Electronic Supplementary Information for Dalton Transactions
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Electronic Supplementary Information

Ferrocene-Thiophene Dyads with Azadiene Spacers: Electrochemical, Electronic and Cation Sensing Properties

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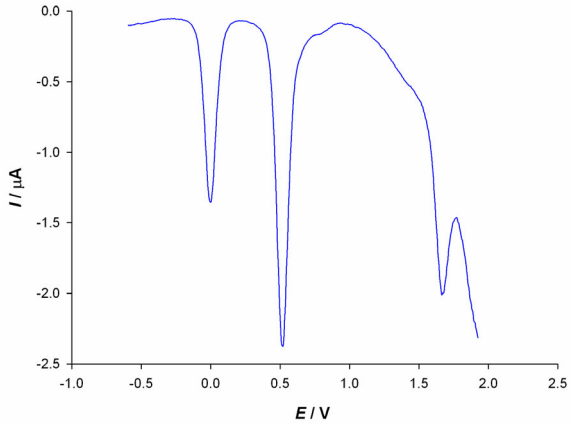

Figure ESI 1a. OSWV of compound **3a** (1mM) in CH_2Cl_2/CH_3CN 3/2 using $[(n\text{-}Bu)_4N]ClO_4$ as supporting electrolyte and decamethylferrocene (DMFc) as internal standard, scanned at 100 mVs^{-1} from -0.7 V to 2 V.

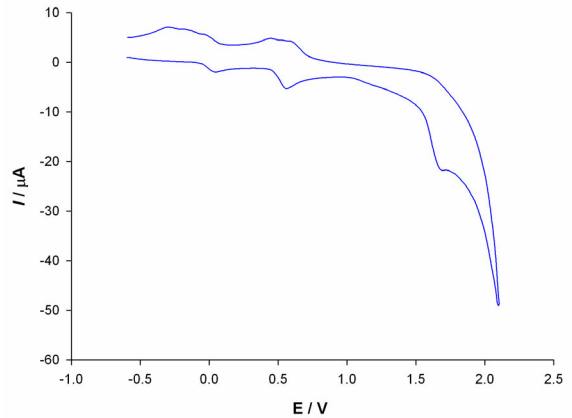

Figure ESI 1b. Cyclic voltammogram of compound **3a** (1mM) in CH_2Cl_2/CH_3CN 3/2 using $[(n\text{-}Bu)_4N]ClO_4$ as supporting electrolyte and decamethylferrocene (DMFc) as internal standard, scanned at 200 mVs^{-1} from -0.7 V to 2 V.

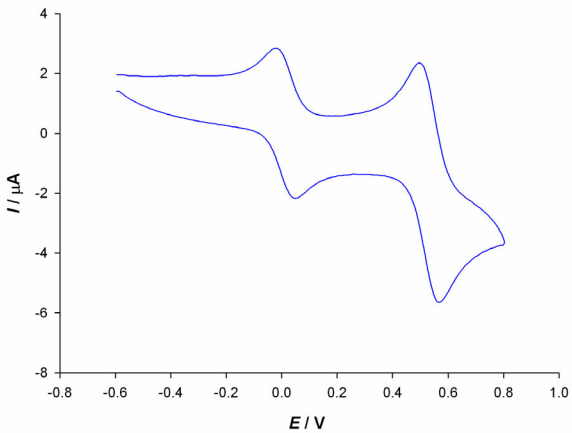

Figure ESI 1c. Cyclic voltammogram of compound **3a** (1mM) in CH_2Cl_2/CH_3CN 3/2 using $[(n\text{-}Bu)_4N]ClO_4$ as supporting electrolyte and decamethylferrocene (DMFc) as internal standard, scanned at 200 mVs^{-1} from -0.7 V to 0.85 V.

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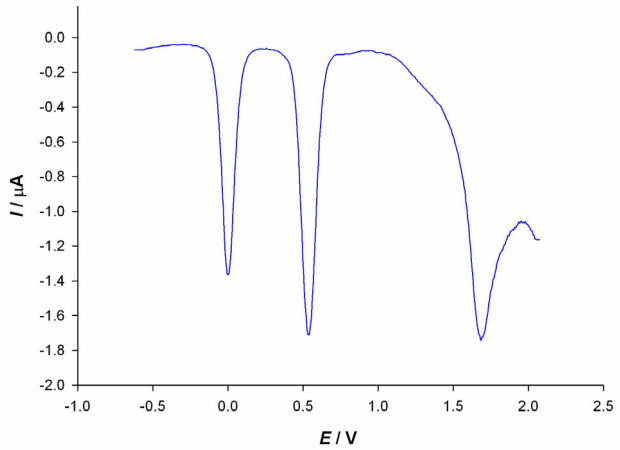

Figure ESI 2a. OSWV of compound **3c** (1mM) in CH_2Cl_2/CH_3CN 3/2 using $[(n\text{-}Bu)_4N]ClO_4$ as supporting electrolyte and decamethylferrocene (DMFc) as internal standard, scanned at 100 mVs^{-1} from -0.7 V to 2 V.

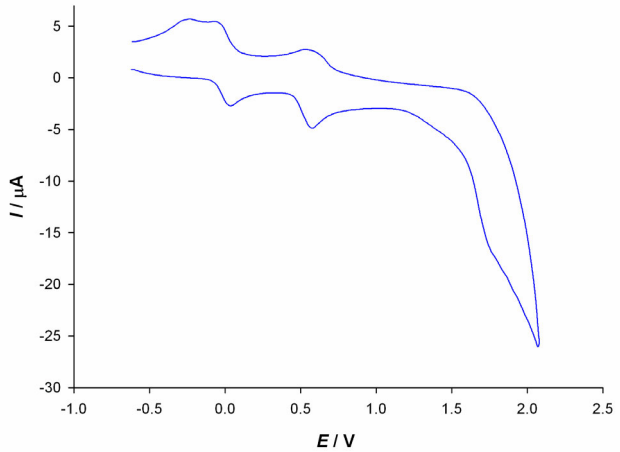

Figure ESI 2b. Cyclic voltammogram of compound **3c** (1mM) in CH_2Cl_2/CH_3CN 3/2 using $[(n\text{-}Bu)_4N]ClO_4$ as supporting electrolyte and decamethylferrocene (DMFc) as internal standard, scanned at 200 mVs^{-1} from -0.7 V to 2 V.

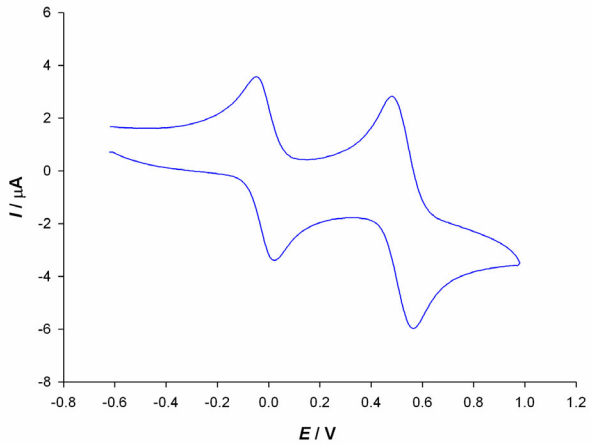

Figure ESI 2c. Cyclic voltammogram of compound **3c** (1mM) in CH_2Cl_2/CH_3CN 3/2 using $[(n\text{-}Bu)_4N]ClO_4$ as supporting electrolyte and decamethylferrocene (DMFc) as internal standard, scanned at 200 mVs^{-1} from -0.7 V to 1 V.

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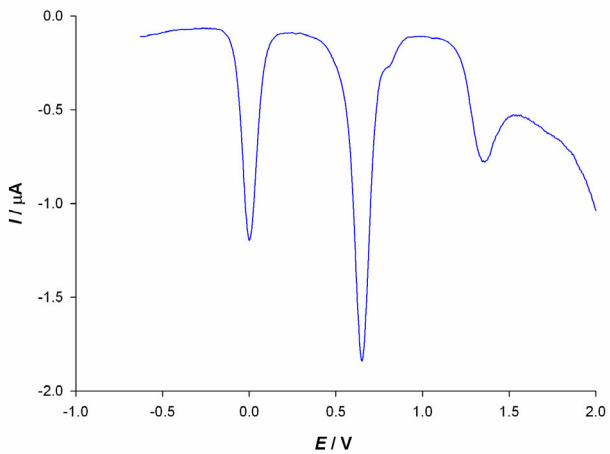

Figure ESI 3a. OSWV of compound **5a** (1mM) in CH_2Cl_2/CH_3CN 3/2 using $[(n\text{-}Bu)_4N]ClO_4$ as supporting electrolyte and decamethylferrocene (DMFc) as internal standard, scanned at 100 mVs^{-1} from -0.7 V to 2 V.

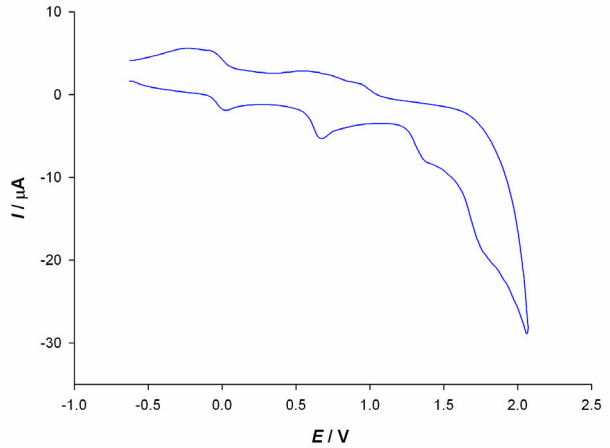

Figure ESI 3b. Cyclic voltammogram of compound **5a** (1mM) in CH_2Cl_2/CH_3CN 3/2 using $[(n\text{-}Bu)_4N]ClO_4$ as supporting electrolyte and decamethylferrocene (DMFc) as internal standard, scanned at 200 mVs^{-1} from -0.7 V to 2 V.

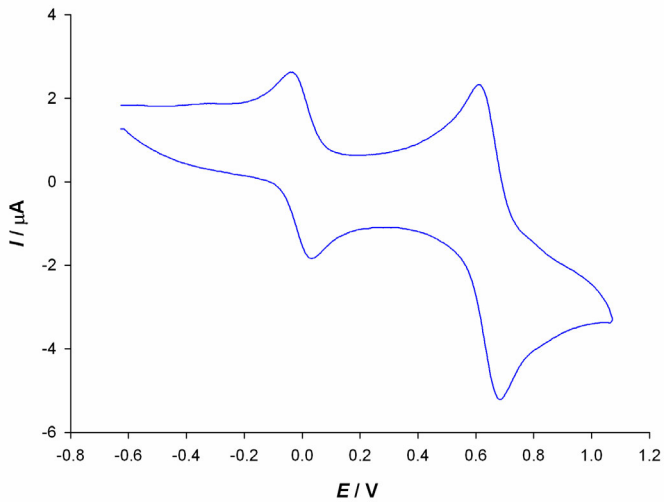

Figure ESI 3c. Cyclic voltammogram of compound **5a** (1mM) in CH_2Cl_2/CH_3CN 3/2 using $[(n\text{-}Bu)_4N]ClO_4$ as supporting electrolyte and decamethylferrocene (DMFc) as internal standard, scanned at 200 mVs^{-1} from -0.7 V to 1.1 V.

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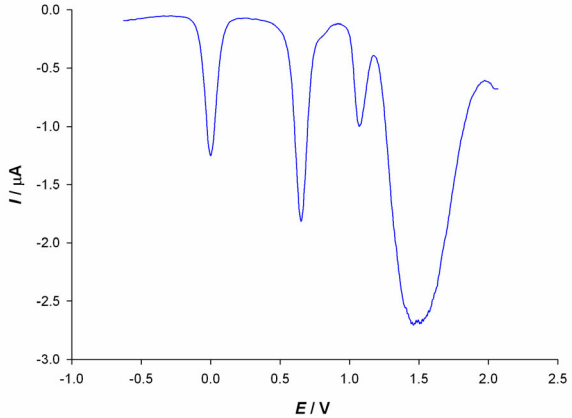

Figure ESI 4a. OSWV of compound **5b** (1mM) in CH_2Cl_2/CH_3CN 3/2 using $[(n\text{-}Bu)_4N]ClO_4$ as supporting electrolyte and decamethylferrocene (DMFc) as internal standard, scanned at 100 mVs^{-1} from -0.7 V to 2 V.

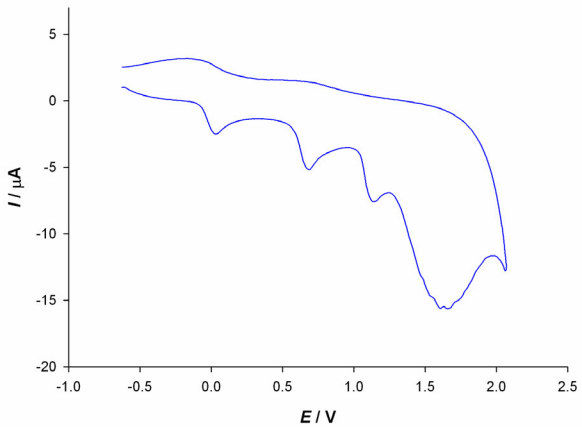

Figure ESI 4b. Cyclic voltammogram of compound **5b** (1mM) in CH_2Cl_2/CH_3CN 3/2 using $[(n\text{-}Bu)_4N]ClO_4$ as supporting electrolyte and decamethylferrocene (DMFc) as internal standard, scanned at 200 mVs^{-1} from -0.7 V to 2 V.

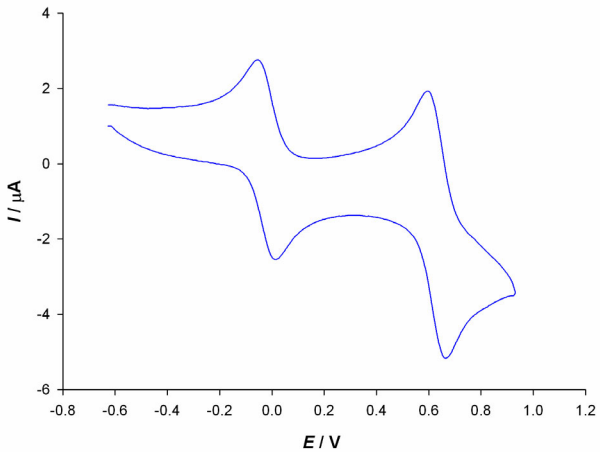

Figure ESI 4c. Cyclic voltammogram of compound **5b** (1mM) in CH_2Cl_2/CH_3CN 3/2 using $[(n\text{-}Bu)_4N]ClO_4$ as supporting electrolyte and decamethylferrocene (DMFc) as internal standard, scanned at 200 mVs^{-1} from -0.7 V to 0.9 V.

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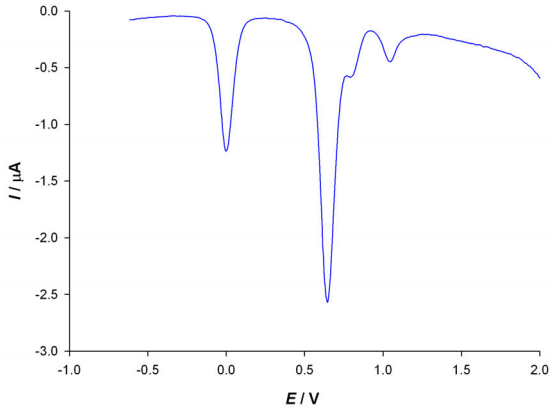

Figure ESI 5a. OSWV of compound **5c** (1mM) in CH_2Cl_2/CH_3CN 3/2 using [(*n*-Bu)$_4$N]ClO_4 as supporting electrolyte and decamethylferrocene (DMFc) as internal standard, scanned at 100 mVs^{-1} from -0.7 V to 2 V.

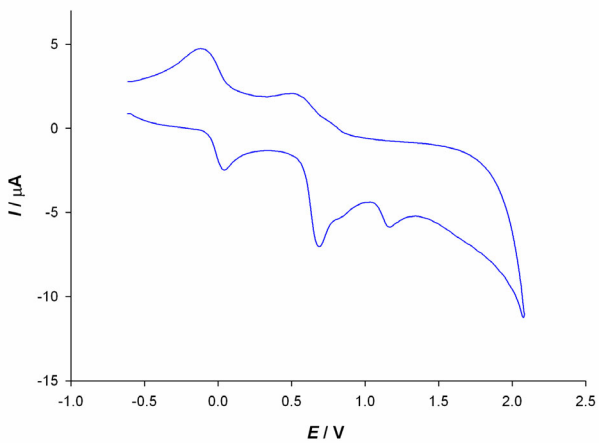

Figure ESI 5b. Cyclic voltammogram of compound **5c** (1mM) in CH_2Cl_2/CH_3CN 3/2 using [(*n*-Bu)$_4$N]ClO_4 as supporting electrolyte and decamethylferrocene (DMFc) as internal standard, scanned at 200 mVs^{-1} from -0.7 V to 2 V.

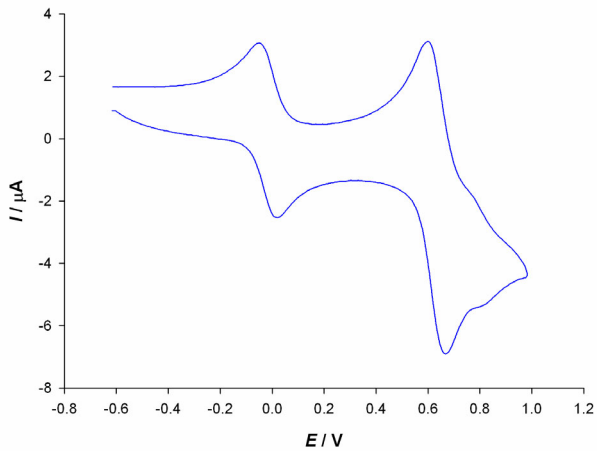

Figure ESI 5c. Cyclic voltammogram of compound **5c** (1mM) in CH_2Cl_2/CH_3CN 3/2 using [(*n*-Bu)$_4$N]ClO_4 as supporting electrolyte and decamethylferrocene (DMFc) as internal standard, scanned at 200 mVs^{-1} from -0.7 V to 1 V.

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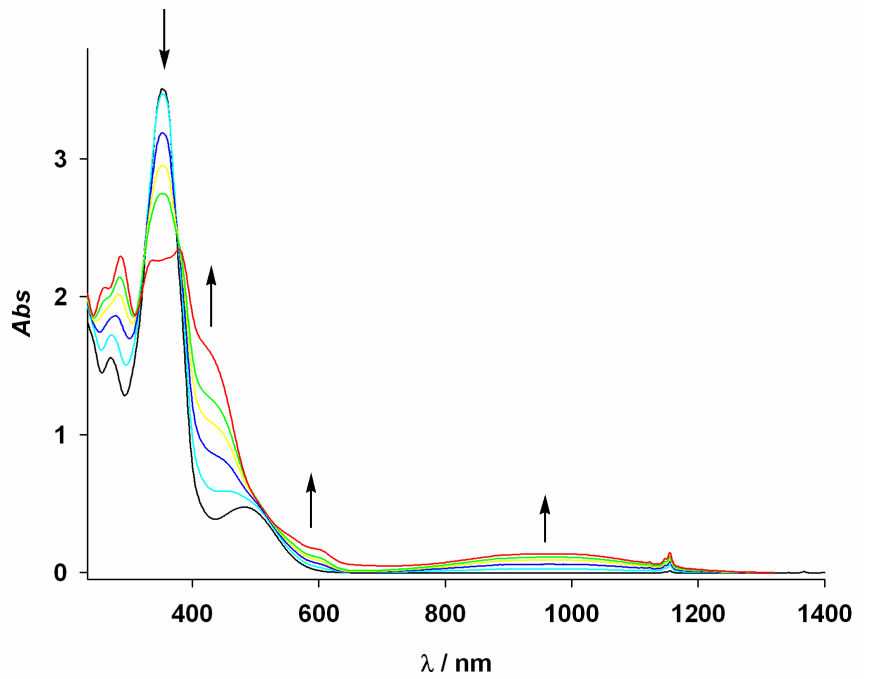

Figure ESI 6. Evolution of Uv-Vis-NIR spectra during the course of the oxidation ($0 \leq n \leq 1$) of compound **3a** (1 mM) in CH_2Cl_2/CH_3CN 3/2 with $[(n\text{-Bu})_4N]PF_6$ (0.15 M) as supporting electrolyte. Arrows indicate absorptions that increase or decrease during the experiment.

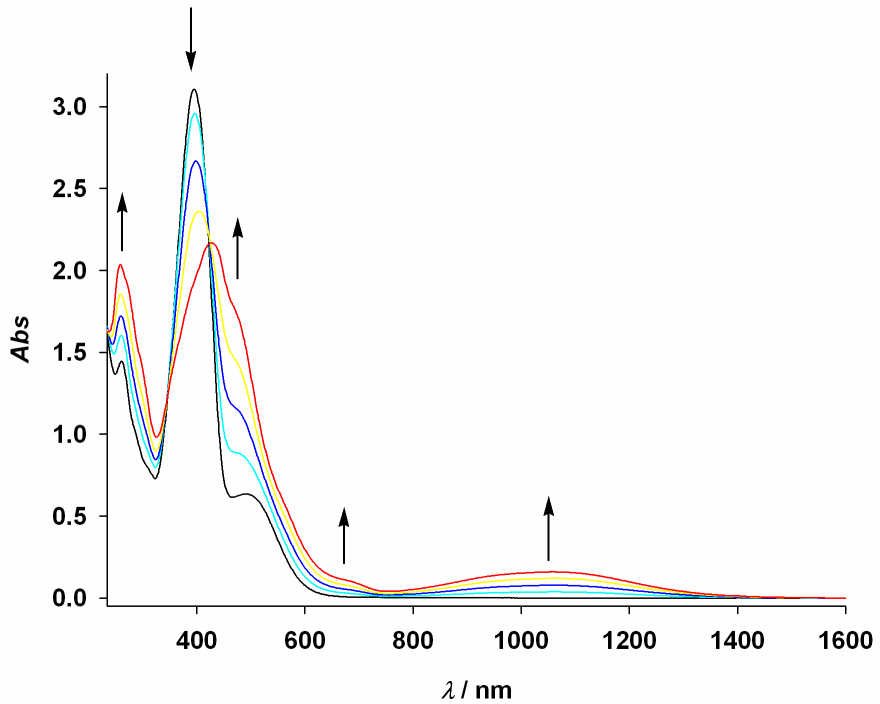

Figure ESI 7. Evolution of Uv-Vis-NIR spectra during the course of the oxidation ($0 \leq n \leq 1$) of compound **3b** (1 mM) in CH_2Cl_2/CH_3CN 3/2 with $[(n\text{-Bu})_4N]PF_6$ (0.15 M) as supporting electrolyte. Arrows indicate absorptions that increase or decrease during the experiment.

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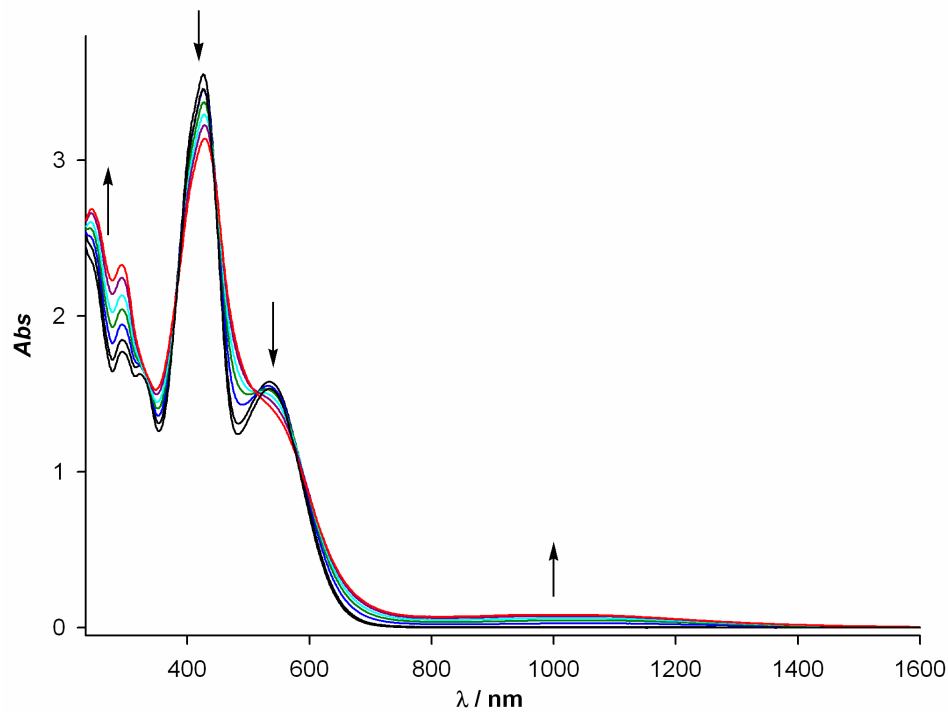

Figure ESI 8. Evolution of Uv-Vis-NIR spectra during the course of the oxidation ($0 \leq n \leq 1$) of compound **3c** (1 mM) in CH_2Cl_2/CH_3CN 3/2 with $[(n\text{-Bu})_4N]PF_6$ (0.15 M) as supporting electrolyte. Arrows indicate absorptions that increase or decrease during the experiment.

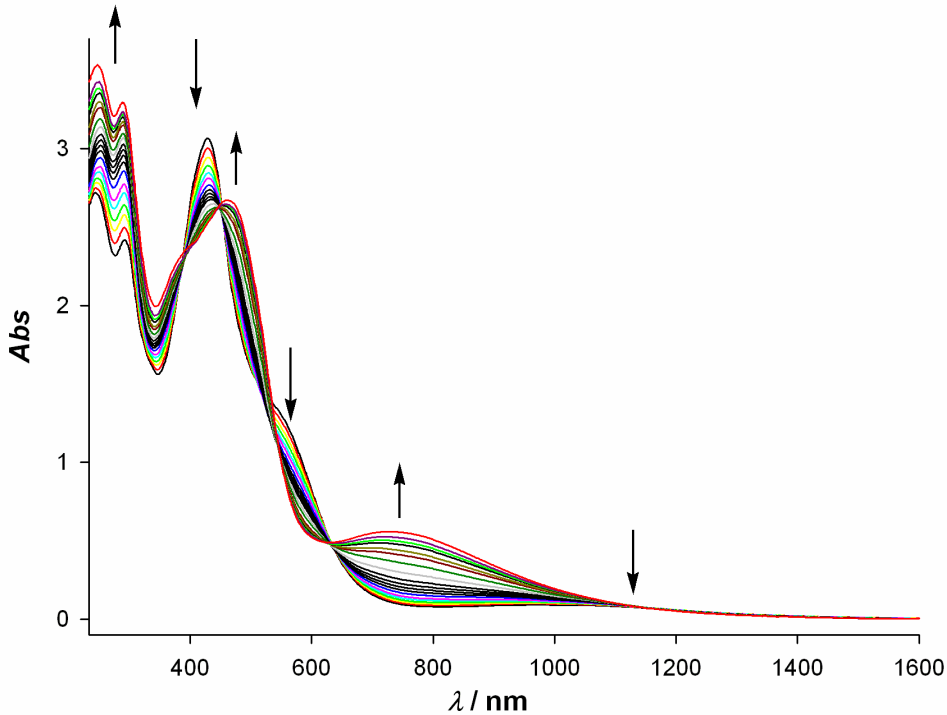

Figure ESI 9. Evolution of Uv-Vis-NIR spectra during the course of the oxidation ($1 \leq n \leq 2$) of compound **3c** (1 mM) in CH_2Cl_2/CH_3CN 3/2 with $[(n\text{-Bu})_4N]PF_6$ (0.15 M) as supporting electrolyte. Arrows indicate absorptions that increase or decrease during the experiment.

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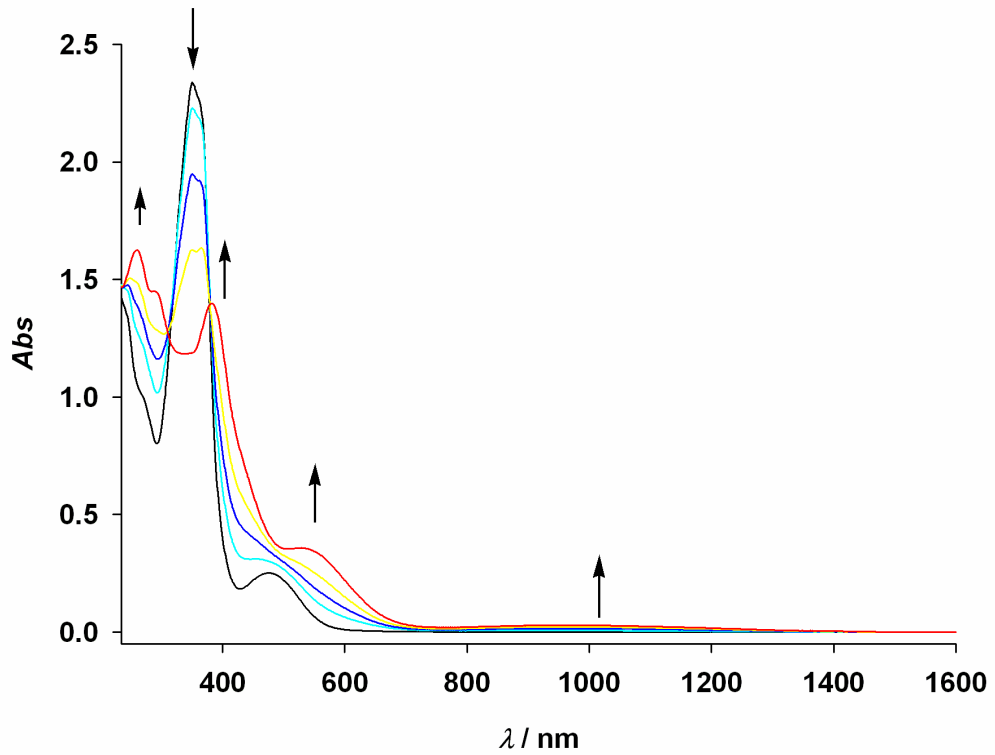

Figure ESI 10. Evolution of Uv-Vis-NIR spectra during the course of the oxidation (0 ≤ n ≤ 1) of compound **5a** (1 mM) in CH_2Cl_2/CH_3CN 3/2 with $[(n\text{-Bu})_4N]PF_6$ (0.15 M) as supporting electrolyte. Arrows indicate absorptions that increase or decrease during the experiment.

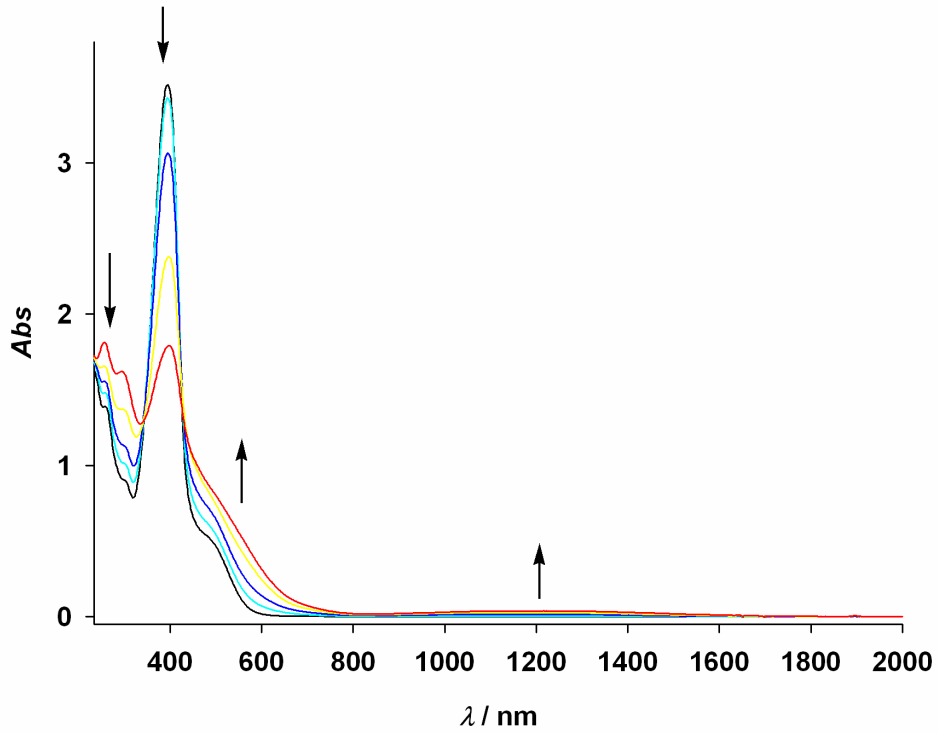

Figure ESI 11. Evolution of Uv-Vis-NIR spectra during the course of the oxidation (0 ≤ n ≤ 1) of compound **5b** (1 mM) in CH_2Cl_2/CH_3CN 3/2 with $[(n\text{-Bu})_4N]PF_6$ (0.15 M) as supporting electrolyte. Arrows indicate absorptions that increase or decrease during the experiment.

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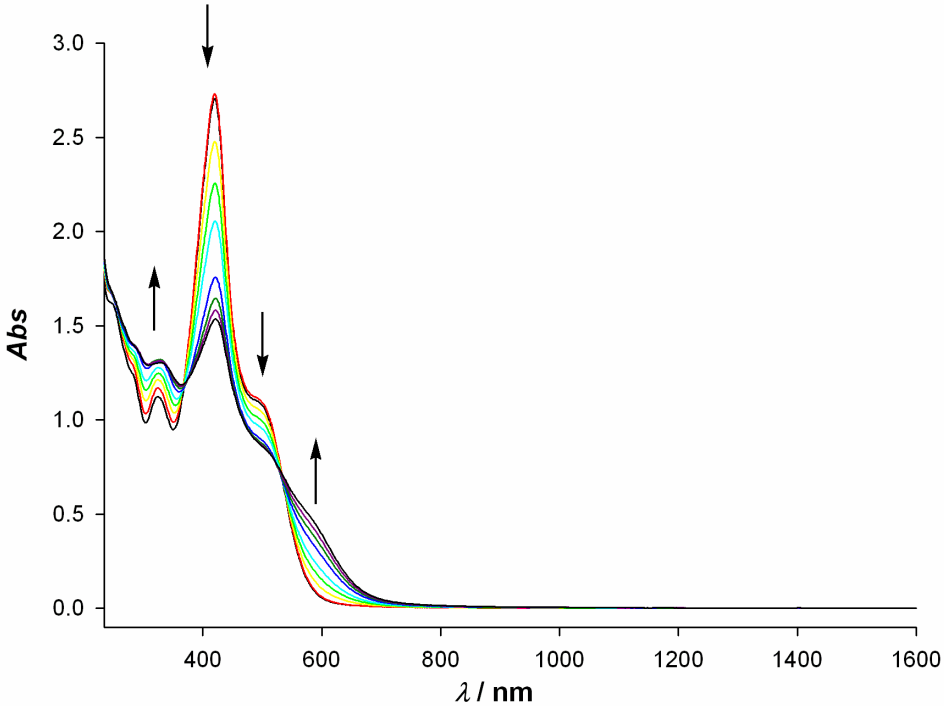

Figure ESI 12. Evolution of Uv-Vis-NIR spectra during the course of the oxidation ($0 \leq n \leq 1$) of compound **5c** (1 mM) in CH_2Cl_2/CH_3CN 3/2 with $[(n\text{-Bu})_4N]PF_6$ (0.15 M) as supporting electrolyte. Arrows indicate absorptions that increase or decrease during the experiment.

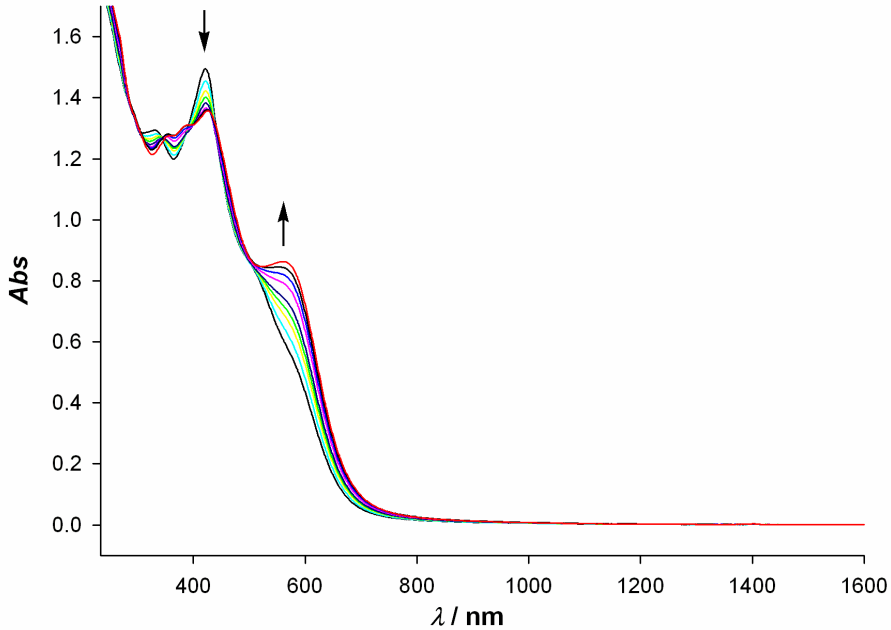

Figure ESI 13. Evolution of Uv-Vis-NIR spectra during the course of the oxidation ($1 \leq n \leq 2$) of compound **5c** (1 mM) in CH_2Cl_2/CH_3CN 3/2 with $[(n\text{-Bu})_4N]PF_6$ (0.15 M) as supporting electrolyte. Arrows indicate absorptions that increase or decrease during the experiment.

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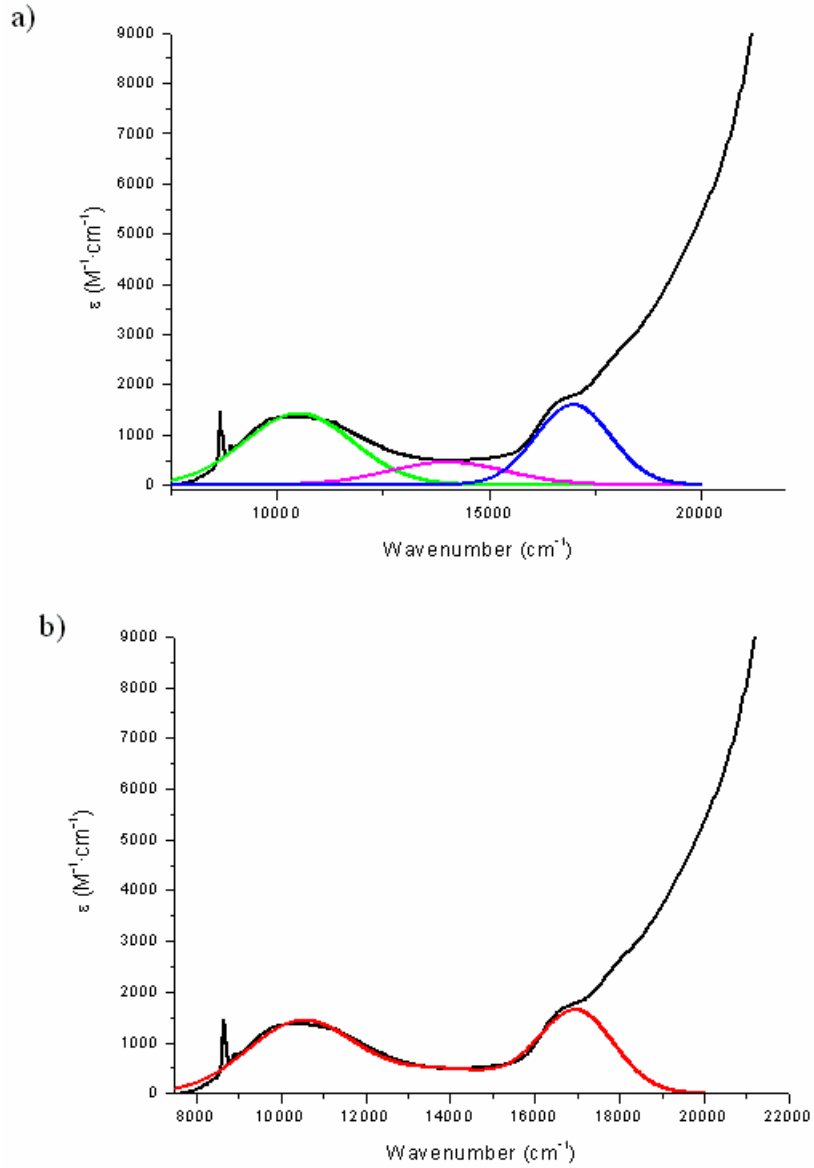

Figure ESI 14. **a)** Deconvolution of NIR spectra of **3a**$^{+\cdot}$. Experimental spectra were deconvoluted by means of tree Gaussian fuctions (green pink and blue lines). **b)** The sum of the Gaussian functions (red line) closely matches the experimental spectrum (black line).

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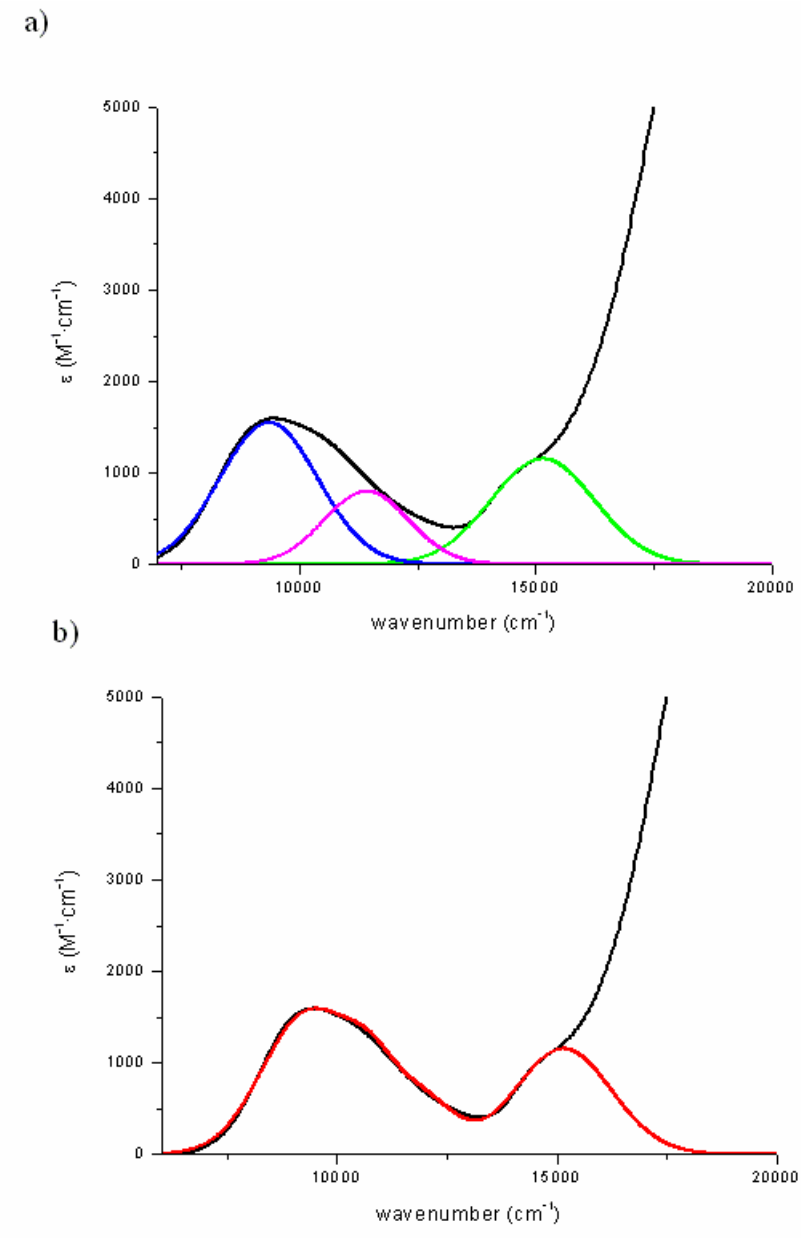

Figure ESI 15 a) Deconvolution of NIR spectra of **3b**$^{+\cdot}$. Experimental spectra were deconvoluted by means of tree Gaussian fuctions (green pink and blue lines). **b)** The sum of the Gaussian functions (red line) closely matches the experimental spectrum (black line).

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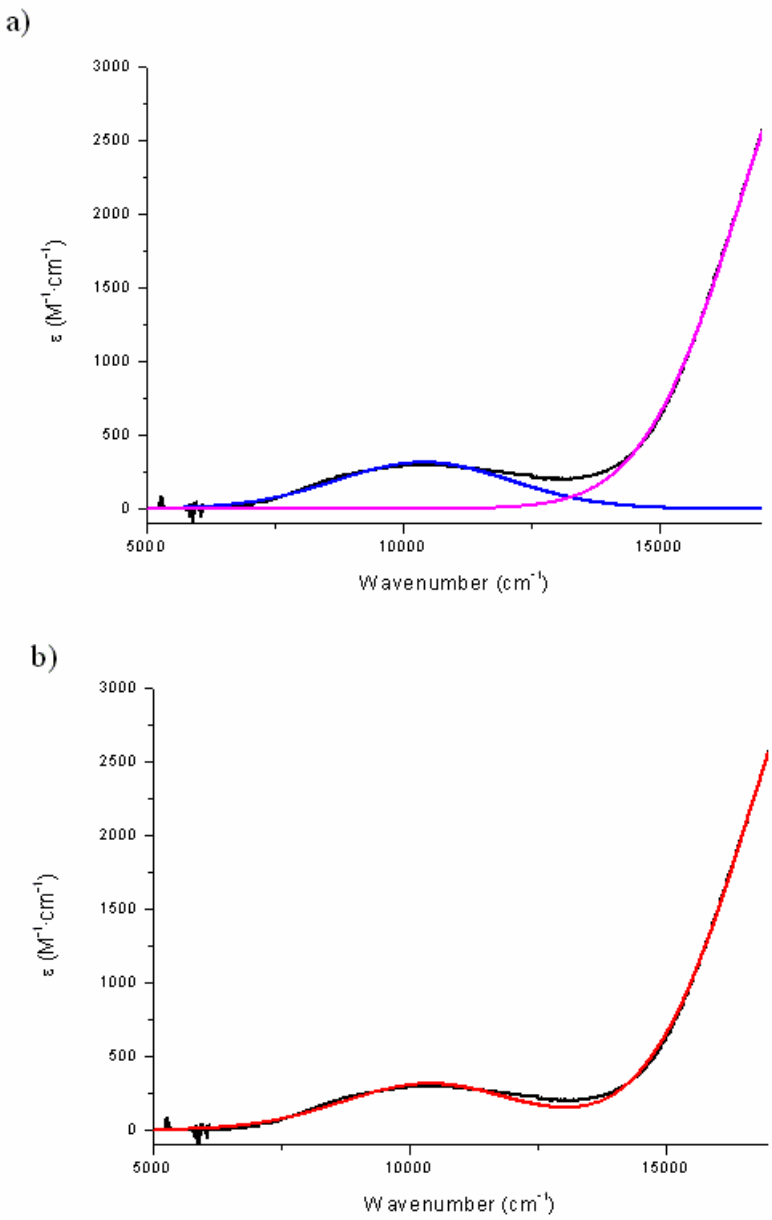

Figure ESI 16. a) Deconvolution of NIR spectra of **5a**$^{+\cdot}$. Experimental spectra were deconvoluted by means of two Gaussian fuctions (pink and blue lines). **b)** The sum of the Gaussian functions (red line) closely matches the experimental spectrum (black line).

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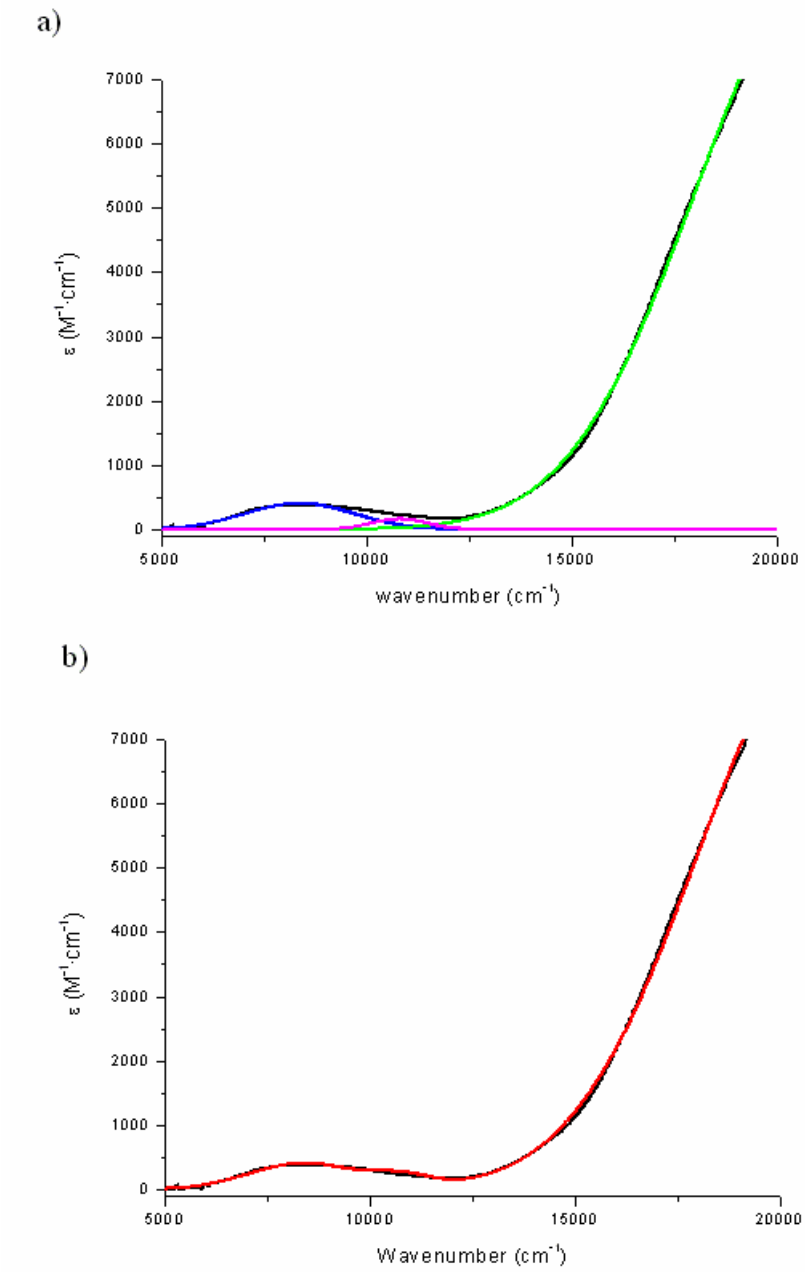

Figure ESI 17. **a)** Deconvolution of NIR spectra of **5b**$^{+\cdot}$. Experimental spectra were deconvoluted by means of tree Gaussian fuctions (green pink and blue lines). **b)** The sum of the Gaussian functions (red line) closely matches the experimental spectrum (black line).

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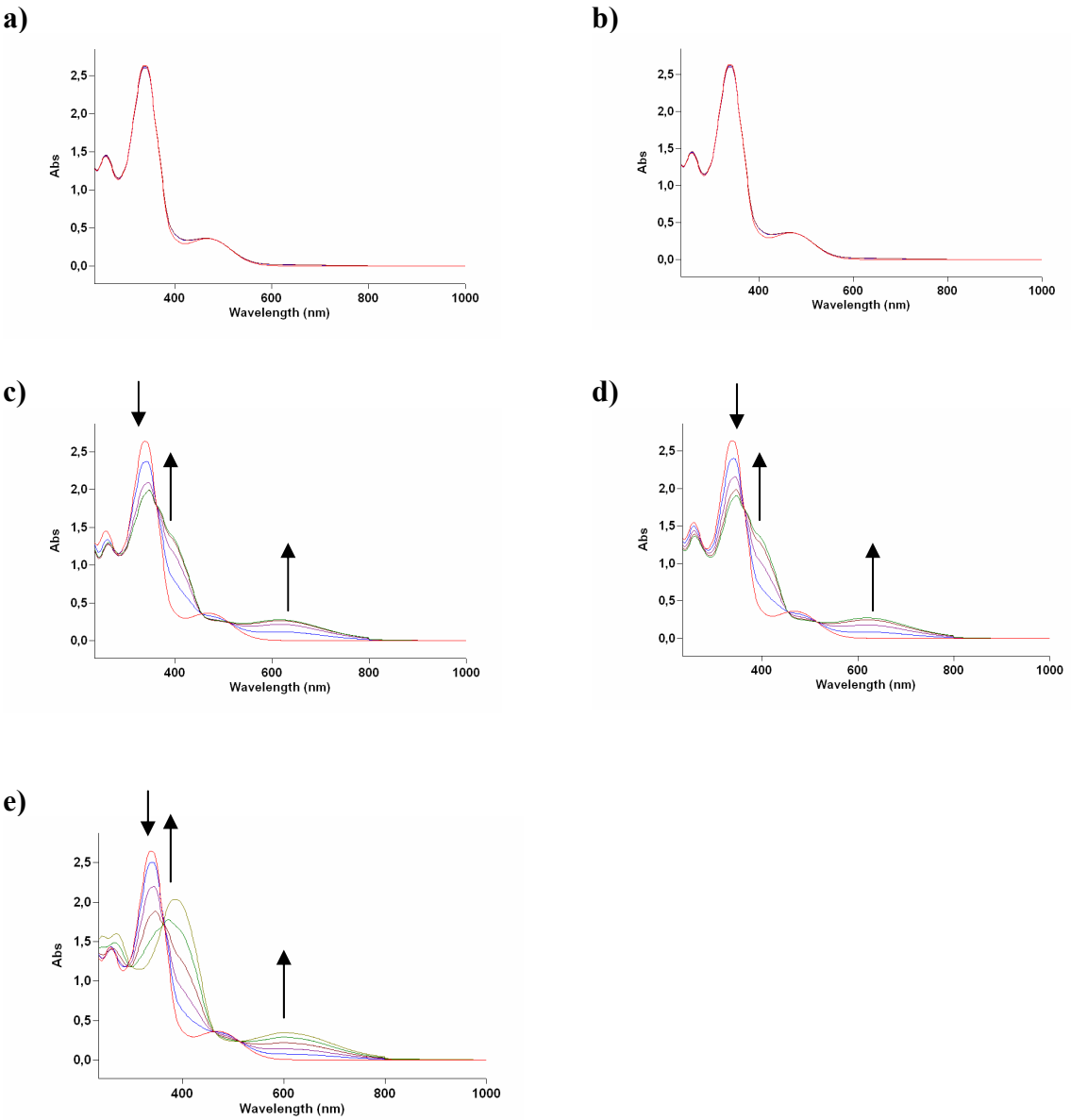

Figure ESI 18. Changes in the absorption spectra of **3a** upon addition of increasing amounts of the appropriate metal cation: **a)** Mg^{+2} from 0 to 1 equiv. **b)** Ca^{+2} from 0 to 1 equiv. **c)** Ni^{+2} from 0 to 0.5 equiv. **d)** Cd^{+2} from 0 to 0.5 equiv. **e)** Hg^{+2} from 0 to 1 equiv.

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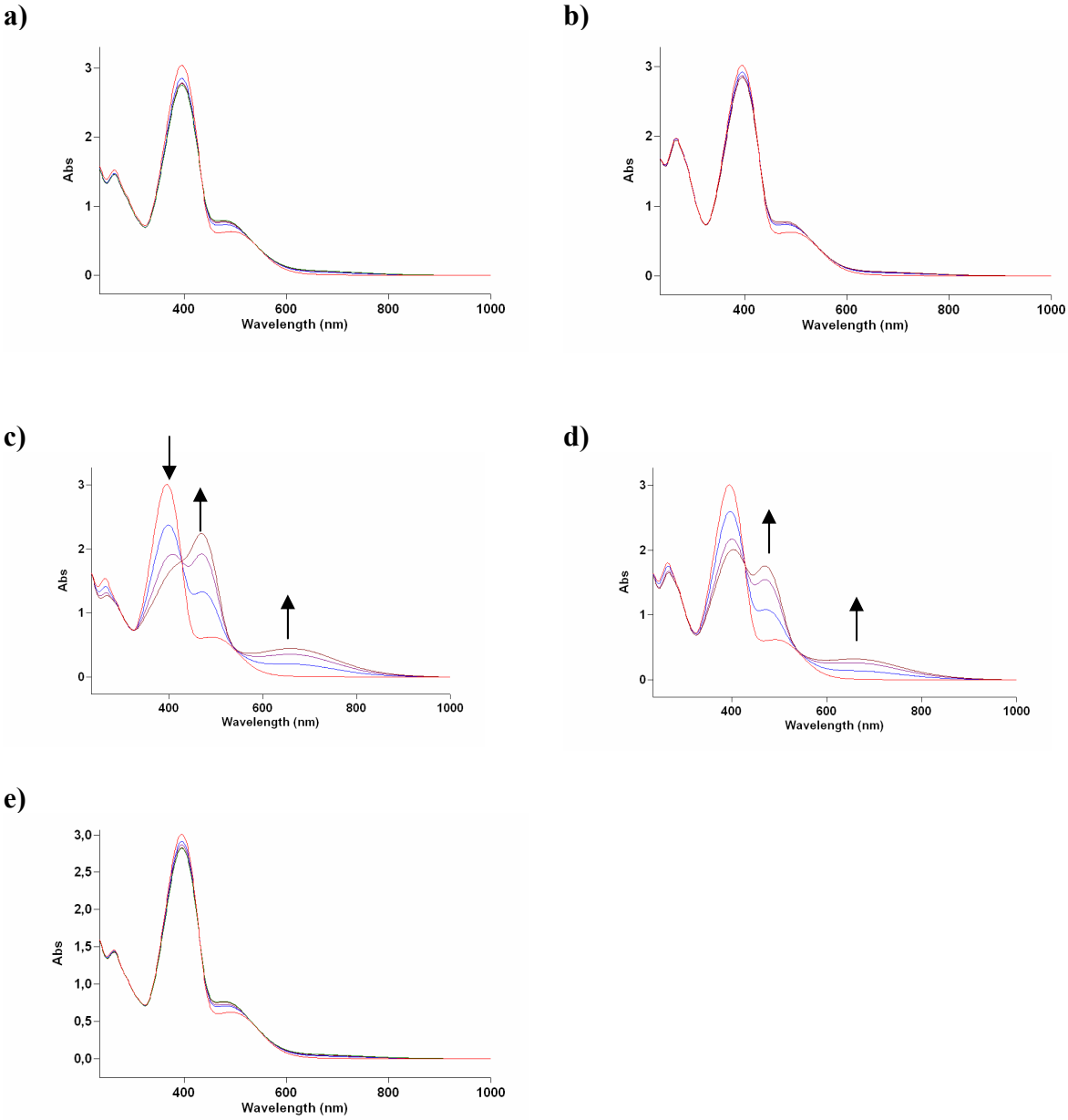

Figure ESI 19. Changes in the absorption spectra of **3b** upon addition of increasing amounts of the appropriate metal cation: **a)** Mg^{+2} from 0 to 1 equiv. **b)** Ca^{+2} from 0 to 1 equiv. **c)** Ni^{+2} from 0 to 0.5 equiv. **d)** Cd^{+2} from 0 to 0.5 equiv. **e)** Hg^{+2} from 0 to 1 equiv.

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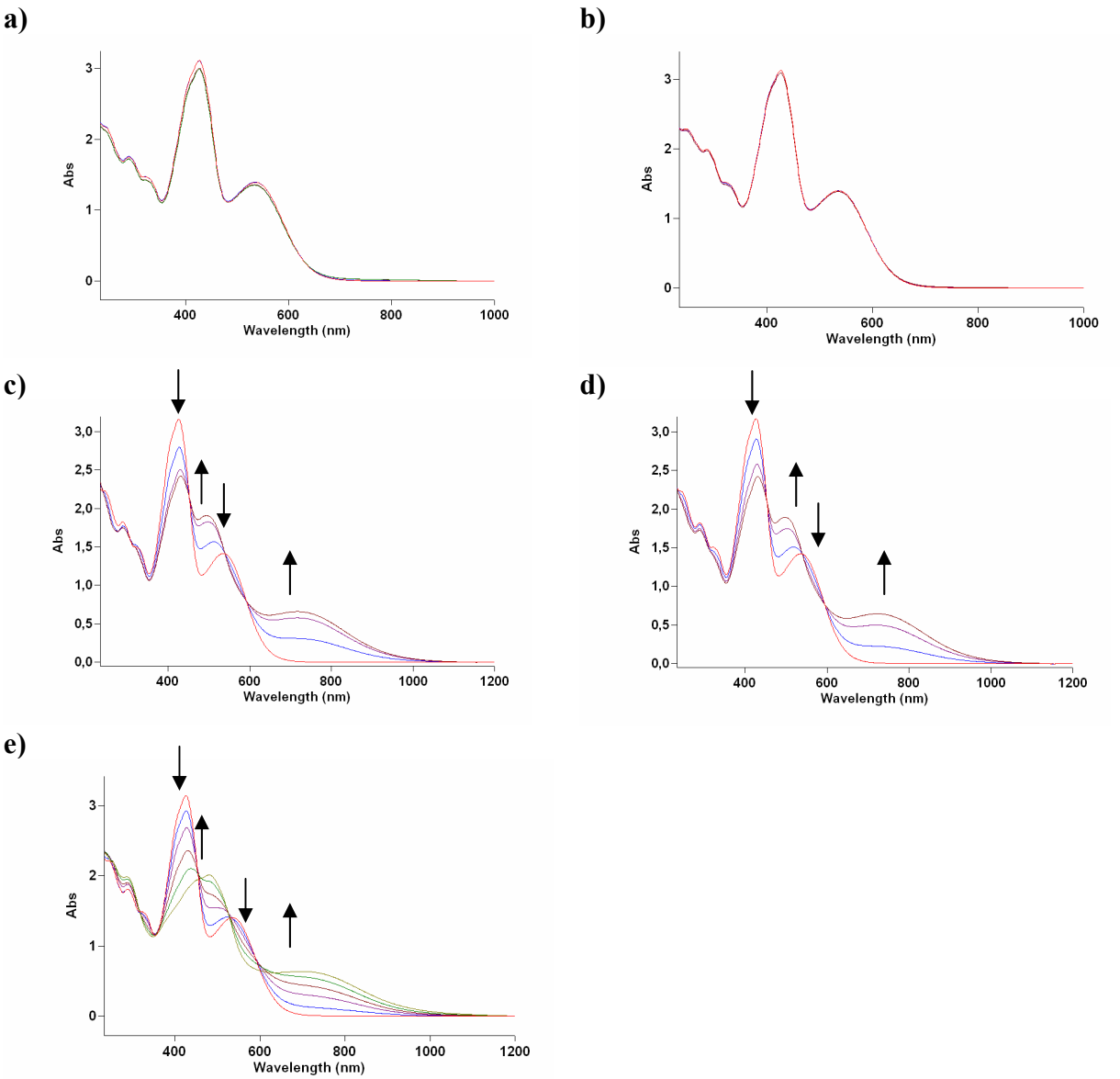

Figure ESI 20. Changes in the absorption spectra of **3c** upon addition of increasing amounts of the appropriate metal cation: **a)** Mg^{+2} from 0 to 1 equiv. **b)** Ca^{+2} from 0 to 1 equiv. **c)** Ni^{+2} from 0 to 0.5 equiv. **d)** Cd^{+2} from 0 to 0.5 equiv. **e)** Hg^{+2} from 0 to 1 equiv.

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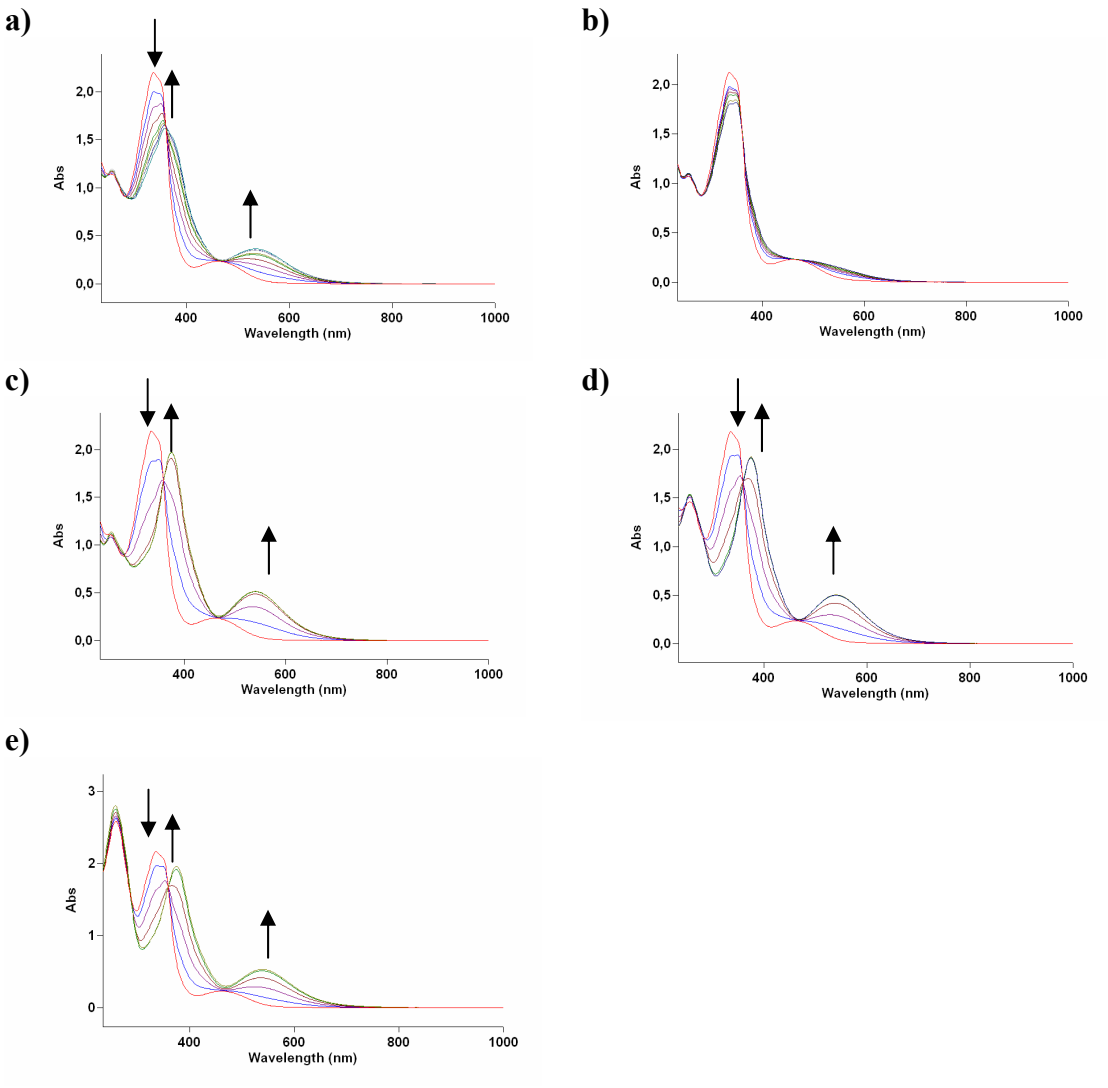

Figure ESI 21. Changes in the absorption spectra of **5a** upon addition of increasing amounts of the appropriate metal cation: **a)** Mg^{+2} from 0 to 1 equiv. **b)** Ca^{+2} from 0 to 1 equiv. **c)** Ni^{+2} from 0 to 0.5 equiv. **d)** Cd^{+2} from 0 to 1 equiv. **e)** Hg^{+2} from 0 to 1 equiv.

a) **b)**

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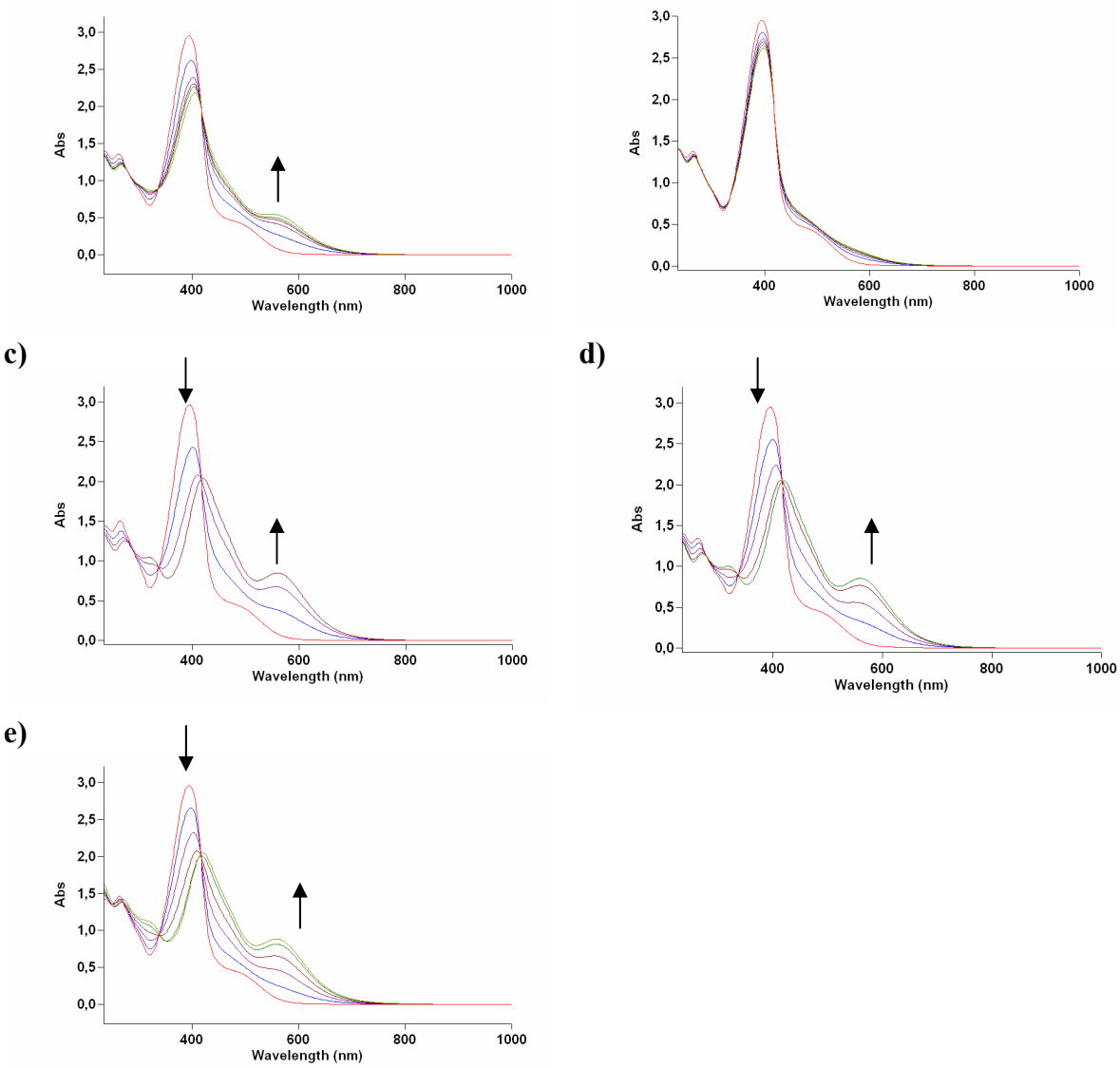

Figure ESI 22. Changes in the absorption spectra of **5b** upon addition of increasing amounts of the appropriate metal cation: **a)** Mg^{+2} from 0 to 1 equiv. **b)** Ca^{+2} from 0 to 1 equiv. **c)** Ni^{+2} from 0 to 0.5 equiv. **d)** Cd^{+2} from 0 to 1 equiv. **e)** Hg^{+2} from 0 to 1 equiv.