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Trisulfur radical anion-triggered stitching thienannulation: rapid access to largely π-extended thienoacenes†

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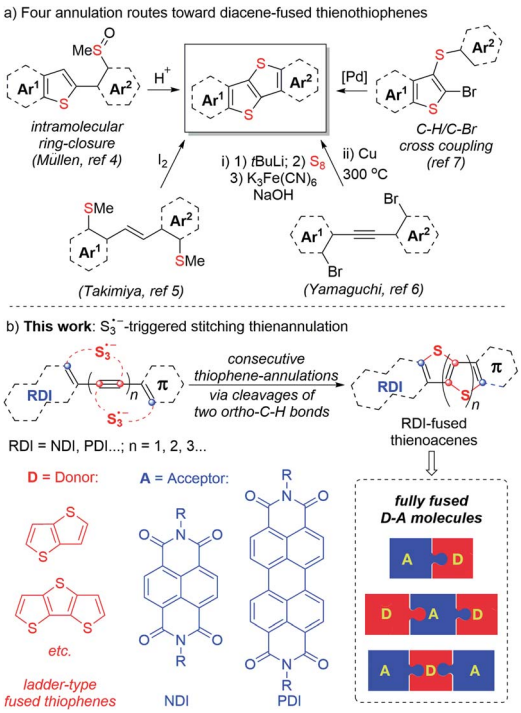
Largely π-extended rylene diimide-fused thienoacenes, a new family of fully fused electron donor–acceptor (D–A) molecules, have been readily synthesized by a novel trisulfur radical anion ($S_3^{\bullet-}$)-triggered stitching thienannulation strategy. The ladder-type fused thiophene cores are constructed in a stitching manner through multiple carbon–sulfur bond formation between acetylenic rylene dyes and $S_3^{\bullet-}$. A detailed mechanistic study of these stitching thienannulations unveiled the multiple reactivities of $S_3^{\bullet-}$. Physical properties of the newly formed D–A, A–D–A, and D–A–D type thienoacenes have also been investigated, which revealed their precisely controllable electronic properties.

Introduction

Largely π-extended thienoacenes, diacene-fused thienothiophenes such as [1]benzothieno[3,2-*b*][1] benzo-thiophene (BTBT) and related compounds constitute a useful class of molecules in the field of organic semiconducting materials due to their rigid planar conformation, well delocalized π-conjugation, unique intermolecular sulfur–sulfur interactions, and improved air stability compared with large acenes.[1,2] To date, four reliable annulation approaches toward these skeletons have been reported (Scheme 1a).[1e,f,3–8] However, each of these methods require the use of uncommon *ortho*-bifunctionalized aromatics as cyclization precursors, which means the options available to access such skeletons are rather limited. In addition, rylene diimides (RDIs) such as naphthalene diimides (NDIs) and perylene diimides (PDIs) represent an important class of n-channel organic semiconductors. Effective π-extensions of the NDI and PDI units are recognized as valuable approaches toward new molecular materials with precisely controlled electronic properties.[9] In this context, fusion of electron-deficient RDI units (acceptors, A) and electron-rich thieno[3,2-*b*]thiophene or other ladder-type fused thiophenes (donors, D) may afford a variety of n-channel, p-channel, and ambipolar materials, depending on their specific electronic structures.[7b,10] As a result, general and efficient synthetic pathways toward these appealing structures are highly desirable.

The trisulfur radical anion ($S_3^{\bullet-}$), as a ubiquitous sulfur-centered radical, has only recently received increasing attention in synthetic chemistry.[11,12] Until now, exploration of its



Scheme 1 Four annulation routes toward diacene-fused thienothiophenes (previous work) and $S_3^{\bullet-}$-triggered stitching thienannulation (this work).

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unique and multiple reactivities and application in the synthesis of useful organosulfur compounds remain limited. Conventionally, intermolecular reactions of normal sulfur-centered radicals, such as thiyl radicals (RS$^{\bullet}$) and sulfonyl radicals ($RSO_2^{\bullet}$), with alkynes predominantly led to the formation of S-functionalized alkene derivatives.[13] In contrast, herein, we discovered that $S_3^{\bullet-}$ could initiate consecutive thiophene-annulations (stitching thienannulation) of arylacetylenic RDIs *via* cleavage of two *ortho*-C–H bonds to afford a host of rylene diimide-fused largely π-extended soluble thienoacenes (Scheme 1b). With controllable electronic structures (D–A type, D–A–D type and A–D–A type), these RDI-fused thienoacenes are promising candidates for high-performance organic semiconductors.[14]

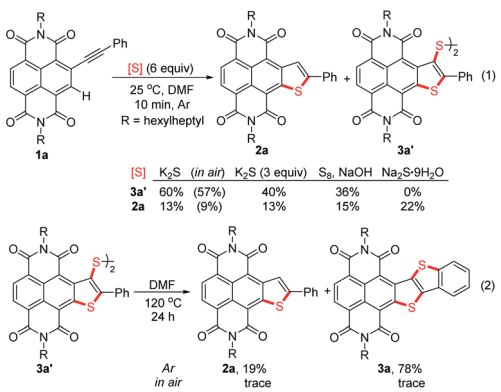
Results and discussion

Stitching thienannulation of phenylethynyl substituted RDIs

In recent years, Takimiya *et al.*,[15] Wang *et al.*[16] and our group[17] have discovered that alkynyl-substituted rylene dyes could undergo direct thiophene–annulation reactions (thienannulations) with Na_2S, S_8 or K_2S to form important thiophene-fused RDIs. Initially, to gain insight into the mechanisms of these thienannulation processes, the reaction of simple phenylethynyl substituted NDI **1a** with different sulfur reagents at room temperature was studied (Scheme 2, eqn (1)). To our surprise, with addition of 6 equiv. of K_2S in *N*,*N*-dimethylformamide (DMF) solution, **1a** was entirely consumed within 10 min and afforded not only a normal thienannulation product **2a** in 13% yield but also an abnormal disulfide product **3a′** in 60% yield (Scheme 2, eqn (1)).[18] The reaction also took place in air and afforded similar results (**2a**, 9%; **3a′**, 57%). Reducing the amount of K_2S to 3 equiv. led to the formation of **3a′** in a lower yield (40%). Treatment of **1a** with S_8 in the presence of NaOH also produced **2a** and **3a′** in 15% and 36% yields, respectively. Previously, $Na_2S{\cdot}9H_2O$ has been recognized as an efficient sulfur source for thienannulation of bis(trimethylsilyl)ethynyl substituted NDI to yield naphtho[2,3-*b*:6,7-*b*′]dithiophene diimide (NDTI).[15,16a] Nonetheless, the reaction of **1a** with 6 equiv. of $Na_2S{\cdot}9H_2O$ at room temperature furnished only **2a** in 22% yield. 38% of **1a** was recovered, and disulfide product **3a′** was not formed at all. Realizing that $S_3^{\bullet-}$ can be generated from the DMF solution of K_2S and the DMF solution of a mixture of elemental sulfur and NaOH at room temperature,[12a,c] we explored whether $S_3^{\bullet-}$ was responsible for this unique thienannulation process. UV-visible spectra of K_2S, S_8/NaOH and $Na_2S{\cdot}9H_2O$ in DMF were all recorded at room temperature (Fig. 1). A characteristic absorption peak of $S_3^{\bullet-}$ at 617 nm (ref. 11) have been found for the DMF solutions of K_2S and S_8/NaOH. Clearly, the yields of **3a′** in the reactions are close related to the concentrations of $S_3^{\bullet-}$ in the solutions, indicating that $S_3^{\bullet-}$ was most likely involved in this reaction process.

More interestingly, later we found that **3a′** could further undergo a direct thienannulation at 120 °C, without the addition of any transition-metal catalysts and additional oxidants,[19] producing an NDI-fused thienoacene product **3a** in 78% yield, accompanied by **2a** in 19% yield (Scheme 2, eqn (2)). Notably, performing this reaction in air was detrimental and 70% of **3a′** was recovered after the reaction.

Motivated by these results, we expected to construct **3a** directly from **1a** *via* a one-pot consecutive thienannulation (stitching thienannulation) process (Table 1). To our delight, direct treatment of **1a** with 6 equiv. of K_2S at 120 °C for 24 h indeed furnished **3a** in 51% yield (entry 1). Higher temperature was found to increase the yield of **3a** to 66% (entry 2). As the amount of K_2S was reduced, the yield of **3a** was decreased, while the yield of **2a** was dramatically increased (entries 3 and 4). Addition of 30 equiv. of H_2O in the reaction had almost no adverse effects on the stitching thienannulation process (entry 5). Other sulfur reagents, such as $Na_2S{\cdot}9H_2O$ and S_8, were also employed as sulfur sources for the synthesis of **3a** albeit with much lower yields (entries 6 and 7). When the reaction between **1a** and S_8 was performed in the presence of 10 equiv. of Et_3N, **2a** was selectively formed in 98% yield (entry 8). Note that the yields of **3a** in these reactions are also close related to the concentrations of $S_3^{\bullet-}$ in the DMF solutions (see Fig. S1†).[20] Gratifyingly, performing the reaction of **1a** with 6 equiv. of K_2S at 25 °C for 10 min and then at 140 °C for 24 h led to the formation of **3a** in 83% yield (entry 9). This is obviously the fastest way to produce diarene-fused thienothiophenes (Scheme 1a).



Scheme 2 Thienannulations of **1a** and **3a′**.

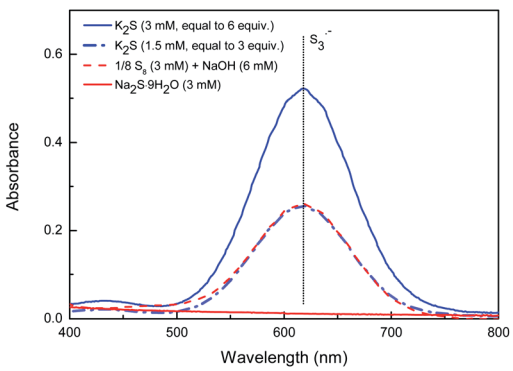
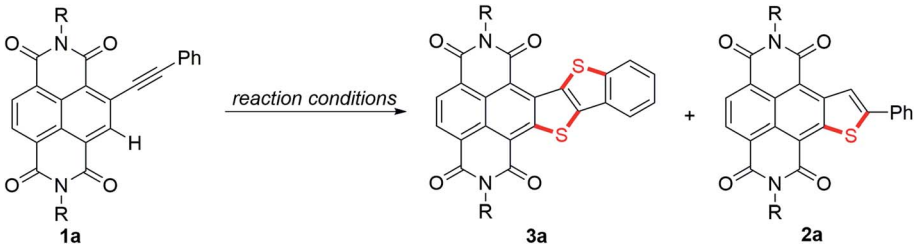


Fig. 1 UV-visible spectra of K_2S, S_8/NaOH and $Na_2S{\cdot}9H_2O$ in DMF.

Table 1 Optimization of reaction conditions[a]



Entry	Reaction conditions (reagent (equiv))	% Yield of **3a**[b]	% Yield of **2a**[b]
1	K_2S (6), 120 °C	51	19
2	K_2S (6), 140 °C	66	16
3	K_2S (4), 140 °C	42	44
4	K_2S (2), 140 °C	10	64
5[c]	K_2S (6), H_2O (30), 140 °C	60	19
6	$Na_2S{\cdot}9H_2O$ (6), 140 °C	20	15
7	S_8 (6), 140 °C	10	71
8	S_8 (6), Et_3N (10), 140 °C	Trace	98
9[d]	K_2S (6), 140 °C	83	16

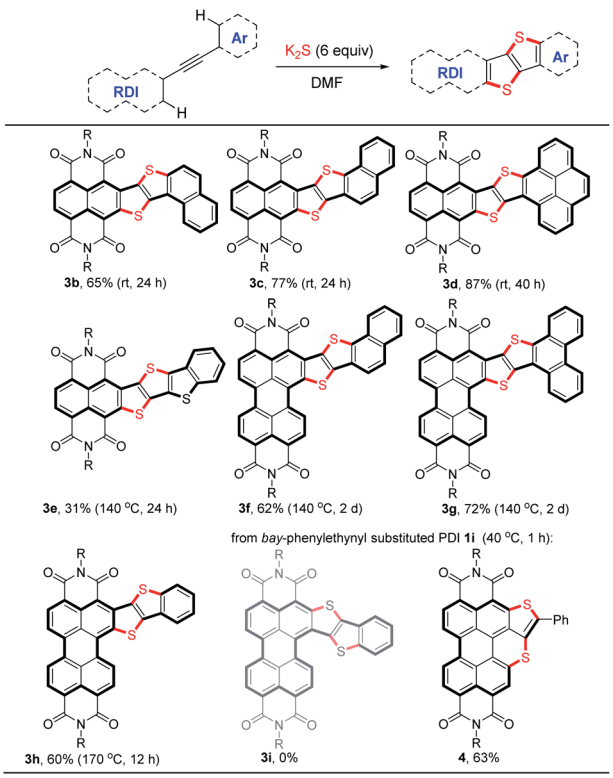
[a] Reactions were run in 0.03 mmol scale for 24 h in Ar (R = hexylheptyl). [b] Isolated yields of **2a** and **3a**. [c] 40 h. [d] Before heating at 140 °C, the reaction mixture was stirred at 25 °C for 10 min.

Substrate scope

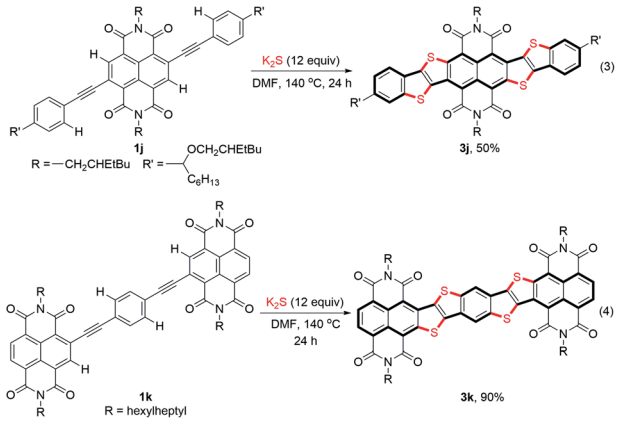
The scope of the double thienannulation was first examined with respect to four arylethynyl substituted NDIs **1b–e**, three *ortho*-arylethynyl substituted PDIs **1f–h**[21] and one *bay*-phenylethynyl substituted PDI **1i** (Table 2). The stitching thienannulations of (1-naphthyl)ethynyl-NDI **1b**, (2-naphthyl)ethynyl-NDI **1c** and (4-pyrenyl)ethynyl-NDI **1d**, all polycyclic aromatic hydrocarbon (PAH) derivatives, proceeded smoothly even at room temperature and afforded the corresponding NDI-fused thienoacenes **3b–d** in good yields (65–87%). The reaction between (2-benzothienyl)ethynyl substituted NDI **1e** and K_2S was performed at 140 °C and furnished **3e** in 31% yield. Besides these acetylenic NDIs, acetylenic PDIs were also susceptible to this transformation. The reactions of (2-naphthyl)ethynyl-PDI **1f** and (9-phenanthryl)ethynyl-PDI **1g** with K_2S were both carried out at 140 °C and afforded the corresponding PDI-fused thienoacenes **3f** and **3g** in 62% and 72% yields, respectively. Compared with the PAH derivatives **1f** and **1g**, less reactive *ortho*-phenylethynyl substituted PDI **1h** underwent double thienannulations at a higher temperature (170 °C), affording the desired product **3h** in 60% yield. In contrast, the reaction of *bay*-phenylethynyl substituted PDI **1i** with K_2S proceeded smoothly at 40 °C and furnished a thienobenzothiopyran product **4** in 63% yield. In this case, the desired PDI-fused thienoacene **3i** was not formed perhaps due to the much higher reactivity of PDI unit compared with phenyl ring during the $S_3^{\bullet-}$-triggered thienannulation.

Ladder-type heteroacenes with planar molecular backbones and zero conformational disorder are potentially promising candidates for many optoelectronic applications.[1f] Using the $S_3^{\bullet-}$-triggered stitching thienannulation approach, two large

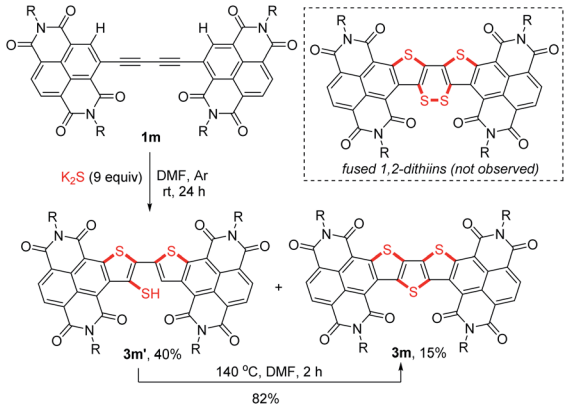
Table 2 Stitching thienannulations of arylacetylenic RDIs[a,b]



[a] Reactions were run in 0.03–0.05 mmol scale in Ar (R = hexylheptyl). [b] Isolated yields of **3** or **4** (reaction temperature and time are shown in parentheses).



Scheme 3 Stitching thienannulations of **1j** and **1k**.



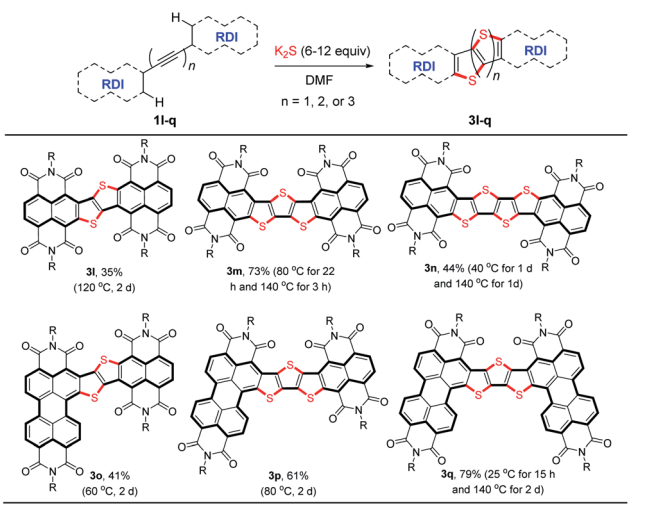
Scheme 4 Consecutive thienannulations of **1m**.

NDI-fused ladder-type thienoacenes **3j** and **3k** could be readily synthesized from the corresponding bisarylethynyl substituted NDI **1j** and *p*-phenylenediyne-linked NDI dimer **1k** in good yields (Scheme 3). Notably, during both of these two reactions, four *ortho*-C–H bonds in the starting compound were cleaved and functionalized in one-pot.

To further explore the potential applications of this stitching thienannulation strategy, ethyne-, butadiyne-, and hexatriyne-bridged RDI dimers **1l–q** were examined (Table 3). With appropriate amounts of K_2S, these oligoyne-tethered RDI dimers could directly undergo double, triple, or even quadruple thienannulations to furnish the corresponding π-extended thienoacenes **3l–q**.[22] The corresponding fused 1,2-dithiin products were not observed.[6a]

To figure out the detailed thienannulation process of oligoyne-bridged RDI dimers, both the reactions of butadiyne-bridged RDI dimer **1m** and **1q** with K_2S were carefully investigated at lower temperatures (Scheme 4 and Table S4†). Treatment of **1m** with 9 equiv. of K_2S in DMF at room temperature afforded not only the triple thienannulation product **3m** in 15% yield, but also a double thienannulation product **3m′** in 40% yield (Scheme 4).[22] Directly heating the DMF solution of **3m′** at 140 °C for 2 h produced **3m** in 82% yield. Similar reactions were also observed for **1q** (Table S4†), which provided insight into the selective formation of π-extended thienoacenes rather than fused 1,2-dithiins.

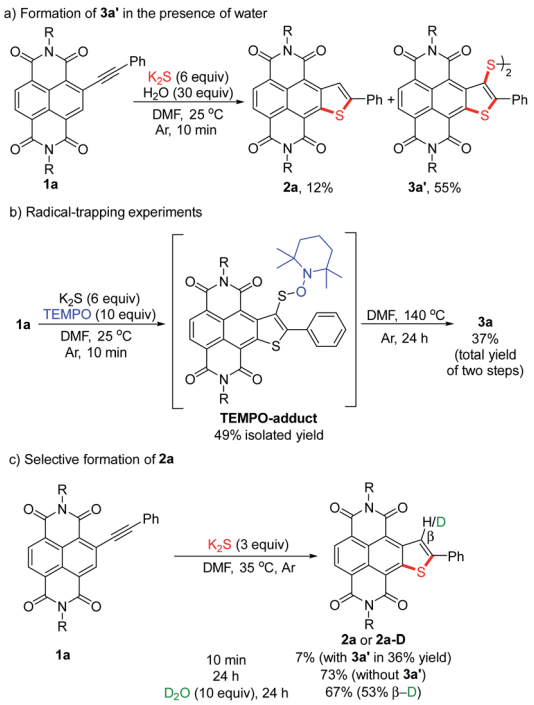
Table 3 Stitching thienannulations of oligoyne-bridged RDI dimers



[a] Reactions were run in 0.02–0.04 mmol scale in Ar (R = hexylheptyl). [b] Isolated yields of **3** (reaction temperatures and times are shown in parentheses).

Further mechanistic studies

To gain a deeper insight into the mechanism of the stitching thienannulation process, we then conducted additional experiments. First, the key step involving the formation of **2a** and **3a′**



Scheme 5 Mechanistic studies on the thienannulation of **1a**: (a) formation of **3a′** in the presence of water, (b) radical-trapping experiments and (c) selective formation of **2a**.

was investigated in detail (Scheme 5). For the reaction of **1a** with 6 equiv. of K_2S at room temperature for 10 min, the presence of 30 equiv. of H_2O did not significantly affect the yields of **2a** and **3a′** (Scheme 5a). When 10 equiv. of TEMPO as radical scavenger was added, a TEMPO-adduct was formed instead of the disulfide **3a′** (Scheme 5b, S2 and Fig. S7†). These results confirmed a radical mechanism. Later, directly heating the isolated TEMPO-adduct in DMF at 140 °C afforded the double thienannulation product **3a**. Based on this result, we speculate that a labile sulfurated thiophene intermediate that could be easily oxidized during work-up in air to produce **3a′** was formed in the reaction. During optimization of the reaction conditions (see Table S1†), we noticed that reducing the amount of K_2S led to the formation of **3a′** in lower yields. Other than that, as the reaction time increased, the yield of **3a′** decreased, while the yield of **2a** increased (for the reaction progresses monitored by UV-vis spectroscopy, see Fig. S5†). This changing trend of the yields is more evident for the reaction performed at a slightly higher temperature. For instance, although treatment of **1a** with 3 equiv. of K_2S at 35 °C for 10 min predominantly produced **3a′** in 36% yield, prolonging the reaction time to 24 h resulted in the selective formation of **2a** in 73% yield (Scheme 5c). Thereafter, the latter transformation was further investigated with a deuteration experiment (Scheme 5c). When adding 10 equiv. of D_2O in the reaction, **2a-D** was isolated in 67% yield with 53% deuterium incorporation at the β-position of the thiophene ring. These results indicate that the labile sulfurated thiophene intermediate can be slowly decomposed in Ar to afford a thiophene anion intermediate which is protonated to afford **2a**.[23] Therefore, based on the substrate scope and the above results, we proposed that the stitching thienannulation should be initiated with the attack of $S_3^{\bullet-}$ on either alkyne or RDI unit and a sulfurated thiophene intermediate is formed as a key intermediate (see Scheme S3† for a plausible mechanism).

Structural and physical properties of RDI-fused thienoacenes

These newly formed D–A (**3a–h**), D–A–D (**3j**) and A–D–A (**3k–q**) type thienoacenes possess three major structural advantages in exploration of excellent organic semiconductors: (1) the conformational rigidity that allows them to have reduced reorganization energies and favorable intermolecular π–π stackings; (2) extended π-conjugation lengths and increased electron delocalization, leading to reduced bandgaps and broadened absorptions; and (3) strong dipole–dipole and sulfur–sulfur interactions which lead to ordered intermolecular arrangements. In addition, these molecules all have good solubilities in common organic solvents, such as CH_2Cl_2, $CHCl_3$, toluene and tetrahydrofuran, which is beneficial for solution processing. To gain a deeper insight into their photophysical properties, UV-vis absorption measurements of **3a–h** and **3j–q** were performed (Fig. S10–S12†). Compared with simple core-unsubstituted NDI, PDI and mono-thiophene-fused NDI **2a**, these RDI-fused thienoacenes exhibited large bathochromic shifts in their UV-vis absorption spectra due to the extension of π-conjugation. Moreover, higher intensities of absorption peaks in the long-wavelength region suggested a strong intramolecular charge

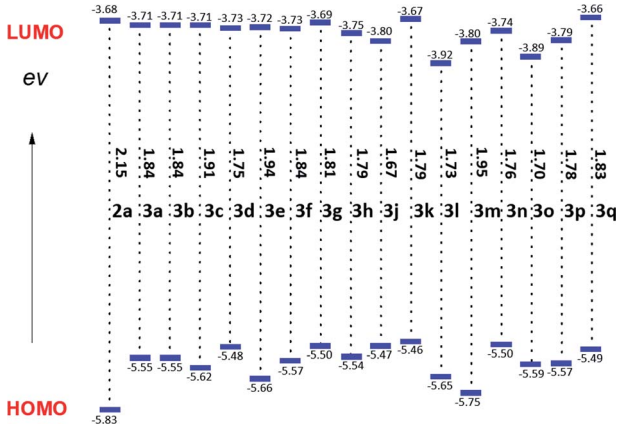


Fig. 2 Energy level diagram of RDI-fused thienoacenes **3a–h** and **3j–q**.

transfer in RDI-fused thienoacenes. Thereafter, the electrochemical properties of **3a–h** and **3j–q** were compared using cyclic voltammetry (Fig. 2, S13–S15 and Table S5†). Compared to **2a**, eight D–A type thienoacenes **3a–h** have similar reduction potentials, whereas their oxidation potentials are finely tuned by the variation of fused-thiophene-ring and conjugation length, indicating that the LUMOs tend to localize on the RDI skeleton and the HOMOs tend to delocalize in the lateral direction.[15] Compared to these asymmetric fused D–A systems, symmetric D–A–D type thienoacene **3j** has an obviously lower LUMO level, indicating its higher electron affinity.[7b] For A–D–A type thienoacenes **3k–q**, the HOMO and LUMO energy levels increase as the donor length increase because the large conjugation enhances the electron donating abilities, resulting in narrowed bandgaps. Moreover, compared to NDI fused A–D–A type thienoacenes, PDI fused counterparts have higher LUMO levels and exhibit more red-shifted UV-vis spectra. All these results suggested that the variation in the relative strengths of donor (ladder-type fused thiophene rings) and acceptor (RDI units), fused-ring number, and ring-fusion sequence in these D–A, D–A–D and A–D–A systems allowed finetuning of their absorption profiles, energy levels and charge–transport properties, which may eventually enable practical applications as organic semiconducting materials.

Conclusions

In conclusion, we have developed a novel $S_3^{\bullet-}$-triggered stitching thienannulation approach for the rapid construction of RDI-fused, largely π-extended thienoacenes from ethyne-, butadiyne-, and hexatriyne-linked π-systems. With this facile and straightforward strategy, thieno[3,2-*b*]thiophene-, dithieno[3,2-*b*:2′,3′-*d*]thiophene and tetrathienoacene substructures can be readily constructed in a stitching manner. Detailed mechanistic studies revealed the unique reactivity of $S_3^{\bullet-}$ and displayed the high reactivities of π-deficient RDI rings toward the radical thienannulation process. Furthermore, interesting properties including planar conformation, extended conjugation and precisely controllable electronic properties are integrated into

these novel fully fused electron donor–acceptor molecules, which are promising candidates for high performance organic semiconductors. These findings are anticipated to provide new opportunities to explore more general methods for the synthesis of useful organosulfur compounds.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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