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Direct synthesis of spirobifluorenes by formal dehydrative coupling of biaryls and fluorenones†

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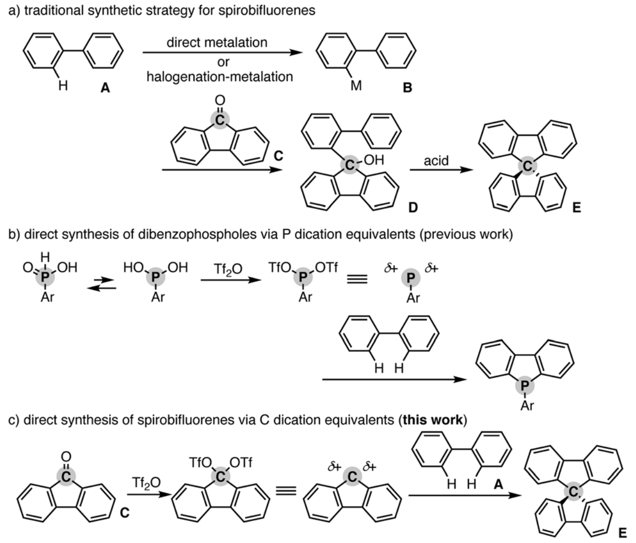
A Tf_2O-mediated, direct dehydrative coupling of (hetero)biaryls and fluorenones proceeds to form the corresponding spirobifluorenes in good to high yields. The reaction system allows the relatively simple nonhalogenated and nonmetalated starting substrates to be directly adopted in the spirocyclisation reaction. In addition, the double cyclisation reaction is easily performed, giving the highly spiro-conjugated aromatic compounds of potent interest in materials chemistry. The preliminary optoelectronic properties of some newly synthesised compounds are also demonstrated.

Introduction

Spiro compounds have received significant attention in the research field of organic optoelectronics.[1] In particular, spirobifluorene (SBF) is a promising structural candidate in the design of organic functional materials such as organic field-effect transistors,[2] light-emitting diodes,[3] and solar cells[4] because of its unique homo-conjugation (spiro-conjugation) increasing the hole transporting ability[5] and rigidity based on the perpendicular arrangement of two π systems that generally provides a high glass temperature (T_g) for the preferable amorphous glassy state.[6] Additionally, in specific cases, SBF has chirality at the spiro carbon and thus intriguing chiroptical properties for application as a circular polarized luminescence (CPL) material.[7] Accordingly, numerous π-conjugated compounds incorporated with the SBF moiety have been designed and synthesised. However, their synthetic method still relies on tedious multistep sequences. In general, the starting simple biaryl **A** is metalated directly or indirectly *via* stepwise halogenation and metalation. The formed metalated biaryl **B** is then coupled with the fluorenone **C** to form the corresponding tertiary alcohol **D**. The final ring closure by the action of a Brønsted or Lewis acid produces the desired SBF **E** (Scheme 1a). Herein, we report a Tf_2O-mediated formal dehydrative coupling of biaryls and fluorenones under relatively mild conditions (in DCE at 40–110 °C). By using this strategy, several hydrocarbon-based and heteroatom-incorporated SBFs are accessible directly without preparation and isolation of any halogenated and metalated intermediates. Moreover, the 1 : 2 couplings of biaryls and fluorenones are also possible, allowing the streamlined synthesis of largely π-extended molecules with two SBF moieties.

Our group recently developed a concise synthetic method for the preparation of dibenzophospholes from simple biaryls and phosphinic acids.[8] The active species is the highly coordinately unsaturated phosphenium dication, which is generated from the phosphinic acid and Tf_2O, and then readily reacts with the simple biaryl to form two C–P bonds in one synthetic operation (Scheme 1b). Inspired by the phosphenium dication chemistry, we envisioned a new synthetic route to the SBF **E** from the simple biaryl **A** and fluorenone **C** *via* a carbon dication: if the


a) traditional synthetic strategy for spirobifluorenes
b) direct synthesis of dibenzophospholes via P dication equivalents (previous work)
c) direct synthesis of spirobifluorenes via C dication equivalents (**this work**)

Scheme 1 (a) General synthetic scheme of spirobifluorenes, (b) direct synthesis of dibenzophospholes from simple biaryls *via* P dication equivalents, and (c) working scenario of direct synthesis of spirobifluorenes from simple biaryls *via* C dication equivalents.

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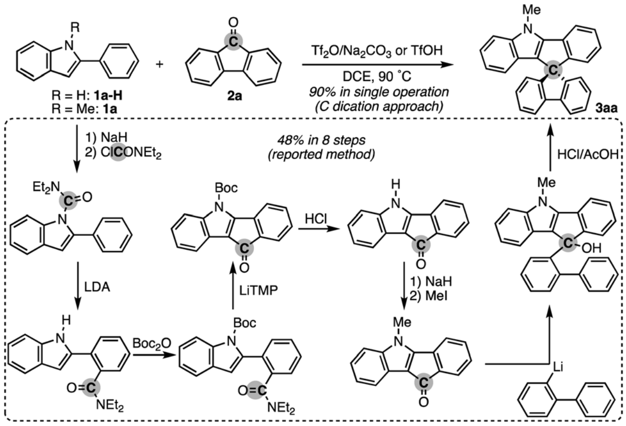
C═O function of fluorenone **C** is activated by Tf_2O, the formed carbon ditriflate can work as a carbon dication equivalent to deliver the SBF **E** directly through double C–C bond formation with the simple bialy **A** (Scheme 1c).[9] We also note that during the course of this study, Wang and Yang reported a related approach to spiro-acridans from fluorenones in the presence of *p*-TsOH as an activator, but the coupling partner was limited to diphenylamine, and the simple (hetero)biaryl was not tested.[10] Moreover, a high reaction temperature (200 °C) was necessary to promote the reaction. Thus, our strategy is complementary to the work by Wang and Yang from the viewpoint of substrate scope.

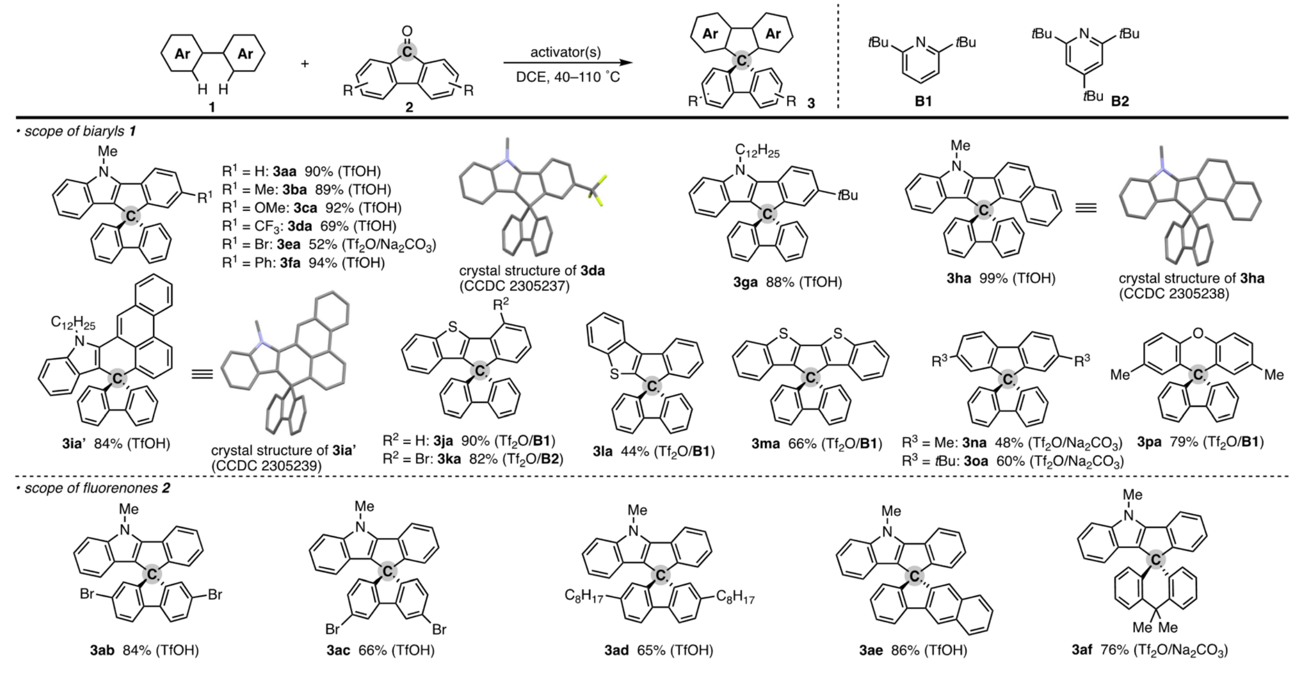


Scheme 2 Comparison of the C dication equivalent strategy (top) *vs.* reported method (bottom) in the synthesis of *N*-incorporated spirobifluorene **3aa**: Boc = *tert*-butoxycarbonyl, LDA = lithium diisopropylamide, and LiTMP = lithium tetramethylpiperidide.

Results and discussion

To test the aforementioned hypothesis, we chose the synthesis of indole-containing SBF **3aa** from 2-phenylindole **1a-H** and fluorenone (**2a**) as the model reaction because the synthesis of **3aa** was achieved but through a long-step sequence, including (1) *N*-carbamoylation, (2) LDA-mediated *N*-to-*C* carbamoyl migration, (3) *N*-Boc protection, (4) directed metalation/intramolecular acylation, (5 and 6) *N*-substituent switch from Boc to Me, (7) coupling with 2-lithiated biphenyl, and (8) ring closure using HCl/AcOH (48% total yield in 8 steps; Scheme 2; bottom route).[11] In sharp contrast, our strategy is much more straightforward: upon treatment with **2a**, Tf_2O, and Na_2CO_3 in heated 1,2-dichloroethane (DCE), the *N*-methylated indole **1a** (readily prepared and commercially available) was directly converted to **3aa** in 90% yield (Scheme 2; top route). In this case, the simple Brønsted acid, TfOH, also promoted the reaction with comparable efficiency. This comparison scheme shows the considerable synthetic advantage of our reaction design based on the carbon dication equivalent (see the ESI† for detailed optimization studies).

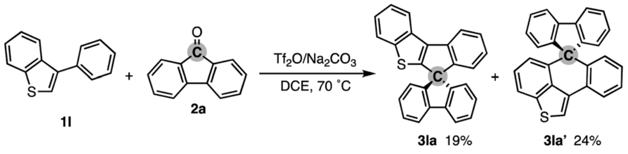
To check the generality of our strategy, we first investigated the scope of biaryls **1** with fluorenone **2a** (Scheme 3). The 2-arylindoles that bear both electron-donating and -withdrawing groups were compatible to form the corresponding *N*-containing SBFs **3ba–fa** in one synthetic operation, where the electro-rich substrates showed better performance (**3aa–ca**, **fa** *vs.* **3da–ea**), reflecting the electrophilic substitution mechanism of this process. The structure of **3da** was determined by X-ray crystallographic analysis (CCDC 2305237).† Additionally, the reaction conditions can obviate the reactive organometallic reagents



Scheme 3 Products of formal dehydrative coupling of simple biaryls **1** and fluorenones **2**. Isolated yields are shown. The activator(s) used is in parentheses. See the ESI† for detailed reaction conditions. In the crystal structures, hydrogens and long alkyl side chains are omitted for clarity.

such as organo-lithiums and -magnesiums, which were inevitable in literature methods,[1] and thus **1e** was transformed to **3ea** with the Ar–Br moiety left intact, which can be a useful synthetic handle for further manipulation. This protocol was also tolerant of the longer alkyl chain on the nitrogen (**3ga**), which is known to generally enhance lipophilicity and solubility and to tune the aromatic π-stacking and π-conjugation of the corresponding oligomers and polymers. In the case of 2-naphthyl-substituted **1h**, the cyclisation occurred selectively at the more sterically congested but more electron-rich C1 position (**3ha**; CCDC 2305238),† again indicating the electronically controlled substitution reaction. In contrast, the higher fused phenanthrene substrate exclusively formed the spiro[4.5] system **3ia′** over the SBF, which was confirmed by the X-ray analysis (CCDC 2305239).† Not only the 2-arylindoles but also several thiophene derivatives could be employed: intriguingly, in these cases the combination of Tf_2O and sterically crowded 2,6-di(*tert*-butyl) pyridines (**B1** and **B2**) uniquely promoted the reaction. For example, 2-arylbenzothiophenes **1j** and **1k** directly afforded the corresponding spirocycles **3ja** and **3ka** in 90 and 82% yields, respectively. Under conditions using Tf_2O/Na_2CO_3 or TfOH, the yields decreased by *ca.* 30% (data not shown). In the reaction of the regioisomeric 3-phenylbenzothiophene (**1l**), the effect of the pyridine base was more remarkable: **B1** provided the desired SBF **3la** exclusively, while the inorganic Na_2CO_3 base formed a mixture of **3la** and its constitutional isomer **3la′** (Scheme 4). The results suggest the involvement of the pyridine base in the C–C bond forming step.[12] Moreover, 2,2′-bisbenzothiophene-based SBF **3ma** was readily accessible under the Tf_2O/**B1** conditions. Particularly notable is the successful use of simple 4,4′-dimethyl- and di(*tert*-butyl)biphenyls to furnish the corresponding spiro hydrocarbons **3na** and **3oa** in synthetically useful yields. Furthermore, the reaction accommodated the synthesis of spiro[fluorene-9,9′-xanthene] from the diaryl ether (**3pa**), which receives significant attention as the core structure in the design of organic electronics and light emitting devices.[13]

In addition to the parent **2a**, several substituted fluorenones were coupled with **1a**: 2,7- and 3,6-dibromofluorenones both were viable to deliver the brominated **3ab** and **3ac** in good yields. In particular, the latter substitution pattern is generally difficult to obtain by the conventional electrophilic bromination of the simple SBF.[1,14] The long alkyl side chain on the fluorenone was also amenable (**3ad**). The reaction of benzofluorenone proceeded smoothly to enable the facile construction of chiral SBF **3ae**. Additionally, the xanthone derivative could also be used, thus providing access to the spiro [4.5] system **3af.**[15]



Scheme 4 Competitive formation of 3la′ from 1l and 2a under Tf_2O/Na_2CO_3 conditions.

The salient advantage of this concise and one-pot strategy is demonstrated more clearly in the attempt to synthesise more conjugated doubly spirocyclic compounds (Fig. 1). The coupling of 2,6-diphenylpyrroloindole **1q** and two equivalent of fluorenone (**2a**) was promoted by simple treatment with TfOH, and the corresponding double spirocycle **3qa** was isolated in a nearly quantitative yield. The 2,6-bis(indole)naphthalene **1r** also reacted with **2a** regioselectively at the C1 and C5 positions under the same conditions to furnish **3ra** as the single isomer in 57% yield. The carbazole also worked as the reactive *N*-heteroaromatic core, and the two-SBF-fused pyrrole **3sa** was formed in the single operation. The structures of three *N*-containing double spirocycles were unambiguously determined by X-ray crystallographic analysis (CCDC 2305240, 2305241, and 2305242).† Promising reactivity was also observed in the synthesis of thiophene-incorporated derivatives: 3,4-diphenylthiophene **1t** was readily converted to **3ta** in 97% yield (CCDC 2305243).† The synthetic route to **3ta** from **1t** was reported, but it required multistep sequences involving stepwise lithiation or stoichiometric halogenation/metalation and suffered from low to moderate overall yield (25–41%).[16] Thus, the straightforward access to **3ta** further shows the beneficial point of our protocol. Moreover, the thienothiophene **1u** and benzothiophene end-capped naphthalenes **1v** and **1w**, which are candidates of the core structure of organic field-effect transistors, could be easily decorated by two-fold spirocyclisation to produce **3ua**, **3vd**, and **3wd** (CCDC 2305244).† A similar 1 : 2 coupling of simple aromatic hydrocarbon, terphenyl **1x**, and fluorenone (**2a**) was also possible, giving **3xa** with exclusive regioselectivity (CCDC 2305245).† While a related structural motif was generally prepared from prefunctionalised terphenyls such as diiodoterphenyls and indenofluorenedione,[17] the present carbon dication strategy enables the direct use of relatively simple precursor **1x.** The double spirocyclisation reaction was applicable to the diaryloxynaphthalene **1y**, and fused spirofluorenexanthene **3ya** of potent interest in materials chemistry[13] was obtained regioselectively in a synthetically acceptable yield.

The optical properties of double spirocycles obtained in Fig. 1 were preliminary surveyed in a solution state (1.0×10^{-5} M $CHCl_3$ solution). Only for the pyrroloindole **3qa**, the spectra were obtained in diluted toluene solution due to its instability in $CHCl_3$. The results are summarized in Fig. 2 and Table 1. In the *N*-containing systems (**3qa**–**3sa**), relatively high quantum yields were obtained probably because of the effective conjugation and rigidity based on the spiro system. In particular, **3qa** and **3ra** showed the absorption peaks in the visible light region and relatively strong blue fluorescence with maxima at $\lambda = 440$ and 469 (**3qa**) and 475 (**3ra**) nm, respectively. On the other hand, thiophene and thienothiophene derivatives **3ta** and **3ua** resulted in poor quantum yields, but the higher fused bisbenzothiophene derivatives **3vd** and **3wd** improved the performance. Additionally, while the figures of both absorption and emission spectra are similar, **3vd** has more intensive absorbance in the long-wavelength region than **3wd**, thus suggesting that the direction of the benzothiophene fusion largely affects photoluminescence efficiency. The hydrocarbon **3xa** also

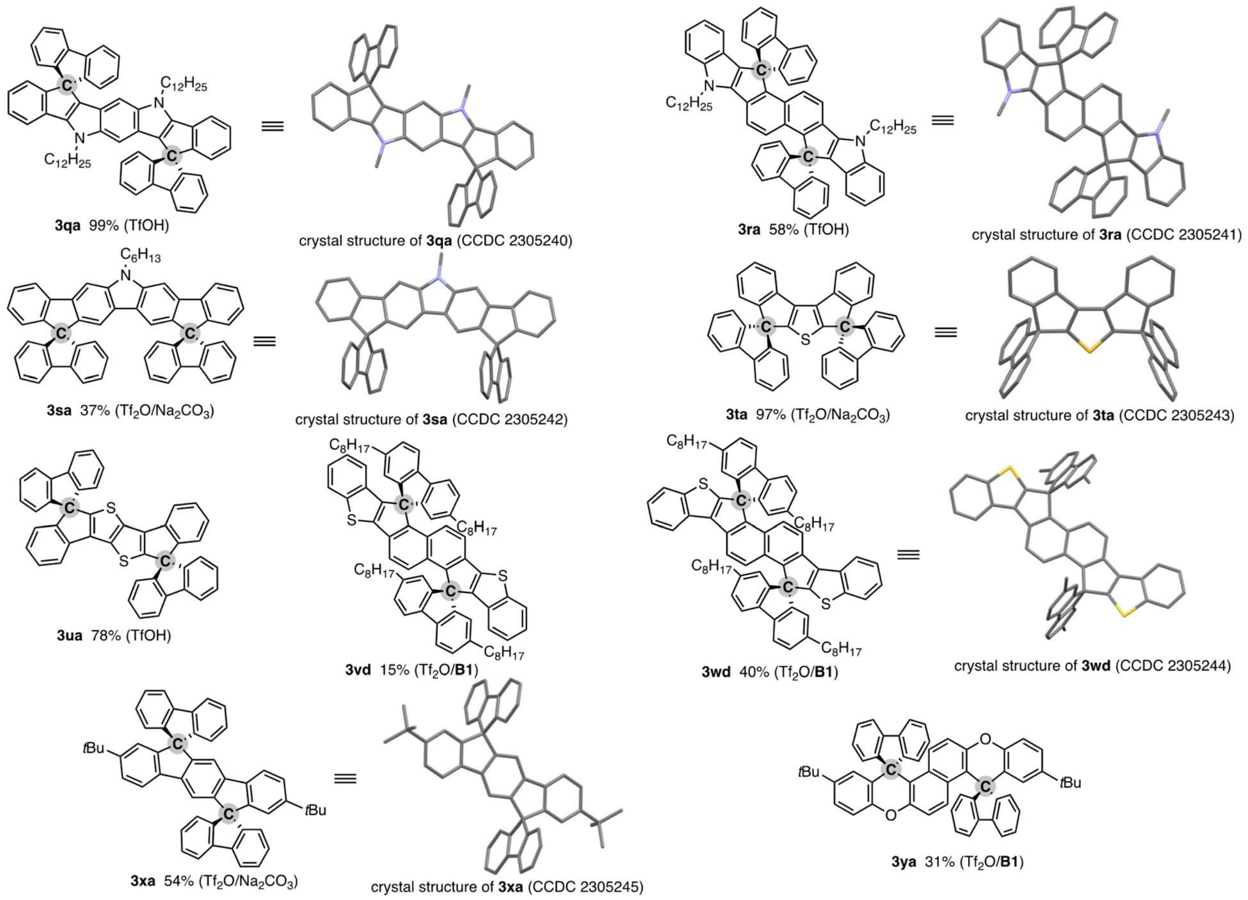


Fig. 1 Products of formal dehydrative coupling of simple biaryls **1** and fluorenones **2**. Isolated yields are shown. The activator(s) used is in parentheses. See the ESI† for detailed reaction conditions. In the crystal structures, hydrogens and long alkyl side chains are omitted for clarity.

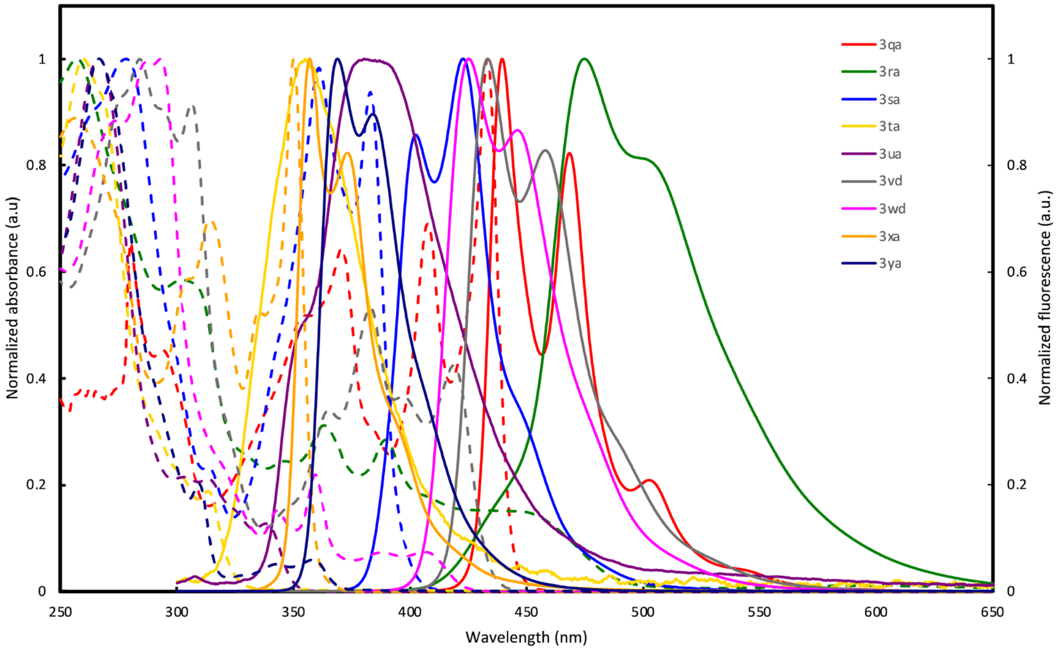


Fig. 2 UV-vis absorption (dashed line) and fluorescence spectra (solid line) of **3qa**, **3ra**, **3sa**, **3ta**, **3ua**, **3vd**, **3wd**, **3xa**, and **3ya** in solution (1.0 × 10^{-5} M).

Table 1 Optical properties of **3qa**, **3ra**, **3sa**, **3ta**, **3ua**, **3vd**, **3wd**, **3xa**, and **3ya**[a]

3	λ_{abs} (nm) (ε (10^4 M^{-1} cm^{-1}))	λ_{Fl}[b] (nm)	Φ (%)
3qa	280 (3.1), 371 (3.0), 408 (3.2), 433 (4.7)	440, 469	83
3ra	303 (3.2), 363 (1.7), 390 (1.6), 447 (0.83)	475	39
3sa	278 (6.1), 361 (6.0), 383 (5.7)	403, 423	49
3ta	260 (4.8), 313 (0.90)	355	4
3ua	266 (7.5), 303 (1.6), 313 (1.6), 338 (0.96)	381	5
3vd	284 (8.0), 306 (7.4), 365 (2.7), 383 (4.3), 397 (2.9), 419 (3.4)	434, 458	48
3wd	287 (9.6), 293 (9.7), 343 (1.5), 359 (2.1), 388 (0.70), 406 (0.71)	425, 446	20
3xa	305 (2.1), 314 (2.5), 335 (1.9), 350 (3.6)	357, 373	43
3ya	266 (7.3), 309 (1.5), 343 (0.37), 358 (0.43)	369, 384	19

[a] Measured in 1.0×10^{-5} M solution of toluene (**3qa**) and $CHCl_3$ (**3ra–3ya**). [b] Excited at λ_{abs}.

resulted in a relatively high quantum yield owing to the incorporation of the perpendicular SBF architecture.

We also examined the electrochemical properties of the *N*- and *S*-containing doubly cyclised SBFs by cyclic voltammetry (CV) in *o*-dichlorobenzene/MeCN (10/1, v/v) with tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) as an electrolyte *versus* ferrocene/ferrocenium ions (Fc/Fc$^+$) (Fig. S23–29†), and their HOMO and LUMO levels were estimated according to the first oxidation potentials and the optical band gaps (E_g^{opt}). The data are summarized in Table 2. The CV of **3qa**, **3ra**, **3vd**, and **3wd** showed two-step, reversible oxidation waves associated with their two pyrrole (**3qa** and **3ra**) and thiophene rings (**3vd** and **3wd**), respectively, and their $E_{ox}^{1/2}$ values are relatively shifted in a negative direction. In particular, the first oxidation potential of **3qa** was significantly lower, which is reflected by the highly rigid and electron-rich two-indene-fused pyrroloindole core. On the other hand, the HOMO–LUMO energy gap is relatively narrow for the two-indole-fused octacyclic system **3ra**, suggesting its larger intramolecular charge transfer ability. Both the HOMO and LUMO levels of regioisomeric **3vd** and **3wd** are almost the same. Thus, in contrast to the photoluminescent properties (Table 1), their electrochemical properties are less dependent on the thiophene ring orientation.

Table 2 Absorption wavelengths, HOMO–LUMO energy gaps and cyclic voltammogram data of compounds **3qa**, **3ra**, **3sa**, **3ta**, **3ua**, **3vd**, and **3wd**

3	λ_{onset}^{abs}[a] (nm)	E_g^{opt}[b] (eV)	$E_{ox}^{1/2}$[c] (V)	E_{HOMO}[d] (eV)	E_{LUMO}[e] (eV)
3qa	440	2.82	0.0085	−4.81	−1.99
3ra	480	2.58	0.309	−5.11	−2.53
3sa	401	3.09	0.665	−5.47	−2.38
3ta	328	3.78	1.05	−5.85	−2.07
3ua	348	3.56	0.843	−5.64	−2.08
3vd	432	2.87	0.647	−5.44	−2.58
3wd	420	2.95	0.628	−5.43	−2.48

[a] Measured in toluene (**3qa**) and $CHCl_3$ (**3ra–3wd**). [b] Determined from the onset of the normalized absorption spectra. [c] Performed in *o*-dichlorobenzene/MeCN (10 : 1, v/v) in the presence of Bu_4NPF_6. ν = 10.0 mV s^{-1} (**3qa**, **3ra**, and **3sa**), 5.0 mV s^{-1} (**3ta**, **3ua**, and **3vd**), and 4.0 mV s^{-1} (**3wd**), *versus* Fc/Fc$^+$. [d] The approximation for the Fc/Fc$^+$ level is −4.8 eV *versus* vacuum: $E_{HOMO} = -4.8 - E_{ox}^{1/2}$. [e] Estimated from E_{HOMO} and E_g^{opt}: $E_{LUMO} = E_{HOMO} + E_g^{opt}$.

Conclusions

We have developed a formal dehydrative coupling reaction of (hetero)biaryls and fluorenone derivatives. The reaction proceeds well under metal-free TfOH- or Tf_2O-promoted conditions, in which two C–C bonds are sequentially formed and the corresponding spirobifluorenes (SBFs) are obtained directly. This protocol does not necessitate any halogenated and metalated starting substrates/intermediates and thus is quite simple, practical, and beneficial from the viewpoint of functional group compatibility. Actually, the reaction was tolerant of the Ar–Br moiety, which can be further functionalised by the established cross-coupling chemistry. Moreover, the present reaction can be applicable to double cyclisation to deliver largely π-conjugated SBFs in one synthetic operation. Given their unique homo-conjugation and rigidity based on the perpendicular arrangement of two π systems, the obtained doubly spiro SBFs are of potent interest in materials chemistry. Further expansion of substrate scope, development of catalytic conditions, and application to chiral SBF molecules are ongoing in our laboratory.

Data availability

All experimental procedures and spectroscopic data can be found in the ESI.†

Author contributions

K. N. and K. H. conceived the idea. Y. K. and K. N. performed all experiments. Y. N. assisted with X-ray analysis. K. H. supervised the project and wrote the manuscript. All the authors discussed the results and commented on the manuscript.

Conflicts of interest

There are no conflicts to declare.

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