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Coordination polymers derived from magnesium and barium complexes of redox-active ligands

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Experimental part

General information.

The starting materials **1a**,[S1] **1b** and **1b**·DME[S2] as well as the products **2a**, **2b**, **3a** and **3b** are sensitive to oxygen and air moisture, so all manipulations on their synthesis, isolation and identification were carried out in a vacuum using glass ampules. 4,4'-Bipyridine (Aldrich) was purified by sublimation. Tetrahydrofuran and 1,2-dimethoxyethane were dried over sodium benzophenone and distilled at low pressure just prior to use. The yields of the products **2a**, **2b** and **3b** were calculated from the starting amount of the dpp-bian, the yield of **3a** was calculated on the starting $[\{(\text{dpp-bian})\text{Mg}(4,4'\text{-bipy})(\text{THF})\}_4(\text{THF})]_m$. The IR spectra were obtained on a FSM-1201 instrument in mineral oil. The ^{1}H NMR spectra were obtained on Avance NEO 300 spectrometer. UV-Vis spectra were recorded on Perkin-Elmer Lambda 25 spectrometer in a Quartz 10 mm cuvette. The ESR spectra were recorded on Magnettech ESR5000 (9.48 GHz). The ESR signals of **3a** and **3b** were simulated using EasySpin (v. 5.2.28) software.[S3] Elemental analysis was performed on a Vario EL Cube analyzer. Thermal analysis in the temperature range 40-500 °C was carried out using a TGA/DSC 3+ METTLER TOLEDO instrument. The experiments were performed under N_2 flow (50 cm^3 min^{-1}) at a 5 K min^{-1} heating rate. The magnetic susceptibilities of polycrystalline samples **2a** and **2b** were measured with a Quantum Design MPMSXL SQUID magnetometer in the temperature range 2-300 K at 5 kOe. Diamagnetic corrections were made using the Pascal constants. The effective magnetic moment was calculated as $\mu_{eff}(T) = [(3k/N_A\mu_B^2)\chi T]^{1/2} \approx (8\chi T)^{1/2}$. Experimental dependencies of $\chi(T)$ have been analyzed by PHI[4] program using Spin Hamiltonian $H = -2\Sigma J_{ij}S_iS_j$.

$[\{(\text{dpp-bian})\text{Mg}(4,4'\text{-bipy})(\text{THF})\}\times 2.5(\text{THF})]_m$ (2a). To a green solution of [(dpp-bian)$Mg(THF)_3$] **1a** (prepared *in situ* from dpp-bian (0.50 g, 1.0 mmol) of and an excess of magnesium (2.4 g, 100 mmol)) in THF (40 ml), a solution of 4,4'-bipyridine (0.16 g, 1.0 mmol) of in THF (10 ml) was added. The reaction mixture turned instantly deep blue. The sealed ampule was left to stay at ambient temperature for 24 h. Dark crystals of compound **2a** were isolated by decantation of the mother liquor. The product was washed twice with cold THF and dried in vacuum. Yield (0.68 g, 73%) Anal. Calcd for $C_{50}H_{56}MgN_4O\times 2.5C_4H_8O$ (933.56): C, 77.19; H, 8.21; N, 6.00. Found: C, 77.07; H, 8.23; N, 5.27. IR (mineral oil): 1719 w, 1668 w, 1639 w, 1598 s, 1532 s, 1445 s, 1422 s, 1357 m, 1316 s, 1293 w, 1276 m, 1252 m, 1220 w, 1200 s, 1184 s, 1139 w, 1101 w, 1068 s, 1040 m, 1020 s, 963 s, 914 m, 873 w, 855 m, 835 w, 820 w, 803 w, 785 w, 771 s, 761 s, 752 m, 736 w, 689 m, 669 m, 618 s, 606 m, 592 w, 577 w, 542 w, 516 w cm^{-1}.

[{(dpp-bian)Ba(4,4'-bipy)(THF)$_2$}×4(THF)]$_m$ (2b). To a brown solution of [(dpp-bian)Ba(THF)$_5$] **1b** (prepared *in situ* from dpp-bian (0.50 g, 1.0 mmol) and an excess of barium (3.5 g, 25.5 mmol)) in THF (40 ml), a solution of 4,4'-bipyridine (0.16 g, 1.0 mmol) in THF (10 ml) was added. The reaction mixture turned instantly deep blue. The sealed ampule was left to stay at ambient temperature for 24 h. Dark crystals of compound **2b** were isolated by decantation of the mother liquor. The product was washed twice with cold THF and dried in vacuum. Yield of **2b** (1.08 g, 88%). Anal. Calcd for $C_{54}H_{64}BaN_4O_2\times4C_4H_8O$ (1226.89): C, 68.53; H, 7.89; N, 4.57. Found: C, 68.49; H, 7.63; N, 4.47. IR (mineral oil): 1671 w, 1585 s, 1529 m, 1442 s, 1414 s, 1407 s, 1353 m, 1337 m, 1313 s, 1267 m, 1249 m, 1216 w, 1198 s, 1181 s, 1143 w, 1105 w, 1071 m, 1038 m, 1009 s, 950 s, 914 w, 837 w, 819 w, 797 w, 785 w, 767 s, 758 s, 690 w, 667 w, 613 w, 599 s, 536 w cm^{-1}.

[{(dpp-bian)Mg(DME)}$_2$(4,4'-bipy)×3.4(DME)] 3a. compound **2a** (0.50 g) was dissolved in DME (20 ml). The sealed ampule was left to stay at ambient temperature for 17 h. Dark crystals of compound **3a** were isolated by decantation of the mother liquor. The product was washed twice with cold DME and dried in vacuum. Yield 0.25 g (29%). Anal. Calcd for $C_{103.6}H_{142}Mg_2N_6O_{10.8}$ (1692.91): C, 73.49; H, 8.45; N, 4.96. Found: C, 73.43; H, 8.41; N, 4.95. IR (mineral oil): 1668 w, 1642 w, 1600 s, 1530 m, 1484 s, 1440 s, 1417 s, 1361 m, 1310 s, 1279 m, 1253 m, 1204 s, 1190 m, 1172 m, 1107 s, 1156 w, 1140 m, 1021 s, 966 s, 918 m, 868 m, 837 w, 817 w, 805 m, 764 m, 752 m, 622 m cm^{-1}.

[{(dpp-bian)Ba(DME)$_2$}$_2$(4,4'-bipy)] 3b. To a solution of [(dpp-bian)Ba(DME)$_{2.5}$] (prepared *in situ* from dpp-bian (0.25 g, 0.5 mmol) and an excess of barium) in DME 15 (ml), a solution of 4,4'-bipyridine (0.04 g, 0.25 mmol) in DME (10 ml) was added. Slow evaporation of the solvent afforded brown crystals of compound **3b**. The product was washed twice with cold DME and dried in vacuum. Yield 0.35 g (79%). Anal. Calcd for $C_{98}Ba_2H_{128}N_6O_8$ (1792.74): C, 65.66; H, 7.20; N, 4.69. Found: C, 65.57; H, 7.18; N, 4.65. IR (mineral oil): 1906 w, 1600 s, 1574 s, 1536 m, 1510 w, 1427 m, 1411 s, 1346 s, 1318 s, 1299 s, 1241 s, 1206 m, 1164 s, 1137 m, 1111 s, 1061 s, 1022 m, 999 m, 981 m, 951 m, 917 s, 882 w, 856 s, 843 s, 802 s, 787 m, 756 s, 738 w, 685 w, 677 m, 630 w, 615 s, 589 m, 554 w, 534 w, 514 w cm^{-1}.

References

S1. I. L. Fedushkin, A. A. Skatova, V. A. Chudakova, G. K. Fukin, S. Dechert, H. Schumann, *Eur. J. Inorg. Chem*., 2003, 3336.

S2. I. L. Fedushkin, A. G. Morozov, O. V. Rassadin, G. K. Fukin, *Chem. Eur. J.,* 2005, **11**, 5749.

S3. S. Stoll, A. Schweiger, *J. Magn. Reson*., 2006, **178**, 42.

S4. N. F. Chilton, R. P. Anderson, L. D. Turner, A. Soncini, K. S. Murray, PHI: *J. Comput. Chem.*, 2013, **34**, 1164.

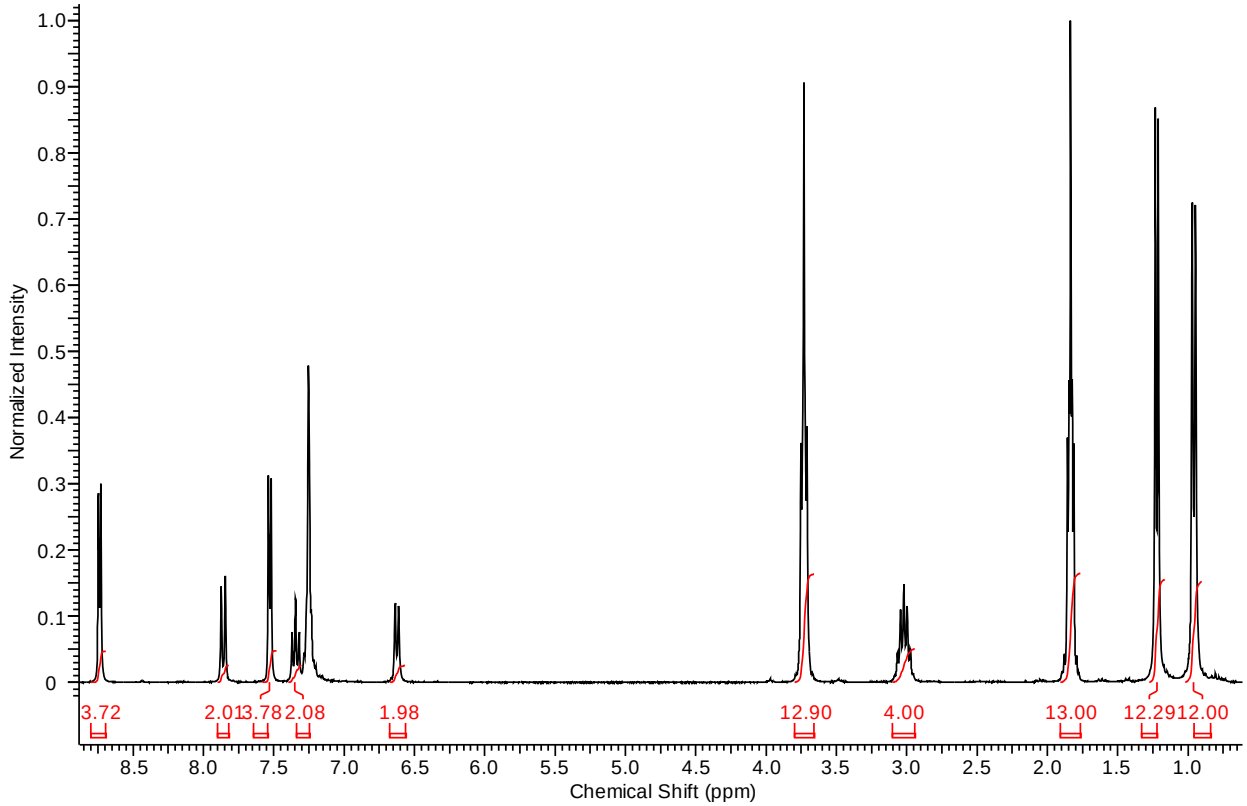

Figure S1. ^{1}H NMR spectrum of the mixtures obtained in the course of oxidative/hydrolytic destruction of **2a** (300 MHz, $CDCl_3$, 298 K).

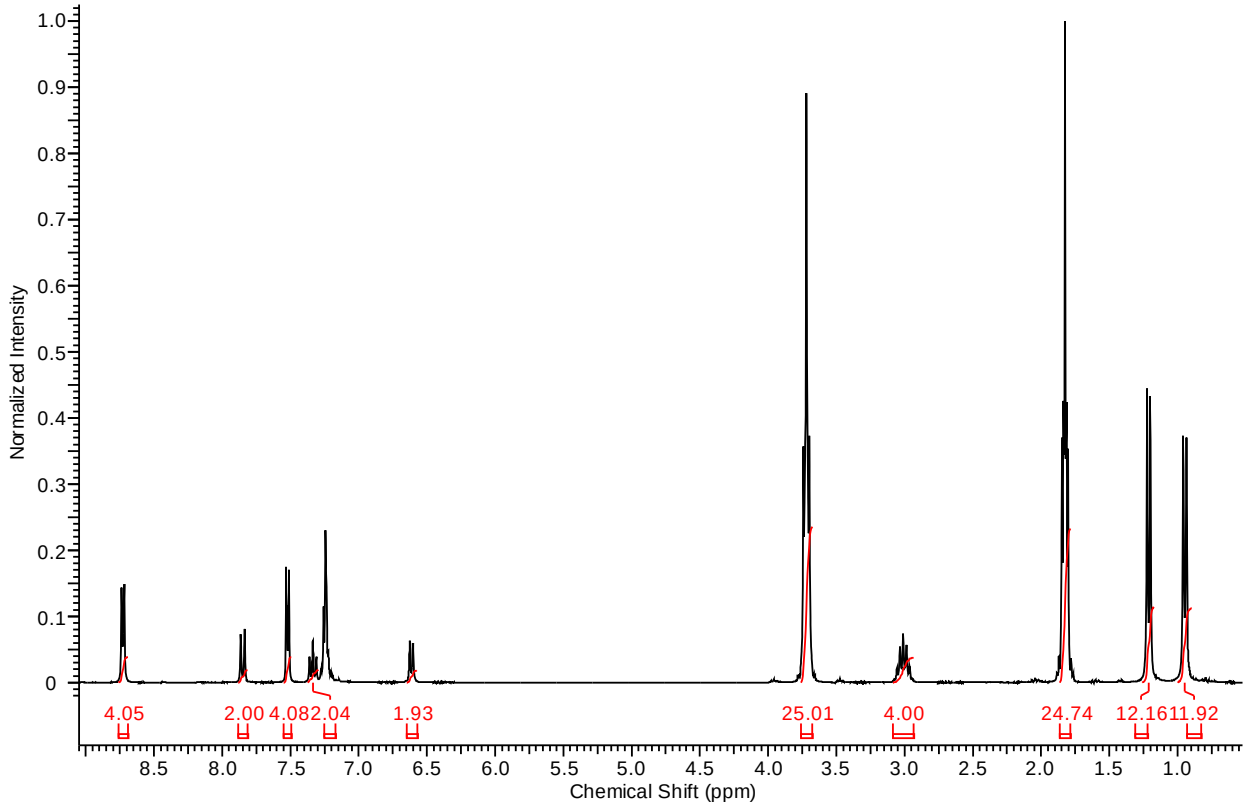

Figure S2. ^{1}H NMR spectrum of the mixtures obtained in the course of oxidative/hydrolytic destruction of **2b** (300 MHz, $CDCl_3$, 298 K).

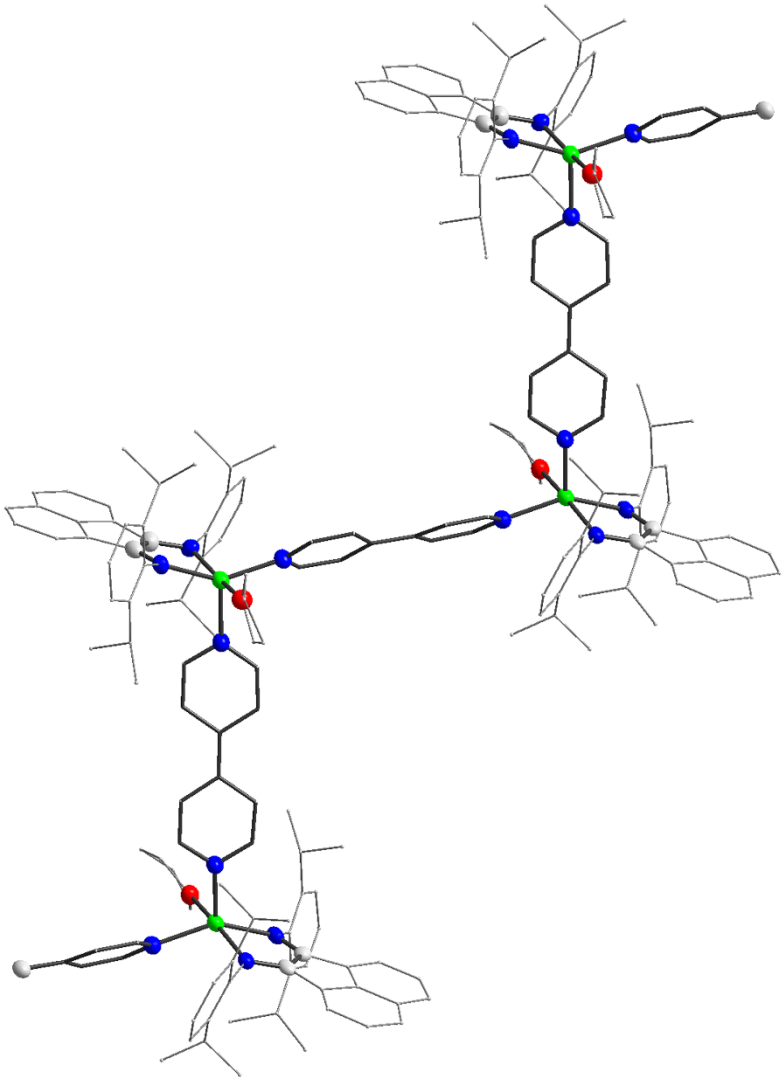

Figure S3. A fragment of 1D coordination polymer **2a**: green – Mg, blue – N, red – O, grey – C. Hydrogen atoms are omitted.

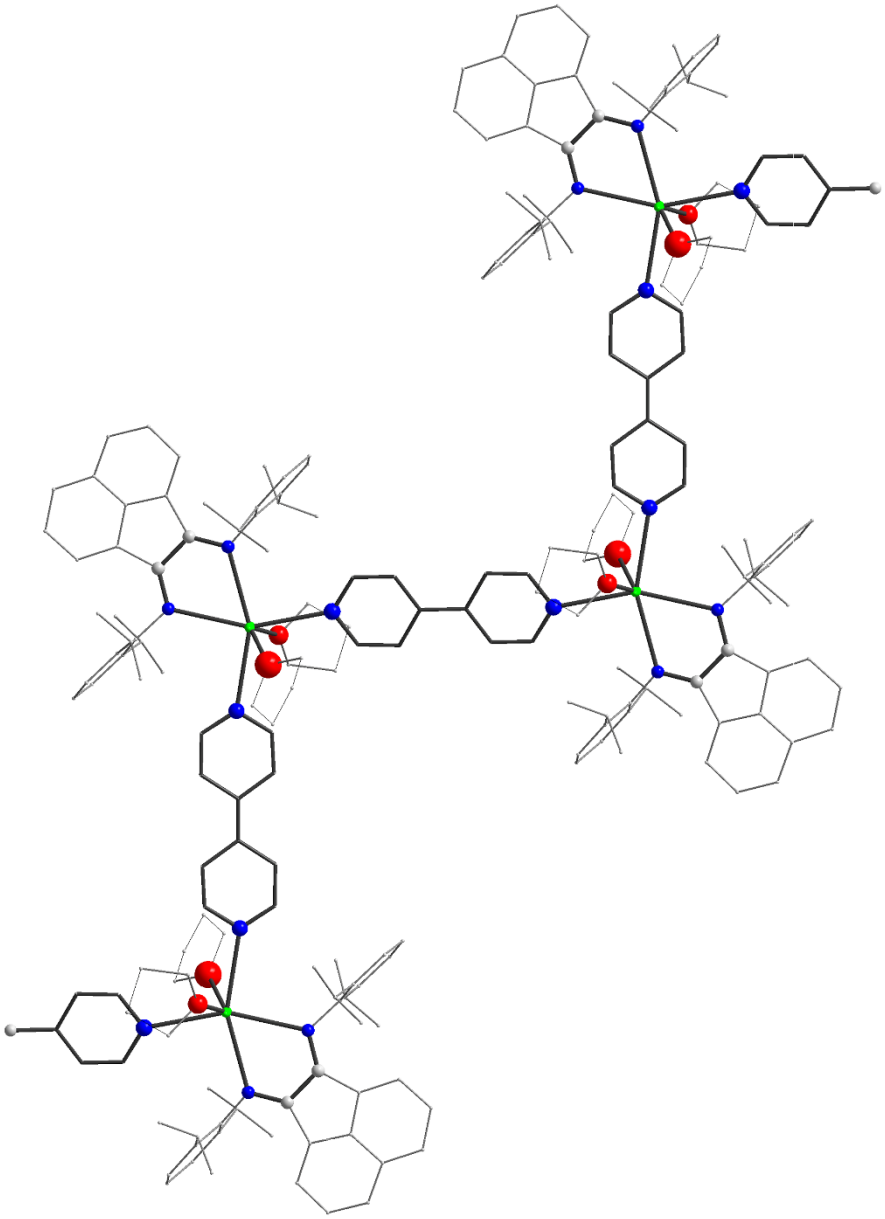

Figure S4. A fragment of 1D coordination polymer **2b** according to the single crystal X-ray analysis: green – Ba, blue – N, red – O, grey – C. Hydrogen atoms are omitted.

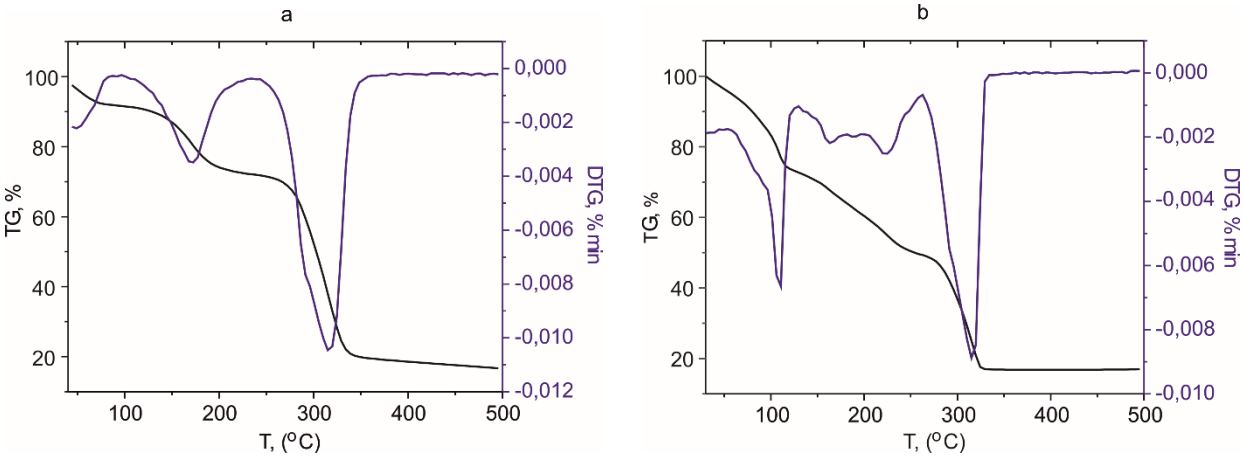

Figure S5. TGA/DTG curves for compounds **2a** (*a*) and **2b** (*b*).

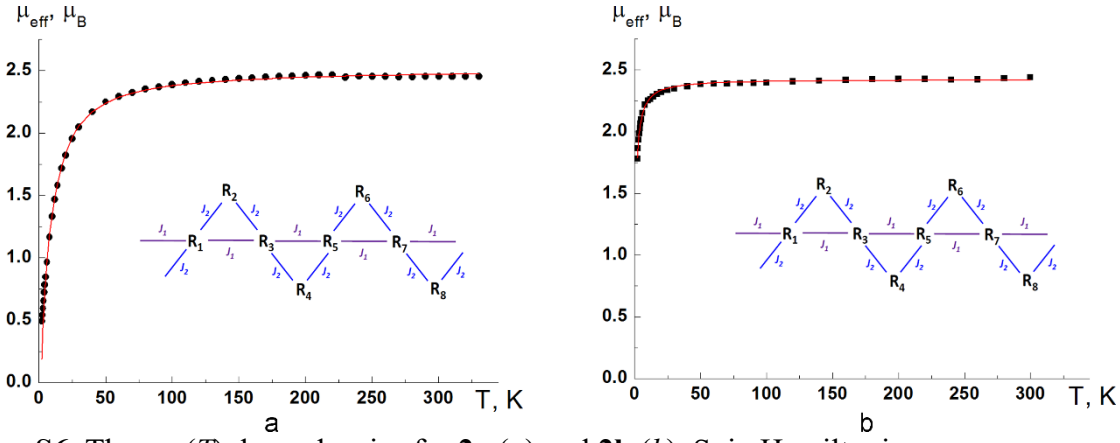

Figure S6. The $\mu_{eff}(T)$ dependencies for **2a** (*a*) and **2b** (*b*). Spin Hamiltonian $H = \sum_{i=1}^{n}(-2J_1S_{2i-1}S_{2i+1} - 2J_2(S_{2i-1}S_{2i} + S_{2i}S_{2i+1}))$ in finite chain approximation with n = 8.

Scheme on the insert represents the model, where symbols R_1, R_3, R_5 and R_7 denote 4,4'-bipy radical-anion, whereas R_2, R_4, R_6 and R_8 represent dpp-bian radical-anion. The J_1 parameter ascribes interaction between only 4,4'-bipy radical-anions, while J_2 parameter characterizes interaction between 4,4'-bipy and dpp-bian radical-anions.

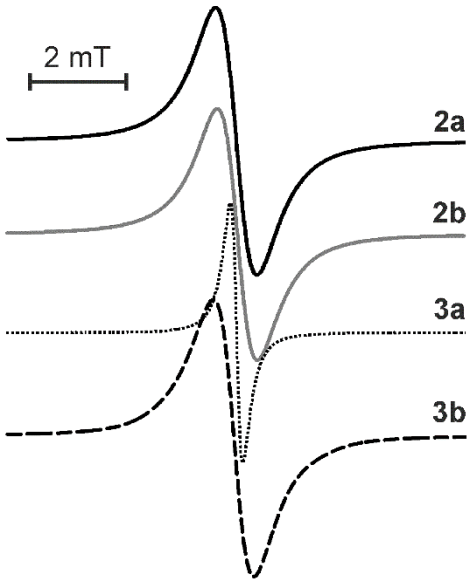

Figure S7. Solid state ESR signals of **2a**, **2b**, **3a** and **3b** at 298 K (line width at 1/2 peak height 1.43, 1.43, 0.48 and 1.46 mT, respectively)

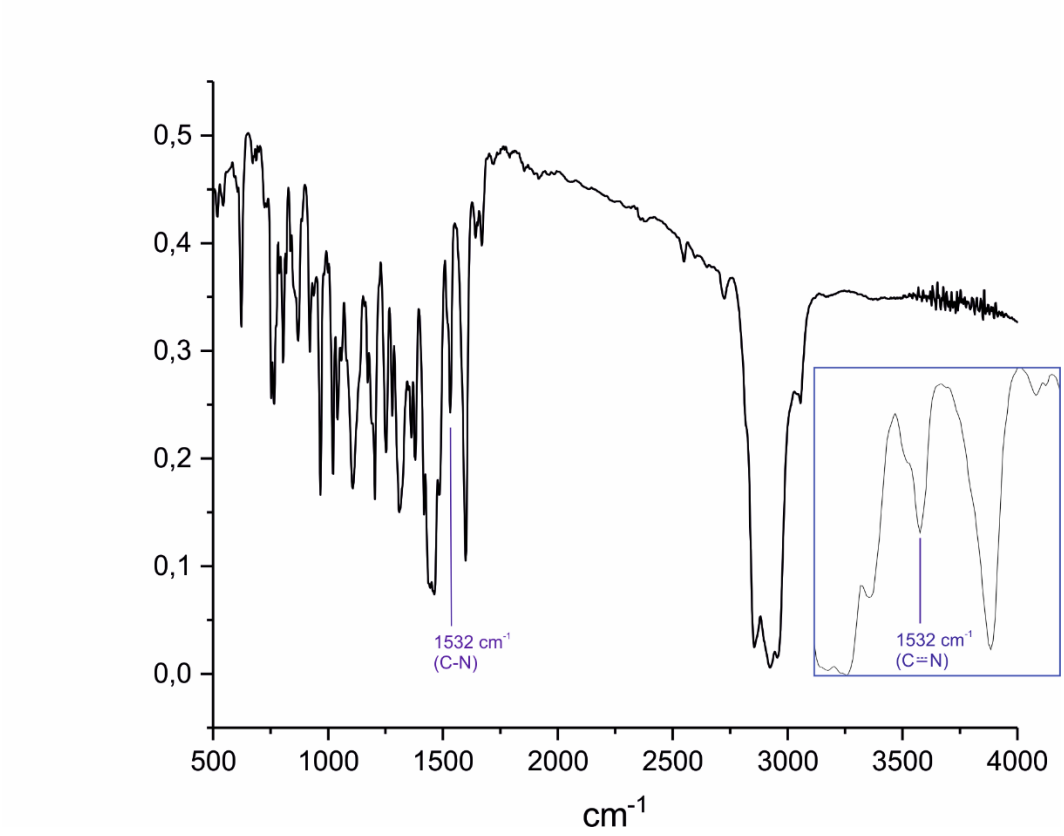

Figure S8. IR spectrum of **3a.**

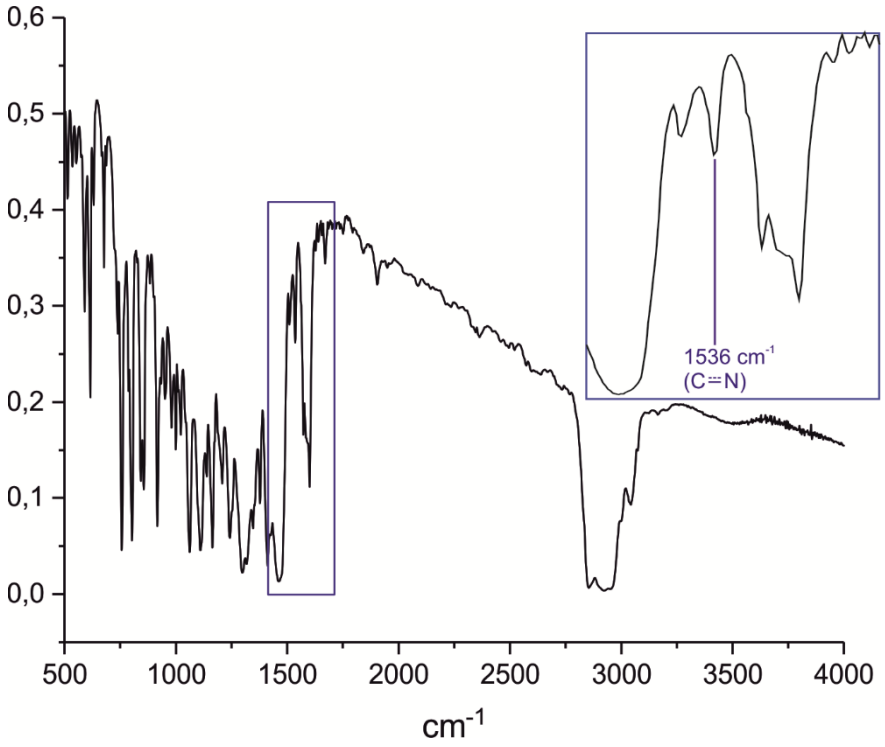

Figure S9. IR spectrum of **3b.**

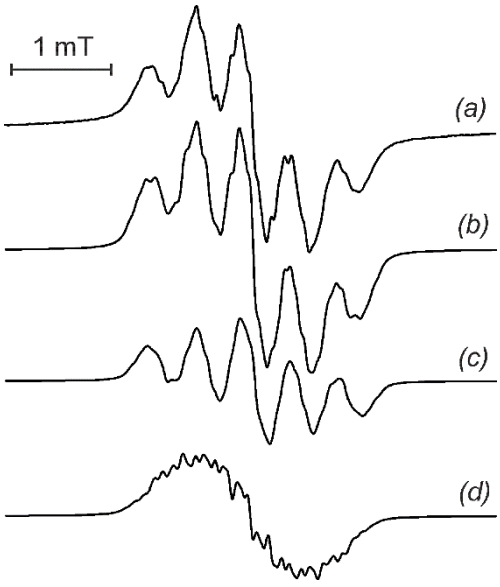

Figure 10. (*a*) ESR signal of **3a** in DME at 298 K; (*b*) simulated superposition of dpp-bian^{1-} and 4,4'-bipy^{1-} ESR signals; (*c*) simulated signal of dpp-bian^{1-} (g = 2.00375, $a_i(2\times^{14}N)$ = 0.454, $a_i(2\times^{1}H)$ = 0.140, $a_i(2\times^{1}H)$ = 0.105, $a_i(2\times^{1}H)$ = 0.067 mT); (*d*) simulated signal of 4,4'-bipy^{1-} (g = 2.00382, $a_i(2\times^{14}N)$ = 0.332, $a_i(4\times^{1}H)$ = 0.198, $a_i(4\times^{1}H)$ = 0.079 mT).

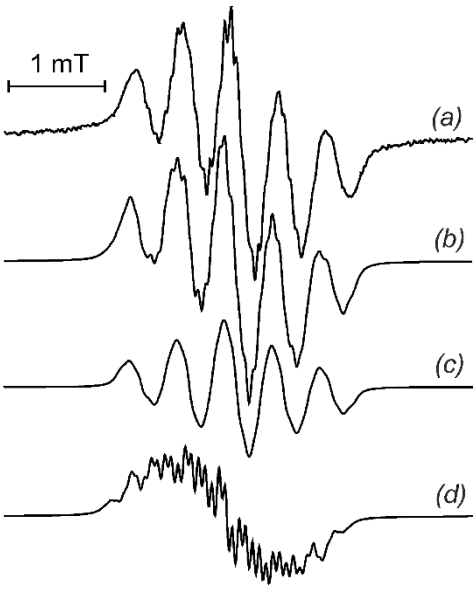

Figure 11. (*a*) ESR signal of **3b** in DME at 298 K; (*b*) simulated superposition of dpp-bian^{1-} and 4,4'-bipy^{1-} ESR signals; (*c*) simulated signal of dpp-bian^{1-} (g = 2.00360, $a_i(2\times^{14}N)$ = 0.491, $a_i(2\times^{1}H)$ = 0.120, $a_i(2\times^{1}H)$ = 0.071 mT); (*d*) simulated signal of 4,4'-bipy^{1-} (g = 2.00418, $a_i(2\times^{14}N)$ = 0.351, $a_i(4\times^{1}H)$ = 0.211, $a_i(4\times^{1}H)$ = 0.062 mT).

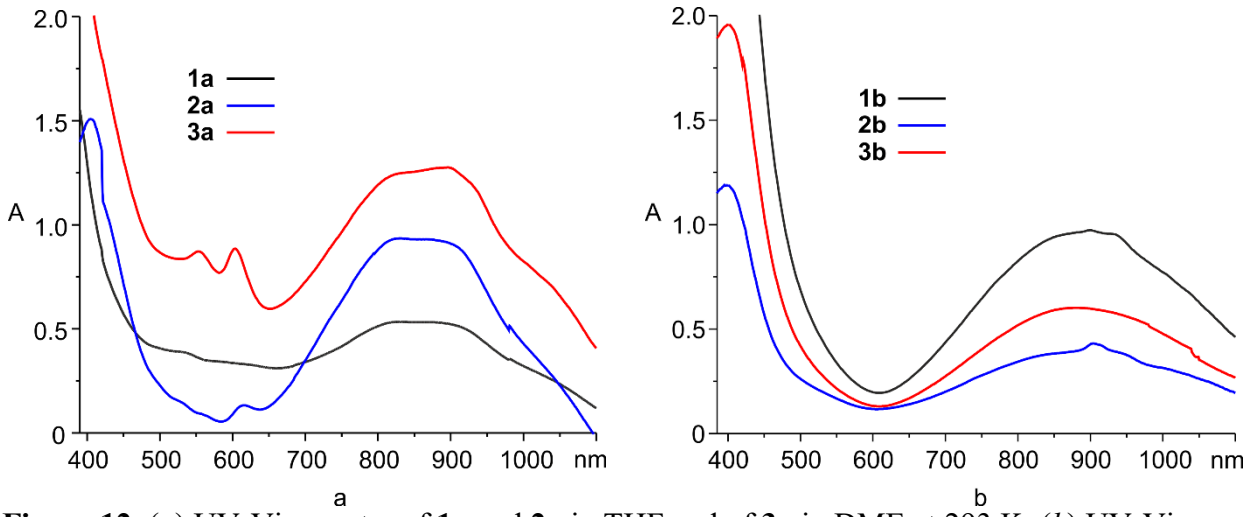

Figure 12. (*a*) UV-Vis spectra of **1a** and **2a** in THF and of **3a** in DME at 293 K; (*b*) UV-Vis spectra of **1b** and **2b** in THF and of **3b** in DME at 293 K.