2{\cdot}8H_20$ dissolved in a CD_3CN (5–50 mL, 0.2–8.0 vol% of CD_3CN in EtOH), at the same temperature. The reaction product was a pale yellow solution and precipitate ($[\mathbf{A}]_i=5.12\times10^{-2}$ M). For spectral characterization, this product was either dissolved in chloroform (for UV-visible and fluorescence spectroscopy) or evaporated to dryness under vacuum, without heating, and a sample dissolved in chloroform (for ^{1}H NMR spectroscopy as well as UV-visible 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 in $CDCl_3$.

9,9-Dihexyl-9*H*-fluorene-2,7-dicarbaldehyde (A): The dialdehyde was synthesized from the corresponding diol,[26] by using the following protocol. Pyridinium chlorochromate (5 g), activated molecular sieves (4 Å; 1 g) and silica gel (1 g) were mixed together in dry methylene chloride (20 mL) and cooled to 0 °C by using an ice bath. A solution of the diol (2 g) in methylene chloride (20 mL) was added dropwise, and the reaction was stirred 4 h at 0 °C and then for a further 12 h at room temperature. The reaction mixture was filtered through a pad of silica gel with methylene chloride as solvent, and then the crude product was evaporated, purified by flash chromatography (solvent system hexane/AcOEt 85:15), and obtained as a white powder. Yield 85 %; m.p. 51–52 °C; elemental analysis calcd (%) for $C_{27}H_{34}O_2$: C 82.82, H 9.01; found: C 82.64, H 8.77; ^{1}H NMR (400 MHz) ($CDCl_3$): $\delta=0.53$–0.59 (m, 4H), 0.76 (t, $^3J=6.8$ Hz, 6H), 0.98–1.13 (m, 12H), 2.08–2.11 (m, 4H), 7.92–7.97 (m, 6H), 10.13 ppm (s, 2H); ^{13}C NMR ($CDCl_3$): $\delta=13.90$, 22.50, 23.75, 29.50, 31.40, 40.00, 55.55, 121.30, 123.35, 130.30, 136.40, 145.60, 152.85, 192.20 ppm; MS (electrospray): m/z (%): 391.3 (100) $[M+H]^+$; HRMS: calcd: 391.2632; found: 391.2592; UV/Vis ($CHCl_3$, 5.05×10^{-5} mol L^{-1}): $\lambda=343$, 329, 311 nm; fluorescence: $\lambda_{max}=416$ nm.

(*E*)-*N*-{{7-[(*E*)-(9*H*-Fluoren-2-ylimino)methyl]-9,9-dihexyl-9*H*-fluoren-2-yl}methylene}-9*H*-fluoren-2-amine (1): The product was synthesized by using the general method and obtained as a bright yellow powder (yield 95 %). M.p. 188–190 °C; ^{1}H NMR (400 MHz) ($CDCl_3$): $\delta=0.65$–0.75 (m, 4H), 0.80 (t, $^3J=6.8$ Hz, 6H), 1.06–1.16 (m, 12H), 2.13–2.18 (m, 4H), 3.99 (s, 4H), 7.36 (qd, $^3J=8.2$ Hz, $^3J=2$ Hz, 4H), 7.41 (t, $^3J=7.6$ Hz, 2H), 7.53 (s, 2H), 7.41 (d, $^3J=7.3$ Hz, 2H), 7.82–7.89 (m, 6H), 7.92–7.95 (m, 2H), 8.03 (s, 2H), 8.68 ppm (s, 2H); ^{13}C NMR ($CDCl_3$): $\delta=14.05$, 22.60, 23.85, 29.70, 31.55, 37.00, 40.35, 117.70, 119.75, 120.25, 120.40, 120.60, 122.60, 125.05, 126.50, 126.85, 128.95, 136.00, 139.90, 141.45, 143.50, 143.60, 144.50, 151.10, 152.25, 160.00 ppm; MS (electrospray): m/z (%): 717.3 (100) $[M+H]^+$; HRMS: calcd: 717.4203; found: 717.4166; UV/Vis ($CHCl_3$, 1.50×10^{-5} mol L^{-1}): $\lambda=394$ nm; fluorescence: $\lambda_{max}=460$ nm.

(*E*)-*N*-{{7-[(*E*)-(Cyclopentylimino)methyl]-9,9-dihexyl-9*H*-fluoren-2-yl}-methylene}cyclopentanamine (2): The product was synthesized by using the general method and obtained as a white powder (yield 88 %). M.p. 88–90 °C; ^{1}H NMR (400 MHz) ($CDCl_3$): $\delta=0.55$–0.62 (m, 4H), 0.77 (t, $^3J=6.8$ Hz, 6H), 0.98–1.13 (m, 12H), 1.71–1.79 (m, 8H), 1.89–1.96 (m, 8H), 2.08–2.11 (m, 4H), 3.78–3.86 (m, 2H), 7.70 (s, 2H), 7074 (s, 4H), 8.39 ppm (s, 2H); ^{13}C NMR ($CDCl_3$): $\delta=14.00$, 22.55, 23.65, 24.75, 29.60, 31.50, 34.50, 40.25, 55.25, 72.15, 120.10, 122.32, 127.46, 135.85, 142.75, 151.70, 159.20 ppm; MS (electrospray): m/z (%): 512.4 (100) $[M+H]^+$; HRMS: calcd: 525.4203; found: 525.4214; UV/Vis ($CHCl_3$, 7.62×10^{-5} mol L^{-1}): $\lambda=342$, 329, 310 nm; fluorescence: $\lambda_{max}=423$ nm.

(*E*)-*N*-{{9,9-Dihexyl-7-[(*E*)-(phenylimino)methyl]-9*H*-fluoren-2-yl}methylene}benzenamine (3): The product was synthesized by using the general method and obtained as a brown-yellow waxy solid (yield 95 %). M.p. 48–50 °C; ^{1}H NMR (400 MHz) ($CDCl_3$): $\delta=0.60$–0.67 (m, 4H), 0.78 (t, $^3J=6.8$ Hz, 6H), 1.03–1.13 (m, 12H), 2.08–2.14 (m, 4H), 7.29–7.31 (m, 6H), 7.43–7.47 (m, 4H), 7.88–7.99 (m, 6H), 8.60 ppm (s, 2H); MS (electrospray): m/z (%): 541.4 (100) $[M+H]^+$; HRMS: calcd: 541.3577; found: 541.3597; UV/Vis (pyridine, 1 g mL^{-1}): $\lambda=400$ nm; fluorescence: $\lambda_{max}=465$ nm.

(*E*+*Z*)-7-[(9*H*-Fluoren-2-ylimino)methyl]-9,9-dihexyl-9*H*-fluorene-2-carbaldehyde (10): The product was synthesized by using the general method and obtained as a bright yellow oil (yield 66 %); ^{1}H NMR (400 MHz) ($CDCl_3$): $\delta=0.57$–0.69 (m, 4H), 0.75–0.80 (m, 6H), 1.05–1.13

(m, 12H), 2.08–2.14 (m, 4H), 3.99 (s, 2H), 7.32–7.38 (m, 2H), 7.44 (t, ^3J = 7.2 Hz, 1H), 7.52 (s, 1H), 7.59 (d, ^3J = 7.5 Hz, 1H), 7.81–7.90 (m, 3H), 7.92–7.98 (m, 4H), 8.02 (br, 1H), 8.68 (s, 1H), 10.12, 10.13 ppm (2s, 1H); ^{13}C NMR ($CDCl_3$): δ = 13.90, 13.95, 14.00, 22.45, 22.55, 22.60, 23.75, 23.80, 29.50, 29.60, 29.65, 31.40, 31.45, 31.55, 36.95, 40.05, 40.20, 55.50, 117.65, 119.75, 120.20, 120.40, 120.55, 120.65, 121.20, 121.30, 122.65, 122.75, 123.20, 123.35, 125.00, 126.55, 126.85, 128.90, 130.30, 130.45, 135.85, 136.45, 136.80, 140.05, 141.35, 142.65, 143.35, 144.50, 145.60, 146.60, 150.90, 152.25, 152.35, 152.80, 152.85, 159.65, 160.00, 192.20, 192.30 ppm; MS (electrospray): m/z (%): 554.4 (100) $[M+H]^+$; HRMS: calcd: 554.3417; found: 554.3392.

Oligomer (4): The product was synthesized by using the general method and obtained as a bright yellow powder (yield 79%); M.p. 226 °C (decomp); ^{1}H NMR (250 MHz, pyridine): δ = 0.72 (br, 14H), 1.02 (br, 30H), 2.24 (br, 8H), 7.45–7.60 (br, 8H), 8.10–8.20 (br, 12H), 8.50 (br, 6H), 8.86 ppm (br, 4H); MS (MALDI-TOF) (n = 1): m/z (%): 1003.6 (100) $[M+H]^+$ (polymeric structures are observed up to n = 10); HRMS (electrospray) (n = 1): calcd: 1003.6612; found: 1003.6668; UV/Vis ($CHCl_3$, 5.42×10^{-6} mol L^{-1}): λ = 408 nm; fluorescence: λ_{max} = 483 nm.

Oligomer (5): The product was synthesized by using the general method and obtained as a bright yellow powder (yield 76%); M.p. (decomposition) 300 °C; ^{1}H NMR (250 MHz; pyridine): δ = 0.72 (br, 14H), 1.03 (br, 30H), 2.24 (br, 8H), 4.95 (br, 6H), 7.45–7.60 (br, 8H), 7.90–8.30 (m, 16H), 8.50–860 (br, 8H), 8.93 ppm (br, 4H); MS (MALDI-TOF) (n = 1): m/z (%): 1292.3 (100) $[M+Na]^+$ (polymeric structures are observed up to n = 10); HRMS (electrospray) (n = 1): calcd: 1267.7514; found: 1267.7508; UV/Vis ($CHCl_3$, 5.36×10^{-6} mol L^{-1}): λ = 414 nm; fluorescence: λ_{max} = 477 nm.

Polymer (6): The product was synthesized by using the general method and obtained as a white powder (yield 95%); M.p. (decomp) 270 °C; ^{1}H NMR(400 MHz) ($CDCl_3$): δ = 0.60 (br, 4H), 0.78 (m, 6H), 1.05–1.13 (m, 12H), 1.62 (br, 2H), 1.90–2.08 (m, 6H), 2.10–2.20 (br, 4H), 3.39 (br, 2H), 2.08–2.11 (m, 4H), 7.75–7.85 (m, 6H), 8.50 ppm (s, 2H); MS (MALDI-TOF; repeated fragments of the main unit): m/z: 470 $[M+H]^+$ (polymeric structures are observed up to n = 14); UV/Vis ($CHCl_3$, 6.68×10^{-5} mol L^{-1}): λ = 345, 331, 309 nm; fluorescence: λ_{max} = 431 (λ_{exit} = 380), λ_{max} = 370 nm (λ_{exit} = 320 nm).

Polymer (7): The product was synthesized by using the general method and obtained as a bright yellow powder (yield 96%); M.p. >360 °C (decomp); ^{1}H NMR (400 MHz) ($CDCl_3$): δ = 0.65 (br, 4H), 0.78 (m, 6H), 1.05–1.13 (m, 12H), 2.10–2.20 (br, 4H), 7.40–7.60 (br, 4H), 7.80–7.95 (br, 4H), 8.02 (s, 2H), 8.67 (s, 2H); MS (MALDI-TOF; repeated fragments of the main unit): m/z: 463 $[M+H]^+$ (polymeric structures are observed up to n = 32); UV/Vis ($CHCl_3$, 1.56×10^{-5} mol L^{-1}): λ = 420 nm; fluorescence: λ_{max} = 490 nm.

Polymer (8): The product was synthesized by using the general method and obtained as a bright yellow powder (yield 98%); M.p. >360 °C (decomp); ^{1}H NMR (400 MHz) ($CDCl_3$): δ = 0.69 (br, 4H), 0.78 (m, 6H), 1.00–1.20 (br, 12H), 2.10–2.20 (br, 4H), 4.00(br, 2H), 7.33–7.40 (m, 2H), 7.40–7.60 (m, 2H), 7.80–8.00 (m, 6H), 8.03 (s, 2H), 8.70 ppm (s, 2H); MS (MALDI-TOF; repeated fragments of the main unit): m/z: 551 $[M+H]^+$ (polymeric structures are observed up to n = 18); UV/Vis ($CHCl_3$, 1.16×10^{-5} mol L^{-1}): λ = 418 nm; fluorescence: λ_{max} = 493 nm.

Polymer (9): The product was synthesized by using the general method and obtained as a bright yellow powder (yield 94%); M.p. >360 °C (decomp); ^{1}H NMR (400 MHz) ($CDCl_3$): δ = 0.65 (br, 4H), 0.78 (m, 6H), 1.00–1.20 (br, 12H), 2.00–2.20 (br, 4H), 7.20 (s, 2H), 7.35 (d, ^3J = 7.3 Hz, 4H), 7.63 (d, ^3J = 7.3 Hz, 4H), 7.83–7.88 (m, 4H), 8.01 (s, 2H), 8.64 ppm (s, 2H); MS (MALDI-TOF; repeated fragments of the main unit): m/z: 565 $[M+H]^+$ (polymeric structures are observed up to n = 25); UV/Vis ($CHCl_3$, 1.15×10^{-5} mol L^{-1}): λ = 422 nm; fluorescence: λ_{max} = 496 nm.

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[16] a) The resonance imine signals were assigned on the basis of the spectra of isolated compounds **1** and **2**; b) before being subjected to exchange, the library was equilibrated for 24 h in chloroform from starting materials; c) when the amount of CF_3CO_2D increases, the rate of the equilibration process is faster than the time necessary for running a proton NMR experiment; these kinetic aspects (b and c are discussed below.

[17] Starting with a 5:2:1 solution of cyclopentylamine/2-aminofluorene/2,7-fluorenedicarboxaldehyde, leads to a system that contains only compound **1** in the same conditions of H^+ concentration and temperature. The use of an equimolar ratio is nevertheless important for further polymerization reactions.

[18] The conversion aspect (Σ Imines/Σ Aldehydes) is not discussed for each H^+ concentration as this ratio is always higher than 97%, except for 10^{-1} M (85%) and for values above 1 M.

[19] For example, at 348 K and for $[CF_3CO_2D]$ = 1 M, bis-imine **1** starts to decompose into the monoaromatic imine monoaldehyde (product

11, see experimental part) and free aldehyde **A**, in agreement with previous observations on the effect on increasing the temperature at high acid concentrations.[9] At the same temperature and for $[CF_3CO_2D] = 0\,\text{M}$, the conversion is not affected but the selectivity is a somewhat lower compared to the 298 K experiment.

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[22] Most of them give a nonselective exchange process together with hydrolysis of the imines bonds ($Ag(OTf)$,$Cu(Otf)_2$, $Ln(Otf)_3$, etc.).

[23] The reaction product was a pale yellow solution and precipitate ($[\mathbf{A}]_i = 5.12 \times 10^{-2}\,\text{M}$). For spectral characterization, this product was either dissolved in chloroform (for UV-visible and fluorescence spectroscopy) or evaporated to dryness under vacuum, without heating, and a sample dissolved in chloroform (for ^1H NMR as well as UV-visible and fluorescence spectral determinations); when both procedures were used they gave the same results. The concentration of the solutions used for NMR spectroscopy was $10^{-4}\,\text{M}$.

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