

Electronic supplementary information for

**Alkylamide-Substituted Tetraphenylethylene: Three Modes of
Fluorescence Based on a Hydrogen-Bonded Excimer**

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1. Experimental Section

General methods

Commercially available reagents and solvents, including dry DMF and CH₂Cl₂, were used as received. Dry triethylamine was prepared by distillation from KOH prior to use. Tetrabromide **2**^[S1] and tetracarboxylic acid **4**^[S2] were prepared from tetraphenylethylene and tetracyanide **3**, respectively, following the published procedures. Column chromatography was performed using silica gel 60 (Merck). ¹H (400 MHz) and ¹³C (100 MHz) NMR spectra were recorded on a Bruker Avance III 400 NMR spectrometer. Chemical shifts (δ) are expressed in ppm relative to tetramethylsilane (¹H 0.00 ppm) or residual nondeuterated solvent (CDCl₃; ¹³C 77.0 ppm) as an internal standard. Mass spectra were recorded on a JMS-700 spectrometer at the NMR and MS Laboratory, Graduate School of Agriculture, Tohoku University. Elemental analyses were performed on a Microcoder JM10 at the Elementary Analysis Laboratory, Institute of Multidisciplinary Research for Advanced Materials, Tohoku University. IR, UV-vis-NIR and Fluorescence spectra were measured on a Thermo Scientific NICOLET 6700 FT-IR, a Perkin Elmer LAMBDA 750, and a Shimadzu RF-6000 spectrometer, respectively.

Preparation of **3**

Tetracyanide **3** was prepared according to the reported method,^[S2] with some modification. A mixture of tetrabromopyrene **2** (2.54 g, 3.92 mmol) and CuCN (2.13 g, 23.8 mmol) in dry DMF (45 mL) was stirred at 150 °C for 65.5 h. After the mixture was allowed to cool to rt, water (250 mL) was added and the resulting suspension was filtered. The collected pale yellow solid was dissolved with ca. 5M aqueous solution of HNO₃ and CHCl₃. The aqueous phase was separated and extracted with CHCl₃. The combined CHCl₃ phase was washed with a sat. aqueous solution of NaHCO₃ and then brine, and dried over MgSO₄. Evaporation of the solvent under reduced pressure gave **3** as a yellow solid. The ¹H NMR spectrum of the obtained solid was consistent with the reported chemical shift (see Figure S9).

Preparation of tetraamide **1**

A mixture of tetracarboxylic acid **4** (1.59 g, 3.14 mmol) in SOCl₂ (50 mL) was stirred at refluxing temperature for 44 h. After the mixture was cooled to rt, excess SOCl₂ was removed by evaporation under reduced pressure. The obtained acid chloride was dissolved in dry CH₂Cl₂ (40 mL). To the solution was added tetradecylamine (3.35 g, 15.7 mmol), followed by Et₃N (2.4 mL, 1.72 mmol). The mixture was stirred at rt for 37 h. The resulting precipitate was collected by filtration and washed with CH₂Cl₂. The obtained solid was recrystallized from toluene/EtOH (1/1) twice to give tetraamide **1** (1.60 g, 40%) as a white solid. Mp 252-253 °C; ¹H NMR (CDCl₃): δ 7.50 (d, *J* = 8.4 Hz,

8H, 8×CH_{Ar}), 7.05 (d, *J* = 8.4 Hz, 8H, 8×CH_{Ar}), 6.04 (t, *J* = 5.4 Hz, 4H, 4×NH), 3.41 (q, *J* = 6.7 Hz, 8H, 4×NHCH₂), 1.67-1.52 (m, 8H, 4×CH₂), 1.43-1.13 (m, 88 H, 44×CH₂), 0.88 (t, *J* = 7.2 Hz, 12H, 4×CH₂). The ¹³C NMR spectrum could not be measured due to its low solubility. IR 3307, 2920, 2850, 1635, 1608, 1548, 1504, 1467, 1435, 1308, 1156, 849, 756, 732, 694, 675 cm⁻¹. HRMS (FAB) calcd for C₈₆H₁₃₇N₄O₄: 1290.0640 [(M + H)⁺]; found: 1290.0638. Anal. Calcd for C₈₆H₁₃₆N₄O₄: C, 80.07; H, 10.63; N, 4.34. Found: C, 80.16; H, 10.60; N, 4.12.

Preparation of tetraester **5**

A mixture of tetracarboxylic acid **4** (1.26 g, 2.49 mmol) in SOCl₂ (50 mL) was stirred at refluxing temperature for 25 h. After the mixture was cooled to rt, excess SOCl₂ was removed by evaporation under reduced pressure. The obtained acid chloride was dissolved in dry CH₂Cl₂ (50 mL). To the solution was added 1-tetradecanol (2.40 g, 11.2 mmol), followed by Et₃N (1.74 mL, 12.2 mmol). The mixture was stirred at rt for 43 h. The mixture was diluted with CH₂Cl₂ and H₂O. After insoluble material was removed by filtration, the aqueous layer was separated and extracted with CH₂Cl₂. The combined organic layer was washed with brine and dried over MgSO₄. The obtained crude product was purified by silica gel column chromatography followed by GPC to give tetraester **5** (724 mg, 22 %) as a pale yellow waxy solid. Mp 62-63 °C; ¹H NMR (CDCl₃): δ 7.80 (d, *J* = 8.7 Hz, 8H, 8×CH_{Ar}), 7.06 (d, *J* = 8.7 Hz, 8H, 8×CH_{Ar}), 4.27 (t, *J* = 6.8 Hz, 8H, 4×OCH₂), 1.73 (quint, *J* = 6.7 Hz, 8H, 4×CH₂), 1.45-1.20 (m, 88H, 44×CH₂), 0.88 (t, *J* = 6.7 Hz, 12H, 4×CH₃). ¹³C NMR (CDCl₃): δ 166.2, 146.8, 141.6, 131.1, 129.3, 129.27, 65.2, 31.9, 29.67, 29.65, 29.63, 29.57, 29.50, 29.34, 29.26, 28.7, 26.0, 22.7, 14.1. IR: 2920, 2851, 1718, 1605, 1468, 1407, 1281, 1177, 1105, 1019, 770, 758, 723 cm⁻¹. HRMS (FAB) calcd for C₈₆H₁₃₃O₈: 1294.0000 [(M + H)⁺]; found: 1293.9998. Anal. Calcd for C₈₆H₁₃₂O₈: C, 79.83; H, 10.28; N, 0.00. Found: C, 79.72; H, 10.50; N 0.10.

Irradiation with UV light

For the UV light irradiation experiments, a Xenon short-arc lamp (Ushio, UXL-500SX) was used as a light source. IR-absorbing (Sigma-Koki, HAF-50S-30H) and UV-absorbing filters (UV-29) were placed in front of the samples to reduce any damage. The sample solutions were placed in a 1-cm quartz cuvette and stirred continuously during the irradiation. The intensity and irradiation area of the UV light were 31 mW cm⁻² and 3.6 cm², respectively.

2. UV-Vis spectra of **1** in CHCl₃ and THF at various concentration condition

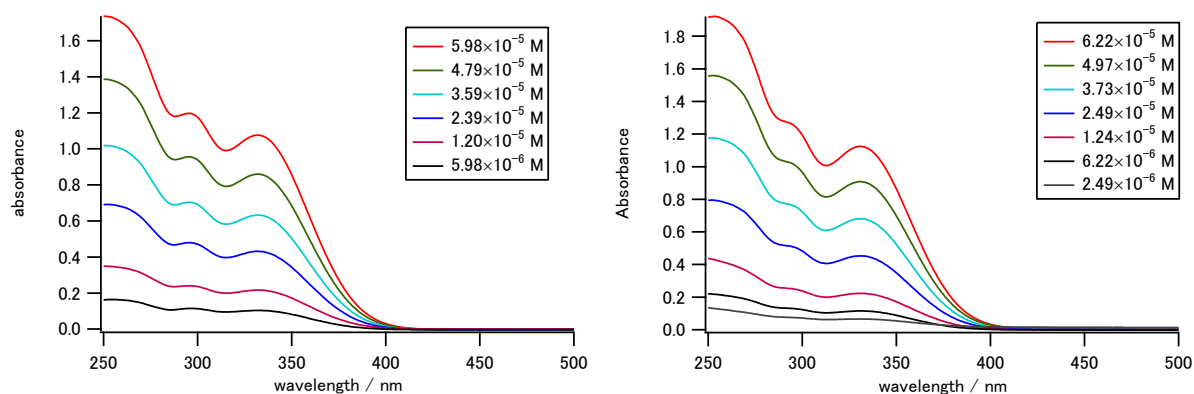


Figure S1 UV-Vis spectra of **1** in CHCl₃ (left) and in THF (right).

3. UV-Vis and fluorescence spectra of **1** in CHCl₃ and THF

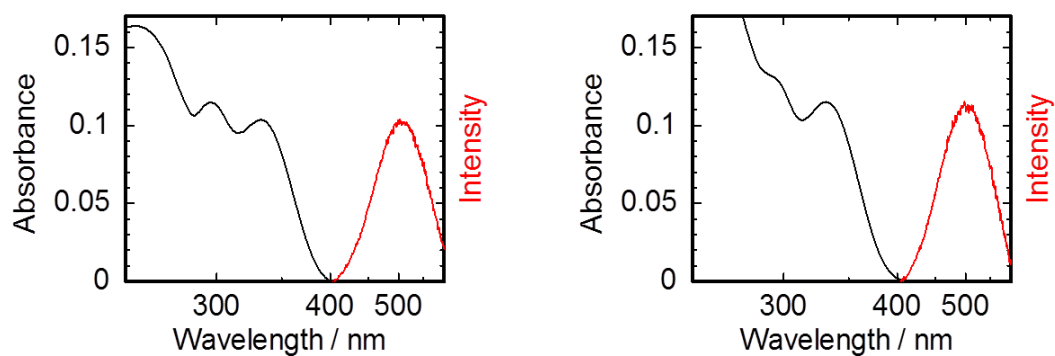


Figure S2 UV-Vis (black) and Fluorescence (red) spectra of **1** in CHCl₃ (left; 5.98×10⁻⁶ M) and in THF (right; 6.22×10⁻⁶ M).

4. Plots of fluorescence intensity against 1-T (T: transmittance)

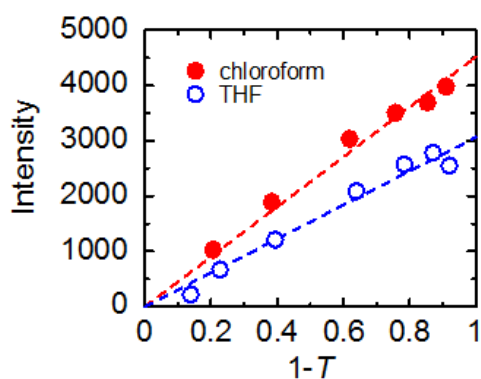


Figure S3 Plot of fluorescence intensity against 1-T (T: transmittance).

5. Fluorescence of **1** in the solid state

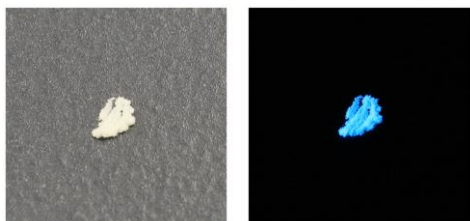


Figure S4 Photos of **1** in the solid state without irradiation of UV-light (left) and with irradiation of 365 nm UV-light (right).

6. Calculated dimer structure of **1**

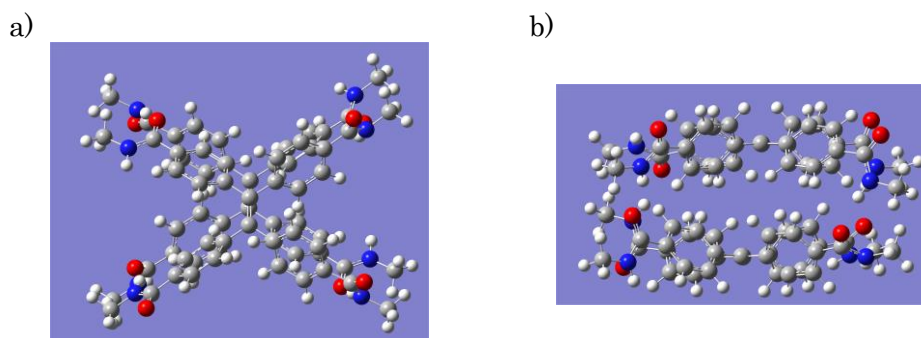


Figure S5 Optimized dimer structure of **1** using DFT calculation at M05/6-31G* level viewed a) along the direction normal to C=C bond and b) along the parallel to the C=C bond. Alkyl groups were replaced with methyl groups. As noted in the manuscript, the benzene rings twist along the Csp²-C_{benzene} bond axis.

7. UV-Vis spectra of **5** in CHCl₃

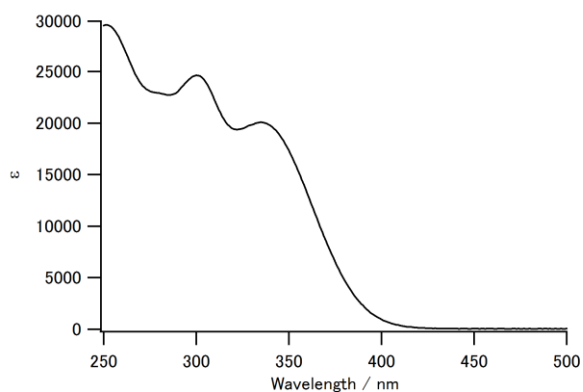


Figure S6 UV-Vis spectra of **5** in CHCl₃.

8. ^1H NMR spectrum of **1**

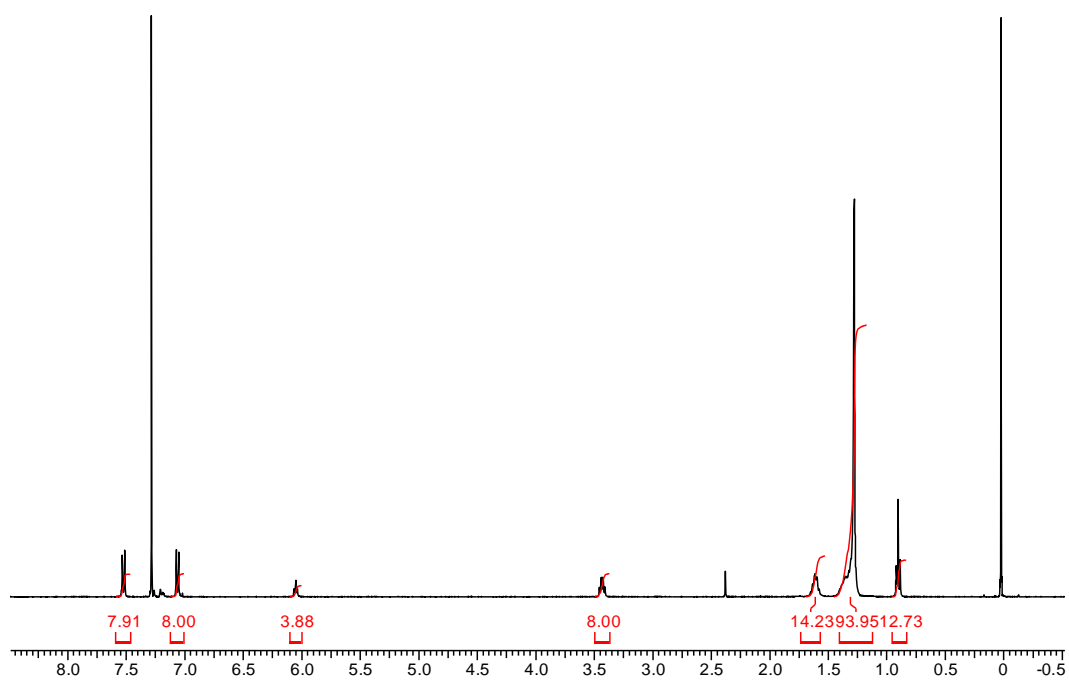


Figure S7 ^1H NMR spectrum of **1** in CDCl_3 .

9. ^1H NMR spectrum of **1** after irradiation of UV-light

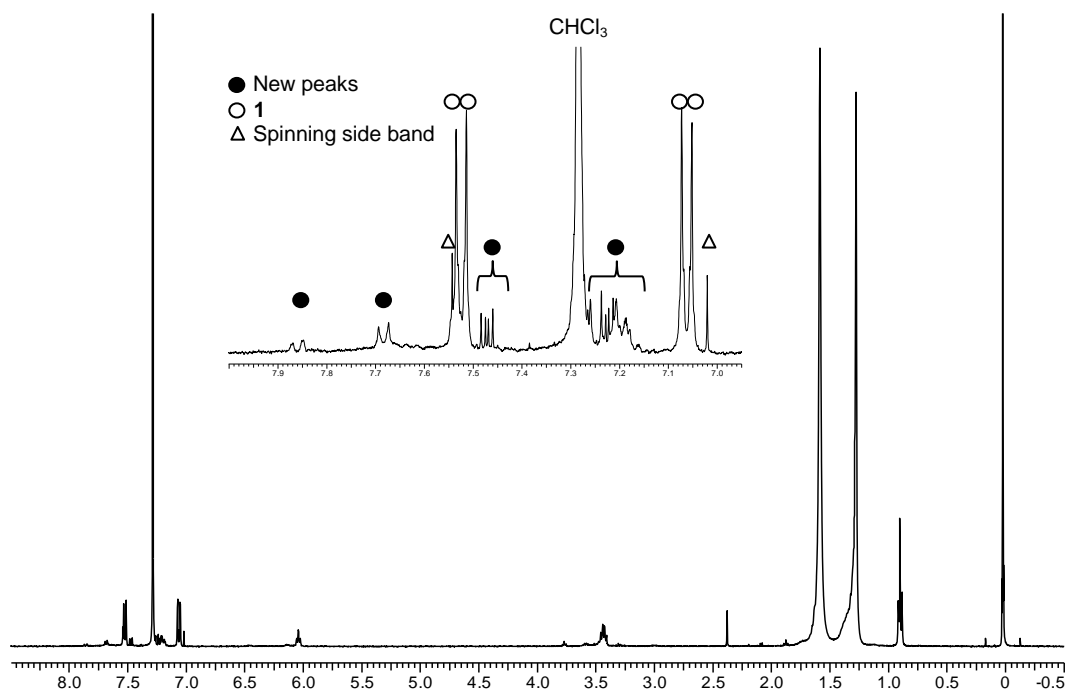


Figure S8 ^1H NMR spectrum of **1** in CDCl_3 (5.2×10^{-4} M) after irradiation of UV-light (6 h). Inset: The magnified spectrum of aromatic region.

10. ^1H NMR spectrum of **3**

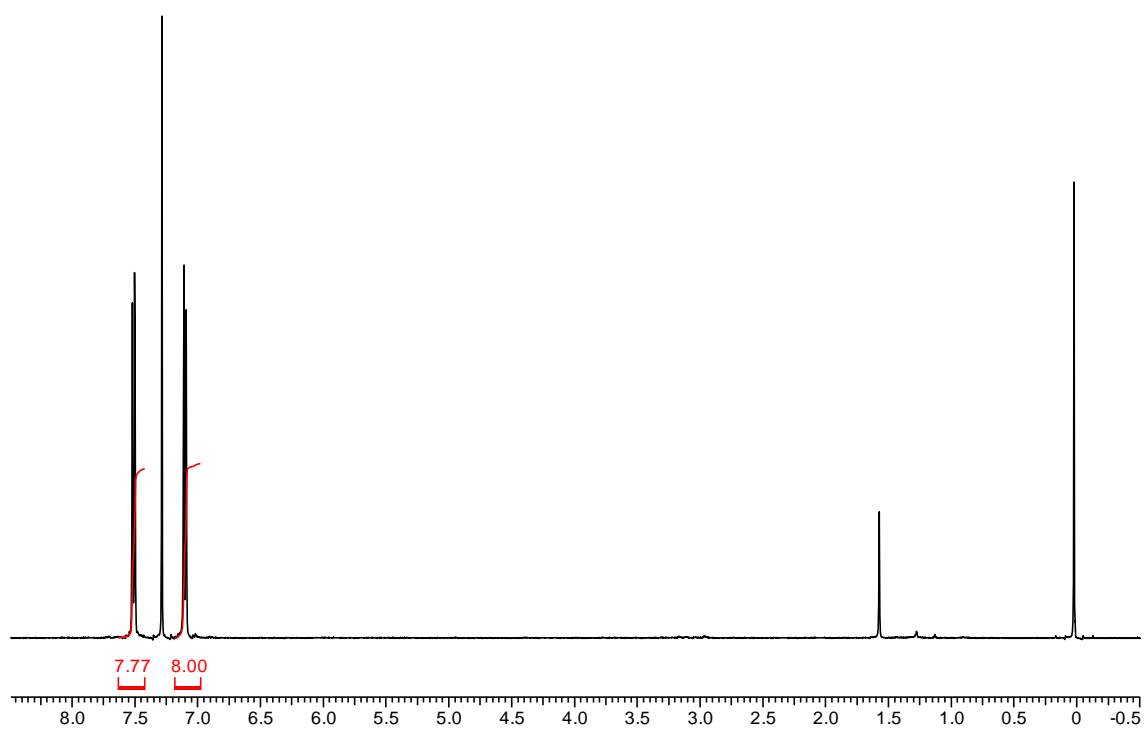


Figure S9 ^1H NMR spectrum of **3** in CDCl_3 .

11. ^1H and ^{13}C NMR spectra of **5**

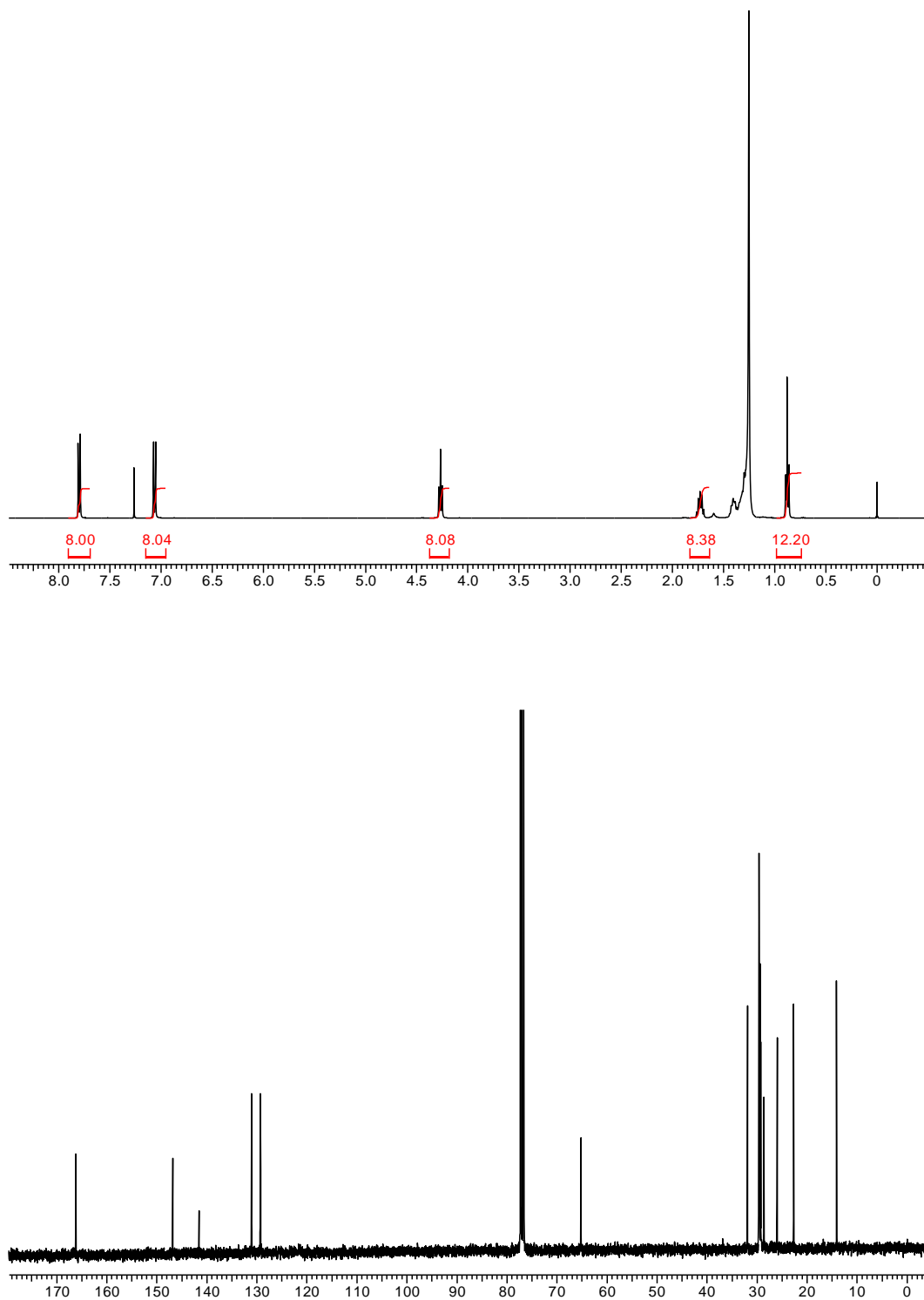


Figure S10 ^1H (top) and ^{13}C (bottom) NMR spectra of **5** in CDCl_3 .

12. References

S1 J. Lu, J. Zhang *J. Mater. Chem. A* **2014**, 2, 13831-13834.

S2 N. B. Shustova, B. D. McCarthy, M. Dincă *J. Am. Chem. Soc.* **2011**, 133, 20126-20129.