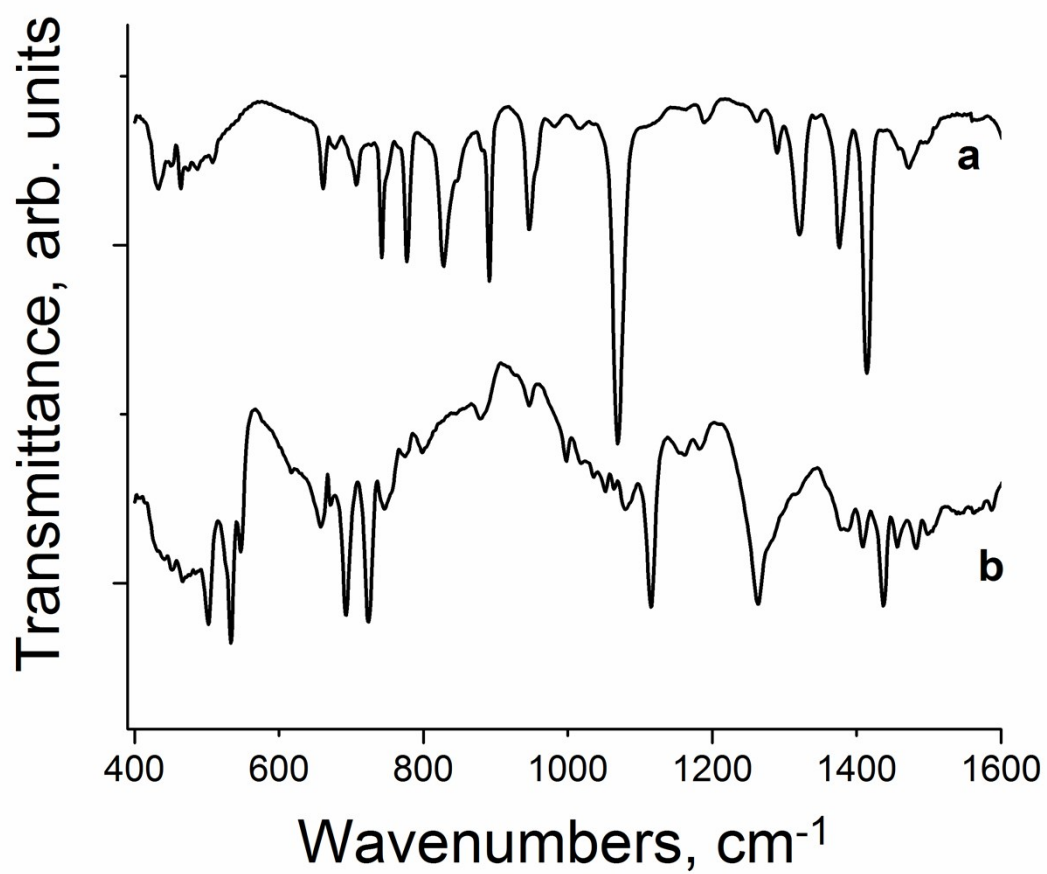


Supporting information.

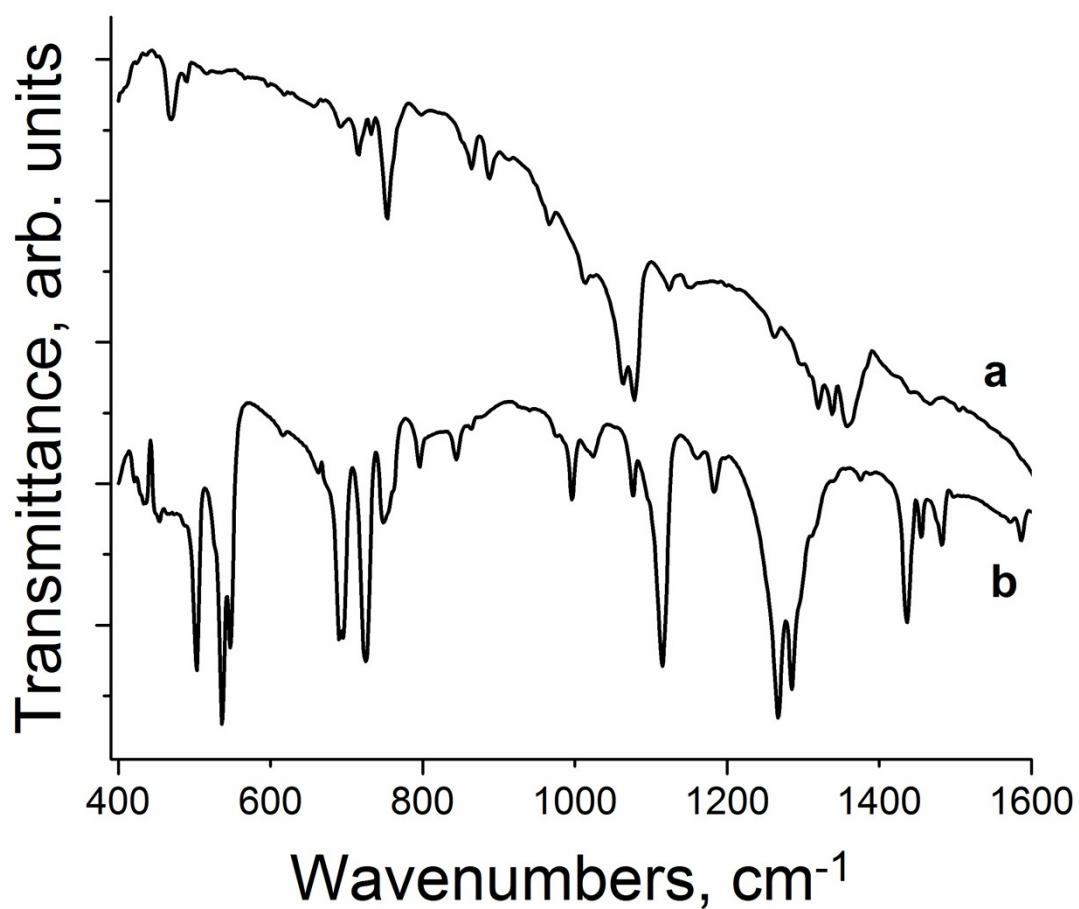
IR spectra

**Table S1.** IR-spectra (cm<sup>-1</sup> in KBr) of starting macrocycles and salts **1-3**.

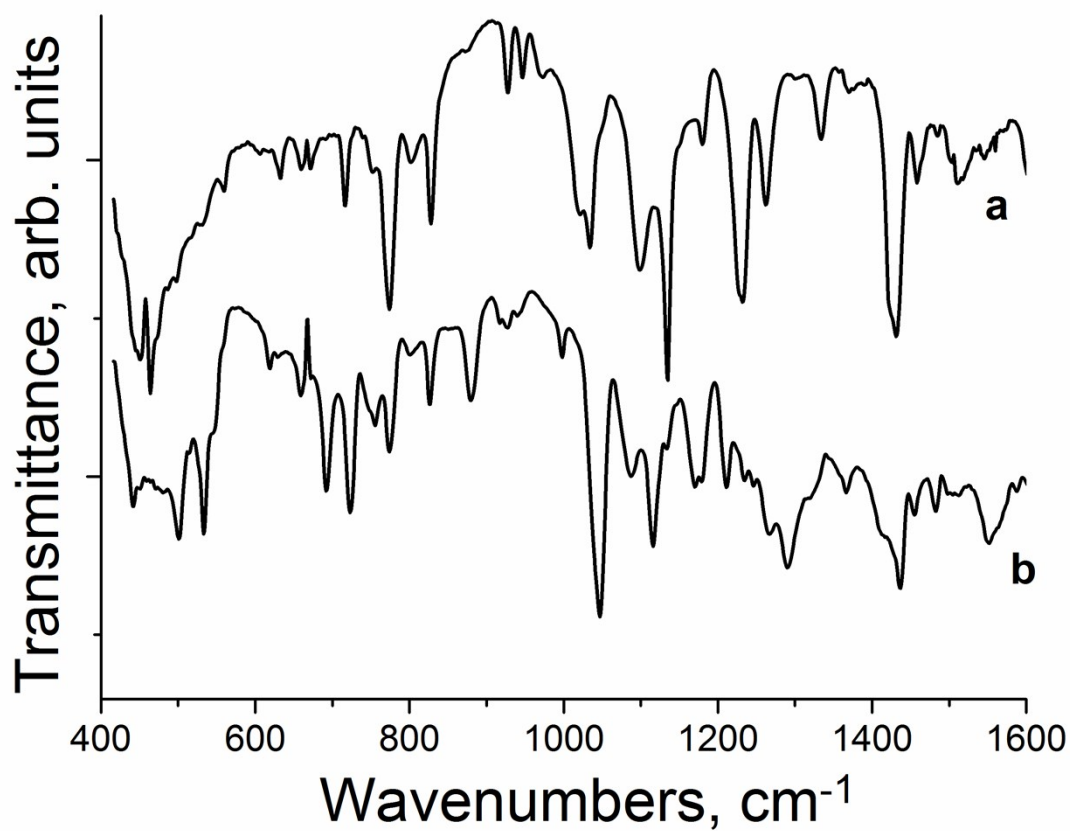
Components	PPN <sup>+</sup>	O=Ti <sup>IV</sup> PcCl <sub>8</sub>	<b>1</b>	Ti <sup>IV</sup> Cl <sub>2</sub> Nc	<b>2</b>	O=Ti <sup>IV</sup> (AceTPrzPz)	<b>3</b>
Macroheterocycle		431w	-	469m	-	449m	442w
		463w	462w	488w	-	464s	-
		659m	656m	514w	-	559w	-
		705m	691s	656w	-	630m	620w
		743m	745m*	690w	692s*	660m	658w
		775m	773w	716m	724s*	675m	-
		829m	799m	733w	-	716m	724s
		890m	878m	752s	-	772s	775m
		946m (Ti=O)	946m	798w	794m	802w	801w
		1017w	(Ti=O)	863m	843m	828m	827m
		1069s	-	886m	-	-	878m
		1188w	1080m	968m	-	927m(Ti=O)	917w(Ti=O)
		1260w	1183w	-	974w (Ti=O)	947m(Ti=O)	927m(Ti=O)
		1289w	1263s*	1077s	1074m	974w(Ti=O)	941w(Ti=O)
		1320m	-	1011m	-	1033s	1048s
		1375m	-	1062s	-	1099m	1088w
		1413s	1383m	1125m	1114s*	1134s	1117m
		1471m	1408m	1153w	1160w	1179m	1177m
		-	1481m*	-	1181m	1229s	1211m
		1603m	1501m	1264m	1267s*	1262m	1266w*
		2922m	1623m	-	1285s	-	1292m
		3087m	-	1318m	-	1333m	-
			-	1338m	-	1369w	1366m
				1358m	-	1431s	1435s*
				1468w	1456m*	1458m	1455w*
				1639m	1630m	1514m	-
				1747w	-	1547w	1553s
					1615s	1608w	
					2851m	-	
					2921m	-	
PPN <sup>+</sup>					501s		500m
		500s			534s		534m
		531s	503m		547s		-
		550s	534s		692s*		692s*
		694m	546w		724s*		724s
		724m	691s		748m*		-
		746m	726s		995m		755m*
		754m	745m*		1023w*		998m
		-	773w		1267s*		-
		1024w	998m		1435s		1266w*
		1250s	-		1480m		1435s*
		1439s	1263s*		-		1481w
		1483m	1435s		1584w		-
		1575w	1481m*				-
		1587m	1563w				-
		1586w					
Solvent					C <sub>6</sub> H <sub>4</sub> Cl <sub>2</sub>		C <sub>6</sub> H <sub>4</sub> Cl <sub>2</sub>
					748m*		658w
			C <sub>6</sub> H <sub>4</sub> Cl <sub>2</sub>		1023w*		755m*
			656m		1114s*		1117m
			745m*		1456m		1455w*
			1115s				
			1455m				C <sub>6</sub> H <sub>5</sub> CN
							692s*
							755m*



**Figure S1.** IR spectra of starting neutral O=Ti<sup>IV</sup>(PcCl<sub>8</sub><sup>2-</sup>) (a) and salt (PPN<sup>+</sup>)<sub>2</sub>{O=Ti<sup>IV</sup>(PcCl<sub>8</sub><sup>4-</sup>)}<sup>2-</sup> (b) in KBr pellet prepared in anaerobic condition.



**Figure S2.** IR spectra of starting neutral  $\text{Ti}^{\text{IV}}\text{Cl}_2\text{Nc}^{2-}$  (a) and salt  $(\text{PPN}^+)\{\text{O}=\text{Ti}^{\text{IV}}(\text{Nc}^{\bullet 3-})\}^{\bullet\bullet}\cdot 2\text{C}_6\text{H}_4\text{Cl}_2$  (2) (b) in KBr pellet prepared in anaerobic condition.



**Figure S3.** IR spectra of starting neutral  $\text{O}=\text{Ti}^{\text{IV}}(\text{AceTPrzPz}^{2-})$  (a) and salt  $(\text{PPN}^+)_2\{\text{O}=\text{Ti}^{\text{IV}}(\text{AceTPrzPz}^{4-})\}^{2-}\cdot 1.3\text{C}_6\text{H}_4\text{Cl}_2\cdot 0.8\text{C}_6\text{H}_4\text{Cl}_2$  (**3**) (b) in KBr pellet prepared in anaerobic condition.