Supplementary Information for

Fe(III) complexes with prolonged luminescence lifetimes and symmetry-breaking charge separation

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Materials and Methods

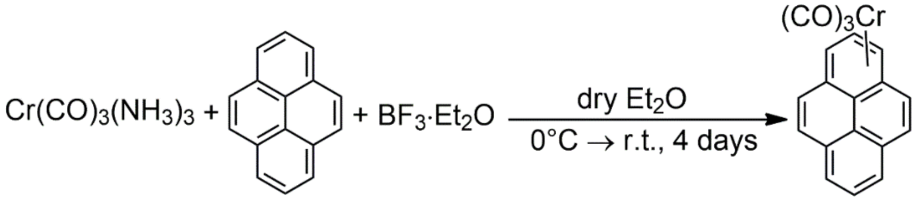
Synthesis and characterization

All the reactions, except metathesis reactions, have been carried out under an inert nitrogen atmosphere. Chromium(0) hexacarbonyl, boron trifluoride diethyl etherate, 2,2,6,6-Tetramethylpiperidine, n-butyllithium, chlorotrimethylsilane solution (2 M in cyclohexane), boron trichloride solution (1.0 M in methylene chloride), 1-methylimidazole, trimethylsilyl trifluoromethanesulfonate, lithium bis(trimethylsilyl)amide, 4-(trimethylsilyl)phenylboronic acid, 1,3-dicyclohexylimidazolium chloride and all dry solvents were purchased from Sigma Aldrich. Iron(II) bromide (ultra dry, 99.995%) was purchased from Thermo Scientific and bis(1,5-cyclooctadiene)nickel(0) (wax encapsulated) was purchased from TCI. The synthesis of 2-(trimethylsilyl)-pyrene (**2-tmspy**) and tri(methylsilyl)phenylboronic acid neopentyl ester (**tmspbanpe)** were performed following literature procedures***R1,R2***. NMR spectra were recorded on a Varian 500 spectrometer, using deuterated solvents (purchased from Sigma-Aldrich) at 295 K and calibrated with the residual NMR solvent: CD_3CN (1.94 ppm for ^1H NMR spectra and 1.32 and 118.26 ppm for ^{13}C NMR spectra) and DMSO-d_6 (2.50 ppm for ^1H NMR spectra and 39.52 ppm for ^{13}C NMR spectra).

Triaminechromium tricarbonyl, **$Cr(CO)_3(NH3)_3$**

Chromium hexacarbonyl (10 g, 45,44 mmol), potassium hydroxide (18 g, 320.80 mmol) and a degassed solvent mixture (ethanol/ n-butanol/ water, 35/5/2 v/v) and heated under reflux for 4 hours. The reaction mixture was cooled to room temperature and placed in an ice bath. A degassed aqueous solution of ammonia (85 mL) was added and after 2 hours of stirring, a yellow solid was isolated through a Schlenk frit (87 %).

(Pyrene)chromium tricarbonyl, **$pyCr(CO)_3$**

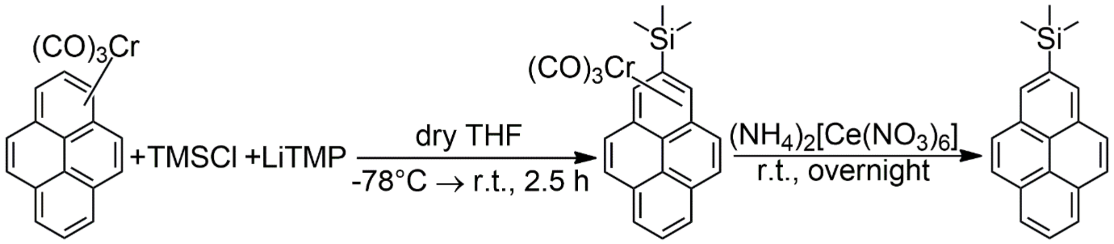


In a two-neck flask charged with **$Cr(CO)_3(NH_3)_3$** (2.08 g, 11.11 mmol), pyrene (2.4 g, 11.87 mmol) and 60 mL of dry diethyl ether, boron trifluoride diethyl etherate (BF_3Et_2O, 45.4 mmol, 5.6 mL, 1.15 g/ml) was added dropwise at 0 °C. The reaction mixture was stirred at room temperature for 4 days and filtered with a Schlenk frit. The precipitate was dissolved in dichloromethane and extracted with an aqueous solution of HCl 1 M. The organic phase was dried over anhydrous magnesium sulfate, rotary evaporated and recrystallized in diethyl ether (45 %).

Lithium 2,2,6,6-tetramethylpiperidide, **LiTMP**

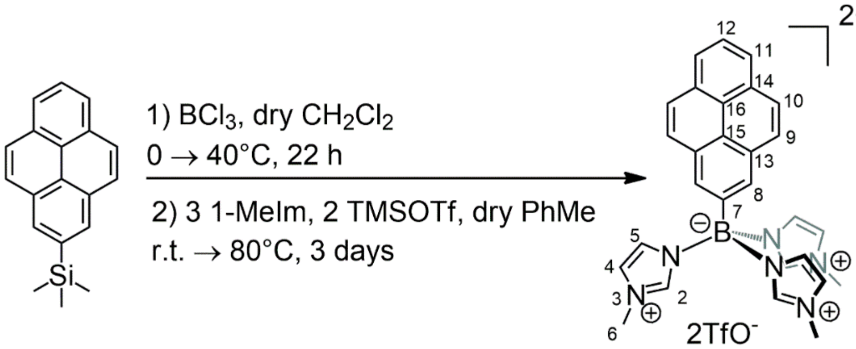
To a solution of 2,2,6,6-Tetramethylpiperidine (3 mL, 17.6 mmol, 0.83 g/mL) in 25 mL of dry tetrahydrofuran was added a solution of n-butyllithium in cyclohexane 2 M (9 mL, 18 mmol) at -78°C. The resulting solution was stirred at room temperature for 30 minutes, obtaining a dark orange **LiTMP** solution.

2-(trimethylsilyl)-pyrene, **2-tmspy**



In a two-neck flask containing **pyCr(CO)$_3$** (1 g, 2.96 mmol) in 30 mL of dry tetrahydrofuran was added, at -78°C, a solution of chlorotrimethylsilane (**TMSCl**, 1.2 mL, 9.44 mmol, 0.856 g/mL) and then the freshly prepared solution of **LiTMP**. After stirring at -78°C for 1.5 hours, it was quenched with 50 mL of HCl 0.3 M, allowed to warm to room temperature, and then after 1 hour diluted with 50 mL of diethyl ether. To decomplex the desired product, a solution of cerium ammonium nitrate, 0.2 M in 25 mL of HCl 0.3 M were added and the resulting mixture was left under constant magnetic stirring overnight. The reaction mixture was acidified with HCl 1 M until pH 1 and extracted with petroleum ether (3 x 100 mL). The resulting organic phase was washed with brine, dried over magnesium sulfate, and concentrated under reduced pressure. The pure compound was isolated by column chromatography on alumina using a hexane/ethyl acetate mixture (95:5 V/V) as eluent, with a yield of 50 %.

2-pyrenyl[tris(3-methylimidazol-1-ylidene)]borate bis(hexafluorophosphate), **pytmeimb (A)**

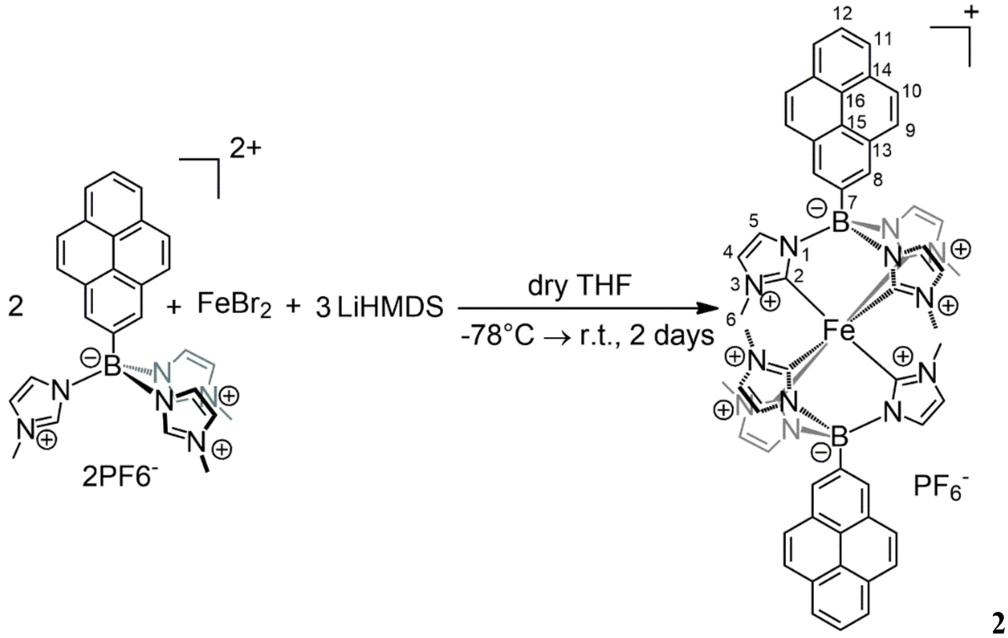


A

To a solution of **2-tmspy** (400 mg, 1.46 mmol) in 3 mL of dry dichloromethane was added at 0°C a solution of boron trichloride 1 M in dichloromethane (4,5 mmol, 4.5 mL). After 1 h, the ice bath was removed, and the reaction mixture was stirred for 19 h, then the temperature was increased to 40°C and the reaction mixture furtherly reacted for 3 h. The solvent was removed under reduced pressure and then 4 mL of toluene and 600 µL of 1-methylimidazole (**1-MeIm**, 7.5 mmol, 1.03 g/mL) were added. After 15 minutes of stirring, a solution of trimethylsilyl trifluoromethanesulfonate (**TMSOTf**, 800 µL, 4.4 mmol, 1.23 g/mL) in 4.5 mL toluene was added dropwise and the reaction mixture was heated to 80°C. After 3 days, the flask contents were concentrated, solubilized in dichloromethane and extracted three times with water. The desired compound, which precipitates, was collected through filtration as trifluoromethanesulfonate salt. It was solubilized in the minimum amount of ethanol and ammonium hexafluorophosphate (233 mg, 1.43 mmol) was added. A white solid was isolated through filtration (61%).

^{1}H NMR (500 MHz, DMSO): δ (ppm) 8.66 (t, 3H, 1.8 Hz, H_2), 8.32 (d, J = 7.7 Hz, 2H, H_{11}), 8.22 (d, J = 9.0 Hz, 2H, H_{10}), 8.13 (d, J = 9.0 Hz, 2H, H_9), 8.10 (t, J = 7.7 Hz, 1H, H_{12}), 8.00 (s, 2H, H_8), 7.87 (t, J = 1.8 Hz, 3H, H_5), 7.55 (t, J = 1.8 Hz , 3H, H_4), 3.86 (s, 9H, H_6); 13C NMR (126 MHz, DMSO) δ (ppm) 139.78 (C_2), 130.79 (C_{14}), 130.34 (C_{15}), 129.38 (C_8), 127.75 (C_9), 127.39 (C_{10}), 126.54 (C_{12}), 125.17 (C_{11}), 124.69 (C_5), 124.15 (C_4), 123.57 ($C_{16,17}$), 35.5 (C_6).

Bis{2-pyrenyl[tris(3-methylimidazol-1-ylidene)]borate}Fe(III) hexafluorophosphate, **[Fe(pytmeimb)$_2$](PF$_6$), 2**

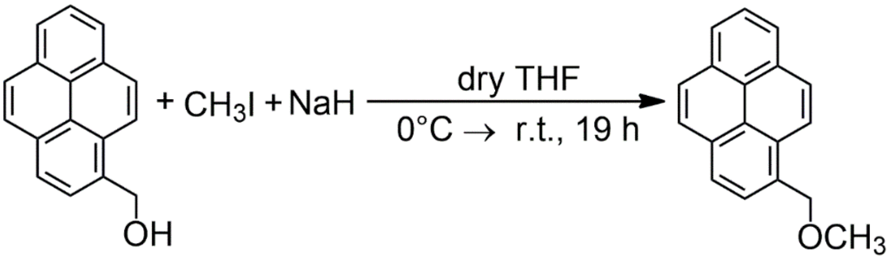


2

(pytmeimb)(PF$_6$)$_2$ (390 mg, 0.52 mmol) was dried under vacuum at 80°C overnight. Dry THF (10 mL) was added at room temperature and then the mixture was cooled at -78°C. A solution of lithium bis(trimethylsilyl)amide 1 M in THF (**LiHMDS**, 2 mL, 2 mmol) was added dropwise and after 40 min of constant magnetic stirring, an anhydrous, freshly prepared, iron(II) bromide solution (prepared sonicating iron(II) bromide (54 mg, 0.25 mmol) in 5 mL of dry THF for 30 minutes in a Schlenk flash) was introduced via cannula. The reaction mixture was allowed to slowly reach room temperature and then was stirred at room temperature for 2 days. Solvents were removed under reduced pressure and the residue was solubilized in acetonitrile and filtered. The resulting solid, solubilized in ethanol, was treated with an excess of ammonium hexafluorophosphate inducing the formation of a red precipitate. Then it was eluted through a size-exclusion column using Sephadex G-10 as stationary phase and dichloromethane as eluent. The compound, solubilized in dichloromethane, was purified on alumina PLC (1.2 mm thickness) using toluene/acetonitrile, 3:1 v/v, as eluent. The product of interest was eluted as a second band, recovered with dichloromethane extractions, concentrated and reprecipitated in diethyl ether. The pure compound was obtained as a dark pink solid with a 15 % yield (43.5 mg).

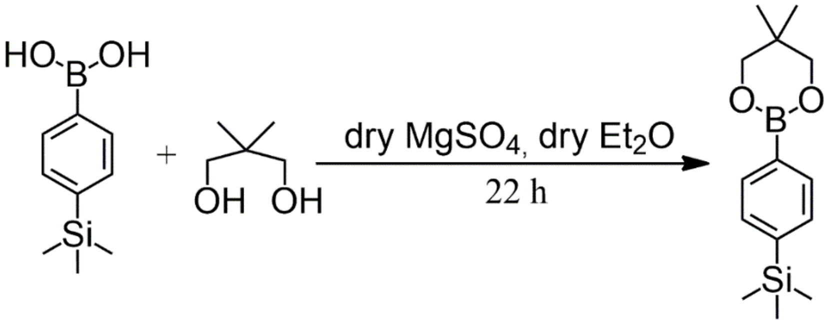
^{1}H NMR (500 MHz, CD_3CN): δ (ppm) 15.66 (s, 4H, H_8), 10.41 (d, *J* = 8.1 Hz, 4H, H_9), 9.38 (d, *J* = 8.1 Hz, 4H, H_{10}), 9.13 (d, *J* = 7.8 Hz, 4H, H_{11}), 8.77 (t, *J* = 7.8 Hz, 2H, H_{12}), 5.14 (s, 18H, H_6), 1.66 (s, 6H, H_5), -12.31 (s, 6H, H_4); ^{13}C NMR (126 MHz, CD_3CN): δ (ppm) 137.34 (C_8), 135.22 (C_{13}), 133.86 (C_{14}), 131.44 (C_9), 129.82 (C_{10}), 128.25 (C_{12}), 126.97 (C_{11}), 49.23 (C_4), 14.76 (C_5), -28.65 (C_6).

2-methoxymethylpyrene, **2-meomepy**



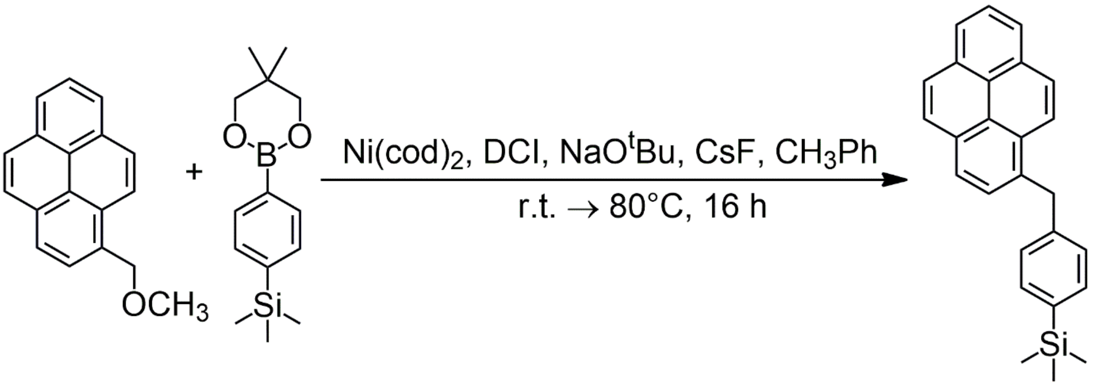
Sodium hydride 60 % w/w in mineral oil (260 mg, 6.50 mmol) was added in 20 mL of dry tetrahydrofuran and then 1-pyrenemethanol (1 g, 4.31 mmol) was introduced at 0°C. The bath was removed and after 1 h of stirring, methyl iodide (400 µL, 2.28 g/mL, 6.4 mmol) was poured to the dispersion. After 19 hours, the reaction was quenched with about 10 mL of methanol and concentrated under reduced pressure. The residue was solubilized in acetone and filtered. The dried filtrate, which forms an orange oil, was chromatographed on silica using petroleum ether/ethyl acetate (95:5) as eluent to isolate the desired product (95 % yield).

Tri(methylsilyl)phenylboronic acid neopentyl ester, **tmspbanpe**



Three freeze-pump-thraw cycles were performed in a two-neck flask containing an excess anhydrous magnesium sulfate (1.3 g, 10.80 mmol), 4-(trimethylsilyl)phenylboronic acid (1 g, 5.15 mmol), neopentyl glycol (542 mg, 5.20 mmol) and 15 mL of dry diethyl ether. After 22 h, the reaction mixture was loaded onto a plug of silica gel, washed with copious amounts of diethyl ether and concentrated under reduced pressure, obtaining an off-white solid (1.33 g, 99 % yield).

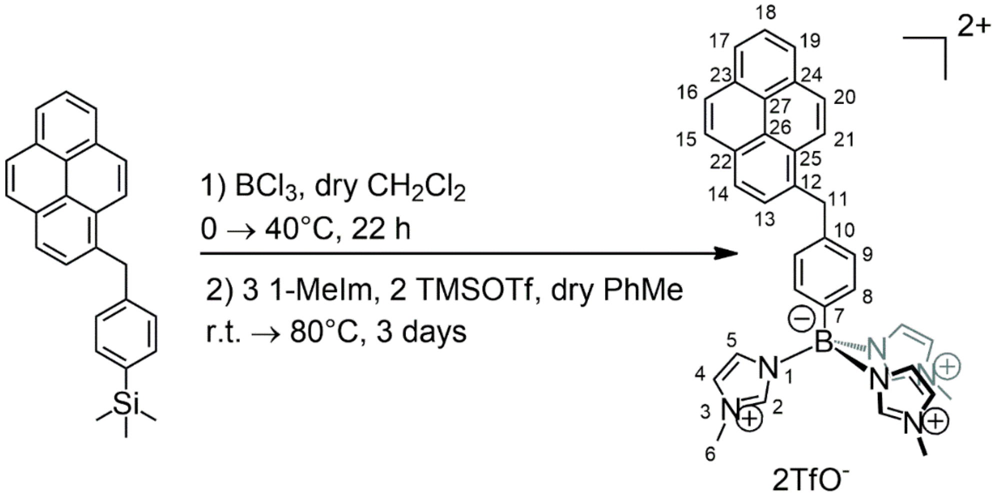
4-[(1-pyrenyl)methyl]phenyl[tris(3-methylimidazol-1-ylidene)]borate} bis(hexafluorophosphate), **pyphtmesi**



In glove box, a two-neck flask was charged with 5 paraffin capsules of bis(1,5-cyclooctadiene)nickel(0) (about 0.25 mmol), 1,3-dicyclohexylimidazolium chloride (**DCI**, 0.50 mmol, 134 mg), sodium tert-butoxide (0.63 mmol, 60 mg) and 4.5 mL toluene. After about 3 min, cesium fluoride (5.00 mmol, 760 mg), **tmspbanpe** (3.75 mmol, 984 mg) and **2-**

meomepy (2.47 mmol, 610 mg) were added sequentially. The flask was removed from the glove box and heated under reflux for 16 h. The reaction crude was placed in a Soxhlet extractor and washed with methanol MeOH for 24 h. The desired product was isolated through PLC on silica using hexane/dichloromethane (3:1 v/v) as mobile phase and diethyl ether for the extraction (260 mg, 32%).

4-(pyrenylmethyl)phenyl[tris(3-methylimidazol-1-ylidene)]borate} bis(hexafluorophosphate), **pyphtmeimb (B)**

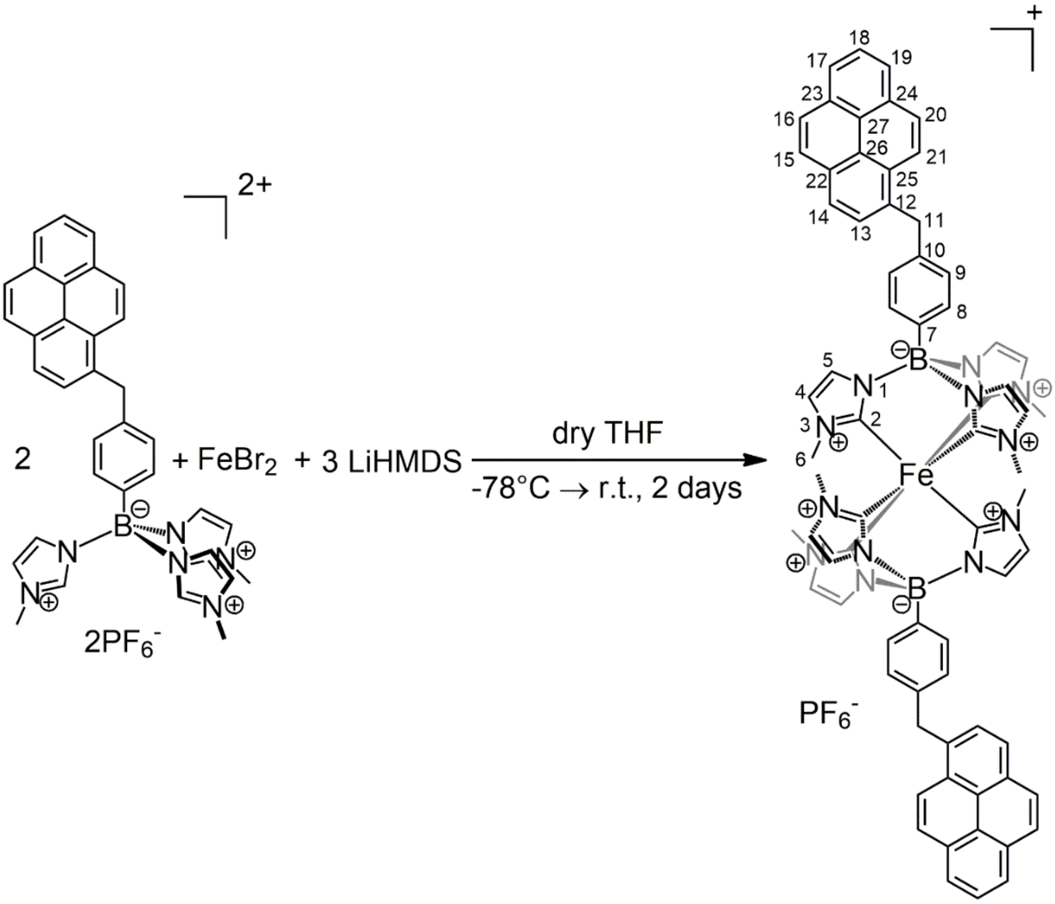


B

The synthetic procedure was the same as that of **pytmeimb,** using 250 mg of **pyphtmesi** (0.714 mmol) in 1.5 mL of dichloromethane, 2,5 mL of boron trichloride 1 M in dichloromethane (2,5 mL), 2 mL of toluene, 300 µL of 1-methylimidazole (**1-MeIm**, 3.8 mmol, 1.03 g/mL) were added. After 15 minutes of stirring, a solution of trimethylsilyl trifluoromethanesulfonate (**TMSOTf**, 400 µL, 2.2 mmol, 1.23 g/mL) in 2 mL toluene was added dropwise and the reaction mixture was heated to 80°C. After 4 days, the solvent was removed. The residue was solubilized in dichloromethane and extracted 3 times with water (3x30 mL). The organic phase was anhydrified with magnesium sulfate and brought to dryness, obtaining a dark brownish oil. This was solubilized in the minimal amount of dichloromethane and allowed to precipitate in diethyl ether. The precipitate was filtered and washed with plenty of diethyl ether, obtaining the ligand as trifluoromethanesulfonate. The solid was solubilized in ethanol and treated with ammonium hexafluorophosphate (174 mg). The desired product, as hexafluorophosphate salt, was isolated through filtration and washed with ethanol and diethyl ether (45%).

^{1}H NMR (500 MHz, DMSO) δ (ppm) 8.51 (t, J = 1.6 Hz, 3H, H_2), 8.44 (d, J = 9.3 Hz, 1H, H_{13}), 8.29 (d, J = 7.8 Hz, 1H, H_{21}), 8.28 (d, J = 7.6 Hz, 2H, $H_{17,19}$), 8.21 (d, J = 9.3 Hz, 1H, H_{14}), 8.16 (dd, J = 9.0 Hz, 2H, $H_{15,16}$), 8.08 (t, J = 7.6 Hz, 2H, H_{18}), 8.06 (d, J = 7.8 Hz, 2H, H_{20}), 7.75 (t, J = 1.6 Hz, 3H, H_5), 7.36 (d, J = 8.2 Hz, 2H, H_8), 7.32 (t, J = 1.6 Hz, 3H, H_4), 7.01 (d, J = 8.2 Hz, 2H, H_9), 4.77 (s, 2H, H_{11}), 3.79 (s, 9H, H_6); ^{13}C NMR (126 MHz, DMSO) δ (ppm) 141.94 (C_2), 139.37(C_{10}), 134.84 (C_{12}), 132.88 (C_9), 130.83 (C_{27}), 130.32 (C_{15}), 129.64 (C_{26}), 128.53 (C_8), 128.43 (C_{20}), 127.48 (C_{14}), 127.40 (C_{15}), 126.84 (C_{16}), 126.31 (C_{18}), 125.21 (C_{21}), 125.05 (C_{19}), 124.95 (C_{17}), 124.46 (C_5), 124.31 ($C_{22,23}$), 123.97 (C_{13}), 123.85 ($C_{24,25}$), 123.82 (C_4), 37.99 (C_{11}), 35.41 (C_6).

Bis{4-(pyrenylmethyl)phenyl[tris(3-methylimidazol-1-ylidene)]borate} Fe(III) hexafluorophosphate, **[Fe(pyphtmeimb)$_2$](PF$_6$), 3**



3

The synthetic procedure was the same as that of [Fe(pytmeimb)$_2$](PF$_6$) using 250 mg of **pyphtmeimb** (0.3 mmol), 7 mL of THF, 1.4 mL of LiHMDS and a solution of iron(II) bromide (32.4 mg, 0.15 mmol in 3.5 mL of dry THF). After 48 h of stirring, the reaction mixture was concentrated under reduced pressure, solubilized in dichloromethane and filtered. The solid was solubilized in ethanol and after the addition of an excess of NH$_4$PF$_6$, the formation of a red solid occurred. The solid was dissolved in the minimum amount of dichloromethane and eluted through a size-exclusion column using Sephadex G10 as stationary phase. Then, it was purified through PLC (1.2 mm thickness) on alumina using toluene/acetonitrile (3:1 V/V) as eluent and dichloromethane. The product of interest was recovered with dichloromethane extractions, concentrated and reprecipitated in diethyl ether, with a yield of 15 % (29 mg).

^{1}H NMR (500 MHz, CD$_3$CN) δ (ppm) 14.55 (d, J = 5.5 Hz, 4H, H$_8$), 10.27 (d, J = 5.5 Hz, 4H, H$_9$), 9.89 (d, J = 9.5 Hz, 2H, H$_{13}$), 9.42 (d, J = 8 Hz, 2H, H$_{21}$), 9.00 (d, J = 8.0 Hz, 2H, H$_{20}$), 8.93 (d, J = 9.5 Hz, 2H, H$_{14}$), 8.61 (dd, 7.9 Hz, 1.1 Hz, 2H, H$_{19}$), 8.58 (d, 9.1 Hz, 2H, H$_{15}$), 8.51 (dd, J = 7.9 Hz, 1.1 Hz, 2H, H$_{17}$), 8.43 (d, J = 9.1 Hz, 2H, H$_{16}$), 8.28 (t, J = 7.9 Hz, 2H, H$_{18}$), 6.49 (s, 4H, H$_{11}$), 4.88 (s, 18H, H$_6$), 1.57 (s, 6H, H$_5$), -12.37 (s, 6H, H$_4$); ^{13}C NMR (126 MHz, CD$_3$CN) δ (ppm) 145.21 (C$_{10}$), 140.68 (C$_8$), 137.77 (C$_{12}$), 132.95 (C$_9$), 130.70 (C$_{21}$), 129.26 (C$_{14}$), 129.01 (C$_{15}$), 128.29 (C$_{16}$), 127.55 (C$_{18}$), 126.97 (C$_{20}$), 126.49 (C$_{19}$), 126.42 (C$_{17}$), 126.16 (C$_{13}$), 49.59 (C$_4$), 41.54 (C$_{11}$), 13.28 (C$_5$), -28.61 (C$_6$).

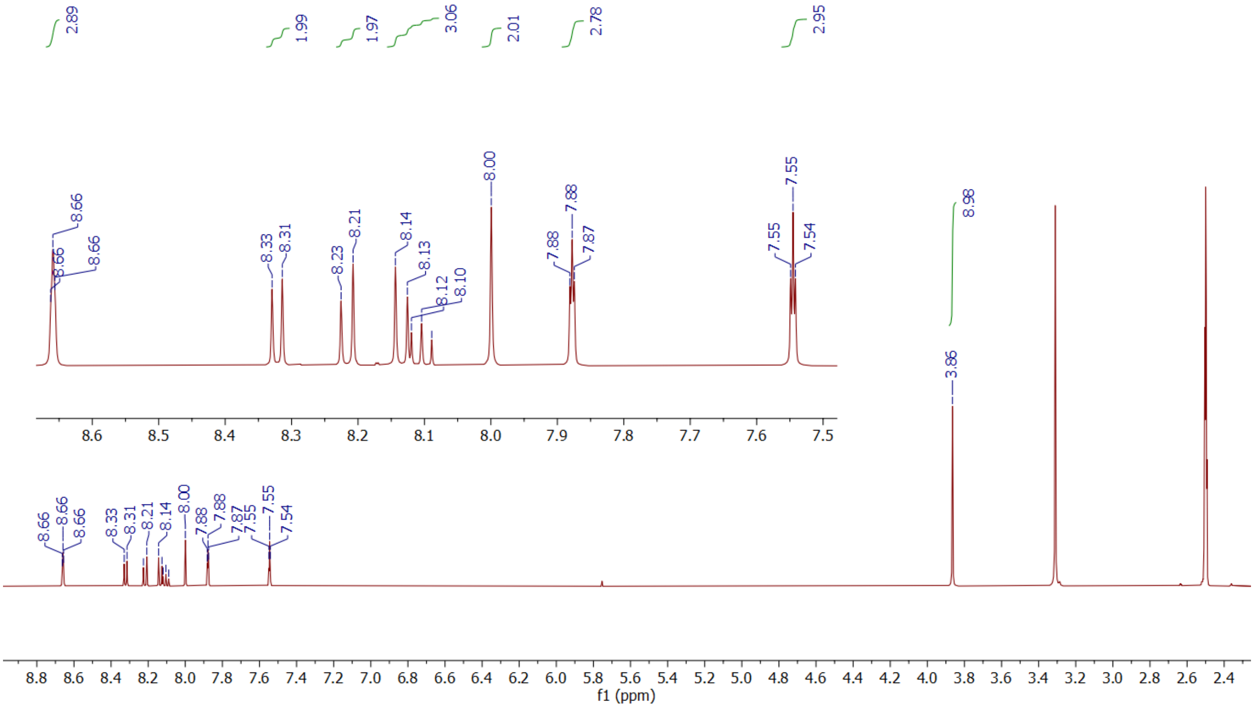


Fig. S1.

^{1}H-NMR spectrum of **A** (5 mM) in DMSO.

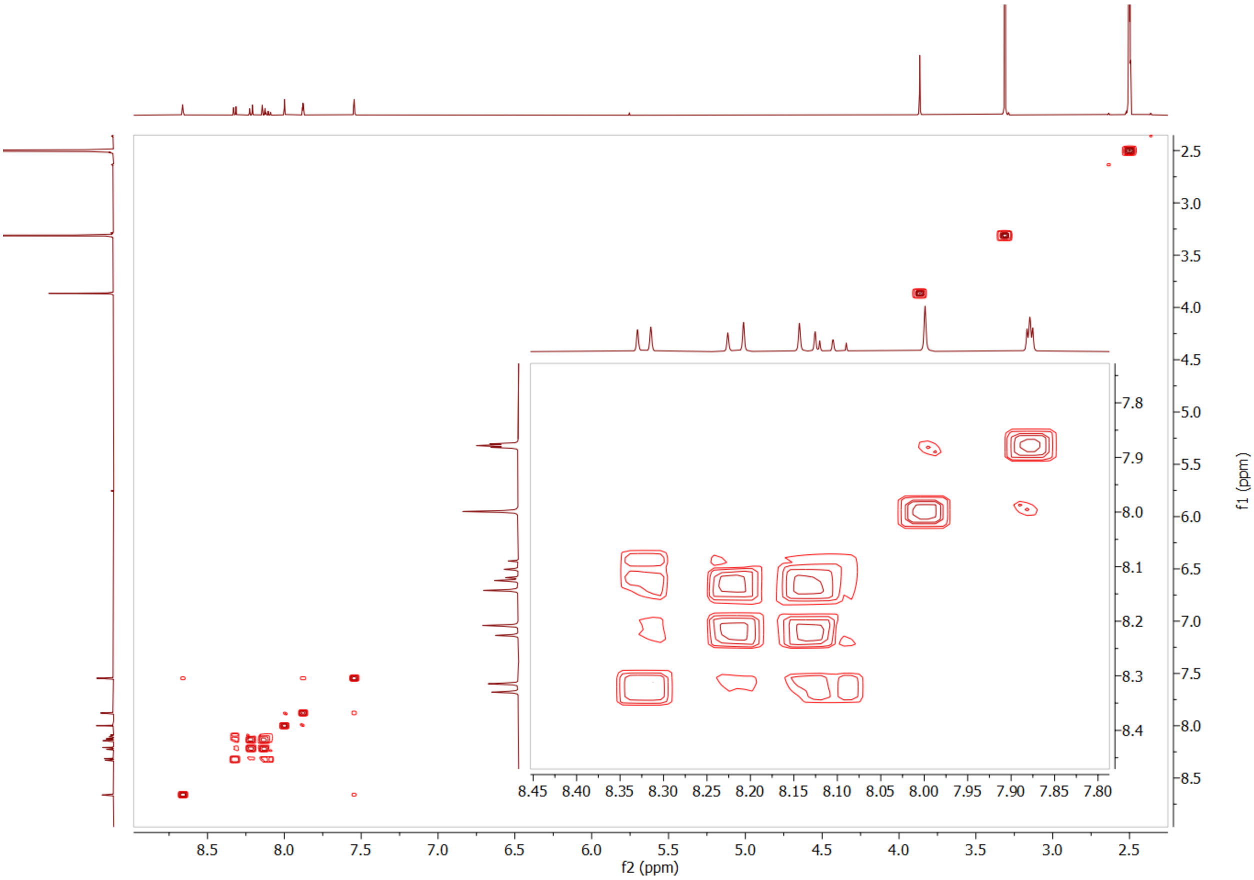


Fig. S2.
gCOSY spectrum of **A** (5 mM) in DMSO.

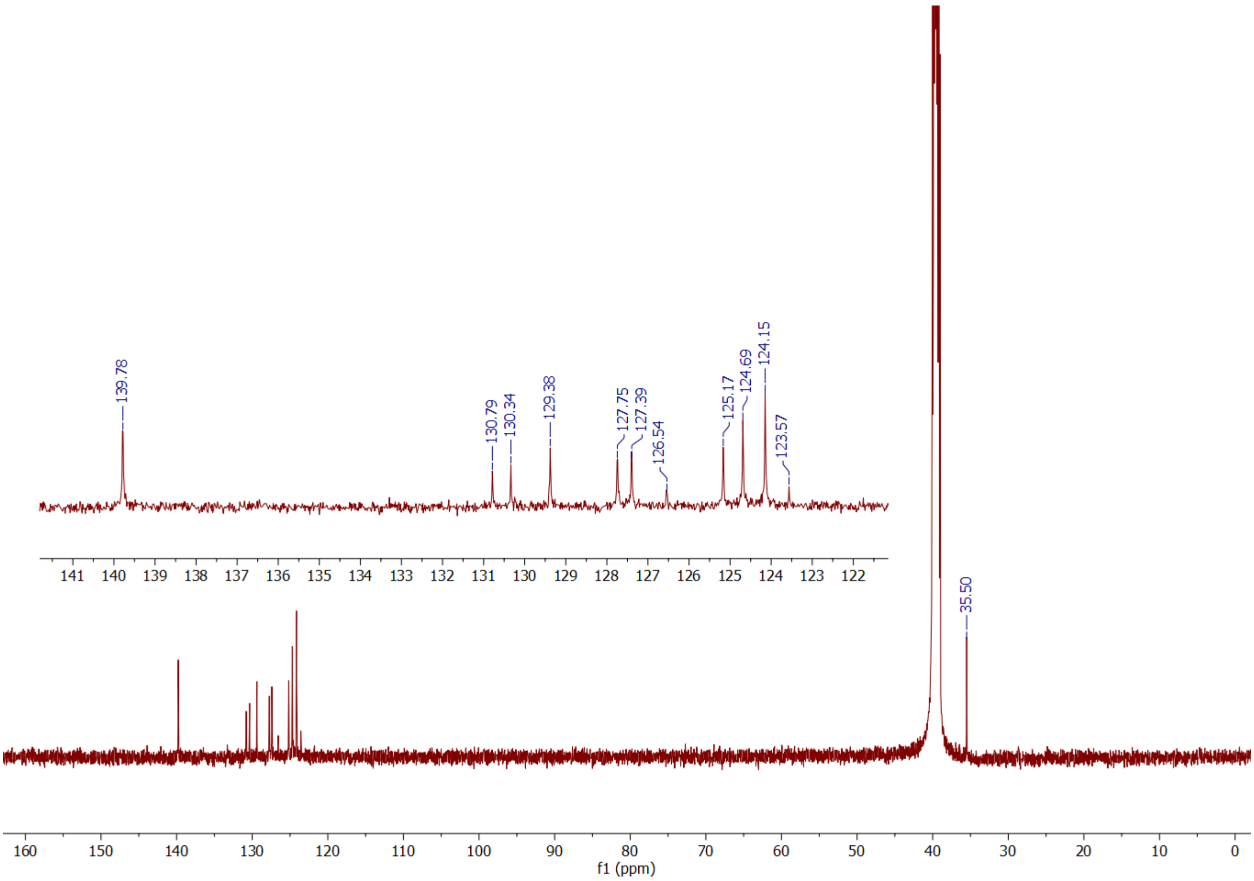


Fig. S3.

^{13}C-NMR spectrum of **A** (15 mM) in DMSO.

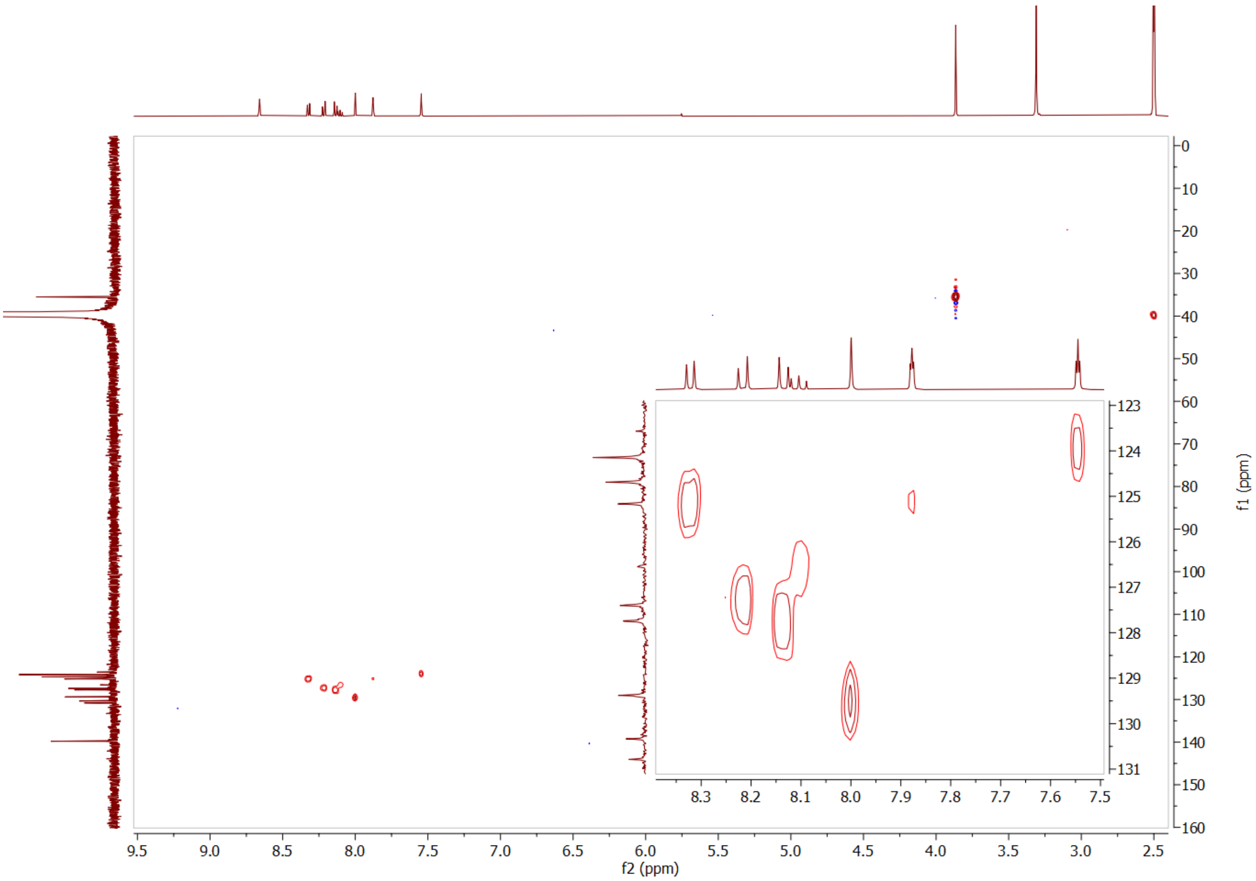


Fig. S4.

gHSQC spectrum of **A** (15 mM) in DMSO.

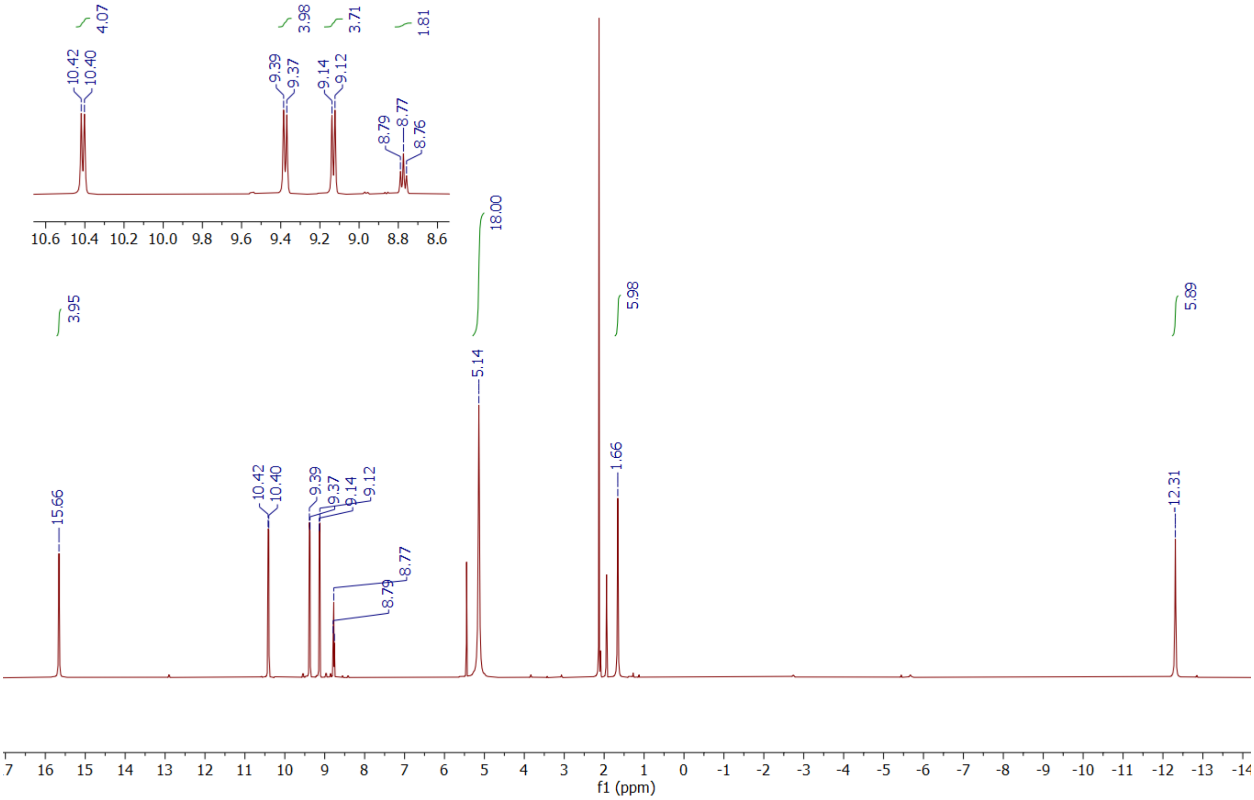


Fig. S5.

^{1}H-NMR spectrum of **2** (4 mM) in CD_3CN.

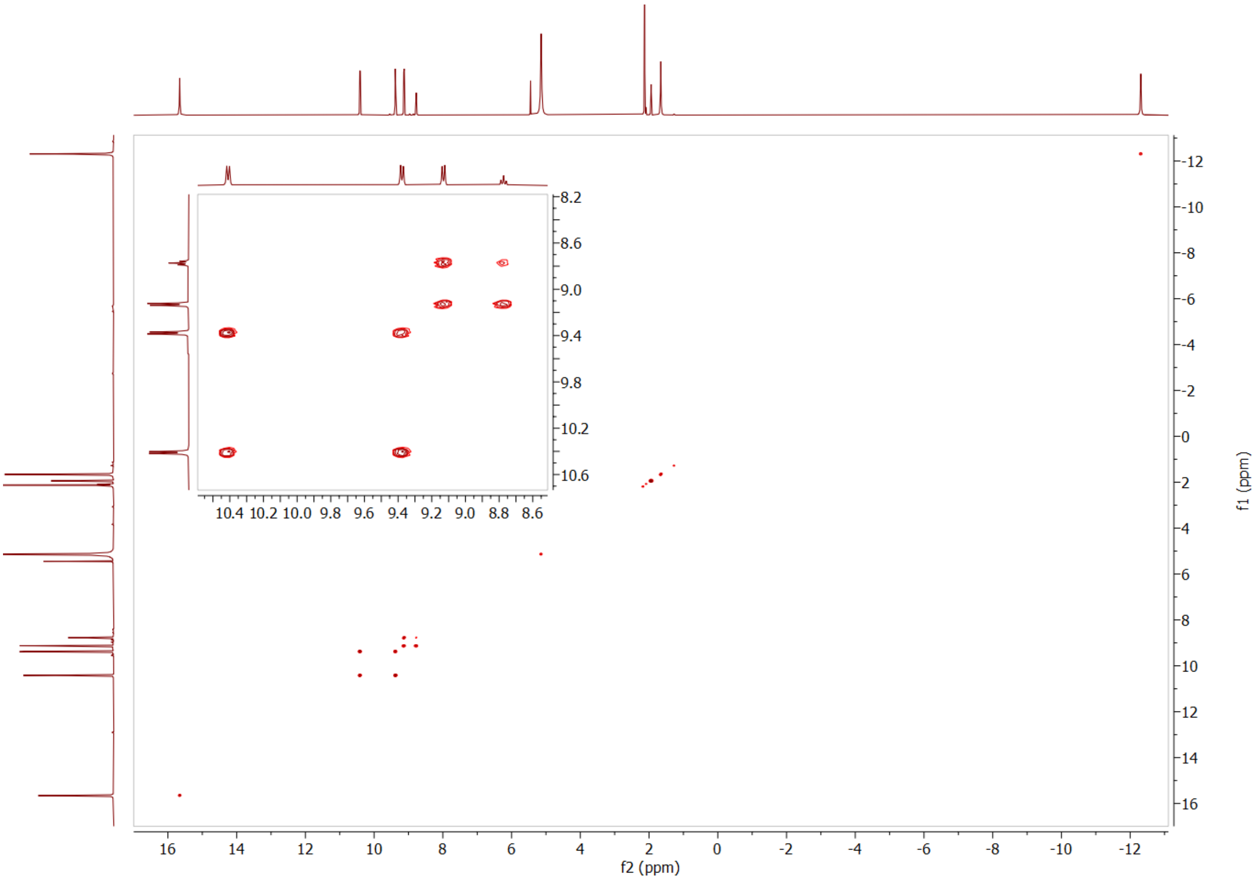


Fig. S6.
gCOSY spectrum of **2** (5 mM) in CD_3CN.

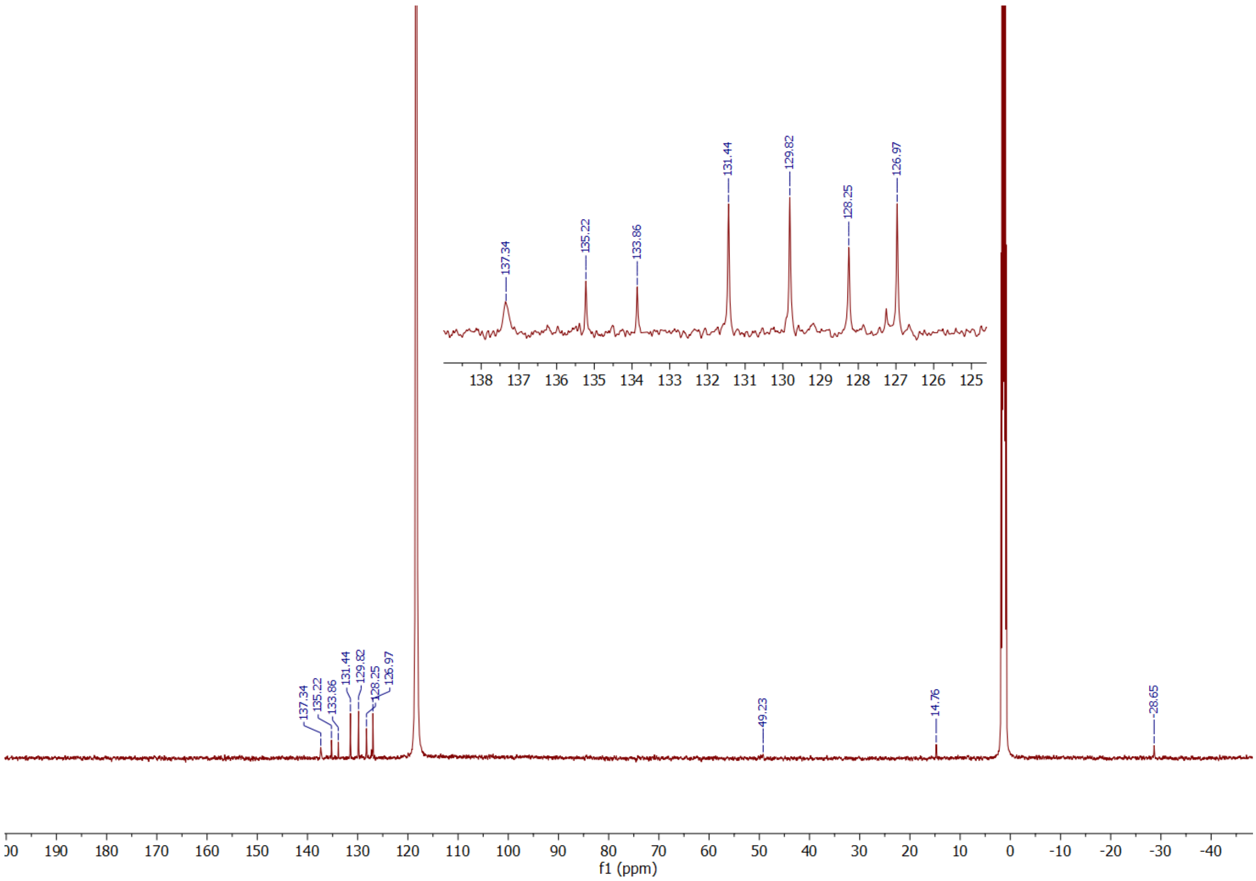


Fig. S7.

^{13}C-NMR spectrum of **2** (10 mM) in CD_3CN.

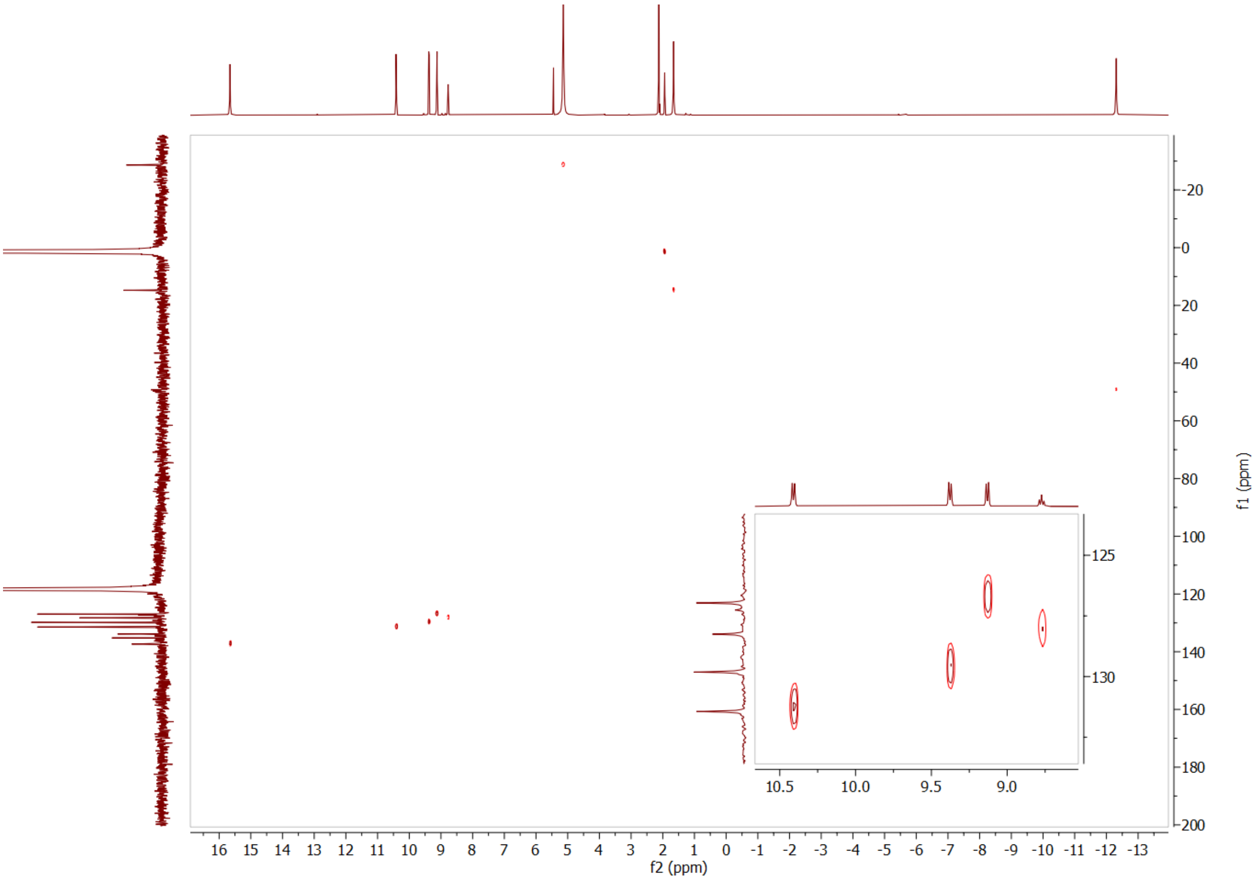


Fig. S8.
HMQC spectrum of **2** (10 mM) in CD_3CN.

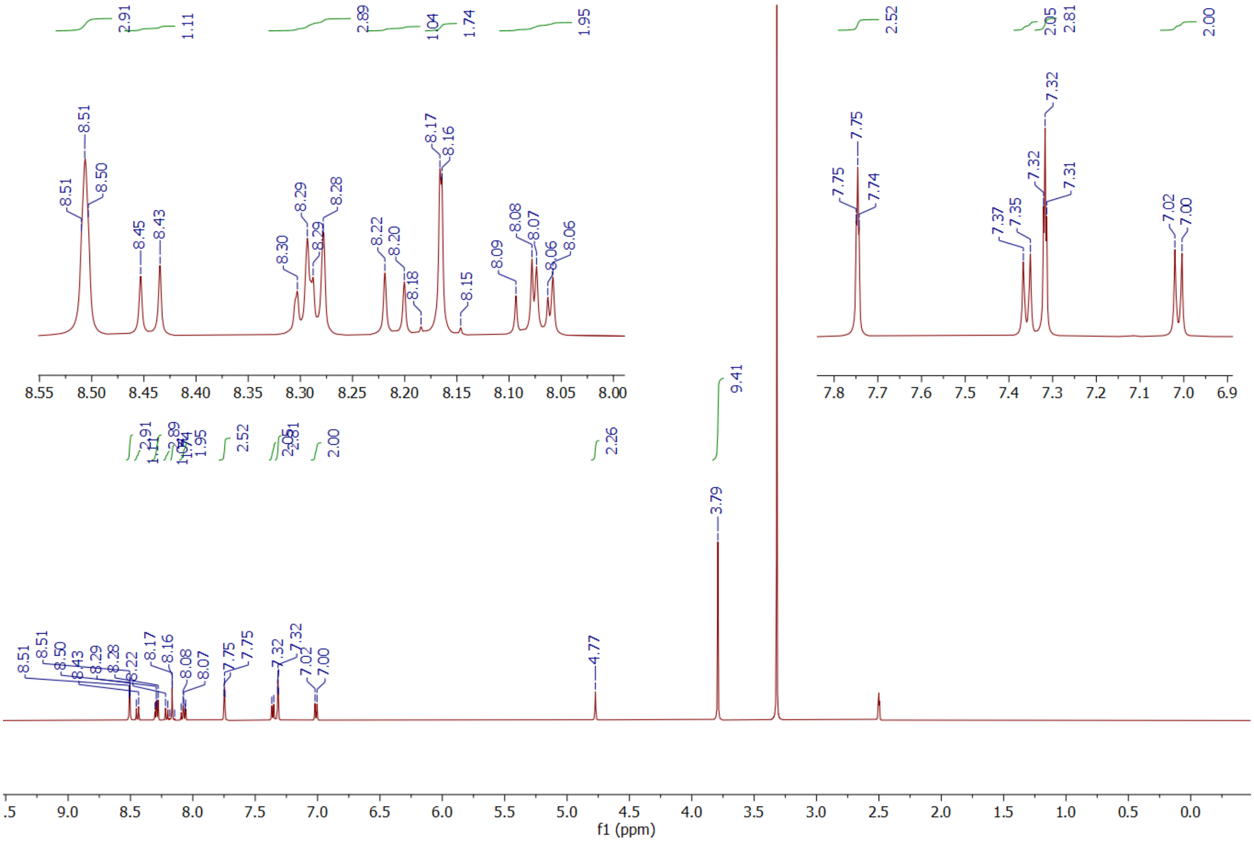


Fig. S9.

^{1}H-NMR spectrum of **B** (5 mM) in DMSO.

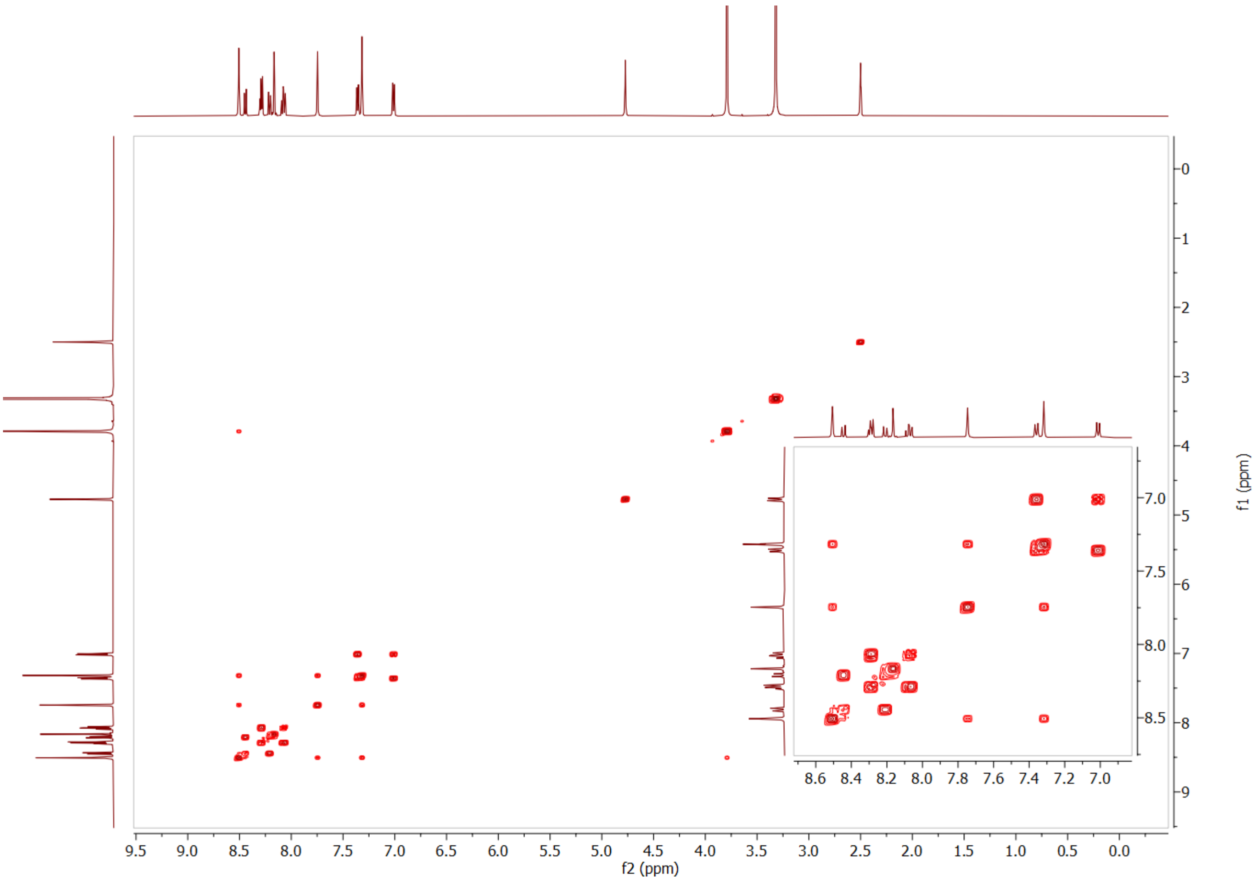


Fig. S10.

gCOSY spectrum of **B** (5 mM) in DMSO.

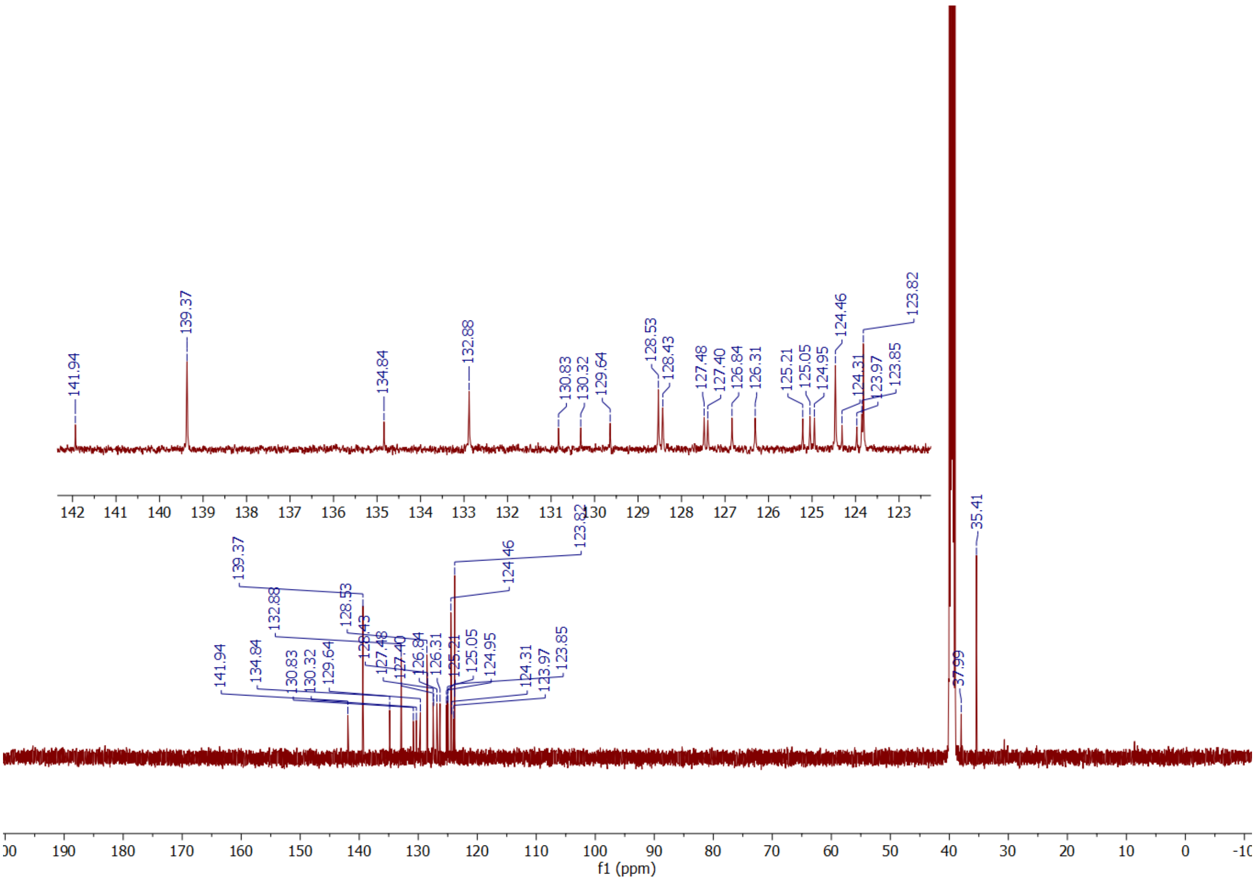


Fig. S11.

^{13}C-NMR spectrum of **B** (15 mM) in DMSO.

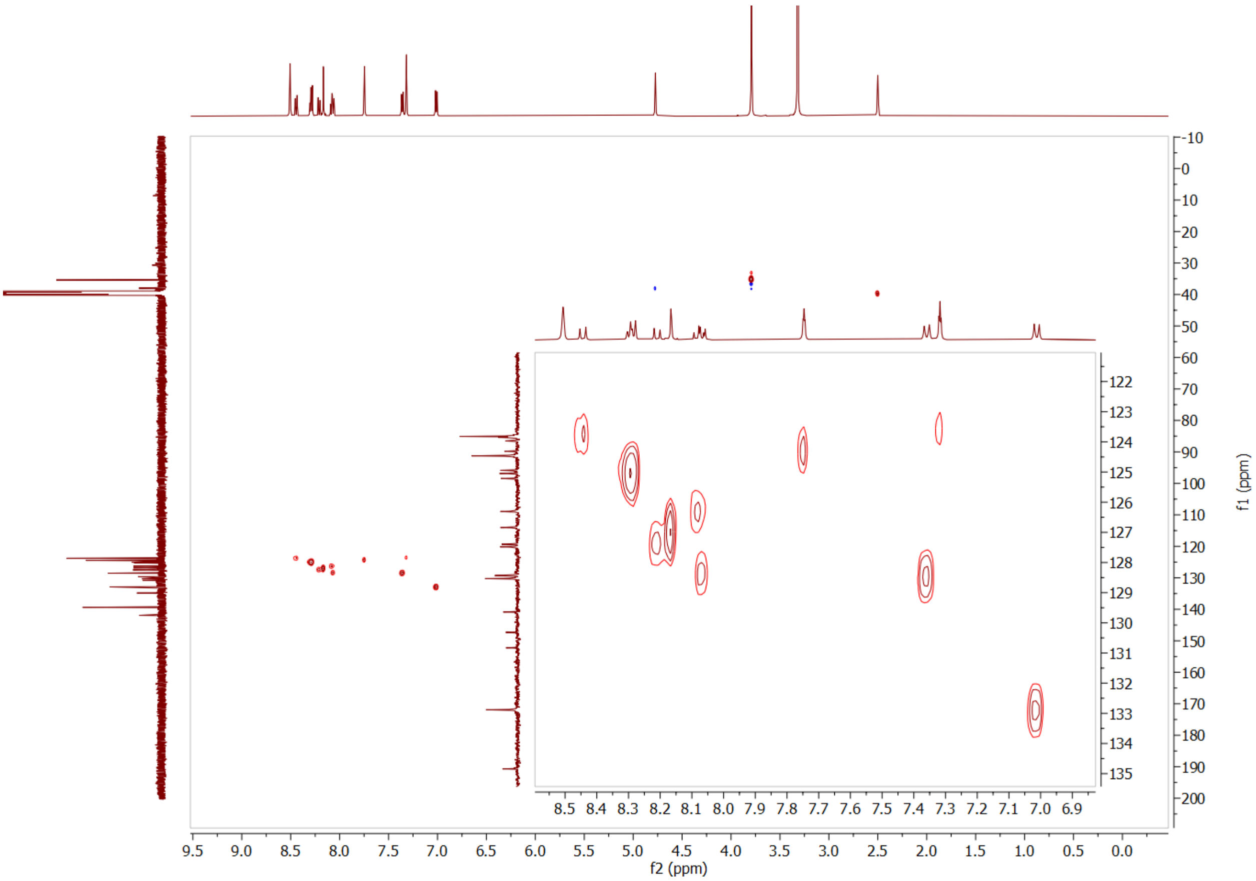


Fig. S12.

gHSQC spectrum of **B** (15 mM) in DMSO.

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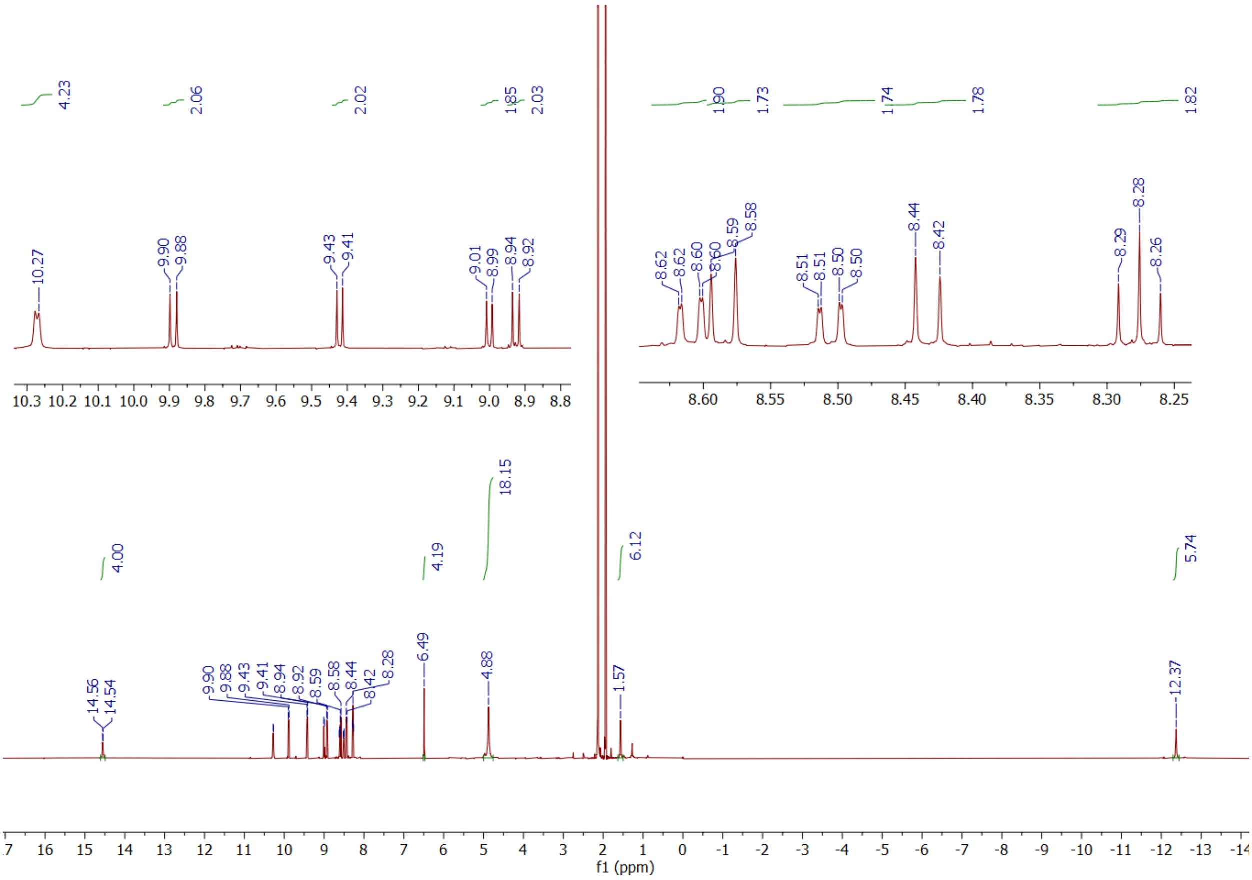

Fig. S13.
^{1}H-NMR spectrum of **3** (4 mM) in CD_3CN.

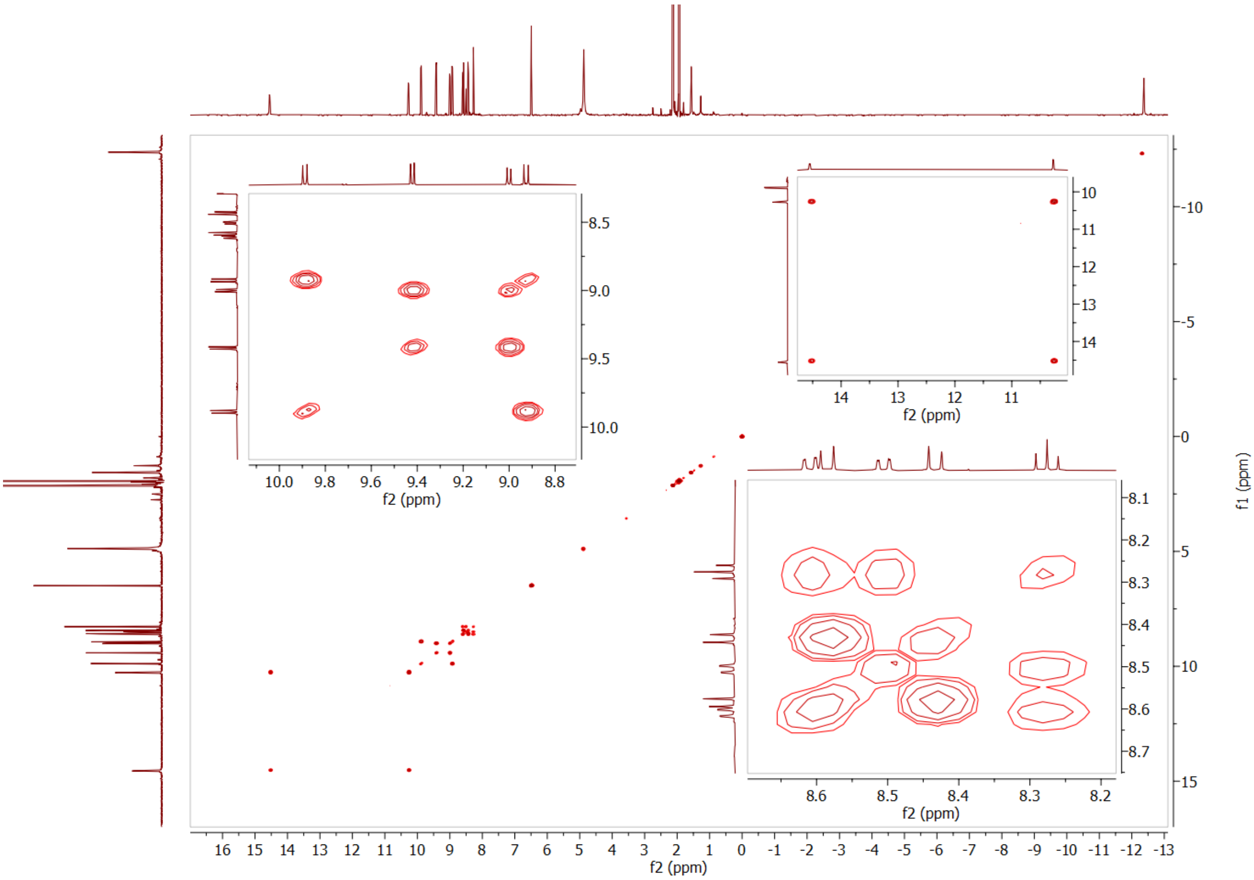

Fig. S14.

gCOSY spectrum of **3** (5 mM) in CD_3CN.

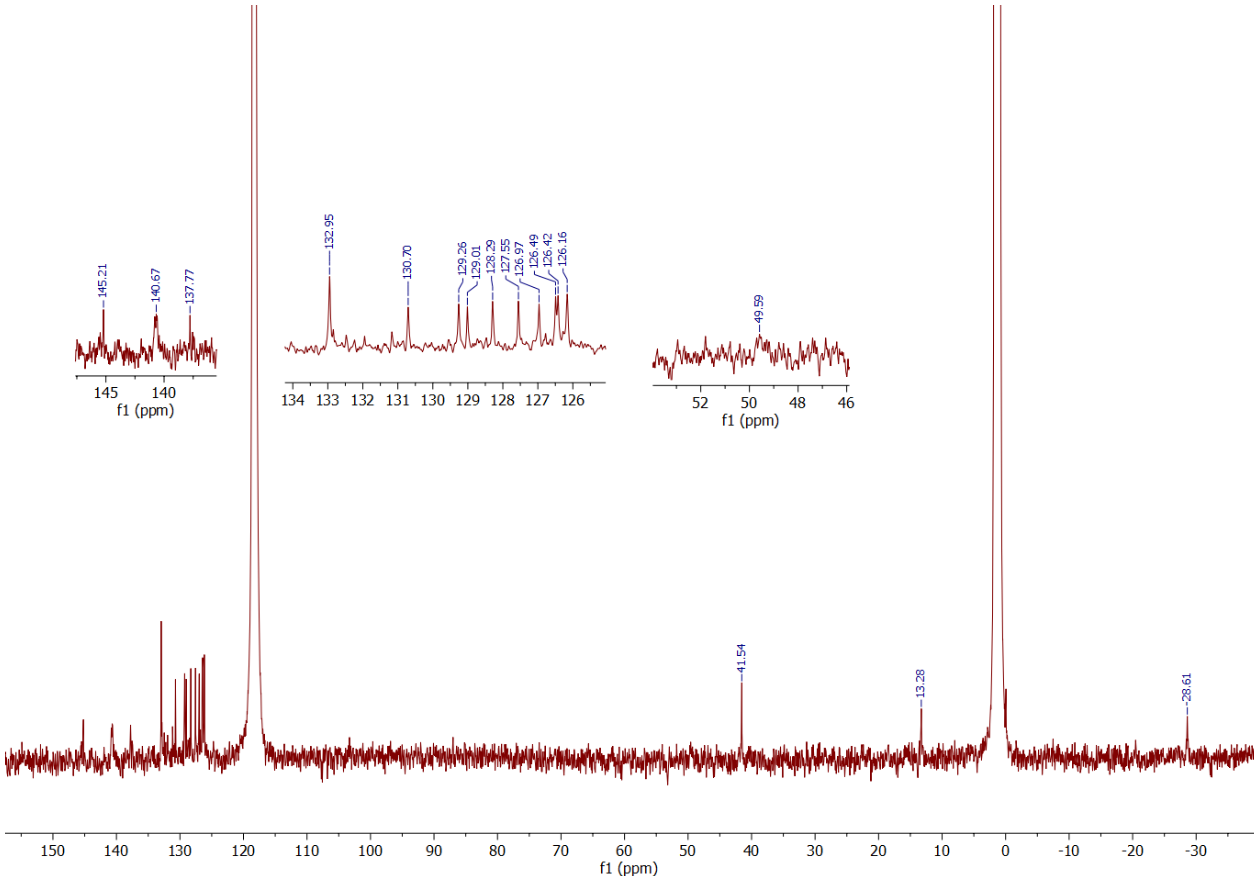

Fig. S15.

^{13}C-NMR spectrum of **3** (10 mM) in CD$_3$CN.

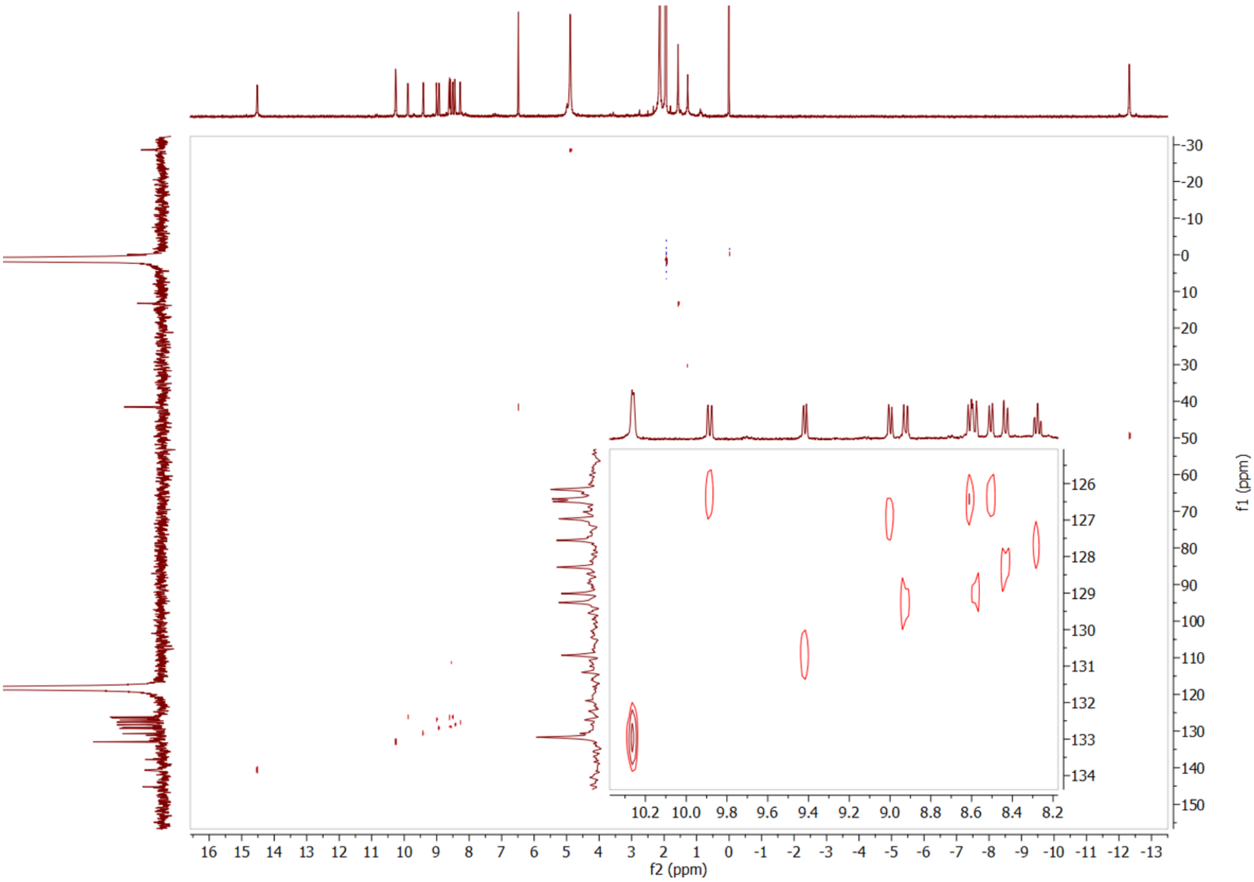

Fig. S16.

HMQC spectrum of **3** (10 mM) in CD_3CN.

Calculation of the rate constants of ^{2}LMCT emission quenching reported in the paper

The quenching rate constant k_q is calculated according to the classical equation S1.
$k_q = (1/\tau') - (1/\tau_0)$ (S1)
As far as **2** in acetonitrile is concerned, in eq. S1 τ' and τ_0 are the emission lifetimes of the shorter-lived emission component of **2**, 0.3 ns, and the emission lifetime of **1**, 2.0 ns, this latter assumed as the model for the emission lifetime of the ^{2}LMCT state of **2** in absence of quenching, respectively. In particular:

$k_q = 1/(0.3\text{x}10^{-9}\text{ s}) - 1/(2\text{x}10^{-9}\text{ s}) = (3.3\text{x}10^9 - 0.5\text{x}10^9)\text{ s}^{-1} = 2.8\text{x}10^9\text{ s}^{-1}$

As far as **3** in dichloromethane is concerned, in eq. S1 τ' and τ_0 are the emission lifetimes of the shorter-lived emission component of **3** (1.5 ns) and the emission lifetime of **1**, 2.4 ns, this latter assumed as the model for the emission lifetime of the ^{2}LMCT state of **3** in absence of quenching in dichloromethane, respectively. In particular:

$k_q = 1/(1.5\text{x}10^{-9}\text{ s}) - 1/(2.4\text{x}10^{-9}\text{ s}) = (0.6\text{x}10^9 - 0.4\text{x}10^9)\text{ s}^{-1} = 2\text{x}10^8\text{ s}^{-1}$

For **2** in dichloromethane, calculation yields:
$k_q = 1/(0.8\text{x}10^{-9}\text{ s}) - 1/(2.4\text{x}10^{-9}\text{ s}) = (1.2\text{x}10^9 - 0.4\text{x}10^9)\text{ s}^{-1} = 8\text{x}10^8\text{ s}^{-1}$

References for Supplementary Information

R1. Morley, J. A. & Woolsey, N. F. Metal arene complexes in organic synthesis. hydroxylation, trimethylsilylation, and carbethoxylation of some polycyclic aromatic hydrocarbons utilizing η^6-arene-chromium tricarbonyl complexes, *J. Org. Chem.*, **57**, 6487-6495 (1992). Doi: 10.1021/jo00050a023.

R2. Matthew, S. C., Glasspoole, B. W., Eisenberger, P. & Crudden, C. M. Synthesis of enantiomerically enriched triarylmethanes by enantiospecific Suzuki–Miyaura cross-coupling reactions, *J. Am. Chem. Soc.*, **136**, 5828-5831 (2014). Doi: 10.1021/ja412159g.

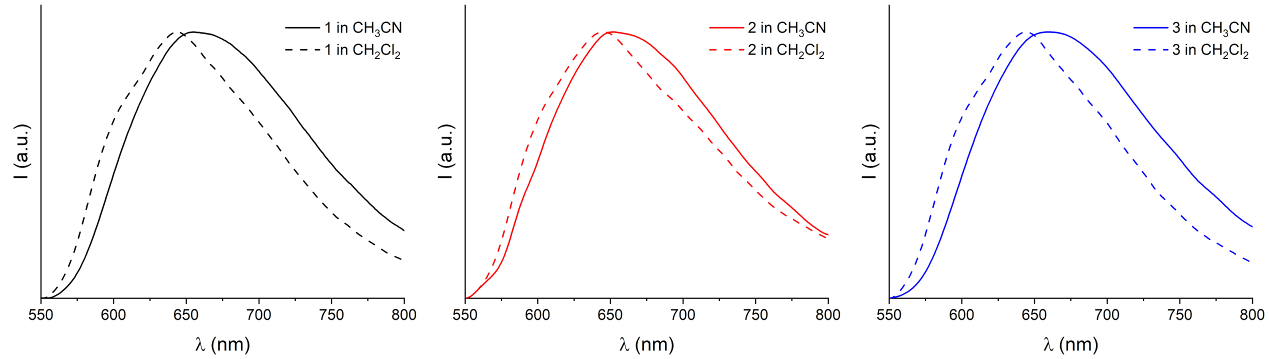

Fig. S17

Normalized emission spectra of **1** (left panel), **2** (middle), and **3** (right) in acetonitrile and dichloromethane fluid solution at room temperature. All spectra are independent of excitation wavelength.

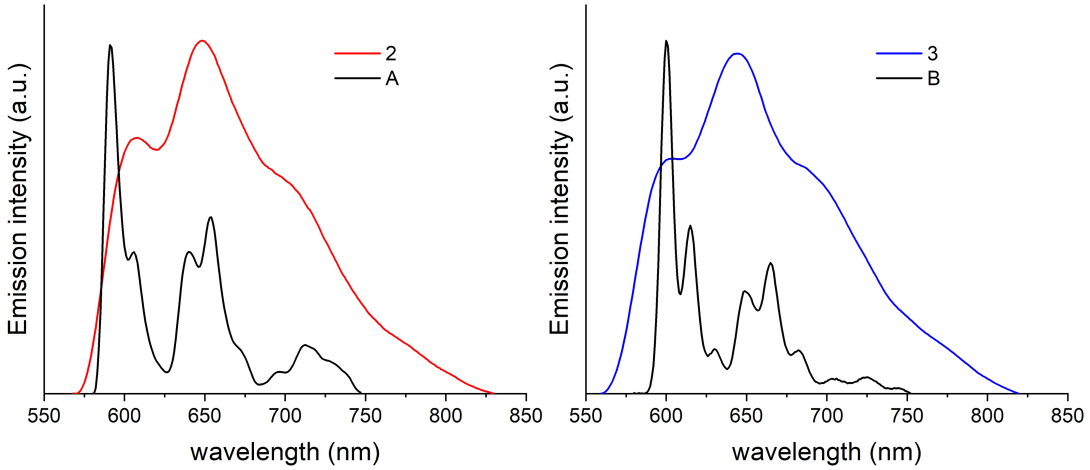

Fig. S18

Emission spectra of **2** and the of free ligand **A** (left panel) and of **3** and of the free ligand **B** (right panel) in EtOH/MeOH 4:1 (v/v) at 77 K. 10 % of iodomethane has been added to **A** and **B** solutions to enhance intersystem crossing and phosphorescence.

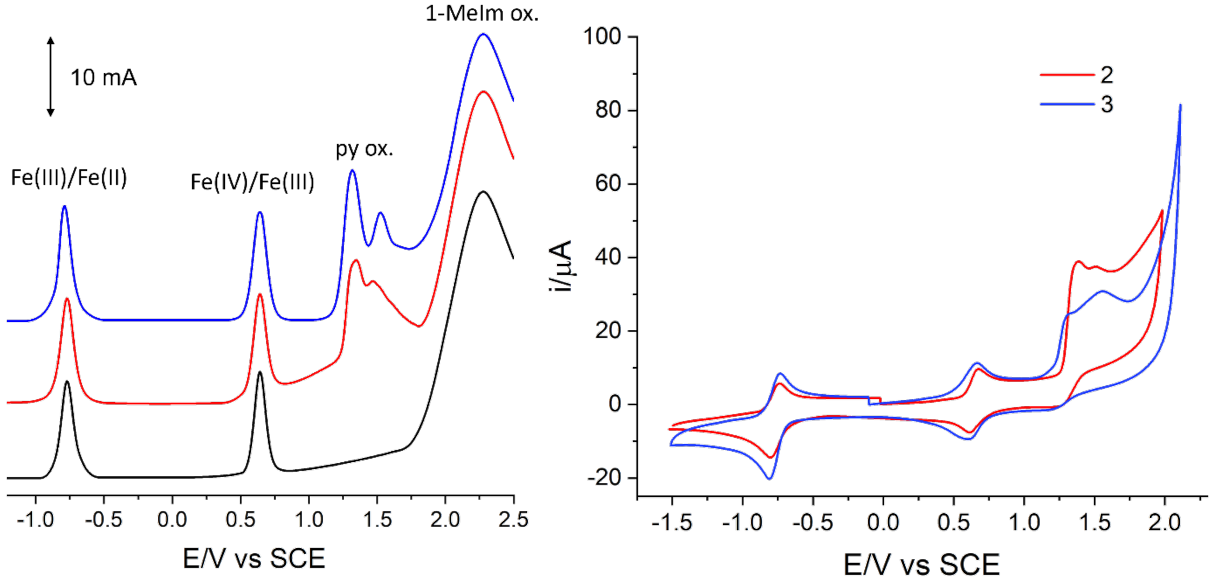

Fig. S19

Left: Differential pulse voltammogram of **1**, **2**, and **3** in acetonitrile (conc.: 0.5 mM; TBAPF$_6$: 0.05 M, scan rate 20 mV/s). Right: Cyclic voltammograms of **2** and **3** in acetonitrile (conc.: 0.5 mM; TBAPF$_6$: 0.05 M, scan rate 200 mV/s). Attribution of the various processes are indicated in figure.

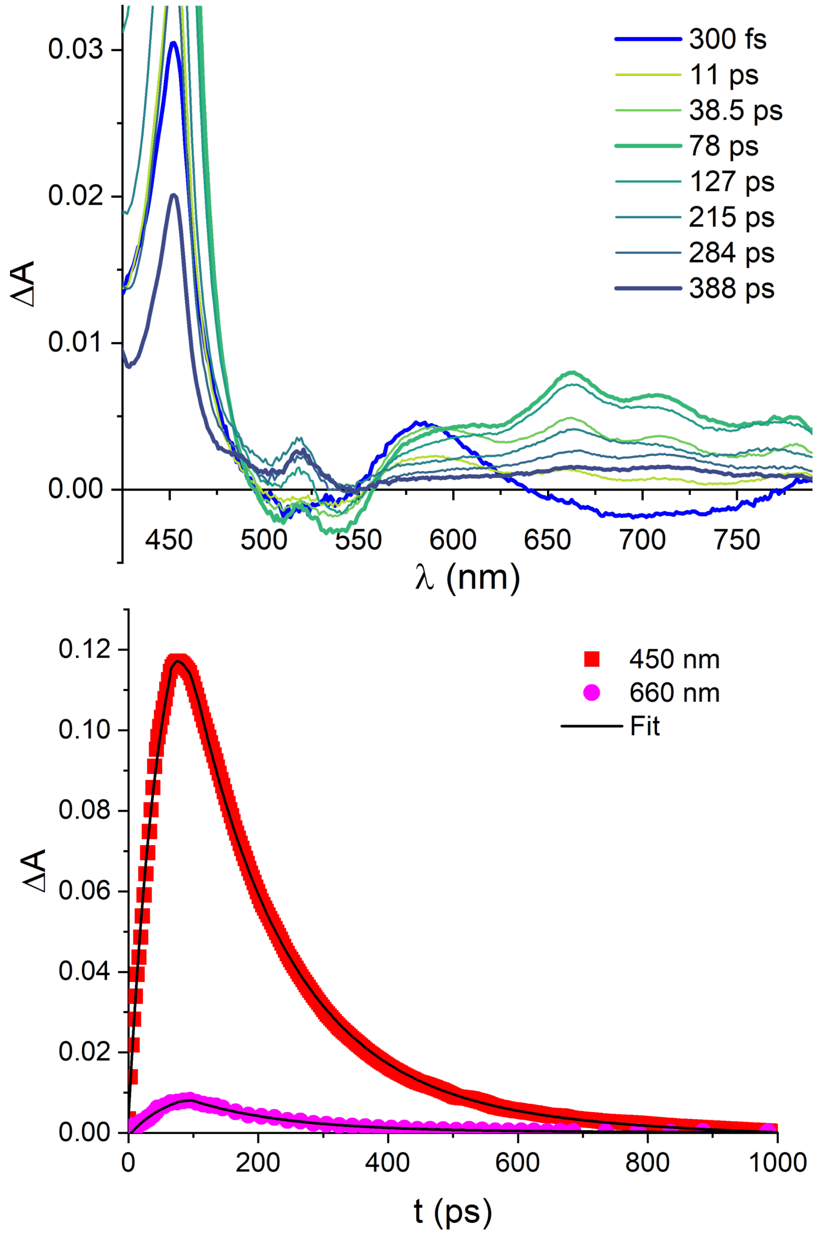

Fig. S20

Top: Pump-probe TASs of **2** in deoxygenated acetonitrile. Bottom: Transient absorption kinetics of **2** in acetonitrile. Symbols are measured data, curves are fits. The data are well fitted with a charge separation time constant of 60 ps and a charge recombination of 250 ps, corresponding to the formation of Fe(II) and Fe(IV) and their subsequent decay, respectively.

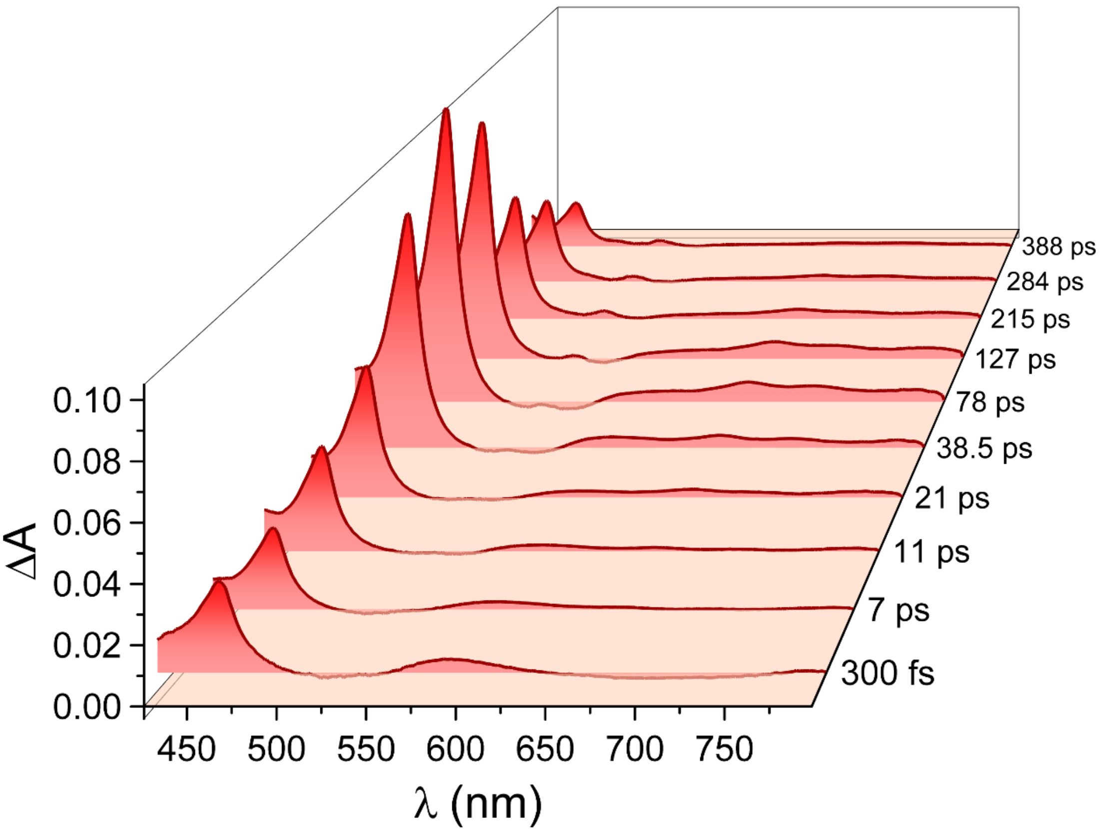

Fig. S21

Pump-probe TASs of **2** in deoxygenated acetonitrile in a full wavelengths scale, to better visualize the transient absorption in the 430-520 nm range.

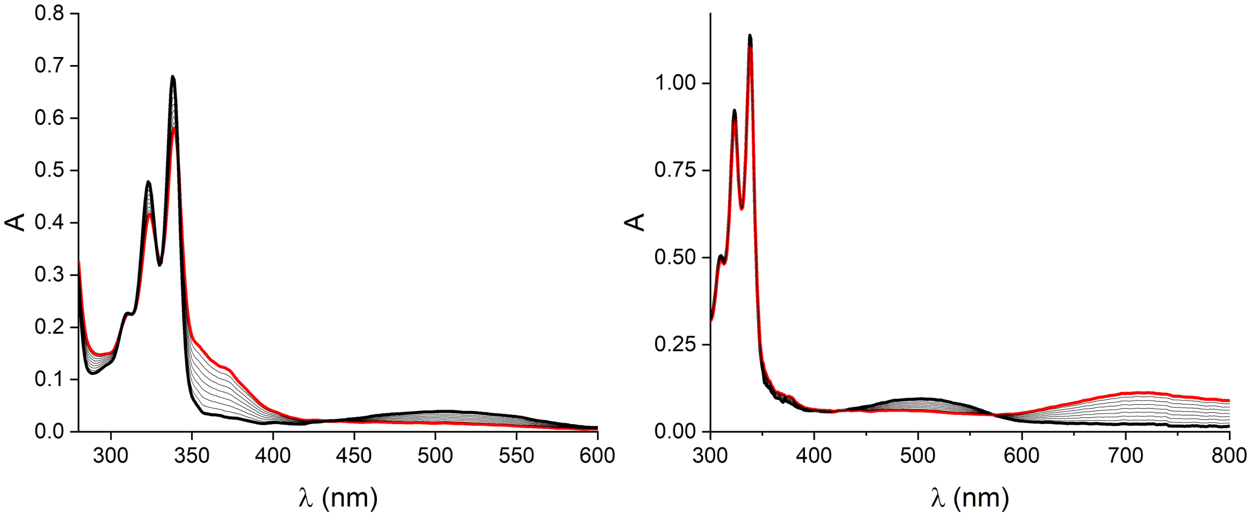

Fig. S22

Left: Absorption spectra of the electrochemically reduced **2** in acetonitrile obtained by applying a -1.1 V potential (**2**: black line: $\mathbf{2_{red}}$: red line). Right: Absorption spectra of the electrochemically oxidized **2** in acetonitrile obtained by applying +1.2 V (**2**: black line: $\mathbf{2_{ox}}$: red line).

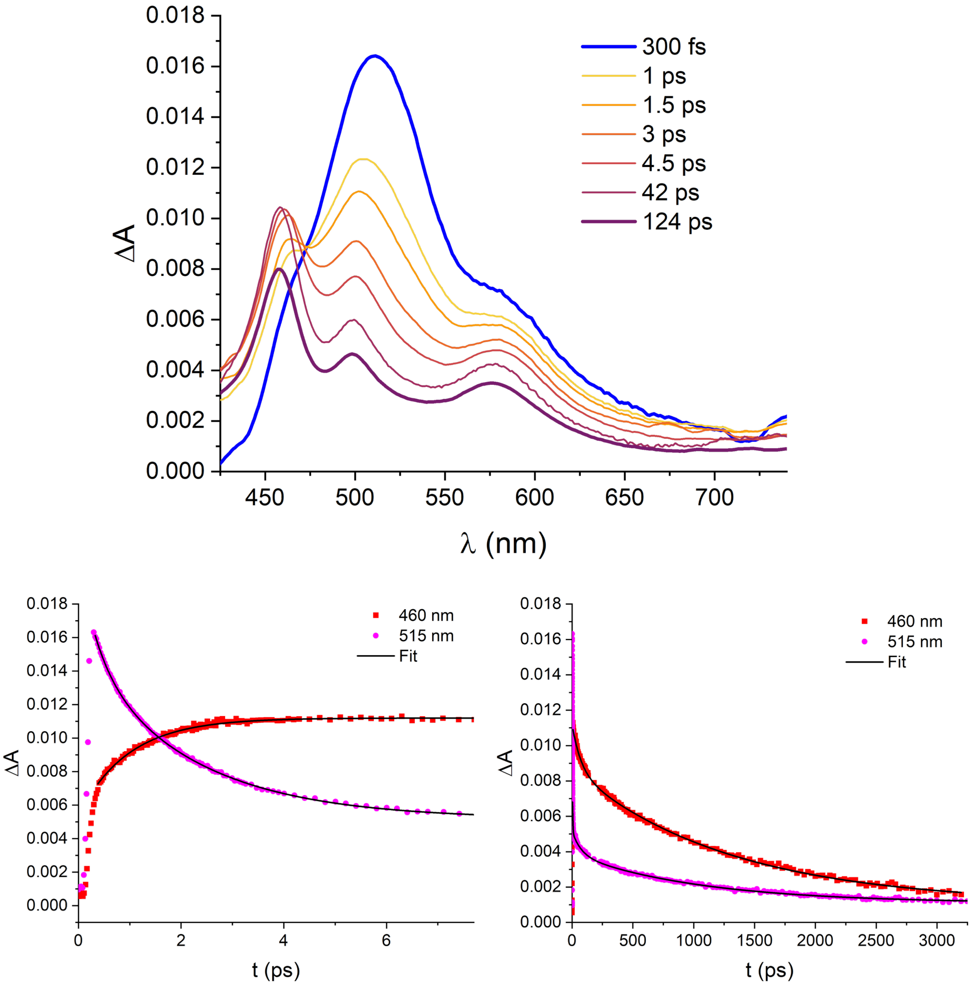

Fig. S23

(Top) Pump-probe TASs of **3** in DCE; (Bottom) kinetics of **3** in DCE: $\tau_1 = 1.5$ ps , τ_2,= 16 ps.: Left: in the early picoseconds to show the conversion of the excimer in the triplet pyrene excited state, Right: in the full scale.

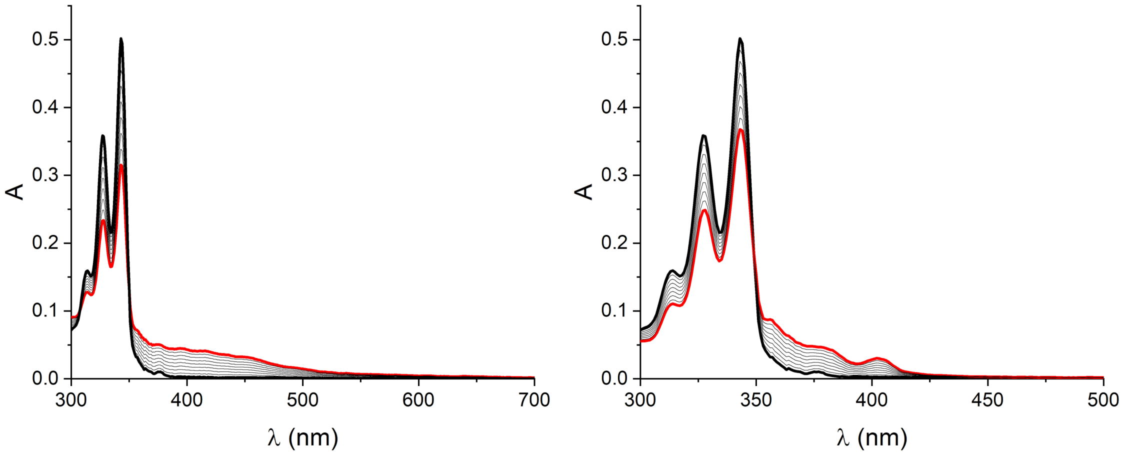

Fig. S24

Left: Absorption spectra of the electrochemically reduced **B** in acetonitrile obtained by applying -1.1 V (**B**: black line: $\mathbf{B}_{\mathbf{red}}$: red line). Right: Absorption spectra of the electrochemically oxidized **2** in acetonitrile obtained by applying +1.1 V (**B**: black line: $\mathbf{B}_{\mathbf{ox}}$: red line).

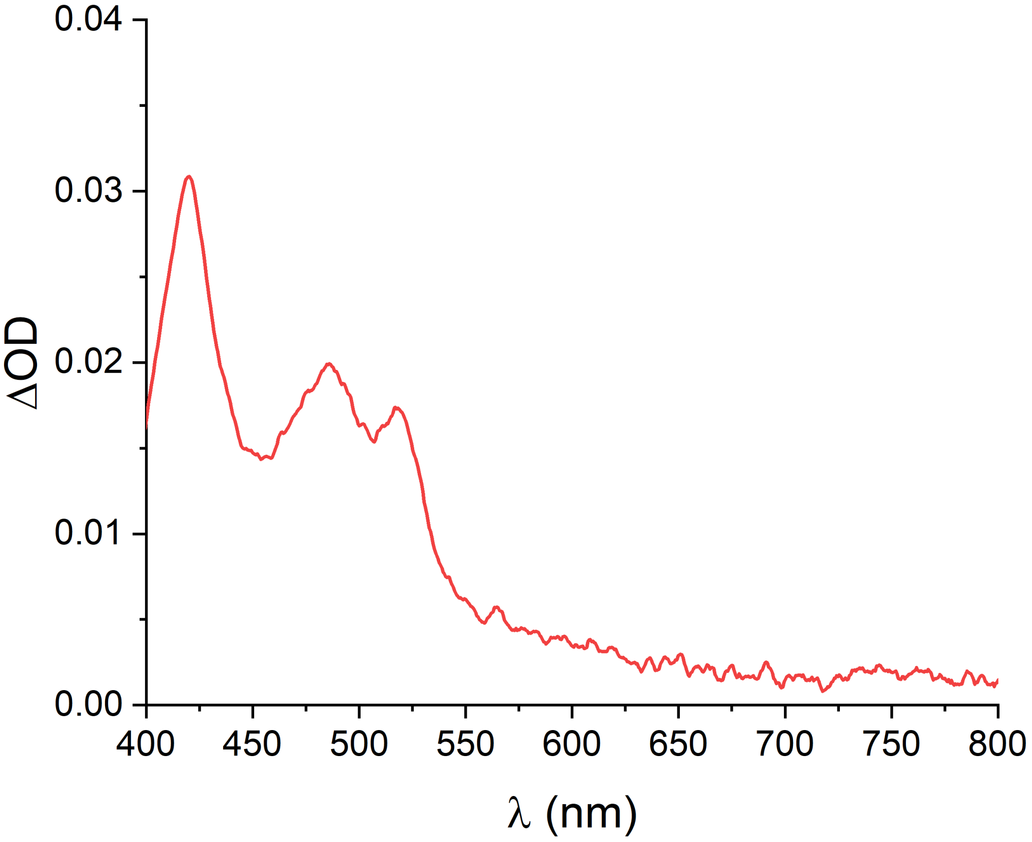

Fig. S25
Nanosecond TAS of **B** in deoxygenated DCE recorded 200 ns following excitation at 355 nm.

Table S1.

Redox data of the new species **2** and **3** and of the model species **1** in acetonitrile. Reported data are vs SCE. Redox processes are reversible, unless otherwise stated. For reversible processes, $E_{1/2}$ is reported, whereas for irreversible processes the DPV peak is given. Attribution of the various processes to specific subunits are shown in Fig. S19.

	E(red), V	E(ox), V		
2	-0.77	+0.64	+1.35[a,b]	+2.28[a]
3	-0.79	+0.64	+1.32[a,b]	+2.28[a]
1	-0.77	+0.64		+2.28[a]

(a) Irreversible process. (b) A further irreversible process follows this peak, probably involving the second pyrene subunit.