

Article

Supplementary Materials: Nonlinear optical properties of porphyrin, fullerene and ferrocene hybrid materials

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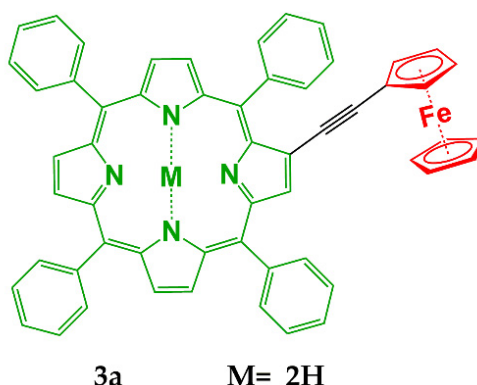
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Experimental

General Methods. ¹H-NMR spectra were recorded as CDCl₃ solutions on a Bruker AM-300 instrument using residual solvent signal as an internal standard. Chemical shifts are given as δ values. FAB mass spectra were measured on a VG-4 spectrometer using m-nitrobenzyl alcohol (NBA) as a matrix. Matrix-assisted laser desorption/ionization time of flight (MALDI-TOF) mass spectra were performed with a MALDI-TOF Reflex IV instrument (Bruker-Daltonics) in reflector mode, using a 337 nm nitrogen laser (8 Hz). A 2 mg/mL 2,5-dihydroxybenzoic acid (gentisic acid) solution in CH₃CN/TFA (0.1% solution) was used as a matrix. Electronic absorption spectra were recorded in CH₂Cl₂ solution at room temperature on a Shimadzu UV 3600 spectrophotometer (Shimadzu Corporation, Kyoto, Japan).

Elemental analyses were carried out with a PerkinElmer CHN 2400 instrument in the Analytical Laboratories of the Department of Chemistry at the University of Milan.

Compound 3a



¹H-NMR (300 MHz, CDCl₃): δ (ppm) 9.02(s, 1H), 8.87(s, 2H), 8.82(m, 3H), 8.73 (m, 1H), 8.24(m, 8H), 7.83(s, 12H), 4.38(s, 3H), 4.27(s, 6H), -2.66(s, 2H).

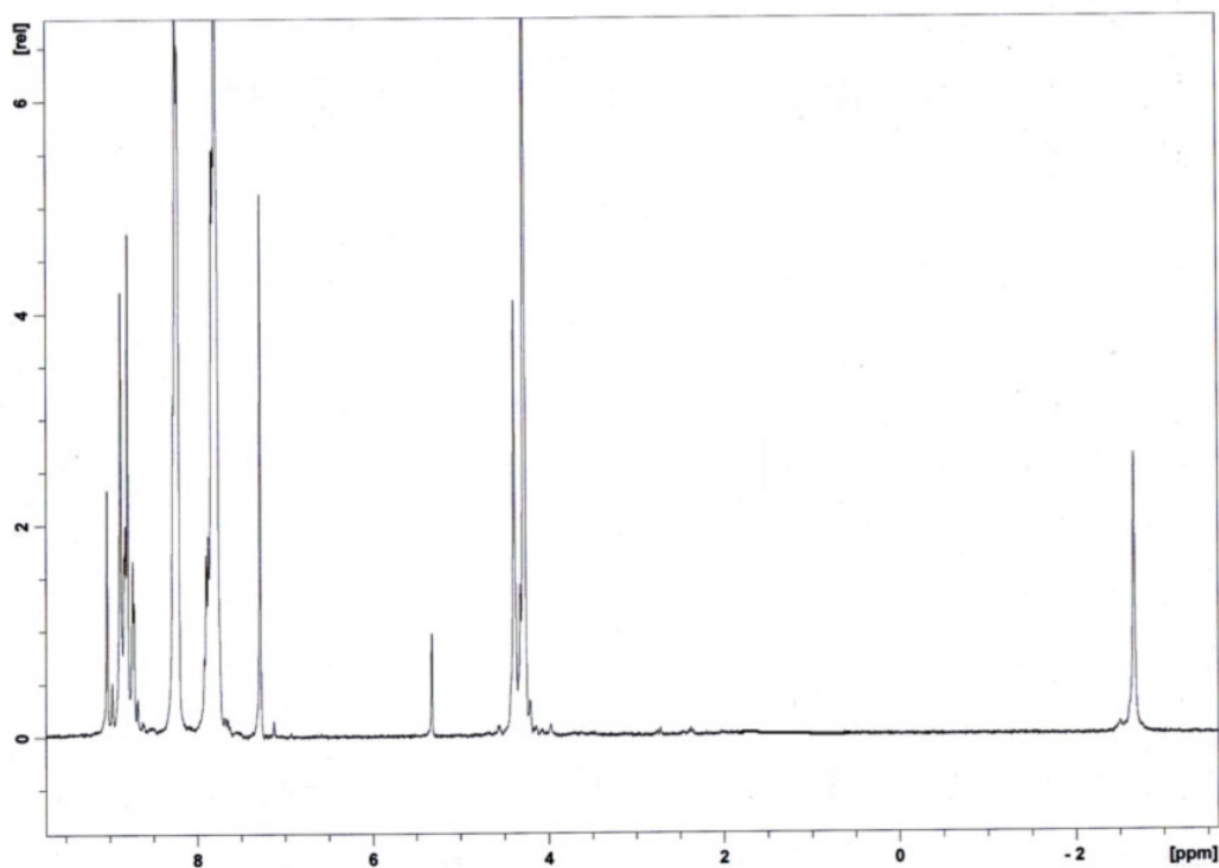


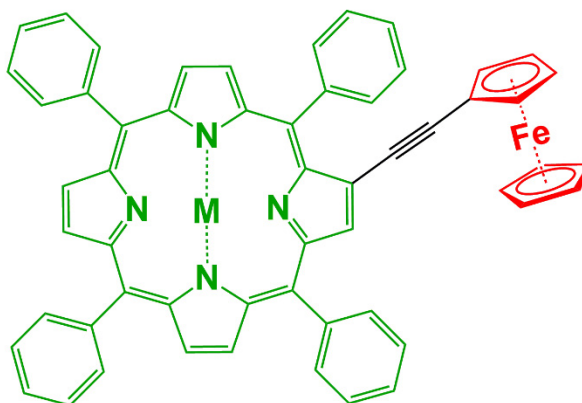
Figure S1. ^1H -NMR spectrum of compound **3a** in CDCl_3 at 300 K at 400 MHz.

MS(FAB+): m/z : 823 $[\text{M}+\text{H}]^+$

Elemental Analysis

Anal. Calcd. for $\text{C}_{56}\text{H}_{38}\text{N}_4\text{Fe}$: C, 81.74; H, 4.65; N, 6.80. Found: C, 81.99; H, 4.64; N, 6.78

Compound **3a**(Zn)



3a(Zn) M= Zn

$^1\text{H-NMR}$ (300 MHz, CDCl_3): $\delta(\text{ppm})$ 9.18(s, 1H), 8.92(m, 4H), 8.82(d, 2H, $J=7.1$ Hz), 8.75(d, 2H, $J=7.1$ Hz), 8.24(m, 8H), 7.80(m, 12H), 4.68(s, 1H), 4.42(s, 2H), 4.25(s, 6H).

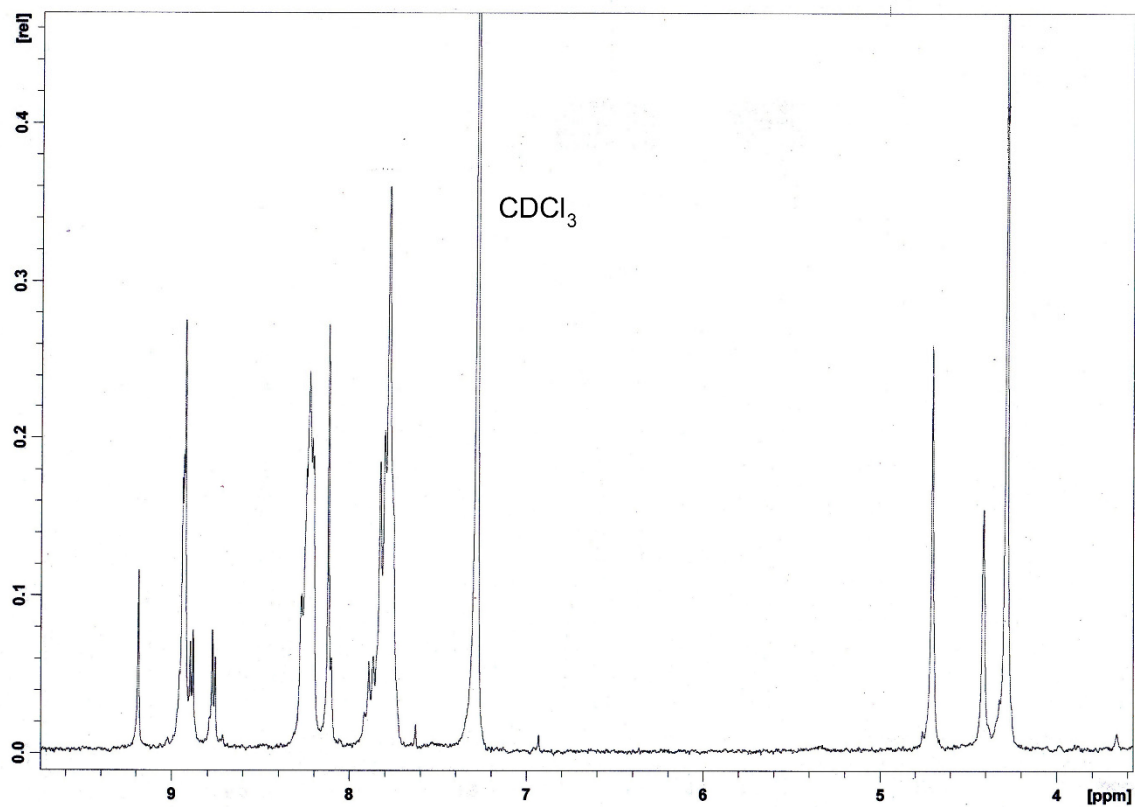


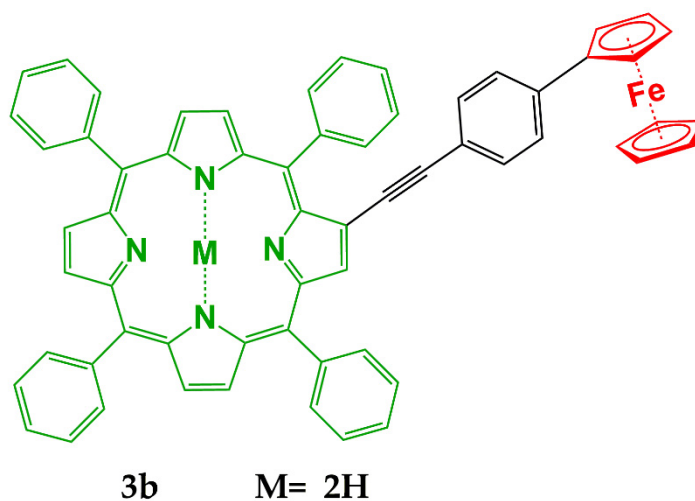
Figure S2. $^1\text{H-NMR}$ spectrum of compound **3a(Zn)** in CDCl_3 at 300 K at 400 MHz. .

MS(FAB $^+$): m/z : 886 $[\text{M}]^+$

Elemental Analysis

Anal. Calcd. for $\text{C}_{56}\text{H}_{36}\text{N}_4\text{FeZn}$: C, 75.90; H, 4.09; N, 6.32. Found: C, 75.67; H, 4.08; N, 6.34

Compound 3b



^1H -NMR (300 MHz, CDCl_3): δ (ppm) 9.09(s,1H), 8.87(s, 2H), 8.82(d, 2H), 8.73(m, 2H), 8.24(m, 8H), 7.83(m, 12H), 7.42(d, 2H, $J=8.3$ Hz), 7.29(d, 2H, $J=8.3$ Hz) 4.65(s, 2H), 4.38(s, 2H), 4.27(s, 5H), -2.66(s, 2H).

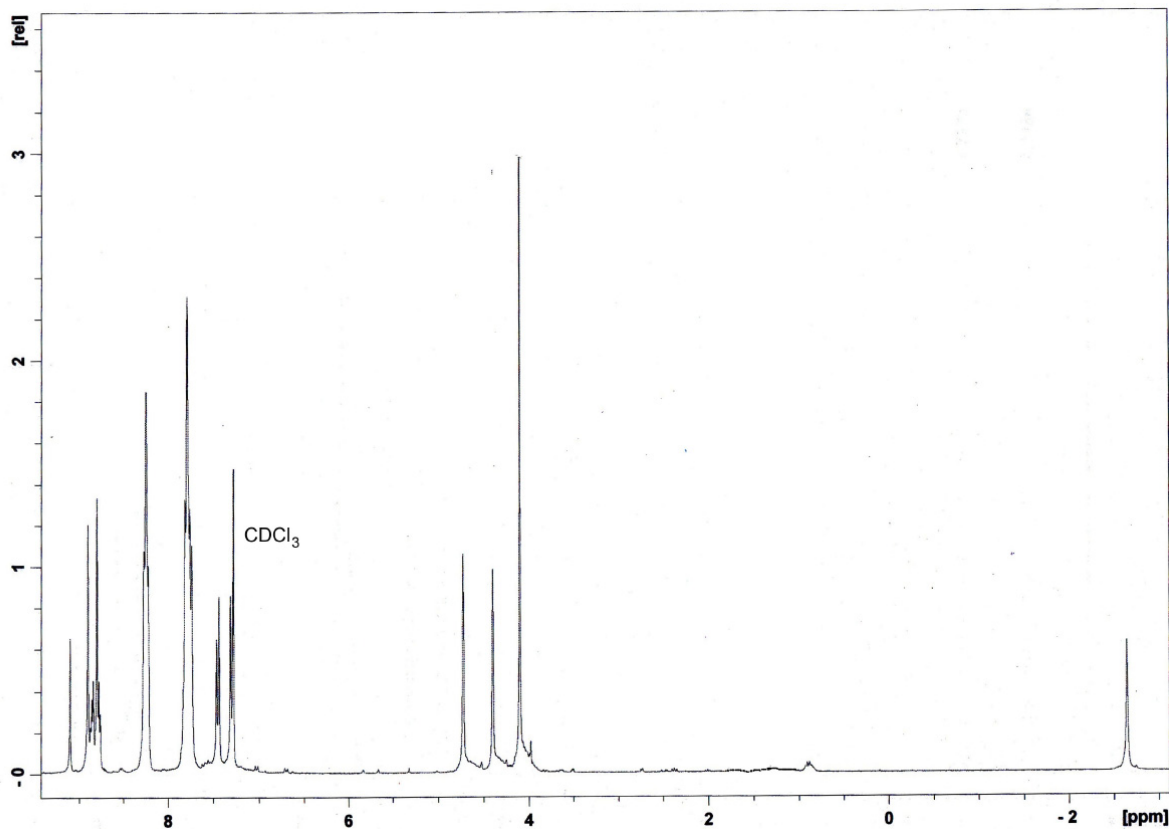


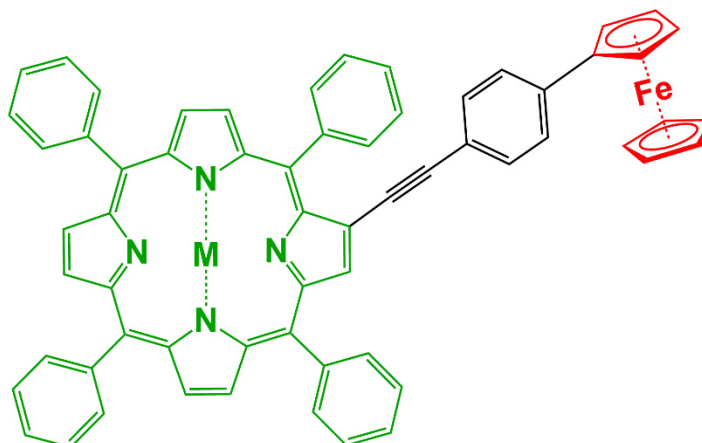
Figure S3. ^1H -NMR spectrum of compound **3b** in CDCl_3 at 300 K at 400 MHz. .

MS(FAB+): m/z : 899 $[\text{M}+\text{H}]^+$

Elemental Analysis

Anal. Calcd. for $\text{C}_{62}\text{H}_{42}\text{N}_4\text{Fe}$: C, 82.84; H, 4.70; N, 6.23. Found: C, 83.09; H, 4.71; N, 6.25

Compound **3b**(Zn)



3b(Zn) M= Zn

$^1\text{H-NMR}$ (300 MHz, CDCl_3): δ (ppm) 9.21(s, 1H), 8.84(m, 5H), 8.82(d, 2H), 8.75(d, 1H), 8.21(m, 8H), 7.75(m, 12H), 7.45(d, 2H), 4.72(s, 2H), 4.39(s, 2H), 4.10(s, 5H).

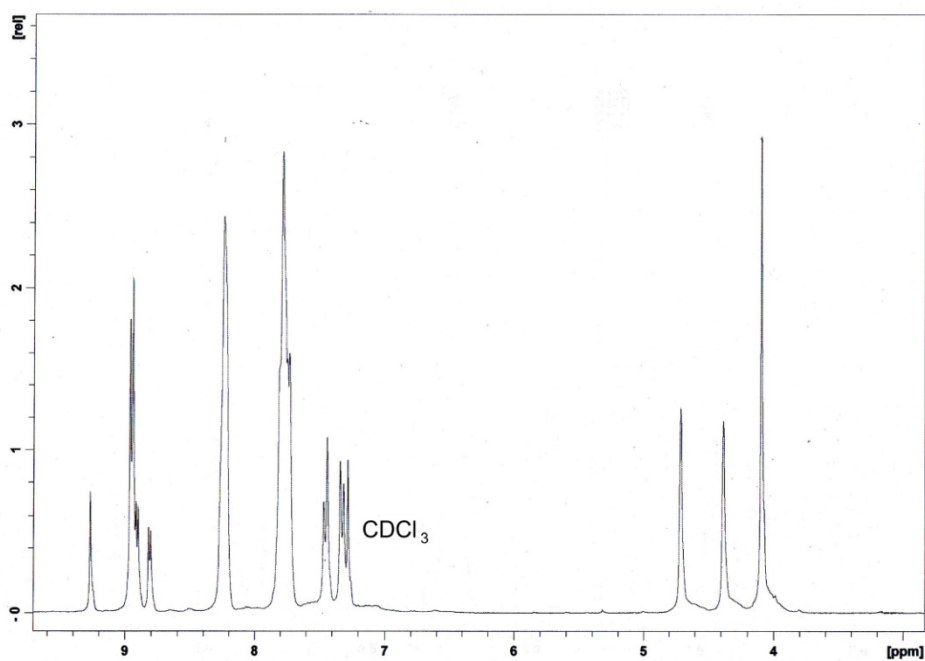


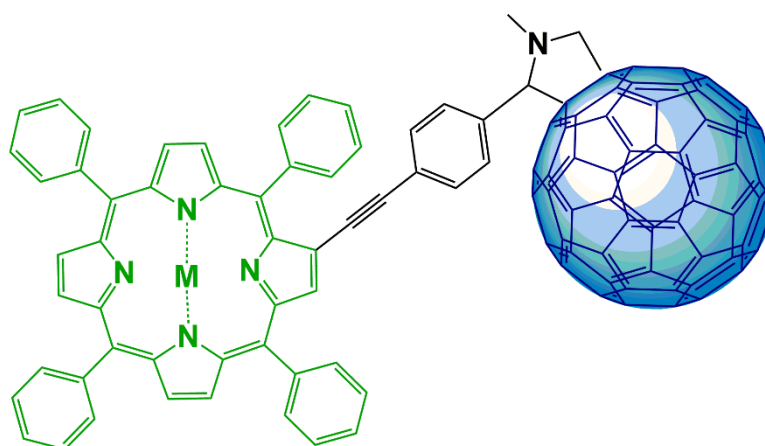
Figure S4. $^1\text{H-NMR}$ spectrum of compound **3b(Zn)** in CDCl_3 at 300 K at 400 MHz. .

MS(FAB $^+$): m/z 963: $[\text{M}+\text{H}]^+$

Elemental Analysis

Anal. Calcd. for $\text{C}_{62}\text{H}_{40}\text{N}_4\text{ZnFe}$: C, 77.38; H, 4.18; N, 5.82. Found: C, 77.15; H, 4.17; N, 5.84

Compound 6-C60

**6-C60****M= 2H**

$^1\text{H-NMR}$ (400 MHz, CDCl_3): δ (ppm) 9.07 (s, 1H), 8.89 (s, 2H), 8.82 (d, 1H; J) 5.1 Hz), 8.79 (s, 2H), 8.73 (d, 1H; J 5.1 Hz), 8.22 (br m, 5H), 7.79 (br m, 15H), 7.61 (br, m, 2H), 7.43 (br, m, 2H), 4.96 (d, 1H; J) 9.2 Hz), 4.89 (s, 1H), 4.22 (d, 1H; J) 9.2 Hz), 2.86 (s, 3H), -2.68 (s, 2H).

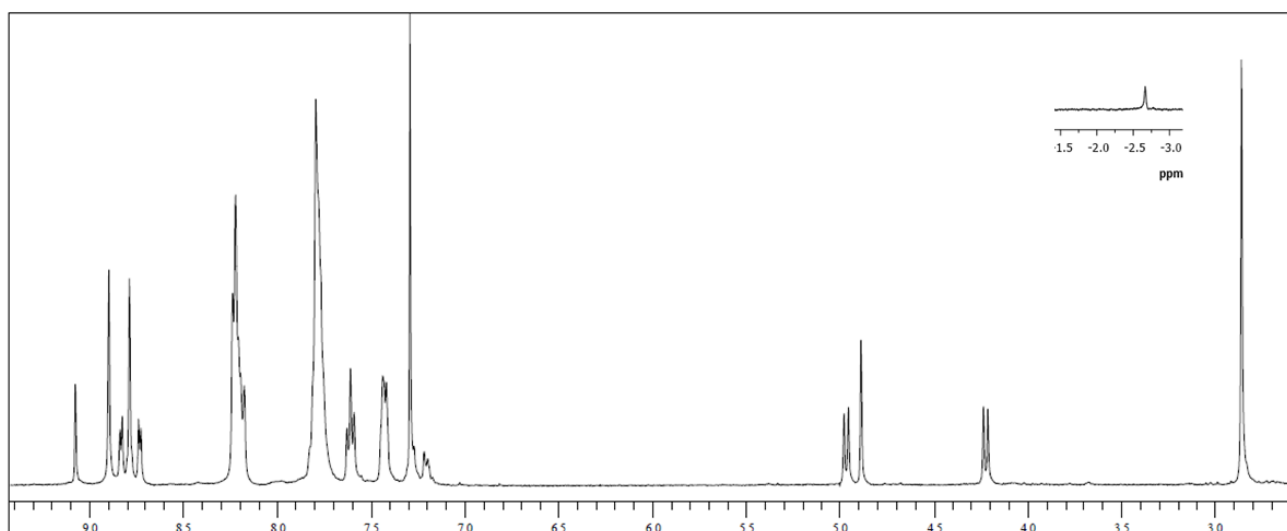


Figure S5. $^1\text{H-NMR}$ spectrum of compound **6-C60** in CDCl_3 at 300 K at 400 MHz.

MS(FAB $^+$): m/z 1491 $[\text{M} + \text{H}]^+$, 769 $[\text{M} - 720]^+$, 720 $[\text{M} - 769]^+$

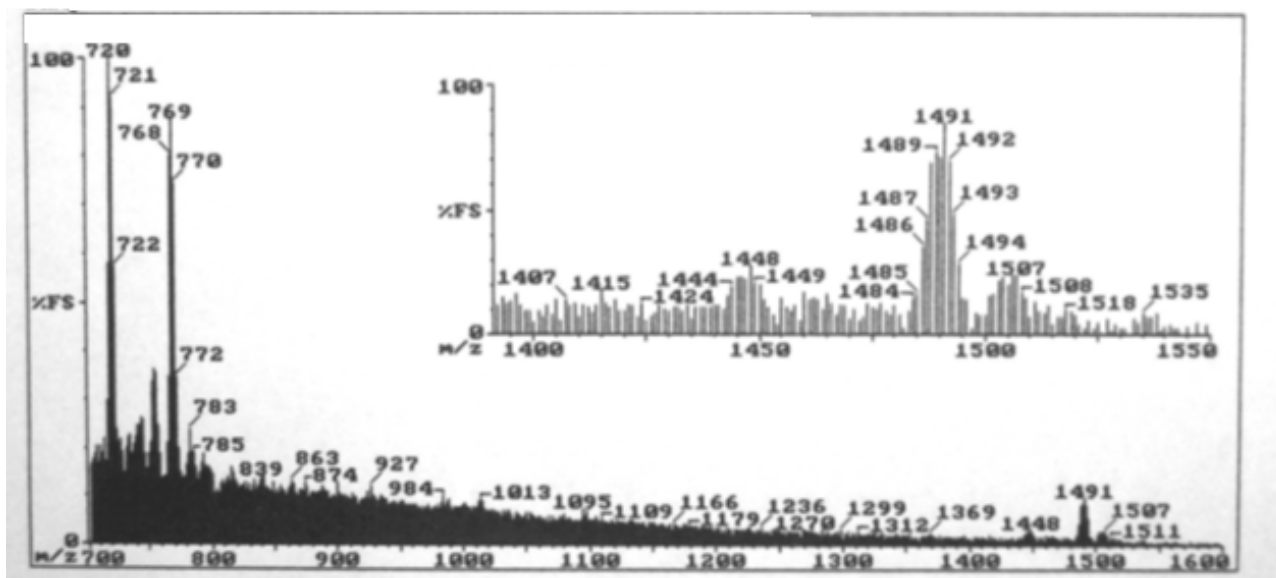


Figure S6. FAB MS spectrum of compound 6-C60 using as matrix NBA.

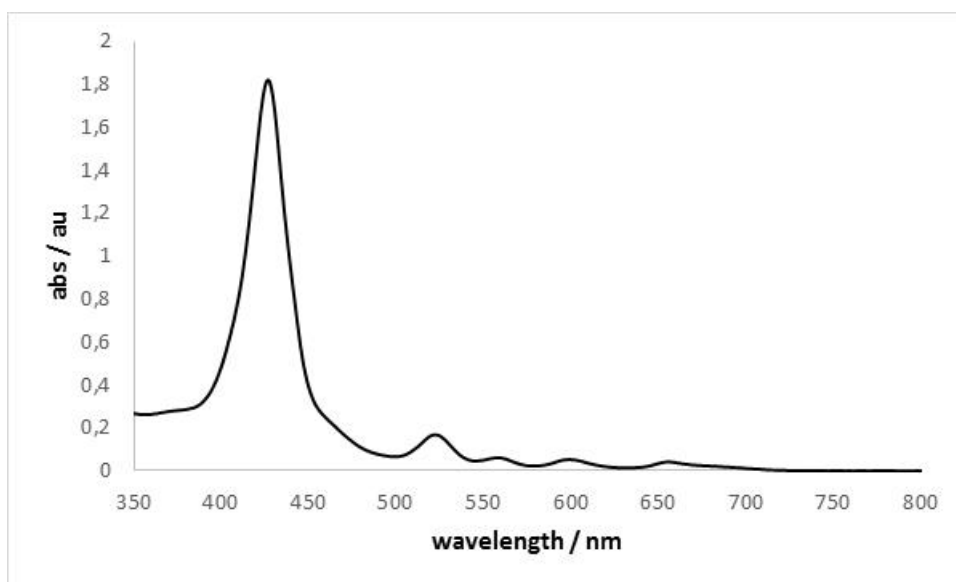
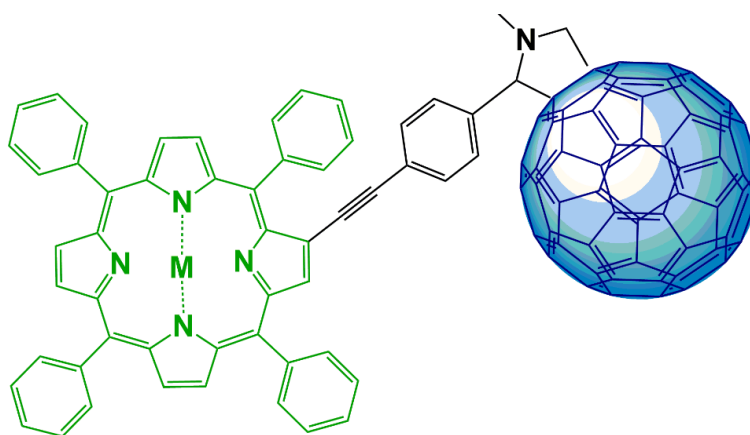


Figure S7. UV-Vis spectrum of compound 6-C60 in CH_2Cl_2 .

Elemental Analysis

Anal. Calcd. for $\text{C}_{115}\text{H}_{40}\text{N}_5$ C, 92.60; H, 2.70; N, 4.70. Found: C, 98.85; H, 2.69; N, 4.72.

Compound 6(Zn)-C60



6(Zn)-C60 M= Zn

$^1\text{H-NMR}$ (400 MHz, CDCl_3): δ (ppm) 9.24 (s, 1H), 8.95 (s, 2H), 8.93 (s, 2H), 8.88 (d, 1H; $J=5.1$ Hz), 8.77 (d, 1H; $J=5.1$ Hz), 8.22 (br m, 3H), 8.16 (br d, 2H; $J=7.2$ Hz), 7.80 (br m, 10H), 7.60 (m, 3H), 7.45–7.40 (br m, 4H), 7.20 (d, 2H; $J=7.2$ Hz), 4.95 (d, 1H; $J=9.2$ Hz), 4.85 (s, 1H), 4.20 (d, 1H; $J=9.2$ Hz), 2.87 (s, 3H).

MS (FAB+): m/z : 1552 $[\text{M}]^+$, 832 $[\text{M}-720]^+$, 720 $[\text{M}-832]^+$

Elemental Analysis

Anal. Calcd. for $\text{C}_{115}\text{H}_{38}\text{N}_5\text{Zn}$ C, 88.83; H, 2.46; N, 4.50, Zn, 4.21 Found: C, 88.57; H, 2.45; N, 4.49.

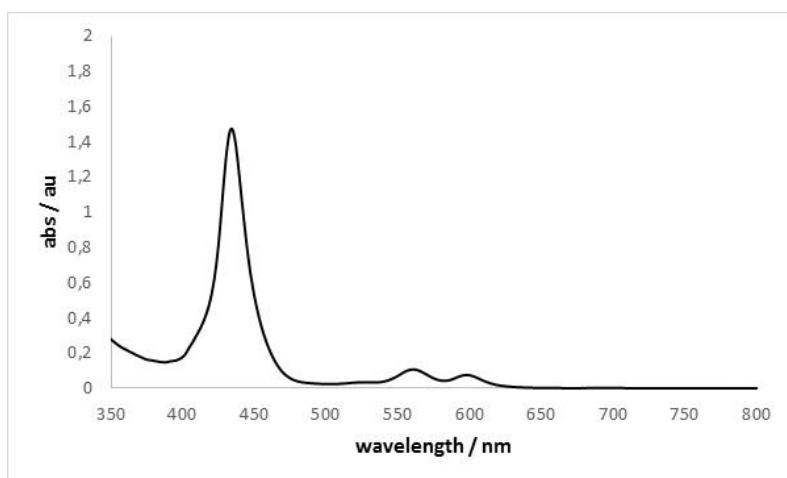
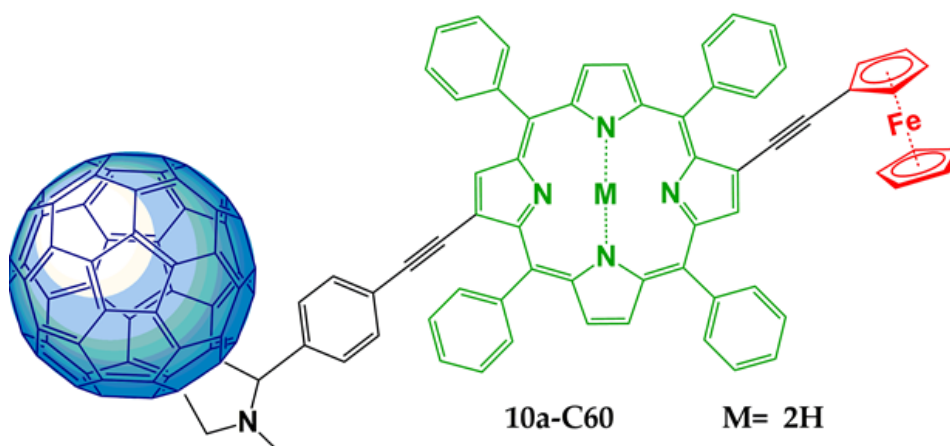


Figure S8. UV-Vis spectrum of compound 6(Zn)-C60 in CH_2Cl_2 .

Compound 10a-C60



$^1\text{H-NMR}$ (300 MHz, CDCl_3): δ (ppm) 9.04 (s, 1H), 8.99 (s, 1H), 8.91 (t, 1H, $J \frac{1}{4}$ 2.9 Hz), 8.87 (t, 1H, 2.9 Hz), 8.84 (s, 1H), 8.78 (t, 1H, $J \frac{1}{4}$ 5.9 Hz), 8.13 (m, 8H), 7.85 (m, 10H), 7.81 (m, 2H), 7.78 (m, 2H), 4.77 (d, 1H, $J \frac{1}{4}$ 8.3 Hz), 4.65 (s, 1H), 4.36 (s, 3H), 4.24 (s, 6H), 3.99 (d, 1H, $J \frac{1}{4}$ 8.3 Hz), 2.74 (s, 3H), -2.69 (s, 1H).

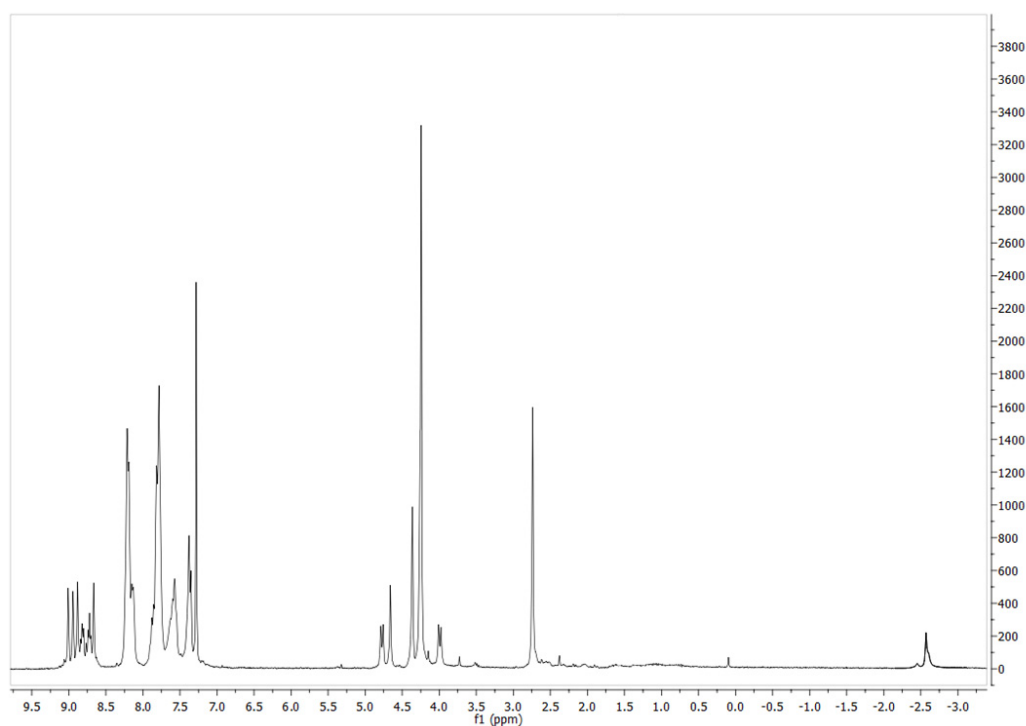


Figure S9. $^1\text{H-NMR}$ spectrum of compound **10a-C60** in CDCl_3 at 300 K at 400 MHz.

MS (MALDI-TOF): m/z : 1699.32 $[\text{M} + \text{H}]^+$

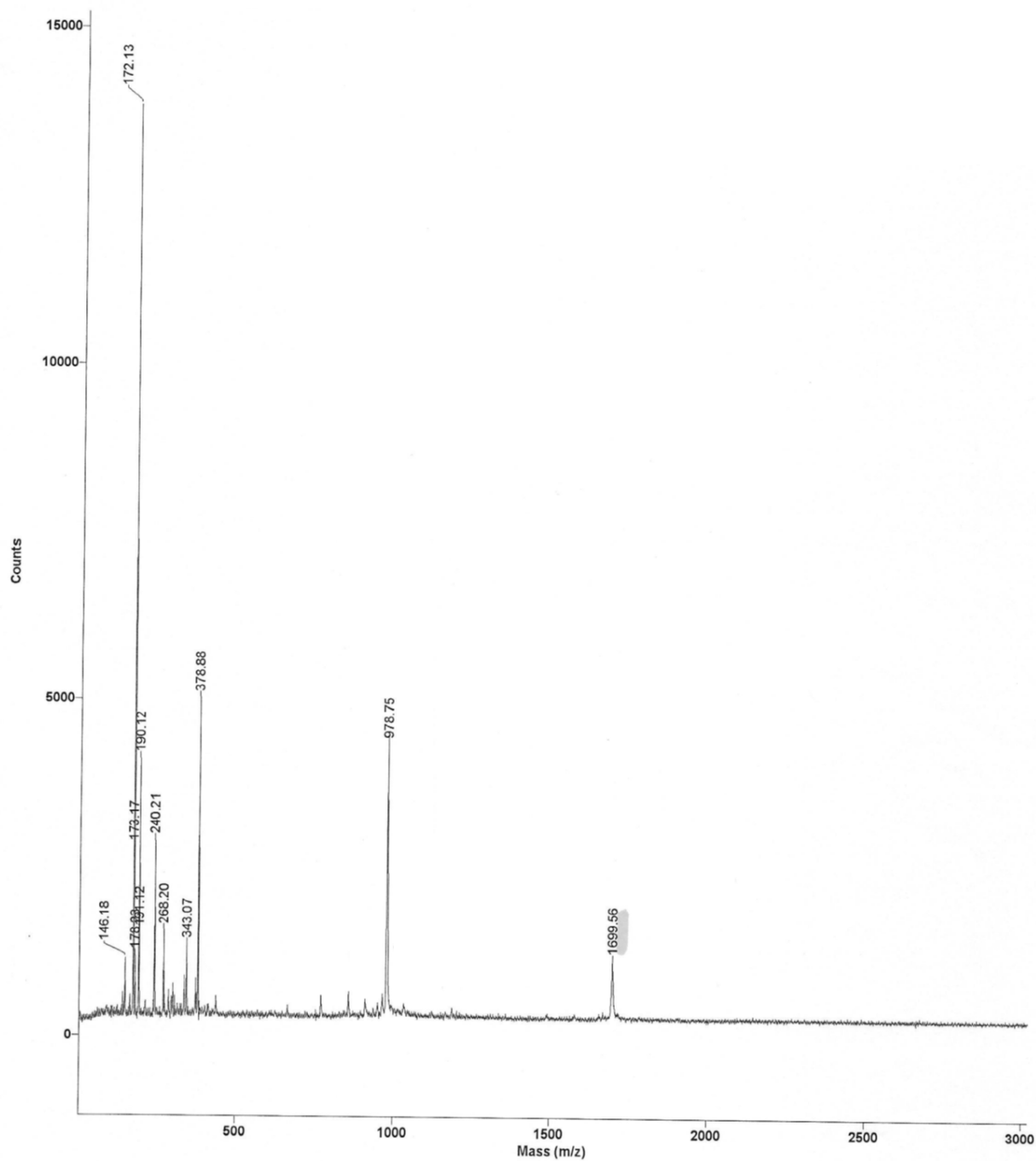
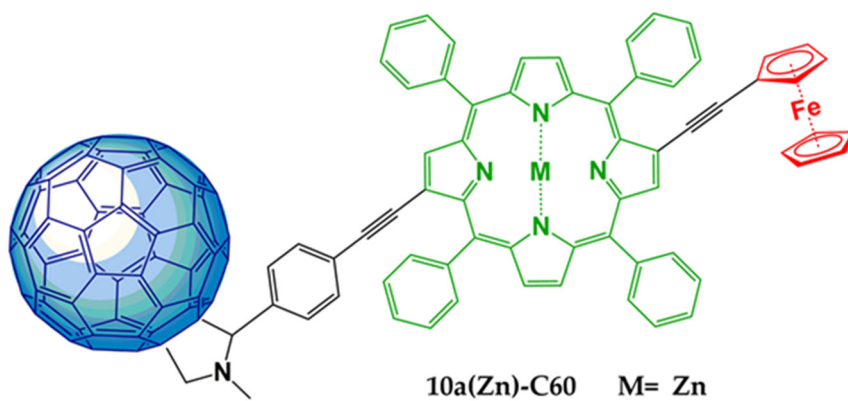


Figure S10. MALDI-TOF MS spectrum of compound **10a-C60** using as matrix gentisic acid.

Elemental Analysis

Anal. Calcd. for $C_{127}H_{47}N_5Fe$: C, 89.80; H, 2.78; N, 4.12. Found: C, 90.07; H, 2.79; N, 4.11.

Compound **10a(Zn)**-C60



$^1\text{H-NMR}$ (300 MHz, CDCl_3): δ (ppm) 9.18 (s, 1H), 9.12 (s, 1H), 8.90 (m, 2H), 8.82 (m, 1H), 8.67 (s, 1H), 8.18 (m, 8H), 7.82 (m, 12H), 7.57 (m, 4H), 7.41 (d, 2H, $J \frac{1}{4} 9.2$ Hz), 4.80 (d, 1H, $J \frac{1}{4} 9$ Hz), 4.66 (s, 1H), 4.39 (s, 3H), 4.26 (s, 6H), 4.03 (d, 1H, $J \frac{1}{4} 9.2$ Hz), 2.80 (s, 3H).

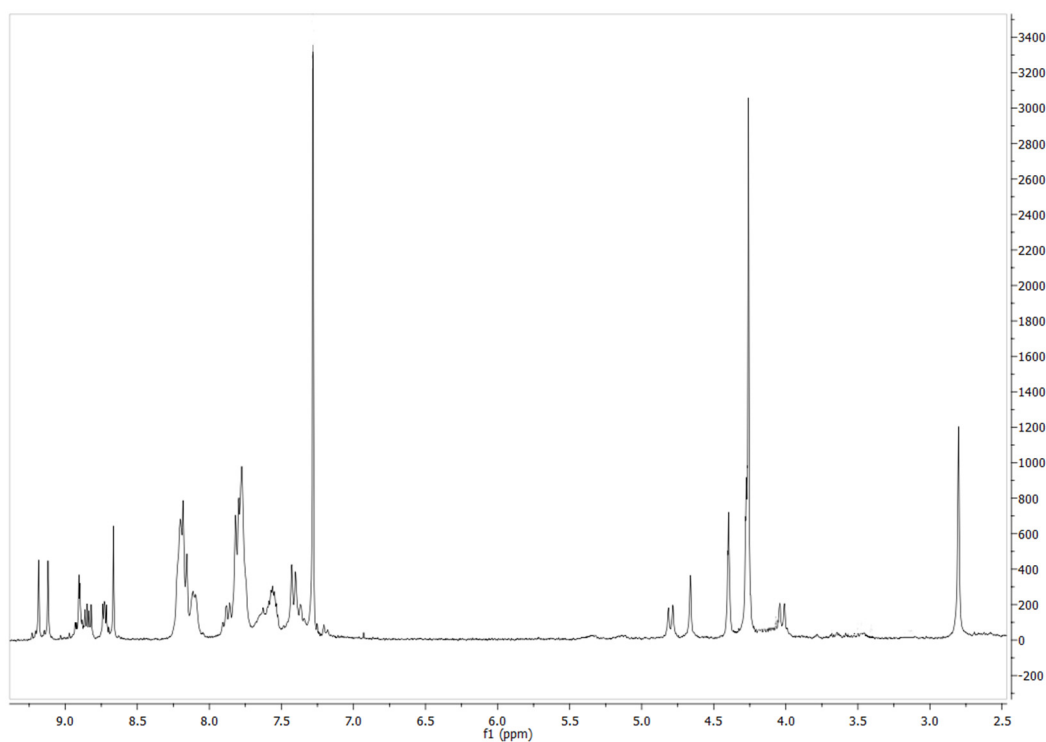


Figure S11. $^1\text{H-NMR}$ spectrum of compound **10a(Zn)-C60** in CDCl_3 at 300 K at 400 MHz. .

MS (MALDI-TOF): m/z : 1041.52 $[\text{M-C60}]^+$

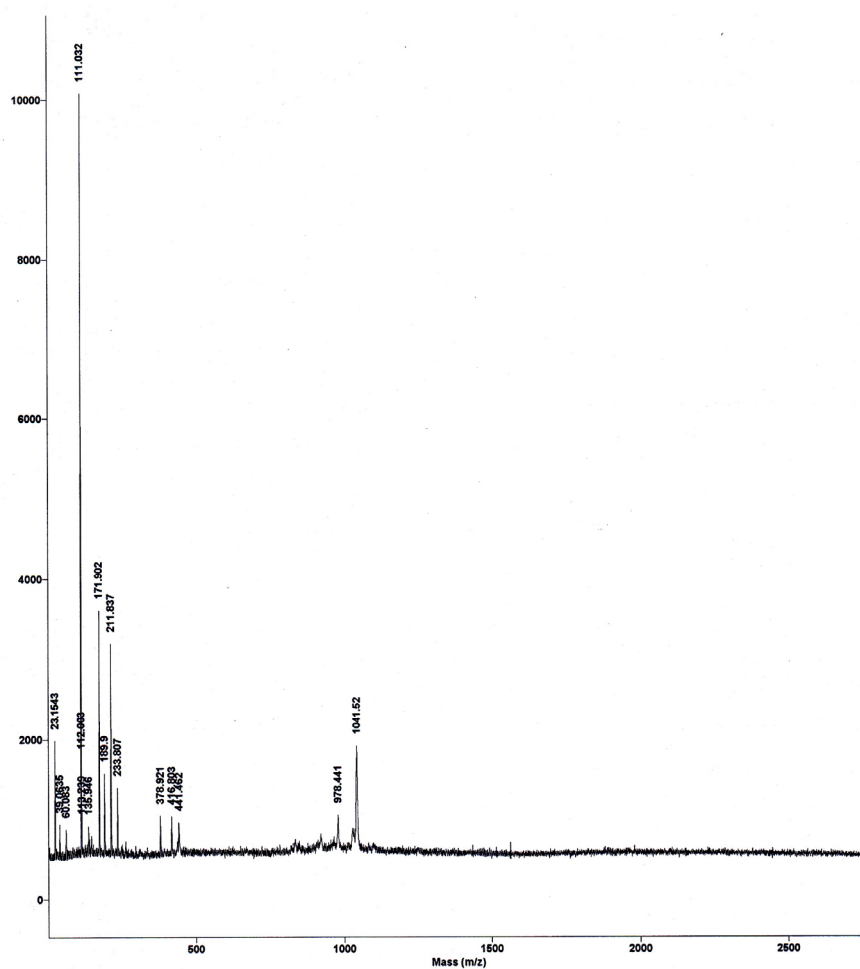
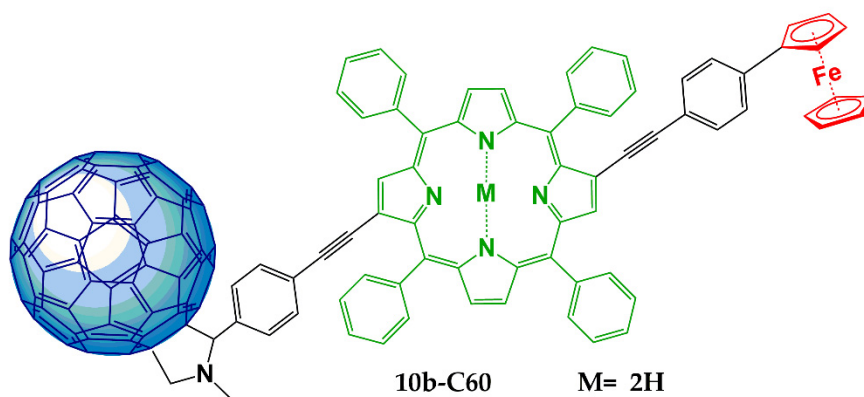


Figure S12. MALDI-TOF MS spectrum of compound **10a-C60** using as matrix gentisic acid.

Elemental Analysis

Anal. Calcd. for $C_{127}H_{45}N_5FeZn$: C, 86.57; H, 2.57; N, 3.97. Found: C, 86.83; H, 2.55; N, 3.99

Compound 10b-C60



^1H -NMR (300 MHz, CDCl_3): δ (ppm) 9.02 (s, 1H), 8.92 (d, 1H, J $\frac{1}{4}$ 1.9 Hz), 8.77 (m, 4H), 8.21 (m, 8H), 7.78 (m, 12H), 7.59 (m, 2H), 7.47 (m, 6H), 4.90 (d, 1H, J $\frac{1}{4}$ 1.3 Hz), 4.81 (s, 1H), 4.70 (s, 2H), 4.38 (s, 2H), 4.14 (d, 1H, J $\frac{1}{4}$ 1.2 Hz), 4.08 (s, 5H), 2.81 (s, 3H), -2.65 (s, 2H).

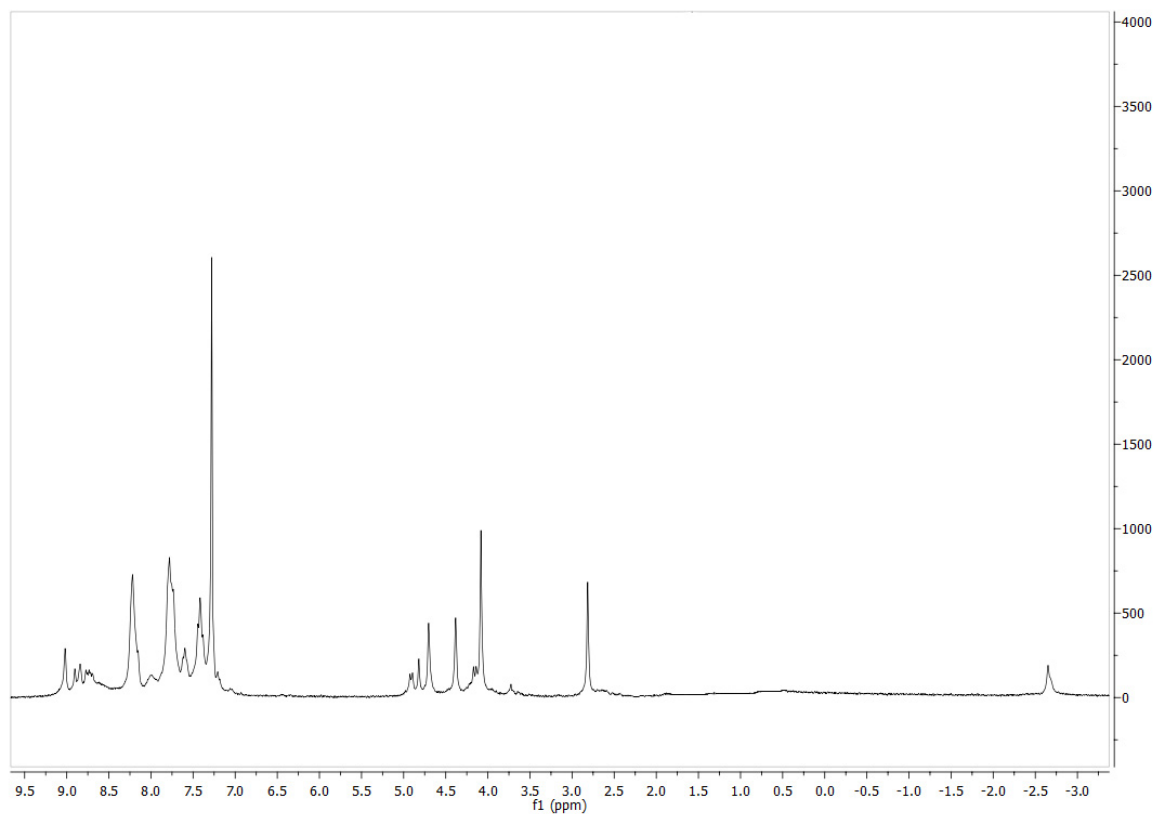


Figure S13. ^1H -NMR spectrum of compound **10b-C60** in CDCl_3 at 300 K at 400 MHz.

MS (MALDI-TOF): m/z : 1775.35 $[\text{M} + \text{H}]^+$, 1055 $[\text{M}-\text{C60}]^+$

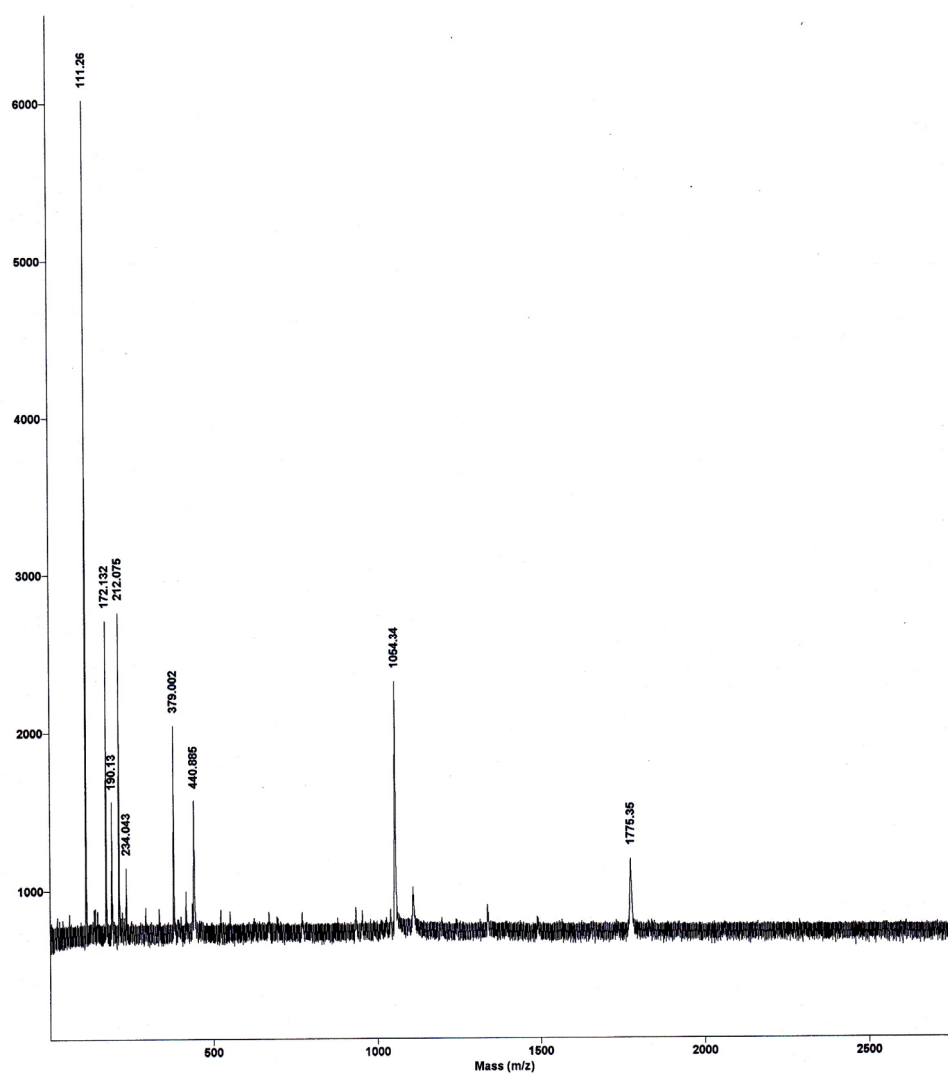
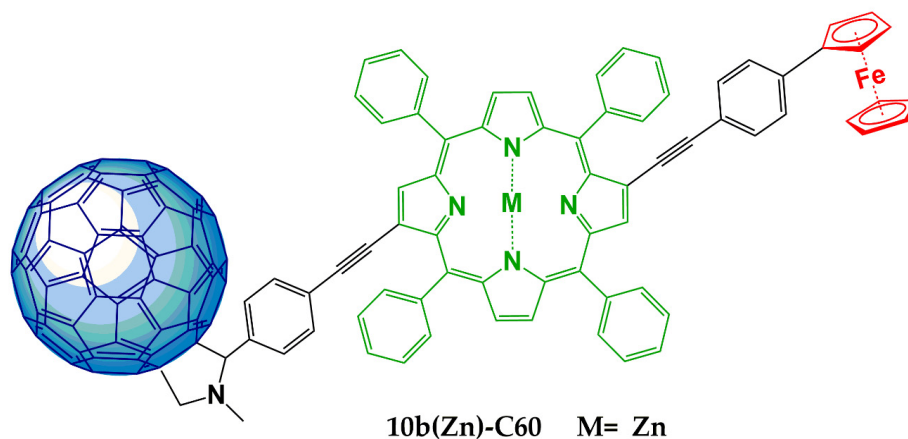


Figure S14. MALDI-TOF MS spectrum of compound **10b-C60** using as matrix gentisic acid.

Elemental Analysis

Anal. Calcd. for $C_{133}H_{51}N_5Fe$: C, 90.01; H, 2.89; N, 3.94. Found: C, 90.28; H, 2.88; N, 3.92.

Compound **10b(Zn)-C60**



$^1\text{H-NMR}$ (300 MHz, CDCl_3): δ (ppm) 9.06 (s, 1H), 9.01 (s, 1H), 8.90 (m, 2H), 8.82 (m, 1H), 8.67 (s, 1H), 8.21 (m, 8H), 7.78 (m, 12H), 7.57 (m, 4H), 7.39 (m, 2H), 7.03 (d, 2H, $J = 6.2$ Hz); 4.84 (d, 1H, $J = 9$ Hz), 4.73 (s, 1H), 4.40 (s, 3H), 4.10 (s, 6H), 4.03 (d, 1H, $J = 9.2$ Hz), 2.77 (s, 3H).

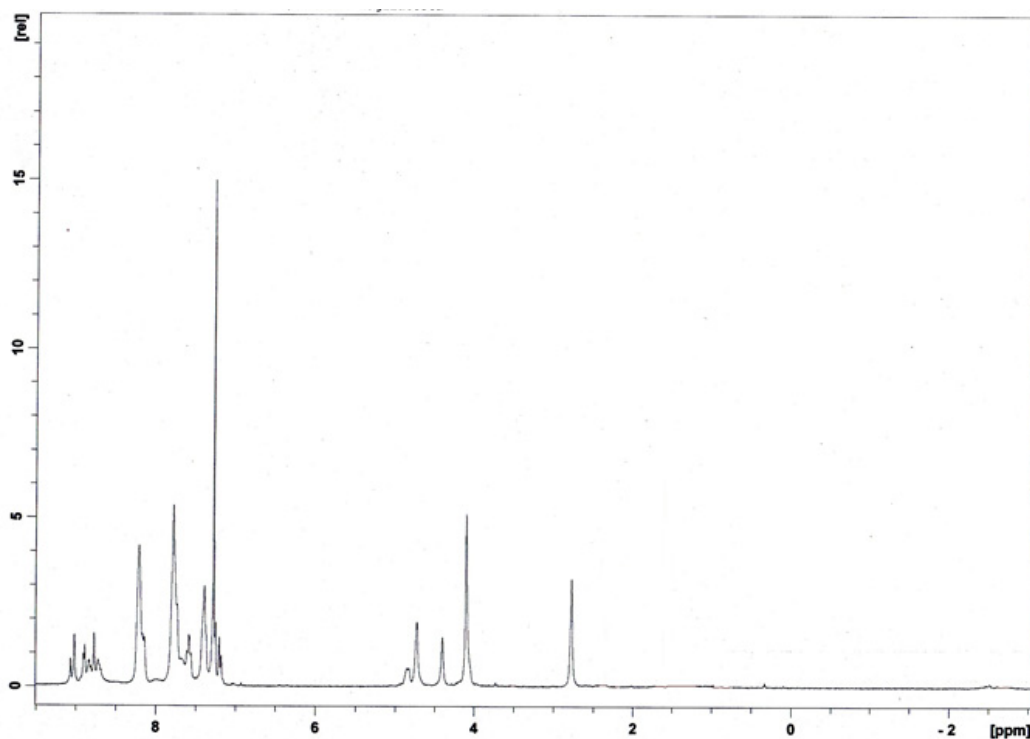


Figure S15. $^1\text{H-NMR}$ spectrum of compound **10b(Zn)-C60** in CDCl_3 at 300 K at 400 MHz.

MS (MALDI-TOF): m/z : 1117.05 $[\text{M-C60}]^+$

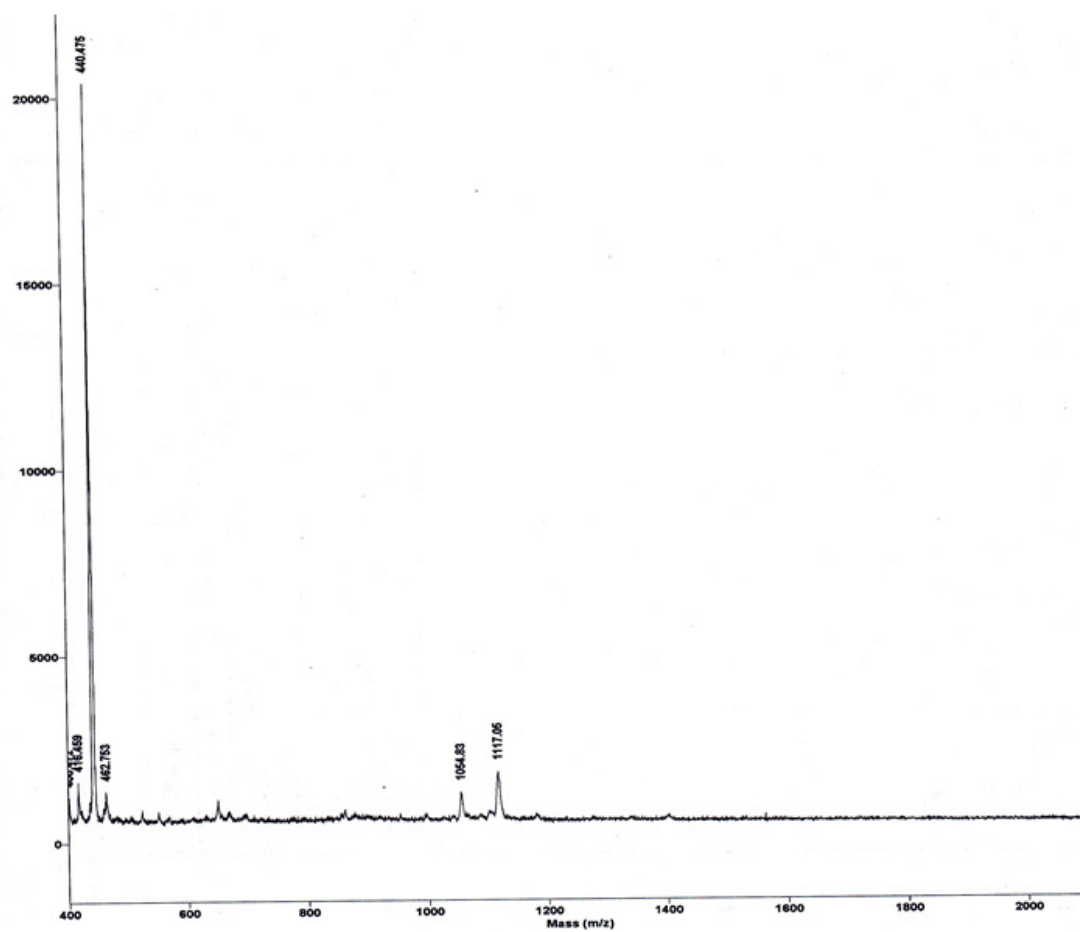


Figure S16. MALDI-TOF MS spectrum of compound **10b(Zn)-C60** using as matrix gentisic acid.

Elemental Analysis

Anal. Calcd. for $C_{133}H_{49}N_5FeZn$: C, 86.90; H, 2.68; N, 3.81. Found: C, 86.64; H, 2.67; N, 3.79.