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Luminescence Quenching of the Excited Tris-bipyridyl Ruthenium(II) Ion by Copper(II)-Cyclodextrin Complexes

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Abstract. The quenching of the luminescence intensity and lifetime of the electronically excited species $\mathrm{Ru(bipy)_3^{2+}}$ by a series of copper (II) cyclodextrin complexes is studied. It is found that conventional Stern–Volmer behaviour is not followed. A modified version of the Stern–Volmer equation, one which assumes purely static quenching, is in good agreement with experimental data. Inclusion of the $\mathrm{Ru(bipy)_3^{2+}}$ by the metallo-cyclodextrin complex is observed to play a key role in the quenching mechanism.

Key words: Cyclodextrin, metallo, quenching, luminescence.

1. Introduction

Cyclodextrins (CDs) are a series of cyclic oligosaccharides composed of six or more glucose units. Their shape is similar to that of a torus, with a hydrophilic exterior and a lipophilic internal cavity. The ability of cyclodextrins to interact with different inorganic and organic species via inclusion within their cavities is widely known [1]. This ability is largely influenced by cavity size. The principle homologues of cyclodextrins have six (α), seven (β) and eight (γ) pyranose rings, giving cavity diameters of 5.7, 7.8 and 9.5 Å respectively. More recently fluorescing and phosphorescing species have been shown to form inclusion complexes with cyclodextrins and complexation has been proven to alter the luminescence characteristics of the species [2, 3]. It was reported that the addition of cyclodextrin to a fluorescer/quencher system may have one of two effects, either depression of dynamic quenching or the acceleration of static quenching [4]. The depression of the dynamic component of quenching may be explained in terms of the separation of the fluorescer and the quencher, only one of the species being included in the cyclodextrin. The acceleration of the static component of quenching, on the other hand, may be interpreted in terms of the formation of a three component ground state complex of the fluorescer, quencher and the cyclodextrin [5–7]. It seems reasonable to expect similar behaviour when the quencher itself is a metallo-cyclodextrin complex.

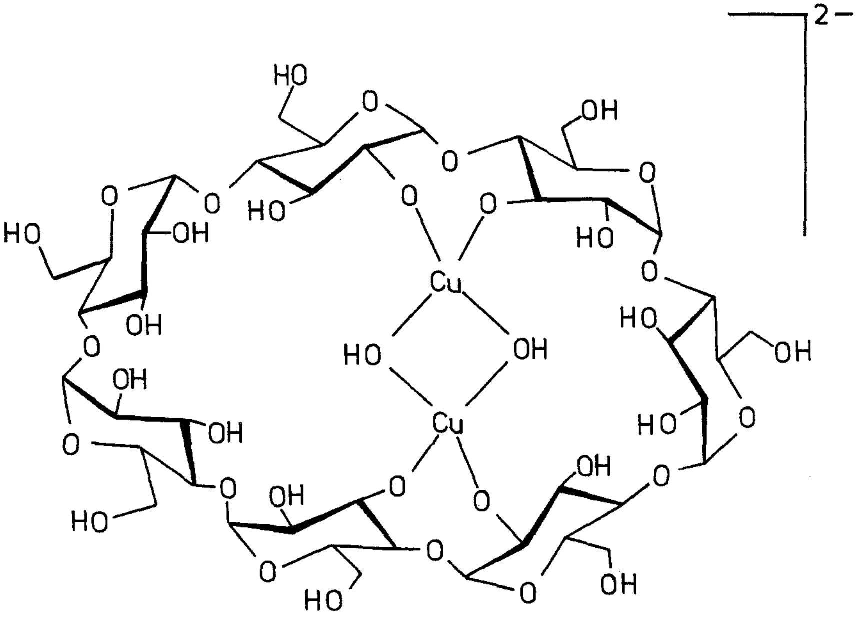

Fig. 1. Proposed binuclear structure of the Cu(II)-βCD complex.

Tris(bipyridyl)ruthenium(II), $[Ru(bipy)_3]^{2+}$, is a widely studied luminescing species. Quenching of its luminescence by many simple metal ions has been reported [8]. Aqueous Cu^{2+} ions quench both the luminescence intensity and lifetime of this species. The quenching mechanism proposed is that of oxidative electron transfer [9–11]. A β-CD complex of copper(II) which features first sphere coordination of Cu(II) has previously been reported [12, 13] (Figure 1). In this paper, the quenching abilities of Cu(II)-CD complexes are investigated and the influence of cavity size on the process is evaluated.

2. Experimental

Trisbipyridyl ruthenium(II) chloride, $Ru(bipy)_3Cl_2$ $5.5H_2O$ was obtained from Sigma Chemicals Ltd. and recrystallised from water before use. NaOH was obtained from Aldrich Ltd. and used without further purification. The syntheses of the Copper(II)-CD complexes are described elsewhere [14].

The luminescence intensity was measured with a Perkin–Elmer L.S.-3 fluorescence spectrometer. Excitation was achieved with 452 nm radiation and emission was recorded at 600 nm. Optically dilute solutions were employed. Emission lifetimes were determined by monitoring the fluorescence decay after excitation by a Coumarin 1 dye laser ($\lambda = 460$ nm) (Oxford lasers EDL 1) pumped by a Lambda Physik E.M.G. 50 excimer (XeCl) (pulse width ca. 15 ns, pulse energy 20–40 mJ).

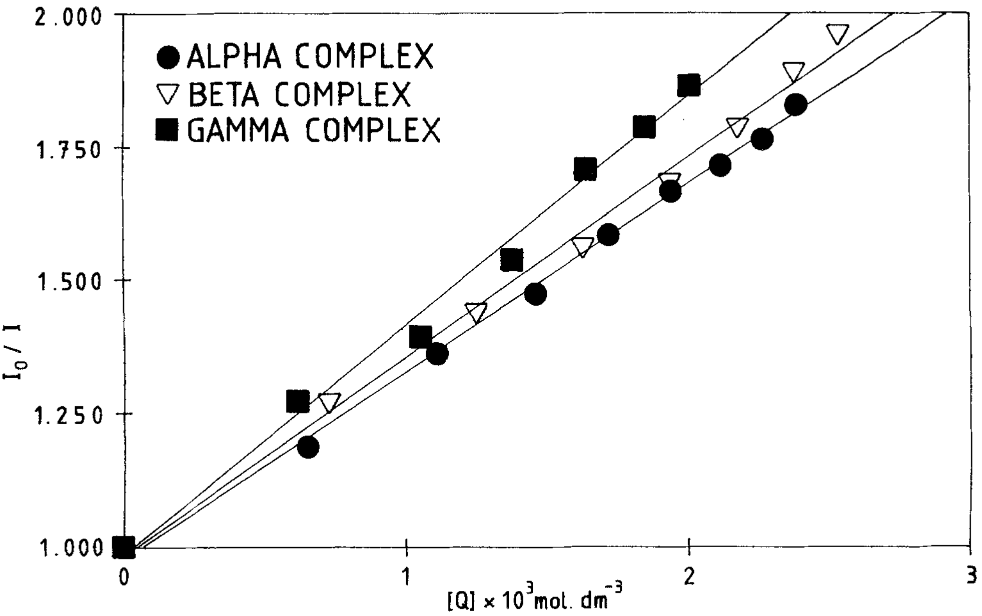

Fig. 2. Stern–Volmer luminescence plots for the quenching of Ru(bipy)_3^{2+*} by Cu(II)-CD complexes.

Fluorescence decays were observed along a 1 cm optical path in a cross beam arrangement, detected on a R298 photo multiplier and recorded on a 125 MHz digital oscilloscope (Philips PM 3311C). The system has a maximum steady-state voltage of 700 mV. In this experiment it was operated at a steady state voltage of less than 100 mV. All experimental values were obtained from air-equilibrated 0.5M NaOH solutions of the donor/quencher species at a temperature of 22°C. Least squares procedures were employed to generate best fit lines.

3. Results and Discussion

Figure 2 presents the conventional Stern–Volmer luminescence plots (1a) for the quenching of the excited state of Ru(bipy)_3^{2+} by the copper cyclodextrin complexes.

$$I_0/I = 1 + K_{sv}[Q] \tag{1a}$$

I_0 – Luminescence at zero quencher concentration
I – Luminescence at quencher concentration $[Q]$
$[Q]$ – Quencher concentration
K_{sv} – Stern Volmer constant.

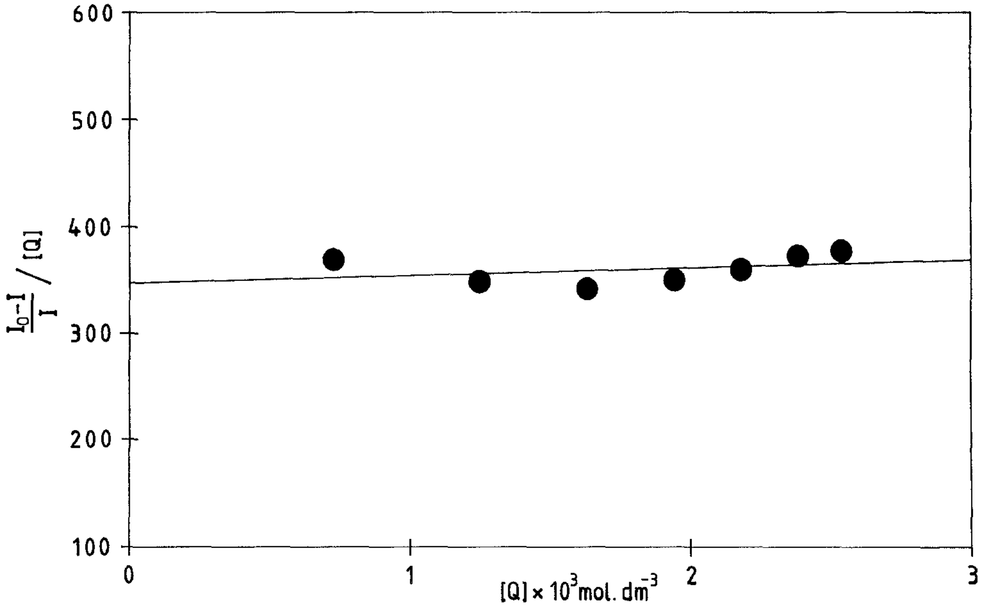

Fig. 3. Extended Stern–Volmer luminescence plot for the $Ru(bipy)_3^{2+*}/Cu(II)$-βCD system.

It should be noted from these plots that the quenching ability of the metallo-CD complexes seems to be dependent on the cavity size, the Cu(II)-γ-CD complex being the most efficient. Another point of interest is the deviation from linearity at increased quencher concentration. The upward curvature is most evident for the complex with the largest cavity size. A deviation from linearity in conventional luminescence Stern–Volmer plots was previously taken to indicate the presence of static quenching in the system [15, 16]. Static quenching is most likely to occur through second sphere interaction via partial inclusion of the bipyridyl ligand in the CD cavity. The nature of the ligand suggests that this would be most feasible for the γ- and least for the α-CD metallo complex.

A more complete expression of the Stern–Volmer relationship, one which takes into account the possibility of both static and dynamic quenching, must therefore be applied to this data in order to obtain an accurate view of the quenching process of these complexes (1b) [17].

$$(I_0 - I)/I = (K_{sv} + K_{ip})[Q] + K_{sv}.K_{ip}[Q]^2 \tag{1b}$$

K_{ip} – Ion pair constant for the formation of the ground state association complex between the donor and the quencher.

A plot of $\{(I_0 - I)/I\}[Q]$ vs. $[Q]$ will therefore yield values of both K_{ip} and K_{sv}. That for the Cu(II)-α-CD complex is shown in Figure 3. It is apparent that

TABLE I. Ion-pair constants for Cu(II)-CD complexes

Quencher	$K_{sv} + K_{ip}$ (mol dm^{-3})$^{-1}$
Cu(II)-αCD	350
Cu(II)-βCD	370
Cu(II)-γCD	430

the product ($K_{ip}.K_{sv}$) approach zero. Similar results were found to apply to the Cu(II)-β and -γ-cyclodextrin complexes also. Values obtained for the intercept ($K_{ip} + K_{sv}$) for the three metallo-CD complexes are shown in Table I.

The quenching ability of a species can also be calculated from a lifetime Stern–Volmer plot (1c)

$$\tau_0/\tau = 1 + K_{sv}[Q] \tag{1c}$$

τ_0 – The lifetime of the excited species in the absence of quencher.
τ – The lifetime of the excited species in the presence of quencher $[Q]$.

The lifetime of the excited species is consequently unaffected by static quenching, this being a ground state interaction. Only the contribution of dynamic quenching to the overall quenching reaction is obtained from this type of plot. The decrease in emission intensity of the excited species as a function of time is monitored and the slope of a plot of ln (Intensity) vs. Time should yield the lifetime of that species. Figures (4) to (6) are studies of the decay of Ru(bipy)$_3^{2+*}$ in the presence of the different Cu(II)-CD quenchers. Table II shows the lifetime values of Ru(bipy)$_3^{2+}$ obtained from these studies. The quencher complexes behave as would be expected. There is no change in the lifetime of the excited species (experimental error 10%) but there is a decrease in concentration of the excited species as the quencher concentration increases. This decrease in excited Ru(bipy)$_3^{2+}$ can be rationalised by the increased formation of a 'dark' ground state association adduct [Ru(bipy)$_3^{2+}$ ... Q] as $[Q]$ increases. If the quenching mechanism is predominantly static as these results indicate, then the dynamic Stern–Volmer constant, K_{sv}, is zero. This implies that the values in Table I are, in fact, the K_{ip} values for the respective metallo-CD complexes.

Drawing the conclusion that the quenching process present is a static one means that conventional Stern–Volmer behaviour cannot therefore be accurately ascribed to these systems. A modified version of the Stern–Volmer equation (1d) has been derived by Patonay *et al.* [18] to describe the quenching of the luminescence of pyrene by cyclodextrin. This derivation is based on two assumptions; (a) that the ground state complexation occurs between one donor and one quencher species and (b) that the quenching mechanism is purely a static one. Results obtained earlier (Figures 4–6) suggest that these conditions are met by the systems described here. This modified version of the Stern–Volmer equation is expressed as follows:

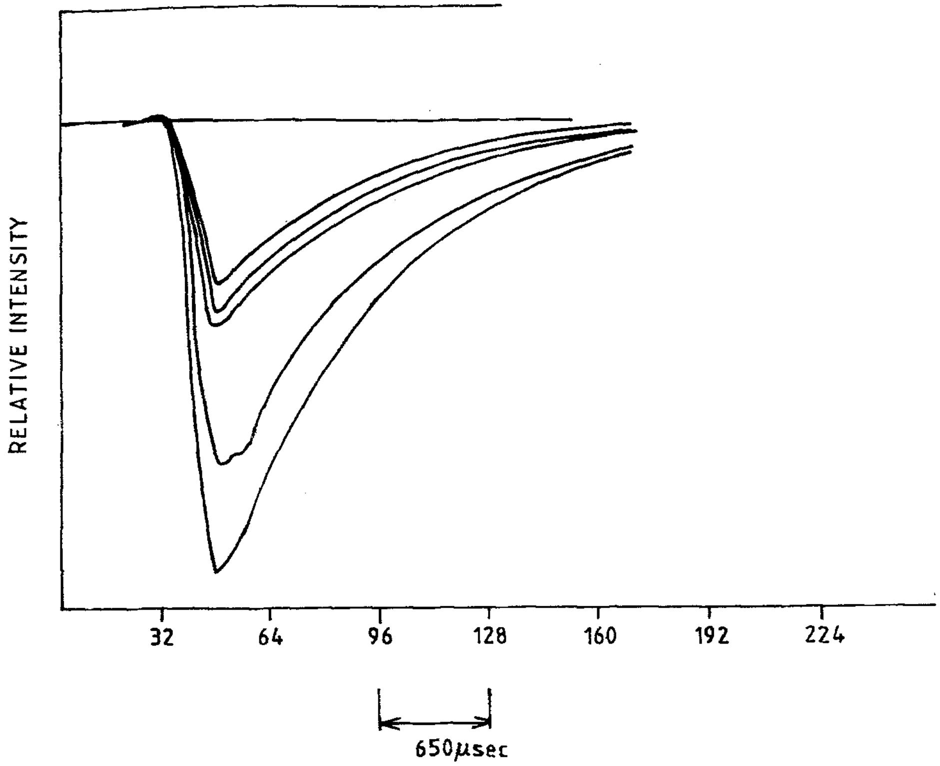

Fig. 4. Luminescence decay plot for the Ru(bipy)_3^{2+*}/Cu(II)-αCD system.

$$\frac{I_0 - I}{I} = \frac{(1-e) + K_{\text{ip}}[Q](1-d)}{e + K_{\text{ip}}[Q]\,d} \tag{1d}$$

d – The fractional quantum yield change of the complexed form of the donor and the quencher.

e – The fractional quantum yield change of the free form of the donor and the quencher.

Figures (7) to (9) show these modified Stern–Volmer plots for all three copper-CD quenchers with both the theoretical line and the experimental points included. The theoretical line was derived using the Simplex routine of Nedler and Mead [19]. The change in relative luminescence of Ru(bipy)_3^{2+} was measured as a function of quencher concentration. This data was substituted into Equation (1d), together with the corresponding K_{ip} values and fitted to best fit curves using the Simplex program. The program optimised the values of d and e for each metallo-CD complex by minimising function (1e).

$$\Sigma(F_{\text{exptl.}} - F_{\text{calc.}})^2 \tag{1e}$$

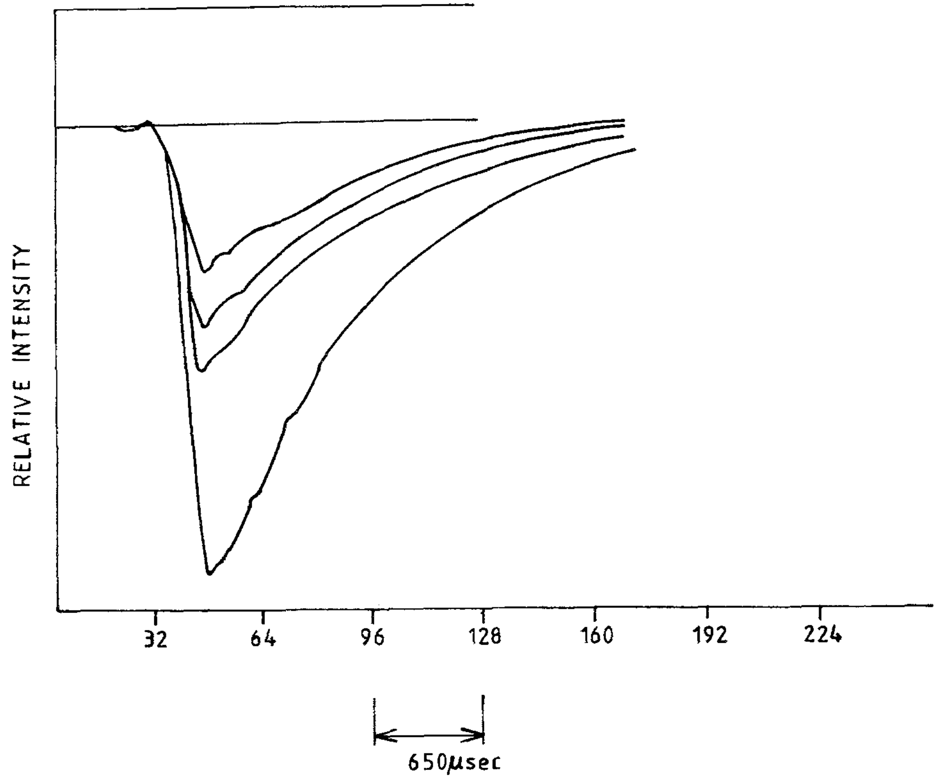

Fig. 5. Luminescence decay plot for the $\mathrm{Ru(bipy)}_3^{2+*}$/Cu(II)-βCD system.

where $F = (I_0 - I)/I$.

The good agreement between the experimental and the theoretical values indicates the suitability of this equation to describe the interaction of $\mathrm{Ru(bipy)}_3^{2+}$ with metallo-CD complexes. The Simplex routine was used to generate values for the co-efficients d and e. These calculated values were the same for each of the three metallo-CD complexes. It was found that *d*, the quantum yield change of the complexed donor and quencher, had a value of zero. This implies that the ground state association species formed between $\mathrm{Ru(bipy)}_3^{2+}$ and each of the metallo-CD complexes is non-fluorescing at the wavelength studied. There were no changes in the quantum yields of the free forms of the donor and quencher species.

4. Conclusion

The quenching of the luminescence of $\mathrm{Ru(bipy)}_3^{2+}$ by these metallo-CD complexes can be described by a relatively simple mechanism, one in which a non-fluorescing ground state association adduct between the donor and the quencher is formed. The assumption that a ground state association adduct is formed between the

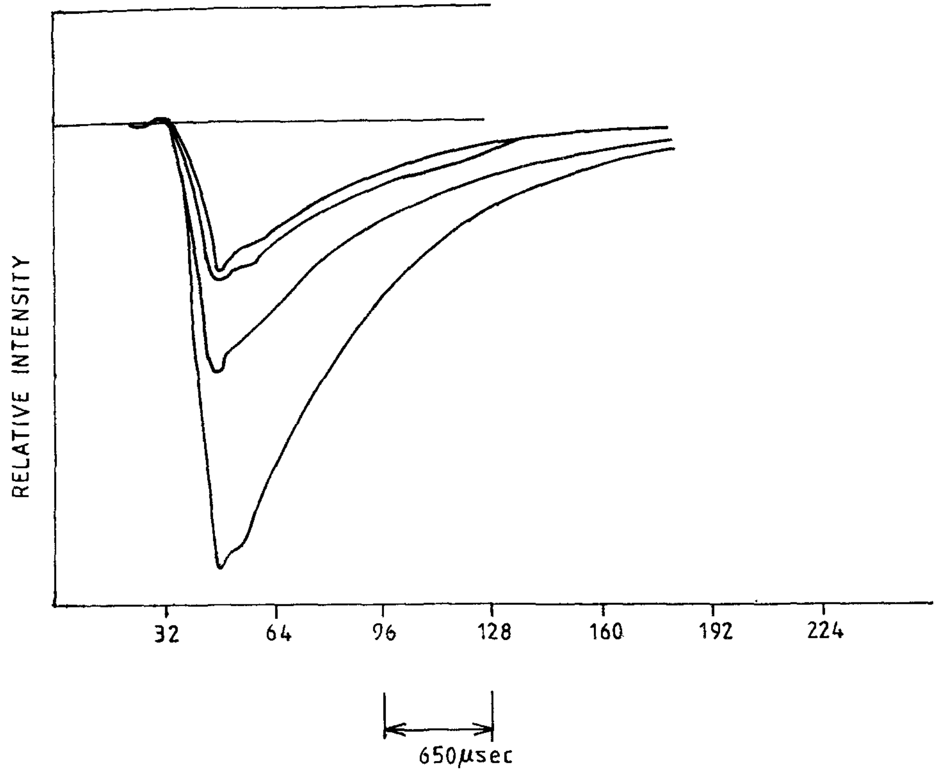

Fig. 6. Luminescence decay plot for the $\mathrm{Ru(bipy)}_3^{2+*}$/Cu(II)-γCD system.

$\mathrm{Ru(bipy)}_3^{2+}$ and the metallo-CD complex is quite a reasonable one. The inclusion of one of the bipyridyl ligands of the $\mathrm{Ru(bipy)}_3^{2+}$, at least partially, in the cavity of the Cu(II)-CD complexes is quite feasible. This would indicate that the greater the cavity dimensions of the Cu(II)-CD complex the more extensive the degree of inclusion of the $\mathrm{Ru(bipy)}_3^{2+}$. It seems reasonable to expect that the greater the degree of inclusion of the donor species the more effective is the quenching of its luminescence. The ion-pair constants (Table I) obtained for the metallo-CD complexes would appear to lend support to this conclusion.

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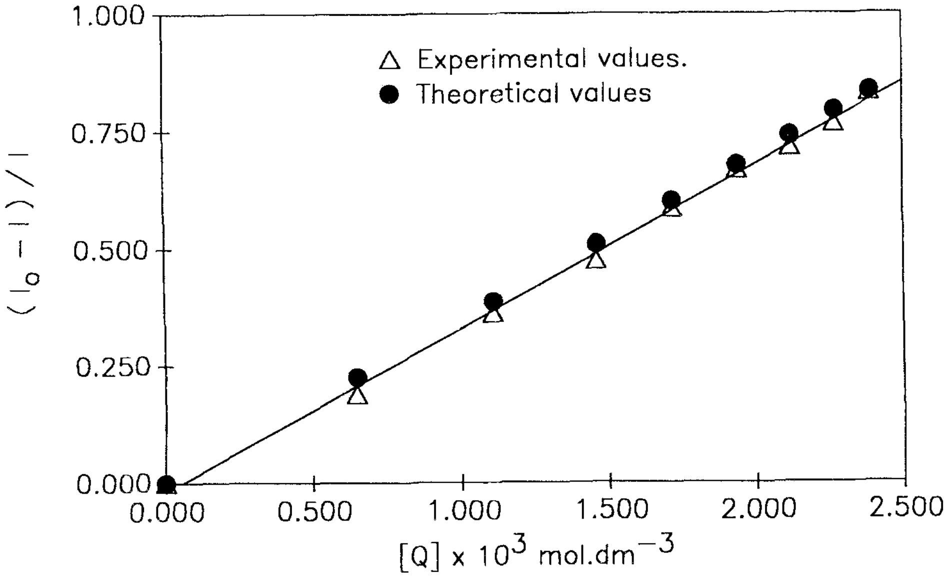

Fig. 7. Modified Stern–Volmer plot for the Cu(II)-αCD system.

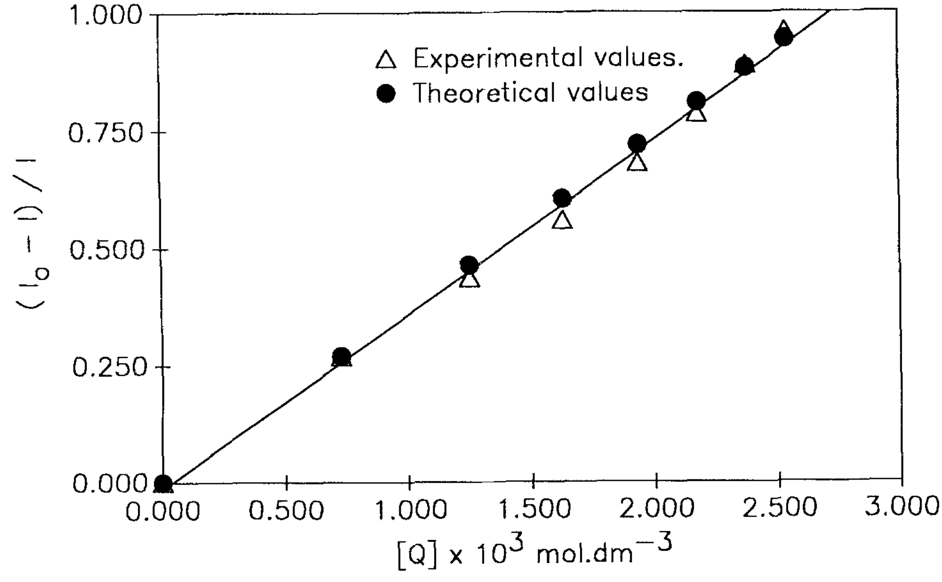

Fig. 8. Modified Stern–Volmer plot for the Cu(II)-βCD system.

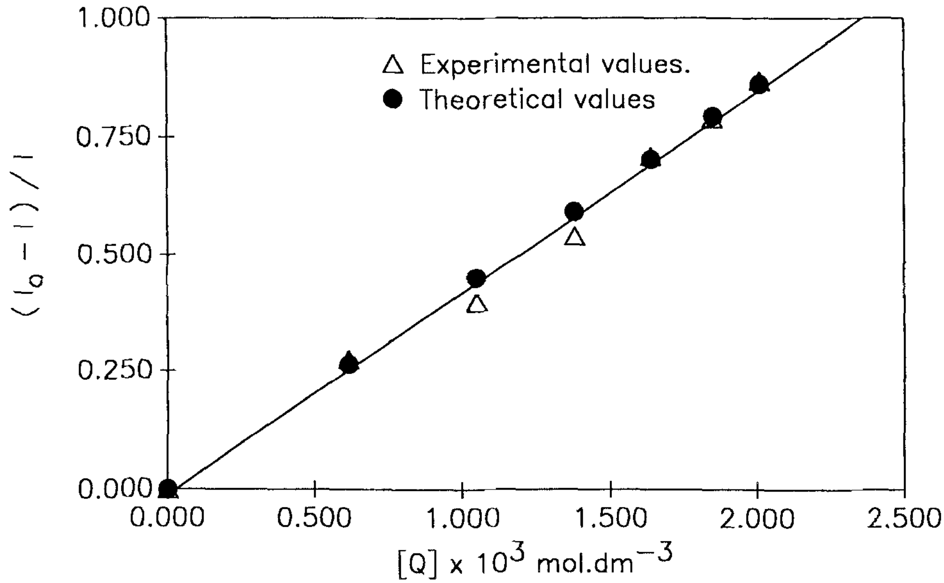

Fig. 9. Modified Stern–Volmer plot for the Cu(II)-γCD system.

TABLE II. The variation of lifetime values of $\mathrm{Ru(bipy)}_3^{2+*}$ as a function of quencher concentration.

Quencher	Quencher conc. (10^3 mol dm^{-3})	Lifetime[a] (ns)
Cu(II)-αCD	0.185	373
Cu(II)-αCD	0.486	363
Cu(II)-αCD	0.898	350
Cu(II)-αCD	1.380	363
Cu(II)-βCD	0.208	366
Cu(II)-βCD	0.569	365
Cu(II)-βCD	1.250	387
Cu(II)-γCD	0.176	374
Cu(II)-γCD	0.851	355
Cu(II)-γCD	1.050	365

[a] The lifetime of $\mathrm{Ru(bipy)}_3^{2+*}$ in air equilibrated 0.5M NaOH at 22°C is 367 ns.

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