Chemiluminescence is often very weak and to use it, or even to investigate it, it is necessary to enhance it. One way to do this is to use fluorescent dyes. So it is necessary to find a link between the properties of the dye and the degree of enhancement achieved. One key property is the fluorescence quantum yield of the dye; this must be greater than the chemiluminescence quantum yield of the original emitter.

There are two processes by which a luminescent signal can be enhanced, depending on the distance separating the emitting molecule (the energy donor) from the dye molecule (the energy acceptor). The Dexter mechanism applies at very short separation distances, for example when molecules collide. This very close approach allows the excited state donor to exchange a high energy electron for one of lower energy, thus returning to the ground state. The ground state acceptor molecule loses the low energy electron and gains one of higher energy, thus entering an excited state. The rate of energy transfer depends on the concentration of acceptor molecules.

For molecules that are further apart (up to 7-10 nm), the Förster mechanism applies. This involves direct transfer of energy from donor to acceptor, rather as a radio antenna transmits energy to a receiver. The relationship between the rate constant of energy transfer ($k_{\text{ET}}$) and the separation distance ($R$) is given by:

$$k_{\text{ET}} = \left( \frac{1}{\tau_D} \right) \left( \frac{R_o}{R} \right)^6$$

where $\tau_D$ is lifetime of the excited state of the donor molecule and $R_o$ is the critical separation constant. The actual rate of energy transfer depends on the rate constant and on the concentrations of donor and acceptor molecules. Also important is the extent of overlap between the emission band of the donor and the absorption bands of the acceptor. This is greatest when the maximum emission wavelength of the donor is close to the maximum absorption wavelength of the acceptor, but it also depends on the shapes of the bands and on the bandwidths. The molecular structure of the donor and acceptor molecules determine the probability of energy transfer.

The chemically initiated electron exchange luminescence model (CIEEL), proposed to explain peroxy-oxalate chemiluminescence\textsuperscript{[1]} (see chapter B5) may sometimes apply to dye enhancement. It has been observed that higher and slimmer chemiluminescence signals, implying a more rapid rate of the light emitting reaction, are obtained when cerium(IV) and rhodamine 6G are premixed before the injection of the sample. Oxidation of rhodamine 6G by cerium(IV) would certainly form excited state cerium(III), but this would add to the baseline and blank signals as well as to the sample peaks; it would therefore not explain the observed premixing effect. It appears that instead an oxidation product of rhodamine 6G is responsible, for this has an opportunity to react with the sample, leading to specifically enhanced analyte signals. There was no advantage in increasing the time available for the pre-oxidation of rhodamine 6G, so it seems likely that the active product is formed on first contact and could be an intermediate formed by single electron transfer. The electron is transferred from this initial oxidation product to the analyte, reducing it back to rhodamine 6G in an excited state, giving us the analyte (A) oxidation:

$$\text{[Rh6G} \rightarrow \text{Rh6G}^{\ast} + e^-]$$

$$\text{[Rh6G}^{\ast} + A \rightarrow \text{Rh6G}^* + A^{\ast}]$$

Emission from excited rhodamine 6G would occur as before. If (as is plausible) this single stage formation of excited rhodamine 6G goes further and faster than the two stages of analyte oxidation by cerium(IV) followed by energy transfer from excited cerium(III) to rhodamine 6G, it would explain the higher and slimmer analyte peaks that were observed.