## Supporting information.

## **IR- spectra. Table S1.** IR-spectra ( $cm^{-1}$ in KBr) of starting compounds, 1 and 2.

| Components   | Cp* <sub>2</sub> Cr | H <sub>3</sub> TPCor | $(Cp*_{2}Cr^{+})(H^{+})(H_{2}TPCor^{\bullet 2^{-}})$ | ${crypt[2,2,2](Na^{+})}$                   |
|--------------|---------------------|----------------------|--|--|
|              | _                   |                      | $C_6H_4Cl_2$ (1)                                     | $(H_2 TPCor^{-}) \cdot 0.5C_6 H_4 Cl_2(2)$ |
| Corrole      |                     | 663m                 | 662w   | 660w                                       |
| Contone      |                     | 669w                 | 668w*  | 668w*                                      |
|              |                     | 700s                 | 700s   | 701s                                       |
|              |                     | 722w                 | 714w 721w  | 7013<br>715w                               |
|              |                     | 752s                 | 754s   | 713 W                                      |
|              |                     | 764m                 | _  | 7558<br>760m                               |
|              |                     | 7888                 | 795s   | 702111                                     |
|              |                     | 819w                 | -  | /88W                                       |
|              |                     | 875w                 | 885  | 820m*                                      |
|              |                     | 064m                 | 058m   | 871w                                       |
|              |                     | 904III<br>087        | 7 <b>5</b> 8111                                      | 970w                                       |
|              |                     | 98/W                 | -  | 987w                                       |
|              |                     | 1011W                | 1003m 1014w  | 1003m                                      |
|              |                     | 1045W                | 1053m  | 1045w                                      |
|              |                     | 1062w                | 10/3m*   | 1073w*                                     |
|              |                     | 1176w                | 1177w  | 1174w                                      |
|              |                     | 1224w                | 1225w  | 1222w                                      |
|              |                     | 1236w                | 1236w  | 1231w                                      |
|              |                     | 1263w                | 1265m*   | 1266w                                      |
|              |                     | 1286w                | -  | 1285w                                      |
|              |                     | 1308w                | -  | 1302m                                      |
|              |                     | 1338w                | 1329m  | 1302m                                      |
|              |                     | 1377w                | 1378m*   | 132 m<br>1375w                             |
|              |                     | 1409w                | 1418w*   | 1417w                                      |
|              |                     | 1439w                | 1436m  | 1417 w<br>1425 w                           |
|              |                     | 1465w                | _  | 1455w                                      |
|              |                     | 1495m                | 1494m  | 1400111                                    |
|              |                     | 1519w                | -  | 1493111                                    |
|              |                     | 151)w                | 15568 15768  | 1521W*                                     |
|              |                     | 1596m                | 1595m  | 1546w                                      |
|              |                     | 2020m                | 3027w  | 1595m                                      |
|              |                     | 2051w                | 3027W  | 3030w                                      |
|              |                     | 2271w                | 3037W  | 3057w                                      |
|              |                     | 55/1W                | -  | -  |
|              |                     | 3404W                | -  | -  |
| Cation       | $Cp*_2Cr$           |                      | Cp* <sub>2</sub> Cr                                  | $cryptand(Na^{+})$                         |
|              | 419w                |                      | -  | 820m*                                      |
|              | 585w                |                      | -  | 850m                                       |
|              | 10225               |                      | 1020m  | 927m                                       |
|              | 10223<br>1068w      |                      | 1073m*   | 939w                                       |
|              | 1262w               |                      | 1265m*   | 1073w*                                     |
|              | 1202w               |                      | -  | 1088s                                      |
|              | 1275                |                      | 1378m*   | 1099s                                      |
|              | 15/38               |                      | 1418w*   | 1128m                                      |
|              | 1414W               |                      | 1423w  | 1356m                                      |
|              | 1423m               |                      | 1441m  | 1521w*                                     |
|              | 1448w               |                      | -  | 2800w                                      |
|              | 1634m               |                      | 2852w  | 2897                                       |
|              | 2852w               |                      | 2911w  | 2957                                       |
|              | 2899w               |                      | 2968w  | 2757 W                                     |
|              | 2955w               |                      |  |  |
|              |                     |                      | 668w*  | 669*                                       |
| $C_6H_4Cl_2$ |                     |                      | 10348  | 1025-m                                     |
|              |                     |                      | 1456m  | 1055M                                      |
|              | 1                   |                      | 1100111  | 1430III                                    |

\* Bands are overlapped, w-weak intensity, m – middle intensity, s – strong intensity.



**Fig. S1.** IR spectra of starting H<sub>3</sub>TPCor; salt {cryptand[2,2,2](Na<sup>+</sup>)}(H<sub>2</sub>TPCor<sup>-</sup>)·0.5C<sub>6</sub>H<sub>4</sub>Cl<sub>2</sub> (**2**) with deprotonated H<sub>2</sub>TPCor<sup>-</sup> anions; complex (Cp\*<sub>2</sub>Cr<sup>+</sup>)(H<sup>+</sup>)·(H<sub>2</sub>TPCor<sup>•2-</sup>)·C<sub>6</sub>H<sub>4</sub>Cl<sub>2</sub> (**1**) with the H<sub>2</sub>TPCor<sup>•2-</sup> radical dianions. Spectra were measured in KBr pellet prepared in anaerobic conditions.

## **Crystal structures**



**Fig. S2.** Crystal structure of {cryptand[2,2,2](Na<sup>+</sup>)}(H<sub>2</sub>TPCor<sup>-</sup>) $\cdot$ 0.5C<sub>6</sub>H<sub>4</sub>Cl<sub>2</sub> (**2**) with deprotonated H<sub>2</sub>TPCor<sup>-</sup> anions. Solvent C<sub>6</sub>H<sub>4</sub>Cl<sub>2</sub> moleculeas are not shown for clarity.

Theoretical calculations.



**Fig. S3.** Calculated structure of the  $H_2TPCor^{\bullet 2-}$  radical dianion.





**Fig. S4.** Temperature dependencies of *g*-factors (a) and linewidths (b) of two EPR signals from polycrystalline **1** attributed to the radical H<sub>2</sub>TPCor<sup> $\bullet$ 2-</sup> dianions in the 4.2-292 K range.