

Supporting Information

Synthesis, physical properties and ion recognition of a novel larger heteroacene with eleven linearly-fused rings and two different types of heteroatoms

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Figure S10 Cyclic voltammogram of the ferrocene standard in NMP solution at the scan rate of 100 mV S^{-1} .

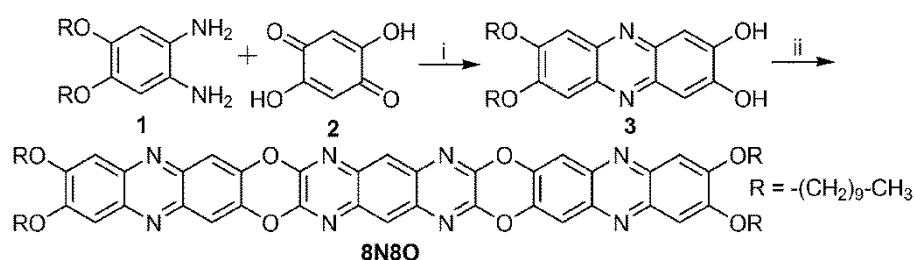
Experimental

Materials

10% Pd/C and hydrazine monohydrate were purchased from Alfa Aesar. 2,5-Dihydroxy-1,4-benzoquinone was purchased from Sigma-Aldrich. 1,2-Bis(decyloxy)-4,5-diaminobenzene was synthesized according to a reported procedure. Other chemicals and solvents were used directly without further purification.

Cyclic voltammetry measurements were carried out on a CHI 604E electrochemical analyzer. Glassy carbon (diameter: 1.6 mm; area 0.02 cm²) was used as a working electrode, platinum wires were used as counter electrode and reference electrode, respectively. Fc⁺/Fc was used as an internal standard. Potentials were recorded versus Fc⁺/Fc in a solution of anhydrous *N*-methyl-2-pyrrolidone (NMP) with 0.1M tetrabutylammonium hexafluorophosphate (TBAPF₆) as a supporting electrolyte at a scan rate of 100 mV s⁻¹.

Experimental Section



Scheme 1. Synthetic route of : (i) CH₃CH₂OH, N₂, reflux, 62%; (ii) 10 equiv CsF, 0.33 equiv 2,3,7,8-tetrachloro-1,4,6,9-tetrazaanthracene, DMF, 80 °C, 10 %.

Synthesis of 7,8-bis(decyloxy)phenazine-2,3-diol (3)

A mixture of 1,2-bis(decyloxy)-4,5-diaminobenzene 1 (840 mg, 2 mmol) and 2,5-dihydroxy-1,4-benzoquinone 2 (308 mg, 2.2 mmol) in refluxing ethanol (v = 100 ml) was stirred 24 h under N₂ atmosphere. The mixture was allowed to cool down to ambient temperature and the obtained precipitate was isolated by filtration and washed with cold methanol and small ethyl ether affording 3 as a red solid (650 mg, 1.24 mmol, yield: 62 %)

^1H NMR (300 MHz, $\text{DMSO-}d_6$) δ 10.48 (s, 2H), 7.29 (s, 2H), 7.22 (s, 2H), 4.16 (t, J = 6.0 Hz, 4H), 1.89 – 1.69 (m, 4H), 1.59 – 1.42 (m, 4H), 1.42 – 1.16 (m, 24H), 0.84 (t, J = 5.6 Hz, 6H).

Synthesis of 2,3,15,16-tetradecyloxy-5,8,10,13,18,21,23,26-octaaza-7,11,20,24-tetraoxohendecacene (8N8O)

A mixture of 7,8-bis(decyloxy)phenazine-2,3-diol **3** (1.57 g, 3 mmol) and CsF (4.53 g, 30 mmol) in 50 mL anhydrous *N,N*-dimethylformamide (DMF) was stirred 2 h under N_2 atmosphere. 2,3,7,8-tetrachloro-1,4,6,9-tetraazaanthracene **4** (320 mg, 1 mmol) was added in 50 mL of anhydrous DMF and the mixture was heated at 80 °C for 3 days. The mixture was allowed to cool down to ambient temperature before pouring into deionised water (500 mL). The obtained precipitate was isolated by filtration and washed with cold ethanol, tetrahydrofuran and small ethyl ether affording compound **8N8O** (122 mg, 0.1 mmol, yield: 10 %).

^1H NMR (400 MHz, TFA) δ 8.71 (s, 2H), 8.25 (s, 4H), 7.67 (s, 4H), 4.46 (t, 8H), 2.04 (m, 8H), 1.64 (m, 8H), 1.39 (m, 48H), 0.86 (t, 12H).

^{13}C NMR (400 MHz, TFA) δ 160.69, 144.73, 144.28, 138.84, 137.76, 132.73, 123.81, 100.07, 71.82, 31.43, 29.03, 28.99, 28.82, 28.66, 27.85, 25.40, 21.98, 12.25

HR-MS (ESI, the isotopomer with one ^{15}N atom): Calcd for $\text{C}_{74}\text{H}_{95}\text{O}_8\text{N}_8$: 1224.7243; Found: 1224.7603.

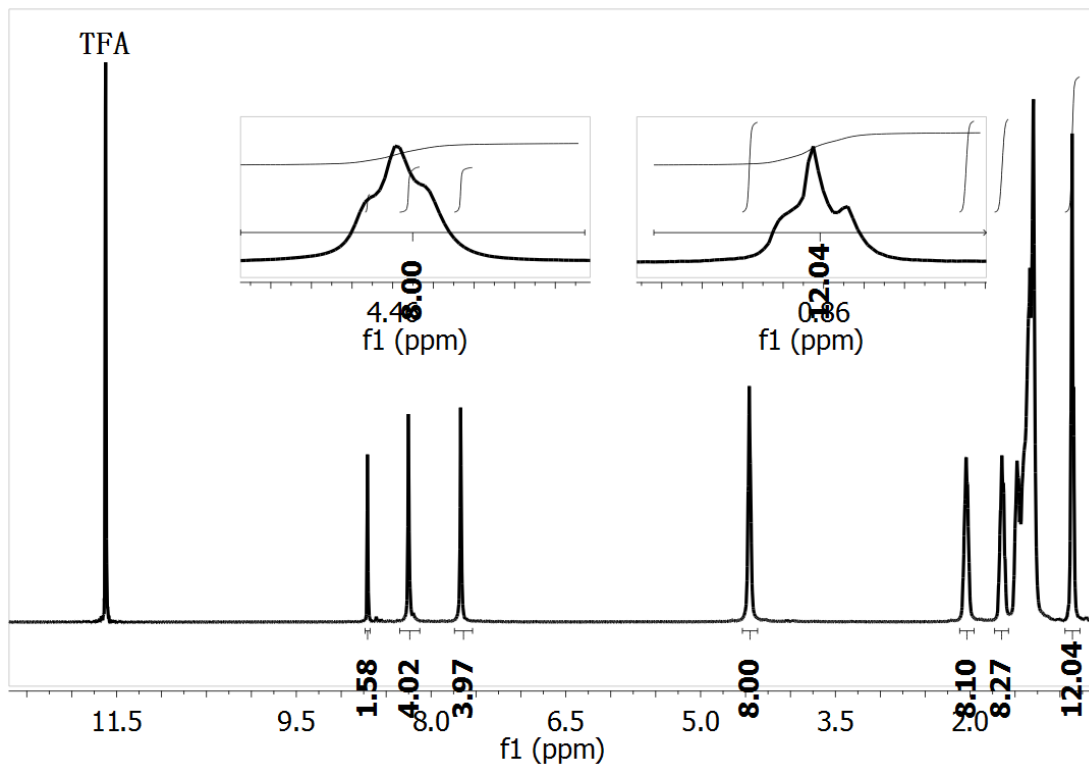


Figure S1 ^1H NMR spectrum of compound **8N8O** in CF_3COOD (TFA).

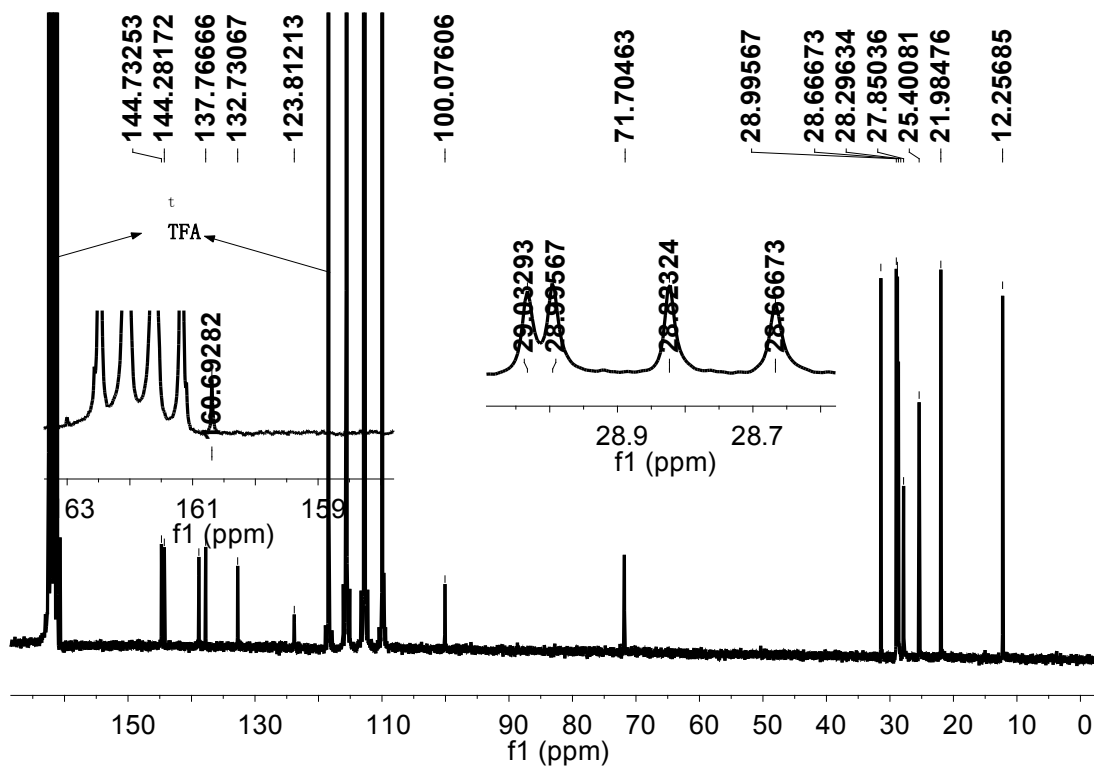


Figure S2 ^{13}C NMR spectrum of compound **8N8O** in TFA.

Single Mass Analysis

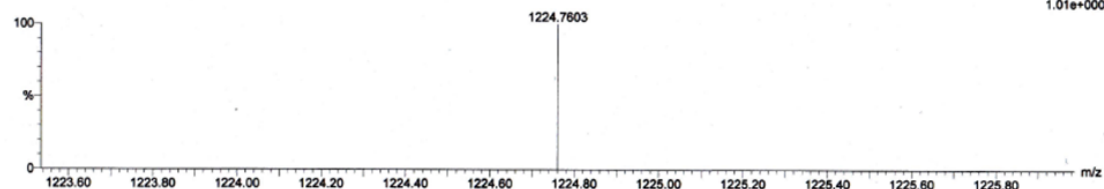
Tolerance = 500.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

1 formula(e) evaluated with 1 results within limits (up to 3 closest results for each mass)

Elements Used:

C: 73-74 H: 94-95 O: 7-8 14N: 1-8 15N: 1-1

C74H95N8O8
G-6 1 (0.045)1: TOF MS ES+
1.01e+000

| Mass | Calc. Mass | mDa | PPM | DBE | i-FIT | i-FIT (Norm) | Formula |
|-----------|------------|------|------|------|-------|--------------|---------------------|
| 1224.7603 | 1224.7243 | 36.0 | 29.4 | 31.5 | 11.1 | 0.0 | C74 H95 O8 14N7 15N |

Figure S3 HRMS spectrum of compound 8N8O.

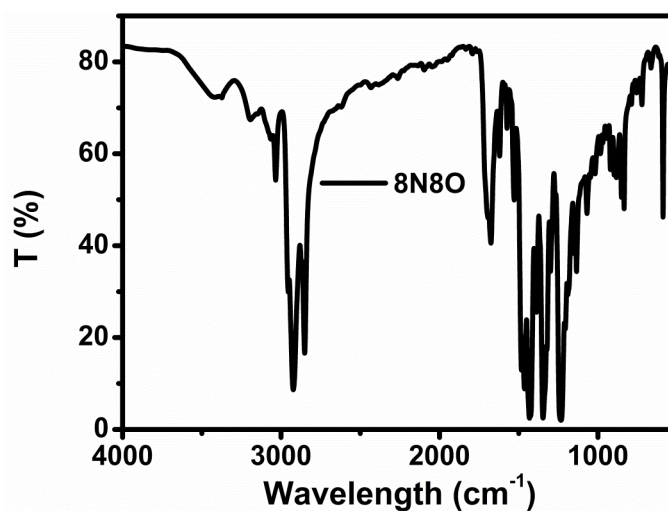
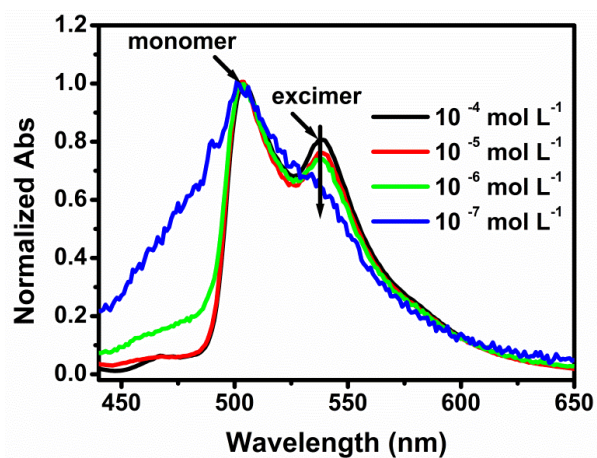


Figure S4 IR spectrum of compound 8N8O.

Figure S5 Normalized emission of compound 8N8O in NMP solution with different concentration ($\lambda_{\text{ex}} = 427 \text{ nm}$).

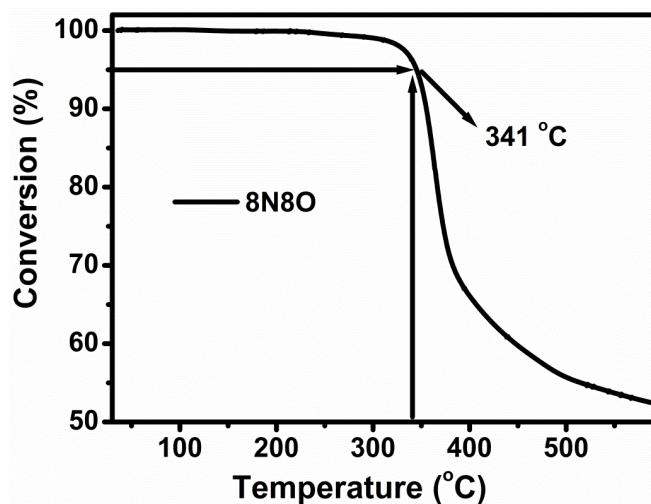


Figure S6 TGA curve of compound **8N8O** with a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$ under N_2 atmosphere.

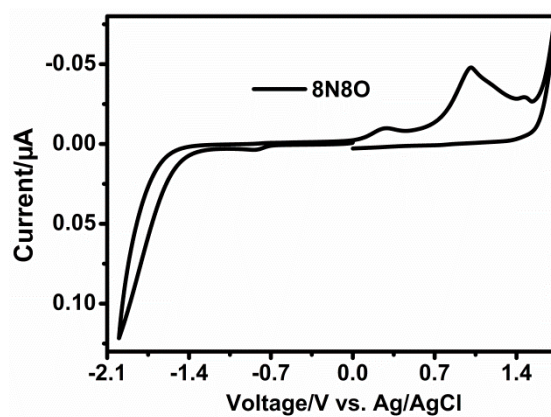


Figure S7 Cyclic voltammogram of compound **8N8O** a 0.1M solution of TBAPF_6 in NMP solution. The scan rate: 100 mV s^{-1} .

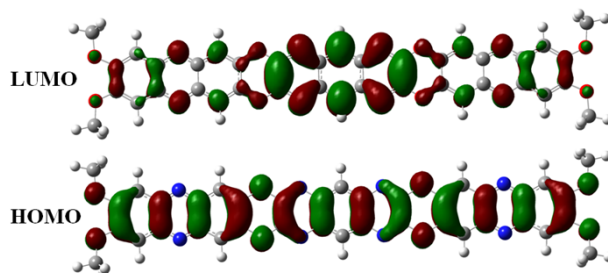


Figure S8 DFT molecular simulation results: HOMO and LUMO of compound **8N8O**.

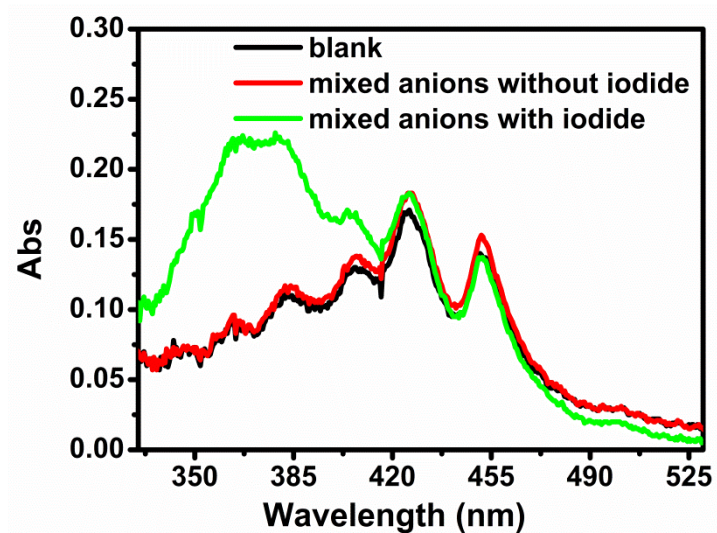


Figure S9 UV/Vis absorption spectra of NMP solutions of compound **8N8O** (10^{-5} mol L $^{-1}$) in the absence (blank) and presence of mixed anions without or with iodide (2×10^{-4} mol L $^{-1}$).

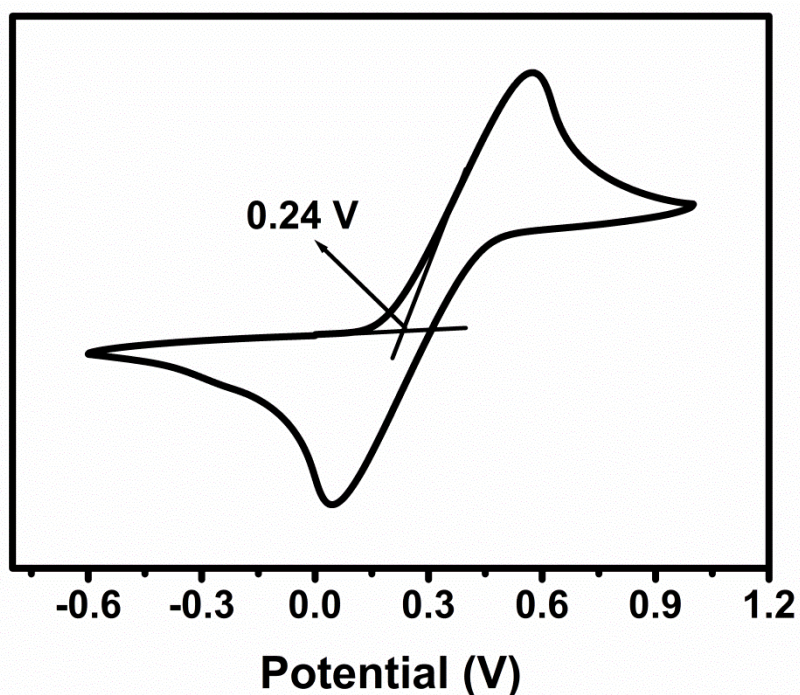


Figure S10 Cyclic voltammogram of the ferrocene standard in NMP solution at the scan rate of 100 mV S $^{-1}$.