Inorganic Chemistry
including bioinorganic chemistry
Inorg. Chem., 1996, 35(5), 1313-1320, DOI:10.1021/ic9509140

Table S1 ESR Parameters and Concentrations of PhCNSNS·[a] at Various Temperatures

temperature t (°C)	T (°K)	h_{pp}[b] (mm)	ΔH_{pp}[b] (G)	I[b]	[PhCNSNS·][c] (M)
+20	293	89	1.80	288	0.0380
+5	278	128	1.44	265	0.0350
-10	263	153	1.28	252	0.0335
-25	248	166	1.19	235	0.0310
-40	233	168	1.14	218	0.0290
-55	218	143	1.12	180	0.0237
-70	203	127	1.07	145	0.0191

(a) PhCNSNS· was generated by reduction of $PhCNSNSAsF_6$ (0.0139 g, 0.0376 mmol) with $SbPh_3$ (0.053 g, 0.15 mmol)/Me_4NCl (0.031 g, 0.28 mmol) in SO_2 (0.055 g)/$CFCl_3$ (1.417 g) mixture.

(b) The h_{pp} and ΔH_{pp} stand for the peak height (arbitrary unit) and peak-to-peak width (in Gauss) respectively for the most upfield peak of the ESR spectra of PhCNSNS· (1:1:1 triplet); the I stands for the intensity of this peak, formulated as

$$I = h_{pp} \times \Delta H_{pp}^2$$

which is directly proportional to the concentration of the PhCNSNS· monomer.

(c) The concentrations (C) of PhCNSNS· at various temperatures are determined using the formula

$$C = (C_0 I)/I_0$$

C_0 and I_0 stand for the concentration and intensity of ESR spectrum of PhCNSNS· at +20 °C respectively. The dimerization of

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(Table S1 continued)

PhCNSNS· at this temperature (ca. 3%) is reasonably negligible, therefore the initial concentration C_0 can be obtained based on the amount of original $PhCNSNSAsF_6$ added.

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Table S2 Equilibria Constants of the Dimerization[a] of PhCNSNS· at Various Temperatures

temperature T(K)	temperature 1/T(10^3K^{-1})	[PhCNSNS·] (M)	[(PhCNSNS·)$_2$][a] (M)	K[a]	lnK
293	3.41	0.0380	------	----	----
278	3.60	0.0350	0.0015	1.22	0.20
263	3.80	0.0335	0.0023	2.05	0.72
248	4.03	0.0310	0.0035	3.64	1.29
233	4.29	0.0290	0.0045	5.35	1.68
218	4.59	0.0237	0.0072	12.8	2.55
203	4.93	0.0191	0.0095	26.04	3.26

a) There is an equilibrium between PhCNSNS· monomer (R) and dimer (R_2) in solution as follows:

$$2\ R \rightleftharpoons R_2$$

The dimerization equilibrium constant (K) can be formulated as

$$K = [R_2]/[R]^2$$

where $[R_2] = 1/2\ ([R]_0 - [R])$, and $[R]_0$ represents the initial concentration of PhCNSNS· radical.

The concentrations of PhCNSNS· monomer [R] at various temperatures were determined by ESR spectroscopy.

The dimerization enthalpy (ΔH_d^0) and entropy (ΔS_d^0) were determined from the slope and intercept of lnK v.s. 1/T plot respectively according to the following equation:

$$\ln K = -\Delta H_d^0/RT + \Delta S_d^0/R$$

The linear relationship of lnK with 1/T (correlation coefficient 0.98) was established by computer regression analysis

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(Table S2 continued)

with

$$\text{slope} = -\Delta H_d^0/R = 2.28(2)\times 10^3$$

$$\text{intercept} = \Delta S_d^0/R = -8.00(9)$$

Therefore, ΔH_d^0 = -19.0(2) kJ/mol and ΔS_d^0 = -66.5(7) kJ/Kmol.

T = 298 K: $\Delta G_{298}^0 = \Delta H_d^0 - 298\Delta S_d^0$ = 817 J/mol

$\Delta G_{298}^0 = -298 \ln K_{298}$ K_{298} = 0.72

At 298 K, the percentage of dimerization of 0.02 M PhCNSNS· is ca. 3%.

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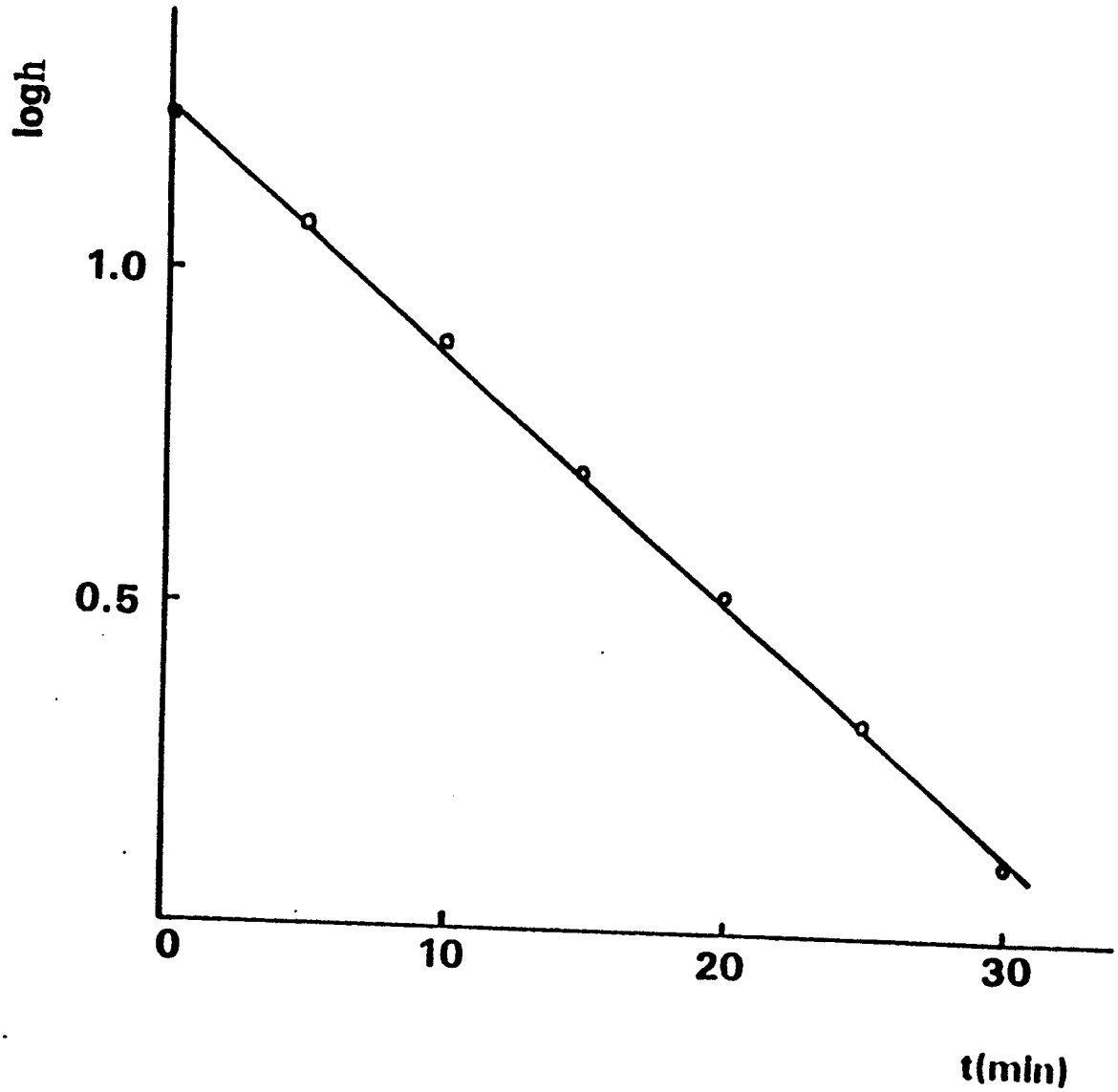

Fig.S1 The change in height (h) of the most upfield peak in ESR spectra of $Bu^tCNSNS^{\cdot}$ with the irradiation (at 254 nm) time.

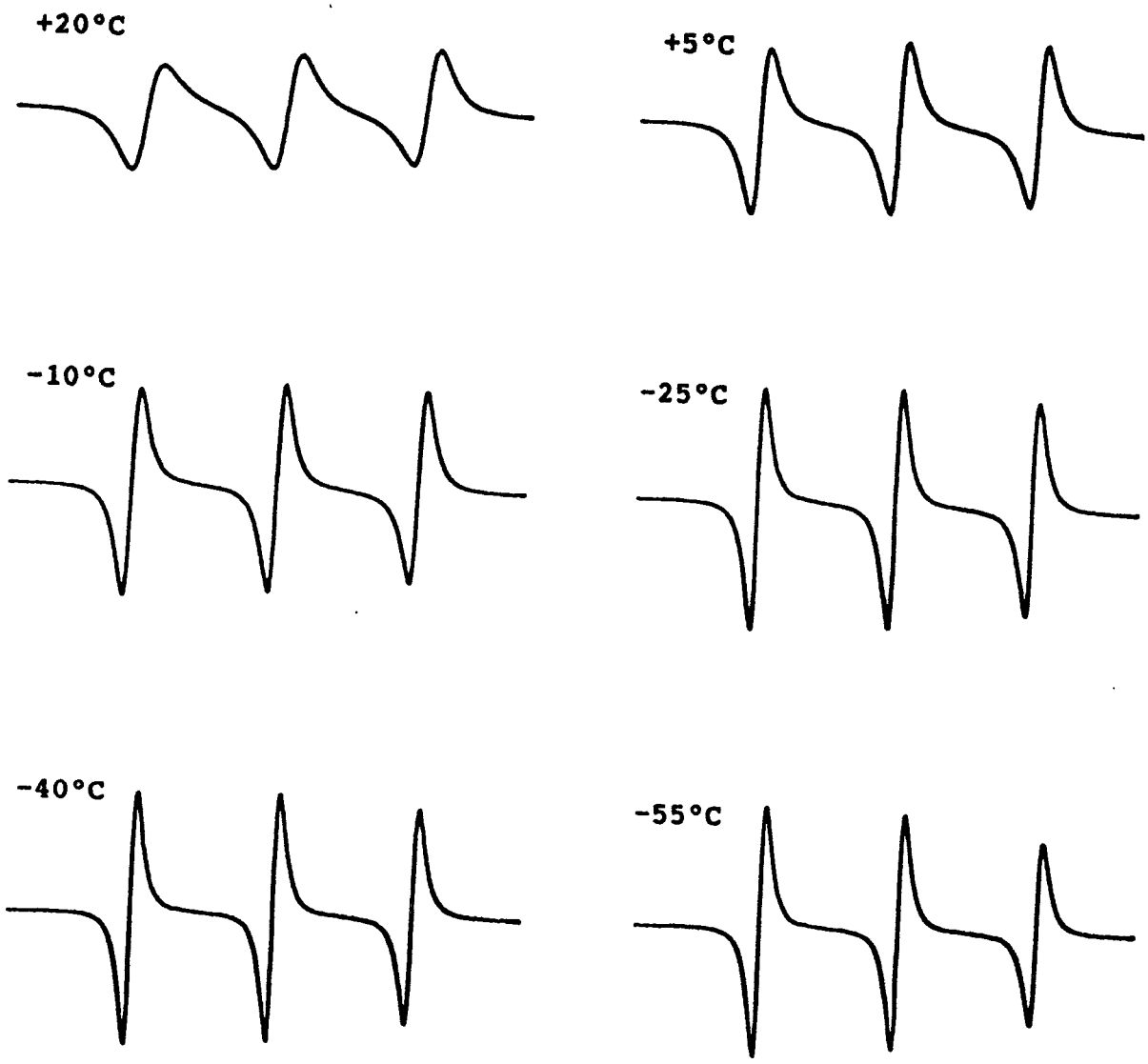

Fig. S2 The ESR spectra of $PhC\overline{NSNS}\cdot$ radical (0.038 M) at various temperatures.

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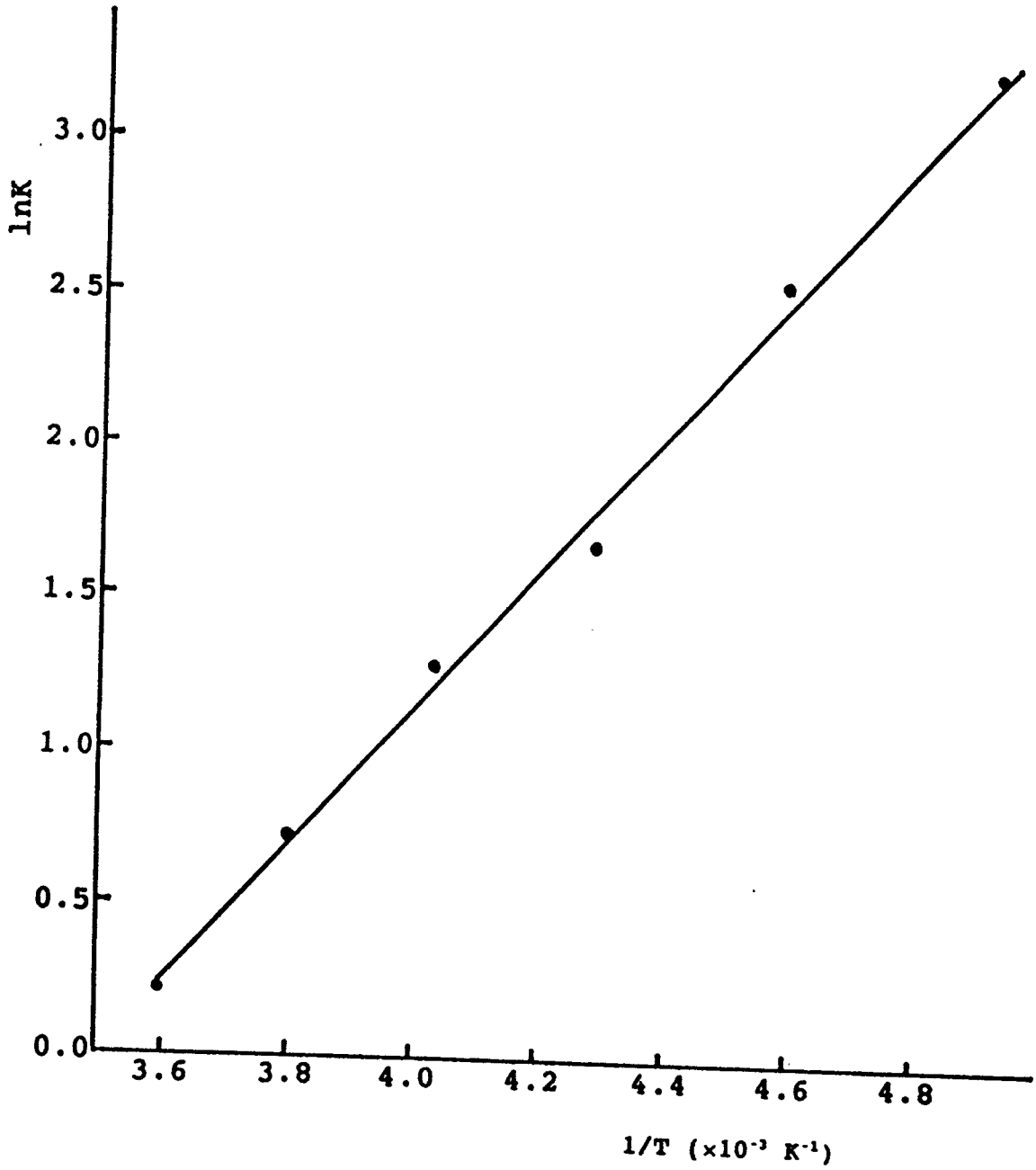

Fig. S3 The plot of logarithm of the equilibrium constant (K) of $PhC\overline{NSNS}\cdot$ dimerization against the reciprocal of the absolute temperature.

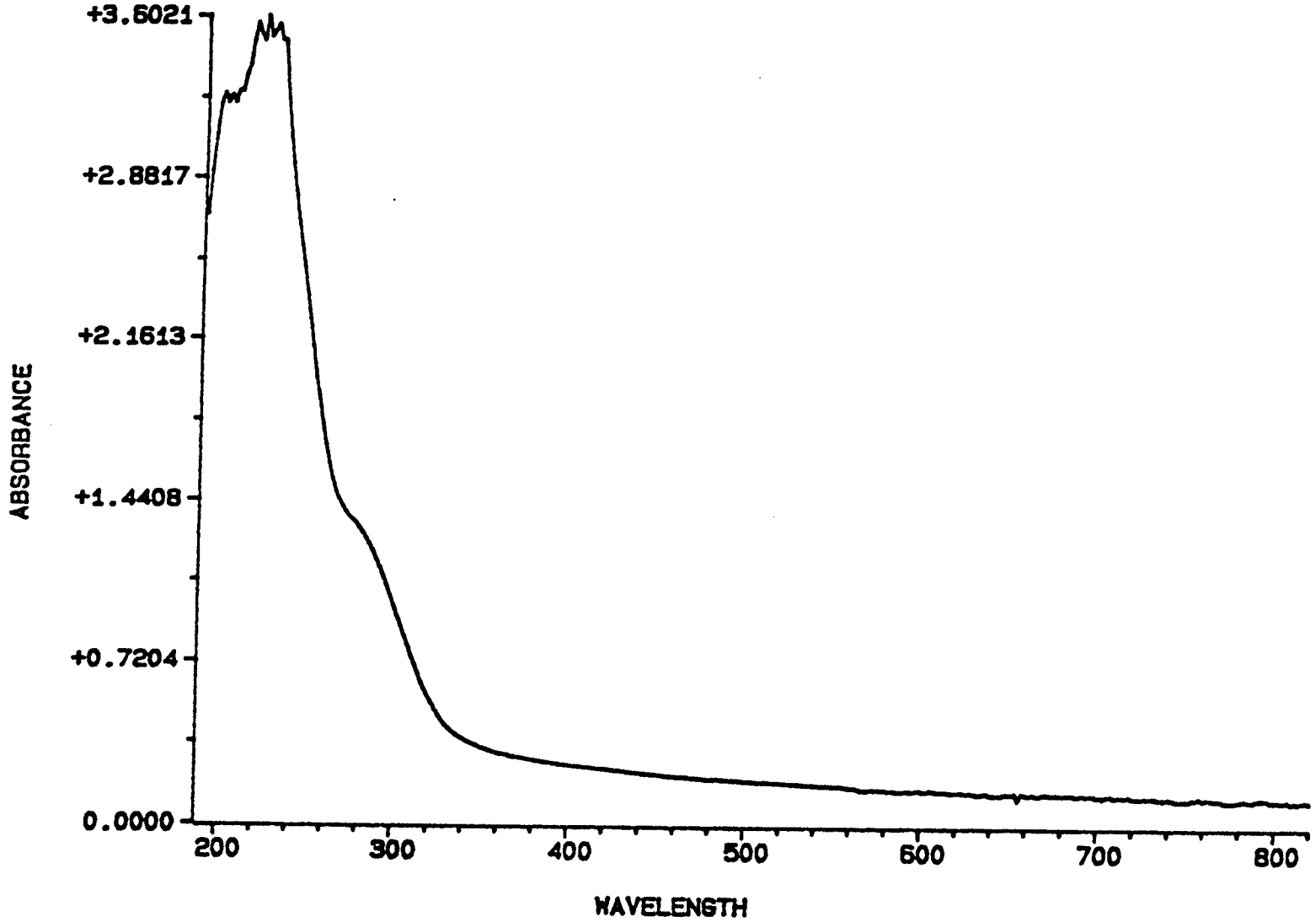

Fig.S4 The UV-Visible spectrum of pure $PhC\overline{NSSN}\cdot$ in $CFCl_3$ (ca. 0.04 M).

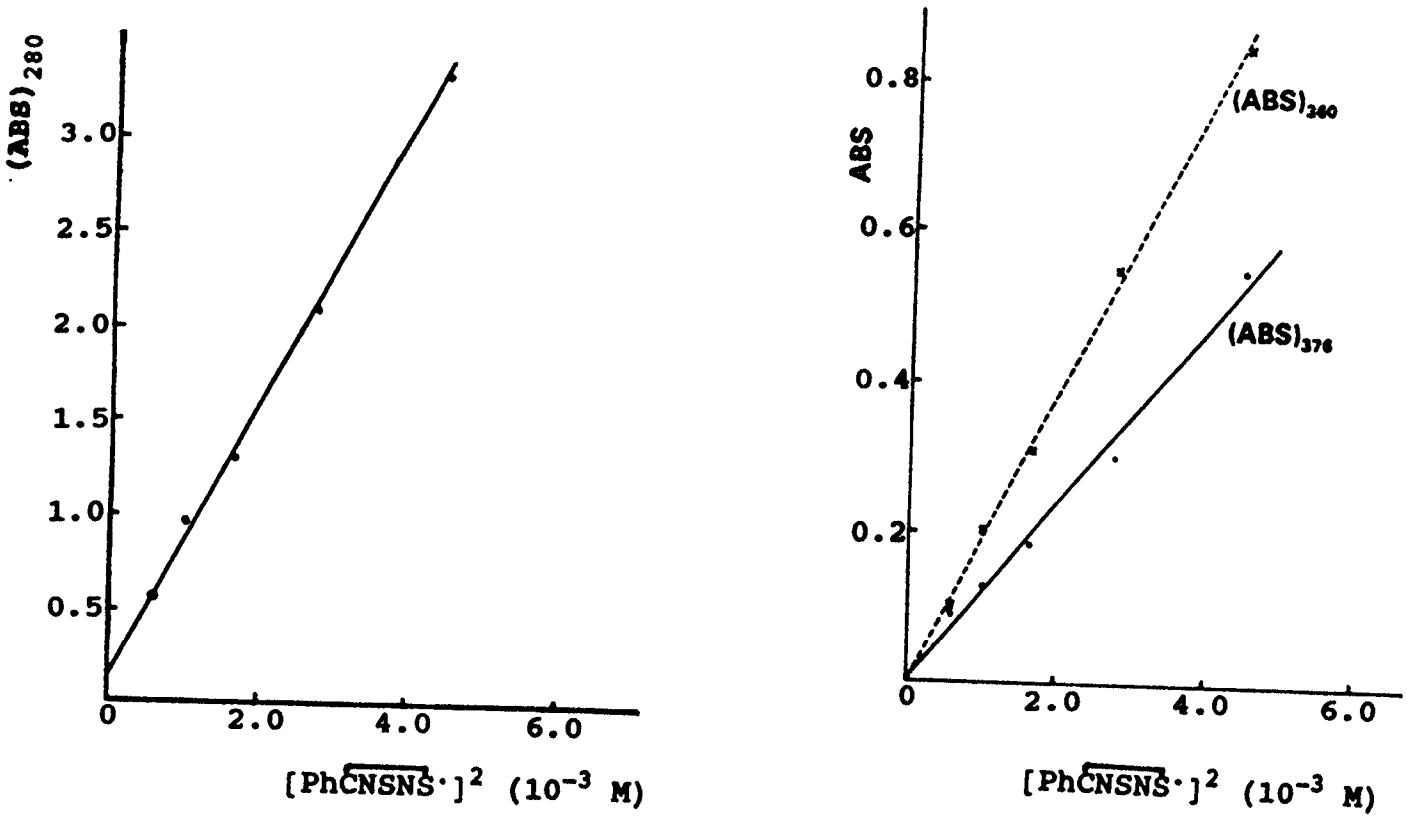

Fig. S5 The relationship between the absorbances of bands (at 280, 360 and 376 nm) in the simulated UV-Vis spectra of PhCNSNS· and the square of the initial concentration of PhCNSNS· (A) monomer $[A]^2$.