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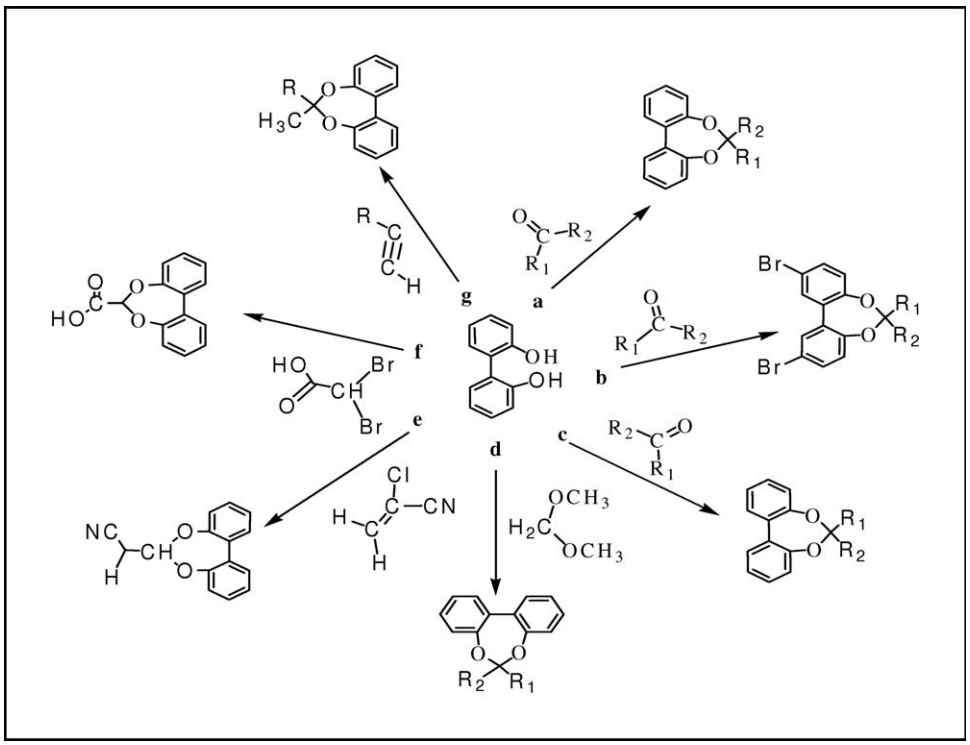

This review presents a survey of synthetic methods and reaction mechanism of the dibenzo[*d*,*f*][1,3] dioxepine derivatives. Furthermore, the influence of the substituent groups in 6,6′-position of dibenzo[*d*,*f*][1,3] dioxepine on their conformation is explored. The functional dibenzo[*d*,*f*][1,3] dioxepine synthetically versatiles substrate, as they can be used for synthesis of a large variety of π-conjugated oligomer and polymer containing heterocyclic compounds, such as dibromination dibenzo[*d*,*f*][1,3] dioxepine derivative as a raw material of synthesis for organic semiconductor polymers. The synthetic and fluorescent property of π-conjugated polymers basic on dibenzo[*d*,*f*][1,3] dioxepine also is explored.

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INTRODUCTION

The dibenzo[*d*,*f*][1,3] dioxepine derivatives are important seven-member-ring type bridged biphenyl compounds and they are very important in pharmaceutical applications [1]. In fact, it has been found that such a structure, which is probably related to their pharmacological activity, is present in many biologically active natural products [2]. Furthermore, the functional dibenzo[*d*,*f*][1,3] dioxepine derivatives could construct π-conjugated polymers, which were used widely in polymer light-emitting diodes [3–5].

To date, the only significant synthetic methods developed for the dibenzo[*d*,*f*][1,3] dioxepines derivatives using 2,2′-dihydroxybiphenyl are the condensation of 2,2′-dihydroxybiphenyl with the appropriate ketone using phosphorus pentoxide [6], the condensation of 2,2′-dihydroxybiphenyl with a dibromoacetate [7], a trans-ketalization [8] or a double Michael addition [9,10] or using $InCl_3$ and $ZrCl_4$ as a catalyst, etc. [11,12].

Thus, focusing on the development of the innovation of synthesis methods and potential application, this

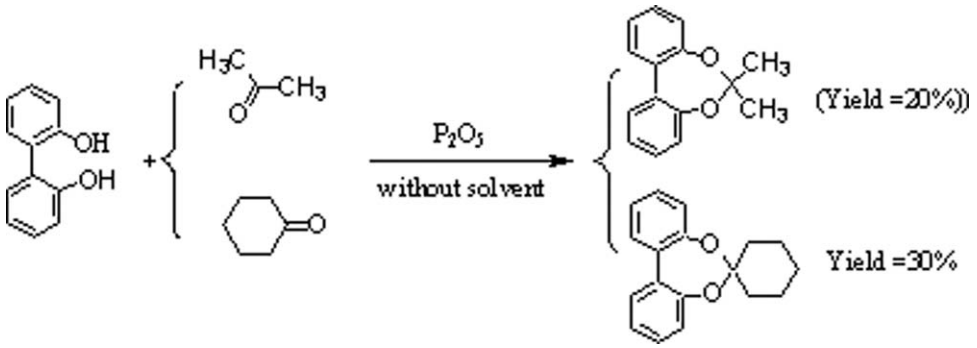


Figure 1. The synthesis routes to dibenzo[*d,f*][1,3] dioxepin using ketone route under without solvent.

article gives a brief review on the synthesis, twisted conformation, and potential application in field of the light-emitting diodes.

SYNTHESIS AND REACTION MECHANISM

Synthesis. Silcox and Zuckerman found the first synthetic way of the dibenzo[*d,f*][1,3] dioxepine derivatives by the intermolecular dehydration–cyclization of 2,2′-dihydroxy biphenyl and the appropriate ketone. The reaction used phosphorus pentoxide as dehydration reagent and without any solvent. The yield of the dibenzo[*d,f*][1,3] dioxepine derivatives is about 20–30% [6]. However, the few ketone allowed preparation of the dibenzo[*d,f*][1,3] dioxepine derivatives due to soluble capability of ketone (Fig. 1).

Hewgill and Hewitt reported the synthesis of the dibenzo[*d,f*][1,3] dioxepine-6-carboxylic acid (Fig. 2) using the condensation of 2,2′-dihydroxy-biphenyl with a dibromoacetate in the presence of sodium hydride [7].

In addition, the dibenzo[*d,f*][1,3]dioxepins could be obtained by transketalization reaction in the presence of toluene-*p*-sulfonic acid with solvent of benzene (Fig. 3) [8]. In contrast with ketone routes, the yield increases evidently (yield $>$ 60%), but the variety of dibenzo[*d,f*][1,3]dioxepins was limited owing to the few varieties of the ketal.

Furthermore, Johnson and Bacon also reported the preparation of the dibenzo[*d,f*][1,3]dioxepins using double Michael addition [10]. For example, treatment of 2,2′-dihydroxybiphenyl with 2-chloroacrylonitrile gave

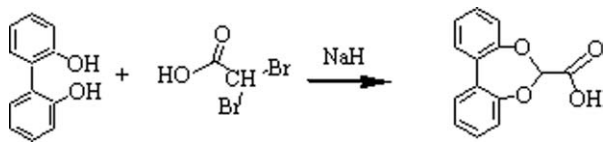


Figure 2. The synthesis routes to dibenzo[*d,f*][1,3] dioxepin using dibromoacetate in the presence of sodium hydride.

the dibenzo[*d,f*][1,3]dioxepin-6-acetonitrile with 47% yield, and treatment of 2,2′-dihydroxybiphenyl with two equivalents of diethyl bromomalonate gave a 95% yield of diethyl dibenzo[d,f][1,3] dioxepin-6,6-dicarboxylate (Fig. 4).

Furthermore, in the presence of catalytic amount of indium(III) chloride (10mol%), 2,2′-dihydroxybiphenyl with ketones or β-keto esters possessing at least one hydrogen atom in the ketone-carbonyl group, to afford some dibenzo[*d,f*][1,3] dioxepines derivatives (Fig. 5) [11].

Moreover, in the presence of $InCl_3$ or $ZrCl_4$, terminal aliphatic and aromatic alkynes easily reacted with 2,2′-dihydroxybiphenyl, leading to 6,6-dialkyl or 6-alkyl-6-aryldibenzo dioxepine derivatives (Fig. 6) [12].

Reaction mechanism using route of theminal alkynes. Figure 7 shows reaction mechanism of the 2,2′-dihydroxybiphenyl with the terminal alkyne [13]. The reaction undergoes a concerted six-membered transition state to form intermediates **4** and **3**. The 2-chloroalkene intermediate **4** is formed by a Markovnikov addition of HCl derived from the nucleophilic interaction between biphenol **1** and $InCl_3$. The final product **5** is afforded by the nucleophilic addition of compound **3** at 2-chloroalkene **4**, which is rapidly followed by an intramolecular cyclization, where an oxacarbenium ion represents the most likely reactive state. Otherwise, 2-chloroalkene **4** might generate a vinyl cation that could react with intermediate **3** to afford the final product **5**.

SYNTHESIS AND TWIST CONFORMATION OF FUNCTIONAL DIBENZO[*d,f*][1,3] DIOXEPINES

Synthesis. Introducing functionalized group Br or —CHO on benzene ring of the dibenzo[*d,f*][1,3] dioxepines affords active positions of reaction [14,15]. Then, luminescent polymers based on dibenzo[*d,f*][1, 3] dioxepine derivatives were constructed by Yamamoto, Suzuki, or Witting reaction. The synthesis of the functional

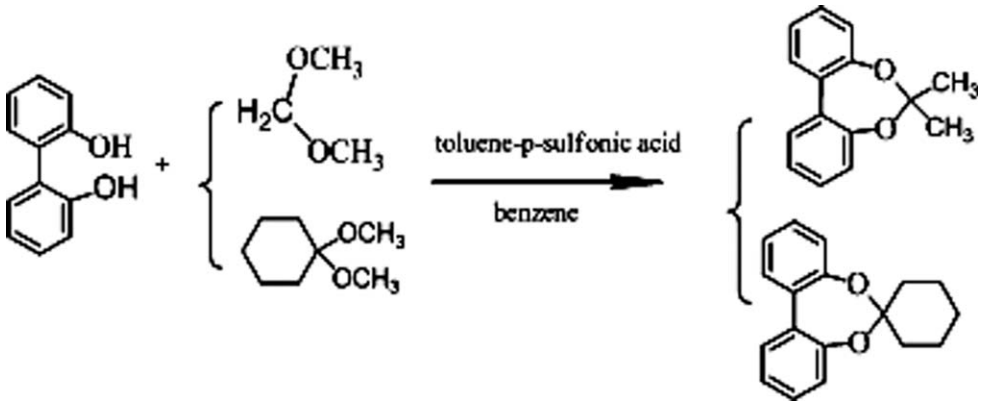


Figure 3. The ketal routes to dibenzo[*d*,*f*][1,3] dioxepin in the presence of toluene-*p*-sulfonic acid.

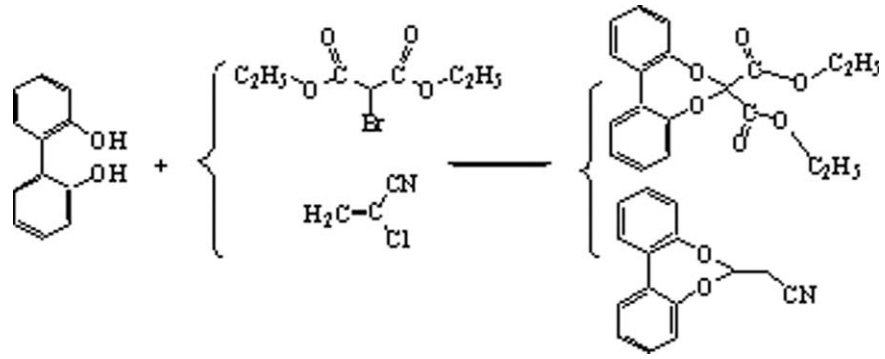
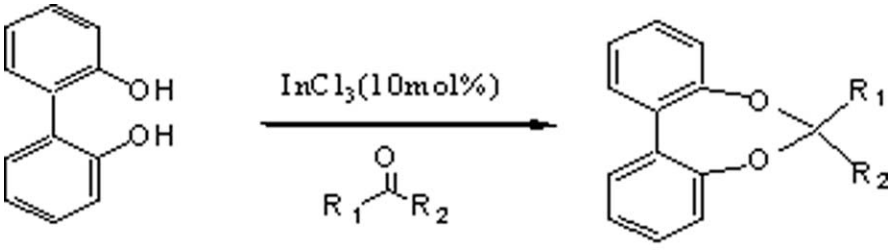


Figure 4. The synthesis routes to dibenzo[*d*,*f*][1,3] dioxepin using double Michael addition.



1 $R_1=CH_3$; $R_2=CH_2COOC_2H_5$,	Yield =25%
2 $R_1=CH_2Cl$; $R_2=CH_2COOC_2H_5$,	Yield=20%
3 $R_1=CH_3$; $R_2=CH_3$;	Yield =30%
4 $R_1=CH_3$; $R_2=CH(CH_3)_2$	Yield =20%
5 $R_1=CH_3$; $R_2=Bz$	Yield=25%
6 $R_1=CH_3$; $R_2=Ph$	Yield=25%
7 $R_1=CH_3$; $R_2=Bu$	Yield=40%
8 $R_1=CH_3$; $R_2=CH(CH_2Ph)COOCH_2CH_3$,	Yield=30%

Figure 5. Ketone routes to the dibenzo[*d*,*f*][1,3] dioxepin using indium(III) chloride as catalytic.

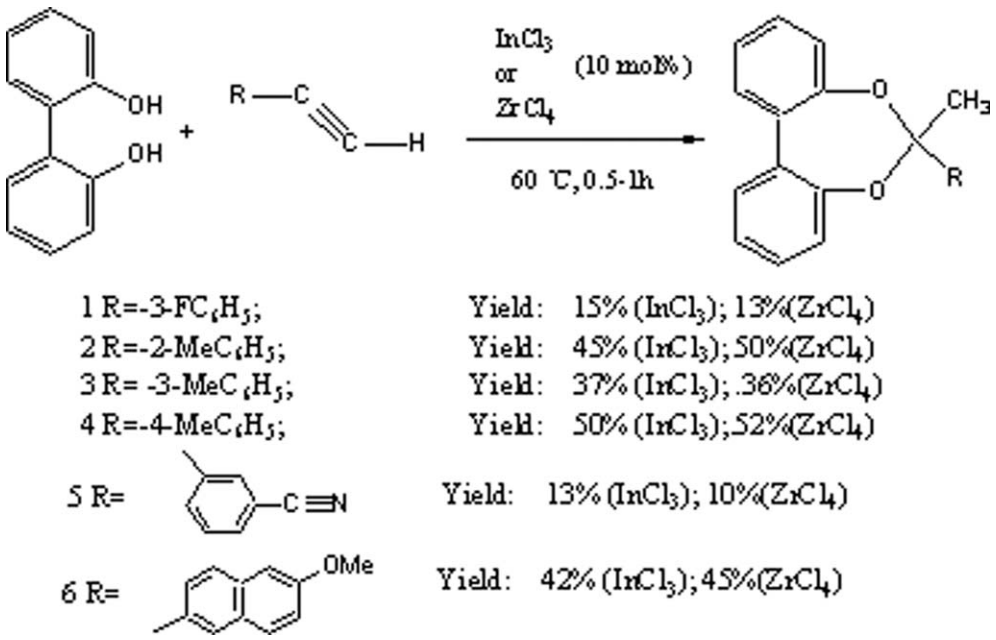


Figure 6. The terminal alkyne routes to dibenzo[*d*,*f*][1,3] dioxepin in the presence of $InCl_3$ or $ZrCl_4$.

dibenzo[*d*,*f*][1,3] dioxepine derivatives was described in Figure 8. The 2,10′-dibromo-dibenzo [*d*,*f*][1,3] dioxepin derivatives **3** were synthesized by the direct bromization of the 2,2′-dihydroxybiphenyl, then using ketone or ketal route. Lithiation **3** with *n*-BuLi and DMF at −78°C, followed by queneching with DMF to give dicarbaldehyde **4** [16].

Twist conformation. The conformation of the bridged biphenyl has an influence on the electronic structure and conjugated degree of conjugated polymer containing the dibenzo[*d*,*f*][1,3] dioxepines [17,18]. Hence, our research groups investigated on conformation of a series of functional dibenzo[*d*,*f*][1,3] dioxepine derivatives and the influence of the substituent groups in 6,6′ position on the twisted angle between the bridged biphenyl. In the crystal structure of these compounds, the two benzene rings of the bridged biphenyl unit are twisted by about 40.0°, and the 7-membered ring is in a

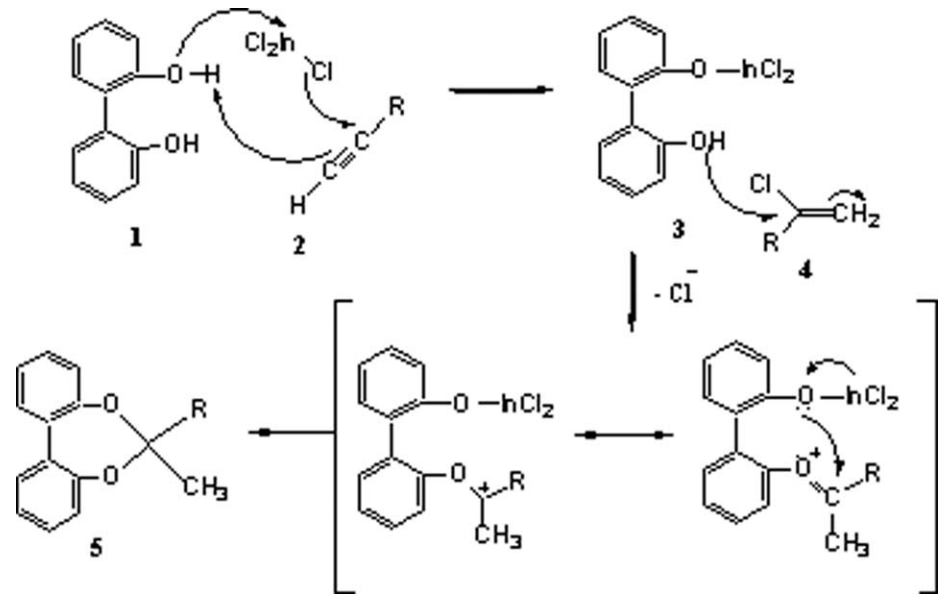


Figure 7. The reaction mechanism of the 2,2′-dihydroxybiphenyl with the terminal alkyne to prepare the dibenzo[*d*,*f*][1,3] dioxepin.

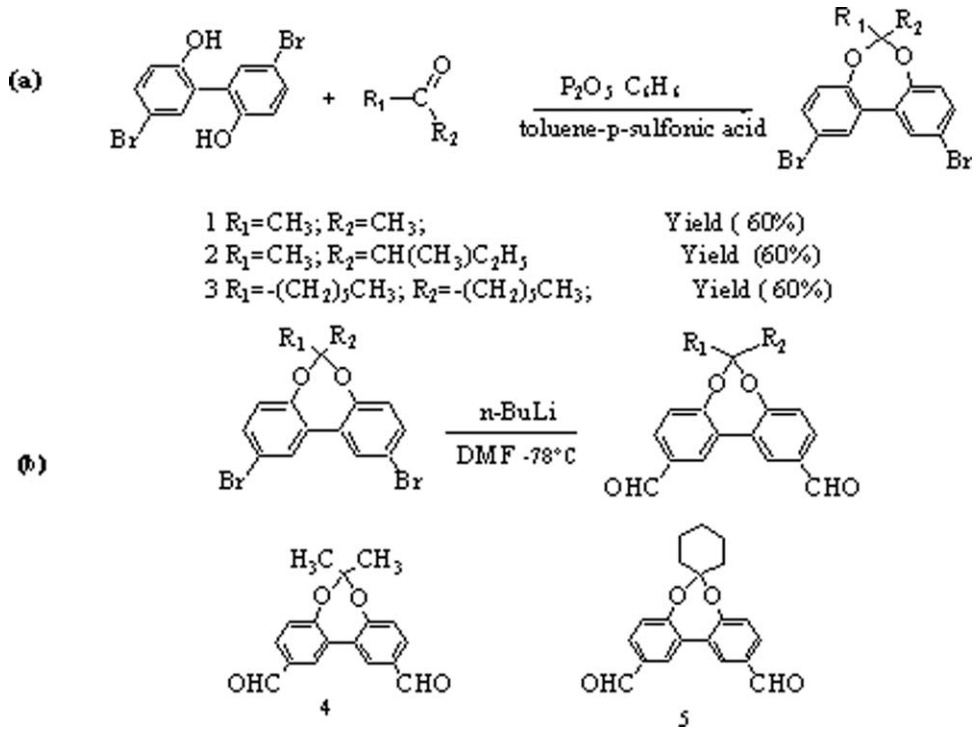


Figure 8. Synthesis of the functional dibenzo[*d*,*f*][1,3] dioxepin containing —Br or CHO groups.

boat conformation [19–21]. The different substituent groups in 6,6′ position could induced the difference of the intermolecular action, which influenced the twisted angle. No obvious intermolecular interaction was observed in a, consequently, the measured θ is in good agreement with its theoretical value, which was

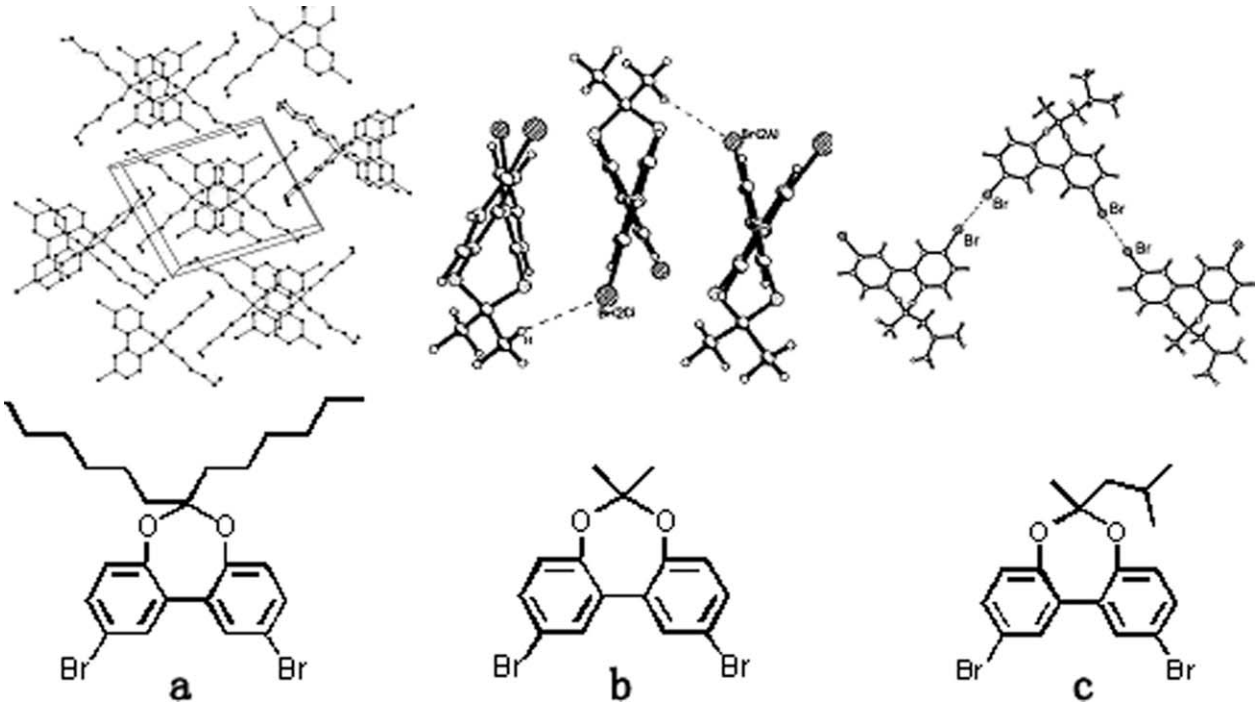


Figure 9. Closest contact between atoms in neighborhood molecules in crystal packing for the functional dibenzo[*d*,*f*][1,3] dioxepin.

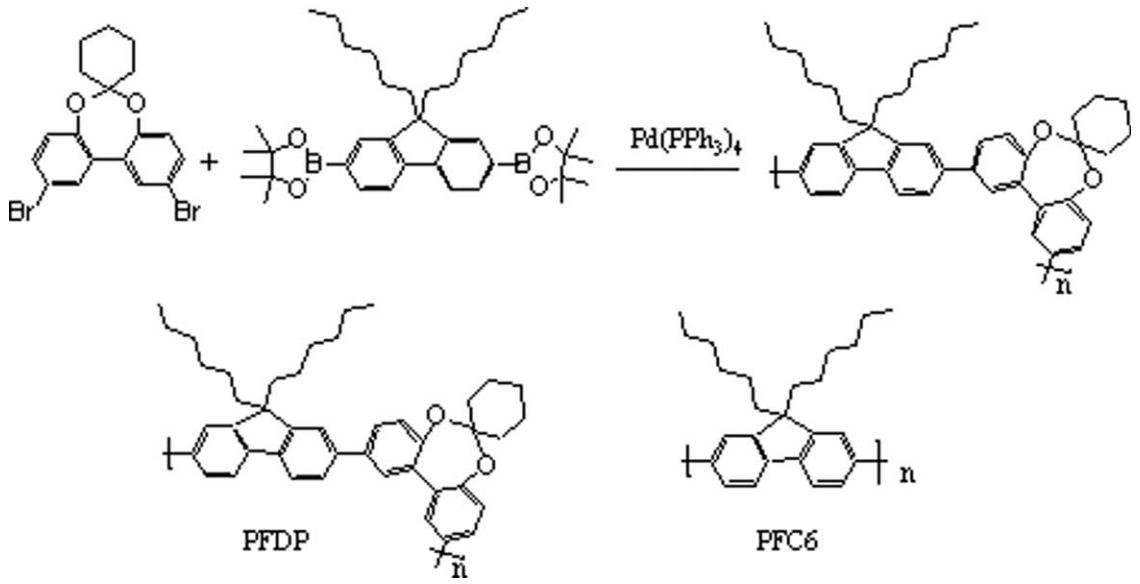


Figure 10. Synthesis of *meta*-linked dibenzo[*d,f*][1,3] dioxepin/fluorene copolymer and chemical structure of PFDP, PCC6.

estimated using UNIVERSAL 1.02 force field in Cerius2 package (4.6). The presence of the intermolecular Br–Br interaction in b induced the decrease of the twisted angle θ compared with theoretical value, and the presence of the intermolecular Br–H interaction in crystal packing c induced increasing of the twisted angle θ compared with their theoretical value (Fig. 9).

APPLICATION IN LUMINESCENCE FIELD

Synthesis and property of fluorene-based copolymer. The new fluorene-based copolymer (PFDP) composed of spiro-cyclohexane-1,6′-dibenzo[*d,f*][1,3] dioxepin segments in the main-chain was synthesized by Suzuki coupling reaction (Fig. 10) [22]. The copolymer was synthesized in a refluxing toluene/aqueous sodium carbonate solution (2 M) containing 1–3 mol % $Pd(PPh_3)_4$ under vigorous stirring for 48 h with yield 83% [23]. The copolymer was a pale-white solid and had good solubility in common organic solvents.

The maximal absorption peak of PFDP in solution is at 328 nm, which is 54 nm blue-shifted to that of poly(9,9-dialkyl-2,7-fluorene) (PFC6) (the chemical structure shows in Fig. 11). The calculated optical bandgap from the absorption onset is 3.26 eV, which is 0.29 eV higher than that of PFC6. The PFDP in solution exhibits strong emission ($\Phi_{f1} = 0.62$) in the ultraviolet spectrum range (peaking at 368 nm and 386 nm) upon irradiation with a 330 nm light. An electroluminescence device from PFDP neat film as an active layer exhibits UV emission which peaks at 395 nm. Furthermore, optimizing the device conditions yields a peak EL quantum efficiency of 0.054% and brightness of 10 cd/m^{-2}.

Synthesis and property of 1,4-phenelenevinylene-based copolymer. Figure 12 shows the synthesis route of 1,4-phenylene vinylene-based copolymer contatining dibenzo[*d,f*][1,3] dioxepine. The copolymerzation of monomer **1** with **2** in the presence of t-Buok in degassed THF gave the copolymer **3** under witting-horner condition at room temperature [24]. The copolymer **3** emitted a strong deep blue fluorescence under UV irradiation and showed two PL peaks at 408 and 430 nm and a shoulder at around 457 nm in dilute solution. As for the peak at 430 nm, there was about 100 nm blue-shift against the prototype poly(1,4-phenylene vinylene). In

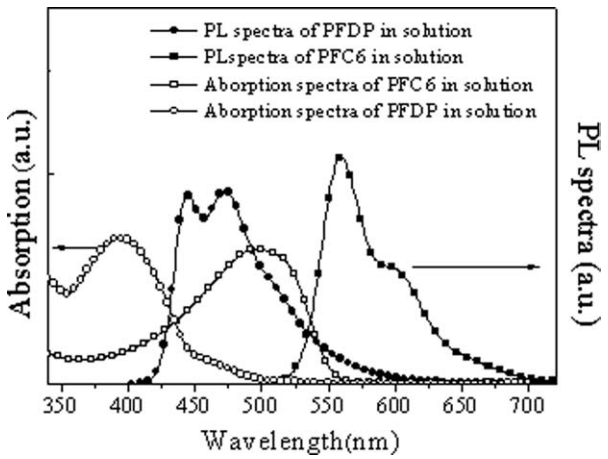


Figure 11. Optical absorption and photoluminescence spectra of PFDP and PFC6 in $CHCl_3$.

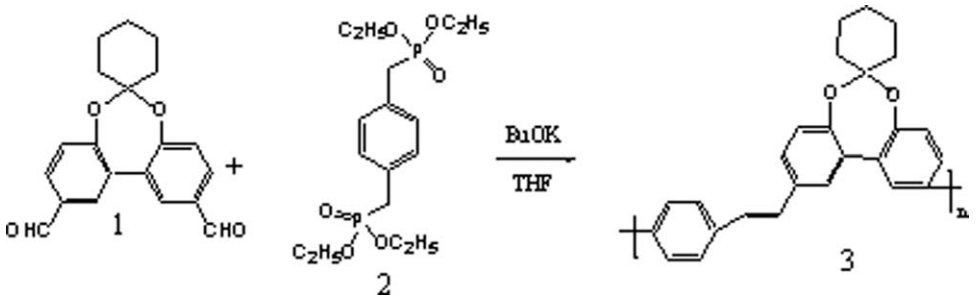


Figure 12. Synthesis of *meta*-linked dibenzo[*d*,*f*][1,3] dioxepin phenylen vinylene copolymer.

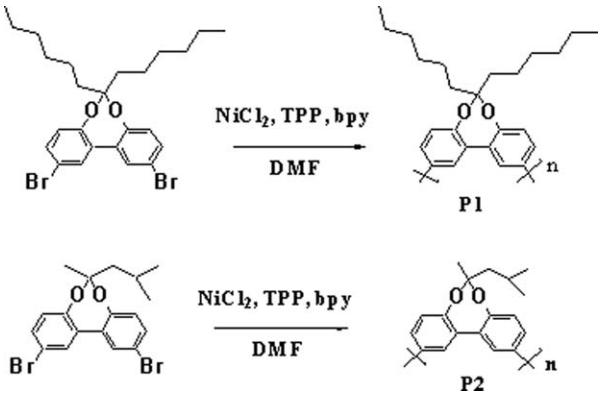


Figure 13. Synthesis of the poly-*meta*-dibenzo[*d*,*f*][1,3] dioxepin derivatives.

contrast with other PPVs [25–27], the most important improvement was that the emission of copolymer 3 in film was at 440 nm, which was just 10 nm red-shift relation to that in dilute solution, and the quantum efficiency was as high as 0.5 in the solid and band which was relatively small.

Synthesis and property of poly-*meta*-dibenzo [*d*,*f*][1,3] dioxepin derivatives. The functional group Br on benzene ring of dibenzo[*d*,*f*][1,3] dioxepine can be constructed by the poly *meta*-dibenzo[*d*,*f*][1,3] dioxepines by the nickel catalyzed coupling reaction (Fig. 13) [28]. The structural and electronic and optical characterizations indicated the planar and twisted conformation existed in the polymer backbone. The polymer exhibits a strong absorption around 256 nm and a weak absorption at about 300 nm. Furthermore, the polymer exhibits a strong UV photoluminescence at 372 nm when the excitation wavelengths are longer than 300 nm (Fig. 14). The ultraviolet-emitting electroluminescence (EL) device with the single layer structure shows EL λ_{max} of the derivative at 370 nm.

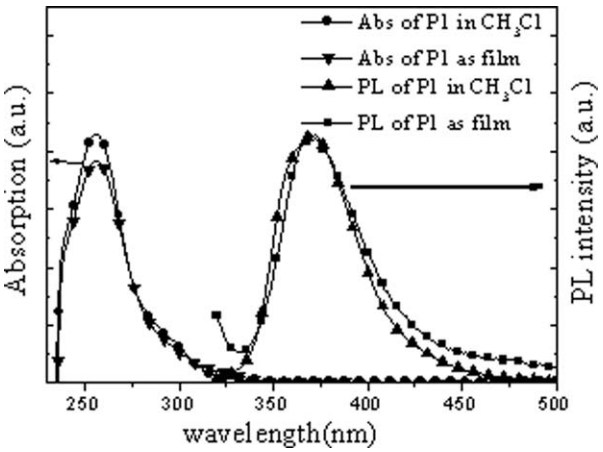


Figure 14. Optical absorption and photoluminescence spectra of the poly-*meta*-dibenzo[*d*,*f*][1,3] dioxepin derivatives.

CONCLUSIONS AND FUTURE DEVELOPMENT

The synthesis, potential application of dibenzo[*d*,*f*][1,3] dioxepine summarized herein indicate that these compounds are certainly worthy of more extensive investigation. The copolymers basic on the twisted bridged biphenyl-dibenzo[*d*,*f*][1,3] dioxepine should candidate for wide-bangap semiconductive materials.

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