



Catalyst-free photocyclization for the synthesis of spiro-fused aromatic organic semiconductor based on SFX

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ARTICLE INFO

Article history:

Received 9 January 2018

Received in revised form

1 March 2018

Accepted 5 March 2018

Available online 6 March 2018

Keywords:

Spiro-fused
Photo-induced
Catalyst-free
Optoelectronic
Semiconductor

ABSTRACT

A green protocol with catalyst-free photo-induced cyclization for the synthesis of a spiro-fused organic semiconductor molecule based on spiro[fluorene-9,9'-xanthene] (SFX) was developed. The photo-physical and electrochemical properties of the spiro-fused compound (DPCzSFX) have been characterized. The results showed that the molecular stability and the property of the charge injecting/transporting were improved due to the cyclization. And the broadening of the emission spectrum in film makes the spiro-fused compound possible for the application as a host in the white phosphorescent organic light-emitting diodes. However, the same reaction for the spirobifluorene-based diphenylamine derivative did not occur under the same condition, which also highlights the importance of the oxygen heteroatom in the ring to the reaction of cyclization.

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1. Introduction

Spirocyclic compounds have attracted considerable attention in recent years in organic optoelectronic devices,^{1–4} such as light-emitting diodes, photovoltaic cells, field-effect transistors, and organic lasers, owing to their high thermal and morphological stabilities, high fluorescent quantum efficiencies, and ambipolar

carrier transporting properties.⁵ Spiro[fluorene-9,9'-xanthene] (SFX), one representative molecule of the spiro family, has been widely studied due to the relatively easy one-pot synthetic method.⁶ Comparing to the typical spirobifluorene (SBF), SFX has more modification sites and higher reactive activity due to the presence of the oxygen heteroatom. A series of researches on SFX derivatives have been reported including organic light-emitting diodes (OLEDs),^{7–9} phosphorescent OLEDs (PhOLEDs),^{10–12} solar cells,^{13,14} organic/polymeric nanoparticles^{15,16} and transistors.¹⁷ However, the steric hindrance of the spiro structure reduces the π - π stacking interaction between molecules and further reduces the molecular charge mobility. Whereas the fused-ring structure such as pentacene is beneficial to the improvement of the charge mobility. Therefore, the fused-ring structural modification on the basis of spiro compounds may be a good protocol to resolve the problem.

Triphenylamine/diphenylamine can be cyclized into carbazole derivatives under photo-catalyzed condition,^{18–20} which is a possible solution to synthesize the fused-ring structure. Although the preparation of carbazole through cyclization has been

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developed for a long time, the photocyclization of the triphenylamine/diphenylamine derivatives is rarely reported in the synthesis of the organic semiconductors. This inspired us to achieve the cyclization of the SFX-based diphenylamine derivative by photo-induced green method and obtain spiro-fused compounds. In our previous work, spiro[fluorene-9,7'-dibenzo[c,h]acridine]-5'-one (SFDBAO) has been synthesized through an eco-friendly visible-light-mediated photooxygenation of spiro[fluorene-9,7'-dibenzo[c,h]acridine] (SFDBA).¹⁵ Furthermore, we explained the idea of green organic semiconductors (GOS) and synthesized a SFX-based fluorescent molecule using a pot-atom-step economic (PASE) reaction.^{2,8} Hereby, we report a new spiro-fused compound, 5',11'-diphenyl-5',11'-dihydrospiro[fluorene-9,8'-pyrano[3,2-c:5,6-c']dicarbazole] (DPCzSFX), based on the idea of GOS. This material was synthesized using photo-induced reaction without extra catalysts and was fully characterized and confirmed by ¹H and ¹³C NMR, MALDITOF-MS, and elemental analysis. Optical and electrochemical properties of the compound were also investigated for the potential application in organic electronics.

2. Results and discussion

2.1. Discovery of the synthesis route

In consideration of the successful synthesis of spiro[fluorene-9,9'-xanthene] (SFX) using 9-fluorenone and phenol via one-pot method,⁶ we did a retrosynthesis analysis of the spiro-fused compound named 5',11'-diphenyl-5',11'-dihydrospiro[fluorene-9,8'-pyrano[3,2-c:5,6-c']dicarbazole] (DPCzSFX) (Scheme 1). Different acid catalysts and reaction temperature were attempted for the synthesis of the spiro-fused compound by one-pot method. However, the targetted cyclized xanthene structure was not obtained.

N3',N3',N6',N6'-tetraphenylspiro[fluorene-9,9'-xanthene]-3',6'-diamine (SFX-3',6'-DDPA) (Fig. 1a) was synthesized as a host material and hole-transporting material in our previous experiments. Photoluminescence (PL) spectrum measurement on SFX-3',6'-DDPA showed that the PL spectra of SFX-3',6'-DDPA changed with the time of illumination of the light source (Fig. 1b). As the duration of xenon lamp illumination increased, the emission intensities at 367 nm and 504 nm decreased and increased, respectively. Based on this phenomenon, we proposed that SFX-3',6'-DDPA might have reacted under the UV illumination and formed other substances. Therefore, another attempt of the photo-induced reaction was made using the SFX-3',6'-DDPA which consists of an oxygen heteroatom in the spiro structure, as shown in Scheme 2. Fortunately, the cyclization reaction occurred as triphenylamine did and the fused-ring structural compound was obtained. This opposed with the reaction of spirobifluorene-based diphenylamine derivative (SBF-2,7-DDPA, Fig. 1a) which does not contain oxygen atom, where the cyclization was not successful. This shows that oxygen heteroatom plays a key role for improving the reactivity of the spiro compound in the photocyclization reaction, which provides more possibilities for the design of new spiro cyclic arenes.

A possible mechanism of cyclization of SFX-3',6'-DDPA was

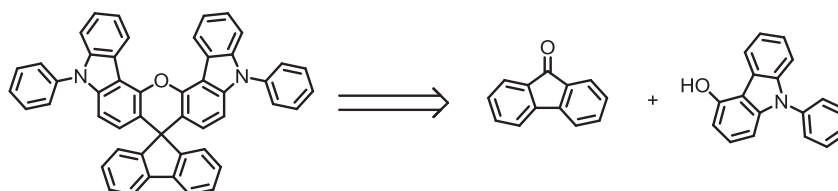
proposed (Scheme 3). SFX-3',6'-DDPA was oxidized to nitrogen cation under illumination and formed carbon anion (1) on the benzene ring of diphenylamine or on the benzene ring of xanthene unit. Subsequently tetra-hydrocarbazole structure (2) was formed by the C-C coupling between ortho-position of oxygen and ortho-position of nitrogen on the diphenylamine unit, whereas the C-C coupling between two benzene rings on the diphenylamine unit was not formed because the product of 3',6'-di(9H-carbazol-9-yl) spiro[fluorene-9,9'-xanthene] was not found in the reaction. Finally, DPCzSFX was obtained via the second oxidation of tetra-hydrocarbazole structure.

2.2. Optical and electrochemical properties of the spiro-fused compound

The absorption spectra of SFX-3',6'-DDPA showed two main absorption bands at 258 nm and 322 nm in dilute dichloromethane solution and its absorption peaks in thin film were close to that in solution (Fig. 2a, Table 1). Whereas DPCzSFX exhibited red-shifted absorption bands where the peaks were at 348 nm in solution and at 347 nm in thin film due to the formation of fused-ring structure. The photoluminescence (PL) emission peak of DPCzSFX was observed at 358 nm with a shoulder peak at 369 nm in solution, which showed slightly blue-shift compared with that of SFX-3',6'-DDPA, unlike photoluminescence behavior of red-shift induced under the continuous illumination, as shown in Fig. 1b. However, the main emission peak of DPCzSFX in thin film exhibited a larger red shift than that in solution and than the emission peak of SFX-3',6'-DDPA in film (Fig. 2a). This shows that there is a strong π - π interaction between DPCzSFX molecules, which is advantageous for the enhancement of the charge mobility. And the wider emission bands from 347 nm to 665 nm made DPCzSFX a potential host for the white PhOLED.

The physical parameters of SFX are from reference [18]. [a] HOMO levels were measured from the onset of oxidation potentials in CH₂Cl₂, LUMO levels were measured from the onset of reduction potentials in THF(tetrahydrofuran); [b] measured in dichloromethane solutions; [c] measured in thin films; [d] calculated from the HOMO and LUMO; [e] estimated from the absorption edges.

Electrochemical properties of the synthesized compounds were measured using cyclic voltammetry (Fig. 2b) to estimate the highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO) and bandgap. The HOMO and LUMO levels of SFX-3',6'-DDPA are −5.42 eV and −1.80 eV and the bandgap is 3.62 eV (Table 1). The higher HOMO level of SFX-3',6'-DDPA means that the molecule has better hole-injection/transport ability, while the higher LUMO level makes the electron-injection/transport ability poorer. After forming the fused-ring structure the HOMO and LUMO levels of DPCzSFX are reduced to −5.54 eV and −2.60 eV, which increases the stability of the molecule. Moreover, the large reduction of the LUMO level is beneficial to the injection/transport of electrons. The bandgap of DPCzSFX was reduced to 2.94 eV compared with that of SFX-3',6'-DDPA, which was consistent with the red-shift in the absorption spectra.



Scheme 1. Retrosynthesis Analysis of the spiro-fused compound (DPCzSFX).

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