

Synthesis, characterization and electrochemistry of the novel metalloporphyrazines annulated with tetrathiafulvalene having pentoxycarbonyl substituents

Fengshou Leng^a, Ruibin Hou^a, Longyi Jin^a, Bingzhu Yin^{*a} and Ren-gen Xiong^{*b}

^a *Key laboratory of Organism Functional Factors of Chanbai Mountain, Yanbian University, Ministry of Education, Yanji 133002, P. R. China*

^b *Ordered Matter Science Research Center, College of Chemistry and Chemical Engineering, Southeast University, Nanjing 210096, P. R. China*

1. Crystal structure of compound **3a**
2. ¹H NMR spectrum of compound **5**
3. MALDI-TOF MS spectrum of compound **5**
4. ESR study of **4**

1. Crystal structure

(1) Crystal structure of **3a**.

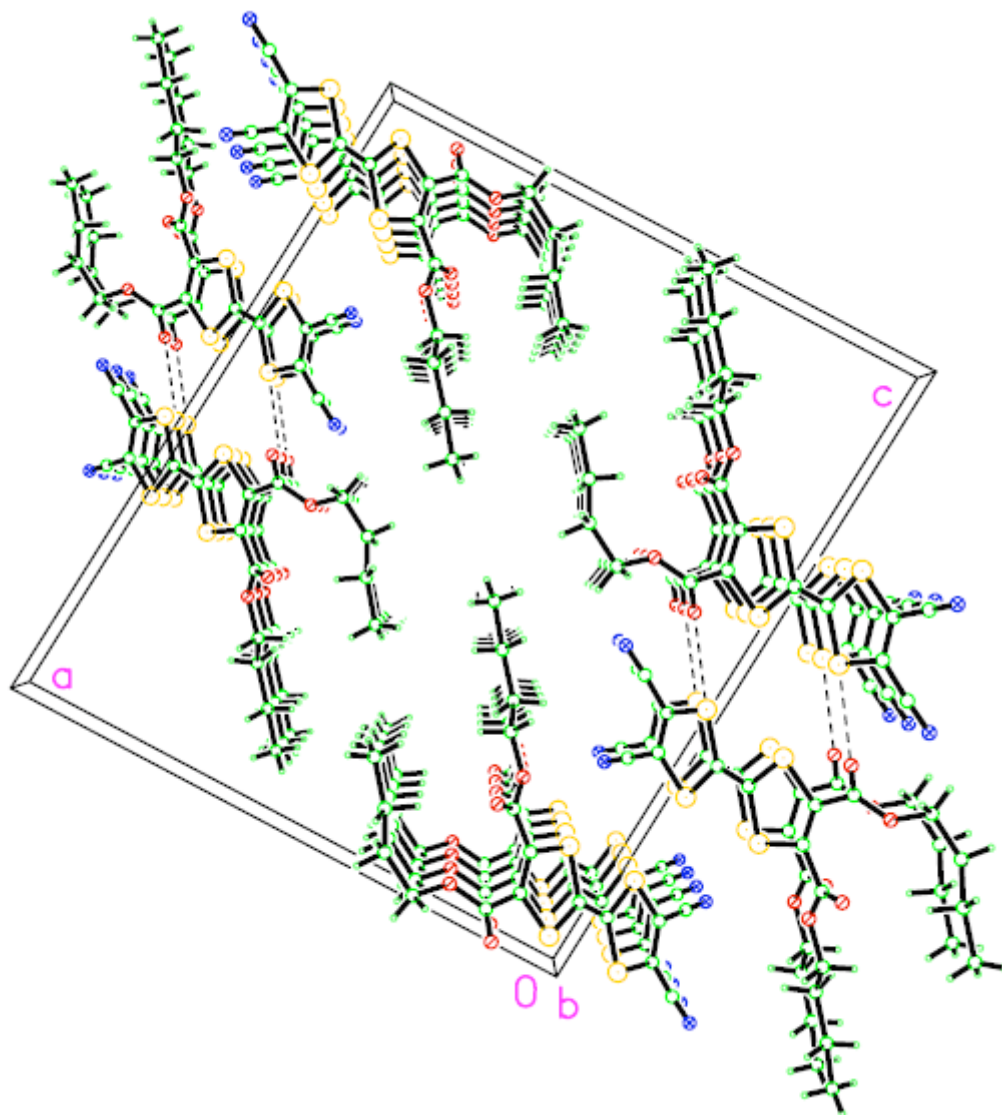


Fig. S1. Packing diagram of **3a**. In the crystal structure, intermolecular S...O interactions [$S3 \cdots O2 = 3.013 \text{ \AA}$] create dimers between neighboring molecules in the ac plane. In addition, weak $\pi \cdots \pi$ stacking interaction exists between adjacent dithiole rings with the centroid-centroid distances of 4.075 \AA forming the chains along the b axis

(2) *Crystal data and structure refinement for 3a.*

Table S1. Crystal data and structure refinement for **3a**

Identification code	123
Empirical formula	C ₁₈ H ₁₈ N ₂ O ₄ S ₄
Formula weight	454.58
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	monoclinic, P2 ₁ /(c)
Unit cell dimensions	a = 20.063(11) Å alpha = 90 deg. b = 5.139(3) Å beta = 94.225(7) deg. c = 23.216(13) Å gamma = 90 deg.
Volume	2387(2) Å ³
Z, Calculated density	4, 1.265 Mg/m ³
Absorption coefficient	0.422 mm ⁻¹
F(000)	944
Crystal size	0.3 x 0.2 x 0.2 mm
Theta range for data collection	1.76 to 26.00 deg.
Limiting indices	-24 ≤ h ≤ 24, -6 ≤ k ≤ 3, -28 ≤ l ≤ 27
Reflections collected/unique	11869/4692 [R(int) = 0.0833]
Completeness to theta = 26.00	99.6%
Refinement method	Full-matrix least-squares on F ²
Data/restraints/parameters	4692/0/253
Goodness-of-fit on F ²	1.005
Final R indices [I > 2σ(I)]	R ₁ = 0.0810, wR ₂ = 0.2159
R indices (all data)	R ₁ = 0.1741, wR ₂ = 0.2392
Largest diff. peak and hole	0.952 and -0.672 e.Å ⁻³

(3) CIF data

Deposition number: CCDC 727217

Summary of Data CCDC 727217

Formula: C18 H18 N2 O4 S4

Unit cell parameters: a 20.063(11) b 5.139(3) c 23.216(13)

alpha 90.00

beta 94.225(7)

gamma 90.00

space group P21/c

data_123

```
_audit_creation_method      SHELXL-97
_chemical_name_systematic
;
?
;
_chemical_name_common        ?
_chemical_melting_point      ?
_chemical_formula_moiety     ?
_chemical_formula_sum
'C18 H18 N2 O4 S4'
_chemical_formula_weight     454.58
```

loop_

```
_atom_type_symbol
_atom_type_description
_atom_type_scatter_dispersion_real
_atom_type_scatter_dispersion_imag
_atom_type_scatter_source
'C' 'C' 0.0033 0.0016
'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
'H' 'H' 0.0000 0.0000
'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
'S' 'S' 0.1246 0.1234
'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
'O' 'O' 0.0106 0.0060
'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
'N' 'N' 0.0061 0.0033
'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
```

```
_symmetry_cell_setting      ?
_symmetry_space_group_name_H-M ?
```

loop_

_symmetry_equiv_pos_as_xyz

'x, y, z'

'-x, y+1/2, -z+1/2'

'-x, -y, -z'

'x, -y-1/2, z-1/2'

_cell_length_a	20.063(11)
_cell_length_b	5.139(3)
_cell_length_c	23.216(13)
_cell_angle_alpha	90.00
_cell_angle_beta	94.225(7)
_cell_angle_gamma	90.00
_cell_volume	2387(2)
_cell_formula_units_Z	4
_cell_measurement_temperature	293(2)
_cell_measurement_reflns_used	?
_cell_measurement_theta_min	?
_cell_measurement_theta_max	?
_exptl_crystal_description	?
_exptl_crystal_colour	?
_exptl_crystal_size_max	?
_exptl_crystal_size_mid	?
_exptl_crystal_size_min	?
_exptl_crystal_density_meas	?
_exptl_crystal_density_diffn	1.265
_exptl_crystal_density_method	'not measured'
_exptl_crystal_F_000	944
_exptl_absorpt_coefficient_mu	0.422
_exptl_absorpt_correction_type	?
_exptl_absorpt_correction_T_min	?
_exptl_absorpt_correction_T_max	?
_exptl_absorpt_process_details	?
_exptl_special_details	
;	
?	
;	
_diffn_ambient_temperature	293(2)
_diffn_radiation_wavelength	0.71073
_diffn_radiation_type	MoK\alpha
_diffn_radiation_source	'fine-focus sealed tube'
_diffn_radiation_monochromator	graphite
_diffn_measurement_device_type	?
_diffn_measurement_method	?

```

_diffrn_detector_area_resol_mean ?
_diffrn_standards_number ?
_diffrn_standards_interval_count ?
_diffrn_standards_interval_time ?
_diffrn_standards_decay_% ?
_diffrn_reflns_number 11869
_diffrn_reflns_av_R_equivalents 0.0833
_diffrn_reflns_av_sigma/netI 0.1308
_diffrn_reflns_limit_h_min -24
_diffrn_reflns_limit_h_max 24
_diffrn_reflns_limit_k_min -6
_diffrn_reflns_limit_k_max 3
_diffrn_reflns_limit_l_min -28
_diffrn_reflns_limit_l_max 27
_diffrn_reflns_theta_min 1.76
_diffrn_reflns_theta_max 26.00
_reflns_number_total 4692
_reflns_number_gt 1849
_reflns_threshold_expression >2sigma(I)

_computing_data_collection ?
_computing_cell_refinement ?
_computing_data_reduction ?
_computing_structure_solution 'SHELXS-97 (Sheldrick, 1990)'
_computing_structure_refinement 'SHELXL-97 (Sheldrick, 1997)'
_computing_molecular_graphics ?
_computing_publication_material ?

```

```
_refine_special_details
```

```
;
```

Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2 , conventional R-factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > 2\text{sigma}(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F , and R-factors based on ALL data will be even larger.

```
;
```

```

_refine_ls_structure_factor_coef Fsqd
_refine_ls_matrix_type full
_refine_ls_weighting_scheme calc
_refine_ls_weighting_details
'calc w=1/[\s^2(Fo^2)+(0.1000P)^2+0.0000P] where P=(Fo^2+2Fc^2)/3'
_atom_sites_solution_primary direct
_atom_sites_solution_secondary difmap

```

_atom_sites_solution_hydrogens	geom
_refine_ls_hydrogen_treatment	mixed
_refine_ls_extinction_method	none
_refine_ls_extinction_coef	?
_refine_ls_number_reflns	4692
_refine_ls_number_parameters	253
_refine_ls_number_restraints	0
_refine_ls_R_factor_all	0.1741
_refine_ls_R_factor_gt	0.0810
_refine_ls_wR_factor_ref	0.2392
_refine_ls_wR_factor_gt	0.2159
_refine_ls_goodness_of_fit_ref	1.005
_refine_ls_restrained_S_all	1.005
_refine_ls_shift/su_max	0.121
_refine_ls_shift/su_mean	0.025

loop_

_atom_site_label	
_atom_site_type_symbol	
_atom_site_fract_x	
_atom_site_fract_y	
_atom_site_fract_z	
_atom_site_U_iso_or_equiv	
_atom_site_adp_type	
_atom_site_occupancy	
_atom_site_symmetry_multiplicity	
_atom_site_calc_flag	
_atom_site_refinement_flags	
_atom_site_disorder_assembly	
_atom_site_disorder_group	

S1 S 0.00622(8) 0.3320(3) 0.31834(6) 0.0596(5) Uani 1 1 d . . .

S2 S -0.07263(8) 0.9423(3) 0.42693(6) 0.0563(5) Uani 1 1 d . . .

S3 S 0.05498(8) 0.5387(4) 0.43452(6) 0.0601(5) Uani 1 1 d . . .

S4 S -0.11555(8) 0.7185(4) 0.31287(7) 0.0618(6) Uani 1 1 d . . .

C1 C -0.1653(3) 0.9611(12) 0.3400(3) 0.0533(16) Uani 1 1 d . . .

C2 C 0.1569(4) 0.1862(14) 0.4359(3) 0.0636(19) Uani 1 1 d . . .

C3 C -0.1469(3) 1.0577(13) 0.3929(2) 0.0518(16) Uani 1 1 d . . .

O3 O -0.2347(2) 0.8715(10) 0.2582(2) 0.0798(15) Uani 1 1 d . . .

C5 C 0.1078(3) -0.0240(15) 0.3256(3) 0.0599(19) Uani 1 1 d . . .

O2 O -0.1503(2) 1.3989(9) 0.4599(2) 0.0771(15) Uani 1 1 d . . .

C7 C -0.0564(3) 0.7124(13) 0.3730(2) 0.0545(17) Uani 1 1 d . . .

C8 C -0.2231(3) 1.0548(18) 0.2988(3) 0.068(2) Uani 1 1 d . . .

C9 C -0.1812(3) 1.2544(14) 0.4281(3) 0.0572(18) Uani 1 1 d . . .

O4 O -0.2472(2) 1.2376(11) 0.4217(2) 0.0879(17) Uani 1 1 d . . .

C11 C -0.0044(3) 0.5511(12) 0.3756(2) 0.0476(15) Uani 1 1 d . . .

C12 C 0.0987(3) 0.2877(13) 0.4052(3) 0.0548(17) Uani 1 1 d . . .

C13 C 0.0760(3) 0.1924(12) 0.3527(2) 0.0545(17) Uani 1 1 d . . .
O1 O -0.2501(3) 1.2654(11) 0.3004(2) 0.0916(18) Uani 1 1 d . . .
N1 N 0.2048(3) 0.0968(14) 0.4583(3) 0.091(2) Uani 1 1 d . . .
N2 N 0.1324(3) -0.1966(13) 0.3049(3) 0.0779(19) Uani 1 1 d . . .
C18 C -0.2880(4) 0.9354(18) 0.2121(4) 0.107(3) Uani 1 1 d . . .
H18A H -0.2720 1.0705 0.1874 0.129 Uiso 1 1 calc R . .
H18B H -0.3269 1.0019 0.2297 0.129 Uiso 1 1 calc R . .
C19 C -0.3076(5) 0.7007(17) 0.1762(4) 0.124(4) Uani 1 1 d . . .
H19A H -0.3186 0.5693 0.2039 0.149 Uiso 1 1 calc R . .
H19B H -0.2664 0.6426 0.1609 0.149 Uiso 1 1 calc R . .
C24 C -0.2864(4) 1.425(2) 0.4539(4) 0.137(4) Uani 1 1 d . . .
H24A H -0.2627 1.5890 0.4579 0.164 Uiso 1 1 calc R . .
H24B H -0.2922 1.3578 0.4923 0.164 Uiso 1 1 calc R . .
C27 C -0.3567(6) 1.468(4) 0.4207(8) 0.286(12) Uani 1 1 d . . .
H27A H -0.3814 1.5428 0.4510 0.343 Uiso 1 1 calc R . .
H27B H -0.3727 1.2904 0.4171 0.343 Uiso 1 1 calc R . .
C32 C -0.3918(11) 1.588(5) 0.3689(6) 0.346(17) Uani 1 1 d . . .
H32A H -0.3529 1.5964 0.3464 0.415 Uiso 1 1 calc R . .
H32B H -0.3942 1.7613 0.3850 0.415 Uiso 1 1 calc R . .
C23 C -0.3641(5) 0.668(3) 0.1228(5) 0.234(10) Uani 1 1 d . . .
H23A H -0.3458 0.7971 0.0978 0.281 Uiso 1 1 calc R . .
H23B H -0.3992 0.7623 0.1405 0.281 Uiso 1 1 calc R . .
C21 C -0.4139(8) 0.521(2) 0.0713(7) 0.290(11) Uani 1 1 d . . .
H21A H -0.4415 0.6483 0.0509 0.435 Uiso 1 1 calc R . .
H21B H -0.4416 0.3957 0.0888 0.435 Uiso 1 1 calc R . .
H21C H -0.3869 0.4338 0.0447 0.435 Uiso 1 1 calc R . .
C20 C -0.4459(6) 1.638(4) 0.3153(8) 0.283(11) Uani 1 1 d . . .
H20A H -0.4243 1.7171 0.2842 0.425 Uiso 1 1 calc R . .
H20B H -0.4803 1.7514 0.3273 0.425 Uiso 1 1 calc R . .
H20C H -0.4653 1.4751 0.3026 0.425 Uiso 1 1 calc R . .

loop_

_atom_site_aniso_label

_atom_site_aniso_U_11

_atom_site_aniso_U_22

_atom_site_aniso_U_33

_atom_site_aniso_U_23

_atom_site_aniso_U_13

_atom_site_aniso_U_12

S1 0.0730(12) 0.0615(12) 0.0435(9) -0.0061(8) -0.0012(8) 0.0097(10)

S2 0.0665(11) 0.0602(11) 0.0414(9) -0.0052(8) -0.0016(8) 0.0043(10)

S3 0.0700(11) 0.0652(12) 0.0444(9) -0.0056(8) -0.0010(8) 0.0093(10)

S4 0.0715(12) 0.0674(13) 0.0450(10) -0.0097(9) -0.0059(8) 0.0083(10)

C1 0.059(4) 0.052(4) 0.049(4) -0.009(3) 0.004(3) -0.002(3)

C2 0.071(5) 0.068(5) 0.052(4) -0.002(4) 0.006(4) 0.009(4)

C3 0.054(4) 0.057(4) 0.044(4) -0.002(3) -0.001(3) 0.005(3)

O3 0.091(4) 0.073(3) 0.068(3) -0.010(3) -0.037(3) 0.008(3)
 C5 0.073(5) 0.065(5) 0.042(4) 0.011(4) 0.007(3) 0.001(4)
 O2 0.087(3) 0.073(4) 0.072(3) -0.025(3) 0.006(3) -0.003(3)
 C7 0.071(4) 0.056(4) 0.037(3) 0.001(3) 0.008(3) -0.011(4)
 C8 0.065(5) 0.086(6) 0.053(4) 0.005(4) -0.005(4) -0.010(5)
 C9 0.065(5) 0.065(5) 0.040(4) -0.002(4) -0.007(3) 0.012(4)
 O4 0.068(3) 0.114(5) 0.081(3) -0.034(3) -0.003(3) 0.015(3)
 C11 0.052(4) 0.050(4) 0.040(3) 0.005(3) -0.003(3) 0.004(3)
 C12 0.057(4) 0.061(4) 0.046(4) 0.009(3) 0.007(3) 0.007(4)
 C13 0.075(4) 0.050(4) 0.039(4) 0.002(3) 0.011(3) 0.004(4)
 O1 0.106(4) 0.084(4) 0.083(4) -0.007(3) -0.008(3) 0.028(4)
 N1 0.095(5) 0.105(6) 0.071(4) -0.006(4) -0.002(4) 0.034(5)
 N2 0.093(5) 0.073(5) 0.069(4) -0.006(4) 0.013(3) 0.013(4)
 C18 0.115(7) 0.099(7) 0.102(7) 0.011(6) -0.034(5) 0.016(6)
 C19 0.162(9) 0.072(6) 0.139(9) -0.040(6) 0.007(7) 0.010(7)
 C24 0.112(7) 0.192(11) 0.111(7) -0.095(8) 0.041(6) 0.007(8)
 C27 0.106(9) 0.37(3) 0.39(3) -0.21(2) 0.048(13) 0.108(13)
 C32 0.62(5) 0.34(3) 0.079(10) -0.054(15) 0.052(16) -0.01(3)
 C23 0.088(7) 0.46(3) 0.152(11) 0.172(14) 0.001(7) 0.120(12)
 C21 0.39(2) 0.120(10) 0.40(3) -0.138(14) 0.261(19) -0.123(14)
 C20 0.126(11) 0.39(3) 0.33(2) -0.08(3) -0.007(13) 0.045(15)

_geom_special_details

;

All esds (except the esd in the dihedral angle between two l.s. planes)
 are estimated using the full covariance matrix. The cell esds are taken
 into account individually in the estimation of esds in distances, angles
 and torsion angles; correlations between esds in cell parameters are only
 used when they are defined by crystal symmetry. An approximate (isotropic)
 treatment of cell esds is used for estimating esds involving l.s. planes.

;

loop_

_geom_bond_atom_site_label_1

_geom_bond_atom_site_label_2

_geom_bond_distance

_geom_bond_site_symmetry_2

_geom_bond_publ_flag

S1 C13 1.716(6) . ?

S1 C11 1.767(6) . ?

S2 C3 1.739(6) . ?

S2 C7 1.769(6) . ?

S3 C12 1.728(6) . ?

S3 C11 1.747(6) . ?

S4 C1 1.744(6) . ?

S4 C7 1.764(6) . ?

C1 C3 1.350(8) . ?
C1 C8 1.525(9) . ?
C2 N1 1.155(8) . ?
C2 C12 1.421(9) . ?
C3 C9 1.499(9) . ?
O3 C8 1.341(8) . ?
O3 C18 1.493(8) . ?
C5 N2 1.138(8) . ?
C5 C13 1.449(9) . ?
O2 C9 1.188(7) . ?
C7 C11 1.331(8) . ?
C8 O1 1.212(8) . ?
C9 O4 1.325(7) . ?
O4 C24 1.480(9) . ?
C12 C13 1.361(8) . ?
C18 C19 1.502(11) . ?
C19 C23 1.626(13) . ?
C24 C27 1.572(15) . ?
C27 C32 1.48(2) . ?
C32 C20 1.609(19) . ?
C23 C21 1.681(17) . ?

loop_

_geom_angle_atom_site_label_1
_geom_angle_atom_site_label_2
_geom_angle_atom_site_label_3
_geom_angle
_geom_angle_site_symmetry_1
_geom_angle_site_symmetry_3
_geom_angle_publ_flag
C13 S1 C11 93.2(3) . . ?
C3 S2 C7 95.8(3) . . ?
C12 S3 C11 93.2(3) . . ?
C1 S4 C7 95.6(3) . . ?
C3 C1 C8 126.8(6) . . ?
C3 C1 S4 117.7(5) . . ?
C8 C1 S4 115.4(5) . . ?
N1 C2 C12 176.6(8) . . ?
C1 C3 C9 129.6(6) . . ?
C1 C3 S2 117.2(5) . . ?
C9 C3 S2 113.2(4) . . ?
C8 O3 C18 115.3(6) . . ?
N2 C5 C13 178.9(7) . . ?
C11 C7 S2 124.6(5) . . ?
C11 C7 S4 121.8(5) . . ?
S2 C7 S4 113.6(4) . . ?

O1 C8 O3 126.5(7) ..?
O1 C8 C1 125.7(7) ..?
O3 C8 C1 107.7(7) ..?
O2 C9 O4 125.6(7) ..?
O2 C9 C3 121.4(6) ..?
O4 C9 C3 113.0(6) ..?
C9 O4 C24 117.7(6) ..?
C7 C11 S3 123.1(5) ..?
C7 C11 S1 119.9(4) ..?
S3 C11 S1 116.9(4) ..?
C13 C12 C2 121.7(6) ..?
C13 C12 S3 118.4(5) ..?
C2 C12 S3 119.9(5) ..?
C12 C13 C5 122.4(6) ..?
C12 C13 S1 118.3(5) ..?
C5 C13 S1 119.3(5) ..?
O3 C18 C19 111.4(7) ..?
C18 C19 C23 130.1(10) ..?
O4 C24 C27 109.5(7) ..?
C24 C27 C32 144.4(19) ..?
C27 C32 C20 161(2) ..?
C19 C23 C21 158.9(13) ..?

_diffn_measured_fraction_theta_max	0.996
_diffn_reflns_theta_full	26.00
_diffn_measured_fraction_theta_full	0.996
_refine_diff_density_max	0.952
_refine_diff_density_min	-0.672
_refine_diff_density_rms	0.086

2. ^1H NMR spectrum of compound 5

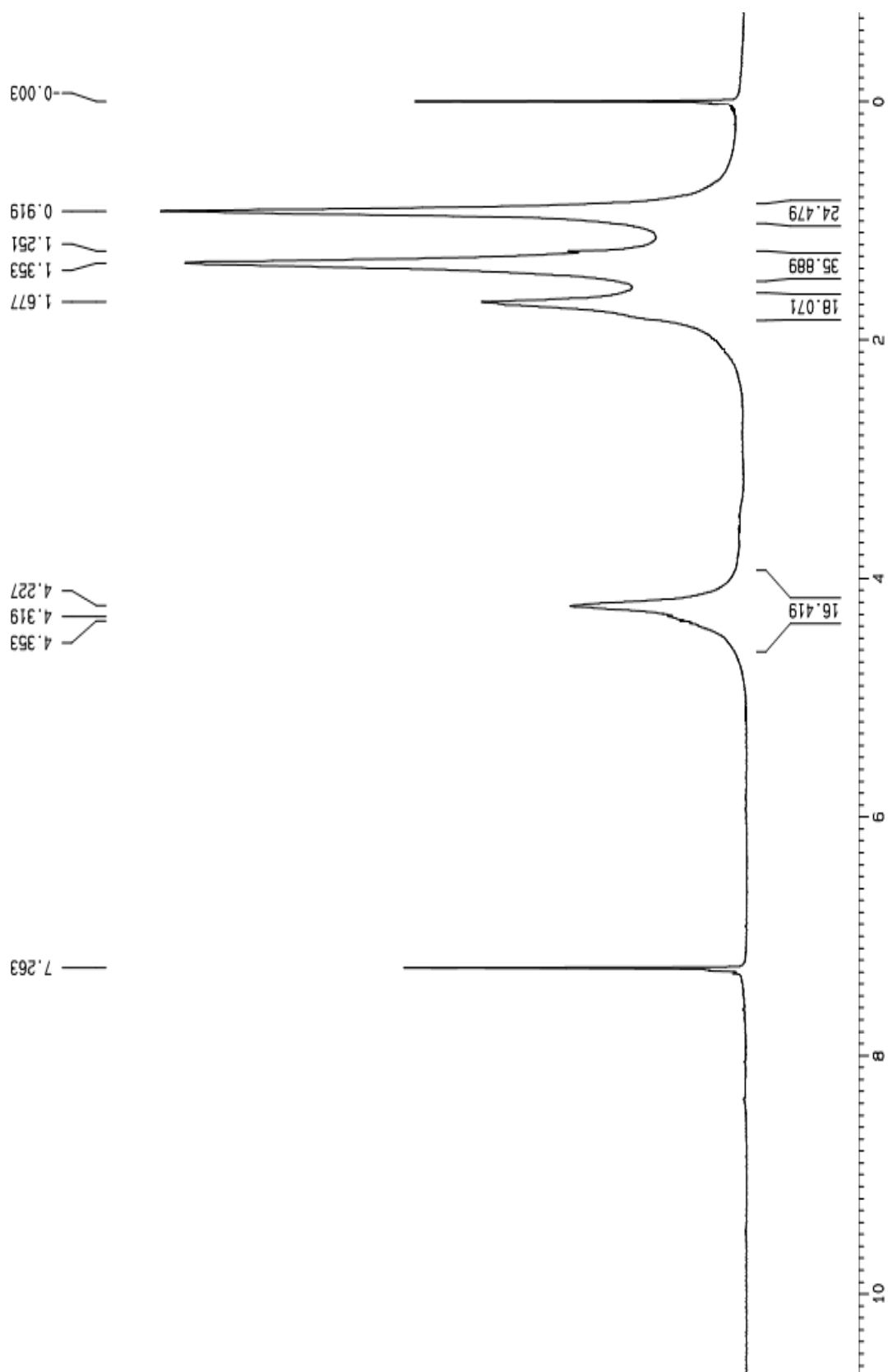


Fig. S2. ^1H NMR spectrum of compound 5

3. MALDI-TOF-MS spectrum of 5

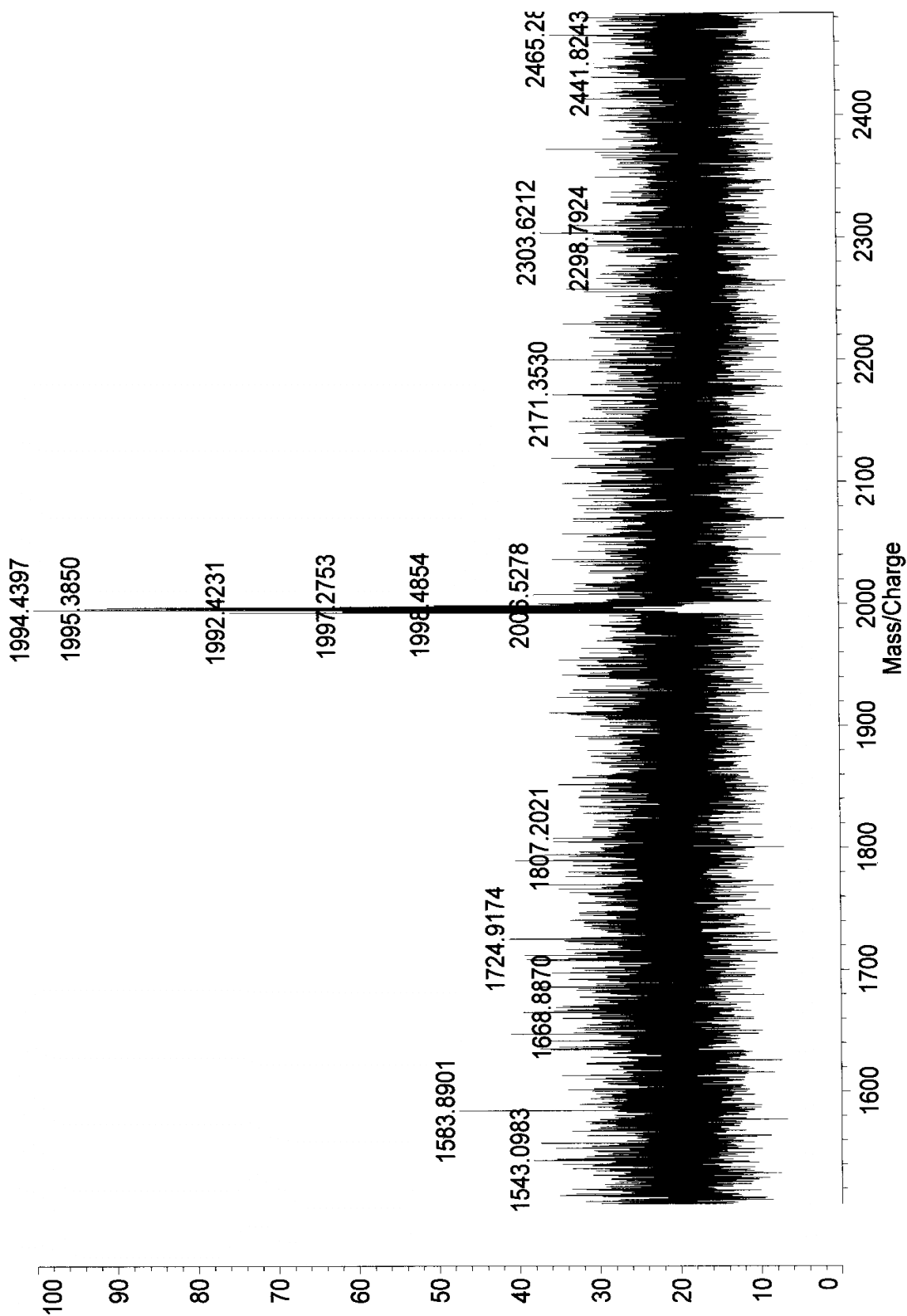


Fig. S3. MALDI-TOF-MS spectrum of 5

4. ESR spectrum of the complex of 4 with F₄TCNQ in CH₂Cl₂ at 25 °C

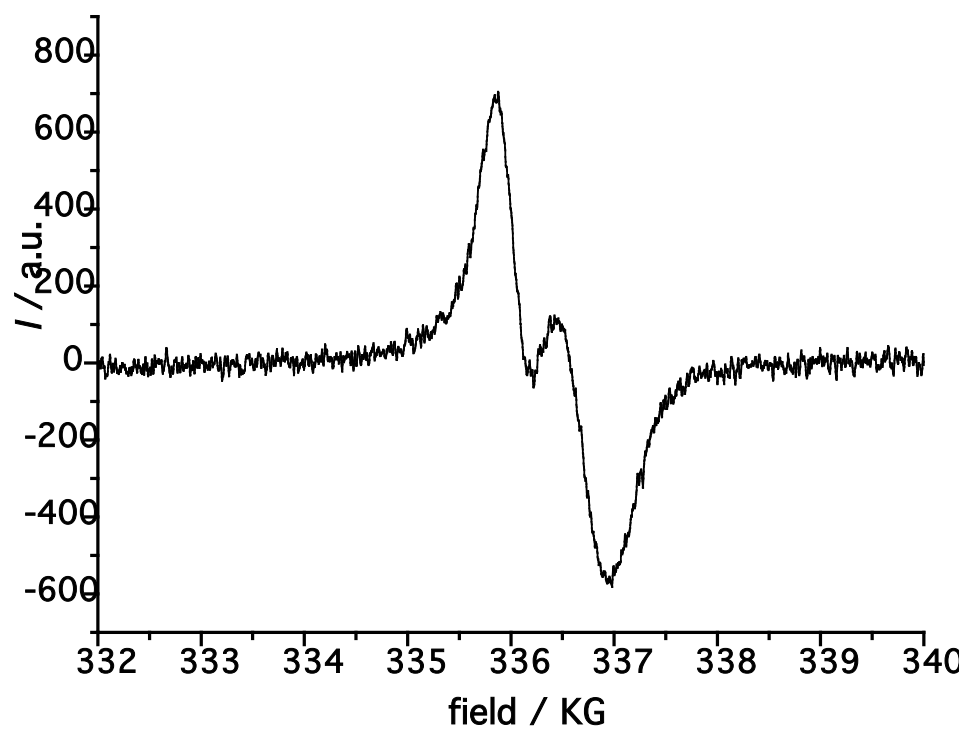


Fig. S4. ESR spectrum of the complex of 4 with F₄TCNQ in CH₂Cl₂ at 25 °C

Copyright of the works in this Journal is vested with World Scientific Publishing. The article is allowed for individual use only and may not be copied, further disseminated, or hosted on any other third party website or repository without the copyright holder's written permission.