Supporting Information:

Ferrocene-based (photo)redox polymerization under long wavelengths

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Synthesis of photoinitiators

All reagents and solvents were purchased from Aldrich or Alfa Aesar and used as received without further purification. Mass spectroscopy was performed by the Spectropole of Aix-Marseille University. ESI mass spectral analyses were recorded with a 3200 QTRAP (Applied Biosystems SCIEX) mass spectrometer. The HRMS mass spectral analysis was performed with a QStar Elite (Applied Biosystems SCIEX) mass spectrometer. Elemental analyses were recorded with a Thermo Finnigan EA 1112 elemental analysis apparatus driven by the Eager 300 software. ^{1}H and ^{13}C NMR spectra were determined at room temperature in 5 mm o.d. tubes on a Bruker Avance 400 spectrometer of the Spectropole: ^{1}H (400 MHz) and ^{13}C (100 MHz). The ^{1}H chemical shifts were referenced to the solvent peaks $CDCl_3$ (7.26 ppm), DMSO (2.49 ppm) and the ^{13}C chemical shifts were referenced to the solvent peak $CDCl_3$ (77 ppm), DMSO (49.5 ppm). All these carbazole photoinitiators were prepared with analytical purity up to accepted standards for new organic compounds (>98%) which was checked by high field NMR analysis. Ferrocenecarboxaldehyde Fe2 was synthesized as previously reported, without modifications and in similar yield [A.F. Neto, J. Miller, V. Faria de Andrade, S.Y. Fujimoto, M.

Maísa de Freitas Afonso, F. Costa Archanjo, V.A. Darin, M.L. Andrade e Silva, Á. Donizete Lanchote Borges, G. Del Ponte, Zeitschrift für anorganische und allgemeine Chemie, 2002, 628, 209–216].

Figure S1. Synthetic pathways to **Fe3-Fe7**.

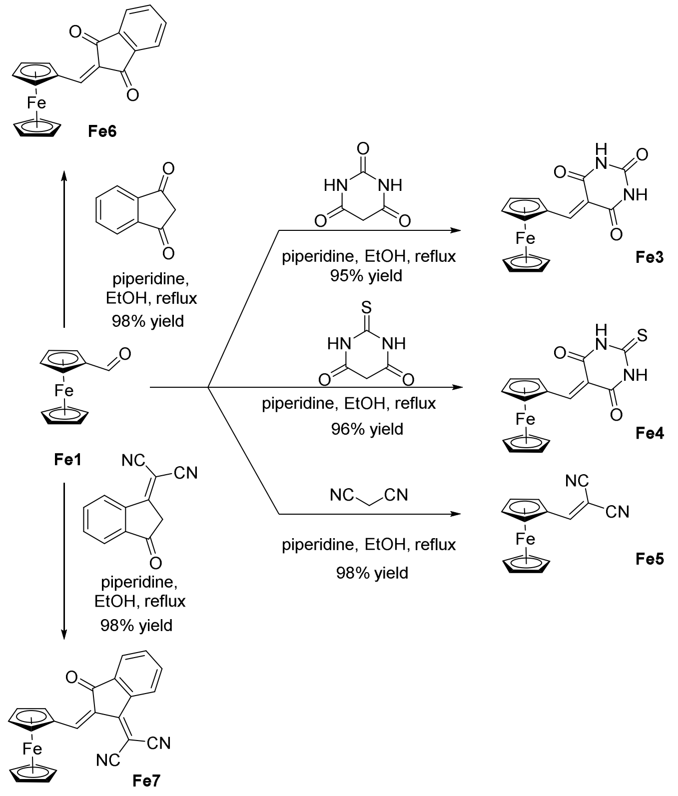
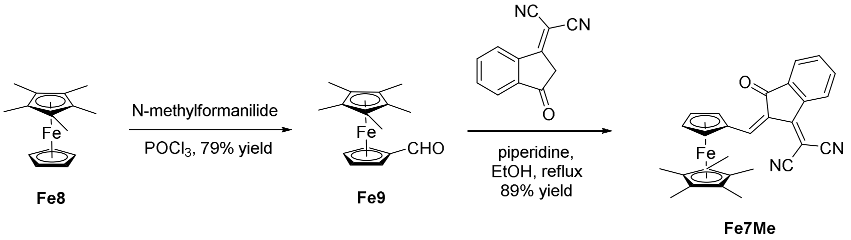
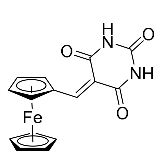


Figure S2. Synthetic pathways to **Fe7Me**.



*Synthesis of [(tetrahydro-2,4,6-trioxo-5(2H)-pyrimidinylidene)methyl]ferrocene **Fe3***

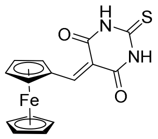


Chemical Formula: $C_{15}H_{12}FeN_2O_3$
Molecular Weight: 324,1170

To a mixture of barbituric acid (0.30 g, 2.34 mmol, M = 128.09 g/mol) and ferrocene-carbaldehyde (0.5 g, 2.34 mmol, 214.00 g/mol) in absolute ethanol (50 mL) was added a few drops of piperidine.

Immediately, the color changed. The solution was introduced in an oil bath preheated at 90°C. Within 10 min, the reaction was finished (TLC control). The solvent was removed under reduced pressure. The residue was purified by column chromatography using DCM as the eluent. The different fractions were combined and the solvent removed under reduced pressure so that approximately 30 mL DCM was remaining. Addition of pentane precipitated a solid that was filtered off, washed several times with pentane and dried under reduced pressure (720 mg, 95% yield). ^{1}H NMR (DMSO-d_6) δ: 4.29 (s, 5H), 4.93 (s, 2H), 5.35 (s, 2H), 8.21 (s, 1H), 10.98 (s, 1H), 11.12 (s, 1H); ^{13}C NMR (DMSO-d_6) δ: 70.5, 75.3, 76.1, 111.3, 150.2, 157.7, 162.1, 163.8; HRMS (ESI MS) m/z: theor: 324.0197 found: 324.0199 ($[M]^{+\cdot}$ detected)

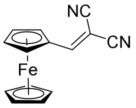
Synthesis of [(tetrahydro-4,6-dioxo-2-thioxo-5(2H)-pyrimidinylidene)methyl]ferrocene ***Fe4***



Chemical Formula: $C_{15}H_{12}FeN_2O_2S$
Molecular Weight: 340,1780

To a mixture of 4,6-dihydroxy-2-mercaptopyrimidine (0.34 g, 2.34 mmol, M = 144.15 g/mol) and ferrocene-carbaldehyde (0.5 g, 2.34 mmol, 214.00 g/mol in absolute ethanol (50 mL) was added a few drops of piperidine. Immediately, the color changed. The solution was introduced in an oil bath preheated at 90°C. Within 10 min, the reaction was finished (TLC control). The solvent was removed under reduced pressure. The residue was purified by column chromatography using DCM as the eluent. The different fractions were combined and the solvent removed under reduced pressure so that approximately 30 mL DCM was remaining. Addition of pentane precipitated a blue-green solid that was filtered off, washed several times with pentane and dried under reduced pressure (764 mg, 96% yield). ^{1}H NMR (DMSO-d_6) δ: 4.33 (s, 5H), 5.04 (s, 2H), 5.39 (s, 2H), 8.26 (s, 1H), 12.09 (s, 1H), 12.21 (s, 1H); ^{13}C NMR (DMSO-d_6) δ: 70.9, 76.0, 76.4, 111.1, 158.1, 159.9, 162.0, 177.8; HRMS (ESI MS) m/z: theor: 339.9969 found: 340.0002 ($[M]^{+\cdot}$ detected)

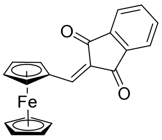
Synthesis of (2,2-dicyanoethenyl)ferrocene ***Fe5***



Chemical Formula: $C_{14}H_{10}FeN_2$
Molecular Weight: 262,0930

To a mixture of malononitrile (0.16 g, 2.34 mmol, M = 66.06 g/mol) and ferrocene-carbaldehyde (0.5 g, 2.34 mmol, 214.00 g/mol) in absolute ethanol (50 mL) was added a few drops of piperidine. Immediately, the color changed. The solution was introduced in an oil bath preheated at 90°C. Within 10 min, the reaction was finished (TLC control). The solvent was removed under reduced pressure. The residue was purified by column chromatography using DCM as the eluent. The different fractions were combined and the solvent removed under reduced pressure so that approximately 30 mL DCM was remaining. Addition of pentane precipitated a solid that was filtered off, washed several times with pentane and dried under reduced pressure (601 mg, 98% yield). ^1H NMR ($CDCl_3$) δ: 4.33 (s, 5H), 4.85 (s, 2H), 4.98 (s, 2H), 7.72 (s, 1H); ^{13}C NMR ($CDCl_3$) δ: 71.3, 71.9, 74.2, 75.4, 114.5, 115.3, 163.4; HRMS (ESI MS) m/z: theor: 262.0193 found: 262.0195 ($[M]^{+\cdot}$ detected).

Synthesis of [(1,3-dihydro-1,3-dioxo-2H-inden-2-ylidene)methyl]ferrocene ***Fe6***

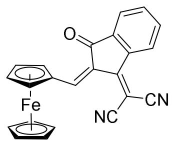


Chemical Formula: $C_{20}H_{14}FeO_2$
Molecular Weight: 342,1750

To a mixture of indane-1,3-dione (0.34 g, 2.34 mmol, M = 146.14 g/mol) and ferrocene-carbaldehyde (0.5 g, 2.34 mmol, 214.00 g/mol) in absolute ethanol (50 mL) was added a few drops of piperidine. Immediately, the color changed. The solution was introduced in an oil bath preheated at 90°C. Within 10 min, the reaction was finished (TLC control). The solvent was removed under reduced pressure. The residue was purified by column chromatography using DCM as the eluent. The different fractions were combined and the solvent removed under reduced pressure so that approximately 30 mL DCM was remaining. Addition of pentane precipitated a solid that was filtered off, washed several times with pentane and dried under reduced pressure (780 mg, 98% yield). ^1H NMR ($CDCl_3$) δ: 4.23 (s, 5H), 4.84-

4.85 (m, 2H), 5.43-5.44 (m, 2H), 7.75-7.79 (m, 2H), 7.88 (s, 1H), 7.93-7.97 (m, 2H); ^{13}C NMR ($CDCl_3$) δ: 70.7, 75.2, 75.3, 76.2, 77.2, 122.6, 122.8, 134.5, 134.6, 139.9, 142.3, 149.4, 189.5, 190.5; HRMS (ESI MS) m/z: theor: 342.0343 found: 342.0342 ($[M]^{+\cdot}$ detected)

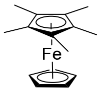
Synthesis of [1-(dicyanomethylene)-1,3-dihydro-3-oxo-2H-inden-2-ylidene]methyl]ferrocene ***Fe7***



Chemical Formula: $C_{23}H_{14}FeN_2O$
Molecular Weight: 390,2230

To a mixture of 2-(3-oxo-2,3-dihydro-1*H*-inden-1-ylidene)malononitrile (1.12 g, 5.79 mmol, M = 194.19 g/mol) and ferrocene-carbaldehyde (1.24 g, 5.79 mmol, 214.00 g/mol) in absolute ethanol (50 mL) was added a few drops of piperidine. Immediately, the color changed. The solution was introduced in an oil bath preheated at 90°C. Within 10 min, the reaction was finished (TLC control). The solvent was removed under reduced pressure. The residue was purified by column chromatography using DCM as the eluent. The different fractions were combined and the solvent removed under reduced pressure so that approximately 30 mL DCM was remaining. Addition of pentane precipitated a solid that was filtered off, washed several times with pentane and dried under reduced pressure (2.19 g, 97% yield). ^{1}H NMR ($CDCl_3$) δ: 4.35 (s, 5H), 5.04 (s, 2H), 5.34 (s, 2H), 7.69-7.78 (m, 2H), 7.86-7.88 (m, 1H), 8.46 (s, 1H), 8.66 (d, 1H, J = 7.0 Hz); ^{13}C NMR ($CDCl_3$) δ: 68.1, 72.0, 76.9, 77.2, 77.7, 115.1, 115.3, 123.3, 123.6, 125.1, 134.2, 134.8, 137.3, 139.4, 149.6, 161.7, 187.2; HRMS (ESI MS) m/z: theor: 390.0456 found: 390.0458 ($[M]^{+\cdot}$ detected)

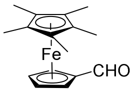
Synthesis of 1,2,3,4,5-pentamethylferrocene ***Fe8***



Chemical Formula: $C_{15}H_{20}Fe$
Molecular Weight: 256,1700

A suspension of anhydrous $FeCl_2$ (4.05 g, 32 mmol M = 126.74 g/mol) in dry THF (200 mL) was vigorously stirred in the dark 1 h to produce $FeCl_2$·THF. Separately, *n*-butyllithium (2.5 M, 12.8 mL, 1 eq.) was added dropwise to pentamethylcyclopentadiene (5 mL, 31.93 mmol, 4.35 g, M = 136.24 g/mol, d = 0.87, 1 eq.) in THF (50 mL) at -78°C and the mixture was then warmed and stirred at room temperature for 2 h. Then, this solution was slowly transferred into the $FeCl_2$·THF solution and stirred at room temperature for 1 h. Then, sodium cyclopentadienylide (2M, 16 mL, 31.93 mmol, 1 eq.) was slowly added to the solution and stirring was maintained overnight. The solution was quenched with water and the solvent removed under reduced pressure. The residue was dissolved in DCM. The organic phase was washed with water several times. The organic phase was dried over magnesium sulfate and the solvent removed under reduced pressure. The targeted pentamethylferrocene was obtained under the form of an orange powder (5.49 g, 67 % yield). ^{1}H NMR ($CDCl_3$) δ: 1.93 (s, 15H), 3.69 (s, 5H); ^{13}C NMR ($CDCl_3$) δ: 11.4, 71.2, 80.2; HRMS (ESI MS) m/z: theor: 256.0914 found: 256.0915 ($[M]^{+\cdot}$ detected). Analyses were consistent with those previously reported in the literature (D. Kang, F. Ricci, R. J. White, K. W. Plaxco, Anal. Chem. 2016, 88, 10452−10458).

Synthesis of 1'-formyl-1,2,3,4,5-pentamethylferrocene ***Fe9***

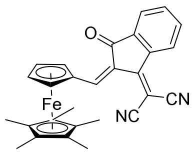


Chemical Formula: $C_{16}H_{20}FeO$
Molecular Weight: 284,1800

1,2,3,4,5-Pentamethylferrocene (2.56 g, 10 mmol, M = 256.17 g/mol) was dissolved in *N*-methylformanilide (20 mL) and phosphorus oxychloride (2.6 g, 1.6 mL, 16.96 mmol, M = 153.33 g/mol, d = 1.645) was added. The solution was stirred at room temperature for 3 days while being protected from light. The reaction mixture was hydrolyzed at 0°C with 100 mL of an aqueous solution of sodium acetate (20%). The solution was stirred for 30 min. at room temperature and the solution was then saturated with sodium chloride and extracted with ether several times. The residue was filtered on a plug of silicagel, providing 1'-formyl-1,2,3,4,5-pentamethylferrocene **Fe9** as a red solid (2.24 g, 79% yield). ^{1}H NMR ($CDCl_3$) δ: 1.83 (s, 15H, CH_3), 4.16 (t, 2H, J = 1.9 Hz), 4.25 (t, 2H, J = 1.9 Hz), 9.70 (s, 1H; CHO); ^{13}C NMR ($CDCl_3$) δ: 11.2, 72.0, 77.6, 80.4, 82.6, 193.9; HRMS (ESI MS) m/z: theor: 284.0864 found:

284.0865 ($[M]^{+\cdot}$ detected). Analyses were consistent with those previously reported in the literature (J. Moreau, L. Challier, N. Lalaoui, F. Mavré, V. Noël, B. Limoges, B. Schöllhorn, C. Fave, Chem. Eur. J. 2014, 20, 2953 – 2959).

Synthesis of 1-[1-(dicyanomethylene)-1,3-dihydro-3-oxo-2H-inden-2-ylidene]methyl]-1′,2′,3′,4′,5′-penta-methylferrocene ***Fe7Me***



Chemical Formula: $C_{28}H_{24}FeN_2O$
Molecular Weight: 460,3580

To a mixture of 2-(3-oxo-2,3-dihydro-1*H*-inden-1-ylidene)malononitrile (1.12 g, 5.79 mmol, M = 194.19 g/mol) and 1'-formyl-1,2,3,4,5-pentamethylferrocene **Fe9** (1.64 g, 5.79 mmol, 284.18 g/mol) in absolute ethanol (50 mL) was added a few drops of piperidine. Immediately, the color changed. The solution was introduced in an oil bath preheated at 90°C. Within 10 min, the reaction was finished (TLC control). The solvent was removed under reduced pressure. The residue was purified by column chromatography using DCM as the eluent. The different fractions were combined and the solvent removed under reduced pressure so that approximately 30 mL DCM was remaining. Addition of pentane precipitated a solid that was filtered off, washed several times with pentane and dried under reduced pressure (2.37 g, 89% yield). ^{1}H NMR ($CDCl_3$) δ: 1.72 (s, 15H), 4.70 (t, 2H, J = 1.9 Hz), 5.02 (s, 2H), 7.67-7.75 (m, 2H), 7.83-7.86 (m, 1H), 8.45 (s, 1H), 8.70-8.73 (m, 1H); ^{13}C NMR ($CDCl_3$) δ: 10.8, 65.3, 72.0, 75.9, 78.6, 80.6, 83.4, 84.8, 115.8, 115.9, 121.7, 123.2, 125.0, 133.7, 134.4, 137.1, 139.7, 149.6, 160.5, 187.8; HRMS (ESI MS) m/z: theor: 460.1238 found: 460.1240 ($[M]^{+\cdot}$ detected).

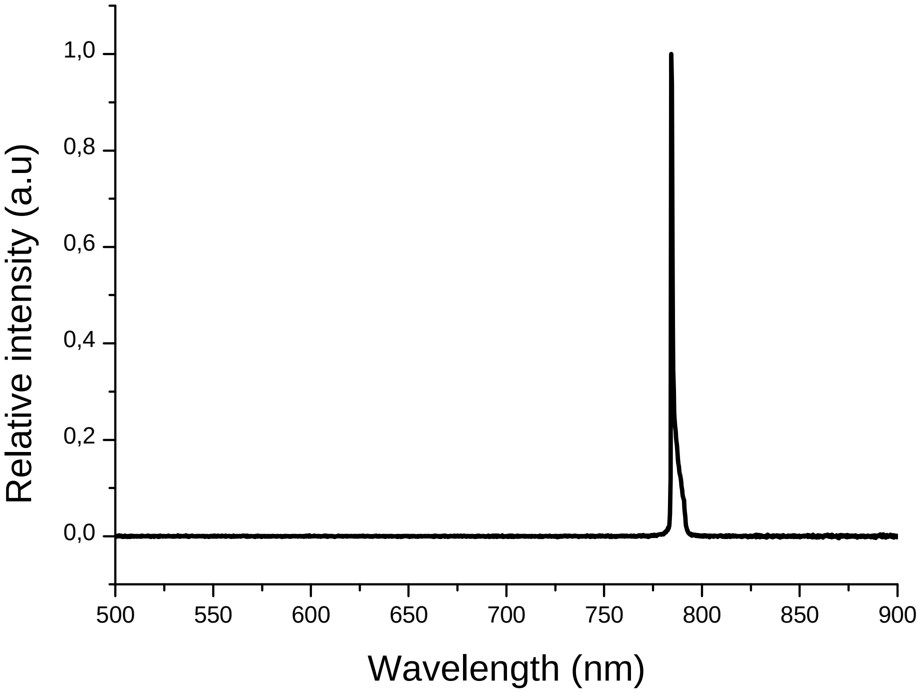
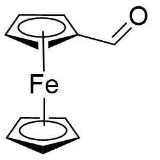


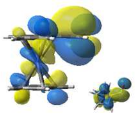
Figure S3: Emission spectra of the laser diode (LD@785 nm) used.

Figure S4: Frontier molecular orbitals and UV-vis calculated spectra of the ferrocene derivatives (UB3LYP/6-31G* level of theory)

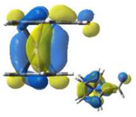
Fe1

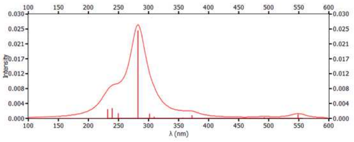


LUMO



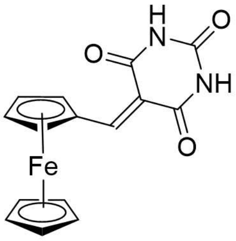
HOMO



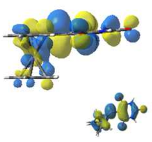


(100 nm < λ < 600 nm)
λ_{max}= 283 nm F= 0.025
λ_{max}= 549 nm F= 0.0012
λ_{max}= 372 nm F= 0.0010

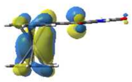
Fe3

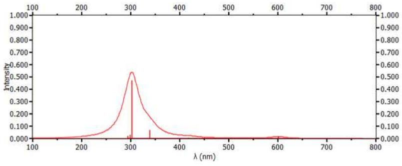


LUMO



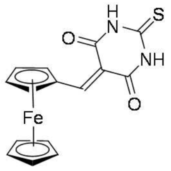
HOMO

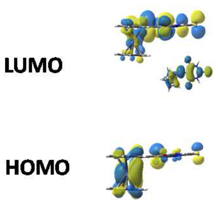


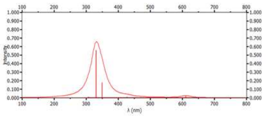


(100 nm < λ < 800 nm)
λ_{max}= 303 nm F= 0.475
λ_{max}= 601 nm F= 0.016

Fe4

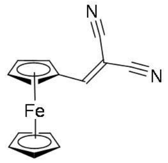


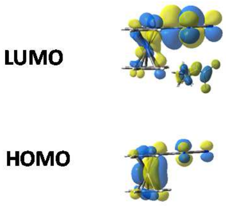


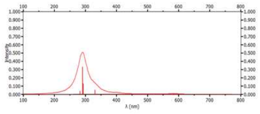


(100 nm <λ < 800 nm)
λ_{max}= 331 nm F= 0.558
λ_{max}= 611 nm F= 0.023

Fe5

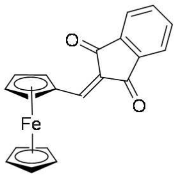


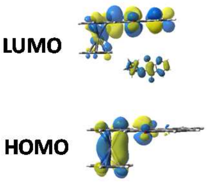


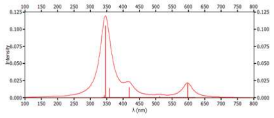


(100 nm <λ < 800 nm)
λ_{max}= 291 nm F= 0.336
λ_{max}= 584 nm F= 0.012

Fe6

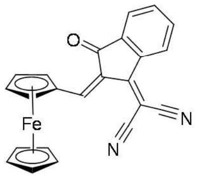


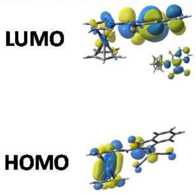


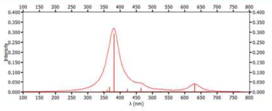


(100 nm <λ < 800 nm)
λ_{max}= 346 nm F= 0.105
λ_{max}= 598 nm F= 0.021
λ_{max}= 419 nm F= 0.015

Fe7

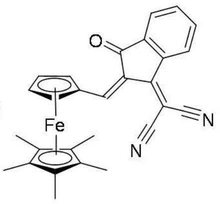


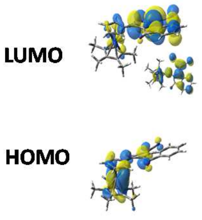


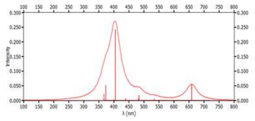


(100 nm <λ < 800 nm)
λ_{max}= 381 nm F= 0.293
λ_{max}= 631 nm F= 0.039
λ_{max}= 465 nm F= 0.023

Fe7Me







(100 nm <λ < 800 nm)
λ_{max}= 405 nm F= 0.243
λ_{max}= 659 nm F= 0.054
λ_{max}= 535 nm F= 0.006

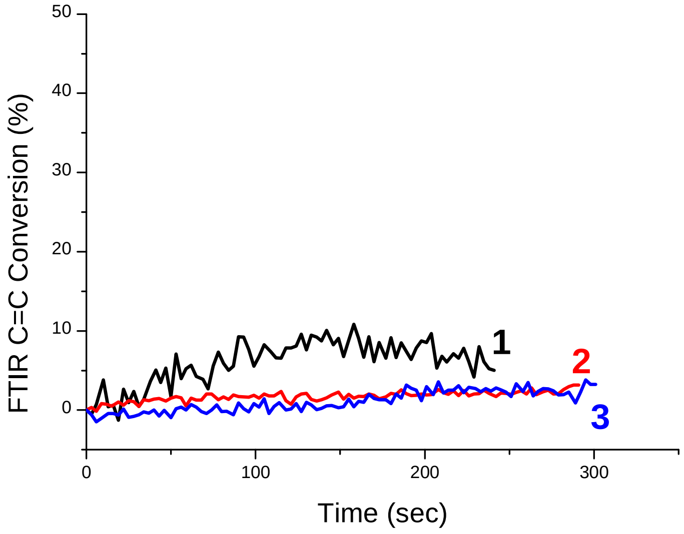


Figure S5: Photopolymerization profiles (methacrylate C=C function conversion vs. irradiation time) measured in RT-FTIR for the resin 2; 1.4 mm thick samples, in air for 2.0 wt% Iod and 0.5 wt% Fe(II) **(1)**: Fe5/Iod upon LED@660nm (80 mW/cm²) irradiation **(2)**: Fe3/Iod upon LED@660nm (80 mW/cm²) irradiation **(3)**: Fe3/Iod upon LED@530nm (30 mW/cm²) irradiation.

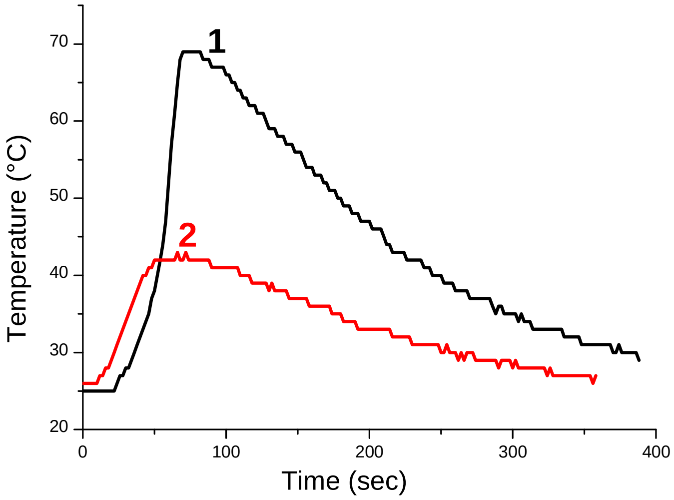


Figure S6: **Redox polymerization:** Optical pyrometric measurements (Temperature vs. mixing time, 4 mm samples), in air in the model methacrylate resin for 2.0 wt% APS (+2.0 wt% water) mixed 1.5 wt% 2dppba and with **(1)** 0.3 wt% Fe and **(2)** 1.3 wt% Fe.

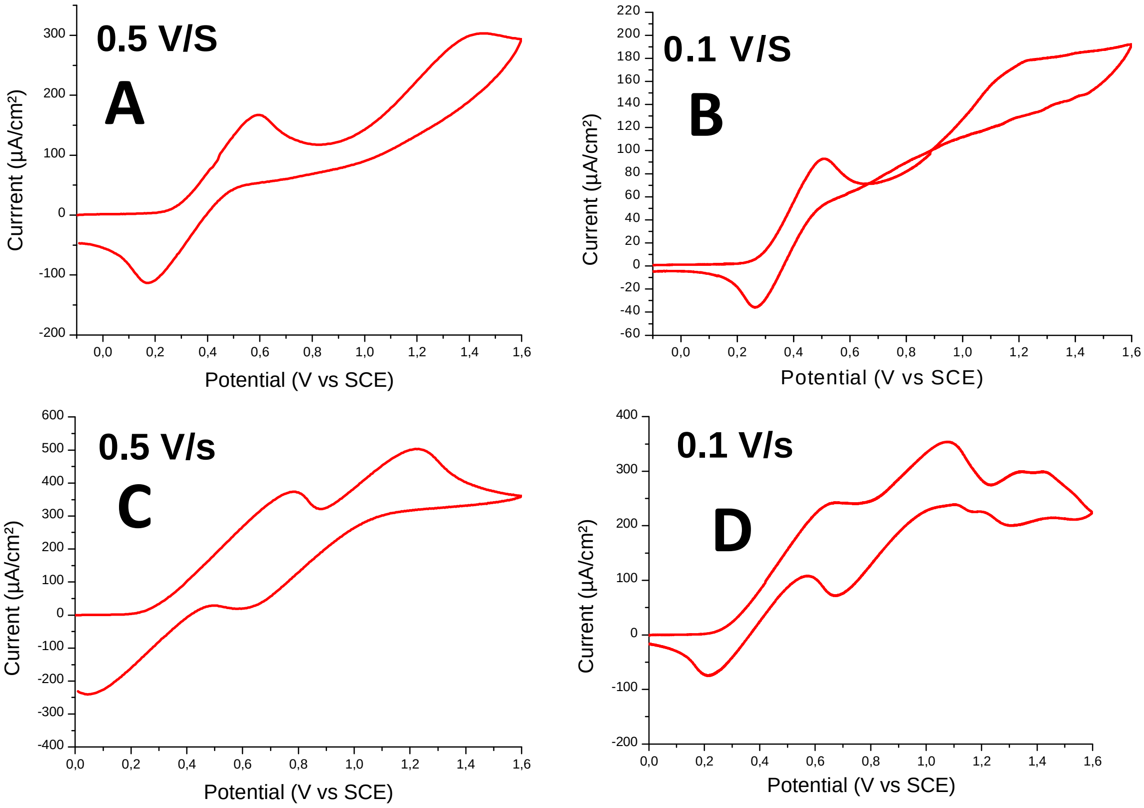


Figure S7: Cyclic voltammetry (CV) experiments in ACN (containing 0.2 M tetrabutylammonium hexafluorophosphate, N_2 degassed)) for **A,B :** Fe + 2dppba and **C,D** Fe + amine (4-*N,N* TMA).