Supporting Information for *Acta Phys. -Chim. Sin.* 2017, *33* (7), 1390−1398
doi: 10.3866/PKU.WHXB201704111

含 TEMPO 配合物的合成、表征、谱学性质及光猝灭机理

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Synthesis, Characterization, Spectroscopic Properties, and Luminescence Quenching Mechanism of a Pt(II) Complex Decorated with a π-Conjugated TEMPO-Terpyridine Ligand System

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1 Synthetic procedures and characterization

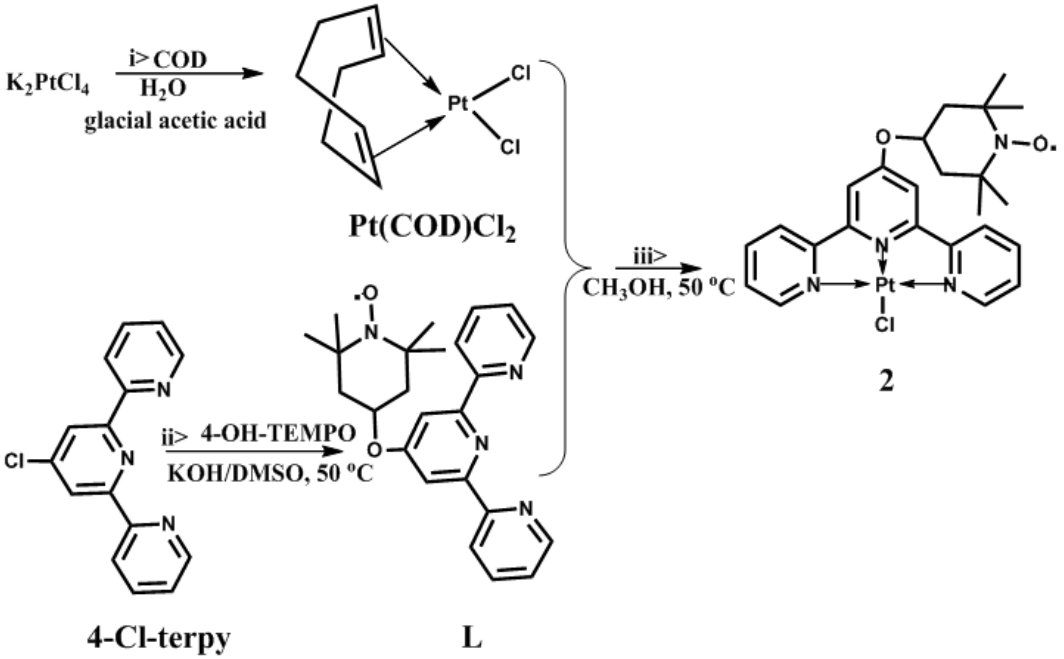

Fig.S1 Synthetic Route for compound 2

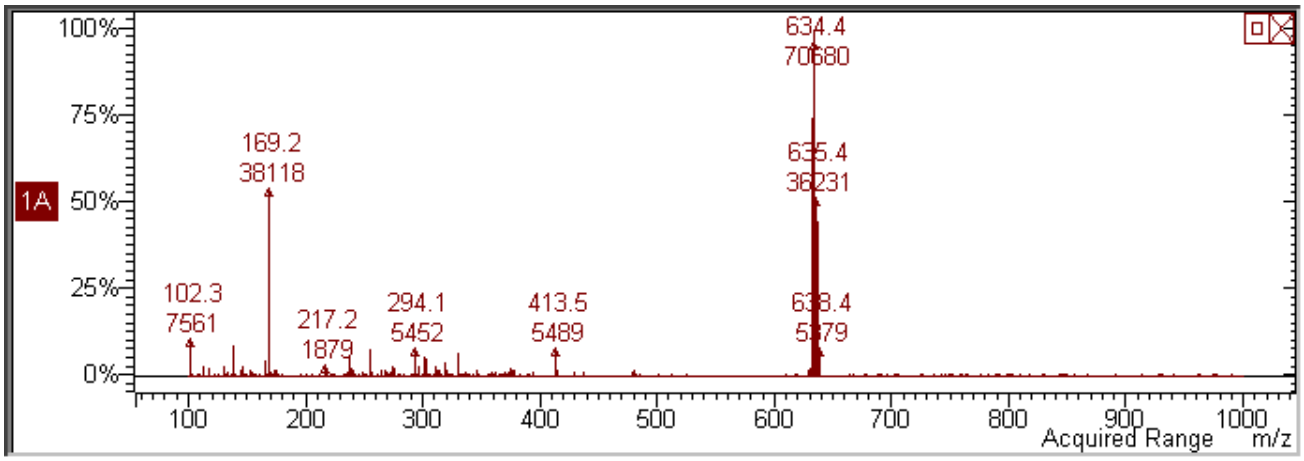

Fig.S2 ESI-MS spectra for compound 2 in CH_3OH

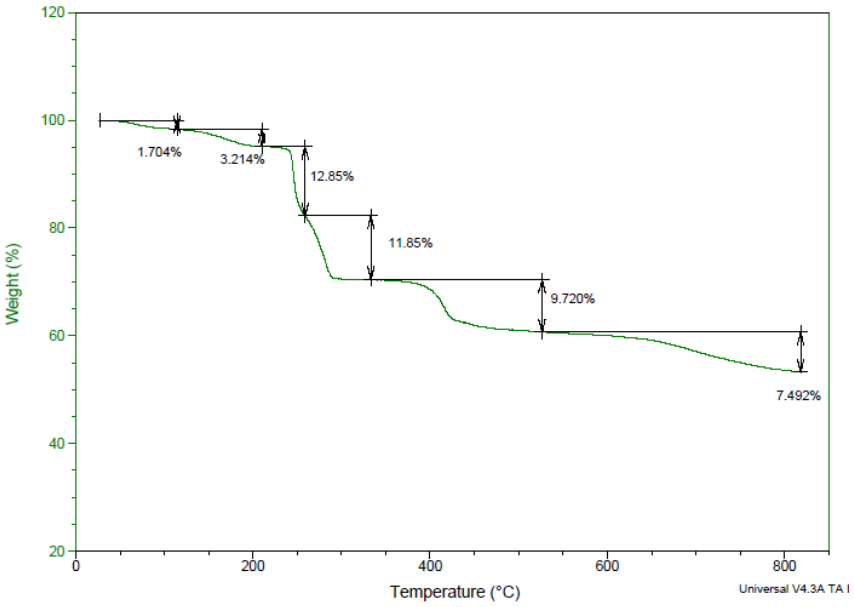

Fig.S3 Thermo gravimetric Analysis (TGA) of compound 2

2 X-ray Crystallographic Studies

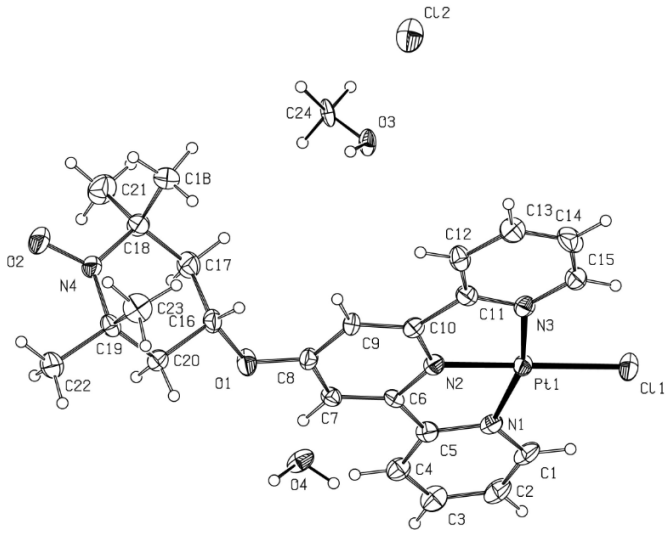

Fig.S4 Structure of the cationic component of [Pt (terpy-TEMPO) Cl].Cl.H_2O.CH_3OH

(compound 2). Selected bond lengths (Å(0.1 nm)) and angles ( ): Pt(1)-N(1) 2.019(5), Pt(1)-N(2) 1.934(5), Pt(1)-N(3) 2.012(5), Pt(1)-Cl(1) 2.296(2), Pt(1)-N(3)-N(2) 80.71(21), Pt(1)-N(1)-N(2) 80.71(21), Pt(1)-N(1)-N(3) 161.42(23), Pt(1)-Cl(1)-N(2) 179.63(15), Pt(1)-Cl(1)-N(3) 99.49(18), Pt(1)-Cl(1)-N(1) 99.08(17); Selected torsion angles: N(2)-Pt(1)-N(1)-C(1) 178.90 (52), N(3)-Pt(1)-N(1)-C(1) 179.15 (53), Cl(1)-Pt(1)-N(1)-C(1) 0.78 (50), N(3)-Pt(1)-N(2)-C(10) 1.91 (41), N(1)-Pt(1)-N(2)-C(10) 178.02 (44), Cl(1)-Pt(1)-N(2)-C(10) 124.82 (25).

Table S1 Crystal data for compound 2

	Calculated	Reported
Volume	1334.95(12)	1334.95(11)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	2(C_{24} H_{27} Cl N_4 O_2 Pt), CH_4 O, 2(Cl), H_2 O	2(C_{24} H_{27} Cl N_4 O_2 Pt), CH_4 O, H_2 O, 2(Cl)
Sum formula	C_{49} H_{60} Cl_4 N_8 O_6 Pt_2	C_{49} H_{60} Cl_4 N_8 O_6 Pt_2
Mr	1389.01	1389.03
Dx/(g·cm^{-3})	1.728	1.728
Z	1	1
Mu/mm^{-1}	5.488	5.488
F000	682.0	682.0
F000’	679.51	-
h,*k*,*l*max	9,14,16	9,14,16
Nref	4884	4852
T_{min},T_{max}	0.596,0.719	0.926,1.000
$T_{min'}$	0.330	-

Bond precision: C-C length = 0.0095 Å; Wavelength = 0.71073 Å; Cell: a = 7.9451(4) Å, b = 12.2121(5) Å, c = 13.9870(8) Å, α = 89.975(4) °, β = 87.286(4) °, γ = 80.000(4) °; Temperature: 293 K; CCDC Ref: 1063015.

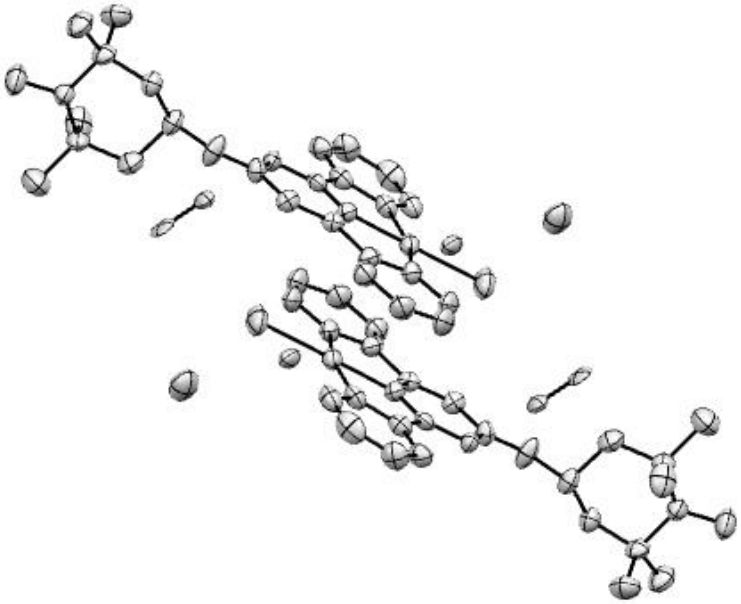

Fig.S5 Stacking arrangement in the solid state for compound 2

3 UV-Vis, fluorescence spectra and fluorescence lifetimes

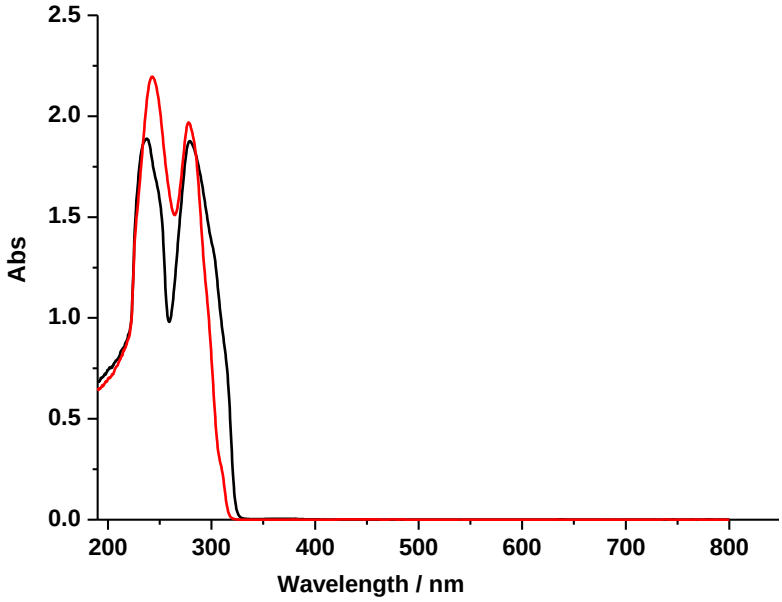

Fig.S6 UV-Vis spectra of 2,2′:6′,2″-terpyridine (black), 2,2′:6′,2″-terpyridine -TEMPO (red)

Table S2 Spectroscopic data for terpy, complex 1 and 2 in DMF and CH_3OH

compounds	Band [λ/nm($10^{-4}\varepsilon_{max}$/(dm^3·mol^{-1}·cm^{-1}))] DMF		Band [λ/nm($10^{-4}\varepsilon_{max}$/(dm^3·mol^{-1}·cm^{-1})] CH_3OH	
	Band A	Band B	Band A	Band B
Terpy	-	279(1.88)	-	281(1.88)
Complex **1**	373(0.18)	279(1.88), 304(0.74), 328(0.95), 343(0.76)	382(0.27)	282(1.47), 306(0.59), 320(0.63), 333(0.88), 349(0.88)
Complex **2**	398(0.23)	286(1.72), 3.5(0.81), 319(0.83), 334(0.99)	402(0.32)	284(1.56), 306(0.63), 317(0.64), 331(0.75)

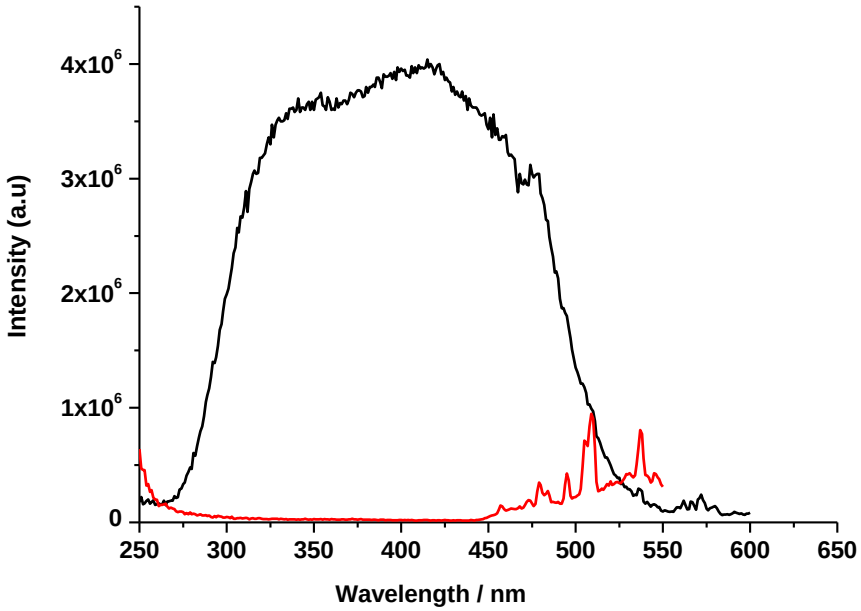

Fig.S7 Excitation spctra of [Pt(terpy)Cl].Cl.2H_2O (black) and [Pt(terpy)-TEMPO].Cl.H_2O .CH_3OH (red) in solid state in 298 K.(emission at 630 nm)

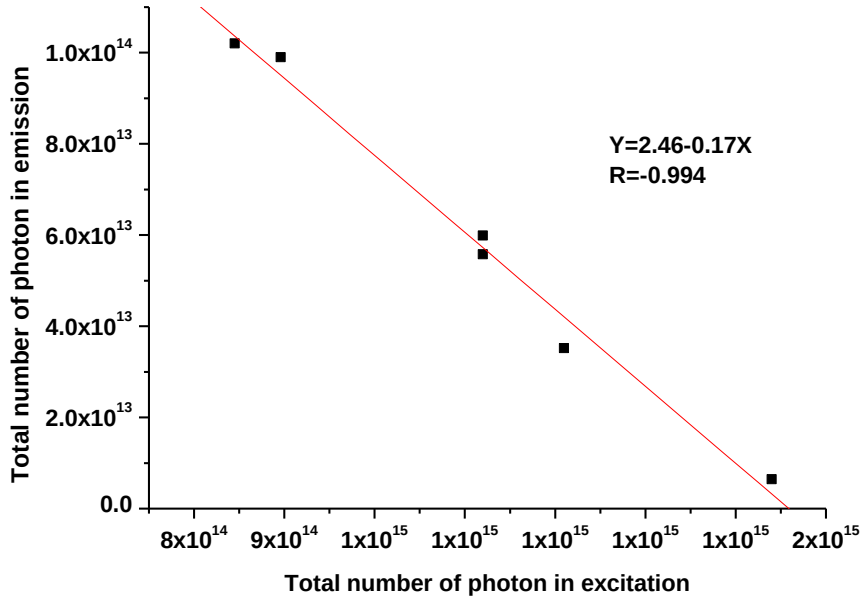

Fig.S8 Quantum yield (φ) of compound 1 in solid state at 298 K

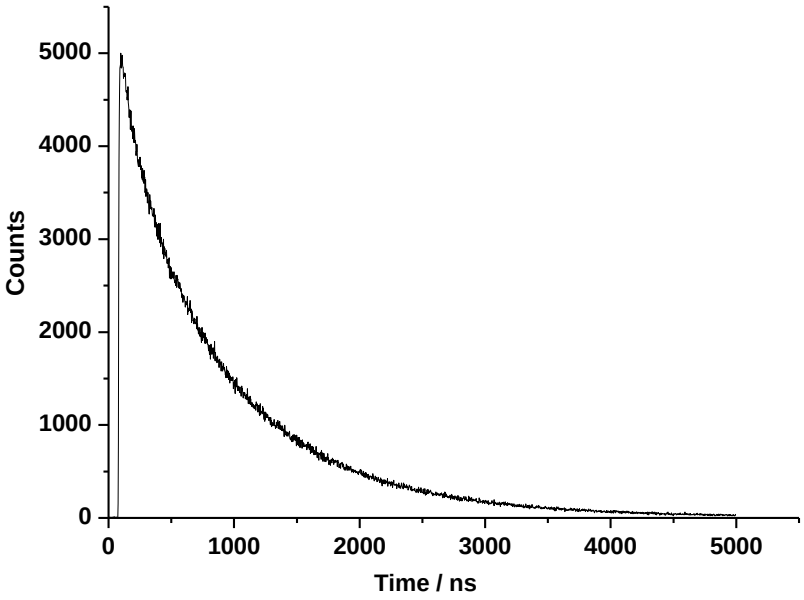

Fig.S9 Lifetime of compound 1 in solid state at 298 K (emission at 630 nm)

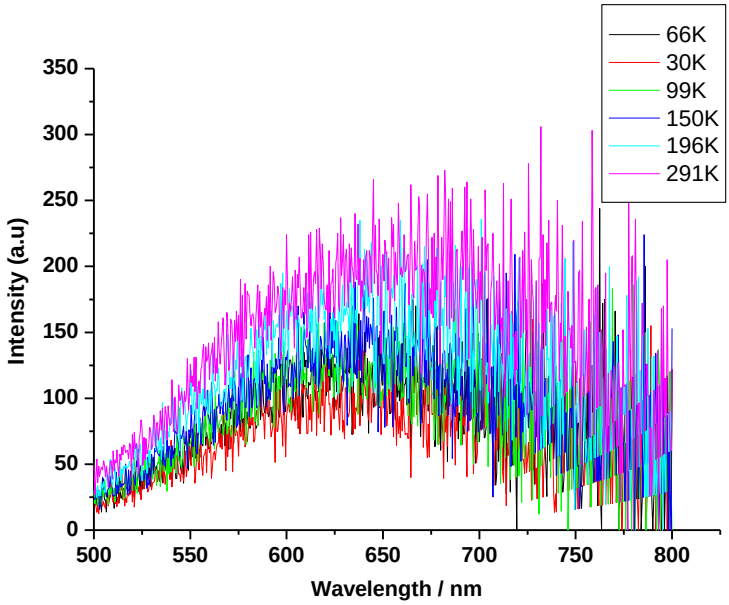

Fig.S10 Luminesence of compound 2 in solid state at different temperatures (30, 66, 99, 150, 196, 290 K, emission at 630 nm)

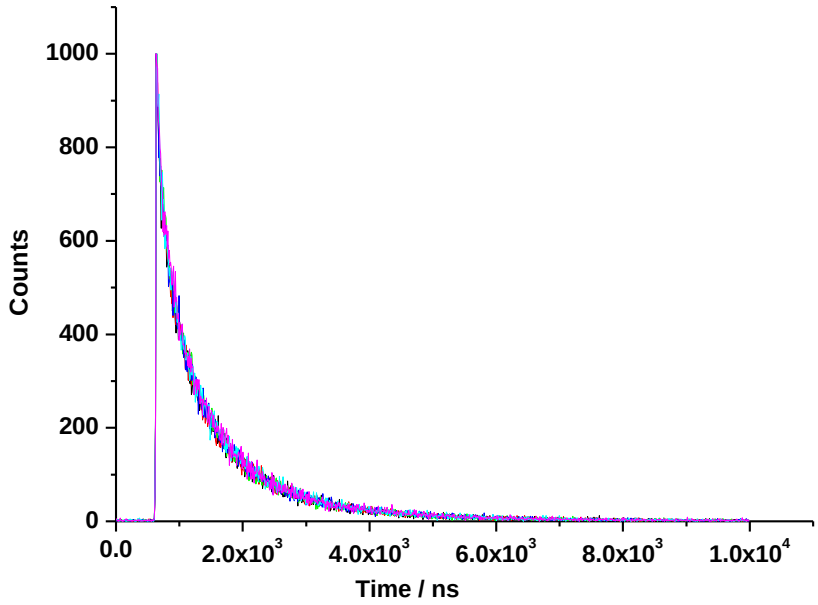

Fig.S11 Lifetimes of compound 2 in solid state at different temperatures (30, 66, 99, 150, 196, 290 K, emission at 630 nm)

Table S3 Lifetimes of compound 2 in solid state at different temperatures (30, 66, 99, 150, 196, 290 K, emission at 630 nm)

T/K / Lifetime/ns	30	66	99	150	196	290
τ_{fitted}	949.06	943.63	927.53	982.27	961.77	957.23

4 Approximate calculation of τ_R

Rotational correlation coefficients (τ_R) may be obtained via analysis of the ESR linewidths and relative intensities. As detailed in ref.,[5] within this regime the relation between τ_R and the spectral parameters is given to a good approximation by the following two expressions [Eq.(1)]:

$$\tau_R = -6.1 \times 10^{-10} \Delta H_{(0)} \left[\sqrt{\frac{I_0}{I_{+1}}} - \sqrt{\frac{I_0}{I_{-1}}} \right]$$
$$= +6.1 \times 10^{-10} \Delta H_{(0)} \left[\sqrt{\frac{I_0}{I_{+1}}} + \sqrt{\frac{I_0}{I_{-1}}} - 2 \right] \quad (1)^6$$

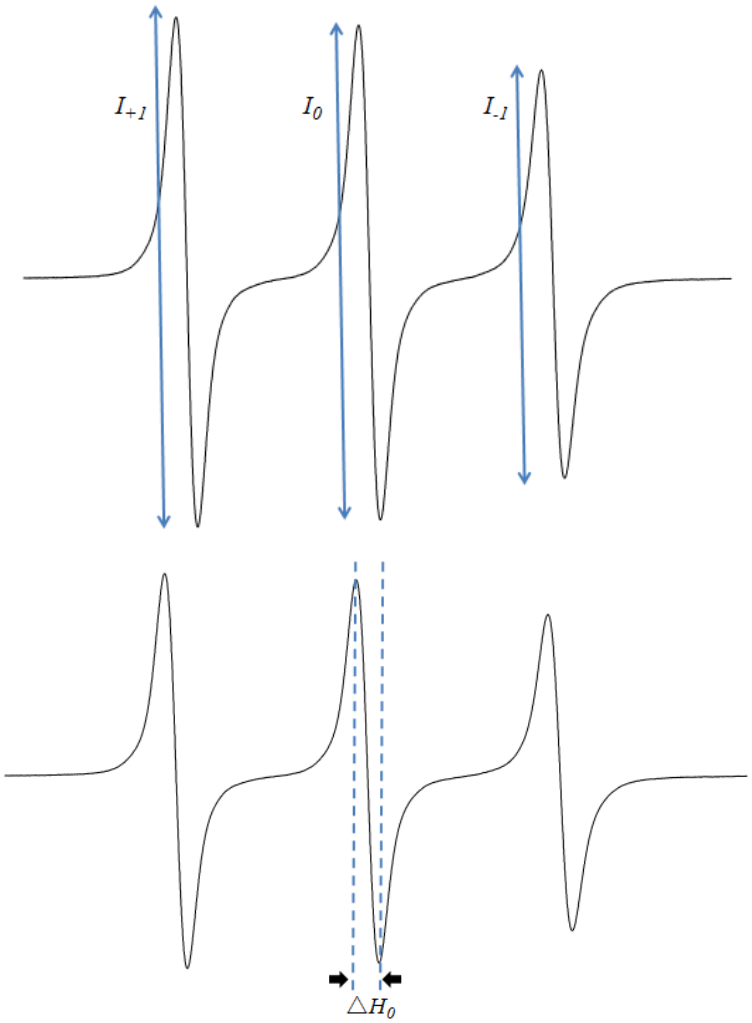

Fig.S12 EPR spectra for 1 × 10^{-3} mol·L^{-1} compound 2 in DMF

Table S4 EPR parameters of 4-OH-TEMPO, Terpy-TEMPO, [Pt(terpy)-TEMPO] .Cl. $H_2O.CH_3OH$ in DMF at 298K, 2 × 10^{-3} mol·L^{-1}

Compounds	A value (G)	g value	τ_R (s)
4-OH-TEMPO	15.68	2.00	2.9×10^{-11}
Terpy-TEMPO	15.50	2.00	1.3×10^{-10}
[Pt(terpy)-TEMPO].Cl.$H_2O.CH_3OH$	15.52	2.00	2.0×10^{-10}

instrumental settings: microwave power, 15.99 mW; modulation amplitude, 1.00 G; modulation frequency, 100 kHz; static field, 3478.00 G; sweep width, 60.00G; receiver gain, 1.59 ×102; time constant, 10.24 msec; conversion time, 42.00 msec; resolution inx, 6144

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