

Supporting Information

A glycyI-substituted porphyrin as a starting compound for the synthesis of a π - π -stacked porphyrin–fullerene dyad with a frozen geometry

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Experimental

General Remarks: $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra were recorded as CDCl_3 solutions on a Bruker AM-300 and Bruker AM-700 instrument respectively 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. GC mass spectra were recorded on a VG-4 spectrometer equipped with a 30 m Supelco SPB-5 capillary column. UV/vis spectra were recorded on a Varian Cary 50 Scan spectrophotometer in toluene solution. Silica gel 60 (70-230 and 230-400 mesh, Merck) was used for column chromatography. High-purity-grade nitrogen and argon gas were purchased from Rivoira. C_{60} was purchased from Term-USA. All other reagents and solvents were from Fluka Chem. Co., Aldrich Chem. Co. or Carlo Erba and were used as received, except where further specified.

5-(phenyl)-dipyrromethane 1: 1 benzaldehyde (2 grams, 1.88×10^{-2} mol) was dissolved in 32 ml (0.46 mol) of pyrrole. The solution was bubbled with nitrogen for 10 minutes and then trifluoroacetic acid (145 ml, 1.88×10^{-3} mol) was added. The reaction was allowed to proceed, protected from light, under inert atmosphere and vigorous stirring at room temperature for 5 minutes, after that, 15 ml of 0.1 M NaOH water solution was added. The resulting mixture was diluted with 70 ml of ethyl acetate and washed several times with water. The organic phase was separated, dried over anhydrous Na_2SO_4 , filtered and the solvent evaporated under vacuum. The excess of pyrrole was removed under vacuum at 50 °C and the resulting pale yellow oil was purified by silica gel column chromatography eluting with CH_2Cl_2 /ethyl acetate = 4:1 containing 1% in volume of triethylamine. The desired product was obtained as pale yellow crystals in a 50% yield (2.1 grams). MS (GC-MS): m/z : 222 [M^+], 156 [$\text{M}-66$] $^+$, 145 [$\text{M}-77$] $^+$; $^1\text{H-NMR}$ (300 MHz, CDCl_3): δ = 7.96 (br s, 2H, NH protons), 7.37-7.24 (superimposed doublets and triplets, 5H, phenyl protons), 6.73 (br m, 2H, CH α to pyrrole NH), 6.19 (br m, 2H, CH β to pyrrole NH), 5.95 (br m, 2H, CH β to pyrrole NH), 5.51 (s, 1H, CH).

5-(2'-nitrophenyl)-10,15,20-triphenyl-porphyrin 2: 2 2-nitro-benzaldehyde (306 mg, 2.03 mmol), benzaldehyde (272 mg, 2.56 mmol) and 5-phenyl-dipyrromethane (884 mg, 4 mmol) were dissolved in 500 ml of freshly distilled (P_2O_5) dichloromethane. The solution was bubbled with a vigorous stream of argon for 10 minutes then 460 ml of a 1.3 M BF_3 methanol solution was added and the mixture was allowed to react under stirring at room temperature in an argon atmosphere for two hours protected from light. *Para*-chloranile (367 mg, 1.5 mmol) was added and the mixture was refluxed for 1.5 hours. Triethylamine, 1.5 ml were added to quench the reaction and the solvent was evaporated under vacuum. The remaining solid was dissolved in the minimum amount of

dichloromethane and passed through a silica gel plug eluting with dichloromethane in order to remove the oligomer by-products. The resulting mixture of porphyrins was purified by silica gel column chromatography eluting with petroleum ether (40-70°)/CH₂Cl₂ = 3:2. The desired porphyrin was recrystallized from dichloromethane/methanol to give 300 mg of pure purple powder (yield 22%). MS (FAB): m/z: 659 [M⁺]; ¹H-NMR (300 MHz, CDCl₃): δ = 8.86 (br s, 8H, β-pyrrole protons), 8.67 (br d, 1H, protons of nitro-substituted phenyl), 8.45 (br d, 1H, protons of nitro-substituted phenyl), 8.29-8.29 (br m, 5H, phenyl protons), 7.97 (br t, 2H, protons of nitro-substituted phenyl), 7.79 (br s, 10H, phenyl protons), -2.70 (s, 2H, NH protons). UV/vis (CHCl₃): λ_{max} (nm) = 420, 517, 551, 590, 648.

5-(2'-aminophenyl)-10,15,20-triphenyl-porphyrin 3:² porphyrin **2** (75 mg, 1.14×10⁻⁴ mol) was dissolved in 16 ml of 1,4-dioxane and then SnCl₂·2H₂O (308 mg, 1.36×10⁻³ mol) and 26 ml of concentrated (37%) HCl were added. The mixture was immersed in a preheated oil bath and allowed to react at 70 °C under argon for 1 hour protected from light. After that the acidic solution was neutralized by adding concentrated ammonia solution, the product was extracted with 2×70 ml portions of ethyl acetate. The organic fractions were combined and washed with water, dried over anhydrous Na₂SO₄, filtered and the solvent was evaporated under vacuum. The desired product was purified through silica gel column chromatography eluting with CHCl₃/petroleum ether (40-70°) = 3:2. The desired porphyrin was recrystallized from dichloromethane/methanol giving 58 mg of purple powder (yield 80%). MS (FAB): m/z: 631 [M+2H]⁺; ¹H-NMR (300 MHz, CDCl₃): δ = 8.95 (d, J = 4.53 Hz, 2H, β-pyrrole protons), 8.91-8.89 (d plus s, 6H, β-pyrrole protons), 8.27 (m, 5H, phenyl protons), 7.93 (d, J = 7.55 Hz, 1H δ to amino group of substituted phenyl), 7.80 (m, 10H, phenyl protons), 7.63 (t, J = 7.55 Hz, 1H γ to amino group of substituted phenyl), 7.21 (t, J = 7.55 Hz, 1H β to amino group of substituted phenyl), 7.13 (d, J = 7.55 Hz, 1H α to amino group of substituted phenyl), -2.68 (s, 2H, NH of tetrapyrrole ring). UV/vis (CHCl₃): λ_{max} (nm) = 419, 515, 550, 589, 646.

5-(2'-ethoxycarbonylmethylamino-phenyl)-10,15,20-triphenylporphyrin 4: The aminoporphyrin **3** (50 mg, 7.9×10⁻⁵ mol) was dissolved in 3 ml of anhydrous DMF and an excess of anhydrous K₂CO₃ was added. The reaction mixture was heated at 80 °C under argon and a solution of 20 mg (9.3×10⁻⁵ mol) of ethyliodoacetate in 2 ml of anhydrous DMF was added dropwise in 1 h. After that the reaction was allowed to proceed for further 12 h and then cooled to room temperature. 60 ml of CHCl₃ were added and the organic phase was washed several times with water (6×40 ml), dried over anhydrous Na₂SO₄, filtered and the solvent was evaporated under vacuum. The desired porphyrin **4** was purified by silica gel column chromatography eluting with CHCl₃/petroleum ether (40-70°) = 1:1 and recrystallized from dichloromethane/methanol giving 32 mg of reddish-purple

powder (yield 56%). MS (FAB): m/z : 715 [M^+]; $^1\text{H-NMR}$ (300 MHz, CDCl_3): δ = 9.00 (d, J = 4.53 Hz, 2H β -pyrrole protons), 8.96-8.94 (d plus s, 6H β -pyrrole protons), 8.30 (br m, 5H phenyl protons), 7.94 (d, J = 7.55 Hz, 1H δ to amino group of substituted phenyl), 7.82 (br m, 10H, phenyl protons), 7.74 (t, J = 7.55 Hz, 1H γ to amino group of substituted phenyl), 7.24 (t, J = 7.55 Hz, 1H β to amino group of substituted phenyl), 7.02 (d, J = 7.55 Hz, 1H α to amino group of substituted phenyl), 4.03 (q, J = 6.80 Hz, 2H, CH_2 of ethyl chain), 3.84 (d, J = 4.53 Hz, 2H, CH_2 α to carboxylic group), 1.11 (t, J = 6.80 Hz, 3H, CH_3 of ethyl chain), -2.60 (s, 2H, NH of tetrapyrrole ring). UV/vis (CHCl_3): λ_{max} (nm) = 419, 516, 550, 588, 648.

5-(2'-carboxymethylamino-phenyl)-10,15,20-triphenylporphyrin 5: porphyrin **4** (26 mg, 3.6×10^{-5} mol) was dissolved in 15 ml of THF and a solution of 75 mg of KOH in 5 ml of water was added dropwise. The mixture was left under argon at room temperature for 4 h, after that was neutralized by adding a diluted hydrochloric acid solution and the organic solution was separated and washed with brine. The organic phase was dried over anhydrous Na_2SO_4 , filtered and the solvent was evaporated under vacuum. The desired product was recrystallized from dichloromethane/hexane affording 24 mg of purple powder (yield 97%). MS (FAB): m/z : 688 [$M+H^+$]; $^1\text{H-NMR}$ (300 MHz, CDCl_3): δ = due to internal acid-base equilibria between the carboxylic group and porphyrin NH protons the signals in the spectrum are completely broadened. UV/vis (Toluene): λ_{max} (nm) = 420, 514, 549, 591, 646.

Dyad 6: glycyI-porphyrin **5** (20 mg, 2.9×10^{-5} mol) and [60]fullerene (42 mg, 5.8×10^{-5} mol) were dissolved in 45 ml of anhydrous toluene. The mixture was stirred under argon until complete dissolution of porphyrin and fullerene. A three-fold excess of benzaldehyde was then added (10 mg, 9.4×10^{-5} mol) and the solution was refluxed under argon for 24 h. After that, the mixture was cooled to room temperature and the solvent evaporated under vacuum. The product was directly purified through silica gel column chromatography eluting with toluene/petroleum ether (40-70°) = 30:70 in order to recover the unreacted fullerene, then with toluene/petroleum ether (40-70°) = 45:55 to recover the dyad **6**. The unreacted porphyrin **5** was recovered by $\text{CH}_3\text{OH}/\text{CHCl}_3$ = 15:85 eluant mixture. The desired compound was obtained in 12% yield (5 mg). MS (FAB): m/z : 1452 [$M+H^+$], 731 [$M-720^+$]; $^1\text{H-NMR}$ (300 MHz, CDCl_3): δ = 9.20-8.97 (series of broadened doublets and multiplets, 8H, β -pyrrole protons), 8.30-7.91 (br m, 5H, phenyl protons), 7.75 (br s, 10H, phenyl protons), 7.47 (br d, 2H, phenyl of pyrrolidine), 7.36 (br m, 3H, phenyl of pyrrolidine), 5.48 (s, 1H, CH of pyrrolidine ring), 3.79 (d, J = 9.82 Hz, 1H of methylene group of pyrrolidine), 3.40 (d, J = 9.82 Hz, 1H of methylene group of pyrrolidine), -2.65 (s, 2H, NH of tetrapyrrole ring). UV/vis (Toluene): λ_{max} (nm) (ϵ $\text{M}^{-1}\text{cm}^{-1}$) = 309 (59100), 331 (58000), 428 (265000), 519 (16000), 553 (7700), 595 (5300), 651 (2800). ^{13}C NMR (700 MHz): δ = 67.19, 68.03, 75.92, 117.92, 120.07,

121.07, 121.33, 123.45, 124.02, 127.35, 128.30, 128.74, 129.04, 130.33, 130.60, 133.16, 134.97, 135.28, 135.43, 135.58, 135.96, 136.48, 137.34, 138.75, 139.31, 139.70, 139.87, 140.61, 140.88, 141.04, 141.24, 141.39, 141.43, 141.61, 141.83, 141.90, 141.99, 142.04, 142.17, 142.41, 142.48, 142.55, 142.60, 142.69, 142.79, 142.85, 143.48, 143.67, 144.18, 144.29, 144.37, 144.60, 145.04, 145.22, 145.27, 145.45, 145.58, 145.70, 146.03, 146.14, 146.26, 147.04, 147.28, 147.51, 149.51, 152.21, 152.57.

***N*-methyl-2-phenyl-3,4-fulleropyrrolidine 7:** ³ [60]fullerene (30 mg, 4.2×10⁻⁵ mol) and benzaldehyde (4 mg, 3.8×10⁻⁵ mol) were dissolved in 25 ml of anhydrous toluene, then *N*-methylglycine (37 mg, 4.2×10⁻⁴ mol) was added and the reaction mixture was refluxed under argon for 12 h. After that, the reaction was cooled to room temperature and the solvent was evaporated under vacuum. The product was purified through silica gel column chromatography eluting with toluene/petroleum ether (40-70°) = 30:70 to recover the excess of fullerene and then with toluene/petroleum ether (40-70°) = 1:1 obtaining 10 mg of the desired product as brown reddish powder (yield 31%). ¹H-NMR (300 MHz, CDCl₃): δ = 7.82 (d, J = 6.80 Hz, 1H, phenyl protons), 7.45 (t, J = 8.31 Hz, 1H, phenyl protons), 7.36 (d, J = 7.55 Hz, 1H, phenyl protons), 7.19 (d, J = 7.55 Hz, 1H, phenyl protons), 5.02 (d, J = 9.06 Hz, 1H, CH₂ of pyrrolidine), 4.96 (s, 1H, CH of pyrrolidine), 4.29 (d, J = 9.06 Hz, 1H, CH₂ of pyrrolidine), 2.84 (s, 3H, N-CH₃ of pyrrolidine). UV/vis (Toluene): λ_{max} (nm) (ε M⁻¹cm⁻¹) = 328 (35800). ¹³C NMR (700 MHz): δ = 40.73, 69.78, 70.76, 84.33, 126.00, 128.92, 129.19, 129.35, 129.73, 130.07, 136.43, 136.55, 137.24, 137.50, 137.67, 140.15, 140.55, 140.85, 140.88, 142.22, 142.39, 142.53, 142.64, 142.69, 142.74, 142.78, 142.81, 142.84, 142.86, 142.95, 142.97, 143.25, 143.26, 143.39, 143.69, 143.85, 145.08, 145.10, 145.30, 145.41, 145.86, 145.92, 145.97, 146.02, 146.04, 146.18, 146.24, 146.48, 146.63, 146.65, 146.80, 146.84, 146.87, 146.91, 146.97, 147.01, 147.19, 147.48, 148.00, 154.12, 154.80, 156.98.

¹H-NMR Spectra

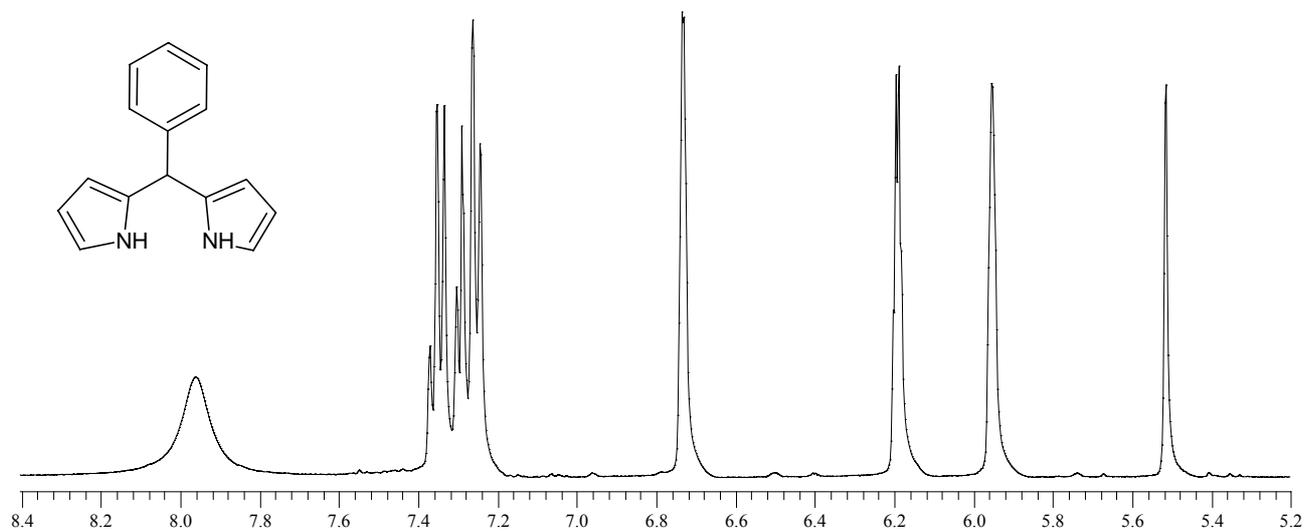


Figure S1. ¹H-NMR spectrum of 5-phenyl-dipyrromethane in CDCl₃ solution.

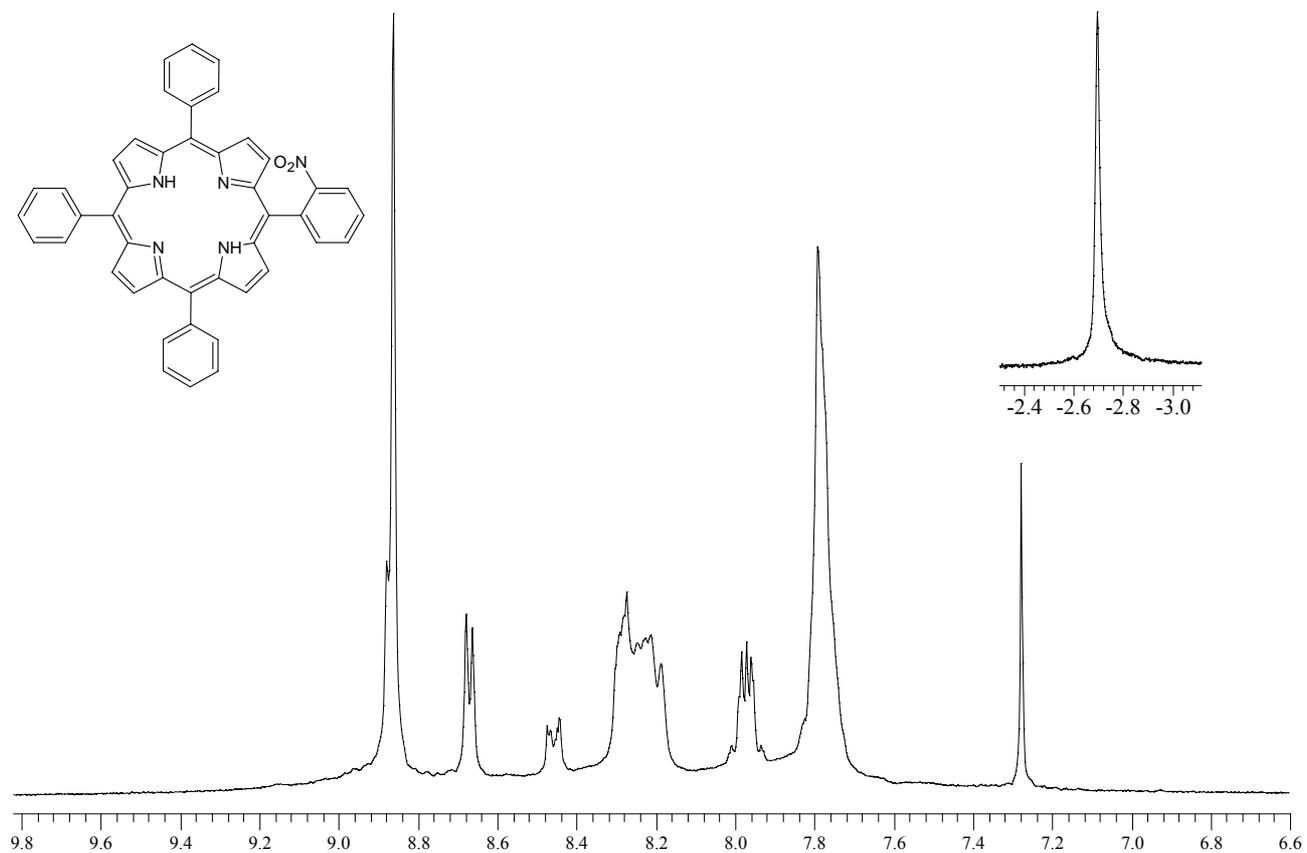


Figure S2. ¹H-NMR spectrum of 5-(2'-nitrophenyl)-10,15,20-triphenylporphyrin in CDCl₃ solution. The NH protons are reported in the inset.

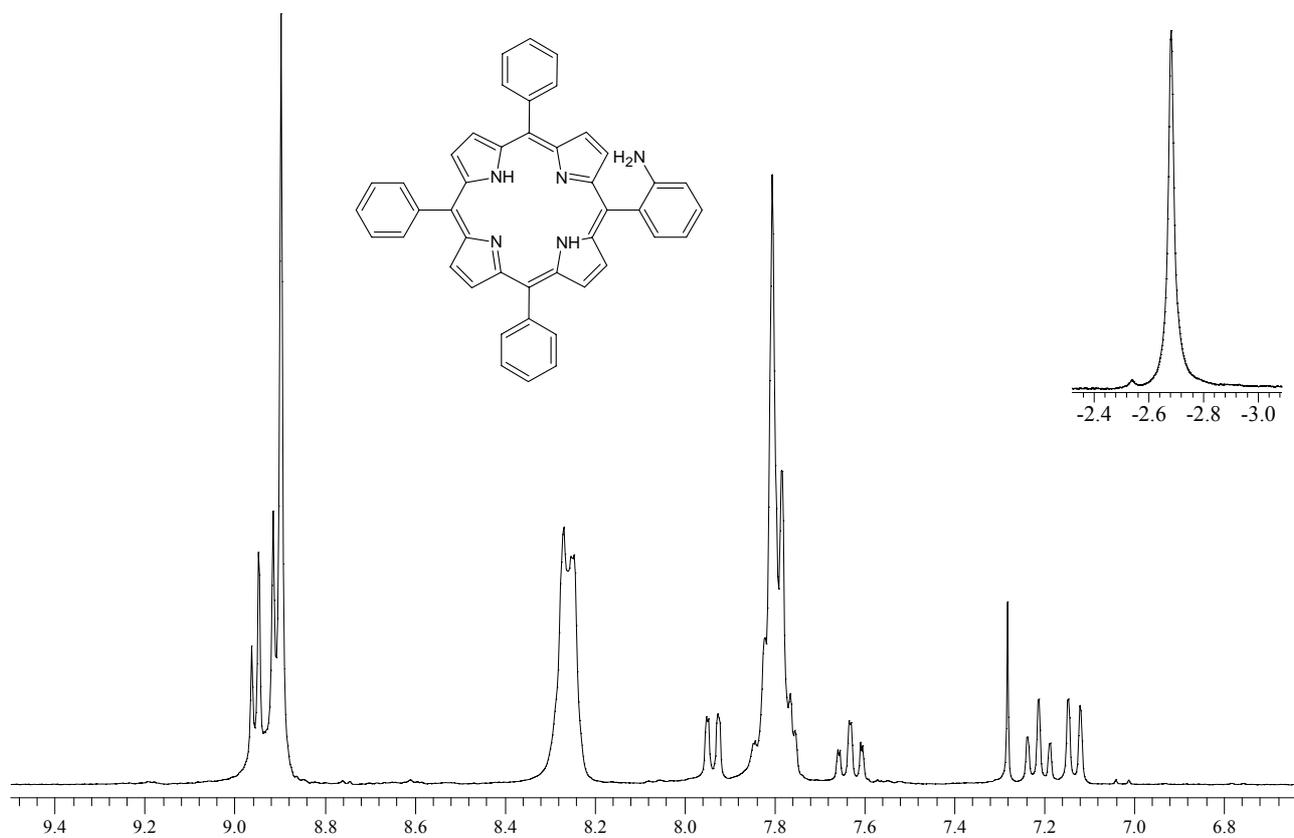


Figure S3. ¹H-NMR spectrum of 5-(2'-aminophenyl)-10,15,20-triphenylporphyrin in CDCl₃ solution. The NH protons are reported in the inset.

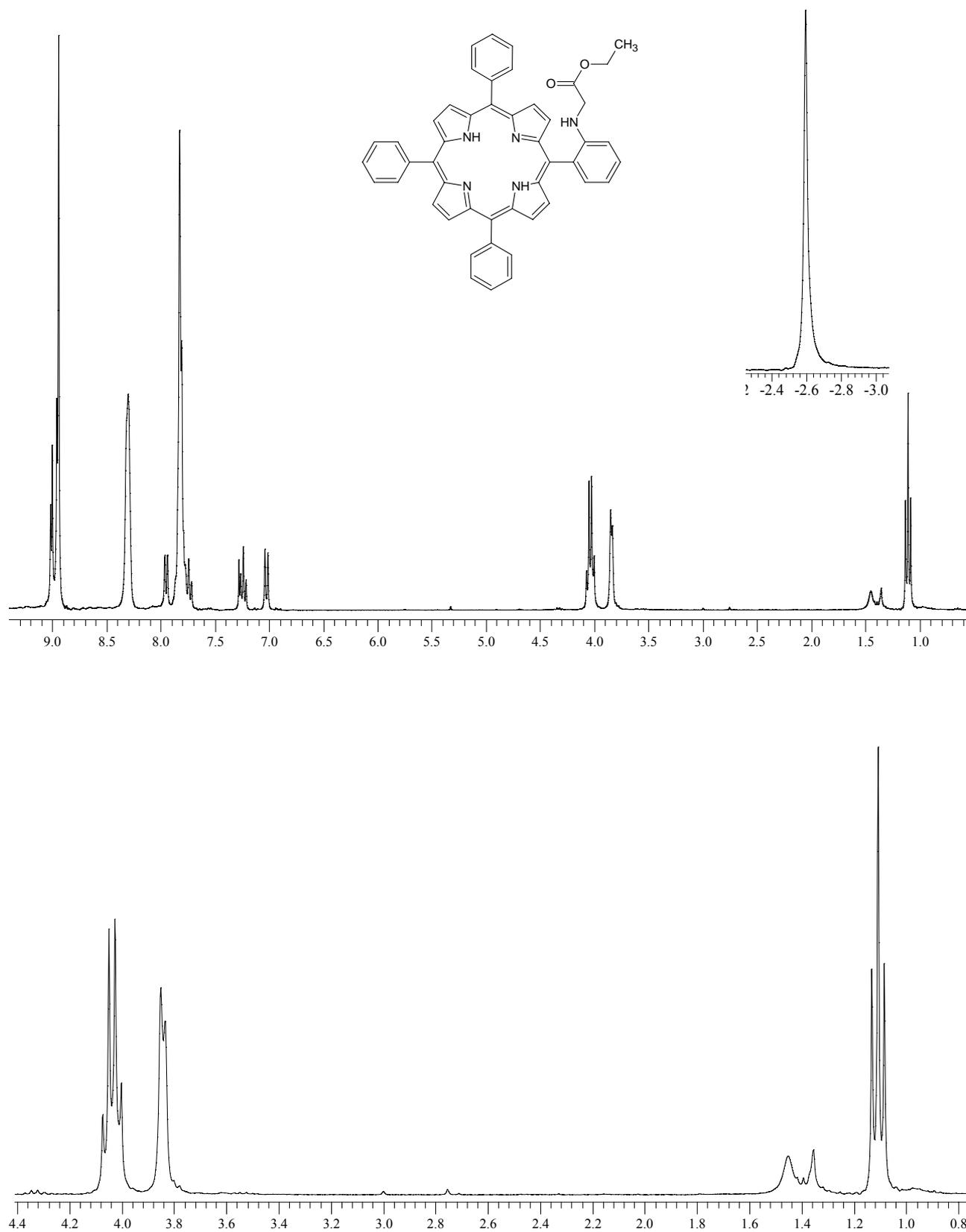


Figure S4. ¹H-NMR spectrum of 5-(2'-ethoxycarbonylmethylaminophenyl)-10,15,20-triphenylporphyrin in CDCl₃ solution (upper part) and magnification (lower part). The NH protons are reported in the inset.

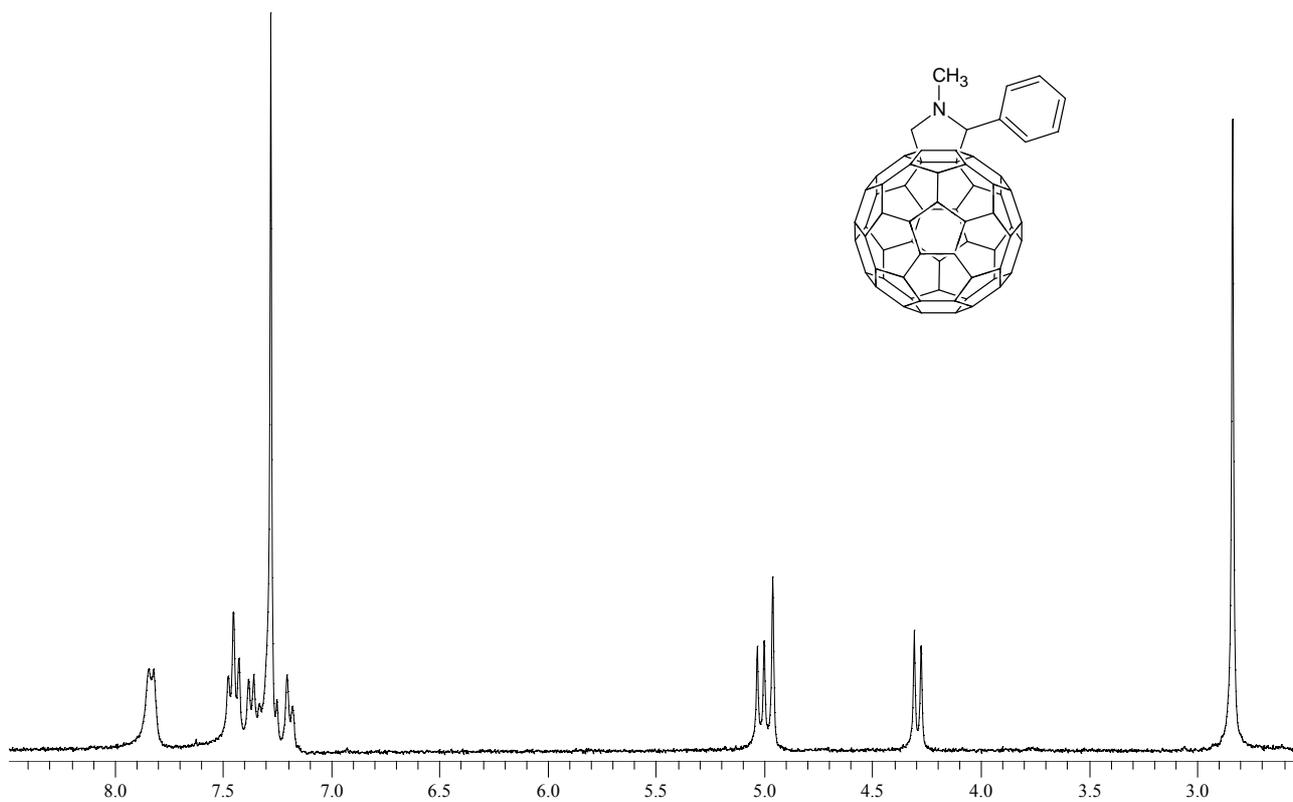


Figure S5. ¹H-NMR spectrum of N-methyl-2-phenyl-3,4-fulleropyrrolidine in CDCl₃ solution.

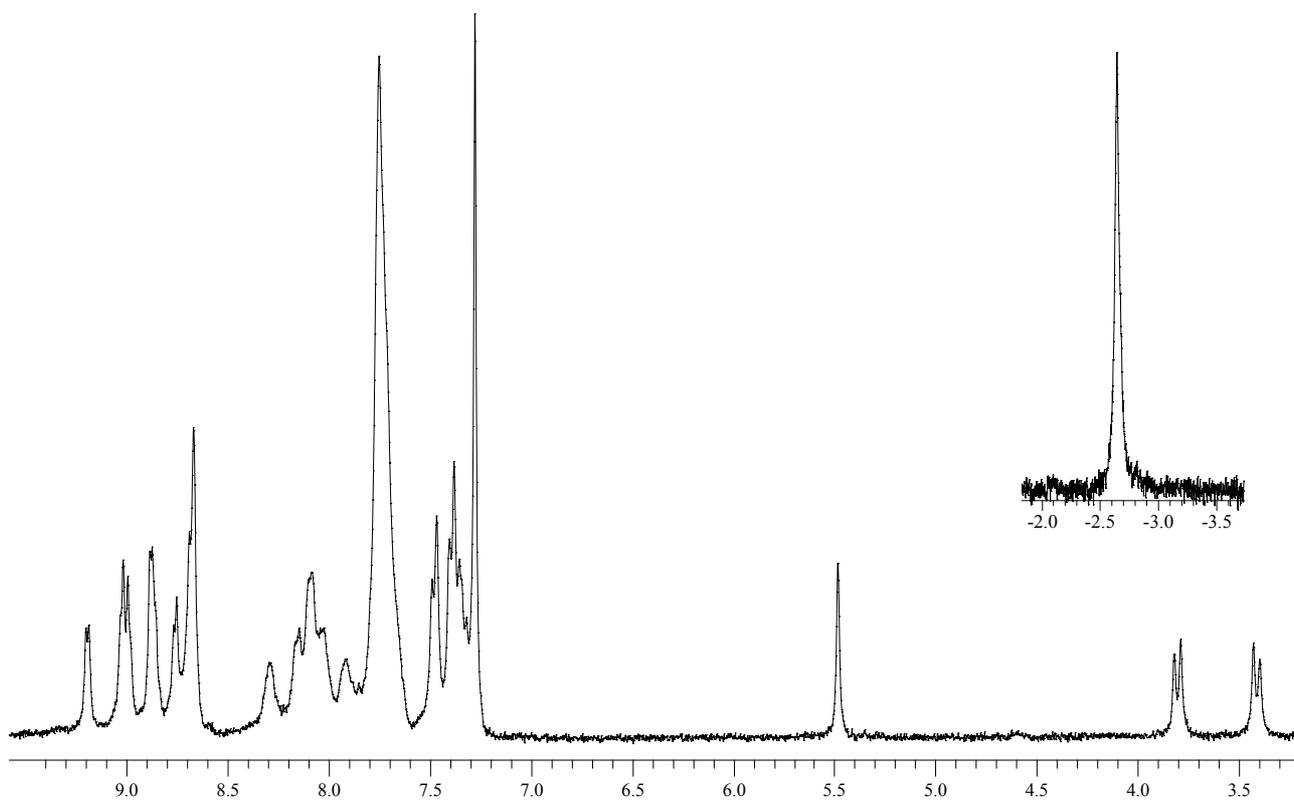
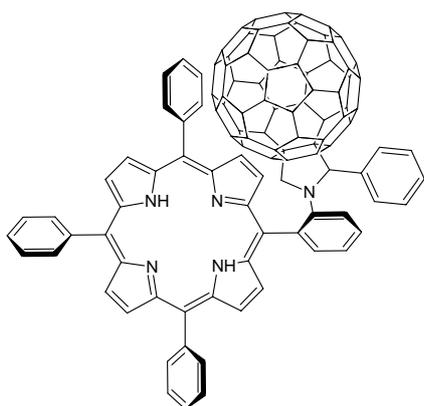


Figure S6. $^1\text{H-NMR}$ spectrum of porphyrin-fullerene dyad **6** in CDCl_3 solution. The NH protons are reported in the inset.

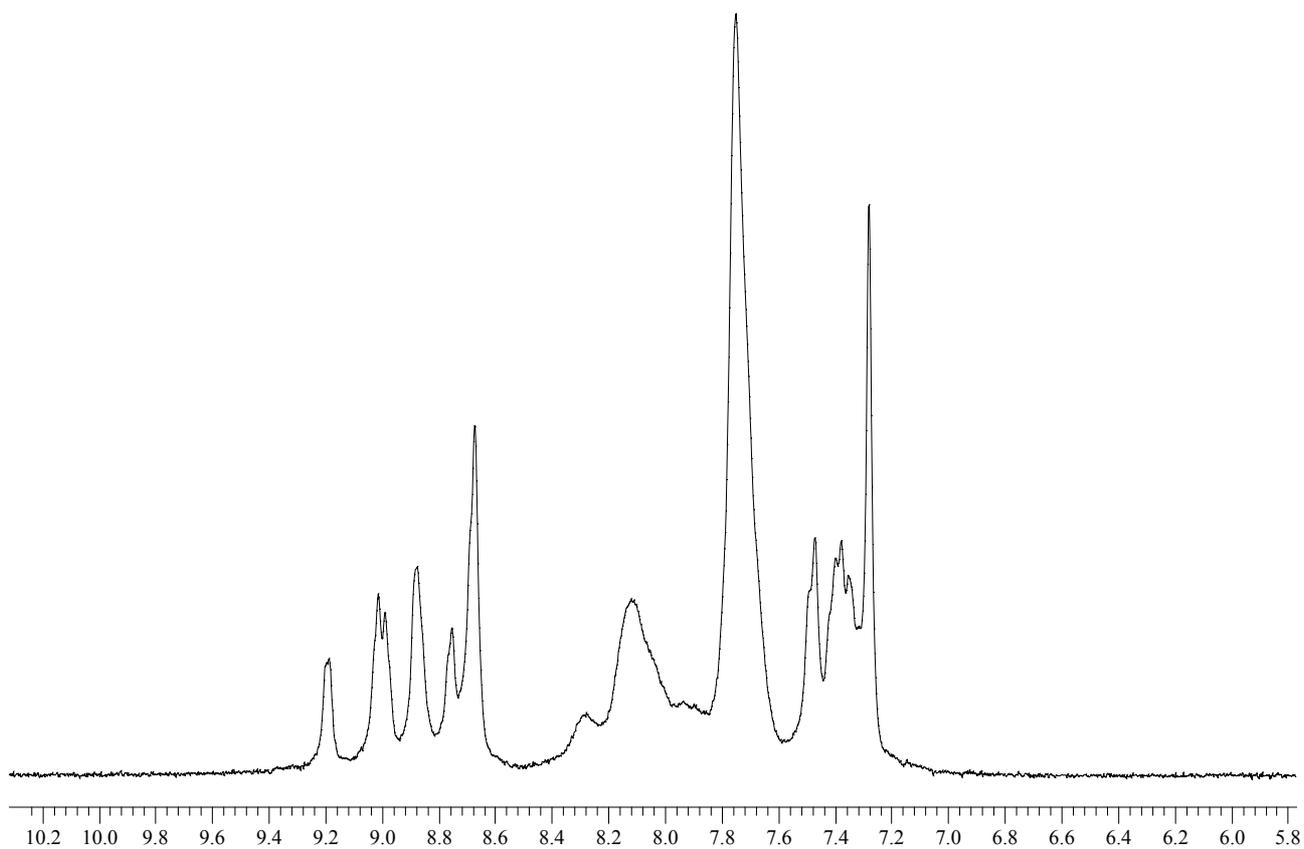


Figure S7. ^1H -NMR spectrum of porphyrin-fullerene dyad **6** in CDCl_3 solution recorded at $45\text{ }^\circ\text{C}$ (Aromatic expansion). Broadened signals are clearly visible respect to the same spectrum recorded at $25\text{ }^\circ\text{C}$ (Figure S6).

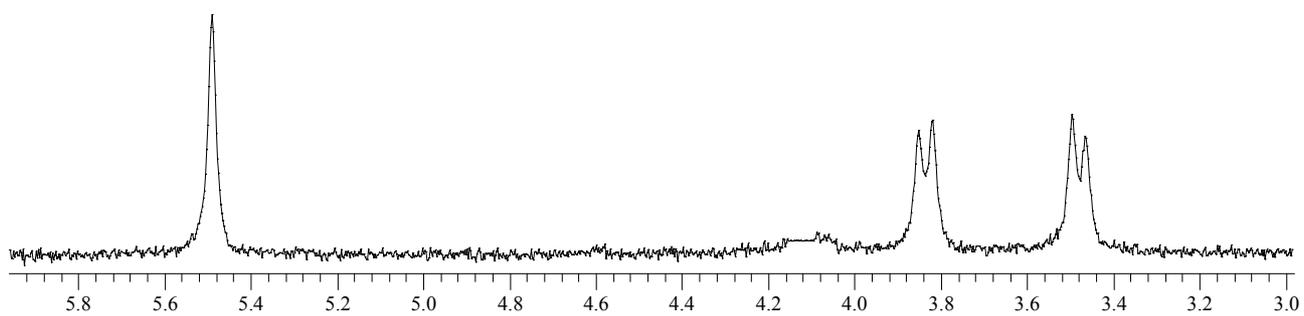


Figure S8. ^1H -NMR spectrum of porphyrin-fullerene dyad **6** in CDCl_3 solution recorded at $45\text{ }^\circ\text{C}$ (Pyrrolidine protons).

FAB and GC Mass Spectra

Scan # : 1742
Mass Peak # : 31 Ret. Time : 18.508
Base Peak : 145.25 (807107)

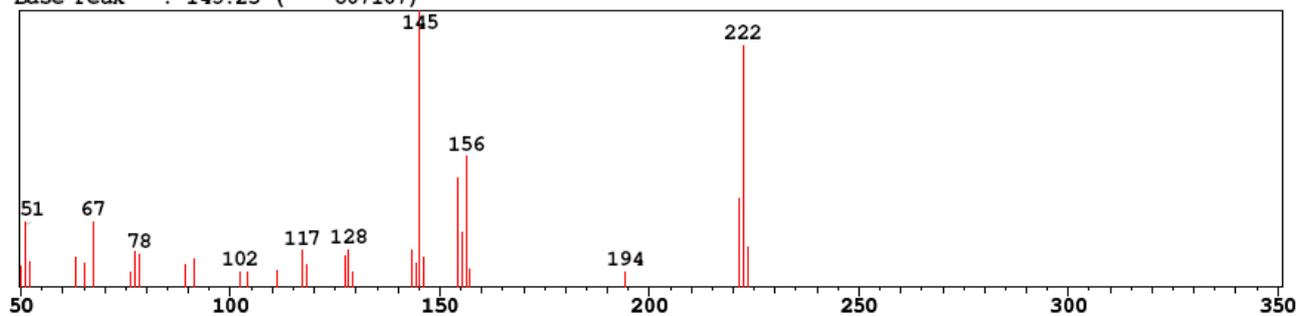


Figure S9. GC-MS spectrum of 5-phenyl-dipyrromethane.

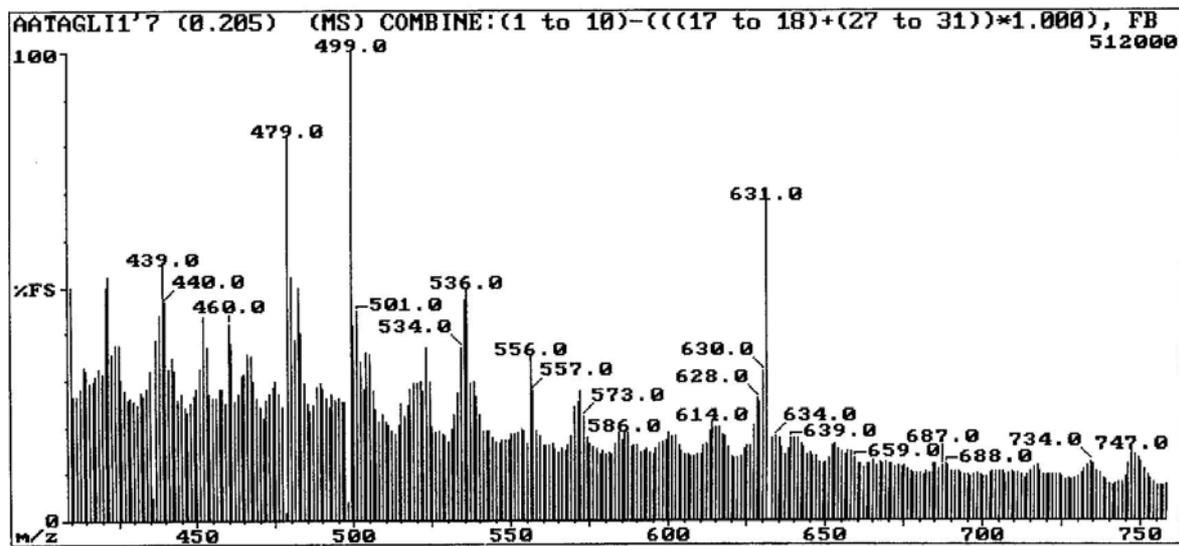


Figure S10. FAB-MS spectrum of 5-(2'-aminophenyl)-10,15,20-triphenylporphyrin.

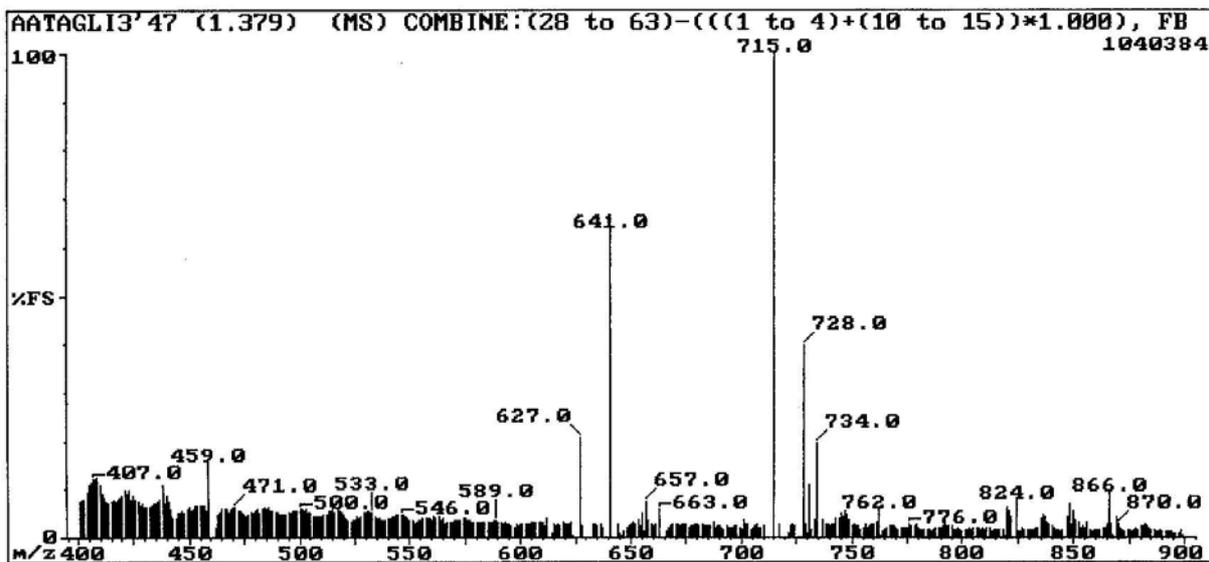


Figure S11. FAB-MS spectrum of 5-(2'-ethoxycarbonylmethylaminophenyl)-10,15,20-triphenylporphyrin.

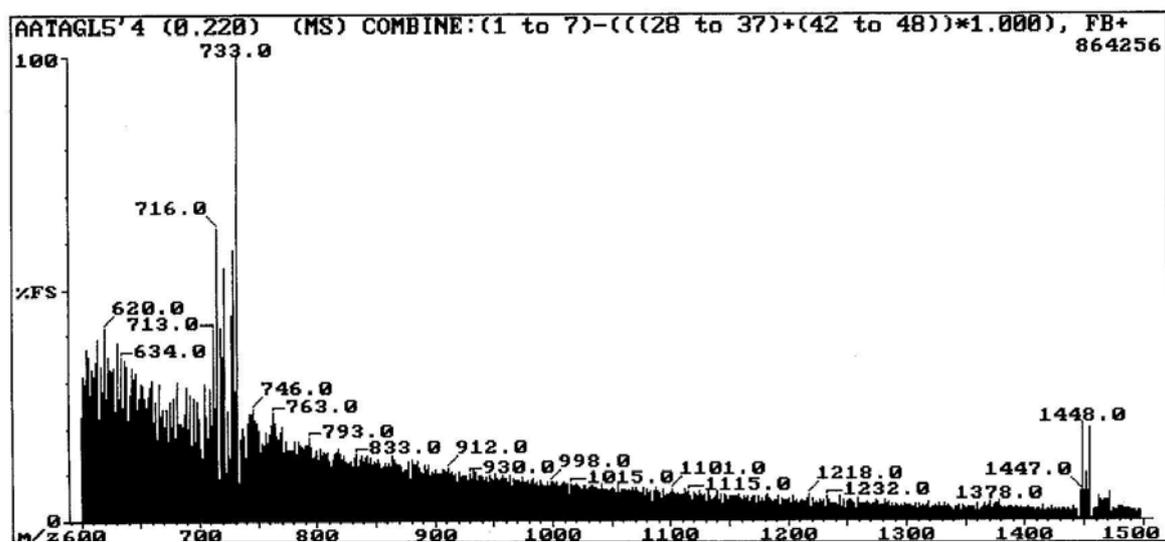


Figure S12. FAB-MS spectrum of porphyrin-fullerene dyad 6.

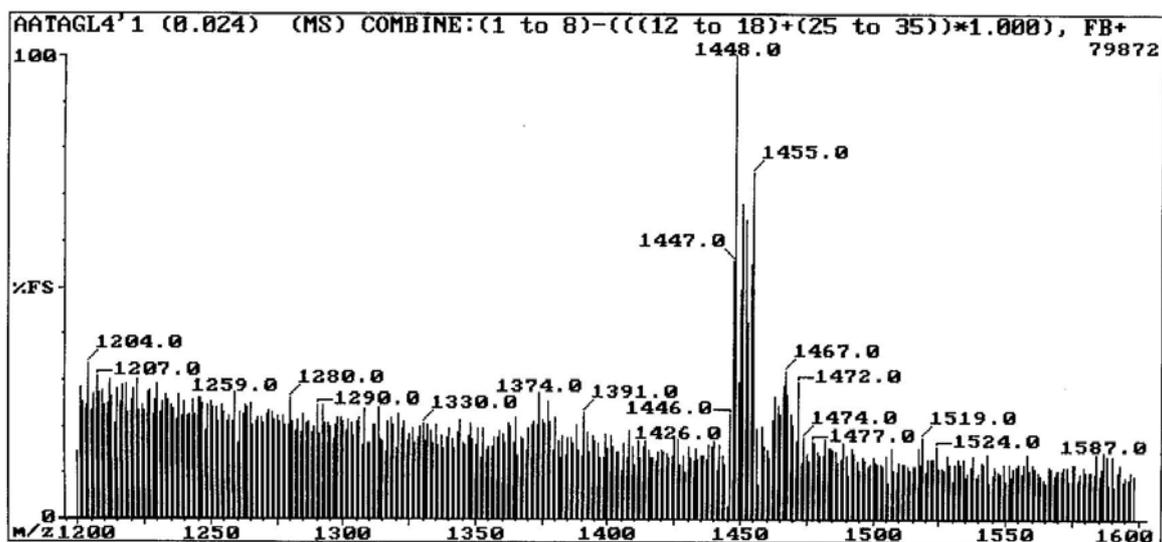


Figure S13. FAB-MS spectrum of porphyrin-fullerene dyad 6 molecular peak.

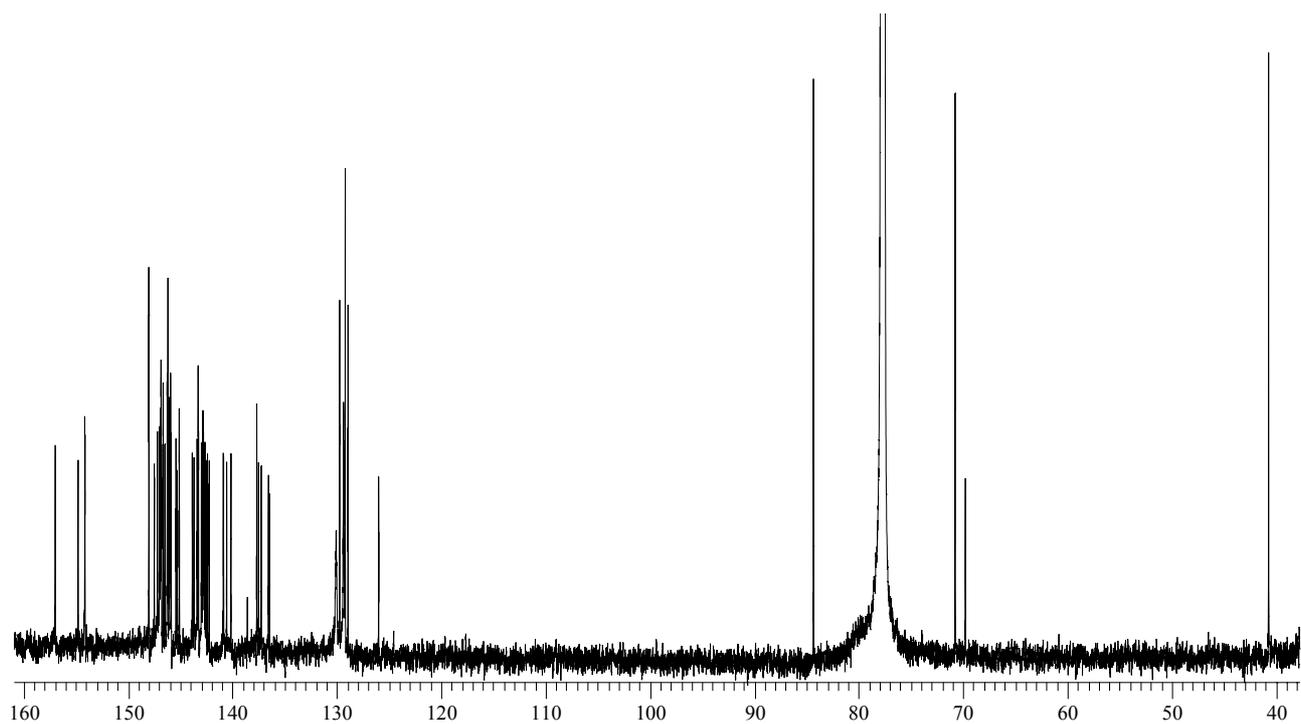


Figure S12. ^{13}C spectrum of reference compound 7 in deuteriochloroform solution.

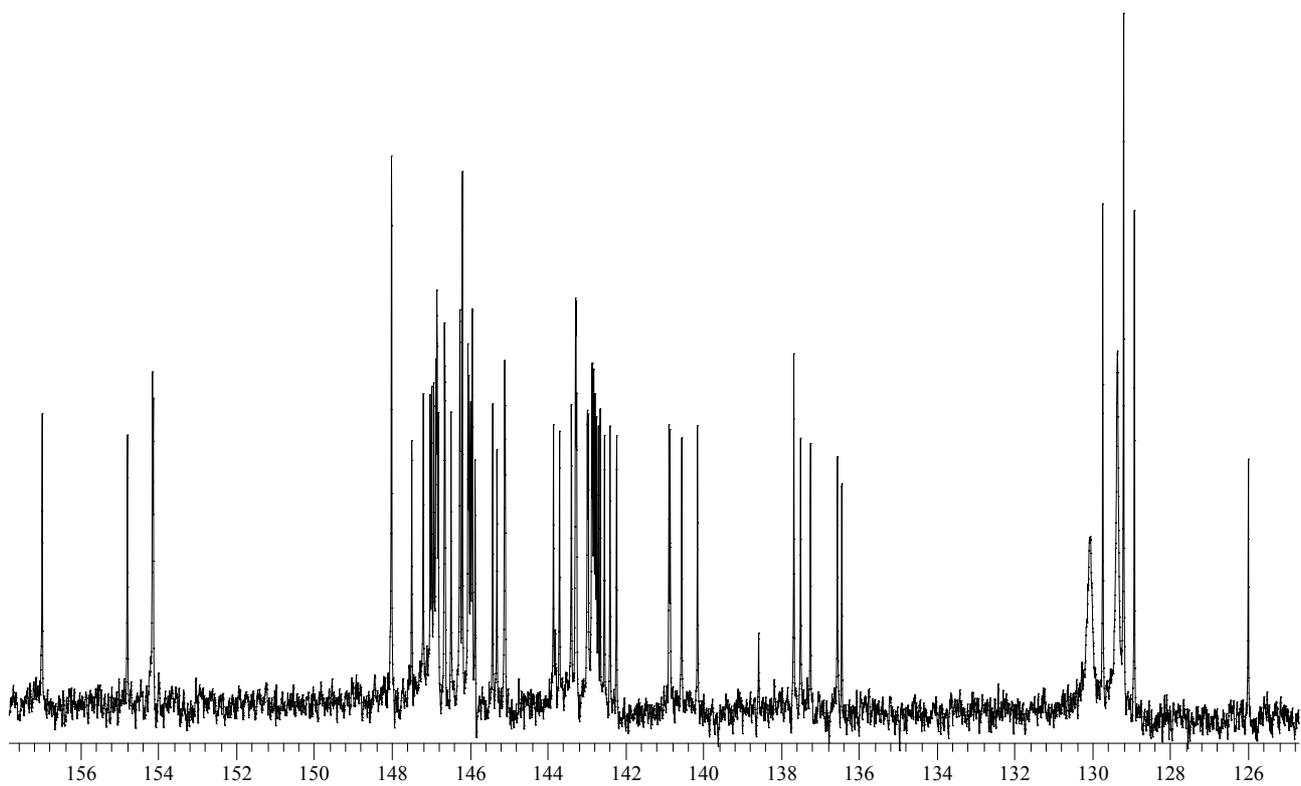


Figure S13. ^{13}C spectrum of reference compound 7, aromatic expansion.

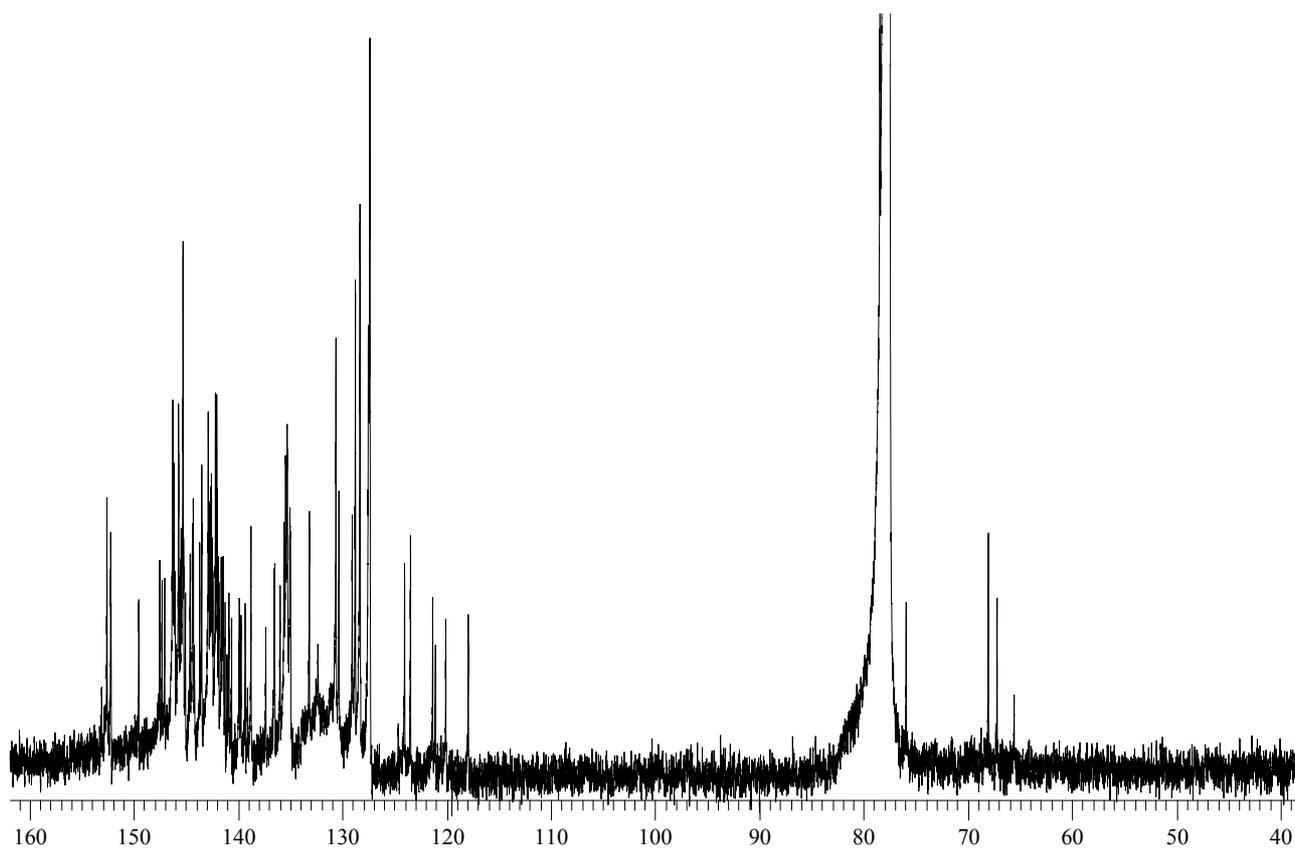


Figure S14. ^{13}C spectrum of porphyrin-fullerene dyad **6** in deuteriochloroform solution.

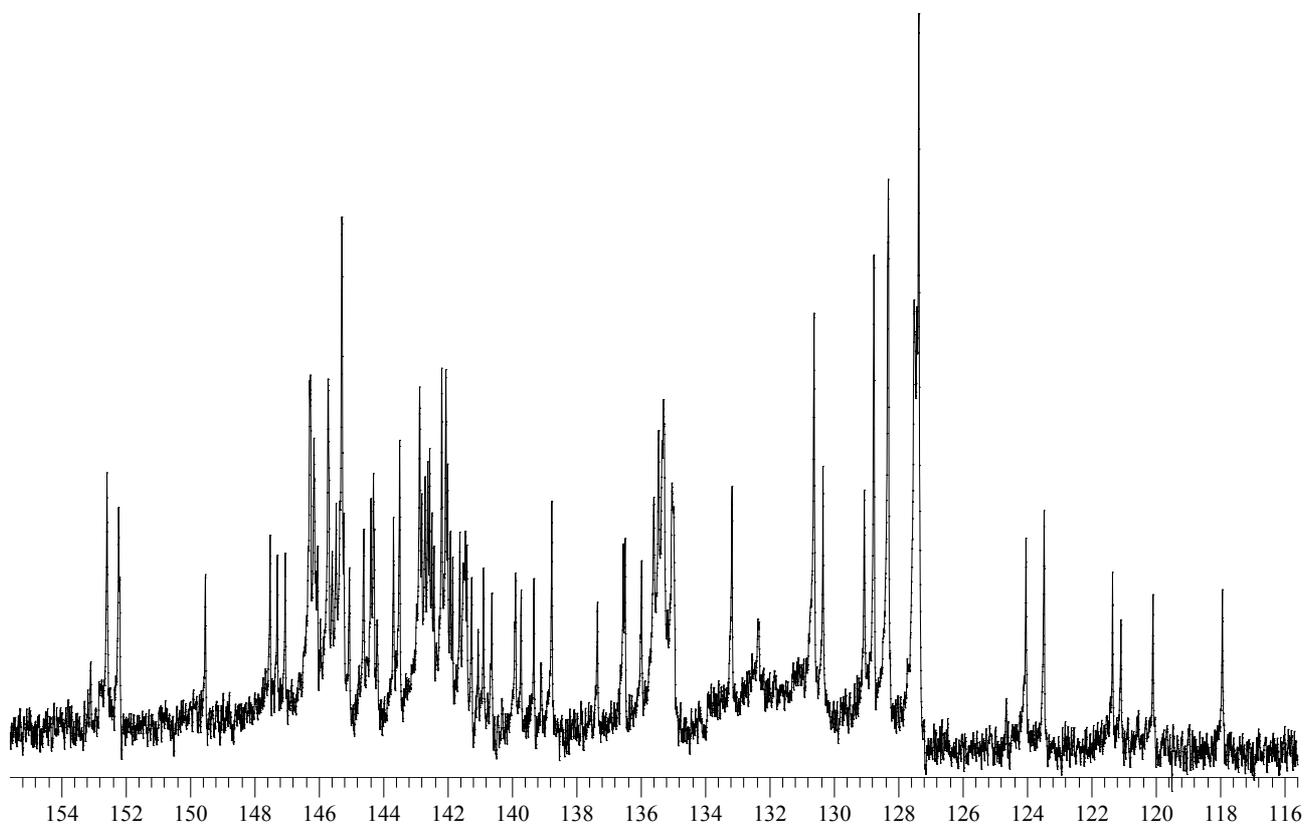


Figure S15. ^{13}C spectrum of porphyrin-fullerene dyad **6**, aromatic expansion.

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2 a) M. Gardner, A. J. Guerin, C. A. Hunter, U. Michelsen, C. Rotger *New. J. Chem.* 1999, **23**, 309 b) R. W. Wagner, T. E. Johnson, J. S. Lindsey *J. Am. Chem. Soc.* 1996, *118*, 11166-11180; c) W.-S. Cho, H.-J. Kim, B. J. Littler, M. A. Miller, C.-H. Lee, J. S. Lindsey *J. Org. Chem.* 1999, **64**, 7890; d) P. D. Rao, S. Dhanalekshmi, B. J. Littler, J. S. Lindsey *J. Org. Chem.* 2000, **65**, 7323.

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