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Dyes and Pigments 51 (2001) 51–55

DYES and PIGMENTS

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Absorption and fluorescence spectral properties of tetra (fluoroalkoxy) metallophthalocyanines

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Received 19 April 2001; received in revised form 20 May 2001; accepted 5 July 2001

Abstract

Absorption and fluorescence spectral properties of some polyfluoroalkoxy metallophthalocyanines are reported for the first time. The absorption spectra and fluorescence spectra are related not only to the central metal and peripheral substituents, but also to the environment. In more polarizable solvents, the absorption and emission maximum blue-shifted, and the fluorescence intensity become lower. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Fluoroalkoxy metallophthalocyanine; UV–visible absorption spectra; Fluorescence spectra; Solvent polarity; Correlation

1. Introduction

Phthalocyanine compounds are very important class of organic materials. The most important and extensive application of phthalocyanines (Pcs) is to be used as colorants, furthermore, Pcs have been widely used as chemical sensors, electrochromism, batteries, semiconductors, catalysts, photochemical hole burning, liquid crystals and nonlinear optics [1,2]. Metallophthalocyanines (MPcs), particularly the aluminum and zinc derivatives, are also currently undergoing clinical trials for use in the photodynamic therapy (PDT) of cancer [3–8]. Compared with the first generation photosensitizers such as hematoporphyrin derivative (HpD), MPcs have a much higher extinction coefficient of the Q band near 670 nm, which makes them be efficiently excited directly through tissue [9,10]. Therefore, MPcs have been widely thought to be ideal photosensitizers for PDT of cancer.

The strong absorption of light by Pcs gives characteristic color, which led to their use as pigments and dyes soon after their discovery and these applications are still of immense commercial importance. For the reasons mentioned above, studying the optical properties of Pcs is still significant. The improved solubility of the studied fluoroalkoxy metallophthalocyanines (Scheme 1), which were characterized by elemental analysis, IR, ^{1}H-NMR and FAB-MS [11], makes it possible to study their spectra properties in different solvents with various polarity, since these properties are important in their applications. For example, in PDT of cancer, the monomers of dyes are mainly responsible for the production of $^1O_2$ [12], and the quantum yield is thought to be one of the leveling factors for photosensitizers [13].

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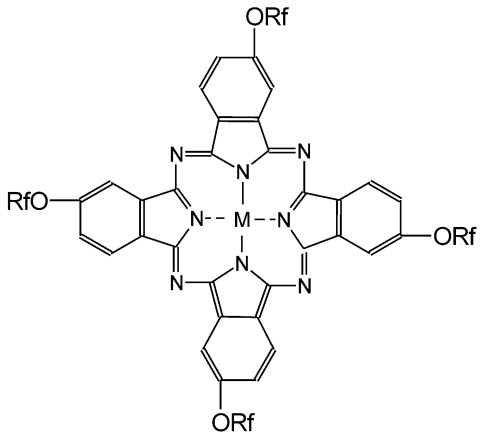
PII: S0143-7208(01)00048-1



1. Rf = CF_3CH_2 -, M = Zn
2. Rf = CF_3CH_2 -, M = Cu
3. Rf = CF_3CH_2 -, M = FeCl
4. Rf = CF_3CH_2 -, M = Mg
5. Rf = CF_3CH_2 -, M = AlCl
6. Rf = CF_3CH_2 -, M = Co
7. Rf = $CF_3CF_2CF_2CH_2$ -, M = Zn

Scheme 1. Structures of fluoroalkoxy metallophthalocyanines.

2. Results and discussion

2.1. Fluorescence spectra

Fluorescence spectral properties of the Pcs have not been received the highly detailed attention given to the absorption spectra, one reason is on the fact that not all Pcs can emit fluorescence when excited, the other is that the fewer application of its fluorescence spectra limits its attraction to researchers. The use of the fluorescence spectral properties in photodiagnosis of cancer has developed a new field [14]. As Pcs show good selectivity towards tumor cell uptake, its emission of a visible light when excited is helpful for the clinic diagnosis. In addition, the fluorescence spectra can reflected the property of compound's singlet excited states, which is related with triplet states for the production of $^1O_2$. Lower quantum yield implies that besides dissipated as heat in the system by internal conversion processes their excitation energy might be easily transferred to triplet excited state for the formation of $^1O_2$.

Zinc (compound **1**, **7**), magnesium (compound **4**) and aluminum (compound **5**) coordinated fluoroalkoxy phthalocyanines show vivid fluorescence, especially magnesium. The fluorescence intensities of copper (compound **2**), iron (compound **3**) and cobalt (compound **6**) centered Pcs are very weak or too weak to be recorded (Table 1). This means that metals with a strong spin-orbit-coupling complexed lead to an enhanced rate of intersystem crossing and subsequently a lowered quantum efficiency of the fluorescent complex.

Compared to the reported fluorescence of unsubstituted phthalocyanines, the fluorescence quantum yield (Φ) of the fluoroalkoxy metallophthalocyanines decreased vividly. For instance, the fluorescence quantum yield of zinc phthalocyanine is 0.3 (chloronaphthalene, 77 K) [15], while the fluorescence quantum yield of its tetra(trifluoroethoxy) substituted derivative (compound **1**) decreased vividly to 0.058 (ethyl acetate, 25 °C), and its tetra (heptafluorobutoxy) substituted derivative (compound **7**), only 0.038 (ethyl acetate, 25 °C); although the recording condition is not on the same. In the case of comparing the emission properties of **1** and **7**, for **7** many different, possible ways of radiationless deactivation (e.g. heavy atom effect, enhanced conversion of excitation energy into rotation/vibration) of the complexes' activated state can lead to a reduced fluorescence intensity.

2.2. Solvent-dependent results

A number of different properties of the environment can be responsible for spectral shifts depending on the properties of the electronic states of the specific solute. In the most widely recognized interaction mechanism, the solute has a large change in dipole moment between the ground and excited electronic states, and its spectra are sensitive to the local electric field generated

Table 1
Fluorescence spectra of fluoroalkoxy metallophthalocyanines

Solvent	Compound **1**[a] λ_{em} (Φ)	Compound **7** λ_{em} (Φ)	Compound **3** λ_{em} (Φ)	Compound **4** λ_{em} (Φ)	Compound **5** λ_{em} (Φ)	Compound **6** λ_{em} (Φ)
Ethyl acetate	687.5 (0.058)	687.1 (0.038)	696.0 (0.004)	702.0 (0.146)	688.4 (0.063)	690.8 (0.006)
Acetone	687.7 (0.047)	687.7 (0.035)	–	–	–	–
Methanol	685.3 (0.031)	687.4 (0.013)	–	–	–	–
Benzene	694.6 (0.085)	693.0 (0.064)	–	–	–	–
Dichloromethane	688.7 (0.052)	–[b]	–	–	–	–
Chloroform	690.5 (0.039)	–	–	–	–	–

[a] Compound **2** shows too weak an intensity to be recorded.
[b] Fluorescence spectra of the compounds in these solvents were not recorded.

Table 2
UV–visible spectra of fluoroalkoxy metallophalocyanines

Compound	Benzene λ_{max} (log ε)	Dichloromethane λ_{max} (log ε)	Chloroform λ_{max} (log ε)	Ethyl acetate λ_{max} (log ε)	Acetone λ_{max} (log ε)	Methanol λ_{max} (log ε)
1	677.0 (5.01)	674.0 (4.61)	674.0 (4.91)	668.8 (5.02)	670.8 (5.04)	669.2 (4.70)
	609.0 (4.25)	608.6 (4.26, sh)	608.8 (4.25)	603.4 (4.27)	603.8 (4.32)	625.4 (4.42)
	356.6 (4.65)	342.4 (4.50)	346.8 (4.66)	346.6 (4.71)	349.2 (4.65)	338.4 (4.66)
2	675.0 (4.51)	670.4 (4.28)	673.8 (4.15)	667.8 (4.45)	665.7 (4.32)	660.8 (4.18, sh)
	612.6 (4.36)	608.0 (4.38)	611.6 (4.10)	607.8 (4.49)	605.5 (4.48)	593.6 (4.40)
	338.2 (4.40)	327.4 (4.63)	329.8 (4.17)	329.8 (4.55)	326.9 (4.54)	320.0 (4.45)
3	699.6 (4.40)	696.4 (4.38, sh)	694.8 (4.36)	695.6 (4.50)	688.0 (4.19, sh)	690.6 (4.47, sh)
	656.2 (4.53)	656.4 (4.51)	663.0 (4.38)	664.6 (4.40, sh)	662.8 (4.29, sh)	665.2 (4.77)
	595.8 (3.98)	608.6 (4.10, sh)	600.4 (4.21, sh)	598.2 (4.25, sh)	627.0 (4.33)	615.4 (4.23, sh)
	328.8 (4.56)	353.4 (4.54)	358.4 (4.42)	346.8 (4.55)	336.4 (4.57)	331.6 (4.67)
4	698.0 (4.84)	694.6 (4.83)	696.8 (4.86)	693.0 (4.86)	691.8 (4.69)	685.8 (3.98, sh)
	660.4 (4.79)	657.8 (4.84)	658.4 (4.83)	656.0 (4.88)	656.0 (4.74)	
	635.0 (4.56)	630.8 (4.70)	639.0 (4.65)	631.2 (4.70)	628.2 (4.69)	
	605.0 (4.40)	602.8 (4.50, sh)	609.2 (4.47, sh)	603.4 (4.57, sh)	602.0 (4.63, sh)	593.8 (4.54)
	328.4 (5.02)	323.6 (5.06)	324.8 (4.80)	325.6 (4.98)	322.8 (4.94)	320.0 (4.68)
5	–[a]	–	–	675.6 (4.84)	676.6 (4.68)	674.4 (4.95)
	–	–	–	608.8 (4.19)	638.8 (4.37)	608.6 (4.27)
	–	–	–	347.0 (4.60)	341.0 (4.70)	356.8 (4.68)
6	–	–	–	659.6 (5.04)	659.0 (5.02)	654.6 (4.72)
	–	–	–	61.25 (4.55, sh)	615.8 (4.68, sh)	617.4 (4.69)
	–	–	–	326.2 (4.85)	325.6 (4.89)	323.6 (4.75)
7	674.4 (5.24)	671.2 (4.47)	672.4 (5.04)	667.0 (5.24)	665.6 (5.24)	667.4 (4.90)
	609.4 (4.59)	609.6 (3.99)	607.2 (4.46)	603.6 (4.59)	603.6 (4.53)	628.2 (4.76)
	356.0 (4.60)	341.8 (4.38)	346.6 (4.84)	346.4 (4.90)	338.0 (4.86)	

[a] Absorption spectra of **5** and **6** in these solvents were not recorded.

by the environment. In this case, the absorption maximum, emission maximum and stokes shift should correlate with the "polarity" of the environment [16, 17].

The UV–visible spectra data of the studied compounds in different solvents are given in Table 2. Compound **1**, for example, the absorption maximum is blue-shifted about 7 nm (from 677.0 nm in benzene to 669.2 nm in methanol), and the absorption coefficient becomes lower (from 5.01 to 4.70) in more polarizable solvent. At the same time, the shoulder absorption presented for the

dimers are red shifted about 16 nm (from 609.0 nm in benzene to 625.4 nm in methanol), and the absorption coefficient becomes higher (from 4.25 to 4.42). The phenomena show that compound **1** has a larger tendency to aggregate in polar solvent methanol than in nonpolar solvent benzene. The absorption characteristics of other compounds are similar to that of compound **1**.

Consistent with absorption spectra of fluoroalkoxy metallophthalocyanines, their fluorescence spectra also correlate with the "polarity" of the environment. As shown in Table 3, the emission maximum of compound **1** is blue-shifted about 10 nm (from 694.6 nm in benzene to 685.3 nm in methanol) and the fluorescence intensity become weaker (from 0.085 to 0.031) with increasing of solvent polarity.

Fig. 1a–b shows some correlations between the absorption maximum or emission maximum of Compound **1** in a number of solvents and E_T (30) [18], a popular empirical measure of solvent polarity, as well as between them and the appropriate function of the solvent index of refraction n [19]. But stokes shift plotted against these two polar scales show no correlations (not shown).

The result show that compound **1** changes in dipole moment upon excitation and is sensitive to the local electric field produced by the environment. It is also affected by changes in dispersion

Table 3
Spectral properties of compound **1** and solvent polarity: excitation maximum, emission maximum (Φ), Stokes shift, E_T (30), n

Solvent	λ_{ex} (nm)	λ_{em} (Φ) (nm)	Stokes shift (K cm^{-1})	E_T (30)[a]	n[b]
Benzene	677.0	694.6 (0.085)	0.37	34.3	1.5010
Dichloromethane	674.0	688.7 (0.052)	0.32	40.7	1.4240
Chloroform	674.0	690.5 (0.039)	0.36	39.1	1.4460
Acetone	670.8	687.5 (0.058)	0.36	42.2	1.3588
Ethyl acetate	668.8	687.7 (0.047)	0.41	38.1	1.3723
Methanol	669.2	685.3 (0.031)	0.35	55.4	1.3288

[a] Ref. [16].
[b] Ref. [17].

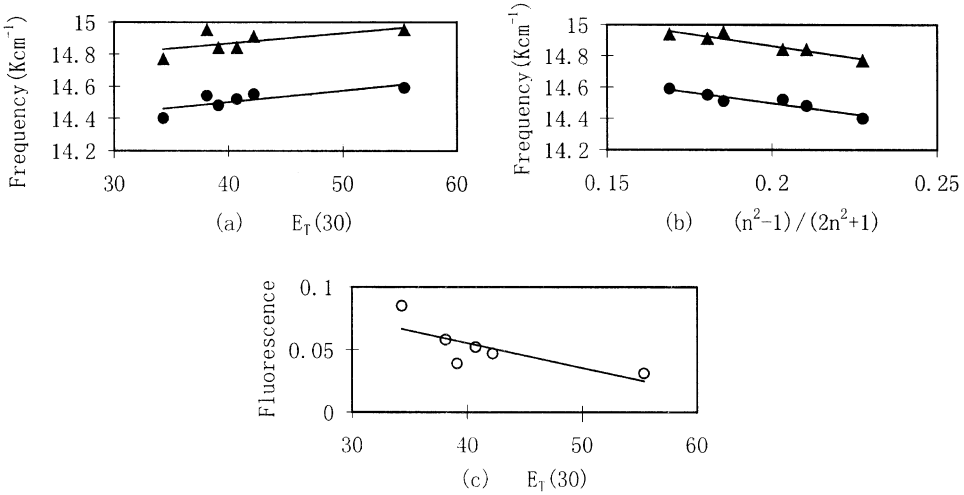


Fig. 1. (a) Excitation maximum (▲) and emission maximum (●) of compound **1** in various solvents vs the E_T (30) polarity scale. (b) Excitation maximum (▲) and emission maximum (●) of compound **1** in various solvents vs a polarizability scale represented by a function of the index of refraction n. (c) Fluorescence quantum yield (Φ) of compound **1** vs the E_T (30) polarity scale. Correlations are found.

interactions with the environment. The fact that the absorption is blue-shifted in more polarizable solvents tells us that the excited states might have a lower polarizability and weaker dispersion interactions than the ground state.

Fig. 1c shows the fluorescence quantum yield in a number of solvents against E_T (30). There also exist correlation. Plot (not shown) against the function of solvent index of refraction n show no correlation. The results show that the fluorescence intensity is sensitive to the local electric field produced by the environment, but not sensitive to the dispersion interactions with the environment.

3. Conclusion

UV–visible spectra and fluorescence spectra of some novel fluoroalkoxy metallophthalocyanines are reported. Environmental factors, mainly solvent polarity, affect their spectra are discussed. The zinc, copper, cobalt and aluminum centered fluoroalkoxy phthalocyanines show characteristic absorptions in the Q-band region without splitting, while the iron and magnesium centered fluoroalkoxy phthalocyanines show broadened or splitted peak in this region. The absorption maximum, emission maximum and fluorescence intensity of the studied compounds correlate with solvent polarity well. In more polarizable solvents, the absorption and emission maximum blue-shifted, and the fluorescence intensity become lower. The influences of peripheral substituents are also discussed. With increasing of the carbon number of the fluoroalkoxy chain, the fluorescence intensity become lower, and the excitation maximum blue-shifted. Plots against empirical polarity scale E_T (30) and index of solvent refraction n show that the absorption and emission maximum are sensitive to the local electric field produced by the environment and also sensitive to the dispersion interactions with the environment.

4. Materials and methods

The studied compounds were synthesized according to Ref. [11]. All solvents employed were of AR grade and were used without further purification.

UV–visible absorption spectra were recorded on a Shimadzu UV-265 spectrophotometer. Fluorescence spectra were measured on a Perkin Elmer LS 50 spectrophotometer, 0.1 M (1 ug/ml) quinoline sulfate monohydrate in 0.1 N sulfuric acid solution was used as a standard ($\Phi = 0.55$, $F = 9.952 \times 10^4$, $A = 0.051$) to determine the fluorescence quantum yield [20–22].

Acknowledgements

The National Natural Science Foundation of China and the Ministry of Education of China financially supported this work.

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