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Short Communication

Fluorescent Properties of Phthalocyanines

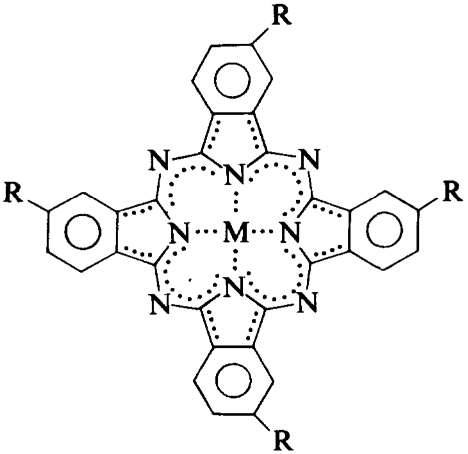
ABSTRACT

A series of ring-substituted phthalocyanines possessing high solubilities in many solvents have been synthesized and their quantum yield and lifetime of fluorescence measured. The relation between fluorescent properties and structural factors, i.e. the central metal ions and the substituents, is summarized. It is found that the fluorescence quantum yield is related to both the central ion and the substituent, whilst the lifetime of fluorescence depends mainly on the central ion and is, generally speaking, independent of the substituent.

1 INTRODUCTION

Phthalocyanines are a class of colorants which are widely used e.g. as pigments, in the dyeing and printing industry, and in solar energy applications.

We have synthesized a series of such compounds, of general formula I



I

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(abbreviated to 'MPcR', where M refers to the central metal ion and R stands for the substituent on the ring). These compounds have greatly improved solubilities in many solvents. Their fluorescent properties, including quantum yield and lifetime, were determined and the relationship between fluorescent properties and structural factors was studied.

2 EXPERIMENTAL

2.1 Synthesis

The following general synthesis, *cf.* Ref. 1, of $ZnPcOC_6H_4$-*p*-C_5H_{11}(t) is illustrative. A mixture of 0·29 g (1 mmol) 4-(*p-tert*-amylphenoxy)phthalonitrile, 0·18 g (3·0 mmol) urea, 0·06 g (0·33 mmol) anhydrous zinc acetate, and about 0·001 g ammonium molybdate was heated to 100°C, when the material became molten. On further heating, the solution bubbled and a green solid precipitated when the temperature reached 150°C. The mixture was kept at 150°C for 2 h and then at 170°C for 2 h, during which time the colour became blackish–green. After heating at 180°C for a further 0·5 h, the reaction mixture was cooled and extracted with chloroform to give 0·2 g crude product. The product was chromatographed on a silica gel column, eluting with chloroform/cyclohexane (8:2) to give the pure dye (MW 1227) (0·12 g, 0·098 mmol, 40% theoretical based on the conversion of the substituted phthalonitrile).

Other derivatives were similarly prepared.

2.2 Fluorescence measurements

The fluorescence of the dyes in DMF (using a concentration of approximately 10^{-5} M) was measured on a Perkin–Elmer LS-5 luminescence spectrometer with a 3600 data station and was calculated according to the equation:

$$\phi = FA_0\phi_0/F_0A$$

where A is the absorbance, F the fluorescence intensity, the subscript 0 refers to the standard dye and ϕ_0(ZnPc) = 0·3.[2] The excitation wavelength was 605 nm, at which wavelength the absorbance of the dyes was 0·05–0·1.

The fluorescence lifetime of the dyes in DMF (about 10^{-5}M) was measured and treated by means of the single-photon counting technique on a Horiba NAES-1100 time-resolved spectrofluorimeter.

3 RESULTS AND DISCUSSION

The relationship between the fluorescence quantum yields and the central metal ions is shown by the data in Table 1, where EN_M is the Pauling electronegativity of the central metal.[3]

It can be seen that the higher the electronegativity of the central metal, the weaker the fluorescence. No fluorescence was observed when the electronegativity of the central metal was higher than 1·8. The relationship for the eight dyes evaluated can be expressed by:

TABLE 1

ϕ and EN_M Values for MPc

Dye	MgPc	ZnPc	CdPc	FePc	CoPc	CuPc	PdPc	PtPc
ϕ	0·6	0·3	0·05	0·004	—	—	—	—
EN_M	1·2	1·6	1·7	1·8	1·8	1·9	2·2	2·2

$$\phi = -0{\cdot}574EN_M + 1{\cdot}153 \qquad (r = 0{\cdot}85)$$

The relationship between the fluorescence quantum yield and the substituents on the ring of ZnPcR is illustrated by Table 2, where σ represents the average Hammett constant of the substituents.[4] It is seen that the more positive the σ value, i.e. the stronger the electron-withdrawing character of the substituent, the smaller is the fluorescence quantum yield. The relationship for the six dyes evaluated is given by

$$\phi = -0{\cdot}320\sigma + 0{\cdot}379 \qquad (r = 0{\cdot}91)$$

The relationship between fluorescence lifetime and the general structural features of the dyes is shown by the data in Table 3, from which it is apparent that the lifetime of the dyes changes significantly with the central metal, whilst changes in the nature of the substituents, R, irrespective of whether they are electron-donating or -withdrawing, does not significantly alter the lifetime. For example, ZnPc and its derivatives all have lifetimes of 3–4 ns.

It can be concluded that in phthalocyanines any change in structural factors which enhances the π-electron density in the conjugated system of

TABLE 2

ϕ and σ Values for ZnPcR

R	OC_6H_5	OC_6H_4-*p*-$C_5H^t_{11}$	H	COOH	$SO_2NHC_4H^n_9$	NO_2
ϕ	0·41	0·46	0·3	0·22	0·21	0·15
σ	−0·034	−0·034	0·000	0·380	0·585	0·744

TABLE 3
Relation of Fluorescence Lifetime with the Structural Factors of Dyes

Dye	$\tau(ns)$
H_2Pc	6·90
MgPc	9·92
ZnPc	4·97
$ZnPcOCH_3$	3·23
$ZnPcOC_6H_5$	3·23
$ZnPcC_6H_4$-*p*-$C_5H_{11}(t)$	3·86
ZnPcCOOH	3·08
$ZnPcSO_2NHC_4H_9$	3·18
$ZnPcSO_2NHC_{14}H_{29}$	3·57
$ZnPcNO_2$	3·58

the dyes may be favourable for increase in the fluorescence quantum yield, whilst the fluorescence lifetime is related mainly to the nature of the central metal, and is essentially independent of the ring substituents.

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