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 selected 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. In order to have a full picture of the situation, the protonation sequence established for L1 by means of the 1H and 13C 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 shifted 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.15

Excimer formation is only observed for the H3L13+ species. Neither the fully protonated species H3L13+ nor the species with lower protonation degrees yield such association. In the case of H3L13+, 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.

†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/

Fig. 1 A—pH dependence of the fluorescence emission of compound L1 at \( \lambda_{\text{exc}} = 287 \text{ nm} \). Protonation sequence determined by 1H NMR is shown in the inset. B—Mole fraction distribution of the protonation states of compound L1 (-----); fluorescence emission at \( \lambda_{\text{exc}} = 287 \text{ nm} \) and \( \lambda_{\text{em}} = 334 \text{ nm} \) (●); fluorescence emission at \( \lambda_{\text{exc}} = 287 \text{ nm} \) and \( \lambda_{\text{em}} = 418 \text{ nm} \) (○).
Intramolecular excimer formation was studied by nanosecond time-resolved fluorescence. Fluorescence decays were monitored at $\lambda_{em} = 315$ nm, where the fluorescence emission is essentially due to the excited monomer, and at $\lambda_{em} = 418$ 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 Scheme 1A and 1B for the triaza receptors L5 and L1, respectively. In both cases, a ground-state equilibrium exists between the fully protonated species (H3L3+) and the mono-unprotonated one (H2L2+). Simultaneous excitation of both H3L3+ and H2L2+ leads to H3L3+* and H2L2+* excited species; the relative proportion of these species will depend on the pH (Fig. 1B). While H1L1+* decays with a lifetime constant to the reciprocal of $k_q$, H2L2+* 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 H2L2+* species is equal $1/(k_q + k_g)$.

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 H1L1+* and H2L2+* 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 H2L12+ and 0.07 for the small amount of the H1L12+ species present at this pH. At pH = 3.2 the two monomers coexist with the excimer. While H2L12+* decays with a lifetime constant to the reciprocal of $k_q$, H2L2+* presents an additional direct quenching to the ground-state by the CT state with $k_g$ (rate constant due to amine quenching); the overall decay for the H2L2+* species is equal $1/(k_q + k_g)$.

by proton from one receptor to the following in size: for L2 it is H2L2+, for L3 it would be H3L3+ and for L4, H4L4+. 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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**Notes and references**

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 $K_{HL\cdot L}$ = 8.38(2), log $K_{H\cdot L\cdot L\cdot L}$ = 7.81(1) and log $K_{H\cdot H\cdot L\cdot L\cdot L}$ = 3.81(3); for L2, log $K_{HL\cdot L\cdot L\cdot L}$ = 9.12(2), log $K_{H\cdot L\cdot L\cdot L\cdot L}$ = 8.22(2), log $K_{H\cdot H\cdot L\cdot L\cdot L\cdot L}$ = 6.01(3) and log $K_{L\cdot L\cdot L\cdot L\cdot L}$ = 3.18(3); for L3: log $K_{H\cdot L\cdot L\cdot L\cdot L}$ = 9.32(1), log $K_{L\cdot L\cdot L\cdot L\cdot L}$ = 8.51(1), log $K_{H\cdot H\cdot L\cdot L\cdot L\cdot L}$ = 7.39(2), log $K_{H\cdot H\cdot H\cdot L\cdot L\cdot L}$ = 4.77(3) and log $K_{H\cdot H\cdot H\cdot L\cdot L\cdot L\cdot L}$ = 2.68(3); for L4 (see ref. 10): log $K_{HL\cdot L\cdot L\cdot L}$ = 10.04(4), log $K_{H\cdot L\cdot L\cdot L\cdot L\cdot L}$ = 8.94(3), log $K_{H\cdot H\cdot L\cdot L\cdot L\cdot L}$ = 8.29(3), log $K_{L\cdot L\cdot L\cdot L\cdot L\cdot L}$ = 6.82(4) and log $K_{L\cdot L\cdot L\cdot L\cdot L\cdot L\cdot L}$ = 4.58(4) and log $K_{H\cdot H\cdot H\cdot L\cdot L\cdot L\cdot L}$ = 2.23(1); for L5: log $K_{HL\cdot L\cdot L\cdot L}$ = 9.72(1), log $K_{H\cdot L\cdot L\cdot L\cdot L\cdot L}$ = 8.21(1) and; log $K_{H\cdot H\cdot L\cdot L\cdot L\cdot L\cdot L}$ = 3.94(2).