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Improved Synthesis of 2,2′-Dibromo-9,9′-spirobifluorene and Its 2,2′-Bisdonor-7,7′-bisacceptor-Substituted Fluorescent Derivatives

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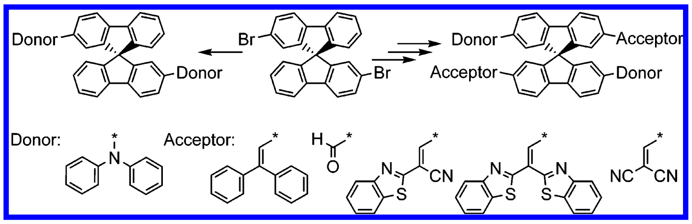
ABSTRACT



Pure 2,2′-Dibromo-9,9′-spirobifluorene was synthesized by a method that did not involve troublesome dibromination of 9,9′-spirobifluorene or Sandmeyer reaction of 2,2′-diamino-9,9′-spirobifluorene. A series of donor–acceptor orthogonally substituted 9,9′-spirobifluorene was subsequently prepared showing rich variation of fluorescence in solution and in solid state.

Although there are abundant optical and electronic molecular materials or polymers that are derived from 2,7-dibromo-9,9′-spirobifluorene,[1] very few materials originate from the closely related isomer 2,2′-dibromo-9,9′-spirobifluorene.[2] This drastic difference is mainly due to the easy preparation of 2,7-dibromo-9,9′-spirobifluorene, which is readily synthesized from 2,7-dibromo-9-fluorenone by reacting with a Grinard reagent of 2-bromobiphenyl.[1b] According to both literature and patent, 2,2′-dibromo-9,9′-spirofluorene can be prepared by direct bromination of 9,9′-spirobifluorene in the presence of a catalytic amount of ferric chloride.[3] However, in our earlier report,[2a] we have encountered difficulty in the preparation and isolation of pure 2,2′-dibromo-9,9′-spirobifluorene.[4] Alternatively, 2,2′-dibromo-9,9′-spirofluorene can be prepared by the replacement of amino group of 2,2′-diamino-9,9′-spirobifluorene by cupric bromide following conventional Sandmeyer procedure.[2a] In addition to biphenyl-, azobenzene-, and phenol-type side products, Sandmeyer reactions are often plagued with position isomers of halide substituent.[5] In this case, 2,2′-dibromo-9,9′-spirobifluorene was obtained together with 2,3′-dibromo-9,9′-spirobifluorene

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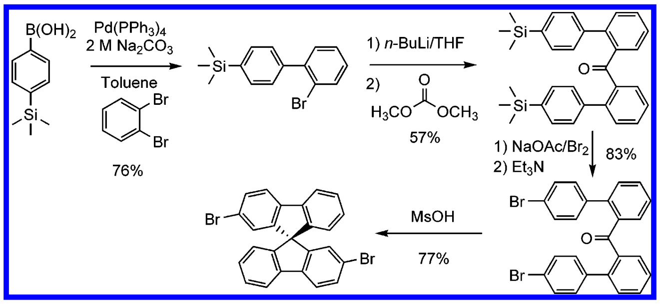
and 2,2,3′-tribromo-9,9′-spirobifluorene as well, and the separation of these isomers remains difficult and greatly hampers materials applications. Here, an improved and reliable synthesis has been developed for the preparation of 2,2′-dibromo-9,9′-spirofluorene. We also illustrate a new series of 2,2′-bisdonor-7,7′-bisacceptor-substituted 9,9′-spirobifluorene compounds as colorful fluorescent materials prepared from now readily accessible and pure 2,2′-dibromo-9,9′-spirofluorene.

The key starting material in the preparation of 2,2′-dibromo-9,9′-spirobifluorene is 4-(trimethylsilyl) benzeneboronic acid, which is commercially available. It can be also readily prepared in a two-step reaction from 1,4-bibromobenzene and chlorotrimethylsilane followed by the treatment of *n*-BuLi and trimethylborate in formation of boronic acid.[6] The desired 2,2′-dibromo-9,9′-spirobifluorene was prepared in 4 steps from 4-(trimethylsilyl)benzeneboronic acid in total overall yields near 30% (Scheme 1). The new preparation first involved the generation of (2′-bromobiphenyl-4-yl)-trimethylsilane and it was easily achieved by Suzuki cross-coupling of (trimethylsilyl)benzeneboronic acid and 1,2-dibromobenzene. The second step of the synthesis led to the ketone-connected dimer of (2′-bromobiphenyl-4-yl)trimethylsilane that was treated with *n*-BuLi and reacted with 0.5 equiv of dimethyl carbonate in a fashion similar to the preparation of bis(3′-methoxybiphenyl-2-yl)methanone.[7] The following bromodesilation of the disilane compound by sodium acetate and bromine easily afforded bis-(4′-bromobiphenyl-2-yl)methanone. The target product was thus obtained by classical Clark and Gomberg method in the present of strong acid of methanesulfonic acid.[8] The 2,2′-dibromo-9,9′-spirobifluorene compound prepared by the new method was pure (see its ^{1}H NMR spectrum in Figure 1) and its chemical structure was firmly identified (see its X-ray crystal structure in Figure 2). The new synthesis method is efficient and reliable. Multigram quantity of 2,2′-dibromo-9,9′-spirobifluorene can be prepared readily (here 4.6 g of the analytically pure product was obtained in one round).

Scheme 1



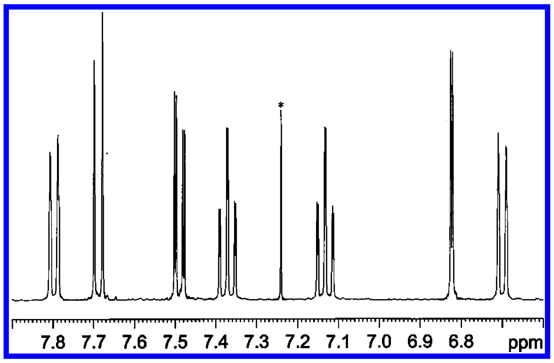


Figure 1. ^{1}H NMR spectra (CDCl$_3$) of 2,2′-dibromo-9.9′-spirobifluorene. Please see ref 2a for the signal assignment.

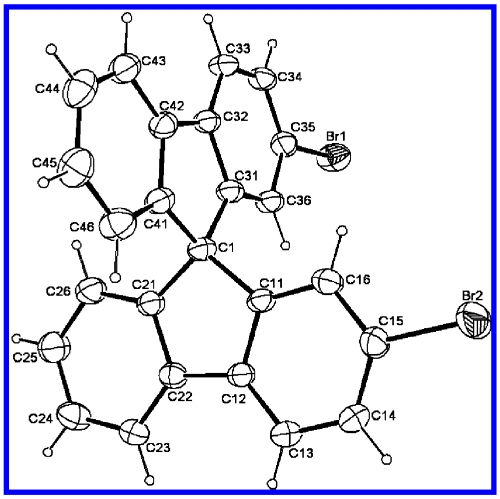


Figure 2. Single-crystal X-ray structure of 2,2′-dibromospirobifluorene.

With a sufficient amount of pure 2,2′-dibromo-9,9′-spirobifluorene, we quickly prepared a series of new fluorescent 9,9′-spirobifluorene derivatives based on orthogonally constructed pair of donor−acceptor substituents

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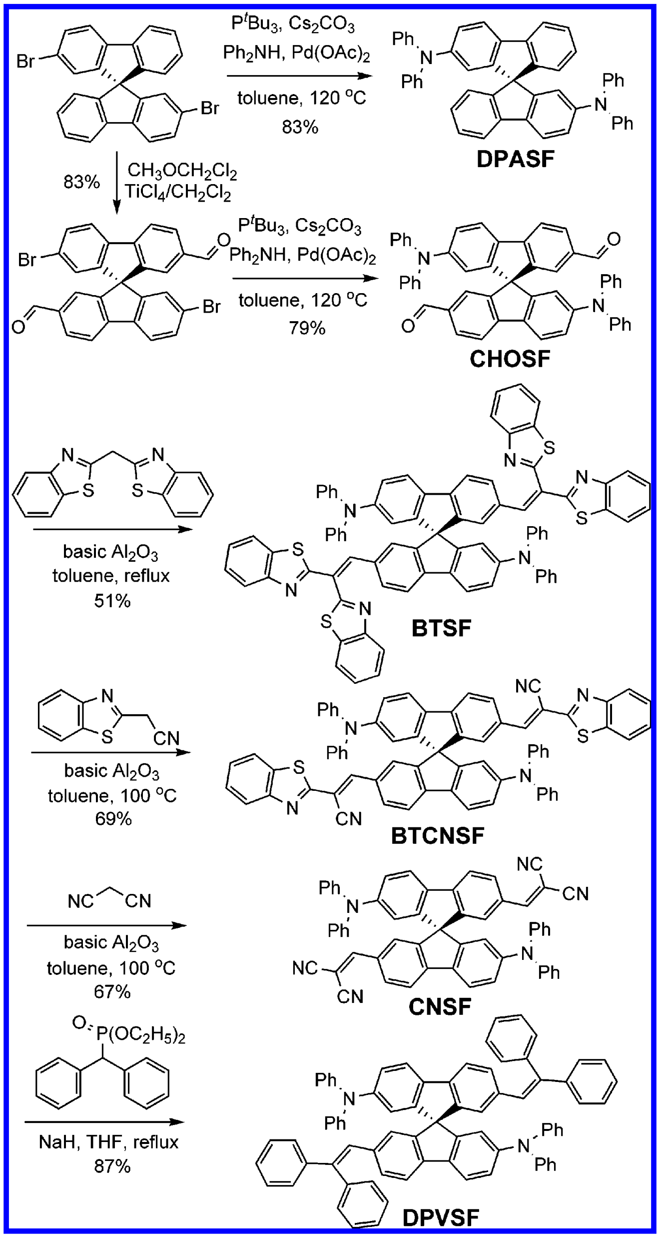
Scheme 2



(Scheme 2). **DPASF** was directly obtained from 2,2′-dibromo-9,9′-spirobifluorene by Pd-catalyzed aromatic amination reaction. Similarly, **CHOSF** was synthesized from 2,2′-dibromo-7,7′-diformyl-9,9′-spirobifluorene, which was easily prepared by the one-step di-formylation of 2,2′-dibromo-9,9′-spirobifluorene carried on using CH_3OCHCl_2/$TiCl_4$ with a 83% yield.[9] Using aldehyde **CHOSF** as the common starting material, various acceptor bisbenzothiazolylvinyl-, benzothiazolylcyanovinyl-, or dicyanovinyl-appended **DPASF**, i.e., **BTSF**, **BTCNSF**, and **CNSF** were smoothly generated in 51−69% yields under Knoevenagel conditions (basic Al_2O_3 in dry toluene). For the synthesis of **DPVSF**, the efficient Horner−Wadsworth−Emmons reaction was conducted for the formation of the C−C double to connect **DPASF** and diethoxy diphenylmethylphosphonate.[10]

Except for **BTSF**, all new donor−acceptor-substituted 9,9′-spirobifluorene compounds showed pronounced fluorescence in solution (Figure 3). Six new spirobifluorenes exhibited fluorescence with varied colors ranging from the deep blue (λ^{fl}_{max} 401 nm) of **DPASF**, sky blue (λ^{fl}_{max} 480 nm) of **DPVSF**, green blue of **CHOSF** (λ^{fl}_{max} 495 nm), yellow orange (λ^{fl}_{max} 549 nm) of **BTSF**, orange red (λ^{fl}_{max} 601 nm) of **BTCNSF**, to the vivid red (λ^{fl}_{max} 620 nm) of **CNSF**. When they were in the form of a solid film, red-shifting fluorescence generally took place. Fluorescence with different brightness was observed for these fluorophores in solution as well in solid state. Qualitatively, solid-state fluorescence intensities (fluorescence quantum yields, ϕ^{fl}s) in general follow the same order as those in solution (Table 1). The strongest fluorescence was found for **DPVSF** and **CHOSF**; DPASF and **CNSF** showed second-rate fluorescence; weak fluorescence or no fluorescence was observed for **BTCNSF** and **BTSF**, respectively. Considering the strong fluorescence in solid state, some of the fluorophores in this report are worth further investigation for potential application of organic

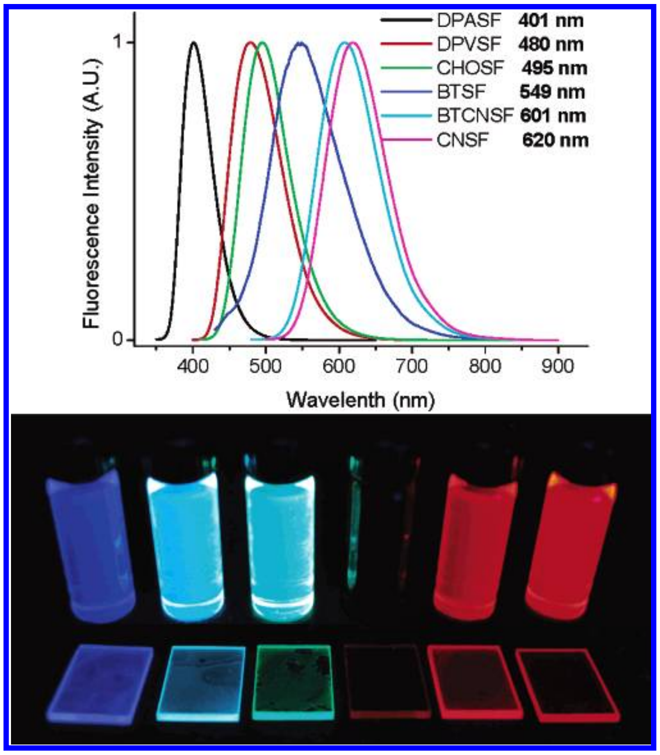


Figure 3. Top: fluorescence spectra of 2,2′-bisdonor-7,7′-bisacceptor-substituted 9,9′-spirobifluorenes in chlorobenzene. Bottom: fluorescence images of the solution (in chlorobenzene) and spin-coated solid films. Note that the fluorescence of **BTSF** (the fourth one from the left) is hardly visible either in solution or as solid film, although it was detectable by fluorescence spectrophotometer.

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Table 1. Fluorescence and Absorption Data of 2,2′-Bisdonor-7,7′-bisaccaptor-Substituted 9,9′-spirobifluorenes

	λ^{fl}_{max} solution[a] (nm)	λ^{fl}_{max} solid (nm)	$\phi^{fl\,b}$ solution[a] (%)	λ^{ab}_{max}, ϵ solution[a] (nm, M^{-1} cm^{-1})
DPASF	401	416	24	353, 42300
DPVSF	480	481	50	385, 84700
CHOSF	495	511	46	402, 49700
BTSF	549	582	~0	433, 59900
BTCNSF	601	627	14	464, 65800
CNSF	620	657	31	481, 66200

[a] In chlorobenzene. [b] Fluorescence quantum yield was measured by the integrating-sphere method described by Mello et al.[11]

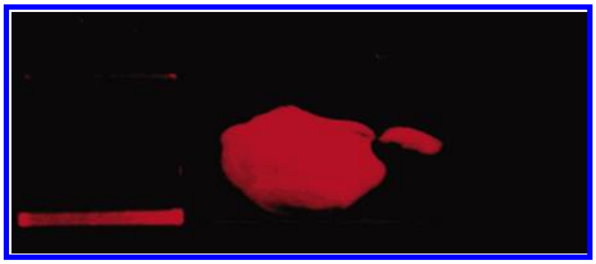

Figure 4. Comparison of the fluorescence intensity of **BTSF** as spin-coated thin film on glass substrate (left), dispersed substance on the surface of silica gel powders (center), and dissolved solute in chlorobenzene (right).

light-emitting diodes (OLEDs). One exceptional case is **BTSF**. Unlike the rest of 9,9′-spirobifluorene fluorophores, **BTSF** is almost nonemissive either in solution or as solid film. Among all new spirobifluorene compounds, the fluorescence of **BTSF** showed largest red-shifting (1032 cm^{-1}) from chlorobenzene solution to solid thin film. When it was dispersed on the surface of silica gel powder, the fluorescence wavelength of **BTSF** was further red-shifted to 649 nm, another enormous red-shifting of 2806 cm^{-1}. Moreover, **BTSF** lit up on the surface of the silica gel (see Figure 4). Such fluorescence behavior usually indicates that there is certain interaction of silica gel and the **BTSF** molecules. Since **BTSF** is the only 9,9′-spirobifluorene fluorophore showing such fluorescence changes, we can deduce that both benzothiazolyl units of **BTSF** are involved in the interaction with silica gel. Further studies are undergoing in order to understand the intriguing fluorescence of **BTSF** and to explore the possible sensor application of the material**.**

In summary, we have successfully demonstrated that 2,2′-dibromo-9,9′-spirobifluorene can be prepared by a new method that does not go through the bromination or Sandmeyer reaction. Multigrams of pure 2,2′-dibromo-9,9′-spirobifluorene can be readily obtained by the new synthetic method without the contamination of bromine-substituent position isomers. From 2,2′-dibromo-9,9′-spirobifluorene we have also synthesized six donor−acceptor-substituted 9,9′-spirobifluorene. These new 9,9′-spirobifluorene derivatives show varied fluorescence color and intensity and they have potential for light-emitting or sensing application.

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Supporting Information Available: Structural characterization and synthetic details of 2,2′-dibromo-9,9′-spirobifluorene and the new donor−acceptor-substituted 9,9′-spirobifluorene derivatives. This material is available free of charge via the Internet at http://pubs.acs.org.

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