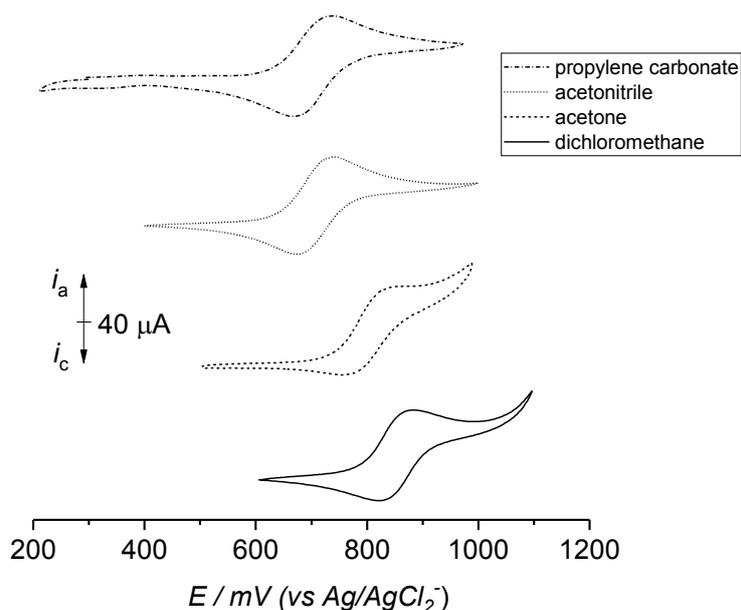




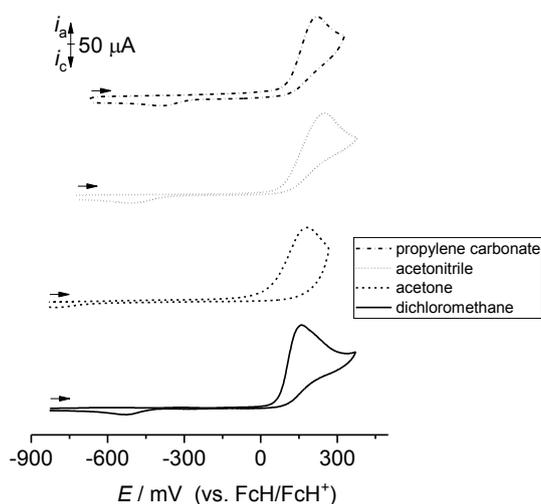
27	Content:		
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65			
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67			
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82	3. References		p18



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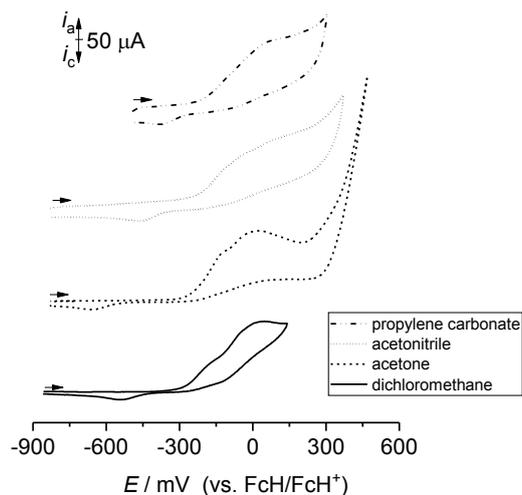
84 **Figure S11.** Cyclic voltammograms (potential area: 200–1200 mV) of ferrocene ( $1.0 \text{ mmol}\cdot\text{L}^{-1}$ ) in dichloromethane  
 85 (solid), acetone (dashed), acetonitrile (dotted) and propylene carbonate (dash-dotted) at  $25 \text{ }^\circ\text{C}$ ; scan rate:  
 86  $100 \text{ mV}\cdot\text{s}^{-1}$ ; supporting electrolyte:  $0.1 \text{ mol}\cdot\text{L}^{-1} [\text{NBu}_4][\text{Cl}]$ ; working electrode: glassy carbon electrode. \*Please  
 87 note that in order to reach reversibility of the ferrocene oxidation in the electrolyte system acetone/ $[\text{NBu}_4][\text{Cl}]$  scan  
 88 rates of  $1.5 \text{ V/s}$  had to be used.  
 89

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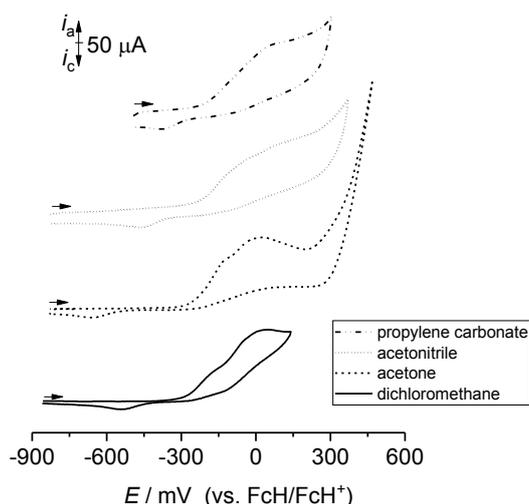
91

92 **Figure S12.** Cyclic voltammograms (potential area: -900–400 mV) of **1** ( $1.0 \text{ mmol}\cdot\text{L}^{-1}$ ) in dichloromethane (solid),  
 93 acetone (dashed), acetonitrile (dotted) and propylene carbonate (dash-dotted) at  $25 \text{ }^\circ\text{C}$ ; scan rate:  $100 \text{ mV}\cdot\text{s}^{-1}$ ;  
 94 supporting electrolyte:  $0.1 \text{ mol}\cdot\text{L}^{-1} [\text{NBu}_4][\text{Cl}]$ ; working electrode: glassy carbon electrode.  
 95



96

97 **Figure S13.** Cyclic voltammograms (potential area: -900–500 mV) of **2** ( $1.0 \text{ mmol}\cdot\text{L}^{-1}$ ) in dichloromethane (solid),  
 98 acetone (dashed), acetonitrile (dotted) and propylene carbonate (dash-dotted) at  $25 \text{ }^\circ\text{C}$ ; scan rate:  $100 \text{ mV}\cdot\text{s}^{-1}$ ;  
 99 supporting electrolyte:  $0.1 \text{ mol}\cdot\text{L}^{-1} [\text{NBu}_4][\text{Cl}]$ ; working electrode: glassy carbon electrode.



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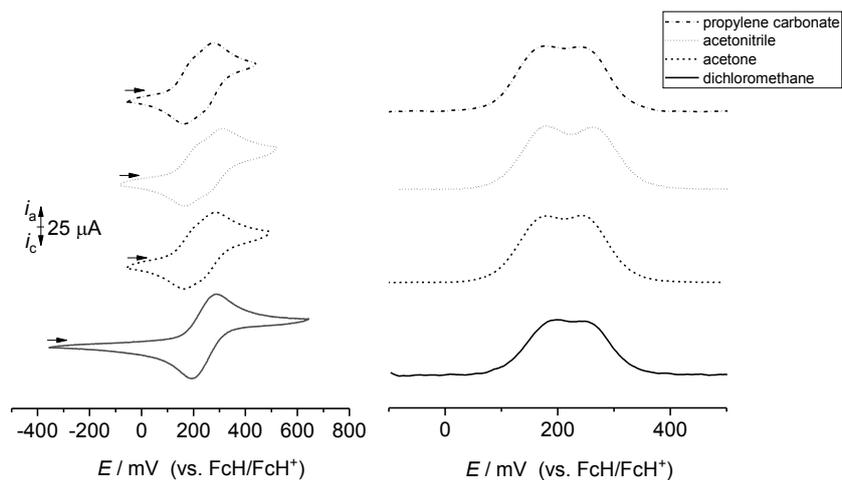
101 **Figure S14.** Cyclic voltammograms (potential area: -900–500 mV) of **3** ( $1.0 \text{ mmol}\cdot\text{L}^{-1}$ ) in dichloromethane (solid),  
 102 acetone (dashed), acetonitrile (dotted) and propylene carbonate (dash-dotted) at  $25 \text{ }^\circ\text{C}$ ; scan rate:  $100 \text{ mV}\cdot\text{s}^{-1}$ ;  
 103 supporting electrolyte:  $0.1 \text{ mol}\cdot\text{L}^{-1} [\text{NBu}_4][\text{Cl}]$ ; working electrode: glassy carbon electrode.

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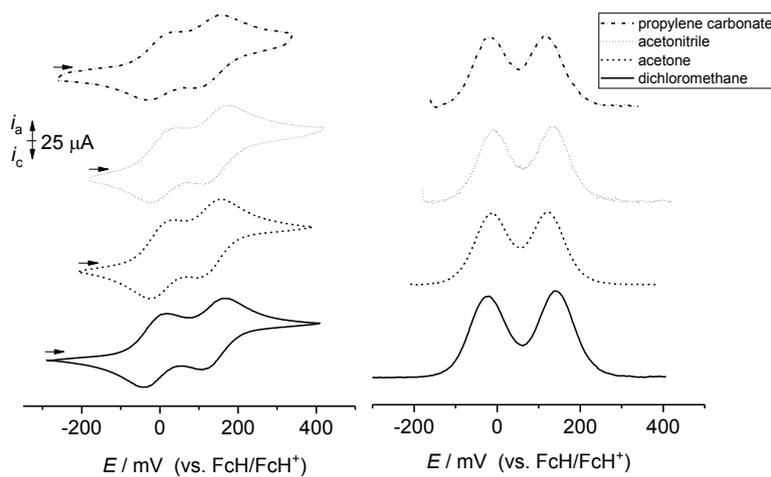
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109 **Figure S15.** Cyclic voltammograms (left; potential area: -400–700 mV; scan rate: 100 mV·s<sup>-1</sup>) and square wave  
 110 voltammograms (right) of **1** (1.0 mmol·L<sup>-1</sup>) in dichloromethane (solid)<sup>1</sup>, acetone (dashed), acetonitrile (dotted) and  
 111 propylene carbonate (dash-dotted) at 25 °C; supporting electrolyte: 0.1 mol·L<sup>-1</sup> [NBu<sub>4</sub>][PF<sub>6</sub>]; working electrode:  
 112 glassy carbon electrode.

113



114

115 **Figure S16.** Cyclic voltammograms (left; potential area: -300–400 mV; scan rate: 100 mV·s<sup>-1</sup>) and square wave  
 116 voltammograms (right) of **2** (1.0 mmol·L<sup>-1</sup>) in dichloromethane (solid), acetone (dashed), acetonitrile (dotted) and  
 117 propylene carbonate (dash-dotted) at 25 °C; supporting electrolyte: 0.1 mol·L<sup>-1</sup> [NBu<sub>4</sub>][PF<sub>6</sub>]; working electrode:  
 118 glassy carbon electrode.

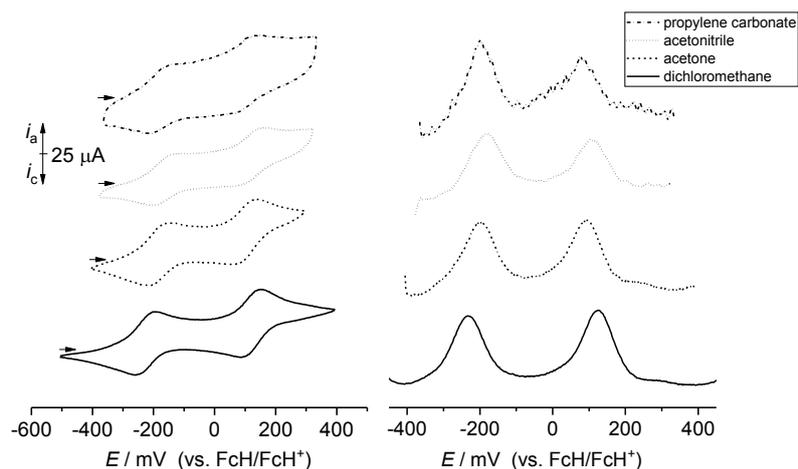
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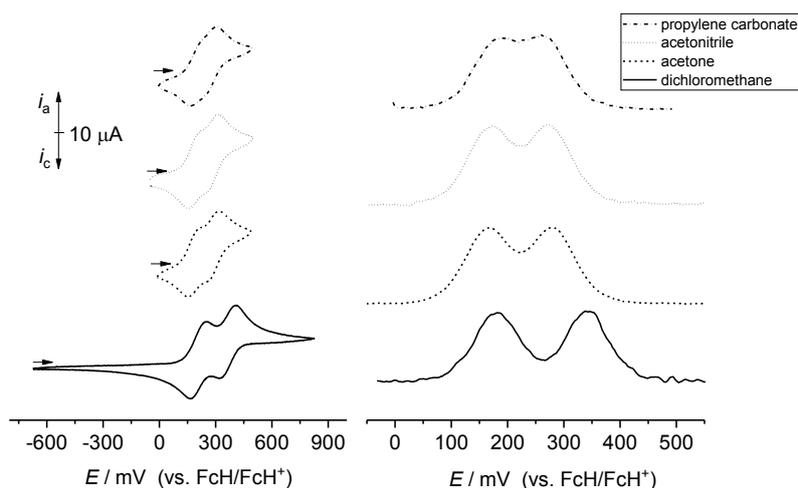
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126 **Figure S17.** Cyclic voltammograms (left; potential area: -500–400 mV; scan rate: 100 mV·s<sup>-1</sup>) and square wave  
 127 voltammograms (right) of **3** (1.0 mmol·L<sup>-1</sup>) in dichloromethane (solid), acetone (dashed), acetonitrile (dotted) and  
 128 propylene carbonate (dash-dotted) at 25 °C; supporting electrolyte: 0.1 mol·L<sup>-1</sup> [NBu<sub>4</sub>][PF<sub>6</sub>]; working electrode:  
 129 glassy carbon electrode.



130

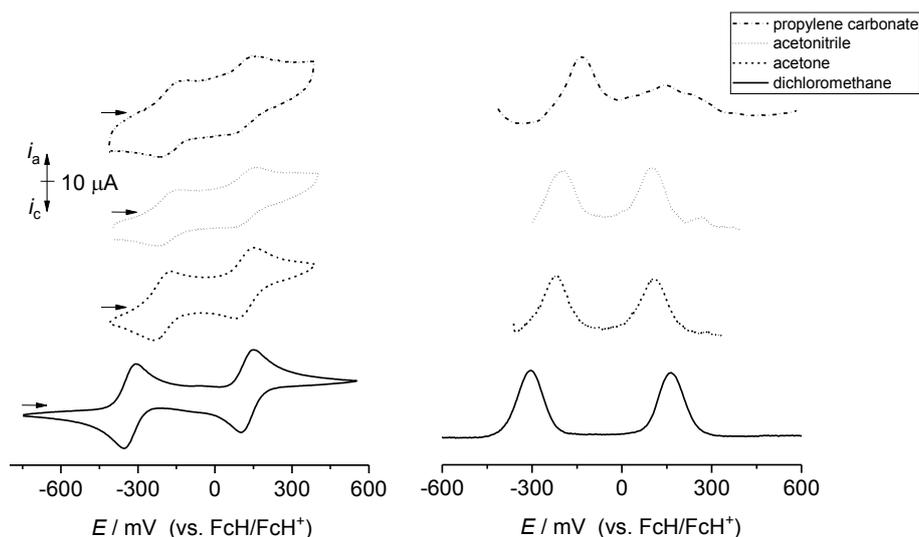
131 **Figure S18.** Cyclic voltammograms (left; potential area: -400–700 mV; scan rate: 100 mV·s<sup>-1</sup>) and square wave  
 132 voltammograms (right) of **1** (1.0 mmol·L<sup>-1</sup>) in dichloromethane (solid)<sup>1</sup>, acetone (dashed), acetonitrile (dotted) and  
 133 propylene carbonate (dash-dotted) at 25 °C; supporting electrolyte: 0.1 mol·L<sup>-1</sup> [NBu<sub>4</sub>][BARF]; working electrode:  
 134 glassy carbon electrode.

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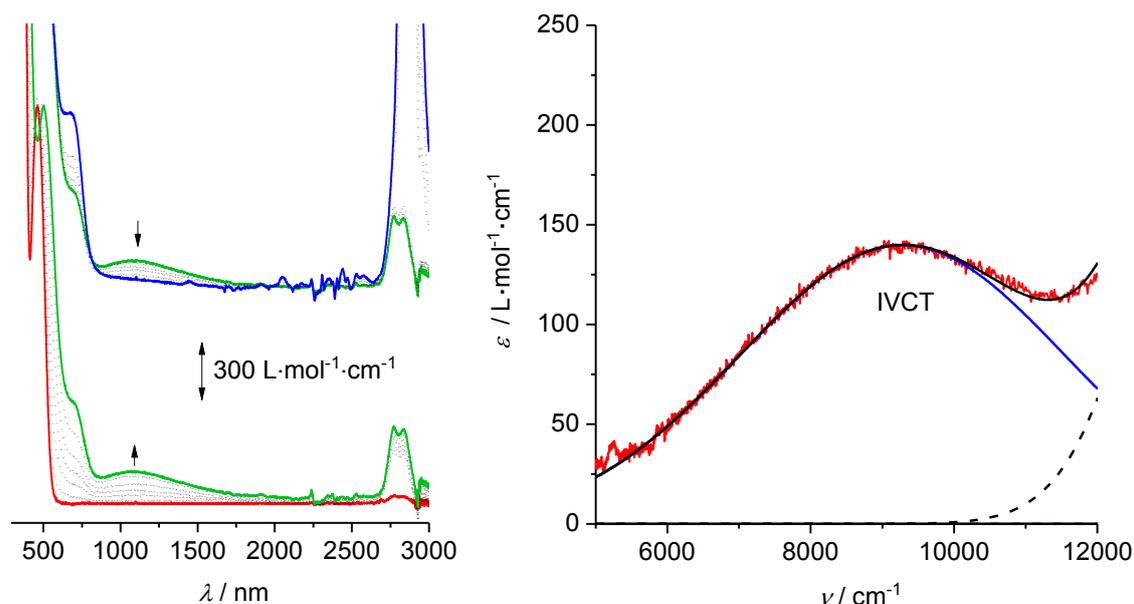
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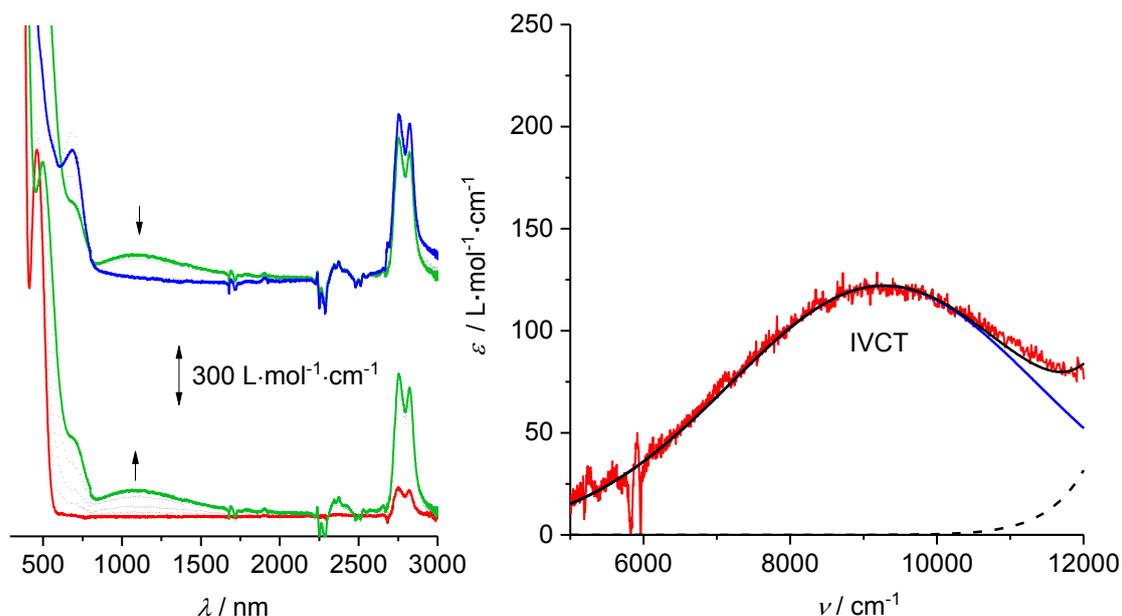
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140 **Figure S19.** Cyclic voltammograms (left; potential area: -400–700 mV; scan rate: 100 mV·s<sup>-1</sup>) and square wave  
 141 voltammograms (right) of **3** (1.0 mmol·L<sup>-1</sup>) in dichloromethane (solid)<sup>2</sup>, acetone (dashed), acetonitrile (dotted) and  
 142 propylene carbonate (dash-dotted) at 25 °C; supporting electrolyte: 0.1 mol·L<sup>-1</sup> [NBu<sub>4</sub>][BArF]; working electrode:  
 143 glassy carbon electrode.



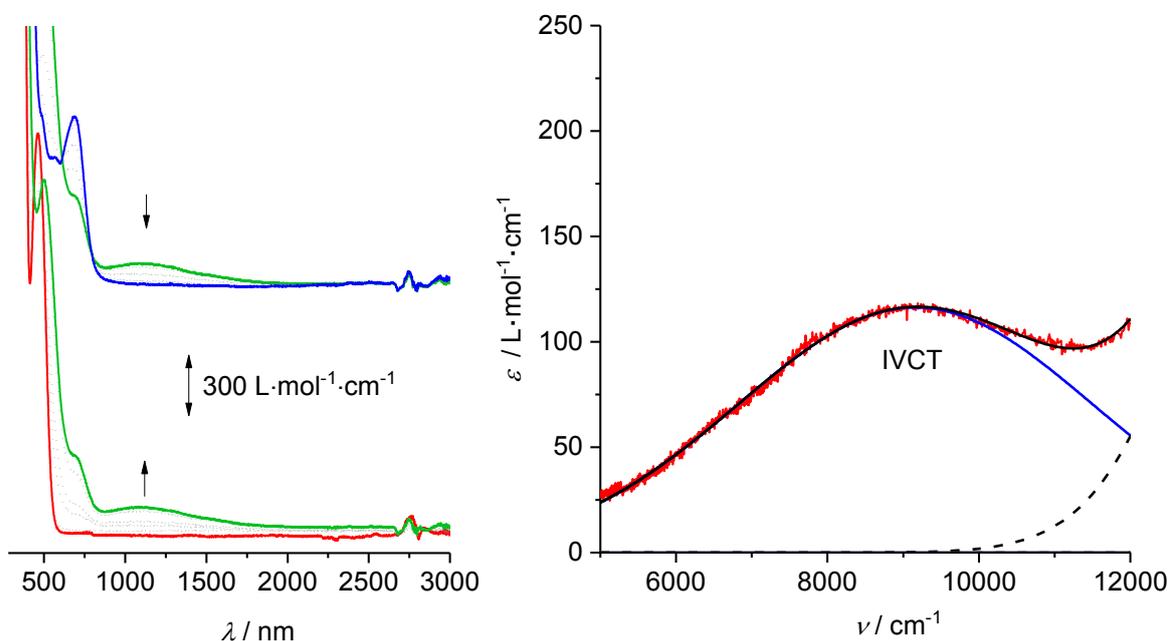
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145 **Figure S10.** Left: UV/Vis-NIR spectra of **1** at 25 °C in acetone (2.0 mmol·L<sup>-1</sup>) at rising potentials (bottom: -200–  
 146 700 mV; top: 700–1300 mV vs Ag/AgCl); [NBu<sub>4</sub>][BArF] as supporting electrolyte (red; **1**, green: **1**<sup>+</sup>, blue: **1**<sup>2+</sup>).  
 147 Right: Deconvolution of the NIR absorptions of **1**<sup>+</sup> using two Gaussian shaped bands determined by  
 148 spectroelectrochemistry in an OTTLE cell (red: experimental spectrum, solid black: sum of Gaussian curves, blue  
 149 IVCT curve).  
 150



151

152 **Figure S11.** Left: UV/Vis-NIR spectra of **1** at 25 °C in acetonitrile ( $2.0 \text{ mmol}\cdot\text{L}^{-1}$ ) at rising potentials  
 153 (bottom:  $-200$ – $675 \text{ mV}$ ; top:  $675$ – $1300 \text{ mV}$  vs Ag/AgCl);  $[\text{NBu}_4][\text{BArF}]$  as supporting electrolyte (red; **1**, green:  $[1]^+$ ,  
 154 blue:  $[1]^{2+}$ ). Right: Deconvolution of the NIR absorptions of  $[1]^+$  using two Gaussian shaped bands determined by  
 155 spectroelectrochemistry in an OTTLE cell (red: experimental spectrum, solid black: sum of Gaussian curves, blue  
 156 IVCT curve).

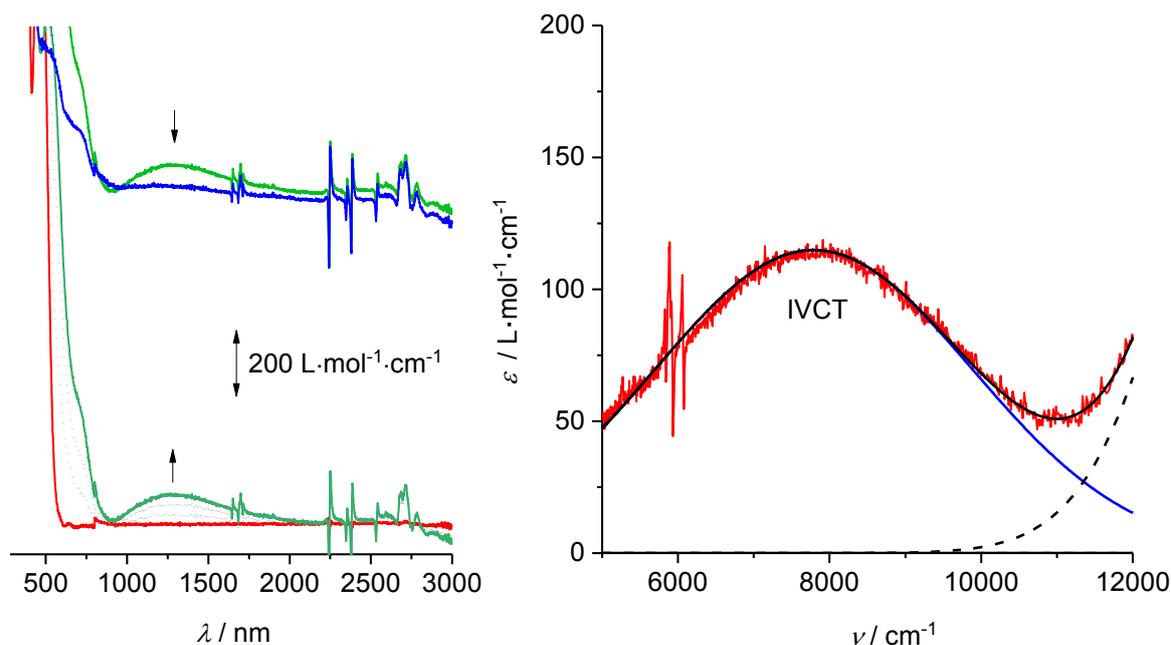


157

158 **Figure S12.** Left: UV/Vis-NIR spectra of **1** at 25 °C in propylene carbonate ( $2.0 \text{ mmol}\cdot\text{L}^{-1}$ ) at rising potentials  
 159 (bottom:  $-200$ – $600 \text{ mV}$ ; top:  $600$ – $1300 \text{ mV}$  vs Ag/AgCl);  $[\text{NBu}_4][\text{BArF}]$  as supporting electrolyte (red; **1**, green:  $[1]^+$ ,  
 160 blue:  $[1]^{2+}$ ). Right: Deconvolution of the NIR absorptions of  $[1]^+$  using two Gaussian shaped bands determined by  
 161 spectroelectrochemistry in an OTTLE cell (red: experimental spectrum, solid black: sum of Gaussian curves, blue  
 162 IVCT curve).

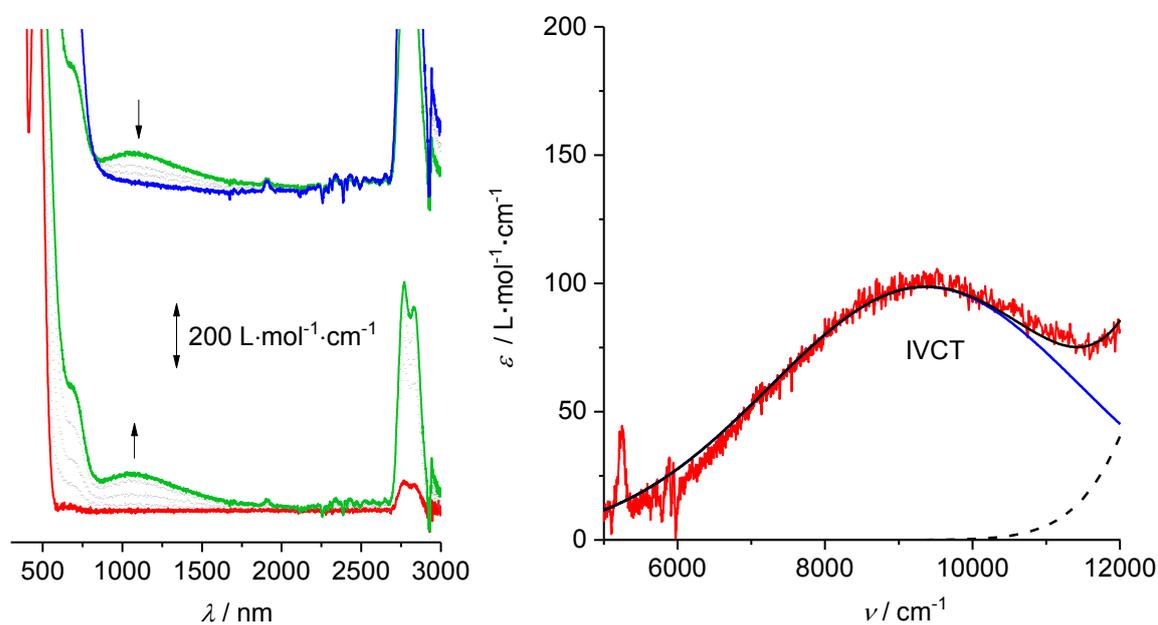
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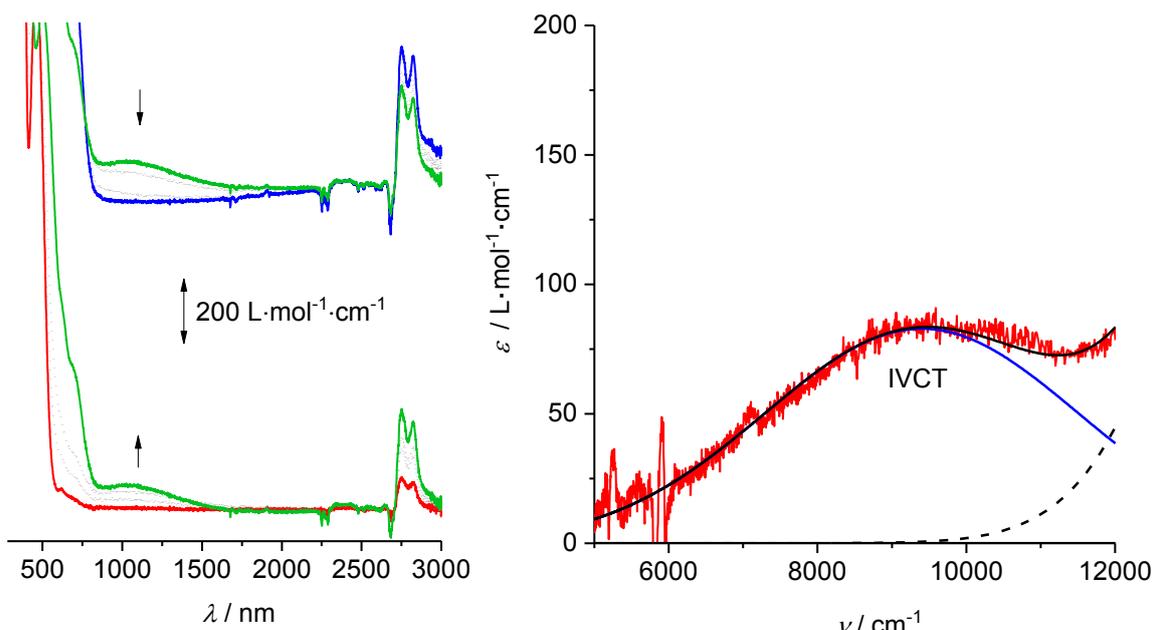
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166 **Figure S113.** Left: UV/Vis-NIR spectra of **1** at 25 °C in dichloromethane (2.0 mmol·L<sup>-1</sup>) at rising potentials (bottom: -200–800 mV; top: 800–1300 mV vs Ag/AgCl); [NBu<sub>4</sub>][PF<sub>6</sub>] as supporting electrolyte (red; **1**), green: **[1]**<sup>+</sup>,  
 167 blue: **[1]**<sup>2+</sup>). Right: Deconvolution of the NIR absorptions of **[1]**<sup>+</sup> using two Gaussian shaped bands determined by  
 168 spectroelectrochemistry in an OTTLE cell (red: experimental spectrum, solid black: sum of Gaussian curves, blue  
 169 IVCT curve).  
 170



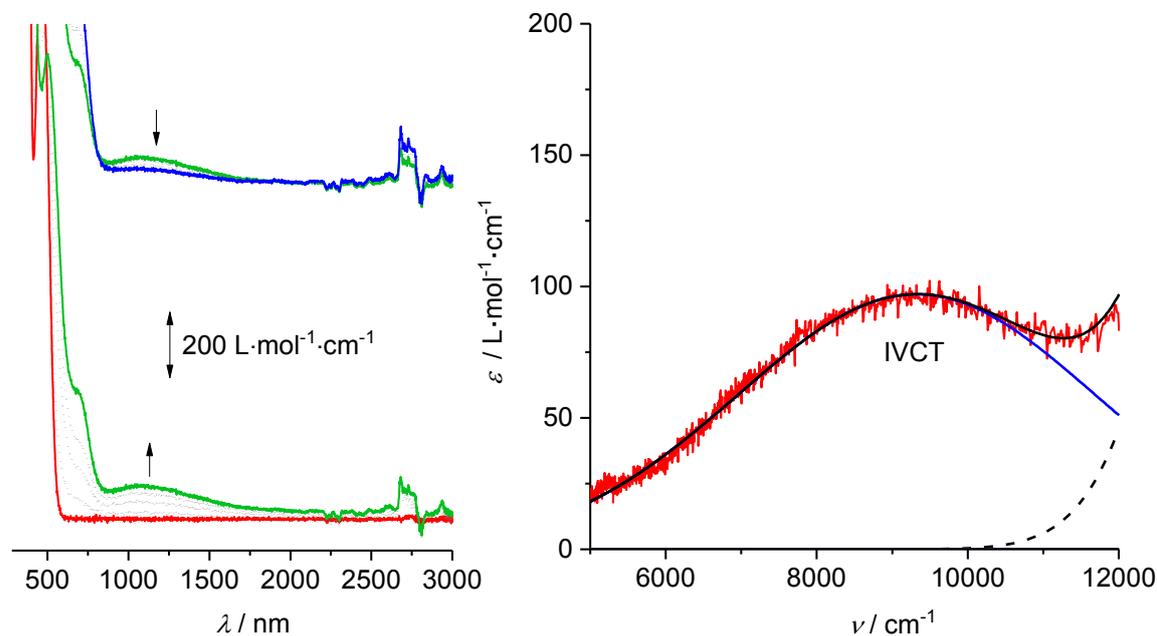
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172 **Figure S114.** Left: UV/Vis-NIR spectra of **1** at 25 °C in acetone (2.0 mmol·L<sup>-1</sup>) at rising potentials (bottom: -200–  
 173 650 mV; top: 650–1300 mV vs Ag/AgCl); [NBu<sub>4</sub>][PF<sub>6</sub>] as supporting electrolyte (red; **1**), green: **[1]**<sup>+</sup>, blue: **[1]**<sup>2+</sup>).  
 174 Right: Deconvolution of the NIR absorptions of **[1]**<sup>+</sup> using two Gaussian shaped bands determined by  
 175 spectroelectrochemistry in an OTTLE cell (red: experimental spectrum, solid black: sum of Gaussian curves, blue  
 176 IVCT curve).  
 177  
 178



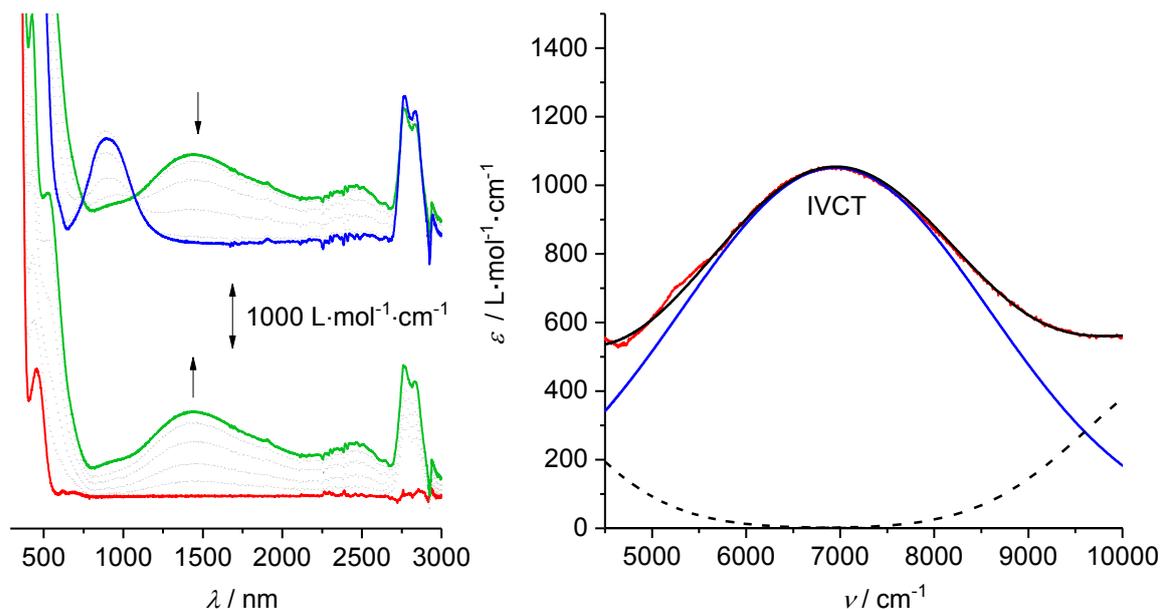
179

180 **Figure S15.** Left: UV/Vis-NIR spectra of **1** at 25 °C in acetonitrile (2.0 mmol·L<sup>-1</sup>) at rising potentials  
 181 (bottom: -200–725 mV; top: 725–1300 mV vs Ag/AgCl); [NBu<sub>4</sub>][PF<sub>6</sub>] as supporting electrolyte (red; [1], green: [1]<sup>+</sup>,  
 182 blue: [1]<sup>2+</sup>). Right: Deconvolution of the NIR absorptions of [1]<sup>+</sup> using two Gaussian shaped bands determined by  
 183 spectroelectrochemistry in an OTTLE cell (red: experimental spectrum, solid black: sum of Gaussian curves, blue  
 184 IVCT curve).



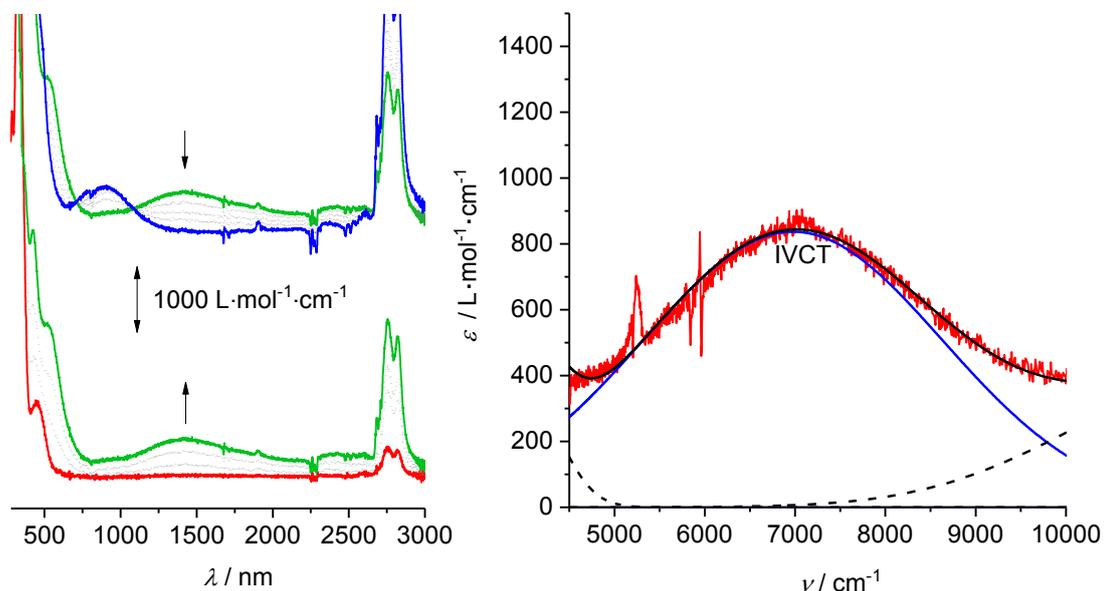
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186 **Figure S16.** Left: UV/Vis-NIR spectra of **1** at 25 °C in propylene carbonate (2.0 mmol·L<sup>-1</sup>) at rising potentials  
 187 (bottom: -200–875 mV; top: 875–1300 mV vs Ag/AgCl); [NBu<sub>4</sub>][PF<sub>6</sub>] as supporting electrolyte (red; [1], green: [1]<sup>+</sup>,  
 188 blue: [1]<sup>2+</sup>). Right: Deconvolution of the NIR absorptions of [1]<sup>+</sup> using two Gaussian shaped bands determined by  
 189 spectroelectrochemistry in an OTTLE cell (red: experimental spectrum, solid black: sum of Gaussian curves, blue  
 190 IVCT curve).  
 191



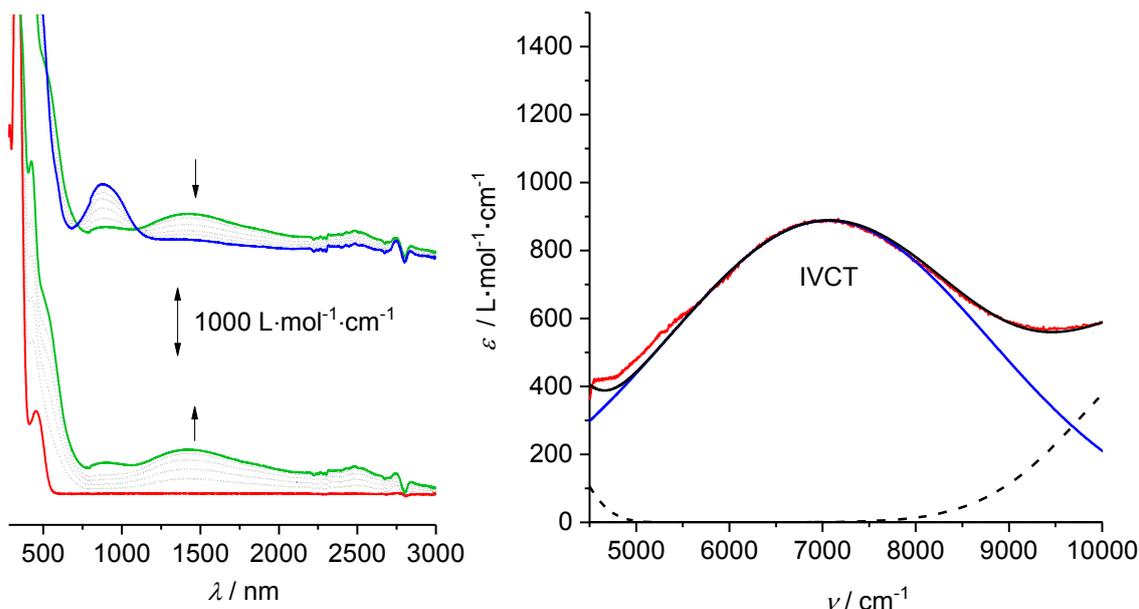
192

193 **Figure S117.** Left: UV/Vis-NIR spectra of **2** at 25 °C in acetone (2.0 mmol·L<sup>-1</sup>) at rising potentials (bottom: -200–  
 194 525 mV; top: 525–1300 mV vs Ag/AgCl); [NBu<sub>4</sub>][BArF] as supporting electrolyte (red; **2**, green: **[2]**<sup>+</sup>, blue: **[2]**<sup>2+</sup>).  
 195 Right: Deconvolution of the NIR absorptions of **[2]**<sup>+</sup> using three Gaussian shaped bands determined by  
 196 spectroelectrochemistry in an OTTLE cell (red: experimental spectrum, solid black: sum of Gaussian curves, blue  
 197 IVCT curve).  
 198



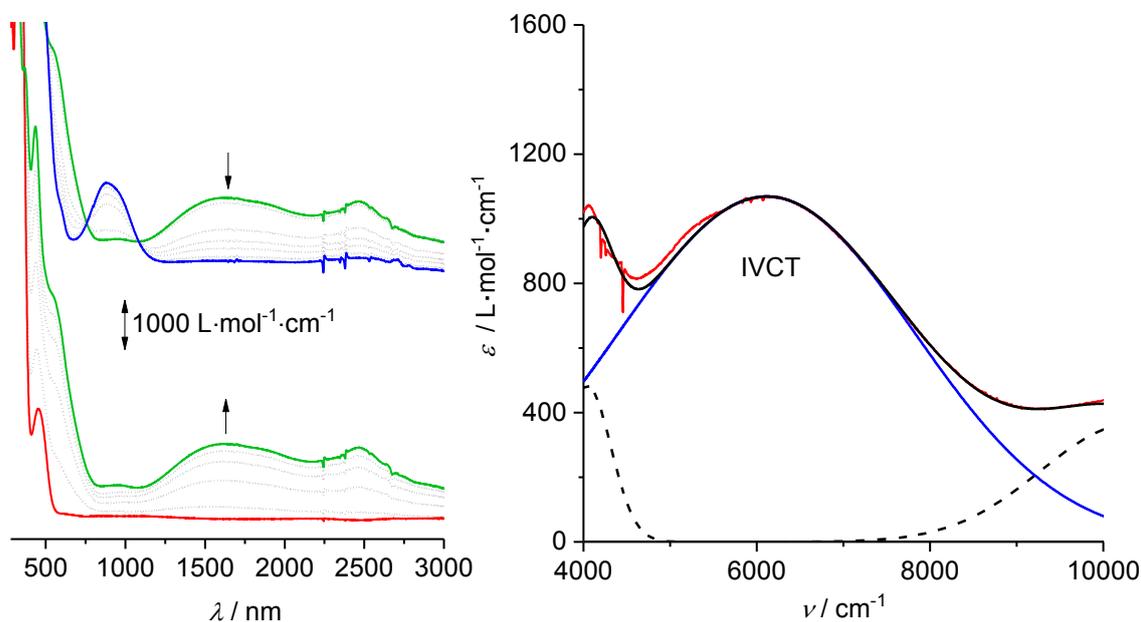
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200 **Figure S118.** Left: UV/Vis-NIR spectra of **2** at 25 °C in acetonitrile (2.0 mmol·L<sup>-1</sup>) at rising potentials  
 201 (bottom: -200–325 mV; top: 325–1300 mV vs Ag/AgCl); [NBu<sub>4</sub>][BArF] as supporting electrolyte (red; **2**, green: **[2]**<sup>+</sup>,  
 202 blue: **[2]**<sup>2+</sup>). Right: Deconvolution of the NIR absorptions of **[2]**<sup>+</sup> using three Gaussian shaped bands determined  
 203 by spectroelectrochemistry in an OTTLE cell (red: experimental spectrum, solid black: sum of Gaussian curves,  
 204 blue IVCT curve).  
 205



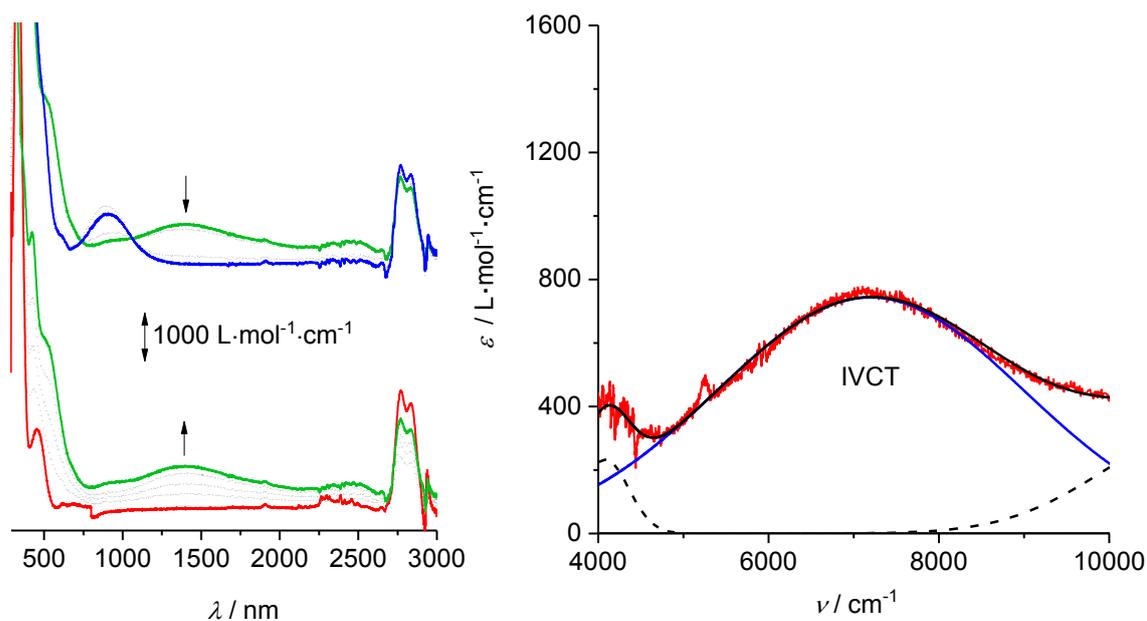
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207 **Figure S119.** Left: UV/Vis-NIR spectra of **2** at 25 °C in propylene carbonate (2.0 mmol·L<sup>-1</sup>) at rising potentials  
 208 (bottom: -200–575 mV; top: 575–1300 mV vs Ag/AgCl); [NBu<sub>4</sub>][BArF] as supporting electrolyte (red; **2**, green: **[2]**<sup>+</sup>,  
 209 blue: **[2]**<sup>2+</sup>). Right: Deconvolution of the NIR absorptions of **[2]**<sup>+</sup> using three Gaussian shaped bands determined  
 210 by spectroelectrochemistry in an OTTLE cell (red: experimental spectrum, solid black: sum of Gaussian curves,  
 211 blue IVCT curve).  
 212



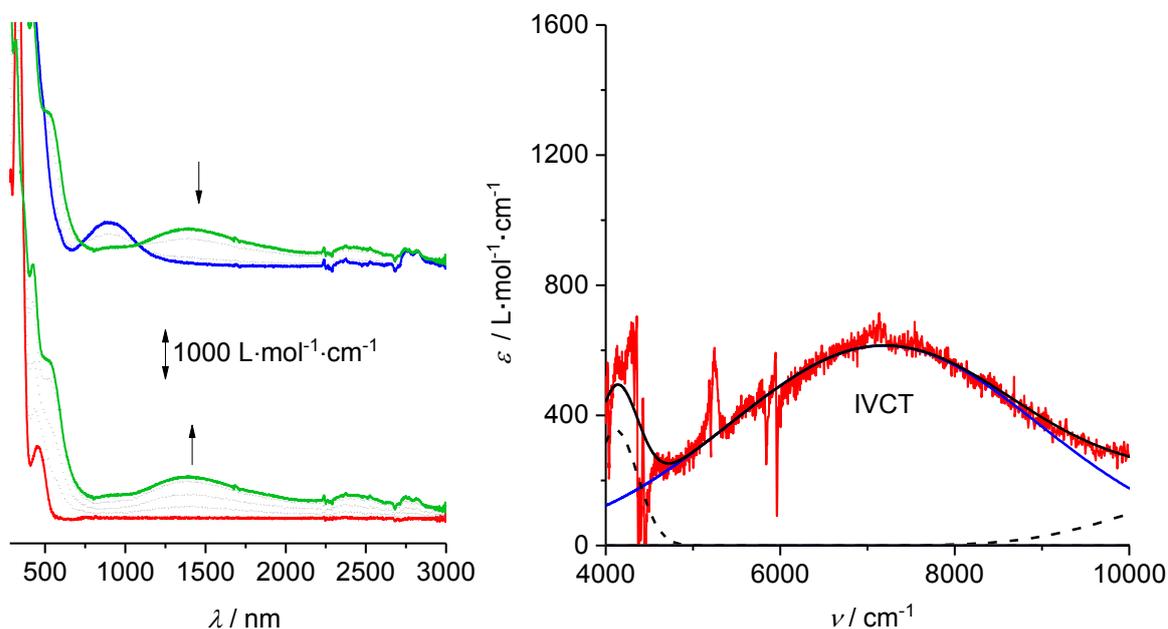
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214 **Figure S120.** Left: UV/Vis-NIR spectra of **2** at 25 °C in dichloromethane (2.0 mmol·L<sup>-1</sup>) at rising potentials  
 215 (bottom: -200–225 mV; top: 225–1300 mV vs Ag/AgCl); [NBu<sub>4</sub>][PF<sub>6</sub>] as supporting electrolyte (red; **2**, green: **[2]**<sup>+</sup>,  
 216 blue: **[2]**<sup>2+</sup>). Right: Deconvolution of the NIR absorptions of **[2]**<sup>+</sup> using three Gaussian shaped bands determined  
 217 by spectroelectrochemistry in an OTTLE cell (red: experimental spectrum, solid black: sum of Gaussian curves,  
 218 blue IVCT curve).



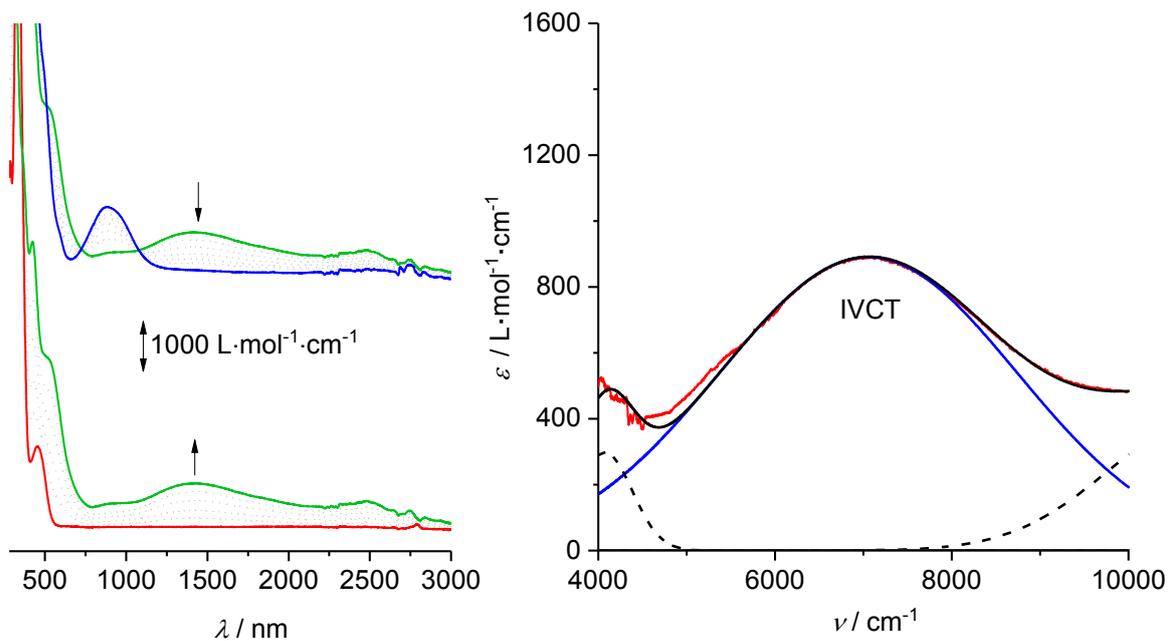
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220 **Figure S121.** Left: UV/Vis-NIR spectra of **2** at 25 °C in acetone ( $2.0 \text{ mmol}\cdot\text{L}^{-1}$ ) at rising potentials (bottom: -200–  
 221 700 mV; top: 700–1300 mV vs Ag/AgCl);  $[\text{NBu}_4][\text{PF}_6]$  as supporting electrolyte (red; **2**), green:  $[\text{2}]^+$ , blue:  $[\text{2}]^{2+}$ ).  
 222 Right: Deconvolution of the NIR absorptions of  $[\text{2}]^+$  using three Gaussian shaped bands determined by  
 223 spectroelectrochemistry in an OTTLE cell (red: experimental spectrum, solid black: sum of Gaussian curves, blue  
 224 IVCT curve).



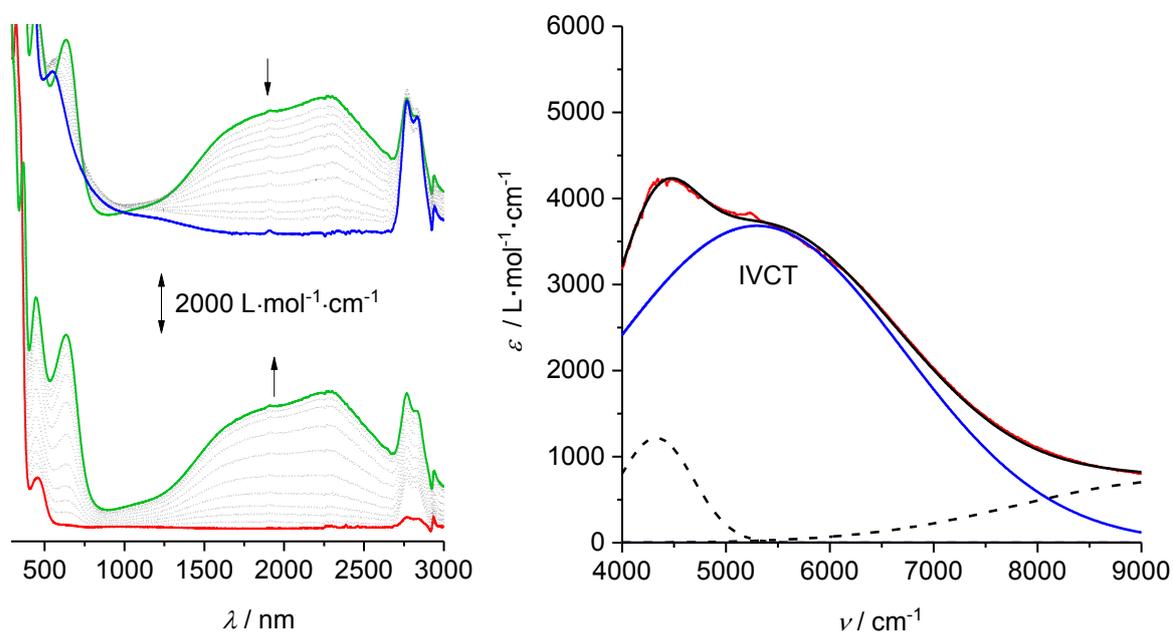
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226 **Figure S122.** Left: UV/Vis-NIR spectra of **2** at 25 °C in acetonitrile ( $2.0 \text{ mmol}\cdot\text{L}^{-1}$ ) at rising potentials  
 227 (bottom: -200–475 mV; top: 475–1300 mV vs Ag/AgCl);  $[\text{NBu}_4][\text{PF}_6]$  as supporting electrolyte (red; **2**), green:  
 228  $[\text{2}]^+$ , blue:  $[\text{2}]^{2+}$ ). Right: Deconvolution of the NIR absorptions of  $[\text{2}]^+$  using three Gaussian shaped bands determined  
 229 by spectroelectrochemistry in an OTTLE cell (red: experimental spectrum, solid black: sum of Gaussian curves,  
 230 blue IVCT curve).



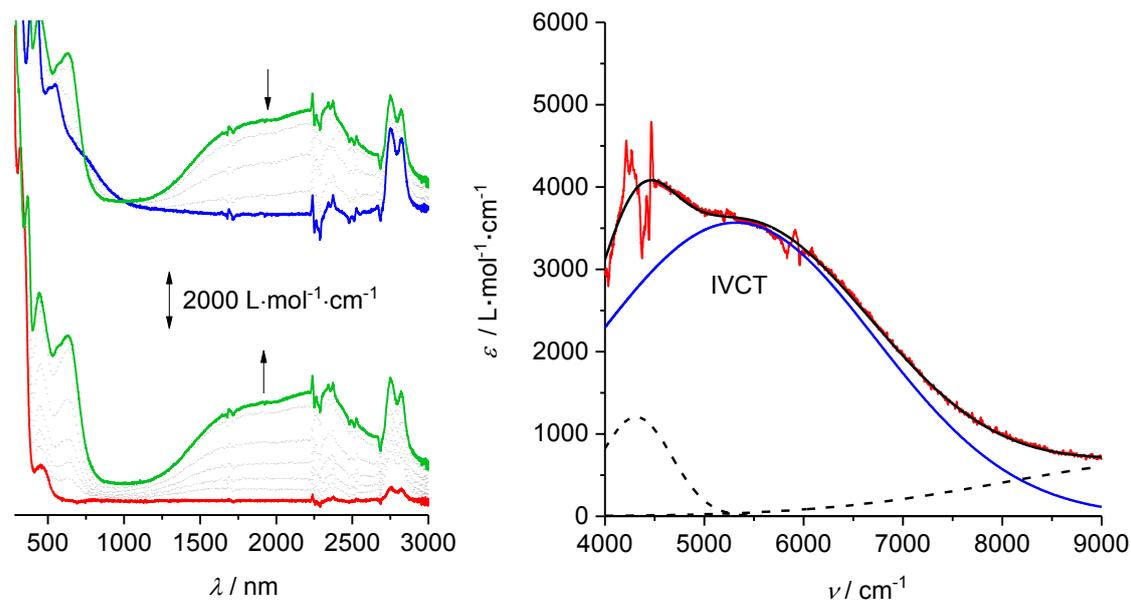
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232 **Figure SI23.** Left: UV/Vis-NIR spectra of **2** at 25 °C in propylene carbonate (2.0 mmol·L<sup>-1</sup>) at rising potentials  
 233 (bottom: -200–650 mV; top: 650–1300 mV vs Ag/AgCl); [NBu<sub>4</sub>][PF<sub>6</sub>] as supporting electrolyte (red; **2**), green: **[2]<sup>+</sup>**,  
 234 blue: **[2]<sup>2+</sup>**). Right: Deconvolution of the NIR absorptions of **[2]<sup>+</sup>** using three Gaussian shaped bands determined  
 235 by spectroelectrochemistry in an OTTLE cell (red: experimental spectrum, solid black: sum of Gaussian curves,  
 236 blue IVCT curve).



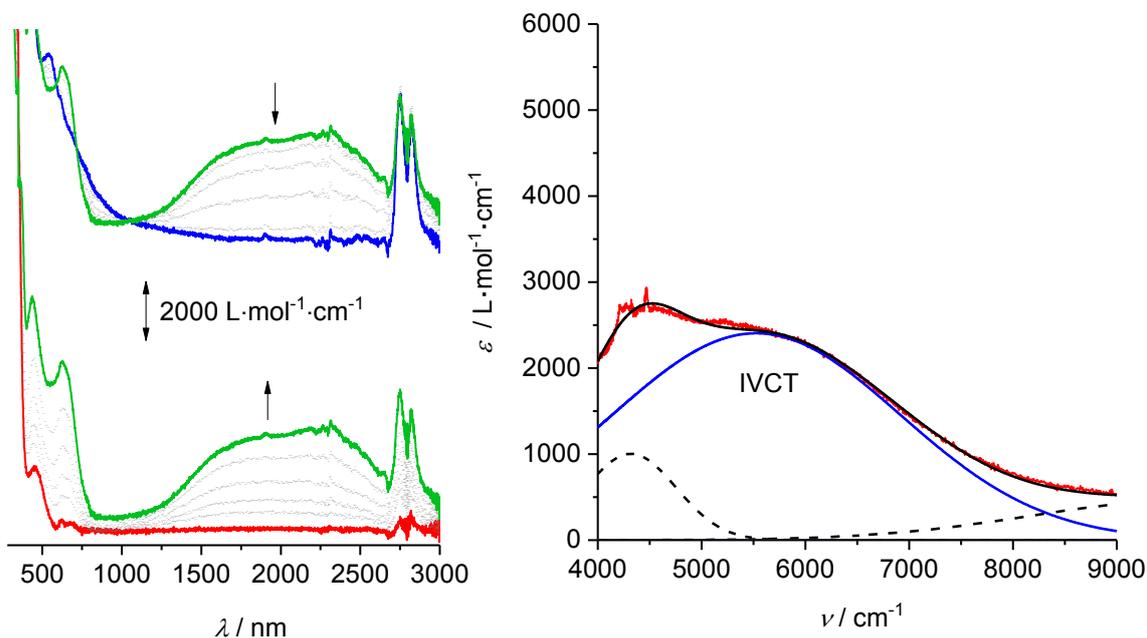
237

238 **Figure SI24.** Left: UV/Vis-NIR spectra of **3** at 25 °C in acetone (1.0 mmol·L<sup>-1</sup>) at rising potentials (bottom: -200–  
 239 400 mV; top: 400–1300 mV vs Ag/AgCl); [NBu<sub>4</sub>][BARF] as supporting electrolyte (red; **3**), green: **[3]<sup>+</sup>**, blue: **[3]<sup>2+</sup>**).  
 240 Right: Deconvolution of the NIR absorptions of **[3]<sup>+</sup>** using three Gaussian shaped bands determined by  
 241 spectroelectrochemistry in an OTTLE cell (red: experimental spectrum, solid black: sum of Gaussian curves, blue  
 242 IVCT curve).  
 243



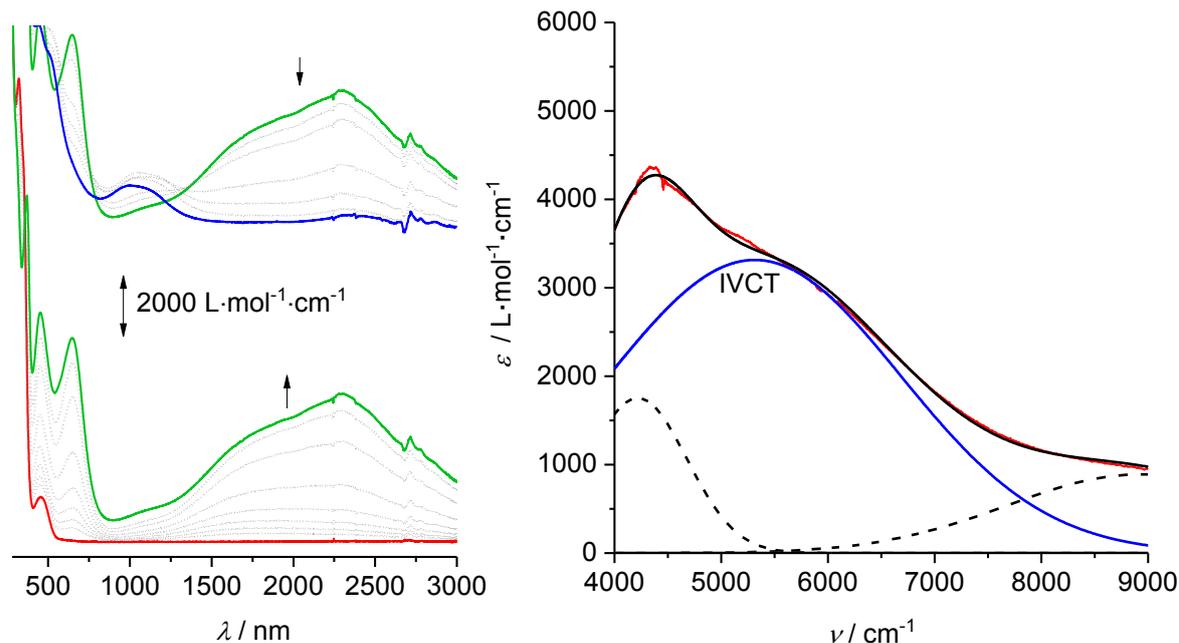
244

245 **Figure SI25.** Left: UV/Vis-NIR spectra of **3** at 25 °C in acetonitrile (1.0 mmol·L<sup>-1</sup>) at rising potentials  
 246 (bottom: -200–225 mV; top: 225–1300 mV vs Ag/AgCl); [NBu<sub>4</sub>][BArF] as supporting electrolyte (red; **3**), green: **[3]<sup>+</sup>**,  
 247 blue: **[3]<sup>2+</sup>**). Right: Deconvolution of the NIR absorptions of **[3]<sup>+</sup>** using three Gaussian shaped bands determined  
 248 by spectroelectrochemistry in an OTTLE cell (red: experimental spectrum, solid black: sum of Gaussian curves,  
 249 blue IVCT curve).



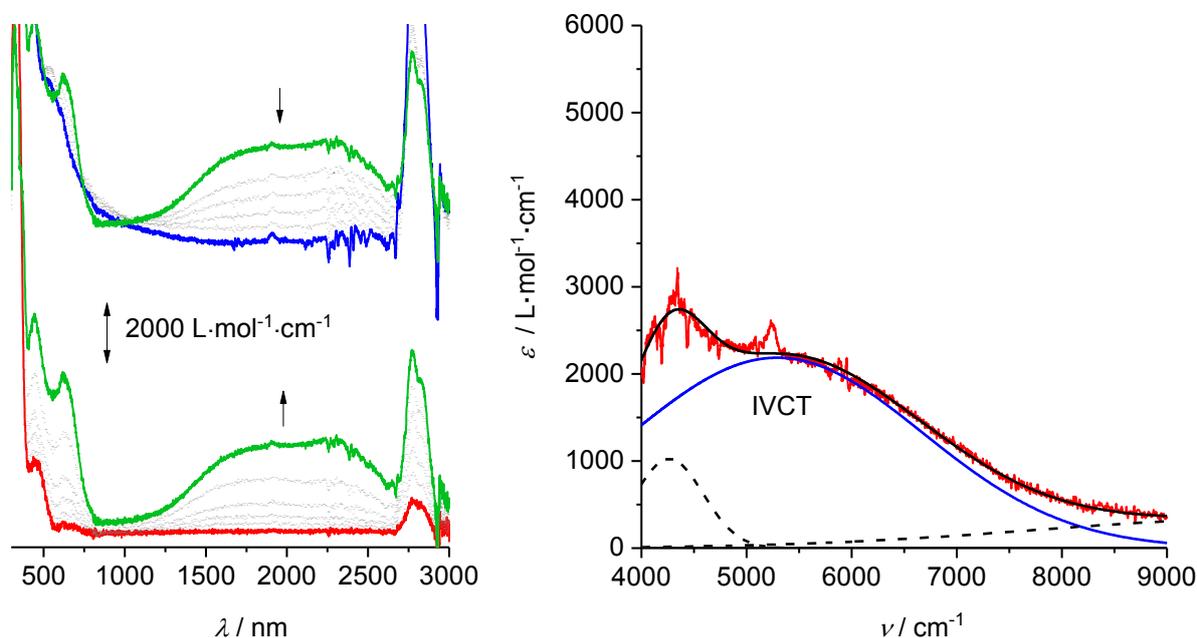
250

251 **Figure SI26.** Left: UV/Vis-NIR spectra of **3** at 25 °C in propylene carbonate (1.0 mmol·L<sup>-1</sup>) at rising potentials  
 252 (bottom: -200–400 mV; top: 400–1300 mV vs Ag/AgCl); [NBu<sub>4</sub>][BArF] as supporting electrolyte (red; **3**), green: **[3]<sup>+</sup>**,  
 253 blue: **[3]<sup>2+</sup>**). Right: Deconvolution of the NIR absorptions of **[3]<sup>+</sup>** using three Gaussian shaped bands determined  
 254 by spectroelectrochemistry in an OTTLE cell (red: experimental spectrum, solid black: sum of Gaussian curves,  
 255 blue IVCT curve).  
 256



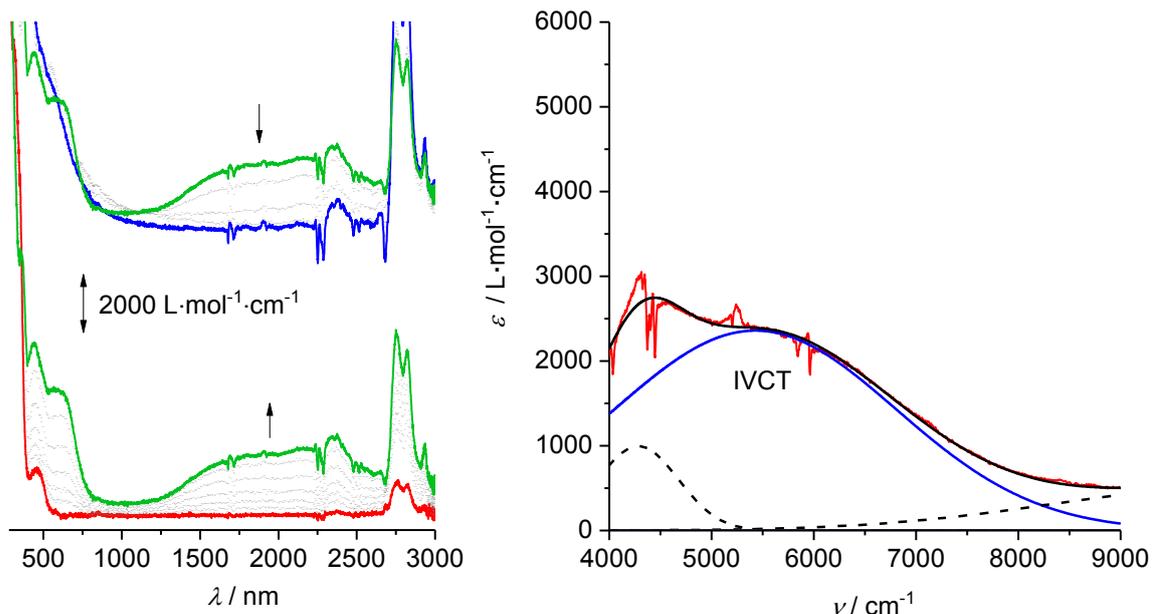
257

258 **Figure SI27.** Left: UV/Vis-NIR spectra of **3** at 25 °C in dichloromethane (1.0 mmol·L<sup>-1</sup>) at rising potentials (bottom: -200–275 mV; top: 275–1300 mV vs Ag/AgCl); [NBu<sub>4</sub>][PF<sub>6</sub>] as supporting electrolyte (red; **3**), green: **[3]<sup>+</sup>**,  
 259 blue: **[3]<sup>2+</sup>**). Right: Deconvolution of the NIR absorptions of **[3]<sup>+</sup>** using three Gaussian shaped bands determined  
 260 by spectroelectrochemistry in an OTTLE cell (red: experimental spectrum, solid black: sum of Gaussian curves,  
 261 blue IVCT curve).  
 262



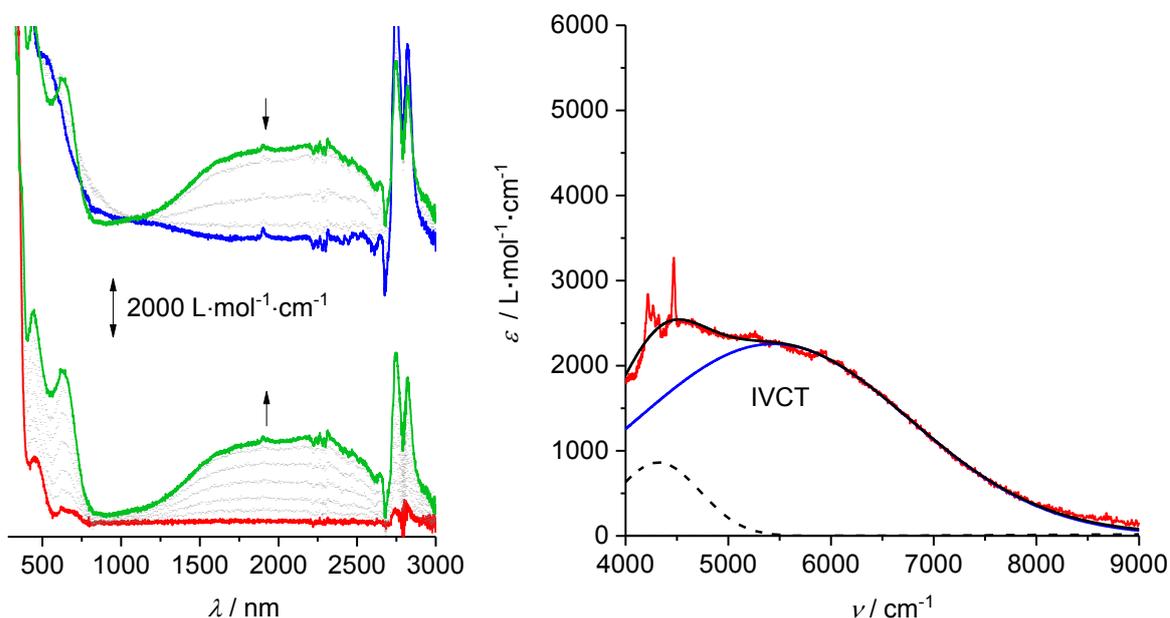
263

264 **Figure SI28.** Left: UV/Vis-NIR spectra of **3** at 25 °C in acetone (1.0 mmol·L<sup>-1</sup>) at rising potentials (bottom: -200–  
 265 350 mV; top: 350–1300 mV vs Ag/AgCl); [NBu<sub>4</sub>][PF<sub>6</sub>] as supporting electrolyte (red; **3**), green: **[3]<sup>+</sup>**, blue: **[3]<sup>2+</sup>**).  
 266 Right: Deconvolution of the NIR absorptions of **[3]<sup>+</sup>** using three Gaussian shaped bands determined by  
 267 spectroelectrochemistry in an OTTLE cell (red: experimental spectrum, solid black: sum of Gaussian curves, blue  
 268 IVCT curve).



269

270 **Figure SI29.** Left: UV/Vis-NIR spectra of **3** at 25 °C in acetonitrile (1.0 mmol·L<sup>-1</sup>) at rising potentials  
 271 (bottom: -200–275 mV; top: 275–1300 mV vs Ag/AgCl); [NBu<sub>4</sub>][PF<sub>6</sub>] as supporting electrolyte (red; [3], green: [3]<sup>+</sup>,  
 272 blue: [3]<sup>2+</sup>). Right: Deconvolution of the NIR absorptions of [3]<sup>+</sup> using three Gaussian shaped bands determined  
 273 by spectroelectrochemistry in an OTTLE cell (red: experimental spectrum, solid black: sum of Gaussian curves,  
 274 blue IVCT curve).



275

276 **Figure SI30.** Left: UV/Vis-NIR spectra of **3** at 25 °C in propylene carbonate (1.0 mmol·L<sup>-1</sup>) at rising potentials  
 277 (bottom: -200–450 mV; top: 450–1300 mV vs Ag/AgCl); [NBu<sub>4</sub>][PF<sub>6</sub>] as supporting electrolyte (red; [3], green: [3]<sup>+</sup>,  
 278 blue: [3]<sup>2+</sup>). Right: Deconvolution of the NIR absorptions of [3]<sup>+</sup> using three Gaussian shaped bands determined  
 279 by spectroelectrochemistry in an OTTLE cell (red: experimental spectrum, solid black: sum of Gaussian curves,  
 280 blue IVCT curve).  
 281

282 **References**

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