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Paper in Celebration for the 2010 Nobel Prize in Chemistry

Diacenaphtho[1,2-*b*;1′,2′-*d*]silole and -pyrrole

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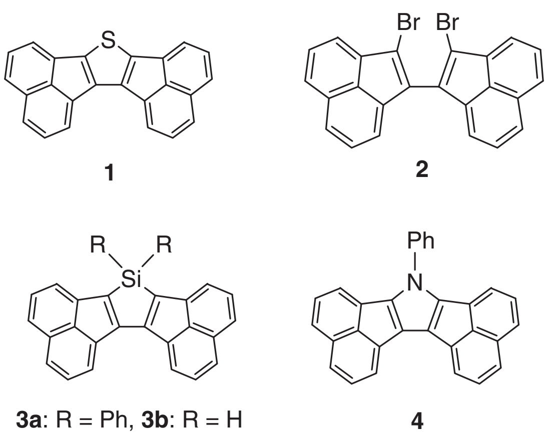
π-Extended silole and pyrrole analogs fused with two acenaphthylene units were synthesized from 2,2′-dibromo-1,1′-biacenaphthylene. The pyrrole was obtained as a stable compound, while the silole was thermally stable, but highly acid-sensitive purple crystals. The molecular structures reveal that both heteroles have a planar π-system and stack to form a head-to-tail dimer structure. Observed electronic and electrochemical properties obviously indicate low LUMO energy level of the silole and high HOMO level of the pyrrole as predicted by DFT calculations.

Recently, polycyclic conjugated systems involving heterole unit(s) have been received much attention for application in organic electronics such as organic field effect transistors (OFET) and organic light-emitting diodes (OLEDs).[1] Diacenaphtheno[1,2-*b*;1′,2′-*d*]thiophene (**1**) is readily prepared by heating acenaphthene with sulfur.[2] Since the first publication in 1939, a variety of studies relating to derivatization,[3] reactivities,[4] and molecular structures[5] have been performed to date. However, no other heterole analogs bearing a diacenaphtheno skeleton have been synthesized, probably due to the lack of appropriate synthetic method.[6] According to recent development of heterole synthesis,[7] 2,2′-dibromo-1,1′-biacenaphthylene (**2**) could serve as a suitable precursor for the corresponding heteroles. We herein discuss the successful synthesis of the π-extended silole **3a** and pyrrole **4** from **2** (Scheme 1) and their electronic and structural properties together with theoretical studies.



1

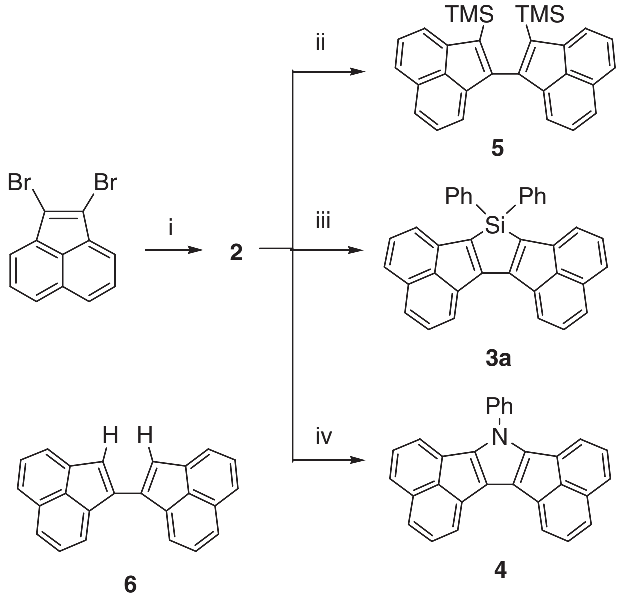
2

3a: R = Ph, **3b**: R = H

4

Scheme 1. Diacenaphtheno[1,2-*b*;1′,2′-*d*]heteroles **1**, **3**, and **4** together with a precursor **2**.

The syntheses of the heteroles are outlined in Scheme 2. Treatment of 1,2-dibromoacenaphthylene[8] with 1 equiv of *n*-BuLi in THF at −78 °C for 1.5 h and subsequent oxidation with $CuCl_2$ afforded 2,2′-dibromo-1,1′-biacenaphthylene (**2**) in 43% yield.[9] Treatment of **2** with 2.2 equiv of *n*-BuLi at −78 °C in THF afforded **5** as a stable solid in 64% yield upon quenching with chlorotrimethylsilane. The result proved the successful generation of corresponding dilithium compound under the reaction conditions. Quenching the dianion with dichlorodiphenylsilane produced a purple solution upon usual aqueous work-up and extraction with toluene. The extract was diluted with hexane to precipitate diphenyl derivative **3a** as purple crystals. It is a fairly thermally stable compound, but chromatographic purification using silica gel lead to decomposition to give 1,1′-biacenaphthylene (**6**)[10] in low yields. Contrary to the purple color of **3a**, disilylated and unsubstituted 1,1′-biacenaphthylenes, **5** and **6**, have pale yellow and yellow colors, respectively. Based on recent intensive studies on the catalytic double *N*-arylation of amines with organic halides,[11,12] $[Pd_2(dba)_3]/t\text{-}Bu_3P/NaO\textit{t}\text{-}Bu$ was first employed for the synthesis of **4** from **2**. The pyrrole **4** was obtained as a sole isolated product in 26%



5

3a

6

4

Scheme 2. Reaction conditions; i) 1 equiv *n*-BuLi, −78 °C, 1.5 h in THF, then, $CuCl_2$ (43%); ii) 2.2 equiv *n*-BuLi, −78 °C, 30 min in THF, then, $(CH_3)_3SiCl$ (64%); iii) 2.2 equiv *n*-BuLi, −78 °C, 30 min in THF, then, Ph_2SiCl_2 (50%); iv) $C_6H_5NH_2$, 9 equiv *t*-BuONa, 0.5 equiv Cy_3P, 8 mol % $[Pd_2(dba)_3]$ in *o*-xylene at 150 °C for 14 h (29%).

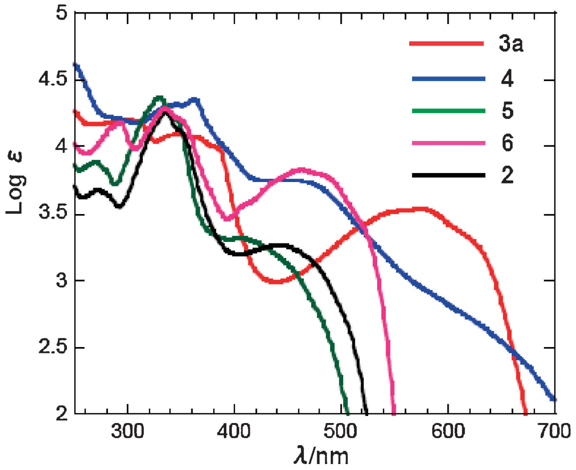


Figure 1. UV spectra of **2**, **3a**, **4**, **5**, and **6** in CH_2Cl_2.

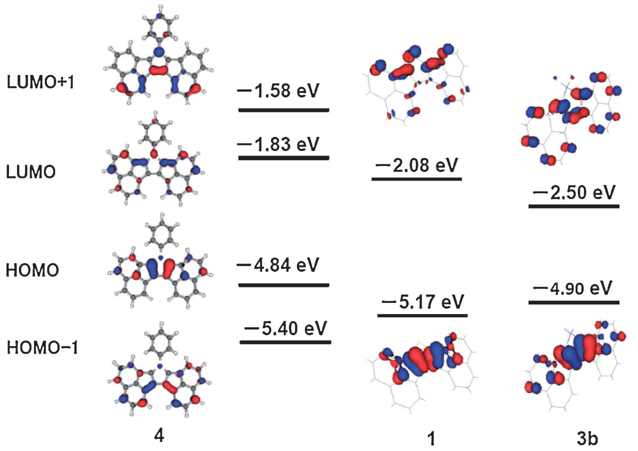


Figure 2. TD-DFT (RB3LYP/6-31G(d)) calculations of **4**, **1**, and **3b**.

yield. When Cy_3P was used as a ligand, the yield was improved slightly (29%). The reaction at relatively low temperature (toluene reflux) did not improve the yield. **4** was fairly stable, dark reddish crystals. ^1H and ^{13}C NMR spectra of the heteroles are consistent with the expected structures.

Figure 1 shows the absorption spectra of **3a** and **4**, and the 1,1′-biacenaphthylenes **2**, **5**, and **6** in CH_2Cl_2. The spectra of all compounds except **4** consist of roughly two absorption bands in the measurable range. The longest absorption maximum of **3a** shows a large bathochromic shift (>100 nm) related to those of **5**, **6**, and the known thiophene **1** (457 nm).[13] On the other hand, the spectrum of **4** consists of three absorption bands. The longest absorption band was observed at about 620 nm as a shoulder peak, and the band almost disappeared in CH_3CN (Figure S1[9]). The solvent effect would be ascribed to the charge-transfer character of the transition.

The optimized structures of heteroles **3b**, **4**, and **1** together with biacenaphthylenes **5** and **6** were calculated with the DFT (RB3LYP/6-31G(d)) basis set and illustrated in Figures S2–S6.[9] Parent silole **3b** (R = H) was employed in place of **3a** as a model compound. The heteroles possess planar π-skeletons, while **5** and **6** have largely twisted structures around the 1,1′-pinch bonds (**5** for 73° and **6** for 40°). The longest absorption of **6** was observed at 55 nm longer wavelength than that of **5**. The relatively large difference can mainly be account for by the largely twisted conformation interrupting the conjugation. The electronic properties of the heteroles were also calculated with TD-DFT (RB3LYP/6-31G(d)).[9,14] The energy diagrams are shown in Figure 2, and Tables S1 and S2.[9] The MO coefficient structures of the HOMO and LUMO of **1** and **4** bearing unshared electron pair(s) on the hetero atoms are quite similar to each other. The HOMO–LUMO gap of **3b** (2.40 eV) is considerably smaller than those of **1** (3.09 eV) and **4** (3.01 eV). Particularly, the LUMO energy level of **3b** is considerably lower than those of **1** and **4**, whereas the differences of HOMO energies are relatively small. The small band gap of **3b** is probably due to the participation of Si–C σ bonds in the π-conjugation of the silole moiety.[1a,1c] This is in accord with the observed absorption spectrum of **3a**. On the other hand, the predicted second absorption of **4** (487 nm, $f = 0.004$) mainly due to the HOMO–LUMO+1 transition is close to the predicted first absorption (498 nm, $f = 0.12$) mainly due to the HOMO–LUMO transition. Because the large MO coefficient locates on the nitrogen atom of **4** in the LUMO+1, the LUMO+1 energy level would be susceptible to the polarity of solvents. Thus, the theoretically assigned LUMO+1 would correspond to the actual LUMO in CH_2Cl_2. In contrast to dibenzosilole[6] and carbazole derivatives,[15] unfortunately, **3a** and **4** show no fluorescence in both solution and the solid state.

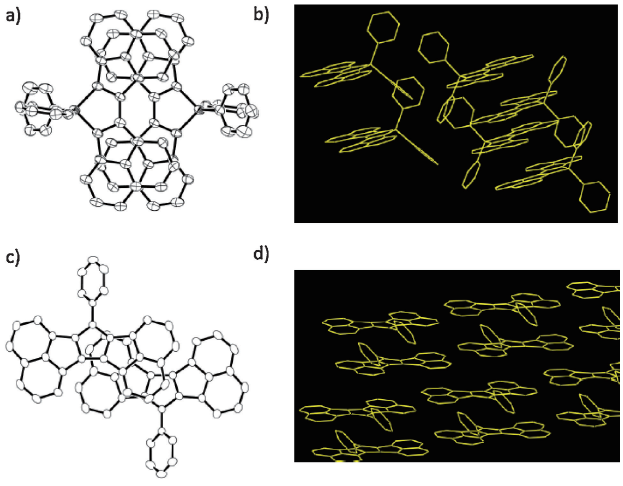


Figure 3. a) ORTEP drawing of a dimer structure of independent two molecules, and b) a molecular packing of **3a**, c) ORTEP drawing of a dimer structure of independent two molecules, and d) a molecular packing of **4**.

Good single crystals of **3a** and **4** were collected by recrystallization from hexane/CH_2Cl_2 solutions, respectively. The crystal of **3a** involves one hexane molecule in one unit cell. The largely disordered hexane molecule increased the *R*1 value. The ORTEP drawings reveal that they have a planar fused ring system as expected (Figure 3).[16] The selected averaged bond lengths and angles of **3a** and **4** together with **1** are listed in Figures S7–S9.[9] **3a** shows middle bond alternation in the silole ring (1.386 and 1.474 Å) in comparison to that of hexaphenylsilole (1.357 and 1.501 Å)[17] and the pyrrole ring of **4** (1.395 and 1.411 Å). The bond lengths of **4** are almost comparable to the thiophene ring of **1** (1.398 and 1.404 Å).[5] The two phenyl substituents of **3a** were tilted almost perpendicular to each other; the protons of the phenyl groups direct toward the π plane of the phenyl groups of neighbor molecules, which formed an intermolecular CH–π interaction network. Moreover, the silole π systems stack well in a head-to-tail manner; the intermolecular distances are considerably short (3.35 and 3.41 Å), which indicated the strong π–π interaction. The molecules construct a one-dimensional columnar structure in the crystal (Figure 3b). On the other hand, the phenyl group of **4** is tilted 53.5° from the pyrrole plane; the protons of phenyl group direct toward the pyrrole π plane of a neighbor molecule. The resulting CH–π interactions build a slipped parallel stacking in the crystal (Figure 3d). The considerably short intermolecular distance (3.39 Å) should also indicate the operation of strong π–π interaction.

The redox properties of heteroles **1**, **3a**, **4**, and the related compounds were examined by cyclic voltammetry (CV) in DMF and CH_2Cl_2 solutions (Table S6[9]). The CV of **3a** in DMF exhibits two reversible reduction waves (−1.60 and −2.10 V), but no oxidation wave was observed in the measurable range (>+1.2 V). On the other hand, the CV of **4** in CH_2Cl_2 exhibited the first reversible and the second irreversible oxidation waves (+0.35 and +1.06 V), and the reduction waves were not observed. The electronic oxidation of **1** readily produced polymeric materials as a film on the surface of the cathode (Figure S12[9]). The relatively high reversibility of oxidation waves indicated that **4** formed stable cationic species.

In conclusion, heretofore unknown diacenaphtheno[1,2-*b*;1′,2′-*d*]silole and -pyrrole derivatives were successfully prepared from 2,2′-dibromo-1,1′-biacenaphthylene (**2**). The crystallographic analyses revealed high planarity of the π-systems, and the electrochemical studies indicated a low energy LUMO level of the silole **3a**, and high energy HOMO level of **4** as predicted by the DFT theoretical calculations. We are currently investigating the potential applications of these compounds for OFETs; the results will be reported in due course.

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14 The molecular geometries of the heteroles were fully optimized at the RB3LYP/6-31G(d) level of theory embedded in the Gaussian 03 software package. The time-dependent calculations were performed on the optimized geometries. Theoretical estimation of $S_0 \rightarrow S_1$ absorption bands were performed with TD-RB3LP/6-31G(d)//RB3LYP/6-31G(d) method.

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16 Selected data for **3a**: Crystal system: Monoclinic, Space group: $P2_1/n$, $a = 22.8451(14)$ Å, $b = 8.2661(4)$ Å, $c = 29.5373(16)$ Å, $\beta = 102.8594(16)°$, $V = 5437.9(5)$ Å^3, $Z = 4$, $\mu = 0.11$ mm^{-1}, $T = 200$ K, $R[F^2 > 2\sigma(F^2)] = 0.096$, $wR(F^2) = 0.270$, $S = 1.05$, Refl/Param. = 12394/721. And for **4**: Crystal system: Triclinic, Space group: $P\bar{1}$, $a = 8.0445(9)$ Å, $b = 11.184(1)$ Å, $c = 11.525(1)$ Å, $\alpha = 83.288(3)°$, $\beta = 74.390(3)°$, $\gamma = 72.725(3)°$, $V = 952.84(16)$ Å^3, $Z = 2$, $\mu = 0.079$ mm^{-1}, $T = 223$ K, $R[F^2 > 2\sigma(F^2)] = 0.0579$, $wR(F^2) = 0.2043$, $S = 1.117$, Refl/Param. = 12394/721. Crystallographic data reported in this manuscript have been deposited with Cambridge Crystallographic Data Centre as supplementary publication No. 842076 for **4** and No. 842077 for **3a**. Copies of the data can be obtained free of charge on application to CCDC, 12, Union Road, Cambridge, CB2 1EZ, U.K. (fax: +44 1223 336033); e-mail: deposit@ccdc.cam.ac.uk.

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