Supplementary Information for:

Doubly N-confused phlorin and phlorinone analogues

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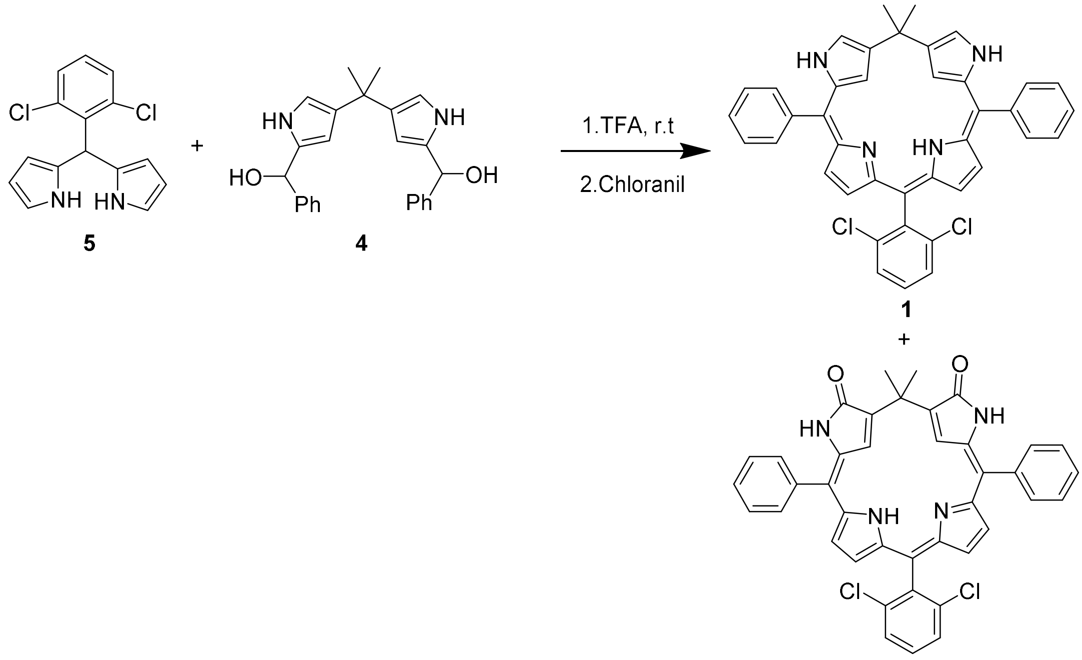
Contents

I. Synthetic Experimental

General

All reagents and solvents were purchased from commercial suppliers and used without further purification. Analytical thin-layer chromatography (TLC) was performed using commercial pre-coated silica gel plates containing a fluorescent indicator. Column chromatography was carried out using silica gel (0.040-0.063 mm). ^{1}H NMR, ^{13}C NMR, and ^{19}F NMR spectra were recorded on Bruker AV400 and AV600 instruments. UV-Vis spectra were measured on a Varian Cary 5000 spectrophotometer. Mass spectra (MS) were taken on Fisher Orbitrap Elite (ESI) or Bruker (Autoflex speed) matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF MS). X-ray crystallographic analyses were carried out on Bruker X8 APEX II or Bruker APEX DUO instruments. Further details of the structures and their refinement are given in a later section.



Scheme S3. Synthesis of compound **1**.

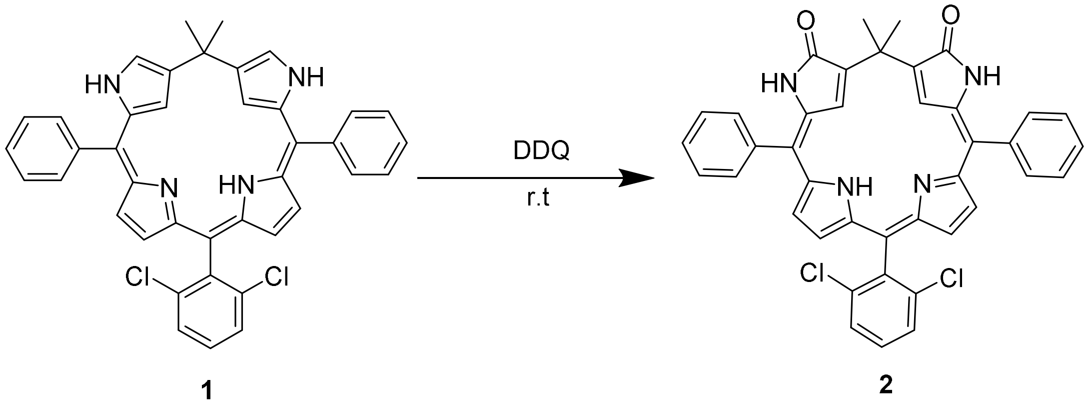
Compound **1**

Dipyrromethane **4** was prepared via the reduction of **3**[S1] with excess $NaBH_4$ at rt. The reaction mixture was quenched with water and extracted using CH_2Cl_2 (DCM). After removal of solvent, **4** was obtained and used directly for the synthesis of **1** without further purification.

To a 50 mL round bottom flask equipped with a stirring bar and septum was added **5** (140mg, 0.4mmol), **4** (120mg， 0.4mmol), and 25 mL $CHCl_3$. After purging with nitrogen, the solution was treated with TFA at rt. The mixture was allowed to react overnight before chloranil was added. The crude material was purified using silica gel chromatography (eluent: 2% MeOH in CH_2Cl_2). After removal of volatiles under reduced presssure, this gave product **1** (21mg, 0.033mmol) in the form of a greenish powder. Yield: 8%. HRMS (ESI, $[M+1]^+$) Calculated for $C_{40}H_{30}Cl_2N_4$: 637.608. Found: 637.608.

^1H NMR (400 MHz, DCM-d_2) δ = 8.04 (s, 2H), 7.58 – 7.43 (m, 13H), 7.35 (t, *J* = 8.1 Hz, 1H), 6.98 (d, *J* = 5.0 Hz, 2H), 6.86 (s, 2H), 6.45 (d, *J* = 5.0 Hz, 2H), 5.96 (s, 2H), 1.76 (s, 6H).

^{13}C NMR (100 MHz, THF-d_8) δ = 147.7, 141.0, 139.5, 139.2, 134.4, 132.9, 132.2, 132.1, 130.0, 128.6, 128.5, 128.2, 126.7, 116.8, 114.6, 102.4, 100.8, 54.7, 30.4.



Scheme S4. Synthesis of compound **2**

Compound **2**

Method A: compound **2** was synthesized and obtained as the side product in the synthesis of **1**. Yield: 1 – 6%.

Method B: To a solution of **1** (15 mg, 0.024 mmmol) in 20 mL $CHCl_3$ was charged 12 μL TFA and DDQ (8 mg, 0.04 mmol). After the reaction mixture was stirred for 2.5 h at rt, the reaction was quenched by the addition of water. The crude productwas purified via silica gel chromatography (eluent: 2% MeOH in CH_2Cl_2). **2** (13 mg, 0.019 mmmol) was obtained as dark blue solid. Yield: 79%. HRMS (ESI, $[M+1]^+$) Calculated for $C_{40}H_{30}Cl_2N_4O_2$: 667.590. Found: 667.591.

^1H NMR (600 MHz, DCM-d_2) δ = 10.38 (s, 1H), 7.77 (s, 2H), 7.61 – 7.35 (m, 13H), 7.23 (s, 2H), 6.45 (s, 2H), 6.27 (d, *J* = 4.2 Hz, 2H), 1.77 (s, 6H).

^{13}C NMR (150 MHz, DCM-d_2) δ = 170.3, 141.6, 137.2, 136.4, 136.4, 135.8, 131.0, 129.8, 129.3, 128.5, 124.8, 118.5, 37.8, 25.2.

II. NMR Spectral Studies

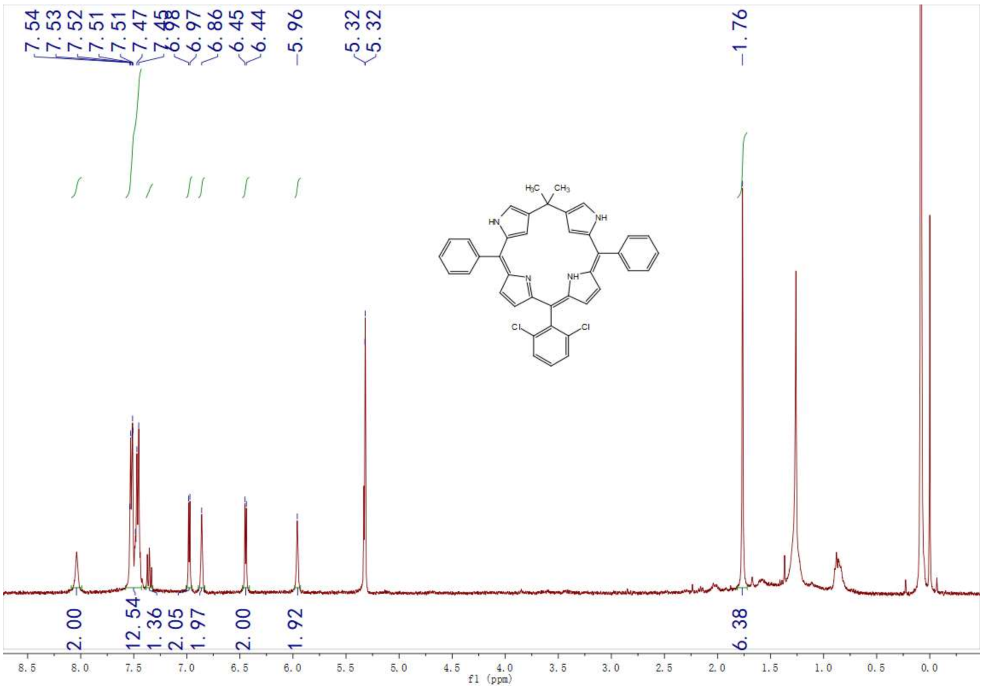


Figure S1. ^{1}H NMR spectrum of **1** recorded in CD_2Cl_2 at rt.

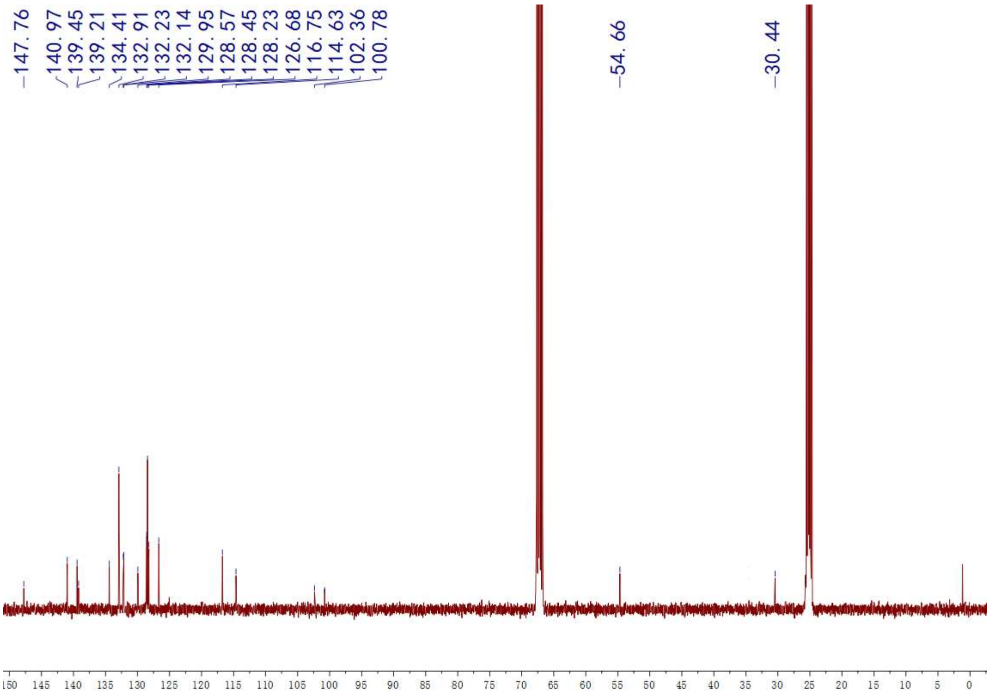


Figure S2. ^{13}C NMR spectrum of **1** recorded in THF-d_8 at rt.

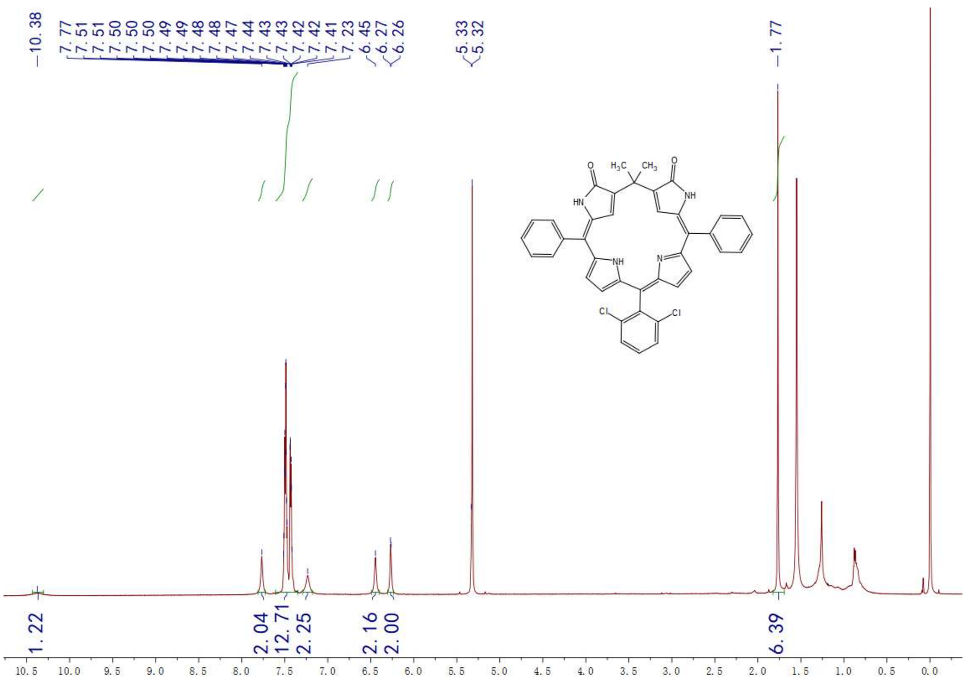


Figure S3. ^{1}H NMR spectrum of **2** recorded in CD_2Cl_2 at rt.

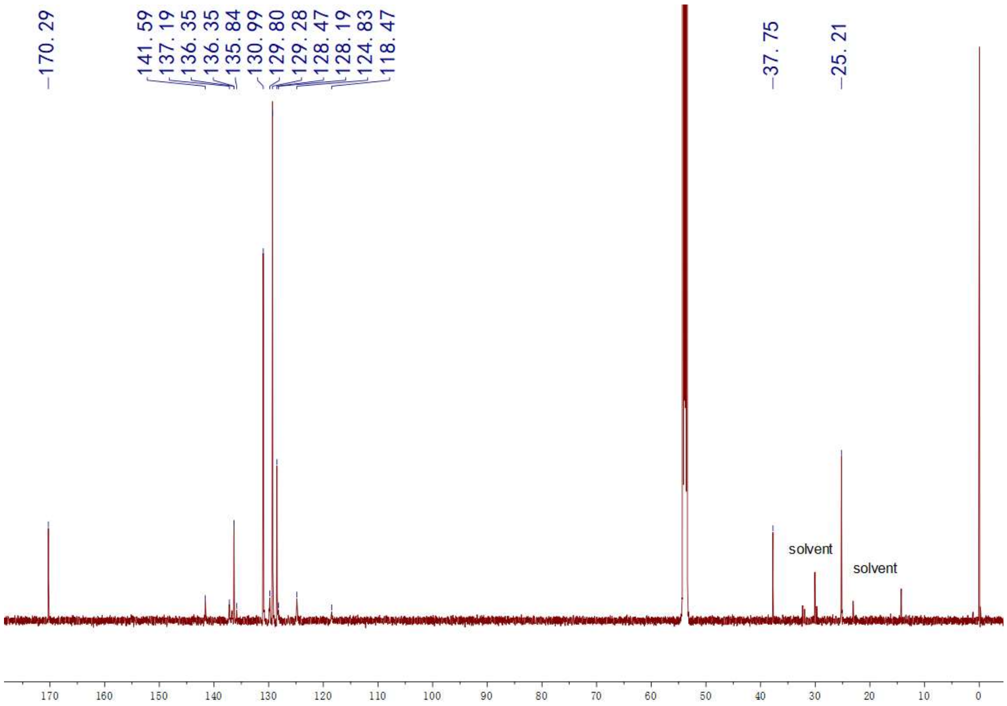


Figure S4. ^{13}C NMR spectrum of **2** recorded in CD_2Cl_2 at rt.

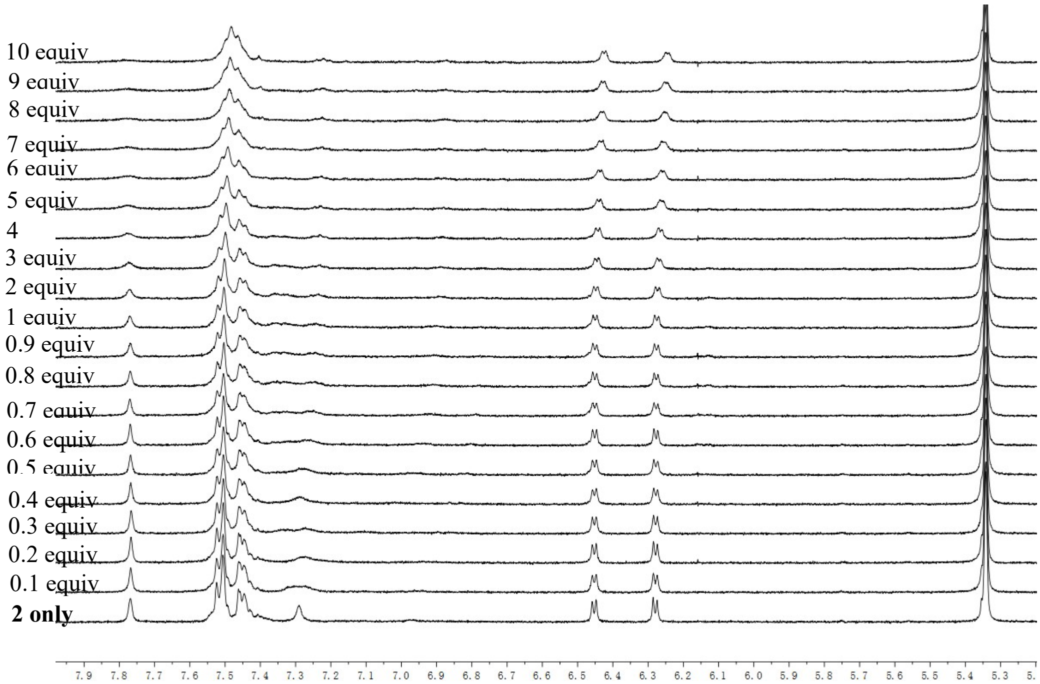


Figure S5: ^{1}HNMR spectra of **2** recorded upon the incremental addition of TBAF in CD_2Cl_2 at rt.

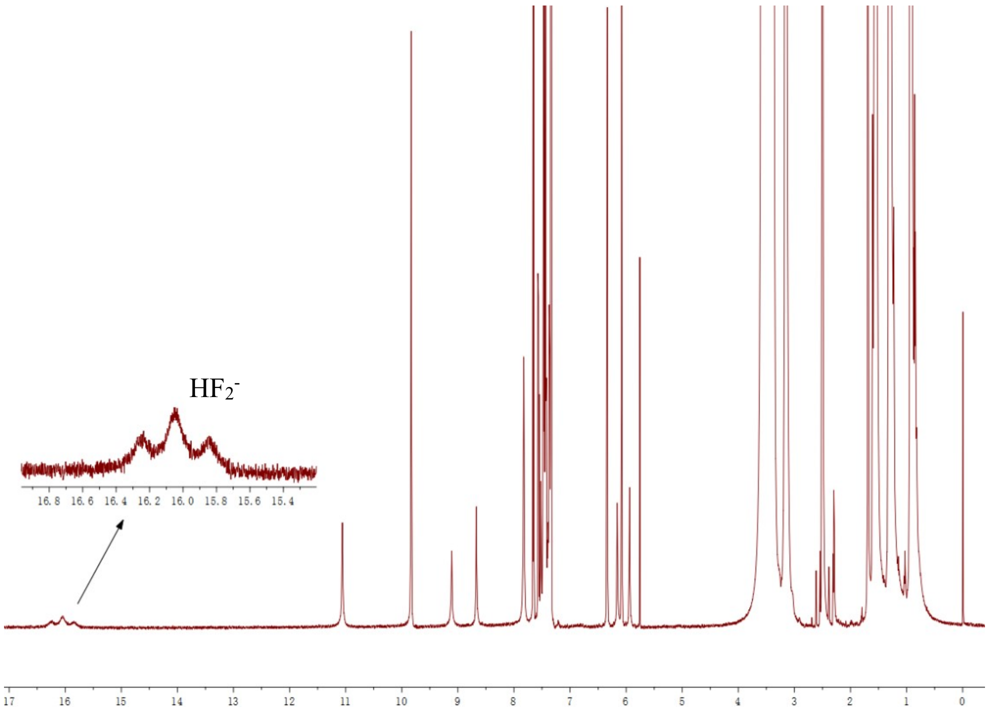


Figure S6: ^{1}H NMR spectrum of **2** recorded in the presence of excess TBAF in DMSO-d_6 at rt.

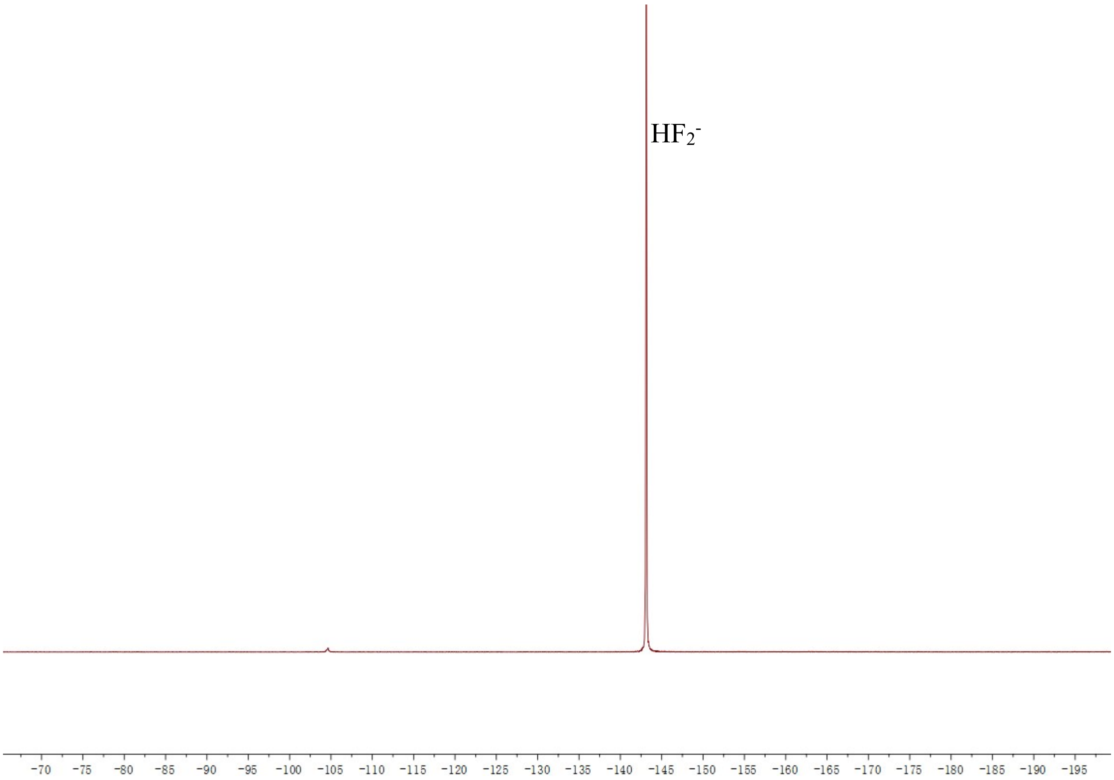


Figure S7: ^{19}F NMR spectrum of **2** recorded in the presence of excess TBAF in DMSO-d_6 at rt.

III. UV-Vis Spectral Studies and Photos

Figure S8: Photos of **1** in DCM, methanol, acetone, ethyl acetate, acetonitrile, THF, DMF and DMSO, respectively.

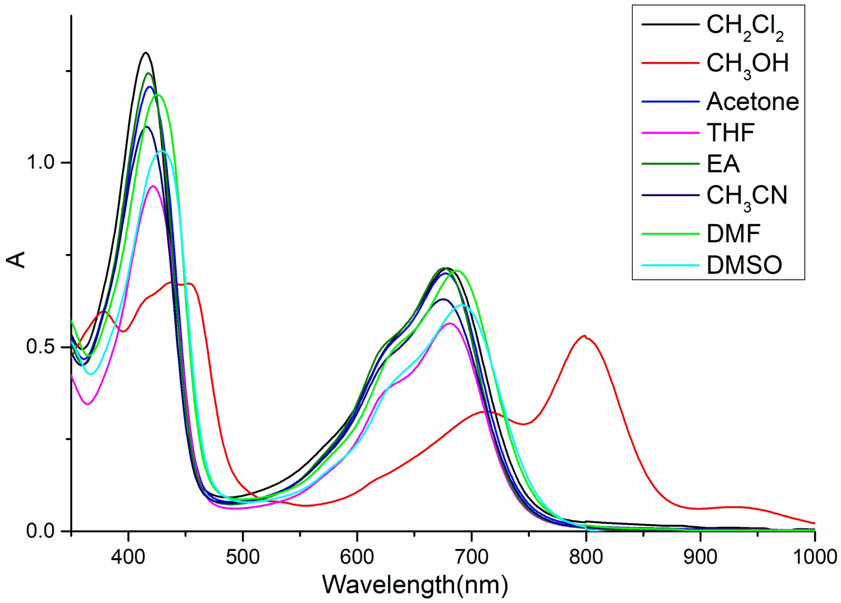


Figure S9: UV-Vis absorption spectra of **1** (3.51×10^{-5}M) recorded in different solvents at rt.

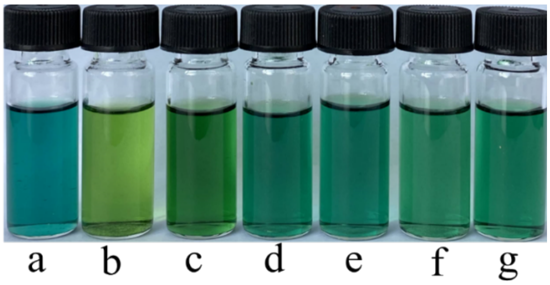


Figure S10: Photos of **1** in DCM, methanol, ethanol, 1-propanol, 2-propanol, 1-butanol and 1-hexanol. respectively.

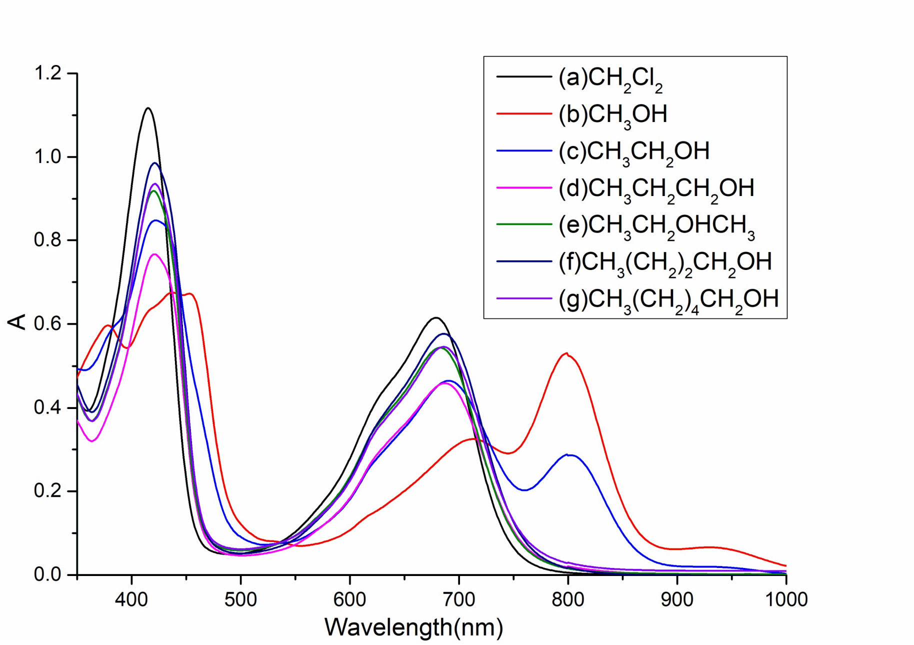


Figure S11: UV-Vis absorption spectra of **1** recorded in different alcohols at rt.

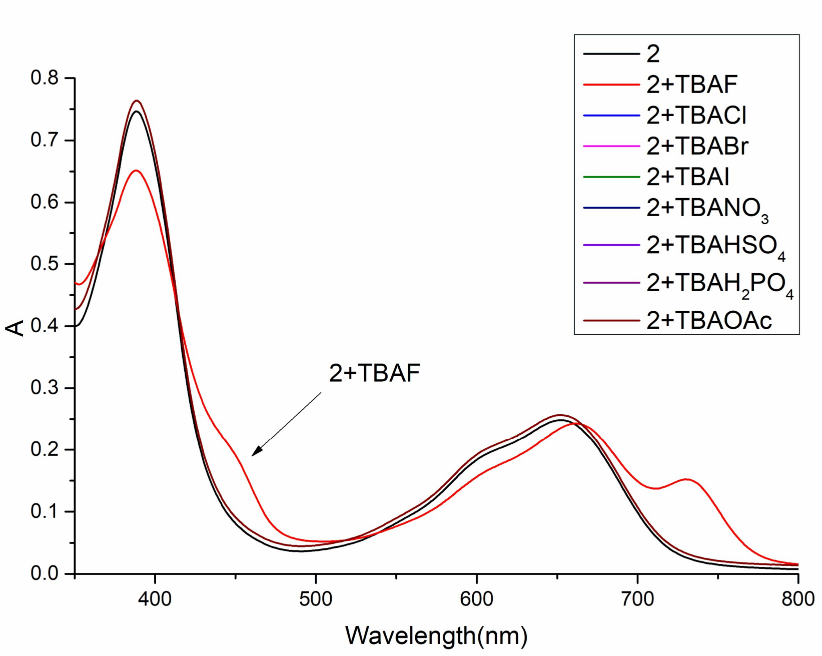


Figure S13: UV-Vis absorption spectra of **2** (5.9 X 10^{-4}M) recorded before and after the addition of excess TBA^+ salts of different anions (F^-, Cl^-, Br^-, I^-, $H_2PO_4^-$, HSO_4^-, ClO_4^-, CH_3COO^-, NO_3^-) in DCM.

Figure S14: Photos of **2** before and after the addition of excess TBA^+ salts of different anions (F^-, Cl^-, Br^-, I^-, $H_2PO_4^-$, HSO_4^- , ClO_4^-, CH_3COO^-, NO_3^-) in DCM.

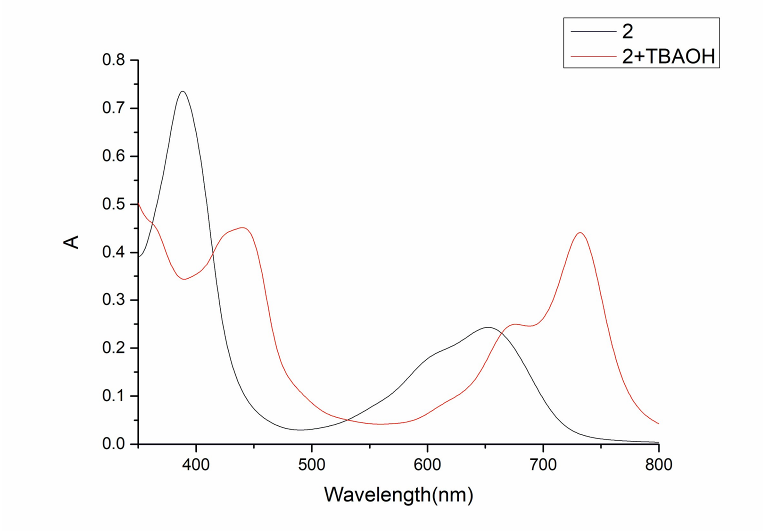


Figure S15 : Changes of UV-Vis absorption of **2** recorded upon the incremental addition of TBAF in DCM (from 1 to 100 equiv).

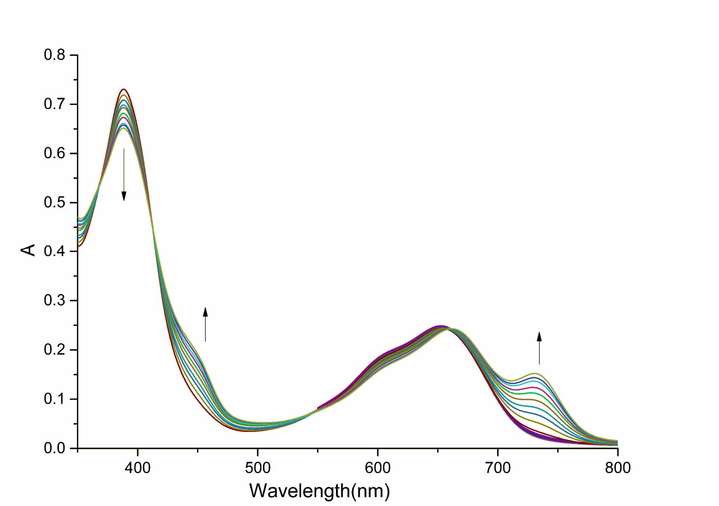


Figure S16: UV-Vis spectra of **2** recorded before and after the addition of excess TBAOH in DCM.

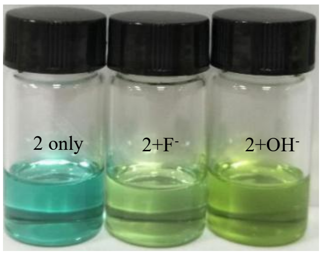


Figure S17. Photos of **2** upon treatment with excess TBAF and TBAOH in DCM.

IV. X-ray Experimental

Compound 1. A black plate crystal of $C_{40}H_{30}N_4Cl_2$ having approximate dimensions of 0.02 x 0.37 x 0.44 mm was mounted on a glass fiber. All measurements were made on a Bruker X8 APEX II diffractometer with graphite monochromated Mo-K radiation. The data were collected at a temperature of -100.0 ± 0.1℃. Of the 30927 reflections that were collected, 4218 were unique (R_{int} = 0.045); equivalent reflections were merged. Data were collected and integrated using the Bruker SAINT software package. The structure was solved by direct methods. All non-hydrogen atoms were refined anisotropically. All C-H hydrogen atoms were placed in calculated positions but were not refined. All N-H hydrogen atoms were located in difference maps and refined isotropically. All refinements were performed using the SHELXTL crystallographic software package Bruker-AXS.

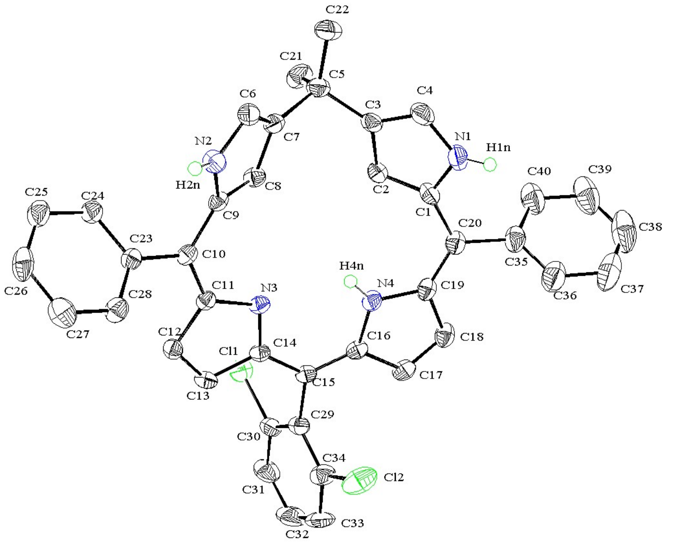


Figure S18. Crystal structure of compound **1**.

Table S1. Crystal data for 1.

Empirical Formula	$C_{40}H_{30}N_4Cl_2$
Formula Weight	637.58
Crystal Color, Habit	black, plate
Crystal Dimensions	0.02 X 0.37 X 0.44mm
Crystal System	monoclinic
Lattice Type	primitive
Lattice Parameters	a = 18.3920(8)Å b = 12.0721(5)Å c = 14.3164(5)Å = 90.0 ^{o} = 90.390(2) ^{o} = 90.0 ^{o} V = 3178.6(2) Å^{3}
Space Group	*P* 2_1/*c* (#14)
Z value	4
D_{calc}	1.332 g/cm^{3}
F_{000}	1328.00
λ(MoKα)	2.41 cm^{-1}

Compound 2. A blue plate crystal of $C_{40}H_{28}N_4O_2Cl_2.C_6H_{14}$ having approximate dimensions of 0.02 x 0.05 x 0.08 mm was mounted on a glass fiber. All measurements were made on a Bruker APEX DUO diffractometer with graphite monochromated Cu-Kα radiation. The data were collected at a temperature of -183.0 ± 0.1℃. Of the 34975 reflections that were collected, 13113 were unique (R_{int} = 0.053); equivalent reflections were merged. Data were collected and integrated using the Bruker SAINT software package. The structure was solved by direct methods. The material crystallizes with two molecules in the asymmetric unit, in addition to two molecules of hexane.

One hexane molecule has disorder that is modeled in two orientations, except for C91, which was split into three orientations. All non-hydrogen atoms except C91Cwere refined anisotropically. NH hydrogens were located in difference maps and refined isotropically. All other hydrogen atoms were placed in calculated positions. All refinements were performed using the SHELXL-97 via the WinGX interface.

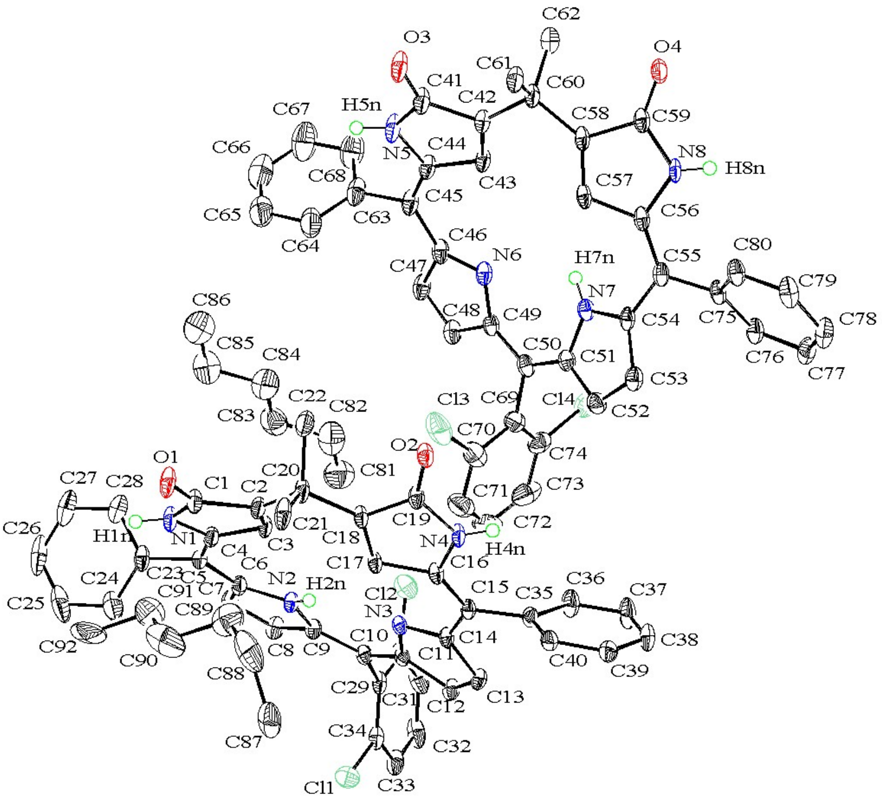


Figure S19. Crystal structure of compound **2**.

Table S2. Crystal data for 2.

Empirical Formula	$C_{46}H_{42}\,N_4O_2$Cl2
Formula Weight	753.74
Crystal Colour, Habit	blue, plate
Crystal Dimensions	0.02 X 0.05 X 0.08 mm
Crystal System	triclinic
Lattice Type	primitive
Lattice Parameters	a = 15.3032(3) Å b = 16.6779(3) Å c = 17.5125(4) Å = 64.714(1)^{o} = 73.361(1)^{o} = 77.895(1)^{o} V = 3852.4(2) Å^{3}
Space Group	*P* -1(#2)
Z value	4
D_{calc}	1.300 g/cm^{3}
F_{000}	1584.00
λ(Cu-Kα)	18.63 cm^{-1}

V. Mass Spectra

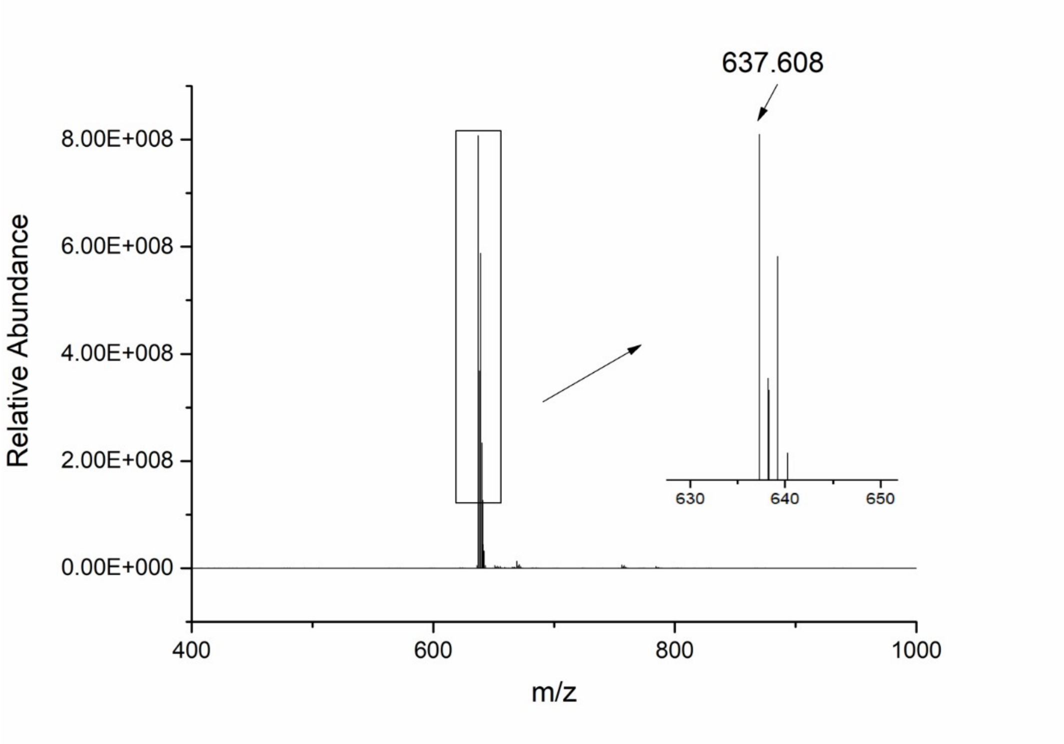


Figure S20. High resolution mass spectrum of **1**.

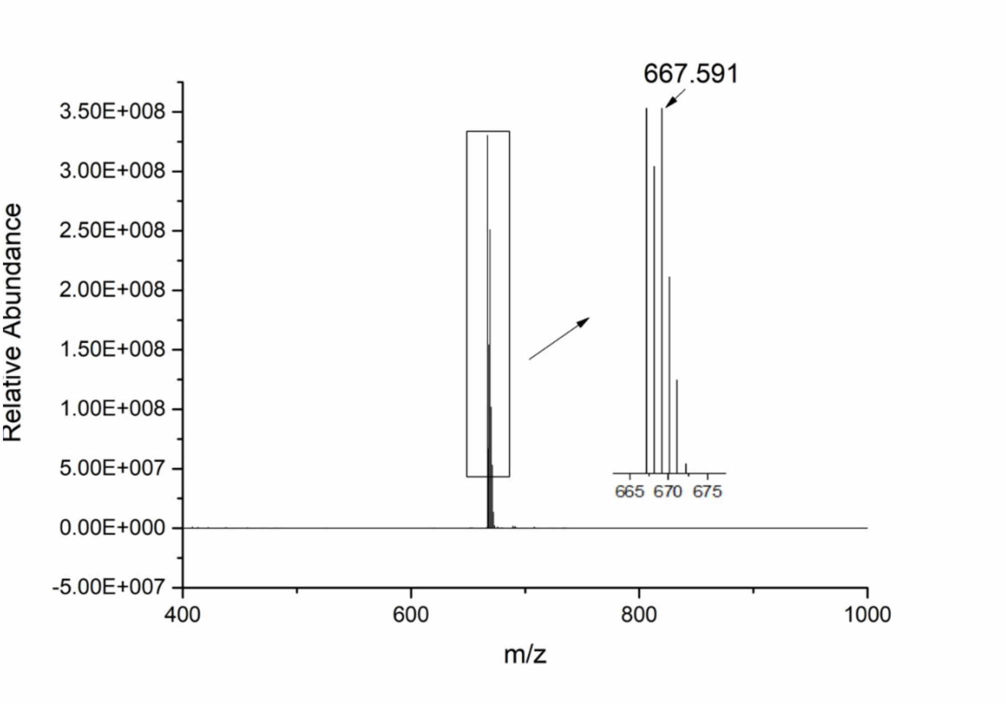


Figure S21. High resolution mass spectrum of **2**.

VI. Electrochemical Studies

Cyclic voltammetry (CV) measurements were carried out at a scan rate of 50 mV/s using 0.1 M TBAPF$_6$ as the supporting electrolyte in dichloromethane (DCM). Experiments were performed in a three-electrode electrochemical cell equipped with a platinum (Pt) working electrode and a Pt wire counter electrode. Ferrocene/ferrocenium (Fc/Fc$^+$) was used as the internal reference.

Table S3. Electrochemical data for N-confused phlorinone **2**.

Oxidation (V)		Reduction (V)		HOMO-LUMO Gap (V)[a]
E_{ox1}	E_{ox2}	E_{red1}	E_{red2}	
-0.07	0.95	-0.85	-1.23	0.78

[a] HOMO−LUMO = E_{ox1}−E_{red1}

VII. Supporting References

1. Zhang, Z.; Chen, Y.; Dolphin, D. *Dalton Trans.* 2012, **41**, 4751–4753.