SUPPORTING INFORMATION

Poly(ether-imide-ester)s Incorporating Sulfur-Containing Amino Acids: A First Step Toward More Sustainable High-Dielectric Polymer Materials

Sebastian Bonardd[1,*], Maksim Bratukhin[2,3], Sara Zanchi[4], Federico Guerrero[1], Florian Le Goupil[4], David Díaz Díaz[2,3], José A. Pomposo[1,5,6], Jon Maiz[1,5,*]

[1] Centro de Física de Materiales (CFM-MPC), CSIC-UPV/EHU, Paseo Manuel de Lardizábal 5, 20018 Donostia-San Sebastián, Spain.

[2] Departamento de Química Orgánica, Universidad de La Laguna, Avda. Astrofísico Francisco Sánchez 3, La Laguna 38206, Tenerife, Spain.

[3] Instituto Universitario de Bio-Orgánica Antonio González, Universidad de La Laguna, Avda. Astrofísico Francisco Sánchez 2, La Laguna 38206, Tenerife, Spain.

[4] Univ. Bordeaux, CNRS, Bordeaux INP, LCPO, UMR 5629, F-33600, Pessac, France.

[5] IKERBASQUE – Basque Foundation for Science, Plaza Euskadi 5, 48009, Bilbao, Spain.

[6] Departamento de Polímeros y Materiales Avanzados: Física, Química y Tecnología, Universidad del País Vasco-Euskal Herriko Unibertsitatea (UPV/EHU), Paseo Manuel de Lardizábal 3, 20018, Donostia-San Sebastián, Spain.

*Corresponding authors: sebastianignacio.bonardd@ehu.eus, jon.maizs@ehu.eus

1. Synthetic procedures

1.1. Synthesis of 4-nitrophthalimide (1b)

The synthesis of 4-nitrophthalimide was performed following Levi's reported protocol, with slight modifications when necessary.[1] In a round-bottom flask immersed in an ice-water bath, 24 mL of nitric acid were added dropwise to 141 mL of sulfuric acid under constant magnetic stirring. After the complete addition of HNO_3, the mixture was stirred until the temperature dropped below 5 °C. Then, 20 g of phthalimide (**1a**, 0.14 mmol) were gradually added in small portions under vigorous stirring, ensuring that the temperature did not exceed 10 °C. Once the addition of 1a was complete, the reaction mixture was allowed to reach room temperature overnight. The resulting yellow-transparent solution was slowly poured into an ice-water mixture, maintaining the temperature below 20 °C. The white precipitate formed was filtered and washed thoroughly with water until the filtrate reached a neutral pH. The solid was air-dried overnight and recrystallized from a 95:5 ethanol:water mixture, yielding 18 g of white crystals. Yield: 69 %

^{1}H-NMR (ppm, DMSO-d_6): 11.83 (s, 1H), 8.60 (d, 1H), 8.43 (s, 1H), 8.07 (d, 1H)

^{13}C-NMR (ppm, DMSO-d_6): 168.01, 167.72, 151.84, 137.77, 134.52, 129.92, 124.95, 118.23

1.2. Synthesis of 4-nitrophthalamide (1c)

In a 250 mL round-bottom flask, 5.00 g of 1b (26.20 mmol) was dissolved in 125 mL of methanol under constant stirring and maintained at 50 °C. The resulting solution was bubbled with a continuous flow of dry NH_3 for 1 hour, generated separately in a glass setup by the controlled addition of a saturated aqueous NH_4Cl solution over solid NaOH. During NH_3 bubbling, a white precipitate formed. After the reaction time was completed, the system was allowed to cool to room temperature, and the precipitated solid was collected by filtration. The solid was then thoroughly washed with methanol and dried at 70 °C for 24 hours, yielding 4.1 g of 1c. Yield: 68 %

^{1}H-NMR (ppm, DMSO-d_6): 8.32 (d, 1H), 8.29 (dd, 1H), 8.05 (s, 1H), 7.99 (s, 1H), 7.71 (d, 1H), 7.62 (s, 2H)

^{13}C-NMR (ppm, DMSO-d_6): 169.17, 168.16, 147.56, 143.13, 137.70, 129.62, 124.85, 122.88

1.3. Synthesis of 4-nitrophthalonitrile (1d)

Based on the protocol reported by Touaiti et al.[2], 25 mL of dry DMF were introduced into a flame-dried round-bottom flask under argon atmosphere and cooled using an ice–salt bath. While maintaining constant stirring, 10.5 mL of thionyl chloride (286 mmol) were added dropwise, ensuring that the temperature did not exceed 5 °C. Then, under a constant flux of argon, 7.5 g of **1c** (35.89 mmol) were added in portions. After completing the addition, the reaction is maintained at 5 °C for 30 minutes before being gradually warmed to room temperature. The reaction is left to proceed for 24 hours, after which the mixture is poured into an ice-water mixture. The formed solid is filtered, washed with abundant water and dried at 75 °C in a vacuum oven for 24 hours, yielding a yellow solid. Yield: 53 %

^{1}H-NMR (ppm, DMSO-d_6): 9.05 (d, 1H), 8.69 (dd, 1H), 8.45 (d, 1H)

^{13}C-NMR (ppm, DMSO-d_6): 150.25, 136.14, 129.34, 129.03, 120.73, 117.10, 115.40, 115.09

1.4. Synthesis of 4,4'-((sulfonylbis(4,1-phenylene))bis(oxy))diphthalonitrile (2a)

The synthesis of **2a** was carried out according to previously reported protocols, with slight variations when required.[3] In a round-bottom flask connected to a reflux system, 3.00 g of **1d** (18.12 mmol) was mixed with 2.00 g of 4,4'-sulfonyl diphenol (9.08 mmol), 5.00 g of K_2CO_3 (36.36 mmol) and 50 mL of DMF. The mixture was heated at 80 °C under constant stirring for 24 hours, after which it was poured into an excess of cold water. The obtained solid was filtered,

washed with abundant water, and dried in a vacuum oven at 80 °C overnight, yielding 3.1 g of a yellowish solid. Yield: 72 %

^{1}H-NMR (ppm, DMSO-d_6): 8.17 (d, 1H), 8.07 (d, 2H), 8.00 (s, 1H), 7.61 (d, 1H), 7.38 (d, 2H)

^{13}C-NMR (ppm, DMSO-d_6): 159.48, 159.20, 137.62, 136.95, 130.82, 124.99, 124.71, 120.65, 117.44, 116.22, 115.73, 110.47.

1.5. Synthesis of 4,4'-((sulfonylbis(4,1-phenylene))bis(oxy))diphthalic acid (2b)

In a two-neck round-bottom flask connected to a reflux system, 3.00 g of **2a** was mixed with 50 mL of ethanol and 50 mL of a 1.5 M KOH aqueous solution. The mixture was vigorously stirred and heated under reflux for 72 hours. The progress of the reaction could be monitored by detecting the release of NH_3 gas using a pH test paper placed at the upper part of the reflux system. After completing the reaction time, the mixture is cooled down and filtered. The obtained solution is diluted with 50 mL of water, chilled in an ice-water bath and acidified until pH 3 using a 6 M HCl aqueous solution. The formed solid is filtered, washed with abundant water and dried at 70 °C in a vacuum oven for 24 hours, yielding 3.00 g of yellowish solid. Yield: 91 %

^{1}H-NMR (ppm, DMSO-d_6): 8.00 (d, 2H), 7.92 (d, 1H), 7.44 (s, 1H), 7.29 (d, 1H), 7.25 (d, 2H)

^{13}C-NMR (ppm, DMSO-d_6): 168.26, 167.89, 160.65, 157.12, 137.22, 136.52, 132.95, 130.56, 129.24, 121.69, 120.35, 119.53

1.6. Synthesis of 5,5'-((sulfonylbis(4,1-phenylene))bis(oxy))bis(isobenzofuran-1,3-dione) (2c)

In a round-bottom flask connected to a reflux system, 2.00 g of **2b** (2.92 mmol) was mixed with 100 mL of acetic anhydride and heated under reflux at 130–140 °C for 24 hours. After the reaction time was completed, the solvent was removed by vacuum distillation, and the resulting solid was mechanically crushed and washed with boiling hexane (in a reflux system) for 1 hour. The solid was then filtered, washed with hexane, and dried in a vacuum oven at 75 °C for 24 hours, yielding 1.2 g of a clear brown solid. Yield: 64 %.

^{1}H-NMR (ppm, DMSO-d_6): 8.00 (m, 3H), 7.47 (s, 1H), 7.29 + 7.25 (m, 3H)

^{13}C-NMR (ppm, DMSO-d_6): 168.20, 167.87, 160.67, 157.10, 137.31, 136.49, 133.25, 130.65, 130.55, 129.44, 121.70, 120.61, 119.52

1.7. Synthesis of EIA-Met

The monomer EIA-Met was synthesized following previously reported protocols with slight modifications.[3] In a reflux system containing 150 mL of acetic acid, 2.00 g of **2c** (3.67 mmol) was mixed with 1.65 g of *D, L*-methionine (11.02 mmol) and stirred at room temperature for 8 hours.

Subsequently, the temperature of the system was raised to 120 °C for 12 hours, observing the dissolution of the solid content of the mixture. After completing the reaction time, the homogeneous mixture was filtered, and two-thirds of the solvent were removed using vacuum distillation. Then, the remaining mixture was poured into a 5 % v/v HCl aqueous solution, achieving the obtainment of a precipitate that was filtered, washed with abundant water and dried in a vacuum oven at 85 °C for 24 hours, yielding a clear brown solid. Yield: 73 %.

^{1}H-NMR (ppm, DMSO-d_6): 8.04 + 7.97 (d + d, 3H), 7.61 + 7.56 (s + d, 2H), 7.34 (d, 2H), 4.94 (m, 1H), 2.37 (m, 2H), 2.02 (s, 3H)

^{13}C-NMR (ppm, DMSO-d_6): 170.84, 167.19, 167.01, 160.84, 160.34, 137.01, 134.68, 130.67, 127.45, 126.74, 120.00, 114.90, 51.23, 30.61, 28.08, 14.91.

1.8. Synthesis of EIA-Met(O_2)

The synthesis of EIA-Met(O_2) was carried out using the same protocol described for the preparation of EIA-Met but replacing D, L-methionine by *D, L*-methionine sulfone (2.00 g, 11 mmol). Yield: 73 %

^{1}H-NMR (ppm, DMSO-d_6): 8.05 + 7.99 (d + d, 3H), 7.62 (s, 1H), 7.57 (d, 1H), 7.33 (d, 2H), 4.95 (m, 1H), 2.95 (s, 3H)

^{13}C-NMR (ppm, DMSO-d_6): 170.22, 167.10, 166.93, 160.79, 160.36, 136.98, 134.71, 130.68, 127.60, 126.42, 125.72, 119.94, 114.92, 51.01, 50.87, 22.28.

1.9. Synthesis of EIA-Ala

The synthesis of EIA-Met(O_2) was carried out using the same protocol described for the preparation of EIA-Met but replacing *D, L*-methionine by *D, L*-Alanine (0.98 g, 11 mmol). Yield: 66 %

^{1}H-NMR (ppm, DMSO-d_6): 8.04 (d, 2H), 7.96 (d, 1H), 7.59 + 7.54 (s + d, 2H), 7.33 (d, 2H), 4.88 (q, 1H), 1.55 (d, 3H)

^{13}C-NMR (ppm, DMSO-d_6): 171.01, 166.40, 166.21, 160.33, 159.89, 136.54, 134.12, 130.20, 127.00, 125.88, 125.25, 119.49, 114.41, 47.14, 14.81.

2.0. Polymerization procedure

The polymerization of the monomers EIA-Met, EIA-Met(O_2), and EIA-Ala was conducted following the procedure reported by Mallakpour et al., with slight modifications.[4] The synthesis of PEIE-Met(O_2) is described below as a representative example.

In a 10 mL dry glass vial equipped with a magnetic stir bar, 0.55 g (2.90 mmol) of p-toluenesulfonyl chloride (TsCl) was introduced under a constant flow of dry argon. The system

was then sealed with a rubber septum, followed by the addition of 1.1 mL of freshly distilled anhydrous pyridine. The mixture was stirred for 30 minutes prior to the dropwise addition of 0.24 mL of anhydrous DMF. Stirring was continued for an additional 30 minutes before use. In parallel, a second solution was prepared in a round-bottom flask equipped with a magnetic stir bar by dissolving 0.50 g (0.58 mmol) of EIA-Met(O_2) in 2.5 mL of anhydrous pyridine. Once complete dissolution of the monomer was achieved, the previously prepared TsCl/pyridine/DMF solution was added dropwise and stirred at room temperature for 30 minutes. Subsequently, a solution containing 0.15 g (0.58 mmol) of 4,4′-sulfonyldiphenol in 1.4 mL of dry pyridine was added dropwise and the reaction mixture was stirred at room temperature for 30 minutes, followed by heating at 120 °C for 4 hours. Upon completion of the reaction, the mixture was cooled to room temperature and poured into 50 mL of methanol, resulting in the precipitation of a solid product. The precipitate was collected by filtration, redissolved in 5 mL of DMF, and subsequently reprecipitated in 50 mL of methanol, with stirring maintained overnight. The final precipitate was filtered, washed thoroughly with methanol, and dried in a vacuum oven at 120 °C for 24 hours.

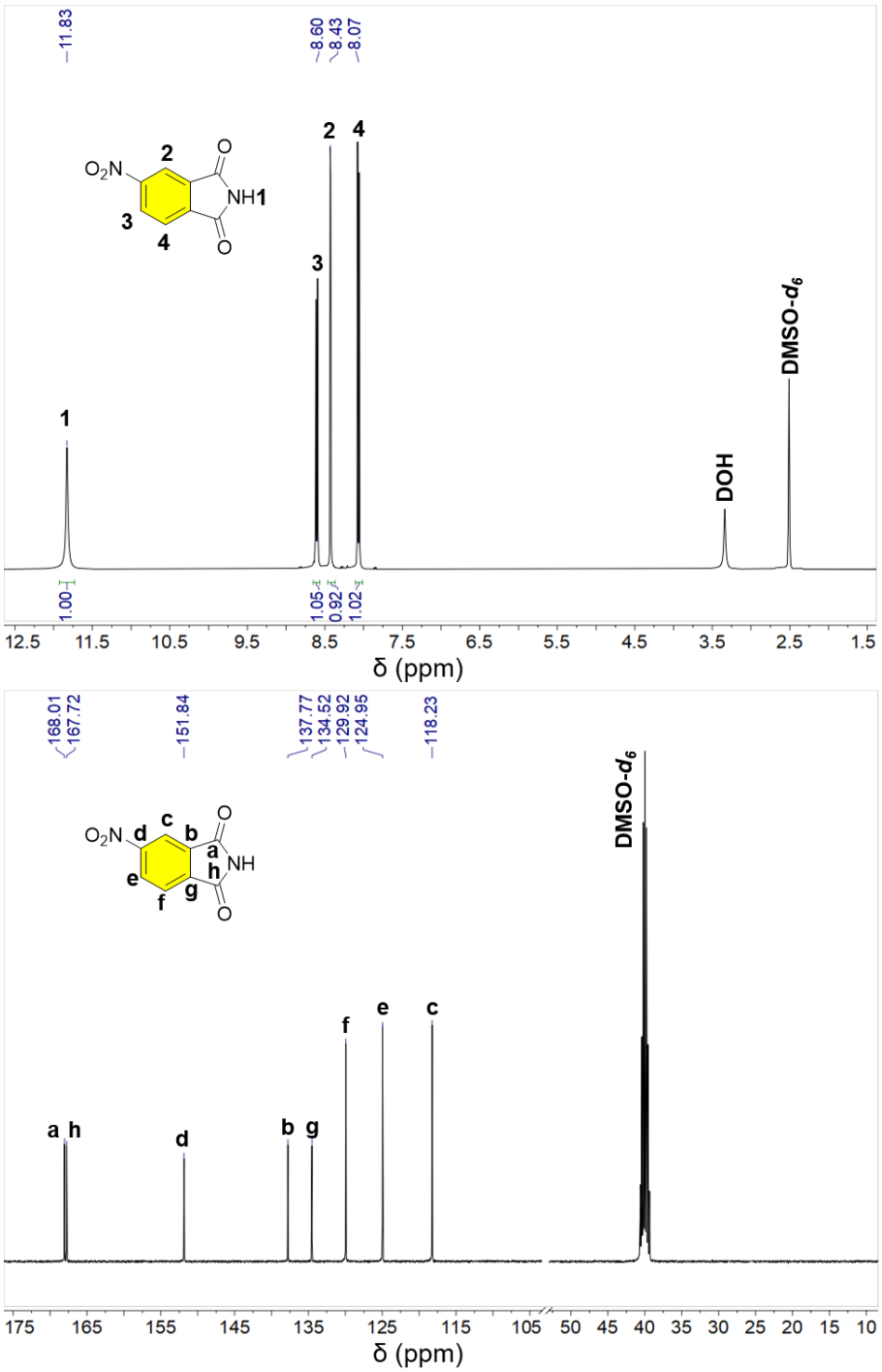

Figure S1. ^{1}H- (up) and ^{13}C-NMR (bottom) spectra recorded for **1b**.

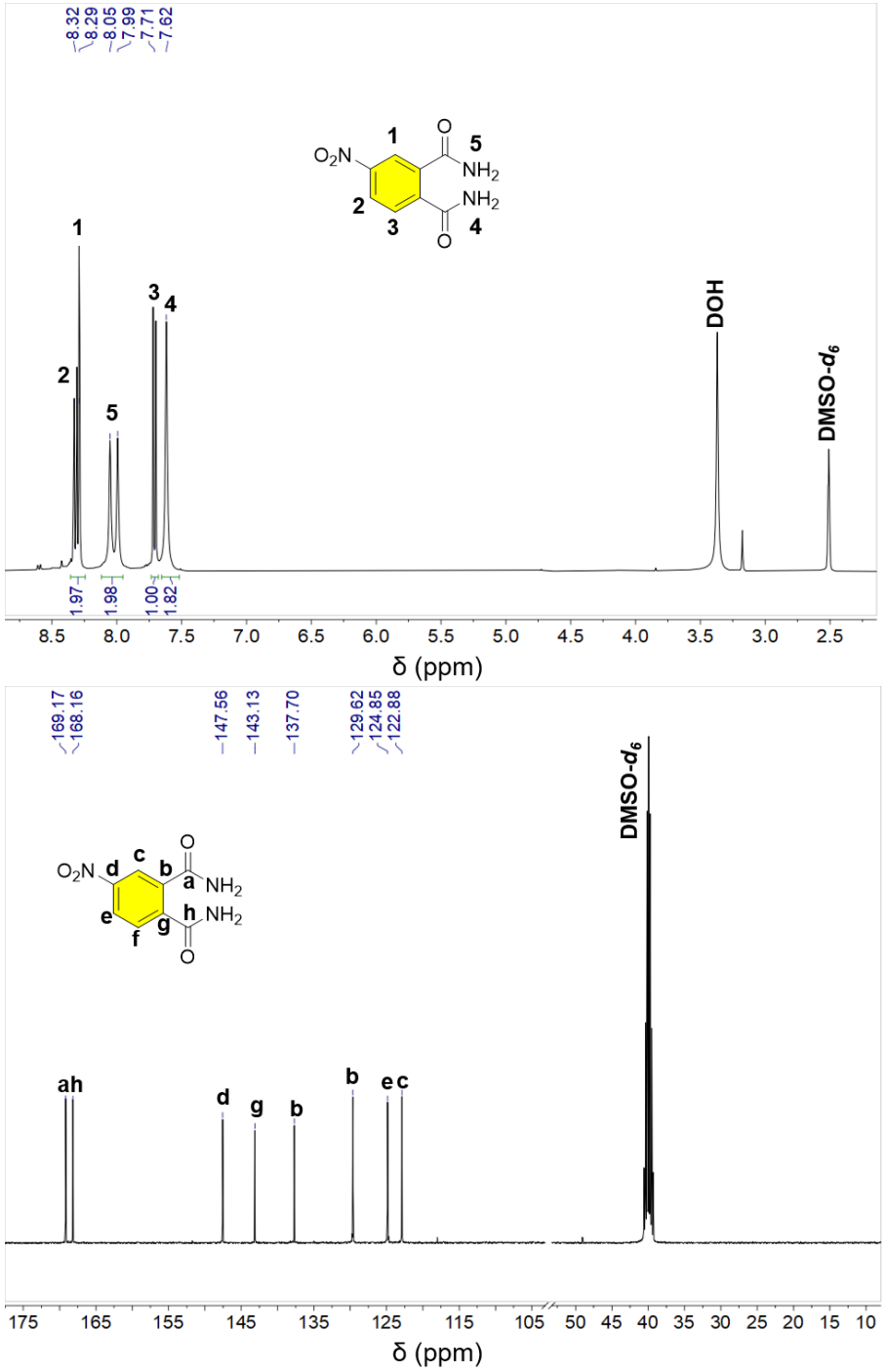

Figure S2. ^{1}H- (up) and ^{13}C-NMR (bottom) spectra recorded for **1c**.

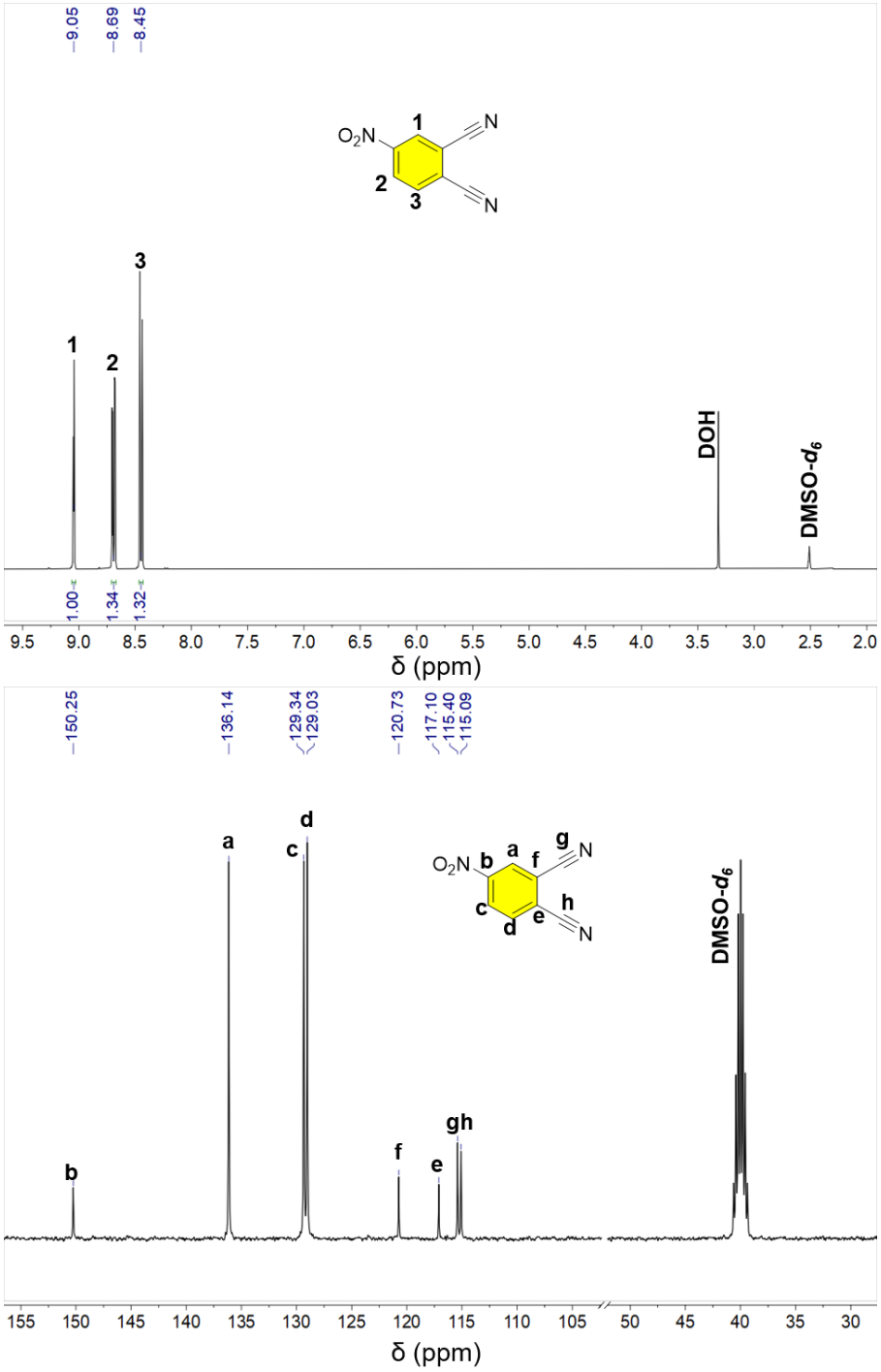

Figure S3. ^{1}H- (up) and ^{13}C-NMR (bottom) spectra recorded for **1d**.

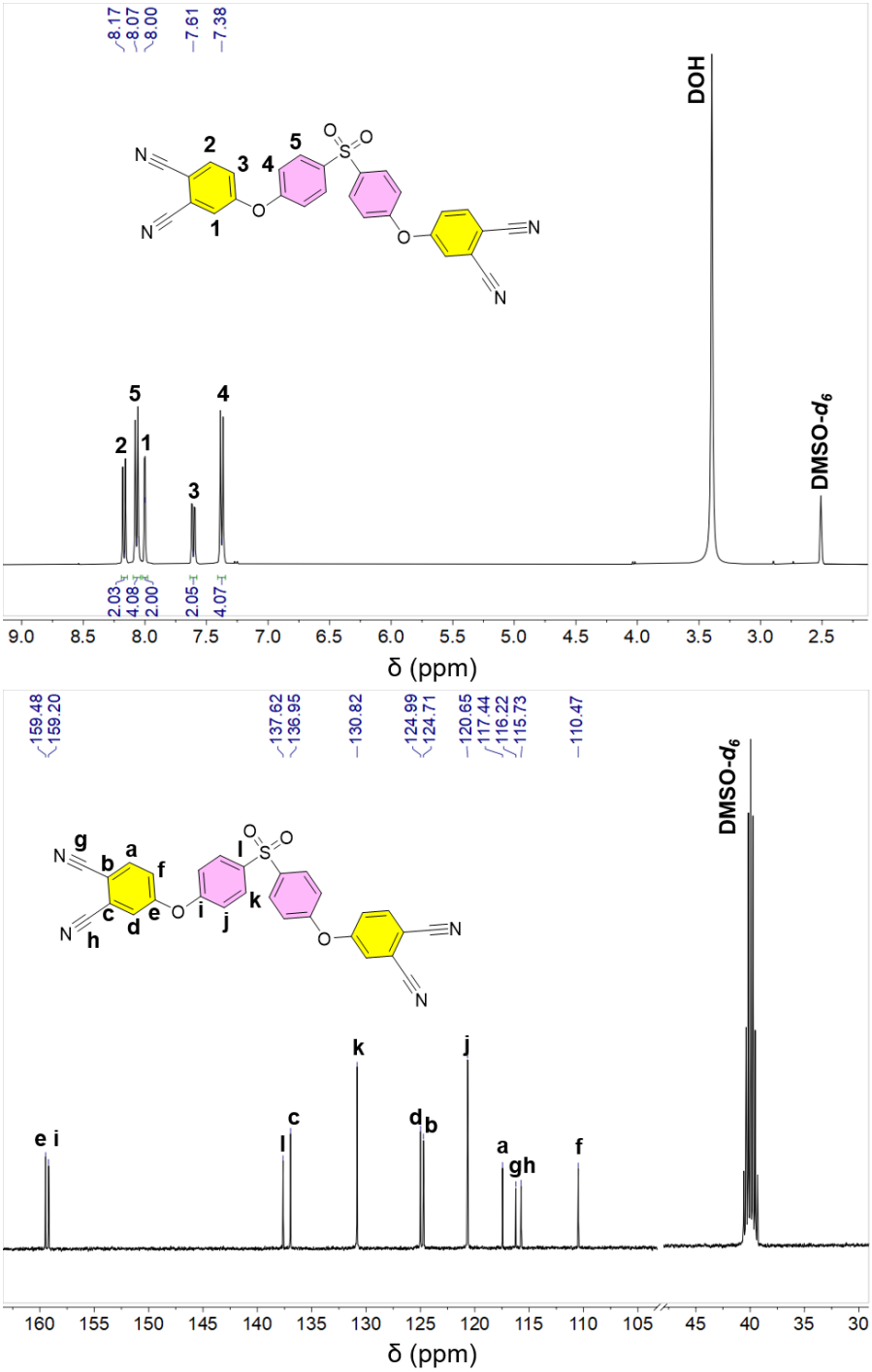

Figure S4. ^{1}H- (up) and ^{13}C-NMR (bottom) spectra recorded for **2a**.

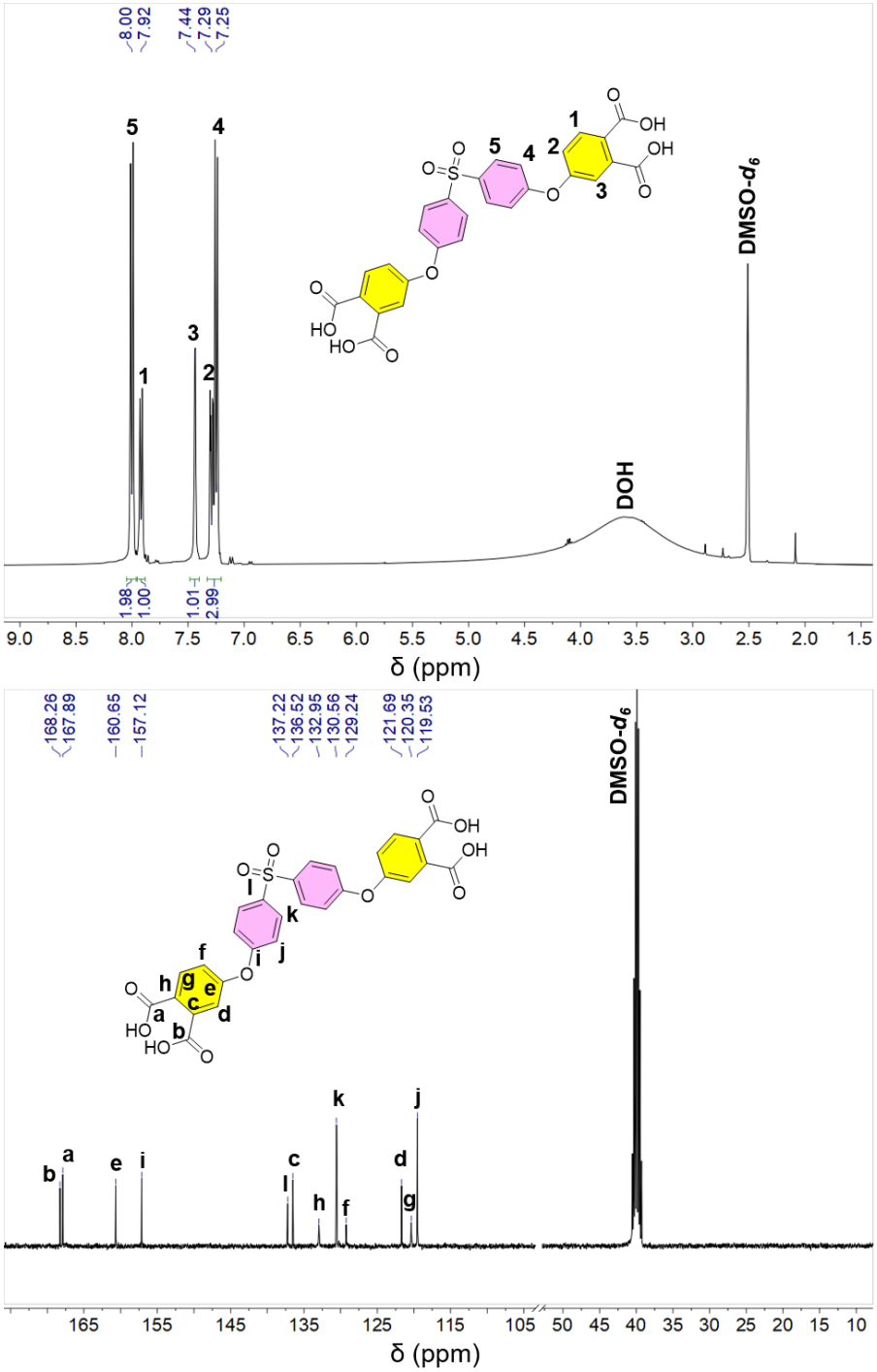

Figure S5. ^{1}H- (up) and ^{13}C-NMR (bottom) spectra recorded for **2b**.

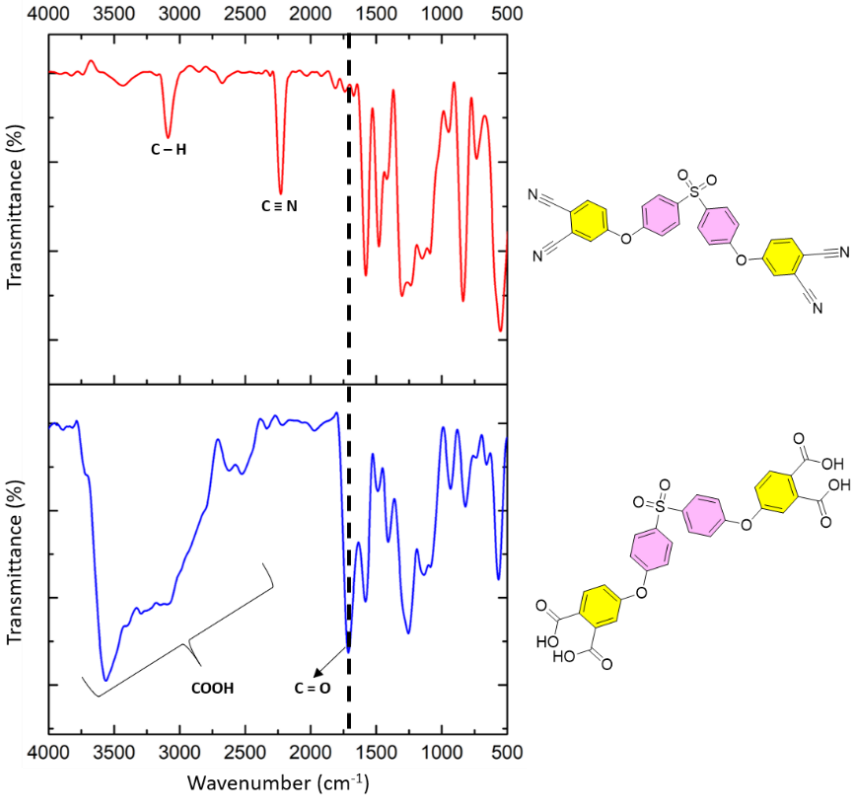

Figure S6. FTIR spectra for 2a (red) and 2b (blue).

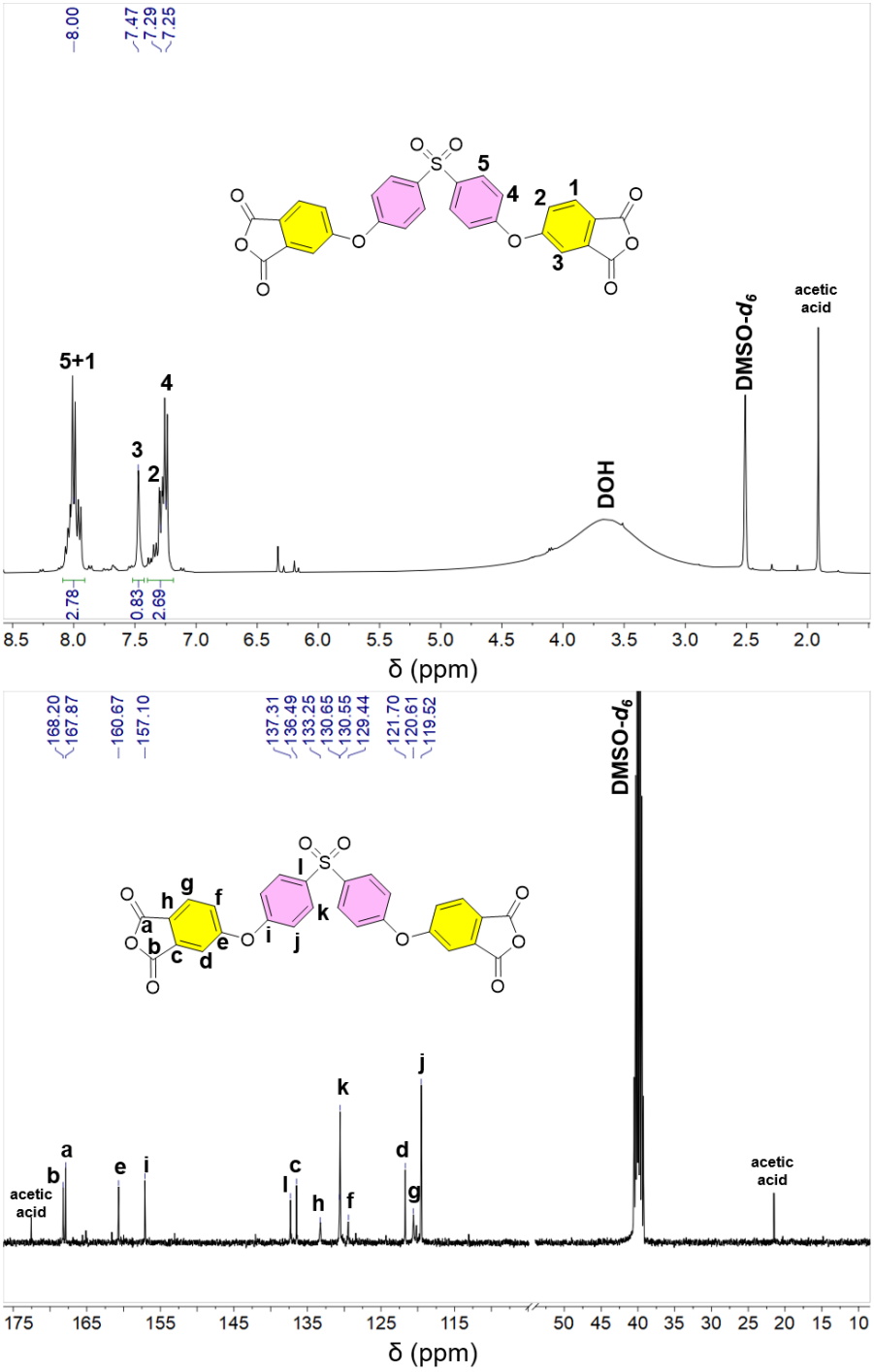

Figure S7. ^{1}H- (up) and ^{13}C-NMR (bottom) spectra recorded for **2c**.

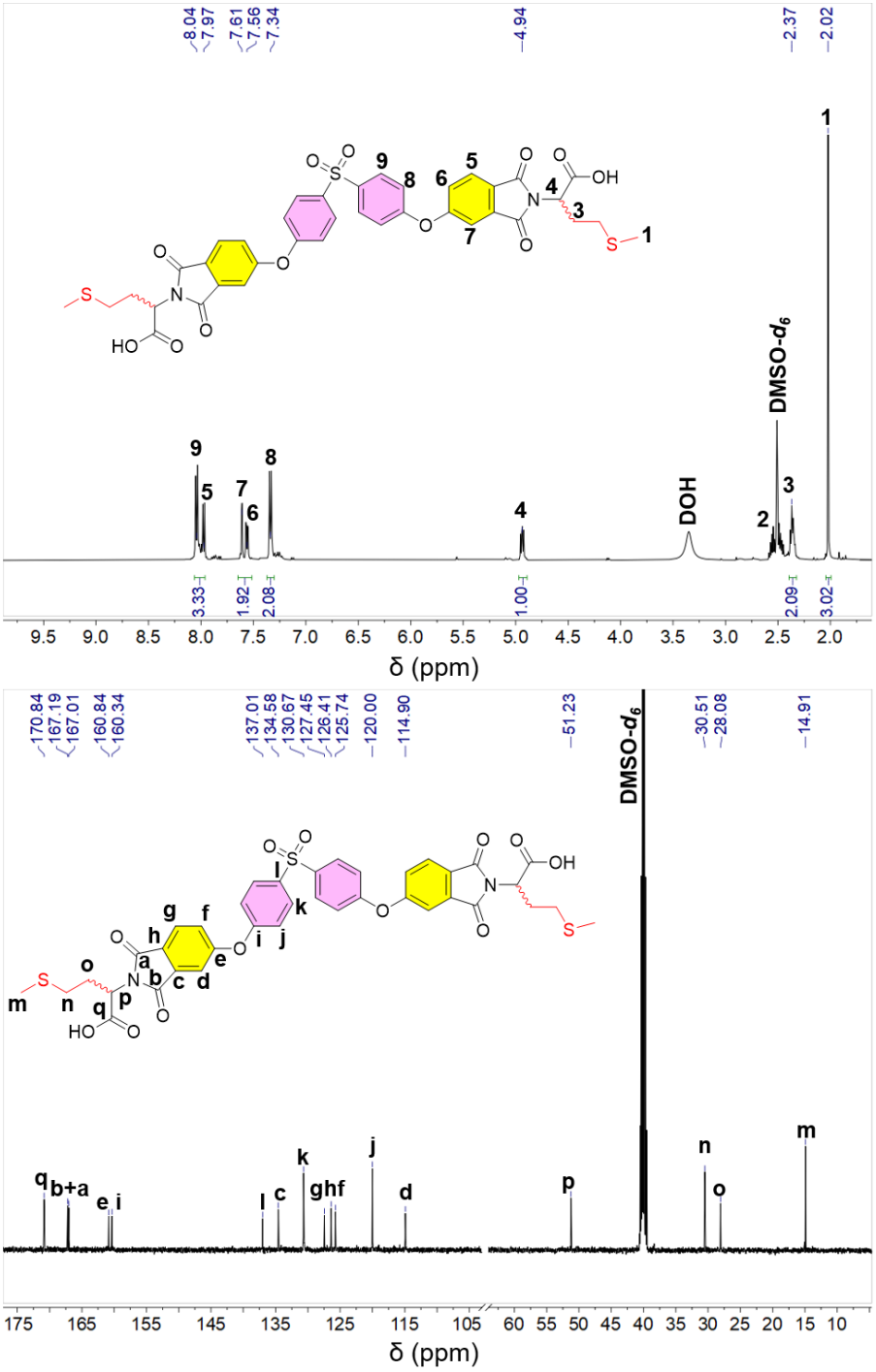

Figure S8. ^{1}H- (up) and ^{13}C-NMR (bottom) spectra recorded for EIA-Met.

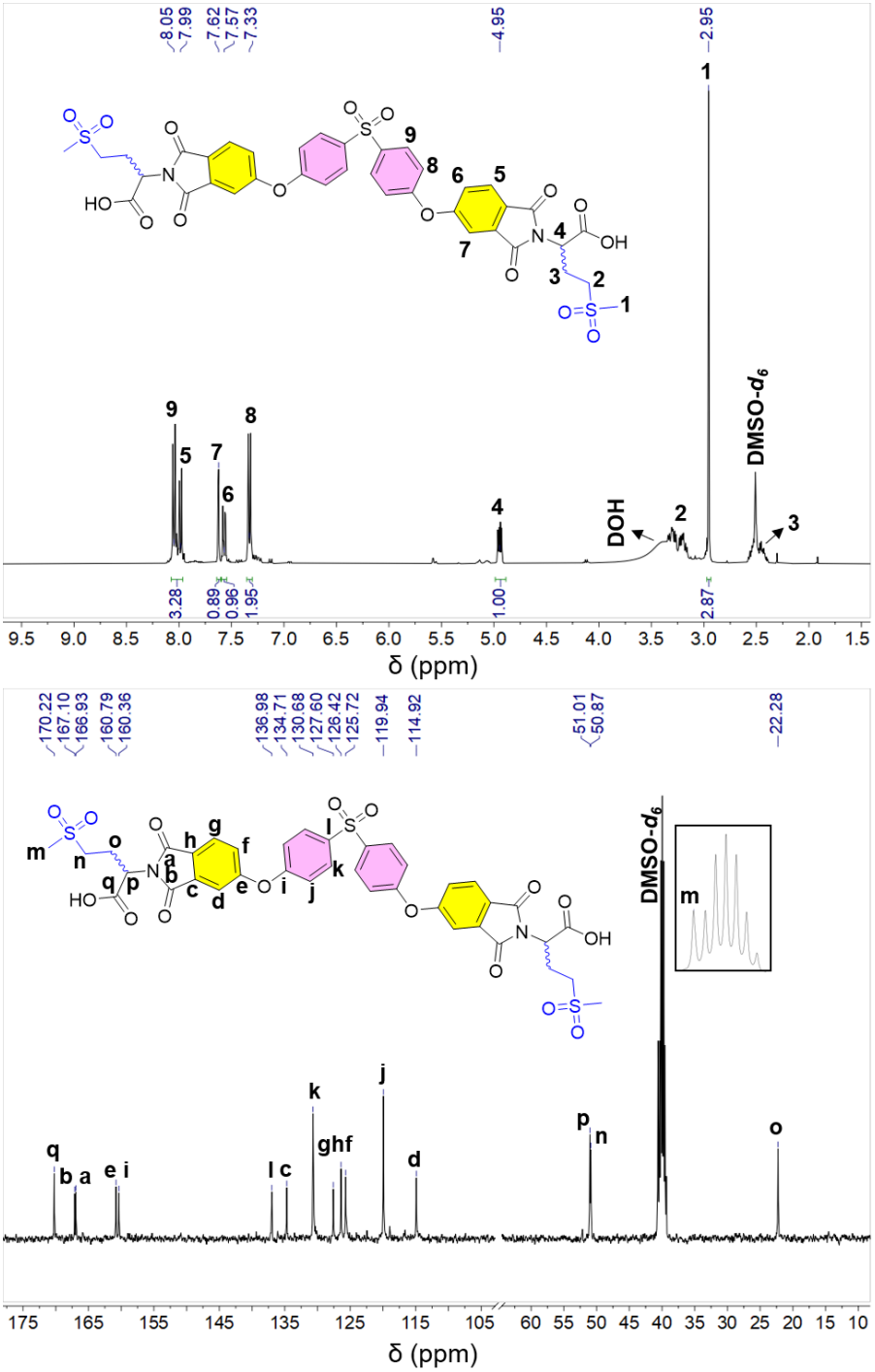

Figure S9. ^{1}H- (up) and ^{13}C-NMR (bottom) spectra recorded for EIA-Met(O_2).

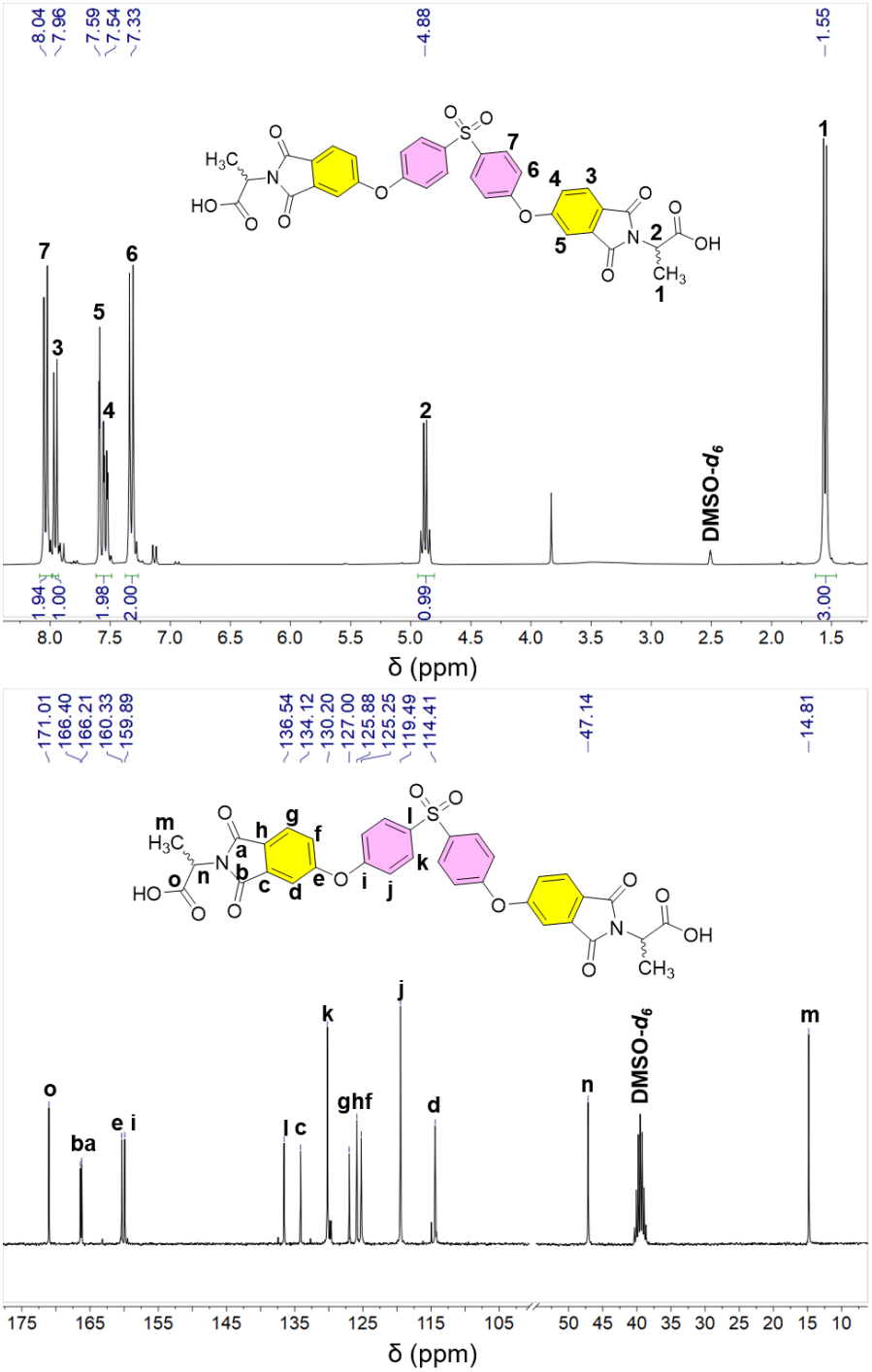

Figure S10. ^{1}H- (up) and ^{13}C-NMR (bottom) spectra recorded for EIA-Ala.

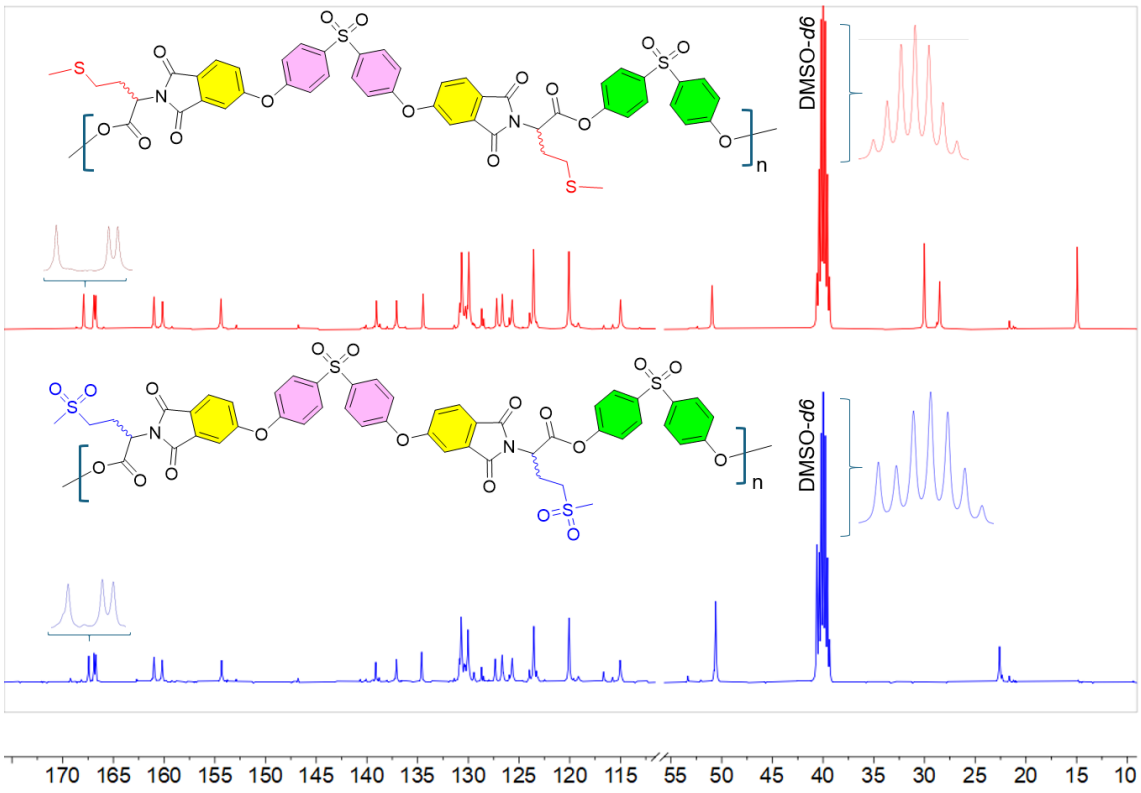

Figure S11. ^{13}C-NMR (bottom) spectra recorded for PEIE-Met (up) and PEIE-Met(O_2) (bottom).

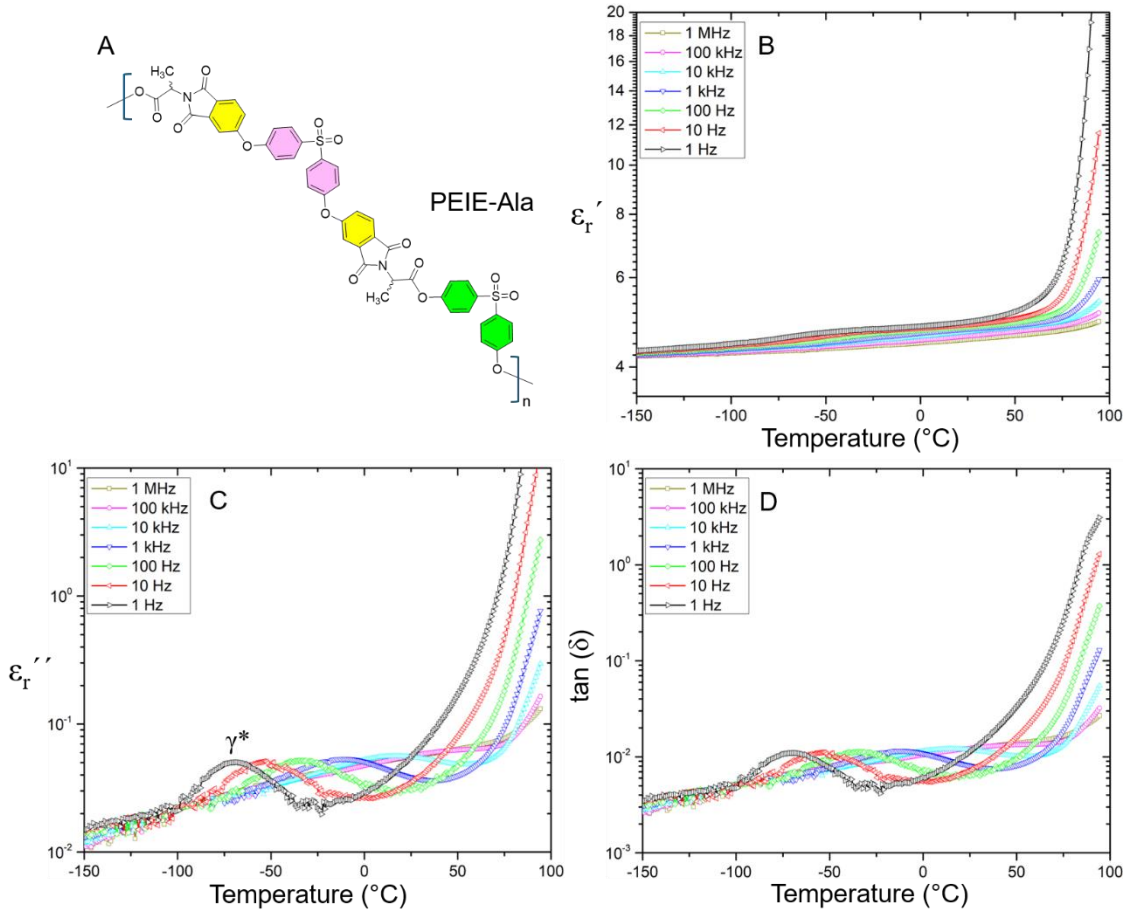

Figure S12. Chemical structure of PEIE-Ala (A) and its ε_r' (B), ε_r'' (C) and tan (δ) (D) isochrones recorded at different frequencies.

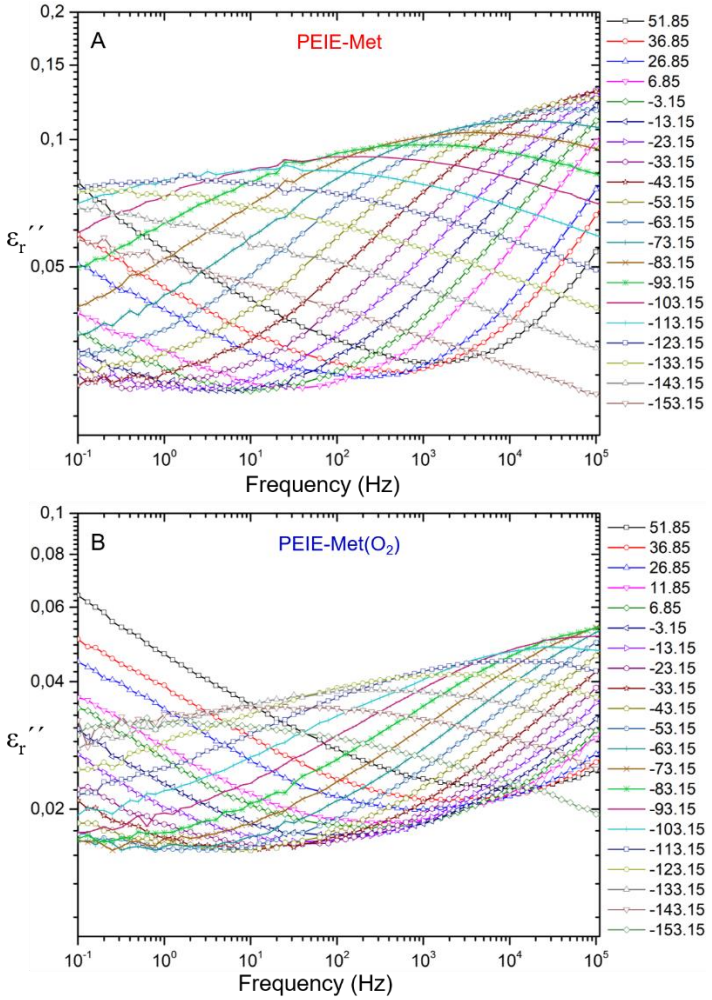

Figure S13. ε_r'' isotherms registered for PEIE-Met (A) and PEIE-Met(O_2) (B).

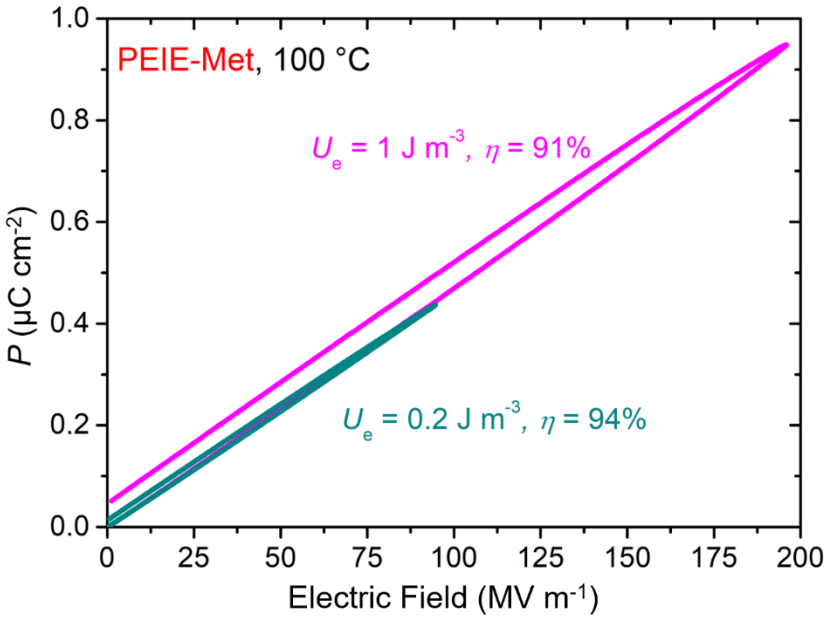

Figure S14. P–E loop measurements performed for PEIE-Met at 100 °C under electric fields of 100 MV/m (dark teal) and 200 MV/m (pink).

Bibliography

1. L. F. Levy and H. Stephen, *Journal of the Chemical Society (Resumed)*, 1931, DOI: 10.1039/JR9310000079., 79-82.
2. S. Touaiti, A. Hajri, M. S. Kahouech, J. Khiari and B. Jamoussi, *Arabian Journal of Chemistry*, 2017, **10**, S1553-S1557.
3. A. Tundidor-Camba, L. H. Tagle, C. A. Terraza, J. Rivera, D. Coll and P. A. Ortiz, *Polymer Bulletin*, 2021, **78**, 4205-4225.
4. S. Mallakpour and H. Seyedjamali, *Amino Acids*, 2008, **34**, 531-538.