Synthesis and electrochromic behavior of a multi-electron redox-active N-heteroheptacenequinone
Synthesis and electrochromic behavior of a multi-electron redox-active N-heteroheptacenequinone†

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We report a novel N-heteroheptacenequinone derivative (C6OAHQC) as a large \(\pi\)-conjugated framework. C6OAHQC shows good electron-accepting behaviour owing to eight electron-deficient imino-N atoms and two carbonyl moieties and excellent solubility in common organic solvents. When a potential between 0 and –2.20 V is applied, C6OAHQC is able to accept four electrons, which is more than fullerene C60 (three electrons) could accept in this voltage range. Moreover, a solution of C6OAHQC and \(\text{Bu}_4\text{NPF}_6\) in CH2Cl2 exhibits a clearly reversible brown-to-green colour change, suggesting that C6OAHQC has potential as an electrochromic material.

Introduction

The introduction of heteroatoms into polycyclic aromatic hydrocarbons (PAHs) has been investigated because novel heteroacenes exhibit different electronic and physical properties to PAH molecules and the molecules in their crystal structures are also packed differently to PAHs.1–7 Among them, we focused on N-heteroacenes in which some of the carbon atoms in PAHs are replaced with nitrogen atoms.8–19 The development of N-heteroacenes based on the oxidised form is necessary in order to expand the series of electron-accepting frameworks. Novel N-heteroacene-based \(\pi\)-conjugated frameworks have been designed and modified by increasing the number of linearly fused rings and by introducing a variety of substituents. The former approach is essential in order to raise HOMO and lower LUMO levels, leading to \(\pi\)-conjugated molecules with low energy band gaps. However, there are some drawbacks associated with this approach, since some N-heteroacenes are unstable in air and UV-vis light and are insoluble in organic solvents.20–25 On the other hand, the introduction of a pyrazine framework comprising two imino-N atoms in the latter approach is a simple method for improving the electron-accepting properties without changing the fundamental planar shape of the \(\pi\)-conjugated framework.11,14 Moreover, both experimental studies and quantum-chemical calculations suggest that the LUMO level is stabilised by increasing the number of imino-N atoms in the \(\pi\)-conjugated framework.24,26,27 However, oxidation from the reduced form to the oxidised form becomes more difficult with the increasing numbers of hydro-N atoms in the framework. To improve the electron-accepting properties, we designed N-heteroacene molecules based on the benzoquinone framework.

Benzoquinone derivatives function as electron acceptors because of their two electron-withdrawing carbonyl groups. Since benzoquinone derivatives behave as organic oxidising agents in organic syntheses and biological systems, the introduction of this framework will effectively improve the electron-accepting properties of the molecule.28–31 A benzoquinone-based N-heteroacene (N-heteroquinone) is composed of both benzoquinone and pyrazine units.32–36 Among them, tetraaza-pentacenequinone (TAPQ) derivatives are products from the oxidation of homofluoridine and are also useful precursors for the preparation of the corresponding N-heteroaazaacenes and trisopropylsilyl-appended derivatives.20,36 Recently, Miao and co-workers reported a simple synthetic route to N-pentacenequinones composed of five linearly fused rings that serve as electron acceptors and \(n\)-type organic semiconductors.32–36 Moreover, the electronic properties and the molecular packing in the crystal state can be tuned by changing the positions of the imino-N atoms in TAPQ. As mentioned above, further modifications are very important for the development of novel electron-accepting functional frameworks based on N-heteroquinone. Herein, we report on the synthesis of an N-heteroheptacenequinone derivative.

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(C6OAHCQ) composed of eight oxidised imino-N atoms (Scheme 1). OAHCQ is very stable in air and UV-vis light in the solid state, and it is very soluble in general organic solvents when appropriate flexible alkoxy-chain substituents are included on its terminal benzene rings. Moreover, the OAHCQ derivative exhibits electrochromic behaviour because of the redox stability arising from its expanded fused-ring structure.

Results and discussion
Molecular design and synthesis
C6OAHCQ, bearing four alkoxy chains, was prepared in high yield through a four-step reaction sequence (Scheme 1). 4,5-Dihexyloxy-1,2-dinitrobenzene (5)37 was treated with N2H4·H2O and Pd/C in EtOH under an Ar atmosphere to give the corresponding reduced dialkoxyphenylene diamine, which was then reacted with diethyl oxalate in dry EtOH to afford pyrazine 4 in 71% yield. Dichloropyrazine 3 was obtained in 91% yield by the reaction of 4 with POCl3 in dimethylaniline (DMA). The treatment of 3 with liquid ammonia in an autoclave for one week afforded diaminopyrazine 2 in quantitative yield; 2 was then reacted with 5,6-dihydroxy-5-cyclohexene-1,2,3,4-tetronedihydrate in acetic acid, followed by NaIO4 and tetrabutylammonium bromide (TBAB) in CH2Cl2 to afford C6OAHCQ in 72% yield.38 The introduction of four flexible alkoxy chains onto the large π-conjugated framework engenders C6OAHCQ with high solubility in common organic solvents, such as CHCl3, CH2Cl2, and EtOAc.

Molecular packing and DFT calculations
A single crystal of C6OAHCQ was grown from a solution of DMSO. As shown in Fig. 1, the single-crystal X-ray analysis of C6OAHCQ(DMSO) reveals that the π-conjugated framework

![Fig. 1](https://example.com/fig1.png)

**Fig. 1**. Crystal structures of C6OAHCQ(DMSO). Dimers A and B are indicated in orange and green, respectively. (a) 1D-Slipped stacking structure of C6OAHCQ molecules along the b axis. Hydrogen atoms and DMSO molecules are omitted for clarity. (b) Dimer structures formed by C6OAHCQ molecules in the 1D slipped stacking structure. Hexyloxy moieties are omitted for clarity. Structures of (c) Dimer A and (d) Dimer B. Hexyloxy moieties and DMSO molecules are omitted for clarity.
adopts an almost planar structure. The structure of C₆OAHCQ shown in Fig. 1a reveals that C₆OAHCQ molecules stack to form a slipped one-dimensional (1D) columnar structure along the b axis; this column is also constructed from two types of dimer structure (Fig. 1b). Dimer A adopts a slipped stack along the short axis of the molecule, as shown in Fig. 1c, while Dimer B is aligned along the long axis of the molecule (Fig. 1d). The shortest distances between stacked molecules are as follows: O(2)⋯C(7) = 3.13(1) Å for Dimer A and C(9)⋯C(14) = 3.29(1) Å for Dimer B. Dimers A and B are alternately stacked along the C₆OAHCQ column, which leads to the formation of the 1D columnar structure shown in Fig. 1a. To further investigate the forces that drive packing within the C₆OAHCQ crystal, the electronic structure of C₆OAHCQ was determined by density functional theory (DFT) calculations at the B3LYP/6-31G* level of theory within the SPARTAN’08 package (Fig. 2a). We used the tetramethoxy-substituted COAHCQ molecule for clarity (Fig. 2a). DFT calculations reveal that COAHCQ accumulates negative charge on the two carbonyl oxygen atoms of its benzoquinone framework and its eight imino-N atoms (Fig. 2b). As a result, the charge is clearly depleted from the aromatic rings substituted by the electron-withdrawing carbonyl and imino-N groups. It should be noted that the observed O(2)⋯C(7) distance in Dimer A is much shorter than the sum of van der Waals radii of C and O (C–O: 3.22 Å),[42,43] which indicates that electrostatic interactions operate between the negatively charged carbonyl groups or imino-N atoms (red colour) and the positively charged rings (blue colour). The shorter intermolecular distances lead to an enhanced transfer integral and more efficient electron-transport behaviour. Therefore, the flexible alkoxy chains at the terminal benzene rings impart significant advantages that improve solubility and molecular arrangements in the crystal state.

Spectroelectrochemical experiments and electrochromic behaviour

The electronic properties of C₆OAHCQ were evaluated by UV-vis absorption spectroscopy in the solution state. The UV-vis absorption spectrum of C₆OAHCQ exhibits its lowest absorption maximum at 500 nm and an absorption edge at 550 nm (Fig. 3a, black solid line); this spectrum is compared to that of TAPQ,[34,35] (Scheme 1, Table 1), an analogue of C₆OAHCQ. TAPQ exhibits an absorption maximum at 356 nm and an absorption onset at 395 nm.[34,35] Hence, C₆OAHCQ exhibits an absorption maximum that is bathochromically shifted by 155 nm compared to that of TAPQ, which suggests that increasing the number of imino-N atoms and expanding the π-conjugated system stabilises the LUMO level of C₆OAHCQ, resulting in a narrower HOMO–LUMO gap compared to that of TAPQ. The experimental result for C₆OAHCQ is in good agreement with that obtained by DFT, in which the LUMO of COAHCQ was found to be mainly located on the carbonyl and imino-N groups of the benzoquinone framework (Fig. 2c), which indicates that the carbonyl and imino-N groups contribute to lowering the energy of the LUMO.

The redox behaviour of C₆OAHCQ was studied by cyclic voltammetry (CV), the results of which are shown in Fig. 3b and S2.[†] The cyclic voltammogram of C₆OAHCQ in CH₂Cl₂ solution containing Bu₄NPF₆ as the electrolyte exhibits reversible two-step reduction waves at the half-wave potentials (E₁/₂) of −0.55 V (1e⁻) and −0.83 V (1e⁻) and two-step reduction waves at −1.67 (1e⁻) and −1.75 V (1e⁻) vs. Fc⁺/Fc. On the other hand, no peak was observed in an anodic potential. The number of electrons transferred from the working electrode to C₆OAHCQ was determined by differential pulse voltammetry (DPV) (Fig. 3b). To determine the electron-accepting moiety involved in the first consecutive two-step reduction, we resorted to DFT calculations (Fig. 2c). The LUMO, LUMO+1, and LUMO+2 orbitals are calculated to clearly reside on the benzoquinone moiety bearing the two carbonyl units, as opposed to the pyrazine moieties with the imino-N atoms (Fig. 2c), which indicates that the first consecutive two-step electron reductions correspond to the formation of radical-anion and dianion species on the benzoquinone moiety, respectively.
C60
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Finally, the optical properties of the C6OAHCQ dianion are
investigated by cyclic voltammetry in a CH2Cl2 solution of
*TAPQ.* C6OAHCQ

Compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>UV-vis absorption/nm</th>
<th>Absorption edge/nm</th>
<th>Redox potential/V vs. Fe/Fe0</th>
<th>E_{LUMO} eV</th>
<th>E_{HOMO} eV</th>
<th>E_{opt} eV</th>
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<tbody>
<tr>
<td>C6OAHCQ</td>
<td>304, 362, 478, 500</td>
<td>550</td>
<td>−0.55</td>
<td>−4.25b</td>
<td>−6.50b</td>
<td>2.25b</td>
</tr>
<tr>
<td>TAPQ</td>
<td>300, 356</td>
<td>395</td>
<td>−1.02</td>
<td>−3.78</td>
<td>−6.92</td>
<td>3.15</td>
</tr>
<tr>
<td>C60d</td>
<td>—</td>
<td>—</td>
<td>−0.98</td>
<td>−1.87</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

*Measured by cyclic voltammetry in a CH2Cl2 solution of Bu4NPF6 (0.10 M). b E_{LUMO} is calculated from the first half-wave potential: E_{LUMO} = −E^1_{1/2} − 4.8 eV. E_{HOMO} is calculated by the following equation: E_{HOMO} = E_{LUMO} − E_{opt} . E_{opt} is estimated from the edge position of the UV-vis absorption spectrum in a CH2Cl2 solution: E_{opt} = 1240/\lambda_{max}. c TAPQ data are taken from ref. 34 and 35. d C60 data are taken from ref. 47 and 48. Half-wave potentials are shown in the region of 0 to −2.2 V.*

Successive two-step two-electron transfers at E^1_{1/2} and E^2_{1/2} are ascribed to two-electron reductions of the two aromatic tetraaza frameworks to form tetranion species. It should be noted that a large gap is observed between the second and the third reduction potentials (ΔE = E^2_{1/2} − E^1_{1/2}), which suggests that the two-electron reduction on the benzoquinone framework delocalizes the negative charge on the molecular entity because the cross-conjugated electronic structure of neutral C6OAHCQ transforms into the fully conjugated structure (Fig. 3c).⁴⁴,⁴⁵ Moreover, since the obtained C6OAHCQ dianion exhibits onsite coulombic repulsion, more negative potential is required in order to accept more electrons for further reduction (Fig. S7†).⁴⁶

We next compared the electrochemical properties and energy levels of C6OAHCQ with those of the TAPQ analogue (Table 1). The LUMO level of C6OAHCQ is much lower than that of TAPQ, in spite of the four electron-donating alkoxy chains. This result suggests that the substitution of two electron-deficient imino-N atoms into the TAPQ framework is more influential than alkoxy-chain substitution. Moreover, the narrower HOMO−LUMO gap (E_g) for C6OAHCQ compared to that of TAPQ is attributed to the expanded π-conjugated system. It should be noted that C6OAHCQ can accept four electrons in the 0 to −2.20 V potential window, which is more than fullerene C60 could accept, a representative electron acceptor that can only accept three electrons.⁴⁷,⁴⁸

C6OAHCQ was subjected to spectroelectrochemical experiments in the same electrolyte used for CV (Fig. 3a). A new absorption band centred at 650 nm gradually appears as the potential is made more negative (i.e., from 0 to −1.20 V), and it is accompanied by a decrease in the absorption band at 500 nm and an increase and a bathochromic shift of the 370 nm band. The presence of two isosbestic points at 463 nm and 524 nm was observed, indicating that an electrochemical reaction, from the neutral to the dianionic species, occurs without decomposition or the generation of by-products. The colour of the C6OAHCQ solution gradually changes from brown to green as the applied potential changes from 0 to −1.20 V; the green colour is assigned to the C6OAHCQ dianion. The initial UV−vis absorption spectrum of neutral C6OAHCQ can be recovered by returning the potential to 0 V in Fig. S3 and S4.† On the other hand, poor colour reversibility is revealed at applied voltages of −0.70 and −2.20 V, which is
attributable to the lower stabilities of the monoanionic and tetraanionic species generated at those potentials, respectively (Fig. S5 and S6†). The good electrochromic reversibility exhibited by C6OAHQCQ between 0 V and −1.20 V strongly indicates that the generated dianionic species is more stable than the monoanionic or tetraanionic species.

Conclusions
We synthesised a novel electron-accepting N-heteroheptacenequinone OAHQCQ derivative as a large π-conjugated framework. The OAHQCQ derivative was composed of eight electron-deficient imino-N atoms and an electron-accepting benzoquinone. The OAHQCQ derivative exhibited reversible four-step, four-electron reduction waves in its CV trace. The number of electrons accepted by C6OAHQCQ in the 0 to −2.20 V window is more than that accepted by electron-accepting fullerene C60. In addition, the OAHQCQ derivative shows electrochromism at negative voltages. Moreover, the HOMO and LUMO energy levels (E_HOMO and E_LUMO) of C6OAHQCQ can be approximately determined from the E_1/2 potentials in its cyclic voltammogram and the absorption edge of its UV-vis spectrum. The E_LUMO of C6OAHQCQ, at −4.29 eV, is comparable to that of the well-known methyl [6,6]-phenyl-C60-butryl electron acceptor (PCBM, −3.8 eV),49 which is expected to function as an n-type semiconductor. The introduction of tetraaza units and the electron-withdrawing benzoquinone is a novel strategy for the design of high-electron-affinity molecules.

Experimental section
General methods
1H and 13C NMR spectra were recorded on a JEOL JNM-LA300 spectrometer. 1H and 13C NMR chemical shifts are referenced against tetramethylsilane (δ = 0.00) and CDCl3 (δ = 77.00), respectively. FT-IR spectra were recorded with a HORIBA FRESExACT-II spectrometer. Matrix-assisted laser desorption/ionisation time-of-flight (MALDI-TOF) mass spectra were collected on a JEOL JMS-S3000 instrument using dithranol as the matrix. Elemental analyses were carried out with a PerkinElmer 2400 Series II CHNS/O analyser. Cyclic voltammetry was carried out in a 0.10 M solution of Bu4NPF6 in CH2Cl2 with glassy-carbon working, Pt counter, and Ag/AgCl reference electrodes using an ALS CHI 600E electrochemical analyser. UV-vis absorption spectra were acquired with a JASCO V-550 UV-vis spectrometer. Spectroelectrochemical studies were conducted in a three-electrode quartz cell with the same electrolyte system as UV using the potentialstat together with a JASCO V-550 spectrometer and a PerkinElmer Lambda35 UV-vis spectrometer. During applying the voltage, Ar gas was flowed into the solution to diffuse the compounds in the cell entirely. Density functional theory (DFT) calculations were carried out using the Wavefunction SPARTAN’08 suite of programs. Ground-state geometries were optimised at the B3LYP/6-31G* level of theory.39–41 Single-crystal X-ray diffraction data for C6OAHQCQ (DMSO) were collected at 173 K on a Bruker Apex II Ultra X-ray diffractometer using Mo Kα radiation (λ = 0.71073 Å). Intensity data were processed using APEX2 software, and the structures were solved using direct methods and refined using SHELXL-2014 (full-matrix least-squares on F2) in APEX2.50,51 The carbon atoms in parts of one hexyloxy group (part A: C38A, C39A, and C40A; part B: C38B, C39B, and C40B) were disordered over two positions. The anisotropic displacement parameters of these atoms were restrained. Crystallographic data files are available from the Cambridge Crystallographic Data Centre (CCDC no. 1871181†).

Synthesis of C6OAHQCQ
2,3-Dihydroxy-6,7-dihexyloxyquinoxaline (4). Hydrazine monohydrate (30.0 g, 60.0 mmol) was added dropwise to a suspension of 4,5-dihydroxy-1,2-dinitrobenzene (5)37 (3.68 g, 10.0 mmol) and Pd/C (1.0 g) in dry EtOH (100 mL) at 0 °C, after which the mixture was refluxed for 24 h. The reaction mixture was filtered through Celite under Ar. After the evaporation of the solvent, the crude product and diethyl oxalate (40.0 mL, large excess) in dry EtOH (50 mL) were refluxed overnight. The reaction solution was cooled to 0 °C, which produced a white precipitate. After filtration, the product was purified by recrystallization, from CHCl3/CH3OH and dried under vacuum to afford 4 as a white solid (2.58 g, 71.2%). MALDI-TOF-MS (dithanol): m/z = 363 ([C6ODHQ]+). Anal. Calcd for [C6ODHQ (H2O)]: C, 64.67%, H, 8.41%, N, 7.54%; Found: C, 65.22%, H, 8.98%, N, 7.49%. 1H NMR (DMSO-δ6/ppm): δ 11.66 (s, 2H), 6.71 (s, 2H), 3.87 (t, J = 4.8 Hz, 4H), 1.67 (quint, J = 4.8 Hz, 4H), 1.41 (m, 4H), 1.29 (m, 8H), 0.88 (t, J = 4.8 Hz, 6H). 13C NMR (DMSO-δ6/ppm): δ 154.91, 144.90, 118.96, 101.43, 68.96, 31.02, 28.74, 25.22, 22.13, 13.91. IR (ATR/cm−1): 3488, 2931, 1670, 1527, 1465, 1396, 1276, 1166, 1147, 1015, 915, 750, 640, 587, 530.

2,3-Dichloro-6,7-dihexyloxyquinoxaline (3). A solution of 4 (3.00 g, 14.0 mmol), POCl3 (13.0 g, 140.0 mmol), and dimethylamine (DMA, 3.5 g, 28.0 mmol) was heated at 125 °C for 24 h. After cooling to r.t., the precipitate was collected by filtration, recrystallized from CHCl3/MeOH, and dried under vacuum to afford 3 as a white solid (3.17 g, 91.0%). MALDI-TOF-MS (dithanol): m/z = 399 ([C6ODCQ]+). Anal. Calcd for [C6ODCQ]: C, 59.26%, H, 3.73%, N, 17.28%; Found: C, 59.21%, H, 3.62%, N, 17.15%. 1H NMR (CDCl3/ppm): δ 7.23 (s, 2H), 4.15 (t, J = 4.8 Hz, 4H), 1.90 (quint, J = 4.8 Hz, 4H), 1.51 (m, 4H), 1.36 (m, 8H), 0.92 (t, J = 4.8 Hz, 6H). 13C NMR (CDCl3/ppm): δ 153.60, 142.14, 137.85, 106.10, 69.32, 31.47, 28.62, 25.61, 22.54, 13.98. IR (ATR/cm−1): 3060, 1558, 1535, 1471, 1305, 1201, 1157, 1111, 1000, 887, 750, 538.

2,3-Diamino-6,7-dihexyloxyquinoxaline (2). A suspension of 3 (1.00 g, 2.50 mmol) in liquid ammonia (15.0 mL) was heated at 130 °C for one week in an autoclave. After the evaporation of NH3, the product was recrystallized from CHCl3/MeOH and dried under vacuum to afford 2 as a yellow solid (0.90 g, quan-titative). MALDI-TOF-MS (dithanol): m/z = 360 ([C6ODAQ]).
Anal. Caled for [C_{6}O_{4}AHCQ](MeOH)_{0.5}: C, 65.39%, H, 9.10%, O, 14.88%; Found: C, 65.33%, H, 9.23%, O, 15.13%. 1H NMR (CDCl3/ppm): δ 7.01 (s, 2H), 4.48 (br, 4H), 4.06 (t, J = 8.8 Hz, 4H), 1.85 (quint, J = 8.8 Hz, 4H), 1.51 (m, 4H), 1.36 (m, 8H), 0.91 (t, J = 8.8 Hz, 6H). 13C NMR (CDCl3/ppm): δ 149.00, 143.05, 132.75, 106.81, 69.02, 31.58, 28.97, 25.69, 22.59, 14.01. IR (ATR/cm−1): 2904, 2854, 1697, 1617, 1556, 1454, 1417, 1384, 1238, 1168, 1087, 838.

2,3-Tetrahydroxy-5,6,9,14,15,17,18-octaazahapteacene-7,16-quinone (C_{6}O_{4}AHCQ). A suspension of 2 (0.31 g, 15.0 mmol) and 5,6-dihydroxy-5-cyclohexene-1,2,3,4-tetrone dihydrate (0.15 g, 7.50 mmol) in dry AcOH (40 mL) was refluxed overnight under Ar. The crude reaction product was collected by filtration, washed with AcOH, H_{2}O, hexane, and EtOH, and dried under vacuum to obtain a green solid. A solution of NaIO_{4} (1.60 g, 75.0 mmol) and tetrabutylammonium bromide (0.024 g, 0.75 mmol) in H_{2}O (30 mL) was added to a solution of the green solid in dry CH_{2}Cl_{2} (30 mL) and stirred for 3 h at room temperature. The reaction mixture was extracted three times with CHCl_{3}, and the combined organic layers were washed with H_{2}O and brine, and dried over anhydrous Na_{2}SO_{4}. After filtration and evaporation of the solvent, the product was purified by crystallization from CHCl_{3}/MeOH, and dried under vacuum to a yellow solid (0.44 g, 72.1%). MALDI-TOF-MS (C_{6}O_{4}AHCQ) m/z = 820 ([C_{6}O_{4}AHCQ]^{4H+}). Anal. Calcd for [C_{6}O_{4}AHCQ]^{0.5}: C, 65.39%, H, 9.10%, O, 14.88%; Found: C, 65.33%, H, 9.23%, O, 15.14%. 1H NMR (CDCl3/ppm): δ 7.01 (s, 2H), 4.35 (t, J = 8.8 Hz, 4H), 1.51 (m, 4H), 1.36 (m, 8H), 0.91 (t, J = 8.8 Hz, 6H). 13C NMR (CDCl3/ppm): δ 149.00, 143.05, 132.75, 106.81, 69.02, 31.58, 28.97, 25.69, 22.59, 14.01.

Notes and references