RSC Advances

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A novel larger stable heteroacene, **8N8O,** has been synthesized and demonstrated to act as an efficient anion sensor for iodide over a wide range of other anions.
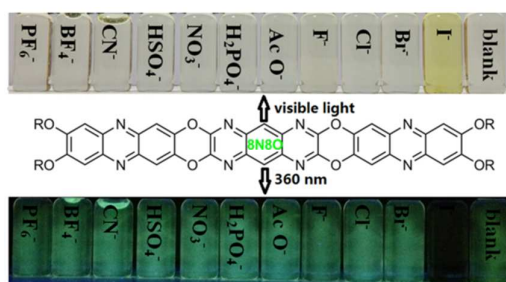
Communication

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

Pei-Yang Gu,[a] Junkuo Gao,[b] Chengyuan Wang,[a] and Qichun Zhang*[a,c]

A novel larger heteroacene, 2,3,15,16-tetradecyloxy-5,8,10,13,18,21,23,26-octaaza-7,11,20,24-tetraoxohendecacene (8N8O) with two different types of heteroatoms (O and N)
10 **and eleven linearly fused rings, has been successfully synthesized and can identify iodide over other anions.**

In past decades, *N*-oligoheteroacenes have attracted a lot of researchers' interests because of their potential applications in n-type organic field effect transistors (OFETs), phototransistor,
15 sensors, organic-light emitting diodes (OLEDs), memory devices, and solar cells.[1] Comparing with their parent systems (plain oligoacenes),[2] *N*-substituted oligoheteroacenes could have more opportunities for scientists to tune their physical properties because the highest occupied molecular orbital (HOMO) - lowest
20 unoccupied molecular orbital (LUMO) gap and HOMO/LUMO positions of oligoheteroacenes strongly depend on the type/position/number of heteroatoms (e.g N, O, P, B, S). Although significant advancements have been witnessed in synthesis, theoretical study, and applications of short
25 heteroacenes, large heteroacenes (n ≥ 7) is still rare.[3] Moreover, introducing two or more types of heteroatoms into the backbone of larger oligoacenes should be more interesting because (1) it should be more challenge to approach them; (2) some unexpected properties could be obtained through carefully selecting the
30 heteroatoms in backbone and tuning their positions; and (3) different heteroatoms could offer more chances to stabilize larger oligoheteroacenes. In this research, we are more interested in large heteroacenes with both oxygen and nitrogen atoms in its backbone due to their relatively-short synthetic steps, reasonable
35 stability, and possible device applications. However, until now, only a few dioxaacenes derivatives (up to six-fused rings) were reported.[4] The curiosity of properties and synthetic possibility strongly encourages us to challenge large heteroacenes (n>7) with two or more different heteroatoms (N/O).
40 Since *N*-substituted heteroacenes are an electron-deficient system, they could act as π acid for anion recognition through anion-π interaction.[5] Actually, non-covalent binding between electron deficient aromatic rings and anions, namely anion-π interaction, has been causing a lot of interests in theoretical and
45 experimental investigations because anion-π interactions play a crucial role in many chemical and biological processes and could have potential applications in medicine and environment.

Recently, we have demonstrated that azaacenes can selectively recognize F^- or $H_2PO_4^-$.[6] Continuing on this direction, we have
50 synthesized a novel heteroacene with eleven linearly-fused rings (2,3,15,16-tetradecyloxy-5,8,10,13,18,21,23,26-octaaza-7,11,20,24-tetraoxohendecacene, abbreviated as **8N8O**), which is the longest one now, and found that it can selectively recognize iodide. Among the range of biologically important anions, iodide
55 plays a vital role in many biological activities such as thyroid gland function.[7] Although a number of studies, which focus on chromogenic and fluorescent recognition of anions, have been published concerning other anions such as fluoride, there are few reports available for the estimation of iodide.[8]
60 In this report, we reported a novel large hetroacene **8N8O**, which have two different types of heteroatoms (O and N) and eleven linear fused-rings. Compound **8N8O** can optically detect the presence of iodide over a wide range of other anions (F^-, Cl^-, Br^-, PF_6^-, HSO_4^-, NO_3^-, BF_4^-, CH_3COO^- (AcO$^-$), CN^-, and $H_2PO_4^-$)
65 based on the "heavy-atom" effect.[9]

The synthetic procedure for the preparation of compound **8N8O** is depicted in **Scheme 1**. The target compound was synthesized in two-step steps: First, the commercially available 2,5-dihydroxy-1,4-benzoquinone was reacted smoothly with 1,2-bis(decyloxy)-
70 4,5-diaminobenzene (0.9 equiv) in alcohol to afford 7,8-bis(decyloxy)phenazine-2,3-diol with yield 62%. Then the as-prepared product was condensed with 2,3,7,8-tetrachloro-1,4,6,9-tetraazaanthracene (0.33 equiv) using cesium fluoride (10 equiv) as the base to yield compound **8N8O** with yield 10%. Compound
75 **8N8O** was fully characterized using ^1H and ^{13}C NMR spectroscopy, infrared spectroscopy (IR) and mass spectrometry.
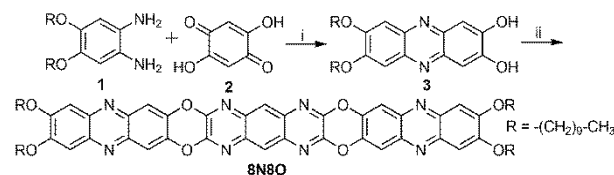
Scheme 1. Synthetic route of : (i) CH_3CH_2OH, N_2, reflux, 62%; (ii) 10 equiv CsF, 0.33 equiv 2,3,7,8-tetrachloro-1,4,6,9-tetraazaanthracene,
80 DMF, 80 °C, 10%.

Figure 1 shows the normalized optical absorption and emission spectra of compound **8N8O**. The absorption spectrum of compound **8N8O** exhibits three prominent bands at 290 nm, 424 nm, and 451 nm in *N*-methyl-2-pyrrolidone (NMP) solution.

which can be ascribed to a localized aromatic π-π* transition, phenazine core,[10] and excimer absorption, respectively. However, there are still three small peaks at shorter wavelength region and the level-off tails at the longer wavelength region, which can be ascribed to the scattering effect of the dye nanoparticles due to the poor solubility of compound **8N8O** in NMP solution. When the solvent was changed from NMP to good solvent trifluoroacetic acid (TFA), there are only two peaks at 283 nm and 492 nm and no level-off tails at the longer wavelength region. TFA dramatically shifts the longer wavelength of compound **8N8O** due to the protonation of N atoms in the framework of compound **8N8O**. Compound **8N8O** emits strong green light at 504 nm and 539 nm in NMP solution. The former is monomer emission and the later is excimer emission, which is confirmed through the emission spectra of compound **8N8O** in NMP solution with different concentration. Normalized emission spectra of compound **8N8O** in NMP solution with different concentration was shown in **Figure S5**, the PL intensity of excimer was decreased with decreasing the concentration. Compound **8N8O** exhibits good thermal stability, with an onset decomposition temperature of ~341 °C (considering the temperature for 5% weight loss, **Figure S6**).
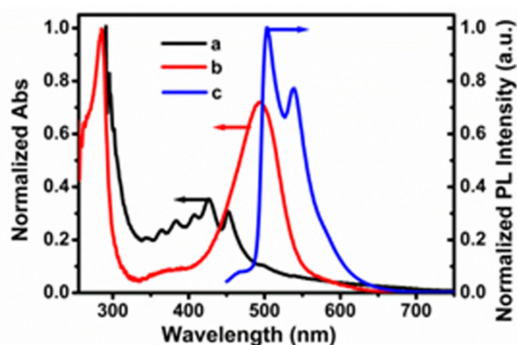

Figure 1 Normalized absorption/emission of compound **8N8O** (a and c in NMP solution, and b in TFA solution, λ_{ex} = 427 nm).

Figure S7 shows the cyclic voltammogram (CV) curve of compound **8N8O** in a 0.1 M solution of tetrabutylammonium hexafluorophosphate (TBAPF$_6$) in anhydrous NMP solution. Cyclic voltammetry measurements were carried out on a CHI 604E electrochemical analyzer. Glassy carbon (diameter: 1.6 mm; area 0.02 cm^2) 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 (TBAPF$_6$) as a supporting electrolyte at a scan rate of 100 mV s^{-1}. The onset oxidation potential for compound 8N8O is 1.0 V, which correspond to the HOMO energy levels of -5.56 eV from the onset oxidation potential with reference to Fc$^+$/Fc (-4.8 eV) using the equation of EHOMO = -[4.8-EFc + Eoxonset] eV. Thus, the LUMO level is estimated to be -3.13 eV using the equation of ELUMO = (EHOMO + Egopt) eV (Egopt = (1240/λoneset) nm, λoneset = 510 nm). Theoretical calculation of compound **8N8O** was performed using the density functional theory (DFT) method of B3LYP with the 6-31G (d)

basis set.[11] Figure S8 shows that the electron density distributions of the HOMO mainly locate on aromatic groups while the LUMO orbital is mainly distributed on tetraazaanthracene, which is a strong electron acceptor. The calculated HOMO and LUMO energy levels for compound **8N8O** are -5.75 eV and -2,56 eV, respectively, which are in agreement with the experimental values (- 5.56 eV and -3.13 eV).
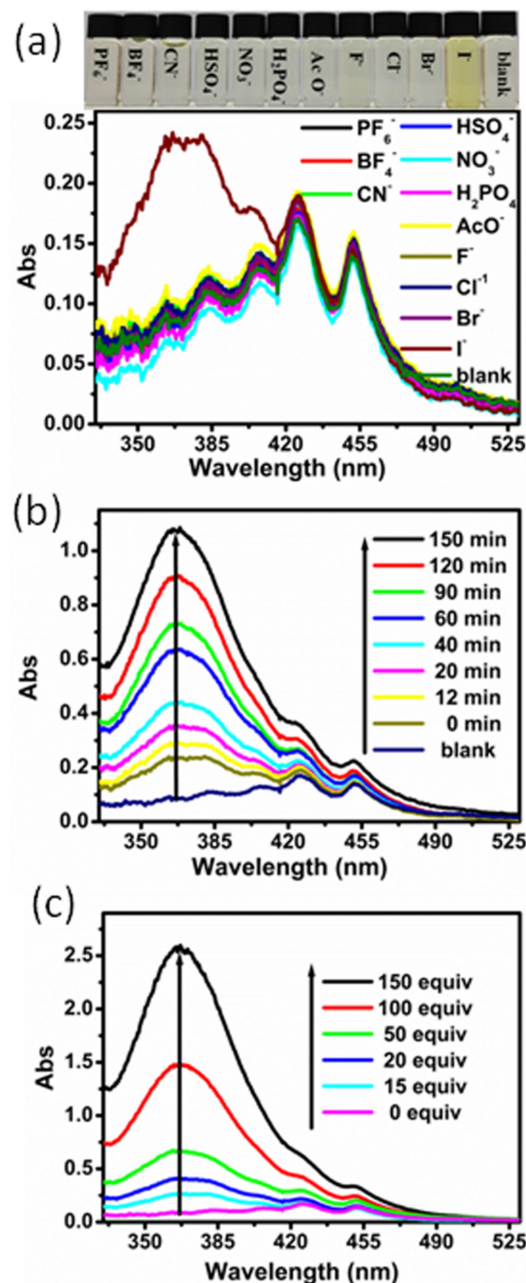
Figure 2 (a) UV/Vis absorption spectra (performed immediately) of NMP solutions of compound **8N8O** (10^{-5} mol L^{-1}) in the absence (blank) and presence of eleven anions (2×10^{-4} mol L^{-1}); (b) UV/Vis absorption spectra of NMP solutions of compound **8N8O** (10^{-5} mol L^{-1}) in the absence (blank) and presence of iodide (2×10^{-4} mol L^{-1}) with increasing time; (c) UV/Vis absorption spectra (performed 30 mins later) of NMP solutions of compound **8N8O** (10^{-5} mol L^{-1}) in presence of different concentration iodide.

The responses of compound **8N8O** to eleven anions (F⁻, Cl⁻, Br⁻, I⁻, PF$_6^-$, HSO$_4^-$, NO$_3^-$, BF$_4^-$, AcO⁻, CN⁻, and H$_2$PO$_4^-$, 2.0×10^{-4} mol L⁻¹) were investigated by UV-vis absorption and fluorescence spectroscopy in NMP solution. **Figure 2a** shows that there are no color change occurred in the presence of ten anions except iodide. Upon addition of iodide, a new absorption band centre at 368 nm was observed, which induced the color change to yellow. Moreover, the absorption intensity at 368 nm increased with increase in time (**Figure 2b**). **Figure 2c** displays the absorption titration spectra of compound **8N8O** with the addition of tetrabutylammonium iodides. Upon addition of iodide, the absorption intensity at 368 nm was increased. Further competition experiments were performed to demonstrate that the coexistence of these ions does not interfere with the detection of iodide. **Figure S9** shows the absorption response of compound **8N8O** towards iodide in the presence of other competitive ions. The absorption spectrum of compound **8N8O** in the presence of mixed anions without iodide was similar to the absorption spectrum in the absence, but a new absorption band centre at 368 nm was observed in the presence of mixed anions with iodide. These results suggest that compound **8N8O** can function as a selective for iodide. This result was confirmed by the emission spectra of compound **8N8O** in the presence of eleven different anions. As shown in **Figure 3a**, upon excitation at 427 nm (the compound **8N8O** maxium absorption in NMP solution), the free and eleven anions compound **8N8O** displays two emission bands centre at 504 nm and 539 nm, respectively, but the PL intensity is quenched in the presence iodide. **Figure 3b/3c** shows that the PL intensity was decreased with increasing time and concentration of iodide.

The changes in the photophysical properties of compound **8N8O** complexation with iodide observed in the UV-vis absorption and fluorescence spectroscopy results are similar to the previous reports, which exhibited that the changes in photophysical properties are due to the "heavy-atom" effect.[9] In addition, there are two types of quenching of the "heavy-atom" effect, one is static quenching through the formation of a complex between a receptor (emitter) and an anion (quencher) and the other is the dynamic quenching due to the random collisions between the emitter and the quencher. In the present investigation, compound **8N8O** shows static quenching upon addition of iodide since a new absorption at 368 nm was observed.
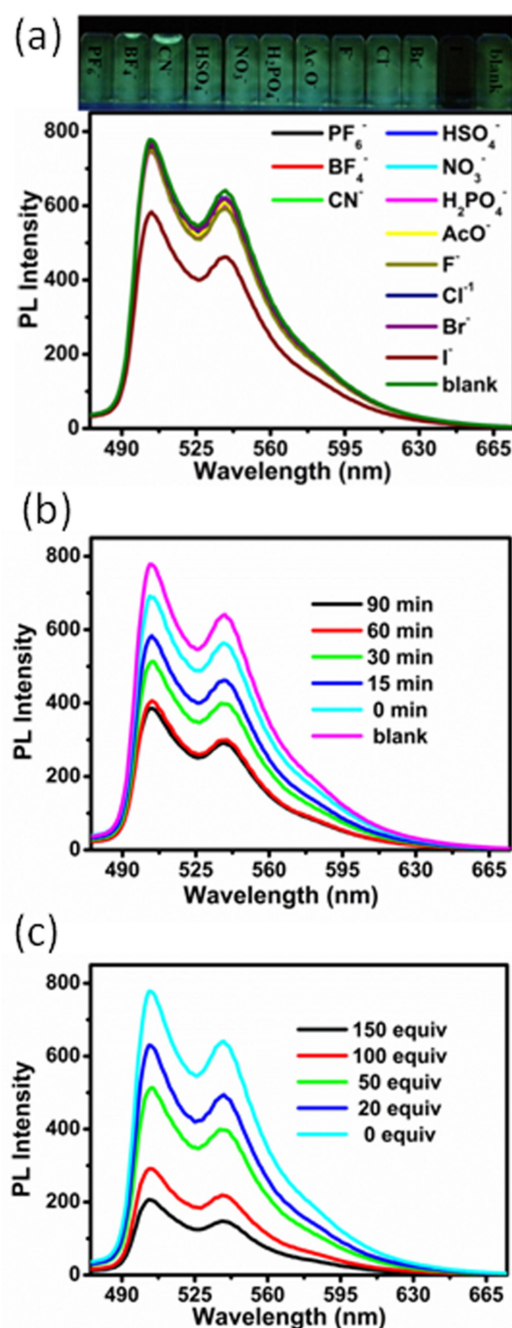
Figure 3 (a) Emission spectra (performed 15 mins later) of NMP solutions of compound **8N8O** (10^{-5} mol L⁻¹) in the absence (blank) and presence of eleven anions (2×10^{-4} mol L⁻¹); (b) Emission spectra of NMP solutions of compound **8N8O** (10^{-5} mol L⁻¹) in the absence (blank) and presence of iodide (2×10^{-4} mol L⁻¹) with increasing time; (c) Emission spectra (performed 30 mins later) of NMP solutions of compound **8N8O** (10^{-5} mol L⁻¹) in presence of different concentration iodide.

In conclusion, we have successfully designed and synthesized a novel heteroacenes, **8N8O**, containing two different types of heteroactoms (nitrogen and oxygen atoms) in its backbones. Interestingly, compound **8N8O** can act as an efficient anion sensor for iodide over a wide range of other anions (F⁻, Cl⁻, Br⁻, PF$_6^-$, HSO$_4^-$, NO$_3^-$, BF$_4^-$, AcO⁻, CN⁻, and H$_2$PO$_4^-$) due to the "heavy-atom" effect.

Notes and references

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