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Accurate fluorescence lifetime predictions of axially substituted silicon phthalocyanines

Suzanne E. Maree[a] and M. David Maree[b]*

[a]Department of Chemistry, University of Zululand, Private Bag X1001, KwaDlangezwa, 3886, Kwa-Zulu Natal, South Africa

[b]Department of Chemistry, Rhodes University, Grahamstown, 6140, South Africa

A convenient method using the Strickler–Berg equation is described for the determination of fluorescence lifetimes for axially substituted silicon phthalocyanines. By utilising only the absorption and emission spectra of these compounds it is possible to determine the fluorescence lifetimes to within 10% accuracy.

Keywords: Strickler–Berg, silicon phthalocyanines, axial substitution, fluorescence lifetime

Einstein found that a relationship exists between the strength of absorption and the spontaneous emission lifetime of atoms in a vacuum. Strickler and Berg[1] extended this theory to include molecules, thus it is possible to determine the natural radiative lifetime, τ_0, of molecules having broad absorption and emission bands using the following equation:

$$1/\tau_0 = 2.880 \text{ x } 10^{-9}\, n^2\, (\int F(\nu)d\nu \times (\int \nu^{-3} F(\nu)d\nu) \times (\varepsilon(\nu)d\ln(\nu))$$

where, ν is the wavenumber in cm^{-1}, $F(\nu)$ is the fluorescence intensity in units of relative numbers of quanta, $\varepsilon(\nu)$ is the molar absorption coefficient at a particular wavenumber and n is the refractive index of the solvent. From the natural radiative lifetime (τ_0) and the fluorescence quantum yield (Φ_F) one may then calculate the actual fluorescence lifetime as: $\tau_F = \Phi_F / \tau_{0.}$ Using software (photochemcad) from Lindsey and co-workers[2] it is possible to determine the fluorescence lifetimes of compounds using their absorbance and fluorescence spectra if Φ_F and $\varepsilon(\nu)$ are known. Axially substituted silicon phthalocyanines are an interesting group of compounds that have found application in nonlinear optics[3] and photodynamic therapy.[4] These phthalocyanines have good fluorescence properties and thus may potentially be used in fluorescence lifetime imaging. Commercial fluorescence lifetime equipment is expensive and cheaper ways are sought to be able to determine these properties. Fluorescence lifetime data are scarce for axially substituted silicon phthalocyanines and recently Beeby *et al.*[5] published data on a series of 11 compounds. We have thus synthesised these molecules reported and obtained their fluorescence as well as absorption data. These data were then used to determine the fluorescence lifetime according to the Strickler-Berg equation and the results are shown in Table 1.

These data show a better than 10% agreement between the experimentally determined values and the Strickler–Berg method. In most cases the Strickler–Berg equation slightly overestimated the fluorescence lifetimes. In the original article by Beeby *et al*, compounds **10** and **11** both had two components in the experimentally determined fluorescence lifetimes. The Strickler–Berg equation predicts that the second component in both cases reflects the more accurate fluorescence lifetime.

Experimental

Absorption and fluorescence spectra were recorded on Perkin Elmer Lambda 15 and SPEX fluoromax spectrophotometers. ^{1}H NMR (400 MHz) spectra were obtained in $CDCl_3$ using a Bruker EMX 400 NMR spectrometer. Dichlorosilicon phthalocyanine, dimethylformamide (DMF), chloroform, deuterated chloroform, 4-*tert*-butylbenzoic acid, 3-thienylacetic acid, 2-methoxyphenylacetic acid, 3-methoxyphenylacetic acid, 4-methoxyphenylacetic acid, 3,4-dimethoxybenzoic acid, 3,4-dimethoxyphenylacetic acid, 3,4-dimethoxyphenylpropanoic acid, 3,4-dimethoxyphenylbutanoic acid, 2,5-dimethoxyphenylacetic acid and 3,4,5-trimethoxyphenylacetic acid were purchased from Aldrich and used as received.

General procedure for preparation of the axially substituted silicon phthalocyanines

Dichlorosilicon phthalocyanine (0.16 mmol) was added to a solution of the relevant acid (0.56 mmol) in DMF and brought to reflux for 3 h. The reaction was quenched with water (10 ml) and the resultant solution filtered. The filtrate was dissolved in chloroform (10 ml) and extracted with solutions of 10% sodium hydroxide (3 × 10ml) and water (3 × 10 ml). The chloroform was evaporated down to 3 ml and the solution applied to TLC plates. The plates were eluted with dichloromethane and the phthalocyanines were removed.

These compounds have been synthesised previously and thus ^{1}H NMR and UV-visible spectra were used as comparison to the published results in order to verify structures. All compounds reported here compared favourably. The data obtained are as follows:

Silicon phthalocyanine bis-(4-tert-butyl)benzoate (**1**)[5]: ^{1}H NMR δ: 9.65 (8H, d, Pc–H), 8.34 (8H, t, Pc–H), 6.27 (4H, d, Ar–H), 5.03 (4H, d, Ar–H), 0.70 (18H, s, CH_3). UV(nm, λ_{max}): 687

Table 1 Comparison of the predicted fluorescence lifetimes from the Strickler–Berg equation with the experimentally determined fluorescence lifetimes from Beeby *et al.*[4]

Compound	Axial ligands (*bis*-)	τ_f (ns) as determined in ref. 5	τ_f (ns) predicted
1	4-*tert*-butylbenzoate	6.7	7.0
2	3-thienylacetate	6.7	7.1
3	2-methoxyphenylacetate	6.8	7.0
4	3-methoxyphenylacetate	6.8	7.0
5	4-methoxyphenylacetate	6.8	6.9
6	3,4-dimethoxybenzoate	6.5	6.4
7	3,4-dimethoxyphenylacetate	6.4	6.4
8	3,4-dimethoxyphenylpropanoate	5.6	6.1
9	3,4-dimethoxyphenylbutanoate	6.2	6.3
10	2,5-dimethoxyphenylacetate	0.96 (5.1*)	5.3
11	3,4,5-trimethoxyphenylacetate	3.8 (2.4*)	2.6

*Compounds **10** and **11** had two components in the lifetime analysis. The values in brackets are the lifetimes due to the second component

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* Correspondent. E-mail: d.m.maree@ru.ac.za

Silicon phthalocyanine bis-(3-thienyl)acetate (**2**)[6]: ^{1}H NMR δ: 9.55 (8H, d, Pc–H), 8.30 (8H, t, Pc–H), 6.09 (1H, m, CH), 4.99 (1H, s, CH), 4.41 (1H, d, CH), 0.67 (2H, s, CH_2). UV(nm, λ_{max}): 686

Silicon phthalocyanine bis-(2-methoxyphenyl)acetate (**3**)[5]: ^{1}H NMR δ: 9.60 (8H, d, Pc–H), 8.32 (8H, t, Pc–H), 6.35 (1H, t, Ar–H), 5.74 (2H, t, Ar–H), 4.84 (1H, d, Ar–H), 2.59 (3H, s, CH_3), 0.67 (2H, s, CH_2). UV(nm, λ_{max}): 685

Silicon phthalocyanine bis-(3-methoxyphenyl)acetate (**4**)[5]: ^{1}H NMR δ: 9.63 (8H, d, Pc–H), 8.34 (8H, t, Pc–H), 6.07 (2H, m, Ar–H), 4.44 (2H, s, Ar–H), 4.37 (2H, t, Ar–H), 3.15 (3H, s, CH_3), 0.69 (2H, s, CH_2). UV(nm, λ_{max}): 685

Silicon phthalocyanine bis-(4-methoxyphenyl)acetate (**5**)[5]: ^{1}H NMR δ: 9.60 (8H, d, Pc–H), 8.37 (8H, t, Pc–H), 5.73 (2H, d, Ar–H), 4.69 (2H, d, Ar–H), 4.37 (2H, t, Ar–H), 3.55 (3H, s, CH_3), 0.60 (2H, s, CH_2). UV(nm, λ_{max}): 688

Silicon phthalocyanine bis-(3,4-dimethoxy)benzoate (**6**)[5]: ^{1}H NMR δ: 9.69 (8H, d, Pc–H), 8.37 (8H, t, Pc–H), 5.66 (1H, s, Ar–H), 4.65 (1H, d, Ar–H), 4.60 (1H, d, Ar–H), 3.25 (3H, s, CH_3), 2.86 (3H, s, CH_3). UV(nm, λ_{max}): 688

Silicon phthalocyanine bis-(3,4-dimethoxyphenyl)acetate (**7**)[5]: ^{1}H NMR δ: 9.60 (8H, d, Pc–H), 8.34 (8H, t, Pc–H), 5.66 (1H, d, Ar–H), 4.45 (1H, s, Ar–H), 4.31 (1H, d, Ar–H), 3.67 (3H, s, CH_3), 3.13 (3H, s, CH_3), 0.60 (2H, s, CH_2). UV(nm, λ_{max}): 686

Silicon phthalocyanine bis-3-(3,4-dimethoxyphenyl)propanoate (**8**)[5]: ^{1}H NMR δ: 9.66 (8H, d, Pc–H), 8.35 (8H, t, Pc–H), 6.05 (1H, d, Ar–H), 5.22 (1H, s, Ar–H), 5.02 (1H, d, Ar–H), 3.69 (3H, s, CH_3), 3.26 (3H, s, CH_3), 0.41 (2H, t, CH_2) –0.32 (2H, t, CH_2). UV(nm, λ_{max}): 685

Silicon phthalocyanine bis-4-(3,4-dimethoxyphenyl)butanoate (**9**)[5]: ^{1}H NMR δ: 9.66 (8H, d, Pc–H), 8.35 (8H, t, Pc–H), 6.22 (1H, d, Ar–H), 5.67 (1H, s, Ar–H), 5.52 (1H, d, Ar–H), 3.69 (3H, s, CH_3), 3.52 (3H, s, CH_3), 0.82 (2H, m, CH_2), 0.66 (2H, m, CH_2), –0.55 (2H, m, CH_2). UV(nm, λ_{max}): 687

Silicon phthalocyanine bis-(2,5-dimethoxyphenyl)acetate (**10**)[5]: ^{1}H NMR δ: 9.64 (8H, d, Pc–H), 8.33 (8H, t, Pc–H), 5.87 (1H, d, Ar–H), 5.64 (1H, d, Ar–H), 4.44 (1H, d, Ar–H), 3.22 (3H, s, CH_3), 2.65 (3H, s, CH_3), 0.71 (2H, s). UV(nm, λ_{max}): 687

Silicon phthalocyanine bis-(3,4,5-trimethoxyphenyl)acetate (**11**)[5]: ^{1}H NMR δ: 9.64 (8H, d, Pc–H), 8.35 (8H, t, Pc–H), 4.11 (2H, s, Ar–H), 3.99 (3H, s, CH_3), 3.35 (6H, s, CH_3), 0.82 (2H, m, CH_2), 0.57 (2H, s, CH_2). UV(nm, λ_{max}): 685

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