Electronic supplementary materials *Mendeleev Commun.*, 2026, **36**, 72–75

New metal-free dye with an acceptor-anchor group of thieno[3,2-*b*]thiophene family for dye-sensitized solar cells

Roman A. Irgashev, Alexander S. Steparuk, Viktor V. Emets, Ekaterina V. Tekshina, Nikita M. Tolkach, Petr I. Lazarenko, Gennady L. Rusinov and Sergey A. Kozyukhin

1. Experimental section

1.1. Materials

All chemicals were purchased from commercial sources and used without further purification. All solvents were dried and distilled according to standard procedures. Compound **3** was prepared in accordance with our previously described procedure.[S1] Compound **4** was obtained from dimethyl 3-hydroxythieno[3,2-*b*]thiophene-2,5-dicarboxylate[S2] using previously described procedure.[S3]

1.2. Characterizations

^{1}H and ^{13}C NMR spectra were recorded on Bruker DRX-400 (400 MHz) and Bruker AVANCE-500 (500 MHz), tetramethylsilane was an internal standard for 1H NMR spectra and residual signals of deuterated solvent DMSO-d_6 (δ 39.5) were references for ^{13}C NMR spectra. Melting points were determined on a Boetius apparatus. Elemental analysis was carried out on a CHN PE 2400 Series II Perkin Elmer Instrument automated analyzer. High-resolution mass spectra were studied on a Bruker maXis Impact HD spectrometer.

The frontier molecular orbitals of the IS-TTCA were calculated using density functional theory. Computing was carried out in the Orca 6.0.0 software package using the DFT B3LYP, 6-311G* method.[S4-S7]

UV/vis spectra were recorded with Shimadzu UV-2600 spectrophotometer. Photoluminescent spectra were recorded on a FS5 Edinburgh Instruments spectrofluorometer. Absolute quantum yields have been measured using integrating sphere SC-30. The emission lifetimes have been measured using TCSPC option of FS5 Edinburgh Instruments spectrofluorometer.

Electrochemical studies were carried out using the Princeton Applied Research 273 potentiostat/galvanostat. The standard three-electrode cell equipped with a SU-2000 glassy carbon disc (0.0078 cm^2) pressed into Teflon as a working electrode, Ag quasi-reference electrode, and a platinum grid (1 cm^2) as a counter electrode were employed. The cyclic voltammograms (CV) were registered in anhydrous tetrahydrofuran with 2.4 mM of analyzed dye and 0.1M Bu_4NPF_6 as supporting electrolyte under high purity argon atmosphere at a scan rate 100 mV s^{-1}.

The current-voltage characteristics of solar cells were determined under irradiation (100 mW cm^{-2}) using a Newport 67005 Arc lamp light source with a Xe lamp. The current density -voltage (*J*/*V*) characteristics were measured using a Keithley 2450 source meter by applying voltage and measuring current. The action spectra of monochromatic incident photon-to-current conversion efficiency (IPCE) for solar cell were performed by using a SCS10-PEC Photoelectrochemistry Measurement System. All measurements were performed at room temperature (20 ± 2 °C).

1.3. Synthesis of dye ***IS-TTCA***

Procedure for the synthesis of compound **5** (dye **IS-TTCA**)

6-Hydroxythieno[3,2-*b*]thiophene-2-carboxylic acid (**4**) (0.115 g, 0.575 mmol) and pyrrolidine (0.1 mL) were added to a solution of carbaldehyde **3** (0.198 g, 0.5 mmol) in glacial acetic acid (7 mL) at continuous stirring at ambient temperature. Then, the reaction mixture was stirred and heated at 120 °C for 1 h. A formed precipitate was collected by filtration, washed with aqueous methanol, and dried to constant mass in air.

5-{[5-(4-Octyl-4H-thieno[3,2-b]indol-2-yl)thiophen-2-yl]methylene}-6-oxo-5,6-dihydrothieno[3,2-b]thiophene-2-carboxylic acid **5** (dye **IS-TTCA**)

Dark green microcrystals, m.p. 301-302 °C, yield 0.235 g (81%).

^{1}H NMR (400 MHz, DMSO-d_6) δ 14.01 (s, 1H), 8.21 (s, 1H), 8.05 (s, 1H), 7.90 (s, 1H), 7.83 (d, *J* = 4.5 Hz, 1H), 7.77 (d, *J* = 7.7 Hz, 1H), 7.63 – 7.55 (m, 2H), 7.33 – 7.27 (m, 1H), 7.17 – 7.11 (m, 1H), 4.38 (t, *J* = 6.8 Hz, 2H), 1.79 (s, 2H), 1.31 – 1.17 (m, 10H), 0.81 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (126 MHz, DMSO-d_6) δ 179.4, 162.1, 149.8, 147.0, 146.1, 145.1, 141.2, 138.4, 135.8, 135.8, 135.8, 134.8, 131.0, 128.6, 127.8, 125.2, 123.4, 120.6, 119.4, 119.0, 115.5, 110.7, 110.0, 44.3, 31.1, 29.1, 28.5, 26.2, 21.9, 13.8.

HRMS (APCI) *m/z* calcd for $C_{30}H_{26}NO_3S_4$ [M-H]$^-$: 576.0801, found: 576.0803.

Anal. calcd for $C_{37}H_{42}N_2O_3S_3$: C, 62.36; H, 4.71, N, 2.42. Found: C, 62.14; H, 4.84, N, 2.55.

1.4. Manufacture of DSSCs

Prior to adsorption of the dyes, the TiO_2 photoanodes (0.36 cm^2 active area, from Ti-Nanoxide T/SP covered by a reflective layer of Ti-Nanoxide R/SP, Solaronix) were heated at 450 °C for 30 min. When the electrodes cooled to 50 °C were immersed in a 0.5 mM tetrahydrofuran solution of the sensitizing dye **IS-TTCA** for 24 h in the dark. The sensitized films were rinsed with isopropyl alcohol to remove excess dyes remaining on the surface and then dried at 50 °C for 10 min. The Pt-counter electrode (Solaronix) and dye-covered TiO_2 electrode were assembled into a sandwich type cell using Meltonix 1170-60 (Solaronix) in a thermal press (Carver) at 100 °C for 3 min. The solar cell was filled with electrolyte through a hole in the cathode. A mixture of in 3-propyl-1-methylimidazolium iodide (PMII, 0.6 M), lithium iodide (LiI, 0.1 M), iodine (I_2, 0.05 M), and 4-(*tert*-butyl)pyridine (TBP, 0.5 M) in 3-methoxypropionitrile was used as the electrolyte. The hole was sealed with thin glass (0.5 mm thickness).

1.5 Frontier molecular orbital diagram of ***IS-TTCA*** *obtained from DFT calculations*

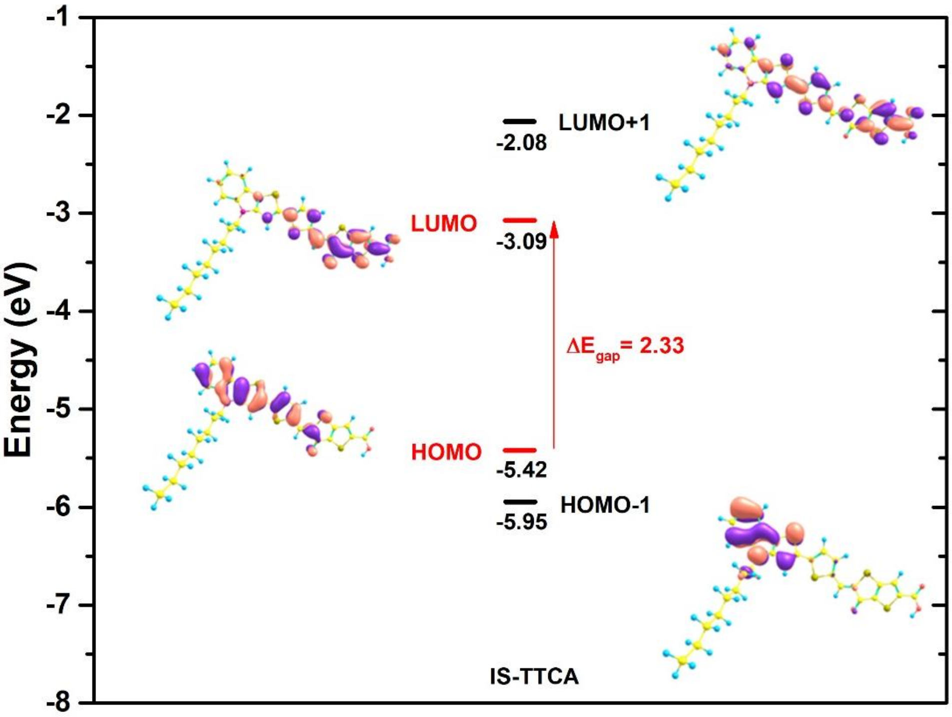

Figure S1 Frontier HOMO and LUMO orbitals of the dye **IS-TTCA**.

2. References

S1. R. A. Irgashev, A. S. Steparuk and G. L. Rusinov, *Org. Biomol. Chem.*, 2018, **16**, 4821; https://doi.org/10.1039/C8OB01110A.

S2. R. A. Irgashev and N. A. Kazin, *Organics*, 2024, **5**, 507; https://doi.org/10.3390/org5040027.

S3. R. A. Irgashev, A. A. Karmatsky, G. L. Rusinov and V. N. Charushin, *Org. Lett.*, 2016, **18**, 804; https://doi.org/10.1021/acs.orglett.6b00081.

S4. F. Neese, *Wiley Interdiscip. Rev.: Comput. Mol. Sci.*, 2022, **12**, e1606; https://doi.org/10.1002/wcms.1606.

S5. F. Neese, F. Wennmohs, A. Hansen and U. Becker, *Chem. Phys.*, 2009, **356**, 98; https://doi.org/10.1016/j.chemphys.2008.10.036.

S6. B. Helmich-Paris, B. de Souza, F. Neese and R. Izsák, *J. Chem. Phys.*, 2021, **155**, 104109; https://doi.org/10.1063/5.0058766.

S7. F. Neese, *J. Comput. Chem.*, 2023, **44**, 381; https://doi.org/10.1002/jcc.26942.

3. Copies of ^{1}H and ^{13}C NMR spectra

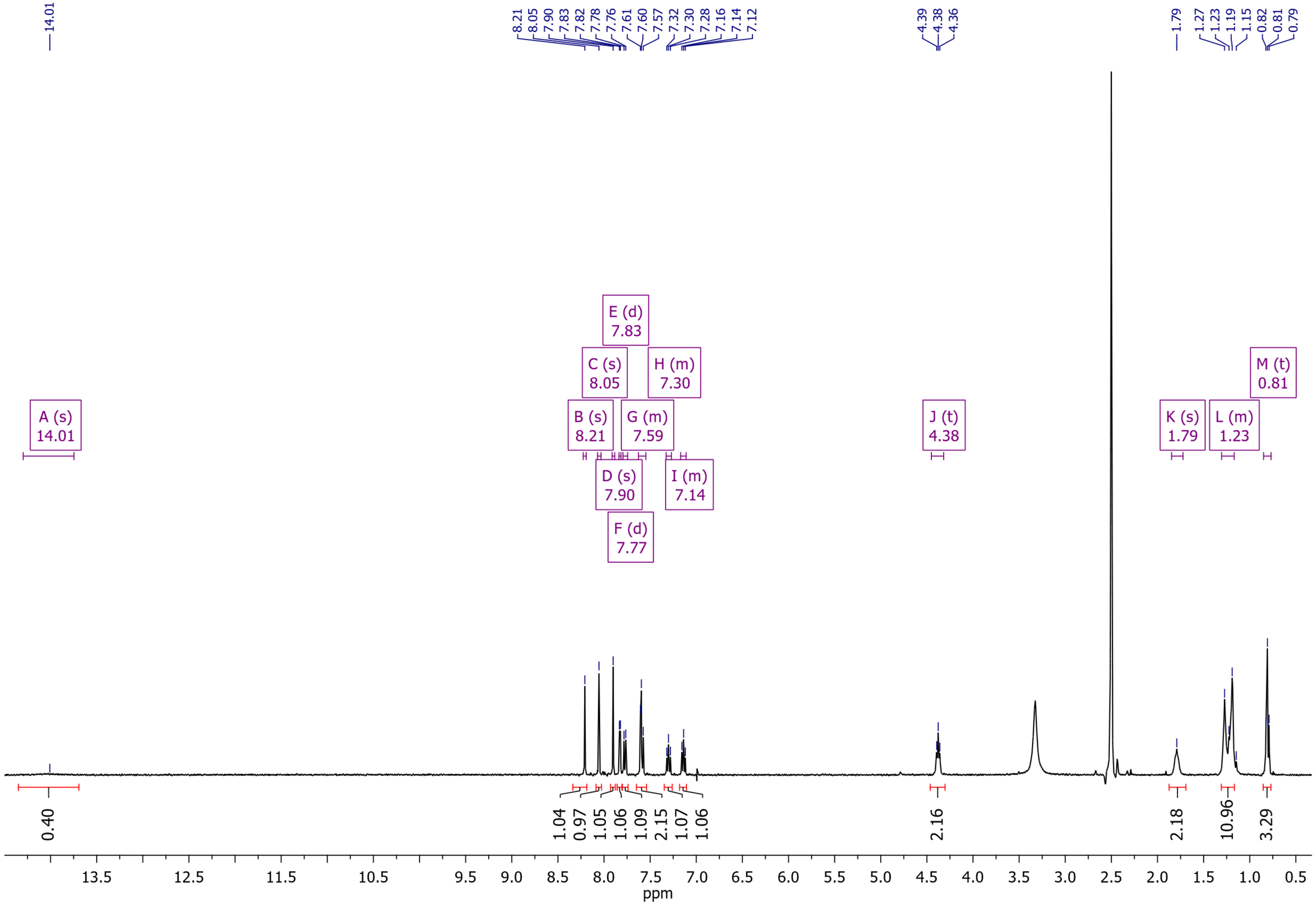

Figure S2. ^{1}H NMR spectrum of compound **5** (dye **IS-TTCA**) in DMSO-d_6

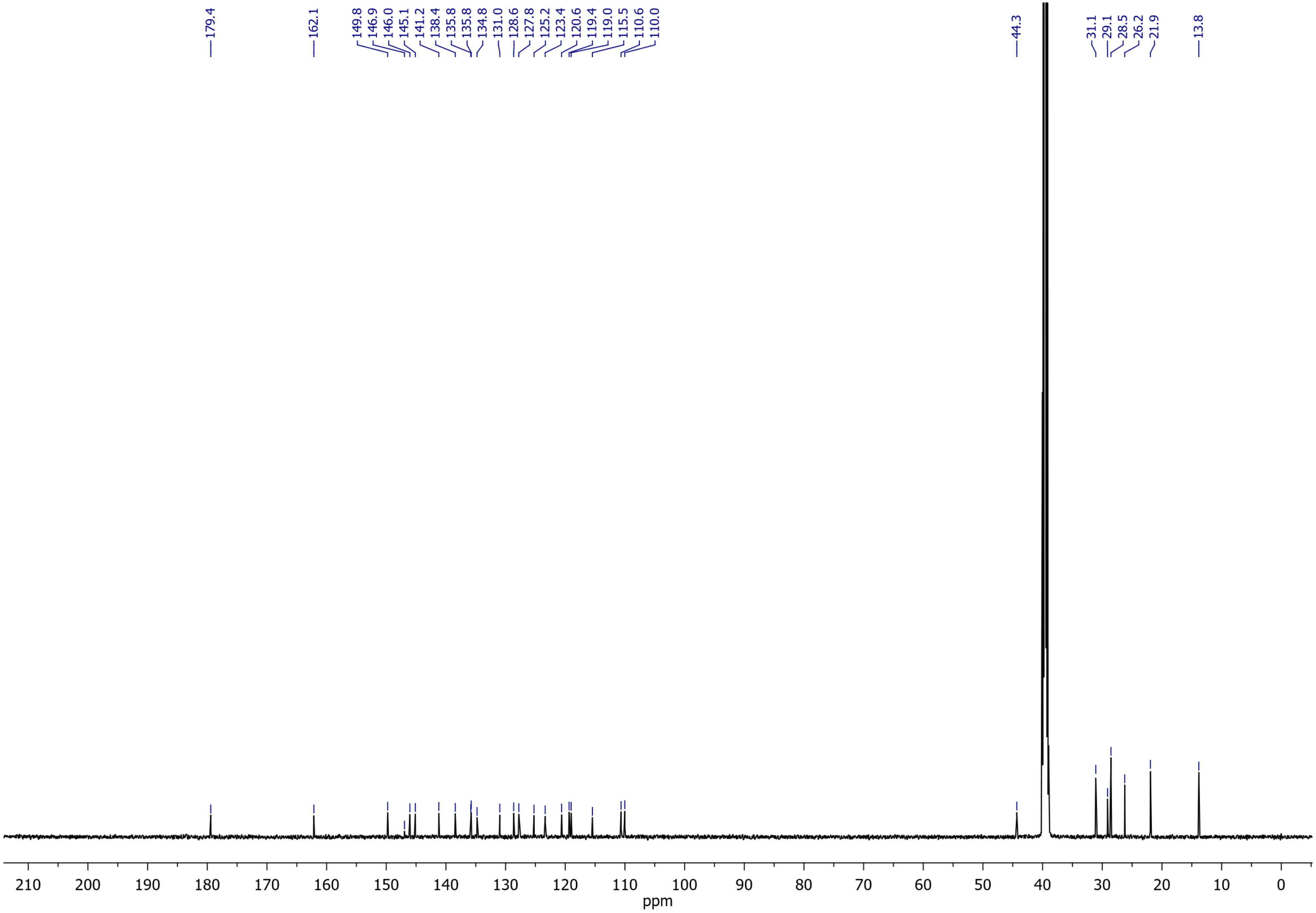

Figure S3. ^{13}C NMR spectrum of compound **5** (dye **IS-TTCA**) in DMSO-d_6