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Polyamines containing naphthyl groups as pH-regulated molecular machines driven by light†

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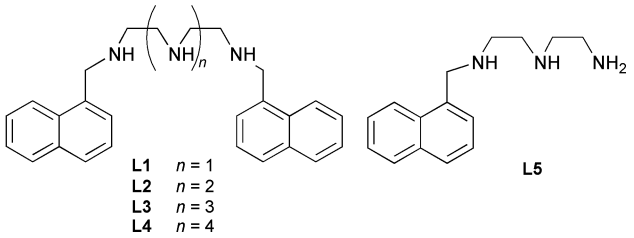
A series of compounds made up by linking methylnaphthalene fragments at both ends of different polyamine chains have shown to behave as pH-regulated molecular machines driven by light and fluorescence emission studies have proved the formation of an excimer between the two naphthalene units whose appearance, fluorescence intensity and decay times depend on the pH value of the media.

Many biological systems can be considered as more or less complex molecular machines operated by chemical or physical stimuli. Examples of this behaviour are found in the triggering effect of many calcium binding proteins or in the astonishing ATP synthase molecular rotor.[1,2] Therefore, in the last few years a lot of research effort has been devoted to identifying systems able to perform molecular motions following chemical or physical inputs.[1–9] Herewith, we communicate on a family of very simple compounds whose molecular movements driven by light can be controlled and even modulated by inputs like the concentration of hydrogen ions and/or metal ions. Compounds L1–L5 have been prepared in good yields by reaction of the



elected polyamine with naphthalene-1-carbaldehyde in ethanol followed by reduction with sodium borohydride.[10]

While the absorption spectra of these compounds do not change significantly with pH, the fluorescence emission intensity dramatically depends on their protonation state (see Fig. 1A for L1). As described for related compounds,[10] the fully protonated forms of L1–L5 exhibit the most intense fluorescence emission. Unprotonated amines are efficient electron transfer quenchers of the aromatic excited state and depending on the distance to the fluorophore can produce a partial or complete quenching. This trend is illustrated in Fig. 1B, where the fluorescence emission intensity monitored at 334 nm is plotted together with the mole fraction distribution of the different protonated species calculated from the protonation constants determined potentiometrically.[11] In order to have a full picture of the situation, the protonation sequence established for L1 by means of the ^{1}H and ^{13}C NMR data has to be taken into account. As shown in Fig. 1B, the first deprotonation that occurs on the central nitrogen atom leads to a partial quenching, *ca.* 80% of the emission of the fully protonated form. Total quenching takes place only upon removing the second proton from one of the side nitrogens. However, the most remarkable feature in the emission spectra of these compounds is the presence of a red-shifted and non-structured band attributable to excimer formation (Fig. 1A). This red shitted band does not appear in the case of the compound containing a single terminal naphthalene (L5), or in the case of an analogue receptor possessing a reinforcing piperazine ring (L6, see ESI). This absence in L5 excludes the possibility of a charge transfer (CT) state involving the deprotonated amine and the fluorophore.[12]

Excimer formation is only observed for the H_2L1^{2+} species. Neither the fully protonated species H_3L1^{3+} nor the species with lower protonation degrees yield such association. In the case of H_3L1^{3+}, this can be ascribed to the large electrostatic repulsion at this stage which prevents the required bending movement while the total quenching of the emission produced in the low protonated species would avoid observing any excimer formation.

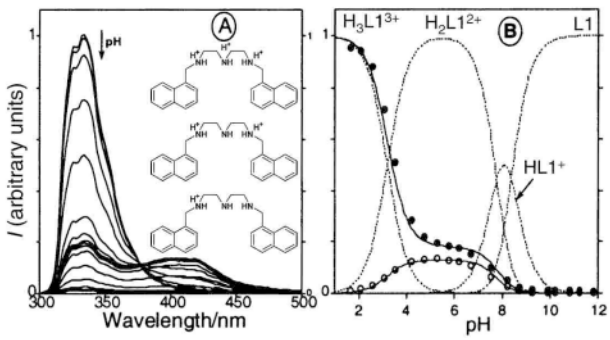
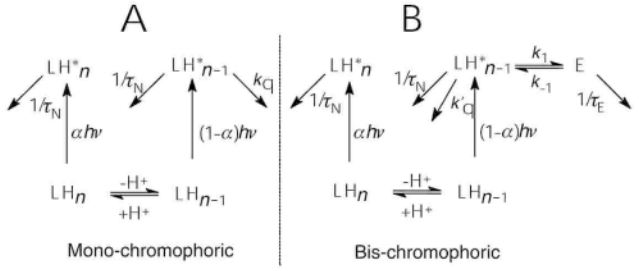


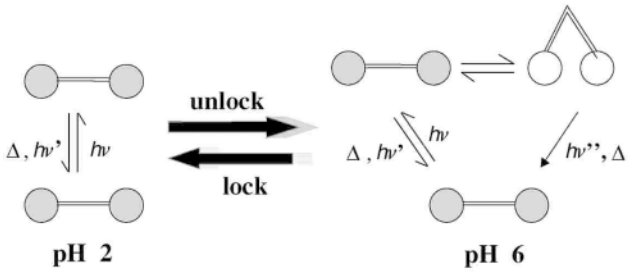
Fig. 1 A—pH dependence of the fluorescence emission of compound L1 at λ_{exc} = 287 nm. Protonation sequence determined by ^{1}H NMR is shown in the inset. B—Mole fraction distribution of the protonation states of compound L1 (-----); fluorescence emission at λ_{exc} = 287 nm and λ_{em} = 334 nm (●); fluorescence emission at λ_{exc} = 287 nm and λ_{em} = 418 nm (○).

† Electronic supplementary information (ESI) available: synthesis and characterisation data for L1–L4, protonation constants and spectra. See http://www.rsc.org/suppdata/cc/b1/b104311k/

 DOI: 10.1039/b104311k



Scheme 1



Scheme 2

Intramolecular excimer formation was studied by nanosecond time-resolved fluorescence. Fluorescence decays were monitored at λ_{em} = 315 nm, where the fluorescence emission is essentially due to the excited monomer, and at λ_{em} = 418 nm, where the excimer emits. Global analysis of the decays can only be properly fitted with sums of two or three exponentials. The fluorescence emission behaviour of the mono-chromophoric and bis-chromophoric systems can be interpreted as depicted in Schemes 1A and 1B for the triaza receptors L5 and L1, respectively. In both cases, a ground-state equilibrium exists between the fully protonated species (H_3L^{3+}) and the mono-unprotonated one (H_2L^{2+}). Simultaneous excitation of both H_3L^{3+} and H_2L^{2+}, leads to H_3L^{3+*} and H_2L^{2+*} excited species; the relative proportion of these species will depend on the pH (Fig. 1B). While H_3L^{3+*} decays with a rate constant equal to the reciprocal of τ_N, H_2L^{2+*} presents an additional direct quenching to the ground-state by the CT state with k_q (rate constant due to amine quenching); the overall decay for the H_2L^{2+*} species is equal to $1/\tau_N + k_q$.

The question arising now is the correct attribution of the observed components of the decay times to the species shown in Fig. 1B for L1. At pH = 4.6, the H_3L1^{3+} and H_2L1^{2+} species coexist with the excimer. At pH = 2.3, where practically no excimer is observed, we have obtained a double-exponential decay with decay times equal to 29.6 and 2.9 ns, and pre-exponential factors, a_i, of respectively 0.93 for H_3L1^{2+} and 0.07 for the small amount of the H_2L1^{2+} species present at this pH. At pH = 3.2 the two monomers coexist with the excimer. While H_2L1^{2+*} with a decay time of 3.4 ns gives rise to the excimer (τ_E = 15.8 ns), the more protonated monomer is found uncoupled with the other emissive species and must unequivocally be attributed to the H_3L1^{3+} species. Also it is worth noting that the negative pre-exponential at λ_{em} = 418 nm is associated with the shorter lifetime (H_2L1^{2+}) and that no negative amplitude is associated with the longer lifetime (H_3L1^{3+}). This once more shows that the H_3L^{3+} species decays with a lifetime identical to the one obtained at pH = 2.3 and to the one of L5 (where no intramolecular excimer formation occurred).[10] For pH = 6.1 the system is now reduced to a bi-exponential decay law since the H_3Ll^{3+} species is absent (see ESI). The H_2L1^{2+*} species will have at this pH two additional deactivation channels: i) electron quenching promoted by unprotonated amino groups, k_q, and ii) excimer formation, k_1. This situation does not apply to the case of H_3L1^{3+*} because excimer formation is forbidden and the only possible deactivation route occurs *via* its natural fluorescence lifetime ($\approx$31 ns). Comparison with the excited state behaviour of L5, where only a double-exponential fit is required, clearly supports the above considerations.

Another interesting aspect is the existence of excited state reversibility of the excimer leading to delayed fluorescence emission because, as reported above, the intermediate lifetime emission can also be detected at 315 nm.

Although the behaviour of L2, L3 and L4 is analogous to that of L1, several aspects deserve comment. The quenching processes and the efficiency of excimer formation are strongly affected by the length of the chain and the protonation states of the molecules. Indeed, the protonation degree for which the ratio excimer–monomer emission is maximum increases proton by proton from one receptor to the following in size; for L2 it is H_2L2^{2+}, for L3 it would be H_3L3^{3+} and for L4, H_4L4^{4+}. In all these species the central nitrogens are unprotonated facilitating the delocalisation of the positive charges along the chain.

All these data clearly point out that the compounds here described are examples of elementary molecular movements driven by light and switched on/off by pH. Scheme 2 for compound L1 illustrates this concept. At pH values below 2, the system is rigid and no bending movement occurs upon light absorption; in this state the system is locked. The unlock step takes place following a pH jump to 6. For this pH value, light absorption by the monomer leads to excimer formation as well as to the back reaction responsible for the delayed fluorescence.

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11 Potentiometric measurements were carried out in 0.15 mol dm^{-3} NaCl at 298.1 ± 0.1 K The program HYPERQUAD (A. Sabatini, A. Vacca and P. Gans, *Coord. Chem. Rev.*, 1992, **120**, 389) was used to derive the values of the protonation constants. Stepwise constants calculated for L1 are: log $K_{HL/H\cdot L}$ = 8.38(2), log $K_{H_2L/HL\cdot H}$ = 7.81(1) and log $K_{H_3L/H_2L\cdot H}$ = 3.81(3); for L2: log $K_{HL/H\cdot L}$ = 9.12(2), log $K_{H_2L/HL\cdot H}$ = 8.22(2), log $K_{H_3L/H_2L\cdot H}$ = 6.01(3) and log $K_{H_4L/H_3L\cdot H}$ = 3.18(3); for L3: log $K_{HL/H\cdot L}$ = 9.32(1), log $K_{H_2L/HL\cdot H}$ = 8.58(1), log $K_{H_3L/H_2L\cdot H}$ = 7.39(2), log $K_{H_4L/H_3L\cdot H}$ = 4.77(3) and log $K_{H_5L/H_4L\cdot H}$ = 2.68(3); for L4 (see ref. 10): log $K_{HL/H\cdot L}$ = 10.04(4), log $K_{H_2L/HL\cdot H}$ = 8.94(3), log $K_{H_3L/H_2L\cdot H}$ = 8.29(3), log $K_{H_4L/H_3L\cdot H}$ = 6.82(4) and log $K_{H_5L/H_4L\cdot H}$ = 4.58(4) and log $K_{H_6L/H_5L\cdot H}$ = 2.23(1); for L5: log $K_{HL/H\cdot L}$ = 9.72(1), log $K_{H_2L/HL\cdot H}$ = 8.21(1) and; log $K_{H_3L/H_2L\cdot H}$ = 3.94(2).
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