Dyes and Pigments, Vol. 28, No. 1, pp. 69–75, 1995
Copyright © 1995 Elsevier Science Ltd
Printed in Great Britain. All rights reserved
0143-7208/95 $9.50 + 0.00

0143-7208(95)00009-7

Q-Band Electronic Absorption of Silicon 2,3-Napthalocyanine Bis(Trihexylsilyloxide) in Various Solvents

Mohammad Yousaf & Mohamed Lazzouni*

SIA Technology Corporation, 337 Turnpike Road,
Southboro, MA 01772, USA

(Received 10 November 1994; accepted 14 December 1994)

ABSTRACT

Silicon 2,3-naphthalocyanine bis(trihexylsilyloxide) has been shown to be an excellent absorber with a narrow band in the near infrared region. Information with respect to the position of the absorption band in various solvents is needed in order to fully exploit the optical properties of this compound and its derivatives in possible applications. This article reports the experimental results of the effect of various solvents on the position of the electronic absorption band (Q-band) in silicon 2,3-naphthalocyanine bis(trihexylsilyloxide). The shifts in nonpolar and polar solvents are accounted for on the basis of known relationships involving refractive indices and dielectric constants of the solvents.

INTRODUCTION

Near infrared absorbing dyes have been reported as having applicability in materials for use in optical recording media, printers, displays, filters, infrared photography, photosensing, and medical and nonlinear optics.[1,2] Properties of particular interest are a strong absorption in the near infrared at similar wavelengths to those of the emission wavelengths of semiconductor lasers, high light fastness, and good resistance to chemical and thermal degradation. Many existing near infrared dyes lack one or more of these characteristics. Naphthalocyanine derivatives

---

* To whom correspondence should be addressed.

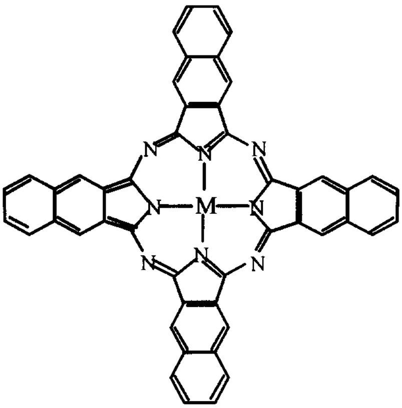

Fig. 1. Structure of 2,3-metallo-naphthalocyanine.

generally meet these requirements and are amongst the various potential candidates which have been proposed for use in the above mentioned applications.[3] Of particular interest are the metallo-naphthalocyanines represented by the structure shown in Fig. 1. The 2,3-isomer is distinguished from the 1,2-isomer in the positioning of the outermost phenyl rings, which in the former case are more symmetrically placed along the four arms of the molecule. Naphthalocyanines based on a large number of elements have been reported, the most common of which are the Al, Cu, Mg and Si complexes. Magnesium 1,2-naphthalocyanine was first reported in 1936 (Ref. 4) and the 2,3-isomer of naphthalocyanine was first synthesized in 1971 (Ref. 5). Referring to Fig. 1, replacement of four outer phenyl rings with double bonds gives what is called a metallo-phthalocyanine and further removal of outer phenyl rings gives tetraazoporphyrin, a well studied class of compounds.[6]

The compounds are usually prepared with alkyl substituents in the outer phenyl rings or ligands attached to the central atom and stretched out normal to the plane of the main molecule, in order to increase the solubility in organic solvents via steric hindrance offered by the heavy and long chain ligands. This increased solubility is required for various applications and a further advantage of such structural modifications is in their ability to alter the position of absorption bands. Various applications and methods employed to synthesize such compounds are described in Refs 7 and 8.

Wheeler *et al.*[9] initially reported silicon 2,3-naphthalocyanine bis(trihexylsilyloxide) (henceforth referred to as SiNc). The structure of this molecule is essentially that shown in Fig. 1, with M representing Si bearing two ligands, $OSi(n\text{-}C_6H_{13})_3$, each one attached to either side of the naphthalocyanine plane. UV/visible absorption and fluorescence spectra of SiNc have been reported[9] in methylene chloride solution.

In a recent communication,[10] we have demonstrated the potential of SiNc for use as a pigment in an invisible, IR-readable printing ink. Both excitation and detection wavelengths lie within the IR region. Some other applications have also been reported.[11–14]

The electronic absorption spectra of SiNc in various solvents are reported in this present work and the results are supported by calculations using known relationships in terms of the refractive indices and the dielectric constants of the solvents used.

EXPERIMENTAL

Figure 2 shows the experimental equipment employed in this study. A tungsten filament illuminates the sample, placed in optical glass cuvettes with path length of 1 mm, through appropriate optics and a chopper. The transmitted light is then passed through a monochromator and is detected by a single element Si detector. The output of the detector is fed to a lock-in amplifier. A concave holographic grating with 1200 grooves mm^{-1} was used in the monochromator which gives a spectral range of 300–850 nm. The grating is blazed at 450 nm in second order. The wavelength accuracy is 1 nm. The monochromator is operated by a stepper motor operating under computer control. The Si detector gives a fairly flat response in the spectral region of interest. Phase sensitive detection using a chopper and lock-in amplifier improves signal to noise ratio and provides the required amplification. SiNc was acquired from the Aldrich Chemical Company (Milwaukee, WI, USA).

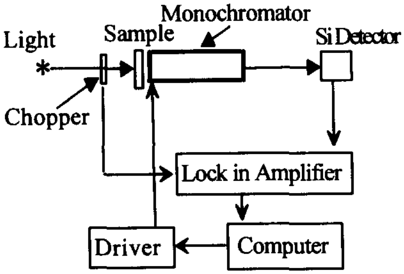

Fig. 2. Experimental equipment for optical spectroscopy.

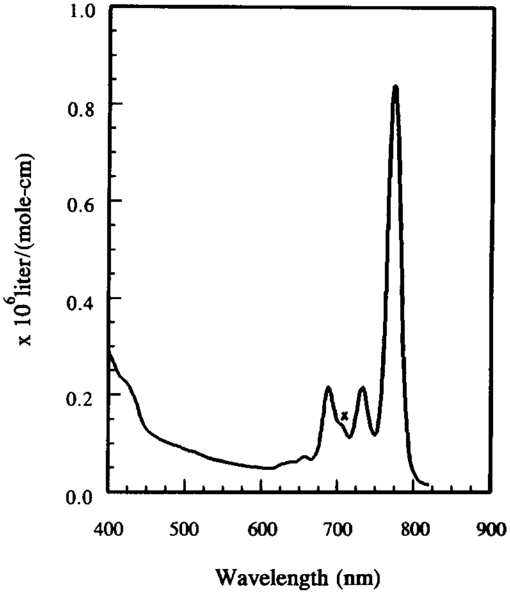

Fig. 3. Visible and near IR absorption spectrum of SiNc in hexane.

RESULTS AND DISCUSSION

Figure 3 shows a typical visible and near IR absorption spectrum of SiNc in hexane. The general features of the spectrum are essentially unchanged from solvent to solvent, except for a shift of the absorption band on the frequency axis. The shoulder marked as 'x' in the middle of two small peaks is, however, not as pronounced in the other solvents used. The positions of the intense and well-defined absorption peaks of the Q-band in various solvents are shown in Table 1. The relationship between the solvent nature and the shift in absorption band (solvatochromism) can be attributed to changes in the electronic distribution, i.e. dipole moment, from the ground state to the excited state of the absorbing molecule.[15] For a nonpolar solute, only dispersion forces (London forces) are operative and this results in a small red shift of the absorption band in a solvent of refractive index n, proportional to $(n^2 - 1)/(2n^2 + 1)$, in wavenumbers, as proposed by Bayliss and McRae.[16,17] In a polar solvent, however, in addition to dispersion forces, the solvent Stark effect contributes significantly to solvatochromism; the shift in wavenumbers is proportional to $(\varepsilon - 1)(2\varepsilon + 1)/\varepsilon$, where ε is the dielectric constant of the solvent.[18] These shifts are measured with respect to the vapor phase absorption, which is not available for SiNc. The position of the Q-band in the vapor phase, and the proportionality constant for nonpolar solvents,

TABLE 1

Experimental and Calculated Spectral Shifts of the *Q*-Band Absorption Peak

Solvent	*n*	*ε*	λ_{max} (+/−0·5 nm)	$\Delta\nu$ (exp)	$\Delta\nu_{calc.}$ (Dispersion)	$\Delta\nu_{calc.}$ (Stark)	$\Delta\nu$ total
Hexane	1·38	1·88	764	800	799	6·7	805·7
Tetrachloroethylene	1·51	2·3	772	935·1	978·9	6·3	985·2
Toluene	1·5	2·38	774	969	965	6·7	971·7
Trichloroethylene	1·48	3·42	772	935·1	940·7	11·1	951·8
Phenetole	1·51	4·22	774	968·6	978·9	14·4	993·3
Chlorobenzene	1·53	5·62	774	968·6	1 003·5	20·1	1 023·6
Cyclohexanol	1·47	9	774	968·6	927·5	33·8	961·3
Pyridine	1·51	12·4	778	1 035	978·9	47·5	1 026·4
Cyclohexanone	1·45	18·3	774	969	900·6	71·1	971·7
Methylethyl ketone	1·38	18·5	770	902	799·7	71·9	871·6
Acetone	1·36	20·7	770	902	768·7	80·7	849·4
Dimethylformamide	1·43	37	776	1 002	872·9	145·9	1 018·8
Ethanol	1·36	24·6	768	867·7	768·7	96·3	865

were then calculated from the experimental spectra in hexane and toluene. The proportionality constant for the Stark effect was derived from the spectrum in acetone. The following results were obtained and used to compute shifts in other solvents (Table 1).

The position of the longest wavelength absorption peak of the *Q*-band in the vapor phase was at 720 nm.

$$\text{For nonpolar solvents } \Delta\nu = 4252(n^2 - 1)/(2n^2 + 1) \tag{1}$$

$$\text{For polar solvents } \Delta\nu = 4252(n^2 - 1)/(2n^2 + 1) + 2(\varepsilon - 1)(2\varepsilon + 1)/\varepsilon \tag{2}$$

For solvents with a small dielectric constant (i.e. nonpolar), the contribution of the Stark effect is either small or negligible, but the effect is appreciable for polar solvents. The calculated shifts were plotted against the experimentally determined values, as shown in Fig. 4; the correlation between the experimental and calculated shifts is good, which not only confirms the validity of the theoretical considerations used, but also enables a prediction to be made of the shift in other solvents.

The proportionality constant estimated above can also be related to the oscillator strength, *f*, of the excitations involved, as described by Bayliss[19] for a nonpolar solvent:

$$\Delta\nu = 10{\cdot}71 \times 10^9\,(f/\nu a^3)(n^2 - 1)/(2n^2 + 1) \tag{3}$$

where a is the radius of the solvent cage around the solute molecule.

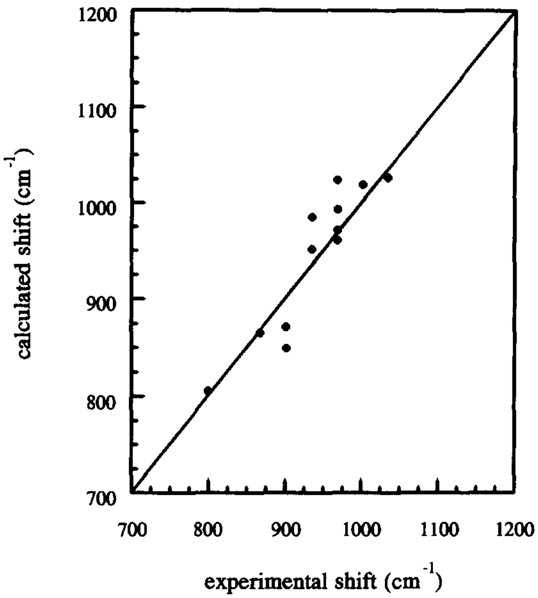

Fig. 4. Experimental versus calculated shifts in the position of the Q-band of SiNc.

Thus, with the proportionality constant equal to 4252·0, we obtain

$$f/a^3 = 5{\cdot}2 \times 10^{-3} \quad (4)$$

A value of $f = 3{\cdot}8$ is obtained if we use $a = 9$Å, the arm length of SiNc.

However, when the solvent molecule is much smaller than the solute molecule, so that it can adjust itself in the 'corners' of the latter, a changes to an 'effective' value which may be very different from the actual one. The effective value of a can be found from eqn (4), if f is computed by other means.

The reflection spectrum from a thin solid film prepared by offset printing on a glossy white paper was reported in our previous communication.[10]

CONCLUSION

Experimental results for the solvatochromic shifts for SiNc are presented in various solvents and the position of the longest wavelength absorption of the Q-band electronic transition is tabulated. The shifts in nonpolar solvents are due to dispersion forces and depend on the refractive index of the solvent. In polar solvents, in addition to the dispersion effect, the Stark effect affects the shift, which depends on the dielectric constant of the solvent. The shifts calculated from its known dependence on refractive indices and dielectric constants agree with the experimental results.

ACKNOWLEDGMENT

The authors acknowledge useful discussions with and a helpful review of this paper by Dr Mohammad Khadim of Hoechst Celanese Corporation, Mount Holly, North Carolina, USA.

REFERENCES

1. Fabian, J., Nakazumi, H. & Matsuoka, M., *Chem. Rev.*, **92** (1992) 1197.
2. Wu, J. W., Heflin, J. R., Norwood, R. A., Wong, K. Y., Zamani-Khamiri, O. & Garito, A. F., *J. Opt. Soc. Am. B*, **6** (1989) 707.
3. Ueno, M. & Yuasa, T., In *Infrared Absorbing dyes*, ed. M. Matsuoka. Plenum Press, New York, 1990.
4. Bradbrook, E. F. & Linstead, R. P., *J. Chem. Soc.*, (1936) 1744.
5. Kovshev, E. I., Puchnova, V. A. & Luk'yanets, E. A., *Zh. Org. Khim.*, **7** (1971) 369.
6. Gouterman, M., *The Porphyrins*. Academic Press, NY, 1978.
7. Tai, S., Hayashi, N., Kamijima, K., Katayoso, M., Akimoto, T. & Hagiwara, H., *European Patent 0 344 891* (1989).
8. Itoh, H., Oguchi, T., Enomoto, K., Nakatsuka, M. & Nishizawa, T., *European Patent 0 313 943* (1988).
9. Wheeler, B. L., Nagasubramanin, G., Bard, A. J., Schechtman, L. A., Dininny, D. R. & Kenney, M. E., *J. Am. Chem. Soc.*, **106** (1984) 7404.
10. Yousaf, M. and Lazzouni, M., *Dyes and Pigments*, **27** (1995) 297.
11. Firey, P. A. & Rodgers, M. A. J., *Photochem. Photobiol.*, **45** (1987) 535.
12. Nikles, D. E., Kuder, J. E. & Jasuta, J. A., *J. Imag. Sci. and Tech.*, **36** (1992) 131.
13. Hayashi, N., Hayashida, S. & Morishita, Y., *J. Imag. Sci. and Tech.*, **36** (1992) 574.
14. Ford, W. E., Rodgers, M. A. J., Schechtman, L. A., Sounik, J. R., Rihter, B. D. & Kenney, M. E., *Inorg. Chem.*, **31** (1992) 3371.
15. Reichardt, C., *Solvent Effects in Organic Chemistry*. Verlag Chemie, Weinheim, 1979.
16. Bayliss, N. S. & McRae, E. G., *J. Phys. Chem.*, **58** (1954) 1002.
17. McRae, E. G., *J. Phys. Chem.*, **61** (1957) 562.
18. Baur, M. E. & Nicol, M., *J. Chem. Phys.*, **44** (1966) 3337.
19. Bayliss, N. S., *J. Chem. Phys.*, **18** (1950) 292.