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Transition-Metal-Free Diarylannulated Sulfide and Selenide Construction via Radical/Anion-Mediated Sulfur−Iodine and Selenium−Iodine Exchange

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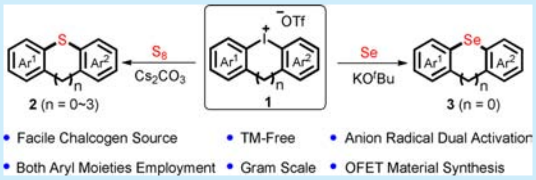
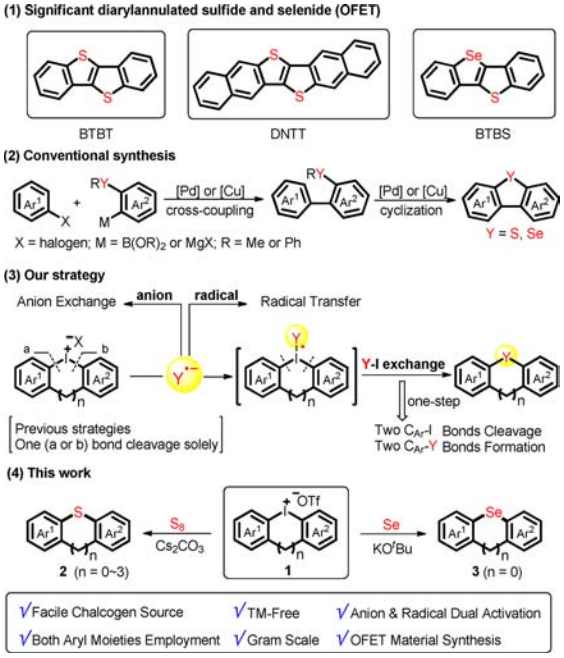
S *Supporting Information*

ABSTRACT: A facile, straightforward protocol was established for diarylannulated sulfide and selenide construction through S−I and Se−I exchange without transition metal assistance. Elemental sulfur and selenium served as the chalcogen source. Diarylannulated sulfides were systematically achieved from a five- to eight-membered ring. A trisulfur radical anion was demonstrated as the initiator for this radical process via electron paramagnetic resonance (EPR) study. OFET molecules [1]benzothieno[3,2-*b*][1]benzothiophene (BTBT) and [1]benzothieno[3,2-*b*][1]benzoselenophene (BTBS) were efficiently established.



Scheme 1. Significant Diarylannulated Sulfides and Selenides and Their Syntheses



Sulfur and selenium atoms play important roles in conjugated organic molecules possessing various electronic and optical properties for optoelectronic devices,[1] such as organic field-effect transistor (OFET),[1b,g,h] organic light-emitting diode (OLED),[1a,b] and organic solar cell (OSC).[1d,e] It resulted from the unique features of sulfur and selenium atoms: (1) higher resonance energy compared to other heteroatoms, such as nitrogen or oxygen,[1i] and (2) higher polarizability leading to excellent charge transport properties.[1c] Diverse sulfur/selenium-containing diarylannulated molecules, such as BTBT, DNTT, and BTBS, are promising motifs for thin film transistors in OFET material science (Scheme 1.1).[2] Conventional synthetic methods for dibenzannulated sulfide and selenide were generally based on cross-coupling between an aromatic thioether and aryl halide with the help of transition metal catalysts, subsequently followed by cyclization (Scheme 1.2).[3] Diaryliodonium salt as an air-/moisture-stable reagent is one of the most efficient arylation reagents in organic synthesis.[4] They have been extensively utilized in transition-metal-catalyzed reactions.[4] Meanwhile, splendid efforts have also been devoted to transition-metal-free arylation with nucleophiles by the Olofsson and Kita groups.[5] Recently, transition-metal-catalyzed utilization of aryls in diaryliodonium salts was demonstrated via cleavage of two C_{Ar}−I bonds.[6] The Greaney group reported the first acyclic diaryliodonium salt for double arylation of indole.[6e] The Yoshikai group reported a facile preparation of bis-iodo compounds from cyclic diaryliodonium salt and elegant synthesis of heterofluorenes.[6d] We envisioned that the radical property in diaryliodonium salts,[7] which is inclined to be initiated through radical species, will lead to the double cleavage of C_{Ar}−I bonds and reformation of new bonds in one step (Scheme 1.3). A bifunctional anion radical, possessing both static effect and radical properties, will drive the radical transfer in a dual activation strategy. Using the concept of transition from inorganic to organic sulfur,[8] we disclosed a radical/anion-mediated diarylannulated sulfide and selenide construction through direct sulfur−iodine and selenium−iodine

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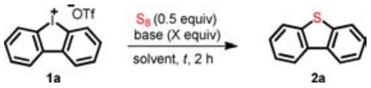
exchange of diaryliodonium salts in transition metal free conditions (Scheme 1.4), which introduce sulfur and selenium in the late stage directly and effectively.

We commenced our concept with testing the interaction between diaryliodonium salt **1a** and elemental sulfur. Unfortunately, there was no desired product **2a** detected when lithium carbonate or sodium carbonate was applied as a base (Table 1, entries 1−2). To our delight, a 47% yield of **2a** was isolated when potassium carbonate was used (Table 1, entry 3). Furthermore, a 78% yield was achieved with stronger base cesium carbonate application (Table 1, entry 4). However, the efficiency was decreased when other kinds of strong bases were tested (Table 1, entries 5−7). The amount of cesium carbonate was also crucial for the transformation (Table 1, entries 8−9). Dimethyl sulfoxide was found to be the best solvent (Table 1, entries 10−12). No improvement was observed when 20 equiv of water were added in order to improve the solubility (Table 1, entry 13). The efficiency of the reaction was dramatically decreased when conducted under open air (Table 1, entry 14), which indicated that the radical system was sensitive to oxygen. Ultimately, the optimized conditions were achieved to afford **2a** in 89% yield under higher temperature (Table 1, entries 15−16).

Table 1. Conditions Optimization of Sulfur−Iodine Exchange[a]

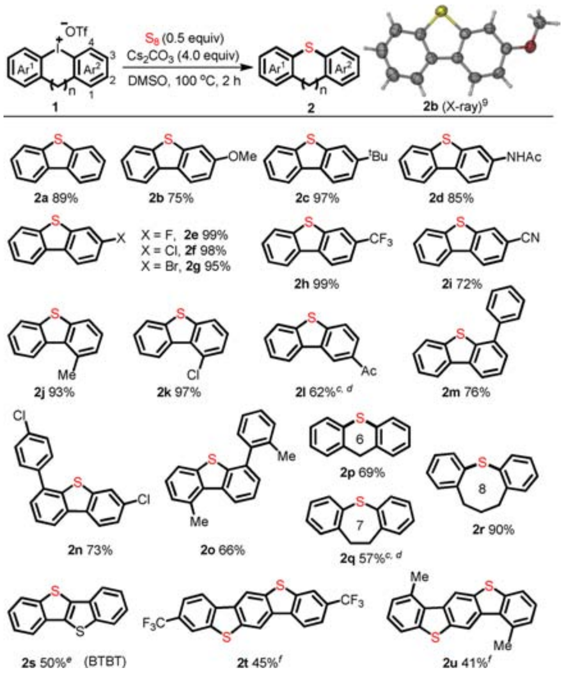


entry	base (X equiv)	solvent	t (°C)	yield (%)[b]
1	Li_2CO_3 (4)	DMSO	80	trace
2	Na_2CO_3 (4)	DMSO	80	trace
3	K_2CO_3 (4)	DMSO	80	47
4	Cs_2CO_3 (4)	DMSO	80	78
5	NaH (4)	DMSO	80	50
6	NaO^{t}Bu (4)	DMSO	80	70
7	KO^{t}Bu (4)	DMSO	80	67
8	Cs_2CO_3 (6)	DMSO	80	46
9	Cs_2CO_3 (2)	DMSO	80	17
10	Cs_2CO_3 (4)	DMF	80	34
11	Cs_2CO_3 (4)	THF	80	trace
12	Cs_2CO_3 (4)	DCE	80	trace
13[c]	Cs_2CO_3 (4)	DMSO	80	75
14[d]	Cs_2CO_3 (4)	DMSO	80	49
15	***Cs_2CO_3 (4)***	***DMSO***	***100***	***89***
16	Cs_2CO_3 (4)	DMSO	120	82

[a] The reactions were carried out with 0.1 mmol of **1a** in 1 mL of solvent. [b] Isolated yields of **2a**. [c] 20 equiv of water were added. [d] Open air.

The sulfur−iodine exchange, exhibiting divergent synthesis of functionalized diarylannulated sulfides including well-known OFET materials, is shown in Scheme 2. A broad range of diaryliodonium salts with electron-donating (**2b**−**2d**)[9] and electron-withdrawing (**2e**−**2i**) substituents at position 3 were efficiently achieved in good to excellent yields. In particular, diaryliodonium salt bearing a bromide moiety, which was liable to oxidative addition with a transition metal, was perfectly tolerated affording **2g** in 95% yield. Switching the substituents to position 1 (**2j**−**2k**), 2 (**2l**), and 4 (**2m**) proved to be entirely compatible. The additional versatility was revealed by employing sterically hindered conjugated groups at position 4, which are beneficial for enhancing carrier mobility in OFET materials (**2m**−**2o**).[1g,h] Six-membered diaryliodonium salt was efficiently transformed into the corresponding 9*H*-thioxanthene **2p**, which is the core structure in biologically active compounds.[10] Remarkably, medium-sized rings of dihydrodibenzothiepine (**2q**, seven-membered) and dihydrodibenzothiocine (**2r**, eight-membered) were more efficiently established via the method, which is a significant challenge in previous synthetic methods. BTBT, a promising organic semiconductor molecule exhibiting outstanding electron mobility in a thin-film transistor setting, was readily synthesized through this atom exchange (**2s**).[2a] Also, bis-iodonium salts formed the corresponding twofold sulfur-containing molecules successfully (**2t**−**2u**), which was an efficient approach for establishing the library of larger π-conjugated organic semiconductor material molecules.[2b]

Scheme 2. Sulfur−Iodine Exchange[a,b]

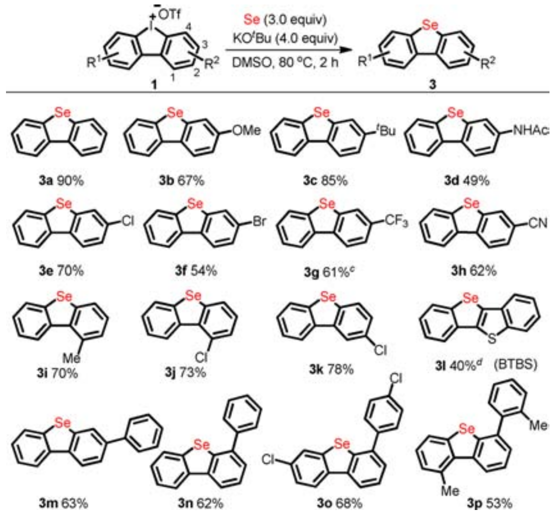


[a] Reaction conditions: **1** (0.1 mmol), S_8 (0.05 mmol) and Cs_2CO_3 (0.4 mmol), in DMSO (1 mL) at 100 °C for 2 h. [b] Isolated yields. [c] 80 °C. [d] 2 equiv of Cs_2CO_3. [e] 2 equiv of KO^{t}Bu were instead of Cs_2CO_3. [f] 8 equiv of KO^{t}Bu were instead of Cs_2CO_3 under 60 °C.

Following the establishment of functionalized diarylannulated sulfides, π-conjugated selenide library was investigated comprehensively (Scheme 3). Due to the relatively weak activity of elemental selenium (compared to elemental sulfur), the stronger base potassium *tert*-butoxide was employed (see Table S1 for details). Diaryliodonium salts bearing electron-rich, -neutral, and -deficient groups proceeded smoothly with elemental selenium to afford the corresponding five-membered diarylannulated selenides prosperously through the current method (**3a**−**3h**). Switching the substituents from position 3 to 1 and 2 could be readily accommodated as well (**3i**−**3k**). It should be noted that the OFET material BTBS could be obtained in this transformation (**3l**) as well.[2e] Diarylannulated selenides with conjugated groups at position 3 and 4, which are significant in the synthesis of π-conjugated materials molecules (**3m**−**3p**), could be well tolerated despite the steric hindrance.

Radical-trapping experiments were conducted by investigating diaryliodonium salt **1a** and 1,1-diphenylethylene **4** under the standard conditions. 2-Diphenylvinyl-2′-iodo-biphenyl **5**[9] was

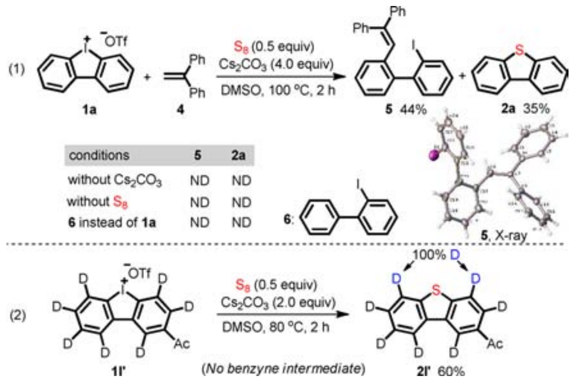
Scheme 3. Selenium−Iodine Exchange[a,b]



[a]Reaction conditions: **1** (0.1 mmol), Se (0.3 mmol), and KO^{t}Bu (0.4 mmol), in DMSO (1 mL) at 80 °C for 2 h. [b]Isolated yields. [c]6 equiv of KO^{t}Bu. [d]2 equiv of KO^{t}Bu under 100 °C.

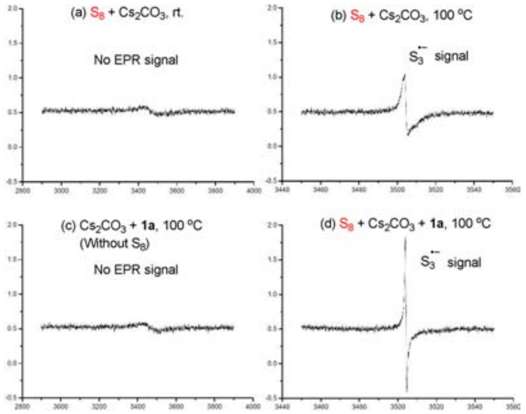
afforded in 44% yield, which provided strong evidence of an aryl radical intermediate being involved in this transformation. **5** and **2a** could not be furnished in the absence of cesium carbonate or elemental sulfur, which indicated that the combination of elemental sulfur and base was indispensable to radical initation (Scheme 4.1). 2-Iodo-biphenyl **6** and **4** could not afford **5** under the standard conditions, which confirmed that the radical-trapped product **5** was not derived from the reductive elimination product of diaryliodonium salt **1a**. H/D exchange was not observed in the product **2l′** when the deuterated diaryliodonium salt **1l′** was launched under the standard conditions of sulfur−iodine exchange (Scheme 4.2), which demonstrated that no benzyne intermediate was formed during the sulfur−iodine exchange process.

Scheme 4. Mechanistic Study



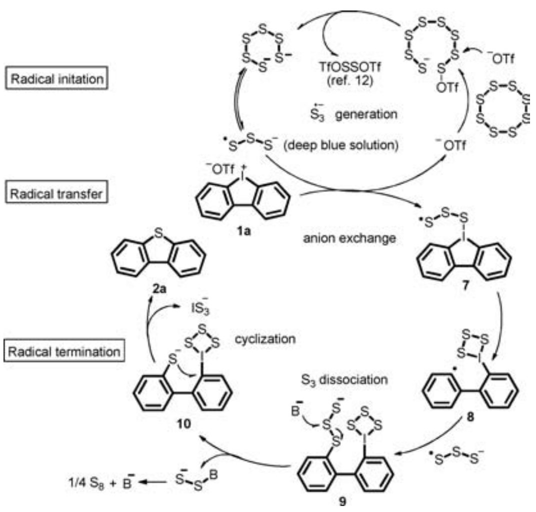
A trisulfur radical anion could be generated through the interaction of elemental sulfur and a base.[11a] EPR studies were carried out to investigate the radical possibility in this transformation. Initially, no EPR signal was observed in the dimethyl sulfoxide solution of elemental sulfur and cesium carbonate mixture at room temperature or the absence of elemental sulfur (Scheme 5a and 5c). A single EPR signal, reported as the trisulfur radical anion,[11] was observed when the reaction temperature increased to 100 °C (Scheme 5b). The same EPR signal was also observed in the system when substrate **1a** was under the standard conditions of sulfur−iodine exchange (Scheme 5d).

Scheme 5. EPR Study



A plausible mechanism that is supported by this experimental evidence is described in Scheme 6. First, elemental sulfur was interacted with the base[11] under the assistance of the anion[12] from diaryliodonium salt to provide the trisulfur radical anion, which was confirmed through EPR experiments. Subsequently, the trisulfur radical anion exchanged with the anion from diaryliodonium salt **1a** to give intermediate **7**. The radical transferred from the trisulfur to the aryl group with the cleavage of C_{Ar}−I generating aryl radical intermediate **8**. It was coupled with another trisulfur radical anion, affording intermediate **9**. This intermediate was dissociated into the thiophenol anion with the help of the base giving intermediate **10**, which underwent intramolecular S_N2 cyclization to afford product **2a** eventually.

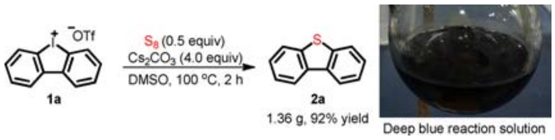
Scheme 6. Plausible Mechanism



In further probing the efficiency and practicability of this exchange approach, **1a** was launched on gram scale to afford the desired product **2a** in 92% yield. The reaction solution showed a deep blue color, which was consistent with trisulfur radical anion phenomena (Scheme 7).[11]

In summary, a convenient and practical protocol was explored for syntheses of diarylannulated sulfides and selenides through sulfur−iodine and selenium−iodine exchange of diaryliodonium salts without transition metal catalysis. Diverse diarylannulated sulfides/selenides were sysmatically achieved, which expands the

Scheme 7. Gram Scale Reaction



synthetic method for unsymmetrical π-conjugated material molecules. Mechanistic study demonstrated that the anion/radical dual activation strategy provided strong compatibility for chalcogen exchange. The trisulfur radical anion initiated the radical initiating step after anion exchange, processed intramolecular radical transfer, and terminated this exchange subsequently. Further explorations of atom exchange reactions are in progress in our laboratory.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b03078.

Experimental procedures; NMR spectral, X-ray, and analytical data for all new compounds (PDF)
Crystallographic data (CIF, CIF)

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Notes

The authors declare no competing financial interest.

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