

Electronic Supplementary Information

Triquinoxalinediol as organic cathode material for rechargeable aqueous zinc-ion batteries

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Material characterization: FT-IR spectroscopy was recorded on IFS66/S (Bruker) using KBr pellets in the wavelength range of 600-4000 cm⁻¹. ¹H and ¹³C NMR spectra were recorded on Avance Neo 600 MHz spectrometer (Bruker) using DMSO-*d*₆ containing 0.03 wt. % tetramethylsilane (TMS) or deuterated trifluoroacetic acid (CF₃COOD) as solvents. Mass spectrometry measurements were recorded on Micromass Q-ToF Premier (Waters) and Bruker UltrafleXtreme MALDI-TOF (Bruker Daltonik) mass spectrometers. For MALDI-TOF MS the samples were first mixed with the matrix dithranol in agate mortar. The solid mixture was then transferred to the MALDI plate using a spatula and the reflective positive ion mode was used to acquire the mass spectra. Calibration was performed externally using a poly(methyl methacrylate) standard (MALDI validation set PMMA, Fluka Analytical). TGA measurements were performed on a TGA/DSC 1 thermogravimetric analyzer (Mettler Toledo, Switzerland) at a heating rate of 10 °C min⁻¹ from 40 to 800 °C in a nitrogen atmosphere. Safety & hazards: Trifluoroacetic acid is strong acid (pK_a=0.52) and volatile (T_B=72.4 °C). It is harmful when inhaled, causes severe burns on skin and is toxic for aquatic organisms.

Electrochemical measurements: Electrochemical measurements were carried out using potentiostat/galvanostat VMP3 (Bio-Logic, France) at room temperature (25 °C).

Battery measurements: The electrodes were prepared by mixing 60 mg of the active material, 30 mg of carbon black (Printex XE2), 10 mg of polytetrafluoroethylene (PTFE) (60 wt. % water dispersion, Aldrich) and 0.5 mL of isopropyl alcohol (IPA). The mixture was ball milled in a planetary ball mill (Retsch PM100) at 300 rpm for 30 min in ambient atmosphere. Obtained slurry was rolled into a thin film on glass and cut into circular discs (φ = 10 mm), which were afterwards dried at 50 °C for 1 day. Swagelok type battery cells were assembled in ambient atmosphere by separating free standing cathode electrodes and zinc foil discs (φ = 10 mm) with 2 pieces (φ = 13 mm) of glass fiber separator (Whatman GF/A) wetted with 3 drops of 4 M ZnSO₄, 1 M ZnSO₄, 2.2 M Zn(OTf)₂ in 70 wt. % PEG in H₂O or 1 M Zn(TFSI)₂ in G2. Different concentrations of ZnSO₄ electrolytes were prepared by dissolving an appropriate amount of zinc sulfate heptahydrate (ZnSO₄·7H₂O) in water. 2.2 M Zn(OTf)₂ in 70 wt. % PEG was prepared according to the literature procedure¹ by dissolving 2 mmol of zinc triflate (Zn(OTf)₂) in 0.7 g of polyethylene glycol 400 (PEG 400) and 0.3 g of water. 1 M Zn(TFSI)₂ in G2 was prepared by dissolving zinc bis(trifluoromethylsulfonyl)imide (Zn(TFSI)₂) in diethyleneglycol dimethyl ether (G2) solvent.

Three-electrode measurements: were done using Ag/AgCl electrode and platinum coil as reference and counter electrode, respectively. Working electrode was obtained by drop-casting slurry composing of 60 wt. % of TQD, 30 wt. % of Super C65 carbon black and 10 wt. % of polyvinylidene fluoride (PVDF) solution (10 mg/mL) in *N*-methyl-2-pyrrolidone (NMP) on glassy carbon electrode and afterwards drying at 50 °C for 2h. Continuous flow of nitrogen ensured oxygen free environment for the measurements. Different concentrations of ZnSO₄ electrolytes were prepared by dissolving an appropriate amount of zinc sulfate heptahydrate (ZnSO₄·7H₂O) in water. 4 M ZnSO₄ + H₂SO₄ (pH = 1) electrolyte was prepared by the addition of H₂SO₄ into 4 M ZnSO₄ until the pH meter (827 pH Lab, Metrohm) measured pH = 1. H₂SO₄ pH = 1 and H₂SO₄ pH = 3.3 electrolyte solutions were obtained by the addition of H₂SO₄ into water until the appropriate pH meter (827 pH Lab, Metrohm) measured

value.

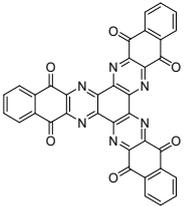
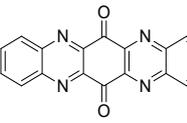
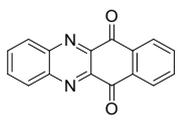
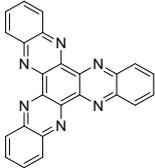
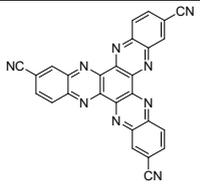
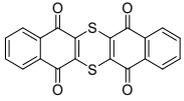
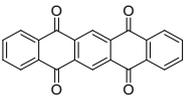
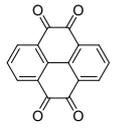
Ex-situ FT-IR characterization of electrodes: FT-IR spectroscopy was recorded on IFS66/S (Bruker) using KBr pellets in the wavelength range of 600-4000 cm^{-1} . TQD cathodes were harvested from Swagelok type cells described in electrochemical measurements with an additional hydrophilic polytetrafluoroethylene (PTFE) membrane separator (0.2 μm pore size, Omnipore), which avoided the contamination with glassy fibers. The cathode electrodes were obtained by disassembling the batteries in different states of charge in an argon-filled glovebox and rinsing them with water to remove the residual electrolyte. Washed electrodes were afterwards dried at 50 $^{\circ}\text{C}$ and mixed with KBr to form the pellet.

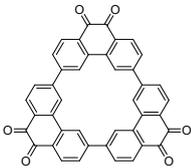
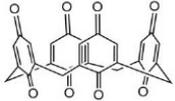
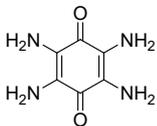
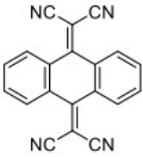
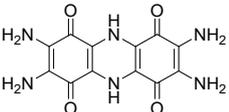
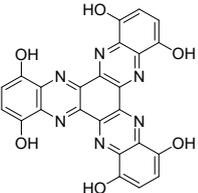
Ex-situ UV-VIS characterization of electrodes: Ex-situ UV-VIS measurements were carried out using LAMBDA 950 (PerkinElmer) with 3 M ZnSO_4 as a blank solution reference in wavelength range of 200-800 nm. TQD cathodes in charged and discharged state were harvested from disassembled batteries in an argon-filled glovebox and submerged in 3 M ZnSO_4 solution for 2 days.

In-situ UV-VIS measurements: In-situ UV-VIS measurements were carried out using LAMBDA 950 (PerkinElmer) with 3 M ZnSO_4 as a blank solution reference in wavelength range of 200-800 nm. In-situ UV-VIS electrochemical cell was constructed from quartz UV-VIS cuvette with zinc strip as anode and TQD electrode slurry pressed on stainless steel mesh as cathode. Platinum wire protruding through the rubber septum was used to connect the zinc anode and cathode mesh to the potentiostat/galvanostat. Before the start of the measurements the solutions were sparged through the rubber septum with argon gas to ensure oxygen-free environment. Afterwards the system was subjected to the galvanostatic cycling at 100 mA g^{-1} in 3 M ZnSO_4 electrolyte in the voltage range of 0.25 V – 1.5 V with simultaneous recording of the UV-VIS spectra in 20 min intervals.

Computational calculations: Density functional theory (DFT) computations were carried out using the B3LYP hybrid density functional with 6-31G* basis set as implemented in Spartan'14 program.

Table S1: Comparison of theoretical and measured reversible capacity in Zn-battery for different positive electrode materials: pyrazines, quinones and nitriles.

Cathode Material	Electrolyte	Theoretical capacity (mAhg ⁻¹ , number of exchanged electrons)	Reversible capacity (mAhg ⁻¹ , Ag ⁻¹)	Reference
 <p>HATNQ</p>	3 M ZnSO ₄	515, 12 e ⁻	482.5, 0.2	[6]
 <p>TAPQ</p>	1 M ZnSO ₄	515, 6 e ⁻	443, 0.05	[7]
 <p>BPD</p>	2 M ZnSO ₄	412, 4 e ⁻	429, 0.05	[8]
 <p>HATN</p>	2 M ZnSO ₄	418, 6e ⁻	370, 0.1	[9]
 <p>HATN-3CN</p>	2 M ZnSO ₄	350, 6e ⁻	320, 0.05	[10]
 <p>DTT</p>	2 M ZnSO ₄	282, 4e ⁻	210.9, 0.05	[11]
 <p>PT</p>	2 M ZnSO ₄	317, 4 e ⁻	220, 0.08	[12]
 <p>PTO</p>	2 M ZnSO ₄	409, 4e ⁻	336, 0.02	[13]

Cathode Material	Electrolyte	Theoretical capacity (mAhg ⁻¹ , number of exchanged electrons)	Reversible capacity (mAhg ⁻¹ , Ag ⁻¹)	Reference
 PQ-Δ	3 M Zn(CF ₃ SO ₃) ₂	260, 6e ⁻	203, 0.03	[14]
 C4Q	3 M Zn(CF ₃ SO ₃) ₂	446, 8e ⁻	335, 0.02	[15]
 TABQ	2 M ZnSO ₄	319, 2e ⁻	203, 0.1	[16]
 TCNAQ	2 M ZnSO ₄	176, 2e ⁻	169, 0.02	[17]
 TCBQ	1 M ZnSO ₄	355, 4e ⁻	369, 0.2	[18]
 TQD	4 M ZnSO ₄	669, 12 e ⁻	503, 0.1	THIS WORK

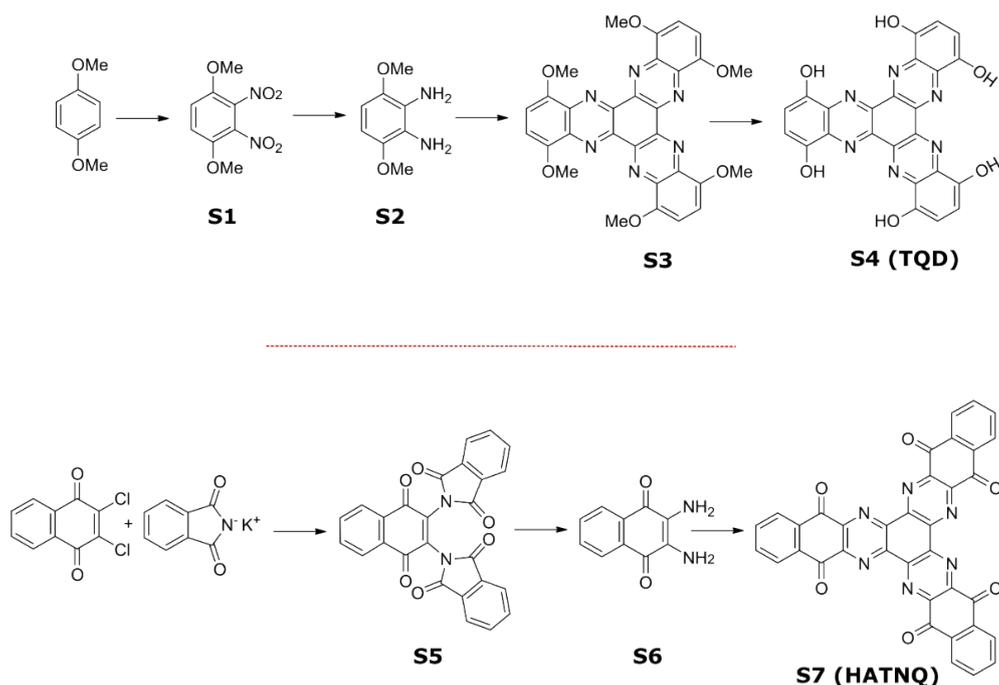


Fig. S1: Synthesis scheme of TQD (top) and HATNQ (bottom).

Synthesis of 1,4-dimethoxy-2,3-dinitrobenzene (S1): The compound was synthesized as previously reported.² Ground 1,4-dimethoxybenzene (18.5 g, 133.9 mmol) was slowly added in portions to 62 wt. % HNO₃ (185 mL) cooled using ice bath. The mixture was left to stir for 1 h in ice bath and for another 1 h at room temperature, upon which it was heated at 100 °C for an additional 1 h. During heating evolution of brown nitrous oxides has been observed. After cooling to room temperature the mixture was filtered and washed with water. Obtained crude product was recrystallized twice from acetic acid to afford final product in the form of yellow crystals in 89 % yield (93 % reported). Safety & hazards: 62 wt. % HNO₃ is considered almost concentrated (68%) nitric acid. It is very strong acid (pK_a= -1.4) and strong oxidizer dissolving most metals, even half precious metals as Cu and Ag. Due to strong oxidizing power, nitric acid reacts with many organic materials violently or even explosively. In contact with skin it causes chemical burns.

¹H NMR (CDCl₃, 600 MHz, δ, ppm): δ 7.21 (s, 2H), 3.94 (s, 6H)

Synthesis of 2,3-diamino-1,4-dimethoxy-benzene (S2): The compound was synthesized using slightly modified literature procedure.³ 1,4-Dimethoxy-2,3-dinitrobenzene (15.0 g, 65.7 mmol) was slowly added to a stirred mixture of granular tin (45.3 g, 381.3 mmol) in 36 wt. % HCl (180 mL). After the addition the mixture was heated at reflux for 2 h. Upon cooling to room temperature the resulting white crystalline solid was filtered. The solid was dissolved in water and the solution made alkaline using 4 M NaOH. Afterwards the solution was extracted using chloroform and filtered through short silica plug. Removal of the solvent under reduced pressure afforded final product in the form of off-white crystals in 78 % yield (95 % reported). Safety & hazards: 4 M NaOH is very strong base that can readily decompose proteins and lipids in living tissue, causing chemical burns and is very dangerous upon contact with eyes.

¹H NMR (DMSO- *d*₆, 600 MHz, δ, ppm): δ 6.15 (s, 2H), 4.10 (s, 4H, -NH₂), 3.68 (s, 6H, -OCH₃)

¹³C NMR (DMSO-*d*₆, 150 MHz, δ, ppm): δ 142.2, 124.0, 99.4, 55.8

Synthesis of 1,4,7,10,13,16-hexamethoxydiquinoxalino[2,3-*a*:2',3'-*c*]phenazine (S3): A mixture of 2,3-diamino-1,4-dimethoxy-benzene (1000 mg, 5.95 mmol) and hexaketocyclohexane octahydrate (599 mg, 1.92 mmol) was added to deoxygenated glacial acetic acid (35 mL). The mixture was heated at 120 °C for 16 h. Upon cooling to room temperature the resulting solid was filtered and washed with ethanol. The filtrate was subjected to evaporation under reduced pressure and the resulting solid heated at 100 °C in 30 wt. % HNO₃ (10 mL) for 2 h. Resulting solid and filtered solid were combined and dried under reduced pressure at 80 °C overnight affording final product in the form of red-orange powder in 92 % yield.

¹H NMR (DMSO- *d*₆, 600 MHz, δ, ppm): δ 7.43 (s, 6H), 4.14 (s, 18H, -OCH₃)

¹³C NMR (DMSO- *d*₆, 150 MHz, δ, ppm): δ 149.3, 142.9, 135.3, 110.9, 56.4

Mass spectrum (ESI, m/z): found [M+H]⁺ 565

Synthesis of diquinoxalino[2,3-*a*:2',3'-*c*]phenazine-1,4,7,10,13,16-hexaol (TQD) (S4): 1 M BBr₃ in DCM (3.7 ml, 3.72 mmol) was dropwise added to a solution of 1,4,7,10,13,16-hexamethoxydiquinoxalino[2,3-*a*:2',3'-*c*]phenazine (300 mg, 0.53 mmol) in anhydrous DCM (15 mL) at -78 °C under inert atmosphere. The mixture was left to warm to room temperature and stirred overnight. Afterwards the reaction was quenched with dropwise addition of methanol (5 mL) at -78 °C. Resulting solid was filtered, washed with ethanol and additionally purified using 24 h Soxhlet extraction with methanol. Obtained product was dried under reduced pressure at 80 °C affording TQD in the form of dark red powder in 90 % yield. Safety & hazards: BBr₃ is very strong lewis acid and volatile. It reacts violently with water and alcohol. Full protection is needed when dealing with this hazardous substance.

¹H NMR (DMSO- *d*₆, 600 MHz, δ, ppm): δ 9.79 (s, 6H, -OH), 7.32 (s, 6H)

¹³C NMR (DMSO- *d*₆, 150 MHz, δ, ppm): δ 146.44, 142.49, 133.62, 113.64

Mass spectrum (MALDI, m/z): found [M+H]⁺ 481 (Fig. S2)

TGA measurements of TQD are presented in Fig. S4 and Fig. S5.

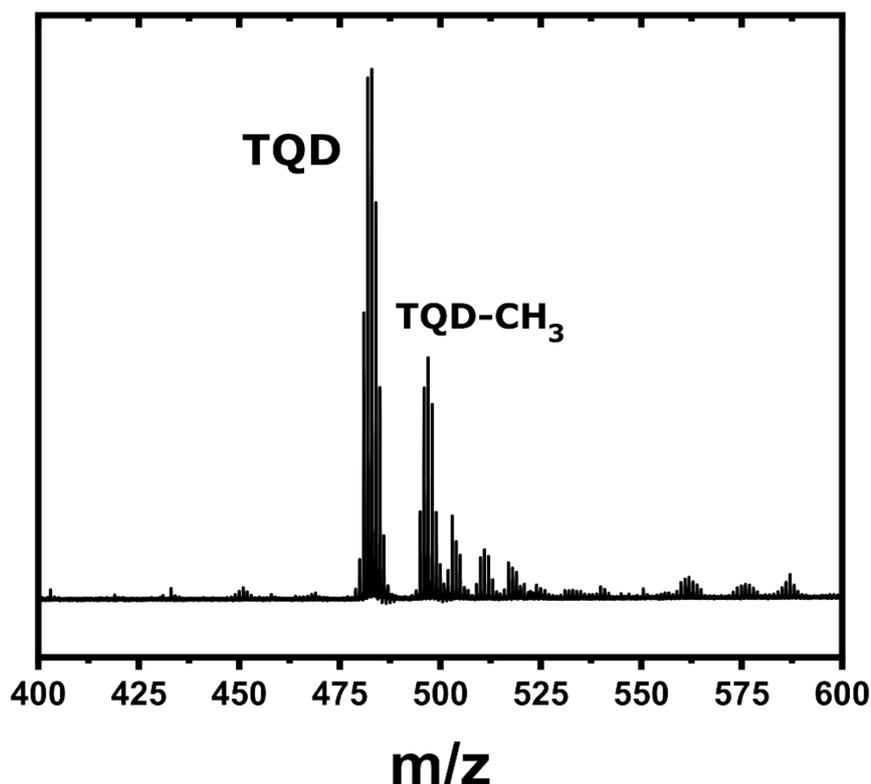


Fig. S2: MALDI-TOF MS spectrum of TQD.

Synthesis of 2,3-diphthalimido-p-naphthoquinone (S5): The compound was synthesized as previously reported.⁴ A mixture of potassium phthalimide (17.1 g, 92.5 mmol) and 2,3-dichloro-p-naphthoquinone (5.0 g, 22.0 mmol) was heated at reflux for 12 h under inert atmosphere. Upon cooling to room temperature the solid was filtered and washed with water and ethanol. Obtained product was dried under reduced pressure overnight to afford the final product in the form of yellow powder in 93 % yield.

¹H NMR (DMSO- *d*₆, 600 MHz, δ , ppm): δ overlapping peaks 8.20-7.92 (m, 12H)

Synthesis of 2,3-diamino-p-naphthoquinone (S6): The compound was synthesized using slightly modified literature procedure.⁴ 2,3-Diphthalimido-p-naphthoquinone (5.0 g, 11.2 mmol) was ground and dispersed in water (330 mL). Afterwards 80 wt. % N₂H₂ (35.7 mL, 909.2 mmol) was slowly added to the mixture and heated at 60 °C for 6 h. Upon cooling to room temperature the product was filtered and washed with water, ethanol and acetone yielding final product in the form of violet powder in 47 % yield (reported 90 %). Safety & hazards: Hydrazine N₂H₂ is a very dangerous chemical. Hydrazine exposure can cause skin irritation and burning, central nervous system depression, blindness, coma, lung and liver damage and death. It is also carcinogen.

¹H NMR (DMSO- *d*₆, 600 MHz, δ , ppm): δ 7.76 (m, 2H), 7.59 (m, 2H), 5.45 (s, 4H, -NH₂)

¹³C NMR (DMSO- *d*₆, 150 MHz, δ , ppm): δ 178.6, 132.8, 131.3, 127.8, 124.7

Synthesis of hexaazatrinaphthalenequinone (HATNQ) (S7): The compound was synthesized as previously reported.⁵ A mixture of 2,3-diamino-p-naphthoquinone (800 mg, 4.3 mmol) and

hexaketocyclohexane hexahydrate (408 mg, 1.3 mmol) was added to deoxygenated glacial acetic acid (20 mL) and heated at 120 °C for 24 h under inert atmosphere. Afterwards the solid was filtered and washed with hot acetic acid, ethanol, acetone and water and dried under reduced pressure overnight. Obtained product was suspended in 25 wt. % HNO₃ (40 mL) and heated at 100 °C for 3 h. Upon cooling to room temperature the solid was filtered, washed with water and dried at 80 °C under reduced pressure overnight yielding final product in the form of yellow powder in 83 % yield (reported 87 %). Safety & hazards: Nitric acid is a very strong acid (pK_a= -1.4) and strong oxidizer, dissolving most metals. Due to strong oxidizing power, nitric acid reacts with many organic materials violently or even explosively. In contact with skin it causes chemical burns.

¹H NMR (CF₃COOD, 600 MHz, δ, ppm): δ 8.64 (m, 6H), 8.09 (m, 6H)

¹³C NMR (DMSO- d₆, 150 MHz, δ, ppm): δ 183.8, 148.6, 147.5, 139.1, 135.5, 131.1

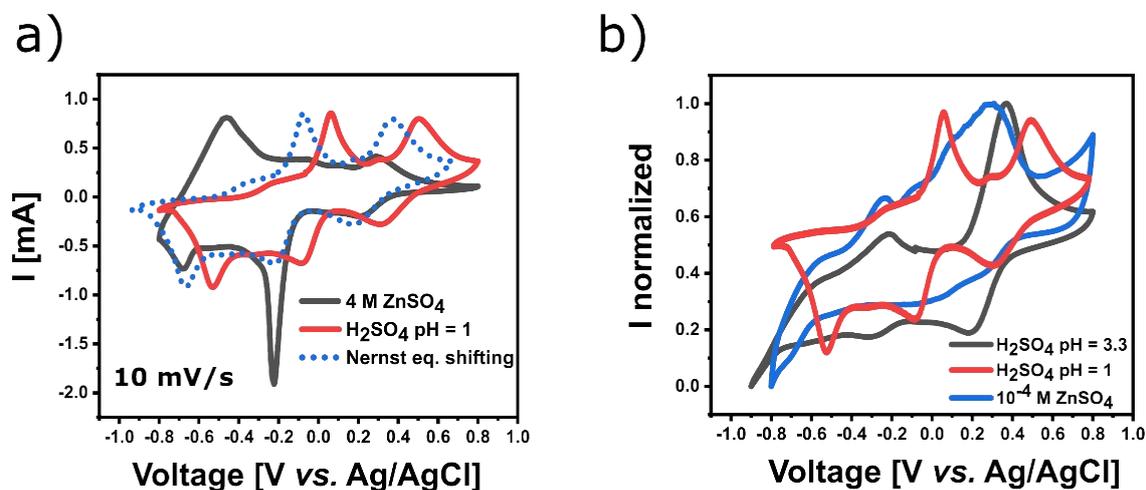


Fig. S3: a) Comparison of CV measurements in 4 M ZnSO₄ (black) and H₂SO₄ (pH = 1) (red), with blue dotted line representing shifting of red curve according to the conditions in H₂SO₄ (pH = 3.3) described by the Nernst equation. b) Comparison of normalized CV curves in H₂SO₄ (pH = 3.3), H₂SO₄ (pH = 1) (red) and 10⁻⁴ M ZnSO₄ (blue).

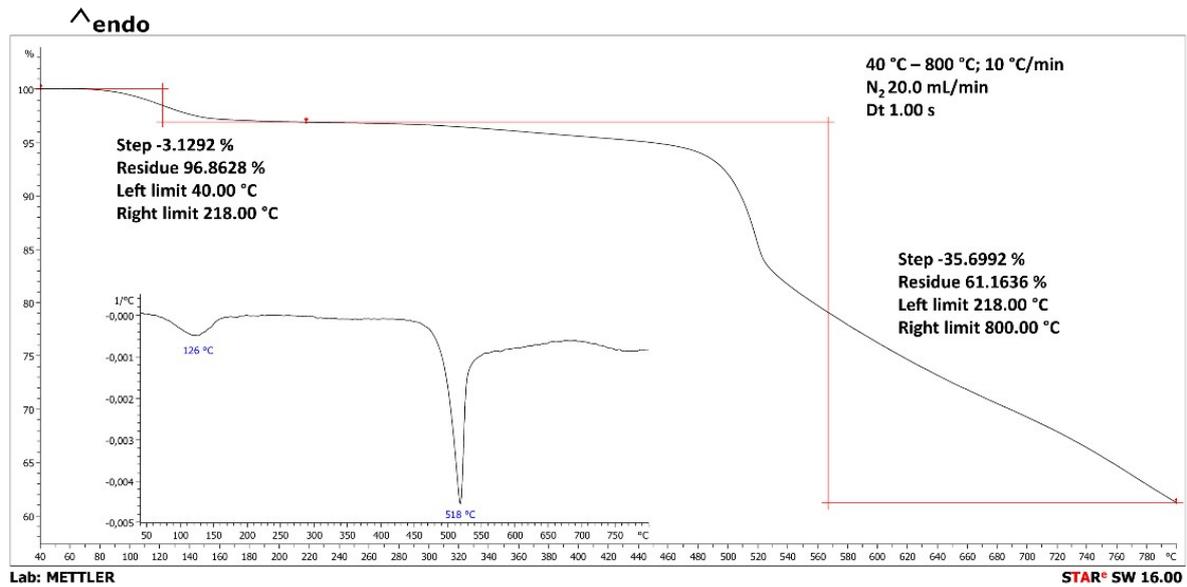


Fig. S4: Thermogravimetric analysis of TQD after drying at 80 °C under reduced pressure.

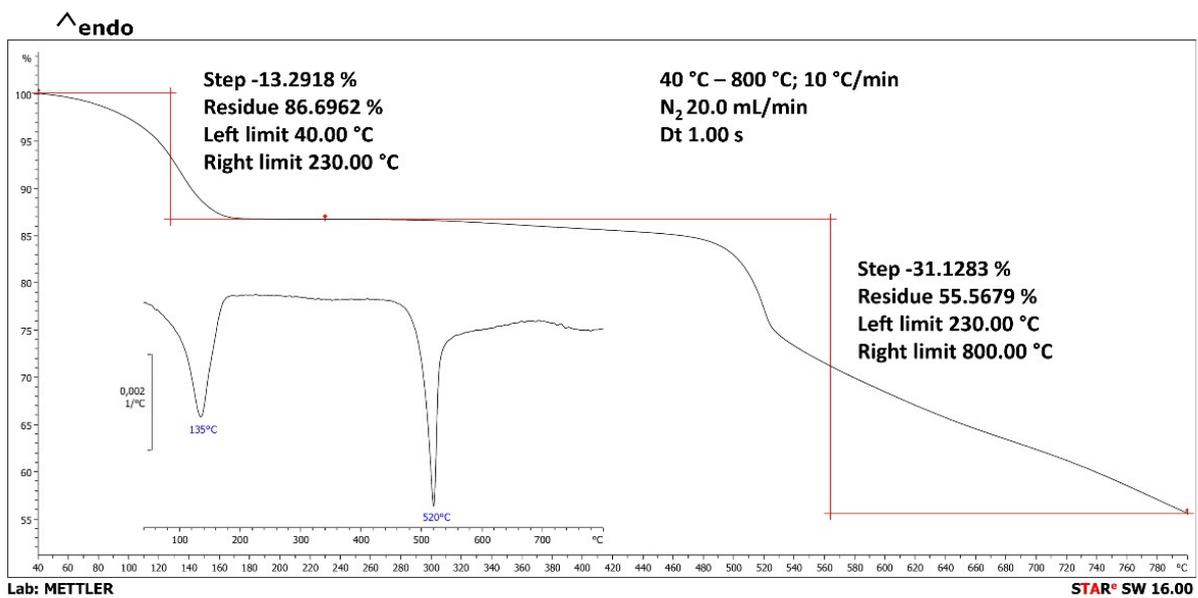
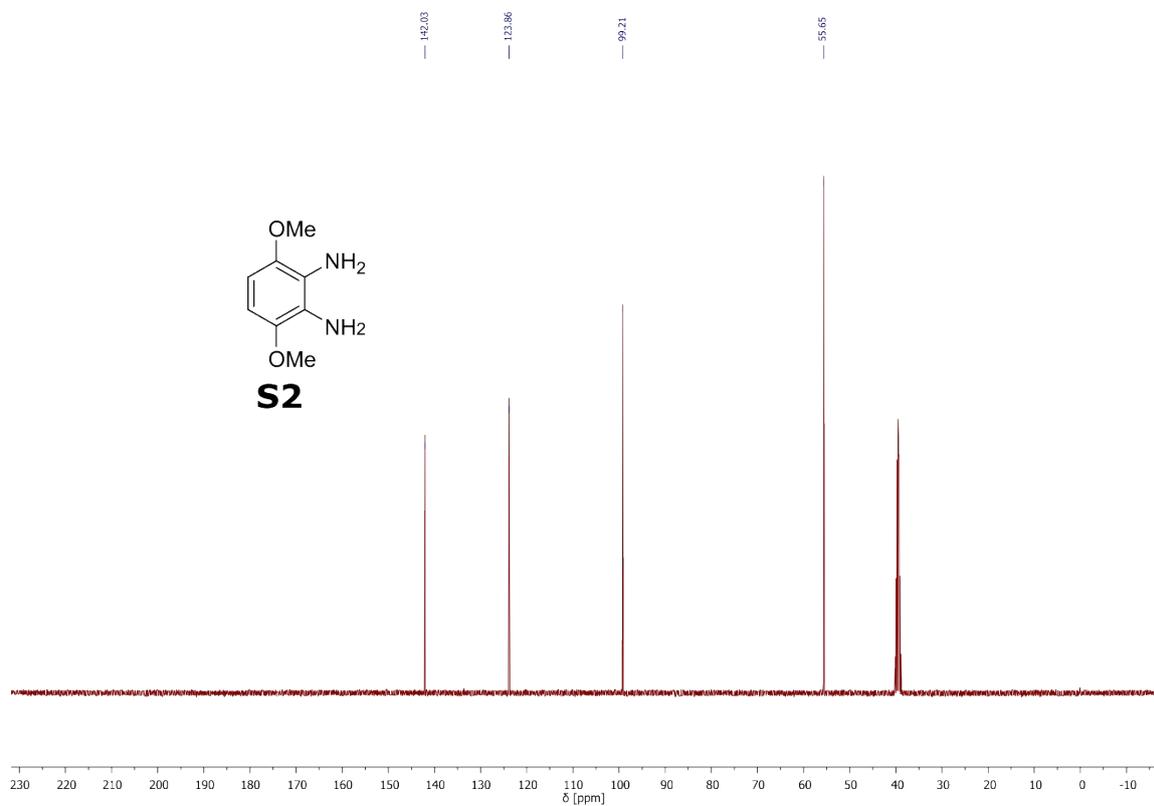
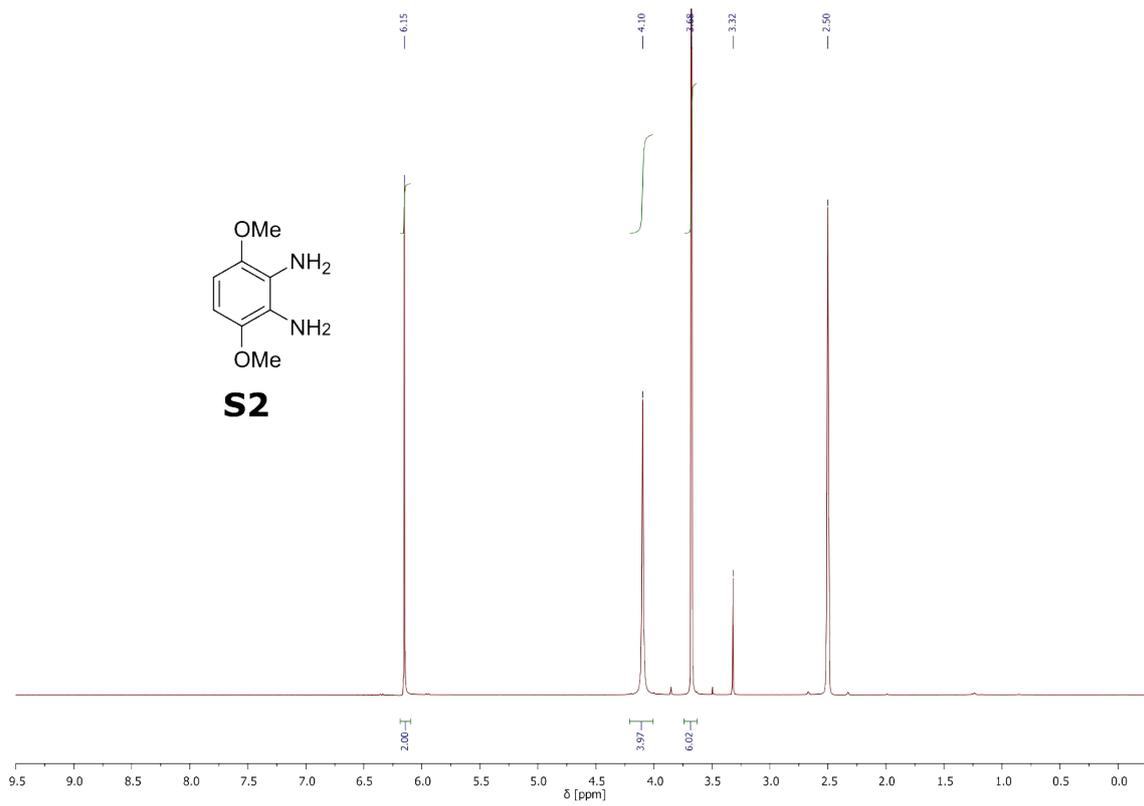
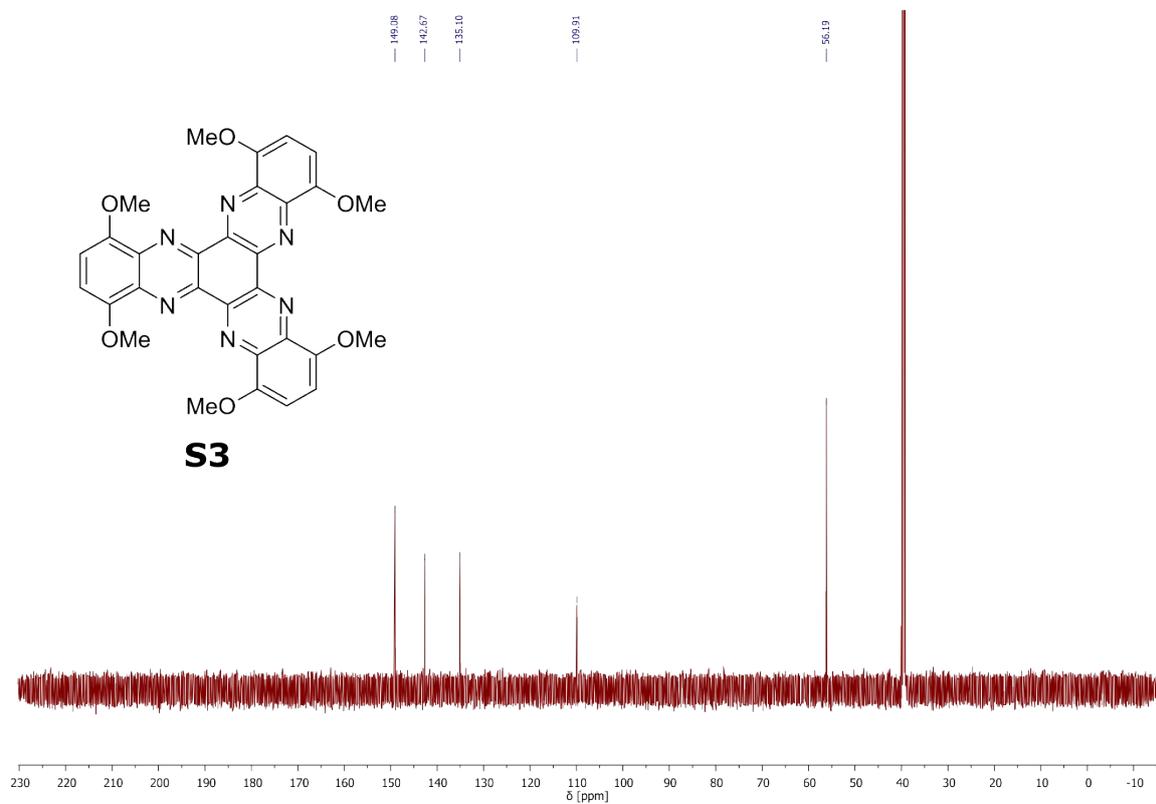
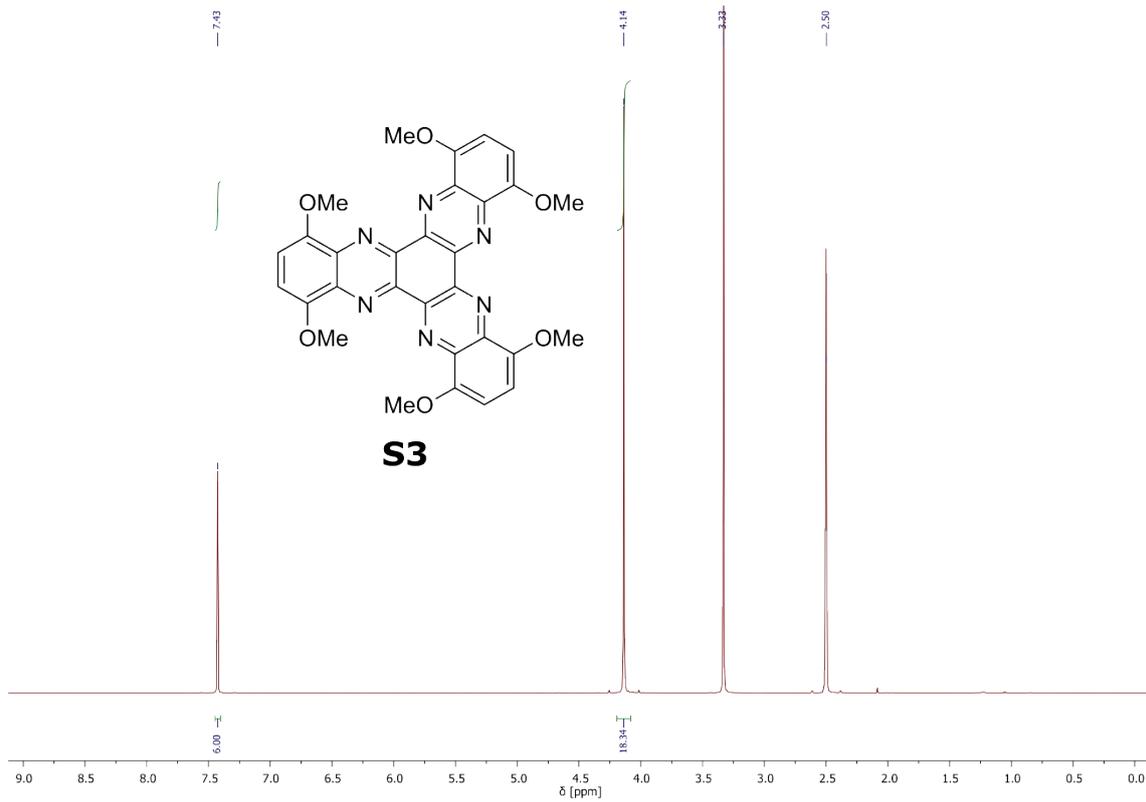
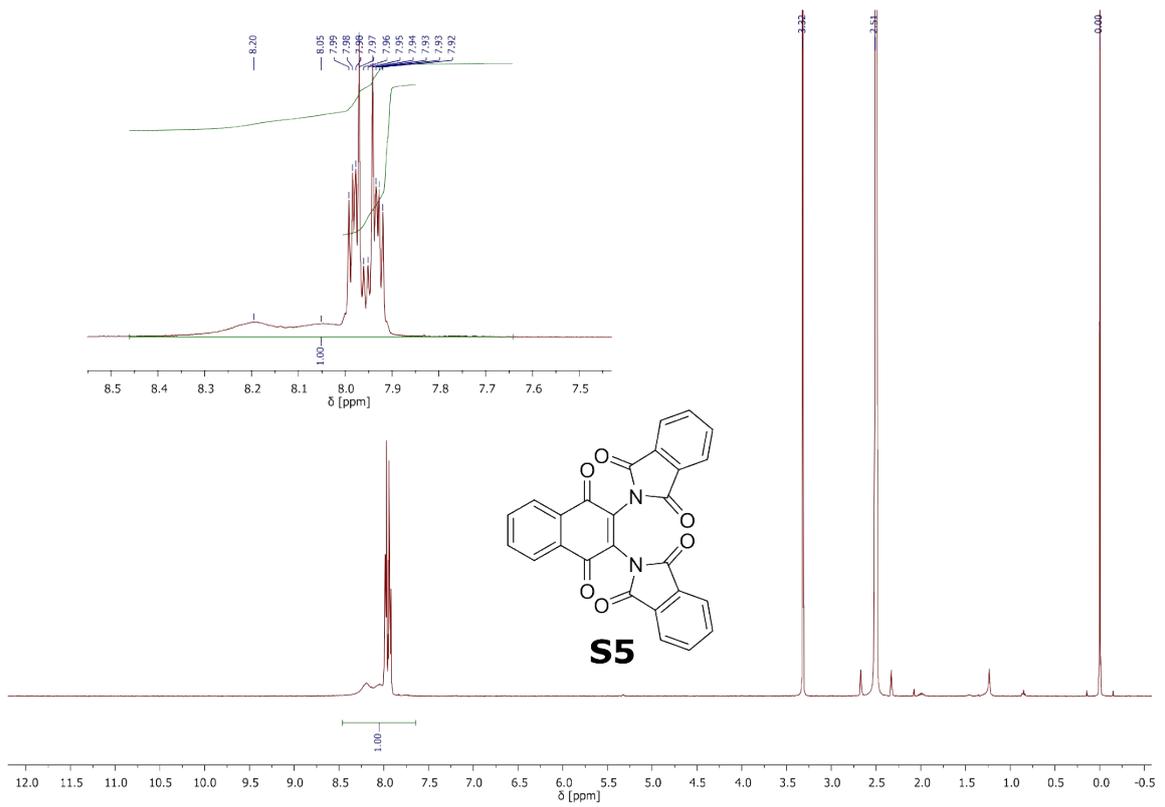
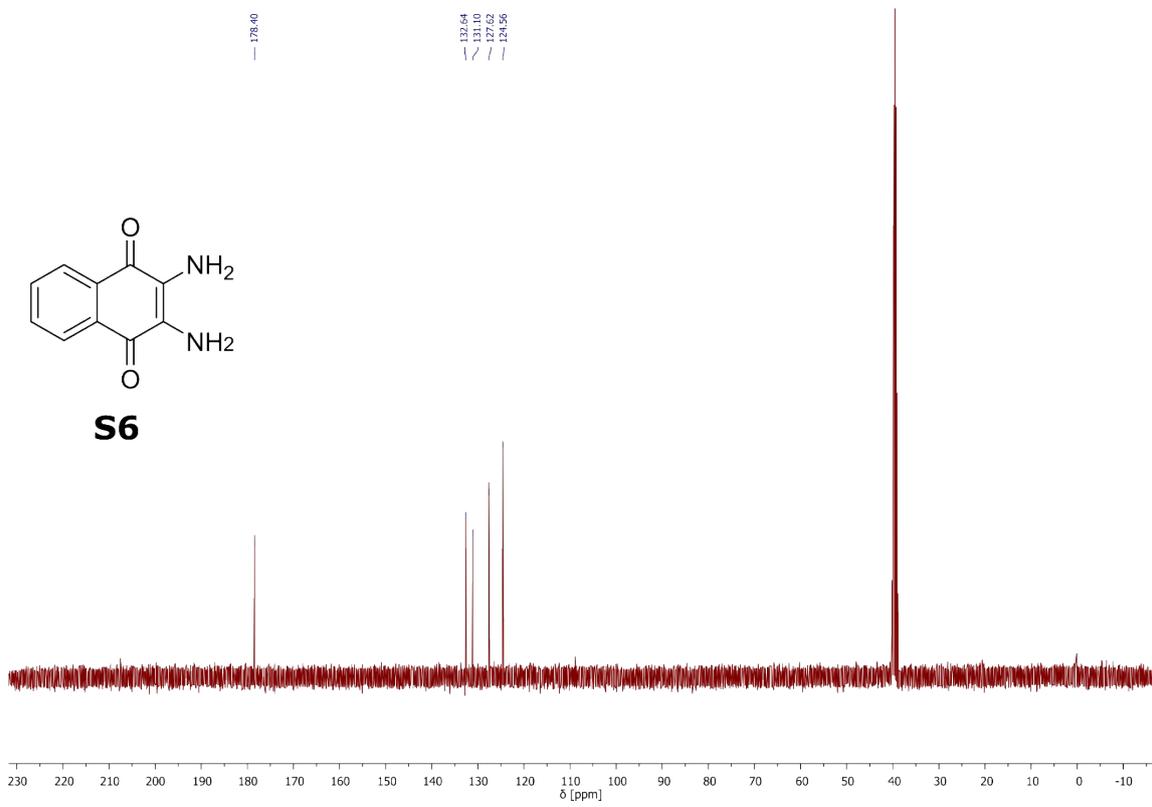
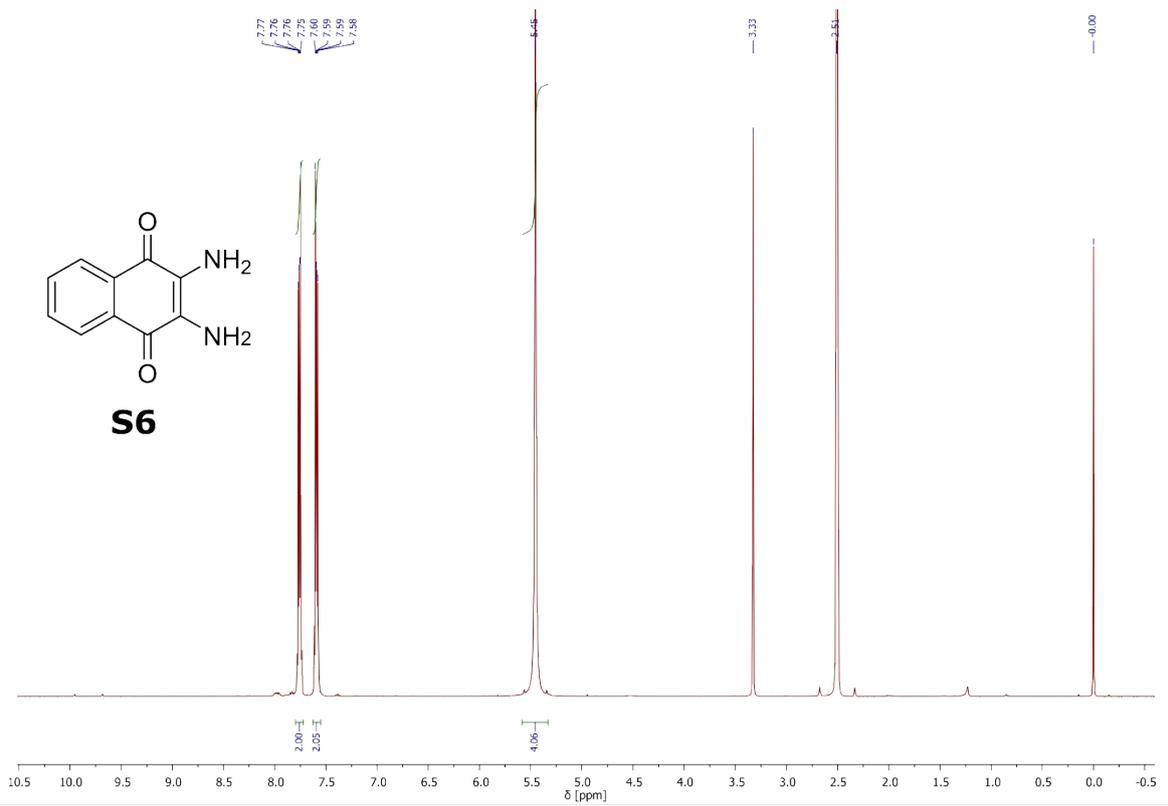


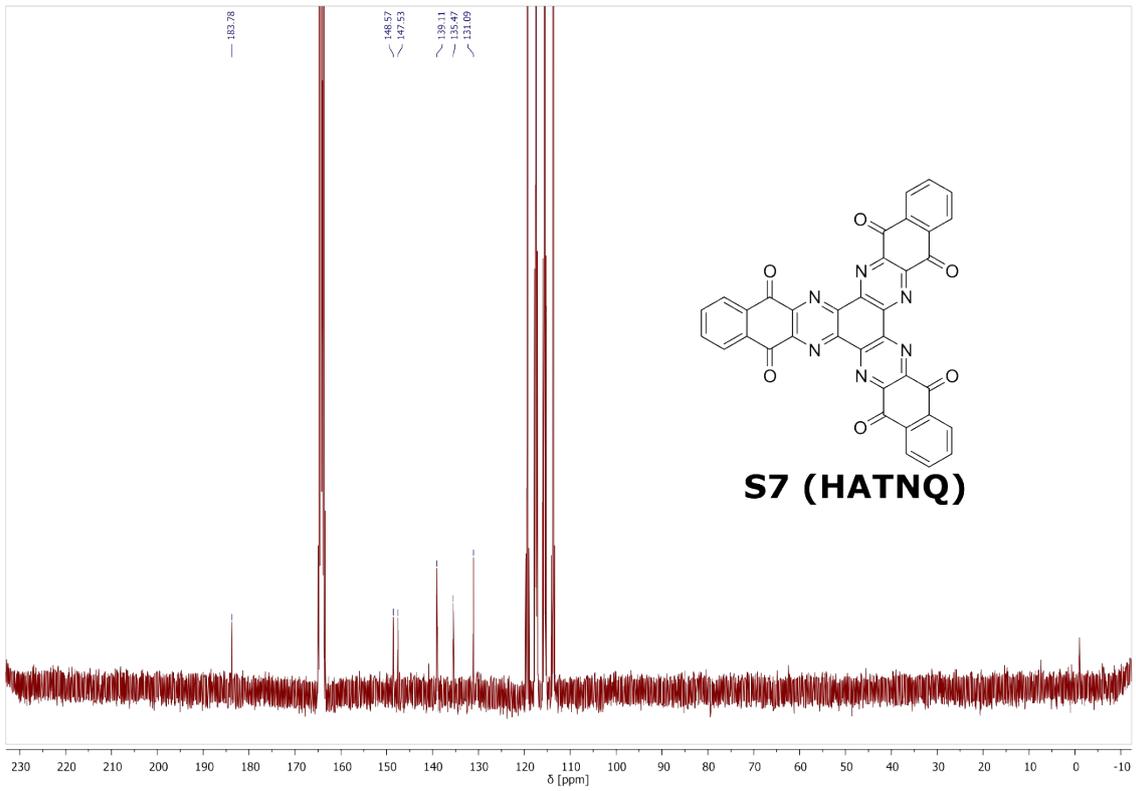
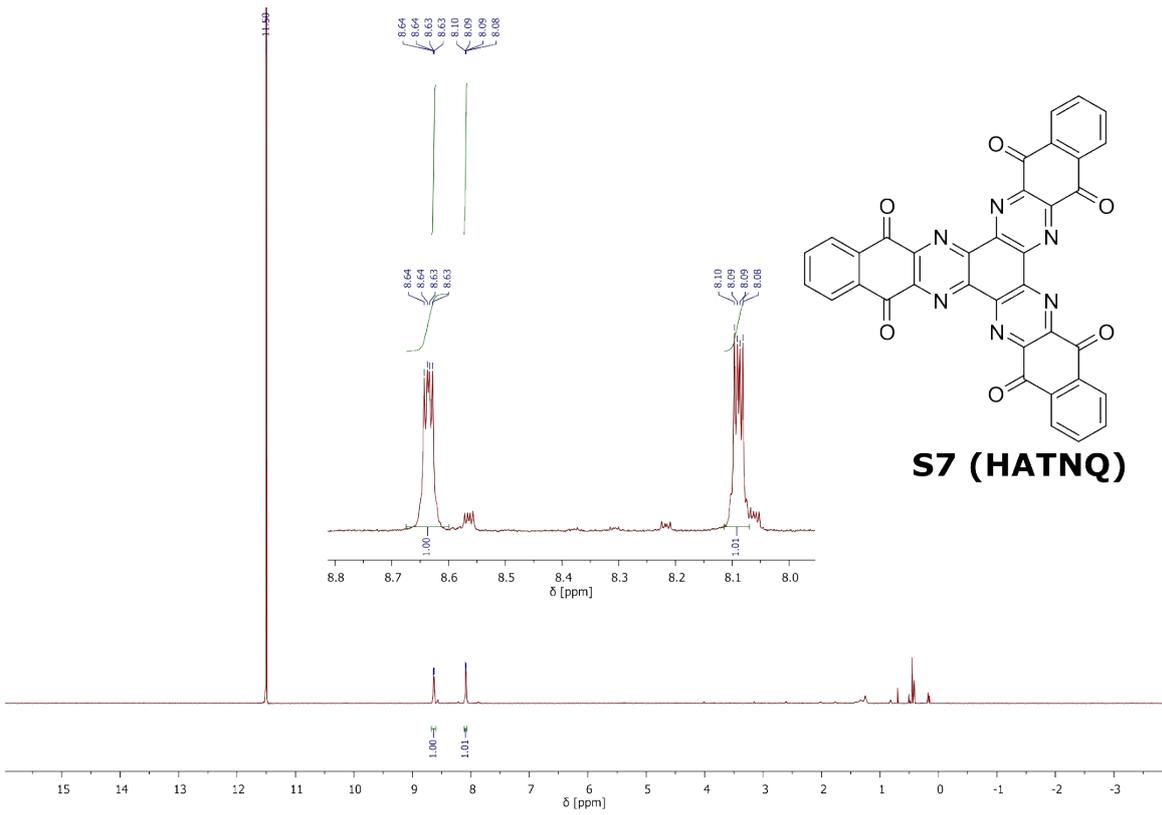
Fig. S5: Thermogravimetric analysis of TQD after three-month storage in air atmosphere. The comparison with dried product (Fig. S4) shows that TQD is highly hygroscopic and care should be taken when preparing the electrodes.











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