Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supplementary Information

Lu(III) bis-phthalocyanines containing carbazole moieties: Synthesis, characterization, electrochemical properties and sensor applications

Hidayet Sarıoğulları, İbrahim F. Sengul, Ayşe Gül Gürek*

Gebze Technical University, Department of Chemistry, 41400 Gebze, Kocaeli-TURKEY

Corresponding Author:

Ayşe Gül Gürek, E-mail :gurek@gtu.edu.t

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***The synthesis of 9-ethyl-9H-carbazol-3-ol* (3)**

Compound **3** was synthesized according to literatures[1].

The compound **2** (1 equiv) were taken in a round bottomed flask and dry methanol was added in nitrogen gas. then hydrogen peroxide (30 % , 1 equiv), concentrated sulphuric acid (0.1 equiv) was added to the flask in 0 °C The mixture was stirred under nitrogen gas at 25 °C for 2 h and then methanol was removed from reaction under vacuum. The crude product was extracted with distilled water and ethyl acetate. Collected organic layer dried over anhydrous sodium sulfate and the volatiles were allowed to remove under vacuum. The crude product was purified by column chromatography on silica gel using CH_2Cl_2 as as the eluent. Compound 3 was obtained as a white solid. Yield: 82%. FT-IR (ATR) ν, cm^{-1}: 3291, (O-H), 3053 (Ar C–H), 2973-2874 (aliphatic C–H), 1630, 1605, 1485, 1471, 1447, 1345, 1315, 1278, 1229, 1147, 1084, 1021, 936, 876. ^{1}H NMR (500 MHz, $CDCl_3$): δ ppm = 8.03 (d,ArH, 1H), 7.57 (s, ArH, 1H), 7.47 (t, ArH, 1H), 7.39 (d, ArH, 1H), 7.29 (d, ArH, 1H), 7.20 (t, ArH, 1H), 7.06 (m, ArH, 1H), 4.34 (q, CH_2, 2H) 1.43 (t, CH_3, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ ppm = 148.87(ArC), 140.63(ArC), 135.10(ArC), 125.75(ArCH), 123.54(ArC), 122.45(ArC), 120.53(ArCH), 118.27(ArCH), 114.59(ArCH), 109.02(ArCH), 108.51(ArCH), 106.00(ArCH), 37.61 (CH_2), 13.82(CH_3) ESI-MS m/z: 212.2$[M+H]^+$, 274,3 $[M+Na+K]^+$, 337.2 $[M+2Na+2K]^+$,486.3$[M+5Na+4K]^+$. calcd. for $C_{14}H_{13}NO$.

Reference

1. Gourab Dey, Pankaj Gaur, Rajanish Giri, Subrata Ghosh, *Chem. Commun*., 2016, 52, 1887-1890.

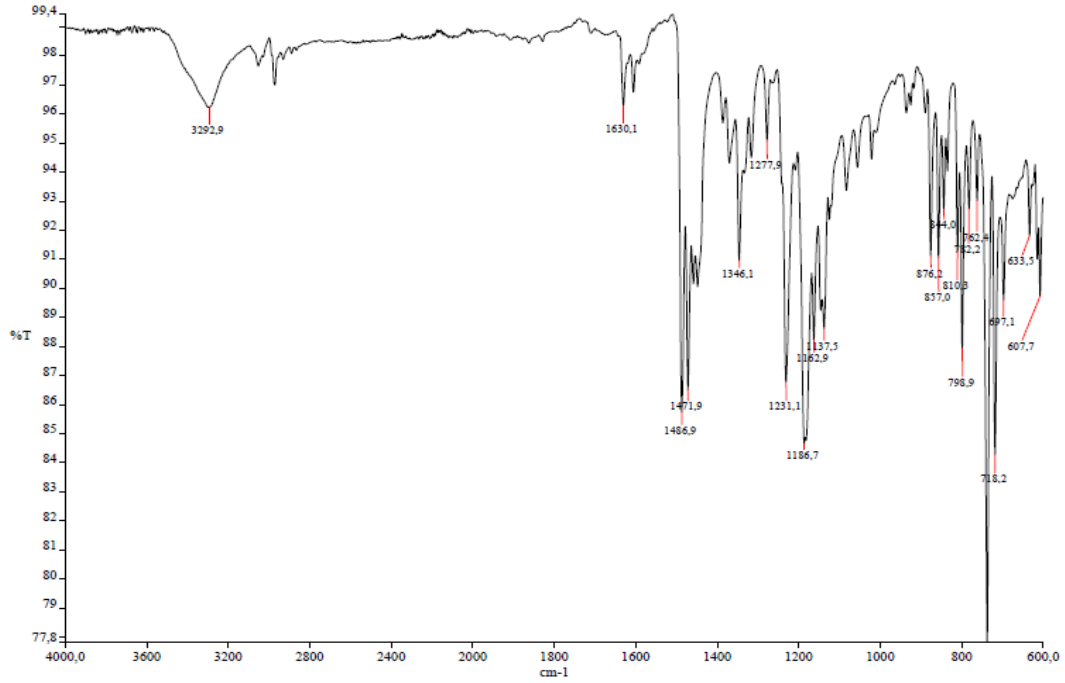


Fig. S1. The FT-IR spectrum of carbazole derivative **3**

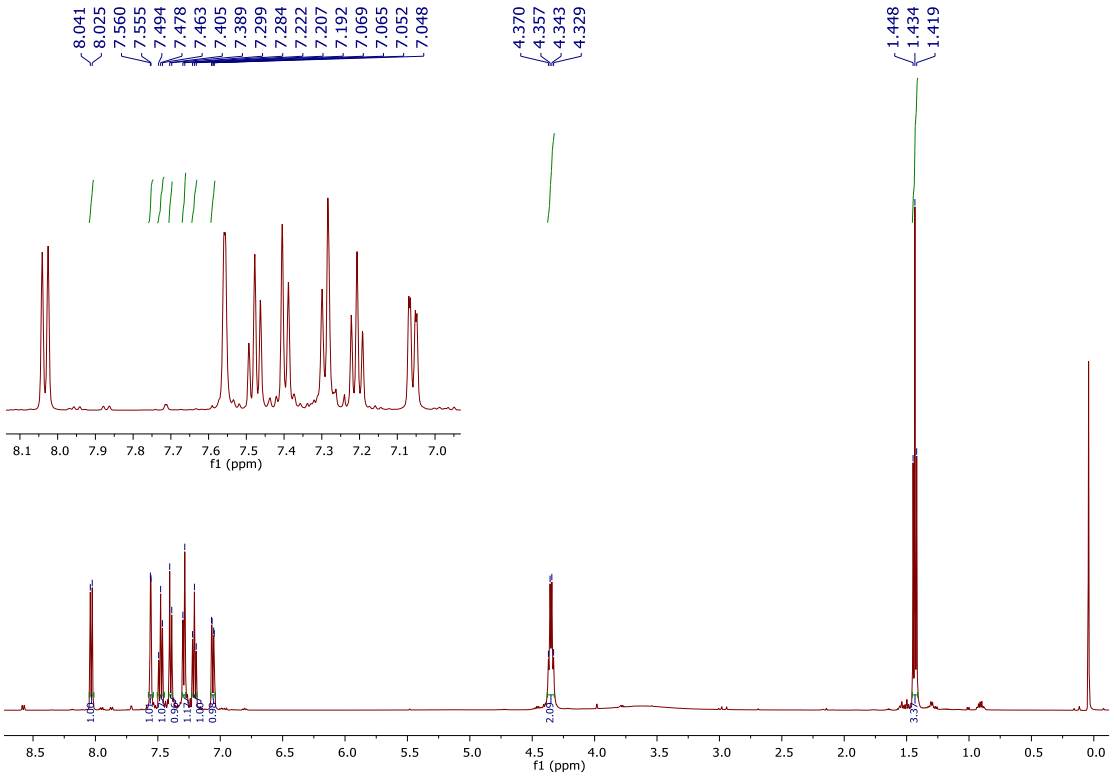


Fig. S2. The ^{1}H-NMR spectrum of carbazole derivative **3** in $CDCl_3$

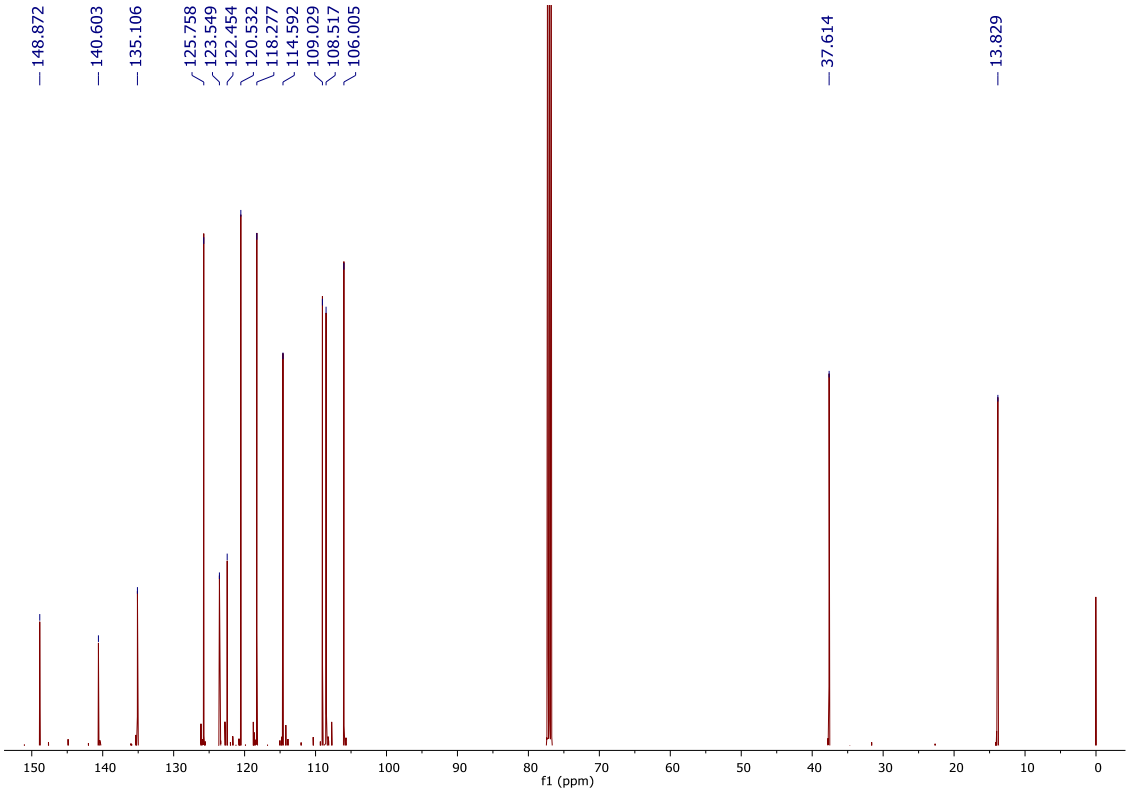


Fig. S3. The ^{13}C-NMR spectrum of carbazole derivative **3** in CDCl

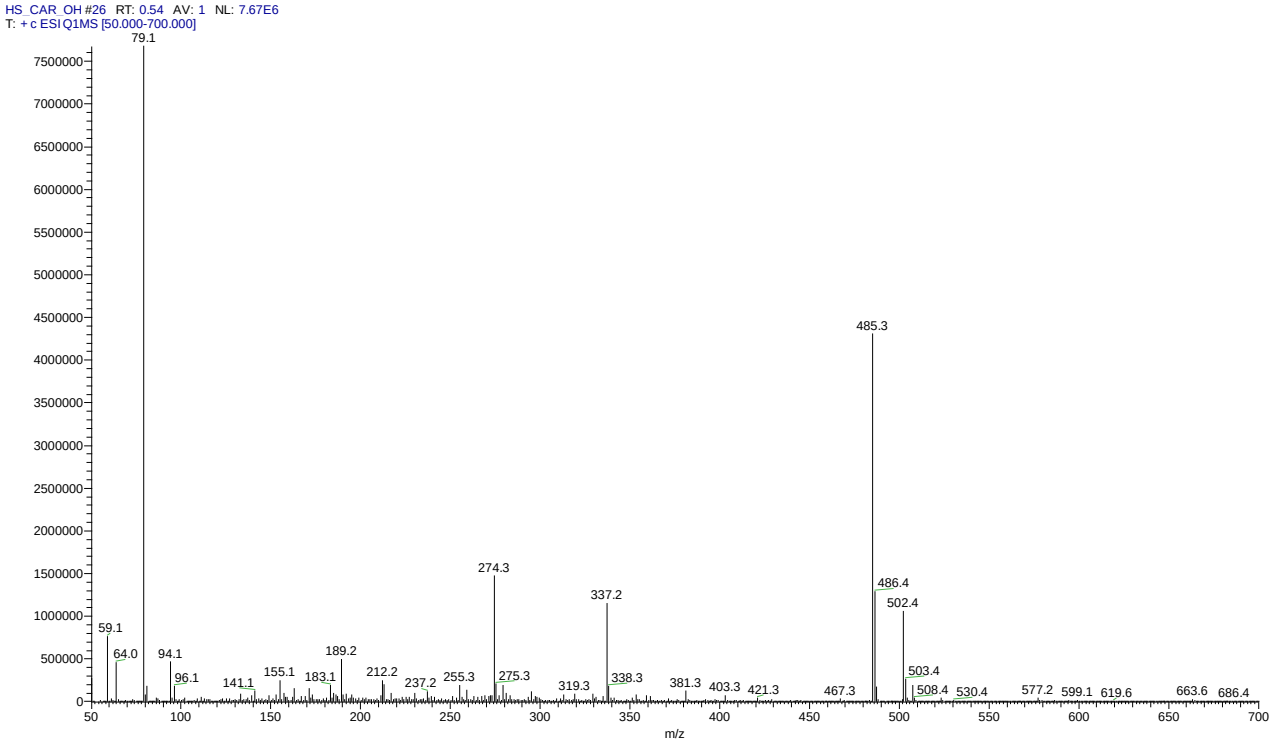


Fig. S4. The ESI-mass spectrum of carbazole derivative **3**

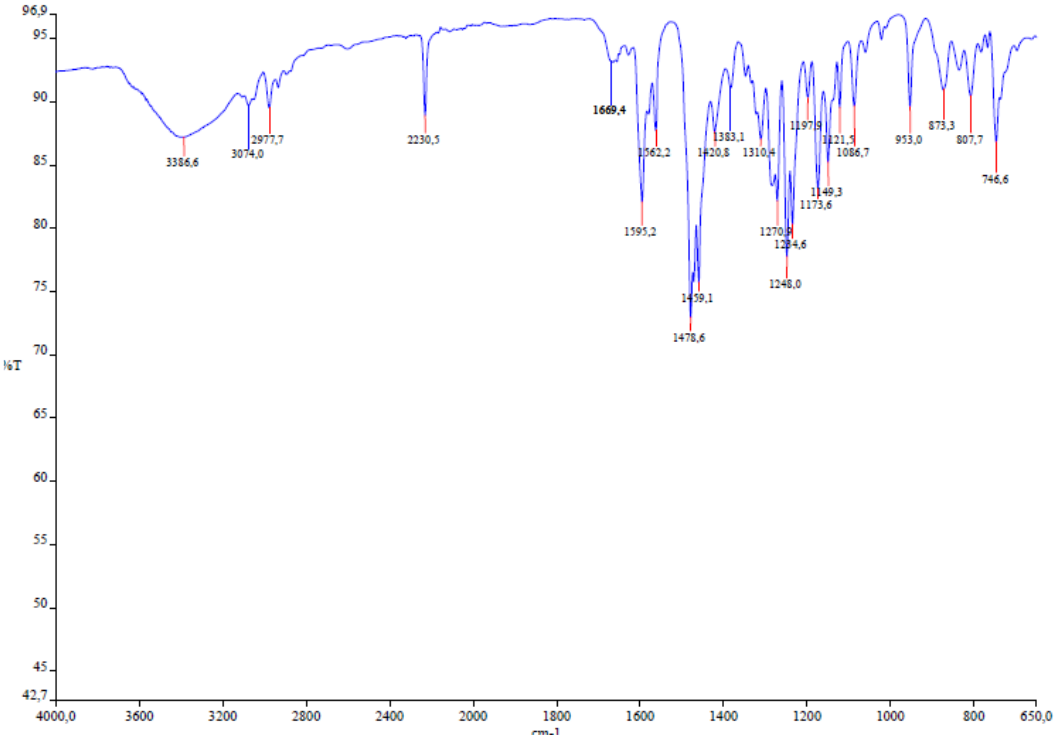


Fig. S5. The FT-IR spectrum of of 4-((9-ethyl-9H-carbazol-3-yl)oxy)-5-hydroxy-phthalonitrile (**5**)

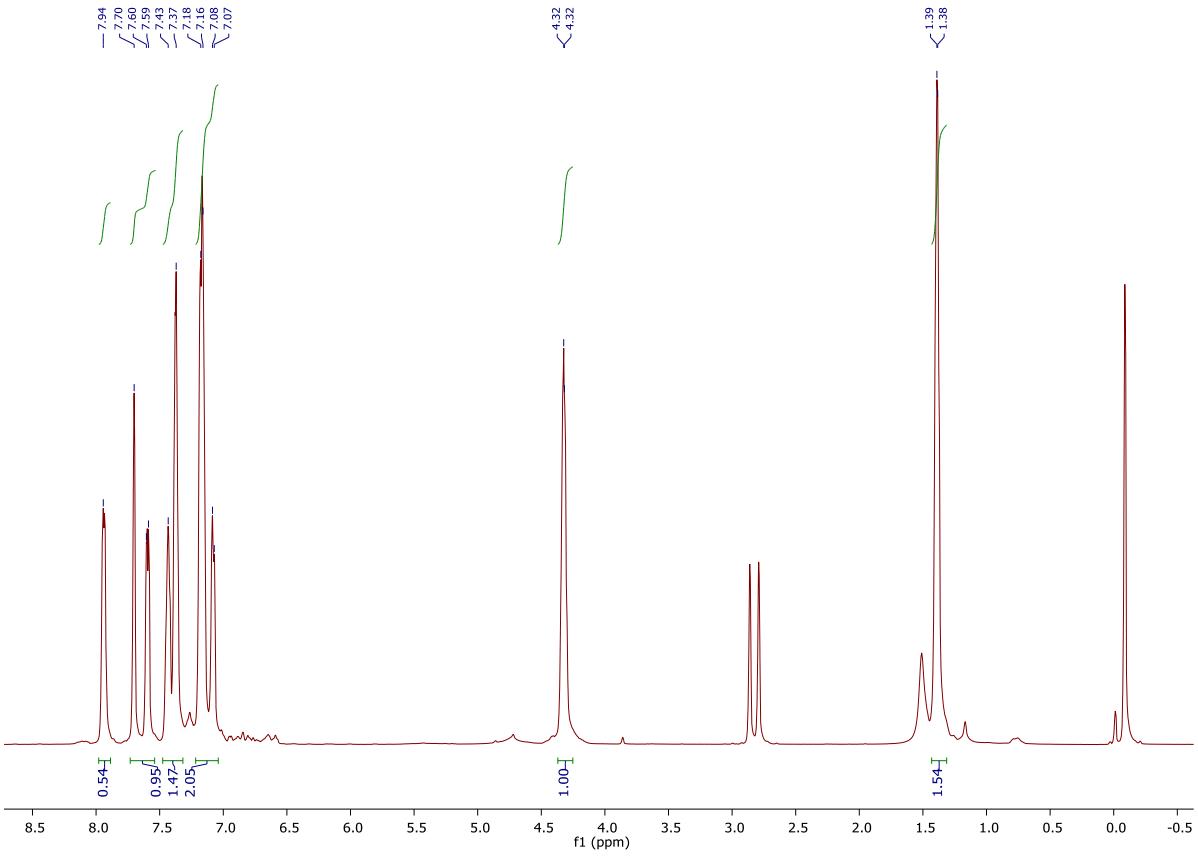


Fig. S6. The ^{1}H-NMR spectrum of 4-((9-ethyl-9H-carbazol-3-yl)oxy)-5-hydroxyphthalonitrile (**5**) in $CDCl_3$

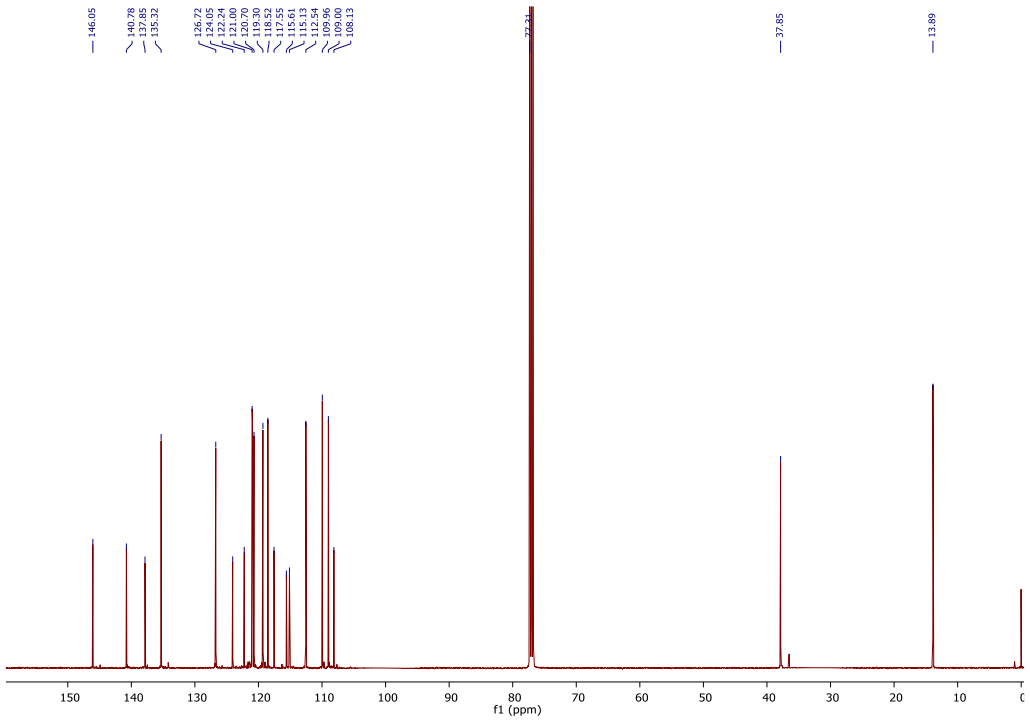


Fig. S7. ^{13}C-NMR spectrum of 4-((9-ethyl-9H-carbazol-3-yl)oxy)-5-hydroxyphthalonitrile (**5**) in $CDCl_3$

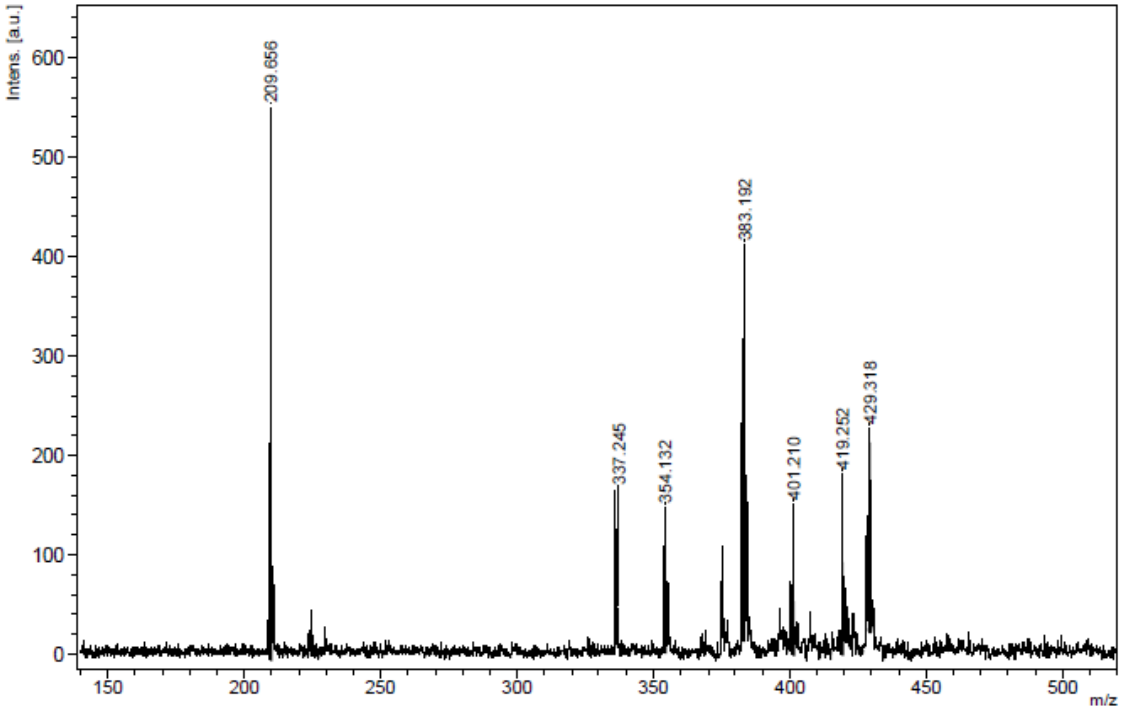


Fig. S8. MALDI-TOF mass spectrum of 4-((9-ethyl-9H-carbazol-3-yl)oxy)-5-hydroxyphthalonitrile (**5**) (matrix:DIT)

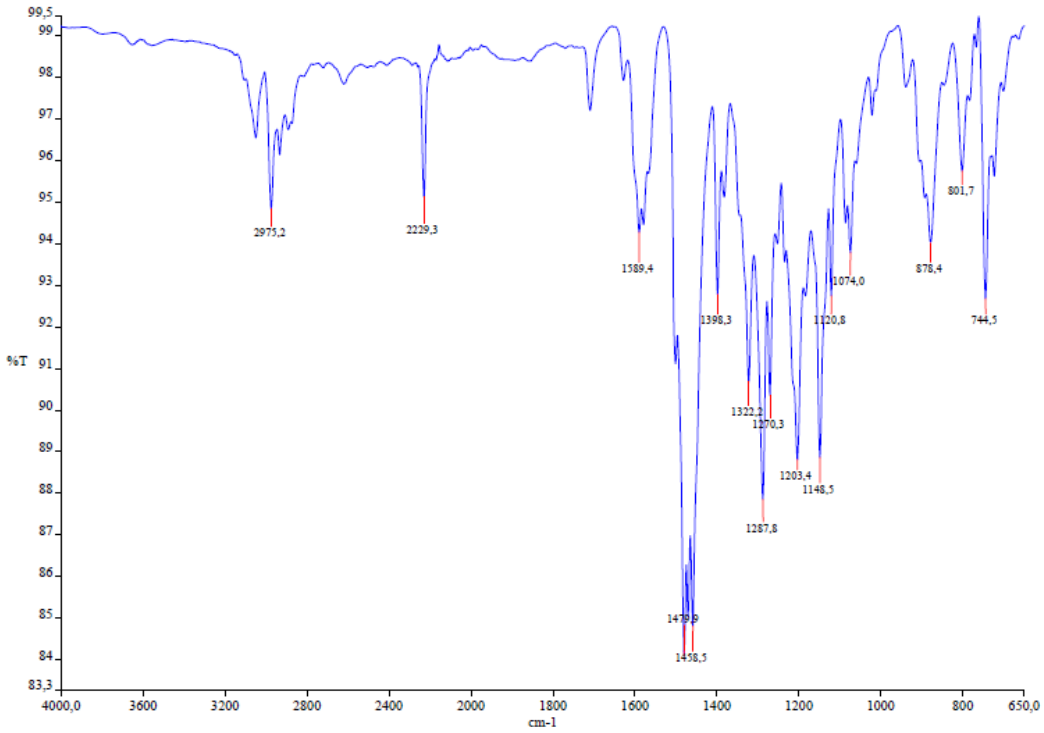


Fig. S9. FT-IR spectrum of 4,5-bis((9-ethyl-9H-carbazol-3-yl)oxy)phthalonitrile (**7**)

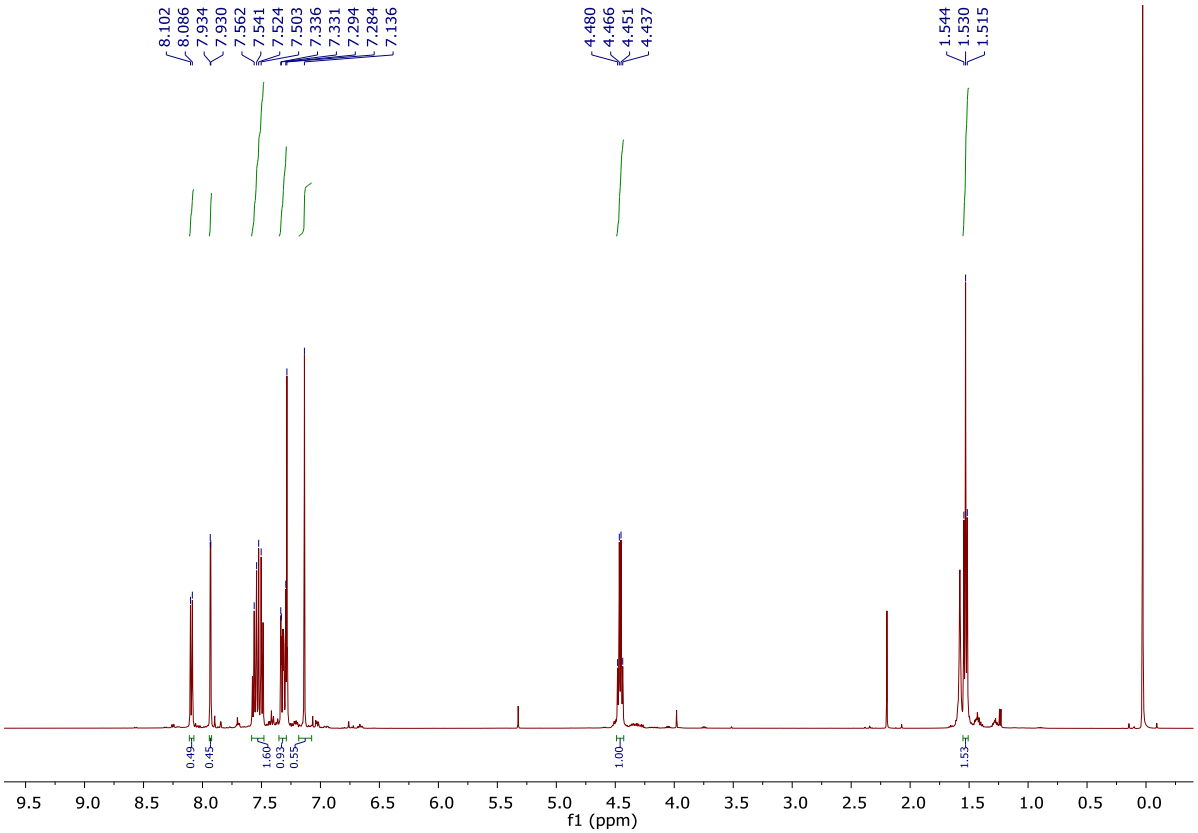


Fig. S10. ^{1}H-NMR spectrum of 4,5-bis((9-ethyl-9H-carbazol-3-yl)oxy)phthalonitrile (**7**) in $CDCl_3$

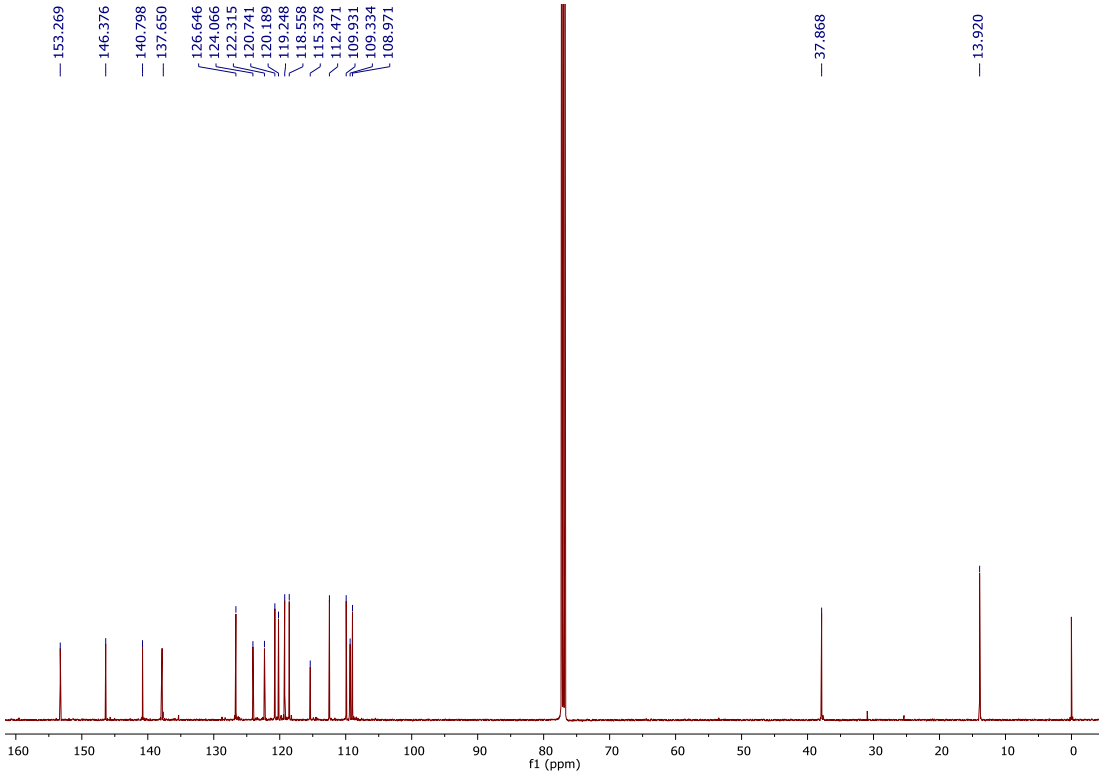


Fig. S11. ^{13}C-NMR spectrum of 4,5-bis((9-ethyl-9H-carbazol-3-yl)oxy)phthalonitrile (**7**) in $CDCl_3$

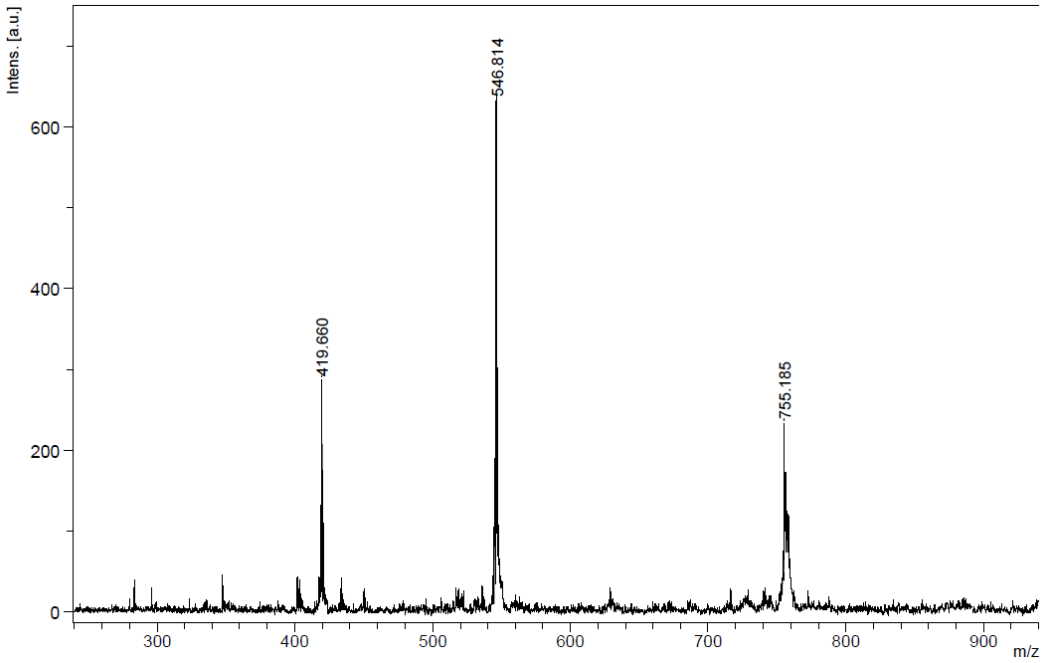


Fig. S12. MALDI-TOF spectrum of 4,5-bis((9-ethyl-9H-carbazol-3-yl)oxy)phthalonitrile (**7**) (matrix:DHB)

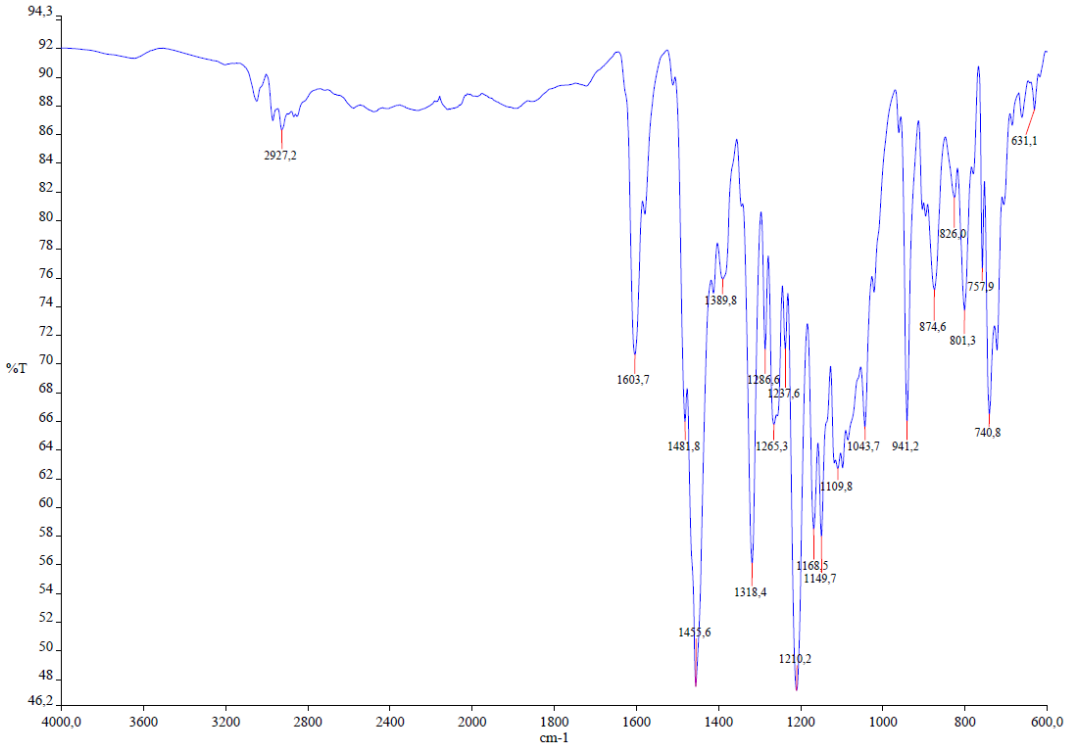


Fig. S13. FTIR spectrum of **Car-Pc$_2$-1**

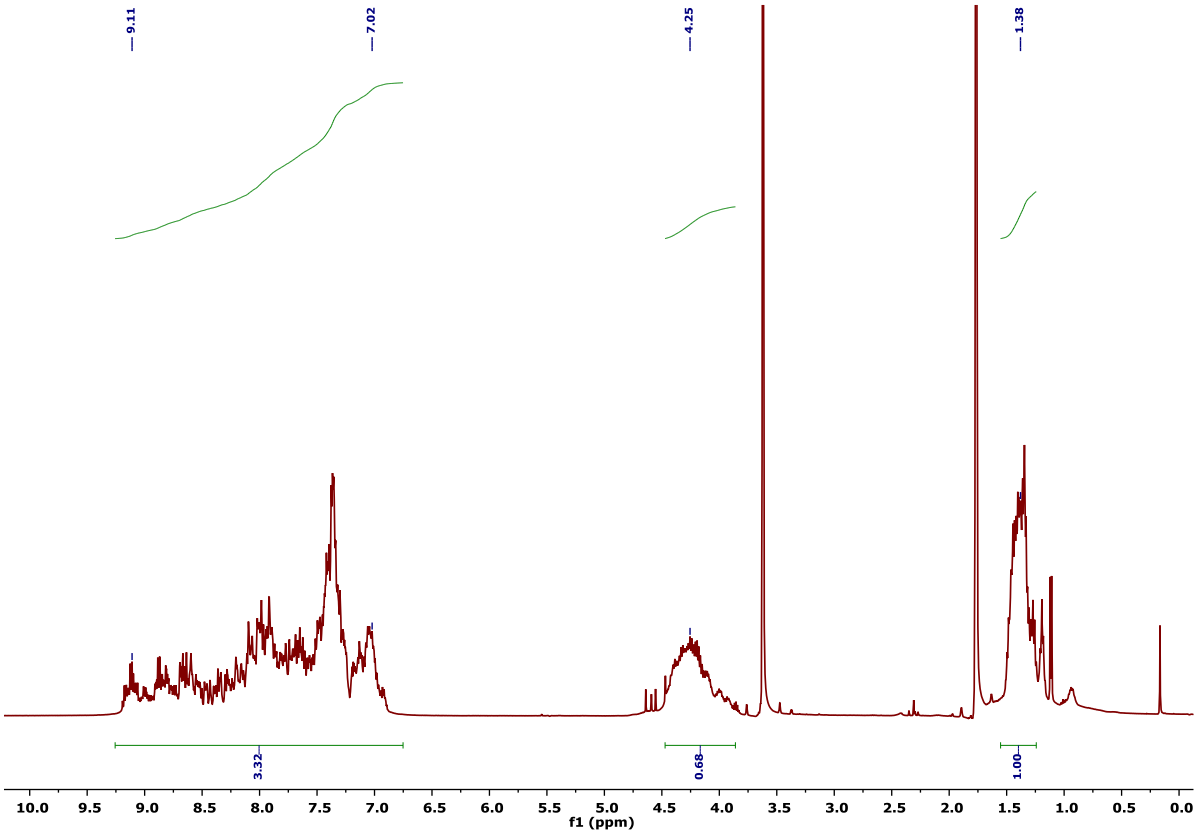


Fig. S14. ^{1}H-NMR spectrum of reduced **Car-Pc$_2$-1** in THF+NaBD$_4$,

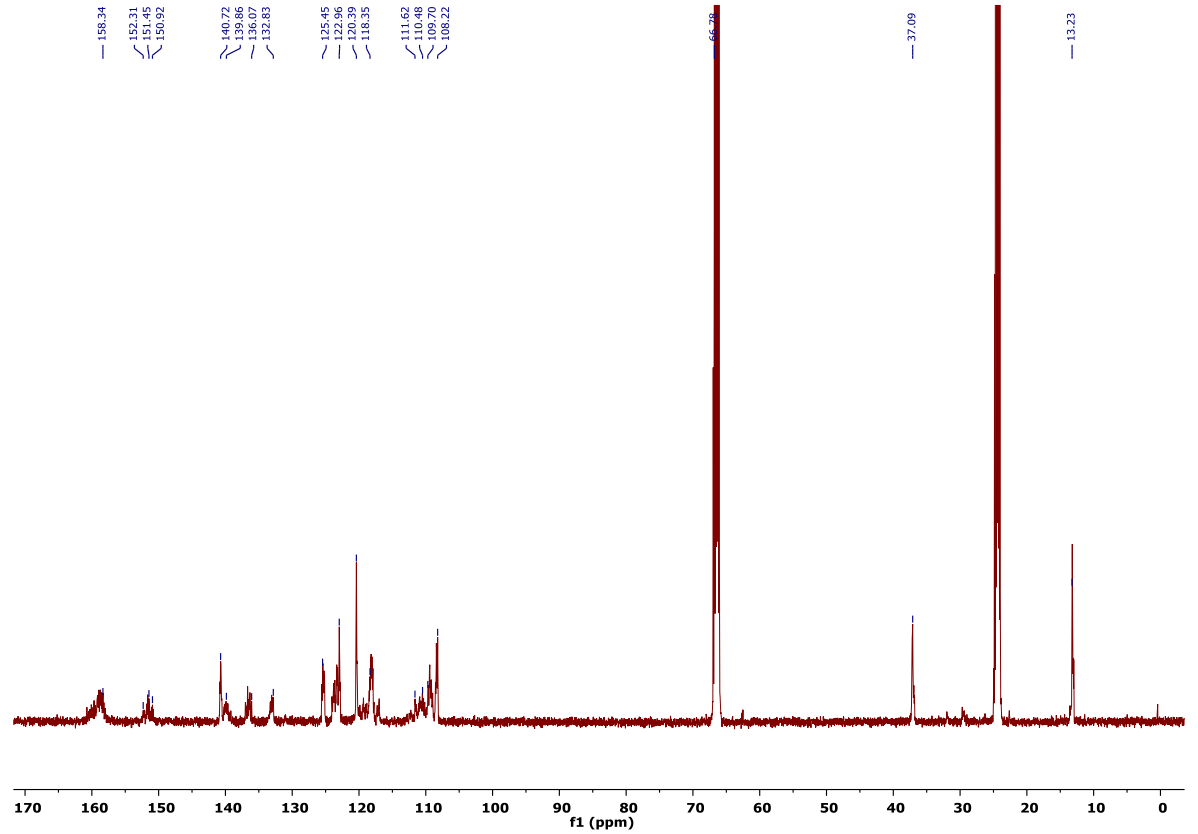


Fig. S15. ^{13}C NMR spectrum of **Car-Pc$_2$-1** in THF-d_8 +NaBD$_4$

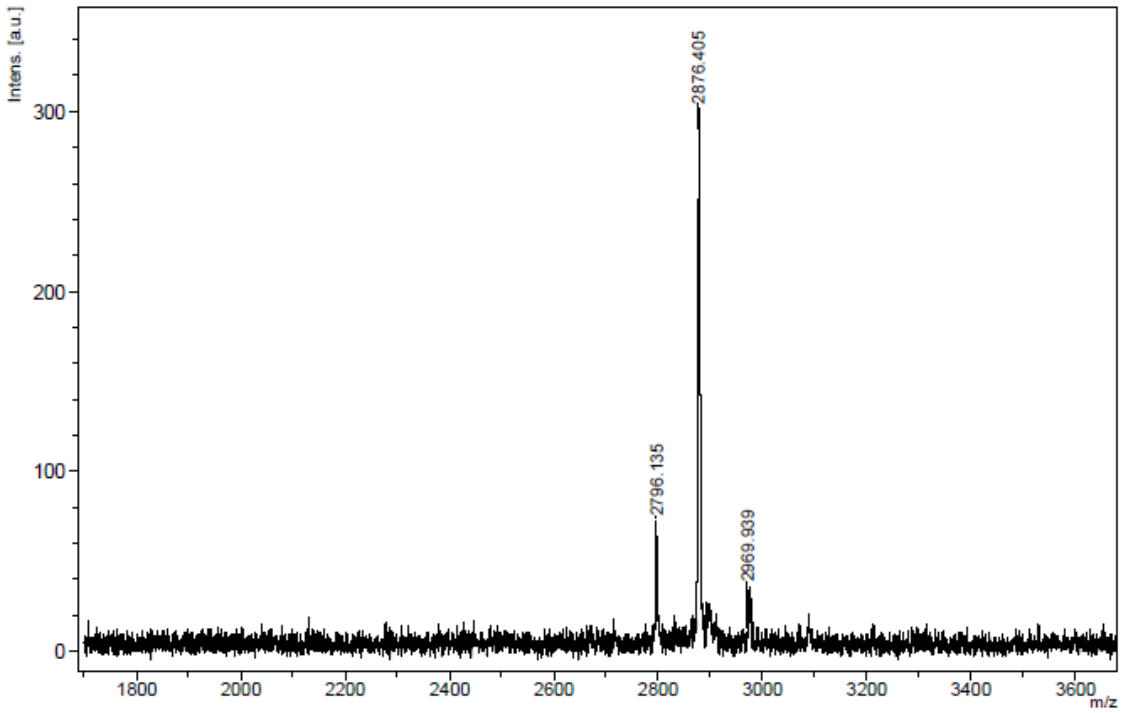


Fig. S16. MALDI-TOF spectrum of **Car-Pc2-1** (matrix:DHB)

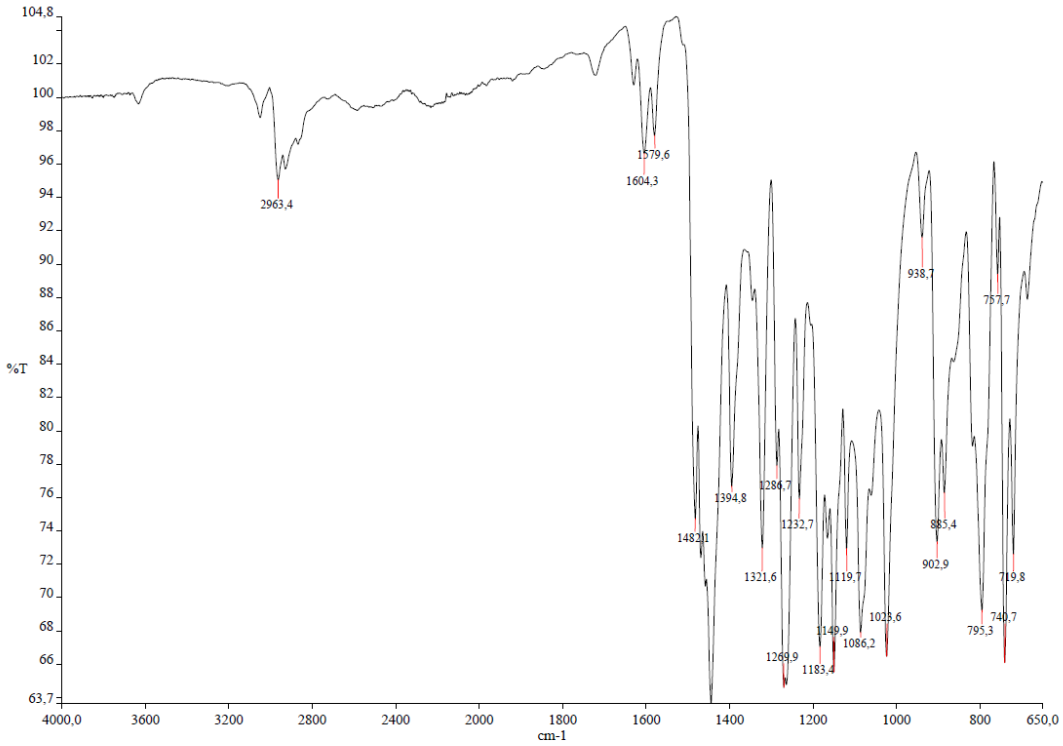


Fig. S17. FTIR spectrum of **Car-Pc2-2**

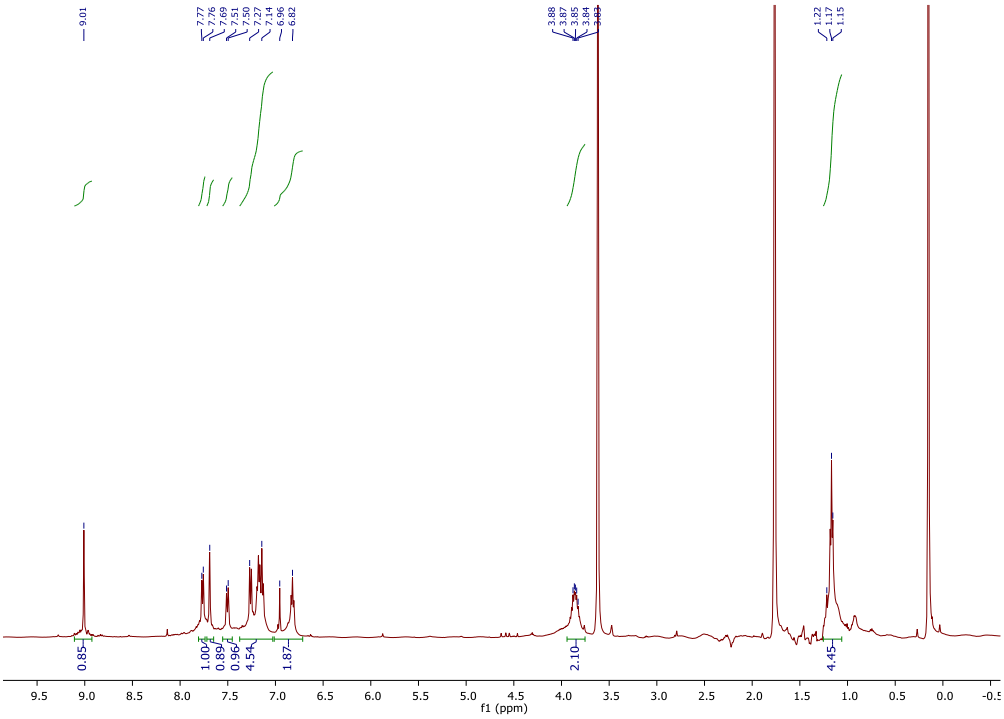


Fig. S18. ^{1}H-NMR spectrum of reduced **Car-Pc$_2$-2** in THF-d_8+ NaBD$_4$

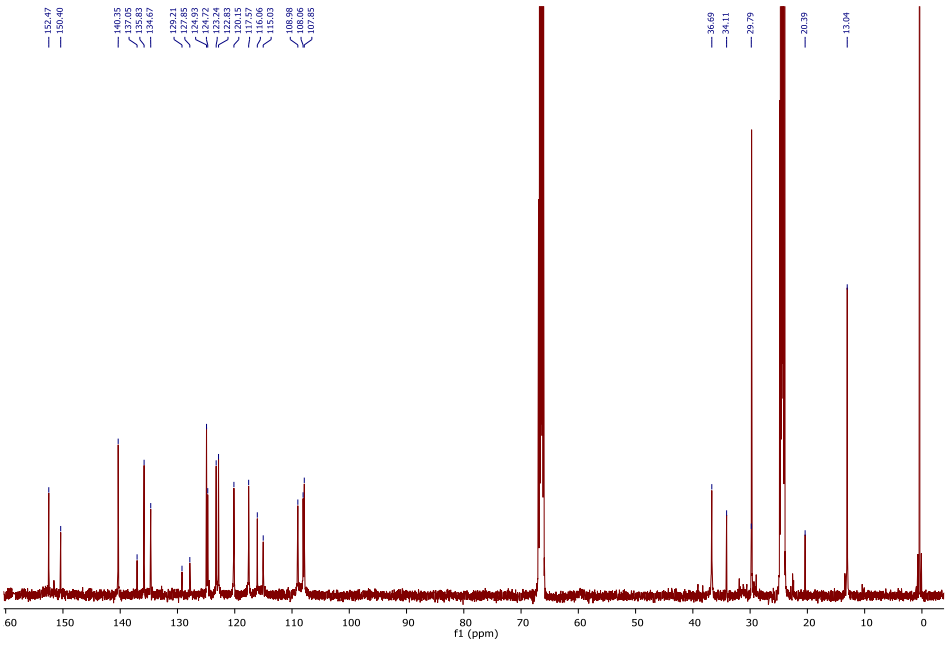


Fig. S19. ^{13}C NMR spectrum of **Car-Pc$_2$-2** in THF-d_8 +NaBD$_4$

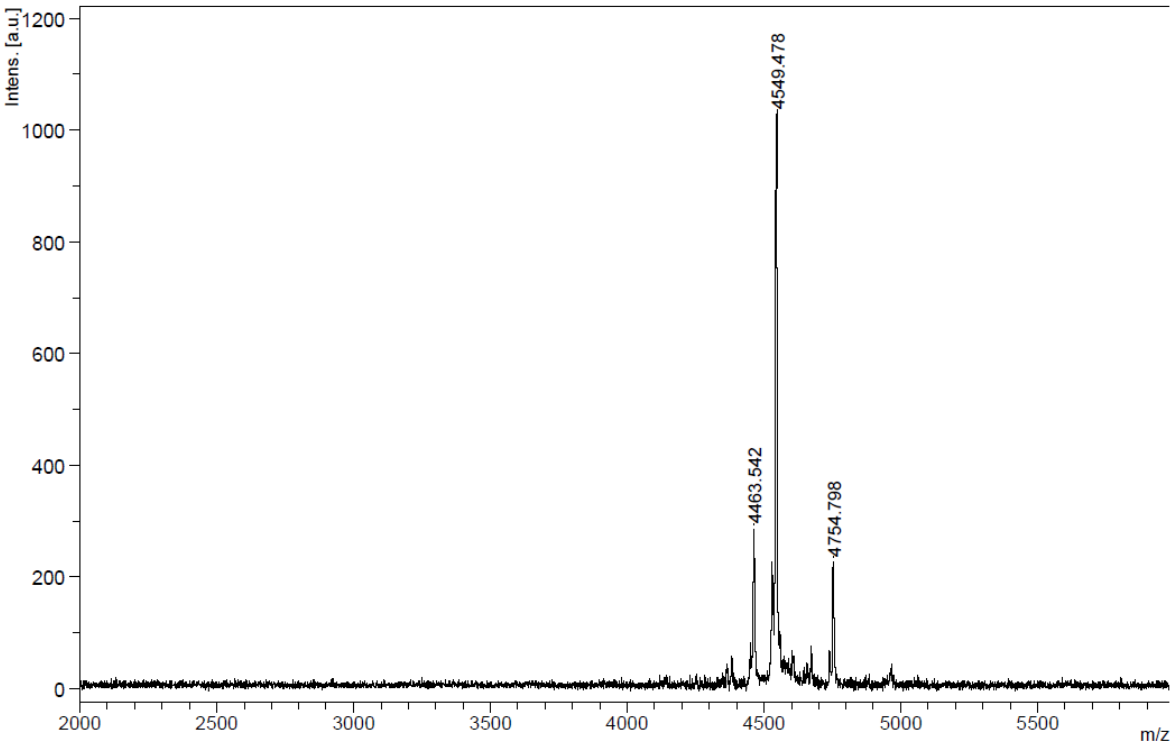


Fig. S20. MALDI-TOF spectrum of **Car-Pc$_2$-2** (matrix:DHB)

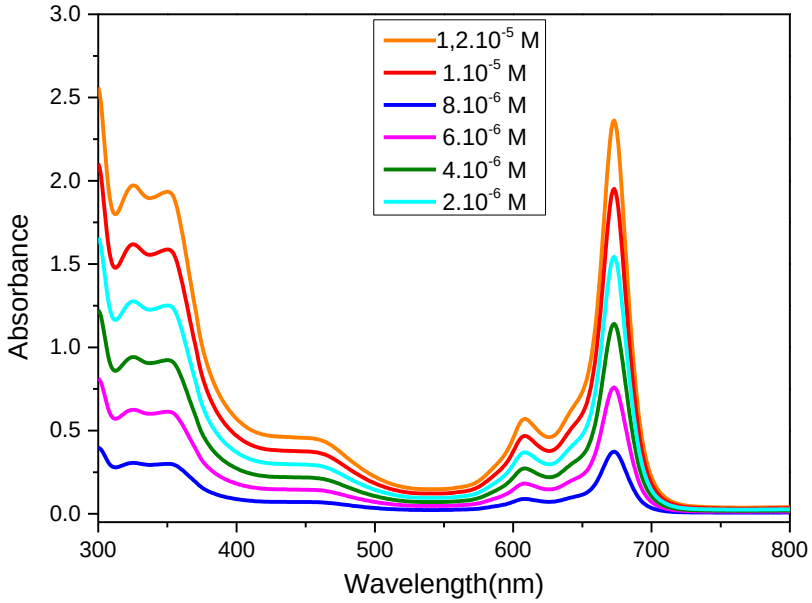


Fig. S21. Electronic absorption spectra of **Car-Pc$_2$-1** in THF at six different concentration.

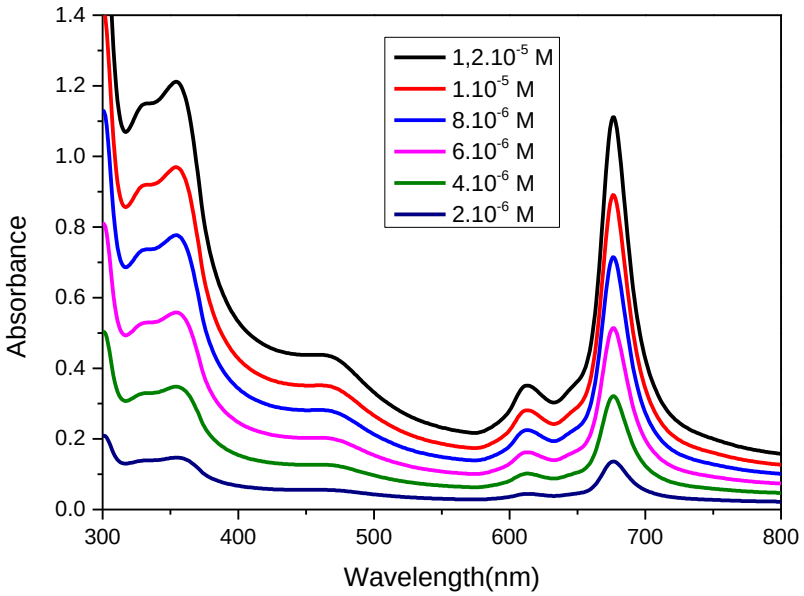


Fig. S22. Electronic absorption spectra of **Car-Pc$_2$-2**in THF at six different concentration.

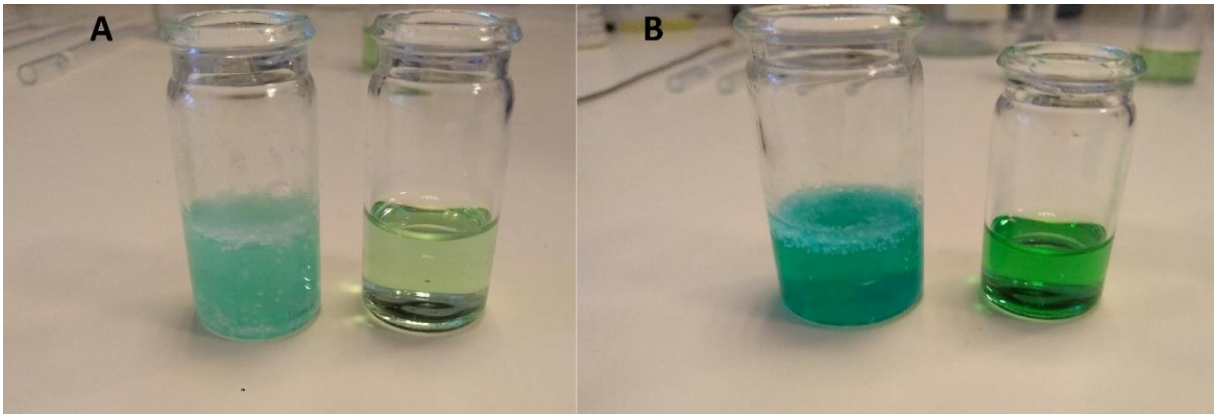


Fig. S23. Reduced (left) and neutral (right) forms of **Car-Pc$_2$-1** (A) and **Car-Pc$_2$-2** (B) bisphthalocyanine derivatives.

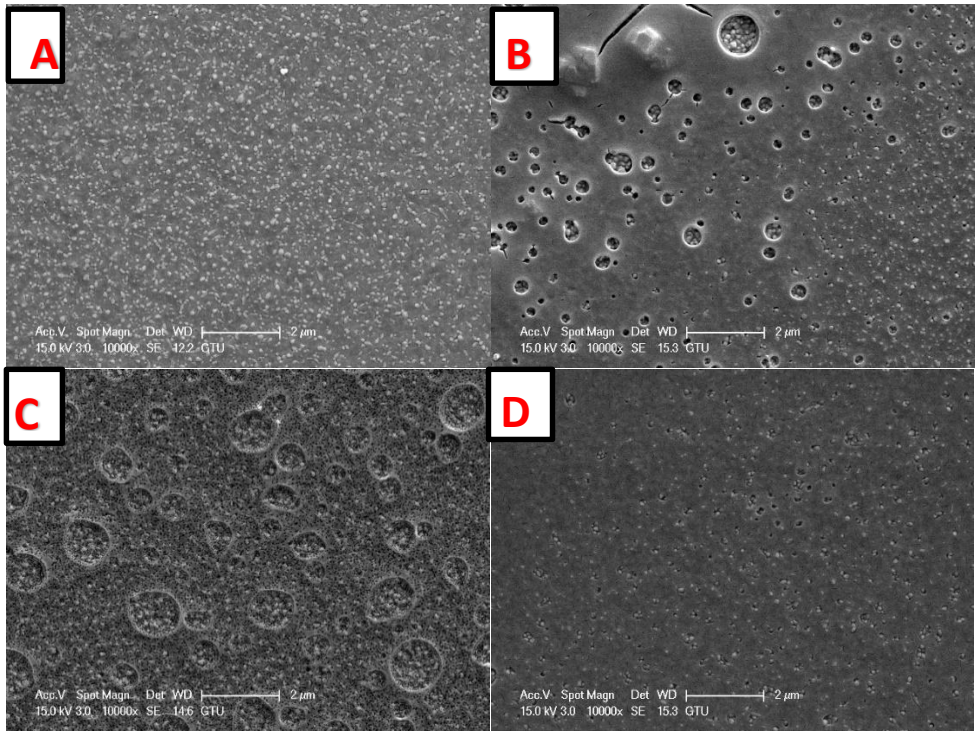
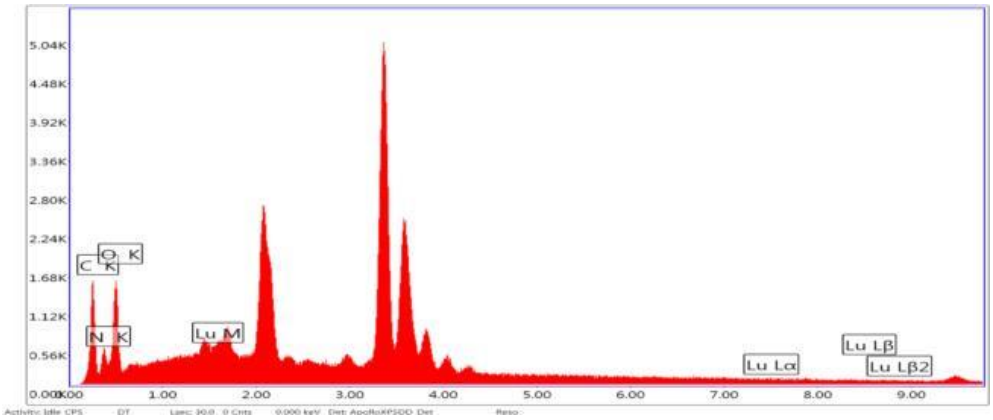
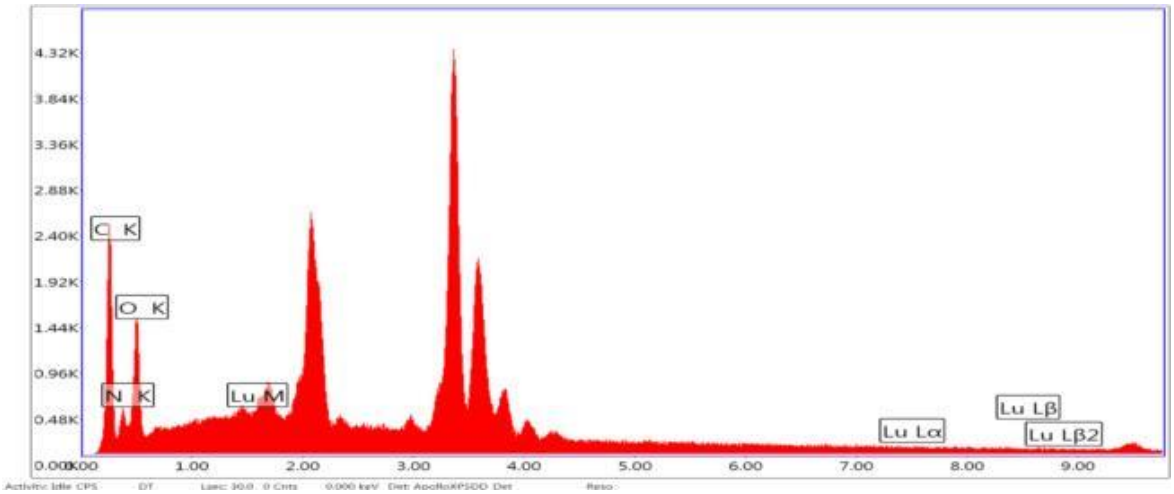


Fig. S24. SEM images of **Car-Pc$_2$-2**(A), **Ply(Car-Pc$_2$-2)** (B), **Grp/Ply(Car-Pc$_2$-2)** (C) and **Grp/Car-Pc$_2$-2**(D) films deposited on FTO electrode



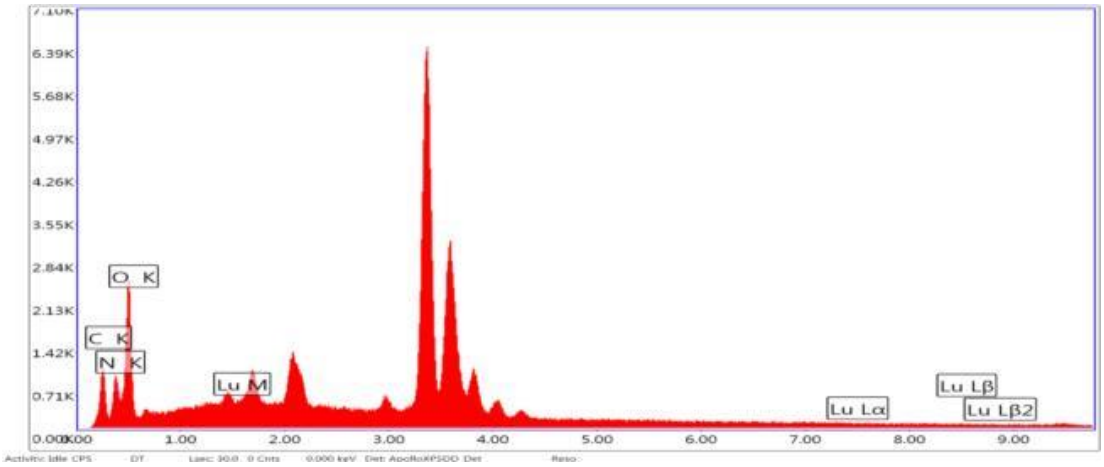
Element	Weight %	Atomic %	Net int.	Net int.Error
C K	29.03	35.65	300.28	0.02
N K	24.04	25.32	89.25	0.04
O K	41.86	38.6	315.21	0.02
LuL	5.07	0.43	8.59	0.53

Fig. S25. EDX image of **Grp/Ply(Car-Pc-1)/GCE**



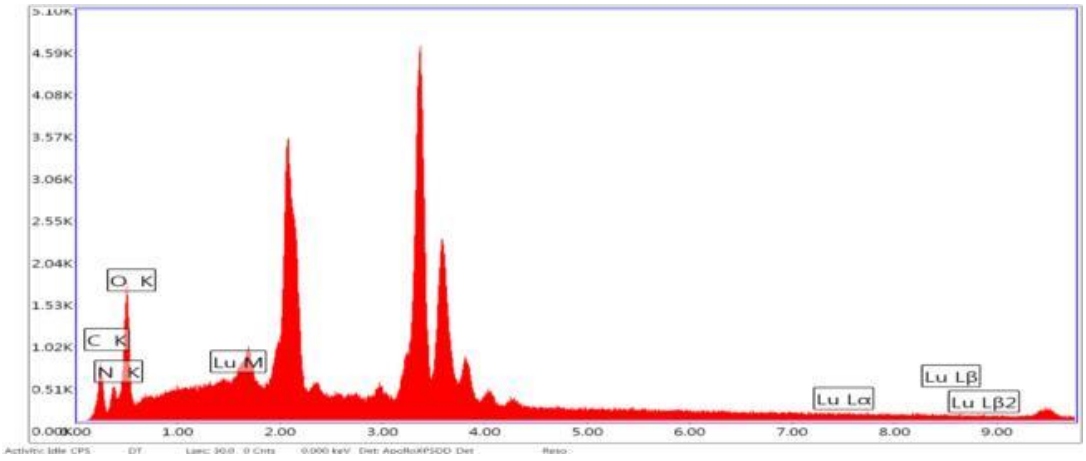
Element	Weight %	Atomic %	Net int.	Net int.Error
C K	36.78	44.02	493.4	0.01
N K	22.51	23.1	84.02	0.04
O K	36.19	32.51	309.91	0.02
LuL	4.53	0.37	9.44	0.53

Fig. S26. EDX image of **Grp/Car-Pc-1/GCE**



Element	Weight %	Atomic %	Net int.	Net int.Error
C K	17.84	22.12	222.62	0.02
N K	28.14	29.93	191.28	0.02
O K	51.24	47.71	529.9	0.01
LuL	2.78	0.24	5.85	0.54

Fig. S27. EDX image of **Grp/Ply(Car-Pc-2)/GCE**



Element	Weight %	Atomic %	Net int.	Net int.Error
C K	21.99	28.18	143.64	0.02
N K	18.92	20.79	58.66	0.05
O K	52.41	50.44	336.72	0.02
LuL	6.69	0.59	7.79	0.53

Fig. S28. EDX image of **Grp/Car-Pc-2/GCE**

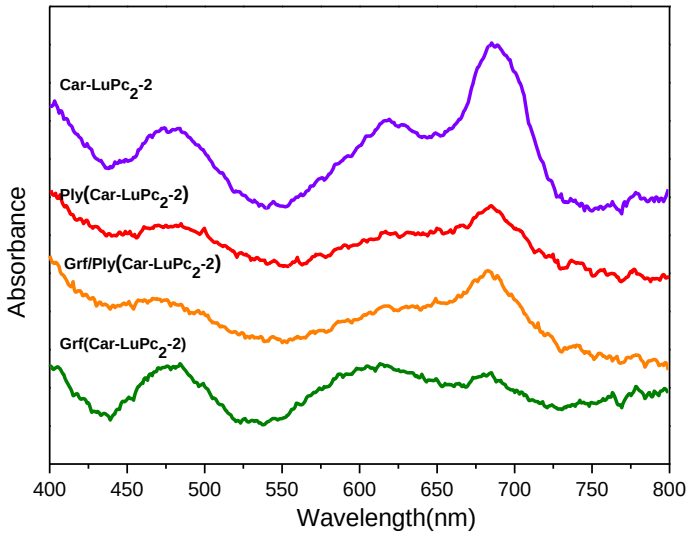


Fig. S29. UV-Vis spectra of **Car-Pc2-2** based films on FTO

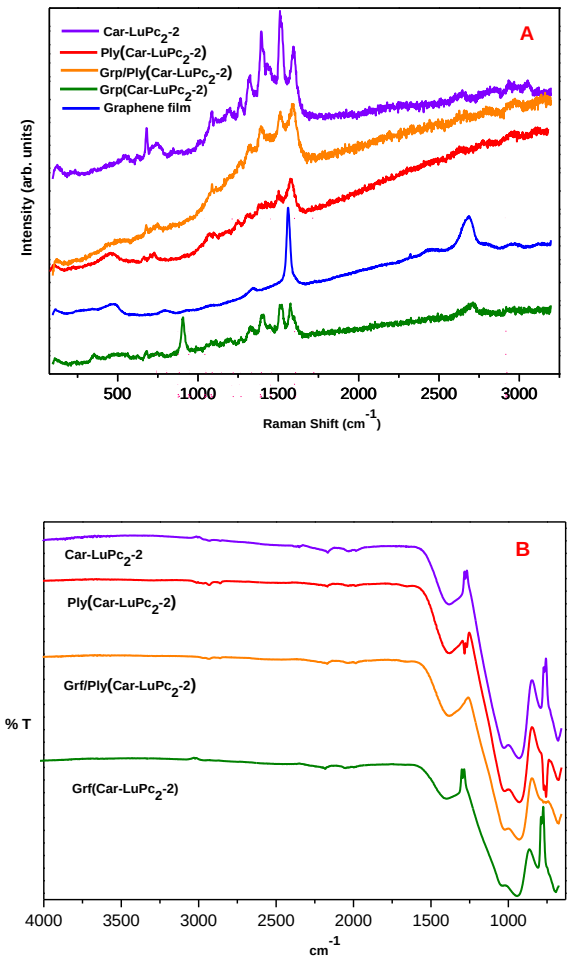


Fig. S30. Raman (A) and FT-IR (B) spectra of **Car-Pc$_2$-2** based films on FTO

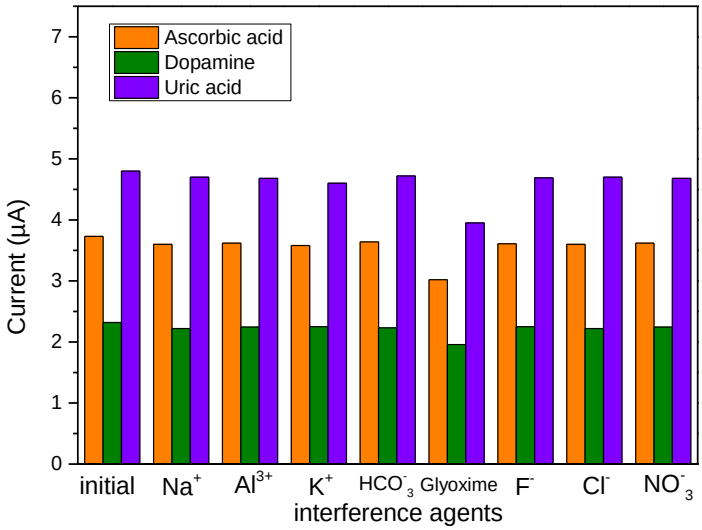


Fig. S31. Effect of the presence of interfering agents on the peak current AA, DA and UA for **Grp/Car-Pc$_2$-2/GCE**

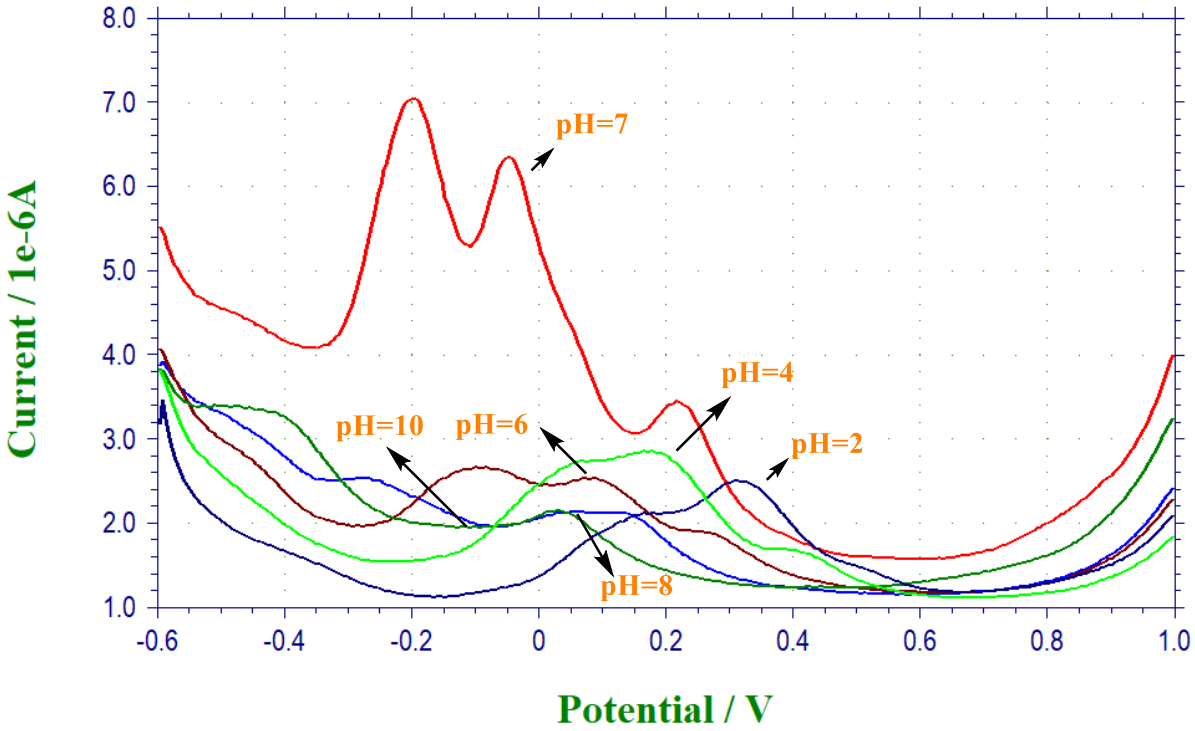


Fig. S32. Typical DPV of 160 μM for AA on **Grp/Car-Pc$_2$-1/GCE** under different pH values.(Potential range: -0.6-1.0 V, pulse period (s): 0.2, quiet time(s): 2, pulse width: 0.05, incr (V): 0.004)