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Versatile Direct Cyclization Constructs Spiro-acridan Derivatives for Highly Efficient TADF emitters

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Abstract: Spiro-acridan (SpA) derivatives possess a great potential in preparing efficient thermally activated delayed fluorescent (TADF) emitters. However, the conventional synthetic routes are cost-expensive and time-consuming. The development of a simple procedure to synthesize SpAs is still in urgent pursuing appreciated by academic and industrial communities. In this contribution, we present a feasible acidcatalyzed solvent-free metal-free cyclization between diarylamines and ketones to construct SpAs. The as-constructed moieties provide a wide possibility to assemble efficient TADF emitters. As an example, D2T-TR with high photoluminescent quantum yield and proper TADF character is applied in organic light emitting diodes (OLEDs) which achieves a maximum external quantum efficiency (EQE) of 27.1%. This work shows us a bright inspiration on developing excellent organic optoelectronic materials and an effective tool to realize it.

hermally activated delayed fluorescent (TADF) emitters have aroused recent interest owing to their great potential in display and lighting,^[1] lasering,^[2] time-resolved imaging,^[3] and scintillators.^[4] Especially in organic light-emitting diodes (OLEDs), TADF emitters have achieved comparable electroluminescent performance to the phosphorescent dyes.^[5–7] Generally, efficient TADF emitters contain donor (D) and acceptor (A) connected together via various kinds of bridges to achieve a small energy difference (ΔE_{ST}) between the first singlet (S₁) and triplet (T₁) excited states in order to activated a fast reversed intersystem crossing (RISC).^[8]

Spiro-acridan (SpA) is one of the most attractive D building blocks in developing TADF emitters.^[9] On one hand, the two perpendicular planes connected via a sp³ hybridized carbon increase the rigidity which will suppress the non-radiative decay and also help avoiding severe aggregation. On the other hand, the central six-membered ring of acridan provides large steric effect when connected with A units

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leading to a sufficient separation of the frontier molecular orbitals (FMOs). Together with a moderate electron donating ability, SpAs earn their unique superiority in assembling TADF emitters with varied emission and high efficiencies.^[10] In addition, the extended structure also endows the emitters with an oriented alignment which further boosts external quantum efficiency (EQE) beyond 30%.^[11] Recent works benefit from the advanced electronic and geometrical characteristics of SpA to construct excellent emitters via spatial confined charge transfer.^[12] Such units show increasing importance in OLEDs application. However, the synthesis of SpAs still involves complex procedures. First, the active N-H of diarylamine generally needs protection before treating with lithium agents (Scheme 1). Then, the following lithium–

1. General synthetic procedure for spiro-acridan



Scheme 1. Comparison of synthetic route by conventional method and this work.

halogen exchanging reaction demands delicate operation under low temperature (e.g. -70°C) to avoid unfavorable side-reactions and extra caution due to the combustible agents. At last, a further ring closing is necessary to afford the final compounds.^[11b,12a] A [2+2] cycloaddition/ring-opening procedure can also generates SpAs, but it usually involves in complicated precursors.^[13] Such cost-expensive and timeconsuming routes make it even more difficult to assemble SpAs with advanced structures. A breakthrough in developing a simple synthetic procedure would benefit revealing full potential of SpAs in organic electronics and the further commercialization.

Herein, we present a feasible preparation of SpA derivatives via an acid-catalyzed metal-free solvent-free ring-cyclizing reaction at an elevated temperature between diarylamines and ketones (such as fluorenones, anthraquinones). Encouragingly, such procedure completes in short

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Communications

time for 30 min heating. Mass production at 15–20 mmol is also verified for model compounds with satisfied yield of 64– 70%. The good tolerance of functional groups ensures myriad possibilities in extending the structure of SpAs. More important, SpAs with multiple amines or ketones also succeed which could greatly extent their variety. To estimate their applications in OLEDs, 10-(4-(*tert*-butyl)phenyl)-10"-(4-(4,6diphenyl-1,3,5-triazin-2-yl)-phenyl)-10H,10"H-dispiro [acridine-9,10'-indeno[2,1-b]fluorene-12',9"-acridine] (D2T-TR) was synthesized and evaluated as an example. EQE as high as 27.1% have been achieved in multi-layered devices illustrating the excellence of D2T-TR as a TADF emitter. This procedure opens a practical perspective for assembling SpAs for organic optoelectronic materials.

The general procedure contains two steps: pre-heating of diarylamines with acid at 140 °C under inner atmosphere for about 15 min, then adding ketones and increasing the temperature for 30 min reaction. Further prolonging the reaction time contributes less to yield but more to the byproducts. One-pot heating of all the agents would also give the demanding compounds but with lower yields. *p*-Toluene-sulfonic acid (TsOH) was used owing to its strong acidity and low oxidability. The reaction is first investigated by screening a series of reacting temperatures. No obvious products obtain when the temperature is below 160 °C. Meanwhile, a sharp increase of unidentifiable byproducts and severe carbonization occurs when the reaction heated higher than 220 °C. The optimized temperature is set at 200 °C.

With the optimized condition, the substrate scope with regards to diarylamines was examined (Supporting Information, Figure S1). As shown in Scheme 2, a series of diarylamines successfully underwent the cyclization with fluorenone (2a, Supporting Information, Figure S2) to afford SpAs in good yields (4a-4g). This protocol shows a tolerance of functional group including symmetrical/unsymmetrical methyl, phenyl, t-butyl and active fluoro/chloro groups which is important for further extension of these molecules. Bromo substituted diarylamine (bis(4-bromophenyl)amine (1j, Supporting Information, Figure S1)) fails the reaction may due to high reactivity of bromo or the active N-para position. This failure also inspires us to lock the para position of diarylamines to avoid unfavorable reactions. Product 4d and 4g were obtained with low yield, which may attribute to the steric hinderance of the bulky t-butyl and m-methyl groups on the substrates. Moreover, model compound 10Hspiro[acridine-9,9'-fluorene] (4a) is performed under scale of 15 mmol with a satisfied yield of 64 % which demonstrates the capability of this procedure in commercial application. As shown in the Supporting Information, Figure S3, compared with 4a, 4b possess a little red-shifted absorption which could ascribe to the electron-donating properties of methyl. Both donors show identical phosphorescence, indicating their same triplet energy level. Such properties suggest 4b could be a useful candidate for TADF emitters.

Next, the scope of fluorenone was explored using di-*p*-tolylamine (**1b**, Supporting Information, Figure S1) with methyl to eliminate the extra active *para* position of arylamines as inspired. Surprisingly, this reaction shows good tolerance with single or double bromo units on fluorenes both



Scheme 2. Scope of substrates with isolated yields, *: yield of mass production (**4a** at 15 mmol, see supporting information, section of synthesis and characterization), **: total yield of the inseparable isomers.

in 2,7- and 3,6-position enabling a huge potential in postfunctionalization. Benzophenone (2j, Supporting Information, Figure S2) with free rotating phenyl also succeeds, indicating the possibility of assembling more flexible ketone agents. Furthermore, anthraquinones (3a-d, Supporting Information, Figure S4) were tested to generalize the variety of ketones. Even better, excellent vield of 80% was reached by 2,7-dimethyl-10H,10'H-spiro[acridine-9,9'-anthracen]-10'one (5a). While, bromo decorated anthraquinones could generate SpAs with moderate yield of 44-48%. Reaction between 1b and 2-bromo-6-phenylanthracene-9,10-dione (3d, Supporting Information, Figure S4) generates inseparable isomers **5d** and **5e** with a molar ratio of 0.85:1 which can be identified in their ¹H NMR spectrum (Supporting Information). Furthermore, the combination of unsymmetrical arylamines and ketones could afford chiral SpAs which can be applied in developing chiral emitters.

The successful assembly of simple SpAs enlightens us to develop more complicated structures. Multi amines N^1 , N^3 -diphenylbenzene-1,3-diamine (**1h**), N^1 , N^3 -di-p-tolylbenzene-1,3-diamine (**1i**, Supporting Information, Figure S1) and ketones indeno[2,1-*b*]fluorene-10,12-dione (**2k**), indeno[1,2-*b*]fluorene-6,12-dione (**2l**, Supporting Information, Figure S2) are examined as example. Multi-amines react well with fluorene with good yields. More importantly, the reaction of **1h** and fluorenone could provide (Scheme 3) *N*-phenyl-10*H*-spiro[acridine-9,9'-fluoren]-3-amine (**4q**) or 5',7'-dihy-

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Scheme 3. Scope of SpAs from multi amines and ketones.

drodispiro[fluorene-9,12'-quinolino[3,2-*b*]acridine-14',9''-fluorene] (**4r**) under the ratio of 1:1 or 1:2 suggesting the controllability of this procedure. Massive synthesis of 2',10'dimethyl-5',7'-dihydrodispiro-[fluorene-9,12'-quinolino[3,2b]acridine-14',9''-fluorene] (**4s**) can be obtained at 20 mmol scale with yield of 70% further revealing its potential in commercialization. Diarylamine equipping with multiketones also shows favorable results. Both **4t** and **4u** can be successfully assembled. Noteworthy, **4r**-**4u** are not reported yet which could ascribe to the complicated synthesis via conventional method. This new procedure provides an easy and effective way to further extend SpAs with more advanced structures.

According to the verification of different substrates, a plausible mechanism of a two-step Friedel–Crafts reaction is speculated. As shown in the Supporting Information, Figure S5, first, an electrophilic attack of protonized fluorenone to 2-positon of diarylamine and the loss of equivalent water gives a carbon cation, which then attacks the other phenyl for cyclization to afford the final compound. In brief summary, this approach could generate SpAs with advanced structures and ensure mass production which demonstrates its potential towards academic and commercial research.

To demonstrate the application of SpAs in TADF emitters, 10H,10"*H*-dispiro[acridine-9,10'-indeno[2,1-b]fluorene-12',9"-acridine], prepared from diphenylamine and indeno[2,1-b]fluorene-10,12-dione (Supporting Information, Scheme S2), was used as an example to assemble D2T-TR (Figure 1a) via Buchwald–Hartwig coupling with 4-bromo-



Figure 1. a) Chemical structure and the twist angle of D2T-TR. b) Distribution of the FMOs calculated with density function theory (DFT) under B3LYP/def2svp level (cyan: LUMO, pink: HOMO, red: HOMO-1), c) Theoretical simulated energy levels of S₁, T₁ and ΔE_{ST} .

triazine. The structure is fully characterized by ¹H, ¹³C NMR and high-resolution mass spectrum. Theoretical simulation shows an almost perpendicular geometry with a dihedral angle of 88° between D and A which ensures a large separation of the FMOs. As expected, the lowest unoccupied molecular orbital (LUMO) is located on electro-deficient triazine (TR) unit and the highest occupied molecular orbital (HOMO) mainly spreads on the other acridan unit connected with t-butylbenzene (Ac2), while HOMO-1 focuses on the acridan directly attached with TR unit (Ac1) (Figure 1b). TR unit may weaken the electron donating property of Ac1 compared with that of Ac2 resulting in such distribution of the FMOs. Natural transition orbital analysis confirms that S1 and T₁ originate from the transition between Ac1 and TR (Supporting Information, Figure S6). The energy of S1 and T_1 are calculated as 2.595 eV and 2.586 eV giving a small ΔE_{sT} value of 9 meV which will ensure a fast triplet up-conversion. Furthermore, a local excited triplet state (³LE) centered at indenofluorene is also observed with energy of 2.658 eV (Supporting Information, Figure S6). Such energetically closed ³LE may also facilitate the RISC process.^[14]

Photophysical property was further investigated using ultraviolet-visible (UV/Vis) absorption and photoluminescence (PL) spectra in solution and in bis[2-(diphenylphosphino)phenyl] ether oxide (DPEPO) doped film with a doping concentration of 20 wt %. The intense absorption in diluted toluene located at 344, 328 and 300 nm is attributed to the local π - π * transition from indenofluorene, TR and Ac units. Weak and broad peak around 400 nm ascribes to charge transfer absorption from Ac1 to TR. The PL spectrum in doped film shows a bluish-green emission at 490 nm and high photoluminescent quantum yield (PLQY) of 99%. The singlet (E_{S1}) and triplet (E_{T1}) energy levels from the onset of fluorescent and phosphorescent spectra are 2.86 eV and 2.76 eV, respectively. Thus, a small $\Delta E_{\rm ST}$ of 0.1 eV is achieved endowing an efficient RISC process in D2T-TR. A transient PL decay spectrum (Figure 2) confirms the TADF characteristic with clear two components of 28 ns and 2.1 µs which originates from prompt and delayed fluorescence. Together with the data of PLQY, the rate constant of radiative decay $(k_{\rm r})$, intersystem crossing $(k_{\rm ISC})$ and RISC $(k_{\rm RISC})$ could be calculated as $1.11 \times 10^7 \text{ s}^{-1}$, $2.48 \times 10^7 \text{ s}^{-1}$ and $1.09 \times 10^5 \text{ s}^{-1}$,



Figure 2. a) UV/Vis absorption in dilute toluene (10^{-5} M) , fluorescence (Fl) and phosphorescence (Ph) spectra in doped film (20 wt% in DPEPO) under room temperature and 77 K, respectively. b) Transient PL decay profile in DPEPO (20 wt%) under inert atmosphere.

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respectively. Fast k_r and k_{RISC} could promote an efficient usage of excitons.^[8]

Considering the FMO levels of D2T-TR estimated from cyclic voltammetry profile (Supporting Information, Table S1 and Figure S8), multi-layer device was fabricated using D2T-TR as emitter under following structure of ITO/MoO₃ (1 nm)/ TAPC (40 nm)/TcTa (10 nm)/mCP (10 nm)/DPEPO: 20 wt % D2T-TR (25 nm)/DPEPO (5 nm)/Bphen (30 nm)/LiF (1 nm)/ Al (1100 nm) by vacuum-deposition to evaluate its EL performance. The energy diagram and chemical structures of (1,1-bis[4-[N, N'-di(p-tolyl)-amino]phenyl]cyclohexane)(TAPC), (4,4',4"-tri(9-carbazoyl)-triphenylamine) (TcTa), 1,3-bis(N-carbazolyl)benzene (mCP), DPEPO, 4,7-diphenyl-1,10-phenanthroline (Bphen) are illustrated in Figure 3. TAPC and TcTa served as hole-transporting layers (HTL) while DPEPO acted as host matrix and Bphen were used as electron transporting layer (ETL). A thin layer of mCP and DPEPO were inserted between respective HTL/emission layer (EML) and EML/ETL to confine excitons. As shown in Figure 3c, EL spectrum exhibits a single blueish-green emission peaked at 490 nm suggesting well confinement of the excitons. The maximum EQE, current efficiency (CE) and power efficiency (PE) reach 27.1%, $69.2 \text{ cd } \text{A}^{-1}$ and 63.9 lm W^{-1} , respectively, thanks to the outstanding PLQY, efficient up-conversion of triplet excitons via TADF mechanism and carefully designed device structure. Relieved efficiency roll-off of 11% at 100 cdm⁻² and 33% at 1000 cdm^{-2} are also observed which could ascribe to the fast RISC process. Such result indicates D2T-TR as an efficient TADF emitter, and more importantly, presents the infinite potential of SpAs.

In conclusion, we have provided a simple metal-free solvent-free strategy to synthesize SpA derivatives with advanced structures featuring fast construction, good controllability and mass production which may help in revealing the potentiality of SpAs in organic electronics. A proof-of-concept TADF emitter D2T-TR is further prepared using the assembled SpA as D unit which exhibits high PLQY, obvious TADF characteristic and consequently acquires excellent EL performance. This work not only demonstrates the wide possibility of SpAs in constructing TADF emitters but also points out a practical way to achieve it.

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Conflict of interest

The authors declare no conflict of interest.



Figure 3. a) Device structure and energy-level diagram of the OLED. b) Chemical structures of the compounds used in devices. c) EL spectra of the device recorded at 10 mAcm⁻², inner: corresponding CIE coordinates. d) Current-density–voltage–brightness (*J-V-L*) profile. e) Power efficiency and EQE vs. brightness curves and efficiency roll-off at 100 cd m⁻² and 1000 cd m⁻².

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Communications



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Fluorescence

H. Liu, Z. Liu, G. Li, H. Huang, C. Zhou, Z. Wang,* C. Yang* _____ **IIII**-IIII

Versatile Direct Cyclization Constructs Spiro-acridan Derivatives for Highly Efficient TADF emitters



A versatile direct cyclization is demonstrated to proceed by substituted diarylamines with various ketones under simple solvent-free and metal-free conditions. It shows huge potential in preparing spiro-acridan derivatives and TADF emitters.

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