

Synthesis, spectra and conductivity of 1-D polymers of nickel(II)- and copper(II)-porphyrazine with sulfur bridges

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The title polymers PNiPzS₄ and PCuPzS₄ were synthesized by reaction of phthalonitrile and 2,3,5,6-tetracyano-1,4-dithiin with corresponding metal salt. Their structures and properties were characterized by associating the experimental results with MO and CI calculations of the dimer molecule as model polymer in the ZINDO method. It has been found that the PNiPzS₄ (or PCuPzS₄) shows the semiconductivity at $T < 253$ K (or 260 K) and $T > 278$ K (or 286 K) and the conductivity increase with a hoist of temperature at 253 K (or 260 K) $< T < 278$ K (or 286 K). The conductivity σ_{298K} of the PNiPzS₄ and PCuPzS₄ under pressure 13.73 MPa is 1.56×10^{-4} and 9.33×10^{-5} S/cm, respectively.

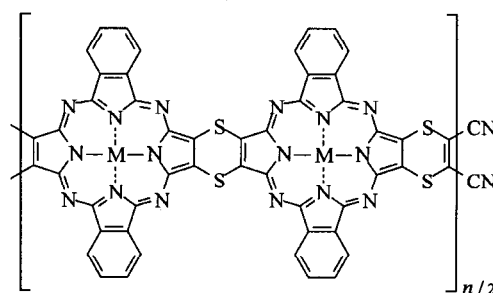
Keywords Metal-porphyrazine, 1-D conjugated polymer, synthesis, ZINDO method

Phthalocyanines (Pcs), porphyrazines (Pzs) and their polymers have been reported in many papers.¹⁻¹¹ These compounds exhibit high thermal stability and unique photoelectric property due to the planar macrocyclic structure and existence of delocalizable conjugated system of π -electrons in the porphyrazines.¹⁻⁴ It has been found that some electronic functions, such as gas-sensitivity, photosensitivity, photoconductivity and electrocatalytic activity, of the metal-thioporphyrazines and their conjugated polymers are more pronounced than those of the corresponding MPcs.⁷⁻¹¹

One of our interests is to design the planar conjugated polymers of metal-porphyrazines (PMPz) with switching points under the control of a changing external field or environment.⁸ In the present work we report the

one-dimensional conjugated polymers of the nickel(II)- and copper(II)-porphyrazine with sulfur bridges and benzo-side groups (PMPzS₄, M = Ni^{II}, Cu^{II}) (Scheme 1). The PMPzS₄ was synthesized by reaction of phthalonitrile (PTN) and 2,3,5,6-tetracyano-1,4-dithiin (TCDT) with corresponding metal chloride respectively. Some properties of the PMPzS₄ were studied by comparison to those of the 1-D polymer (PMS₄Pz) of metal-porphyrazine with carbon bridges and sulfur side groups,⁷ the 2-D polymer (PMS₈Pz) of metal-porphyrazine with sulfur bridges,⁹ and the 1-D polymer (PMPc) of metal-phthalocyanine with carbon bridges.⁵

Scheme 1 Structure of polymer PMPzS₄ (M = Ni^{II}, Cu^{II})



Experimental

Material and reagent

Phthalonitrile (PTN, A. R.) was purchased from

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Fluka in Switzerland. Urea (A. R.) was purchased from Chongqing chemical reagent factory. $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CuCl}_2 \cdot 6\text{H}_2\text{O}$ (A. R.) and ammonium molybdate (A. R.) were bought from Shanghai purchase stage of chemical reagents. All solvents (A. R.) were commercial products.

2,3,5,6-Tetracyano-1,4-dithiin (TCDT) was prepared according to the literature method,¹² melting point 207–208 °C. λ_{max} (in methylene chloride, nm): 243, 277, 315, 331. ν_{max} (in KBr, cm^{-1}): 2230 (C \equiv N), 1520 (C=C), 983, 881 (C-C, C-S). Anal. $\text{C}_8\text{N}_4\text{S}_2$. Calcd: C, 44.43; N, 25.91. Found: C, 44.10; N, 26.18.

Synthesis of the polymer PMPzS₄

Polymeric nickel(II)-tetrathioporphyrazine PNiPzS₄ To a mixture of milled phthalonitrile (2.60 g, 0.02 mol), TCDT (2.16 g, 0.01 mol), $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (2.45 g, 0.01 mol), urea (0.2 g) and ammonium molybdate (0.2 g) was added quinoline (100 mL). Under nitrogen atmosphere the mixture was stirred for 10 min, and then was refluxed for 4.5 h. The cooled suspension was filtered and washed with hydrochloric acid (6 M), water and acetone respectively until the filtrate was colorless. After the solid was extracted by pyridine, deposition of the extractive solution in water was filtered. The black solid was washed with water and acetone until the filtrate was colorless. The extraction-filtration-wash procedure was repeated three times. The product PNiPzS₄ was dried at 110 °C and 130 Pa over P_2O_5 for 24 h to 2.1 g of black crystallites (yield 39.5%, calculated based on TCDT). UV-Vis absorption λ_{max} (nm, log ϵ in $\text{Ni}(\text{C}_{24}\text{H}_8\text{N}_8\text{S}_2)$), in H_2SO_4 : 772 (4.13), 690 (3.86), 424sh, 302(4.42), 240(4.42), 198 (4.18); in DMSO: 667 (3.71), 439 (3.75), 264 (4.23). Fluorescence spectra λ_{max} (nm, in DMSO): Ex 365, Em 460. IR absorption ν_{max} (cm^{-1} , in KBr): 2218w(C \equiv N); 1609ms, 1561ms, 1532s, 1470ms, 1430s(C=C, C=N); 949m, 916m, 873m(C—C, C—S); 1485ms, 1469ms, 1410ms, 1377m, 1333s, 1164ms, 1123ms, 1070ms, 1033ms(macrocycl. skel). DTA (T , K): Endotherm, 383w, 751m; Exotherm, 836w, 1007s. Anal. $[\text{Ni}(\text{C}_{24}\text{H}_8\text{N}_8\text{S}_2) \cdot 2\text{H}_2\text{O}]_n$. Calcd: C, 50.82; H, 2.13; N, 19.75; Ni 10.35. Found: C, 51.25; H, 2.58; N, 17.89; Ni, 9.92.

Polymeric copper(II)-tetrathioporphyrazine PCuPzS₄⁸ was synthesized from $\text{CuCl}_2 \cdot 6\text{H}_2\text{O}$ by the method mentioned above. The yield was 38.7%. UV-Vis absorption ν_{max} (nm, log ϵ in $\text{Cu}(\text{C}_{24}\text{H}_8\text{N}_8\text{S}_2)$), in H_2SO_4 : 787(3.44), 700sh, 395(4.20), 310(4.34), 238 (4.51), 197(4.59); in DMSO: 674(3.40), 652sh, 455(3.91), 267 (4.20). Fluorescence spectra ν_{max} (nm, in DMSO,): Ex 336, Em 480. IR absorption ν_{max} (cm^{-1} , in KBr): 2210w(C(N); 1611ms, 1547ms, 1523s, 1467ms, 1443s(C=C, C=N); 946m, 919m, 878m (C—C, C—S); 1486ms, 1426s, 1379m, 1323s, 1165ms, 1121ms, 1076ms, 1036ms(macrocycl. skel). EPR (powder, RT): $g_{\parallel}^1 = 2.176$, $g_{\parallel}^2 = 1.881$, $g_{\perp}^1 = 2.066$, $g_{\perp}^2 = 1.992$; $J = -0.106 \text{ cm}^{-1}$, $|D| = 0.048 \text{ cm}^{-1}$. DTA (T , K): Endotherm, 385w, 768m; Exotherm, 837w, 970s. Anal. $[\text{Cu}(\text{C}_{24}\text{H}_8\text{N}_8\text{S}_2) \cdot 2\text{H}_2\text{O}]_n$. Calcd: C, 50.39; H, 2.11; N, 19.59; Cu, 11.11. Found: C, 49.96; H, 2.54; N, 17.94; Cu, 10.86.

Measurements

Analyses of C, H, N were performed on a Perkin-Elmer 240B elemental autoanalyzer. Metal content was determined by titration with EDTA. Surface feature was observed on a JEOL100CX II transmission electron microscope. Thermal analysis was conducted on a Rigaku TAS100 thermal analyzer. Infrared spectra were recorded on an N-240 spectrophotometer. Fluorescence spectra were recorded on a Shimadzu FR-5000 spectrofluorophotometer. EPR spectra were measured using a Bruker ER-200-D-SPC 10/12 EPR spectrometer at X-band frequencies. Conductivity measurement was performed using two-probe geometry in pressed powder pellets.

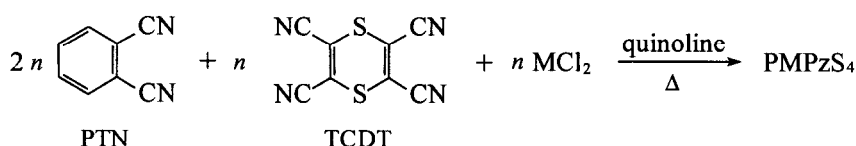
Molecular orbital theoretical calculations

All calculations were performed using the HyperChem 5.11 program system¹³ on an Acer 518 TX (Intel Pentium II 400 MHz, 64 MB, 6.4 GB) computer. A dimer ($n = 2$ in Scheme 1), nickel-contained dimer (1) or copper-contained dimer (2), was selected as a model polymer for molecular orbital (MO) calculations of PMPzS₄. The molecular structure of the dimer was obtained by geometry optimization using the ZINDO/1 method in both the C—S single bonds and conjugated dithiin

rings. The structure was then used to obtain calculated the electronic structures and UV-Vis spectra using the ZINDO/S method. The configuration interaction (CI) calculations of the multiconfigurations were performed using RHF method in a given spin multiplicity and a given number-pair (n_{00} , n_{U0}) of the lowest occupied and highest unoccupied MOs.

Results and discussion

Scheme 2 Reaction process of synthesis



Both the polymer PNiPzS_4 and PCuPzS_4 are soluble in concentrated H_2SO_4 , pyridine and DMSO, slightly soluble in quinoline, and insoluble in water and organic solvents. DTA curves of the polymers under a nitrogen atmosphere exhibit a weak endothermal peak in the region $343 \text{ K} < T < 615 \text{ K}$, which corresponds to the weight loss of the water and a weak sublimation effect of the sample in TG. The two exothermal peaks in the region $830 \text{ K} < T < 1010 \text{ K}$ correspond to the thermolysis of the sample. The IR spectra show a set of characteristic absorption bands of the macrocyclic skeleton vibrations at $1485\text{--}1033 \text{ cm}^{-1}$ and a weak $\nu(\text{C}\equiv\text{N})$ band at $\sim 2215 \text{ cm}^{-1}$. As compared with the starting material TCDT, the wavenumber of the $\nu(\text{C}\equiv\text{N})$ is decreased and a new band at $\sim 918 \text{ cm}^{-1}$ belongs to $\nu(\text{C}\text{--}\text{C})$ and $\nu(\text{C}\text{--}\text{S})$ in the PMPzS_4 . The EPR spectra of the PCuPzS_4 powder at room-temperature showed a signal with obvious axis-symmetry and zero-field splitting due to the spin-spin coupling and the magnetic exchange interaction.^{7,8} It turns out that the PNiPzS_4 and PCuPzS_4 molecules contain the end groups as shown in Scheme 1.

Electronic spectra

The electronic spectra of the PNiPzS_4 are very simi-

Synthesis and elementary properties

By comparison with the synthesis of polymers MPcs ^{4,5} the template reaction of synthesizing PMPzS_4 shown in Scheme 2 proceeded easily under moderate conditions. The main product was regarded as the polymer PMPzS_4 . The yield was moderate due to the slight solubility of the product in quinoline. Possible impurities such as the monomeric MPcs , MS8Pzs , two-dimensional and irregular polymers were removed by extraction with various solvents.

lar to those of the PCuPzS_4 . The absorption spectra of PMPzS_4 in H_2SO_4 , as well as DMSO, show a set of strong *B*-bands in the ultraviolet region and a set of stronger *Q*-bands in the visible region, which is similar to those of the 1-D polymeric copper(II)-tetrathiopyrphrazine PCuS_4Pz .⁷ These spectra exhibit the characteristic absorption of 1-D polymers of MPcs .⁵ But by comparison with the latter the *Q*-bands move slightly (see Table 1) due to the effect of the sulfur atoms on the $\pi\text{--}\pi^*$ transitions of the conjugated Pz macrocycles. From Table 1 we can see that the wavelengths of the *Q*-bands decrease with the increase of an average number of sulfur atoms on Pz from the 1-D polymeric metal-phthalocyanine (PMPc) to the 2-D polymeric metal-octathiopyrphrazine (PMS_8Pz).^{9,10}

The PMPzS_4 in DMSO and H_2SO_4 exhibit a strong fluorescent band under excitation of ultraviolet light. As an example, Fig. 1 shows the emission spectra under $\lambda = 365 \text{ nm}$ excitation and the excitation spectra for $\lambda = 476 \text{ nm}$ (PNiPzS_4) and 480 nm (PCuPzS_4) emission in fluorescence spectra in the PMPzS_4 of DMSO at room-temperature. The half-width of the fluorescent emission band is 123 nm. This shows that the PMPzS_4 has a comparatively strong ability to transform the ultraviolet light into visible light.

Table 1 Q-bands λ_{\max} in H_2SO_4 and conductivity σ_{RT} in solid of some conjugated polymers of porphyrazine

Polymer	Average number of sulfur atoms on Pz	Q-band λ_{\max} (nm)	σ_{RT} (S/cm)	Note
PNiPc	0	776, 738	2.59×10^{-6}	Ref. 5
PNiPzS ₄	2	772, 690	1.56×10^{-4}	Present work
PNiS ₄ Pz	4	746, 583	1.86×10^{-5}	<i>cf.</i> Ref. 7 ^a
PNiS ₈ Pz	8	~ 680	2.76×10^{-3}	Ref. 9
PCuPc	0	771 (?) ^b	1.52×10^{-4} (?) ^b	Ref. 5
PCuPzS ₄	2	787, 700	9.33×10^{-5}	Present work
PCuS ₄ Pz	4	767, 656	1.31×10^{-6}	Ref. 7
PCuS ₈ Pz	8	563	5.83×10^{-6}	Ref. 9, 10

^a The work will be reported, in which the structure of the polymer is similar to that of the PCuS₄Pz in Ref. 7.

^b The Q-bands λ_{\max} of PCuPc must be greater than those of PNiPc, and σ_{RT} of PCuPc must be less than those of PNiPc.

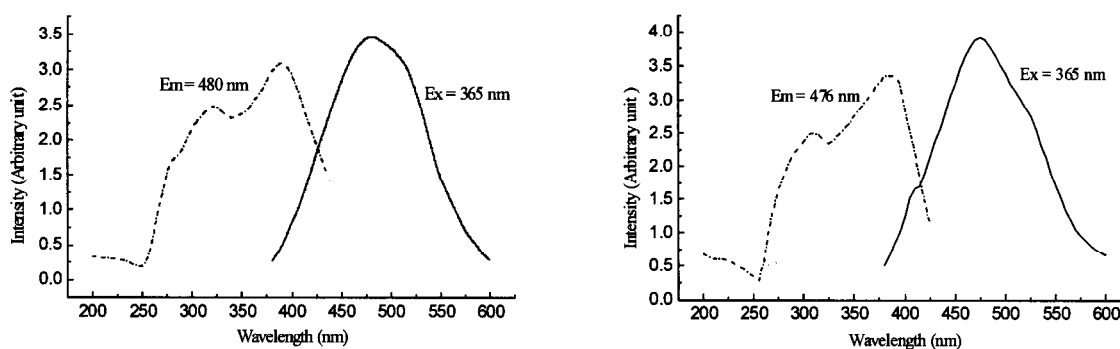


Fig. 1 Fluorescent spectra of PNiPzS₄ (left) and PCuPzS₄ (right) in DMSO at room-temperature. - - - - Excitation spectrum for $\lambda = 476$ nm emission, — Emission spectrum under $\lambda = 365$ nm excitation.

Electric conductivity

From Table 1 we can see that the room-temperature conductivity σ_{RT} of the polymers of porphyrazine goes up with the increase of an average number of sulfur atoms on Pz from the 1-D PMPc to the 2-D PMS₈Pz. But the σ_{RT} of the PMPzS₄ with sulfur bridges is greater than that of the 1-D polymer PMS₄Pz with carbon bridges and sulfur side groups.⁷ The σ_{RT} of the PMPzS₄ increases steadily with the increase of pressure (Fig. 2). Fig. 2 shows the temperature dependence of the conductivity of the PMPzS₄ under constant pressure. In both the region $T < 253$ K (PNiPzS₄) or $T < 260$ K (PCuPzS₄) and the region $T > 278$ K (PNiPzS₄) or $T > 286$ K (PCuPzS₄) the formula of the intrinsic semiconductivity is satisfied:

$$\sigma = \sigma_0 \exp(-\Delta E/kT)$$

But in the region of $253 \text{ K} < T < 278 \text{ K}$ (PNiPzS₄) or $260 \text{ K} < T < 286 \text{ K}$ (PCuPzS₄) it exhibits obviously the

partial character of the metallic conductivity, *i. e.*, the conductivity increases with a hoist of temperature. The existence of the two newly found turn points proves that the polymer PMPzS₄ is an intrinsic 1-D semiconductor. This polymer PMPzS₄ with the switching points is certainly useful in some high technical fields.

Theoretical analysis

Symmetry of the dimeric molecules **1** and **2** belongs to the point group C_{2v} . The ZINDO calculations showed that the conjugated structure of the dithiin rings stabilized the model dimers **1** and **2** for ~ 200 kJ/mol than the C—S single bonds. This was proved by the band at $\sim 918 \text{ cm}^{-1}$ in IR spectra of the PMPzS₄. The ground state of the model molecules approaches to a lower spin (see Table 2). As shown in Fig. 3, the metal 3d orbitals have contributions to higher occupied and lower unoccupied MOs. For example, $43b_1$ (HOMO) of **1** contains the atomic orbital as $-0.0067 d_{yz} - 0.0023 d_{xy}$ of

Ni, and $42a_2$ of **1** contains $-0.0032 d_{yz} - 0.0079 d_{xy}$ of Ni.

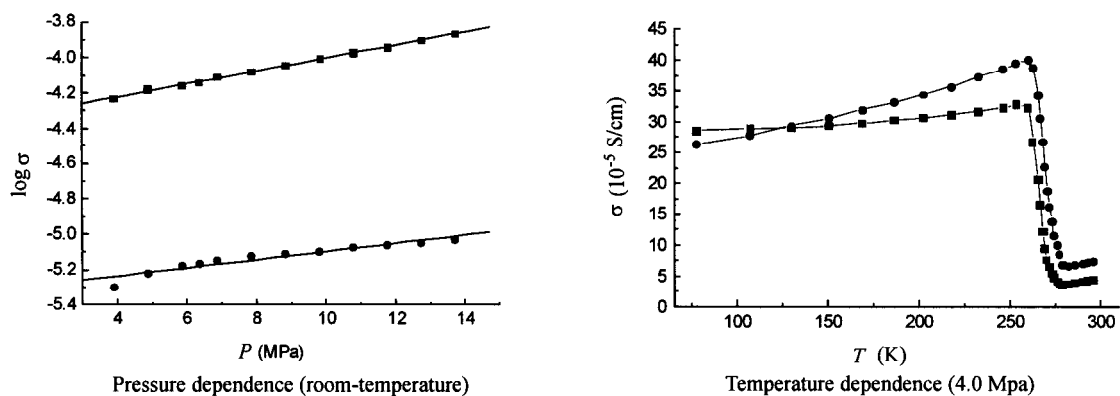


Fig. 2 Conductivity plots of polymer PMPzS₄: ■ PNiPzS₄; ● PCuPzS₄.

Calculated electronic spectra for the number-pair, $n_{00} = 5$ and $n_{U0} = 5$, are basically in agreement with the experimental absorption in solution. By an increase of the number n_{00} and n_{U0} theoretical spectra have only a less effect on the *Q*- and *B*-band transitions. Main results calculated for the given number-pair ($n_{00} = 8$ and

$n_{U0} = 12$) of the gaseous dimer and the assigning transition to observed absorption bands of PMPzS₄ solutions are listed in Table 3. It follows that the conjugated structure of the dithiin rings in the PMPzS₄ is useful to heighten the stability and conductivity. Spin of the ground state of the PMPzS₄ is relatively low.

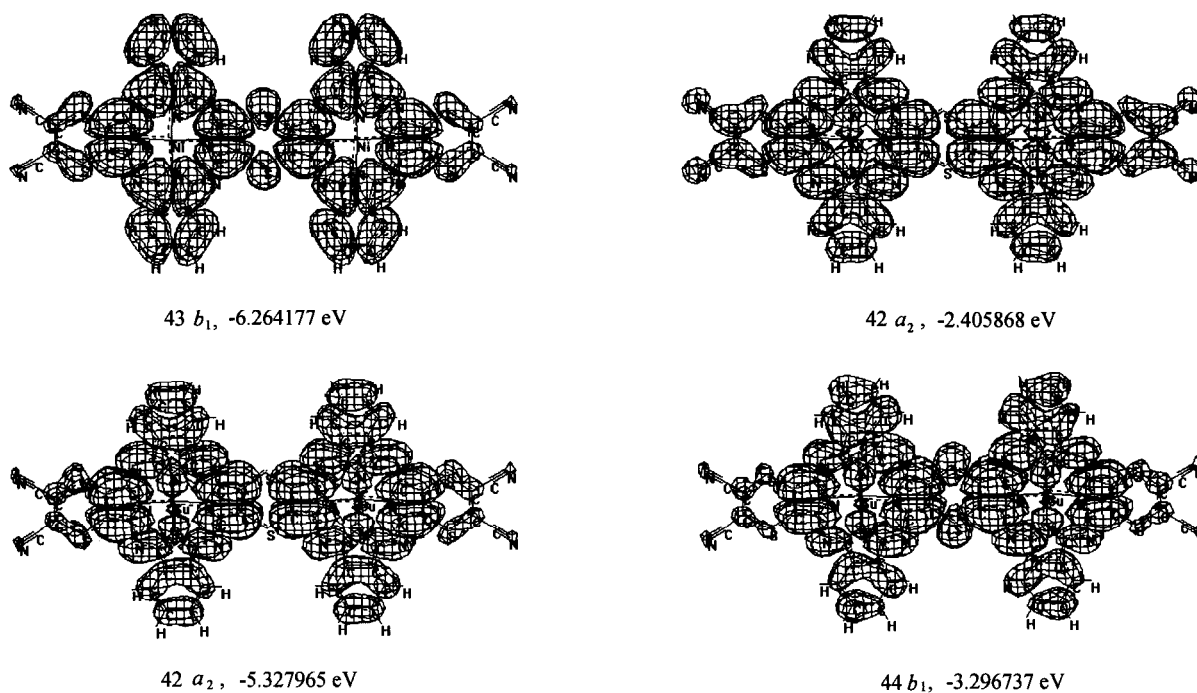


Fig. 3 3-D isosurface graph and energy of HOMO (left) and LUMO (right) of the model dimers with the symmetry C_{2v} .

Conclusions

The 1-D conjugated polymers PMPzS₄ (M = Ni^{II}, Cu^{II}) of the metal-porphyrine with sulfur bridges and benzo-side groups have been synthesized under gentle condition. The structure and properties of PMPzS₄ have

been discussed by associating the experimental results with MO and CI calculations of the dimer molecule as model polymer by the ZINDO method. It has been found that the temperature dependence of the conductivity of the PMPzS₄ shows the two switching points. The conjugated structure of sulfur bridges in PMPzS₄ is much advantageous to heighten the stability and conductivity.

Table 2 Calculated total energy E_{total} , binding energy E_{bind} , heat of formation E_{form} and Ni net charge $Q(\text{Ni})$ of the model dimeric molecule with conjugated dithiin rings in a given spin

Dimer	Spin (S)	$-E_{\text{total}}$ (kJ/mol)	$-E_{\text{bind}}$ (kJ/mol)	$-E_{\text{form}}$ (kJ/mol)	$Q(\text{Ni})$
1	0	1676268.383	339493.980	283962.897	-0.0251
1	1	1676167.218	339392.816	283861.733	-0.0305
2	0	1725487.643	354722.930	299376.846	0.3160
2	1	1725481.495	354716.782	299370.698	0.3158

Table 3 Number (N_0), spin (S), transition wavelength (λ_{max}) and oscillator strength of characteristic excitation states calculated for number pair ($n_{00} = 8$ and $n_{10} = 12$) of the gaseous dimer with ground state spin 1, and the assignment transition to observed absorption bands of PMPzS₄ solution of H₂SO₄ and DMSO

Model polymer 1				Model polymer 2				Observed absorption band	
No.	State S	λ_{max} (nm)	Oscillator strength	No.	State S	λ_{max} (nm)	Oscillator strength	PNiPzS ₄	PCuPzS ₄
7	1.32	839.2	0.0276	11	1.02	854.6	0.0736	772(4.13) ^a	787(3.44) ^a
8	1.30	820.4	0.0044	12	1.07	839.9	0.0615	690(3.86) ^a	700sh ^a
10	1.01	714.6	0.0032	18	1.12	741.3	0.0353		
11	1.02	654.2	0.2162	20	1.31	681.6	0.1327	667(3.71) ^b	674(3.40) ^b
13	1.01	580.0	0.0653	24	1.08	634.1	0.0156		652sh ^b
19	1.19	502.9	0.2685	25	1.14	629.1	0.0666		
21	1.17	495.9	0.1485	37	1.35	521.0	0.0512		
22	1.06	495.2	1.3246	40	1.05	484.8	0.1813	439(3.75) ^b	455(3.91) ^b
27	1.01	441.9	0.2178	45	1.05	448.5	0.0184	424 sh ^a	
28	1.36	439.1	0.0573	46	1.05	443.3	0.0101		395(4.18) ^a
48	1.19	350.3	0.1207	72	1.12	349.6	0.0153		
62	1.02	309.1	1.1750	77	1.28	325.1	0.0029	302(4.42) ^a	310(4.34) ^a
70	1.12	285.5	0.5439	103	1.13	287.9	0.0058	264(4.23) ^b	267(4.25) ^b
78	1.39	253.5	0.0508	111	1.14	275.0	0.0041		
96	1.10	228.8	0.2269	115	1.04	267.1	0.0093	240(4.58) ^a	238(4.51) ^a
98	1.05	228.3	0.3458	118	1.02	260.0	0.0167		
104	1.09	223.9	0.0174	139	1.49	231.3	0.0042		
134	1.01	204.8	0.0241	158	1.24	218.6	0.0024	198(4.81) ^a	197(4.59) ^a

^a In concentrated H₂SO₄. ^b In DMSO.

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