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# Fluorescence Quenching of Viologen on Xanthene Dyes in Dyads

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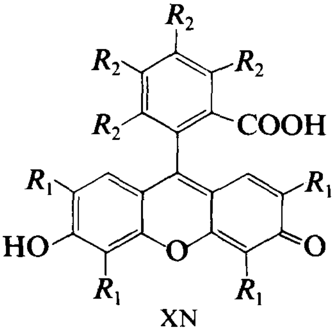
## *ABSTRACT*

*Many dyads containing xanthene dyes and viologens linked with different spacers were synthesized and characterized. The fluorescence quantum yields of dyes in the dyads were measured and the quenching efficiencies were calculated by comparison with dye models and discussed with respect to structural factors.*

## 1 INTRODUCTION

Xanthene (XN) dyes, typified by fluorescein (FL), eosin (EO), erythrosin (ER) and Rose Bengal (RB) all exhibit fluorescence, although the strength varies from dye to dye, and may be used as photosensitizers.[1,2] On the other hand, viologen (VL) is a powerful electron acceptor.[3]



XN

| XN | $R_1$ | $R_2$ |
|---|---|---|
| FL | H | H |
| EO | Br | H |
| ER | I | H |
| RB | I | Cl |

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We report here the synthesis and characterization of some dyads derived from XN dyes and VL. The fluorescence quantum yields ($QY_f$) of the dyes in the dyads were measured and compared with model compounds; the quenching efficiencies are discussed from the viewpoint of structural features.

## 2 RESULTS AND DISCUSSION

The $QY_f$ values of model compound and of dyads, and the calculated $EF_q$ values in dyads, are listed in Table 1. It is apparent that, in dyads, the fluorescence of XN dyes is significantly quenched by VL; the range of $EF_q$ values was 0·48–0·91.

In solution, the XN dye and VL can form a ground state complex which does not emit;[4,5] however, when the XN is excited, it can transfer an electron to VL.[3] These processes may decrease the dye fluorescence. In dyads however, irrespective of the processes involved, the quenching should depend on the dye properties, the distance between XN and VL, and the conformation of the dyads.[3,6,7]

Comparing compounds **10**, **11**, **12** and **13** in Table 1, in which only the dye part differs, the quenching efficiency of VL is decreased in an order consistent with the order of the $QY_f$ value, i.e. the stronger the fluorescence of the dye, the more it is quenched by VL.

When comparing compounds **4**, **5**, **6**, **7** and **8**, in which only the number of methylene groups varies (from 2 to 6), and the other parts of

**TABLE 1**

| *No.* | *Compounds* | $QY_f$ | $EF_q$ |
|---|---|---|---|
| **1** | FLEt | 0·32 | |
| **2** | EOEt | 0·27 | |
| **3** | EREt | 0·11 | |
| **4** | RBEt | 0·10 | |
| **5** | EO-2-VL-4 | 0·14 | 0·48 |
| **6** | EO-3-VL-4 | 0·073 | 0·73 |
| **7** | EO-4-VL-4 | 0·036 | 0·87 |
| **8** | EO-5-VL-4 | 0·066 | 0·76 |
| **9** | EO-6-VL-4 | 0·097 | 0·64 |
| **10** | FL-4-VL-16 | 0·030 | 0·91 |
| **11** | EO-4-VL-16 | 0·035 | 0·87 |
| **12** | ER-4-VL-16 | 0·016 | 0·85 |
| **13** | RB-4-VL-16 | 0·021 | 0·79 |
| **14** | EO-4-VL | 0·030 | 0·89 |

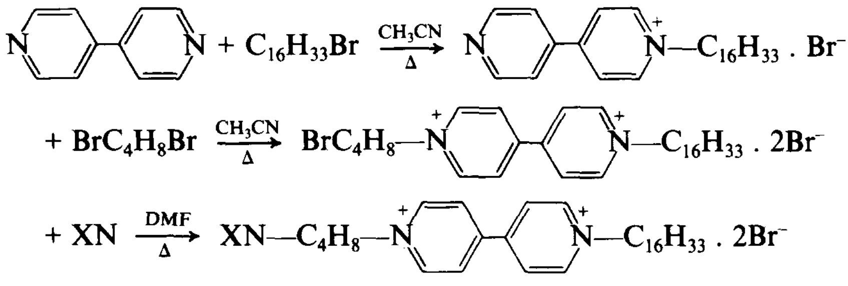
the dyads are the same, dyad **6**, which possesses a butylene spacer, has the highest $EF_q$. Although the linking chains between XN and VL are flexible, they still have a definite conformation in any specific solvent.[7] From the data above, when $n = 4$ for dyad **6** the moieties EO and VL are most suitably matched.[3]

In the dyads **14**, **6** and **11**, in which only the VL part is varied, the $EF_q$ values are essentially the same. The $EF_q$ of **14**, in which VL exists in a monocation form without a substituent on the other end, is a little better than that of the others. This implies that the accepting ability of the monocation VL is sufficient, and that the bulky substituent at the other end of the system may hinder the best match between EO and VL.

## 3 EXPERIMENTAL

### 3.1 Synthesis and characterization

The ethyl esters of the four XN dyes were used as reference models of the XN dyes in dyads. They were synthesized by esterification of the disodium salt of the XN dye with ethyl iodide.[8] A typical synthetic path for the dyads is shown below.

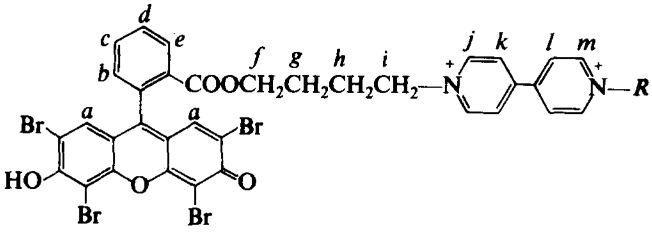


(XN-4-VL-16)

The process is typified by that for EO-4-VL-16, viz. 1-bromohexadecane and 4,4'-bipyridine (two molar ratio) were refluxed for 12 h in acetonitrile, causing 4-hexadecyl bipyridinium bromide to precipitate when the solution was cooled to room temperature. After filtration, the yellow-green residue was washed with benzene to remove excess bipyridine. The resulting monobromide was then refluxed with a five-fold molar excess of 1,4-dibromobutane in $CH_3CN$ for 10 h. A green solid was formed; this was filtered and washed three times with benzene and then with $CH_3CN$. The dibromide thus obtained was then mixed with EO in *N*,*N*-dimethylformamide and heated for 8 h at 95°C. DMF was distilled off under

TABLE 2

$^1H$ NMR data of EO-4-VL, EO-4-VL-4 and EO-4-VL-16



| R | *EO-4-VL* | | | *EO-4-VL-4* | | | *EO-4-VL-16* | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | *n o p q*<br>$—CH_2CH_2CH_2CH_3$ | | | *n o p q*<br>$—CH_2CH_2(CH_2)_{13}CH_3$ | | |
| *a* | 6·96 | s | 2H | 6·92 | s | 2H | 6·91 | s | 2H |
| *b* | 7·48 | d | 1H | 7·48 | d | 1H | 7·44 | d | 1H |
| *c* | 7·81 | t | 1H | 7·79 | t | 1H | 7·77 | t | 1H |
| *d* | 7·89 | t | 1H | 7·86 | t | 1H | 7·85 | t | 1H |
| *e* | 8·21 | d | 1H | 8·20 | d | 1H | 8·16 | d | 1H |
| *f* | 4·05 | t | 2H | 4·05 | t | 2H | 4·02 | t | 2H |
| *g* | 1·40 | m | 2H | 1·32–1·37 | m | 2H | 1·30 | m | 2H |
| *h* | 1·69 | m | 2H | 1·98 | m | 2H | 1·96 | m | 2H |
| *i* | 4·49 | t | 2H | 4·71 | t | 2H | 4·69 | t | 2H |
| *j* | 9·07 | d | 2H | 9·42 | d | 2H | 9·42 | d | 2H |
| *k* | 8·56 | d | 2H | 8·86 | d | 2H | 8·86 | d | 2H |
| *l* | 8·09 | d | 2H | 8·68 | d | 2H | 8·67 | d | 2H |
| *m* | 8·88 | d | 2H | 9·17 | d | 2H | 9·14 | d | 2H |
| *n* | | | | 4·50 | t | 2H | 4·51 | t | 2H |
| *o* | | | | 1·57 | t | 2H | 1·56 | t | 2H |
| *p* | | | | 1·32–1·37 | m | 2H | 1·22 | m | 26H |
| *q* | | | | 0·94 | t | 3H | 0·84 | t | 3H |

reduced pressure and the residue was washed with acetone. The product was initially separated on an aluminium oxide column and then further purified on a silica gel column using methanol and tetrahydrofuran (3 : 2, v/v) as eluant.

Other dyads were similarly synthesized. Typical $^1H$ NMR data (in DMSO-$d_6$) are given in Table 2.

## 3.2 General

Absorption spectra were measured on a Hitachi 557 UV/Vis spectrophotometer, $^1H$ NMR on a Varian XL-400 (with TMS as internal standard) and fluorescence spectra on a Perkin-Elmer LS-5 with a 3600 data station.

*N*,*N*-dimethylformamide (DMF) was re-distilled and collected at 152°C. The concentration used for the dyes was about $10^{-6}$ M.

$QY_f$ values were measured and calculated according to the relationship

$$QY_f = (FA_0/F_0A)QY_{f0}$$

in which $A$ is absorbance, $F$ represents the area of the fluorescence spectrum, and subscript 0 refers to the standard substance. Taking EO as standard, $QY_{f0}(EO) = 0{\cdot}48$.[1]

The quantum efficiency of fluorescence quenching ($EF_q$) is defined by

$$EF_q = (QY_{f0} - QY_f)/QY_{f0}$$

in which subscript 0 stands for $QY_f$ in the absence of quencher, i.e. the $QY_f$ of the model compounds.

## ACKNOWLEDGEMENT

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