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The Unusual Spectrum of the Mixture of Tin-octabutoxy Naphthalocyanine and $SnCl_2$ in CH_2Cl_2

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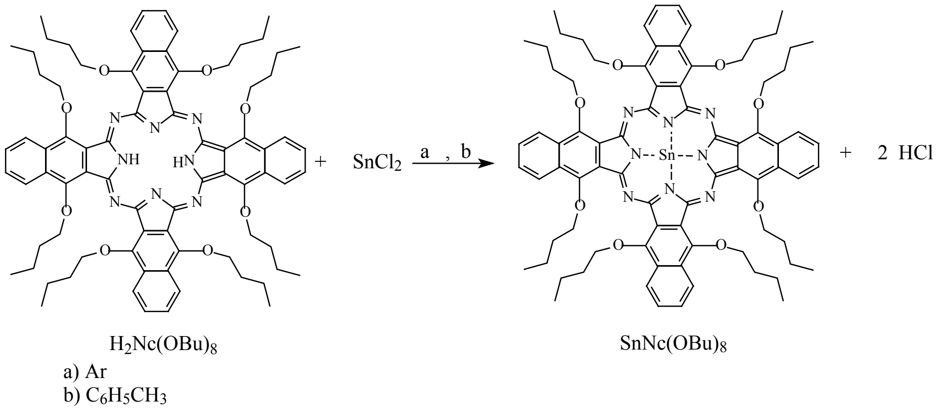
Abstract: The Q-band position of tin-centered 5, 9, 14, 18, 23, 27, 32, 36-octabutoxy 2, 3-phthalocyanine($SnNc(OBu)_8$) exhibits dramatic red-shift as mixed with $SnCl_2$ in CH_2Cl_2.

Keywords: Q-band, $SnNc(OBu)_8$, red-shift.

We have prepared tin-centered 5, 9, 14, 18, 23, 27, 32, 36-octabutoxy-2, 3-naphthalocyanine ($SnNc(OBu)_8$) and studied its photochemical properties with and without $SnCl_2$. The mixture of $SnNc(OBu)_8$ and $SnCl_2$ in CH_2Cl_2 has a Q-band absorption at a wavelength of 1044 nm in dichloromethane with an extinction coefficient of 1.1×10^5 $mol^{-1}\cdot L\cdot cm^{-1}$. This property of near infrared absorption opens the window of an array of potential use in many fields, especially as infrared light absorbers[1-2].

Typical procedure for preparation of $SnNc(OBu)_8$: $H_2Nc(OBu)_8$ was dissolved in toluene and mixed with $SnCl_2$ powder. The reaction mixture reactants was sealed in an

Figure 1 The synthesis of $SnNc(OBu)_8$



a) Ar
b) $C_6H_5CH_3$

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argon flushed round bottomed flask and heated to reflux for 30 min. The obtained SnNc(OBu)$_8$ was then purified by column chromatography(silica gel, 5:1 chloroform/ ethyl acetate). The resulting solution was filtered and evaporated to dryness with a rotary evaporator (60℃,~30Torr). The MS-FAB, elemental analysis, NMR, UV-Vis and IR spectra analysis results were as expected.

MS(FAB): *m/z* 1408 [M$^+$]; Elemental analysis; Calcd. for $SnC_{80}H_{88}N_8O_8$ (%): C 68.25, H 6.25, N 7.97. Found: C 68.23, H 6.25, N 7.94.

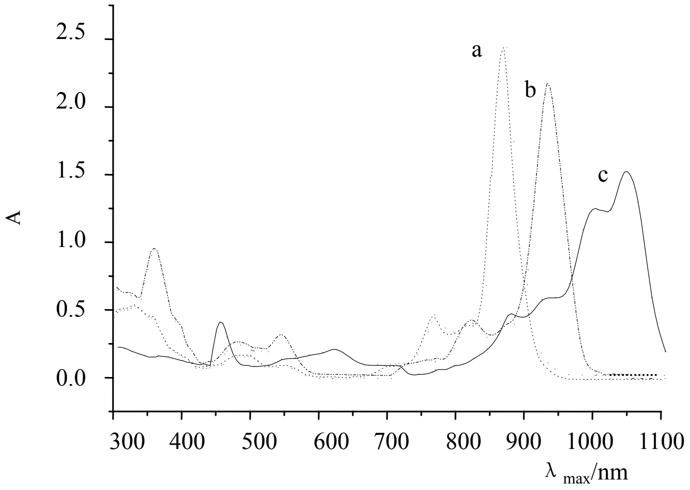
The electronic absorption spectra were recorded on a Perkin Elmer Lambda 40P spectrophotometer in dichloromethane. The observed data of $H_2Nc(OBu)_8$, SnNc(OBu)$_8$ and the mixture of SnNc(OBu)$_8$ and $SnCl_2$ were collected on **Table 1**.

As shown on **Figure 2**, compared to $H_2Nc(OBu)_8$[3], the Q-band of SnNc(OBu)$_8$ has a red shift of 68 nm, which can be attributed to the ligand-to-metal charge transfer between Sn^{2+} and Nc(OBu)$_8$[4]. If 60 times of molar ratio of $SnCl_2$ is added to the solution of SnNc(OBu)$_8$, the Q-band was red-shifted further upto 1044 nm.

Table 1 *Q*-Band maxima of $H_2Nc(OBu)_8$, SnNc(OBu)$_8$, the mixture of SnNc(OBu)$_8$ and $SnCl_2$ in dichloromethane （c=1.35×10^{-5}mol/L）

	λ_{max}(nm)
$H_2Nc(OBu)_8$	863.99
SnNc(OBu)$_8$	930.04
mixture of SnNc(OBu)$_8$ and $SnCl_2$	1044.05

Figure 2 The visible-near infrared spectra of $H_2Nc(OBu)_8$, SnNc(OBu)$_8$ and the mixture of SnNc(OBu)$_8$ and $SnCl_2$ in CH_2Cl_2



a. $H_2Nc(OBu)_8$
b. SnNc(OBu)$_8$
c. The mixture of SnNc(OBu)$_8$ and $SnCl_2$

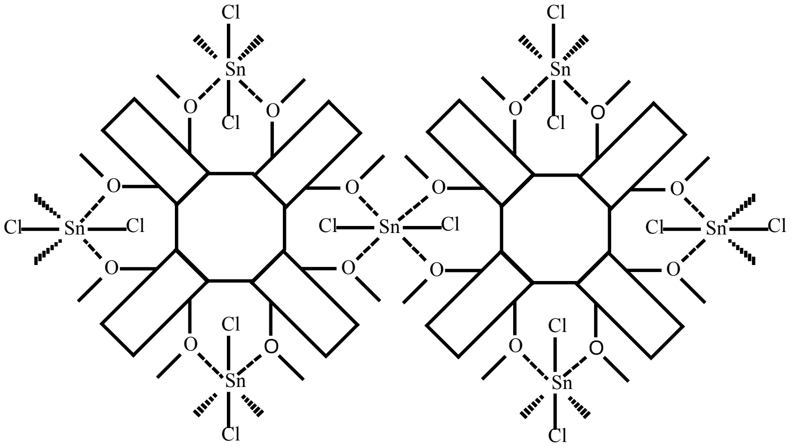
Table 2 The ^1H NMR data of $SnNc(OBu)_8$ and the mixture (CD_2Cl_2, δ ppm)

	proton	
	$SnNc(OBu)_8$	mixture of $SnNc(OBu)_8$ and $SnCl_2$
1,4,10,13,19,22,28,31-ArH	9.02	9.02
2,3,11,12,20,21,29,30-ArH	8.00	8.00
OR-1 CH_2	3.66	3.78
OR-2 CH_2	2.87	3.69
OR-3 CH_2	2.52	3.06
OR CH_3	1.29	1.29

The ^1H NMR of $SnNc(OBu)_8$ and the mixture of $SnNc(OBu)_8$ and $SnCl_2$ were separately recorded in CD_2Cl_2 on a Varian Mercury VX-300 FT NMR spectrometer, using TMS as reference.

As shown in **Table 2**, after $SnNc(OBu)_8$ was mixed with $SnCl_2$, the positions of the butoxy protons in $SnNc(OBu)_8$ were significantly shifted to low field, especially for the protons of OR-1 CH_2 ,OR-2 CH_2 ,OR-3 CH_2. The variation ranges from 0.09 to 0.82 ppm. This is possibly caused by the formation of a fast exchanging dimer with a possible structure as shown in **Figure 3**. As the formation of this coordination environment, the interaction of oxygen atoms from the butoxy groups of $Nc(OBu)_8$ weakens the Sn-Cl bond, causing higher ionic character. So the axial orbitals of Sn are almost empty and could overlap with the p orbitals of oxygen atom, which is conjugated with the Nc ring system. These interactions might lead to an even larger conjugate system formation. This super-delocalized structure[1] is probably the main reason of the dramatic red shift of Q-band of the mixture.

Figure 3 The proposed super-delocalized structure of the mixture of $SnNc(OBu)_8$ and $SnCl_2$



Because of the relatively weak interaction between oxygen atoms of the butoxy groups, the exo-coordination bond complex is relatively unstable. The addition of more solvent will reduce the tendency of these coordination, even destroy the exo-coordination complex. The observation also demonstrated this expectation. With the addition of more solvent, the saturated solution will blue-shift the Q-band to its original position.

In conclusion, examination of the electronic absorption of the mixture of $SnNc(OBu)_8$ and $SnCl_2$ made in the study shows that the Q-band of the mixture appears at an unusual wavelength. The fast exchanging of the exo-coordination environment makes the NMR indistinguishable for different types of butoxy groups. This mixture, with its unusual but effective absorption in near infrared region, can be expected to be used as an outstanding infrared light absorber.

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