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Energy transfer between polyamine chains bearing naphthalene terminal units and $K_3[Co(CN)_6]$: an example of a molecular photoreactor

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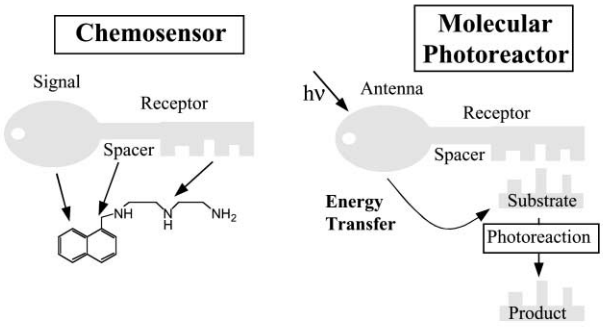
Molecular photoreactors consisting of polyamine chains (receptors) bearing terminal naphthalene units (antennae) are described. The receptors are used to bind the substrate hexacyanocobaltate(III) and the antennae to transfer energy to the complex and thus promote a photoaquation reaction.

Introduction

In recent years we have been devoted to the study of chemosensors constituted by polyamine chains bearing benzene, naphthalene or anthracene fluorophores at their terminii, see one example in Scheme 1.[1–3] These molecules contain; i) a receptor unit which is playing the role of recognising and binding a given target substrate, together with ii) a signalling unit, capable of either producing a signal or significantly altering its intensity following the binding of the substrate, and finally iii), a spacer unit, see Scheme 1. One necessary requirement for having a good chemosensor is the absence of thermal or photochemical reactions induced by the analysis procedure that might occur along the detection procedure. With fluorescent chemosensors, chelation enhancement of the fluorescence (CHEF) or chelation enhancement of the quenching (CHEQ) are rather common responses to the binding of the substrate in the receptor unit.[1–5]



Scheme 1

Polyamine chains are of particular interest due to their ambivalent capability as receptors. This is reflected in their ability to co-ordinate metal ions, when a sufficient number of deprotonated amino groups is available or, alternatively, if the number of protonated amino groups is sufficiently high, to co-ordinate anionic species.[2]

The signalling mechanism is based on the fact that the nitrogens of the polyamine chain can efficiently quench the fluorescence emission of the terminal fluorophores by an electron transfer process (from the amine lone pairs to the excited fluorophore). Whenever a target substrate (*e.g.* Zn^{2+}, H^+) coordinates to the chain receptor, the nitrogen lone pairs become involved in the binding, therefore preventing the electron transfer process to occur. Suppression of the fluorescence emission (from the partially protonated chemosensors) can also occur upon coordination of several metals,[3] *e.g.* Cu^{2+}.

Although the occurrence of a photoreaction in the substrate induced by the excited fluorophore results in a drawback reaction for a chemosensor, such a process can be explored in order to design a molecular photoreactor, Scheme 1. To achieve this goal, the fluorescent unit should behave as an antenna device in order to transfer energy to the susbtrate bound in the receptor unit. The usefulness of this process depends on the existence of some advantages when compared with the direct reaction of the substrate, as for example, i) a larger molar absorption coefficient of the antenna unit when compared with the substrate, ii) photosensitization of reactive states of the substrate by exciting the antenna at lower energies than those accessible by direct irradiation of the substrate. If in addition the substrate is more weakly bound to the receptor than the product, a photocatalytic centre can emerge.

Several years ago it was shown that the fully protonated forms of macrocyclic polyamine receptors, *e.g.* [24]ane-$N_6H_6^{6+}$ and [32]ane-$N_8H_8^{8+}$ give rise to 1 : 1 adducts with $[Co(CN)_6]^{3-}$ and other cyanide complexes.[6–8] On the other hand, the quantum yield for the photodissociation aquation reaction of $[Co(CN)_6]^{3-}$ (see below) was reduced by factors of two or three when [24]ane-$N_6H_6^{6+}$ or [32]ane-$N_8H_8^{8+}$ were respectively present.[6,7]

$$[Co(CN)_6]^{3-} + H_3O^+ + h\nu \longrightarrow [Co(CN)_5(H_2O)]^{2-} + HCN$$

Such discrete quenching effects were taken as an indication of defined structures involving, respectively, three and four of the cyanide ligands linked by hydrogen bonds to the protonated

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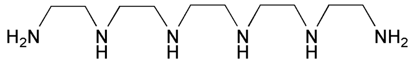
Table 1 Logarithm of the stability constants (log K_s) for the interaction of the receptors L2–L5 and L7–L10 (L) with $[Co(CN)_6]^{3-}$ (A) determined at 298.0 ± 0.1 K in 0.15 mol dm^{-3} NaCl

Entry	Reaction[a]	L2	L3	L4	L5	L7	L8	L9	L10
1	$A + H + L \rightleftharpoons HAL$[a]	—	12.3(1)	13.4(1)	—	—	13.28(6)	13.22(2)	13.50(3)
2	$A + 2H + L \rightleftharpoons H_2AL$	—	21.90(3)	22.80(7)	23.04(5)	—	22.41(4)	22.34(2)	22.96(2)
3	$A + 3H + L \rightleftharpoons H_3AL$	25.58(3)[b]	28.94(3)	31.22(8)	32.21(3)	23.93(8)	30.15(6)	30.64(2)	31.74(2)
4	$A + 4H + L \rightleftharpoons H_4AL$	—	32.84(4)	37.51(9)	40.36(3)	—	33.86(7)	37.29(4)	39.54(2)
5	$A + 5H + L \rightleftharpoons H_5AL$	—	—	41.1(1)	46.42(5)	—	—	41.01(4)	45.52(3)
6	$A + 6H + L \rightleftharpoons H_6AL$	—	—	—	49.63(5)	—	—	—	49.09(3)
7	$A + HL \rightleftharpoons HAL$	—	2.8	3.7	—	—	4.2	3.9	3.8
8	$A + H_2L \rightleftharpoons H_2AL$	—	3.5	4.1	3.3	—	5.1	4.4	4.4
9	$A + H_3L \rightleftharpoons H_3AL$	3.6	4.3	4.5	3.7	3.9	6.8	5.4	4.9
10	$A + H_4L \rightleftharpoons H_4AL$	—	4.9	5.8	4.4	—	7.3	7.2	5.8
11	$A + H_5L \rightleftharpoons H_5AL$	—	—	6.6	5.2	—	—	8.3	6.8
12	$A + H_6L \rightleftharpoons H_6AL$	—	—	—	6.1	—	—	—	7.9

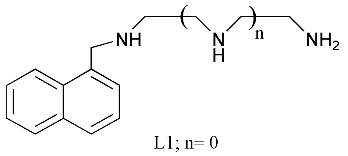
[a] Charges omitted for clarity. [b] Values in parentheses are standard deviations in the last significant figure.

nitrogens of the polyamine.[6,7] The photoaquation reaction of hexacyanocobaltate (III) can consequently be used as a structural probe in solution for this and other adducts involving polyamine chains.

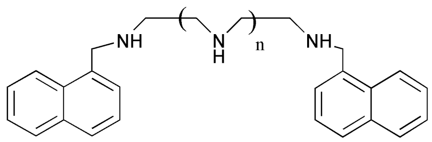
In the present work we report on the interaction of a series of polyamine chains bearing one or two naphthalene terminal units, L1 to L10, with hexacyanocobaltate(III). These polyamine receptors behave as chemosensors in the sense that their fluorescence emission intensity and lifetimes can change upon co-ordination to different substrates. Consideration of the present system lies on the observation of a strong quenching effect of the fully protonated forms of Ln compounds upon coordination with $[Co(CN)_6]^{3-}$, leading to the photoaquation of the complex, thus suggesting the possibility of exploring the system as a molecular photoreactor.



L0



L1; n= 0
L2; n= 1
L3; n= 2
L4; n= 3
L5; n= 4



L6; n= 0
L7; n= 1
L8; n= 2
L9; n= 3
L10; n= 4

Experimental

The syntheses of the compounds are reported elsewhere.[1,5,9] The electronic spectra were recorded on a Shimadzu UV-2501PC spectrophotometer equipped with a 1 cm cell thermostatted at 298 K. Fluorescence emission was measured by means of a SPEX Fluorolog spectrophotometer. In the irradiation experiments light excitation was performed by a medium pressure mercury arc lamp (Müller Elektronic Optic). Interference filters (Oriel) were used to select narrow spectral ranges with maximum wavelength at 313 nm. The irradiated solution was contained in a 1 cm spectrophotometric quartz cell under magnetic stirring. The intensity of the incident light (1.1×10^{-6} Einstein min^{-1} at 313 nm) was measured by ferrioxalate actinometry.[10] Nanosecond time resolved fluorescence measurements were carried out with the time correlated single photon counting technique as described elsewhere.[11]

The potentiometric titrations were carried out at 298.1 ± 0.1 K in 0.15 mol dm^{-3} NaCl. The experimental procedure (burette, potentiometer, cell, stirrer, microcomputer, *etc.*) has been fully described elsewhere.[12] The acquisition of the emf data was performed with the computer program PASAT.[13] The reference electrode was an Ag/AgCl electrode in saturated KCl solution. The glass electrode was calibrated as a hydrogen-ion concentration probe by titration of previously standardized amounts of HCl with CO_2-free NaOH solutions and determining the equivalent point by the Gran's method,[14] which gives the standard potential, E^{01}, and the ionic product of water ($pK_W = 13.73(1)$). NaCl was used as the supporting electrolyte instead of the most usual $NaClO_4$ due to the higher solubility of the receptors in this medium.

The computer program HYPERQUAD,[15] was used to calculate the protonation and stability constants. The titration curves for each system (*ca.* 100 experimental points corresponding to at least three measurements, pH range investigated 2–10, concentration of $[Co(CN)_6]^{3-}$ and L ranging from 1×10^{-3} to 5×10^{-3} mol dm^{-3}) were treated either as a single set or as separated curves without significant variations in the values of the stability constants. Finally, the sets of data were merged together and treated simultaneously to give the final stability constants.

Results and discussion

Potentiometric studies

Table 1 shows the cumulative and stepwise stability constants obtained for the interaction of the anion $[Co(CN)_6]^{3-}$ determined in 0.15 mol dm^{-3} NaCl at 298.1 K by means of the computer program HYPERQUAD.[15]

The first aspect to be discussed regards the choice of the ionic strength used. As supporting electrolytes contain anions themselves, in our case chloride anions, these will compete to some extent with the anionic substrate subject of the study and, therefore, the constants presented are always relative values. Nevertheless, these constants are self-consistent since the ionic strength is kept constant for all the studied systems and allow comparison between them and with other systems studied under the same conditions.

Since $[Co(CN)_6]^{3-}$ does not experience any protonation throughout the pH range analysed (2.5–11), the cumulative constants can be decomposed into the successive stability constants for the equilibria, $[Co(CN)_6]^{3-} + H_jL^{j+} = \{([Co(CN)_6])\cdot H_jL\}^{(j-3)+}$, log K_s, (entries 7–12 in Table 1)

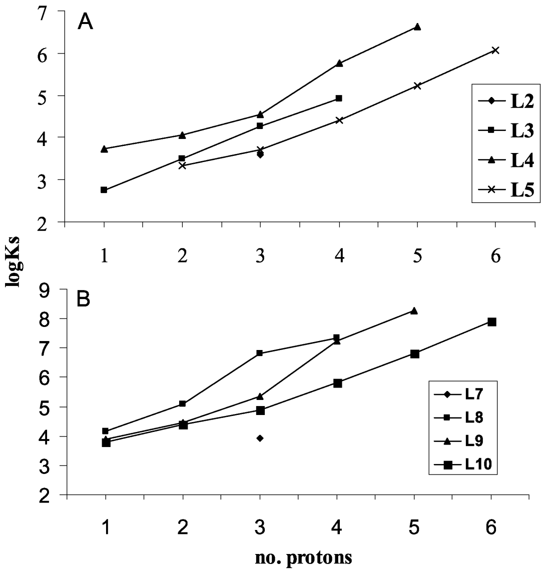


Fig. 1 Plot of log K_s *vs.* protonation degree of the adducts for mononaphthyl derivatives L2–L5 (A) and bisnaphthyl derivatives L7–L10 (B).

that are representative of the processes actually occurring in solution.

The analysis of the values of the constants allows one to derive some general trends for the interaction between $[Co(CN)_6]^{3-}$ and the polyamines considered here. Firstly, in all the systems studied the stability of the adducts formed increases with the degree of protonation, indicating the major role that charge–charge interactions play in these interactions (Table 1, Fig. 1). Secondly, it is generally observed that the receptors displaying naphthyl fragments at both ends (L7–L10) interact more strongly than the analogous ligands with just one naphthylic moiety. For instance, for protonation degree 3 (entry 9), the log K_s value for the tetramine L8 with two naphthyl groups is 6.8 while that for L3 is just 4.3. For a given degree of protonation the maximum stability for the receptors with just one naphthyl group is found for L4, with five amino groups; for those with two naphthyl groups L8, with four nitrogen atoms, displays the largest stability constant (see Figs. 1A and 1B).

The larger stability of the bis(naphthyl) derivatives can be explained in terms of their greater hydrophobicity that may cause a larger solvophobic effect that will reinforce the interaction between the partners. Hydrogen-bonding formation between the polyammonium sites of the receptor and the cyanide groups should also be favoured in the more hydrophobic environment provided by the receptors with two naphthyl groups. The different compounds required for achieving the highest stability in both series has to be related to the relative disposition and matching between host and guest species. Nevertheless, when comparing the constants for a given protonation degree, it can be observed that the introduction of a sixth polyammonium group (L5 or L10) does not yield a higher stability in any of the two series of receptors.

Fluorescence emission studies

The fluorescence emission spectrum of compound L5 at pH = 2.0 is presented in Fig. 2A. In accordance with previous work, this emission is characteristic of the naphthalene unit, reaching its maximum intensity for the fully protonated form.[1,2,5] Increasing the pH leads to partial deprotonation of the polyamine nitrogens and to a quenching effect, explained by an electron transfer reaction from the amine lone pairs to the excited naphthalene moiety. On the other hand, the fluorescence emission of the fully protonated species is quenched by addition of hexacyanocobaltate(III). In Fig. 2, the Stern–Volmer plot of the adduct formed between L5 and $[Co(CN)_6]^{3-}$, $\{L5H_6[Co(CN)_6]\}^{3+}$, is reported.

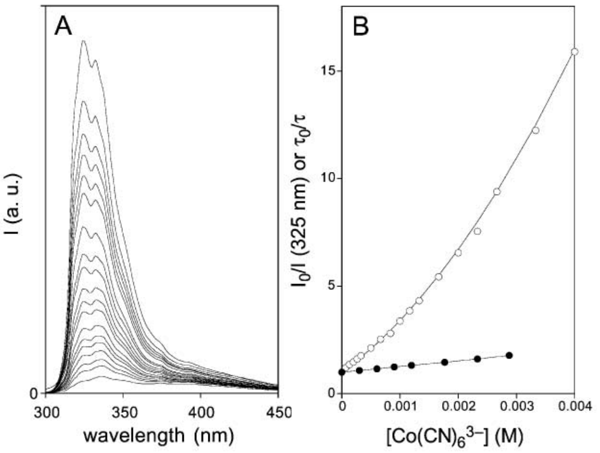


Fig. 2 (A) Fluorescence emission spectra of compound L5 at pH = 2.0, 0.15 mol dm^{-3} NaCl, upon addition of hexacyanocobaltate(III); (B) Stern–Volmer plot based on fluorescence emission intensities (○) and lifetimes (●).

The positive shift observed in the fluorescence emission intensity I_0/I ratio of the Stern–Volmer plot clearly shows the existence of a static quenching due to the formation of a ground state adduct.[16] This type of adduct was previously reported[6,7] for other polyamine chains and macrocycles, the respective driving force resulting from the hydrogen bond interaction of the cyanide ligands of the complex with the protonated nitrogens of the polyamine, as well as by the electrostatic attraction between the positively charged $L5H_6{}^{6+}$ and the negatively charged hexacyanocobaltate(III).

In order to assess the photoaquation quantum yield of the cobalt complex without interference from the energy transfer, we used a simple polyamine chain as model compound, L0, analogous to L5 but lacking aromatic groups. The obtained value of Φ = 0.23 leads to a ratio, R = 1.3, for the photoaquation quantum yield in the absence and in the presence of L0. This value for R does not allow distinction between the involvement of one or two hydrogen bonds. The lack of a discrete number of hydrogen bonds can in principle be explained by the larger mobility of the open chain when compared with a macrocycle. The Φ value in the presence of L0 is in good agreement with the 0.22 value reported by Lehn and Balzani using the same cobalt complex and the linear polyamine 21-$N_6H_6{}^{6+}$ (identical to L0 but with propylene instead of ethylene spacers).[6]

The results mentioned above can be interpreted by two different emission quenching mechanisms of the polyamine receptors (L), by the hexacyanocobaltate(III) complex, (Q): a dynamic quenching, eqns. (1) to (4), and a static quenching, eqns. (1) to (3), (6) and (7).

$$L \xrightarrow{hv} L^* \tag{1}$$

$$L^* \xrightarrow{k_f} L + hv \tag{2}$$

$$L^* \xrightarrow{k_{ic}} L + \Delta \tag{3}$$

$$L^* + Q \xrightarrow{k_q} \text{Quenching} \tag{4}$$

According to eqn. (4) the excited state species must diffuse in order to encounter a molecule of Q prior to deactivation, giving rise to the well known Stern–Volmer kinetics,[16] which can be analysed through eqn. (5),

$$\frac{I_0}{I} = 1 + k_q \tau_0 [Q] \tag{5}$$

Table 2 Association constants of compounds L1 to L10 with $K_3[Co(CN)_6]$ in aqueous 0.15 mol dm^{-3} NaCl at pH = 2.0

	L1	L2	L3	L4	L5	L6	L7	L8	L9	L10
logK_s	2.5	2.8	3.0	3.1	3.3	2.4	2.8	2.9	3.1	3.3

where I is the fluorescence emission for a given concentration of quencher [Q], I_0 the fluorescence emission in the absence of quencher, k_q the quenching rate constant, eqn. (4), and τ_0 the lifetime in the absence of quencher.

Another possible route to the emission quenching is the existence of a ground-state association between the emissive species and the quencher (static quenching). Both quenching mechanisms are accounted for through eqn. (8),[16]

$$L + Q \xleftrightarrow{K_s} LQ \tag{6}$$

$$LQ \xrightarrow{h\nu} \text{Quenching} \tag{7}$$

$$\frac{I_0}{I} = (1 + k_q\tau_0[Q])(1 + K'[Q]) \tag{8}$$

where K' is an equilibrium constant defined in eqn. (9), and K_s is the equilibrium constant defined in eqn. (6), with ε_{LQ} and ε_L being respectively the molar absorption coefficients of the adducts LQ and L.

$$K' = K_s\frac{\varepsilon_{LQ}}{\varepsilon_L} \tag{9}$$

In the present family of adducts we have not detected any significant changes in the absorption spectra of Ln upon addition of the complex, and by consequence, K' can be considered to be identical to K_s. Another way to distinguish between static and dynamic quenching is to plot the ratio τ/τ_0 (where τ and τ_0 are respectively the lifetimes in the presence and absence of quencher) *vs.* [Q]. In this system the lifetime is not dependent on the static quenching, because it clearly fits to eqn. (10).

$$\frac{\tau_0}{\tau} = 1 + k_q\tau_0[Q] \tag{10}$$

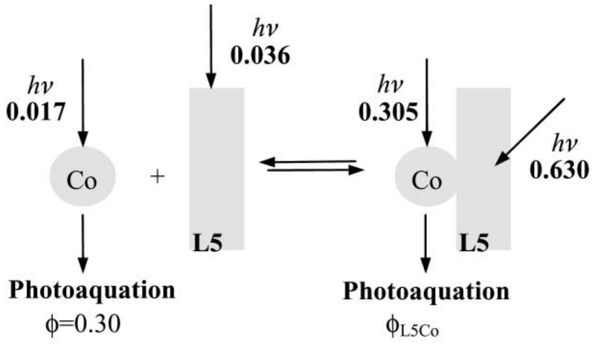
The data reported in Fig. 2B allow the determinination of the the dynamic quenching rate constant through eqn. (10), leading to a value of $k_q = 1.1 \times 10^{10}$ mol^{-1} dm^3 s^{-1}. This value essentially deals with the quenching of L5 (2.0×10^{-5} mol dm^{-3}) by the free hexacyanocobaltate(III). Within experimental error, this value is identical for all the adducts. A fitting of the experimental data reported in Fig. 2B by means of eqn. (8) allows the determination of the association constant for the adducts, K_s. The results are reported in Table 2.

Comparison of the association constants measured by potentiometry (Table 1) and fluorimetry (Table 2) reveal differences that reach several orders of magnitude (*e.g.* L5). In order to clarify this point we carried out fluorimetric experiments for L5 in the absence of added NaCl leading to log K_{ip} = 5.0. This result shows that the association constant depends dramatically on the ratio $[Cl^-]/[K_3Co(CN)_6]$, indicating that the Cl^- anion competes with $Co(CN)_6^{3-}$ for the ligand. As a consequence, the constants from potentiometric experiments (0.15 mol dm^{-3} NaCl, ratio = 150, log K_{ip} = 6.1) are higher than those obtained from fluorimetric data ([HCl] = 0.01 mol dm^{-3}, [NaCl] = 0, ratio = 500, log K_{ip} = 5.0 and [HCl] = 0.01 mol dm^{-3}, [NaCl] = 0.15 mol dm^{-3}, ratio = 8000, log K_{ip} = 3.3). At this point, it must be stressed that the hydrophobic/hydrophilic balance changes very importantly with the ratio $[Cl^-]/[K_3Co(CN)_6]$ and this can affect the mono- and bis-chromophoric compounds to different extents. This could partly explain the much reduced differences between the constants of L1–L5 and those of L6–L10 found in the fluorimetric measurements, Table 2, when compared with potentiometric data, Table 1.

The most interesting feature of this system is however the quantitative analysis of the photoaquation quantum yields of hexacyanocobaltate(III) in the presence of the receptors. In order to have the most feasible data the compound with the largest association constant, L5, was used. In the case of L10 we were unable to carry out the experiment due to adduct precipitation. In a typical experiment, aqueous 0.15 mol dm^{-3} NaCl solutions with concentrations of $[L5H_6^{6+}] = [Co(CN)_6^{3-}] = 3.0 \times 10^{-3}$ mol dm^{-3}, at pH = 2.0, (94.7% of adduct) were irradiated with a mercury arc lamp at 313 nm. The formation of the pentacyanoaquo complex was followed by monitoring the optical density changes at 380 nm (λ_{max} of the photoproduct $[Co(CN)_5(H_2O)]^{2-}$). The obtained value for the quantum yield of the reaction, calculated on the basis of the total absorbed light at initial time (t = 0), was 0.17. This value is lower than that of the free hexacyanocobaltate(III) obtained under the same experimental conditions (Φ = 0.30).[6,7] It is however much higher than what would be expected on the basis of the fraction of total absorbed light (32.6%) that excites the $[Co(CN)_6^{3-}]$ moiety ($0.322 \times 0.30 = 0.097$), immediately suggesting energy transfer processes to be involved.

As observed, the absorption spectra of the mixture of hexacyanocobaltate(III) and L5 is identical to the sum of the two individual components and, consequently, no charge transfer processes in the ground state should be expected to occur.

The fraction of light absorbed by each species in the studied solution is represented in Scheme 2. The observed quantum yield can be considered as the sum of several parcels arising from direct absorption of light by the cobalt complex and from energy transfer upon absorption of light by the ligand, eqn. (11).



Scheme 2

$$\Phi_{obs} = 0.017 \times 0.30 + 0.305 \times \Phi_{L5Co} + 0.036 \times 0.041 \times 0.30 + 0.036 \times 0.43 \times \Phi_{L5Co} + 0.630 \times \eta_{L5 \longleftarrow Co} \times \Phi_{L5Co} \tag{11}$$

The free cobalt complex contributes with 0.017×0.30 and the cobalt complex involved in the adduct contributes with $0.305 \times \Phi_{L5Co}$ by direct absorption of light. The photoaquation quantum yield inside the adduct, Φ_{L5Co}, has the upper limit of 0.30 and these two parcels contribute at maximum with 0.097 for the observed quantum yield. On this basis, the observed quantum yield for photoproduct formation can only be explained if upon irradiation of L5 energy is transferred from the ligand to the metal complex.

Time resolved fluorescence measurements (Fig. 2B) allow the calculation of the dynamic energy transfer efficiency from free L5 to free $[Co(CN)_6]^{3-}$. Indeed, through the ratio $k_q\tau_0[Q]/(1 + k_q\tau_0[Q]) = 268 \times 1.6 \times 10^{-4}/(1 + 268 \times 1.6 \times 10^{-4})$, a value of η(free L5 ⟶ free Co) = 0.041 is obtained. The contribution of this process to the overall quantum yield is $0.036 \times 0.041 \times 0.30 = 0.0004$, which is still insufficient to explain the observed quantum yield. Assuming an identical (diffusional) k_q for dynamic energy transfer from free L5 to the adduct, a maximum contribution of $0.036 \times 0.43 \times 0.30 = 0.005$ to the overall quantum yield is expected.

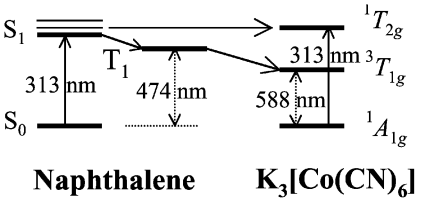
Inspection of both parcels of the dynamic contribution shows that these processes contribute no more than 3% to the total quantum yield, and can thus be neglected.

At this point there are two unknowns: $\eta_{L5 \longrightarrow Co}$ and Φ_{L5Co}. In a first approach, Φ_{L5Co} can be assumed to be identical to the photoaquation quantum yield observed in the presence of the model compound L0. In this case a value of $\eta_{L5 \longrightarrow Co} = 0.63$ is obtained. On the basis of Förster's R_0 value[17] for this donor–acceptor system (13 Å), the mean distance between the naphthalene and the cobalt complex to achieve an energy transfer efficiency of $\eta_{L5 \longrightarrow Co} = 0.63$, would be ≈11 Å, which is higher than ≈7 Å calculated from molecular modelling.[18]

On the other hand, if this last distance is used, an efficiency of 0.98 is obtained for $\eta_{L5 \longrightarrow Co}$ which leads to $\eta_{L5Co} = 0.18$ for the photoaquation reaction. This value is significantly different from 0.23 obtained with the model compound L0. Indeed, the naphthalene aromatic moiety in L5 may affect the way the polyamine chain wraps the cobalt complex and the quantum yield may be different. A reduction in the quantum yield for hexacyanocobaltate(III) photoaquation from 0.30 to values around 0.15 was observed with polyamine ligands containing benzene as fluorophore.[19]

In any case, contribution from dynamic energy transfer for the observed quantum yield is negligible compared to the static contribution. The guest photoreaction sensitised by the host is the main contribution for the observed quantum yield and the supramolecular system constituted by L5 and hexacyanocobaltate(III) may be described as a molecular photoreactor.[20]

The photoaquation reaction of hexacyanocobaltate(III) is known to occur from its triplet state, $^3T_{1g}$.[21] In particular, photosensitization of the hexacyanocobaltate(III) triplet by biacetyl has been reported.[22,23] In our system both singlet–singlet and triplet–triplet energy transfer processes are thermodynamically allowed (Scheme 3).



Scheme 3

Conclusions

Host–guest supramolecular systems can be explored as molecular photoreactors if the host behaves as an antenna and sensitises a photochemical reaction of the guest. This has been explored with cyclodextrins substituted with naphthalenes by Valeur and Lehn.[20] The system reported in the present work shows the possibility of carrying out the photoaquation of hexacyanocobaltate(III) by direct excitation of the naphthalene unit attached to the polyamine chain, and illustrates this concept as depicted in Scheme 1. In general, a molecular photoreactor can be transformed into a molecular photocatalytic centre if the receptor unit binds the substrate strongly and the photoproduct weakly. In the system described in this work the substrate (3− charged) is bound more strongly to the receptor than the photoproduct (2− charged) but the difference is still not enough to obtain a good turnover. The optimisation of these parameters, in order to achieve a more efficient model system, is now underway.

Acknowledgements

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