

Deposition of loosely bound organic D-A- π -A' dyes on sensitized TiO₂ film: a possible strategy to suppress charge recombination and enhance power conversion efficiency in dye-sensitized solar cells

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1. Dye sensitized solar cell fabrication

Double layer films of interconnected TiO₂ particles on the fluorine-doped SnO₂ (FTO) conducting glass electrode were used as mesoporous photoanodes, which consist of a 10 μm thick film of TiO₂ particles with diameter of 20 nm sized and 4 μm thick of scattering anatase particles with diameter of 100 nm (Solaronix). The TiO₂ particles double layer films were first treated with TiCl₄ solution (40 mM) at 70 °C for 30 min. After being washed with DI water and absolute ethanol, the TiO₂ films were further thermally annealed at 500 °C for 30 min. The TiO₂ electrode was cooled to at 80 °C and then immersed into a dye solution in ethanol/CHCl₃ (4:1) containing chenodeoxycholic acid, CDCA for 12 hours at room temperature. After washing with ethanol and drying by high pure nitrogen gas, the stained TiO₂ electrodes were assembled with thermally platinized conducting glass electrodes with 60 μm thick gaskets. Counter electrode were prepared by adding two drops of platinum salt solution (Dyesol, MS006220) on FTO and the heated at 400 °C for 20 min. The liquid electrolyte consisted of 0.6 M 1,3-dimethylimidazolium iodide, 0.03 M iodine, 0.05 M LiI, 0.05 M guanidinium thiocyanate, and 0.5 M 4-tert-butylpyridine in 15/85 (v/v) mixture of valeronitrile and acetonitrile.

2. Photovoltaic characterization of the dye sensitized solar cell

The air mass (AM) 1.5-irradiance of 100 mW /cm² was provided by a solar simulator, which consists of a 300 W xenon light source (Oriel, U.S.A.) and an optical shutter connected to Keithley meter which is automated with I-V station from Newport. The light intensity was calibrated with a silicon diode reference cell 91150V (Oriel, U.S.A.). The mismatch between the simulated and the true solar spectra was corrected with the light filter 81094 (Oriel, U.S.A.). The current-voltage performance of the cell under these conditions were tested with four-wire connection mode by sourcing external potential bias to the cell and measuring the generated photocurrent with a Keithley 2400 digital source meter. The test results were acquired with Oriel IV test station software. The incident photon-to-electron conversion efficiency (IPCE) was characterized by using Oriel Quantum Efficiency Measurement Kit, consisted with a 300W xenon lamp, Merlin lock-in amplifier, Cornerstone 260 monochromator and a silicon detector. The measuring process was automated with TracQ software from Newport.

3. Materials and general methods

Solvents: Anhydrous toluene and MeCN were purchased from Aldrich. Pd(OAc)₂ (99+%) was purchased from Strem Chemicals. Pivalic acid and P^tBu₂Me·HBF₄ were purchased from Acros and Alfa Aesar, respectively, and used as received. **1** was synthesized by direct arylation of 5,6-difluoro-2,1,3-benzothiadiazole (DFBT);¹ **2** was made by following literature procedure.²

¹H and ¹³C NMR spectra were acquired in CDCl₃ using a Bruker AMX-400 spectrometer and the signals were referenced using the solvent peak (7.27 ppm for ¹H NMR and 77.0 ppm for ¹³C NMR) or tetramethylsilane (TMS, 0.0 ppm) as an internal standard. ¹⁹F NMR spectra (376 MHz) were recorded using trifluoro-toluene as an external standard (δ -63.73 ppm).

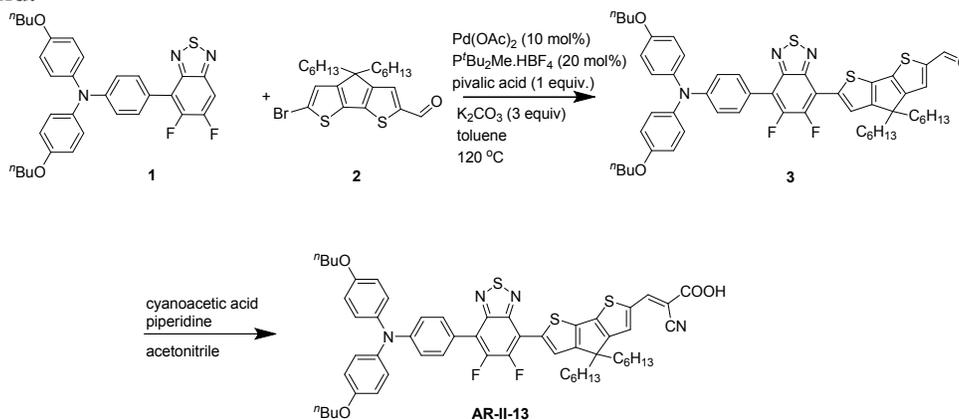
Chromatographic separations were performed using standard flash column chromatography methods using silica gel purchased from Sorbent Technologies (60 Å, 32-63 μm). Mass spectra were recorded on an Applied Biosystems 4700 Proteomics Analyzer at the Mass Spectrometry Facility at the Georgia Institute of Technology. Elemental analyses were performed by Atlantic

Microlabs. UV-Vis-NIR spectra were recorded in 1 cm quartz cuvette using a Varian Cary 5E spectrometer. Steady-state fluorescence measurement was performed on a single-photon-counting spectrofluorimeter from Horiba-Jovin-Yvon (Fluorolog 3).

Electrochemical measurements were carried out under nitrogen in dry deoxygenated 0.1 M tetra-*n*-butylammonium hexafluorophosphate in dichloromethane (ca. 10^{-4} M of analyte) using a conventional three-electrode cell with a glassy carbon working electrode, platinum wire counter electrode, and a Ag wire coated with AgCl as pseudo-reference electrode. Potentials were referenced to ferrocenium/ferrocene. Cyclic voltammograms were recorded at a scan rate of 50 mV.s⁻¹.

4. Synthesis of AR-II-13

The synthesis of **AR-II-13** is shown in the following scheme. Use recently-developed sequential direct arylations of DFBT,¹ **3** was quickly synthesized in an efficient manner. Final Knoevenagel condensation with cyanoacetic acid in the presence of piperidine gave target dye as a black solid.



6-(7-(4-(Bis(4-butoxyphenyl)amino)phenyl)-5,6-difluorobenzo[*c*][1,2,5]thiadiazol-4-yl)-4,4-dihexyl-4*H*-cyclopenta[1,2-*b*:5,4-*b'*]dithiophene-2-carbaldehyde (**3**)

Pd(OAc)₂ (17 mg, 0.075 mmol), P^{*t*}Bu₂Me.HBF₄ (37 mg, 0.15 mmol), pivalic acid (76 mg, 0.75 mmol), potassium carbonate (310 mg, 2.25 mmol), **1** (420 mg, 0.75 mmol), and **2** (480 mg, 1.05 mmol) were weighed in air and added to a 50 mL Schlenk flask, followed by adding toluene (4 mL). The resulting mixture was purged with N₂ for 30 min, screw-capped, and heated in an oil bath at 120 °C. After TLC analysis showed completion of the reaction (18 h), the resulting mixture was cooled to room temperature, diluted with DCM (100 mL), and filtered through Celite® (20 mL). The filtrate was purified with silica gel chromatography (300 mL of silica gel, 16% CH₂Cl₂ in hexane as eluent) to provide **3** as an orange solid (313 mg, 45%). ¹H NMR (400 MHz, CDCl₃) δ 9.87 (s, 1H), 8.18 (s, 1H), 7.68 (d, *J* = 8 Hz, 2H), 7.61 (s, 1H), 7.15 (d, *J* = 8 Hz, 4H), 7.03 (d, *J* = 8 Hz, 2H), 6.90 (d, *J* = 8 Hz, 4H), 3.96 (t, *J* = 5 Hz, 4H), 1.99 – 1.92 (m, 4H), 1.88 – 1.79 (m, 4H), 1.60 – 1.55 (m, 8H), 1.20 – 1.12 (m, 8H), 1.05 – 0.95 (m, 10H), 0.81 (m, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 182.66, 162.12, 158.96, 156.14, 151.28 (t, *J* = 18 Hz), 149.63 (dd, *J* = 187, 9 Hz), 149.62, 148.86, 147.21, 144.24, 139.81, 139.16, 139.09, 136.50 (dd, *J* = 2, 2 Hz), 131.29, 129.91, 127.48, 124.77, 120.67, 118.40, 118.06 (d, *J* = 12 Hz), 115.40, 111.80 (d, *J* = 12 Hz), 67.94, 54.24, 37.73, 31.56, 31.40, 29.61, 24.62, 22.58, 19.29, 14.02,

13.89. ^{19}F NMR (376 MHz, CDCl_3) δ -126.55 (d, $J_{\text{FF}} = 19$ Hz), -134.64 (d, $J_{\text{FF}} = 19$ Hz). HRMS (MALDI) m/z : Calcd for $\text{C}_{54}\text{H}_{59}\text{F}_2\text{N}_3\text{O}_3\text{S}_3$ (M^+), 931.3691; Found, 931.3693. Anal. Calcd for $\text{C}_{54}\text{H}_{59}\text{F}_2\text{N}_3\text{O}_3\text{S}_3$: C, 69.57; H, 6.38; N, 4.51. Found: C, 69.48; H, 6.43; N, 4.43.

(*E*)-3-(6-(7-(4-(Bis(4-butoxyphenyl)amino)phenyl)-5,6-difluorobenzo[*c*][1,2,5]thiadiazol-4-yl)-4,4-dihexyl-4*H*-cyclopenta[1,2-*b*:5,4-*b'*]dithiophen-2-yl)-2-cyanoacrylic acid (**AR-II-13**)
Cyanoacetic acid (36.5 mg, 0.43 mmol), **3** (200 mg, 0.22 mmol), piperidine (80 μL), and acetonitrile (32 mL) were added to a 50 mL two-necked flask. The resulting suspension was purged with N_2 for 10 min and heated to reflux in an oil bath. After TLC analysis showed completion of the reaction (3 h), the resulting mixture was cooled to room temperature, diluted with DCM (100 mL), and filtered through Celite[®] (5 mL). The filtrate was purified with silica gel chromatography (210 mL of silica gel, gradient eluent from pure CH_2Cl_2 to 6% MeOH and 4% AcOH in DCM) to provide **AR-II-13** as a black solid (160 mg, 75%). ^1H NMR (400 MHz, CDCl_3) δ 8.35 (s, 1H), 8.21 (s, 1H), 7.72 (s, 1H), 7.68 (d, $J = 9.0$ Hz, 2H), 7.15 (d, $J = 9.0$ Hz, 4H), 7.03 (d, $J = 9.0$ Hz, 2H), 6.87 (d, $J = 9.0$ Hz, 4H), 3.96 (t, $J = 6.0$ Hz, 4H), 1.97 (d, $J = 6.0$ Hz, 4H), 1.73 (m, 4H), 1.47 (m, 4H), 1.17 (br, 12H), 0.96 (m, 10H), 0.81 (m, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 163.25, 159.84, 156.09, 150.38 (m), 149.55, 148.49 (m), 148.19 (m), 139.72, 138.96 (m), 138.27 (m), 137.15, 131.33 (m), 127.47, 124.62, 120.48, 118.22, 116.56, 115.37, 111.46 (m), 67.92, 54.32, 37.70, 31.56, 31.38, 29.59, 24.71, 22.58, 19.27, 14.02, 13.88 (seven aromatic resonances not observed, presumably due to overlap). ^{19}F NMR (376 MHz, CDCl_3) δ -125.90 (d, $J_{\text{FF}} = 19$ Hz), -134.68 (d, $J_{\text{FF}} = 19$ Hz). HRMS (MALDI) m/z : Calcd for $\text{C}_{57}\text{H}_{60}\text{F}_2\text{N}_4\text{O}_4\text{S}_3$ (M^+), 998.3773; Found, 998.3745. Anal. Calcd for $\text{C}_{57}\text{H}_{60}\text{F}_2\text{N}_4\text{O}_4\text{S}_3$: C, 68.51; H, 6.05; N, 5.61. Found: C, 68.48; H, 6.10; N, 5.49.

5. Photophysical properties of compound AR-II-13

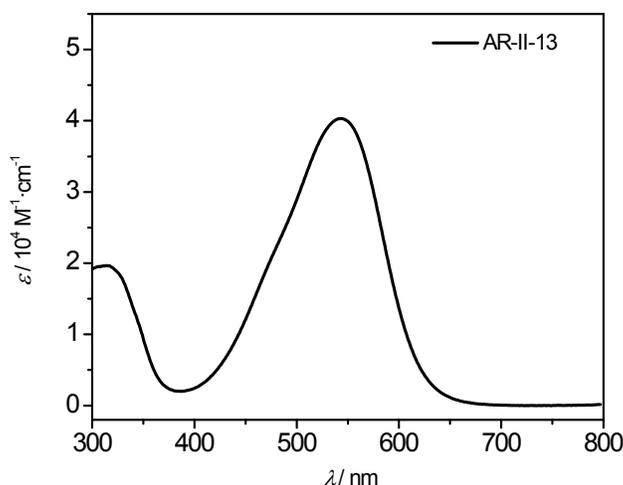


Figure S1. Absorption spectra of **AR-II-13** in chloroform/methanol mixed solution ($v/v = 4/1$).

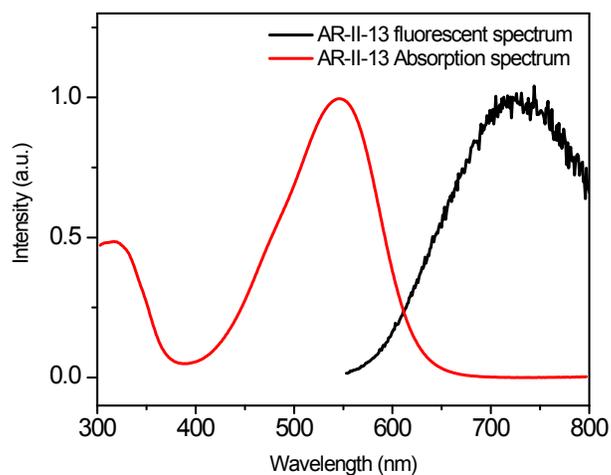


Figure S2. Normalized UV-Vis absorption and emission spectra ($\lambda_{\text{ex}} = 520$ nm) of compounds **AR-II-13** in chloroform/methanol mixed solution (v/v = 4/1). The optical bandgap, 2.02 eV, was roughly estimated from the intersection.

6. Cyclic voltammetry of AR-II-13

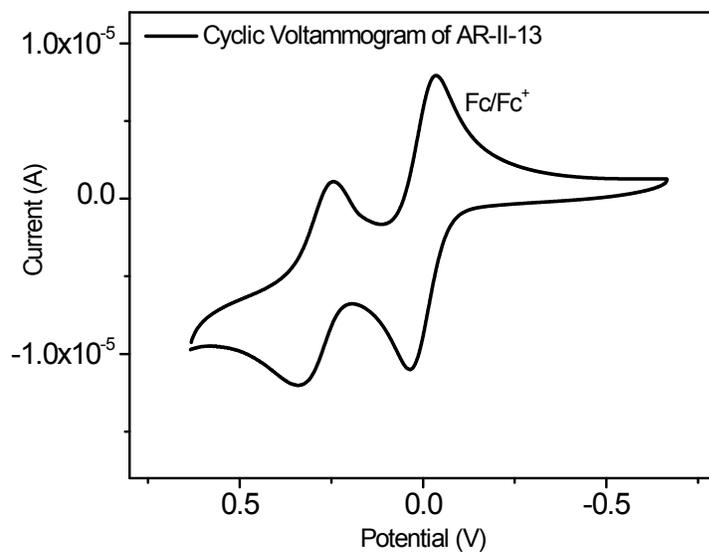


Figure S3. Cyclic voltammograms of **AR-II-13** conducted in 0.1 M $n\text{Bu}_4\text{NPF}_6$ in CH_2Cl_2 with $\text{Cp}_2\text{Fe}^{+/0}$ as internal reference at a scan rate of 50 mV s^{-1} .

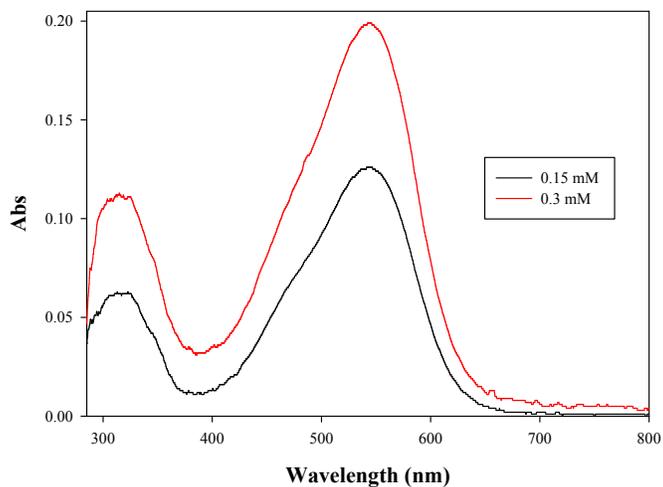
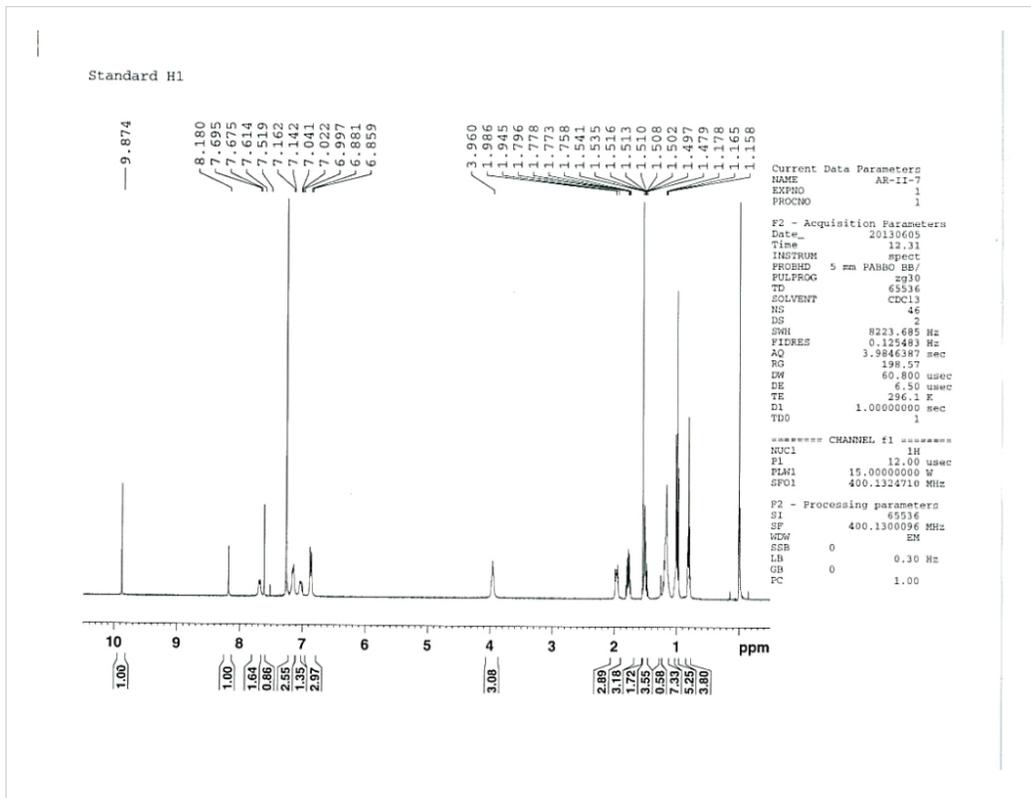


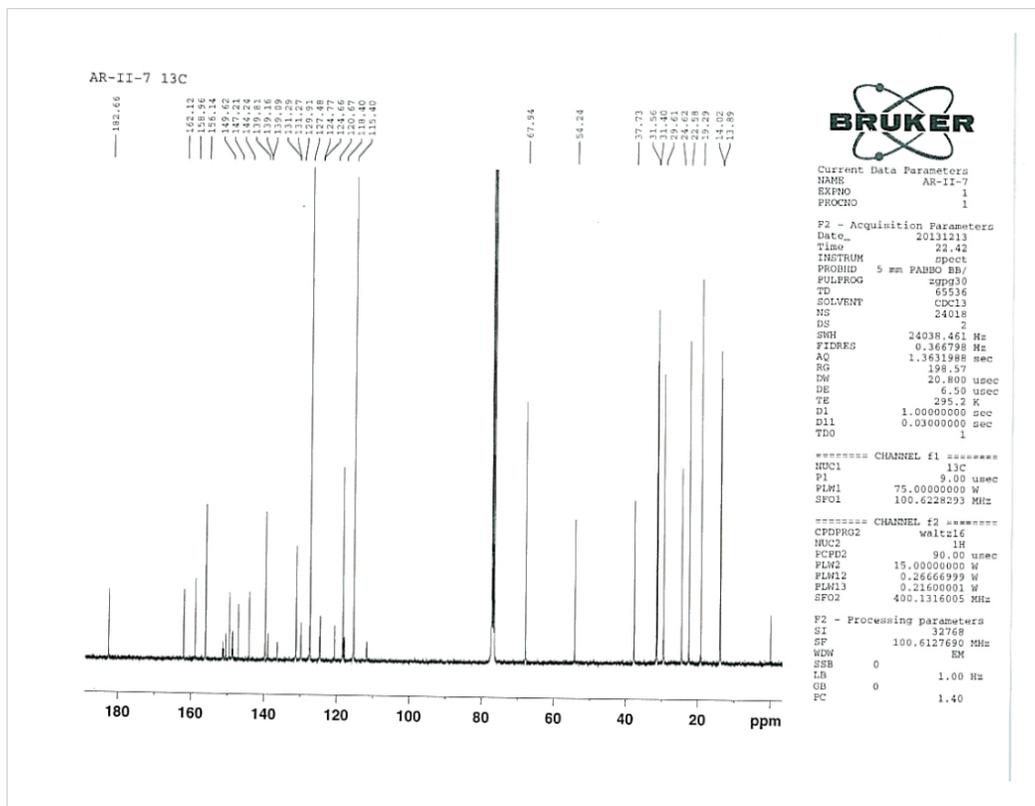
Figure S4. UV-vis spectra of **AR-II-13** free dye loading on TiO_2 film upon ethanol wash, which was dissolved in ethanol/chloroform mixture solution from TiO_2 film: the amount of dye loading is 4.96×10^{-8} mol from 0.3 mM dye solution: 3.1×10^{-8} mol from 0.15 mM dye solution.

7. NMR spectra of new compounds

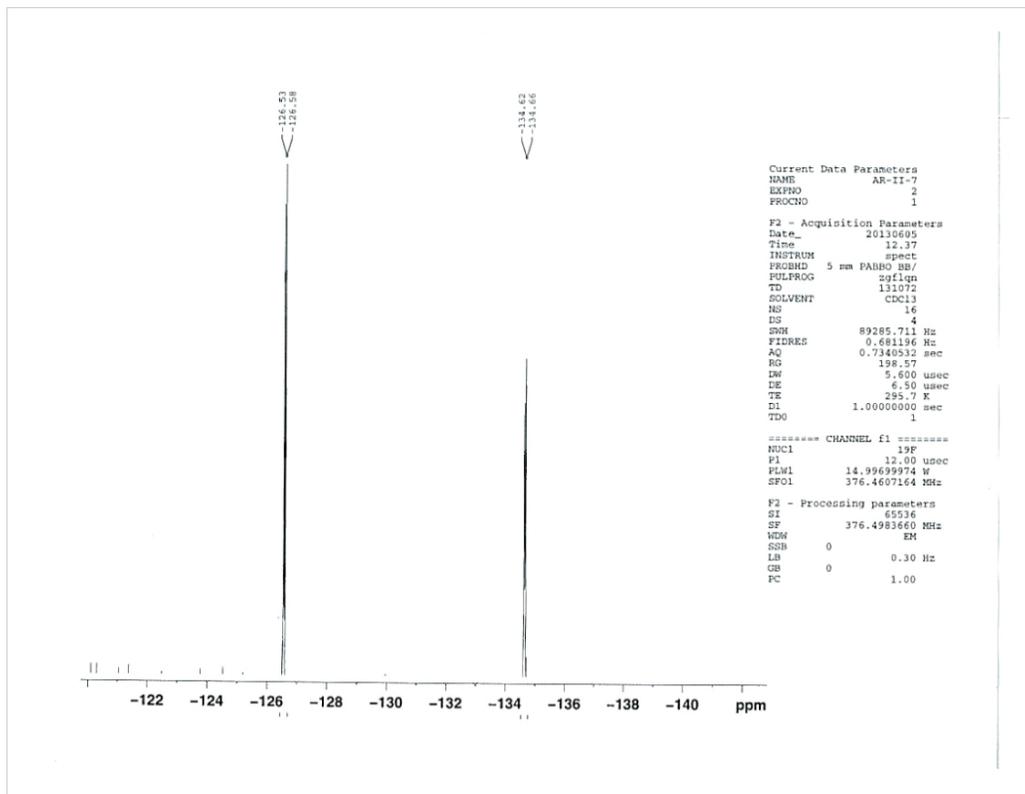
¹H NMR of 3



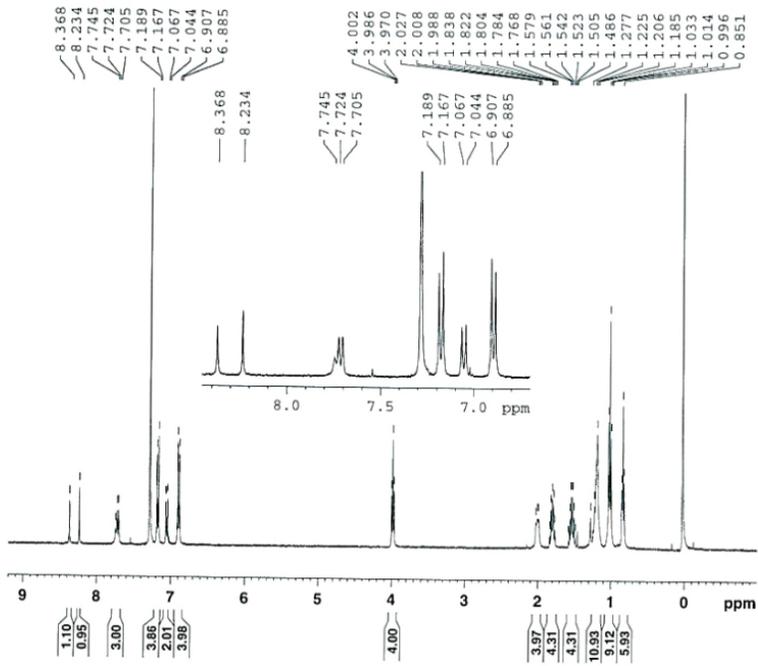
¹³C NMR of 3



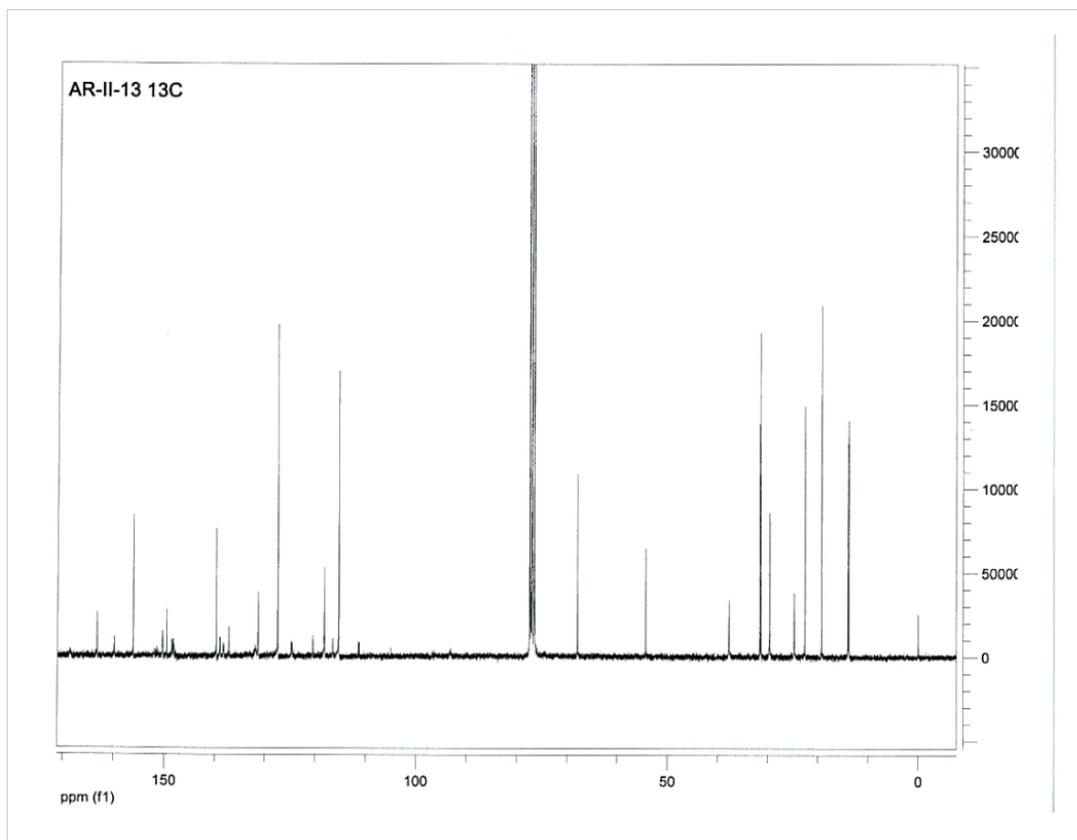
¹⁹F NMR of 3

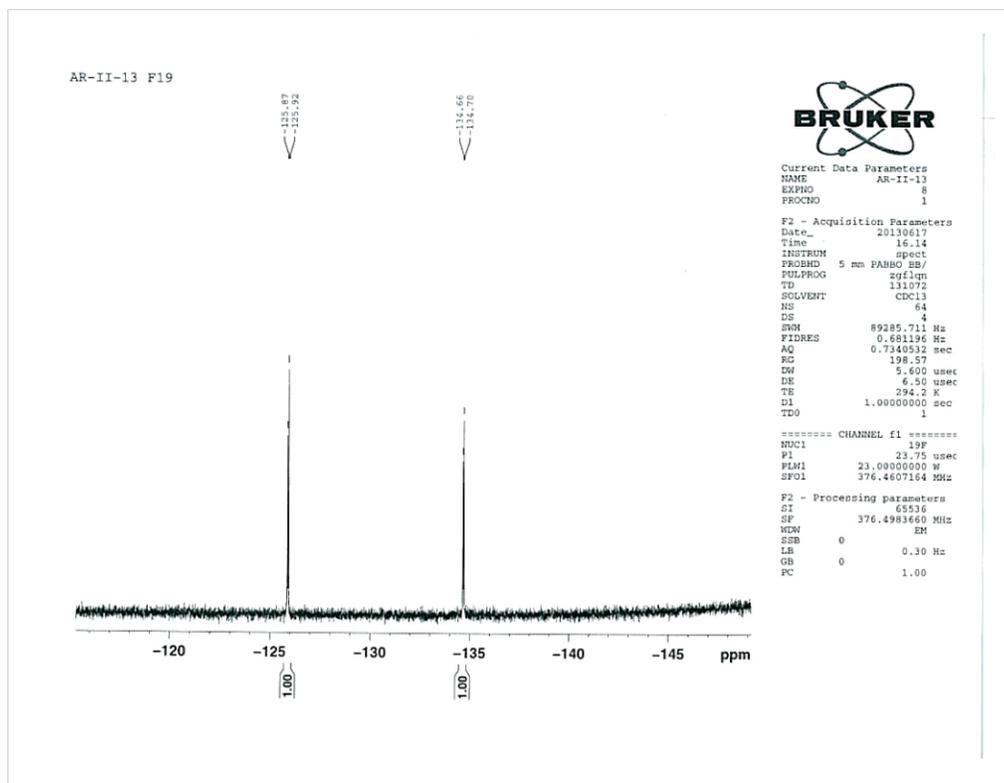


AR-II-13 CDC13



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RG 198.57
EW 60.800
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GB 0
PC 1.00





References for supporting information

1. J. Zhang, W. Chen, A. J. Rojas, E. V. Jucov, T. V. Timofeeva, T. C. Parker, S. Barlow and S. R. Marder, *J. Am. Chem. Soc.*, 2013, **135**, 16376-16379.
2. R. Li, J. Liu, N. Cai, M. Zhang and P. Wang, *J. Phys. Chem. B*, 2010, **114**, 4461-4464.