

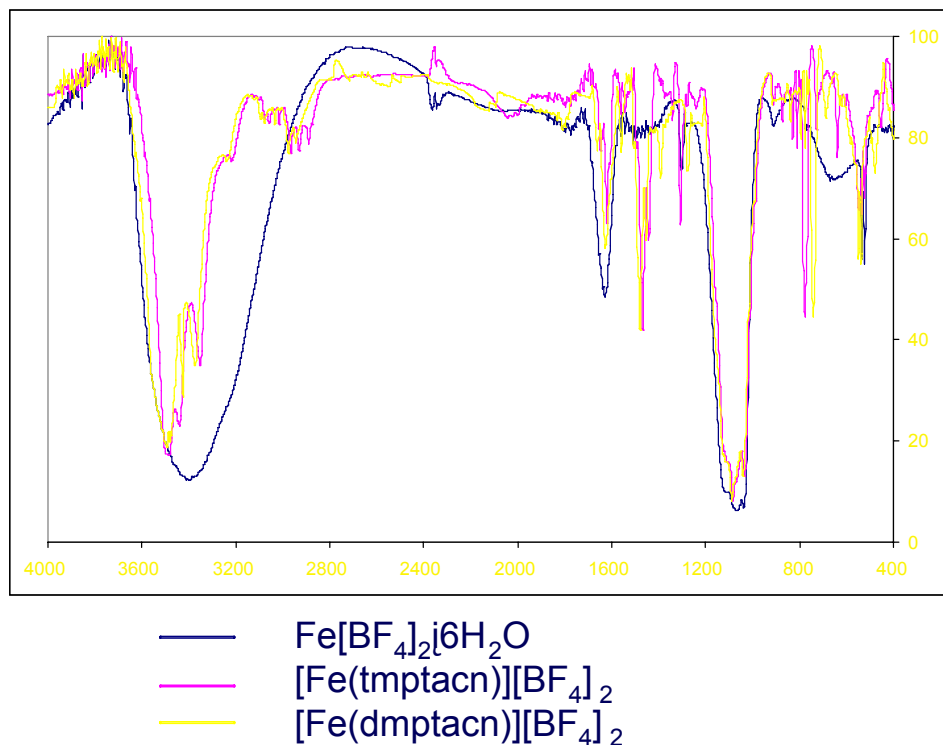
Supplementary Information

Significant relaxivity gap between a low-spin and a high-spin iron(II) complex of structural similarity: an attractive off/on system for the potential design of responsive MRI probes

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Experimental

IR analysis :



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X-ray analysis of compound 5 :

Crystal data

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$C_{18}H_{26}N_5 \cdot H_2O \cdot Cl$	$Z = 4$
$M_r = 365.91$	$D_x = 1.209 \text{ Mg m}^{-3}$
Monoclinic, $P12_1/c1$	Mo $K\alpha$ radiation
$a = 7.9048 (7) \text{ \AA}$	Cell parameters from 1493 reflections
$b = 10.0563 (11) \text{ \AA}$	$\theta = 1.0\text{--}27.9^\circ$
$c = 25.406 (3) \text{ \AA}$	$\mu = 0.21 \text{ mm}^{-1}$
$\beta = 95.440 (5)^\circ$	$T = 293 \text{ K}$
$V = 2010.5 (3) \text{ \AA}^3$	Block, colorless

Data collection

Area diffractometer $R_{\text{int}} = 0.042$

ϕ & ω scans	$\theta_{\max} = 28.1^\circ$
Absorption correction: none	$h = -9 \rightarrow 10$
$T_{\min} = 0, T_{\max} = 0$	$k = -13 \rightarrow 12$
4819 measured reflections	$l = -33 \rightarrow 33$
3452 independent reflections	0 standard reflections
1443 reflections with $I > 2.0\sigma(I)$	every . reflections

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Refinement

Refinement on F	H atoms constrained to parent site
$R[F^2 > 2\sigma(F^2)] = 0.051$	Calculated weights Method = Modified Sheldrick $w = 1/[\sigma^2(F^2) + (0.02P)^2 + 0.03P]$, where $P = (\max(F_o^2, 0) + 2F_c^2)/3$
$wR(F^2) = 0.079$	$(\Delta/\sigma)_{\max} < 0.0001$
$S = 1.07$	$\Delta\rho_{\max} = 0.24 \text{ e } \text{\AA}^{-1}$
1915 reflections	$\Delta\rho_{\min} = -0.21 \text{ e } \text{\AA}^{-1}$
227 parameters	Extinction correction: Larson (1970), Equation 22

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Geometric parameters (\AA , $^\circ$)

N2—C7	1.429 (5)	N9—C19	1.332 (7)
N2—C8	1.444 (5)	C10—C13	1.492 (6)
N2—C13	1.448 (5)	C10—C15	1.377 (6)
N3—C10	1.332 (6)	C14—C18	1.496 (6)
N3—C22	1.335 (6)	C15—C24	1.369 (8)
N4—C12	1.454 (6)	C16—C17	1.367 (7)
N4—C14	1.474 (5)	C16—C20	1.504 (7)
N4—C20	1.467 (5)	C17—C25	1.375 (7)
N5—C11	1.493 (5)	C19—C21	1.355 (8)
N5—C18	1.486 (5)	C21—C25	1.360 (8)
C7—C12	1.533 (6)	C22—C23	1.355 (7)
C8—C11	1.503 (6)	C23—C24	1.365 (8)
N9—C16	1.315 (6)		

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C7—N2—C8	116.5 (4)	C10—C13—N2	114.0 (4)
C7—N2—C13	115.6 (4)	N4—C14—C18	109.9 (4)
C8—N2—C13	115.0 (4)	C10—C15—C24	119.4 (6)
C10—N3—C22	116.9 (4)	N9—C16—C17	121.4 (5)
C12—N4—C14	114.1 (4)	N9—C16—C20	115.8 (5)
C12—N4—C20	112.1 (4)	C17—C16—C20	122.8 (5)
C14—N4—C20	110.5 (4)	C16—C17—C25	119.9 (5)
C11—N5—C18	116.1 (3)	C14—C18—N5	111.1 (4)
N2—C7—C12	112.5 (3)	N9—C19—C21	125.1 (6)
N2—C8—C11	111.0 (4)	C16—C20—N4	113.1 (4)

C16—N9—C19	117.6 (5)	C19—C21—C25	116.9 (6)
N3—C10—C13	118.2 (4)	N3—C22—C23	124.3 (5)
N3—C10—C15	122.1 (5)	C22—C23—C24	118.4 (5)
C13—C10—C15	119.7 (5)	C15—C24—C23	118.9 (6)
C8—C11—N5	110.0 (3)	C17—C25—C21	119.2 (6)
C7—C12—N4	113.0 (4)		

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Hydrogen-bond parameters (Å, °)

	<i>D—H</i>	<i>H...A</i>	<i>D...A</i>	<i>D—H...A</i>
N5—H1...N3	0.88	2.26	3.016 (8)	144

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LCMS analysis

⁴⁵ $[\text{Fe}(\text{tpnacn})][\text{BF}_4]_2$ (**1**, LS)

$\text{C}_{24}\text{H}_{30}\text{N}_6\text{Fe}$: $m = 458.19$; $m/2 = 229$; $m + \text{HCOO}^- = 503$; $m + 2 \text{HCOO}^- + \text{Na}^+ = 571$.

Chromatographic conditions :

Column : Synergi Polar-RP (Phenomenex), 4μ , 80A° , 150×4.60 mm.

⁵⁰ Mobile phase : A = 0.1% formic acid in water

B = Acetonitrile

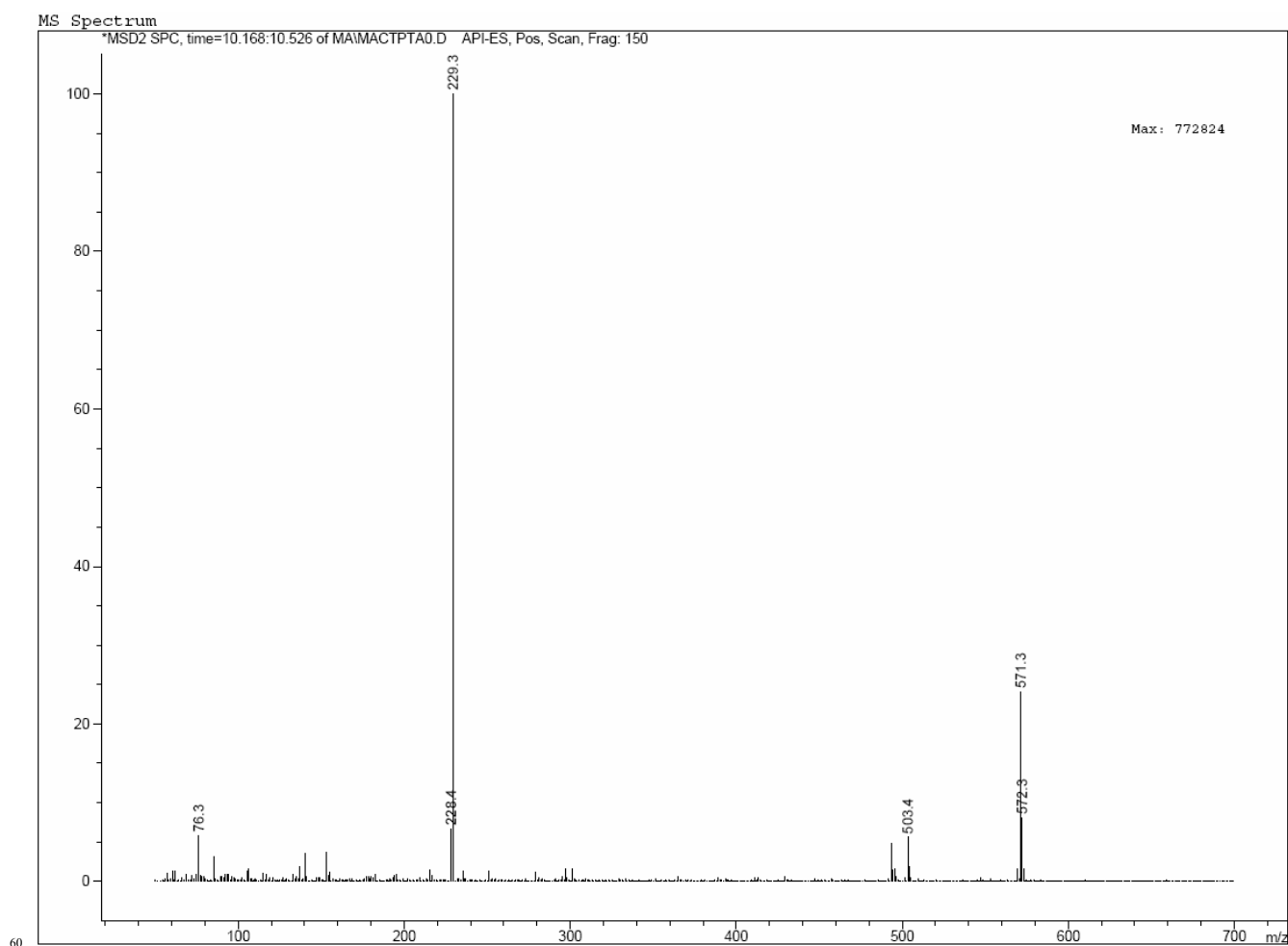
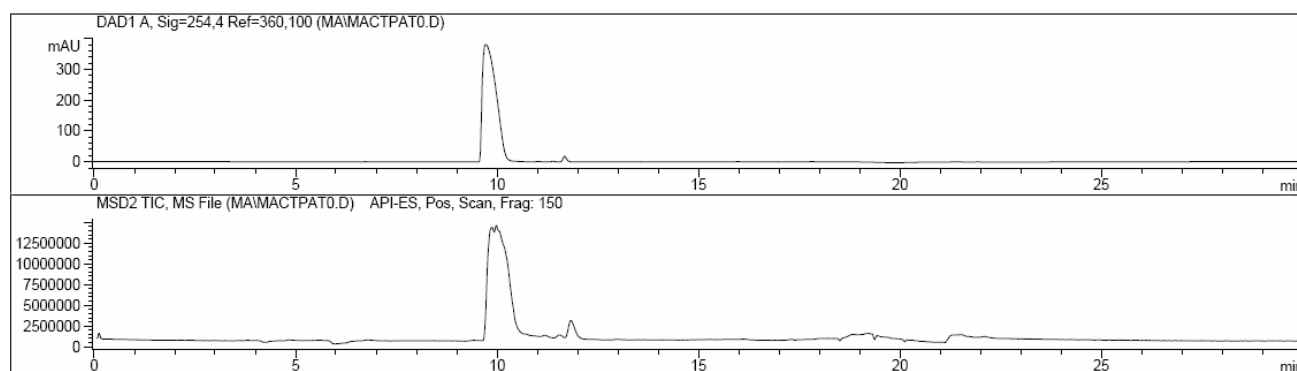
Isocratic: 90% A

Flow Rate: 0.3 mL/min

Column temp: 25°C

⁵⁵ DAD: 254 nm, reference = 360.

Mass analysis : API-ESI, scan mode



LCMS analysis

[Fe(dptacn)][BF₄]₂ (**2**, HS)

C₁₈H₂₅FeN₅ : m = 367.15; m/2 = 183; m + HCOO⁻ = 412; m + 2 HCOO⁻ + Na⁺ = 480.

65 Chromatographic conditions :

Column : Synergi Polar-RP (Phenomenex), 4μ, 80A°, 150 x 4.60 mm.

Mobile phase : A = 0.1% formic acid in water

B = Acetonitrile

Isocratic: 90% A

70 Flow Rate: 0.3 mL/mn

Column temp: 25°C

DAD: 254 nm, reference = 360.

Mass analysis : API-ESI, scan mode

