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Deep-Blue Thermally Activated Delayed Fluorescence (TADF) Emitters for Light-Emitting Electrochemical Cells (LEECs)

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SUPPORTING INFORMATION

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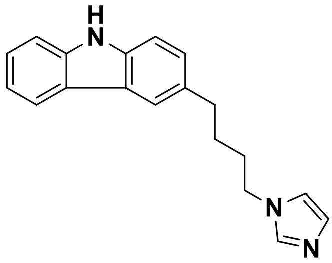
Experimental Section

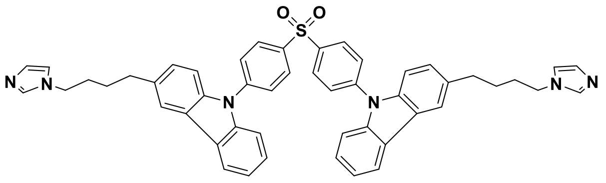
General Synthetic Procedures. All the commercially available chemicals and reagent grade solvents were used as received. Air-sensitive reactions were performed using standard Schlenk techniques under a nitrogen atmosphere. Anhydrous THF was obtained from a solvent purification system. Flash column chromatography was carried out using silica gel (60 Å, 40-63 µm). Analytical thin-layer-chromatography (TLC) was performed with silica plates with aluminum backings (250 µm with F-254 indicator). TLC visualization was accomplished by 254/365 nm UV lamp. ^{1}H, ^{13}C and ^{19}F NMR spectra in $CDCl_3$, CD_2Cl_2 or DMSO-*d*6 were recorded on a NMR spectrometer (300 or 400 MHz for ^{1}H, 76 or 101 MHz for ^{13}C and 282 MHz for ^{19}F). Melting points were measured using open-ended capillaries and are uncorrected. High-resolution mass spectrometry (HRMS) was performed by the EPSRC National Mass Spectrometry Service Centre (NMSSC), Swansea University. Elemental analyses were performed by Mr. Stephen Boyer, London Metropolitan University.

CzC$_4$Im, 1:



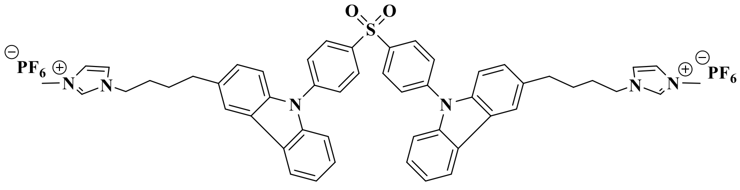
The synthesis of the title compound has been reported previously.[1]

(CzC$_4$Im)$_2$DPS, 2:



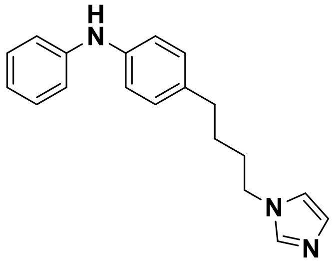
CzC$_4$Im (500 mg, 1.73 mmol, 2 equiv.) and sodium hydride (60% in mineral oil, 104 mg, 2.60 mmol, 3 equiv.) were mixed in dry DMF (5 mL) and stirred for 15 mins. Bis(4-fluorophenyl)sulfone (220 mg, 0.87 mmol, 1 equiv) was added and the mixture was heated at 100°C under nitrogen for 6 hours. The reaction mixture was poured into ice water (5 mL) and extracted with DCM (3 x 10 mL). The combined organic layers were dried with anhydrous sodium sulphate and purified by column chromatography (silica, DCM: Hexanes: Triethylamine = 4: 1: 10%) to afford the title compound. White solid. **Yield**: 64%. **R$_f$:** 0.23 (Acetone : Triethylamine = 9: 1 on silica). **Mp**: 115-116 °C. **^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm)**: 8.29 (d, *J* = 8.7 Hz, 4 H), 8.13 (d, *J* = 7.6 Hz, 2 H), 7.91 (s, 2 H), 7.84 (d, *J* = 8.7, 4 H), 7.63-7.43 (m, 8 H), 7.35 (t, J = 7.9 Hz, 2 H), 7.23 (dd, *J* = 8.4, 1.6 Hz, 2 H), 7.08 (s, 2 H), 6.92 (s, 2 H), 3.98 (t, d = 6.9 Hz, 2 H), 2.85 (t, J = 7.3 Hz, 2 H), 1.92-1.85 (m, 2 H), 1.78-1.71 (m, 2 H). **^{13}C NMR (101 MHz, CDCl$_3$) δ (ppm)**: 142.8, 140.2, 139.2, 138.5, 134.4, 129.7, 127.0, 126.9, 126.4, 124.2, 123.9, 121.0, 120.5, 119.9, 109.7, 109.6, 47.0, 35.3, 30.6, 29.0. **HR-MS (**ESI) **[M+H]$^+$ Calculated:** (C$_{50}$H$_{44}$N$_6$O$_2$S) 793.3319; **Found:** 793.3322.

imCzDPS:



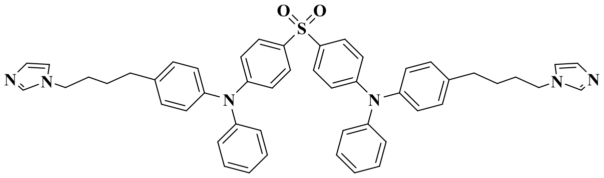
(C$_Z$C$_4$Im)DPS (200 mg, 0.25 mmol, 1 equiv.) and methyl iodide (108 mg, 0.75 mmol, 3 equiv.) was mixed in acetonitrile (5 mL) and heated at 40 °C for 2 hours. After cooling, the reaction mixture was poured into saturated aqueous solution (10 mL) of ammonium hexafluorophosphate to obtain the title compound which was then washed with distilled water and dried thoroughly. White solid. **Yield**: 96%. **Mp**: decomposed at 187 °C. **^{1}H NMR (300 MHz, DMSO-*d6*) δ (ppm)**: 9.08 (s, 2 H), 8.33 (d, *J* = 8.6 Hz, 4 H), 8.21 (d, *J* = 7.7 Hz, 2 H), 8.06 (s, 2 H), 7.97 (d, *J* = 8.7, 4 H), 7.76 (s, 2 H), 7.68 (s, 2 H), 7.56-7.27 (m, 10 H), 4.20 (t, *J* = 7.0, 4 H), 3.82 (s, 3 H), 2.80 (t, *J* = 7.2 Hz, 4 H), 1.89-1.79 (m, 4 H), 1.68-1.59 (m, 4 H). **^{13}C NMR (76 MHz, DMSO-*d6*) δ (ppm)**: 146.2, 143.5, 140.9, 139.9, 139.2, 135.0, 130.4, 127.6, 127.5, 127.0, 124.9, 124.5, 122.2, 120.5, 111.0, 47.2, 37.4, 35.5, 30.8, 29.1. **^{19}F NMR (282 MHz, DMSO-*d6*) δ (ppm)**: -68.9, -71.4. **HR-MS (**ESI) **[M]$^{2+}$ Calculated:** ($C_{50}H_{50}N_6O_2S$) 411.1852; **Found:** 411.1845.

TPAC$_4$Im, **3**:



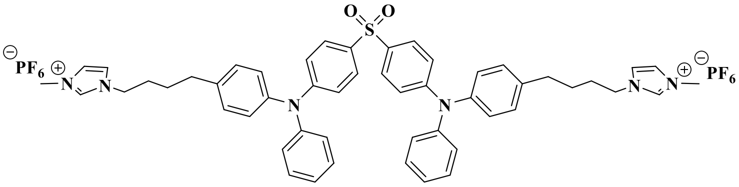
The title compound was accomplished using the same procedure as **C$_Z$C$_4$Im**, **1**,[1] except diphenylamine was used instead of carbazole. White solid. **R$_f$:** 0.16 (EA on silica). **Mp**: 134-135 °C. **^{1}H NMR (300 MHz, CDCl$_3$) δ (ppm)**: 7.42 (s, 1 H), 7.23-7.18 (m, 2 H), 7.05 (d, J = 8.5 Hz, 2 H), 6.98-6.92 (m, 7 H), 3.94 (t, *J* = 7.0, 2 H), 2.59 (t, *J* = 6.8, 2 H), 1.86-1.76 (m, 2 H), 1.65-1.55 (m, 2 H). **^{13}C NMR (76 MHz, CDCl$_3$) δ (ppm)**: 141.0, 139.2, 138.2, 133.6, 130.5, 127.4, 126.8, 124.5, 124.1, 121.2, 120.6, 120.3, 119.8, 111.5, 111.4, 47.4, 30.9, 29.3, 20.1. **HR-MS (**ESI) **[M+H]$^+$ Calculated:** ($C_{19}H_{22}N_3$) 292.1808; **Found:** 292.1806.

(TPAC$_4$Im)DPS, 4:



The title compound was synthesized from **TPAC$_4$Im 3** and Bis(4-fluorophenyl)sulfone in an analogous fashion to **(C$_Z$C$_4$Im)DPS, 2.** White solid. **Yield**: 42%. **R*f*:** 0.17 (Acetone : Triethylamine = 9: 1 on silica). **Mp**: 97-98 °C. **^{1}H NMR (300 MHz, CDCl$_3$) δ (ppm)**: 7.43 (s, 1 H), 7.19-6.88 (m, 10 H), 6.87-6.75 (m, 4 H), 3.95 (t, *J* = 7.1 Hz, 2 H), 2.58 (t, *J* = 6.9 Hz, 2 H), 1.85-1.76 (m, 2 H), 1.64-1.53 (m, 2 H). **^{13}C NMR (76 MHz, CDCl$_3$) δ (ppm)**: 141.1, 140.2, 139.5, 138.4, 135.7, 134.7, 134.0, 130.6, 127.9, 127.8, 127.3, 125.1, 124.7, 121.8, 121.4, 120.8, 110.4, 47.3, 30.8, 29.2, 19.1.

imDPADPS:



The title compound was synthesized from **(TPAC$_4$Im)DPS, 4** in an analogous fashion to **imCzDPS.** White solid. **Yield**: 93%. **Mp**: 171-172 °C. **^{1}H NMR (300 MHz, CD$_2$Cl$_2$) δ (ppm)**: 8.54 (s, 2 H), 7.63 (d, J = 8.9 Hz, 4 H), 7.36-7.28 (m, 8 H), 7.18-7.12 (m, 10 H), 7.06 (d, J = 8.4 Hz, 4 H), 6.94 (d, J = 8.9 Hz, 4 H), 4.21 (t, J = 7.4 Hz, 4 H), 3.94 (s, 6 H), 2.67 (t, d = 7.0 Hz, 4 H), 2.00-1.90 (m, 4 H), 1.73-1.65 (m, 4 H). **^{13}C NMR (76 MHz, DMSO-*d6*) δ (ppm)**: 144.0, 143.0, 142.3, 141.2, 138.4, 137.4, 136.7, 133.3, 130.5, 130.4, 129.8, 127.6, 127.2, 124.3, 123.8, 123.2, 112.6, 47.9, 37.8, 31.0, 29.4, 19.4. **^{19}F NMR (282 MHz, CD_2Cl_2) δ (ppm)**: -71.2, -73.7. **HR-MS (**ESI) **$[M-PF_6]^+$ Calculated:** ($C_{52}H_{54}F_6N_6O_2PS$) 917.3665; **Found:** 917.3657.

Photophysical measurements. Optically dilute solutions of concentrations in the order of 10^{-5} or 10^{-6} M were prepared in HPLC grade acetonitrile for absorption and emission analyses. Absorption spectra were recorded at room temperature on a double beam spectrophotometer. Molar absorptivity values were determined by linear regression analysis from at least four solutions of different concentrations within the range of 10^{-4} to 10^{-5} M. Aerated solutions were prepared by using aerated solvent with prior air bubbling for 5 min whereas degassed solutions were prepared via five freeze-pump-thaw cycles prior to emission analysis using a home-made cuvette extended solvent bulb designed for cryogenic degassing. Steady state emission and time-resolved emission spectra were recorded at 298 K. Samples were excited at 360 nm for steady state measurements and at 378 nm for time-resolved measurements. Photoluminescence quantum yields for solutions were determined using the optically dilute method[2] in which four sample solutions with absorbance at 360 nm being ca. 0.10, 0.080, 0.060 and 0.040 were used. Their emission intensities were compared with those of a reference, quinine sulfate, whose quantum yield (Φ_r) in 1 *N* H_2SO_4 was taken as 54.6%.[3] The quantum yield of sample, Φ_s, can be determined by the equation $\Phi_s = \Phi_r(A_r/A_s)((I_s/I_r)(n_s/n_r)^2$, where A stands for the absorbance at the excitation wavelength (λ_{exc}: 360 nm), I is the integrated area under the corrected emission curve and n is the refractive index of the solvent, with the subscripts "s" and "r" representing sample and reference respectively. An integrating sphere was employed for quantum yield measurements for thin film samples.

Electrochemistry measurements. Cyclic Voltammetry (CV) analysis was performed on a potentiostat. Samples were prepared as MeCN solutions, which were degassed by sparging with MeCN-saturated nitrogen gas for 15 minutes prior to measurements. All measurements were performed in 0.1 M MeCN solution of tetrabutylammonium hexafluorophosphate (nBu$_4$NPF$_6$). An Ag/Ag$^+$ electrode was used as the reference electrode while a platinum electrode and a platinum wire (Pt/Pt$^+$) were used as the working electrode and counter electrode, respectively. The redox potentials are reported relative to a saturated calomel electrode (SCE) with a ferrocenium/ferrocene (Fc$^+$/Fc) redox couple as the internal standard (0.38 V vs SCE).[4]

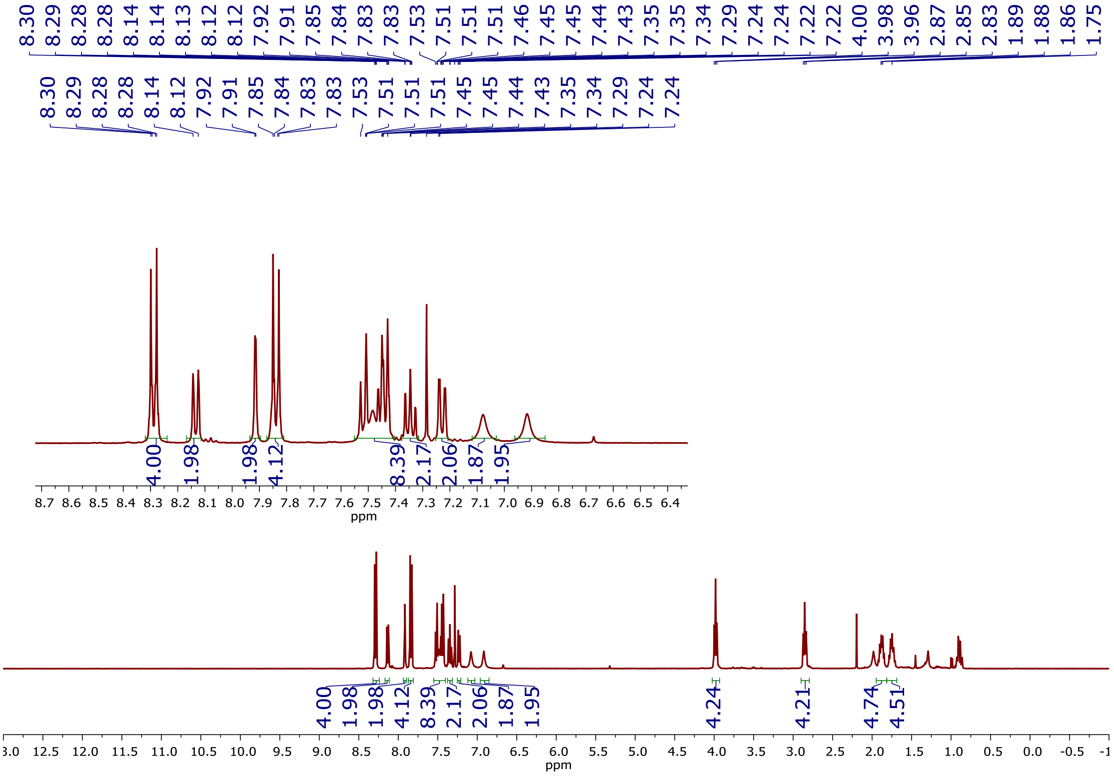


Figure **S1**. ^{1}H NMR spectrum of **(CzC$_4$Im)DPS**.

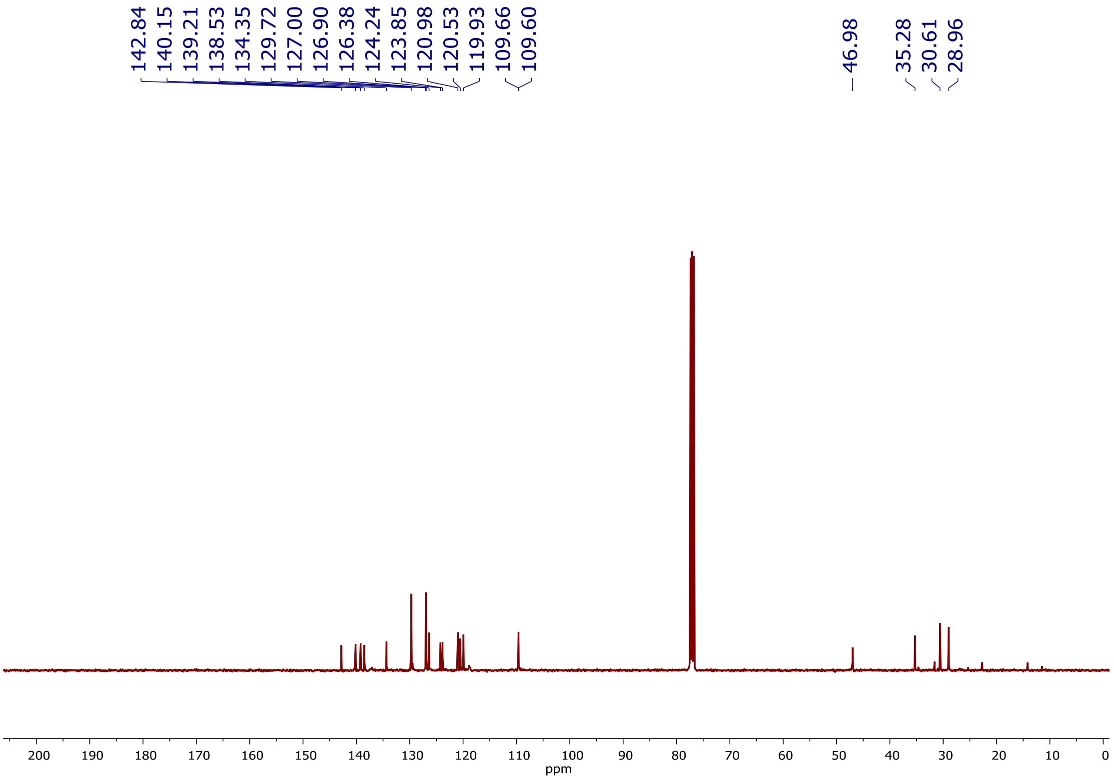


Figure **S2**. ^{13}C NMR spectrum of **(CzC$_4$Im)DPS**.

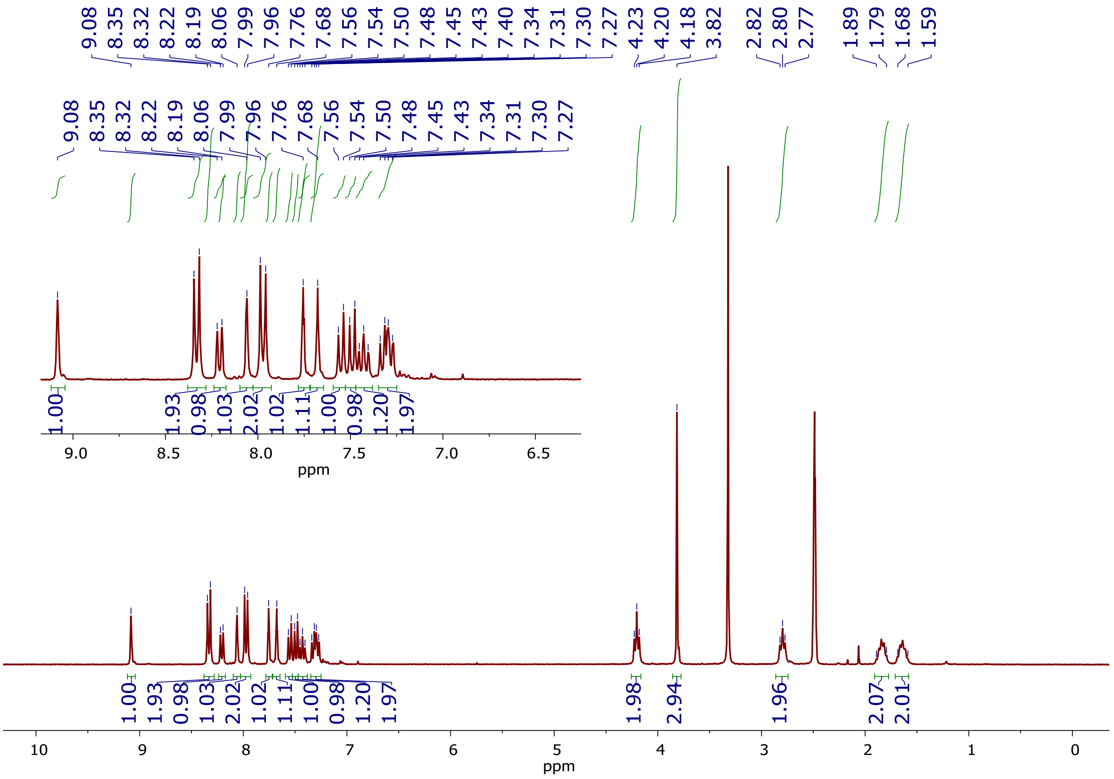


Figure **S3**. ^{1}H NMR spectrum of **imCzDPS**.

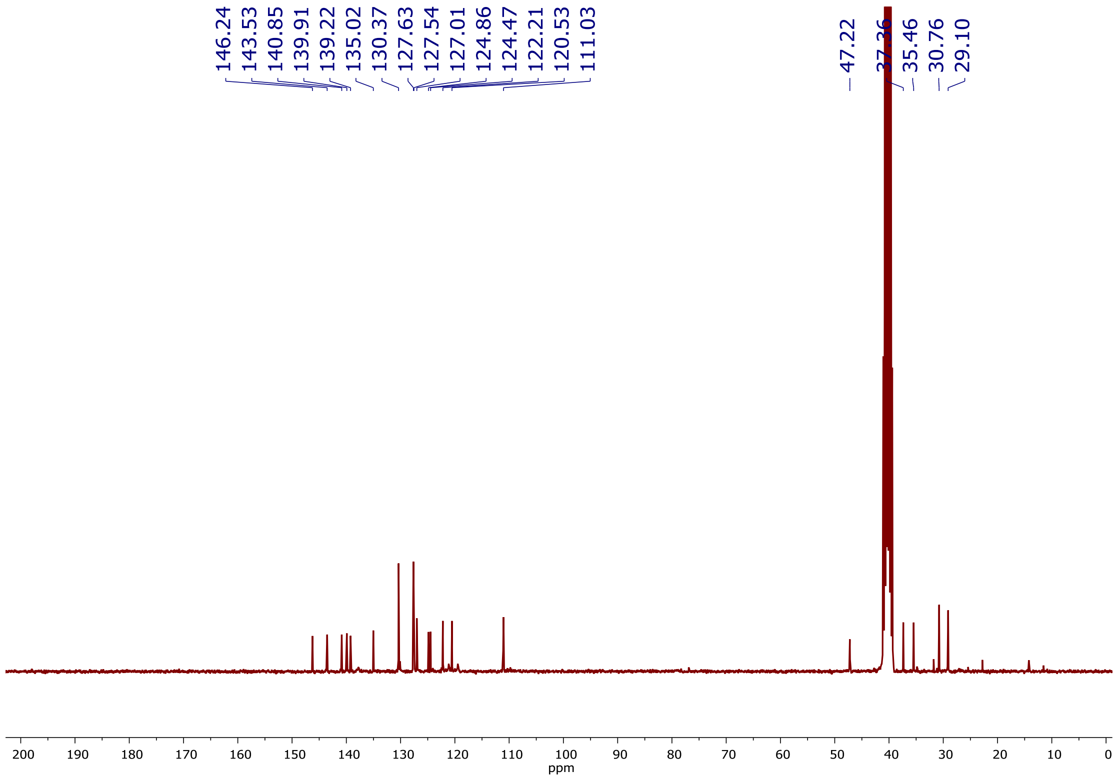


Figure **S4**. ^{13}C NMR spectrum of **imCzDPS**.

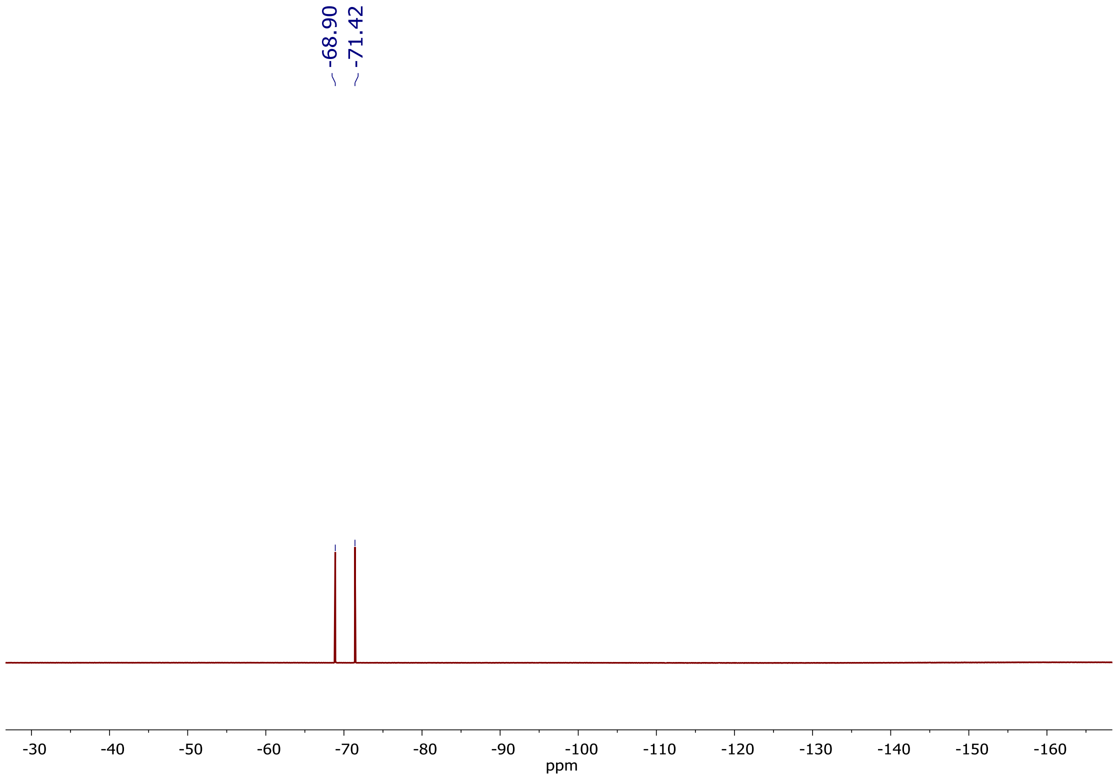


Figure **S5**. ^{19}F NMR spectrum of **imCzDPS**.

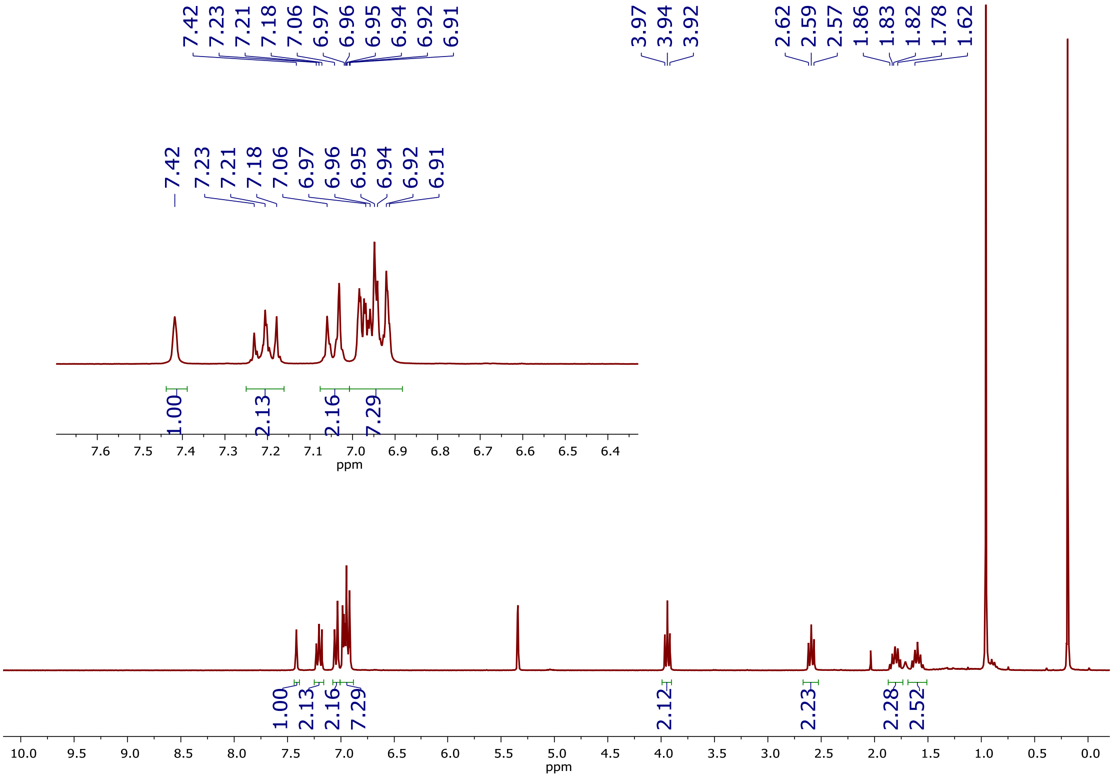


Figure **S6**. ^{1}H NMR spectrum of **TPAC$_4$Im**.

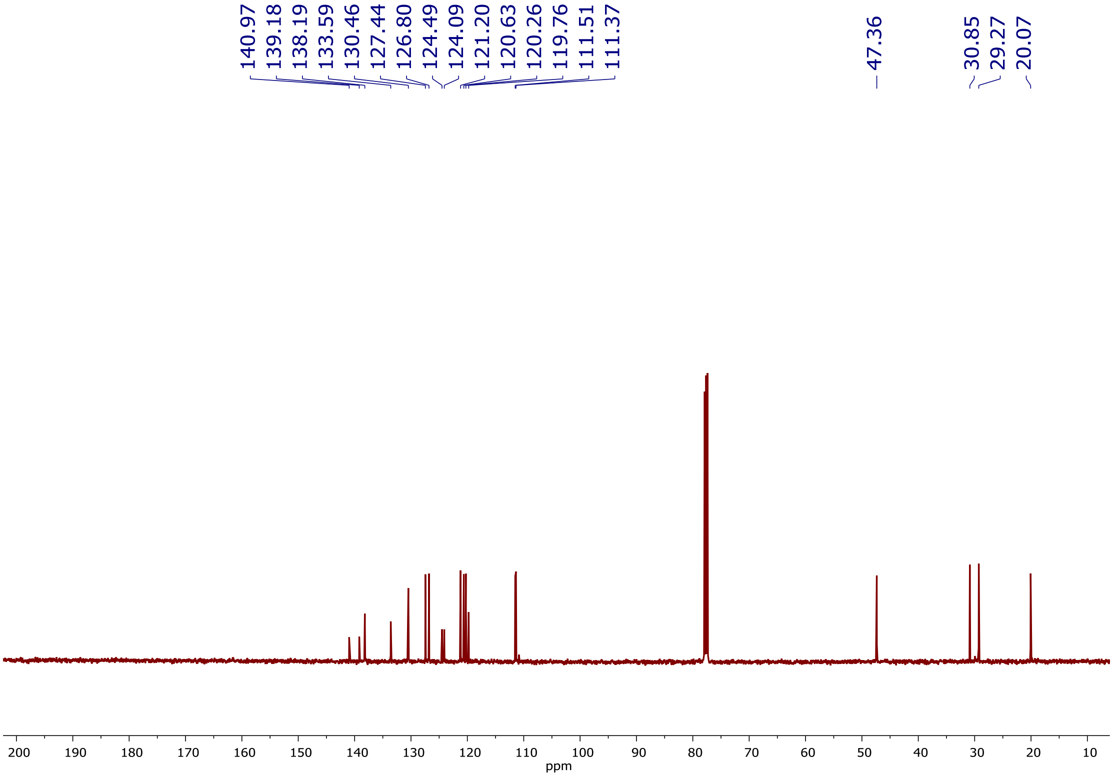


Figure **S7**. ^{13}C NMR spectrum of **TPAC$_4$Im**.

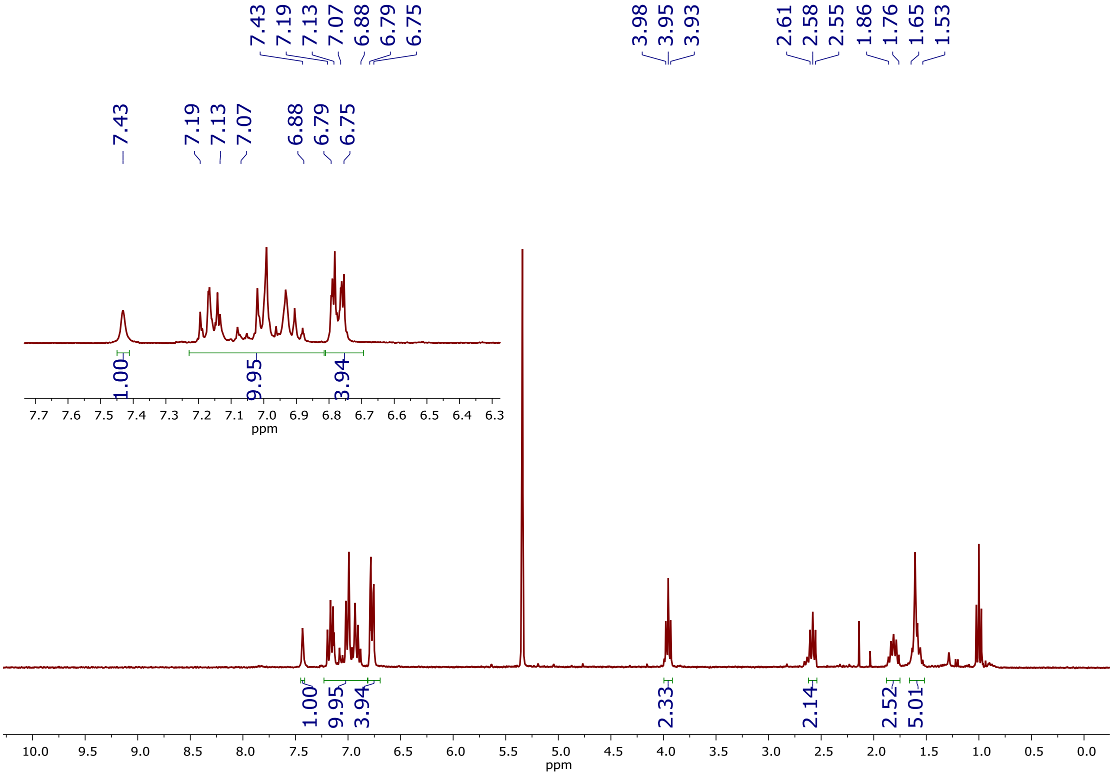


Figure **S8**. ^{1}H NMR spectrum of **(TPAC$_4$Im)DPS**.

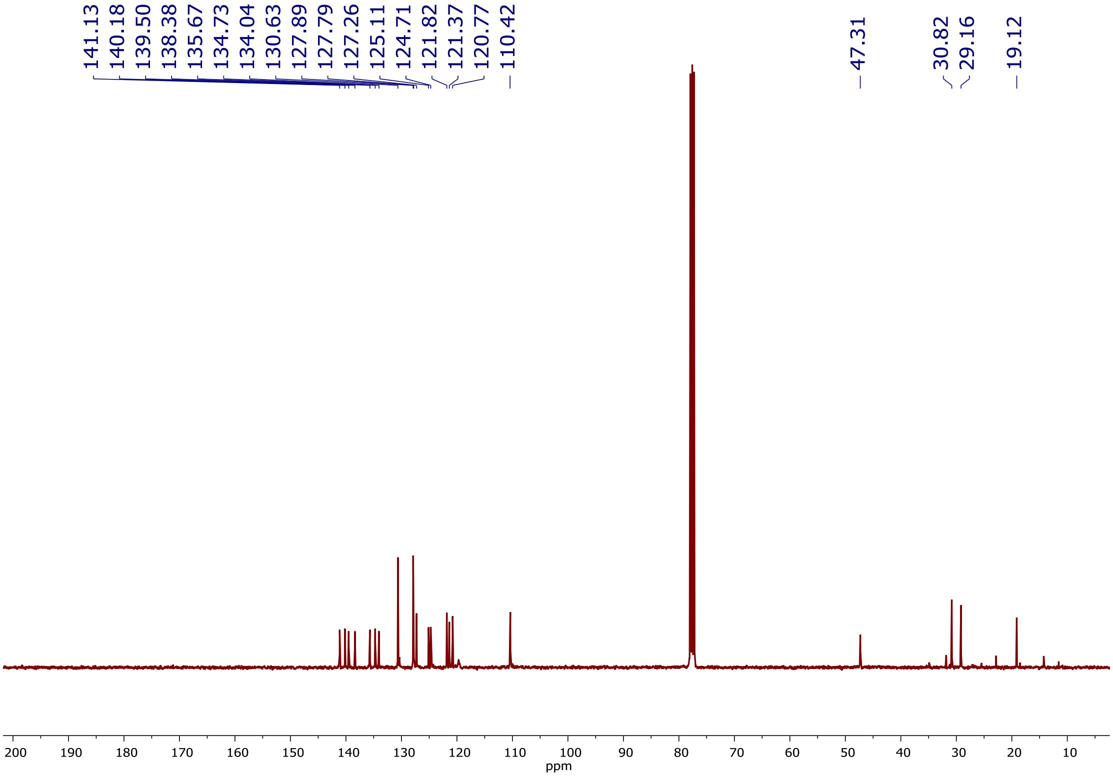


Figure **S9**. ^{13}C NMR spectrum of **(TPAC$_4$Im)DPS**.

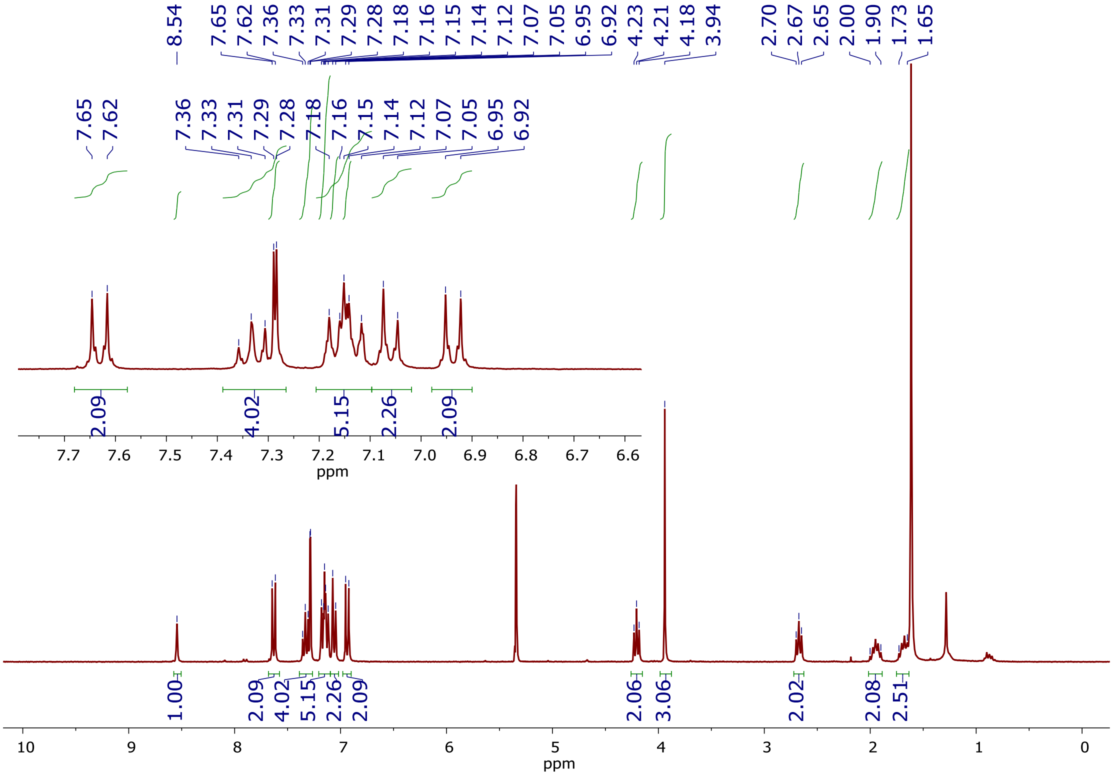


Figure **S10**. ^{1}H NMR spectrum of **imDPADPS**.

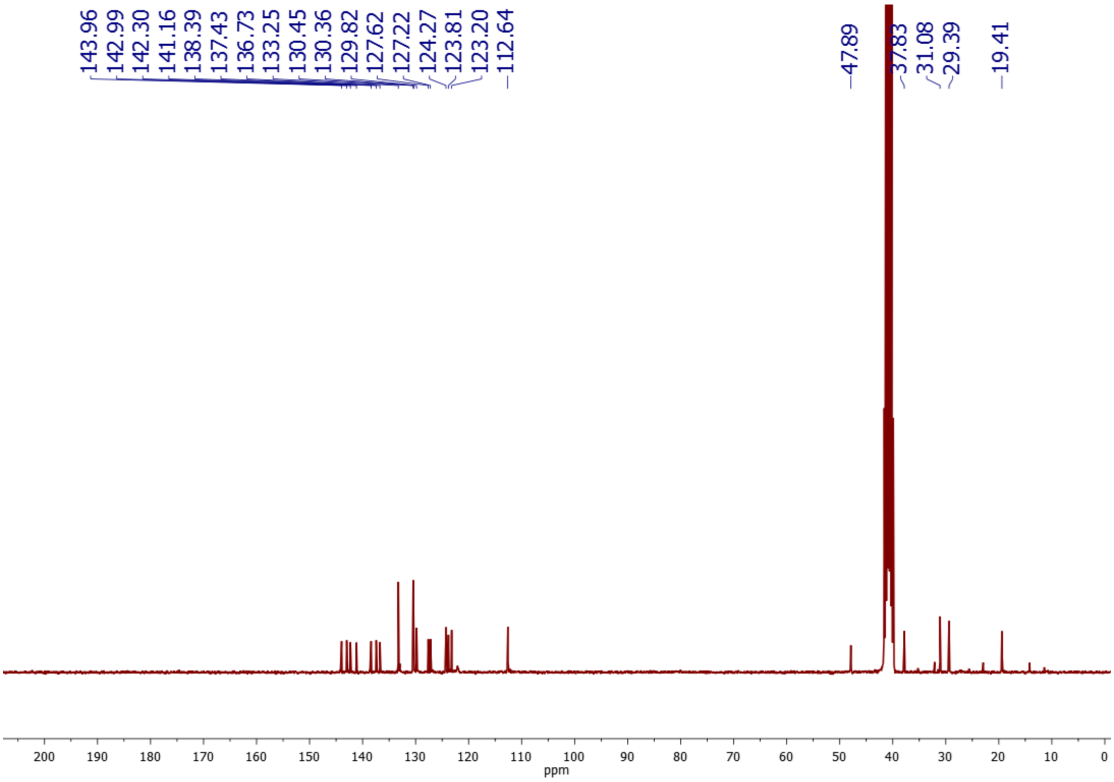


Figure **S11**. ^{13}C NMR spectrum of **imDPADPS**.

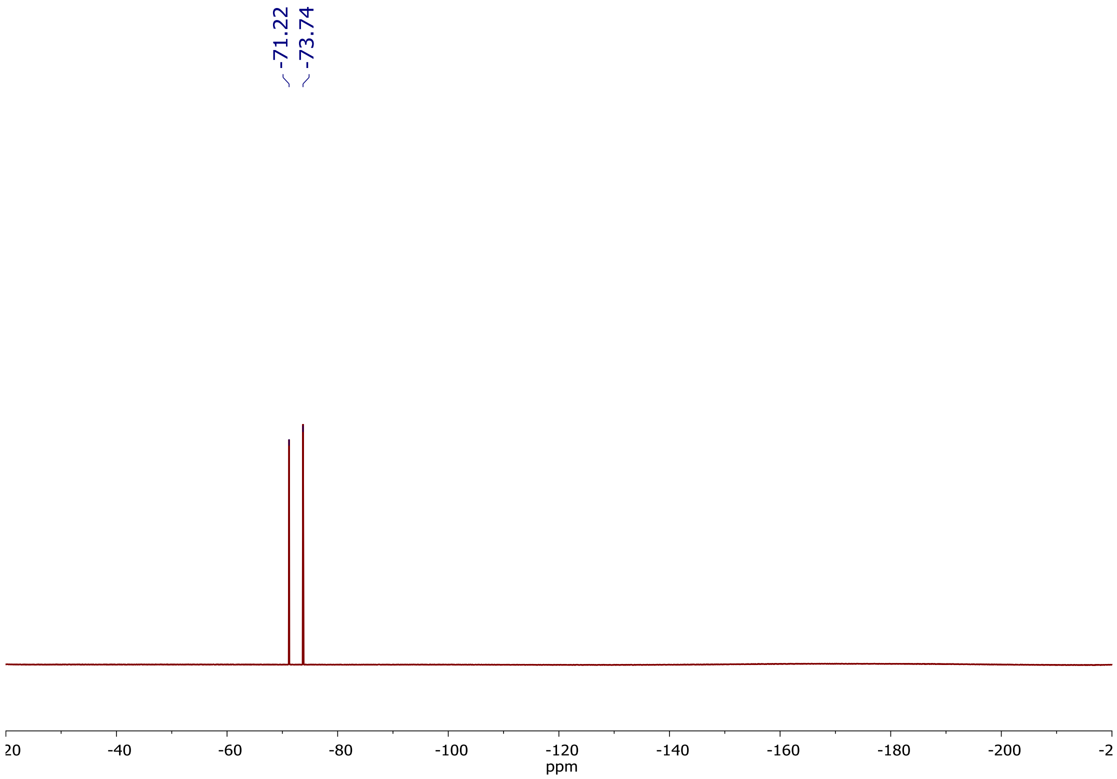


Figure **S12**. ^{19}F NMR spectrum of **imDPADPS**.

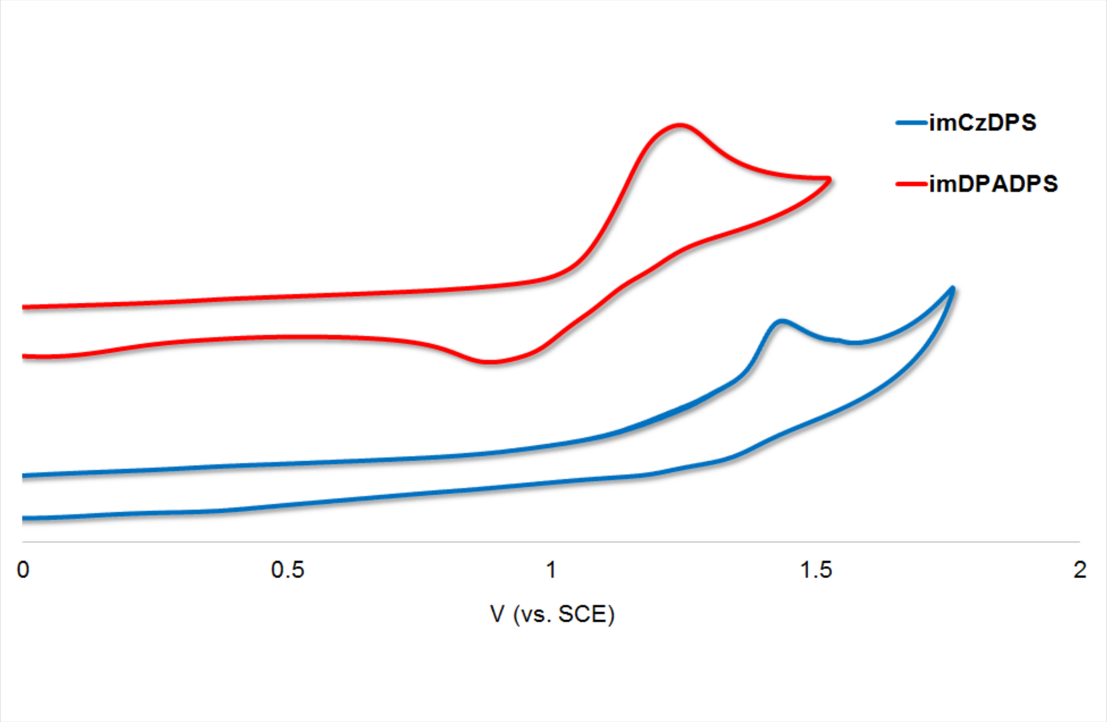


Figure **S13**. Cyclic voltammograms of **imCzDPS and imDPADPS** in degassed MeCN under argon with 0.1 M *n*-Bu_4NPF_6 as the supporting electrolyte.

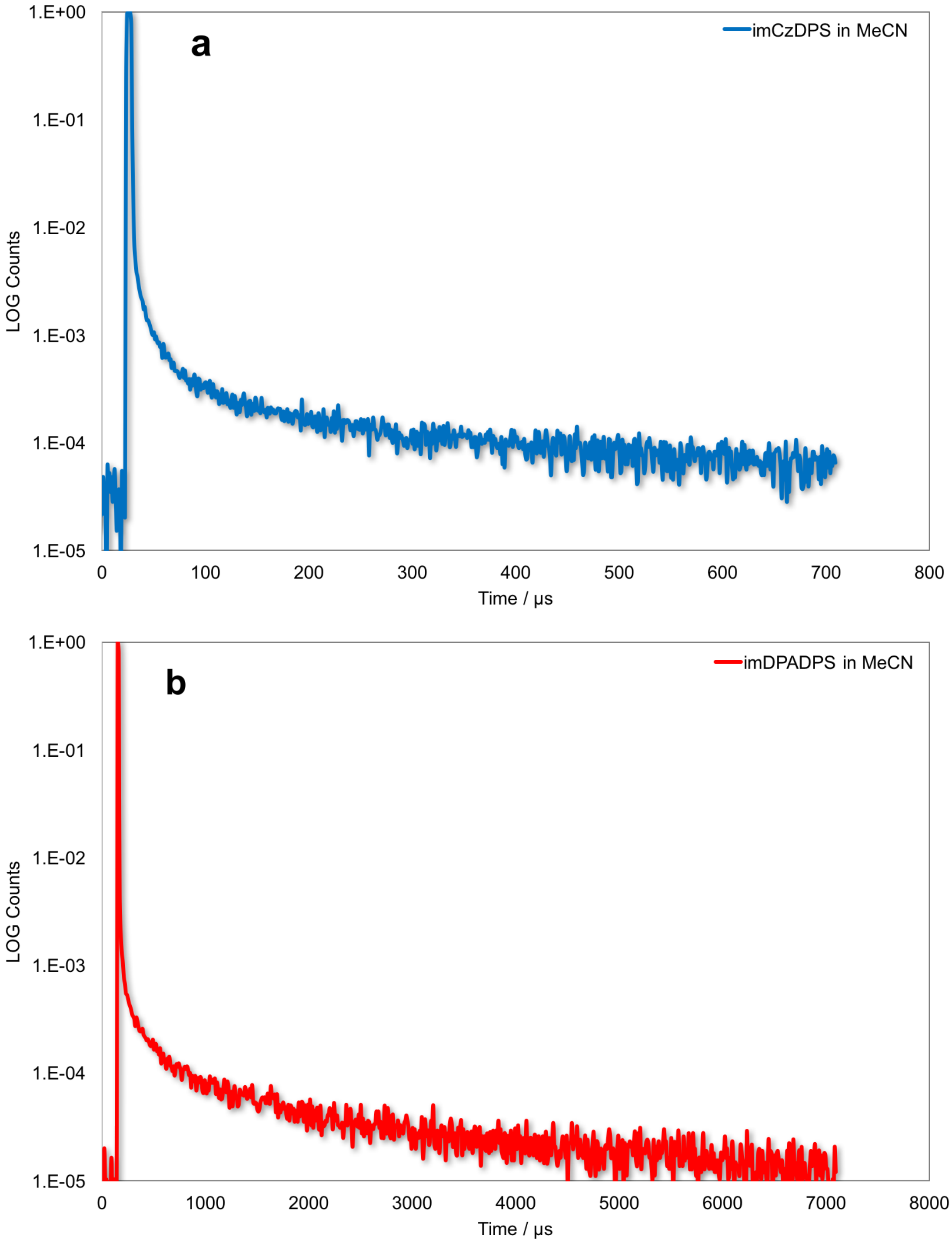


Figure **S14**. Emission decays of **imCzDPS** (a) and **imDPADPS** (b) in degassed MeCN.

References

(1). M. Y. Wong, G. J. Hedley, G. Xie, L. S. Kölln, I. D. W. Samuel, A. Pertegás, H. J. Bolink and E. Zysman-Colman, *Chem. Mater.*, 2015, **27**, 6535-6542.
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(4). V. V. Pavlishchuk and A. W. Addison, *Inorg. Chim. Acta*, 2000, **298**, 97-102.