**Supporting Information**

**Experimental**

*General procedures*

The reagents used, $FeCl_2 \cdot 4H_2O$, $\alpha$-benzyldioxime, $BF_3 \cdot O(C_2H_5)_2$, sorbents, organic bases and solvents were obtained commercially (SAF). Dibromoglyoxime (denoted as $Br_2GmH_2$) was obtained by known procedure[1]. Initial bis-dioximate complex **1** was prepared as described earlier[2].

Analytical data (C, H, N content) were obtained with a Carlo Erba model 1106 microanalyzer. Iron content was determined spectrophotometrically. Bromine content was determined by Shoeniger mercurimetric titration.

MALDI-TOF mass spectra were recorded in both the positive and negative spectral regions using a MALDI-TOF-MS Bruker Autoflex mass spectrometer in reflecto-mol mode. The ionization was induced by UV-laser with wavelength 336 nm. The sample was applied to a nickel plate, 2,5-dihydroxybenzoic acid and nitroaniline were used as the matrixes. The accuracy of measurements was 0.1%.

IR spectra of the solid samples (KBr tablets) in the range 400 – 4000 $cm^{-1}$ were recorded with a Perkin Elmer FT-IR Spectrum BX II spectrometer.

UV-vis spectra of the solutions in dichloromethane (5 ml) were recorded in the range 230 – 900 nm with a Lambda 9 Perkin Elmer spectrophotometer. The individual Gaussian components of these spectra were calculated using the SPECTRA program.

$^1H$ and $^{13}C\{^1H\}$ NMR spectra of the complexes obtained were recorded from their $CD_2Cl_2$ solutions using a Bruker Avance 600 FT-spectrometer.

*Syntheses*

**$FeBd_2(Br_2Gm)(BF)_2$ (2)**.

$BF_3 \bullet O(C_2H_5)_2$ (7.1 ml, 56 mmol) was dissolved in nitromethane (30 ml) and triethylamine (5.8 ml, 42 mmol) was added dropwise to this stirring solution under argon. Then complex **1** (10 g, 14 mmol) and dibromoglyoxime (3.66 g, 15 ml) were added to the stirring reaction mixture. The red solution / suspension

obtained was intensively stirred and heated with partial distillation of a solvent (approximately 25 ml) for 30 min; the reaction course was controlled by TLC (eluent: dichloromethane – hexane 2:1 mixture). The reaction mixture was then cooled to room temperature and the precipitate formed was filtered off. The solid product was washed with methanol (75 ml, in three portions), diethyl ether (40 ml, in two portions) and hexane (20 ml), and extracted with dichloromethane. The filtered extract was evaporated to dryness, the solid residue was washed with hexane (20 ml) and dried *in vacuo*. Yield: 9.1 g (78%).

**$\{FeBd_2((BrGm)(BF)_2\}_2$ (3)**.

Complex $FeBd_2(Br_2Gm)(BF)_2$ (**2**) (3.01 g, 3.6 mmol) was dissolved/suspended in HMPA (30 ml) at 100°C and $[Cu(CH_3CN)_4](BF_4)$ (4.54 g, 14.4 mmol) was portionally added for 20 min to the stirring reaction mixture under argon; the reaction course was controlled by TLC (eluent: dichloromethane – hexane 3:1 mixture). Then the reaction mixture was cooled to room temperature and precipitated with 2% aqueous hydrochloric acid. The precipitate formed was filtered off, washed with methanol and dissolved in dichloromethane (30 ml). The solution was dried with $Na_2SO_4$, filtered through silica gel Silasorb SPH-300 (30-mm layer, eluent: dichloromethane) and precipitated with hexane (70 ml). The precipitate was filtered off, washed with methanol and diethyl ether, and dried *in vacuo*. Yield: 2.01 g (74%).

**$\{FeBd_2(((CH_2)_5N)Gm)(BF)_2\}_2$ (4)**

Complex $\{FeBd_2(BrGm)(BF)_2\}_2$ (**3**) (0.060 g, 0.04 mmol) was dissolved in DMSO (2.5 ml) at 70°C, and piperidine (0.027 g, 0.3 mmol) was added to the stirring reaction mixture under argon. The reaction mixture was stirred for 4 h and then precipitated with 4% aqueous KCl solution (20 ml). The precipitate formed was filtered off, washed with water, methanol and diethyl ether, and dried *in vacuo*. Yield: 0.058 g (95%).

**{$FeBd_2$(*meta*-$HOOCC_6H_4SGm$)$(BF)_2$}$_2$ (5)**

Complex **3** (0.43 g, 0.28 mmol) and *meta*-mercaptobenzoic acid (0.13 g, 8.4 mmol) were dissolved in DMF (7 ml), and triethylamine (0.45 ml, 3.2 mmol) was added dropwise to the stirring reaction mixture under argon. The reaction mixture was stirred for 30 min and then precipitated with mixed 2% HCl and 4% KCl aqueous solution (100 ml). The precipitate formed was filtered off, washed with water, methanol and diethyl ether, and dried *in vacuo*. Yield: 0.43 g (92%).

**{$FeBd_2$(*para*-$HOOCC_6H_4SGm$)$(BF)_2$}$_2$ (6)**

Complex **3** (0.20 g, 0.13 mmol) and *para*-mercaptobenzoic acid (0.06 g, 0.39 mmol) were dissolved in DMF (4 ml), and triethylamine (0.09 ml, 0.65 mmol) was added dropwise to the stirring reaction mixture under argon. The reaction mixture was stirred for 30 min and then precipitated with mixed 2% HCl and 4% KCl aqueous solution (50 ml). The precipitate formed was filtered off, washed with water and methanol, and dried *in air*. The solid was dissolved/suspended in dichloromethane (35 ml) and precipitated with diethyl ether (70 ml). The precipitate was washed with diethyl ether and hexane, and dried *in vacuo*. Yield: 0.185 g (94%).

**{$FeBd_2$($NH_2Gm$)$(BF)_2$}$_2$ (7)**

Complex **3** (0.25 g, 0.17 mmol), THF (2 ml) and liquid ammonia (2 ml) were placed in 7 ml-volume steel autoclave at – 40°C. The reaction mixture was autoclaved at 70°C for 2 h, then cooled to – 40°C and evaporated to dryness. The solid residue was dissolved in dichloromethane, the solution was filtered through a silica gel (Silasorb SPH-300, 30-mm layer, eluent: dichloromethane) and precipitated with hexane. The precipitate formed was filtered off, washed with methanol and dried *in vacuo*. Yield: 0.11 g (47%).

**{$FeBd_2$($CH_3O(CH_2)_2NHGm$)$(BF)_2$}$_2$ (8)**

Complex **3** (0.60 g, 0.04 mmol) was dissolved in DMF (3 ml), and 2-methoxyethylamine (0.10 ml, 1.3 mmol) was added to the stirring reaction mixture under argon. The reaction mixture was stirred for 24 h and then precipitated with 0.5% aqueous HCl solution (30 ml). The precipitate formed was extracted with chloroform, the extract was evaporated to a small volume (~ 2 ml) and precipitated with hexane. The precipitate was filtered off, washed with diethyl ether and hexane, and dried *in vacuo*. Yield: 0.033 g (55%).

**X-ray crystallography.**

Single crystals of the complexes **2** · $CH_2Cl_2$, **3** · 3 $C_6H_6$ and **4** · 5 $C_6H_6$ were grown from dichloromethane – hexane and benzene – isooctane mixtures, respectively, at room temperature. The intensities of reflections were measured at 100(2) K with a Bruker Apex II CCD diffractometer using graphite monochromated Mo – Kα radiation ($\lambda$ = 0.71073 Å). Transmission coefficients were determined using SADABS program[3]. The structures were solved by the direct method and refined by full-matrix least squares against $F^2$. Non-hydrogen atoms were refined in anisotropic approximation except disordered species, namely the solvate molecule in the clathrochelate **2** · $CH_2Cl_2$, the carbon atoms of one disordered phenyl group and those of all the solvate molecules in the crystal **4** · 5 $C_6H_6$. The solvate molecule in the crystal **2** · $CH_2Cl_2$ and one of the phenyl groups in the molecule **4** are disordered over two sites with site occupations 0.4 : 0.6 and 0.3 : 0.7, respectively. The best available crystal of the clathrochelate **4** · 5 $C_6H_6$ had a very weak reflection ability of the single crystal that was obtained in a form of needles; thus, a number of restraints were applied to refine the geometry of the structure correctly. The C – C distance at the C38s atom and the N – C distance at the N13 atom were fixed at 1.49 and 1.42 Å, and thermal ellipsoids of a number of the atoms were restricted so that their $U_{ij}$ components approximate to isotropic behavior. Positions of the hydrogen atoms were calculated geometrically. The H(C) atoms were included in the refinement by the

riding model with $U_{iso}$(H) = $nU_{eq}$(C), where $n$ = 1.5 for methyl groups and 1.2 for the other atoms.

All calculations were made using the SHELXTL PLUS 5 program package[4]. The crystallographic data and experimental details are listed in Table SI1. CCDC 889585 – 889587 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/conts/retrieving.html.

*Computational methods*

The docking study was performed using AutoDock VINA package[5]. The structure of T7 RNA polymerase transcription complexes with PDB code 1S77 was taken from Protein Data Bank and prepared for the docking calculations using the GUI ADT (v.1.5.4)[6]. Since the binding site was not known, the grid size was chosen to cover all the surface of the transcription complex. Default docking parameters were used, and modifications in the exhaustiveness of the search did not change the results significantly. The docking results were clustered on the basis of the RMSD between the coordinates of the atoms, and the conformers with the best scores were chosen for speculation regarding the detailed binding patterns. The molecular representations were generated using PyMol software[7].

**Analytical and Spectral Data**

**2.** *Anal*. calc. for $C_{30}H_{20}N_6O_6B_2F_2Br_2Fe$ (%): C, 43.11; H, 2.41; N, 10.06; Fe, 6.68; Br, 19.12. Found (%):C, 43.04; H, 2.35; N, 10.13; Fe, 6.77; Br, 18.91. MS (MALDI-TOF): *m/z*(I, %) (positive range) 676(15) $[ M - 2Br]^{+\bullet}$, 836(100) $[ M ]^{+\bullet}$, 859(20) $[ M + Na^+ ]^+$, 875(10) $[ M + K^+ ]^+$; (negative range) – 836 $[ M ]^{-\bullet}$. $^1$H NMR ($CD_2Cl_2$) δ (ppm): 7.32 (m, 20H, Ph). $^{13}C\{^1H\}$ NMR ($CD_2Cl_2$) $\delta$ (ppm): 123.41 (s, BrC=N), 127.98, 130.05, 130.44, 130.80 (all s, Ph), 157.46 (PhC=N). IR (KBr), ν/cm$^{-1}$ 914, 1000, 1066 ν(N – O), 1219m ν(B – O) + ν(B – F), 1546 ν(BrC = N), 1579 ν(PhC = N). UV-vis ($CH_2Cl_2$): $\lambda_{max}$/nm (ε ·10$^{-3}$ mol$^{-1}$·L·cm$^{-1}$) 264(28), 285(6.2), 299(10), 329(3.4), 386(3.5), 440(3.4), 470(30).

**3** *Anal*. calc. for $C_{60}H_{40}N_{12}O_{12}B_4F_4Br_2Fe_2$ (%): C, 47.63; H, 2.64; N, 10.06; Fe, 7.40. Found (%): C, 47.54; H, 2.70; N, 10.00; Fe, 7.23. MS (MALDI-TOF): *m/z*(I, %) (positive range, matrix: DHB) 1512(5) $[ M ]^{+\bullet}$, 1523(100) $[ M + Na^+ ]^+$, 1551(25) $[ M + K^+ ]^+$, 1597(70) $[ M + Rb^+ ]^+$, 1645(100) $[ M + Cs^+ ]^+$; (negative range, matrix: nitroaniline) – 1512 $[ M ]^{-\bullet}$. $^1$H NMR ($CD_2Cl_2$) δ (ppm): 7.26 (m, 40H, Ph). $^{13}C\{^1H\}$ NMR ($CD_2Cl_2$) δ (ppm): 119.58 (s, BrC=N), 128.30, 128.19, 128.12, 128.10 (all s, *m*-Ph), 128.99, 128.91, 128.84, 128.81 (all s, *ipso*-Ph), 130.63, 130.57, 130.50 (all s, *p*-Ph), 130.78, 130.72, 130.67 (all s, *o*-Ph), 157.92, 157.85, 157.82, 157.44 (all s, PhC=N). IR (KBr), ν/cm$^{-1}$ 932m, 1066, 1110, 1142 ν(N – O), 1219m ν(B – O) + ν(B – F), 1549m ν(BrC = N) + ν(C – C = N), 1581 ν(PhC = N). UV-vis ($CH_2Cl_2$): $\lambda_{max}$/nm (ε · 10$^{-3}$ mol$^{-1}$·L·cm$^{-1}$) 239(33), 263(21), 282(18), 301(12), 388(7.0), 435(9.8), 461(18), 509(25).

**4** *Anal*. calc. for $C_{70}H_{60}N_{14}O_{12}B_4F_4Fe_2$ (%): C, 55.30; H, 3.98; N, 12.90; Fe, 7.35. Found (%): C, 55.48; H, 3.83; N, 12.80; Fe, 7.24. MS (MALDI-TOF): *m/z*(I, %) 1521(100) $[ M ]^{+\bullet}$, 1544(55) $[ M + Na^+ ]^+$, 1560(75) $[ M + K^+ ]^+$. $^1$H NMR ($CD_2Cl_2$) δ (ppm): 1.44 (m, 8H, β-piperidine), 2.42 (m, 4H, γ-piperidine), 3.30 (m, 8H, α-

piperidine), 7.11 (m, 4H, Ph), 7.16 (m, 4H, Ph), 7.25 (m, 4H, Ph), 7.37 (m, 4H, Ph). $^{13}C\{^{1}H\}$ NMR ($CD_2Cl_2$) δ (ppm): 23.68 (s, γ-piperidine), 26.23 (s, β-piperidine), 50.99 (s, α-piperidine), (s, BrC=N), 128.11, 128.09, 127.96, 127.92 (all s, *m*-Ph), 129.28, 129.14, 129.11, 129.03 (all s, *ipso*-Ph), 130.30, 130.21, 130.11 (all s, *p*-Ph), 130.83, 130.69, 130.58, 130.38 (all s, *o*-Ph), 143.80 (s, N=C-C=N), 152.48 (s, N-C=N), 158.43, 157.73, 156.91, 156.68 (all s, PhC=N). IR (KBr), ν/cm$^{-1}$ 923, 941, 992, 1061, 1110, 1133, 1152, 1182 ν(N – O), 1211m ν(B – O) + ν(B – F), 1589m ν(C = N). UV-vis ($CH_2Cl_2$): $\lambda_{max}$/nm (ε · $10^{-3}$ mol$^{-1}$·L·cm$^{-1}$) 253(41), 266(4.3), 288(31), 310(10), 399(7.0), 477(12), 489(21), 545(18).

**5** *Anal*. calc. for $C_{64}H_{50}N_{12}O_{16}B_4F_4S_2Fe_2$ (%): C, 53.60; H, 3.05; N, 10.14. Found (%): C, 53.49; H, 3.15; N, 10.06. MS (MALDI-TOF): *m/z*(I, %) (positive range) 1599(35) [ M – $COO^-$ – O ]$^+$, 1643(95) [ M – O ]$^{+\bullet}$, 1659(100) [ M ]$^{+\bullet}$, 1682(70) [ M + $Na^+$ ]$^+$, 1698(6) [ M + $K^+$ ]$^+$; (negative range) – 1506(20) [ M – $HCOOC_6H_4S$ ]$^{-\bullet}$, – 1659(100) [ M ]$^{-\bullet}$. $^{1}H$ NMR ($CD_2Cl_2$) δ (ppm): 7.09 (m, 8H, Ph), 7.16 (m, 4H, $C_6H_4$), 7.21 (m, 16H, Ph), 7.29 (m, 16H, Ph), 7.63 (m, 4H, $C_6H_4$). $^{13}C\{^{1}H\}$ NMR ($CD_2Cl_2$) δ (ppm): 128.13, 127.98, 127.96 (all s, *m*-Ph), 128.24, 128.28 (s, $C_6H_4$), 129.15, 129.08, 129.01 (all s, *ipso*-Ph), 130.25, 130.18, 130.00, 129.77 (all s, *p*-Ph), 130.91, 130.69, 130.44 (all s, *o*-Ph), 133.24, 133.17, 133.04 (all s, $C_6H_4$), 139.44 (s, S-C=N), 145.45 (s, N=C-C=N), 156.71, 156.83, 156.90, 157.35 (all s, PhC=N), 169.61 (s, COOH). IR (KBr), ν/cm$^{-1}$ 928, 1066, 1109, 1147 ν(N – O), 1218m ν(B – O) + ν(B – F), 1554 ν(C – C = N) + ν(SC = N), 1595 ν(PhC = N). UV-vis ($CH_2Cl_2$): $\lambda_{max}$/nm, (ε·$10^{-3}$ mol$^{-1}$·L·cm$^{-1}$) 245(42), 270(28), 296(21), 358(6.8), 442(14), 465(17), 519(11), 526(16).

**6** *Anal*. calc. for $C_{64}H_{50}N_{12}O_{16}B_4F_4S_2Fe_2$ (%): C, 53.60; H, 3.05; N, 10.14. Found (%): C, 53.60; H, 3.09; N, 10.16; Fe. MS (MALDI-TOF): *m/z*(I, %) (positive range) 1599(30) [ M – $COO^-$ – O ]$^+$, 1643(90) [ M – O ]$^{+\bullet}$, 1659(100) [ M ]$^{+\bullet}$, 1682(50)

[ M + $Na^+$ ]$^+$, 1698(35) [ M + $K^+$ ]$^+$; (negative range) – 1586(90) [ M – COOH – CO ]$^{-\bullet}$, – 1659(100) [ M ]$^{-\bullet}$. $^1$H NMR ($CD_2Cl_2$) δ (ppm): 6.50 (d, 4H, $C_6H_4$), 7.18 (d, 4H, $C_6H_4$), 7.22 (m, 8H, Ph), 7.29 (m, 16H, Ph), 7.38 (m, 16H, Ph). $^{13}$C{$^1$H} NMR ($CD_2Cl_2$) δ (ppm): 124.28 (s, $C_6H_4$), 127.13 (s, $C_6H_4$), 128.07, 128.13, 128.42, 128.54 (all s, *m*-Ph), 128.67, 128.74, 128.83 (all s, *ipso*-Ph), 130.19, 130.39, 130.67 (all s, *o*-Ph), 130.55, 130.91, 130.99 (all s, *p*-Ph), 138.92 (s, $C_6H_4$), 139.13 (s, S-C=N), 144.60 (s, N=C-C=N), 156.94, 157.59, 157.76, 157.83 (all s, PhC=N), 171.58 (s, COOH). IR (KBr), ν/$cm^{-1}$ 930, 1068, 1110, 1144 ν(N – O), 1218m ν(B – O) + ν(B – F), 1554 ν(C – C = N) + ν(SC = N), 1593 ν(PhC = N). UV-vis ($CH_2Cl_2$): $\lambda_{max}$/nm, (ε·$10^{-3}$ $mol^{-1}$·L·$cm^{-1}$) 238(12), 269(35), 302(10), 362(4.7), 416(4.6), 458(15), 512(13), 530(5.8).

**7** *Anal*. calc. for $C_{60}H_{44}N_{14}O_{12}B_4F_4Fe_2$ (%): C, 52.07; H, 3.20; N, 14.17. Found (%):C, 51.96; H, 3.10; N, 14.12. MS (MALDI-TOF): *m/z*(I, %) (positive range) 1337(10) [ M – O – 2$NH_2$ ]$^{+\bullet}$, 1369(75) [ M – $NH_2$ ]$^{+\bullet}$, 1385(100) [ M ]$^{+\bullet}$, 1408(35) [ M + $Na^+$ ]$^+$, 1424(40) [ M + $K^+$ ]$^+$; (negative range) – 1369(90) [ M – $NH_2$ ]$^{-\bullet}$, – 1385(100) [ M ]$^{-\bullet}$. $^1$H NMR ($CD_2Cl_2$) δ (ppm): 5.83 (d, 4H, $NH_2$), 7.27 (m, 40H, Ph). $^{13}$C{$^1$H} NMR ($CD_2Cl_2$) δ (ppm): 128.26, 128.12, 128.06 (all s, *m*-Ph), 129.16, 129.09, 129.02, 128.96 (all s, *ipso*-Ph), 130.52, 130.37, 130.35 (all s, *p*-Ph), 130.74, 130.64, 130.58, 130.49 (all s, *o*-Ph), 139.01 (s, N-C=N), 149.97 (s, N=C-C=N), 158.59, 156.45, 156.41 (all s, PhC=N). IR (KBr), ν/$cm^{-1}$ 930, 1059, 1108, 1159 ν(N – O), 1213m ν(B – O) + ν(B – F), 1545 ν(C – C = N) + ν(NC = N), 1580m ν(PhC = N), 1638 δ(N – H), 3377 ν(N – H). UV-vis ($CH_2Cl_2$): $\lambda_{max}$/nm (ε ·$10^{-3}$ $mol^{-1}$·L·$cm^{-1}$) 264(27), 285(10), 296(18), 323(9.0), 382(6.4), 442(8.7), 478(20), 508(14), 568(18), 598(5.8).

**8** *Anal*. calc. for $C_{66}H_{56}N_{14}O_{14}B_4F_4Fe_2$ (%): C, 52.84; H, 3.76; N, 13.07. Found (%):C, 52.66; H, 3.88; N, 12.92. MS (MALDI-TOF): *m/z*(I, %) (positive range) 1485(30) [ M – O ]$^{+\bullet}$, 1501(100) [ M ]$^{+\bullet}$, 1524(35) [ M + $Na^+$ ]$^+$, 1540(25)

$[ M + K^+ ]^+$. $^1H$ NMR ($CD_2Cl_2$) δ (ppm): 3.15 (s, 6H, $CH_3$), 3.15 (m, 8H, $CH_2CH_2$), 7.23 (m, 40H, Ph). $^{13}C\{^1H\}$ NMR ($CD_2Cl_2$) δ (ppm): 46.20 (s, $NCH_2$), 60.72 (s, $CH_3$), 73.58 (s, $OCH_2$), 130.06, 130.00, 129.93 (all s, *m*-Ph), 131.32, 131.28, 131.21, 131.19 (all s, *ipso*-Ph), 132.21, 132.17, 132.09, 132.01 (all s, *p*-Ph), 132.67, 132.59, 132.56, 132.46 (all s, *o*-Ph), 141.72 (s, N-C=N), 152.54 (s, N=C-C=N), 159.98, 159.77, 158.92, 158.25 (all s, PhC=N). UV-vis ($CH_2Cl_2$): $\lambda_{max}$/nm ($\varepsilon \cdot 10^{-3}$ $mol^{-1} \cdot L \cdot cm^{-1}$) 251(28), 276(34), 292(8.4), 357(9.1), 427(9.0), 474(140), 500(22), 555(12), 645(4.1).

***In vitro transcription assay.*** The *in vitro* assay with the T7 RNA polymerase was performed using the Fermentas transcription protocol optimized for a screening of the inhibitors[8]. The reaction mixture (20 μl) contained the linearized DNA template (0.5 μg of pTZ19R plasmid with a 341 bp insert cloned in the Ecl136II site), ribonucleoside triphosphate (2 mM), ribonuclease inhibitor (10 U), T7 RNA polymerase (12 U) in the presence of Tris-HCl (40 mM, pH 7.9), $MgCl_2$ (6 mM), spermidine (2 mM), NaCl (10 mM) and dithiothreitol (10 mM). The solution of a compound under study in DMSO was added to the reaction mixture, and this mixture was incubated at 37ºC for 1 h. Then the reaction was stopped by cooling up to – 20ºC, and the products were separated by an electrophoresis in 1.2% agarose gel in TBE buffer supplemented with ethidium bromide (0.5 $\mu g \cdot ml^{-1}$) and visualized using a standard UV-transilluminator. The stained gels were photographed with a FujiFilm FinePix S5600 digital camera, and the images were processed with a TotallLab 1.10 and Origin 7 software. The 50% inhibitory concentration values ($IC_{50}$) were obtained from a plot of the compound concentration *versus* a percent of the synthesized RNA transcript compared with that of the control reaction (no inhibitor added). At least three independent experiments were carried out for each complex studied at each concentration.

**Table SI1.** Crystallographic data and experimental details for the complexes **2** · $CH_2Cl_2$, **3** · 3 $C_6H_6$ and **4** · 5 $C_6H_6$.

| | **2** · $CH_2Cl_2$ | **3** · 3 $C_6H_6$ | **4** · 5 $C_6H_6$ |
|---|---|---|---|
| Empirical formula | $C_{31}H_{22}B_2Br_2F_2FeN_6O_6Cl_2$ | $C_{78}H_{58}B_4Br_2F_4Fe_2N_{12}O_{12}$ | $C_{100}H_{90}B_4F_4Fe_2N_{14}O_{12}$ |
| Formula weight | 920.74 | 1746.12 | 1910.80 |
| Crystal size (mm) | 0.32 × 0.15 × 0.13 | 0.22 × 0.10 × 0.08 | 0.28 × 0.06 × 0.05 |
| *a* (Å) | 13.913 (2) | 28.3891 (12) | 12.040 (7) |
| *b* (Å) | 17.521 (2) | 28.3891 (12) | 19.399 (12) |
| *c* (Å) | 16.0443 (17) | 18.8932 (17) | 23.44 (2) |
| α (°) | 90 | 90 | 107.911 (13) |
| β (°) | 96.463 (4) | 90 | 96.646 (13) |
| γ (°) | 90 | 90 | 105.862 (9) |
| *V* (Å$^3$) | 3886.1 (9) | 15226.8 (16) | 4891 (6) |
| *Z* | 4 | 8 | 2 |
| Crystal system | monoclinic | tetragonal | triclinic |
| Space group | $P2_1/n$ | $I4_1/a$ | $P\bar{1}$ |
| $D_{cal}$ (g cm$^{-3}$) | 1.574 | 1.523 | 1.299 |
| μ (mm$^{-1}$) | 2.64 | 1.51 | 0.37 |
| Min / max transmis. coef. | 0.630 / 0.705 | 0.832 / 0.889 | 0.974 / 0.980 |
| Reflections collected | 57472 | 82003 | 41467 |
| Independent reflections ($R_{int}$) | 9354 (0.030) | 8696 (0.145) | 17181 (0.141) |
| Reflections with [$I > 2\sigma(I)$] | 7867 | 4872 | 4953 |
| $R[F^2 > 2\sigma(F^2)]$ | 0.067 | 0.048 | 0.119 |
| $wR(F^2)$ | 0.195 | 0.103 | 0.289 |
| *S* | 1.00 | 1.00 | 1.02 |
| No. of parameters | 468 | 454 | 914 |
| No. of restraints | 4 | 0 | 543 |
| Weighting scheme | $w = 1/[\sigma^2(F_o^2) + (0.1P)^2 + 25.P]$, $P = (F_o^2 + 2F_c^2)/3$ | $w = 1/[\sigma^2(F_o^2) + (0.035P)^2 + 1.8P]$, $P = (F_o^2 + 2F_c^2)/3$ | $w = 1/[\sigma^2(F_o^2) + (0.060P)^2 + 10.P]$, $P = (F_o^2 + 2F_c^2)/3$ |
| Largest diff. peak and hole (e Å$^{-3}$) | 2.71 and – 1.64 | 1.05 and – 1.11 | 1.30 and – 1.25 |

**Table SI2**. Main geometrical parameters of the clathrochelates **2** – **4**.

| Parameter | **2** | **3** | **4**[a] |
|---|---|---|---|
| Fe – $N_{1,3,5}$ (Å) | 1.917(4)[b], 1.904(4), 1.904(4) | 1.893(3)[b], 1.896(3), 1.903(3) | 1.927(9) / 1.850(10)[b], 1.831(9) / 1.855(10), 1.836(9)[b] / 1.928(9) |
| Fe – $N_{2,4,6}$ (Å) | 1.921(4)[b], 1.910(4), 1.910(4) | 1.876(3)[b], 1.890(3), 1.899(3) | 1.829(9) / 1.925(9), 1.880(9) / 1.901(9), 1.947(10) / 1.896(9) |
| | *av.* 1.911 | *av.* 1.893 | *av.* 1.875 / 1.893 |
| $\varphi$ (°) | 22.5 | 27.7 | 27.8 / 26.3 |
| $\alpha$ (°) | 39.4 | 39.3 | 38.9 / 39.2 |
| *h* (Å) | 2.33 | 2.29 | 2.24 / 2.29 |

[a] Bis-clathrochelate molecule **4** contains two independent cage moieties; their parameters are divided by slash. The N(7) – N(12) atoms correspond to the N(1) – N(6) atoms, respectively.

[b] The distances for the functionalized ribbed fragments.

**Table SI3.** The UV-vis spectra ($\lambda_{max}$/nm, $\varepsilon \cdot 10^{-3}$ mol$^{-1}$·L·cm$^3$) of the macrobicyclic precursor **3**, its bis-clathrochelate derivatives **4** – **8** and their monoclathrochelate analogs

| | $\lambda_1$ | $\lambda_2$ | $\lambda_3$ | $\lambda_4$ | $\lambda_5$ | $\lambda_6$ | $\lambda_7$ | $\lambda_8$ | $\lambda_9$ | $\lambda_{10}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| **2** | 264(28) | 285(6.2) | 299(10) | 329(3.4) | 386(3.5) | 440(3.4) | 470(30) | | | |
| **3** | 239(33) | 263(21) | 282(18) | 301(12) | 388(7.0) | 435(9.8) | 461(18) | 509(25) | | |
| **4** | 253(41) | 266(4.3) | 288(31) | 310(10) | 399(7.0) | 477(12) | 489(21) | 545(18) | | |
| **5** | 245(42) | 270(28) | 296(21) | 358(6.8) | | 442(14) | 465(17) | 519(11) | 526(16) | |
| **6** | 238(12) | 269(35) | 302(10) | 362(4.7) | | 416(4.6) | 458(15) | 512(13) | 530(5.8) | |
| **7** | 264(27) | 285(10) | 296(18) | 323(9.0) | 382(6.4) | 442(8.7) | 478(20) | 508(14) | 568(18) | 598(5.8) |
| **8** | 251(28) | 276(34) | 292(8.4) | 357(9.1) | | 427(9.0) | 474(140) | 500(22) | 555(12) | 645(4.1) |
| $FeBd_4(NH_2)_2(BF)_2$* | 248(17) | 266(7.9) | 291(13) | 338(3.1) | 374(2.9) | 425(5.3) | 475(5.8) | 511(12) | 576(1.0) | |
| $FeBd_4$(S-*m*-$C_6H_4CO_2H)_2(BF)_2$* | 203(24) | 221(26) | 246(27) | 278(14) | 299(6.1) | 399(3.3) | 455(6.4) | 476(12) | 509(10) | |
| $FeBd_4$(S-*p*-$C_6H_4CO_2H)_2(BF)_2$* | 198(52) | 225(27) | 265(17) | 288(7.6) | 306(6.7) | 403(2.9) | 450(4.0) | 475(7.8) | 508(8.3) | |

* *data from [9]*

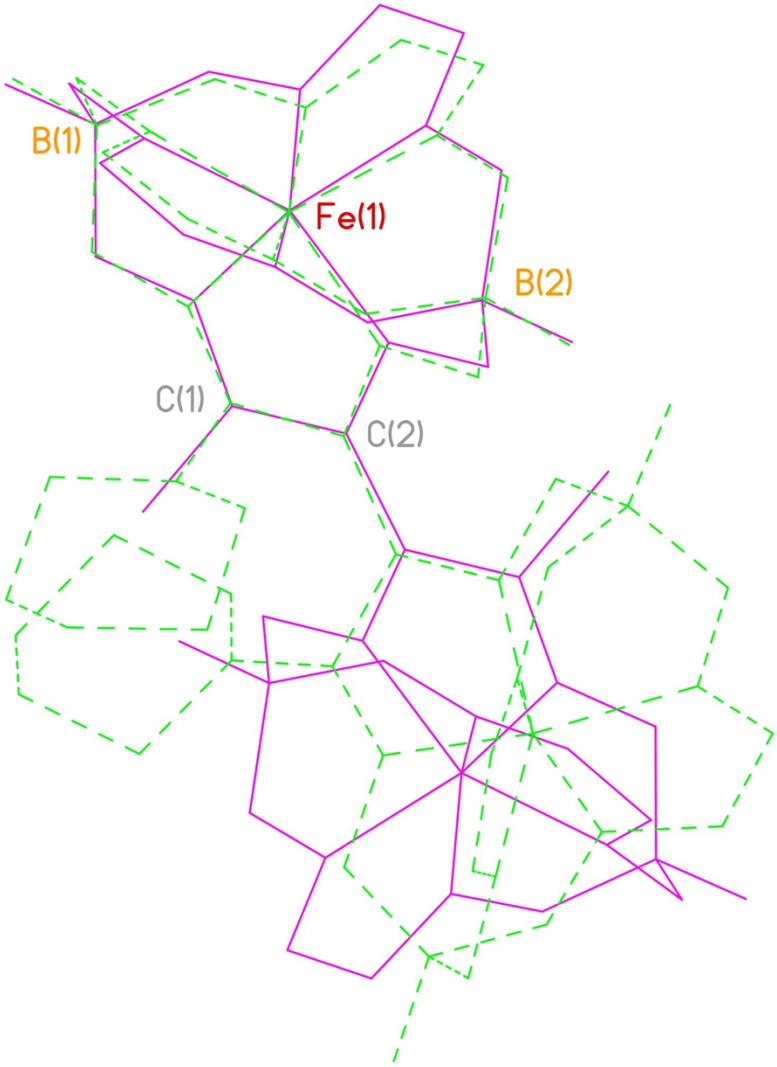


**Fig. SI1.** Comparisons of the molecular views of the bis-macrobicyclic frameworks **3** (red solid line) and **4** (green dashed line). Their superimposed atoms are Fe1, B1, B2, C1 and C2, and Fe1, B2, B1, C6 and C5, respectively.

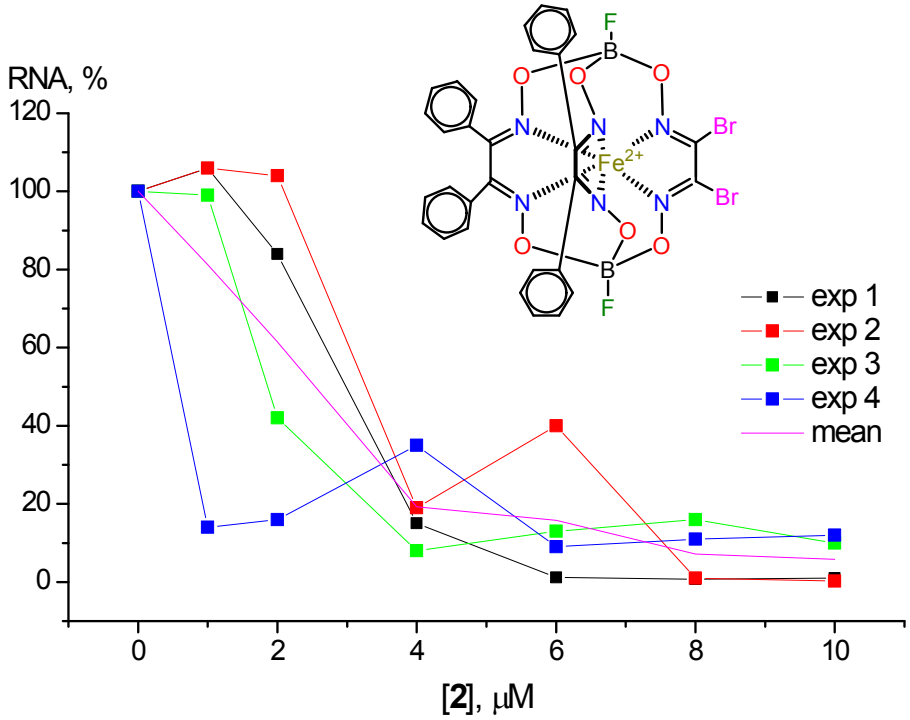


**Figure SI2.** Plot of T7 RNAP inhibitor activity of the monoclathrochelate precursor **2** *versus* its concentration.

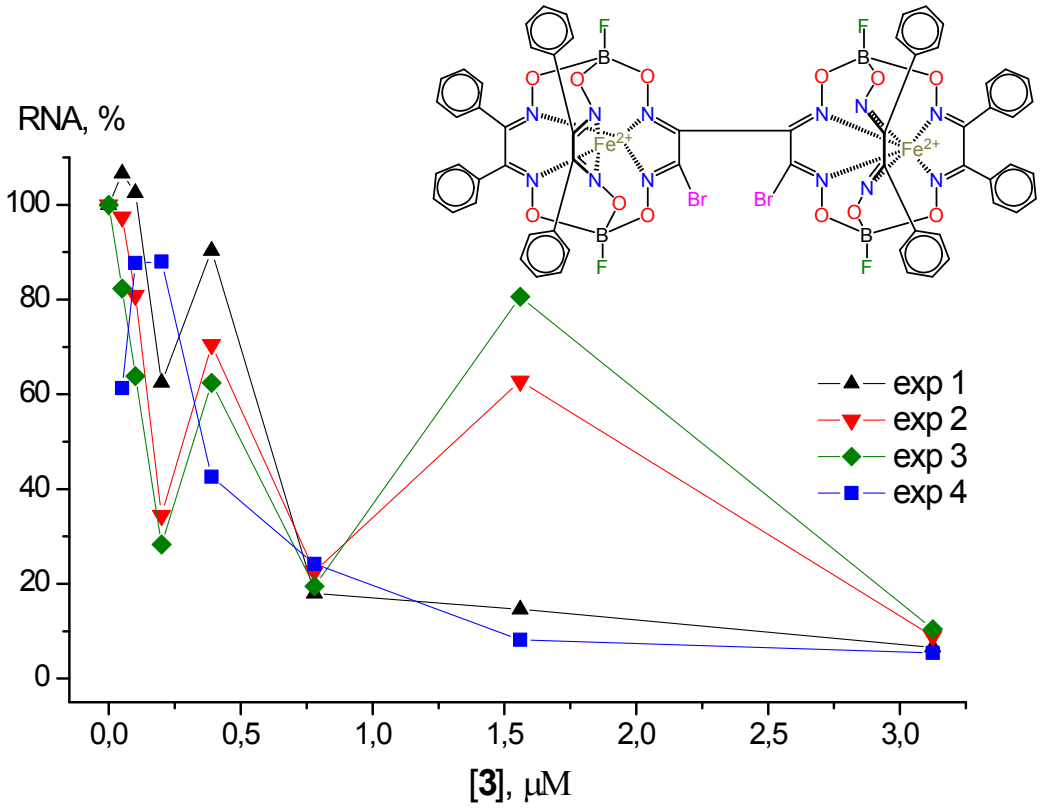


**Figure SI3.** Plot of T7 RNAP inhibitor activity of the bis-clathrochelate **3** *versus* its concentration.

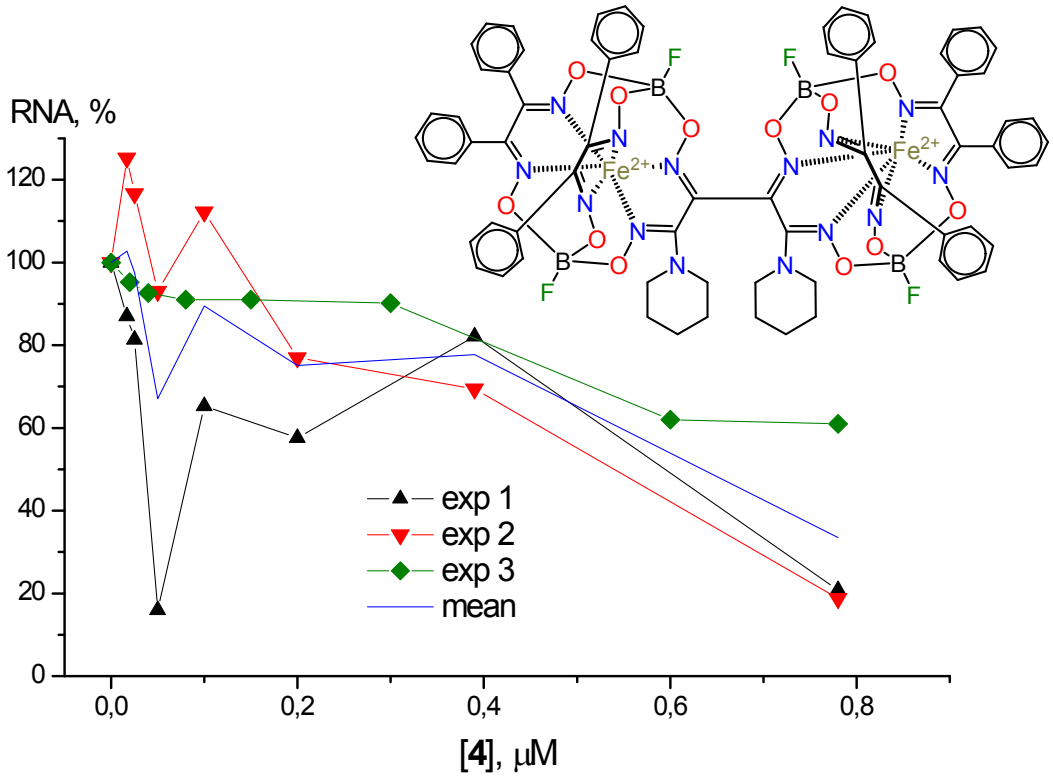


**Figure SI4.** Plot of T7 RNAP inhibitor activity of the bis-clathrochelate **4** *versus* its concentration.

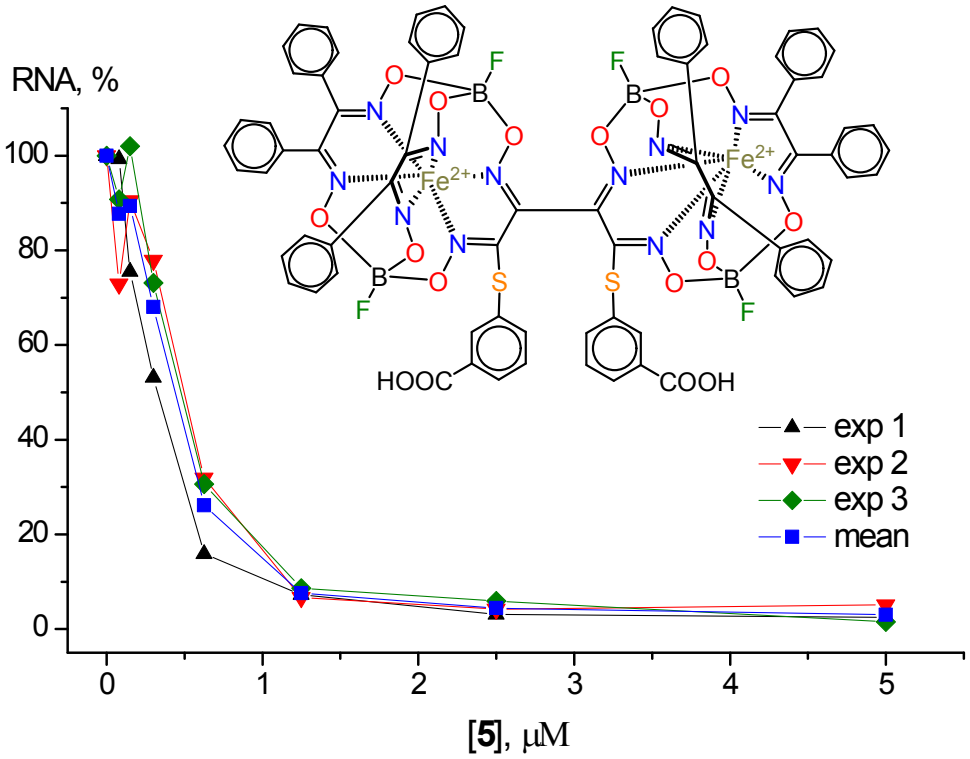


**Figure SI5.** Plot of T7 RNAP inhibitor activity of the bis-clathrochelate **5** *versus* its concentration.

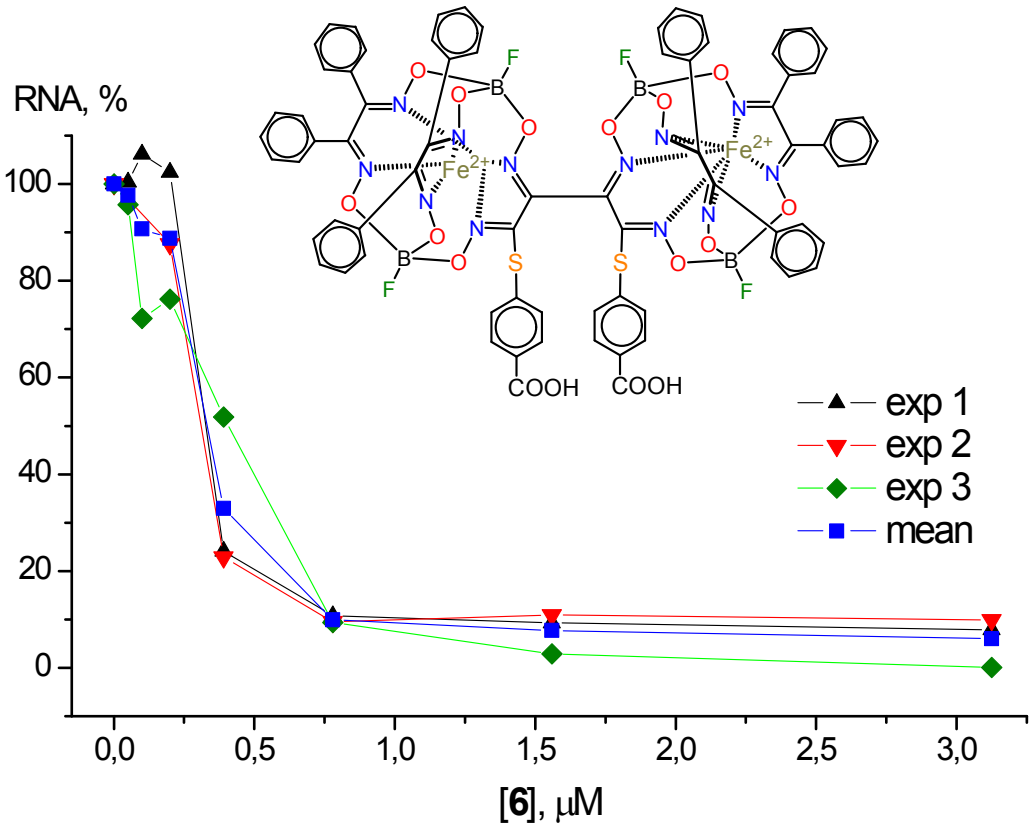


**Figure SI6.** Plot of T7 RNAP inhibitor activity of the bis-clathrochelate **6** *versus* its concentration.

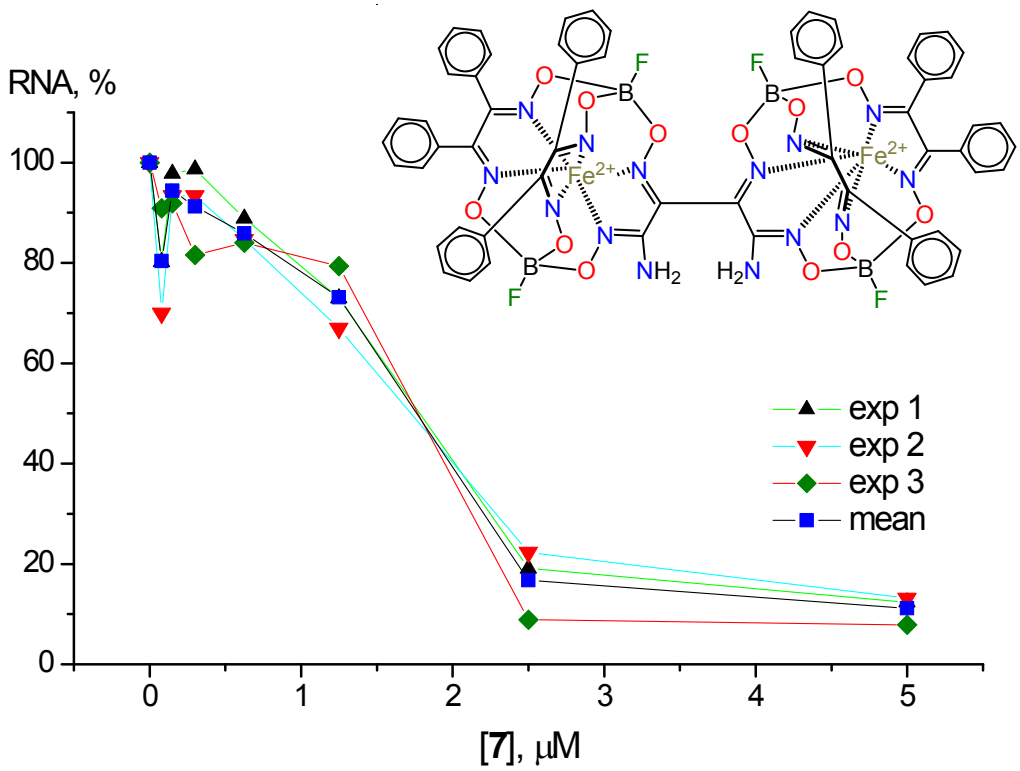


**Figure SI7.** Plot of T7 RNAP inhibitor activity of the bis-clathrochelate **7** *versus* its concentration.

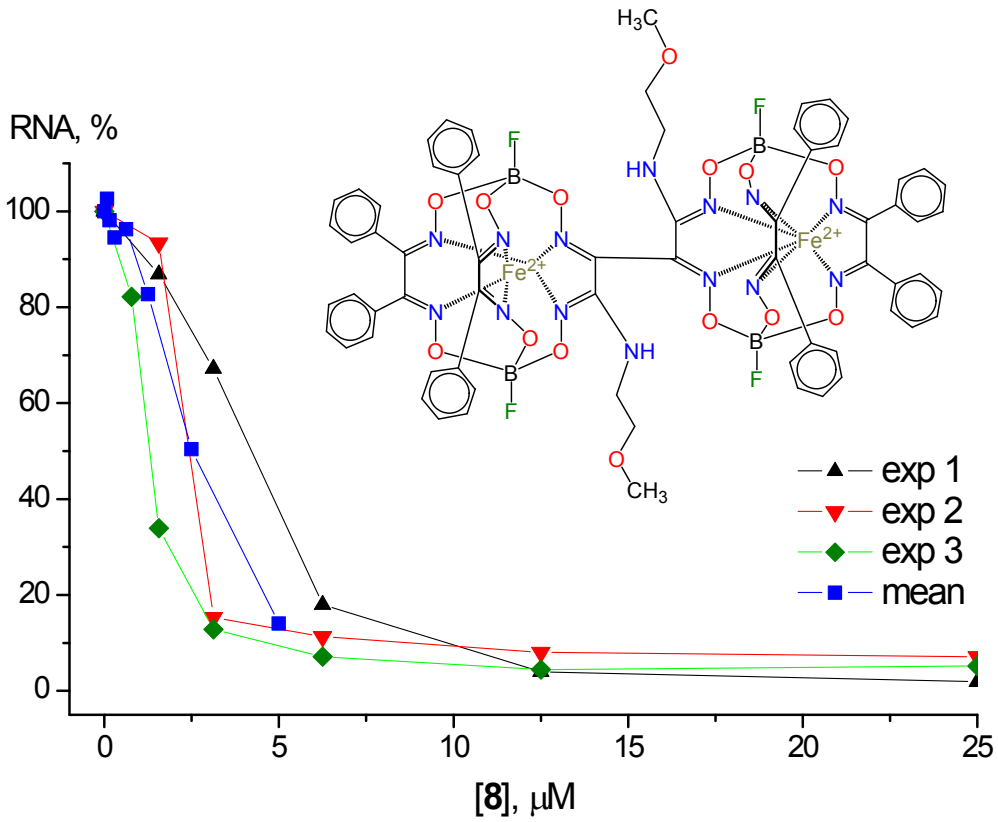


**Figure SI8.** Plot of T7 RNAP inhibitor activity of the bis-clathrochelate **8** *versus* its concentration.

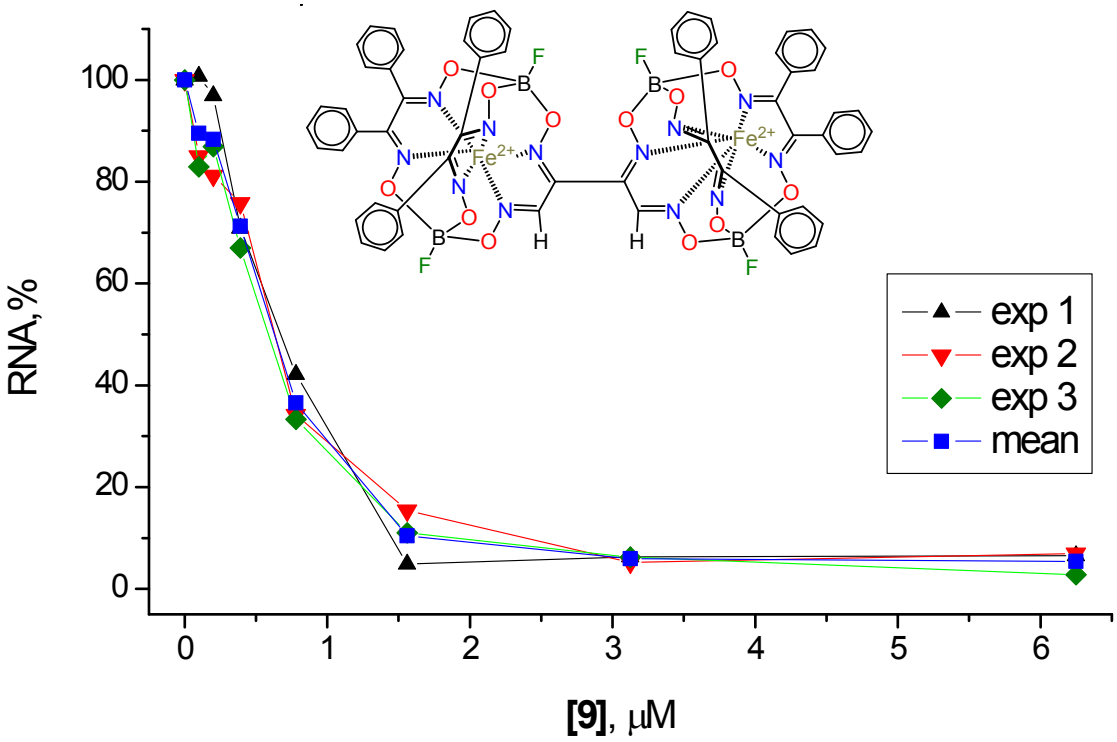


**Figure SI9.** Plot of T7 RNAP inhibitor activity of the bis-clathrochelate **9** *versus* its concentration.

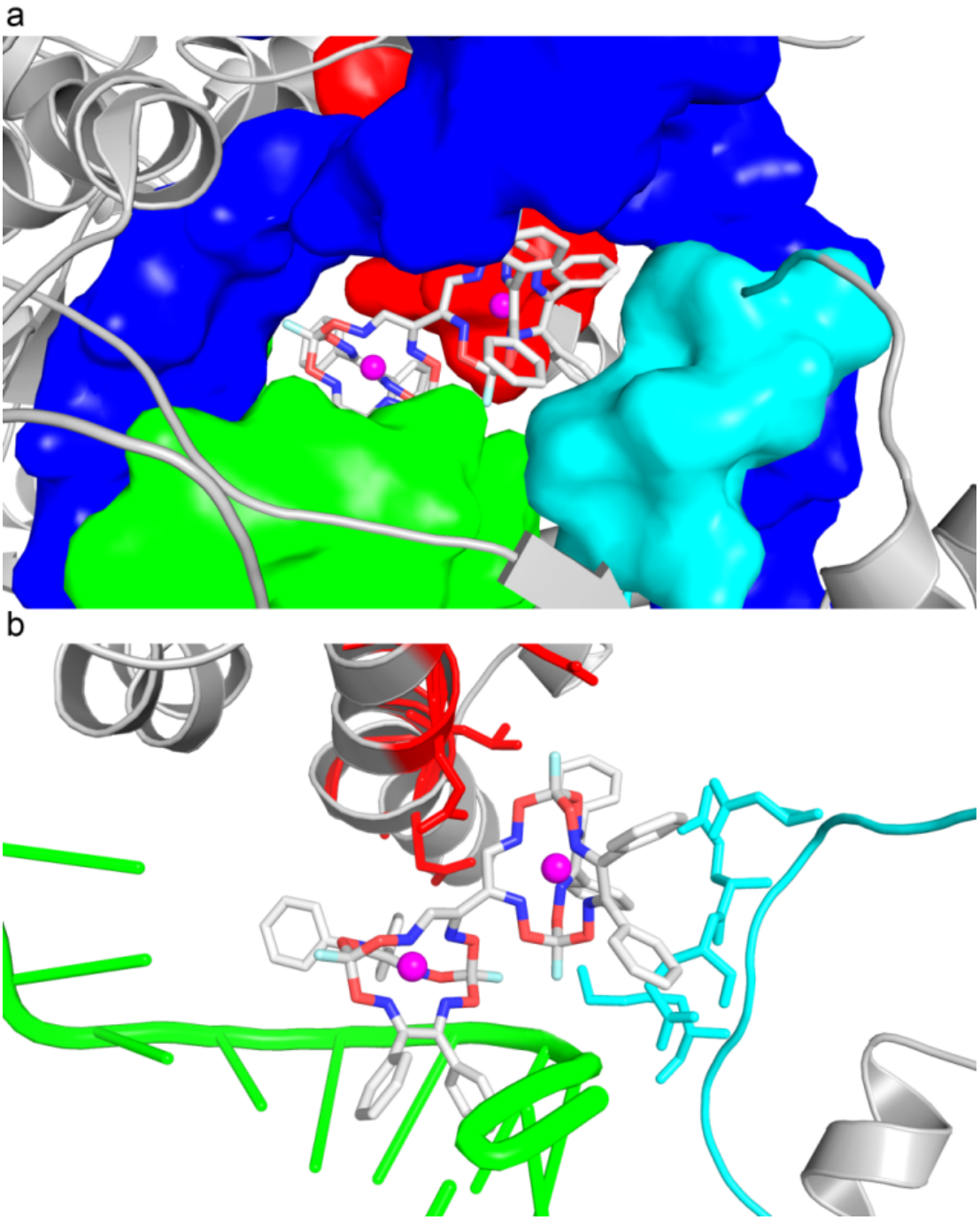


**Fig. S10**. Inhibition mode as predicted by molecular docking: (a) the best-scoring solution for the bis-clathrochelate **9** (DNA (blue) and RNA (green) are shown as surfaces); (b) the side view of the best docking solution for the complex **9** (DNA is not shown, helix is shown in red, loop in cyan).

## Supplementary Information references


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