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Generation and pH dependent superquenching of poly(amido) carboxylate dendrons hosting a single “focal point” pyrene

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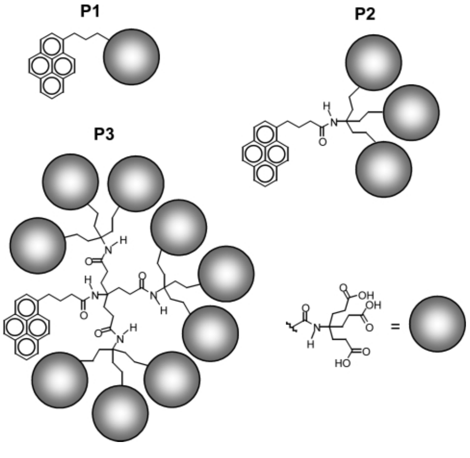
Both pH and generation number play deterministic roles in the luminescence quenching efficiency of analytes toward a series of water-soluble, monopyrenyl poly(amido) carboxylate dendrons, with clear implications toward switchable or programmable chemosensors.

Dendrimers are highly branched and complex, yet structurally perfect, polymers exbiting a tree-like topology first prepared by iterative ‘cascade’ synthesis. With coined names as divergent as ‘cauliflower polymers’, ‘crowned arborals’, ‘starburst polymers’ and ‘molecular fractals’, the initial interest in dendrimers was perhaps due to their aesthetic appeal and for the fact that they were interesting synthetic targets against which ambitious chemists could test their mettle. Due to their highly specific synthesis, however, dendrimers and dendritic materials possess unique features that set them apart from classical polymers.[1] Quickly, researchers realized this potential and sought to exploit their unique properties by employing dendrimers as building blocks in nanoscale devices and functional materials (for background on some recent activity in these areas, see ref. 2). In the hands of able chemists, dendrimers have made outstanding progress in areas as far reaching as multielectron redox catalysis,[3] nonlinear photonics,[4] light harvesting,[5,6] gene and drug delivery,[7] and as components of magnetic resonance imaging (MRI) contrast agents[8] and biomimetic scaffolds.[9] Photoactive dendrimers, in particular, offer the promise of both providing information on the dendritic structure and superstructure as well as performing useful functions such as signal amplification for efficient sensor design.[10–13]

In the present work, we report on the photophysical behavior, as functions of pH and quenching agent, of first, second and third generation asymmetric dendrons prepared by a Newkome or divergent growth approach. Our dendrons are functionalized at their periphery with multiple carboxylic acid groups rendering them water-soluble and are decorated with a *single*, focally-located fluorescent pyrene unit. This work extends our earlier studies[10] and complements recent reports from the Balzani and Vögtle laboratories.[11] Each trifurcated pyrene-labeled dendron **P*n***, where $n = 1, 2$, or 3, is the generation number, comprises 3^n carboxylate units in the periphery and $(3^n - 1)/2$ amides in the interior. Thus, as shown in Scheme 1, **P3** contains 13 amide linkages and 27 surface carboxylates while **P1** contains only 1 and 3, respectively.

In order to probe the relative structural permeabilities of **P*n*** and the effects of protonation on such, we employed several quenchers, including nitromethane, iodide and lead ion, toward the single pyrene residue attached at the first branching point of **P1**–**P3**. Results for the addition of Pb^{2+} (as $Pb(NO_3)_2$) to a 10^{-5} M solution of **P*n*** in water at pH 1.0, 4.0 and 7.0 are shown in Fig. 1.† Although not shown, significant upward curvature of Stern–Volmer plots at high [Pb^{2+}] for **P2** and **P3** suggests an apparent static component to the quenching, often interpreted as a ‘sphere of action’ within which the probability of quenching is unity. For ease of comparison, only **P*n***/Pb^{2+} data for a truncated [Pb^{2+}] range for which a linear Stern–Volmer model is followed are shown. At low [Pb^{2+}], the correlation coefficients of Stern–Volmer plots for **P2** and **P3** fall in the range from 0.985–0.999. It is immediately apparent from Fig. 1 that both pH and generation number have a remarkable influence on quenching efficacy. For **P3** at pH 7, the fact that the experimental Stern–Volmer quenching curve is asymptotic to the condition [Pb^{2+}]/**P3** = 1 is noteworthy and suggests the formation of a 1 : 1 Pb^{2+}/**P3** species resulting in complete quenching.



Scheme 1 Chemical structures of the carboxylate-terminated poly(amido) dendrons **P*n*** (n = 1–3) studied.

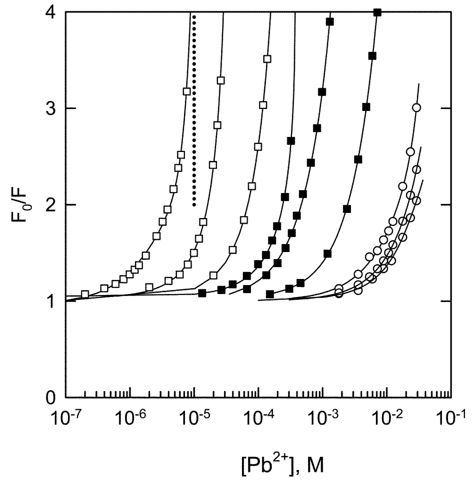


Fig. 1 Stern–Volmer quenching profiles for 10^{-5} M **P*n*** in water. The associated dendron generation numbers increase from n = 1 to 3 from left to right at pH 1 (○) and increase from right to left for pH 4 (■) and 7 (□). The vertical dotted line identifies a [Pb^{2+}]/[**P*n***] ratio of unity.‡

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Fig. 2 provides a comparison of the pH and generation dependent **P*n***/Q Stern–Volmer quenching constants for Pb^{2+} with those of I$^-$ and MeNO$_2$. For the neutral quencher MeNO$_2$, K_{SV} decreases with generation number reflecting the progressive shielding offered by the dendritic branches (‘site isolation’). This is as expected and is fully consistent with the increase in quantum yield from 0.65 to 0.82 and the corresponding decrease in the pyrene vibronic band ratio (I_1/I_3) from 1.75 to 1.68 upon increasing the generation number from 1 to 2 to 3 for quencher-free **P*n*** in water at pH 7. While the dendritic network does provide some barrier to diffusion for MeNO$_2$ (for example, at pH 11, K_{SV} decreases from *ca.* 600 M^{-1} to 245 M^{-1} in going from **P1** to **P3**), the impact of protonation is even slighter, with the highest quenching constants observed at pH 1 for all **P*n***.

By comparison, the protonation state of **P*n*** plays a key role in determining K_{SV} for I$^-$ mediated quenching. This is particularly the case for **P3** where the quenching constants are 2, 22 and 202 M^{-1} for pH 11, 4 and 1, respectively. At pH 11, presumably the carboxylic acid groups at the periphery are fully ionized presenting a Coulombic repulsive barrier to the approach of I$^-$. The higher surface charge density for **P3** is also perfectly in line with this dendritic species more effectively repelling anionic species at high pH.[11] In contrast, at pH 1 where the internal aliphatic amides are expected to be largely protonated, this effect works in reverse and offsets the protective ‘firewall’ of **P3**.

We now turn our attention to Pb^{2+} based quenching of **P*n***. In the case of Pb^{2+}, due to its high charge density, the protonation state of **P*n*** wholly determines the quenching efficiency: $K_{SV} = 36$ M^{-1} for **P3** at pH 1 and $K_{SV} = 2.4 \times 10^5$ M^{-1} for the same dendron at pH 7, a nearly four orders of magnitude increase in the quenching efficiency, that is, ‘superquenching’. This ‘switching’ behaviour can be rationalized in a similar way to that of the I$^-$ results. Essentially, at near neutral pH the negative surface charge density of **P3** acts as an electrostatic sponge for approaching Pb^{2+}. Once a Pb^{2+} ion becomes electrostatically bound to the dendron’s surface to form a 1 : 1 adduct (*vide supra*) efficient heavy atom and/or electron transfer quenching of the semi-buried pyrene residue ensues. Such a static mechanism is plausible, given the excited-state lifetime of **P*n*** (*ca.* 130 ns; see ref. 10). That is, the Pb^{2+} concentrations used here are too small to cause sizeable effects in the case of purely diffusion-controlled quenching. At pH 1, on the other hand, the cationic **P*n*** core (*i.e.*, protonated amide groups) staves off any approach of Pb^{2+} and the quencher becomes ineffective as a result.

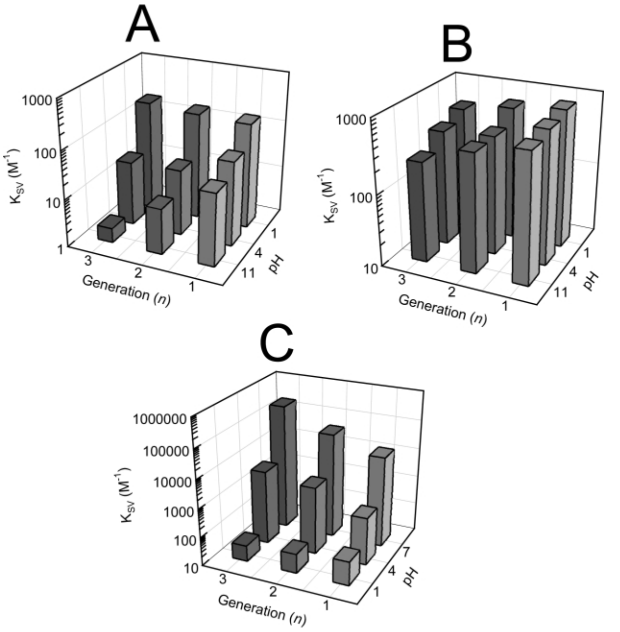

Fig. 2 Effects of dendron generation number and pH on the observed Stern–Volmer quenching constants for various quenchers in aqueous solution: (A) I$^-$ (B) nitromethane (C) Pb^{2+}.§ Sample solutions were freeze–pump–thaw degassed several times to remove residual oxygen.

Although the selectivity has not been evaluated, clearly **P3** is a highly sensitive chemosensor for Pb^{2+} determination in aqueous media at/near neutral pH. For the **P3** level used here, the limit of detection (LOD) is well below 10 ppb, the level defined by the World Health Organization for safe drinking water. Importantly, the LOD can be lowered by a decade or more simply by utilizing a lower concentration of **P3**.

Notes and references

† The pH of the aqueous dendron solutions was controlled by addition of 10^{-2} or 10^{-4} M solutions of HNO$_3$ or NaOH. For the Pb^{2+} quenching experiments, we were limited to *ca.* pH 7 and below due to precipitation of Pb(OH)$_2$ (s) at high pH; $K_{sp} \approx 10^{-16}$.

‡ The equipment used has been described elsewhere.[14] Raw emission spectra were background corrected for Raman scatter using appropriate **P*n***-free aqueous blanks. In all experiments, the concentration of **P*n*** was 10^{-5} M. The excitation and emission wavelengths were 337 and 372 nm, respectively; a 2 nm spectral bandpass was used for both.

§ The degree of quenching is most simply expressed within the Stern–Volmer formalism $F_0/F = 1 + K_{SV}[Q]$, where F_0 and F are the fluorescence intensities in the absence and presence of quencher, K_{SV} is the Stern–Volmer quenching constant, and $[Q]$ is the analytical concentration of quencher.

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