# Unprecedented Photochromism of Ferrocene-Aryl Dicyanovinylenes

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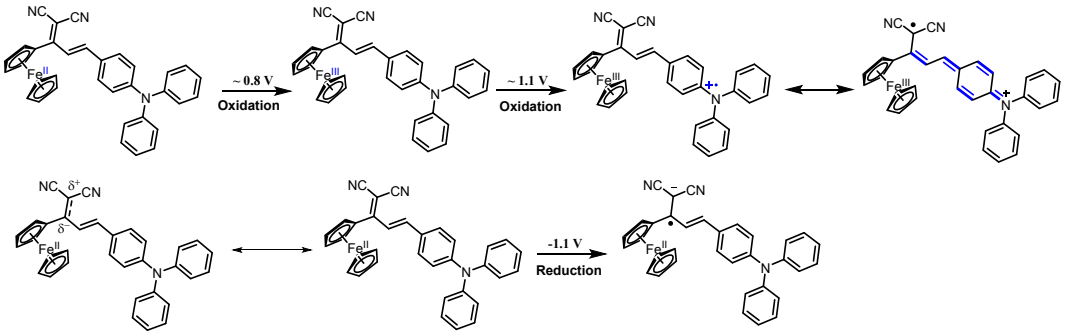



**Fig. S1** Redox Mechanism of $\mathbf{M_2}$.

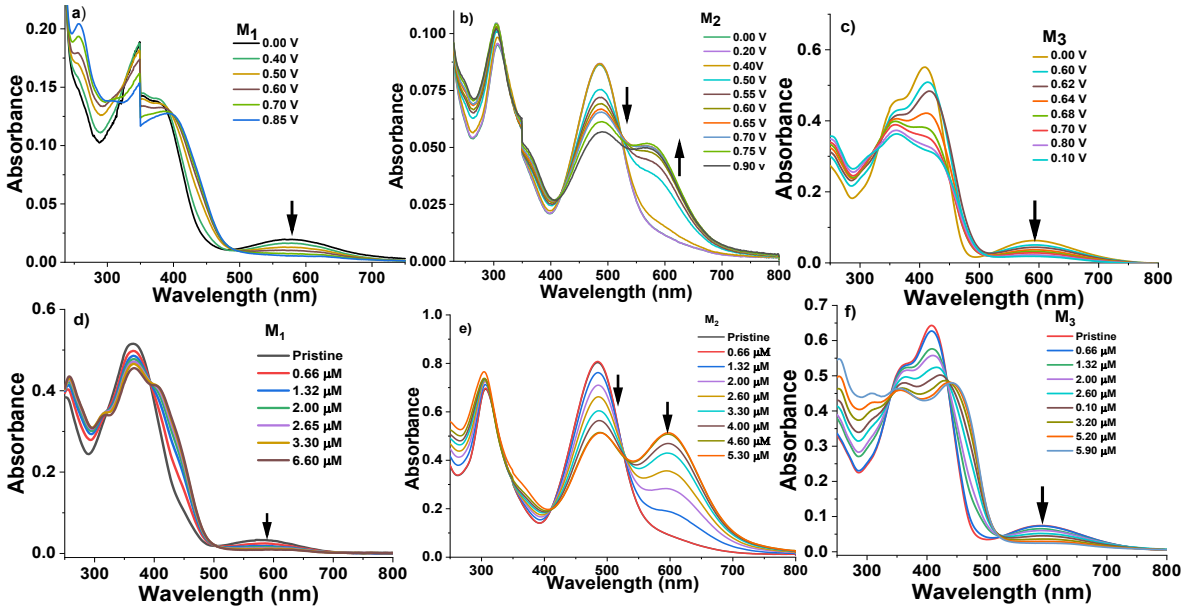



**Fig. S2** Spectroelectrochemical (a-c) & chemical (d-f) oxidation (Iron perchlorate $1 \times 10^{-4}$ M) spectra of $\mathbf{M_1}$-$\mathbf{M_3}$ measured in dichloromethane

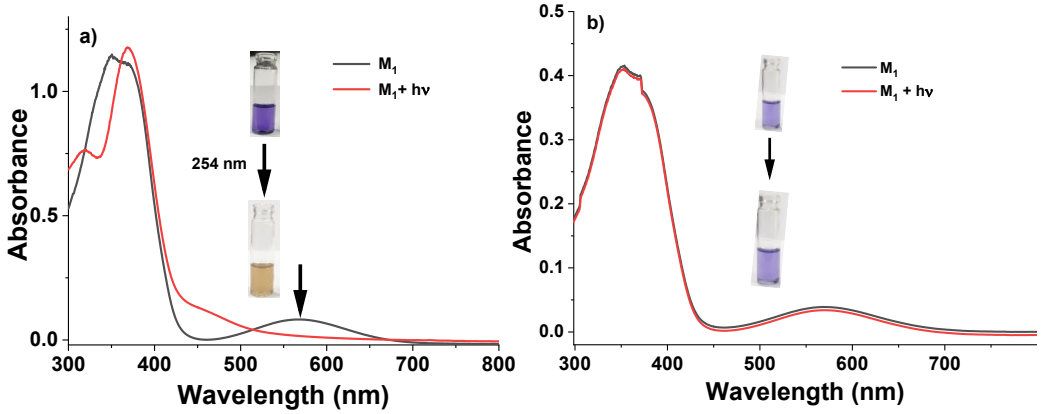



**Fig. S3** UV/vis spectral changes of a) $\mathbf{M_1}$ upon irradiation with 254 nm in a) $CCl_4$ b) Toluene

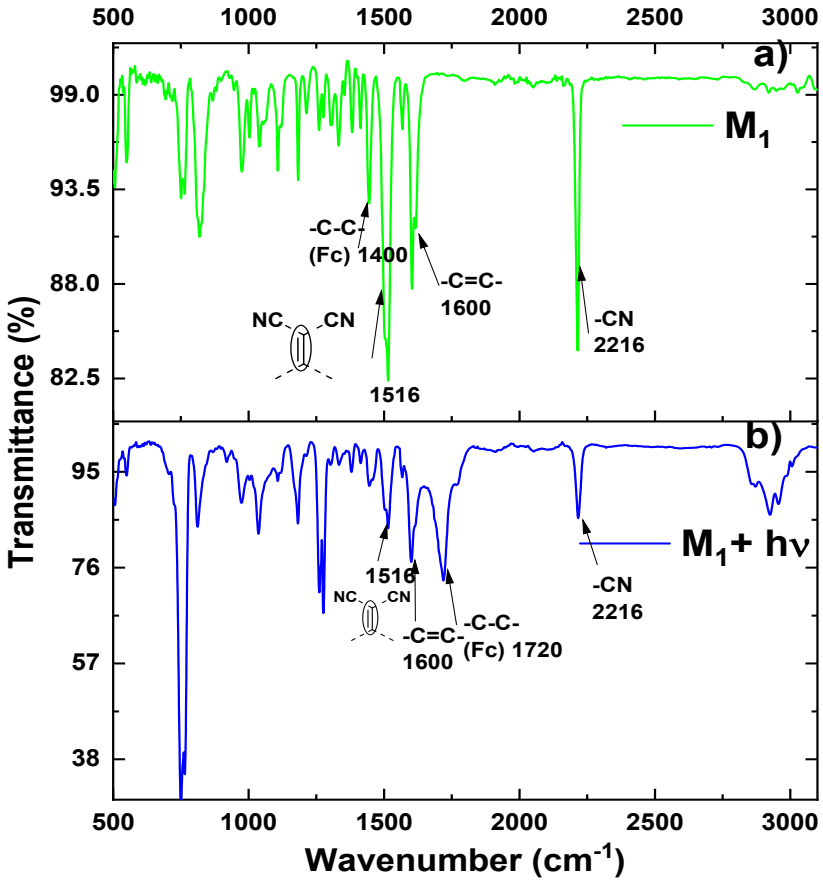



**Fig. S4** FTIR spectra of compound $\mathbf{M_1}$ a) before b) after irradiating with 254 nm light.

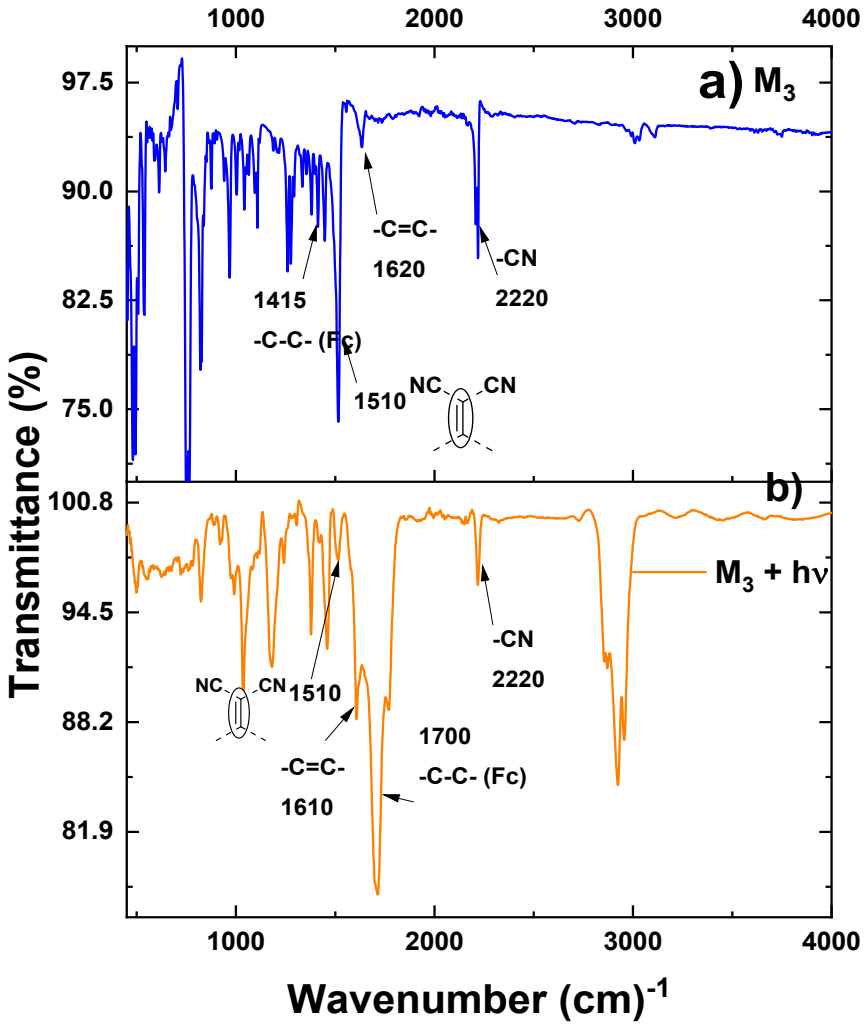



**Fig. S5** FTIR spectra of compound $\mathbf{M_3}$ a) before b) after irradiating with 254 nm light

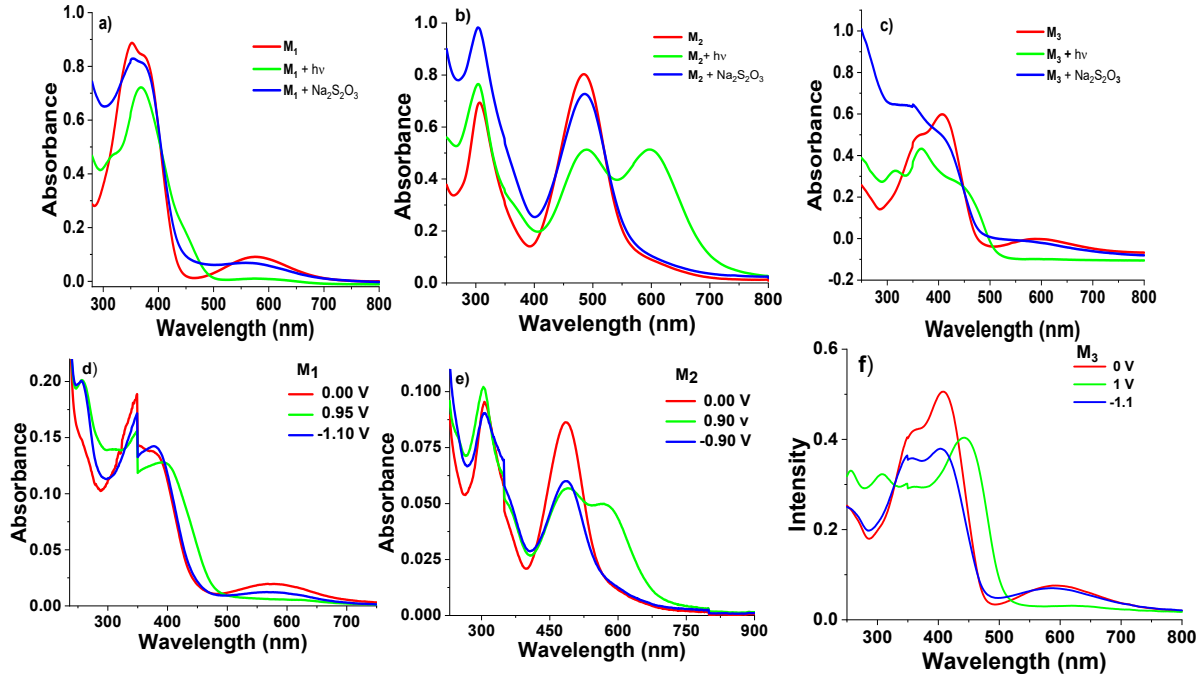


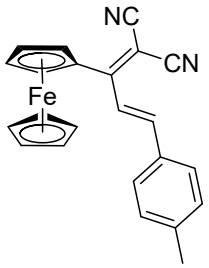

**Fig. S6** i) Chemical (a-c) and Electrochemical (d-f) reversibility of **$M_1$-$M_3$** measured in dichloromethane

# Experimental section

General Procedure of **$M_1$-$M_3$**

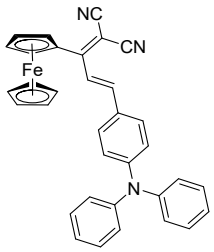
In a 25 mL round bottom flask, compound **Fc-d** (0.36 mmol), aromatic aldehyde (0.36 mmol) and catalytic amounts of piperidine were added and mixed with 10 mL of ethanol. The flask was heated to reflux for 12 hours. At the end of the time, the reaction mixture was brought to room temperature and poured into water. The resultant solid was filtered and purified by silica gel column chromatography with dichloromethane/petroleum ether (1/1, v/v) as an eluent.

(E)-2-(1-ferrocenyl-3-(p-tolyl) allylidene)malononitrile (**$M_1$**):

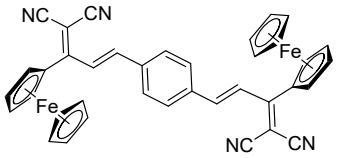



Blue solid (82 %), HRMS (QTOF): m/z calcd for $C_{23}H_{18}FeN_2$ ([M+]): 378.0819; found m/z: 378.0795; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, $^3J_{H\text{-}H}$ = 15.9 Hz, 1H), 7.47 (d, $^3J_{H\text{-}H}$ = 7.9 Hz, 2H), 7.24 (d, $^3J_{H\text{-}H}$ = 8.0 Hz, 2H), 7.20 (d, $^3J_{H\text{-}H}$ = 15.9 Hz, 1H), 5.01 (t, $^3J_{H\text{-}H}$, 2.0 Hz, 2H), 4.75

(t, $^{3}J_{H-H}$, 2.0 Hz, 2H), 4.33 (s, 5H), 2.41 (s, 3H).{$^{1}$H}$^{13}$C NMR (101 MHz, $CDCl_3$) δ 172.51, 144.55, 141.62, 132.18, 130.04, 128.24, 123.52, 115.98, 115.21, 74.97, 73.09, 71.93, 71.45, 21.67.

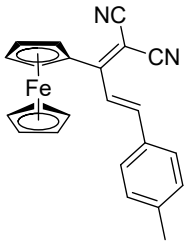



(E)-2-(3-(4-(diphenylamino)phenyl)-1-ferrocenyl-allylidene)malononitrile (**$M_2$**): Orange solid (81%), HRMS (QTOF) : m/z calcd for $C_{34}H_{25}FeN_3$ ([M+H]): 532.1471; found m/z: 532.1446; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, $^{3}J_{H-H}$ = 15.8 Hz, 1H), 7.42 (d, $^{3}J_{H-H}$ = 8.8 Hz, 2H), 7.34 – 7.29 (m, 4H), 7.16 – 7.10 (m, 7H), 7.02 (d, $^{3}J_{H-H}$ = 8.8 Hz, 2H), 4.98 (t, $^{3}J_{H-H}$ = 2.0 Hz, 2H), 4.72 (t, $^{3}J_{H-H}$, 2.0 Hz, 2H), 4.31 (s, 5H). {$^{1}$H}$^{13}$C NMR (101 MHz, $CDCl_3$) δ 172.09, 150.58, 146.59, 144.49, 129.63, 129.56, 127.57, 125.69, 124.51, 121.78, 121.36, 116.26, 115.50, 73.87, 72.64, 71.84, 71.28.




2,2'-((2E,2'E)-1,4-phenylenebis(1-ferrocene-2-en-3-yl-1-ylidene)dimalononitrile (**$M_3$**): Green solid (78%), $^{1}$H NMR (400 MHz, $CDCl_3$), HRMS (QTOF): m/z calcd for $C_{38}H_{26}Fe_2N_4$ [(M+)]: 650.0856; found m/z: 650.0844; δ 7.62 (s, 4H), 7.55 (d, *J* = 16.0 Hz, 2H), 7.30 (d, *J* = 16.0 Hz, 2H), 5.05 – 5.00 (m, 4H), 4.82 – 4.77 (m, 4H), 4.35 (s, 10H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 172.04, 142.70, 136.94, 128.82, 125.89, 115.72, 77.30, 73.44, 71.87, 71.52.

# Spectral data

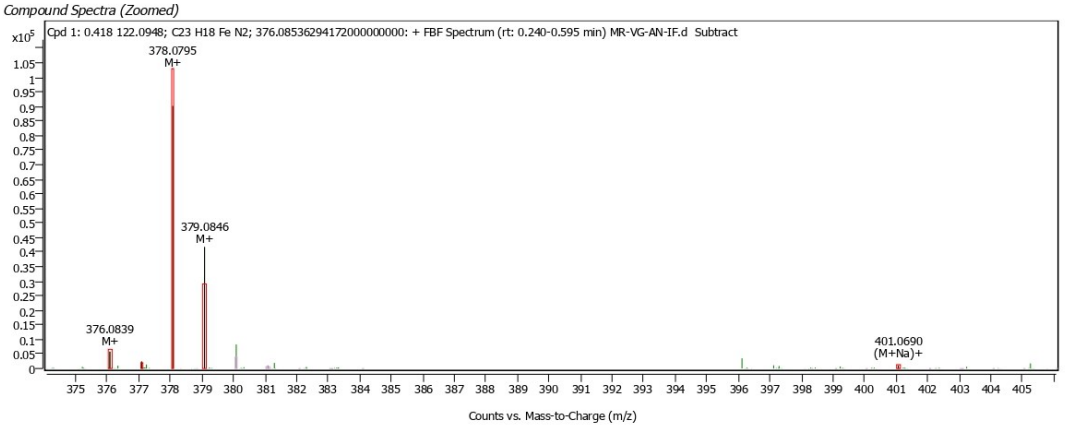



**Compound Details**

**Cpd. 1: C23 H18 Fe N2**

| Formula | m/z | Observed M/Z | Difference_Da | Difference_PPM | Score |
|---|---|---|---|---|---|
| C23 H18 Fe N2 | 378.0795 | 378.079499037288 | -1.25034727972206 | -3.32462585888758 | 67.59 |

*Compound Spectra (Zoomed)*




**MassHunter Qual 10.0**
**(End of Report)**

**Fig. S7** HRMS of compound $\mathbf{M_1}$

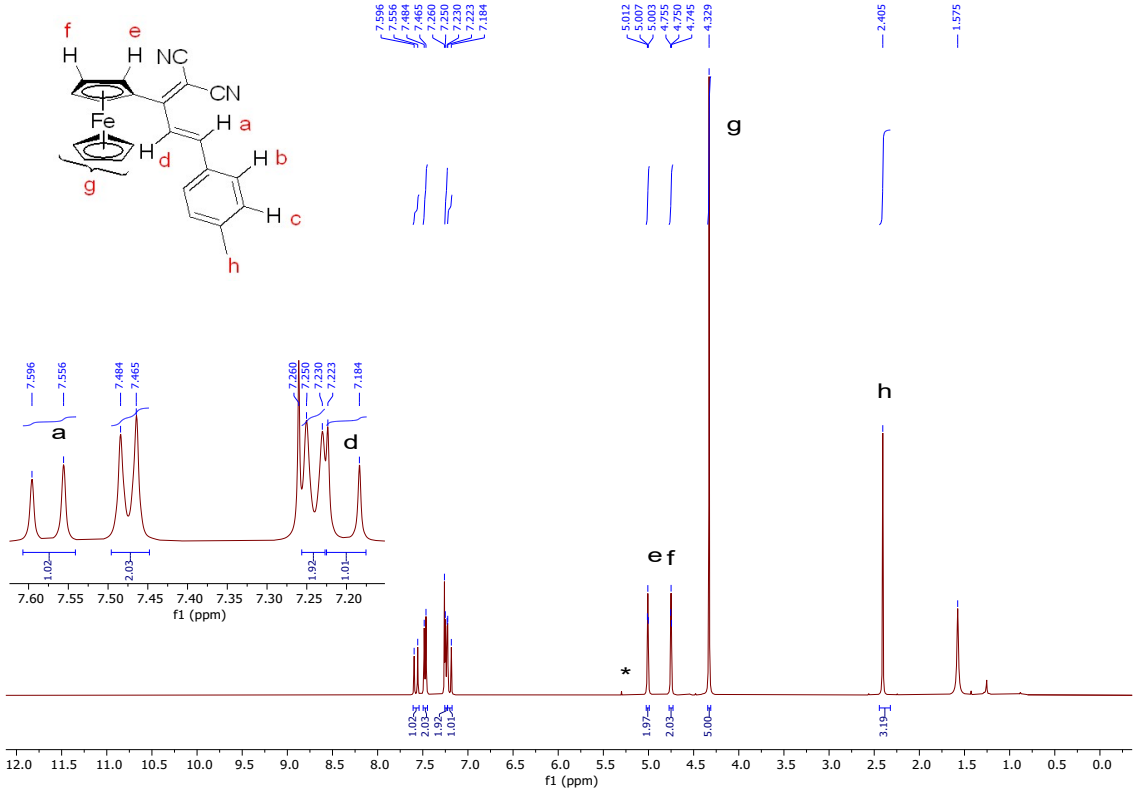



**Fig. S8** $^{1}$H NMR spectrum of compound $\mathbf{M_1}$ (400 MHz, $CDCl_3$)

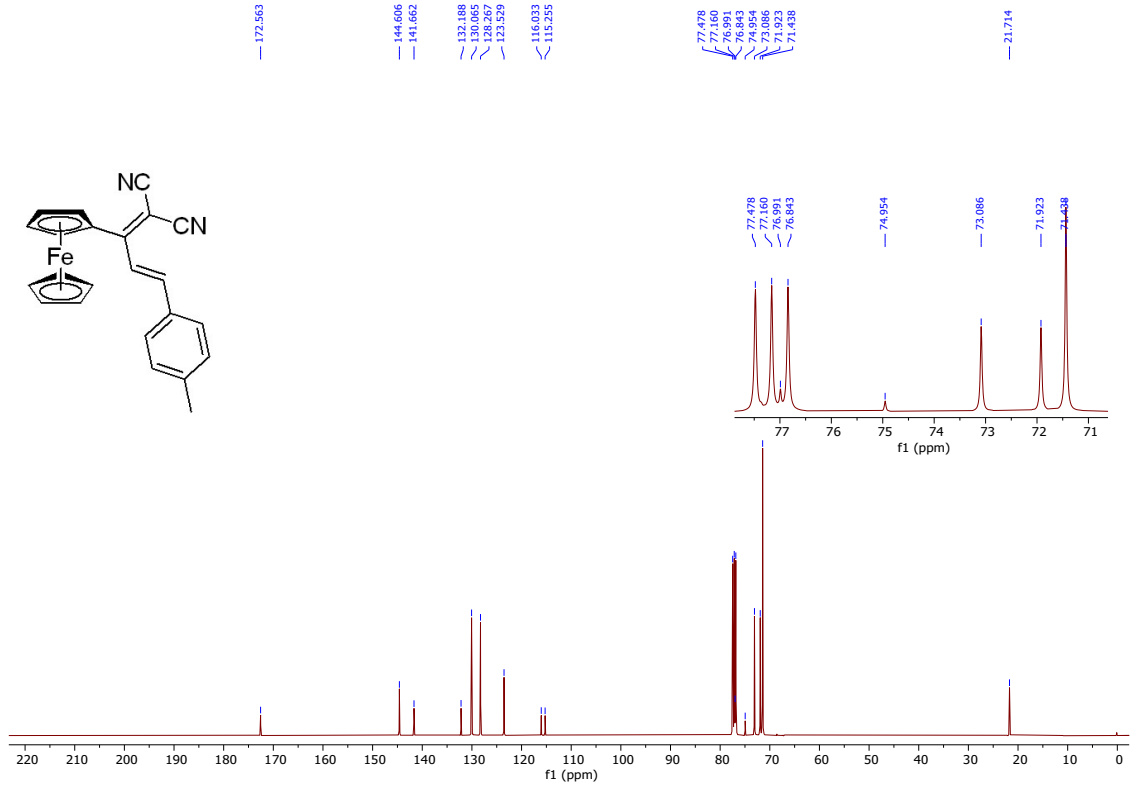



**Fig. S9** $\{^{1}H\}^{13}C$ NMR spectrum of compound $\mathbf{M_1}$ (101 MHz, $CDCl_3$)

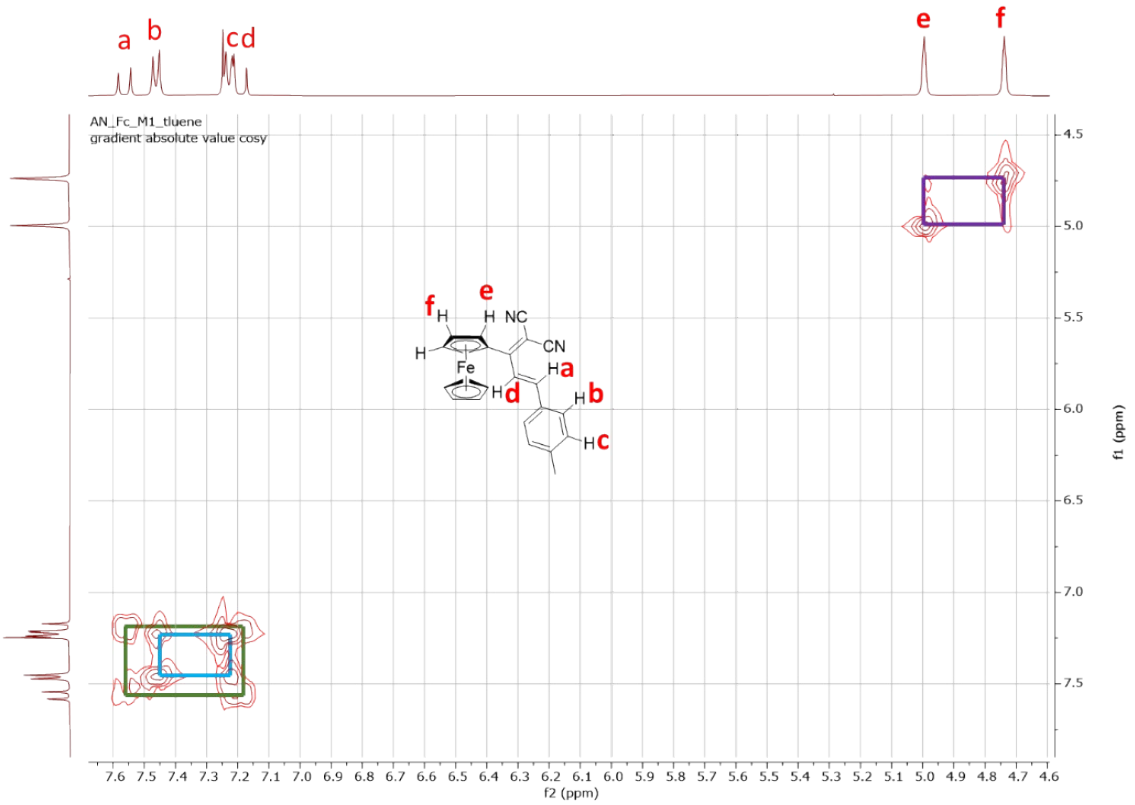
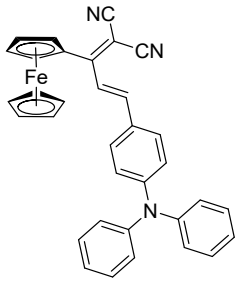



**Fig. S10** $^{1}$H-$^{1}$H, COSY NMR spectrum of compound $\mathbf{M_1}$ (400 MHz, $CDCl_3$)

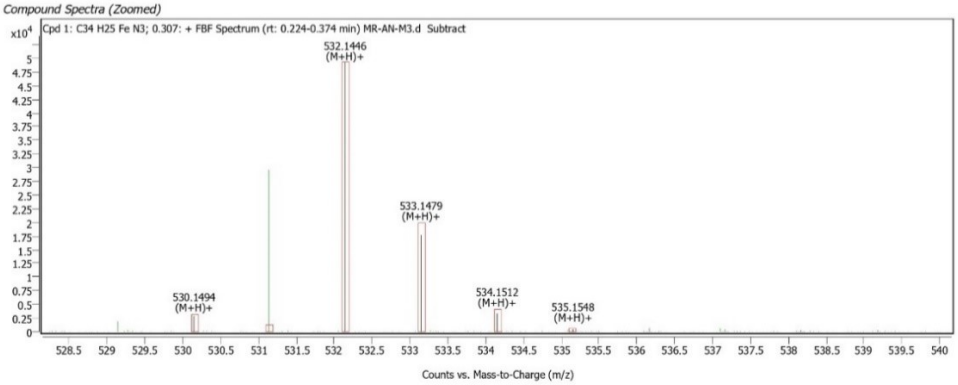



**Compound Details**

**Cpd. 1: C34 H25 Fe N3**

| Formula | m/z | Observed M/Z | Difference_Da | Difference_PPM | Score |
|---|---|---|---|---|---|
| C34 H25 Fe N3 | 532.1446 | 532.144572478966 | -2.39376402282687 | -4.52383837001366 | 75.86 |

*Compound Spectra (Zoomed)*




**MassHunter Qual 10.0**
**(End of Report)**

**Fig. S11** HRMS of compound $\mathbf{M_2}$

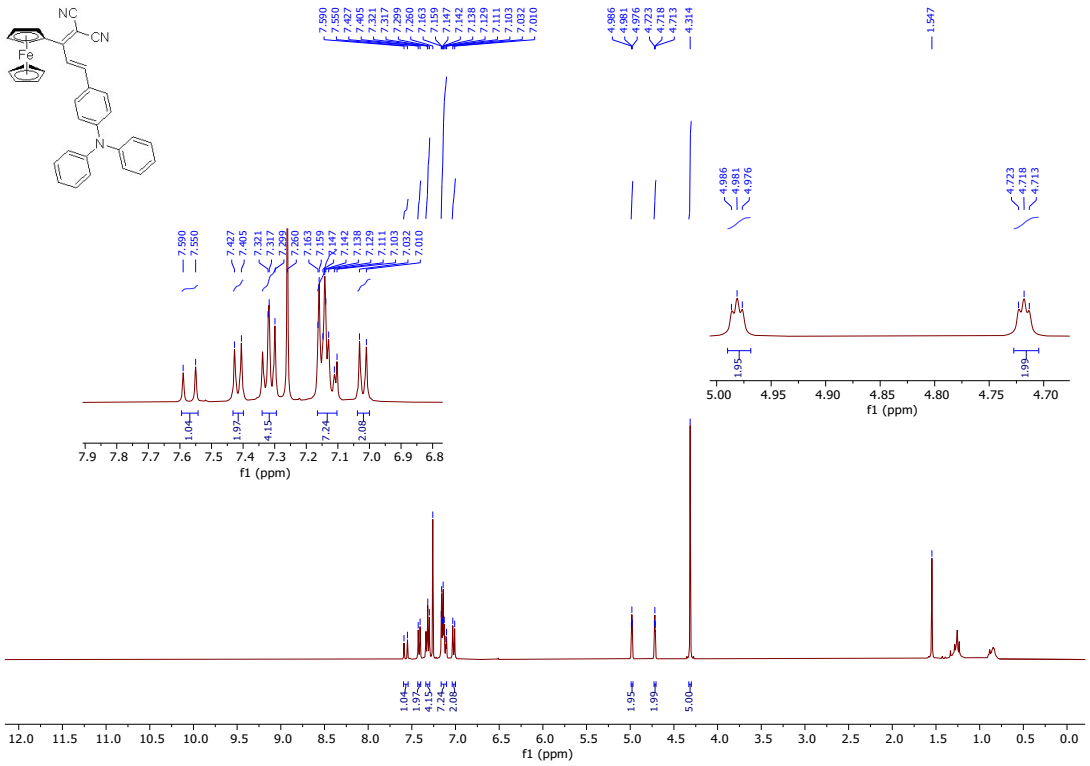



**Fig. S12** $^1$H NMR spectrum of Compound $\mathbf{M_2}$ (400 MHz, $CDCl_3$)

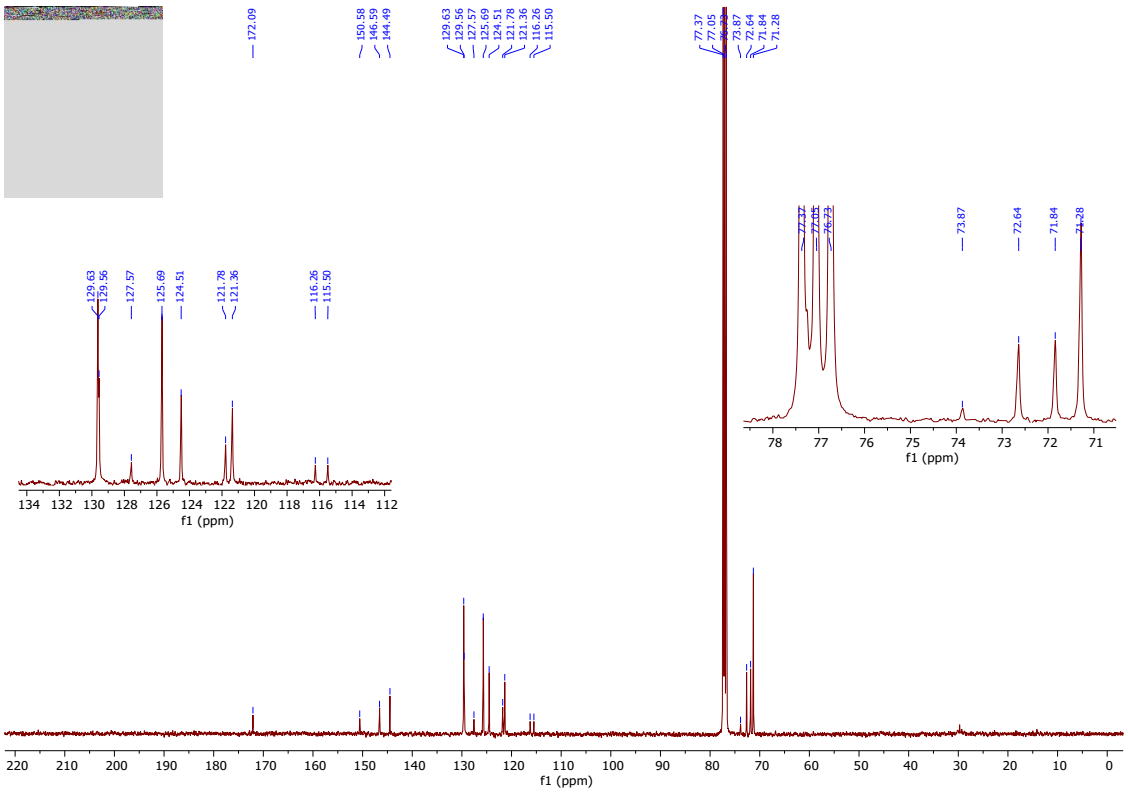



**Fig. S13** $\{^1H\}^{13}C$ NMR spectrum of Compound $\mathbf{M_2}$ (101 MHz, $CDCl_3$)

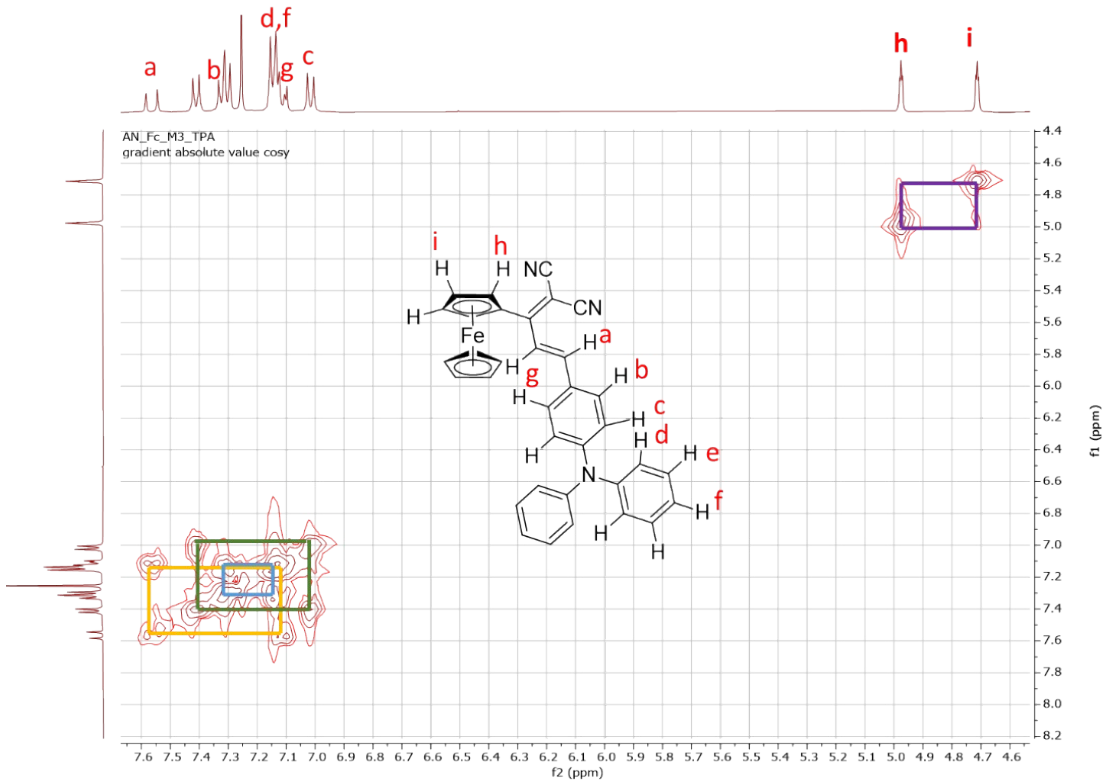
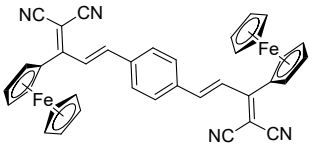



**Fig. S14** $^1H$-$^1H$, COSY NMR spectrum of compound $\mathbf{M_2}$ (400 MHz, $CDCl_3$)




**Compound Details**

**Cpd. 1: C38 H26 Fe2 N4**

| Formula | m/z | Observed M/Z | Difference_Da | Difference_PPM | Score |
|---|---|---|---|---|---|
| C38 H26 Fe2 N4 | 650.0844 | 650.084351631536 | -0.259268031868487 | -0.401284704873722 | 81.84 |

*Compound Spectra (Zoomed)*

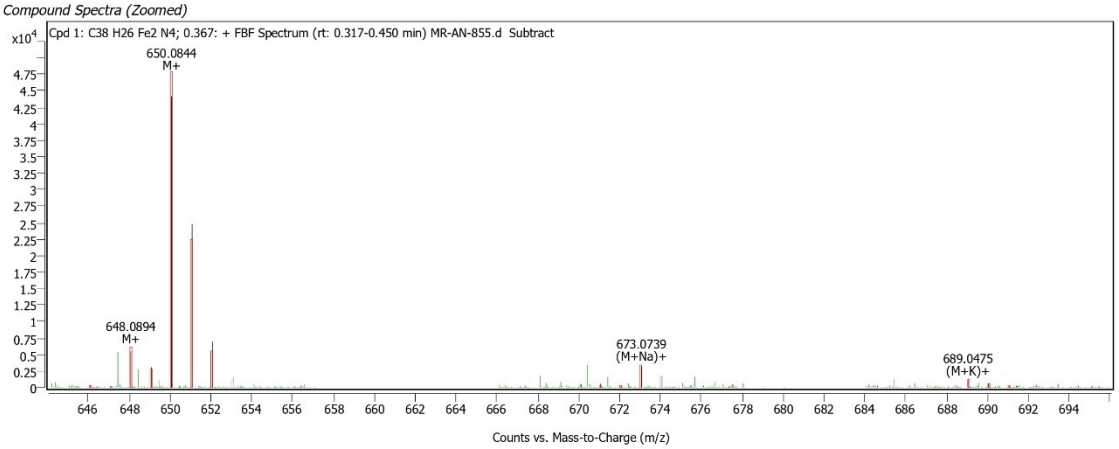



**Fig. S15** HRMS of compound $\mathbf{M_3}$

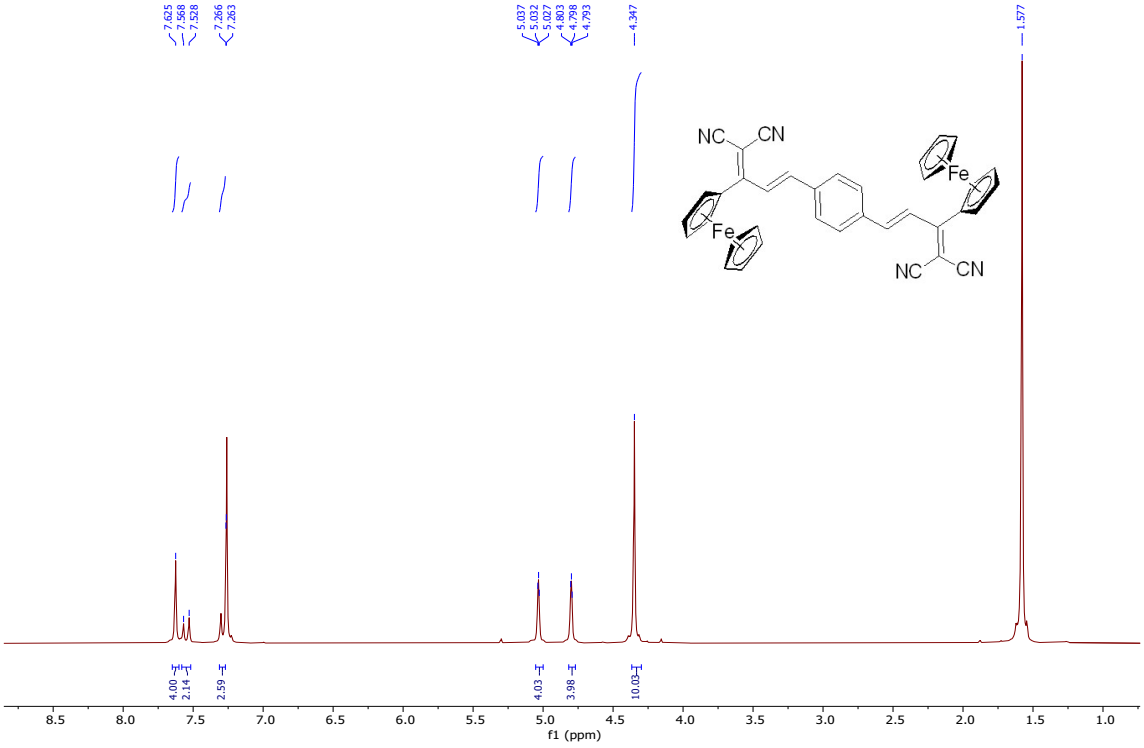



**Fig. S16** $^1$H NMR spectrum of compound $\mathbf{M_3}$ (400 MHz, $CDCl_3$)

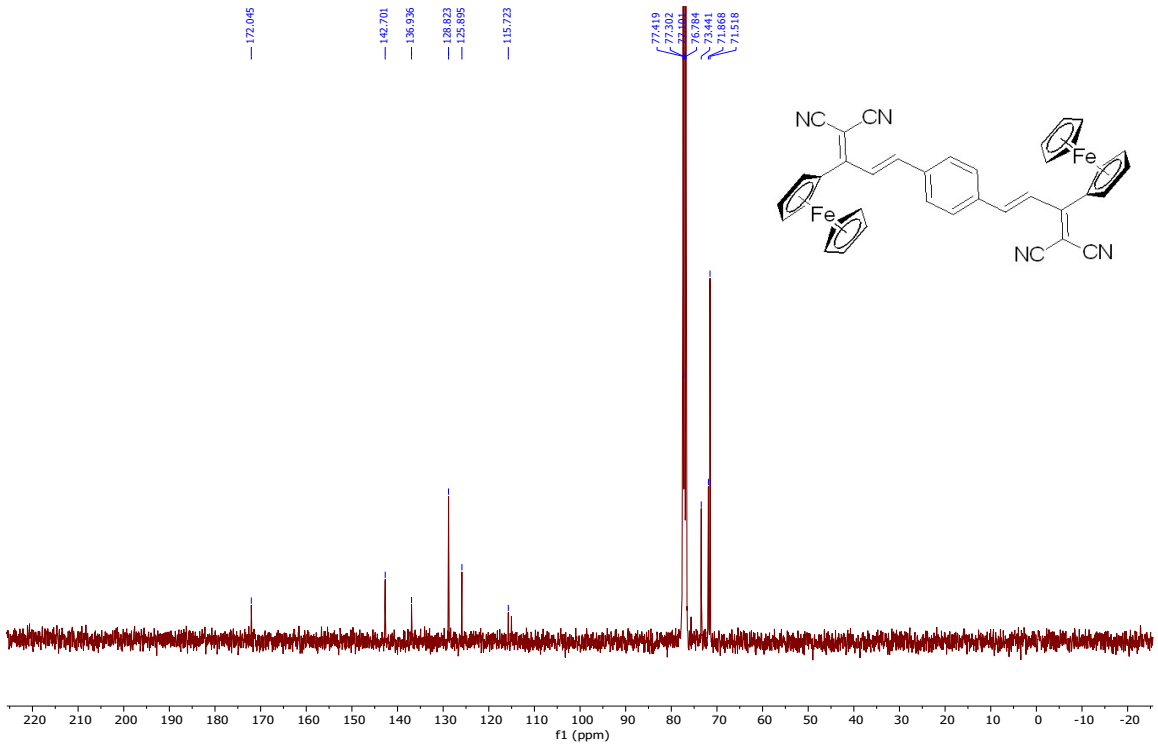



**Fig. S17** $\{^1H\}^{13}C$ NMR spectrum of Compound $\mathbf{M_3}$ (101 MHz, $CDCl_3$)