

Supporting Materials for

Electrochemical investigation of iron-catalyzed atom transfer radical polymerization

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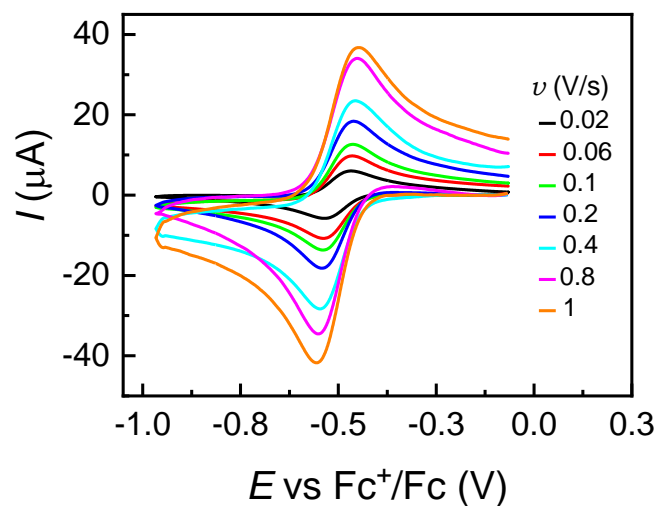


Figure S1. Cyclic voltammetry of 0.93 mM FeCl₃ in DMF + 0.1 M Et₄NBF₄ + 20 mM Et₄NCl, recorded on a GC electrode at different scan rates at $T = 25$ °C.

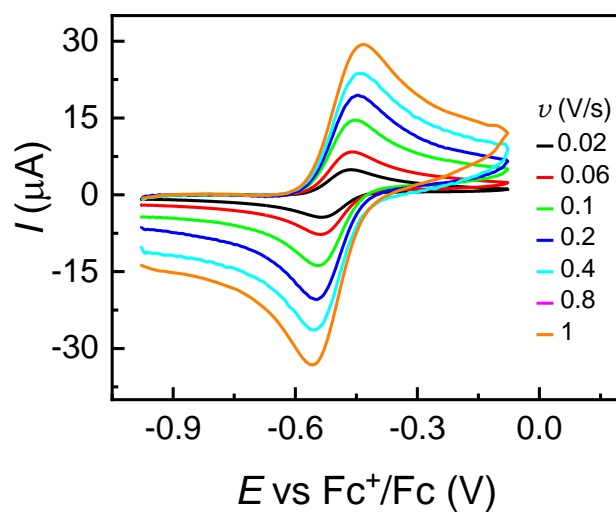


Figure S2. Cyclic voltammetry of 1.83 mM FeCl₂ in DMF + 0.1 M Et₄NBF₄ + 20 mM Et₄NCl, recorded on a GC electrode at different scan rates at $T = 25$ °C.

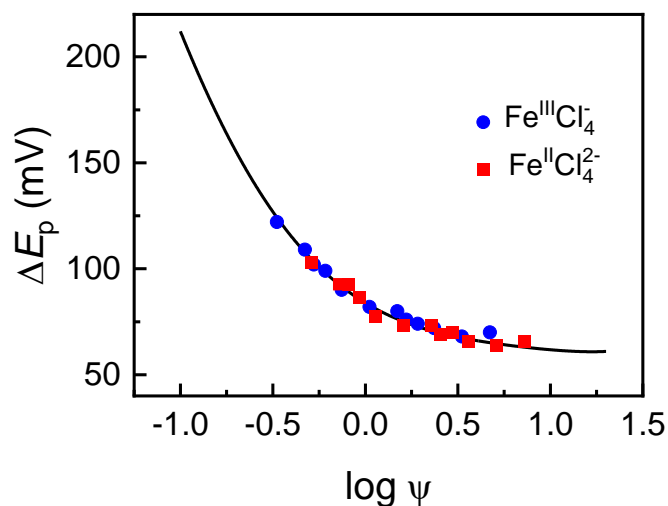


Figure S3. Fitting of experimental data obtained from cyclic voltammetry of FeCl_4^- and FeCl_4^{2-} on a theoretical working curve (solid line) for the determination of k° in DMF + 0.1 M Et_4NBF_4 at $T = 25^\circ\text{C}$. The dimensionless parameter ψ is defined as:

$$\psi = \frac{(D_{\text{Ox}}/D_{\text{Red}})^{\alpha/2} k^\circ}{((nF/RT)\pi D_{\text{Ox}} v)^{1/2}}$$

α was assumed to be 0.5, whereas D_{ox} and D_{red} were measured as $(8.0 \pm 0.8) \times 10^{-6} \text{ cm}^2\text{s}^{-1}$ and $(2.3 \pm 0.1) \times 10^{-6} \text{ cm}^2\text{s}^{-1}$.

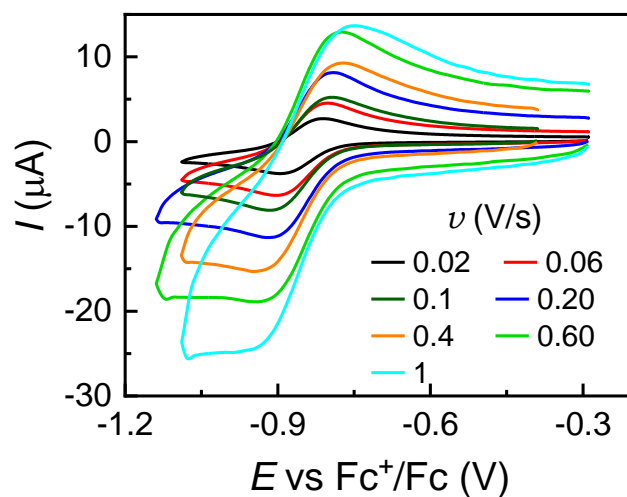


Figure S4. Cyclic voltammetry of 1.0 mM $\text{Fe}^{\text{III}}\text{L}(\text{Cl})$ in DMF + 0.1 M Et_4NBF_4 + 30 mM Et_4NCl , recorded on a GC electrode at different scan rates at $T = 25^\circ\text{C}$.

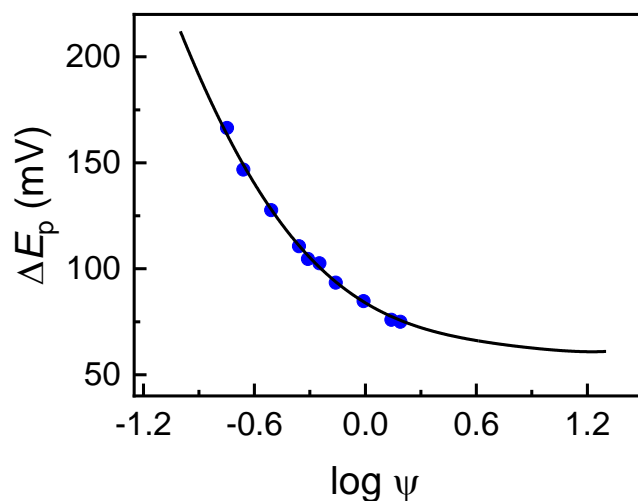


Figure S5. Fitting of experimental data obtained from cyclic voltammetry of $\text{Fe}^{\text{III}}\text{L}(\text{Cl})$ on a theoretical working curve (solid line) for the determination of k° in DMF + 0.1 M Et_4NBF_4 at $T = 25^\circ\text{C}$. α was assume to be 0.5, whereas the value of D measured for $\text{Fe}^{\text{III}}\text{L}(\text{Cl})$ ($(8.0 \pm 0.8) \times 10^{-6} \text{ cm}^2\text{s}^{-1}$) was used for both oxidation states of the complex.

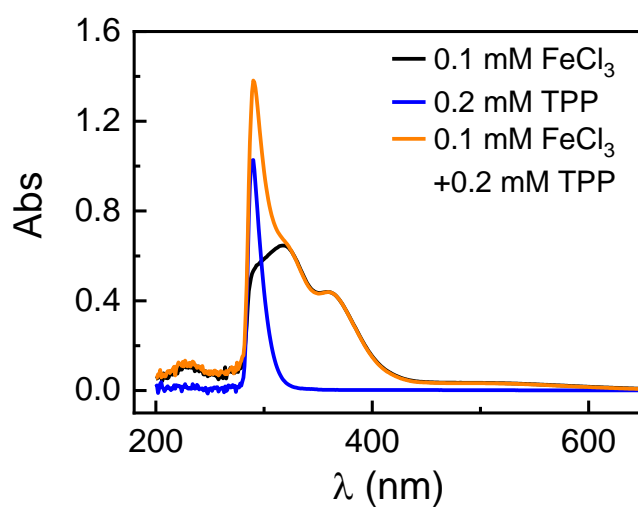


Figure S6. UV-vis spectra of 0.1 mM FeCl_3 , 0.2 mM TPP and a mixture of 0.1 mM FeCl_3 + 0.2 mM TPP, in DMF (path length = 1 cm).

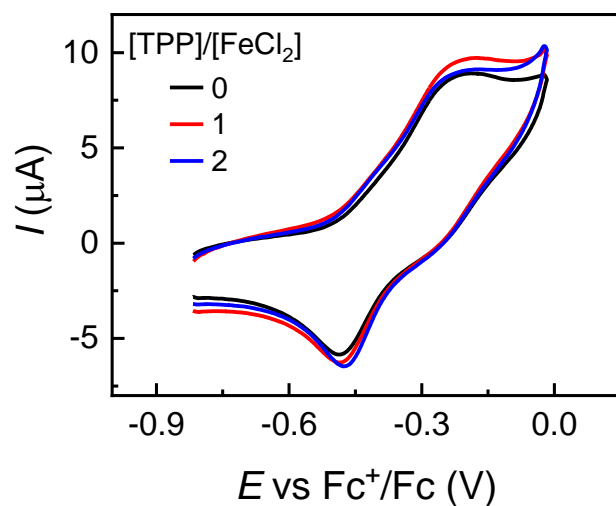


Figure S7. Cyclic voltammetry of 1.08 mM FeCl₂ in DMF + 0.1 M Et₄NBF₄, recorded on a GC electrode in the absence and presence of triphenylphosphine (TPP) at $v = 0.2$ V/s and $T = 25$ °C.

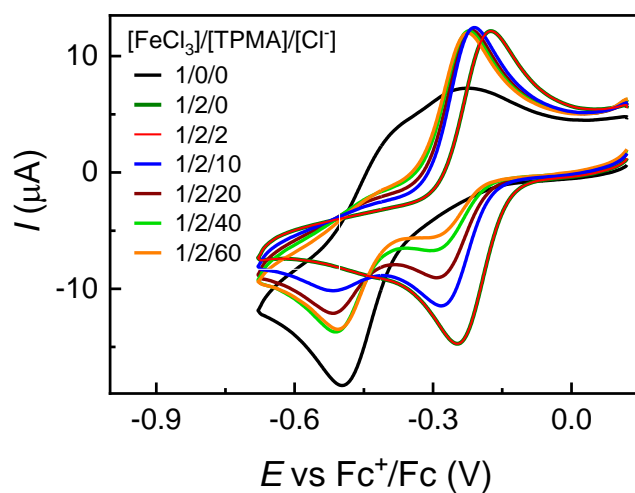


Figure S8. Cyclic voltammetry of 1.1 mM FeCl₃ in DMF + 0.1 M Et₄NBF₄ recorded on a GC electrode at $v = 0.2$ V/s and $T = 25$ °C, before and after addition of TPMA and Et₄NCl.

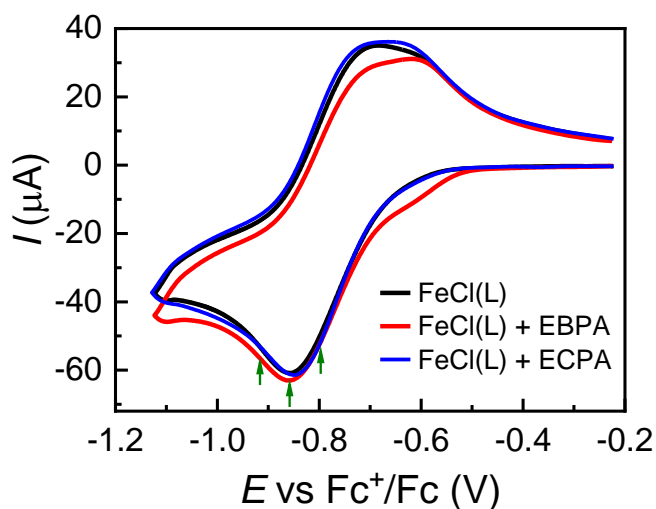


Figure S9. Cyclic voltammetry of 5 mM $\text{Fe}^{\text{III}}\text{L}(\text{Cl})$ in DMF/MMA (50/50, v/v) + 0.1 M Et_4NBF_4 recorded on a GC electrode at $v = 0.2$ V/s and $T = 50$ °C, in the absence (black line) and presence of 15 mM ECPA (blue line) or 15 mM EBPA (red line). The arrows indicate E_{app} values used during *e*ATRP: $E_{\text{app}} = E_p + 0.06$ V, E_p and $E_p - 0.06$ V.

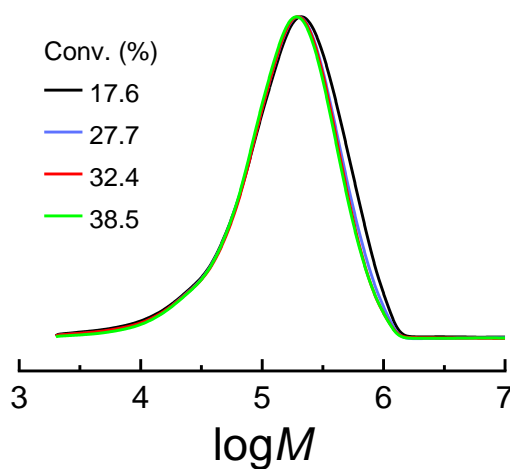


Figure S10. GPC traces of PMMA samples taken at different monomer conversions during *e*ATRP of MMA mediated by $\text{Fe}^{\text{III}}\text{L}(\text{Cl})$ in DMF/MMA (50/50, v/v) + 0.1 M Et_4NBF_4 with EBPA as initiator performed at 50 °C and $E_{\text{app}} = E_p + 0.06$ V. Other conditions: $[\text{MMA}]:[\text{RX}]:[\text{Fe}^{\text{III}}\text{L}(\text{Cl})] = 100:0.32:0.11$, with $[\text{Fe}^{\text{III}}\text{L}(\text{Cl})] = 5$ mM.

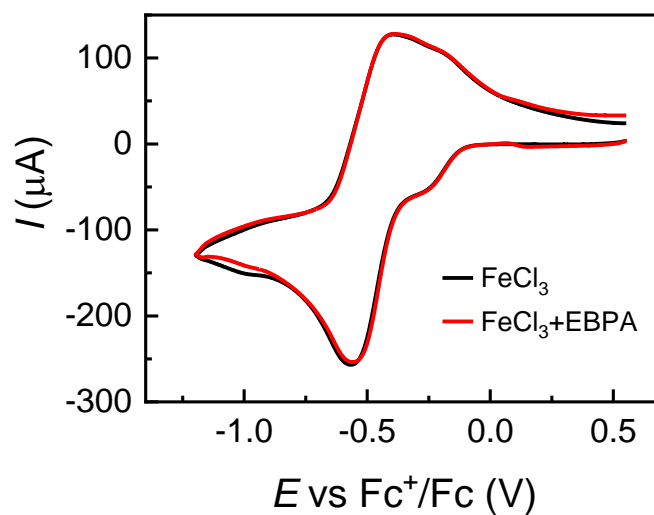


Figure S11. Cyclic voltammetry of 11.75 mM $\text{Fe}^{\text{III}}\text{Cl}_3$ in DMF/MMA (50/50, v/v) + 0.1 M Et_4NBF_4 recorded on a GC electrode at $v = 0.2 \text{ V/s}$ and $T = 55^\circ\text{C}$, in the absence (black line) and presence of 47 mM EBPA (red line).

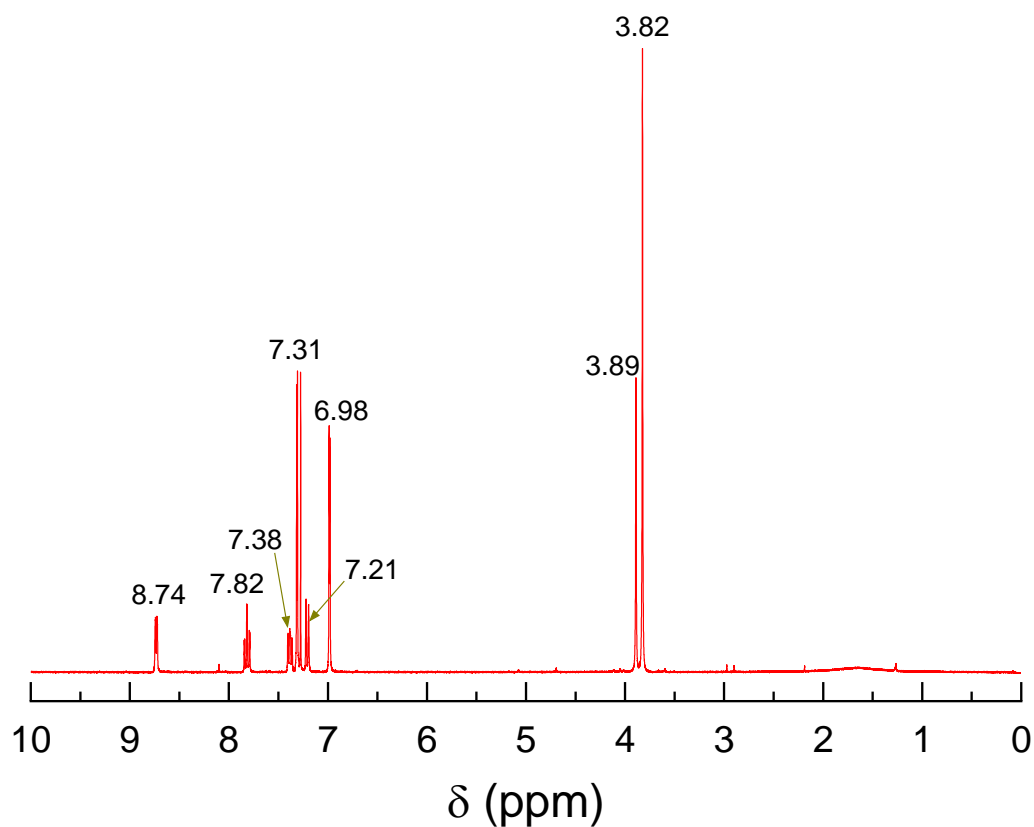


Figure S12. ^1H NMR spectrum (300 MHz, CDCl_3) of 2-pyridylamino-*N,N*-bis(2-methylene-4,6-dichlorophenol).

Table S1. ¹H NMR spectral data of 2-pyridylamino-*N,N*-bis(2-methylene-4,6-dichlorophenol).

Chemical shift (ppm), multiplicity, number of protons	
This work	Literature ¹
8.74, d, 1H	8.69, d, 1H
7.82, ddd, 1H	7.78, ddd, 1H
7.38, dd, 1H	7.34, dd, 1H
7.31, d, 2H	7.28, s, 2H
7.21, d, 1H	7.16, d, 1H
6.98, d, 2H	6.94, s, 2H
3.89, s, 2H	3.85, s, 2H
3.82, s, 4H	3.79, s, 4H

¹Reference 1.**Table S2.** Elemental analysis of chloro(2-pyridylamino-*N,N*-bis(2-methylene-4,6-dichlorophenolate))iron(III).

Element	Predicted (wt%)	Experimental (wt%)
C	43.88	44.46
H	2.58	2.89
N	5.12	4.99

References

- 1) Reckling, A.M.; Martin, D.; Dawe, L.N.; Decken, A.; Kozak, C.M. Structure and C–C Cross-Coupling Reactivity of Iron(III) Complexes of Halogenated Amine-Bis(Phenolate) Ligands. *J Organomet Chem* **2011**, 696, 787–794.