

Supporting Information

Excited State Dynamics of Thermally Activated Delayed Fluorescence from an Excited State Intramolecular Proton Transfer System

Yun Long*, Masashi Mamada^{†,‡,§}, Chunyong Li*, Paloma Lays dos Santos*, Marco Colella*, Andrew Danos*, Chihaya Adachi^{†,‡,§,||}, Andrew Monkman^{*^}

*Department of Physics, Durham University, South Road, Durham DH1 3LE, United Kingdom

[†]Center for Organic Photonics and Electronics Research (OPERA), Kyushu University 744 Motoooka, Nishi, Fukuoka 819-0395, Japan

[‡]JST, ERATO, Adachi Molecular Exciton Engineering Project c/o Center for Organic Photonics and Electronics Research (OPERA), Kyushu University, Nishi, Fukuoka 819-0395, Japan

[§]Academia-Industry Molecular Systems for Devices Research and Education Center (AIMS), Kyushu University, Nishi, Fukuoka 819-0395, Japan

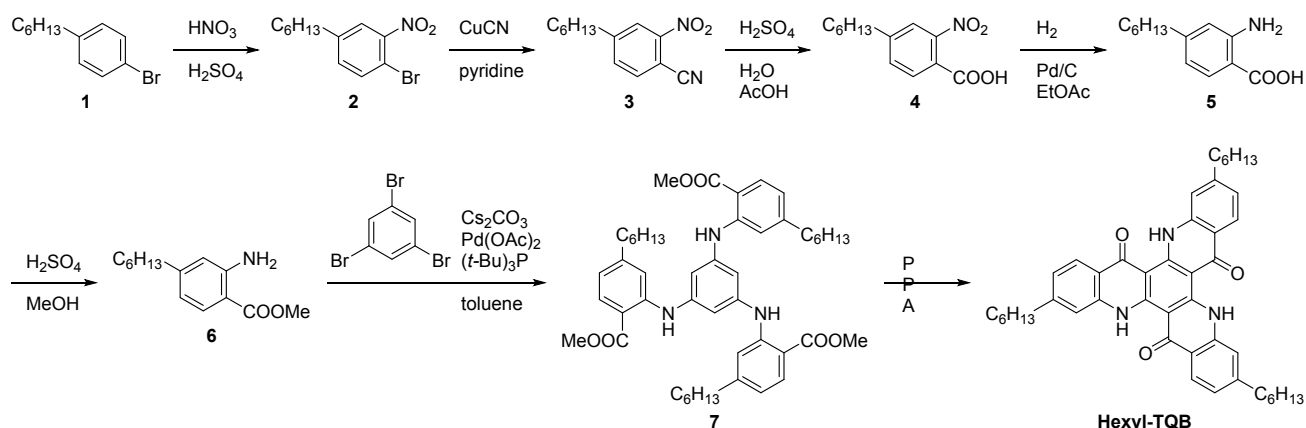
^{||} International Institute for Carbon Neutral Energy Research (WPI-I2CNER), Kyushu University, Nishi, Fukuoka 819-0395, Japan

[^]Email: a.p.monkman@durham.ac.uk

Methods S1. Synthesis

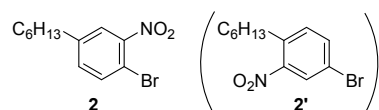
The reagents and solvents for the synthesis were purchased from Tokyo Kasei Co., Ltd. (TCI), WAKO Chemical Industries, Kanto Chemicals, and Sigma-Aldrich, and were used as received unless otherwise noted.

Reagents	CAS No.	Supplier, code and Grade
1-Bromo-4-hexylbenzene	23703-22-2	Tokyo Kasei Co., Ltd., B1606, >90.0%
Nitric acid (1.38)	7697-37-2	WAKO Chemical Industries, 141-01366, 60%
Copper cyanide	544-92-3	WAKO Chemical Industries, 032-19152, >98.0%
Ammonia solution	1336-21-6	WAKO Chemical Industries, 016-03146
Pd/C 10%	7440-05-3	Aldrich Chemical Co., 330108
1,3,5-Tribromobenzene	626-39-1	Tokyo Kasei Co., Ltd., T0347, >98.0%
Cesium carbonate	534-17-8	WAKO Chemical Industries, 038-06545, >95.0%
Palladium(II) acetate	3375-31-3	WAKO Chemical Industries, 163-24702
Tri- <i>tert</i> -butylphosphine	13716-12-6	Tokyo Kasei Co., Ltd., T1912, >95.0%
Polyphosphoric acid	8017-16-1	Merck Millipore Corporation, 807471, 83.0-87.0%



Scheme S1. Synthesis of Hexyl-TQB

Procedure for the synthesis of **2**



Compound **2** was synthesized by modifying the literature¹

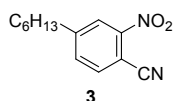
A solution of 1-bromo-4-hexylbenzene (16.4 g, 68.1 mmol) in sulfuric acid (35 ml) was cooled in an ice bath. To this solution was added nitric acid ($d = 1.38$, 60–61 wt%, 5.2 ml, 68.3 mmol). The ice bath was removed, and the mixture was stirred at room temperature for 20 min. A further portion of nitric acid was added (0.2 ml, 2.63 mmol) and the mixture was stirred for a further 20 min. The mixture was poured into K_2CO_3 aq, which was extracted with EtOAc. The organic phase was washed with saturated K_2CO_3 aq, water and brine, then dried and concentrated. The crude product was purified by column chromatography on a silica gel using hexane/EtOAc (20:1 v/v) mixture to give isomeric product **2** and byproduct **2'** as colorless liquid.

Product **2** ($R_f = 0.40$): 1-bromo-4-hexyl-2-nitrobenzene (9.87 g, 50.7%). 1H -NMR: δ /ppm (500 MHz, $CDCl_3$, Me_4Si) = 7.65 (s, 1H, $J = 2.1$ Hz); 7.61 (d, 1H, $J = 8.2$ Hz); 7.24 (d, 1H, $J = 8.2$ Hz, $J = 2.1$ Hz); 2.64 (t, 2H, $J = 7.8$ Hz); 1.64–1.58 (m, 2H); 1.35–1.26 (m, 6H); 0.88 (t, 3H, $J = 6.8$ Hz). ^{13}C -NMR: δ /ppm (125 MHz, $CDCl_3$) = 149.82, 144.20, 134.83, 133.53, 125.49, 111.25, 35.16, 31.73, 31.67, 30.93, 28.85, 22.65, 14.17. MS/ASAP: m/z 285 (M^+ , 100%). Anal. Calcd. For $C_{12}H_{16}BrNO_2$: C, 50.37; H, 5.64; Br, 27.92; N, 4.89; O, 11.18. Found: C, 50.48; H, 5.68; N, 4.94.

Byproduct **2'** ($R_f = 0.52$): 4-bromo-1-hexyl-2-nitrobenzene (8.19 g, 42.0%). 1H -NMR: δ /ppm (500 MHz, $CDCl_3$, Me_4Si) = 8.01 (s, 1H); 7.61 (d, 1H, $J = 8.3$ Hz); 7.22 (d, 1H, $J = 8.3$ Hz); 2.82 (t, 2H, $J = 7.9$ Hz); 1.63–1.56 (m, 2H); 1.39–1.26 (m, 6H); 0.88 (t, 3H, $J = 6.9$ Hz). ^{13}C -NMR: δ /ppm (125 MHz, $CDCl_3$) = 149.93, 136.86, 135.84, 133.37, 127.56, 119.68, 32.69, 31.62, 30.65, 29.29, 22.67, 14.17. MS/ASAP: m/z 285 (M^+ , 100%).

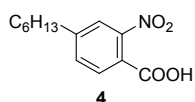
¹ W. Liu, H. J. Lim, and T. V. RajanBabu, *J. Am. Chem. Soc.* **2012**, *134*, 5496–5499.

Procedure for the synthesis of **3**



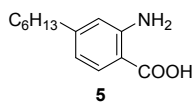
A mixture of compound **2** (3.76 g, 13.1 mmol) and copper (I) cyanide (1.32 g, 14.7 mmol) in pyridine (50 ml) was stirred at 150 °C for 60 h. After cooling, ammonia solution was added, and the mixture was extracted with DCM, dried over anhydrous Na₂SO₄, and concentrated to dryness. The crude material was purified by column chromatography on a silica gel using hexane/EtOAc (5:1 v/v) mixture (*R*_f = 0.25) to give a brown liquid (2.73 g, 89.5%). ¹H-NMR: δ/ppm (500 MHz, CDCl₃, Me₄Si) = 8.13 (s, 1H); 7.81 (d, 1H, *J* = 7.9 Hz); 7.60 (d, 1H, *J* = 7.9 Hz); 2.79 (t, 2H, *J* = 7.8 Hz); 1.70–1.64 (m, 2H); 1.36–1.28 (m, 6H); 0.89 (t, 3H, *J* = 6.9 Hz). ¹³C-NMR: δ/ppm (125 MHz, CDCl₃) = 150.66, 148.76, 135.47, 134.30, 125.47, 115.34, 105.36, 36.00, 31.61, 30.73, 28.86, 22.61, 14.14. MS/ASAP: *m/z* 232 (M⁺, 100%). Anal. Calcd. For C₁₃H₁₆N₂O₂: C, 67.22; H, 6.94; N, 12.06; O, 13.78. Found: C, 67.41; H, 6.97; N, 11.97.

Procedure for the synthesis of **4**



A solution of compound **3** (7.00 g, 30.1 mmol) in H₂O (15 ml), AcOH (30 ml), and conc. H₂SO₄ (15 ml) was stirred at 110 °C for 20 h. After cooling, water was added, and the solid was collected by filtration, washed with water and dried. The crude material was dissolved in a mixture of aqueous NaOH solution and MeOH and washed with DCM. To an aqueous solution was added conc. HCl and extracted with DCM, washed with water, dried over anhydrous Na₂SO₄, and concentrated to dryness to give a colorless solid (5.11 g, 67.5%). Mp: 77–79 °C. ¹H-NMR: δ/ppm (500 MHz, CDCl₃, Me₄Si) = 7.83 (d, 1H, *J* = 7.9 Hz); 7.60 (s, 1H, *J* = 1.7 Hz); 7.47 (d, 1H, *J* = 7.9 Hz, *J* = 1.7 Hz); 2.73 (t, 2H, *J* = 7.8 Hz); 1.69–1.63 (m, 2H); 1.37–1.29 (m, 6H); 0.89 (t, 3H, *J* = 6.9 Hz). ¹³C-NMR: δ/ppm (125 MHz, CDCl₃) = 169.82, 149.77, 149.75, 132.27, 130.89, 123.72, 122.47, 35.79, 31.67, 30.83, 28.91, 22.65, 14.18. Anal. Calcd. For C₁₃H₁₇NO₄: C, 62.14; H, 6.82; N, 5.57; O, 25.47. Found: C, 62.10; H, 6.79; N, 5.59.

Procedure for the synthesis of **5**



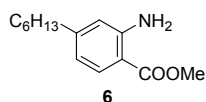
Compound **5** was synthesized by modifying the literature²

Palladium 10% on Carbon (Pd/C, 0.28 g) was added to a solution of compound **4** (5.11 g, 20.3 mmol) in EtOAc (100 ml), and the solution was saturated with hydrogen for 12 h at room temperature. The reaction mixture was filtered through a Celite pad and the solution was concentrated to dryness. The crude material was purified by column chromatography on a silica gel using hexane/EtOAc (1:1 v/v) mixture (*R*_f = 0.27, fluorescent) as eluent to

² M. Chwastek, M. Pieczykolan, and S. Stecko, *J. Org. Chem.* **2016**, *81*, 9046–9074.

give a to give a colorless solid (4.39 g, 97.5%). Mp: 91–96 °C. ¹H-NMR: δ /ppm (500 MHz, CDCl₃, Me₄Si) = 7.83 (d, 1H, J = 8.2 Hz); 6.52 (d, 1H, J = 8.2 Hz, J = 1.6 Hz); 6.48 (s, 1H, J = 1.6 Hz); 2.52 (t, 2H, J = 7.7 Hz); 1.62–1.57 (m, 2H); 1.36–1.28 (m, 6H); 0.89 (t, 3H, J = 6.8 Hz). ¹³C-NMR: δ /ppm (125 MHz, CDCl₃) = 173.64, 151.32, 151.14, 132.19, 117.54, 116.38, 107.56, 36.23, 31.84, 30.82, 29.14, 22.73, 14.24. Anal. Calcd. For C₁₃H₁₉NO₂: C, 70.56; H, 8.65; N, 6.33; O, 14.46. Found: C, 70.37; H, 8.58; N, 6.30.

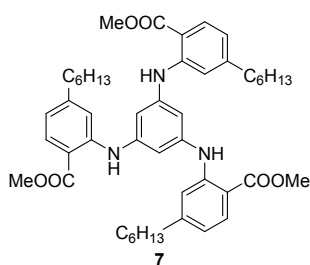
Procedure for the synthesis of **6**



Compound **6** was synthesized by modifying the literature³

To a stirred solution of conc. H₂SO₄ (20 mL) in MeOH (50 mL) was added compound **5** (4.39 g, 19.8 mmol). The mixture was stirred at 70 °C overnight and then allowed to cool down to room temperature. The mixture was neutralized with a saturated aqueous solution of Na₂CO₃ and extracted with DCM, dried over anhydrous Na₂SO₄, and concentrated to dryness. The crude material was purified by column chromatography on a silica gel using DCM (R_f = 0.4, fluorescent) as eluent to give a pale yellow oil (2.79 g, 59.7%). ¹H-NMR: δ /ppm (500 MHz, CDCl₃, Me₄Si) = 7.75 (d, 1H, J = 8.7 Hz); 6.48 (d, 1H, J = 8.7 Hz, J = 1.6 Hz); 6.47 (s, 1H, J = 1.6 Hz); 3.85 (s, 3H); 2.50 (t, 2H, J = 7.7 Hz); 1.61–1.56 (m, 2H); 1.33–1.26 (m, 6H); 0.88 (t, 3H, J = 6.8 Hz). ¹³C-NMR: δ /ppm (125 MHz, CDCl₃) = 168.71, 150.60, 149.97, 131.26, 117.31, 116.34, 108.74, 51.51, 36.14, 31.84, 30.88, 29.12, 22.73, 14.23. MS/ASAP: m/z 235 (M⁺, 100%). Anal. Calcd. For C₁₄H₂₁NO₂: C, 71.46; H, 9.00; N, 5.95; O, 13.60. Found: C, 71.53; H, 9.02; N, 6.02.

Procedure for the synthesis of **7**



Compound **7** was synthesized by modifying the literature⁴

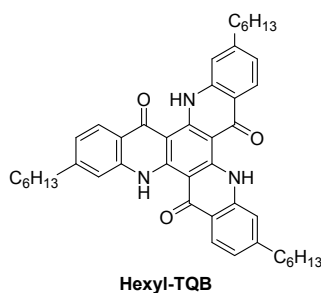
The mixture of 1,3,5-tribromobenzene (1.13 g, 3.60 mmol), compound **6** (2.58 g, 11.0 mmol), cesium carbonate (6.03 g, 18.5 mmol), and Pd(OAc)₂ (0.097 g, 0.43 mmol) was placed in a two-neck flask and purged with argon. Toluene was added and then tri-*tert*-butylphosphine (0.265 g, 1.31 mmol) was added. The reaction mixture was refluxed for 3 days. After cooling, the mixture was filtered, washed with toluene and an aqueous solution of NH₄Cl. The organic phase was collected, dried over Na₂SO₄ and concentrated to dryness. The crude product was purified

³ C. Bosset, R. Coffinier, P. A. Peixoto, M. E. Assal, K. Miqueu, J.-M. Sotiropoulos, L. Pouységu, and S. Quideau, *Angew. Chem. Int. Ed.* **2014**, *53*, 9860–9864.

⁴ F. Qiu, F. Zhang, R. Tang, Y. Fu, X. Wang, S. Han, X. Zhuang, and X. Feng, *Org. Lett.* **2016**, *18*, 1398–1401.

by column chromatography on a silica gel using DCM/hexane (1:1 v/v) mixture ($R_f = 0.25$) as eluent to give a colorless oil (2.33 g, 83.2%). $^1\text{H-NMR}$: δ /ppm (500 MHz, CDCl_3 , Me_4Si) = 9.44 (s, 3H); 7.86 (d, 3H, $J = 8.2$ Hz); 7.15 (s, 3H, $J = 1.6$ Hz); 6.84 (s, 3H); 6.59 (d, 3H, $J = 8.2$ Hz, $J = 1.6$ Hz); 3.88 (s, 9H); 2.53 (t, 6H, $J = 7.7$ Hz); 1.57–1.51 (m, 6H); 1.32–1.23 (m, 18H); 0.84 (t, 9H, $J = 6.8$ Hz). $^{13}\text{C-NMR}$: δ /ppm (125 MHz, CDCl_3) = 168.95, 150.06, 147.50, 143.26, 131.67, 118.30, 114.82, 110.33, 109.88, 51.77, 36.61, 31.81, 31.12, 29.15, 22.70, 14.20. MS/ASAP: m/z 777 (M^+ , 100%). Anal. Calcd. For $\text{C}_{48}\text{H}_{63}\text{N}_3\text{O}_6$: C, 74.10; H, 8.16; N, 5.40; O, 12.34. Found: C, 74.03; H, 8.13; N, 5.36.

Procedure for the synthesis of Hexyl-TQB



A mixture of compound **7** (2.23 g, 2.86 mmol) and polyphosphoric acid (50 g) was heated at 150 °C overnight. After cooling, ice-cold water was added and the precipitate was filtered, washed with water, MeOH. The crude was purified by column chromatography on a silica gel using DCM ($R_f = 0.7$) as eluent to give a pale yellow solid (1.72 g, 88.0%). Mp: 195–199 °C. 5% Weight loss temperature: 466 °C. $^1\text{H-NMR}$: δ /ppm (500 MHz, CDCl_3 , Me_4Si) = 15.42 (s, 3H); 8.09 (d, 3H, $J = 8.2$ Hz); 7.19 (s, 3H, $J = 1.6$ Hz); 7.06 (d, 3H, $J = 8.2$ Hz, $J = 1.6$ Hz); 2.67 (t, 6H, $J = 7.8$ Hz); 1.72–1.66 (m, 6H); 1.42–1.34 (m, 18H); 0.94 (t, 9H, $J = 7.0$ Hz). $^{13}\text{C-NMR}$: δ /ppm (125 MHz, CDCl_3) = 178.26, 149.24, 147.17, 138.31, 125.44, 125.11, 121.29, 117.44, 99.39, 36.28, 31.88, 30.80, 29.22, 22.77, 14.28. MS/ASAP: m/z 681 (M^+ , 100%). Anal. Calcd. For $\text{C}_{45}\text{H}_{51}\text{N}_3\text{O}_3$: C, 79.26; H, 7.54; N, 6.16; O, 7.04. Found: C, 79.04; H, 7.51; N, 6.11.

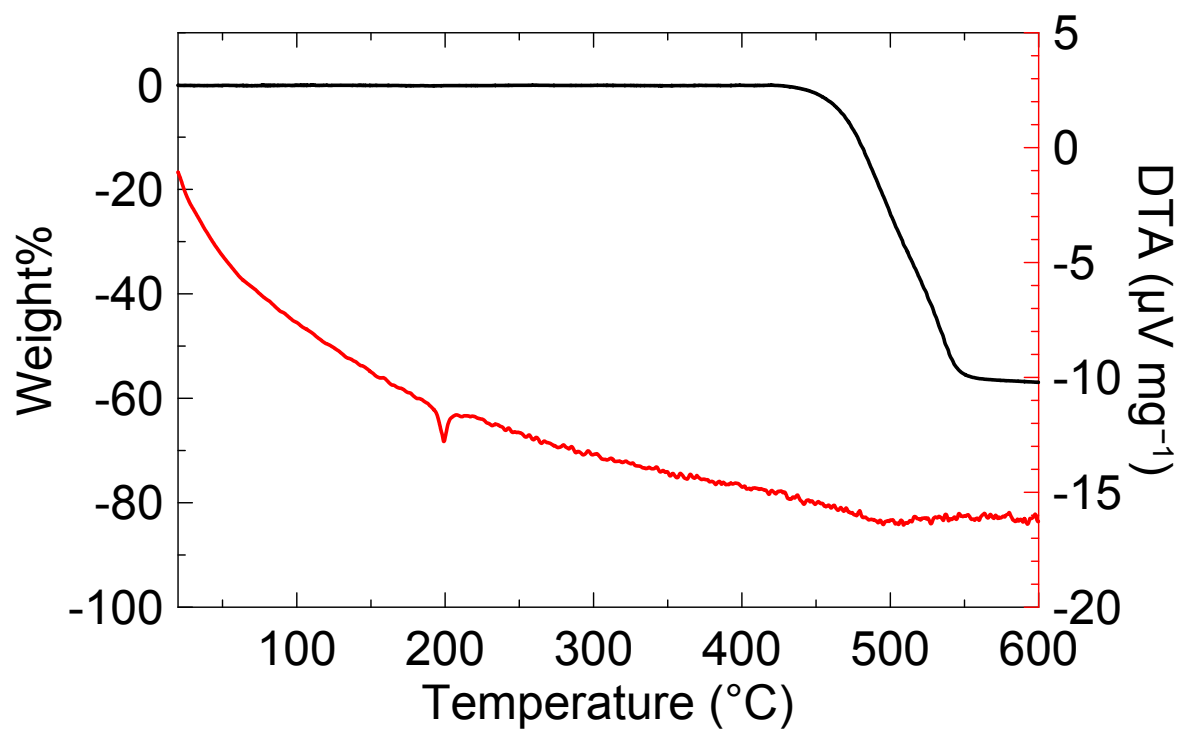
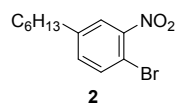
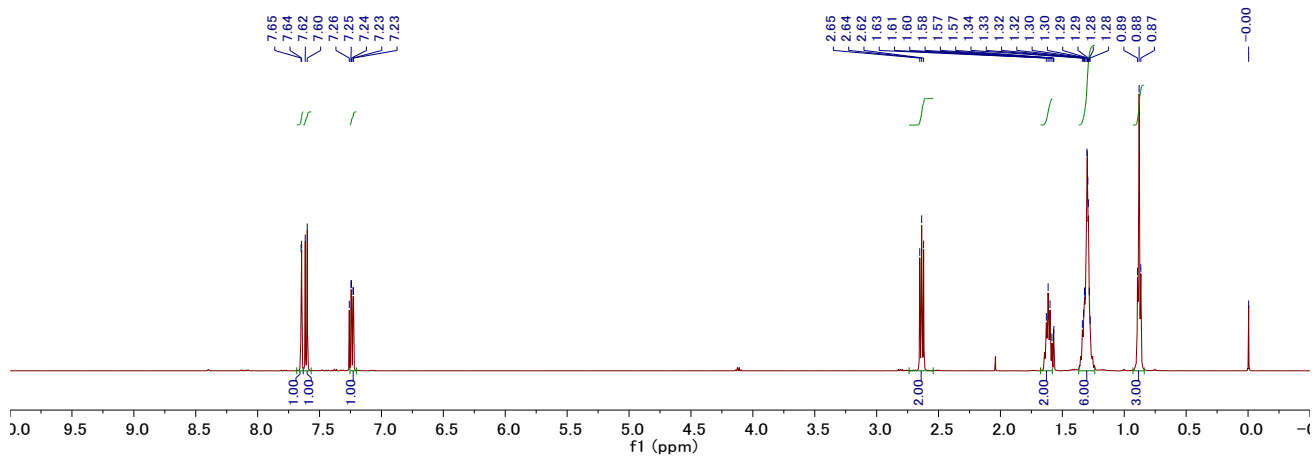


Figure S1. Thermogravimetric (TG) and differential thermal analysis (DTA) at ambient pressure for Hexyl-TQB.

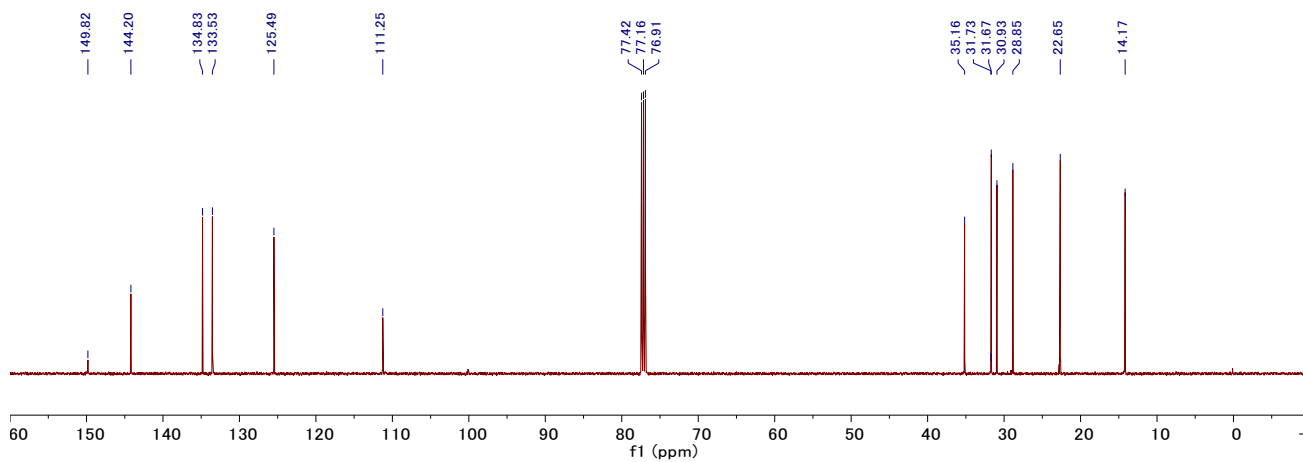
Data S1. NMR spectra

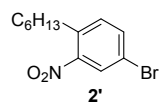


¹H-NMR spectrum (500 MHz, CDCl₃, 300 K)

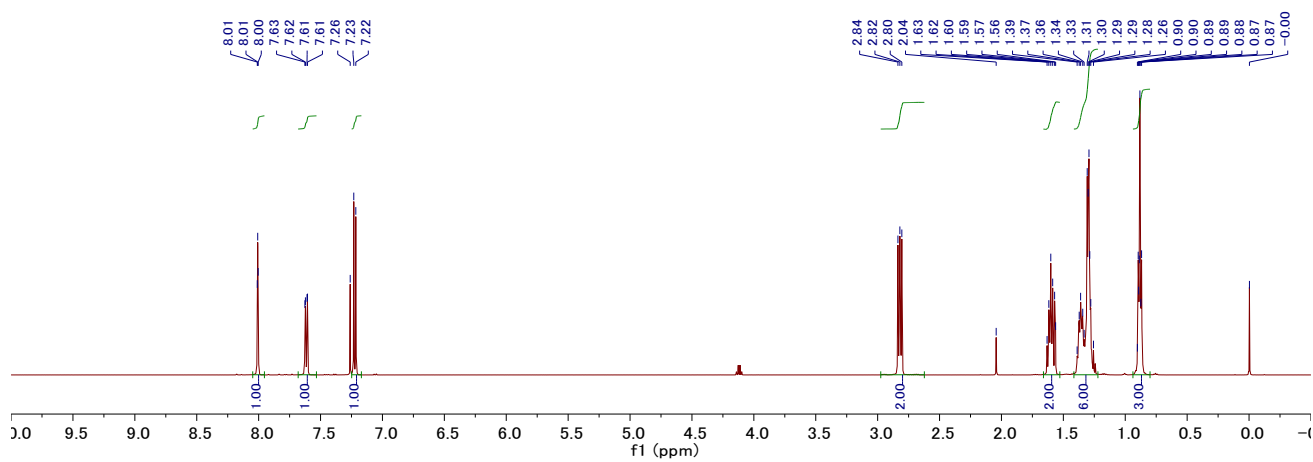


¹³C-NMR spectra (125 MHz, CDCl₃, 300 K)

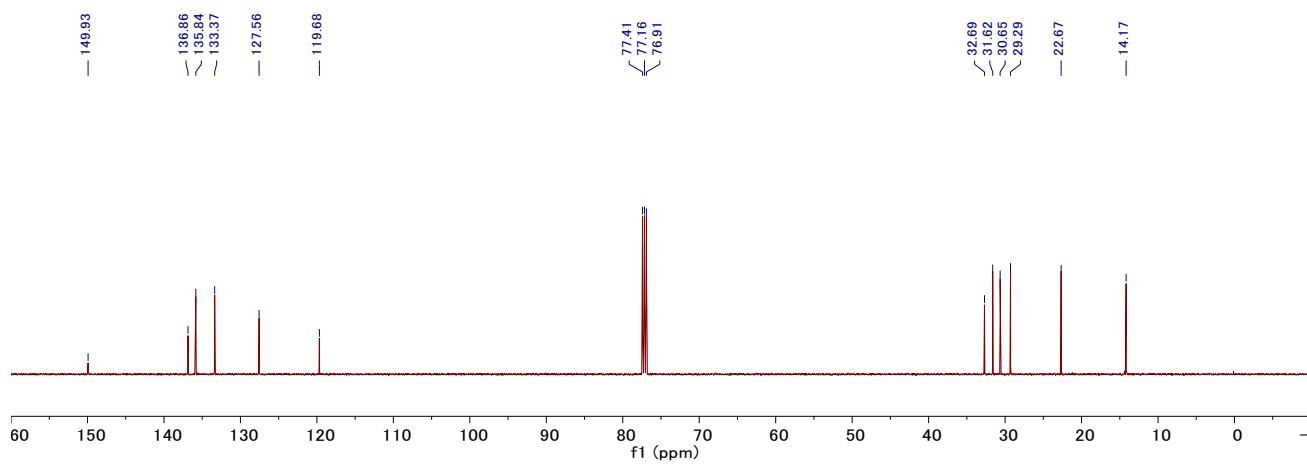


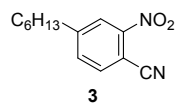


^1H -NMR spectrum (500 MHz, CDCl_3 , 300 K)

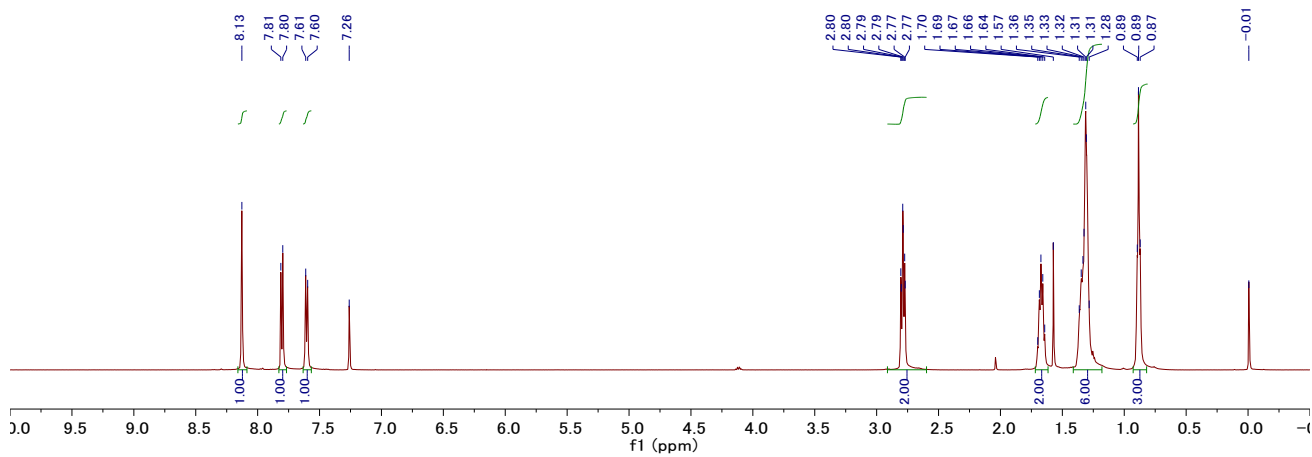


^{13}C -NMR spectra (125 MHz, CDCl_3 , 300 K)

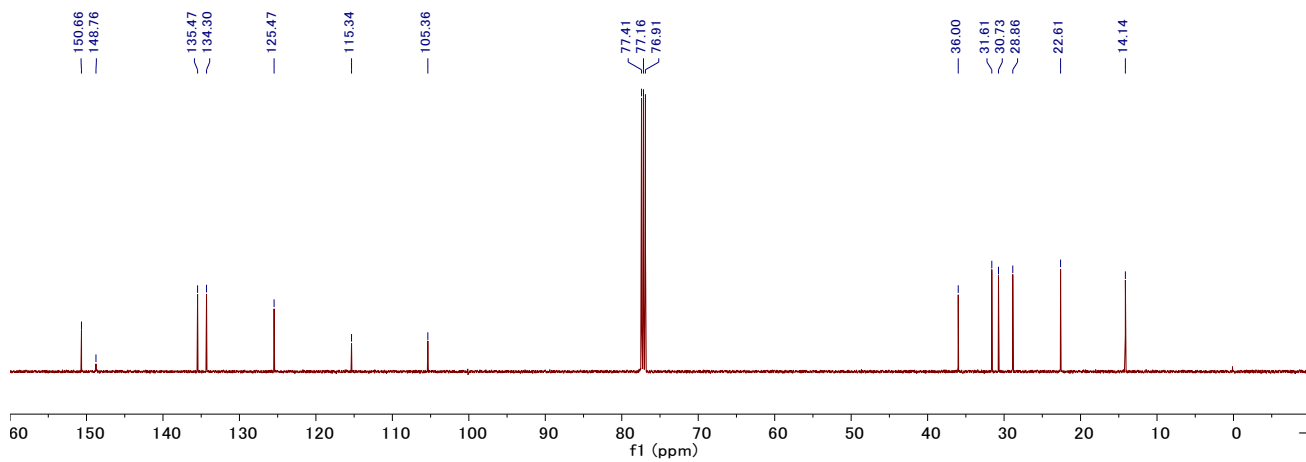


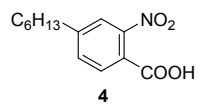


^1H -NMR spectrum (500 MHz, CDCl_3 , 300 K)

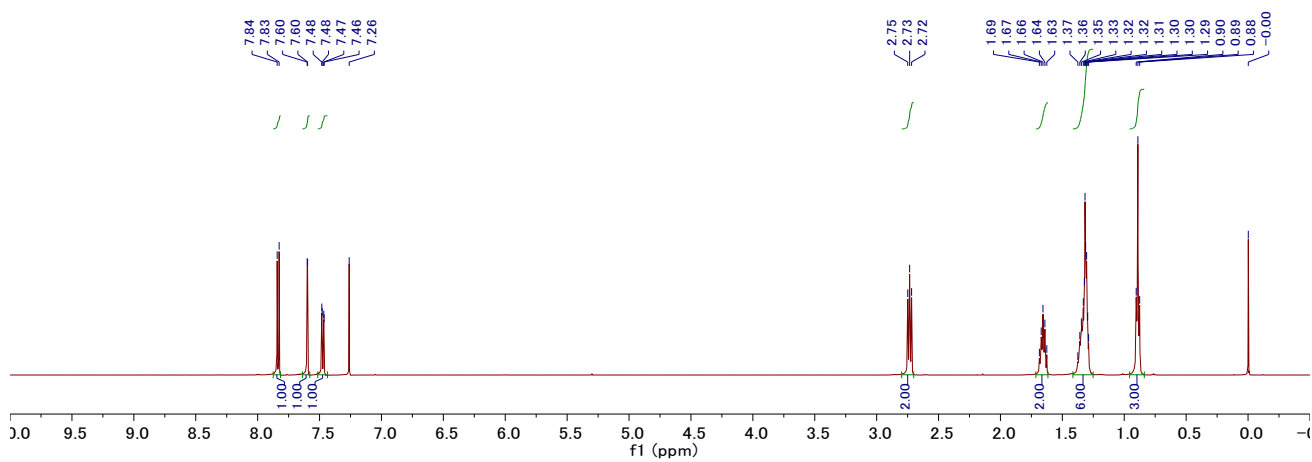


^{13}C -NMR spectra (125 MHz, CDCl_3 , 300 K)

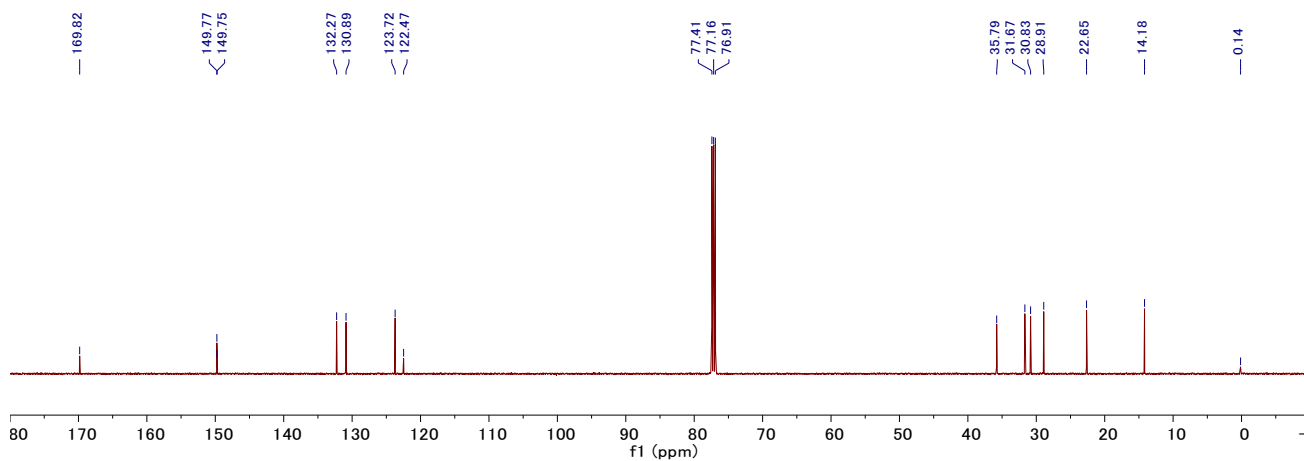


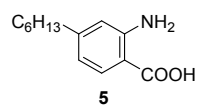


^1H -NMR spectrum (500 MHz, CDCl_3 , 300 K)

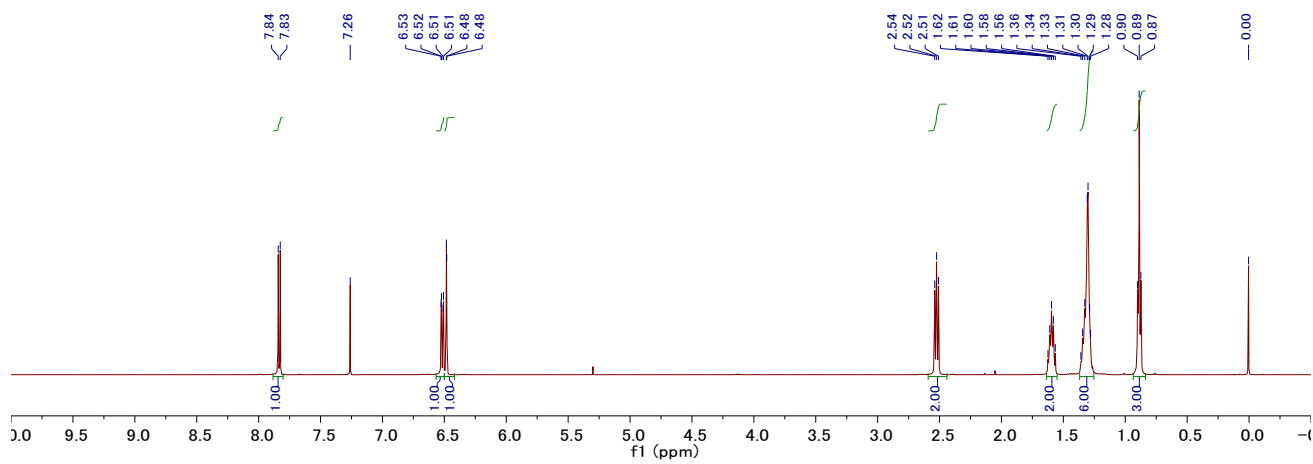


^{13}C -NMR spectra (125 MHz, CDCl_3 , 300 K)

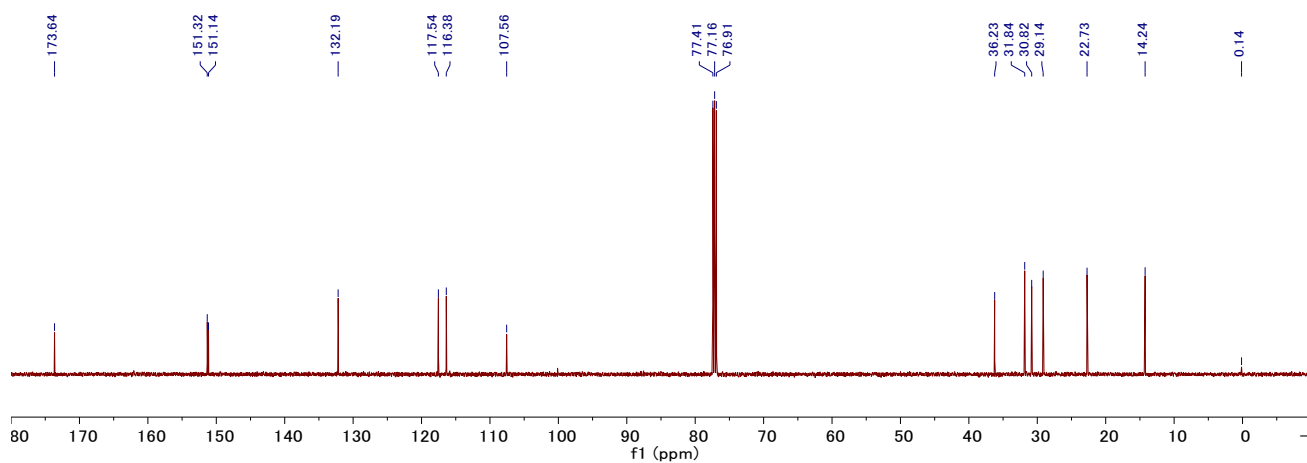


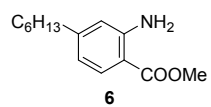


^1H -NMR spectrum (500 MHz, CDCl_3 , 300 K)

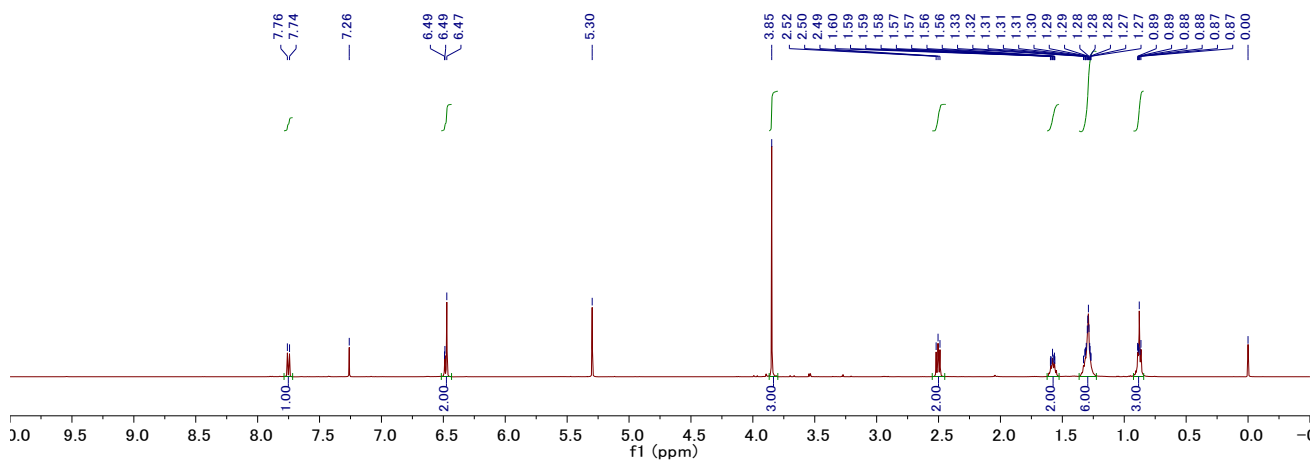


^{13}C -NMR spectra (125 MHz, CDCl_3 , 300 K)

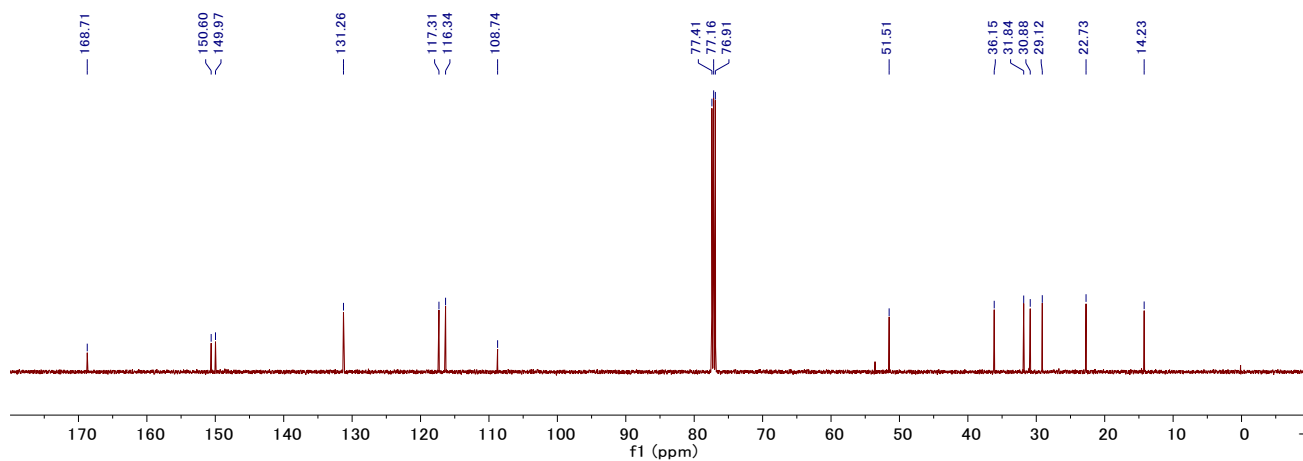


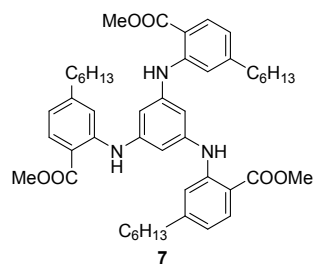


^1H -NMR spectrum (500 MHz, CDCl_3 , 300 K)

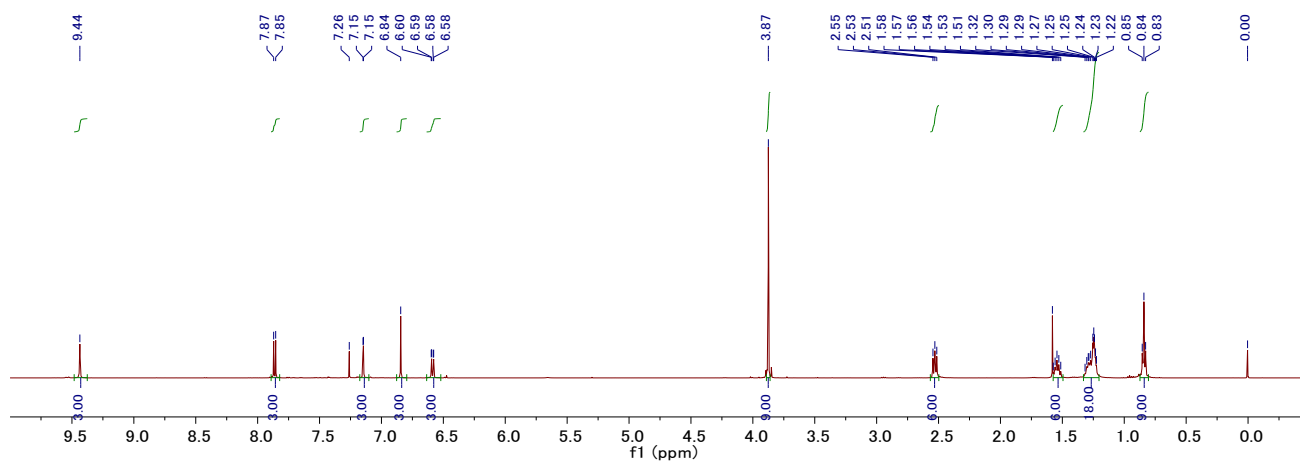


^{13}C -NMR spectra (125 MHz, CDCl_3 , 300 K)

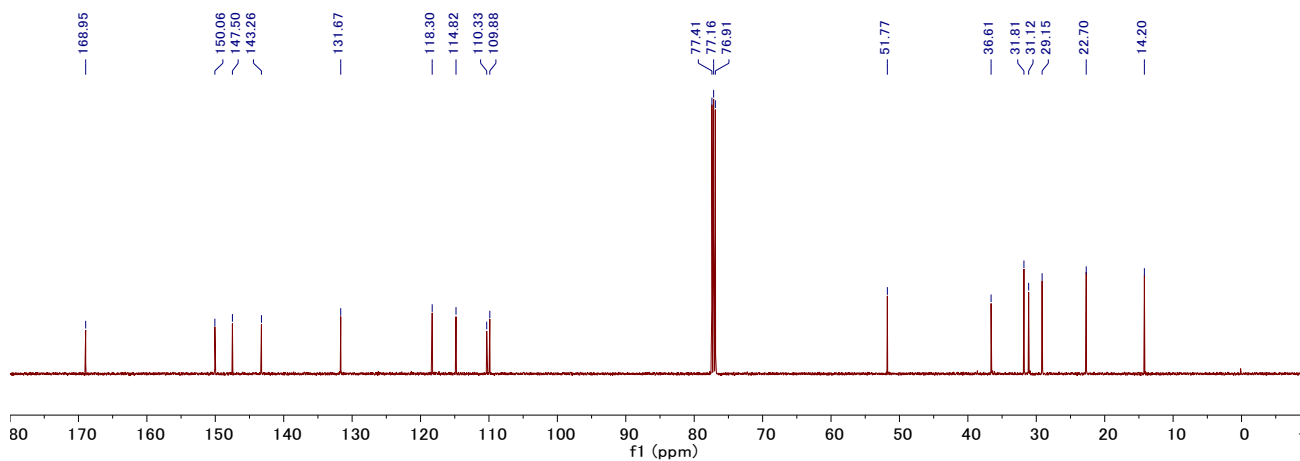


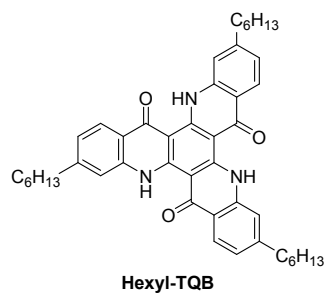


^1H -NMR spectrum (500 MHz, CDCl_3 , 300 K)

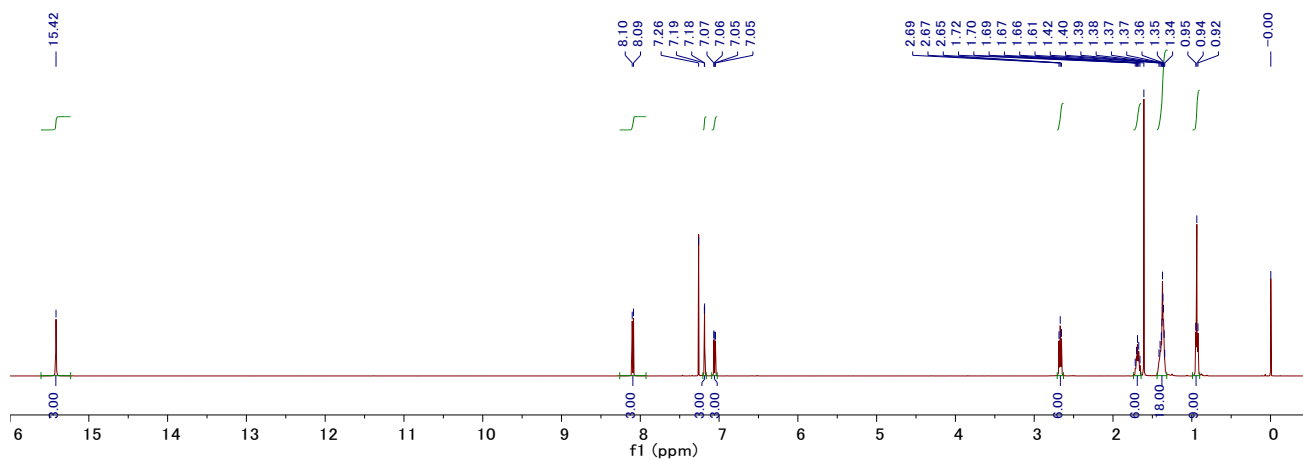


^{13}C -NMR spectra (125 MHz, CDCl_3 , 300 K)

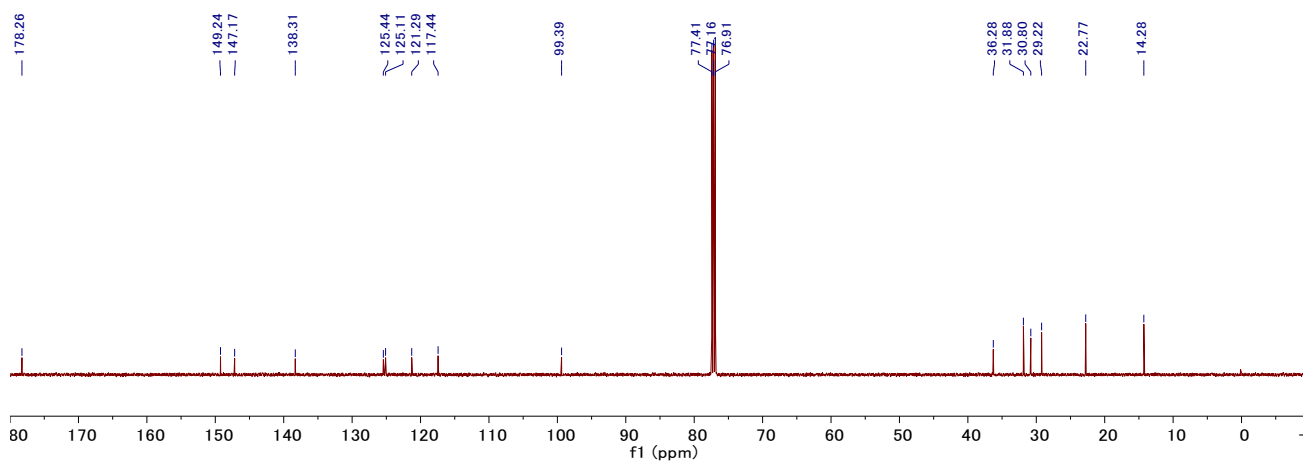




¹H-NMR spectrum (500 MHz, CDCl₃, 300 K)



¹³C-NMR spectra (125 MHz, CDCl₃, 300 K)



Experimental Methods:

- Sample preparation

Films of neat TQB and TQB doped in DPEPO host were made by drop casting onto transparent sapphire substrates from solutions which were prepared as follows: Stock solutions of TQB (concentration 3mg/ml) and DPEPO (2mg/ml) were prepared by dissolving the corresponding materials in toluene solution overnight at 60°C (using magnetic stirrers) to ensure complete dissolution. To make the solution from which the TQB-doped DPEPO films were drop cast, volumes of each stock solution were blended together with a emitter:host ratio to give films of 10 wt%.

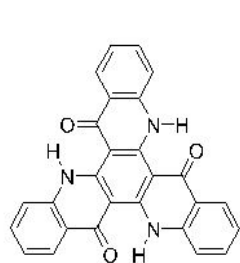
The film of 'regular' (non-hexyl) TQB in zeonex matrix was made by doctor blade coating onto transparent sapphire substrate. Stock solution of TQB was prepared by dissolving the material in toluene at a nominal 1mg/ml concentration. Due to poor solubility, the solution was then filtered to remove undissolved solids before being blended with an equal volume of zeonex solution (180mg/ml) and blade cast. The films produced in this way were therefore lower than 0.5 wt%. Despite this low concentration we find that the additional film thickness associated with blade coating gave sufficient absorption to allow optical measurements.

- Photophysical characterisation

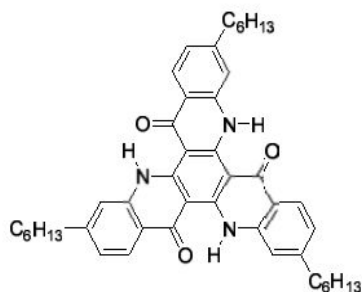
Absorption spectra for films and solutions were collected using a double beam Shimadzu UV-3600 UV/VIS/NIR spectrophotometer. Steady state photoluminescence spectra were collected using a Jobin-Yvon Fluoromax-4 fluorimeter.

- Transient Absorption and Time-Resolved Photoluminescence

Transient absorption measurements were carried out using a pump-probe spectrometer, in which an actinic YAG 355 nm laser (with pulse width 4 ns) acted as the pump source for measuring dynamics on the nanosecond scale, whilst for picosecond measurements, the pump beam was supplied by a Pharos Yb:KGW femtosecond laser directed using an Optical Delay Line (from Thorlabs.) The probe beam was a white light continuum generated by passing the Pharos Yb:KGW femtosecond laser beam through a sapphire plate, with measuring range between 500-800 nm. Time-resolved photoluminescence spectra and decays were measured using a nanosecond gated spectrograph-coupled iCCD (Stanford) using an Nd:YAG laser emitting at 355 nm (EKSPLA) as an excitation source, along with a gated 4 Picos iCCD camera.



TQB



TQB-Hexyl

PLQY in toluene with
N₂ bubbling
TQB: 59%
TQB-Hexyl: 66%

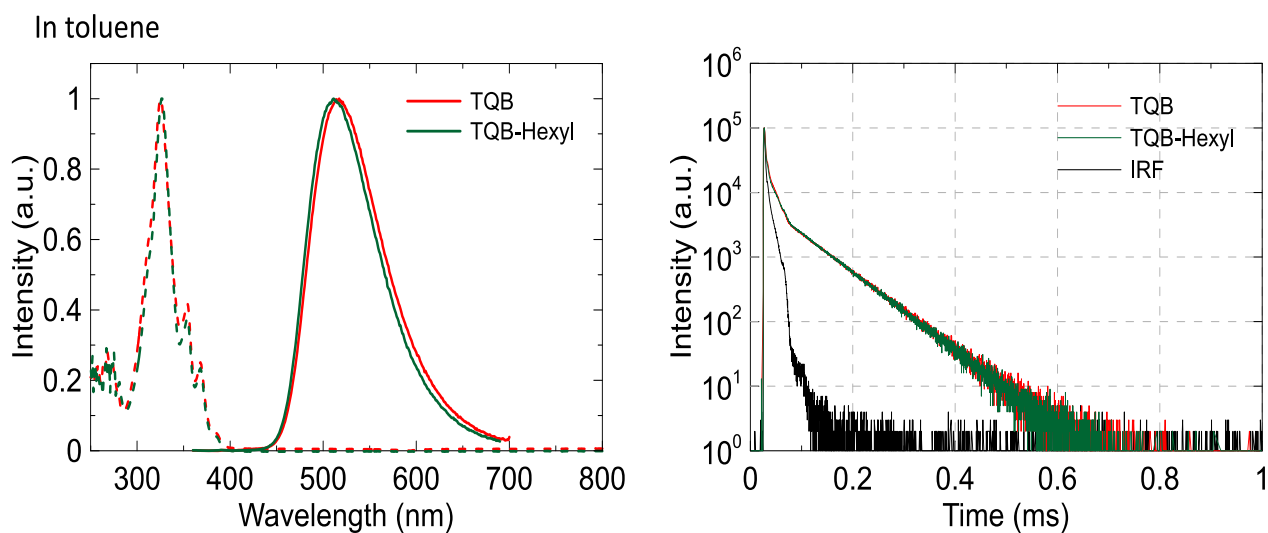


Figure S2: Comparison of structures, absorption (dashed line) and emission (solid line, 340nm excitation), and emission lifetimes of TQB and hexyl-TQN in toluene. Emission decays were collected using a Hamamatsu Photonics Quantaurs-Tau C11367-03 with 340nm excitation and 520nm emission collection. Emission was detected with a photomultiplier after being dispersed with a monochromator. Time to amplifier converter (TAC) was used with a multichannel analyser (MCA) to perform TCSPC

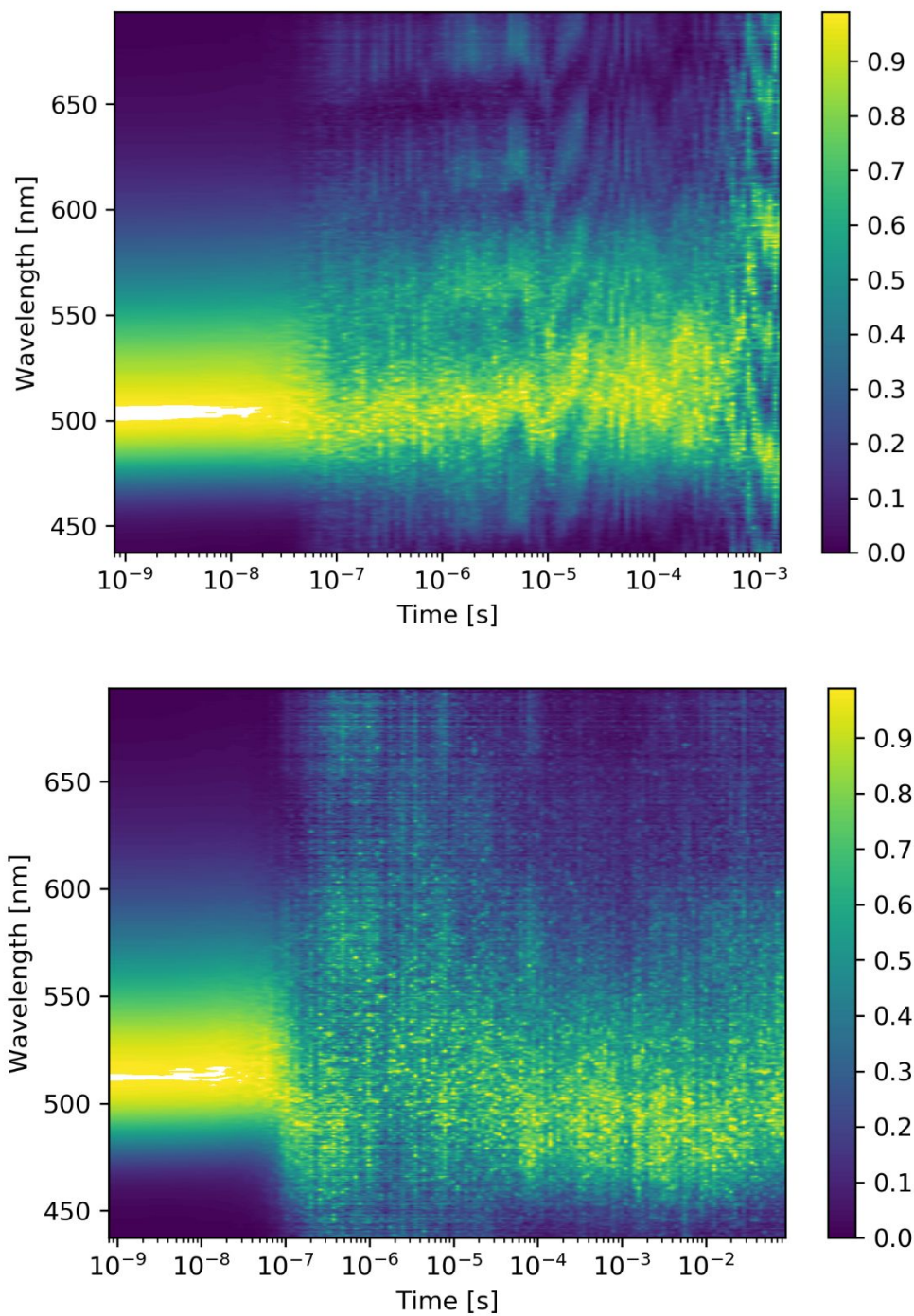


Figure S3: Normalised time-resolved emission spectra of TQB in DPEPO at 300K (top) and 80K (bottom). Although signal to noise ratios vary at different times, the emission bandshape and onset do not vary over the timescales investigated (ns-ms).

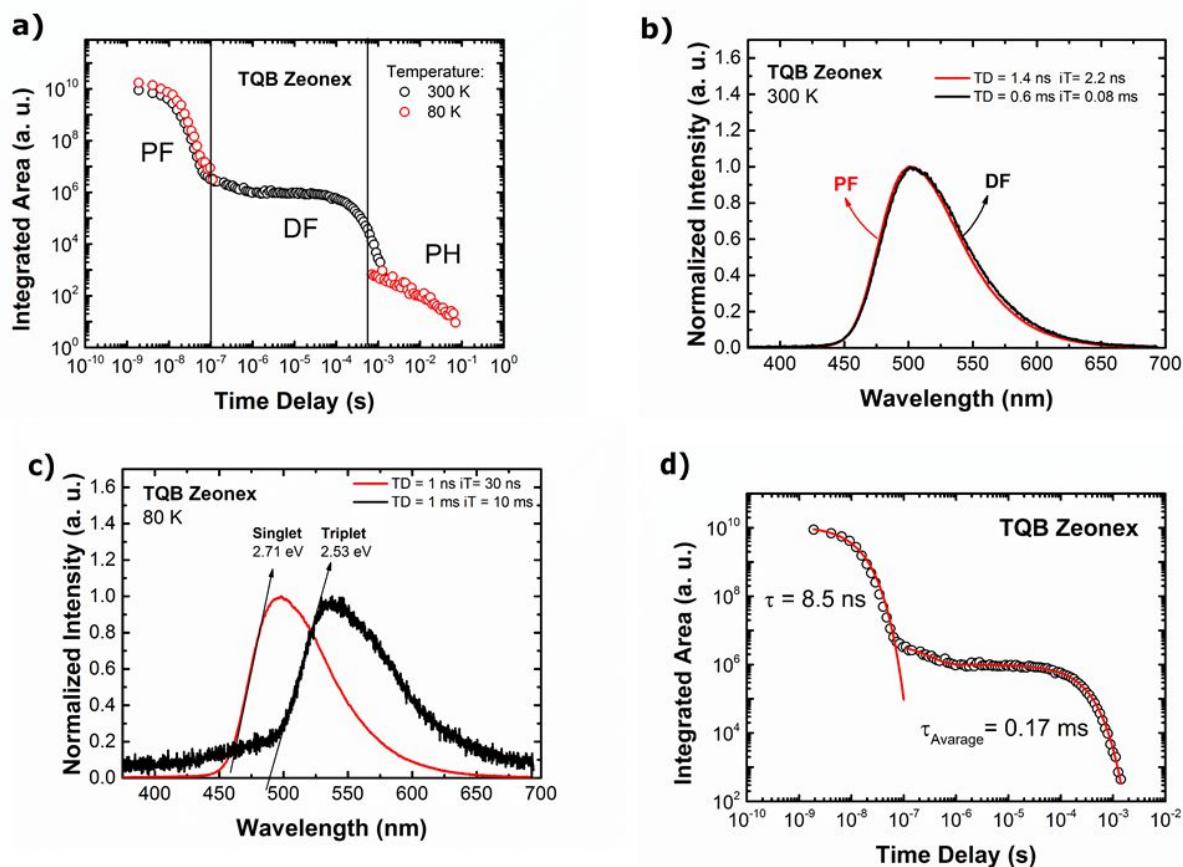


Figure S4: Emission decay kinetics and spectra of plain (non-hexyl) TQB in zeonex: a) comparison of emission decays at 300K and 80K b) representative PF and DF spectra at 300K c) representative PF and DF spectra at 80K, with band onsets indicated to give the singlet and triplet energies d) exponential lifetime fitting of emission decay at 300K.

We suggest that the observation of phosphorescence solely in zeonex may be due to its intermediate rigidity – flexible enough to allow vibrational modes associated SOC and T1 emission (modes restricted in DPEPO), but rigid enough to prevent vibrational relaxation of T1 that quenches phosphorescence in liquid toluene.